Classical S-matrix calculation for vibrationally inelastic transitions in three dimensional collisions of Li$^+$ with H$_2$ *

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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 deactivation of H$_2$ from the initial state ($n_f$, $j_f$) = (1, 0) to final states ($n_f$, $j_f$), $n_f$ = 0, $j_f$ = 0, 2, 4,... 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 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—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. 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.

Classical S-matrix theory—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 for treating this problem which are also "semiclassical" in nature. Some of these 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 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 decoupling of the translational motion and inelastic dynamics itself—are particularly poor in the case of low collision energy and a weak inelastic transition.

Section II first summarizes the theory with particular attention to the "partial averaging" analysis, and Sec. III discusses some aspects of the numerical methods involved. The results for the 1-0 vibrational deactivation of H$_2$ by Li$^+$ are presented in Sec. IV and compared to the coupled channel quantum mechanical results of Schaefer and Lester. 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, and the partial averaging technique has also been discussed briefly. 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 $n_1j_1-n_2j_2$ vibrational—rotational transition,

$$A + BC(n_1j_1) \rightarrow A + BC(n_2j_2), \quad (2.1)$$
summed and averaged over the $m$ components of the rotational states, is given by
\[ \sigma_{m_2=m_1} (E_1) = \frac{\pi}{k^2} \sum \left( \frac{2J+1}{2^m} \right)^{\frac{1}{2}} \left| \frac{\delta(n_2,j_2)}{\delta(n_1,j_1)} \right|^2, \] 
(2.2)

where $n$, $j$, and $I$ denote vibrational, rotational, and orbital angular momentum quantum numbers, respectively; $\pi$ is the total angular momentum quantum number, $E_1 = \hbar^2 k^2 / 2\mu$ is the initial collision energy, and $E = E_1 + \epsilon(n_1,j_1)$ the total energy.

Because of the sums over the various quantum number labels in Eq. (2.2), it has been noted\(^\text{12}\) that interference effects in the $S$-matrix elements which are prominent in individual matrix elements are often quenched. If interference effects are discarded and if the $n_1 j_1 \rightarrow n_2 j_2$ transition is classically allowed, then the square modulus of the classical $S$-matrix element is given by\(^\text{5}\)
\[ S_{nm_2=nm_1} (J,E) = \left( 2\pi \right)^{\frac{1}{2}} \left| \frac{\delta(n_2,j_2)}{\delta(n_1,j_1)} \right|^2, \] 
(2.3)

The meaning of the Jacobian determinant in Eq. (2.3) is the usual\(^\text{1}\): A complete set of initial conditions for the $A + BC$ classical trajectory are, in action-angle variables, $E$, $J$, $n_1$, $j_1$, $l_1$, $\theta_{n_1}$, $\phi_{j_1}$, and $\mu_{l_1}$, 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 $\theta_{n_1}$, $\phi_{j_1}$, and $\mu_{l_1}$ are chosen so that the final quantum numbers resulting from the trajectory are the desired integer values, i.e., so that the equations
\[ n_2 (\theta_{n_2}, \phi_{j_2}, \mu_{l_2}) = n_2, \] 
\[ j_2 (\theta_{n_2}, \phi_{j_2}, \mu_{l_2}) = j_2, \] 
\[ l_2 (\theta_{n_2}, \phi_{j_2}, \mu_{l_2}) = l_2, \] 
(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 necessarily 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
\[ \sigma_{m_2=m_1} (E_1) = \frac{\pi}{k^2} \sum \left( \frac{2J+1}{2^m} \right)^{\frac{1}{2}} \left| \frac{\delta(n_2,j_2)}{\delta(n_1,j_1)} \right|^2, \] 
(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\(^\text{13}\) about $n_2$ and $j_2$, i.e., to assume
\[ \sigma_{m_2=m_1} (E_1) = \frac{\pi}{k^2} \sum \left( \frac{2J+1}{2^m} \right)^{\frac{1}{2}} \left| \frac{\delta(n_2,j_2)}{\delta(n_1,j_1)} \right|^2, \] 
(2.6)

