

Vibrational deactivation in planar ion-neutral collisions. A classical trajectory study of the fixed orientation angle approximation

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Vibrational deactivation of O_2^+ ($v=1$) in low-energy collisions with Kr is studied within the framework of planar classical mechanics. An approximation in which the relative orientation of the diatom is fixed fails to describe the extent of vibrational deactivation found in exact planar dynamics. We also consider planar Li^+/N_2 ($v=1$) collisions. For this system, in contrast to Kr/O_2^+ , the vibrational energy transfer is described quite accurately in the fixed-angle approximation.

1. Introduction

There has been much recent interest in the deactivation of vibrationally excited ions in low-energy collisions with neutrals [1]. For several such systems, the vibrational quenching rate shows pronounced deviations from standard Landau-Teller behavior [2] at collision energies smaller than 1.0 eV or so [1]. In some cases, notably Kr/O_2^+ [3], a minimum is observed in the quenching rate versus collision energy (see fig. 3 of ref. [3]).

The origin of the upturn in quenching rate at very low collision energies has been the subject of some discussion [1,4,5]. According to the mechanism proposed by Ferguson [1], vibrational deactivation at very low collision energies proceeds via transient orbiting complexes, formed by transfer of energy from translation into rotational degrees of freedom. Vibrational quenching then occurs upon vibrational predissociation of the orbiting complexes [1]. At higher collision energies, deactivation by direct, impulsive collisions presumably takes over. Classical trajectory studies have shown that deactivation by

both direct and complex forming collisions occurs at low collision energies [5,6].

On the basis of an approximate quantum-mechanical study of vibrational quenching in Li^+/N_2 [4], Tanner and Maricq have however concluded that complex formation and rotational degrees of freedom play no role in the deactivation process [4], and that deviations from standard LT behavior are due solely to the influence of the attractive component of the potential upon an effectively one-dimensional vibrational deactivation probability. They have also proposed a modified Landau-Teller expression to fit the energy dependence of the quenching rate coefficient for Kr/O_2^+ in the energy range of interest. The utility of such expressions is discussed elsewhere [6].

Quantum close-coupling (CC) calculations of vibrational quenching in Kr/O_2^+ including all rotational channels are impractical at present. Rotational decoupling schemes such as the centrifugal sudden approximation (CSA) or infinite-order sudden approximation (IOSA) have long been used to reduce the computational effort required by CC calculations of rotational and vibration-rotation energy transfer in atom-diatom collisions (for reviews, see refs. [7-9]). Tanner and Maricq have applied a combination of the IOSA and the distorted wave approximation to treat vibrational deactivation in Li^+ /

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N_2 , and have mass-scaled these results to describe the Kr/O_2^+ system [4].

Conditions for the validity of the CSA and IOSA for a given system are discussed in refs. [7,8]. In Kr/O_2^+ there is experimental evidence [10] for a chemical well approximately 0.33 eV deep. The existence of the well together with long-range attraction argues against the validity of the CSA for treating rotational energy transfer. On the other hand, the CSA may well be useful for describing vibrational energy transfer occurring via hard, short-range collisions. The H-LL mass combination in Kr/O_2^+ is the worst possible for validity of the IOSA, other factors being equal.

A key aspect of the IOSA calculation of Tanner and Maricq [4] is the solution of the vibrational CC problem at fixed orientation angle [4] (cf. ref. [7]). The vibrational deactivation cross section is then obtained by averaging fixed-angle cross sections over orientation angle [4]. Use of the fixed-angle approximation (FAA) obviously precludes formation of orbiting complexes via T→R energy transfer.

In the absence of quantum CC calculations for comparison, it is natural to investigate the validity of the various sudden approximations using classical mechanics. The classical analogues of the CSA and the IOSA have been considered in refs. [11–13]. Although the classical CS and IOS approximations do not reduce computation time as drastically as the corresponding quantum approximations, they can be used to test the validity of the corresponding quantum approximations subject to the usual limitations of classical and semiclassical methods [14].

In the present paper, we investigate the validity of the classical FAA in the simplest possible context, namely planar collisions. We study vibrational deactivation in Kr/O_2^+ using planar classical dynamics with and without the FAA. We also perform corresponding calculations for Li^+/N_2 .

Use of planar dynamics is of course a severe restriction. Consideration of planar collisions however reduces the number of degrees of freedom to a minimum while allowing inclusion of diatom rotation, thereby facilitating detailed investigation of the dynamics of vibrational deactivation [6]. Moreover, effective 3D vibrational deactivation cross sections extracted from our planar calculations on Kr/O_2^+ have the same dependence on energy as that observed experimentally [3] and in the 3D trajectory

calculations of Tosi et al. [5]. Although a detailed investigation of the relation between planar and 3D dynamics for the systems treated here would be highly desirable, it is our hope that our results provide at least some indication of the validity of the corresponding quantum approximation in the 3D problem.

