

Sampling the Initial Conditions for Quasiclassical Trajectory Studies of Vibrational Predissociation Dynamics

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Abstract. A method is proposed for selecting initial conditions in order to study the classical dynamics of vibrational predissociation of van der Waals (vdW) clusters. The method starts from the quantum initial state of the system, which is used to sample and weight the initial positions of the different modes. The initial values of the associated momenta are calculated in such a way that they correspond with the total energy and angular momentum of the system initial state, at which the classical trajectory simulation is to be carried out. An application to the case of $\text{Cl}_2\text{—He}_2$ is presented and discussed.

Key words: Sampling initial conditions, vibrational predissociation, van der Waals clusters.

1. Introduction

In the last decade the experimental time-resolved pump-probe techniques have experienced an enormous advance in its application to the field of chemical reaction dynamics [1–11]. This type of experiment makes it possible to follow in real time the course of a reaction occurring in the picosecond or even in the subpicosecond time scale. Detailed information on the time-evolution of a chemical process provides a great deal of physical insight into the dynamics involved and how the reaction proceeds. In addition, time-resolved data may complement other type of dynamical information like that obtained by frequency domain spectroscopic experiments.

Cluster systems composed of several rare-gas atoms weakly bound to a molecule acting as a chromophore present several interesting features. By gradually increasing the cluster size it is possible to establish a bridge between the gas-phase limit and the condensed-matter regime. This allows one to investigate fundamental questions such as the mechanisms of energy transfer from the electronically or vibrationally excited chemical bond (or bonds) to the solvent, the influence of the weak solvation interactions on the molecule dissociation, and the effect of caging and recombination of the chemical impurity induced by the solvent [8].

Clusters with a halogen diatomic molecule weakly bound to one or more rare-gas atoms have been extensively investigated by means of frequency-domain experi-

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ment [2–15]. The pioneering experiments of Levy and co-workers on $I_2\text{---He}_n$ ($n = 1\text{--}3$) [16] and $I_2\text{---Ne}_n$ ($n = 1\text{--}7$) [17] measured binding energies, predissociation linewidths and lifetimes, and spectral band shifts in order to explore the structure, possible coordination effects, and energy transfer mechanisms in these systems. The dynamics of complexes with diatomic molecules different than I_2 , like $Br_2\text{---Ne}_n$ ($n = 1\text{--}3$) [18], $ICl\text{---Ne}_n$ ($n = 1\text{--}5$) [19], $Cl_2\text{---Ne}_n$ ($n = 1\text{--}3$) [20], and $Cl_2\text{---He}_n$ ($n = 1\text{--}2$) [21], have also been investigated. The characterization of rare gas–halogen potentials has also been the subject of several experiments [22–24].

The great deal of experimental work mentioned above has generated a rich body of dynamical information in the frequency domain. Consequently, the theoretical analysis of this information has been carried out mostly using time-independent methodologies. Exact close-coupling calculations on several triatomic systems have been reported in the literature [25–27]. Unfortunately, exact quantum methods are limited by the fact that the computational effort required grows very rapidly with the number of system modes. Several approximate methods have been suggested, including Golden Rule approaches [27, 28] and a variety of sudden approximation, [29–32]. The appearance of time-domain experimental data, along with the development of techniques for the efficient solution of the time-dependent Schrödinger equation [33–36] gave a great impetus to the use of time-dependent approaches. Exact [37–40] and approximate [41–47] time-dependent methods have been applied to van der Waals clusters, most of them triatomic and tetraatomic systems. However, a quantum dynamical treatment of a four-atom system including the full dimensionality, even for zero total angular momentum, becomes extremely costly.

Classical Molecular Dynamics (MD) simulations make the problem tractable [48–50], and provide at the very least a qualitative insight into the dynamics. In the classical scheme, prior to the study of the dynamics, an initial state must be specified in the form of initial conditions of the classical trajectories to be integrated. The aim of this work is to propose a technique to select such initial conditions and to apply it to the $Cl_2(B, v)\text{---He}_2$ cluster.