When this averaging procedure is carried out, Eq. (2.5) becomes
\[ \sigma_{m_2=m_1} (E_1) = \frac{\pi}{k^2} \sum \left( \frac{2J+1}{2^m} \right)^{\frac{1}{2}} \left| \frac{\delta(n_2,j_2)}{\delta(n_1,j_1)} \right|^2, \] 
(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 $(\theta_{n_2}, \phi_{j_2}, \mu_{l_2})$, i.e.,
\[ \int dn_2 \int dj_2 \int dl_2 = \int d\theta_{n_2} \int d\phi_{j_2} \int d\mu_{l_2} \left| \frac{\delta(n_2,j_2)}{\delta(n_1,j_1)} \right|^2, \] 
(2.8)

introduces a Jacobian factor which exactly cancels the one in Eq. (2.7). Equation (2.7) thus becomes
\[ \sigma_{m_2=m_1} (E_1) = \frac{\pi}{k^2} \sum \left( \frac{2J+1}{2^m} \right)^{\frac{1}{2}} \left| \frac{\delta(n_2,j_2)}{\delta(n_1,j_1)} \right|^2 \] 
(2.9)

where the characteristic function $\chi$ is 1 if the final vibrational and rotational quantum numbers which result from the trajectory with the indicated initial conditions fall in the increments\(^\text{13}\) $(n_2 - \frac{1}{2}, n_2 + \frac{1}{2})$ and $(j_2 - \frac{1}{2}, j_2 + \frac{1}{2})$, respectively, and 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 $n_2 (\theta_{n_2}, \phi_{j_2}, \mu_{l_2})$ and $j_2 (\theta_{n_2}, \phi_{j_2}, \mu_{l_2})$ 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 quasiclassical trajectory procedure\(^\text{1}\) 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
\[
I_1 = 0 - \infty, \quad J = |j_1 I_1| - (j_1 + I_1),
\]
and one normally replaces \(I_1\) by the impact parameter \(b\),
\[
b = (I_1 + \frac{1}{2})/k_1,
\]
and \(J\) by the variable \(x\)
\[
J = \frac{x}{[2(j_1 + I_1 + 1)]} = [(j_1 - j_1)x + (2j_1 + 1)(2j_1 + 1)x]^{1/2}.
\]
In addition, the impact parameter integral is cutoff at some value \(b_{\text{max}}\) beyond which no trajectories lead to the transition of interest. Since
\[
\sigma_{n_{I_{I_{I_1}}}m_{I_{I_{I_1}}}}(E_r) = \pi b_{\text{max}} \int_0^{\pi} d\xi \int_0^{\pi} d\eta \int_0^{\pi} d\eta' \int_0^{\pi} d\phi \int_0^{\pi} d\phi' \int_0^{\pi} d\phi'' \int_0^{\pi} d\phi''' \chi_{n_{I_{I_{I_1}}}m_{I_{I_{I_1}}}}(\eta, \eta', \eta'', \phi, \phi', \phi'') \chi_{m_{I_{I_{I_1}}}n_{I_{I_{I_1}}}}(\eta, \eta', \eta'', \phi, \phi', \phi''),
\]
(2.10)
Since all five integrals have the limits \((0, 1)\), the Monte Carlo evaluation of Eq. (2.10) is straightforward. If Eq.
(2.10) is also summed over final rotational states,
\[
\sigma_{n_{I_{I_{I_1}}}m_{I_{I_{I_1}}}}(E_r) = \sum_{J_{II}} \sigma_{n_{I_{I_{I_1}}}m_{I_{I_{I_1}}}}(E_r),
\]
then one obtains
\[
\sigma_{n_{I_{I_{I_1}}}m_{I_{I_{I_1}}}}(E_r) = \pi b_{\text{max}} \int_0^{\pi} d\xi \int_0^{\pi} d\eta \int_0^{\pi} d\eta' \int_0^{\pi} d\phi \int_0^{\pi} d\phi' \int_0^{\pi} d\phi'' \int_0^{\pi} d\phi''' \chi_{n_{I_{I_{I_1}}}m_{I_{I_{I_1}}}}(\eta, \eta', \eta'', \phi, \phi', \phi'') \chi_{m_{I_{I_{I_1}}}n_{I_{I_{I_1}}}}(\eta, \eta', \eta'', \phi, \phi', \phi''),
\]
(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 \([h_2 - \frac{1}{2}, h_2 + \frac{1}{2}]\), and 0 otherwise.

