A classical model for electronically non-adiabatic collision processes is applied to E → V energy transfer in a collinear system, A + BC (ν = 1) → A* + BC (ν = 0), resembling Br−H₂. The model, which treats electronic as well as translational, rotational, and vibrational degrees of freedom by classical mechanics, describes the resonance features in this process reasonably well.

1. Introduction

A series of papers [1–5] over the last few years has developed and applied a classical model for treating electronically non-adiabatic processes in molecular collisions. The novel feature of this model is that electronic, as well as heavy-particle (i.e. translation, rotation, and vibration) degrees of freedom are described by classical mechanics, and its attractiveness from a practical point of view is that calculations can be carried out within the framework of standard Monte Carlo classical trajectory methodology [6].

One of the motivations for developing this completely classical model was the realization [7] that “mixed” dynamical models — i.e. those which characterize some degrees of freedom by classical mechanics and others by quantum mechanics — fail to describe some features of the dynamics correctly. The very popular and often successful surface-hopping model [8], for example, which treats heavy-particle motion classically but electronic degrees of freedom quantum mechanically (as states, i.e. distinct potential energy surfaces), is unable to describe resonance effects between electronic and heavy-particle degrees of freedom. Such resonance effects are important in the quenching of excited fluorine atoms (2P₁/2) by collision with H₂ [9] because the 404 cm⁻¹ excitation energy of fluorine is roughly equal (within ≈10%) to the energy of the 0 → 2 rotational excitation of H₂. Similarly, Br* (2P₁/2) is thought [10] to be quenched efficiently by H₂ because the vibrational quantum of H₂ approximately matches the 3685 cm⁻¹ excitation energy of bromine. Since the classical model [1–5] treats all degrees of freedom on the same dynamical footing, i.e. by classical mechanics, it has been reasoned that it should be able to describe these aspects of resonance energy transfer at least qualitatively correctly. To see how quantitative the model is, however, requires numerical applications, and such is the purpose of this paper.

Earlier calculations [4] have shown that the classical model does indeed provide a reasonably good description of the resonance effect between electronic and rotational degrees of freedom in F−H₂ collisions,

\[ F^*(2P_{1/2}) + H₂ (ν = 0) \rightarrow F(2P_{3/2}) + H₂ (ν = 2). \quad (1) \]

The cross section for this process is much larger at low collision energies than for quenching by a comparable inert-gas atom that does not have rotational degrees of freedom. The present paper considers a simple model of electronic–vibrational energy transfer that would pertain, for example, to the quenching of Br* by H₂,

\[ Br^*(2P_{1/2}) + H₂ (ν = 0) \rightarrow Br(2P_{3/2}) + H₂ (ν = 1). \quad (2) \]

The particular example we consider is the collinear version of such a system for which Lee et al. [11] have recently carried out quantum-mechanical coupled-
channel calculations. Lee et al.'s calculations provide the exact results for this model problem, which can thus serve as a benchmark to see how well the classical model is able to describe such non-adiabatic processes.

Section 2 defines the system treated by Lee et al. and briefly summarizes the classical model as it applies to this example. The results are discussed in section 3.

2. The model

Lee et al. [11] consider a collinear atom–diatomic collision system, A + BC, with two potential energy surfaces, i.e. two electronic states, corresponding to ground and excited states of the atom A. The 2 × 2 diabatic interaction potential surface matrix is

\[
\begin{pmatrix}
V_{00}(R, r) & V_{01}(R, r) \\
V_{10}(R, r) & V_{11}(R, r)
\end{pmatrix} = \begin{pmatrix}
\lambda/3 & \lambda^{1/2}\lambda/3 \\
\lambda^{1/2}\lambda/3 & -\lambda/3
\end{pmatrix}
\]

where \( r \) is the vibrational coordinate of BC and \( R \) the translational coordinate, the distance of A to the center of mass of BC. It is useful to make a unitary transformation of this potential matrix to diagonalize the first term, the atomic part of the interaction that survives as \( R \to \infty \). The appropriate unitary transformation matrix is

\[
U = \begin{pmatrix}
(\frac{\lambda}{3})^{1/2} & (\frac{\lambda}{3})^{1/2} \\
-(\frac{\lambda}{3})^{1/2} & (\frac{\lambda}{3})^{1/2}
\end{pmatrix}
\]

and for the transformed potential matrix \( \tilde{V} \),

\[ \tilde{V} \approx U^\dagger \cdot V \cdot U \]

one obtains

\[
\begin{pmatrix}
\tilde{V}_{00} & \tilde{V}_{01} \\
\tilde{V}_{10} & \tilde{V}_{11}
\end{pmatrix} = \begin{pmatrix}
0 & 0 \\
0 & \lambda
\end{pmatrix}
\]

