

A hybrid classical/quantum approach to cluster fragmentation dynamics: Application to the vibrational predissociation of He₂Cl₂

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A new hybrid classical/quantum method is proposed and applied to investigate the vibrational predissociation (VP) dynamics of the He₂Cl₂ complex. The full dimensionality of the system (assuming zero total angular momentum) is included in the method. The VP process of He₂Cl₂ is dominated by a sequential mechanism of dissociation of the two van der Waals bonds. The hybrid approach describes the first weak bond fragmentation classically, and the second one quantum mechanically. The rotational distribution of the Cl₂ fragment is calculated both with the hybrid method and with a fully classical trajectory simulation, and compared with the experimental distribution. The hybrid distribution is found to agree very well with the experimental one, and to involve a substantial improvement with respect to the classical result. © 1998 American Institute of Physics. [S0021-9606(98)01105-2]

I. INTRODUCTION

Clusters composed of atomic and/or molecular species held together by weak van der Waals (vdW) forces have been a subject of great interest in the last years. The study of these systems can help understand the nature of vdW interactions, which play a central role in more complex condensed-matter systems. Aggregates containing chemical impurities solvated by rare-gas atoms allow one to explore characteristic effects of condensed matter like caging or recombination of the dissociating chemical subsystem (upon excitation) induced by the solvent. In this sense, vdW clusters provide a bridge between the gas-phase regime¹ and the condensed-matter environment,^{2,3} which can be approached by gradually increasing the cluster size. The advantage is that the smaller number of degrees of freedom involved in the cluster makes it easier to extract detailed information about chemical processes occurring in condensed phase.

The fragmentation dynamics of rare-gas clusters with molecular impurities has been extensively studied experimentally using pump-probe techniques. Essentially two types of experiments have been carried out. One type includes high-resolution spectroscopic experiments in the frequency domain, which provide detailed and specific state-to-state dynamical information.⁴⁻⁷ A variety of vdW complexes of halogen diatomic molecules bound to rare-gas atoms like He_nI₂ ($n = 1-3$),⁸ Ne_nI₂ ($n = 1-7$),⁹ Ne_nBr₂ ($n = 1-3$),^{10,11} Ne_nICl ($n = 1-3$),¹² Ne_nCl₂ ($n = 1-3$),¹³ and He_nCl₂ ($n = 1,2$),¹⁴ have been investigated with these techniques. The second type of experiments, more recently developed, are based on real-time methodologies.^{1,15-17} They allow one to follow and probe the dynamical evolution with subpicosecond resolution, giving rise to what is called femtochemis-

try. The two kinds of experimental techniques have experienced an enormous advance, which still continues, and provide complementary information on the dynamics of the fragmentation process.

On the theoretical side, the development of efficient techniques¹⁸⁻²¹ to solve the Schrödinger equation has meant a great advance in the field of vdW clusters. Exact full-dimensional quantum calculations, both time-dependent and time-independent ones, are currently performed on triatomic systems,^{22,23} even for nonzero total angular momentum. Tetra-atomic clusters have also been investigated quantum mechanically, although assuming reduced-dimensionality models.^{24,25} Regrettably, already for tetra-atomic systems an exact, full-dimensional treatment is in general out of reach at the present date.

One way to approach a full-dimensionality treatment of tetra-atomic clusters is to use quantum approaches which assume some sort of decoupling scheme for the modes of the system, such that the computational effort is reduced. A quantum description is then preserved for all the modes, in an approximate fashion. On the other extreme, a classical treatment of the dynamics allows for a fully coupled description of all degrees of freedom at a reasonable price. In this case, however, the accuracy of the results is generally lower, and problems inherent to the classical methodology, like the violation of the zero-point energy requirement,²⁶ may arise. Hybrid methods combine both quantum and classical approaches, to obtain an optimum compromise between accuracy and cost.

In the present work, a hybrid method mixing a classical and a quantum description of the dynamics is proposed to study the vibrational predissociation of the He₂Cl₂ vdW complex, including the full dimensionality for $\mathbf{J}=0$. The fragmentation dynamics of such a system consists basically

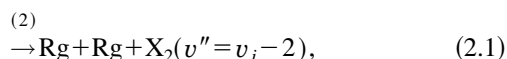
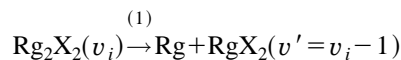
of a sequential dissociation process of the two vdW bonds.¹⁴ The bottleneck of a quantum mechanical treatment of this process is the first dissociation step, in which all the modes (six for $\mathbf{J}=0$) of the tetra-atomic cluster are involved. Once the first vdW bond breaking, $\text{He}_2\text{Cl}_2 \rightarrow \text{He} + \text{HeCl}_2$, takes place, the second fragmentation, $\text{HeCl}_2 \rightarrow \text{Cl}_2 + \text{He}$, is a tractable problem with quantum methods.

