

Prediction of Asymmetric Resonance in the Photodissociation Spectrum of SH

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Asymmetric resonance is an intriguing phenomenon. This interesting feature is now well known to be due to the interplay of the discrete and continuum states.¹ Experimental and theoretical treatments of asymmetric resonances yielded invaluable information on the dynamics of photoionization² processes of many atoms and molecules. Although observations of the asymmetric resonances in the photodissociation processes were relatively rare, quite numerous reports were recently made on the asymmetric resonances in photodissociation spectra of molecules such as H₂,³ NO,⁴ FNO,⁵ Cs₂,⁶ O₂,⁷ Na₂.⁸ Theoretical predictions were also made for the OH molecule.⁹⁻¹³ Systematic analysis of the shape of resonances not only yielded profound insight into the detailed dynamics of indirect dissociation processes, but also showed that the properties of the photofragments may strongly change near the asymmetric resonance.^{5, 9-12}

In the present paper, we show that asymmetric resonance may be observed for the dissociation of the SH molecule by carrying out close-coupling computation of the photodissociation spectra. We predict that the effects of quantum interference could produce asymmetric resonance in the predissociation of the A²Σ⁺ state of the SH molecule at energies above the threshold to S(¹D), proposing highly desirable experiments on this important molecule.

The theory was described in detail in Ref. 9. It includes all the interactions (except the hyperfine interactions) between the electronic states participating in the process, treat the complicated angular momentum couplings, and also analyze the asymptotic scattering states in a proper way. Two kinds of basis functions are used in the calculations to evaluate the total Hamiltonian. Hund's case (a) basis function of parity *p*, |JMCAΣ*p*> is employed to evaluate the electronic Hamiltonian, which is diagonal in this basis. *J* is the total angular momentum, *M* is its component along the space-fixed axis, *S* is the total spin, and *C* denotes any other electronic state labels. Other Hund's case basis functions can also be employed to give identical results, as long as all of the interactions are included in the calculations. The asymptotic basis functions |JM*f*l*c**s**j**f**H*>, are used to evaluate the spin-orbit Hamiltonian and the rotational part $I(I+1)/2\mu r^2$, since they are diagonal in this basis. Here *j*_S (*j*_H) are the total electronic angular momentum of the sulfur (hydrogen) fragment and *l* and *μ* is the orbital angular momentum and its projection along the SF axis, respectively, $j = j_S + j_H$, and *c*_S denotes extra quantum numbers needed to describe the electronic states of sulfur besides *j*_S (that is, *S* and *A*). The two basis functions are related to each other by *r*-independent transfor-

mation matrices $\langle j|c_S j_S |C A S \Sigma p \rangle_{j..}$, which is the most important ingredient of the theory. The continuum wavefunction is propagated in the ABO basis |JMCAΣ*p*> using the Renormalized Numerov method. Propagation was carried out to *R*=25 bohr, and the number of integration steps was increased to 3000 in order to ascertain convergence. The transition amplitudes in ABO basis are transformed into the asymptotic basis |JM*f*l*c**s**j**f**H*> by the two frame transformation matrices at the end of the propagation and boundary conditions are imposed. The potentials obtained by Manaa¹⁴ are employed for X²Π, ⁴Σ⁻, ²Σ⁻ and ⁴Π states. The potential for the A²Σ⁺ state is that given by Ashfold.¹⁵ The ²Δ and ²Π and states are represented by the potential curves of Park and Sun.¹⁶

Figure 1 depicts the potential curves of the electronic states included in the present calculations. Zero of the energy is defined as the statistical average of the energy splittings of S(³P_{*j*}, *j*=0, 1, 2) in Figure 1. The X²Π, ⁴Σ⁻, ²Σ⁻ and ⁴Π states correlate with S(³P), while the A²Σ⁺, ²Δ and ²Π states correlate with S(¹D). The predissociation of the A²Σ⁺ state results from the spin-orbit couplings of this state with the three repulsive ⁴Σ⁻, ²Σ⁻ and ⁴Π states. At energies between thresholds to S(³P) and S(¹D), the dynamics is described as pre-