B. Classically forbidden case

If the \((n_{I_{I_{I_1}}}) - (n_{I_{I_{I_1}}})\) 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 Sec. II, A, 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 an exponential damping factor:
\[
|S_{n_{I_{I_{I_1}}}}(J, E)|^2 = \left(\frac{2\pi}{|B_{n_{I_{I_{I_1}}}}|}\right)^{1/2} \exp(-2\text{Im}\Phi),
\]
(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 \(\eta, \eta', \eta''\), and \(\eta''\),

The partial averaging idea, therefore, is to average over the final rotational quantum number as was done in subsection 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 final quantum condition by initial conditions, which are much easier to deal with computationally.) With Eq.
(2.13), the cross section—summed over final \(J_z\) becomes
\[
\sigma_{n_{I_{I_{I_1}}}m_{I_{I_{I_1}}}}(E_r) = \frac{\pi}{k_1(2j_1 + 1)} \int dJ \int dI_1 \int dI_2 \int dI_3 \left(\frac{2J_1 + 1}{2\pi}\right)^3 \left|\frac{\psi_{n_{I_{I_{I_1}}}m_{I_{I_{I_1}}}}}{\psi_{n_{I_{I_{I_1}}}m_{I_{I_{I_1}}}}}(\eta, \eta', \eta'', \phi, \phi', \phi'')\right|^2 \exp(-2\text{Im}\Phi),
\]
(2.14)
J. Chem. Phys., Vol. 61, No. 12, 15 December 1974
and since
\[ (d\tilde{q}_1 d\tilde{q}_1)_{m_1 n_1} = d\tilde{q}_1 d\tilde{q}_1 \left( \frac{a(\tilde{q}_1, \tilde{q}_1)_{m_1 n_1}}{a(\tilde{q}_1, \tilde{q}_1)_{n_1 n_1}} \right) \frac{\delta(n_1 n_2 j_2)}{\delta(n_2 n_1)} \frac{\delta(\tilde{q}_1 \tilde{q}_1)}{(m_2 / \delta q_{m_2})_{n_1}}. \]
Eq. (2.14) becomes
\[ \sigma_{n_2 \rightarrow n_1}(E_i) = \frac{\pi}{k^2 (2j + 1)} \int d\tilde{q}_1 \int d\tilde{q}_1 \left( \frac{d(\tilde{q}_1 \tilde{q}_1)}{2\pi} \right)^2 \int d(\tilde{q}_1 \tilde{q}_1) / (2\pi) \left( \frac{d(\tilde{q}_1 \tilde{q}_1)}{2\pi} \right)^2 \exp(-2 Im\phi). \]

In Eq. (2.15) \( \tilde{q}_m \) is not integrated over as in Eq. (2.12) of Sec. II A but must be chosen to be that specific (complex) value for which
\[ n_2(\tilde{q}_m; \tilde{q}_{j_1}, \tilde{q}_{j_1}, l_1, l_1, \ldots, E_i) = n_2. \] (2.16)