The organization of the paper is as follows. In Section 2 we briefly describe the potential surface and the quasiclassical methodology applied. Section 3 describes the model proposed to obtain the initial conditions. Finally, Section 4 presents and discusses distributions of the different modes of $Cl_2(B, v)\text{---He}_2$.

2. Quasiclassical Methodology

The VP process in the $Cl_2(B, v)\text{---He}_2$ cluster occurs upon laser excitation from the ground state to a well-defined vibrational level v ($v \neq 0$) in the electronic B state of the Cl_2 chromophore. The metastable state $Cl_2^*(B, v)\text{---He}_2$ prepared in this way decays to a dissociation continuum giving the products $Cl_2(B, v' = v - m) + 2He$, where $m \geq 2$. Such metastable state is the one to be reproduced by the initial conditions in a classical calculation.

2.1. CLASSICAL HAMILTONIAN AND POTENTIAL-ENERGY SURFACE

In the present work bond coordinates (\mathbf{r} , \mathbf{R}_1 , \mathbf{R}_2) have been used, where \mathbf{r} is the vector associated with the Cl—Cl bond, and \mathbf{R}_1 , \mathbf{R}_2 are the vectors between the Cl_2 center of mass and the two He atoms, respectively. In these coordinates the classical Hamiltonian can be expressed as

$$H = \frac{\mathbf{P}_r^2}{2\mu_{\text{Cl}_2}} + \frac{\mathbf{P}_1^2}{2\mu_{\text{Cl}_2-\text{He}}} + \frac{\mathbf{P}_2^2}{2\mu_{\text{Cl}_2-\text{He}}} + \frac{\mathbf{P}_1 \cdot \mathbf{P}_2}{2m_{\text{Cl}}} + V(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2), \quad (1)$$

where \mathbf{P}_r , \mathbf{P}_1 , and \mathbf{P}_2 are the conjugate momenta associated with \mathbf{r} , \mathbf{R}_1 , and \mathbf{R}_2 , respectively, and $\mu_{\text{Cl}_2} = m_{\text{Cl}}/2$, $\mu_{\text{Cl}_2-\text{He}} = 2m_{\text{Cl}}m_{\text{He}}/(2m_{\text{Cl}} + m_{\text{He}})$ are the corresponding reduced masses. By choosing a body-fixed frame with the z -axis always coinciding with the \mathbf{r} direction, and using a polar coordinate representation where $\mathbf{R}_i = (R_i, \theta_i, \phi_i)$, the Hamiltonian in the case of total angular momentum $\mathbf{J} = 0$ takes the more specific form

$$\begin{aligned} H^{(J=0)} = & \frac{1}{2\mu_{\text{Cl}_2}} \left[P_r^2 + \frac{\mathbf{j}^2}{r^2} \right] + \frac{1}{2\mu_{\text{Cl}_2-\text{He}}} \left[P_{R_1}^2 + \frac{\mathbf{l}_1^2}{R_1^2} \right] + \\ & + \frac{1}{2\mu_{\text{Cl}_2-\text{He}}} \left[P_{R_2}^2 + \frac{\mathbf{l}_2^2}{R_2^2} \right] + \frac{\mathbf{P}_1 \cdot \mathbf{P}_2}{2m_{\text{Cl}}} + \\ & + V_{\text{Cl}_2}(r) + V_{\text{Cl}_2-\text{He}}(r, R_1, \theta_1) + V_{\text{Cl}_2-\text{He}}(r, R_2, \theta_2) + \\ & + V_{\text{He-He}}(R_1, R_2, \cos \gamma), \end{aligned} \quad (2)$$

