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Interaction of NH($X\,^3\Sigma^-$) Molecules with Rubidium Atoms: Implications for Sympathetic Cooling and the Formation of Extremely Polar Molecules

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The Rb-NH interaction is investigated as a prototype for interactions between alkali-metal atoms and stable molecules. For spin-aligned Rb and NH that interact on a quartet surface ($^4A''$), the interaction is relatively weak, with a well depth of 0.078 eV. However, there are also doublet surfaces of ion-pair character that are very much deeper (well depth 1.372 eV). They may be important for atom-molecule collision rates and offer the possibility of forming strongly dipolar molecules by photoassociation. Similar deeply bound ion-pair states are likely to exist for other alkali atom-molecule pairs.

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There is great interest in the production and trapping of translationally cold molecules and in the possibility of achieving quantum degeneracy in molecular gases [1–4]. There is special interest in dipolar quantum gases [5], where the trap geometry controls the attractive or repulsive nature of the anisotropic dipole-dipole interaction. Important goals in this area include Bose-Einstein condensation of dipolar gases [6], realization of phase transitions of such gases in optical lattices [7], and formation of superfluid pairs and observation of the Bardeen-Cooper-Schrieffer (BCS) transition to a superfluid state in dipolar Fermi gases [8]. The electric dipole moments of ultracold polar molecules could also be used as qubits in quantum computation [9].

One very promising route for the production of cold dipolar molecules is molecular beam deceleration [10]. Meijer and co-workers have developed a decelerator based on the molecular Stark effect and switched inhomogeneous electric fields [11] and have used it to slow a beam of ND_3 molecules and trap them at a temperature around 25 mK [12]. Beam deceleration is also applicable to other polar molecules, such as OH [13] and H_2O, but is typically likely to achieve temperatures only of the order of 1 mK. To cool the molecules further, towards temperatures where quantum degeneracy might be achieved, another cooling technique is needed. One possible route is sympathetic cooling by thermal contact with a cold atomic gas such as ^{87}Rb [14].

The purpose of the present Letter is to investigate the potential energy surfaces for interaction of a polar molecule with an alkali atom, in order to help understand collisions in molecule-alkali atom mixtures. For this prototype study, we choose NH ($X\,^3\Sigma^-$) interacting with with Rb (^2S). This system is topical because Meijer and co-workers [15] have recently proposed a scheme for the production of ultracold NH molecules in their ground vibronic state. In this scheme, NH molecules in their long-lived $a^1\Delta$ metastable state are first slowed in a Stark decelerator. The molecules are then excited to the $v = 0$ level of the $A\,^3\Pi$ excited state, allowed to decay spontaneously to the $v = 0$ level of the $X\,^3\Sigma^-$ ground state, and finally trapped magnetically.

An important and general point is that many molecule-alkali atom systems have deeply bound electronic states with ion-pair character. Alkali-metal atoms have low ionization energies, while molecules containing electronegative elements such as C, N, and O and the halogens often have a low-lying unoccupied orbital that can accept an extra electron relatively easily. There is thus an ion-pair state (Rb^+NH^- in the present case) that is asymptotically not far above the energy of the neutrals. Because of the Coulomb attraction between the ions, the potential surface for the ion-pair state cuts down fast in energy with decreasing separation, and around the equilibrium geometry is often the lowest electronic state. As we see below, this is the case for RbNH.

The $X\,^3\Sigma^-$ ground state of NH has two electrons with parallel spins in π antibonding orbitals. At collinear geometries (with $C_{\infty v}$ point group symmetry), there are two electronic states of RbNH, $^4\Sigma^-$ and $^2\Sigma^-$, which correlate with the NH($X\,^3\Sigma^-$) + Rb(^2S) dissociation limit. At nonlinear geometries (with C_s symmetry), these two states become $^4A''$ and $^2A''$. These states are principally bound by dispersion forces. However, as mentioned above, there is also an ion-pair threshold $Rb^+(^1S)$ + $NH^-(^2\Pi)$ less than 4 eV above the neutral threshold. The resulting $^2\Pi$ ion-pair state of RbNH is subject to the Renner-Teller effect and splits at nonlinear geometries into two states with the electron hole either in the triatomic plane ($^2A'$) or perpendicular to it ($^2A''$). There are thus two $^2A''$ states, one of ion-pair character and one dispersion-bound, which form a conical intersection at linear geometries, where one has $^2\Pi$ and the other $^2\Sigma^-$ symmetry. [This is a conical intersection on the two-dimensional surface obtained when the NH bond length r_{NH} is fixed; in three dimensions, the two surfaces intersect on a seam at linear geometries.]

