Intramolecular dynamics of some van der Waals dimers

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(Received 1 December 1978)

In this paper we consider the problem of intramolecular vibrational energy flow from a conventional bond to a van der Waals bond in a linear AB–CD van der Waals molecule, where AB and CD are conventional diatomics. A model for collinear vibrational predissociation of AB–CD on a single ground state potential surface was developed. The vibrational predissociation of a van der Waals heterodimer, consisting of a pair of distinct diatomics, can be described in terms of a simple exponential decay of a single discrete zero order state which corresponds to excited bond modes, into a dissociative continuum. The dependence on the vibrational predissociation rate of the heterodimer on the parameters of the molecular bonds and of the van der Waals bond is elucidated. The details of the intramolecular dynamics of a homodimer, consisting of a pair of identical diatomics, are determined by the excitation conditions. Optical infrared short time excitation is expected to result in a coherent, in phase, superposition of degenerate bond modes, which will subsequently exhibit a simple exponential time evolution, the decay rate being determined by the resonance width. Collisional excitation of the dimer is expected to result in an incoherent initial superposition of degenerate bond modes, the subsequent time evolution being determined by the discrete–discrete coupling and by the widths of the metastable states. Model calculations were performed for the nuclear dynamics of collisionally excited linear halogen dimers $A_2 \cdots A_2 (A = F, Cl, Br, I)$. The linear $(Cl_2)_2$, $(Br_2)_2$, and $(I_2)_2$ dimers are characterized by negligibly small discrete–discrete coupling terms whereupon the nuclear dynamics of these van der Waals molecules is determined by exponential decay due to vibrational predissociation, without direct energy exchange between the bond modes. For the $(F_2)_2$ linear dimer the discrete–discrete coupling terms overwhelm the widths of the resonances and the system will exhibit efficient direct energy exchange between the molecular bond modes before the occurrence of vibrational predissociation. Model calculations for the vibrational predissociation lifetimes for the halogen dimers reveal remarkably long lifetimes, which can be accounted for in terms of the energy gap law for vibrational predissociation. Our results account for the ineffective process of intramolecular vibrational energy flow discovered by Dixon and Herschbach in the $(Cl_2)_2$ dimer.

I. INTRODUCTION

Dixon and Herschbach[1] have observed remarkably long lifetimes for the vibrational predissociation (VP) of a vibrationally excited $Cl_2 \cdots Cl_2$ van der Waals dimer. They were able to set a lower limit of the VP lifetime τ by observing that the dimer in a supersonic beam survived the transit time from the point of collisional vibrational excitation up to the point of detection, without undergoing fragmentation. Thus, for the Cl_2-Cl_2 dimer, $\tau \geq 10^{-4}$ sec and this van der Waals molecule undergoes $\sim 10^8-10^9$ vibrations of the Cl_2 subunit, whose vibrational energy exceeds the dissociation energy of the van der Waals bond, before bond breaking occurs. The ineffective process of intramolecular vibrational energy flow from a conventional chemical bond to a van der Waals bond is a problem of considerable current interest in the area of intramolecular dynamics. This physical situation is relevant for the understanding of nonstatistical vibrational energy redistribution in polyatomic molecules,[2] which pertains to basic chemical processes such as unimolecular reactions[3] and multiphoton photodissociation.[4]

As pointed out by Dixon and Herschbach,[1] the surprisingly long lifetime of the Cl_2-Cl_2 dimer can be attributed to very weak coupling for vibration to translation energy transfer in this system. The VP lifetime τ $(=\tau_0 Z_{01})$ was phenomenologically represented[1,5] as a product of the translational–vibrational energy transfer probability per collision Z_{01} and $\tau_0 \cong 10^{-12\pm1}$ sec, which corresponds to the duration of a collision. This approach for VP of a van der Waals bond bears a close analogy to the phenomenological "half-collision" concept,[6] which was invoked to describe photofragmentation of ordinary chemical bonds. We have recently investigated the intramolecular dynamics of VP of linear[7] and T-shaped[8] triatomic $X \cdots BC$ van der Waals molecules, where BC, characterized by the frequency ω_{BC}, is a conventional diatomic while X represents a rare gas atom. We have derived an energy gap law $\ln(1/\tau) \propto \omega_{BC}^{1/2}$ for the VP process, whereupon the mismatch between the molecular frequency and the frequency of the van der Waals bond severely inhibits the VP process. The stability of the Cl_2-Cl_2 dimer with respect to VP can be qualitatively rationalized in terms of our energy gap law.

In this paper, we present a theoretical study of VP of linear van der Waals dimers $AB \cdots CD$, where AB and CD are normal molecules. We have conducted a detailed analysis of the intramolecular energy flow as well as explored the VP rates in such model systems. In van der Waals molecules, the relevant part of the potential surface is relatively simple and may be estimated, in principle, from spectroscopic data for the molecular constituents and for the van der Waals molecule. Such information is not yet available for van der Waals dimers, and we shall restrict our discussion to model systems involving linear complexes. The present theo-

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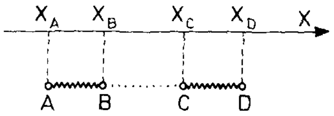

FIG. 1. Coordinate system used to describe the one-dimensional motion of two ordinary diatomic molecules AB and CD coupled through a van der Waals interaction.

ry of fragmentation of a van der Waals bond, together with the intelligent guesses regarding the potential surface, provides a fairly complete theoretical description of VP on a single potential surface. This theoretical approach to breaking of van der Waals bonds will be useful for the elucidation of the features of fragmentation of chemical bonds.

II. MODEL SYSTEM

A. Dissection of the Hamiltonian

We consider two ordinary diatomic molecules AB and CD restricted to one-dimensional motion (Fig. 1). The interaction potential between the atoms B and C represents the van der Waals bond. The Hamiltonian for the nuclear motion on the ground state electronic potential surface is

$$H=-\frac{\hbar^2}{2}\sum_{i=A,B,C,D} m_i^{-1}\partial^2/\partial X_i^2 + V_{AB}(X_B-X_A)+V_{CD}(X_D-X_C)+V_{BC}(X_C-X_B) . \quad (1)$$

It will be now convenient to define the following coordinates:

$$X_{c.m.}=\sum_{i=A,B,C,D} m_i X_i/M , \quad M=\sum_{i=A,B,C,D} m_i , \quad (2a)$$

$$X_{AB}=X_B-X_A , \quad X_{CD}=X_D-X_C , \quad (2b)$$

$$X_{AB,CD}=-(m_B X_B+m_A X_A)/(m_A+m_B) + (m_C X_C+m_D X_D)/(m_C+m_D) , \quad (2c)$$

which correspond to the position of the center of mass of the whole system [Eq. (2a)], the internal interatomic distances of the two diatomic molecules AB and CD [Eq. (2b)], and the distance between the centers of mass of AB and CD [Eq. (2c)]. After separation of the center of mass motion, the Hamiltonian defined in Eq. (1) assumes the form

$$H=-\frac{\hbar^2}{2\mu_{AB}}\frac{\partial^2}{\partial X_{AB}^2}-\frac{\hbar^2}{2\mu_{CD}}\frac{\partial^2}{\partial X_{CD}^2}-\frac{\hbar^2}{2\mu_{AB,CD}}\frac{\partial^2}{\partial X_{AB,CD}^2} \times V_{AB}(X_{AB})+V_{CD}(X_{CD})+V_{BC}(X_{AB,CD} -\gamma_{AB}X_{AB}-\gamma_{CD}X_{CD}) , \quad (3)$$

where

$$\mu_{AB}=m_A m_B/(m_A+m_B) , \quad \mu_{CD}=m_C m_D/(m_C+m_D) , \quad (4a)$$

$$\mu_{AB,CD}=(m_A+m_B)(m_C+m_D)/M , \quad (4b)$$

$$\gamma_{AB}=m_A/(m_A+m_B) , \quad \gamma_{CD}=m_D/(m_C+m_D) . \quad (4c)$$

The intramolecular potentials $V_{AB}(X_{AB})$ and $V_{CD}(X_{CD})$ for the normal AB and CD bonds, respectively, will be represented either in terms of a harmonic potential or of a Morse potential. The van der Waals interaction V_{BC} was specified in terms of a Morse potential

$$V_{BC}(X_{BC})=D_{BC}\{\exp[-2\alpha_{BC}(X_{BC}-\bar{X}_{BC})] - 2\exp[-\alpha_{BC}(X_{BC}-\bar{X}_{BC})]\} , \quad (5)$$

where D_{BC} and $\bar{X}_{BC}$ are the dissociation energy and the equilibrium distance, respectively. The effective frequency for the van der Waals bond is $\omega_{BC}=(\mu_{AB,CD})^{-1} \times(\partial^2 V_{BC}/\partial X_{AB,CD}^2)$ while the characteristic inverse length for the van der Waals bond is $\alpha_{BC}=\omega_{BC}(\mu_{AB,CD}/2D_{BC})$. Finally, the number of bound states in the van der Waals bond is $N=(K_{BC}+1/2)$, where $K_{BC}=(2D_{BC}/\hbar\omega_{BC})$. In Table I, we present a compilation of the Morse potential parameters for van der Waals complexes $X_2 \cdots X_2$ between homonuclear halogen diatomics. We note in passing that, in the present work on dimers as well as in our previous study[7] on $X \cdots BC$ van der Waals molecules, we have represented the van der Waals bond in terms of a Morse potential. We have recently studied[8(b)] the dynamics of VP of the $He \cdots I_2$ molecule using both a Morse potential as well as a modified Buckingham type potential, the latter potential accounts properly for the long-range part of the van der Waals interaction. These calculations have demonstrated that the dynamics of the VP process is determined by the short range part of the interaction potential, being insensitive to the long-range form of the interaction. Thus, the Morse potential is adequate for the study of VP in $X_2 \cdots X_2$ van der Waals dimers.

The Hamiltonian (3) will be now separated in the following manner:

TABLE I. Potential parameters for $X_2 \cdots X_2$ van der Waals dimers.

	Parameters of the diatomic fragments[a]		Parameters of the van der Waals bond[b]			
Dimer	ω_{AB} (cm^{-1})	ωX_{AB} (cm^{-1})	ω_{BC} (cm^{-1})	D_{BC} (cm^{-1})	α_{BC} (Å^{-1})	Number of bond levels
$(F_2)_2$	802	4	27.3	77.8	1.64	6
$(Cl_2)_2$	564.9	4	33.	334.	1.3	20
$(Br_2)_2$	325.2	1	24.7	361.4	1.41	29
$(I_2)_2$	214.6	6	17.2	382.	1.2	45

[a] The frequencies and anharmonic factors for the diatomic fragments have been taken from Ref. 9.
[b] The parameters for the VDW bond for $(F_2)_2$, $(Br_2)_2$, and $(I_2)_2$ have been obtained from viscosity data reported in Ref. 10. For $(Cl_2)_2$, we have used the estimate given in Ref. 1.

$$H=H_0+\mathcal{V}\ . \tag{6}$$

We define the zero-order Hamiltonian

$$\begin{aligned}H_0=&-\frac{\hbar^2}{\partial\mu_{\mathrm{AB}}}\frac{\partial^2}{\partial X_{\mathrm{AB}}^2}-\frac{\hbar^2}{2\mu_{\mathrm{CD}}}\frac{\partial^2}{\partial X_{\mathrm{CD}}^2}-\frac{\hbar^2}{2\mu_{\mathrm{AB,CD}}}\frac{\partial^2}{\partial X_{\mathrm{AB,CD}}^2}\\&+V_{\mathrm{AB}}(X_{\mathrm{AB}})+V_{\mathrm{CD}}(X_{\mathrm{CD}})+V_{\mathrm{BC}}(X_{\mathrm{AB,CD}}\\&\qquad-\gamma_{\mathrm{AB}}\bar{X}_{\mathrm{AB}}-\gamma_{\mathrm{CD}}\bar{X}_{\mathrm{CD}})\ ,\end{aligned} \tag{7}$$

where $\bar{X}_{\mathrm{AB}}$ and $\bar{X}_{\mathrm{CD}}$ are the equilibrium interatomic distances for molecules AB and CD, respectively. This zero-order Hamiltonian incorporates three independent contributions; two contributions from the vibrating AB and CD normal bonds and a third contribution which corresponds to the relative motion of the fragments. This zero-order Hamiltonian is separable and its spectrum consists of discrete and continuum eigenvalues corresponding to the eigenfunctions $|n_{\mathrm{AB}}, n_{\mathrm{CD}}, l\rangle$ and $|n_{\mathrm{AB}}, n_{\mathrm{CD}}, \epsilon\rangle$, respectively, where n_{AB} and n_{CD} are quantum numbers associated to the internal vibrational motion of molecules AB and CD, respectively, l is a discrete quantum number characterizing the bound states of the van der Waals bond, and ϵ is the relative kinetic energy the diatomic fragments AB and CD. Such a representation of zero-order states in terms of bond modes is adequate for the heterodimer. The residual perturbation term is

$$\begin{aligned}\mathcal{V}=H-H_0=&\ V_{\mathrm{BC}}(X_{\mathrm{AB,CD}}-\gamma_{\mathrm{AB}}X_{\mathrm{AB}}-\gamma_{\mathrm{CD}}X_{\mathrm{CD}})\\&-V_{\mathrm{BC}}(X_{\mathrm{AB,CD}}-\gamma_{\mathrm{AB}}\bar{X}_{\mathrm{AB}}-\gamma_{\mathrm{CD}}\bar{X}_{\mathrm{CD}})\ .\end{aligned} \tag{8}$$

In what follows, we shall be interested in the nuclear dynamics of a heterodimer which consists of a van der Waals pair of distinct diatomic molecules AB and CD. Under these circumstances, the zero-order basis consisting of discrete states $\{|n_{\mathrm{AB}}, n_{\mathrm{CD}}, l\rangle\}$ and of continuum states $\{|n_{\mathrm{AB}}, n_{\mathrm{CD}}, \epsilon\rangle\}$ provides an adequate starting point for the study of the VP process. In the case of a homodimer, consisting of two identical diatomic molecules, the situation is more complicated because of degeneracy and we shall return to this problem in Sec. IV.

