Time Dependent Quantum Mechanical Calculations of the Dissociation Dynamics of the Cluster He_n-I_2.

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Abstract

A time dependent quantum mechanical framework is used to examine the dissociation dynamics of van der Waals clusters, in particular the He_n-I_2 system. The time dependent approach exploits the time scale separation between the He motion and the I_2 vibration. The formalism used is the Time Dependent Self Consistent Field (TDSCF). In this picture, in which the He degrees of freedom are moving in the average field of the I_2 molecule and vice versa, the equations of motion are solved by the Fourier grid method which calculates the operation of the operators constituting the Hamiltonian locally. The result is a very fast convergence with respect to grid size. The TDSCF approximation is tested for the collinear $He-I_2$ system by comparing to an exact time dependent propagation. Good results were obtained for low vibrational excitation of the I_2 bond. For higher excitations the TDSCF approximation could not account for the fast dephasing part of the autocorrelation function, nevertheless the long time behavior responsible for the dissociation was represented well. The TDSCF approach was then applied to calculate the dissociation of T-shaped and X-shaped He_n-I_2 clusters. The basis of this approximation is the weak interaction between the He atoms, and the extra averaging due to increase in the number of particles. Results show very small dependence of dissociation rate on cluster size in contrast to an RRKM picture. The symmetry of the He wavefunction to exchange is investigated. A scheme to incorporate part of the correlations responsible for collective motion which are missing in the simple TDSCF approach is presented. This scheme is based on a projection operator approach and the time dependent variational principle. On the basis of symmetry it is predicted that the dissociation rate of a cluster consisting of He^3 will be faster than a cluster of He^4.

J. Jortner et al. (eds.), Large Finite Systems, 53–66.

I. Introduction

Dissociation of van der Waals clusters has received considerable attention both experimentally and theoretically. The introduction of the seeded supersonic beam, in combination with new laser spectroscopic techniques, enabled the detailed study of the dissociation dynamics of these clusters [1]. These studies of a well-defined isolated system inspired considerable theoretical work [1][2]. The "text book" cluster of He_n-I_2, which was also one of the first to be produced, is the subject of this study. While this system has been studied both classically [2] and quantum mechanically [3], nevertheless it is still a source of fundamental questions on the nature of these van der Waals clusters.

In this work a time dependent quantum mechanical approach is used to elucidate the following problems:
1) The relation between the cluster size and dissociation rate.
2) The role of quantum effects at the low temperatures of the experiment and in particular the role played by the symmetry to particle exchange of the He_n part of the wavefunction.
3) Classical studies [4[[5] have found that the energy transfer is dominated by bottlenecks. How does this behavior manifest itself in a quantum regime?

The study of van der Waals clusters through a time dependent picture is appealing because of the ability to interpret the dynamical process while following the evolution. Moreover the time dependent treatment is directly comparable to classical trajectory results which allows an easy identification of quantum effects. Numerical time dependent techniques have advanced considerably recently, enabling exact quantum mechanical detailed studies. The time dependent quantum mechanical method used in this work is the Fourier method [6][7]. This method has fast convergence properties and is very flexible. Numerical efficiency is obtained because of the Fast Fourier Transform (FFT) algorithm which is well suited for parallel and vector computers.

The time dependent approach is also the source of a dynamical mean field approximation. The Fourier method allows a simple direct implementation of a Time Dependent Self Consistent Field (TDSCF) formulation [8]. The time dependent approach gives a superior mean field approximation to the static SCF due to the ability to include as a time correlation many of the omitted static correlations. This approximation is found to be accurate in the study of van der Waals clusters because of the natural time scale separation between the molecular degrees of freedom and the surrounding rare gas atoms. It is also expected that the quality of the approximation should increase with the cluster size due to the extra averaging with the increase in the number of cluster atoms. Classical and semiclassical TDSCF studies of similar systems have been tried previously [9][10], but the validity of these approximations could not be tested directly, therefore a full quantum mechanical time dependent study of the collinear dissociation of the $He-I_2$ molecule has been carried out. In that study a direct comparison of the exact and TDSCF wavefunctions was done [11]. That work proves the validity of the TDSCF approximation for treating wan der Waals clusters. This study is directed at understanding the behavior of He clusters at low temperature where a quantum picture is necessary. In particular we want to shed light on the three fundamental questions posed previously.

This paper is divided as follows. Section II describes the use of the Fourier method and the development of the TDSCF approximation for collinear He $-I_2$. Section III describes the dissociation dynamics of large T-shaped and X-shaped clusters. Section IV develops a systematic procedure to include correlations omitted in the simple TDSCF approach. Section V summarizes the results.

II. The collinear He$-$I$_2$ as a test of the validity of the TDSCF approximation.

The dissociation of the collinear He$-$I$_2$ system is used to demonstrate the quality of the time dependent self consistent field approximation for van der Waals clusters. This is done by comparing an exact solution of the time dependent Schrödinger equation for the collinear system to the approximate TDSCF approach.

