A closecoupling infinite order sudden approximation (IOSA) to study vibrational predissociation of the HeI2 van der Waals molecule

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We apply in this paper a model related to the "infinite order sudden approximation" to treat the vibrational predissociation of the HeI$_2$ van der Waals molecule. For each configuration, the stretching motions within the complex are exactly solved in the close-coupling formalism. The bending motion is then considered in an approximate way and averaged predissociation rates are obtained. Our results are compared with the experiment and also with previous models.

I. INTRODUCTION

A great deal of theoretical effort is being addressed to the elucidation of the mechanism of energy transfer which occurs in vibrational predissociation (VP) of polyatomic molecules. In particular, it is well known the role played by van der Waals (VDW) molecules in this context. HeI$_2$(B) is one of the most carefully studied systems. This complex provides an excellent example of VP consisting in the flow of vibrational energy stored in the I$_2$ molecule to the VDW bond leading to its fragmentation.

Several theoretical models have been used in order to explain the experimental[1] behavior of the VP rates as a function of the vibrational excitation of the diatomic subunit: (a) Close-coupling calculations in the collinear[2] and T-shaped[3] configurations; (b) approximate three-dimensional (3D) quantal calculations using a distorted-wave treatment for vibration and sudden approach for rotational motions[4]; (c) quasiclassical trajectory calculations[5]; and (d) A full photodissociation process calculation[6] in the framework of the infinite order sudden approximation (IOSA) by using the artificial channel method.[7]

In the He–I$_2$ photodissociation process, we can recognize three steps: (1) complex formation, where the I$_2$ subunit is in its ground electronic and vibrational state; (2) optical excitation to a precise vibrational level v in the B excited state of I$_2$; and (3) predissociation, that results in He and I$_2$ fragments, where I$_2$ is in a vibrational level $v' < v$ of the B state.

Traditionally, because the excitation is much faster than the dissociation, the process was assumed[2–5] to be almost independent of step (2). Hence, the initial situation was considered to correspond to a quasibound level of the He–I$_2$ (B,v) complex. Subsequently, the couplings of this level with different He + I$_2$($B,v' < v$) continua give rise to dissociation of the molecule.

On the other hand, Shapiro *et al.*[6] have concluded that the separation of steps (2) and (3) cannot be done within the IOSA due to effects arising from the interference between direct photodissociation and predissociation processes. Hence, the calculations of these authors involve both electronic states, He–I$_2$(X) and He–I$_2$(B), together with a transition dipole operator in the IOSA framework. Shapiro *et al.*[6] claim that a predissociation linewidth Γ, calculated in step (3), depending on the atom–diatom orientation θ, is

meaningless because the librational time is even smaller than the lifetime of the complex.

Our point of view is, however, that in a time-independent treatment, time only becomes meaningful as associated to energy uncertainties. Therefore, provided that energies associated to rotational motions are much lower than vibrational ones within the complex, an adiabatic angular approximation is justified. After that, the variation in θ is taken into account by using a proper distribution of this quantity.

As regards the relative importance of direct photodissociation, it strongly depends on the potential surfaces assumed. In fact, the surface corresponding to B state in Ref. 6 is quite different of that used in Refs. 2–4.

Based on these reasons, and in line with previous works,[2–4] we assume the independency of VP process on the excitation step. We then extend collinear[2] and T-shaped[3] calculations to a collection of relative atom–diatom orientations. The method consists in exactly solving stretching motions, at each θ fixed orientation, by means of close-coupling (CC) calculations. The angular-dependent energy positions of the corresponding scattering resonances will be considered as the effective bending potentials. Taking into account the rotational terms neglected in θ-fixed CC calculations, triatomic energy levels and angular wave functions are obtained. These functions are then used to carry out an average of θ-dependent widths, yielding final VP rates. This treatment of VP and the results obtained are shown and discussed in following sections.

