Cold heteromolecular dipolar collisions

Brian C. Sawyer,[1] Benjamin K. Stuhl,[1] Mark Yeo,[1] Timur V. Tscherbul,[2, *] Matthew T. Hummon,[1] Yong Xia,[1, †] Jacek Kłos,[3] David Patterson,[2] John M. Doyle,[2] and Jun Ye[1]

[1] JILA, National Institute of Standards and Technology and the University of Colorado
Department of Physics, University of Colorado, Boulder, Colorado 80309-0440, USA
[2] Department of Physics, Harvard University, Harvard-MIT Center for Ultracold Atoms, Cambridge, Massachusetts 02138, USA
[3] Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742-2021, USA

I.   ABSOLUTE DENSITY CALIBRATION OF THE COLD ND$_3$ BEAM

Determining absolute densities of neutral atomic or molecular samples from amplified ion currents produced via resonance-enhanced multiphoton ionization (REMPI) is often difficult. When multiple photons are used to excite an atom or molecule to an intermediate electronic state, the saturation behavior of the given transition makes ionization efficiency rather sensitive to excitation laser parameters such as waist size and transverse beam profile. The use of pulsed dye lasers for REMPI renders accurate determination of these parameters unlikely. Microchannel plate (MCP) detectors, which boast current gains of $\sim 10^6 - 10^9$, are commonly used to amplify ion signals as part of a time-of-flight mass spectrometer (ToFMS). Unfortunately, the gain of a given MCP assembly can change over the lifetime of the unit and vacuum breaks or complete replacement of the MCP stack would all require careful re-characterization of the system gain for reliable calibrations.

In order to accurately calibrate the density of our cold, guided ND$_3$ buffer gas beam, we choose to compare the amplified 2+1 REMPI ion yield from the cold beam to that of a calculable thermal source of ND$_3$ molecules introduced into the ionization region. This procedure makes the density measurement insensitive to long-term fluctuations in MCP gain and laser size/profile since both the cold beam ion yield and the density scaling factor obtained from the thermal signal include these effects. Since REMPI laser parameters and buffer gas source flux can change on a daily basis, this density calibration is performed for each realization of the collision experiment to allow for consistent averaging of many cross section measurements. We determine the density, n, of ND$_3$ using

$$n = \frac{S_{\mathrm{b}}(\nu)}{S_{\mathrm{th}}(\nu')C_{\mathrm{overlap}}(\nu')} \times \frac{P}{k_B T} \times f_{JK}(T) \times C_{\mathrm{pressure}} \tag{1}$$

where $S_{\mathrm{b}}(\nu)$ is the amplified ion signal for a given REMPI line of cold ND$_3$ at a laser single-photon energy of ν, $S_{\mathrm{th}}(\nu')$ is the amplified ion signal from the thermal ND$_3$ at pressure P and temperature T, k_B is Boltzmann's constant, and $f_{JK}(T)$ is the thermal fraction of ND$_3$ molecules in the state J, K at temperature T. The constants $C_{\mathrm{overlap}}(\nu')$ and C_{pressure} allow one to correct for the requisite overlap of transition lines in the hot spectrum and pressure differences at different positions in the vacuum chamber, respectively. In principle, the frequencies ν and ν' need not be identical so long as the laser beam profile and position are stable over the range $(\nu - \nu')$ and we account for the relative transition strength.

