sites of hydrogen-bonded hydroxyls. Formate formation caused surface carbonates to disappear and did not displace the isolated hydroxyls, suggesting that the formate species was adsorbed on a zinc site on the nonpolar ZnO plane. The formation of adsorbed formaldehyde and methoxy groups caused the isolated hydroxyls to disappear, indicating that these species were adsorbed on zinc sites on the polar ZnO plane. Formaldehyde was produced during methanol decomposition on a polar ZnO surface but not on any other surface. The type I hydroxyl at 3524 cm$^{-1}$ apparently exists on an energetic surface or defect site. Because both formic acid and methanol adsorption produced this hydroxyl species, it can be proposed that stepped surfaces between polar and nonpolar planes are the sites for this type of hydroxyl group.

Conclusions

The adsorption of methanol, formaldehyde, and formic acid on binary Cu/ZnO and ternary Cu/ZnO/Cr$_2$O$_3$ catalysts provided an improved understanding of the nature of reaction intermediates in methanol synthesis. Infrared spectra of formate and methoxy species on these catalysts were very similar to formate and methoxy species on pure zinc oxide. The behavior of surface hydroxyl groups indicated how the adsorbate interacted with the catalyst surface. Thus it was possible to establish that the bidentate formate species was adsorbed on the nonpolar ZnO surface, whereas the adsorbed formaldehyde and methoxy species were adsorbed on the same sites on polar ZnO surfaces. The methanol synthesis reaction is structure sensitive because the intermediates occur on different crystal planes. This study indicates that the adsorbed formaldehyde species would be unstable at methanol synthesis conditions, i.e., temperatures above 200 °C. On the basis of microscopic reversibility of chemical reactions, the hydrogen from the surface hydroxyls at 3524 cm$^{-1}$ would hydrogenate methoxy groups to form methanol.

Acknowledgment. This work was conducted through the Ames Laboratory which is operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.

Registry No. Cu, 7440-50-8; ZnO, 1314-13-2; Cr$_2$O$_3$, 1308-38-9; methanol, 67-56-1; formaldehyde, 50-00-0; formic acid, 64-18-6.

Rotational Predissociation of Model Atom–Diatomic Complexes

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The rotational predissociation and intramolecular energy transfer rates of model atom–diatomic complexes are determined via classical trajectory methods. For those systems whose quantum mechanical lifetimes have also been computed, the ensemble-averaged classical decay rates are in surprisingly good agreement. Underlying details of the energy transfer mechanism are examined with coordinate-momentum pair distribution density and autocorrelation function techniques. The pair distribution densities are useful for gaining insight into where the collection of trajectories tend to accumulate. The correlation functions allow one to observe, for ensembles of trajectories, energy transfers which occur at regular frequencies. These two probes of the intramolecular energy transfer process provided considerable information about the model van der Waals species treated here. They allowed us to identify when, in a typical trajectory's path, energy transfer takes place. However, they also indicated the presence of other energy transfer events whose nature we do not yet comprehend.

I. Introduction

The rates of rotational predissociation of several model triatomic van der Waals complexes were previously studied quantum mechanically in our laboratory using the complex coordinate rotation method (CR). With the scientific community's growing interest in using classical mechanics to study molecular-level dynamical processes, we were interested in results obtained using classical trajectory calculations on these same model systems. We studied three model systems. One of the systems (system I) provides a model for the Ar–H$_2$ complex which has a weakly anisotropic atom–diatomic potential energy. The second system is slightly more anisotropic and is chosen to approximately represent the reduced mass and well depth of Xe–H$_2$ but with an unrealistically large anisotropy. The third system is an even more strongly anisotropic model for the adatom, so that energy transfer rates could be examined as both the initial vibrational and rotational energies were varied.

These three systems span a wide range of anisotropies and well depths. They all involve small atom–diatomic relative reduced masses with large diatomic rotational constants, which means that quantum effects would be expected to be quite important. In our opinion, it is precisely in such situations that comparisons between quantum and classical mechanical results are most interesting. In other words, it is most intriguing to examine systems where classical dynamics might be expected to fail; such cases provide the best data for critically evaluating the connection between quantum and classical mechanics.

In the present study, we determined the predissociation lifetimes of several internal (vibration–rotation) states of the model atom–diatomic van der Waals (vdW) complexes by monitoring ensembles of trajectories whose initial conditions are selected to replicate internal quantum states of the complex. By graphing the number of trajectories remaining undissociated as a function of time we extract the decay-kinetics information. In an attempt to better characterize the lifetime for which energy is transferred between modes, we further analyzed the energy transfer process by using coordinate-momentum pair distributions, by monitoring selected individual trajectories, and by calculating correlation functions of relevant dynamical variables. These probes of the system dynamics constitute much of what is novel about the present work.

We emphasize that our interest here lies not in performing accurate calculations on realistic vdW molecules. The calculations we are carrying out should be viewed as model studies on arti-
Predissociation Model of Atom–Diatom Complexes

Figure 1. Geometry of the diatomic molecule and adatom. $R$ is the bond length of the diatom, $r$ is the distance between the adatom and the center of mass of the diatom, and $\theta$ is the angle between the $\mathbf{F}$ and $\mathbf{R}$ vectors.

Artificially chosen model systems which are qualitatively representative of vDW molecules. The value of such studies lies in the new knowledge and insight they can provide about trends in quantum-classical correspondence or in energy transfer rates as various molecular parameters are adjusted.

The classical trajectories used in this work involve motion on model atom–rigid homonuclear diatomic potential energy surfaces. The angle dependence of the vDW potential is written as a two-term expansion in Legendre polynomials, containing only the even terms $P_0$ and $P_2$ since the diatomic molecules being considered are homonuclear. The two-term expansion implies that these model van der Waals systems involve weakly to moderately anisotropic potentials. Hence, our potentials are two-term sums consisting of a spherical part $V_0(r)$ which is independent of orientation and an anisotropic part $P_2(\cos \theta)V_2(r)$ which is dependent on the orientation of the diatomic molecule. The adatom–diatom separation $r$ and internal angle $\theta$ are displayed in Figure 1.

Our classical trajectories begin with the adatom of the complex in a particular (approximate) vibrational state $v$ and with the diatomic molecule in a particular (approximate) excited rotational state $J$. The total angular momentum $J_{\text{total}}$ of the complex is constrained to be zero (in order to generate results to compare to our earlier quantal results which involved only $J_{\text{total}} = 0$), so the diatomic’s angular momentum is offset by the orbiting motion of the adatom.