\mathbf{j} , \mathbf{l}_1 and \mathbf{l}_2 being the angular momenta associated with \mathbf{r} , \mathbf{R}_1 , and \mathbf{R}_2 , respectively. Other definitions used in Equation (2) are $\cos \gamma = \sin \theta_1 \sin \theta_2 \cos \phi + \cos \theta_1 \cos \theta_2$, $\phi = \phi_1 - \phi_2$, and the expanded expression of $\mathbf{P}_1 \cdot \mathbf{P}_2$ is

$$\begin{aligned} \mathbf{P}_1 \cdot \mathbf{P}_2 = & P_{R_1} P_{R_2} \cos \gamma - \frac{\cos \phi}{R_1 R_2 \sin \theta_1 \sin \theta_2} P_\phi^2 + \\ & + \frac{\cos \theta_1 \cos \theta_2 \cos \phi + \sin \theta_1 \sin \theta_2}{R_1 R_2} P_{\theta_1} P_{\theta_2} + \\ & + \frac{\sin \theta_1 \cos \theta_2 \cos \phi - \cos \theta_1 \sin \theta_2}{R_2} P_{R_1} P_{\theta_2} + \\ & + \frac{\cos \theta_1 \sin \theta_2 \cos \phi - \sin \theta_1 \cos \theta_2}{R_1} P_{R_2} P_{\theta_1} - \frac{\sin \theta_1 \sin \phi}{R_2 \sin \theta_2} P_{R_1} P_\phi - \\ & - \frac{\sin \theta_2 \sin \phi}{R_1 \sin \theta_1} P_{R_2} P_\phi - \frac{\cos \theta_1 \sin \phi}{R_1 R_2 \sin \theta_2} P_{\theta_1} P_\phi - \frac{\cos \theta_2 \sin \phi}{R_1 R_2 \sin \theta_1} P_{\theta_2} P_\phi. \end{aligned}$$

In order to integrate the trajectories it is necessary to solve the Hamilton equations corresponding to the above Hamiltonian.

Regarding the potential-energy surface for the B state of the Cl_2 — He_2 cluster, an addition of atom—atom interactions

$$V = V_{\text{Cl}_2} + V_{\text{Cl}_2-\text{He}_1} + V_{\text{Cl}_2-\text{He}_2} + V_{\text{He}_1-\text{He}_2}.$$

Table I. Morse potential parameters used in this work.

	D (cm ⁻¹)	α (Å ⁻¹)	R_{eq} (Å)
Cl—Cl	3176.4	2.345	2.435
Cl—He	16.2	1.5	3.8
He—He	7.61	2.126	2.963

was used.

The Cl₂ interaction potential, is described by a Morse analytical form with the parameters reported in Ref. [51]. The $V_{\text{Cl}_2\text{--He}_i}$ ($i = 1, 2$) potentials were expressed as a sum of two Cl—He_{*i*} interactions,

$$V_{\text{Cl}_2\text{--He}_i} = V_{\text{Cl--He}_i} + V_{\text{Cl--He}_i},$$

where each $V_{\text{Cl--He}_i}$ interaction is also described by a Morse function. The corresponding Morse parameters were taken from the potential of Ref. [22]. Finally, a Morse function was also used for the He—He interaction whose parameters were obtained by fitting the more complicate analytical form of Aziz and Slaman [52]. All the Morse potential parameters are listed in Table I.

3. Initial Conditions

As discussed above, the first step in studying the dynamics of the cluster is to obtain the initial conditions for each classical trajectory. From a methodological point of view, a classical distribution for the initial state could be used for the sake of consistency. However, the goal in this work is not to test the applicability of Classical Mechanics, but to describe the dynamics of a system with six coupled degrees of freedom as realistically as possible. It is well known that for the ground states the classical and quantal distributions are very different. It is expected that the quantum description will be the most realistic one. In this sense, to introduce the proper quantification in the initial state we start with a quantum calculation of the Cl₂—He₂ complex, including the full dimensionality (six degrees of freedom) for $\mathbf{J} = 0$. This calculation employs a variational method described elsewhere [53]. A diabatic separation of the Cl₂ vibration is assumed, but the full coupling between all the vdW modes is taken into account in the variational calculation. The diabatic separation is justified because of the frequency mismatch between the diatomic and the vdW vibrations. From the resonance wave function calculated in this way, the quantum-mechanical probability distributions for all the modes are obtained, and used to weight the initial positions selected by random sampling [53(b)].

