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Influence of rotation on the vibrational predissociation of the van der Waals molecule HeI_2

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We apply a rotational decoupling scheme related to the infinite order sudden approximation to treat vibrational predissociation of the triatomic van der Waals molecule HeI_2 . The potential surface is described by the sum of three Morse potentials between individual bonds. The total rate for vibrational predissociation as a function of vibrational excitation is compared with the results obtained for the colinear and T-shaped models. Final rotational distributions for the I_2 fragment are also obtained.

I. INTRODUCTION

The vibrational predissociation of van der Waals molecules¹⁻³ provides a unique and clear example of intramolecular vibrational redistribution on a single electronic potential energy surface. Furthermore, the study of quasibound states of van der Waals molecules are of importance in the vibrational relaxation of gases at low temperatures⁴ and in supersonic beams and jets.⁵ Recently detailed experimental studies on the $\text{HeI}_2(B)$ molecule have been conducted.⁶ The vibrational predissociation lifetimes have been determined from the linewidths Γ (HWHM) of the R branch heads in the fluorescence excitation spectra. It has been found that the dependence of Γ on the vibrational quantum number of $\text{I}_2(B)$ follows an almost quadratic law^{6(d)}

$$\Gamma = 0.555 \times 10^{-4} v_1^2 + 0.174 \times 10^{-5} v_1^3 (\text{cm}^{-1}) \quad (1)$$

for $12 \leq v_1 \leq 26$. The corresponding lifetimes varied from 221 ps at $v_1 = 12$ to 38 ps at $v_1 = 26$. We have recently⁷ performed numerical calculations of the linewidths for the T-shaped $\text{HeI}_2(B)$ molecule by solving the close-coupled equation for nuclear motion.

The linewidths were obtained from the energy dependence of the scattering matrix. The potential surface was represented in terms of three pairwise interatomic interactions. The I-I interaction was described by a Morse potential while the two He-I interactions were represented in terms of Morse or Buckingham potentials. The dynamics of vibrational predissociation was shown to be largely insensitive to the long-range part of the interaction potential and we concluded that the Morse form was adequate for the description of this process.⁷ The theoretical dependence of the linewidths on the excess vibrational energy of the molecular I_2 bond was in good agreement with the experimental data of Eq. (1). Tentative fits of the absolute value of the experimental linewidths lead to rough estimates of the potential parameters for the van der Waals bond in HeI_2 . It is clear however, that a precise conformation between theory and experiment requires the consideration of the rotation-

al degrees of freedom of the molecule. The aim of this work is to provide an approximate treatment for incorporating these effects on the vibrational predissociation of the triatomic van der Waals molecule HeI_2 . The approximation used is closely related to the "rotational infinite order sudden approximation" used in scattering problems.⁸⁻¹⁰ The method is presented in Sec. II. In Sec. III application is made to the van der Waals molecule $\text{HeI}_2(B)$. The results are compared with those obtained for the colinear and T-shaped models. Final rotational distributions for the I_2 fragment are also obtained.

II. MODEL FOR ROTATIONAL-VIBRATIONAL PREDISSOCIATION OF TRIATOMIC VAN DER WAALS MOLECULES

We consider a triatomic van der Waals molecule $\text{X} \cdots \text{BC}$, where X is a rare-gas atom and BC is a chemical bonded diatomic molecule. The Hamiltonian for nuclear motion, after separation of the center of mass of the whole system, may be written as

$$H = \frac{\hbar^2}{2\mu_{\text{X,BC}}} \left(-\frac{\partial^2}{\partial R_{\text{X,BC}}^2} + \frac{l^2}{R_{\text{X,BC}}^2} \right) + \frac{\hbar^2}{2\mu_{\text{BC}}} \left(-\frac{\partial^2}{\partial R_{\text{BC}}^2} + \frac{j^2}{R_{\text{BC}}^2} \right) + U_{\text{BC}}(R_{\text{BC}}) + V(R_{\text{X,BC}}, R_{\text{BC}}, \gamma), \quad (2)$$

where $R_{\text{X,BC}}$ is the distance between X and the center of mass of BC, R_{BC} is the internuclear distance for BC, while γ is the angle between the two vectors $\mathbf{R}_{\text{X,BC}}$ and $\mathbf{R}_{\text{BC}}$. The $\mu_{\text{X,BC}}$ and μ_{BC} factors are the corresponding reduced masses. Finally, l and j are the two angular momentum operators (in units of $\hbar$) associated with $\mathbf{R}_{\text{X,BC}}$ and $\mathbf{R}_{\text{BC}}$, respectively. In Eq. (2), $U_{\text{BC}}(R_{\text{BC}})$ is the intramolecular potential interaction for the "free" diatomic molecule BC while V is the van der Waals interaction. We thus have $V \rightarrow 0$ as $R_{\text{X,BC}} \rightarrow \infty$.

