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SMR/115 - 67**

WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

(21 January - 22 March 1985)

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Topical Meeting on Multiphoton Processes

# INTRAMOLECULAR DYNAMICS OF VAN DER WAALS COMPLEXES

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# Intramolecular Dynamics of van der Waals Complexes

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## 1. Introduction

Van der Waals molecules are weakly bound complexes held together by attractive intermolecular interactions. The term "van der Waals molecule" is not restricted to the stabilization of an aggregate by dispersive, London-type, forces but pertains to a broad class of intermolecular clustering due to electrostatic forces, charge transfer interactions, hydrogen bonding, etc. The primary characteristics of the van der Waals molecules are their low ($10 - 500\ cm^{-1}$) dissociation energies, their large bond-length, as well as the retention of the individual properties of the atomic or molecular constituents within the aggregate.

The low dissociation energy implies that a single photon (even infrared) will usually be enough to break the van der Waals bond. On the other hand, the retention of the individual properties of the constituents makes direct photodissociation being negligeable and fragmentation proceeds via vibrational (and/or rotational) predissociation. This offers a unique, and for the first time clear, example of vibrational predissociation on a single electronic surface.

The elucidation of vibrational predissociation in complexes involving polyatomic molecules may provide important insights into the general problem of unimolecular reactions. Also, vibrational and rotational predissociation in van der Waals molecules is the "half-collision" analog of collision-induced relaxation. Both processes involve the same interactions, but they differ in that the collision-induced relaxation must occur at energies above a threshold for vibrational or rotational excitation of the fragments, while predissociation occurs at energies below that threshold. The comparison between the results of these two types of experiments is therefore of general interest.

It is the purpose of this lecture to summarize the recent theoretical developments in the area of intramolecular dynamics of van der Waals molecules, exploring the photophysical consequences of the reactive processes occurring on a single nuclear potential energy surface of a weakly-bound complex.

## 2. General Theory

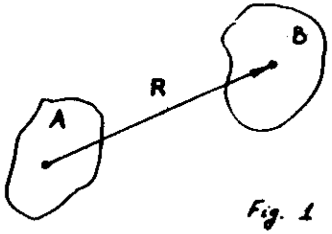

Fig. 1

Let consider the general problem of two molecules A and B interacting via van der Waals forces. The total Hamiltonian can be written (after separation of the motion of the center of mass of the whole system):

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dR^2} + H_A + H_B + H_{A-B} \qquad (1)$$

where R is the distance between the two centers of mass and m is the reduced mass for the relative motion:

$$m = \frac{m_A\, m_B}{m_A + m_B} \qquad (2)$$

In eq. (1), $H_A$ and $H_B$ are the Hamiltonians for the "free" A and B molecules, respectively, while $H_{A-B}$ is the intermolecular van der Waals interaction. Thus $H_{A-B} \to 0$ for $R \to \infty$. We shall define by $\chi_v(r)$ the rovibrational wavefunctions of $(H_A + H_B)$, where r denotes a collection of internal degrees of freedom of A and B molecules. Thus $\chi_v(r)$ represents the internal vibrations and rotations of A and B for $R \to \infty$, and it obeys the eigenvalue equation:

$$(H_A + H_B)\,\chi_v(r) = E_v\, \chi_v(r) \qquad (3)$$

To proceed with the description of the intramolecular dynamics we have to define an appropriate zero-order Hamiltonian. To accomplish this goal we use the distorted-wave treatment where the zero-order Hamiltonian is :

$$(4) \qquad H_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dR^2} + (H_A + H_B) + \sum_v \overline{H}^{(v)}_{A-B}(R)\,|\chi_v\rangle\langle\chi_v|$$

where $\overline{H}_{A-B}(R)$ is the average of the intermolecular interaction $H_{A-B}(R,r)$ over the rovibrational wavefunctions $\chi_v(r)$, i.e.,

$$(5) \qquad \overline{H}^{(v)}_{A-B} = \langle \chi_v | H_{A-B} | \chi_v \rangle$$

