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Citation: [The Journal of Chemical Physics](#) **104**, 1047 (1996); doi: 10.1063/1.470830

View online: <http://dx.doi.org/10.1063/1.470830>

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Quantum-mechanical study of the $\text{I}_2\text{-Ne}$ vibrational predissociation dynamics: A three-dimensional time-dependent self-consistent-field approach

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(Received 15 September 1995; accepted 12 October 1995)

A three-dimensional time-dependent self-consistent-field (TDSCF) approach is proposed to study the vibrational predissociation of the $\text{I}_2(B)\text{-Ne}$ van der Waals (vdW) complex. Jacobian coordinates are used within the assumption of zero-total angular momentum. In the method the total wave function is factorized such that the bending mode of the system is explicitly separated, while the coupling between the remaining two degrees of freedom is treated exactly. The decay dynamics of several resonances corresponding to different initial vibrational states of I_2 is investigated through long-time wave packet propagations. Calculated resonance lifetimes are compared to experimental data and found to be in quantitative agreement with them. The results show that predissociation of the complex is mainly governed by the coupling between the I_2 and the vdW stretching vibrations, whereas the bending mode has a rather weak effect on the dynamics. The good quality of the TDSCF description of this long-time dynamical process is due to the adaptation of the decoupling approximations applied in the method to the physical situation of the system. The validity of the approach is discussed in the light of the results. © 1996 American Institute of Physics. [S0021-9606(96)03303-4]

I. INTRODUCTION

The application of time-resolved pump-probe experimental techniques to the field of chemical reaction dynamics has experienced a great impulse in the last years.¹⁻¹⁰ Such techniques allow the possibility of monitoring a chemical process in real time with a subpicosecond resolution, and probing directly the reaction intermediates. A large variety of chemical reactions have been investigated through time-resolved experiments, among them the photoinduced dissociation of weakly bound van der Waals (vdW) clusters.^{3,5,7(b)} More specifically, real-time techniques have been applied in recent years to explore the vibrational predissociation (VP) of vdW systems,⁵ which was extensively studied in the past by means of frequency-domain spectroscopic experiments.¹¹⁻¹³

The increasing availability of experimental data in the time domain has stimulated the theoretical efforts in the direction of developing time-dependent methods to rationalize such information. In this sense, a number of algorithms to solve efficiently the time-dependent Schrödinger equation has been proposed,¹⁴⁻²⁰ and exact, full-dimensional quantum treatments of triatomic complexes (assuming zero-total angular momentum) have been reported in the literature.^{21,22} Also time-dependent quantum calculations of tetra-atomic vdW clusters were carried out on restricted-dimensionality models.^{21(b),23} However, the fast scaling of the computational effort required by exact quantum methods as the number of coordinates increases, reduces their applicability to small systems involving few degrees of freedom. In addition, the vibrational predissociation of vdW clusters is a rather long-time process, which typically ranges from a few picoseconds to several hundreds. This implies long-time numerical propagations, and therefore the use of large grids for the dissoci-

ating coordinates. In practice, a full-dimensional quantum calculation of a vdW system with more than four atoms becomes intractable at present, and several difficulties are found even for many tetraatomic complexes.

In order to overcome the restrictions associated with the high computational cost of exact treatments, several approximate methods have been suggested. Most of them apply a scheme of factorization of the exact wave function, as a way of reducing the effective dimensionality of the problem. Among the different approaches, the time-dependent self-consistent-field (TDSCF) approximation²⁴ has received a great deal of attention in the last recent years. In this method the wave function can be either totally or partially factorized. Then, based on a mean-field approximation, each separated mode or group of modes generates an instantaneous mean-field potential in which the motion of the remaining modes takes place. The mean potentials allow for partial coupling and energy exchange between the separated degrees of freedom along the time propagation. The TDSCF scheme has been applied to chemical reaction dynamics in different forms, the most common of which is perhaps the quantum single-configuration (SC) version.²⁵⁻²⁸ Also hybrid quantum/classical^{26,29-36} and quantum/semiclassical^{37,38} variations of the SC TDSCF approach have been proposed. The factorization of the exact wave function assumed in the SC TDSCF method implies a loss of correlation or interaction between the separated modes. As a consequence, the approximate TDSCF wave function gradually dephases and deteriorates with respect to the exact one with increasing time of propagation.²⁶ Based on similar ideas to those applied in electronic structure theory, several improvements of the SC TDSCF scheme have been suggested, including configuration interaction,³⁹ multiconfiguration TDSCF,⁴⁰⁻⁴⁴ and

perturbation-theory⁴⁵ corrections. Some of the above SC versions of the TDSCF method were applied to simulate the vibrational predissociation of vdW complexes.^{23(c),25,29,31} Reduced-dimensionality models were currently assumed in these calculations. Also a three-dimensional multiconfiguration TDSCF treatment of the Cl_2 -Ne VP dynamics was recently reported,^{44(a)} and good agreement with previous time-dependent and time-independent calculations, as well as with experiment was found.

