Non-Lorentzian resonance and product control in two-photon photodissociation

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Abstract
We demonstrate that detuning in two-photon processes can yield non-Lorentzian resonances in the photodissociation spectra by accurately computing the second-order transition amplitudes. Both the one-colour and the two-colour processes are discussed. In one-colour two-photon processes, non-Lorentzian resonances may be obtained due to the detunings in the intermediate and final states, when the final states are predissociating. The product branching ratios may change significantly in the vicinity of non-Lorentzian resonances when the built-in interference in the final state manifold affects the dynamics. In two-colour two-photon processes, quantum interference between the \((\nu_1 + \nu_2)\) and \((\nu_2 + \nu_1)\) processes can give rapidly changing product branching ratios near the non-Lorentzian resonances, suggesting the potential of controlling product distributions in two-photon photodissociation processes.

1. Introduction

Resonance [1] is the concept bridging molecular spectroscopy and reaction dynamics, since it can be described as a discrete state embedded in a continuum. The characteristics of the resonance, such as position and width, can provide a wealth of invaluable information on the molecule. The Lorentzian resonances [2], for which these latter two 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 non-Lorentzian resonances, lineshape is another important characteristics, in addition to position and width. One well known type of non-Lorentzian resonance is the Fano profile [3], which has been a focus of many experimental and theoretical studies. The origin of the Fano profile is the quantum interference between multiple dynamic pathways. Although observations of this interesting feature in the photodissociation processes have been rather infrequent compared with those for autoionization [4–11], numerous reports have recently appeared on asymmetric
resonances in the photodissociation spectra of the molecules such as $H_2$ [12, 13], NO [14], FNO [15–17], $Cs_2$ [18, 19] and $O_2$ [20]. Although most asymmetric resonances were observed experimentally or predicted for Feshbach-type resonances, shape resonances [21] are also known to yield them. Despite the importance of resonance in the dynamic processes of molecules, the dynamical aspects of the resonance have not yet been fully investigated.

The dynamics of photodissociation near the non-Lorentzian resonances began to be elucidated only very recently in relation to control of photoproducts both in photoionization and photodissociation processes. In photoionization, Wang et al [22] showed that interference between two indistinguishable two-colour two-photon routes (employing two different photon frequencies) can give product state control in the ionization of the barium atom, and Nakajima et al [23] demonstrated theoretically that this control scheme can give an asymmetric resonance near which the product state distributions change considerably. Pratt [24] also showed similar results for the photoionization of NO. In the photodissociation of molecules, Chen et al [25] proposed that two distinct resonant two-photon routes, employing four different photon frequencies, can give quantum interference and product control in the dissociation of $Na_2$. In one-photon dissociation, it was predicted that the scalar [26–28] (such as the total cross section and the product branching ratios) and vector [29–32] properties (angular distribution, orientation and alignment) of photodissociation may exhibit rapid variations near the Fano profile or overlapping resonances. Although photoionization and photodissociation processes are similar in principle, there are several notable differences. The origin of these differences is, of course, the presence of nuclear degrees of freedom in the latter process. In photoionization, it is the transition dipole moments that may affect the quantum interference in $(2 + 2)$ control methods, as discussed by Nakajima et al [23]. In contrast, the Franck–Condon factors may give very important additional effects on the photodissociation processes. For example, in photodissociation spectra, the interactions of two electronic states may lead to rapidly changing signs ($q$-reversal) of the asymmetry parameters of the resonances due to the presence of oscillating Franck–Condon factors in the transition amplitudes [18, 19]. These interesting features are lacking in the photoionization processes, and therefore, detailed analysis of the effects of Franck–Condon factors on the quantum interference in a $(2 + 2)$-type control scheme would be highly valuable.

In this work, we describe non-Lorentzian resonances that can be observed in two-photon processes. We treat both the one- and two-colour processes, and systematically examine the dynamics of photodissociation near the non-Lorentzian resonances. The focus will be on the effects of nuclear degrees of freedom and the Franck–Condon factors on quantum interference. In one-colour two-photon processes, we show that the product branching ratios may rapidly change near the non-Lorentzian resonance, similarly to the corresponding one-photon processes [26–32], when the final dissociative states, coupled with the final bound state, carry oscillator strength from the intermediate states. In two-colour two-photon processes, we show that the interference between the $(v_1 + v_2)$ and $(v_2 + v_1)$ pathways, which is a special case of a four-colour scheme proposed by Shapiro et al [25], can give rapidly changing product branching ratios near the non-Lorentzian resonances. We demonstrate that this effect may be observed as the result of the difference between the Franck–Condon overlap integrals for transitions from the intermediate resonances and the final continuum states, when the energies of excitation are monitored near the two resonances belonging to the same electronic state.
2. Theory and computational methods