The starting point of this comparison is the two-dimensional Schrödinger equation in atomic units:

$$i\frac{\partial\psi}{\partial t} = \hat{\mathbf{H}}\psi \tag{2.1}$$

subject to the initial condition in which the vibrational bond of I$_2$ is excited. The Hamiltonian can be written

$$\hat{\mathbf{H}} = \frac{1}{2}\left(\hat{\mathbf{P}}^2_{r_1} + \hat{\mathbf{P}}^2_{r_2}\right) + \hat{\mathbf{V}}(r_1,r_2) \tag{2.2}$$

using a mass scaled coordinate system for which: $r_1 = aR_{\mathrm{He-I_2}}$ and $r_2 = bR_{\mathrm{I-I}}$, where:

$$a = \left(\frac{m_1(m_2+m_3)}{(m_1+m_2+m_3)}\right)^{1/2} \qquad b = \left(\frac{m_3(m_1+m_2)}{(m_1+m_2+m_3)}\right)^{1/2} \tag{2.3}$$

$m_1 = m_{\mathrm{He}}$ and $m_2 = m_3 = m_{\mathrm{I}}$.

Examining equation (2.3) one can identify the r_1 coordinate as predominantly a He motion and r_2 as a relative I$_2$ motion.

A direct numerical solution of the Schrödinger equation is based on a discretization scheme in which all operators constituting the Hamiltonian operators are calculated locally. This is done by representing the wavefunction on a grid. In configuration space the potential operator is local and therefore its operation is just a multiplication of the value of the wavefunction at a grid point with the value of the potential at that point. The kinetic energy operator is calculated locally in momentum space. The transformation from coordinate space to momentum space is done by a discrete Fast Fourier Transform (FFT). As a result the classical phase space is discretized by rectangular cells of area h . The time propagation operator is expanded in a Chebychev polynomial:

$$\hat{\mathrm{U}}(t) = e^{-i\hat{\mathbf{H}}t} = \sum_{n}^{N} a_n \phi_n(-i\hat{\mathbf{H}}t/R) \tag{2.4}$$

where ϕ_n is the complex Chebychev polynomial which is calculated by its recursion relation, a_n are expansion coefficients, and R is the range of eigenvalues of $\hat{\mathbf{H}}$ represented on the grid multiplied by t. The details of the method can be found elsewhere [12]. The initial wavefunction was chosen as a product form in the r_1 and r_2 coordinates where, for the He degree of freedom, a Morse initial wavefunction was chosen and for the I$_2$ coordinate the eigenfunction problem was solved on a one-dimensional grid by a relaxation method described previously [13]. This procedure overcame the numerical difficulties of calculating high order Morse wavefunctions [14][15].

The TDSCF equations for the collinear He$-$I$_2$.

The TDSCF idea in quantum mechanics manifests itself by the product form for the wavefunction:

$$\psi(r_1,r_2) = \phi(r_1)\chi(r_2)e^{i\sigma(t)} \tag{2.5}$$

and normalization:

$$<\phi|\phi> = 1 \quad , \quad <\chi|\chi> = 1. \tag{2.6}$$

The phase convention is chosen such that $\sigma(t) = \int_0^t <H>dt'$ where $<H>$ is the total energy of the system. This convention enables a direct comparison to the exact two-dimensional propagation. The choice of the r_1 and r_2 coordinates is critical to the success of the TDSCF as well as static SCF methods [16]. The choice of equation (2.3) reflects the physical intuition that the He degree of freedom is separated from the I$_2$ motion. The equations of motion are generated by the Hamiltonian. In order to save storage in a computer code, the sum of products form for the interaction potential is used

$$\hat{\mathbf{H}}(r_1,r_2) = \hat{\mathbf{H}}_1(r_1) + \hat{\mathbf{H}}_2(r_2) + \sum_i \hat{\mathbf{V}}_1^{\,i}(r_1)\hat{\mathbf{V}}_2^{\,i}(r_2) \tag{2.7}$$

Inserting (2.5) into the Schrödinger equation (2.1):

$$\begin{aligned} i\frac{\partial\psi(r_1,r_2)}{\partial t} &= i\frac{\partial\phi(r_1)}{\partial t}\chi(r_2) + i\phi(r_1)\frac{\partial\chi(r_2)}{\partial t} \\ &= \chi(r_2)\hat{\mathbf{H}}_1(r_1)\phi(r_1) + \phi(r_1)\hat{\mathbf{H}}_2(r_2)\chi(r_2) + \sum_i \hat{\mathbf{V}}_1^{\,i}(r_1)\hat{\mathbf{V}}_2^{\,i}(r_2)\phi(r_1)\chi(r_2) \end{aligned} \tag{2.8}$$

