Widths and Positions of Isolated Resonances in the Predissociation of SH: Quantal Treatments

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The predissociating resonances are treated for the SH molecule by quantal method. The isolated resonances (N' = 0, v' = 0-6) are predicted to be highly Lorentzian. The widths and positions of the isolated resonances are computed as functions of v'. The magnitudes and signs of the widths and the shifts as functions of v' are discussed in terms of the distance of the resonance from the crossing points between the bound state ($A^2\Sigma^+$) and the repulsive states ($^4\Sigma^-$, $^2\Sigma^-$ and $^4\Pi$).

Keywords : Resonance, Predissociation, SH.

Introduction

Predissociation is an interesting phenomenon occurring due to the failure of the Born-Oppenheimer approximation. Crossing between bound and repulsive potential surfaces causes the mixing of the corresponding electronic states, and it gives several important effects on the photoabsorption spectra. First, the energy levels of the bound electronic state broaden, appearing as broad resonances in the spectra, and second, they shift from the unperturbed positions. Since these characteristic features of the resonance are related to the interactions between the bound and dissociative states in useful way (for example, the width is proportional to the square of the interaction: see Eq. (1) below), measurements on these properties would give detailed knowledge on non-Born-Oppenheimer interactions.

SH is an important molecule playing major role in atmospheric[1] and combustion[2] reactions. Since the three repulsive ($^4\Sigma^-$, $^2\Sigma^-$ and $^4\Pi$) electronic states cross a bound ($A^2\Sigma^+$) state, the predissociation is a very complicated multichannel phenomenon, and the interactions between these repulsive states would also affect the dynamics, in addition to the spin-orbit couplings between the $A^2\Sigma^+$ state and the three repulsive states. The effects of these interactions may show up in important properties of the photofragment (sulfur atom), such as the branching ratios and angular distributions.[3-6]

In this work, we focus on the widths and positions of the resonances in the total photodissociation spectra of SH, since these are the two most important characteristics of the resonance. We study the v' = 0 to v' = 6 resonances (N' = 0) and compute the widths and shifts as functions of the vibrational quantum number v' by employing close coupling methods. We show that the general trends of these properties can easily be understood in terms of the distance of the resonances from the crossing points. We only consider isolated resonances here, since other effects may significantly complicate the analysis on overlapping resonances. We examine several interesting behaviors of these properties as functions of v', and give discussions based on the distance of the resonance from the crossing points between the bound state ($A^2\Sigma^+$) and the repulsive states ($^4\Sigma^-$, $^2\Sigma^-$ and $^4\Pi$), by invoking the mathematical expressions of the widths and shifts of the resonance.

Theory

The theory employed here was described in detail in Ref. 3. The basic ingredient of the theory is the frame transformation matrix that connects the adiabatic Born-Oppenheimer (ABO) states to the atomic term. Since two atomic terms (S(^{3}P) and S(^{1}D)) are involved in the photodissociation of SH, two transformation matrices are constructed and employed in the present work. Two basis sets are employed to describe the dissociation dynamics in the molecular and asymptotic region, respectively. The first basis (ABO basis) is a space-fixed basis derived from Hund's coupling cases. Hund’s case (a) basis is used here. The second basis set, which is called ‘asymptotic’ molecular basis, diagonalizes the total Hamiltonian at infinite internuclear distances. These two basis sets are related to each other by r-independent transformation matrix. Close-coupled equations are solved for the continuum wave function. Photodissociation amplitudes to a specific fine structure component of the sulfur atom are computed by the Golden Rule. The potential curves of the $X^2\Pi$, $^4\Sigma^-$, $^2\Sigma^-$ and the $^4\Pi$ states are those given by Manaa.[7] The $2^2\Pi$ and the $^2\Delta$ states are taken from the work by Park and Sun.[8] The potential curve for the $A^2\Sigma^+$ state is that given by Ashfold and co-workers.[9] The transition dipole moments for the optical transitions from the initial $X^2\Pi$ state to the $A^2\Sigma^+$, $^2\Sigma^-$, $2^2\Pi$ and $^2\Delta$ states were obtained by employing the effective valence shell Hamiltonian method. The values of the spin-orbit couplings are taken from the *ab initio* work by Manaa.[7] Propagation of the scattering wave function is carried out by Renormalized Numerov method,[10] and appropriate boundary conditions are