We compute the second-order transition amplitudes of the two-photon photodissociation processes,

\[ T_{fi} = \int \frac{\langle f | j \rangle \langle j | i \rangle}{E_i + h\nu_1 - E_j + i\varepsilon_j} \]

where the sum (integration) is over the eigenstate \(| j \rangle\) of the intermediate state Hamiltonian, \(E_i\) is the energy of the initial state \(| i \rangle\), \(\nu_1\) is the photon frequency, \(\varepsilon_j\) denotes the width of the intermediate resonance, 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 [38, 39] of the Green operator \(G^{(+)}\),

\[ G^{(+)} = \int \frac{\langle j | j \rangle}{E_i + h\nu_1 - E_j + i\varepsilon_j} \]

is employed to compute the transition amplitudes in equation (1).

The Green operator \(G^{(+)}\) is calculated by employing an efficient numerical method that was described in [40]. In brief, the Schrödinger equations for the intermediate and the final states are solved simultaneously. The Green operator \(G^{(+)}\) is expressed in terms of the regular and irregular solutions of the second intermediate manifold Hamiltonian. A special procedure is taken to ensure the linear independence of these two solutions in the classically forbidden region. The Green operator \(G^{(+)}\) and the final state wavefunction \(| f \rangle\) are propagated simultaneously with respect to the interparticle distance \(R\), and the two sets of asymptotic analysis are carried out at the end of the propagation, imposing appropriate boundary conditions on \(G^{(+)}\) and \(| f \rangle\). 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.

The detunings from the intermediate and final bound states are defined, respectively, as

\[ \Delta_j = E_i + h\nu_1 - E_j \]  (3a)

and

\[ \Delta_f = E_i + h\nu_1 + h\nu_2 - E_f. \]  (3b)

In two-colour \((\nu_1 \neq \nu_2)\) two-photon processes, the \((\nu_1 + \nu_2)\) and \((\nu_2 + \nu_1)\) pathways are indistinguishable, and there may exist effects of quantum interference due to coherent excitation via these two processes. The transition amplitudes in this case can be expressed as

\[ T_{fi} = \int \frac{\langle f | j \rangle \langle j | i \rangle}{E_i + h\nu_1 - E_j + i\varepsilon_j} + \int \frac{\langle f | j' \rangle \langle j' | i \rangle}{E_i + h\nu_2 - E_{j'} + i\varepsilon_{j'}}. \]  (4)

Although this expression may be simplified to a single term when only one intermediate resonance dominates in each of the two terms in equation (4), we compute (4) without approximation in order to be able to treat the general situations in which many intermediate resonances overlap and contribute more or less equally.

3. Results

We adopt a realistic model system 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 in order to demonstrate for general situations where there is more than
one dissociation products correlated to the final dissociative states. This model system is depicted in figure 1. The ground state is a harmonic oscillator state with a vibrational quantum of 200 cm\(^{-1}\). The reduced mass of the system is 40 amu. The system is assumed to be photoexcited from the vibrationally ground level \((v_i = 0)\) in the initial electronically ground state both in the one-colour and in two-colour cases presented below. The final bound state is a displaced (by 0.3 \(a_0\)) harmonic oscillator state with the same vibrational quantum as the ground state. The bottom of the ground state potential is defined as the zero of energy. The final repulsive states are described by exponential potentials \((V = -A \exp(-F(R + a)) + V_0)\).