With our choice of the internal wavefunctions $\chi_v(r)$, the equations above define completely the problem in the so-called "diabatic" distorted-wave treatment. The residual interaction :

$$(6) \qquad V = H - H_0 = H_{A-B} - \sum_v \overline{H}^{(v)}_{A-B}\,|\chi_v\rangle\langle\chi_v|$$

defines and induces the nonradiative intramolecular transitions. The zero-order Hamiltonian (4) is separable and its eigenstates correspond to discrete states ( see fig. 2 )

$$(7) \qquad \Psi_{v,\ell}(R,r) = \chi_v(r)\,\phi^{(v)}_\ell(R)$$

and continuum states :

$$(8) \qquad \Psi_{v,\varepsilon}(R,r) = \chi_v(r)\,\phi^{(v)}_\varepsilon(R)$$

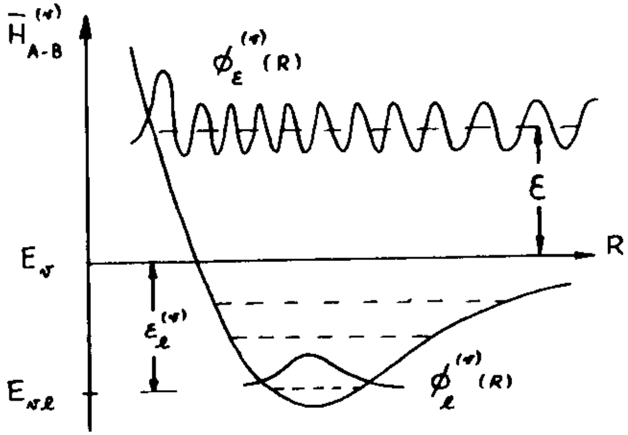

Fig. 2

where $\varepsilon$ is the relative kinetic energy of the fragments. From (3), (4), (7) and (8), we thus have

$$(9) \qquad H_0\,\Psi_{v,\ell} = \left(E_v - \varepsilon^{(v)}_\ell\right)\Psi_{v,\ell} = E_{v\ell}\,\Psi_{v,\ell}$$

and

$$(10) \qquad H_0\,\Psi_{v,\varepsilon} = (E_v + \varepsilon)\,\Psi_{v,\varepsilon}$$

These zero-order nuclear diabatic states are coupled by V (eq. 6), the relevant discrete-discrete (d-d), discrete-continuum (d-c), and continuum-continuum (c-c) coupling terms are ( see fig. 3) :

$$(11) \qquad V^{d-d}_{v'\ell',v\ell} = \langle \Psi_{v'\ell'} | V | \Psi_{v\ell} \rangle \qquad v \neq v'$$

$$V^{d-c}_{v'\ell', v\varepsilon} \equiv \langle \psi_{v'\ell'} | V | \psi_{v\varepsilon} \rangle \qquad v \neq v' \tag{12}$$

$$V^{c-c}_{v'\varepsilon', v\varepsilon} \equiv \langle \psi_{v'\varepsilon'} | V | \psi_{v\varepsilon} \rangle \qquad v \neq v' \tag{13}$$

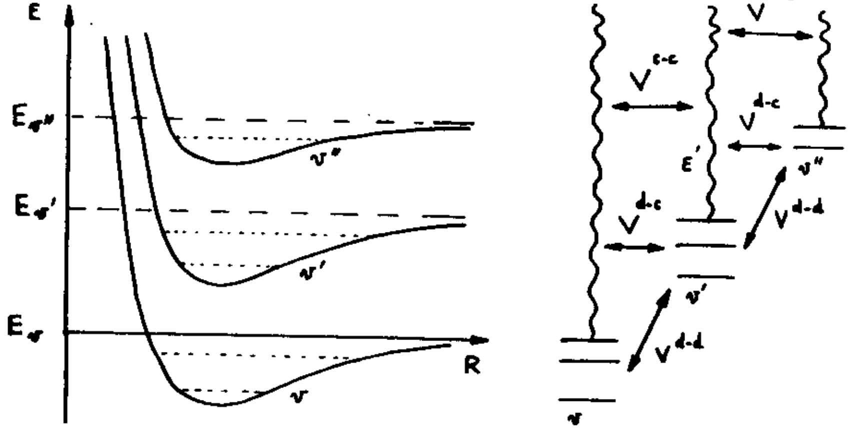

Fig. 3

In the simplest analytical models the following simplifying assumptions are invoked :

1. Discrete - discrete interactions are neglected
2. Continuum - continuum couplings are treated as second-order perturbations ( the "half - collision" model ).
3. The square of the modulus of the discrete - continuum coupling terms $| V^{d-c}_{v'\ell', v\varepsilon} |^2$ (which are given in units of energy if the continuum wavefunctions $\psi_{v\varepsilon}$ are energy normalized), are assumed to be appreciably smaller than the energy spacing between the discrete levels, i.e.,

$$| V^{d-c}_{v'\ell', v\varepsilon} |^2 \ll | E_{v'\ell'} - E_{v''\ell''} | \quad \forall\ v'' \text{ and } \ell'' \tag{14}$$

Thus, in those simple models all interference effects between resonances are disregarded.

