Extreme ultraviolet laser excitation of molecular nitrogen: Perturbations and predissociation

VRIJE UNIVERSITEIT

Extreme ultraviolet laser excitation of molecular nitrogen: Perturbations and predissociation

ACADEMISCH PROEFSCHRIFT

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Chapter 1

Introduction

The molecule of interest in this Thesis is molecular nitrogen (N_2) , a closed shell diatomic molecule consisting of two nitrogen atoms. 78 % of the Earth's atmosphere consists of molecular nitrogen and also low abundances of N₂ have been found in the atmospheres of Venus and Mars. Furthermore, N₂ is a major constituent in the atmospheres of Titan and Triton, satellites of Saturn and Neptune, respectively.

 N_2 hardly absorbs visible and ultraviolet (UV) radiation. The solar radiation with $\lambda \lesssim 310 \text{ nm}^1$ impinging on the Earth's atmosphere is absorbed by the various other molecular gaseous constituents, and is thus prevented from reaching the Earth's surface. In Fig. 1.1, the altitude in the Earth's atmosphere is shown at which solar radiation is attenuated by a factor of 37 % (e^{-1}) . The species causing significant absorption are also shown, with ozone (O_3) the main absorber in the range $\sim 200-310$ nm. At shorter wavelengths, in the vacuum ultraviolet (VUV) from $\sim 100-200$ nm, absorption by O₂ becomes important, but in the extreme ultraviolet (XUV) at wavelengths below 100 nm, N_2 dominates the absorption of solar radiation, which occurs at altitudes near 150 km. The complex structure occurring in this wavelength range in Fig. 1.1 is associated with absorption transitions of N_2 from the ground state to several excited electronic states, which have many strong mutual interactions. Furthermore, upon excitation many of these excited states undergo predissociation, i.e., these states couple with other dissociative states and the molecule falls apart, producing N atoms and thus influencing the atmospheric photochemical processes.

In this Thesis, N_2 is studied experimentally using state-of-the-art XUV laser systems to investigate the complex energetic structure and interactions of the excited

¹In this Thesis, wavelength λ (in nm or Å) and frequency ν (in Hz) are used to describe the electromagnetic radiation, with the relationships: 1 nm = 10 Å and $\nu = c/\lambda$, where c is the speed of light. However in most cases, the wavenumber in units of cm⁻¹ is used in the traditional loose definition, referring to level energies, transition energies or transition frequencies. In the latter case the wavenumber equals $1/\lambda$, where the wavelength is considered in vacuum.



Figure 1.1: Altitude at which vertically incident radiation is attenuated by e^{-1} in the Earth's atmosphere. Dashed lines: spectral regions where particular species have significant extinction. Arrows: ionization thresholds. Right: atmospheric regions. Figure is kindly supplied by R. R. Meier (Ref. [1]).

electronic states leading to the complex spectral structure indicated in Fig. 1.1 in the range 90 – 100 nm. Also, the predissociation behaviour of these states is extensively studied in this Thesis. Further in this Introduction, information is presented on the electronic states of N₂ (Sec. 1.1), on N₂ in planetary atmospheres and space (Sec. 1.2), while an outline of the Thesis is given in Sec. 1.3.

1.1 N_2 and its electronic states

Molecular nitrogen is a closed shell diatomic molecule, consisting of 2 nitrogen atoms. The nitrogen atom has 7 electrons and its ground state has the configuration $1s^22s^22p^3$. The molecular-orbital (MO) configuration for the $X^1\Sigma_g^+$ ground state of N₂ is

$$(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^4 (3\sigma_g)^2.$$
(1.1)

 N_2 is one of the most stable molecules in nature, since it has an excess of bonding electrons. By ionizing N_2 , the number of bonding electrons decreases and therefore, N_2^+ is less stable and has a slightly longer bond length compared with N_2 . Potential energy curves of many of the electronic states of N_2 and N_2^+ are displayed in Fig. 1.2. More detailed potential energy diagrams for states of singlet *ungerade* symmetry $({}^{1}\Sigma_{u}^+$ and ${}^{1}\Pi_{u})$ are given further on in this Thesis in Fig. 2.1 and for some ${}^{1}\Pi_{u}$ and ${}^{3}\Pi_{u}$ states in Fig. 10.1. Principal MO configurations for the lowest Rydberg states converging on the $X^{2}\Sigma_{q}^{+}$ core of N_2^+ are:

$$a''^{1}\Sigma_{g}^{+}, E^{3}\Sigma_{g}^{+}: (1\sigma_{g})^{2}(1\sigma_{u})^{2}(2\sigma_{g})^{2}(2\sigma_{u})^{2}(1\pi_{u})^{4}(3\sigma_{g})3s\sigma_{g},$$
(1.2)

$$c'^{1}\Sigma_{u}^{+}, D^{3}\Sigma_{u}^{+}: (1\sigma_{g})^{2}(1\sigma_{u})^{2}(2\sigma_{g})^{2}(2\sigma_{u})^{2}(1\pi_{u})^{4}(3\sigma_{g})3p\sigma_{u},$$
(1.3)

$$c^{1}\Pi_{u}, G^{3}\Pi_{u}: (1\sigma_{g})^{2}(1\sigma_{u})^{2}(2\sigma_{g})^{2}(2\sigma_{u})^{2}(1\pi_{u})^{4}(3\sigma_{g})3p\pi_{u},$$
(1.4)

for the lowest Rydberg states converging on the $A^2 \Pi_u$ core of N_2^+ :

$$o^{1}\Pi_{u}, F^{3}\Pi_{u}: (1\sigma_{g})^{2}(1\sigma_{u})^{2}(2\sigma_{g})^{2}(2\sigma_{u})^{2}(1\pi_{u})^{3}(3\sigma_{g})^{2}3s\sigma_{g},$$
(1.5)

and for the valence states of relevance in this Thesis:

$$b'^{1}\Sigma_{u}^{+}:(1\sigma_{g})^{2}(1\sigma_{u})^{2}(2\sigma_{g})^{2}(2\sigma_{u})^{2}(1\pi_{u})^{3}(3\sigma_{g})^{2}(1\pi_{g}),$$
(1.6)

$$b'^{1}\Sigma_{u}^{+}: (1\sigma_{g})^{2}(1\sigma_{u})^{2}(2\sigma_{g})^{2}(2\sigma_{u})^{2}(1\pi_{u})^{4}(3\sigma_{g})(3\sigma_{u}),$$
(1.7)

$$b^{1}\Pi_{u}, C^{3}\Pi_{u}: (1\sigma_{g})^{2}(1\sigma_{u})^{2}(2\sigma_{g})^{2}(2\sigma_{u})(1\pi_{u})^{4}(3\sigma_{g})^{2}(1\pi_{g}),$$
(1.8)

$$b^{1}\Pi_{u}, C^{3}\Pi_{u}, C'^{3}\Pi_{u}: (1\sigma_{g})^{2}(1\sigma_{u})^{2}(2\sigma_{g})^{2}(2\sigma_{u})^{2}(1\pi_{u})^{3}(3\sigma_{g})(1\pi_{g})^{2}.$$
 (1.9)

Actually, the Rydberg states given above are the first members of Rydberg series, which, in the case of the singlet *ungerade* states, are labeled as $c'_{n+1}{}^{1}\Sigma^{+}_{u}$, $c_{n}{}^{1}\Pi_{u}$ and $o_{n}{}^{1}\Pi_{u}$, where *n* is the principal quantum number of the Rydberg states.² The potential energy curves of the $a''{}^{1}\Sigma^{+}_{g}$ and $D^{3}\Sigma^{+}_{u}$ states are not shown in Fig. 1.2 but are located near the $E^{3}\Sigma^{+}_{g}$ and $c'{}^{1}\Sigma^{+}_{u}$ states, respectively. Also, the $F^{3}\Pi_{u}$ and $G^{3}\Pi_{u}$ states are not shown but are just below the $o^{1}\Pi_{u}$ and $c^{1}\Pi_{u}$ states, respectively.

Since N₂ is a homonuclear diatomic molecule, the vibration-rotation and pure rotation spectra are not allowed, hence N₂ exhibits no infrared spectrum. However, the very weak $v = 1 \leftarrow 0$ quadrupole spectrum has been observed by Reuter *et al.* [3]. N₂ is transparent in the visible and ultraviolet domain except for weak bands of the Lyman-Birge-Hopfield (LBH) system $(a^1\Pi_g - X^1\Sigma_g^+)$ at 150 – 180 nm and the even weaker Vegard-Kaplan (VK) system $(A^3\Sigma_u^+ - X^1\Sigma_g^+)$ at 200 nm. For more information on the $a^1\Pi_g$ and $A^3\Sigma_u^+$ states, we refer to the extensive review on the nitrogen molecule by Lofthus and Krupenie [4]. The oscillator strength in the LBH system is associated with magnetic dipole and electric quadrupole transition

²The c'_4 and c_3 Rydberg states are often labeled as c' and c, respectively, and the o_3 Rydberg state as o.



Figure 1.2: Potential-energy curves for most of the electronic states of N_2 and N_2^+ . Figure is taken from Ref. [2].

moments, while the VK system is very weak because of its spin-forbidden singlet-triplet nature.

Electric dipole-allowed transitions from the $X^1\Sigma_q^+$ ground state are connected to the singlet ungerade states $[(c'_{n+1}, b')^1 \Sigma_u^+$ and $(c_n, o_n, b)^1 \Pi_u]$. These transitions occur in the XUV domain between 79.5 nm (ionization threshold) and 100 nm and transitions beyond the ionization limit have also been observed in absorption [5]. These states are strongly mixed, resulting in an irregular structure and intensity distribution. Strong electrostatic homogeneous interactions occur between states of the same symmetry (between the ${}^{1}\Sigma_{u}^{+}$ states and between the ${}^{1}\Pi_{u}$ states), together with heterogeneous rotational interactions (interaction between the electronic orbital and total rotational angular momenta) between the ${}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{u}$ states. Homogeneous perturbations between Rydberg and valence states are also called Rydberg-valence interactions. The interactions range in strength from strong, where entire electronic states interact with each other, to weak local perturbations, where a limited number of levels (mostly two levels) couple with each other near level-crossing regions. The strongest electrostatic interactions are already manifest in the fact that the dominant MO configuration of the $b^1\Pi_u$ state (and also for $C^3\Pi_u$) changes from configuration (1.8) to (1.9) in the range 1.3-1.4 Å and cause the unusually shaped potential curves for these states. The $b'^1 \Sigma_u^+$ state is also associated with two MO configurations: (1.6) and (1.7). The singlet *ungerade* states and the perturbations between them are key topics in this Thesis and for more information, including an extensive background, see for example Chapter 2 and Refs. cited therein.

Most singlet ungerade states predissociate, i.e., these are bound states but, due to coupling with a dissociative continuum, the molecule falls apart. As will be discussed in Chapter 10, the predissociation of the lowest ${}^{1}\Pi_{u}$ states is governed by spin-orbit coupling (interaction between the electronic orbital angular momentum and the electron spin) with the ${}^{3}\Pi_{u}$ manifold. Electrostatic homogeneous perturbations in the ${}^{3}\Pi_{u}$ manifold and rotational heterogeneous **S**-uncoupling between the ${}^{3}\Pi_{u\Omega=0,1,2}$ sublevels (interaction between the electron spin and the total rotational angular momentum) complicate the predissociation mechanism.

In this Thesis, a focus is made on the electronic states of singlet and triplet *ungerade* symmetry between $100\,000 - 109\,000$ cm⁻¹ to investigate all these interactions and predissociation effects.

1.2 N_2 in planetary atmospheres and space

1.2.1 N_2 in the Earth's atmosphere

The major constituents of the Earth's atmosphere are molecular nitrogen (78 %) and molecular oxygen (21 %), the former being the molecule of interest in this Thesis. Since on Earth, 1 out of 273 N atoms is the heavier ¹⁵N isotope, the majority of

the N₂ molecules are of the main isotopomer ¹⁴N₂. N₂ dominates two processes in the Earth's atmosphere, namely Rayleigh scattering due to its high abundance and second, as already mentioned in the beginning of the introduction, N₂ shields the Earth's surface from harmful XUV solar radiation with wavelengths $\lambda < 100$ nm by photo-excitation, photodissociation and photo-ionization processes [1]. As shown in Fig. 1.1, where the altitude at which solar radiation is attenuated by e^{-1} in the Earth's atmosphere is presented, N₂ absorbs the radiation just below 100 nm at an altitude of ~150 km in the thermosphere. The complex structure introduced by N₂ in Fig. 1.1 is associated with electric dipole transitions from the $X^1\Sigma_g^+$ ground state to the heavily mixed singlet ungerade $[(c'_{n+1}, b')^1\Sigma_u^+ \text{ and } (c_n, o_n, b)^1\Pi_u]$ Rydberg and valence states (see Fig. 2.1 for potential-energy curves). The perturbations between these states cause an irregular structure and intensity distribution (see Sec. 1.1 and Chapter 2).

In the Earth's atmosphere, the singlet *ungerade* states are also excited by collisions with electrons (electron impact excitation). Upon excitation, whether that is by absorbing a photon or by electron impact, most singlet *ungerade* states predissociate and N atoms are formed. In fact, these processes are the main source of N atoms in the thermosphere. Walter *et al.* [6] determined in a photofragment spectroscopic study that levels below 112 200 cm⁻¹ dissociate into $N(^2D^0)+N(^4S^0)$ atomic products, while levels above 112 200 cm⁻¹ dissociate into $N(^2P^0)+N(^4S^0)$. This behaviour of the two predissociation channels is governed by the structure of the triplet manifold, which is responsible for the predissociation. Ground state $N(^4S^0)+N(^4S^0)$ products are not formed in the predissociation of the singlet *ungerade* states. The metastable $N(^2D^0)$ and $N(^2P^0)$ atoms and $N(^4S^0)$ atoms with a high kinetic energy can react with O₂, yielding NO and $O(^1D)$. The $O(^1D)$ atoms can react further to form OH.

Emission of N₂ has been observed in the Earth's daytime airglow (dayglow) [1]. Observed transitions are from the Second Positive (2 PG) $C^3\Pi_u - B^3\Pi_g$, the VK and the LBH systems, with electron impact as the main excitation source since transitions from the ground state to the upper states of these systems are electric dipole forbidden. A significant population of the $A^3\Sigma_u^+$ upper state of the VK system comes from cascade from the *C*, *B* and *W* triplet states, the latter of ${}^3\Delta_u$ symmetry. The 2 PG and VK systems dominate the near UV range between 300 and 450 nm of the dayglow together with the First Negative (1 NG) $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system of N₂⁺. The most intense LBH bands occur in the far UV range near 150 nm with weaker bands in the middle UV range above 200 nm. For more information on the excited states of N₂ and N₂⁺ mentioned here, see Ref. [4] (for potential energy curves see Fig. 1.2).

Transitions involving singlet *ungerade* upper states have also been observed in the Earth's dayglow: the Birge-Hopfield I (BH I) $b^1\Pi_u - X^1\Sigma_g^+$, Birge-Hopfield II (BH II) $b'^1\Sigma_u^+ - X^1\Sigma_g^+$ and the Carroll-Yoshino (CY) $c'_4{}^1\Sigma_u^+ - X^1\Sigma_g^+$ systems [1, 7]. These systems have been extensively studied in this Thesis. Because solar XUV radiation is weak, electron impact excitation is the main source for populating these singlet *ungerade* states in the Earth's atmosphere. The *b* state predissociates quite strongly for all vibrational levels, except for v' = 1 (as discussed in Chapter 3). Therefore emission from only b(v' = 1) to several v'' levels of the ground X state has been observed. The radiative decay of b(v' = 1) to the ground X state is distributed over the entire vibrational manifold of the X state, with ~10% decay to the v'' = 0ground state level (see Fig. 3.5). The emitted (1,0)-band photons are likely to be reabsorbed because of the large optical depth (depending on absorption cross section and number density) of this band, and some multiple scattering occurs. But since b(v' = 1) mostly decays to ground state levels with v'' > 0 this effect of radiation trapping for BH I (1,0) is smaller than for CY(0,0) (see below).

The (0,0) band emission of the CY $c'_4 - X$ system in the dayglow and the aurora (see below) was found to be rather weak compared to the excitation rate of $c'_4(0)$, which does not predissociate strongly. About 90% of the emitted radiation of this level decays to the v'' = 0 ground state level and CY(0,0) has one of the largest oscillator strengths reported for the singlet ungerade states [8, 9] and thus, radiation trapping occurs. Stevens et al. [10] solved the mystery of the missing radiation by developing a resonant fluorescent scattering model for this band including multiple scattering effects, excitation and all loss processes: branching to CY(0,v''), branching to the Gaydon-Herman (GH) $c'_4{}^1\Sigma^+_u - a^1\Pi_q$ system, escape to space, absorption by O_2 and predissociation. It was found that branching to CY(0,1), followed by absorption by the overlapping BH I b - X (2,0) band, is a very important loss process since the b(2) level is 100% predissociated. Also, predissociation of $c'_4(0)$ is important and has recently been investigated in detail by Liu et al. [11]. Estimated predissociation yields are negligibly small for J = 0 - 2 and are between 0.2 and 0.5 for J = 4 - 23. Stevens et al. showed that the CY(0,0) band indeed undergoes multiple scattering, resulting in higher probabilities of the other loss processes. This radiation trapping explains the weak CY(0,0) emission.

Fluorescence from N_2 has also been observed in the aurora borealis (northern light) and aurora australis (southern light) near the magnetic poles of the Earth. The aurora is created by collisions of charged particles from the solar wind, e.g., electrons and protons, with N_2 and other atmospheric species, resulting in the population of excited states and the occurrence of fluorescence. These charged particles are introduced into the atmosphere near the poles by the Earth's magnetic field.

Many transitions in N₂ have been observed in the aurora: the VK and 2 PG systems in the UV, the First Positive (1 PG) $B^3\Pi_g - A^3\Sigma_u^+$ system, the infrared afterglow $B'^3\Sigma_u^- - B^3\Pi_g$ (IRA), and the Wu-Benesch (WB) $W^3\Delta_u - B^3\Pi_g$ systems in the visible and the infrared [12]; the GH system around 350 nm [13, 14], the LBH system in the far UV, and the BH I in the XUV [1]. The CY system has not been positively assigned in the aurora. Perhaps Feldman and Gentieu [15] and Paresce *et al.* [16] observed CY(0,0) and (0,1) very weakly, but, also in the aurora, radiation trapping (see above) causes a significant CY emission loss.

1.2.2 N_2 in other planetary atmospheres

 N_2 has also been found in low abundance in the atmospheres of the planets Venus (3.5 %) and Mars (2.7 %) [17]. In the atmospheres of Titan [18] and Triton [19], moons of Saturn and Neptune, respectively, N_2 is a major constituent and XUV emissions of N_2 have been observed by the ultraviolet spectrometers (UVS) on the Voyager spacecrafts. In the case of Titan, Strobel and Shemansky [18] observed relatively strong emissions of the CY(0-1,0) and (3-4,0), the BH I(1,v''), LBH, BH II(9,0) and (17,0) and $c_3 - X(2,0)$ bands. However, Stevens [20] employed a multi-scattering model, similar to that for the Earth's dayglow (see Section 1.2.1), and found that radiation trapping should occur for the CY(0,0) band in Titan's atmosphere, resulting in a much lower calculated emission intensity for this band than observed by Strobel and Shemansky, while for the CY(0,1) band the calculated and observed data agree well. The model of Stevens also predicted relatively intense emission lines of N I, formed by photodissociative ionization and electron impact processes on N_2 , near 95.32 and 96.45 nm,³ which have already been identified in the Earth's dayglow [7], with the weak CY(0,0) band in between. Stevens argued that the region near CY(0,0) was misassigned in the Voyager data and that the strong emission in this region corresponds to a combination of these N I lines, together with other N_2 bands and the weak CY(0,0) band. The Ultraviolet Imaging Spectrograph Subsystem experiment [21] on the Cassini mission (see below) should be able to solve this question.

Titan is interesting because its atmosphere has many similarities with that of the prebiotic Earth, before life put O_2 into the atmosphere. Hydrocarbon-rich elements have been detected in Titan's atmosphere by infrared spectroscopy, elements which are building blocks for amino acids. The molecule of interest in this Thesis, N_2 , plays a role as quencher of other species and in the formation of HCN. First, N atoms and N⁺ ions are formed by electron-impact dissociation and ionization of N₂. Then, N⁺ reacts with CH₄, yielding H₂CN⁺ and two H atoms, and subsequent dissociative recombination of H₂CN⁺ with an electron gives HCN. The nitrogen compounds HCCCN and C_2N_2 are produced in secondary reactions [17]. Vervack *et al.* [22], reanalyzed the Voyager UVS data and developed an XUV transmission model for Titan's upper atmosphere from which densities of N₂, CH₄, C₂H₂, HCN and other species, and atmospheric temperatures, were obtained. Lammer *et al.* [23] investigated all possible sources of nitrogen isotope fractionation to explain Titan's ¹⁵N enrichment of about 4.5 times the value on Earth, while Owen [24] discussed in detail the origin of Titan's atmosphere.

Currently, the Cassini-Huygens mission to Saturn and its moons is in progress to investigate the Saturn system in detail, using many different instruments on

³These N I lines in the XUV domain have recently been measured (see Chapter 11) with a precision of 0.005 cm⁻¹. These new measurements may be useful for future investigations of the Earth's dayglow and aurora and XUV emissions on Titan (Cassini mission).

board the Cassini Spacecraft orbiter and the Huygens probe, which has landed on Titan [25]. The Ultraviolet Imaging Spectrograph Subsystem [21] on Cassini will investigate the XUV emission of Titan's atmosphere, including most likely many N_2 bands (see above), while the ${}^{15}N/{}^{14}N$ isotope ratio may be verified using the results obtained with the Gas Chromatograph and Mass Spectrometer (GCMS) instrument on the Huygens probe.

1.2.3 N_2 in space

Absorption of N₂ has been observed only just recently for the first time in the interstellar medium [26, 27]. While observations of many other molecules have been reported, N₂ has, not surprisingly, been undetected in the interstellar medium until 2004, although chemical models for dense (dark) and diffuse interstellar clouds predict the presence of N₂ in significant abundances. N₂ does not have allowed rotational and vibrational transitions and the electronic transitions occur in the XUV domain, which makes it difficult to measure. However, recently a weak signal was observed near 95.86 nm in the interstellar medium, in the line of sight towards HD 124314, a star in the constellation of Centaurus, using the Far Ultraviolet Spectroscopic Explorer (FUSE) satellite. The absorption was assigned as the CY $c'_4 - X(0,0)$ band. The nearby $c_3 - X(0,0)$ band could not be found because of overlap with H₂ lines. The determined N₂ column density and N₂/H₂ ratio (in the 10^{-7} range) do not fit with models for diffuse or dense clouds, and hence the N₂ chemistry models for these clouds are possibly inadequate.

1.3 Outline of Thesis

Following the Introduction, comprehensive laser-spectroscopic experimental studies are presented on the singlet and triplet ungerade states $({}^{1}\Sigma_{u}^{+}, {}^{1}\Pi_{u}, {}^{3}\Sigma_{u}^{+}, {}^{3}\Pi_{u})$ of N₂ in the XUV domain between 100 000 – 109 000 cm⁻¹. The experimental work has been performed using the XUV laser systems at the Laser Centre Vrije Universiteit Amsterdam, while the interpretation and theoretical analysis has been done in close collaboration with B.R. Lewis and coworkers (Canberra, The Australian National University) who are involved in developing models for the level structure and dissociation dynamics of the excited states of the nitrogen molecule. The main goals of the collaborative project are to investigate the structure of the singlet and triplet *ungerade* states, including all the perturbations between the states, and to elucidate the predissociation mechanism of the singlet *ungerade* states, which is, as discussed later in this Thesis (Chapter 10), governed by coupling with the ${}^{3}\Pi_{u}$ states. The dynamic interaction between experimentalists and theorists was fruitful and helped focusing on problems of interest and importance.

The understanding of the structure and predissociation dynamics of the singlet

and triplet *ungerade* states of N_2 will help in understanding the radiation budget, airglow and auroral observations, N atom formation and other (photo-)chemical processes in the N₂-rich atmospheres of the Earth, Titan and Triton, and is useful for interpreting, not only atmospheric, but also interstellar observations.

The experimental part of the N_2 project is presented in Chapters 2 – 9. In Chapter 2 and the Appendix, the dipole-allowed 1 XUV + 1 UV ionization spectrum is presented of the isotopomers ${}^{15}N_2$ and ${}^{14}N^{15}N$, consisting of ${}^{1}\Pi_u - X^{1}\Sigma_q^+$ and ${}^{1}\Sigma_{u}^{+} - X^{1}\Sigma_{a}^{+}$ transitions. In Chapters 3 and 4, direct time-domain pump-probe lifetime measurements on several singlet ungerade states are presented. These measurements were performed with the picosecond XUV laser system at the Lund Laser Centre in collaboration with A. Johansson, A. L'Huillier and C.-G. Wahlström. Chapter 3 focuses only on the relatively long-lived $b^1 \Pi_u(v=1)$ level in ¹⁴N₂, suggesting a predissociation yield for this level. Chapters 5 and 6 contain frequencydomain linewidth/lifetime measurements on singlet ungerade states performed in Amsterdam, showing isotopic variations. The dynamic ranges of the two laser systems are complementary. The time-domain Lund setup is applicable for lifetimes >200 ps, while lifetimes shorter than 800 ps can be determined with the frequencydomain Amsterdam setup. A reanalysis of the $o^1 \Pi_u(v=1)/b^1 \Pi_u(v=9)$ Rydbergvalence complex in N₂, including the perturbation between the two levels, is given in Chapter 7. Newly observed triplet ungerade states and accidental singlet-triplet interactions are discussed in Chapters 8 and 9.

The theoretical part of the N₂ project is summarized in Chapter 10, where the predissociation mechanism of the singlet *ungerade* states, developed by Lewis and coworkers, is discussed. The experimental results in Chapters 2-9 are used (or will be used in future) as key inputs in the theoretical predissociation model. Finally, Chapter 11 presents high precision frequency calibration measurements on N I lines in the XUV domain.

Chapter 2

Extreme ultraviolet laser excitation of isotopic molecular nitrogen: The dipole-allowed spectrum of ${}^{15}N_2$ and ${}^{14}N^{15}N$

Extreme ultraviolet + ultraviolet (XUV + UV) two-photon ionization spectra of the $b^1 \Pi_u(v=0-9)$, $c_3{}^1 \Pi_u(v=0,1)$, $o^1 \Pi_u(v=0,1)$, $c'_4{}^1 \Sigma_u^+(v=1)$ and $b'{}^1 \Sigma_u^+(v=0,1)$ 1, 3 - 6) states of ¹⁵N₂ were recorded with a resolution of 0.3 cm⁻¹ full-width at half-maximum (FWHM). In addition, the $b^1\Pi_u(v=1,5-7)$ states of ¹⁴N¹⁵N were investigated with the same laser source. Furthermore, using an ultra-narrow bandwidth XUV laser [$\sim 250 \text{ MHz}$ ($\sim 0.01 \text{ cm}^{-1}$) FWHM], XUV + UV ionization spectra of the $b^1 \Pi_u(v=0-1,5-7), c_3^1 \Pi_u(v=0), o^1 \Pi_u(v=0), c'_4^1 \Sigma_u^+(v=0)$ and $b'^{1}\Sigma_{u}^{+}(v=1)$ states of ¹⁵N₂ were recorded in order to better resolve the band-head regions. For ¹⁴N¹⁵N, ultra-high resolution spectra of the $b^1\Pi_u(v=0-1,5-6)$, $c_3{}^1\Pi_u(v=0)$ and $b'{}^1\Sigma_u^+(v=1)$ states were recorded. Rotational analyses were performed for each band, revealing perturbations arising from the effects of Rydbergvalence interactions in the ${}^{1}\Pi_{u}$ and ${}^{1}\Sigma_{u}^{+}$ states, and rotational coupling between the ${}^{1}\Pi_{u}$ and ${}^{1}\Sigma_{u}^{+}$ manifolds. Finally, a comprehensive perturbation model, based on the diabatic-potential representation used previously for $^{14}N_2$, and involving diagonalization of the full interaction matrix for all Rydberg and valence states of ${}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{u}$ symmetry in the energy window 100 000–110 000 cm⁻¹, was constructed. Term values for ${}^{15}N_2$ and ${}^{14}N^{15}N$ computed using this model were found to be in good agreement with experiment.

2.1 Introduction

Molecular nitrogen dominates atmospheric absorption in the extreme ultraviolet (XUV) spectral region for wavelengths immediately below 100 nm. N₂ shields the Earth's surface from XUV radiation through photodissociation, photoexcitation and photoionization processes, in which the singlet ungerade $({}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{u})$ states play significant roles [1]. These processes occur predominantly in the upper-atmospheric layers above 100 km. At those altitudes, the singlet ungerade states are not only populated via photo-excitation, but also via electron-collision-induced excitation processes occur, their rates providing key inputs for models explaining the radiation budget of the Earth's atmosphere. Such processes are also important in the nitrogen-rich atmospheres of the satellites Titan and Triton, of Saturn and Neptune, respectively.

Predissociation of the singlet *ungerade* states is likely to occur *via* coupling with (pre-)dissociating valence states of triplet character [6, 28]. However, the predissociation mechanisms and the singlet-triplet coupling are not understood at present. The isotopic study of the singlet *ungerade* states reported here and in subsequent works is important for further characterization of the molecular potentials and interactions that must be included in realistic predissociation models for N₂. Laboratory investigations of the spectra and predissociation rates for different N₂ isotopomers are also relevant to an understanding of differences in isotopic abundances in nitrogen-rich planetary atmospheres. For example, in the Earth's atmosphere, only 1 out of 273 nitrogen atoms is the heavier ¹⁵N isotope. On Titan [23], the ¹⁵N atom is enriched 4.5 times compared to the Earth, while on Mars [29, 30] the ¹⁵N enrichment factor is 1.6.

Molecular nitrogen is almost transparent in the visible and the ultraviolet domains. However, strong electric-dipole-allowed absorption occurs in the XUV region with $\lambda \leq 100\,$ nm, down to the first ionization limit at 79.5 nm and beyond. Lefebvre-Brion [31], Dressler [32] and Carroll and Collins [33] showed that the allowed spectrum consists of transitions from the ground state $X^{1}\Sigma_{g}^{+}$ to the $c'_{n}{}^{1}\Sigma_{u}^{+}$ and $c_{n}{}^{1}\Pi_{u}$ Rydberg series converging on the ionic ground state $X^{2}\Sigma_{g}^{+}$, where n is the principal quantum number, the $o_{n}{}^{1}\Pi_{u}$ Rydberg series converging on the $A^{2}\Pi_{u}$ state of the ion, and the valence states $b'{}^{1}\Sigma_{u}^{+}$ and $b^{1}\Pi_{u}$. Potential-energy curves for the relevant electronic states of N₂ are shown in Fig. 2.1. It should be noted that there are alternative nomenclatures in use for some of these states. In particular, o_{3} is commonly known as o.

The N₂ absorption spectrum in the XUV domain shows many irregularities, not only in the rovibronic structure, but also in the intensity distribution. Indeed, the spectrum was not understood for many years due to the complications introduced by strong interactions between the singlet *ungerade* states in this region. Stahel *et al.* [34] modelled the $(c'_4, c'_5 \text{ and } b')^1 \Sigma_u^+$ and $(c_3, o \text{ and } b)^1 \Pi_u$ states in a diabatic representation and showed that the principal irregularities are due to homogeneous



Figure 2.1: Potential-energy curves for relevant singlet electronic states of N₂, shown in a diabatic (crossing) representation. Full curves: ${}^{1}\Pi_{u}$ states. Dashed curves: ${}^{1}\Sigma_{u}^{+}$ states. The energy scale is referenced to a zero defined by the v = 0, J = 0 level of the $X {}^{1}\Sigma_{a}^{+}$ state (not shown).

interactions within each of the two manifolds of states, mainly of Rydberg-valence type. Furthermore, heterogeneous interactions between the ${}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{u}$ manifolds also add to the complexity of the spectra. Helm *et al.* [28], Edwards *et al.* [35], Walter *et al.* [36] and Ubachs *et al.* [37] extended the work of Stahel *et al.* [34] by including these heterogeneous interactions in their calculations. The interactions between the $c'_{n+1}{}^{1}\Sigma_{u}^{+}$ and $c_{n}{}^{1}\Pi_{u}$ Rydberg states, which are members of p complexes, were analyzed using **L**-uncoupling theory by Carroll and Yoshino [38]. More recently, a comprehensive *ab initio* study of the three lowest ${}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{u}$ states and their mutual interactions has been performed by Spelsberg and Meyer [39].

The isotopomers ¹⁴N¹⁵N and ¹⁵N₂ have not been studied experimentally as extensively as the main isotopomer ¹⁴N₂. In the case of the $X^{1}\Sigma_{g}^{+}$ state, accurate molecular constants for ¹⁴N₂ and ¹⁵N₂ were obtained in a high-resolution coherent Raman spectroscopy experiment by Orlov *et al.* [40] while in a more recent Fouriertransform-Raman experiment, Bendtsen [41] determined the molecular constants of $^{14}\rm N^{15}N$ and $^{15}\rm N_2$ with even better accuracy.

In the case of the excited states in the XUV, the vibrational isotope shifts for ¹⁵N₂ have been investigated by Ogawa *et al.* [42, 43] in a classical absorption experiment. Yoshino *et al.* [44] measured the isotope shifts for the Q bandheads of the $o_n{}^1\Pi_u(v = 0 - 4)$ levels for both ${}^{14}N{}^{15}N$ and ${}^{15}N_2$. Mahon-Smith and Carroll [45] measured vibrational isotope shifts for ${}^{15}N_2$ in transitions between electronically-excited states. Rotationally-resolved spectra accessing the $c'_4{}^1\Sigma_u^+(v = 0)$ and $b'{}^1\Sigma_u^+(v = 1)$ levels of ${}^{14}N{}^{15}N$ and ${}^{15}N_2$ were recorded by Yoshino and Tanaka [46] who analyzed the homogeneous interaction between these states for the different isotopomers. Hajim and Carroll [47, 48] calculated the vibronic energies and the interaction energies of the $c'_4{}^1\Sigma_u^+$ and $b'{}^1\Sigma_u^+$ states of ${}^{15}N_2$; their results were compared with unpublished results of Yoshino in Ref. [47].

In this article, an XUV + UV spectroscopic study of singlet ungerade states of the isotopomers ¹⁴N¹⁵N and ¹⁵N₂ in the 100 000–108 000 cm⁻¹ region is reported. While much of the study was performed with high resolution (~ 3×10^5 resolving power), in some cases ultra-high resolution was employed (~ 10^7 resolving power). Molecular parameters and isotope shifts have been determined from the rotationally-resolved spectra. Finally, using the model originally developed for ¹⁴N₂ by Stahel *et al.* [34], including heterogeneous interactions, we have computed term values for the relevant states of ¹⁵N₂ and ¹⁴N¹⁵N. Using the diabatic potential energy curves and couplings employed for ¹⁴N₂ [34], we find good agreement between the experimental and computed results for ¹⁵N₂ and ¹⁴N¹⁵N. The present paper, one in a series, is intended to broadly summarize the isotopic results and identify the effects of the principal interactions. The original line assignments leading to the results presented here are available separately *via* the EPAPS data depository of the AIP (see the Appendix). Future reports will focus on excited-state predissociation lifetimes and on the effects of singlet-triplet interactions in the XUV spectrum.

2.2 Experiment

The experimental system has been described in detail elsewhere [49, 50] and only the key features will be summarized here. We employ an XUV source which is based on harmonic upconversion, using two laser systems: a pulsed dye laser (PDL) with high resolution [XUV bandwidth ~9 GHz (~0.3 cm⁻¹) full-width at halfmaximum (FWHM)] for undertaking survey spectra; and an ultra-high resolution pulsed-dye-amplifier (PDA) yielding an XUV bandwidth of ~250 MHz (~0.01 cm⁻¹ FWHM) for measuring precise line positions and widths and to enable resolution of the congested band heads. A scheme of the experimental setup, including the PDL-based and PDA-based systems, is presented in Fig. 2.2.

Both tunable pulsed laser systems, the PDL (Quanta-Ray PDL3), as well as the



Figure 2.2: Scheme of the experimental setup. Dashed line: PDL-based setup. Full line: PDA-based setup. After the frequency doubling in the KDP crystal, the PDL-based and PDA-based setups are similar. EM: electron-multiplier. TOF setup: time-of-flight setup. See the text for more information.

home-built PDA, are pumped by the second harmonic of a pulsed Nd:YAG laser. In such a system, a range of dyes can be used to cover a broad wavelength range in the red-yellow region with a short wavelength limit of 545 nm. The PDA is injection seeded by the output of a Spectra Physics 380D cw-ring-dye laser, pumped by a cw 532 nm Millennia laser. In the configuration employed, the short-wavelength cut-off of this cw-system is at 566 nm, thereby also reducing the accessible wavelength range of the PDA.

The XUV radiation is generated in the same way for both laser systems, by frequency doubling the visible pulsed output in a KDP crystal, and then frequency tripling the resulting UV beam in a pulsed xenon jet. For the PDL and PDA sources, the lower wavelength limits in the XUV are 91 nm and 94.3 nm, respectively. At long wavelengths, both the PDL and PDA systems can be tuned to 600 nm, thus allowing the lowest dipole-allowed states in N_2 to be accessed in the XUV near 100 nm.

The generated XUV beam and the UV beam propagate collinearly into the interaction chamber, where they are perpendicularly crossed with a skimmed and pulsed beam of N₂. For the measurements with the PDL system, the distance between the nozzle and the skimmer was decreased to only a few mm, in order to increase the number of N₂ molecules in the interaction zone. In this way, the weaker bands of $^{15}N_2$ and some strong bands of $^{14}N^{15}N$ could be observed. For $^{14}N^{15}N$, only strong bands were observed because natural N₂ gas was used, containing only 0.74% ¹⁴N¹⁵N. For the ¹⁵N₂ experiments, a 99.40% ¹⁵N isotopically enriched gas sample (Euriso-top) was used, enabling weak bands to be observed. For all PDL scans, the highest achievable laser power was used, i.e., 40 mJ/pulse in the UV, to enhance the signal of weak lines which otherwise could not be observed. In experiments with the ultra-high resolution PDA source, the nozzle-skimmer distance was increased to a maximum of 150 mm to reduce the Doppler broadening, enabling more precise measurement of the transition frequencies and linewidths.

The N_2 spectra were recorded using 1 XUV + 1 UV two-photon ionization spectroscopy. The XUV photon excites the N₂ molecules from the ground state to the states under investigation and, subsequently, the UV photon ionizes the molecule forming N_2^+ , which is detected using a time-of-flight (TOF) electron-multiplier detection system. It should be noted that the signal intensities for the spectral lines recorded in 1 XUV + 1 UV two-photon ionization do not directly reflect the cross sections of the single-XUV-photon-induced bound-bound transitions. The UV-laserinduced photoionization step also influences the signal intensities, particularly when autoionizing resonances are probed in the continuum above the ionization potential. No signatures of such resonances were found, however. Furthermore, the N_2^+ signal intensity is strongly dependent on the lifetime of the intermediate (target) state. If the lifetime is shorter than the duration of the laser pulse (3 ns for XUV, 5 ns for UV), e.g., as a result of predissociation, the signal drops considerably. This phenomenon has been discussed in quantitative terms by Eikema et al. [51]. The N_2^+ ions are accelerated in the TOF apparatus, allowing for mass selective detection of the different isotopomers of N_2 (masses 28, 29 and 30). Nevertheless, the signal of the much more abundant ${}^{14}N_2$ was more than an order of magnitude higher than that of the ${}^{14}N^{15}N$ isotopomer. In cases where the ${}^{14}N^{15}N$ isotopomer has features that spectrally coincide with ${}^{14}N_2$ lines, the mass-selectivity is limited by the strong signal from the main isotopomer for two reasons: the large number of ions created give rise to a Coulomb explosion and the large mass-28 signals saturate the detector. In regions without spectral overlap the ¹⁴N¹⁵N features were more favorably recorded.

The absolute frequency-calibration procedures employed have been discussed elsewhere for the PDL-based [49] and PDA-based [52] XUV sources. In both cases, frequency calibration is performed in the visible and the result is multiplied by a factor of 6 to account for the subsequent harmonic conversion. The frequency of the PDL is determined by simultaneously recording a Doppler-broadened I₂ absorption spectrum which is compared with an iodine atlas [53]. The frequency of the PDA is determined by simultaneously recording fringes from a stabilized étalon (free spectral range 148.9567 MHz) and an I₂ saturated-absorption spectrum, using the output of the cw-ring dye laser. Reference lines for the I₂ spectrum are taken from an accurate list of saturated resonances produced in our laboratory [54, 55] or from calculations [56].

In some of the spectra recorded with the PDL source, line broadening associated

with the AC-Stark effect was observed, sometimes yielding asymmetric line shapes. This phenomenon was not investigated in detail, but the AC-Stark-induced shifts were compensated for by comparison with spectra obtained using the PDA source. For several bands, low-J lines were recorded with the PDA, while the entire band was recorded using the PDL at high laser intensity. Line positions from the PDA source were systematically lower by $\Delta_{PDL-PDA} \approx 0.05 - 0.20 \text{ cm}^{-1}$. Based on the observations with both systems, the PDL data were corrected for the AC-Stark shift, for those bands where ultra-high resolution PDA data were available. Due to the uncertain Stark shifts, the absolute wave-number uncertainty for the lines recorded with the PDL-based XUV source is $\pm 0.2 \text{ cm}^{-1}$, significantly worse than the calibration uncertainty of $\pm 0.05 \text{ cm}^{-1}$. The absolute calibration uncertainty for the PDA source is $\pm 0.003 \text{ cm}^{-1}$. This value represents a lower limit to the uncertainty for the narrowest spectral lines recorded. For lines where lifetime and/or Doppler broadening is of importance, the uncertainty is $\pm 0.02 \text{ cm}^{-1}$.

2.3 Analysis of spectra

Using the PDL system, rotationally-resolved spectra of transitions from $X^{1}\Sigma_{g}^{+}(v = 0)$ to the $b^{1}\Pi_{u}(v = 0, -9)$, $c_{3}^{1}\Pi_{u}(v = 0, 1)$, $o^{1}\Pi_{u}(v = 0, 1)$, $c'_{4}^{1}\Sigma_{u}^{+}(v = 1)$ and $b'^{1}\Sigma_{u}^{+}(v = 1, 3 - 6)$ states of $^{15}N_{2}$ and the $b^{1}\Pi_{u}(v = 1, 5 - 7)$ states of $^{14}N^{15}N$ were recorded. With the much narrower-bandwidth PDA source, spectra for transitions to the $b^{1}\Pi_{u}(v = 0, -1, 5 - 7)$, $c_{3}^{1}\Pi_{u}(v = 0)$, $o^{1}\Pi_{u}(v = 0)$, $c'_{4}^{1}\Sigma_{u}^{+}(v = 0)$ and $b'^{1}\Sigma_{u}^{+}(v = 1)$ states of $^{15}N_{2}$ and the $b^{1}\Pi_{u}(v = 0 - 1, 5 - 6)$, $c_{3}^{1}\Pi_{u}(v = 0)$ and $b'^{1}\Sigma_{u}^{+}(v = 1)$ states of $^{14}N^{15}N$ were recorded in order to resolve the band-head regions.

Since the nozzle-skimmer distance was increased in the PDA-based measurements, to minimize the Doppler width and improve the spectral resolution, the rotational temperature was low and transitions arising from only those groundstate levels with $J'' \leq 5$ could be observed. The difference in resolution of the two laser systems is illustrated in Figs. 2.3 and 2.4, in which spectra of the b - X(1,0)band of ${}^{15}N_2$, recorded with the PDL source, and the b - X(5,0) band of ${}^{15}N_2$ obtained with the PDA system, are shown, respectively. Line widths of ~ 0.3 cm⁻¹ FWHM are observed in the PDL-based recordings if the excited state is not severely predissociated. This value is predominantly due to the laser bandwidth, but includes a contribution from Doppler broadening and is independent of the specific nozzle-skimmer distance chosen. The line widths for the PDA-based recordings are partially determined by the laser-source bandwidth (250 MHz FWHM) and partially by Doppler broadening which depends on the nozzle-skimmer distance. The minimum line width measured was 300 MHz FWHM, corresponding to the case of no predissociation.

Rotational lines in the P, Q, and R-branches of all bands were assigned us-



Figure 2.3: 1 XUV + 1 UV ionization spectrum and line assignments for the ${}^{15}N_2 \ b^1\Pi_u - X^1\Sigma_g^+$ (1,0) band, recorded using PDL-based XUV source with a resolution of ~0.3 cm⁻¹(9 GHz) FWHM.



Figure 2.4: 1 XUV + 1 UV ionization spectrum of the $^{15}\mathrm{N}_2~b^1\Pi_u-X^1\Sigma_g^+$ (5,0) band-head region, recorded using PDA-based XUV source with a resolution of $\sim 0.01~\mathrm{cm}^{-1}(\sim 250~\mathrm{MHz})$ FWHM. For this level, little lifetime broadening occurs and the observed line width reflects the instrumental width.

ing ground-state combination differences and guidance provided by the effects of nuclear-spin statistics on the appearance of spectra. For ¹⁴N₂, the nuclear spin I = 1, which results in a 2:1 intensity alternation of the even:odd rotational lines. Conversely, for ¹⁵N₂ I = 1/2 and the odd lines are three times stronger than the even lines. Because ¹⁴N¹⁵N is not a homonuclear diatomic molecule, no intensity alternation occurs in this case. Rotational line assignments and corresponding wave numbers for all bands studied are listed in Tables which have been lodged with the EPAPS data depository of the AIP (see the Appendix). As an example, transition energies for the $b^{1}\Pi_{u} - X^{1}\Sigma_{a}^{+}(1,0)$ band of ¹⁵N₂ are listed in Table 2.1.

Term values for the rovibrational levels of the excited ${}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{u}$ states accessed in this work were determined from the experimental transition energies using $X {}^{1}\Sigma_{g}^{+}(v=0)$ terms obtained from the spectroscopic constants of Bendtsen [41] for both ${}^{15}N_{2}$ and ${}^{14}N^{15}N$. Effective spectroscopic parameters for the isotopomers were determined by least-squares fitting polynomial expressions in J to the experimental rotational terms. We eschew the use of the terminology "spectroscopic constant" in relation to the excited states considered here since, for the most part, the observed levels are significantly perturbed, thus limiting or removing the mechanical significance normally attributed to these constants. Moreover, for the same reason, the number of polynomial terms necessary to reproduce the experimental results to an acceptable accuracy was, in many cases, found to be greater than usual, and the values of the polynomial coefficients were dependent on the number of terms.

Therefore, in the case of the excited states with ${}^{1}\Sigma_{u}^{+}$ symmetry, the terms are taken to have the form:

$$T(J,e) = \nu_0 + Bx - Dx^2 + Hx^3 + H'x^4, \qquad (2.1)$$

where x = J(J+1), ν_0 is the band origin, B, D, H, and H' are rotational parameters, and we note that all rotational levels are of e parity [57]. The terms for the excited states with ${}^{1}\Pi_{u}$ symmetry are represented as:

$$T(J,f) = \nu_0 + By - Dy^2 + Hy^3 + H'y^4, \qquad (2.2)$$

for the f-parity levels, and

$$T(J,e) = T(J,f) + \Delta T_{ef}(J), \qquad (2.3)$$

for the *e*-parity levels, where y = x - 1 and the Λ -doubling is taken as:

$$\Delta T_{ef}(J) = qy + q'y^2 + q''y^3 + q'''y^4, \qquad (2.4)$$

where q, q', q'' and q''' are Λ -doubling parameters. The e levels of the excited state are accessed in the P- and R-branch transitions (J = J'' - 1 and J = J'' + 1,respectively), while the f levels are accessed in the Q-branch transitions (J = J''), absent in the case of the ${}^{1}\Sigma_{u}^{+} - X {}^{1}\Sigma_{g}^{+}$ bands.

