Vibrational deactivation in Kr/O$_2^+$ collisions: Role of complex formation and potential anisotropy

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We report a theoretical study of vibrational deactivation of the diatomic ion O$_2^+$ ($v=1$) by low-energy (<1 eV) collisions with Kr. It is shown that one-dimensional collision models are not able to reproduce the experimentally observed minimum in the deactivation rate as a function of collision energy, even when attractive interactions are included. Classical trajectory calculations on an empirical potential surface lead to good agreement with experiment, confirming the essential role of rotational degrees of freedom in the deactivation process. We find that the upturn in the deactivation rate at low energies is due to the formation of orbiting complexes, as suggested by Ferguson. Our results show that the energy dependence of the association (complex formation) rate is an important factor in determining that of the deactivation rate at low collision energies, whereas orbiting complex lifetimes show relatively little variation over the energy range studied. At very low collision energies, our computed deactivation rate becomes independent of energy, in accord with recent experiments of Hawley and Smith. We also investigate the role of potential anisotropy in the deactivation process. It is suggested that the decrease in deactivation rate with increased potential well width (i.e., decreasing anisotropy) is due to the elimination of a transient resonance between hindered rotation and diatom vibration.

I. INTRODUCTION

An understanding of the dynamics of thermal ion-neutral collisions is important for many processes involving ions, such as ion-molecule reactions and vibrational quenching. Consider, for example, the deactivation of a vibrationally excited ion $AB^+$ ($v$) by collision with a neutral species $C$. The usual Landau-Teller (LT) model for $V\rightarrow T$ energy transfer based on purely repulsive interactions predicts a monotonic increase in quenching rate with collision energy. Recent experiments using ion flow drift tube techniques have shown that, for the ion-neutral pair $N_2^+/He$ at collision energies larger than ~0.25 eV, the vibrational quenching rate is fitted well by standard LT theory. That is, a plot of $\ln(k_{\text{quench}})$ versus $T^{-1/3}$ is linear over almost all of the observed energy range. For several other ion-neutral pairs studied to date, however, the vibrational deactivation rate is not in accord with simple LT predictions at any energy. For $O_2^+ (v=1)/Kr$, the deactivation rate as a function of collision energy exhibits a minimum, first decreasing and then increasing with increasing collision energy. A minimum in the quenching rate is also seen in drift tube experiments on NO$^+$ ($v=1$)/CH$_4$ (Ref. 12) and for very low-temperature collisions of NO$^+$ ($v=1$) with He, Ar, and N$_2$ in a free jet flow. Many other ion-neutral pairs exhibit vibrational deactivation rates well in excess of those found in typical neutral-neutral systems. Deviations from LT theory are also found for neutral-neutral systems such as HCl-HCl, where strong attractive forces are present.

To explain the anomalous behavior of the vibrational deactivation probability found for $O_2^+/Kr$, the following mechanism has been proposed by Ferguson:

\[ AB^+ (v) + C \rightarrow [AB^+ (v) \cdots C]^* \rightarrow AB^+ (v' < v) + C. \]  

(1)

The first step consists of an associative collision between the ion and the neutral to form an "orbiting" complex. This orbiting complex may then dissociate to yield either the ion $AB^+ (v)$ in its initial vibrational state (unimolecular decay of the orbiting complex, rate constant $k_a$), or in a state with fewer vibrational quanta (vibrational predissociation of the orbiting complex, rate constant $k_{up}$). The steady-state quenching rate constant $k_q$ is

\[ k_q = k_a \frac{k_{up}}{k_{up} + k_u}, \]  

(2)

i.e., the rate coefficient for orbiting complex formation times the branching ratio for vibrational predissociation. Ferguson assumes that the association rate, $k_a$, is approximately equal to the Langevin collision rate for capture of nonpolar neutrals of polarizability $\alpha$ by a charged species,

\[ k_a \approx k_i = 2\pi \left( \frac{\alpha}{M} \right)^{1/2} \]  

(3)

($M$ is the atom/diatom reduced mass, see the following), and therefore is temperature independent.

In the limit that vibrational predissociation is much slower than unimolecular decay, $k_{up} > k_u$, the quenching rate coefficient is

\[ k_q \approx \frac{k_a k_{up}}{k_u} \approx k_a k_{up} \tau_u , \]  

(4)

where $\tau_u$ is the unimolecular decay lifetime of the orbiting complex.


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In Ferguson's mechanism, the enhanced vibrational quenching probability at low collision energies is a consequence of repeated collisions of the partners during the lifetime of the complex, so that each complex-forming collision is effectively equivalent to several direct collisions. The initial decrease in $k_q$ with relative collision energy is then ascribed to a rapid decrease in the lifetime of the orbiting complex (i.e., increase in $k_u$) with increasing internal energy. At higher collision energies, deactivation by direct ion-neutral collisions presumably takes over as the dominant mechanism, although the efficiency of these collisions is higher than predicted by simple LT considerations for $V \rightarrow T$ energy transfer.

Ferguson has correlated the rate of vibrational deactivation according to scheme (1) with that for three-body association:

$$k'_u AB^+ + C \rightarrow [AB^+ \cdots C]^* \rightarrow [AB^+ \cdots C].$$

The steady-state rate coefficient $k^{(3)}$ for three-body association

$$k^{(3)} = \frac{k'_u k'_3}{k'_u + k'_3 [M]}$$

becomes

$$\frac{k'_u k'_3}{k'_u} = k'_u k'_3 \tau'_u$$

for short-lived complexes ($k'_u \equiv 1/\tau'_u \gg k'_3 [M]$). Assuming $\tau_u \sim \tau'_u$ and $k_u \sim k'_u$ gives

$$k_q = \frac{k^{(3)} k_{vp}}{k'_u}.$$  

An approximately linear relation between $k_q$ and $k^{(3)}$ has, in fact, been found by Ferguson. Assuming efficient collisional deactivation, measured values of $k_q$ and $k^{(3)}$ then yield values for the vibrational predissociation rate $k_{vp}$ in the range $10^9$–$10^{11}$ s$^{-1}$.

In the limit of very low collision energies, where the orbiting complex is extremely long-lived, $k_{vp} \gg k_u$, and

$$k_q \sim k_2,$$

so that the quenching rate is equal to the association rate. If the complex formation rate is approximately equal to the Langevin capture rate at very low collision energies, we expect the vibrational quenching rate to become temperature independent for collisions of ions with polarizable nonpolar neutrals. Such behavior has very recently been observed by Hawley and Smith for collisions of NO$^+$ with Ar and N$_2$.

