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Configuration Interaction Theory and van der Waals Predissociation

Chun-Woo Lee

Department of Chemistry, Ajou University, Suwon 441-749, Korea

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Golden-rule like formulas have been used without theoretical basis to calculate the resonance lifetimes and final state distributions in the predissociation of van der Waals molecules. Here we present their theoretical basis by extending Fano's configuration interaction theory. Such extensions were independently done by Farnoux [*Phys. Rev.* 1985, 25, 287] but his work, unfortunately, was not well known outside some small group of people in the field of Auger spectroscopy. Since my extension is easier to understand than his, it is presented here. Theoretical basis of Golden rule like formulas used in the predissociation of van der Waals molecules was obtained by using such extensions. Factors responsible for several aspects of predissociation dynamics, such as variations of dynamics as functions of resonance lifetimes, or variations in shapes of final quantum state distributions of photofragments around resonances, were identified. Parameters, or dynamical information that could be obtained from the measurement of partial cross section spectra were accordingly determined. The theory was applied to the vibrational predissociation of triatomic van der Waals molecules and its result was compared with those calculated by close-coupling method. An example where Golden-rule like expression fails and branching ratios vary greatly around a resonance was considered.

Introduction

Photofragmentation processes provide a wealth of information on the molecular dissociation dynamics. They could be visualized as half collision processes but their study as a means of obtaining molecular dissociation dynamics have advantages over molecular beam collision experiments. For example, complicated and rich resonance structures are commonly observed in the photofragmentation spectra while not many resonances are identified in the collision experiments. Predissociation spectra of van der Waals molecules with the accompanying final quantum state distributions of photofragments, in particular, have served as the only experimental tool to provide the full features of anisotropic intermolecular potentials, as intermolecular potentials in van der Waals systems are weak and therefore only a few channels are involved in predissociation processes.³ Still, scattering calculations on such predissociation spectra are not easy and Golden-rule like formulas have been used to calculate lifetimes and final quantum state distributions of photofragments.⁴ The Golden-rule like formula provides the detour to the repeated calculations at the finely divided energy mesh points around resonances and directly calculates resonance widths. Though

it has been successfully applied, its theoretical basis is not known yet. It is one of the purposes of this paper to find out in what conditions the Golden-rule like formula could be applied and when it fails by making use of Fano's configuration interaction theory. Another purpose of this paper is to show that analytical solutions for the predissociation processes can be obtained in Fano's configuration interaction theory and many questions on predissociation could be answered in general terms.

Fano showed that the following profile formula parameterizes the photodissociation (including photoionization) spectra:¹²

$$\sigma(\epsilon) = \sigma_0 \frac{(q + \epsilon)^2}{1 + \epsilon^2}, \quad (1)$$

where ϵ is the reduced energy defined by $(E - E_r)/(\Gamma/2)$; E_r and \hbar/Γ represent the resonance energy and the mean life time of the quasi-bound state, respectively; σ_0 represents the photofragmentation cross section to the continuum state that does not interact with the quasibound-bound state; q is an index that characterizes the line profile. This formula shows that measurement of photodissociation spectra provides us with the information on σ_0 , E_r , Γ , and q . It strictly

holds for the system of one discrete state and one continuum. Formulas for the total photodissociation cross sections for the system in which configuration interactions of arbitrary number of discrete states with arbitrary number of continua are accounted for, are also known by the work of Fano (this will be referred to as Ref. 1).

With the advent of powerful laser sources and efficient detection methods, internal state distributions of photofragments are resolved in modern experiments, yielding photodissociation partial cross section spectra.³ These partial cross section spectrum data contain richer information on the dissociation dynamics. F. Combet-Farnoux² and, independently I derived the formulas similar to Fano-Beutler one for the partial cross section spectra. As F. Combet-Farnoux and I used different methods, and as my derivation is simpler, I will describe my derivation below.

From this work, it is found that, even for the system of one discrete state and many continua, Fano-Beutler profile formula can be applied to represent the photodissociation partial cross section spectra but with different profile indices that are now generally complex numbers.

Import of this work is in the determination of parameters, or dynamical information, that can be obtained from the partial cross section spectra.

Section II summarizes the Fano theory of configuration interaction which provides the basis for this work. Section III applies the boundary conditions to obtain the wavefunctions that describe the state resolved photodissociation spectra. In Section IV, partial cross section formulas are obtained in a Fano-Beutler profile form. Physical discussions are given for these formulas. Section V considers the application of the theory to the vibrational predissociation of triatomic van der Waals molecules.

Configuration Interaction Theory for One Discrete and Many Continua

Here we are interested in the predissociation of an isolated resonance state ϕ into several energetically accessible final states $\psi_E^{(-)}$ (the minus in the superindex means that ψ satisfies an incoming boundary condition). This system is called one discrete state and several continua by Fano. He obtained the analytical diagonalization of the hamiltonian for this system. He first considered a discrete state ϕ and several continua $\{\psi_E^{(-)}\}$ that are assumed to prediagonalize the hamiltonian H but couple together *via* the interaction matrices $\langle\phi|H|\psi_E^{(-)}\rangle$ *i.e.*

$$\langle\phi|H|\phi\rangle = E_0$$

$$\langle\psi_E^{(-)}|H|\psi_{E'}^{(-)}\rangle = E\delta_{EE'}\delta(E-E'), \quad (j, j' = 1, 2, \dots, N)$$

$$\langle\psi_E^{(-)}|H|\phi\rangle = V_E, \quad (j = 1, 2, \dots, N). \quad (2)$$

In other words, H is assumed to be diagonalized in each subspace spanned by ϕ or $\{\psi_E^{(-)}\}$ but not in the whole space spanned by $\{\phi, \{\psi_E^{(-)}\}\}$.

The key observation made in Ref. 1 and emphasized later in Ref. 2 is that only a certain superposition of continuum wavefunctions gives a nonzero interaction matrix element with ϕ . Let us consider an interaction matrix element of ϕ with $\psi_E^{(-)}$

$$\langle\psi_E^{(-)}|H|\phi\rangle = \sum_j b_{jE}^{(\lambda)} V_{jE} = [b^{(\lambda)}]^* \cdot V, \quad (3)$$

with a normalization condition

$$[b^{(\lambda)}]^* \cdot b^{(\lambda)} = \sum_{j=1}^N |b_{jE}^{(\lambda)}|^2 = 1. \quad (4)$$

$b^{(\lambda)}$ and V may be considered as vectors. Since $b^{(\lambda)}$ changes only its direction with its length fixed to unity by (4), the maximum value of $\langle\psi_E^{(-)}|H|\phi\rangle$, the scalar product of $b^{(\lambda)}$ and V , is obtained when the unit vector $b^{(\lambda)}$ is parallel to V *i.e.* when $\psi_E^{(-)}$ is given by a superposition

$$\psi_E^{(a)} = \frac{\sum_k V_{kE} \psi_E^{(-k)}}{(\sum_k |V_{kE}|^2)^{1/2}}. \quad (5)$$

