Prospects for producing ultracold NH$_3$ molecules by sympathetic cooling:
A survey of interaction potentials

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We investigate the possibility of producing ultracold NH$_3$ molecules by sympathetic cooling in a bath of ultracold atoms. We consider the interactions of NH$_3$ with alkali-metal and alkaline-earth-metal atoms, and with Xe, using ab initio coupled-cluster calculations. For Rb-NH$_3$ and Xe-NH$_3$ we develop full potential energy surfaces, while for the other systems we characterize the stationary points (global and local minima and saddle points). We also calculate isotropic and anisotropic van der Waals $C_6$ coefficients for all the systems. The potential energy surfaces for interaction of NH$_3$ with alkali-metal and alkaline-earth-metal atoms all show deep potential wells and strong anisotropies. The well depths vary from 887 cm$^{-1}$ for Mg-NH$_3$ to 5104 cm$^{-1}$ for Li-NH$_3$. This suggests that all these systems will exhibit strong inelasticity whenever inelastic collisions are energetically allowed and that sympathetic cooling will work only when both the atoms and the molecules are already in their lowest internal states. Xe-NH$_3$ is more weakly bound and less anisotropic.

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I. INTRODUCTION

There is great interest at present in producing samples of cold molecules (below 1 K) and ultracold molecules (below 1 mK). Such molecules have many potential applications. High-precision measurements on ultracold molecules might be used to measure quantities of fundamental physics interest, such as the electric dipole moment of the electron [1] and the time dependence of fundamental constants such as the electron/proton mass ratio [2]. Ultracold molecules are a stepping stone to ultracold quantum gases [3] and might have applications in quantum information and quantum computing [4].

There are two basic approaches to producing ultracold molecules. In direct methods such as Stark deceleration [5,6] and helium buffer-gas cooling [7], preexisting molecules are cooled from higher temperatures and trapped in electrostatic or magnetic traps. In indirect methods [8], laser-cooled atoms that are already ultracold are paired up to form molecules by either photoassociation [9] or tuning through magnetic Feshbach resonances [10].

Indirect methods have already been used extensively to produce ultracold molecules at temperatures below 1 µK. However, they are limited to molecules formed from atoms that can themselves be cooled to such temperatures. Direct methods are far more general than indirect methods and can in principle be applied to a very wide range of molecules. However, at present direct methods are limited to temperatures in the range 10–100 mK, which is outside the ultracold regime. There is much current research directed at finding second-stage cooling methods to bridge the gap and eventually allow directly cooled molecules to reach the region below 1 µK where quantum gases can form.

One of the most promising second-stage cooling methods that has been proposed is sympathetic cooling. The hope is that, if a sample of cold molecules is brought into contact with a gas of ultracold atoms, thermalization will occur and the molecules will be cooled towards the temperature of the atoms. Sympathetic cooling has already been used successfully to cool atomic species such as $^7$Li [11] and $^{41}$K [12], but has not yet been applied to neutral molecules.

Sympathetic cooling relies on thermalization occurring before molecules are lost from the trap. Thermalization requires elastic collisions between atoms and molecules to redistribute translational energy. However, electrostatic and magnetic traps rely on Stark and Zeeman splittings and trapped atoms and molecules are not usually in their absolute ground state in the applied field. Any inelastic collision that converts internal energy into translational energy is likely to kick both colliding species out of the trap. The ratio of elastic to inelastic cross sections is thus crucial, and a commonly stated rule of thumb is that sympathetic cooling will not work unless elastic cross sections are a factor of 10–100 greater than inelastic cross sections for the states concerned.

Inelastic cross sections for atom-atom collisions are sometimes strongly suppressed by angular momentum constraints. In particular, for $s$-wave collisions (end-over-end angular momentum $L=0$), pairs of atoms in spin-stretched states (with the maximum possible values of the total angular momentum $F$ and its projection $|M_F|$) can undergo inelastic collisions only by changing $L$. Cross sections for such processes are very small because, for atoms in $S$ states, the only interaction that can change $L$ is the weak dipolar coupling between the electron spins. However, for molecular collisions the situation is different: the anisotropy of the intermolecular potential can change $L$, and this is usually much stronger than spin-spin coupling.