II. THEORY

We are interested in the quantum mechanical equation of motion for the X $\cdots$ BC system. The Hamiltonian for nuclear motion, after separation of the center of mass of the whole system, may be written as[4(a)]

$$H = \frac{\hbar^2}{2\mu_{\text{X,BC}}} \left(-\frac{\partial^2}{\partial R_{\text{X,BC}}^2} + \frac{\mathbf{l}^2}{R_{\text{X,BC}}^2} \right)$$
$$+ \frac{\hbar^2}{2\mu_{\text{BC}}} \left(-\frac{\partial^2}{\partial R_{\text{BC}}^2} + \frac{\mathbf{j}^2}{R_{\text{BC}}^2} \right)$$
$$+ \mathscr{U}_{\text{BC}}(R_{\text{BC}}) + V(R_{\text{X,BC}}, R_{\text{BC}}, \theta), \qquad (1)$$

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 θ is the angle between the two vectors $\mathbf{R}_{\text{BC}}$ and $\mathbf{R}_{\text{X,BC}}$. The

$\mu_{X,BC}$ and μ_{BC} factors are the corresponding reduced masses. Finally, **l** and **j** are angular momentum operators associated with $R_{X,BC}$ and R_{BC}, respectively. $U_{BC}(R_{BC})$ is the intramolecular potential interaction for the "free" diatomic molecule BC while V is the van der Waals interaction. We thus have $V \to 0$ as $R_{X,BC} \to \infty$.

We consider here the HeI₂ complex where the process of VP involves mainly the coupling between the vibration of the diatomic subunit and the VDW stretching. A model related to the IOSA has been applied to treat rotational motions. It is assumed in this model that vibrational motions are much faster than rotational ones. For this system, it is particularly acceptable because the vibrational frequencies for the I₂ and He–I₂ stretch motions are ~ 125 and ~ 6 cm^{-1}, respectively, while the rotational constants associated to the I₂ and the complex are ~ 0.037 and ~ 0.27 cm^{-1}, respectively.[3(a)] Hence, the rotational motion can be considered as adiabatic and, therefore, we can take θ, the bending angle, as a parameter.

With all this in mind, we write the total wave function as

$$\Phi(\mathbf{R}_{X,BC}, \mathbf{R}_{BC}) = \Psi(R_{X,BC}, R_{BC}; \theta) \chi(\hat{R}_{X,BC}, \hat{R}_{BC}) \quad (2)$$

$\hat{R}_{X,BC}$ and $\hat{R}_{BC}$ being unit vectors in the $\mathbf{R}_{X,BC}$ and $\mathbf{R}_{BC}$ directions, respectively, and apply the adiabatic approximation

$$\begin{aligned} \mathbf{l}^2 \Phi &\simeq \Psi \mathbf{l}^2 \chi, \\ \mathbf{j}^2 \Phi &\simeq \Psi \mathbf{j}^2 \chi, \end{aligned} \quad (3)$$

i.e., we neglect the effect of the angular momentum operators on $\Psi(R_{X,BC}, R_{BC}; \theta)$ function. Then Ψ, describing the triatomic motion depending on θ as a parameter, is a solution of the following equation:

$$H_\theta \Psi(R_{X,BC}, R_{BC}; \theta) = E\Psi(R_{X,BC}, R_{BC}; \theta), \quad (4)$$

where

$$\begin{aligned} H_\theta = {} & -\frac{\hbar^2}{2\mu_{X,BC}} \frac{\partial^2}{\partial R_{X,BC}^2} - \frac{\hbar^2}{2\mu_{BC}} \frac{\partial^2}{\partial R_{BC}^2} \\ & + \mathcal{U}_{BC}(R_{BC}) + V(R_{X,BC}, R_{BC}; \theta). \end{aligned} \quad (5)$$

