Rotational Quenching in Ionic Systems at Ultracold Temperatures

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The behavior of the rotational quenching for a molecular ion in collision with closed-shell neutral gases is investigated. We confirm that Wigner's threshold law for inelastic scattering holds in the presence of a long-range interaction due to polarization forces decreasing as the inverse fourth power of the distance but find that, because of the contributions of the higher angular momenta, its range of applicability is markedly reduced when compared to the scattering by neutral species. The calculations of the quenching cross sections make evident the special features of ionic systems at ultralow collision energies and yield rate coefficients of the order of 10^{-9} cm^3 s^{-1}, much larger than those found for the quenching of neutral molecules.

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The possibility of obtaining and storing samples of ultracold molecules is opening new perspectives in chemistry. While optical cooling can be readily achieved for dilute atomic samples of alkali and alkaline-earth metals [1] and of metastable helium [2,3], its application to molecules is complicated by the absence of closed optical transitions. Molecules irradiated with laser light would be optically pumped into dark states well before translational cooling is completed [4]. A variety of methods has been discussed to obtain ultracold molecules. Among them, the photoassociation (PA) of translationally cold atoms has been considered [5,6]. Refined versions of PA including effects from Feshbach resonances [7] and processes involving two-photon Raman [8] schemes have also been proposed. Raman PA of cold atoms has been experimentally verified and realized for Cs_2 [9], Na_2 [10], and Rb_2 [11]. Theoretical treatments of the dynamical and chemical behavior of an atomic-molecular Bose-Einstein condensate predict a class of interesting phenomena [12] that could be the subject of experimental investigation. Recent studies are probing ultracold atomic systems in which electric charges may play an important role [13]. These include ultracold plasmas [14], ultracold Rydberg gases [15], as well as ionization experiments [16].

It is important, in the framework of theoretical and experimental discussions of cold molecules, to analyze the behavior of rotational quenching cross sections in the ultracold temperature limit, particularly so for ionic systems which have been seldom studied. Indeed, a correct modeling of the low-energy dynamics in these systems could be helpful to better understand microscopic nucleation in cold rare gas clusters where often the accretion core is deemed to be an ionic molecule [17]. An interesting class of experiments has been performed [18,19] and a variety of theoretical approaches has been attempted [20,21] to explain the experimental data and the magic numbers they seem to reveal. The efficient quenching of the internal degrees of freedom of the ionic core could explain the high rates of evaporation of the neutral solvation shells and the survival of the final stable geometric configurations. It is essentially the same dynamics which controls the collisional cooling of such systems in the ultralow energy temperatures reached in a cold trap environment.

Theoretical studies on the low energies dynamics between atoms and molecules have been performed for the several neutral systems H-H_2 [22,23], He-H_2 [24–26], He-CO [27–29], and He-O_2 [30]. Each of these studies has provided cross sections and rates for rovibrational quenching and proved their behavior to be in agreement with the limiting Wigner law. The behavior of the cross section at ultralow energies is mostly determined by the long-range tail of the potential for a neutral-neutral collision as shown in Ref. [25]. Here we investigate the inelastic and elastic cross sections in the case of long-range interactions such as those occurring in a collision between a charged molecule and a neutral atom. The anisotropy of our potentials is strong in the short-range region while the long-range potentials are determined by the polarizability of the atom.

The theoretical analysis of a low-energy inelastic collision can be achieved by performing a series of close coupling calculations for decreasing energies and then extracting from the resulting cross sections the complex scattering length

$$a_{\nu j} = \alpha_{\nu j} + i\beta_{\nu j}, \tag{1}$$

where ν and j are the initial quantum numbers of the molecular state. The imaginary part can be obtained from the total quenching cross section in the limit of zero kinetic energy [22]

$$\beta_{\nu j} = \lim_{k_{\nu j} \to 0} \frac{k_{\nu j} \sigma_{\nu j}^{in}(E)}{4\pi}, \tag{2}$$

where $k_{\nu j}$ is the relative velocity wave vector between the collision partners. The imaginary part of the scattering length yields the zero temperature quenching rate coefficient

$$C_{\nu j}(T \to 0) = \frac{4\pi \hbar \beta_{\nu j}}{\mu}, \tag{3}$$

where μ is the reduced mass of the system. Equation (2) is a form of the Wigner threshold law, which in general states that the total (and the state-to-state) inelastic cross section for a deexcitation collision diverges in the limit of zero kinetic energy as the inverse of the initial relative velocity between the colliding partners. Wigner's law should hold for all potentials that vanish at infinity faster than R^{-3}.