We shall now construct the zero-order "nuclear diabatic" basis set for treating vibrational predissociation as^{11,12}

$$\psi_{v_1}(\mathbf{R}_{\text{X,BC}}, \mathbf{R}_{\text{BC}}) = \chi_{v_1}(R_{\text{BC}}) \varphi(\mathbf{R}_{\text{X,BC}}, \hat{\mathbf{R}}_{\text{BC}}), \quad (3)$$

where $\hat{\mathbf{R}}_{\text{BC}}$ is the unit vector associated to $\mathbf{R}_{\text{BC}}$. The function $\chi_{v_1}(R_{\text{BC}})$ is the solution of the BC intramolecular Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu_{\text{BC}}} \frac{\partial^2}{\partial R_{\text{BC}}^2} + U_{\text{BC}}(R_{\text{BC}}) \right] \chi_{v_1} = E_{\text{BC}}(v_1) \chi_{v_1}, \quad (4)$$

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corresponding to vibrational quantum number v_1 , while $\phi(R_{\text{X,BC}}, \gamma)$ is the solution of

$$\left[\frac{\hbar^2}{2\mu_{\text{X,BC}}} \left(-\frac{\partial^2}{\partial R_{\text{X,BC}}^2} + \frac{l^2}{R_{\text{X,BC}}^2} \right) + V(R_{\text{X,BC}}, \gamma) + B j^2 \right] \times \phi(R_{\text{X,BC}}, \gamma) = \epsilon \phi(R_{\text{X,BC}}, \gamma), \quad (5)$$

where

$$V(R_{\text{X,BC}}, \gamma) = V(R_{\text{X,BC}}, \bar{R}_{\text{BC}}, \gamma) \quad (6)$$

and

$$B = \frac{\hbar^2}{2\mu_{\text{BC}} \bar{R}_{\text{BC}}^2}. \quad (7)$$

The zero-order equation (5) has discrete $\epsilon < 0$ as well as continuum $\epsilon > 0$ solutions. The overall process of vibrational predissociation involves the decay of one of these discrete, quasibound states into the continuum of other v_1 channels induced by the couplings neglected in the Hamiltonian. Using the "golden-rule" approximation, we will then write for the vibrational predissociation linewidths

$$\Gamma_{v_1} = \pi \sum_{v_1' < v_1} |\langle \psi_{v_1}^{\text{discrete}} | V | \psi_{v_1'}^{\text{continuum}} \rangle|^2 \quad (8)$$

for energy-normalized continuum wave functions. We turn now to the determination of the solutions of Eq. (5). We shall treat differently the discrete and the continuum wave functions. For the discrete wave functions we use the fact that the wave function is sensitive mainly to the details of the potential surface in the region of the well.⁷ We replace then $R_{\text{X,BC}}$ in the centrifugal term of Eq. (5) by some equilibrium distance $\bar{R}_{\text{X,BC}}$. We then write the functions ϕ as

$$\phi_{v_2}(R_{\text{X,BC}}, \hat{R}_{\text{BC}}) = \phi_{v_2}(R_{\text{X,BC}}, \gamma) F_{v_2}(\hat{R}_{\text{X,BC}}, \hat{R}_{\text{BC}}), \quad (9)$$

where $\phi(R_{\text{X,BC}}, \gamma)$ is the solution of

$$\left[-\frac{\hbar^2}{2\mu_{\text{X,BC}}} \frac{\partial^2}{\partial R_{\text{X,BC}}^2} + V(R_{\text{X,BC}}, \gamma) \right] \phi_{v_2}(R_{\text{X,BC}}, \gamma) = W_{v_2}(\gamma) \phi_{v_2}(R_{\text{X,BC}}, \gamma), \quad (10)$$

where v_2 is the vibrational quantum number for the van der Waals bond stretch.