Multipling by $\chi^*(r_2)$ and integrating on the r_2 variable using the normalization condition $\frac{\partial}{\partial t}<\phi|\phi> = 0$ and the fact that the r.h.s. is Hermitian one obtains the TDSCF equations:

$$i\frac{\partial\phi(r_1)}{\partial t} = \hat{\mathbf{H}}_1^{SCF}(r_1)\phi(r_1) \tag{2.9}$$

and:

$$i\frac{\partial\chi(r_2)}{\partial t} = \hat{\mathbf{H}}_2^{SCF}(r_2)\chi(r_2)$$

where:

$$\hat{\mathbf{H}}_1^{SCF}(r_1) = \hat{\mathbf{H}}_1(r_1) + <\chi(r_2)|\hat{\mathbf{H}}_2(r_2)|\chi(r_2)> + \sum_i <\chi(r_2)|\hat{\mathbf{V}}_2^{\,i}(r_2)|\chi(r_2)>\hat{\mathbf{V}}_1^{\,i}(r_1)$$

and:

$$\hat{\mathbf{H}}_2^{SCF}(r_2) = \hat{\mathbf{H}}_2(r_2) + <\phi(r_1)|\hat{\mathbf{H}}_1(r_1)|\phi(r_1)> + \sum_i <\phi(r_1)|\hat{\mathbf{V}}_1^{\,i}(r_1)|\phi(r_1)>\hat{\mathbf{V}}_2^{\,i}(r_2)$$

$$\mathbf{H}_i(r_i) = \frac{\hat{\mathbf{P}}_{r_i}^2}{2} + \hat{\mathbf{V}}(r_i) \qquad i = 1\ ,\ 2$$

The equation is solved by constructing a grid for the r_1 and r_2 coordinates. On this grid the operations of equation (2.9) are calculated. The $\hat{\mathbf{H}}_i$ operator in equation (2.9) is calculated by the Fourier method for one degree of freedom. The second term is the average energy of the complementary degree of freedom. The third operation in equation (2.9) is a sum of potential terms multiplied by averages of potential terms from the other degree of freedom. Summing up these contributions completes the Hamiltonian operation. The propagation in time is done simultaneously in both degrees of freedom by the second order differencing scheme (SOD) [6][7].

$$\phi(t+\Delta t) \approx \phi(t-\Delta t) - 2i\,\Delta t\,\hat{\mathbf{H}}_{\mathrm{SCF}}\phi(t) \tag{2.10}$$

where $\hat{\mathbf{H}}_{\mathrm{SCF}}$ is the operator on the r.h.s. of equation (2.9). A similar propagation scheme exists for χ. Use of the SOD propagating method is employed because the operators of equation (2.9) become time dependent and the Chebychev scheme cannot handle the time ordering operation involved. This scheme preserves the norm of both wavefunctions since $\hat{\mathbf{H}}_{\mathrm{SCF}}$ is Hermitian. The total energy becomes the expectation value

$$E = \langle\phi|\hat{\mathbf{H}}_{\mathrm{SCF}}(r_1)|\phi\rangle = \langle\chi|\hat{\mathbf{H}}_{\mathrm{SCF}}(r_2)|\chi\rangle \tag{2.11}$$

and is conserved in time. The second order propagation scheme requires two initial conditions $\phi(0\cdot\Delta t)$ and $\phi(1\cdot\Delta t)$. The scheme is therefore started by a second order Runga-Kutta propagation.

Results.

A typical calculation starts by constructing an initial wavefunction on the grid. The initial wavefunction was a product of the ground state of a Morse in the He direction and an excited vibrational state in the I_2 direction calculated by a relaxation method [13]. The potential was a Morse potential in the $R_{\mathrm{He-I}}$ and in the $R_{\mathrm{I-I}}$ coordinates, the parameters were adopted from reference [3], other details of the calculation as well as a more extensive discussion of the results can be found in reference [11]. The same initial wavefunction was propagated by the direct Fourier method with the Chebychev scheme and by the TDSCF method. Figure 1 compares propagation of both schemes for $v=5$, $v=11$, and $v=22$ vibrational initial states of I_2 by displaying the overlap:

$$b(t) = |\langle\psi(r_1,r_2)|\phi(r_1)\chi(r_2)\rangle|^2 \tag{2.12}$$

as a function of time.

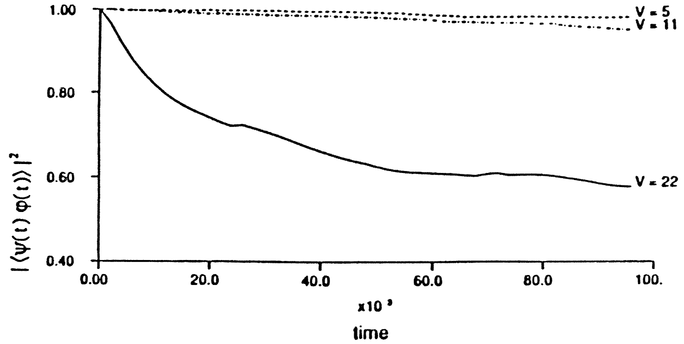

Figure 1: The overlap between the TDSCF wavefunction and the exact wavefunction as a function of time for the initial vibration of the I_2, v=5, v=11, and v=22.