The rate of energy transfer from the diatomic’s rotation to the adatom’s motion results in the metastability of such states of the complex. Since the adatom–diatom potential is dominated by its spherical term ($V_0(r)$), the coupling of the rotational and vibrational modes is rather weak and the energy transfer is slow. It is also the weak to moderate anisotropy of $V(r,\theta)$ which allows us to approximately label the initially prepared metastable state by the vibrational and rotational quantum numbers, $v$ and $J$. Upon creation of the system in such a state, there is enough total energy for the complex to dissociate, but some of it is trapped in the nondissociative rotational motion of the molecule. The energy is transferred from the rotational mode into the adatom’s vibrational mode due to the anisotropic term ($V_2(r)P_2(\cos \theta)$) of the potential, which couples the two degrees of freedom, and dissociation eventually occurs. We were interested in the rates of decay of various initial ($v, J$) states and the branching ratios for production of the diatomic in various final rotational states. We also wanted to gain a clearer physical picture of the energy transfer process which gives rise to the dissociation of these complexes.

We proceed now to discuss, in section II, the specific atom–diatom potentials employed; our computational methods are treated in section III. Then, in section IV, we analyze our results and discuss the mechanism of energy transfer which seems to be operative. Section V contains our concluding remarks.

II. Specification of the Atom–Diatom Potentials

The model van der Waals complexes treated here consist of a homonuclear diatomic molecule and an adatom. As shown in Figure 1, the potential energy is a function of three variables: $R$, $r$, and $\theta$. $R$ is the bond length of the diatom, $r$ is the distance between the atom and the center of mass of the diatom, and $\theta$ is the angle between the $\mathbf{F}$ and $\mathbf{R}$ vectors. We are restricting our attention, as was done in the earlier quantum study, to situations in which the complex’s total angular momentum vanishes ($J_{\text{total}} = 0$).

TABLE I: Parameters of vDW Complexes

<table>
<thead>
<tr>
<th>System</th>
<th>$\mu$, amu</th>
<th>$B_0$, cm$^{-1}$</th>
<th>$c$, cm$^{-1}$</th>
<th>$a_0$</th>
<th>$b_0$</th>
<th>$a_1$</th>
<th>$b_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.9191</td>
<td>60.0</td>
<td>53.938</td>
<td>3.2423</td>
<td>1.00</td>
<td>0.1184</td>
<td>0.1192</td>
</tr>
<tr>
<td>II</td>
<td>1.981</td>
<td>60.551</td>
<td>60.408</td>
<td>3.4745</td>
<td>1.00</td>
<td>0.09</td>
<td>0.1192</td>
</tr>
<tr>
<td>III</td>
<td>1.3405</td>
<td>60.967</td>
<td>384.097</td>
<td>3.00</td>
<td>1.00</td>
<td>0.00</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Figure 2. The potential energy diagram for the vDW complex of system III containing the spherical part $V_0(r)$ and the anisotropic part $V_2(r)$. The four bound states (---) are also shown and occur at energies of $-272$, $-116$, $-34$, and $-4$ cm$^{-1}$.

0). Hence, the internal angular motion can be thought of as the rotation of the diatom within the triatomic complex, which is balanced by the tumbling or orbiting of the adatom relative to the diatom. Furthermore, the diatomic’s bond length ($R$) is held constant in this model study of rotational predissociation. Hence, the functional form of the potential $V(r,\theta)$ is a sum of two terms: a spherical part, $V_0(r)$, and an anisotropic part, $V_2(r)P_2(\cos \theta)$

$$V(r,\theta) = V_0(r) + V_2(r)P_2(\cos \theta)$$

(1)

where $P_2(\cos \theta)$ is the second Legendre polynomial. For systems II and III, $V_0(r)$ and $V_2(r)$ are given in the Lennard-Jones form

$$V_{0,2}(r) = 4[a_0(\alpha/r)^{12} - a_2(\alpha/r)^6]$$

and for system I, which is chosen to represent Ar–H$_2$, $V_0(r)$ and $V_2(r)$ are of the form

$$V_{0,2}(r) = (27/4)[a_0(\alpha/r)^{12} - a_2(\alpha/r)^6]$$

which is similar to the Lennard-Jones but whose 12,8 power law mimics the experimental data better than the 12,6 power law does. $V(r,\theta)$ is designed to be even in $\cos \theta$ because the diatom is homonuclear. The $V_0$ potentials of the three model systems can support one, two, and four bound states, respectively. The numerical values of the parameters defining $V(r,\theta)$ for all three systems are given in Table I and $V_0$ and $V_2$ for the most strongly anisotropic system III, are shown pictorially in Figure 2.

The restrictions to zero total angular momentum and fixed diatomic bond length were made primarily to permit direct comparison with the results of the earlier quantum study where these restrictions greatly reduced the computational difficulty of the project. The constant-$R$ restriction is physically reasonable because, at the total energies considered here, excitation of the diatomic’s vibrational motion is not probable if the diatomic has a vibrational spacing greater than 1200 cm$^{-1}$. The $J_{\text{total}} = 0$ restriction

(3) From an analysis of the infrared spectrum measured by McKellar and Welsh (J. Chem. Phys., 55, 595 (1971))) a potential was obtained by Dunker and Gordon (J. Chem. Phys., 68, 700 (1978)) to which Beswick and Requena fit a Morse potential (J. Chem. Phys., 72, 3018 (1980)). Bašić (Z. Bašić, Ph.D. Thesis, University of Utah, 1981) found that the 12,8 power law fit the Morse potential better than the 12,6 power law.
is not made on any physical grounds; certainly at experimentally
relevant temperatures, many values of $J_f$ are Boltzmann populated.
$J_f = 0$, which is insensitive only to permutational energies with
the quantum results, means that the adatom is tumbling relative to
the center of mass of the diatom. Tumbling quantum numbers
$(l)$ of 2 or 4 correspond to centrifugal potential energies $h^2[l(l+1)/2]u^2$ of approximately $16.7l(l+1)/μ^2$ cm$^{-1}$ with $μ$
the system's reduced mass, in amu and $r$ in Å. In the region of
the interfragment separation where $V_o(r)$ is substantial, this contribu-
tion to the interfragment effective radial potential ranges from
0.2 to 8.5 cm$^{-1}$ for $l = 2, 4$ for systems I, II, and III.

