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Isotopic variation of experimental lifetimes for the lowest $^1\Pi_u$ states of N_2

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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 linewidth measurements in the frequency domain. Extreme ultraviolet (XUV)+UV two-photon ionization spectra of the $b\,^1\Pi_u(v=0\text{–}1,5\text{–}7)$ and $c_3\,^1\Pi_u(v=0)$ states of $^{14}N_2$, $b\,^1\Pi_u(v=0\text{–}1,5\text{–}6)$ and $c_3\,^1\Pi_u(v=0)$ states of $^{14}N^{15}N$, and $b\,^1\Pi_u(v=0\text{–}7)$, $c_3\,^1\Pi_u(v=0)$, and $o\,^1\Pi_u(v=0)$ states of $^{15}N_2$ are recorded at ultrahigh resolution, using a narrow band tunable XUV-laser source. Lifetimes are derived from the linewidths of single rotationally resolved spectral lines after deconvolution of the instrument function. The observed lifetimes depend on the vibrational quantum number and are found to be strongly isotope dependent. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1869985]

I. 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,[2–12] some showing rotational dependence.[13] 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 coupled-channel Schrödinger equation model describing the predissociation process which is presented in an accompanying paper.[14]

Lifetimes of the singlet *ungerade* states in N_2 have been measured using a wide variety of sophisticated experimental techniques. Laser-induced photofragment translational spectroscopy was performed in various studies[4,6–8,10,12] 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,[15] or via a vacuum ultraviolet-laser based pump-probe technique.[13,16,17] In an elegant application of the Hanle effect[18] 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 long-lived $a''\,^1\Sigma_g^+$ state.[19]

In our previous linewidth 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 (Refs. 3 and 20) 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.[9,11] This enabled the determination of linewidths for states with lifetimes shorter than ~800 ps. We have extended these measurements to include the molecular isotopomers in the present experiments.

II. EXPERIMENT

The experimental setup has already been described in our previous measurement of perturbations in the isotopic line positions (Ref. 21) and therefore will not be explained in detail here. The laser system employed a pulsed dye amplifier (PDA) injection seeded by a narrow band, tunable cw dye laser. The PDA output was first frequency doubled into the UV using a potassium dihydrogen phosphate crystal, and then frequency tripled into the XUV using a pulsed xenon jet. The resulting copropagating 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 $Nd:VO_4$ 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 linewidth measurements are consequently less accurate. This configuration was especially used for $^{14}N^{15}N$ since the natural abundance (0.74%)

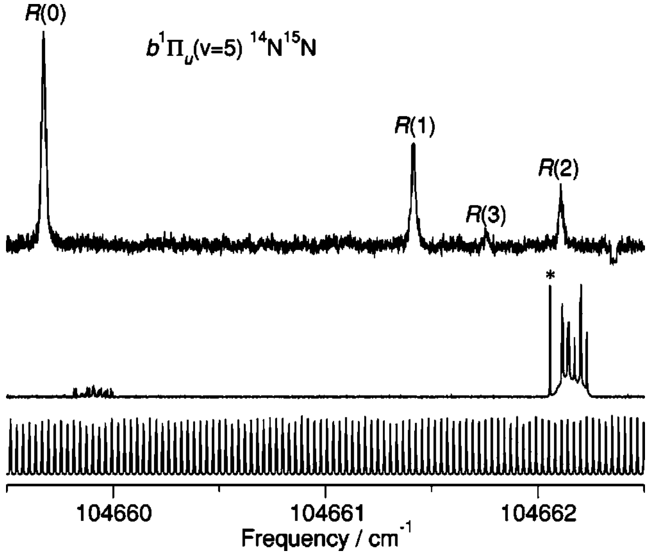

FIG. 1. Upper curve: 1 XUV+1 UV ionization spectrum for the $^{14}N^{15}N$ $b\,^1\Pi_u$-$X\,^1\Sigma_g^+$ (5,0) band recorded in natural abundance. The width of the lines is instrument limited. Middle curve: Simultaneously recorded I_2 saturation spectrum. The line marked with an asterisk is the "*t*" hyperfine component of the *B*-*X* (18-1)*P*(64) line of I_2 at 17 443.676 16 cm^{-1}, used for absolute calibration. Lower curve: Simultaneously recorded étalon markers.

in N_2 is very low. For $^{15}N_2$ a 99.40% isotopically enriched gas sample (Euriso-top) enabled larger nozzle-skimmer distances to be used.

The cw injection laser frequency was calibrated by simultaneously recording an accurate I_2 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. 1, which shows the $^{14}N^{15}N$ $b\,^1\Pi_u$-$X\,^1\Sigma_g^+$ (5,0) band. The saturated absorption line positions provided absolute frequency calibration, while relative frequency intervals are obtained from the étalon spectrum.