2. Systems and methods

2.1. Hamiltonian

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

$$\mathcal{H} = \frac{p_s^2}{2\mu} + \frac{p_r^2}{2M} + \frac{p_\gamma^2}{2\mu s^2} + \frac{(J - p_\gamma)^2}{2Mr^2} + V(r, s, \gamma). \quad (1)$$

The coordinates are s , the bond length of the diatom, r , the distance from the atom to the diatom center of mass, and γ , the angle between the diatom axis and the vector from the diatom center of mass to the atom. Note that $0 \leq \gamma \leq 2\pi$ for planar motion. Momenta conjugate to these coordinates are p_s , p_r and p_γ , respectively. The reduced mass of the diatom is μ 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 γ .

2.2. Kr/O_2^+ potential

We use the potential developed for the Kr/O_2^+ system in our previous paper [6], which is based on the potential used in the work of Tosi et al. [5]. This potential successfully reproduces the observed dependence of the vibrational quenching rate on the relative translational energy E_t [3] in the Kr/O_2^+ system, and is also consistent with experimental data on the angle and depth of the strong interaction between the Kr atom and the O_2^+ diatom [10].

The potential function consists of three parts:

$$V(r, s, \gamma) = V_{O_2^+} + V_{\text{isotropic}} + V_{\text{anisotropic}}. \quad (2)$$

The first term $V_{O_2^+}$ describes a Morse potential for the isolated O_2^+ diatomic, with parameters deter-

mined from spectroscopic data [15]. The second term $V_{\text{isotropic}}$ consists of a long-range ion/induced-dipole attraction plus a short-range exponential repulsion term. The third term $V_{\text{anisotropic}}$ models the strong "chemical" interaction between Kr and O_2^+ . The potential function eq. (2) is described in detail in ref. [6]; contours are shown in fig. 1a.

2.3. Li^+/N_2 potential

Following Tanner and Maricq [4], we use the Li^+/N_2 potential of Billing [16], which is a 19 pa-

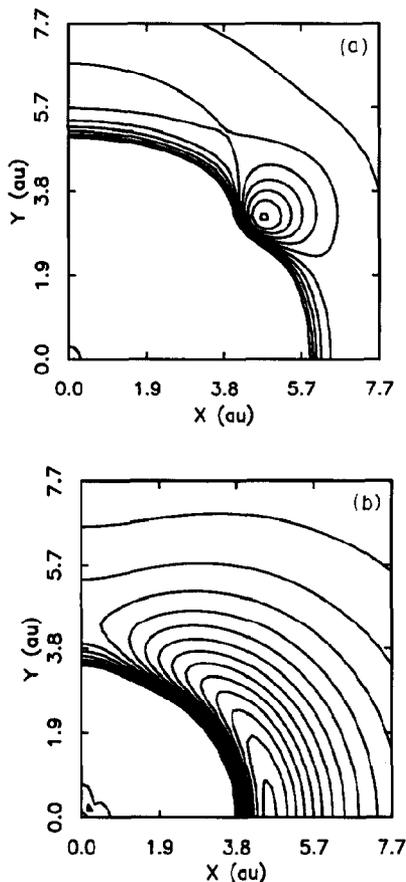


Fig. 1. (a) Contour plot of the Kr/O_2^+ potential [6]. The O_2^+ molecule lies along the x axis, with the midpoint of the O-O bond at the origin. The O-O bond length is fixed at $s=s_e=2.109$ au. Contours are at multiples of 0.046 eV. (b) Contour plot for the Li^+/N_2 potential [16]. The N_2 molecule lies along the x axis, with the midpoint of the N-N bond at the origin. The N-N bond length is fixed at $s=s_e=2.067$ au. Contours are at multiples of 0.046 eV.

rameter fit to an ab initio potential energy surface. The form of this potential is given in ref. [16]. A contour plot is shown in fig. 1b, where contours are at 0.046 eV intervals as in fig. 1a. Note that the interaction well depth of this potential is much deeper (about 0.6 eV) than that for the Kr/O_2^+ potential.

2.4. Classical fixed-angle approximation

The FAA considered here is an essential part of the classical IOSA as discussed by Mulloney and Schatz [12] (see also ref. [13]), and our treatment closely follows ref. [12]. In the planar FAA, the rotor degree of freedom is frozen, thereby reducing the number of degrees of freedom by one. Operationally, both orbital angular momentum p_l and rotor angular momentum p_y are held fixed along a trajectory, and are taken to have their initial values l and j , respectively [12]. The Hamiltonian for planar motion in this approximation is then

$$\mathcal{H}_{\text{FAA}} = \frac{p_s^2}{2\mu} + \frac{p_r^2}{2M} + \frac{j^2}{2\mu s^2} + \frac{(J-j)^2}{2Mr^2} + V(r, s; \gamma_i) \quad (3)$$

As the Hamiltonian is independent of the dynamical variable p_γ , the angle γ remains fixed at its initial value, γ_i , and V depends only parametrically on γ_i . Vibrational energy transfer probabilities are calculated by ensemble averaging over the rotor orientation γ_i .

