

# Perpendicular vibrational predissociation of T-shaped van der Waals molecules

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In this paper we present a numerical quantum mechanical study for vibrational predissociation on a single electronic potential surface of a T-shaped van der Waals molecule



where X is a rare-gas atom while BC is a conventional diatomic molecule. The rare-gas atom is constrained to move on a line perpendicular to the interatomic axis of the BC molecule. The interaction between X and atoms B and C is represented by a sum of Morse atom-atom potentials. The close-coupling scattering equations were solved numerically and the vibrational predissociation rates were related to the widths of the resulting resonances. The method is applied to the HeI<sub>2</sub> (B) van der Waals complex. We also present numerical results for the vibrational relaxation of linear X...B-C molecules where the three atoms are restricted to move on a single line. Good correspondence with the approximate (distorted wave) analytical results previously derived by us for ArI<sub>2</sub>, NeI<sub>2</sub>, and HeI<sub>2</sub> is obtained.

## I. INTRODUCTION

The vibrational predissociation (VP) on a single electronic adiabatic surface of polyatomic molecules is of considerable interest for the understanding of vibrational redistribution and intramolecular vibrational energy flow following optical excitation or collision excitation of the molecule. The currently available direct information on this process is very sparse as it is very often difficult to distinguish between VP and electronic predissociation. Recently Smalley, Levy, and Wharton<sup>1</sup> have provided a pioneering study of the photodissociation of van der Waals complexes (HeI<sub>2</sub>, NeI<sub>2</sub>, ArI<sub>2</sub>, HeNO<sub>2</sub>), some of which provide unique examples for VP on a single electronic potential surface. This photodissociation process was documented for vibrationally excited states of the ground electronic state and for vibrationally excited levels of an excited electronic configuration. In the case of a van der Waals molecule (VDWM) X... (BC) where BC is a conventional diatomic molecule and X is a rare-gas atom, the laser optical excitation produces electronic-vibrational excited states of the BC bond and subsequently intramolecular relaxation processes will induce the breaking of the X... (BC) van der Waals bond which are characterized by very weak dissociation energies, typically of the order of 10–200 cm<sup>-1</sup>. This VP process competes with radiative decay to the ground electronic state.

The currently available<sup>1</sup> experimental information about VP processes in HeI<sub>2</sub>, NeI<sub>2</sub>, and ArI<sub>2</sub>, are

(a) The VP rate of HeI<sub>2</sub> in the electronically-excited state B<sup>3</sup>Π is  $< 5 \times 10^9 \text{ sec}^{-1}$  for  $n=7$  (where  $n$  is the vibrational quantum number for the I-I stretch mode) increasing with  $n$  to  $\sim 5 \times 10^{10} \text{ sec}^{-1}$  for  $n=27$ .<sup>1a</sup>

(b) The VP rate in the  $n=1$  vibrational level of the ground X<sup>1</sup>Σ electronic state of HeI<sub>2</sub> is  $> 5 \times 10^6 \text{ sec}^{-1}$ .<sup>1a</sup>

(c) The propensity rule  $\Delta n = -1$  for VP was established.<sup>1b,1c</sup>

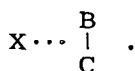
(d) The occurrence of VP in NeI<sub>2</sub> (B) and in high  $n > 11$  states of ArI<sub>2</sub> (B) has been demonstrated.<sup>1d</sup>

Recently, we have advanced<sup>2</sup> a quantum mechanical model for VP of a linear triatomic VDWM, X...BC. The zero-order states for the internal motion were chosen as products of a vibrational wavefunction for the BC bond and a bound (or unbound) nuclear wavefunction representing the motion of X relative to the center of mass of the BC molecule which has been frozen at its equilibrium configuration. The residual interaction representing the deviation between the total interaction potential of X with the vibrating BC molecule and the interaction of X with the frozen diatomic induces discrete-continuum and continuum-continuum couplings. On the basis of the analysis of these coupling terms we have asserted that the zero-order resonance widths are usually small relative to their spacings and, furthermore, that continuum-continuum coupling prevails essentially only between adjacent continua. The dynamics of VP was then reduced to the problem of the decay of a single discrete state into a manifold of adjacently coupled continua. Closed analytical expressions for the rate of VP of a linear VDWM and for the vibrational distribution of the BC product were derived incorporating the effects of discrete-continuum and continuum-continuum coupling.

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From the study of the dependence of the VP rate on the molecular parameters of the van der Waals bond and on the molecular frequency and masses of the BC molecule we were able to elucidate the gross features of the VP process. We have established an energy gap law for the dependence of the VP rate on the molecular frequency of the BC bond, predicted a superlinear dependence of the VP rate on the vibrational quantum number, and provided proper justification for the propensity rule  $\Delta n = -1$ . Our previous study is, however, based on a colinear configuration model where the three atoms move on a line and is clearly inappropriate for describing VP processes for  $\text{HeI}_2$  complex, which is characterized by a nonlinear  $T$ -shaped configuration.

In this paper we study the VP dynamics of a  $T$ -shaped VDWM considering a rare-gas atom X constrained to move on a line perpendicular to the interatomic axis of the BC molecule. In contrast to the colinear case, this problem does not result in an analytical solution, and numerical methods have to be applied. One of these methods involves the use of conventional scattering solutions of the Schrödinger equation resting on the numerical solutions of the resulting close-coupling equations. Alternative procedures for treating similar breakdown processes have been presented in the literature.<sup>3</sup> From the study of the probabilities for inelastic transitions in the collision of X with BC, it is possible to extract information about the quasibound states of the triatomics.<sup>4</sup> These states (also called resonances, collision complexes, compound states, metastable states) manifest themselves as dips or peaks at energies which approximately correspond to their zero-order energies. The widths of these resonances can then be related to the rate for VP. This method was applied by us for the investigation of the features of VP of  $T$ -shaped VDWM



A by-product of this study involves the application of these numerical techniques to the case of colinear VP and in this way to provide a test for the accuracy of the approximate analytical results obtained in our previous work<sup>2b</sup> (hereafter referred to as Paper I). We have found good correspondence between exact numerical and approximate analytical results for the three linear systems ( $\text{ArI}_2$ ,  $\text{NeI}_2$ , and  $\text{HeI}_2$ ) previously studied by us.

