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Mechanism of Collisional Spin Relaxation in $^3\Sigma$ Molecules

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We measure and theoretically determine the effect of molecular rotational splitting on Zeeman relaxation rates in collisions of cold $^3\Sigma$ molecules with helium atoms in a magnetic field. All four stable isotopomers of the imidogen (NH) molecule are magnetically trapped and studied in collisions with ^3He and ^4He . The ^4He data support the predicted $1/B_e^2$ dependence of the collision-induced Zeeman relaxation rate coefficient on the molecular rotational constant B_e . The measured ^3He rate coefficients are much larger than the ^4He coefficients, depend less strongly on B_e , and theoretical analysis indicates they are strongly affected by a shape resonance. The results demonstrate the influence of molecular structure on collisional energy transfer at low temperatures.

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The development of experimental techniques for cooling molecular ensembles to subKelvin temperatures has opened up possibilities to study collision dynamics of molecules in a new, previously inaccessible, regime. Elastic and inelastic scattering of molecules at such low temperatures is sensitive to external electromagnetic fields as well as fine and hyperfine interactions, of negligible importance in thermal collisions. Cold collisions hold the promise of being exploited to study a new class of processes including chemical reactions induced by fine non-adiabatic interactions [1], field control of intermolecular interactions [2], effect of the geometric phase on collision dynamics [3] and the effect of long-range intermolecular interactions in determining chemical reactions [4]. Cooling techniques also allow for the preparation of molecules in a single quantum state and enable experimental tests of fundamental theories of molecular dynamics. Of particular importance for the experimental work on thermal isolation of molecular ensembles in magnetic traps and collisional cooling of molecules to ultracold temperatures is the theory of collision-induced Zeeman relaxation [5]. Quantum mechanical calculations of Krems and Dalgarno showed that the rates of Zeeman relaxation in collisions of open-shell molecules in Σ electronic states with cold atoms are very sensitive to the rotational constant of the molecules, which can be used to identify the range of molecules amenable to dissipative cooling in magnetic traps based on their rotational structure. In this Letter, we present the first experimental study of the effect of the rotational constant on the magnetic Zeeman relaxation.

Zeeman transitions in Σ -state molecules are thought to be induced by second-order interactions of the electron spin with the rotational angular momentum [5]. The same interactions give rise to an intricate interplay of the fine structure couplings and the couplings induced by electrostatic interaction forces between molecules, which

can be used to engineer novel quantum phases with molecules trapped on optical lattices [6] or develop schemes for quantum information processing based on state-dependent interactions between molecules [7]. It is therefore extremely important to validate by experimental measurements the theory of these interactions subject to uncertainties due to inaccuracies of quantum chemistry calculations. In the present work, we study collisions of magnetically trapped imidogen (NH) molecules with helium atoms. Our experimental data not only exemplify the effects of internal molecular structure on collision-induced Zeeman relaxation of $^3\Sigma$ molecules, but also provide evidence for the role of scattering resonances in a multiple-partial-wave collision regime and provide benchmark results for tests of *ab initio* theories of molecular dynamics at cold temperatures.

In this work, we vary the rotational constant of the molecule (B_e) by changing the NH isotopomers and the reduced mass of the collision system by changing the isotope of He. We present the measurement data for all eight isotopic combinations of the imidogen-helium collision system ($^A\text{N}^B\text{H} - ^C\text{He}$). The predicted $1/B_e^2$ dependence of the inelastic cross section [8] fits well for the ^4He data, supporting the model that the couplings between rotational states of the molecule drive helium induced Zeeman relaxation. The measured ^3He inelastic collision rate coefficient is found to be much larger than that for ^4He , and the ^3He data show a weaker dependence on the molecular rotational splitting. Based on quantum mechanical calculations, we show that the anomalous behavior of the ^3He -induced Zeeman relaxation rate coefficient of imidogen can be attributed to the presence of a predicted shape resonance [8,9].