III. Computational Methods Used

A. Initial Coordinates and Momenta. To simulate the behavior
of each of the metastable internal energy levels of the vdW
complex, 10$^4$ classical trajectories were run. Each of these internal
states are labeled by an adatom vibrational quantum number $v$
and a diatom rotational quantum number $J$ which, because $J_f$
= 0, equals the adatom's tumbling quantum number $l$. The fact
that the spherical part ($V_o$) of the potential $V(r,θ)$ dominates the
anisotropic part ($V_v$) (see Figure 2) for all three systems, allows
the quantum numbers $v$ and $J$ to be used to approximately specify
initial conditions. It also suggests that it is reasonable to use
solutions to the separate diatom rotational and adatom vibrational
(with $V(r) = V_v(r)$) Schrödinger equations as the approximate
radial and angular eigenstates corresponding to various ($v, J$
) levels. Hence, in selecting initial coordinates and momenta for use
in the classical trajectories, only the dominant term, $V_v$, was used in
determining the radial distributions. As described previously,
the $h^2[l(l+1)/2μ^2$ term contributes at most 8.5 cm$^{-1}$ to the initial
potential; therefore, the radial-coordinate distributions were
calculated with eigenfunctions of only the $V_v$ term. The angular
motion of the diatom relative to the atom is approximated as that of
a free rigid rotor and hence the angular-coordinate distributions
are described by the usual spherical harmonics. The squares of
these rotational and vibrational wave functions were then used to
generate weighting factors for choosing classical-trajectory initial
coordinates. The values of $r$ considered in choosing the initial
coordinates ranged from approximately 4 to 14 bohrs; outside of
these ranges, the radial probability was essentially zero. The angles
θ were allowed to range from 0 to 90°; since the diatomic molecule
is homonuclear, $θ$ and 180° − $θ$ have identical probabilities. The
magnitudes of the initial momenta, $P_r$ and $P_θ$, were determined
by knowing the classical kinetic energy of the system in each of
the two approximately separable degrees of freedom at any given point
($r, φ$). The directions (signs) of the momenta were determined
randomly.

It should be stressed that although the tumbling centrifugal
potential is small (<8.5 cm$^{-1}$ for $J = 2, 4$) and is neglected in
choosing the initial coordinates and momenta, this contribution
to the complex's total energy is fully and properly incorporated
into our classical trajectory calculations of the time evolution of
the system.

B. Integration of Classical Trajectories. For any approximate
$v J$ energy level, 10$^4$ ($θ$, $r$, $P_θ$, $P_r$) initial values were obtained as
outlined above. The classical equations of motion were integrated
by using a sixth-order Gears hybrid predictor-corrector numerical
integration method$^4$ with a time step of $2 \times 10^{-12}$ s. This time
step was arrived at by insisting that our trajectories regenerate
the same classical path when run in reverse. By examining the
range of the potential surfaces, we determined that once $r$
reached 20 bohrs for systems II and III, the complex was irreversibly
dissociated if the total energy was above the dissociation limit
and the radial momentum was greater than zero. Therefore, the
conditions $r > 20$ bohr and $P_r > 0$ were used as our definition of
when dissociation had occurred for systems II and III. For
system I (the model for the Ar–H$_2$ complex), our definition of
when dissociation had occurred was $r > 13$ bohr and $P_r > 0$.

Subsequent to dissociation, the final rotational state $J_f$ of the
diatomic molecule was recorded. Since classical mechanics need
not yield rotational energies which are quantized, the fraction of
trajectories in each $J_f$ state had to be decided by binning them
thereinto only to permit comparison with the quantum results.

To simulate the behavior of each of the metastable internal energy levels of the vdW complex, 10$^4$ classical trajectories were run. Each of these internal states are labeled by an adatom vibrational quantum number $v$ and a diatom rotational quantum number $J$ which, because $J_f = 0$, equals the adatom's tumbling quantum number $l$. The fact that the spherical part ($V_o$) of the potential $V(r,θ)$ dominates the anisotropic part ($V_v$) (see Figure 2) for all three systems, allows the quantum numbers $v$ and $J$ to be used to approximately specify initial conditions. It also suggests that it is reasonable to use solutions to the separate diatom rotational and adatom vibrational (with $V(r) = V_v(r)$) Schrödinger equations as the approximate radial and angular eigenstates corresponding to various ($v, J$) levels. Hence, in selecting initial coordinates and momenta for use in the classical trajectories, only the dominant term, $V_v$, was used in determining the radial distributions. As described previously, the $h^2[l(l+1)/2μ^2$ term contributes at most 8.5 cm$^{-1}$ to the initial potential; therefore, the radial-coordinate distributions were calculated with eigenfunctions of only the $V_v$ term. The angular motion of the diatom relative to the atom is approximated as that of a free rigid rotor and hence the angular-coordinate distributions are described by the usual spherical harmonics. The squares of these rotational and vibrational wave functions were then used to generate weighting factors for choosing classical-trajectory initial coordinates. The values of $r$ considered in choosing the initial coordinates ranged from approximately 4 to 14 bohrs; outside of these ranges, the radial probability was essentially zero. The angles $θ$ were allowed to range from 0 to 90°; since the diatomic molecule is homonuclear, $θ$ and 180° − $θ$ have identical probabilities. The magnitudes of the initial momenta, $P_r$ and $P_θ$, were determined by knowing the classical kinetic energy of the system in each of the two approximately separable degrees of freedom at any given point ($r, φ$). The directions (signs) of the momenta were determined randomly.

It should be stressed that although the tumbling centrifugal potential is small (<8.5 cm$^{-1}$ for $J = 2, 4$) and is neglected in choosing the initial coordinates and momenta, this contribution to the complex's total energy is fully and properly incorporated into our classical trajectory calculations of the time evolution of the system.

B. Integration of Classical Trajectories. For any approximate $v J$ energy level, 10$^4$ ($θ$, $r$, $P_θ$, $P_r$) initial values were obtained as outlined above. The classical equations of motion were integrated by using a sixth-order Gears hybrid predictor-corrector numerical integration method$^4$ with a time step of $2 \times 10^{-12}$ s. This time step was arrived at by insisting that our trajectories regenerate the same classical path when run in reverse. By examining the range of the potential surfaces, we determined that once $r$ reached 20 bohrs for systems II and III, the complex was irreversibly dissociated if the total energy was above the dissociation limit and the radial momentum was greater than zero. Therefore, the conditions $r > 20$ bohr and $P_r > 0$ were used as our definition of when dissociation had occurred for systems II and III. For system I (the model for the Ar–H$_2$ complex), our definition of when dissociation had occurred was $r > 13$ bohr and $P_r > 0$.