## II. GENERAL FORMALISM

We consider a triatomic system  $\text{X} \cdots \text{BC}$  where X is a rare gas atom and BC a conventional diatomic molecule, restricted to move on a single adiabatic electronic potential surface. If the diatomic molecule BC is assumed to be bounded for all energies considered, a natural set of internal coordinates for describing continuum wavefunctions of the three-atom system involves the interatomic distance  $\mathbf{R}_{\text{BC}}$  and the distance  $\mathbf{R}_{\text{X,BC}}$  between the center of mass of the diatomic and the atom X. In terms of these coordinates the nuclear Hamiltonian assumes the form

$$H = -\frac{\hbar^2}{2\mu_{\text{X,BC}}} \nabla_{\mathbf{R}_{\text{X,BC}}}^2 - \frac{\hbar^2}{2\mu_{\text{BC}}} \nabla_{\mathbf{R}_{\text{BC}}}^2$$

$$+ V(\mathbf{R}_{\text{BC}}) + V(\mathbf{R}_{\text{BC}}, \mathbf{R}_{\text{X,BC}}), \quad (1)$$

where

$$\lim_{\mathbf{R}_{\text{X,BC}} \rightarrow \infty} V(\mathbf{R}_{\text{BC}}, \mathbf{R}_{\text{X,BC}}) = 0 \quad (2)$$

and

$$\begin{aligned} \mu_{\text{X,BC}} &= m_{\text{X}}(m_{\text{B}} + m_{\text{C}}) / (m_{\text{X}} + m_{\text{B}} + m_{\text{C}}); \\ \mu_{\text{BC}} &= m_{\text{B}} m_{\text{C}} / (m_{\text{B}} + m_{\text{C}}). \end{aligned} \quad (3)$$

In the potential coupling scheme the nuclear wavefunction at total energy  $E$  is expanded in terms of the eigenstates  $\phi_n(\mathbf{R}_{\text{BC}})$  of the asymptotic Hamiltonian for the diatomic BC

$$\left( -\frac{\hbar^2}{2\mu_{\text{BC}}} \nabla_{\mathbf{R}_{\text{BC}}}^2 + V(\mathbf{R}_{\text{BC}}) \right) \phi_n(\mathbf{R}_{\text{BC}}) = \epsilon_n \phi_n(\mathbf{R}_{\text{BC}}). \quad (4)$$

Explicitly

$$\Psi_E(\mathbf{R}_{\text{BC}}, \mathbf{R}_{\text{X,BC}}) = \sum_n \phi_n(\mathbf{R}_{\text{BC}}) \chi_{nE}(\mathbf{R}_{\text{X,BC}}). \quad (5)$$

After substitution of this expansion in the Schrödinger equation, we obtain the set of the familiar close-coupled equations

$$\begin{aligned} \left( -\frac{\hbar^2}{2\mu_{\text{X,BC}}} \nabla_{\mathbf{R}_{\text{X,BC}}}^2 + U_{nn}(\mathbf{R}_{\text{X,BC}}) + (\epsilon_n - E) \right) \chi_{nE}(\mathbf{R}_{\text{X,BC}}) \\ = -\sum_{n' \neq n} U_{nn'}(\mathbf{R}_{\text{X,BC}}) \chi_{n'E}(\mathbf{R}_{\text{X,BC}}), \end{aligned} \quad (6)$$

where

$$U_{nn'}(\mathbf{R}_{\text{X,BC}}) = \int \phi_n^*(\mathbf{R}_{\text{BC}}) V(\mathbf{R}_{\text{BC}}, \mathbf{R}_{\text{X,BC}}) \phi_{n'}(\mathbf{R}_{\text{BC}}) d\mathbf{R}_{\text{BC}}. \quad (7)$$

These coupled differential equations (6) may now be solved by any of the currently available<sup>5</sup> numerical integration methods. These algorithms usually give the elements of the  $S$ -matrix. The absolute value squared of the elements of the  $S$ -matrix, namely  $|S_{nn'}(E)|^2$ , for a collision between atom X and diatomic BC at total energy  $E$ , gives the probability for BC, which initially was at the distant past in the state  $n$ , to be after the collision in the state  $n'$ . The coupled equations (6) involve, for a given total energy  $E$ , open ( $(E - \epsilon_n) > 0$ ) and closed [ $(E - \epsilon_n) < 0$ ] channels. Provided that a diagonal potential term  $U_{nn}$  has a minimum, then it can be shown that the absolute value squared of the  $S$ -matrix exhibits resonances located at approximately the position of the bound states in this  $U_{nn}$  potential. In the case of van der Waals complexes  $\text{X} \cdots \text{BC}$  where BC is a normal diatomic and X a rare-gas atom, which are characterized by the potential surfaces as described in Paper I,<sup>2</sup> the widths of the resonances specify the VP rate, experimentally determined for the VP process of the VDWM.

