Low-temperature collisions of NH($X\,^3\Sigma^-$) molecules with He atoms in a magnetic field: An *ab initio* study

R. V. Krems,[1,2,*] H. R. Sadeghpour,[2] A. Dalgarno,[2] D. Zgid,[3] J. Kłos,[4] and G. Chałasiński[3,†]

[1]*Harvard-MIT Center for Ultracold Atoms, Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA*
[2]*ITAMP, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138, USA*
[3]*Faculty of Chemistry, Warsaw University, Pasteura 1, 03-093 Warszawa, Poland*
[4]*Institute of Theoretical Chemistry, NSRIM, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands*

Ab initio calculations of cross sections and rate constants for elastic scattering and Zeeman relaxation in collisions of NH($X\,^3\Sigma^-$) molecules with ^{3}He atoms in a magnetic field are presented and the mechanism for Zeeman transitions in ground-state $^3\Sigma$ molecules is established. The potential surface for He-NH interaction is obtained using all-electron coupled-cluster calculations with single, double, and noniterative triple excitations in a basis set augmented by bond functions. The ratio of the rates for elastic energy transfer and Zeeman relaxation in NH-^{3}He collisions exceeds 10^5 at temperatures between 0.5 and 1 K.

The development of techniques for the production of ultracold atoms has generated a resurgence in atomic collision physics. New fields of research such as coherent control of atomic processes, quantum information, and matter wave interferometry make extensive use of ultracold atoms [1,2]. A major thrust of the research is now to create ultracold molecules. The creation and trapping of ultracold molecules will be a revolution in molecular physics. Spectroscopic measurements of unprecedented precision, manipulation of chemical reactions, and molecular Bose-Einstein condensation may become possible.

Ultracold molecules can be produced by photoassociation of atoms at microkelvin temperatures [3–7], molecular beam deceleration [8–10] or buffer-gas loading [11,12] followed by evaporative cooling in a magnetic trap. Buffer-gas loading is applicable to any paramagnetic species and is potentially the most general method of cooling molecules. It employs a gas of ^{3}He atoms and involves the capture of molecules in a magnetic trap. Magnetic trapping selects molecules in the highest-energy Zeeman level and the efficiency of buffer-gas loading depends on the relative rates of elastic energy transfer and Zeeman relaxation in collisions with ^{3}He atoms.

The buffer-gas method was used to load CaH molecules in a magnetic trap at a temperature $T\sim0.4$ K [12]. The ground state of the CaH molecule has $^2\Sigma^+$ symmetry and its magnetic moment is 1 Bohr magneton. In order to capture a large number of $^2\Sigma$ molecules, the trapping field should be quite high which poses experimental difficulties. The technique may be more effective when applied to molecules with larger spin and an experiment is underway for magnetic trapping of NH($X\,^3\Sigma^-$) molecules [13]. The success of the experiment depends upon the collisional properties of NH in ^{3}He gas. Bohn and coworkers [14–16] showed that collisionally induced Zeeman relaxation in $O_2(^3\Sigma^-)$+He collisions is slow but it is not clear if the conclusions are applicable to NH molecules.

We have demonstrated recently that spin-flip relaxation in rotationally ground-state $^2\Sigma$ molecules is induced by collisions with He atoms through coupling to rotationally excited molecular levels [17] and accordingly spin-flipping transitions may be more efficient in heteronuclear diatoms. A further enhancement may arise from the presence of a strong spin-spin interaction [18]. We have suggested [18] that the Zeeman relaxation in collisions of $^3\Sigma$ molecules with structureless atoms is determined by the electrostatic atom-molecule interaction which couples the $N=0$ and $N=2$ rotational states that are mixed by the spin-spin interaction, and the electrostatic interaction in the $N=2$ state. Verification of this suggestion would establish the mechanism of spin-flipping transitions in $^3\Sigma$ molecules in collisions with structureless targets.

In this Rapid Communication, we report the first results for the elastic energy transfer and Zeeman relaxation in collisions of ground-state NH molecules with ^{3}He atoms in a magnetic field, based on a He-NH interaction potential, computed using an accurate *ab initio* method. We employed a close coupling technique using the fully uncoupled space-fixed representation [18] to make predictions for experiments on the buffer-gas loading of NH, and we establish the mechanism of Zeeman transitions in NH-He collisions.

