Vibrational predissociation lifetimes of the van der Waals molecule HeI$_2$

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In this paper we present a quantum mechanical study of the rates of vibrational predissociation of the T-shaped HeI$_2$(B) van der Waals molecule. The van der Waals bond is characterized in terms of Morse type atom–atom interaction and by a Buckingham type atom–atom potential. The dynamics of vibrational predissociation is shown to be insensitive to the long-range part of the van der Waals potential and the Morse form is adequate for the description of this process. The close-coupling equations for nuclear motion are solved by standard numerical methods and the vibrational predissociation rates are related to the widths of the resulting resonances. The superlinear theoretical dependence of the vibrational predissociation rates on the excess vibrational energy of the molecular I$_2$ bond is in good agreement with the experimental data. The relative contribution of intramolecular and of intermolecular terms to this superlinear dependence are elucidated, demonstrating the effects of the anharmonicity of the molecular bond on the intramolecular dynamics.

I. INTRODUCTION

There has been considerable recent interest in the intramolecular dynamics of vibrational redistribution and vibrational energy flow in polyatomic molecules. Recent experimental studies of vibrational predissociation (VP) of the van der Waals molecules (VDWM) HeI$_2$,[1] ArI$_2$,[2] HeNO$_2$,[3] (Cl$_2$)$_2$,[4] and (N$_2$O)[5] provide interesting examples for energy acquisition within a normal chemical bond followed by intramolecular vibrational energy redistribution which results in the fragmentation of the van der Waals bond. In the VDWM's the optical or collisional excitation process is well defined and can be well controled and the resulting dynamic intramolecular relaxation provides a unique example for VP on a single and simple potential energy surface. The understanding of VP of VDWM's is relevant for the elucidation of the general features of bond breaking processes in chemical systems.

Recent theoretical studies by Ashton and Child[6] and by Beswick and Jortner[7] addressed themselves to the dynamics of VP of VDWM. Ewing[8] has analyzed in the same spirit the role of van der Waals molecules in vibrational relaxation processes. A related problem concerns the diffuse bands observed in the infrared absorption spectra of hydrogen bonding systems.[9] We have recently[7(c)] performed numerical calculations of the VP rates for linear and T-shaped X–I$_2$ (X = He, Ne, Ar) VDWM's by solving the close-coupled equations for nuclear motion on a single potential surface. The VP rates were obtained from the energy dependence of the scattering matrix. The potential surface for VDWM's was represented in terms of a harmonic potential for the I$_2$ stretching vibration and a Morse-type atom–atom interaction for the van der Waals bond. Clustering evidence and spectroscopic data[10] seem to indicate a T-shaped equilibrium configuration for the He–I$_2$ complex. The potential parameters for the calculation of the VP of the T-shaped He–I$_2$ VDWM were derived from two sources: (a) Using the compilation of semiempirical Lennard–Jones potential parameters,[11] and (b) utilizing the spectroscopic data[1(a)] for the energy separation ΔE_{10} between the $l = 1$ and the $l = 0$ vibrational states in the van der Waals bond which results in a value of 13.5 cm^{-1} for the dissociation energy of the VDWM. The latter potential parameters resulted in theoretical predictions of VP rates for the T-shaped HeI$_2$ VDWM which were in order-of-magnitude agreement with the semiquantitative experimental data which were available at that time.[1(a)] It was clear that the theory requires some refinement to include the effects of the anharmonicity of the normal molecular bond on the VP rate, which according to our energy gap law was expected to result in a superlinear dependence of the rate on the vibrational quantum number of the molecular bond. Recently Johnson, Wharton, and Levy[1(c)] have determined the VP lifetimes of the HeI$_2$ VDWM produced in a supersonic free expansion, from the linewidths Γ_v (HWHM) of the R branch heads in the fluorescence excitation spectra. The dependence of Γ_v on the vibrational quantum numbers of I$_2$ ($B\,^3\Pi$) were fit by the superlinear relationship

$$\Gamma_v = 0.555 \times 10^{-4} v^2 + 0.174 v^3 \ (\text{cm}^{-1}),$$

for $12 \le v \le 26$. The corresponding lifetimes varied from 221 psec at $v = 12$ to 38 psec at $v = 26$. These accurate data call for a confrontation of our theory with experimental facts.