The "root-search" problem which complicates the application of classical \( S \)-matrix theory to three dimensional collision systems 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 Sec. II A can also be carried out here, and Eq. (2.15) then takes on the simpler form
\[ \sigma_{n_2 \rightarrow n_1}(E_i) = \pi n_2^2 \int_0^1 d\theta \int_0^1 d\tilde{q}_1 \left( \frac{d(\tilde{q}_1 \tilde{q}_1)}{2\pi} \right)^2 \times \left( \frac{d(\tilde{q}_1 \tilde{q}_1)}{2\pi} \right)^2 \frac{d(\tilde{q}_1 \tilde{q}_1)}{2\pi} \end{array} P_{n_2 n_1}(j_1 \tilde{q}_{j_1}, \tilde{q}_{j_1}; E_i), \]
where \( P_{n_2 n_1}(j_1 \tilde{q}_{j_1}, \tilde{q}_{j_1}; E_i) = (2\pi \delta(n_2 \delta q_{m_2}) \right)^{-1} \exp(-2 Im\phi). \)

(2.17)
The vibrational transition probability function defined by Eq. (2.16) has the structure of a collinear vibrational transition probability 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, namely a "gas kinetic cross section" multiplied by an average vibrational transition probability: here one sees precisely what this "average vibrational transition probability" is.

Equation (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
\[ \sigma_{n_2 \rightarrow n_1}(E_i) = \int d(\cos \theta) \sigma_{n_2 \rightarrow n_1}(\theta, E_i) \]
\[ = \int d(\cos \theta) \sigma_{n_2 \rightarrow n_1}(\theta, E_i), \]
(2.19)
(2.20)
to obtain the \( n_1 j_1 - n_2 j_2 \) cross section differential in final rotational state and in scattering angle, i.e., \( \sigma_{n_2 \rightarrow n_1}(\theta) \), one simply defines a set of \( j_2 \) boxes and \( \cos \theta \) 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 \( \cos \theta \) box which corresponds to the final values of \( j_2 \) and \( \cos \theta \) for the trajectory which satisfies Eq. (2.16), i.e., the one from which the transition probability in Eq. (2.16) is constructed. The distributions in \( j_2 \) and \( \cos \theta \) are thus obtained simultaneously with the calculation of the integral cross section \( \sigma_{n_2 \rightarrow n_1}(\theta) \), 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 is might require only 50 Monte Carlo points, for example, to evaluate the integral cross section to within 10% statistical error, but a larger number of points would be required to obtain the distribution of final rotational states, \( \sigma_{n_2 \rightarrow n_1}(\theta) \), and a still larger number of points to obtain the "doubly differential" cross section \( \sigma_{n_2 \rightarrow n_1}(\theta) \) differential in \( j_2 \) and \( \theta \) 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 quantities with less detailed calculations. By way of contrast, in a completely 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., \( n_2, \tilde{q}_{m_2}, \tilde{q}_{m_2}, l_1, \tilde{q}_{l_1}, l_1, \tilde{q}_{l_1}, \ldots \)), 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., \( n_2, \tilde{q}_{m_2}, l_1, \ldots \)). Appendix C of Ref. 12 gives the expressions for the initial values of the Cartesian variables in terms of the action-angle variables (see also Sec. II.B of Ref. 10). With regard to the transformation at the end of the trajectory, the final angular momentum variables \( j_2 \) and
\[ j_{2} \cdot \frac{1}{2} = (p_{2} \cdot p_{2} + p_{2} \cdot p_{2})^{1/2}, \]
\[ i_{2} \cdot \frac{1}{2} = (p_{2} \cdot p_{2} + p_{2} \cdot p_{2})^{1/2}, \]
where \( p_{2} \) and \( p_{2} \) are the Cartesian variables of the diatom and \( p_{2} \) and \( p_{2} \) 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
\[ \epsilon = (p_{2} \cdot p_{2})/2m, \]
\( \epsilon \) being the vibrational potential of the diatom, and then solving the equation
\[ \epsilon = \epsilon_{2} \]
(3.1)
for \( \epsilon_{2} \) (since \( \epsilon_{2} \) is known), where \( \epsilon \) is the WKB energy level formula for the diatom; it is usually known as a Dunham expansion. Alternatively, with \( \epsilon_{2} \) known from Eq. (3.1), \( \epsilon_{2} \) can be computed directly from the WKB quantum condition:
\[ \epsilon_{2} = \int_{r_{0}}^{r} dr \left[ 2m (\epsilon_{2} - \epsilon) \right]^{1/2} \]
(3.2)

