Variation of photofragment angular distributions near the isolated Lorentzian resonances: Influence of the continuum-continuum interaction

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The variation of the product angular distributions near isolated Lorentzian resonances is theoretically analyzed. We show that interactions between the asymptotically degenerate dissociative states can give a monotonic variation of the anisotropy parameters of $O(^3P_j, \ j=0,1,2)$ with different slopes near isolated Lorentzian resonance in the predissociation of the OH molecule. The anisotropy parameters are shown to change near the resonance even in the simplest situation where the predissociation occurs through only one dissociative state, noninteracting to the first order with other asymptotically degenerate states. This finding is attributed to second- and higher-order interactions. [S1050-2947(98)09509-2]

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I. INTRODUCTION

The dynamics of predissociation is very different from the direct (off-resonance) dissociation processes in many respects. In direct dissociations dynamic observables such as the product branching ratios or angular distributions rapidly approach diabatic limit values [1] at energies well above the dissociation threshold. An interesting dynamics is expected to be observed only at near-threshold energies as a consequence of the influence of nonadiabatic interactions among the asymptotically degenerate states at large internuclear distances called the recoupling region. The measurement of dynamic properties at intermediate energies easily provides information on the symmetry of the excitation process and the dissociation mechanism [1]. On the other hand, very interesting dynamics exist both at near-threshold energies and at intermediate energies in predissociation processes. The familiar occurrence of resonance is a typical dynamic consequence of predissociation at intermediate energies, which is caused by the interactions between bound (gateway) states and the dissociation continua.

Dynamics in the vicinity of isolated Lorentzian resonance may look intuitively simple. Indeed, we have shown [2] that the product branching ratios do not change as functions of the energy across the symmetric (Lorentzian) resonances. This observation simply stems from the fact that for Lorentzian resonances the partial cross sections to photoproducts exhibit resonances whose linewidths and positions are identical to those of the total cross section. However, recent experimental and theoretical studies indicate that the dynamics near the simplest (isolated and Lorentzian) type of resonances may not be simple at all, as a consequence of the interactions among dissociative states. For example, these interactions were predicted [3] to affect the line shape of asymmetric resonances. The very interesting observations by Liyanage *et al.* [4] on the very diverse (adiabatic, diabatic, and intermediate) patterns (depending on the nature of the gateway state) of the branching ratios of the Cl-atom fine-structure states produced in HCl predissociation were proposed [5] to arise from the interactions among dissociative states carrying the quantum flux in the photodissociation pro-

cesses. These type of interactions were also shown to affect the magnitude of the molecular phase [6] in (ω_1,ω_3) coherent control.

While interactions between discrete and continuum states are well known to be the origin of the phenomena of predissociation and autoionization [7], the effects of the coupling between dissociative states (when there exists more than one dissociative states carrying the quantum flux) have rarely been treated in indirect dissociation processes. In Fano's [8] classic treatment, for example, continuum states were assumed to be ''prediagonalized'' before interacting with discrete states. When more than one kind of photofragment can be produced from the predissociation process, several Born-Oppenheimer states may correspond to these products, and the nonadiabatic coupling between the dissociative electronic states may significantly affect the dynamics [1]. Considering that the vector properties of photodissociation are more sensitive indicators [1] of the dynamics than the scalar properties, it will be very interesting to examine how they would be affected by the interaction among the asymptotically degenerate dissociative states in the vicinity of resonance. The most fundamental question would be whether the vector properties would remain constant near isolated Lorentzian resonances like the scalar properties (product branching ratios) treated earlier [2,3].

We address this important question in the present work. We show that the anisotropy parameters may exhibit a significant variation near isolated Lorentzian resonances even in the absence of quantum interference between direct and indirect dissociation pathways. This finding is attributed to interactions among the asymptotically degenerate dissociative states. Eliminating these asymptotic couplings gives an identical variation of anisotropy parameters across the resonances. However, we show that very gradual changes still persist even in this simplest situation, where only a single noninteracting dissociative state is mostly responsible for the dissociation.

II. THEORY AND COMPUTATIONAL METHODS

In this work we treat vector properties [1,9–15] of photofragments for predissociation processes of OH. The potential

FIG. 1. Potential-energy curves of OH. The zero of energy is defined as the baricenter of the energies of the triplet oxygen-atom fine-structure states.

FIG. 2. Partial cross sections (solid and dotted lines) and the product branching ratios (dashed lines) $O(^3P_j$, $j=0,1,2)$ near *isolated Lorentzian* resonance corresponding to the $N=2$ and $\nu'=9$ levels of the $A\,^2\Sigma^+$ state. The initial ground state is the $X\,^2\Pi_{3/2}^-$ state, with $J_i=\frac{7}{2}$ and $\nu_i=0$.