The other $N-1$ superpositions orthogonal to $\psi_E^{(a)}$ yield zero of $\langle\psi_E^{(-)}|H|\phi\rangle$ which implies that these superpositions still form the eigenfunctions of Hamiltonian in the whole space spanned both by ϕ and $\psi_E^{(-k)}$ as well as in the subspace. They will be denoted as $\Psi^{(i)}$ in order to emphasize that they are eigenfunctions in the whole space. Only $\psi_E^{(a)}$ interacts with the discrete state ϕ and thus needs a diagonalization. The analytical diagonalization is obtained in Ref. 1 and yields the following eigenfunction

$$\Psi_E^{(a)} = a(E)\phi + \sum_j \int dE' b_{jE'}^{(a)} \psi_E^{(-j')} \quad (6)$$

where

$$b_{jE'}^{(a)} = V_{jE'} \left[\frac{P}{E-E'} + z(E)\delta(E-E') \right] a(E). \quad (7)$$

The coefficients $a(E)$ and $z(E)$ are given by

$$|a(E)|^2 = \frac{1}{(\pi^2 + z^2) \sum_k |V_{kE}|^2} = \frac{1}{[(E-E_0-F)^2 + \pi^2 (\sum_k |V_{kE}|^2)]}, \quad (8)$$

$$z(E) = \frac{E-E_0-F(E)}{\sum_k |V_{kE}|^2} = \pi\epsilon, \quad (9)$$

$$F(E) = P \int \frac{\sum_k |V_{kE'}|^2}{E-E'} dE'. \quad (10)$$

By using the phase shift Δ due to configuration interaction of $\psi_E^{(-)}$ with ϕ and a modified discrete state Φ

$$\tan\Delta = -\frac{\pi}{z(E)} = -\frac{1}{\epsilon},$$

$$\Phi = \phi + P \int dE' \frac{\sum_k V_{kE'} \psi_E^{(-k)}}{E-E'}, \quad (11)$$

Eq. (6) can be rewritten as

$$\Psi_E^{(a)} = \Phi \frac{\sin\Delta}{\pi(\sum_k |V_{kE}|^2)^{1/2}} - \psi_E^{(a)} \cos\Delta. \quad (12)$$

In Ref. 1 and 2, the main interest was in the total photodissociation cross section. Total cross section is simply given as an incoherent sum as

$$\sum_\lambda |\langle\Psi_E^{(\lambda)}|T|i\rangle|^2 = |\langle\Psi_E^{(a)}|T|i\rangle|^2 + \sum_{\lambda \neq a} |\langle\Psi_E^{(\lambda)}|T|i\rangle|^2, \quad (13)$$

where i and T denote the initial state and transition dipole

operator, respectively. The interference between different eigensolutions is not needed. The absorption spectra then shows a simple functional dependence on photon energy:

$$\sigma(\varepsilon) = \sigma_a \frac{(q + \varepsilon)^2}{\varepsilon^2 + 1} + \sigma_b, \quad (14)$$

where the line profile parameter q and the reduced energy ε are defined as

$$q = \frac{(\Phi|T|i)}{\pi(\Psi_E^{(a)}|T|i)(\sum_k |V_{kE}|^2)^{1/2}} \quad (15)$$

$$\varepsilon = \frac{E - E_a - F}{\pi \sum_k |V_{kE}|^2} = \frac{E - E_a - F}{\Gamma/2} \quad (16)$$

σ_a and σ_b denote the following

$$\sigma_a = |(\Psi_E^{(a)}|T|i)|^2, \quad (17)$$

$$\sigma_b = \sum_{\lambda \neq a} |(\Psi_E^{(\lambda)}|T|i)|^2. \quad (18)$$

The line profile parameter q is real since the only complex value functions $\Psi_E^{(a)}$ in Eq. (15) always appear as a form $\sum_j |\Psi_E^{(j)}|(\Psi_E^{(j)}|T|i)|$ which is real.

In this work, our interest is in the photodissociation spectra at which internal state distribution of photofragments is analyzed. Cross section formulas for the production of each fragment can no longer be written as an incoherent sum as in Eq. (13). For those, we have to calculate the transition matrix elements in which the final states wavefunctions that satisfy the photodissociation (incoming wave) boundary conditions are input. This is the topic of the next section. Before that, let us first rewrite (6) or (12) into the form convenient for the application of boundary conditions at the asymptotic region, *i.e.*

$$\Psi_E^{(a)} = \phi \frac{\sin \Delta}{\pi(\sum_k |V_{kE}|^2)^{1/2}} + (\bar{\Psi}_E^{(a)} \sin \Delta - \Psi_E^{(a)} \cos \Delta), \quad (19)$$

where $\bar{\Psi}_E^{(a)}$ lags $\Psi_E^{(a)}$ in phase by 90° at large radius and is defined as

$$\bar{\Psi}_E^{(a)} = \frac{1}{\pi(\sum_k |V_{kE}|^2)^{1/2}} P \int \frac{\sum_k V_{kE} \Psi_E^{(k)}}{E - E'} dE'. \quad (20)$$

Final State Wavefunctions Compatible with Boundary Conditions

The solutions $\Psi^{(\lambda)}$ ($\lambda = 1, 2, \dots, N$) described in the previous section, though diagonalizing the hamiltonian, do not necessarily represent the states observed. Their superpositions that satisfy the boundary conditions appropriate to the observed observables should be considered. For the partial cross sections of final states j of fragments in photodissociation, we have to seek the wavefunctions

$$\Psi_E^{(j)} = \sum_{\lambda} \Psi^{(\lambda)} A_{\lambda j}, \quad (21)$$

that satisfy the incoming wave boundary conditions

$$\Psi_E^{(j)} \rightarrow \sum_j \phi_j(\omega) \sqrt{\frac{m_j}{2\pi k_j}} (e^{ik_j R} \delta_{j'j} + e^{-ik_j R} S_{j'j}^0), \quad (22)$$

where R denotes the coordinate along which the photodissociation takes place; ω stands for the other remaining coordinates; ϕ_j denote the channel states of photofragments with quantum numbers j' specifying the channel states; m denotes the reduced mass of the system composed of photofragments; k_j is the wavenumber for the relative motion of fragments in channel j' .

