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Double continuum fragmentation in the vibrational predissociation $X \cdots BC(v) \cdots Y \rightarrow BC(v' < v) + X + Y$ of van der Waals complexes: A perturbative treatment

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We present an approximate quantal model to study the double continuum problem arising in the complete fragmentation of $X \cdots BC(v) \cdots Y$ van der Waals (vdW) complexes, where BC is a conventional diatomic molecule vibrationally excited and X and Y are rare gas atoms, through vibrational predissociation (VP). Assuming a near equilibrium geometry of the complex and using an adiabatic approximation for describing the oscillation in the angle formed by the $BC \cdots X$ and $BC \cdots Y$ weak bonds, the rates for complete fragmentation are expressed in the frame of Fermi's "Golden Rule". Double continuum wave functions may be obtained by a perturbative treatment that allows one to take properly into account the symmetry of the problem in the particular and very frequent case $X \equiv Y$.

I. INTRODUCTION

The structure and dynamics of vdW complexes containing a chemical bond and two or more rare gas atoms, $BC \cdots X_n$, is receiving increasing attention from both the experimental¹⁻⁴ and theoretical⁵⁻⁷ points of view. In particular, for $n=2$, the main goals of the theoretical calculations are to elucidate the competition in the flow of energy from the vibrationally excited BC molecule towards each weak bond and its dependence on the initial excited state. The quantal treatments^{6(b),7} assume the dissociation of the complex to be sequential, that is, the simultaneous breaking up of both weak bonds is not considered. However, there are four different channels leading to complete fragmentation of a $X \cdots BC \cdots Y$ complex via VP,

Channels (a) and (b) constitute a sequential mechanism where the complete dissociation requires the loss of two vibrational quanta by BC to take place. Channel (c) involves a double continuum fragmentation and, with the exception of energy constraints, may proceed via the loss of one vibrational quantum. When the interaction between rare gases supports bound levels, channel (d) accounts for the possibility that two diatomic fragments emerge via the loss, in principle, of one vibrational quantum by BC.

We have studied,⁷ for the $He \cdots I_2(B) \cdots Ne$ system the first part of channels (a) and (b), the second part representing the VP of a triatomic complex. Although the calculations carried out were approximate, we think that a

similar study on channels (c) and (d) may be useful in order to estimate their relative importance in the VP process of the four-body complex. Of course, this does not exclude the convenience of a rigorous treatment of the full problem, connected to a reactive scattering, by using e.g., hyperspherical coordinates⁸ or a time-dependent wave packet propagation method⁹ able to handle cases of several fragmentation channels quite naturally,¹⁰ which seems more promising.

Recently, Janda *et al.*⁴ have detected the presence of channels (c) and (d) in the VP of Ne_2Cl_2 . In our opinion, since the $Ne \cdots Ne$ interaction supports bound levels, channel (d) seems to be more probable than (c). This case may be studied within a "Golden Rule" treatment by using the coordinates considered by Hutson, Beswick, and Halberstadt¹¹ in the calculation of spectroscopic parameters for the complex Ar_2HCl , and involves the presence of only one continuum in the distance between the center of mass of Ar_2 and that of HCl . In this work we focus our attention on channel (c) involving a double continuum fragmentation. This problem has been extensively treated in connection with ionization of atomic targets by electronic or positronic projectiles¹²⁻¹⁴ as well as inelastic breakup (d, pn) and transfer ($^3He, pp$) nuclear reactions.^{15,16} However, all these are collisional processes and have been studied using Jacobi coordinates. To the best of our knowledge, no attempt has been made to treat such a fragmentation phenomenon as that discussed here, where, in order to compare double continuum fragmentation rates with those associated with single dissociation mechanisms, we use bond $BC-X$ and $BC-Y$ coordinates as in Ref. 7.

The paper is organized as follows. We show in Sec. II how, within a "Golden Rule" frame, the rate for double continuum dissociation may be expressed through a quadrature on the relative kinetic energy of one of frag-

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ments, the only “trouble” resting on the description of the double continuum wave function, that is presented in Sec. III. Although a project to use discretization of continua is in progress, we are not now in position to estimate “exact” two-dimensional double continuum wave functions. Hence, we show in Sec. IV a numerical comparison among exact and perturbative continuum wave functions up to the first order for a one dimensional simulation of the $\text{He} \cdots \text{I}_2 \cdots \text{He}$ problem, and also an estimate of double continuum rates in this case.

II. RATES FOR DOUBLE CONTINUUM DISSOCIATION

We consider a complex $\text{X} \cdots \text{BC} \cdots \text{Y}$, where the atoms X and Y are restricted to move on a plane perpendicular to the nonrotating BC molecule. Using valence coordinates $(r, \mathbf{R}_1, \mathbf{R}_2)$, with r being the BC bondlength and $\mathbf{R}_1$ and $\mathbf{R}_2$ vectors going from the BC center of mass to X and Y, respectively, after a diabatic separation of BC vibrations and an adiabatic one in the oscillation of the angle $\gamma = \arccos(\mathbf{R}_1 \mathbf{R}_2 / R_1 R_2)$, the problem reduces to obtain the solutions of the Schrödinger equation for an effective two dimensional stretching Hamiltonian at selected values of γ , see Eq. (9) of Ref. 7,

$$\mathcal{H}^{(v)}(R_1, R_2, \gamma) = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial R_2^2} + V_{vv}(R_1, R_2, \gamma) \quad (1)$$