It is thus crucial to investigate the anisotropy of the interaction potential for systems that are candidates for sympathetic cooling experiments. In experimental terms, the easiest systems to work with are those in which molecules that can be cooled by Stark deceleration (such as NH$_3$, OH, and NH) interact with atoms that can be laser cooled (such as alkali-metal and alkaline-earth-metal atoms). There has been exten-
sive work on low-energy collisions of molecules with helium atoms [13–19], but relatively little on collisions with alkali-metal and alkaline-earth-metal atoms. Soldán and Hutson [20] investigated the potential energy surfaces for Rb+NH and identified deeply bound ion-pair states as well as weakly bound covalent states. They suggested that the ion-pair states might hinder sympathetic cooling. Lara et al. [21,22] subsequently calculated full potential energy surfaces for Rb + OH, for both ion-pair states and covalent states, and used them to investigate low-energy elastic and inelastic cross sections, including spin-orbit coupling and nuclear spin splittings. They found that even for the covalent states the potential energy surfaces had anisotropies of the order of 500 cm⁻¹ and that this was sufficient to make the inelastic cross sections larger than elastic cross sections at temperatures below 10 mK. Tacconi et al. [23] have recently carried out analogous calculations on Rb+NH, though without considering nuclear spin. There has also been a considerable amount of work on collisions between alkali-metal atoms and the corresponding dimers [24–29].

One way around the problem of inelastic collisions is to work with atoms and molecules that are in their absolute ground state in the trapping field. However, this is quite limiting: only optical dipole traps and alternating current traps [30] can trap such molecules. It is therefore highly desirable to seek systems in which the potential energy surface is only weakly anisotropic. The purpose of the present paper is to survey the possibilities for collision partners to use in sympathetic cooling of NH₃ (or ND₃), which is one of the easiest molecules for Stark deceleration. Even if sympathetic cooling proves to be impractical for a particular system, the combination of laser cooling for atoms and Stark deceleration for molecules offers opportunities for studying molecular collisions in a new low-energy regime. For example, experiments are under way at the University of Colorado [31] to study collisions between decelerated NH₃ molecules and laser-cooled Rb atoms.

The energy levels of NH₃ and ND₃ are characterized by rotational quantum numbers J and K and a label ± that describes tunneling between the two equivalent umbrella configurations [32]. The molecules that can be slowed by Stark deceleration are those in states with |K| > 0 (usually J = 1, |K| = 1). Both rotationally inelastic collisions and those that change the tunneling quantum number are driven by the anisotropy of the interaction potential [33,34].

The alkali-metal atom+NH₃ systems have not been extensively studied theoretically, though there has been experimental interest in the spectroscopy of Li-NH₂ as a prototype metal-atom–Lewis-base complex [35]. Lim et al. [36] recently calculated electrical properties and infrared spectra for complexes of NH₃ with alkali-metal atoms from K to Fr and gave the equilibrium structures of their global minima. However, to our knowledge, no complete potential energy surfaces have been published for any of these systems. The alkaline-earth-metal+NH₃ have been studied even less, and except for an early study of the Be-NH₃ system [37] there are no previous results available.

II. Ab Initio METHODS

The interaction energy of two monomers A and B is defined as

\[ E_{\text{tot}}^A = E_{\text{tot}} - E_{\text{tot}}^B \]

where \( E_{\text{tot}}^A \) is the total energy of the dimer and \( E_{\text{tot}} \) and \( E_{\text{tot}}^B \) are the total energies of the isolated monomers. Since the interaction energy is dominated at long range by intermolecular correlation (dispersion), \textit{ab initio} calculations of the interaction energy must include electronic correlation effects at the highest possible level [38] and must be carried out with large basis sets augmented by diffuse functions. At present, the coupled-cluster (CC) method with single, double, and noniterative triple excitations (CCSD(T)) provides the best compromise between high accuracy and computational cost. In the present paper, we carry out coupled-cluster calculations using the MOLPRO package [39]. All interaction energies are corrected for basis-set superposition error (BSSE) with the counterpoise method of Boys and Bernardi [40].

Standard coupled-cluster methods are reliable only when the wave function is dominated by a single electronic configuration. This is often an issue for molecular systems with low-lying excited states. In order to check the reliability of CC calculations, it is necessary to monitor the norm of the \( T_1 \) operator [41] (measured by the \( T_1 \) diagnostic). In the case of metal-NH₃ systems this is relatively large, especially when the atom approaches the lone pair of the NH₃ molecule, but the convergence of the CC equations is fast and converged CCSD results are very close to benchmark multireference configuration interaction (MRCl-SD) calculations with size-extensivity corrections. Thus we consider CC results reliable.