The SC TDSCF approximation appears as an attractive tool to study realistic systems for which more refined configuration interaction or multiconfiguration TDSCF approaches may become prohibitively expensive. In this light, a better knowledge on the applicability and limitations of this method is desirable. As mentioned above, the SC TDSCF approach is usually a good short-time approximation which deteriorates with time. Interesting questions arise about how long and in what conditions this method remains accurate when applied to long-time processes like the vibrational predissociation of vdW systems. The main source of error in the TDSCF approach is originated in the separation of modes assumed in the wave function. Therefore, the larger is the extent to which the wave function is factorized, the poorer is expected to be the quality of the TDSCF results. The limit of a TDSCF treatment assuming a completely factorized wave function will work well only for those systems in which the modes are well separated physically. This is not the case for most of the systems, where usually some of the modes are more strongly coupled and underlie significant energy exchange along the dynamical process. This situation suggests that we apply a TDSCF decoupling scheme in which only those modes interacting more weakly are explicitly separated, and the main couplings are described as accurately as possible. The above scheme was recently applied in 3D TDSCF calculations to simulate the transition-state dynamics of hydrogen transfer²⁷ following electron photodetachment from $ClHCl^-$, and the Ar-HCl photodissociation.²⁸ Comparison of the TDSCF results with exact calculations showed a quantitative agreement in both works. These calculations encouragingly support the TDSCF scheme discussed above, at least for short-time processes (<1 ps) like those studied in Refs. 27 and 28. To investigate the applicability of a similar TDSCF approach to longer-time processes appears as a challenging task.

In the present work a 3D quantum SC TDSCF approach is proposed to study the VP dynamics of the I_2 -Ne complex. In the method zero-total angular momentum is assumed, and Jacobian coordinates are used to represent the three modes of this triatomic system; the I_2 stretch, the vdW stretch, and the vdW bending mode. Experimental results^{5(a)} seem to indicate that the fragmentation of the complex occurs via direct predissociation, essentially governed by the coupling between the iodine stretching vibration and the reactive vdW stretch mode. The bending coordinate would play a secondary role as a “bath mode,” affecting rather weakly the dissociation dynamics. The above physical picture suggests a factorization scheme where only the bending mode is explicitly separated, while the coupling between the two stretching vibra-

tions is treated exactly. The TDSCF approach proposed here to describe the $I_2(B)$ -Ne dissociation dynamics is based on this type of factorization, and its validity will be discussed below by comparing with the available experimental data.^{5(a)}

The paper is organized as follows: In Sec. II we present the potential surface used in the calculations, and the details of the TDSCF method. In Sec. III the results are shown and discussed. Some conclusions are given in Sec. IV.

II. THEORETICAL APPROACH

A. Potential-energy surface and initial state

Vibrational predissociation of the I_2 -Ne cluster occurs upon vibroelectronic excitation of the iodine to the $(B, v_i > 0)$ state. The laser prepares a resonance state of the complex which is coupled to a continuum and decays with time, producing the cluster fragmentation,

The I_2 -Ne potential surface used in the present calculations to simulate the above process has been described in detail elsewhere.⁴⁶ Therefore, we will give just a brief summary here. The potential is represented as a sum of atom-atom interactions, where the two I-Ne interactions are taken to be Morse functions, and the I-I potential is the functional form of Gruebele and Zewail.⁴⁷ The Morse parameters of the I-Ne potential were adjusted with an approximate dynamical quantum model⁴⁶ in order to reproduce the experimental lifetimes of Zewail and co-workers.^{5(a)} The adjusted parameters are $D=40.75$ cm⁻¹, $d_e=4.36$ Å, and $\alpha=1.56$ Å⁻¹. Very similar parameters were obtained in a fit carried out by Gray with a time-dependent exact method.^{21(b)} The small differences are probably due to the different I-I potentials and dynamical approaches (to a lesser extent) used in the fits of Refs. 21(b) and 46.

The initial resonance states of the I_2 -Ne cluster associated with the I_2 vibrational excitations studied in this work were calculated variationally on the above potential surface. A diabatic separation of the I_2 stretching mode was assumed in the calculation of the resonance states. This approximation, only applied in the characterization of the initial state, is justified because of the frequency difference between the chemical and the vdW modes.