A simple parametrization of these resonances can be obtained by using partitioning techniques and the Feshbach formalism.<sup>7</sup> Neglecting for a moment the couplings between closed and open channels, we obtain a system of coupled equations for the closed channels which if solved exactly results in a set of (zero-order) discrete eigenfunctions  $\Psi_i$  corresponding to the bound

states of the complex. The projection operator  $\hat{P}$  is then defined by

$$\hat{P} = \sum_i |\Psi_i\rangle\langle\Psi_i| \quad (8)$$

For the open channels we define zero-order ingoing plane waves solutions of the asymptotic Hamiltonian

$$\left(-\frac{\hbar^2}{2\mu_{X,BC}} \nabla_{R_{X,BC}}^2 + (\epsilon_n - E)\right) \chi_{nE}^0(R_{X,BC}) = 0, \quad (9)$$

and we define the complement of  $\hat{P}$  to be

$$\hat{Q} = \sum_n \int dE |\Psi_{nE}\rangle\langle\Psi_{nE}| \quad (10)$$

with

$$\langle R_{X,BC}, R_{BC} | \Psi_{nE}\rangle = \phi_n(R_{BC}) \chi_{nE}^0(R_{X,BC}). \quad (11)$$

In terms of this complete set, the Hamiltonian assumes the form

$$H = H_0 + V \quad (12)$$

with

$$\begin{aligned} H_0 &= \sum_i E_i |\Psi_i\rangle\langle\Psi_i| + \sum_n \int dE |\Psi_{nE}\rangle\langle\Psi_{nE}| E \\ &= \hat{P} H_0 \hat{P} + \hat{Q} H_0 \hat{Q}, \end{aligned} \quad (13)$$

and

$$V = \hat{P} V \hat{Q} + \hat{Q} V \hat{Q} + \hat{Q} V \hat{P}, \quad (14)$$

where there is no term in  $\hat{P} V \hat{P}$  as  $\hat{P}$  has been chosen to diagonalize  $\hat{P} H \hat{P}$ . The matrix elements of  $V$  are

$$\begin{aligned} \langle \Psi_i | V | \Psi_{nE}\rangle &= \int d\mathbf{R}_{BC} d\mathbf{R}_{X,BC} \langle \Psi_i | \mathbf{R}_{BC}, \mathbf{R}_{X,BC}\rangle \\ &\quad \times V(\mathbf{R}_{BC}, \mathbf{R}_{X,BC}) \phi_n(\mathbf{R}_{BC}) \chi_{nE}^0(\mathbf{R}_{X,BC}) \end{aligned} \quad (15a)$$

for bound-continuum coupling, and

$$\begin{aligned} \langle \Psi_{nE} | V | \Psi_{n'E'}\rangle &= \int d\mathbf{R}_{BC} d\mathbf{R}_{X,BC} \phi_n^*(\mathbf{R}_{BC}) \\ &\quad \times \chi_{nE}^{0*}(\mathbf{R}_{X,BC}) V(\mathbf{R}_{BC}, \mathbf{R}_{X,BC}) \\ &\quad \times \phi_{n'}(\mathbf{R}_{BC}) \chi_{n'E'}^0(\mathbf{R}_{X,BC}) \end{aligned} \quad (15b)$$

for continuum-continuum coupling. The  $S$ -matrix is now defined in the usual way,

$$S_{nn'}(E) = \delta_{nn'} - 2i\pi T_{nn'}(E), \quad (16)$$

where  $T_{nn'}(E)$  are on-the-energy-shell matrix elements  $\langle \Psi_{nE} | T(E) | \Psi_{n'E}\rangle$  of the transition operator

$$T(E) = V + V G^*(E) V = V + V G_0^*(E) T(E). \quad (17)$$

In Eq. (19)  $G^*$  and  $G_0^*$  stand for the resolvent operators

$$G^*(E) = (E^* - H)^{-1}, \quad G_0^*(E) = (E^* - H_0)^{-1}, \quad (18)$$

with  $E^* = E + i\epsilon$ , and it is implied that the limit  $\epsilon \rightarrow 0^+$  is to be taken at the end of the calculations. It can be shown<sup>8</sup> that the projection  $\hat{Q} T \hat{Q}$  can be written in the form

$$\hat{Q} T(E) \hat{Q} = \hat{Q} R(E) \hat{Q} + \hat{Q} R(E) \hat{P} (E^* - H_0 - \hat{P} R(E) \hat{P})^{-1} \hat{P} R(E) \hat{Q}, \quad (19)$$

where the level shift operator  $R(E)$  is defined by

$$R(E) = V + V \hat{Q} (E^* - \hat{Q} H \hat{Q})^{-1} \hat{Q} V. \quad (20)$$

This operator only involves continuum-continuum interactions and therefore is expected to vary slowly with energy in the region of a resonance. In particular, the first term on the right-hand side of Eq. (19) is equal to the transition operator  $T^d$  for a collision process in which the bound states are neglected,

$$T^d \equiv \hat{Q} R(E) \hat{Q} = \hat{Q} V \hat{Q} + \hat{Q} V \hat{Q} (E^* - \hat{Q} H \hat{Q})^{-1} \hat{Q} V \hat{Q}, \quad (21)$$

and represents the operator for direct transitions between open channels. On the other hand, the second term on the right-hand side of Eq. (19) exhibits peaks due to the presence of the energy dependent denominator. Defining  $\Delta$  and  $\Gamma$  as the Hermitian and negative value of the anti-Hermitian part of  $\hat{P} R \hat{P}$ , respectively, namely

$$\Delta = \hat{P} V \hat{Q} \phi (E - \hat{Q} H \hat{Q})^{-1} \hat{Q} V \hat{P} \quad (22)$$

and

$$\Gamma = \hat{P} V \hat{Q} \delta(E - \hat{Q} H \hat{Q}) \hat{Q} V \hat{P}, \quad (23)$$

