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CLASSICAL S-MATRIX CALCULATION FOR VIBRATIONALLY INELASTIC TRANSITIONS IN THREE DIMENSIONAL COLLISIONS OF Li^+ WITH H_2*

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ABSTRACT

The "partially averaged" version of classical S-matrix theory is applied to three-dimensional collisions of Li^+ with H_2. For an initial collision energy of 0.684 eV cross sections for the vibrational de-activation of H_2 from the initial state $(n_1,j_1) = (1, 0)$ to final states (n_2,j_2), $n_2 = 0$, $j_2 = 0, 2, 4,\ldots$ are computed and compared with the recent quantum mechanical coupled channel calculations of Schaefer and Lester. The agreement is quite good, indicating that this approach is an accurate and practical way of describing these weak, "classically forbidden" processes which cannot be treated by ordinary classical trajectory methods.

I. INTRODUCTION.

Vibrationally inelastic processes in three dimensional A + BC collision systems at low energy present an extremely difficult task for molecular collision theory. Because such transitions are typically "classically forbidden" (i.e., weak) processes, it is in general not possible to employ the usual classical trajectory methods[1] that work well for describing "classically allowed" , or strong transitions. Since the process is weak, one might think that quantum mechanical perturbation theory (i.e., the distorted wave Born approximation) would be applicable--as it is for the collinear version of the problem[2]--but in the three dimensional A + BC system there are typically a large number of rotational states that are strongly coupled, invalidating the normal distorted wave Born approximation.[3] It is this feature--the large number of strongly coupled rotational states--which also makes the complete quantum mechanical approach, i.e., a coupled channel calculation, often impractical unless dynamical approximations are introduced to simplify it.[4]

Classical S-matrix theory[5]--a semiclassical model which combines exact classical dynamics (i.e., numerically computed trajectories) and the quantum principle of superposition--turns out to be well suited for this situation, for as will be seen below, it is possible to cast it in a form that allows one to treat classical-like rotational degrees of freedom within the spirit of a normal trajectory calculation, while simultaneously quantizing the quantum-like vibrational degree of freedom

semiclassically. It is important, too, that this "partial averaging" technique entails no dynamical approximations; the only approximations beyond that of classical S-matrix theory itself are neglect of interference effects, which are presumably quenched by the average over various quantum states, and the assumption that there are a large number (i.e., more than two or three) of final rotational states populated by the vibrationally inelastic transition. The practical simplifications that result from this "partially averaged" version of the theory are substantial and appear to make it quite a practical and accurate way of calculating cross sections for these processes.

There are a number of other approaches[6-8] for treating this problem which are also "semiclassical" in nature. Some of these[6] are various versions of the classical path, or impact parameter model in which a classical trajectory is assumed for the translational motion, this determining a time-dependent perturbation for the internal degrees of freedom; inelastic transitions are then described by a time-dependent Schrödinger equation for the internal degrees of freedom. Other models[7] use full classical trajectories and invoke a correspondence between the average classical and the average quantum mechanical energy transfer. Although these approaches may be useful in some situations, it is clear that they involve dynamical approximations which invalidate their general applicability; these dynamical approximations--primarily a de-coupling of the translational motion and inelastic dynamics itself--are particularly poor in the case of low collision energy and a weak inelastic transition.

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Section II first summarizes the theory with particular attention to the "partial averaging" analysis, and Section III discusses some aspects of the numerical methods involved. The results for the $1 \rightarrow 0$ vibrational deactivation of H_2 by Li^+ are presented in Section IV and compared to the coupled channel quantum mechanical results of Schaefer and Lester.[9] These are the most extensive coupled channel calculations yet carried out for any three dimensional A + BC collision process, and the excellent agreement between these values and the present semiclassical results is quite encouraging.

II. THEORETICAL SUMMARY; PARTIAL AVERAGING.

The expressions pertinent to the application of classical S-matrix theory to nonreactive A + BC collisions in three dimensions have been given previously,[5,10] and the partial averaging technique has also been discussed briefly.[10,11] Here we wish to summarize the appropriate expressions and to describe the partial averaging idea more fully. In doing so, it is illustrative to consider first the case of a classically allowed transition.

A. Classically Allowed Case.

The integral cross section for the $n_1 j_1 \rightarrow n_2 j_2$ vibrational-rotational transition,

$$A + BC(n_1 j_1) \rightarrow A + BC(n_2 j_2) \quad , \tag{2.1}$$

summed and averaged over the m-components of the rotational states, is given by

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) = \frac{\pi}{k_1^{\,2}(2j_1 + 1)} \sum_{J,\ell_1,\ell_2} (2J+1) \left| S_{n_2 j_2 \ell_2, n_1 j_1 \ell_1}(J,E) \right|^2 , \tag{2.2}$$

where n, j, and ℓ denote vibrational, rotational, and orbital angular momentum quantum numbers, respectively; J is the total angular momentum quantum number, $E_1 = \hbar^2 k_1^{\,2}/2\mu$ is the initial collision energy, and $E = E_1 + \varepsilon(n_1, j_1)$ the total energy.

Because of the sums over the various quantum number labels in Eq. (2.2), it has been noted[5,12] that interference effects in the S-matrix elements--which are prominent in <u>individual</u> matrix

elements--are often quenched. If interference effects are discarded--and if the $n_1 j_1 \to n_2 j_2$ transition is classically allowed--then the square modulus of the classical S-matrix element is given by[5]

$$|S_{n_2 j_2 \ell_2, n_1 j_1 \ell_1}(J,E)|^2 = \left[(2\pi)^3 \left| \frac{\partial(n_2 j_2 \ell_2)}{\partial(\bar{q}_{n_1} \bar{q}_{j_1} \bar{q}_{\ell_1})} \right| \right]^{-1} . \qquad (2.3)$$

The meaning of the Jacobian determinant in Eq. (2.3) is the usual:[5] A complete set of initial conditions for the A + BC classical trajectory are, in action-angle variables, E, J, n_1, j_1, ℓ_1, $\bar{q}_{n_1}$, $\bar{q}_{j_1}$ and $\bar{q}_{\ell_1}$, the small q's being the angle variables conjugate to the corresponding action variables, or "quantum numbers"; with n_1, j_1, and ℓ_1 (and J and E) held fixed, the initial angle variables $\bar{q}_{n_1}$, $\bar{q}_{j_1}$, and $\bar{q}_{\ell_1}$ are chosen so that the final quantum numbers resulting from the trajectory are the desired integer values, i.e., so that the equations

$$\begin{aligned} n_2(\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1}) &= n_2 \\ j_2(\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1}) &= j_2 \\ \ell_2(\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1}) &= \ell_2 \end{aligned} \qquad (2.4)$$

are satisfied. (n_2, j_2 and ℓ_2, written without arguments, are specific integer values; written with arguments, they are the specific final values--not necessary integral--which result from the classical trajectory with the indicated initial conditions.) The Jacobian in Eq. (2.3) is evaluated at the root of Eq. (2.4).