B. Intramolecular coupling for a heterodimer

The VP dynamics of a heteronuclear dimer on the ground state potential surface can be considered by defining a preparation process where only the discrete zero-order states $|n_{\mathrm{AB}}, n_{\mathrm{CD}}, l\rangle$ are amenable to excitation, while the continuum states $|n'_{\mathrm{AB}}, n'_{\mathrm{BC}}, \epsilon\rangle$ are inactive. This assumption is justified for optical infrared excitation of the dimer and seems to be sensible also for collisional excitation. To provide a complete picture of the VP of a heterodimer, three types of coupling terms between the zero-order states, which are induced by the perturbation (8), have to be considered (see Fig. 2). These consist of discrete–discrete (*d*–*d*), discrete–continuum (*d*–*c*), and continuum–continuum (*c*–*c*) interaction. The coupling terms

$$\begin{aligned}&\mathcal{V}^{u-v}_{n_{\mathrm{AB}},n_{\mathrm{CD}}\alpha,n'_{\mathrm{AB}},n'_{\mathrm{CD}},\beta}\equiv\langle n_{\mathrm{AB}}n_{\mathrm{CD}}\alpha|\mathcal{V}|n'_{\mathrm{AB}}n'_{\mathrm{CD}}\beta\rangle\ ,\\&u,v\equiv d\text{ and }c\ ,\quad \alpha,\beta\equiv l\text{ and }\epsilon\end{aligned} \tag{9}$$

can be evaluated in an analytical form for the potential surface defined by Eqs. (5)–(7). The technical details

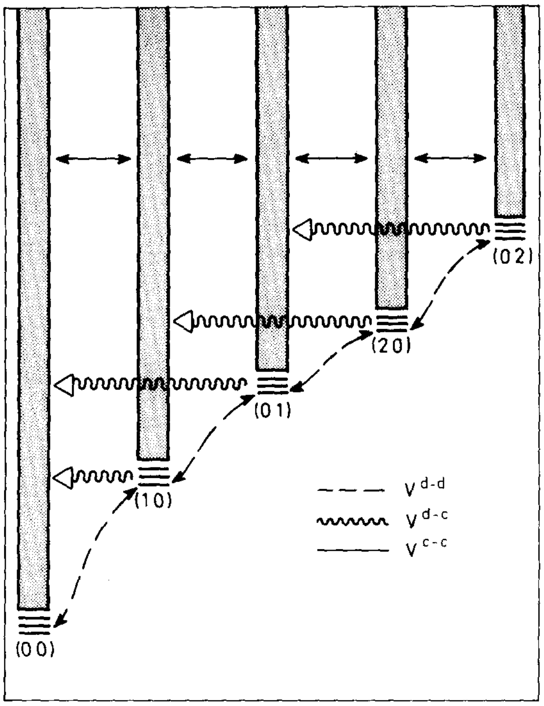

FIG. 2. Zero-order states and coupling terms for a heterodimer AB···CD. The manifolds are labeled by the vibrational quantum numbers (n_{AB}, n_{CD}) associated with the two diatomics AB and CD.

are similar to those given in our previous work.[7] The *d*–*d* coupling will turn out to be of minor interest in the case of a heterodimer; however, it may be crucial in determining the nuclear dynamics of homodimer and therefore we shall present the result

$$\begin{aligned}\mathcal{V}^{d-d}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l,n'_{\mathrm{AB}}n'_{\mathrm{CD}}l'}=&\ (A^{(2)}_{n_{\mathrm{AB}}n_{\mathrm{CD}},n'_{\mathrm{AB}}n'_{\mathrm{CD}}}C^{(2)}_{ll'}\\&-2A^{(1)}_{n_{\mathrm{AB}}n_{\mathrm{CD}},n'_{\mathrm{AB}}n'}C^{(1)}_{ll'})\ ,\end{aligned} \tag{10}$$

where

$$\begin{aligned}A^{(p)}_{n_{\mathrm{AB}}n_{\mathrm{CD}},n'_{\mathrm{AB}}n'_{\mathrm{CD}}}=&\ \langle n_{\mathrm{AB}}n_{\mathrm{CD}}|(\exp\{p\alpha_{\mathrm{BC}}[\gamma_{\mathrm{AB}}(X_{\mathrm{AB}}-\bar{X}_{\mathrm{AB}})\\&+\gamma_{\mathrm{CD}}(X_{\mathrm{CD}}-\bar{X}_{\mathrm{CD}})]\}-1)|n'_{\mathrm{AB}}n'_{\mathrm{CD}}\rangle\ ,\quad p=1,2\end{aligned} \tag{11}$$

and

$$C^{(1)}_{ll'}=(D_{\mathrm{BC}}/2K_{\mathrm{BC}})\left[\frac{(2K_{\mathrm{BC}}-2l-1)(2K_{\mathrm{BC}}-2l'-1)}{l!l'!\,\Gamma(2K_{\mathrm{BC}}-l)\Gamma(2K_{\mathrm{BC}}-l')}\right]^{1/2}\ , \tag{12}$$

$$\begin{aligned}&C^{(2)}_{ll'}=(C^{(1)}_{ll'}/2K_{\mathrm{BC}})[l'(2K_{\mathrm{BC}}-l'-1)-l(2K_{\mathrm{BC}}-l-1)+2K_{\mathrm{BC}}]\ ,\\&\quad l'>l-1\ .\end{aligned} \tag{13}$$

These discrete–discrete terms were found on the basis of numerical calculations to be exceedingly small relative to the energy spacing between the discrete energy levels of the heterodimer

$$|E_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}-E_{n'_{\mathrm{AB}}n'_{\mathrm{CD}}l'}|\gg\mathcal{V}^{d-d}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l,n'_{\mathrm{AB}}n'_{\mathrm{CD}}l'}\ . \tag{14}$$

Condition (14) is expected to be satisfied for most of the bound vibrational states of the heterodimer excluding perhaps only those $n_{\mathrm{AB}}n_{\mathrm{CD}}$ states near the dissociation limit of the normal chemical bonds in which we are not interested at present. Accordingly, *d*–*d* interaction can be safely neglected.

Next, we briefly consider the continuum–continuum coupling. Our previous calculations[7] on the X ⋯ BC van der Waals molecules demonstrated that the effects of c–c interactions somewhat modify the quantitative features of the VP at high vibrational energies of the molecular bond. For vibrational quantum number of the molecular bond $n = 10$–20, the c–c interaction leads to a retardation of the VP rate by a numerical factor of ~ 2–3 relative to the simple golden rule expression.[7] As we shall be interested in VP following low vibrational excitations of the heterodimer, i.e., $n_{AB}n_{CD} = 1$–5, the effects of c–c coupling can be safely disregarded.

We are left with the effects of discrete–continuum interactions which determine the VP rate of the heterodimer. The d–c coupling terms can be expressed in the form[7]

$$\mathcal{V}^{d-c}_{n_{AB}n_{CD}l,\,n'_{AB}n'_{CD}\epsilon} = A^{(2)}_{n_{AB}n_{CD},\,n'_{AB}n'_{CD}}C^{(2)}_{l\epsilon} - 2A^{(1)}_{n_{AB}n_{CD},\,n'_{AB}n'_{CD}}C^{(1)}_{l\epsilon}, \tag{15}$$

where the coefficients $A^{(p)}_{n_{AB}n_{CD},\,n'_{AB}n'_{CD}}$ $(p = 1, 2)$ are given by Eq. (11) while

$$C^{(1)}_{l\epsilon} = (1/2)\left[(D_{BC}/2)\sinh(2\pi\theta_\epsilon)\,\frac{(2K_{BC}-2l-1)}{l!\,\Gamma(2K_{BC}-l)}\right]^{1/2} \times \frac{|\Gamma(\frac{1}{2}+K_{BC}-i\theta_\epsilon)|}{[\cos^2(\pi K_{BC})+\sinh^2(\pi\theta_\epsilon)]^{1/2}} \tag{16}$$

and

$$C^{(2)}_{l\epsilon} = (C^{(1)}_{l\epsilon}/2K_{BC})[(K_{BC}-l-1/2)^2+\theta^2_\epsilon+2K_{BC}], \tag{17}$$

where $\Gamma(Z)$ stands for the Gamma function of the complex variable Z and where we have introduced the following definitions:

$$K_{BC} = (\hbar\alpha_{BC})^{-1}(2\mu_{AB,CD}D_{BC})^{1/2} = 2D_{BC}/\hbar\omega_{BC}, \tag{18a}$$

$$\omega_{BC} = \alpha_{BC}(2D_{BC}/\mu_{AB,CD})^{1/2}, \tag{18b}$$

$$\theta_\epsilon = (\hbar\alpha_{BC})^{-1}(2\mu_{AB,CD}\epsilon)^{1/2} = 2\sqrt{D_{BC}\epsilon}/\hbar\omega_{BC}, \tag{18c}$$

ϵ being the final relative kinetic energy between fragments AB and CD, i.e.,

$$\epsilon = E - W_{AB}(n'_{AB}) - W_{CD}(n'_{CD}), \tag{19}$$

where E is the total energy, $W_{AB}(n'_{AB})$ is the internal vibrational energy of AB in the state corresponding to n'_{AB}, and $W_{CD}(n'_{CD})$ is the internal energy of CD in the vibrational level labelled by n'_{CD}. Provided that we are interested only in the coupling on the energy shell, then

$$E = W_{AB}(n_{AB}) + W_{CD}(n_{CD}) - (\hbar\omega_{BC}/2K_{BC})(K_{BC}-l-\tfrac{1}{2})^2. \tag{20}$$

The half-width for the decay of the metastable state $|n_{AB}n_{CD}l\rangle$ of the heterodimer via VP is given in terms of the familiar golden rule result

$$\Gamma_{n_{AB}n_{CD}l} = \sum_{n'_{AB}}\sum_{n'_{CD}} |\mathcal{V}^{d-c}_{n_{AB}n_{CD}l,\,n'_{AB}n'_{CD}\epsilon}|^2, \tag{21}$$

where the energy ϵ is taken on the energy shell, according to Eqs. (19) and (20). The summation in Eq. (21) is taken over all open channels. Now, provided that interference effects can be neglected, i.e., the spacing between resonances originating from various $|n_{AB}n_{CD}l\rangle$ zero-order levels considerably exceeds their widths, the decay of each metastable state is exponential, being characterized by the decay time

$$\tau = \hbar/\Gamma_{n_{AB}n_{CD}l}. \tag{22}$$

We are now in a position to provide simple explicit relation for the VP rate of a heterodimer.

III. VIBRATIONAL PREDISSOCIATION DYNAMICS OF A HETERODIMER

We shall now consider the features of the VP process of the heterodimer. We shall handle a simple model where the intermolecular AB and BC potentials are taken to be harmonic and where a linearization approximation is introduced for the d–c interaction, which is handled to first order in the internal displacements. The d–c coupling within the framework of the linearization approximation was previously considered by Coulson and Robertson,[11(a)] by Ewing[11(b)] and by us.[7] The linear approximation together with the harmonic model for the intramolecular potentials are adequate for low vibrational excitations of the normal bond modes X_{AB} and X_{CD}, in which we are interested. In the harmonic model for the AB and BC potentials, we have

$$W_{AB}(n_{AB}) = \hbar\omega_{AB}(n_{AB}+\tfrac{1}{2});\quad W_{CD}(n_{CD}) = \hbar\omega_{CD}(n_{CD}+\tfrac{1}{2}), \tag{23}$$

where ω_{AB} and ω_{CD} are the frequencies of molecules AB and CD respectively. Substituting Eq. (23) into Eqs. (19) and (20), and using this relation in Eqs. (18), we obtain the discrete–continuum coupling (15) in the harmonic model

$$\mathcal{V}^{d-c}_{n_{AB}n_{CD}l,\,n'_{AB}n'_{CD}\epsilon} = C^{(1)}_{l\epsilon}\{A^{(2)}_{n_{AB}n_{CD},\,n'_{AB}n'_{CD}}[1+(\hbar\omega_{AB}/\hbar\omega_{BC})(n_{AB}-n'_{AB})+(\hbar\omega_{CD}/\hbar_{BC})(n_{CD}-n'_{CD})] - 2A^{(1)}_{n_{AB}n_{CD},\,n'_{AB}n'_{CD}}\}. \tag{24}$$

