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Time-Domain Measurement of Spontaneous Vibrational Decay of Magnetically Trapped NH

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The $\nu = 1 \rightarrow 0$ radiative lifetime of $\text{NH}(X^3\Sigma^-, \nu = 1, N = 0)$ is determined to be $\tau_{\text{rad,exp.}} = 37.0 \pm 0.5_{\text{stat}}^{+2.0}_{-0.8\text{syst}}$ ms, corresponding to a transition dipole moment of $|\mu_{10}| = 0.0540_{-0.0018}^{+0.0009}$ D. To achieve sufficiently long observation times, $\text{NH}(X^3\Sigma^-, \nu = 1)$ radicals are magnetically trapped using helium buffer-gas loading. The rate constant for background helium-induced collisional quenching was determined to be $k_{\nu=1} < 3.9 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$, which yields the quoted systematic uncertainty on $\tau_{\text{rad,exp.}}$. With a new *ab initio* dipole moment function and a Rydberg-Klein-Rees potential, we calculate a lifetime of 36.99 ms, in agreement with our experimental value.

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Measurement of molecular abundances in astrophysical, atmospheric, and chemical settings is critical to the discovery of new physics. A myriad of techniques are used to accomplish this. One, in particular, infrared absorption spectroscopy, studies light passing through a sample (e.g., an atmosphere or stellar cloud) to determine total absorption. In combination with transition strengths measured in the lab, molecular density can be determined. However, measurement of transition strengths for rovibrational transitions of radicals is particularly difficult due to imprecise knowledge of the radical density [1]. One approach that removes the need for absolute density calibration is time-domain or linewidth measurement of the transition lifetime. This approach has been seldom used for weak transitions because measurement of lifetimes longer than a few milliseconds is difficult; the long measurement time required can be limited by collisional quenching or transit time. These experimental limitations have contributed to the increasing importance of *ab initio* calculations in determining transition strengths [2].

One “striking” example of the need for improved experimental methods and verification of *ab initio* techniques is the case of imidogen (NH). The NH vibrational radiative lifetime τ_{rad} is a vital number for astrophysical studies since the $\Delta\nu = 1$ transitions of the $X^3\Sigma^-$ state fall in the $3 \mu\text{m}$ atmospheric transmission window. The absolute line strength of the 0-1 vibration-rotation (V - R) transition (A_{10}) plays a crucial role in determining the nitrogen abundance in cool stars [3–6], which, in turn, is tied to questions of stellar evolution and internal mixing. The estimated absolute nitrogen abundance of the sun is based on atomic nitrogen (NI) lines and NH V - R absorption [7]. The lack of precise knowledge of A_{10} is the dominant source of uncertainty in observed abundances based on V - R lines [8]. Despite their importance, measurements of the NH V - R transition strengths are particularly lacking [8–10].

Chackerian, Jr. *et al.* [11] have made the only published laboratory measurement of τ_{rad} for NH using a spectroscopic technique [1,12]. This experimental determination and the published theoretical values [2,8,10,13,14] cover a range spanning nearly 50%.

In this Letter we report a direct time-domain measurement and *ab initio* theoretical calculation of the spontaneous emission lifetime of vibrationally excited $\text{NH}(\nu = 1, N = 0)$ radicals. NH ($\nu = 1$ and $\nu = 0$) is loaded into a magnetic trap using ^3He buffer-gas loading. The trap lifetime of $\text{NH}(\nu = 1)$ is measured to be $\tau_{\text{trap},\nu=1} = 33.5 \pm 0.5$ ms, dominated by the radiative lifetime ($\tau_{\text{rad},10}$). Corrections to the measured lifetime due to the finite trap evaporation (determined from our measured $\text{NH}(\nu = 0)$ lifetime) and the possibility of background helium collisional quenching ($k_{\nu=1}$) result in $\tau_{\text{rad,exp.}} = 37.0 \pm 0.5_{\text{stat}}^{+2.0}_{-0.8\text{syst}}$ ms, in agreement with our calculated value of 36.99 ms. We also measure a tight bound on the helium-induced $\text{NH}(\nu = 1)$ collisional quenching rate coefficient of $k_{\nu=1} < 3.9 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$.