To understand the origin of the intermolecular forces we also consider the interaction energies obtained at the Hartree-Fock level, which neglects electron correlation. The comparison between Hartree-Fock and coupled-cluster results thus provides information about the role of dispersion and other correlation effects. For some systems we also analyze the components of the intermolecular interactions using symmetry-adopted perturbation theory [42] (SAPT). The first-order SAPT corrections (electrostatic and exchange terms) are computed from Hartree-Fock monomer wave functions, while the dispersion energy is evaluated with the coupled Hartree-Fock approach [43] without full spin adaptation. These calculations are carried out using the SAPT006 [44] program.

We are interested principally in the collisions of cold ammonia molecules with atoms at energies that are much too low for vibrational excitation to occur. Such collisions are governed by an effective potential that is vibrationally averaged over the ground-state vibrational wave function of NH₃. For the present purpose it is adequate to represent this by a potential calculated with the NH₃ molecule frozen at a geometry that represents the ground state. In the present paper we use a geometry derived from the high-resolution infrared spectra [45]: the molecule is taken to have \( C_{3v} \) symmetry with N-H bond lengths of 1.913 Å and an H-N-H angle of 106.7°. Intermolecular geometries are specified in Jacobi coordinates: \( R \) is the distance from the center of mass of NH₃ to the atom, while \( \theta \) is the angle between the intermolecular vector and the \( C_3 \) axis of the NH₃ molecule (with \( \theta = 0° \) corresponding to the atom approaching towards the lone pair
of NH₃). Finally, χ is the dihedral angle between the plane containing the C₃ axis and an NH bond and that containing the C₃ axis and the intermolecular vector.

Table I gives the lowest excitation energies, dipole polarizabilities, and ionization energies of the atoms studied in this paper. The neutral alkali-metal and alkaline-earth-metal atoms (denoted below as A and Ae, respectively) have particularly low excitation energies, resulting from small separations between energy levels corresponding to ns and np or (n−1)d configurations. Since the gap between the ground and excited states is small, the atoms have very large polarizabilities. Hence, we expect particularly strong induction and dispersion interactions. The alkali-metal and alkaline-earth-metal atoms also have low ionization energies Eᵢ. Since the atomic orbital wave functions vanish at long range as exp(−Eᵢ/r), the wave functions and densities are very diffuse, and this causes a large overlap between monomers even at relatively large separations. Finally, because of the low ionization energies, alkali-metal and alkaline-earth-metal atoms have a strong tendency to form charge-transfer complexes.

The basis sets used in the ab initio calculations are as follows. For Be, Li, Mg, Na, and Ca atoms we use all-electron cc-pVTZ basis sets [55] (correlation-consistent polarized valence triple-zeta) augmented by even-tempered diffuse exponents, while for potassium we use the correlation-valence CVTZ basis set of Feller et al. [56]. For Rb, Sr, and Xe we handle only the outermost electrons explicitly, with the core electrons represented by effective core potentials (ECPs). For Rb we use the small-core effective core potential ECP28MWB with a basis set based on that of Ref. [57], which was optimized to recover the static dipole polarizability. We modified this slightly to account for intramonomer electronic correlation effects by removing 0.07 f and adding 0.001049 s, 0.0024 p, 4.5 and 0.016667 d, 1.9 and 0.655 f, and 0.95 and 0.3167 g functions. The basis set for Sr is taken from Ref. [58]. For Xe we use the basis set given by Lozeille et al. [53], which was found to be excellent for polarizabilities and hyperpolarizabilities. For each system we added a set of midbond functions with exponents sp:

<table>
<thead>
<tr>
<th>Atom</th>
<th>dipole polarizability (units of a₀³)</th>
<th>Ref.</th>
<th>Lowest excitation energy (cm⁻¹)</th>
<th>Ionization energy (cm⁻¹)</th>
<th>C₆ coefficient (units of E₀aₒ⁶)</th>
<th>Ref.</th>
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<td>Li</td>
<td>164</td>
<td>[47]</td>
<td>14904</td>
<td>43487</td>
<td>1395</td>
<td>[48]</td>
</tr>
<tr>
<td>Na</td>
<td>162</td>
<td>[49]</td>
<td>16956</td>
<td>41449</td>
<td>1561</td>
<td>[48]</td>
</tr>
<tr>
<td>K</td>
<td>293</td>
<td>[49]</td>
<td>12985</td>
<td>35010</td>
<td>3921</td>
<td>[50]</td>
</tr>
<tr>
<td>Rb</td>
<td>319</td>
<td>[49]</td>
<td>12578</td>
<td>33691</td>
<td>4707</td>
<td>[51]</td>
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<tr>
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<td></td>
<td>21978</td>
<td>75193</td>
<td>213</td>
<td>[48]</td>
</tr>
<tr>
<td>Mg</td>
<td>71</td>
<td>[48]</td>
<td>21850</td>
<td>61671</td>
<td>629</td>
<td>[48]</td>
</tr>
<tr>
<td>Ca</td>
<td>159</td>
<td>[48]</td>
<td>15157</td>
<td>49305</td>
<td>2221</td>
<td>[52]</td>
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<td>[48]</td>
<td>14317</td>
<td>45932</td>
<td>3250</td>
<td>[48]</td>
</tr>
<tr>
<td>Xe</td>
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<td>[53]</td>
<td>67068</td>
<td>97834</td>
<td>286</td>
<td>[54]</td>
</tr>
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</table>

To reduce the computational effort we calculate the interaction potential only for χ=0⁰ and χ=60⁰ and approximate the leading terms V₀(R,θ) and V₃(R,θ) by sum and difference potentials,

\[
V₀(R,θ,χ) = \sum_{k=0}^{∞} V₃k(R,θ) \cos 3k\chi.
\] (2)

V₀ can be viewed as the interaction potential averaged over χ, while V₃ describes the variation of the potential with respect to rotation about the C₃ axis of NH₃; V₃ is referred to below as the noncylindrical term.

A. Alkali-metal atom+NH₃ interactions

The potential energy surface for Rb-NH₃ is shown in Fig. 1. CCSD(T) calculations were carried out at χ=0⁰ and 60⁰, at values of θ corresponding to a 20-point Gauss-Lobatto quadrature. The grid included R values from 3.5a₀ to 12a₀ with a step of 0.5a₀ and from 12a₀ to 15a₀ with a step of 0.5a₀. There is a deep minimum (1862 cm⁻¹) at R=5.90a₀ and θ=0⁰, corresponding to approach of Rb towards the NH₃ lone
pair. The potential is much shallower at other geometries, with a saddle point near $\theta = 110^\circ$ and a shallow secondary minimum at $\theta = 180^\circ$. The noncylindrical term $V_3(R, \theta)$ is relatively weak, at least in the low-energy classically allowed region defined by $V_0 < 0$.

The overall shape of the other $A$-$NH_3$ potentials is quite similar. In each case there is a deep minimum around $\theta = 0^\circ$ and a shallow secondary minimum for $\theta = 180^\circ$. Table II gives the well depths and equilibrium distances. For the alkali metals the well depth of the global minimum decreases down the periodic table, from 5104 cm$^{-1}$ for Li to 1862 cm$^{-1}$ for Rb, and the equilibrium distance increases from 3.91$a_0$ for Li to 5.90$a_0$ for Rb. The changes in the properties of the

![Diagram](a)

![Diagram](b)

**FIG. 1.** The interaction potential of Rb-$NH_3$ from CCSD(T) calculations: $V_0(R, \theta)$ component (upper panel) and $V_3(R, \theta)$ component (lower panel). Contours are labeled in cm$^{-1}$. To aid visualization, $V_3$ is plotted only in the energetically accessible region defined by $V_0 < 0$.

**TABLE II.** Equilibrium distances and well depths for alkali-metal atom+$NH_3$ systems from CCSD(T) calculations.

<table>
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<th>$\theta=0^\circ$</th>
<th>$\theta=180^\circ$</th>
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<tr>
<td></td>
<td>$R_e$ (units of $a_0$)</td>
<td>$D_e$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>Li</td>
<td>3.91</td>
<td>5104</td>
</tr>
<tr>
<td>Na</td>
<td>4.73</td>
<td>2359</td>
</tr>
<tr>
<td>K</td>
<td>5.52</td>
<td>2161</td>
</tr>
<tr>
<td>Rb</td>
<td>5.90</td>
<td>1862</td>
</tr>
</tbody>
</table>

