sites of hydrogen-bonded hydroxyls.¹³ 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.¹⁵ 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/Cr₂O₃ 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_2O_3 , 1308-38-9; methanol, 67-56-1; formaldehyde, 50-00-0; formic acid, 64-18-6.

Rotational Predissociation of Model Atom–Diatom Complexes

Regina F. Frey, James O. Jensen, and Jack Simons*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 (Received: August 15, 1984)

The rotational predissociation and intramolecular energy transfer rates of model atom-diatom 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 mechanically¹ in our laboratory using the complex coordinate rotation method (CR).² 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-H₂ complex which has a weakly anisotropic atom-diatom potential energy. The second system is slightly more anisotropic and is chosen to approximately represent the reduced mass and well depth of Xe-H₂ but with an unrealistically large anisotropy. The third system is an even more strongly anisotropic system and is not intended to accurately represent any particular noble gas-homonuclear diatom complex. Its reduced mass and well depth were chosen to yield several bound vibrational states 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-diatom relative reduced

masses with large diatom 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 atomdiatom 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 time scale over 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-

⁽¹⁴⁾ Morimoto, T.; Morishige, K. J. Phys. Chem. 1975, 79, 1573.

⁽¹⁵⁾ Cheng, W. H.; Akhter, S.; Kung, H. H. J. Catal. 1983, 82, 341.

Z. Baĉić and J. Simons, Int. J. Quantum Chem. Symp., 14, 467 (1980).
 Proceedings of the 1977 Sanibel Workshop on Complex Scaling, Int. J. Quantum Chem., 14, 343-542 (1978).



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 θ is the angle between the \vec{r} and \vec{R} vectors.

ficially 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 diatom potential energy surfaces. The angle dependence of the vdW potential is written as a twoterm 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 θ 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_{T} of the complex is constrained to be zero (in order to generate results to compare to our earlier quantal results¹ which involved only $J_{\rm T} = 0$), so the diatom's angular momentum is offset by the orbiting motion of the adatom. The rate of energy transfer from the diatom'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_0P_0) , the coupling of the vibrational and rotational 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 diatom 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 atomdiatom 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 θ . R is the bond length of the diatom, r is the distance between the atom and the center of mass of the diatom, and θ is the angle between the \vec{r} and \vec{R} vectors. We are restricting our attention, as was done in the earlier quantum study,¹ to situations in which the complex's *total* angular momentum vanishes ($J_T =$

TABLE I: Parameters of vdW Complexes

	system I	system II	system III
μ , amu B_d , cm^{-1}	1.9191 60.0	1.981 60.551	1.3405 60.967 284.007
ε, cm σ, Å	3.2423	3.4745	3.00
<i>a</i> ₀	1.00	1.00	1.00
b_0	1.00	1.00	1.00
<i>a</i> ₂	0.1184	0.09	0.00
<i>b</i> ₂	0.1192	0.5	0.15
200			11
140			
80 - \			_
20 -	\		
5 -100	/		-
- 160 -			-
-220 -			-
-280	/		
-340 -	/		4
-400			
5.5	7.# 9.3 ra	dius (Bohr)	15.0

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

$$V_{0,2}(r) = 4\epsilon [b_{0,2}(\sigma/r)^{12} - a_{0,2}(\sigma/r)^6]$$

and for system I, which is chosen to represent Ar-H₂, $V_0(r)$ and $V_2(r)$ are of the form

