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Experimental verification of strong rotational dependence of fluorescence and predissociation yield in the $b\,^1\Pi_u(v = 1)$ level of $^{14}N_2$

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New, rotationally resolved fluorescence-excitation spectra confirm coupled-channel Schrödinger-equation predictions of strong rotational dependence of the fluorescence and predissociation yields in the $b(v = 1)$ level of $^{14}N_2$. © *2012 American Institute of Physics*. [doi:10.1063/1.3676781]

The $b\,^1\Pi_u(v = 1)$ level of N_2 is of particular interest because it is the only b-state level which decays principally radiatively, rather than by predissociation. As a result, $b(v = 1)$ leads to prominent features in the fluorescence spectrum of N_2, induced both by extreme-ultraviolet (EUV) radiation,[1,2] and electron impact.[3] Furthermore, $b(v = 1)$ is important in aeronomical processes in the terrestrial and planetary atmospheres, corresponding bands having been observed in the earth's dayglow and aurora, and in the atmosphere of Titan.[4]

Recently, building on a coupled-channel Schrödinger-equation (CSE) treatment of the interacting Rydberg and valence states of N_2,[5,6] Lewis *et al.*[7] calculated predissociation and radiative linewidths for $b(v = 1)$ which suggested a very strong dependence of the predissociation quantum yield on the rotational quantum number J. However, experimental support for that prediction has been marginal due to a dearth of rotationally resolved lifetime or linewidth measurements.[7] The few existing $b(v = 1)$ lifetime measurements have arisen from picosecond pump-probe laser spectroscopy[7,8] and fluorescence-excitation spectroscopy following direct EUV excitation.[1] These low-resolution experiments yield rotationally averaged lifetimes corresponding to the narrow range $J \approx 3$–6, limiting the ability to test the theoretical prediction of strong J dependence.

Here, we report the first rotationally resolved fluorescence-excitation spectrum (FES) of the $b\,^1\Pi_u - X\,^1\Sigma_g^+(1, 0)$ band of N_2, following direct synchrotron EUV excitation. The relative J dependence of the fluorescence quantum yield is estimated by comparison with the corresponding photoabsorption spectrum (PAS). The results confirm the theoretical prediction of very strong rotational dependence, albeit with some differences in detail.

The experimental apparatus and procedure have been described elsewhere.[2,9] Briefly, the U9 Undulator Beamline Facility at the 1.5 GeV electron storage ring of the National Synchrotron Radiation Research Center, Hsinchu, Taiwan, was employed as the source of EUV radiation. This beamline is equipped with a 6-m cylindrical grating monochromator, resulting in a potential resolving power of $\sim 10^5$ at 16 eV using a 1600 g/mm grating.[10] The high-order synchrotron radiation is filtered out by a rare-gas cell installed in the beamline.[10] Gaseous N_2 (Matheson, 99.995% purity) was passed through an effusive gas cell, operated at room temperature (298 K), into the interaction region which was isolated from the beamline by differential pumping. The incident EUV radiation was monitored using a Ni mesh, the transmitted radiation by a Cu plate, and the vacuum-ultraviolet fluorescence in the 115–200-nm region by a solar-blind photomultiplier (Hamamatsu R1459, CsI photocathode). The fluorescence so captured covers emissions from part of the resonance fluorescence of the b–X transition, the b–a emission, and the subsequent a–X (Lyman-Birge-Hopfield) emission.