With Eq. (2.3), Eq. (2.2) becomes

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) = \frac{\pi}{k_1^{\,2}(2j_1 + 1)} \int dJ \int d\ell_1 \int d\ell_2 \, \frac{(2J + 1)}{(2\pi)^3} \left| \frac{\partial(n_2 j_2 \ell_2)}{\partial(\bar{q}_{n_1} \bar{q}_{j_1} \bar{q}_{\ell_1})} \right|^{-1} , \quad (2.5)$$

where it has been assumed that enough integer values contribute to the sums over ℓ_1, ℓ_2, and J to replace the sums by integrals. Furthermore, if there are at least a few values of n_2 and j_2 that are classically allowed transitions from the initial state (n_1, j_1), then it is reasonable--and greatly simplifies matters--to treat n_2 and j_2 as continuous variables and to average Eq. (2.5) over a quantum number width[13] about n_2 and j_2, i.e., to assume

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) \simeq \int_{n_2 - \frac{1}{2}}^{n_2 + \frac{1}{2}} dn_2 \int_{j_2 - \frac{1}{2}}^{j_2 + \frac{1}{2}} dj_2 \; \sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) \quad . \qquad (2.6)$$

Carrying out this averaging procedure, Eq. (2.5) becomes

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) = \frac{\pi}{k_1^{\,2}(2j_1 + 1)} \int dJ \int d\ell_1 \int dn_2 \int dj_2 \int d\ell_2 \, \frac{(2J + 1)}{(2\pi)^3} \left| \frac{\partial(n_2 j_2 \ell_2)}{\partial(\bar{q}_{n_1} \bar{q}_{j_1} \bar{q}_{\ell_1})} \right|^{-1} \quad (2.7)$$

and the simplification resulting from this averaging procedure is now clear: Eq. (2.7) involves an integral over all final quantum numbers n_2, j_2 and ℓ_2, so that a change of variables of integration from (n_2, j_2, ℓ_2) to their conjugate initial conditions $(\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1})$--i.e.,

$$\int dn_2 \int dj_2 \int d\ell_2 = \int d\bar{q}_{n_1} \int d\bar{q}_{j_1} \int d\bar{q}_{\ell_1} \left| \frac{\partial(n_2 j_2 \ell_2)}{\partial(\bar{q}_{n_1} \bar{q}_{j_1} \bar{q}_{\ell_1})} \right| \tag{2.8}$$

--introduces a Jacobian factor which <u>exactly</u> <u>cancels</u> the one in Eq. (2.7). Eq. (2.7) thus becomes

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) = \frac{\pi}{k_1^{\,2}(2j_1 + 1)} \int d\ell_1 \int dJ \int d\bar{q}_{n_1} \int d\bar{q}_{j_1} \int d\bar{q}_{\ell_1} \frac{(2J + 1)}{(2\pi)^3}$$

$$\chi_{n_2 j_2 \leftarrow n_1 j_1}(\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1}, \ell_1, J, E) \tag{2.9}$$

where the characteristic function χ is 1 if the final vibrational and rotational quantum numbers which result from the trajectory with the indicated initial conditions fall in the increments[13] $(n_2 - \frac{1}{2}, n_2 + \frac{1}{2})$ and $(j_2 - \frac{1}{2}, j_2 + \frac{1}{2})$, respectively, and is 0 otherwise. The most important practical advantage of Eq. (2.9) is that all reference to double-end boundary conditions--i.e., the root-search problem, Eq. (2.4)--has been eliminated, and it is now necessary to deal with trajectories only through their initial conditions. In practice, too, one sweeps all the integration variables, i.e., the initial conditions, through their complete domains, assigning the final values of n_2 $(\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1})$ and $j_2(\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1})$ to the appropriate quantum number "boxes", thus generating in one calculation the cross sections from (n_1, j_1) to all classically allowed final states.

The reader will recognize that the above prescription is the standard quasi-classical trajectory procedure[1] if the integrals

are evaluated by Monte Carlo methods. To see this even more concretely, note that the limits of integration for ℓ_1 and J are

$$\ell_1 = 0 \to \infty$$

$$J = |j_1 - \ell_1| \to (j_1 + \ell_1) \quad ,$$

and one normally replaces ℓ_1 by the impact parameter b,

$$b \equiv (\ell_1 + \tfrac{1}{2})/k_1 \quad ,$$

and J by the variable z

$$J + \frac{1}{2} = \left[(\ell_1 - j_1)^2 + (2\ell_1 + 1)\ (2j_1 + 1)z\right]^{\frac{1}{2}} \quad .$$

In addition, the impact parameter integral is cut off at some value b_{max} beyond which no trajectories lead to the transition of interest; since

$$\pi \int_0^{b_{max}} db\ 2b = \pi\ b_{max}^2 \int_0^1 d\xi \quad ,$$

where

$$\xi = (b/b_{max})^2 \quad ,$$

or

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$$\ell_1 + \frac{1}{2} = k_1 \, b_{max} \sqrt{\xi} \quad ;$$

these changes of variables replace Eq. (2.9) by

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) = \pi b_{max}^2 \int_0^1 d\xi \int_0^1 dz \int_0^1 d(\bar{q}_{n_1}/2\pi) \int_0^1 d(\bar{q}_{j_1}/2\pi) \int_0^1 d(\bar{q}_{\ell_1}/2\pi)$$

$$\chi_{n_2 j_2 \leftarrow n_1 j_1}(\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1}, \ell_1, J, E) \quad . \qquad (2.10)$$

Since all five integrals have the limits (0, 1), the Monte Carlo evaluation of Eq. (2.10) is straight forward. If Eq. (2.10) is also summed over final rotational states,

$$\sigma_{n_2 \leftarrow n_1 j_1}(E_1) \equiv \sum_{j_2} \sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) \quad , \qquad (2.11)$$

then one obtains

$$\sigma_{n_2 \leftarrow n_1 j_1}(E_1) = \pi b_{max}^2 \int_0^1 d\xi \int_0^1 dz \int_0^1 d(\bar{q}_{n_1}/2\pi) \int_0^1 d(\bar{q}_{j_1}/2\pi) \int_0^1 d(\bar{q}_{\ell_1}/2\pi)$$

$$\chi_{n_2 \leftarrow n_1 j_1}(\bar{q}_{n_1}, \bar{q}_{\ell_1}, \bar{q}_{j_1}, \ell_1, J, E) \quad , \qquad (2.12)$$

where the characteristic function here is 1 if the final vibrational quantum number resulting from the classical trajectory with the indicated initial conditions is in the interval $(n_2 - \frac{1}{2}, n_2 + \frac{1}{2})$, and is 0 otherwise.