In the hybrid method proposed here, the strategy followed is to describe the first vdW bond dissociation by quasiclassical trajectories (QCT), which allow us to include all the pertinent degrees of freedom. The trajectories start from initial conditions generated with a quantum-mechanically calculated initial state of the tetra-atomic cluster. A classical propagation is carried out until the first vdW bond breaks, producing an atomic He fragment and a triatomic HeCl₂ complex in a given rovibrational state. The whole set of trajectories provides a distribution of triatomic states. The classical distribution is then used to weight quantum dynamical calculations of the HeCl₂ intermediate complex, starting from the initial triatomic states contained in the distribution. Specifically, in our method calculations of close-coupled equations are performed on the different HeCl₂ states populated to obtain the final magnitudes of interest. The close-coupling method has proven to be very efficient for triatomic systems involving both $\mathbf{J}=0$ and $\mathbf{J}\neq 0$ initial states, which is the present case. The observable on which we focus is the rotational distribution of the Cl₂ fragment, which has been measured by Janda's group.¹⁴ Such detailed data provides a demanding test of the hybrid approach.

The paper is structured as follows. In Sec. II the hybrid method is described. In Sec. III the potential used in the calculations is presented, and the results are shown and discussed. Finally, some concluding remarks are given in Sec. IV.

II. THEORY

In this work, we consider a sequential mechanism for fragmentation of a Rg₂X₂ tetra-atomic cluster (Rg=rare gas, X₂=halogen diatomic molecule):



where v_i denotes the (nearly exact) quantum number for the X₂ vibrational motion within the complex. There are several other fragmentation paths which are energetically allowed and some times observed for these kinds of complexes.^{1,13} either Rg+Rg or Rg₂ can be produced; the mechanism may be a direct vibrational predissociation or it can be mediated by a vibrational-energy redistribution process; vibrational quantum transfer may range from $\Delta v = -1$ to -3 . It is, however, clear that a sequential mechanism [two independent vibrational predissociation (VP) processes] is the main one, as the dominant coupling is usually that between the X₂ vibrational mode and the vdW stretching mode.^{1,13} Hence the

diatom loses one vibrational quantum for each bond breaking. A sequential mechanism is consistent with the observation¹⁴ for He₂Cl₂ since the main product channel is Cl₂($v_i - 2$) (92%), even though for the $\Delta v = -1$ channel there is more than enough energy available to break both vdW bonds.

We have performed a mixed simulation of reaction (2.1) applied to the He₂Cl₂ system in which the first (1) and (2) steps are studied by means of quasiclassical trajectories and three-dimensional quantum mechanical calculations, respectively. By analyzing final product distributions of the QCT run (producing He+HeCl₂), such distributions can be turned into "initial conditions" for the subsequent quantal simulation. The central assumption here is that the quantity of interest (the rotational distribution of the diatomic fragment, in this work) may be written as

$$p_j = \sum_{\nu} \mathcal{D}_{\nu}^{(\text{cl})} p_j^{\nu(q)}, \quad (2.2)$$

where j indicates the diatomic rotational quantum number, $\mathcal{D}_{\nu}^{(\text{cl})}$ is the classical probability for the HeCl₂ intermediate to be in a quantum state labeled by ν , and $p_j^{\nu(q)}$ is the quantal Cl₂ rotational distribution for the fragmentation of a quasi-bound state ν of HeCl₂($v_i - 1$). The label ν is further decomposed in J (hereafter J will denote the total angular momentum of the triatomic complex, unless otherwise specified) and α , a global number indicating the rovibrational excitation for each value of J . In this way, the classical distribution is factorized as

$$\mathcal{D}_{\nu}^{(\text{cl})} = \mathcal{P}_J \mathcal{A}_{\alpha}^J, \quad (2.3)$$

where \mathcal{P}_J is the rotational population of the intermediate HeCl₂ and \mathcal{A}_{α}^J is the rovibrational probability distribution for a given J (α comprises the vdW vibrational excitation as well as the rotational sublevel).

This section is divided in two parts. First, the quasiclassical approach is outlined. Second, the time-independent quantal formulation for the second fragmentation process is described. The procedure for the calculation of the classical distribution $\mathcal{D}_{\nu}^{(\text{cl})}$ is discussed in Sec. III.

A. Quasiclassical methodology

In the classical description of the He₂Cl₂ predissociation dynamics, bond coordinates ($\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2$) were used, with \mathbf{r} being the vector associated with the Cl-Cl bond, and $\mathbf{R}_1, \mathbf{R}_2$ being the vectors between the Cl₂ center of mass and the two He atoms, respectively. In such coordinates the classical Hamiltonian is written as

$$H = \frac{\mathbf{P}_{\mathbf{r}}^2}{2\mu_{\text{Cl}_2}} + \frac{\mathbf{P}_{\mathbf{R}_1}^2}{2\mu_{\text{HeCl}_2}} + \frac{\mathbf{P}_{\mathbf{R}_2}^2}{2\mu_{\text{HeCl}_2}} + \frac{\mathbf{P}_1 \cdot \mathbf{P}_2}{2m_{\text{Cl}}} + V(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2), \quad (2.4)$$

where $\mathbf{P}_{\mathbf{r}}$, $\mathbf{P}_{\mathbf{R}_1}$, and $\mathbf{P}_{\mathbf{R}_2}$ are the conjugate momenta associated with \mathbf{r} , \mathbf{R}_1 , and \mathbf{R}_2 , respectively, and $\mu_{\text{Cl}_2} = m_{\text{Cl}}/2$, $\mu_{\text{HeCl}_2} = 2m_{\text{Cl}}m_{\text{He}}/(2m_{\text{Cl}} + m_{\text{He}})$ are the corresponding reduced masses. In a body-fixed frame with the z axis always ori-