Let us first rewrite $\Psi_E^{(j)}$:

$$\begin{aligned} \Psi_E^{(j)} &= \sum_{\lambda} \Psi^{(\lambda)} A_{\lambda j} = \Psi_E^{(a)} A_{aj} + \sum_{\lambda \neq a} \Psi^{(\lambda)} A_{\lambda j} \\ &= \Psi_E^{(a)} A_{aj} + \sum_{\lambda \neq a} \sum_{j'} \Psi_E^{(j')} b_{j'E}^{(\lambda)} A_{\lambda j}. \end{aligned} \quad (23)$$

At large R , the asymptotic form of $\Psi_E^{(a)}$ is obtained from (19) with ϕ going to zero:

$$\Psi_E^{(a)} \rightarrow \bar{\Psi}_E^{(a)} \sin \Delta - \Psi_E^{(a)} \cos \Delta, \quad (24)$$

where $\bar{\Psi}_E^{(a)}$ is given as a linear combination of $\Psi_E^{(k)}$ which satisfy the boundary condition similar to $\Psi_E^{(a)}$:

$$\bar{\Psi}_E^{(a)} \rightarrow \sum_j \phi_j(\omega) \sqrt{\frac{m_j}{2\pi k_j}} (e^{ik_j R} \delta_{j'j} + e^{-ik_j R} S_{j'j}^0), \quad (25)$$

with $S_{j'j}^0$ replaced by $S_{j'j}^a$. The background scattering matrix $S_{j'j}^a$ may be obtained by solving close coupling equations. The boundary conditions for $\bar{\Psi}_E^{(a)}$ is conveniently obtained by differentiating $\Psi_E^{(a)}$ with respect to R and multiplying by -1 as it lags $\Psi_E^{(a)}$ in phase by 90° :

$$\bar{\Psi}_E^{(a)} \rightarrow \sum_j \phi_j(\omega) \sqrt{\frac{m_j}{2\pi k_j}} i (-e^{ik_j R} \delta_{j'j} + e^{-ik_j R} S_{j'j}^a), \quad (26)$$

Substituting (26), (25) and (24) into (23) and then applying the boundary condition (22) to (23), we obtain

$$-\frac{V_{jE} e^{i\Delta} A_{aj}}{(\sum_k |V_{kE}|^2)^{1/2}} + \sum_{\lambda \neq a} b_{j'E}^{(\lambda)} A_{\lambda j} = \delta_{j'j}, \quad (27)$$

$$\sum_j [S_{j'j}^a \left(-\frac{V_{jE}}{(\sum_k |V_{kE}|^2)^{1/2}} e^{-i\Delta} A_{aj} + \sum_{\lambda \neq a} b_{j'E}^{(\lambda)} A_{\lambda j} \right)] = S_{j'j}. \quad (28)$$

Eq. (27) determines the coefficients $A_{\lambda j}$ and Eq. (28) yields the formulas for the scattering cross sections $S_{j'j}$. In order to obtain the coefficients $A_{\lambda j}$, we need not invert (27). Multiplying $V_{j'E}$ on both sides of (27) and summing over j' , we obtain

$$-(\sum_k |V_{kE}|^2)^{1/2} e^{i\Delta} A_{aj} + \sum_{\lambda \neq a} \left(\sum_j b_{j'E}^{(\lambda)} V_{j'E}^* \right) A_{\lambda j} = V_{j'E}^*. \quad (29)$$

By applying the fact that $\Psi_E^{(\lambda)}$ ($\lambda \neq a$) have zero interaction matrix elements with ϕ *i.e.*

$$\sum_j b_{j'E}^{(\lambda)} V_{j'E}^* = (\phi|H|\Psi_E^{(\lambda)}) = 0, \text{ for } \lambda \neq a, \quad (30)$$

into (29), we get A_{aj} as

$$A_{aj} = -\frac{V_{j'E}^* e^{-i\Delta}}{(\sum_k |V_{kE}|^2)^{1/2}}. \quad (31)$$

In order to determine the remaining coefficients $A_{\lambda j}$ ($\lambda \neq a$), at first it looks as if we have to know the coefficients $b_{j'E}^{(\lambda)}$ which could be determined by applying the condition that $\Psi_E^{(a)}$ are orthogonal with each other. It turns out to be not the case. Since

$$\begin{aligned} \Psi_E^{-\langle i \rangle} &= \sum_{\lambda} \Psi^{(\lambda)} A_{\lambda j} = \Psi_E^{(g)} A_{gj} + \sum_{\lambda(\neq g)} \Psi^{(\lambda)} A_{\lambda j} \\ &= \Psi_E^{(g)} A_{gj} + \sum_j \left[\Psi_E^{-\langle j \rangle} \left(\sum_{\lambda(\neq g)} b_{jE}^{(\lambda)} A_{\lambda j} \right) \right], \end{aligned} \quad (32)$$

partial cross section measurements are only affected by the combination $\sum_{\lambda(\neq g)} b_{jE}^{(\lambda)} A_{\lambda j}$, which is easily obtained from (27) as

$$\begin{aligned} \sum_{\lambda(\neq g)} b_{jE}^{(\lambda)} A_{\lambda j} &= \delta_{ji} + \frac{V_{jE}}{(\sum_k |V_{kE}|^2)^{1/2}} e^{i\Delta} A_{gj} \\ &= \delta_{ji} - \frac{V_{jE} V_{jE}^*}{\sum_k |V_{kE}|^2}. \end{aligned} \quad (33)$$

Then the final wavefunctions that satisfy the incoming wave boundary conditions are given by

$$\begin{aligned} \Psi_E^{-\langle i \rangle} &= -\frac{V_{jE}^*}{(\sum_k |V_{kE}|^2)^{1/2}} e^{-i\Delta} \Psi_E^{(g)} + \Psi_E^{-\langle i \rangle} - \frac{V_{jE}^* \sum_j V_{jE} \Psi_E^{-\langle j \rangle}}{\sum_k |V_{kE}|^2} \\ &= \Psi_E^{-\langle i \rangle} - \frac{V_{jE}^*}{(\sum_k |V_{kE}|^2)^{1/2}} (e^{-i\Delta} \Psi_E^{(g)} + \Psi_E^{(g)}), \\ &= \underbrace{[1 - |\Psi_E^{(g)}\langle \Psi_E^{(g)} | \rangle|]}_{\text{background}} \Psi_E^{-\langle i \rangle} - \underbrace{e^{-i\Delta} (\Psi_E^{(g)} | \Psi_E^{-\langle i \rangle}) \Psi_E^{(g)}}_{\text{resonance}} \end{aligned} \quad (34)$$

The second equality is obtained by utilizing the definitions of $\Psi_E^{(g)}$. The third equality tells us that $\Psi_E^{(g)}$ consists of two contributions, the background contribution deprived of $\Psi_E^{(g)}$ and the resonance contribution. By substitution of (6) into (34), we obtain the formula that shows the energy dependence explicitly. That is,

$$\Psi_E^{-\langle i \rangle} = \Psi_E^{-\langle i \rangle} - e^{-i\Delta} \sin\Delta \frac{V_{jE}^*}{(\sum_k |V_{kE}|^2)^{1/2}} \left[\frac{\Phi}{\pi(\sum_k |V_{kE}|^2)^{1/2}} + i\Psi_E^{(g)} \right]. \quad (35)$$

