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Citation: The Journal of Chemical Physics 104, 8405 (1996); doi: 10.1063/1.471590 View online: http://dx.doi.org/10.1063/1.471590 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/104/21?ver=pdfcov Published by the AIP Publishing

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Quasiclassical dynamics of the $I_2 - Ne_2$ vibrational predissociation: A comparison with experiment

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(Received 29 December 1995; accepted 27 February 1996)

The vibrational predissociation dynamics of the $I_2(B,v)$ -Ne₂ complex is investigated for several vibrational levels of I_2 , using a quasiclassical trajectory approach. The time evolution of the population of nascent I₂ fragments is calculated. A model is proposed which reproduces the results of the classical trajectories, and allows to obtain the lifetimes associated with the dissociation of the two van der Waals (vdW) bonds. The classical lifetimes are higher in general than the experimental ones of Zewail and co-workers [J. Chem. Phys. 97, 8048 (1992)]. The classical method appears to overestimate mechanisms of energy redistribution between the modes, which slow down the dissociation of the cluster. However, the behavior of the lifetimes with the initial iodine vibrational excitation is in very good agreement with experiment. A sequential path of fragmentation of the two weak bonds via direct predissociation is found to dominate, producing $I_2(B, v-2)+2Ne$ fragments. Although with smaller probability, alternative dissociation paths are observed involving statistical mechanisms of internal energy redistribution. In these paths, the energy initially transferred by the iodine heats the vdW modes without breaking the complex. Further energy transfer produces either simultaneous or sequential dissociation of the two weak bonds in a rather evaporative way, populating the v-2 and v-3 exit channels. © 1996 American Institute of Physics. [S0021-9606(96)01421-3]

I. INTRODUCTION

In the last decade the experimental time-resolved pumpprobe techniques have experienced an enormous advance in its application to the field of chemical reaction dynamics.^{1–11} This type of experiments make posible 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 about the dynamics involved and how the reaction proceeds. In addition, time-resolved data may complement other type of dynamical information like that obtained by frecuency domain spectroscopic experiments.

A large variety of chemical species has been studied by means of real-time techniques, ranging from small clusters of rare-gas atoms with chemical impurities⁵ to molecules embedded in condensed-matter environments like rare-gas solutions⁸ or matrices.¹¹ Among them, cluster systems composed of several rare-gas atoms weakly bound to a molecule acting as a cromophore, 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. It allows to investigate fundamental questions like 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 a one or more rare-gas atoms have been extensively investigated means by of frequency-domain experiments.¹²⁻¹⁵ The pioneering experiments of Levy and co-workers on I_2 -He_n $(n=1-3)^{16}$ and I_2 -Ne_n $(n=1-7)^{17}$ 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-Ne_n (n=1-3),¹⁸ ICl-Ne_n (n=1-5),¹⁹ Cl₂-Ne_n (n=1-3),²⁰ Cl₂-He_n (n=1-2),²¹ was also investigated. The characterization of rare-gas-halogen potentials has been also the subject of several experiments.²²⁻²⁴

The great deal of experimental work above mentioned 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 timeindependent 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 approximations.²⁹⁻³² The appearance of time-domain experimental data, along with the development of techniques to solve efficiently the time-dependent Schödinger equation³³⁻³⁶ gave a great impulse to the use of timedependent 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.

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In a series of papers⁵ Zewail and co-workers have reported real-time experiments on the vibrational predissociation (VP) of the I_2 -Ne_n (n=1-4) clusters. Using picosecond pump-probe (LIF) and molecular beam techniques,48 they measured the state-to-state rates of VP for specific vibrational levels of the diatomic by monitoring the rise of nascent I₂ along time. These experiments explored the transition from the "small molecule" case (the triatomic complex) to the "large molecule" regime (clusters with several raregas atoms).

In the small I_2 –Ne cluster the predissociation dynamics is basically dominated by the coupling between the vibrationally excited I₂ stretching mode and the reactive, dissociating vdW stretching mode.⁴⁶ In the case of I_2 -Ne_n clusters with n > 1, the diatomic cromophore is coupled to dissociating modes and also to a number of nondissociating "bath modes' which increases with n, and may play an important role in the dynamics. In fact, the mechanism of cluster dissociation can be affected by these bath modes, potential acceptors of the I_2 vibrational energy.

