

Predissociative decay of the $c'_4 \ ^1\Sigma_u^+$, $v = 0$ state of N_2

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Abstract

In a laser spectroscopic study the lifetime of the $c'_4 \ ^1\Sigma_u^+$, $v = 0$ state is determined at $\tau = 535 \pm 100$ ps and a predissociation fraction of $28_{-18}^{+30}\%$ is inferred. For the $b' \ ^1\Sigma_u^+$, $v = 0$ state $\tau = 630 \pm 100$ ps is found, which means that this state cannot mediate the predissociation of the $c'_4(0)$ state. For the $c_3 \ ^1\Pi_u$, $v = 0$ state $\tau = 70 \pm 5$ ps and the predissociation fraction of 90% provides an explanation for the increased predissociation at higher rotational levels of the $c'_4 \ ^1\Sigma_u^+$, $v = 0$ state.

1. Introduction

In spectra recorded by the Voyager I and II missions flying by Titan and Triton [1,2] the $c'_4 \ ^1\Sigma_u^+ - X \ ^1\Sigma_g^+$ (0, 0) band of N_2 at 95.8 nm was found to be the strongest emission feature in the extreme ultraviolet (XUV) spectral range. The $c'_4 \ ^1\Sigma_u^+ - X \ ^1\Sigma_g^+$ system in the XUV and similarly the $c'_4 \ ^1\Sigma_u^+ - a \ ^1\Pi_g$ system in the near UV are of major importance for processes in the aurora and dayglow of the Earth's atmosphere. In the aurora only weak emission is seen from $c'_4(0)$ and the missing radiation from this state has been identified as a serious concern for the energy budget in auroras [3]. A full understanding of energy deposition processes in N_2 is essential for the modelling of planetary atmospheric phenomena [4], and for these problems the decay of the $c'_4(0)$ state appears to be crucial. In this study we present accurate lifetime measurements of this $c'_4(0)$ state, from which a predissociation fraction is inferred, that sheds new light on the missing radiation problem.

The $c'_4 \ ^1\Sigma_u^+$, $v = 0$ Rydberg state is one of the many excited singlet states in the energy range 100000–115000 cm^{-1} . The Rydberg and valence states of singlet character are known to be strongly mixed [5] and a number of investigations have been performed to chart the dynamic behaviour of these states [6–10]. The spectroscopy of $c'_4(0)$ is, in addition, complicated by the ℓ -uncoupling of Rydberg states [11]. Specifically, $c'_4(0)$ forms a 3p-complex with the $c_3 \ ^1\Pi_u$, $v = 0$ Rydberg state and homogeneously interacts with the $b' \ ^1\Sigma_u^+$, $v = 1$ state [12], while the $b \ ^1\Pi_u$ states are heterogeneously coupled. The $c'_4(0)$ state is considered to be the state with the lowest dissociation yield, although the precise values for the emission and dissociation rates are in dispute. In an early study Zipf and McLaughlin [13] found that the $c'_4 \ ^1\Sigma_u^+$ state predissociated by 15%. In the work of Ajello et al. [7] emission cross sections were derived from medium resolution studies, resulting in a predissociation yield of 10%. For vibrational levels $v = 0-5$ of $c'_4 \ ^1\Sigma_u^+$ an equally low predissociation yield was estimated. This is in contradiction with the