Table 2.1: Observed transition energies for the $b^1 \Pi_u - X^1 \Sigma_g^+(1,0)$ band of ¹⁵N₂. 101 000 cm⁻¹ has to be added to listed values for transition energies. Wave numbers given to three decimal places are from narrowbandwidth pulsed dye-laser (PDA) spectra, those to two decimal places are from pulsed dye-laser (PDL) spectra. Wave numbers derived from blended lines are flagged with an asterisk (*), those from shoulders in the spectra by s and those from weak features by w. Deviations from transition energies calculated using a least-squares fit of Eqs. (2.2-2.4) to the corresponding term values are also shown ($\Delta_{\rm oc} = {\rm obs. - calc.}$). All values in cm⁻¹.

J	R(J)	$\Delta_{\rm oc}$	Q(J)	$\Delta_{\rm oc}$	P(J)	$\Delta_{\rm oc}$
0	458.455	-0.004				
1	$460.014 \mathrm{s}$	0.009	454.737	-0.007		
2	460.465	0.001	452.565	-0.009	447.17	-0.14
3	459.890s	0.053	449.310	-0.009	441.35	-0.08
4	458.04	-0.08	444.88	-0.10	434.39	-0.07
5	455.336	0.016	439.57	0.02	426.39	-0.01
6	451.48	0.05	433.10^{*}	0.07	417.13s	-0.13
7	446.35	-0.10	425.42	-0.01	406.99^{*}	-0.05
8	440.40	0.03	$416.80 \mathrm{s}$	0.07	395.66s	-0.05
9	433.10^{*}	-0.09	406.99^{*}	0.04	383.30	-0.01
10	424.96s	0.03	396.12s	0.06	370.02	0.21
11	415.54	-0.02	384.09	0.01	355.18	-0.05
12	405.13	0.04	371.26	0.25	339.49	-0.05
13	393.44	-0.07	356.84	0.01	322.75	-0.01
14	380.86	0.03	341.52	-0.04	304.92	0.05
15	367.16	0.12	325.16	-0.01	285.91	0.01
16	352.05	-0.09	307.69	0.01	265.83	0.01
17	336.11	0.00	289.12	0.05	244.43	-0.19
18	318.90	-0.06	269.41	0.06	222.36	0.04
19	300.74	0.05	248.45	-0.06	198.91	0.00
20	281.30	0.01	226.51	-0.03	174.38w	0.01
21	260.79	0.03	203.34	-0.11	148.66	-0.06
22	239.04w	-0.04	179.22w	-0.01		
23	216.20	-0.07	153.84	-0.03	094.02w	-0.02
24			127.38w	0.01		
25	167.29w	0.10	099.78w	0.05		

From the least-squares fits, spectroscopic parameters for the $b'^{1}\Sigma_{u}^{+}(v=1,3-6)$ and $c'_{4}{}^{1}\Sigma_{u}^{+}(v=1)$ states of ${}^{15}N_{2}$ and the $b'^{1}\Sigma_{u}^{+}(v=1)$ state of ${}^{14}N^{15}N$ were determined and the results are listed in Table 2.2. For the $c'_{4}{}^{1}\Sigma_{u}^{+}(v=0)$ state of ${}^{15}N_{2}$, only a few R(J) lines were measured with the PDA system, yielding, however, an accurate determination of the band origin. Spectroscopic parameters for the ${}^{1}\Pi_{u}$ states, obtained from the least-squares fits, are given in Table 2.3, for ${}^{15}N_{2}$, and Table 2.4, for ${}^{14}N^{15}N$. Term values derived from the PDL-based measurements, as well as the more accurate data from the PDA-based source, were simultaneously included in the fitting routines, taking account of the PDL–PDA shift, and using proper weighting of the uncertainties.

The isotopic spectroscopic parameters in Tables 2.2, 2.3 and 2.4 display the effects of perturbations, just as in the well-known case of $^{14}N_2$. In our analysis, we have taken the following approach. (1) For the stronger perturbations, where level crossings are not so apparent, we follow the rotational term series to as high a J value as possible, thus requiring additional polynomial terms in the fitting procedure. In these cases, of course, the electronic character of each level changes significantly over the full range of J. (2) For weaker perturbations, we follow the terms through the level crossing, neglecting the small range of J values around the perturbed crossing region. The ranges of J values included in the fits are indicated in Tables 2.2, 2.3 and 2.4. Our principal aim is to provide spectroscopic parameters which enable the reproduction of the experimental term values over as wide a range of rotation as possible, to a level of precision commensurate with the relative experimental uncertainties.

Specific effects of perturbations manifest in Tables 2.2, 2.3 and 2.4 include irregularities in vibrational spacings and B values, together with widely varying D and q values. Some of these effects are summarized in Fig. 2.5, and particular cases are discussed in more detail in Sec. 2.5. Principally, they are caused by Rydberg-valence interactions within the ${}^{1}\Pi_{u}$ and ${}^{1}\Sigma_{u}^{+}$ manifolds, together with rotational coupling between these manifolds. In the simplest possible view, anomalously large values of D, e.g., for b(v = 4) of ¹⁵N₂ in Table 2.3, indicate either homogeneous perturbation by a level with a smaller B value, or heterogeneous perturbation, both from above. Conversely, a negative D value, e.g., for b(v = 8) of ¹⁵N₂ in Table 2.3, indicates either homogeneous perturbation by a level with a larger B value, or a heterogeneous perturbation, both from below. A large-magnitude Λ -doubling parameter |q|for a ${}^{1}\Pi_{u}$ state indicates a significant heterogeneous interaction between the ${}^{1}\Pi_{u}$ e-level and one of the ${}^{1}\Sigma_{u}^{+}$ states. In principle, the ${}^{1}\Pi_{u}$ f-levels could be shifted in interactions with ${}^{1}\Sigma_{u}^{-}$ states, but such states have not been reported for the 100000–110000 cm⁻¹ region in N₂. Hence a positive q-value, e.g., for b(v = 5) of $^{15}N_2$ in Table 2.3, signifies that the $^{1}\Pi_u$ level is dominantly perturbed by a lowerlying ${}^{1}\Sigma_{u}^{+}$ level, while in case of a negative q-value, e.g., for $c_{3}(v=0)$ of ${}^{15}N_{2}$ in Table 2.3, the most strongly interacting ${}^{1}\Sigma_{u}^{+}$ level lies energetically above the ${}^{1}\Pi_{u}$ level.

Table 2.2: Spectr	roscopic parame	eters for the	${}^{1}\Sigma_{u}^{+}$ states	of ${}^{15}N_2$ and	$^{14}\mathrm{N^{15}N}.$ All values in c	m^{-1} .
Level	B	$D \times 10^6$	$H \times 10^8$	$H' \times 10^{10}$	$\nu_0{}^a$	$J_{\max}{}^{b}$
$b'^{1}\Sigma_{u}^{+}(v=1)$ ¹⁵ N ₂	1.07334(18)	-29(6)			104419.8989(12)	R(8), P(5)
$b'^{1}\Sigma_{u}^{+}(v=3)$ ¹⁵ N ₂	1.0797(4)	21.2(10)			105824.40(3)	R(19), P(17)
$b'^{1}\Sigma_{u}^{+}(v=4)^{c}$ ¹⁵ N ₂	1.1683(21)	-155(22)	122(8)	-16.0(10)	106567.84(6)	R(14), P(21)
$b'^{1}\Sigma_{u}^{+}(v=5)$ ¹⁵ N ₂	1.0870(8)	23.3(84)	3.3(3)		107227.45(4)	R(25), P(27)
$b'^{1}\Sigma_{u}^{+}(v=6)$ ¹⁵ N ₂	1.132(1)	79(6)	6.3(9)		107874.97(4)	R(20), P(18)
$c'_4{}^1\Sigma_u^+(v=0) {}^{15}\mathrm{N}_2$	1.78902(7)	p89			104326.2679(9)	R(3)
$c'_4{}^1\Sigma_u^+(v=1) {}^{15}\mathrm{N}_2$	1.605(2)	19(12)	-122(4)	10.2(3)	106308.01(5)	R(23), P(21)
$b'^{1}\Sigma_{u}^{+}(v=1)$ ¹⁴ N ¹⁵ N	1.1124(3)	-7(7)			104419.009(2)	R(5), P(2)
a Numbers in parentheses	s indicate 1σ fittin	g uncertaintie	s, in units of	the last signific	ant figure. Absolute uncerta	inties in band origins are higher
(see discussion at end of §	Sec. 2.2).					
^b Highest- J'' rotational-b	ranch lines include	ed in fit are in	dicated.			

 c J=21,22,24,26 omitted from fit due to perturbation with $c'_4 \, ^1\Sigma^+_u(v=1)$ and $c_3 \, ^1\Pi_u(v=1)$ states.

 d Fixed at D constant of Yoshino and Tanaka [46].

.2.3) are omitted from nt. 2 10c,101,101 (rotational perturbation, see 5

^d H' = $-1.7(2) \times 10^{-10}$, $q'' = 9.8(1.3) \times 10^{-8}$.

 $^{e}~q^{\prime\prime}=2.3(4)\times10^{-7},~q^{\prime\prime\prime}=-2.6(4)\times10^{-10}.~J=4f,5f,6f$ are blended and omitted from fit.

 $f q'' = -1.56(4) \times 10^{-8}.$

 g $H' = 1.35(17) \times 10^{-10}$, $q'' = 1.55(6) \times 10^{-6}$, $q''' = -1.08(4) \times 10^{-9}$. J = 3-11 for both e and f levels (rotational perturbation, see Sec. 2.5.2.5) omitted from fit.

 $h q'' = -1.10(5) \times 10^{-7}$. Deperturbed (see Sec. 2.5.2.4).

able 2.4: Spectr	oscopic para	meters for t	the Π_u stat	tes of ¹⁴ N ¹	^o N. All val	lues in cm^{-1} .	
Level	B	$D \times 10^6$	$H\times 10^8$	$q \times 10^3$	$q' \times 10^6$	$\nu_0{}^a$	$J_{\max}{}^b$
$b^1 \Pi_u (v=5)$	1.3883(2)	-24.2(3)	2.0(2)	8.6(4)	36.6(15)	104658.273(5)	R(8), Q(20), P(18)
$b^1 \Pi_u (v=6)$	1.3156(3)	9(3)		1.1(2)		105292.5305(7)	R(8), Q(10), P(5)
$b^1 \Pi_u (v = 7)$	1.2960(7)	-24(4)		-0.6(4)		106046.349(4)	R(9), Q(14), P(12)
$c_3{}^1\Pi_u(v=0)$	1.455(2)	-6(8)		-24(2)		104106.370(7)	R(7),Q(2)
^{a} See footnote (a	a) to Table 2.2 .						

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 b See footnote (b) to Table 2.2.



Figure 2.5: Perturbations in the spectroscopic parameters of ${}^{15}N_2$. (a) Reduced band origins for $b {}^1\Pi_u$ state. A linear term in v has been subtracted to emphasize the perturbations. (b) B values for the $b {}^1\Pi_u$ and $c_3 {}^1\Pi_u (v = 0)$ states. (c) D values for the $b {}^1\Pi_u$ state.

2.4 Theory

A theoretical framework within which the perturbations as well as the intensities in the dipole-allowed spectrum of ${}^{14}N_2$ could be explained was published in the seminal paper by Stahel et al. [34]. Vibronic matrix diagonalization and close-coupling methods were applied separately to three ${}^{1}\Sigma_{u}^{+}(b', c'_{4}, c'_{5})$ states and three ${}^{1}\Pi_{u}(b,$ (c_3, o) states in a diabatic representation. A perturbation model was built separately for each symmetry, taking into account the Rydberg-valence interactions. Later on, rotational coupling, i.e. heterogeneous interactions between states of ${}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{u}$ symmetry, were included in extended models by Helm et al. [28], Edwards et al. [35] and Ubachs et al. [37]. These models accounted for J-dependent effects and also the A-doubling in the ${}^{1}\Pi_{u}$ states. In the present study, the procedures of Ref. [37] used for ${}^{14}N_2$ have been applied to the ${}^{15}N_2$ and ${}^{14}N^{15}N$ isotopomers. The same RKR diabatic potentials generated from molecular constants given by Stahel et al. [34] and the same Rydberg-valence coupling strengths have been used, since the diabatic potentials and coupling strengths, of electronic character, can be considered as invariant for different isotopomers. Thus, for each isotopomer and for each rotational quantum number J, coupled equations have been solved simultaneously for six states of both ${}^{1}\Pi_{u}$ and ${}^{1}\Sigma_{u}^{+}$ symmetries, with a centrifugal term added to the diabatic potentials and including only the most important heterogeneous interaction term $-(\hbar^2/\mu R^2)\sqrt{J(J+1)}$ between the c'_4 and c_3 states. Both terms, being mass dependent, clearly vary with the isotopomer under consideration. This calculation provides the term values of the rotational e components of the ${}^{1}\Pi_{u}$ states, the only components affected by the heterogeneous interaction. To obtain the corresponding components of f symmetry, and consequently the Λ -doublings of the ${}^{1}\Pi_{\mu}$ states, a similar calculation has been performed for each J, with the same electronic coupling strengths, but without including the heterogeneous interaction term. The reduced masses used were $\mu(^{15}N_2) = 7.5000544865$ a.m.u. and $\mu(^{14}N^{15}N) = 7.242226813$ a.m.u. [4]. It is worth recalling that, as in Ref. [37], the Fourier grid Hamiltonian method [58], an efficient and accurate method for bound state problems has been applied. The advantage of this method is in providing all the eigen values and the coupled-channels wavefunctions in one single diagonalization of the Hamiltonian matrix expressed in a discrete variable representation. As outlined previously [37], for each energy value indexed by k and given J, the coupled-channels radial wavefunction is given by a six-component vector, each component corresponding to a given electronic diabatic state e $(e = b, c_3, o, b', c'_4, c'_5)$:

$$\chi_k^d(R) = \{\chi_{ek}^d(R), \chi_{e'k}^d(R), \ldots\},$$
(2.5)

The percentage of the electronic character e is obtained directly by:

$$P_e^k = \int_0^\infty |\chi_{ek}^d(R)|^2 dR.$$
 (2.6)


Figure 2.6: Comparison between experimental and calculated rovibronic term values for the ${}^{1}\Pi_{u}(e)$ and ${}^{1}\Sigma_{u}^{+}$ states of ${}^{15}N_{2}$. Solid curves: calculated term values for the ${}^{1}\Pi_{u}(e)$ states. Dashed curves: calculated term values for the ${}^{1}\Sigma_{u}^{+}$ states. Open circles: experimental term values.

The electronic component takes into account not only the bound vibrational states but also the vibrational continuum. The calculation for J = 0 yields the perturbed band origins. In principle, rotational parameters can be derived by fitting the results obtained for a set of *J*-values to a polynomial. This has been done for a number of states during the course of analysis and some of these rotational

Table 2.5: Calculated band origins ν_0 and rotational parameters B ,
obtained from the comprehensive perturbation model, for the singlet
ungerade states of ${}^{15}N_2$. Deviations Δ from the experimental values
are also indicated. All values in $\rm cm^{-1}$.

Level	$ u_0$	Δu_0	B	ΔB
	model	calcobs.	model	calcobs.
$b^1 \Pi_u (v = 0)$	100838.088	-6.641	1.3130	-0.0344
$b^1 \Pi_u (v=1)$	101471.808	14.666	1.2996	-0.0157
$b^1 \Pi_u (v=2)$	102135.720	5.50	1.2885	-0.0105
$b^1 \Pi_u (v=3)$	102815.508	-3.67	1.2862	-0.0066
$b^1 \Pi_u (v=4)$	103483.531	-3.21	1.3158	-0.0047
$b'^1 \Sigma_u^+(v=0)$	103698.483		1.0803	
$c_3{}^1\Pi_u(v=0)$	104075.404	4.058	1.4046	0.0065
$c'_4{}^1\Sigma_u^+(v=0)$	104329.699	3.431	1.7867	-0.0023
$b'^1 \Sigma_u^+ (v=1)$	104416.495	-3.404	1.0741	0.0008
$b^1 \Pi_u (v=5)$	104608.546	-5.956	1.3673	0.0245
$b'^1 \Sigma_u^+ (v=2)$	105127.642		1.0667	
$b^1 \Pi_u (v = 6)$	105234.038	-1.894	1.2643	-0.0042
$o^1 \Pi_u (v = 0)$	105661.170	14.48	1.5738	-0.0084
$b'^1 \Sigma_u^+ (v=3)$	105826.844	2.44	1.0726	-0.0071
$b^1 \Pi_u (v=7)$	105965.810	-14.259	1.2443	-0.0160
$c'_4{}^1\Sigma_u^+(v=1)$	106306.961	-1.05	1.6498	0.045
$c_3{}^1\Pi_u(v=1)$	106456.420	6.08	1.6307	0.0405
$b'^1 \Sigma_u^+ (v = 4)$	106565.300	-2.54	1.1408	-0.0275
$b^1 \Pi_u (v=8)$	106737.598	-27.16	1.2595	-0.0127
$b'^1 \Sigma_u^+ (v=5)$	107230.487	3.04	1.0755	-0.0115
$b^1 \Pi_u (v=9)$	107438.341	-6.78	1.1568	0.0001
$o^1 \Pi_u (v=1)$	107575.750	-2.40	1.5845	-0.0350
$b'^1 \Sigma_u^+ (v = 6)$	107877.546	2.58	1.1291	-0.003
$b^1 \Pi_u (v = 10)$	108157.169		1.1259	
$c'_4{}^1\Sigma_u^+(v=2)$	108381.354		1.3738	
$c_3^{\ 1}\Pi_u(v=2)$	108587.796		1.7210	
$b'^1 \Sigma_u^+(v=7)$	108792.718		1.2197	
$b^1 \Pi_u (v = 11)$	108872.210		1.1060	
$b'^1 \Sigma_u^+(v=8)$	109386.783		1.0674	
$o^1 \Pi_u (v=2)$	109430.677		1.5419	
$b^1 \Pi_u (v = 12)$	109578.467		1.0883	
${b'}^1 \Sigma_u^+ (v=9)$	110032.076		1.0375	
$b^1 \Pi_u (v = 13)$	110255.672		1.0574	
$c'_4{}^1\Sigma_u^+(v=3)$	110486.892		1.6313	
$c_3{}^1\Pi_u(v=3)$	110633.689		1.6700	

Table 2.6: Calculated band origins ν_0 and rotational parameters B, obtained from the comprehensive perturbation model, for the singlet ungerade states of ¹⁴N¹⁵N. Deviations Δ from the experimental values are also indicated. All values in cm⁻¹.

Level	$ u_0$	$\Delta \nu_0$	B	ΔB
	model	calcobs.	model	calcobs.
$b^1 \Pi_u (v = 0)$	100823.749		1.3595	
$b^1 \Pi_u (v=1)$	101469.292		1.3455	
$b^1 \Pi_u (v=2)$	102145.790		1.3339	
$b^1 \Pi_u (v=3)$	102838.068		1.3320	
$b^1 \Pi_u (v=4)$	103516.116		1.3660	
$b'^1 \Sigma_u^+ (v=0)$	103684.821		1.1187	
$c_3{}^1\Pi_u(v=0)$	104111.146	4.776	1.4606	0.006
$c'_4{}^1\Sigma_u^+(v=0)$	104327.640		1.8497	
$b'^1 \Sigma_u^+ (v=1)$	104415.428	-3.581	1.1125	0.0001
$b^1 \Pi_u (v=5)$	104652.988	-5.285	1.4089	0.0206
$b'^1 \Sigma_u^+(v=2)$	105138.809		1.1045	
$b^1 \Pi_u (v=6)$	105292.593	0.063	1.3077	-0.0079
$o^1 \Pi_u (v = 0)$	105670.635		1.6319	
$b'^1 \Sigma_u^+(v=3)$	105849.472		1.1117	
$b^1 \Pi_u (v=7)$	106037.459	-8.890	1.2821	-0.0139
$c'_{4}{}^{1}\Sigma_{u}^{+}(v=1)$	106337.397		1.7002	
$c_3{}^1\Pi_u(v=1)$	106493.141		1.7025	
$b'^1 \Sigma_u^+ (v=4)$	106604.364		1.1859	
$b^1 \Pi_u (v = 8)$	106825.700		1.2812	
$b'^1 \Sigma_u^+ (v=5)$	107279.719		1.1135	
$b^1 \Pi_u (v=9)$	107542.079		1.1941	
$o^1 \Pi_u (v=1)$	107605.417		1.6389	
$b'^1 \Sigma_u^+ (v = 6)$	107939.255		1.1656	
$b^1 \Pi_u (v = 10)$	108271.946		1.1616	
$c'_4{}^1\Sigma_u^+(v=2)$	108457.126		1.4196	
$c_3{}^1\Pi_u(v=2)$	108652.739		1.7804	
$b'^1 \Sigma_u^+ (v = 7)$	108869.575		1.2688	
$b^1 \Pi_u (v = 11)$	108998.444		1.1396	
$b'^1 \Sigma_u^+ (v = 8)$	109469.218		1.1042	
$o^1 \Pi_u (v=2)$	109493.941		1.6056	
$b^1 \Pi_u (v = 12)$	109711.747		1.1102	
$b'^1 \Sigma_u^+ (v=9)$	110121.647		1.0772	
$b^1 \Pi_u (v = 13)$	110399.274		1.0886	
$c'_4{}^1\Sigma_u^+(v=3)$	110574.578		1.6618	
$c_3{}^1\Pi_u(v=3)$	110733.375		1.7331	

parameters are given in Sec. 2.5. However, for the most part, to be consistent with the case of ¹⁴N₂ [34], the model rotational parameter *B* of each state has been calculated as the mean value of the operator $h/8\pi^2 c\mu R^2$ using the channel wavefunction with J = 0. The model band origins and *B*-values for ¹⁵N₂ and ¹⁴N¹⁵N, listed in Tables 2.5 and 2.6, respectively, are found to be in fairly good agreement with experiment, with deviations of the same order as found in the case of ¹⁴N₂ [34]. The model rotational term values for ¹⁵N₂ (curves) are compared in Fig. 2.6 with our experimental values (open circles). Inspection of Fig. 2.6 reveals the most prominent local interactions. Besides the well-known rotationally-dependent interaction between $c'_4(0)$ and b'(1) [46, 52, 59], avoided crossings clearly occur between o(0) and b(7), between o(0) and b'(3), between $c_3(1)$ and b(8), and between b'(4) and $c'_4(1)$.

2.5 Discussion

2.5.1 Isotope shifts

The vibrational isotope shifts for ¹⁵N₂ and ¹⁴N¹⁵N are defined as the band origin in ¹⁴N₂ minus the band origin in ¹⁵N₂ or ¹⁴N¹⁵N, respectively. Isotope shifts derived from the present experimental measurements for the ¹ Σ_u^+ and ¹ Π_u states are listed in Tables 2.7 and 2.8. In determining the isotope shifts, the band origins of ¹⁴N₂ were taken from Ref. [59] for $b'^1\Sigma_u^+(v=1)$ and $c'_4{}^1\Sigma_u^+(v=0)$, Ref. [60] for $b'^1\Sigma_u^+(v=3-6)$ and $c'_4{}^1\Sigma_u^+(v=1)$, Ref. [61] for $b^1\Pi_u(v=0)$, Ref. [62] for $b^1\Pi_u(v=1)$, Ref. [33] for $b^1\Pi_u(v=2-5,9)$, Ref. [49] for $b^1\Pi_u(v=6-8)$ and $o^1\Pi_u(v=1)$, Ref. [59] for $c_3{}^1\Pi_u(v=0)$, Ref. [34] for $c_3{}^1\Pi_u(v=1)$, and Ref. [44] for $o^1\Pi_u(v=1)$. The band origins taken from some of these works [33, 34, 44, 49, 59] have been corrected to account for the different energy representation used previously.

In Tables 2.7 and 2.8, the isotope shifts are compared with literature values, and with values calculated using the perturbation model discussed in Sec. 2.4. The isotope shift of the corresponding band origin is negative for the $b^1\Pi_u(v=0-1)$ levels because the isotope shift of the ground state $X^1\Sigma_g^+(v=0, J=0)$ is larger than that of the excited states.

Reduced experimental ${}^{14}N_2 - {}^{15}N_2$ isotope shifts for vibrational levels of the $b^1\Pi_u$ valence state, plotted in Fig. 2.7, are irregular, deviating from the smooth vibrational dependence expected for an unperturbed state. The experimental isotope-shift perturbations are in excellent agreement with our model calculations, which are also shown in Fig. 2.7 (note that the small systematic difference between the vibrational dependences of the experimental and computed isotope shifts has been removed to facilitate this comparison of the perturbation behavior). The isotope-shift perturbations become more noticeable for $v \geq 4$, where small shifts for the low-v levels of the c_3 Rydberg state, together with larger shifts for the higher-v

Table 2.7: Isotope shifts of band origins for the ${}^{1}\Sigma_{u}^{+}$ states (see text for ${}^{14}N_{2}$ references). Observed shifts are compared with literature data and with the comprehensive perturbation model calculations. All values in cm⁻¹.

Level	$^{15}N_2$	${}^{15}N_{2}$	$^{15}N_2$	${ m ^{14}N^{15}N}$	${ m ^{14}N^{15}N}$	${}^{14}\mathrm{N}{}^{15}\mathrm{N}$
	obs.	previous	model	obs.	previous	model
$b'^1 \Sigma_u^+ (v=1)$	-1.99	-1.0 [47]	-2.03	-1.10	-0.8 [46]	-1.00
		-2.0 [46]				
		-0.3 [42]				
$b'^{1}\Sigma_{u}^{+}(v=3)$	44.8	44.2 [47]	44.90			22.24
$b'^1 \Sigma_u^+ (v = 4)$	79.1	$79.9 \ [47]$	77.69			38.59
		80.2 [42]				
$b'^1 \Sigma_u^+ (v=5)$	99.3	89.2 [47]	97.82			48.56
		100.3 [42]				
$b'^1 \Sigma_u^+ (v = 6)$	124.3	123.8 [47]	122.65			60.90
		129.3 [42]				
$c'_4{}^1\Sigma_u^+(v=0)$	-3.36	-3.4 [47]	-4.01		-1.7 [46]	-1.99
		-3.5[46]				
$c'_4{}^1\Sigma_u^+(v=1)$	61.5	69.0[47]	60.49			30.02
		62.4 [42]				

levels of the b state, result in differential effects which influence the pattern of Rydberg-valence energy degeneracies and consequent perturbation behavior.

Isotope shifts for the Rydberg ${}^{1}\Pi_{u}$ states are also significantly perturbed, particularly for the v = 0 levels. An inspection of Table 2.8 shows ${}^{14}N_2 - {}^{15}N_2$ isotope shifts of 68.64 cm⁻¹ and 37.96 cm⁻¹, respectively, for $c_3(0)$ and o(0), much higher than the near-zero value expected for an unperturbed v = 0 level. The positive perturbations observed in the low-v Rydberg isotope shifts contrast with the predominantly negative perturbations found for the $b{}^{1}\Pi_{u}$ valence levels of higher v, supporting the mutual Rydberg-valence nature of these perturbations.

2.5.2 The ${}^{1}\Pi_{u}$ levels of ${}^{15}N_{2}$

The ${}^{1}\Pi_{u}$ states of ${}^{15}N_{2}$ undergo strong homogeneous interactions with each other and strong heterogeneous interactions with states of ${}^{1}\Sigma_{u}^{+}$ symmetry. For most ${}^{1}\Pi_{u}$ levels of ${}^{15}N_{2}$, the perturbations are due to interactions with several other states and/or levels. Some distinction can be made between the strong vibronic interactions that cause entire rotational manifolds to be shifted by several hundreds of cm⁻¹, such as the interaction between $c_{3}{}^{1}\Pi_{u}(v=0)$ and the $b^{1}\Pi_{u}$ levels, but

Table 2.8: Isotope shifts of band origins for the ${}^{1}\Pi_{u}$ states (see text for
$^{14}\mathrm{N}_2$ references). Observed shifts are compared with literature data
and with the comprehensive perturbation model calculations. All val-
ues in cm^{-1} .

Level	$^{15}N_2$	${}^{15}N_{2}$	$^{15}N_2$	${}^{14}\mathrm{N}{}^{15}\mathrm{N}$	${}^{14}\mathrm{N}{}^{15}\mathrm{N}$
	obs.	previous	model	obs.	model
$b^1 \Pi_u (v=0)$	-26.466	-24.8 [42]	-28.35	-13.34 [61]	-14.04
$b^1 \Pi_u (v=1)$	-4.140	-4.3 [42]	-4.88	-1.95 [61]	-2.40
$b^1 \Pi_u (v=2)$	22.9	15.7 [42]	20.09		9.99
$b^1 \Pi_u (v=3)$	45.8	$39 \ [42]$	44.84		22.24
$b^1 \Pi_u (v=4)$	63.5	66.1 [42]	64.49		31.87
$b^1 \Pi_u (v=5)$	87.1	89.3 [42]	88.22	43.4	43.74
$b^1 \Pi_u (v=6)$	111.45	$106.1 \ [42]$	115.04	54.85	56.45
$b^1 \Pi_u (v=7)$	130.90	$137.4 \ [42]$	141.88	64.62	70.20
$b^1\Pi_u(v=8)$	169.62	178 [32]	175.71		87.58
$b^1 \Pi_u (v=9)$	199.6	$182.6 \ [42]$	209.70		105.93
$c_3{}^1\Pi_u(v=0)$	68.64	68.5 [42]	70.36	33.62	34.58
$c_3{}^1\Pi_u(v=1)$	79.2	79.7 [42]	73.44		36.68
$o^1 \Pi_u (v = 0)$	37.96	49.7 [42]	19.25	$17.2 \ [44]$	9.75
		$37.8 \ [44]$			
$o^1 \Pi_u (v = 1)$	61.1	$70.6 \ [42]$	54.72	41.9 [44]	25.02
		42.7 [44]			

there are also somewhat weaker interactions that give rise to local perturbations near crossing points. These points can be identified from the plot of term values in Fig. 2.6. In the following sections, these interactions are discussed for several groups of levels.

2.5.2.1 $b^1 \Pi_u (v = 0)$

As observed in the case of ¹⁴N₂ [33, 61], even allowing for considerable experimental uncertainty due to the low range of J values accessed, our D value for ¹⁵N₂ is significantly higher than those observed for b(v = 1, 2). Contrary to the suggestion of Carroll and Collins [33] that this effect is due to a strong perturbation of b(v = 0)by an undetermined state, our calculations support the view that the high D value is a property of the uncoupled *b*-state potential-energy curve, which has an unusual shape due to a configurational change near its minimum (see Fig. 2.1) [39].



Figure 2.7: Perturbations in the ${}^{14}N_2 - {}^{15}N_2$ isotopic shifts for the $b {}^1\Pi_u$ state. Solid circles: Experimental. Open circles joined by solid lines: Model calculations. To facilitate presentation of the perturbations, the experimental and computed isotope shifts have been reduced by the subtraction of separate linear terms in v.

2.5.2.2 $b^1 \Pi_u (v = 1 - 3)$

There is no significant perturbation visible in the rotational structure of the b - X(1-3,0) bands. For example, the $b^1\Pi_u(v=1)$ level, which has been found to be well described by an unperturbed rotational progression for ${}^{14}N_2$ by Ubachs *et al.* [61], behaves similarly in the case of ${}^{15}N_2$, as shown in Table 2.1. However, a global perturbation by the higher-lying $c_3 {}^1\Pi_u$ state causes an overall shift of these *b*-state levels downwards by about 200 cm⁻¹. This shift, however, has little effect on the rotational structure which can still be described using only two rotational parameters. According to Ref. [61], rotational levels of the ${}^{14}N_2 \ b^1\Pi_u(v=3)$ state are diffuse and broadened due to the short lifetime of this level. As has been found elsewhere by Robbe [63], the broadening of this level in ${}^{15}N_2$ is much smaller than in ${}^{14}N_2$. The isotope-dependent lifetimes and predissociative behavior of the ${}^1\Pi_u$

2.5.2.3 $b^1 \Pi_u (v = 4 - 5)$ and $c_3^1 \Pi_u (v = 0)$

The $b^1\Pi_u(v=4-5)$ valence-state levels interact strongly with the $c_3{}^1\Pi_u(v=0)$ Rydberg level which lies between them. This homogeneous interaction pushes the b(4 and 5) levels downwards and upwards in energy, respectively, perturbing the corresponding origins as shown in Fig. 2.5(a). The perturbation model predicts for the b(4), b(5) and $c_3(0)$ states level shifts of -157.96 cm^{-1} , $+224.00 \text{ cm}^{-1}$ and -187.42 cm^{-1} , respectively, relative to their unperturbed positions (diabatic term values). The effects of the severe Rydberg-valence mixing are particularly noticeable in the *B* values, which are fairly similar for all three levels, as shown in Fig. 2.5(b) and as illustrated by the near-parallel term-value plots in Fig. 2.6. In the absence of an interaction, the *B* value for $c_3(0)$ predicted by the diabatic model is much higher: 1.8277 cm⁻¹, characteristic of a v = 0 member of a Rydberg series converging on the ground state of the ion, while the predicted *B* values for b(4) and b(5) are much smaller: 1.2278 cm⁻¹ and 1.2100 cm⁻¹, respectively. Furthermore, the same interaction is responsible for the widely differing *D* values for b(4), which is significantly larger than expected for an unperturbed level, and for b(5), which is of even greater magnitude and *negative*, as shown in Fig. 2.5(c).

There is also significant Λ -doubling in this region, which indicates heterogeneous interaction with ${}^{1}\Sigma_{\mu}^{+}$ states. First, the $b'{}^{1}\Sigma_{\mu}^{+}(v=0)$ state lies just above b(4), shifting its e levels to lower energies, increasingly as J increases, while leaving the flevels unaffected, and resulting in a negative q value for b(4). Second, as in ¹⁴N₂ [33], the b(5) and $c_3(0)$ states have relatively strong heterogeneous interactions with the $c'_4(0)$ and b'(1) states, which lie between them. The result is that the e levels of the b(5) state are pushed upwards in energy and those of the $c_3(0)$ state are shifted downwards. Therefore, the Λ -doubling parameter q is negative for $c_3(0)$ and positive for b(5), with almost the same magnitude. Fits of calculated rotational term values to Eqs. (2.2), (2.3) and (2.4), with the same numbers of J levels and parameters as in the experimental fits, lead to the following results for the B, D and q parameters: (1) b(4): $B = 1.3143 \text{ cm}^{-1}$, $D = 35.7 \times 10^{-6} \text{ cm}^{-1}$ and $q = -1.94 \times 10^{-3} \text{ cm}^{-1}$. (2) b(5): $B = 1.3674 \text{ cm}^{-1}$, $D = -40.0 \times 10^{-6} \text{ cm}^{-1}$ and $q = 11.5 \times 10^{-3} \text{ cm}^{-1}$. (3) $c_3(0)$: $B = 1.4056 \text{ cm}^{-1}$, $D = 54.04 \times 10^{-6} \text{ cm}^{-1}$ and $q = -14.75 \times 10^{-3} \text{ cm}^{-1}$. Overall, these parameters are in reasonably good agreement with those obtained from the experimental fits, given in Table 2.3.

Finally, we note that we have observed new, weak local perturbations and extra lines in spectra of the b - X(4, 0) band for both ${}^{15}N_2$ and ${}^{14}N_2$. These perturbations occur in both the P and R branches [e levels of b(4)] and in the Q branch (f levels), most prominently in the J = 15e region for ${}^{15}N_2$ and at J = 18e for ${}^{14}N_2$. The latter perturbation has also been observed in synchrotron-based photoabsorption spectra by Stark [64]. There is no known singlet state of N₂ energetically located so as to be able to cause these local perturbations, which will be assigned and analyzed elsewhere.

2.5.2.4 $b^1 \Pi_u (v = 6 - 7)$ and $o^1 \Pi_u (v = 0)$

The $b^1 \Pi_u (v = 6 \text{ and } 7)$ valence levels interact with the $o^1 \Pi_u (v = 0)$ Rydberg level. As already mentioned by Yoshino *et al.* [44], the interactions in ${}^{14}N_2$ of o(0) with b(6 and 7) are equally strong, but opposite in sign. In contrast, in ${}^{15}N_2$ the b(7) level lies closer to o(0) than does b(6) [44], resulting in much stronger interaction between b(7) and o(0) than between b(6) and o(0). A plot of the experimental term values in the b(7) - o(0) region, shown in Fig. 2.8, demonstrates the effects of the avoided crossing between these two levels as the o(0) Rydberg level approaches the b(7) valence level from below with increasing J, including a tendency towards the two term series becoming parallel as the mixing increases. In fact, at J values higher than those in the avoided-crossing region (J > 25, according to the perturbation model) the upper term series, labeled b(7) in Fig. 2.8, has predominantly Rydberg character, while the lower has predominantly valence character. The same interaction is responsible for the negative D value for b(7), the large D value for o(0), and the need for a cubic polynomial to accurately represent the b(7) rotational terms (see Table 2.3).



Figure 2.8: Experimental rotational term values for the $o \, {}^{1}\Pi_{u}(v = 0)$, $b \, {}^{1}\Pi_{u}(v = 7)$, and $b' \, {}^{1}\Sigma_{u}^{+}(v = 3)$ states of ${}^{15}N_{2}$. Solid curves: ${}^{1}\Pi_{u}(e)$ levels. Solid circles: ${}^{1}\Pi_{u}(f)$ levels. Dashed curves: ${}^{1}\Sigma_{u}^{+}$ (e levels only). A strongly-avoided Rydberg-valence crossing occurs between the o(0) and b(7) levels.

While the Λ -doubling in b(7) is small and regular, the heterogeneous interaction between $o^1 \Pi_u(v=0)$ and $b' \, {}^1\Sigma_u^+(v=3)$, whose term series crosses that of o(0) from



Figure 2.9: Reduced term values in the region of the o(0)-b'(3) crossing [Solid circles: o(0, e). Open circles: o(0, f). Solid triangles: b'(3) (e levels only.)], including the results of an effective two-level deperturbation of the e-level interaction [Solid line: o(0). Dashed line: b'(3).]. A quadratic in J(J+1) has been subtracted from all terms so that the deperturbed o(0, e) levels lie on the zero line.

above, near J = 19, results in significant perturbation of the *e* levels of o(0), leaving the *f* levels untouched, as illustrated in Fig. 2.9, where we have also shown the results of a local two-level deperturbation of the *e*-level crossing region. Although the experimental data are insufficient to allow one to distinguish between a homogeneous or heterogeneous perturbation, we can safely assume that this ${}^{1}\Sigma_{0} - {}^{1}\Pi_{1}$ interaction is heterogeneous, in which case the deperturbation implies an effective two-level interaction matrix element $H_{12} = -0.21\sqrt{J(J+1)}$ cm⁻¹.

It is well known that it is hazardous to rely on intensities in ionization spectra as indicators of photoabsorption intensities. However, even with this proviso, our spectra indicate an interesting anomaly in the *R*-branch intensities associated with the o(0)-b'(3) crossing region: *R*-branch lines in b'-X(3,0) are excessively weak for excited-state *J* values immediately below the crossing region, and are abnormally strong for *J* values immediately above the crossing region. It is likely that this is an example of the well-known P - R intensity anomalies caused by quantum interference between the amplitudes for dipole-allowed transitions into coupled ${}^{1}\Sigma$ and ${}^{1}\Pi$ states, as discussed, e.g., by Lefebvre-Brion and Field [57]. Unfortunately, however, due to limitations in the spectra, we are unable to confirm the opposite



Figure 2.10: Experimental rotational term values for the $c_3 {}^1\Pi_u(v=1)$ and $b {}^1\Pi_u(v=8)$ states, and the $c'_4 {}^1\Sigma^+_u(v=1)$ and $b' {}^1\Sigma^+_u(v=4)$ states of ${}^{15}N_2$. Solid curves: ${}^1\Pi_u(e)$ levels. Solid circles: ${}^1\Pi_u(f)$ levels. Dashed curves: ${}^1\Sigma^+_u(e)$ levels only). Strongly-avoided Rydberg-valence crossings occur for each symmetry.

intensity behavior expected in the b' - X(3,0) P branch, and the opposite P - R behavior expected in the o - X(0,0) band crossing region.

We note also that we have observed new, weak local perturbations in o(0), specifically in the J = 3e - 4e region, and also in the J = 10 - 14 region for both the *e* and *f* levels. These regions were either deperturbed or excluded from the corresponding spectroscopic-parameter fits in Table 2.3. As in the case of b(4), we will consider these particular perturbations elsewhere.

2.5.2.5 $b^1 \Pi_u(v=8)$ and $c_3^1 \Pi_u(v=1)$

Experimental rotational terms for the $b(8) - c_3(1)$ region are shown in Fig. 2.10. The $b^1\Pi_u(v=8)$ valence level is perturbed from below by the $c_3{}^1\Pi_u(v=1)$ Rydberg level, a strongly-avoided crossing between these two levels occurring near J = 19 with $H_{12} = 126 \text{ cm}^{-1}$. As in the case of the $b(5) - c_3(0)$ interaction, significant perturbations occur in the *B* values for these levels, the *D* value for the lower level $c_3(1)$ is elevated, the *D* value for the upper level b(8) is large and negative, and additional polynomial terms are required to reproduce the experimental term values. Also shown in Fig. 2.10 are experimental terms for the $b'{}^{1}\Sigma_{u}^{+}(v=4)$ valence level and the $c'_{4}{}^{1}\Sigma_{u}^{+}(v=1)$ Rydberg level which play secondary roles in perturbing



Figure 2.11: Observed A-doubling in the $b^{1}\Pi_{u}(v = 8)$ valence and $c_{3}{}^{1}\Pi_{u}(v = 1)$ Rydberg states.

these ${}^{1}\Pi_{u}$ states. These ${}^{1}\Sigma_{u}^{+}$ levels themselves exhibit a strong mutual homogeneous interaction, resulting in an avoided crossing near J = 16 with $H_{12} = 94$ cm⁻¹, as is clear from Fig. 2.10.

In ¹⁴N₂, the Λ -doubling in the $c_3(1)$ state has been attributed to an interaction with the b'(4) state [65]. The experimental Λ -doubling in the $c_3(1)$ and b(8) states of ¹⁵N₂, shown in Fig. 2.11, is significant, displaying a degree of complexity well beyond the usual linear dependence on J(J+1). In the case of the b(8) level (solid circles in Fig. 2.11), the Λ -doubling is primarily caused by heterogeneous interactions with the lower-lying $c'_4(1)$ and b'(4) states, the b(8, e) levels being perturbed upwards with a greater than linear dependence on J(J+1). The Λ -doubling in the $c_3(1)$ level (open circles in Fig. 2.11) shows clear evidence of being affected by the Rydbergvalence interaction between the $b'^1 \Sigma_u^+(v=4)$ valence and $c'_4 \Sigma_u^+(v=1)$ Rydberg states which lie above and below $c_3(1)$, respectively, post interaction (see Fig. 2.10), producing perturbations in the $c_3(1, e)$ levels of opposite signs. For very low J values, the $c_3(1, e)$ levels are predominantly perturbed upwards, due to the strong rotational interaction with the $c'_4(1)$ state which is a member of the same p complex [57], despite its lying further away from $c_3(1)$ than does b'(4). On the other hand, for higher J, as the valence level b'(4) approaches the Rydberg level $c_3(1)$ more closely, the predominant effect becomes a downward perturbation of the $c_3(1, e)$ levels by b'(4), this effect maximizing near J = 19, corresponding to the region of closest approach of the $c_3(1)$ and b'(4) levels, which do not cross because of the strongly-



Figure 2.12: 1 XUV + 1 UV ionization spectrum of the ${}^{15}N_2 \ b^1\Pi_u - X^1\Sigma_g^+$ (8,0) band, recorded with PDL-based XUV source. Note that the R(0) and P(2) lines were not observed. Lines marked with * are from the $b' \,{}^1\Sigma_u^+ - X \,{}^1\Sigma_g^+(5,0)$ band: P(22), R(25), P(25), and P(27), respectively, in order of decreasing energy. Note the AC-Stark-induced asymmetry in the spectral lines.

avoided crossings in both the ${}^{1}\Pi_{u}$ and ${}^{1}\Sigma_{u}^{+}$ levels.

We note in passing that the slightly scattered points in Fig. 2.11 at low-J values for the $c_3(1)$ state result from further weak local perturbations. There appear to be three perturbations in the range J < 12, in both the e and f levels, similar to one of the groups of perturbations observed for o(0) and mentioned in Sec. 2.5.2.4. These perturbations will be analyzed further elsewhere.

There is also a perturbation visible in the intensity distribution of the b-X(8,0)band, the spectrum of which is shown in Fig. 2.12. Rotational lines for all branches exciting low-J levels are significantly less intense than rotational lines to higher-Jlevels, an effect unrelated to laser power levels. This perturbation in intensity occurs due to a destructive quantum-interference effect between the ${}^{1}\Pi_{u}$ Rydberg and valence transition amplitudes. Vibrational intensity anomalies observed in the b-Xsystem of ${}^{14}N_{2}$ [66], including an intensity minimum for the (8,0) band, are known to result from these Rydberg-valence interactions, having been treated successfully semi-empirically by Stahel *et al.* [34], and by Spelsberg and Meyer using *ab initio* methods [39]. These interference effects have a strong rotational dependence: in the the case of ${}^{14}N_{2}$, Carroll and Collins [33] note that the intensities of lines in the (8,0) band with intermediate J drop markedly before increasing again at higher J; in the present case of ${}^{15}N_{2}$, evidently the destructive interference effect maximizes at low J. We have found this observed isotopic and J dependence to be qualitatively consistent with predictions based on the ${}^{1}\Pi_{u}$ Rydberg-valence interaction model of Spelsberg and Meyer [39]. The alternative explanation of our observations for ${}^{15}N_{2}$, namely that the low-J levels of b(8) are heavily predissociated due to an accidental perturbation by a short-lived level of another electronic state, is unlikely since no detectable broadening is observed. Furthermore, we know of no such level near the energy of the b(8) bandhead.

2.5.2.6 $b^1 \Pi_u(v=9)$ and $o^1 \Pi_u(v=1)$

In ¹⁴N₂, the rotationless o(1) Rydberg level lies slightly below the b(9) valence level, the higher Rydberg *B* value and homogeneous Rydberg-valence interaction resulting in a weakly-avoided crossing ($H_{12} = 8.1 \text{ cm}^{-1}$) in the corresponding rotational term series [44]. In ¹⁵N₂, the order of these levels is reversed and their energy separation is increased substantially, as illustrated in Fig. 2.6. As a result, their degree of mutual perturbation decreases significantly and they can, in effect, be regarded as independent levels.

For example, the b(9) level is very well behaved, with no local perturbations evident in its rotational structure, a *B* value appropriate to an unperturbed valence state, a very small *D* value, no additional polynomial terms necessary to describe its rotational energies, and negligible Λ -doubling. Similar comments apply to the o(1) level, where the *B* value is typical of an unperturbed Rydberg state, with the exception of a detectable amount of Λ -doubling (q < 0), likely caused by heterogeneous interaction with the higher-lying $b'^{1}\Sigma_{u}^{+}(v = 6)$ valence level which has a smaller *B* value.

2.5.3 The ${}^{1}\Pi_{u}$ states of ${}^{14}N^{15}N$

Practical considerations limit the amount of data obtainable for the mixed isotopomer. For the few ${}^{1}\Pi_{u}$ states of ${}^{14}N^{15}N$ studied, the derived spectroscopic parameters in Table 2.4 show the same general behavior as found for ${}^{14}N_{2}$ and ${}^{15}N_{2}$. For example, the $b{}^{1}\Pi_{u}(v = 5)$ and $c_{3}{}^{1}\Pi_{u}(v = 0)$ states exhibit a strong homogeneous interaction, and a large, negative D value is found for b(5). A-doubling is also present in these states, which can be explained in the same way as for ${}^{14}N_{2}$ and ${}^{15}N_{2}$.

