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Published in:
Journal of Chemical Physics

DOI:
10.1063/1.2137722

2005

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Citation: J. Chem. Phys. **123**, 236101 (2005); doi: 10.1063/1.2137722
View online: http://dx.doi.org/10.1063/1.2137722
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v123/i23
Published by the American Institute of Physics.

Lifetime and predissociation yield of $^{14}N_2$ $b\,^1\Pi_u(v=1)$ revisited: Effects of rotation

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(Received 26 September 2005; accepted 24 October 2005; published online 21 December 2005)

[DOI: 10.1063/1.2137722]

The $b\,^1\Pi_u(v=1)$ state leads to the second-strongest feature in the fluorescence-excitation spectrum of N_2 excited by synchrotron radiation in the extreme ultraviolet (EUV).[1] The $b\,^1\Pi_u - X\,^1\Sigma_g^+(1,v'')$ progression is also a prominent feature in the electron-impact-induced fluorescence spectrum of N_2,[2] and is important in aeronomical processes in the terrestrial and planetary atmospheres, bands having been observed in the Earth's dayglow and aurora, and in the atmosphere of Titan.[3]

The particular importance of $b(v=1)$ arises because it is the only b-state level which decays principally radiatively, rather than by predissociation. Recently, Sprengers *et al.*[4] determined experimentally a lifetime of 2.61(10) ns for this level, using an EUV-laser-based pump-probe scheme, and deduced a corresponding predissociation yield of ~28% following a semiempirical calculation of 3.61 ns for the radiative lifetime. The lifetime of Ref. 4 differs significantly from the value 1.75(26) ns measured by Oertel *et al.*,[1] a difference for which there is currently no explanation.

The first quantitative model for the predissociation of the lowest b-state levels of N_2, based on a coupled-channel Schrödinger-equation (CSE) treatment of the interacting $b,c,o\,^1\Pi_u$, and $C,C'\,^3\Pi_u$ states, was developed by Lewis *et al.*[5] Recently, Haverd *et al.*[6] have extended this model to consider the effects of molecular rotation on the predissociation linewidths of the $^1\Pi_u$ levels and the band oscillator strengths for the $^1\Pi_u - X\,^1\Sigma_g^+(v,0)$ transitions, finding excellent agreement with the experimental data of Stark *et al.*[7]

Here, building on these recent developments, we perform CSE calculations of the J dependences of the radiative, predissociative, and total lifetimes of the $b(v=1)$ level of N_2, and, by comparison with experiment, show that the apparent discrepancy between the results of Sprengers *et al.*[4] and Oertel *et al.*[1] is an artifact, caused by a significant J dependence of the lifetime, together with differing experimental conditions. This comparison is facilitated by the analysis of further EUV pump-probe data, not included in Ref. 4. In addition, the $b(v=1)$ predissociation yield is shown to have an extremely strong J dependence, leading to significant consequences for the interpretation of N_2 fluorescence spectra and aeronomical data.

The CSE model employed here has been described in detail elsewhere.[5,6] Briefly, the model comprises the $b\,^1\Pi_u$ valence state, the $c,o\,^1\Pi_u$ Rydberg states, and the $C,C'\,^3\Pi_u$ valence states, coupled by mutual electrostatic interactions within the singlet and triplet manifolds and spin-orbit interactions between the manifolds. The radial Schrödinger equation for the coupled $^{1,3}\Pi_u$ states is solved numerically, yielding the coupled-channel wave functions for the excited states, which are then combined with the ground-state radial wave function and diabatic b, c, $o-X$ electronic transition moments, in order to form the total photodissociation cross section. The rotational dependence of the cross section is evaluated by including centrifugal terms in the ground- and excited-state Hamiltonians. Oscillator strengths and predissociation linewidths are deduced from the computed CSE cross sections by fitting Fano profiles.

