Fluorescence spectra of $\text{NH}_2 \; \tilde{X}^2B_1 \leftarrow \tilde{A}^2A_1 \; \Sigma$ bands: Experiment and theory

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We report new calculations and measurements of fluorescence properties of the title system, which is important in astrochemical processes. Dispersed fluorescence spectra show extensive $\tilde{X}^2B_1$ vibrational progressions that depend on the initial $\tilde{A}^2A_1$ state. Observed and calculated $(0, \nu'_2, 0) \Sigma$ lifetimes are in good accord, save for $\nu'_2 = 4$ (bent molecule notation), and calculated $(1, \nu'_2 = 2, 0) \Sigma$ lifetimes are longer than the $(0, \nu'_2, 0) \Sigma$ ones. The calculated laser-induced fluorescence spectrum is compared with experimental absorption data and with previous calculations, finding that the present treatment underestimates the intensity of the $(0, 0, 0) \Sigma$ band. © 2003 American Institute of Physics. [DOI: 10.1063/1.1580112]

I. INTRODUCTION

Since the detailed analysis by Dressler and Ramsay, the $\text{NH}_2 \; \tilde{X}^2B_1 \leftarrow \tilde{A}^2A_1$, electronic spectra have been extensively studied both experimentally and theoretically. $\text{NH}_2$ is indeed a small molecule that allows detailed investigations, and is the best known example where Renner-Teller (RT) effects can be measured and calculated. Energy levels are known with great accuracy, but absorption and fluorescence intensities are much less well known, and depend critically on the initial state and its population. Experimentally, absorption and fluorescence intensities can be measured and calculated. Energy levels are known with great accuracy, but absorption and fluorescence intensities are much less well known, and depend critically on the initial state and its population. Experimentally, absorption intensities in the Ar matrix at 4.2 K, dispersed fluorescence (DF) spectra of the $\tilde{A}^2A_1(0, 0, 0)$ and $(0, 1, 0) \Pi$ bands (bent molecule notation), and radiative lifetimes up to $\sim 19000 \text{ cm}^{-1}$ have been measured. Theoretically, some dipole moments and lifetimes were calculated by Jungen et al. (JHM), Bueken et al., and Jensen et al. (JKB). The first two studies were limited to an effective one-dimension (1D) bending treatment, and while Ref. 3 is very recent, the published data allow one to obtain only a part of the absorption spectrum.

Using the bent molecule notation, this paper presents new theoretical and experimental studies concerning fluorescence properties of $\tilde{A}^2A_1(0, \nu'_2, 0)$ and $(1, \nu'_2 = 2, 0) \Sigma$ bands, which are quite important in astrochemical processes. We calculated state-to-state fluorescence rates of DF spectra, radiative lifetimes, and laser-induced fluorescence (LIF) intensities, using a 3D vibrational method that neglects the activity of the molecular rotation but considers stretch–bend interactions. We compare the calculated $\tau$ with precise new measurements for $\Sigma$ bands, reported here for the first time and encompassing levels up to $\nu'_2 = 12$ at $\sim 31000 \text{ cm}^{-1}$, RT effects are thus omitted in the theoretical study and are minimal for the observed values.

II. CALCULATIONS

Let $|i\rangle$ and $|f\rangle$ be the initial and final states of a fluorescence transition, $\hbar \omega_{ji}$ their energy difference, and $\mu$ the electric dipole moment. Fluorescence rates $\gamma_{fi}$, lifetimes $\tau_i$, and LIF intensities $I_i^{\text{LIF}}$ are equal to

$$
\gamma_{fi} = \frac{4|\psi_{fi}|^2}{3\hbar c} |\langle f | \mu | i \rangle|^2, \quad \tau_i = \frac{1}{\sum_f \gamma_{fi}},
$$

(1)

$$
I_i^{\text{LIF}} = \sigma_{ji}^\text{ABS} \left[ 1 - \exp(-t^{\text{exc}}/\tau_i) \right] \omega_{ji} |\langle f | \mu | 0 \rangle|^2 \times \left[ 1 - \exp(-t^{\text{exc}}/\tau_i) \right],
$$

(2)

where $\sigma_{ji}^\text{ABS}$ are absorption cross sections from the ground state $|0\rangle$ and $t^{\text{exc}}$ is the acquisition time of the experiment.