ented along the \mathbf{r} direction, and using a polar coordinate representation, $\mathbf{R}_i = (R_i, \theta_i, \phi_i)$, the above Hamiltonian can be expressed as^{26(b)}

$$H = \frac{1}{2\mu_{\text{Cl}_2}} \left[P_r^2 + \frac{\mathbf{j}^2}{r^2} \right] + \frac{1}{2\mu_{\text{HeCl}_2}} \left[P_{R_1}^2 + \frac{\mathbf{I}_1^2}{R_1^2} \right] + \frac{1}{2\mu_{\text{HeCl}_2}} \left[P_{R_2}^2 + \frac{\mathbf{I}_2^2}{R_2^2} \right] + \frac{\mathbf{P}_1 \cdot \mathbf{P}_2}{2m_{\text{Cl}}} + V_{\text{Cl}_2}(r) + V_{\text{HeCl}_2}(r, R_1, \theta_1) + V_{\text{HeCl}_2}(r, R_2, \theta_2) + V_{\text{HeHe}}(R_1, R_2, \cos \gamma). \quad (2.5)$$

In Eq. (2.5) \mathbf{j} , \mathbf{I}_1 , and \mathbf{I}_2 are the angular momentum operators associated with the rotational motions of the chemical and the two vdW bonds, respectively, and

$$\cos \gamma = \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2) + \cos \theta_1 \cos \theta_2.$$

Prior to the simulation of the predissociation dynamics, a set of initial conditions representing the initial state of the He₂Cl₂ system must be generated. A detailed account of the quasiclassical method of sampling of initial conditions for tetra-atomic clusters of this type has been given elsewhere.^{26(b),27} Here we will summarize the procedure briefly. First, the quantum mechanical state associated with a resonance of interest of He₂Cl₂ is calculated variationally.²⁸ The resonance wave function obtained (actually, the squared modulus) is used as a distribution to weight initial positions randomly selected. Then, initial momenta are produced such that the total energy (the quantum resonance energy) and the total angular momentum of the system are conserved.

Starting from this set of initial conditions, classical trajectories are integrated until the first vdW bond dissociates. At this point, positions and momenta of all the system modes are stored in order to extract the classical distribution of states that will be used as initial states in the further quantum calculations (see Sec. III). In order to obtain the classical rotational distribution of the Cl₂ fragment, integration of the classical trajectories is resumed until fragmentation of the remaining weak bond occurs, leaving the products Cl₂ + He + He.

B. Quantal methodology

The Hamiltonian for the HeCl₂ system is written in Jacobi coordinates as

$$H = \frac{\hbar^2}{2\mu_{\text{Cl}_2}} \left[-\frac{\partial^2}{\partial r^2} + \frac{\mathbf{j}^2}{r^2} \right] + \frac{\hbar^2}{2\mu_{\text{HeCl}_2}} \left[-\frac{\partial^2}{\partial R^2} + \frac{\mathbf{I}^2}{R^2} \right] + V_{\text{Cl}_2}(r) + V_{\text{HeCl}_2}(r, R, \theta), \quad (2.6)$$

where \mathbf{r} is the vector joining the two Cl nuclei and \mathbf{R} is the vector from the center of mass of Cl₂ to He, respectively, μ_{Cl_2} and μ_{HeCl_2} are the corresponding reduced masses, and θ is the angle between \mathbf{r} and \mathbf{R} . The angular momenta associated with such vectors are $\mathbf{I}(\mathbf{R})$ and $\mathbf{j}(\mathbf{r})$ and they couple to give the total triatom angular momentum \mathbf{J} (all angular mo-

menta being in units of \hbar). Finally, V_{Cl_2} and V_{HeCl_2} are intramolecular and vdW intermolecular interaction potentials.

For the present purposes, we basically need to describe a set of initial rovibrational quasibound states $\{J, \alpha\}$ in the $v_i - 1$ Cl₂ vibrational state and their coupling with the dissociative continuum, in order to obtain the fragment rotational distributions. The initial quasibound states are given here within the vibrational diabatic approximation:²⁹

$$\Psi^{Jav'}(\mathbf{r}, \mathbf{R}) = \chi_{v'}(r) \Phi^{Jav'}(\hat{\mathbf{r}}, \mathbf{R}) \quad (2.7)$$

where $\hat{\mathbf{r}}$ represents the orientation of \mathbf{r} (i.e., a unitary vector along the direction of \mathbf{r}), $\chi_{v'}(r)$ is the $(v' = v_i - 1)$ diatomic wave function [eigenfunction of $-(\hbar^2/2\mu_{\text{Cl}_2})\partial^2/\partial r^2 + V_{\text{Cl}_2}(r)$], and $\Phi^{Jav'}(\hat{\mathbf{r}}, \mathbf{R})$ is a discrete eigenstate of the triatomic Hamiltonian averaged on the diatomic vibrational motion

$$\langle v' | H | v' \rangle \Phi^{Jav'} = E^{Jav'} \Phi^{Jav'}, \quad (2.8)$$

$E^{Jav'}$ being the energy of the vdW motion. Equation (2.8) is solved by diagonalization of the corresponding Hamiltonian matrix, using an expansion of Φ in a suitable radial-angular basis set. Label α above could be further decomposed in $(\epsilon_i, \epsilon_j, m)$, where ϵ_i and ϵ_j are the coordinate inversion and Cl₂ nuclei exchange parity numbers, respectively. Calculations are performed in blocks for different values of J , $\epsilon_i \pm 1$, $\epsilon_j = \pm 1$, and m indicates the m th eigenstate within each parity block.