III. RESULTS

In the photodissociation of the OH molecule, quantum interference between the direct dissociation pathway (via $^2\Sigma^-$) and the indirect pathway (via $A\,^2\Sigma^+$) would give asymmetric resonances [2,3] for the $\nu'\geqslant 7$ vibrational levels of the $A\,^2\Sigma^+$ state, since both the dissociative $^2\Sigma^-$ and the bound $A\,^2\Sigma^+$ states are optically coupled with the ground $X\,^2\Pi$ state. In order to examine the product angular distributions near isolated Lorentzian resonance, however, we eliminate the effects of quantum interference by employing vanishing transition dipole moments for transitions from the initial $X\,^2\Pi$ state to the repulsive $^2\Sigma^-$ state. The resulting dynamics is the "pure" predissociation of the $A\,^2\Sigma^+$ state by coupling with the three repulsive $^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$ states. It should be noted that the latter three repulsive states can interact with each other by spin-orbit and Coriolis interactions. The behavior of the scalar properties [2,3] (total cross section and product branching ratios) are simple in this situation: The resonances are Lorentzian, and the product branching ratios are independent of energy near the resonance as depicted in Fig. 2. Figure 3 depicts the product angular distributions for this purely indirect dissociation processes. It can be seen that the anisotropy parameters exhibit significant variation, and that the slopes of the variations are different from each other. The changes in the anisotropy parameters near isolated Lorentzian resonances are monotonic, in contrast to the more drastic (exhibiting maxima) changes of the vector properties across the asymmetric resonances shown in earlier works [9].

In order to elucidate the underlying mechanism for this very intriguing variation of the product angular distribution shown in Fig. 3, we investigate the situation where predissociation occurs by a single channel ($^4\Sigma^-$ state). This is achieved by employing vanishing spin-orbit couplings between $A\,^2\Sigma^+$ and the other two repulsive $^2\Sigma^-$ and $^4\Pi$ states. The $^4\Sigma^-$ state, however, is still allowed to interact with the other two repulsive $^2\Sigma^-$ and $^4\Pi$ states in asymptotic region in this *single-channel* dissociation. The resulting anisotropy parameters are depicted in Fig. 4. The

curves of the electronic states included in the present calculations are depicted in Fig. 1. Two oxygen terms, $O(^3P)$ and $O(^1D)$, are involved in the dynamic process considered in this work. The ground state $X\,^2\Pi$ and the repulsive states $^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$ correlate with the triplet oxygen $O(^3P)$, while the $A\,^2\Sigma^+$, $^2\Delta$, and $2\,^2\Pi$ states correlate with the singlet oxygen $O(^1D)$ term. The $A\,^2\Sigma^+$ state, correlating with $O(^1D)$, crosses with the repulsive states $^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$ that dissociate to $O(^3P)$. Predissociation of the $A\,^2\Sigma^+$ state results from spin-orbit couplings between the bound state $A\,^2\Sigma^+$ and the three repulsive states $^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$. The optical transition considered in the present work is from the vibrationally ground level of the $X\,^2\Pi$ state to the $\nu'=9$ level of the $A\,^2\Sigma^+$ state, and the transition energy is about 6.3 eV.

The frame transformation matrices [1], which connect the adiabatic Born-Oppenheimer (ABO) states to the corresponding atomic term limits, are the most important element of the theory. Since the spin-orbit interactions between the $A\,^2\Sigma^+$ state and the $^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$ states do not vanish at infinite internuclear distances in the OH molecule, *two* transformation matrices must be constructed, each of which describes the correlation between ABO states and the corresponding atomic term limits [$O(^3P)$ and $O(^1D)$], as shown in Ref. [2(a)]. It must be noted that the theory can include a variety of interactions (except the hyperfine couplings), and that it studies their effects on the photodissociation dynamics.

A continuum wave function (14×14 matrix) of good parity is propagated using the renormalized Numerov method [16], and appropriate boundary conditions are imposed at the end of the propagation. The transition amplitudes for dissociation to a specific fine-structure component of the oxygen atom is calculated by applying the golden rule. The potentials and the spin-orbit interactions employed in the present study were described in Ref. [2(a)].

FIG. 3. Angular distributions of $O(^3P_j, \ j=0,1,2)$ near the *isolated Lorentzian* resonance corresponding to the $N=2$ and $\nu'=9$ levels of the $A \ ^2\Sigma^+$ state. Direct dissociation via the $^2\Sigma^-$ state is eliminated. Predissociation occurs by the spin-orbit coupling between the $A \ ^2\Sigma^+$ state and the three dissociative ($^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$) states. The initial ground state is the $X \ ^2\Pi_{3/2}^-$ state, with $J_i=\frac{7}{2}$ and $v_i=0$.

angular distributions exhibit monotonic parallel variations near the resonance, with small differences in the values of the anisotropy parameters in this situation. Thus, even in this single-channel dissociation, it seems that the nonadiabatic (spin-orbit and Coriolis) interactions between the $^4\Sigma^-$ state, which carries the quantum flux, and the $^2\Sigma^-$ and $^4\Pi$ states, can yield small differences in the anisotropy parameters of $O(^3P_j, \ j=0,1,2)$.