It is necessary to simulate the 2+1 REMPI spectrum of ND$_3$ in order to accurately assign a value for C_{overlap}. Therefore, we calculate all positions and line strengths for 2^5_0 REMPI rotational transitions using $J'', J' < 20$ and assuming that the two-photon transition strengths are determined exclusively by the transition hyperpolarizability tensor $\mathbf{T}^2_{\pm 1}$ [1]. When describing 2+1 REMPI transitions, we use $|J'', K''\rangle$ and $|J', K'\rangle$ to represent the ground $\tilde{X}^1A'_1(v_2 = 0)$ and intermediate $\tilde{B}^1E''(v_2 = 5)$ molecular states, respectively. Molecular constants for the ground state are obtained from Ref. [2] while constants for the intermediate level are taken from Ref. [3]. Accounting for mixing of transition strengths due to l-uncoupling (mixed $K, K + 2$ states) at high-J [4], we obtain the simulated spectrum of Fig. 1a shown in red. Accompanying the spectrum simulation is the measured thermal spectrum (black points) taken at a pressure $P = 2.5 \times 10^{-7}$ Torr and laser pulse energy of 3 mJ. A 30 cm lens is placed one focal distance from the magnetic trap center. When calibrating the cold ND$_3$ beam, we restrict P to below 10^{-6} Torr to avoid nonlinearities in the response of our calibrated quadrupole mass spectrometer (Stanford Research Systems RGA200) and MCP detector.

---

*ITAMP, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138, USA
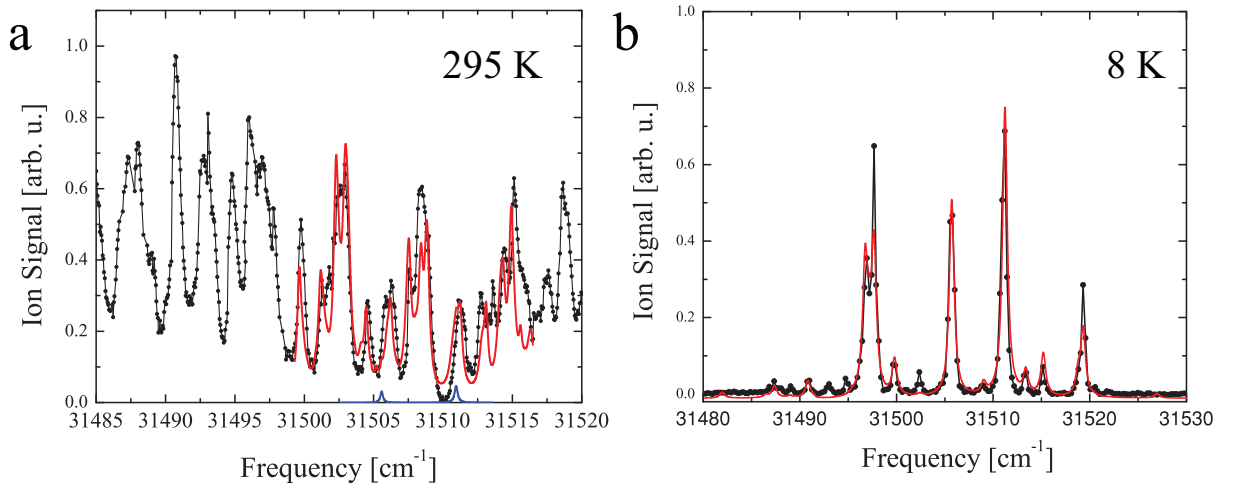†Department of Physics, East China Normal University, Shanghai 200062, China

FIG. 1: **Measured and simulated ND$_3$ spectra.** (a) Measured (black points) and simulated (red line) ND$_3$ spectra at 295 K. The experimental 2+1 REMPI spectrum was taken within the OH-ND$_3$ collision region. The relative strengths and line positions for two of the $|J'', K''\rangle = |1,1\rangle$ transitions at the single-photon frequencies of 31505.6 cm^{-1} and 31510.9 cm^{-1} are shown in blue (to scale). (b) Measured (black points) and simulated (red line) spectrum of a guided ND$_3$ beam with a rotational temperature of 8 K.