2.5.4 The ${}^{1}\Sigma_{u}^{+}$ states of ${}^{15}N_{2}$ and ${}^{14}N^{15}N_{2}$

The $b'^{1}\Sigma_{u}^{+}(v=1)$ states in both ${}^{15}N_{2}$ and ${}^{14}N^{15}N$ suffer local perturbation by the $c'_{4}{}^{1}\Sigma_{u}^{+}(v=0)$ state. The homogeneous interaction between these two levels has already been examined for ${}^{14}N_{2}$, in high resolution, by the Amsterdam group [52, 59] and by Yoshino *et al.* [46] for the various isotopomers. Narrow spectral lines with the ultra-high resolution system could only be recorded for the lowest J values in these two levels, not reaching the avoided-crossing region. Since the lower-resolution data, recorded with the PDL for b'(1) and higher J levels of $c'_4(0)$, are not more accurate than those of Ref. [46], no attempt was made at an improved analysis of the avoided-crossing region.

Interactions involving several of the higher vibrational levels of the $b'^1 \Sigma_u^+$ and $c'_4{}^1 \Sigma_u^+$ states have been discussed in Sec. 2.5.2. Overall, the *B* values for $b'^1 \Sigma_u^+$ increase with *v*, contrary to the behavior expected for a normal, unperturbed state. Mixing with the Rydberg state $c'_4{}^1 \Sigma_u^+$ is responsible for this behavior.

2.6 Conclusions

An XUV-laser-spectroscopic study of the ${}^{1}\Pi_{u}$ and ${}^{1}\Sigma_{u}^{+}$ states of the isotopomers ${}^{15}N_{2}$ and ${}^{14}N^{15}N$ has been performed. New data on 26 absorption bands have been obtained with the highest resolving power and precision achievable using presentday XUV-laser technology. New molecular spectroscopic parameters and precise isotope shifts have been determined, which will help to inform future models of the molecular structure, interactions, and dynamics of N₂.

While the overall pattern of strong Rydberg-valence perturbations in the ${}^{1}\Pi_{u}$ and ${}^{1}\Sigma_{u}^{+}$ states, together with rotational coupling between the ${}^{1}\Pi_{u}$ and ${}^{1}\Sigma_{u}^{+}$ manifolds, is found to be similar in ${}^{15}N_{2}$ to that known previously for ${}^{14}N_{2}$, there are many significantly isotope-dependent aspects. With the aid of a comprehensive perturbation model, which is based on parameters used previously for ${}^{14}N_{2}$ and includes Rydberg-valence interactions and rotational coupling simultaneously, we have found that the present experimental results for ${}^{15}N_{2}$ can be reproduced to a similar level of accuracy as achieved for ${}^{14}N_{2}$.

In a future publication, experimental studies of the lifetimes of the ${}^{1}\Pi_{u}$ states of the different isotopomers of N₂ will be presented, providing insight into the isotope dependence of the predissociation behavior for these states. In a further study, the singlet-triplet interactions which are responsible for the several weak local perturbations seen here for the first time in ${}^{15}N_2$, and which have not been reported previously in ${}^{14}N_2$, will be discussed.

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Chapter 3

Lifetime and predissociation yield of ${}^{14}N_2$ $b \ {}^{1}\Pi_u(v=1)$

The lifetime of the $b \ ^1\Pi_u(v=1)$ state in $^{14}N_2$ has been determined experimentally using a laser-based pump-probe scheme and an exceptionally long lifetime of 2.61 ns was found. Semiempirical close-coupling calculations of the radiative lifetime, which include Rydberg-valence interactions in the singlet manifold, are consistent with this large value, giving a value of 3.61 ns and suggesting a predissociation yield of ~ 28% for this level of the *b* state.

3.1 Introduction

The dipole-allowed absorption spectrum of molecular nitrogen sets in at wavelengths $\lambda < 100$ nm and is governed by transitions from the ground state $X^{-1}\Sigma_g^+$ to two valence states, $b'^{-1}\Sigma_u^+$ and $b^{-1}\Pi_u$, two *np*-Rydberg series $c'_{n+1}^{--1}\Sigma_u^+$ and $c_n^{--1}\Pi_u$, converging on the ionic ground state, and an *ns*-Rydberg series $o_n^{--1}\Pi_u$, converging on the first-excited ionic state. The combined effect of these mutually interacting states is to shield the Earth's atmosphere below 100 km from hazardous extreme ultraviolet (XUV) radiation. Knowledge of the competition between the N₂ deexcitation processes of fluorescence and predissociation, obtained from electron-impact [66, 67, 68] or photoexcitation experiments (see below) is of great practical importance in view of the roles of these processes in atmospheric radiative transport [1] and ionospheric chemistry.

Furthermore, studies of the spectroscopy and decay dynamics of N₂ states in the XUV are important in providing advances in our understanding of fundamental molecular problems. In particular, the ${}^{1}\Pi_{u}$ symmetry states of N₂ present a textbook example of Rydberg-valence and Rydberg-Rydberg interactions, widely discussed previously for the main isotopomer ${}^{14}N_{2}$ in Refs. [31, 32, 33, 34, 57]. The dipole-allowed spectrum of ${}^{14}N_2$ has been extensively studied, but there are sufficient outstanding problems, e.g., the determination of absolute oscillator strengths, for such studies to be ongoing [64]. Dipole-allowed ionization spectra for the isotopomers ${}^{15}N_2$ and, to a lesser extent, ${}^{14}N^{15}N$ have also been studied recently by Sprengers *et al.* [69].

An understanding of the predissociation mechanisms for the ${}^{1}\Pi_{u}$ (and ${}^{1}\Sigma_{u}^{+}$) states remains one of the major outstanding problems in N₂ structure and dynamics. While it is likely that the ultimate dissociation channel is a ${}^{3}\Pi_{u}$ continuum, despite attempts over many years to establish these mechanisms, no quantitative predissociation model exists to explain the seemingly erratic dependence of ${}^{1}\Pi_{u}$ predissociation rates on the vibrational quantum number, in particular, for the $b {}^{1}\Pi_{u}$ valence state. The development of such a model requires, not only an improved theoretical understanding of the interactions between the ${}^{1}\Pi_{u}$ states of N₂ (Rydberg-valence, Rydberg-Rydberg, and valence-valence), but also a reliable experimental database for all isotopomers. Considering the wide range of applicable predissociation rates, such a database would benefit from direct (Doppler-free) line-width measurements, for the broader levels, and direct lifetime measurements, for the narrow $b {}^{1}\Pi_{u}(v = 1)$ state in ${}^{14}N_{2}$.

Several experimental studies have been performed on line widths and lifetimes of the ${}^{1}\Pi_{\mu}$ states, but the picture is presently incomplete and there are many inconsistencies in the results. Line widths for the lower-energy ${}^{1}\Pi_{u}$ states, including the low-v levels of the b state, were determined by Leoni and Dressler [70] who analyzed photoelectric scans of the absorption bands taken at many pressures. Predissociation lifetimes for excited states of ${}^{1}\Pi_{u}$ symmetry were determined by Ubachs and coworkers [49, 52, 61, 62] using narrowband XUV-laser excitation, while Kawamoto et al. [65] studied predissociation of the $c_3(v=1)$ level using near-infrared excitation from the long-lived $a'' \, {}^{1}\Sigma_{a}^{+}$ metastable state. Helm, Cosby and coworkers determined dissociation quantum yields of somewhat higher-lying vibronic states of ${}^{1}\Pi_{u}$ symmetry using laser-induced photofragment spectroscopy, after population of the metastable state via charge exchange [6, 28, 36, 71, 72]. Buijsse and Van der Zande also used the photo-fragment technique [73], as well as the Hanle effect [74], to investigate in detail rotational-state effects in the predissociation of the $e^{-1}\Pi_u(v=0)$ state, which is also known as $c_4^{-1}\Pi_u(v=0)$. Direct time-domain lifetime measurements of N_2 excited states have also been performed using short pulses from a synchrotron source; lifetimes of $o_3(v=2)$ and b(v=0-1) were determined [75].

From an atmospheric perspective, there are two vibronic states that behave differently from all the others. Both the $c'_4 \, {}^1\Sigma^+_u(v=0)$ and $b \, {}^1\Pi_u(v=1)$ states predissociate only to a minor extent, and XUV radiation is redistributed and scattered after excitation of these states. While the $c'_4 \, {}^1\Sigma^+_u(v=0)$ Rydberg state radiates 90% back to the $X \, {}^1\Sigma^+_g(v=0)$ ground state, absorption into the $b \, {}^1\Pi_u(v=1)$ valence state induces fluorescence that is shifted to longer wavelengths. Accurate measurements of these lifetimes may help to elucidate the competition between predissociation and radiation in N_2 in the Earth's atmosphere.

In the present study, a picosecond laser system is used in a pump-probe configuration to study the lifetime of the $b \ {}^{1}\Pi_{u}(v=1)$ level in ${}^{14}N_{2}$. This study follows previous work [37] on lifetime measurements for the $c'_{4} \ {}^{1}\Sigma^{+}_{u}(v=0-2)$ states of ${}^{14}N_{2}$ and is part of a collaborative experimental and theoretical program intended to unravel the Rydberg-valence and singlet-triplet interactions of N₂ in the 100 000– 110 000 cm⁻¹ region. A theoretical model, based on Rydberg-valence interaction, is used to provide an explanation for the exceptionally long b(v=1) lifetime found experimentally.

3.2 Experimental method and data analysis

A detailed description of the picosecond XUV-radiation source, the pump-probe 1XUV + 1UV two-photon ionization scheme for direct time-domain measurements of excited-state lifetimes, and its application to excited states in N_2 , has been given previously [37]. Briefly, the infrared (IR) output of a distributed-feedback dye laser (DFDL), pumped by the frequency doubled output of a mode-locked Nd:YAG laser, was amplified in a titanium-sapphire crystal and frequency doubled to the ultraviolet (UV) in a KD*P crystal. Higher harmonic generation was then achieved by focusing the UV beam and the remaining IR beam into a pulsed krypton jet. To reach the desired wavelength, the 8th harmonic of the IR beam was produced by wave-mixing IR and UV photons; one of the processes yielding the 8th harmonic is: $\nu_{\rm XUV} = 3\nu_{\rm UV} + 2\nu_{\rm IR}$. The 8th harmonic was selected by a spherical grating, sent to the interaction region, refocused and crossed with a pulsed N_2 beam. The output of the DFDL was tuned by varying the temperature of the dye solution, allowing the XUV to be scanned over an absorption in N_2 . The XUV pump photon excited the molecules from the ground state to the excited state under investigation, while a delayable probe beam, the frequency tripled 355-nm output of the same mode-locked Nd:YAG laser, was focused into the interaction region, ionizing the excited N_2 molecules. The resulting ions were accelerated by an electric field, passed through a time-of-flight (TOF) analyzer, and detected by an electron multiplier. Lifetime measurements were performed by temporally delaying the UV pulse with an optical rail and by measuring the intensity of the corresponding ion signal, which was averaged over 300 pulses. 1XUV + 1UV ionization spectra of the excited states studied were obtained by scanning the XUV wavelength with zero time delay between the XUV and UV pulses.

Since an unexpectedly long lifetime was found for the $b \, {}^{1}\Pi_{u}(v=1)$ state in ${}^{14}N_{2}$, two dedicated measurement series were performed on the $b \, {}^{1}\Pi_{u}(v=1)$ state in ${}^{14}N_{2}$ with a two-year time interval to verify the results. Measurements on the possible effects of radiation trapping were also performed for the $c'_4 \, {}^1\Sigma^+_u(v=0)$ state, which has a larger oscillator strength, and which decays 90% into the v = 0 level of the ground state. For this state, radiative trapping should be a much stronger effect, but no sign of increased lifetime was observed in the pressure range used. Since radiative decay of the b(v=1) state is distributed over a vibrational manifold, with only ~10% decay to the v = 0 ground-state level, the effects of radiative trapping should be smaller than for $c'_4(v=0)$.

An important limiting characteristic of the laser system is its bandwidth of $\Delta\lambda_{\rm XUV} \approx 0.01$ nm in the XUV domain, which does not allow for full resolution of rotational structure in the N₂ bands. Nevertheless, the laser can be set to probe a limited number of lines within the band envelope, thus allowing for some rotational sensitivity. Previously, the temporal resolution of the apparatus was estimated from streak camera measurements of the IR laser pulses used for the generation of the XUV radiation via harmonic upconversion [37]. Here, in Fig. 3.1, we show a pumpprobe delay scan for the b(v = 4) state of N₂, which is known to have a lifetime of 11–18 ps [61, 62]. The resulting convoluted width of 107 ps full-width at halfmaximum (FWHM) represents, in fact, the instrument function of our pump-probe setup in the temporal domain. This value is in good agreement with an actual measurement of pulse durations by a streak camera yielding a convoluted width of 95 ps [37].



Figure 3.1: Pump-probe delay scan with the XUV laser fixed at $\lambda =$ 96.56 nm, probing the shortlived $b \, {}^{1}\Pi_{u}(v=4)$ level in ${}^{14}N_{2}$. The data have been centered around $\Delta T = 0$ and fitted to a Gaussian, yielding an effective instrument width of 107 ps FWHM.



Figure 3.2: Spectrum of the $b {}^{1}\Pi_{u} - X {}^{1}\Sigma_{g}^{+}(1,0)$ band in ${}^{14}N_{2}$. Full line: observed spectrum. Dashed line: calculated spectrum at T = 80 K. Vertical sticks: line strengths of individual rotational lines.

Several fitting procedures were applied to the lifetime decay curves to derive estimates for the decay times and their uncertainties. The first method was analogous to that of Ref. [37], involving Monte Carlo simulations of the distribution of errors. Furthermore, the rate-equation model used in Ref. [76] and a method similar to that in Ref. [77] were applied.

Simulations of the recorded excitation spectra were made by convolving a stick spectrum, representing the relative rotational line strengths, with the bandwidth of the laser system. A rotational temperature of 80 K, together with appropriate Hönl-London factors, was employed and account was taken of the effect of nuclearspin statistics on the rotational line strengths. The ranges of J levels probed during the lifetime measurements were estimated from the calculated spectra. The simulated spectrum of b(v = 1), in comparison with the experimental spectrum, is shown in Fig. 3.2. Some rotational structure is resolved experimentally for higher J levels, mainly because the R, Q and P lines accidentally coincide. We note that our simulations are somewhat crude, not including the effects of Rydberg-valence, and ${}^{1}\Pi_{u} - {}^{1}\Sigma_{u}^{+}$ interactions on the rotational line strengths, nor the effects of Jdependent predissociation on the ionization quantum yield. These effects are likely to be small, however, for b(v = 1), the main subject of this study.

3.3 Results and Discussion

A typical b(v = 1) decay transient is reproduced in Fig. 3.3. No evidence for a rotational dependence of the lifetime was found. Most measurements were performed near 98.57 nm, thus probing low J levels (see Fig. 3.2). A mean lifetime of 2635 ± 150 ps was found in the first measurement campaign, which yielded nine independent decay transients in the range 2359-2841 ps, consistent with a statistical distribution. During the second independent validation campaign, lifetimes of 2525 ± 150 ps were observed, an average over three measurements, confirming the long lifetime. A statistical analysis of all measurements yielded a final value of 2610 ± 100 ps.

In previous studies, values for the lifetime of b(v = 1) in ¹⁴N₂ were determined as 1700±250 ps [75] and 1100±300 ps [62]. In the latter study, the line widths of single rotational levels were investigated. In Ref. [62], it was stated that the wavelength resolution of the XUV laser was barely sufficient to enable the deconvolution of molecular lifetime effects from the observed widths. Furthermore, the possibility of hyperfine structure should be considered. Here, we conclude that the estimate of the instrument width in Ref. [62] was too optimistic. The picosecond XUV laser at Lund certainly provides much better accuracy for lifetimes in the dynamic range >500 ps, and hence the present value should be more trustworthy. For the discrepancy with the value obtained by Oertel *et al.* [75], we have no explanation.

It is of interest, especially in view of this discrepancy, to see whether the long b(v = 1) lifetime determined here is compatible with estimates of the radiative lifetime of this level based on known oscillator strengths.

The relationship between the band oscillator strength $f_{v'v''}$ and the corresponding radiative decay channel is given by [78]:

$$f_{v'v''} = \frac{2 - \delta_{0\Lambda'}}{2 - \delta_{0\Lambda''}} 4\pi\epsilon_0 \frac{m_e c}{8\pi^2 e^2} \lambda_{v'v''}^2 A_{v'v''}, \qquad (3.1)$$

where v' and v'' denote vibrational levels in the upper and lower electronic states, $\lambda_{v'v''}$ is the transition wavelength, $A_{v'v''}$ is the state-to-state radiative decay rate, and the other symbols have their usual meanings. As pointed out by Morton and Noreau [78], in the case of a ${}^{1}\Pi \leftarrow {}^{1}\Sigma^{+}$ transition, the phenomenon of Λ -doubling has to be taken into account explicitly, and, since $\delta_{0\Lambda} = 1$ for Σ states and 0 otherwise, the degeneracy prefactor in Eq. (3.1) takes the value 2.

The radiative lifetime $\tau_{v'}^{\text{rad}}$ of the single vibrational level v' is given by:

$$\frac{1}{\tau_{v'}^{\text{rad}}} = A_{v'} = \sum_{v''} A_{v'v''}^X + \sum_{e,v''} A_{v'v''}^e.$$
(3.2)

The summations in Eq. (3.2) take into account that the excited state may decay to many vibrational levels v'' of both the ground state X and other excited states e.

In the case of the $b^{1}\Pi_{u}(v=1)$ state, of principal interest here, dipole-allowed radiative decay can occur energetically, not only to the ground state $X^{1}\Sigma_{q}^{+}$, but



Figure 3.3: Lifetime decay measurement for the $b \, {}^{1}\Pi_{u}(v = 1)$ state of ${}^{14}N_{2}$. Full line: fit to observed data; Dashed line: time response function of the two laser pulses combined.

also to the $a \,{}^{1}\Pi_{g}$, $a'' \,{}^{1}\Sigma_{g}^{+}$, and II ${}^{1}\Sigma_{g}^{+}$ states, the latter of which is only known theoretically [79]. The b - a(1,0) transition has been observed experimentally [80]. Inspection of Eq. (3.1) shows that, for a given oscillator strength, the contribution to the decay rate is inversely proportional to the square of the transition wavelength. Hence, there is likely to be a significantly smaller contribution from the $b \,{}^{1}\Pi_{u} - a''$, II ${}^{1}\Sigma_{g}^{+}$ transitions, which occur in the far-IR and visible, respectively, than from the $b \,{}^{1}\Pi_{u} - a \,{}^{1}\Pi_{g}$ transition, which lies in the near-UV. Therefore, here we consider only the b - X and b - a decay channels and take the b(v = 1) radiative lifetime to be given by:

$$\frac{1}{\tau_1^{\text{rad}}} = A_1 = \sum_{v''} A_{1v''}^X + \sum_{v''} A_{1v''}^a.$$
(3.3)

Combining Eqs. (3.1) and (3.3), with appropriate degeneracy factors for the two electronic transitions, one may write:

$$\frac{1}{\tau_1^{\text{rad}}} = A_1 = \frac{8\pi e^2}{4\epsilon_0 m_e c} \sum_{\nu''} \left[\frac{f_{1\nu''}^{bX}}{2(\lambda_{1\nu''}^{bX})^2} \right] \\
+ \frac{8\pi e^2}{4\epsilon_0 m_e c} \sum_{\nu''} \left[\frac{f_{1\nu''}^{ba}}{(\lambda_{1\nu''}^{ba})^2} \right].$$
(3.4)

In order to compute the oscillator-strength array for the b - X transition, we employed the diabatic ${}^{1}\Pi_{u}$ potential-energy curves and couplings, and the ${}^{1}\Pi_{u} - X$ electronic transition moments of Spelsberg and Meyer [39] in a rotationless, coupled-



Figure 3.4: Oscillator strengths for the b - X(v' = 0 - 5, 0) bands. Solid line vertices: Coupled-channel rotationless calculations, performed as described in the text. Solid circles: Absolute optical values of Stark *et al.* [64, 81]. Crosses: Electron-scattering values of Geiger and Schröder [66], scaled to agree with the computed value for the (4,0) band.

channel (CC) treatment of the Rydberg-valence and Rydberg-Rydberg interactions. As is well-known [34], the ${}^{1}\Pi_{u} - X$ oscillator strengths in N₂ display strong interference effects due to these interactions. As expected, our computed CC oscillator strengths $f_{v'0}^{bX}$ behave similarly to the band strengths computed by Spelsberg and Meyer [39], which correctly reproduce the *relative* trends in the experimental results of Geiger and Schröder [66]. However, it was necessary to scale the oscillator strengths by a factor of 0.75, equivalent to reducing the Spelsberg and Meyer transition moments by 13.4%, in order to optimize agreement with the absolute optical oscillator strengths of Stark *et al.* [64, 81] for the b - X(v' = 0 - 5, 0) bands. These reduced diabatic electronic transition moments were used for all subsequent calculations of $f_{v'v''}^{bX}$.

In Fig. 3.4, the computed b - X(v' = 0 - 5, 0) oscillator strengths are compared with the absolute optical values of Stark *et al.* [81], including a preliminary low-Jvalue for the (5,0) band [64], and also with the electron-scattering intensities of Geiger and Schröder [66]. The latter are scaled to agree with the computed (4,0) oscillator strength of 0.0655. Agreement is excellent with each experimental data set



Figure 3.5: Branching ratios for the b - X(1, v'') fluorescence channels. Solid line vertices: Coupled-channel rotationless calculations, performed as described in the text. Solid circles: Experimental values of James *et al.* [68]. Open circles: Experimental values of Zipf and Gorman [82].

and it is likely that the residual uncertainties in the computed oscillator strengths, and in the corresponding transition rates discussed below, are on the order of those applicable to the optical values to which they are scaled, i.e., $\sim 10\%$.

Having thus "calibrated" our CC computational model, we then computed the oscillator strengths connecting b(v = 1) to the lowest 22 levels of the ground state, i.e., $f_{1v''}^{bX}$, which were then converted into the corresponding transition rates $A_{1v''}^X$ using the first term in Eq. (3.4). In Fig. 3.5, the computed relative fluorescence branching ratios $R_{1v''}^X = A_{1v''}^X / \sum_{v''} A_{1v''}^X$ are compared with the experimental branching ratios of James *et al.* [68] and Zipf and Gorman [82]. In the range v'' = 0 - 9, excellent agreement is found with Zipf and Gorman [82], and reasonable agreement with James *et al.* [68], but the (1,0) and (1,1) branching ratios of the latter work are not supported by the present calculations. The computed total transition rate from b(v = 1) to the first 22 levels of the ground state is $\sum_{v''} A_{1v''}^X = (2.60 \pm 0.26) \times 10^8 \text{ s}^{-1}$.

In principle, CC calculations should also be used to estimate the contribution of fluorescence to the $a \,{}^{1}\Pi_{g}$ state to the radiative lifetime of b(v = 1), but there is no information available on the magnitudes or phases of the corresponding diabatic electronic transition moments. Therefore, we performed an uncoupled, rotationless "adiabatic" calculation of the b - a(1, v'') oscillator strengths, employing Rydberg-Klein-Rees potential-energy curves for the b and a states [4], together with an R-dependent electronic transition moment assumed to be the same as that applying to the isoconfigurational $C^{3}\Pi_{u} - B^{3}\Pi_{g}$ transition [83]. The b - a fluorescence is found to be dominated by the (1,0) transition, with significant contributions only for v'' < 7. The total transition rate, computed according to the second term in Eq. (3.4), is $\sum_{v''} A^{a}_{1v''} = (0.17 \pm 0.09) \times 10^{8} \text{ s}^{-1}$, only $\sim 7\%$ of the b - X rate, with the large estimated relative uncertainty arising from the inevitable uncertainty in the assumed b - a electronic transition moment.

Combining the computed rates for the two decay channels, we find a total transition rate $A_1 = (2.77 \pm 0.28) \times 10^8 \text{ s}^{-1}$, corresponding to a radiative lifetime $\tau_1^{\text{rad}} = 3.61 \pm 0.37$ ns. The difference between this radiative lifetime and the observed lifetime of 2.61 ± 0.10 ns can be explained by residual predissociation of the b(v = 1) level. In the case of predissociation, the true lifetime is related to the radiative lifetime according to:

$$\tau = \tau^{\rm rad} (1 - \eta^{\rm pre}), \tag{3.5}$$

where η^{pre} is the predissociation yield of the excited state. Using the present values for τ_1 and τ_1^{rad} in Eq. (3.5) gives an estimate for the predissociation yield of $\eta_1^{\text{pre}} = 0.28 \pm 0.10$. This value differs significantly from the value of 0.105 given by James *et al.* [68], but this disagreement is no cause for concern. James *et al.* [68] derive their value from two quantities: an experimental emission cross section, with a stated uncertainty of 22%, and an excitation cross section which is scaled assuming a b - X(4,0) band oscillator strength of 0.055, based on an old optical measurement [84]. If we rescale the excitation cross section of James *et al.* [68] using our oscillator strength of 0.0655, based on a fit to more recent optical data [64, 81], their emission cross section then implies a predissociation yield of 0.25 \pm 0.30, in good agreement with our result, but with a significantly greater uncertainty.

3.4 Conclusions

A direct time-domain pump-probe lifetime measurement has been performed on the $b^{1}\Pi_{u}(v=1)$ level in ¹⁴N₂, yielding a lifetime of 2.61 ns. The measured lifetime is consistent with our coupled-channel calculation of the corresponding radiative lifetime, 3.61 ns, together with a predissociation yield of 28%.

In principle, a separate calculation of the predissociation lifetime is possible. However, the specific predissociation mechanisms for the dipole-accessible states of N₂ are yet to be identified, and, certainly, a comprehensive predissociation model is completely lacking. In any case, the reliable calculation of such a small predissociation linewidth ($\sim 0.0006 \text{ cm}^{-1}$ FWHM) for a single vibrational level among many significantly broader levels would be very difficult. A predissociation model, including isotopic effects, and involving Rydberg-valence, Rydberg-Rydberg, spin-orbit, and rotational interactions, is currently being developed by some of the present authors. Our b(v = 1) predissociation-yield estimate may be useful in informing the development of that new predissociation model.

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Chapter 4

Pump-probe lifetime measurements on singlet *ungerade* states in molecular nitrogen

Excited-state lifetimes for a number of vibronic states of ${}^{1}\Pi_{u}$ symmetry in molecular nitrogen have been determined experimentally in a laser-based pump-probe scheme using a coherent and tunable extreme ultraviolet source based on harmonic generation. States investigated in ${}^{14}N_2$ were $b {}^{1}\Pi_u(v = 6 - 9)$, of valence character, and $c_3 {}^{1}\Pi_u(v = 1)$ and $o_3 {}^{1}\Pi_u(v = 1)$, of Rydberg character. In the case of $b {}^{1}\Pi_u(v = 7)$ and $c_3 {}^{1}\Pi_u(v = 1)$, rotationally dependent predissociation was observed. States studied in ${}^{15}N_2$ were $b {}^{1}\Pi_u(v = 5)$ and $c_3 {}^{1}\Pi_u(v = 1)$; in addition, lifetimes of the $c'_4 {}^{1}\Sigma^+_u(v = 0, 1)$ and $b' {}^{1}\Sigma^+_u(v = 1)$ states were determined. The lifetimes show a dependence on the vibrational quantum number and isotope.

4.1 Introduction

The excited states in N₂ which are accessible from the ground state $X^{1}\Sigma_{g}^{+}$ via dipole-allowed transitions are of singlet *ungerade* $({}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{u})$ symmetry, with corresponding transition frequencies in the extreme ultraviolet (XUV) spectral region. Absorption by N₂ in the upper layers of the atmosphere shields the Earth's surface from XUV solar radiation. The ${}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{u}$ states in N₂ undergo predissociation by coupling with triplet *ungerade* states, mainly of ${}^{3}\Pi_{u}$ symmetry. An understanding of the predissociation mechanism is currently lacking and, therefore, experimental values for the lifetimes of the singlet *ungerade* states provide valuable new information to validate models describing the predissociation process. An understanding of the predissociation in N₂ is also important for knowledge of the radiation budget and photochemistry in the Earth's atmosphere [1]. Many line-width and lifetime measurements have been carried out previously for the main isotopomer ¹⁴N₂ [6, 28, 36, 37, 49, 52, 61, 62, 65, 70, 71, 72, 73, 74, 75, 85], but the data set is not yet complete and many disagreements exist. Moreover, no lifetime measurements of the singlet *ungerade* states in ¹⁵N₂ have been reported previously. In the present study, a picosecond laser system was used in a pumpprobe configuration to study lifetimes of a number of states: $b^{-1}\Pi_u(v = 6 - 9)$, $c_3^{-1}\Pi_u(v = 1)$ and $o_3^{-1}\Pi_u(v = 1)$, in ¹⁴N₂, and $b^{-1}\Pi_u(v = 5)$, $c_3^{-1}\Pi_u(v = 1)$, $c'_4^{-1}\Sigma_u^+(v = 0, 1)$ and $b'^{-1}\Sigma_u^+(v = 1)$, in ¹⁵N₂. The same experimental setup has been used previously to measure lifetimes of the $c'_4^{-1}\Sigma_u^+(v = 0 - 2)$ [37] and $b^{-1}\Pi_u(v =$ 1) [85] states in ¹⁴N₂. The lifetimes obtained here are, wherever possible, compared with literature data from previous measurements.

4.2 Experimental method and data analysis

The experimental setup has been described in detail in Refs. [37, 85]. Briefly, the frequency-doubled output of a mode-locked Nd:YAG laser pumped a distributedfeedback dye laser (DFDL), and its infrared (IR) output was amplified in a titaniumsapphire crystal and frequency doubled in a KD*P crystal to produce ultraviolet (UV) radiation. The 8th harmonic of the fundamental IR beam was obtained by focusing the temporally and spatially overlapping UV and IR beams in a pulsed krypton jet. The most probable wave-mixing process to produce the 8th harmonic was: $\nu_{\rm XUV} = 3\nu_{\rm UV} + 2\nu_{\rm IR}$. The 8th harmonic, selected by a grating, was refocused in the interaction chamber, where it crossed a pulsed N_2 beam. At resonance, the XUV pump beam excited the N_2 molecules, and a probe beam, the frequencytripled 355 nm output of the mode-locked Nd:YAG laser, ionised the N₂ molecules. The resulting N_2^+ ions were accelerated and mass-selected in a time-of-flight (TOF) drift tube and detected by an electron multiplier. A 98%-atom ¹⁵N isotopicallyenriched gas sample (ISOTEC) was used for the measurements on ¹⁵N₂. Lifetime measurements were carried out by delaying the probe beam on an optical rail and by measuring the ion signal over 300 pulses as a function of time delay. 1 XUV +1 UV excitation spectra were recorded at zero time delay between pump and probe pulses. Smooth scanning was accomplished by varying the temperature of the dye in the DFDL and simultaneously monitoring the wavelength of the fundamental on a Burleigh wavelength meter.

Important characteristics of the XUV laser were the bandwidth, $\Delta \lambda_{\text{XUV}} \approx 0.01$ nm, and the pulse duration, estimated at 100 ps [37, 85]. The broad bandwidth meant that rotational structure could not be fully resolved and that selected groups of J levels were probed simultaneously during the lifetime measurements. The lifetimes and their uncertainties were obtained by fitting exponential decay functions to the observed data, having allowed for the limited temporal resolution of the experimental setup (see Ref. [85]). The average lifetimes and uncertainties



Figure 4.1: Spectrum of the $c_3 \, {}^{1}\Pi_u - X \, {}^{1}\Sigma_g^+(1,0)$ and $c'_4 \, {}^{1}\Sigma_u^+ - X \, {}^{1}\Sigma_g^+(1,0)$ bands in ${}^{15}N_2$. Dashed line: observed spectrum. Full line: calculated spectrum at T = 130 K. Vertical sticks: line strengths of individual rotational lines. Perturbations [69] are not included in the simulation.

obtained from a number of recordings are listed in Tables 4.1 and 4.2, for the levels in ${}^{14}N_2$ and ${}^{15}N_2$, respectively.

The excitation spectra were simulated by convolving the estimated bandwidth of the XUV laser with a stick spectrum representing the relative rotational line strengths, assuming and accounting for an approximate rotational temperature between 80 and 150 K, Hönl-London factors for ${}^{1}\Pi_{u} - {}^{1}\Sigma_{g}^{+}$ and ${}^{1}\Sigma_{u}^{+} - {}^{1}\Sigma_{g}^{+}$ transitions and nuclear-spin statistics on the rotational line strengths for ${}^{14}N_{2}$ and ${}^{15}N_{2}$, but ignoring possible perturbation effects. The resulting population distributions are strongly dependent on experimental conditions (e.g. nozzle-skimmer distance and gas pulse delay setting) and do not exactly obey a pure Boltzmann distribution. From these simulated spectra, the ranges of J levels probed in the lifetime measurements were estimated. An example of a simulated spectrum, in comparison with the experimental spectrum, is shown for the $c_3 \, {}^{1}\Pi_u - X \, {}^{1}\Sigma_g^+(1,0)$ and $c'_4 \, {}^{1}\Sigma_u^+ - X \, {}^{1}\Sigma_g^+(1,0)$ bands of ${}^{15}N_2$ in Fig. 4.1. A lifetime decay curve for the $c_3 \, {}^{1}\Pi_u(v=1)$ level of ${}^{15}N_2$ is shown in Fig. 4.2.

State	v	$\tau (ps)$	$\lambda ~({ m nm})$	Rot. lines	Previous results (ps)
$b \ ^1 \Pi_u$	6	380 ± 40	94.91 – 94.93		$350 \pm 75 \ [62], >150 \ [4]$
	7 a	550 ± 40	94.236	R(0-2)	>150 [49]
		500 ± 40	94.246	R(5), Q(2)	
		320 ± 40	94.262	R(8), Q(5)	
		250 ± 40	94.296	R(11), Q(9), P(7)	
	x	95 ± 70	93.51 – 93.52		>150 [49]
	q 6	$\leq 50 - 110$	92.88 - 92.90		
$c_3 \ ^1\Pi_u$	1^{a}	170 ± 30	93.86 - 93.88	R(0-13), Q(1-6), P(2-3)	230 c $(J = 1)$ [65]
		100 ± 70	93.90	Q(10), P(6)	$37 \ c \ (J=8) \ [65]$
$0_3 \ ^1 \Pi_{m}$	1^{b}	$\leq 50-110$	92.88 - 92.90		

Table 4.1:
Lifetimes
for some
${}^{1}\Pi_{u}$
states
\mathbf{of}
${}^{14}N_2.$

^b Blended bands.

 c See Sec. 4.3.1.

State	v	$ au~(\mathrm{ps})$
$c'_4 \ ^1\Sigma^+_u$	0	660 ± 40
	1	530 ± 50
$b' \ ^1\Sigma_u^+$	1	760 ± 60
$b \ ^1\Pi_u$	5	820 ± 60
$c_3 \ ^1\Pi_u$	1^{a}	1000 ± 100

Table 4.2: Lifetimes for some singlet *ungerade* states of $^{15}N_2$.

 a Indication of shorter lifetimes at high *J*-values.



Figure 4.2: Lifetime decay measurement for the $c_3 \, {}^{1}\Pi_u(v=1)$ level in ${}^{15}N_2$ recorded at the band head. Full line: fit to observed data; Dashed line: time response function of the two laser pulses combined.

4.3 Results

4.3.1 Lifetime measurements for ¹⁴N₂

Several levels of ${}^{1}\Pi_{u}$ symmetry were investigated in ${}^{14}N_{2}$. For b(v = 6), single exponential decays with an average lifetime of 380 ± 40 ps were observed. This value, obtained with the present Lund time-domain pump-probe setup, is consistent with the 350 ± 75 ps deduced from previous line-width experiments with the Amsterdam narrow-band XUV setup [62]. Lifetimes of ~350 ps fall just in the dynamic range where both experiments deliver unambiguous and accurate results. It is therefore reassuring for the consistency of the methods that good agreement is found for b(v = 6). Our b(v = 6) lifetime is also consistent with Ref. [49], where a lower limit of 150 ps was found.

For the b(v = 7) state, lifetime measurements were performed at four wavelength settings, probing different sets of rotational levels (see Table 4.1). At the longer wavelengths, where higher rotational states were probed, a lower signal intensity was obtained; hence the relative uncertainty is larger. These measurements demonstrate a strong decrease of excited-state lifetime for higher rotational quantum numbers in b(v = 7). As is detailed in Table 4.1, there is a steady decrease in lifetime from ~550 ps for J = 1-3, down to ~250 ps for $J \sim 9$. Since, at most wavelength settings, e- and f-parity levels were probed simultaneously, a possible parity dependence of the lifetime can neither be proven nor ruled out. Finally, our b(v = 7) lifetimes are consistent with the results of Ref. [49] which found a lower limit of 150 ps.

Although the b - X(8,0) transition has a small oscillator strength as a result of Rydberg-valence interference [34], the signal strength was sufficient to perform a lifetime measurement on b(v = 8). However, the observed lifetime is at the edge of the dynamic range of the system, on the order of 95 ps. In Ref. [49], no line broadening was observed and their estimated lower limit of 150 ps is not too far off from our result.

The b(v = 9) and $o_3(v = 1)$ levels are overlapped and, due to the limited wavelength resolution of the XUV laser, these states could not be resolved from each other. Observed lifetimes vary from lower than 50 ps to 110 ps, giving only an indicative value of the lifetimes for these two levels. No other lifetime measurements have been previously reported for these states.

Pump-probe decay transients were recorded for $c_3(v = 1)$ at three wavelengths. A value of 170 ps was found at $\lambda = 93.86$ and 93.88 nm, where many lines pile up: in this window there is the entire R branch as well as Q(1-6) and P(2-3). At 93.90 nm, higher-J lines were probed, centered on Q(10) and P(6). At this wavelength, the lifetime is too short for an accurate determination. Nevertheless, a clear shortening of the lifetime is found for higher J. This result may be compared with the findings of Kawamoto *et al.* [65], who measured line widths in the c - a''(1,0)band. These authors found line widths increasing quadratically with J for both the e- and f-parity components, with an effective parity-averaged Lorentzian width of 0.023 cm⁻¹ full-width at half-maximum (FWHM) at J = 1, and 0.14 cm⁻¹ FWHM at J = 8, corresponding to lifetimes of 230 ps and 37 ps, respectively. The latter lifetime is too short to measure accurately with our setup. However, the present lifetimes, including the observed decrease with increasing J, are in quite good agreement with the results of Kawamoto *et al.*

4.3.2 Lifetime measurements for ¹⁵N₂

Two states of ${}^{1}\Pi_{u}$ symmetry were studied in ${}^{15}N_{2}$. A lifetime of 820±60 ps was found for b(v = 5), a factor of four higher than the lifetime of this level in ${}^{14}N_{2}$ [62]. The lifetime of the $c_{3}(v = 1)$ Rydberg state was also found to be isotope dependent. In ${}^{15}N_{2}$, a lifetime of 1000 ± 100 ps was measured at the band head of the Rbranch, as shown in Fig. 4.2, where a lifetime decay curve is presented. At higher Jlevels, bi-exponential decay curves were observed, with components of ~ 1 ns and ~ 300 ps. Although the observation of short-lived components underlying long-lived ones is unambiguous, the spectral assignment of these features in a low-resolution spectrum is difficult, particularly in view of the overlap of $c_{3}(v = 1)$ and $c'_{4}(v = 1)$ (see Fig. 4.1) and the strong perturbations in $c_{3}(v = 1)$ [69].

In addition, three states of ${}^{1}\Sigma_{u}^{+}$ symmetry were studied in ${}^{15}N_{2}$. The $c'_{4} {}^{1}\Sigma_{u}^{+}(v = 0)$ Rydberg state has an average lifetime of 660 ± 40 ps. Rotational levels up to J = 11 were probed, but no significant J dependence of the lifetime was found, contrary to the J dependence observed for $c'_{4}(v = 0)$ in ${}^{14}N_{2}$ [37, 86]. One pumpprobe delay scan was performed at 95.795 nm, exciting the R(7) and P(4-5) lines of the $b' {}^{1}\Sigma_{u}^{+}(v = 1)$ valence state. The observed lifetime of this level is somewhat larger, 760 ± 60 ps. The longer lifetime of b'(v = 1) compared with $c'_{4}(v = 0)$, was also found for ${}^{14}N_{2}$ in a frequency-domain line-width experiment [52]. The average lifetime of the vibrational level $c'_{4} {}^{1}\Sigma_{u}^{+}(v = 1)$ was found to be 530 ± 50 ps. The lifetime of this level is isotope dependent; the lifetime in ${}^{14}N_{2}$ is 330 ± 35 ps [37], significantly lower.

4.4 Discussion and Conclusions

Direct time-domain pump-probe lifetime measurements have been performed on several ${}^{1}\Pi_{u}$ states in ${}^{14}N_{2}$ and also, for the first time, in the isotopomer ${}^{15}N_{2}$. In ${}^{15}N_{2}$, the $c'_{4} {}^{1}\Sigma_{u}^{+}(v=0,1)$ and $b' {}^{1}\Sigma_{u}^{+}(v=1)$ states were also studied. The present lifetime measurements on ${}^{1}\Pi_{u}$ and some ${}^{1}\Sigma_{u}^{+}$ states of the isotopomers of molecular nitrogen provide further examples of the erratic dependences on vibrational and rotational quantum numbers observed in many previous studies [6, 28, 36, 37, 49, 52, 61, 62, 65, 70, 71, 72, 73, 74, 75, 85]. Aspects of such behaviour have been attributed to the effects of Rydberg-valence interaction. For example, Rydbergvalence interactions between the states of ${}^{1}\Sigma_{u}^{+}$ symmetry have been invoked to explain the behaviour of the lowest three vibrational levels in the $c'_{4} {}^{1}\Sigma_{u}^{+}$ state [37]. The experimental lifetimes are also found to be different for the isotopomers of N₂. The lifetime of $b {}^{1}\Pi_{u}(v = 7)$ in ${}^{14}N_{2}$ is *J*-dependent: four different sets of *J* levels were probed and a decrease of the lifetime with *J* was found. Similarly, a *J*-dependence was found for the $c_{3} {}^{1}\Pi_{u}(v = 1)$ level in ${}^{14}N_{2}$. For $c'_{4} {}^{1}\Sigma_{u}^{+}(v = 0)$ in ${}^{15}N_{2}$, no *J*-dependence was observed, contrary to findings in ${}^{14}N_{2}$ [37, 86]. All the present observations of excited-state lifetimes provide valuable input information for a comprehensive predissociation model, based on Rydberg-valence and singlettriplet interactions, which is currently being developed by some of the authors.

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Chapter 5

Isotopic variation of experimental lifetimes for the lowest ${}^{1}\Pi_{u}$ states of N_{2}

Lifetimes of several ${}^{1}\Pi_{u}$ states of the three natural isotopomers of molecular nitrogen, ${}^{14}N_2$, ${}^{14}N^{15}N$ and ${}^{15}N_2$, are determined via line width measurements in the frequency domain. XUV + UV two-photon ionization spectra of the $b{}^{1}\Pi_{u}(v =$ 0-1, 5-7) and $c_3{}^{1}\Pi_u(v = 0)$ states of ${}^{14}N_2$, $b{}^{1}\Pi_u(v = 0-1, 5-6)$ and $c_3{}^{1}\Pi_u(v = 0)$ states of ${}^{14}N^{15}N$ and $b{}^{1}\Pi_u(v = 0-7)$, $c_3{}^{1}\Pi_u(v = 0)$ and $o{}^{1}\Pi_u(v = 0)$ states of ${}^{15}N_2$ are recorded at ultra-high resolution, using a narrowband tunable XUV-laser source. Lifetimes are derived from the line widths of single rotationally-resolved spectral lines after deconvolution of the instrument function. The observed lifetimes dependent.

5.1 Introduction

In the Earth's atmosphere, molecular nitrogen is the main absorber of extreme ultraviolet (XUV) solar radiation [1]. The absorption is associated with dipole-allowed excitation of singlet ungerade $(c'_n {}^1\Sigma_u^+, b'{}^1\Sigma_u^+, c_n {}^1\Pi_u, o_n {}^1\Pi_u$ and $b^1\Pi_u$, where *n* is the principal quantum number) states, which are known to undergo strong predissociation [6, 28, 36, 52, 61, 62, 68, 70, 71, 72, 73], some showing rotational dependence [37]. The rates of predissociation of these levels are key inputs in the radiation budget of the Earth's atmosphere, but the applicable predissociation mechanisms are far from being understood at present. This paper adds to the database on lifetimes and predissociation rates pertaining to the excited states of the dipole-allowed bands in nitrogen, with a special focus on the less abundant natural isotopomers (${}^{14}N^{15}N$ and ${}^{15}N_2$). The isotopic variations provide a sensitive test for a coupledchannel Schrödinger equation model describing the predissociation process which is presented in an accompanying paper [87]. Lifetimes of the singlet ungerade states in N₂ have been measured using a wide variety of sophisticated experimental techniques. Laser-induced photo-fragment translational spectroscopy was performed in various studies [6, 28, 36, 71, 72, 73] that also provided direct information on the predissociation yields. Direct time domain studies have also been performed, either via the delayed coincidence technique combined with synchrotron radiation [75], or via a VUV-laser based pump-probe technique [37, 85, 88]. In an elegant application of the Hanle effect [74] lifetimes within a several nanosecond time window were determined for some states. In another experiment determination of the natural lifetime was achieved through a line broadening study in the near-infrared range with discharge preparation of the longlived $a''^{1}\Sigma_{a}^{+}$ state [65].

In our previous line width studies on molecular nitrogen, high-resolution XUV + UV two-photon ionization spectra were recorded using a tunable XUV-laser source initially with a bandwidth of ~10 GHz [49, 61] full-width at half-maximum (FWHM, all further widths and bandwidths in this paper are FWHM) and later with an improved bandwidth of ~250 MHz [52, 62]. This enabled the determination of line widths for states with lifetimes shorter than ~800 ps. We have extended these measurements to include the molecular isotopomers in the present experiments.

5.2 Experimental

The experimental setup has already been described in our previous measurement of perturbations in the isotopic line positions [69] and therefore will not be explained in detail here. The laser system employed a pulsed dye amplifier (PDA) injection-seeded by a narrowband, tunable cw dye laser. The PDA output was first frequency-doubled into the UV using a KDP crystal, and then frequency tripled into the XUV using a pulsed xenon jet. The resulting co-propagating radiation was used to perform 1 XUV + 1 UV ionization measurements in a nitrogen jet emitted from a pulsed nozzle source. In the present setup a Millennia-V Nd:VO₄ laser (at 532 nm) was used for pumping the cw dye laser. This limits the tunability of the XUV-laser setup to $\lambda > 94.2$ nm.

The pulsed jet nozzle-skimmer distance could be varied during the measurements from 0 to 150 mm to trade off signal level against the transverse Doppler width. For the strongest lines, the largest distance was chosen to better collimate the skimmed molecular beam and reduce the Doppler broadening. Conversely, the nozzle could be moved adjacent to the skimmer for some very weak lines to maximize the signal level. In the latter configuration, there is significantly more Doppler broadening and the line width measurements are consequently less accurate. This configuration was especially used for ¹⁴N¹⁵N since the natural abundance (0.74%) in N₂ is very low. For ¹⁵N₂ a 99.40% isotopically enriched gas sample (Euriso-top) enabled larger nozzle-skimmer distances to be used.