We expand the wave function as

$$\Psi(R_{X,BC}, R_{BC}; \theta) = \sum_v \phi_v(R_{BC}) \varphi_{vE}(R_{X,BC}; \theta), \quad (6)$$

where $\phi_v(R_{BC})$ are vibrational eigenfunctions for the free BC molecule which will be represented by eigenfunctions of the Morse potential. After substitution of expansion (6) into the Schrödinger equation (4), we obtain the set of close-coupling equations

$$\left[-\frac{\hbar^2}{2\mu_{X,BC}} \frac{\partial^2}{\partial R_{X,BC}^2} + \mathcal{U}_{v,v}(R_{X,BC}) + (\epsilon_v - E) \right]$$
$$\times \varphi_{vE}(R_{X,BC}; \theta) = -\sum_{v' \neq v} \mathcal{U}_{v,v'}(R_{X,BC}) \varphi_{vE}(R_{X,BC}; \theta), \quad (7)$$

where

$$\mathcal{U}_{v,v'}(R_{X,BC})$$
$$= \int dR_{BC}\, \phi_v^*(R_{BC}) V(R_{X,BC}, R_{BC}; \theta) \phi_{v'}(R_{BC}) \quad (8)$$

and ϵ_v is the energy of the free BC molecule in the vibrational

state v. The coupled differential equations may be solved by some of the currently available numerical integration methods [see Ref. 3(a)].

In order to avoid time consuming, numerical evaluation of integrals was performed. We have expanded the van der Waals potential $V(R_{X,BC}, R_{BC}; \theta)$ in a Taylor series up to second term around the equilibrium position $\overline{R}_{BC}$ of the BC diatomic molecule. The integrals (8) can be written as

$$\begin{aligned} \langle \phi_v | V(R_{X,BC}, R_{BC}; \theta) | \phi_{v'} \rangle &\simeq \langle \phi_v | V(R_{X,BC}, \overline{R}_{BC}; \theta) | \phi_{v'} \rangle \\ & + \frac{\partial V}{\partial R_{BC}} \bigg|_{\overline{R}_{BC}} \langle \phi_v | (R_{BC} - \overline{R}_{BC}) | \phi_{v'} \rangle \\ & + \frac{1}{2} \frac{\partial^2 V}{\partial R_{BC}^2} \bigg|_{\overline{R}_{BC}} \langle \phi_v | (R_{BC} - \overline{R}_{BC})^2 | \phi_{v'} \rangle, \end{aligned} \quad (9)$$

where the integrals $\langle \phi_v | (R_{BC} - \overline{R}_{BC})^l | \phi_{v'} \rangle$ with $l = 1,2$, were numerically calculated.[8]

Now, by solving the close-coupling equations at each θ value, positions of resonances sustained by the v channel, $E_{vn}(\theta)$ and rates for VP, $\Gamma_{vn}(\theta)$, were obtained by fitting a Lorentzian function of the energy to the probability $|S_{(v-2)\leftarrow(v-1)}(E)|^2$ as in a previous work[3(a)] and also by using a more accurate procedure.[3(b)] These quantities are indexed by means of the two quantum numbers v and n associated with the R_{BC} and $R_{X,BC}$ stretching motions, respectively.

We turn now to calculate energies of triatomic predissociating levels together with their corresponding widths, that is reached by evaluating the angular part of the wave function for discrete states.

As in previous works,[4] a total angular momentum $J = 0$ is considered, and this quantum number is omitted by simplicity.