Omitting the molecular rotation and using $\tilde{X}^2B_1$ and $\tilde{A}^2A_1$ multireference configuration-interaction potentials, Born–Oppenheimer $\Sigma$ vibrational states and levels were calculated in primitive and optimized finite basis representations, as described in detail in Ref. 15. Levels up to $\sim 35000 \text{ cm}^{-1}$ above the ground one were converged within 0.1 cm$^{-1}$, employing 91 and 71 primitive functions for the stretching and bending modes, respectively, and 2556 and 1491 optimized functions for $\tilde{X}^2B_1$ and $\tilde{A}^2A_1$, respectively. The active component of $\mu$ is perpendicular to the $\text{NH}_2$ plane, and the electronic transition moment is approximated as

$$
\mu_{21} = \mu_0 \cos(\theta/2),
$$

(3)

where 1 and 2 label $\tilde{X}^2B_1$ and $\tilde{A}^2A_1$, respectively, $\mu_0$ is a constant, and $\theta$ is the bending angle.

III. EXPERIMENTS

The apparatus consisted of a cubic, black-anodized aluminum vacuum chamber evacuated by a 6 in. water-baffled diffusion pump (Varian VHS-6) and equipped with a molecular beam source and laser induced fluorescence detection assembly. The $\text{NH}_2$ radicals were generated by a pulsed elec-
trical discharge through a ~1% mixture of NH₃ in Ar that was premixed in a stainless steel cylinder. Details of the nozzle design were reported elsewhere. The typical back- was premixed in a stainless steel cylinder. Details of the absolute wavelength calibration. The Nd:YAG laser fundamental into an Fe–Ne optogalvanic lamp for electrical discharge through a ballast resistor. The timing of laser, nozzle, and discharge firing was controlled by a digital delay generator (Stanford Research Systems DG535), which generated the variable width gate pulse for the high voltage pulser (Directed Energy GRX-1.5K-E).

The laser system consisted of an etalon narrowed dye laser (Lambda-Physik Scanmate 2E) pumped by the second or third harmonic of an injection seeded Nd:YAG laser (Continuum Powerlite 7010). Wavelengths between ~320 and 375 nm were generated by doubling the dye laser output in a BBO crystal, while those between ~375 nm and 440 nm were generated by mixing the dye fundamental with the Nd:YAG fundamental in a second BBO crystal. Wavelengths between ~440 and 520 nm were generated via the use of appropriate dyes pumped with the Nd:YAG third harmonic. Typical pulse energies were ~200–300 μJ in a ~3 mm diam beam. A quartz window was used to direct a portion of the dye laser fundamental into an Fe–Ne optogalvanic lamp for absolute wavelength calibration. The Nd:YAG laser frequency (9397.44 cm⁻¹) was determined by calibrating the sum frequency against lines of an Fe–Ar optogalvanic lamp.

The laser beam crossed the molecular beam at right angles at a distance of ~10 mm (~20 exit orifice diameters) downstream. Fluorescence was collected by a two-lens F/1.5 condenser assembly, and filtered via an appropriate long-pass cutoff filter (Corion) prior to striking a photomultiplier tube detector (Oriel) held at typically ~600 V. The PMT signal was terminated into 50 Ω, and digitized at a typical sampling rate of 250 MHz. For lifetime measurements, the molecular beam was oriented at 180° to the detection assembly to minimize the effects of molecular fly-out from the detector field of view. This arrangement was found to give single exponential decays over several fluorescence lifetimes for all transitions probed, as illustrated in Fig. 1. The lifetime was deter-

mined via linear regression analysis over typically three or more fluorescence lifetimes. Waveforms were averaged over 2500 laser shots, with six waveforms typically collected for each transition.

IV. RESULTS AND DISCUSSION

Figure 2 reports the calculated state-to-state fluorescence rates γᵢ (DF spectra) of the high lying A^2Σ⁺₁ bands (0,10,0) and (1,8,0). Because both initial A^2Σ⁺₁ states are quite excited, their DF spectra show long and inverted progressions of the final X^2B₁ vibrational species. The first spectrum is dominated by the X^2B₁(0,v'₂,0) bending progression, which peaks at v₂''=2 and 3, and extends up to v₂''=10. It also shows some weaker X^2B₁(1,v'₀,0) bands for v₂''=2, and is in good agreement with the experimental DF spectrum of A^2Σ⁺₁(0,10,0)Π. On the contrary, the A^2Σ⁺₁ state with ν'₁=1 decays mostly towards X^2B₁(1,ν'₂,0) stretch–bend bands, populating preferentially the (1,1,0) level owing to the common symmetric-stretch excitation. These different product distributions thus allow a clear observation of two X^2B₁ vibrational progressions. The rates γᵢ depend more on the transition moments μᵢ than on the frequencies |ωᵢ| and are larger for ν'₁=0 than for ν'₁=1, because the pure bending A^2Σ⁺₁ species has larger μ'₁ with X^2B₁ states and emits preferentially higher-frequency photons. This behavior is general for A^2Σ⁺₁(0,ν₂',0) and (1,ν₂',−2,0) bands, is preferred at low ν₂', where the vibrational mixing is small, and is the origin of the smaller lifetimes of the (0,ν₂',0) progression with respect to the (1,ν₂',−2,0) one, as we shall see below.

