Inelastic Collisions of Ultracold Polar Molecules

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The collisional stability of ultracold polar molecules in electrostatic traps is considered. Rate constants for collisions that drive molecules from weak-field-seeking to strong-field-seeking states are estimated using a simple model. The rates are found to be quite large, of order $10^{-12} - 10^{-10}$ cm$^3$/sec, and moreover to grow rapidly in an externally applied electric field. It is argued that these results are generic for polar molecules, and that therefore polar molecules should be trapped by other than electrostatic means.

Recently Bethlem et al. broadened the scope of ultracold AMO physics by cooling and electrostatically trapping ND$_3$ molecules [1,2]. This achievement is notable both for the complexity of the species trapped and for the generality of the Stark slowing technique, which could in principle cool any polar molecule. This technique is therefore now on a par with other experimental methods for producing cold molecular gases, such as photoassociation [3] and buffer-gas cooling [4], as well as photoproduction of molecular ions in a Paul trap [5].

The electrostatic trap demonstrated in Ref. [1] raises anew questions of collisional stability that are familiar in the context of magnetic trapping of atoms [1]. An electrostatic trap can only confine dipoles that are in their weak-field seeking states, since Maxwell’s equations permit a local field minimum but not a field maximum. Thus the dipoles are susceptible to orientation-changing collisions that populate the strong-field seeking, untrapped states. In the case of magnetic trapping of alkali atoms a standard remedy against collisional losses is to prepare the atoms in their stretched spin states, whereby the dominant spin-exchange collisional processes are absent. Atomic spins can then only change their orientation via spin-spin dipolar processes, which are weak because of the inherent weakness of magnetic dipolar interactions.

The purpose of this Rapid Communication is to point out that polar molecules are not as immune to dipolar relaxation as are magnetic atoms, simply because electric dipoles have a much stronger interaction. Indeed, the force between a pair of $d = 1$ Debye (0.39 atomic units) electric dipoles is $\sim 3 \times 10^3$ times larger than that between a pair of $\mu = 1 \mu_B$ magnetic dipoles. The basic physics of electric dipolar relaxation lies in the competition between the dipoles’ interaction with the electric field when they are far apart, $-\vec{d} \cdot \vec{E}$, and with each other when they are closer together, $\sim d_1 \cdot d_2 / R^3$. At small values of intermolecular separation $R$ the dipoles will tend to lock on their intermolecular axis rather than on the lab-fixed axis set by $\vec{E}$; the competition between these tendencies scrambles the orientation of the molecular dipoles. The resulting state-changing collisions can in principle be suppressed by a field strong enough to maintain the dipolar orientation. This will happen, roughly, if $d\vec{E} > d^2 / R^3$ for small values of $R$. Still, for $d = 1$ Debye dipoles at a typical collision distance $R \approx 10$ atomic units (a.u.), an electric field of $10^6$ V/cm would be required to maintain dipolar orientation. Thus very large laboratory fields may exert some mitigating influence, but are unlikely to arrest relaxation altogether.

To quantify this general argument this paper presents detailed calculations using a simplified model of collisions. In general the physics of cold molecular collisions will be quite complex, intertwining rotational, electronic, nuclear spin, and perhaps even vibrational degrees of freedom. However, to establish orders of magnitude for dipolar relaxation rate constants it suffices to focus on orientational degrees of freedom, and to account only for the dominant dipole-dipole interaction between molecules. Accordingly, a simplified “toy” model is used here, which has zero spin and nuclear spin. The molecules are assumed to be diatomic rigid rotors with electric dipole moments $d = 1$ Debye along their molecular axes. The electronic ground state of the molecules is assumed to be $^1\Pi$, so that it possesses a $\Lambda$-doublet of parity eigenstates. The splitting of this doublet is assumed to have a “typical” value of $\Delta = 10^{-3}$ cm$^{-1}$, and the lower-energy state is assumed to have even parity.

At ultracold temperatures and in zero electric field the molecules occupy parity eigenstates, hence exhibit no permanent dipole moment. The dipole moment only become apparent when the field is large enough to significantly mix states of different parity, thus “activating” the dipoles. This occurs at a field value where the Stark effect transforms from quadratic to linear, at $\sim 100$ V/cm in the present model (Figure 1). For fields below this value the molecules are fairly weakly interacting, whereas above this value the molecules have extremely strong dipole couplings. Thus in the $\Lambda$-doubled state collisions can be manipulated using modest electric fields, in contrast to the $\sim 10^6$ V/cm fields required to influence cold atomic collisions [6]. These arguments also apply to molecules with $^{2S+1}\Sigma$ electronic symmetry when $S > 0$ and the molecule exhibits an $\Omega$-doubling [6], as well as to ND$_3$.