B. Classically Forbidden Case.

If the $(n_1 j_1) \to (n_2 j_2)$ transition is classically forbidden--i.e., if there are no real-valued classical trajectories at the given values of J and E which connect these initial and final quantum numbers--then the above prescription is clearly not applicable; it gives a cross section of 0, which is consistent in that the cross section is indeed small, but which is not a useful estimate. Some of the simplifying steps discussed above in Section IIA, however, are still valid.

Because of the sums in Eq. (2.2) it is still a good approximation to assume that interference terms in the S-matrix elements are quenched. If so, then Eq. (2.3) for the square modulus of a classical S-matrix element is modified only by the addition of a exponential damping factor:[5]

$$|S_{n_2 j_2 \ell_2, n_1 j_1 \ell_1}(J,E)|^2 = \left[(2\pi)^3 \left| \frac{\partial(n_2 j_2 \ell_2)}{\partial(\bar{q}_{n_1} \bar{q}_{j_1} \bar{q}_{\ell_1})} \right| \right]^{-1} \exp(-2 \operatorname{Im} \Phi) \ , \quad (2.13)$$

units being used throughout such that $\hbar = 1$. This damping factor arises because the classical trajectory which satisfies the correct initial and final quantum conditions is complex-valued, i.e., the values of $\bar{q}_{n_1}$, $\bar{q}_{j_1}$, and $\bar{q}_{\ell_1}$ which satisfy Eq. (2.4) are complex; the action integral Φ along such a trajectory is complex-valued, and the imaginary part of this action integral is the exponent of the damping factor. One sees, therefore, that the term "classically forbidden" is a generalization of the concept of "tunneling" to dynamical systems of

more than one degree of freedom. Reference 5 has a more extensive discussion of classically forbidden processes.

Even though it is now not possible to treat the final vibrational quantum number n_2 as a continuous variable--because the S-matrix elements change exponentially for different final integer values of n_2--it is still usually the case that a number of final rotational states have comparable transition probabilities for a given vibrational transition. The reason for this is that at energies for vibrationally inelastic processes to be possible, rotationally inelastic transitions are usually strong, classically allowed-like. (Rotationally inelastic transitions are, in fact, essentially <u>always</u> classically allowed processes.[14])

The <u>partial</u> averaging idea, therefore, is to average over the final rotational quantum number as was done in part A, but not over the final vibrational quantum number. (One wishes to average over as many final quantum numbers as is allowable since it replaces the <u>final</u> quantum condition by <u>initial</u> conditions, which are much easier to deal with computationally). With Eq. (2.13), the cross section--summed over final j_2--becomes

$$\sigma_{n_2 \leftarrow n_1 j_1}(E_1) = \frac{\pi}{k_1^{\,2}(2j_1 + 1} \int dJ \int d\ell_1 \int d\ell_2 \int dj_2$$

$$\times \frac{(2J + 1)}{(2\pi)^3} \left| \frac{\partial(n_2 j_2 \ell_2)}{\partial(\bar{q}_{n_1} \bar{q}_{j_1} \bar{q}_{\ell_1})} \right|^{-1} \exp(-2 \text{ Im } \Phi) \quad , \qquad (2.14)$$

and since

$$(dj_2\, d\ell_2)_{n_2,n_1} = d\bar{q}_{j_1}\, d\bar{q}_{\ell_1} \left(\frac{\partial(j_2,\ell_2)}{\partial(\bar{q}_{j_1}\bar{q}_{\ell_1})}\right)_{n_2,n_1}$$

$$= d\bar{q}_{j_1}\, d\bar{q}_{\ell_1} \frac{\partial(n_2 j_2 \ell_2)}{\partial(\bar{q}_{n_1}\bar{q}_{j_1}\bar{q}_{\ell_1})} \Bigg/ \left(\frac{\partial n_2}{\partial \bar{q}_{n_1}}\right)_{n_1} ,$$

Eq. (2.14) becomes

$$\sigma_{n_2 \leftarrow n_1 j_1}(E_1) = \frac{\pi}{k_1^{\,2}(2j_1 + 1)} \int d\ell_1 \int dJ \int d(\bar{q}_{j_1}/2\pi) \int d(\bar{q}_{\ell_1}/2\pi)$$

$$\times \left[2\pi \left|\frac{\partial n_2}{\partial \bar{q}_{n_1}}\right|\right]^{-1} \exp\,(-2\ \mathrm{Im}\ \Phi) \quad . \tag{2.15}$$

In Eq. (2.15) $\bar{q}_{n_1}$ is not integrated over--as in Eq. (2.12) of Section IIA--but must be chosen to be that specific (complex) value for which

$$n_2(\bar{q}_{n_1};\ \bar{q}_{j_1},\bar{q}_{\ell_1},\ell_1,j_1,J,E_1) = n_2 \quad . \tag{2.16}$$

The "root-search" problem which complicates the application of classical S-matrix theory to three dimensional collision systems[10] has thus not been completely eliminated, but has been reduced to a one dimensional root-search which must be carried out many times.

The same changes of variables introduced in Section IIA can also be carried out here, and Eq. (2.15) then takes on the simpler form

$$\sigma_{n_2 \leftarrow n_1 j_1}(E_1) = \pi b_{max}^2 \int_0^1 d\xi \int_0^1 dz \int_0^1 d(\bar{q}_{j_1}/2\pi) \int_0^1 d(\bar{q}_{\ell_1}/2\pi)\, P_{n_2,n_1}(j_1 \ell_1 \bar{q}_{j_1} \bar{q}_{\ell_1}; JE_1), \tag{2.17}$$

where

$$P_{n_2,n_1}(j_1 \ell_1 \bar{q}_{j_1} \bar{q}_{\ell_1}; JE_1) \equiv \left[2\pi \left|\frac{\partial n_2}{\partial \bar{q}_{n_1}}\right|\right]^{-1} \exp\,(-2\ \mathrm{Im}\ \Phi) \quad . \tag{2.18}$$

The vibrational transition probability function defined by Eq. (2.18) has the structure of a collinear vibrational transition probability[15] which depends parametrically on the initial conditions of the other degrees of freedom. The analogy to a collinear transition probability is purely formal, however, for Eqs. (2.17) and (2.18) involve no dynamical approximations beyond that of classical S-matrix theory itself, the neglect of interference terms, and the assumption that enough j_2 values have comparable probability that a sum over integer values of j_2 can be replaced by an integral. It is interesting, nevertheless, that Eq. (2.17) does have the phenomenological form often assumed,[16] namely a "gas kinetic cross section", πb_{max}^2, multiplied by an average vibrational transition probability; here one sees precisely what this "average vibrational transition probability" is.