with the reduced triatomic masses $\mu_1 = m_X(m_B + m_C)/(m_X + m_B + m_C)$, $\mu_2 = m_Y(m_B + m_C)/(m_Y + m_B + m_C)$. Here V_{vv} stands for an average of the potential energy function V in a given vibrational state v of the isolated BC molecule. [Note that to avoid unnecessary complications, the cross term $-\cos \gamma/(m_B + m_C) \partial^2/\partial R_1 \partial R_2$ has been neglected; it would be included in the angular part.] Representing the potential V by an addition of potentials corresponding to T-shaped X-BC and Y-BC triatomic molecules plus the X-Y interaction,

$$V(r, R_1, R_2, \gamma) = V_{\text{X-BC}}(R_1, r) + V_{\text{Y-BC}}(R_2, r) + V_{\text{X-Y}}(R_1, R_2, \gamma)$$

the averaged potential V_{vv} is

$$V_{vv}(R_1, R_2, \gamma) = \langle v | (V_{\text{X-BC}} + V_{\text{Y-BC}}) | v \rangle + V_{\text{X-Y}} \quad (2)$$

and the Hamiltonian (1) may be rewritten as

$$\mathcal{H}^{(v)}(R_1, R_2, \gamma) = h_X^{(v)}(R_1) + h_Y^{(v)}(R_2) + V_{\text{X-Y}}(R_1, R_2, \gamma), \quad (3)$$

where

$$h_X^{(v)} = -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial R_1^2} + \langle v | V_{\text{X-BC}} | v \rangle,$$

$$h_Y^{(v)} = -\frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial R_2^2} + \langle v | V_{\text{Y-BC}} | v \rangle. \quad (4)$$

The discrete spectrum of $\mathcal{H}^{(v)}$ may be obtained by representing it in a basis of products $\{\xi_m^{(v)}(R_1) \cdot \eta_n^{(v)}(R_2)\}_{m,n}$ of eigenfunctions of $h_X^{(v)}$, $\{\xi_m\}$, and $h_Y^{(v)}$, $\{\eta_n\}$, and diagonalizing the resulting matrix. Discrete wave functions become linear combinations,

$$\varphi_{v,\kappa}^{\text{dis}}(R_1, R_2, \gamma) = \sum_{m,n} a_{m,n}^{(v,\kappa)}(\gamma) \xi_m^{(v)}(R_1) \eta_n^{(v)}(R_2), \quad (5)$$

where κ is a two-dimensional vibrational quantum number, with γ -dependent associated eigenvalues $W_\kappa^{(v)}(\gamma)$ that constitute, by varying γ , effective potentials for the angular motion. [Note that an averaged term

$$-\frac{\cos \gamma}{(m_B + m_C)} \left(\varphi_{v,\kappa}^{\text{dis}} \left| \frac{\partial^2}{\partial R_1 \partial R_2} \right| \varphi_{v,\kappa}^{\text{dis}} \right)$$

must now be added to $W_\kappa^{(v)}$ in Eq. (A1) of Ref. 7.]

Let us suppose that we have obtained an acceptable double continuum (dc) wave function for a Hamiltonian $\mathcal{H}^{(v')}$ of type (3), with $v' < v$,

$$\mathcal{H}^{(v')} \varphi_{v',\epsilon_X,\epsilon_Y}^{\text{dc}}(R_1, R_2, \gamma) = E \varphi_{v',\epsilon_X,\epsilon_Y}^{\text{dc}}(R_1, R_2, \gamma), \quad (6)$$

normalized to a product of δ functions in energy

$$\langle \varphi_{v',\epsilon_X,\epsilon_Y}^{\text{dc}} | \varphi_{v',\epsilon_X,\epsilon_Y}^{\text{dc}} \rangle = \delta(\epsilon_X - \epsilon_X) \delta(\epsilon_Y - \epsilon_Y), \quad (7)$$

where ϵ_X stands for the relative kinetic energy between X and BC. Similarly, ϵ_Y is the relative kinetic energy Y-BC. The total available energy E , equal to the difference of energy between levels v and v' of the isolated BC molecule plus $W_\kappa^{(v)}(\gamma)$, must be

$$E = E_{\text{BC}}(v) - E_{\text{BC}}(v') + W_\kappa^{(v)}(\gamma) = \epsilon_X + \epsilon_Y. \quad (8)$$

In the frame of the Golden Rule, the “probability” in a broad sense of X and Y escaping at the same time with energies ϵ_X and $\epsilon_Y = E - \epsilon_X$ would be proportional to the square of the discrete-dc coupling,

$$\mathbf{P}(\epsilon_X; \gamma) = \pi \left| \langle \varphi_{v,\kappa}^{\text{dis}} | V_{vv'} | \varphi_{v',\epsilon_X,E-\epsilon_X}^{\text{dc}} \rangle_{R_1, R_2} \right|^2, \quad (9)$$

where the quadrature is taken over R_1 and R_2 and

$$V_{vv'}(R_1, R_2) = \langle v | V_{\text{X-BC}}(r, R_1) + V_{\text{Y-BC}}(r, R_2) | v' \rangle_r$$

is the relevant potential coupling.

Obviously, the energy available E can be shared between both rare gas atoms in all the possible ways restricted to condition (8). Assuming that *no interference* among these ways takes place, the rate for dc fragmentation may be evaluated by integrating over all of them,

$$\Gamma_{v,\kappa-v',E}^{\text{dc}}(\gamma) = \int_0^E d\epsilon_X \mathbf{P}_{v,\kappa-v',E}(\epsilon_X; \gamma). \quad (10)$$

Now, by performing this quadrature at selected values of γ and further averaging on the angular functions obtained in solving the discrete problem,⁷ the rate for vibrational predissociation of the complex yielding three fragments—two rare atoms and the diatomic molecule—may be calculated.