where  $\phi$  denotes the "Cauchy Principal Part distribution," we can write

$$\hat{Q} T(E) \hat{Q} = T^d + \hat{Q} R \hat{P} (E - (H_0 + \Delta) + i\Gamma)^{-1} \hat{P} R \hat{Q}, \quad (24)$$

where the weak dependence on energy of the operator  $R$  has been omitted. If the resonances do not overlap, i. e., if

$$\Gamma_i, \Gamma_j \ll |(E_i + \Delta_i) - E_j + \Delta_j| \quad (25)$$

for all  $i$  and  $j$ , for energies  $E$  in the vicinity of  $E_i$ , the probability for a transition from  $n$  to  $n'$  channel with  $n \neq n'$  will be given approximately by

$$P_{nn'}(E) = S_{nn'}(E)^2 \approx 4\pi^2 \left| T_{nn'}^d + \frac{R_{ni} R_{in'}}{E - (E_i + \Delta_i) + i\Gamma_i} \right|^2, \quad (26)$$

where

$$T_{nn'}^d \equiv \langle \Psi_{nE} | T^d | \Psi_{n'E}\rangle, \quad (27a)$$

$$R_{ni} \equiv \langle \Psi_{nE} | R | \Psi_i\rangle, \quad (27b)$$

$$\Delta_i - i\Gamma_i \equiv \langle \Psi_i | R | \Psi_i\rangle. \quad (27c)$$

The final expression (26) which is valid for an isolated resonance results in the general dispersion formula<sup>9</sup>

$$P_{nn'}(E) = C + \frac{(\Gamma_i)B + (E - E_i - \Delta_i)A}{(E - E_i - \Delta_i)^2 + \Gamma_i^2}, \quad (28)$$

with

$$C = 4\pi^2 |T_{nn'}^d|^2, \quad (29)$$

$$B = 4\pi^2 [ |R_{ni} R_{in'}|^2 \Gamma_i^{-1} - 2 \text{Im}(T_{nn'}^d R_{ni}^* R_{in'}^*) ],$$

$$A = 8\pi^2 \text{Re}(T_{nn'}^d R_{ni}^* R_{in'}^*).$$

Comparing now the expression for  $\Gamma_i$ , Eq. (27c), with those given in Paper I for the VP rate  $\Gamma_{ni}$  (of a zero-order bound state  $|nl\rangle$  characterized by the quantum numbers  $n$  and  $l$  for the BC mode and for the van der Waals bond, respectively) it is immediately apparent that the two quantities will be identical provided that we can identify the approximate zero-order state  $|n, l\rangle$  (see Paper I) with the state  $|\Psi_i\rangle$  defined above. A fit of the energy dependence of the probabilities  $P_{nn'}(E)$  will

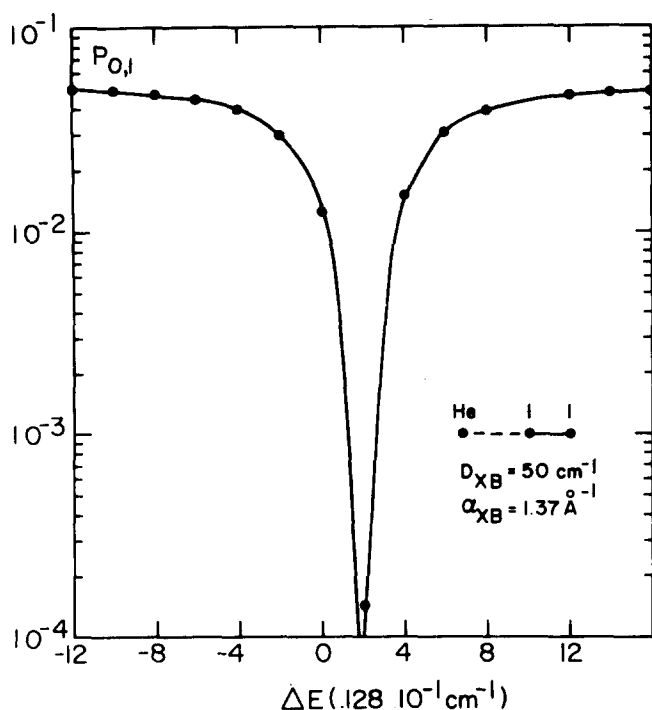


FIG. 1. Transition probability  $P_{01}$  between vibrational states  $n=0$  and  $n=1$  of  $I_2$  for the colinear collision of He with  $I_2(B)$  in the region of a resonance corresponding to the closed channel  $n=2$ . The total energy is measured from the approximate position of level  $n=2$  and  $l=0$  given by Eq. (38).

then yield  $\Gamma_i$  [Eq. (27c)], which can be considered as the exact half-width of the level  $|\Psi_i\rangle$  in contrast to the approximate half-width derived in Paper I. From the fit of the energy dependence of  $P_{nn'}(E)$  we can also evaluate the true position of the levels,  $(E_i + \Delta_i)$ , and the transition probability  $C = 4\pi^2 |T_{nn'}^2|$  for continuum-continuum transitions. This procedure will be applied to the colinear case in Sec. III where comparisons with the approximate results presented in Paper I will be discussed. Finally, in Sec. IV we will study the perpendicular VP problem.

### III. COLINEAR VIBRATIONAL PREDISSOCIATION AND COMPARISON WITH THE DISTORTED-WAVE ANALYTICAL RESULTS

In the colinear case, the coordinate  $R_{x,BC}$  defined in Sec. II is

$$R_{x,BC} = R_{XB} + \gamma R_{BC}; \quad \gamma = m_C / (m_B + m_C), \quad (30)$$

so that the nuclear Hamiltonian, Eq. (1), assumes the form

$$H = -\frac{\hbar^2}{2\mu_{x,BC}} \left( \frac{\partial^2}{\partial R_{x,BC}^2} \right) - \frac{\hbar^2}{2\mu_{BC}} \left( \frac{\partial^2}{\partial R_{BC}^2} \right) + V_{BC}(R_{BC}) + V_{XB}(R_{x,BC} - \gamma R_{BC}), \quad (31)$$

where we have assumed that in the colinear configuration the potential energy surface can be approximated by the sum of two terms,  $V_{BC}$  and  $V_{XB}$ , which depend on the interatomic distances  $R_{BC}$  and  $R_{XB}$ , respectively.