These points pertain to the description of the energy levels. An additional assumption is usually invoke to specify the "preparation" of the vibrationally excited state which undergoes predissociation :

4. Only the discrete zero-order excited states carry oscillator strength from the ground ( initial ) state : $\psi_{v_0\ell_0}$. The optical excitation of the van der Waals molecule is thus described in terms of the radiative coupling $\psi_{v_0\ell_0} \xrightarrow{h\nu} \psi_{v'\ell'}$ between zero-order discrete levels. The transition moments to the continuum states that correspond to the radiative couplings $\psi_{v_0\ell_0} \xrightarrow{h\nu} \psi_{v'\varepsilon'}$ are assumed to be negligibly small. Thus, there is no possible interference between direct dissociation and predissociation, and Fano type resonances will not occur.

In fig. 4 the level scheme and coupling terms, according to assumptions 1 to 4, are represented. It should be emphasized that these simplifying assumptions have to be relaxed in many cases, and in the following sections we shall consider more general situations. Nevertheless, the main features of vibrational and rotational predissociation in van der Waals complexes are represented in this model.

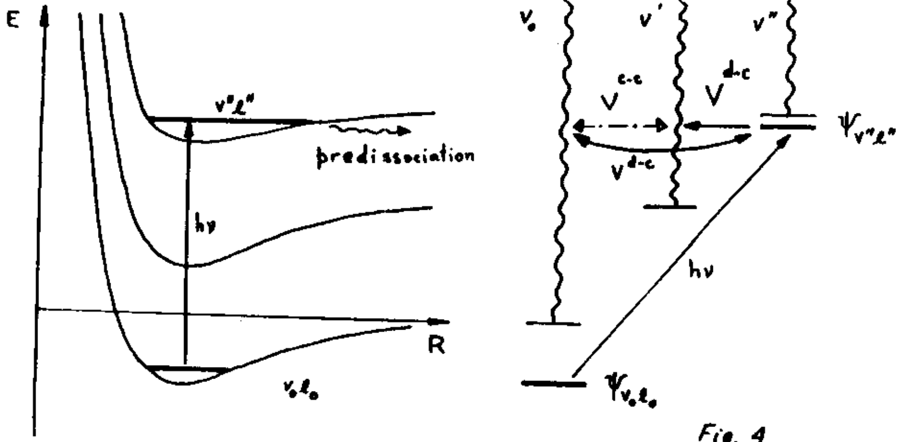

Fig. 4

From fig. 4 it is clear that the problem has been reduced to a discrete level $\Psi_{v''\ell''}$, excited from the initial state $\Psi_{v_0\ell_0}$ by photon absorption, and coupled by $V^{d-c}$ to the continua $\Psi_{v'\varepsilon'}$ and $\Psi_{v_0\ell_0}$. The solution of this problem is well known. Neglecting in first approximation $V^{c-c}$, the partial photodissociation cross section from the initial state $\Psi_{v_0\ell_0}$ to the final state $\chi_{v'}$ of the fragments at total energy $E \equiv E_{v_0\ell_0} + h\nu = E_{v'} + \varepsilon'$, is:[1]

$$\sigma(E) = \frac{2\pi}{\hbar c} \left|\langle \Psi_{v_0\ell_0} | H_{int} | \Psi_{v''\ell''} \rangle\right|^2 \frac{\left| V^{d-c}_{v''\ell'',v'\varepsilon'} \right|^2}{(E - E_{v''\ell''})^2 + \Gamma^2_{v''\ell''}} \tag{15}$$

where $H_{int}$ is the radiative interaction, and $\Gamma_{v''\ell''}$ is the linewidth (HWHM) given by the golden-rule expression:

$$\Gamma_{v''\ell''} = \pi \sum_{v'} \left| V^{d-c}_{v''\ell'',v'\varepsilon'} \right|^2 \tag{16}$$