B. The TDSCF formalism

In the method proposed here Jacobian coordinates (r, R, θ) are used to represent the I_2 -Ne system, where r is the I-I distance, R is the separation between the Ne atom and the I_2 center-of-mass, and θ is the angle between the vectors associated with the r and R coordinates. It is assumed in the calculations that the total angular momentum of the system is zero. For convenience the following standard definition of the total wave function is adopted,

$$\Psi(r, R, \theta) = \Phi(r, R, \theta)/rR, \quad (1)$$

such that the Hamiltonian for the reduced wave function $\Phi(r, R, \theta)$ is (in atomic units)

$$\hat{H}(r, R, \theta) = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial r^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial R^2} + \left(\frac{1}{2\mu_1 r^2} + \frac{1}{2\mu_2 R^2} \right) \times \hat{j}^2 + V_{I_2}(r) + W(r, R, \theta). \quad (2)$$

In Eq. (2) μ_1 and μ_2 are the reduced masses corresponding to I₂ and I₂-Ne, respectively, and $\hat{j}$ is the angular momentum operator. The potential surface has been divided in two terms, one corresponding to the isolated I₂ diatom, $V_{I_2}(r)$, and the other, $W(r, R, \theta)$, representing the vdW interaction potential. The solution of the time-dependent Schrödinger equation,

$$i \frac{\partial \Phi(r, R, \theta, t)}{\partial t} = \hat{H} \Phi(r, R, \theta, t), \quad (3)$$

would provide the exact time evolution of the system. In the TDSCF formalism proposed in this work the total wave function is factorized in the following way:

$$\Phi^{\text{TDSCF}}(r, R, \theta, t) = \psi(r, R, t) \phi(\theta, t) e^{i\gamma(t)}. \quad (4)$$

The factor $e^{i\gamma(t)}$ in Eq. (4) is a coordinate-independent phase factor^{48,49} of no importance for the purpose of this study. The above scheme of factorization of the TDSCF wave function ensures an accurate treatment of the coupling between the r and R modes, which is the one governing the predissociation dynamics.

Substitution of the TDSCF wave function of Eq. (4) in Eq. (3) leads to the new time-dependent Schrödinger equations which are satisfied by $\psi(r, R, t)$ and $\phi(\theta, t)$,

$$i \frac{\partial \psi(r, R, t)}{\partial t} = \hat{H}_1^{\text{eff}}(r, R, t) \psi(r, R, t), \quad (5)$$

$$i \frac{\partial \phi(\theta, t)}{\partial t} = \hat{H}_2^{\text{eff}}(\theta, t) \phi(\theta, t), \quad (6)$$

where

$$\begin{aligned} \hat{H}_1^{\text{eff}}(r, R, t) &= \langle \phi(\theta, t) | \hat{H}(r, R, \theta) | \phi(\theta, t) \rangle \\ &= -\frac{1}{2\mu_1} \frac{\partial^2}{\partial r^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial R^2} + \left(\frac{1}{2\mu_1 r^2} + \frac{1}{2\mu_2 R^2} \right) \\ &\quad \times \langle \phi(\theta, t) | \hat{j}^2 | \phi(\theta, t) \rangle \\ &\quad + V_{I_2}(r) + \langle \phi(\theta, t) | W(r, R, \theta) | \phi(\theta, t) \rangle \end{aligned} \quad (7)$$

and

$$\begin{aligned} \hat{H}_2^{\text{eff}}(\theta, t) &= \langle \psi(r, R, t) | \hat{H}(r, R, \theta) | \psi(r, R, t) \rangle \\ &= \left\langle \psi(r, R, t) \left| \frac{1}{2\mu_1 r^2} + \frac{1}{2\mu_2 R^2} \right| \psi(r, R, t) \right\rangle \hat{j}^2 \\ &\quad + \langle \psi(r, R, t) | W(r, R, \theta) | \psi(r, R, t) \rangle \end{aligned} \quad (8)$$

are time-dependent effective Hamiltonians. Equations (5)–(8) are the TDSCF equations, and by solving them self-consistently the time evolution of the $\psi(r, R, t)$ and $\phi(\theta, t)$ wave packets is obtained. The effective Hamiltonians allow

for energy exchange between the two wave functions, which makes possible a partial coupling between the explicitly separated modes along the time propagation.

In order to solve Eq. (5) we can take advantage of the fact that the I₂ vibration mode has a discrete spectrum, and remains bound during all the predissociation process. This suggests to expand the r dependence of $\psi(r, R, t)$ on a basis set $\{\chi_v(r, t)\}$, where

$$\chi_v(r, t) = \chi_v(r) e^{-iE_v t}$$

and $\chi_v(r)$ are the vibrational eigenfunctions of the isolated I₂ molecule in the B electronic state with associated energy levels E_v , satisfying the equation

$$\left[-\frac{1}{2\mu_1} \frac{\partial^2}{\partial r^2} + V_{I_2}(r) \right] \chi_v(r) = E_v \chi_v(r).$$

Thus, the wave packet $\psi(r, R, t)$ can be expressed as

$$\psi(r, R, t) = \sum_v C_v(R, t) \chi_v(r) e^{-iE_v t}, \quad (9)$$

where the R dependence is explicitly included in the time-dependent complex coefficients $C_v(R, t)$ of the expansion.