Next, we utilize the linearization approximation, expanding the exponentials in Eq. (11) up to linear terms in the intramolecular displacements $(X_{AB}-\bar{X}_{AB})$ and $(X_{CD}-\bar{X}_{CD})$, resulting in

$$\begin{aligned} A^{(p)}_{n_{AB}n_{CD},\,n'_{AB}n'_{CD}} \cong p\alpha_{BC}\{&\gamma_{AB}(\hbar/2\mu_{AB}\omega_{AB})^{1/2}[n^{1/2}_{AB}\delta_{n_{AB},\,n'_{AB}+1}+(n_{AB}+1)^{1/2}\delta_{n_{AB}+1,\,n'_{AB}}]\delta_{n_{CD}n'_{CD}} \\ &+\gamma_{CD}(\hbar/2\mu_{CD}\omega_{CD})^{1/2}[n^{1/2}_{CD}\delta_{n_{CD},\,n'_{CD}+1}+(n_{CD}+1)^{1/2}\delta_{n_{CD}+1,\,n'_{CD}}]\delta_{n_{AB}n'_{AB}}\},\quad p=1,2. \end{aligned} \tag{25}$$

The discrete–continuum coupling on the energy shell assumes the form

$$\begin{aligned} \mathcal{V}^{d-c}_{n_{AB}n_{CD}l,\,n'_{AB}n'_{CD}\epsilon} = {}&(\alpha_{BC}/\omega_{BC})[(D_{BC}/2)\sinh(2\pi\theta_\epsilon)(2K_{BC}-2l-1)/l!\,\Gamma(2K_{BC}-l]^{1/2}\,|\Gamma(\tfrac{1}{2}+K_{BC}-i\theta_\epsilon)| \\ &\times[\cos^2(\pi K_{BC})+\sinh^2(\pi\theta_\epsilon)]^{-1/2}[\omega_{AB}(n_{AB}-n'_{AB})+\omega_{CD}(n_{CD}-n'_{CD})]C_{n_{AB}n'_{AB},\,n_{CD}n'_{CD}}, \end{aligned} \tag{26}$$

with

$$\begin{aligned} C_{n_{AB}n'_{AB},\,n_{CD}n'_{CD}} = {}&\gamma_{AB}(\hbar/2\mu_{AB}\omega_{AB})^{1/2}[n^{1/2}_{AB}\delta_{n_{AB},\,n'_{AB}+1}+(n_{AB}+1)^{1/2}\delta_{n_{AB}+1,\,n'_{AB}}]\delta_{n_{CD}n'_{CD}} \\ &+\gamma_{CD}(\hbar/2\mu_{CD}\omega_{CD})^{1/2}[n^{1/2}_{CD}\delta_{n_{CD},\,n'_{CD}+1}+(n_{CD}+1)^{1/2}\delta_{n_{CD}+1,\,n'_{CD}}]\delta_{n_{AB}n'_{AB}}. \end{aligned} \tag{27}$$

Consequently, Eqs. (26) and (27) result in the propensity rules for discrete–continuum coupling

$$\Delta n_{\mathrm{AB}}=0\,,\qquad \Delta n_{\mathrm{CD}}=\pm 1\,,$$
$$\Delta n_{\mathrm{CD}}=0\,,\qquad \Delta n_{\mathrm{AB}}=\pm 1\,, \tag{28}$$

with the condition that

$$\epsilon=\hbar\omega_{\mathrm{AB}}(n_{\mathrm{AB}}-n'_{\mathrm{AB}})+\hbar\omega_{\mathrm{CD}}(n_{\mathrm{CD}}-n'_{\mathrm{CD}})-\hbar\omega_{\mathrm{BC}}/2K_{\mathrm{BC}})(K_{\mathrm{BC}}-l-\tfrac{1}{2})^2>0\,, \tag{29}$$

which implies, therefore, that nonvanishing discrete–continuum coupling originates from two combinations $\Delta n_{\mathrm{AB}}=0$, $\Delta n_{\mathrm{CD}}=+1$ and $\Delta n_{\mathrm{CD}}=0$, $\Delta n_{\mathrm{AB}}=+1$. These propensity rules determine the channels which contribute to the resonance width (21), and to the decay time (22). According to Eq. (28), the decay problem reduces just to the simple case of parallel decay of a simple discrete state into two continua. From Eqs. (26)–(29) together with Eq. (21), we obtain the total width for VP of the heterodimer

$$\Gamma_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}=\Gamma^{(1)}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}+\Gamma^{(2)}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}\,, \tag{30}$$

where the partial widths for the channels specified by the propensity rules Eq. (28) are given by

$$\begin{aligned}\Gamma^{(1)}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}&\equiv\pi\left|\mathcal{V}^{d-c}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l,(n_{\mathrm{AB}}-1)n_{\mathrm{CD}}\epsilon}\right|^2\\&=(\pi/8)\hbar\omega_{\mathrm{AB}}n_{\mathrm{AB}}m_1[(2K_{\mathrm{BC}}-2l-1)/l!\,\Gamma(2K_{\mathrm{BC}}-l)]\\&\quad\times\{\sinh(2\pi y_1)/[\cos^2(\pi K_{\mathrm{BC}})+\sinh^2(\pi y_1)]\}\\&\quad\times|\Gamma(K_{\mathrm{BC}}+\tfrac{1}{2}-iy_1)|^2\,,\end{aligned} \tag{31}$$

where

$$m_1=(m_{\mathrm{C}}+m_{\mathrm{D}})m_{\mathrm{A}}/m_{\mathrm{B}}M\,, \tag{32a}$$

$$y_1=[\beta_1-(K_{\mathrm{BC}}-l-\tfrac{1}{2})^2]^{1/2}\,, \tag{32b}$$

$$\beta_1=4D_{\mathrm{BC}}\omega_{\mathrm{AB}}/\hbar\omega^2_{\mathrm{BC}}=2\omega_{\mathrm{AB}}\mu_{\mathrm{AB,CD}}/\hbar\alpha^2_{\mathrm{BC}} \tag{32c}$$

if $y_1^2>0$; otherwise $\Gamma^{(1)}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}=0$, and

$$\begin{aligned}\Gamma^{(2)}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}&\equiv\pi\left|\mathcal{V}^{d-c}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l,n_{\mathrm{AB}}(n_{\mathrm{CD}}-1)\epsilon}\right|^2\\&=(\pi/8)\hbar\omega_{\mathrm{CD}}n_{\mathrm{CD}}m_2[(2K_{\mathrm{BC}}-2l-1)/l!\,\Gamma(2K_{\mathrm{BC}}-l)]\\&\quad\times\{\sinh(2\pi y_2)/[\cos^2(\pi K_{\mathrm{BC}})+\sinh^2(\pi y_2)]\}\\&\quad\times|\Gamma(K_{\mathrm{BC}}+\tfrac{1}{2}-iy_2)|^2\,,\end{aligned} \tag{33}$$

with

$$m_2=(m_{\mathrm{A}}+m_{\mathrm{B}})m_{\mathrm{D}}/m_{\mathrm{C}}M\,, \tag{34a}$$

$$y_2=[\beta_2-(K_{\mathrm{BC}}-l-\tfrac{1}{2})^2]^{1/2}\,, \tag{34b}$$

$$\beta_2=4D_{\mathrm{BC}}\omega_{\mathrm{CD}}/\hbar\omega^2_{\mathrm{BC}}=2\omega_{\mathrm{CD}}\mu_{\mathrm{AB,CD}}/\hbar\alpha^2_{\mathrm{BC}}\,, \tag{34c}$$

if $y_2^2\geq 0$; while, otherwise, $\Gamma^{(2)}_{n_{\mathrm{AB}}n_{\mathrm{CD}}}=0$.

Equations (30)–(34) constitute our final result for the VP of a heterodimer. To explore the characteristics of the VP dynamics of this system, we shall be interested in the situation $y_1\gg 1$ and $y_2\gg 1$, as for the van der Waals dimer $\omega_{\mathrm{AB}}/\omega_{\mathrm{BC}}\gg 1$ as well as $\omega_{\mathrm{CD}}/\omega_{\mathrm{BC}}\gg 1$, so that according to Eqs. (32c) and (34c), $\beta_1,\beta_2\gg 1$. Utilizing the expansion of the gamma function, the partial widths $\Gamma^{(j)}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}$ $(j=1,2)$ can be recast in the approximate form[7,11]

$$\Gamma^{(1)}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}\simeq\pi^2\hbar\omega_{\mathrm{AB}}n_{\mathrm{AB}}m_1[(N-l-1)/l!\,(2N-l-1)!]\times y_1^{2N-1}\exp(-\pi y_1) \tag{35a}$$

and

$$\Gamma^{(2)}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}\simeq\pi^2\hbar\omega_{\mathrm{CD}}n_{\mathrm{CD}}m_2[(N-l-1)/l!\,(2N-l-1)!]\times y_2^{2N-1}\exp(-\pi y_2)\,. \tag{35b}$$

The VP rate is roughly given by

$$\Gamma_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}\cong\pi^2[(N-l-1)/l!\,(2N-l-1)!][\hbar\omega_{\mathrm{AB}}n_{\mathrm{AB}}m_1y_1^{2N-1}\times\exp(-\pi y_1)+\hbar\omega_{\mathrm{CD}}n_{\mathrm{CD}}m_2y_2^{2N-1}\exp(-\pi y_2)]\,. \tag{36}$$

From these relations, the following conclusions emerge:

(1) Energy gap law (EGL): For large values of l in the range $l\lesssim N-1$, we can take $y_1\simeq\beta_1^{1/2}$ and $y_2\simeq\beta_2^{1/2}$ and the VP rate assumes the form

$$\Gamma_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}\propto\hbar\omega_{\mathrm{AB}}n_{\mathrm{AB}}m_1\exp[-\pi\beta_1^{1/2}+(N-\tfrac{1}{2})\ln\beta_1]+\hbar\omega_{\mathrm{CD}}n_{\mathrm{CD}}m_2\exp[-\pi\beta_2^{1/2}+(N-\tfrac{1}{2})\ln\beta_2]\,. \tag{37}$$

Utilizing Eqs. (32c) and (34c), we get

$$\Gamma_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}\propto\hbar\omega_{\mathrm{AB}}n_{\mathrm{AB}}m_1\beta_1^{[N-(1/2)]}\exp[-2\pi\hbar^{-1/2}(D^{1/2}_{\mathrm{BC}}/\omega_{\mathrm{BC}})\omega^{1/2}_{\mathrm{AB}}]+\hbar\omega_{\mathrm{CD}}n_{\mathrm{CD}}m_2\beta_2^{[N-(1/2)]}\exp[-2\pi\hbar^{-1/2}(D^{1/2}_{\mathrm{BC}}/\omega_{\mathrm{BC}})\omega^{1/2}_{\mathrm{CD}}]\,. \tag{37a}$$

Equation (37) exhibits the EGL for the VP of the heterodimer. Each of the partial widths which together determine the VP rate exhibits a strong exponential dependence on the vibrational frequency of the corresponding molecular modes.

(2) Energetic parameters of the van der Waals bond: The two partial widths are determined by the parameter $(D^{1/2}_{\mathrm{BC}}/\omega_{\mathrm{BC}})$ for the weak intermolecular bond.

(3) Dependence on l: From Eq. (36) together with Eqs. (32b) and (34b), it is apparent that, for high values of $l\lesssim(N-1)$, the two partial decay widths increase with decreasing l.

(4) Dependence on the internal vibrational quantum number: It is evident from Eq. (36) that each of the two partial widths exhibits a linear dependence of the corresponding vibrational quantum number n_{AB} and n_{CD} of the two bond modes. This linear dependence is, of course, common to all problems involving harmonic oscillator models, and is a consequence of the harmonic approximation. For low values of n_{AB} and of n_{CD}, this linear dependence constitutes a reasonable zero-order description; however, in general, anharmonicity effects for the local bond modes are expected to result in a superlinear dependence of the VP rate on n_{AB} and on n_{CD}.

(5) A limiting situation: For a heterodimer characterized by the bond frequencies $\omega_{\mathrm{AB}}\ll\omega_{\mathrm{CD}}$, then for a metastable state characterized by $n_{\mathrm{AB}}\neq 0$ we have

$$\Gamma^{(2)}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}\gg\Gamma^{(1)}_{n_{\mathrm{AB}}n_{\mathrm{CD}}l} \tag{37}$$

and we obtain for the VP rate

$$\begin{aligned}\Gamma_{n_{\mathrm{AB}}n_{\mathrm{CD}}l}&=(\pi/8)\hbar\omega_{\mathrm{AB}}n_{\mathrm{AB}}m_1[(2K_{\mathrm{BC}}-2l-1)/l!\,\Gamma(2K_{\mathrm{BC}}-l)]\\&\quad\times\{\sinh(2\pi y_1)/[\cos^2(\pi K_{\mathrm{BC}})+\sinh^2(\pi y_1)]\}\\&\quad\times|\Gamma(K_{\mathrm{BC}}+\tfrac{1}{2}-iy_1)|^2\,.\end{aligned} \tag{38}$$

This is just the result for VP of a linear triatomic van der Waals molecules AB ⋯ X,[7] where the high-frequency molecule CD is now replaced by an effective atom X, where mass equals $m_C + m_D$ and the $B \cdots C$ van der Waals bond.