$$V_{0,2}(r) = (27/4)\epsilon [b_{0,2}(\sigma/r)^{12} - a_{0,2}(\sigma/r)^8]$$

which is similar to the Lennard-Jones but whose 12,8 power law mimics the experimental data³ 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 diatom 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 diatom's vibrational motion is not probable if the diatom has a vibrational spacing greater than 1200 cm⁻¹. The $J_T = 0$ 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)). Baĉić (Z. Baĉić, 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_T are Boltzmann populated. $J_T = 0$, which is imposed only to permit comparison 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 $\hbar^2 l(l + 1)/2\mu r^2$ of approximately $16.7l(l + 1)/\mu r^2$ cm⁻¹ with μ , the system's reduced mass, in amu and r in Å. In the region of the interfragment separation where $V_0(r)$ is substantial, this contribution 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, 10⁴ classical trajectories were run. Each of these internal states are labeled by an adatom vibrational quantum number vand a diatom rotational quantum number J which, because J_{T} = 0, equals the adatom's tumbling quantum number *l*. The fact that the spherical part (V_0) of the potential $V(r,\theta)$ dominates the anisotropic part (V_2) (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 $V(r) \approx V_0(r)$) 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_0 , was used in determining the radial distributions. As described previously, the $\hbar^2 l(l+1)/2\mu r^2$ 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_0 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 $180^\circ - \theta$ have identical probabilities. The magnitudes of the initial momenta, P_{θ} and P_{r} , 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,θ) . 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 ($\theta, r, P_{\theta}, P_r$) 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 method⁴ with a time step of 2×10^{-15} 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-H₂ 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 monitored. 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 histogramming the continuous values of J inferred from the rotational energies of the fragment diatom to the nearest integer. It was thus possible to determine what fraction of the dissociated trajectories left the diatomic molecule in any specific rotational level, J_f . By monitoring 10⁴ classical trajectories for each (v,J), the fraction of trajectories that did not dissociate before time t was determined. Graphs were constructed of these fractions as functions of time for each initial (v,J) level and each value of J_f . These decay graphs were then used to evaluate the lifetime (τ) of the state (v,J,J_f) being studied. These data are given and discussed in section IV.

The classical trajectory simulations described above follow rather traditional lines in that they monitor the final outcome $(J_{\rm f}\tau)$ of a collection of trajectories whose initial conditions are chosen to replicate a specified (approximate) quantum state. In attempting to understand the physical origins of observed final-state distributions and decay rates of the various systems considered here, it became necessary to develop tools which allow us to focus on the dynamical behavior of the trajectories as they are evolving. This could, of course, be accomplished by visually monitoring the time development of each of the 10^4 trajectories for each v,J state. In our opinion, this approach is, at best, very inefficient. What is needed are methods which allow one to acquire averaged data about the evolution of many trajectories so that the typical behavior can be separated from the exceptional.

In an attempt to create such trajectory monitoring devices, we followed two distinct paths. First, we decided to construct dynamically evolving density distribution graphs over pairs of coordinates or momenta for the ensemble of trajectories characterizing each state. For example, to construct the r,P, pair distribution graph we monitor the evolution of $\sim 10^3$ trajectories (for each v,J) and we stop the trajectory at regularly (and finely) spaced intervals. At each halting of the trajectory, we tabulate r and P, and place a dot on the r,P, graph where each of the trajectories existed in r,P, space. By monitoring the *density* of dots in r,P, space as time evolves, we hoped to find regions of this r,P, subspace which were stable in the sense that they often contained high dot densities.

Our second approach involved looking at the development of ensemble-averaged correlation functions involving variables which, if mode-mode coupling were absent (i.e., $V_2 = 0$), would identically vanish. In particular, we chose to study the correlation function of the rate of change of the rotor's angular momentum. Our hope was to find *periodic structures* in the correlation function (or peaks in its Fourier transform) which we could assign to mode-mode energy transfer rates. To limit the amount of data generated to an amount which illustrates the essential features of our two probes of intermode dynamics, we focus most of our attention on the J = 2 states of each system. Let us now turn to a more detailed description of how our pair distribution densities and correlation functions were constructed.

C. Coordinate-Momentum Pair Distribution Studies. To study in further detail the rate and mechanism of energy transfer between the two active modes of the model vdW systems, we decided to tabulate and plot various pair distributions of the coordinates and momenta as the trajectories proceeded. Here we focus our attention on system III since the data in section IV shows this system has an unusually slowly dissociating state (v=3,J=2) on which this method for probing dynamical evolution offers the most promise. Therefore, to illustrate the use of the pair distribution method, we feel it is adequate to consider this case alone.

We decided to carry out our study as a function of evolving diatomic rotation angle θ rather than as a function of time, because, as we discovered in our correlation function study (which is described later), the intermode energy transfer seems to occur more regularly in θ space than in time space. We ran, for each initial state (v,J), 1000 classical trajectories with the same type of distribution of initial conditions and definition of final conditions as were used in the correlation function study described later.