Formulas for Photodissociation Partial Cross Section

Photodissociation partial cross sections into final states j are obtained from a modulus square of the transition dipole matrix elements

$$\begin{aligned} \langle \Psi_E^{-\langle i \rangle} | T | i \rangle &= \\ \langle \Psi_E^{-\langle i \rangle} | T | i \rangle &= e^{i\Delta} \sin\Delta \frac{V_{jE}}{(\sum_k |V_{kE}|^2)^{1/2}} \left[\frac{\langle \Phi | T | i \rangle}{\pi(\sum_k |V_{kE}|^2)^{1/2}} - i \langle \Psi_E^{(g)} | T | i \rangle \right]. \end{aligned} \quad (36)$$

(Note that excitation energy of photon is not multiplied to the square of the transition dipole matrix. It may not be important in the study of resonance since resonances are usually sharp.) By substitution of (15) and (16) into (36), and taking a modulus square of (36), we obtain the formulas for the partial cross sections into final states j as a function of reduced energy ε :

$$\sigma_j = \sigma_j^b \frac{|\varepsilon + q_j|^2}{\varepsilon^2 + 1} = \sigma_j^b \frac{[\varepsilon + R_j(q_j)]^2}{\varepsilon^2 + 1} + \sigma_j^r \frac{[I_n(q_j)]^2}{\varepsilon^2 + 1}. \quad (37)$$

Though the apparent form of Eq. (37) is identical to the Fano-Beutler profile formula, it is different from that because q_j are now complex numbers and depend on j . Spectral shapes of the partial photodissociation cross sections are deter-

mined by incoherent sums of two terms. One is identical to the Fano-Beutler formula with the line profile index replaced by $R_j(q_j)$. The other term is given as a Lorentzian shape and its magnitude is proportional to the square of the imaginary part of q_j . The larger either the imaginary part or the real part of q_j is, the more the spectra become close to Lorentzian shapes. This case will be considered again later when we discuss the theoretical basis of Golden-rule like expression in the vibrational predissociation of van der Waals molecules. If the imaginary part of q_j is not zero, the spectra always contain Lorentzian shapes whose widths are the same for all partial cross sections.

Notice that there is no σ_b -like contribution in Eq. (37). In (37), σ_j^r denotes $|\langle \Psi_E^{-\langle i \rangle} | T | i \rangle|^2$ and is the partial cross section to the final state j in the absence of Φ i.e. the direct (background) partial cross section to j ; q_j is defined as

$$\begin{aligned} q_j &= i + \frac{V_{jE}}{(\sum_k |V_{kE}|^2)^{1/2}} \frac{\langle \Psi_E^{(g)} | T | i \rangle}{\langle \Psi_E^{-\langle i \rangle} | T | i \rangle} (q - i) \\ &\equiv i + \rho_j (q - i), \end{aligned} \quad (38)$$

and its real part determines the line profile for the photodissociation spectra into final state j (q_j is assumed to be a slowly varying function of energy). Its imaginary part incoherently contributes to the partial cross section and its contribution is given as a Lorentzian shape.

The parameter ρ_j defined in (38) may be rewritten as

$$\rho_j = \frac{(i | T | \Psi_E^{-\langle i \rangle}) (\Psi_E^{-\langle i \rangle} | H | \Phi) \sum_k (\Phi | H | \Psi_E^{-\langle k \rangle}) (\Psi_E^{-\langle k \rangle} | T | i)}{(i | T | \Psi_E^{-\langle i \rangle}) (\Psi_E^{-\langle i \rangle} | T | i) \sum_k (\Phi | H | \Psi_E^{-\langle k \rangle}) (\Psi_E^{-\langle k \rangle} | H | \Phi)}. \quad (39)$$

With the presence of summations over j in both numerator and denominator, it would represent the correlation coefficient between the sets of matrix elements $(\Psi_E^{-\langle i \rangle} | T | i)$ and $(\Psi_E^{-\langle k \rangle} | H | \Phi)$, defined as ρ in Ref. 2. Or, by noting

$$\langle \Psi_E^{-\langle i \rangle} | \Psi_E^{(g)} \rangle = \frac{V_{jE}}{(\sum_k |V_{kE}|^2)^{1/2}} \quad (40)$$

ρ_j may be rewritten as

$$\rho_j = \frac{\langle \Psi_E^{-\langle i \rangle} | \Psi_E^{(g)} \rangle \langle \Psi_E^{(g)} | T | i \rangle}{\langle \Psi_E^{-\langle i \rangle} | T | i \rangle} = \frac{P_o \langle \Psi_E^{-\langle i \rangle} | T | i \rangle}{\langle \Psi_E^{-\langle i \rangle} | T | i \rangle} \quad (41)$$

where P_o represents a projection operator to the state $\Psi_E^{(g)}$ and defined as $|\Psi_E^{(g)}\langle \Psi_E^{(g)} | \rangle|$. Thus ρ_j may be viewed as the ratio between the transition dipole moments from the ground state to $\Psi_E^{-\langle i \rangle}$ projected to $\Psi_E^{(g)}$ and to $\Psi_E^{-\langle i \rangle}$ itself. ρ_j is unity when $\Psi_E^{-\langle i \rangle}$ is identical to $\Psi_E^{(g)}$.

Eq. (38) tells us that line profile indices $R_j(q_j)$ are generally different for different partial photodissociation cross sections and thus branching ratio among photodissociated states may vary greatly around resonances as a function of energy. But we recall that the interaction of continua with a discrete state occurs only through $\Psi_E^{(g)}$. That means the factors that determine line profiles for photodissociation cross sections should be the same for different partial photodissociation cross sections. In order to see this, we rewrite q_j by making use of Eq. (34) instead of Eq. (35).

$$\begin{aligned} \langle \Psi_E^{-\langle i \rangle} | T | i \rangle &= [\langle \Psi_E^{-\langle i \rangle} | T | i \rangle - \langle \Psi_E^{-\langle i \rangle} | \Psi_E^{(g)} \rangle \langle \Psi_E^{(g)} | T | i \rangle] \\ &\quad - e^{-i\Delta} \langle \Psi_E^{-\langle i \rangle} | \Psi_E^{(g)} \rangle \left[\frac{\sin\Delta}{(\sum_k |V_{kE}|^2)^{1/2}} \langle \Phi | T | i \rangle - \cos\Delta \langle \Psi_E^{(g)} | T | i \rangle \right] \end{aligned} \quad (42)$$

The first bracket denotes the contribution from background and the second denotes one from the quasi-bound state $\Psi_E^{(j)}$. From Eq. (42), we obtain

$$\sigma_j = \sigma_j^0 \frac{[\varepsilon(1-\rho_j) + \rho_j(q+\varepsilon)]^2}{\varepsilon^2 + 1} \\ = |1-\rho_j|^2 + \frac{|\rho_j|^2(\varepsilon+q)^2}{1+\varepsilon^2} + (\text{cross term}) \quad (43)$$

The first term in Eq. (43) is the background contribution and is very insensitive to variation of energy and the second term is the one from the quasi-bound state $\Psi_E^{(j)}$ and its line profile is independent of the photodissociation channel j in contrast to $R_i(q_j)$. Thus the above equation tells us that the different line profile indices for different partial photodissociation cross section originate from the different projections of $\Psi_E^{(j)}$ to $\Psi_E^{(0)}$ as j varies.