The interatomic interaction  $V_{BC}$  is represented here by a harmonic potential,

$$V_{BC}(R_{BC}) = \frac{1}{2} \mu_{BC} \omega_{BC}^2 (R_{BC} - \bar{R}_{BC})^2, \quad (32)$$

while the van der Waals bond is characterized by a Morse potential

$$V_{XB}(R_{XB}) = D_{XB} \left\{ \exp[-2\alpha_{XB}(R_{XB} - \bar{R}_{XB})] - 2 \exp[-\alpha_{XB}(R_{XB} - \bar{R}_{XB})] \right\}. \quad (33)$$

The close-coupled equations, Eqs. (6) and (7), are now

$$\left[ -\frac{\hbar^2}{2\mu_{x,BC}} \left( \frac{\partial^2}{\partial R_{x,BC}^2} \right) + U_{nn'}(R_{x,BC}) + \hbar \omega_{BC} \left( n + \frac{1}{2} \right) - E \right] \chi_{nE} = -\sum_{n' \neq n} U_{nn'}(R_{x,BC}) \chi_{n'E}(R_{x,BC}), \quad (34)$$

with

$$U_{nn'} = D_{XB} \left\{ A_{nn'}^{(2)} \exp[-2\alpha_{XB}(R_{x,BC} - \bar{R}_{x,BC})] - 2 A_{nn'}^{(1)} \exp[-\alpha_{XB}(R_{x,BC} - \bar{R}_{x,BC})] \right\}, \quad (35)$$

where

$$\bar{R}_{x,BC} = \bar{R}_{XB} + \gamma \bar{R}_{BC}, \quad (36)$$

and the integrals  $A_{nn'}^{(1)}$  and  $A_{nn'}^{(2)}$  are defined by

$$A_{nn'}^{(j)} = \int_{-\infty}^{\infty} \phi_n(R_{BC}) \exp[j\alpha_{XB}(R_{BC} - \bar{R}_{BC})] \phi_{n'}(R_{BC}) dR_{BC}, \quad (37)$$

with  $j=1, 2$  and where  $\phi_n, \phi_{n'}$  represent the eigenfunctions of the harmonic oscillator potential (32). Explicit expressions for the integral in Eq. (37) have been given elsewhere.<sup>10</sup>

The close-coupled equations (34) have been solved numerically subjected to the usual scattering boundary conditions. A typical plot of the probability  $P_{01}$  for transition between states  $n=0$  and  $n=1$  in the region of a resonance corresponding to the closed channel  $n=2$  is depicted in Fig. 1. The energy scale for the probability  $P_{01}(E)$  is represented relative to the approximate position  $E_{n,l}$  of the resonance, as given by a variational calculation,<sup>11</sup> namely

$$E_{n,l} = \hbar \omega_{BC} \left( n + \frac{1}{2} \right) - \frac{\hbar^2 \alpha_{XB}^2}{2\mu_{x,BC}} \left( K' - l - \frac{1}{2} \right)^2, \quad (38)$$

where

$$K' = K A_{nn}^{(1)} / (A_{nn}^{(2)})^{1/2}; \quad K = (2D_{XB} \mu_{x,BC})^{1/2} / \hbar \alpha_{XB}. \quad (39)$$

The  $P_{01}(E)$  curve has been fitted to Eq. (28) and in this way the half-width  $\Gamma_{n,l}^{\text{num}}$  is obtained. We have conducted a series of calculations for VP of linear VDWMS,  $XI_2(B)$  ( $X = \text{Ar, Ne, He}$ ) using the parameters of Paper I. The numerical results are presented in Table I. The frequency  $\omega_{XB}$  is defined by

$$\omega_{XB} = \alpha_{XB} (2D_{XB} / \mu_{x,BC})^{1/2}, \quad (40)$$

but it should not be confused with the energy spacing between levels  $(n, l=0)$  and  $(n, l=1)$  which is given approximately by

$$E_{n,1} - E_{n,0} \approx \hbar \omega_{XB} (1 - K^{-1}). \quad (41)$$

$N$  is the number of bound states.  $\Delta E_{n,l}$  in Table I gives

TABLE I. Comparison between numerical and distorted wave half-widths for some model colinear van der Waals molecules.