We employ two different sets of intermediate and final states for the one- and two-colour cases. For the \textit{one-colour} process, the parameters for the two final dissociative states are \(A = 1 \text{ cm}^{-1}\), \(F = 2.9 \text{ cm}^{-1}\), \(a = 1.0 \text{ } a_0\), \(V_0 = 13450 \text{ cm}^{-1}\) (product channel I), and \(F = 3.0 \text{ cm}^{-1}\), \(a = 1.0 \text{ } a_0\), \(V_0 = 13400 \text{ cm}^{-1}\) (product channel II), and they interact with the final harmonic oscillator state by the interactions of 200 cm\(^{-1}\) \(\times \exp(-f(R - 0.9)^2)\) and 320 cm\(^{-1}\) \(\times \exp(-f(R - 0.6)^2)\), respectively. They also interact with each other by 50 cm\(^{-1}\) \(\times \exp(-f(R - 0.6)^2)\) \((f = 1 \text{ } a_0^{-1})\). The intermediate states consist of a harmonic oscillator state (identical to the ground state, but displaced by 0.2 \(a_0\)), and a repulsive state \((V = -A \exp(-F(R + 0.5)) + V_0)\), where \(A = 1 \text{ cm}^{-1}\), \(F = 3.0 \text{ cm}^{-1}\), and \(V_0 = 7600 \text{ cm}^{-1}\). The intermediate bound state is allowed to predissociate by coupling with the intermediate repulsive state by the interactions of 200 cm\(^{-1}\) \(\times \exp(-f(R - 0.9)^2)\). The vertical displacements of the intermediate and final state harmonic oscillator potentials from the ground state potential are 9980 and 19500 cm\(^{-1}\), respectively. The model system for the \textit{two-colour} process is similar to that for the one-colour case, except that the final bound state is eliminated. The parameters for the two final dissociative states are \(A = 1 \text{ cm}^{-1}\), \(F = 3.05 \text{ cm}^{-1}\), \(a = 0.5 \text{ } a_0\), \(V_0 = 14450 \text{ cm}^{-1}\) (product channel I), and \(F = 3.0 \text{ cm}^{-1}\), \(a = 1.0 \text{ } a_0\), \(V_0 = 14400 \text{ cm}^{-1}\) (product channel II), while those for the intermediate repulsive state are \(A = 1 \text{ cm}^{-1}\), \(F = 3.0 \text{ cm}^{-1}\), \(a = 1.1 \text{ } a_0\), \(V_0 = 7600 \text{ cm}^{-1}\). The vertical displacement of the intermediate state harmonic oscillator potential from the ground state potential is 10005 cm\(^{-1}\). Couplings between the potentials are identical to those for the one-colour case.

\[
\text{Figure 1. Schematic diagram of the potential curves.}
\]
We adopt the predissociating intermediate states in order to treat situations that are as
general as possible. Only intermediate bound state is allowed to optically couple to the ground
state with transition dipole moment of unity in all the computations presented in this work.
When the widths of the intermediate resonances are only due to the radiative decay, the radiative
widths of the intermediate resonances may be easily incorporated by employing proper value for
$\varepsilon_j$ in equation (1). It should also be pointed out that the present computations may treat the two-
photon processes near the overlapping resonances in which several intermediate resonances
may contribute, since the sum over the intermediate resonances in equation (1) may be carried
out in a trivial way by employing our method.

In an earlier work [41], we showed that the one-colour two-photon spectra can be non-
Lorentzian in certain cases (for example, when the 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 non-zero, and other transitions are assumed to vanish. This choice strictly
eliminates the effects of the quantum interference). In the absence of this built-in quantum
interference, Lorentzian resonance may be obtained when the zeros of detunings from the
intermediate ($\Delta_1$) and final bound states ($\Delta_f$) coincide at one frequency (see figure 1 in [41]).
The non-Lorentzian resonances were not the results of the effects of quantum interference, and
consequently, they were different from the Fano profiles. The branching ratios do not change
near the resonance, and the dynamics near this type of non-Lorentzian resonances is very
much like that near the isolated Lorentzian resonances. When there exist the effects of built-in
interference, however, non-Lorentzian resonances may also display rapidly changing product
branching ratios in one-colour two-photon processes, as depicted in figure 2, which is obtained
when the transition dipole moments from the intermediate bound state to the final dissociative
states do not vanish (the ratios of the transition dipole moments from the intermediate harmonic
oscillator state to the final harmonic oscillator and the final two repulsive potentials are taken to
be 1:10:10). In this situation, the indirect dissociation pathway via the final harmonic oscillator
state and the direct route by excitation to the final repulsive states interefer, allowing the product
branching ratios to change rapidly as functions of the excitation frequency. It must be noted
that the quantum interference in this case is built-in in the molecule, while it is an experimental
parameter in the well known $(\omega_1, \omega_2)$ coherent control methods [42–50] that were pioneered
by Shapiro and Brumer [42–45], and confirmed by Elliott and co-workers [46], Gordon and
co-workers [48–50], and by Shapiro, Brumer and co-workers [42]. 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 detuning. The
asymmetric resonance depicted in figure 2 for two-photon process may be fitted by invoking the ‘generalized multiphoton asymmetry parameter’ recently introduced by Gordon, Seideman
and co-workers [51].