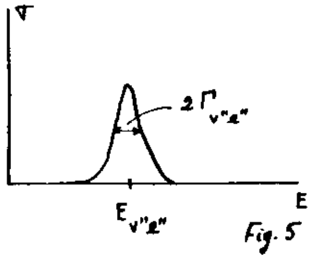

Fig. 5

If all the coupling matrix elements are slowly varying functions of the energy, (15) gives the usual Lorentzian predissociation profile centered at $E = E_{v''\ell''}$ with total width $2\Gamma_{v''\ell''}$.

The situation we are describing here corresponds to energy-resolved experiments, characterized by infinite spectral resolution and corresponding to a time-independent experiment. In the case of time-resolved experiments, characterized by infinite time resolution and instantaneous excitation, the observable is the lifetime of the discrete state $\Psi_{v''\ell''}$. One obtains:

$$\tau_{v''\ell''} = \hbar / 2\Gamma_{v''\ell''} \tag{17}$$

Another observable is the relative vibrational and rotational distribution of the fragments among the different open channels. In both experiments it will be given by[1]:

$$P_{v'} = \pi \left| V^{d-c}_{v''\ell'',v'\varepsilon'} \right|^2 / \Gamma_{v''\ell''} \tag{18}$$

Up to now we have disregarded the effects of the continuum-continuum interactions. The role of continuum-continuum couplings, sometimes referred to as final-state interactions, is crucial for a quantitative description of the predissociation dynamics. We shall now proceed to provide a general treatment. We start by partitionning the Hilbert space into two parts,

$$P = |\Psi_{v''\ell''}\rangle\langle\Psi_{v''\ell''}| \tag{19}$$

$$Q = \sum_{v'} \int d\varepsilon' \; |\psi_{v'\varepsilon'}\rangle\langle\psi_{v'\varepsilon'}| \tag{20}$$

In the case of the time-resolved experiment, after the excitation has taken place, the initial condition $|\psi(t=0)\rangle = |\psi_{v''\ell''}\rangle$ is invoked and the probability for dissociation at time $t$ is given by,

$$p_{v'}(t) = \int d\varepsilon' \; |\langle\psi_{v'\varepsilon'}| U(t,0) |\psi_{v''\ell''}\rangle|^2 \tag{21}$$

where $U(t,0)$ is the time evolution operator. Using the resolvent operator method,

$$p_{v'}(t) = (4\pi^2)^{-1} \int d\varepsilon' \left| \int_{-\infty}^{\infty} dE \; \langle\psi_{v'\varepsilon'}| G^+(E) |\psi_{v''\ell''}\rangle \, e^{-\frac{iEt}{\hbar}} \right|^2 \tag{22}$$

where

$$G^+(E) = (E + i\eta - H)^{-1} \quad ; \quad \eta \to 0^+ \tag{23}$$

Thus, from (22) and (19)-(20), the dissociation probability can be expressed in terms of the matrix elements of the operator $QG^+(E)P$. This can be expressed as[1]:

$$QG^+(E)P = (E + i\eta - QH_0Q)^{-1} \, Q\mathcal{R}P \; P(E + i\eta - H_0 - P\mathcal{R}P)^{-1} \tag{24}$$

where

$$\mathcal{R} = V + V(E + i\eta - QHQ)^{-1} V \tag{25}$$

We may now perform the integration in (22) by invoking the usual assumptions regarding the weak dependence of $\mathcal{R}$ on the energy and the negligible effects of the thresholds. The probability distribution is then given by

$$p_{v'}(t) = \frac{\pi}{\Gamma_{v''\ell''}} |\langle\psi_{v'\varepsilon'}| \mathcal{R} |\psi_{v''\ell''}\rangle|^2 \left[1 - e^{-2\Gamma_{v''\ell''} t/\hbar}\right] \tag{26}$$

where $\Gamma_{v''\ell''}$ is now given by:

$$\Gamma_{v''\ell''} = \pi \sum_{v'} |\langle\psi_{v''\ell''}| \mathcal{R} |\psi_{v'\varepsilon'}|^2 \tag{27}$$