In the following, all the discussion is referred to the $v = 13$ vibrational level of Cl₂. In the scheme adopted here to select the initial conditions of the r vibration, this mode is separated from the vdW ones, similarly as in the variational calculation

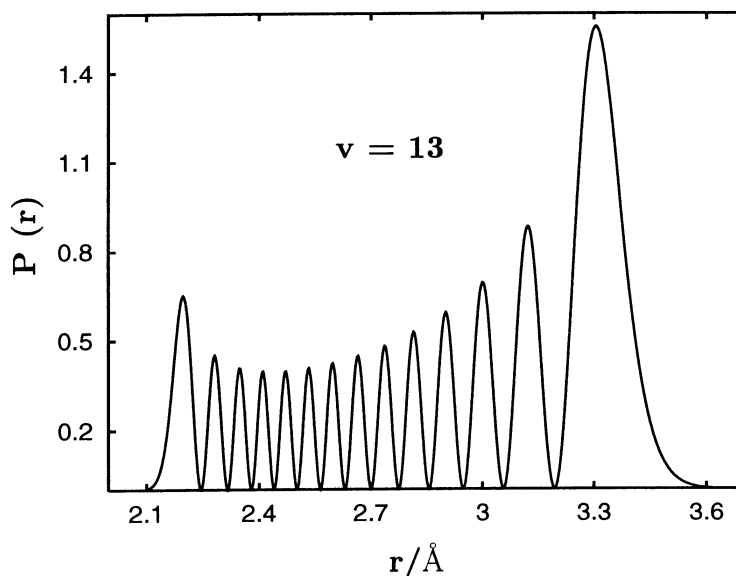


Figure 1. Quantum probability distribution of the r mode.

of the initial resonance state. The quantal probability distribution corresponding with r is displayed in Figure 1. Using this distribution to select and weight initial positions of r , the associated initial momenta can be calculated by means of

$$P_r = \pm \sqrt{2\mu_{\text{Cl}_2}[E_v - V_{\text{Cl}_2}(r)]},$$

where E_v is the energy of the diatomic vibrational level v , and the corresponding sign of these momenta is further selected at random. The resulting initial positions and corresponding momenta for the Cl_2 vibration are represented in Figure 2. In this drawing, although only the border is meaningful, the non-zero probability regions have been shadowed in order to stress the nodal structure. As can be seen, both figures reflect the same nodal pattern, that of the $v = 13$ level.

Now, initial distributions of positions and momenta for the vdW vibrations still remain to be obtained. Figures 3 and 4 show the quantum probability distributions of the modes R_i , θ_i ($i = 1, 2$) and γ , and Figure 5 displays the quantum rotational distributions associated with the Cl_2 (j) and the two vdW bonds (l_i , $i = 1, 2$). These distributions are employed to sample initial positions of the vdW modes, values of the quantum numbers j and l_i ($i = 1, 2$). Only the values fulfilling the constraint $|l_1 - l_2| < j < l_1 + l_2$ are accepted in order to ensure a given total angular momentum ($\mathbf{J} = 0$ in the case study here) for the initial conditions.

The initial angular momenta P_{θ_1} , P_{θ_2} , and P_ϕ are then obtained by solving the following system of equations,

