

Asymmetric Resonance in Apparently Direct Photodissociation

Sungyul Lee

Department of Chemistry, Kyunghee University, Kyungki-Do 449-701, Korea

Received November 20, 1999

The phenomenon of asymmetric resonance is attracting considerable attention recently. Quite numerous reports were made on the observation of asymmetric resonances in photodissociation spectra of molecules such as H₂ [Ref. 1], FNO [Ref. 2], Cs₂ [Ref. 3, 4] and O₂.⁵ Systematic analysis of the line shape yielded profound insight into the dynamics of photodissociation. Since the theoretical treatment of Fano⁶ in 1961, this very interesting feature has been attributed to the interference between the multiple fragmentation pathways. It is now widely known in the community of molecular spectroscopy and dynamics that one may observe the asymmetric resonances when both the discrete and the continuum state are coherently accessed from the initial state.

What is still not well understood is, however, the fact that the asymmetric resonances may also be observed even when the optical transition to the discrete states are forbidden, as long as the continuum state is coupled with the discrete states. Although this can be inferred from Ref. 6, no explicit comment has been made on this point to our knowledge. This latter situation may be very tricky to deal with when analyzing experimental observations. Since the discrete states do not carry oscillator strength from the initial (usually the ground) state, predissociation in the ordinary sense does not apply here. The situation apparently looks like direct dissociation, and one may attempt to analyze the dynamics in terms of the high energy recoil limit approximation.^{7,8} This approach would not be appropriate, as we discuss below. What one may actually observe is a very sharp asymmetric resonance superimposed on broad background, but the spectrum is not simple overlap of the two components either. Product branching ratios and the vector properties (such as the product angular distributions) may exhibit very abrupt changes near the resonance. These facts clearly require more careful analysis of the experimental observations in apparently simple dissociation processes involving the continuum states. In this paper we treat this very interesting case by employing the predissociation of the OH molecule as a model case.

We begin with Fano's expression⁶ of the transition amplitude from the initial state i to the final state Ψ_E of the system,

$$\langle \Psi_E | T | i \rangle = \frac{1}{\pi V_{E'}} \langle \varphi | T | i \rangle \sin \Delta + \frac{1}{\pi V_{E'}} PP \int dE' V_{E'}^* \langle \Psi_{E'} | T | i \rangle \sin \Delta - \langle \Psi_{E'} | T | i \rangle \cos \Delta. \quad (1)$$

Here φ is the zeroth-order (unperturbed) discrete state, $\Psi_{E'}$ is the zeroth-order continuum state, T is the optical transition operator, PP denotes the principal part, and V_E is the

interaction between the discrete and the continuum states,

$$V_E = \langle \varphi | H | \Psi_E \rangle. \quad (2)$$

The parameter Δ is defined as

$$\Delta = -\arctan \frac{\pi |V_E|^2}{E - E_\varphi - F(E)}, \quad (3)$$

where E_φ is the energy of the unperturbed discrete state and $F(E)$ is the shift of the resonance from the unperturbed position. Difference in the dependence of the $\sin \Delta$ and the $\cos \Delta$ terms on the energy E yields the asymmetric line shape.

Now, when the optical transition to the discrete state is forbidden, that is, when

$$\langle \varphi | T | i \rangle = 0, \quad (4)$$

Eq. (1) is simplified to

$$\langle \Psi_E | T | i \rangle = \frac{1}{\pi V_{E'}} PP \int dE' \frac{V_{E'}^* \langle \Psi_{E'} | T | i \rangle}{E - E'} \sin \Delta - \langle \Psi_{E'} | T | i \rangle \cos \Delta. \quad (5)$$

It can be seen that this expression still retains the $\sin \Delta$ term, which can interfere with the $\cos \Delta$ term. The $\sin \Delta$ term in Eq. 5 is to be multiplied by the following expression that resembles a second order transition amplitude,

$$PP \int dE' \frac{\langle \varphi | H | \Psi_{E'} \rangle \langle \Psi_{E'} | T | i \rangle}{E - E'}. \quad (6)$$

Now, this expression implies that the transition can occur from the initial state to the discrete state φ by a second order process: transition from i to Ψ_E is due to optical transition, and subsequent transition from Ψ_E to φ occurs by discrete-continuum interaction V_E . This term interferes with the direct excitation to the continuum (the second term on the right hand side of Eq. (5)). This effect is to be understood in light of the fact that the zeroth order discrete states are mixed up with the continuum state by discrete-continuum interactions.