The fluorescence signal and the incident and transmitted EUV intensities were recorded as a function of primary photon wavelength for each set of experimental conditions. The relative FES was obtained by dividing the fluorescence signal by the corresponding incident photon intensity. In the present work, we used entrance and exit slit widths of 10 μm and 20 μm, respectively, to provide a resolving power of 4×10^4, corresponding to a spectral resolution of 0.0024 nm (2.5 cm^{-1}) full-width at half-maximum (FWHM) in the 98.5-nm region. Wavelength calibration was provided by reference to the b–$X(1, 0)$ PAS of Yoshino.[11]

In order to properly analyze the experimental FES and estimate the J dependence of the fluorescence quantum yield, it is necessary to have an accurate knowledge of the corresponding rotationally resolved PAS. While the present experiment yields a simultaneous relative transmittance spectrum, background variations and the effects of limited experimental resolution limit its utility. Therefore, a theoretical calculation of the photoabsorption cross section performed at infinite resolving power is preferred. Here, we perform a CSE cross-section calculation, using, without change, the N_2 model of Lewis and co-workers which has been described in detail in Refs. 5 and 6. Briefly, the model comprises the $b\,^1\Pi_u$ valence

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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 photoabsorption cross section. The rotational dependence of the cross section is evaluated by including centrifugal terms in the ground- and excited-state Hamiltonians. Finally, the 298 K PAS is formed by combining individual rotational-branch cross sections using appropriate Hönl-London and Boltzmann factors, followed by accounting for Doppler broadening via convolution with a Gaussian.

Rotational line strengths in an experimental FES are influenced, not only by the photoabsorption cross section and the J dependences of the radiative and predissociation lifetimes, but also by unwanted instrumental effects, including variations in fluorescence detection efficiency and pressure-dependent preabsorption and collisional quenching.[2] In the present experiment, the detection efficiency is constant over the narrow wavelength range of the band. Experimental scans were undertaken for a number of N_2 pressures. For source pressures $\leq$200 mTorr, it was found that the relative FES line strengths became invariant, allowing the neglect of preabsorption and collisional quenching in the analysis. Under these conditions, the relative line strengths in the FES differ from those in the PAS only by the fluorescence-quantum-yield factor $\eta(J) = \Gamma^{\rm rad}(J)/[\Gamma^{\rm rad}(J) + \Gamma^{\rm pre}(J)]$, where $\Gamma^{\rm rad}(J)$ and $\Gamma^{\rm pre}(J)$ are the radiative and predissociative linewidths, respectively.[12]

In Fig. 1, the experimental b–$X(1, 0)$ FES (solid circles), taken at 200 mTorr source pressure to maximize the signal-to-noise ratio, is compared with a PAS (dashed curve), calculated assuming $\eta(J) = 1$ and degraded to the experimental resolution. A large difference in the relative line strengths is observed, reaching a factor of five over the full range of the scan. Therefore, it can be reliably inferred that the $b(v = 1)$ fluorescence quantum yield must be significantly J-dependent. Using an iterative procedure which includes a smooth functional J dependence for η as the only fitting parameter, it is possible to reproduce the relative intensities in the experimental FES at the $\pm$5% level, leading to the solid curve in Fig. 1.[13] The resultant optimized $\eta(J)$ is shown in Fig. 2(b) (solid curve),[14] scaled in the region of $J \approx 3$ to be consistent with the experimental $b(v = 1)$ natural linewidth of Ref. 8 and the radiative linewidth calculated in Ref. 7. The corresponding natural linewidth is shown in Fig. 2(a) (solid curve).