By summing σ_j over j , we obtain the total cross section formula as

$$\sigma_{\text{tot}} = |(\Psi_E^{(0)}|T|\hat{i})|^2 + \sum_j |(\Psi_E^{-(j)}|T|\hat{i})|^2 - |(\Psi_E^{(0)}|T|\hat{i})|^2 \\ = |(\Psi_E^{(0)}|T|\hat{i})|^2 \frac{(\varepsilon+q)^2}{1+\varepsilon^2} + \sum_j |(\Psi_E^{-(j)}|T|\hat{i})|^2 - |(\Psi_E^{(0)}|T|\hat{i})|^2 \\ \equiv \sigma_a \frac{(\varepsilon+q)^2}{1+\varepsilon^2} + \sigma_b \quad (44)$$

which shows explicitly the forms of σ_a and σ_b in (14). Other useful relations are

$$q = \frac{\sum_j \sigma_j^0 R_i(q_j)}{\sigma_a} \\ q^2 = \frac{\sum_j \sigma_j^0 |q_j|^2 - \sigma_b}{\sigma_a} \quad (45)$$

We notice that ρ_j is unity when

$$(\Psi_E^{-(j)}|T|\hat{i}) \propto (\Psi_E^{-(j)}|H|\phi). \quad (46)$$

In other words, when the distribution of $(\Psi_E^{-(j)}|T|\hat{i})$ is completely correlated with that of $(\Psi_E^{-(j)}|H|\phi)$. In this case, all partial cross sections have the same line profiles (*i.e.* same q). The final state distribution, or branching ratio, remains constant with the variation of energy. Otherwise, *i.e.* if two sets of distributions $(\Psi_E^{-(j)}|T|\hat{i})$ and $(\Psi_E^{-(j)}|H|\phi)$ are not correlated, partial cross sections will have different line profiles q_j and the final state distribution will vary with the variation of energy. In particular, quite different final state distributions may be expected in front and behind the resonance energy in the energy range $\varepsilon \sim 1$ if the signs of q_j are alternating with j . But we have to be cautious for this assertion when q_j have large absolute magnitudes. When the absolute magnitudes of q_j are large, partial photodissociation spectra resemble Lorentzian shapes and the differences in the values of q_j do not affect the spectral shapes much.

Eq. (37) tells us that all partial cross sections have the identical half-width given by $\Gamma = 2\pi \sum_k |V_{kE}|^2$. Note that the half-widths for the partial cross section into j are not given by $\Gamma_j = 2\pi |V_{jE}|^2$. This derives from the fact that only one specific superposition may interact with a bound state.

If the direct photodissociation has much smaller magnitudes than that of resonance photodissociation, then from the definition (15) the value of q becomes very large and

$$q_j \approx \rho_j q. \quad (47)$$

In the energy range near resonance

$$\sigma_j \approx \sigma_j^0 \frac{q_j^2}{\varepsilon^2 + 1} = \frac{|V_{jE}|^2}{\sum_k |V_{kE}|^2} |(\Psi_E^{(0)}|T|\hat{i})|^2 q^2. \quad (48)$$

Since $|(\Psi_E^{(0)}|T|\hat{i})|^2$ and q do not depend on j , final state distribution will be determined solely by $|V_{jE}|^2$. Appendix A shows that the interaction matrices V_{jE} are reduced in case of the vibrational predissociation of van der Waals molecules as

$$V_{jE} = (\Psi_E^{-(j)}|V|\phi). \quad (49)$$

Thus golden rule type calculation commonly performed for the vibrational predissociation of van der Waals molecules relies on the negligible contribution of the background or direct photodissociation.

Let us now examine the effects of life times on photodissociation dynamics. If the lifetime is long ($\Gamma \ll 1$), photodissociation dynamics may not depend on the ground state wavefunctions. In this case, q is large as can be seen from the definition. Then $q_j \approx \rho_j q$. In this case, dissociation dynamics can be well described by Golden-rule like expression. The final state distributions are hardly affected by the wavefunction before photoabsorption. In the short time limit ($\Gamma \gg 1$), $q \ll 1$ and Eq. (43) becomes $\sigma_j \sim |1-\rho_j|^2$ near resonance since ε is close to near resonance and the second and third terms may be neglected. Since

$$\sum_j |1-\rho_j|^2 = \sum_j \sigma_j^0 - \sigma_a = \sigma_b \quad (50)$$

we see that short time limit is just equal to the direct photodissociation.

We see from (37) that the partial cross section spectra for photodissociation provide us with the information on E_ϕ , σ_j^0 , $R_i(q_j)$, $[I_m(q_j)]^2$, and Γ . From the total photodissociation spectra for which the formula may be obtained by summing (37) over j and are given in (14), we easily obtain the information on σ_a , σ_b , E_ϕ , and Γ . Values of $|V_{jE}|$ may be obtained from Eq. (38). Partial information on the sign of V_{jE} may be provided by the sign of ρ_j .

The remaining condition (28) obtained by applying the boundary condition provides the formulas for scattering matrices as shown in Appendix B. In contrast to the photodissociation partial cross section formulas, the formulas for this have been derived repeatedly in the past by different procedures and are well known.

Application of the Result to the Triatomic van der Waals Predissociation

Let us now consider the application of the above result to vibrational predissociations of triatomic van der Waals molecules considered in Ref. 6 where Golden-rule like expression for calculating resonance life times, final state distributions can be applied. The previous section tells us about the theoretical background on the Golden-rule like expression. Previous section provides us with additional information on the partial cross sections as a function of energy besides life times of the resonance states and final state distributions.

Let us briefly describe the system used for the calculation.