Finally, we isolate the residual effects of the nonadiabatic (spin-orbit and Coriolis) interactions by eliminating the *direct* (that is, first order) interactions among the dissociative states ($^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$), and obtain the anisotropy parameters depicted in Fig. 5. Now, all the differences in anisotropy parameters of $O(^3P_j, \ j=0,1,2)$ vanish, and they
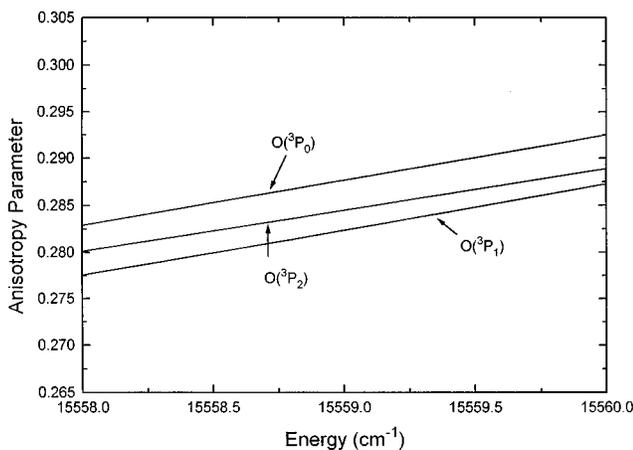
FIG. 4. Angular distributions of $O(^3P_j, \ j=0,1,2)$ near *isolated Lorentzian* resonance corresponding to the $N=2$ and $\nu'=9$ levels of the $A \ ^2\Sigma^+$ state. Direct dissociation via the $^2\Sigma^-$ state is eliminated. Predissociation is allowed to occur only by the spin-orbit coupling between the $A \ ^2\Sigma^+$ and $^4\Sigma^-$ states. Asymptotic couplings between the three dissociative ($^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$) states are *retained*. The initial ground state is the $X \ ^2\Pi_{3/2}^-$ state, with $J_i=\frac{7}{2}$ and $v_i=0$.
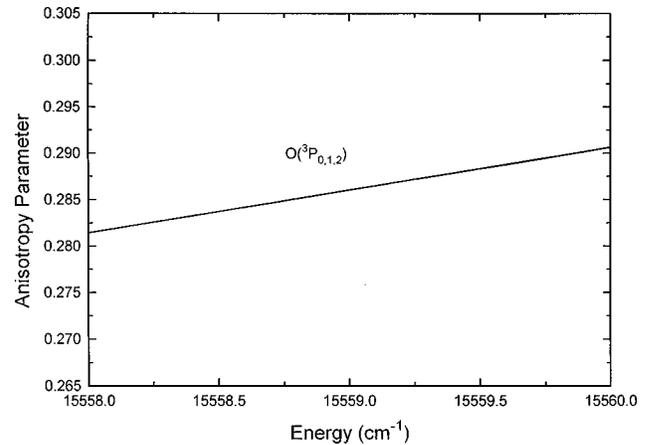
FIG. 5. Identical to Fig. 4, but with the asymptotic couplings between the three dissociative ($^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$) states *removed*.

show identical, very slow and monotonic variation near the resonance. Thus it clearly shows that the differences between the values of the anisotropy parameters of $O(^3P_j, \ j=0,1,2)$ shown in Fig. 4 can be attributed to the direct interactions among the asymptotically degenerate dissociative states. It is very intriguing that the anisotropy parameters still exhibit a small degree of variation near the resonance even in this simplest situation. We emphasize that the predissociation occurs only by a single channel ($^4\Sigma^-$ state), and that the $^4\Sigma^-$ state does not directly interact with other repulsive states in this hypothetical scheme. Thus it may seem that the other dissociation channels are ''spectators'' that would not affect the dynamics at all. However, it should be noted that the $^4\Sigma^-$ state can still interact with other repulsive states in an *indirect* (second- and higher-order) way through the bound $A \ ^2\Sigma^+$ state near the crossing points. This latter type of interaction between continuum states has rarely been discussed although, it was shown that the second- or higher-order interactions between resonances (via continuum states) may affect the shape of asymmetric resonances in the predissociation of Cs_2 [17]. Although this effect is weak in the present case, it may yield a more rapid variation of photofragment angular distributions for systems with large coupling between the gateway and the dissociative states, and consequently with larger coupling among the dissociative states.

IV. CONCLUSIONS

The calculations presented in this paper demonstrate that the anisotropy parameters of the photofragments may exhibit significant variation across *isolated Lorentzian* resonances due to several different kinds of interactions between the dissociative states. The present findings clearly indicate that the interactions between the dissociative states in predissociation can significantly affect the vector properties of photodissociation. It is shown that the interactions between dissociation channels can give different variation of the anisotropy parameters of $O(^3P_j, \ j=0,1,2)$. First-order interactions among the asymptotically degenerate states are also shown to result in parallel variation of the anisotropy parameters. Only eliminating these effects gave identical anisotropy parameters of $O(^3P_j, \ j=0,1,2)$ near the reso-

nance. Even in this simplest case, second- and higher-order interactions among the repulsive states are shown to yield a very gradual variation. Thus, as a limiting case of this very intriguing trend, it can be concluded that the product angular distributions are independent of energy near isolated Lorentzian resonances, only when the predissociation occurs through a single, noninteracting (to any order) dissociative state. It must also be pointed out that this limiting case will correspond to the semiclassical case recently treated by in Ref. [18].

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