III. DOUBLE CONTINUUM WAVE FUNCTIONS

A. Simple approach

As a first attempt, we may propose for dc wave functions, satisfying Eqs. (6) and (7), the following product,

$$\varphi_{v', \epsilon_X, E - \epsilon_X}^{\text{dc}}(R_1, R_2; \gamma) = \xi_{\epsilon_X}^{(v')} (R_1) \eta_{\epsilon_X, E - \epsilon_X}^{(v')} (R_2; \gamma), \quad (11)$$

where $\xi_{\epsilon_X}^{(v')}$ is a continuum wave function of $h_X^{(v')}$, Eq. (4), with a typical sine behavior at long distances and energy normalization,

$$\langle \xi_{\epsilon_X}^{(v')} | \xi_{\epsilon_X}^{(v')} \rangle = \delta(\epsilon_X - \epsilon_X).$$

By considering the quadrature over R_1

$$\langle \xi_{\epsilon_X}^{(v')} | \mathcal{H}^{(v')} | \varphi_{v', \epsilon_X, E - \epsilon_X}^{\text{dc}} \rangle_{R_1}$$

with $\xi_{\epsilon_X}^{(v')}$ also a continuum wave function of $h_X^{(v')}$ corresponding to an energy ϵ_X' in the range $(0, E)$, the following equation for η in Eq. (11) is obtained

$$[(\epsilon_X' + h_Y^{(v')}) \delta(\epsilon_X' - \epsilon_X) + \langle \xi_{\epsilon_X'}^{(v')} | V_{X-Y} | \xi_{\epsilon_X}^{(v')} \rangle] \eta^{(v')} = E \delta(\epsilon_X' - \epsilon_X) \eta^{(v')}.$$

Therefore, after integration over ϵ_X' , the $\eta^{(v')}$ function becomes a continuum wave function of the modified Hamiltonian

$$h_Y^{(v')} = h_Y^{(v')} + \int_0^E d\epsilon_X' \langle \xi_{\epsilon_X'}^{(v')} | V_{X-Y} | \xi_{\epsilon_X}^{(v')} \rangle_{R_1} \quad (12)$$

with energy $\epsilon_Y = E - \epsilon_X$. This resembles a first step of a SCF procedure¹⁷ successfully used in discrete problems. Unfortunately, iteration of this process is not energy conserving, i.e., the energy E changes. This is the goal in the discrete case, the energy going to a discrete level in the convergence limit. However, in the continuum part of spectrum, this is a serious hinderance since the disposal energy E must remain constant. Physically, the model assumes that the Y particle “feels” all the X–Y interaction, while X is escaping only on the X–BC(v') potential energy curve. Of course, depending on the situation, i.e., the relative strength of X–BC(v') and Y–BC(v') interactions, this may result acceptable. On the contrary, this treatment becomes formally unsatisfactory in the frequent case $X \equiv Y$, for which Eq. (19) yields different “probabilities”,

$$P(\epsilon_X; \gamma) \neq P(E - \epsilon_X; \gamma) \quad (13)$$

since $\varphi_{v', \epsilon_X, E - \epsilon_X}^{\text{dc}}$ is, in principle, different from $\varphi_{v', E - \epsilon_X, \epsilon_X}^{\text{dc}}$.

B. Perturbative continuum wave functions: One-dimensional case

In one-dimensional problems the search for continuum wave functions at energy $E > 0$ corresponding to a Hamiltonian

$$H = H_0 + V,$$

provided that the corresponding ones for H_0 are already known, constitutes the usual scattering problem with the formal Lippmann–Schwinger solution

$$\varphi_E^{(\pm)}(x) = \varphi_E^0(x) + G_0^{(\pm)}(E) V \varphi_E^{(\pm)}(x). \quad (14)$$

Here, φ_E^0 is a standing wave continuum function of H_0 , i.e., it asymptotically behaves as a sine function and is normalized in energy to a δ function, and $G_0^{(\pm)}$ stands for the resolvent operator

$$G_0^{(\pm)}(E) = \lim_{\epsilon \rightarrow 0^+} (E - H_0 \pm i\epsilon)^{-1}.$$

Introducing now the unit operator

$$\mathcal{I} = \int dE' |\varphi_{E'}^0\rangle \langle \varphi_{E'}^0| + \sum_n |\varphi_n^0\rangle \langle \varphi_n^0|,$$

where the sum runs over discrete states of H_0 , the desired solution $\varphi_E^{(\pm)}$, that now becomes an incoming (—) or outgoing (+) continuum wave function, satisfies the following integral equation:

$$\begin{aligned} \varphi_E^{(\pm)}(x) = & [1 \mp i\pi \langle \varphi_E^0 | V | \varphi_E^{(\pm)} \rangle] \varphi_E^0(x) \\ & + \mathcal{P} \int dE' \frac{\langle \varphi_{E'}^0 | V | \varphi_E^{(\pm)} \rangle}{E - E'} \varphi_{E'}^0(x) \\ & + \sum_n \frac{\langle \varphi_n^0 | V | \varphi_E^{(\pm)} \rangle}{E - E_n} \varphi_n^0(x) \end{aligned} \quad (15)$$

where “ $\mathcal{P}$ ” denotes “principal part”, i.e., integration on the real E' axis except at $E' = E$. Substitution of $\varphi_E^{(\pm)}$ on the right-hand side of Eq. (15) by φ_E^0 leads to the first-order Born approximation,

$$\begin{aligned} \varphi_E^{(\pm)}(x) \simeq & [1 \mp i\pi V_{EE}] \varphi_E^0(x) \\ & + \mathcal{P} \int dE' \frac{V_{EE}}{E - E'} \varphi_{E'}^0(x) \\ & + \sum_n \frac{V_{nE}}{E - E_n} \varphi_n^0(x), \end{aligned} \quad (16)$$

where $V_{EE} = \langle \varphi_E^0 | V | \varphi_E^0 \rangle$ and $V_{nE} = \langle \varphi_n^0 | V | \varphi_E^0 \rangle$. Iteration of this process gives rise to the well-known Born expansion.