Table I provides a summary of the measured lifetimes τᵢ for Σ bands, which decrease from ~8 μs for (0,4,0) to ~1.6 μs for (0,12,0), reflecting the cubic energy dependence of the spontaneous emission rate. Little variation with rotational or
spin-rotational state is observed, as we avoided including lifetimes for any rovibronic levels that could be identified as perturbed from our fluorescence excitation measurements. Despite the fact that the molecule is undergoing large-perturbations from the present calculations overestimate the strength of the Fermi resonance.

We compare in Fig. 3 experimental (averaged values of Table I, full line) and calculated (dotted line) lifetimes of $\tilde{A}^2A_1$ bands, plotting also the calculated $\tau$ ($\nu'_2 = 5$) that was not measured here. The calculated $\tau$ were fitted to those observed, finding $\mu_0 = 0.3035$ a.u. in Eq. (3). This value gives a transition moment $\mu_{21} = 0.19$ a.u. at the ground state equilibrium angle of 102.4°, smaller than the recent JKB (Ref. 3) $ab initio$ value of 0.29 a.u., but in agreement with 0.18 and $\sim$0.20 a.u. of Refs. 10 and 11. Figure 3 shows that the calculated lifetime at $\nu'_2 = 4$ is overestimated with respect to the observed one, owing to a too small transition moment with the $\tilde{A}^2B_1(0,0,0)$ state. The agreement between calculated and observed $\tau$ is better at $\nu'_2 = 6$, 7, and 8, and then decreases slightly at higher bending quanta, where the calculated lifetimes are systematically smaller by $\sim$26%. This last finding suggests that some weak interactions may be present in the high-energy spectrum, possibly of rovibronic or Fermi-resonance type, which the calculations underestimate. Overall, the calculated lifetimes have an average error of $\sim$23%, which is certainly acceptable given the approximations of the theoretical treatment and the large errors that calculated $\tau$ can have.\(^{13}\)

Table II reports $\tilde{A}^2A_1$ lifetimes of the $(0,\nu'_2,0)$ and $(1,\nu'_2, 2)\Sigma$ bands, plotting also the calculated $\tau$ ($\nu'_2 = 5$) that was not measured here. The calculated $\tau$ were fitted to those observed, finding $\mu_0 = 0.3035$ a.u. in Eq. (3). This value gives a transition moment $\mu_{21} = 0.19$ a.u. at the ground state equilibrium angle of 102.4°, smaller than the recent JKB (Ref. 3) $ab initio$ value of 0.29 a.u., but in agreement with 0.18 and $\sim$0.20 a.u. of Refs. 10 and 11. Figure 3 shows that the calculated lifetime at $\nu'_2 = 4$ is overestimated with respect to the observed one, owing to a too small transition moment with the $\tilde{A}^2B_1(0,0,0)$ state. The agreement between calculated and observed $\tau$ is better at $\nu'_2 = 6$, 7, and 8, and then decreases slightly at higher bending quanta, where the calculated lifetimes are systematically smaller by $\sim$26%. This last finding suggests that some weak interactions may be present in the high-energy spectrum, possibly of rovibronic or Fermi-resonance type, which the calculations underestimate. Overall, the calculated lifetimes have an average error of $\sim$23%, which is certainly acceptable given the approximations of the theoretical treatment and the large errors that calculated $\tau$ can have.\(^{13}\)

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Table II reports $\tilde{A}^2A_1$ lifetimes of the $(0,\nu'_2,0)\Sigma$ and $(1,\nu'_2, 2)\Sigma$ progressions, calculated both in the present work and in JHM (Ref. 10) with a 1D bending model. We use $\mu_0 = 0.2855$ a.u. for the JHM data, according to their Eqs. (15) and (18). The present $\tau$ values of the $(1,\nu'_2, 0)\Sigma$ bands have been obtained for the first time. Our calculated $\tau$ for $\nu'_2 = 2$ and 3 are in good agreement with the experimental values of $45.6 \pm 5.7$ and $23 \pm 4$ $\mu$s,\(^{2,4}\) and our calculated lifetimes of $\nu'_2 = 5$ and 8 are larger than those of $\nu'_2 = 4$ and 7, respectively, contrary to the inverse cubic energy dependence of $\tau$. The bands with $\nu'_2 = 5$ and 8 have indeed a mixed bending-symmetric stretch character, owing to $(0,5,0)-(1,3,0)$ and $(0,8,0)-(1,6,0)$ Fermi resonances that increase their lifetimes. This finding explains why the average observed lifetime of $\nu'_2 = 8$ is slightly longer than that of $\nu'_2 = 7$ (Table I). Our calculated $\tau$ ($\nu'_2 = 5$) is larger than that measured in another work ($8.1 \pm 2$ $\mu$s),\(^{2,7}\) probably because the present calculations overestimate the strength of the $(0,5,0)-(1,3,0)$ Fermi resonance.