In this paper we present a detailed calculation for the perpendicular VP of the T-shaped HeI$_2$ molecule incorporating the anharmonicity effects in the I$_2$ molecular bond. The close-coupling equations for this problem are presented in Sec. II. We have introduced a linear expansion of the interaction potential in powers of the

displacements with respect to the equilibrium internuclear distance of I_2, retaining only the linear term. Numerical tests of this linearization approximation show that it is adequate, the difference between the linearized and exact results being less than 20% even for large v. The linear approximation provides some further insight into the dynamics of VP, as the VP rates are essentially determined by a product of an intramolecular term involving only structural properties of the I_2 diatomic molecule, and an intermolecular term which depends on the parameters of the van der Waals potential and on the final relative kinetic energy of the recoiling fragments, elucidating their relative contributions to the dependence of the VP rate on the excess vibrational energy of the normal molecular bond. We present in Sec. III the results of the calculations within the framework of the linearization approximation and elucidate the effect of the intermolecular and of intramolecular factors on the v dependence of the VP rates when the molecular I_2 bond is anharmonic. Using the potential parameters of our previous work,[7(a),(b)] we show that the numerical integration of the close-coupling equations reproduce very well this v dependence of the VP rates, however, the calculated VP rates are smaller by a numerical factor of ~3 than the experimental values. Accordingly in Sec. IV we have attempted to fit the experimental Γ_v values by modifying the parameters of the He–I_2 van der Waals bond. A central practical problem concerning the validity of our model for VP pertains to the use of a Morse potential to represent the van der Waals interaction. In Sec. V we explore this problem concluding that VP dynamics for the lowest level is essentially determined by the short range part of the van der Waals potentials, so that the Morse function is adequate. Finally, in Sec. VI we examine the validity of the different assumptions underlying our theory of VP and VDWM's. In particular, we address ourselves to the validity of the dumbbell model and to the relation between these T-shaped configuration calculations and the Rotational Infinite Order Sudden Approximation[9] (RIOSA) used in collision problems.

II. CLOSE-COUPLING EQUATIONS FOR VIBRATIONAL PREDISSOCIATION

We consider the quantum mechanical equation of motion for three particles X, B, C in a T-shaped configuration where X is restricted to move on a line perpendicular to the interparticle axis BC. The Hamiltonian can be written as,

$$H = -\frac{\hbar^2}{2\mu_{\text{X,BC}}}\frac{\partial^2}{\partial R_{\text{X,BC}}^2} - \frac{\hbar^2}{2\mu_{\text{BC}}}\frac{\partial^2}{\partial R_{\text{BC}}^2} + V_{\text{BC}}(R_{\text{BC}}) + V(R_{\text{X,BC}}, R_{\text{BC}}) \quad (1)$$

where $R_{\text{X,BC}}$ and R_{BC} are the distance between X and the center of mass of BC, and the distance between B and C, respectively. V_{BC} is the potential energy for the normal BC bond which will be characterized in terms of a Morse potential, while V is the intramolecular potential for the van der Waals bond. The reduced masses are defined by: $\mu_{\text{X,BC}} = m_{\text{X}}(m_{\text{B}} + m_{\text{C}})/(m_{\text{X}} + m_{\text{B}} + m_{\text{C}})$ and $\mu_{\text{BC}} = m_{\text{B}}m_{\text{C}}/(m_{\text{B}} + m_{\text{C}})$. We expand the nuclear wave function for total energy E as

$$\psi_E(R_{\text{BC}}, R_{\text{X,BC}}) = \sum_v \phi_v(R_{\text{BC}})\chi_{vE}(R_{\text{X,BC}}), \quad (2)$$

where $\phi_v(R_{\text{BC}})$ are the vibrational eigenfunctions for "free" molecule BC, which will be represented by eigenfunctions of the Morse potential. After substitution of expansion (2) into the Schrödinger equation, we obtain the set of close-coupling equations

$$\left[\frac{-\hbar^2}{2\mu_{\text{X,BC}}}\frac{\partial^2}{\partial R_{\text{X,BC}}^2} + U_{vv}(R_{\text{X,BC}}) + (\epsilon_v - E)\right]\chi_{vE}(R_{\text{X,BC}})$$

$$= -\sum_{v' \neq v} U_{vv'}(R_{\text{X,BC}})\chi_{v'E}(R_{\text{X,BC}}), \quad (3)$$

where

$$U_{vv'}(R_{\text{X,BC}}) = \int dR_{\text{BC}}\phi_v^*(R_{\text{BC}})V(R_{\text{BC}}, R_{\text{X,BC}})\phi_{v'}(R_{\text{BC}}), \quad (4)$$

and ϵ_v is the energy of the free BC molecule in the vibrational state v. The coupled differential equations (3) may be solved by any of the currently available numerical integration methods.[13] In order to avoid time consuming numerical evaluation of integrals (4) we shall adopt a linearization approximation, expanding the van der Waals potential $V(R_{\text{BC}}, R_{\text{X,BC}})$ in a Taylor series around the equilibrium position $\overline{R}_{\text{BC}}$ of the diatomic molecule BC. The integrals (4) can be then handled analytically. In the present work, we have kept the first two terms in the expansion of the potential retaining the linear term in the intramolecular displacement of the normal BC bond,

$$V(R_{\text{BC}}, R_{\text{X,BC}}) = V(\overline{R}_{\text{BC}}, R_{\text{X,BC}}) + \frac{\partial V}{\partial R_{\text{BC}}}\bigg|_{\overline{R}_{\text{BC}}}(R_{\text{BC}} - \overline{R}_{\text{BC}}). \quad (5)$$