Our experimental apparatus is described in detail elsewhere [9]. A molecular beam of imidogen radicals is loaded into a cryogenic buffer-gas cell through a 1 cm

diameter molecular beam entrance aperture. The buffer-gas cell is thermally connected to a ^3He refrigerator through a copper heat link, and resides in the bore of a superconducting anti-Helmholtz magnet. The trap magnet creates a spherical quadrupole field up to 3.9 T deep centered inside the buffer-gas cell. Molecules entering the cell collide with the cold helium buffer gas and the low-field seeking (LFS) molecules fall into the magnetic trap. The buffer gas is continuously supplied to the cell by a fill line that is thermally connected to the ^3He refrigerator. The buffer-gas density is set by the flow rate and the conductance out of the molecular beam input aperture. The buffer-gas density is monitored and controlled by a flow controller at room temperature, and the buffer-gas density has been calibrated previously [9].

Trapped radicals are detected using laser-induced fluorescence (LIF). A cw dye laser is frequency doubled to provide 336 nm excitation light for imidogen. The beam enters and exits the cell through windows in the side, and fluorescence is also collected through a window in the side of the cell perpendicular to the excitation beam. Fluorescence from the trap region is imaged onto the face of a photomultiplier tube operating in photon-counting mode. In this work, detection takes place via LIF excited on the $A^3\Pi_2(v=0, J=2) \leftarrow X^3\Sigma^-(v''=0, J''=1)$ transition from the LFS Zeeman sublevel of the rotational ground state.

The molecular beam of radicals is produced in a dc glow discharge of ammonia [10] and each imidogen isotopomer is created by using a different isotopic variant of ammonia as the stagnation gas ($^{14}\text{NH}_3$ for ^{14}NH , $^{15}\text{ND}_3$ for ^{15}ND , etc.). Isotopic purity levels for all four gases are higher than 95% and we are unable to detect impurity contributions in the LIF signal. Buffer-gas isotopes are interchanged by feeding from different bottles, and the helium isotopic purity is 99.95% or better. In the experiments with ^4He , the temperature of the cell is kept above 700 mK to prevent saturation of the vapor pressure. The isotope shifts for all four stable isotopomers of imidogen make spectroscopic distinction between them possible, even in the presence of the magnetic trapping field. The observed shifts of the $A^3\Pi_2(v=0, N=1, J=2) \leftarrow X^3\Sigma^-(v''=0, N''=0, J''=1)$ transition from the dominant isotopomer (^{14}NH) are $+11.70\text{ cm}^{-1}$ (^{14}ND), $+0.12\text{ cm}^{-1}$ (^{15}NH), and $+11.83\text{ cm}^{-1}$ (^{15}ND).

Figure 1 shows the trap lifetime of ^{14}NH as a function of ^4He density at 740 mK. The lifetime is measured by fitting a single-exponential to the fluorescence signal [9]. In the low-density regime on the left side, the trap lifetime increases with buffer-gas density. This is because the buffer gas enforces diffusive motion of the molecules, effectively making them slower to exit the trap. The lifetime then reaches a maximum as collision-induced Zeeman relaxation becomes more frequent and decreases as $1/n$ for high buffer-gas densities (n). The solid curve is a two-parameter

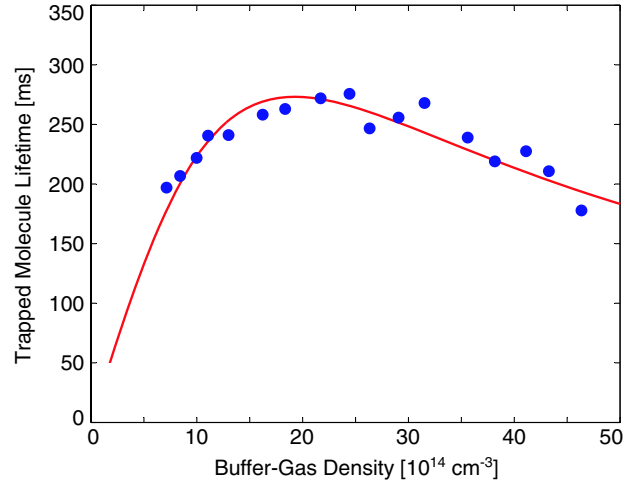


FIG. 1 (color online). Measured trap lifetime vs buffer-gas density for ^{14}NH with ^4He at 740 mK. The solid curve is fit to extract a collision-induced Zeeman relaxation rate coefficient.

fit to the data of the form $1/\tau_{\text{eff}} = A/n + nk_{\text{ZR}}$ where τ_{eff} is the trap lifetime, A is a fitting parameter describing the influence of elastic collisions and trap depth on the lifetime, and k_{ZR} is the collision-induced Zeeman relaxation rate coefficient. We measure k_{ZR} by fitting the trap lifetime as a function of buffer-gas density for each of the eight imidogen-helium collision pairs.