The dissociative wave functions are written as

$$\Psi_{v_f j_f \Omega_f E}^{(J \epsilon_i \epsilon_j)}(\mathbf{r}, \mathbf{R}) = \sum_{v_j, j_j, \Omega_j} \phi_{v_j j_j \Omega_j}^{v_f j_f \Omega_f E}(R) \chi_{v'}(r) \Theta_{j_j \Omega_j}^{(J \epsilon_i \epsilon_j)}(\hat{\mathbf{r}}, \hat{\mathbf{R}}), \quad (2.9)$$

where $\Theta_{j_j \Omega_j}^{J p_i p_j}$ represent a free rotor basis set (in a body-fixed frame where the z axis is parallel to \mathbf{R}), with Ω being the projection of \mathbf{J} and \mathbf{j} onto the body fixed z axis. Note that several diatomic vibrational states are included in the expansion given by Eq. (2.9). Functions $\phi_{v_j j_j \Omega_j}^{v_f j_f \Omega_f E}(R)$ are the amplitudes to be found, which correlate with the outgoing channels labeled by the rovibrational state (v_j, j_j) (with $v_j < v'$). They are obtained by converting the Schrödinger equation [for Eq. (2.6)] into a set of close-coupled equations, which are actually solved by accumulation (using Numerov's propagator³⁰) of the overlap between the dissociative function and the quasibound state $\Psi^{Jav'}$.³¹ After application of the appropriate boundary conditions,^{32,33} such an overlap

$$S_{v_f j_f}^{Jav'}(E) = \sum_{\Omega_f} |\langle \Psi^{Jav'} | \Psi_{v_f j_f \Omega_f E}^J \rangle|^2 \quad (2.10)$$

gives the line shape for fragmentation products (v_f, j_f) as a function of E , for an initial state (J, α, v') . Position and lifetimes of the resonances may be extracted (when they are isolated) by fitting the total line shape (summed over v_f and j_f) to a Lorentzian function. Finally, the rotational distribution for the product manifold $v_f = v_i - 2$ is given by

$$p_{j_f}^{J\alpha}(E) = \frac{S_{v_f j_f}^{Jav'}(E)}{\sum_{j_f} S_{v_f j_f}^{Jav'}(E)}. \quad (2.11)$$

For isolated resonances such rotational distributions are almost independent on E , and can be calculated at any energy near the resonant peak.

To summarize, the quantum calculations on HeCl₂ are used to obtain the quasibound states $\Psi^{Jav'}$, their energies $E^{Jav'}$, and the corresponding final product state distribution following dissociation of the triatomic system. The quantum product state dimensions are combined using the rovibrational distribution of the intermediate complex HeCl₂ obtained from a quasiclassical calculation for the first step, He₂Cl₂ → HeCl₂ + He, with the knowledge of the $\Psi^{Jav'}$ and $E^{Jav'}$.

III. RESULTS AND DISCUSSION

A. Potential-energy surface

The vibrational predissociation of the He₂Cl₂ complex takes place upon laser excitation from the ground state to a well-defined vibrational level $v_i \neq 0$ in the electronic state B of the Cl₂ diatomic. To a good approximation, this process can be modeled as occurring on the single potential-energy surface of the B state. The potential surface of such a state is represented as the following sum,

$$V = V_{\text{Cl}_2} + V_{\text{He}_a\text{Cl}_2} + V_{\text{He}_b\text{Cl}_2} + V_{\text{He}_a\text{He}_b}$$

The Cl₂ interaction potential is described by a Morse function with parameters³⁴ $D = 3176.4 \text{ cm}^{-1}$, $\alpha = 2.345 \text{ \AA}^{-1}$, and $r_{\text{eq}} = 2.435 \text{ \AA}$. The $V_{\text{He}_i\text{Cl}_2}$ ($i = a, b$) potentials are expressed as a sum of two He_{*i*}-Cl interactions,

$$V_{\text{He}_i\text{Cl}_2} = V_{\text{He}_i\text{Cl}_a} + V_{\text{He}_i\text{Cl}_b}$$

where each $V_{\text{He}_i\text{Cl}_j}$ ($j = a, b$) term is also described by a Morse functional form. The Morse parameters of Ref. 35 were used in this case. Finally, also a Morse potential represents the He-He interaction, whose parameters were obtained by fitting the analytical form of Aziz *et al.*³⁶ These parameters are³⁷ $D = 7.61 \text{ cm}^{-1}$, $\alpha = 2.126 \text{ \AA}^{-1}$, and $R_{\text{eq}} = 2.963 \text{ \AA}$.

B. Quasiclassical dynamics

The vibrational predissociation dynamics of the He₂Cl₂ (B, v_i) complex has been simulated starting from the resonance state associated with the $v_i = 13$ vibrational level of Cl₂. A set of 10 000 trajectories was integrated using a GEAR algorithm with a variable time step. Trajectories are run up to a maximum time of 300 ps per vdW bond dissociation. A vdW bond is considered dissociated when the corresponding distance reaches 12 Å. Energy conservation of the trajectories is of the order of 10^{-8} cm^{-1} .