Notice that Eq. (9) is a rotational "adiabatic" function depending parametrically on γ . We are interested here in systems like HeI_2 for which the rotational motion is much slower than the vibrational motion of the van der Waals bond. We may then apply the adiabatic approximation

$$l^2 \phi = \phi l^2 F, \quad (11a)$$

$$j^2 \phi = \phi j^2 F, \quad (11b)$$

and neglect the effect of the angular momentum operators on the vibrational wave function $\phi(R_{\text{X,BC}}, \gamma)$. Introducing now Eq. (9) into Eq. (5) and using Eq. (11), we obtain, after multiplication by ϕ^* and integration over $R_{\text{X,BC}}$,

$$[b l^2 + B j^2 + W_{v_2}(\gamma)] F_{v_2, v_3} = \epsilon_{v_2, v_3} F_{v_2, v_3}, \quad (12)$$

with

$$b = \frac{\hbar^2}{2\mu_{\text{X,BC}} \bar{R}_{\text{X,BC}}^2} \quad (13)$$

The additional quantum number v_3 appearing in Eq. (12) corresponds to bending (libration or hindered rotation) of the complex. The solution of Eq. (12) is now straightforward by expansion of F in any complete rotational basis set and diagonalization. We have chosen here the "body-fixed" system of Refs. 13–15, so that

$$F_{v_2, v_3}(\hat{R}_{\text{X,BC}}, \hat{R}_{\text{BC}}) = \sum C_{j\Omega}^{(v_2, v_3)} \langle \hat{R}_{\text{X,BC}}, \hat{R}_{\text{BC}} | JM; \Omega \rangle, \quad (14)$$

with

$$\langle \hat{R}_{\text{X,BC}}, \hat{R}_{\text{BC}} | JM; \Omega \rangle = \left(\frac{2J+1}{4\pi} \right)^{1/2} D_{j\Omega}^{J*}(\phi, \theta, 0) Y_{j\Omega}(\gamma, \psi), \quad (15)$$

where J is the total angular momentum quantum number associated to the operator $\mathbf{J} = \mathbf{j} + 1$, M corresponds to the projection of $\mathbf{J}$ on the space-fixed z axis, j is the rotational quantum number associated to $\mathbf{j}$ and referred to the body-fixed system of coordinates, while Ω is the "tumbling"¹⁵ angular momentum quantum number corresponding to the component of $\mathbf{J}$ on the body-fixed z axis (i.e., $\mathbf{R}_{\text{X,BC}}$). The function $D_{j\Omega}^{J*}(\phi, \theta, 0)$ is an element of the Wigner rotation matrix¹⁶ with θ and ϕ being the polar angles of $\mathbf{R}_{\text{X,BC}}$ in the "space-fixed" system of coordinates, while $Y_{j\Omega}$ is a spherical harmonic function depending on the polar angles γ and ψ of $\mathbf{R}_{\text{BC}}$ with respect to the body-fixed system of reference. The states $|JMj\Omega\rangle$ are eigenstates of the angular momentum operators $\mathbf{J}^2$, $\mathbf{J} \cdot \mathbf{z}^{\text{SF}}$, $\mathbf{j}^2$, and $\mathbf{J} \cdot \mathbf{R}_{\text{X,BC}}$ with eigenvalues J , M , j , and Ω , respectively. J and M are good quantum numbers for this problem but not j and Ω . The sum in Eq. (14) is thus restricted to j and Ω . The matrix elements of the operators l^2 and j^2 in the body-fixed basis set $|JMj\Omega\rangle$ are given by^{13–15}

$$\langle JMj\Omega | j^2 | JMj'\Omega' \rangle = \delta_{jj'} \delta_{\Omega\Omega'} j(j+1), \quad (16)$$

$$\langle JMj\Omega | l^2 | JMj'\Omega' \rangle = \delta_{jj'} \{ \delta_{\Omega\Omega'} [J(J+1) + j(j+1) - 2\Omega^2] - \delta_{\Omega\pm 1, \Omega'} [J(J+1) - \Omega(\Omega\pm 1)]^{1/2} [j(j+1) - \Omega(\Omega\pm 1)]^{1/2} \}.$$