| System               | $D_{XB}$<br>( $\text{cm}^{-1}$ ) | $\alpha_{XB}$<br>( $\text{\AA}^{-1}$ ) | $\omega_{XB}$<br>( $\text{cm}^{-1}$ ) | $E_{n1} - E_{n0}$<br>( $\text{cm}^{-1}$ ) | $N$  | $n$       | $l$                  | $\Delta E_{n,l}$<br>( $\text{cm}^{-1}$ ) | $\Gamma_{n,l}^{\text{num}}$<br>( $\text{cm}^{-1}$ ) | $\Gamma_{n,l}^{\text{DW}}$<br>( $\text{cm}^{-1}$ ) |           |           |           |           |           |
|----------------------|----------------------------------|--|---------------------------------------|---|------|-----------|----------------------|--|---|--|-----------|-----------|-----------|-----------|-----------|
| ArI <sub>2</sub> (B) | 200                              | 2.02                                   | 40                                    | 36  | 10   | 2         | 2                    | 0.30                                     | $10^{-1}$   | 0.26   | 0.32      |           |           |           |           |
|                      |                                  |  |                                       |   |      |           | 3                    | -0.55                                    | $10^{-1}$   | 0.34   | 0.41      |           |           |           |           |
|                      |                                  |  |                                       |   |      |           | 4                    | -0.17                                    |   | 0.38   | 0.45      |           |           |           |           |
|                      |                                  |  |                                       |   |      |           | 5                    | -0.12                                    |   | 0.39   | 0.45      |           |           |           |           |
|                      |                                  |  |                                       |   |      |           | 6                    | -0.24                                    |   | 0.35   | 0.40      |           |           |           |           |
|                      |                                  |  |                                       |   |      |           | 7                    | -0.24                                    |   | 0.23   | 0.32      |           |           |           |           |
|                      |                                  |  |                                       |   |      |           | NeI <sub>2</sub> (B) | 100                                      | 1.31  | 25   | 22        | 8         | 2         | 0         | 0.78      |
| 1                    | -0.26                            | $10^{-2}$                              | 0.37                                  | $10^{-2}$                                 | 0.46 | $10^{-2}$ |                      |  |   |  |           |           |           |           |           |
| 2                    | -0.90                            | $10^{-2}$                              | 0.67                                  | $10^{-2}$                                 | 0.78 | $10^{-2}$ |                      |  |   |  |           |           |           |           |           |
| 3                    | -0.12                            | $10^{-1}$                              | 0.87                                  | $10^{-2}$                                 | 0.10 | $10^{-1}$ |                      |  |   |  |           |           |           |           |           |
| 4                    | -0.12                            | $10^{-1}$                              | 0.93                                  | $10^{-2}$                                 | 0.11 | $10^{-1}$ |                      |  |   |  |           |           |           |           |           |
| HeI <sub>2</sub> (B) | 50                               | 1.37                                   | 40                                    | 24  | 2    | 2         | 0                    | 0.22                                     | $10^{-1}$   | 0.42   | $10^{-1}$ | 0.44      | $10^{-1}$ |           |           |
|                      |                                  |  |                                       |   |      |           | 1                    | 0.11                                     | $10^{-1}$   | 0.38   | $10^{-1}$ | 0.40      | $10^{-1}$ |           |           |
|                      |                                  |  |                                       |   |      |           | 10                   | 0  | 0.18  |  | 0.16      | 0.20      |           |           |           |
|                      |                                  |  |                                       |   |      |           | 1                    | 0.96                                     | $10^{-1}$   |  | 0.16      | 0.18      |           |           |           |
|                      |                                  |  |                                       |   |      |           | 20                   | 0  | 0.29  |  | 0.35      | 0.37      |           |           |           |
|                      | 1                                | 0.20                                   |                                       |   | 0.30 | 0.33      |                      |  |   |  |           |           |           |           |           |
|                      | 14                               | 1.18                                   | 18                                    | 6.4                                       | 2    | 2         | 2                    | 0  | 0.17  | $10^{-2}$  | 0.12      | $10^{-2}$ | 0.12      | $10^{-2}$ |           |
|                      |                                  |  |                                       |   |      |           |                      | 1  | 0.12  | $10^{-3}$  | 0.81      | $10^{-4}$ | 0.10      | $10^{-3}$ |           |
|                      |                                  |  |                                       |   |      |           |                      | 10                                       | 0   | 0.12   | $10^{-1}$ | 0.57      | $10^{-2}$ | 0.60      | $10^{-2}$ |
|                      |                                  |  |                                       |   |      |           |                      | 1  | 0.72  | $10^{-3}$  | 0.36      | $10^{-3}$ | 0.49      | $10^{-3}$ |           |
|                      |                                  |  |                                       |   |      |           |                      | 20                                       | 0   | 0.24   | $10^{-1}$ | 0.11      | $10^{-1}$ | 0.12      | $10^{-1}$ |
|                      |                                  |  |                                       |   |      |           |                      | 1  | 0.11  | $10^{-2}$  | 0.49      | $10^{-3}$ | 0.95      | $10^{-3}$ |           |
|                      |                                  |  |                                       |   |      |           |                      | 30                                       | 0   | 0.35   | $10^{-1}$ | 0.15      | $10^{-1}$ | 0.17      | $10^{-1}$ |
|                      |                                  |  |                                       |   |      |           |                      | 1  | 0.93  | $10^{-3}$  | 0.44      | $10^{-3}$ | 0.14      | $10^{-2}$ |           |

the numerical result for the position of the resonance with respect to the approximate result, Eq. (38). Finally,  $\Gamma_{n,l}^{\text{num}}$  and  $\Gamma_{n,l}^{\text{DW}}$  represent the numerical value obtained herein and the analytical distorted wave (see Paper I) half-width of the resonance, respectively. The total rate for VP is then given by  $2\Gamma_{n,l}/\hbar$ . From the results of Table I, we conclude that the distorted wave treatment provides a very good estimate of the exact VP rates.