The mechanism of Eq. (1) raises several interesting dynamical questions. Ion-neutral interactions are typically intermediate in strength between weak van der Waals interactions and ordinary chemical bonds, and have accurately known long-range attractive components (ion/induced-dipole, ion quadrupole, etc.). Several theories of Langevin type are available to calculate the total capture rate (that is, the rate of passage over the centrifugal barrier) in the presence of long-range attractive forces, but the dynamics of subsequent complex formation and decay is not fully understood (cf. Ref. 19). The fundamental process involved in formation of orbiting complexes is transfer of energy from relative translation of the ion and neutral species into and out of internal degrees of freedom. The orbiting complex $[AB^+ \cdots C]^*$ in the proposed mechanism, Eq. (1), is assumed to be formed by transfer of energy from translation to internal rotation; the reverse process of complex decay then occurs by rotational predissociation. If complex formation is important for vibrational deactivation at low energies, then rotational decoupling approximations such as the infinite order sudden approximation (IOSA) would not be expected to describe the quenching process accurately.

Several theoretical studies have addressed Ferguson's mechanism. Tanner and Maricq have made a quantum-mechanical study of vibrational deactivation in N$_2$/Li$^+$, taken as a model for NO$^+$/He. Using the IOS/distorted wave (DW) approximations, the deactivation cross section was found to exhibit a minimum as a function of collisional energy $E_c$. Moreover, Tanner and Maricq concluded that the anomalous behavior of the deactivation cross section as a function of collision energy seen in Kr/O$_2^+$, for example, could be explained in terms of a LT type expression for $V \rightarrow T$ energy transfer modified to incorporate the effects of attractive interactions, and that complex formation and rotational degrees of freedom play no role in the deactivation process. Tanner and Maricq's analysis of vibrational quenching is discussed in more detail below. A modified LT treatment has also been given by Parson.

Tosi et al. made a classical trajectory study of vibrational deactivation in Kr/O$_2^+$, and were able to reproduce the observed dependence of the deactivation rate on collision energy. Significant complex formation was found at low energies, and an increasing fraction of vibrational deactivation occurred via orbiting complexes with decreasing $E_c$. Nevertheless, direct collisions made the dominant contribution to deactivation even at the lowest energies studied (cf. Ref. 27). The preponderance of $V \rightarrow R$ and $V \rightarrow R,T$ over $V \rightarrow T$ energy transfer however suggested the essential importance of rotational degrees of freedom. Classical trajectory studies of vibrational quenching in collisions of N$_2^+$ ($v = 1$) with He have been made by Zenevich et al., while Goldfield has recently made a quantum-mechanical wave-packet study of the Kr/O$_2^+$ system. Based on scaling arguments and the results of trajectory calculations on H$^+ +$H$_2$, Brass and Schlier have suggested that energy transfer into diatomic vibration is essential for the formation of long-lived complexes. In the present paper we further examine the role of vibrational quenching via direct versus complex forming collisions in the Kr/O$_2^+$ system. Our study is carried out using classical trajectories on a potential surface similar to that used by Tosi et al. Ferguson's mechanism is reexamined, in particular, the interplay between orbiting complex
formation and decay and vibrational predissociation. The role of potential anisotropy is also explored.\textsuperscript{20,21}

In Section II we discuss in some detail the possibility of fitting experimental quenching rate data for $\text{Kr}/\text{O}_2^+$ using deactivation probabilities obtained from one-dimensional models such as Lennard–Teller theory modified to incorporate attractive interactions. The $\text{Kr}/\text{O}_2^+$ Hamiltonian and the classical trajectory methodology used in this paper are presented in Sec. III, while Sec. IV gives our trajectory results. Discussion and conclusions are given in Sec. V.

II. CAN ONE-DIMENSIONAL MODELS FIT THE EXPERIMENTAL DATA?

Before turning to a description of our classical trajectory studies on the $\text{Kr}/\text{O}_2^+$ system, we first address the important question: Is it possible to fit the experimental rate constants for quenching of vibrationally excited $\text{O}_2^+$ by $\text{Kr}$ as a function of collision energy\textsuperscript{11} using LT-type expressions (or, more generally, expressions derived from one-dimensional models)? That is, can a satisfactory fit to the experimental data be obtained without invoking the formation of orbiting complexes? A satisfactory fit to the data must not only reproduce the observed shape of the experimental rate curve for physically appropriate parameter values, but should also yield absolute rate values in reasonable accord with experiment.

Tanner and Marić have given a critical discussion of Ferguson's proposed mechanism for vibrational relaxation of diatomic ions via transient ion/neutral complex formation, and have argued that it is possible to fit the $\text{Kr}/\text{O}_2^+$ data using a modified LT expression.\textsuperscript{22} The $\text{Li}^+/$N$_2$ ($\nu=1$) system, for which an \textit{ab initio} surface is available,\textsuperscript{32} was chosen as a model for vibrational relaxation in NO$^+$/He collisions. Coupled-channel equations for vibrationally inelastic collisions in Li$^+$/N$_2$ ($\nu=1$) were solved using the DWA, and the IOSA was used to decouple rotational channels. The DWA/IOSA quantum calculations of Tanner and Marić showed that the cross section for vibrational relaxation of N$_2$ ($\nu=1$) exhibits a minimum as a function of energy (Fig. 1 of Ref. 22). Moreover, even the $s$-wave cross section ($\ell=0$) was found to have a minimum.\textsuperscript{22} On this basis, Tanner and Marić concluded that "transfer of energy to molecular rotation, which would play a role in stabilizing a transient complex ... , therefore does not contribute to the unusual dependence of cross section on energy."\textsuperscript{22}

Furthermore, Tanner and Marić concluded that the anomalous behavior of the vibrational deactivation cross section as a function of collision energy for $\text{Kr}/\text{O}_2^+$ (Ref. 11) could be reproduced both by a suitable scaling of the Li$^+$/N$_2$ DWA/IOSA results and by a LT type expression for $V \to T$ energy transfer modified to incorporate the effects of attractive interactions, so that complex formation and rotational degrees of freedom play no role in the deactivation process.\textsuperscript{24}