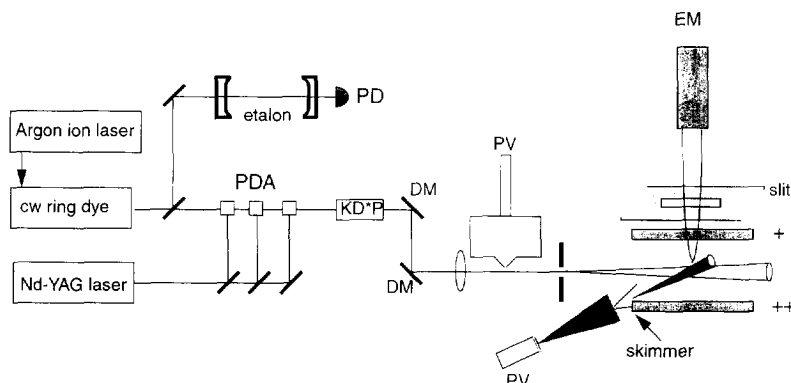


Fig. 1. Schematic representation of the experimental apparatus. The chosen geometry reduces the Doppler broadening to a minimum. KD*P is a frequency doubling crystal. PDA: pulsed-dye amplifier; PV: pulsed valves; PD: photodiode; EM: electron multiplier for the detection of N_2^+ ions.

work of Kam et al. [9], who derived a lifetime of 190 ps for $c'_4 \ ^1\Sigma_u^+$, $v = 3$, implying a larger predissociation yield for this state. Helm et al. [8] directly measured the dissociation products of the $c'_4 \ ^1\Sigma_u^+$, $v = 4$ state, deriving lifetimes varying from 340 ps for $J = 1$ to below 100 ps for $J > 15$. Moreover, they concluded that the admixture of $b' \ ^1\Sigma_u^+$ character ($v = 13$ in this case) mediates the predissociation. Shemansky et al. [14] thereupon reinvestigated the predissociation of $c'_4(0)$ resulting in an overall predissociation yield of 15%, based on an assumption that levels with $J < 5$ are not affected by predissociation. An important perspective is that in these studies [7,8] predissociation of the $c'_4 \ ^1\Sigma_u^+$, $v = 0$ state is believed to be induced by its coupling to the $b' \ ^1\Sigma_u^+$, $v = 1$ state. In view of the local mixing of these states near $J = 10$ [12] this would imply a strong rotational dependence of the predissociation process. In the present work an ultra-narrow band XUV-radiation source is applied to measure the lifetimes of the rotationally resolved levels of the $c'_4 \ ^1\Sigma_u^+$, $v = 0$ state and the interacting $c_3 \ ^1\Pi_u$, $v = 0$ and $b' \ ^1\Sigma_u^+$, $v = 1$ states.

2. Experiments and results

The set-up of the spectrometer, involving a laser-based extreme ultraviolet (XUV) tunable radiation source, with an ultra-narrow bandwidth of below 250 MHz, is schematically shown in Fig. 1. The output

of a stabilized cw-ring-laser in the range 570–580 nm is pulse-amplified employing a powerful Nd-YAG laser. Nearly Fourier-transform limited pulses are generated, frequency-doubled in a nonlinear crystal and subsequently tripled in a xenon gas jet. The N_2 molecules are resonantly excited and detected via 1 XUV + 1 UV photoionization as described previously [12,15]. The source was used for the recording of linewidths of selected rotational transitions of the N_2 bands in the range 95–96 nm. A spectrum of the R(0) line of the c'_4 -X (0, 0) band is shown in Fig. 2 with a simultaneous recording of etalon markers. These markers of a stabilized etalon (free spectral

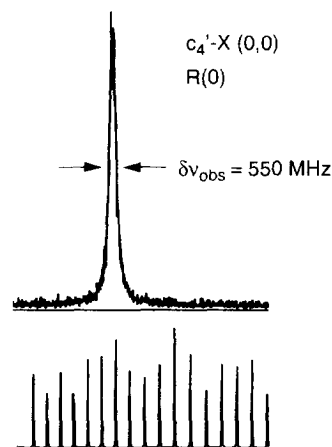


Fig. 2. Recorded spectrum of the R(0) line in the $c'_4 \ ^1\Sigma_u^+ - X \ ^1\Sigma_g^+$ (0,0) band of N_2 at $\lambda = 95.85$ nm, and below simultaneously recorded etalon markers.