(6) Nature of the linearization approximation: The linearization approximation amounts to retaining only the first-order linear terms in nuclear displacements for the intramolecular contributions to the d–c coupling $A^{(p)}$ [Eq. (11)]. Such approximation results in one-quantum transitions, as is evident from Eq. (28), resulting in the conversion of vibrational energy to translational energy, i.e., a $V \to T$ process. A cursory examination of Eqs. (11) and (25) indicates that the first-order expansion of the intramolecular contribution is justified provided that $Z = \alpha_{BC}\langle R^2\rangle^{1/2} \ll 1$, where α_{BC} is the range parameter for the van der Waals bond and $\langle R^2\rangle^{1/2} = (\hbar/\mu\omega)^{1/2}$, with $\mu(\equiv \mu_{AB}$ or $\mu_{CD})$ and $\omega(\equiv \omega_{AB}$ or $\omega_{CD})$ representing typical molecular reduced mass and molecular frequency, respectively, and $\langle R^2\rangle^{1/2}$ represents the rms displacement of the zero-point intramolecular vibration. For typical values of $\alpha_{BC} \sim 2$ Å^{-1} and $\langle R^2\rangle^{1/2} \sim 0.1$ Å, $Z \sim 0.05$ and the linear term dominates in the expansion of $A^{(p)}$.

(7) Vibration–vibration transfer. High-order terms in the expansion of $A^{(p)}$ [Eq. (11)], may sometimes lead to significant contribution to the VP rate and, in particular, result in a new mechanism for the VP process. For example, the second-order term in nuclear displacements $(X_{AB} - \bar{X}_{AB})$ and $(X_{CD} - \bar{X}_{CD})$ will result in two-quantum jumps $\Delta n_{AB} = \pm 1$ and $\Delta n_{CD} = \mp 1$. Such second-order contribution corresponds to the conversion of vibrational energy of AB to vibrational energy of CD (provided that $\hbar\omega_{AB} > \hbar\omega_{CD}$), while the energy balance is made up by translational energy. This mechanism involves a $V \to V + T$ process. The relative kinetic energy of the two fragments can now be considerably lower than for the case of $V \to T$ transfer. Under these circumstances, the intermolecular contributions $C^{(1)}$ and $C^{(2)}$ [Eqs. (12) and (13), respectively] to the d–c coupling, which essentially determine our energy gap law, will result in an appreciable contribution of the second-order term to the VP rate. We conclude that, for some systems when $\hbar(\omega_{AB} - \omega_{CD})$ is relatively low, the $V \to V + T$ process can be efficient.

The theory of VP of linear heterodimers $AB \cdots CD$ constitutes an extension of the theory of the nuclear dynamics of linear triatomic van der Waals molecules previously considered by us.[7] The characteristics of the VP process of the heterodimer bear a close analogy to that of the triatomic van der Waals molecule, except that in the present case two parallel effective decay channels for each metastable state are involved. Of considerable interest is the problem of the nuclear dynamics of a homodimer, which will exhibit some new physical features, and which will now be considered.

IV. VIBRATIONAL PREDISSOCIATION DYNAMICS OF A HOMODIMER

A. The degeneracy problem

The VP dynamics of a heterodimer involves essentially the decay of a single, isolated, discrete zero-order state into several continua. In this case, the discrete–discrete coupling terms are negligible according to Eq. (14), whereupon the VP process can be adequately characterized in terms of a simple single exponential decay law. In the case of a homodimer, a new physical effect should be considered, which stems from the degeneracy of some of the zero-order state. Consider, for example, the local mode description of a homodimer whose bond zero-order states will be denoted by $|n_1 n_2 l\rangle$, where n_1 and n_2 represent the vibrational quantum numbers of the two diatomic fragments. The pairs of zero-order states $|n_1 n_2 l\rangle$ and $|n_2 n_1 l\rangle$ are degenerate. Under these circumstances, even a small discrete–discrete coupling term between zero-order degenerate states can go a far way in determining the intramolecular dynamics of the homodimer. In what follows, we shall address ourselves to the problem of the intramolecular VP dynamics of a homodimer in an attempt to answer the following questions:

(1) What are the energetic parameters which determine the VP dynamics? They are evidently the resonance half-width and the d–d coupling.

(2) When are the VP processes characterized by an oscillatory nonexponential decay which is amenable to experimental observation?

To answer these questions, we shall proceed in three steps. First, we shall discuss some zero-order basis sets which can be used for the study of the VP of the homodimer. These basis sets will be introduced without alluding to any real physical situation. For each basis set, we shall obtain different values of the resonance half-width and of the d–d coupling term. However, now the resonance half-width does not represent an exponential decay probability, different basis sets will result in different energetic parameters, and the characteristics of the VP dynamics depends on the initially excited metastable state. Second, we shall define excitation processes which result in physically meaningful initial conditions for the dynamic problem. These initial conditions will determine the subsequent time evolution of the system. Third, we shall develop a complete theory of intramolecular dynamics and apply it to the problem at hand.

B. Basis sets for the homodimer

We shall now consider three sets of zero-order states which are appropriate for the description of the intramolecular dynamics of the homodimer. For each basis set, we shall provide explicit expressions for the discrete–discrete coupling terms and for the half-width of the resonance.

1. *The local mode basis*

This basis set consisting of discrete states $|n_1 n_2 l\rangle$ and of continuum states $|n_1 n_2 \epsilon\rangle$ was already considered in Sec. II and is displayed in Fig. 3(a) for the $AB \cdots BC$ or for the $AB \cdots AB$ homodimer. When a harmonic approximation is adopted for the potential energy surfaces of the two AB subunits, all the states with the same l and for which $n_1 + n_2 = M$ are degenerate. Part of this degeneracy is accidental and can be lifted by de-

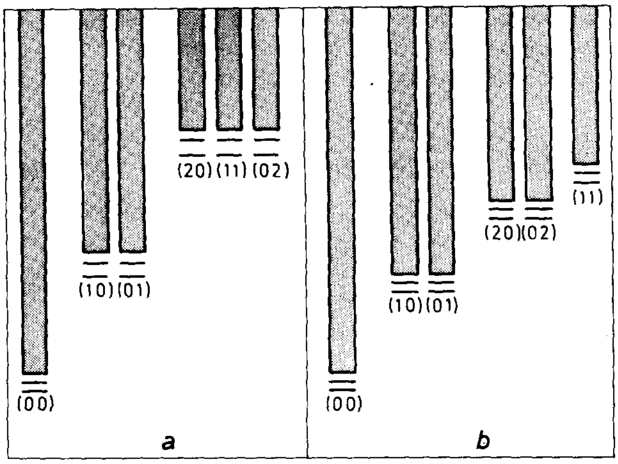

FIG. 3. Local mode basis sets for the study of intramolecular dynamics of the homodimer AB···AB: (a) Harmonic approximation; (b) anharmonic molecules. The labels ($n_{\mathrm{AB}}\ n'_{\mathrm{AB}}$) specify different vibrational levels of the individual subunits AB.

scribing the molecular bond modes in terms of more realistic anharmonic potential. Now the (permutation) symmetry determines that degeneracy prevails between the pairs of discrete states $|n_1n_2l\rangle$ and $|n_2n_1l\rangle$, and similarly for continuum states [see Fig. 3(b)]. As anharmonicity defects for the intramolecular AB modes are expected to be of the order of a few cm^{-1}, the accidental degeneracy is practically completely lifted and we can disregard d–d coupling between states which were accidentally degenerate in the harmonic description.

Consider now the half-widths of the resonances for a homodimer consisting of two identical AB diatomics. These half-widths of the resonances will be presented in the harmonic approximation for the bond modes, which is adequate for low values of n_1 and of n_2. For the linear arrangement AB··· BA which is characterized by a center of inversion symmetry, we can immediately utilize Eqs. (30)–(34) to obtain

$$\begin{aligned}\Gamma_{n_1n_2l} &= (\pi/8)\hbar\omega_{\mathrm{AB}}m_1[(2K_{\mathrm{BB}}-2l-1)/l!\,\Gamma(2K_{\mathrm{BB}}-l)]\\ &\quad\times\sinh(2\pi y_1)/[\cos^2(\pi K_{\mathrm{BB}})+\sinh^2(\pi y_1)]\}\\ &\quad\times|\Gamma(K_{\mathrm{BB}}+\tfrac{1}{2}-iy_1)|^2(n_1+n_2)\,, \qquad (39)\end{aligned}$$

with $m_1=m_{\mathrm{A}}/2m_{\mathrm{B}}$. For this homodimer, $\Gamma_{n_1n_2l}=\Gamma_{n_2n_1l}$ as the two molecular subunits are equivalent. For the configuration AB(n_1)··· AB(n_2), the half-width is given by

$$\begin{aligned}\Gamma_{n_1n_2l} &= (\pi/8)\hbar\omega_{\mathrm{AB}}[(2K_{\mathrm{BC}}-2l-1)/l!\,\Gamma(2K_{\mathrm{BC}}-l)]\\ &\quad\times\{\sinh(2\pi y_1)/[\cos^2(\pi K_{\mathrm{BC}})+\sinh^2(\pi y_1)]\}\\ &\quad\times|\Gamma(K_{\mathrm{BC}}+\tfrac{1}{2}-iy_1)|^2(n_1m_1+n_2m_2)\,, \qquad (40)\end{aligned}$$

where

$$m_1=m_{\mathrm{A}}/2m_{\mathrm{B}}\,,\qquad m_2=m_{\mathrm{B}}/2m_{\mathrm{A}}\,. \qquad (40\mathrm{a})$$

The resonance half-widths given in terms of Eqs. (39) and (40) for the homodimer exhibit a characteristic energy gap law, a typical dependence on the parameters of the van der Waals bond and of the molecular bonds, which is similar to that obtained for the heterodimer.

In order to predict the time evolution of the degenerate discrete levels such as $|n_1n_2l\rangle$ and $|n_2n_1l\rangle$, it is necessary to study the appropriate discrete–discrete couplings which may no longer be negligible. Obviously, we shall have to consider only coupling term of the type $\mathcal{V}^{d-d}_{n_1n_2l,n_2n_1l}$ with the same value of l; all the other d–d couplings are still negligible. The general form of the d–d coupling terms is given in terms of Eq. (10) and (11), where we now set $n_{\mathrm{AB}}=n'_{\mathrm{CD}}=n_1$ and $n_{\mathrm{CD}}=n'_{\mathrm{AB}}=n_2$. We are interested in the case $l=l'$, whereupon Eqs. (10) and (11) yield

$$C^{(2)}_{ll'}=C^{(1)}_{ll'} \qquad (41)$$

Equation (41) implies that utilization of the linearization approximation, i.e., expanding $A^{(p)}_{n_1n_2,n_2n_1}$ ($p=1,2$) [Eq. (11)], to first order in the intramolecular displacements results in $\mathcal{V}^{d-d}_{n_1n_2l,n_2n_1l}=0$. The linearization approximation results in the vanishing of the d–d coupling between degenerate states which are characterized by the same value of l; this effect will be exhibited irrespective of the specific form of the potential for the bond modes and it will happen both for harmonic and anharmonic description of the AB potential. We conclude that the coupling between zero-order discrete degenerate levels originates from high-order terms in the intramolecular displacements which contribute to Eq. (10). These calculations have to be carried out by direct integration of Eq. (11), which was performed by us (see Sec. VI).

2. *The miniexciton basis*

A traditional way to treat degenerate zero-order excited states involving vibrational or electronic excitations in dimers and in molecular aggregates[12] rests on the construction of symmetry adopted wave functions with the interaction lifting the degeneracy. We shall adopt a similar approach here, which bears a close analogy to exciton theory applied to the homodimer, i.e., a miniexicton. We shall consider the subset of discrete zero-order states $|n_1n_2l\rangle$ and, in this subspace of the Hilbert space, we shall construct the symmetry adapted functions from each pair of degenerate bond-mode states

$$\begin{aligned}|(+)n_1n_2l\rangle &= 2^{-1/2}(|n_1n_2l\rangle+|n_2n_1l\rangle)\,,\\ |(-)n_1n_2l\rangle &= 2^{-1/2}(|n_1n_2l\rangle-|n_2n_1l\rangle)\,. \qquad (42)\end{aligned}$$

This basis will be referred to as the miniexciton basis set. As we shall be interested in the homodimers of the halogen dimers A_2–A_2 ($A\equiv$ F, Cl, Br, I), we shall avoid unnecessary complication and from now on consider the linear AB··· BA dimer only. Each pair of the $|(+)\rangle$ and $|(-)\rangle$ states in Eq. (42) is now uncoupled with respect to d–d interaction

$$\mathcal{V}^{d-d}_{(+)n_1n_2l,(-)n_2n_1l}=0\,. \qquad (43)$$

The degeneracy is split and the (zero-order) energies of the discrete states are $E(+)_{n_1n_2l}=-\mathcal{V}^{d-d}_{n_1n_2l,n_2n_1l}$ and $E(-)_{n_1n_2l}=\mathcal{V}^{d-d}_{n_1n_2l,n_2n_1l}$. The half-widths of the resonances are readily obtained from Eqs. (39) and (40) in the form

$$\begin{aligned}\Gamma_{(+)n_1n_2l} &= 2\Gamma_{n_1n_2l}\,,\\ \Gamma_{(-)n_1n_2l} &= 0\,. \qquad (44)\end{aligned}$$

It is interesting to note that each $|(-)\rangle$ discrete state is stable with respect to direct decay into the continuum due to destructive interference. As these $|(-)\rangle$ states are not coupled to $|(+)\rangle$ states in view of Eq. (43), we expect the $|(-)\rangle$ levels to constitute truly "isolated" states which are stable with respect to intramolecular decay.