Figure 5.1: Upper curve: 1 XUV + 1 UV ionization spectrum for the ${}^{14}\mathrm{N}{}^{15}\mathrm{N}$ $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}$ (5,0) band recorded in natural abundance. The width of the lines is instrument limited. Middle curve: Simultaneously recorded I₂ saturation spectrum. The line marked with an asterisk is the "t" hyperfine component of the B - X (18-1)P64 line of I₂ at 17443.67616 cm⁻¹, used for absolute calibration. Lower curve: Simultaneously recorded étalon markers.

The cw injection laser frequency was calibrated by simultaneously recording an accurate I₂ saturated-absorption spectrum together with fringes from a stabilized étalon (free spectral range 148.957 MHz). An example of such a calibrated spectrum is given in Fig. 5.1, which shows the ¹⁴N¹⁵N $b^1\Pi_u - X^1\Sigma_g^+$ (5,0) band. The saturated absorption line positions provided absolute frequency calibration, while relative frequency intervals are obtained from the étalon spectrum.

5.3 Results and analysis

5.3.1 Line positions

The above technique enabled line positions to be determined to an accuracy of $\pm 0.003 \text{ cm}^{-1}$ for the narrower resonances. The lines which show Doppler and/or lifetime broadening, have a larger uncertainty of $\pm 0.02 \text{ cm}^{-1}$. We have already presented line positions for the majority of the bands for ¹⁵N₂ and several levels

in ¹⁴N¹⁵N in Ref. [69]. Accurate line positions of $b^1\Pi_u(v=1)$ in ¹⁴N₂ were given in Ref. [62]. However, we present here some additional line assignments for the $b^1\Pi_u(v=0,5-7)$ and $c_3{}^1\Pi_u(v=0)$ levels in ¹⁴N₂ and the $b^1\Pi_u(v=0-1)$ levels in ¹⁴N¹⁵N in Table 5.1. Our line positions presented here are the most accurate up to date and many overlapping lines, especially in the band head of the *R* branches, could be resolved for the first time. However, no fitting procedures were performed to obtain molecular constants since only a few lines of every band were measured and all levels have already been analyzed previously [33, 49, 59, 61].

5.3.2 Line widths

Figure 5.2 is an example of the dramatic variation in the line widths observed for different isotopomers. Shown here are the $b^1\Pi_u(v=1)$ band for ${}^{14}N_2$ and ${}^{15}N_2$, the former being instrument limited, while the latter exhibits a Lorentzian line profile due to lifetime broadening. Note that the *R*-branch is clearly resolved for ${}^{14}N_2$, while for ${}^{15}N_2$ the R(1) and R(3) lines are overlapped.

The instrument width, comprising the laser bandwidth and the residual Doppler broadening (due to the transverse velocity spread of the pulsed nozzle source), was determined by analyzing the narrow, well-resolved spectrum of the $b^1\Pi_u(v=1)$ level in ${}^{14}N_2$ shown in Fig. 5.2. This level is known to be long lived (2610 \pm 100 ps [85]) and consequently the instrument width dominates. The instrument widths thus obtained are shown in Fig. 5.3 as a function of nozzle-skimmer distance. As can be seen, the instrument width asymptotes to ~250 MHz for large distances where the Doppler broadening contribution becomes less important. We therefore conclude that the laser bandwidth is no greater than ~250 MHz. The instrument width contributions from the laser line width and from Doppler broadening would be expected to be characterized by Gaussian profiles. However, even instrument-limited line profiles such as those shown for the $b^1\Pi_u(v=1)$ in ${}^{14}N_2$ exhibited some additional intensity in the far wings and were found to be fitted best by a Voigt profile.

Various procedures were followed, in a stepwise fashion, to deduce the lifetimes of the excited states under investigation. After a determination of natural lifetime broadening parameters Γ excited state lifetimes were deduced via:

$$\tau = 1/2\pi\Gamma\tag{5.1}$$

First, lines which are predominantly lifetime broadened were fitted accurately using a Lorentzian profile, but for line profiles in which the instrument width contributed significantly, a Voigt profile was used. There exist no straightforward procedures to deconvolute a Voigt-shaped instrument function from an observed line profile, whether that is a Voigt profile or close to a Lorentzian profile. When the instrument function is Gaussian-like the natural line width Γ may be deduced from the observed

Table 5.1: Additional observed transition frequencies (in cm⁻¹) for the $b^1\Pi_u - X^1\Sigma_g^+$ (v,0) bands in ¹⁴N₂ and ¹⁴N¹⁵N and the $c_3{}^1\Pi_u(v=0)$ level in ¹⁴N₂. No P(J) lines were measured. Line marked with s is derived from the shoulder of a neighboring line in the spectrum. Line marked with s' in ¹⁴N¹⁵N is derived from the shoulder of a ¹⁴N₂ line. Lines given in less significant digits have undergone lifetime and/or Doppler broadening.

Level	J	R(J)	Q(J)
$b^1 \Pi_u (v=0)^{-14} \mathrm{N}_2$	0	100819.72	
	1	100821.54	100815.75
	2	100822.26	
$b^1 \Pi_u (v=5)^{-14} \mathrm{N}_2$	0	104702.726	
	1	104704.470	
	2	104705.121	
	3	104704.689	
	4	104703.176	
$b^{1}\Pi_{u}(v=6)^{-14}N_{2}$	0	105348.645	
	1	105350.129	105344.664
	2	105350.364	105342.165
	3	105349.348	
	5	105343.551	
$b^{1}\Pi_{u}(v=7)^{-14}N_{2}$	0	106112.229	
	1	106113.617	106108.248
	2	106113.710	106105.660
	3	106112.502	
$c_3{}^1\Pi_u(v=0){}^{14}\mathrm{N}_2$	0	104141.48	
	1	104143.43	104137.57
	2	104144.34	104135.63
	3	104144.24s	
	4	104143.13	
$b^{1}\Pi_{u}(v=0)^{-14}\mathrm{N}^{15}\mathrm{N}$	0	100833.22	
	1	100834.96	
	2	100835.67	
	3	100835.32	
	4	100833.92	
$b^{1}\Pi_{u}(v=1)^{-14}\mathrm{N}^{15}\mathrm{N}$	0	$101456.39\mathrm{s'}$	
	1	101458.00	101452.55
	2	101458.47	
	3	101457.82	
	5	101453.14	



Figure 5.2: 1 XUV + 1 UV ionization spectrum for the $b^1\Pi_u - X^1\Sigma_g^+$ (1,0) band. (a) ¹⁴N₂. Nozzle-skimmer distance = 150 mm. The width of the lines is instrument limited. (b) ¹⁵N₂. Nozzle-skimmer distance = 40 mm. Due to the significantly greater lifetime broadening, R(1) and R(3) are not resolved.

Voigt profile [89]:

$$\Gamma = \Delta \nu_{obs} - (\Delta \nu_{instr}^G)^2 / \Delta \nu_{obs}$$
(5.2)

For those examples where the nozzle-skimmer separation is small, and the Doppler contribution is decisive, this approximation will yield a reasonably accurate value for Γ . In other cases it will give a first estimate.

Second, for the analysis of very short-lived excited states, giving rise to large Lorentzian-shaped line widths Eq. (5.2) may be employed as well, but it should



Figure 5.3: Instrument width (FWHM) of the PDA-based XUV source as a function of nozzle-skimmer distance using 2 bars N_2 backing pressure. The error bars indicate 1σ uncertainties.

be noted that it will give a slight overestimate of the natural lifetime broadening parameter, because the instrument width has some Lorentzian content. If the instrument function were to be exactly Lorentzian one might use:

$$\Gamma = \Delta \nu_{obs} - \Delta \nu_{instr}^L \tag{5.3}$$

In fact, since the instrument function is Voigt-shaped, with Lorentzian and Gaussian content, the true value will be in between results obtained with Eqs. (5.2) and (5.3). Using both equations, estimates for Γ as well as uncertainties are derived.

Finally, a numerical procedure is followed, particularly for those lines where the observed widths do not exceed the instrument width too much, and as an independent check on the procedures described above for a number of examples. The instrument width, as measured for $b^1 \Pi_u (v = 1)$ lines under specific conditions of nozzle-skimmer separation, was fitted to a Voigt-shaped function, thereby retrieving two parameters representing the Lorentzian and Gaussian content. These parameters represent in full the instrument shape function. Subsequently this function was convoluted with a Lorentzian function $f_l(\Gamma)$ for the lifetime broadening effect. The result of this convolution was then fitted, in a least-squares routine, to the recorded line profiles for the other excited states, thereby determining Γ . By varying Γ in the convolution procedure using $f_l(\Gamma)$ an estimate of the resulting uncertainty can be established as well. Table 5.2 shows the resulting values of the lifetimes, using Eq. (5.1), and their uncertainties, which represent the principal results of the present paper.

u:z: Experimenta hire data. All data	tvnically per	a une isonopomers	In $I < 5$	and 172. 111	e mennes are compare
Level	$^{14}N_{2}$	$^{14}\mathrm{N}_2$	$^{14}\mathrm{N}^{15}\mathrm{N}$	$^{15}\mathrm{N}_{2}$	$^{15}\mathrm{N}_2$
	τ (ps) obs.	τ (ps) previous	τ (ps) obs.	τ (ps) obs.	τ (ps) previous
$b^1 \Pi_u (v=0)$	31 ± 4	$16 \pm 3 [61]$	80 ± 25	40 ± 7	
$b^1 \Pi_u (v=1)$	>800	$1750 \pm 260 \ [75]$	180 ± 100	34 ± 5	
		$2610 \pm 100 \; [85]$			
$b^1 \Pi_u (v=2)$		10 ± 2 [61]		6.9 ± 0.8	
$b^1 \Pi_u (v=3)$		$1.6 \pm 0.3 \; [61]$		7.7 ± 1.0	
$b^1 \Pi_u (v=4)$		18 ± 1 [62]		10 ± 2	
$b^1 \Pi_u (v=5)$	230 ± 45	$205 \pm 25 \; [62]$	>800	>800	$820 \pm 60 \; [88]$
$b^1 \Pi_u (v=6)$	325 ± 80	$350 \pm 75 \; [62]$	600 ± 200	780 ± 280	
		380 ± 40 [88]			
$b^1 \Pi_u (v = 7)$	550 ± 170	$550^{a} \pm 40$ [88]		660 ± 210	
$c_3{}^1\Pi_u(v=0)$	66 ± 6	67 ± 7 $[52]$	47 ± 10	29 ± 4	
$o^1 \Pi_u (v=0)$		$240 \pm 50 \; [62]$		280 ± 65	

literat Table 5.2: E: .) + al lifati ÷ + 2 14N₂ 14N15N 15 N₂ Ę ∍ lifati: red with

^a Lifetime obtained from lines R(0-2). Rotational state dependent lifetime reported in Ref. [88]. See Sec. 5.4.



Figure 5.4: Experimental lifetimes of the $b^1\Pi_u(v=0-7)$ levels in ${}^{14}N_2$, ${}^{14}N^{15}N$ and ${}^{15}N_2$. Solid circles: ${}^{14}N_2$, stars: ${}^{14}N^{15}N$ and open circles: ${}^{15}N_2$. Note the logarithmic vertical scale. For ${}^{14}N_2$, the lifetime of b(1) is taken from Ref. [85] and those of b(2-4) from Ref. [61]. The lifetime of b(5) in ${}^{15}N_2$ is taken from Ref. [88].

For each vibronically excited state, lifetimes were determined for a few rotational levels limited to low-J values. Since no evidence was found of possible J-dependent effects, averages were taken over those J levels investigated. Hence the lifetimes, as listed in Table 5.2, represent this average over the values obtained for the individual spectroscopic lines pertaining to a certain vibronic state.

Figure 5.4 provides a comparison of the most accurate lifetimes for the $b^1\Pi_u(v = 0-7)$ levels in ¹⁴N₂ and ¹⁵N₂. For ¹⁴N¹⁵N only lifetimes for the $b^1\Pi_u(v = 0-1, 5-6)$ were observed, since nitrogen in natural abundance (0.74%) was used to record ¹⁴N¹⁵N spectra. Therefore, only strong bands and levels with a relatively long lifetime could be investigated in ¹⁴N¹⁵N. In a 1 XUV + 1 UV ionization scheme, the observed ion signal depends on the lifetime of the intermediate level. For short-lived levels (due to predissociation), there is a competition between predissociation and ionization, resulting in lower ion yields. Figure 5.4 again indicates the dramatic variation of lifetimes both between the different isotopes, and as a function of vibrational quantum number.

5.4 Discussion

The line broadening technique presented here, is suitable for lifetimes shorter than ~800 ps. Therefore, for levels which are instrument limited, only a lower limit of >800 ps is given for the lifetime e.g. for $b^1\Pi_u(v=1)$ in ${}^{14}N_2$. In a previous study on line broadening in N₂ performed with a similar experimental setup [62], the instrument width and the dynamic range of applicability were estimated rather optimistically. Ubachs *et al.* [62] estimated for $b^1\Pi_u(v=1)$ in ${}^{14}N_2$ a lifetime of 1.0 \pm 0.3 ns. Later, more accurate pump-probe time-domain measurements [85] yielded $\tau = 2610 \pm 100$ ps, beyond the limit of applicability of the XUV line broadening measurements. In the present study, lifetimes >500 ps have relatively large errors and for these lifetimes, the direct time-domain pump-probe lifetime measurements performed previously [37, 85, 88] are more accurate. Lifetimes >200 ps can also be determined with the pump-probe method so the dynamic range of the two systems is complementary.

The lifetimes given in Table 5.2 and Fig. 5.4 are clearly isotope dependent. However, no lifetime differences were observed between J_e levels (R and P branches) and J_f levels (Q branches). The levels are discussed separately below for each state.

5.4.1 $b^1\Pi_u$ state

The lifetime of the $b^1\Pi_u(v=0)$ level is isotope dependent, with the largest value occurring for ${}^{14}N^{15}N$: 80 ± 25 ps. The lifetimes of the other isotopomers are approximately half this value: 31 ± 4 ps and 40 ± 7 ps for ${}^{14}N_2$ and ${}^{15}N_2$, respectively. Ubachs *et al.* [61] determined a lifetime of 16 ± 3 ps for this level in ${}^{14}N_2$ (also from line width studies), which is about half that of the present measurement. Since the present instrument bandwidth is much narrower (~0.01 cm⁻¹, c.f. ~0.28 cm⁻¹ in Ref. [61]), the lifetimes presented here are considered to be more accurate.

A significant isotope dependence is found for the $b^1\Pi_u(v=1)$ level. The most accurate lifetime for this level in ¹⁴N₂ is 2610 ± 100 ps, determined in a direct timedomain pump-probe experiment [85]. In the present experiment, no natural line broadening was observable for this level in ¹⁴N₂, which enabled the determination of the instrument width (see Sec. 5.3). Only a lower limit of $\tau > 800$ ps can be estimated in this study. A significant decrease in the lifetime occurs for the heavier isotopomers, 180 ± 100 ps for ¹⁴N¹⁵N and 34 ± 5 ps for ¹⁵N₂ i.e. almost 2 orders of magnitude difference between ¹⁴N₂ and ¹⁵N₂. In Fig. 5.2, two-photon ionization spectra are shown for b(1) in ¹⁴N₂ and ¹⁵N₂ respectively. Besides the clear difference in the widths of the lines, the spectra in ¹⁵N₂. This is due to competition between predissociation and ionization of the N₂ molecules in the excited b(1) level, yielding a much less efficient ionization channel, i.e. weaker signal, for b(1) in ¹⁵N₂ than in ¹⁴N₂. The lifetime of the $b^1\Pi_u(v=2)$ level is short. Ubachs *et al.* [61] determined a lifetime of 10 ± 2 ps for b(2) in ¹⁴N₂. For ¹⁵N₂, we found a slightly shorter lifetime of 6.9 \pm 0.8 ps. No lifetime measurements could be performed on b(2) in ¹⁴N¹⁵N because of weak signal levels.

The $b^1\Pi_u(v=3)$ level is very short lived in ${}^{14}N_2$: 1.6 ± 0.3 ps [61]. We found that in ${}^{15}N_2$, the lines of b(3) are less broadened and correspond to a lifetime of 7.7 ± 1.0 ps. If similarly large line widths are present for b(3) in ${}^{14}N^{15}N$, then this explains why this level was not observed. This is one of the shortest-lived states found in the present study, and represents a minimum in the lifetime of the *b* state (see Fig. 5.4).

The short lifetime of the $b^1\Pi_u(v=4)$ level is slightly isotope dependent. b(4) is longer lived in ¹⁴N₂ (18 ± 1 ps [61]) than in ¹⁵N₂ (10 ± 2 ps, measured here). Again, the short lifetimes probably explain why no signals pertaining to b(4) in ¹⁴N¹⁵N were observed.

For $b^1\Pi_u(v=5)$ a lifetime of 230 ± 45 ps was observed in ${}^{14}N_2$, in very good agreement (see Table 5.2) with the previous measurement performed using the same experimental apparatus [62]. This level is much longer lived in the isotopomers ${}^{14}N^{15}N$ and ${}^{15}N_2$, for which only instrument-limited line widths were observed. Therefore we can only give a lower limit of $\tau > 800$ for b(5) in these heavier isotopomers. A previous time-domain pump-probe lifetime measurement [88] of b(5)in ${}^{15}N_2$ showed a lifetime of 820 ± 60 ps, consistent with the present observation. b(5) is one of the longest lived levels in ${}^{14}N^{15}N$ and ${}^{15}N_2$.

The lifetime of $b^1 \Pi_u (v = 6)$ increases from ${}^{14}N_2$ to ${}^{15}N_2$ with that of ${}^{14}N^{15}N$ in between. A lifetime of 325 ± 80 ps was measured for ${}^{14}N_2$, also in agreement with previous work [62, 88] (see Table 5.2). The lifetime increases to 600 ± 200 ps and 780 ± 280 ps in ${}^{14}N^{15}N$ and ${}^{15}N_2$, respectively.

For $b^1\Pi_u(v = 7)$, 1 XUV + 1 UV ionization spectra were only recorded in ${}^{14}N_2$ and ${}^{15}N_2$, giving lifetimes of 550 ± 170 ps and 660 ± 210 ps, respectively. The lifetime in ${}^{14}N_2$ is in excellent agreement with a previous time-domain pumpprobe lifetime measurement [88] of 550 ± 40 ps. In Ref. [88], a rotational state dependent lifetime of b(7) in ${}^{14}N_2$ was observed. The value of 550 ± 40 ps belongs to a measurement on $J_e = 1 - 3$, while a second measurement on $J_e = 6$, $J_f = 2$ gave 500 ± 40 ps. The lifetime decreases at higher J levels [88]. In our measurement on b(7) in ${}^{14}N_2$, only the lines R(0-2) and Q(1-2) were measured, which showed no J-dependence for these low J levels.

Generally, the lifetimes of the $b^1\Pi_u$ state levels depend strongly on v and isotopomer. The strongest isotopic dependence is found for b(1). The lifetimes of the valence $b^1\Pi_u$ levels have a minimum near v = 3 in both ${}^{14}N_2$ and ${}^{15}N_2$ and the lifetimes of b(5-7) are significantly higher than the lifetimes of the other levels, except b(1) in ${}^{14}N_2$ (see Fig. 5.4).

5.4.2 $\ \ ^{1}\Pi_{u}$ Rydberg states

Two Rydberg states of ${}^{1}\Pi_{u}$ symmetry were also investigated. First of all, the Rydberg $c_{3}{}^{1}\Pi_{u}(v = 0)$ state has a fairly short lifetime: 66 ± 6 ps, 47 ± 10 ps and 29 ± 4 ps in ${}^{14}N_{2}$, ${}^{14}N^{15}N$ and ${}^{15}N_{2}$, respectively, showing a decrease of the lifetime towards the heavier isotopomers. A previous lifetime measurement [52] on $c_{3}(0)$ in ${}^{14}N_{2}$ yielded 67 ± 7 ps, in excellent agreement with the present value.

Another Rydberg state with ${}^{1}\Pi_{u}$ symmetry is the $o^{1}\Pi_{u}(v=0)$ state, which was only investigated in ${}^{15}N_{2}$ and for which a lifetime of 280 ± 65 ps was measured. This lifetime is comparable with that in ${}^{14}N_{2}$, namely 240 ± 50 ps measured by Ubachs *et al.* [62].

5.5 Conclusions

Frequency domain line width measurements have been performed on a number of ${}^{1}\Pi_{u}$ states in the isotopomers ${}^{14}N_{2}$, ${}^{14}N^{15}N$ and ${}^{15}N_{2}$. Most levels were significantly broadened, and the lifetimes thereby derived were found to be strongly isotope- and vibrational level-dependent. The lifetimes of the $b^{1}\Pi_{u}(v = 0 - 7)$ levels for ${}^{14}N_{2}$ and ${}^{15}N_{2}$ clearly show a minimum near v = 2 - 4.

The behaviour of the line widths as a function of isotopomer and vibrational level provides important information on predissociation rates which dominate for the levels studied. These data are key inputs for a comprehensive predissociation model, based on coupled-channel Schrödinger equation techniques, which is presented in an accompanying paper [87].

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Chapter 6

Lifetimes and transition frequencies of several singlet *ungerade* states in N_2 between $106\,000 - 109\,000$ cm⁻¹

Using a narrow-band tunable XUV source, ultrahigh resolution 1 XUV + 1 UV twophoton ionisation spectra were recorded of transitions to several singlet *ungerade* states in ¹⁴N₂ and ¹⁵N₂ in the range 106 000 – 109 000 cm⁻¹. The natural linewidths of the individual rotational spectral lines were determined and the resulting lifetimes were found to depend on vibrational level and for the $c_3^{1}\Pi_u(v = 1)$ level also on isotope. Furthermore, accurate transition frequencies were determined and for several bands, lines near bandhead regions were resolved for the first time.

6.1 Introduction

The dipole-allowed transitions in molecular nitrogen from the ground state $X^1\Sigma_g^+$, accessing excited states of singlet *ungerade* symmetry $(c'_4{}^1\Sigma_u^+, b'{}^1\Sigma_u^+, c_3{}^1\Pi_u, o^1\Pi_u$ and $b^1\Pi_u$), lie in the extreme ultraviolet (XUV) spectral domain. Strong Rydbergvalence and rotational interactions perturb the structure and intensity distribution [34, 39, 69], while additional spin-orbit interactions with triplet *ungerade* states cause predissociation of the singlet states. A large number of linewidth and lifetime measurements (see [90] and references cited therein) show a predissociation rate strongly depending on vibrational level and isotope. Lewis *et al.* [87] explained the predissociation for the $b^1\Pi_u(v = 0 - 6)$ and $c_3{}^1\Pi_u(v = 0)$ states, lying in the energetic range 100 000 - 106 000 cm⁻¹, in terms of interactions with the $C^3\Pi_u$ and $C'{}^3\Pi_u$ states. To extend their theoretical predissociation model to higher singlet states, more information is required (and recently became available [91, 92]) on the $F^3\Pi_u$ and $G^3\Pi_u$ states, which are supposed to play significant roles at higher energies [87]. Secondly, a comprehensive set of linewidth and lifetime measurements on singlet *ungerade* states at these higher energies is required to give a detailed picture of the predissociation behaviour and to explain the underlying mechanisms. Recently, linewidth measurements of several singlet *ungerade* states in the region $109\,000 - 112\,000$ cm⁻¹ were reported [93, 94] and here we present new frequency domain linewidth measurements on the singlet *ungerade* states between $106\,000 - 109\,000$ cm⁻¹. The present ultra-high resolution 1 XUV + 1 UV two-photon ionisation spectra also yield accurate line positions and several lines near bandhead regions are resolved for the first time.

6.2 Experiment

This Paper reports on an extension of previous experiments on linewidths in the N_2 spectra using the ultrahigh resolution XUV laser in Amsterdam [90]. Now the system has been modified to produce XUV radiation at energies exceeding $106\,000$ cm^{-1} . The extension has been documented before [95] and will only be briefly described here. The output of a narrow-band tunable cw ring dye laser, pumped by a 532-nm Millennia-V laser, was amplified in a pulsed dye amplifier (PDA), which was in turn pumped with the second harmonic of a pulsed Nd:YAG laser. The output of the PDA was mixed with a $\sim 100 \text{ mJ/pulse 532-nm}$ green beam (15 % from the same narrow-band injection-seeded Nd:YAG laser used to pump the PDA) in a KD*P crystal to generate UV radiation with typical powers of 10 - 15 mJ/pulse. XUV radiation was produced by nonresonant frequency tripling the UV in a xenon gas jet obeying the following relation: $\omega_{XUV} = 3\omega_{PDA} + 3\omega_{Nd;YAG}$. Absolute frequency calibration of ω_{PDA} was done by applying I₂ saturation spectroscopy on the cw ring dye laser output, while relative calibration was achieved with an étalon. Calibration of $\omega_{Nd;YAG}$ was performed with an ATOS wavemeter. The XUV beam was perpendicularly crossed with a skimmed N_2 supersonic jet and the N_2^+ ions formed in the 1 XUV + 1 UV ionisation scheme were accelerated to a electronmultiplier detector in a time-of-flight setup. A 99.40 % isotopically enriched gas sample (Euriso-top) was used for the ${}^{15}N_2$ measurements.

Philip *et al.* [95] deduced a XUV source bandwidth of 300 MHz at full width at half maximum (FWHM) (all further widths and bandwidths in this Paper are FWHM) by measuring a long-lived krypton resonance at a nozzle-skimmer distance of 150 mm. This is the same bandwidth determined from measurements applying the third harmonic of the frequency-doubled output of the PDA corresponding to $\omega_{XUV} = 6\omega_{PDA}$ [90]. For strong signal levels, a nozzle-skimmer distance of 150 mm was used also for the N₂ studies, but for weaker lines, this distance was decreased resulting in extended Doppler broadening and less accurate measurements. In worst cases, the nozzle was located only a few mm before the skimmer to obtain a sufficient signal-to-noise ratio. In the subsequent data analysis, the same function of the instrument width against nozzle-skimmer distance as given in [90] was used, in which the XUV bandwidth is constant and the Doppler width depends on the nozzle-skimmer geometry.

6.3 Results

With the present setup, 1 XUV + 1 UV two-photon ionisation spectra were recorded, probing the $b^1 \Pi_u(v=10)$, $c_3{}^1 \Pi_u(v=1,2)$, $c_4{}^1 \Sigma_u^+(v=1,2)$ and $b'{}^1 \Sigma_u^+(v=4,6)$ states in ¹⁴N₂ and the $b^1\Pi_u(v=9)$, $c_3{}^1\Pi_u(v=1)$, $o^1\Pi_u(v=1)$, $c'_4{}^1\Sigma_u^+(v=1)$ and $b'^{1}\Sigma_{u}^{+}(v=5,6)$ states in ¹⁵N₂. Examples of spectra are shown in Figs. 6.1 and 6.2 for the $c'_4 \Sigma^+_u - X^1 \Sigma^+_a$ (2,0) and $b^1 \Pi_u - X^1 \Sigma^+_a$ (10,0) bands, respectively. In Fig. 6.2 and its caption, the procedure is demonstrated to convert the online calibrated frequency ω_{PDA} (scanned) and $\omega_{Nd;YAG}$ (fixed) into a scale for the XUV-frequencies. Not all levels in the energy range $106\,000 - 109\,000$ cm⁻¹ are presented here because of several reasons. Raw data were obtained for b(9) and o(1) in ¹⁴N₂, but the strong mutual perturbation [44] requires further analysis before the lines can be assigned unambiguously and the predissociation behaviour presented. Also the $c_3(1)$ level in ${}^{15}N_2$ has local interactions but in this case with a triplet state [69] and here only a value of the lifetime is given, while a detailed analysis of the perturbations will be presented elsewhere. No signal levels corresponding to the transitions to b(8) in both ¹⁴N₂ and ¹⁵N₂ and b'(4) in ¹⁵N₂ were detected, probably because of a lack of sufficient XUV power. We note here that in the present XUV-production scheme involving $\omega_{XUV} = 3\omega_{PDA} + 3\omega_{Nd;YAG}$, the XUV intensity is less than in the sextupling $(\omega_{XUV} = 6\omega_{PDA})$ scheme [90]. Excited states $b(10), c_3(2)$ and $c'_4(2)$ in ${}^{15}N_2$ were not investigated because the energy positions of the bandheads are not known to sufficient accuracy to attempt an ultra-high resolution study; searching for these lines would consume too much expensive ${}^{15}N_2$ gas. Finally, b'(5) in ${}^{14}N_2$ was already presented in [95].

6.3.1 Line positions

The observed transition frequencies and assignments are tabulated for $^{14}N_2$ and $^{15}N_2$ in Tables 6.1 and 6.2, respectively. The absolute accuracy of the spectral measurements is estimated at $\pm 0.01 \text{ cm}^{-1}$ [95], significantly larger than the accuracy of $\pm 0.003 \text{ cm}^{-1}$ in our other studies on N₂ [69, 90]. The higher uncertainty is associated with the limited accuracy of the ATOS wavemeter and small drifts of $\omega_{Nd;YAG}$ during the scans [95]. These estimates are for the narrower resonances, while for lines with a significant Doppler contribution or lifetime broadening, a lower accuracy of $\pm 0.02 \text{ cm}^{-1}$ is estimated. Note that the resolving power, i.e. bandwidth, of the setups with $\omega_{XUV} = 3\omega_{PDA} + 3\omega_{Nd;YAG}$ and $\omega_{XUV} = 6\omega_{PDA}$ are similar, notwithstanding the fact that the accuracies are different.

Level	J	R(J)	Q(J)	P(J)
$b^1 \Pi_u (v = 10)$	0	108374.040		
	1	108374.911	108370.063	
	2	108374.236	108366.956	
	3	108372.003		
	4	108368.199		
$c_3{}^1\Pi_u(v=1)$	0	106531.442		
	1	106534.334	106527.443	
	2		106526.323	
$c_3{}^1\Pi_u(v=2)$	0	108698.00		
$c_4'{}^1\Sigma_u^+(v=1)$	0	106371.966		
$c_4'{}^1\Sigma_u^+(v=2)$	0	108547.605		
	1	108549.305		
	2	108549.858		
	3	108549.264		
	4	108547.510		
$b'^1 \Sigma_u^+ (v = 4)$	0	106649.145		
	1	106650.228		
	2	106649.903		
$b'^1 \Sigma_u^+(v=6)$	0	108000.93^*		
	1			107994.49
	2	108000.93^*		107988.94
	3	107998.65		
	4	107994.73		
	5	107989.23		

Table 6.1: Observed transition frequencies (in cm⁻¹) in ${}^{14}N_2$. Lines marked with * are blended lines in the spectrum. Lines given in less significant digits have undergone lifetime and/or Doppler broadening.



Figure 6.1: 1 XUV + 1 UV ionisation spectrum for the ${}^{14}N_2 c'_4{}^1\Sigma^+_u - X^1\Sigma^+_g$ (2,0) band. The R(0) and R(4) lines and the R(1-3) lines are resolved for the first time. Left spectrum is recorded with a smaller nozzle-skimmer distance than the spectrum at the right, i.e. the widths are slightly larger in the left spectrum due to increased Doppler broadening.

Table 6.2: Observed transition frequencies (in cm^{-1}) in $^{15}\text{N}_2$. Lines given in less significant digits have undergone lifetime and/or Doppler broadening.

Level	J	R(J)	Q(J)
$b^1\Pi_u(v=9)$	1	107446.97	107442.34
$o^1 \Pi_u (v = 1)$	1	107582.40	107575.92
$c_4'{}^1\Sigma_u^+(v=1)$	1	106313.887	
$b'^1 \Sigma_u^+ (v=5)$	0	107229.574	
	1	107230.200	
	2	107229.284	
${b'}^1 \Sigma_u^+ (v = 6)$	1	107877.81	

For most nozzle-skimmer geometries, a low rotational temperature in the gas expansion only allowed population of low rotational levels with $J \leq 5$. Near the *R*-branch bandheads regions, many individual lines were resolved for the first time. For example, the R(0) and R(4) and the R(1-3) of the $c'_4 - X$ (2,0) band in ¹⁴N₂ are clearly separated (see Fig. 6.1) and also the R(0) and R(2) lines of the b - X (10,0) band in ¹⁴N₂ are resolved for the first time (see Fig. 6.2). These levels have all been

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Figure 6.2: Upper spectrum: 1 XUV + 1 UV ionisation spectrum for the ¹⁴N₂ $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}$ (10,0) band. Nozzle-skimmer distance = 40 mm. The lines are lifetime broadened and clearly show a dominant Lorentzian contribution. The R(0) and R(2) lines are resolved for the first time. Lower spectrum: (a) Simultaneously recorded I₂ saturation spectrum. The line marked with an asterisk is the "t" hyperfine component of the B - X (19-2)P56 line of I₂ at 17 336.22109 cm⁻¹, used for absolute calibration of ω_{PDA} . (b) Simultaneously recorded étalon markers for relative calibration of ω_{PDA} . Three photons of the green beam, with an energy of $\omega_{Nd:YAG} = 18788.3766$ cm⁻¹, has to be added to obtain the frequency $\omega_{XUV} = 3\omega_{PDA} + 3\omega_{Nd:YAG}$ shown in the upper curve.

measured and analyzed before with a lower resolution for ${}^{14}N_2$ [33, 49, 60, 65, 96, 97] and ${}^{15}N_2$ [69]. To identify the resolved lines, transition frequencies were calculated from the known molecular constants. Since only a limited amount of lines were measured, no attempts were made to improve the molecular constants.

6.3.2 Linewidths

From the recorded 1 XUV + 1 UV ionisation spectra, linewidths for the individual rotational lines of all bands were determined using the same procedures and instrument function as in [90] to deconvolve the instrument function from the observed widths to obtain natural linewidths Γ . Subsequently, lifetimes were derived using $\tau = 1/2\pi\Gamma$ and the results for the various states investigated are tabulated for both $^{14}N_2$ and $^{15}N_2$ in Table 6.3. For the small range of low J levels studied ($J \leq 5$) no evidences of J-dependences were found. Also no differences in lifetime between Π^+ or e parity levels (observed in R and P branches) and Π^- or f parity levels (Q branches) were observed, in the case of the ${}^{1}\Pi_u$ states.

6.3.2.1 ${}^{1}\Pi_{u}$ states

One vibrational level of the $b^1\Pi_u$ state was investigated in ${}^{14}N_2$, namely b(10), providing the first reported lifetime for this level of 100 ± 15 ps. In ${}^{15}N_2$, the b(9)level was studied, yielding a lifetime of 46 ± 7 ps. This value is only derived from several scans of the Q(1) line, corresponding to f symmetry levels. Because of a low signal-to-noise ratio, no accurate linewidths of R (and P) lines were determined and hence, the present lifetime of b(9) in ${}^{15}N_2$ applies to f parity levels only.

The $c_3{}^1\Pi_u$ Rydberg state was studied for vibrational levels v = 1, 2 in ${}^{14}N_2$ and v = 1 in ${}^{15}N_2$. A significant isotope dependence is found for $c_3(1)$, as shown in Fig. 6.3. Clearly lifetime broadened lines were observed in ${}^{14}N_2$ giving a lifetime of 155 ± 30 ps, while in the heavier isotopomer, nearly instrument limited widths were found. This gives only a lower limit of $\tau > 800$ ps for $c_3(1)$ in ${}^{15}N_2$. Previous time-domain lifetime measurements [88] give similar results: 170 ± 30 ps and 1000 ± 100 ps for ${}^{14}N_2$ and ${}^{15}N_2$, respectively, showing that this level in ${}^{15}N_2$ is indeed one of the longest lived singlet *ungerade* states in N₂ in the region below 112 000 cm⁻¹. Obviously, high-*n* Rydberg states, used in zero-kinetic energy experiments, have much longer lifetimes even into the μ s range [98, 99].

Although in a previous direct time-domain pump-probe lifetime study [88] individual rotational lines were unresolved, some evidence of a *J*-dependence was found for the lifetime of $c_3(1)$ in ¹⁴N₂. At higher *J* levels a shorter lifetime was observed but no accurate lifetime determination could be performed. Kawamoto *et al.* [65] also investigated this level in ¹⁴N₂ by measuring linewidths in the c - a''(1,0) band and found a decrease in the lifetime with *J*: 230 ps at J = 1 and 37 ps at J = 8(see for more information [88]).

The $c_3(2)$ level was measured for ¹⁴N₂ yielding a lifetime of 62 ± 10 ps, about two times smaller than that of $c_3(1)$ in ¹⁴N₂. The $o^1\Pi_u(v=1)$ Rydberg level was studied in ¹⁵N₂ resulting in a lifetime of 27 ± 6 ps. For the latter two states no previous results have been reported.

6.3.2.2 ${}^{1}\Sigma_{u}^{+}$ states

Two states of ${}^{1}\Sigma_{u}^{+}$ symmetry were investigated, the $c'_{4}{}^{1}\Sigma_{u}^{+}$ Rydberg state and the $b'{}^{1}\Sigma_{u}^{+}$ valence state. For $c'_{4}(1)$, lifetimes of 270 ± 70 and 310 ± 80 ps were derived for ${}^{14}N_{2}$ and ${}^{15}N_{2}$, respectively, showing no significant isotope dependence at the present level of accuracy. Time-domain pump-probe lifetime measurements give

o.a: Experimentan	n nav rasno fi	ost atti tit / sattina	topomers $- n_2$ and	$u = 1N_2$. The H	retimes are compa
ure data. All data	typically per	tain to rotational l	levels $J \leq 5$.		
Level	$^{14}\mathrm{N}_2$	$^{14}\mathrm{N}_2$	$ m ^{14}N^{15}N$	$^{15}\mathrm{N}_{2}$	$^{15}\mathrm{N}_2$
	τ (ps) obs.	τ (ps) previous	τ (ps) previous	τ (ps) obs.	τ (ps) previous
$b^1 \Pi_u (v=9)$		$\leq 50 - 110$ [88]		46 ± 7	
$b^1 \Pi_u (v = 10)$	100 ± 15				
$c_3{}^1\Pi_u(v=1)$	155 ± 30	$170 \pm 30 \; [88]$		>800	1000 ± 100 [88]
		230^{a} [65]			
$c_3{}^1\Pi_u(v=2)$	62 ± 10				
$o^1 \Pi_u (v=1)$		$\leq 50 - 110$ [88]		27 ± 6	
$c_4'^1 \Sigma_u^+ (v=1)$	270 ± 70	$330 \pm 35 \; [37]$	$240 \pm 35 \; [37]$	310 ± 80	$530\pm50[88]$
$c_4'^1 \Sigma_u^+ (v=2)$	530 ± 150	$675 \pm 50 \; [37]$			
		650 [75]			
$b'^1 \Sigma_u^+ (v = 4)$	160 ± 70				
$b'^1 \Sigma_u^+ (v=5)$		$210 \pm 25 \; [95]$		250 ± 80	
		280 [75]			
$b'^1 \Sigma_u^+ (v = 6)$	60 ± 10			55 ± 10	
a Lifetime for $J =$	= 1. see [88] for	more information			

Table 6.3: literature ŗ ÷ 2 J lifati . Ł 14N15Nļ ared with



Figure 6.3: Isotope dependent width of the $c_3{}^1\Pi_u - X^1\Sigma_g^+$ (1,0) R(0) line. Left spectrum: ${}^{14}N_2$: line is lifetime broadened. Right spectrum: ${}^{15}N_2$: width is nearly instrument limited.

lifetimes of 330 ± 35 ps [37] and 530 ± 50 ps [88] for ¹⁴N₂ and ¹⁵N₂, respectively. The ¹⁴N₂ results agree well, while for ¹⁵N₂ differing results are found from linebroadening and pump-probe techniques. We cannot provide a definite explanation for this discrepancy. However, in the pump-probe experiment the bandwidth of the laser is rather limited, to an effect that for ¹⁵N₂ some high J lines in the $c_3 - X(1,0)$ band are excited when probing $c'_4(1)$. Meanwhile, it has been established that the lifetime for $c_3(1)$ in ¹⁵N₂ is as long as 1000 ± 100 ps [88], hence even a small signal admixture from these longer-lived states could affect the lifetime observed for $c'_4(1)$ in ¹⁵N₂. In the present line-broadening study singly-resolved rotational levels are studied. In addition we note that in the current study similar lifetimes were observed for $c'_4(1)$ in ¹⁴N₂ and ¹⁵N₂. Since the lifetime of $c'_4(1)$ in ¹⁴N¹⁵N is in the same range (240 ± 35 ps [37]), it may be deduced that for this particular state there is no isotope dependence.

A value of 530 ± 150 ps was determined for the lifetime of the $c'_4(2)$ level in $^{14}N_2$. Only a small broadening was observed compared to the instrument width, causing a large uncertainty in the lifetime determination. The present technique is applicable for lifetimes lower than ~800 ps, but lifetimes longer than 400 ps are determined more accurately using time-domain pump-probe experiments as have been performed in Lund [37, 85, 88]. In view of the relatively high uncertainty in the present lifetime of $c'_4(2)$, there is still reasonable agreement with previous data: 675 ± 50 ps [37] and 650 ps [75].

For the $b'^1 \Sigma_u^+$ state, lifetimes of the v = 4 - 6 vibrational levels were determined.

For the b'(4) level, here only studied in ¹⁴N₂, a lifetime of 160 ± 70 ps was obtained. Ubachs *et al.* [37] assumed a lifetime of 60 - 80 ps for b'(4) to explain the lifetime of $c'_4(1)$ in a Rydberg-valence mixing perturbation model, which seems to be a reasonable estimate. The lifetime of b'(5) in ¹⁴N₂ was already measured with the same setup [95], giving a value of 210 ± 25 ps, not too far off from a value of 280 ps measured by Oertel *et al.* [75]. In the present study, a lifetime of this level in ¹⁵N₂ of 250 ± 80 ps was obtained, hence showing no isotope dependence. Similarly for b'(6), no difference in lifetime of the isotopomers was found, with lifetimes of 60 ± 10 and 55 ± 10 ps in ¹⁴N₂ and ¹⁵N₂, respectively. The lifetime of b'(6) is certainly shorter than those of b'(4) and b'(5).

6.4 Discussion and conclusions

Lifetimes of singlet ungerade states between $106\,000 - 109\,000 \text{ cm}^{-1}$ in $^{14}\text{N}_2$ and $^{15}\text{N}_2$ have been determined experimentally from linewidth measurements in the frequency domain. The lifetimes provide information about the predissociation rates and for virtually all excited states in N₂ in the region below $112\,000 \text{ cm}^{-1}$, predissociation dominates radiative decay; for high-*n* Rydberg states the situation is known to be different [98, 99]. In the present study, lifetimes are found to depend on vibrational level and for the $c_3{}^1\Pi_u(v=1)$ level also on isotope. Using the coupled-channel Schrödinger equation (CSE) technique, Lewis *et al.* [87] combined the $(b, c_3, o){}^1\Pi_u$ and $(C, C'){}^3\Pi_u$ states in a five-channel CSE model, including all the electrostatic and spin-orbit interactions, to explain the predissociation of the $b{}^1\Pi_u(v=0-6)$ and $c_3{}^1\Pi_u(v=0)$ states. For these ${}^1\Pi_u$ states the predissociation is governed by the $(C, C'){}^3\Pi_u$ states. To extend their model on the ${}^{1,3}\Pi_u$ states to higher energies, i.e. to the region of the states studied here, more information on the ${}^3\Pi_u$ manifold is necessary. Recent rotationally resolved experiments on the $F{}^3\Pi_u$ [91] and $G{}^3\Pi_u$ [92] states are valuable since the F and G states play a significant role at these energies.

A comprehensive predissociation model including singlets and triplets, as was reported for the states of ${}^{1}\Pi_{u}$ symmetry [87], is not yet developed for the ${}^{1}\Sigma_{u}^{+}$ states. However, Ubachs *et al.* [37] explained lifetimes of $c'_{4}{}^{1}\Sigma_{u}^{+}(v=0-2)$ in ${}^{14}N_{2}$ from a perspective of Rydberg-valence mixing in the ${}^{1}\Sigma_{u}^{+}$ manifold. The pure c'_{4} Rydberg state is assumed to be unpredissociated, while Rydberg-valence mixing with the predissociating b' valence state (possibly by coupling with triplet states) shortens the lifetimes of the Rydberg state levels. For example for the specific level $c'_{4}(1)$, Ubachs *et al.* showed that this level is strongly mixed with the b' state with a dominant b'(4) admixture and assuming a lifetime of 60 – 80 ps for b'(4), they explained the shortening of an estimated radiative lifetime of 740 ps to their observed $c'_{4}(1)$ lifetime of 330 ps. Their assumed b'(4) lifetime is not that far off from the present b'(4) result of 160 ± 70 ps.

In general, the dependence of the lifetime behaves in a seemingly erratic way

for the manifolds of ${}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{u}$ symmetry. However, comprehensive perturbation models involving singlet and triplet states are able to explain the lifetimes, as was demonstrated by Lewis *et al.* [87] for a number of ${}^{1}\Pi_{u}$ states in the limited energetic range below 106 000 cm⁻¹. Such models should be extended now to include ${}^{1}\Pi_{u}$ states at higher energies and ${}^{1}\Sigma_{u}^{+}$ states. The presently obtained lifetimes can be used as key inputs for these levels.

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Chapter 7

Reanalysis of the $o^{1}\Pi_{u}(v=1)/b^{1}\Pi_{u}(v=9)$ Rydberg-valence complex in N₂

The $b^1\Pi_u(v=9)$ valence state and the $o^1\Pi_u(v=1)$ Rydberg state of molecular nitrogen are investigated by laser-based 1 XUV + 1 UV two-photon ionization. The high resolution and frequency accuracy obtained allow for an improved analysis of the homogeneous perturbation between both states of ${}^1\Pi_u$ symmetry. At high rotational states (J > 20) an additional heterogeneous perturbation is found with the $b'{}^1\Sigma_u^+(v=6)$ state, which is analyzed as well. In addition to spectra of ${}^{14}N_2$ also spectra of ${}^{14}N^{15}N$ have been studied from a natural nitrogen gas sample. Predissociation rates for some low-J levels were determined from line broadening.

7.1 Introduction

The dipole-allowed absorption spectrum of molecular nitrogen in the extreme ultraviolet wavelength region was initially thought to consist of a multitude of electronic band structures, until the true nature of the excited states was unraveled [31, 32, 33]. The complexity of the XUV spectrum appears to be a result of Rydberg-valence mixing between a limited number of singlet *ungerade* states lying at excitation energies just above 100 000 cm⁻¹ in the molecule. There is one valence state each of ${}^{1}\Sigma_{u}^{+}$ and of ${}^{1}\Pi_{u}$ symmetries (referred to as $b'{}^{1}\Sigma_{u}^{+}$ and $b^{1}\Pi_{u}$ states) and there exist Rydberg series converging on the first $X^{2}\Sigma_{g}^{+}$ ionization limit in the N₂⁺ ion (the $c'_{n+1}{}^{1}\Sigma_{u}^{+}$ and $c_{n}{}^{1}\Pi_{u}$ series) and the $o_{n}{}^{1}\Pi_{u}$ series¹ converging on the $A^{2}\Pi_{u}$ ionization limit in the ion (see Fig. 2.1). In the pivotal study by Stahel *et al.* [34] a model of Rydberg-valence interactions was presented that provided a quantitative explanation for the perturbations in positions of band origins, the seemingly erratic behavior of rotational constants, and for the pattern of band intensities strongly

¹The o_3 Rydberg state is often labeled as o.

deviating from Franck-Condon factors. In addition to homogeneous perturbations in which states of equal symmetry are coupled also the effects of heterogeneous perturbations, *i.e.* coupling between states of ${}^{1}\Pi_{u}$ and ${}^{1}\Sigma_{u}^{+}$ symmetries were included in subsequent further refined analyses [35], therewith improving the quantitative agreement between theory and experiment.