Since the degree of asymmetry of the resonance may depend on the relative signs of the
transition dipole moments to the discrete and continuum states it deserves some attention here.
Fano’s formula for an isolated asymmetric resonance is

$$q = \frac{\langle \phi | T | i \rangle + P \int dE' \langle \psi | H | \psi_{E'} \rangle \langle \psi_{E'} | T | i \rangle / (E - E')} {\pi \langle \psi | H | \psi_{E} \rangle \langle \psi_{E} | T | i \rangle}$$

(5)

$|\phi\rangle$ represents the discrete state, $|\psi_{E'}\rangle$ is the continuum state, $|i\rangle$ is the initial state, $T$ is
the transition operator and $P$ denotes the principal part of the integral. $\langle \psi | H | \psi_{E} \rangle$ is the
coupling between the discrete state and the continuum (see [3, 18, 19]). $\langle \psi_{E'} | T | i \rangle$ and $\langle \psi_{E} | T | i \rangle$
are the transition dipole moments from the initial state to the discrete and continuum state,
respectively. If the principal part in the numerator ($P \int dE' \ldots$) is negligible, as is assumed
in many works in the literature, then the role of the relative signs of the two transition dipole
moments is straightforward: if one of them changes sign, the sign of the $q$ parameter will reverse. When the transition dipole moment to the discrete state is also small (as was the case for Cs$_2$ [18, 19]), however, it becomes complicated, since the numerator of equation (5) contains both of the transition dipole moments. For example, if $\langle \psi | T | i \rangle$ vanishes, then the transition dipole moment to the continuum state $\langle \psi_E | T | i \rangle$ cancels out in the numerator and denominator in equation (5), and thus the sign of $q$ will remain unchanged with respect to the sign change of $\langle \psi_E | T | i \rangle$.

For two-colour two-photon processes, the situation can be quite different, because the system can be excited from $|i\rangle$ to $|f\rangle$ coherently via the two indistinguishable processes $|i\rangle \xrightarrow{\nu_1} \{ |j\rangle \} \xrightarrow{\nu_2} |f\rangle$ and $|i\rangle \xrightarrow{\nu_2} \{ |j'\rangle \} \xrightarrow{\nu_1} |f\rangle$ if the two lasers are coincident at the time, as recently shown by several groups [22–24] for photoionization processes. The difference in the transition dipole moments between the intermediate resonances and the final continuum states (correlating with different products) gives rise to asymmetric lineshape and variation of the product distribution near the resonance in photoionization of atoms. On the other hand, in two-photon dissociation processes, different Franck–Condon overlaps in the amplitudes for transitions from the intermediate resonances and the final continuum states can also yield rapid changes in the product branching ratios, as demonstrated below. The transition amplitude is to be computed as the coherent sum of these two processes, as given by equation (4). In actual experiments, the frequency $\nu_2$ is fixed near a resonance, and $\nu_1$ is scanned across another resonance.

Figure 3 depicts the two-photon spectra in a hypothetical situation where only the $|i\rangle \xrightarrow{\nu_1} \{ |j\rangle \} \xrightarrow{\nu_2} |f\rangle$ process contributes. The ground state is assumed to be excited by $\nu_1$ to energies near the $v' = 0$ resonance of the intermediate states, and subsequently to the final state by $\nu_2$. This situation may be realized when the detuning $\Delta_{II}$ from the intermediate level in the second pathway $|i\rangle \xrightarrow{\nu_2} \{ |j'\rangle \} \xrightarrow{\nu_1} |f\rangle$ is much larger than the detuning in the

