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Structure and dynamics of small $I_2 \dots He_n$ van der Waals clusters ($n = 1-9$)

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Energetics and dynamics of van der Waals (vdW) $I_2 \dots He_n$ clusters are studied in an approximate way by using a model that considers $2n + 1$ degrees of freedom, that is, the I_2 stretch and the $2n$ stretching and bending modes of the He atoms restricted to move along a plane perpendicular to the I_2 axis. For $n = 2, 3$ a configuration-interaction treatment is carried out to obtain energy levels. For $n = 4-8$, ground-level energies are estimated from those corresponding to $n = 2, 3$ and the geometric relationships among the n vdW bonds. A quasiclassical trajectory approach is used to study the dynamics of these clusters, and lifetimes and half-widths for vibrational predissociation have been calculated for $n = 1-9$. A large increase in the half-width of $n = 9$ with respect to the cases $n = 1-8$ is observed, which would imply the existence of a first coordination shell for He about I_2 containing eight atoms. Also, it is found that the mechanisms of dissociation for these clusters become statistical as the number of vdW bonds increases.

I. INTRODUCTION

In the last few years considerable attention has been paid to the study of atomic¹⁻³ and molecular^{4,5} clusters in order to establish their structure and dynamical behavior. Different techniques have been used such as Monte Carlo and molecular-dynamics simulations,^{1,2} and the density-functional formalism,^{6,7} among other approaches. van der Waals (vdW) clusters constitute one of the most studied types of cluster. They can be complexes composed of just noble-gas atoms weakly bound to each other by vdW forces or also bound to molecules with one or more chemical bonds. Several experimental⁸⁻¹⁰ and theoretical¹¹⁻¹³ studies on such systems can be found in the literature. Specifically, a great amount of the research effort has been concerned with the predissociation process of triatomic vdW clusters as $BC \dots X$,¹⁴⁻¹⁷ where X is a rare-gas atom and BC is a conventional diatomic molecule. In this process, part of the internal energy of BC is transferred to the vdW bond causing its break up.¹⁸⁻²⁰

In more recent work, tetra-atomic clusters such as $X \dots BC \dots Y$, with Y also being a rare-gas atom, have been studied from both dynamic and static points of view, fixing some degrees of freedom in the first case²¹⁻²⁴ and including all the vdW modes in the second one.²⁵

Although experimentalists have studied clusters such as $I_2 \dots X_n$, with $X = He, Ne$ and $n > 2$,^{8(b),8(d)} there are no theoretical papers about such complexes involving more than two vdW bonds at the present moment. The aim of this paper is to develop a theoretical model to study $I_2 \dots X_n$ systems with $n \geq 2$. Some approximations are included in order to reduce the large number of degrees of freedom involved when n increases, since by including all of them the problem would become intractable. So, assuming a near-equilibrium geometry of the complex, the X atoms only are allowed to move along a plane perpendicular to the I_2 axis. This assumption is justified by early results²⁵ and will be discussed later. On the other hand, the I_2 rotation is neglected in our

model because of the smallness of the corresponding rotational constant and the weakness of the coupling between that rotation and the vdW bending modes.¹⁷

We have chosen bond coordinates to write the Hamiltonian, taking the I_2 bond as a quantization axis. The kinetic coupling terms between vdW modes, which are divided by two times the iodine mass, have been neglected.

Dynamical calculations of vibrational predissociation (VP) rates through Fermi's golden rule have been carried out for $I_2 \dots He$ and $I_2 \dots He_2$ at the bending equilibrium configurations. However, the main dynamical calculations have been performed in the framework of a quasiclassical trajectory (QCT) method that uses the above static results to establish the initial conditions. So, lifetimes and half-widths for the VP of clusters $I_2 \dots He_n$, with $n = 1-9$, were calculated at the near-equilibrium geometry already mentioned.

The organization of the paper is the following. In Sec. II the formalism and its approximations are developed, and in Sec. III the potential-energy surface used together with the details of the calculations are described, and our results are presented and discussed. Brief concluding remarks are presented in Sec. IV.

II. THEORETICAL TREATMENT

A. Obtaining the energy levels

After separating the center of mass of the whole system, we may write the Hamiltonian for the nuclear motion of a $BC \dots X_n$ system as²⁵

$$H = H_{BC} + \sum_i h_i + \sum_{i < j} V_{X_i X_j} + \Theta \left(\frac{1}{2m_I} \right), \quad (1)$$

where H_{BC} is the BC diatomic Hamiltonian

$$H_{BC} = -\frac{\hbar^2}{2\mu_{BC}} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2\mu_{BC} r^2} j^2 + V_{BC}(r), \quad (2)$$

h_i is the Hamiltonian describing the motion of the vdW bond $BC \dots X_i$

$$h_i = -\frac{\hbar^2}{2\mu_{\text{BC},X}} \frac{\partial^2}{\partial R_i^2} + \frac{\hbar^2}{2\mu_{\text{BC},X} R_i^2} l_i^2 + V_{\text{BC-X}}(r, R_i, \theta_i), \quad (3)$$

$V_{\text{X-X}_j}(R_i, R_j, \theta_i, \theta_j, \phi_i, \phi_j)$ is the interaction potential between the rare-gas atoms X_i and X_j , and the term $\Theta(1/2m_i)$ symbolizes the coupling terms between kinetic operators which are neglected in our model. In the above equations, r is the BC internuclear distance, R_i is the distance between X_i and the center of mass (CM) of BC, θ_i is the angle subtended between the $\mathbf{r}$ and $\mathbf{R}_i$ vectors, and ϕ_i is the rotation angle around the BC internuclear axis. The terms $V_{\text{BC}}(r)$ and $V_{\text{BC-X}}(r, R_i, \theta_i)$ are the diatomic and the BC...X interaction potentials; the factors μ_{BC} and $\mu_{\text{BC},X}$ are reduced masses of BC and BC...X, respectively, and j and l are angular momentum operators associated with the rotation of BC and the vdW bond, respectively.

As was mentioned before, the rotation of the BC diatom is neglected in our formalism. In addition, its vibration is separated from the other motions by applying a diabatic distorted-wave approach. So, we first determine the vibrational state of $H_{\text{BC}}(r)$ for a given vibrational quantum number v of BC. Then, the remaining part of H depending on r is averaged between the v -dependent wave functions of $H_{\text{BC}}(r)$, $\chi_v(r)$.

Once the stretching motion of BC has been separated, we proceed to the study of the vdW bond motion by finding the eigenstates of h_i . Due to the difference between the frequency of the stretching ($\sim 6 \text{ cm}^{-1}$) and the rotational constant ($\sim 0.27 \text{ cm}^{-1}$) for the $\text{I}_2\cdots\text{He}$ vdW bond,^{11(b)} we may adiabatically separate the motions of both coordinates R and θ , taking θ as a parameter. We are interested in the T-shaped configuration $\theta = \pi/2$. Then, we solve the following Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu_{\text{BC},X}} \frac{\partial^2}{\partial R_i^2} + V_{\text{BC-X}}^{(v)}(R_i, \bar{\theta}_i) \right] \Psi_\kappa^{(v)}(R_i, \bar{\theta}_i) = \mathcal{E}_\kappa^{(v)}(\bar{\theta}_i) \Psi_\kappa^{(v)}(R_i, \bar{\theta}_i) \quad (4)$$

for the value $\bar{\theta}_i = \pi/2$. In Eq. (4) the term $V_{\text{BC-X}}^{(v)}(R_i, \bar{\theta}_i)$ symbolizes the average of $V_{\text{BC-X}}(r, R_i, \bar{\theta}_i)$ between the stretching vibrational wave functions of BC,

$$V_{\text{BC-X}}^{(v)}(R_i, \bar{\theta}_i) = \langle \chi_v(r) | V_{\text{BC-X}}(r, R_i, \bar{\theta}_i) | \chi_v(r) \rangle,$$

and κ is the vdW stretching vibrational quantum number.