Using this model with the electronic transition moments of Ref. 8, but reduced by 13.4% in order to optimize agreement with experimental oscillator strengths,[4,9] we have computed the $b(v=1,J)-X(v''=0,J)$ oscillator strengths, thereby extending the $b(v=1)$ radiative lifetime calculation of Ref. 4 to nonzero J.[10] The results, shown in Fig. 1(a) (long-dashed curve), show only a small J dependence; the lifetime τ_{rad} increasing from 3.6 ns at $J=1$ to 4.0 ns at $J=25$. On the other hand, predissociation linewidths Γ_{pre} calculated for the $b(v=1,J)$ levels[11] show an extremely strong rotational dependence, increasing from ~0.0003 cm^{-1} full width at half maximum (FWHM) at $J=1$ to 0.10 cm^{-1} FWHM at $J=25$. Predissociative lifetimes τ_{pre} determined from these linewidths using the relation $\tau_{\mathrm{pre}}(\mathrm{ps})=5.309/\Gamma_{\mathrm{pre}}(\mathrm{cm}^{-1}\ \mathrm{FWHM})$ are also shown in Fig. 1(a) (dashed curve). "Total" effective $b(v=1)$ lifetimes τ, where $1/\tau=1/\tau_{\mathrm{rad}}+1/\tau_{\mathrm{pre}}$, also shown in Fig. 1(a) (solid curve), vary from 2.9 ns at $J=1$ to 53 ps at $J=25$. This rapid lifetime shortening with increasing J translates into a rapidly increasing predissociation yield η^{pre}, where $\tau=\tau_{\mathrm{rad}}(1-\eta^{\mathrm{pre}})$, shown in Fig. 1(b), with the yield increasing from <20% at $J=1$ to ~100% at $J=25$.[12]

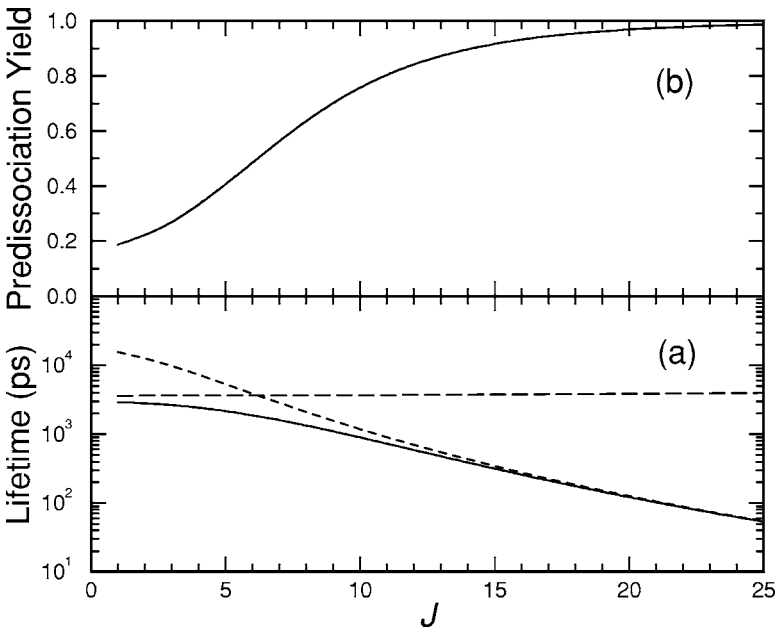

FIG. 1. (a) Rotational dependence of CSE lifetimes for the $b\,^1\Pi_u(v=1)$ level of $^{14}N_2$. Long-dashed curve: radiative lifetime, dashed curve: predissociative lifetime, and solid curve: "total" lifetime. (b) Rotational dependence of CSE predissociation yield.

Such a large rotational effect will obviously have to be taken into account when interpreting N_2 fluorescence spectra, in particular, when attempting to attribute "rotational" temperatures, and will also have consequences in terrestrial and planetary aeronomy. A similar effect has recently been deduced indirectly for the other aeronomically important state of N_2, $c'\,^1\Sigma_u^+(v=0)$, by Liu *et al.*,[13] from an analysis of rotationally resolved electron-impact emission spectra. Since the $^1\Sigma_u^+$ states of N_2 rotationally couple to the $^1\Pi_u$ manifold, which spin-orbit couples to the $^3\Pi_u$ manifold, which, in turn, provides the predissociation route,[5] a strong rotational dependence of the predissociation yield is not surprising for $c'(v=0)$. On the other hand, in the case of $b(v=1)$, the strong rotational dependence must be attributed to the effects of Rydberg-valence interactions, together with the indirect mechanism of predissociation by the $C,C'\,^3\Pi_u$ states, effects which are already known to produce strong dependences of $^1\Pi_u$ predissociation on vibrational quantum number and N_2 isotopomer.[5] Such rotational effects would be expected to be strongest, in a relative sense, for the longest-lived levels, such as $b(v=1)$.