Subsequent to dissociation, the final rotational state $J_f$ of the diatomic molecule was recorded. Since classical mechanics need
point. At dissociation, the final rotational state $J_f$ of the diatomic molecule was determined and pair distribution graphs for each 2s interval were plotted for each value of $J_f$. Plots were constructed of $P_r, r$, and $P_\theta, \theta$ vs. $P_\theta, \theta$ vs. $r$, and $P_\theta, \theta$ vs. $r \theta = 2\pi$. We examined these graphs involving all of the 1000 trajectories characterizing each $(\nu,J)$ state and looked for patterns or correlations among the different variables. In particular, we were looking for patterns which either remained stationary or appeared and disappeared at regular intervals (in $\theta$ space).

D. Correlation Function Studies. To examine other aspects of the energy transfer process, we also calculated the autocorrelation function involving the derivative of the rotor’s angular momentum with respect to $\theta$, $dP_\theta/d\theta$, which is evaluated throughout any trajectory propagation as $(dP_\theta/dt)(dt/d\theta)$, was chosen as a variable to examine because it would be zero if no energy transfer were present. When $dP_\theta/dt$ is positive, energy is flowing into the diatom from the adatom. This occurs when $dP_\theta/d\theta$ is positive and $dt/d\theta$ is positive or when $dP_\theta/d\theta$ is negative and $dt/d\theta$ is negative. When $dP_\theta/d\theta$ is positive and $dt/d\theta$ is negative or when $dP_\theta/d\theta$ is negative and $dt/d\theta$ is positive, $dP_\theta/dt$ is negative and leaving is happening. By examining the autocorrelation between the starting value of $dP_\theta/d\theta$ and $dP_\theta/dt$ in the energy transfer process and we determine the range of rotational periods over which $dP_\theta/d\theta$ varies. The rate of decay of the $(dP_\theta/d\theta(\theta = 0) dP_\theta/d\theta(\theta))$ correlation function contains information both about the rate of dissociation of the vdW complex (since at dissociation $dP_\theta/d\theta \rightarrow 0$) and about loss of phase or coherence information. That is, $dP_\theta/d\theta$ can, as the trajectory dynamics proceeds, become uncorrelated with its initial value simply via coupling with the adatom’s vibrational motion.

Our decision to consider the autocorrelation of $dP_\theta/d\theta$ requires further explanation. At first we examined the time-space autocorrelation of $dP_\theta/dt$, but found that neither it nor its Fourier frequency transform contained clear structures. We decided to consider $dP_\theta/d\theta$ because we speculated that intermode energy transfer might occur more regularly in $\theta$ space than in time space. As the results described in section IV demonstrate, our “guess” was correct. The autocorrelation function in $\theta$ space shows well-defined structures some of which we have been able to exploit in our attempt to understand how the intermode energy transfer occurs (classically). There are, however, some structures in these correlation functions which we have not yet been able to assign to dynamical events.

For any initial $(\nu,J)$ level, 1000 classical trajectories were run with initial conditions determined as outlined in section III. To construct each of the $\theta$-space correlation functions, the trajectory results were digitized by using a $\theta$ step size of 0.8 rad, and a total of 1024 steps were employed. The number of $\theta$ steps and therefore step size was dictated by the fact that the fast Fourier transform routine which we used to frequency analyze the $\theta$ correlation function required the number of steps to be a power of two. We constructed graphs of the intensity of the autocorrelation function vs. $\theta$ as well as of the power spectra obtained by taking the Fourier transforms of the correlation functions. The details of how our correlation functions were computed are given in Appendix A and the results are contained in section IV.

Before closing this section on methodology, it should be pointed out that the pair distribution density is designed to uncover cause-and-effect relationships between pairs of dynamical variables and to detect regions of coordinate or momentum space where trajectories tend to accumulate. The correlation function method is designed to detect dynamical events which repeatedly occur at regular intervals in $\theta$ space.

IV. Results

A. Predissociation Rates. 1. Lifetimes. In Table II, we have listed the classical decay lifetimes and final $J_f$ branching ratios

![Table II: Decay Kinetics and Relevant Time Scales](#)

Table II: Decay Kinetics and Relevant Time Scales

<p>| System III: Initial $J = 2$ (Rotational Period = 0.091 ps); Rotor Energy, 366 cm$^{-1}$ |</p>
<table>
<thead>
<tr>
<th>Energy levels (vibrational periods)</th>
<th>% $\text{trajectories giving } J_r$</th>
<th>$r$, ps, of traj giving $J_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v = 3$ (4.8 ps)</td>
<td>$-4$</td>
<td>56 44 0</td>
</tr>
<tr>
<td>$v = 2$ (1.0 ps)</td>
<td>$-34$</td>
<td>52 48 0</td>
</tr>
<tr>
<td>$v = 1$ (0.41 ps)</td>
<td>$-116$</td>
<td>30 70 0</td>
</tr>
<tr>
<td>$v = 0$ (0.21 ps)</td>
<td>$-272$</td>
<td>0 60 40</td>
</tr>
</tbody>
</table>

<p>| System III: Initial $J = 4$ (Rotational Period = 0.027 ps); Rotor Energy, 1220 cm$^{-1}$ |</p>
<table>
<thead>
<tr>
<th>Energy levels (vibrational periods)</th>
<th>% $\text{trajectories giving } J_r$</th>
<th>$r$, ps, of traj giving $J_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v = 3$ (4.8 ps)</td>
<td>100 0 0</td>
<td></td>
</tr>
<tr>
<td>$v = 2$ (1.0 ps)</td>
<td>100 0 0</td>
<td></td>
</tr>
<tr>
<td>$v = 1$ (0.41 ps)</td>
<td>100 0 0</td>
<td></td>
</tr>
<tr>
<td>$v = 0$ (0.21 ps)</td>
<td>32 68 0</td>
<td></td>
</tr>
</tbody>
</table>

4Only 6% of the total number of molecules dissociated within the duration of our classical trajectories; hence on accurate estimate of the lifetime is impossible.

of various states $(\nu,J)$ of systems II and III. The lifetime $(r)$ is defined as the time necessary for the limited population of 10$^4$ trajectories to decrease by $e^{-1}$. These classical lifetimes were determined by fitting the decay kinetics resulting from our trajectories to an exponential decay profile $(N/N_0) = e^{-t/\tau}$ having an induction time, $\tau_0$ (see, for example, Figure 3). We found that for systems II and III, our results for all of the $(\nu,J)$ states fit such a single exponential functional form. The induction time $(\tau_0)$ is needed in our fitting procedure because our definition of dissociation $(r > 20 \text{ bohr})$ and $P_r > 0$ for systems II and III is not fulfilled until a trajectory is well outside the range of the $P(r,\theta)$ potential and it simply takes a finite amount of time $(\tau_0)$ for any trajectory to reach $r > 20 \text{ bohr}$.