Eq. (2.17) corresponds to a sum over final rotational states, but it is clear how one can obtain the distribution of final rotational states--and also the differential cross section--within a classical Monte Carlo framework. Since

$$\sigma_{n_2 \leftarrow n_1 j_1}(E_1) = \int dj_2\ \ \sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) \tag{2.19}$$

$$= \int dj_2 \int d(\cos\theta) \quad \sigma_{n_2 j_2 \leftarrow n_1 j_1}(\theta, E_1) \quad , \tag{2.20}$$

to obtain the $n_1 j_1 \rightarrow n_2$ cross section differential in final rotational state and in scattering angle--i.e., $\sigma_{n_2 j_2 \leftarrow n_1 j_1}(\theta)$--one simply defines a set of "j_2-boxes" and "cos θ-boxes"; with the integration variables in Eq. (2.17) chosen by Monte Carlo, the numerical value of the integrand--i.e., the vibrational transition probability--is assigned to the j_2- and cos θ-box which corresponds to the final values of j_2 and cos θ for the trajectory which satisfies Eq. (2.16), i.e., the one from which the transition probability in Eq. (2.18) is constructed. The distributions in j_2 and cos θ are thus obtained simultaneously with the calculation of the integral cross section $\sigma_{n_2 \leftarrow n_1 j_1}$, the only limitations being the usual Monte Carlo ones--i.e., the more detailed the quantities desired the more Monte Carlo points are required. Thus it might require only 50 Monte Carlo points, for example, to evaluate the integral cross section to within 10 % statistical error, but a large number of points would be required to obtain the distribution of final rotational states, $\sigma_{n_2 j_2 \leftarrow n_1 j_1}$, and a still larger number of points to obtain the "doubly differential" cross section, $\sigma_{n_2 j_2 \leftarrow n_1 j_1}(\theta)$, differential in j_2 and θ, to within 10 % statistical error. The situation is thus much like an experiment: The more highly resolved the information sought, the more effort required to obtain it. This is, however, a highly desirable feature of the theory, for it means that one may obtain less detailed

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quantities with less detailed calculations. By way of contrast, in a complete rigorous quantum mechanical theory it is never possible to obtain averaged cross sections without first computing the most detailed cross sections and then proceeding to average them.

III. COMPUTATIONAL ASPECTS.

A. Numerical Integration of Complex-Valued Trajectories.

Although the formalism of classical S-matrix theory deals with initial and final values of action-angle variables, it is actually most convenient to carry out the numerical integration of Hamilton's equations in cartesian coordinates and momenta. The procedure is that one specifies initial conditions in terms of action-angle variables (e.g., $n_1, \bar{q}_{n_1}, j_1, \bar{q}_{j_1}, \ell_1, \bar{q}_{\ell_1} \ldots$), transforms these into initial conditions for the cartesian variables, carries out the numerical integration of the trajectory in cartesian variables, and at the end of the trajectory transforms the final values of the cartesian variables into final values of the action-angle variables (e.g., $n_2, j_2, \ell_2 \ldots$). Appendix C of reference 12 gives the expressions for the initial values of the cartesian variables in terms of the action-angle variables (see also Section II B of reference 10). With regard to the transformation at the end of the trajectory, the final angular momentum variables j_2 and ℓ_2 are easily determined from the cartesian variables by using the classical relations

$$j_2 + \frac{1}{2} = [(\underset{\sim}{r}_2 \times \underset{\sim}{p}_2) \cdot (\underset{\sim}{r}_2 \times \underset{\sim}{p}_2)]^{1/2}$$

$$\ell_2 + \frac{1}{2} = [(\underset{\sim}{R}_2 \times \underset{\sim}{P}_2) \cdot (\underset{\sim}{R}_2 \times \underset{\sim}{P}_2)]^{1/2} \quad ,$$

where $(\underset{\sim}{r}_2, \underset{\sim}{p}_2)$ are the cartesian variables of the diatom and $(\underset{\sim}{R}_2, \underset{\sim}{P}_2)$ the cartesian variables for the atom-diatom separation at the end of the trajectory.

The final vibrational quantum number is determined from the cartesian variables by first computing the total energy of the diatom

$$\varepsilon_2 = (\underset{\sim}{p}_2 \cdot \underset{\sim}{p}_2)/2m + v(r_2) \quad , \tag{3.1}$$

v(r) being the vibrational potential of the diatom, and then solving the equation

$$\varepsilon(n_2, j_2) = \varepsilon_2 \tag{3.2}$$

for n_2 (since j_2 is known), where $\varepsilon(n,j)$ is the WKB energy level formula for the diatom; it is usually known as a Dunham expansion. Alternatively, with ε_2 known from Eq. (3.1) n_2 can be computed directly from the WKB quantum condition:

$$(n_2 + \tfrac{1}{2})\pi = \int_{r_<}^{r_>} dr \, \{2m\,[\varepsilon_2 - v(r)] - j_2^{\,2}/r^2\}^{1/2} \quad . \tag{3.3}$$

To a large extent the actual numerical integration of complex-valued trajectories is the same as for ordinary real-valued ones; this is possible by taking advantage of the complex arithmetic capabilities of FORTRAN IV. Thus it is only necessary to declare all the coordinates and momenta, and the time increment, to be COMPLEX variables and use essentially the same numerical integration algorithm[17] - e.g., Runge-Kutta, Adams-Moulton, etc. - as used for real-valued trajectories. Since it is often convenient, however, to vary the direction in the complex time plane of the

complex time increment, Miller and George[18] developed a variable step-size-predictor-corrector algorithm; it has the variable step-size and self-starting advantages of Runge-Kutta routines with the efficiency of a predictor-corrector (e.g., Adams-Moulton) method. Appendix C of reference 18 gives the predictor and corrector formulae for the fifth order [error $\sim O(h^6)$] version of the algorithm; used in the PECE mode,[17] the integrator has excellent stability characteristics.

The principal feature which distinguishes the numerical integration of complex-valued trajectories from real-valued ones lies in the flexibility one has in choosing the complex time path along which time is incremented. Although the quantities from which the classical S-matrix is constructed are analytic functions and thus independent of the particular time path,[5] there are practical considerations that restrict the choice. Thus although translational coordinates behave as low order polynomials in time, so that nothing drastic happens to them when t becomes complex, the vibrational coordinate is oscillatory -

$$r(t) - r_{eq} \sim \cos(\omega t + \eta)$$

- so that it can become exponentially large along a complex time path. The complex time path must be chosen, therefore, in order to stabilize the vibrational motion.