This linearization approximation has been tested by solving the coupled equations (3) with a potential of the form,

$$V(R_{\text{BC}}, R_{\text{X,BC}}) = D\{\exp[-\alpha(R_{\text{X,BC}} - \overline{R}_{\text{X,BC}})$$

$$+ \alpha(R_{\text{BC}} - \overline{R}_{\text{BC}})/2] - 1\}, \quad (6)$$

for which the matrix elements defined in Eq. (4) are known (see the Appendix). We have compared the results of this integration using the full potential (6) and the linearized expansion (5). Some results for the $HeI_2(B)$ system using a typical set of parameters D, α, $\overline{R}_{\text{X,BC}}$ are shown in Fig. 1, where we present the energy dependence of the square of the scattering amplitude connecting channels $v = 19$ and $v = 18$ in the neighborhood of the resonance corresponding to the lowest quasibound state of the $v = 20$ channel. For the sake of comparison the zero of the energy scale has been defined by the position of the dip of the resonance for the full potential (6) and for its linearized version. Actually, there is an energy shift of ~0.24 cm⁻¹ between the positions of the two dips. The two curves look very similar. The widths obtained by fitting these curves to a general dispersion profile according to the methodology presented in our previous work,[7(c)] differ by less than 20%. In view of the uncertainty in the potential parameter, such an error is acceptable and the linearization approximation is adequate for calculations of the VP rates.
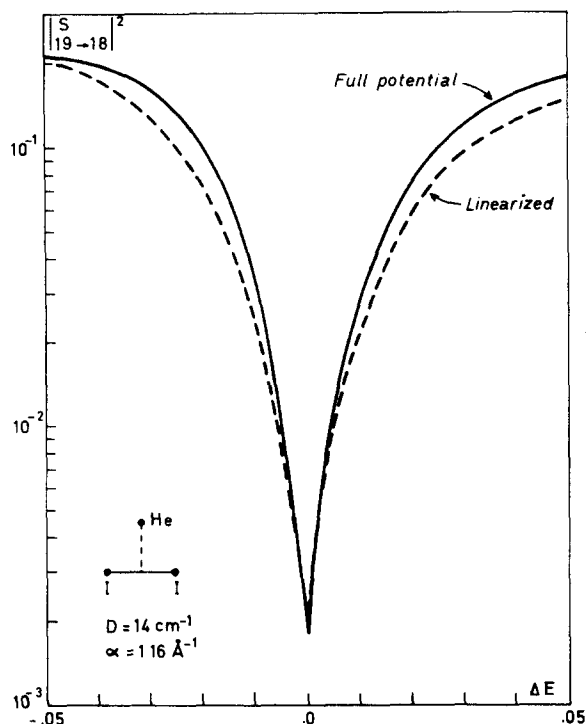
FIG. 1. Transition probability between vibrational states $v = 19$ and $v = 18$ of I$_2$ for the perpendicular collision of He with I$_2$ (B) in the energy region of a resonance corresponding to the closed channel $v = 20$. The total energy is measured from the center of the resonance in wave numbers. The full line corresponds to a calculation using the potential of Eq. (6) while the dashed line coresponds to the linearized potential given by Eq. (5). E is the total energy in cm^{-1} measured from the center of the line.

III. VIBRATIONAL PREDISSOCIATION RATES

Before alluding to numerical calculations for the T-shaped HeI$_2$(B) VDWM it is instructive to advance a simple perturbation type argument, which will elucidate the gross features of the dependence of the VP rate on the excess vibrational energy of the BC bond. We shall use the Golden rule rate for the VP process with distorted wave basis set. The distorted wave basis is obtained by retaining only one term in the sum giving the total wave function (2) and $\chi(R_{X,BC})$ is the solutions of the homogeneous part of Eqs. (3). Such approach has been shown to yield values of Γ_v in very good agreement with the numerical results obtained from the brute force solution of the close-coupling equations in the case of colinear configuration and a harmonic diatomic BC.[7(c)] Two types of functions can be constructed from this zero-order distorted-wave basis: (a) discrete, bound, vibrational states of the VDWM