The overlap criteria for comparison of wavefunctions is a more strict test of the approximation than commonly used average quantaities such as the dissociation rate or average energy.

Lifetimes of the different states can be estimated by the autocorrelation function [17][18]:

$$a(t) = |\langle\psi(0)|\psi(t)\rangle|^2 \qquad (2.13)$$

Figure 2 displays the autocorrelation function as a function of time for both the exact and TDSCF wavefunctions.

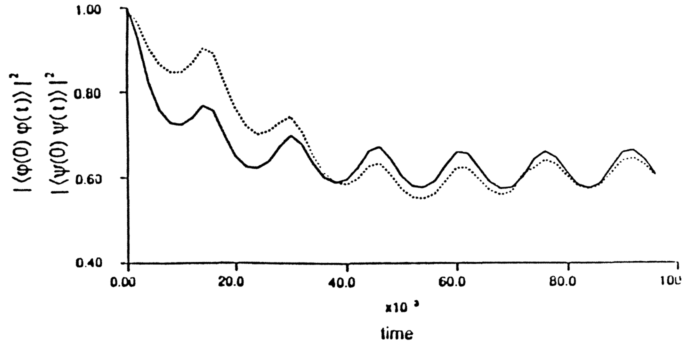

Figure 2: The autocorrelation function as a function of time for the solid line is the exact result and the dashed line is the TDSCF approximation. the initial state is v=22.

Figure 3 shows the exact vs the TDSCF wavefunction superimposed at 40000 au for v=5 .

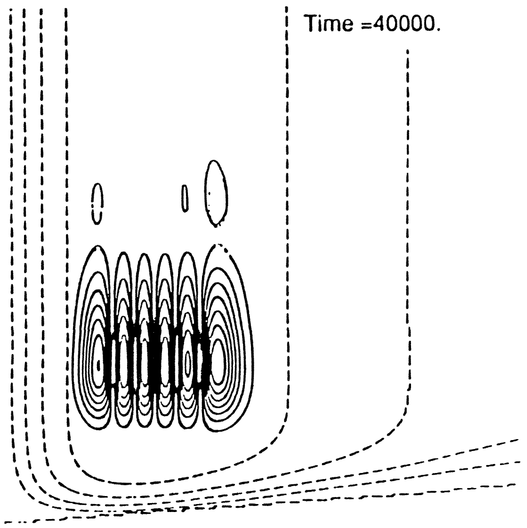

Figure 3: A contour plot of the wavefunction on the potential at t=40000 a.u. (approximately 1 p.s.) for v=5. The solid line is the exact result and the dotted line is the TDSCF approximation. The vertical direction is r_1 and the horizontal direction r_2. The potential is drawn as a dashed line

Upon examining the plots it can be concluded that the TDSCF wavefunction compares well with the exact evolution. Deviations are found for the $v=22$ I_2 initial state. The reason is that for this highly excited state part of the wavefunction penetrates into the classically forbidden region. The result is a fast initial dephasing of the wavefunction which is not well represented in the TDSCF wavefunction. The long time behavior manifested by the superposition of the I_2 vibrations on the He vibrations is represented quite well.

The success of the TDSCF approximation for the collinear He-I_2 is encouraging to the use of this approximation for larger clusters. It is expected that the quality of the method should improve due to the extra averaging when more particles are bunched around the central I_2.

III. The T-shaped and X-shaped He_n-I_2 clusters.

Experimental evidence suggests [1] that the He$-I_2$ molecule has a T shape. It is speculated that additional He atoms will stay on the same plane demonstrated by the X shape of He_2-I_2 displayed in Figure 4.

The TDSCF equations of motion for the T-shaped molecule are identical to equation (2.9). The mass scaling in equation (2.3) is changed to account for the different geometry : $b=(\tfrac{1}{2}m_I)^{\frac{1}{2}}$. The He-$I_2$ potential is expanded to second order in $R_3 = R_{I-I} - (R_{I-I})_{eq}$ in order to preserve the product form of the potential in equation (2.7).

The equations of motion for the X-shaped cluster are solved in the set of coordinates represented in Figure 4.

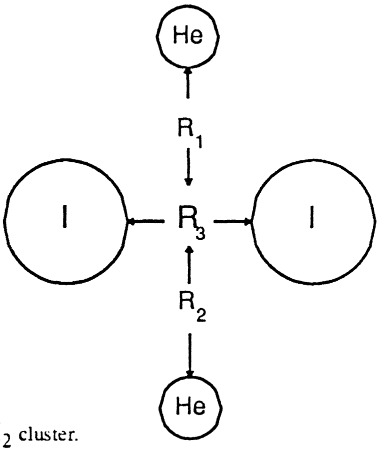

Figure 4: Coordinate set of the X-shaped He_2-I_2 cluster.