The matrix elements of $W(\gamma)$ may be obtained by first expanding the function in terms of Legendre polynomials $P_\lambda(\cos\gamma)$, i.e.,

$$W_{v_2}(\gamma) = \sum_\lambda a_\lambda P_\lambda(\cos\gamma) \quad (17)$$

and then using the analytic expression^{13–15}

$$\langle JMj\Omega | P_\lambda(\cos\gamma) | JMj'\Omega' \rangle = \delta_{\Omega\Omega'} \left(\frac{2j'+1}{2j+1} \right)^{1/2} \times C \langle j'0\lambda 0 | j'\lambda j 0 \rangle C \langle j'\lambda\Omega 0 | j'\lambda j \Omega \rangle, \quad (18)$$

where $C \langle j_1 M_1 j_2 M_2 | j_1 j_2 j_3 M_3 \rangle$ are Clebsch–Gordan coefficients.¹⁶ Once all the matrix elements of l^2 , j^2 , and $W(\gamma)$ have been calculated, the coefficients $C_{j\Omega}^{(v_2, v_3)}$ of Eq. (14) are simply obtained by diagonalization of Eq. (12). We turn now to the determination of the continuum wave functions. We shall use the infinite-order sudden approximation.^{8–10} In this method Eq. (5) is simplified by making the approximations

$$j^2\psi = j_0(j_0 + 1)\psi, \quad (19)$$

$$l^2\psi = l_0(l_0 + 1)\psi, \quad (20)$$

where j_0 and l_0 are constants whose choice depends on the initial conditions. In our case we are dealing with low rotational excitation so that j_0 and l_0 may be chosen to be zero. We then write the functions φ as

$$\varphi(\mathbf{R}_{\text{X,BC}}, \hat{R}_{\text{BC}}) = \phi_\epsilon(R_{\text{X,BC}}; \gamma) \langle \hat{R}_{\text{X,BC}}, \hat{R}_{\text{BC}} | JMj\Omega \rangle, \quad (21)$$

with ϕ_ϵ obeying the Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu_{\text{X,BC}}} \frac{\partial^2}{\partial R_{\text{X,BC}}^2} + V(R_{\text{X,BC}}, \gamma) \right] \phi_\epsilon(R_{\text{X,BC}}; \gamma) = \epsilon \phi_\epsilon(R_{\text{X,BC}}; \gamma), \quad (22)$$

where ϵ is the relative kinetic energy between the fragments.

We are now in position to calculate the linewidths from Eq. (8). Neglecting the small contribution of the centrifugal terms, we obtain for the total linewidth of the level specified by vibrational quantum numbers v_1 , v_2 , and v_3 :

$$\Gamma_{v_1, v_2, v_3} = \pi \sum_{v_1', j'} \left| \sum_{j\Omega} C_{j\Omega}^{(v_2 v_3)} \langle JMj\Omega | V_{v_1 v_2, v_1' \epsilon}^{d-c}(\gamma) | JMj' \Omega \rangle \right|^2, \quad (23)$$

where

$$V_{v_1 v_2, v_1' \epsilon}^{d-c}(\gamma) = \langle \phi_{v_2}(R_{\text{X,BC}}; \gamma) \chi_{v_1}(R_{\text{BC}}) | V(R_{\text{X,BC}}, R_{\text{BC}}, \gamma) | \phi_{v_1}(R_{\text{X,BC}}; \gamma) \chi_{v_1'}(R_{\text{BC}}) \rangle \quad (24)$$

is a "distorted-wave" discrete-continuum coupling. These coupling terms are similar to those of the fixed-configuration calculations.^{11,12} In particular for $\gamma=0$, Eq. (24) is the expression for the distorted-wave discrete-continuum couplings in the colinear model.^{11(a),12}

We now address ourselves to the determination of the final vibrational and rotational distribution of the diatomic fragment BC. Using again the simple golden-rule model, we obtain that the probability for detecting the diatomic fragment BC in the state specified by the vibrational quantum number v_1' and rotational quantum number j' , if the initial state was specified by the quantum numbers v_1 , v_2 , and v_3 is¹¹

$$P_{v_1 v_2 v_3 \rightarrow v_1' j'} = \frac{\pi \left| \sum_{j\Omega} C_{j\Omega}^{(v_2 v_3)} \langle JMj\Omega | V_{v_1 v_2, v_1' \epsilon}^{d-c}(\gamma) | JMj' \Omega \rangle \right|^2}{\Gamma_{v_1 v_2 v_3}}, \quad (25)$$

with $\Gamma_{v_1 v_2 v_3}$ given by Eq. (23).