Roughly speaking one can think of two limiting types of fragmentation mechanisms. One of such types is the socalled "sequential mechanism," through which the vdW bonds break directly one at a time via VP. This mechanism could imply a direct flux of the I₂ vibrational energy to the reactive modes, and a rather weak effect of the bath modes in the fragmentation process, similarly to the case of the triatomic complex. The other limiting situation is a mechanism of statistical nature. The I₂ moiety can loose energy which redistributes to both the reactive and nonreactive modes, "heating" the cluster and being inefficient to produce direct fragmentation. Then dissociation of the rare-gas atoms can occur by VP, evaporation, or both. Strong couplings of the I₂ cromophore to the nonreactive vdW modes would be the origin of a statistical mechanism of dissociation. Competition between the sequential and the statistical mechanism is also possible. In this light, it is interesting to investigate how and to what extent the cluster size (and therefore the number of bath modes) can affect the mechanism of fragmentation.

The aim of this work is to investigate the VP dynamics of the I₂-Ne₂ cluster and the mechanism through which it occurs. The time-resolved data of Zewail and co-workers pose a strong motivation for a theoretical study of this complex. To this purpose, a quasiclassical molecular dynamics (MD) treatment has been applied which uses the initial state calculated quantum mechanically to select the initial conditions, and then runs classical trajectories to analyze the dynamics. A quantum dynamical treatment of a four-atom system including the full dimensionality, even for zero total angular momentum becomes extremely costly. Classical MD simulations make the problems tractable, and provide at the very least a qualitative insight on the dynamics.

Quasiclassical studies of clusters like I_2 -He_n and I_2 -Ne_n (n=1-9) were carried out earlier by the authors, ^{49,50} assuming a restricted configuration where some of the bending modes were frozen at their equilibrium positions. In these works energy redistribution (IVR) was found to play a significant role with increasing cluster size. In a recent study⁵¹ a

TABLE I. Morse potential parameters used in this work.

	$D (\mathrm{cm}^{-1})$	α (Å ⁻¹)	$R_{\rm eq}$ (Å)
I–Ne	40.75	1.56	4.36
Ne-Ne	29.36	2.088	3.091

new potential energy surface was developed by fitting it to the experimental data of Ref. 5(a), and was applied to investigate the VP of the $I_2(B,v)$ -Ne complex. The present work is the continuation of that of Ref. 51 using the new potential surface for I₂-Ne₂, and including all the modes corresponding to zero total angular momentum.

The organization of the paper is the following. In Sec. II we briefly describe the potential surface and the quasiclassical methodology applied. In Sec. III the results are presented and discussed. Finally, in Sec. IV some conclusions are drawn.

II. QUASICLASSICAL METHODOLOGY

The VP process in the I2-Ne2 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 I₂ cromophore. The metastable state $I_2^*(B,v)$ -Ne₂ prepared in this way decays to a dissociation continuum giving the products $I_2(B, v' = v - m) + 2Ne$, where $m \ge 2$. Thus to a good approximation, this process can be modeled as taking place on a single potential-energy surface, that of the B state. This assumption is made in our calculations.

A. Potential-energy surface

The *B* state potential surface for the I_2 -Ne₂ cluster was represented as an addition of atom-atom interactions

$$V = V_{I_2} + V_{I_2 - Ne_1} + V_{I_2 - Ne_2} + V_{Ne_1 - Ne_2}$$

For the V_{I_2} interaction potential the analytical form reported in Ref. 52 was used.⁵³ This potential was inverted from ultrafast laser experiments by analyzing the coherences of the wave packet in the temporal transients of the I_2 molecule. Regarding the $V_{I_2-Ne_i}$ potentials, they were expressed as a sum of two I-Ne; interactions,

$$V_{I_2-Ne_i} = V_{I-Ne_i} + V_{I+Ne_i},$$

where each V_{I-Ne_i} interaction is described by a Morse function. The corresponding Morse parameters were fitted with a quantum-mechanical method in order to reproduce the experimental lifetimes of the I₂-Ne complex reported in Ref. 5(a). The fitting of this potential has been described elsewhere⁵¹ and will not be discussed here. Finally, a Morse function was also used for the Ne-Ne interaction whose parameters were obtained by fitting the more complicate analytical form of Aziz and Slaman.⁵⁴ All the Morse potential parameters are listed in Table I.