Either when the first weak bond breaks or when the established maximum time of integration is reached, the positions and momenta of all the modes of the system are stored for each trajectory. The above set of positions and momenta contain all the dynamical information necessary to determine the classical distribution of states of the intermediate triatomic complex HeCl₂.

Before discussing how the HeCl₂ distribution of states is obtained, some technical aspects should be pointed out. Not all the trajectories contribute to the distribution. In particular, those trajectories which reach the maximum time of integration without producing fragmentation of any vdW bond are removed. In addition, we note that the expansion of Eq. (2.2) only includes quasibound states of the intermediate HeCl₂ cluster. Therefore trajectories describing continuum states do not contribute to this expansion. These trajectories are identified by observing that the vdW bond energy is above the dissociation energy limit of HeCl₂. Finally, a number of trajectories suffer from violation of the zero-point-energy (ZPE) requirement in the vdW modes. ZPE problems were also found in classical calculations of the NeI₂ and Ne₂I₂ VP dynamics.²⁶ In the case of He₂Cl₂ the ZPE effect is more dramatic, since the ZPE of each vdW stretch mode is comparable with its dissociation energy. The ZPE problem manifests itself in the present system in that one vdW bond is dissociated at the expense of the ZPE of the other weak bond, without (or with little) change of the initial Cl₂ vibrational energy. Trajectories showing such a behavior are clearly unphysical and must be discarded. This is done by imposing the restriction of considering as valid only those trajectories in which the Cl₂ diatomic losses an amount of energy of at least 15% of the vibrational quantum, $E = 0.15 (E_{v=13} - E_{v=12})$, in the first dissociation step. This energy E is somewhat larger than the dissociation energy of one vdW bond. We ensure in this way that the first weak bond fragmentation occurs via energy transfer from the Cl₂ stretch vibration, as physically expected, and not from the ZPE of the other vdW bond.

After removing the spurious trajectories as discussed above, we are left with a set of 4317 relevant trajectories from which the classical distribution of quasibound states of HeCl₂ ($B, v' = 12$) is to be extracted. In the following we will discuss how this distribution is obtained.

The first step consists of a variational calculation of the quantum-mechanical quasibound states of the triatomic HeCl₂ complex. Now, if the HeCl₂ intermediate cluster was described by a wave packet, the projection of this wave packet onto the calculated quasibound states would provide the desired state distribution. A classical calculation, however, gives as a result a distribution of positions and momenta for HeCl₂, which cannot be projected in the usual way. Therefore a sort of "approximate projection" of such a distribution has to be carried out. This approximate projection is the connecting point between the classical and the quantum treatments in our hybrid approach.

In order to match the classical and the quantum schemes it is desirable to make as few assumptions as possible. Actually, there are two quantities which are well defined both for the quantum resonance states and for the classical distribution of trajectories describing the intermediate HeCl₂: the energy and the total angular momentum. We chose, therefore, to use these two quantities to connect the classical trajectory information and the triatomic quantum states.

The trajectories are thus classified according to the total angular momentum of the intermediate HeCl₂ complex. A

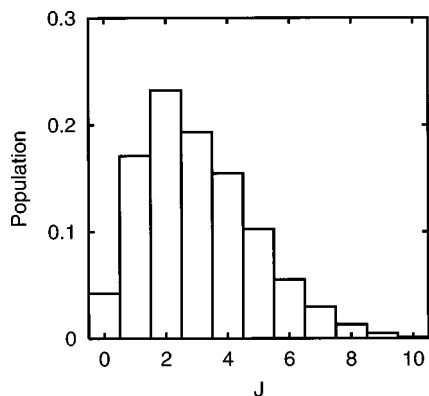


FIG. 1. Classical total angular momentum distribution of the intermediate HeCl₂ complex.

classical distribution of J is generated and displayed in Fig. 1. The distributions associated with the different angular momenta within He₂Cl₂ are very cold in the initial resonance state.^{27,28} Taking this into account, the J distribution of Fig. 1 shows some rotational excitation, caused by the first vdW bond fragmentation.

Now, for each set of trajectories corresponding with a given value of J , an additional HeCl₂ energy distribution is calculated. The histogram of Fig. 2 shows the energy distribution associated with $J=2$, which is the maximum of the J distribution. It is found that the distribution has a Gaussian-like shape. The energy distributions for the other J values are very similar to this (with the only difference being that the center of the Gaussian slightly shifts to higher energies as J increases) and will not be shown. In Fig. 2 the zero of the energy axis coincides with the dissociation energy limit of the vdW bond (the vibrational energy of Cl₂ in $v'=12$ has been subtracted, so only the vdW bond energy is shown in this axis). For the sake of visualizing the Gaussian shape of the distribution, the trajectories with vdW bond energy above the dissociation limit are also shown in the figure. As mentioned above, however, these trajectories will not be included in the calculation of $\mathcal{D}_v^{(cl)}$. The distribution of Fig. 2 (and also those associated with the remaining J values) shows a non-negligible population at energies below the ZPE of the

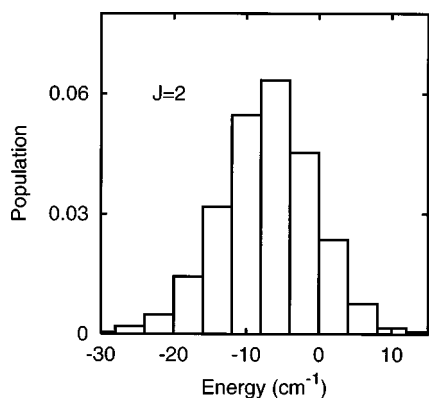


FIG. 2. Classical vdW energy distribution of the intermediate HeCl₂ associated with the total angular momentum $J=2$. See text for details.

vdW bond (ZPE = -12.59 cm⁻¹). This result was expected since that energy region is classically allowed.