III. APPLICATION TO THE HeI₂(B) VAN DER WAALS MOLECULE

In this section we will apply our general expressions (23)–(25) to the van der Waals molecule HeI₂ in the electronically excited $B^3\pi$ configuration. This system has been studied experimentally⁶ as well as theoretically,^{7,11} the last being limited however to fixed (colinear or perpendicular) configurations. The van der Waals interaction will be specified in terms of two pairwise

interactions between the He atom and each one of the iodine atoms, i.e.,

$$V(R_{\text{X,BC}}, R_{\text{BC}}, \gamma) = U_{\text{HeI}}(R_{\text{XB}}) + U_{\text{HeI}}(R_{\text{XC}}), \quad (26)$$

where the interparticle distances R_{XB} and R_{XC} are related to the dissociation coordinates $R_{\text{X,BC}}$, R_{BC} , and γ by the trigonometric relations

$$R_{\text{XB}} = (R_{\text{X,BC}}^2 + R_{\text{BC}}^2 - 2\xi_{\text{C}} R_{\text{BC}} R_{\text{X,BC}} \cos\gamma)^{1/2}, \quad (27a)$$

$$R_{\text{XC}} = (R_{\text{X,BC}}^2 + R_{\text{BC}}^2 + 2\xi_{\text{B}} R_{\text{BC}} R_{\text{X,BC}} \cos\gamma)^{1/2}, \quad (27b)$$

with

$$\xi_{\text{Y}} = \frac{m_{\text{Y}}}{m_{\text{B}} + m_{\text{C}}}, \quad \text{Y = B or C.} \quad (28)$$

The individual interactions U_{HeI} have been specified by Morse potentials

$$U_{\text{HeI}}(R) = D \{ \exp[-2\alpha(R - R_0)] - 2 \exp[-\alpha(R - R_0)] \}. \quad (29)$$

We now expand the potential (26) in a Taylor series around the equilibrium position $\bar{R}_{\text{BC}}$ of the diatomic molecule BC, i.e.,

$$V(R_{\text{X,BC}}, R_{\text{BC}}, \gamma) = \sum_n \frac{\partial^n V(R_{\text{X,BC}}, R_{\text{BC}}, \gamma)}{\partial R_{\text{BC}}^n} \bigg|_{\bar{R}_{\text{BC}}} \frac{(R_{\text{BC}} - \bar{R}_{\text{BC}})^n}{n!}. \quad (30)$$

The intramolecular potential for BC is represented by a Morse potential with parameters obtained from the literature.^{17,18} The matrix elements of $(R_{\text{BC}} - \bar{R}_{\text{BC}})^n$ between Morse oscillator wave functions are known.^{19–21} Finally, for each γ we may fit the $\partial^n V / \partial R_{\text{BC}}^n$ factors in terms of Morse and exponential functions of $R_{\text{X,BC}}$.

We will then have after this fitting procedure that $V(R_{\text{X,BC}}, \gamma)$ of Eq. (6) will be given by

$$V(R_{\text{X,BC}}, \gamma) = D(v) \{ \exp\{-2\alpha(\gamma)[R_{\text{X,BC}} - \bar{R}(\gamma)]\} - 2 \exp\{-\alpha(\gamma)[R_{\text{X,BC}} - \bar{R}(\gamma)]\} \} \quad (31)$$

and using the well-known wave functions and eigenvalues for the Morse potentials,²¹ we get

$$W_{v_2}(\gamma) = -\frac{\hbar^2 \alpha^2(\gamma)}{2\mu_{\text{X,BC}}} [K(\gamma) - V_2 - \frac{1}{2}], \quad (32)$$

with

$$K(\gamma) = [2\mu_{\text{X,BC}} D(\gamma)]^{1/2} / \hbar \alpha(\gamma). \quad (33)$$

For the HeI₂ system it has been found⁷ that the linearization approximation, which consists of keeping only the first two terms in the Taylor expansion of the potential, is adequate. If this approximation is performed in Eq. (24), we obtain

$$V_{v_1 v_2, v_1' \epsilon}^{d-c}(\gamma) = \langle \chi_{v_1} | (R_{\text{BC}} - \bar{R}_{\text{BC}}) | \chi_{v_1'} \rangle \times \langle \phi_{v_2} | \frac{\partial V(R_{\text{X,BC}}, R_{\text{BC}}, \gamma)}{\partial R_{\text{BC}}} \bigg|_{\bar{R}_{\text{BC}}} | \phi_\epsilon \rangle \quad (34)$$

and we see that like in the fixed-configuration calculations⁷ the discrete-continuum couplings consist in the product of an intermolecular term depending on the