$$\psi_{vl,E}^{bound} = \phi_v(R_{BC})\chi_l(R_{X,BC}),\qquad(7)$$

where v is the vibrational quantum number of the BC bond, while l corresponds to the discrete vibrational quantum number of the van der Waals bond. The total energy of these bound states are $E = \epsilon_v + \epsilon_l$, where ϵ_v and ϵ_l correspond to the energies of the discrete levels ϕ_v and χ_l, respectively; (b) continuum states of the fragments X + BC

$$\psi_{v'\epsilon,E}^{unbound} = \phi_{v'}(R_{BC})\chi_\epsilon(R_{X,BC}),\qquad(8)$$

where ϵ designates the relative kinetic energy of the recoiling fragments. The continuum states are characterized by the energies $E = \epsilon_{v'} + \epsilon$. The Golden rule will then yield for the vibrational predissociation rate from the initial state v, l to the final channel v', ϵ

$$\Gamma_{vl \to v'} = \pi \left| \langle \psi_{vl,E}^{bound} | V | \psi_{v'\epsilon,E}^{unbound} \rangle \right|^2 ,\qquad(9)$$

and using the expansion (5) we obtain

$$\Gamma_{vl \to v'} = \pi \left| \langle \chi_l | \partial V/\partial R_{BC} |_{\bar{R}_{BC}} | \chi_\epsilon \rangle \right|^2$$
$$\otimes \left| \langle \phi_v | (R_{BC} - \bar{R}_{BC}) | \phi_{v'} \rangle \right|^2 ,\qquad(10)$$

and we see that the individual VP rate $v \to v'$ consist in the product of an intermolecular term depending on the parameters van der Waals interaction potential and on the final relative kinetic energy of recoiling fragments, and an intramolecular factor which depends only on intrinsic properties, (i.e., frequency and anharmonicity), of the normal BC bond. It should be noted that this intramolecular term is the responsible for the propensity rule, as even for an anharmonic BC potential the matrix elements $|\langle \phi_v | (R_{BC} - \bar{R}_{BC}) | \phi_{v'} \rangle|^2$ will strongly favor the transition with $v' = v - 1$. Thus $\Gamma_{vl} \cong \Gamma_{vl \to (v-1)}$ constitutes a reasonable first-order description of the VP rate.

We can now determine the relative contributions of the intramolecular term and of the intermolecular term to the dependence of the VP rate on the excess vibrational energy of the normal molecular bond. When a harmonic model is used for the BC potential, as done in our previous work,[7(c)] the intermolecular factor is independent of the vibrational excitation, as the relative kinetic energy of the recoiling fragment is constant, and the intramolecular factor is solely responsible for the v dependence of $\Gamma_{vl} \propto v$. For an anharmonic BC bond the linear v dependence of the intramolecular contribution is not significantly modified for sufficient low values of v. For a Morse type BC potential the intramolecular contribution is (see Appendix)

$$\left| \langle \phi_v | (R_{BC} - \bar{R}_{BC}) | \phi_{v-1} \rangle \right|^2$$
$$\propto \frac{(2K_{BC} - 2v + 1)(2K_{BC} - 2v - 1)}{(2K_{BC} - v)(K_{BC} - v)^2} v ,\qquad(11)$$