Using mass scaled coordinates,

$$r_1 = a\,R_{He^1-I_2} \qquad r_2 = a\,R_{He^2-I_2} \qquad r_3 = b\,R_{I\ I} \qquad (3.1)$$

where:

$$a = \left(\frac{m_1(m_2 + 2m_3)}{(m_1+m_2+2m_3)}\right)^{\frac{1}{2}} \qquad b = \left(\tfrac{1}{2}m_3\right)^{\frac{1}{2}}$$

$m_1 = m_2 = m_{He}$ and $m_3 = m_I$,

the kinetic energy operator becomes:

$$\hat{\mathbf{T}} = \frac{1}{2}\left(\hat{\mathbf{P}}_1^2 + \hat{\mathbf{P}}_2^2 + \delta\hat{\mathbf{P}}_1\hat{\mathbf{P}}_2 + \hat{\mathbf{P}}_3^2\right) \tag{3.2}$$

and δ the kinetic energy coupling term is

$$\delta = \left(\frac{m_1 m_2}{(2m_3 + m_2)(2m_3 + m_1)}\right)^{1/2} \tag{3.3}$$

The potential energy is a sum of the I-I potential and the two He-I_2 potentials. The He-He potential is neglected because it is expected to be very small. The TDSCF wavefunction for this system becomes:

$$\psi(r_1,r_2,r_3) = \phi(r_1)\phi(r_2)\chi(r_3) \tag{3.4}$$

One should notice that the TDSCF wavefunction is symmetric to the exchange of the He atoms 1 and 2. Therefore only one TDSCF equations of motion for the He atoms has to be solved:

$$i\frac{\partial\phi(r)}{\partial t} = \hat{\mathbf{H}}_{12}(r)^{SCF}\phi(r) \tag{3.5a}$$

where:

$$\hat{\mathbf{H}}_{12}^{SCF}(r) = \hat{\mathbf{H}}_{12}(r) + <\chi(r_3)|\hat{\mathbf{H}}_3(r_3)|\chi(r_3)> + \sum_i <\chi(r_3)|\hat{\mathbf{V}}_3^{\,i}(r_3)|\chi(r_3)>\hat{\mathbf{V}}_{12}^{\,i}(r)$$
$$+ \frac{\delta}{2}<\phi(r)|\hat{\mathbf{P}}_r(r)|\phi(r)>\hat{\mathbf{P}}_r(r) + <\phi(r)|\hat{\mathbf{H}}_{12}(r)|\phi(r)>$$

and:

$$\hat{\mathbf{H}}_{12}(r) = \frac{\hat{\mathbf{P}}_r^2}{2} + \hat{\mathbf{V}}(r)$$

The equation of motion for the I_2 degree of freedom becomes:

$$i\frac{\partial\chi(r_3)}{\partial t} = \hat{\mathbf{H}}_3^{SCF}(r_3)\chi(r_3) \tag{3.5b}$$

where

$$\hat{\mathbf{H}}_3^{SCF}(r_3) = \hat{\mathbf{H}}_3(r_3) + 2<\phi(r)|\hat{\mathbf{H}}_{12}(r)|\phi(r)>$$
$$+ 2\sum_i <\phi(r)|\hat{\mathbf{V}}_{12}^{\,i}(r)|\phi(r)>\hat{\mathbf{V}}_3^{\,i}(r_3) + \frac{\delta}{2}<\phi(r)|\hat{\mathbf{P}}_r(r)|\phi(r)>^2$$

and

$$\hat{\mathbf{H}}_3(r_3) = \frac{\hat{\mathbf{P}}_3^2}{2} + \hat{\mathbf{V}}(r_3)$$

Very similar equations are obtained for larger clusters where the mass scaling and δ parameter change. For the system under consideration the heavy I_2 atoms serve as a kinetic energy block similar to the situation in the light heavy light triatomic molecule. To a first approximation one can use $\delta = 0$ instead of $\delta = 2/131$. Using this approximation the main difference as a function of cluster size comes through the conservation of energy terms inherent in the TDSCF equations. The He atoms are only subject to the forces exerted by the central I_2 and no correlations between the different He atoms is assumed.

Results.

Calculations were performed for cluster sizes n=1 , n=2, and n=4, for $\nu=23$. Figure 5 displays the autocorrelation function as a function of time.

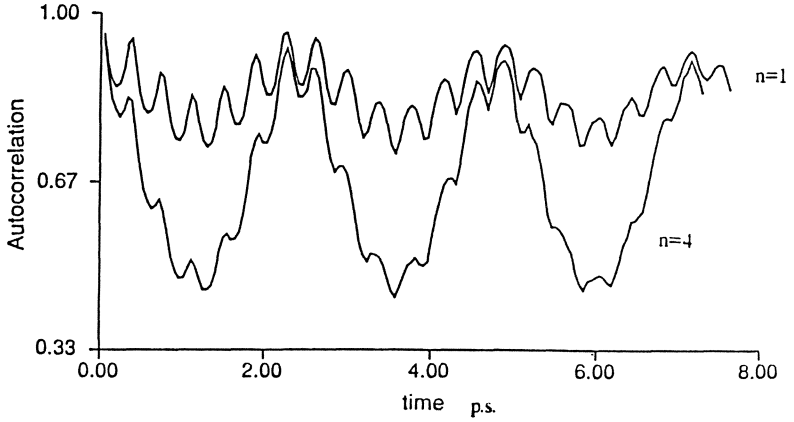

Figure 5: The autocorrelation function $|\langle\psi(t)|\psi(0)\rangle|^2$ as a function of time for n=1 and n=4 size clusters.