$$l_1^2 = P_{\theta_1}^2 + \frac{P_\phi^2}{\sin^2 \theta_1}, \quad (3)$$

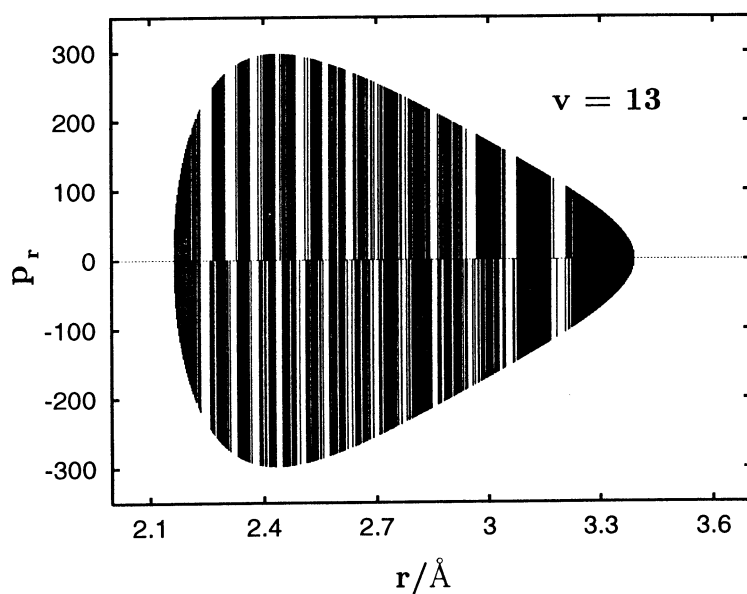


Figure 2. Initial distribution of positions and momenta associated with the r mode.

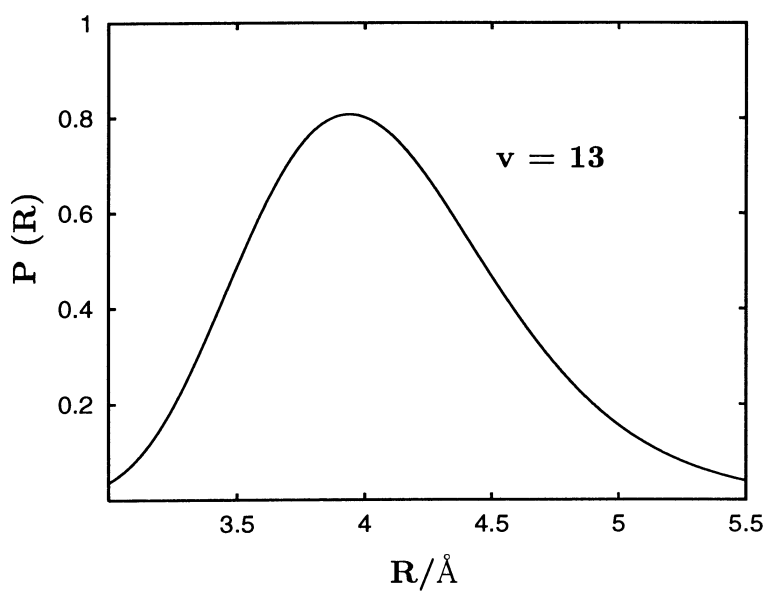


Figure 3. Quantum probability distribution of the R ($R = R_1, R_2$) vdW modes.

$$l_2^2 = P_{\theta_2}^2 + \frac{P_\phi^2}{\sin^2 \theta_2}, \quad (4)$$

$$j^2 = l_1^2 + l_2^2 + l_1 \cdot l_2 = P_{\theta_1}^2 + P_{\theta_2}^2 + 2P_{\theta_1}P_{\theta_3} \cos \phi -$$

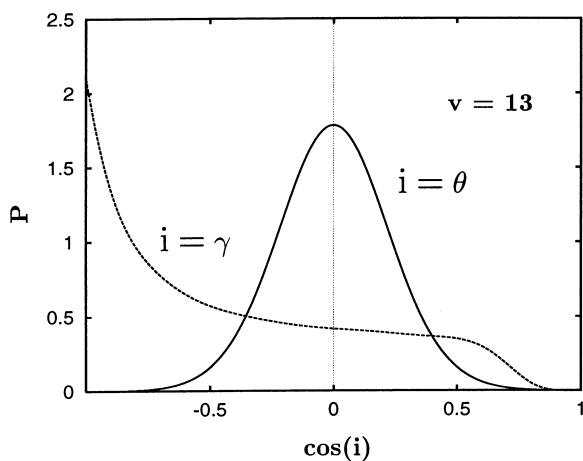


Figure 4. Quantum probability distributions associated with the θ ($\theta = \theta_1, \theta_2$) and γ angles.