The angular part of the total wave function associated to the Hamiltonian H still remains to be found. Until now, we have allowed variation of the vdW stretching degrees of freedom, R_i , in order to find the eigenstates of h_i . However, when we try to study BC... X_n clusters with $n > 2$, handling the Hamiltonian H as expressed in Eq. (1) becomes a prohibitively difficult problem due to the large number of degrees of freedom involved, which are coupled by the term $\sum_{i < j} V_{\text{X-X}_j}$. Hence, it is necessary to do some type of approximation in order to reduce the number of variables to be handled. In a previous work²⁵ by our group on tetraatomic clusters $\text{I}_2\cdots\text{X}_2$ ($\text{X} = \text{He}, \text{Ne}$) including all the vdW modes, we observed that the maximum probability density of finding an X atom in a volume element dv was located in a narrow range of θ (centered at $\theta = \pi/2$ in both cases, $\text{X} = \text{He},$

Ne) and R (centered at $R = 3.86 \text{ \AA}$ for $\text{X} = \text{He}$) coordinates. The probability density decreases very quickly as we get away from the centers of the ranges. Thus, the stretching- and bending-mode amplitudes are rather small, and the motion of the rare-gas atoms basically takes place on a plane perpendicular to the I_2 axis. Therefore, it is reasonable to fix all the R_i and θ_i coordinates at the above equilibrium values in order to find the angular wave function. These results justify the near-equilibrium geometry chosen for the complexes throughout this paper. An insight of the error committed by making such an approximation will be given in the next section. Now, we obtain this angular function as a solution of the following Schrödinger equation, in which the Hamiltonian is the remaining part of H depending on the ϕ_i coordinates,

$$\left[\sum_i^n -\frac{\hbar^2}{2\mu_{\text{BC},X} \bar{R}_i^2 \sin^2 \bar{\theta}_i} \frac{\partial^2}{\partial \phi_i^2} + \sum_{i < j}^n V_{\text{X-X}_j}(\bar{R}_i, \bar{R}_j, \bar{\theta}_i, \bar{\theta}_j, \phi_i, \phi_j) \right] \times \mathcal{F}_l(\phi_1, \dots, \phi_n) = \epsilon_l \mathcal{F}_l(\phi_1, \dots, \phi_n), \quad (5)$$

where l is the quantum number associated with the vdW bending motion on the ϕ_i coordinates. In Ref. 25 for $\text{I}_2\cdots\text{X}_2$, the R_i coordinates were not fixed, but the terms $\hbar^2/(2\mu_{\text{BC},X} R_i^2 \sin^2 \bar{\theta}_i)$ and $V_{\text{X-X}_j}$ were averaged between the stretching wave functions $\Psi_\kappa^{(v)}(R_i, \bar{\theta}_i)$. However, both approximations yield similar results due to the small amplitude of the vdW stretch.

The solution of Eq. (5) is reached in a configuration-interaction (CI) scheme using a basis set built up with configurations, each one of them being the product of n imaginary exponentials

$$\Xi_{\lambda_1, \dots, \lambda_n}(\phi_1, \dots, \phi_n) = \prod_{j=1}^n e^{i\lambda_j \phi_j},$$

the angular function $\mathcal{F}_l$ being an expansion in such basis functions

$$\mathcal{F}_l(\phi_1, \dots, \phi_n) = \sum_{\lambda_1, \dots, \lambda_n} a_{\lambda_1, \dots, \lambda_n}^{(l)} \times \Xi_{\lambda_1, \dots, \lambda_n}(\phi_1, \dots, \phi_n), \quad (6)$$

where $\lambda_1, \dots, \lambda_n$ are quantum numbers associated with the projections over the BC axis of the vdW bending motions in the ϕ_i coordinates. The coefficients of expansion Eq. (6) are variationally found by diagonalization of the matrix representing the Hamiltonian appearing in Eq. (5) in the above basis set.

Although we have remarkably reduced the number of degrees of freedom by fixing the R_i and θ_i coordinates, it still remains large when the number of rare-gas atoms increases. As a consequence, it becomes costly to carry out a CI treatment for $n > 3$. So, in order to estimate the ground-level energy of clusters with $n \geq 4$, we have applied a rough approximation based on geometric relationships between the vdW bonds. In Ref. 25, the equilibrium angle ϕ between both vdW bonds of $\text{I}_2\cdots\text{X}_2$ ($\phi = \phi_2 - \phi_1$) was found to be $\phi \sim 45^\circ$. Therefore, it is reasonable to suppose that the most stable arrangement of n He atoms on the plane perpendicular to I_2

is that in which the j th He is separated from both the $(j-1)$ th and the $(j+1)$ th ones by relative angles of $\sim 45^\circ$. For the $I_2 \dots \text{He}_2$ case, there is only one pairwise potential interaction between He atoms, $V_{\text{He-He}}(\phi_2 - \phi_1)$. So, we may separate the energy obtained for the ground level of $I_2 \dots \text{He}_2$ by means of a CI treatment, E_2^{CI} , in two contributions

$$E_2^{\text{CI}} = 2\mathcal{E}_0^{(v)} + V_2, \quad (7a)$$

where $\mathcal{E}_0^{(v)}$ is the triatomic ground-level energy at $\theta = \pi/2$ and V_2 would represent some average of the interaction $V_{\text{He-He}}$ between the different configurations involved in the CI treatment.²⁶ Hence, the V_2 contribution can be estimated from Eq. (7a). For the $I_2 \dots \text{He}_3$ system we find three pairwise interactions between He atoms, two of them between adjacent atoms, $V_{12}(\phi_2 - \phi_1)$ and $V_{23}(\phi_3 - \phi_2)$, and the third one involving nonadjacent atoms, $V_{13}(\phi_3 - \phi_1)$. Following the above discussion, in the equilibrium configuration the adjacent atoms would be separated by about 45° from each other, while the relative angle between the nonadjacent atoms would be $\sim 90^\circ$. So then, we may think of the $I_2 \dots \text{He}_3$ ground-level energy as an addition of three different terms,

$$E_3^{\text{CI}} = 3\mathcal{E}_0^{(v)} + 2V_2 + V_3, \quad (7b)$$

where V_3 is some average of $V_{13}(\phi_3 - \phi_1)$ and can be obtained from this expression. Now, by assuming the above arrangement for the He atoms, and neglecting those pairwise interactions V_{ij} for which the relative angle between the i and j He atoms is greater than 90° (that is, for distances between both atoms placed on the asymptote of the V_{ij} potential curve), we approximate the ground-level energy for clusters with $n \geq 4$ as

$$E_n = n\mathcal{E}_0^{(v)} + mV_2 + kV_3, \quad (8)$$

where m and k are the number of adjacent and nonadjacent interactions, respectively, being easily obtained from geometric considerations.