The results of the measurements are summarized in Table I and are best interpreted in the context of theory put forth in Ref. [5]. Krems and Dalgarno demonstrated that collision-induced spin depolarization in $^3\Sigma$ molecules is mediated by a small admixture of the anisotropic rotational state $|N=2\rangle$ in the rotational ground state (nominally $|N=0\rangle$) of the molecule due to the spin-spin interaction. The electrostatic interaction with helium (V_{He}) cannot directly couple different Zeeman sublevels of an $|N=0\rangle$ rotational state, but there can be a nonzero off-diagonal contribution $\langle N=2|V_{\text{He}}|N=0\rangle$ to the

TABLE I. Zeeman relaxation rate coefficients for imidogen in collisions with helium in units of $10^{-15}\text{ cm}^3\text{ s}^{-1}$. The quoted uncertainties are statistical. The uncertainty in the absolute buffer-gas density results in a systematic uncertainty of $\pm 30\%$ for all measurements. The last two columns show the results of our calculations and the values in parentheses are calculated with the interaction anisotropy multiplied by 1.6

Collision Species	$^3\text{He}^a$	$^4\text{He}^b$	$^3\text{He}^c$	$^4\text{He}^d$
^{14}NH	4.5 ± 0.3	1.1 ± 0.1	0.56 (2.1)	0.23 (0.76)
^{15}NH	5.1 ± 0.4	1.4 ± 0.2	0.61 (2.3)	0.27 (0.87)
^{14}ND	9.3 ± 0.8	4.0 ± 0.7	2.17 (9.1)	1.03 (3.9)
^{15}ND	13.0 ± 0.8	2.8 ± 0.6	2.32 (9.1)	1.18 (4.3)

^aExperiment: $T = 580\text{--}633\text{ mK}$.

^bExperiment: $T = 720\text{--}741\text{ mK}$.

^cTheory: $T = 600\text{ mK}$.

^dTheory: $T = 700\text{ mK}$.

Zeeman transition probability for $^3\Sigma$ molecules due to the $N = 2$ contribution. The admixture of $|N = 2\rangle$ in the ground rotational state is determined to first order by the ratio λ_{SS}/B_e , where λ_{SS} is the spin-spin interaction constant. The collision-induced Zeeman relaxation cross section is then predicted to scale as λ_{SS}^2/B_e^2 [8]. This is in direct contrast with $^2\Sigma$ molecules, where the collision-induced Zeeman transition is induced by the spin-rotation interaction in the molecule, and is predicted to scale as γ_{SR}^2/B_e^4 .

To show the dependence of the rate coefficients on B_e , we plot k_{ZR} extracted from our data vs $1/B_e^2$ in Fig. 2. The solid curves are one-parameter fits to a B_e^{-2} scaling of the inelastic rate coefficient. The measured data for ^4He are in good agreement with the scaling prediction. While the scaling for ^3He does not follow $1/B_e^2$, in all cases, decreasing the imidogen rotational constant by a factor of ≈ 2 (through $\text{H} \rightarrow \text{D}$ substitution) still dramatically increases the Zeeman relaxation rate.

In order to fully understand the experimental observations and their implications, we computed the Zeeman relaxation rate coefficients for each pair of the collision partners using a rigorous quantum scattering approach described in Ref. [11]. The calculations are based on the most accurate NH-He interaction potential borrowed from Ref. [8]. The rate coefficients in the temperature interval $T = 0.2\text{--}1$ K were obtained from the cross sections calculated at 300 collision energies from 0.01 to 1.5 cm^{-1} and summed over all final spin states of NH. Table I shows that the computed rate coefficients for Zeeman relaxation are smaller than the measured values by a factor between 2.3 and 8. At the same time, the computed cross section for

