LETTER TO THE EDITOR

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

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Abstract
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 12 levels in the $2p^2 3d$ and $2p^2 4s$ 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 ^{14}N and ^{15}N yield accurate values for transition isotope shifts, which reveal large specific-mass shifts almost to the extent of cancelling 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 [1, 2], 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 [1, 2] and southern hemispheres [3, 4], 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 [5]. 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 [6]. 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 [7].

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 [8], we now turn to a high-accuracy calibration study of 12 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 ^{14}N is a matter of controversy [9].

The XUV spectrum of N I was investigated in the early days of quantum mechanics by Compton and Boyce [10], who covered the entire range of 50–120 nm. Since then a number of investigators focused on the nitrogen spectrum. Herzberg [11] performed a high-resolution investigation, probing levels of the $(2p^2 4s)\,^4P$ and $(2p^2 3d)\,^4D$ manifolds directly in emission at an absolute accuracy 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 [12, 13], 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} [14].

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 set-up 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 I$_2$ standard in the visible range, we refer to [15]. The operation of the same system for a calibration of C I lines (for both ^{12}C and ^{13}C) was demonstrated recently [8].

A beam of atomic nitrogen was produced in a pulsed expansion from a source equipped with a high-voltage discharge as described in [16]. About 20% of N$_2$ in He was used for optimal discharge operation, where the nitrogen part was premixed from naturally occurring nitrogen ^{14}N$_2$ with a sample of 99% isotopically enriched ^{15}N$_2$ 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 $(2p^3)\,^4S_{3/2}$–$(2p^2 3d)\,^4P_{3/2}$ transition for both ^{14}N and ^{15}N is shown in figure 1. The spectra are obtained by laser excitation combined with time-of-flight mass separation. By this means the spectra for ^{14}N and ^{15}N are recorded simultaneously from the same atomic beam, although the spectral traces for both isotopes appear distinct, as shown in figure 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 $6 \times \lambda_{\mathrm{XUV}}$. In table 1, the resulting transition frequencies are listed with the uncertainties,
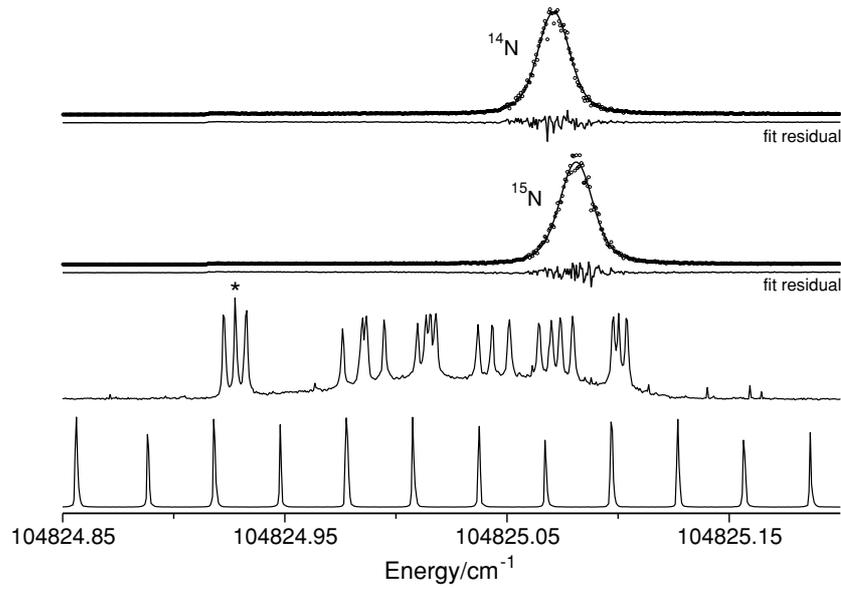
Figure 1. Recordings of the $(2p^3)\,{}^4S_{3/2}$–$(2p^23d)\,{}^4P_{5/2}$ transition for ^{14}N and ^{15}N. The line fits, superimposed on the data points (open circles) as well as the fit residuals are shown. The calibration line marked with an asterisk is the t-hyperfine component of the P43 line in the B–X(18-1) band of I$_2$ 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.

Table 1. Resulting frequency calibration 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. For ^{14}N a comparison is made with literature values from [11, 14]. All values in cm^{-1}.