The minima corresponding to approach at the hydrogen end $NH_3$ is 1973 cm$^{-1}$ deep, while the dispersion-bound minimum is 100.5 cm$^{-1}$ deep. The overall shape of the other $A$-$NH_3$ potentials is quite similar. In each case there is a deep minimum around $\theta = 0^\circ$ and a shallow secondary minimum for $\theta = 180^\circ$. Table II gives the well depths and equilibrium distances. For the alkali metals the well depth of the global minimum decreases down the periodic table, from 5104 cm$^{-1}$ for Li to 1862 cm$^{-1}$ for Rb, and the equilibrium distance increases from 3.91$a_0$ for Li to 5.90$a_0$ for Rb. The changes in the properties of the

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shallow secondary minima are much smaller, with well depths close to 100 cm$^{-1}$ for all the alkali metals. Our results for the species containing K and Rb are in good agreement with the CCSD(T) calculations of Lim et al. [36]; they obtained slightly different values of the binding energies of K-$NH_3$ and Rb-$NH_3$ (2210 cm$^{-1}$ and 1950 cm$^{-1}$, respectively), but their results are not corrected for BSSE. It should also be noted that their binding energies are for relaxed $NH_3$ geometries.

The deep wells and large anisotropies of the $A$-$NH_3$ potentials will produce strong coupling between the different $NH_3$ rotational and inversion states during collisions. All these systems are therefore likely to have large inelastic cross sections. It is thus unlikely that sympathetic cooling of $NH_3$ with alkali-metal atoms will be successful unless both the atoms and the molecules are already in their lowest internal states for the symmetry concerned.

**B. Alkaline-earth-metal atom+$NH_3$ interactions**

We originally hoped that the potentials for systems containing alkaline-earth-metal atoms would be more weakly bound and less anisotropic than for those containing alkali-metal atoms. However, this proved not to be the case, at least for the heavier alkaline-earth-metal atoms that are most suitable for laser cooling. The results for the $Ae$-$NH_3$ systems are summarized in Table III. The shapes of the potential energy surfaces are generally similar to those for $A$-$NH_3$ systems. For Ca and Sr, the depths of the global minima are 3229 and 3141 cm$^{-1}$ respectively; these are both deeper than for the corresponding alkali-metal atom. For Mg, however, the well depth is considerably shallower at only 887.5 cm$^{-1}$. The minima corresponding to approach at the hydrogen end of $NH_3$ are slightly deeper than for the alkali metals, ranging from 115.7 for Mg to 131.6 cm$^{-1}$ for Sr. On the other hand, the interaction potential for Be-$NH_3$ resembles those for Ca-$NH_3$ and Sr-$NH_3$ more than that for Mg-$NH_3$; the global minimum is 1973 cm$^{-1}$ deep, while the dispersion-bound minimum is 100.5 cm$^{-1}$ deep. The equilibrium distance for Be-$NH_3$ at $\theta = 0^\circ$ (3.57$a_0$) is also much shorter than for the other $Ae$-$NH_3$ systems and is comparable to that for Li-$NH_3$.

**C. Origin of bonding in metal-atom+$NH_3$ systems**

It is important to understand the large difference between the metal-lone-pair bond energies between Mg and the other group-1 and -2 atoms considered here. Table IV gives
the interaction energies at the Hartree-Fock, CCSD, and CCSD(T) levels at the positions of the CCSD(T) global and secondary minima for Li-NH₃, Mg-NH₃, and Ca-NH₃. For all these systems the Hartree-Fock interaction energies are positive for the shallow secondary minima, indicating that the shallow wells are dominated by dispersion forces. At the global minima, however, Mg-NH₃ is repulsive at the Hartree-Fock level while the other two systems are strongly attractive. There is thus strong chemical bonding in Li-NH₃ and Ca-NH₃ that is absent in Mg-NH₃.

The qualitative differences between Mg and the other atoms can be understood if we consider how the energy of the highest occupied molecular orbital (HOMO) differs for the different atom-NH₃ systems. Figure 2 shows the two highest occupied molecular orbitals of each system. As we separate the monomers to infinity, these two orbitals become HOMOs of the atom and the NH₃ molecule. For any alkali-metal atom, the strong A-NH₃ bond can be explained as a chemical bond of order one-half, since we have a doubly occupied bonding orbital and a singly occupied antibonding orbital [see Fig. 2(a)]. However, this explanation does not apply to the alkaline-earth-metal atoms, where the antibonding orbital is doubly occupied. The net bonding in Ca-NH₃ arises because the bonding orbital is shifted down in energy considerably more than the antibonding orbital is shifted up. Conversely, in Mg-NH₃, the contributions from the bonding and antibonding orbitals are closely balanced. The difference can probably be attributed to the participation of np orbitals; as shown in Table I, the $S \rightarrow P$ splitting is considerably smaller in Ca than in Mg. Thus Mg-NH₃ is bound mainly by dispersion forces whereas Ca-NH₃ has substantial chemical bonding.

