

Behavior of Angular Distributions of $S(^3P)$ Near Multichannel Asymmetric Resonance in the Photodissociation of SH

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Most resonances observed in chemical physics are for pre-dissociation processes due to either curve crossing (Feshbach-type resonance) or potential barrier (shape resonance). The origin of these types of resonance is quite well understood: They correspond to rovibrational levels of bound electronic state perturbed by interactions with continuum states.^{1,2} The latter interactions cause position shifts and broadening of the resonance.³ Recently, however, new kind of resonance was predicted to occur due to very complicated interplay of many electronic states correlating to identical or different atomic terms. The first example studied was CH^+ . Freed and co-workers⁴ predicted that multichannel resonances may appear in the photodissociation spectrum due to interactions among different adiabatic Born-Oppenheimer (ABO) states correlating with the same atomic term ($C(^2P)$ in the case of CH^+). This type of resonances is different from the conventional ones in that they may be observed above the dissociation threshold. Therefore, they do not correspond to any rovibrational levels and cannot be assigned definite vibrational quantum numbers. Scalar properties (such as product branching ratios) or vector properties (angular distributions, orientation and alignment) may display extensive changes near this near-threshold multichannel type resonance.⁴

In the present article, we show that the angular distributions of the sulfur atom fine structure states $S(^3P_j, j = 0, 1, 2)$ may exhibit such rapid changes near the multichannel resonance in the photodissociation of the SH molecule, proposing highly desirable experiments on this important molecule. We compute the anisotropy parameters β_D of $S(^3P_j, j = 0, 1, 2)$ by employing close coupled methods for photodissociation amplitudes.

The theory was described in detail in Ref. 5. 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 , $|JMCA\Sigma p\rangle$ 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 $|JMf/c_s j_H\rangle$, are used to evaluate the spin-orbit Hamiltonian and the rotational part $l(l-1)/2\mu^2$, 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 transformation matrices $\langle j|c_s j_H|CA\Sigma p\rangle$, which is the most important ingredient of the theory. The continuum wavefunction is propagated in the ABO basis $|JMCA\Sigma p\rangle$ using the Renormalized Numerov method.⁶ 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 $|JMf/c_s j_H\rangle$ by the two frame transformation matrices at the end of the propagation and boundary conditions are imposed. The potentials obtained by Manaa⁷ are employed for $X^2\Pi$, $^4\Sigma^-$, $^2\Sigma^-$ and $^4\Pi$ states. The potential for the $A^2\Sigma^+$ state is that given by Ashfold.⁸ The $^2\Delta$ and $2^2\Pi$ and states are represented by the potential curves of Park and Sun.⁹

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 $X^2\Pi$, $^4\Sigma^-$, $^2\Sigma^-$ and $^4\Pi$ states correlate with $S(^3P)$, while the $A^2\Sigma^+$, $^2\Delta$ and $2^2\Pi$ states correlate with $S(^1D)$. Figure 2 shows a multichannel resonance excited from the ($J_r = 11.5$ and $v_r = 0$) level of the ground $X^2\Pi$ state. Since it lies above the threshold to $S(^1D)$, it does not correspond to any rovibrational level of the $A^2\Sigma^+$ state. It is also different from conventional shape resonance, but it is rather attributed to very complicated interplay among ABO states correlating with $S(^3P)$ and $S(^1D)$, as we discussed before.¹⁰ 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. The resonance given in Figure 2 is clearly asymmetric,^{1,5,11-21} indicating that very interesting dynamics may be predicted to occur near it. Partial cross sections to each of the fine structure states of $S(^3P)$ are also depicted in Figure 2. Since they display different degree of asymmetry, the branching ratios for $S(^3P_j, j = 0, 1, 2)$ change considerably near the resonance.