At θ intervals of $2n\pi$ (n = 0, 1, 2, ...), we stopped each trajectory and tabulated the coordinates and momenta ($r, \theta, P_r, P_{\theta}$) at that

⁽⁴⁾ C. W. Gear, SIAM J. Num. Anal., 213, 69 (1965).

point. At dissociation, the final rotational state J_f of the diatomic molecule was determined and pair distribution graphs for each 2π interval were plotted for each value of J_f . Plots were constructed of P_r vs. r, P_r vs. P_{θ} , θ vs. P_{θ} , θ vs. r, and P_{θ} vs. r at $\theta = 2n\pi$. We examined these graphs involving all of the 1000 trajectories characterizing each (v, 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 θ space).

D. Correlation Function Studies. To examine other aspects of the energy transfer process, we also calculated the autocorrelation function⁵ involving the derivative of the rotor's angular momentum with respect to θ . $dP_{\theta}/d\theta$, 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_{θ}/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_{θ}/dt is negative and energy is leaving the rotor. By examining the autocorrelation between the starting value of $dP_{\theta}/d\theta$ and $dP_{\theta}/d\theta$ later in the trajectory, we gain information about the rate of decay 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 $\langle dP_{\theta}/d\theta \ (\theta = 0) \ dP_{\theta}/d\theta \ (\theta) \rangle$ 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_{θ}/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 θ space than in time space. As the results described in section IV demonstrate, our "guess" was correct. The autocorrelation function in θ 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 (v,J) level, 1000 classical trajectories were run with initial conditions determined as outlined in section III. To construct each of the θ -space correlation functions, the trajectory results were digitized by using a θ step size of 0.8 rad, and a total of 1024 steps were employed. The number of θ steps and therefore step size was dictated by the fact that the fast Fourier transform routine which we used to frequency analyze the θ correlation function required the number of steps to be a power of two. We constructed graphs of the intensity of the autocorrelation function vs. θ 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 θ 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

System III: Initial J = 2 (Rotational Period = 0.091 ps); Rotor Energy, 366 cm⁻¹

energy levels (vibrnl	vibrnl energy.	% traj in J _f			$ au$, ps, of traj giving $J_{\rm f}$		
periods)	cm ⁻¹	$\overline{J} = 2$	J = 1	J = 0	J = 2	J = 1	J = 0
v = 3 (4.8 ps)	-4	56	44	0	2.7	2.2	
v = 2 (1.0 ps)	-34	52	48	0	1.6	0.81	
v = 1 (0.41 ps)	-116	30	70	0	1.8	1.4	
v = 0 (0.21 ps)	-272	0	60	40		2.7	3.1

System III: Initial J = 4 (Rotational Period = 0.027 ps); Rotor Energy, 1220 cm⁻¹

energy levels	% tra	j in J_{f}	$ au$, ps, of traj giving $J_{ m f}$		
(vibrnl periods)	J = 4	J = 3	$\overline{J} = 4$	J = 3	
v = 3 (4.8 ps)	100	0	2.7		
v = 2 (1.0 ps)	100	0	2.2		
v = 1 (0.41 ps)	100	0	3.6		
$v = 0 (0.21 \text{ ps})^a$	32	68			

System II: Initial J = 2 (Rotational Period = 0.092 ps); Rotor Energy, 363 cm⁻¹

energy levels (vibrn)	vibrnl energy.	% traj in $J_{\rm f}$ $ au$,		τ, ps,	ps, traj giving $J_{\rm f}$		
periods)	cm ⁻¹	J=2 .	J = 1	$\overline{J} = 0$	$\overline{J} = 2$	J = 1	J = 0
v = 1 (4.6 ps)	-4	100			14		
v = 0 (0.95 ps)	-31	100			21		
C	lassical ar	nd Coordin	ate Re	otation	Lifetim	es	
	I		. 11		avatar	- III	

system I	system II	system III		
classical, -	classical, 21 ps	classical, 3.1 ps		
CR, 300 ps	CR, 21 ps	CR, 2.0 ps		