B. Quantal half-widths for vibrational predissociation of $\text{BC} \dots \text{X}_n$ ($n=1,2$)

Rates of VP have been calculated for $I_2 \dots \text{He}_n$ ($n=1,2$) using Fermi's golden rule at fixed configurations of the bend-

ing angles (the T-shaped one, with $\theta = \pi/2$ for $I_2 \dots \text{He}$, and that corresponding to the equilibrium value of γ for $I_2 \dots \text{He}_2$, $\gamma = \phi_2 - \phi_1$).

Once the I_2 stretch has been diabatically separated, we have to obtain discrete and continuum states of the vdW stretching motion for $I_2 \dots \text{He}_2$. Discrete wave functions are solutions of the following equation:

$$\left[-\frac{\hbar^2}{2\mu_{\text{BC-X}}} \left(\frac{\partial^2}{\partial R_1^2} + \frac{\partial^2}{\partial R_2^2} \right) - \frac{\hbar^2 \cos \bar{\gamma}}{m_B + m_C} \frac{\partial^2}{\partial R_1 \partial R_2} + V^{(v,v)}(R_1, R_2, \bar{\gamma}) \right] \Psi_\kappa^{(v)}(R_1, R_2, \bar{\gamma}) = \mathcal{E}_\kappa^{(v)}(\bar{\gamma}) \Psi_\kappa^{(v)}(R_1, R_2, \bar{\gamma}), \quad (9)$$

with

$$V^{(v,v)}(R_1, R_2, \bar{\gamma}) = V_{\text{BC-X}}^{(v,v)}(R_1) + V_{\text{BC-X}}^{(v,v)}(R_2) + V_{\text{X-X}}(R_1, R_2, \bar{\gamma}).$$

In the above equations $\bar{\gamma}$ is the equilibrium value of γ , and κ is a quantum number that accounts for the two-dimensional stretching problem. Notice that a kinetic coupling term (the third one) between the vdW stretch modes has been included in Eq. (9). The discrete solutions of Eq. (9) can be obtained by expanding Ψ as

$$\Psi_\kappa^{(v)\text{dis}}(R_1, R_2, \bar{\gamma}) = \sum_{m,n} a_{m,n}^{(v,\kappa)}(\bar{\gamma}) \varphi_m^{(v)}(R_1) \varphi_n^{(v)}(R_2), \quad (10)$$

where the φ 's are discrete triatomic stretching functions

$$\left[-\frac{\hbar^2}{2\mu_{\text{BC-X}}} \frac{\partial^2}{\partial R^2} + V_{\text{BC-X}}^{(v,v)}(R) \right] \varphi_m^{(v)}(R) = E_{\text{BC-X}}^{(v,m)} \varphi_m^{(v)}(R). \quad (11)$$

Now the coefficients $a_{m,n}^{(v,\kappa)}$ of the expansion Eq. (10) are obtained by diagonalizing the matrix

$$H_{m,n;m',n'}^{(v)}(\bar{\gamma}) = [E_{\text{BC-X}}^{(v,m)} + E_{\text{BC-X}}^{(v,n)}] \delta_{m,m'} \delta_{n,n'} - \frac{\hbar^2 \cos \bar{\gamma}}{m_B + m_C} \left[\frac{\langle \varphi_m^{(v)}(R_1) | dV_{\text{BC-X}}^{(v,v)}(R_1)/dR_1 | \varphi_{m'}^{(v)}(R_1) \rangle}{E_{\text{BC-X}}^{(v,m)} - E_{\text{BC-X}}^{(v,m')}} \right. \\ \times (1 - \delta_{m,m'}) \frac{\langle \varphi_n^{(v)}(R_2) | dV_{\text{BC-X}}^{(v,v)}(R_2)/dR_2 | \varphi_{n'}^{(v)}(R_2) \rangle}{E_{\text{BC-X}}^{(v,n)} - E_{\text{BC-X}}^{(v,n')}} (1 - \delta_{n,n'}) \left. \right] \\ + \langle \varphi_m^{(v)}(R_1) \varphi_n^{(v)}(R_2) | V_{\text{X-X}}(R_1, R_2, \bar{\gamma}) | \varphi_{m'}^{(v)}(R_1) \varphi_{n'}^{(v)}(R_2) \rangle. \quad (12)$$

The continuum solutions of Eq. (9) are functions describing the atom X plus a triatomic fragment $\text{BC} \dots \text{X}$ in a given stretching n'' state, with BC being in a lower $v' < v$ vibrational level. They may be written as a product

$$\Psi_{\epsilon_1, n''}^{(v')\text{cont}}(R_1, R_2, \bar{\gamma}) = \varphi_{\epsilon_1}^{(v', n'')}(R_1, \bar{\gamma}) \varphi_{n''}^{(v')}(R_2), \quad (13)$$

where $\varphi_{n''}^{(v')}$ is defined by Eq. (9) and $\varphi_{\epsilon_1}^{(v', n'')}$ is the solution of

$$\left[-\frac{\hbar^2}{2\mu_{\text{BC-X}}} \frac{\partial^2}{\partial R_1^2} + V_{\text{BC-X}}^{(v',v')}(R_1) + \langle \varphi_{n''}^{(v')}(R_2) \right. \\ \times \left. | V_{\text{X-X}}(R_1, R_2, \bar{\gamma}) | \varphi_{n''}^{(v')}(R_2) \rangle - \epsilon_1 \right] \varphi_{\epsilon_1}^{(v', n'')}(R_1, \bar{\gamma}) = 0, \quad (14)$$

calculated on the energy shell, i.e.,

$$\epsilon_1 = (E_{BC}^{(v)} - E_{BC}^{(v')}) + \epsilon_{\kappa}^{(v)}(\gamma) - E_{BC-X}^{(v',n^*)}.$$

with ϵ_1 being the kinetic energy between the fragments. There are similar equations for the fragmentation of the bond associated to R_2 .