Use of the IOSA to decouple rotational degrees of freedom of course precludes from the outset an assessment of the importance of rotational degrees of freedom for vibrational quenching. In the absence of a solution to the full quantum-mechanical coupled channels problem, the validity of the IOSA or related decoupling approximations such as the coupled states approximation is difficult to judge. It is nevertheless relatively straightforward to investigate the validity of rotational decoupling approximations within classical mechanics (see, for example Refs. 21 and 33). A study of classical rotational decoupling approximations for vibrational deactivation in ion-neutral collisions is currently in progress.\textsuperscript{34}

The usual LT expression for the probability of vibrational deactivation in a single collinear collision between a diatom (reduced mass $\mu$, vibrational quantum $\hbar \nu$) in the $\nu=1$ state and an atom (atom-diatom reduced mass $M$) interacting via a purely repulsive exponential interaction with range parameter $\alpha$ is\textsuperscript{5,6}

$$p_{\ell=0}^{LT} = \frac{8\pi^2 \mu M}{\alpha^2 \hbar} \exp\left( -\frac{4\pi \mu M}{\hbar k_1} \right), \quad (10)$$

where $k_1 = (2ME_1)^{1/2}/\hbar$ and $k_0 = (2ME_1+\hbar \nu)^{1/2}/\hbar$ are the initial and final wave numbers, respectively. This expression can be derived in a variety of ways;\textsuperscript{25} it is, for example, the classical limit (2$\pi \nu_0/\alpha \to 1$ and $2\pi k_1/\alpha \to 1$) of the quantum-mechanical expression of Jackson and Mott,\textsuperscript{35} which is obtained using the DWA. Tanner and Marić suggested an empirical modification to Eq. (10) to account for the influence of an attractive component of the atom/diatom interaction.\textsuperscript{22} The modification involves (a) replacing the collision energy $E_1$ with $E_1 + \epsilon$, where $\epsilon$ is the depth of the potential well and (b) replacing $\alpha$ by minus the logarithmic derivative of the potential relative to the potential minimum.\textsuperscript{22} To compute the deactivation rate, it is necessary to calculate a deactivation cross section which must then be multiplied by the relative collision velocity. Marić and Tanner apparently obtained a deactivation cross section for $s$-wave scattering by multiplying their modified LT probability by $\pi/k_1^2$; the resulting cross section has a minimum as a function of $E_1$. It is claimed that this expression (suitably scaled) evaluated for a Morse interaction potential is able to provide a reasonable fit to cross-section data extracted from experimental rate constant results on $\text{Kr}/\text{O}_2^+$ and to their DWA/IOSA calculations for $\text{Li}^+$/N$_2$ (cf. Fig. 3 of Ref. 22).

Several comments are in order here. We first note that an expression for the quantum vibrational deactivation probability with a Morse interaction potential

$$V(R) = D(e^{-2\alpha(R-R_0)} - 2e^{-\alpha(R-R_0)}) \quad (11)$$

has been derived by Lennard-Jones and Devonshire within the first-order DWA (Ref. 36) (see also Ref. 37):

$$\rho_{\ell=0}^{LT} = \frac{\hbar}{2\omega_\ell} k^2 \pi^2 (\nu_0^2 - \nu^2)^2 \times \frac{\sinh(2\pi \nu_1) \sin(2\pi \nu_0)}{\cosh(2\pi \nu_1) - \cosh(2\pi \nu_0)} \frac{(A_{\ell_1} + A_{\ell_0})^2}{A_{\ell_1} A_{\ell_0}}, \quad (12)$$

where
It is of interest to examine \( p_{I=0}^{\text{LJD}} \) as a function of \( E_t \) and to compare its behavior with the modified LT expression proposed by Maricq and Tanner, as the latter expression is an approximation to the former.

In Fig. 1 we plot \( p_{I=0}^{\text{LJD}} \) versus \( E_t \) for a Morse interaction potential with parameters appropriate for Kr/O\(_2^+\) (\( \kappa = 1.45 \) a.u., \( D = 0.33 \) eV; see Sec. III). The first-order DWA gives probabilities greater then unity for collision energies greater than an eV or so. The LJD deactivation probability decreases monotonically with energy, becoming nearly constant for \( E_t \sim 0.01 \) eV. We have followed the LJD deactivation probability down to much lower collision energies (\( \sim 10^{-7} \) eV), and have verified that it has the \( E_t^{1/2} \) dependence required by the "1/\( v \) law" in the low-energy limit where scattering is predominantly \( s \) wave.\(^{2,5} \)

The full deactivation cross section can be estimated by multiplying the collinear deactivation probability by the Langevin capture cross section \( \sigma_L = \frac{v^2}{k_1} \), \( q = \frac{k}{k_1} \).

\[ \sigma_{I=0}(\gamma) = \frac{\pi}{k_1^2} \sum_{l=0}^{l_{\text{max}}} (2l+1)p_{I=0}(\gamma), \]  

(15)

where the sum is over partial waves with orbital angular momentum \( l \), and collisions with \( l > l_{\text{max}} \) have negligible deactivation probability \( p_{I=0}(\gamma) \). The full deactivation cross section is obtained by averaging Eq. (15) over all orientations \( \gamma \). The \( s \)-wave (\( l=0 \)) contribution to the cross section \( \sigma_{I=0} \) is approximated by multiplying the collinear deactivation probability by \( \sigma_L/k_1^2 \) [cf. Eq. (10) of Ref. 22]

\[ \sigma_{I=0} = \frac{\pi}{k_1^2} p_{I=0}. \]

(16)

The full deactivation cross section can be estimated by multiplying the collinear deactivation probability by the Langevin capture cross section \( \sigma_L = 2\pi(\alpha/2E_t)^{1/2} \)

\[ \sigma_{I=0}^{\text{L}} = 2\pi\left(\frac{\alpha}{2E_t}\right)^{1/2} p_{I=0}, \]

(17)

where \( \alpha \) is the polarizability of the neutral species (Kr in the present case). Classically, this approximation assumes that all collisions with impact parameter out to \( b_{\text{max}} = l_{\text{max}}/k_1 \) lead to equally efficient quenching. The maximum impact parameter \( b_{\text{max}} \sim E_t^{1/4} \).