There are a variety of ways of stabilizing the vibrational motion, but the most satisfactory procedure we have found to date is to head the oscillator always toward its next equilibrium

position. Thus at time t_n the values r_n, $\dot{r}_n$, $\ddot{r}_n$, [$r_n = r(t_n)$, etc.] are known, so that for t near t_n one has the approximation

$$r(t) = r_n + r_n\,(t - t_n) + \frac{1}{2}\,\ddot{r}_n\,(t - t_n)^2 \quad , \tag{3.4}$$

and one wishes to choose the next time, t_{n+1}, so that

$$r(t_{n+1}) = r_{eq} \quad ; \tag{3.5}$$

solving Eqs. (3.4) and (3.5) gives

$$\Delta t \equiv t_{n+1} - t_n$$

$$= (\ddot{r}_n)^{-1}\,\{-\,\dot{r}_n \pm [\dot{r}_n^{\,2} + 2\ddot{r}_n\,(r_{eq} - r_n)]^{1/2}\} \quad , \tag{3.6}$$

with the ± sign chosen to insure $\mathrm{Re}(\Delta t) > 0$.[19] Actually one wishes only to cause r(t) to head in the <u>direction</u> of r_{eq}; thus the new time increment is chosen to have the <u>phase</u> of that in Eq. (3.6) but the magnitude determined by the truncation error estimate of the integrater.[18] If Δt is given by Eq. (3.6), then the new time increment is thus chosen as

$$h(\Delta t)/|\Delta t| \quad ,$$

where $|\Delta t|$ is the complex absolute value of Δt and h is the magnitude of time increment allowed by the integrater.

The above algorithm for choosing the complex time path is used throughout the entire trajectory except at the conclusion where the time path is chosen so as to terminate the trajectory as a vibrational turning point.

B. Satisfying the Boundary Conditions.

There is one complicating feature that has not yet been mentioned. The integrals over j_2 and ℓ_2 in Eq. (2.14) are over real values of these quantities, so that when changing to integration variables $\bar{q}_{j_1}$ and $\bar{q}_{\ell_1}$ the integrals over these variables must be contour integrals, i.e.,

$$\int dj_2 \int d\ell_2 = \int_{C_1} d\bar{q}_{j_1} \int_{C_2} d\bar{q}_{\ell_1} \frac{\partial(j_2\ell_2)}{\partial(\bar{q}_{j_1}\bar{q}_{\ell_1})} \tag{3.7}$$

$$= \int_{C_1} |d\bar{q}_{j_1}| \int_{C_2} |d\bar{q}_{\ell_1}| \left|\frac{\partial(j_2\ell_2)}{\partial(\bar{q}_{j_1}\bar{q}_{\ell_1})}\right|$$

$$= \int_{C_1} |d\bar{q}_{j_1}| \int_{C_2} |d\bar{q}_{\ell_1}| \left|\frac{\partial(n_2 j_2 \ell_2)}{\partial(\bar{q}_{n_1}\bar{q}_{j_1}\bar{q}_{\ell_1})}\right| \left|\left(\frac{\partial n_2}{\partial \bar{q}_{n_1}}\right)_{n_1}\right|^{-1},$$

where the contours C_1 and C_2 must be chosen so that $j_2\ (\bar{q}_{j_1}, \bar{q}_{\ell_1})$ and $\ell_2\ (\bar{q}_{j_1}, \bar{q}_{\ell_1})$ remain real along them. (The integrand in Eq. (2.14) is not an analytic function--it is the square modulus of one--so that the value of the integral depends on the integration path.) By the usual arc length formula, however,

$$|d\bar{q}_{j_1}| = d(\mathrm{Re}\ \bar{q}_{j_1}) \left[1 + \left(\frac{d(\mathrm{Im}\ \bar{q}_{j_1})}{d(\mathrm{Re}\ \bar{q}_{j_1})}\right)^2\right]^{1/2}$$

$$|d\bar{q}_{\ell_1}| = d(\mathrm{Re}\ \bar{q}_{\ell_1}) \left[1 + \left(\frac{d(\mathrm{Im}\ \bar{q}_{\ell_1})}{d(\mathrm{Re}\ \bar{q}_{\ell_1})}\right)^2\right]^{1/2} . \tag{3.8}$$

It is possible, therefore, to integrate with respect to Re $\bar{q}_{j_1}$ and Re $\bar{q}_{\ell_1}$, provided Im $\bar{q}_{j_1}$ and Im $\bar{q}_{\ell_1}$ are chosen at each integration point to satisfy

$$\mathrm{Im}\ j_2\ (\bar{q}_{j_1}, \bar{q}_{\ell_1}) = 0$$

$$\mathrm{Im}\ \ell_2\ (\bar{q}_{j_1}, \bar{q}_{\ell_1}) = 0 \quad , \tag{3.9}$$

and provided the arc length factors of Eq. (3.8) are inserted in the integrand.

Taking this feature into account, Eq. (2.17) is replaced by

$$\sigma_{n_2 \leftarrow n_1 j_1}(E_1) = \pi b_{max}^2 \int_0^1 d\xi \int_0^1 dz \int_0^1 d\ (\mathrm{Re}\ \bar{q}_{j_1}/2\pi) \int_0^1 d\ (\mathrm{Re}\ \bar{q}_{\ell_1}/2\pi)$$

$$\times\ A_\ell\ A_j \left[2\pi \left|\frac{\partial n_2}{\partial \bar{q}_{n_1}}\right|\right]^{-1} \exp\ (-2\mathrm{Im}\Phi) \quad , \tag{3.10}$$

where

$$A_j = \left[1 + \left(\frac{d(\mathrm{Im}\ \bar{q}_{j_1})}{d(\mathrm{Re}\ \bar{q}_{j_1})}\right)^2\right]^{1/2}$$

$$A_\ell = \left[1 + \left(\frac{d(\mathrm{Im}\ \bar{q}_{\ell_1})}{d(\mathrm{Re}\ \bar{q}_{\ell_1})}\right)^2\right]^{1/2} .$$

For each value of the integration variables in Eq. (3.10) one must thus choose the four variables $\bar{q}_{n_1} \equiv \text{Re}\ \bar{q}_{n_1} + i\ \text{Im}\ \bar{q}_{n_1}$, $\text{Im}\ \bar{q}_{j_1}$, and $\text{Im}\ \bar{q}_{\ell_1}$ so that the four equations

$$\text{Re}\ n_2\ (\text{Re}\ \bar{q}_{n_1},\ \text{Im}\ \bar{q}_{n_1},\ \text{Im}\ \bar{q}_{j_1},\ \text{Im}\ \bar{q}_{\ell_1}) = n_2 \tag{3.11 a}$$

$$\text{Im}\ n_2\ (\text{Re}\ \bar{q}_{n_1},\ \text{Im}\ \bar{q}_{n_1},\ \text{Im}\ \bar{q}_{j_1},\ \text{Im}\ \bar{q}_{\ell_1}) = 0 \tag{3.11 b}$$

$$\text{Im}\ j_2\ (\text{Re}\ \bar{q}_{n_1},\ \text{Im}\ \bar{q}_{n_1},\ \text{Im}\ \bar{q}_{j_1},\ \text{Im}\ \bar{q}_{\ell_1}) = 0 \tag{3.11 c}$$

$$\text{Im}\ \ell_2\ (\text{Re}\ \bar{q}_{n_1},\ \text{Im}\ \bar{q}_{n_1},\ \text{Im}\ \bar{q}_{j_1},\ \text{Im}\ \bar{q}_{\ell_1}) = 0 \quad . \tag{3.11 d}$$