The main feature seen in the autocorrelation function is the superposition of the He and I_2 vibrations. The larger amplitude of the He_4 cluster is only the result of the larger cluster size. When examining the autocorrelation functions of an individual He atom very small differences in the autocorrelation are found as a function of cluster size. This result demonstrates the almost perfect separability between the I_2 degree of freedom and the He degrees of freedom. One way to picture the problem is to think of the I_2 vibrations as a time varying force driving the He atoms out almost independently. The I_2 frequency is much higher than the He frequency with a frequency mismatch of approximately 19/3 and the high excitation of the I_2 molecule enables it to act as an energy sink. This situation is opposed to the situation explored by Brown and Wyatt [19] in which a Morse oscillator was driven by a constant frequency comparable to the vibrational spacings. In their study bottlenecks to the dissociation were found. Brown and Wyatt reasoned that these bottlenecks are produced while the molecule acquires energy and its frequency changes, causing a frequency mismatch with the driving frequency. This mismatch in the two frequencies has to go through the golden mean which is the most difficult irrational number to be approximated by a rational product [20]. Classical studies on this system [4-5] also found bottleneck-type restrictions in the classical phase space. Considering the evidence concerning the quantum calculations [3], which show a monotonic increase in the dissociation rate as a function of the initial vibrational excitation, no evidence for bottlenecks is found.

IV. Correlations and symmetry.

The approximation inherent in the TDSCF method is of a separate motion for each degree of freedom in an effective time dependent Hamiltonian. Correlations between degrees of freedom exist only as time correlations i.e. energy can flow back and forth between the individual degrees of freedom. Two types of spatial correlations should be considered: He - I_2 correlations and He - He correlations which are also associated with the symmetry to exchange. Although the He$-I_2$ correlations are weak some correlation still persists. As a demonstration of this effect one can consider the collinear He$-I_2$ molecule in the $R_{\mathrm{He-I}}$ and R_{I_2} coordinates. In these coordinates the TDSCF initial state is an eigenstate of the TDSCF Hamiltonian. Therefore the TDSCF wavefunction does not dissociate. Examining the exact dynamics one finds that dissociation occurs through a highly correlated motion which originates in the soft turning point of the I_2. This is an example of a rare correlated event which in this choice of coordinates is the only route to dissociation. It is therefore desirable to amend the simple TDSCF method by including the important correlations without increasing the dimensionality of the calculations. This task can be done by adding configurations to the simple product wavefunction.

The symmetry to exchange manifests itself by requiring that the He wavefunction be symmetric to exchange of two He atoms for He^4. For He^4 this symmetry can only manifest itself if the He motion is correlated with other He atoms. Considering the He - He correlations two types of interactions can lead to correlations: a kinetic energy coupling, equations (3.2)-(3.3), and a potential coupling term which is dominantly an excluded volume term which is present in a full 3-D description. The question one wants to answer is the influence of symmetry on the dissociation rate. Considering the picture manifested by the calculations where the He motion is uncorrelated and the dissociation is impulsive, symmetry plays no role. For larger clusters ($n \geq 3$) excluded volume interactions can lead to a correlated He motion. It is expected that this correlated motion should resist the I_2 driving, resulting in a longer lifetime. An opposite extreme is an RRKM picture where phase space has to fill up before dissociation can start. For this case the symmetry reduces the density of states and therefore increases the dissociation rate.

A more involved picture can be found for He^3 clusters because He^3 are fermions. Therefore the total wavefunction has to be antisymmetric including also the nuclear spin contribution. The situation is in analogy to the electronic structure of the He atom where the He^3 atoms play the role of the electrons and the I_2 the role of the positive charge. This picture leads to the conclusion that when a third He^3 atom is added it can only occupy an excited state, and as a result the system is already partially excited, with a higher dissociation rate. Another kinematic isotopic effect which also enhances the He^3 cluster dissociation is that being lighter than He^4, its vibrational frequency is higher by a factor of 1.15. This will lead to a more efficient energy transfer from the I_2 vibration to the He motion. One can conclude that the main effects of symmetry are present only for larger He clusters.

The addition of configurations to the wavefunction is the most simple way to include some correlations. This addition increases the number of coupled equations that have to be solved without increasing the dimensionality. The Multi-Configuration TDSCF (MC-TDSCF) approach is demonstrated for the symmetric He^4 cluster. A similar approach can be used to include He-I_2 correlations. A simple TDSCF approximation is assumed for the separation of the I_2 motion.