By introducing this expansion in Eq. (5), and after some algebra, a set of time-dependent coupled equations are obtained for the expansion coefficients $C_v(R, t)$,

$$\begin{aligned} i \frac{\partial C_v(R, t)}{\partial t} &= \left[-\frac{1}{2\mu_2} \frac{\partial^2}{\partial R^2} + \frac{A(t)}{2\mu_2 R^2} \right] C_v(R, t) \\ &\quad + \sum_{v'} [A(t) B_{vv'} + V_{vv'}(R, t)] \\ &\quad \times e^{-i(E_{v'} - E_v)t} C_{v'}(R, t), \end{aligned} \quad (10)$$

where

$$A(t) = \langle \phi(\theta, t) | \hat{j}^2 | \phi(\theta, t) \rangle, \quad (11)$$

$$B_{vv'} = \left\langle \chi_v(r) \left| \frac{1}{2\mu_1 r^2} \right| \chi_{v'}(r) \right\rangle, \quad (12)$$

$$V_{vv'}(R, t) = \langle \chi_v(r) \phi(\theta, t) | W(r, R, \theta) | \phi(\theta, t) \chi_{v'}(r) \rangle. \quad (13)$$

Following a similar procedure, by substituting the basis set expansion of $\psi(r, R, t)$ in Eq. (8), the time-dependent Schrödinger equation of $\phi(\theta, t)$ [Eq. (6)] takes the new form

$$i \frac{\partial \phi(\theta, t)}{\partial t} = [b(t) \hat{j}^2 + V(\theta, t)] \phi(\theta, t), \quad (14)$$

with

FIG. 1. Decay curves of the initial v -state population corresponding to the $v=23$ resonance of the I₂-Ne complex, vs time. The curves are calculated using different basis set expansions with three (solid line), four (dotted line), five (long-dashed line), and six (short-dashed line) I₂ vibrational eigenfunctions. See text for details.

$$b(t) = \sum_{vv'} \left\langle \chi_v(r) \left| \frac{1}{2\mu_1 r^2} \right| \chi_{v'}(r) \right\rangle \times \langle C_v(R, t) | C_{v'}(R, t) \rangle e^{-i(E_{v'} - E_v)t} + \sum_v \left\langle C_v(R, t) \left| \frac{1}{2\mu_2 R^2} \right| C_v(R, t) \right\rangle, \quad (15)$$

$$V(\theta, t) = \sum_{vv'} \langle C_v(R, t) | V_{vv'}(R, \theta) | C_{v'}(R, t) \rangle \times e^{-i(E_{v'} - E_v)t}, \quad (16)$$

$$V_{vv'}(R, \theta) = \langle \chi_v(r) | W(r, R, \theta) | \chi_{v'}(r) \rangle.$$

Now Eqs. (10)–(16) are the new TDSCF equations. For a vdW system of the type BC-X (BC=diatomic, X=rare gas atom), only a few vibrational states are usually needed in the basis set expansion of the $\psi(r, R, t)$ wave packet.^{21,22,44(a)} Thus, the problem of solving a two-dimensional time-dependent Schrödinger equation, Eq. (5), reduces to solve a few one-dimensional time-dependent coupled equations. Therefore the basis set representation of the r coordinate means, in practice, a substantial reduction of the computational effort required to propagate $\psi(r, R, t)$, as compared to the case of using a grid representation for this coordinate. In this sense we also note that all the quadratures involving the basis functions $\chi_v(r)$ need to be carried out only once in the calculations, and can be saved in memory storage.

C. Computational details

In order to determine the size of the basis set expansion of Eq. (9), convergence tests were performed including three ($\chi_v, \chi_{v-1}, \chi_{v-2}$), four ($\chi_{v+1}, \chi_v, \chi_{v-1}, \chi_{v-2}$), five ($\chi_{v+2}, \dots, \chi_{v-2}$), and six ($\chi_{v+2}, \dots, \chi_{v-3}$) I₂ vibrational eigenfunctions in the basis. The population decay $|\langle C_v(R, t) | C_v(R, t) \rangle_R|$ was calculated for the complex resonance corresponding to $v=23$ with the above basis sets, and

is shown in Fig. 1 vs time. A trend of convergence is found for the basis sets including 4, 5, and 6 basis functions, which give nearly indistinguishable decay curves for the 45 ps of time propagation. The three-state basis set also provides good results in the short-time region (the first few picoseconds), but tends to slow down the decay of the population at longer times, probably as a consequence of being less flexible. Since the results produced by the basis sets with 4, 5, and 6 vibrational functions seem to be similarly accurate, a four-state expansion of $\psi(r, R, t)$ will be used in the remaining calculations reported in this paper.