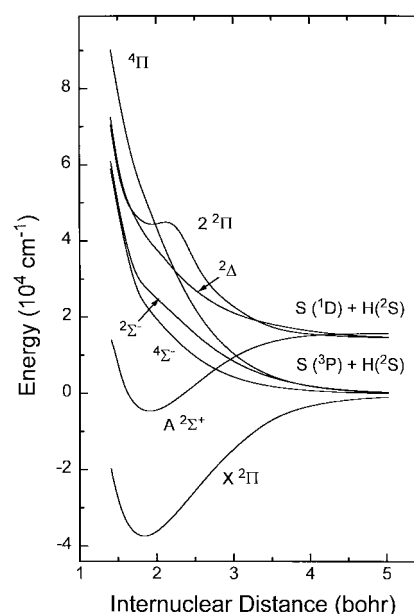


Figure 1. *Ab initio* Potential energy curves of SH. Zero of the energy is defined as the baricenter of the energies of S(³P_{*j*}, *j*=0, 1, 2).

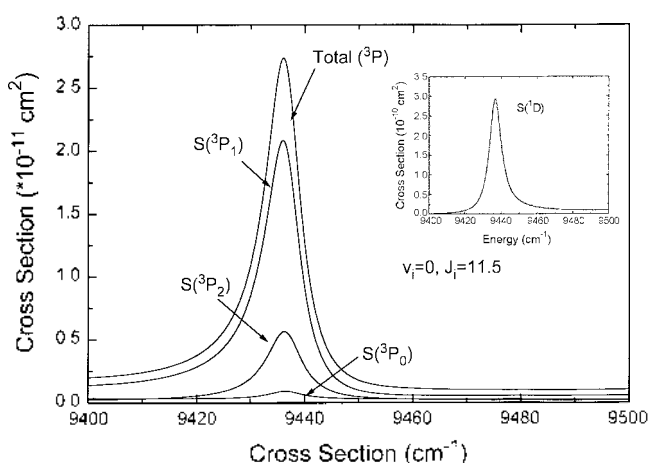


Figure 2. A threshold resonance lying above the threshold to $S(^1D)$, reached from the initial ground $X^2\Pi^+_{2,3}$ state ($J_i=11.5$ and $v_i=0$).

dissociation of the $A^2\Sigma^-$ state by the three dissociative $^4\Sigma^-$, $^3\Sigma^-$ and $^4\Pi$ states. Since both of the binding $A^2\Sigma^-$ and dissociative $^3\Sigma^-$ state are optically coupled with the ground $X^2\Pi$ state, and since these two excited states interact by spin-orbit couplings, absorption spectrum in this energy regime may exhibit asymmetric resonance as a result of the quantum interference between two indistinguishable pathways: that is, between the indirect dissociation path *via* the $A^2\Sigma^+$ state and the direct path *via* the $^3\Sigma^-$ state.

For most of the resonances, the Franck-Condon factor for the $^3\Sigma^-$ - $X^2\Pi$ transition is highly unfavorable, giving only minor contribution to the direct dissociation pathway. Therefore, the dissociation is dominated by predissociation of the $A^2\Sigma^+$ state by the three repulsive $^4\Sigma^-$, $^3\Sigma^-$ and $^4\Pi$ states, and the resonances are essentially Lorentzian. However, we find that for the resonances lying above the threshold to $S(^1D)$ the contribution of the dissociative $^3\Sigma^-$ pathway becomes sufficiently appreciable due to the increased $^3\Sigma^-$ - $X^2\Pi$ vibrational overlap to give asymmetric resonance. Fig. 2 shows such a resonance reached from the initial ground $X^2\Pi_{2,3}$ state ($J_i=11.5$ and $v_i=0$). The resonances in the total as well as in the partial cross sections to each of the sulfur fine structure components exhibit asymmetric features. The dissociation to $S(^1D)$ is open at energies near this resonance, and the spectrum for dissociation to this state of the sulfur atom is also given in Figure 2. It is interesting to see that the shape of the asymmetric resonances in the spectrum for dissociation to $S(^3P)$ and $S(^1D)$ are different. For $S(^3P)$ the q -parameter is negative, while that for dissociation to $S(^1D)$ is positive.