where $K_{BC} = \omega_{BC}/2(\omega X_e)_{BC}$, with ω_{BC} being the frequency of the BC bond and $(\omega X_e)_{BC}$ its anharmonicity. $(K_{BC} + \frac{1}{2})$ represents the number of bound levels in the molecular potential. For I$_2$(B) we get $K_{BC} = 76.7$. Thus for sufficiently low values of $v < K_{BC}$ as we are concerned with here ($v = 12-26$) we expect that the intramolecular contribution, Eq. (11), for an anharmonic BC bond is still proportional to v. This is apparent from a numerical evaluation of the intramolecular contribution presented in Fig. 2. This anharmonicity effects do not affect the nature of the intramolecular contribution to Γ_{vl}. An additional contribution to the v dependence of the VP rate for an anharmonic BC potential is expected to originate from the intermolecular contribution to Eq. (10). This intermolecular contribution originates from a dynamic effect which is determined by the relative kinetic energy of the fragments. As v increases the relative velocity decreases, because of the anharmonicity of the
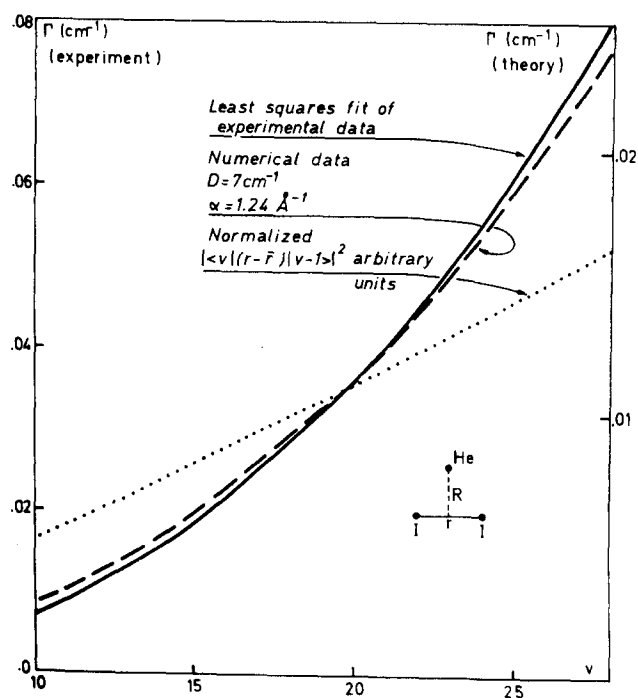
FIG. 2. Dependence of the vibrational predissociation line-widths $\Gamma_{v,J}$ ($l = 0$) on the vibrational quantum number v of the I_2 (B) diatomic molecule in the T-shaped van der Waals complex HeI₂. The full line corresponds to the experimental data of Johnson, Wharton, and Levy,[1(c)] while the dashed line is the result of the numerical integration of the close-coupling equations (3) using the molecular parameters given in the text. The dotted line corresponds to the intramolecular contribution given by Eq. (11).

BC potential, and accordingly Γ_{vl} is enhanced. In order to obtain a quantitative estimate of the intermolecular contribution to Γ_{vl} numerical calculation of the VP rate were performed, which of course incorporate both the intermolecular and the intramolecular contribution. In Fig. 2, we display the results for the VP rates $\Gamma_{v,l}$ ($l = 0$) obtained by numerical integration of the close-coupling equations (3) using the molecular parameters[14]

$$\omega_{BC} = 128. \text{ cm}^{-1} ,$$
$$(\omega Xe)_{BC} = 0.834 \text{ cm}^{-1} , \tag{12}$$

for the I_2 molecule, and the following potential parameters for the T-shaped He–I_2 bond

$$\alpha = 1.25 \text{ Å}^{-1} ,$$
$$\overline{R}_{XB} = 4 \text{ Å} , \tag{13}$$
$$D = 7 \text{ cm}^{-1} ,$$

which were advocated in our previous work.[7(c)] The v dependence of the calculated VP rates is superlinear being well accounted by the empirical relation $\Gamma_{v,l=0}$ = Av^2, in the range $v = 10$–30. This v dependence of the VP rates is in excellent qualitative agreement with the experimental data of Johnson, Wharton, and Levy.[1(c)] As we have already convinced ourselves that the intramolecular contribution results in a linear v dependence, it is apparent that an additional v dependence of Γ_{vl} originates from the dynamic effects inherent in the intermolecular contribution to the VP rates. This is a

novel and interesting anharmonicity effect on intramolecular dynamics.

IV. NUMERICAL RESULTS FOR VP RATES

The functional form of the dependence of the VP rates on the excess vibrational energy of the molecular bond is faithfully reproduced by our theory. It should be however noted (see Fig. 2) that the absolute values of the VP rates calculated for the potential parameters (12) are lower by a numerical factor of ~3 than the experimental values.[1(c)] It should be borne in mind that these potential parameters are rather approximate and it is interesting to vary the potential parameters to find out to what extent the general correlation $\Gamma_v \propto v^2$ will be affected and whether a self-consistent set of potential parameters can be obtained, which provide a quantitative fit of the experimental data.

In our numerical calculations we have taken a dumbbell model potential for the van der Waals bond

$$V = V_{XB}(R_{XB}) + V_{XC}(R_{XC}) \tag{14a}$$

which is represented in terms of a sum of two interactions between the rare gas atom X and each of the atoms the BC molecule. In our case we have a T-shaped configuration and an homonuclear diatomic, so that

$$R_{XB} \equiv R_{XC} = [R_{X,BC}^2 + R_{BC}^2/4]^{1/2} , \tag{14b}$$

and $V_{XB} \equiv V_{XC}$. We have specified the interactions V_{XB} and V_{XC} by Morse-type potentials

$$V_{XB}(R_{XB}) = D \exp[-2(R_{XB} - \overline{R}_{XB})]$$
$$- 2 \exp[-(R_{XB} - \overline{R}_{XB})] . \tag{14c}$$