Different considerations apply to the Be atom, which is a notoriously difficult case for electronic structure theory [59]. Although the potential energy surfaces are qualitatively similar for the Be-NH₃, Ca-NH₃, and Sr-NH₃ systems at the CCSD(T) level, the origin of the strong bonding is probably different in Be-NH₃. In this case the Hartree-Fock and CCSD potential energy curves for $\theta=0^\circ$ show a double-minimum structure, with a shallow long-range minimum separated from the global minimum by a barrier. This suggests a sudden change in chemical character as the Be atom approaches N. At the Hartree-Fock level the maximum has an energy of 730 cm⁻¹ at $R=4.88\,a_0$. The long-range minimum at the Hartree-Fock level is 18.4 cm⁻¹ deep at $R=9.02\,a_0$, while at the CCSD level it is 138 cm⁻¹ deep at $R=6.5\,a_0$. Despite this peculiar behavior, the CC calculations showed no convergence problems or unusually large T1 diagnostics. However, our results for Be-NH₃ disagree with those of Chalasinski and co-workers [37], who carried out fourth-order Moller-Plesset (MP4) calculations and found a global minimum that corresponds to the outer minimum on the CCSD potential energy curve. They did not find the inner minimum, which turned out to be the global minimum in our calculations.

As mentioned before, the feature of the potential energy surfaces that is important for elastic and inelastic collision ratios is the anisotropy. In order to understand the origin of the anisotropies better, we carried out additional calculations based on SAPT. Figures 3–5 show the electrostatic, first-order exchange, and dispersion components of the interaction energy $V_0$ for Na-NH₃ and Mg-NH₃, averaged over $\chi$ as in Eq. (3). The calculations were performed at a fixed $R$ value of $6\,a_0$, which is in an attractive region for $\theta=0^\circ$ and a repulsive region for $\theta=180^\circ$. Figures 3–5 show clearly that it is the first-order interaction energy that is responsible for most of the anisotropy in the valence overlap region. This is caused by a very large difference between the electrostatic attraction near the lone-pair site and near hydrogen sites (see Fig. 3). This difference is significantly larger than that in the exchange energy. The anisotropy of the dispersion interaction (plotted in Fig. 5), is even weaker.

The three components of $V_0$ are shown for Na-NH₃ and Mg-NH₃ in Fig. 6. The exchange energy is very strongly
noncylindrical, especially for Mg-NH$_3$. The large difference in the exchange component between Mg-NH$_3$ and Na-NH$_3$ can be explained by the closed-shell character of the Mg atom and the much stronger Pauli repulsion between hydrogens of NH$_3$ and Mg. The electrostatic and dispersion contributions to $V_3$ are much more similar for the two systems.

D. Xe+NH$_3$ interaction

The potential energy surfaces for all the metal-NH$_3$ systems investigated above have disappointingly large anisotropies. It is likely that all these systems will exhibit large inelastic cross sections for any initial state where inelasticity is possible. We therefore decided to consider other possible collision partners for sympathetic cooling of NH$_3$. Barker [60] has suggested an experiment in which Xe is first laser cooled in its metastable $^3P_2$ state and then transferred to its ground $^1S_0$ state by laser excitation followed by spontaneous emission. Since ground-state Xe has a fairly large dipole polarizability, it can be held in an optical dipole trap and might be used for sympathetic cooling. In this subsection we investigate the Xe-NH$_3$ interaction in order to evaluate its potential in this respect.

Interactions between noble gases and ammonia have been studied extensively. The interaction between He and NH$_3$ is important in understanding the spectroscopy of NH$_3$ molecules in helium nanodroplets [61]. The most recent $ab$ initio calculations of Hodges and Wheatley [62,63] gave a global minimum about 33 cm$^{-1}$ deep at $R=6a_0$, $\theta=90^\circ$, and $\chi=60^\circ$. The interaction of Ar with NH$_3$ has been studied even more extensively, both experimentally [64] and by $ab$ initio methods [65,66]. Inversion of vibration-rotation-tunneling spectra [64] gave a minimum 147 cm$^{-1}$ deep at $R=6.5a_0$, $\theta=97^\circ$, and $\chi=60^\circ$, while the $ab$ initio MP4 (fourth-order Møller-Plesset) calculations of Tao and Klemperer [66] gave a global minimum 130 cm$^{-1}$ deep at $R=6.85a_0$, $\theta=90^\circ$, and $\chi=60^\circ$. The Ne-NH$_3$ system was investigated through MP4 calculations by van Wijngaarden and Jäger [67], who obtained a global minimum 63 cm$^{-1}$ deep at $R=6.1a_0$, $\theta=90^\circ$, and $\chi=60^\circ$. For Kr-NH$_3$, Chalásinski et al. [68] obtained a global minimum 108 cm$^{-1}$ deep at $R=7.2a_0$, $\theta=100^\circ$, and $\chi=60^\circ$. However, their results were based on calculations at the MP2 level and may not reproduce the dispersion energy accurately.

