Non-Lorentzian Resonance Due to the Detuning in One-Color Two-Photon Photodissociation

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Non-Lorentzian resonance is predicted to occur in two-photon photoabsorption processes due to the detuning off the intermediate levels. This type of non-Lorentzian resonance is distinct from the asymmetric resonance resulting from the effects of quantum interference between competing indistinguishable dynamic pathways. The product distributions are shown to be constant near this type of resonance.

Introduction

Resonance[1] is the concept bridging the molecular spectroscopy and the reaction dynamics, since it can be described as discrete state imbedded in continuum. The characteristics of the resonance, such as the position and width, can provide a wealth of invaluable information on the molecule. The Lorentzian resonances,[2] for which these two latter parameters are of primary importance, have been studied intensively. In contrast, studies on non-Lorentzian resonances were relatively rare, because their importance was not appreciated very much. For the non-Lorentzian resonances, line shape is another important characteristics, in addition to position and width.

One type of non-Lorentzian resonances is the so-called Fano profile,[3] which has been a focus of many experimental and theoretical studies. Although observations of this interesting feature in the photodissociation processes have been rather infrequent compared with those for autoionization,[4] quite numerous reports were recently made on the asymmetric resonances in photodissociation spectra of the molecules such as H₂ [Ref. 5], NO [Ref. 6], FNO [Ref. 7], Cs₂ [Ref. 8], and O₂ [9]. The origin of the asymmetric resonance is well known to be the quantum interference between multiple dynamic pathways. Although most asymmetric resonances were experimentally observed or predicted for Feshbach type resonances, shape resonances[10] were also known to yield them. Overlapping resonance[11] is another type of non-Lorentzian resonances that begins to attract a lot of attention recently. While most of these non-Lorentzian resonances were studied in one-photon processes, investigation on them in multiphoton processes were very rare to our best knowledge. One may intuitively assume that the asymmetric resonances in multiphoton processes be due to the effects of quantum interference as in one-photon processes, but this supposition may not be true. Indeed, we show in the present work that there may be another origin of non-Lorentzian resonances in two-photon processes. Further discussions on this type of resonance in connection to product control will be given in subsequent publications.

In this work, we describe non-Lorentzian resonances that can be observed in one-color two-photon[12-14] photodissociation processes. We show that this type of non-Lorentzian

resonances is not due to the effects of the quantum interference, but that they result from detuning in the multiphoton photoabsorption processes. We first employ a simple phenomenological argument to introduce this type of asymmetric resonances, and then proceed to detailed computation on realistic model systems. We discuss the significance of the present study in connection with the control of photodissociation processes.

We compute the second order transition amplitudes of the two-photon photodissociation processes.[15]

$$T_{fi} = \lim_{\varepsilon \to 0} \int_j \frac{\langle f|i\rangle\langle j|i\rangle}{E_i + h\nu_1 - E_j + i\varepsilon} \, . \tag{1}$$

where $|j\rangle$ is the eigenstate of the intermediate state Hamiltonian, E_i is the energy of the initial state $|i\rangle$, ν_1 is the photon frequency, and $|f\rangle$ is the final (scattering) state. Here it is assumed that the transition dipole moments are incorporated in $|i\rangle$ and $|f\rangle$. The energy eigenstate representation of the Green's operator $G^{(-)}$,

$$G^{(-)} = \lim_{\varepsilon \to 0} \int_j \frac{|j\rangle\langle j|}{E_i + h\nu_1 - E_j + i\varepsilon} \, . \tag{2}$$

is employed to compute the transition amplitudes in Eq. (1). The Green's operator $G^{(-)}$ is calculated by employing an efficient numerical method that was described in Ref. [16]. It should be pointed out that, although model potentials (exponential and harmonic oscillator potentials) are employed in this work for simplicity, the numerical method can treat arbitrary potentials for real molecules.

When the energy of the photon is such that only one intermediate resonance significantly contributes, the transition amplitude in Eq. (1) can be simplified to

$$T_{fi} = \frac{\langle f|j\rangle\ \langle j|i\rangle}{E_i + h\nu_1 - E_j + i\varepsilon_j} \, . \tag{3}$$

The transition probability can be expressed as

$$|T_{fi}|^2 = \frac{|\langle f|j\rangle|^2\ |\langle j|i\rangle|^2}{|E_i + h\nu_1 - E_j + i\varepsilon_j|^2} \, . \tag{4}$$