Now, half-widths for VP of $BC...X_2$ in a given κ state may be obtained by applying Fermi's golden rule. Then, for breaking up any $BC...X$ bond we have

$$\begin{aligned} \Gamma_{v,\kappa}^x(\bar{\gamma}) &= 2\pi \sum_{v' < v} \sum_{n^*} |\langle \Psi_{\kappa}^{(v)\text{dis}} | \chi_v | V | \chi_{v'} \rangle \langle \Psi_{\epsilon_1, n^*}^{(v')\text{cont}} |^2 \\ &= 2\pi \sum_{v' < v} \sum_{n^*} \left| \sum_{m,n} a_{m,n}^{(v,\kappa)}(\bar{\gamma}) [\langle \varphi_n^{(v)} | \varphi_n^{(v')} \rangle \right. \\ &\quad \times \langle \varphi_m^{(v)} | V_{BC-X}^{(v,v')} | \varphi_{\epsilon_1}^{(v',n^*)} \rangle \\ &\quad \left. + \langle \varphi_m^{(v)} | \varphi_{\epsilon_1}^{(v',n^*)} \rangle \langle \varphi_n^{(v)} | V_{BC-X}^{(v,v')} | \varphi_{n^*}^{(v')} \rangle \right|^2. \quad (15) \end{aligned}$$

The treatment for a triatomic $BC...X$ system is very similar, although some differences remain since there is only one vdW bond. The discrete states $\Psi_{\kappa}^{(v)\text{dis}}$ are in this case the discrete solutions of Eq. (11)

$$\Psi_{\kappa}^{(v)\text{dis}}(R) = \varphi_n^{(v)}(R),$$

and the continuum functions describing the X atom plus the I_2 fragment are energy normalized solutions of

$$\left[-\frac{\hbar^2}{2\mu_{BC,X}} \frac{\partial^2}{\partial R^2} + V_{BC-X}^{(v,v')}(R) - \epsilon \right] \varphi_{\epsilon}^{(v')}(R) = 0.$$

Then, we can express the half-width for VP of $BC...X$ in a given n state as

$$\Gamma_{v,n}^x = \pi \sum_{v' < v} |\langle \varphi_n^{(v)} | V_{BC-X}^{(v,v')} | \varphi_{\epsilon}^{(v')} \rangle|^2. \quad (16)$$

C. Quasiclassical trajectory approach for vibrational predissociation of $BC...X_n$ ($n=1-9$)

The dynamics of VP for $BC...X_n$ clusters with $n=1-9$ has been studied by means of a QCT approach. As in Sec. II A, the X atoms are constrained to move on a plane perpendicular to BC. After separating the CM of the whole system we may write the classical Hamiltonian for a $BC...X_n$ system as

$$\begin{aligned} H &= \frac{P_r^2}{2\mu_{BC}} + V_{BC}(r) + \sum_{i=1}^n \left[\frac{1}{2\mu_{BC,X_i}} \left(P_{R_i}^2 + \frac{P_{\bar{\theta}_i}^2}{R_i^2} \right) + V_{BC-X_i}(r, R_i, \bar{\theta}_i) \right] \\ &\quad + \sum_{i < j}^n \left[\frac{\cos(\phi_i - \phi_j)}{m_B + m_C} \left(P_{R_i} P_{R_j} + \frac{P_{\phi_i} P_{\phi_j}}{R_i R_j} \right) + \frac{\sin(\phi_i - \phi_j)}{m_B + m_C} \left(\frac{P_{R_i} P_{\phi_j}}{R_j} - \frac{R_{R_j} P_{\phi_i}}{R_i} \right) + V_{X_i-X_j}(R_i, R_j, \bar{\theta}_i, \bar{\theta}_j, \phi_i, \phi_j) \right], \quad (17) \end{aligned}$$

where the P 's are the conjugate momenta to the respective coordinates, $\bar{\theta}_i = \pi/2$, and all the other symbols are already known. In the above Hamiltonian, all the kinetic coupling terms between vdW modes have been taken into account. In spite of being neglected in getting ground-energy levels of the different clusters, their contribution at this stage may be important since the trajectories can, in principle, explore highly excited states. The corresponding Hamilton equations constitute a set of $4n+2$ first-order coupled differential equations, which are numerically solved once the relevant initial conditions have been established. The above accounts for $n > 1$, since for the case $n=1$ only the r and R degrees of freedom have been considered.

We initially consider the vibrational energy stored in the BC molecule as being the corresponding v state of a nonrotating Morse oscillator, $E_{BC}(v)$. Since there is a large difference between the frequency of BC (I_2 in our case) and the dissociation energy of the complex,^{11(b)} the diatomic molecule practically conserves its individuality within the complex. Hence, the initial interdiatomic distance r is selected according to the following expression²⁷:

$$r = \bar{r} - \frac{1}{\alpha} \ln \left[\frac{-2a}{b + (b^2 - 4ac)^{1/2} \sin 2\pi S} \right], \quad (18)$$

where $a = E_{BC} - D$, $b = 2D$, $c = -D$, and S is a random number uniformly distributed in the range $[0,1]$. Here, E_{BC} is the energy of the vibrational quantum level v relative to the minimum of the well and D , α , and $\bar{r}$ are Morse parameters of

the diatomic molecule. The initial conjugate momentum P_r is

$$P_r = \pm [2\mu_{BC}(E_{BC}(v) - V_{BC}(r))]^{1/2}. \quad (19)$$

As regards the choice of the R_i distances, and the associated momenta, we take advantage of the fact that the quantal energy of a $BC...X_n$ cluster is close to the simple addition of triatomic energies, as will be discussed in the next section. Thus, we fix each triatom at its corresponding ground-level quantal energy $\mathcal{E}_0^{(v)}$, previously calculated by solving Eq. (4). The relevant distances are obtained at random according to the distribution defined by the squared modulus of the corresponding wave function $|\Psi_0^{(v)}|^2$, which is peaked at the equilibrium value of the vdW stretching coordinate. The P_{R_i} momenta are calculated by means of

$$P_{R_i} = \pm [2\mu_{BC,X_i}(\mathcal{E}_0^{(v)} - V_{BC-X_i}(r, R_i, \bar{\theta}_i))]^{1/2}. \quad (20)$$

In order to find the ϕ_i initial values we take into account the fact that the He atoms mainly interact with adjacent ones, making the interactions with nonadjacent atoms much less important. It allows us to select relative angles $\phi_{ij} = \phi_i - \phi_j$ between pairs of adjacent atoms i, j , from which the ϕ_i and ϕ_j angles can be obtained later. In this sense, we rely the previous results of Ref. 25, where it was found that the two-particle probability density function, as a function of $\phi = \phi_2 - \phi_1$, was peaked at $\phi \sim 45^\circ$ for $I_2...He_2$, as was already mentioned. So, the different ϕ_{ij} ($\phi_{21}, \phi_{32}, \phi_{43}, \dots, \phi_{nn-1}$) are obtained at random within a

range of 10° centered at 45° for $n = 1-8$. The range we have taken for $n = 9$ is centered at 40° in order to approach the more realistic situation in which the nearest angle to the equilibrium one between adjacent atoms, can only be 40° when there are nine atoms moving along the same plane. Once the ϕ_{ij} relative angles have been selected, by fixing ϕ_1 at $\phi_1 = 0^\circ$, the rest of the ϕ_i angles are easily found. We calculate the initial P_{ϕ_i} momenta in the following way:

$$P_{\phi_i} = \pm [2\mu_{BC,X_i} R_i^2 (E_\phi - V_{X_i-X_j}(R_i, R_j, \bar{\theta}_i, \bar{\theta}_j, \phi_i, \phi_j))]^{1/2}, \quad (21)$$

where it is assumed that $P_{\phi_i} = 0$ and

$$E_\phi = E_2^{CI} - 2\mathcal{E}_0^{(v)}.$$

In order to calculate the different conjugate momenta, Eqs. (19)–(21) must satisfy the following inequality:

$$E - V \geq 0,$$

with $E = E_{BC}$, $\mathcal{E}_0^{(v)}$, E_ϕ and $V = V_{BC}$, V_{BC-X_i} , $V_{X_i-X_j}$, respectively. If the above expression is not fulfilled, the random selection of the corresponding coordinate is iterated. The positive or negative sign of the momenta is also randomly selected.