We employed in the present study two rigid rotor potential energy surfaces (PES's) expressed in the usual Jacobi coordinates R and θ, calculated earlier in our group using *ab initio* methods [21,31]. The long-range points were fitted to the multipolar expansion for the electrostatic interactions for which we employed the experimental values of the dipole polarizabilities α of the neutral atoms [$\alpha(\text{He}) = 1.38$ a.u. [21] and $\alpha(\text{Ne}) = 2.67$ a.u. [31]] that interact with their homonuclear parent ions ($\text{He}_2{}^+$ and $\text{Ne}_2{}^+$):

$$E_{ab}(R, \theta) = V(R, \theta) - V_a - \frac{\alpha}{2R^4}, \tag{4}$$

where E_{ab} are the total energies obtained from the *ab initio* calculations: they extend out to an outer limiting $R_{\max}$ value (5 Å for He and 7 Å for Ne) beyond which the He/Ne atomic polarizabilities are used to generate the full interaction. Here V_a is the asymptotic potential or the isolated diatom. Since the *ab initio* calculation could not be extended to the large-R region we employed a least squares fitting of the above expression to produce the interaction potential $V(R, \theta)$ with the correct large-R dependence. The two surfaces are reported in Fig. 1. The potential presents a minimum at larger distances for the $\text{Ne}_3{}^+$ surface as expected by the larger size of the Ne atoms. The corresponding attractive well is deeper for the Ne system at small angles ($\theta = 0°$-$\theta = 30°$), while the opposite is true for larger angles. Therefore, a more marked anisotropy occurs for the Ne system than for the He case.

The anisotropy of the potential energy surfaces (the source of rotational inelasticity) can be described by expanding in Legendre polynomials according to

$$V(R, \theta) = \sum_{\lambda} V_{\lambda}(R) P_{\lambda}(\cos\theta). \tag{5}$$

The spherical term V_0 has a similar depth of (~ 500 cm^{-1}), but the $\text{Ne}_2{}^+$-Ne interaction has its minimum at larger R values. The attractive regions of the higher order terms are pushed to larger R in the case of Ne compared to He although the V_λ coefficients have much stronger attractive tails for the Ne system than for the He. The Legendre expansion converges less rapidly for Ne because the surface has a larger anisotropy as exemplified by the presence of weaker minima at higher θ values. Enough multipolar coefficients were included to reproduce the angular PES's within a few percent of the directly computed values (four terms for He and seven for Ne).

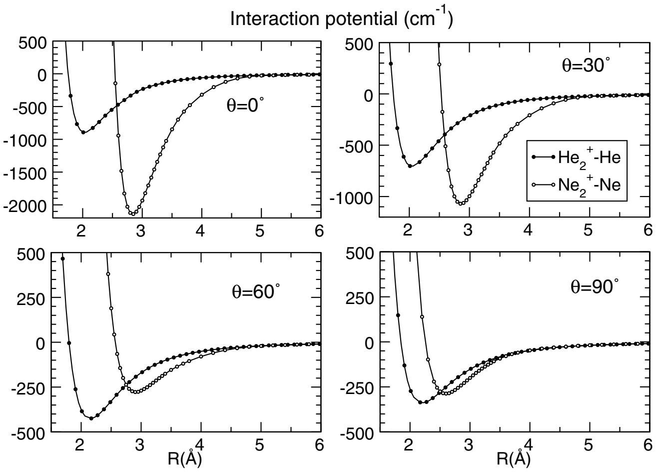

FIG. 1. Interaction potentials for $\text{Ne}_2{}^+$-Ne and $\text{He}_2{}^+$-He as a function of R for four different orientations.

We solved the close coupled (CC) equations in the rigid rotor approximation, which excludes the possibility of vibrational transitions and reactive collisions but should yield reliable results for pure rotational transitions. For a given partial wave of angular momentum l and initial internal quantum angular number j the total angular quantum number J ranges from $|j - l|$ to $j + l$. For s-wave scattering with $l = 0$, $J = j$.