2.5. Selection of initial conditions

Two different trajectory ensembles are used in this paper. The first is that used in our previous study of the Kr/O_2^+ system [6]. At each collision energy 3000 trajectories were run, with a two-dimensional Boltzmann weighted distribution of integral p_y^0 values used for the O_2^+ rotor, corresponding to a rotor temperature of 300 K. For each value of the rotor angular momentum, s^0 and p_s^0 values were chosen uniformly in vibrational angle at fixed vibrational action $J_{\text{vib}}=1.5\hbar$. The angle γ^0 was randomly chosen between 0 and π . The impact parameter b was chosen randomly in the interval $-b_{\text{max}}$ to b_{max} , where b_{max} is a value of impact parameter beyond which vibrational inelasticity is negligible in the exact classical dynamics. Trajectories with final vibrational action

J_{vib} between 0 and $1.0\hbar$ were considered to be deactivated. This set of initial conditions was used to calculate the vibrational quenching cross length for Kr/O_2^+ ($\nu=1$) using both exact planar classical dynamics and the planar fixed-angle approximation.

In the second ensemble, the initial rotor angular momentum p_y^0 was not thermally averaged, but had the same initial value for all trajectories in the ensemble.

Vibrational deactivation is classically dynamically forbidden for Li^+/N_2 , so that as a measure of the deactivation efficiency we compute the sum of the absolute values of the differences between the initial and final vibrational actions of each trajectory divided by the total number of trajectories in the ensemble:

$$\overline{|\Delta J_{\text{vib}}|} = \frac{1}{N} \sum_{n=1}^N |J_{\text{vib}}^{(f)}(n) - J_{\text{vib}}^{(i)}(n)|. \quad (4)$$

3. Results

3.1. Kr/O_2^+

Our classical trajectory results for the vibrational deactivation cross length σ_{planar} (appropriate for planar dynamics) as a function of the collisional energy E_i are shown in fig. 2. The exact planar classical

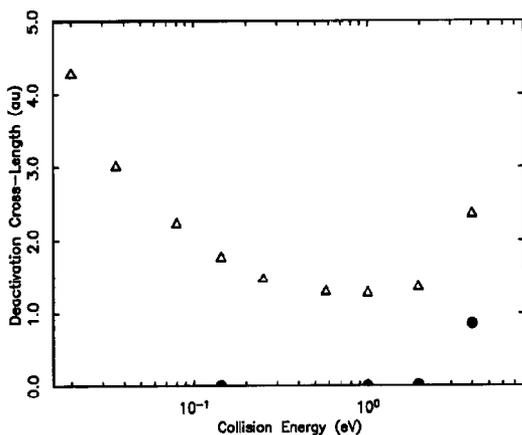


Fig. 2. Vibrational deactivation cross length for $\text{O}_2^+(\nu=1)/\text{Kr}$ as a function of collision energy E_i . (Δ) Exact planar classical; (\bullet) classical planar fixed-angle approximation.

trajectory results are compared with those obtained in the FAA.

The fixed angle results show negligible vibrational deactivation for energies below 1 eV, in marked contrast to the exact planar case. We conclude that the FAA is unable to describe vibrational energy transfer in planar Kr/O_2^+ collisions at low collision energies. The fixed orientation angle approximation is an essential part of the IOSA as applied to vibrational deactivation [4]. The fact that the FAA is so poor at low collision energies is consistent with the suggestion that active involvement of rotational degrees of freedom is essential for vibrational deactivation in the Kr/O_2^+ system [1].

3.2. Li^+/N_2

The vibrational deactivation of N_2 by collision with Li^+ is at a given energy much less probable than quenching in the Kr/O_2^+ system. In fact, just as for He/N_2^+ [17], vibrational deactivation in Li^+/N_2 is classically dynamically forbidden at thermal collision energies [14] (it is classically dynamically allowed for Kr/O_2^+). In fig. 3 we therefore plot the average absolute change in vibrational action as a function of collision energy E_i obtained for planar dynamics with and without the FAA for an initial rotor action of $2\hbar$. This plot shows that the planar FAA results follow the trend of exact planar me-