At this stage we will not pay attention to the divergence problem of the Born series¹⁸ appearing in the very low energy regime. We shall instead focus our attention on the first order perturbative expression, Eq. (16). Choosing the incoming solution, as usual in photofragmentation processes,¹⁹ we have asymptotically

$$\begin{aligned} \varphi_E^{(-)}(x) \sim & (1 + i\pi V_{EE}) \sin(\kappa_E x + \delta_0) \\ & - \pi V_{EE} \cos(\kappa_E x + \delta_0), \end{aligned} \quad (17)$$

where $\kappa_E = \sqrt{2\mu E}$ is the relevant inverse wavelength, δ_0 the phase shift produced by H_0 and use has been made of the relation²⁰

$$\mathcal{P} \int dE' \frac{V_{EE'}}{E - E'} \sin(\kappa_{E'}x + \delta_0) \sim_{x \rightarrow \infty} -\pi V_{EE} \cos(\kappa_E x + \delta_0) \quad (18)$$

Now, replacing the sine and cosine functions by their well-known expressions in terms of exponential functions, we obtain

$$\varphi_E^{(-)}(x) \sim_{x \rightarrow \infty} \frac{1}{2i} \{ e^{i(\kappa_E x + \delta_0)} - (1 + 2i\pi V_{EE}) e^{-i(\kappa_E x + \delta_0)} \},$$

where, as long as the first-order perturbation approximation holds, the factor $1 + 2i\pi V_{EE}$ may be identified with the complex conjugate of the relevant scattering matrix, i.e.,

$$1 + 2i\pi V_{EE} \simeq e^{i2\pi V_{EE}} = e^{-i\Delta}. \quad (19)$$

$\Delta = -\pi V_{EE}$ is the phase shift due to the perturbation V . Now, the incoming solution can be rewritten in terms of that of a standing wave:

$$\varphi_E^{(-)}(x) \sim_{x \rightarrow \infty} e^{-i\Delta} \sin(\kappa_E x + \delta_0 + \Delta)$$

or

$$\varphi_E(x) = \varphi_E^{(-)}(x) e^{i\Delta} \sim_{x \rightarrow \infty} \sin(\kappa_E x + \delta_0 + \Delta). \quad (20)$$

Hence, by replacing $\varphi_E^{(-)}$ by its expression, Eq. (16),

$$\begin{aligned} \varphi_E(x) &= e^{-i\pi V_{EE}} \left\{ (1 + i\pi V_{EE}) \varphi_E^0(x) + \mathcal{P} \int \dots + \sum \dots \right\} \\ &\simeq (1 - i\pi V_{EE}) \{ \dots \} \end{aligned}$$

and retaining only first-order terms, we obtain

$$\begin{aligned} \varphi_E(x) &= \varphi_E^0(x) + \mathcal{P} \int dE' \frac{V_{EE'}}{E - E'} \varphi_E^0(x) \\ &+ \sum_n \frac{V_{nE}}{E - E_n} \varphi_n^0(x). \end{aligned} \quad (21)$$

This constitutes our first-order standing wave solution in terms of the (assumed) known spectrum of H_0 . In fact, taking in Eq. (21) the limit $x \rightarrow \infty$, and using Eq. (18), we have

$$\begin{aligned} \varphi_E(x) &\sim_{x \rightarrow \infty} \sin(\kappa_E x + \delta_0) \\ &- \pi V_{EE} \cos(\kappa_E x + \delta_0) \\ &\quad \text{1st order} \\ &\simeq \sin(\kappa_E x + \delta_0 - \pi V_{EE}) \end{aligned}$$

in complete agreement with Eq. (20). Thus, expression (21) tells us that the standing wave solution of the scattering problem, up to the first order in the Born series, reduces to the real part of the corresponding incoming or outgoing wave. From Eq. (21) we can also see how small will be the contribution of the last term, arising from the

discrete spectrum of H_0 , for medium and high energies. Although this is outside the scope of this work, the last term suggests the possibility of partially avoiding the divergence problem of the Born series at low energies by using a distorted-wave approximation, i.e., starting from a zero-order Hamiltonian including bound levels, instead of making the usual assumption that H_0 has only continuum eigenstates.¹⁸

C. Perturbative double continuum wave functions

The literal translation from the one- to two-dimensional case reads as follows: We want to obtain stationary dc wave functions of energy $E = \epsilon_x + \epsilon_y$ for a Hamiltonian

$$H(x, y) = h_X(x) + h_Y(y) + V_{X-Y}(x, y),$$

where h_X and h_Y are assumed to have known spectra and V_{X-Y} stands for a “small” perturbation. The procedure to reach them will be, however, somewhat different, except that only the real part will be retained as a solution. We start by writing

$$\begin{aligned} \Psi_E^{(\epsilon_x \epsilon_y)}(x, y) &= \xi_{\epsilon_x}(x) \eta_{\epsilon_y}(y) \\ &+ \int \int d\epsilon'_x d\epsilon'_y b_{\epsilon'_x \epsilon'_y} \xi_{\epsilon'_x}(x) \eta_{\epsilon'_y}(y) \\ &+ \sum_{nm} a_{nm} \xi_n(x) \eta_m(y), \end{aligned} \quad (22)$$