Now a few comments are due on the small oscillations displayed by the population decay curves of Fig. 1, independently on the basis set employed. For an isolated resonance one would expect a monotonically decaying population, with no oscillations. Such undulations were also found in calculations of resonance decay in the HCO radical⁵⁰ and in the Cl₂-Ne complex,^{44(a)} where the same type of expansion in diatomic vibrational eigenfunctions was used. The oscillating behavior of the population is due to the fact that the initial state does not correspond to a pure resonance, but to a mixing of resonances,⁵⁰ as a consequence of the diabatic separation of the r coordinate. The small intensity of the oscillations and the exponentiality of the decay indicates, however, that a single resonance (the one of interest) dominates in the initial state.

The set of time-dependent coupled equations [Eq. (10)] was solved numerically by using the Fourier method.^{15(b),17,19} Following this method, the $C_v(R, t)$ coefficients are represented on a grid on which the Hamiltonian operations are calculated locally. A grid representation of the R coordinate is more convenient than a basis set expansion since this mode is a dissociative one. A grid of 1980 equally-spaced points was used for this coordinate, with $5.7 \text{ a.u.} \leq R \leq 377.8 \text{ a.u.}$ Such a large grid ensures no reflection of the wave packet for the 45 ps of temporal propagation carried out in all the calculations. The $C_v(R, t)$ coefficients were propagated using the Chebychev polynomial expansion method,^{16,17} combined with fast Fourier transform (FFT) techniques to evaluate the action of the kinetic-energy operator on the coefficients. In order to solve Eq. (14), the propagation of the $\phi(\theta, t)$ wave packet was also carried out with the Chebychev scheme. In this case the action of the Hamiltonian operator was evaluated using the discrete variable representation (DVR) theory.¹⁸ In the DVR formulation a finite basis representation (FBR) is chosen such that the kinetic-energy terms are diagonal. Then a grid or DVR is defined from the quadrature points associated with the FBR which leads to a diagonal representation of the potential-energy function. For the present problem, a Legendre polynomial FBR was used, and a grid of 90 points corresponding to a Gauss-Legendre quadrature was employed for θ in the range $0 \leq \theta \leq 180^\circ$. The unitary Legendre transform relates the two representations,^{51,52} which allow to calculate locally the Hamiltonian operations on $\phi(\theta, t)$. Two different time steps $\Delta t_1 = 0.1 \text{ ps}$ and $\Delta t_2 = 0.05 \text{ ps}$ were used to solve Eqs. (10) and (14), respectively. At every time step Δt_2 the effective Hamiltonians $\hat{H}_1^{\text{eff}}$ and $\hat{H}_2^{\text{eff}}$ were recalculated according to

FIG. 2. Time evolution of the population in the v , $v-1$, $v-2$, and $v+1$ vibrational states of iodine for the $v=19$ resonance decay. The population of the $v+1$ state is not appreciated at the scale of the figure. Also an exponential fit [Eq. (17)] to the decay curve of the v -state population is shown. See text for details.

Eqs. (11)–(13), (15), and (16). All the integrals over the $\chi_v(r)$ functions were calculated with a Simpson quadrature using 1000 points in the range $4.7 \text{ a.u.} \leq r \leq 7.7 \text{ a.u.}$ Conservation of total energy and norm was better than 0.0006%. Each wave packet propagation up to 45 ps took 162 cpu min on an IBM RISC 6000/350 workstation.

III. RESULTS AND DISCUSSION

A. Three-dimensional TDSCF calculations

The vibrational predissociation dynamics of the I₂-Ne complex has been studied for five resonances corresponding to the $v=19$ – 23 vibrational excitations of the I₂ diatomic molecule. For each resonance, the time evolution of the population $|\langle C_i(R,t) | C_i(R,t) \rangle_R|$ ($i=v+1, v, v-1, v-2$) associated with the I₂ vibrational states of the basis set has been calculated. They are shown in Figs. 2, 3, and 4 for three of the resonances studied, those corresponding to the vibrational excitations $v=19$, $v=21$, and $v=23$, respectively. The evolution of the vibrational populations is qualitatively simi-

FIG. 3. Same as Fig. 2 but for the $v=21$ resonance decay.