The influence of ion-pair states on collisions of alkali-metal atoms and similar species has been called the "harpoon" mechanism [16]. If the electron transfer takes place at long range, as is often the case, large collision cross sections result. The range of the harpooning is determined by the position R_X of the crossing point (conical intersection). This can be estimated from

$$\Delta E_0 = \frac{e^2}{4\pi\varepsilon_0 R_X}, \quad (1)$$

where ΔE_0 is the difference between the Rb ionization energy and the NH^- vertical ionization energy (NH electron affinity). The experimental values for the Rb ionization potential and the NH vertical electron affinity are 4.177 eV [17] and 0.387 eV, respectively; the latter is obtained from the adiabatic NH electron affinity (0.381 eV) [18] and a calculated value of the difference between the zero-point energies of NH and NH^- (0.006 eV) [19]. This gives an estimate of $R_X \approx 3.79$ Å. Because in $NH^-(^2\Pi)$ the negative charge is concentrated on the nitrogen atom, R_X represents the distance between N and Rb.

The nature of the dispersion-bound and ion-pair states depends on the electron configuration of the molecular partner. For Rb-OH, for example, the dispersion-bound states are $^1\Pi$ and $^3\Pi$ at linear geometries, splitting into $^1A'$, $^1A''$, $^3A'$, and $^3A''$ at nonlinear geometries, while the ion-pair state is a closed-shell singlet ($^1\Sigma^+$ or $^1A'$). As for Rb-NH, therefore, there is no ion-pair state for the highest allowed spin multiplicity. For Rb-CH, the dispersion-bound states are the same, but there are many more ion-pair states arising from a π^2 configuration: $^3\Sigma^-$ ($^3A''$), $^1\Delta$ ($^1A'$ and $^1A''$), and $^1\Sigma^+$ ($^1A'$). The only dispersion-bound state that does not have an ion-pair counterpart in this case is the $^3A'$ state. In Rb-HF, the lowest ion-pair state does not come deep enough to cross below the dispersion-bound state, because HF is a closed-shell molecule without a low-lying unoccupied orbital.

The high values of the dipole polarizabilities for alkali-metal atoms imply large dispersion forces. Because of this, the crossing point is in the classically allowed region of the dispersion-bound state for many molecule-alkali atom systems. This is the case for RbNH. The "harpooning" is thus a barrierless process, and no tunneling is required for the charge transfer.

To obtain a more quantitative picture of the RbNH electronic states, we have carried out *ab initio* calculations at the CASSCF/MRCI level (complete active space self-consistent field/multireference configuration interaction). For N and H, we used the aug-cc-pVTZ basis sets of Dunning [20] in uncontracted form, and for Rb we used two different approaches: (i) the quasirelativistic small-core effective core potential (ECP) ECP28MWB [21] with the valence basis set from Ref. [22]; the (10,3) active space covers all the occupied orbitals on N and H and all the large-valence and 5*p* orbitals on Rb, and (ii) the large-core ECP ECP36SDF [23] with a new valence basis set and including the core polarization term [24]; this allows a larger (13,5) active space covering Rb orbitals from 5*s* to 6*p* (including 4*d*), as well as the occupied orbitals on N and H. This gives better Rb excitation energies and is thus more suitable for excited-state calculations. Only the electrons in the 1*s* orbital on N were excluded from the correlation calculations. All the calculations were performed using the MOLPRO package [25].

Figure 1 shows the lowest few curves calculated with the small-core ECP for Rb-N-H angles of 180° and 170° (for fixed NH bond length). The minimum on the quartet surface is at a depth of 0.078 eV at $r_{\mathrm{RbN}} = 3.26$ Å, while that on the doublet ion-pair surface is at a depth of $D_e = 1.372$ eV at $r_{\mathrm{RbN}} = 2.53$ Å. At linear geometries the $^2\Pi$ and $^2\Sigma^-$ curves cross at $R_X = 3.77$ Å. At nonlinear geometries the crossing is replaced by an avoided crossing. Note that the minimum of the $^2\Sigma^-$ curve is at a shorter Rb-N distance (around 3.4 Å) than the crossing point, so that at 170° the $1\,^2A''$ curve has just one minimum.

The collisional processes in Rb-NH mixtures will depend greatly on the magnetic states that are present. If

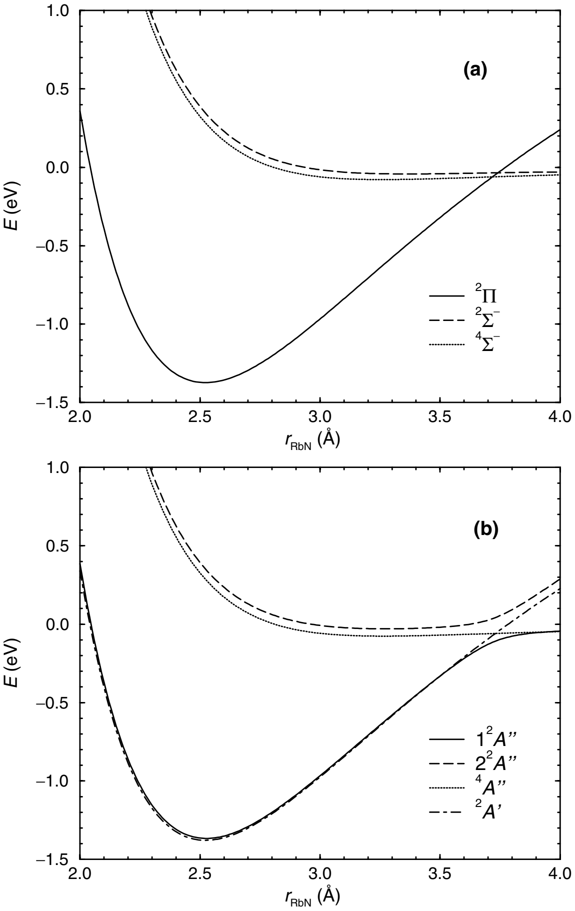

FIG. 1. CASSCF(10,3)/MRCI potential energy curves of RbNH with fixed $r_{\mathrm{NH}} = 1.0308$ Å and fixed Rb-N-H angle of 180° (a) and 170° (b). (a) At linear geometries the crossing point is at 3.77 Å. (b) At nonlinear geometries the crossing is avoided.