Finally, it is necessary to consider the experimental $b(v=1)$ lifetimes. In view of the above, the concept of a single lifetime becomes invalid, and the crucial issue is the effective value of J associated with a particular measurement. The fluorescence measurements of Ref. 1 appear to have been performed on a gaseous N_2 sample at room temperature. If room-temperature rotational line intensities[14] are weighted with the CSE fluorescence yield $1-\eta^{\mathrm{pre}}$, we obtain a weighted mean of $J=5.8$ applicable to the measurements of Oertel *et al.*[1] Sprengers *et al.*[4] reported an effective rotational temperature of 80 K for their 1 EUV + 1 UV ionization spectrum, which implicitly includes the effects of η^{pre}, and reported only pump-probe decay traces taken at 98.57 nm, probing the (1,0) bandhead region. Using 80 K rotational line intensities for the lines in this region, we find a weighted mean of $J=3.3$. Here, we report the analysis of two additional traces taken in the 98.61 nm region, yielding a mean lifetime of 1.97(10) ns and probing levels with a weighted mean of $J=6.5$. Total decay linewidths associated with all of these measurements, shown in Fig. 2 (circles), are in excellent agreement with our computed total linewidth (solid curve), thus removing the discrepancies that appear to exist if J dependence is not considered. Of course, direct measurements of the predissociation yield are highly desirable, in order to confirm in detail our prediction of linewidths and predissociation yields which increase rapidly as J increases (and lifetimes which decrease rapidly).

This work was supported by Australian Research Council Discovery Program Grant No. DP0558962 and the European Community, through the Access to Research Infrastructures action of the Improving Human Potential Program, Contract No. HPRI-CT-1999-00041.

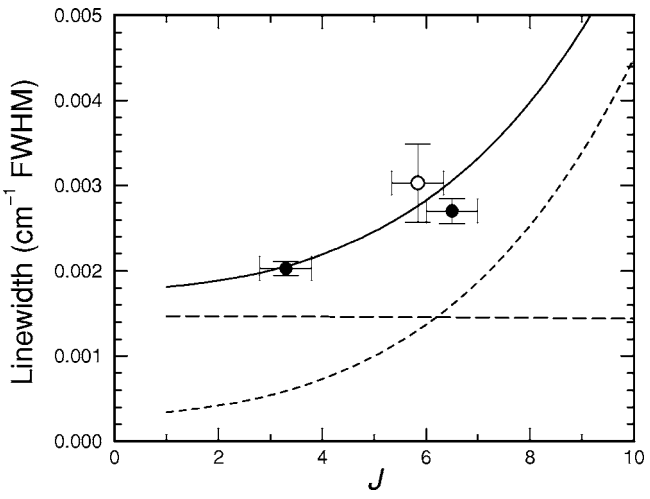

FIG. 2. Comparison between experimental (circles) and CSE (curves) rotational dependences of linewidths for the $b\,^1\Pi_u(v=1)$ level of $^{14}N_2$. Solid circles: widths from experimental lifetimes of Ref. 4 and this work, open circle: width from experimental lifetime of Ref. 1, long-dashed curve: radiative width, dashed curve: predissociative width, and solid curve: total width.

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[10] Lifetimes were calculated using Eq. (4) of Ref. 4, assuming the same $\sim 7\%$ branching to the $a\,^1\Pi_g$ state.
[11] These CSE predissociation linewidths were also summarized graphically in Ref. 6.
[12] Due to inevitable uncertainty in the calculation of very narrow predissociation linewidths, the relative uncertainty in the yield increases significantly as J decreases, reaching possibly $\sim 50\%$ at $J=1$.
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[14] The intensities used are the products of $^1\Pi_u - {}^1\Sigma_g^+$ Hönl-London factors and 295 K Boltzmann factors.