It is easy to see that Eq. (3.11) must be imposed if one is to obtain meaningful results. Thus the trajectory corresponding to the initial values $\bar{q}_{j_1}$ and $\bar{q}_{\ell_1}$ is clearly the same if these angle variables have added to them arbitraty multiples of 2π--i.e., if

$$\bar{q}_{j_1} \to \bar{q}_{j_1} + 2\pi m_1$$

$$\bar{q}_{\ell_1} \to \bar{q}_{\ell_1} + 2\pi m_2 \quad ,$$

m_1 and m_2 being arbitrary integers--while the imaginary part of the action integral Φ,

$$\Phi \equiv - \int dt\ [R(t)\ \frac{dP_R(t)}{dt} + q_n(t)\ \frac{dn(t)}{dt} + q_j(t)\ \frac{dj(t)}{dt} + q_\ell(t)\ \frac{d\ell(t)}{dt}] \tag{3.12}$$

changes according to

$$\mathrm{Im}\ \Phi \rightarrow \mathrm{Im}\ \Phi - 2\pi m_1\ \mathrm{Im}\ (\Delta j) - 2\pi m_2\ \mathrm{Im}\ (\Delta \ell) \quad ,$$

where

$$\Delta \ell = \ell_2\ (\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1}) - \ell_1$$

$$\Delta j = j_2\ (\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1}) - j_1 \quad .$$

There is clearly no physical significance to which 2π increment $\bar{q}_{j_1}$ and $\bar{q}_{\ell_1}$ are chosen from, i.e., to the values of m_1 and m_2, so that Im Φ would not be uniquely determined if Im Δj and Im $\Delta \ell$ were not 0. Eq. (3.11), however, insures that they are 0 so that Im Φ is indeed uniquely defined.

Since one must solve Eqs. (3.11) many times--once for each set of the Monte Carlo-chosen integration variables (ξ, z, Re $\bar{q}_{j_1}$, Re $\bar{q}_{\ell_1}$)--it is clear that one needs an efficient way of solving them. Many methods were tried but no completely satisfactory procedure was found; i.e., it was possible to solve Eqs. (3.11) for many sets of integration variables but no automated procedure was found that could routinely find the root with a small number (less than 10) of iterations.

For the number of special cases for which Eqs. (3.11) were solved, however, it always observed that Im $\bar{q}_{j_1}$ and Im $\bar{q}_{\ell_1}$ were small (less than 0.05), with Im $\bar{q}_{n_1}$ being much larger (about 0.5); i.e., the classically forbidden character of the transition is associated primarily with the vibrational degree of freedom, as expected. To simplify the calculation, therefore, it was decided

to allow $\bar{q}_{j_1}$ and $\bar{q}_{\ell_1}$ to remain completely real, i.e., not to vary Im $\bar{q}_{j_1}$ and Im $\bar{q}_{\ell_1}$ in order to satisfy Eq. (3.11 c) and (3.11 d). In order to obtain a unique value for Im Φ it is then necessary to drop the terms $q_j(dj/dt)$ and $q_\ell(d\ell/dt)$ from the integrand of Eq. (3.12); this is consistent with the assumption that the complex-valued part of the trajectory is concentrated primarily in the vibrational degree of freedom. The imaginary part of Φ is thus taken to be

$$\begin{aligned} \mathrm{Im}\,\Phi &= -\,\mathrm{Im} \int_{t_1}^{t_2} dt \quad [R\dot{P}_R + q_n\dot{n}] \qquad (3.13) \\ &= -\,\mathrm{Im}\,[f_2(r,n)\,\Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} dt\,(R\dot{P}_R - p_r\dot{r})] \\ &= -\,\mathrm{Im}\,[f_2(r,n)\,\Big|_{t_1}^{t_2} - p_r r\,\Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} dt\,(R\dot{P}_R + r\dot{p}_r)] \quad , \end{aligned}$$

where $f_2(r,n)$ is the generator of the transformation between the vibrational radial coordinate and momentum (r,p_r) and the vibrational action-angle variables (n,q_n); since the trajectory is actually begun and ended at a vibrational turning point, the imaginary part f_2 at t_1 and t_2 vanishes, as does p_r, and since

$$\dot{P}_R R = \dot{\underset{\sim}{P}} \cdot \underset{\sim}{R} \equiv \dot{P}_X X + \dot{P}_Y Y + \dot{P}_Z Z$$

$$\dot{p}_r r = \dot{\underset{\sim}{p}} \cdot \underset{\sim}{r} \equiv \dot{p}_x x + \dot{p}_y y + \dot{p}_z z \quad ,$$

the imaginary part of the action integral is

$$\mathrm{Im}\,\Phi = -\,\mathrm{Im}\int_{t_1}^{t_2} dt\,(\underset{\sim}{R}\cdot\dot{\underset{\sim}{P}} + \underset{\sim}{r}\cdot\dot{\underset{\sim}{p}}) \quad . \tag{3.14}$$

In practice, the imaginary part of Φ is obtained as

$$\mathrm{Im}\,\Phi = \mathrm{Im}\,\chi(t_2) \quad , \tag{3.15}$$

where $\chi(t)$ is obtained by adding one extra differential equation to the twelve first order equations for the trajectory in cartesian coordinates,

$$\dot{\chi}(t) = -\,\underset{\sim}{R}(t)\cdot\dot{\underset{\sim}{P}}(t) - \underset{\sim}{r}(t)\cdot\dot{\underset{\sim}{p}}(t) \quad , \tag{3.16}$$

with the initial condition

$$\chi(t_1) = 0 \quad . \tag{3.17}$$

With these approximations--namely that $\bar{q}_{j_1}$ and $\bar{q}_{\ell_1}$ are taken to be real and consistent with this the action integral is defined by Eq. (3.14)--it is now only necessary to solve the one complex equation

$$n_2(\bar{q}_{n_1}) = n_2 \tag{3.18}$$

for each given set of integration variables in Eq. (2.17). This is easily accomplished by first evaluating $n_2(\bar{q}_{n_1})$ for the three real values (involving completely real trajectories) $\bar{q}_{n_1} = 0$,

$2\pi/3$, and $4\pi/3$; these values determine the three coefficients in the functional form

$$n_2(\bar{q}_{n_1}) = a_o + a_1 \cos \bar{q}_{n_1} + b_1 \sin \bar{q}_{n_1} \quad . \tag{3.19}$$

With the fit to $n_2(\bar{q}_{n_1})$ given by Eq. (3.19) one solves Eq. (3.18) for the approximate complex value of $\bar{q}_{n_1}$, runs a complex trajectory to evaluate the exact $n_2(\bar{q}_{n_1})$ at this value, uses this value and two previous ones to redetermine the coefficients in Eq. (3.19) and iterates the procedure. It usually takes only 3 to 5 complex trajectories, after the 3 real ones, to find the root of Eq. (3.18) and evaluate the vibrational transition probability function of Eq. (2.18).