System I, the model for the Ar–H$_2$ complex, did not dissociate (by our definition) even within the maximum duration $2 \times 10^{10}$ s permitted in our trajectories. Trajectories of system I tended to move out to the region where $r > 13 \text{ bohr}$, but their radial momenta $(P_r)$ became smaller and smaller so that they could not fulfill our definition of dissociation within our specified maximum time period. We believe that such trajectories were on their way to dissociation and would eventually have dissociated, but not within our maximum time period. For this reason alone, determining the rate of decay or lifetime of model system I is extremely difficult if one insists on doing so by monitoring the dissociation of individual classical trajectories. Recall that system I is the least anisotropic and hence is likely to have the smallest mode-mode energy transfer rates. As a result, trajectories tend to acquire very little radial $(r,P_r)$ energy in the excess of the complex’s dissociation energy. This makes their asymptotic rate of decay very slow and, hence, difficult for us to monitor using classical trajectory methods. As noted in Table II, the quantal coordinate rotation lifetime of this system $(\nu=0,J=2)$ is 300 ps, only 1.5 times the maximum duration of our classical trajectories. One would therefore have

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expected a measurable fraction of the $10^4$ classical trajectories to have dissociated within our numerical experiment. This observation further supports our belief that many of our trajectories actually were "on their way" to dissociation. It is thus our very strict definition of dissociation which causes difficulty when attempting to extract the decay lifetime of this very long lived system.

2. Dependence of Lifetime on $J$. From our trajectory calculations on systems II and III, we found the lifetimes to depend on the initial atom–diatom vibrational state and the initial diatomic rotational state $(v,J)$ as well as the final diatomic rotational state $(J_f)$, but in a manner which does not simply depend on the amount of total energy. For example, in system III the complex initially in $J = 4$ does not dissociate faster than the complex in the same vibrational state but initially in $J = 2$, even though the complex has much more total energy with $J = 4$ than with $J = 2$. It was also observed (see Table II) that system III in the vibrational state $v = 3$ with the rotor initially in $J = 2$ or $J = 4$ has a long lifetime, even though for $v = 3$, a transfer of only 4 cm$^{-1}$ to the vibrational mode could result in dissociation. Comparing, again in system III, the lifetimes belonging to different vibrational states all of which have $J = 2$ initially, we observe no general trend except that the lifetimes of states $v = 1$ and $v = 2$ are comparatively shorter than those of $v = 0$ or $v = 3$ (more than 1.5 times as short). This pattern is not seen in the decay rates of states of system II, where, as we go to higher energy vibrational states, the lifetimes monotonically decrease. Moreover, the rates of decay of all states in system III are faster than those of system II. This is not surprising since system III is considerably more anisotropic and hence more mode coupled.

These findings are not unexpected since it is well-known that energy content is not the only factor governing mode–mode energy transfer; the momenta or relative phases of the two modes are at least as important to consider. From a quantum mechanical viewpoint, the rate of energy transfer should be related to the strength of the coupling integral $\langle \phi_d | V_{d, P} | \phi_p \rangle$. Here $\phi_d$ is the initial rotation–vibration wave function discussed in section IIIA and $\phi_p$ is the final rotational wave function multiplied by a dissociative continuum function of $r$ having asymptotic momentum $p$. The presence of the $P_c(\cos \theta)$ angular dependence can couple $J_f$ and $J_i$ pairs which differ by no more than two units of angular momentum. Of course, for homonuclear molecules, only even $J$ and $I$ can occur. This means that for $J = 2$, $4$, $J_f$ can be only $0, 2, 4$. Energy considerations require $J_f$ to be less than $J$ since energy must flow from the rotor into the adatom's motion. The vibrational contribution to the above coupling integral involves integration over $r$ of a product of three factors: the $V_{d,P}(r)$ (e.g., Figure 2), the bound vibrational wave function $\psi_v(r)$ for state $v$, and a continuum function $\psi_p(r)$. For this radial integral to be nonvanishing it is necessary that $\psi_v(r)$ and $\psi_p(r)$ have similar local deBroglie wavelengths ($\lambda$) or kinetic energy. If a large amount of energy is transferred from the rotor to the adatom, $\psi_v$ will have a considerably shorter local $\lambda$ than will $\psi_p$, thereby causing the coupling integral to be small. Combining these two observations, we see that there is a competition between the angular contributions to the coupling integral which favor $J = 2 \rightarrow J_f = 0$ or $J = 4 \rightarrow J_f = 2$, 0 transitions and the radial contributions which favor the least change in local kinetic energy. Although these observations are made from the point of view of quantum mechanics, we feel that they also rationalize our observed data of Table II. In our classical mechanical world, conservation of momentum along the $r$ coordinate plays the role of $\psi_v$ and $\psi_p$ having similar local deBroglie wavelengths. The amount by which the wavelengths of $\psi_v$ and $\psi_p$ (or the corresponding $r$ momenta) can differ is determined by the magnitude of $V_{d,P}(r)$.

3. Branching Ratios. The branching ratios for the production of various final rotational states $J_f$ shown in Table II display a tendency for the complex to transfer little excess energy to the relative translational motion; most of the excess energy is preserved in rotation of the diatom. For example, even for the most strongly anisotropic system III, in $(v=2, J=2)$, the $366 - 34 = 332$ cm$^{-1}$ of excess energy would, if retained in the diatom's rotation, correspond to a maximum expected (classical) $J_f$ value of $J_f(J_f + 1) = 61 = 332$ or $J_f = 1.89$. The observed distribution of $52\%$ $J_f = 2$ and $48\%$ $J_f = 1$ corresponds to an average $J_f$ of 1.52. The difference between the maximum $J_f = 1.89$ and the observed $J_f = 1.52$ represents the amount of energy which has gone into relative translational motion. For system III in $(v=3, J=2)$ the corresponding maximum $J_f$ is 1.99 and the observed average $J_f$ is 1.56. In this case somewhat more energy has been deposited into relative translational motion. As discussed above, the tendency to deposit little excess kinetic energy into the adatom's motion can be rationalized in terms of the quantum mechanical coupling integral involving $\psi_{v_p} \psi_v$ and $V_{d,P}(r)$. Transfer of little excess kinetic energy to the adatom results in similar local deBroglie wavelengths for $\psi_{v_p}$ and $\psi_v$.