Excited state	^{14}N (Obs)	Δ ([11])	Δ ([14])	^{15}N (Obs)
$(2p^24s)\,{}^4P_{1/2}$	103 622.4773 (50)	−0.009 (20)	−0.052 (40)	103 622.4825 (40)
$(2p^24s)\,{}^4P_{3/2}$	103 667.1214 (50)	−0.021 (20)	−0.053 (40)	103 667.1255 (40)
$(2p^24s)\,{}^4P_{5/2}$	103 735.4527 (50)	−0.020 (20)	−0.042 (40)	103 735.4572 (40)
$(2p^23d)\,{}^2F_{5/2}$	104 810.3324 (50)		−0.045 (40)	104 810.3429 (40)
$(2p^23d)\,{}^4P_{5/2}$	104 825.0699 (50)		−0.051 (40)	104 825.0844 (40)
$(2p^23d)\,{}^4P_{3/2}$	104 859.6952 (50)		−0.051 (40)	104 859.7094 (40)
$(2p^23d)\,{}^4P_{1/2}$	104 886.0687 (50)		−0.051 (40)	104 886.0828 (40)
$(2p^23d)\,{}^4D_{1/2}$	104 984.3238 (50)	−0.007 (20)	−0.062 (40)	104 984.3391 (40)
$(2p^23d)\,{}^4D_{3/2}$	104 996.2343 (50)	−0.001 (20)	−0.056 (40)	104 996.2487 (40)
$(2p^23d)\,{}^4D_{5/2}$	105 008.5141 (50)	−0.004 (20)	−0.048 (40)	105 008.5297 (40)
$(2p^23d)\,{}^2D_{3/2}$	105 119.8419 (50)		−0.054 (40)	105 119.8541 (40)
$(2p^23d)\,{}^2D_{5/2}$	105 143.6799 (50)		−0.046 (40)	105 143.6913 (40)

including a statistical error from averaging over at least three recordings and estimating the systematic uncertainty [8, 15]. 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 [11, 14]. These uncertainties are mainly determined by systematic effects related to

Table 2. Resulting isotope shifts from relative frequency measurements 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	Δ_{IS} ($^{15}N-^{14}N$)
$2p^2 4s\,^4P_{1/2}$	160 (60)
$2p^2 4s\,^4P_{3/2}$	130 (40)
$2p^2 4s\,^4P_{5/2}$	140 (50)
$2p^2 3d\,^2F_{5/2}$	310 (20)
$2p^2 3d\,^4P_{5/2}$	320 (20)
$2p^2 3d\,^4P_{3/2}$	340 (20)
$2p^2 3d\,^4P_{1/2}$	320 (30)
$2p^2 3d\,^4D_{1/2}$	440 (20)
$2p^2 3d\,^4D_{3/2}$	430 (20)
$2p^2 3d\,^4D_{5/2}$	470 (20)
$2p^2 3d\,^2D_{3/2}$	370 (20)
$2p^2 3d\,^2D_{5/2}$	340 (30)

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 [15]. The present data on the transition frequencies are on average lower in energy by $-0.010\ \text{cm}^{-1}$ with respect to the values of [11], in agreement with the cited error of $0.020\ \text{cm}^{-1}$. Similarly, the present values for the 12 transitions are on average $-0.051\ \text{cm}^{-1}$ lower than those of [14], therewith slightly exceeding the cited uncertainty of $0.040\ \text{cm}^{-1}$.

The line widths of the atomic resonances are in the range 450–650 MHz, larger than the bandwidth of the XUV source ($\approx 300\ \text{MHz}$). 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 [17, 18], 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 [8], where lifetime broadening was the dominant broadening effect. The $(2p^3)\,^4S_{3/2}$ ground state in ^{14}N is split into a hyperfine triplet spanning 42 MHz, while in ^{15}N it is split into a doublet spanning 29 MHz [19] 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 (^{14}N) and 45 MHz (^{15}N) were determined [20]. 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 line widths. In figure 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 ^{14}N and ^{15}N 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 the determination of line centres. The values are listed in table 2 in units of MHz. The $^{15}N-^{14}N$ 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 ^{15}N 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 [20]. 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 12 resonance lines in the spectrum of N I, for both ^{14}N and ^{15}N 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.

Acknowledgments

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