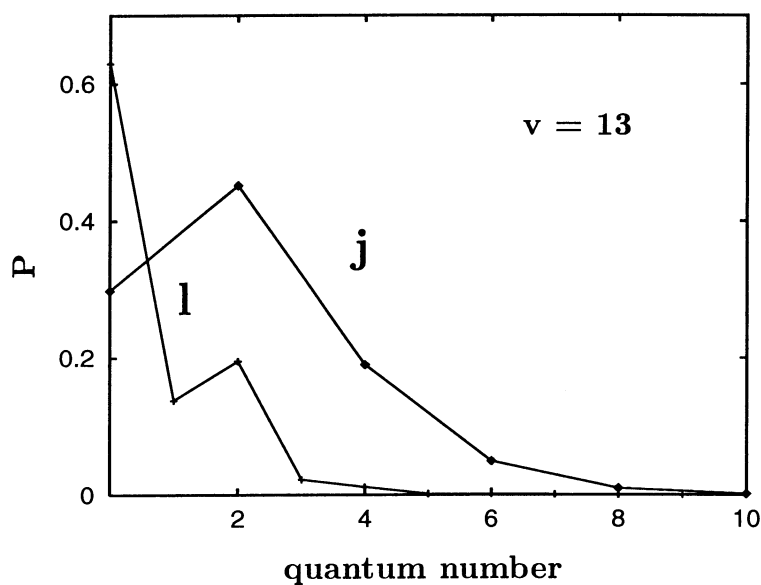


Figure 5. Distributions of the rotational quantum numbers j and l ($l = l_1, l_2$).

$$\begin{aligned}
 & -2 \sin \phi \left(\frac{\cos \theta_2}{\sin \theta_2} P_{\theta_1} + \frac{\cos \theta_1}{\sin \theta_1} P_{\theta_2} \right) P_{\phi} + \\
 & + \left(\frac{1}{\sin^2 \theta_1} + \frac{1}{\sin^2 \theta_2} - 2 \cos \phi \frac{\cos \theta_1 \cos \theta_2}{\sin \theta_1 \sin \theta_2} - 2 \right) P_{\phi}^2, \quad (5)
 \end{aligned}$$

By introducing Equations (3) and (4) into Equation (5), a fourth-order polynomial in P_{ϕ} is obtained. Each root of this polynomial constitutes an initial value of P_{ϕ} (which already includes the sign). Introducing that value P_{ϕ} in Equations (3)

and (4) gives the initial P_{θ_1} and P_{θ_2} , whose signs are randomly selected. In this way the calculated initial values of P_{θ_1} , P_{θ_2} , and P_{ϕ} are compatible with a prespecified total angular momentum of the system.

Finally, initial values for P_{R_1} and P_{R_2} are calculated by an iterative method. In a first stage, both momenta are obtained with the expression

$$P_{R_i} = \pm \sqrt{2\mu_{\text{Cl}_2\text{-He}}[E_0^{(v)} - V_{\text{Cl}_2\text{-He}}(\tau, R_i, \theta_i)]}, \quad (i = 1, 2), \quad (6)$$

where $E_0^{(v)}$ is the vdW ground state energy of the triatomic $\text{Cl}_2\text{-He}$ system in a Cl_2 vibrational level v . The \pm sign of the momenta is selected at random.

At this point initial values for the positions and momenta of all the system modes have been selected. However, the contribution of the $\mathbf{P}_1 \cdot \mathbf{P}_2$ and $V_{\text{He-He}}$ terms has so far been neglected in the total energy of the system. This causes the $\text{Cl}_2\text{-He}_2$ total energy associated with the initial conditions generated above to be slightly different from that calculated quantum-mechanically. To match the energy of the quantum initial state we must incorporate the two terms previously neglected. The terms $\mathbf{P}_1 \cdot \mathbf{P}_2$ and $V_{\text{He-He}}$ are not separable in order to distribute their energy contribution among all the vdW modes. We then chose to distribute such energy difference only among the P_{R_1} and P_{R_2} momenta. To do so, P_{R_1} and P_{R_2} are redefined as