where ξ_{ϵ_x} , ξ_n are standing continuum and discrete wave functions of h_X , respectively, and likewise η_{ϵ_y} and η_m with respect to h_Y . By calculating the matrix element

$$\begin{aligned} \langle \xi_n \eta_m | H | \Psi_E^{(\epsilon_x \epsilon_y)} \rangle &= E \langle \xi_n \eta_m | \Psi_E^{(\epsilon_x \epsilon_y)} \rangle \\ &= E a_{nm} = (E_n + E_m) a_{nm} \\ &+ \langle \xi_n \eta_m | V_{X-Y} | \Psi_E^{(E_x E_y)} \rangle, \end{aligned}$$

we obtain

$$a_{nm} = \frac{\langle \xi_n \eta_m | V_{X-Y} | \Psi_E^{(\epsilon_x \epsilon_y)} \rangle}{E - (E_n + E_m)}.$$

Also,

$$\begin{aligned} \langle \xi_{\epsilon'_x} \eta_{\epsilon'_y} | H | \Psi_E^{(\epsilon_x \epsilon_y)} \rangle &= [\delta(\epsilon'_x - \epsilon_x) \delta(\epsilon'_y - \epsilon_y) + b_{\epsilon'_x \epsilon'_y}] E \\ &= (\epsilon'_x + \epsilon'_y) [\delta(\epsilon'_x - \epsilon_x) \delta(\epsilon'_y - \epsilon_y) + b_{\epsilon'_x \epsilon'_y}] \\ &+ \langle \xi_{\epsilon'_x} \eta_{\epsilon'_y} | V_{X-Y} | \Psi_E^{(\epsilon_x \epsilon_y)} \rangle. \end{aligned}$$

Thus,

$$\begin{aligned} [E - (\epsilon'_x + \epsilon'_y)] [\delta(\epsilon'_x - \epsilon_x) \delta(\epsilon'_y - \epsilon_y) + b_{\epsilon'_x \epsilon'_y}] \\ = \langle \xi_{\epsilon'_x} \eta_{\epsilon'_y} | V_{X-Y} | \Psi_E^{(\epsilon_x \epsilon_y)} \rangle \end{aligned}$$

since $\epsilon_x + \epsilon_y = E$, we obtain

$$\begin{aligned}
\Psi_E^{(\epsilon_x \epsilon_y)}(x, y) &= \xi_{\epsilon_x}(x) \eta_{\epsilon_y}(y) + \int_0^E d\epsilon'_x [\mathcal{P}_{\epsilon'_y \neq E - \epsilon'_x} \\
&\times \int d\epsilon'_y \frac{\langle \xi_{\epsilon'_x} \eta_{\epsilon'_y} | V_{X-Y} | \Psi_E^{(\epsilon_x \epsilon_y)} \rangle}{E - \epsilon'_x - \epsilon'_y} \xi_{\epsilon'_x}(x) \\
&\times \eta_{\epsilon'_y}(y) + i\pi \langle \xi_{\epsilon'_x} \eta_{E - \epsilon'_x} | V_{X-Y} | \Psi_E^{(\epsilon_x \epsilon_y)} \rangle \xi_{\epsilon'_x}(x) \\
&\times \eta_{E - \epsilon'_x}(y)] + \sum_{nm} \frac{\langle \xi_n \eta_m | V_{X-Y} | \Psi_E^{(\epsilon_x \epsilon_y)} \rangle}{E - E_n - E_m} \xi_n(x) \eta_m(y).
\end{aligned}$$

Replacing in the right-hand side of this expression $\Psi_E^{(\epsilon_x \epsilon_y)}$ by the first term $\xi_{\epsilon_x} \eta_{\epsilon_y}$, we have the first-order perturbation,

$$\begin{aligned}
\Psi_{E, \epsilon_x}^{(-)} &\simeq \xi_{\epsilon_x} \eta_{E - \epsilon_x} + \int d\epsilon'_x \mathcal{P}_{\epsilon'_y \neq E - \epsilon'_x} \\
&\times \int d\epsilon'_y \frac{V_{\epsilon'_x \epsilon'_y; \epsilon_x E - \epsilon_x}^{X-Y}}{E - \epsilon'_x - \epsilon'_y} \xi_{\epsilon'_x} \eta_{\epsilon'_y} \\
&+ i\pi \int_0^E d\epsilon'_x V_{(\epsilon'_x E - \epsilon'_x; \epsilon_x E - \epsilon_x) \xi_{\epsilon'_x} X-Y}^{\epsilon'_x \eta_{E - \epsilon'_x}} \\
&+ \sum_{nm} \frac{V_{n, m; \epsilon_x E - \epsilon_x}^{X-Y}}{E - E_n - E_m} \xi_n \eta_m.
\end{aligned}$$

Accounting for only the real part of this equation, we obtain the stationary solution

$$\begin{aligned}
\Psi_{E, \epsilon_x} &\simeq \xi_{\epsilon_x} \eta_{E - \epsilon_x} + \mathcal{P} \int \int d\epsilon'_x d\epsilon'_y \frac{V_{\epsilon'_x \epsilon'_y; \epsilon_x E - \epsilon_x}^{X-Y}}{E - \epsilon'_x - \epsilon'_y} \\
&\times \xi_{\epsilon'_x} \eta_{\epsilon'_y} + \sum_{nm} \frac{V_{n, m; \epsilon_x E - \epsilon_x}^{X-Y}}{E - E_n - E_m} \xi_n \eta_m, \quad (23)
\end{aligned}$$

where the principal part $\mathcal{P}$ extends the double integration over all the values ϵ'_x, ϵ'_y except those couples such that $\epsilon'_x + \epsilon'_y = E$, and the V symbols stand for obvious double integrations over x and y , for instance,

$$\begin{aligned}
V_{\epsilon'_x \epsilon'_y; \epsilon_x E - \epsilon_x}^{X-Y} &= \langle \xi_{\epsilon'_x}(x) \eta_{\epsilon'_y}(y) | V_{X-Y}(x, y) | \xi_{\epsilon_x}(x) \eta_{E - \epsilon_x}(y) \rangle.
\end{aligned}$$

Expression (23) constitutes our final result for perturbative stationary dc wave functions. Indeed, for $X \equiv Y$, i.e., $h_X \equiv h_Y$, the proper symmetry is automatically accounted for in this treatment.

