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

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The \( \nu = 1 \rightarrow 0 \) radiative lifetime of 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 \( |\mu_{10}| = 0.0540^{+0.0009}_{-0.0009} \text{D} \). To achieve sufficiently long observation times, 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 \emph{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 \emph{ab initio} calculations in determining transition strengths [2].

One “striking” example of the need for improved experimental methods and verification of \emph{ab initio} techniques is the case of imidogen (NH). The NH vibrational radiative lifetime \( \tau_{\text{rad}} \) 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 (N\( _{i} \)) 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, \emph{et al.} [11] have made the only published laboratory measurement of \( \tau_{\text{rad}} \) 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 \emph{ab initio} theoretical calculation of the spontaneous emission lifetime of vibrationally excited NH(\( \nu = 1, N = 0 \)) radicals. NH (\( \nu = 1 \) and \( \nu = 0 \)) is loaded into a magnetic trap using \( ^3\text{He} \) buffer-gas loading. The trap lifetime of NH(\( \nu = 1 \)) is measured to be \( \tau_{\text{rad},\nu=1} = 33.5 \pm 0.5 \text{ ms}, \) dominated by the radiative lifetime (\( \tau_{\text{rad},10} \)). Corrections to the measured lifetime due to the finite trap evaporation (determined from our measured 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 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 CaH(\( \nu = 0 \)). It was discovered that both \( \nu = 0 \) and \( \nu = 1 \) states were coolable and CaH(\( \nu = 1 \)) persisted in the buffer gas as long as 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 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 \emph{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 $\Sigma$ 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 along with $N_{\text{He}}$ along with $N_{\text{NH}}$ is about 0.04 cm$^{-3}$ s$^{-1}$. About the same as that described in Ref. [19]. Briefly, NH radicals associating ammonia in a dc glow discharge is in the $N = 0$ state. We do not detect any $N_{\text{He}} = 3.6 \times 10^{14}$ cm$^{-3}$. The measurement is done at the low end of our workable buffer-gas density range, reducing the effect of finite trap lifetime on the expected value of $\tau_{\text{rad,exp}}$. Data are obtained from 1041 trapping cycles, yielding a measured NH($v = 1$) trap lifetime of $\tau_{\text{trap},v=1} = 33.5$ ms with a standard error of 0.5 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 ($\tau_{\text{hold}}$) as well as additional loss mechanisms unique to the vibrationally excited molecules ($\tau_{\text{loss}}$) must be taken into account. $\tau_{\text{rad,exp}}$ can be written

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

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

![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 $\rightarrow$ X transition (see inset).](image1)

![FIG. 2 (color online). Measured trap lifetime for NH($v = 0$) (closed circles, $\tau_{\text{hold}}$) and NH($v = 1$) (open circles, $\tau_{\text{trap},v=1}$). The solid curve is a fit to the expected functional form [19].](image2)
magnetic moment of NH(ν = 1) is identical to NH(ν = 0), this gives a simple correction of Δτ = +3.5 ± 0.1 ms. Among the possible mechanisms that would cause population changes in NH(ν = 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 ν = 1 state is different from the ν = 0 state, it would manifest itself with the same functional dependence on n_He as direct ν = 1 → 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(ν = 1) (after correcting τ_{trap,ν=1} for the trap hold time). This attempted fit results in a collisional-quenching rate coefficient of 1.1 ± 2.8 × 10^{-15} cm^3 s^{-1}, consistent with zero. This implies an upper limit on the collisional quenching rate coefficient for NH(ν = 1) of k_{v-1} < 3.9 × 10^{-15} cm^3 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 ν = 1 than ν = 0. This is the dominant systematic uncertainty in our measurement, which yields a final value of τ_{rad,exp} = 37.0 ± 0.5_{stat} ^{+2.0}_{-0.8yst} 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, μ_{10} = ⟨φ_{ν=1,N=0}|μ|φ_{ν=0,N=1}⟩ where φ_{ν,N} is the vibrational wave function. The spontaneous emission lifetime can be written in terms of the vibrational transition dipole moment as

\[
τ_{rad,10} = \frac{3c^2e^2}{4αω^2}|⟨φ_{ν=1,N=0}(r) |μ(r) |φ_{ν=0,N=1}(r)⟩|^2. \tag{2}
\]

where α is the fine-structure constant and ω is the transition frequency. The final rotational state for the decay to ν = 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 ω = 3092.88 cm^{-1} from spectroscopic constants in the literature [23,24] gives us a measured value of |μ_{10}| = 0.0540^{+0.0009}_{-0.0018} D.

Comparison of our experimental value of τ_{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(ν = 1). The vibrational wave function φ_{ν=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 φ_{ν=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 μ(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 1σ - 6σ, 1π - 3π, and 1δ - 2δ 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-excitation were included and the aug-cc-pV6Z basis was used. The dipole was obtained in a finite field calculation with electric fields of ±10^{-4} E_0/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(ν = 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 $|\mu_{10}| = 0.0648 \pm 0.008 \text{ D}$, which they present with a calculated $ab$ initio value [11] of $|\mu_{10}| = 0.0594 \text{ D}$. These transition dipole moments are inconsistent with our result of $|\mu_{10}| = 0.0540 \pm 0.0008 \text{ D}$. Grevesse et al. provide a plot of the calculated dipole moment matrix element (including rotation) vs. $N''$ that gives a value of $|\mu_{10}| > 0.06 \text{ D}$ 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 $0.0528 < |\mu_{10}| < 0.0618 \text{ D}$ [2]. Das et al. calculate and oscillator strength corresponding to $|\mu_{10}| = 0.0526 \text{ D}$ [14].

Our measured lifetime $T_{\text{rad,exp}} = 37.0 \pm 0.5 \text{ s}_{\text{stat}} + 0.20\text{ s}_{\text{sys}} \text{ ms}$ can also be compared to published values of the Einstein A coefficient using $A_{10}^{-1} = T_{\text{rad,10}}$. Rosmus and Werner [13] calculate $A_{10}^{-1} = 28.7 \pm 4 \text{ ms}$, and Dodd et al. [10] calculate $A_{10}^{-1} = 19.3 \text{ ms}$. 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 $X^3\Sigma^{-}(\nu = 1, N = 0)$ 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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6 D. L. Lambert (private communication).


20 LD688 dye in EPH, frequency doubled in BBO in an external build-up cavity.


24 To reproduce the term values in Table I of [23] we had to assume this sign convention in Table II: $B_0 = Y_{01}$, $\alpha_c = -Y_{11}$, $\gamma_c = Y_{21}$, $\delta_c = -Y_{31}$, and $\epsilon_c = Y_{41}$.