A multi-configuration symmetric wavefunction is chosen which has the form

$$\psi(r_1,r_2,r_3) \;=\; \chi(r_3)\Big(N_1\phi_a(r_1)\phi_a(r_2) + N_2\phi_b(r_1)\phi_b(r_2) + N_3(\,\phi_a(r_1)\phi_b(r_2) + \phi_a(r_2)\phi_b(r_1)\,)\Big) \tag{4.1}$$

where the χ and ϕ wavefunctions are normalized:

$$<\chi|\chi> = 1 \quad , \quad <\phi_i|\phi_j> = \delta_{ij}$$

where $i\ ,\ j = a\ ,\ b$ and N_1, N_2 and N_3 are normalization constants. The indices a and b can be interpreted as channel indices. The choice of the wavefunctions is related to a projection operator $\hat{\mathbf{P}}$ which defines the desired correlation. The projection operator is symmetric to particle exchange and operates in the tensor product Hilbert space of the two particles:

$$\hat{\mathbf{P}} \;=\; \hat{\mathbf{P}}_1\,\hat{\mathbf{P}}_2 \tag{4.2}$$

and

$$\hat{\mathbf{P}}_1\phi_a(r_1) \;=\; \phi_a(r_1) \quad , \quad \hat{\mathbf{P}}_1\phi_b(r_1) \;=\; 0$$

with a similar relation for $\hat{\mathbf{P}}_2$. Defining $\hat{\mathbf{Q}} = \hat{\mathbf{I}} - \hat{\mathbf{P}}$ one obtains from the Schrödinger equation (2.1) the coupled equations

$$\begin{aligned} i\hat{\mathbf{P}}\frac{\partial\psi}{\partial t} &= \hat{\mathbf{P}}\hat{\mathbf{H}}\left(\hat{\mathbf{P}}+\hat{\mathbf{Q}}\right)\psi \\ i\hat{\mathbf{Q}}\frac{\partial\psi}{\partial t} &= \hat{\mathbf{Q}}\hat{\mathbf{H}}\left(\hat{\mathbf{P}}+\hat{\mathbf{Q}}\right)\psi \end{aligned} \tag{4.3}$$

The following Hamiltonian is now used:

$$\hat{\mathbf{H}} \;=\; \hat{\mathbf{H}}^s(r_1)+\hat{\mathbf{H}}^s(r_2) + \hat{\mathbf{H}}^\delta(r_1)\hat{\mathbf{H}}^\delta(r_2) + \hat{\mathbf{V}}(r_1)\hat{\mathbf{V}}(r_2) \tag{4.4}$$

where $\hat{\mathbf{H}}^s(r_i)$ is the single particle Hamiltonian of particle i. $\hat{\mathbf{H}}^\delta(r_i)$ is the kinetic energy coupling term, and $\hat{\mathbf{V}}(r_i)$ is the potential energy coupling term. Using the time dependent variational principle and the norm conservation one obtains the equations of motion for ϕ_a and ϕ_b (for simplicity the dependence on r_3 is omitted from the equations).

$$\begin{aligned} i\frac{\partial\phi_a}{\partial t} &= \hat{\mathbf{H}}^{SCF}_{aa}\phi_a + \hat{\mathbf{H}}^{SCF}_{ab}\phi_b \\ i\frac{\partial\phi_b}{\partial t} &= \hat{\mathbf{H}}^{SCF}_{bb}\phi_b + \hat{\mathbf{H}}^{SCF}_{ba}\phi_a \end{aligned} \tag{4.5}$$

where

$$
\begin{aligned}
\hat{\mathbf{H}}_{aa}^{SCF} = {} & -\frac{N_2}{N_3}<\phi_a|\hat{\mathbf{H}}^s|\phi_b> - <\phi_a|\hat{\mathbf{H}}^s|\phi_a> + \hat{\mathbf{P}}\hat{\mathbf{H}}^s \\
& + \frac{N_1}{N_3}<\phi_b|\hat{\mathbf{H}}^\delta|\phi_a>\hat{\mathbf{P}}\hat{\mathbf{H}}^\delta + <\phi_b|\hat{\mathbf{H}}^\delta|\phi_b>\hat{\mathbf{P}}\hat{\mathbf{H}}^\delta + \frac{N_1}{N_3}<\phi_b|\hat{\mathbf{V}}|\phi_a>\hat{\mathbf{P}}\hat{\mathbf{V}} \\
& + <\phi_b|\hat{\mathbf{V}}|\phi_b>\hat{\mathbf{P}}\hat{\mathbf{V}} - \frac{N_2}{N_3}<\phi_a|\hat{\mathbf{H}}^\delta|\phi_b> <\phi_b|\hat{\mathbf{H}}^\delta|\phi_b> \\
& - <\phi_a|\hat{\mathbf{H}}^\delta|\phi_a> <\phi_b|\hat{\mathbf{H}}^\delta|\phi_b> - \frac{N_2}{N_3}<\phi_a|\hat{\mathbf{V}}|\phi_b> <\phi_b|\hat{\mathbf{V}}|\phi_b> \\
& - <\phi_a|\hat{\mathbf{V}}|\phi_a> <\phi_b|\hat{\mathbf{V}}|\phi_b> - \frac{N_1}{N_3}<\phi_a|\hat{\mathbf{H}}^\delta|\phi_a> <\phi_b|\hat{\mathbf{H}}^\delta|\phi_a> \\
& - <\phi_a|\hat{\mathbf{H}}^\delta|\phi_b>^2 - \frac{N_1}{N_3}<\phi_a|\hat{\mathbf{V}}|\phi_a> <\phi_b|\hat{\mathbf{V}}|\phi_a> - <\phi_a|\hat{\mathbf{V}}|\phi_b>^2
\end{aligned}
\tag{4.6}
$$