Table 1. Parameters for the Model Intermolecular System A-B₂

(a) Reduced mass between A and B ₂		
$m = 6756.8$ a.u.		
(b) Morse potential parameter		
$D_{AB} = 0.0034$ eV	$D_{CM} = 0.00195$ eV	
$\alpha_{AB} = 1.0$ a.u. ⁻¹	$\alpha_{CM} = 1.0$ a.u. ⁻¹	
$R_{AB}^{(0)} = 6.82$ a.u.	$R_{CM}^{(0)} = 6.65$ a.u.	
(c) van der Waals potential parameter		
$C_{60} = 0.75$ eV(a.u.) ⁻⁶		
$C_{62} = 0.119$ eV(a.u.) ⁻⁶		
$C_{80} = 1.58$ eV(a.u.) ⁻⁸		
$C_{82} = 0.8$ eV(a.u.) ⁻⁸		

Triatomic van der Waals molecules considered are restricted to rare gas-homonuclear halogen like diatomic molecules. Empirical potentials for them like NeCl₂, HeCl₂^{3,7} are well established owing to the state-to-state measurements available for them. The interaction potential between A and B₂ in AB₂ triatomic system used by Halberstadt *et al.*⁸ for NeCl₂ system has the following form (a slightly modified form for HeCl₂)

$$V(R, r, \gamma) = V_M(R, r, \gamma), \quad \text{when } R \leq R',$$

$$V(R, r, \gamma) = V_{vdW}(r, \gamma) + (V_M - V_{vdW})e^{-\alpha \left(\frac{R-R'}{R}\right)^2}, \quad \text{when } R \geq R', \quad (51)$$

in the Jacobi coordinates R, r, γ that denote the distance between A and the center of mass of B₂, the bond distance of B₂, and the angle between \vec{R} and \vec{r} , respectively. $V_M(R, r, \gamma)$ and V_{vdW} are given as

$$V_M(R, r, \gamma) = D_{AB} \sum_{i=1}^2 \left\{ \left[e^{-\alpha_{AB}(R_{AB_i} - R_{AB}^{(0)})} - 1 \right]^2 - 1 \right\}^2 \quad (52)$$

$$+ D_{CM} \left\{ \left[e^{-\alpha_{CM}(R - R_{CM}^{(0)})} - 1 \right]^2 - 1 \right\}^2, \quad (53)$$

$$V_{vdW}(R, \gamma) = -\frac{C_6(\gamma)}{R^6} - \frac{C_8(\gamma)}{R^8}, \quad (54)$$

where R_{AB_i} is the distance between A and i^{th} B atom, R is same as above, and other parameters are constants that are adjusted to yield the best fit to the experimental values. Two Legendre terms are retained for $C_6(\gamma)$ and $C_8(\gamma)$, *e.g.*,

$$C_6(\gamma) = C_{60} + C_{62}P_2(\cos\gamma). \quad (55)$$

R' is chosen as the inflection point of the atom-atom Morse potentials and given by $R' = R_{CM}^{(0)} + \ln 2 / \alpha_{CM}$. The values of parameters used in this paper are slightly different from those of Ref. 8 and given in Table 1.

With this interaction potential, the Hamiltonian for the triatomic van der Waals molecules AB₂ is given in the Jacobi coordinates by⁹

$$H = -\frac{1}{2m} \frac{\partial^2}{\partial R^2} + \frac{\vec{j}^2}{2\mu r^2} + \frac{\vec{l}^2}{2mR^2} + V(R, r, \gamma) + H_{B_2}(r), \quad (56)$$

where

$$H_{B_2}(r) = -\frac{1}{2\mu r^2} \frac{\partial^2}{\partial r^2} + V_{B_2}(r), \quad (57)$$

denotes the vibrational Hamiltonian of B₂, m and μ denote the reduced mass of A and the center of mass of B₂ and

Table 2. Diatomic Molecular Parameters

Vibrational frequency	ω_e	0.0162 eV
Rotational constant	B	0.01758 meV
Equilibrium bond length	r_e	3.044 a.u.
Reduced mass	μ	32576.6 a.u.

of B₂, respectively; \vec{j} , the angular momentum operator of B₂; and \vec{l} , the orbital angular momentum operator of the relative motion of A and the center of mass of B₂. Typical values of diatomic molecular parameters of B₂ are given in Table 2.

The values of total angular momentum operator $\vec{J} = \vec{j} + \vec{l}$, as is well known both experimentally and theoretically, do not affect the predissociation dynamics much and is set to zero hereafter. This simplifies the Hamiltonian as \vec{l} can be set to \vec{j} .

When the wavefunctions $\Psi^{-\langle i \rangle}(R, r, \gamma)$ to the dissociation channel $i = \{v\}$ are expanded into base functions $\Phi_i(r, \gamma) = \langle r | v \rangle Y_{\nu}(\gamma, 0)$ as

$$\Psi_i(R, r, \gamma) = \sum_{\gamma} \Phi_{i\gamma}(r, \gamma) \chi_{i\gamma}(R), \quad (58)$$

the close-coupling equations are given as

$$\left[-\frac{1}{2m} \frac{d^2}{dR^2} - k_i^2 + \frac{\vec{j}^2}{2mR^2} \right] \chi_{i\gamma}(R) + \sum_{\gamma'} V_{i\gamma\gamma'}(R) \chi_{i\gamma'}(R) = 0, \quad (59)$$

with

$$k_i^2 = 2m \left[E - B_j(j+1) - (v + \frac{1}{2})\omega_0 \right], \quad (60)$$

and

$$V_{i\gamma\gamma'}(R) = \int d\gamma \sin\gamma \int dr \Phi_{i\gamma}(r, \gamma) V(R, r, \gamma) \Phi_{i\gamma'}^*(r, \gamma). \quad (61)$$

The above close coupling equations are solved by De Vogelaere algorithm.¹⁰ Usual calculations of partial photodissociation cross sections around resonances are usually done by solving close coupling equations at first at coarse energy mesh points. If abrupt changes in photodissociation cross sections are found, then close coupling calculations at much finer energy mesh points are done to find the smooth curves of photodissociation cross sections around resonances. These kinds of calculations are very time-consuming since usually resonances are very sharp and very fine energy mesh points calculations are usually needed. The beauty of the configuration interaction theory developed in the previous sections lies in that in most cases one energy point calculation is enough to find the behaviours of photodissociation cross sections around resonances if bound states are known.

Bound states are obtained by including only closed channels and by starting to solve close coupling equations at both ends and then by propagating the solutions ϕ_a and ϕ_b toward matching radius. The values of solutions ϕ_a , ϕ_b and their first derivatives $d\phi_a/dR$, $d\phi_b/dR$ should match at the matching radius. Besides this bound state, the configuration interaction theory need the continuum solutions $\psi_E^{-\langle i \rangle}$ of close-coupled equations among open channels alone. Then as we saw in the previous sections, Schrödinger equations for the combined space $\{\phi, \{\psi_E^{-\langle i \rangle}\}\}$ are solved analytically.