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—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 developed a variable step-size predictor–corrector algorithm; it has the variable stepsize and self-starting advantages of Runge–Kutta routines with the efficiency of a predictor–corrector (e.g., Adams–Moulton) method, Appendix C of Ref. 18 gives the predictor and corrector formula for the fifth order [error \( \sim O(h^{5}) \)] version of the algorithm; used in the PECE mode, 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, \( \tau \) 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 \( \tau \) becomes complex, the vibrational coordinate is oscillatory,
\[ r(t) = r_{n} - \cos(\omega t + \eta), \]
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 \( r_{n}, \dot{r}_{n}, \dot{r}_{n}, \quad r_{n+1}, \dot{r}_{n+1}, \dot{r}_{n+1}, \) etc. are known, so that for \( t \) near \( t_{n} \) one has the approximation
\[ r(t) = r_{n} + \dot{r}_{n}(t - t_{n}) + \frac{1}{2}\ddot{r}_{n}(t - t_{n})^{2}, \]
(3.4)
and one wishes to choose the next time \( t_{n+1} \) so that
\[ r(t_{n+1}) = r_{n+1}; \]
(3.5)

solving Eq. (3.4) and (3.5) gives
\[ \Delta t = t_{n+1} - t_{n} = \left( \frac{\dot{r}_{n}}{\ddot{r}_{n}} \right) \frac{1}{\frac{1}{2} \ddot{r}_{n}^{2} + 2 \dddot{r}_{n}(r_{n+1} - r_{n})^{1/2}}, \]
(3.6)
with the sign chosen to ensure \( \text{Re} (\Delta t) > 0 \). Actually one wishes only to cause \( r(t) \) to head in the direction of \( \Delta r \); thus the new time increment is chosen to have the phase of that in Eq. (3.6) but the magnitude determined by the truncation error estimate of the integrator. If \( \Delta t \) is given by Eq. (3.6), then the new time increment is thus chosen as
\[ h(\Delta t)/|\Delta t|, \]
where \( |\Delta t| \) is the complex absolute value of \( \Delta t \) and \( h \) is the magnitude of time increment allowed by the integrator.

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 \( i_{2} \) and \( i_{2} \) in Eq. (2.14) are over real values of these quantities, so that when changing to integration variables \( \xi \) and \( \xi \), the integrals over these variables must be contour integrals, i.e.,
\[ \int d\xi \int d\xi = \int_{C_{1}} d\xi_{1} \int_{C_{2}} d\xi_{2} \int_{C_{1}} d\xi_{1} \int_{C_{2}} d\xi_{2} \frac{g(j_{2} j_{2})}{g(\xi_{1}, \xi_{1})}, \]
\[ = \int_{C_{1}} d\xi_{1} \int_{C_{2}} d\xi_{2} \frac{g(j_{2} j_{2})}{g(\xi_{1}, \xi_{1})} \frac{d\xi_{1}}{\xi_{1}}, \]
\[ = \int_{C_{1}} d\xi_{1} \int_{C_{2}} d\xi_{2} \frac{\partial}{\partial \xi_{1}} \frac{g(j_{2} j_{2})}{g(\xi_{1}, \xi_{1})} \left( \frac{d\xi_{1}}{\xi_{1}} \right)^{-1}, \]
(3.7)