The constant $C_{\mathrm{overlap}}(\nu') \leq 1$ is the fraction of ions produced from the state J, K within the background of other lines overlapping ν' in the thermal room-temperature spectrum. At $T = 295$ K, the most populous angular momentum states are $J = 5 - 6$. As such, ions resulting from REMPI of the $|1,1\rangle$ state make up a fraction of the total ion yield at a given line position ν'. We use the $\tilde{B}|2,0\rangle \leftarrow \tilde{X}|1,1\rangle$ line at a single-photon frequency of 31505.6 cm^{-1} to perform all density calibrations described in this article. The position and relative ion yield of this transition is shown in blue in Fig. 1a. Integrating ion yield over the range of the REMPI laser FWHM of 0.1 cm^{-1}, we obtain $C_{\mathrm{overlap}}(31505.6 \text{ cm}^{-1}) = 0.24$. Any discrepancy between the simulated and measured 295 K spectra at this line position is addressed in the following section concerning error estimation of C_{overlap}. For comparison, we include a measured (black) cold ND$_3$ spectrum and corresponding simulation (red) in Fig. 1b. The cold beam spectrum reflects a rotational temperature of 8 K.

To compute the Boltzmann fraction $f_{JK}(T)$ in Eq. 1, we use the following expression for symmetric top molecules [5]

$$f_{JK}(T) = \frac{1}{2Z} \sum_{J,K} S(I = 1, K)(2J + 1) \exp\left(-U_{JK}/k_B T\right) \tag{2}$$

where Z is the partition function and $S(I, K)$ is the degeneracy due to the three identical D atoms each possessing nuclear spin $I = 1$. The remaining terms comprise the standard Boltzmann fraction for a $|J,K\rangle$ state of energy U_{JK}. The extra factor of two multiplying the partition function is necessary since the 2_0^5 transitions in ND$_3$ connect only antisymmetric $v_2 = 0$ levels with $v_2 = 5$ intermediate rotational states, while our pressure measurement is sensitive to all states. Using this formula, we obtain $f_{11}(295 \text{ K}) = 4.45 \times 10^{-3}$.

The constant C_{pressure} is the ratio of actual pressure in the magnetic trap to measured pressure at the quadrupole mass spectrometer (QMS) when gas is leaked into the trap chamber. To quantify this term, we physically move our QMS from its customary position between the OH magnetic trap and turbomolecular pump to a port parallel to the trap itself. Using a calibrated mass flow controller, we inject Ne through the usual ND$_3$ leak valve port and measure the pressure at each QMS position. Repeating this procedure multiple times, we obtain $C_{\mathrm{pressure}} = 1.4(1)$. Neon gas is substituted for ND$_3$ in this measurement due to their identical mass and neon's chemical compatibility with the mass flow controller. Under molecular flow conditions, the identical mass of Ne will yield the same pressure differentials as ND$_3$.

A. Estimating the error of C_{overlap}

The positions and relative ion yields of the two transitions with $\nu_1' = 31510.9$ cm^{-1} and $\nu_2' = 31505.6$ cm^{-1} are plotted as the blue line in Fig. 1a. To estimate the systematic error of our line overlap correction factor $C_{\mathrm{overlap}}(\nu')$, we compare the spectrum simulation results of Fig. 1a with an experimental measurement of the thermal spectrum at

295 K. To obtain $\rho = C_{\mathrm{overlap}}(\nu_1')/C_{\mathrm{overlap}}(\nu_2')$, we measure the ion yield of the 295 K ND_3 at ν_1' and ν_2' corresponding to distinct REMPI transitions from the $|1,1\rangle$ antisymmetric ground state. We compare this measured ratio of C_{overlap} with that predicted by the spectroscopy simulation ($\rho_{\mathrm{sim}} = 0.70$). Our measured ρ_{exp} of 0.83 thus represents a 16% fractional disagreement for the determination of C_{overlap}, which we take as a systematic uncertainty.

---

[1] R. N. Dixon, J. M. Bayley, and M. N. R. Ashfold, Chem. Phys. **84**, 21 (1984).
[2] L. Fusina and G. D. Lonardo, J. Mol. Spectrosc. **112**, 211 (1985).
[3] R. N. Dixon, J. M. Bayley, and M. N. R. Ashfold, Chem. Phys. Lett. **332**, 85 (2000).
[4] M. N. R. Ashfold, R. N. Dixon, R. J. Stickland, and C. M. Western, Chem. Phys. Lett. **138**, 201 (1987).
[5] C. H. Townes and A. L. Schawlow, *Microwave spectroscopy* (Dover Publications, Inc., New York, 1975).