In Fig. 2 we compare quenching rates calculated in the way just described with experimental quenching rate coefficients for Kr/O\(_2^+\) as a function of collision energy. The \( s \)-wave deactivation rate curves estimated using either the LJD or Tanner and Maricq deactivation probabilities for a Morse potential show the same qualitative trend as the experimental points. In particular, the theoretical curves have shallow minima in the vicinity of \( E_t \sim 0.1 \) eV. The \( s \)-wave deactivation rates are however over 2 orders of magnitude smaller than the experimental rates. This is not surprising, since many partial waves will contribute to the
scattering cross section even at the lowest experimentally relevant energies for a heavy collision partner such as Kr. Deactivation rates calculated using the Langevin collision cross section are comparable to experimental values over most of the energy range of interest (first-order DWA deactivation probabilities are larger than unity for $E_t$ greater than about 1 eV). The calculated rates however decrease monotonically as $E_t$ decreases, and so do not show a minimum.

The nonappearance of a minimum may be understood by noting that the Langevin cross section is proportional to $E_t^{-1/2}$, whereas the s-wave cross section is proportional to $E_t^{-1}$. The more gradual decrease with increasing $E_t$ in the former case is offset by the increase in $p_{1-o}$ with $E_t$.

We have also examined the deactivation rates for vibrational deactivation in Li$^+$/N$_2$ ($v=1$) collisions, calculated from the DWA/IOSA cross sections of Tanner and Maricq. Although the Li$^+$/N$_2$ ($v=1$) rate (not shown) does exhibit a very shallow minimum, the upturn in the rate at lower collision energies is nowhere near as pronounced as that found for Kr/O$_2^+$.11

We therefore conclude that the experimental quenching rate data for Kr/O$_2^+$ cannot be satisfactorily fitted using expressions derived for one-dimensional collisions, even when the attractive part of the interaction is taken into account. This conclusion, although at variance with that of Tanner and Maricq,22 is certainly consistent with the work of Tosi et al.26 and with the trajectory results presented below.

III. THE SYSTEM

A. Hamiltonian

We consider the classical dynamics of planar atom-diatom collisions, with Hamiltonian

$$H = \frac{p_s^2}{2\mu} + \frac{p_r^2}{2M} + \frac{(J-p_r)^2}{2\mu r^2} + V(r, s, \gamma).$$

(18)

The coordinates are $s$, the bond length of the diatom O$_2^+$, $r$, the distance from the Kr atom to the diatom center of mass, and $\gamma$, the angle between the diatom axis and the vector from the diatom center of mass to the atom. Note that $0<\gamma<2\pi$ for planar motion. Momenta conjugate to these coordinates are $p_s$, $p_r$, and $p_\gamma$ respectively. The reduced mass of the diatom is $\mu$ and the reduced mass of the atom-diatom system is $M$. $J$ is the total angular momentum for rotation in the plane and is a constant of the motion. $V$ is the potential energy, a function of the three coordinates $r$, $s$, and $\gamma$.

B. Potential for Kr/O$_2^+$

The model potential used in the classical trajectory calculations of Tosi et al. successfully reproduced the observed dependence of the vibrational quenching rate on the relative translational energy $E_t$ in Kr/O$_2^+$.23 The anisotropy or angular width of the potential well was found to be an important factor in determining whether or not the trajectory calculations yielded a minimum in the vibrational quenching rate. A well width of approximately 40° gave a minimum at the experimental energy of ~0.3 eV.

Tosi et al. did not give an explicit analytical form for their potential surface. The functional form used here corresponds closely to the qualitative description given in Ref. 25, and is chosen to match quantitatively all relevant features. For example, our potential function has a Kr/O$_2^+$ well depth of approximately 0.33 eV, with Kr–O–O bond angle around 139°.40

The potential function used in the present paper is composed of three parts:

$$V(r, s, \gamma) = V_{O_2^+} + V_{\text{isotropic}} + V_{\text{anisotropic}}.$$  

(19)

The first term $V_{O_2^+}$ describes a Morse potential for the isolated O$_2^+$ diatomic, with parameters determined from spectroscopic data41

$$V_{O_2^+}(s) = D \left( e^{-\beta(s-s_c)} - e^{-\beta(s-s_c)} - 2 \right).$$  

(20)

The second term $V_{\text{isotropic}}$ consists of a long-range ion/induced-dipole attraction plus a short-range exponential repulsion term

$$V_{\text{isotropic}}(r) = C e^{-\alpha r} - \frac{\alpha}{2r^2}.$$  

(21)

This interaction term, which is independent of the coordinates $s$ and $\gamma$, yields a well depth of $-0.13$ eV at $r \approx 6$ bohr. The third term $V_{\text{anisotropic}}$ models the strong "chemical" interaction between Kr and O$_2^+$

$$V_{\text{anisotropic}}(r, s, \gamma) = D_2 e^{-\kappa(r-r_0)} \left[ e^{-\kappa(r-r_0)} - 2 f_1(\gamma) \right] + D_2 e^{-\kappa(r-r_0)} \left[ e^{-\kappa(r-r_0)} - 2 f_2(\gamma) \right].$$  

(22)

Here, $r_{1,2}$ are the distances from the Kr atom to the two O atoms. The interaction term is a sum of Morse potentials in which the attractive parts are multiplied by functions $f_{1,2}(\gamma)$ of the form

$$f_n(\gamma) = e^{-a(\cos(\gamma - \gamma_n)} + e^{a(\cos(\gamma + \gamma_n))}, \quad n = 1, 2.$$  

(23)

The functions $f_n$ are peaked at $\gamma = \pm \gamma_n$ where $\gamma_1 = 33.9^\circ$ and $\gamma_2 = 146.1^\circ$ correspond to the positions of the chemical wells at each end of the O$_2^+$ molecule. The parameter $a$ controls the angular width of the chemical well, i.e., the anisotropy of the interaction potential.

Values of the potential parameters are given in Table I. The contour plot of the full potential Eq. (19) in Fig. 3 with $s=s_c$ is very similar to that given by Tosi et al. in Fig. 1 of Ref. 75.

C. Selection of trajectory initial conditions

Ensembles of classical trajectories are used in standard fashion to compute vibrational deactivation cross sections and rates as a function of relative translational energy $E_t$. For the Kr/O$_2^+$ system considered here, vibrational deactivation of the $v=1$ state of O$_2^+$ is classically a dynamically allowed process42 at all energies down to the lowest stud-
TABLE I. Potential parameters (atomic units).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>$\beta$</td>
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</tr>
<tr>
<td>$\gamma$</td>
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<td>$D$</td>
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<td>$\beta$</td>
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<tr>
<td>$C$</td>
<td>38.5 hartree</td>
</tr>
<tr>
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<td>7.3502 $\times 10^{-3}$ hartree</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>1.45 bohr$^{-1}$</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>5.0 bohr</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>75.0</td>
</tr>
</tbody>
</table>

ied. In contrast to systems such as He/N$_2^+$, it is therefore not necessary to resort to devices such as the moment method for extracting vibrational deactivation probabilities from classical trajectory calculations.