Numerical calculations of the VP rates for $l = 0$ for several values of the potential parameters are presented in Fig. 3. We note that increasing the parameter D (notice that $2D$ gives the minimum of the potential surface) results in an enhancement of the VP rate. We have also performed calculations with slightly different values of α. These calculations give an idea of the sensibility of the vibrational predissociation rate to changes in the potential parameters of the van der Waals bond. In Fig. 4 we have displayed two possible theoretical fits of the experimental data. For α in the range 1.1–1.2 Å^{-1}, D is in the range 13–18 cm^{-1}. The dissociation energy of the van der Waals complex (being equal to $2D$ minus the zero point energy of the van der Waals bond) will be in the range 20–30 cm^{-1}. We shall return in Sec. VI to discuss these potential parameters.

V. ALTERNATIVE POTENTIAL FUNCTIONS FOR THE VAN DER WAALS BOND

An interesting question which arises concerning the validity of the present model for VP pertains to the utilization of Morse potentials for representing the van der Waals interaction. This is a reasonable description at small and at intermediate distances but certainly very poor one for long-range interactions, where the usual R^{-6}, R^{-8}, dependence due to dispersion forces is expected. However, the VP dynamics is essentially determined by bound-continuum interaction, so that one can hope that the VP rates will be essentially determined by
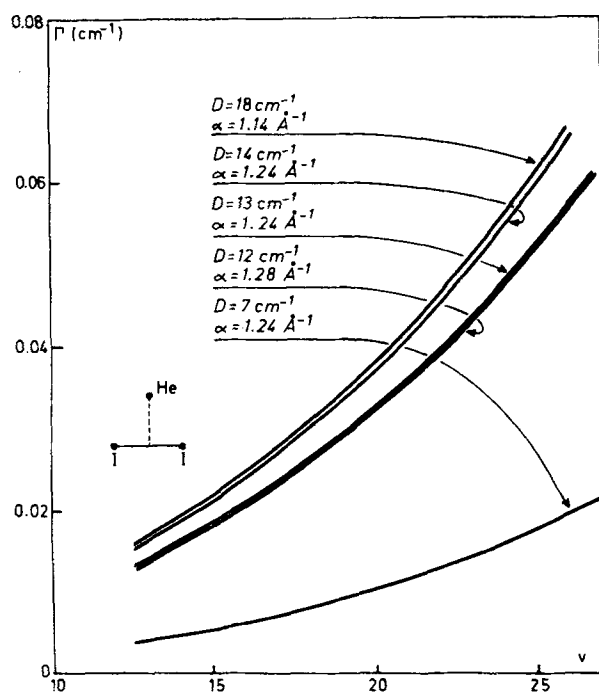
FIG. 3. Numerical calculations of the vibrational predissociation rates for the T-shaped HeI$_2$ complex as a function of the vibrational quantum number v of the I$_2$ (B) diatomic molecule. The parameters D and α correspond to the Morse potential Eq. (14c) with $\bar{R}_{XB} = 4$ Å.

TABLE I. Comparison between vibrational predissociation rates obtained with Morse and Buckingham potentials.

Parameters of the Morse potential[a] [see Eq. (14)]	v	Morse Γ_v (cm^{-1})	Buck. Γ_v (cm^{-1})
$D = 13$ cm^{-1}, $\alpha = 1.24$ Å^{-1}, $\bar{R}_{XB} = 4$ Å	15	0.19×10^{-1}	0.20×10^{-1}
	20	0.33×10^{-1}	0.34×10^{-1}
	25	0.53×10^{-1}	0.55×10^{-1}
$D = 7$ cm^{-1}, $\alpha = 1.24$ Å^{-2}, $\bar{R}_{XB} = 4$ Å	15	0.61×10^{-2}	0.64×10^{-2}
	20	0.11×10^{-1}	0.11×10^{-1}
	25	0.18×10^{-1}	0.19×10^{-1}

[a]The parameters of the Buckingham potentials have been determined following the procedure described in the text. See Eqs. (15)–(16).

VI. CONCLUDING REMARKS

We have presented numerical calculations for the VP rates of HeI$_2$(B), which rest on the following assumptions:

(1) We use a dumbbell model potential, the total van der Waals potential being represented by the sum of two atom–atom interactions.

(2) The system is restricted to vibrational motion in a fixed T-shaped configuration.

(3) Rotational effects have been disregarded.