In addition to the comprehensive analyses describing the overall level structure of dipole-allowed transitions in nitrogen also local perturbation analyses were performed focusing on particular crossings that can then be parameterized at the accuracy level of the experimental data. Yoshino and co-workers analyzed a number of such local perturbations, most of which had one of the vibrational $o_3{}^1\Pi_u$ and $o_4{}^1\Pi_u$ states as perturbation partner [44]. A further example of a detailed treatment of a local perturbation in the N₂ spectrum is that of a rather large set of levels $c'_5{}^1\Sigma_u^+(v=0)$ and $c_5{}^1\Pi_u(v=0)$ Rydberg states interacting with a number of valence states of ${}^1\Pi_u$ and ${}^1\Sigma_u^+$ symmetry [100]. The typical perturbation, observed as a pronounced feature in many nitrogen spectra, of the $c'_4{}^1\Sigma_u^+(v=0)$ and $b'{}^1\Sigma_u^+(v=1)$ levels was analyzed by Yoshino and Tanaka, based on classical spectroscopic data [46], and later based on XUV-laser data by Levelt and Ubachs [59]. Several local perturbation analyses in ${}^{15}N_2$, for example of the $o_3{}^1\Pi_u(v=0)/b'{}^1\Sigma_u^+(v=3)$ crossing, are already presented in Chapter 2.

In the present study, the $o^1 \Pi_u(v=1)/b^1 \Pi_u(v=9)$ Rydberg-valence complex has been studied using 1 XUV + 1 UV two-photon ionization employing XUVlaser systems at differing resolution, providing detailed information on the rotational structure. An improved rotational analysis, including the perturbation, is proposed which differs from the previous, classical spectrometer-based investigation by Yoshino *et al.* [44]. Furthermore, linewidth measurements are presented for the first time, giving information on the predissociation behavior of these levels. In addition to the recording of the b - X(9,0) and o - X(1,0) bands in the main $^{14}N_2$ isotopomer, these bands were also investigated for $^{14}N^{15}N$ and a rotational analysis is made. In the mixed isotopomer $^{14}N^{15}N$, the perturbation in the spectrum does not appear in the pronounced form of an anti-crossing. Since at high rotational states the homogenous perturbation complex of the two $^1\Pi_u$ states undergoes a heterogeneous interaction with the $b'^1\Sigma_u^+(v=6)$ state, as already noticed by Yoshino *et al.* [44], the b'(6) level in $^{14}N_2$ is also included in the present study.

7.2 Experiment

Laser-based 1 XUV + 1 UV two-photon ionization spectroscopy was employed to study the excitation spectrum of molecular nitrogen in the range $\lambda = 92.9 - 93.5$ nm. This range covers the two interacting states $b^1\Pi_u(v=9)$ and $o^1\Pi_u(v=1)$. The experimental method, including a description of the lasers, vacuum setup, molecular beam configuration, time-of-flight (TOF) detection scheme and calibration procedures, has been documented before. Two different laser systems were used, a PDL (pulsed dye laser) based XUV source, delivering an XUV-bandwidth of $\sim 0.3 \text{ cm}^{-1}$ at full-width-half-maximum (FWHM), and a PDA (pulsed dye amplifier) based XUV-source, delivering an XUV-bandwidth of $\sim 0.01 \text{ cm}^{-1}$.

The PDL based system and its application to the spectroscopy of N₂ was described in Refs. [49, 69]. Essential ingredients are that the 6th harmonic of a pulsed dye laser was used, that was calibrated against the reference standard of the Doppler-broadened linear absorption spectrum of molecular iodine [53]. The absolute wavenumber uncertainty in the XUV for these data is ± 0.1 cm⁻¹ for resolved lines. The PDA-based system was used in a frequency mixing scheme $\omega_{XUV} =$ $3(\omega_{PDA} + \omega_{532})$, where ω_{532} is the frequency-doubled output of an injection-seeded Nd:YAG laser. It was documented previously how this frequency-mixing scheme produces a bandwidth of ~0.01 cm⁻¹ in the XUV-range [95, 101]. The intensity for XUV-production within the mixing scheme is much lower, and signal levels are accordingly decreased. Even though the molecular beam densities were increased, this scheme could only be used for calibration (and line width measurements) of a few low-J lines. In the view of the lifetime-broadening encountered in the b(9)and o(1) levels in ¹⁴N₂ (see section 7.4.2) the absolute accuracy is limited to ~0.04 cm⁻¹.

The 1 XUV + 1 UV two-photon ionization time-of-flight (TOF) experiment has some characteristics that were favorably employed in the present study. Massseparation can be combined with laser excitation to unravel the contributions to the spectrum of the main $^{14}N_2$ isotopomer from the mixed $^{14}N^{15}N$ species. Even in the case of using natural nitrogen as a probe gas, containing only 0.74% $^{14}N^{15}N$, resolved lines at the bandheads of the b(9) and o(1) levels could be observed. By changing the relative triggers for the pulsed valve, producing the nitrogen beam, and the laser pulse, as well as varying the nozzle-skimmer distance, the rotational temperature in the molecular beam could be controlled to measure independent spectra of cold (10 - 20 K) and warm (up to 180 K) samples. The latter option has greatly helped in the assignment of the spectral lines.

The wavelength range was extended to $\lambda = 92.59 - 92.87$ nm to also cover excitation of the $b'^{1}\Sigma_{u}^{+}(v=6)$ state of ¹⁴N₂ that was investigated under similar conditions in a molecular beam with the PDL-based XUV-source.

7.3 Analysis of spectra

Using the PDL-based XUV source, rotationally resolved spectra of the $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(9,0)$ and $o^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(1,0)$ bands in ¹⁴N₂ were recorded at mass 28 in the TOF spectrum with low and high rotational temperatures, which was achieved by varying the timing of the N₂ supersonic beam. In Fig. 7.1 the two spectra are compared and line assignments are shown. Similar laser excitation spectra,



Figure 7.1: 1 XUV + 1 UV ionization spectrum and line assignments for the $b^1\Pi_u - X^1\Sigma_g^+(9,0)$ and $o^1\Pi_u - X^1\Sigma_g^+(1,0)$ bands in ¹⁴N₂ in high [spectrum (a)] and in low [spectrum (b)] rotational temperature molecular beams. Note that several lines were not observed because of blending by stronger lines. In the region in spectrum (a) marked with an asterisk, two separate scans are joined and intensities of the two scans should not be compared.

with the gate in the TOF set at mass 29, were recorded from a molecular beam of natural nitrogen. Fig. 7.2 shows such a recording displaying weak lines of the $b^1\Pi_u - X^1\Sigma_g^+(9,0)$ and $o^1\Pi_u - X^1\Sigma_g^+(1,0)$ bands in ¹⁴N¹⁵N. The trace for ¹⁴N¹⁵N is still dominated by the spectrum of ¹⁴N₂ due to the fact that the mass-resolution in the TOF is not sufficient for a full discrimination.

Using the narrower-bandwidth frequency mixing PDA-based XUV source, spectra of the b - X(9,0) and o - X(1,0) bands in ¹⁴N₂ were recorded for some low J lines. Recordings of the Q(2) b - X(9,0) and Q(1) o - X(1,0) lines in ¹⁴N₂ obtained with the PDA-based XUV source are shown in Fig. 7.3. Signal levels for the b(9) level are low because of the competition between predissociation and ionization in the 1 + 1 two-photon ionization detection scheme and the rather low XUV/UV intensity levels in the frequency mixing scheme employed.

Transition energies and line assignments for the o(1) and b(9) levels (see below)



Figure 7.2: 1 XUV + 1 UV ionization spectrum and line assignments for the $b^1\Pi_u - X^1\Sigma_g^+(9,0)$ and $o^1\Pi_u - X^1\Sigma_g^+(1,0)$ bands in ${}^{14}N^{15}N$, recorded using the PDL-based XUV source. (a) Recording at mass 29 in the TOF spectrum. Large mass-28 signals of ${}^{14}N_2$ are also present in the spectrum due to a limited mass-selectivity of the TOF apparatus. Some channel averaging has been performed to improve the signal-tonoise ratio. (b) Recording at mass 28 in the TOF spectrum, showing lines of the $b^1\Pi_u - X^1\Sigma_g^+(9,0)$ and $o^1\Pi_u - X^1\Sigma_g^+(1,0)$ bands in ${}^{14}N_2$.

are presented in Tables 7.1 and 7.2 for ${}^{14}N_2$ and in Table 7.3 for ${}^{14}N^{15}N$. Term values and spectroscopic parameters were determined from the experimental transition energies using least-squares fitting procedures. The terms of the ground state $X^1\Sigma_g^+$ are represented as

$$E(J) = B[J(J+1)] - D[J(J+1)]^2 + H[J(J+1)]^3$$
(7.1)

where B is the rotational constant, and D and H centrifugal distortion parameters. Spectroscopic parameters of Trickl *et al.* [102] and Bendtsen [41] were used for the $X^1\Sigma_g^+$ state of ${}^{14}N_2$ and ${}^{14}N^{15}N$, respectively. The terms of the excited ${}^{1}\Pi_u$ states are taken to have the form

$$E(J,f) = \nu_0 + B[J(J+1) - 1] - D[J(J+1) - 1]^2$$
(7.2)

for the *f*-parity levels, where ν_0 is the band origin, and

$$E(J,e) = E(J,f) + \Delta E_{ef}(J), \qquad (7.3)$$

for the e-parity levels. Furthermore, the Λ -doubling is represented by

$$\Delta E_{ef}(J) = q[J(J+1) - 1], \tag{7.4}$$



Figure 7.3: 1 XUV + 1 UV ionization spectra of the Q(2) $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(9,0)$ and Q(1) $o^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(1,0)$ lines in ¹⁴N₂ recorded using the PDA-based XUV source, showing the different lifetime broadening observed for b(9) and o(1).

where q is the Λ -doubling parameter. Λ -doubling is neglected in the analysis of the ¹⁴N¹⁵N results because of a limited amount of rovibrational lines observed.

The b(9) and o(1) levels in ¹⁴N₂ give rise to an avoided crossing in the rotational structure, resulting from a homogeneous perturbation. A deperturbation analysis is performed by diagonalizing for each J_e and J_f the matrix

$$\begin{pmatrix}
E_{b9} & H_{b9o1} \\
H_{b9o1} & E_{o1}
\end{pmatrix},$$
(7.5)

where the diagonal elements are the term energies of b(9) and o(1) given by equations (7.2-7.4) and the off-diagonal element H_{b9o1} is the two-level homogeneous interaction parameter.

Results of an excitation spectrum of the $b'^{1}\Sigma_{u}^{+}(v=6)$ state of ${}^{14}N_{2}$ are shown in Fig. 7.4. Although at higher *J*-values a perturbation is found, the assignment of the lines in this ${}^{1}\Sigma_{u}^{+} - {}^{1}\Sigma_{g}^{+}$ band, allowing only *P* and *R* lines, is straightforward. The rotational constants for ground and excited states are such that *P* and *R* lines overlap within the resolution of the experiment up to R(12)/P(9). The observed line positions for the $b'^{1}\Sigma_{u}^{+} - X^{1}\Sigma_{g}^{+}(6,0)$ band are listed in Table 7.4. Spectroscopic parameters for b'(6) in ${}^{14}N_{2}$ were determined using a least-squares fitting procedure, in which the ground state terms are represented using eq. 7.1 and those of the excited

Table 7.1: Observed transition frequencies (in cm⁻¹) for the $b^1\Pi_u - X^1\Sigma_g^+(9,0)$ band in ¹⁴N₂. Wave numbers given to three decimal places are from narrow-bandwidth PDA spectra, those to two decimal places are from PDL spectra. Wave numbers derived from blended lines are flagged with an asterisk (*).

Level	J	R(J)	Q(J)	P(J)
$b^1\Pi_u(v=9)$	0	107654.320		
	1	107656.05^*	107650.44	
	2	107656.05^*	107647.840	107642.51
	3	107656.05^*	107644.35	
	4	107635.07	107639.99	
	5	107632.68		
	6			
	7		107599.57	
	8	107611.15		107567.72
	9		107575.50	107552.81
	10		107560.92	107535.75
	11			107517.27
	12	107558.87	107526.76	107497.19
	13	107541.69	107507.11	107474.92
	14	107523.19	107486.11	107451.60
	15	107503.00	107463.34	107427.06
	16	107481.33	107439.41	107400.01
	17	107458.27	107413.73	
	18	107433.80	107386.64	
	19	107407.65		
	20	107380.08		

 $b'^1 \Sigma_u^+(v=6)$ level are given by:

$$E(J) = \nu_0 + B[J(J+1)] - D[J(J+1)]^2 + H[J(J+1)]^3.$$
(7.6)

The resulting spectroscopic parameters for o(1), b(9) and b'(6) are listed in Table 7.5.

7.4 Discussion

7.4.1 The b(9)/o(1) complex in ¹⁴N₂

In Fig. 7.5 reduced experimental term values are plotted for b(9) and o(1) levels in ¹⁴N₂ based on the assignments to be discussed below. An avoided crossing is

Table 7.2: Observed transition frequencies (in cm⁻¹) for the $o^1 \Pi_u - X^1 \Sigma_g^+(1,0)$ band in ¹⁴N₂. Wave numbers given to three decimal places are from narrow-bandwidth PDA spectra, those to two decimal places are from PDL spectra. Wave numbers derived from blended lines are flagged with an asterisk (*).

Level	J	R(J)	Q(J)	P(J)
$o^1 \Pi_u (v=1)$	0	107632.68		
	1	107634.995	107628.614	
	2	107636.456	107627.16	107620.71^*
	3	107636.58	107624.56*	107615.19
	4	107654.69	107620.71^*	107608.59
	5	107653.69	107635.04^*	107601.02
	6	107652.43	107629.72	107610.96
	7	107651.09	107624.56^*	107601.84
	8	107649.70	107619.31	107592.70
	9	107647.88	107614.02	107583.44
	10	107645.84	107608.46	107573.95^*
	11	107643.31	107602.25	107564.45
	12		107596.05	107554.39
	13		107588.98	107543.92
	14		107581.59	107532.98
	15		107573.95^*	107521.55
	16	107623.26	107565.41	107509.59
	17	107617.70	107556.49	107497.19
	18		107547.21	107484.34
	19	107605.05	107537.22	107470.87
	20	107597.75	107526.76	107456.95
	21		107516.14	107442.29
	22		107504.67	107427.03
	23		107492.65	107411.20
	24		107480.16	107394.53

clearly visible with a maximum energy shift of 8.5 cm⁻¹ at J = 4 as a token of the homogeneous interaction between the two levels. In this Figure only the (e)-parity levels of both ${}^{1}\Pi_{u}$ states are displayed, but within the scales given, the (f)-parity components overlay the points in the figure.

The present line assignments in the b(9)/o(1) complex in ¹⁴N₂ differ with the previous study of Yoshino *et al.* [44] First, the labeling of the levels before the crossing (J = 1 - 4) is the opposite, but this is just a matter of nomenclature. We

Table 7.3: Observed transition frequencies (in cm⁻¹) for the $b^1\Pi_u - X^1\Sigma_g^+(9,0)$ and $o^1\Pi_u - X^1\Sigma_g^+(1,0)$ bands in ¹⁴N¹⁵N. Wave numbers derived from blended lines are flagged with an asterisk (*), that from a blended line of ¹⁴N₂ with *' and those from shoulders of a ¹⁴N₂ line with s'.

Level	J	R(J)	Q(J)
$b^1 \Pi_u (v=9)$	0	$107547.80^{*}{ m s'}$	
	1	107548.61	$107543.74{ m s}'$
	2	$107547.80^*{ m s'}$	107541.05
	3	107546.15	107536.57
	4		107530.82
	5	107537.93	
$o^1 \Pi_u (v=1)$	0	$107610.23 { m s}'$	
	1	107613.10	107606.41
	2		107605.37
	3	107617.26	107603.82
	4	107618.49	107601.86^{*}
	5		107599.23



Figure 7.4: 1 XUV + 1 UV ionization spectrum and line assignments for the $b'^{1}\Sigma_{u}^{+} - X^{1}\Sigma_{g}^{+}(6,0)$ band in ¹⁴N₂, recorded using the PDL-based XUV source.

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Table 7.4: Observed transition frequencies (in cm⁻¹) for the $b'^1 \Sigma_u^+ - X^1 \Sigma_g^+(6,0)$ band in ¹⁴N₂. Wave numbers derived from blended lines are flagged with an asterisk (*).

Level	J	R(J)	P(J)
$b'^1 \Sigma_u^+ (v=6)$	0	108000.93^a	
	1	108001.80	107994.49^{a}
	2	108000.93^a	107988.94^a
	3	107998.65^a	107982.30^*
	4	107994.73^a	107973.25^*
	5	107989.23^a	107963.02^*
	6	107982.30^*	107951.07^*
	7	107973.25^*	107937.43^*
	8	107963.02^*	107922.44^*
	9	107951.07^*	107905.61^*
	10	107937.43^*	107887.74
	11	107922.44^*	107867.64
	12	107905.61^*	107846.03
	13	107886.73	107822.77
	14	107866.28	107797.62
	15	107844.27	107771.52
	16	107820.74	107743.23
	17	107794.84	
	18	107767.93	107681.70
	20	107708.80	

^a Data taken from PDA-based measurements (Chapter 6).

Table 7.5: Molecular parameters of the $b^1 \Pi_u(v=9)$ and $o^1 \Pi_u(v=1)$ states of ¹⁴N₂ and ¹⁴N¹⁵N and the $b'^{1}\Sigma_{\mu}^{+}(v=6)$ state of ¹⁴N₂. All values in $\rm cm^{-1}$.

Level	B	$D \times 10^6$	$q \times 10^3$	$ u_0$
$b^1 \Pi_u (v=9)^{a-14} N_2$	1.2278(6)	-5.1(1.4)	0.48(19)	107647.70(6)
$o^1 \Pi_u (v=1)^{a-14} \mathcal{N}_2$	1.7349(5)	13.6(1.0)	-2.60(17)	107636.32(4)
$b^{1}\Pi_{u}(v=9)^{-14}\mathrm{N}^{15}\mathrm{N}$	1.198(3)	10^{b}		107546.50(7)
$o^{1}\Pi_{u}(v=1)$ ¹⁴ N ¹⁵ N	1.669(3)	10^{b}		107608.58(5)
$b'^{1}\Sigma_{u}^{+}(v=6)^{c} {}^{14}\mathrm{N}_{2}$	1.2032(9)	61(7)		107998.49(2)

^a Deperturbation of homogeneous interaction between b(9) and o(1) in ¹⁴N₂ implies an effective two-level interaction matrix element $H_{b9o1} = 9.44(2) \text{ cm}^{-1}$. ^b Fixed.

 c H = 1.3(1.4) × 10^{-8}.



Figure 7.5: Reduced term values of the $b^1 \Pi_u(v=9)/o^1 \Pi_u(v=1)$ crossing in ${}^{14}N_2$ (e levels only), including the results of an effective twolevel deperturbation. The terms are reduced such that the deperturbed b(9) levels lie on the zero line.

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Figure 7.6: Calculated o(1) mixing factors for the $o^1 \Pi_u(v=1)$ and $b^1 \Pi_u(v=9)$ levels of ${}^{14}N_2$.

have assigned the b(9) and o(1) term values to the energy levels with the highest mixing factor of the corresponding level. Thus as shown in Fig. 7.5, for J levels before the crossing, the highest term values belong to b(9) and after the crossing $(J \ge 5)$, to o(1). The lowest term values are, within the chosen definition, assigned as o(1) and b(9) for J values before and after the perturbation, respectively. Yoshino *et al.* [44] had, in contrast, assigned all the highest and lowest term values as o(1)and b(9). The mixing factors as following from the diagonalization procedure using equation (7.5) are presented in Fig. 7.6.

Besides this difference in nomenclature, we have made a new rotational assignment. For $J \ge 5$, the assignments of the current and previous (Yoshino *et al.* [44]) studies are the same but for lines going to J' = 1 - 4 of the excited states, we present a re-assignment as shown in Tables 7.1 and 7.2. These re-assignments are based on several considerations.

The separate spectra recorded with a relatively high and a low rotational temperature, allow for the lines to be assigned as low or high J. For example, a line found at 107 629.50 cm⁻¹ is assigned as Q(1) b(9) by Yoshino *et al.*, but appears as strong in the present spectrum of the warm beam, and can therefore not originate from J'' = 1. This line is in fact Q(6) of o(1) and should be weak in the 'cold' spectrum, which is indeed the case. The same argument can be made for the line at 107 652.3 cm⁻¹ which was assigned as a blended line of R(0) and R(6) of o(1) by Yoshino *et al.* [44]. This line only corresponds to R(6) of o(1) and the R(0) line of b(9) is indeed observed at 107 654.320 cm⁻¹ in the present study, in agreement with
the deperturbation analysis. Furthermore, from the 'cold' spectrum it is obvious that the strong lines at 107 650.44 and 107 647.840 cm⁻¹ are Q(1) and Q(2) of b(9), respectively, and that the assignment of the latter line as Q(1) by Yoshino *et al.* [44] is not correct. Also the intense line at 107 632.68 cm⁻¹ is certainly a blend of R(0)of o(1) and R(5) of b(9) and not only the latter. The line at 107 634.995 cm⁻¹ is not the R(0) line but the R(1) line of o(1).

Secondly, the PDA-based measurements are performed with a rather low rotational temperature, so that only lines originating from J'' = 0 - 2 in the ground state strongly appear with possible weak lines from J'' = 3, 4. This is confirmed in measurements of the b - X(10,0) band in ¹⁴N₂ [101], recorded under the same experimental conditions. This explains why a line at 107 629.50 cm⁻¹, labeled as Q(1)b(9) by Yoshino *et al.* [44], was not observed in the study with the PDA-system and the cold beam; that line is now assigned as the Q(6) of o(1). Also the region near 107 639.8 cm⁻¹ was scanned, initially searching for R(2-3) as in the assignment of Ref. [44], but no lines were observed. Now it is clear that this line is in fact the Q(4) line of b(9), which is expected to be very weak under the conditions employed.

The arguments given above support the present assignment of the rotational lines probing J' = 1 - 4 levels in the b(9) - o(1) complex. The assignments of rotational lines probing b(9) given by Carroll and Collins [33] are erroneous, as already discussed by Yoshino *et al.* [44]. Of course the most convincing argument for the present line assignment and analysis is the reproducibility of all lines in the fitting procedure using equations (7.1-7.5). With 113 lines included in the fit, a χ^2 of less than 50 is found when uncertainties of singly resolved lines are put at the estimated values, and somewhat higher for blended lines. This shows that the assignments are unambiguous and that the uncertainties are even underestimated.

The deperturbed rotational constant of o(1), $B = 1.7349 \text{ cm}^{-1}$, is in excellent agreement with what is expected for a Rydberg state converging on the $A^2 \Pi_u$ ionic state $[B(A, v = 0) = 1.735 \text{ cm}^{-1}, B(A, v = 1) = 1.716 \text{ cm}^{-1}[103]]$, as is the case for the $3s\sigma_a o^1 \Pi_u$ state. The B value of b(9) is significantly lower, B = 1.2278 cm^{-1} , and is appropriate for an unperturbed valence $b^1 \Pi_u$ state. The deperturbed molecular parameters of b(9) and o(1), tabulated in Table 7.5, show additional perturbations. First the D value of b(9) is small and negative, comparable to the D value of -5.5×10^{-3} cm⁻¹ in ¹⁵N₂, reported in Ref. [69]. This may indicate a weak homogeneous perturbation by a level with a larger B value from below. Second, the A-doubling parameter of o(1) has a large magnitude and is negative, which indicates that the *e*-parity levels are pushed downwards for high J levels (J > 20), while the f-parity levels are untouched. This is due to a heterogeneous interaction with the higher-lying $b'^1 \Sigma_u^+(v=6)$ valence level, which approaches o(1) from above with increasing J since b'(6) has a smaller B value than o(1), as already discussed by Yoshino et al. [44]. The b'(6) state was only studied for levels up to J = 21 and for o(1) up to J = 23, 24. The crossing between o(1) and b'(6) occurs at higher J levels than the levels studied here and therefore, no deperturbation analysis is performed.

The only clear effect of the heterogeneous interaction in the present study is the significant Λ -doubling observed for o(1). This heterogeneous interaction between o(1) and b'(6) has also been reported in ¹⁵N₂ [69].

7.4.2 Predissociation linewidths

From the PDA-based spectra, predissociation linewidths Γ were determined by deconvolving the instrument width from the observed widths as explained in Ref. [90] and are tabulated in Table 7.6.

The determined predissociation linewidths of individual rotational levels of b(9)and o(1) in ¹⁴N₂ are 0.22 - 0.25 cm⁻¹ and ~ 0.05 cm⁻¹, respectively, showing a significant difference for the two states (see Fig. 7.3). Only the widths of J = 1, 2of b(9) and J = 1 - 3 of o(1) were measured, thus only restricting to J levels before the crossing. No J and e/f-parity dependences, including effects on the widths of the perturbation between the two levels, were found. Possibly, for the most heavily mixed J = 4 - 5 levels (see Fig. 7.6) there is a perturbation effect on the widths, but these J levels could not be observed with the narrowband PDA-based laser system.

From the measured natural linewidths Γ , lifetimes τ of the excited state levels are derived using $\tau = 1/2\pi\Gamma$, resulting in average lifetimes of 23 ± 5 ps and 105 ± 30 ps for b(9) and o(1), respectively. The lifetimes agree with time-domain pump-probe lifetime measurements [88]. In Ref. [88], the rotational structure of the b(9)/o(1)complex was not resolved and lifetimes observed varied from lower than 50 ps to 110 ps. From the present study it can be decided unambiguously that b(9) belongs to the pump-probe lifetimes lower than 50 ps and o(1) to the value of 110 ps.

The lifetimes of these two levels in ${}^{15}N_2$ have been determined with the same frequency mixing PDA-based XUV source in Ref. [101]. For b(9) in ${}^{15}N_2$ a lifetime of 46 ± 7 ps was found, applying to the *f*-parity levels only, a factor 2 higher than in ${}^{14}N_2$. Also the lifetime of o(1) is isotope dependent: a lifetime of 27 ± 6 ps was obtained for this level in ${}^{15}N_2$ in Ref. [101], a factor 4 lower than in ${}^{14}N_2$.

Table 7.6: Experimental predissociation linewidths (in cm⁻¹ FWHM) for the $b^1\Pi_u(v=9)$ and $o^1\Pi_u(v=1)$ levels of ¹⁴N₂.

Level	J	Γ_e	Γ_f
$b^1 \Pi_u (v=9)$	1	0.25(4)	
	2		0.22(2)
$o^1 \Pi_u (v=1)$	1		0.05(1)
	2	0.06(1)	
	3	0.04(1)	

The two lifetimes obtained in this study extend the database (see Refs. [90, 101] and references cited therein) on lifetimes of the singlet *ungerade* states $({}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{u})$ in N₂, which is important in understanding the predissociation behavior of these states (see Chapter 10). These two lifetimes again show that the lifetimes of the singlet *ungerade* states in N₂ depend on vibrational level (see for other lifetimes the database cited above) and that isotopic differences in lifetimes generally occur for these states.

7.4.3 The isotopic states

The b(9) and o(1) levels in ¹⁴N¹⁵N do not cross because the b(9) level shifts more downwards in energy than the o(1) level by the isotopic substitution. Therefore in ¹⁴N¹⁵N, the order of the two states is the reverse and the lower-lying b(9) level with a smaller *B* value does not cross the higher-lying o(1), which has a larger *B* value. These states has been studied in ¹⁵N₂ in Ref. [69] and the b(9) level has shifted even more downwards in energy compared to o(1) than in ¹⁴N¹⁵N and also no crossing exists. The *B* values are slightly lower in the heavier isotopomers due to the increasing reduced mass. The *B* values and band origins of b(9) and o(1)of ¹⁴N¹⁵N in Table 7.5 are in reasonable agreement with calculated values from a comprehensive perturbation model [69].

Vibrational isotope shifts are defined as the band origin in ${}^{14}N_2$ minus that in the heavier isotopomer and are given for both ${}^{14}N^{15}N$ and ${}^{15}N_2$ in Table 7.7. Yoshino *et al.* [44] determined isotope shifts of the *Q*-branch heads of the o-X(1,0)system for ${}^{14}N^{15}N$ and ${}^{15}N_2$, but because of the incorrect assignment of the ${}^{14}N_2$ head, these previous isotope shifts are not discussed here. Note that the *Q*-branch head in ${}^{14}N^{15}N$ of Yoshino *et al.* nicely agrees with the present line position for Q(1). The ${}^{15}N_2$ isotope shifts in Ref. [69] are also not correct since the ${}^{14}N_2$ band origins of Yoshino *et al.* were used.

Table 7.7: Isotope shifts of band origins (in cm⁻¹) for the $b^1 \Pi_u(v=9)$ and $o^1 \Pi_u(v=1)$ levels.

Level	$^{14}\mathrm{N}^{15}\mathrm{N}$	${}^{15}\mathrm{N}_2{}^a$
$b^1\Pi_u(v=9)$	101.20	202.58
$o^1 \Pi_u (v=1)$	27.74	58.17

^{*a*} Band origins of ${}^{15}N_2$ were taken from Ref. [69].

7.5 Conclusions

An 1 XUV + 1 UV ionization spectroscopic study on the $o^1 \Pi_u (v=1)/b^1 \Pi_u (v=9)$ Rydberg-valence complex in ¹⁴N₂ has been performed and a new rotational analysis has been made of the homogeneous perturbation between the two levels, resulting in new rotational line assignments and spectroscopic parameters. Furthermore, the $b'^{1}\Sigma_{u}^{+}(v=6)$ level in ¹⁴N₂ and its heterogeneous interaction with o(1) has been investigated as well. Also, the b(9) and o(1) levels in ¹⁴N¹⁵N have been studied, showing no homogeneous perturbation between the two levels, at least not in the form of an avoided crossing, because the order of the levels is the reverse compared with ${}^{14}N_2$ and the levels are much more separated in energy due to the different isotope shifts of the levels. It is noted that the present model for o(1)/b(9), that provides an explanation for the line positions at the level of accuracy of the experiment, is a *local* two-state deperturbation analysis. The two levels are also part of strong Rydberg-valence interactions with the entire manifold of singlet ungerade states, as described in Refs. [34, 39, 87]. From linewidths measurements for ${}^{14}N_2$, lifetimes have been determined, which are different for the b(9) and o(1) levels. These lifetimes are important in developing and extending predissociation models (see Chapter 10) for the ${}^{1}\Pi_{u}$ states of N₂.

Chapter 8

Optical observation of the $3s\sigma_g F^3\Pi_u$ Rydberg state of N_2

Using ultrahigh-resolution 1 XUV + 1 UV two-photon ionization laser spectroscopy, the $F^{3}\Pi_{u} \leftarrow X^{1}\Sigma_{g}^{+}(0,0)$ transition of N₂ has been optically observed for the first time, and the $3s\sigma_{g}F^{3}\Pi_{u}(v=0)$ Rydberg level fully characterized with rotational resolution. The experimental spectroscopic parameters and predissociation level widths suggest strong interactions between the F state and the $3p\pi_{u}G^{3}\Pi_{u}$ Rydberg and $C'^{3}\Pi_{u}$ valence states, analogous to those well-known in the case of the isoconfigurational ${}^{1}\Pi_{u}$ states.

8.1 Introduction

Knowledge of N₂ spectroscopy and dissociation dynamics in the extreme ultraviolet (XUV) region is essential for a proper understanding of the radiative and photochemical processes occurring in nitrogen-rich planetary atmospheres. The lowest dipole-allowed transitions from the $X^{1}\Sigma_{g}^{+}$ state of N₂, which occur above ~ 100 000 cm⁻¹ in the XUV, result from the excitation of highly-mixed Rydberg and valence states of ${}^{1}\Pi_{u}$ and ${}^{1}\Sigma_{u}^{+}$ symmetry [34, 39]. While these states and their interactions have been well studied, both experimentally and theoretically, their predissociation mechanisms are not well understood. For example, although it has been confirmed very recently that the lowest ${}^{1}\Pi_{u}$ states of N₂ predissociate by spin-orbit coupling to the ${}^{3}\Pi_{u}$ manifold [87], experimental information on the spectroscopy and dissociation dynamics of the relevant ${}^{3}\Pi_{u}$ states is very limited. In particular, lack of information on the ${}^{3}\Pi_{u}$ *Rydberg* states has restricted the N₂ predissociation model of Ref. [87] to a consideration of only the lowest ${}^{1}\Pi_{u}$ levels.

The lowest Rydberg states of N₂ which are members of series converging on the $X^{2}\Sigma_{g}^{+}$ core of N₂⁺ are the well-known gerade states $3s\sigma_{g} a''^{1}\Sigma_{g}^{+}$ and $3s\sigma_{g} E^{3}\Sigma_{g}^{+}$,

with v = 0 levels near 99 000 cm⁻¹ and 96 000 cm⁻¹, respectively [103]. The lowest ungerade Rydberg states arise from the 3p-complex [57] in the 103 000–105 000 cm⁻¹ energy region, comprising $3p\sigma_u c'^{1}\Sigma_u^+$, $3p\sigma_u D^{3}\Sigma_u^+$, $3p\pi_u c^{1}\Pi_u$, and $3p\pi_u G^{3}\Pi_u$. While only the first three of these states are known from optical spectroscopy [103], the nomenclature G for the ${}^{3}\Pi_u$ state has been employed for some time [70, 104, 105, 106, 107], somewhat confusingly, given the use of the same nomenclature for the ${}^{3}\Delta_g$ valence state of N₂ near 88 000 cm⁻¹ [103]. The lowest Rydberg states of N₂ which are members of series converging on the $A^{2}\Pi_u$ core of N₂⁺ are the $3s\sigma_g o^{1}\Pi_u$ and $3s\sigma_g F^{3}\Pi_u$ states, in the 105 000–106 000 cm⁻¹ energy region. The c and o states are the Rydberg members of the ${}^{1}\Pi_u$ manifold accessed in the first allowed transitions of N₂, while the F and G states are the Rydberg members of the ${}^{3}\Pi_u$ manifold responsible for the ${}^{1}\Pi_u$ predissociation.

The ${}^{3}\Pi_{u} \leftarrow X {}^{1}\Sigma_{g}^{+}$ transitions of N₂ are optically forbidden and the only previously published assignments of levels of the *F* and *G* states have been in lowresolution electron energy-loss (EEL) [104, 105, 106] and photofragment (PF) [107] spectra. These assignments, which were not based on rotational analyses since the applicable experimental bandwidths were $\geq 200 \text{ cm}^{-1}$ full-width at half-maximum (FWHM), must, therefore, remain in doubt. In particular, the question of the vibrational numbering of the F(v) levels has been controversial, with Leoni and Dressler [70] invoking a diffuse F(v = 0) level near 102 900 cm⁻¹ in order to explain the strong predissociation of the $b {}^{1}\Pi_{u}(v = 3)$ valence level, while Robbe [63] argued against this assignment, suggesting, on theoretical grounds, that the F(v = 0) level lay at a significantly higher energy. This matter has been settled convincingly only by the PF study of van der Kamp *et al.* [107], who found the F(v = 0) level at 104 500(160) cm⁻¹. ¹

Here, we present the results of an ultrahigh-resolution laser-spectroscopic study of the $F \leftarrow X(0,0)$ transition of ¹⁴N₂. This dipole-forbidden transition becomes observable, apparently through the indirect spin-orbit borrowing of intensity from the dipole-allowed $b \leftarrow X(5,0)$ transition, facilitated by the near-degeneracy of the F(v = 0) and b(v = 5) levels in the normal isotopomer. This study represents the first reported observation of the F state in an optical transition, and is the first to provide spin- and rotationally-resolved spectroscopic data. In addition, the excellent experimental resolution enables the F(v = 0) predissociation level widths to be determined for the first time, information expected to be crucial to the extension of N₂ predissociation models to higher energies than presently applicable.

¹Throughout this work, numbers in parentheses represent 1σ uncertainties, in units of the least significant figure.

8.2 Experimental method

The experimental setup was similar to the system used in our previous ultrahighresolution laser-spectroscopic studies of N_2 [69, 90], except that the system was modified and significantly improved in order to observe the extremely weak signal levels expected for a dipole-forbidden transition, such as $F \leftarrow X(0,0)$. Briefly, a narrowband tunable dye laser, pumped by a 532-nm Millennia-V laser, injection seeded a pulsed dye amplifier (PDA). The Nd:YAG pump laser for the PDA was changed from a Spectra-Physics GCR-5 to a Spectra-Physics GCR-330, which gives higher energies (750 mJ per pulse and 1 J per pulse, respectively) and has a better beam profile. The PDA configuration was slightly changed to improve the overlap of the pump beam with the seed laser in the dye cells. A carefully optimized mixture of Rhodamine 6G and Rhodamine B was used as dye mixture in the PDA, since the dyes individually did not cover the required wavelength range (572.0-573.5 nm). A KD*P crystal frequency doubled the output of the PDA into the UV and, subsequent frequency tripling in a pulsed N_2 jet generated XUV radiation. In our previous experiments, a xenon jet was used but, at these particular wavelengths (95.40–95.55 nm), more XUV was produced with N_2 as the tripling medium. These changes and optimizations resulted in typical UV powers of 50 mJ per pulse. The collinearly propagating XUV and remaining UV beams were crossed with a pulsed N_2 jet in a separate chamber where the spectroscopic measurements were performed. The $F \leftarrow X(0,0)$ band was recorded using 1 XUV + 1 UV two-photon ionization spectroscopy, where the XUV photon accessed the F - X transition and, subsequently, the UV photon ionized the excited molecules. The resultant N_2^+ ions were detected in a time-of-flight electron-multiplier detection system. The distance between the nozzle and the skimmer was decreased to a few mm to increase the ion signal. This resulted in the N₂ gas pressure increasing in the interaction chamber to 4×10^{-5} mbar, with typical pressures of 3 bar behind the nozzle. Only with this nozzle-skimmer configuration and gas pressure were N_2^+ ions corresponding to F(v=0) excitation detected. An étalon and an I₂-saturated absorption setup provided absolute frequency calibration, which was performed in the visible using the output of the cw-ring dye laser.

In Fig. 8.1, the instrumental width of the experimental system is demonstrated using a scan over the R(1) line of the $b' {}^{1}\Sigma_{u}^{+} \leftarrow X {}^{1}\Sigma_{g}^{+}(2,0)$ transition in ${}^{14}N_{2}$, performed under the same experimental conditions as for the F - X(0,0) measurements. This line was measured also with the nozzle located 10 cm from the skimmer and compared with scans over low-rotational lines from the $b \leftarrow X(1,0)$ band. The b(v = 1) level in ${}^{14}N_{2}$ is long-lived ($\tau = 2610(100)$ ps [85]) and, therefore, the experimental widths of lines reaching this level are mainly instrument limited [90]. The R(1) line of b' - X(2,0) was, with the nozzle at 10 cm, only marginally broader than the b - X(1,0) lines. Therefore, the scan over the b' - X(2,0) line in Fig. 8.1 essentially defines the instrumental width applicable to the F - X(0,0) measurements. Fitting of a Voigt profile to the scan (effective resolution 0.057 cm⁻¹ FWHM) yielded a Doppler component of 0.041(1) cm⁻¹ FWHM, together with a Lorentz component of 0.029(2) cm⁻¹ FWHM. These values were used in the analysis of all experimental F - X(0, 0) profiles.



Figure 8.1: 1 XUV + 1 UV ionization spectrum of the R(1) line of the b' - X(2,0) band in ¹⁴N₂ (open circles), recorded under the same experimental conditions as used for the F - X(0,0) measurements, fitted with a Voigt profile (solid line). The very small asymmetry of the line is possibly due to a slight misalignment of the nozzle and skimmer.

8.3 Results and discussion

In a number of short experimental scans over the region 104 705–104 765 cm⁻¹, we observed structure which, as will be become clear, was due to the F - X(0,0)transition. These results are summarized in the composite spectrum of Fig. 8.2, in which some channel averaging has been performed for clarity, while not significantly compromising the widths of the narrowest features. The F - X(0,0) lines are notably diffuse, characterized by near-Lorentzian line shapes, indicating a strong degree of predissociation of the F(v = 0) level. Four narrower lines, marked with asterisks in Fig. 8.2, contaminate the spectrum. These lines have distinctly different profiles from the F - X(0,0) lines, and are characterized by an essentially Gaussian line shape with a FWHM of ~ 0.25 cm⁻¹, corresponding to the room-temperature Doppler profile of the N₂ background gas. They are high-rotational lines from



Figure 8.2: Composite 1 XUV + 1 UV ionization spectrum of the F - X(0,0) band of ¹⁴N₂, including partial line assignments for the three spin subbands. The P and Q branches of the low-energy subband are not detectable, as they are obscured by the rapidly rising signal from the dipole-allowed transition b - X(5,0) (extreme left of figure), while the higher R-branch lines in the high-energy subband are too weak to observe (extreme right of figure). Narrower lines marked with an asterisk are high-rotational lines from higher-lying dipole-allowed transitions (see text).

higher-lying allowed transitions, specifically, P(21), R(23), and P(20) from the b' - X(2,0) band, at 104 712.61 cm⁻¹, 104 738.27 cm⁻¹, and 104 750.48 cm⁻¹, respectively, and P(29) from the b - X(6,0) band at 104 726.37 cm⁻¹.

The clearest features in Fig. 8.2 are P, Q, and R branches in the central region, near 104 730 cm⁻¹. Combination differences confirm that these arise from the ground state of ¹⁴N₂, and they can be associated with the central $F(v = 0, \Omega = 1) - X(v = 0)$ subband. In the low-energy region of Fig. 8.2, near 104 710 cm⁻¹, a returning R-branch can be identified, corresponding to the $F(v = 0, \Omega = 2) - X(v = 0)$ subband, since we could not find any corresponding R(0) transition. Finally, in the high-energy region of Fig. 8.2, near 104 755 cm⁻¹, an overlapped Q head, together with R(0), and, possibly, R(1) lines, appear very weakly, corresponding to the $F(v = 0, \Omega = 0) - X(v = 0)$ subband. These observations confirm that the ³ Π_u upper state of the observed transition is inverted, as indeed expected for the



Figure 8.3: Typical ionization spectrum of the R(0) line of the central F - X(0,0) subband (solid line), fitted with a Voigt profile (open line). Assumption of an instrumental profile as in Fig. 8.1 yields a predissociation linewidth of 0.45 cm⁻¹ FWHM.

 $3s\sigma_g F^3\Pi_u$ Rydberg state, the first member of a series converging on the firstexcited state of N_2^+ , $A^2\Pi_u$, which is known to be inverted [108].

The individual scan segments in Fig. 8.2 were not all performed with the same experimental sensitivity. Nevertheless, it was clear that the subband intensities decreased significantly as their energy increased, consistent with the view that the F - X(0,0) transition borrows its intensity from the lower-lying dipole-allowed b - X(5,0) transition. For example, the b(v = 5) level at 104 700 cm⁻¹ is nearly degenerate with the $F(v = 0, \Omega = 2)$ sublevel, but some 50 cm⁻¹ lower in energy than $F(v = 0, \Omega = 0)$, leading to much greater intensity borrowing in the former case. The most likely coupling mechanism leading to the intensity borrowing is indirect spin-orbit coupling between the $b^{1}\Pi_{u}(v = 5, \Omega = 1)$ and $F^{3}\Pi_{u}(v = 0, \Omega = 1)$ levels, assisted by rotation-dependent **S**-uncoupling between the *F*-state triplet sublevels.

In order to obtain precise experimental line positions and predissociation widths, we performed Voigt profile analyses on the individual F - X(0,0) lines, using a least-squares fitting procedure and correcting for the effects of instrumental resolution, including Doppler broadening. A typical fit is shown in Fig. 8.3, for the case of the R(0) line of the central subband, yielding a residual Lorentzian linewidth of 0.45 cm⁻¹ FWHM, attributable to predissociation. In the case of significantly overlapped pairs of lines, e.g., the R(3) and R(4) lines of the lower subband, the individual linewidths were tied to a single value, determined by the fit, together with the individual line positions, albeit with greater uncertainties. In the case of the Q branch of the upper subband, which contains six lines, the individual line spacings were fixed according to an initial estimate of the appropriate F-state rotational constant, and a single linewidth and overall position were determined by the fit, nominally associated with the Q(2) line, the peak of which was distinguishable in the experimental spectrum. The resultant experimental line positions and predissociation linewidths are summarized in Tables 8.1 and 8.2, respectively, the greater uncertainties associated with the analysis of blended or weak features. Finally, the transition wave numbers in Table 8.1 were combined with the appropriate $^{14}N_2$ ground-state terms [40], to form rotational term values for the F(v = 0) state, which were then fitted using the $^{3}\Pi$ Hamiltonian of Brown and Merer [109], yielding the spectroscopic parameters given in Table 8.3.

Table 8.1: Wave numbers for rotational lines observed in the $F^{3}\Pi_{u} \leftarrow X^{1}\Sigma_{g}^{+}(0,0)$ band system of ¹⁴N₂, in cm⁻¹. Uncertainties include calibration and statistical contributions.

Ω'	J''	P(J'')	Q(J'')	R(J'')
0	0			$104\ 757.133(17)$
	1			$104\ 761.406(35)$
	2	$104\ 745.180(35)$	$104\ 753.636(17)$	
1	0			$104\ 733.656(11)$
	1		$104 \ 729.664(12)$	$104\ 736.703(11)$
	2	$104\ 721.711(11)$	$104\ 728.742(11)$	$104\ 739.336(11)$
	3	$104\ 716.820(13)$	$104\ 727.398(11)$	$104\ 741.570(11)$
	4		$104\ 725.672(11)$	$104\ 743.469(11)$
	5		$104\ 723.578(19)$	$104\ 744.992(28)$
	6		$104\ 721.141(12)$	$104\ 746.156(12)$
	7		$104\ 718.359(25)$	$104\ 747.016(32)$
	8			104 747.500(32)
2	1			$104\ 708.117(12)$
	2			$104\ 709.641(11)$
	3			$104\ 710.438(19)$
	4			$104\ 710.625(18)$
	5			104 710.117(30)

The experimental F(v = 0)-state energy in Table 8.3, $\nu_0 = 104$ 727 cm⁻¹, differs from previous PF [107] and EEL² [104, 105, 106] values by ~ 230 cm⁻¹ and ~ 10 - 40 cm⁻¹, respectively, differences within, or similar to, the combined

²The previous EEL studies had misassigned F(v = 0) as F(v = 1).

	$\Omega =$	= 0	$\Omega =$	= 1	$\Omega = 2$
J	Γ_e	Γ_f	Γ_e	Γ_f	Γ_e
1	0.57(8)		0.45(3)	0.41(4)	
2			0.45(3)	0.45(3)	0.35(3)
3			0.46(3)	0.45(4)	0.40(3)
4		0.48(6)	0.48(4)	0.45(3)	
5			0.51(4)	0.45(5)	0.39(4)
6			0.49(10)	0.34(4)	
7			0.46(5)	0.46(10)	

Table 8.2: Experimental predissociation level widths for the $F^{3}\Pi_{u}(v = 0)$ state of ¹⁴N₂, in cm⁻¹ FWHM.

Table 8.3: Experimental spectroscopic parameters for the $F^{3}\Pi_{u}(v = 0)$ state of ¹⁴N₂, in cm⁻¹.