parameters of the van der Waals interaction potential and on the final relative kinetic energy of the recoiling fragments, and an intramolecular factor which depends only on the properties of the "free" I_2 molecule. This factor is responsible for the strong propensity rule $v_1' = v_1 - 1$ found in the experiments.⁶ Expanding now

$$\left. \frac{\partial V(R_{X,BC}, R_{BC}, \gamma)}{\partial R_{BC}} \right|_{\bar{R}_{BC}} = \sum_m b_m(\gamma) e^{-\beta_m(\gamma) R_{X,BC}}, \quad (35)$$

all the matrix elements in Eq. (34) are analytically known.^{7,22} It should be noticed at this point that, since we are fitting the effective potentials $V(R_{X,BC}, \bar{R}_{BC}, \gamma)$ and $\partial V / \partial R_{BC} |_{\bar{R}_{BC}}$ by Morse or exponential functions, there is no restriction to the form of the original intermolecular potential energy surface $V(R_{X,BC}, R_{BC}, \gamma)$. In particular, we are not restricted to the pairwise assumption of Eq. (26) or to the Morse functional form for the individual interatomic potentials in Eq. (29). In the absence of detailed knowledge of the potential surface, however, the pairwise assumption of Eq. (26) is likely to be a reasonable approximation for a system like HeI_2 . The Morse functional forms for the individual interatomic interactions [Eq. (29)] have been chosen in order to make contact with our previous calculations.⁷ We have shown⁷ that the linewidths are largely insensitive to the long-range part of the potential (at least for the lower bound levels of the van der Waals bond) and that the Morse potentials provide an adequate representation of the van der Waals interaction in the region of the well. We are not attempting here to reproduce the experimental results for $\text{HeI}_2(B)$, by adjusting the intermolecular potential parameters in Eq. (29), but rather to study the effect of rotational motion for some typical, reasonable, values of the interaction constants. Consequently, we have chosen two sets of values for D , α , and R_0 which were used in our previous work⁷:

FIG. 1. Lowest effective potential for the bending motion $W_{v_2=0}(\gamma)$ of the $\text{HeI}_2(B)$ molecule. The parameters of the intermolecular potential energy surface are $D = 18 \text{ cm}^{-1}$, $\alpha = 1.14 \text{ \AA}^{-1}$, and $R_0 = 4 \text{ \AA}$. The equilibrium internuclear distance of the $\text{I}_2(B)$ bond is taken to be $\bar{R}_{BC} = 3.016 \text{ \AA}$ from Ref. 18. The first three levels supported by this potential are indicated as horizontal lines.

FIG. 2. Energy level diagram for some bound and quasibound states of the van der Waals molecule $\text{HeI}_2(B)$. The energy represented is $\epsilon_{v_2 v_3}$ [see Eq. (12) in the text] and is relative to the vibrational energy of the $\text{I}_2(B)$ bond. The parameters of the intermolecular potential energy surface are the same as those in Fig. 1.

$$D = 7 \text{ cm}^{-1}, \quad \alpha = 1.24 \text{ \AA}^{-1}, \quad R_0 = 4 \text{ \AA}, \quad (36a)$$

$$D = 18 \text{ cm}^{-1}, \quad \alpha = 1.14 \text{ \AA}^{-1}, \quad R_0 = 4 \text{ \AA}. \quad (36b)$$

The frequency and anharmonicity of the $\text{I}_2(B)$ bond have been taken from the literature¹⁷ and the equilibrium internuclear distance used was¹⁸ $\bar{R}_{BC} = 3.016 \text{ \AA}$. We have performed the calculation for a set of 11 values of $\gamma = n\pi/10$, $n = 0, 1, \dots, 10$ (for symmetry reasons only the range $0 \leq \gamma \leq \pi/2$ needs to be considered here). In Fig. 1 we have represented the eigenvalue $W_{v_2=0}$ of Eq. (10), which is given in Eq. (32), as a function of γ for the parameters (36b). This function constitutes an effective potential for the bending motion [see Eq. (12)]. Three levels of this potential are also represented on Fig. 1. We notice that the $v_3 = 0$ level corresponds to bending vibrations with rather small amplitude oscillations around $\gamma = \pi/2$. This is expected since the pairwise potential of Eq. (26) has its minimum for $\gamma = \pi/2$. The first excited level $v_3 = 1$ has much larger oscillating amplitudes, while the second excited level $v_3 = 2$ is almost a free rotating state.