(4) The potential is expanded in powers of the displacement from the equilibrium interatomic distance of I$_2$, up to the linear term.
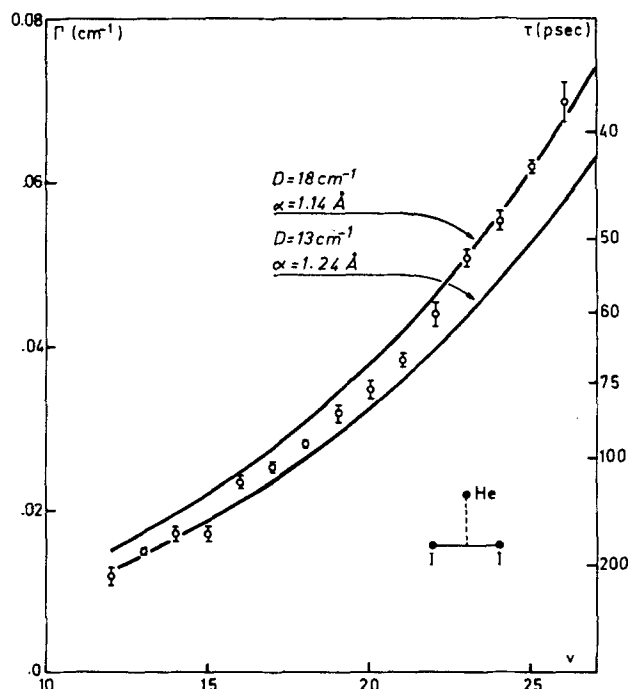
the details of the potential at internuclear distances corresponding to the minimum of the potential surface. In order to investigate this cardinal point we have repeated the numerical calculations using the modified Buckingham potential

$$V_{XB}(R_{XB}) = A \exp(-\beta R_{XB}) - C R_{XB}^{-6} \qquad (15)$$

for the van der Waals bond. The parameters A, C, and β have been chosen in such a way so that the potential function and its second derivative at the equilibrium position will be equal to the corresponding values for the Morse potential. This prescription results in the relations

$$A = 6 D e^{\gamma}/(\gamma - 6) ,$$

$$C = D \bar{R}_{XB}^{-6} \gamma/(\gamma - 6),$$

$$\gamma = 7/2 + \gamma'/6 + [(7/2 + \gamma'/6)^2 - 2\gamma'^2]^{1/2} , \qquad (16)$$

$$\gamma = \beta \bar{R}_{XB} ; \qquad \gamma' = \alpha \bar{R}_{XB} .$$

In Table I we present the results of the numerical integration of close-coupling equations using potentials (14) and (15) for two different sets of parameters α and D ($\bar{R}_{XB} = 4$ Å). The calculated VP rates are insensitive to the form of the potential at large distances. This is to be expected since the rates for VP are essentially determined by the overlap between a continuum wavefunction and a bound state, so that the only nonvanishing contribution originates from the region of the potential well. We conclude that for the determination of VP rates the Morse potential provides a reasonable description of the van der Waals interaction.

FIG. 4. Two possible numerical fits of the experimental data of Johnson, Wharton, and Levy[1(c)] for vibrational predissociation linewidths of the T-shaped HeI$_2$ (B) van der Waals complex. The parameters D and α correspond to the Morse potential Eq. (14c) with $\bar{R}_{XB} = 4$ Å. The parameters for the diatomic molecule I$_2$ (B) are taken from spectroscopic data.[14]

Furthermore while confronting our results with the experimental data we have assumed that:

(5) The measured linewidth correspond to pure vibrational predissociation occurring on a single adiabatic potential surface.

(6) The photodissociation is assumed to proceed by two well defined processes: a "preparation" of a single metastable state and the subsequent decay of this non-stationary state via VP.

Assumption (1) is likely to be a good approximation for a VDWM. Assumptions (2) and (3) should be critically examined. These can be related to the rotational infinite order sudden approximation[12] (RIOSA) used in collision problems, in which the vibrational motion is considered to be much faster than rotation. For a system like HeI$_2$ this will be particularly acceptable as the vibrational frequencies for the I–I stretch and for the He $\cdots$ I$_2$ motion are 128 cm^{-1} and ~6 cm^{-1}, respectively, while the rotational constants associated to the I$_2$ and the complex are 0.037 cm^{-1} and 0.27 cm^{-1}, respectively. The rotational motion can be considered in that case as adiabatic and θ the angle between the interatomic axis of I$_2$ and the line between the He atom and the center of mass of I$_2$ ($\theta = \frac{1}{2}\pi$ for T-shaped configuration) can be taken as a parameter. We will get then a vibrational predissociation amplitude which depends parametrically on θ. The final result is obtained after an average over θ. Further work in this direction is under progress. We have shown in Sec. II that the linearization approximation (4) introduces an error of <20%. For the purpose of our approximate fits of the VP rates this is an acceptable error. The calculation can be however easily improved by incorporating additional terms in the expansion (5). Assumption (5) seems to be borne out by the experimental results of Smalley et al. If a second decay channel of induced electronic predissociation