$$P_{R_1} = P_{R_1}^{\text{app}} + \Delta_1,$$

and

$$P_{R_2} = P_{R_2}^{\text{app}} + \Delta_2,$$

where $P_{R_1}^{\text{app}}$ and $P_{R_2}^{\text{app}}$ are the approximate momenta calculated with Equation (6), and Δ_1 and Δ_2 are the variations of P_{R_1} and P_{R_2} , respectively, responsible for absorbing the energy difference. Replacing the new definition of P_{R_1} and P_{R_2} in the expression of the total energy (including the $\mathbf{P}_1 \cdot \mathbf{P}_2$ and $V_{\text{He-He}}$ terms) we get a quadratic form in the unknowns Δ_1 and Δ_2 . Such an equation is solved iteratively by introducing the constraint that the ratio between Δ_1 and Δ_2 is the same as that between $P_{R_1}^{\text{app}}$ and $P_{R_2}^{\text{app}}$. The final values of Δ_1 and Δ_2 make it possible to fit the energy of the quantum initial state within a desired convergence criterion. In this way, the total energy of the initial conditions now properly matches the quantum resonance energy.

Distributions including 2000 initial conditions for the vdW modes were calculated with the above method. Figure 6 shows the distribution associated with the momenta P_R and the positions R ($R = R_1, R_2$), which corresponds with the quantum distribution of Figure 3. The distributions associated with the angular modes θ ($\theta = \theta_1, \theta_2$) and ϕ are displayed in Figures 7 and 8, respectively. These distributions reflect a strong quantization of the angular momenta, as a result of

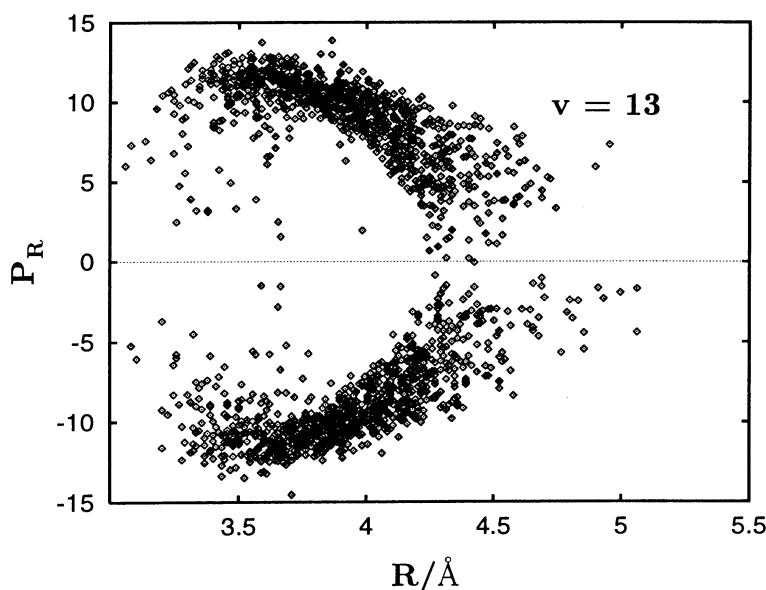


Figure 6. Initial distribution of positions and momenta associated with the R ($R = R_1, R_2$) vdW modes.

using the quantum probability distributions of Figure 5 to select the values of l_1 , l_2 and j that enter in the system of Equations (3)–(5). In fact, the high quantum probability of low rotational numbers l_1, j has its counterpart in low values of the angular momenta in the initial conditions.

The initial conditions generated with the method previously described conform an initial state compatible both in total energy and total angular momentum with the quantum initial state from which they come. Such initial conditions can be employed now as the starting point of a classical trajectory simulation of the predissociation dynamics of $\text{Cl}_2\text{—He}_2$. Work in this direction is in progress.