We now demonstrate this explicitly by computing the photodissociation spectrum of the OH molecule. Figure 1 depicts the relevant potential curves. The bound A²Σ⁺ state and the repulsive ²Σ⁻ state are optically accessible from the ground X²Π state. In order to demonstrate the situation discussed above, however, we assume that the A²Σ⁺-X²Π transition dipole moment vanishes. Thus, the X²Π state is optically excited only to the repulsive ²Σ⁻ state, which is interacting with the A²Σ⁺ state by the spin-orbit and rotational couplings. The role played by the optically dark ⁴Σ⁻

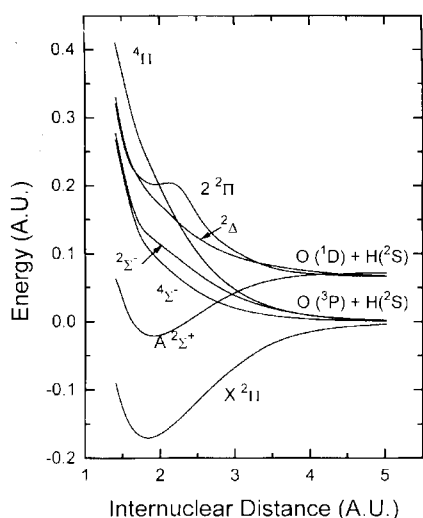


Figure 1. Potential energy curves of OH. The zero of energy is defined as the baricenter of the energies of the triplet oxygen atom fine structure states.

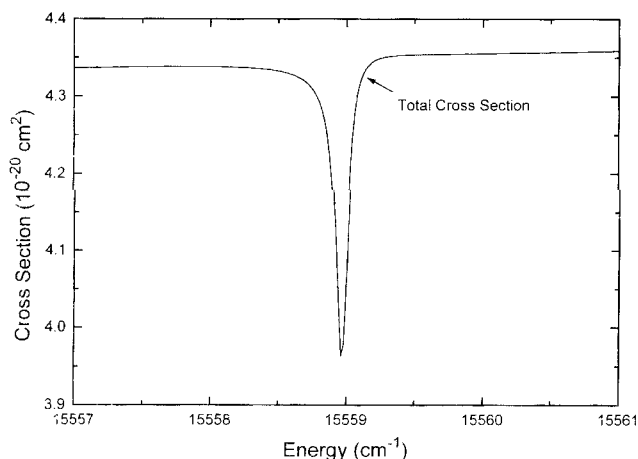


Figure 2. Total cross section near the isolated resonance corresponding to the ($J_f = 7/2$ and $\nu_f = 9$) of the $A^2\Sigma^+$ state. The initial ground state is the $X^2\Pi_{3/2}$ state with ($J_i = 7/2$ and $\nu_i = 0$). Optical transition is assumed to occur only to the $^2\Sigma^-$ state.

and $^4\Pi$ states were discussed elsewhere in detail.^{7,8}

Figure 2 depicts the total photodissociation cross section calculated for transitions from the ($J_i = 7/2$ and $\nu_i = 0$) level of the ground state. The resonance corresponding to ($J_f = 7/2$ and $\nu_f = 9$) level of the $A^2\Sigma^+$ state is shown to be highly asymmetric. The resonance in fact looks like a window, indicating that the quantum interference is destructive here.