Assuming the energy positions of the resonances, $E_{vn}(\theta)$, to be effective potentials for the bending motion and taking into account the rotational terms, the angular part of the wave function (2), χ, is the solution to the following equation:

$$\left[\frac{\hbar^2 \mathbf{l}^2}{2\mu_{X,BC} \overline{R}_{X,BC}^2} + \frac{\hbar^2 \mathbf{j}^2}{2\mu_{BC} \overline{R}_{X,BC}^2} + E_{vn}(\theta) \right]$$
$$\times \chi_{vnm}(\hat{R}_{X,BC}, \hat{R}_{BC})$$
$$= \epsilon_{vnm} \chi_{vnm}(\hat{R}_{X,BC}, \hat{R}_{BC}), \quad (10)$$

where m represents the quantum number associated to the bending motion. In Eq. (10) we have used the fact that discrete wave functions are mainly sensitive to the details of the potential surface in the region of the well. Hence, we have replaced $R_{X,BC}$ and R_{BC} in the rotational terms by reasonable equilibrium distances $\overline{R}_{X,BC}$ and $\overline{R}_{BC}$, respectively. Once the χ function is expanded in terms of an appropriate rotational basis set, the corresponding coefficients together with the triatomic levels ϵ_{vnm} are then obtained by simple diagonalization of Eq. (10).

A convenient rotational basis set is provided by the "body fixed" representation.[9] All the necessary matrix elements in this basis are analytically known[9] if the $E_{vn}(\theta)$ potential is expanded in terms of Legendre polynomials.[10]

For a triatomic level specified by the three quantum

numbers v, n, and m, we may obtain the associated VP rate, by using the corresponding χ angular function, as an average given by

$$\Gamma_{vnm} = \langle \chi_{vnm} | \Gamma_{vn}(\theta) | \chi_{vnm} \rangle. \tag{11}$$

We note this equation is also reached starting with the "Golden Rule" expression previously used[4] if the discrete-continuum couplings appearing in Eq. (23) of Ref. 4(a) are substituted by effective couplings $V_{vn}(\theta)$ such as

$$\pi | V_{vn}(\theta) |^2 = \Gamma_{vn}(\theta), \tag{12}$$

so that, the difference between the treatment of Ref. 4 and that developed here arises from using in the former a diabatic approximation to describe the diatomic vibrational motion. As a consequence, all couplings except the discrete continuum are neglected. On the contrary, CC treatment includes every kind of couplings yielding different effective potentials, and hence χ angular functions, together with different $\Gamma(\theta)$ values.

III. RESULTS

As it was already mentioned, a total angular momentum $J = 0$ has been considered along all the calculations. The potential was the same previously used.[4(b)] Seven θ values equally spaced over the range $[0,\pi/2]$ were taken, while the vibrational quantum number of I_2, v, was varied from 20 up to 35. For each θ value, we have focused our attention on that metastable level labeled by the quantum numbers v and $n = 0$, corresponding to the first resonance found in the CC calculation. In order to get convergency, two closed channels $(v,v + 1)$ together with three open ones $(v - 1,...,v - 3)$ were included.

In order to test the expansion of the potential (9) we have performed two calculations for $\theta = \pi/2$ (*T*-shaped) and $v = 20$. When we consider the expansion up to linear term we get $\Gamma = 0.071$ cm^{-1} while a value of $\Gamma = 0.070$ cm^{-1} is obtained when the quadratic term is also included. Therefore, the rates are almost insensitive to an expansion larger than the linear one.