^aOnly 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 (v,J) of systems II and III. The lifetime (τ) is defined as the time necessary for the limited population of 10⁴ 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 $(N/N_0 = e^{-(t-t_0)/\tau})$ having an induction time, t_0 (see, for example, Figure 3). We found that for systems II and III, our results for *all* of the (v,J) states fit such a single exponential functional form. The induction time (t_0) is needed in our fitting procedure because our definition of dissociation (r > 20 bohr and $P_r > 0$ for systems II and III) is not fulfilled until a trajectory is well outside the range of the $V(r,\theta)$ potential and it simply takes a finite amount of time (t_0) for any trajectory to reach r > 20 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 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 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 (in v=0, J=2) is 300 ps, only 1.5 times the maximum duration of our classical trajectories. One would therefore have

⁽⁵⁾ A. Papoulis, "Probability, Random Variables, and Stochastic Processes", McGraw-Hill, New York, 1965.



Figure 3. Typical graphs of the single exponential fit of our classical trajectories for systems III and II, respectively.

expected a measurable fraction of the 10⁴ 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 v,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 $\langle \psi_{Jv} | V_2 P_2 | \psi_{Jv} \rangle$. Here ψ_{Jv} is the initial rotation-vibration wave function discussed in section IIIA and $\psi_{J_{tp}}$ is the final rotational wave function multiplied by a dissociative continuum function of r having asymptotic momentum p. The presence of the $P_2(\cos \theta)$ angular dependence can couple $J_{\rm f}$ and J pairs which differ by no more than two units of angular momentum. Of course, for homonuclear molecules, only even J and J_f 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 $V_2(r)$ (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 (λ) or kinetic energy. If a large amount of energy is transferred from the rotor to the adatom, ψ_p will have a considerably shorter local λ than will ψ_v , 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 ψ_p and ψ_v having similar local deBroglie wavelengths. The amount by which the wavelengths of ψ_p and ψ_v (or the corresponding r momenta) can differ is determined by the magnitude of $V_2(r)$.

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) $J_{\rm f}$ value of $J_{\rm f}(J_{\rm f})$ + 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 $J_{\rm f}$ is 1.99 and the observed average $J_{\rm f}$ is 1.56. In this case somewhat more energy has been deposited into relative translation. 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 ψ_p , ψ_v , and $V_2(r)$. Transfer of little excess kinetic energy to the adatom results in similar local deBroglie wavelengths for ψ_p and ψ_v .

4. Comparison with Quantum Lifetimes. Baĉiĉ et al.¹ 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





Figure 4. A series of graphs of P, vs. radius from the coordinate-momentum pair distribution study for the (v=3, J=2) state of system III.

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 (v=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 IIIC. 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_r

vs. P_{θ} (see Figure 5). Let us first examine both the (r,P_r) and (P_r,P_{θ}) 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 θ) 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 $-0.01 < P_r < 0.6$ Moreover, at $\theta = 22\pi$, the bottom line (7 < r < 13 bohr



and $-0.06 < P_r < -0.01$) partially decomposes. This bottom line reappears gradually over another interval of 22π (see Figure 4d) at which time the hook θ has essentially become part of the bottom line, and the top line is still absent. As seen in Figure 4e, after another interval of 22π ($\theta = 66\pi$), the bottom line has again disappeared and the hook⁷ is slowly disappearing. Hence, there seems to be a pattern of stability and then instability of the bottom line occurring at an interval of 22π .⁸ 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, vs. P_{θ} (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_{θ} values and at higher P, 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

⁽⁶⁾ P_r is in units of (hartrees × atomic mass units)^{1/2} or 4.6 × 10² (cm⁻¹ × atomic mass units)^{1/2}.

⁽⁷⁾ This hook is also present when the molecule is in the state (v=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 (v=2,J=2), but at a faster rate than for the state (v=3,J=2).