B. Classical Hamiltonian and method

In the classical treatment of I_2 -Ne₂ applied in this work bond coordinates ($\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2$) have been used, where \mathbf{r} is the vector associated with the I–I bond, and $\mathbf{R}_1, \mathbf{R}_2$ are the vectors between the I_2 center of mass and the two Ne atoms, respectively. In these coordinates the classical Hamiltonian can be expressed as

$$H = \frac{\mathbf{P}_{\mathbf{r}}^{2}}{2\mu_{I_{2}}} + \frac{\mathbf{P}_{\mathbf{1}}^{2}}{2\mu_{I_{2}-Ne}} + \frac{\mathbf{P}_{\mathbf{2}}^{2}}{2\mu_{I_{2}-Ne}} + \frac{\mathbf{P}_{\mathbf{1}} \cdot \mathbf{P}_{\mathbf{2}}}{2m_{I}} + V(\mathbf{r}, \mathbf{R}_{\mathbf{1}}, \mathbf{R}_{\mathbf{2}}),$$
(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 $\mu_{I_2} = m_{I}/2$, $\mu_{I_2-Ne} = 2m_{I}m_{Ne}/(2m_I + m_{Ne})$ 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

$$H^{(J=0)} = \frac{1}{2\mu_{I_2}} \left[P_r^2 + \frac{\mathbf{j}^2}{r^2} \right] + \frac{1}{2\mu_{I_2-Ne}} \left[P_{R_1}^2 + \frac{\mathbf{l}_1^2}{R_1^2} \right] + \frac{1}{2\mu_{I_2-Ne}} \left[P_{R_2}^2 + \frac{\mathbf{l}_2^2}{R_2^2} \right] + \frac{\mathbf{P}_1 \cdot \mathbf{P}_2}{2m_1} + V_{I_2}(r)$$

+
$$V_{I_2-Ne}(r, R_1, \theta_1) + V_{I_2-Ne}(r, R_2, \theta_2)$$

+ $V_{Ne-Ne}(R_1, R_2, \cos \gamma),$ (2)

being

$$\mathbf{l}_{1}^{0} = P_{\theta_{1}}^{2} + \frac{P_{\phi}^{2}}{\sin^{2}\theta_{1}},\tag{3}$$

$$\mathbf{l}_{2}^{2} = P_{\theta_{2}}^{2} + \frac{P_{\phi}^{2}}{\sin^{2}\theta_{2}},\tag{4}$$

$$\mathbf{j}^{2} = \mathbf{I}_{1}^{2} + \mathbf{I}_{2}^{2} + \mathbf{I}_{1} \cdot \mathbf{I}_{2} = P_{\theta_{1}}^{2} + P_{\theta_{2}}^{2} + 2P_{\theta_{1}}P_{\theta_{2}} \cos \phi - 2$$

$$\times \sin \phi \left(\frac{\cos \theta_{2}}{\sin \theta_{2}} P_{\theta_{1}} + \frac{\cos \theta_{1}}{\sin \theta_{1}} P_{\theta_{2}} \right) P_{\phi} + \left(\frac{1}{\sin^{2} \theta_{1}} + \frac{1}{\sin^{2} \theta_{2}} - 2\cos \phi \frac{\cos \theta_{1} \cos \theta_{2}}{\sin \theta_{1} \sin \theta_{2}} - 2 \right) P_{\phi}^{2}, \quad (5)$$