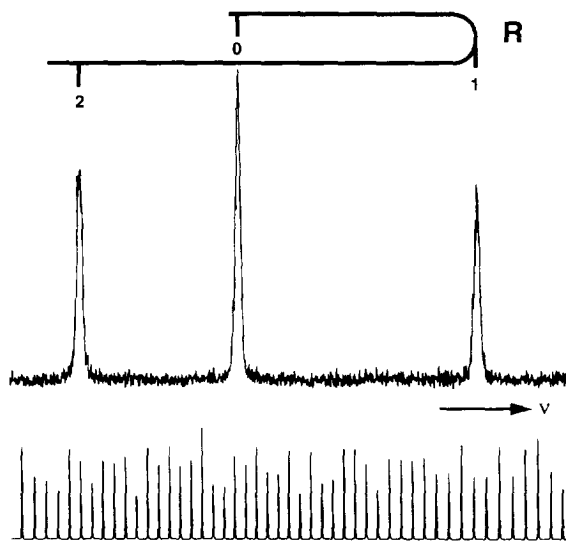


Fig. 3. Spectrum of the R-branch bandhead region in the $b'1\Sigma_u^+ - X1\Sigma_g^-(1,0)$ band of N_2 at $\lambda = 95.75$ nm.

range 148.9560 (5) MHz) recorded at the fundamental wavelength also provide a relative frequency scale in the XUV range, since the frequencies in the XUV correspond to exactly six times the frequency of the visible laser [16]. In Fig. 3 the bandhead region of the $b'-X(1,0)$ band with R(0), R(1) and R(2) lines is displayed. Similarly in Fig. 4 the bandhead region of the $c_3-X(0,0)$ band is presented, where even in the highest resolution the R(2) and

R(3) lines overlap at the bandhead. With the R-branch lines, probing the $1\Pi_u(e)$ components, also the Q(1) line, probing the opposite symmetry (f) component is shown. The lines in the $c_3-X(0,0)$ band are by far the broadest recorded in the present study. The linewidths of all the observed resonances were determined in a computerized fit of the data to a Voigt profile. Results for the derived linewidths are collected in Table 1.

In lifetime studies the true natural lifetime, corresponding to both radiative and dissociative decay effects, may be shortened by quenching collisions. Under the presently chosen conditions of a molecular beam, at distances of over 100 nozzle diameters, no collisions occur. Moreover, the background pressure is about 10^{-7} mbar and thus the kinetic collision time is much longer than any excited state lifetime. Kam et al. [9] have estimated the collisional broadening at these pressures for the $c_4'1\Sigma_u^+$ state to be below 1 MHz. On the other hand, the effective lifetime may be enlarged by radiation trapping effects, particularly, for the $c_4'1\Sigma_u^+$, $v=0$ state, which emits predominantly in the (0,0) band. However, this phenomenon only gives a larger value for the lifetime if it is measured via fluorescence decay. The width of the absorption line is not affected and therefore our results are unperturbed.

In order to obtain a minimum instrumental linewidth the effect of Doppler broadening was

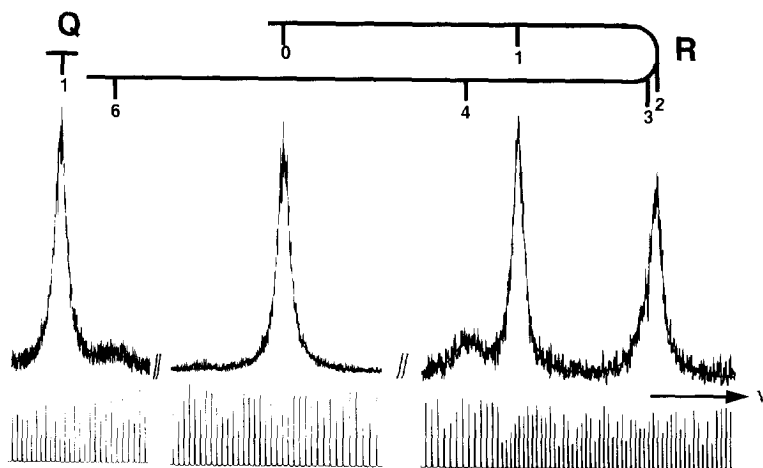


Fig. 4. Spectrum of the bandhead region in the $c_31\Pi_u - X1\Sigma_g^+(0,0)$ band of N_2 at $\lambda = 96.02$ nm.