A trajectory is considered as dissociated when one of the R_i distances becomes larger than a certain value $R_{\max}$, for which the corresponding vdW interaction is negligible. Also, the trajectories are terminated if the time exceeds a given $T_{\max}$.

The distribution of trajectories is fitted to an exponential law of decay¹³

$$N_{ND} = N_T e^{-t/\tau}, \quad (22)$$

where N_T is the total number of trajectories, N_{ND} is the number of nondissociated ones at time t , and τ is the lifetime of the cluster. Once the lifetime is obtained, the half-width for VP is calculated as

$$\Gamma = \frac{\hbar}{2\tau}. \quad (23)$$

III. CALCULATIONS AND RESULTS

A. Potential-energy surface

As in previous work on vdW clusters,^{22,24,25} we represent the potential-energy surface (PES) as an addition of pairwise atom–atom interactions

$$V = V_{BC} + \sum_i V_{BC-X_i} + \sum_{i < j} V_{X_i-X_j},$$

with

$$V_{BC-X_i} = V_{B-X_i} + V_{C-X_i}.$$

A Morse function is used to describe each atom–atom interaction, since this functional form has been proved to work fairly well for vdW systems^{11(b)}

$$V_k(R_k) = D_k [e^{-2\alpha_k(R_k - \bar{R}_k)} - 2e^{-\alpha_k(R_k - \bar{R}_k)}],$$

with D_k , α_k , and $\bar{R}_k$ being the Morse parameters for the different interactions, where $k = BC$, $B-X_i$, $C-X_i$, X_i-X_j , and

$$R_{BC} = r,$$

$$R_{B-X_i} = \left(R_i^2 + \frac{r^2}{4} + 2R_i r \cos \theta_i\right)^{1/2},$$

$$R_{C-X_i} = \left(R_i^2 + \frac{r^2}{4} - 2R_i r \cos \theta_i\right)^{1/2},$$

$$R_{X_i-X_j} = (R_i^2 + R_j^2 - 2R_i R_j \cos \gamma_{ij})^{1/2},$$

where

$$\cos \gamma_{ij} = \cos \theta_i \cos \theta_j + \sin \theta_i \sin \theta_j \cos(\phi_i - \phi_j).$$

In Table I we list the Morse parameters used to describe the I–I,²⁸ I–He,²⁹ and He–He (Ref. 30) interactions.

B. Details of the calculations

We solve Eq. (4) using a grid of $N = 3000$ points for R with $R_{\min} = 4.0$ a.u. and $R_{\max} = 30.0$ a.u. by means of a Truhlar algorithm^{31(a)} further improved by a Numerov method.^{31(b)} In order to estimate the $V_{BC-X}^{(v)}$ averages appearing in Eq. (4), the interaction potential $V_{BC-X}(r, R_i, \theta_i)$ is expanded in a Taylor series up to third order about the $\bar{r}$ equilibrium value.

All the integrals involving the different ϕ_i coordinates were numerically evaluated by means of a Gauss–Legendre quadrature. The advantages of this method of integration have been already discussed elsewhere.²⁵ A 20-point quadrature for each coordinate was used in this work.

Expansions [Eq. (6)] composed of 63 and 17 configurations (that is, 125 and 139 basis functions, respectively) were used for the $n = 2$ and $n = 3$ cases, respectively. These sizes for the CI expansion yield an energy convergence of 10^{-4} cm⁻¹ for $n = 2$ and 10^{-5} cm⁻¹ for $n = 3$. The method of diagonalization used was a standard Jacobi one.

With respect to QCT calculations, Hamilton equations have been numerically solved by using an Adams–Moulton integrator initiated by a fourth-order Runge–Kutta–Gill integrator with a time step $\Delta t = 0.4 \times 10^{-15}$ s. Here, we take $50 \times 10^{-12}/n$ s as the maximum total time of every trajectory, which is equivalent to 125 000/ n cycles of integration. For the value of $R_{\max}$ we have chosen 12.5 Å. These parameters lead to stable values of the final magnitudes, the conservation in total energy being of the order of 10^{-11} cm⁻¹.

C. Results and discussion

All the calculations reported in this paper have been carried out for the diatomic vibrational level $v = 28$. By solving Eq. (4) at $\theta = \pi/2$, we found two stretching energy levels separated by about 17 cm⁻¹. For the energy-level calculations only the ground level was used ($\mathcal{E}_0^{(v)} = -18.570\,53$ cm⁻¹), while in the expansion Eq. (10) employed for the

TABLE I. Morse potential parameters used in this work.

	D (cm ⁻¹)	α (Å ⁻¹)	R_{eq} (Å)
I–I	5168.72	1.834	3.0247
I–He	16.5	1.5	4.0
He–He	7.61	2.126	2.963

dynamical treatment of $I_2\cdots He_2$, both energy levels were taken into account. Then, in order to solve Eq. (5), the R_i degrees of freedom were fixed at their equilibrium values, according to the discussion of Sec. II A, and the energy levels of $I_2\cdots He_2$ and $I_2\cdots He_3$ systems were calculated by means of a CI approach. The ground-level energy of these systems is reported in Table II. The configurations used in the CI treatment have been previously selected and only those with Σ symmetry have been employed in expansion Eq. (6). These Σ configurations consist of products of n imaginary exponentials, $e^{i\lambda_i\phi_i}$ such that the addition of the different λ_j equals zero.

Comparison of the ground-level energy of $I_2\cdots He_2$ obtained in this work with the results of Ref. 25 provides some information about how well the approximation of "freezing" the R_i and θ_i coordinates at the above equilibrium values works. In Ref. 25 calculations of the energy levels of $I_2\cdots He_2$ were also carried out with the X atoms moving along the plane perpendicular to the I_2 axis, but there the R_i degrees of freedom were allowed to vary. The ground-level energy found in that case was -37.1942 cm^{-1} , which agrees fairly well with our result. This means, therefore, that fixing the vdW stretching coordinates at $\bar{R}_i = 3.86\text{ \AA}$ becomes a good approximation. However, considering the bending motion on the θ_i coordinates has a greater influence on the energy, since calculations of Ref. 25 taking into account all the vdW modes (i.e., with all the R_i , θ_i , and ϕ_i varying) yield a ground-level energy of -28.9661 cm^{-1} for $I_2\cdots He_2$.

Now, by making use of the Eqs. (7a) and (7b), and taking the values of Table II previously obtained for E_2^{CI} and E_3^{CI} , we estimate the contributions of V_2 and V_3 as $V_2 = -0.17446\text{ cm}^{-1}$ and $V_3 = 1.06371\text{ cm}^{-1}$. Note that the energy corresponding to the V_2 term is less than zero while the V_3 one is positive. It is a consequence of the fact that the ground energy is slightly lower than $n\mathcal{E}_0^{(v)}$ for $n = 2$ ($2\mathcal{E}_0^{(v)} = -37.14106\text{ cm}^{-1}$), but the situation is just the opposite for the $I_2\cdots He_3$ case ($3\mathcal{E}_0^{(v)} = -55.71159\text{ cm}^{-1}$). By introducing in Eq. (8) these values together with the corresponding n , m , and k numbers, we estimate the ground energies E_n for $I_2\cdots He_n$ systems with $n > 3$. They are shown in Table II together with $n\mathcal{E}_0^{(v)}$ and the m and k values corresponding to each n one. These energies E_n result practically equal to $n\mathcal{E}_0^{(v)}$, the small differences coming from the very weak interactions between rare atoms. This fact was taken into account in computing the initial conditions for the QCT treatment, as previously mentioned in Sec. II C.