Linewidths for VP at $v = 20$ are plotted vs the θ bending angle in Fig. 1. We show two kinds of calculations: (a) including diagonal terms $\langle \phi_v | (R_{BC} - \bar{R}_{BC}) | \phi_v \rangle$ (WD) and (b) without them (ND). The last approximation becomes exact when an harmonic oscillator describes the diatomic fragment and has largely been used in the past. In spite of calculation, (a) involves a better approximation, and the results obtained through calculation (b) are expected to be more plausible since the parameters describing the VDW interaction were fitted by means of this kind of approach in a *T*-shaped configuration[3(a)] in order to get the experimental rates. Each one of these calculations yields different behaviors: while the first one gives rise to a maximum at $\theta = \pi/2$, the largest value excluding the diagonal term is reached at the collinear configuration. In any case, the linewidths are very sensitive to the angle variation, but a minimum about $\theta = \pi/3$ is found, whatever the approach used. This is in agreement with the analytical discrete-continuum couplings obtained through the approximate 3D quantal model.[4] In fact, those couplings—as functions of θ—went from positive to negative values about $\theta = \pi/3$.
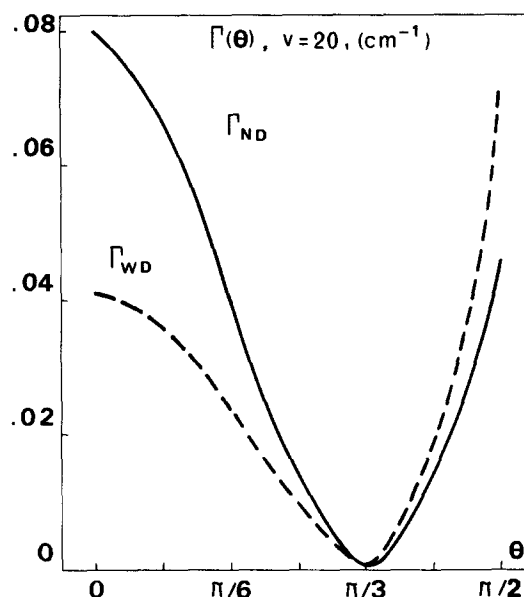

FIG. 1. Linewidths for VP at $v = 20$—as a function of the bending angle, θ—using the two kinds of calculations: Γ_{WD} (dashed line) and Γ_{ND} (full line). See the text.

In contrast of the different results obtained through WD and ND calculations concerned with widths, both approaches lead to very close resonance energies. In Fig. 2 we plot the energies $E_{v = 20,n = 0}$ vs θ, i.e., the effective bending potential corresponding to the ground VDW stretching level. Also in this figure we represent triatomic energies $\epsilon_{20,0,m}$, with $m = 0,1,2$, lying below zero. They were obtained by solving the bending equation (10). The angular basis set used to carry out the corresponding diagonalization included rotational diatomic states up to $j = 12$. Those triatomic levels are very close to the ones previously reported.[4(a)] In particular, for the ground state $\epsilon_{20,0,0}$, we obtain a value of $- 20.20$ cm^{-1}. If we compare this result with that reached
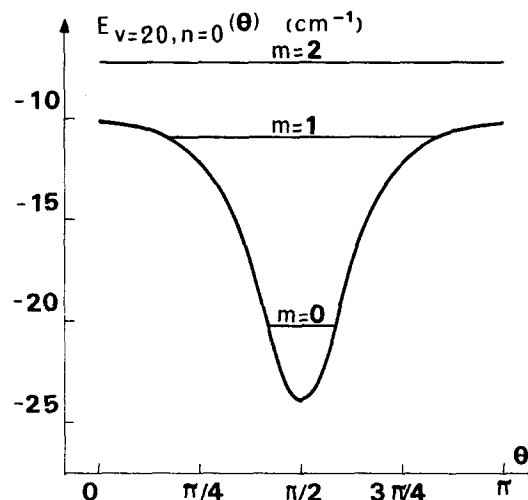

FIG. 2. Effective potential for the bending motion of HeI₂(B) molecule for $v = 20$ and $n = 0$. The horizontal lines represent the triatomic energy levels $\epsilon_{20,0,m}$ ($m = 0,1,2$). See the text.

TABLE I. VP linewidths calculated (expressed in cm^{-1}) for $v = 20, 23$, and 26 obtained through the ND approach at collinear (coll), perpendicular (T-shaped) configurations and the averaged 3D values. Also, it is included the corresponding values of Ref. 4(a).