Param.	This work	Previous work
$ u_0 $	$104\ 727.41(10)^a$	$\nu_0 = 104 \ 500(160) \ (\text{Ref.} \ [107])$
B	1.8028(1)	$\nu_0 = 104 \ 690(40) \ (\text{Ref.} [104])$
A	-21.82(1)	$\nu_0 = 104 \ 690(40) \ (\text{Ref.} [105])$
λ	0.302(3)	$\nu_0 = 104 \ 740(40) \ (\text{Ref.} [106])$
0	0.072(5)	
p	0.0046(14)	
q	-0.0021(8)	
a D + +	1 5	(1)/2 + 2D = 104.720.01(10) = 1

^{*a*} Rotationless F_2 energy = $\nu_0 - 4\lambda/3 + 2B = 104\ 730.61(10)\ \mathrm{cm}^{-1}$.

experimental uncertainties in each case, but the present measurement is much more precise. The rotational constant, $B = 1.803 \text{ cm}^{-1}$, is consistent with our Rydbergstate assignment, but is a little greater than expected for a Rydberg state built on the $A^2\Pi_u$ ionic core $(B(A, v = 0) = 1.735 \text{ cm}^{-1} [103])$, suggesting significant mixing with a state carrying a higher rotational constant, such as the $3p\pi_u G^3\Pi_u$ Rydberg state, the lowest member of a series converging on the $X^2\Sigma_g^+$ ionic core $(B(X, v = 0) = 1.922 \text{ cm}^{-1} [103])$. The spin-orbit coupling constant, $A = -21.8 \text{ cm}^{-1}$, while consistent with the expectation of an inverted F state, has a magnitude somewhat less than that expected for a Rydberg ${}^3\Pi_u$ state built on the $A^2\Pi_u$ ionic core, i.e., $A \approx \frac{1}{2}A[N_2^+(A^2\Pi_u)] \approx -37 \text{ cm}^{-1} [57, 87]$, suggesting mixing with a state having a more positive A value. This difference is also consistent with mixing between the F and G states, since a Rydberg ${}^3\Pi_u$ state built on the $X^2\Sigma_g^+$ ionic core would be expected to have $A = a_{3p\pi_u} \approx \zeta_{3p_N} \approx +2 \text{ cm}^{-1} [57, 87]$. a and ζ are single-electron molecular and atomic spin-orbit parameters, respectively.

The mixing postulated above between the F and G states can be confirmed semiquantitatively. If we consider a simple two-level interaction between "pure" Rydberg F(v = 0) and G(v = 0) states having $B = 1.735 \text{ cm}^{-1}$, $A = -37 \text{ cm}^{-1}$, and B = 1.922 cm⁻¹, A = +2 cm⁻¹, respectively, with leading wave-function coefficients of 0.82^{3} , then the effective values for the mixed F level will become $B = 0.82^2 \times 1.735 + (1 - 0.82^2) \times 1.922 = 1.796 \text{ cm}^{-1}$, and, by similar reasoning, $A = -24.2 \text{ cm}^{-1}$. These values are in good agreement with our experimental values of 1.803 cm^{-1} and -21.8 cm^{-1} , respectively. Similarly, the effective values for the correspondingly-mixed G level will be $B = 1.861 \text{ cm}^{-1}$ and $A = -10.8 \text{ cm}^{-1}$, the G state becoming *inverted* due to the interaction. We have recently become aware of an unpublished ultrahigh-resolution study of the $G^{3}\Pi_{u} \leftarrow E^{3}\Sigma_{a}^{+}(0,0)$ transition, using near-infrared diode-laser spectroscopy, which yielded the results $B = 1.864 \text{ cm}^{-1}$ and $A = -8.17 \text{ cm}^{-1}$, for the G(v = 0) level [92, 110]. The Refs. [92, 110] B value for the G(v = 0) state has been adjusted to be consistent with the same Brown and Merer Hamiltonian (Ref. [109]) that we have used here for analysis of the F(v=0) state. So, our two-level model of strong mixing between F(v=0) and G(v=0) is in good agreement also for the G state.

Using similar arguments, it is possible also to explain the observed value of λ in Table 8.3. The effective spin-spin constant $\lambda^{\text{eff}} = \lambda^{\text{SS}} + \lambda^{\text{SO}}$, where λ^{SS} is the true spin-spin constant and λ^{SO} is the contribution from second-order isoconfigurational spin-orbit interaction [57]. Semiempirical estimates [57] in the case of the "pure" $\pi_u^3 \sigma_q F^3 \Pi_u(v=0)$ state yield: $\lambda^{SS} = -3\eta/2 = -0.21 \text{ cm}^{-1}$, where $\eta = 0.14 \text{ cm}^{-1}$ is the atomic spin-spin parameter for N [57]; $\lambda^{SO} = A^2/2\Delta E = 0.72 \text{ cm}^{-1}$, where $A = -37 \text{ cm}^{-1}$ is the spin-orbit constant for the pure F state, and $\Delta E = 950 \text{ cm}^{-1}$ is the energy separation between the isoconfigurational $F^{3}\Pi_{u}(v=0)$ and $o^{1}\Pi_{u}(v=0)$ 0) levels; and thus $\lambda^{\text{eff}} = 0.51 \text{ cm}^{-1}$. In the case of the "pure" $\sigma_q \pi_u G^3 \Pi_u (v=0)$ state, $\lambda^{\text{eff}} = \lambda^{\text{SS}} = -0.21 \text{ cm}^{-1}$ [57], since λ^{SO} is negligible, owing to the low A value for the G state, which is a member of a Rydberg series converging on a closed-shell ionic core. If we now introduce the mixing postulated above between the F(v = 0) and G(v = 0) states, in the case of the mixed F state, we find $\lambda^{\text{eff}} = 0.82^2 \times 0.51 + (1 - 0.82^2) \times (-0.21) = +0.27 \text{ cm}^{-1}$, in good agreement with the experimental value of 0.30 cm^{-1} in Table 8.3, and confirming the dominant role of $\lambda^{\rm SO}$, which certainly determines the sign of the observed effective spin-spin constant. Similarly, in the case of the mixed G state, $\lambda^{\text{eff}} = +0.03 \text{ cm}^{-1}$, in good agreement with the experimental value of Refs. [92, 110] (-0.011 cm^{-1}) . Thus, in this latter case, the true spin-spin constant of the pure G state is essentially counterbalanced by the isoconfigurational spin-orbit contribution borrowed from the F state, giving a near-zero effective value. Overall, it is clear that a simple $\sim 2:1$ mixing between the F(v=0) and G(v=0) levels is all that is needed to semiquantitatively explain the observed B, A, and λ values for each level.

 $^{^{3}\}mathrm{A}$ coefficient of 0.82 results in the best overall fit of this simple model to experiment.

The experimental predissociation level widths in Table 8.2 show little rotational dependence, no e/f-parity dependence, and only a slight tendency to decrease as Ω increases from 0 to 2. The most likely predissociation mechanism is electrostatic interaction with the $C' {}^{3}\Pi_{u}$ valence state, rather than a spin-orbit process. The C' potential-energy curve crosses the outer limb of the F-state curve well above the v = 0 level [87], so a strong, possibly multistate, interaction will be required to explain the large average experimental predissociation level width of ~ 0.45 cm⁻¹ FWHM.

8.4 Summary and conclusions

We have optically observed the F - X(0, 0) transition for the first time and characterized the $3s\sigma_g F^3\Pi_u(v=0)$ Rydberg level with rotational resolution. The experimental spectroscopic parameters and predissociation level widths suggest strong interactions between the F state and the $3p\pi_u G^3\Pi_u$ Rydberg and $C'{}^3\Pi_u$ valence states, analogous to those well-known in the case of the isoconfigurational ${}^1\Pi_u$ states [34, 39, 87]. This new experimental information will prove valuable in the extension of existing N₂ coupled-channel predissociation models [87] to higher energies.

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Chapter 9

Newly observed triplet states and singlet-triplet interactions in the XUV spectrum of N_2

9.1 Introduction

Using the PDL-based and the PDA-based XUV sources, as described before in this Thesis (see for example Chapters 2 and 6), several hitherto unobserved triplet states and singlet-triplet interactions were found in N₂. Transitions from the $X^1\Sigma_g^+$ ground state to these triplet ungerade (${}^{3}\Sigma_u^+$ and ${}^{3}\Pi_u$) states are forbidden by the $\Delta S = 0$ selection rule. However, due to local spin-orbit interactions with ${}^{1}\Pi_u$ states, which carry large oscillator strengths in excitation from the ground state, transitions to some triplet ungerade states borrow intensity and become observable. The first optical observation of the $F^{3}\Pi_u(v=0)$ level in ${}^{14}N_2$ has already been reported in Chapter 8, while in this Chapter, results on several other triplet states are presented, including transition energies, line assignments, linewidths and rotational and local deperturbation analyses.

The absolute wavenumber uncertainty for the lines recorded with the PDL-based XUV system is $\pm 0.2 \text{ cm}^{-1}$, while for the PDA-based source the uncertainty is $\pm 0.003 \text{ cm}^{-1}$. For those PDA spectra showing significant lifetime and/or Doppler broadening, the uncertainty increases to $\pm 0.02 \text{ cm}^{-1}$. Some of the PDA-based measurements were performed with a nozzle-skimmer distance of 150 mm to reduce the Doppler broadening. However, due to the low rotational temperature in the gas expansion, only low rotational levels were populated and only levels with $J \leq 5$ were studied. To observe higher J levels, the nozzle-skimmer distance was reduced to 0 mm to increase the signal sensitivity and the rotational temperature of the gas jet, producing, however, also a significant increase in Doppler broadening (see

As already mentioned in Chapters 2 and 6, a perturbation is found in the $c_3{}^1\Pi_u(v = 1)$ level near J = 1 - 12 in ${}^{15}N_2$, for both e and f parity levels. The PDL-based spectrum has already been presented in Chapter 2 and the Appendix, while the PDA-based results have briefly been discussed in Chapter 6, without interpreting this perturbation in detail. Note that these PDA-based measurements were performed using the frequency mixing scheme: $\omega_{XUV} = 3\omega_{PDA} + 3\omega_{Nd:YAG}$ and the absolute wavenumber uncertainty (in the XUV) is ± 0.01 cm⁻¹ for the narrowest spectral lines (see Chapter 6), while for lines where Doppler broadening is of importance, the uncertainty is ± 0.02 cm⁻¹.

Here, a more detailed picture is given of this perturbation. For both e and f parity levels, three crossings are found in the range J = 1 - 12; between J = 3, 4, J = 7, 8 and J = 10, 11 and some extra weak lines appear in the XUV spectrum near the first crossing. A crossing with a higher lying ${}^{3}\Pi_{u}$ valence state with a smaller B value is the most likely candidate. The perturbation is then governed by a weak spin-orbit interaction. From the coupled-channel Schrödinger equations (CSE) model (see Chapter 10), the perturbing state is identified as the $C^{3}\Pi_{u}$ valence state, with v = 14 the most probable vibrational level, and with crossings of the sublevels $C_{\Omega=2/0}$ at $J = 3, 4, C_{\Omega=1}$ at J = 7, 8 and $C_{\Omega=0/2}$ at J = 10, 11. It is not known yet if the C(14) level is inverted or not, so that the lowest crossing near J = 3, 4 can be due to $C_{\Omega=0} - X$ or $C_{\Omega=2} - X$ subband. Since the Λ -doubling found experimentally for the lowest sublevel is small (see below), the preferable assignment is $C_{\Omega=2}$ and C(14) is preferably inverted. In the present study, the lowest sublevel is labeled as $C_{\Omega=2/0}$ and the highest sublevel as $C_{\Omega=0/2}$.

PDA-based 1 XUV + 1 UV ionization spectra of the lowest J lines of the R and Q branches of the $c_3{}^1\Pi_u - X^1\Sigma_g^+$ (1,0) band in ${}^{15}N_2$, together with several lines of the $C^3\Pi_{u\Omega=2/0} - X^1\Sigma_g^+$ (14,0) band are presented in Figs. 9.1 and 9.2. Observed transition energies and line assignments of the $c_3 - X(1,0)$ and $C_{\Omega=2/0} - X(14,0)$ bands in ${}^{15}N_2$ are given in Tables 9.1 and 9.2, respectively. Reduced term values of the f parity levels of $c_3(1)$ and $C_{\Omega=2/0}(14)$ are presented in Fig. 9.3, clearly showing the level shifts near the crossings. In Figs. 9.1 and 9.2, the effect of the lowest crossing near J = 3, 4 is also visible. Due to the perturbation, the lines are shifted in energy and the result is that the R(3-5) lines are very close to each other and Q(4) is significantly shifted towards Q(3). Hence, the rotational structure is irregular. Although it is hazardous to rely on intensities, it is obvious that Q(4) in Fig. 9.2 is weaker than expected. Although for ${}^{15}N_2$ the nuclear spin I = 1/2

Table 9.1: Observed transition energies for the $c_3{}^1\Pi_u - X^1\Sigma_g^+$ (1,0) band in ${}^{15}N_2$ from PDA spectra, together with $c_3{}^1\Pi_u(v=1)$ term values. Lines marked with s are derived from the shoulder of a neighbouring line in the spectrum. All values in cm⁻¹.

J''	R(J)	Q(J)	P(J)	J	T_e	T_{f}
0	106452.040					
1	106454.582	106448.308		1	106452.038	106452.023
2	106456.473	106447.097	106440.890	2	106458.306	106458.243
3	106459.297	106445.243	106436.024	3	106467.619	106467.534
4	106459.352	106444.390	106430.503	4	106481.590	106481.541
5	$106459.278\mathrm{s}$	106440.610	106425.868	5	106496.503	106496.334
6	106457.908	106436.772	106418.497	6	106515.005	106514.783
7	$106458.952\mathrm{s}$	106431.826	106410.996	7	106535.917	106535.837
8	106456.479	106429.360	106402.192	8	106562.946	106563.083
9	106453.177	$106423.209\mathrm{s}$	106395.800	9	106590.191	$106590.355\mathrm{s}$
10		106416.511	106385.901	10	106620.317	106620.790
11	106445.968	$106411.254\mathrm{s}$	106375.190	11	106655.805	$106656.374\mathrm{s}$
12	106439.869	106402.685	106366.137	12	106691.086	106692.353
13	106432.629	106393.808	106353.161	13	106729.532	106731.731
14	106424.178	106384.035	106339.650	14	106770.552	106773.917
15	106414.487	106373.227		15	106814.060	106818.770
16	106403.663	106361.225		16	106860.030	106866.131
17	106391.881	106347.961		17	106908.569	106915.928
				18	106959.848	

Table 9.2: Observed transition energies for the $C^3 \Pi_{u\Omega=2/0} - X^1 \Sigma_g^+$ (14,0) band in ¹⁵N₂ from PDA spectra, together with $C^3 \Pi_{u\Omega=2/0}(v =$ 14) term values. Line marked with s is derived from the shoulder of a neighbouring line in the spectrum. All values in cm⁻¹.

J''	R(J)	Q(J)	P(J)	J	T_e	T_{f}
3	106456.706	106449.940		3	106472.250	106472.231
4		106441.796	106435.099	4	106478.996	106478.947
5		106434.179	$106423.271\mathrm{s}$	5		106489.903



Figure 9.1: 1 XUV + 1 UV ionization spectrum for the R branch of the $c_3{}^1\Pi_u - X^1\Sigma_g^+(1,0)$ band in ${}^{15}N_2$ recorded with the PDA-based XUV source. (a): recording with nozzle-skimmer distance = 150 mm. (b): recording with nozzle-skimmer distance = 0 mm. Due to the perturbation, the R(3) line of the $C^3\Pi_{u\Omega=2/0} - X^1\Sigma_g^+(14,0)$ band becomes observable and the R lines of the $c_3 - X(1,0)$ band show an irregular structure.

and even lines are three times weaker than odd lines, Q(4) is weaker than Q(3) and Q(5) by more than a factor of three. Its weakness is due to the perturbation by the C(14) state. As can be seen in Fig. 9.3, J = 4 of $c_3(1)$ is strongly perturbed by and is thus mixed with $C_{\Omega=2/0}(14)$, resulting in J = 4 of $c_3(1)$ having some triplet C(14) character and the $Q(4) c_3 - X(1, 0)$ line losing some of its intensity. Additionally, the width of this line becomes larger due to the mixing with the triplet state (see below) and hence, this line appears even more weakly in the 1 XUV + 1 UV ionization spectrum, because of the competition between predissociation and ionization. On the other hand, for example, R(3), Q(4) and P(5) of $C_{\Omega=2/0}-X(14,0)$ appear in the spectrum. Because of the spin-orbit interaction, J = 4 of $C_{\Omega=2/0}(14)$ has significant singlet $c_3(1)$ character and the R(3), Q(4) and P(5) lines of $C_{\Omega=2/0} - X(14,0)$ borrow intensity from the spin-allowed $c_3 - X(1,0)$ transition. In addition, other lines of $C_{\Omega=2/0} - X(14,0)$ were found, corresponding to J = 3,5 of the upper state, which are also affected by the perturbation.

A local deperturbation analysis of the $C_{\Omega=2/0}(14)/c_3(1)$ crossing yields the following molecular parameters for $C_{\Omega=2/0}(14)$ (in cm⁻¹): $C_{\Omega=2/0e}$: $\nu_0 = 106\,459.7(2)$, $B_{\text{eff}} = 1.016(13), H_{12} = 1.27(4), C_{\Omega=2/0f}$: $\nu_0 = 106\,459.7(1), B_{\text{eff}} = 1.017(3)$ and



Figure 9.2: 1 XUV + 1 UV ionization spectrum for the Q branch of the $c_3{}^1\Pi_u - X^1\Sigma_g^+(1,0)$ band in ${}^{15}N_2$ recorded with the PDA-based XUV source. Nozzle-skimmer distance = 150 mm, except for the scan labeled with an asterisk: nozzle-skimmer distance = 0 mm. Due to the perturbation, the Q(3,4) lines of the $C^3\Pi_{u\Omega=2/0} - X^1\Sigma_g^+(14,0)$ band becomes observable and the Q lines of the $c_3 - X(1,0)$ band show an irregular structure.

 $H_{12} = 1.28(3)$. Since this local crossing occurs at low J, a determination of the origin is justified. There is no measurable difference between the e and f levels and the low B value is consistent with the identification of the C valence state. There is only a small Λ -doubling observed for $C_{\Omega=2/0}(14)$ (see Table 9.2) and thus the more preferable assignment is $\Omega = 2$.

From the PDA-based results with a nozzle-skimmer distance of 150 mm, natural linewidths Γ were deduced by deconvolving the instrument width from the observed widths (see Chapter 5 for more information on the instrument width and the deconvolution procedures). Not only were widths of $c_3 - X(1,0)$ lines determined, but also the widths of two $C_{\Omega=2/0} - X(14,0)$ lines, R(3) and Q(4). For the measurements with a nozzle-skimmer distance of 0 mm, the lines were heavily affected by Doppler broadening and no accurate linewidths could be determined. Natural linewidths are tabulated in Table 9.3 and level widths are presented in Fig. 9.4. Since only a slight lifetime broadening was observed for $c_3(1)$ compared with the instrument width, the uncertainties in the widths are relatively large. The $C_{\Omega=2/0}(14)$ lines are broader, and hence the widths deduced are more accurate. The perturbation also has an effect on the widths for $c_3(1)$. As shown in Fig. 9.4, the widths of levels



Figure 9.3: Reduced term values for f parity levels in the region of the $c_3(1) - C(14)$ crossing in ¹⁵N₂. Term values have been reduced so that the $c_3(1)$ levels lie on the zero line. Closed circles: $c_3(1)$. Open circles: C(14), $\Omega = 2$ or $\Omega = 0$. No levels of the other substates of C(14) were observed; however, crossings of C(14), $\Omega = 1$ and $\Omega = 0/2$ with $c_3(1)$ are highlighted by arrows.

J = 3, 4 are larger than for the other J levels. The levels J = 3, 4 are most strongly mixed with $C_{\Omega=2/0}(14)$ (see above) and have a significant character contribution of the predissociating triplet C state, thereby increasing the width of these levels. The widths determined here of $C_{\Omega=2/0}(14)$ should also be affected by the interaction. The mixing with the longer lived $c_3(1)$ level should narrow the widths of the $C_{\Omega=2/0}(14)$ levels near the crossing, but this effect is not observable from the present data.

A lifetime of 1000 ± 100 ps (width: 0.005 cm^{-1}) was measured at the *R* branch band head for $c_3(1)$ in ¹⁵N₂ in a direct time-domain pump-probe experiment, described in Chapter 4. The present widths agree with this, except for J = 3, 4 which are strongly mixed with the triplet *C* state. In the pump-probe study in Chapter 4, bi-exponential decay curves were found for higher *J* levels with components of ~1 ns and ~300 ps. Not only the perturbation described above should be taken into account to explain the component of ~300 ps, but also the overlap with the $c'_4 {}^1\Sigma^+_u(v = 1)$ level, which has a lifetime (in ${}^{15}N_2$) of 310 ± 80 ps (see Chapters 4 and 6).

band	J''	$\Gamma_{R(J)}$	$\Gamma_{Q(J)}$	$\Gamma_{P(J)}$
$c_3{}^1\Pi_u - X^1\Sigma_g^+$ (1,0)	0	0.004(2)		
	1	0.010(3)	0.007(3)	
	2	0.012(4)	0.006(3)	0.005(3)
	3		0.012(4)	0.009(3)
	4	0.005(3)	0.013(4)	
	5		0.005(3)	
$C^{3}\Pi_{u\Omega=2/0} - X^{1}\Sigma_{q}^{+}$ (14,0)	3	0.049(5)		
. 5	4		0.040(6)	

Table 9.3: Observed natural linewidths for the $c_3{}^1\Pi_u - X^1\Sigma_g^+$ (1,0) and $C^3\Pi_{u\Omega=2/0} - X^1\Sigma_g^+$ (14,0) bands in ${}^{15}N_2$. All values in cm⁻¹.



Figure 9.4: Experimental predissociation level widths for the $c_3{}^1\Pi_u(v = 1)$ state of ${}^{15}N_2$. Crosses: *e* parity levels. Solid circles: *f* parity levels.

9.3 $D^{3}\Sigma_{u}^{+}(v=0)$ in ¹⁴N₂

Using the PDL-based and PDA-based XUV sources, the $3p\sigma_u D^3 \Sigma_u^+$ state, which is a Rydberg state converging on the $X^2 \Sigma_g^+$ state of N_2^+ , similar to the $3p\sigma_u c'_4{}^1 \Sigma_u^+$ Rydberg state, was investigated also. The D state is the upper state of the Fourth Positive system [4] $(D^3 \Sigma_u^+ - B^3 \Pi_g)$ and has, furthermore, been optically studied by Kanamori *et al.* [111] who observed the $D^3 \Sigma_u^+ - E^3 \Sigma_g^+(0,0)$ and (1,1) transitions in ${}^{14}N_2$ using near-infrared diode laser absorption spectroscopy. Here, the electricdipole forbidden $D^3 \Sigma_u^+ - X^1 \Sigma_g^+(0,0)$ transition was observed in ${}^{14}N_2$. In the main isotopomer, the D(0) level lies very close to $b^1 \Pi_u (v = 4)$. Therefore, the D - X(0,0) transition has the possibility of borrowing intensity from the allowed $b^1 \Pi_u - X^1 \Sigma_g^+(4,0)$ transition. PDL-based and PDA-based spectra are presented in Figs. 9.5 and 9.6, respectively, and line positions are tabulated in Table 9.4.

A rotational analysis of the D - X(0, 0) transition in ¹⁴N₂ yielded the spectroscopic parameters (in cm⁻¹): $\nu_0 = 103\,572.667(6)$, B = 1.9609(6), $D = 1.1(12) \times 10^{-5}$, $\lambda = -0.036(6)$ and $\gamma = 0.018(2)$, in excellent agreement with the more accurate measurements of Kanamori *et al.*, except that the present D value is not determined well since only low J levels were studied. However, this is the first time that the D - X transition has been observed optically and the present data give the first absolute band origin for D - X(0,0) in ¹⁴N₂. Furthermore, by combining ν_0 of D - X(0,0) and the D - E(0,0) band origin of Kanamori *et al.*, the absolute energy for the $E^3\Sigma_g^+(v = 0)$ level is determined to be 95774.446(6) cm⁻¹, more precise than the previous value of Carroll and Doheny [112]. The $3s\sigma_g E^3\Sigma_g^+$ state is the lowest Rydberg state converging on the $X^2\Sigma_q^+$ state of N₂⁺.

No lifetime broadening was observed in the present study, with all linewidths instrument limited. Kanamori *et al.* also observed no lifetime broadening. Kurzweg *et al.* [113] measured a lifetime of 14.1 ± 1.0 ns for the D(0) state in ¹⁴N₂, arguing that this level does not undergo predissociation and explaining why no additional line broadening was observed.

9.4 $D^{3}\Sigma_{u}^{+}(v=1)$ in ${}^{15}\mathbf{N}_{2}$

In ¹⁵N₂, the $D^3\Sigma_u^+(v=1)$ level was observed due to a crossing with the $o^1\Pi_u(v=0)$ level. Because of intensity borrowing due to the interaction, lines of the $D^3\Sigma_u^+ - X^1\Sigma_g^+(1,0)$ band appeared between lines of the dipole allowed $o^1\Pi_u - X^1\Sigma_g^+(0,0)$ band. An 1 XUV + 1 UV ionization spectrum of the *R* branches of the o - X(0,0) and D - X(1,0) bands is shown in Fig. 9.7. Line positions and line assignments of the o - X(0,0) band have already been presented in Chapter 2 and the Appendix and those of the D - X(1,0) band are given in Table 9.5.

As shown in Fig. 9.8, where reduced term values of o(0) and D(1) near the crossing region are presented, only the F_2 , e parity levels of $D^3 \Sigma_u^+(v=1)$ cross



Figure 9.5: 1 XUV + 1 UV ionization spectrum of the $D^{3}\Sigma_{u}^{+}(v=0)$ - $X^{1}\Sigma_{g}^{+}(v=0)$ band in ¹⁴N₂, recorded with the PDL-based XUV source. The rising signal level at the left side of the spectrum is from the bandhead of the much stronger $b^{1}\Pi_{u}(v=4) - X^{1}\Sigma_{g}^{+}(v=0)$ transition. The lines marked with an asterisk are high J lines of $c_{3}^{1}\Pi_{u}(v=0) - X^{1}\Sigma_{g}^{+}(v=0)$.

Table 9.4: Observed transition energies for the $D^3\Sigma_u^+ - X^1\Sigma_g^+$ (0,0) band in ¹⁴N₂. Wavenumbers given to three decimal places are from PDA spectra, those to two decimal places are from PDL spectra. Lines marked with an asterisk are derived from blended lines. All values in cm⁻¹.

J''	R(J)	$^{R}Q(J)$	$^{P}Q(J)$	P(J)
0	103576.587			
1	103580.452^*	103580.452^*	103568.734	
2	103584.259^*	103584.259^*	103564.717	103564.654
3	103588.002	103587.978	103560.72^*	103560.72^*
4	103591.697	103591.647		
5	103595.323	103595.256		
6	103599.01^*	103599.01^*		
8	103605.66^*	103605.66^*		
10	103612.53^*	103612.53^*		



Figure 9.6: 1 XUV + 1 UV ionization spectrum of the $D^{3}\Sigma_{u}^{+}(v=0)$ - $X^{1}\Sigma_{g}^{+}(v=0)$ band in ¹⁴N₂ recorded with the PDA-based XUV source. Left: recording of ^RQ(4) and R(4). Right: recording of P(2) and ^PQ(2).



Figure 9.7: 1 XUV + 1 UV ionization spectrum of the R branches of the $o^1\Pi_u - X^1\Sigma_g^+(0,0)$ and $D^3\Sigma_u^+ - X^1\Sigma_g^+(1,0)$ bands in ${}^{15}N_2$, recorded with the PDA-based XUV source. Nozzle-skimmer distance = 150 mm, except for the scan labeled with an asterisk: nozzle-skimmer distance = 0 mm.

rom F ıeighb	^o DL spectra. Li ouring line in t	nes marked wi he spectrum, 1	th an asterisk espectively. A	and s are deriv ll values in cm ⁻	ed fr -1.	om blended lir	ies and from th	ie shoulder of a
J''	R(J)	$^RQ(J)$	$^PQ(J)$	P(J)	N	$T(F_1)$	$T(F_2)$	$T(F_3)$
0	105645.016				0	105641.716		
1	105648.260	105648.742	105638.001		Ч		105645.015	
2	105651.174s			105633.868	0		105651.975	105652.457
3	105655.520			$105629.675 \mathrm{s}$	°		$105662.319{ m s}$	
4	105657.838			105625.170s	4		105677.811	
5	105660.217			105622.082	5		105694.988	
9	105662.45			105616.99	9		105715.940	
2				105611.92	~		105740.46	

term values. Wavenumbers given to three decimal places are from PDA spectra, those to two decimal places are Table 9.5: Observed transition energies for the $D^3 \Sigma_u^+ - X^1 \Sigma_g^+$ (1,0) band in ¹⁵N₂, together with $D^3 \Sigma_u^+ (v = 1)$ ļ د --د -. : : . ÷ fror nei



Figure 9.8: Reduced term values for e and f parity levels in the region of the o(0) - D(1) crossing in ¹⁵N₂. Term values have been reduced so that the o(0) f parity levels lie on the zero line. The two D(1), f level series, which are located above and under the D(1), e level series do not cross o(0).

the $o^1 \Pi_u (v = 0)$ level near J = 3, 4. Therefore, only the *e* parity levels of o(0) are perturbed strongly, leading to the *R* and *P* branches of the o - X(0, 0) band showing an irregular structure that is not present in the *Q* branch. For example, the *R*(2) and *R*(3) lines are very close to each other, and are just resolved in the lowest XUV spectrum of Fig. 9.7. Furthermore, the F_2 levels of D(1) are more strongly mixed with o(0) than the F_1 , *f* and F_3 , *f* parity levels, thus $D(F_2) - X(1, 0)$ transitions (*R* and *P* branches) borrow much more intensity than the transitions to the F_1 and F_3 levels. In fact, only two very weak lines corresponding to F_1 and F_3 levels of D(1)

A local deperturbation analysis of the D(1)/o(0) e level crossing yields the following molecular parameters for D(1), e (in cm⁻¹): $\nu_0 = 105\,641.80(4)$, B = 1.762(3) and $D = 5.3(4.7) \times 10^{-5}$ and the interaction matrix element $H_{12} = 1.01(2)$. The large B value is consistent with the assignment of the D Rydberg state.

Lifetime broadening was observed for o(0), while the D - X(1,0) lines show instrument limited linewidths (~0.010-0.015 cm⁻¹). The natural linewidths and lifetime of o(0) have already been presented in Chapter 5. No effect introduced by the o(0)/D(1) perturbation on the linewidth was observed. Kanamori *et al.* [111] investigated the $D^{3}\Sigma_{u}^{+} - E^{3}\Sigma_{g}^{+}(1,1)$ transition of ¹⁴N₂ in absorption and observed a linewidth increasing quadratically with J for F_{1} levels of D(1), with widths of <0.02 cm⁻¹ for J < 4, ~0.05 cm⁻¹ for J = 4, and increasing further to as much as ~0.3 cm⁻¹ for J > 10. Because of the broadening, the F_2 and F_3 components could not be resolved. Kanamori *et al.* argued that the predissociation of D(1) is caused by a *J*-dependent heterogeneous interaction, such as **L**-uncoupling with a ${}^{3}\Pi_{u}$ state. However, the results of Kanamori *et al.* are for ${}^{14}N_2$ and the predissociation of D(1) in ${}^{15}N_2$ may be different. In the present PDA-based study, only F_1 , F_2 and F_3 widths for J = 1, and F_2 widths for J = 2 - 4 were measured with a large nozzle-skimmer distance (thus reducing Doppler broadening), but no increase with J was found for $J \leq 4$. The F_2 levels J = 5, 6 of D(1) were only measured with a small nozzle-skimmer distance and, because of the larger Doppler widths and the poor signal to noise ratio, no accurate widths could be determined. The present results do not rule out the possibility of a J-dependent predissociation for D(1) in ${}^{15}N_2$. The range of J levels studied here is limited and it is possible for higher Jlevels not investigated here to exhibit a J-dependence. In any case, the broadening determined by Kanamori *et al.* for J = 4 in ${}^{14}N_2$ is significantly larger than the presently observed widths for ${}^{15}N_2$.

9.5 $C^3 \Pi_u (v = 13)$ in ${}^{15}\mathbf{N}_2$

Other small irregularities in the rotational structure of o(0) were found near J=10-14, for both e and f levels (see the reduced term energies in Fig. 9.8). The levels are only slightly shifted in energy, except for J = 10 which undergoes the strongest perturbation, with a downward shift in energy of ~0.15 cm⁻¹ for both e and f levels. Another effect of the perturbation on J = 10 was observed on the intensities. In the PDL-based XUV spectrum, the lines R(9), Q(10) and P(11) were found to be rather weak compared with other lines of the o - X(0,0) band. In the PDA-based spectrum, weak R(9) and Q(10) lines were found while no search for P(11) was performed. A PDA-based spectrum of the R(8-11) region of the o - X(0,0) band is presented in Fig. 9.9, showing the weakness of R(9) compared with, for example, R(8). Although intensities are hazardous to rely on in a 1 XUV + 1 UV ionization study, R(9) is clearly weak, certainly in view of the nuclear spin statistics in ¹⁵N₂, in which the odd lines are three times stronger than the even lines.

The CSE model (see Chapter 10) predicts the $C^3\Pi_u(v = 13)$ level as the perturber, but it is not possible to perform a local deperturbation analysis to confirm this, due to the non-observation of extra lines. The C(13) level must certainly be short-lived in order to explain the weakness of the R(9), Q(10) and P(11) lines of o - X(0,0). These lines are also likely to show additional lifetime broadening due to the coupling with the short-lived perturber, but no indication of such broadening could be observed. The spectra were measured with a nozzle-skimmer distance of 0 mm and the linewidths are highly affected by Doppler broadening. Especially for lines with J > 6, signal from N₂ background gas (width ~0.25 cm⁻¹) contributes to the line intensity and no accurate determination of the natural linewidths is



Figure 9.9: 1 XUV + 1 UV ionization spectrum of the R(8-11) region of the $o^1\Pi_u - X^1\Sigma_g^+(0,0)$ band in ${}^{15}N_2$ recorded with the PDA-based XUV source, showing the weakness of R(9). Lines marked with an asterisk are from the $D^3\Sigma_u^+ - X^1\Sigma_g^+(1,0)$ band (see Fig. 9.7). Nozzleskimmer distance = 0 mm.

possible. However, the widths of these lines are smaller than 0.25 cm^{-1} .

Note that the increasing difference in energy between the e and f levels of o(v = 0) with increasing J (see Fig. 9.8) is due to Λ -doubling. In addition, near J = 19, a crossing with $b'^{1}\Sigma_{u}^{+}(v = 3)$ occurs and this heterogeneous perturbation disturbs the e parity rotational structure (see Chapter 2).

9.6 $G^3 \Pi_u (v=0)$ in ${}^{14}\mathbf{N}_2$ and ${}^{15}\mathbf{N}_2$

As described in Chapter 2, a perturbation was observed in the $b^1\Pi_u(v=4)$ level near J = 18e, f and J = 15e, f in ¹⁴N₂ and ¹⁵N₂, respectively. This perturbation in ¹⁴N₂ has also been noted by Stark *et al.* [9], except that the weak f level perturbation was not noticed and no identification of the perturber state was made. CSE model predictions (see Chapter 10) identified the $G^3\Pi_{u\Omega=0}(v=0)$ level as the perturber. The $3p\pi_u G^3\Pi_u$ Rydberg state converges on the $X^2\Sigma_g^+$ core of N₂⁺, similar to the $3p\pi_u c_3^{-1}\Pi_u$ state. The $G^3\Pi_u - E^3\Sigma_g^+(0,0)$ transition in ¹⁴N₂ has recently been studied in detail by Hashimoto *et al.* [92, 110]. In Fig. 9.10, PDL-based spectra are shown of the b - X(4,0) band, including assignments of the extra lines corresponding to transitions into the perturber state. Observed transition energies and line assignments of the $G_{\Omega=0} - X(0,0)$ band in ¹⁴N₂ and ¹⁵N₂ are given in Table 9.6.



Figure 9.10: 1 XUV + 1 UV ionization spectrum of the $b^{1}\Pi_{u}$ – $X^{1}\Sigma_{g}^{+}(4,0)$ band in ¹⁴N₂ [spectrum (a)] and ¹⁵N₂ [spectrum (b)] recorded with the PDL-based XUV source. The extra lines belonging to the $G^{3}\Pi_{u\Omega=0} - X^{1}\Sigma_{g}^{+}(0,0)$ band are indicated.

A detailed analysis of the b(4)/G(0) perturbation is in progress, including data obtained with the PDA-based XUV source and the ¹⁴N₂ data (including oscillator strengths) from Stark *et al.* [9]. Here only the results of a deperturbation analysis of the $b(4)/G_{\Omega=0}(0)$ crossing in ¹⁵N₂ near J = 15 is presented. The deperturbed molecular parameters of $G_{\Omega=0}(0)$ in ¹⁵N₂ are (in cm⁻¹): $G_{\Omega=0e}$: $B_{\text{eff}} = 1.94(2)$, $H_{12} = 1.65(5), G_{\Omega=0f}$: $B_{\text{eff}} = 1.90(2), H_{12} = 1.5(1)$. No determination of the origins is justified, since the crossing occurs at high J. The high B values are consistent Table 9.6: Observed transition energies for the $G^3 \Pi_{u\Omega=0} - X^1 \Sigma_g^+$ (0,0) band in ¹⁴N₂ and ¹⁵N₂ from PDL spectra, together with $G^3 \Pi_{u\Omega=0} (v = 0)$ term values. Lines marked with s are derived from the shoulder of a neighbouring line in the spectrum and those marked with an asterisk are blended. All values in cm⁻¹.

$J^{\prime\prime}$	R(J)	Q(J)	P(J)	J	T_e	T_{f}
$^{14}N_2$						
16	103417.45			16		
17	103422.94			17	103958.19	
18		103335.46		18	104031.21	104015.22
19		103334.29		19		104089.50
${}^{15}N_{2}$						
11	103396.40^*			11		
12	103400.90^*	$103345.58\mathrm{s}$		12	103641.52	103635.25
13	103405.37	$103345.21\mathrm{s}$	103303.60	13	103690.57	103683.13
14	103408.33	103344.53	103300.69	14	103743.29	103734.41
15			103297.75	15	103798.21	
16		$103343.81\mathrm{s}$	103293.30	16		103848.72

with the assignment to the G Rydberg state.

The G - X(0,0) lines indicated in Fig. 9.10 in ¹⁵N₂ are surprisingly narrow and intense, compared with those in ${}^{14}N_2$ and compared with the b - X(4, 0) lines. Possibly in ${}^{15}N_2$, quantum interference effects narrow some G(0) J levels near the crossing, while this effect is much less (or not at all) pronounced in ${}^{14}N_2$. Note that in a 1 XUV + 1 UV ionization study, signal intensities depend on the lifetime, i.e. width, of the intermediate level studied. Competition between predissociation and ionization occurs, resulting in a decrease of the signal intensity observed for levels with a larger width (shorter lifetime). In ${}^{15}N_2$, the b(4) level is strongly predissociated [90], while the J levels of G(0) near the crossing are narrower than those of b(4) (see above). Therefore, the G - X(0,0) lines observed in ¹⁵N₂ are more intense than the b - X(4,0) lines belonging to the same J levels, even if the G - X(0,0) lines borrow their intensity from the b - X(4,0) lines. In Fig. 9.11, ratios of the strengths of the extra G - X(0,0) lines / main b - X(4,0) lines in ¹⁵N₂ of connecting pairs of R, P and Q lines in the PDL-based spectrum are presented as a function of the energy difference $\Delta E[G(0) - b(4)]$ from the crossing point. This ratio peaks around 10 cm⁻¹ below the crossing point. In this region, the G(0) levels are very narrow due to the interference effects, resulting in a strong enhancement in the ionization signal.



Figure 9.11: Ratios of the strengths of the extra G - X(0,0) lines / main b - X(4,0) lines $[I_{G(0)}/I_{b(4)}]$ in ¹⁵N₂ of connecting pairs of R, P and Q lines in the PDL-based spectrum, as a function of energy difference $\Delta E[G(0) - b(4)]$ from the crossing point.

9.7 Discussion and conclusions

The interactions of $c_3{}^1\Pi_u(v=1)$ with $C^3\Pi_u(v=14)$ in ${}^{15}N_2$, $o^1\Pi_u(v=0)$ with $C^3\Pi_u(v=13)$ in ${}^{15}N_2$ and between $b^1\Pi_u(v=4)$ and $G^3\Pi_u(v=0)$ in ${}^{14}N_2$ and ${}^{15}N_2$ presented here, are extremely valuable for elucidating the predissociation mechanism of the ${}^1\Pi_u$ states and especially for extending the mechanism towards higher energies (the predissociation of the ${}^1\Pi_u$ states is governed by interaction with the ${}^3\Pi_u$ manifold, see Chapter 10). The presently obtained information about these crossings, including line positions, linewidths, rotational constants and interaction parameters, may be used as input data for the predissociation model, just as for the $F^3\Pi_u(v=0)$ data in ${}^{14}N_2$ in Chapter 8.

The Rydberg $D^3\Sigma_u^+(v=0)$ level in ¹⁴N₂ and the $D^3\Sigma_u^+(v=1)$ level in ¹⁵N₂ presented here, further enlarge the knowledge about N₂ spectroscopy and dynamics. Kanamori *et al.* [111] already determined that D(0) in ¹⁴N₂ does not undergo strong predissociation, while for D(1) in the main isotopomer, a rotational dependent predissociation was found which is possibly governed by rotational coupling with the ³ Π_u manifold. Because only a limited range of low J levels was studied here, such as effect was not found here for D(1) in ¹⁵N₂.

Chapter 10

Predissociation mechanism for the singlet ungerade states of N_2

In this Chapter, a model is presented to explain the predissociation phenomena of the nitrogen molecule. Most of the singlet *ungerade* states in the XUV domain studied in this Thesis, which are accessed by electric-dipole transitions from the $X^1\Sigma_g^+$ state, undergo predissociation, i.e. these bound states couple to a dissociative continuum and the molecule falls apart. The rates of predissociation for the various rovibronic states exhibit a seemingly erratic behaviour, which is in addition strongly dependent on isotopic constitution of the molecule and in many cases also on rotational quantum number. No singlet ungerade $({}^{1}\Sigma_{u}, {}^{1}\Pi_{u}, {}^{1}\Delta_{u})$ continua exist in this energy range and thus, predissociation is most likely caused by interactions with triplet states. Recently, Lewis and coworkers succeeded in explaining quantitatively the predissociative behaviour of the lowest ${}^{1}\Pi_{u}$ states, namely $b^{1}\Pi_{u}(v=0-6)$ and $c^1 \Pi_u (v = 0)$, which was found to be governed by spin-orbit interactions with the $C^3\Pi_u$ and the $C'^3\Pi_u$ states [87, 114]. In this energy range, no ${}^3\Sigma_u^+$ states exist that can cause predissociation of these ${}^{1}\Pi_{u}$ states. A diabatic potential energy diagram of the relevant $^{1,3}\Pi_u$ states is given in Fig. 10.1, associated with the following molecular-orbital (MO) configurations

$$c^{1}\Pi_{u}, G^{3}\Pi_{u}: (1\sigma_{g})^{2}(1\sigma_{u})^{2}(2\sigma_{g})^{2}(2\sigma_{u})^{2}(1\pi_{u})^{4}(3\sigma_{g})3p\pi_{u}$$
(10.1)

$$p^{1}\Pi_{u}, F^{3}\Pi_{u}: (1\sigma_{g})^{2}(1\sigma_{u})^{2}(2\sigma_{g})^{2}(2\sigma_{u})^{2}(1\pi_{u})^{3}(3\sigma_{g})^{2}3s\sigma_{g}$$
(10.2)

$$b^{1}\Pi_{u}, C^{3}\Pi_{u}: (1\sigma_{g})^{2}(1\sigma_{u})^{2}(2\sigma_{g})^{2}(2\sigma_{u})(1\pi_{u})^{4}(3\sigma_{g})^{2}(1\pi_{g})$$
(10.3)

$$b^{1}\Pi_{u}, C^{3}\Pi_{u}, C'^{3}\Pi_{u}: (1\sigma_{g})^{2}(1\sigma_{u})^{2}(2\sigma_{g})^{2}(2\sigma_{u})^{2}(1\pi_{u})^{3}(3\sigma_{g})(1\pi_{g})^{2}$$
(10.4)

The c and G states are Rydberg states converging on the $X^2\Sigma_g^+$ ionic core, while the o and F Rydberg states converge on the $A^2\Pi_u$ state of N_2^+ . The potential curves of the F and G states are not shown in Fig. 10.1 but are located just below the singlet



Figure 10.1: Potential energy diagram of the $(b, c, o)^1 \Pi_u$ (solid curves) and $(C, C')^3 \Pi_u$ states (dashed curves) of N₂. Potential energy curves are in the diabatic representation and are obtained from the CSE model. Vibrational levels are also presented. Figure is kindly supplied by B. R. Lewis (Ref. [114])

Rydberg *o* and *c* states, respectively. The potential curves of the *b* and *C* states are unusually shaped because of a change of MO configuration (10.3) to configuration (10.4) in the range 1.3-1.4 Å. There are strong electrostatic interactions between the ${}^{1}\Pi_{u}$ states given above, as well as between the *C* and *C'* triplet states. The ${}^{1}\Pi_{u}$ and ${}^{3}\Pi_{u\Omega=1}$ states are coupled by spin-orbit interactions with the most important couplings between the isoconfigurational pairs of singlet and triplet states, i.e., between the *b* and *C*, *b* and *C'* (weak), *c* and *G* (weak), and *o* and *F* states.

Since there is a lack of detailed information on the F and G states,¹ the predissociation model of Lewis and coworkers only applies to ${}^{1}\Pi_{u}$ states below ~ 105500 cm⁻¹, thus b(v = 0 - 6) and c(v = 0). In this region, the F and G states are supposed to have only a minor influence on the predissociation, and hence only spin-orbit couplings between the b state and the C and C' states are of relevance.

Lewis and coworkers used a coupled-channel Schrödinger equations (CSE) model [115, 116] to unravel the predissociation mechanism of the lowest ${}^{1}\Pi_{u}$ states of N₂.

¹Previously the F and G states have only been found in low resolution electron-energy-loss and photofragment spectra (see Refs. in Chapter 8), but recently, the F(v = 0) (Chapter 8) and G(v = 0) (Ref. [92] and Chapter 9) levels have been characterized with rotational resolution.

First, a five-channel CSE model was employed of the $(b, c, o)^1 \Pi_u$ and the $(C, C')^3 \Pi_u$ states without the effects of rotation [87]. Lewis and coworkers used the diabatic potential energy curves for the b, c and o states from the *ab initio* semi-empirical study of Spelsberg and Meyer [39], and diabatic curves for the C and C' states derived from adiabatic curves from the *ab initio* calculations of Partridge (see Ref. [87]), as starting points for their optimization. More recently, the CSE model was extended to include rotational effects and, not only were the ${}^3\Pi_{u\Omega=1}$ sublevels, which spin-orbit couple with the ${}^1\Pi_{u\Omega=1}$ levels, included in the CSE model, but also the ${}^3\Pi_{u\Omega=0,1,2}$ sublevels. Therefore, the CSE model was extended to a nine-channel model [114]. For the C' state the spin-orbit constant was fixed at A = 0 cm⁻¹, thus the potentials of the three C' sublevels were taken to be identical, while for the Cstate $A \approx 15$ cm⁻¹. Since the ${}^1\Sigma_u^+$ states were excluded, the model only applies to f parity levels, neglecting the e parity levels and corresponding Λ -doubling effects.