Selection of initial conditions for individual trajectories is straightforward. For given relative translational velocity $v$, $E_t = Mv^2/2$, the Kr atom is placed a large distance ($R = 60$ a.u.) from the O$_2^+$ center of mass. Values for the O$_2^+$ angular momentum $p_\rho$, the orientation $\gamma'$, and the impact parameter $b$ are then chosen, and

$$p_\rho = \frac{MvR}{\rho}.$$

The impact parameter distribution is taken to be uniform in the interval $-b_{\text{max}}$ to $b_{\text{max}}$, as appropriate for planar dynamics. The maximum value of the impact parameter, $b_{\text{max}}$, beyond which the vibrational deactivation probability is negligible, is energy dependent, and can be estimated using the Langevin formula for the critical impact parameter in ion/induced-dipole collisions. At each energy $b_{\text{max}}$ is, however, determined numerically. The angle $\gamma'$ is chosen randomly in the interval $0-\pi$ (the angle range is halved due to the symmetry of the diatom). A two-dimensional Boltzmann weighted distribution of (positive) integral $p_\rho^0$ values was used for the O$_2^+$ rotor, corresponding to a rotational temperature of 300 K.

For given $p_\rho^0$ it is necessary to determine $p_s$ and $s$ values corresponding to the quasiclassical action $J_s = 1.5\hbar$ for the initial vibrational state $v=1$ of the rotating Morse O$_2^+$ oscillator. The vibrational action $J_s$ is a conserved quantity in the absence of the coupling term $V_{\text{anisotropic}}$. Even though rotational and vibrational energies are not individually conserved during a cycle of the vibrational motion, a numerical method is used to calculate initial conditions for the rotating Morse oscillator with $v=1$ for arbitrary $p_\rho^0$. With the Kr atom held fixed a large distance from the O$_2^+$ diatom, for a given value of $p_\rho^0$, the initial vibrational energy is varied until the vibrational action (as determined by numerical quadrature over ten vibrational periods) is 1.500$\hbar$. Once the appropriate value of the vibrational energy is determined, it is fixed and $s$ and $p_s$ values output at constant time (i.e., angle) intervals over one period of the vibration. This procedure yields a set of $(s, p_s)$ values uniformly spaced in vibrational phase angle for a trajectory with a given $p_\rho^0$ and fixed vibrational action. Sets of $s$ and $p_s$ values are generated in this way and stored for each integral value of $p_\rho$ from 0$\hbar$ to 16$\hbar$.

For each value of $E_p$ an ensemble of 3000 trajectories is run. The final vibrational and rotational actions are binned in the usual quasiclassical fashion. Vibrational deactivation occurs if the final value of the vibrational action $J_s$ lies between 0.0 and 1.0.

D. Opacity functions and rate coefficients

For given $E_p$ the trajectory ensemble averages over vibrational phase, diatom angular momentum, diatom orientation, and impact parameter. Trajectory results are conveniently represented by computing the opacity function $\Pi(b)$.

In terms of the opacity function, the planar deactivation cross section (cross length) is defined as

$$\sigma_{\text{planar}} = 2 \int_0^\infty db \Pi(b).$$

$\Pi(b)$ is a probability distribution for “successful” collisions. If trajectories densely and uniformly sample $b$, and if $\Delta N_s(b)$ is the number of successful (deactivating in this case) collisions and $\Delta N(b)$ is the total number of trajectories with impact parameter in the range $b \pm (\Delta b/2)$, then $\Pi(b)$ is approximated by

$$\Pi(b) \approx \frac{\Delta N_s(b)}{\Delta N(b)}.$$

Converting the integral to a summation over bins of width $\Delta b$ gives

$$\sigma_{\text{planar}} \approx 2 \sum_i \Delta b \frac{\Delta N_s(b_i)}{\Delta N(b_i)}.$$

If the trajectories uniformly sample impact parameter and if $b_{\text{max}}$ is a suitably large impact parameter such that any trajectory with an impact parameter larger than $b_{\text{max}}$ has zero probability of deactivation, then $\Delta N(b)$ is given by

\[\text{FIG. 3. Contour plot of the Kr/O}_2^+\text{ potential surface, Eq. (19). The O}_2^+\text{ molecule lies along the x axis, with the midpoint of the O-O bond at the origin. The O-O bond length is fixed at } s = 2.4 \text{ bohr. Contours are at multiples of } 0.046 \text{ eV (cf. Ref. 26).}\]
The expression for the cross length then becomes

\[ \sigma_{\text{planar}} \approx \frac{2b_{\text{max}}}{N} \sum \Delta N_i, \]

(28)

where the summation is over bins \( i \), or

\[ \sigma_{\text{planar}} \approx \frac{2b_{\text{max}}}{N} \sum \chi_{ik} \]

(29)

where the summation is over individual trajectories, and the characteristic function \( \chi \) is unity for a deactivating trajectory and zero otherwise. The cross length for complex formation is defined analogously; complex forming trajectories are defined to be those with one or more outer turning points in the relative coordinate \( r \).

To compare our planar computations with experimentally determined quenching rates, we must obtain an effective three-dimensional cross section using our planar results. In terms of the opacity function, the three-dimensional cross section is

\[ \sigma_{3D} = 2\pi \int_0^{\infty} db \Pi_{3D}(b)b. \]

(30)

In the spirit of the centrifugal sudden approximation, we now assume that

\[ \Pi_{3D}(b) \approx \Pi(b), \]

(31)

i.e., the opacity function for three-dimensional collisions can be approximated by that obtained in our planar calculations. In terms of a sum over bins \( i \)

\[ \sigma_{3D} \approx 2\pi \frac{b_{\text{max}}}{N} \sum b_i \Delta N_i, \]

(32)

where the summation is over bins \( i \), or as a sum over individual trajectories \( k \),

\[ \sigma_{3D} \approx 2\pi \frac{b_{\text{max}}}{N} \sum \chi_k b_k, \]

(33)

In terms of the effective three-dimensional cross section, the deactivation rate is estimated as

\[ k_q = u \sigma_{3D}. \]

(34)

The use of the planar opacity function to calculate a three-dimensional cross section leads to an overestimate of the deactivation rate (see Sec. IV). A possible explanation is that the planar calculation cannot account for relatively inefficient collisions in which the rotor is oriented out of plane.