diminishing in intensity until most of the trajectories have dissociated. At $\theta = 22\pi$ (Figure 5c), the arc is still present, but the bottom of the vertical line ($-0.06 < P_r < -0.01$) has disappeared. This disappearance occurs at the same θ value as when the bottom line in the P, vs. r graph (Figure 4) disappeared. After another interval of 22π , 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_r vs. r. Again, after an interval of 22π , 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_r vs. r graph, there exists a pattern of oscillating stability and instability in the bottom of the vertical line in the P_r vs. P_{θ} data which also occurs at an interval of 22π .⁸ Also in the P_r vs. P_θ series of graphs, there is an arc structure which is present throughout the trajectories.⁹ This structure involves P_{θ} between 0.035 and 0.04510 and P, between 0.04 and 0.06 for the final rotational state $J_f = 1$; while for the final rotational state $J_f = 2$, P_{θ} 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_r vs. r and the movement of the bottom of the vertical line in the graphs P_r vs. P_{θ} 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 of P_r vs. P_{θ} . Based upon the ten single trajectories with initial conditions appropriate to this structure, it seems that the arc consists of trajectories which have gained P_r at the expense of P_{θ} and are on their way to dissociation. The arc persists because, as molecules dissociate, others come in to the same regions of $P_r - P_{\theta}$ 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



Figure 6. Typical graphs of the autocorrelation function $\langle (dP_{\theta}/d\theta) (\theta=0), dP_{\theta}/d\theta(\theta) \rangle$ for systems I, II, and III, respectively.

being in the probed region of space at any time.

C. Correlation Functions. 1. General Features. The calculation of the θ -space correlation functions discussed in section IIID involved averages over $\sim 10^3$ trajectories whose initial condition distributions were discussed earlier. $dP_{\theta}/d\theta$ was chosen to correlate against itself because it is nonzero only when energy transfer is taking place (i.e., P_{θ} would be constant for a freely rotating diatom). In computing these correlation functions, we chose to work in θ space rather than in the time domain because we were interested in seeing if certain regions of coordinate space were important in the energy transfer dynamics. Figure 6 shows graphs of the autocorrelation function vs. θ which are typical for the states in systems I, II, and III,¹¹ respectively. Comparing the correlation

⁽⁹⁾ This occurs for the state (v=2,J=2) at the same ranges of P_r and P_{θ} as for the state (v=3,J=2) but, for the state (v=2,J=2), the arc appears and disappears in a θ interval between $4-8\pi$.

⁽¹⁰⁾ $P_{\theta} = \hbar (J(J+1))^{1/2}$. In our program, P_{θ} has units of hartrees × our atomic time units (1 atomic time unit = 1.03×10^{-15} s) or 4.5×10^{-26} erg s.

⁽¹¹⁾ The state $(v=3,J_t=1)$ for system III does not have the same form as the other states for system III.

TABLE III: Comparison of Kinetic Lifetimes (τ) and Correlation-Function Decay Times (τ_c) for System III (J = 2)

	no. of rotn $(\theta_3/2\pi)$ for J_f		τ_c in J_f , ps			τ in $J_{\rm f}$, ps			
v	$\overline{J=2}$	J = 1	J = 0	J = 2	J = 1	J = 0	$\overline{J=2}$	J = 1	J = 0
3	17			2.1			2.7	2.2	
2	13	16		1.7	2.1		1.6	.81	
1	15	10		2.0	1.3		1.8	1.4	
0		19	35		2.4	3.2		2.7	3.1

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 π radian. The bands are separated by 21 rad for the state (v=0,J=2) shown in Figure 6b and by 256 rad for (v=1,J=2). The width of each band is 31 rad for (v=0,J=2) and 44 rad for (v=1,J=2).

For both systems I (Figure 6a) and III (Figure 6c), there are peaks occurring approximately every π 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.¹² All of the states for system III were found to have correlation functions whose envelopes fit a single exponential decay profile in θ 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.¹³

The fact that the correlation functions of *all* states of all three systems display strong features at $\theta = n\pi$ (n = 1, 2, ...) 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 $dP_{\theta}/d\theta$ correlation function at integral multiples of π can only be properly interpreted in terms of the collection of trajectories which constitute the ensemble. Simply put, at each multiple of π , 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 (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 predissociation lifetimes, but not to high precision and not equally well in all cases. In particular, the state $(v=2,J=2,J_f=1)$ shows a large deviation between these approximate correlation-function decay times and the classical-trajectory decay times. However, it must be kept in mind that the times inferred from the θ -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_{θ} (\dot{P}_{θ}) with itself to determine decay rates in the time domain instead of in θ space. We found that the decay lifetimes in the time domain agree more closely with the classical predissociation lifetimes than do the decay lifetimes in θ 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_{θ} 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 θ 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 θ -space correlation graphs. The above correlation-function-based results have thus revealed dynamical features that occur at regular intervals in θ 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 predissociation 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 (v=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 $Ar-H_2$ 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 θ -space correlation functions approximate decay times (from the envelope decay of the correlation functions) which seem to agree with the classical predissociation 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. If not

⁽¹²⁾ The absence of an exponential decay in system I is likely due to the fact that the molecule is not dissociating within the maximum time period of our trajectories as was discussed in section IIID.