Having obtained the angular momentum and energy distributions we proceed to establish the contribution $\mathcal{D}_v^{(cl)}$ of each HeCl₂ quasibound state to the fragmentation dynamics into Cl₂+He products.

Once the first vdW bond is fragmented, the integration of the trajectories is continued in order to simulate the dissociation of the second weak bond. Classical lifetimes for the two vdW bond fragmentations are calculated by fitting the decaying population of the tetra-atomic and the triatomic complex, respectively, to an exponential form. The estimated values are $\tau_1 = 17$ ps and $\tau_2 = 41$ ps. These lifetimes seem to be underestimated by comparison with the quantum lifetimes calculated for the quasibound triatomic states (see Sec. III C). We stress, however, that the classical lifetimes keep the rate $\tau_1 \approx 1/2\tau_2$, which is consistent with a predominantly sequential mechanism of dissociation.

C. Quantal dynamics

Quantal calculations for the fragmentation of HeCl₂ were conducted with total angular momenta ranging from $J=0$ to 7. According to the previous classical results (see Fig. 1), such states account for more than 97% of the total triatom population. Calculations were carried out for all initial states whose zero-order energy is below the He+Cl₂(v') dissociation limit.

In order to obtain the initial quasibound states $\Phi^{Jav'}$, (with $v'=12$), ten numerical functions for the radial coordinate and 12 free rotor functions (for j =even or odd, depending on the parity block) were used in the basis set expansion. A graph of the obtained zero-order energy levels (up to 162) is shown in Fig. 3, for the different triatomic angular momenta. The density of states is rather large, particularly for energies above ≈ -6 cm⁻¹. In order to assign such levels to vdW bend or stretch excitations, reduced density functions, $D^{J\alpha}(x)$, ($x=R, \cos\theta$) were also computed (they are obtained by integrating $|\Phi^{Jav'}|^2$ over all the coordinates except x). In Fig. 4, such radial and angular density functions for $J=0$ are depicted. It can be seen that, although both radial and angular distributions are correlated, all excited states correspond to excitations in the angular degree of freedom. In this way, label n in Fig. 4 indicates the number of nodes in the bending mode. For low J values, it is found that each ($J=0, n$) level splits into $2J+1$ sublevels, whose probability distributions in the vibrational degrees of freedom (R and $\cos\theta$) are very similar to the corresponding one for $J=0$. For higher angular momenta and particularly for high-energy levels, such a decoupling between vibration and overall rotation breaks down and thus there are some levels that cannot be related to a specific bending excitation of the vdW bond.

For each initial quasibound state, the fragmentation dynamics was solved by calculation of the overlap between the initial state and the dissociative wave function [Eq. (2.10)]. Close-coupled equations were integrated from 1.0 to 18.5 Å with a total number of 1024 steps, and including three vibrational channels ($v=v_i-1, v_i-2, v_i-3$) with 12 rotational

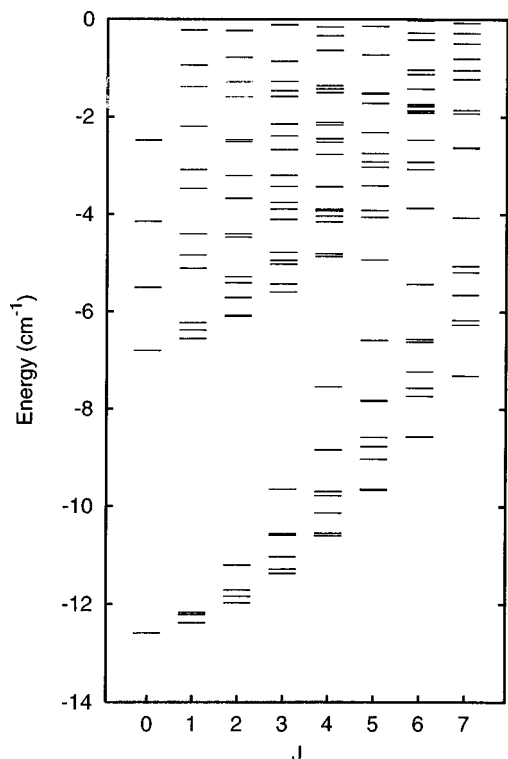


FIG. 3. Energy level diagram of the quasibound states of HeCl₂($v'=12$) for all the values of the total angular momentum included in the calculations.