The V_2 and V_3 contributions have been calculated assuming that the He atoms have enough space in the plane where they are moving to arrange at their equilibrium angle with respect to the adjacent atoms, that is, at $\sim 45^\circ$ for all the equivalent pairs of adjacent atoms. Geometrically, this is possible up to $n = 8$, the pictorial image being a circumference divided in eight portions, where the vdW bonds would be placed at the sides of the portions. However, the situation changes for $n = 9$, since introducing the ninth atom implies that the angle between adjacent atoms cannot be 45° yet for all the pairs (the nearest angle to the equilibrium one for adjacent atoms is now 40°). Hence, the V_2 and the V_3 estimates are no longer valid for $n = 9$, and the ground energy of

TABLE II. Ground-level energies (in cm^{-1}) for $I_2\cdots He_n$ clusters. Those energies for $n = 2, 3$ have been calculated using a CI treatment, while the remaining ones have been estimated following a geometric model. The values of $n\mathcal{E}_0^{(v)}$ are presented in the second column. See the text for more details. Besides, the number of terms V_2 and V_3 (m and k , respectively) involved in the calculation of E_n , for $n > 4$, are given in the last two columns.

E_n	$n\mathcal{E}_0^{(v)}$	n	m	k
-18.570 53	-18.570 53	1		
-37.315 52	-37.141 06	2		
-54.996 81	-55.711 59	3		
-72.678 07	-74.282 12	4	3	2
-90.359 35	-92.852 65	5	4	3
-108.040 62	-111.433 18	6	5	4
-124.658 19	-129.993 71	7	6	6
-141.450 21	-148.564 24	8	8	8

$I_2\cdots He_9$ cannot be evaluated in this way.

With regard to dynamical calculations, half-widths for VP of $I_2\cdots He$ and $I_2\cdots He_2$ have been computed at the equilibrium configurations in the bending angles³² ($\theta = \pi/2$ for $I_2\cdots He$ and $\theta_1 = \theta_2 = \pi/2$, $\phi = \phi_2 - \phi_1 = 47.2^\circ$ for $I_2\cdots He_2$). The half-width for breaking up the vdW bond in $I_2\cdots He$ calculated by means of Eq. (16) is $\Gamma = 0.219184\text{ cm}^{-1}$. With respect to the $I_2\cdots He_2$ system, some remarks should be made about Eq. (15). So, we have $\langle \varphi_n^{(v)} | \varphi_n^{(v')} \rangle \approx 1$ for $n = n'$, since the discrete stretching wave functions for v and $v' = v - 1$ are very similar, while the overlap integral $\langle \varphi_m^{(v)} | \varphi_{\epsilon_1}^{(v', n')} \rangle \approx 0$. Then, the mean contribution to Γ is due to the first term of Eq. (15). All the allowed states of the exiting triatomic fragments are taken into account in Eq. (15). However, for the ground tetratomic stretching level $\kappa = 0$, the dominant contribution comes from the triatomic ground state, that is, those coefficients $a_{m,n}^{(v,0)}$ in expansion Eq. (10) which are different from $a_{0,0}^{(v,0)}$ are negligible. Therefore, the breaking up of one vdW bond mainly yields a triatomic fragment in its ground level with the I_2 partner deexcited by one vibrational quantum. This fact appears to be reflected by the results obtained for the half-widths corresponding to the situations when the triatomic fragment is either in its ground or excited level after the breakup. So, in the first case the partial half-width is $\Gamma_p^{n''=0} = 2\Gamma_{0,0}^{He,n''=0} = 0.40812\text{ cm}^{-1}$, while for the excited-level case we have a remarkably smaller one, $\Gamma_p^{n''=1} = 0.92 \times 10^{-5}\text{ cm}^{-1}$. The total half-width for $I_2\cdots He_2$ is the sum of these two partial rates, $\Gamma_t = 0.408136\text{ cm}^{-1}$, which practically equals $\Gamma_p^{n''=0}$.

Since a quantal treatment of the dynamics becomes very complicated for $n > 2$, we have applied a quasiclassical trajectory approach to study the VP process of $I_2\cdots He_n$ clusters with $n = 1-9$. So, once the initial conditions have been established, we have integrated the corresponding set of Hamilton equations for each value of n . In Figs. 1 and 2 we show typical plots of $\ln(N_{\text{ND}}/N_T)$ vs the trajectory time (which are fitted to straight lines) for $n = 2$ and $n = 7$. In Table III we report the total number of trajectories, N_T , used in each linear fit (third column) together with the corresponding correlation coefficient (last column). It is observed to be in very good agreement with the assumed exponential law of decay,

FIG. 1. Plot of $\ln(N_{ND}/N_T)$ vs the trajectory time for $I_2\cdots He_2$. The number N_T of the trajectories used in the plot is reported in Table III.

the fit corresponding to $n = 8$ being somewhat poorer, but still acceptable. In the second column of Table III we present the number of trajectories that actually were calculated, N_T^{calc} . Resting on physical grounds, from this number we have only considered, in order to carry out the linear fits, those trajectories for which the I_2 molecule has lost at least one vibrational quantum (that is, N_T) according to a usual box quantization procedure.

By taking a range centered at 40° for the ϕ_{ij} angles, when finding the ϕ_i initial conditions for $n = 9$, some initial ϕ_{ij} angles take values for which the pairwise interaction between He atoms is repulsive. As a consequence of these repulsive initial conditions, the corresponding trajectories dissociate in a very short time, before that the I_2 molecule has time to transfer at least one vibrational quantum to some vdW bond. This is the reason for which from 1852 trajectories calculated for $n = 9$, only 590 remain valid after the box quantization is applied (see Table III).

From the above linear fits we obtain the lifetimes τ corresponding to each $I_2\cdots He_n$ cluster. They are presented in Table IV together with their standard deviations, $(SD)_\tau$. We observe a gradual decreasing of τ as n increases. The decreasing is more remarkable from $n = 1$ to $n = 3$, and

FIG. 2. Same as Fig. 1 for $I_2\cdots He_7$.

TABLE III. Total number of trajectories calculated, N_T^{calc} (second column), and number of trajectories used to carry out the linear fits, N_T , after the usual box quantization (third column, see the text), for each value of n . Also, the correlation coefficients for each linear fit are reported in the last column of the table.

n	N_T^{calc}	N_T	Correlation coefficient
1	3000	981	-0.9903
2	1000	756	-0.9986
3	837	739	-0.9946
4	780	731	-0.9905
5	756	723	-0.9887
6	733	708	-0.9768
7	706	678	-0.9745
8	803	671	-0.8934
9	1852	590	-0.9639

takes place smoothly from $n = 3$ to $n = 8$. From $n = 8$ to $n = 9$ we find an abrupt jump in the lifetime. We have also calculated the average time $\bar{t}$ of the N_T trajectories used for each linear fit. They are displayed in Table IV together with their corresponding standard deviations $(SD)_\tau$. Although the values of $\bar{t}$ are quantitatively different from those of τ , the qualitative behavior depending on n is exactly the same, also showing a strong decrease from $I_2\cdots He_8$ to $I_2\cdots He_9$. It is interesting to emphasize at this point that the sharp decrease of the lifetime for the $n = 9$ cluster is not a mere artifact of the incidentally repulsive initial conditions already mentioned, since the loss of one vibrational quantum by I_2 is required by each trajectory included in the fit.