3. The normal mode basis

This basis is obtained by adopting the conventional procedure for constructing normal modes for the intramolecular motion of the homodimer, which rests on the formation of symmetric and antisymmetric combination of the displacements in the bond modes.[13] This approach rests on the harmonic model for the AB bond modes. Thus, in this description, both accidental and symmetry determined degeneracies will be exhibited for the homodimer. This intrinsic limitation of the normal mode basis prevents us from using it in our general treatment of the VP dynamics. Appendix A is devoted to a comprehensive discussion of the normal mode basis and to a comparison of the results obtained for this basis with those derived for the harmonic bond mode basis.

C. "Preparation" of metastable states of the homodimer

We have first defined two useful basis sets, the bond mode basis and the miniexciton basis, which will be used for the subsequent treatment of intramolecular dynamics of the linear homodimer on its ground state potential surface. The physical preparation of the "initially excited" state is of cardinal importance, as this will determine the intramolecular dynamics. For example, we have already noted that the $|(-)n_1n_2l\rangle$ miniexciton states are stable with respect to time evolution. Thus, if such a $|(-)n_1n_2l\rangle$ state could be initially prepared, it will not exhibit intramolecular time evolution. This is not surprising, as other examples of states which are stable with respect to subsequent decay are well known in related areas of molecular and of solid-state physics. To provide a simple analogy, let us recall that, in the simple didactic theory of Frenkel[13] exciton states, all the states with $\mathbf{k}\neq 0$ are stable with respect to radiative decay to the ground state. The cardinal question in relation to our problem is whether such a stable state can be excited in a heterodimer. The answer usually is negative. To be more specific, let us consider two limiting excitation modes of the homodimer, which result in reasonably well-defined "initial" metastable states.

1. Optical excitation

We shall consider optical excitation of the homodimer by infrared radiation as we are concerned with vibrational excitation on the ground state potential surface. To consider properly a "short time" excitation process, we have to specify which of the zero-order states carries oscillator strength from the ground state. We invoke the reasonable assumption that only the discrete zero-order states carry oscillator strength from the ground state $|n_1=0, n_2=0, l=0\rangle$. Accordingly, we have to consider radiative coupling with the discrete subspace of the Hilbert space where the miniexciton basis provides a diagonal representation of the Hamiltonian. Thus, two optical excitation processes should be considered for each nearly degenerate pair

$$|n_1=0, n_2=0, l=0\rangle \to |(+)n_1n_2l\rangle \;, \tag{45a}$$

$$|n_1=0, n_2=0, l=0\rangle \to |(-)n_1n_2l\rangle \;. \tag{45b}$$

For the linear homodimer, only the optical transition (45a), where the transition moments of the two subunits are in phase, is allowed while the transition (45b), where the transition moments of the time subunits cancel, is forbidden. This state of affairs bears a close analogy to exciton theory.[13] On the other hand, when the optical excitation of a nondegenerate state is considered, such as $|n_1=n, n_2=nl\rangle$, this discrete zero-order state is initially prepared by optical excitation. We conclude that optical excitation results in the initial selection of the $|(+)n_1n_2l\rangle$ state from each degenerate pairs and in the initial excitation of a discrete nondegenerate state. These metastable states will exhibit subsequent time evolution.

Finally, we would like to comment on the nature of the transition moments of the two subunits (TMTS) whose superposition determines the total transition moment for infrared excitation. For a homodimer consisting of two heteronuclear diatomics AB, each of these TMTS corresponds to the infrared transition moment of the AB molecule. For a homodimer $A_2\cdots A_2$ consisting of a pair of homonuclear diatomics, the infrared transition moment of each "isolated" A_2 molecule vanishes. In this case, charge transfer vibronic type mixing[14] will lead to finite TMTS. Infrared absorption of several homodimers, such as $(H_2)_2$, $(N_2)_2$, and $(O_2)_2$, has been recorded.[15]

2. Collisional excitation

Excitation of the homodimer by collision will result in an incoherent superposition of zero-order degenerate states, which can be expressed as

$$|a\rangle = A\,|n_1n_2l\rangle + B\,|n_2n_1l\rangle \;, \tag{46}$$

where the constant coefficients determined by the experimental collisional excitation A and B are uncorrelated, in contrast to the case of optical excitation. We can immediately construct the complementary state to Eq. (46) which cannot be initially excited in that particular excitation experiment

$$|b\rangle = C\,|n_1n_2l\rangle + D\,|n_2n_1l\rangle \;, \tag{47}$$

where the constant coefficients C and D are related to the "experimental" coefficients A and B via the conventional orthonormality relations

$$\begin{aligned} &|C|^2+|D|^2=1\,, \\ &AC^*+BD^*=0\,. \end{aligned} \tag{48}$$

The relevant energetic parameter which determine the intramolecular dynamics of the homodimer are

$$\begin{aligned} &\mathcal{V}_{ba}^{d-d}=\mathcal{V}_{n_1n_2l,\,n_2n_1l}^{d-d}(AD^*+BC^*)\,, \\ &\Gamma_a=(A^2+B^2)\Gamma_{n_1n_2l}\,, \qquad \Gamma_b=(C^2+D^2)\Gamma_{n_1n_2l}\,. \end{aligned} \tag{50}$$

As the coefficients A and B do not bear any phase relationship, it is apparent from Eqs. (49) and (50) that a reasonable description of the intramolecular dynamics can be based on a bond mode state as an initial state. This is justified as now for incoherent excitation $(A^2 + B^2) \sim 1$ and $(AD^* + BC^*) \sim 1$, so that the energetic parameters calculated for an initially excited bond mode and thus the subsequent time evolution of the system will faithfully reproduce the VP dynamics of the collisionally excited homodimer.

V. TIME EVOLUTION OF QUASIDEGENERATE STATES

From the foregoing discussion, we conclude that a reasonable description of a physically meaningful excitation condition of the homodimer in an energy range containing a degenerate (in the bond mode basis) or nearly degenerate (in the miniexciton bond) pair of zero-order discrete levels can be specified by the initial condition

$$\Psi(0) = |(+)n_1 n_2 l\rangle \tag{51}$$

for a coherent optical excitation, and

$$\Psi(0) = |n_1 n_2 l\rangle \tag{52}$$

for collisional incoherent excitation. In defining these initial conditions, we have asserted that the duration of the short time optical or collisional excitation is short relative to the energy spread of the two zero-order levels. Such separation between excitation and subsequent time evolution is acceptable in the modern theory of relaxation phenomena.[16,17] The problem we are facing is essentially that of the dynamics of two coupled levels, which will be denoted by $|\alpha\rangle$ and $|\beta\rangle$ and which are coupled to a common continuum $\{|\epsilon\rangle\}$. These time coupled levels are given by Eq. (45) for the case of optical excitation and by Eqs. (46) and (47) for collisional excitation. We shall first consider the general formalism of the dynamics of such two-level systems. The discrete-continuum coupling terms are $v_{\alpha\epsilon}$ and $v_{\beta\epsilon}$ and the corresponding half-widths, which specify the discrete-continuum couplings, are given in terms of the elements of the off-diagonal decay matrix. The diagonal terms are

$$\Gamma_{\alpha\alpha} = \pi |\mathcal{V}_{\alpha\epsilon}|^2 , \tag{53a}$$

$$\Gamma_{\beta\beta} = \pi |\mathcal{V}_{\beta\epsilon}|^2 , \tag{53b}$$

while the off-diagonal terms are given by

$$\Gamma_{\alpha\beta} = \Gamma^*_{\beta\alpha} = \pi V_{\alpha\epsilon} V_{\epsilon\beta} . \tag{53c}$$

These off-diagonal terms [Eq. (53c)] are related to the diagonal terms by

$$\Gamma_{\alpha\beta}\Gamma_{\beta\alpha} = \Gamma_{\alpha\alpha}\Gamma_{\beta\beta}/\pi . \tag{53d}$$

The discrete-discrete coupling among the states $|\alpha\rangle$ and $|\beta\rangle$ is denoted by $\mathcal{V}_{\alpha\beta}$. The initial condition is $\Psi(0) = |\alpha\rangle$, where $|\alpha\rangle$ is given in terms of either Eq. (51) or (52). The probability $P_\alpha^{(\alpha)}(t)$ for the system to remain in the initial state $|\alpha\rangle$ at time t is

$$P_\alpha^{(\alpha)}(t) = |\langle\alpha| e^{-iHt/\hbar} |\alpha\rangle|^2 , \tag{54}$$

while the probability to populate the $|\beta\rangle$ state at time t is

$$P_\beta^{(\alpha)}(t) = |\langle\beta| e^{-iHt/\hbar} |\alpha\rangle|^2 . \tag{55}$$

The VP probability $P_{\mathrm{VP}}^{(\alpha)}(t)$ is given in terms of the population probability of all the continuum states, which in view of basic conservation relations is given by

$$P_{\mathrm{VP}}^{(\alpha)}(t) = 1 - P_\alpha^{(\alpha)}(t) - P_\beta^{(\beta)}(t) . \tag{56}$$

The time evolution of the two level system is well known.[16] In Appendix B, we present a detailed treatment of the dynamics of two discrete levels interacting among themselves and coupled to a common continuum. In what follows, we shall just quote the essential results. Two limiting cases will be of interest for the elucidation of the VP dynamics of heterodimers.

A. Case (A)

Two quasidegenerate levels are coupled to a common continuum

$$\Gamma_\alpha, \Gamma_\beta \gg V_{\alpha\beta} \tag{57}$$

so that the resonances widths considerably exceed the d–d coupling. Under these conditions, the decay pattern of the system is exponential and no oscillatory terms are exhibited. As we demonstrate in Appendix B, in this case

$$\begin{aligned} P_\alpha^{(\alpha)}(t) &= (\Gamma_{\alpha\alpha} + \Gamma_{\beta\beta})^{-2}\{\Gamma_{\beta\beta} + \Gamma_{\alpha\alpha}\exp[-(\Gamma_{\alpha\alpha} + \Gamma_{\beta\beta})t/\hbar]\}^2 , \\ P_\beta^{(\alpha)}(t) &= (\Gamma_{\alpha\alpha} + \Gamma_{\beta\beta})^{-2}\Gamma_{\alpha\alpha}\Gamma_{\beta\beta}\{1 - \exp[-(\Gamma_{\alpha\alpha} + \Gamma_{\beta\beta})t/\hbar]\}^2 . \end{aligned} \tag{58}$$

The VP probability is

$$\begin{aligned} P_{\mathrm{VP}}^{(\alpha)}(t) &= 1 - (\Gamma_{\alpha\alpha} + \Gamma_{\beta\beta})^{-1}[\Gamma_{\beta\beta} + \Gamma_{\alpha\alpha}\exp(-2\gamma t)] , \\ \gamma &= (\Gamma_{\alpha\alpha} + \Gamma_{\beta\beta})/\hbar , \end{aligned} \tag{59}$$

while the VP yield at $t = \infty$ is given by

$$P_{\mathrm{VP}}^{(\alpha)}(t = \infty) = \Gamma_{\alpha\alpha}/(\Gamma_{\alpha\alpha} + \Gamma_{\beta\beta}) . \tag{60}$$

Four comments are now in order. First, the time evolution of a two-level system where the resonance widths exceed the d–d coupling exhibits a nontrivial decay pattern, not just a simple exponential decay. Second, in the limit $\Gamma_\beta = 0$, the simple exponential decay law

$$\begin{aligned} P_\alpha^{(\alpha)}(t) &= \exp(-2\Gamma_{\alpha\alpha}t/\hbar) , \\ P_\beta^{(\alpha)}(t) &= 0 , \\ P_{\mathrm{VP}}^{(\alpha)}(t) &= 1 - \exp(-2\Gamma_{\alpha\alpha}t/\hbar) \end{aligned} \tag{61}$$

is regained while the $|\beta\rangle$ state is not populated. Third, in general, when $\Gamma_\beta \neq 0$, the $|\beta\rangle$ state is populated not by direct coupling between $|\alpha\rangle$ and $|\beta\rangle$ but by indirect coupling between these discrete states via the continuum. Fourth, in general case, the VP yield is smaller than unity.

B. Case (B)

Two effectively coupled levels weakly are coupled to a joint continuum

$$\Gamma_{\alpha\alpha}, \Gamma_{\beta\beta} \ll V_{\alpha\beta} ; \tag{62}$$

thus, the d–d coupling considerably exceeds the decay widths. For short times $t \ll \hbar\Gamma_{\alpha\alpha}^{-1}, \hbar\Gamma_{\beta\beta}^{-1}$, the time evolution of the system, is oscillatory

$$\begin{aligned} P_\alpha^{(\alpha)}(t) &= \cos^2(\mathcal{V}_{\alpha\beta}t/\hbar) , \\ P_\beta^{(\alpha)}(t) &= \sin^2(\mathcal{V}_{\alpha\beta}t/\hbar) , \end{aligned} \tag{63}$$

with $\mathcal{V}_{\alpha\beta}$ determining the oscillation frequency (see Appendix B). The intramolecular dynamics will now involve quasiperiodic energy exchange between the zero-order states $|\alpha\rangle$ and $|\beta\rangle$. Only for sufficiently long times of the order of the decay widths Γ_α and Γ_β will effective damping be exhibited. The decay is so slow relative to the period of the oscillations that in this limit the oscillatory behavior cannot be observed by monitoring the VP decay as the fast oscillations will be smeared out.

In Appendix B, we provide a general solution to the dynamics of the two level system, which in general exhibits oscillatory decay. Several additional interesting features of the dynamics are known[16] such as the appearance of a double pole when $\Gamma_{\alpha\alpha}=\Gamma_{\beta\beta}=2\mathcal{V}_{\alpha\beta}$. However, for the elucidation of the main features of VP dynamics of homodimers, the two limiting cases considered above are sufficient at present.