FIG. 4. Same as Fig. 2 but for the $v=23$ resonance decay.

lar for all the resonances. Initially only the vibrational state v is populated. This population decays with time and is transferred to the other vibrational states, reflecting the energy transfer from the I₂ vibration to the vdW modes, which causes the predissociation of the complex. As seen in the figures, the dominant predissociation channel is that in which the iodine loses one quantum of vibrational energy, $\Delta v=1$. Decay to the $v-2$ state (the $\Delta v=2$ channel) is far less probable (by about a factor of 15) than that to the $v-1$ state, although still significant. The population of the $v+1$ vibrational state remains very small, of the order of 10^{-3} , along all the propagation, and cannot be appreciated at the scale of the figures. The above picture is consistent with previous time-dependent results for related triatomic vdW complexes.^{21(a),44(a)}

For a unimolecular decomposition process like this, the decay of the initial resonance state is expected to show an exponential behavior.⁵³ This is reflected in the time evolution of the v -state populations of Figs. 2–4, which can be fitted to the following law,

$$P_v(t) = e^{-\Gamma t}, \quad (17)$$

where Γ is the vibrational predissociation half-width, and is related to the lifetime through

$$\tau = \frac{1}{\Gamma}. \quad (18)$$

The fitting curves $P_v(t)$ are displayed in Figs. 2–4, and the excellent agreement with the TDSCF populations confirms that they decay exponentially. Associated VP lifetimes were calculated from Eqs. (17) and (18) for all the resonances studied, and they are presented in Table I (third column), along with the experimental ones^{5(a)} (second column). For the sake of comparison, both the experimental and the calculated lifetimes are also plotted in Fig. 5 vs the initially prepared vibrational excitation of I₂. As seen from both Table I and Fig. 5, very good, quantitative agreement is found between the experimental and the TDSCF lifetimes, most of which are within the experimental error range. These results strongly support the validity of the present TDSCF

TABLE I. Experimental and calculated 3D TDSCF and 2D lifetimes for several resonance states of the I₂–Ne complex. Experimental error bars are also given. See text for details.

v	$\tau^{\text{exp}}(\text{ps})$	$\tau^{\text{TDSCF}}(\text{ps})$	$\tau^{\text{2D}}(\text{ps})$
19	87±4	100.0	96.5
20	78±4	84.5	81.0
21	69±6	71.5	68.5
22	58±3	60.5	58.0
23	53±3	51.5	49.0

formulation, despite the long-time propagation involved in the calculations. Two main factors contribute essentially to the good performance of the method. First, the coupling between the r and R modes is treated exactly. This coupling governs the energy transfer from the I₂ vibration to the reactive vdW stretching mode, and therefore the predissociation process. A TDSCF description assuming an explicit separation of these two modes is expected to produce significantly poorer results for such a long-time calculation. In fact, the I₂–Ne vibrational predissociation was studied applying a hybrid quantum/classical TDSCF scheme where the r mode was treated quantum mechanically (using a basis set expansion, like in this work), and the vdW modes were described classically.⁵⁴ In this calculation only the I₂ vibration was explicitly separated, while the vdW degrees of freedom remained coupled during the propagation. The results predicted a much slower and less exponential decay of the initial resonance population than in the present calculations. The TDSCF separation of relatively strong vdW couplings (like the r – R one) may be not accurate enough in order to describe quantitatively processes involving long-time dynamics (of several picoseconds). The second factor is related to the influence of the bending mode on the predissociation dynamics of the I₂–Ne cluster. The agreement between the experiment and the TDSCF results, despite the explicit factorization of the θ coordinate, seems to indicate that this mode has a little

effect on the dynamics, rather behaving as a “spectator” mode. This point will be analyzed in more detail in next paragraph.

B. Two-dimensional calculations

In order to estimate the effect of the bending mode on the vibrational predissociation of I₂–Ne, two-dimensional dynamical calculations were carried out including only the stretching vibrations associated with the r and R coordinates. These calculations were similar to the 3D ones discussed above. They consisted of solving Eqs. (10)–(13) using the same basis set expansion of Eq. (9) (with four vibrational basis functions) for $\psi(r, R, t)$. The only difference is that the initial wave packet $\phi_{\text{in}}(\theta, t=0)$ is not propagated along time, as previously done through Eqs. (14)–(16). The initial distribution in θ , $\phi_{\text{in}}(\theta, t=0)$ is used to carry out the averages over the bending coordinate in Eq. (7), or equivalently, in Eqs. (11)–(13), which define the Hamiltonian of the set of coupled equations, Eq. (10). Note that this Hamiltonian is time-independent now since $\phi_{\text{in}}(\theta)$ does not change with time. We stress that these calculations can be viewed as exact 2D calculations provided that the basis set expansion is converged, as shown in Fig. 1. By averaging over $\phi_{\text{in}}(\theta, t=0)$ in Eqs. (11)–(13) the zero-point energy of the bending mode is introduced in the calculation. This ensures that the 2D calculations are carried out at the same resonance energies as the 3D TDSCF ones.