In 1998 our group demonstrated the first magnetic trapping of molecules [15] by buffer-gas loading $\text{CaH}(\nu = 0)$. It was discovered that both $\nu = 0$ and $\nu = 1$ states were coolable and $\text{CaH}(\nu = 1)$ persisted in the buffer gas as long as $\text{CaH}(\nu = 0)$ [16]. In 2005, the Meijer group in Berlin used a very different method, Stark deceleration [17] and optical pumping, to electrostatically trap $\text{OH}(\nu = 1)$ and perform the first vibrational lifetime measurement of cold trapped molecules [18]. Their measurement improved the precision of the experimentally determined Einstein A coefficient A_{10} to better than 4% and was in agreement with their *ab initio* calculated value. Our group recently demonstrated trapping of $^3\Sigma$ state molecules with the buffer-gas loading of ground-state NH into a magnetic trap [19]. The large splitting between levels of opposite

parity in molecules in Σ states makes them unsuitable for Stark deceleration due to nonlinear Stark shifts [17] but well suited for buffer-gas loading.

The experimental apparatus and method is essentially the same as that described in Ref. [19]. Briefly, NH radicals are loaded into a magnetic trap from a molecular beam. About $\approx 10\%$ of the NH produced in the beam by dissociating ammonia in a dc glow discharge is in the $v = 1$ state. We do not detect any NH($v = 2$). The NH($v = 1$) along with NH($v = 0$) enter the magnetic trap, which is inside a cold buffer-gas cell. The flow rate of buffer gas into the cell is controlled to set the buffer-gas density at a constant level. Low-field seeking molecules fall into the 3.9 T magnetic trap and are detected using either laser-induced fluorescence (LIF) or laser absorption on the $A \leftrightarrow X$ transition. Laser absorption spectroscopy indicates that we typically trap more than 2×10^8 NH($v = 0$) molecules. The excitation laser is a 672 nm cw dye laser frequency doubled to 336 nm [20]. Thermalization of the external and rotational motion of the NH proceeds rapidly, as can be verified from their trapped lifetime and the Zeeman-broadened spectrum [19].

NH($v = 0$) and NH($v = 1$) are detected from the rotational ground state ($N = 0$) on the diagonal vibrational lines of the R_1 $A \leftrightarrow X$ transition. Figure 1 shows a measurement of the number of trapped NH($v = 1$) versus time, i.e., the fluorescence observed due to our continuous excitation of the $A \leftrightarrow X$ transition. Lifetimes are measured by χ^2 -fitting the fluorescence to a single exponential and the measured lifetime does not depend on laser power in this range. Figure 2 shows the measured trap lifetime of both NH($v = 1$) and NH($v = 0$) vs buffer-gas density at a temperature of 615 mK. The vibrational ground-state lifetime shows the previously studied dependence on buffer-gas density [19]. At low buffer-gas densities, the helium

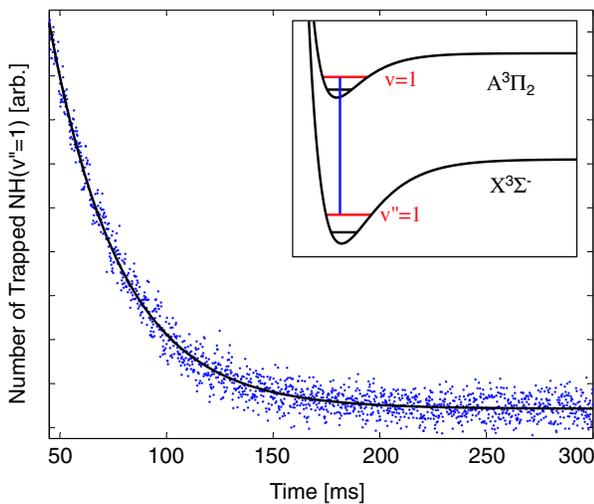


FIG. 1 (color online). Vibrationally excited trapped molecule density vs time. The population of the NH $X^3\Sigma^-(v'' = 1, N = 0)$ molecules is monitored using laser-induced fluorescence on the 1-1 band of the $A \leftrightarrow X$ transition (see inset).

enhances the trap lifetime by enforcing diffusive motion of the trapped molecules. As the buffer-gas density is increased further, the lifetime is suppressed due to the higher frequency of Zeeman relaxation collisions with helium. In contrast, the measured lifetime of the $v = 1$ state ($\tau_{\text{trap}, v=1}$) shows very little buffer-gas density dependence, as is expected for spontaneous radiative decay.