Figure 1 shows the electric field dependence of the lowest-lying energy levels in the model molecules. Although both $N = 1$ and $N = 2$ rotational levels are
shown, the calculations below focus exclusively on the $N = 1$ levels. Their low-$E$ behavior is shown in the inset, labeled by the pair of quantum numbers $|M_N|, p$. Here $p$ stands for the parity in zero field, while $|M_N|$ denotes the magnitude of the molecular rotation’s magnetic quantum number referred to the laboratory axis; the $M_N = 1$ and $M_N = -1$ levels are degenerate even in an electric field. In an electrostatic trap of the kind used by Bethlem et al. the trapped states are the weak-field seekers, i.e., those whose Stark energy rises with rising field. These are the $|M_N|, p = |1, -1\rangle$ states in the model.

The Hamiltonian for collisions between the molecules consists of four terms in this model,

$$\hat{H} = \hat{T} + \hat{H}_{\text{fs}} + \hat{H}_{\text{field}} + \hat{H}_{\text{dip-dip}},$$

(1)

Here $\hat{T}$ represents the kinetic energy, $\hat{H}_{\text{fs}}$ the molecular fine structure including the $A$-doubling, and the last two terms are the electric field interaction and the dipole-dipole interaction between molecules:

$$\hat{H}_{\text{field}} = -\langle \hat{d}_1 + \hat{d}_2 \rangle \cdot \vec{E},$$

(2)

$$\hat{H}_{\text{dip-dip}} = \frac{\hat{d}_1 \cdot \hat{d}_2 - 3(\hat{R} \cdot \hat{d}_1)(\hat{R} \cdot \hat{d}_2)}{R^3},$$

(3)

where $\hat{R}$ denotes the orientation of the vector joining the center-of-mass of the molecules. Dispersion and exchange potentials are neglected here since they are of secondary importance to dipolar interactions at large $R$. To avoid problems with the singularity of $1/R^3$ at $R = 0$, vanishing boundary conditions are imposed at a cutoff radius $R_0 = 10$ a.u., where the potentials are deep compared to $\Delta$.

In the scattering calculation the molecules are assumed to be identical bosons, so that only even partial waves are relevant. Only the partial waves $L = 0$ and $L = 2$ are included explicitly, even though in principle all partial waves are coupled together by strong anisotropic interactions. However, the neglected higher-$L$ partial waves can be shown, in the Born approximation, to fall off rapidly with $L$ [1]. Cross sections for processes that change molecular channel $|i\rangle$ into channel $|i'\rangle$ are given as in Ref. [11]:

$$\sigma_{i \rightarrow i'} = \frac{\pi}{k_i^2} \sum_{LM, L'M_L} |\langle i, LM|T|i' L'M_L' \rangle|^2,$$

(4)

where $T$ is the T-matrix for scattering and $k_i$ is the incident wave number. Because of the incoherent sum in (4), contributions arising from $L = 0$ and $L = 2$ incident partial waves can be presented individually. All results, for both elastic and state-changing collisions will be reported as event rate coefficients,

$$K_{i \rightarrow i'} = v_i \sigma_{i \rightarrow i'},$$

(5)

where $v_i$ is the incident relative velocity of the collision partners.

Although state-changing collisions are primarily of interest here, it is useful first to consider elastic scattering of polar molecules, to illustrate the enormous influence of the electric field. Figure 2 shows the elastic scattering rate constant $K_{\text{el}}$ for molecules in their $|M_N, p\rangle = |1, -1\rangle$ state. Figure 2(a) depicts the low-field limit ($E = 0$ V/cm), while Fig. 2(b) shows a higher-field limit ($E = 200$ V/cm), where the Stark effect is linear. These rate constants are separated into their s-wave (solid line) and d-wave (dashed line) contributions.

In both the low- and high-field regimes the s-wave rate has the familiar $K_{\text{el}} \propto E^{1/2}$ threshold behavior as a function of collision energy $E$, arising from the Wigner threshold law. For the d-waves, however, the threshold dependence changes dramatically, falling off as $K_{\text{el}} \propto E^{5/2}$ at low field but as $K_{\text{el}} \propto E^{1/2}$ at higher fields. This behavior has to do with qualitative differences in the long-range intermolecular potentials. In the low-field limit, the asymptotic molecular states are parity eigenstates, hence have no dipole moment. At large values of $R$, where the dipole-dipole interaction energy becomes less than the $A$-doubling energy, the dipole-dipole $1/R^3$ potential is thus effectively absent. By contrast, in the high-field regime parity eigenstates are mixed at large $R$ and the $1/R^3$ potential is activated. It is well known [2,13] that a $1/R^3$ potential contributes a long-range scattering phase shift that is proportional to the wave number $k$ for all partial waves $L > 0$, thus yielding a $K_{\text{el}} \propto E^{1/2}$ threshold law.