![Figure 2. Cross sections (full curves) and branching ratios (broken curves) in the one-colour two-photon process obtained when the built-in quantum interference is in effect. The branching ratios change near the non-Lorentzian resonances.](image-url)
first pathway $\Delta_{I}$, and thus, the first term dominates in equation (4). We treat this case in order to show the positions and widths of the resonances, which will be useful for subsequent discussions. The resonances centred at 10 093 and at 10 296 cm$^{-1}$ correspond to $v' = 0$ and 1 of the intermediate bound potential, respectively. These resonances are shifted from their zeroth-order positions (10 105 and 10 305 cm$^{-1}$) due to the coupling with the intermediate repulsive state. The model potentials adopted for computation for figure 3 are those employed for two-colour process described above with the exception that the harmonic oscillator potential (broken one) in the final state manifold is eliminated. Thus, the final states are direct dissociating (off resonance). The halfwidths of the two resonances corresponding to $v' = 0$ and 1 are 7 and 40 cm$^{-1}$, respectively. Since only a single dissociation channel $(|i\rangle \overset{v_1}{\rightarrow} |j\rangle \overset{v_2}{\rightarrow} |f\rangle)$ contributes in this case, the resonances are highly Lorentzian, with slight asymmetry due to the effects of detuning (see [41]). Figure 4 depicts the spectra and the branching ratios obtained when both of the two-photon pathways $(|i\rangle \overset{v_1}{\rightarrow} |j\rangle \overset{v_2}{\rightarrow} |f\rangle)$ are taken into consideration. Here $v_2$ is fixed at 10 310 cm$^{-1}$, about 14 cm$^{-1}$ higher in energy than the peak of the $v' = 1$ resonance, and $v_1$ is scanned across the $v' = 0$ resonance. The partial cross sections are clearly asymmetric, and the branching ratios exhibit gradual changes near the resonance. Figure 5 depicts a similar situation, but with $v_2$ fixed at 10 280 cm$^{-1}$, which is located in the lower frequency portion of the $v' = 1$ resonance. The partial cross sections exhibit a higher degree of asymmetry, and the branching ratios show more frequent variations. It can be seen that the lineshape of the resonance and the variation of the product branching ratios can be very different, depending on the detuning $\Delta_{II}$.

In photodissociation, there may exist many close-lying resonances in the intermediate manifold in contrast to atomic photoionization processes [22–24], making this scheme of product control highly desirable. The simplest case will be two-colour two-photon excitation...
Figure 4. Cross sections (full curves) and branching ratios (broken curves) in the two-colour two-photon process obtained for $v_2 = 10310 \text{ cm}^{-1}$ ($\Delta_{1II} = 14 \text{ cm}^{-1}$).

Figure 5. Cross sections (full curves) and branching ratios (broken curves) in the two-colour two-photon process obtained for $v_2 = 10280 \text{ cm}^{-1}$ ($\Delta_{1II} = -16 \text{ cm}^{-1}$).

via the intermediate bound states, which can be either predissociating, as in the present case, or not. In the present situation, the intermediate resonances arise from coupling between the intermediate bound and repulsive states. When the intermediate bound states are not predissociating, it is the radiative decay that can yield the intermediate resonances. It should
be noted that the \( v' = 0 \) and 1 resonances treated here belong to the same electronic state. Consequently, transition dipole moments from the ground state to these two intermediate resonances (\( v' = 0 \) and 1) are identical. For transitions from the intermediate resonances to final continua, both the transition dipole moments and the Franck–Condon overlap integrals may be different. When the two final continuum states belong to the same electronic states (for example, when different spin–orbit components of a Born–Oppenheimer state dissociate to different fine structure states of atoms), however, only the Franck–Condon overlap integrals may be different. Since we employ the same transition dipole moments for transitions from the intermediate to the final states, the rapid variations of the product branching ratios exhibited in figures 4 and 5 are the result of the different Franck–Condon overlap integrals. On the other hand, the two intermediate resonances may well belong to different electronic states, in which case both the differences in the transition dipole moments and the Franck–Condon overlap integrals would contribute. It is also worth noting that changing the intensities of the radiation fields does not affect the product branching ratios, since the overall intensity of the two coherent processes will be identical, being the product of the two intensities. Likewise, the phase difference of the radiation fields will not affect the results, since the phases cancel out in equation (4). Detuning from the intermediate resonances will solely determine the lineshapes and the product distributions in the present scheme. This scheme of product control is simplification of that proposed by Chen et al [25], in which radiations with four different frequencies (\( \nu_1 + \nu_2, \nu_3 + \nu_4 \)) are employed to yield product control.

4. Conclusions

We have demonstrated that non-Lorentzian resonance may indeed be observed due to the effects of detuning in two-photon processes. We have also shown that the presence of quantum interference effects between two coherent pathways can display rapidly changing product branching ratios both in one-colour and in two-colour two-photon processes. It will be very interesting to confirm the findings in this work for photodissociation processes of molecules.

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