$$\text{HeI}_2^*(B) \rightarrow \text{He} + 2\text{I} \tag{17}$$

will significantly contribute to the linewidth a strong irregular vibrational dependence of the linewidth is expected to be exhibited. The situation is completely different for the ArI$_2$ VDWM where electronic relaxation competes with VP[2]. Finally, assumption (5) has already been discussed in our previous work[1(a)] and seems to be justified in view of the spectroscopic data of Smalley et al.

We conclude that the fits of the experimental VP rates in terms of our theory provide rough estimates of the potential parameters for the van der Waals bond in HeI$_2$(B). We have obtained a dissociation energy of the range 20–30 cm^{-1}, when using a parameter α [see Eq. (14c)] in the range 1.1–1.2 Å^{-1}. Recent experimental data[10] indicate that the dissociation energy of the HeI$_2$(B) van der Waals complex is <18.5 cm^{-1}. On the other hand our "best" potential parameters result in $\Delta E_{01} = 13$ cm^{-1} for the energy spacing between the $l = 1$ and $l = 0$ states which is higher than the experimental value $\Delta E_{01} = 6$ cm^{-1} reported by Smalley et al.[1(a)] This discrepancy will be settled after a further examination of rotational effects on the energetics and dynamics of VDWM's.

APPENDIX

We are interested in the matrix elements

$$A_{vv'} = \int dR_{BC}\phi_v^*(R_{BC})\exp[-\gamma(R_{BC} - \overline{R}_{BC})]\phi_{v'}(R_{BC}), \tag{A1}$$

where ϕ_v and $\phi_{v'}$ are the vibrational eigenfunctions of the "free" molecule BC. For a Morse potential of the form

$$V_{BC}(R_{BC}) = D_{BC}\{\exp[-2\alpha_{BC}(R_{BC} - \overline{R}_{BC})] - 2\exp[-\alpha_{BC}(R_{BC} - \overline{R}_{BC})]\}, \tag{A2}$$

the matrix elements (A1) are given by[15] (for $v \geq v'$)

$$A_{vv'} = \left[\frac{(v')!(2K_{BC} - 2v' - 1)(2K_{BC} - 2v - 1)\Gamma(2K_{BC} - v')}{(v)!\Gamma(2K_{BC} - v)}\right]^{1/2}$$
$$\times (2K_{BC})^{\gamma/\alpha_{BC}}\sum_{m=0}^{v'}(-1)^{m+v'-v}\frac{\Gamma(v' + \gamma/\alpha_{BC} - m + 1)}{m!(v' - m)!}$$
$$\times \frac{\Gamma(-v' - v - \gamma/\alpha_{BC} + m + 2K_{BC} - 1)}{\Gamma(2K_{BC} - 2v' + m)\Gamma(1 + \gamma/\alpha_{BC} + v' - v - m)}, \tag{A3}$$

where $K_{BC} = (\hbar\alpha_{BC})^{-1}(2\mu_{BC}D_{BC})^{1/2}$. The parameter α_{BC} and D_{BC} are related to the frequency ω_{BC} and the anharmonicity $(\omega\chi_e)_{BC}$ of the diatomic molecule by the relations

$$\omega_{BC} = \alpha_{BC}(2D_{BC}/\mu_{BC})^{1/2}, \tag{A3'}$$

$$(\omega\chi_e)_{BC} = \frac{\hbar\omega_{BC}}{2K_{BC}},$$

and can then be obtained from spectroscopic data.[11] The matrix element

$$B_{vv'} = \int dR_{BC}\phi_v^*(R_{BC})[R_{BC} - \overline{R}_{BC}]\phi_{v'}(R_{BC}) \tag{A4}$$

for $v \neq v'$, can be obtained by taking the limit $\gamma \rightarrow 0$ in Eq. (A3). The result is (see also Ref. 16)

$$B_{vv'} = (-1)^{v+v'}\frac{[(v)!(2K_{BC} - 2v - 1)(2K_{BC} - 2v' - 1)]^{1/2}}{\alpha_{BC}(v' - v)(2K_{BC} - v - v' - 1)}$$
$$\times \left[\frac{\Gamma(2K_{BC} - v)}{(v')!\Gamma(2K_{BC} - v')}\right]^{1/2}. \tag{A5}$$

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