 $\phi = \phi_1 - \phi_2,$

 $\cos \gamma = \sin \theta_1 \sin \theta_2 \cos \phi + \cos \theta_1 \cos \theta_2$,

$$\begin{split} \mathbf{P_1} \cdot \mathbf{P_2} &= P_{R_1} P_{R_2} \cos \gamma - \frac{\cos \phi}{R_1 R_2 \sin \theta_1 \sin \theta_2} P_{\phi}^2 + \frac{\cos \theta_1 \cos \theta_2 \cos \phi + \sin \theta_1 \sin \theta_2}{R_1 R_2} P_{\theta_1} P_{\theta_2} \\ &+ \frac{\sin \theta_1 \cos \theta_2 \cos \phi - \cos \theta_1 \sin \theta_2}{R_2} P_{R_1} P_{\theta_2} + \frac{\cos \theta_1 \sin \theta_2 \cos \phi - \sin \theta_1 \cos \theta_2}{R_1} P_{R_2} P_{R_1} P_{\theta_2} \\ &- \frac{\sin \theta_1 \sin \phi}{R_2 \sin \theta_2} P_{R_1} P_{\phi} - \frac{\sin \theta_2 \sin \phi}{R_1 \sin \theta_1} P_{R_2} P_{\phi} - \frac{\cos \theta_1 \sin \phi}{R_1 R_2 \sin \theta_2} P_{\theta_1} P_{\phi} - \frac{\cos \theta_2 \sin \phi}{R_1 R_2 \sin \theta_1} P_{\theta_2} P_{\phi}. \end{split}$$

From the Hamiltonian of Eq. (2) the corresponding Hamilton equations are derived and integrated using a GEAR algorithm with a variable time step. Trajectories are run up to a maximum time of 600 ps. A vdW bond is considered dissociated when the corresponding distance R_i reaches 12 Å. Energy conservation of the trajectories is of the order of 10^{-8} cm⁻¹.

C. Initial conditions

Prior to study the dynamics it is necessary to characterize the initial resonance state of the cluster, e.g., to generate a set of initial conditions from which the classical trajectories will start. In the quasiclassical treatment employed here each resonance state studied has been calculated variationally including the full dimensionality (six degrees of freedom) of the I_2 -Ne₂ complex⁵⁵ for **J**=0. A diabatic separation of the I_2 vibration was assumed, but the full coupling between all the vdW modes was taken into account in the variational calculation. This diabatic separation is justified because of the frequency mismatch between the diatomic and the vdW vibrations. From the resonance wave function calculated this way, the quantum-mechanical probability distributions for all the modes are obtained and used to weight the initial positions selected by random sampling.^{55(b)}

Once the initial positions have been selected, the initial momenta can be calculated. The approximation of considering an isolated I_2 molecule is again assumed to calculate P_r , which is expressed as

$$P_r = \pm \sqrt{2\mu_{\rm I_2}[E_v - V_{\rm I_2}(r)]},$$

where E_v is the energy of the diatomic vibrational level v, and the value of r has been previously generated with the corresponding quantum probability distribution. The initial angular momenta P_{θ_1} , P_{θ_2} , and P_{ϕ} were obtained by solving the system of Eqs. (3)–(5). Sets of l_1 , l_2 , and j values were randomly selected following the distributions of the quantum

J. Chem. Phys., Vol. 104, No. 21, 1 June 1996 This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms of the initial resonance state, and introduced in the above system of equations. Only the values which fulfill the restriction $|l_1-l_2| < j < l_1+l_2$ were accepted in order to ensure a total angular momentum **J**=0 for the initial conditions. Finally, the P_{R_1} and P_{R_2} initial values were calculated with the expression

$$P_{R_i} = \pm \sqrt{2\mu_{I_2-Ne}[E_0^{(v)} - V_{I_2-Ne}(r, R_i, \theta_i)]},$$

where $E_0^{(v)}$ is the vdW ground state energy of the triatomic I₂-Ne system in a I₂ vibrational level v.

In the calculation of the initial momenta described above energy contribution of the $V_{\text{Ne-Ne}}$ potential term has not been considered. This causes the I₂-Ne₂ resonance energy associated with the initial conditions generated above to be slightly different from that calculated quantum mechanically. Unfortunately it is not possible to separate the energy contribution of $V_{\text{Ne-Ne}}$ in order to distribute it among the vdW modes. To include this energy contribution in the initial conditions we adopted here the approximation of randomly sharing it between the vdW stretching momenta, P_{R_1} and P_{R_2} . In this way, the energy of the initial conditions now matches the quantum resonance energy. The directions (the \pm sign) of the momenta were also selected at random.