IV. RESULTS

A. One-dimensional simulation

In order to check the reliability of the two-dimensional perturbative dc wave functions, we present a one-dimensional simulation of the He-I₂-He problem, as a starting point, by using the approximation of Sec. III B. Such simulation consists in fixing one He atom at its equi-

librium distance from I₂. Both weak bonds, placed in a normal plane to the iodine axis, form an angle γ . In this way, the escaping He atom feels the interaction with I₂ as well as that of the other "static" He atom, described by means of model Morse potentials,

$$U_i = D_i \{ \exp[2\alpha_i(\bar{R}_i - R_i)] - 2 \exp[\alpha_i(\bar{R}_i - R_i)] \},$$

where $i=1,2$ stands for He-I₂ and He-He interactions, respectively. The first of them is taken from the He-I Morse potential^{21a} by simply multiplying by two the corresponding well depth, while keeping unaltered the characteristic inverse length and the equilibrium distance, i.e.,

$$D_1 = 33 \text{ cm}^{-1}, \quad \alpha_1 = 1.5 \text{ \AA}^{-1}, \quad \bar{R}_1 = 4.0 \text{ \AA}.$$

The He-He potential is taken from the literature.^{21b}

$$D_2 = 3.785(-5) \text{ a.u.}, \quad \alpha_2 = 1.17 \text{ a.u.}, \quad \bar{R}_2 = 5.59 \text{ a.u.}$$

The He-He distance can be expressed in terms of R_1 , the He-I₂ distance, and the angle γ by the trigonometric relation

$$R_2 = [R_1^2 + \bar{R}_1^2 - 2R_1\bar{R}_1 \cos \gamma]^{1/2}.$$

Of course, either the zeroth-order problem,

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR_1^2} + U_1(R_1) \right] \varphi_E^0(R_1) = E \varphi_E^0(R_1), \quad (24)$$

or the full one

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR_1^2} + U_1(R_1) + U_2(R_1, \gamma) \right] \varphi_E(R_1) = E \varphi_E(R_1) \quad (25)$$

can be numerically solved by outward Numerov propagation of the solution and matching of it to sine forms at long distances.²² For an energy $E = 48.6 \text{ cm}^{-1}$, that roughly corresponds to the available energy in the complete fragmentation of the tetraatomic complex with I₂ in the $v=24$ vibrational level, emerging in the $v=23$ one, and for different values of γ , we have obtained the full solution [Eq. (25)], the zeroth-order approximation [Eq. (24)], and the first order perturbative one [Eq. (21)]. In order to estimate the accuracy of the successive levels of approximation, two kinds of quantities have been calculated: the phase shifts and the relative distances between approximations and the full solution defined by

$$I^{(j)} = \frac{\|\varphi_E^{(j)} - \varphi_E\|}{\|\varphi_E\|}, \quad j=0,1, \quad \|\varphi\| = \left[\int_{\text{RIN}}^{\text{RFIN}} \varphi^2 dx \right]^{1/2}.$$

A grid of 2000 points in the range [$\text{RIN} = 4 \text{ a.u.}$, $\text{RFIN} = 20 \text{ a.u.}$] has been used to perform zeroth order and exact calculations, while 20 points of a Gauss-Chebyshev quadrature in the range $[0, 2E]$ proved sufficient to achieve convergency of Eq. (21), where the V_{EE} terms were evaluated through a $h/3$ Simpson rule, h being the integration step. Since the energy E is far from bound levels of H_0 , the last term in that equation was neglected at this stage.

FIG. 1. 1D simulation of the He-I₂-He system: Phase shifts at different angles between both weak bonds of the exact continuum wavefunction (dots) the zeroth order wavefunction (crosses) and the first order perturbative one (open circles).

The results for phase shifts and relative distances are plotted in Figs. 1 and 2, respectively, as functions of the angle. For $\gamma < 40^\circ$ the perturbative method does not work since the relative distances become greater than unity, which means an error larger than 100%. In fact for low angles the rare atoms feel a high repulsion and the “perturbation” is no longer small. However, even in this problematic region one can observe that the first order phase shift changes in the right way, i.e., it deviates from the zeroth-order value, which is completely wrong, and approaches the exact one. For $\gamma > 40^\circ$, both kinds of results show the encouraging behavior of the first order approximation. Indeed, for large γ values, e.g. 90° , even the zeroth order becomes sufficiently accurate. All these results may be qualitatively understood by examining the interaction felt by the escaping He atom as a function of the angle and the distance to I₂, that is plotted in Fig. 3. In the region of high angular values, this interaction practically coincides with the He-I₂ potential, i.e., the He-He interaction results negligible. On the contrary, as γ decreases, the repulsion is more and more important and the full interaction becomes no longer attractive.

FIG. 2. 1D simulation of the He-I₂-He system: relative distances between the zeroth order (dots) or the first order perturbative wavefunctions (open circles) and the exact one as functions of the angle formed by the weak bonds.