4. Comparison with Quantum Lifetimes. Bačić et al. studied these same three model systems in the lowest-energy dissociating state $(v=0, J=2)$ using the quantal coordinate rotation (CR) method. Comparing (see Table II) our classical-decay lifetimes in the $(v=0, J=2)$ state for each system with the corresponding CR lifetimes, we find that the decay times compare quite well. For system III, the two lifetimes differ by a factor of 1.6; in system II, the comparison is even better. Of course, we could not compare the lifetimes for system I since we were unable to obtain a classical lifetime for this system for reasons explained above.

In summary, our classical trajectory simulations yield lifetimes which agree unexpectedly well with the quantum results in those few cases (systems II and III, $v=0, J=2$) where data permits comparison. System I's long lifetime makes classical trajectory simulation difficult and thus suggests that more clever definitions of dissociation be developed. Although the trends in the observed classical decay lifetimes of systems II and III in various initial $(v, J)$ states and for various final $J_f$ states are not surprising, we felt that further study of the physical nature of the mode–mode energy transfer process was important. Therefore, we undertook...
the pair distribution and correlation function studies described earlier. The results of our efforts along these lines are contained in the following two subsections.

B. Coordinate-Momentum Pair Distribution Densities. 1. Observation of Interesting Structures. As previously described, our discussion of the pair distribution study focuses on the state \((\nu=3, J=2)\) of system III, since it was in this state that the observed patterns were most pronounced. Hence it is for this one state that we illustrate the usefulness of the pair distribution density data.

Approximately 1000 classical trajectories were run with their initial conditions selected as described earlier. These trajectories were used to construct various pair distribution density graphs as described in section IIIIC. After viewing all of the resulting data, there seemed to us to be four interesting features arising in the pair distribution graphs of \(P_r\) vs. \(r\) (see Figure 4) and \(P_t\) vs. \(P_t\) (see Figure 5). Let us first examine both the \((r, P_r)\) and \((P_t, P_t)\) series of graphs and point out the interesting characteristics. Then we can proceed to attempt to explain those characteristics in terms of the dynamical behavior of the two coupled modes.

First, let us look at the series of graphs for \(P_r\) vs. \(r\). Initially (Figure 4a), this pair distribution density has a shape which is entirely determined by the procedure we use to select initial conditions. It consists of two smooth curves (a top line and a bottom line) which are joined in a “hook”. As time (or \(\theta\)) evolves, the density of points constituting the top line monotonically decreases while the density of points forming the bottom line and the “hook” remain essentially constant (Figure 4b). At approximately \(\theta = 22\pi\) (Figure 4c), the top line is still decomposed and the hook has been elongated to \(13 < r < 16\) bohr and \(-0.01 < P_r < 0\). Moreover, at \(\theta = 22\pi\), the bottom line (\(7 < r < 13\) bohr}

Figure 4. A series of graphs of \(P_r\) vs. radius from the coordinate-momentum pair distribution study for the \((\nu=3, J=2)\) state of system III.
Figure 5. A series of graphs of $P_r$ vs. $P_\theta$ from the coordinate-momentum pair distribution study for the $(\nu=3, J=2, J_{pl}=1)$ state of system III.

and $-0.06 < P_\theta < -0.01$) partially decomposes. This bottom line reappears gradually over another interval of $2\pi$ (see Figure 4d) at which time the hook $\theta$ has essentially become part of the bottom line, and the top line is still absent. As seen in Figure 4e, after another interval of $2\pi$ ($\theta = 66\pi$), the bottom line has again disappeared and the hook is slowly disappearing. Hence, there seems to be a pattern of stability and then instability of the bottom line occurring at an interval of $2\pi$.

The points on this bottom line consist of inward moving trajectories ($P_r < 0$) having $r > \sigma$ bohr.

Now let us describe the second series of graphs which involve $P_r$ vs. $P_\theta$ (Figure 5). Initially (Figure 5a), this pair distribution involves a single vertical line which again is not surprising based upon our choice of initial conditions. Almost immediately, at $\theta = 2\pi$ (Figure 5b), an arc of points begins to form at smaller $P_\theta$ values and at higher $P_r$ values. The points in this arc arise because energy has been transferred from the angular mode into the radial mode. This arc persists throughout the rest of the graphs without

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(6) $P_r$ is in units of (hartrees x atomic mass units)$^{1/2}$ or $4.6 \times 10^7$ (cm$^{-1}$ x atomic mass units)$^{1/2}$.

(7) This hook is also present when the molecule is in the state $(\nu=2, J=2)$, but it does not exist for very long ($\sim 8\pi$) for this state.

(8) This pattern also occurs for the state $(\nu=2, J=2)$, but at a faster rate than for the state $(\nu=3, J=2)$. 
diminishing in intensity until most of the trajectories have dissi-
ated. At \( \theta = 22\pi \) (Figure 5c), the arc is still present, but the bottom of the vertical line (\(-0.06 < P, < -0.01\)) has disappeared. This disappearance occurs at the same \( \theta \) value as when the bottom line in the \( P, \) vs. \( r \) graph (Figure 4) disappeared. After another interval of \( 22\pi \), at \( \theta = 44\pi \) (Figure 5d), the bottom of the vertical line has reappeared, analogous to the reappearance of the bottom line in the graph of \( P, \) vs. \( r. \) Again, after an interval of \( 22\pi \), at \( \theta = 66\pi \) (Figure 5e), the bottom of the vertical line has once more disappeared. Analogous to the behavior of the bottom line in the \( P, \) vs. \( r \) graph, there exists a pattern of oscillating stability and instability in the bottom of the vertical line in the \( P, \) vs. \( P, \) data which also occurs at an interval of \( 22\pi.\) Also in the \( P, \) vs. \( P, \) series of graphs, there is an arc structure which is present throughout the trajectories.\(^9\) This structure involves \( P, \) between 0.035 and 0.045\(^9\) and \( P, \) between 0.04 and 0.06 for the final rotational state \( J, = 1 \) while for the final rotational state \( J, = 2, \) \( P, \) has a range 0.045-0.055 with \( P, \) being between 0.01 and 0.04.