elastic collisions of ^{14}NH with ^3He is in excellent agreement with the experimental measurement (cf., Refs. [8,9]). This indicates that the isotropic part of the He-NH interaction potential from Ref. [8] is accurate but the anisotropy of the atom-molecule potential may be significantly underestimated. In order to elucidate the effects of the interaction anisotropy on the Zeeman relaxation process, we recomputed the rate coefficients with the interaction potential anisotropy multiplied by 1.6. The 60% change of the interaction anisotropy enhances the rate coefficients for Zeeman relaxation to a great extent but leaves the rate coefficients for elastic collisions almost unaffected. The rate coefficients calculated with the modified potential agree to within 30% with the experimental data for all collision systems except $^{14}\text{NH} - ^3\text{He}$ and $^{15}\text{NH} - ^3\text{He}$. The measured effect of the NH/ND isotopic substitution on collisions with ^3He is thus again in marked disagreement with theory.

Table I demonstrates that the rates of Zeeman relaxation in collisions of NH and ND molecules with ^3He , both measured and calculated, are consistently larger than in collisions with ^4He . The effect of nuclear spin of ^3He should be negligible [12]. This enhancement suggests the presence of scattering resonances. Figure 3(a) shows the cross section for the dominant $|M_S = 1\rangle \rightarrow |M_S = -1\rangle$ transition in the ground rotational state of NH induced by collisions with ^3He atoms computed as a function of the incident collision energy and the magnetic field magnitude. The cross section displays a single resonance peak that splits into two at finite magnetic field. The higher-energy resonance is insensitive to the magnetic field, which suggests that it is a shape resonance in the incoming collision channel. The low-energy resonance can be classified as a shape resonance in the outgoing collision channel [13]. The $|M_S = -1\rangle$ state is $4\mu_0 B$ lower in energy than the initial $|M_S = 1\rangle$ state, where μ_0 is the Bohr magneton, and the splitting between the resonances in Fig. 3(a) increases linearly with the magnetic field strength. The cross sections for collisions of ND and ^3He display a similar resonance pattern. However, the cross sections calculated for Zeeman relaxation in collisions of NH and ND molecules with ^4He show no resonance structures in the energy interval $0.1\text{--}1.5$ cm^{-1} corresponding to the temperature of the experimental measurements.

The shape resonances affect the temperature dependence of the Zeeman relaxation rates and modify the scaling of the rates with B_e (see Fig. 3). To verify this, we recomputed the rate constants for Zeeman relaxation with the interaction potential multiplied by 1.1. Figures 3(b) and 3(c) display the ratios of the spin relaxation rates $k_{\text{ND}}/k_{\text{NH}}$ for ND and NH at a magnetic field of 0.1 T computed both with the original and modified potentials. The calculated ratios for collisions with ^4He are in excellent agreement with the experimental data and the $1/B_e^2$ scaling law. We focus here on the ^{14}N data, but Table I shows that the

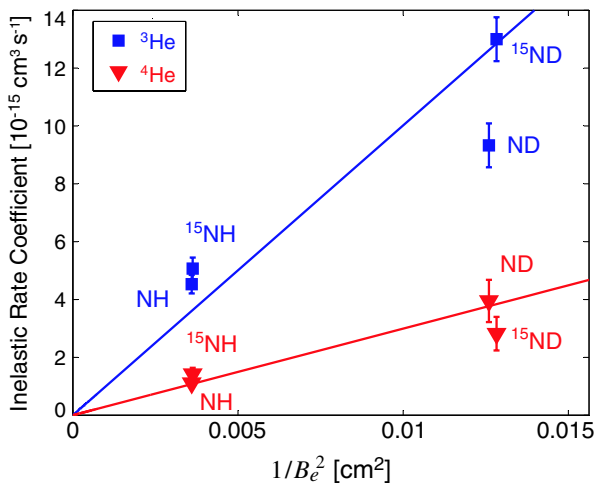


FIG. 2 (color online). Collision-induced Zeeman relaxation (inelastic collision) rate coefficient as a function of the rotational constant (B_e) of the imidogen radical. The solid lines are one-parameter fits to a $1/B_e^2$ scaling law for the inelastic collision rate coefficients. The rotational constants for ^{15}N -bearing isotopomers are estimated from the ^{14}N -bearing rotational constants and the reduced masses: $B_e' = B_e \times \mu/\mu'$.