In Fig. 2 we have represented, for the same parameters, several bound states of the complex ($\epsilon_{v_2 v_3} < 0$) together with some rotational quasibound levels. For the potential parameters used here there are only two bound stretching states ($v_2 = 0, 1$). The $v_2 = 0$ manifold supports four bending bound levels ($v_3 = 0, 1, 2, 3$) while the $v_2 = 1$ has only two bending bound levels ($v_3 = 0, 1$). Altogether there are six bound states of the molecule for $J = 0$. Notice that the first excited state ($v_2 = 0, v_3 = 1$) corre-

sponds to the excitation of the bending and not of the stretching. In Fig. 2 we also compare the approximate first two energies obtained using the present method with the exact eigenvalues of Eq. (5) obtained by a diagonalization of the Hamiltonian. We notice the very good correspondence between approximate and exact results, the error being in the two cases of the order of 1%. For $v_1=0$ all the levels with $\epsilon_{v_2v_3} < 0$ will correspond to true bound states of the complex, while those with $\epsilon_{v_2v_3} > 0$ will correspond to quasibound states decaying by predissociation induced by the couplings neglected in the approximations leading from Eqs. (5)–(12), i.e., the adiabatic rotational approximation of Eqs. (11) and the replacement of $R_{X,BC}$ by $\bar{R}_{X,BC}$ in the centrifugal terms. These processes will not be considered here. In this paper, we are interested instead in the vibrational predissociation of the lowest bound state $v_2=v_3=0$ for an excited vibrational state of the I_2 bond:

We now turn to the calculation of the total widths $\Gamma_{v_1v_2v_3}$, according to Eq. (8). In Figs. 3 and 4 we present the linewidths for the $v_2=v_3=0$ of the $\text{HeI}_2(B)$ molecule as a function of the vibrational quantum number v_1 of the I_2

FIG. 3. Vibrational predissociation linewidths for the $\text{HeI}_2(B)$ molecule as a function of the stretching quantum number v_1 corresponding to the vibration of the I_2 bond. The other quantum numbers v_2 and v_3 as well as the total angular momentum J are equal to zero. The parameters of the intermolecular potential energy surface are $D=7 \text{ cm}^{-1}$, $\alpha=1.24 \text{ Å}^{-1}$, $R_0=4 \text{ Å}$, and $\bar{R}_{ac}=3.016 \text{ Å}$. The frequency and anharmonicity of the I_2 bond are taken from Ref. 17: $\omega_e=125,273 \text{ cm}^{-1}$, $\omega_e x_e=0.7016 \text{ cm}^{-1}$. The curve labeled 3-Dimensional corresponds to the results of the approximate treatment for treating the effect of rotations, presented in this work. The curves labeled *colinear* and *perpendicular* are the results obtained for fixed angular configurations $\gamma=0$ and $\gamma=\pi/2$.

FIG. 4. Same as Fig. 3 for the parameters $D=18 \text{ cm}^{-1}$, $\alpha=1.14 \text{ Å}^{-1}$.

bond, for the two set of parameters given in Eqs. (36). The results denoted 3-Dimensional are those obtained with the present method and they are compared with those obtained for the colinear and perpendicular models.^{7,11} We notice that the effect of rotations is to narrow the line. The colinear model gives the largest linewidths while the perpendicular calculations give some intermediate values.

Finally, in Fig. 5 we have represented the final rotational distribution of the I_2 fragments for the two sets of parameters given in Eqs. (36). The quantum numbers of the predissociated state are $v_1=25$, $v_2=0$, $v_3=0$, and $J=0$. The distribution has a maximum for $j'=2$ [j' being the final rotational quantum number of the $\text{I}_2(B)$ fragment] and a width of about 2 being broader for the potential with larger D (i.e., with larger anisotropy). The fraction of energy going to rotation is thus very small owing to the very small rotational constant of the I_2 fragment. For the parameter of Eq. (36a) we get $E_{\text{rot}}=0.3 \text{ cm}^{-1}$ while for those of Eq. (36b), $E_{\text{rot}}=0.4 \text{ cm}^{-1}$.