III. RESULTS AND DISCUSSION

A. Vibrational predissociation lifetimes

The vibrational predissociation dynamics of the $I_2(B,v)$ -Ne₂ cluster has been studied for several vibrational levels of I₂ in the range v = 17-23. A set of 1000 trajectories was integrated for each vibrational excitation. From the trajectories corresponding to each vibrational level v one can obtain the quantity $N_{\rm ND}(t)/N_I$, where $N_{\rm ND}(t)$ is the number of nondissociated trajectories at time t, and N_T is the total number of trajectories. By dissociated trajectories we mean those trajectories in which total dissociation of the two vdW bonds occurs, leading to I₂ as one of the products. Trajectories where only one weak bond has broken are considered nondissociated ones. Thus the magnitude $P(t) = 1 - N_{\rm ND}(t)/N_T$ represents the probability of nascent I₂ formation with time, and it is displayed in Figs. 1-3 for the v = 17, v = 20, and v = 23 initial vibrational levels of iodine, respectively. The most prominent feature of the calculated population curves of nascent I_2 is that they take a period of several picoseconds to begin to rise from zero. The longer is the lifetime associated with an initial vibrational level, the longer is the time delay in the rise of the corresponding population curve. After that time a nearly exponential rise is found for all the curves.

A similar result was obtained in quasiclassical calculations of the $I_2(B,v)$ -Ne vibrational predissociation.⁵¹ In that work, the origin of the slow down in the I_2 -Ne fragmentation was attributed to energy exchange mechanisms between the I_2 and the vdW modes. Through these mechanisms, the energy would flow between the chemical and the weak bonds in the two directions, in a continuous (not quantized) fashion along the process. Classically, the I_2 subunit may loose only



FIG. 1. Probability of nascent I_2 formation versus time for the v = 17 initial vibrational excitation of I_2 . The circles represent the calculated trajectories, and the solid line corresponds to a fit to Eq. (11) using the model described in the text.

a fraction of a quantum of vibrational energy, which is not enough to break the vdW bond. This leaves the complex temporarily in a state where the vdW modes are partially excited and the iodine partially de-excited. Such a state is probably more inefficient to produce dissociation than the initial resonance one, and eventually the energy returns to I_2 before it has time to loose the additional energy needed to dissociate the vdW bond. The result is an increase in the lifetime of the complex. In addition, zero-point energy effects were found to play in the same direction in Ref. 51. The vdW modes may eventually fall below their zero-point level, transferring energy to the diatomic molecule, which is thus slightly excited over its initial level v. Again the complex in this state is likely to have a longer lifetime.

The effects discussed above are mainly originated in the limitations inherent to the classical methodology applied, and cause an overestimation of the energy exchange mechanisms between the different modes. As a consequence, the



FIG. 2. Same as Fig. 1 but for the v=20 initial vibrational excitation of iodine.



FIG. 3. Same as Fig. 1 but for the v = 23 initial vibrational excitation of iodine.

fragmentation process is artificially delayed. Such a behavior, manifested in the triatomic cluster, is found to be more pronounced in the I_2 -Ne₂ predissociation dynamics predicted classically. This is not surprising since, similarly to the physical (nonartificial) energy exchange mechanisms, the effect of the artificial ones is expected to increase with increasing number of modes and couplings between them. The fact that the time delay displayed in Figs. 1–3 depends on the initial resonance state studied, and therefore on the specific couplings associated with that state, supports the above argument.

A detailed analysis of the trajectories calculated shows the following situation. Dissociation of one vdW bond occurs in most of the trajectories ($\geq 99\%$) within the time of integration, for all the iodine vibrational excitations studied. A delay in the formation of nascent I₂-Ne complexes is already detected at this stage. However, the number of trajectories leading to final I₂ products decreases appreciably, more significantly for the lower diatomic vibrational excitations, as shown in Figs. 1-3. This is explained because some of the trajectories take a long time until the first weak bond breaks, and then the maximum time of integration is reached before dissociation of the second vdW bond. In addition, following the discussion given above, the nascent I2-Ne intermediate complexes may be produced in energy states rather inefficient for further dissociation. The result is that the curves of Figs. 1-3 exhibit a time delay associated with a markedly nonexponential rise. As a consequence, these curves cannot be fitted neither to a single exponential rising function, nor to a sum of two exponentials, each of them describing the dissociation of one vdW bond.^{5(c)}