Table 3. Comparison Between Spectral Parameters Obtained by Configuration Theory and Obtained by Close-Coupled Method

	configuration	close-coupled
E_0 (eV)	0.01320262	0.01320249
Γ (eV)	2.193×10^{-6}	2.193×10^{-6}
σ_a (eV $^{-1}$)	0.877	0.879
σ_b (eV $^{-1}$)	0.399	24.86
q	-349.8	-349.8

Table 4. Comparison Between Line Profile Indices of Partial Photodissociation Cross Sections Obtained by Configuration Theory and by Close-Coupled Method

j	configuration			close-coupled		
	σ_j^0	$R_c(q_j)$	$[I_w(q_j)]^2$	σ_j^0	$R_c(q_j)$	$[I_w(q_j)]^2$
0	0.221	-356	24280	0.219	-358	24920
2	0.279	-233	169	0.281	-233	-48
4	0.305	-171	23810	0.310	-173	23040
6	0.282	-275	10930	0.281	-275	11390
8	0.154	-248	34190	0.150	-248	36880
10	0.035	143	76130	0.034	125	81320

The calculation of photodissociation spectra needs a ground wavefunction. Its radial and angular functions are simply assumed to be of Gaussian types like

$$\Psi_{\alpha}(R, r, \gamma) = \frac{1}{2} \{ \exp[-a_R(R-R_c)^2] + \exp[-a_R(R+R_c)^2] \} \\ \times \exp[-a_\gamma(\gamma-\gamma_c)^2] \langle r | n=0 \rangle \\ \equiv \Phi_R(R) \Phi_\gamma(\gamma) \langle r | n=0 \rangle, \quad (62)$$

where a_R and a_γ are related to the standard deviations δ_R and δ_γ of radial and angular functions by $a_R \delta_R^2 = 4 \ln 2$ and $a_\gamma \delta_\gamma^2 = 4 \ln 2$. Values used for R_c , γ_c , δ_R , and δ_γ are 3.5 Å, 90°, 0.5 Å, 20°, respectively.

Total and partial photodissociation cross sections are calculated by both configuration interaction theory and close-coupled equations with the parameters given in Table 1 and 2 and with other information given above. The results are summarized in terms of E_0 , Γ , σ_a , σ_b , q , $R_c(q_j)$, $[I_w(q_j)]^2$, and σ_j and presented in Table 3, 4, and 5.

In the calculation of the line profile index q by configuration interaction theory, Φ defined in Eq. (11) is simply replaced by ϕ . Data fittings of the partial and total photodissociation cross sections obtained by close-coupled method to Fano-Beutler formula given in Eq. (37) are done by Levenberg-Marquardt method described in Ref. 11. All the parameters, E_0 , Γ , σ_a , σ_b , q , $R_c(q_j)$, $[I_w(q_j)]^2$, and σ_j are fitted. The total and partial photodissociation cross sections obtained in configuration interaction theory as Eq. (14), (16), (37) need the quantity F defined like following

$$F = \frac{1}{2\pi} P \int_{-\infty}^{\infty} \frac{\Gamma(E')}{E' - E_0} dE'. \quad (63)$$

The upper limit of the integration can not be sent to infinity

Table 5. Comparison Between Final State Distributions Obtained by Configuration Interaction Theory and by Close-Coupled Method

j	configuration	close-coupled
0	1	1
2	0.455	0.456
4	0.479	0.489
6	0.725	0.728
8	0.440	0.438
10	0.100	0.100

in the actual calculation since Γ is not constant as a function of energy but has a small negative slope. On the other hand, the lower limit can not go to infinite since the energy can not be smaller than the lowest asymptotic energy of dissociation channels. The numerical value of integration with the parameters of Table 1 and 2 in the interval $[E - \Gamma/2, E + \Gamma/2]$ is obtained as -2.37×10^{-10} eV. It is ten thousands smaller than the value of Γ and it may be argued that F may be neglected. But the difference in E_0 in two methods shown in Table 3 tells us that it is not. According to configuration interaction theory, the difference comes from F . The integration interval may be set to $[E - \text{the lowest energy of dissociation channel}, E + \text{the lowest energy of dissociation channel}]$. Then the value of F is approximately given by $-2.37 \times 10^{-10} \omega_0/\Gamma \approx 2 \times 10^{-6}$ eV, 10 times larger than the actual value. More study on this is needed. Since it is not critical in this study, we will not consider it anymore.

In contrast to F , the integration appearing in the definition of Φ in Eq. (11) may be neglected since q and q_j calculated by both methods agree quite well as can be seen in Table 3, 4, and 5.

Tables show that the agreements between the two methods are excellent except for the background cross section σ_b and $[I_w(q_j)]^2$. The discrepancy in the values of the former may be ignored since the variation of the values of σ_b from 0.399 to 24.86 eV $^{-1}$ hardly affects the value of σ_{tot} which is 107580 eV $^{-1}$. The agreements in the latter are usually good except for $j=2$, though the agreements are not as good as in other quantities.

The final state distribution shown for configuration interaction theory in Table 5 is actually the one of $|V_{jE}|^2$ as claimed in Golden-rule like expression. The table shows that Golden-rule like expression holds quite well in this case. This agreement comes from the fact that in the present model system excitation to discrete state is much larger than that to continua as can be seen from the large value -350 of q . The large value of q means that the total photodissociation spectrum are of Lorentzian shape. This situation is the same for each photodissociation spectra. Though values of $R_c(q_j)$ differ from each other, their absolute values are large and all can be represented by Lorentzian curve very well. Thus the final state distributions (or branching ratio) do not change around the resonance.

Configuration theory tells us that if the excitations to continua have comparable size to that to the discrete state, then Golden-rule like expression may no longer be used to calculate the final state distribution. Besides that, it tells us that

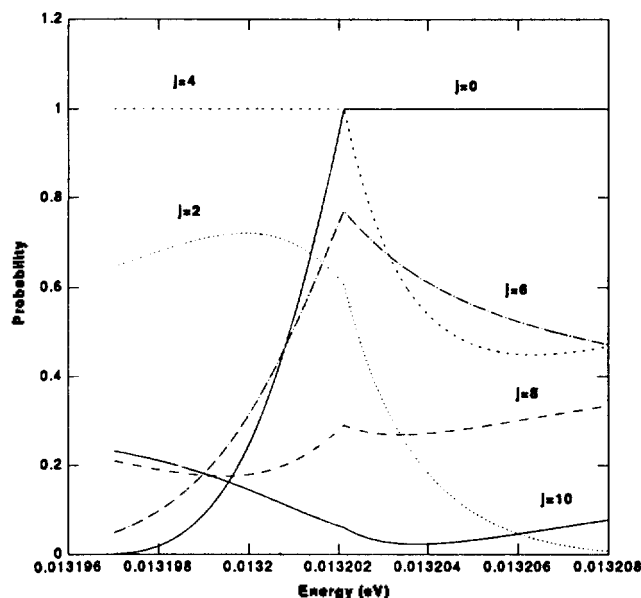


Figure 1. Distributions of probabilities of finding the diatomic photofragments whose rotational quantum numbers are j when $\gamma_e = 45^\circ$.