The total Hamiltonian of the He-NH complex in a magnetic field can be written as [19]

$$H = -\frac{1}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{\mathbf{l}^2}{2\mu R^2} + V(\mathbf{R},\mathbf{r}) + \frac{\mathbf{N}^2}{2\mu_{\mathrm{NH}}r^2} + \gamma\mathbf{N}\cdot\mathbf{S}$$
$$+ \frac{2}{3}\lambda_{\mathrm{SS}}\left[\frac{4\pi}{5}\right]^{1/2}\sqrt{6}\sum_q (-1)^q Y_{2-q}(\hat{r})[\mathbf{S}\otimes\mathbf{S}]_q^{(2)}$$
$$+ 2\mu_0\mathbf{B}\cdot\mathbf{S}, \tag{1}$$

where $\mathbf{R}$ is the vector joining the center of mass of the molecule with the He atom, $\mathbf{r}$ is the separation vector of NH, μ and μ_{NH} are the reduced masses of the He-NH complex and the NH molecule, respectively, $\mathbf{l}$ is the orbital angular mo-

*Electronic mail: rkrems@cfa.harvard.edu

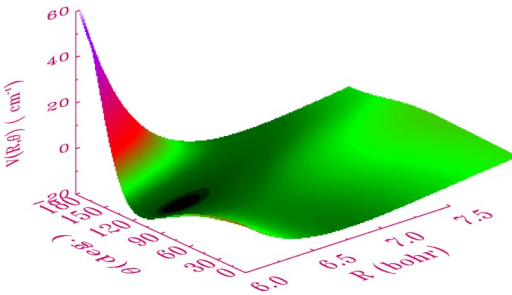†Also at Department of Chemistry, Oakland University, Rochester, MI 48309, USA.

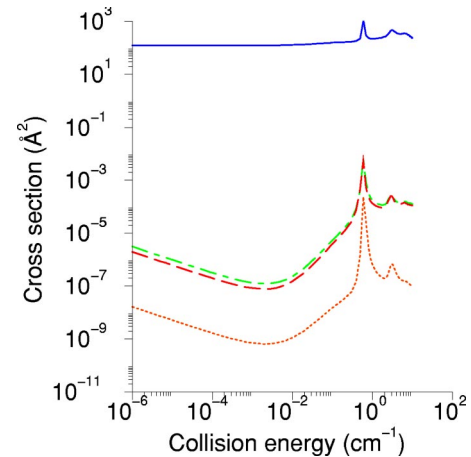FIG. 1. Potential-energy surface for He-NH interaction.

FIG. 2. Cross sections for elastic (full curve) and inelastic $m_j = 1 \rightarrow m_j' = -1$ (dashed curve) scattering of NH by ^{3}He in a magnetic field of 100 G. Cross sections for the Zeeman transition computed without the $N = 2$ level (dotted curve) and without odd rotational levels (dot-dashed curve) are also shown. $1 \text{ cm}^{-1} = 0.695 \text{ K}$.

mentum for the collision, **N** and **S** are the rotational and spin angular momenta of NH, γ and λ_{SS} are the phenomenological spin-rotation and spin-spin interaction constants, **B** is the magnetic field, and μ_0 is the Bohr magneton. For the NH molecule, $\gamma = -0.054\,67 \text{ cm}^{-1}$ and $\lambda_{SS} = 0.9197 \text{ cm}^{-1}$ [20]. The matrix elements of Hamiltonian (1) can be evaluated analytically [18] in the product basis $|NM_N\rangle|SM_S\rangle|lm_l\rangle$ upon expanding the interaction potential $V(\mathbf{R}, \mathbf{r})$ in a Legendre series, where M_N, M_S, and m_l are the projections of **N**, **S** and **l**, respectively, on the magnetic field axis. The vibrational motion of NH is neglected and the interatomic separation r is fixed at the equilibrium distance of 1.96 bohrs.

The potential for the He-NH interaction was computed on a two-dimensional (2D) grid of 870 points in the range of atom-molecule separation $3 \leq R \leq 15$ a.u. All-electron calculations using the spin-restricted coupled-cluster method [21–23] were performed with the aug-cc-pvQZ basis set [24–26] augmented with an extended $3s3p2d2f1g$ set of bond functions with the exponents sp: 0.94, 0.34, 0.12; df :0.64, 0.23; g: 0.35 [27]. The relative error of the computation was estimated to be within 5% (cf. also Ref. [28]). To avoid uncertainties due to 2D fitting, the potential energy was computed at 30 Gauss-Legendre quadrature points and the potential surface was expanded in Legendre polynomials. The dependence of the expansion terms on R was then fitted to analytical expressions that mimic the correct asymptotic form of the interaction energy. The average error of the resulting representation of the surface is less than 0.04% and the maximum error of the analytical fit is less than 0.83%.

The potential-energy surface for the He-NH interaction (Fig. 1) is remarkably flat. The lowest energy of the potential is -19.80 cm^{-1} at the interparticle separation $R = 6.33$ bohrs and the relative orientation angle $\Theta = 117.67$ deg. The zero of Θ corresponds to the collinear He-NH approach. A series of 12 Legendre polynomials sufficed to represent the angular dependence of the potential-energy surface.