where the contours \( C_{1} \) and \( C_{2} \) must be chosen so that \( j_{2}(\xi_{1}, \xi_{1}) \) and \( \xi(\xi_{1}, \xi_{1}) \) 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,
\[ |d\xi_{1}| = d(\text{Re} \xi_{1}) \left( \int_{C_{1}} d(\text{Re} \xi_{1}) \right)^{1/2}, \]

\[ |d\xi_{2}| = d(\text{Re} \xi_{2}) \left( \int_{C_{2}} d(\text{Re} \xi_{2}) \right)^{1/2}, \]

\[ \text{J. Chem. Phys., Vol. 61, No. 12, 15 December 1974} \]
\[ |d\bar{q}_{i1}| = d(\text{Re}\bar{q}_{i1}) \left[ 1 + \left( \frac{d(\text{Im}\bar{q}_{i1})}{d(\text{Re}\bar{q}_{i1})} \right)^{1/2} \right]^{1/2}. \]  

(3.8)

It is possible, therefore, to integrate with respect to \( \text{Re}\bar{q}_{i1} \) and \( \text{Re}\bar{q}_{i1} \), provided \( \text{Im}\bar{q}_{i1} \) and \( \text{Im}\bar{q}_{i1} \) are chosen at each integration point to satisfy

\[ \text{Im}\bar{q}_{i1} = 0, \]

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

\[ \sigma_{n_{1}-n_{1}}(E_{1}) = \beta_{n_{1},n_{1}}^{2} \int_{0}^{1} d\xi \int_{0}^{1} d(\text{Re}\bar{q}_{i2}/2\pi) \int_{0}^{1} d(\text{Re}\bar{q}_{i3}/2\pi) A_{i} A_{j}(2\pi |\delta_{n_{1}}/\delta_{n_{1}}|)^{-1} \exp(-2i\Phi), \]

(3.10)

where

\[ A_{j} = \left[ 1 + \left( \frac{d(\text{Im}\bar{q}_{i1})}{d(\text{Re}\bar{q}_{i1})} \right)^{1/2} \right]^{1/2}, \]

\[ A_{i} = \left[ 1 + \left( \frac{d(\text{Im}\bar{q}_{i1})}{d(\text{Re}\bar{q}_{i1})} \right)^{1/2} \right]^{1/2}. \]

For each value of the integration variables in Eq. (3.10) one must choose the four variables \( \bar{q}_{i1} = \text{Re}\bar{q}_{i1} + i \text{Im}\bar{q}_{i1} \), \( \bar{q}_{i1} \), and \( \text{Im}\bar{q}_{i1} \), so that the four equations are satisfied:

\[ \text{Re}\bar{q}_{i2}(\text{Re}\bar{q}_{i1}, \text{Im}\bar{q}_{i1}, \text{Im}\bar{q}_{i1}, \text{Im}\bar{q}_{i1}) = n_{2}, \]

(3.11a)

\[ \text{Im}\bar{q}_{i2}(\text{Re}\bar{q}_{i1}, \text{Im}\bar{q}_{i1}, \text{Im}\bar{q}_{i1}, \text{Im}\bar{q}_{i1}) = 0, \]

(3.11b)

\[ \text{Im}\bar{q}_{i3}(\text{Re}\bar{q}_{i1}, \text{Im}\bar{q}_{i1}, \text{Im}\bar{q}_{i1}, \text{Im}\bar{q}_{i1}) = 0, \]

(3.11c)

\[ \text{Im}\bar{q}_{i3}(\text{Re}\bar{q}_{i1}, \text{Im}\bar{q}_{i1}, \text{Im}\bar{q}_{i1}, \text{Im}\bar{q}_{i1}) = 0. \]

(3.11d)