Figure 3 shows trap lifetimes for NH($v = 0$) and NH($v = 1$) as the temperature of the buffer gas is varied. The NH($v = 0$) data show the expected strong dependence of lifetime on trap depth, as described in Ref. [19]. In contrast, the NH($v = 1$) trap lifetime changes by less than 5 ms over this range, which again demonstrates that the lifetime is not dominated by either trap depth or collisions. This is again consistent with spontaneous radiative decay.

The spontaneous radiative lifetime of NH($v = 1$) is measured using the following procedure. We repeatedly measure the lifetime of trapped NH($v = 1$) at 615 mK with buffer-gas density $n_{\text{He}} = 3.6 \times 10^{14} \text{ cm}^{-3}$. This measurement is done at the low end of our workable buffer-gas density range, reducing the effect of finite trap lifetime on the measured value of $\tau_{\text{rad,exp}}$. Data are obtained from 1041 trapping cycles, yielding a measured NH($v = 1$) trap lifetime of $\tau_{\text{trap}, v=1} = 33.5 \text{ ms}$ with a standard error of $\pm 0.5 \text{ ms}$.

In order to extract the $1 \rightarrow 0$ spontaneous radiative lifetime ($\tau_{\text{rad,exp}}$) from the measured trap lifetime ($\tau_{\text{trap}, v=1}$), the finite hold time of the trap (τ_{hold}) as well as additional loss mechanisms unique to the vibrationally excited molecules (τ_{loss}) must be taken into account. $\tau_{\text{rad,exp}}$ can be written

$$\tau_{\text{rad,exp}} = \frac{1}{\tau_{\text{trap}, v=1}^{-1} - \tau_{\text{hold}}^{-1} - \tau_{\text{loss}}^{-1}}. \quad (1)$$

The finite trap hold time effects are measured directly by observing the trap lifetime of NH($v = 0$). Given that the

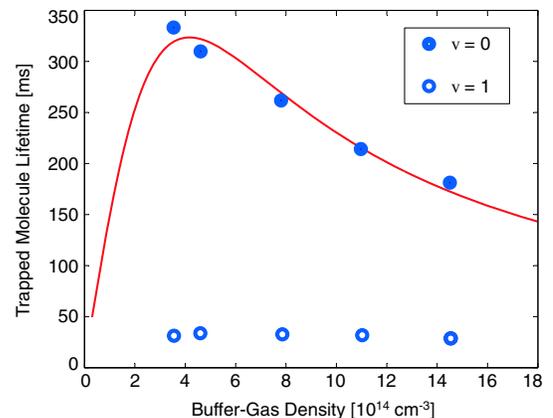


FIG. 2 (color online). Measured trap lifetime for NH($v = 0$) (closed circles, τ_{hold}) and NH($v = 1$) (open circles, $\tau_{\text{trap}, v=1}$). The solid curve is a fit to the expected functional form [19].

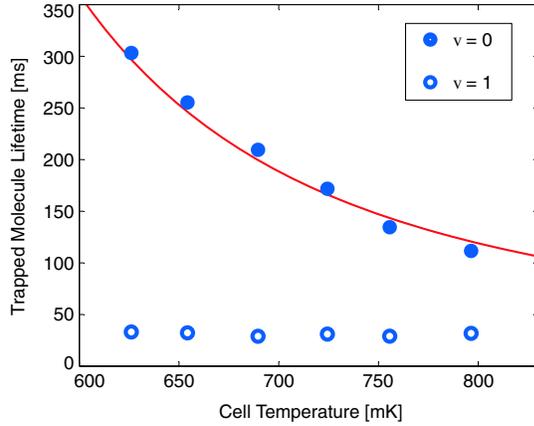


FIG. 3 (color online). Measured trap lifetimes for the ground (closed circles) and first vibrationally excited states (open circles) of NH vs buffer-gas temperature. The $v = 0$ molecules show the previously studied strong dependence on temperature and the solid curve is a fit to the expected functional form [19].

magnetic moment of NH($v = 1$) is identical to NH($v = 0$), this gives a simple correction of $\Delta\tau = +3.5 \pm 0.1$ ms.