2. Probing Interesting Structures with Selected Trajectories.

To examine the behavior of those trajectories which existed in each of the above-mentioned structures (i.e., the lines, hook, and arc) we ran, for each structure, approximately ten single trajectories having initial conditions placing the trajectory within the structure. Based upon analyzing the ten trajectories lying within the hook in the graphs \( P, \) vs. \( r, \) it seems that such trajectories are on their way to dissociation but have not yet transferred enough energy from the angular mode into the radial mode to dissociate; as a result the adatom eventually comes back in and hits the repulsive wall in order to exchange more energy. The adatom then goes out to the outer edge of the potential once more. If enough energy has been transferred, the molecule dissociates; otherwise, the adatom again comes back in toward the inner wall where energy is once again transferred. This cycle seems to continue until enough energy has been transferred for dissociation to occur.

The pattern of stability and instability shown in the movement of the bottom line in the graphs \( P, \) vs. \( r \) and the movement of the bottom of the vertical line in the graphs \( P, \) vs. \( P, \) was examined in a similar fashion. From the 20 single trajectories mimicking these conditions, there seems to be two connections: the disappearance of both lines occurs when the adatom is at the outer edge of the potential, whereas the appearance of both lines occurs when the adatom is very near the repulsive wall. These relationships make sense since, when the adatom is at the outer part of the potential, the radius increases and the radial momentum decreases, which implies that the bottom line (corresponding to a large magnitude of the radial momentum) should disappear. Similarly, when the molecule approaches the wall, there is an increase in the magnitude of the radial momentum, as a result of which the bottom lines should be present.

The last structure examined via individual trajectory methods is the arc formed in the graphs \( P, \) vs. \( P, \) and the movement of the bottom of the vertical line in the graphs \( P, \) vs. \( P, \) was examined in a similar fashion. From the 20 single trajectories having initial conditions appropriate to this structure, it seems that the arc consists of trajectories which have gained \( P, \) at the expense of \( P, \) and are on their way to dissociation. The arc persists because, as molecules dissociate, others come in to the same regions of \( P, - P, \) space to replace those that were lost.

It should be noted that the pair distribution graphs, whose use is illustrated above, are designed to detect regions of coordinate and momentum space in which the ensemble of trajectories build up as revealed through high dot densities. As revealed by examining the behavior of individual trajectories, the high dot densities observed are not due to each trajectory spending long times in the region of coordinate-momentum space being probed; rather they are due to many trajectories from among the ensemble of graphs having initial conditions placing the trajectory within the structures. Based upon analyzing the ten trajectories lying within the structure, it seems that such trajectories are on their way to dissociation but have not yet transferred enough energy from the angular mode into the radial mode to dissociate; as a result the adatom eventually comes back in and hits the repulsive wall in order to exchange more energy. The adatom then goes out to the outer edge of the potential once more. If enough energy has been transferred, the molecule dissociates; otherwise, the adatom again comes back in toward the inner wall where energy is once again transferred. This cycle seems to continue until enough energy has been transferred for dissociation to occur.

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functions of the three systems, it can be seen that the graphs for systems I (Figure 6a) and III (Figure 6c) are reasonably similar while that for system II (Figure 6b) seems to be quite different.

The autocorrelation function shown in Figure 6b, which is typical for all of the states in system II, consists of a series of separated pulses or bands and, within each band, a set of peaks occurring every \( \pi \) radian. The bands are separated by 21 rad for the state \((\nu=0,J=2)\) shown in Figure 6b and by 256 rad for \((\nu=1,J=2)\). The width of each band is 31 rad for \((\nu=0,J=2)\) and 44 rad for \((\nu=1,J=2)\).

For both systems I (Figure 6a) and III (Figure 6c), there are peaks occurring approximately every \( \pi \) and a slower modulation which has a period of about 125 rad. The autocorrelation functions for system III also contain a set of extra intense peaks which occur with a period of approximately 12 rad as well as a slow decay of the envelope function. The latter two features are not present in the autocorrelation graph for system I. All of the states for system III were found to have correlation functions whose envelopes fit a single exponential decay profile in \( \theta \) space. From these fits, approximate correlation decay "lifetimes" (in radians) were determined and have been listed in Table III along with the classical lifetimes (in picoseconds) which were discussed earlier in this section.

The fact that the correlation functions of all states of all three systems display strong features at \( \theta = n\pi \) (\( n = 1, 2, \ldots \)) indicated an energy transfer process which occurs every half rotation of the diatom. This does not imply that each trajectory involves giving and taking of energy by the rotor every half rotation; the correlation functions display the behavior of the entire ensemble of trajectories. As discussed in section IVB, each trajectory seems to display energy transfer only when the adatom closely approaches the rotor. Hence the appearance of alternating positive and negative contributions to the \( \Delta P_\theta/\Delta \theta \) correlation function at integral multiples of \( \pi \) can only be properly interpreted in terms of the collection of trajectories which constitute the ensemble. Simply put, at each multiple of \( \pi \), some fraction of the trajectories are spatially arranged to permit efficient energy transfer; that is, some of the adatoms are close to their partner diatoms.

The other structures displayed by the above correlation functions indicate that other factors are modulating the energy transfer rates at frequencies which correspond to those of the extra intense spikes or slow modulation feature pointed out earlier. Thus far, we have been unable to correlate these features with any natural frequencies (e.g., the rotor period or adatom vibrational period or their difference or any reasonable estimate of a Rabi frequency) of the two coupled degrees of freedom. We thus feel that the correlation function studies have given us valuable insight which, when combined with the pair distribution and individual trajectory data, allow us to present a clear picture of the operative energy transfer mechanism. However, they have also provided us with data suggestive of more detail in the energy transfer process which we have not been able to interpret.

2. Envelope Decay Times. The decay lifetimes of the correlation functions for system III are seen in Table III to vary from 10 to 35 rotations depending on the initial vibrational state and the final rotational state of the complex. We can, by assuming a rotational period which remains constant throughout the decay process, convert the number of rotations into approximate decay times (in picoseconds). These times, which are also listed in Table III, seem to agree with the classical-trajectory pseudodissociation lifetimes, but not to high precision and not equally well in all cases. In particular, the state \((\nu=2,J=2,J_f=1)\) shows a large deviation between these approximate correlation-decay lifetime values and the classical-decay times. However, it must be kept in mind that the times inferred from the \( \theta \)-space decay rates of our correlation functions are only rough estimates since they involve the (very approximate) assumption of constant rotational velocity throughout the decay. To further check on the connection between the envelope decay time and the classical dissociation time of the complex, we correlated the time derivative of \( P_\theta \) with itself to determine decay rates in the time domain instead of in \( \theta \) space. We found that the decay lifetimes in the time domain agree more closely with the classical pseudodissociation lifetimes than do the decay lifetimes in \( \theta \) space. Hence, the envelope decay in the correlation function likely arises from the dissociation of the complex which then produces a free rotor for which \( P_\theta \) is constant.