Although we would like to have been able to solve Eq. (3.11) and use Eq. (3.10), the approximation of leaving $\bar{q}_{j_1}$ and $\bar{q}_{\ell_1}$ real, and for consistency modifying the expression for Im Φ, seems for this system to make little difference in the results, certainly no more than 10 - 20% in the final cross sections. In other cases--perhaps those involving stronger rotational-vibrational coupling, such as HCℓ + Ar--it may be necessary to re-examine this approximation. Better yet, perhaps better numerical algorithms will be devised to obviate the necessity for invoking it.

IV. RESULTS AND DISCUSSION.

The interaction potential for the $Li^+ - H_2$ system was taken to be the same as that used by Schaefer and Lester[9] in their quantum mechanical coupled channel calculations. For the vibrational potential of H_2--which must be added to the interaction potential to obtain the total potential energy function--a Morse function was used; an accurate fit of the Kolos-Wolniewicz H_2 potential was also used in some test calculations, and this made neglible difference.

Figure 1 shows the cross sections for vibrational de-activation of H_2 by Li^+--i.e., $\sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1)$ for $(n_1, j_1) = (1,0)$ and $n_2 = 0$--for an initial collision energy $E_1 = 0.684$ eV. The values labeled SC are the present semiclassical results, and the error bars indicate the statistical error in the Monte Carlo evaluation of Eq. (2.17); 1000 Monte Carlo points were used.

The points designated QMI in Fig. 1 are the results of Schaefer and Lester's[9] quantum mechanical calculation with a coupled channel expansion including the states

$$n = 0;\ j = 0, 2, 4, 6, 8, 10 \qquad (4.1)$$
$$n = 1;\ j = 0, 2, 4$$
$$n = 2;\ j = 0, 2 \quad .$$

The values labeled QM II are their results[20] obtained by adding one additional rotational state to each vibrational manifold: $j = 12$ for $n = 0$, $j = 6$ for $n = 1$, and $j = 4$ for $n = 2$.

The large change in the quantum results with this increase in basis set seems to indicate that the coupled channel expansion is still some ways from convergence, a rather disconcerting observation since the basis set already produces up to 75 coupled channels! (It should be noted that Schaefer and Lester[9] were primarily interested in pure rotational transitions, $n_1 = n_2$, and their results do indicate the expansion to be converged for these processes.) Another possibility is that the difference between the QM I and QM II results is due to numerical error, for the algorithm used for solving the coupled equations does not seem well suited for treating processes with small transition probabilities.[21,22]

The cross section summed over final rotational states, $\sigma_{n_2 \leftarrow n_1 j_1}$ for $(n_1, j_1) = (1,0)$ and $n_2 = 0$, is 1.87 a_o^2, 1.15 a_o^2, and 0.83 a_o^2, respectively, for the QM I, QM II, and semiclassical calculations. Within the uncertainty of the quantum mechanical results, therefore, the semiclassical cross sections are in excellent agreement with the quantum values, both in magnitude and in the distribution of rotational states (Fig. 1) populated in the vibrational de-activation.

The distribution in scattering angle, i.e., the differential cross section, for the $1 \rightarrow 0$ vibrational de-activation was also obtained within the classical Monte Carlo framework. It is qualitatively the same for each final rotational state, so only the total result, summed over j_2, is shown in Fig. 2; i.e., the quantity shown is

$$\sigma_{n_2 \leftarrow n_1 j_1}(\theta) = \sum_{j_2} \sigma_{n_2 j_2 \leftarrow n_1 j_1}(\theta) \quad . \tag{4.2}$$

The result is hard sphere-like (i.e., isotropic) except for a narrow peak in the forward direction.

Finally, it is interesting to ask what the rotational state distribution in Fig. 1 signifies about the dynamics of the inelastic process. First, one sees that a substantial amount of the energy released by the vibrational de-activation goes into rotational excitation. The amount of rotational excitation is considerably less than that of a "resonant" process (no change in translational energy), however, for that would demand a final rotational state $j_2 = 8$. Another interesting comparison is to a <u>statistical</u> distribution of final rotational states; this corresponds to

$$\sigma_{0j_2 \leftarrow 10}(E_1) \propto (2j_2 + 1)\ [E - \varepsilon(0,j_2)] \quad , \tag{4.3}$$

where E is the total energy and $\varepsilon(0,j_2)$ the vibrational-rotational energy of H_2 for $n = 0$ and $j = j_2$. This distribution, normalized to the semiclassical cross section, is the dashed line in Fig. 1. The amount of rotational excitation is thus also much less than that based simply on available phase space.

V. CONCLUDING REMARKS.

The partially averaged version of classical S-matrix theory thus appears to be an accurate and practical method for describing classically forbidden vibrationally inelastic processes in three-dimensional A + BC collision systems. The primary advantage of the approach is that one can treat the classical-like rotational degrees of freedom within the usual Monte-Carlo framework, while quantizing the vibrational degree of freedom within the classical S-matrix framework, all without the necessity of introducing any approximations to the dynamics itself. Many of the practical difficulties of applying the classical S-matrix model to three-dimensional collision systems are thus circumvented, and the computational efficiency of the approach is comparable to that of ordinary trajectory methods.

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† Camille and Henry Dreyfus Teacher-Scholar.