In the CSE model [116], the diabatic-basis coupled Schrödinger equations

$$\left\{\mathbf{I}\frac{d^2}{dR^2} + \frac{2\mu}{\hbar^2}[E\mathbf{I} - \mathbf{V}(R) - \mathbf{V}^{ROT}(R)]\right\}\chi_{EJ}(R) = 0$$
(10.5)

were solved numerically for each J to give the coupled-channel radial wave function matrix $\chi_{EJ}(R)$, where R is the internuclear distance, μ the reduced mass and \mathbf{I} is the identity matrix. The symmetric diabatic potential matrix $\mathbf{V}(R)$ is given by

$$\begin{pmatrix} V_b & H_{bc}^{el} & H_{bo}^{el} & 0 & H_{bC}^{so} & 0 & 0 & H_{bC'}^{so} & 0 \\ H_{bc}^{el} & V_c & H_{co}^{el} & 0 & 0 & 0 & 0 & 0 & 0 \\ H_{bo}^{el} & H_{co}^{el} & V_o & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & V_{C_{\Omega=0}} & H^{JS} & 0 & H_{CC'}^{el} & 0 & 0 \\ H_{bC}^{so} & 0 & 0 & H^{JS} & V_{C_{\Omega=1}} & H^{JS} & 0 & H_{CC'}^{el} & 0 \\ 0 & 0 & 0 & 0 & H^{JS} & V_{C_{\Omega=2}} & 0 & 0 & H_{CC'}^{el} & 0 \\ 0 & 0 & 0 & 0 & H_{CC'}^{el} & 0 & 0 & H_{CC'}^{JS} & 0 \\ H_{bC'}^{so} & 0 & 0 & 0 & H_{CC'}^{el} & 0 & H^{JS} & 0 \\ H_{bC'}^{so} & 0 & 0 & 0 & H_{CC'}^{el} & 0 & H^{JS} & V_{C_{\Omega=1}} & H^{JS} \\ 0 & 0 & 0 & 0 & 0 & H_{CC'}^{el} & 0 & H^{JS} & V_{C_{\Omega=2}} \end{pmatrix},$$

where the diagonal elements are the diabatic electronic potential energy curves with

$$V_k(R) = \langle \Phi_k | \mathbf{H}^{el} | \Phi_k \rangle \tag{10.7}$$

and the off-diagonal elements represent the interaction parameters between the states with electrostatic couplings: H_{bc}^{el} , H_{bo}^{el} , H_{co}^{el} and $H_{CC'}^{el}$, spin-orbit couplings: H_{bC}^{so} and $H_{bC'}^{so}$ and rotational **S** uncoupling terms between the ${}^{3}\Pi_{u\Omega}$ sublevels:

$$H^{JS}(\Omega, \Omega + 1) = -\sqrt{2}B(R)\sqrt{J(J+1) - \Omega(\Omega + 1)}$$
(10.8)

where $B(R) = \hbar/(2\mu R^2)$ cm⁻¹. In eq. (10.5), $\mathbf{V}^{ROT}(R)$ is a diagonal matrix with elements

$$V_{kk}^{ROT}(R) = \langle \Phi_k | \mathbf{H}^{ROT} | \Phi_k \rangle$$
(10.9)

where \mathbf{H}^{ROT} is the rotational part of the Hamiltonian.

Subsequently, the photodissociation cross section $\sigma_{EJ \leftarrow iv''J''\Omega''}$ from the initial uncoupled state Φ_i into the coupled states Φ_k at an energy E and rotation J was taken as [116]

$$\sigma_{EJ \leftarrow iv''J''\Omega''} \approx g\nu |\langle \chi_{EJ}(R) | \mathbf{M} | \chi_{iv''J''\Omega''}(R) \rangle|^2$$
(10.10)

where g is a degeneracy factor, ν is the transition energy, $\chi_{EJ}(R)$ is the coupledchannel radial wave function matrix, $\chi_{iv''J''\Omega''}(R)$ is the initial state vibrational wavefunction, and **M** is the transition vector containing diabatic electronic transition moments and rotational components. Note that only the transitions from the $X^1\Sigma_g^+$ ground state to the $(b, c, o)^1\Pi_u$ states have nonzero diabatic electronic transition moments and that the ${}^3\Pi_{u\Omega=1}$ states borrow intensity from these transitions by spin-orbit coupling. The ${}^3\Pi_u$ states with $\Omega=0,2$ borrow intensity from ${}^3\Pi_{u\Omega=1}$ by **S** uncoupling. Finally, different isotopomers were studied, simply by changing the reduced mass.

From the computed cross sections, transition energies, rotational constants, predissociation linewidths and oscillator strengths were deduced, which were iteratively compared with an experimental database to optimize the parameters of the CSE model. The experimental database contains data from many different sources, but mainly experimental data presented in this Thesis (transition energies, predissociation linewidths/lifetimes, including isotopic data of ${}^{15}N_2$ and to a lesser extent of ${}^{14}N^{15}N$ [Chapters 2, 3, 4 and 5]) and data from G. Stark (transition energies, linewidths and oscillator strengths [9]). The isotopic dependences found in the experimental data, were very helpful in testing the model.

From these computations, Lewis and coworkers showed that the spin-orbit interaction parameter H^{so} between b and C is significantly larger than for b and C'and that the indirect process of spin-orbit coupling with the C state, together with electrostatic coupling of the C state with the continuum of the C' state, is the main predissociation mechanism of these lowest ${}^{1}\Pi_{u}$ states. The contribution of the direct process of spin-orbit interaction with the C' state is negligibly small in the predissociation process.

The CSE model results and the experimental database are in very good agreement (see Refs. [87, 114, 117]). For example, the erratic behavior of rotationless lifetime on vibrational level and isotopomer as was measured experimentally (see Chapter 5), is very well reproduced, even the very strong isotope dependence of the lifetime of b(1). In another example, Stark [9, 114] observed a rotational dependence for the linewidth of b(3) in ¹⁴N₂, which increases with J until J = 11, and then decreases. The CSE model only reproduced this behavior if the triplet structure (Ω =0,1,2) is included. There is an accidental degeneracy between b(3) and C(9), and C(9) is predicted to be very short-lived by the CSE model. Local interactions of b(3) with all the triplet C(9) sublevels occur, resulting in this typical J dependence in the linewidth of b(3). The degeneracy between b(3) and C(9) is shown in
Fig. 10.1 and explains why the lifetime for b(3) in ¹⁴N₂ is the lowest compared to all the other singlet *ungerade* states in this energetic region.

The CSE model predicted a J dependence of the linewidth of b(1) in ¹⁴N₂ [117], which has been found to be one of the longest-lived states of N₂ in this energetic region. However, there was still a discrepancy: the experimental lifetime presented in this Thesis (Chapter 3) is 2.61 ns, while Oertel *et al.* [75] reported a value of 1.75 ns. However, the two lifetimes correspond to different ranges of J. The lifetime of 2.61 ns belongs to J levels near J = 3, while the value of Oertel applies to higher J levels near J = 6. This J dependence is well reproduced by the CSE model, thus removing the discrepancy. An additional value for the lifetime of b(1) of 1.97 ns near J = 6, 7, measured with the same experimental setup as described in Chapter 3, agrees with this J dependence [117].

In the future, the CSE model will be extended towards higher energies to explain the predissociation of the higher ${}^{1}\Pi_{u}$ states. As was mentioned before, the $F^{3}\Pi_{u}$ and $G^{3}\Pi_{u}$ states are expected to play crucial roles in the predissociation mechanism for the ${}^{1}\Pi_{u}$ states at higher energies. Recently, F(v = 0) (Chapter 8), G(v = 0) (Ref. [92] and Chapter 9) and other triplet levels (Chapter 9) have been characterized with rotational resolution and predissociation level widths have been determined. At higher energies, it is possible that ${}^{3}\Sigma_{u}^{+}$ states are involved in the predissociation process and if so, these ${}^{3}\Sigma_{u}^{+}$ states have to be included in the model. Furthermore, the experimental database of the singlet *ungerade* states, including transition energies and linewidths, has been extended towards higher energies: $106000 - 109000 \text{ cm}^{-1}$ (Chapter 6) and $109000 - 112000 \text{ cm}^{-1}$ [93, 94]. Using all these new experimental data, the CSE model may be able to explain the predissociative behavior of the ${}^{1}\Pi_{u}$ states at these higher energies.

Another possible extension of the predissociation model is the inclusion of the ${}^{1}\Sigma_{u}^{+}$ states and rotational interactions between the ${}^{1}\Sigma_{u}^{+}$ and ${}^{1}\Pi_{u}$ states. Models containing the ${}^{1}\Pi_{u}$ and ${}^{1}\Sigma_{u}^{+}$ states and the heterogeneous rotational interactions between them already exist (see Refs. [28, 35, 36, 37] and Chapter 2), but the triplet states have yet to be included in these models. The predissociative behaviours of the ${}^{1}\Sigma_{u}^{+}$ states are likely to show J dependences, since the ${}^{1}\Sigma_{u}^{+}$ states rotationally couple with the ${}^{1}\Pi_{u}$ states, which in turn couple with the ${}^{3}\Pi_{u}$ continuum. However, this is still a hypothesis and future studies should clarify this. The predissociation of the $c_{4}'{}^{1}\Sigma_{u}^{+}$ (v = 0.1, 2) Rydberg levels in ${}^{14}N_{2}$ (including J dependences) has been investigated by Ubachs *et al.* [37], and was explained in terms of Rydberg-valence mixing with the predissociating $b'{}^{1}\Sigma_{u}^{+}$ and $b^{1}\Pi_{u}$ valence states. For $c_{4}'(0)$ in ${}^{14}N_{2}$, a shortening of the lifetime with increasing J was found by Ubachs *et al.*, in agreement with the findings of Liu *et al.* [11], who found a J dependent predissociation yield.

Finally, the predissociation mechanism developed by Lewis and coworkers is important in understanding the radiative and photochemical processes in the N_2 rich atmospheres of the Earth, Titan and Triton (see Chapter 1).

Chapter 11

High precision frequency calibration of N I lines in the XUV domain

With the use of a narrowband and tunable extreme ultraviolet laser source transition frequencies in the spectrum of neutral atomic nitrogen were measured for transitions originating from the $(2p^3)$ ${}^4S_{3/2}$ ground state to twelve levels in the $2p^23d$ and $2p^24s$ configurations in the wavelength range 95.1-96.5 nm. The present laboratory calibrations, performed at an absolute accuracy of 0.005 cm⁻¹ or 5×10^{-8} , should be useful for comparison with nitrogen absorption features observed in quasars for assessment of possible temporal variation of the fine structure constant. Simultaneous recordings of spectra for both ¹⁴N and ¹⁵N yield accurate values for transition isotope shifts, that reveal large specific-mass shifts almost to the extent of canceling the isotope shifts.

With the recent claims on a possible variation of the fine structure constant $\alpha = e^2/4\pi\epsilon_0\hbar c$ on a cosmological time scale, deduced from comparisons between laboratory spectra and high-resolution data from quasi-stellar objects [118, 119], a renewed interest has arisen in obtaining transition frequencies of the strong resonance lines of atoms and ions measured at the highest precision. Although the claim of variability of α has been disputed, based on differing findings on the northern [118, 119] and southern hemispheres [120, 121], this issue which touches upon the very foundations of physics is sufficiently important to be pursued in all details. With the use of the many-multiplet method, adding lines to the comparison-database may result in improved constraints on the temporal behaviour of α , particularly when these lines have a spread in relativistic fine structure splittings. But as was noted, the laboratory (or zero-redshift) values for quite a number of spectral lines are not known at sufficient precision for reliable comparison with astrophysical data [122]. Currently two distinct strategies are being followed to probe a possible

variation of α , and from both methods a rate of change is found on the order of 10^{-15} per year or smaller. For clarity we explain that absorption data of cold interstellar clouds in the path of emitting quasar systems are probed with accuracies of $10^{-6} - 10^{-7}$, using echelle-grating based spectrometers attached to large telescopes. Several of those absorbing clouds lie at redshifts of z = 3 representing a look-back time of more than 10 Billion years. Hence a comparison with laboratory data obtained in the modern epoch yields a multiplication factor of 10^{10} for detection of a rate of change of α , and laboratory data of accuracy better than 10^{-7} can be considered exact for the purpose of comparison with quasar data. A second strategy involves measuring spectral lines in the laboratory at time intervals of one to several years. Then spectral accuracies on the order of 10^{-15} are required to set an upper limit on the rate of change of α of 2×10^{-15} per year [123]. Another method for probing possible variations of fundamental and dimensionless constants of nature (such as the proton-to-electron mass ratio μ) is pursued by comparing the spectrum of molecular hydrogen over wide time intervals [124].

After a similar investigation on the C I line at 94.5 nm achieving an absolute accuracy of 4×10^{-8} with the use of the Amsterdam narrowband and tunable extreme ultraviolet (XUV) laser system [125], we now turn to a high-accuracy calibration study of twelve resonance lines in the spectrum of N I near 95-96 nm, including a determination of the isotope shift. Neutral nitrogen has been observed in so-called damped Lyman- α systems, where the nucleo-synthetic origin of ¹⁴N is a matter of controversy [126].

The XUV spectrum of N I was investigated in the early days of quantum mechanics by Compton and Boyce [127], who covered the entire range of 50-120 nm. Since then a number of investigators focused on the nitrogen spectrum. Herzberg [128] performed a high-resolution investigation, probing levels of the $(2p^24s)^{4}P$ and $(2p^23d)^{4}D$ manifolds directly in emission at an absolute accuracy of of 0.0002 Å or 0.02 cm^{-1} . Alternatively the level energies of the highly excited states were derived from the investigation of combination differences after measuring large numbers of spectral lines in the visible and near-infrared ranges. On the basis of the spectra of Eriksson and coworker [129, 130], as well as from some new measurements, Kaufman and Ward succeeded in determining the level energies of all levels included in the present study to an accuracy of 0.04 cm^{-1} [131].

The aim of the present investigation is to further improve upon the calibration accuracy of the resonance lines in the XUV-domain such that in comparison with quasar and other astrophysical data the laboratory or rest-frame frequencies can be considered exact. The use of the Amsterdam narrowband and tunable XUV laser-setup has been described extensively, including its limitations in providing frequency calibrations. For discussions on the effects of frequency chirp in pulsed dye amplifiers used in the production of highly energetic laser pulses; the generation of narrowband XUV-radiation; the method of 1 XUV + 1 UV photoionization detection; possible effects of residual Doppler and AC-Stark shifts; and the frequency calibration against the Doppler-free I₂-standard in the visible range, we refer to Ref. [132]. The operation of the same system for a calibration of C I lines (for both 12 C and 13 C) was demonstrated recently [125].



Figure 11.1: Recordings of the $(2p^3) {}^4S_{3/2} - (2p^23d) {}^4P_{5/2}$ transition for ¹⁴N and ¹⁵N. The line fits, superimposed on the data points (open circles), as well as the fit residuals are shown. The calibration line marked with an asterisk is the *t*-hyperfine component of the P43 line in the B-X(18-1) band of I₂ at 17 470.821 290 cm⁻¹ measured by saturated absorption spectroscopy. The lower trace represents markers of an étalon used for the frequency calibration procedure.

A beam of atomic nitrogen was produced in a pulsed expansion from a source equipped with a high-voltage discharge as described in Ref. [133]. About 20% of N₂ in He was used for optimal discharge operation, where the nitrogen part was premixed from naturally-occuring nitrogen ¹⁴N₂ with a sample of 99% isotopically enriched ¹⁵N₂ in a 50%/50% mixture. The nozzle-discharge expansion was positioned at a distance of 10 cm from a skimmer to obtain a highly collimated atomic beam which is perpendicularly crossed with the laser beams to obtain Doppler-free spectra. An example of recordings of the $(2p^3)^4S_{3/2}$ - $(2p^23d)^4P_{5/2}$ transition for both ¹⁴N and ¹⁵N is shown in Fig. 11.1. The spectra are obtained by laser excitation combined with time-of-flight mass separation. By this means the spectra for ¹⁴N and ¹⁵N are recorded simultaneously from the same atomic beam, although the

o the listed excited	states, with uncertai	nties given in p	arentheses. For	¹⁴ N a comparison is
re values from Refs.	[128, 131]. All values	in cm^{-1} .		
Excited state	14 N (Obs.)	Δ (Ref. [128])	Δ (Ref. [131])	$^{15}\mathrm{N}\left(\mathrm{Obs.} ight)$
$(2p^24s) {}^4\mathrm{P}_{1/2}$	103622.4773(50)	-0.009(20)	-0.052(40)	103622.4825(40)
$(2p^24s) {}^4\mathrm{P}_{3/2}$	103667.1214(50)	-0.021(20)	-0.053(40)	103667.1255(40)
$(2p^24s){}^4\mathrm{P}_{5/2}$	103735.4527(50)	-0.020(20)	-0.042(40)	103735.4572(40)
$(2p^2 3d) {}^2{ m F}_{5/2}$	104810.3324(50)		-0.045(40)	104810.3429(40)
$(2p^2 3d)~^4{ m P}_{5/2}$	104825.0699(50)		-0.051(40)	104825.0844(40)
$(2p^2 3d) {}^4\mathrm{P}_{3/2}$	104859.6952(50)		-0.051(40)	104859.7094(40)
$(2p^2 3d) {}^4\mathrm{P}_{1/2}$	104886.0687(50)		-0.051(40)	104886.0828(40)
$(2p^2 3d) {}^4 ext{D}_{1/2}$	104984.3238(50)	-0.007(20)	-0.062(40)	104984.3391(40)
$(2p^2 3d) {}^4 ext{D}_{3/2}$	104996.2343(50)	-0.001(20)	-0.056(40)	104996.2487(40)
$(2p^2 3d) {}^4 ext{D}_{5/2}$	105008.5141(50)	-0.004(20)	-0.048(40)	105008.5297(40)
$(2p^2 3d)^2 \mathrm{D}_{3/2}$	105119.8419(50)		-0.054(40)	105119.8541(40)
$(2p^2 3d) {}^2\mathrm{D}_{5/2}$	105143.6799(50)		-0.046(40)	105143.6913(40)

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spectral traces for both isotopes appear distinct, as shown in Fig. 11.1. The transition frequencies were determined by line-fitting with the use of frequency markers from a calibrated and stabilized étalon, and the simultaneous measurement of I_2 calibration lines, recorded at the fundamental wavelength of the laser system at $6 \times \lambda_{XUV}$. In Table 11.1, the resulting transition frequencies are listed with the uncertainties, including a statistical error from averaging over at least three recordings and estimating the systematic uncertainty [125, 132]. The accuracy of the absolute calibrations in the present study is at the 5×10^{-8} level, and hence a factor of 4 and 8 more accurate than the previous classical studies [128, 131]. These uncertainties are mainly determined by systematic effects related to frequency chirp in the dye amplifiers, the possible first-order Doppler shifts as a result of imperfect perpendicular alignment of the laser and atomic beams, and the AC-Stark effect. These effects were estimated and treated experimentally by methods described before [132]. The present data on the transition frequencies are on average lower in energy by -0.010 cm^{-1} with respect to the values of Ref. [128], in agreement with the cited error of 0.020 cm^{-1} . Similarly the present values for the twelve transitions are on average -0.051 cm^{-1} lower than those of Ref. [131], therewith slightly exceeding the cited uncertainty of 0.040 cm^{-1} .

The linewidths of the atomic resonances are in the range 450 - 650 MHz, larger than the bandwidth of the XUV source (≈ 300 MHz). In the chosen geometry of the beam configuration, Doppler broadening adds slightly to the instrument width. For the upper states in the 4s and 3d manifolds of N I lifetimes of 11 ns and 7 ns are reported [134, 135], giving rise to lifetime broadenings of 14 and 22 MHz, so only marginally contributing to the observed widths in the present experiment. This is in contrast to the investigation of the C I resonance line [125], where lifetime broadening was the dominant broadening effect. The $(2p^3)^4S_{3/2}$ ground state in ¹⁴N is split into a hyperfine triplet spanning 42 MHz, while in ¹⁵N it is split into a doublet spanning 29 MHz [136] by the magnetic dipole interaction term. For the 4s and 3d excited states no information exists for the hyperfine structure, but for the $(2p^2)3s^4P$ level hyperfine constants of 61 MHz (¹⁴N) and 45 MHz (¹⁵N) were determined [137]. Such effects of hyperfine structure should not be observable in the present XUV excitation scheme, at least not in terms of splittings or asymmetries, but might add somewhat to the linewidths. In Fig. 11.1 the residuals from fits of the observed line shapes to Voigt profiles are plotted. These residuals do not exhibit significant asymmetries that might be caused by underlying hyperfine structure. Also fits were performed with skewed Voigt functions, to detect asymmetries; also this procedure did not yield a significant effect.

Since the ¹⁴N and ¹⁵N spectra are recorded simultaneously under identical conditions, the isotope shifts (IS) can be derived from relative frequency measurements, which are not affected by most of the systematic contributions to the uncertainty in the absolute calibration. Hence, the uncertainties in the values for the IS, depend mainly on the statistical uncertainties related to the fitting of the line profiles and

Table 11.2: Resulting isotope shifts from relative frequency measure-
ments for transitions from the $(2p^3)$ ${}^4S_{3/2}$ electronic ground state in
the N atom to the listed excited states, with uncertainties given in
parentheses. Values are given in MHz.

Excited state	$\Delta_{\rm IS} \left({\rm ^{15}N} - {\rm ^{14}N} \right)$
$2p^2 4s {}^4 ext{P}_{1/2}$	160(60)
$2p^2 4s {}^4 ext{P}_{3/2}$	130(40)
$2p^2 4s {}^4 ext{P}_{5/2}$	140(50)
$2p^2 3d {}^2\mathrm{F}_{5/2}$	310(20)
$2p^2 3d {}^4 ext{P}_{5/2}$	320(20)
$2p^2 3d {}^4\mathrm{P}_{3/2}$	340(20)
$2p^2 3d {}^4\mathrm{P}_{1/2}$	320(30)
$2p^2 3d {}^4\mathrm{D}_{1/2}$	440(20)
$2p^2 3d {}^4\mathrm{D}_{3/2}$	430(20)
$2p^2 3d {}^4 ext{D}_{5/2}$	470(20)
$2p^2 3d {}^2\mathrm{D}_{3/2}$	370(20)
$2p^2 3d {}^2\mathrm{D}_{5/2}$	340(30)

the determination of line centres. The values are listed in Table 11.2 in units of MHz. The ¹⁵N - ¹⁴N isotope shifts are in the range between 120 and 470 MHz, or 0.004 and 0.016 cm⁻¹, where the Bohr shift (or the normal mass-shift contribution to the IS) for these XUV-transitions should amount to 0.27 cm⁻¹. Hence, the specific mass-shift (SMS) contribution to the isotope shift for these lines is negative, exceeds 7.5 GHz, and almost cancels the effect of the Bohr shift. This implies that in astrophysical observation of these lines the ¹⁵N component will always be fully overlapped. This large and negative SMS-contribution in nitrogen is consistent with previous measurements on isotope shifts in the near-infrared spectral range. In the case of the $(2p^23s)^4P$ - $(2p^3)^4P$ transitions SMS contributions of -2.5 GHz were found to give rise to negative isotope shifts in the nitrogen atom [137]. So far no isotope measurements involving the $2p^24s$ and $2p^23d$ configurations, nor results on *ab initio* calculations of IS in atomic nitrogen, have been reported.

In conclusion, we report on a frequency calibration in the XUV-domain of twelve resonance lines in the spectrum of N I, for both ¹⁴N and ¹⁵N isotopes, at the 5×10^{-8} accuracy level. These results should be useful for comparison with highly redshifted quasar absorption lines of atomic nitrogen in order to test a possible variation of the fine structure constant, and may encourage performing first principle calculations on the anomalous isotope shift behaviour in this atom.

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Appendix: Data archive

Extreme ultraviolet laser excitation of isotopic molecular nitrogen: The dipole-allowed spectrum of ${}^{15}N_2$ and ${}^{14}N^{15}N$

This supplementary data archive contains the rotational line assignments and wave numbers for the ionization spectra discussed in the above article in The Journal of *Chemical Physics*, hereafter called *I* (Chapter 2). Recommended term values are also given for the excited states, leading to the spectroscopic parameters given in I. The term values of the $X^{1}\Sigma_{a}^{+}(v=0)$ ground states of ${}^{15}N_{2}$ and ${}^{14}N^{15}N$ are tabulated in Table 3 up to J = 30. The term values of the ground state are calculated using the rotational constants of Bendtsen [J. Ram. Spectrosc. 32, 989 (2001)]. Line positions and term values of the excited states of ${}^{15}N_2$ and ${}^{14}N^{15}N$ studied are tabulated in Tables 4–24 and 25–29, respectively. Wave numbers given to three decimal places are from narrow-bandwidth pulsed dye-laser (PDA) spectra, those to two decimal places are from pulsed dye-laser (PDL) spectra. Wavenumbers derived from blended lines are flagged with an asterisk (*), those from shoulders in the spectra by s, those from weak features by w, and doubtful assignments by ?. Line positions and term values of ${}^{14}N^{15}N$ which are blended with a ${}^{14}N_2$ line are labeled with *' (s' for shoulder). Wave numbers from PDA data which are relatively broad due to lifetime broadening or Doppler broadening are indicated with b. However, these relatively broad lines from the PDA data are significantly narrower than the lines from the PDL data.

In some of the spectra recorded with the PDL source, line broadening associated with the AC-Stark effect was observed, sometimes yielding asymmetric line shapes. This phenomenon was not investigated in detail, but the AC-Stark-induced shifts were compensated for by comparison with spectra obtained using the PDA source. For several bands, low-J lines were recorded with the PDA, while the entire band was recorded using the PDL at high laser intensity. Line positions from the PDA source were systematically lower by $\Delta_{\rm PDL-PDA} \approx 0.05 - 0.20 \text{ cm}^{-1}$. Based on the observations with both systems, the PDL data were corrected for the AC-Stark shift, for those bands where ultra-high resolution PDA data were available. The PDL shifts are given in the captions of the tables. Due to the uncertain Stark shifts, the absolute wave-number uncertainty for the lines recorded with the PDL-based XUV source is ± 0.2 cm⁻¹, significantly worse than the calibration uncertainty of ± 0.05 cm⁻¹. The absolute calibration uncertainty for the PDA source is ± 0.003 cm⁻¹. This value represents a lower limit to the uncertainty for the narrowest spectral lines recorded. For lines where lifetime and/or Doppler broadening is of importance, the uncertainty is ± 0.02 cm⁻¹.

$^{14}N^{1}$	^o N. All values	$\sin \mathrm{cm}^{-1}$.			
J	$T_e(J)$ ¹⁵ N ₂	$T_e(J)$ ¹⁴ N ¹⁵ N	J	$T_e(J)$ ¹⁵ N ₂	$T_e(J)$ ¹⁴ N ¹⁵ N
0	0	0	16	504.906	522.826
1	3.715	3.847	17	567.967	588.123
2	11.146	11.541	18	634.726	657.249
3	22.291	23.083	19	705.179	730.199
4	37.151	38.470	20	779.325	806.972
5	55.724	57.703	21	857.161	887.565
6	78.011	80.782	22	938.684	971.976
7	104.011	107.705	23	1023.893	1060.202
8	133.723	138.472	24	1112.784	1152.239
9	167.146	173.082	25	1205.354	1248.085
10	204.279	211.532	26	1301.601	1347.736
11	245.120	253.823	27	1401.521	1451.190
12	289.668	299.953	28	1505.111	1558.442
13	337.923	349.920	29	1612.367	1669.489
14	389.882	403.722	30	1723.288	1784.328
15	445.543	461.358			

Table 3: Term values for the $X^{1}\Sigma_{g}^{+}(v=0)$ ground states of ${}^{15}N_{2}$ and ${}^{14}N^{15}N$. All values in cm⁻¹.

Table 4: Rotational line assignments and wave numbers for the $b \, {}^{1}\Pi_{u} - X \, {}^{1}\Sigma_{g}^{+}(0,0)$ band of ${}^{15}N_{2}$, together with $b \, {}^{1}\Pi_{u}(v = 0)$ term values. PDL shift is -0.03 cm^{-1} .

$J^{\prime\prime}$	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	100846.073					
1	100847.751	100842.31		1	100846.073	100846.02
2	100848.380	100840.31	100834.88	2	100851.466	100851.46
3	100848.021	100837.23	100829.12	3	100859.526	100859.52
4	100846.65	100833.18	100822.16^*	4	100870.312	100870.33
5	100844.11	100828.02	100814.62^*	5	100883.74	100883.74
6		100822.16^*	100805.68	6	100899.89^*	100900.17
7	100836.06	100814.62^*	100795.94	7	100918.90^*	100918.63
8		100806.30	100785.18	8	100940.07	100940.03
9	100823.77	100797.10		9		100964.25
10				10	100990.92	
11		$100775.70\mathrm{w}$		11		$101020.82\mathrm{w}$

Table 5: Rotational line assignments and wave numbers for the $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(1,0)$ band of ¹⁵N₂, together with $b^{1}\Pi_{u}(v = 1)$ term values. PDL shift is -0.09 cm^{-1} .

J''	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	$101458.455\mathrm{b}$					
1	$101460.014\mathrm{sb}$	$101454.737\mathrm{b}$		1	$101458.455\mathrm{b}$	$101458.452\mathrm{b}$
2	$101460.465{\rm b}$	$101452.565\mathrm{b}$	101447.17	2	$101463.729\mathrm{b}$	$101463.711\mathrm{b}$
3	$101459.890\mathrm{sb}$	$101449.310\mathrm{b}$	101441.35	3	$101471.611\mathrm{b}$	$101471.601\mathrm{b}$
4	101458.04	101444.88	101434.39	4	$101482.181\mathrm{b}$	101482.03
5	$101455.336\mathrm{b}$	101439.57	101426.39	5	101495.17	101495.29
6	101451.48	101433.10^*	$101417.13\mathrm{s}$	6	$101511.060{ m b}$	101511.12^*
7	101446.35	101425.42	101406.99^*	7	101529.44	101529.43
8	101440.40	$101416.80\mathrm{s}$	$101395.66\mathrm{s}$	8	101550.40	$101550.52\mathrm{s}$
9	101433.10^*	101406.99^*	101383.30	9	101574.21	101574.13^*
10	$101424.96\mathrm{s}$	$101396.12\mathrm{s}$	101370.02	10	101600.27	$101600.40\mathrm{s}$
11	101415.54	101384.09	101355.18	11	101629.20	101629.21
12	101405.13	101371.26	101339.49	12	101660.67	101660.93
13	101393.44	101356.84	101322.75	13	101694.80	101694.77
14	101380.86	101341.52	101304.92	14	101731.41	101731.40
15	101367.16	101325.16	101285.91	15	101770.74	101770.70
16	101352.05	101307.69	101265.83	16	101812.55	101812.59
17	101336.11	101289.12	101244.43	17	101857.02	101857.08
18	101318.90	101269.41	101222.36	18	101904.08	101904.14
19	101300.74	101248.45	101198.91	19	101953.66	101953.63
20	101281.30	101226.51	$101174.38\mathrm{w}$	20	102005.87	102005.84
21	101260.79	101203.34	101148.66	21	102060.63	102060.51
22	$101239.04\mathrm{w}$	$101179.22\mathrm{w}$		22	102117.93	102117.90w
23	101216.20	101153.84	$101094.02\mathrm{w}$	23	$102177.73\mathrm{w}$	102177.73
24		101127.38w		24	102240.09	$102240.17\mathrm{w}$
25	$101167.29\mathrm{w}$	$101099.78\mathrm{w}$		25		$102305.13\mathrm{w}$
26				26	$102372.64\mathrm{w}$	

	$X^{1}\Sigma_{g}^{+}(2,0)$ b	and of ${}^{15}N_2$, to	by both b by the product of the p	$h^{\perp}\Pi_{u}$	(v=2) term va	alues. No
	PDL shift app	plied.				
J''	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	102131.34^*					
1	102132.97^*	102127.81^*		1	102131.34^*	102131.53
2	102132.97^*	102125.58		2	102136.64	102136.73
3	102132.97^*	102122.32	102114.29	3	102144.25	102144.61
4	102131.34^*	102117.92^*	102107.22	4	102155.09	102155.07

Table 6: Rotational line assignments and wave numbers for the $b^{1}\Pi_{u} - V^{1}\Sigma^{+}(2,0)$ hand of ¹⁵N = together with $b^{1}\Pi_{u}(u, -2)$ term values. No

0	102131.34^*					
1	102132.97^*	102127.81^*		1	102131.34^*	102131.53^*
2	102132.97^*	102125.58		2	102136.64	102136.73
3	102132.97^*	102122.32	102114.29	3	102144.25	102144.61
4	102131.34^*	102117.92^*	102107.22	4	102155.09	102155.07^*
5	102127.81^*	102112.00^*	102099.18	5	102168.49^*	102167.72^*
6	$102123.54\mathrm{s}$	102105.58		6	102183.54*	102183.59
7	102117.92^*	102097.50		7	$102201.55\mathrm{s}$	102201.52
8	102112.00^*	102088.71		8	102221.93^*	102222.43
9	$102104.49\mathrm{s}$	102078.83		9	102245.72^*	102245.97
10	$102095.75\mathrm{w}$	102067.60		10	$102271.64\mathrm{s}$	102271.88
11	102085.88	102055.13		11	$102300.02\mathrm{w}$	102300.25
12	$102075.08\mathrm{w}$	102041.47		12	102331.00	102331.14
13	102062.87	102026.52		13	$102364.74\mathrm{w}$	102364.44
14	102049.44w	102010.70		14	102400.79	102400.58
15	$102035.36\mathrm{w}$	101994.06		15	$102439.32\mathrm{w}$	102439.60
16		$101975.81\mathrm{w}$		16	$102480.90\mathrm{w}$	$102480.72\mathrm{w}$
17	$102003.16\mathrm{w}$	$101956.50\mathrm{w}$		17		$102524.47\mathrm{w}$
18				18	$102571.12\mathrm{w}$	
19	$101965.86\mathrm{w}$			19		
20				20	$102671.03\mathrm{w}$	

Table 7: Rotational line assignments and wave numbers for the $b \,{}^{1}\Pi_{u} - X \,{}^{1}\Sigma_{g}^{+}(3,0)$ band of ${}^{15}N_{2}$, together with $b \,{}^{1}\Pi_{u}(v=3)$ term values. No PDL shift applied.

J''	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	$102820.79\mathrm{s}$					
1	102821.77^*	102816.65^*		1	$102820.66\mathrm{s}$	102820.37^*
2	102821.77^*	102814.45	$102809.38\mathrm{sw}$	2	102825.56	102825.60
3	102821.77^*	102811.10	102803.34	3	102833.17	102833.39
4	$102819.60\mathrm{s}$	102806.79^*	102796.26	4	102843.89	102843.94^*
5	102816.65^*	102800.84	102787.99	5	102856.75	102856.56
6	$102812.08\mathrm{s}$	102794.22	102778.74	6	$102872.20^{*}{ m s}$	102872.23
7	102806.79^*	102786.19	$102768.00\mathrm{s}$	7	$102890.07\mathrm{s}$	102890.21
8		102777.22	$102756.32\mathrm{s}$	8	102910.80^*	102910.95
9	102792.71	102766.83		9	102933.79^*	102933.97
10	102783.88	$102755.47\mathrm{s}$	102729.51^*	10	102959.76	$102959.75\mathrm{s}$
11	102773.82	102743.19	102714.54^*	11	102988.16	102988.31
12	$102762.71\mathrm{w}$	102729.51^*	102698.49^*	12	103019.07	103019.18^*
13	102750.42	102714.54^*	102681.26^*	13	$103052.53\mathrm{w}$	103052.46^*
14	$102736.95\mathrm{w}$	102698.49^*	$102662.81^* \mathrm{w}$	14	103088.54	103088.37^*
15	102722.25	102681.26^*	102643.19^*	15	$103126.83\mathrm{w}$	103126.81^*
16		$102662.81^* \mathrm{w}$		16	103167.80	$103167.71^*\mathrm{w}$
17	$102689.27\mathrm{w}$	102643.19^*	$102599.84 \mathrm{sw}$	17		103211.16^*
18		$102623.10\mathrm{w}$		18	$103257.23\mathrm{w}$	$103257.83\mathrm{w}$
19	$102651.78\mathrm{w}$	$102601.07\mathrm{sw}$		19		$103306.24\mathrm{sw}$
20				20	$103356.96\mathrm{w}$	

Table 8: Rotational line assignments and wave numbers for the $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(4,0)$ band of ¹⁵N₂, together with $b^{1}\Pi_{u}(v = 4)$ term values. PDL shift is -0.18 cm^{-1} .

$J^{\prime\prime}$	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	103488.08					
1	103489.61	103484.45^*		1	103488.08	103488.17^*
2	$103490.23\mathrm{s}$	103482.26		2	103493.34	103493.41
3	$103489.29\mathrm{s}$	103478.99	103471.05	3	$103501.29\mathrm{s}$	103501.28
4	103487.75	103474.60	$103464.05\mathrm{s}$	4	$103511.60\mathrm{s}$	103511.75
5	$103484.90s^*$	103469.43	$103455.89\mathrm{s}$	5	103524.90	103525.15
6	103481.27	103462.84	103446.65^*	6	103540.69^*	103540.85
7	103476.26	103455.31	103436.75^*	7	103559.28	103559.32
8		103446.65^*	$103425.25\mathrm{s}$	8	103580.27	103580.37^*
9	$103463.34\mathrm{s}$	103436.75^*	$103413.21\mathrm{s}$	9	103603.72	103603.90^*
10	$103454.66\mathrm{s}$	103425.97	103399.44	10	103630.20	103630.25
11	103445.32	103414.03	103385.08	11	103658.96	103659.15
12	103434.82	103400.86	103369.30	12	103690.54	103690.53
13	103423.17	103386.87	103352.69	13	103724.57	103724.79
14	$103411.57\mathrm{s}$	103371.48	103334.76	14	103761.10	103761.36
15	103396.08^*	103355.10	103315.56	15	$103801.45\mathrm{s}$	103800.64
16	103380.88	103337.05	$103296.55\mathrm{s}$	16	103841.68	103841.96
17	103364.42	103318.38	103273.72	17	103885.86	103886.35
18	$103346.82\mathrm{s}$	$103298.41\mathrm{s}$	$103251.19\mathrm{w}$	18	103932.54	$103933.14\mathrm{s}$
19	103328.09	103277.10	103227.51	19	$103981.83 \mathrm{ws}$	103982.28
20	$103308.64\mathrm{w}$	$103254.82\mathrm{w}$	$103202.79\mathrm{w}$	20	104033.41	$104034.15\mathrm{w}$
21	$103286.83\mathrm{s}$	103231.08	103176.37	21	$104087.53\mathrm{w}$	104088.24
22		$103206.33\mathrm{w}$	$103148.74\mathrm{w}$	22	104144.06	$104145.01\mathrm{w}$
23		103180.28	103120.17	23		104204.17
25		103123.61		25		104328.96

	PDL shift is -	-0.20 cm^{-1} .				
J''	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	104615.82					
1	104617.573	104612.133		1	104615.82	104615.848
2	104618.289	104610.075	104604.67	2	104621.288	104621.221
3	104618.011	104606.984	$104598.79\mathrm{s}$	3	104629.435	104629.275
4	104616.82	104602.88	$104592.13\mathrm{s}$	4	104640.302	104640.03
5	104614.42	104597.77	104584.60^*	5	104653.92	104653.49
6	104611.31	$104591.60\mathrm{s}$	104575.86	6	104670.16	$104669.61\mathrm{s}$
7	104607.092	104584.60^*	104566.15	7	104689.27	104688.61^*
8	$104601.94\mathrm{s}$	104576.47	104555.51	8	104711.103	104710.20
9	104595.94	104567.27	104543.96	9	104735.67	104734.42
10	104588.97	104557.20	104531.40	10	104763.04	104761.48
11	104581.08	104546.10	104517.87	11	104793.24	104791.22
12	104572.37	104534.10	104503.57	12	104826.16	104823.77
13	104562.95	104521.13	104488.20	13	104862.12	104859.05
14	104552.39	104507.19	104472.32	14	104900.83	104897.08
15	104541.64	104492.24	104455.24	15	104942.41	104937.79
16		104476.76	104437.64	16	104987.19	104981.67
17		104459.69		17		105027.66
18		104442.11		18		105076.84

Table 9: Rotational line assignments and wave numbers for the $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(5,0)$ band of ¹⁵N₂, together with $b^{1}\Pi_{u}(v = 5)$ term values. PDL shift is -0.20 cm^{-1} .

Table 10: Rotational line assignments and wave numbers for the $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(6,0)$ band of ¹⁵N₂, together with $b^{1}\Pi_{u}(v=6)$ term values. PDL shift is -0.13 cm^{-1} .

$J^{\prime\prime}$	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	105237.202					•••
1	105238.567	105233.484		1	105237.202	105237.199
2	105238.760	105231.129	105226.26	2	105242.282	105242.275
3	105237.777	105227.597	105220.12	3	105249.906	105249.888
4	105235.64	105223.05	105212.77	4	105260.068	105260.20
5	105232.286	105217.08	105204.37	5	105272.76	105272.80
6	105227.779	105210.10	105194.71	6	105288.010	105288.11
7	105222.22	105201.68	105184.01	7	105305.790	105305.69
8	105215.31	105192.35	105172.03	8	105326.25	105326.08
9	105207.35	105181.75	105159.12	9	105349.04	105348.90
10	105197.95	105169.90	105144.76	10	105374.44	105374.18
11	105187.73	105157.06	105129.26	11	105402.36	105402.18
12	105176.25	105142.88	105112.81	12	105432.85	105432.55
13	105163.67	105127.59		13	105465.92	105465.52
14	105149.71	105111.10		14	105501.60	105500.98
15	105134.83			15	105539.59	
16	$105118.35\mathrm{w}$			16	105580.37	
17				17	$105623.25\mathrm{w}$	

Table 11: Rotational line assignments and wave numbers for the $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(7,0)$ band of ¹⁵N₂, together with $b^{1}\Pi_{u}(v=7)$ term values. PDL shift is -0.19 cm^{-1} .

$J^{\prime\prime}$	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	105981.332					
1	105982.652	105977.619		1	105981.332	105981.334
2	105982.782	105975.231	105970.16	2	105986.367	105986.377
3	105981.722	105971.55^*	105964.06	3	105993.927	105993.84^*
4	105979.473	105966.90	105956.84	4	106004.131	106004.05
5	105976.033	105960.93	105948.25	5	106016.624	106016.65
6	105971.55^*	105953.80	105938.60	6	106031.758	106031.81
7	105965.63	105945.40	105927.76	7	106049.43	106049.41
8	105958.74	105936.00	105915.71	8	106069.59	106069.72
9	105950.56	105925.44	105902.40	9	106092.41	106092.59
10	105941.28	105913.54	105888.07	10	106117.72	106117.82
11	105930.99	105900.54	105872.61	11	106145.56	106145.66
12	105919.72	105886.60	$105855.91{ m s}^*$	12	106176.12	106176.27
13	105907.08	105871.50	105838.23^*	13	106209.29	106209.42
14	105893.64	$105855.42s^*$	105819.31	14	106245.05	$106245.30s^*$
15	105879.23	105838.23^*	105799.54	15	106283.52	106283.77^*
16	105863.80	105820.17	105778.61^*	16	106324.70	106325.08
17	105847.69	105801.32	105756.67	17	106368.67	106369.29
18	105830.65	105781.45	105733.90	18	106415.62	106416.18
19	105812.94	105760.90	105710.40	19	106465.28	106466.08
20	105794.77	105739.69	105685.86	20	106518.16	106519.02
21	105776.18	105718.18	105661.03	21	106574.10	106575.34
22	105757.38	105696.19	105635.36^*	22	106633.39	106634.87
23	105738.33	105674.08	105609.53	23	106696.07	106697.97
24	$105719.56\mathrm{s}$			24	106762.21	
25	105700.99		105556.83	25	$106832.36\mathrm{s}$	
26				26	106906.35	

J''	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
1	106767.40	$106762.34\mathrm{s}$		1		$106766.06\mathrm{s}$
2	$106767.87\mathrm{s}$	106760.01		2	106771.12	106771.16
3	106766.84	106756.58	106748.98^*	3	106778.82	106778.87
4	106764.89	106752.07^*	106741.67	4	106789.12	106789.22^*
5	106761.80	106746.26^*	106733.39	5	106802.03	106801.98^*
6	106757.58	106739.05^*	106724.01	6	106817.52	106817.06^*
$\overline{7}$	106752.38^*	106731.20	$106713.44\mathrm{s}$	7	106835.59	106835.21
8	106746.26^*	106722.07^*	106701.98^*	8	106856.31^*	106855.79^*
9	106739.05^*	106712.16^*	106689.09^*	9	$106879.90\mathrm{s}$	106879.31^*
10	$106730.87\mathrm{s}$	106701.08	$106675.62\mathrm{s}$	10	106906.15	106905.36
11	106722.07^*	106689.09^*	106661.03	11	106935.28	106934.21^*
12	106712.16^*	106676.30	106645.62	12	106967.23	106965.97
13	106701.98^*	106662.54	106629.30	13	107002.07	107000.46
14	106691.03	106648.21	106612.19	14	107040.07	107038.09
15	106679.76	106633.13	106594.53	15	107081.01	107078.67
16	106667.92	106617.60	106576.20	16	107125.27	107122.51
17	106656.11	106601.57	106557.28	17	107172.83	107169.54
18	106644.24	106585.05		18	107224.06	107219.78
19	106632.04	$106568.48s^*$	106518.86	19	107278.97	$107273.66s^*$
20	106620.09	$106551.81\mathrm{s}$	$106499.60\mathrm{s}$	20	107337.23	107331.14
21	106608.16			21	107399.42	
22				22	107465.33	

Table 12: Rotational line assignments and wave numbers for the $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(8,0)$ band of ¹⁵N₂, together with $b^{1}\Pi_{u}(v=8)$ term values. No PDL shift applied.

Table 13: Rotational line assignments and wave numbers for the $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(9,0)$ band of ¹⁵N₂, together with $b^{1}\Pi_{u}(v=9)$ term values. No PDL shift applied.

J''	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	107446.19					
1	107447.10^*	107442.61		1	107446.19	107446.33
2	107447.10^*	107439.75		2	107450.95	107450.90
3	107444.83	107435.51	107428.66	3	107457.84	107457.80
4	107441.58	107429.97	107420.69	4	107467.14	107467.12
5	107436.79	107423.06^*	107411.44	5	107478.73	107478.78^*
6	107430.70	107414.58^*	107400.72	6	107492.48	107492.59^*
7	107423.06^*	107404.72	107388.43	7	107508.69	107508.73
8	107414.58^*	107393.43	107374.95	8	107527.35	107527.15
9	$107404.17\mathrm{s}$	107380.99	107360.21	9	107548.15	107548.14
10	107392.48	107366.96	107343.87	10	107571.18	107571.24
11	107379.54	107351.73	107326.06	11	107596.75	107596.85
12	107365.02	107334.90	107307.08	12	107624.67	107624.57
13	107349.46	107316.71	107286.73	13	107654.69	107654.63
14		107297.26	107264.80	14	107687.25	107687.14
15	107313.47	107276.27	107241.57	15		107721.81
16	107293.52	107254.15		16	107759.01	107759.06
17	107272.35			17	107798.43	
18				18	107840.32	

Table 14: Rotational line assignments and wave numbers for the $c_3 {}^1\Pi_u - X {}^1\Sigma_g^+(0,0)$ band of ${}^{15}N_2$, together with $c_3 {}^1\Pi_u(v=0)$ term values. PDL shift is -0.08 cm^{-1} .