Table 1

Observed linewidths $\Delta\nu_{\text{obs}}$, derived natural widths Γ and lifetimes τ for various excited states in N_2 as obtained in the present study and a comparison with data from previous experiments. In the last column deduced values for the radiative lifetimes are given

State		Present study			Previous studies		Radiative lifetime
		$\Delta\nu_{\text{obs}}$ (MHz)	Γ (MHz)	τ (ps)	τ (ps)	τ (ps)	τ_{rad} (ps)
$c'_4 \ ^1\Sigma_u^+, v=0$	$J=1$	525 ± 30	310 ± 60	510 (100)	900 (200) ^a	1130 ^b	740 ^c
	$J=2$	500 ± 50	185 ± 60	560 (100)			
$b' \ ^1\Sigma_u^+, v=1$	$J=1$	472 ± 20	255 ± 50	625 (120)		1130 ^b	720 ^d
	$J=2$	475 ± 20	260 ± 50	610 (120)			
	$J=3$	445 ± 30	230 ± 60	690 (180)			
$c_3 \ ^1\Pi_u^+, v=0$	$J=1$	2410 ± 100	2200 ± 150	72 (5)			
$c_3 \ ^1\Pi_u^-, v=0$	$J=1$	2740 ± 150	2530 ± 180	63 (5)			

^a From Ref. [19]; $c'_4(0)$ and $b'(1)$ were not resolved.

^b From Ref. [6]; $c'_4(0)$ and $b'(1)$ were not resolved.

^c Value derived from quoted Einstein coefficient $A_0 = 1.350 \text{ ns}^{-1}$ in Ref. [7].

^d Derived from oscillator strength $f = 0.321$ [7] and Franck–Condon factors [20]; see text.

largely suppressed in a crossed molecular beam/laser beam configuration. Moreover, a large (10 cm) distance was chosen between nozzle and skimmer, and the orifice of both nozzle and skimmer were as small as 1 mm in diameter. The distance between skimmer and interaction zone was another 10 cm. Furthermore, only the central part of the interaction zone is imaged onto the particle detector, by placing a 1 mm slit in the time-of-flight zone, such that particles excited off-axis and contributing to the Doppler wings, are not detected. In this geometry the molecular beam is highly collimated (10 mrad) and a Doppler width of 50 MHz is estimated for the N_2 lines. Due to these experimental constraints only the lowest rotational states could be investigated, in contrast to a previous study [12].

The instrumental width of the XUV-laser spectrometer was determined by measuring the $5p^6\text{--}6s'$ resonance line in krypton at 95.34 nm (upper state lifetime 100 ns) in the same set-up. Under conditions of a tightly skimmed molecular beam, where the residual Doppler effects are strongly reduced, the calibration of the instrumental width resulted in a value of 250 ± 30 MHz. The resulting 250 MHz includes a minor contribution from residual Doppler effects. The instrument profile registered was fitted to a symmetric function and stored in the computer for a deconvolution analysis. The instrument function shows some intensity in its wings, so it resem-