Therefore, from this one-dimensional simulation we may expect the two-dimensional perturbative treatment of dc fragmentation to be applicable at least to systems like the one tested here. In addition, there is nothing dramatic in the behavior observed at low angles since, within an adiabatic angular treatment, this region has a negligible contribution to the final averaged rates owing to the small probability to find the complex there (see, for instance, Fig. 1 in Ref. 7).

B. Two-dimensional double continuum rates

The approximations developed in the preceding sections have been numerically tested on the He-I₂ ($v=24$)—He complex, where the rare gas atoms are restricted to move on a perpendicular plane to the iodine and the angle between He-I₂ bonds is fixed at its equilibrium value, $\gamma \simeq 41^\circ$.

In order to obtain the metastable ground van der Waals level as well as single and double fragmentation rates, the remaining potential, once the iodine stretching vibration has been diabatically separated, is expanded in a Taylor series up to the linear term around the I₂ equilibrium bondlength.

With the exception of the averaging and potential coupling calculations, that become analytical after the expansion mentioned above, all the necessary integrals have been numerically evaluated by Gauss-Chebyshev quadratures using 50 points in distances and 20 points in energies, that suffice to obtain six correct decimal figures.

Following the same variational procedure described in Ref. 7, the relevant averaged two-dimensional Hamiltonian is represented in a basis of products of numerical discrete states corresponding to T-shaped He-I₂ triatomic molecules, the tetraatomic discrete states being obtained by further diagonalization of the corresponding matrix. In the particular configuration accounted for here, the triatomic He-I₂ shows two stretching van der Waals levels placed at -19.10 and -2.214 wave numbers with respect to the I₂ vibrational energy at $v=24$. For $v=23$, as a manifestation of the blue-shift variation, they appear at -19.05 and -2.189 wave numbers, respectively. Hence, the lowest of the four tetraatomic levels obtained by diagonalization has an energy of -44.46 cm^{-1} measured from the I₂ ($v=24$) vibrational level.

Complete fragmentation rates (CFR) were evaluated following the procedure outlined in Sec. II by using as dc wave functions those obtained through the simple approach of Sec. III A, and also the zeroth and first-order perturbative ones of Sec. III C. In Fig. 4 we plot the “probabilities” [Eq. (9)] of complete fragmentation obtained in the three ways as a function of the relative kinetic energy of one of the escaping rare atoms relative to that of I₂ in a lower vibrational state $v=23$. As can be seen, the zeroth- and first-order perturbative results are very close, owing to the small contribution of the He-He interaction, with values almost constant in all the energy range, although one can see a weak propensity for both He atoms to escape with very different energy. Of course, the energy distribution in

FIG. 3. 1D simulation of the He-I₂-He system: Variation of the interaction felt by escaping rare atom as a function of the distance R to the center of mass of iodine and of the angle between the weak bonds.

these two cases becomes completely symmetrical. As expected from inequality (13), this requirement is not fulfilled in the simple approach calculations, and the distribution of “probabilities” becomes asymmetrical with sharp variations depending on the energy. However, a similar tendency to the escape of the He fragments with very different energy is more acute in this case. After averaging Eq. (10) in energy the rates for complete fragmentation within the perturbative scheme in zeroth and first order remain very close, 0.000 043 and 0.000 040 cm⁻¹, respectively, while the simple approach yields a value of 0.000 111 cm⁻¹, almost three times larger. This kind of wrong result is not surprising since the symmetry conditions imposed by the system must be fulfilled.

FIG. 4. 2D complete fragmentation of the He-I₂-He system: Dependence of the “probability” of escape one He atom on its relative kinetic energy with respect the iodine while the other He atom escapes with a complementary relative energy. Stars: simple approach; triangles: zeroth order approximation; open circles: first order perturbative approximation. The total available energy is 48.62 cm⁻¹.

With the aim of estimating relative probabilities of fragmentation, single fragmentation rates (SFR) were evaluated by using the scheme already applied to the He-I₂-Ne complex,⁷ except that in the present case only the breaking up of one of the rare atom-iodine bonds needs to be studied. In this way, the SFR for He-I₂($\nu = 24$)-He becomes 0.554 028 cm⁻¹, the most important part, (0.552 413 cm⁻¹), corresponding to a triatomic He-I₂($\nu = 23$) fragment in its ground van der Waals level, and the rest (0.001 615 cm⁻¹) to a stretching excited complex.

Assuming the first-order perturbative value is the correct one for describing the complete fragmentation of the complex, we obtain for this process the almost negligible probability

$$P_{\text{CFR}} = \frac{\Gamma_{\text{CFR}}}{\Gamma_{\text{SFR}} + \Gamma_{\text{CFR}}} = 8 \times 10^{-5}$$

and, because the He-He does not support bound levels, the sequential mechanism of dissociation dominates in this complex. We do not expect that the full calculation, including several angles and further averaging, is going to change qualitatively this estimate. On the other hand, a larger expansion of the potential up to the third order, achieving convergency, as well as the consideration of the $\Delta v = -2$ channel, modifies the values of $\Gamma_{\text{SFR}} (\sim 0.3 \text{ cm}^{-1})$ and $\Gamma_{\text{CFR}} (\sim 1 \times 10^{-5} \text{ cm}^{-1})$ but the probability of complete fragmentation remains extremely small ($P_{\text{CFR}} \sim 3 \times 10^{-5}$). In addition, anharmonicity effects of the iodine vibration may play an important role in sharing the fragmentation rate between both, sequential and direct or complete mechanisms. Hence calculations in different regions of initial vibrational excitation of iodine within the tetraatomic complex could be interesting.

