Cold N + NH Collisions in a Magnetic Trap

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We present an experimental and theoretical study of atom-molecule collisions in a mixture of cold, trapped N atoms and NH molecules at a temperature of ~600 mK. We measure a small N + NH trap loss rate coefficient of $k_{loss}^{(N+NH)} = 9(5)(3) \times 10^{-13}$ cm$^3$ s$^{-1}$. Accurate quantum scattering calculations based on $ab$ initio interaction potentials are in agreement with experiment and indicate the magnetic dipole interaction to be the dominant loss mechanism. Our theory further indicates the ratio of N + NH elastic-to-inelastic collisions remains large (> 100) into the mK regime.

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spherical quadrupole magnetic trap. In the bore of the solenoids resides a cryogenic buffer gas cell held at 500 mK. N and NH are produced in a molecular beam using a dc glow discharge and enter the trapping region through a 1 cm diameter aperture in the buffer gas cell. N and NH thermalize with 3He buffer gas to 500 mK and fall into the trap. The initial buffer gas density at time of loading of 10^{15} \text{ cm}^{-3} is produced using a cryogenic reservoir with fast actuating valve [26] to inject buffer gas through a 3.8 cm diameter aperture in the cell. After trap loading, the valve is closed, and the buffer gas exits primarily back out through the larger aperture, yielding background helium densities of 10^{12} \text{ cm}^{-3}, corresponding to NH trap lifetimes of several seconds.

Detection of trapped N is performed using two-photon absorption laser induced fluorescence from the ground \((2p^3)^1S_{3/2}\) state to the excited \((3p)^4S_{3/2}\) state at 96750 \text{ cm}^{-1}. NH is detected via laser induced fluorescence, as described in [19]. We initially load NH with densities on the order of 10^{10} \text{ cm}^{-3}. Accurate knowledge of the absolute NH density is unnecessary as the NH density is much smaller than the N density in all our measurements. To determine the N density without relying on imprecise fluorescence collection measurements, the two-photon absorption laser induced fluorescence signal is calibrated using N + N collisional loss measurements [27]. We load \(5 \times 10^{11}\) N atoms into the trap with peak densities of 10^{12} \text{ cm}^{-3}.

Figure 1 shows a typical NH trapping decay. At time \(t = 0\) s, N and NH are coloaded into the magnetic trap. For the first 2 s, the NH trap loss is rapid due to the collisions with background helium gas during the pump out of buffer gas from the cell. By \(t = 5\) s the NH trap loss reaches a steady rate, with typical 1/e lifetimes of about 3 s. Since the excitation laser for the N detection causes additional loss of the trapped NH, we measure the trapped N density at \(t = 15\) s.

To measure N + NH collisions, we observe the NH trap loss over a range of cotrapped N densities. The trapped N density is varied by changing the ratio of molecular

\[
\Gamma_{\text{NH}} = \frac{\Gamma_{\text{loss}}}{4} n_N + \Gamma_{\text{He}}
\]

where \(n_N\) is the peak nitrogen density, \(\Gamma_{\text{He}}\) is the NH loss rate attributable to collisions with background helium gas, and \(k_{\text{loss}}^{\text{(N+NH)}}\) is the N + NH loss rate coefficient. The factor of 14(\pm 0.4) arises from averaging the N and NH densities over the volume of the magnetic trap [27]. We find from this fit that \(k_{\text{loss}}^{\text{(N+NH)}} = 9(5)(3) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}\). The uncertainties in \(k_{\text{loss}}^{\text{(N+NH)}}\) are statistical and systematic, respectively, where the systematic uncertainty is dominated by the N density calibration [27]. The N + NH loss rate coefficient has contributions from both elastic (evaporative) and inelastic N + NH collisions [27], but their individual contributions cannot be determined by a single measurement. Therefore, our measurement of \(k_{\text{loss}}^{\text{(N+NH)}}\) is an upper limit on the inelastic N + NH rate coefficient. From the following theoretical analysis of N + NH elastic scattering and trap loss dynamics, we estimate elastic collisions contribute up to 60% to the total value of \(k_{\text{loss}}^{\text{(N+NH)}}\).

To interpret the experimental observations and explore the possibility of sympathetic cooling of NH molecules by collisions with cotrapped N atoms, we performed rigorous quantum scattering calculations of N + NH collisions in an external magnetic field. The Hamiltonian of the atom-molecule collision complex may be written (\(\hbar = 1\))

\[
\hat{H} = -\frac{1}{2}\mu \frac{\partial^2}{\partial R^2} + \sum_{S=1/2}^{5/2} V_S(R, r, \theta)\hat{S}M_S\hat{\Delta}M_S + \frac{\mu \alpha^2}{2R^2} \sum_q X_2^q(\hat{R})[\hat{S}_{\text{NH}} \otimes \hat{S}_{\text{N}}]_{2q}^2 + \hat{H}_{\text{NH}} + \hat{H}_N.
\]

FIG. 1 (color online). NH trap decay taken at a trap depth of 3.9 T and cell temperature 570 mK. The solid line is a fit to the form \(n_N = A \exp(-\Gamma_{\text{NH}} t)\). The fit to the exponential decay was performed over the range of 5.5 to 10 s.