III. RESULTS AND ANALYSIS

A. Line positions

The above technique enabled line positions to be determined to an accuracy of ±0.003 cm^{-1} for the narrower resonances. The lines which show Doppler and/or lifetime broadening have a larger uncertainty of ±0.02 cm^{-1}. We have already presented line positions for the majority of the bands for $^{15}N_2$ and several levels in $^{14}N^{15}N$ in Ref. 21. Accurate line positions of $b\,^1\Pi_u(v=1)$ in $^{14}N_2$ were given in Ref. 11. However, we present here some additional line assignments for the $b\,^1\Pi_u(v=0,5\text{–}7)$ and $c_3\,^1\Pi_u(v=0)$ levels in $^{14}N_2$ and the $b\,^1\Pi_u(v=0\text{–}1)$ levels in $^{14}N^{15}N$ in Table I. 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.[3,20,22,23]

TABLE I. Additional observed transition frequencies (in cm^{-1}) for the $b\,^1\Pi_u$-$X\,^1\Sigma_g^+(v,0)$ bands in $^{14}N_2$ and $^{14}N^{15}N$ and the $c_3\,^1\Pi_u(v=0)$ level in $^{14}N_2$. 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 $^{14}N^{15}N$ is derived from the shoulder of a $^{14}N_2$ line. Lines given in less significant digits have undergone lifetime and/or Doppler broadening.

Level	J	$R(J)$	$Q(J)$
$b\,^1\Pi_u(v=0)$ $^{14}N_2$	0	100 819.72	
	1	100 821.54	100 815.75
	2	100 822.26	
$b\,^1\Pi_u(v=5)$ $^{14}N_2$	0	104 702.726	
	1	104 704.470	
	2	104 705.121	
	3	104 704.689	
	4	104 703.176	
$b\,^1\Pi_u(v=6)$ $^{14}N_2$	0	105 348.645	
	1	105 350.129	105 344.664
	2	105 350.364	105 342.165
	3	105 349.348	
	5	105 343.551	
$b\,^1\Pi_u(v=7)$ $^{14}N_2$	0	106 112.229	
	1	106 113.617	106 108.248
	2	106 113.710	106 105.660
	3	106 112.502	
$c_3\,^1\Pi_u(v=0)$ $^{14}N_2$	0	104 141.48	
	1	104 143.43	104 137.57
	2	104 144.34	104 135.63
	3	104 144.24*s*	
	4	104 143.13	
$b\,^1\Pi_u(v=0)$ $^{14}N^{15}N$	0	100 833.22	
	1	100 834.96	
	2	100 835.67	
	3	100 835.32	
	4	100 833.92	
$b\,^1\Pi_u(v=1)$ $^{14}N^{15}N$	0	101 456.39*s'*	
	1	101 458.00	101 452.55
	2	101 458.47	
	3	101 457.82	
	5	101 453.14	

B. Linewidths

Figure 2 is an example of the dramatic variation in the linewidths 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. 2. This level is known to be long lived [2610±100 ps (Ref. 16)] and consequently the instrument width dominates. The instrument widths thus obtained are shown in Fig. 3 as a function of