Since the resonance shown in Figure 2 lies above the threshold to $S(^1D)$, it does not correspond to the rovibra-

tional levels of the $A^2\Sigma^+$ state. It rather seems to correspond to the shape resonance attributable to the centrifugal barrier of the dissociative states, since similar calculations with lower J do not display such resonances. It is, however, different from ordinary shape resonance, since the effects of the asymptotic interactions are also seen. For example, it should be noted that the resonance is seen both in the cross section for dissociation to $S(^3P)$ and to $S(^1D)$ in Figure 2. If the resonance is due to the centrifugal barrier of only one of the dissociative states, cross sections for dissociation to $S(^3P)$ or to $S(^1D)$ would exhibit resonance. Therefore, it seems to be of multichannel character, as shown by Freed and co-workers for the threshold resonances in the photodissociation of CH^+ .¹⁷ More discussions will be reported in subsequent publications.

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References

1. Fano, U. *Phys. Rev.* **1961**, *61*, 1866.
2. Lefebvre-Brion, H.; Field, R. W. *Perturbations in the Spectra of Diatomic Molecules*; Academic Press: New York, 1986.
3. Glass-Maujean, M.; Breton, J.; Guyon, P. M. *Chem. Phys. Lett.* **1979**, *63*, 591.
4. Ashfold, M. N. R.; Dixon, R. N.; Prince, J. D.; Tutchter, B.; Western, C. M. *J. Chem. Soc., Faraday Trans. II* **1986**, *82*, 1257.
5. Brandon, J. T.; Reid, S. A.; Robie, D. C.; Reisler, H. *J. Chem. Phys.* **1992**, *97*, 5246.
6. Kim, B.; Yoshihara, K. *J. Chem. Phys.* **1993**, *99*, 1433.
7. Lewis, B. R.; Banerjee, S. S.; Gibson, S. T. *J. Chem. Phys.* **1995**, *102*, 6631.
8. Liu, Y.; Li, J.; Gao, H.; Chen, D.; Li, L.; Field, R. W.; Lyyra, A. M. *J. Chem. Phys.* **1998**, *108*, 2269.
9. Lee, S. *J. Chem. Phys.* **1995**, *103*, 3501.
10. Lee, S. *Chem. Phys. Lett.* **1995**, *240*, 595; **1995**, *243*, 250.
11. Lee, S. *J. Chem. Phys.* **1996**, *104*, 1912; **1996**, *105*, 10782; **1997**, *107*, 1388; **1999**, *111*, 6407.
12. Lee, S. *Phys. Rev. A* **1996**, *54*, R4621; **1998**, *58*, 4981.
13. Lee, S. *Bull. Korean Chem. Soc.* **1995**, *16*, 387; **2000**, *21*, 497.
14. Riad Manaa, M. *Int. J. Quant. Chem. Quantum Chem. Symp.* **1995**, *29*, 577.
15. Wheeler, M. D.; Orr-Ewing, A. J.; Ashfold, M. N. R. *J. Chem. Phys.* **1997**, *107*, 7591.
16. Park, J. K.; Sun, H. *Chem. Phys. Lett.* **1992**, *194*, 485.
17. Williams, C. J.; Freed, K. F.; Singer, S. J.; Band, Y. B. *Faraday Discuss. Chem. Soc.* **1986**, *82*, 4762; Williams, C. J.; Freed, K. F. *J. Chem. Phys.* **1986**, *85*, 2699.