The close coupling equations for He-NH scattering were propagated in the $|NM_N\rangle|SM_S\rangle|lm_l\rangle$ basis using the log-derivative method of Johnson and Manolopoulos [29]. The Hamiltonian matrix is not diagonal in this basis when $R = \infty$, and the propagation matrix was transformed numerically to the representation in which the asymptotic Hamiltonian $H(R = \infty)$ is diagonal, before construction of the scattering S matrix.

The rotational angular momentum N is not a good quantum number in $^3\Sigma$ molecules [19]. The spin-spin interaction

couples states with N and $N' = N \pm 2$ and the ground state of the NH molecule in the absence of a magnetic field is characterized by the total angular momentum j, its space-fixed projection m_j and a phenomenological quantum number n [18,19]. Interaction with magnetic fields couples states with different values of j or n so that the only good quantum number of the NH molecule in a magnetic field is m_j. The ground state of NH is split in a triplet of Zeeman levels; the state with $m_j = 1$ is trappable in a magnetic field and transitions to the states with $m_j = 0$ and $m_j = -1$ lead to trap loss.

Figure 2 depicts cross sections for elastic energy transfer and Zeeman relaxation in collisions of NH($m_j = 1$) with ^{3}He in a magnetic field $B = 100$ G. Only the cross section for the dominant $m_j = 1 \rightarrow m_j' = -1$ inelastic transition is presented. The rate constant is $1.93 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for elastic scattering and $4.20 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ for inelastic relaxation at a temperature $T = 0.5$ K. Five rotational energy levels ($N = 0$–4) were coupled for these calculations giving results accurate to within 15%. The rate for elastic collisions is large and the elastic-to-inelastic ratio is more than 10^5, indicating that the buffer-gas loading of NH molecules in a magnetic trap will be efficient.

The cross sections show resonant structure in the energy interval 0.3–4 cm^{-1}. Six states of orbital angular momentum $l = 0$–5 were included in the calculations at these energies. The cross sections do not show any resonance enhancement with only three states, $l = 0, 1$, and 2, whereas adding the $l = 3$ state produces the large peak at the collision energy of 0.6 cm^{-1}. Thus all the peaks in Fig. 2 arise from shape resonances and the $l = 3$ shape resonance is responsible for the largest peak.

The energy of the last bound state supported by the He-NH potential is 0.761 cm^{-1} below the dissociation threshold so that the scattering length should not be very sensitive to small changes in the interaction potential. We have repeated the calculations of the cross sections at
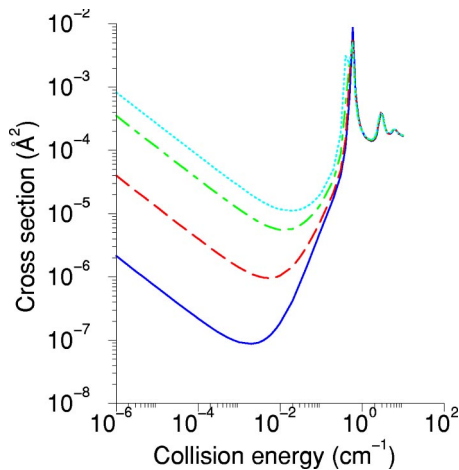
FIG. 3. Cross sections for Zeeman relaxation of NH($m_j=1$) by collisions with ^{3}He in a magnetic field of 100 G (full curve), 300 G (long-dashed curve), 700 G (dot-dashed curve), and 1000 G (dotted curve). 1 cm^{-1}=0.695 K.

FIG. 4. Rate constants for rotational relaxation of NH in the five excited rotational energy levels induced by collisions with ^{3}He at a temperature of 0.5 K at zero magnetic field.

$B=100$ G with the potential multiplied by 0.9 and 1.1. Variation of the potential by 10% changes the elastic cross section at zero energy by 50–80% and the spin-flip cross sections by a factor of 3–4.

Figure 3 shows cross sections for the $m_j=1\rightarrow m_j'=-1$ relaxation computed at different magnetic-field strengths. The m_j levels are split in a magnetic field and the cross sections for m_j-changing transitions increase to infinity in agreement with the Wigner law [30,31] when the collision energy vanishes. Increasing the magnetic field enhances the cross sections at threshold energies but does not affect collisions at energies >0.1 cm^{-1}. The increase of the threshold cross sections for Zeeman transitions with magnetic field has been explained by Tiesinga *et al.* [32] and Volpi and Bohn [16]. When the energy defect between the initial and final scattering states is small, the height of the centrifugal barrier in the final state can be larger than the initial energy of the system and the inelastic collision is suppressed by the centrifugal maximum in the outgoing channel. Increasing the energy gap between the initial and final states with magnetic field increases the probability of escaping over the barrier. Varying the magnetic field from 100 to 1000 G has little effect on the rate constants for elastic and inelastic collisions of NH with He at temperatures larger than 0.5 K.