Among the possible mechanisms that would cause population changes in NH($v = 1$), background helium collision-induced loss is the only likely mechanism we can identify for our system. We will refer to this loss mechanism as vibrational quenching, although it should be noted that if the collision-induced Zeeman relaxation for the $v = 1$ state is different from the $v = 0$ state, it would manifest itself with the same functional dependence on n_{He} as direct $v = 1 \rightarrow 0$ quenching. In order to quantify this possible effect, we fit the data in Fig. 2 assuming as a free parameter helium collision-induced loss of NH($v = 1$) (after correcting $\tau_{\text{trap},v=1}$ for the trap hold time). This attempted fit results in a collisional-quenching rate coefficient of $1.1 \pm 2.8 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$, consistent with zero. This implies an upper limit on the collisional quenching rate coefficient for NH($v = 1$) of $k_{v=1} < 3.9 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ and a consequent systematic correction of the lifetime from this possible effect of between -0.8 and $+2.0$ ms, where the negative value would correspond to slower Zeeman relaxation for $v = 1$ than $v = 0$. This is the dominant systematic uncertainty in our measurement, which yields a final value of $\tau_{\text{rad,exp.}} = 37.0 \pm 0.5_{\text{stat}}^{+2.0}_{-0.8_{\text{syst}}}$ ms. Fractional corrections to the lifetime from blackbody radiation [21], hyperfine splitting [22] and Zeeman shifts [22] are calculated to be negligible ($< 10^{-4}$).

We can use this measurement to extract the dipole matrix element for this transition, $\mu_{10} \equiv \langle \phi_{v=1,N=0} | \mu | \phi_{v=0,N=1} \rangle$ where $\phi_{v,N}$ is the vibrational wave function. The spontaneous emission lifetime can be written in terms of the vibrational transition dipole moment as

$$\tau_{\text{rad},10} = \frac{3c^2 e^2}{4\alpha\omega^3} |\langle \phi_{v=1,N=0}(r) | \mu(r) | \phi_{v=0,N=1}(r) \rangle|^{-2}, \quad (2)$$

where α is the fine-structure constant and ω is the transition frequency. The final rotational state for the decay to $v = 0$ is $N = 1$ due to the parity selection rule. We calculate the contribution to the lifetime from the $N = 3$ final state to be negligible ($< 10^{-5}$). Taking $\omega = 3092.88 \text{ cm}^{-1}$ from spectroscopic constants in the literature [23,24] gives us a measured value of $|\mu_{10}| = 0.0540^{+0.0009}_{-0.0018}$ D.

Comparison of our experimental value of $\tau_{\text{rad,exp.}}$ to theory is crucial to claim resolution of the conflicting published measured and theoretical values. To obtain a state-of-the-art calculated value we perform an *ab initio* calculation of the spontaneous emission lifetime of NH($v = 1$). The vibrational wave function $\phi_{v=1,N=0}(r)$ was computed by solving the one-dimensional Schrödinger equation with the sinc-function discrete variable representation method [25]. The radial potential was constructed with the Rydberg-Klein-Rees (RKR) method [26], using the Dunham parameters from Ram *et al.* [23,24]. To compute $\phi_{v=0,N=1}(r)$ the centrifugal term was added to the potential. The MOLPRO program package [27] was used to compute the r -dependent electric dipole moment function $\mu(r)$. We used the internally contracted multireference single and double excitation configuration interaction (MRCI) method [28] and the aug-cc-pV6Z one electron basis. The orbitals were obtained in a complete active space self consistent field (CASSCF) calculation. The active space consisted of the $1\sigma - 6\sigma$, $1\pi - 3\pi$, and $1\delta - 2\delta$ orbitals. All CASSCF configurations were used as reference configurations in the MRCI calculation. The result is a calculated spontaneous emission lifetime of 36.99 ms, in excellent agreement with our measured value.