The final (relative) probability distribution of the fragments is

$$P_{v'} \equiv \frac{p_{v'}(t=\infty)}{\sum_{v'} p_{v'}(t=\infty)} = \frac{\pi}{\Gamma_{v''\ell''}} |\langle\psi_{v'\varepsilon'}| \mathcal{R} |\psi_{v''\ell''}\rangle|^2 \tag{28}$$

It is possible to separate formally the contribution of the continuum-continuum interaction by defining a transition $T^{c\text{-}c}$ operator which acts only in the $Q$ subspace

$$T^{c\text{-}c} \equiv Q\mathcal{R}Q = V^{c\text{-}c} + V^{c\text{-}c}(E + i\eta - QHQ)^{-1} V^{c\text{-}c} \tag{29}$$

The operator $Q\mathcal{R}P$ takes the form[1]:

$$Q\mathcal{R}P = \left[1 + T^{c\text{-}c}(E + i\eta - QH_0Q)^{-1}\right] V^{c\text{-}d} \tag{30}$$

Neglecting the off-shell contributions of the operator $(E + i\eta - QH_0Q)^{-1}$, which amounts to the assumption that the coupling varies slowly with energy, we obtain:

$$P_{v'} = \frac{\pi}{\Gamma_{v''\ell''}} \left| \sum_{v} \bar{S}_{v'v} \; V^{d\text{-}c\,*}_{v''\ell'',v\varepsilon} \right|^2 \tag{31}$$

where $\bar{S}$ is the so-called half-collision scattering matrix :

$$\bar{S} = 1 - i\pi T^{c\text{-}c} \tag{32}$$

Similarly, the total width $\Gamma_{v''\ell''}$ can be written :

$$\Gamma_{v''\ell''} = \pi \, \mathrm{Re}\left[ \sum_{vv'} V^{d\text{-}c}_{v''\ell'', v\varepsilon} \; \bar{S}_{vv'} \; V^{d\text{-}c\,*}_{v''\ell'', v'\varepsilon'} \right] \tag{33}$$

Eqs. (31) to (33) provide a theory of vibrational and/or rotational predissociation on a single electronic potential energy surface, which incorporates both the effects of discrete-continuum couplings as well as the effects of continuum-continuum couplings (final-state interactions). This description involves basically feeding of the continuum states, induced by the $V^{d\text{-}c}$ couplings, and "half-collision" transitions within the dissociative final states represented by $\bar{S}$ and which originates from the continuum-continuum couplings. If the final-state interactions are neglected, then from (32) we obtain $\bar{S} = 1$ and eqs. (31) and (33) reduce to our simplified model eqs. (18) and (16), respectively.

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* The usual scattering matrix in collision theory is defined by : $S = 1 - 2i\pi T^{c\text{-}c}$. Thus, the relation between "half" and "full" collision matrices is : $\bar{S} = (1 + S)/2$

## 3. Analytical model

Before alluding to more detailed calculations it is instructive to advance a simple model of potential surfaces and couplings, which will elucidate the gross features of the dependence of the rates (lifetimes) and final energy distribution of the fragments, on the intramolecular as well as on the intermolecular parameters. For this, we shall consider a triatomic system X... BC where X is a rare gas atom and BC a conventional molecule. We consider the following vibrational predissociation process :

$$X\ldots BC\,(v''\ell'') \xrightarrow{\Gamma_{v''\ell''}} X + BC\,(v' < v'') \tag{34}$$

where $v'$ is the vibrational quantum number of the BC molecule.

Let expand the intermolecular interaction $H_{X\text{-}BC}$ in a Taylor series around the equilibrium position $r_e$ of the diatomic molecule BC, keeping only the linear term in the intramolecular displacement of the BC bond. For harmonic vibrational wavefunctions $\chi_v(r)$ we then get (see eq.(6))

$$V = \left( \frac{\partial H_{X\text{-}BC}}{\partial r} \right)_{r_e} (r - r_e) \tag{35}$$