IV. DISCUSSION OF THE RESULTS

We have presented an approximate quantum mechanical treatment of the effect of rotations on the vibrational predissociation of the van der Waals molecule HeI_2 . The method is closely related to the *rotational infinite order sudden approximation*⁸⁻¹⁰ used in scattering problems. In particular, for the bound states, the approximation may be considered as an adiabatic decoupling between rotations and stretching vibrations. The HeI_2 molecule, with its small rotational constant, should constitute a suitable system for the application of these approximations. The fact that the approximate positions of the bound states of the complex are given so accurately

FIG. 5. Final states rotational distribution of the $\text{I}_2(\text{B})$ fragments in the vibrational predissociation of the $\text{HeI}_2(\text{B})$ molecule. The quantum numbers of the predissociated states are $v_1=25$, $v_2=0$, $v_3=0$, and $J=0$. The values of the parameters D , α , and R_0 are indicated in the figure. All other constants are as in Fig. 3.

(see Fig. 2) constitutes a strong indication in favor of this assumption. We have shown that the first excited level of the complex for $J=0$ corresponds to the excitation of the bending motion rather than excitation of the van der Waals stretching. This is a confirmation of an earlier suggestion by Levy.²³ The energy difference between the first excited level and the ground state for the parameters of Eq. (36b) is 9.1 cm^{-1} . This is to be compared with the experimental result of 6 cm^{-1} . Sharfin *et al.*^{6(d)} have also determined the dissociation energy to be $W_0 < 18.5\text{ cm}^{-1}$. From Fig. 2 we obtain $W_0 = 20.6\text{ cm}^{-1}$ for the parameters of Eq. (36b). This set of parameters therefore gives results in approximate correspondence with the spectroscopic data. They also give good estimates of the absolute value of the experimental linewidths when used in the perpendicular model.⁷ From Fig. 4 it is seen that the effect of the rotations is to change the results obtained in the perpendicular model by a factor of 2–3. The parameters D , α , and R_0 should therefore be adjusted again in order to fit simultaneously the absolute values of the widths and the spectroscopic data.⁶ This work is now in progress.

It should be stressed at this point that the results presented in Figs. 3 and 4 indicate that for an order of magnitude estimate of the widths the colinear and perpendicular models are adequate. In particular, since we are using a dumbbell model for the potential, the T-shaped configuration is favored and the perpendicular model gives results which only differ by a factor of 2–3

from the three-dimensional values. It should also be noticed here that all the models give a quasiquadratic dependence of the linewidths as a function of v_1 , in good correspondence with the experimental data⁶ [see also Eq. (1)]. Recently, Ramaswamy and DePristo²⁴ have presented a *scaling theoretical analysis*²⁵ of the dependence of the vibrational predissociation linewidths as a function of the vibrational excitation, concluding that for this system (and likely for many others) the van der Waals bond potential (and therefore the anisotropy of the total potential energy surface) is unimportant for the scaling of the linewidths. Thus, only the absolute value of the linewidths are sensitive to the details of the potential. This point is borne out by our previous model calculations.⁷

We have also obtained final rotational distributions for the $\text{I}_2(\text{B})$ fragments. The distribution shows very little rotational excitation and that the fraction of the available energy going to rotational energy of the I_2 fragment is small compared with the energy going to translational motion. We therefore conclude on the basis of the calculations presented here that vibrational predissociation in the HeI_2 molecule is essentially a *half-collision* pure V - T process.²⁶ It should be noticed, however, that all the calculations in this paper have been conducted for total angular momentum $J=0$. In the actual experiments an initial rotational distribution exists.⁶ The rotational temperature associated with this distribution is, however, very low so we may expect that the general features of the results presented in this work will remain unchanged.

Note added in proof: E. Segev and M. Shapiro (to be published) have pointed out to us that there are more excited bound levels of the system than those indicated in Figs. 1 and 2. The levels presented in Figs. 1 and 2 correspond to linear combinations of basis states with even values of the angular momentum quantum number l which, because of symmetry, are uncoupled from the odd. Therefore, there is another manifold of excited bending levels corresponding to odd values of l . The lowest energy level of the system remains, however, the one which we consider here. Recently Blazy *et al.* [J. Chem. Phys. **72**, 2439 (1980)] have determined accurately the dissociation energy of the $\text{HeI}_2(\text{B})$ complex with the result $W_0 = 14.5\text{ cm}^{-1}$. For symmetry reasons they have also ruled out the possibility that the first excited state they are seeing would correspond to bending excitation. Further work is needed in order to elucidate this interesting aspect of the energetics of the HeI_2 van der Waals molecules.

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