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 \( \bar{q}_{i1} \) and \( \bar{q}_{i1} \) is clearly the same if these angle variables have added to them arbitrary multiples of 2\( \pi \), i. e., if

\[ \bar{q}_{i1} = \bar{q}_{i1} + 2m_{1}, \quad \bar{q}_{i1} = \bar{q}_{i1} + 2m_{2}, \]

where \( m_{1} \) and \( m_{2} \) being arbitrary integers, while the imaginary part of the action integral

\[ \Phi = \int_{t_{1}}^{t_{2}} dt \left( R(t) \frac{dP(t)}{dt} + q_{i}(t) \frac{d\theta_{i}(t)}{dt} \right) \]

changes according to

\[ \text{Im}\Phi = -\text{Im}\Phi - 2\pi m_{1} \text{Im}(\Delta t) - 2\pi m_{2} \text{Im}(\Delta t) \]

(3.12)

where

\[ \Delta t = \int_{t_{1}}^{t_{2}} (\bar{q}_{i1} - \bar{q}_{i1} - \bar{q}_{i1} - t_{1}), \]

\[ \Delta t = \int_{t_{1}}^{t_{2}} (\bar{q}_{i1} - \bar{q}_{i1} - \bar{q}_{i1} - t_{1}). \]

There is clearly no physical significance to which \( 2\pi \) increment \( \bar{q}_{i1} \) and \( \bar{q}_{i1} \) are chosen from, i. e., to the values of \( m_{1} \) and \( m_{2} \), so that \( \text{Im}\Phi \) would not be uniquely determined if \( \text{Im}\Delta t \) and \( \text{Im}\Delta t \) were not 0. Equation (3.11), however, ensures that they are 0, so that \( \text{Im}\Phi \) is indeed uniquely defined.

Since one must solve Eqs. (3.11) many times—one for each set of the Monte Carlo-chosen integration vari-
where $\chi(t)$ is obtained by adding one extra differential equation to the twelve first order equations for the trajectory in Cartesian coordinates,

$$\dot{\chi}(t) = -R(t) \cdot \dot{\chi}(t) - \chi(t) \cdot \ddot{\chi}(t),$$  
(3, 16)

with the initial condition

$$\chi(t_0) = 0.$$  
(3, 17)

With these approximations—namely, that $\bar{q}_{i_1}$ and $\bar{q}_{i_1}$ are taken to be real and, consistently with this, the action integral is defined by Eq. (3, 14)—it is now only necessary to solve the one complex equation

$$n_0(\bar{q}_n) = n_m,$$  
(3, 18)

for each given set of integration variables in Eq. (2, 17). This is easily accomplished by first evaluating $n_0(\bar{q}_n)$ for the three real values (involving completely real trajectories) $\bar{q}_n = 0, \frac{3}{4} \pi$, and $\frac{3}{4} \pi$; these values determine the three coefficients in the functional form

$$n_0(\bar{q}_n) = a_0 + a_1 \cos \bar{q}_n + b_1 \sin \bar{q}_n.$$  
(3, 19)

With the fit to $n_0(\bar{q}_n)$ given by Eq. (3, 19) one solves Eq. (3, 18) for the approximate complex value of $\bar{q}_n$, runs a complex trajectory to evaluate the exact $n_0(\bar{q}_n)$ at this value, uses this value and two previous ones to rederive the coefficients in Eq. (3, 19) and iterates the procedure. It usually takes only three to five complex trajectories, after the three 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 $\bar{q}_{i_1}$ and $\bar{q}_{i_1}$ real, and for consistency modifying the expression for Im $\delta$, 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 reexamine 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 Koless–Wolniewicz H$_2$ potential was also used in some test calculations, and this made negligible difference.