Introducing (35) into (16), we obtain :

$$\Gamma_{v''\ell''} = \pi \sum_{v'} \left| \left\langle \phi^{(v'')}_{\ell''} \right| \left( \frac{\partial H_{X\text{-}BC}}{\partial r} \right)_{r_e} \left| \phi^{(v')}_{\varepsilon'} \right\rangle \right|^2 \left| \langle \chi_{v''} | (r - r_e) | \chi_{v'} \rangle \right|^2 \tag{36}$$

so that the predissociation rate is approximated by the product of an intermolecular term, depending on the parameters of the van der Waals interaction potential and on the final relative kinetic energy of the recoiling fragments $\varepsilon'$ (determined by conservation of the energy), and an intramolecular factor which depends only on intrinsic properties (i.e., frequency and masses) of the normal BC bond. It should be noted that the intramolecular term will give a strong propensity rule $\Delta v = v' - v'' = -1$. This has actually been observed in the experiments.[2,3]

To proceed further the calculation of the matrix elements $\langle \phi^{(v'')}_{\ell''} | \left( \frac{\partial H_{X-BC}}{\partial r} \right)_{r_0} | \phi^{(v')}_{\varepsilon'} \rangle$ is necessary. For this purpose the van der Waals interaction needs to be specified. The simplest choice leading to analytical expressions, is to consider a Morse function of the form $D\{ e^{-2\alpha(R-R_e)} - 2 e^{-\alpha(R-R_e)} \}$. The final result for the predissociation rate is[1]:

(37) $$\Gamma_{v''\ell''} = (\pi/8)\, \hbar \omega_{BC}\, (m/\mu)\, v'' \left\{ \frac{\sinh(2\pi\theta)}{\cos^2 \pi K + \sinh^2(\pi\theta)} \right\} \times \left[ \frac{2K - 2\ell'' - 1}{\ell''!\, \Gamma(2K - \ell'')} \right] \left| \Gamma(K + 1/2 - i\theta) \right|^2$$

where $\mu$ is the reduced mass of BC, $K$ is the Morse parameter:

(38) $$K \equiv \frac{2D}{\hbar\omega} = (2mD)^{1/2} / \hbar\alpha$$

while $\theta$ is defined by:

(39) $$\theta \equiv 2(D\varepsilon)^{1/2} / \hbar\omega = (2m\varepsilon)^{1/2} / \hbar\alpha$$

For large values of $\theta$, $\Gamma_{v''\ell''}$ can be approximate by[1]:

(40) $$\Gamma_{v''\ell''} \propto e^{-\pi\theta} = e^{-\pi(2m\varepsilon)^{1/2}/\hbar\alpha}$$

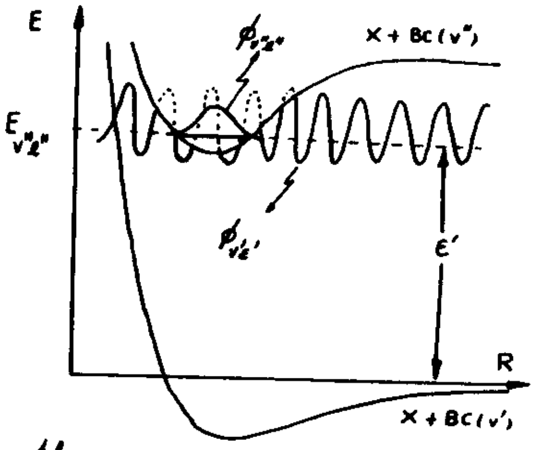

Fig. 6

Thus the linewidth is expected to decrease fast with increasing the excess energy $\varepsilon'$, which is determined by the conservation of energy. We thus expect that the vibrational predissociation rate will be severely retarded when there is an appreciable mismatch between the molecular frequency and the dissociation energy of the van der Waals bond. This result has been referred as the "energy gap law".[1] It has also been noted that $\Gamma_{v''\ell''}$ in eq. (40) contains $p = (2m\varepsilon)^{1/2}$, i.e., the relative translational momentum of the departing fragments, so that it may be appropriate to refer to the relation (40) as the "momentum gap law".[4]

It is easy to rationalize the exponential dependence of $\Gamma_{v''\ell''}$ on the translational momentum in terms of the semiclassical approximation. The final wavefunction will be a rapid oscillating function of R if $p$ is large (see Fig. 6). The rate for predissociation is essentially determined by the overlap between the bound initial state and this rapid oscillating wavefunction. The nuclear overlap integral is just expressed in the form $\exp(-bp)$, where $b$ is some constant. Thus the rate will decrease fast with increasing $p$.

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