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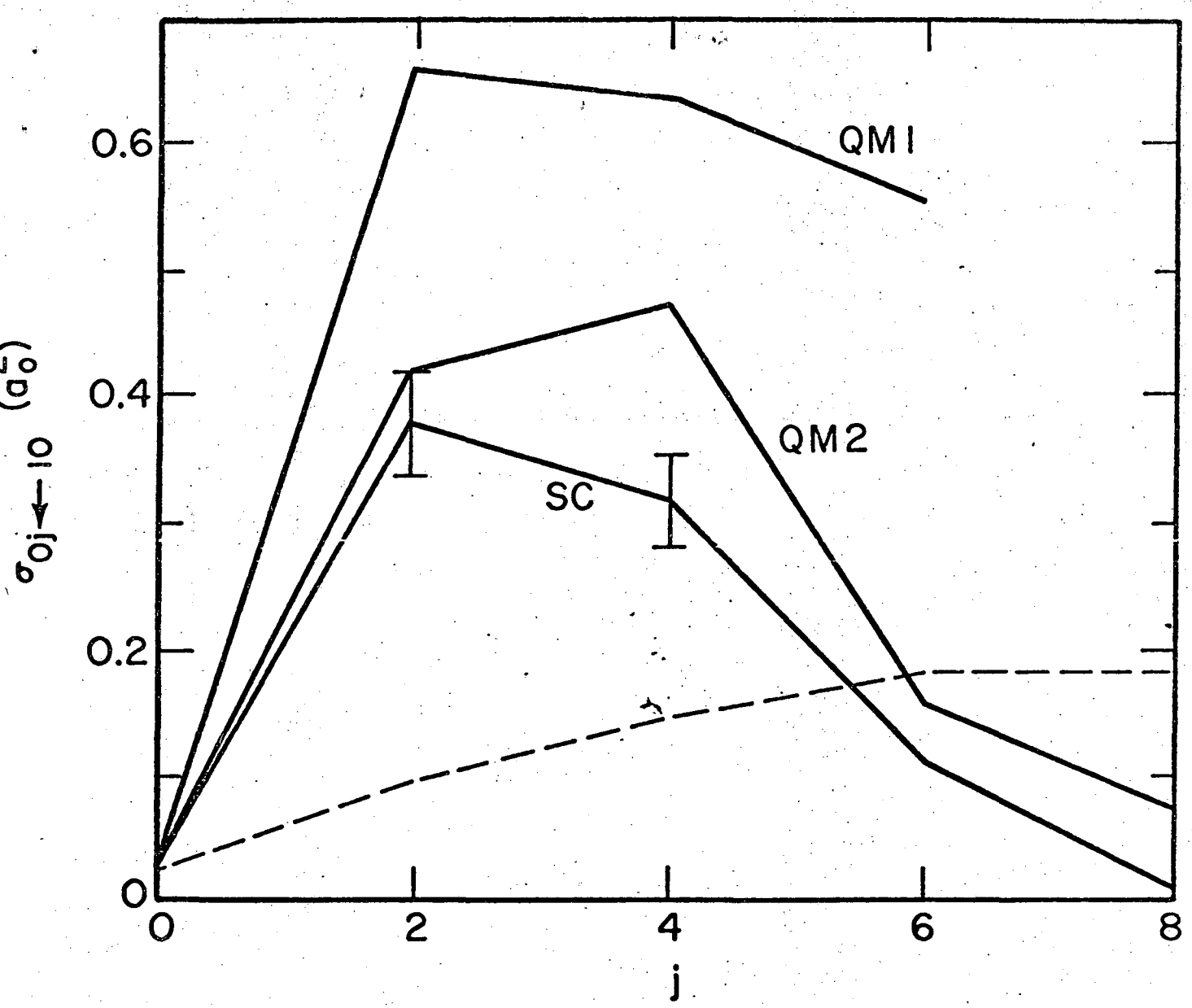
FIGURE CAPTIONS

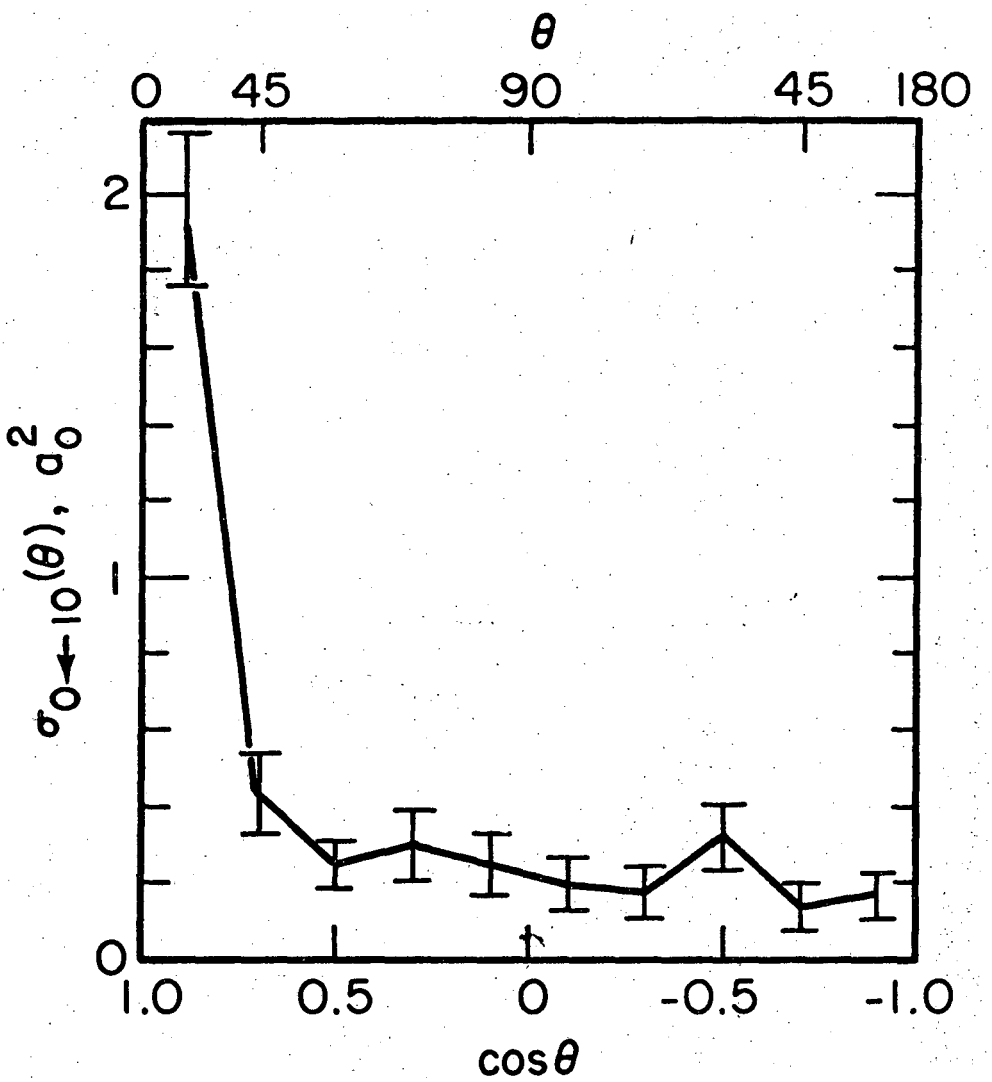
Figure 1. Cross sections for the (1,0) → (0,j) vibrational de-activation of H_2 by Li^+ at an initial collision energy of 0.684 eV. QM I and QM II label the quantum mechanical results of Schaefer and Lester (ref. 9) with two different basis sets, SC designates the semiclassical results of this paper, and STAT is the statistical distribution of Eq. (4.3) (normalized to the SC total cross section).

Figure 2. The angular distribution, or differential cross section for the same process as in Figure 1, summed over final rotational states.



XBL 748-6935

Fig. 1



XBL 748-6934

Fig. 2

0 0 0 0 4 2 0 1 4 9 7

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