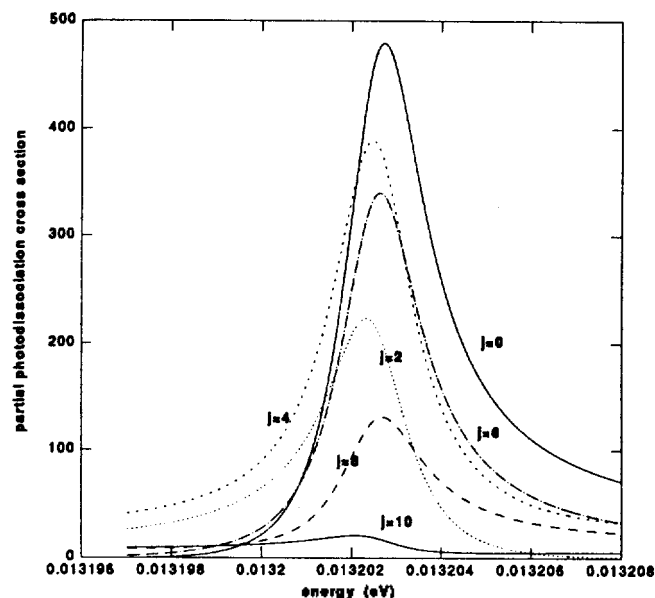


Figure 2. Energy dependencies of partial photodissociation cross sections σ_j around the resonance energy 0.0132025 eV when $\gamma_e = 45^\circ$.

line profile indices may now become very small and final state distributions may change greatly around a resonance. In order to confirm this, we arbitrarily change the shape of the ground wavefunction so that now transitions to continua are no longer smaller than that to a bound state. This is achieved by changing the value of γ_e from 90° to 45° .

The results of such calculations are shown in Figures 1, 2 and Tables 6 and 7. Table 7 shows that Golden-rule like expression can no longer be used to calculate the final state distributions. Figure 1 shows that the final state distributions

Table 6. Spectral Parameters when $\gamma_e = 45^\circ$

	total cross section	partial cross sections			
		j	σ_j^e	$R_e(q_j)$	$[I_m(q_j)]^2$
E_0 (eV)	0.01320262	0	0.679	5.0	0.1
Γ (eV)	2.193×10^{-6}	2	0.199	-6.3	1.2
σ_a (eV $^{-1}$)	0.26	4	0.851	-0.5	16.6
σ_b (eV $^{-1}$)	2.34	6	0.183	8.2	0.02
q	14.5	8	0.429	0.7	8.2
		10	0.259	-0.8	2.1

Table 7. Comparison Between Final State Distributions σ_j/σ_{\max} Obtained by Configuration Interaction Theory and by Golden-rule Like Expression when $\gamma_e = 45^\circ$

j	configuration interaction theory		Golden-rule
	$E=0.013202$ eV	$E=0.0132025$ eV	
0	0.25	1.00	1.00
2	0.72	0.48	0.46
4	1.00	0.84	0.49
6	0.32	0.73	0.73
8	0.18	0.28	0.44
10	0.14	0.04	0.10

vary greatly around the resonance. Such variations in final state distributions may be analyzed by line profile parameters $R_e(q_j)$ and $[I_m(q_j)]^2$. Values of $R_e(q_j)$ for $j=0, 6,$ and 8 are positive numbers and those for $j=2, 4,$ and 10 are negative ones. This means that $j=0, 6,$ and 8 contribute relatively more when $E > E_0$ than when $E < E_0$. Figure 2 shows such behavior graphically. Notice the asymmetry of each partial photodissociation cross section spectrum.

Conclusion and Discussion

There are several interesting questions on the photodissociation dynamics around resonances. What are the effects of the life times on the final state distributions? Do the initial states before photoabsorption affect the photodissociation dynamics as they do by way of reflection principles in direct photodissociation? Photodissociation cross sections vary rapidly around resonances. Then do final state distributions also vary rapidly around resonances? Normally, they do not vary much around resonances. What are dynamical parameters responsible for such variations? Photodissociation spectra exhibit rich structures around resonances. Then what dynamical information can we extract from these rich structures? In vibrational predissociation of van der Waals molecules, Golden-rule like expression is known to approximate quite well final state distributions. What is the theoretical basis for this? When and in what conditions does it hold?

All the above questions are answered here by deriving the general partial photodissociation cross section formulas given by Eq. (37). For example, let us consider the effect of the life times on the final state distributions.

In the long lived complex, the value of line profile index

q defined in Eq. (15) is so large that spectral shapes of partial photodissociation cross sections are proportional to the square of transition dipole moment to the projected state of $\psi_E^{(q)}$ to $\psi_E^{(q)}$. Such projections given by Eq. (48) are energy insensitive and final state distributions are the same around resonances.

Parameters that determine partial photodissociation spectral shapes are identified. Different partial cross sections are found to have different spectral shapes in contrast to the fact that continua interact with a discrete state *via* one type continuum function $\psi_E^{(q)}$ and photodissociation to $\psi_E^{(q)}$ can be described by one kind of spectral shape (*i.e.* q). The cause for different spectral shapes is found to derive from the fact that dissociation to channel states $\psi_E^{(q)}$ is influenced by the discrete state *via* the projection of $\psi_E^{(q)}$ to $\psi_E^{(q)}$ and such projections are different from channels to channels.

Golden-rule like expression is found to hold when photodissociation is dominated by the transition to discrete states.

The theory is applied to the model system of vibrational predissociation of triatomic van der Waals molecules. The results are compared with those obtained from close-coupled equations. Agreements are quite good. A case where transitions to continua can not be ignored is considered and it is shown that Golden-rule like expression can no longer be used.

In conclusion, the configuration interaction theory developed here is found to be very powerful and is able to disentangle dynamical quantities responsible for the spectral shapes of partial photodissociation cross sections, to find out the theoretical basis for the Golden-rule like expression, and so on.

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Appendix A

Eq. (56) may be partitioned as $H_0 + V(R, r, \gamma)$, where H_0 are defined as

$$H_0 = -\frac{1}{2m} \frac{\partial^2}{\partial R^2} + \frac{\vec{j}^2}{2\mu r^2} + \frac{\vec{l}^2}{2mR^2} + H_{B_2}(r). \quad (56)$$

In the $\Delta v = v - v' = 1$ vibrational predissociation, $(\phi_v | H_0 | \psi_E^{(v'j)})$ becomes zero as H_0 does not contain the linear or odd power terms of r (we assume a harmonic approximation for the diatomic vibrational motion). The only term that contains the linear or odd power terms of r is $V(R, r, \gamma)$. Therefore,

$$(\phi_v | H | \psi_E^{(v'j)}) = (\phi_v | V | \psi_E^{(v'j)}). \quad (65)$$

Appendix B

Eq. (28) becomes after substitution of Eq. (38)

$$\begin{aligned} S_{j'j} &= S_{j'j}^0 + \sum_j S_{j'j}^0 \frac{V_{j'E} V_j^*}{\sum_k |V_{kE}|^2} (e^{-2\delta} - 1) \\ &= S_{j'j}^0 + 2i \sum_j S_{j'j}^0 \frac{V_{j'E} V_j^*}{E - E_0 - F - i\pi \sum_k |V_{kE}|^2} \end{aligned} \quad (66)$$

This differs from formulas of other people in that i is replaced by $-i$. This amounts to the replacement of S matrix into their complex conjugates and derives from the adaptation of incoming wave boundary condition instead of outgoing wave boundary condition.