The one-photon transition probability $|\langle f|j\rangle|^2$ for the transition from the intermediate state $|j\rangle$ to the final state $|f\rangle$ can be described, in the absence of the effects of quan-

tum interference, by the Lorentzian function,

$$|\langle f | j \rangle|^2 = \frac{A\Gamma}{E_i - h\nu_1 + h\nu_2 - E_f + \Gamma^2} , \tag{5}$$

where ν_1 and ν_2 are the frequencies of the two photons, Γ is the width of the Lorentzian function, E_f is the energy of the final state, and A is the proportionality factor. Defining the two detunings as

$$\Delta_j = E_i + h\nu_1 - E_j \tag{6a}$$

and

$$\Delta_f = E_i - h\nu_1 + h\nu_2 - E_f = E_i + 2h\nu_1 - E_f , \tag{6b}$$

($\nu_1 = \nu_2$ in one-color two-photon processes) the transition probability is obtained as

$$|T_{fi}|^2 = \frac{A\Gamma F_{ij}}{(\Delta_j^2 + \varepsilon_j^2)(\Delta_f^2 + \Gamma^2)} , \tag{7}$$

where F_{ij} is the Franck-Condon factor of the transition from $|i\rangle$ to $|j\rangle$.

We begin with a phenomenological description of the resonance in Eq. (7). Of the four parameters, Δ_j and Δ_f, ε_j and Γ, only the detunings Δ_j and Δ_f are functions of the frequency of the photon. Depending on the detunings Δ_j and Δ_f, the transition probability may exhibit a variety of non-Lorentzian shapes. Figure 1 depicts several absorption spectra, based on Eq. (7), for different set of the parameters Δ_j and Δ_f, ε_j and Γ. It can be seen that the resulting resonance is Lorentzian only when the zero of the two detunings Δ_j and Δ_f coincide at one frequency. In other cases, the resonances are all non-Lorentzian. It should be noted that one of these resonances even exhibits two peaks.

In more general situations where there is more than one dissociation products correlated with the final dissociative states, more complicated model is required to describe the dynamics, and the transition amplitudes as described in Eq. (1) must be evaluated. Thus we adopt a realistic model sys-
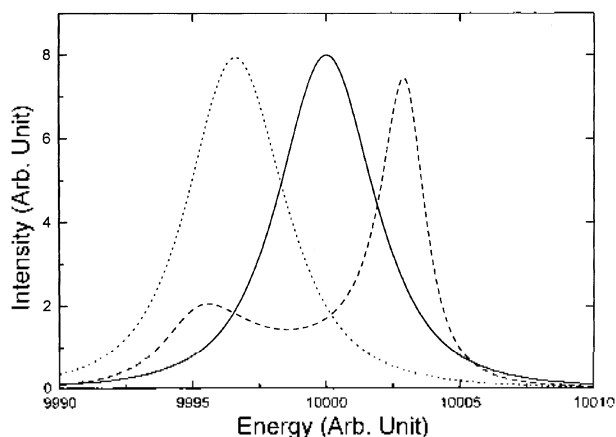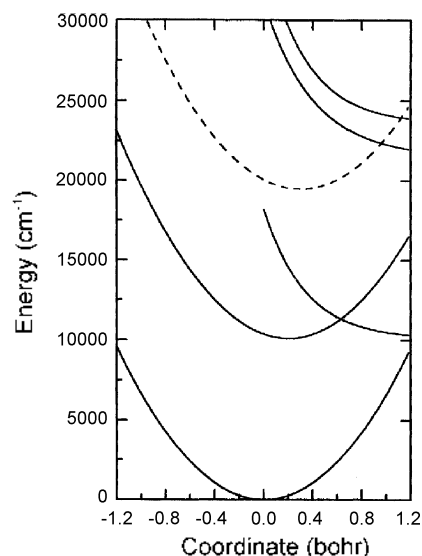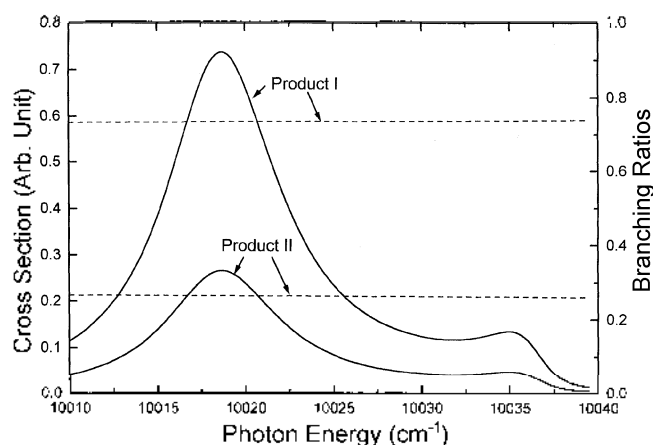