In order to reproduce the results of the calculated trajectories we have applied the following kinetic model:

$$\overset{\gamma}{\underset{k \to 0}{\longrightarrow}} \overset{\alpha}{\underset{k \to 0}{\longrightarrow}} \overset{\beta}{\underset{k \to 0}{\longrightarrow}} N_2,$$
 (6)

where N_4 is the population of the tetraatomic complex $I_2(B,v)$ -Ne₂ initially prepared, and N_3 and N_2 are the popu-

lations of the nascent $I_2(B, v' < v)$ -Ne and $I_2(B, v'' < v)$ species, respectively. By n_4 we denote an intermediate state of I_2 -Ne₂ where the iodine has transferred a fraction of a quantum of vibrational energy to the vdW modes. In Eq. (6) α , β , and γ are the rate constants associated with the three steps involved. The double arrow connecting N_4 and n_4 symbolizes the energy exchange mechanisms by which the energy can flow from the I_2 stretch vibration to the weak modes, and viceversa. To simplify the model we have assumed the same rate γ for the two directions of this energy flow.

In our model, the time evolution of the above populations is governed by the following first-order coupled equations:

$$\frac{dN_4}{dt} = -\gamma N_4 + \gamma n_4, \tag{7a}$$

$$\frac{dn_4}{dt} = \gamma N_4 - \gamma n_4 - \alpha n_4, \tag{7b}$$

$$\frac{dN_3}{dt} = \alpha n_4 - \beta N_3, \tag{7c}$$

$$\frac{dN_2}{dt} = \beta N_3, \tag{7d}$$

with the initial conditions $N_4(t=0)=1$, $n_4(t=0)=N_3(t=0)=N_2(t=0)=0$. Solution of Eqs.(7) is given by

$$N_4(t) = \frac{e^{-Qt}}{2q} \left[\left(q + \frac{\alpha}{2} \right) e^{qt} + \left(q - \frac{\alpha}{2} \right) e^{-qt} \right], \tag{8}$$

$$n_4(t) = \frac{\gamma}{2q} e^{-Qt} (e^{qt} - e^{-qt}), \tag{9}$$

$$N_{3}(t) = Ae^{-\beta t} + \frac{\alpha\gamma}{2q} \left[\frac{e^{-(Q-q)t}}{q-Q+\beta} + \frac{e^{-(Q+q)t}}{q+Q-\beta} \right],$$
(10)

and

$$N_2(t) = 1 - N_4(t) - n_4(t) - N_3(t), \qquad (11)$$

where

$$Q = \gamma + (\alpha/2),$$

$$q = \left(\gamma^2 + \frac{\alpha^2}{4}\right)^{1/2},$$

$$A = \frac{\alpha\gamma}{(\beta - Q)^2 - q^2}.$$

The function $N_2(t)$ of Eq. (11), which depends on the three rates α , β , and γ describes the time evolution of the nascent I₂ population. A least squares fit of the rising curves obtained from the calculated trajectories to $N_2(t)$ provides the rate constants for dissociation of the two vdW bonds. The fitting curves are shown along with the classical ones in Figs. 1–3 for v=17, v=20, and v=23, respectively. The fits are reasonably good in the whole range of time integration, thus indicating that the model suggested reproduces the main features of the classical results.

TABLE II. Calculated and experimental lifetimes associated with the first (τ_1) and the second (τ_2) vdW bond dissociation, for the different vibrational levels of I₂ studied. The experimental error is also included in the table.

υ	$ au_1^{\mathrm{cal}}~(\mathrm{ps})$	$ au_1^{\exp}$ (ps)	$ au_2^{ m cal}~(m ps)$	$ au_2^{\exp}$ (ps)
17	107.7	84±8	220.1	165 ± 12
18	83.8	65 ± 5	165.9	139±9
19	77.3	47 ± 4	109.5	97±4
20	62.7	41 ± 2	88.0	91±4
21	53.3	38 ± 5	75.1	86±5
22	40.6	23 ± 3	73.9	76±5
23	34.4	19±3	59.8	44±5