V. CONCLUSIONS

We have presented an approximate treatment to estimate complete fragmentation rates of tetraatomic $X \cdots BC \cdots Y$ van der Waals complexes through vibrational predissociation. They are being evaluated by quadrature on the kinetic energy of one of the escaping rare gas atoms of the corresponding "Golden-Rule" probabilities. Besides a simple approach to describe dc wave functions including the X-Y interaction, we propose a first-order Born expression that accounts for the proper symmetry of the problem in the particular and important case $X=Y$. A one-dimensional perturbative simulation on the He-I₂-He complex demonstrates the feasibility of applying this scheme in the two dimensional case. Numerical estimates of complete fragmentation rate in that system stress the necessity of accounting for the symmetry of the problem, although at the level of approximation used and for medium initial vibrational excitations of the diatomic considered here, the complete dissociation seems to be an almost forbidden channel of fragmentation of the complex.

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- ¹ (a) W. Sharfin, K. E. Johnson, L. Wharton, and D. H. Levy, *J. Chem. Phys.* **71**, 1292 (1979); (b) J. E. Kenny, K. E. Johnson, W. Sharfin, and D. H. Levy, *ibid.* **72**, 1109 (1980); (c) K. E. Johnson, W. Sharfin, and D. H. Levy, *ibid.* **74**, 163 (1981).
- ² J. C. Drobits and M. I. Lester, *J. Chem. Phys.* **86**, 1662 (1987).
- ³ B. A. Schwartz, D. E. Brinza, C. M. Western, and K. C. Janda, *J. Phys. Chem.* **88**, 6272 (1984).
- ⁴ S. R. Hair, J. I. Cline, C. R. Bieler, and K. C. Janda, *J. Chem. Phys.* **90**, 2935 (1989).
- ⁵ (a) G. C. Schatz, V. Buch, M. A. Ratner, and R. B. Gerber, *J. Chem. Phys.* **79**, 1808 (1983); (b) M. A. Ratner and R. B. Gerber, *ibid.* **90**, 20 (1986).
- ⁶ (a) N. Martín, G. Delgado-Barrio, P. Villarreal, P. Mareca, and S. Miret Artés, *J. Mol. Struct.* **142**, 501 (1986); (b) G. Delgado-Barrio, P. Villarreal, A. Varadé, N. Martín and A. García-Vela, in *Structure and Dynamics of Weakly Bound Molecular Complexes*. NATO ASI Series C, Vol. 212, edited by A. Weber (Reidel, Dordrecht, 1987), p. 573.
- ⁷ P. Villarreal, A. Varadé, and G. Delgado-Barrio, *J. Chem. Phys.* **90**, 2648 (1989).
- ⁸ (a) R. Schinke and V. Engel, *Chem. Phys. Lett.* **124**, 504 (1986); (b) K. C. Kulander, *Chem. Phys. Lett.* **129**, 353 (1986).
- ⁹ E. J. Heller, *Acc. Chem. Res.* **14**, 368 (1981).
- ¹⁰ (a) K. C. Kulander and A. E. Orel, *J. Chem. Phys.* **85**, 834 (1986); (b) M. Jacon, O. Atabek, and C. Leforestier, *J. Chem. Phys.* **91**, 1585 (1989).
- ¹¹ J. M. Hutson, J. A. Beswick, and N. Halberstadt, *J. Chem. Phys.* **90**, 1337 (1989).
- ¹² H. Ehrhardt, K. Jung, G. Knoth, and P. Schlemmer, *Z. Phys. D* **1**, 3 (1986).
- ¹³ M. K. Srivastava and S. Sharma, *Phys. Rev. A* **37**, 628 (1988) and references therein.
- ¹⁴ M. Brauner, J. S. Briggs, and H. Klar, *J. Phys. B: At. Mol. Phys.* **22**, 2265 (1989).
- ¹⁵ (a) H. Amakawa and T. Tamura, *Phys. Rev. C* **26**, 904 (1982); (b) H. Amakawa, N. Austern, and C. M. Vincent, *Phys. Rev. C* **29**, 699 (1984); (c) N. Austern, *Phys. Rev. C* **30**, 1130 (1984); (d) N. Austern, *Direct Nuclear Reaction Theories* (Wiley, New York, 1970).
- ¹⁶ M. Yahiro, J. A. Tostevin, and R. C. Johnson, *Phys. Rev. Lett.* **62**, 133 (1989).
- ¹⁷ R. B. Gerber and M. A. Ratner, *Advan. Chem. Phys.* **LXX**(1), 97 (1988).
- ¹⁸ From the pioneering works of S. Weinberg, *Phys. Rev.* **130**, 776 (1963); **131**, 440 (1963), introducing the concept of "quasiparticles" to overcome this serious difficulty, several works have been addressed in the same direction. See, e.g., the formal theory of equivalent potentials in solids developed by J. Rubio and F. García-Moliner, *Proc. Phys. Soc.* **91**, 739 (1967); **92**, 206 (1967).
- ¹⁹ G. G. Balint-Kurti and M. Shapiro, *Chem. Phys.* **61**, 137 (1981).
- ²⁰ U. Fano, *Phys. Rev.* **124**, 1866 (1961).
- ²¹ (a) E. de Pablo, M. S. Guijarro, P. Villarreal, P. Mareca, and G. Delgado-Barrio, *An. Fis.* **A80**, 210 (1984); (b) M. C. Donnamaría, E. A. Castro, and M. Fernández, *J. Chem. Phys.* **80**, 1179 (1983).
- ²² O. Roncero, S. Miret-Artés, G. Delgado-Barrio, and P. Villarreal, *J. Chem. Phys.* **85**, 2084 (1986).