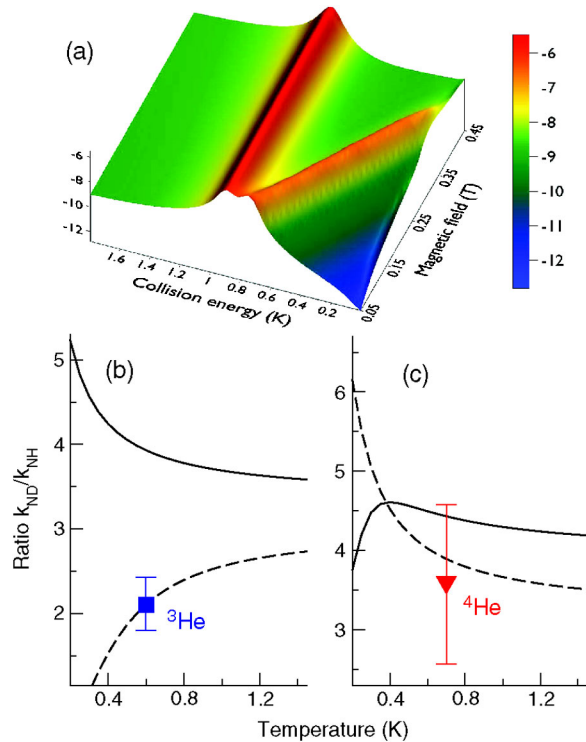


FIG. 3 (color online). Upper panel (a): The logarithm of the cross section for the $|M_S = 1\rangle \rightarrow |M_S = -1\rangle$ transition in collisions with ^3He atoms as a function of the magnetic field and collision energy. Lower panel: The calculated ratios of the Zeeman relaxation rate coefficients $k_{\text{ND}}/k_{\text{NH}}$ for ^3He (b) and ^4He (c) obtained with the original NH-He interaction potential (full lines) and with the potential multiplied by 1.1 (dashed lines). The experimental data are shown as symbols.

predicted rates for ^{15}N are similar. For ^3He , the results obtained with the original potential overestimate the measured $k_{\text{ND}}/k_{\text{NH}}$ ratio by a factor of 2 (cf., Table I) but the results obtained with the modified potential agree well with the measurements. Multiplying the potential by 1.1 moves the resonance structure to lower energies and changes the temperature dependence of the rate coefficients dramatically, weakening the dependence on B_e . The agreement between our data and the scaled potential suggests that the imidogen-helium potential used for our calculation is too shallow.

In conclusion, we have trapped both fermionic (NH, ^{15}ND) and bosonic (ND, ^{15}NH) imidogen radicals in a magnetic trap using buffer-gas loading. We have measured the Zeeman relaxation rate coefficients for all stable isotopomers of NH in collision with both stable isotopes of helium at ≈ 650 mK. The experiments show that the Zeeman relaxation rates for $^3\Sigma$ molecules in the ground rotational state are sensitive to the rotational constant of the molecule. The observed scaling behavior of the collision-

induced Zeeman relaxation rate, which is compatible with the prediction of $1/B_e^2$, has important implications for sympathetic cooling of magnetically trapped molecules, and suggests that $^3\Sigma$ molecules with large rotational splitting will be more stable against spin-projection changing collisions. Furthermore, the rotational constant of NH can be identified as a general marker in the magnetic trapping landscape— $^3\Sigma$ molecules with smaller rotational constants will generally be difficult to cool collisionally in a magnetic trap.

Our study also underlines the role of multiple partial-wave scattering in collision dynamics at cold temperatures. The results of rigorous quantum calculations demonstrate that the collision dynamics of NH and ND molecules with ^3He at the temperatures of our measurements are modified by a scattering shape resonance. The resonance enhances the inelastic collision rate, alters the temperature dependence of the collision rate coefficients and modifies the dependence on the rotational constant. Identification of resonances in candidate collisional cooling systems will therefore be an important guide for future experiments using sympathetic and evaporative cooling to reach the ultracold regime.

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