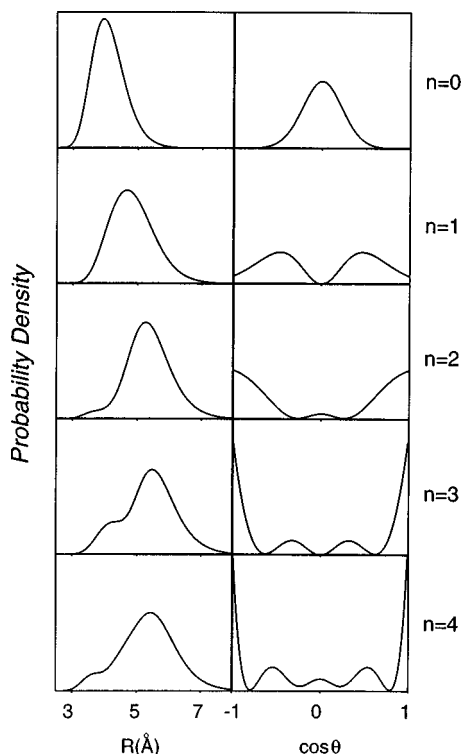


FIG. 4. Probability density of the five quasibound states of HeCl₂($v=12$) for $J=0$ versus the vdW coordinates R and $\cos \theta$. The energy levels of these states are displayed in the first column of Fig. 3.

channels each in the expansion given in Eq. (2.9) (including only three vibrational channels is good enough in order to obtain correct rotational distributions for the v_i-2 channel). The calculated lifetimes are between 75 and 150 ps, the larger ones corresponding to the first excited vdW state, whereas the ground state has a range of lifetimes (for the different overall rotation excitations) of about 78 ps. The vibrational population of the $\Delta v = -1$ channel was found to vary between 91% to 96% for the different states. Cl₂ rotational populations for that channel were stored for comparison with the experimental result after proper weighting using the classical triatomic state distribution.

D. Combining classical and quantal schemes: Fragment rotational distributions

As indicated in Eq. (2.3), the classical probability distribution $\mathcal{D}_{J\alpha}$ is given by the product of the rotational population \mathcal{P}_J (already obtained and shown in Fig. 1) and the rovibrational probability distribution \mathcal{A}_α^J . The latter has been obtained by making use of the classical energy distribution for each value of the triatom angular momentum J . The normalized distribution is written as

$$\mathcal{A}_\alpha^J = \frac{D_J^{\text{cl}}(E^{J\alpha v'})}{\sum_\alpha D_J^{\text{cl}}(E^{J\alpha v'})}, \quad (3.1)$$

where $D_J^{\text{cl}}(E^{J\alpha v'})$ is the classical density of states at energy $E^{J\alpha}$ corresponding to the quantum quasibound state (J, α) . Since the classical energy distributions exhibit Gaussian-like shapes (as mentioned when discussing Fig. 2), we have proceeded using a Gaussian distribution in Eq. (3.1) after fitting the energy histogram for each J to such an analytical function. The rovibrational populations obtained in this way are found to be nearly equally weighted within each J block. This is because the spectrum of quantum energy levels lies at the center of the classical distribution D_J^{cl} and not at its wings (compare, for instance, the classical distribution of Fig. 2 with the $J=2$ energy spectrum of Fig. 3).

In Fig. 5, classical distributions in the vdW degrees of freedom are presented in comparison with hybrid distributions corresponding with the superposition of quantum HeCl₂ quasibound states:

$$D^J(x) = \sum_\alpha \mathcal{A}_\alpha^J D^{J\alpha}(x), \quad (3.2)$$

where $x = R, \cos \theta$ and $D^{J\alpha}(x)$ is a reduced density function for quantum state (J, α) . As can be seen, both classical and hybrid distributions are fairly similar and present the same trend as J increases. This shows that the energy criterion followed to obtain rovibrational populations $\{\mathcal{A}_\alpha^J\}$ is reasonable, as it succeeds in correctly reproducing the probability density in the internal vdW degrees of freedom. Notice in Fig. 5 that, with increasing J , the probability density is reduced at the wings of the distribution in $\cos \theta$ and, in turn, the radial distribution becomes more compact. This behavior can be understood in terms of energy disposal. Indeed, since the classical energy distributions are found to be fairly simi-

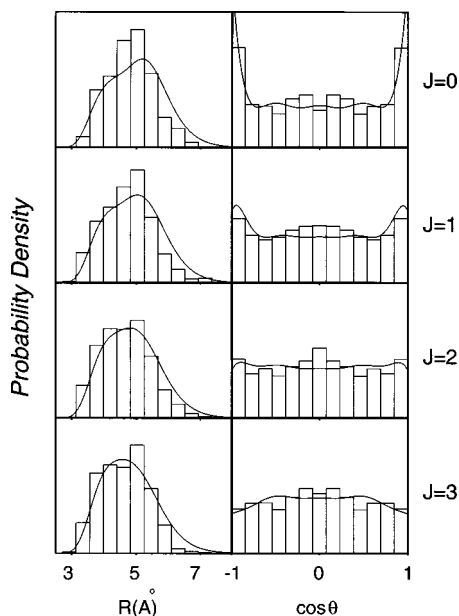


FIG. 5. Probability density associated with the vdW coordinates R and $\cos \theta$ of the HeCl₂ intermediate for $J=0-3$. The histogram represents the classical trajectory result, while the solid line is calculated with the expansion given by Eq. (3.2). Classical distributions were symmetrized with respect to the operation $\cos \theta \rightarrow -\cos \theta$. See text for details.

lar for all J states, there is less energy available for internal excitation as rotational excitation increases. Thus the population of bending excited states (which are the ones giving larger intensity at the wings of the angular distributions) diminishes when J becomes larger.