and

$$
\begin{aligned}
\hat{\mathbf{H}}_{ab}^{SCF} = {} & \frac{N_2}{N_3}\hat{\mathbf{P}}\hat{\mathbf{H}}^s + \frac{N_2}{N_3}<\phi_b|\hat{\mathbf{H}}^\delta|\phi_b>\hat{\mathbf{P}}\hat{\mathbf{H}}^\delta + <\phi_b|\hat{\mathbf{H}}^\delta|\phi_a>\hat{\mathbf{P}}\hat{\mathbf{H}}^\delta \\
& + \frac{N_2}{N_3}<\phi_b|\hat{\mathbf{V}}|\phi_b>\hat{\mathbf{P}}\hat{\mathbf{V}} + <\phi_b|\hat{\mathbf{V}}|\phi_a>\hat{\mathbf{P}}\hat{\mathbf{V}}
\end{aligned}
\tag{4.7}
$$

A similar equation is found for $\hat{\mathbf{H}}_{bb}^{SCF}$. Simultaneously with equation (4.5) one solves the equations of motion for the terms N_1, N_2, and N_3

$$
\begin{aligned}
i\frac{\partial N_1}{\partial t} = {} & 2N_1<\phi_a|\hat{\mathbf{H}}^s|\phi_a> + 2N_3<\phi_a|\hat{\mathbf{H}}^s|\phi_b> + N_1<\phi_a|\hat{\mathbf{H}}^\delta|\phi_a>^2 \\
& + 2N_3<\phi_a|\hat{\mathbf{H}}^\delta|\phi_b><\phi_a|\hat{\mathbf{H}}^\delta|\phi_a> + N_1<\phi_a|\hat{\mathbf{V}}|\phi_a>^2 \\
& + 2N_3<\phi_a|\hat{\mathbf{V}}|\phi_a><\phi_a|\hat{\mathbf{V}}|\phi_b> + N_2<\phi_a|\hat{\mathbf{H}}^\delta|\phi_b>^2 + N_2<\phi_a|\hat{\mathbf{V}}|\phi_b>^2
\end{aligned}
\tag{4.8}
$$

A similar equation exists for N_2. N_3 can then be calculated from the total normalization condition.

The set of equations (4.5)-(4.8) can be readily implemented. Only two one-dimensional partial differential equations (4.5) need be solved. This formalism allows flexiblity in the choice of projected states and should prove useful for many different scattering phenomena.

V. Conclusions.

This paper presents a framework for calculating the dissociation dynamics of van der Waals clusters. Considering quantum calculations for large systems with many degrees of freedom a mean field approach seems the only alternative. The approach adopted here of a TDSCF approximation relies on the physical picture in which a time scale separation exists between the He motion and the I_2 degrees of freedom. This basic approximation can be amended by including part of the correlations as more configurations without increasing the dimensionality of the problem. The procedure is not limited by the number of configurations. By a proper choice of projection operators all important correlations can be included while still maintaining the feasiblity of the calculation, even for relatively large systems.

From a numerical point of view the TDSCF method saves much computation time by decomposing one n-dimensional problem into n 1-dimensional problems. For the collinear He-I_2 calculation a reduction of a factor of ten was found. An exact calculation for larger clusters would not be feasible on the minicomputer used for this calculation. The TDSCF algorithm is also very well suited for parallel computation. By assigning one processor to each degree of freedom the processors carry out a lot of computation independently, with only a very small amount of communication between them.

The simple TDSCF calculation shows that the dissociation rate depends very little on cluster size. An impulsive model of the dissociation therefore results. This is in contrast to an RRKM picture which would predict a decrease in the dissociation rate. The emerging picture is of a He atom driven out of its well by a periodic fast perturbation.

Considering the role of symmetry in $_3$He clusters it is expected that different dissociation rates can be found for He^4 than He^3 for clusters with more than three He atoms.

Acknowledgment:

We want to thank the organizers of the Jerusalem Symposium for stimulating this work, and to A. Ben-Shaul, R. S. Berry, J. A. Beswick, and J. Jortner for helpful discussions. The Fritz Haber Research Center is supported by the Minerva Gesellschaft für die Forschung, GmbH München, BRD. R. K. acknowledges support by grants from the U.S. - Israel Binational Science Foundation.

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