4. Conclusions

A method to sample initial positions and momenta to be used in a classical trajectory treatment of the dynamics has been proposed and applied to the $\text{Cl}_2\text{—He}_2$ vdW cluster. In the model suggested the quantum probability distributions associated with the initial state of the system are used to sample and weight the initial positions of the modes. Then the initial values of the associated momenta are calculated in such a way that they properly match the total energy and angular momentum of the quantum initial state. In the calculations reported here an initial state corresponding to zero total angular momentum was studied, but the method allows to treat states with total angular momentum different from zero.

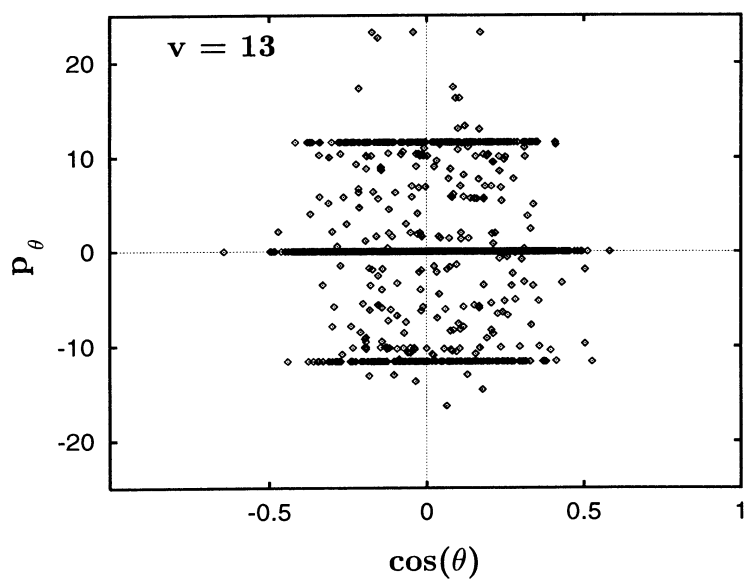


Figure 7. Initial distribution of angles and angular momenta associated with the θ ($\theta = \theta_1, \theta_2$) vdW modes.

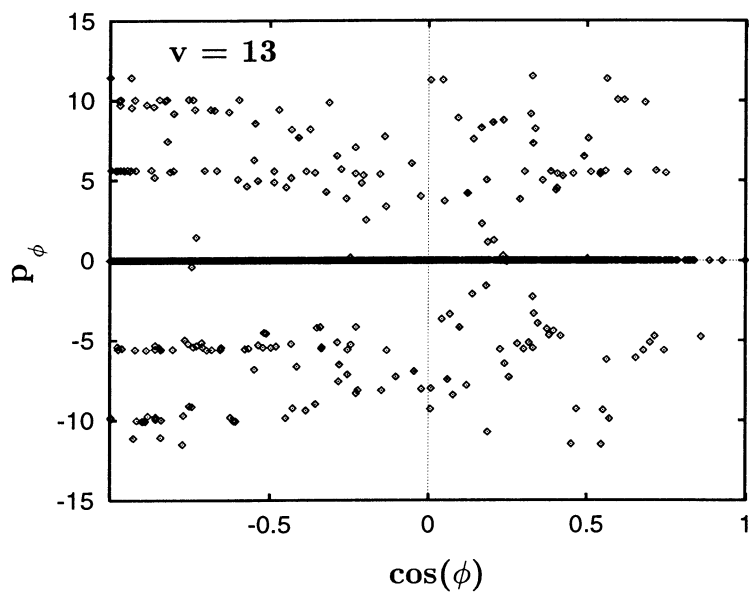


Figure 8. Initial distribution of angles and angular momenta associated with the ϕ mode.

The method proposed in this work can be viewed as a tool to transform an initial state calculated quantum-mechanically into initial conditions for classical trajectories, keeping the main features of the quantum state. Extending the present

technique to systems larger than tetraatomic ones still requires more work, but we believe it is feasible. In that sense, the application of this method to many-mode initial states obtained from quantum Monte Carlo approaches [54] appears as a very interesting direction.

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