IV. RESULTS

A. The quenching rate coefficient

Figure 4 shows our calculated quenching rate coefficient \( k_q \) as a function of the collision energy \( E_r \). The potential surface used is that described in Sec. III. The plot shows a broad minimum in the region of 0.33 eV, which is the depth of the chemical well between Kr and \( \text{O}_2^+ \). It can be seen from Fig. 4 that the behavior of our theoretical rate coefficient \( k_q \) is in reasonable agreement with the experimental results of Kriegl et al., in particular, the upturn in the rate at the lowest experimental collision energies is well reproduced. Our use of planar trajectory results to define an effective three-dimensional cross section overestimates the rate coefficient by a factor of \( \sim 6 \) (the theoretical results have been scaled to match the experimental point at \( E = 0.147 \) eV).

These results therefore confirm the finding of Tosi et al. that quasiclassical trajectory calculations with a suitable model potential surface are able to reproduce the observed dependence of the quenching rate coefficient on relative translational energy. Moreover, at very low collision energies, our trajectory results show a leveling off of the rate coefficient in accord with the recent experiments of Hawley and Smith. In the rest of this paper we examine the mechanism of deactivation in further detail.

B. Collisional energy transfer

The average energy transfer into or out of translation, rotation, and vibration was calculated separately for deactivating and nondeactivating trajectories. These values are plotted as a function of the collision energy in Fig. 5.

Several broad trends can be seen in Fig. 5. At high collision energies, all trajectories gain rotational energy and lose translational energy. Trajectories for which vibrational deactivation occurs lose more translational energy than nondeactivating trajectories.

A strong correlation between rotational excitation and excitation of stretching vibrations has previously been found by Kreutz and Flynn in collisions of fast H atoms with \( \text{CO}_2 \). For this system, a simple breathing ellipsoid model provides a useful basis for analysis of experimental results. In essence, excitation of stretching modes of \( \text{CO}_2 \) is most probable for those collisions in which the momentum transfer has a significant component along the \( \text{CO}_2 \) (semi-major) axis. Such collisions, which occur predominantly...
C. Single versus multiple turning point collisions

In Fig. 6 we decompose the total vibrational quenching rate of Fig. 4 into contributions from trajectories with a single turning point (STP) in the relative coordinate $r$ and those with multiple turning points (MTP); these are complex forming by definition. There is a substantial contribution to vibrational quenching from STP (i.e., direct) trajectories down to the very lowest energies (cf. Fig. 7 of Ref. 26), so that deactivation occurs both by direct collisions and via formation of transient complexes even at low energies. The importance of Ferguson's mechanism for explaining the experimental rate data is, however, apparent when we note that the quenching rate due to single turning point trajectories alone shows no upturn in rate at lower energies (cf. Fig. 6), tending instead to a constant value for energies below about 0.1 eV. Note that, at the lowest collision energy studied (0.005 eV), the MTP contribution to the quenching rate itself levels off.

For potentials that tend asymptotically to isotropic ion-induced-dipole form, such as that studied here, the rate of "capture" collisions (i.e., those in which the partners are able to pass over the centrifugal barrier) will at very low collision energies tend to a constant value given by the Langevin rate $2\pi(\alpha/M)^{1/2}$. At low energies, therefore, a constant fraction of the trajectories passing over the centrifugal barrier leads to deactivation of the $O_2^+$ vibration in a single encounter, resulting in a constant value of the direct contribution to the deactivation rate. On the other hand, the contribution of MTP collisions to the rate increases rapidly as $E_d$ decreases and this increase is ascribed in Ferguson's mechanism to the combination of a constant (essentially Langevin) rate for complex formation [$k_c$ Eq. (2)] with an increasing unimolecular decay lifetime for orbiting complexes [$\tau_m$ Eq. (4)].

To shed further light on the vibrational quenching mechanism, we have examined opacity functions $II(b)$ for quenching by different types of trajectory. Figure 7 shows that the opacity function for STP trajectories is flat out to $b_{max}$ and approximately constant for three different energies in the low-energy regime, whereas the opacity function for MTP trajectories is not constant but increases as the collision energy is decreased. Once over the centrifugal barrier, then, trajectories at low energies have an intrinsic probability of deactivating by a direct collision that is essentially independent of collision energy and impact parameter. This lack of dependence of the value of the opacity function on $E_d$ for STP collisions, although inconsistent with the standard LT model, is consistent with a modified LT picture, in which the effective collision kinetic energy...
is gained by rolling into the potential well. For small enough $E$, this effective kinetic energy is independent of $E_t$. As $E_t \to 0$, an increasing fraction of those trajectories that do not deactivate upon the first close encounter are subsequently "turned back," leading to a larger fraction of MTP collisions (Fig. 8).

D. Capture rates, complex lifetimes, and deactivation rates

We now examine in more detail the dynamics of vibrational deactivation of $O_2^+$ by formation of transient orbiting complexes. In Ferguson’s kinetic model,\textsuperscript{10} the rate of formation of orbiting complexes is taken to be approximately equal to the Langevin capture rate, which is independent of $E_t$ for ion-induced-dipole potentials. The observed increase in deactivation rate with decreasing relative translational energy is, in this model, a consequence of the increase in rotational predissociation lifetime $\tau_u$ with decreasing complex energy [Eq. (4)].\textsuperscript{10}

To investigate the validity of this picture, we have calculated $[O_2^+ \cdot \cdot \cdot Kr]$\textsuperscript{8} complex formation rates and complex lifetimes as a function of collision energy $E_t$. Recall that we define a complex forming trajectory to be one having one or more outer turning points in the relative coordinate $r$. In Fig. 9 we plot the effective three-dimensional association (complex formation) rate derived from our planar trajectory calculations as a function of translational energy $E_t$. It can be seen that, far from being approximately constant over the energy range of interest, the rate increases rapidly as $E_t$ decreases before leveling off (cf. Ref. 19). Moreover, even at the lowest collision energy studied ($10^{-2}$ eV), the complex formation rate is only about one-half of the Langevin capture rate (cf. Ref. 19).