This “switching on” of the dipolar interaction in the presence of a field also manifests itself in the inelastic rate constants, which are shown in Figure 3. This figure shows the sum $K_{\text{relax}} = \sum_{i, i'} K_{i \rightarrow i'}$ of all the rate constants for collisions of $|M_N, p\rangle = |1, -1\rangle$ molecules in which at least one molecule relaxes into one of the strong-field-seeking states $|M_N, p\rangle = |0, -1\rangle$, $|0, +1\rangle$, or $|1, +1\rangle$ (see Fig. 1). Again both the $E = 0$ V/cm and $E = 200$ V/cm cases are shown, and the rates are separated into $L = 0$ and $L = 2$ initial states. These relaxation rates are dominated by exothermic processes which exhibit their own characteristic threshold behavior. The rates for $L = 0$ partial waves become independent of energy at threshold, while the behavior of $L = 2$ partial waves transforms from the usual Wigner result $K_{\text{relax}} \propto E^2$ at low field, to a $K_{\text{relax}} \propto E$ behavior at high field when the dipoles are activated [14].

More significantly, the values of the loss rate constant are substantially boosted by the presence of an electric field, even for s-wave collisions. This is simply because the strong dipolar interactions that drive inelastic transitions are also made stronger in an electric field. Figure 4 shows the threshold relaxation rate as a function of electric field. Even at low field the rates are fairly large, since dipole interactions are still present at small $R$. As the field grows to $E \sim 100$ V/cm, where the dipoles turn on, the rates rise sharply. In the particular model considered here the rates are boosted nearly two orders of magnitude by the field.
Weak-electric-field seeking states should quite generally suffer these large loss rates. Quantum mechanically this follows from the fact that the large-$R$ Hamiltonian $\hat{H}_{\text{fs}} + \hat{H}_{\text{field}}$ is diagonal in the laboratory frame, while the interaction Hamiltonian $\hat{H}_{\text{dip-dip}}$ is diagonal in the body frame that joins the centers-of-mass of the two molecules. The former is stronger at large separations $R$, while the latter dominates at small $R$. Molecules that start out in eigenstates of $\hat{H}_{\text{fs}} + \hat{H}_{\text{field}}$ are thus distributed over all the different states of $\hat{H}_{\text{dip-dip}}$ during the collision, and re-assembled into an assortment of eigenstates of $\hat{H}_{\text{fs}} + \hat{H}_{\text{field}}$ as the molecules separate. Since the asymptotic states are completely deconstructed and reconstructed during this collision, in general it is expected that the probability for inelastic scattering is roughly the same as that for elastic scattering, and that therefore the rates are comparable.

This is of course the same kind of physics that governs spin-exchange collisions in the alkali atoms, which are driven by the competition between hyperfine-plus-erns spin-exchange collisions in the alkali atoms, which are completely deconstructed and reconstructed during the collision, and that therefore the rates are comparable.

In conclusion, dipolar molecules electrostatically trapped in weak-field-seeking states are susceptible to state-changing collisions that can rapidly deplete the trapped gas. Moreover, these rates can grow in the presence of the trapping electric field, which effectively turns on the full dipolar coupling at large intermolecular separation. Although this conclusion has been demonstrated using a particular toy model, the physics is quite general and should apply to any polar species. It is therefore recommended that dipolar molecules be trapped in strong-field-seeking states, where inelastic channels are absent at low temperatures. This kind of trapping cannot be achieved in a static trap, but would require a time-varying electric field. Magnetic dipoles in strong-field-seeking states have indeed been confined in such traps, using either time-varying fields or microwave cavities. A more conventional magnetic trap may also be useful, although the influence of the electric dipoles on losses in magnetic traps would have to be explored.

More broadly, an externally applied electric field is seen to have a profound influence on the collision dynamics of ultracold polar molecules, even to the extent of altering the threshold behavior. Preliminary results on the properties of quantum degenerate gases with dipolar interactions have been reported in the literature. More detailed scattering calculations are required to help shape the study of these unusual substances.

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FIG. 1. Stark energy levels for the model molecules, which have $^1\Pi$ electronic symmetry. This paper concentrates on collisions between molecules in their $|M, p\rangle = |+1, -\rangle$ states, which are weak-field seekers (see inset).

FIG. 2. Elastic scattering rate constants for $|M_N, p\rangle = |+1, -\rangle$ molecules. Shown are results for low-field [$\mathcal{E} = 0$ V/cm in (a)] and high-field [$\mathcal{E} = 200$ V/cm in (b)] regimes. Notice that in the presence of an electric field the $d$-wave ($L = 2$) rate is significantly boosted, and acquires a $K_{el} \propto E^{1/2}$ threshold behavior.

FIG. 3. Dipolar relaxation rate constants for $|M_N, p\rangle = |+1, -\rangle$ molecules, at the same field values as in Fig. 2. The rates are substantially higher in the presence of an electric field, as explained in the text.
FIG. 4. Electric field dependence of the total relaxation rates for molecules initially in their $|M_N, p⟩ = |+1, −⟩$ state, in the zero-collision-energy limit. These rates rise sharply by $\mathcal{E} = 100$ V/cm, where the molecular dipoles are “activated” by a suitable admixture of parity eigenstates.