For the He system we employed nine rotational levels and for the Ne system 32 with ten partial waves for both. The highest rotational level of $\text{He}_2{}^+$ is $j = 16$ and of $\text{Ne}_2{}^+$ is $j = 62$. The rotational constants are 7.211 cm^{-1} for He [32] and 0.554 cm^{-1} for Ne [33]. In both cases we integrated the equations from 0.5 Å out to 500 Å. The matching R values were arranged to change automatically for $l \neq 0$ incoming waves, to avoid the presence of imaginary local wave vectors at the matching point. The solution of the CC equations was accomplished by the use of a new propagator we have developed [34] that is based on the variable phase equations for mutichannel scattering [35,36] and is particularly efficient for long-range interactions. The propagator is a hybrid method which uses a standard log-derivative approach at short range and the variable phase equations at long range.

The quenching cross sections for the rotational deexcitation of $\text{He}_2{}^+$ by He are shown in Fig. 2 as a function of the collision energy for the transitions from $j = 2$, 4, and 6 with $\Delta j = 0$, 2, and 4. The cross sections for the transitions involving the $\Delta j = 2$ jump are all of the

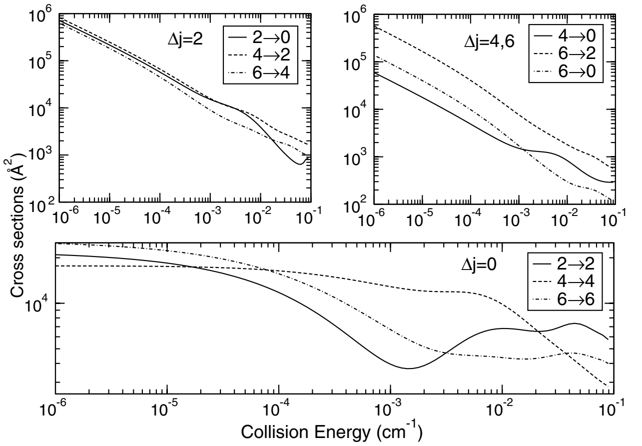

FIG. 2. Quenching cross sections for He_2^+-He. Upper-left panel: transitions involving a single quantum jump. Upper-right panel: transitions involving double and triple jumps. Lower panel: elastic transitions.

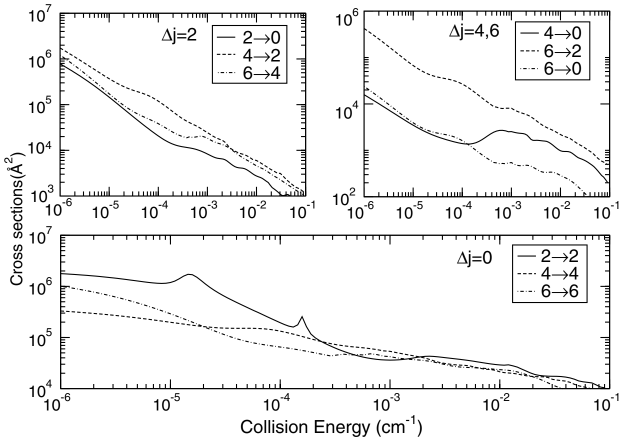

FIG. 3. Quenching cross sections for Ne_2^+-Ne. Upper-left panel: transitions involving a single jump. Upper-right panel: transitions involving double and triple jumps. Lower panel: elastic transitions.

same order of magnitude and reach the Wigner regime at an energy of 10^{-4} cm^{-1}. The energy is small compared to neutral-neutral collisions, where the Wigner law's regime applies at energies below 10^{-2} cm^{-1} [27,29,30]. The difference is due to the long-range tail of the polarization potential which enhances contributions from higher partial waves.

A more complex behavior occurs for transitions with $\Delta j > 2$. The cross section for the $6 \rightarrow 0$ transitions is an order of magnitude larger than the one for the $\Delta j = 4$ transitions shown in Fig. 2. The anisotropic coefficients V_λ decrease rapidly with λ, and their direct interaction does not drive large changes in j. The large changes in j must be a result of multiple dynamical couplings between adjacent rotational levels. At ultralow energies the long interaction time corresponds to several rotations of the target ion.