The lifetime of an orbiting complex is defined as the time between the first and last inner turning points in $r$.\textsuperscript{19,44} Direct trajectories have zero lifetime by definition. The lifetime distribution for an ensemble of trajectories at fixed $E_t$ can often be reasonably well approximated on a timescale of several picoseconds as an exponential function. Complex lifetimes thus determined are given in Table II. It is apparent that complex lifetimes do not increase drastically over the range of $E_t$ for which orbiting complexes are formed (the range is from 2.0–5.0 ps). Deactivating MTP trajectories have lifetimes that are noticeably longer on the average than nondeactivating MTP trajectories (Table II).

Our computations show that the increase in complex rotational predissociation lifetimes ($\tau_u$) with decreasing
collisional energy \( E_t \) is neither the only nor even the most significant factor accounting for the anomalous quenching behavior of the Kr/O\(_2^+\) system. The dominant factor is the rapid increase in complex formation rate with decreasing collision energy. Even at the lowest collision energies, the complex formation rate coefficient \( k_c \) is only roughly half the value of the Langevin capture rate coefficient. These findings and those of others (Ref. 19 and references therein) on the translational energy dependence of the association rate are of some general interest, as kinetic schemes for ion-molecule reaction rates typically assume that the rate of complex formation is approximately constant and equal to the Langevin capture rate.\(^{47-49}\)

At very low collision energies, the ion-neutral association rate becomes rate determining [cf. Eq. (9)], and the quenching rate will then show the same temperature dependence as the association rate. An approach of the quenching rate to a constant value at very low collision energies has recently been seen experimentally by Hawley and Smith.\(^{13}\)

We have also determined the effect of the O\(_2^+\) vibrational degree of freedom on complex formation by calculating formation rates and lifetimes for trajectory ensembles in which the O\(_2^+\) vibration is frozen. Freezing the vibrational degree of freedom results in a decrease in the complex formation rate and slight changes in lifetimes (Table II). Although complex lifetimes do change in the presence of vibration, neither the directions nor the magnitudes of the changes support the view that storage of energy in diatom vibration is essential for the formation of transient complexes.\(^{30}\) This conclusion is consistent with our computations on the ion-molecule system Na\(^+\)/N\(_2\),\(^{34}\) where the presence or absence of vibration is found to have no effect on the complex lifetime. (In a trajectory study of Cl\(^-\)/CH\(_3\)Cl association, Vande Linde and Hase have found that excitation of CH\(_3\)Cl modes has only a minor effect on lifetimes of Cl\(^-\) ⋯ CH\(_3\)Cl complexes.\(^{50}\) The Kr/O\(_2^+\) complex formation rate does, however, increase noticeably in the presence of vibration. This increase may be understood by noting that, for complex formation (multiple turning points in \( r \)) to occur at low collision energies \( E_t \), it is necessary to transfer only a small amount of energy out of translation into internal degrees of freedom. Classically, even a very small amount of energy transfer into diatom vibration facilitates complex formation.

**TABLE II.** Orbiting complex unimolecular decay lifetimes (picoseconds) and formation probabilities obtained using classical trajectories with and without inclusion of diatom vibration. \( \tau_{\text{tot}} \), complex lifetime for whole ensemble; \( \tau_{\text{vib}} \), lifetime for trajectories that undergo vibrational deactivation; \( \tau_{\text{un}} \), lifetime for nondeactivating trajectories. At high collision energies (marked by an asterisk), lifetime estimates are unreliable due to poor statistics. Complex formation probability \( p_c \), is the ratio of the effective 3D complex formation cross section to \( \pi r_{\text{eff}}^2 \) (cf. Sec. II).

<table>
<thead>
<tr>
<th>( E_t ) (eV)</th>
<th>Vibration included</th>
<th>Vibrationless</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau_{\text{tot}} )</td>
<td>( \tau_{\text{vib}} )</td>
</tr>
<tr>
<td>0.250*</td>
<td>2.02</td>
<td>2.02</td>
</tr>
<tr>
<td>0.143*</td>
<td>2.22</td>
<td>2.13</td>
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<tr>
<td>0.080</td>
<td>2.96</td>
<td>3.39</td>
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<tr>
<td>0.036</td>
<td>4.12</td>
<td>4.73</td>
</tr>
<tr>
<td>0.020</td>
<td>4.10</td>
<td>4.91</td>
</tr>
<tr>
<td>0.010</td>
<td>5.08</td>
<td>6.01</td>
</tr>
</tbody>
</table>

**E. Rotor orientation at inner turning point and trajectory funnelling**

For STP trajectories, there is a strong correlation between vibrational deactivation and the orientation of the diatom (\( \gamma \)) at the inner turning point. Trajectories that deactivate are more likely to approach such that the Kr atom is at or near the chemical well (Fig. 10). All STP trajectories are "funneled" either into one of the deep chemical wells or into one of the two shallow troughs at 90° and 270°, but deactivation occurs solely for those trajectories that access the chemical wells. Trajectory funnelling is most pronounced at low collision energies (Fig. 11).
F. Role of potential anisotropy

The role of potential anisotropy in determining the lifetimes of transient ion-neutral complexes has recently been discussed by Schelling and Castleman and by Brass and Schlier. Tosi et al. have shown that widening the chemical wells in their Kr/O$_2^+$ potential leads to a disappearance of the minimum in the deactivation rate as a function of $E_r$. Variation of the parameter $a$ in our Kr/O$_2^+$ potential of Eq. (19) enables the width of the chemical well to be changed and so allows us to study the effects of potential anisotropy on the quenching dynamics. The potential of Fig. 3 (henceforth, potential I) has $a = 75$. Trajectory calculations were made for two other values of $a$. Potential II ($a = 50$) has somewhat wider chemical wells than potential I [Fig. 12(a)], while potential III ($a = 25$) has very wide wells [Fig. 12(b)]. For potential II, there is a very shallow minimum in $k_d$ versus $E_r$ while for potential III we observe no deactivation at all for collision energies below 0.25 eV (Fig. 13). The angular width of the chemical well in the Kr/O$_2^+$ potential is therefore an important factor in determining the dependence of the quenching rate on collision energy at low energies.