bles a Lorentzian rather than a Gaussian profile. Deconvolution of the instrumental width may be performed analytically. In the case of a Lorentzian instrument function $\Delta\nu_{\text{instr}}$ the natural lifetime broadening Γ follows from: $\Gamma = \Delta\nu_{\text{obs}} - \Delta\nu_{\text{instr}}$, while in the case of a Gaussian instrument function under specific approximations and assumptions the following relation can be used [17]: $\Gamma = \Delta\nu_{\text{obs}} - (\Delta\nu_{\text{instr}})^2 / \Delta\nu_{\text{obs}}$. Both equations were used to derive an upper and a lower limit for the lifetimes. Apart from these analytical methods also a computerized numerical deconvolution procedure was followed. The functional form of the measured krypton line was deconvoluted from the observed N_2 features in order to extract the lifetimes. From the numerical deconvolution tests we find that subtraction of approximately 215 MHz from the observed widths of the N_2 lines yields the most reliable values for the natural linewidths of the recorded N_2 features. This fact quantitatively expresses that the instrument function resembles a Lorentzian. Due to the uncertainty associated with the deconvolution procedure rather large error margins result for the natural linewidths. The values of the deconvoluted widths Γ are presented in Table 1 as well.

The lifetimes of the excited states of N_2 can then simply be derived from the natural linewidths via the relation $\tau = 1/2\pi\Gamma$. The thus obtained lifetimes are also listed in Table 1. This procedure of straightfor-

wardly converting broadening into a lifetime is valid only if no spectroscopic substructure exists within the line profile. The influence of nuclear spin-rotation and hyperfine coupling was discussed by Kam et al. [9] for the case of the $c'_4 \ ^1\Sigma_u^+$, $v = 3$ state, and based on their considerations we conclude that these contributions are also negligible for $c'_4 \ ^1\Sigma_u^+$, $v = 0$.

3. Discussion

For the $c'_4 \ ^1\Sigma_u^+$, $v = 0$ state a lifetime was determined in two previous experiments in which $c'_4(0)$ and $b'(1)$ were not resolved. Oertel et al. [6] observed fluorescence decay from a static gas sample at 10^{-2} Torr. At these high pressures, particularly, for an almost purely radiative transition with estimated decay fractions of 72% [7] in the c'_4 -X (0, 0) band, strong radiation trapping is expected to lengthen the effectively measured lifetime. Filipelli et al. [18] experimentally found the phenomenon of radiation trapping to become important for $c'_4(0)$ at pressures exceeding 10^{-4} Torr. The value of 900 ps of Hesser and Dressler [19] is, even considering the stated uncertainty of 22%, outside the error limits of the present study. From the comprehensive study of Ajello et al. [7] parameters follow, which can be translated to a radiative lifetime of 740 ps for $c'_4(0)$. We note that this value is in contradiction with the larger values of Oertel et al. [6] and Hesser and Dressler [19], that include predissociative as well as radiative effects. If our averaged value of 535 ± 100 ps for the $J = 1$ and 2 levels is compared with the result of Ajello et al. a predissociation decay fraction of $28_{-18}^{+30}\%$ follows. This value is consistent, considering the error margins, with that of Zipf and McLaughlin [13], who find 15% dissociative decay. Ajello et al. [7] found less than 10% predissociation for $c'_4(0)$. In the recent study of Shemansky et al. [14] a dissociative decay of 15% was found, which was presumed, however, to be due to the predissociation of states with higher J values. For $J < 5$ they assumed the absence of predissociation. We note the present study gives rotationally resolved information on predissociation fractions pertaining to the low $J = 1$ and 2 rotational levels.

Meier [3] and Ajello et al. [7] point out the possibility of an interaction with the $b' \ ^1\Sigma_u^+$ state