FIG. 2 (color online). NH loss rate vs cotrapped N density. The (red) line is a fit of the data to Eq. (1). The vertical error bars represent 1 standard deviation intervals from the fit for \(\Gamma_{\text{NH}}\) as shown in Fig. 1. The horizontal error bars represent the change in N density over the interrogation time of 5.5 to 10 s. The calibration of the peak N density (horizontal axis scale) contains an overall uncertainty of 30%.
where \(\mu\) is the reduced mass of the complex, \(R = |\mathbf{R}|\) is the \(N + NH\) separation vector, \(r\) is the internuclear distance in \(NH\), \(\theta\) is the angle between the vectors \(\mathbf{R}\) and \(\mathbf{r}\), \(V_S(R, r, \theta)\) is the interaction potential of the \(N + NH\) collision complex, \(\hat{S}\) is the total spin of the complex, and \(M_S\) is its projection on the magnetic field axis. The last two terms in the Hamiltonian describe noninteracting collision partners in the presence of an external magnetic field of strength \(B\) \[28\]. The term proportional to \(R^{-3}\) represents the magnetic dipole interaction \[27,28\].

The interaction of \(NH(^3\Sigma)\) molecules with \(N(^4\Sigma_{1/2})\) atoms gives rise to three adiabatic potential energy surfaces (PESs) with \(S = 1/2, 3/2\), and \(5/2\). Since in our experiments both atoms and molecules are confined in a static magnetic trap, the incident collision channel is the maximally spin-stretched Zeeman state \(|M_{SNH} = 1\rangle \otimes |M_{SN} = 3/2\rangle\) with \(S = 5/2\). We neglect the weak couplings between the electronic states of different \(S\) arising from the fine-structure terms in \(\hat{H}_{NH}\) and off-diagonal matrix elements of the magnetic dipole interaction \[27,28\].

To evaluate the PES for the \(S = 5/2\) electronic state of \(N-NH\), we use the partially spin-restricted coupled cluster method with single, double, and noniterative triple excitations \[29\] using quadruple-zeta basis set \((\text{aug-cc-pvqz})\) \[30\] augmented with \(3s3p2d2f1g\) bond functions placed in the middle of the intermolecular distance. A contour plot of the calculated PES is shown in Fig. 3. The PES has a global minimum \(87.83 \text{ cm}^{-1}\) deep in the linear N-NH configuration \((R = 7.02 a_0, \theta = 0)\) and a secondary minimum of \(77.52 \text{ cm}^{-1}\) in the H-N configuration \((R = 6.61 a_0, \theta = 180^\circ)\) separated by a barrier \(39.6 \text{ cm}^{-1}\) high located at \(\theta = 92^\circ\).

To solve the scattering problem, we expand the wave function of the collision complex in a direct-product basis set \(|\langle \mathbf{N}M_N \rangle |S_{NH}M_{SNH}\rangle |S_M \rangle |M_{SM}\rangle |\ell \ell_M\rangle\), where \(\mathbf{N}\) is the rotational angular momentum of \(NH\), and \(M_N, M_{SNH}, M_{SN},\) and \(m_\ell\) are the projections of \(\hat{N}, \hat{S}_{NH}, \hat{S}_N,\) and \(\ell\) on the magnetic field axis. We solve the resulting close-coupled equations numerically for each value of the total angular momentum projection \(M = M_N + M_{SNH} + M_{SN} + m_\ell\) for collision energies between \(10^{-4}\) and \(1 \text{ cm}^{-1}\) and extract the \(S\)-matrix elements and scattering cross sections. Large basis sets with \(N = 0-5\) and \(\ell = 0-8\) are used to ensure that the results are converged to \(<5\%\).