Optical excitation of a metastable state of the homodimer corresponds to the initial state $|\alpha\rangle=|(+)n_1n_2l\rangle$; the complementary state β is just $|(-)n_1n_2l\rangle$, whereupon $\mathcal{V}_{\alpha\beta}=0$ and $\Gamma_\beta=0$. As the d–d coupling vanishes identically, it is apparent that the time evolution following optical excitation of the homodimer corresponds to case (A) of a pair of quasidegenerate levels coupled to a common quasicontinuum. Furthermore, as $\Gamma_\beta=0$, the decay pattern of the optically excited initial state is described in terms of a simple exponential decay, the VP rate being given by $2\Gamma_\alpha/\hbar=4\Gamma_{n_1n_2l}/\hbar$.

Collisional excitation of a metastable state of the homodimer can be described as resulting in the initial state $|\alpha\rangle=|n_1n_2l\rangle$, the complementary state being $|\beta\rangle=|n_2n_1l\rangle$. Now, $\mathcal{V}^{d-d}_{\alpha\beta}=\mathcal{V}^{d-d}_{n_1n_2l,n_2n_1l}$ is finite and $\Gamma_\alpha=\Gamma_\beta=\Gamma_{n_1n_2l}$ [Eq. (39)]. The nuclear dynamics can correspond either to case (A) or to case (B) or even to an intermediate situation of oscillatory decay. In order to confront the theory with the experimental results of Dixon and Herschbach,[1] where a collisional excitation of the Cl_2–Cl_2 van der Waals homodimer was performed, it will be interesting to obtain information concerning the energetic parameters which determine the VP dynamics of this and similar systems.

VI. MODEL CALCULATIONS OF VIBRATIONAL PREDISSOCIATION OF HALOGEN DIMERS

We shall now consider the VP of halogen dimers A_2–A_2 ($A\equiv F, Cl, Br, I$) on the ground state potential surface, adopting our simple model for nuclear dynamics of homodimer excited by collisions. The structures of the halogen dimers are not yet known, so that we have resorted to model calculations for linear homodimers. The energetic parameters which determine the VP dynamics were evaluated numerically, $\mathcal{V}^{d-d}_{n_1n_2l,n_2n_1l}$ was calculated using Eqs. (10) and (11) without invoking the linearization approximation, while $\Gamma_{n_1n_2l}$ was calculated from Eq. (39). The spectroscopic and structural input data are summarized in Table I. To explore that gross features of the nuclear dynamics, we present in Table II some numerical results for the discrete–discrete coupling terms and for the half-widths of the resonance for VP of halogen dimers in the low lying vibrational states of the bond modes. From these results, it is apparent that off resonance interactions between zero-order states characterized by different values of l are negligible relative to the energy spacing between the zero-order levels. Thus, we have to consider discrete–discrete coupling only between degenerate zero-order levels.

From a cursory examination of the energetic data for degenerate zero-order states for the halogen dimers, it is immediately apparent that they fall into two categories (a) The $(Cl_2)_2$, $(Br_2)_2$, and $(I_2)_2$ homodimers are characterized by negligibly small discrete–discrete coupling terms. For these dimers, condition (57) is well satisfied and the nuclear dynamics of these systems following collisional excitation is characterized by case (A). Thus, the VP process of these dimers will exhibit a nontrivial exponential decay determined by Eqs. (59) and (60). In this case, no oscillatory energy exchange between the bond modes will be exhibited as the discrete–discrete coupling is too weak. The only exchange mechanism between the bond modes pertains to high-order coupling via the common dissociative channel. The widths $\Gamma_{n_2n_2l}$ provide a proper rule of the thumb characterization of the VP decay rates. All the states of these homodimers listed in Table II are metastable with respect to VP, except the $|n_1=1, n_2=0, l=0\rangle$ state of $(Br_2)_2$, which is located below the dissociation threshold that corresponds to the $|n_1=0, n_2=0, \epsilon=0\rangle$ state. (b) The $(F_2)_2$ homodimer is characterized by discrete–discrete coupling terms which overwhelm the widths of the zero-order degenerate states, whereupon condition (62) is strictly obeyed and this system corresponds to case (B). In this case, collisional excitation will result in direct energy exchange between the bond modes as the VP decay is inefficient. The dimer collisionally excited into one bond mode will play a game of "musical chairs," oscillating 10^8–10^9 times between the two bond modes, before VP occurs. In this case, the oscillations are too fast to be interrogated by following the VP decay, which will occur on the time scale $\sim\hbar/\Gamma_{n_1n_2l}$.

To gain some insight into the time scale which characterizes the VP process in linear halogen dimers, some further numerical model calculations were performed. In Fig. 4, we portray the l dependence of the half-width of the resonances of the $(Cl_2)_2$ homodimer for several vibrational states. These results qualitatively demonstrate the enhancement of the VP rate with increasing the excess vibrational energy of the dimer. The dependence of the VP rate on the vibrational quantum number l of the bound states in the van der Waals bond reveals an increase of the VP rate with decreasing l at high l values until a maximum is reached at $l=\bar{l}$. This pattern is analogous to that previously obtained by us for VP of triatomic linear van der Waals molecules.[7] To gain some insight into the semiquantitative aspects of the VP dynamics, we present in Fig. 5 the reciprocal decay widths for the VP of the $|n_1=1, n_2=0, l\rangle$ zero-order state at $l=\bar{l}$ for the halogen dimers. For the $(Cl_2)_2$, $(Br_2)_2$, and $(I_2)_2$ dimers which correspond to class (A), these reciprocal decay widths indeed represent the lifetimes with respect to VP, while for the $(F_2)_2$ dimer which belongs to class (B), again the reciprocal width marks the time scale for VP, after averaging over the

TABLE II. Discrete–discrete coupling terms and half-widths of resonances for VP of linear van der Waals dimers of the homonuclear halogen diatomics.

Molecule	Levels n_{AB}	n_{CD}	n'_{AB}	n'_{CD}	l	Energy difference (cm^{-1})	d–d Couplings (cm^{-1})	$\Gamma_{n_{AB}n_{CD}l}$ (cm^{-1})
$(F_2)_2$	1	0	0	1	0	0	0.15×10^{-4}	0.62×10^{-12}
					1	22.5	0.43×10^{-4}	
					1	0	0.25×10^{-3}	0.26×10^{-11}
					2	17.7	0.48×10^{-3}	
					2	0	0.14×10^{-2}	0.56×10^{-11}
					3	12.9	0.19×10^{-2}	
					3	0	0.35×10^{-2}	0.74×10^{-11}
					4	8.1	0.35×10^{-2}	
					4	0	0.44×10^{-2}	0.59×10^{-11}
					5	3.4	0.20×10^{-2}	
					5	0	0.11×10^{-2}	0.11×10^{-11}
$(Cl_2)_2$	1	0	0	1	0	0	0.48×10^{-44}	0.18×10^{-12}
					0	31.4	0.30×10^{-43}	
					10	0	0.20×10^{-34}	0.80×10^{-9}
					11	15.1	0.30×10^{-34}	
					19	7.6	0.49×10^{-33}	
					19	0	0.36×10^{-33}	0.28×10^{-9}
$(Br_2)_2$	1	0	0	1	0	0	0.19×10^{-74}	0
					1	23.7	0.14×10^{-73}	
	1	0	0	1	10	0	0.66×10^{-63}	0.2×10^{-7}
					11	15.4	0.13×10^{-62}	
	1	0	0	1	20	0	0.19×10^{-58}	0.1×10^{-6}
					21	7.	0.24×10^{-58}	
$(I_2)_2$	1	0	0	1	11			0.46×10^{-8}
					16			0.22×10^{-7}
					20		$<10^{-78}$	0.50×10^{-7}
					24			0.88×10^{-7}
					28			0.12×10^{-6}
					32			0.13×10^{-6}
					36			0.11×10^{-6}

fast energy-exchange oscillation. The effective lifetimes for VP of linear $(A_2)_2$ halogen dimer exhibit the following features: (1) The lifetimes are remarkably long, being in the range of 10^{-1} sec for $(F_2)_2$ to 10^{-5} sec for $(I_2)_2$. (2) For the $(Cl_2)_2$, $(Br_2)_2$, and $(I_2)_2$ dimers, efficient intramolecular energy flow between the bond modes is not exhibited on the remarkably long time scale of 10^{-3}–10^{-5} sec. (3) The low values of the lifetimes and their dependence on the chemical composition of the dimer can be adequately rationalized in terms of our energy gap law for VP, i.e., $\ln\tau \propto \omega^{1/2}$. (4) The

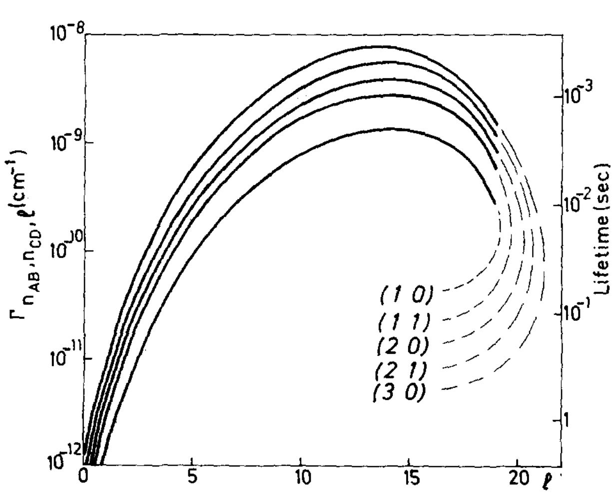

FIG. 4. Dependence of the half-width of the resonances of the $(Cl_2)_2$ homodimer for several vibrational states on the quantum number l, corresponding to bound motion along the van der Waals coordinate.

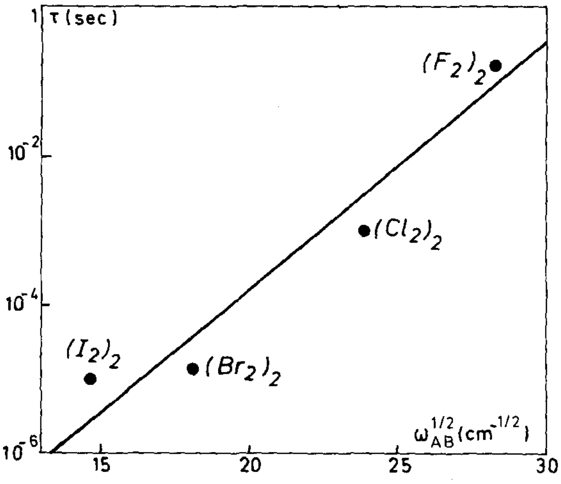

FIG. 5. Reciprocal decay widths and lifetimes for vibrational predissociation of the $|n_1=1,\ n_2=0,\ l\rangle$ zero-order state at $l=\bar{l}$ for the halogen dimers.

lifetime of 10^{-3} sec evaluated for the $|n_1=1,\ n_2=0,\ l=\bar{l}\rangle$ state of the $(Cl_2)_2$ dimer is in fortuitous agreement with the experimental value $\tau \geq 10^{-4}$ sec of Dixon and Herschbach.[1] This numerical agreement should not be taken seriously because of four reasons. First, the structure of the $(Cl_2)_2$ homodimer is unknown and the linear model utilized herein provides only a qualitative description of the VP process. Second, the potential parameters of the van der Waals bond were not yet established and the VP rate is very sensitive to these parameters, as is apparent from our energy gap law. Third, rotational effects were not incorporated in our treatment. Fourth, the experimental collisional excitation method employed by Dixon and Herschbach[1] does not select a single l state and, as is apparent from Fig. 4, the VP rate exhibits a strong dependence on l. The lifetime of $\tau=10^{-3}$ sec evaluated for linear $(Cl_2)_2$ at $l=\bar{l}$ constitutes a lower limit for the VP lifetime of a model system, which is consistent with the currently available information on the nuclear dynamics of the $(Cl_2)_2$ dimer in real life. The goal of the present theory is not to provide numerical results, as it is too primitive for that purpose, but rather to elucidate the characteristics of the intramolecular dynamics of a new and interesting class of chemical systems.

Note added in proof: After the completion of this work we have become aware of a recent theoretical contribution, by G. Ewing,[18] to the related field of VP of hydrogen bonded molecules. He shows that the VP process is inefficient when there are unfavorable Franck–Condon overlaps between the vibrational wave functions for the bound complex and the wave functions which describe the fragments. Also the effect of internal degrees of freedom of the fragments on the VP rate is discussed, in accord with our general conclusions and which rest on the energy gap law.

ACKNOWLEDGMENTS

We are indebted to Professor D. Dixon for a provocative discussion and to Professor D. R. Herschbach for communicating to us some of his results prior to publication and for stimulating correspondence. One of us (J. A. B.) is indebted to the Chemical Physics Department, the Weizmann Institute of Science, for their kind hospitality during the completion of this work.