For systems I and II, the envelope decay is not seen in our correlation functions probably because the decay lifetimes for these two systems (in all internal states) are 10-100 times those for system III and our correlation functions do not extend to such large \( \theta \) values.

We also constructed graphs of the Fourier "frequency" transforms of each of the above autocorrelation functions. From these graphs, we observed peaks in the "frequency" \((1/\theta)\) space which correspond to the modulations observed in the \( \theta \)-space correlation graphs. The above correlation-function-based results have thus revealed dynamical features that occur at regular intervals in \( \theta \) space. This information has proven useful in complementing the insights gained from the pair distribution density and individual trajectory studies.

V. Concluding Remarks

From our classical trajectory calculations on the rotational pseudodissociation rates of three model vdW systems, we found that the decay kinetics of all the states of systems II and III fit a single exponential functional form. Comparing the classical lifetimes of the \((\nu=0,J=2)\) states of systems II and III to those obtained by quantal coordinate rotation methods, we found surprisingly good agreement. The lifetimes differ by no more than a factor of 1.6. System I, the model for the \( \text{Ar-H}_2 \) complex, did not dissociate by our definition, even though we believe that many of the trajectories were "on their way" to dissociation. It seems that the difficulty with system I's decay kinetics arises from our definition of dissociation when applied to very long-lived systems; our classical trajectories simply cannot be followed long enough to allow our definition to be useful. For system III, we were also able to extract from our \( \theta \)-space correlation functions approximate decay times (from the envelope decay of the correlation functions) which seem to agree with the classical pseudodissociation lifetimes.

Aside from wanting to determine decay times of the systems by using classical trajectories, we were also interested in probing the mechanism of the energy transfer process. To study this, we decided to monitor the trajectories by using two different devices: the pair distribution density method and the correlation function method.

As stated previously, the pair distribution density method shows cause and effect relationships between pairs of dynamical variables and detects regions of coordinate or momentum space where trajectories from the ensemble tend to accumulate. From examining the structures found in the pair distribution study, it seems that the energy exchange process involves the adatom first moving to the outer part of the potential; if there is not enough energy in the radial motion to cause the molecule to dissociate, the adatom eventually returns to the inner part of the adatom–diatom potential where energy can be transferred. If enough energy is then transferred to the adatom's radial mode, the adatom will move away from the diatom and the molecule will dissociate.
An ab-Initio Study of the Isotropic and Anisotropic Potential Energy Surfaces of the He–H₂ Interaction

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An accurate ab-initio potential surface of the ground-state He–H₂ interaction has been computed. Computations were performed with large optimized basis sets (up to 105 functions) using the SCF-PNOCI-CEPA2 method. The study covers the range of \( R = 2.0 \; \text{a}_0 \) to \( R = 15.0 \; \text{a}_0 \) for the He–H₂ separation and \( r = 1.449 \; \text{a}_0 \) for the H–H separation using molecular orientations of \( \theta = 0^\circ \), \( 45^\circ \), and \( 90^\circ \). Additional computations at \( r = 1.28 \) and \( 1.618 \; \text{a}_0 \) for \( R = 3.0 \), 5.0, 6.5, and 8.0 \( \text{a}_0 \) at the above orientations were carried out to investigate the contribution of H₂ zero point vibrational energy change to the potential surface. Comments are made about the origin of “damping” of the van der Waals expansion in this interaction.

Introduction

Although the He–H₂ system presents us with the simplest example of a closed-shell anisotropic interaction, considerable computational effort is required to accurately represent the various contributions to the potential energy surface within the presently available ab-initio formalisms. The most accurate and comprehensive method available to determine such van der Waals interactions is to proceed with a supramolecule calculation including the effects of electron correlation and to take the difference of total energies. One of the major difficulties with this type of calculation is that the various components of the interaction (i.e., the SCF energy and the intra- and intermolecular correlation energies) are dominated by different characteristics of the electronic structure and are thus dependent on different aspects of the orbital basis set expansion chosen to represent the final electronic wavefunction. This means that a large basis set is required to accurately represent these components and the interaction between them.

It is still prohibitively expensive to compute the entire potential surface with a complete treatment of electron correlation effects and a single large basis set that will give the desired accuracy in all regions of the interaction, so reasonable approximations need to be invoked which minimize the loss of accuracy over the various regions of the interaction.

In the repulsive region of the interaction, for \( R < \sim 5.0 \; \text{a}_0 \), a reasonable approximation to the interaction can be obtained from

\[ \text{C}(\theta) = \left\{ \frac{dP_{\theta}}{d\theta} (\theta=0), \frac{dP_{\theta}}{d\theta} (\theta) \right\} \]

In order to maximize our efficiency in calculating correlation functions, we used each classical trajectory several times in the averaging process. This was done by arbitrarily choosing several points along the trajectory to define the initial conditions \( \theta = 0 \). The first 40 points of each trajectory were considered to be 40 different initial conditions in calculating the correlation function. (In some cases, the trajectory did not last even 40 \( \theta \) steps, in which case fewer than 40 initial conditions were used.) Each of these 40 initial conditions was weighted by a factor \( W_x \) corresponding to the factor determined by the quantum mechanical wave functions for rotation and vibration as described in the text. We integrated Hamilton's equations in steps of constant \( \theta \) (0.8 rad) and considered each trajectory to formally have a length of 40 + \( 2^{10} \) steps in \( \theta \) space. In practice, most trajectories dissociated before reaching 1064 \( \theta \) steps and hence, for efficiency, were not integrated to the end. If a trajectory dissociated before 1064 steps, it was assumed that \( dP_{\theta}/d\theta \) was zero for all points after that. The correlation function was then calculated in discrete form as follows:

\[ C_j = \frac{1}{N_T} \sum_{i=1}^{100} \sum_{k=1}^{N_j} W_i \left\{ \frac{dP_{\theta}}{d\theta} \right\}_{j+k-1}, \; j = 1, 1024 \]

where \( N_j \) is either the number of \( \theta \) points prior to the dissociation of the \( j \)th trajectory or 40 whichever is smaller:

\[ N_j = \min (40, n_j) \]

\[ N_T = \sum_{i=1}^{100} N_j \]

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