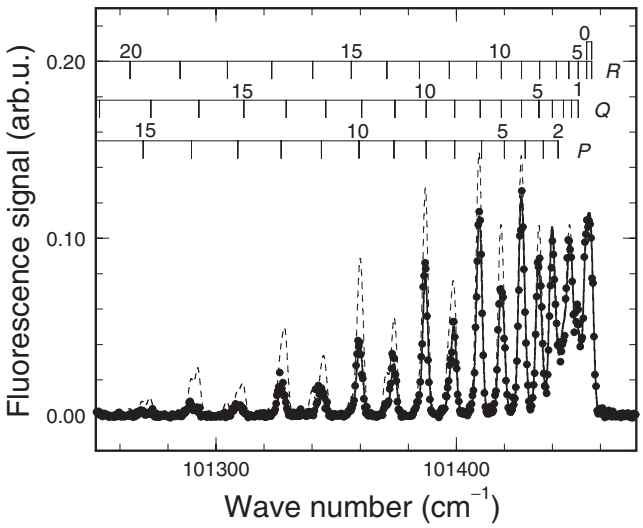

FIG. 1. High-resolution fluorescence excitation spectra for the $b\,^1\Pi_u - X\,^1\Sigma_g^+(1, 0)$ band of N_2. Circles: Experimental spectrum. Solid curve: Model spectrum assuming J-dependent fluorescence yield (solid curve of Fig. 2(b)). Dashed curve: Model spectrum assuming J-independent yield. The spectra are normalized in the region of the R head.

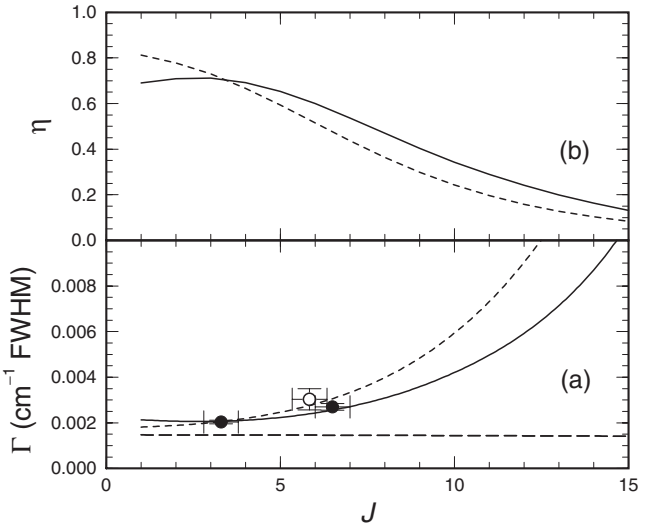

FIG. 2. J dependence of linewidth and fluorescence quantum yield in the $b\,^1\Pi_u(v = 1)$ level of N_2. (a) Long-dashed and dashed curves: Calculated radiative and total linewidths, respectively (Ref. 7). Open circle: Total width from experimental lifetime of Ref. 1. Solid circles: Total widths from experimental lifetimes of Refs. 7 and 8. Solid curve: Form of dependence implied by present FES (Fig. 1), normalized to the experimental width for $J \approx 3$ (Ref. 8). (b) Dashed curve: Calculated fluoresence quantum yield (Ref. 7). Solid curve: Yield implied by present FES.

These results, derived from experiment, are in reasonable agreement with the full-CSE theoretical predictions of Ref. 7 (dashed curves in Fig. 2), with better agreement possible by a small shift of the theoretical results towards higher J values. However, further work is required to determine whether the difference in behavior at low J requires improvement of the CSE model of Ref. 7, or is an unexpected experimental effect, perhaps due to J dependence of the fluorescence angular distribution. Nevertheless, overall, a strong J dependence of fluorescence and predissociation yields, and predissociation linewidth in the $b(v = 1)$ level of N_2 is confirmed. Clearly, this effect must be taken into account in planetary applications, particularly when inferring rotational temperatures.

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[11]K. Yoshino, see http://cfa-www.harvard.edu/amp/ampdata/cfamols.html for cross sections and line lists.
[12]This conclusion assumes that the angular distribution of the fluorescence is not J-dependent.
[13]The calculated 298 K PAS yields a transmittance spectrum, which, when degraded to the experimental resolution of 2.5 cm^{-1} FWHM and assuming an N_2 column density of $\sim 1.5 \times 10^{14}$ cm^{-2}, is in good agreement with the experimental spectrum, verifying the applicable rotational temperature to within 2 K. The peak apparent absorption is only $\sim$2%, and the negligible effect of instrumental preabsorption is verified.
[14]Due to overlapping rotational lines in the FES of Fig. 1, the main uncertainties in the inferred $\eta(J)$ relate to the associated J values, significantly worse at low J because of more severe overlapping.