Figure 4(a) shows the cross sections for elastic energy transfer and inelastic relaxation in \(N + NH\) collisions. The cross sections increase with decreasing collision energy before reaching a maximum at \(E_C \sim 2 \text{ mK}\), which we identify as a shape resonance supported by the centrifugal barrier with \(\ell = 1\) in the incident collision channel. At \(E_C < 0.1 \text{ mK}\) the inelastic cross sections assume the characteristic \(E_C^{-1/2}\) dependence on collision energy, and the elastic cross sections become constant, according to the Wigner threshold law. By thermally averaging the cross sections in Fig. 4(a), we obtain elastic and inelastic rate constants at the experimental temperature of \(570 \text{ mK}\) of \(k_{el} = 2.2 \times 10^{-10} \text{ cm}^3 \text{s}^{-1}\), \(k_{in} = 4.1 \times 10^{-13} \text{ cm}^3 \text{s}^{-1}\). The fraction of elastic \(N + NH\) collisions that lead to trap loss is less than \(3 \times 10^{-3}\) \[27\], leading to a total trap loss rate coefficient \(k_{\text{loss}-\text{theory}} = (4-11) \times 10^{-13} \text{ cm}^3 \text{s}^{-1}\), in good agreement with the experimental value of \(k_{\text{loss}-\text{experiment}} = 9(5)(3) \times 10^{-13} \text{ cm}^3 \text{s}^{-1}\). The ratio \(\gamma = k_{el}/k_{in}\) is shown in Fig. 4(b) as a function of temperature. The ratio remains large \((\gamma > 100)\) over the temperature range \(\sim 10 \text{ mK} - 1 \text{ K}\), which indicates that

![Ab Initio Interaction PES](image)

**FIG. 3** (color online). Contour plot of the \textit{ab initio} interaction PES for the fully spin-polarized \(S = 5/2\) state of \(N + NH\) calculated in this work. The NH bond distance is fixed at its equilibrium value \(r = 1.958 a_0\). Energies are in units of \(\text{cm}^{-1}\).
NH can be sympathetically cooled by elastic collisions with spin-polarized N down to the millidegrees Kelvin regime. As shown in Fig. 4(b), an increasing magnetic field suppresses inelastic relaxation, so that $\gamma$ remains high ($\sim 50$) even at $T = 1$ mK. The suppression occurs due to an increase of the energy gap between the initial and final collision channels with increasing magnetic field\[27,31]. Although the current experiment, at a temperature of 600 mK, is not sensitive to this suppression, applying a strong uniform magnetic field of order 1 T may be used to stabilize spin-polarized atom-molecule mixtures against collisonal losses at temperatures below 100 mK, thereby enhancing the efficiency of sympathetic cooling.

Inelastic collisions of $^{3}\Sigma$ molecules with open-shell atoms like N can occur due to (i) spin-dependent couplings arising from an interplay between the anisotropy of the atom-molecule interaction potential and the intramolecular spin-spin interaction [5,28], and (ii) direct couplings between atomic and molecular Zeeman levels induced by the long-range magnetic dipole interaction. The magnetic dipole interaction [27] can thus be more efficient in inducing inelastic relaxation than other spin-dependent couplings. Figure 4(a) shows that omitting the magnetic dipole interaction from scattering calculations reduces the inelastic cross sections by a factor of $\sim 10$, confirming that Zeeman transitions in N + NH collisions are indeed driven by the magnetic dipole interaction. In our experiments, both N and NH collision partners are fully spin-polarized, so the chemical reaction $N + NH \rightarrow N_2 + H$ is spin-forbidden and can only proceed via nonadiabatic transitions between different electronic states of the N-NH complex in the entrance reaction channel mediated by the fine-structure and magnetic dipole coupling terms of the Hamiltonian. Our observed value for $k_{\text{loss}}^{(\text{N+NH})}$ is much smaller than the calculated reaction rate for spin-unpolarized reactants ($k_{\text{reaction}} \sim 3 \times 10^{-11}$ cm$^3$/s at $T = 1$ K) [32]. Since our measurements are consistent with theoretical predictions that ignore the reaction channel, we conclude that chemical exchange processes in spin-polarized N + NH mixtures occur at a slow rate, and do not contribute to the trap loss dynamics. This finding shows that inelastic relaxation in N + NH collisions occurs via the same mechanism as dipolar relaxation in spin-polarized atomic gases [27].

In conclusion, we have measured a small N + NH trap loss rate coefficient of $9.5(3) \times 10^{-13}$ cm$^3$/s$^{-1}$ at a temperature of $\sim 600$ mK. To interpret experimental observations, we have carried out accurate \textit{ab initio} quantum scattering calculations of Zeeman relaxation in N + NH collisions in a magnetic field and find theory and experiment to agree. Our calculations show that the ratio of N + NH elastic-to-inelastic collisions remains large ($> 100$) over the temperature range $\sim 10$ mK–1 K, which indicates that it may be possible to sympathetically cool NH down to the millidegrees Kelvin regime via elastic collisions with (evaporatively cooled [27]) spin-polarized N. If this conclusion holds for other paramagnetic molecules such as the highly polar CaH and SrF in their electronic ground states of $^{3}\Sigma$ symmetry, it may be possible to create large samples of these molecules via collisional cooling with N in a magnetic trap.

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