APPENDIX A. THE NORMAL MODES BASIS

We consider a van der Waals homodimer AB ⋯ CD, where B≡C and D≡A. We shall define the normal coordinates[13]

$$R_s = 2^{-1/2}(X_{AB}+X_{CD}), \tag{A1}$$

$$R_{as} = 2^{-1/2}(X_{AB}-X_{CD}). \tag{A2}$$

After separating the motion of the center of mass, the Hamiltonian is

$$H = -\frac{\hbar^2}{2}\left[m^{-1}\frac{\partial^2}{\partial R^2}+\mu^{-1}\left(\frac{\partial^2}{\partial R_s^2}+\frac{\partial^2}{\partial R_{as}^2}\right)\right]+V(R,R_s,R_{as}), \tag{A3}$$

where

$$R = X_{BC}+\frac{m_A}{m_A+m_B}(X_{AB}+X_{CD}). \tag{A4}$$

The reduced mass is

$$\mu = m_A m_B/(m_A+m_B) \tag{A5}$$

and m is the average mass

$$m=(m_A+m_B)/2. \tag{A6}$$

If we assume now that the interaction V can be represented as the sum of three interatomic potentials between neighboring atoms, i.e.,

$$V(R,R_s,R_{as}) = V_{AB}[2^{-1/2}(R_s+R_{as})] + V_{BC}(R-\gamma R_s)+V_{CD}[2^{-1/2}(R_s-R_{as})], \tag{A7}$$

then, in the harmonic approximation for the interatomic potential V_{AB},

$$V(R,R_s,R_{as}) = \tfrac{1}{2}k_{AB}[(R_s-\bar{R}_s)^2+(R_{as}-\bar{R}_{as})^2] + V_{BC}(R-\gamma R_s), \tag{A8}$$

with $\gamma = 2^{1/2}m_A/(m_A+m_B)$, so that the asymmetric mode becomes separable. The substitution

$$\psi(R_s,R_{as},R) = \phi(R,R_s)\chi(R_{as}) \tag{A9}$$

in the Hamiltonian (A3) with V given by Eq. (A8) results in

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2}-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R_s^2}+\tfrac{1}{2}k_{AB}(R_s-\bar{R}_s)^2+V(R-\gamma R_s)\right] \times\phi(R,R_s) = E_s\phi(R,R_s) \tag{A10a}$$

and

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R_{as}^2}+\tfrac{1}{2}k_{AB}(R_{as}-\bar{R}_{as})^2\right]\chi(R_{as}) = E_{as}\chi(R_{as}). \tag{A10b}$$

The zero-order discrete states are now written in the form

$$\psi_{n_s n_{as} l} \equiv \langle R_s,R_{as},R\,|\,n_s n_{as}\epsilon\rangle = \chi_{n_s}(R_s)\chi_{n_{as}}(R_{as})\varphi_l(R), \tag{A11}$$

with $\chi_{n_s}(R_s)$ and $\chi_{n_{as}}(R_{as})$ representing harmonic oscillator wave functions with energy $\hbar\omega_{AB}(n_s+\frac{1}{2})$ and $\hbar\omega_{AB}(n_{as}+\frac{1}{2})$, respectively. The frequency ω_{AB} of the diatomic molecule AB is $\omega_{AB}=(k_{AB}/\mu)^{1/2}$. The functions $\varphi_l(R)$ are the bound solutions of the equation

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2}+V(R-\gamma\bar{R}_s)\right]\varphi_l(R) = \epsilon_l\varphi_l(R) \tag{A12}$$

and we have for the total energy of the bound states

$$E=\epsilon_l+\hbar\omega_{AB}(n_s+n_{as}+1), \qquad \epsilon_l<0. \tag{A13}$$

The continuum wave functions are written in the same form as Eq. (A11):

$$\psi_{n_s n_{as}} = \chi_{n_s}(R_s)\chi_{n_{as}}(R_{as})\varphi_\epsilon(R), \tag{A14}$$

with the energies of the continuum states being given by

$$E=\epsilon+\hbar\omega_{AB}(n_s+n_{as}+1), \qquad \epsilon>0. \tag{A15}$$

Equations (A13) and (A15) imply that levels obtained by interchanging n_s and n_{as} or from any other combination of of n_s and n_{as} which gives the same total value of $M=(n_s+n_{as})$ will be degenerate. However, all the states which correspond to different values of n_{as} are completely uncoupled. As the total Hamiltonian is separable in the R_{as} coordinate, then all the eigenvalues which correspond to a single value of n_{as}, which constitutes a good quantum number of the system, span an independent subspace in Hilbert space. Thus, all states characterized by different values of n_s (discrete) and ϵ (continuum) quantum numbers for the n_s zero-order states and which correspond to the single value of n_{as} will exhibit an independent time evolution.

The discrete–continuum coupling in the normal mode basis is

$$\mathcal{V}^{d-c}_{n_s l, n_s' \epsilon} = \langle n_s l | [V(R-\gamma R_s) - V(R-\gamma \bar{R}_s)] | n_s' \epsilon\rangle \,, \tag{A16}$$

where we have omitted the quantum number n_{as} for the reasons given above. It should be understood that we are dealing with a particular subspace corresponding to a given value of n_{as}.

Using a Morse potential of the form given in Eq. (5) (with BC≡BB) for the van der Waals bond, we obtain

$$\mathcal{V}^{d-c}_{n_s l, n_s' \epsilon} = B^{(2)}_{n_s n_s'} C^{(2)}_{l\epsilon} - 2B^{(1)}_{n_s n_s'} C^{(1)}_{l\epsilon} \,, \tag{A17}$$

with

$$B^{(j)}_{n_s n_s'} = \langle n_s | \{\exp[j\alpha_{\mathrm{BC}}\gamma(R_s - \bar{R}_s)] - 1\} | n_s'\rangle \,, \qquad j = 1, 2 \,, \tag{A18}$$

while $C^{(j)}_{l\epsilon}$, $j = 1, 2$ is given in Eqs. (16) and (17) (with BC≡BB everywhere). We have on the energy shell

$$\epsilon = \hbar\omega_{\mathrm{AB}}(n_s - n_s') - \frac{\hbar\omega_{\mathrm{BC}}}{2K_{\mathrm{BC}}}\,(K_{\mathrm{BC}} - l - \tfrac{1}{2})^2 \,. \tag{A19}$$

We must impose the condition $\epsilon > 0$, so that $n_s > n_s'$.

In the linearization approximation, we get for the coefficient in Eq. (A18) the following:

$$B^{(j)}_{n_s n_s'} \simeq j\alpha_{\mathrm{BC}}\gamma(\hbar n_s/2\mu\omega_{\mathrm{AB}})^{1/2}\delta_{n_s, n_s'+1} \,, \qquad j = 1, 2 \tag{A20}$$

and substituting this result into Eq. (A17) and using Eqs. (16) and (17), we obtain on the energy shell

$$\begin{aligned}\mathcal{V}^{d-c}_{n_s l, n_s' \epsilon} = {} & \frac{D_{\mathrm{BC}}\omega_{\mathrm{AB}}}{\omega_{\mathrm{BC}}}\,\alpha_{\mathrm{BC}}\gamma(\hbar n_s/2\mu\omega_{\mathrm{AB}})^{1/2} \\ & \times\left[(D_{\mathrm{BC}}/2)\sinh(2\pi\theta_\epsilon)\,\frac{(2K_{\mathrm{BC}} - 2l - 1)}{l!\,\Gamma(2K_{\mathrm{BC}} - l)}\right]^{1/2} \\ & |\Gamma(\tfrac{1}{2} + K_{\mathrm{BC}} - i\theta_\epsilon)| / [\cos^2(\pi K_{\mathrm{BC}}) + \sinh^2(\pi\theta_\epsilon)]^{1/2} \,.\end{aligned} \tag{A21}$$

The width for a discrete level (n_{as}, n_s, l) is then given by

$$\begin{aligned}\Gamma_{n_{as} n_s l} \equiv \pi|\mathcal{V}^{d-c}_{n_s l, n_s' \epsilon}|^2 = {} & 2(\pi/8)\hbar\omega_{\mathrm{AB}} m_1 n_s [(2K_{\mathrm{BC}} - 2l - 1)/ \\ & l!\,\Gamma(2K_{\mathrm{BC}} - l)]\{\sinh(2\pi y_1)/[\cos^2(\pi K_{\mathrm{BC}}) \\ & + \sinh^2(\pi y_1)]\}|\Gamma(K_{\mathrm{BC}} + \tfrac{1}{2} - iy_1)|^2\end{aligned} \tag{A22}$$

if $y_1^2 > 0$, and $\Gamma_{n_{as} n_s l} = 0$ otherwise. In Eq. (A22), we have defined

$$m_1 = m_{\mathrm{A}}/2m_{\mathrm{B}} \,, \tag{A23a}$$

$$y_1 = [\beta_1 - (K_{\mathrm{BC}} - l - \tfrac{1}{2})^2]^{1/2} \,, \tag{A23b}$$

$$\beta_1 = 4D_{\mathrm{BC}}\omega_{\mathrm{AB}}/\hbar\omega^2_{\mathrm{BC}} \,. \tag{A23c}$$

We shall now confront the result for the resonance width in the normal mode basis with the result obtained in Sec. IV for the local mode basis comparing Eqs. (39) with Eq. (A22); we conclude that

$$\Gamma_{n_1 n_2 l}/(n_1 + n_2) = \Gamma_{n_s n_{as} l}/2n_s \,, \tag{A24}$$

where $n_1 n_2$ refer to vibrational quantum numbers for the two AB bonds, while n_s and n_{as} refer to the quantum numbers corresponding to the normal coordinates R_s and R_{as}, respectively.

It is now easy to prove the equivalence of the normal mode expansion and the harmonic local mode basis. We note that there is a unitary transformation between the two sets of wave functions

$$|n_s, M - n_s\rangle = \sum_{n_s=0}^{M} C^M_{n_s n_1} |n_1, M - n_1\rangle \,, \tag{A25a}$$

$$|n_1, M - n_1\rangle = \sum_{n_s=0}^{M} C^M_{n_1 n_s} |n_s, M - n_s\rangle \,, \tag{A25b}$$

with

$$C^M_{n_1 n_s} = 2^{-M/2}\left[\frac{n_s!\,(M - n_s)!}{n_1!\,(M - n_1)!}\right]^{1/2} \sum_{j=0}^{M-n_1} (-1)^{M-n_1-j} \binom{M - n_1}{j}\binom{n_1}{n_s - j} . \tag{A26}$$

The proof follows from the explicit form of the harmonic oscillator wave function

$$\chi_n(x) = C_n H_n(x)\exp(-x^2/2) \,, \tag{A27}$$

with

$$H_n(x) = \frac{d^n}{d\xi^n}\, e^{-\xi^2 + 2x\xi}\Big|_{\xi=0} \,,$$

$$C_n = 2^{-n/2}(n!)^{-1/2}\left(\frac{\mu\omega}{\hbar\pi}\right)^{1/4} . \tag{A28}$$

A wave function $\langle R_1, R_2 | n_1, M - n_1\rangle$ is, in our case,

$$\begin{aligned}\langle R_1, R_2 | n_1, M - n_1\rangle = {} & C_{n_1} C_{M-n_1}\,\frac{d^{n_2}}{d\xi_1^{n_1}}\,\frac{d^{M-n_1}}{d\xi_2^{M-n_1}} \\ & \times\exp(-\xi_1^2 - \xi_2^2 + 2x_1\xi_1 + 2x_2\xi_2 - x_1^2/2 - x_2^2/2)\big|_{\xi_1, \xi_2 = 0} \,,\end{aligned} \tag{A29}$$

where

$$x_1 = (\mu\omega_{\mathrm{AB}}/\hbar)^{1/2}(R_1 - \bar{R}_1) \,, \qquad x_2 = (\mu\omega_{\mathrm{AB}}/\hbar)^{1/2}(R_2 - \bar{R}_2) \,, \tag{A30}$$

defining the dimensionless normal coordinates

$$x_s = (\mu\omega_{\mathrm{AB}}/\hbar)^{1/2}(R_s - \bar{R}_s) \,, \qquad x_{as} = (\mu\omega_{\mathrm{AB}}/\hbar)^{1/2}(R_{as} - \bar{R}_{as}) \,, \tag{A31a}$$

and

$$\xi_s = 2^{-1/2}(\xi_1 + \xi_2) \,, \qquad \xi_{as} = 2^{-1/2}(\xi_1 - \xi_2) \,. \tag{A31b}$$

We obtain

$$\langle R_1 R_2 | n_1 M - n_1\rangle = C_{n_1} C_{M-n_1}\left(\frac{d}{d\xi_s} + \frac{d}{\partial\xi_{as}}\right)^{n_1} 2^{-n_1/2}\left(\frac{d}{d\xi_s} - \frac{d}{\partial\xi_{as}}\right)^{M-n_1} 2^{-M+n_1}\exp(-\xi_s^2 - \xi_{as}^2 + 2x_s\xi_s + 2x_{as}\xi_{as} - x_s^2/2 - x_{as}^2/2)\big|_{\xi_s \xi_{as} = 0} \tag{A32}$$

and therefore

$$\begin{aligned}\langle R_1 R_2 | n_1 M - n_1\rangle = {} & (\mu\omega_{\mathrm{AB}}/\hbar\pi)^{1/2} 2^{-M}[n_1!\,(M - n_1)!]^{-1/2} \\ & \times\sum_{i=0}^{n_1}\sum_{j=0}^{M-n_1}\binom{n_1}{i}\binom{M - n_1}{j}(-1)^{M-n_1-j}\,\frac{d^{i+j}}{d\xi_s^{i+j}}\,\frac{d^{M-(i+j)}}{d\xi_{as}^{M-(i+j)}}\exp(-\xi_s^2 - \xi_{as}^2 + 2x_s\xi_s + 2x_{as}\xi_{as} - x_s^2/2 - x_{as}^2/2)\big|_{\xi_s \xi_{as} = 0} \,.\end{aligned} \tag{A33}$$