J''	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	$104072.725\mathrm{b}$					
1	$104074.547\mathrm{b}$	$104069.052 \mathrm{b}^{*}$		1	$104072.725{\rm b}$	$104072.767\mathrm{b^*}$
2	$104075.316\mathrm{b}^*$	$104067.199\mathrm{b}$	$104061.48\mathrm{s}$	2	$104078.262\mathrm{b}$	$104078.345\mathrm{b}$
3	$104075.316\mathrm{b}^*$	$104064.421\mathrm{b}$	104056.07^*	3	$104086.462\mathrm{b}$	$104086.712\mathrm{b}$
4	$104074.306\mathrm{b}$	104060.76^*	104049.32	4	$104097.607{\rm b}$	104097.91^*
5	$104072.224\mathrm{b}$	104056.07^*	104041.90	5	$104111.457\mathrm{b}$	104111.79^*
6	104069.17^*	104050.54	104033.40	6	$104127.948\mathrm{b}$	104128.55
7	$104065.334\mathrm{b}$	104044.06	104023.90	7	104147.22	104148.07
8	104060.76^*	104036.61	104013.53	8	$104169.345\mathrm{b}$	104170.33
9	104054.52	104028.26	104002.25	9	104194.32	104195.41
10	104047.78	104018.84	103989.87	10	104221.65	104223.12
11	104040.02	104008.52	103976.52	11	104252.02	104253.64
12	104031.25	103997.34	103962.31	12	104285.15	104287.01
13	104021.40	103985.08	103947.23	13	104320.91	104323.00
14	104010.72	103971.97^*	103931.02	14	104359.36	104361.85^*
15	103998.93	103957.55^*	103913.87	15	104400.53	104403.09^*
16		103942.18	103895.56	16	104444.41	104447.09
17	103971.97^*	103925.78	103876.38	17	104491.00	104493.74
18	103957.55^*	103908.43	103856.28	18	104540.07	104543.15
19	103941.14	103889.88	103835.03	19	104592.08	104595.06
20	103923.81	103870.26	$103812.55\mathrm{w}$	20	104646.35	104649.58
21	103905.65	103849.48	103789.21	21	104703.21	104706.64
22	103886.08	103827.62	$103764.60\mathrm{w}$	22	104762.84	104766.31
23	103865.29	103804.17	$103738.98\mathrm{w}$	23	104824.76	104828.07
24	$103843.62\mathrm{w}$	$103780.15\mathrm{w}$		24	104889.29	$104892.94\mathrm{w}$
25	103820.18	103754.43	$103684.05\mathrm{w}$	25	$104956.41\mathrm{w}$	104959.79
26	$103795.77\mathrm{w}$	$103727.53\mathrm{w}$		26	105025.53	$105029.14\mathrm{w}$
27		$103699.30\mathrm{w}$		27	$105097.37\mathrm{w}$	$105100.82\mathrm{w}$

Table 15: Rotational line assignments and wave numbers for the $c_3 {}^1\Pi_u - X {}^1\Sigma_g^+(1,0)$ band of ${}^{15}N_2$, together with $c_3 {}^1\Pi_u(v=1)$ term values. No PDL shift applied.

J''	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	106452.06					
1	106454.66	106448.34		1	106452.06	106452.06
2	106456.59^*	106447.13	$106441.04\mathrm{s}$	2	106458.35	106458.28
3	106459.37^*	106445.28	106436.02	3	106467.70	106467.57
4	106459.37^*	$106444.30\mathrm{s}$	106430.55	4	106481.56	$106481.45\mathrm{s}$
5	106459.37^*	106440.59	106425.84	5	106496.61	106496.31
6		106436.74	106418.60	6	106515.09^*	106514.75
7	$106458.86\mathrm{s}$	106431.85	106411.08^*	7		106535.86
8	106456.59^*	106429.21		8	106562.98	106562.93
9	$106453.06\mathrm{s}$	106423.22	106395.84	9	106590.21	106590.37
10	$106451.77\mathrm{s}$	106416.52	106385.93	10	106620.28	106620.80
11	$106445.98\mathrm{s}$	106411.08^*	106375.16	11	$106656.02\mathrm{s}$	106656.20^*
12	$106439.61\mathrm{ws}$	106402.73^*	$106366.33\mathrm{s}$	12	106691.12	106692.40^*
13	106432.62	106393.84	106353.19	13	106729.39	106731.76
14	106424.06	106384.02	106339.51	14	106770.56	106773.90
15	106414.52	106373.17	106325.03	15	106813.97	106818.71
16	106403.72	106361.24	$106309.10\mathrm{s}$	16	106860.10	106866.15
17	106391.87	106347.92	106292.17	17	106908.61	106915.89
18	106379.15	106333.27	106273.86	18	106959.87	106968.00
19	106365.47	106317.11	106254.71	19	107013.93	107022.29
20	106350.56	106299.10	106234.66	20	107070.68	107078.43
21	106334.16	106279.51	106213.53	21	107129.89	107136.67
22		106258.11	$106191.36\mathrm{w}$	22	107191.37	107196.79
23		106234.67^*	106167.51	23	$107254.57\mathrm{w}$	107258.56^*
24		$106209.50\mathrm{w}$	$106141.79\mathrm{w}$	24	107319.98^*	$107322.28\mathrm{w}$
25		106182.29	106114.63^*	25	$107385.68\mathrm{w}$	107387.64
26		$106153.37\mathrm{w}$	$106084.08\mathrm{w}$	26		$107454.97\mathrm{w}$
27		$106122.10\mathrm{w}$		27		$107523.62\mathrm{w}$

Table 16: Rotational line assignments and wave numbers for the $o^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(0,0)$ band of ¹⁵N₂, together with $o^{1}\Pi_{u}(v=0)$ term values. PDL shift is -0.19 cm^{-1} .

J''	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	105648.544					
1	105651.206	105644.602		1	105648.543	105648.317
2	$105653.434\mathrm{s}$	105643.485	105637.396	2	105654.921	105654.631
3	$105653.459\mathrm{s}$	105641.820	105632.630	3	$105664.579\mathrm{s}$	105664.111
4	105654.744	$105639.595\mathrm{w}$	105627.424	4	$105675.751\mathrm{s}$	105676.746
5	$105655.185\mathrm{w}$	$105636.805\mathrm{w}$	$105620.017 {\rm s}$	5	105691.895	105692.529
6	105654.946	105633.444	105613.875	6	105710.910	105711.455
7	105654.072	105629.507	105606.889	7	105732.961	105733.518
8	105652.574	105624.985	105599.240	8	105758.088	105758.708
9	$105650.364\mathrm{w}$	$105619.860\mathrm{s}$	105590.946	9	105786.302	$105787.006 {\rm s}$
10	$105647.731\mathrm{w}$	$105613.963\mathrm{s}$	105582.027	10	$105817.511{\rm w}$	$105818.242\mathrm{s}$
11	105644.271	105607.847	105572.39	11	$105852.011 {\rm w}$	105852.967
12	105640.217	105600.828	105562.33	12	$105889.392\mathrm{w}$	105890.496
13	105635.314	105593.191	105551.37	13	105929.887	105931.114
14		105584.809	$105540.12\mathrm{w}$	14	105973.239	105974.691
15	105623.275	105575.686		15		106021.229
16	$105615.86\mathrm{w}$	105565.95		16	106068.821	106070.86
17	$105607.07\mathrm{s}$	105555.54		17	$106120.77\mathrm{w}$	106123.51
18	105602.10			18	$106175.04\mathrm{s}$	
19	105589.49			19	106236.83	
20				20	106294.68	
21	105564.54			21		
22				22	106421.71	

Table 17: Rotational line assignments and wave numbers for the $o^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(1,0)$ band of ¹⁵N₂, together with $o^{1}\Pi_{u}(v=1)$ term values. No PDL shift applied.

J''	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	107579.76					
1	107582.59	107575.99		1	107579.76	107579.71
2	107584.81	107575.08	$107568.66\mathrm{s}$	2	107586.30	107586.23
3	107586.61	107573.62	107564.00	3	107595.96	107595.91
4	$107587.92 \mathrm{ws}^*$	107571.75	$107558.82\mathrm{s}$	4	107608.95	107608.90
5	107588.81^*	107569.41	107553.28	5	107625.11	107625.13
6	$107589.24s^*$	107566.62	107547.10	6	107644.50	107644.63
7	107588.81^*	107563.22	107540.49	7	107667.10^*	107667.23
8	107588.42^*	107559.36	107533.23^*	8	107692.93	107693.08
9	$107587.28\mathrm{s}$	107555.15	107525.79	9	107722.04	107722.30
10		107550.34	107517.76	10	107754.45	107754.62
11	$107583.59\mathrm{s}$	107545.07	107509.33	11	107789.95	107790.19
12	107580.94^*	$107539.27\mathrm{s}$	107500.29	12	107828.81	$107828.94\mathrm{s}$
13	107577.83	107533.23^*	107490.88	13	107870.66	107871.15^*
14		$107526.30\mathrm{s}$	107480.83	14	107915.89	$107916.18\mathrm{s}$
15	$107570.25\mathrm{s}$	107519.17	107470.35	15	107964.31	107964.71
16		107511.59	107459.41	16	$108015.82\mathrm{s}$	108016.50
17	$107560.64\mathrm{s}$	107503.48	$107447.89\mathrm{s}$	17		108071.45
18		107494.90		18	$108128.61\mathrm{s}$	108129.63
19	107548.66	107485.77		19	108189.77	108190.95
20		$107476.18s^*$	$107410.45\mathrm{s}$	20	108253.88	$108255.51s^*$
21		107466.05	107396.74	21		108323.21
22		107455.46		22		108394.14

Table 18: Rotational line assignments and wave numbers for the $b' {}^{1}\Sigma_{u}^{+} - X {}^{1}\Sigma_{g}^{+}(1,0)$ band of ${}^{15}N_{2}$, together with $b' {}^{1}\Sigma_{u}^{+}(v=1)$ term values. PDL shift is -0.08 cm^{-1} .

J''	R(J'')	P(J'')	J	$T_e(J)$
0	104422.045		0	104419.90
1	104422.626	104416.18	1	104422.045
2	104421.637		2	104426.341
3	104419.27^*	104404.17	3	104432.783
4	104414.98	104395.67	4	104441.50
5	104409.31	104385.71	5	104452.13
6	104402.05		6	104465.03
7	104393.38		7	104480.06
8	104383.00		8	104497.39
9			9	104516.72

Table 19: Rotational line assignments and wave numbers for the $b' {}^{1}\Sigma_{u}^{+} - X {}^{1}\Sigma_{g}^{+}(3,0)$ band of ${}^{15}N_{2}$, together with $b' {}^{1}\Sigma_{u}^{+}(v=3)$ term values. PDL shift is -0.19 cm^{-1} .

J''	R(J'')	P(J'')	J	$T_e(J)$
0	$105826.41s^*$		0	$105824.43 \mathrm{sw}$
1	105827.06	$105820.71\mathrm{sw}$	1	105826.48
2	$105826.17s^*$	105815.33	2	105830.83
3	105823.67	105808.59	3	105837.42s
4	105819.30^*	$105800.27\mathrm{sw}$	4	105845.98
5	105813.90	105790.27	5	
6	105806.92	105778.62^*	6	105869.66
7	105798.07	105765.68	7	105884.91
8	105787.80	105751.17	8	105902.03
9	$105775.71\mathrm{s}$	105734.84	9	105921.46
10	$105762.34\mathrm{s}$	105717.14	10	105943.05
11	105747.25	105697.93	11	105966.53
12	105730.67	105676.87	12	105992.40
13	105712.31	$105654.480\mathrm{w}$	13	106020.33
14	$105692.61\mathrm{w}$	$105630.430{\rm w}$	14	106050.23
15	105671.11?	105604.68	15	106082.52
16		105577.65	16	106116.77
17	$105624.210\mathrm{w}$	105548.81	17	
18	105593.569		18	$106192.181\mathrm{w}$
19	105568.08		19	106228.298
20			20	106 273.27

Table 20: Rotational line assignments and wave numbers for the $b' {}^{1}\Sigma_{u}^{+} - X {}^{1}\Sigma_{g}^{+}(4,0)$ band of ${}^{15}N_{2}$, together with $b' {}^{1}\Sigma_{u}^{+}(v=4)$ term values. No PDL shift applied.

J''	R(J'')	P(J'')	J	$T_e(J)$
0	106570.47^*		0	
1	$106571.31s^*$		1	106570.47^*
2	106570.47^*		2	$106574.92s^*$
3	$106568.92s^*$	$106552.51s^*$	3	106581.83
4	106565.79	106544.68	4	106591.21^*
5	106561.51	106535.49^*	5	106603.03
6	106555.97	106525.11	6	106617.27
7	106549.24	106513.30	7	106634.00
8	$106541.33\mathrm{w}$	106500.30	8	106653.21
9	106532.45	106486.03	9	106675.03
10	106522.81	106470.75	10	106699.59
11	$106512.36\mathrm{s}$		11	106727.09
12	$106501.47\mathrm{s}$		12	$106757.49\mathrm{s}$
13	106490.34		13	106791.17
14	$106478.96\mathrm{s}$	106401.29	14	106828.24
15		106382.66	15	106868.82
16		106363.92	16	106912.80
17		106344.84	17	$106960.94\mathrm{s}$
18		$106326.21\mathrm{s}$	18	107012.52
19		106307.34	19	$107067.75 \mathrm{sw}$
20		$106288.43s^*$	20	107126.63
21	106398.55^*	106269.47	21	$107189.09\mathrm{w}$
22		$106250.41\mathrm{w}$	22	107255.70
23	$106377.02\mathrm{sw}$	106231.81	23	
24			24	107400.84
25	$106356.88\mathrm{w}$	106195.49	25	107479.63
26		106178.03	26	$107562.14\mathrm{w}$
27		$106160.53{ m w}$	27	

Table 21: Rotational line assignments and wave numbers for the $b' {}^{1}\Sigma_{u}^{+} - X {}^{1}\Sigma_{g}^{+}(5,0)$ band of ${}^{15}N_{2}$, together with $b' {}^{1}\Sigma_{u}^{+}(v=5)$ term values. No PDL shift applied. $J'' \quad R(J'') \qquad P(J'') \qquad J \qquad T_{e}(J)$

J''	R(J'')	P(J'')	J	$T_e(J)$
0			0	107227.44
1	107230.24	107223.72	1	107229.73
2	$107229.43\mathrm{s}$	$107218.58\mathrm{s}$	2	107234.00
3	107226.74	107211.74	3	107240.56
4	$107222.86\mathrm{s}$	107203.41	4	107249.10
5	107217.33	107193.45	5	107260.06
6	107210.30	107182.05	6	107272.99
$\overline{7}$	107201.59	107168.91	$\overline{7}$	107288.31
8	107191.28		8	107305.60
9	107179.67		9	107325.00
10	107166.16		10	107346.81
11			11	107370.44
17			17	107558.95
18		106924.22	18	107597.92
19		106892.74	19	107639.04
20		106859.72	20	107682.31
21	106918.59	106825.15	21	107727.87
22	106887.15	106789.19	22	107775.76
23	106854.45	$106751.75\mathrm{s}$	23	107825.84
24	106820.31	$106712.89s^*$	24	107878.28
25	106785.10	106672.85	25	107933.11
26			26	107990.49
27		$106589.01\mathrm{w}$	27	

Table 22: Rotational line assignments and wave numbers for the $b' {}^{1}\Sigma_{u}^{+} - X {}^{1}\Sigma_{g}^{+}(6,0)$ band of ${}^{15}N_{2}$, together with $b' {}^{1}\Sigma_{u}^{+}(v=6)$ term values. No PDL shift applied.

J''	R(J'')	P(J'')	J	$T_e(J)$
0	$107877.12s^*$		0	$107875.00s^*$
1	107878.02	$107871.28s^*$	1	$107877.15\mathrm{s}$
2	$107877.36s^*$	$107866.00\mathrm{s}$	2	107881.76
3	107875.38	107859.49	3	$107888.47\mathrm{s}$
4	$107871.84s^*$	$107851.32\mathrm{s}$	4	107897.64
5	107866.63	107841.88	5	$107908.96s^*$
6	$107860.10\mathrm{s}$	$107830.92s^*$	6	107922.40
7	107852.02	107818.43	7	$107938.11\mathrm{s}$
8	$107842.60\mathrm{s}$	107804.66^*	8	107956.04
9	$107831.47s^*$	107788.91^*	9	$107976.32\mathrm{s}$
10	$107818.94\mathrm{s}$	107771.97^*	10	107998.54
11	107804.66^*	107753.42^*	11	$108023.09\mathrm{s}$
12	107788.91^*	$107733.29\mathrm{s}$	12	108049.90
13	107771.97^*	107711.97	13	108078.88
14	107753.42^*	107689.00	14	108109.69
15	107732.69	107664.15	15	108142.96
16	$107710.56\mathrm{s}$	107638.06	16	108178.27
17	107687.54	107610.36	17	$108215.59\mathrm{s}$
18	$107662.59\mathrm{s}$	$107580.97\mathrm{ws}$	18	108255.51
19	107635.93		19	$108297.31\mathrm{s}$
20	107607.98		20	108341.12
21			21	108 387.31

Table 23: Rotational line assignments and wave numbers for the $c'_4 {}^1\Sigma^+_u - X {}^1\Sigma^+_g(0,0)$ band of ${}^{15}N_2$, together with $c'_4 {}^1\Sigma^+_u(v=0)$ term values.

J''	R(J'')	J	$T_e(J)$
0	104329.845	0	
1	104333.285	1	104329.845
2	104336.581	2	104337.000
3	104339.730	3	104347.727
4		4	104362.021

Table 24: Rotational line assignments and wave numbers for the $c'_4 \, {}^{1}\Sigma^+_u - X \, {}^{1}\Sigma^+_g(1,0)$ band of ${}^{15}N_2$, together with $c'_4 \, {}^{1}\Sigma^+_u(v=1)$ term values. No PDL shift applied.

J''	R(J'')	P(J'')	J	$T_e(J)$
0	106311.13		0	106307.90
1	106313.86	106304.18	1	106311.10
2	106316.16	106299.92	2	106317.60
3	106317.85^*	106295.32	3	106327.35
4	106319.00^*	106290.24	4	106340.09
5	106319.65^*	106284.37	5	106356.21
6	106319.65^*	106278.20	6	106375.34
7	106319.00^*	106271.33	7	106397.79
8	106317.85^*	106264.07	8	106423.04
9	106315.60	106255.90	9	106451.47
10	106312.58	106247.19	10	106482.73
11	106308.65	106237.60	11	106516.87
12	$106303.47\mathrm{s}$	106227.21	12	106553.78
13	106296.82	106215.85	13	106593.04
14	106288.78	106203.16	14	106634.81
15	$106278.59\mathrm{s}$	106189.32	15	106678.64
16	$106266.34\mathrm{w}$	106173.72	16	106724.22
17	$106251.71\mathrm{w}$	106156.26	17	106771.19
18	106234.65^*	106136.40	18	$106819.68\mathrm{w}$
19	$106214.50\mathrm{ws}$	106114.63^*	19	106869.17
20	$106191.34\mathrm{w}$	106089.85	20	106919.79
21	106166.38	106062.63	21	$106970.67\mathrm{w}$
22	106138.28		22	107023.54
23	106108.07		23	107076.96
24			24	107131.96

$J^{\prime\prime}$	R(J'')	$Q(J^{\prime\prime})$	P(J'')	J	$T_e(J)$	$T_f(J)$
0	104659.674					
1	104661.418	104655.805		1	104659.674	104659.652
2	104662.110	$104\ 653.661$	$104648.17\mathrm{w}$	2	104665.265	104665.202
3	104661.760	104650.51^{*}	104642.07	3	104673.651	104673.59*
4	104660.371	104646.18	104635.23	4	104684.843	104684.65
5	104657.91	104640.70	104627.00^{**}	5	104698.841	104698.40
6	$104654.44\mathrm{s}$	104634.44	104618.45^*	6	104715.67	104715.23
7	$104649.79s^*$	104627.00^{**}	104608.02	7	$104735.18 { m ss'}$	104734.71^{**}
8	$104644.54\mathrm{w}$	104618.45^*	$104596.66\mathrm{s'}$	8	$104757.60 \mathrm{s's}^{*}$	104756.92^*
9		104609.02	104584.62s'	9	104783.10	104782.10
10		$104598.28\mathrm{s'}$	104571.66	10	104811.26	$104809.81{ m s}'$
11		104586.71	104557.43	11	104842.44	104840.54
12		$104\ 574.09$	104542.48	12	$104876.25 { m s'}$	104874.04
13		104560.59	$104526.33{ m s}'$	13	104913.10	104910.51
14			104509.38	14	$104952.95\mathrm{s'w}$	
15		$104530.50\mathrm{s'w}$	$104491.59\mathrm{s'w}$	15	$104995.78\mathrm{s'w}$	$104991.86\mathrm{s'w}$
16		$104513.88{ m s}'$	$104472.95\mathrm{s'w}$	16	$105041.60\mathrm{w}$	$105036.71{ m s}'$
17		$104496.39\mathrm{w}$	$104453.47\mathrm{w}$	17	$105090.73\mathrm{w}$	$105084.51\mathrm{w}$
18			$104433.48\mathrm{w}$	18		
19		$104458.88\mathrm{w}$		19		$105189.08\mathrm{w}$
20		$104438.56\mathrm{w}$		20		$105245.53\mathrm{w}$

Table 25: Rotational line assignments and wave numbers for the $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(5,0)$ band of ¹⁴N¹⁵N, together with $b^{1}\Pi_{u}(v=5)$ term values. PDL shift is -0.14 cm^{-1} .

Table 26: Rotational line assignments and wave numbers for the $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(6,0)$ band of ¹⁴N¹⁵N, together with $b^{1}\Pi_{u}(v=6)$ term values. PDL shift is -0.16 cm^{-1} .

$J^{\prime\prime}$	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	105293.848					
1	105295.267	105289.997		1	105293.848	105293.844
2	105295.472	105287.567	$105282.35\mathrm{w}$	2	105299.114	105299.108
3	105294.461	$105283.95 \mathrm{s}^{\prime*}$		3	105307.013	$105307.04\mathrm{s}^{\prime*}$
4	105292.13^{*}	105279.13^{*}	$105268.57\mathrm{w}$	4	105317.544	105317.60^*
5	$105288.73\mathrm{ss'}$	105273.03	$105259.88\mathrm{w}$	5	105330.60^{*}	105330.74
6	$105283.95 \mathrm{s}^{\prime *}$	105265.62^{*}		6	$105346.44\mathrm{ss'}$	105346.41^{*}
$\overline{7}$	$105278.26\mathrm{s}$	105257.11		7	$105364.74s'^*$	105364.82
8	$105271.20\mathrm{w}$			8	$105385.97\mathrm{s}$	
9		$105236.43\mathrm{w}$		9	$105409.68\mathrm{w}$	$105409.51\mathrm{w}$
10		$105224.33\mathrm{w}$		10		$105435.86\mathrm{w}$

Table 27: Rotational line assignments and wave numbers for the $b^{1}\Pi_{u} - X^{1}\Sigma_{g}^{+}(7,0)$ band of ¹⁴N¹⁵N, together with $b^{1}\Pi_{u}(v=7)$ term values. No PDL shift applied.

$J^{\prime\prime}$	R(J'')	Q(J'')	P(J'')	J	$T_e(J)$	$T_f(J)$
0	106047.77^*					
1	106048.93^*	106043.72		1	106047.71	106047.57
2	106048.93^*	$106041.289 \mathrm{bs'}$	106036.11	2	106052.77	$106052.830\mathrm{bs'}$
3	106047.77^*	106037.51	106029.68	3	106060.52	106060.60
4	106045.46	106032.47	106022.09	4	106070.89	106070.94
5	$106041.81\mathrm{s}$	106026.21	106013.22	5	106083.94	106083.91
6	$106036.91\mathrm{s}$	106018.66	106003.17	6	106099.53	106099.44
7	106030.73	106010.04	105991.84	7	106117.66	106117.74
8	106023.38	106000.14	105979.16	8	106138.43	106138.61
9	106014.71	105988.85	105965.34	9	106161.86	106161.94
10		105976.35	105950.35	10	106187.67	106187.88
11		105962.72	105933.74	11	106216.52	106216.54
12		105947.81	105916.56	12		106247.76
13		105931.70		13		106281.62
14		105914.58		14		106318.30

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Table 28: Rotational line assignments and wave numbers for the $c_3 {}^{1}\Pi_u - X {}^{1}\Sigma_g^+(0,0)$ band of ${}^{14}N^{15}N$, together with $c_3 {}^{1}\Pi_u(v=0)$ term values.

J''	R(J'')	Q(J'')	J	$T_e(J)$	$T_f(J)$
0	$104107.794{\rm b}$				
1	$104109.669{\rm b}$	$104103.991{ m b}$	1	$104107.794{\rm b}$	$104107.838\mathrm{b}$
2	$104110.521\mathrm{b}^*$	$104102.099\mathrm{b}$	2	$104113.516\mathrm{b}$	$104113.640\mathrm{b}$
3	$104110.521\mathrm{b}^*$		3	$104122.062b^*$	
4	$104109.396{\rm b}$		4	$104133.604\mathrm{b}^*$	
5	$104107.335{\rm b}$		5	$104147.866{\rm b}$	
6	$104104.274\mathrm{b}$		6	$104165.038\mathrm{b}$	
7	$104100.269{\rm b}$		7	$104185.056{\rm b}$	
8			8	$104207.974{\rm b}$	

Table 29: Rotational line assignments and wave numbers for the $b' {}^{1}\Sigma_{u}^{+} - X {}^{1}\Sigma_{g}^{+}(1,0)$ band of ${}^{14}N^{15}N$, together with $b' {}^{1}\Sigma_{u}^{+}(v = 1)$ term values.

	J''	R(J'')	P(J'')	J	$T_e(J)$
	0	104421.228s'		0	
	1	104421.840		1	104421.233
	2	104420.817	104409.696	2	104425.687
	3	104418.177		3	104432.358
	4	104413.916		4	104441.260
	5	104408.039		5	104452.386
_	6			6	104465.742

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Publications

The following scientific publications are reproduced in this thesis:

Chapter 2: Extreme ultraviolet laser excitation of isotopic molecular nitrogen: The dipole-allowed spectrum of ${}^{15}N_2$ and ${}^{14}N^{15}N$, J.P. Sprengers, W. Ubachs, K.G.H. Baldwin, B.R. Lewis, and W.-Ü L. Tchang-Brillet, *J. Chem. Phys.* **119** (2003) 3160. Data archive (EPAPS Document No. E-JCPSA6-119-012330, http://www.aip.org/pubservs/epaps.html) is presented in the **Appendix**.

Chapter 3: Lifetime and predissociation yield of ${}^{14}N_2 \ b^1\Pi_u(v=1)$, J.P. Sprengers, W. Ubachs, A. Johansson, A. L'Huillier, C.-G. Wahlström, R. Lang, B.R. Lewis, and S.T. Gibson, *J. Chem. Phys.* **120** (2004) 8973. This paper also appeared in the *Virtual Journal of Ultrafast Science*.

Chapter 4: Pump-probe lifetime measurements on singlet *ungerade* states in molecular nitrogen,

J.P. Sprengers, A. Johansson, A. L'Huillier, C.-G. Wahlström, B.R. Lewis, and W. Ubachs, *Chem. Phys. Lett.* **389** (2004) 348.

Chapter 5: Isotopic variation of experimental lifetimes for the lowest ${}^{1}\Pi_{u}$ states of N₂,

J.P. Sprengers, W. Ubachs, and K.G.H. Baldwin, *J. Chem. Phys.* **122** (2005) 144301.

Chapter 6: Lifetimes and transition frequencies of several singlet *ungerade* states in N_2 between 106000-109000 cm⁻¹,

J.P. Sprengers and W. Ubachs, J. Mol. Spectrosc. 235 (2006) 176.

Chapter 7: Reanalysis of the $o^1 \Pi_u(v=1)/b^1 \Pi_u(v=9)$ Rydberg-valence complex in N₂, to be published.

Chapter 8: Optical observation of the $3s\sigma_g F^3\Pi_u$ Rydberg state of N₂, J.P. Sprengers, E. Reinhold, W. Ubachs, K.G.H. Baldwin, and B.R. Lewis, *J. Chem. Phys.* **123** 144315 (2005).

Chapter 9: Newly observed triplet states and singlet-triplet interactions in the

XUV spectrum of N_2 , to be published.

Chapter 11: High precision frequency calibration of N I lines in the XUV domain, E.J. Salumbides, J.P. Sprengers, E. Reinhold, and W. Ubachs, *J. Phys. B* 38 (2005) L383.

Other publications and contributions:

• The $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of CF starting from highly excited vibrational states,

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- Highly accurate transition frequencies in the H₂ Lyman and Werner absorption bands,
 J. Philip, J.P. Sprengers, Th. Pielage, C.A. de Lange, W. Ubachs, and E. Reinhold, *Can. J. Chem.* 82 (2004) 713.
- Lifetime and predissociation yield of ${}^{14}\mathrm{N}_2~b^1\Pi_u(v=1)$ revisited: effects of rotation,

B.R. Lewis, S.T. Gibson, J.P. Sprengers, W. Ubachs, A. Johansson, and C.-G. Wahlström, *J. Chem. Phys.* **123** (2005) 236101.

Summary

The major constituent of the Earth's atmosphere is molecular nitrogen (N_2) , in which ¹⁴N₂ is the main isotopomer (only 1 out of 273 nitrogen atom is the heavier ¹⁵N atom). This molecule shields the Earth's surface from harmful extreme ultraviolet (XUV) solar radiation with wavelengths $\lambda < 100$ nm by photo-excitation, photodissociation and photo-ionization processes. N₂ is also involved in other processes in the Earth's atmosphere: it dominates the Rayleigh scattering because of its high abundance and emission of N₂ has been observed in the daytime airglow and the aurora. Also in the atmospheres of Titan and Triton, satellites of Saturn and Neptune, respectively, N₂ is a major constituent and emission of N₂ has been observed. Currently, the Cassini-Huygens mission to the Saturn system is under way, including an investigation of Titan's N₂-rich atmosphere. Recently, absorption of N₂ has been observed for the first time in interstellar medium using the Far Ultraviolet Spectroscopic Explorer (FUSE) satellite. In Chapter 1, some aspects of N₂ in planetary atmospheres and space are reviewed.

 N_2 is almost transparent in the visible and the ultraviolet domains and strong electric-dipole allowed absorption occurs in the XUV domain with $\lambda < 100$ nm, consisting of transitions from the singlet ground state with gerade symmetry $(X^1\Sigma_g^+)$ to excited singlet states with ungerade symmetry $({}^1\Sigma_u^+$ and ${}^1\Pi_u)$. These excited states can be distinguished into Rydberg states, which converge on states of the ion N_2^+ and valence states which are located at larger internuclear distances. Strong electrostatic and rotational interactions occur between these states resulting in a complex XUV absorption spectrum, with not only irregularities in the rovibronic structure but also in the intensity distribution.

Most of the singlet ungerade states predissociate, i.e, these bound states couple with other (pre-)dissociating states and the molecule falls apart. The predissociation occurs via spin-orbit coupling with triplet states with ungerade symmetry $({}^{3}\Pi_{u})$. Upon excitation of the singlet ungerade states in the Earth's atmosphere, whether by absorption or by electron impact processes, the excited states emit a photon or predissociate. Predissociation of N₂ is a major source of N atoms and furthermore, the rates of these competing emission and predissociation processes provide key inputs for radiation budget models of the Earth's atmosphere.

In this Thesis, the structure of the excited singlet and triplet *ungerade* states of N₂ are studied experimentally, including all the different perturbations between them and the predissociative behavior. Most of the experiments are carried out using the XUV laser facility at the Laser Centre Vrije Universiteit, Amsterdam. Two different nanosecond pulsed XUV sources are employed, both based on harmonic upconversion: a pulsed dye laser (PDL) based XUV source [XUV bandwidth $\sim 0.3 \text{ cm}^{-1}$ full-width at half-maximum (FWHM)] and a pulsed dye amplifier (PDA) based XUV source [XUV bandwidth ~0.01 cm⁻¹]. The N₂ spectra are recorded using 1 XUV + 1 UV ionization spectroscopy, in which the XUV photon excites the molecule from the ground state to the excited state and the UV photon subsequently ionizes the molecule to form detectable N₂⁺ ions.

Experimental studies on the singlet *ungerade* states in N₂, using the PDL-based and PDA-based XUV sources, are presented in Chapters 2, 5, 6 and 7. In Chapter 2 and the Appendix, the dipole-allowed spectrum of ¹⁵N₂ and to a lesser extent of ¹⁴N¹⁵N between 100 000 – 108 000 cm⁻¹ is presented, including rotational analyses and revealing electrostatic and rotational perturbations. The overall pattern of the perturbations is found to be similar to that for the well-known ¹⁴N₂ isotopomer, but also many isotope dependent aspects are found due to the different isotope shifts for the rovibronic states. Furthermore, a comprehensive perturbation model of the singlet *ungerade* states is presented in Chapter 2 for ¹⁵N₂ and ¹⁴N¹⁵N, showing good agreement with experiment.

In Chapters 5 and 6, lifetimes of the singlet ungerade states (mostly of ${}^{1}\Pi_{u}$ symmetry) between 100 000–106 000 cm⁻¹ and 106 000–109 000 cm⁻¹ are reported, respectively. Natural linewidths are derived from the observed linewidths of single rotationally-resolved spectral lines recorded with the PDA-based XUV source after deconvolving of the instrument width. Subsequently, lifetimes are deduced from the natural linewidths. Note that in Chapter 6, the output of the PDA is mixed with the 532 nm output of a nanosecond pulsed injection-seeded Nd:YAG laser before further harmonic upconversion to the XUV. Most of the levels show significant lifetime broadening and the lifetimes are found to be strongly dependent on vibrational level and isotopomer. The lifetimes give new information on the predissociation rates which dominate the radiative decay for the levels studied.

In Chapter 7, the Rydberg-valence complex $o^1 \Pi_u (v=1)/b^1 \Pi_u (v=9)$ is studied. In ¹⁴N₂, these two levels tend to cross each other, resulting in a local electrostatic perturbation. In this Chapter, a new rotational assignment, a reanalysis of the local perturbation and linewidths/lifetimes are given. Also a spectrum of these two levels in ¹⁴N¹⁵N is reported, showing no local perturbation.

In Chapters 8 and 9, transitions from the $X^1\Sigma_g^+$ ground state to several triplet ungerade states are studied with the PDL-based and PDA-based XUV sources. These singlet-triplet transitions are optically forbidden but since some of the triplet ungerade states locally interact with singlet ungerade states, which are optically allowed for transitions from the ground state, transitions to some triplet ungerade states borrow intensity and become observable. In Chapter 8, the first optical observation of the $F^3\Pi_u(v=0)$ Rydberg state in ¹⁴N₂ is presented, including a full characterization with rotational resolution and a determination of the predissociation level widths. In Chapter 9, observations of other triplet ungerade states are reported: the $D^3\Sigma_u^+$ and $G^3\Pi_u$ Rydberg states and the $C^3\Pi_u$ valence state. Transition energies, line assignments, linewidths and rotational (deperturbation) analyses are given.

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 N_2 is also investigated with the picosecond XUV laser system at the Lund Laser Centre, Sweden. With this laser system, the rotational structure is not resolved but it is suitable to perform direct time domain pump-probe lifetime measurements for a selected range of rotational levels. In the pump-probe scheme, a XUV photon excites the molecule to the state under investigation and a UV photon ionizes the molecule and by delaying the UV photon, lifetime decay curves are recorded from which lifetime values are derived. This system is applicable for lifetimes >200 ps, while with the Amsterdam setup lifetimes shorter than 800 ps can be determined. The two systems are therefore complementary. Using the Lund picosecond XUV setup, lifetimes of several singlet ungerade states are determined in ${}^{14}N_2$ and ${}^{15}N_2$ and are discussed in Chapters 3 and 4. The experimental lifetimes again show the erratic dependence on vibrational and in some cases also on rotational quantum number. Isotopic differences in lifetime are found as well. Chapter 3 only focuses on the relatively long-lived $b^1 \Pi_u (v = 1)$ level in ¹⁴N₂, including semiempirical closecoupling calculations of the radiative lifetime and determining a predissociation vield for this level.

In Chapter 10, a coupled-channel Schrödinger equations (CSE) predissociation model, developed by Lewis and coworkers, is discussed for the singlet ungerade (only ${}^{1}\Pi_{u}$) states below ~ 105700 cm⁻¹, in which the experimental data (transition energies, linewidths/lifetimes) presented in Chapters 2 - 9 are used (or will be used in future) as key inputs. All the ${}^{1}\Pi_{u}$ and ${}^{3}\Pi_{u}$ states and all the different interactions are included in the model. From the computed photodissociation cross sections, transition energies, predissociation linewidths and oscillator strengths are deduced and iteratively compared with the experimental database to optimize the model parameters. The isotopic dependences found in the experimental data are very helpful in testing the model. The model and experimental results are in very good agreement, the isotopic dependences are nicely reproduced by the model. The model shows that the predissociation of the lowest ${}^{1}\Pi_{u}$ states is governed by spin-orbit coupling with the $C^3 \Pi_u$ state, which electrostatically couples with the continuum of the $C^{\prime 3}\Pi_{u}$ state. The isotopic differences of the lifetimes are due to the different isotope shifts of the levels, resulting in different interactions contributions and predissociation rates. Also further extensions of the model are proposed in Chapter 10. Since more information is obtained on the ${}^{3}\Pi_{u}$ manifold $[(F, G, C)^{3}\Pi_{u}]$ states, see Chapters 8 and 9], an extension of the model towards higher energies is maybe possible. Furthermore, the ${}^{1}\Sigma_{n}^{+}$ states are not yet included in the model, but may be so in future to explain their predissociation behavior.

Finally, Chapter 11 contains high precision frequency calibration measurements on N I lines, performed using the Amsterdam PDA-based XUV source. A beam of N atoms is produced by discharging a mixture of N_2 and helium in a pulsed expansion and several N I lines are observed in the XUV domain. To explain the small isotope shifts observed, large specific-mass shifts are proposed which almost cancel the effect of the normal mass-shift contribution to the isotope shift (Bohr shift). These laboratory calibrations may be useful for comparison with N I lines observed in quasars to determine a possible temporal variation of the fine structure constant α .

Samenvatting

De samenvatting van dit proefschrift met de titel "Extreem ultraviolet laser excitatie van molekulair stikstof: storingen en predissociatie" is niet een directe vertaling van de summary in de Engelse taal. Terwijl in de summary uitgebreid wordt ingegaan op specifieke metingen, heb ik getracht om de Nederlandstalige samenvatting enigzins te populariseren.

In dit proefschrift wordt het stikstof molekuul (N_2) bestudeerd met de hulp van laser opstellingen. Onderzoek naar N_2 is van atmosferisch belang. De aardse atmosfeer bestaat hoofdzakelijk uit N_2 (78 %) en molekulair zuurstof (O_2 , 21 %). N_2 speelt een aanzienlijke rol in een aantal processen in de aardse atmosfeer. Door de overvloed aan N_2 , domineert dit molekuul bijvoorbeeld de Rayleigh verstrooiing van het zonlicht. Aangezien blauw licht meer verstrooid wordt dan rood licht, heeft de lucht een blauwe kleur.

Verder absorbeert N_2 nagenoeg geen zonlicht in het zichtbare en het ultraviolette (UV) deel van het spectrum. En dat is maar goed ook, anders zou er geen zonlicht op het aardse oppervlak vallen. Ozon (O_3) absorbeert de schadelijke UV straling. Straling met een nog kortere golflengte dan UV noemen we eXtreme UltraViolette straling (XUV) en nu blijkt dat voornamelijk N_2 deze energetische straling absorbeert in de aardse atmosfeer zodat de straling de oppervlakte niet bereikt. Tijdens dit proces wordt een electron in een hogere baan van het N_2 molekuul gebracht, de toestand van het molekuul verandert en het molekuul belandt in een aangeslagen toestand. Deze toestanden hebben bepaalde symmetrie eigenschappen en alleen overgangen tussen toestanden met bepaalde symmetrieën zijn toegestaan. Voor één-foton (straling) overgangen in N_2 vanaf de grond toestand (singlet gerade symmetrie) geldt dat alleen toestanden met singlet ungerade symmetrie aangeslagen kunnen worden. Gerade en ungerade geven bepaalde kenmerken aan van inversie-symmetrie van het molekuul en singlet betekent dat alle electronen gepaard zijn. Om deze singlet ungerade toestanden te bereiken zijn energetische XUV fotonen nodig, de lagere aangeslagen toestanden van N_2 hebben andere symmetrieën en zijn dus niet toestaan voor één-foton overgangen vanaf de grond toestand.

De aangeslagen toestanden in N_2 met singlet *ungerade* symmetrie hebben sterke interacties met elkaar. Door deze storingen schuiven de toestanden op in energie en is de structuur van de toestanden hoogst onregelmatig. Verschillende soorten storingen treden op en hierdoor is het XUV absorptiespectrum van N_2 zeer gecompliceerd, waaronder ook onregelmatigheden in de overgangssterkten. Nadat de molekulen aangeslagen zijn kunnen ze vervallen naar lagere toestanden door een foton uit te zenden, ionisatie kan optreden, maar veel toestanden blijken echter na een zeer korte tijd uit elkaar te vallen waardoor N atomen onstaan. Veel toestanden van N_2 zijn predissociatief, d.w.z. het zijn gebonden toestanden maar door storingen (interacties) met andere (pre-)dissociatieve toestanden krijgen ze een kans om uit een te vallen. Deze predissociatieve toestanden hebben een bepaalde levensduur en hebben een duidelijke structuur. Als een molekuul zich echter in een dissociatieve toestand bevindt dan valt het molekuul direct uit elkaar en zo'n toestand heeft geen structuur. Voor deze singlet toestanden in N_2 blijkt dat de interactie met een aantal (pre-)dissociatieve triplet *ungerade* toestanden verantwoordelijk is voor de predissociatie. De triplet eigenschap betekent dat niet alle electronen in het molekuul gepaard zijn. In de aardse atmosfeer blijkt dat predissociatie van N_2 één van de belangrijkste bronnen van N atomen is. Voor atmosfeer modellen is het belangrijk om te weten te komen wat de competitie tussen deze verschillende vervalkanalen is. Zendt het molekuul straling uit of krijgt het daar de kans niet toe omdat het molekuul al voortijdig predissocieert? De voornaamste doelen van dit proefschrift zijn het ophelderen van de complexe structuur van de singlet *ungerade* toestanden, waaronder alle storingen en het onderzoeken van de predissociatie effecten van deze toestanden.

Het laser centrum van de Vrije Universiteit beschikt over een heel smalbandige gepulste XUV laser [pulsduur 5 ns (0.000000005 seconden)]. Door niet-lineaire processen toe te passen op de laser straal van een kleurstoflaser wordt XUV straling geproduceerd en dit systeem is ideaal om experimenten aan N₂ mee uit te voeren. De XUV laser straal wordt gekruist met een bundel van N₂ molekulen, waardoor de molekulen de XUV straling kunnen absorberen. De absorptie wordt waargenomen doordat toegevoegde UV straling de aangeslagen toestanden ioniseert, waardoor N₂⁺ ionen onstaan die gedetecteerd kunnen worden. Door de golflengte (de kleur) van de laser te veranderen kan een groot deel van het XUV spectrum gemeten worden. Verder worden verschillende isotopen van N₂ onderzocht. Isotopen zijn atomen van hetzelfde element maar met een verschillende samenstelling. Het is interessant om te onderzoeken of er isotoop afhankelijkheden zijn in de structuur, de storingen en de predissociatie effecten.

Het opgenomen complexe spectrum wordt zorgvuldig geanalyseerd, waaronder de opheldering van de storingen tussen de aangeslagen toestanden en isotoop afhankelijkheden. Veel toestanden van N₂ zijn bovendien breder in energie dan de bandbreedte van de XUV laser. Door de predissociatie hebben deze toestanden een korte levensduur, in het picoseconde bereik (1 ps = 0.0000000000001 s), en vanwege het Heisenberg onzekerheids principe hebben deze toestanden dan een grotere onzekerheid in energie. Dit wordt levensduurverbreding genoemd. Door deze verbreding nauwkeurig te bepalen voor de verschillende toestanden van N₂ kunnen van deze toestanden de levensduur bepaald worden, wat informatie geeft over hun predissociatie eigenschappen. Het blijkt dat de levensduur sterk varieert voor de verschillende toestanden en door de experimenten voor verschillende isotopen van N₂ uit te voeren, blijkt bovendien dat de levensduur van de toestanden afhankelijk is van de isotoop. Levensduur metingen werden ook uitgevoerd met de picoseconde XUV laser in Lund, Zweden. Door de UV pulsen (dat de aangeslagen singlet toestanden ioniseert) ten opzichte van de XUV pulsen te vertragen kunnen vervalsprocessen gemeten worden (door het meten van de N_2^+ ionen), waaruit de levensduur van de toestand bepaald kan worden. De technieken in Amsterdam en Lund zijn aanvullend en van veel toestanden van N_2 is zo de levensduur bepaald.

Nu weer terug naar het XUV spectrum opgenomen in Amsterdam. De overgangen van de grond toestand naar triplet *ungerade* toestanden zijn niet toegestaan, maar omdat sommige daarvan een storing hebben met een singlet toestand, krijgen sommige van de triplet toestanden wat singlet karakter, waardoor de overgangen zwak waarneembaar zijn. Een aantal triplet toestanden zijn daarom waarneembaar in het XUV absorptie spectrum en worden ook uitvoerig bestudeerd, voornamelijk omdat deze triplet toestanden verantwoordelijk zijn voor de predissociatie van de singlet toestanden.

Met behulp van alle bovengenoemde verkregen informatie: structuur, storingen en levensduren van de singlet toestanden en triplet toestanden is een model ontwikkeld dat de predissociatie van een bepaalde groep singlet toestanden verklaard. Het blijkt dat voor deze groep singlet toestanden dit proces beheerst wordt door de interactie met een aantal (pre-)dissociatieve triplet toestanden, waardoor de singlet toestanden een kans krijgen om uit elkaar te vallen. De opheldering van de structuur, storingen en predissociatie effecten in het XUV absorptie spectrum van N_2 is belangrijk voor het begrijpen van stralings en chemische processen in de aardse atmosfeer. De atmosferen van Titan and Triton, manen van respectievelijk Saturnus en Neptunus, bestaan ook grotendeels uit N_2 en de verkregen resultaten van dit proefschrift zullen ook voor het begrijpen van die planetaire atmosferen zeer waardevol zijn. Met behulp van het Cassini-Huygens ruimtevaartuig, dat op dit moment Saturnus and Titan onderzoekt, zal namelijk ook Titan's N₂-rijke atmosfeer bestudereerd worden en de resultaten van dit proefschrift zijn hierbij van groot belang voor het onderzoek naar de stralings, predissociatie en scheikundige processen in Titan's atmosfeer.

Ten slotte nog iets heel anders. Door N_2 molekulen uit elkaar te laten vallen met een ontlading, hebben we N atomen geproduceerd en hebben we op een soortgelijke manier als voor N_2 , een aantal absorpties van N atomen met de XUV laser gemeten. Een nauwkeurige bepaling van deze N atoom absorpties is van belang om vast te stellen of bepaalde fundamentele natuurconstanten eigenlijk wel constant zijn in de tijd. Deze constanten zijn de basis van de huidige natuurkunde en eventuele tijdsvariaties van deze constanten zullen van grote invloed zijn op ons beeld van de natuurkunde. Onderzoek hieraan wordt gedaan door nu gemeten absorpties in bijvoorbeeld ons laser centrum met hele oude absorpties te vergelijken, die uit het licht van sterren en quasars, dat nu pas de aarde bereikt, opgespoord kunnen worden. Sommige van de absorpties waargenomen in de extreem oude astrofysische objecten zijn wel 12 miljard jaar oud. Door de nu gemeten en de oude absorpties te vergelijken kan bepaald worden of de structuur van de atomen en molekulen veranderd is, wat een verandering in de tijd van enkele natuurconstanten zou betekenen. Dit onderzoek staat echter nog in de kinderschoenen en er kan nog geen conclusie gemaakt worden of er een tijdsvariatie bestaat van de natuurconstanten.

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