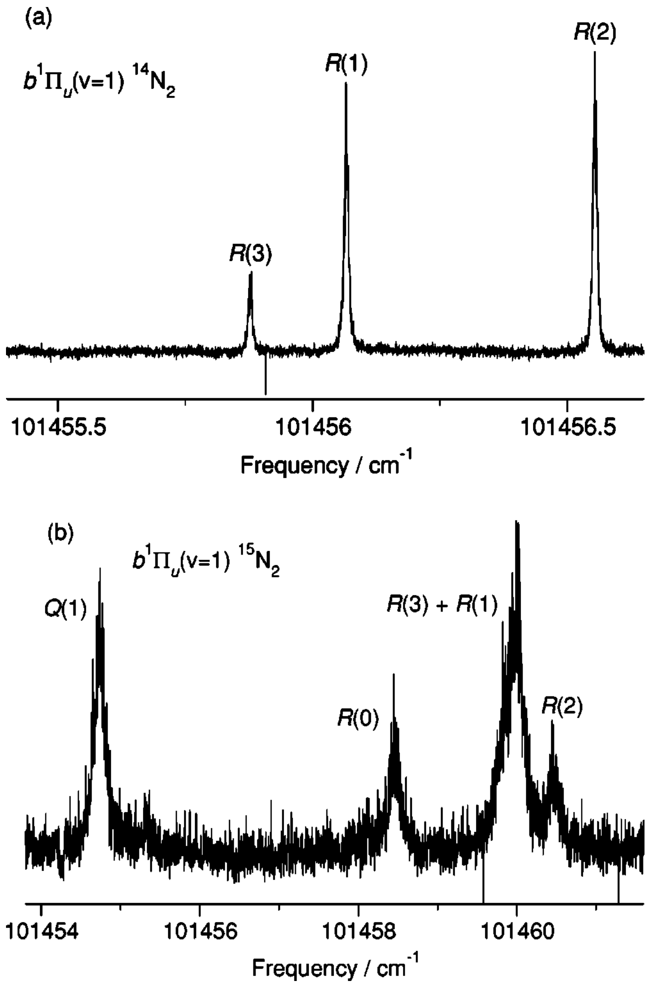

FIG. 2. 1 XUV+1 UV ionization spectrum for the $b\,^1\Pi_u$-$X\,^1\Sigma_g^+$ (1,0) band. (a) $^{14}N_2$: Nozzle-skimmer distance=150 mm. The width of the lines is instrument limited. (b) $^{15}N_2$: Nozzle-skimmer distance=40 mm. Due to the significantly greater lifetime broadening, $R(1)$ and $R(3)$ are not resolved.

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 linewidth 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.

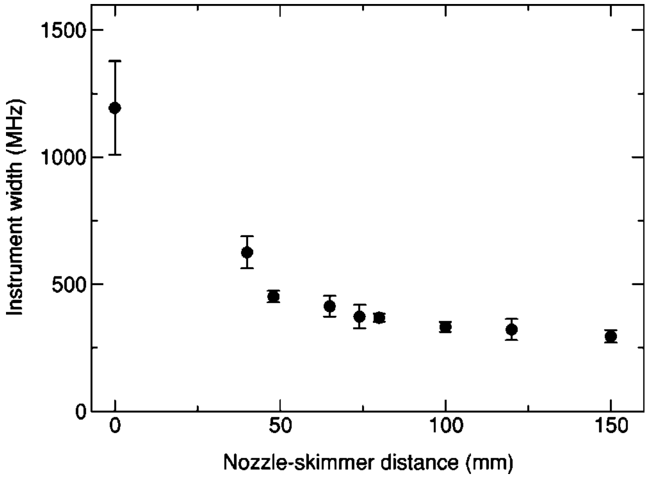

FIG. 3. Instrument width (FWHM) of the PDA-based XUV source as a function of nozzle-skimmer distance using 2 bars N_2 backing pressure. The error bars indicate 1σ uncertainties.

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,

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

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 linewidth Γ may be deduced from the observed Voigt profile:[24]

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

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 linewidths, Eq. (2), may be employed as well, but it should 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

$$\Gamma = \Delta\nu_{obs} - \Delta\nu_{instr}^{L}. \tag{3}$$

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. (2) and (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 II shows the

TABLE II. Experimental lifetimes τ for the isotopomers $^{14}N_2$, $^{14}N^{15}N$, and $^{15}N_2$. The lifetimes are compared with literature data. All data typically pertain to rotational levels $J \leq 5$.

Level	$^{14}N_2$ τ (ps) obs.	$^{14}N_2$ τ (ps) previous	$^{14}N^{15}N$ τ (ps) obs.	$^{15}N_2$ τ (ps) obs.	$^{15}N_2$ τ (ps) previous
$b\,^1\Pi_u(v=0)$	31±4	16[3]±3	80±25	40±7	
$b\,^1\Pi_u(v=1)$	>800	1750[15]±260 2610[16]±100	180±100	34±5	
$b\,^1\Pi_u(v=2)$		10[3]±2		6.9±0.8	
$b\,^1\Pi_u(v=3)$		1.6[3]±0.3		7.7±1.0	
$b\,^1\Pi_u(v=4)$		18[11]±1		10±2	
$b\,^1\Pi_u(v=5)$	230±45	205[11]±25	>800	>800	820[17]±60
$b\,^1\Pi_u(v=6)$	325±80	350[11]±75 380[17]±40	600±200	780±280	
$b\,^1\Pi_u(v=7)$	550±170	550[17]±40[a]		660±210	
$c_3\,^1\Pi_u(v=0)$	66±6	67[9]±7	47±10	29±4	
$o\,^1\Pi_u(v=0)$		240[11]±50		280±65	

[a] Lifetime obtained from lines $R(0–2)$. Rotational state dependent lifetime reported in Ref. 17. See Sec. IV.

resulting values of the lifetimes, using Eq. (1), and their uncertainties, which represent the principal results of the present paper.

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 II, represent this average over the values obtained for the individual spectroscopic lines pertaining to a certain vibronic state.

Figure 4 provides a comparison of the most accurate lifetimes for the $b\,^1\Pi_u(v=0–7)$ levels in $^{14}N_2$ and $^{15}N_2$. For $^{14}N^{15}N$ 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 $^{14}N^{15}N$ spectra. Therefore, only strong bands and levels with a relatively long lifetime could be investigated in $^{14}N^{15}N$. 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 4 again indicates the dramatic variation of lifetimes both between the different isotopes, and as a function of vibrational quantum number.