Two-dimensional simulations were performed for the resonances associated with the $v=19$ –23 vibrational states of I₂. In each case the wave packet was propagated up to 45 ps, same as for the 3D calculations, using the Chebychev expansion method. Resonance lifetimes were calculated with Eqs. (17) and (18), and they are shown in Table I (fourth column) and Fig. 5. The agreement between the experimental and the 2D results is apparently better in general (except for $v=23$) than that between the experiment and the 3D TDSCF calculations. This is rather an accidental result, due to the following reason. The 2D lifetimes are expected to be lower than the 3D ones, because in the 2D calculations the I₂ energy can only be transferred to the dissociating vdW stretching, which makes the dissociation process more efficient. In the three-dimensional case part of the I₂ vibrational energy goes to the nonreactive, bath mode θ , delaying the dissociation of the complex. Since most of the TDSCF lifetimes are somewhat larger than the experimental ones, the lower (but very similar to the TDSCF results) 2D values turn out to be closer to experiment. The case of $v=23$, where the TDSCF lifetime is below the experimental value, and closer to it than the 2D result, supports the above argument.

The interesting result arising from the 2D calculations is that the difference between the 3D TDSCF and the 2D lifetimes is both small and essentially constant (about 3 ps in average) for the five resonances studied. The interpretation of this result is that the bending mode has a very weak effect on the dissociation dynamics of the I₂–Ne cluster. This is so to the extent that including or not the bending degree of freedom in the dynamical calculation does not change sig-

FIG. 5. Plot of the experimental (with error bars) and calculated resonance lifetimes presented in Table I vs the initial I₂ vibrational level.

FIG. 6. Snapshots of the TDSCF wave packet probability density in the R mode for four different times.

nificantly the value of the calculated lifetime. This fact greatly contributes to the accuracy of the TDSCF method proposed for the long dissociation process studied here. The physical picture emerging from the above results is that the vibrational predissociation of I₂-Ne is primarily governed by direct energy transfer from the iodine vibration to the vdW stretch. The bending mode plays a discrete spectator role as an acceptor of a small portion of the vibrational energy initially stored in the chemical bond.

C. TDSCF wave packet evolution

Analysis of the TDSCF wave packet time evolution is very enlightening in order to visualize the dynamical course of the I₂-Ne predissociation. In the following we shall analyze separately the evolution of the three modes involved in the calculation. Since the decay dynamics is very similar for all the resonances studied, we chose that corresponding to $v=23$ to carry out the analysis. The temporal behavior of the iodine vibration is reflected by the evolution of the square modulus of the expansion coefficients appearing in Eq. (9), which is displayed in Fig. 4 for the $v=23$ resonance. Such evolution was already discussed in the beginning of this section.

Four snapshots of the evolving probability density in the R coordinate along the predissociation process are presented in Fig. 6. In this figure the quantity $P(R,t)=|C_i(R,t)|^2$ is shown for the dissociation channel $i=v-1=22$, which is the dominant one. At $t=0$ the wave packet component corresponding to the $v-1$ exit channel has zero amplitude. As time passes amplitude is developed as a consequence of predissociation. In the four instants displayed in Fig. 6, the $v-1$ wave packet component presents a structure of peaks which spreads out towards larger distances as dissociation proceeds. Among the different peaks, the first one always appears at the same R distance (~ 7 a.u.), nearly coinciding with the

FIG. 7. Probability density of the TDSCF wave packet versus the angular coordinate for several time instants.

position of the classical inner turning point of the vdW stretch vibration. Such a peak seems to be the source from which the remaining peaks of the structure split away. The following picture of the predissociation dynamics is consistent with the results of Fig. 6. When the initial resonance wave function visits the interaction region of the v and $v-1$ vibrational states, the vdW coupling acts transferring an amount of wave packet amplitude (the first peak in the snapshots of Fig. 6) to the $v-1$ channel. This amplitude then spreads out and moves away towards the dissociation limit. Successive pumps of amplitude along the process gradually build up the dissociating wave shown in the figure. The same behavior takes place in the dissociation through the $v-2$ exit channel (not shown here), although with much smaller intensity. The regularity of the structure of peaks of Fig. 6, along with the fact that the number of peaks increases roughly proportionally with time, indicates that predissociation is governed by the interaction between the periodic iodine and vdW stretch vibrations. A similar type of dynamics has been found in calculations on the predissociation of the related Cl₂-Ne complex.^{44(a)}

The dynamical evolution of the bending mode is shown in Fig. 7, where the probability density

$$P(\theta,t)=|\phi(\theta,t)|^2 \sin \theta,$$

is plotted for several time instants. The $\phi(\theta,t)$ wave packet dynamics consists essentially of a periodic “breathing” motion, along which both the initial shape and width of the packet do not significantly change. Such restricted motion of $\phi(\theta,t)$ is associated with exchange of small amounts of energy between the bending mode and the other degrees of freedom during the dissociation process. The time evolution of $\phi(\theta,t)$ thus reflects a bath mode dynamics of the bending coordinate, which does not affect much the fragmentation of the complex.