From the lifetimes the associated half-widths for VP, Γ , may be calculated by means of Eq. (23). In Fig. 3 we show a plot of Γ as a function of n . We find that the QCT rate for $I_2\cdots X$ (0.438 cm^{-1}) is higher than that calculated with Fermi's golden rule approach (0.219 cm^{-1}) in Sec. II B by a factor of 2, while the experimental value^{8(e)} for $v = 28$ is about 0.08 cm^{-1} . In both cases only 2 degrees of freedom are taken into account, that is, the stretching motions of I_2 and the vdW bond. In Ref. 33 a rate of $\Gamma \approx 0.50\text{ cm}^{-1}$, very close to our result, has been obtained for $I_2\cdots He$, using a QCT treatment very similar to that employed in this work, in

TABLE IV. Lifetimes (τ) and average times ($\bar{t}$, see the text) for VP together with their standard deviations $[(SD)_\tau$ and $(SD)_\bar{t}$, respectively] for $n = 1-9$. The units are ps.

n	τ	$(SD)_\tau$	$\bar{t}$	$(SD)_\bar{t}$
1	6.046	± 0.059	6.91	± 0.14
2	4.645	± 0.083	5.51	± 0.10
3	4.040	± 0.108	4.82	± 0.07
4	3.862	± 0.118	4.59	± 0.06
5	3.621	± 0.133	4.27	± 0.05
6	3.569	± 0.143	4.18	± 0.04
7	3.376	± 0.163	3.92	± 0.04
8	3.081	± 0.133	3.56	± 0.04
9	1.367	± 0.0073	1.33	± 0.05

FIG. 3. Plot of the half-width for VP vs the number of helium atoms, n for $n = 1$ –9 (dots), and fit of $\Gamma(n)$ to the curve $\Gamma(n) = 0.452n^{0.298}$ (solid line) for $n = 1$ to $n = 8$. Error bars (the standard deviation) have been added to each value of $\Gamma(n)$.

which the same degrees of freedom are considered in the T-shaped configuration. As is known,^{12(a),31} the rates provided for quantal as well as QCT calculations decrease as the number of degrees of freedom considered is increased, since the stability of the system increases with the additional degrees of freedom. So, the difference between our quantal and QCT rates and the experimental value may be due to the fact that only two degrees of freedom were considered, and this would affect in a more dramatic way the QCT treatment. In fact, three-dimensional QCT calculations^{13(b)} for $\text{I}_2\cdots\text{He}$ yield results which agree fairly well with experimental ones. In the QCT calculations for $n \geq 2$ we have considered one more degree of freedom per vdW bond (the one corresponding to the ϕ_i coordinate), and therefore we expect to obtain more reliable rates than for $n = 1$. So, for $n = 2$, the quantal rate (0.408 cm^{-1}) is lower than the QCT one (0.570 cm^{-1}), but this difference is expected since the quantal rate is calculated for a fixed configuration, the equilibrium one, in the coordinate $\gamma = \phi_2 - \phi_1$, while in the calculation of the QCT rate the ϕ_1 and ϕ_2 degrees of freedom are allowed to vary. There are no calculations available in the literature to compare with our results for $n \geq 3$.

The above remarks are relevant in order to estimate how quantitative our results are, but actually we are mainly interested in the qualitative behavior of the half-width as a function of the size of the cluster. So, in Fig. 3 we can see that the half-width (dots) smoothly increases with n up to $n = 8$, and at $n = 9$ a sudden jump is observed (from 0.860 cm^{-1} for $n = 8$ to 1.938 cm^{-1} for $n = 9$) as in the case of both the lifetime and the average time vs n . The abrupt jump that happens for $n = 9$ suggests the existence of a first coordination shell for the He atoms around I_2 , which would contain eight rare-gas atoms arranged in equivalent positions in a plane perpendicular to I_2 with angles of 45° between the vdW bonds. Such a result is closely related with that of Kenny *et al.*^{8(b)} about $\text{I}_2\cdots\text{Ne}_n$ ($n = 1$ –7). In that work, they ob-

served that a band-shift rule is fulfilled for $n = 1$ to $n = 6$, and it is broken down for $n = 7$. Thus, they infer that there exists a first coordination shell about I_2 with six Ne atoms occupying equivalent sites. Two geometric structures consistent with their observation were proposed: a belt model with six Ne atoms encircling the I_2 molecule (equivalent to the geometry used in the present work), and an ethane model with three Ne atoms over each I atom as in an ordinary ethane molecule. Our choice of a belt configuration rests on previous structural results²⁵ as was mentioned before. Moreover, some experimental studies on other vdW clusters such as $\text{I}_2\cdots\text{He}_n$ ($n = 1$ –3),^{8(d)} $\text{Br}_2\cdots\text{Ne}_n$ ($n = 1$ –3),^{9(f)} $\text{ICl}\cdots\text{Ne}_n$ ($n = 1$ –5),^{10(e)} and $\text{Cl}_2\cdots\text{Ne}_n$ ($n = 2, 3$),^{9(g)} also point in the same direction. In all of these works the rare-gas atoms were found to occupy equivalent positions, and a belt model with the rare atoms encircling the diatomic molecule satisfies this requirement.

These coordination numbers for $\text{BC}\cdots\text{X}_n$ vdW clusters [$n = 8$ in our case, $n = 6$ in the case of Ref. 8(b)] are in some way equivalent to the magic numbers found when other kinds of vdW clusters, those only composed by rare-gas atoms without any chemical bond, are studied.¹ It is in the sense that the addition of a single atom to a magic, or coordination, number cluster can dramatically alter the behavior of some physical or chemical properties (such as the melting behavior in Ar_n clusters,¹ the half-width in our case, or the band shift^{8(b)} in $\text{I}_2\cdots\text{Ne}_n$) of the new cluster.