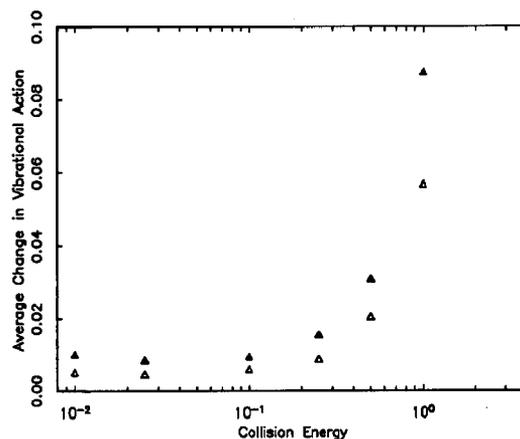


Fig. 3. Average magnitude of vibrational action change for $\text{Li}^+/\text{N}_2(\nu=1)$ as a function of collision energy E_i . (\blacktriangle) Exact planar classical; (\triangle) classical planar fixed-angle approximation.

chanics as a function of E_i quite closely, although the vibrational inelasticity is smaller in the FAA. At very low energies there is a slight upturn in the inelasticity for both exact planar and FAA trajectories. The classical FAA therefore qualitatively reproduces the extent of vibrational energy transfer in planar Li^+/N_2 .

Our results show that the classical FAA is a useful approximation for Li^+/N_2 , and we may conclude that rotational degrees of freedom are not as important as they are for Kr/O_2^+ .

3.3. Comparison of Kr/O_2^+ and Li^+/N_2

There are as yet no experimental data on the collision energy dependence of the quenching rate at low collision energies for Li^+/N_2 (although deactivation rates have been measured at high energies [18]), so that the extent of anomalous quenching is unknown. Vibrational deactivation is moreover dynamically forbidden in classical mechanics [14]. We can nevertheless compare our planar classical trajectory results for the two systems Kr/O_2^+ and Li^+/N_2 .

The classical planar dynamics of these two systems shows striking differences. Classical trajectory calculations for Kr/O_2^+ are able to reproduce the nonmonotonic experimental behaviour of the quenching rate coefficient as a function of collision energy [5,6]. Within the approximation of planar dynamics, the classical FAA fails completely for Kr/O_2^+ . For Li^+/N_2 , on the other hand, classical planar FAA calculations are in quite reasonable, though not quantitative, agreement with exact planar trajectory results.

In our previous work on the Kr/O_2^+ system [6], we have shown that the anisotropy of the interaction potential has a strong influence on the probability of vibrational deactivation at low collision energies (cf. also ref. [5]). Furthermore, we indicated that this effect could be due to the importance in vibrational deactivation of transient resonances between bending (libration/hindered rotation) and diatom stretching [6]. Reduction of potential anisotropy leads to a softening of the libration mode and lower bending frequencies, which are not as effective in coupling to vibration [6]. Comparing the potential contours for Kr/O_2^+ and Li^+/N_2 (figs. 1a and 1b) we see that, although the interaction well depth in Li^+/N_2 is greater than in Kr/O_2^+ , the Li^+/N_2 well

is much broader. It is then reasonable that the smaller anisotropy of the Li^+/N_2 potential reduces the importance of the type of rotation-vibration interaction that occurs in Kr/O_2^+ .

4. Conclusions

We have investigated the accuracy of a classical fixed orientation angle approximation for describing vibrational deactivation in planar ion-neutral collisions. We emphasize again that use of planar dynamics is a drastic approximation.

The following results and conclusions were obtained:

(1) We recall that both 3D [5] and planar [6] classical trajectory treatments of vibrational quenching in Kr/O_2^+ collisions are able to reproduce the experimentally observed [3] non-monotonic dependence of the deactivation rate on collision energy. The planar classical fixed angle approximation however fails completely to describe vibrational energy transfer at low collision energies in Kr/O_2^+ . Active involvement of the rotational degree of freedom is essential for classical vibrational deactivation at low collision energies in planar Kr/O_2^+ .

(2) Planar trajectory studies of vibrational deactivation in Li^+/N_2 show that, in contrast to Kr/O_2^+ , this process is classically dynamically forbidden in the energy range of interest.

(3) The classical planar FAA for Li^+/N_2 gives results in qualitative agreement with exact planar trajectory results for the average magnitude of the change in vibrational action, although the FAA consistently underestimates the vibrational inelasticity.

(4) The above points lead us to conclude that, in the planar approximation at least, the mechanism of vibrational energy transfer in Li^+/N_2 is different from that in Kr/O_2^+ . Rotation-vibration and rotation-translation interaction appears to be much less important in Li^+/N_2 , and the classical FAA is of some utility in treating the deactivation.

It remains for future work to study the validity of rotational decoupling approximations for vibrational deactivation in the 3D case. The results obtained here for planar collisions however suggest that the use of mass-scaled quantum DWA/IOSA results

for Li^+/N_2 to describe vibrational deactivation in Kr/O_2^+ should be viewed with some caution [4].

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