The dissociation lifetimes of each weak bond of the I_2 -Ne₂ complex are related to the inverse of the rates α and β ,

$$\tau_1 = \frac{1}{\alpha}, \tau_2 = \frac{1}{\beta},$$

where τ_1 corresponds to the first dissociated bond and τ_2 to the second one. Such lifetimes are presented in Table II along with the experimental ones. They are also plotted in Fig. 4 versus the I₂ vibrational level for the sake of comparison. A qualitative agreement is found between the experiment and the calculations. The calculated τ_1 values are clearly overestimated, while those of τ_2 are in general closer to the experimental data. A possible reason is that part of the time delay associated to the step $N_4 \rightleftharpoons^{\gamma} n_4$ in our model, is absorbed in the lifetime of the first bond dissociation, which therefore increases.

Despite the fact that the comparison between the present results and the experiment is only qualitative, we stress that the variation of the lifetimes with the iodine vibrational level is predicted in very good agreement with the experimental one. The same result was found in previous classical calculations on the I_2 -Ne cluster.⁵¹ It reflects that in this case



FIG. 4. Calculated (solid lines) and experimental (dashed lines) predissociation lifetimes associated with the first (circles) and second (squares) vdW bond breaking, versus the iodine vibrational level v. Error bars are displayed for the experimental data.

classical mechanics is able to predict at least the general features of the dynamics in agreement with experiment. A quantitative description of more specific magnitudes can be prevented, however, by the limitations of the classical methodology.

B. Dissociation mechanisms

As pointed out in Sec. I to this article, one of the most interesting issues about the predissociation of I₂-Ne₂ concerns the characterization of the mechanism through which fragmentation occurs. Two basic paths are possible in principle. In one of them the two weak bonds would break sequentially, via direct predissociation. The other path would involve internal energy redistribution (IVR) mechanisms of statistical nature between the modes, prior to the complex fragmentation. For the iodine vibrational excitations studied here, one vibrational quantum of energy is required to dissociate each vdW bond of I2-Ne2. It means that in the sequential mechanism the I₂ moiety should loose two vibrational quanta in order to dissociate the cluster. In the case of the statistical path of dissociation the diatomic molecule should transfer more than two quanta, since part of the energy is redistributed between the vdW modes, being inefficient to cause dissociation.

Our calculations show that the dominating exit channel is v-2 for all the vibrational levels studied, with a probability $\geq 90\%$. Actually, the fraction of trajectories leading to the channel v-3 ranges from 0.2% for v=17 up to $\sim 11\%$ for v=23. A quantization criterion of the classical I₂ vibrational energy has been applied to carry out the above estimation. Following this criterion, those trajectories in which the iodine looses more than n-1/2 vibrational quanta are assigned to the v-n exit channel. The increasing population of the v-3 channel with the vibrational excitation of I₂ is consistent with decreasing dissociation lifetimes as the initial level vincreases.

The above results indicate that the sequential path dominates in the predissociation of I_2 –Ne₂, although IVR mechanisms take place to some extent for high initial vibrational excitations. This is in agreement with the findings of recent quantum-mechanical calculations using a model of four degrees of freedom for the I_2 –Ne₂ cluster.^{40,47} In a sequential mechanism via direct predissociation, the probability of the first vdW bond breaking is expected to be about two times that of the second one, which implies that $\tau_1 \sim \tau_2/2$. Such a behavior is found in the experimental data.^{5(c)} In our results of Table II a similar trend also emerges, although in a less clear way. This is likely to be due to the classical overestimation of the τ_1 values as a consequence of the artificial energy exchange mechanisms.

In addition to the main dissociation path, the sequential one through direct predissociation, alternative fragmentation mechanisms are found in our calculations, which are related to IVR effects. One of them involves simultaneous breaking of the two weak bonds. Such a mechanism may lead either to I_2+2Ne or I_2+Ne_2 products. The iodine may transfer one quantum of vibrational energy which redistributes among the vdW modes, heating the complex without producing dissociation at all. Then, further transfer and redistribution of a second quantum, or even a third one produces the final dissociation of the complex into the above fragments. The probability of this dissociation path is rather small, ranging from 0.6% (v=17) to 1% (v=23) of Ne₂ products, and from 1% (v=17) to 2.3% (v=23) of simultaneous formation of I₂+Ne+Ne fragments. We note that a small probability (~1%) of finding Ne₂ diatomics has also been predicted by quantum calculations⁴⁰ in the same range of I₂ vibrational levels.