The cross sections for the Ne systems are reported in Fig. 3. The effects of multiple transitions are more evident for Ne as expected for a system with a denser rotational spectrum and stronger $P_2(\cos\theta)$ anisotropy. The region in which the cross section behaves as $1/v$ is not reached until energies below 10^{-6} cm^{-1}, because of the the larger polarizability and extended long-range interaction.

The difference between the Ne and He systems arises mostly from the greater magnitude of the polarizability of Ne and the heavier mass, which both lead to an increased contribution from large values of l.

The long-range potential scatters higher angular momentum partial waves than does one of shorter range: classically trajectories with large impact parameters are deflected only by the long-range part of the interaction. In Fig. 4 we report the energy dependence of the $J = 0$, 1, and 2 cross sections for both systems for the transition $j = 2 \rightarrow j' = 0$ and show in the inset the dominant l value for each J. The longer range potential of the Ne system scatters incoming waves with $l > 0$ more effectively though their contribution does vanish in the limit of low energies where Wigner's law for s waves applies. However, lower energies are required to access the Wigner law regime.

We present in Table I the real and imaginary parts of the scattering lengths together with the limiting values of the rate constants for the quenching process. Some of the real contributions to the scattering lengths are large and positive showing the presence of bound states of the composite systems with energies close to the dissociation threshold, as can be expected for such strongly interacting partners. The large quenching rate coefficients of order 10^{-9}–10^{-10} cm^3 s^{-1} attained at zero temperature may cause significant loss in trapping experiments but enhance the possibility of measuring the cross sections by means of ion storage experiments.

The present study constitutes a first attempt to analyze the behavior of rotational collisional quenching in ionic

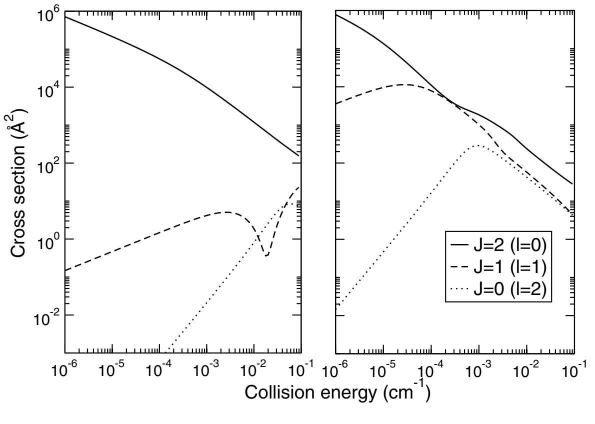

FIG. 4. Partial contributions to the $2 \rightarrow 0$ deexcitation cross sections for the first three values of J for the He system (left panel) and for the Ne (right panel) as a function of collision energy. The dominant value of l for each J is indicated.

TABLE I. Scattering lengths and rate constants.

Initial j	α_j (Å)	β_j (Å)	$C_j(T \rightarrow 0)$ ($\mathrm{cm^3\,s^{-1}}$)
$\mathrm{He_2}^+$-He			
2	-33.9	22.6	6.7×10^{-10}
4	$+24.8$	28.0	8.4×10^{-10}
6	-14.1	42.1	1.2×10^{-9}
$\mathrm{Ne_2}^+$-Ne			
2	$+371.6$	55.5	3.3×10^{-10}
4	$+103.6$	124.5	7.3×10^{-10}
6	-256.7	117.9	7.0×10^{-10}

molecular encounters in very low relative energy regimes. We have chosen for this case study the ionic, homonuclear rare gas systems $\mathrm{Ne_2}^+ + \mathrm{Ne}$ and $\mathrm{He_2}^+ + \mathrm{He}$ which are also of interest because of the role they play when modeling ionic nucleation in rare gas clusters [31,37–39]. The calculations demonstrate that the region in which the Wigner law applies is reached for ionic systems at much lower collision energies than for neutral particles and that the quenching rate coefficients as T tends to zero are of the order of 10^{-9} $\mathrm{cm^3\,s^{-1}}$, considerably larger than for neutral atom-molecule systems. We expect that also in reactive events with ionic partners the rotational excitation will play a significant role.

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