Finally, we report on the calculated rotational populations of the Cl₂ fragment in comparison with experiment. These results are collected in Fig. 6. The quasiclassical distribution (shown as a histogram) is much colder than the experimental one (in filled squares), even though both distri-

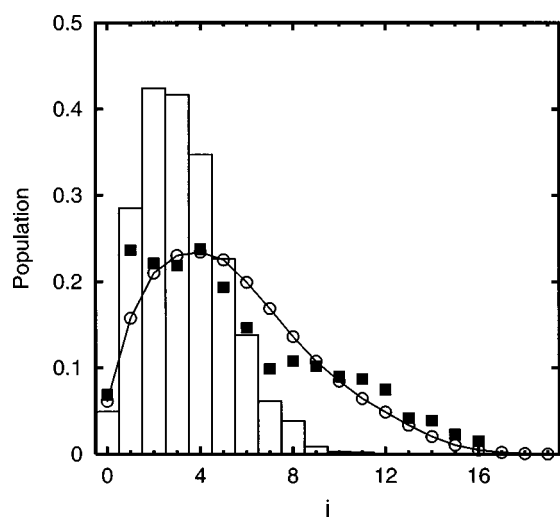


FIG. 6. Rotational distributions of the Cl₂($v_f=11$) fragment. The experimental measurements from Ref. 14 (filled squares), the classical distribution (histogram), and the classical/quantum distribution (open circles connected by solid line) are displayed. Even and odd j distributions are independently normalized to 1.

butions have their maximum values at the same region. On the other hand, the hybrid classical/quantum population reproduces the overall behavior and the extent of the experimental rotational excitation quite well. Thus the mixed approach certainly improves the more qualitative QCT result. Experiment gives, however, a more structured population distribution: it can be noticed that experimental population falls quite rapidly in the $4 < j < 8$ range to exhibit a large tail for $j > 8$ whereas the theoretical distribution is smoother in that region (it even seems that the experimental distribution displays a slight bimodal shape with a minimum at $j=6$). We do not think that the origin of this minor difference comes from not having used a realistic enough potential-energy surface, since it has been checked that the rotational populations for the process HeCl₂($J=0, \alpha = \text{ground}$) \rightarrow He + Cl₂ compare very well with measurements previously reported.³⁸ Also, it seems unlikely that inaccuracies on the He-He interaction or the neglect of many-body terms can give large uncertainties in the calculations. Instead, we believe that the classical treatment of the first fragmentation step is not accurate enough to reproduce such details in the final result. In the first place, it could be possible that the rotational classical distributions (both for triatomic and diatomic product) are somewhat too cold. This can be due to the fact that only few trajectories lose a complete vibrational quantum in the Cl₂ stretch, and therefore there is, on average, less energy available to distribute among the fragments, including the rotational degree of freedom. Another point is that a classical treatment cannot account for a rotational bimodal distribution (whether it occurred in either the triatom or the diatom distribution), since it has been shown that this is a pure quantum interference effect.^{23(b),39} A further analysis of the different contributions of the set of initial quasi-bound states to the final weighted rotational distribution also indicates that the classical distribution in the internal vdW modes may slightly overestimate the extent of the bending excitation. A rovibrational distribution having a somewhat larger weight in the ground vdW state would give a slightly more structured Cl₂ rotational distribution.

IV. CONCLUDING REMARKS

A hybrid classical/quantum approach is proposed to study the vibrational predissociation dynamics of the He₂Cl₂ vdW cluster, including the full dimensionality for zero total angular momentum. The method takes advantage of the fact that the VP process of He₂Cl₂ occurs primarily through a sequential mechanism of dissociation of the two vdW bonds. Therefore the strategy followed in the hybrid approach consists of treating the first weak bond fragmentation classically, and the second one quantum mechanically.

The first stage of the process, He₂Cl₂(B, v_i) \rightarrow HeCl₂(B, v_i-1) + He, is described classically starting from a quantum initial state for the resonance of He₂Cl₂ associated with $v_i=13$. The advantage of the classical trajectory treatment is that its computational cost is low enough as to include all the degrees of freedom of the tetra-atomic cluster. The classical calculation of the first dissociation step

provides a distribution of quasibound states for the intermediate HeCl₂(*B*, *v_i* - 1) complex.

The second weak bond fragmentation is described quantum mechanically by means of close-coupling calculations for each quasibound state contained in the state distribution. Further weighting of the quantum results with the classical state distribution gives the final magnitudes of interest. Hence, in the present hybrid method, the connection between the classical and the quantum dynamical schemes is established through the classical state distribution of triatomic quasibound states.

The rotational distribution of the Cl₂(*B*, *v_i* - 2) fragment is calculated both with the hybrid method and with a classical simulation, and compared with the experimental measurements. The agreement between the hybrid and the experimental distributions is found to be at least semiquantitative, while the classical result is only qualitative. Therefore, although the first fragmentation step of the process is treated classically, the quantum description of the second dissociation clearly improves the result with respect to the completely classical simulation.

The present hybrid approach reproduces the dynamics of a tetra-atomic system like He₂Cl₂, including the full dimensionality, at a semiquantitative level of description with a reasonable (not very high) computational cost. In this work the method was applied to an initial state of He₂Cl₂ with zero total angular momentum. We stress, however, that the hybrid approach is also able to describe the decay dynamics of *J* ≠ 0 initial tetra-atomic states, with little additional computational effort in the classical trajectory integration. We therefore envision numerous applications for the method presented here.

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