As expected, the JHM (Ref. 10) lifetimes are smaller
than ours (save for $\nu'_2 = 9$), because that previous work neglects bend–stretch interactions that increase $\tau$.

For $2\nu'_1 + \nu'_2 \leq 8$, $\tau (\nu'_1 = 1)$ are up to four times larger than those of the pure bending bands, except for the Fermi resonances $(0,5,0)\rightarrow(1,3,0)$ and $(0,8,0)\rightarrow(1,6,0)$. As shown above, this result is due to $(0,\nu'_2,0)$ preferred Franck-Condon access to lower $\tilde{X}^2B_1$ vibrational states. For $2\nu'_1 + \nu'_2 \geq 9$, this trend is somewhat reduced, owing to the mixings of the vibrational modes and the general lowering of $\tau$ at high energies. We also remark that there is a striking similarity between the calculated lifetimes of $(0,\nu'_2,0)$ and $(1,\nu'_2,0)$, which suggests that $\tau$ is strongly governed by the $\nu'_2$ bending quantum number, except for $(1,3,0)$ in Fermi-resonance with $(0,5,0)$.

Figure 4 shows the $\tilde{X}^2B_1\rightarrow\tilde{A}^2A_1$ calculated LIF spectrum of $\Sigma$ bands, obtained with an acquisition time $t^{\text{acq}} = 16\mu s$ according to Fig. 1. As in the gas-phase absorption spectrum, the LIF intensity is dominated by a long and regular $\tilde{A}^2A_1(0,\nu'_2,0)$ bending progression, owing to very different equilibrium $\theta$ values of the electronic states. The intensity dip at $\nu'_2 = 5$ is due to the $(0,5,0)\rightarrow(1,3,0)$ Fermi resonance, and the strongest LIF intensity at $\nu'_2 = 6$ is consistent with the largest calculated absorption intensity for this state. Satellite lines of each $\tilde{A}^2A_1(2\nu'_1 + \nu'_2)$ polycad correspond to symmetric stretch–bending combination bands $(1,\nu'_2, -2,0)$, and the polycads are well separated in energy up to $\sim 27\,000\,\text{cm}^{-1}$, i.e., the vibrational spectrum does not show significant perturbations save that at $\nu'_2 = 5$.

The calculated LIF and absorption intensities are maximal at $\nu'_2 = 6$, whereas the strongest feature observed in gas-phase absorption corresponds to $(0,4,0)$ $\Sigma$ bands. This difference is mainly due our potentials that were calculated for describing the $\text{N}+\text{H}_2$ collision, and thus behave correctly in the full configurational space but are not optimized for spectroscopic purposes. Molecular rotation, and therefore selection rules $J = 0 \rightarrow \nu' = 0$ and $\Delta K = \pm 1$ and RT effects, should be also important, because $\text{NH}_2$ absorption intensities depend strongly on the initial $|i\rangle$ and final $|j\rangle$ rotational states, on the population of $|i\rangle$, and on whether $\text{NH}_2$ is in thermal equilibrium or not.

Optimizing the potentials with respect to the observed bands and taking into account the RT coupling, JHM (Ref. 10) and JKB (Ref. 3) correctly found that the maximum absorption intensity is due to the $\Sigma$ band with $\nu'_2 = 4$. Using Eq. (2) and the JHM lifetimes of Table II, the maximum LIF intensity calculated in Ref. 10 is for $(0,5,0)\Sigma$ band.

Equation (3) of the electronic transition moment is another, minor source of calculation error, because $\cos(\theta/2)$ overweighs bent geometries, whereas the $\tilde{A}^2A_1$ vibrational states are maximal at linearity. Assuming a constant $\mu_{21}$, in agreement with the Condon approximation but in contrast to the selection rule that imposes a zero moment at linearity, the $\tilde{A}^2A_1(0,4,0)$ band is preferred in absorption.

Calculations of fluorescence spectra using the JKB (Ref. 3) vibronic transition moments, which take into account the molecular rotation and the RT coupling, and comparisons with lifetime measurements for $K \neq 0$ are currently in progress.

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