both NH($X\,^3\Sigma^-$) and Rb(^2S) are in spin-stretched states ($|M_F| = F = F_{\max}$), collisions will take place on the $^4A''$ surface. If the NH($X\,^3\Sigma^-$) molecules are initially in their ground rovibrational state ($v = 0, N = 0, J = 1, M = 1$) [15], only elastic and reorientation (spin-changing) atom-molecule collisions can occur. Under these circumstances, trap loss will be caused only by spin-changing collisions and by three-body recombination processes.

If the species present are not in spin-stretched states, collisions will also involve the doublet surfaces. In this case, the harpoon mechanism may be important and may enhance the rates of reorientation collisions. In addition, the transient collision complexes formed during the collision will be highly polar and may be expected to have enhanced interactions with other species. Three-body collision rates may thus be large. Collisions with third bodies might also result in vibrational quenching and formation of bound RbNH($^2\Pi$) molecules with ionic character, and consequently in trap loss. However, because of the short-range nature of this type of three-body recombination (which can occur only when the distance between the N and Rb is smaller than R_X), it cannot be described in terms of the fragment-fragment scattering lengths and a three-body parameter.

The existence of ion-pair states also offers the possibility of producing extremely polar molecules. The electric dipole moment of RbNH($^2\Pi$) varies from 8.7 to 15.3 D between the potential minimum and the crossing point. Such molecules would provide a valuable probe of low-temperature physics of dipolar gases, because phenomena related to dipole-dipole interactions, such as linking of polar molecules [26], will be significantly enhanced. Figure 2 shows a possible photoassociation scheme involving an excited $^2\Pi$ state that correlates with NH($^3\Sigma^-$) + Rb(^2P). The corresponding potential curve has an unusual square-bottomed shape because of an avoided crossing with the $^2\Pi$ ion-pair state. Because of this, it has vibrational states that have good Franck-Condon overlap with both low-energy continuum states on the lowest $^2\Sigma^-$ state and low-lying vibrational states of the $^2\Pi$ ion-pair state. There are several vibrational levels of the excited $^2\Pi$ state that are good candidates for this scheme; the $v' = 18$ state shown in Fig. 2 has a vibrational overlap of 0.17 to the $v'' = 0$ ion-pair ground state. The electronic transition moment is also favorable, at around 0.1 D near the potential minimum. It thus seems entirely feasible to produce Rb$^+$NH$^-$ by a pump-dump scheme or even by excitation followed by spontaneous emission. The wavelengths required for the pump and dump lasers (ca. 800 and 420 nm, respectively) are in easily accessible spectral regions.

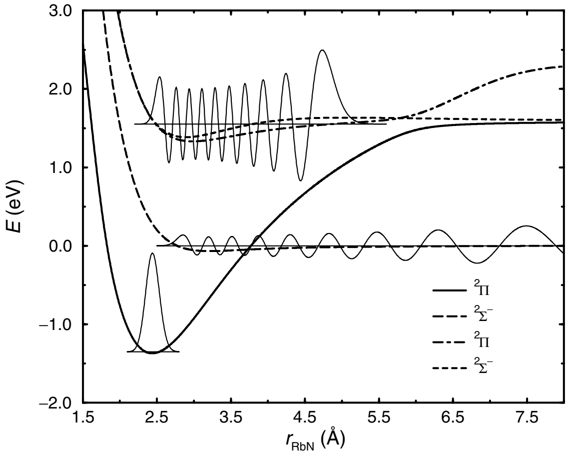

FIG. 2. CASSCF(13,5)/MRCI large-core potential energy curves of RbNH with fixed $r_{\rm NH} = 1.0308$ Å and fixed Rb-N-H angle of 180°. The large-core calculations underestimate repulsion [21], so the curves here are scaled in energy and distance to match D_e and R_X from small-core calculations.

In conclusion, ion-pair states are likely to have important consequences for the physics of sympathetic cooling of molecules. They provide additional mechanisms for inelastic collisions and three-body recombination but also offer the possibility of creating extremely dipolar molecules. A detailed theoretical investigation of Rb-molecule collisions will require full calculations on the interacting surfaces and either an explicitly nonadiabatic treatment of the collision dynamics or unraveling of the surfaces to produce a diabatic representation. We are currently working on this, but it is outside the scope of the present paper.

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[25] MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles with contributions from others; for more information, see the www page http://www.tc.bham.ac.uk/molpro/

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