A fragmentation path which involves a combination of IVR effects and sequential dissociation is also observed in the calculations reported here. It accounts for most of the trajectories dissociating through the channel v-3. In this case the transfer of the first I₂ vibrational quantum excites the complex as in the simultaneous breaking mechanism, and then two additional quanta dissociate the vdW bonds sequentially.

The alternative fragmentation paths discussed above could be interpreted as evaporation phenomena, where the dissociation of the complex is due to statistical energy redistribution rather than to direct vibrational predissociation. The experimental observation of nascent $I_2(v'=v-3)$ species seems to point in this direction.

IV. CONCLUSIONS

The vibrational predissociation of the $I_2(B,v)$ – Ne₂ complex has been studied in the range v = 17-23 of I₂ vibrational excitations. A quasiclassical method is used which select the initial conditions from the quantum distributions of the initial resonance state. From the integrated trajectories the variation of the nascent I₂ fragment population with time is calculated. A significant time delay is found in the rise of the population curves, which increases with decreasing iodine initial vibrational level. The delay in the predissociation process is due mainly to artificial energy exchange mechanisms between the chemical and the vdW modes. These mechanisms are originated in limitations of the classical method, like the lack of quantization of the energy transferred, and zero-point energy effects. Through such mechanisms the energy of the system, initially in a resonance state, is relocated in a different energy state which is more inefficient to produce dissociation of the complex.

A first-order kinetic model has been proposed in order to rationalize the results obtained from the classical trajectories. In this model the dissociation of I_2 -Ne is assumed to occur in three steps. In a first step the system undergoes energy transfer from the I_2 subunit to the vdW degrees of freedom, and vice versa. This step accounts for the artificial energy exchange mechanisms causing the time delay in the dissociation. In a second and third step dissociation of the two vdW bonds take place. The nascent I_2 populations calculated with this model are found to fit reasonably well those obtained from the classical trajectories in the range of time studied. This supports the assumptions introduced in the model. weak bonds have been calculated from the I_2 population curves fitted with the kinetic model. They are found to be in qualitative agreement with the experimental ones. The classical lifetimes are in general overestimated with respect to the experimental values, as a consequence of the artificial time delay. However, the behavior of the calculated lifetimes with the I_2 vibrational excitation appears to be in very good accord with that observed experimentally. Therefore, classical mechanics is able to reproduce the general behavior of the dynamics in the present case, but it fails at a quantitative level of description.

Mechanistic issues were also investigated in this work. A sequential fragmentation path via direct predissociation leading to $I_2(B,v'=v-2)+2Ne$ products is found to be the dominating one for all the vibrational levels studied. This result agrees both with experimental data and with quantum calculations on this system.

Additional paths of dissociation are also predicted by the calculations. They are related to statistical IVR mechanisms, by means of which the energy initially transferred by the I₂ heats the vdW modes, but do not cause dissociation. An excited intermediate complex $[I_2(B,v'=v-1)-Ne_2]^*$ is formed as a result. Further energy transfer from the chemical bond may produce: (a) Simultaneous breaking of the two vdW bonds to yield either $I_2(B,v')+2Ne$ or $I_2(B,v')+Ne_2$ products, with v'=v-2,v-3; (b) Sequential dissociation of the cluster into $I_2(B,v'=v-3)+2Ne$ fragments. The formation of Ne₂ diatomics is also predicted by quantum results, which seems to confirm the existence of alternative reaction paths involving IVR effects.

The probability of this type of evaporation mechanisms is still small as compared to that of the dominating sequential dissociation path, in the case of I_2 -Ne₂. However, it is expected to grow for larger cluster sizes involving an increasing number of vdW bath modes. Investigation on this line merits further work.

ACKNOWLEDGMENTS

This work was supported by DGICYT, Spain, under Grant No. PB92-0053, and by Comunidad Autónoma de Madrid, under Grant No. 064/92. J.R.S. is also grateful to the Instituto de Cooperación Iberoamericana, Spain, for a fellowship.

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