Figure 3 shows the anisotropy parameters β_D of $S(^3P_j,$

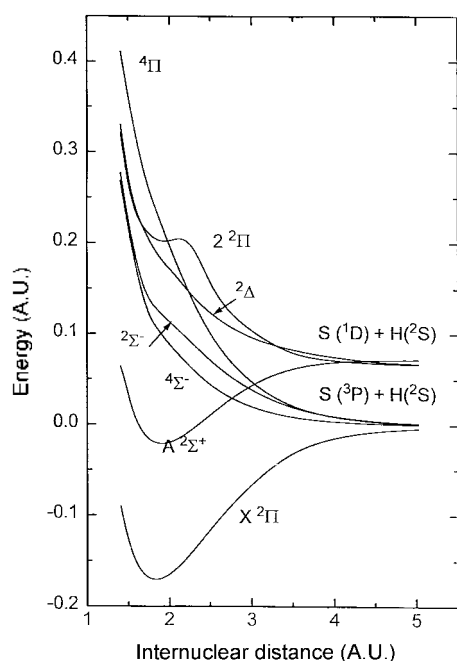


Figure 1. *Ab initio* Potential energy curves of SH. Zero of the energy is defined as the baricenter of the energies of $S(^3P_j, j = 0, 1, 2)$.

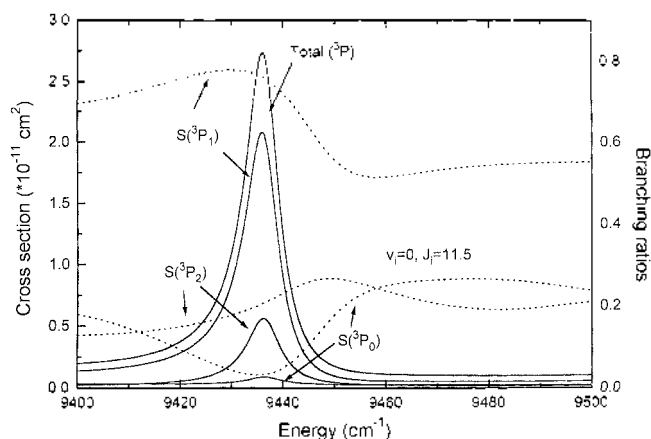


Figure 2. Threshold resonance lying above the threshold to $S(^1D)$, reached from the initial ground $X^2\Pi^+_{2,3}$ state ($J_r = 11.5$ and $v_r = 0$).

$j = 0, 1, 2$) produced from photodissociation of SH near the resonance. The values of β_D are very different from each other, and they change rapidly near the resonance. Far from the resonance, the anisotropy parameters approach the value of (-1) which is the high energy recoil limit value for perpendicular ($|\Delta\Omega| = 1, \Pi \leftarrow \Sigma$) electronic transition. Near the resonance, however, β_D 's for $S(^3P_j, j = 0, 1, 2)$ increase to 0.7 and 0.5, respectively, as a result of interactions of ABO states depicted in Figure 1 and the effects of intensity borrowing of the optically dark states from the bright states ($A^2\Sigma^+, ^2\Sigma^-, 2^2\Pi$ and $^2\Delta$). Different values of β_D 's for $S(^3P_j, j = 0, 1, 2)$ near the resonance suggests that angular resolution of photofragments may be possible near the multichannel resonance.

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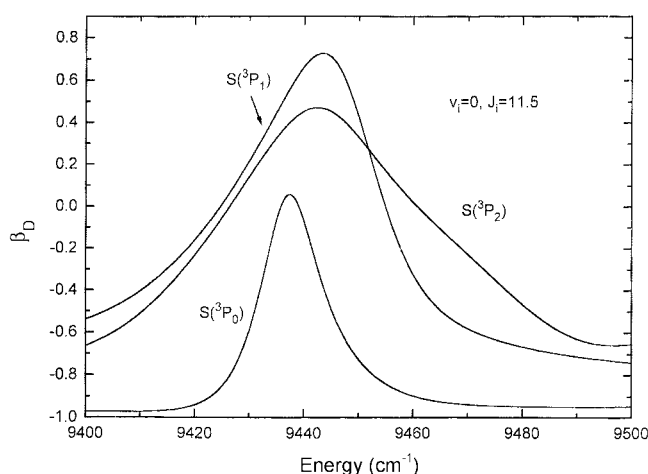


Figure 3. Anisotropy parameters of $S(^3P_j, j = 0, 1, 2)$ near the threshold resonance shown in Figure 2.

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