Figure 2. Schematic diagram of the model potential curves.

tem that consists of two interacting (one is bound, the other is repulsive) intermediate states, and three interacting (two of them are repulsive and the other is bound) final states. This model system is depicted in Figure 2. The ground state is a harmonic oscillator state with vibrational quantum of 200 cm^{-1}. The reduced mass of the system is 40 amu. The final bound state is a displaced (by 0.3 bohr) harmonic oscillator state with the same vibrational quantum. Each of the two final dissociative states interacts with the final harmonic oscillator state by 100 $cm^{-1} \times \exp(-(R-3)^2)$. The radiative decay width of the intermediate resonance may be treated simply by employing proper value for ε_j. The parameters for these two final dissociative states ($V = -\exp(-F(R+a))$) are $F = 2.5$ bohr^{-1}, $a = 3.0$ bohr (product channel I), and $F = 3.0$ bohr^{-1}, $a = 2.5$ bohr (product channel II). It is assumed in this model that these two final dissociative states are not coupled. The intermediate states consist of a harmonic oscillator state (identical to the ground state, but displaced by 0.2 bohr), and a repulsive state ($V = -\exp(-F(R+a))$). The intermediate bound state is allowed to predissociate by coupling with the intermediate repulsive state by the interactions of 100 $cm^{-1} \times \exp(-(R-3)^2)$. The vertical displacements of the intermediate and final state harmonic oscillator potentials are such that the energy from the bottom of the wells are 67 cm^{-1} and 83 cm^{-1}, respectively, when the system is excited to the bottom of the final harmonic oscillator potential.

Transition moment from the ground state to the bound intermediate state, and that from the bound intermediate state to the final bound state are taken to be nonzero (we set them to unity for convenience). Other transitions are assumed to vanish. This choice strictly eliminates the effects of the quantum interference (for example, allowing optical transition from the initial state to the intermediate or final continuum state (see Figure 2), coupled with the bound states, may give rise to quantum interference: see Ref. 19). Consequently, the one-photon spectra for transition from the ground state to the intermediate manifold, and that from the

Figure 1. Line profiles computed by Eq. (7) for one-color two-photon process: Solid line: $\Gamma = \varepsilon_j = 5$ cm^{-1}, $E_j = 10000$ cm^{-1}, $E_f = 20000$ cm^{-1}. Dotted line: $\Gamma = \varepsilon_j = 5$ cm^{-1}, $E_j = 9997$ cm^{-1}, $E_f = 19993$ cm^{-1}. Dashed line: $\Gamma = \varepsilon_j = 2$ cm^{-1}, $E_j = 9995$ cm^{-1}, $E_f = 20006$ cm^{-1}.

Figure 3. Cross Sections (solid lines) and branching ratios (dashes) in *one-color* two-photon process obtained in the absence of the built-in quantum interference. The branching ratios do not change in the vicinity of the non-Lorentzian resonances. The origin of energy is taken to be the bottom of the ground state potential.

bound intermediate state to final states are Lorentzian. The resulting *two*-photon spectrum for transition from the ground state to the final states is not symmetric (that is, non-Lorentzian), however, due to the effects of the two detunings Δ_i and Δ_f.

Figure 3 clearly shows that the one-color two-photon spectra can be non-Lorentzian. The partial cross sections for the product channels I and II exhibit splittings due to the effect of the detunings. It must be noted that the present type of non-Lorentzian resonances are not the results of the effects of quantum interference, and consequently, they are different from the Fano profiles. It is very noteworthy that the line shapes of the two partial cross sections depicted in Figure 3 are very similar to each other. The important consequence of this observation is that the branching ratios (the ratio of the dissociation cross sections to product I and II to total cross sections) do *not* change near the resonance, as also shown in Figure 3. In that sense, the dynamics near this type of non-Lorentzian resonances is very much like that of isolated Lorentzian resonances. This is in radical contrast to the dynamics in the vicinity of the Fano profiles, where all the properties of the photofragments exhibit rapid changes.[17-19] On the other hand, in the absence of this built-in quantum interference, the effects of the detuning in the intermediate excitation step in the first example will not bring difference between the partial cross sections to the product, since the dependence of the detunings on the energy in the denominator of Eq. (7) will distort the partial cross sections from the Lorentzian line shapes in an identical fashion, yielding identical line shapes and constant branching ratios across the reso-

nance. Thus, in actual two-photon experiments, the measurements of the product branching ratios could conveniently distinguish between the effects of the built-in quantum interference and the effects of the detunings.

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