Figure 7 shows the interaction potential for Xe-NH$_3$ from our CCSD(T) calculations. The potential energy surface differs qualitatively from those for metal-NH$_3$ potentials studied in the previous subsection and behaves analogously to those for other Rg-NH$_3$ systems. The $V_0$ surface for Xe-NH$_3$ has only one minimum, 173.5 cm$^{-1}$ deep, at $R=7.65a_0$ and $\theta=66^\circ$. The global minimum for the nonexpanded surface is 196.8 cm$^{-1}$ deep, at $R=7.35a_0$, $\theta=81^\circ$, and $\chi=60^\circ$. There are saddle points at both $C_{3y}$ configurations. For $\theta=0$ the saddle point is 166.2 cm$^{-1}$ deep at $R=7.73a_0$, while for $\theta=180^\circ$ the saddle point is 134.1 cm$^{-1}$ deep at $R=7.93a_0$. The major binding arises from the dispersion energy, and at the Hartree-Fock level we observe only a small attraction (a few cm$^{-1}$) at large distances, due to weak induction forces which behave asymptotically as $-C_R^{-6}$. Near the van der Waals minimum predicted by CCSD(T), the Hartree-Fock energy is repulsive.
FIG. 7. The interaction potential of Xe-NH3 from CCSD(T) calculations: \( V_0(R,\theta) \) component (upper panel) and \( V_1(R,\theta) \) component (lower panel). Contours are labeled in cm\(^{-1}\). To aid visualization, \( V_3 \) is plotted only in the energetically accessible region defined by \( V_0 < 0 \).

The \( V_0 \) surface for Xe-NH3 system thus has an anisotropy of only about 60 cm\(^{-1}\) between the potential minimum and the higher of the two saddle points. This is considerably smaller than for Rb-OH or any of the metal-NH3 systems studied here, but still substantial compared to the rotational constant of NH3, \( b=6.35 \text{ cm}^{-1} \) for rotation about an axis perpendicular to \( C_3 \).

E. Long-range forces

Long-range forces are very important in cold and ultracold collisions. We therefore carried out separate calculations of the van der Waals coefficients for the interactions. The isotropic \( C_{6,0} \) and anisotropic \( C_{6,2} \) dispersion coefficients for the interaction of atom \( A \) and symmetric top molecule \( B \) may be written in terms of the dynamic polarizabilities of the monomers, evaluated at imaginary frequencies [69],

\[
C_{6,0}^{\text{disp}} = \frac{3}{\pi} \int_0^{\infty} \alpha_A(iau)\bar{\alpha}_B(iau)du,
\]

\[
C_{6,2}^{\text{disp}} = \frac{1}{\pi} \int_0^{\infty} \alpha_A(iau)\Delta\alpha_B(iau)du,
\]

where \( \bar{\alpha} = \frac{1}{3}(2\alpha_{xx} + \alpha_{yy}) \) is the isotropic polarizability and \( \Delta\alpha = \alpha_{zz} - \alpha_{xx} \) is the polarizability anisotropy. The induction contributions to the van der Waals coefficients are

\[
C_{6,0}^{\text{ind}} = C_{6,2}^{\text{ind}} = \alpha_A\mu^2,
\]

where the dipole moment \( \mu \) is 0.579\( a_0 \) for NH3 [70].