FIG. 8. Iodine rotational distributions versus the rotational state j for the resonances corresponding to the $v=19$, $v=21$, and $v=23$ initial vibrational excitations of I_2 .

D. Rotational distributions

Among the observables of interest from which one can extract dynamical information on the I_2 -Ne predissociation are the vibrational and rotational distributions of the I_2 fragment. Vibrational distributions of the diatomic product can be inferred from Figs. 2–4, which show that the $v-1$ channel is clearly the dominant exit channel, as already discussed. Iodine rotational distributions are displayed in Fig. 8 vs the rotational quantum number j for the resonances associated with the $v=19$, $v=21$, and $v=23$ initial states. Only even j states are populated, as corresponds to a homonuclear diatomic molecule. Although the dissociation process is not completely over at 45 ps, the fact that the $\phi(\theta, t)$ wave function does change little during the dissociation process justifies to calculate a I_2 rotational distribution at this stage. In fact, this was checked by following the time evolution of the $I_2(v=23)$ rotational distribution, not finding significant changes along time. We therefore believe that the distributions of Fig. 8 are converged to practical effects. The three rotational distributions are very similar, peaking at very low j states (either $j=0$ or $j=2$, but with nearly the same intensity in both states). The intensity of the distributions decreases rapidly with j , and only the few first states are appreciably populated. The calculated distributions of Fig. 8, quite similar to the j -distributions of the initial $\phi(\theta)$ wave packet, indicate that very little bending excitation occurs during the predissociation of the I_2 -Ne cluster. This result is consistent with the behavior of the $\phi(\theta, t)$ wave function discussed above, and once again is the reflection of the limited role of the bending mode in the dissociation dynamics.

IV. CONCLUSIONS

A quantum single-configuration TDSCF approach in three dimensions is proposed to study the vibrational predissociation of the $I_2(B)$ -Ne cluster.

Jacobian coordinates are used in the method, assuming zero-total angular momentum. Factorization of the total wave function is introduced by the TDSCF scheme by explicitly separating the angular degree of freedom, while the coupling between the two stretch modes is treated exactly. Still a partial coupling between the factorized modes is allowed in the method through mean-field potentials appearing in the equations of motion. The decay dynamics of the resonance wave functions corresponding to the $v=19$ – 23 initial vibrational states of I_2 is propagated up to 45 ps. An exponential decay of the resonance population is predicted by the simulations. Calculated resonance lifetimes are found to agree quantitatively with experimental ones. Analysis of the TDSCF wave packet dynamics indicates that predissociation occurs essentially through direct energy transfer from the iodine vibration to the vdW stretch mode. The θ degree of freedom has little effect on the cluster fragmentation, behaving as a bath mode to which only small portions of the I_2 vibrational energy are transferred. This is confirmed by the low bending excitation found in the calculated iodine rotational distributions. Resonance lifetimes calculated with a two-dimensional model not including the angular coordinate turn out to be very similar to the 3D TDSCF ones, which also corroborates the spectator role played by the bending mode in the I_2 -Ne dissociation.

The results presented here show that the suggested TDSCF approach describes the $I_2(B)$ -Ne vibrational predissociation at a quantitative level of accuracy, as compared with experiment, even when a long-time propagation is involved in the calculations. Two main factors contribute to the good performance of the method. On the one hand, the $r-R$ coupling, which governs the predissociation dynamics, is treated exactly. On the other hand, the mode explicitly separated has a minor effect on the fragmentation of the vdW complex. As a consequence, the decoupling approximation applied to that mode causes only a little distortion on the TDSCF results. The implication is that a single-configuration TDSCF description of a long-time process may become quantitative provided that (a) the most relevant couplings of the system are treated accurately; (b) separation schemes are applied only to the physically less coupled modes. Application of the present method to triatomic vdW systems with a bending mode more active dynamically, as well as to larger clusters should be very interesting in order to check further its validity.

ACKNOWLEDGMENTS

This work was supported by DGICYT, Spain, under Grant No. PB92-0053, and by Comunidad Autónoma de Madrid, under Grant No. 064/92.

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