We have shown by a formal derivation [18] that the Zeeman levels of a ground-state $^3\Sigma$ molecule are coupled by the electrostatic interaction of the $N=0$ and $N=2$ rotational levels and through integrals of the type $\langle N=2|V(\mathbf{r},\mathbf{R})|N=2\rangle$. The derivation suggests that the spin-flipping Zeeman transitions in $^3\Sigma$ molecules are determined by the admixture of the excited $N=2$ state in the ground molecular level. Figure 2 confirms this suggestion. It shows that if the $N=2$ level is omitted from the calculations, the rate of the Zeeman transitions decreases by more than two orders of magnitude and that if all odd rotational energy levels of NH are neglected, the Zeeman relaxation remains almost unaffected. We have found also that the cross sections for Zeeman relaxation undergo a negligible change if the $\gamma\mathbf{N}\cdot\mathbf{S}$ term is omitted from
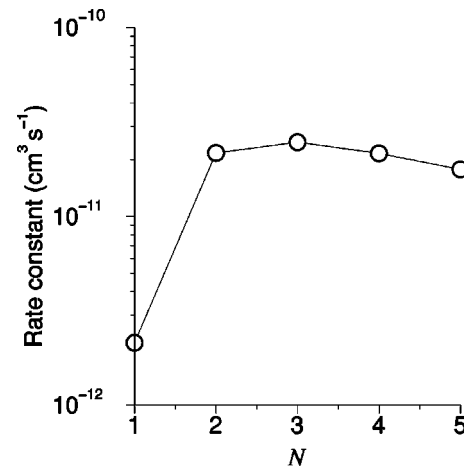
Hamiltonian (1) and that they vary quadratically with the spin-spin interaction constant λ_{SS}.

The experimental measurements provide rate constants for energy transport rather than elastic scattering [11,12]. The cross section for energy transport in elastic $m_j=1\rightarrow m_j=1$ collisions is defined as follows:

$$\sigma_t=\frac{1}{4\pi}\int d\hat{R}_i\int d\hat{R}\frac{d\sigma_{m_j\rightarrow m_j}}{d\hat{R}_i d\hat{R}}[1-\cos\Theta], \qquad (2)$$

where $d\sigma_{m_j\rightarrow m_j}/d\hat{R}_i d\hat{R}$ is the doubly differential cross section depending on the direction of the initial ($\hat{R}_i$) and final ($\hat{R}$) collision fluxes, Θ is the angle between $\hat{R}_i$ and $\hat{R}$, and $d\hat{R}$ denotes the spherical volume element. The cross section (2) is the same as the elastic cross section of Fig. 2 in the ultracold limit and is smaller than the elastic cross section at higher collision energies. The corresponding rate coefficient is 1.49×10^{-10} cm^{-1} s^{-1} at 0.5 K.

Recent experiments demonstrated that it is possible to measure rate constants for rotational relaxation in atom-molecule collisions at subkelvin temperatures [12]. For future comparison with experiment, we present in Fig. 4 the rate constants for rotational relaxation of NH in the five excited rotational energy levels by collisions with ^{3}He at 0.5 K. Interaction with magnetic fields, spin-rotation coupling, and spin-spin interaction were neglected for these calculations. The accuracy of the results should be within a factor of two. The rate for relaxation of NH($N=1$) is about one order of magnitude smaller than the rates for relaxation of NH in higher rotational levels. The rotational relaxation is fast so that most molecules in the buffer-gas experiment will be in the rotational ground state.

In summary, the potential-energy surface for the He-NH interaction and calculations for Zeeman relaxation in collisions of a heteronuclear diatomic molecule with structureless atoms have been presented. The Zeeman relaxation in NH-He collisions in weak magnetic fields is at least five

orders of magnitude slower than the elastic energy transfer which suggests that buffer-gas loading of NH molecules in a magnetic trap should be efficient. We have demonstrated that the Zeeman transitions in the ground-state $^3\Sigma$ molecules are induced by the admixture of the $N=2$ state that arises from the spin-spin interaction. The efficiency of the Zeeman relaxation depends on the strength of the spin-spin interaction and the relative separation of the $N=0$ and $N=2$ levels in the molecule. Zeeman transitions will be slower in molecules with smaller ratios

$$\frac{\lambda_{SS}}{E_{N=2}-E_{N=0}}, \tag{3}$$

where E_N denotes the rotational energy of the molecule in state N. A review of properties of diatomic molecules [19] shows that NH is among the best candidates for buffer-gas loading experiments.

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