Now,

$$\langle R_s, R_{as} | n_s, M-n_s\rangle = (\mu\omega_{\rm AB}/\hbar\pi)^{1/2} 2^{-M/2}[n_s!(M-n_s)!]^{-1/2} \frac{d^{n_s}}{d\xi_s^{n_s}} \frac{d^{M-n_s}}{d\xi_{as}^{M-n_s}} \exp(-\xi_s^2-\xi_{as}^2+2x_s\xi_s+2x_{as}\xi_{as}-x_s^2/2-x_{as}^2/2) \tag{A34}$$

so that

$$\langle R_1, R_2 | n_1, M-n_1\rangle = 2^{-M/2}[n_1!(M-n_1)!]^{-1/2} \sum_{n_s=0}^{M} \sum_{j=0}^{M-n_1} \binom{n_1}{n_s-j}\binom{M-n_1}{j} (-1)^{M-n_1-j}[n_s!(M-n_s)!]^{1/2}\langle R_s, R_{as}|n_s M-n_1\rangle \ . \tag{A35}$$

From Eq. (A25), it follows that

$$\Gamma_{n_1,M-n_1,l} = \left(\sum_{n_s=0}^{M} C_{n_1 n_s}^{M} \Gamma_{n_s,M-n_s,l}^{1/2}\right)^2 , \tag{A36}$$

and using Eq. (A24), we obtain

$$\Gamma_{n_1,M-n_1,l} = \left(\sum_{n_s=0}^{M} C_{n_1 n_s}^{M} 2^{1/2}\Gamma_{n_1,M-n_1,l}^{1/2} n_s^{1/2}/M^{1/2}\right)^2 = \frac{2}{M}\left(\sum_{n_s=0}^{M} C_{n_1 n_s}^{M} n_s^{1/2}\right)^2 \Gamma_{n_1,M-n_1,l} , \tag{A37}$$

so that

$$\left|\sum_{n_s=0}^{M} C_{n_1 n_s}^{M} n_s^{1/2}\right| = \left(\frac{M}{2}\right)^{1/2} , \tag{A38}$$

which implies that

$$\left|\sum_{n_s=0}^{M} \sum_{j=0}^{M-n_1} [n_s!(M-n_s)!]^{1/2} n_s^{1/2}(-1)^j \binom{M-n_1}{j}\binom{n_1}{n_s-j}\right| = [2^{M-1}Mn_1!(M-n_1)!]^{1/2} \ . \tag{A39}$$

APPENDIX B. TIME EVOLUTION OF TWO CLOSE-LYING LEVELS COUPLED TO A CONTINUUM

We consider two discrete levels $|\alpha\rangle$ and $|\beta\rangle$ coupled to a common continuum $\{|\epsilon\rangle\}$. Let P be the projection operator

$$P = |\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta| \tag{B1}$$

and Q its supplement in the space defined by the Hamiltonian

$$H = H_0 + \mathcal{V} , \tag{B2}$$

where H_0 does not couple P with Q.

From the definition of the resolvent operator

$$(E-H)G = 1 , \tag{B3}$$

we obtain

$$(E-PHP)PGP - PVQQGP = 1 \tag{B4}$$

and

$$(E-QHQ)QGP - QVPPGP = 0 , \tag{B5}$$

where the only assumption is $PH_0Q = 0$. Note that H need not to be diagonal in the subspaces spanned by the projection operators P and Q. In fact, these relations are completely general and it is not necessary to write $H = H_0 + \mathcal{V}$. Then in Eqs. (B4)–(B5), we replace PVQ and QVP by PHQ and QHP, respectively, and the rest of the argument is invariant. From Eq. (B5), we get

$$QGP = (E-QHQ)^{-1}QVPPGP \tag{B6}$$

and substituting Eq. (B6) into (B5),

$$PGP = [E-PHP-PVQ(E-QHQ)^{-1}QVP]^{-1} \ . \tag{B7}$$

For the special form of the projection operator (B1) and (B7), these general relations result in

$$[E-E_\alpha-R_{\alpha\alpha}(E)]G_{\alpha\alpha} - [V_{\alpha\beta}+R_{\alpha\beta}(E)]G_{\beta\alpha} = 1 \tag{B8}$$

and

$$-[V_{\beta\alpha}+R_{\beta\alpha}(E)]G_{\alpha\alpha} + [E-E_\beta-R_{\beta\beta}(E)]G_{\beta\alpha} = 0 , \tag{B9}$$

where we have defined

$$E_i = \langle i|H_0|i\rangle + \langle i|V|i\rangle = \langle i|H|i\rangle , \tag{B10}$$

$$R_{ij}(E) = \langle i|VQ(E-QHQ)^{-1}QV|j\rangle \tag{B11}$$

$$V_{ij} = \langle i|V|j\rangle , \qquad i,j \equiv \alpha,\beta \ . \tag{B12}$$

From Eqs. (B8) and (B9), we obtain

$$G_{\beta\alpha} = \frac{[V_{\beta\alpha}+R_{\beta\alpha}(E)]}{E-E_\beta-R_{\beta\beta}(E)} G_{\alpha\alpha} \tag{B13}$$

and

$$G_{\alpha\alpha} = \left\{E-E_\alpha-R_{\alpha\alpha}(E) - \frac{[V_{\alpha\beta}+R_{\alpha\beta}(E)][V_{\beta\alpha}+R_{\beta\alpha}(E)]}{E-E_\beta-R_{\beta\beta}(E)}\right\}^{-1} \tag{B14}$$

and similar expressions for $G_{\beta\beta}$ and $G_{\alpha\beta}$.

If the Q subspace belongs completely to a continuous spectrum, then

$$R_{ij}(E) = \Delta_{ij}(E) - i\Gamma_{ij}(E) \tag{B15}$$

and we obtain finally

$$G_{\alpha\alpha}(E) = [E-E_\beta-\Delta_{\beta\beta}(E)+i\Gamma_{\beta\beta}(E)]/\{[E-E_\alpha-\Delta_{\alpha\alpha}(E)+i\Gamma_{\alpha\alpha}(E)][E-E_\beta-\Delta_{\beta\beta}(E)+i\Gamma_{\beta\beta}(E)] + [V_{\alpha\beta}+\Delta_{\alpha\beta}(E)-i\Gamma_{\alpha\beta}(E)][V_{\beta\alpha}+\Delta_{\beta\alpha}(E)-i\Gamma_{\beta\alpha}(E)]\} \tag{B16}$$

and

$$G_{\beta\alpha} = [V_{\beta\alpha}+\Delta_{\beta\alpha}(E)-i\Gamma_{\beta\alpha}(E)]/\{[E-E_\alpha-\Delta_{\alpha\alpha}(E)+i\Gamma_{\alpha\alpha}(E)][E-E_\beta-\Delta_{\beta\beta}(E) + i\Gamma_{\beta\beta}(E)] + [V_{\alpha\beta}+\Delta_{\alpha\beta}(E)-i\Gamma_{\alpha\beta}(E)][V_{\beta\alpha}+\Delta_{\beta\alpha}(E)-i\Gamma_{\beta\alpha}(E)]\} \ . \tag{B17}$$

The Green's functions (B16) and (B17) which determine the time evolution of the system can be expressed in the compact form

$$G_{\alpha\alpha}(E)=[E-\tilde{E}_\beta+i\Gamma_{\beta\beta}(E)]/(E-E_+)(E-E_-)\,, \tag{B16a}$$

$$G_{\beta\alpha}(E)=\frac{[\tilde{V}_{\beta\alpha}-i\Gamma_{\beta\alpha}(E)]}{(E-E_+)(E-E_-)}\,, \tag{B17a}$$

where E_+ and E_- are the poles of the Green's functions obtained in terms of the roots of the quadratic equation

$$\begin{aligned}&[E-\tilde{E}_\alpha+i\Gamma_{\alpha\alpha}(E)][E-\tilde{E}_\beta+i\Gamma_{\beta\beta}(E)]\\&\quad+[\tilde{V}_{\alpha\beta}-i\Gamma_{\alpha\beta}(E)][\tilde{V}_{\beta\alpha}-i\Gamma_{\beta\alpha}(E)]=0\,,\end{aligned} \tag{B18}$$

where we have defined the shifted energies and coupling terms

$$\tilde{E}_\alpha=E_\alpha+\Delta_{\alpha\alpha}(E)\,, \tag{B19a}$$

$$\tilde{E}_\beta=E_\beta+\Delta_{\beta\beta}(E)\,, \tag{B19b}$$

$$\tilde{V}_{\alpha\beta}=V_{\alpha\beta}+\Delta_{\alpha\beta}(E)\,, \tag{B19c}$$

$$\tilde{V}_{\beta\alpha}=V_{\beta\alpha}+\Delta_{\beta\alpha}(E)\,. \tag{B19d}$$

Assuming that the level shifts $\Delta(E)$ and the level widths $\Gamma(E)$ are slowly dependent functions of E, we obtain the explicit solutions

$$\begin{aligned}E_\pm=\frac{\tilde{E}_\alpha+\tilde{E}_\beta-i(\Gamma_{\alpha\alpha}+\Gamma_{\beta\beta})}{2}\pm\Bigg\{\left[\frac{\tilde{E}_\alpha-\tilde{E}_\beta-i(\Gamma_{\alpha\alpha}-\Gamma_{\beta\beta})}{2}\right]^2\\-(\tilde{V}_{\alpha\beta}-i\Gamma_{\alpha\beta})(\tilde{V}_{\beta\alpha}-i\Gamma_{\beta\alpha})\Bigg\}^{1/2}\,.\end{aligned} \tag{B20}$$

Invoking the initial condition $\Psi(t=0)=|\alpha\rangle$, the probability $P_\alpha^{(\alpha)}(t)$ to be in the $|\alpha\rangle$ state at time t is

$$P_\alpha^{(\alpha)}(t)=\left|(2\pi i)^{-1}\int_0^\infty dE\exp(-iEt/\hbar)G_{\alpha\alpha}(E)\right|^2\,, \tag{B21}$$

while the probability to be in the $|\beta\rangle$ state at time t is given by

$$P_\beta^{(\alpha)}(t)=\left|(2\pi i)^{-1}\int_0^\infty dE\exp(-iEt/\hbar)G_{\beta\alpha}(E)\right|^2\,. \tag{B22}$$

Now, the total probability for VP up to time t is

$$P_{\mathrm{VP}}^{(\alpha)}(t)=1-P_\alpha^{(\alpha)}(t)-P_\beta^{(\alpha)}(t)\,. \tag{B23}$$

From Eqs. (B16)–(B22), we obtain the general results for the time evolution of the system

$$\begin{aligned}P_\alpha^{(\alpha)}(t)=&\,|(E_+-E_-)|^{-2}|(E_+-\tilde{E}_\beta+i\Gamma_{\beta\beta})\exp(-iE_+t/\hbar)\\&-(E_--\tilde{E}_\beta+i\Gamma_{\beta\beta})\exp(-iE_-t/\hbar)|^2\,,\end{aligned} \tag{B24}$$

$$\begin{aligned}P_\beta^{(\alpha)}(t)=&\,(V_{\beta\alpha}^2+\Gamma_{\beta\alpha}^2)|(E_+-E_-)|^{-2}|\exp(-iE_+t/\hbar)\\&-\exp(-iE_-t/\hbar)|^2\,,\end{aligned} \tag{B25}$$

and

$$\begin{aligned}P_{\mathrm{VP}}^{(\alpha)}(t)=&\,|(E_+-E_-)|^{-2}[|(E_+-\tilde{E}_\beta+i\Gamma_{\beta\beta})\exp(-iE_+t/\hbar)\\&-(E_--\tilde{E}_\beta+i\Gamma_{\beta\beta})\exp(-iE_-t/\hbar)|^2+(V_{\beta\alpha}^2+\Gamma_{\beta\alpha}^2)\\&\times|\exp(-iE_+t/\hbar)-\exp(-iE_-t/\hbar)|^2]\,.\end{aligned} \tag{B26}$$

Two limiting cases will be now considered.

I. Case (A)

We have two quasidegenerate levels $(\tilde{E}_\alpha\sim\tilde{E}_\beta)$ with

$$\Gamma_\alpha,\Gamma_\beta\gg V_{\alpha\beta}\,, \tag{B27}$$

so that the resonances widths considerably exceed the d–d coupling. Under these conditions,

$$E_+\sim\tilde{E}_\alpha\sim\tilde{E}_\beta\,, \tag{B28a}$$

$$E_-\sim\tilde{E}_\alpha-i(\Gamma_{\alpha\alpha}+\Gamma_{\beta\beta})\,, \tag{B28b}$$

and replacing Eq. (B28a) and (B28b) in Eqs. (B24)–(B26), we obtain the final results for this case given in Eqs. (58)–(60) of Sec. V.

II. Case (B)

The d–d coupling considerably exceeds the decay widths, i.e.,

$$\Gamma_{\alpha\alpha},\Gamma_{\beta\beta}\ll V_{\alpha\beta}\,. \tag{B29}$$

In this case, we get

$$E_\pm=E_\alpha\pm i|V_{\alpha\beta}|\,, \tag{B30}$$

and introducing Eq. (B30) into Eqs. (B24)–(B26), we obtain the results given in Eqs. (63) of Sec. V.

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