The integrals in Eqs. 4 were evaluated using the method given by Amos et al. [71]. The dynamic polarizabilities of NH3 were obtained using coupled Kohn-Sham theory with the asymptotically corrected PBE0 functional [72] and doubly augmented d-aug-cc-pVTZ basis sets [55]. To get the dynamic polarizabilities for the alkali-metal atoms, we adjusted the fraction of exchange, exact exchange, and correlation fraction in the PBE0 functional in such a way as to recover the atom-atom \( C_6 \) coefficients (see Table I). Our coupled Kohn-Sham program does not allow us to use core potentials to calculate dynamic polarizabilities. For Rb we therefore performed all-electron calculations with the pVTZ basis set of Sadlej [73] combined with the Douglas-Kroll approximation [74]. The dynamic polarizabilities obtained in this way were tested by comparing \( C_6 \) coefficients for \( A-\text{Ar} \) and \( A-\text{Xe} \) systems with those obtained by Mitroy and Zhang [75]. The maximum error was found to be +6.3% (for Na-Xe) while the average error is less than +3%. For alkaline-earth-metal and Xe atoms the frequency-dependent dipole polarizabilities were obtained from time-independent coupled-cluster linear response functions [76,77].

The resulting \( C_6 \) coefficients are shown in Table V. For the alkali-metal and alkaline-earth-metal atoms, the isotropic dispersion coefficients \( C_{6,0}^{\text{disp}} \) are fairly large because of the large atomic polarizabilities. The anisotropies in the dispersion coefficients are much smaller, because of the small atomic polarizabilities. The anisotropies in the dispersion coefficients are much smaller, because of the small polarizability anisotropy of NH3 (2.1\( a_0^3 \)) compared to its isotropic polarizability (14.6\( a_0^3 \)). The induction van der Waals coefficients are large and account for 10%–25% of the total \( C_{6,0} \) and 70%–90% of the total \( C_{6,2} \). It may be noted that \( C_{6,0}^{\text{disp}} \) for Rb-NH3 is somewhat larger than \( C_{6,0}^{\text{disp}} \) for Rb-OH [22]. As one might expect, the Xe-NH3 long-range interaction has slightly different character from the \( A-\text{Ar} \) and \( Ae-\text{NH}_3 \) systems. The \( C_{6,0}^{\text{disp}} \) coefficient is still large, but the total anisotropy (in particular the dispersion anisotropy) is much smaller.

<table>
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<tr>
<th>Element</th>
<th>( C_{6,0}^{\text{disp}} )</th>
<th>( C_{6,2}^{\text{disp}} )</th>
<th>( C_{6,0}^{\text{ind}} )</th>
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<td>55.0</td>
</tr>
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<tr>
<td>Xe</td>
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</table>
IV. CONCLUSIONS

We have investigated the intermolecular potential energy surfaces for interaction of NH$_3$ with several different atoms that might be used for sympathetic cooling. Both rotationally inelastic collisions and those that change the tunneling quantum number are governed by the anisotropy of the interaction potential. For interaction with all the alkali-metal and alkaline-earth-metal atoms, we found deep minima and strong anisotropies. The shallowest potential is for Mg-NH$_3$, but even there the anisotropy in the well depth is close to 800 cm$^{-1}$. This is likely to cause strong inelastic collisions for all initial states for which they are energetically and symmetry allowed. Accordingly, we consider that none of the alkali metals and alkaline earth metals are good prospects for sympathetic cooling of NH$_3$ unless both the atoms and the molecules are in their lowest states in the trapping field for the symmetry concerned. This suggests that sympathetic cooling would need to be carried out in either optical or alternating current traps.

A somewhat more promising system for sympathetic cooling is Xe-NH$_3$, for which the global minimum is calculated to be 196.8 cm$^{-1}$ deep at an off-axis geometry. The Xe-NH$_3$ system is relatively weakly anisotropic, with the saddle points for C$_{3v}$ geometries only 30.6 and 62.7 cm$^{-1}$ higher than the global minimum. In future work we will use the interaction potential to calculate low-energy elastic and inelastic cross sections, in order to predict whether sympathetic cooling of NH$_3$ by Xe is likely to be feasible.

Even if sympathetic cooling proves to be impossible for these systems, there is much to be learnt from collisions between velocity-controlled beams of molecules and laser-cooled atoms. There are opportunities to explore low-energy inelastic processes in novel collisional regimes and to probe scattering resonances in unprecedented detail. We therefore intend to use the potential energy surfaces developed here to carry out inelastic collision calculations to explore these effects and assist in the interpretation of collision experiments.

ACKNOWLEDGMENTS

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[31] H. J. Lewandowski (private communication).
PROSPECTS FOR PRODUCING ULTRACOLD NH₃/H₂O₈51/H₂O₈51


[60] P. F. Barker (private communication).