\[ + \exp[-\alpha(R - \frac{1}{2}r - \rho_0)] \begin{pmatrix}
A_{00} & A_{01} \\
A_{10} & A_{11}
\end{pmatrix}, \] (6)

where

\[ A_{00} = \frac{1}{3}A_0 + \frac{1}{3}A_1, \]

\[ A_{01} = \frac{1}{2}A_0 + \frac{3}{2}A_1, \] (7a)

\[ A_{10} = A_{10}(2^{1/2}/3)(A_1 - A_0), \] (7b)

\[ A_{01} = \frac{1}{2}A_0 + \frac{3}{2}A_1 \cdot (2^{1/2}/3)(A_1 - A_0). \] (7c)

The classical model [1–5] for the electronic degrees of freedom replaces the diabatic potential matrix \( \tilde{V}_{N,N'}(R, r) \), \( N, N' = 0, 1 \) of eqs (7) by a classical electronic hamiltonian \( \tilde{V}(R, r, N, Q) \) which is defined in terms of the matrix elements by

\[ \tilde{V}(R, r, N, Q) = N\tilde{V}_{11}(R, r) + (1 - N)\tilde{V}_{00}(R, r) \]

\[ + 2\tilde{V}_{01}(R, r)[(N + \frac{1}{2})(\frac{3}{2} - N)]^{1/2} \cos Q. \] (8)

\( N, Q \) are the classical action–angle variables [12] for the electronic degrees of freedom; i.e. \( N \) is the classical electronic quantum number. With eq. (6) one notes that as \( R \to \infty \), eq. (8) becomes

\[ \tilde{V}(R \to \infty, r, N, Q) = N\lambda, \] (9)

thus \( N \) is a conserved quantity in the asymptotic region, with \( N = 0 \) corresponding to the ground electronic state of atom A (with energy 0) and \( N = 1 \) to the excited state \( \Lambda^* \) (with energy \( \lambda \)).

To obtain the classical hamiltonian for the complete system one adds to \( \tilde{V}(R, r, N, Q) \) the potential energy for free vibrational motion of BC and the kinetic energy for vibration and translation, and with eqs. (6) and (8) this gives

\[
H(P, R, p, r, N, Q) = \frac{p^2}{2\mu} + \frac{r^2}{2m} + \frac{1}{2}m\omega^2(r - r_0)^2 \]

\[ + \lambda N^2 + \exp[-\alpha(R - \frac{1}{2}r - \rho_0)] \{(1 - N)\tilde{A}_{00} + N\tilde{A}_{11} \}
\]

\[ + 2\tilde{A}_{01}[N + \frac{1}{2}][(\frac{3}{2} - N)]^{1/2} \cos Q], \] (10)

where \( m \) and \( \mu \) are the reduced masses for BC vibration and A–BC translation, respectively. To obtain the final form of the classical hamiltonian one replaces the vibrational coordinate and momentum \( (r, p) \) by their action–angle variables [12] \( (n, q) \),

\[ r - r_0 = [(2n + 1)m\omega]^{1/2} \cos q, \] (11a)

\[ p = -[(2n + 1)m\omega]^{1/2} \sin q \] (11b)

giving
The results presented in the next section correspond to implementation of the classical model within the framework of both the standard histogram approach \cite{6,13} and also the classical moment method \cite{14,15}. Thus to compute the probability for the following vibration-to-electronic transition,

\[ A + BC(n = 1) \rightarrow A^* + BC(n = 0) , \]

one integrates Hamilton's equations (generated from the hamiltonian of eq. (12) with initial conditions

\[ n(t_1) = 1 \equiv n_1 , \quad N(t_1) = 0 \equiv N_1 , \]

\[ q(t_1) = q_1 , \quad Q(t_1) = Q_1 , \quad R(t_1) = \text{large} , \]

\[ P(t_1) = - (2\mu[E - (n_1 + \frac{1}{2})\omega - N_1])^{1/2} . \]

If \( n_2(q_1, Q_1) \) and \( N_2(q_1, Q_1) \) are the final vibrational and electronic quantum numbers, respectively, that result from a classical trajectory with these initial conditions, then the histogram approximation to the transition probability is

\[ P_{n_2N_2-n_1N_1} = (2\pi)^{-2} \int_0^{2\pi} dq_1 \int_0^{2\pi} dQ_1 \chi(q_1, Q_1) \]

where \( \chi = 1 \) if \( |n_2(q_1, Q_1) - n_2| \leq \frac{1}{2} \) and \( |N_2(q_1, Q_1) - N_2| \leq \frac{1}{2} \), and \( \chi = 0 \) zero otherwise. The classical moment method, on the other hand, determines the transition probabilities by equating the lower-order classical moments of the quantum-number changes to their quantum-mechanical expressions,