causing predissociation of $c'_4(0)$. Ajello et al. report a 84% dissociative decay for the $b' \ ^1\Sigma_u^+$ state. Similarly, Helm et al. [8] conjecture that predissociation in higher vibrational levels of $c'_4 \ ^1\Sigma_u^+$ is caused by an admixture of $b' \ ^1\Sigma_u^+$ character. The present measurements result in narrower lines for the $b'(1)$ state than for $c'_4(0)$. The longer lifetime deduced for the $b'(1)$ state is significant notwithstanding the large error bars on the absolute values in Table 1, resulting from the deconvolution procedure. This result contradicts previous findings, in particular the large dissociation fraction of $b' \ ^1\Sigma_u^+$. Zipf and McLaughlin [13] report an oscillator strength of $f = 0.311$ for the b' -X system, while Ajello et al. [7] report $f = 0.321$. The oscillator strengths for the b' -X and c'_4 -X systems ($f = 0.223$ for the latter from Ref. [7]) should not be directly compared in terms of lifetimes, since the $b' \ ^1\Sigma_u^+$ valence state radiates at longer wavelengths than the $c'_4 \ ^1\Sigma_u^+$ Rydberg state. Based on the oscillator strength $f = 0.321$ and the Franck-Condon factors for the b' -X (1, v') bands [20] a radiative lifetime of 720 ps is calculated for $b'(1)$. Here radiative decay into levels $X \ ^1\Sigma_g^+$, $v'' > 21$ and the continuum, not included in Ref. [20] is estimated at 7%. The contribution of decay into higher lying gerade electronic states [21] is neglected. This calculation in combination with the observed data yields a predissociation fraction of $13_{-13}^{+25}\%$ for $b'(1)$. Since $b' \ ^1\Sigma_u^+$, $v = 1$ predissociates less than $c'_4 \ ^1\Sigma_u^+$, $v = 0$, it follows that the predissociation of $c'_4(0)$ is not caused by an interaction with $b'(1)$.

The lifetime of the $c_3 \ ^1\Pi_u$, $v = 0$ state is the shortest of the states studied. Because of the large broadening the deconvolution procedure gives only a small contribution to the uncertainty. If the radiative decay of this state is assumed to be equal to that of the $c'_4(0)$ state, its counterpart in the 3p-Rydberg complex, then a 90% dissociation fraction results for this state. It has not been discussed in the literature that the ℓ -uncoupling phenomenon may provide an explanation for a rotationally dependent predissociation of $c'_4(0)$. Based on the perturbation analysis of Ref. [12] it is calculated that ℓ -uncoupling mixes 4% $c_3 \ ^1\Pi_u$ character into $c'_4 \ ^1\Sigma_u^+$ at $v = 0$ and $J = 15$. Due to the rapid predissociation of $c_3(0)$ this mixing causes increasing predissociation in $c'_4(0)$ for increasing J to the amount of a 4% predissociation fraction at $J = 15$. In the study of Shemansky et al. [14] such

an increased predissociation at higher J in $c'_4(0)$ was postulated, although a link to ℓ -uncoupling with the $c_3(0)$ state was not made.

4. Conclusion

Disputes on the decay dynamics and predissociation of the N_2 singlet states should be resolved before the next generation of high resolution XUV-imaging spacecraft is launched to study planetary atmospheres. In this study we have proven that the $c'_4 \ ^1\Sigma_u^+$, $v = 0$ state indeed predissociates. Quantitatively, a predissociation fraction of $28_{-18}^{+30}\%$ is derived. From a comparison with $b' \ ^1\Sigma_u^+$, $v = 1$ it follows that $c'_4(0)$ predissociates by a larger fraction. Hence it is concluded that predissociation in $c'_4(0)$ can not be caused by mixing with the $b' \ ^1\Sigma_u^+$ valence state. As a consequence of the large predissociation rate of the $c_3 \ ^1\Pi_u$, $v = 0$ state an increasing predissociation fraction for higher J levels in $c'_4 \ ^1\Sigma_u^+$, $v = 0$ is induced. These findings may have important consequences for the modeling of planetary atmospheres. Specifically, it may explain the unexpectedly low XUV-emission in the aurora and the day-glow of the Earth. A predissociation fraction of $> 10\%$ already causes a lower emission yield, particularly, when this effect is amplified via radiation trapping in an optically dense medium.

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