Figure 1 shows the cross sections for vibrational deactivation of H$_2$ by Li$^+$, i.e., $\sigma_{n_f \rightarrow n_i}$ (Eq. 1) for $(n_1, j_1) = (1, 0)$ and $n_2 = 0$, for an initial collision energy $E_i = 0.684$ 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 QM in Fig. 1 are the results of Schaefer and Lester$^9$ quantum mechanical calculations with a coupled channel expansion including the states

$$n = 0, \ j = 0, 2, 4, 6, 8, 10$$

$$n = 1, \ j = 0, 2, 4$$

$$n = 2, \ j = 0, 2.$$

The values labeled QM II are their results 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 QM I and QM II results is due to numerical errors, for the algorithm used for solving the coupled equations does not seem well suited for treating processes with small transition probabilities.

The cross section summed over final rotational states, $\sigma_{n_f \rightarrow n_i}$, for $(n_1, j_1) = (1, 0)$ and $n_2 = 0$, is 1.87 $a_0$, 1.15 $a_0^2$, and 0.83 $a_0^3$, 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 deactivation.

The distribution in scattering angle, i.e., the differential cross section, for the 1–0 vibrational deactivation was also obtained within the classical Monte Carlo.
The angular distribution, or differential cross section for the same process as in Fig. 1, summed over final rotational states.

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 deexcitation goes into rotational excitation. The amount of rotational excitation considered less than that of a "resonant" process (no change in translational energy), however, for that demand a final rotational state \( j_2 = 8 \). Another interesting comparison is to a statistical distribution of final rotational states: this corresponds to

\[
\sigma_{n\rightarrow n_2j_2}(\theta) = \sum_{j_2} \sigma_{n_2j_2 \rightarrow n_2j_2}(\theta)
\]

(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 deactivation proceeds 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 demand a final rotational state \( j_2 = 8 \). Another interesting comparison is to a statistical distribution of final rotational states: this corresponds to

\[
\sigma_{n\rightarrow n_2j_2}(E) = (2j_2 + 1)[E - \epsilon(0,j_2)]
\]

(4.3)

where \( E \) is the total energy and \( \epsilon(0,j_2) \) 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 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.
2 See, for example, R. E. Roberts, J. Chem. Phys. 55, 100 (1971), and earlier work cited therein.
3 The DWBA would presumably be applicable if a multichannel distortion potential matrix were used, one which describes rotationally inelastic processes within each vibrational manifold.
4 Some recent approaches to reducing the number of coupled equations are those by (a) H. Rabitz, J. Chem. Phys. 57, 1718 (1972); (b) H. Rabitz and G. Zagar, ibid., 59, 1973; (c) T. T. Pack, ibid., 69, 633 (1974); (d) F. McGuire and D. J. Kouri, ibid., 60, 2488 (1974).
6 For a review of many of these approaches, see D. Rapp and T. Kassal, Chem. Rev. 69, 61 (1969). Some recent examples of the classical path model are those by (a) T. A. Dillon and J. C. Stephenson, Phys. Rev. A 6, 1460 (1972); (b) J. Chem. Phys. 55, 2056 (1973); 58, 3848 (1973); (c) G. B. Sörens, ibid., 57, 5241 (1972); (c) W. B. Neilson and R. G. Gordon, ibid., 58, 4313 (1972).
7 Some recent examples of the application of this model are (a) G. C. Berend, R. L. Thommerson, and S. W. Benson, J. Chem. Phys. 57, 3601 (1972); (b) G. C. Berend and R. L. Thommerson, ibid., 58, 3230 (1973); 58, 3454 (1973); (c) M. Rubinson, B. Czerep, and J. P. Steinfield, 60, 3062 (1974).
13 If the diatom is homonuclear, so that \( \Delta \) is required to be even, then the width of the rotational quantum number box is of course taken to be \( \Delta \), rather than \( l \).
16 See, for example, K. F. Herzfeld and T. A. Litovitch, Absorption and Dispersion of Ultrasonic Waves (Academic, New York, 1959).
19 This ensures that the trajectory does not back up to a prior real time at which the equilibrium position was passed.
20 J. Schaeffer and W. A. Lester (unpublished).
21 J. A. Lester (private communication).
22 G. Wolken (private communication).