\[ M_{\alpha,\beta} = (2\pi)^{-2} \int_0^{2\pi} dq_1 \int_0^{2\pi} dQ_1 [n_2(q_1, Q_1) - n_1]^\alpha \]

\[ \times [N_2(q_1, Q_1) - N_1]^\beta \]

\[ = \sum_{n_2,N_2} (n_2-n_1)^\alpha(N_2-N_1)^\beta P_{n_2N_2-n_1N_1} , \]

where one must invert these equations algebraically to express the transition probabilities in terms of the classical moments. The results depend on how many terms are retained in the sum over final quantum state and thus on how many moments are used to determine the transition probabilities, the rule of thumb is to include all \((n_2, N_2)\) values for states that are "classically allowed" transitions from the initial state \((n_1, N_1)\).

Since \( N_2 \) can only take on values 0 and 1, it is clear that one should use moments with \( \beta = 0, 1 \). For the present system with initial state \((n_1, N_1) = (1, 0)\), \( n_2(q_1, Q_1) \) attains values corresponding to \( n_2 = 0, 1, 2 \), so this suggests using moments with \( \alpha = 0, 1, 2 \), and thus was indeed found to be the best choice, i.e. using more or fewer moments of \( \Delta n \) does not give as good agreement with quantum-mechanical results. Using these moments, therefore, one obtains the following expression for the \((10 \rightarrow 01)\) transition probability \( \text{eq. (13)} \),

\[ P_{01-10} = \frac{1}{2}(M_{21} - M_{11}) \]

\[ = (2\pi)^{-2} \int_0^{2\pi} dq_1 \int_0^{2\pi} dQ_1 N_2(q_1, Q_1) \]

\[ \times [1 - n_2(q_1, Q_1)] [1 - \frac{1}{2}n_2(q_1, Q_1)] . \]

The parameters in the classical hamiltonian, eq. (12), which correspond to Lee et al.'s \cite{11} calculations are

\[ \omega = 0.02 , \quad \alpha = 3 , \]

\[ R_0 = 4.7 , \quad A_{00} = \frac{1}{3} \times 10^{-5} , \]

\[ m = 1000 , \quad A_{11} = \frac{13}{3} \times 10^{-5} , \]

\[ \mu = 3896.1 , \quad A_{01} = (2^{3/2}/3) \times 10^{-5} . \]

These values, in atomic units, correspond roughly to the \( \text{Br} - H_2 \) system. The parameter \( \lambda \), the \( A \rightarrow A^* \) excitation energy, is varied in these model calculations to assess the significance of resonance in the electronic-vibrational energy transfer. Exact resonance, for example, corresponds to \( \lambda = \omega = 0.02 \), so for very low translational energies, where resonance considerations are most important, one would expect the transition probability for eq. (13) to be largest for \( \lambda \approx 0.02 \). By varying \( \lambda \) one can see how prominent the resonance effect is and how well the classical model is able to describe it.
Results and discussion

Figs 1–3 show the transition probability for eq (13) as a function of the atomic excitation energy \( \lambda \), for an initial translational energy \( E_{\text{tr}} = 0.01 \text{ eV} \). The solid curve is the exact quantum result of Lee et al [11], the dashed curve the result given by the classical model with the histogram approximation [eq (15)], and the dotted curve the result of the classical model with the moment method [eq (17)].

As expected, the resonance structure is sharpest at the lowest translational energy; i.e., in fig. 1 the transition probability peaks sharply at \( \lambda \approx 0.02 \). At higher translational energy the resonance structure broadens and shifts.

The significant point to note is that this classical model correctly describes the resonance features in this process, and in particular the moment version of the classical model is in excellent agreement with the quantum-mechanical results. The results of the histogram approach show the correct qualitative features of the resonance structure but are not as satisfactory quantitatively. The shortcomings of the histogram approach are perhaps not unexpected since so few final states are populated in this example.

It is extremely encouraging that this classical model for electronic degrees of freedom is able to describe this electronically inelastic process so well. If this degree of accuracy proves to be typical, then one has a dynamically consistent classical trajectory model for treating both electronically non-adiabatic as well as adiabatic collision processes.

Acknowledgement

The authors would like to thank Professor T.F. George and his associates for providing us with the quantum-mechanical results at the lowest energy \( E_{\text{tr}} = 0.01 \text{ eV} \), which were not originally computed and reported in ref. [11]. This work has been supported in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of
Energy under contract No. W-7405-Eng-48. All calculations were carried out on a Harris H800 minicomputer funded by a National Science Foundation Grant CHE-79-20181

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