#### IV. STUDY OF THE VIBRATIONAL PREDISSOCIATION FOR THE PERPENDICULAR CONFIGURATION

We consider now the perpendicular VP case of a VDWM



(with  $B \equiv C$ ) consisting of a rare-gas atom X bound to a homonuclear diatomic BC and where X moves on a line perpendicular to the BC axis. The coordinate  $R_{X,BC}$  defined in Sec. II as the distance of X from the center of mass of BC is

$$R_{X,BC} = (R_{XB}^2 - \frac{1}{4}R_{BC}^2)^{1/2}; \quad B \equiv C. \quad (42)$$

Thus the nuclear Hamiltonian, Eq. (1), takes the form

$$H = -\frac{\hbar^2}{2\mu_{X,BC}} \left( \frac{\partial^2}{\partial R_{X,BC}^2} \right) - \frac{\hbar^2}{2\mu_{BC}} \left( \frac{\partial^2}{\partial R_{BC}^2} \right) + V_{BC}(R_{BC}) + 2V_{XB}[(R_{X,BC}^2 + \frac{1}{4}R_{BC}^2)^{1/2}]; \quad B \equiv C \quad (43)$$

where the factor 2 in the last term of Eq. (43) originates from the sum of two identical interactions between X and atoms B and C  $\equiv$  B. The potentials  $V_{BC}$  and  $V_{XB} \equiv V_{XC}$  are given by Eqs. (32) and (33). Using the reasonable approximation

$$(R_{X,BC}^2 + \frac{1}{4}R_{BC}^2)^{1/2} \approx (R_{X,BC}^2 + \frac{1}{4}\bar{R}_{BC}^2)^{1/2} + (R_{X,BC}^2 + \frac{1}{4}\bar{R}_{BC}^2)^{-1/2} \bar{R}_{BC} (R_{BC} - \bar{R}_{BC}), \quad (44)$$

the close-coupled equations, Eqs. (6) and (7), assume the form (34) with

$$U_{nn'} = 2D_{XB}(B_{nn'}^{(2)}) \exp\{-2\alpha_{XB}[(R_{X,BC}^2 + \frac{1}{4}\bar{R}_{BC}^2)^{1/2} - \bar{R}_{XB}]\} - 2B_{nn'}^{(1)} \exp\{-\alpha_{XB}[(R_{X,BC}^2 + \frac{1}{4}\bar{R}_{BC}^2)^{1/2} - \bar{R}_{XB}]\}, \quad (45)$$

and where

$$B_{nn'}^{(j)} = \int_{-\infty}^{\infty} \phi_n(R_{BC}) \exp\{j\alpha_{XB}(R_{X,BC}^2 + \frac{1}{4}\bar{R}_{BC}^2)^{-1/2} \times \bar{R}_{BC}(R_{BC} - \bar{R}_{BC})\} \phi_{n'}(R_{BC}) dR_{BC}, \quad (46)$$

with  $j \equiv 1, 2$  and where  $\phi_n, \phi_{n'}$  are the eigenfunctions of the harmonic potential (32). Explicit expression for the integrals defined in Eq. (46) has been given in Ref. 10. Note that now, in contrast to the collinear case, the coefficients  $B_{nn'}^{(j)}$  depend on  $R_{X,BC}$ . The approximate position of the bound states can be obtained by making use of the approximation

$$(R_{X,BC}^2 + \frac{1}{4}\bar{R}_{BC}^2)^{1/2} \approx (\bar{R}_{X,BC}^2 + \frac{1}{4}\bar{R}_{BC}^2)^{1/2} + (\bar{R}_{X,BC}^2 + \frac{1}{4}\bar{R}_{BC}^2)^{-1/2} \bar{R}_{X,BC} (R_{X,BC} - \bar{R}_{X,BC}) \quad (47)$$

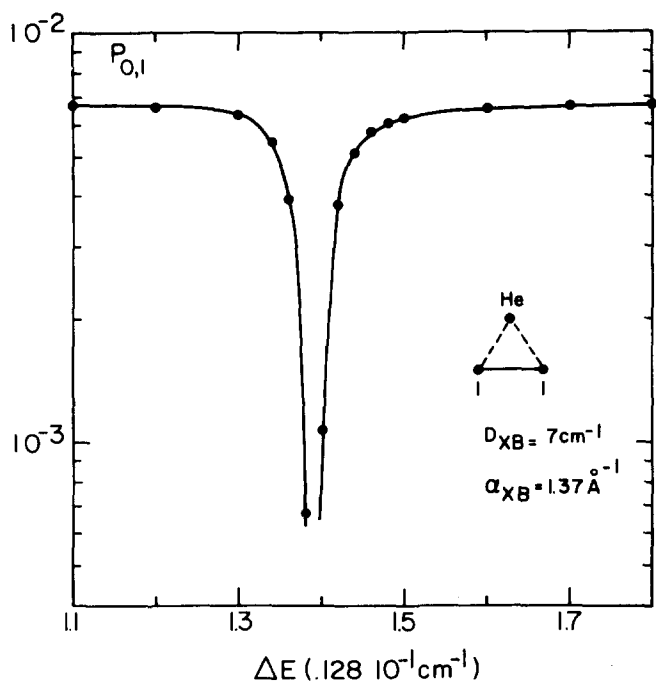


FIG. 2. Transition probability  $P_{01}$  between vibrational states  $n=0$  and  $n=1$  of  $I_2$  for the perpendicular collision of He with  $I_2$  (B), in the region of a resonance corresponding to the closed channel  $n=2$ . The total energy is measured from the approximate position of level  $n=2$  and  $l=0$  given by Eq. (48).

in Eq. (45) and by just replacing  $R_{x,BC}$  by the equilibrium value  $\bar{R}_{x,BC}$  in Eq. (46). In analogy to Eq. (38) we now have for the approximate position for the resonance which defines the origin of the energy scale

$$E_{n1} \approx \hbar\omega_{BC}(n + \frac{1}{2}) - \frac{\hbar^2 \alpha'_{XB}{}^2}{2\mu_{x,BC}} (K'' - l - \frac{1}{2})^2$$

$$\alpha'_{XB} = \alpha_{XB} (\bar{R}_{x,BC}^2 + \frac{1}{4} \bar{R}_{BC}^2)^{-1/2} \bar{R}_{x,BC}$$

$$K'' = \left( \frac{4D_{XB} \mu_{x,BC}}{\hbar^2 \alpha_{XB}^2} \right)^{1/2} \frac{B_{nn}^{(1)}}{(B_{nn}^{(2)})^{1/2}} \quad (48)$$