	Reference 4(a)			Our results		
v	Coll	T-shaped	3D	Coll	T-shaped	3D
20	0.058	0.032	0.011	0.080	0.046	0.029
23	0.077	0.041	0.014	0.102	0.063	0.039
26	0.100	0.052	0.019	0.133	0.085	0.052

by means of a calculation solving exactly the $R_{X,BC}$ and θ motions, R_{BC} being fixed, a difference of 0.43 cm^{-1} is found. Moreover, using the angular function associated, $\chi_{20,0,0}$, we find a total contribution of rotational terms in this state of 1.55 cm^{-1}. Therefore, these results provide us reliability in the angular adiabatic approximation applied in this work. However, this approach is expected to be poorer and poorer as more excited bending levels are considered.

For the ground VDW level $n = m = 0$ and $v = 20,23,26$ we report in Table I tridimensional VP widths obtained by using Eq. (11) within the ND approach. Also in this table we show collinear and perpendicular widths, together with the corresponding values of Ref. 4(a). In both cases, whatever be v, the rates decrease following the sequence: collinear, T-shaped, and 3D. This behavior is not surprising within our treatment since a minimum of the rates near $\theta = \pi/3$ is ever found. So that, an additional degree of freedom supplies more stability to the complex because the 3D lifetimes are longer than T-shaped or collinear values. Also, from this table, we notice the present 3D rates are higher, by a factor ~2.7, than the previous ones,[4(a)] being closer to the experimental data.[1(a)] Hence, we may stress the importance of treating these kinds of problems using CC calculations compared with traditional Golden Rule approaches. In fact, although very close energetic results are found in both types of calculations, a big difference between the associated rates are obtained.

Finally, linewidths for VP are displayed vs the initial diatomic vibrational quantum number, v, in Fig. 3. In this figure we show the theoretical values, within the already mentioned approaches WD and ND averaged over the θ angle, together with the experimental results.[1(a)] As can be seen, both VP rates are in qualitative agreement with the experiment since they also follow an almost quadratic law as a function of the initial excitation. However, due to the potential parameters used in this work, the presumably better approximation gives poorer results, as it was already pointed out. Thus, in order to get a real agreement with the experiment, we must improve the corresponding parameters.

As a word of conclusion, the procedure presented in this work constitutes a very efficient alternative way to describe the dynamics of VDW complexes formed by a light atom and a heavy diatomic molecule. This encourages us to extend this type of treatment to more complicated systems in which
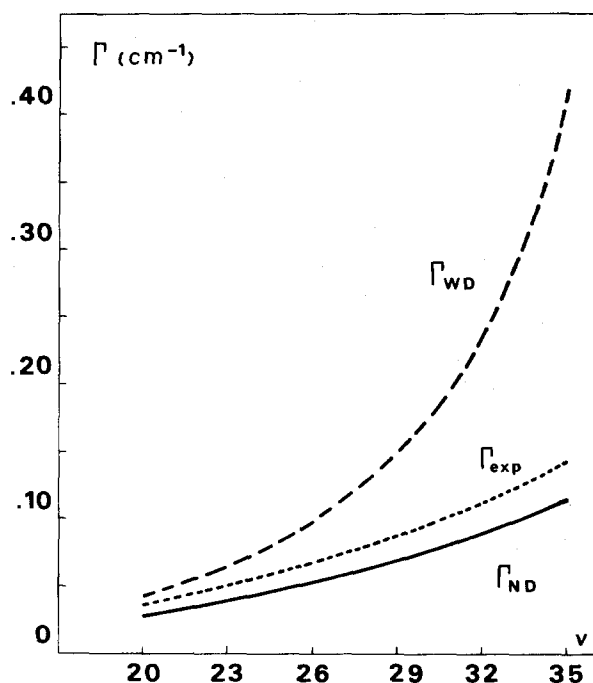

FIG. 3. Vibrational predissociation linewidths for the HeI₂(B) molecule as a function of the vibrational quantum number of I₂ subunit v. The curves labeled Γ_{WD} (dashed line) and Γ_{ND} (full line) are our results. The curve labeled Γ_{exp} (dotted line) is the experimental one of Ref. 1(a).

one motion might be considered as much slower than the other ones.

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