The dynamic consequence of the asymmetry of the resonance shown in Figure 2 may be significant. Since the present example is a multichannel dissociation, the product branching ratios and the vector properties would show rapid variation near the resonance, as discussed in previous publications. Figure 3 shows that the anisotropy parameters of the angular distributions of $O(^3P_j, j = 0, 1, 2)$ exhibit sharp changes near the resonance. The values of the anisotropy parameters differ from each other near the resonance, and exhibit maxima and minima. On the other hand, at off-reso-

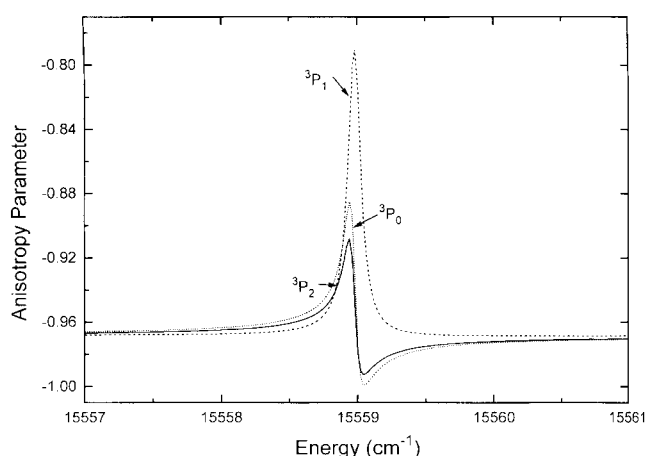


Figure 3. Anisotropy parameters of the angular distributions of $O(^3P_j, j = 0, 1, 2)$ near the isolated resonance depicted in Fig. 2.

nance energies, the anisotropy parameters all approach the high energy recoil limit value of -1 (the $^2\Sigma^- - X^2\Pi$ transition is perpendicular), indicating that the dissociation is mostly direct in this case. However, near the resonance, such a simplified interpretation is not appropriate.

This situation may be frequently encountered in many real molecules. In many experiments, the absence of the bound electronic states optically coupled with the ground state near the excitation energies may tempt one to regard the process as a simple direct dissociation. However, our present analysis clearly demonstrates that the "dark" bound states may significantly influence the process when they interact with the dissociative states. Therefore, analysis of the experimental observations should be carried out carefully, and should employ full quantum treatments, as demonstrated in the present work.

Acknowledgment. This work was supported by the Korea Science and Engineering Foundation (1999-1-121-001-5).

References

1. Glass-Maujean, M.; Breton, J.; Guyon, P. M. *Chem. Phys. Lett.* **1979**, *63*, 591.
2. Brandon, J. T.; Reid, S. A.; Robie, D. C.; Reisler, H. J. *Chem. Phys.* **1992**, *97*, 5246.
3. Kim, B.; Yoshihara, K.; Lee, S. *Phys. Rev. Lett.* **1994**, *43*, 424.
4. Kim, B.; Yoshihara, K. *J. Chem. Phys.* **1993**, *99*, 1433.
5. Lewis, B. R.; Banerjee, S. S.; Gibson, S. T. *J. Chem. Phys.* **1995**, *102*, 6631.
6. Fano, U. *Phys. Rev.* **1961**, *124*, 1866.
7. Singer, S. J.; Freed, K. F.; Band, Y. B. *Adv. Chem. Phys.* **1985**, *61*, 1; *J. Chem. Phys.* **1983**, *79*, 6060.
8. Lee, S. *Chem. Phys. Lett.* **1995**, *240*, 595; *ibid.* **1995**, *243*, 250; *Bull. Korean Chem. Soc.* **1995**, *16*, 801; *J. Chem. Phys.* **1995**, *103*, 3501; *ibid.* **1996**, *104*, 1912; *ibid.* **1996**, *104*, 7914; *ibid.* **1996**, *105*, 10782; *ibid.* **1997**, *107*, 1388; *J. Phys. Chem.* **1995**, *99*, 13380; *Phys. Rev. A* **1996**, *54*, R4621; *J. Chem. Phys.* **1999**, *111*, 6407.