To get an indication of the accuracy of the *ab initio* calculation we computed the spectroscopic constants and the lifetime using the MRCI potential instead of the RKR potential. This results in a transition frequency that is 0.44% too high, a ground-state rotational constant that is 0.48% too high and a computed lifetime of 37.29 ms.

Another indication of the accuracy of the *ab initio* calculation was obtained by computing the dipole function with the partially spin restricted coupled cluster method with single and double excitations and a perturbative treatment of the triples [RCCSD(T)] [29–31]. This is a single reference method and the orbitals were taken from a restricted Hartree Fock calculation. Core-excitations were included and the aug-cc-pV6Z basis was used. The dipole was obtained in a finite field calculation with electric fields of $\pm 10^{-4} E_h/a_0$. With the vibrational wave functions computed for the RKR potential this results in a lifetime of 37.39 ms. The transition frequency computed with the RCCSD(T) potential is 0.73% too high.

Using the MRCI dipole moment function we also computed the NH($v = 0$) *permanent* dipole moment. The result, 1.5246 D, is 10% larger than the 1974 experimental value of 1.38 ± 0.07 D [32] but it agrees well with the 1996 *ab initio* value of 1.536 D Paldus and Li [33], who already express doubt about the experimental value.

While both our measured and calculated values for the transition dipole moment agree, they differ significantly from previously published values. Chackerian, Jr. *et al.* [11] have observed the Herman-Wallis effect and combined their spectroscopic data with the 1974 measured value of the static dipole moment of ground-state NH [32]. This results in a measured value for the transition dipole moment of $|\mu_{10}| = 0.0648 \pm 0.008$ D, which they present with a calculated *ab initio* value [11] of $|\mu_{10}| = 0.0594$ D. These transition dipole moments are inconsistent with our result of $|\mu_{10}| = 0.0540^{+0.0009}_{-0.0018}$ D. Grevesse *et al.* provide a plot of the calculated dipole moment matrix element (including rotation) vs. N'' that gives a value of $|\mu_{10}| > 0.06$ D for $N'' = 1$ [8]. Cantarella *et al.* use a series of different published potentials and dipole moment functions to calculate dipole matrix elements falling in the range of $0.0528 \leq |\mu_{10}| \leq 0.0618$ D [2]. Das *et al.* calculate and oscillator strength corresponding to $|\mu_{10}| = 0.0526$ D [14].

Our measured lifetime $\tau_{\text{rad,exp.}} = 37.0 \pm 0.5^{+2.0}_{\text{stat}-0.8\text{syst}}$ ms can also be compared to published values of the Einstein A coefficient using $A_{10}^{-1} = \tau_{\text{rad,10}}$. Rosmus and Werner [13] calculate $A_{10}^{-1} = 28.7 \pm 4$ ms, and Dodd *et al.* [10] calculate $A_{10}^{-1} = 19.3$ ms. Both of these calculations neglect rotation, and we find convergence for our calculated value only after inclusion of the large basis and active space described above. Despite these discrepancies, our measurement is in agreement with our *ab initio* calculated value and we believe this new value to be the most accurate yet reported.

In conclusion, we have measured the spontaneous emission lifetime of the $X^3\Sigma^-(v=1, N=0)$ state of the NH radical in a magnetic trap and performed a new *ab initio* calculation and find these in good agreement. This new value can be used to calibrate molecular densities in spectroscopic measurements on the NH $1 \leftrightarrow 0$ transition. Since previously published values for the transition dipole matrix element are almost all larger than our measured value, it is likely that NH densities that have been inferred from $V-R$ absorption on this line are lower than the actual density of NH radicals. We estimate that current solar nitrogen abundance estimates derived from this transition [7,8,34] will require a correction of about 30%.

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