Experimental results reported by Sharfin *et al.*^{8(d)} show that the vibrational predissociation of the $\text{I}_2\cdots\text{He}_2$ complex is predominantly a sequential two-step process involving the independent dissociation of He atoms. That is, although one vibrational quantum of I_2 has enough energy [for the vibrational levels of I_2 studied in Ref. 8(d)] to break up both vdW bonds, as an effect of the dynamics of dissociation of this complex, two quanta are required. The implication is that the breaking up of one vdW bond is independent of the presence or absence of the other He, and then they postulate that the half-width for $\text{I}_2\cdots\text{He}_2$ should be twice that for $\text{I}_2\cdots\text{He}$ as a result consistent with their observations. If this behavior is expected to be fulfilled also for clusters with $n > 2$, we should observe a linear behavior for $\Gamma(n)$ of the type

$$\Gamma(n) \approx \Gamma(1)n.$$

However, it is not found when we fit our half-widths as a function of n to a curve (solid line in Fig. 3). It is observed that they approximately follow the law

$$\Gamma(n) \propto n^{1/3}$$

(see caption of Fig. 3 for a more exact equation) up to $n = 8$, which remarkably separates from linearity. This behavior for $\Gamma(n)$ suggests a mechanism of statistical redistribution of the energy as n increases (the number of vdW molecules available to store energy increases with the cluster size), decreasing the efficiency of the dissociation. This mechanism was proposed to explain the same statistical nature observed for the dissociation of $\text{I}_2\cdots\text{Ne}_n$ clusters.^{8(b)} As discussed by Hair *et al.*^{9(g)} for $\text{Cl}_2\cdots\text{Ne}_n$ ($n = 2, 3$) clusters, the observation of multiple reaction pathways, such as double continuum dissociation³⁴ yielding 2Ne and Ne_2 fragments, also denotes statistical nature for dissociation of these clusters. In

this sense a non-negligible portion of double continuum dissociation to 2He products has been detected in our calculations. There is no possibility of finding He₂ because this dimer has no bound states. The above results are meaningful since we are observing a dissociation behavior for I₂...He_n clusters very similar to that for clusters with Ne atoms, in which the dissociation of the different vdW bond does not occur independently due to the stronger couplings between them. It would indicate that the dissociation of the different He atoms becomes more dependent as *n* increases. The following fact confirms the above conclusion. Notice that we are actually studying the dissociation of only one vdW bond, that is, our trajectories are terminated when the first vdW bond dissociates. So, if dissociation of the different He atoms was independent when *n* increases, we should observe the channel $\Delta v = -1$ (that for which I₂ loses only one vibrational quantum) to be the dominant one for all the *n* values. This is found for *n* = 2 (of course for *n* = 1), but not for higher *n*. In fact, we have seen that for *n* = 3 the $\Delta v = -2$ channel becomes almost as probable as the $\Delta v = -1$ one, and for *n* > 3 the channel losing two quanta dominates more up to *n* = 7. As the cluster grows $\Delta v = -3$ and even $\Delta v = -4$ channels become open (with small probability). For *n* = 8 the system returns to a situation in which the $\Delta v = -1$ and $\Delta v = -2$ channels are comparable (still slightly more dominant for the $\Delta v = -2$ one), and for *n* = 9 the $\Delta v = -1$ exiting channel becomes the dominant one again. This different dissociation behavior for the cluster with nine atoms, as compared with smaller clusters, provides one more indication that the ninth rare atom is not equivalent to the other eight ones.

All of the above results enable us to think of the appearance of efficient intramolecular vibrational relaxation (IVR) mechanisms between the chemical and the vdW bonds, and between the vdW bonds themselves, which play a relevant role as *n* increases. It would explain the variation of Γ with *n* observed, and therefore the statistical nature of the dissociation for I₂...He_n clusters. It turns out, then, that although dissociation of vdW bonds is mainly independent for small I₂...He_n clusters (*n* = 1, 2 as observed by Sharfin *et al.*^{8(d)}), when many He atoms are present it has the effect of making the fragmentation of each vdW bond more dependent on the other bonds.

It is possible to get a simple estimate of the IVR time by assuming the total lifetime τ (second column in Table IV) to be

$$\tau = \tau_{\text{IVR}} + \tau_{\text{DIS}},$$

where τ_{IVR} is the IVR time and τ_{DIS} would be just the time in which dissociation occurs. Provided that no IVR exists, $\Gamma_{\text{DIS}}(n)$ would follow a linear behavior,

$$\Gamma_{\text{DIS}}(n) = \Gamma(1)n = 0.44n,$$

and then, using Eq. (23), we have

$$\tau_{\text{DIS}} = \frac{\hbar}{2\Gamma_{\text{DIS}}},$$

and therefore

$$\tau_{\text{IVR}} = \tau - \frac{\hbar}{0.88n}.$$

TABLE V. Estimates of τ_{IVR} and τ_{DIS} (in ps) for *n* = 2–9 (see Sec. III C). In the last column of the table the percentage of τ_{IVR} in the total lifetime τ is displayed.

<i>n</i>	τ_{DIS}	τ_{IVR}	Percent
2	3.01	1.63	35
3	2.01	2.03	50
4	1.51	2.35	61
5	1.20	2.42	67
6	1.00	2.57	72
7	0.86	2.52	75
8	0.75	2.33	76
9	0.67	0.70	51

Table V displays the estimates of τ_{IVR} and τ_{DIS} calculated in this way for *n* = 2–9, together with the percentage of τ_{IVR} in the total lifetime τ (fourth column). We see that *n* = 2 is the only case in which $\tau_{\text{DIS}} > \tau_{\text{IVR}}$ (with the smaller percentage), while for *n* ≥ 3 the opposite behavior, $\tau_{\text{IVR}} > \tau_{\text{DIS}}$ is found (for *n* = 3 they are still comparable). The percentage is observed to increase with *n* up to *n* = 8. Again, *n* = 9 means the breaking down of the general behavior with $\tau_{\text{IVR}} \approx \tau_{\text{DIS}}$. The interaction of this ninth atom with the other ones and with the I₂ molecule seems to be weaker. A possibility consistent with our results is that this atom is in the first excited stretching state, at a longer distance from the I₂ center of mass than the other rare atoms. The estimates of Table V show in a somewhat more quantitative way the relevant role played by redistribution of statistical nature in the dissociation of I₂...He_n clusters as the cluster size increases.

Our model constrains the motions of the vdW bonds to a plane perpendicular to I₂, and perhaps introducing the other degrees of freedom that we have fixed, that is to say, the bending modes out of this plane (in the θ_i coordinates), may vary the number of He atoms in the coordination shell about I₂ somewhat. Further work on this line would be valuable.

IV. CONCLUDING REMARKS

In this paper we have presented an approximate quantal model to study the discrete energy spectrum of small I₂...He_n clusters (*n* = 1–8). Relying on previous results on I₂...He₂, it is assumed that a near-equilibrium geometry exists where the motions of the He atoms are only allowed to take place on a plane perpendicular to the I₂ axis. Energy levels for I₂...He₂ and I₂...He₃ are calculated with a CI treatment. Then, using the ground energy levels obtained for these two clusters, and by means of geometric considerations, the ground-level energies corresponding to clusters with *n* ≥ 4 are estimated. Lifetimes and half-widths for VP of I₂...He_n with *n* = 1–9 have also been calculated by applying a QCT treatment. A sudden jump in both magnitudes for *n* = 9 suggests that there exists a first coordination shell for the helium atoms about I₂, containing eight atoms in equivalent positions. Also, we have found that the half-width varies with *n* as approximately the inverse of the cubic root of *n* from *n* = 1 to *n* = 8. It points out that there appear to exist

internal vibrational relaxation mechanisms which cause the efficiency of the dissociation reaction to decrease as the cluster size increases. Further work introducing the degrees of freedom not considered here, as well as extending the calculations to systems with other rare-gas atoms, seems to be very promising and interesting in order to check for similar behavior of the half-width for VP vs n and the existence of arrangements in coordination shells of the noble atoms for other vdW clusters.

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