⁽¹³⁾ The state (v=3,J=2,J=1) for system III shows no simple exponential decay form; therefore, an approximate decay lifetime could not be determined.

enough energy is transferred to the radial mode, the adatom again moves back to the diatom where it can undergo energy transfer once more. As seen by monitoring the single trajectories, there is not a gradual transfer of energy throughout the adatom-diatom relative motion. Rather, the energy transfer occurs in bursts everytime the adatom closely approaches the diatom. At such close encounters, energy can be transferred either from the radial to the angular mode or from the angular to the radial mode.

The second method we used in probing the energy transfer dynamics involved correlation functions which are designed to detect dynamical events which repeatedly occur at regular intervals. From these correlation studies, we observed some interesting structures when the correlation functions were examined in θ space instead of in time space. While we could not explain all of the structures observed in the resulting correlation functions or their Fourier transforms, we did observe that energy did not transfer gradually. The peaks occurring in the correlation graphs every π rad indicate that, at every π , some diatom is transferring energy to or from its corresponding adatom. That is, for any one vdW molecule, the energy transfer does not occur every π but at every π , some molecule's diatom among our ensemble is exchanging energy with its partner adatom.

The two methods for examining the mechanism of the energy transfer process provided insight into when energy transfer takes place. However, the correlation functions revealed that, in the energy transfer process, other events also occur which we do not yet understand.

Acknowledgment. We acknowledge the computational assistance of Ms. J. Ozment and helpful conversations on correlation functions with Prof. Joel Harris. The authors also acknowledge the financial support of the National Science Foundation (Grant 8206845), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the U.S. Army Research Office (Grant DAAG2984K0086).

Appendix A

In this section we describe some of the details of our calculation of the correlation functions defined as

$$C(\theta) = \left\langle \frac{\mathrm{d}P_{\theta}}{\mathrm{d}\theta} (\theta = 0), \frac{\mathrm{d}P_{\theta}}{\mathrm{d}\theta}(\theta) \right\rangle$$

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 θ steps, in which case fewer than 40 initial conditions were used.) Each of these 40 initial conditions was weighted by a factor W_n 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 θ (0.8 rad) and considered each trajectory to formally have a length of 40 + 2^{10} steps in θ space. In practice, most trajectories dissociated before reaching 1064 θ 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:

$$C_{j} = \frac{1}{N_{\rm T}} \sum_{l=1}^{1000} \sum_{k=1}^{N_{l}} W_{k} \left\langle \left(\frac{\mathrm{d}P_{\theta}}{\mathrm{d}\theta} \right)_{k} \left(\frac{\mathrm{d}P_{\theta}}{\mathrm{d}\theta} \right)_{k+j-1} \right\rangle, \quad j = 1,1024$$

where N_1 is either the number of θ points prior to the dissociation of the *l*th trajectory or 40 whichever is smaller:

$$N_l = \min(40, n_l)$$

$$N_{\rm T} = \sum_{l=1}^{1000} N_l$$

Registry No. Ar, 7440-37-1; Xe, 7440-63-3; H₂, 1333-74-0.

An ab-Initio Study of the Isotropic and Anisotropic Potential Energy Surfaces of the H_2 Interaction

Ulrich E. Senff* and Peter G. Burton

Chemistry Department, University of Wollongong, Wollongong, N.S.W. 2500, Australia (Received: September 17, 1984)

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 $R = 2.0 a_0$ to $R = 15.0 a_0$ for the He-H₂ separation and $r = 1.449 a_0$ for the H-H separation using molecular orientations of $\theta = 0^\circ$, 45°, and 90°. Additional computations at r = 1.28 and 1.618 a_0 for R = 3.0, 5.0, 6.5, and 8.0 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 supermolecule 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 $R < \sim 5.0 a_0$, a reasonable approximation to the interaction can be obtained from