The close-coupled equations (34) together with Eqs. (45) and (46) have been solved numerically<sup>5</sup> as in the colinear case. In Fig. 2 we have portrayed a typical plot of the probability  $P_{01}$  for transitions between states  $n=0$  and  $n=1$  in the region of a resonance corresponding to the closed channel  $n=2$ . The probability is represented

in function of the energy difference with respect to the approximate position of the quasibound state given by Eq. (48). By fitting this curve to the Eq. (28) we obtain the half-width  $\Gamma_{n1}^{num}$  of this state. We have also conducted a series of calculations for  $HeI_2$  (B) using approximately the same parameter  $\alpha_{XB}$  as in the colinear case, which has been estimated from the Lennard-Jones potential reported by Secrest and Eastes<sup>12</sup> (see Paper I). The equilibrium distances,  $\bar{R}_{XB}$  and  $\bar{R}_{BC}$ , were chosen respectively equal to 4 Å and 3.02 Å. On the other hand, in order to have the same total interaction energy for the  $T$ -shaped VDWM, the van der Waals dissociation energy  $D_{XB}$  in Eq. (33) should be divided by two in the perpendicular configuration. The results of these calculations are presented in Table II, together with the VP rates ( $2\Gamma_{n1}^{num}/\hbar$ ) and the exact position of the resonance  $\Delta_{n1}$  measured from the approximate energy given by Eq. (48).

## V. DISCUSSION

From the results presented in Secs. III and IV, several conclusions emerge:

(1) The analytical results obtained by the use of the distorted wave approximation of Paper I provide very good estimates of the actual VP rates in the linear case.

(2) The VP rates for the  $T$ -shaped  $HeI_2$  (B) are usually smaller (almost one order of magnitude) than those corresponding to the model linear  $HeI_2$  (B) VDWM, provided that the total  $X \dots BC$  interaction is taken to be the same, i. e.,

$$D_{BX}^{colinear} = 2D_{BX}^{T-shaped}$$

(3) When the B-C potential is harmonic we find that the dependence of VP rates on the vibrational quantum number  $n$  is almost linear with a slight effect of continuum-continuum interactions, for colinear as well as for  $T$ -shaped VDWMs.

(4) The approximate position of the resonances in both cases are very well estimated from the variational formulas, Eqs. (38) and (48).

We are now able to confront the theoretical VP rates obtained for the  $T$ -shaped  $HeI_2$  (B) VDWM with the experimental data of Smalley, Levy and Wharton.<sup>1</sup> They have determined a VP rate of  $HeI_2$  in the electronically

TABLE II. VP rates for model  $T$ -shaped  $HeI_2$  (B) van der Waals.

| $D_{XB}$<br>( $cm^{-1}$ ) | $\alpha_{XB}$<br>( $\text{Å}^{-1}$ ) | $E_{n1} - E_{n0}$<br>( $cm^{-1}$ ) | $n$ | $l$ | $\Delta E_{n1}$<br>( $cm^{-1}$ ) | $\Gamma_{n1}^{num}$<br>( $cm^{-1}$ ) | VP rate:<br>$2\Gamma_{n1}/\hbar$<br>( $sec^{-1}$ ) |
|---------------------------|--------------------------------------|------------------------------------|-----|-----|----------------------------------|--------------------------------------|--|
| 25                        | 1.25                                 | 22.3                               | 2   | 0   | $0.43 \cdot 10^{-1}$             | $0.41 \cdot 10^{-2}$                 | $0.15 \cdot 10^{10}$                               |
|                           |                                      |                                    | 10  | 0   | 0.15                             | $0.20 \cdot 10^{-1}$                 | $0.75 \cdot 10^{10}$                               |
|                           |                                      |                                    | 20  | 0   | 0.28                             | $0.40 \cdot 10^{-1}$                 | $0.15 \cdot 10^{11}$                               |
|                           |                                      |                                    | 30  | 0   | 0.40                             | $0.59 \cdot 10^{-1}$                 | $0.22 \cdot 10^{11}$                               |
| 7                         | 1.25                                 | 6.5                                | 2   | 0   | $0.18 \cdot 10^{-1}$             | $0.33 \cdot 10^{-3}$                 | $0.12 \cdot 10^9$                                  |
|                           |                                      |                                    | 10  | 0   | $0.42 \cdot 10^{-1}$             | $0.16 \cdot 10^{-2}$                 | $0.60 \cdot 10^9$                                  |
|                           |                                      |                                    | 20  | 0   | $0.73 \cdot 10^{-1}$             | $0.32 \cdot 10^{-2}$                 | $0.12 \cdot 10^{10}$                               |
|                           |                                      |                                    | 30  | 0   | 0.10                             | $0.48 \cdot 10^{-2}$                 | $0.18 \cdot 10^{10}$                               |

excited state  $B^3\Pi$  of  $5 \times 10^9 \text{ sec}^{-1}$  for  $n=7$  to  $5 \times 10^{10} \text{ sec}^{-1}$  for  $n=27$ . From Table II we conclude that the best fit is obtained with the parameters  $D_{\text{XB}} = 27 \text{ cm}^{-1}$  and  $\alpha_{\text{XB}} = 1.25 \text{ \AA}^{-1}$  which correspond to an estimate from the Lennard-Jones potential parameters presented by Secrest and Eastes<sup>12</sup> (see Paper I). The experimental dependence on  $n$  is, however, superlinear, a fact that can easily be taken into account if one considers the anharmonicity of the BC bond. This point has already been discussed in Paper I in connection with the colinear model. We are currently performing some similar numerical simulations including the anharmonicity of the BC bond.

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