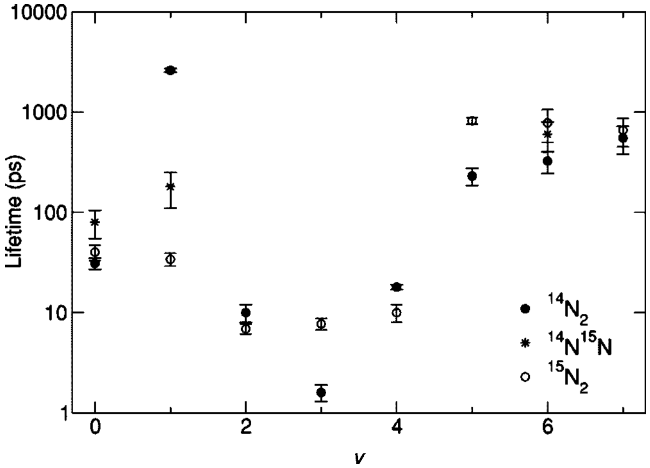

FIG. 4. Experimental lifetimes of the $b\,^1\Pi_u(v=0–7)$ levels in $^{14}N_2$, $^{14}N^{15}N$, and $^{15}N_2$. Solid circles, $^{14}N_2$; stars, $^{14}N^{15}N$; and open circles, $^{15}N_2$. Note the logarithmic vertical scale. For $^{14}N_2$, the lifetime of $b(1)$ is taken from Ref. 16 and those of $b(2–4)$ from Ref. 3. The lifetime of $b(5)$ in $^{15}N_2$ is taken from Ref. 17.

IV. 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 N_2 performed with a similar experimental setup,[11] the instrument width and the dynamic range of applicability were estimated rather optimistically. Ubachs *et al.*[11] estimated for $b\,^1\Pi_u(v=1)$ in $^{14}N_2$ a lifetime of 1.0±0.3 ns. Later, more accurate pump-probe time-domain measurements[16] yielded $\tau=2610\pm100$ 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[13,16,17] 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 II and Fig. 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.

A. $b\,^1\Pi_u$ 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 of this value: 31±4 ps and 40±7 ps for $^{14}N_2$ and $^{15}N_2$, respectively. Ubachs *et al.*[3] determined a lifetime of 16±3 ps for this level in $^{14}N_2$ (also from linewidth 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. 3), 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

$^{14}N_2$ is 2610±100 ps, determined in a direct time-domain pump-probe experiment.[16] In the present experiment, no natural line broadening was observable for this level in $^{14}N_2$, which enabled the determination of the instrument width (see Sec. II). 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 $^{14}N^{15}N$ and 34±5 ps for $^{15}N_2$, i.e., almost two orders of magnitude difference between $^{14}N_2$ and $^{15}N_2$. In Fig. 2 two-photon ionization spectra are shown for $b(1)$ in $^{14}N_2$ and $^{15}N_2$, respectively. Besides the clear difference in the widths of the lines, the spectra in $^{15}N_2$ exhibit more noise, which is the result of the much weaker signal for $^{15}N_2$. This is due to competition between predissociation and ionization of the N_2 molecules in the excited $b(1)$ level, yielding a much less efficient ionization channel, i.e., weaker signal, for $b(1)$ in $^{15}N_2$ than in $^{14}N_2$.

The lifetime of the $b\,^1\Pi_u(v=2)$ level is short. Ubachs *et al.*[3] determined a lifetime of 10±2 ps for $b(2)$ in $^{14}N_2$. For $^{15}N_2$, we found a slightly shorter lifetime of 6.9±0.8 ps. No lifetime measurements could be performed on $b(2)$ in $^{14}N^{15}N$ 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.[3] 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 linewidths 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. 4).

The short lifetime of the $b\,^1\Pi_u(v=4)$ level is slightly isotope dependent. $b(4)$ is longer lived in $^{14}N_2$(18±1 ps[3]) than in $^{15}N_2$ (10±2 ps, measured here). Again, the short lifetimes probably explain why no signals pertaining to $b(4)$ in $^{14}N^{15}N$ 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 II) with the previous measurement performed using the same experimental apparatus.[11] This level is much longer lived in the isotopomers $^{14}N^{15}N$ and $^{15}N_2$, for which only instrument-limited linewidths 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[17] 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[11,17] (see Table II). 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 pump-probe lifetime measurement[17] of 550±40 ps. In Ref. 17, 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.[17] 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. 4).

B. $^1\Pi_u$ 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[9] 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.*[11]

V. CONCLUSIONS

Frequency domain linewidth 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 behavior of the linewidths 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.[14]

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