We have attempted to identify the dynamical origin of the anisotropy dependence of the quenching rate. One possibility is that a decrease of potential anisotropy reduces the ion-neutral association rate, thereby reducing the magnitude of the MTP contribution to the deactivation rate. Our trajectory results show that the complex formation rate is not drastically affected by changing the potential anisotropy over the range considered here. Although there is a slight decrease in complex formation rate as the well is widened, the complex formation rate at the lowest collision energy is comparable for all three potentials (Table III). The decrease of deactivation rate at low collision energies for the less anisotropic potentials is not due therefore to inhibition of complex formation. Another possibility is that complex lifetimes are significantly reduced by decreasing the potential anisotropy. Complex lifetimes for the least anisotropic potential (potential III) are several picoseconds longer than those of the other two potentials at low collision energies. As reduced anisotropy implies reduced rotation-translation coupling, it is reasonable that the rotational predissociation lifetime of an orbiting complex will, once formed, be on average longer for potential III than for potential I. It is clear then that changes in ion-
neutral association rates and orbiting complex lifetimes cannot account for the decrease in deactivation rate at low energies with decreasing potential anisotropy.

Our trajectory results show that at low collision energies all deactivating trajectories (both STP and MTP) have at least one turning point in the angle $\gamma$. We have therefore examined the effect of potential anisotropy on the nature of the librational or rocking motion. In Fig. 14(a) we show a distribution of bending frequencies, where the latter were estimated by taking the inverse of twice the time between two successive turning points in $\gamma$ (changes in sign of $p_\gamma$). Care was taken to ensure that the time intervals corresponded to genuine libration in a particular well, rather than motion from one well to another. The librational frequencies were then binned and the fraction of oscillations at a given frequency plotted. Fig. 14(a) shows the distribution of bending frequencies for potentials I, II, and III, where the collisional energy for all three ensembles is 0.01 eV. There is a marked trend towards lower frequencies as the potential well is widened. In Fig. 14(b) we show the distribution of frequencies for deactivating trajectories for potentials I and II; that is, we plot the distribution of librational frequencies estimated for the half cycle just prior to deactivation. It can be seen that deactivating trajectories have higher average bending frequencies on average, approximately $1$ to $5$ the zeroth order vibrational frequency for $O_2^+$ ($v=1$). Our results suggest that particular vibration-libration resonances may be responsible for deactivation at low collision energies. The softening of the bending vibration upon reduction of the potential anisotropy then eliminates the resonances, reducing the quenching rate. More work is, however, required to elucidate the detailed dynamics of the quenching process.

TABLE III. Complex formation rates (a.u.) and lifetimes (picoseconds) for potentials I, II, and III. At high collision energies (marked by an asterisk), lifetime estimates are unreliable due to poor statistics.

<table>
<thead>
<tr>
<th>$E_c$ (eV)</th>
<th>Potential I</th>
<th>Potential II</th>
<th>Potential III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_c$</td>
<td>$\tau_{tot}$</td>
<td>$k_c$</td>
</tr>
<tr>
<td>0.250*</td>
<td>0.0034</td>
<td>2.02</td>
<td>0.0028</td>
</tr>
<tr>
<td>0.143*</td>
<td>0.0131</td>
<td>2.22</td>
<td>0.0096</td>
</tr>
<tr>
<td>0.080</td>
<td>0.0271</td>
<td>2.96</td>
<td>0.0264</td>
</tr>
<tr>
<td>0.036</td>
<td>0.0475</td>
<td>4.12</td>
<td>0.0473</td>
</tr>
<tr>
<td>0.020</td>
<td>0.0548</td>
<td>4.10</td>
<td>0.0576</td>
</tr>
<tr>
<td>0.010</td>
<td>0.0630</td>
<td>5.08</td>
<td>0.0625</td>
</tr>
</tbody>
</table>

V. CONCLUSION AND SUMMARY

The conclusions of our classical trajectory study of vibrational quenching in $O_2^+$/Kr collisions are as follows.

1. We were unable to obtain a satisfactory fit to experimental rate data using one-dimensional transition probabilities, such as the Lennard-Jones/Devonshire or modified Landau-Teller expressions, even when the interaction potential has a minimum (e.g., Morse potential). These results confirm the importance of rotational degrees of freedom in the quenching process.

2. Our quasiclassical trajectory calculations are able to reproduce the observed behavior of the vibrational quenching rate coefficient $k_q$ as a function of collision energy $E_c$ in Kr/$O_2^+$ collisions, in particular, the existence of a minimum, thereby confirming the results of Tosi et al. 25,26

3. At high energies, Kr/$O_2^+$ collisions transfer energy from translation into rotation, whereas at low collision energies both translation and rotation gain energy from vibration.

4. The upturn in the quenching rate at low energies is strictly due to the increasing contribution of complex forming (multiple turning point) trajectories with decreasing $E_c$, as suggested by Ferguson.10 Removing the contribution to the quenching rate from MTP trajectories eliminates the minimum.

5. A major factor governing the translational energy dependence of the quenching rate via complex formation is the marked $E_c$ dependence of the ion-neutral association rate in the energy range of interest. Even at the lowest collision energy studied ($5 \times 10^{-3}$ eV), the association cross section is only one-half of the Langevin value (cf. Ref. 19). This finding is in contrast to the picture of Fer-
guson, in which only the energy dependence of the orbiting complex unimolecular decay lifetime is considered.

(6) Ion-neutral complex lifetimes are of the order of several picoseconds, and vary by a factor of 3 over the energy range of interest. Complex lifetimes are insensitive to the presence or absence of the diatomic vibrational mode.

(7) The quenching rate at low collision energies is very sensitive to variations in potential anisotropy (i.e., the angular width of the potential well). Decreasing the potential anisotropy greatly reduces the quenching rate. This reduction in quenching rate is due neither to a decrease in ion-neutral association rate nor to a decrease in complex lifetime. Our results suggest that the softening of the librational or rocking mode upon widening of the potential well greatly reduces the possibility of resonance with the diatomic vibration, but further work is required on this aspect of the problem.

ACKNOWLEDGMENTS

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1. Interactions between Ions and Molecules, edited by P. Ausloos (Plenum, New York, 1974).
24. R. Parson (private communication).
39. Miklavc’s result [Eq. (48) of Ref. 37] agrees with Cottrell’s semiclassical treatment [Eqs. (6.9)–(6.14) of Ref. 3 except for an extra factor of 4 in the argument of the arctan in Miklavc’s expression, which appears to be due to an algebraic error. Cottrell’s quantum mechanical expression does not tend to his (correct) semiclassical expression, as his expression for the quantum-mechanical transition probability [Eq. (6.54) of Ref. 3] is incorrectly reported from a paper of Blyth (Eq. (1.6) of Ref. 51).