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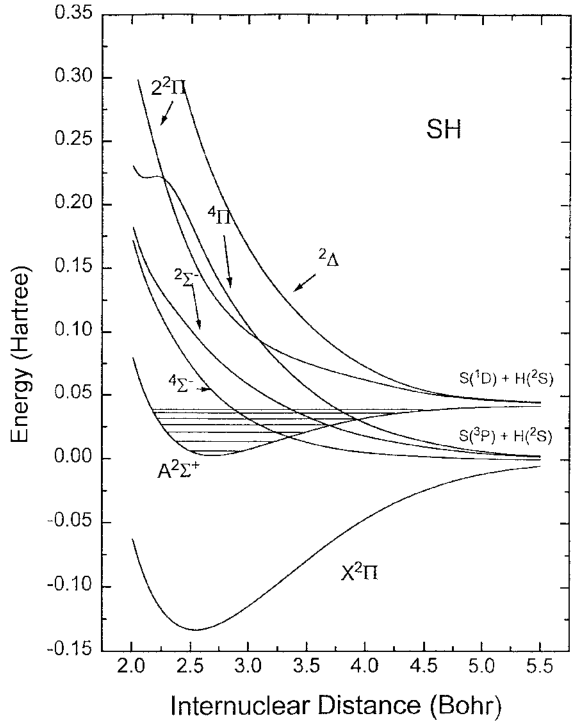

Figure 1. Potential curves of SH. The zero of energy is defined as the statistical average of the energies of S(^{3}P$_j$, j = 0, 1, 2).

imposed at sufficiently large internuclear distance.

Results

The potential curves of the electronic states included in the present calculations are depicted in Figure 1. The X$^2\Pi$, $^4\Sigma^-$, $^2\Sigma^-$ and the $^4\Pi$ states correlate with S(^{3}P), while the A$^2\Sigma^+$, 2$^2\Pi$ and the $^2\Delta$ states correlate with S(^{1}D) term. There are three fine structure states for S(^{3}P), ^{3}P$_2$, ^{3}P$_1$ and ^{3}P$_0$. Of these levels, S(^{3}P$_2$) is of the lowest energy. The zero of energy in Figure 1 is defined as the baricenter of these three fine structure states of S(^{3}P). The A$^2\Sigma^+$, $^2\Sigma^-$, 2$^2\Pi$ and $^2\Delta$ states carry oscillator strengths from the ground X$^2\Pi$ state. The bound A$^2\Sigma^+$ state crosses with the three repulsive $^4\Sigma^-$, $^2\Sigma^-$ and the $^4\Pi$ states at R = 3.34, 3.70 and 3.96 bohr, respectively. These crossing points lie at the energy of 3775, 5706 and 6804 cm^{-1}, respectively. Spin-orbit couplings between the bound A$^2\Sigma^+$ state and the three repulsive $^4\Sigma^-$, $^2\Sigma^-$ and the $^4\Pi$ states account for the predissociating resonances considered here. The magnitudes of these spin-orbit couplings at the crossing points are 52, 59 and -150 cm^{-1}, respectively. Although the ground X$^2\Pi$ state and the A$^2\Sigma^+$ state do not cross in the normal sense, spin-orbit coupling between these two states are also included in the present work.

Figure 2 depicts a typical predissociating resonance obtained here, which corresponds to the v' = 5 and N' = 0 level of the A$^2\Sigma^+$ state (N' is the rotational quantum number of the Hund's case (b) state, $N' = J'-S'$), reached from the ground X$^2\Pi^-_{3/2}$ state with v_i = 0, J_i = 1.5 (v_i and J_i are the vibrational quantum number and the total angular momentum quantum number, respectively, of the ground X$^2\Pi$ state). The resonance is highly Lorentzian, indicating that no significant changes will be observed for the branching ratios of S(^{3}P$_j$, j = 0, 1, 2) near this resonance. The width (half width at half maximum) of this resonance is 0.9 cm^{-1}, and the shift from its zeroth order (unperturbed) position, computed is +6.27 cm^{-1}. It should be noted that the unperturbed position here (and in Table 1) is the energy of the eigenstate of the A$^2\Sigma^+$ state that is *not* coupled with other electronic states. In this paper we computed it by Cooley's procedure.[11] Since the N' = 0 level of the A$^2\Sigma^+$ state can only be accessible from the X$^2\Pi^-_{3/2}$ (v_i = 0, J_i = 1.5) state, and since the other states reachable from this initial state (those with N' = 2) are separated from this resonance by much more than the width, it can be considered as isolated resonance.

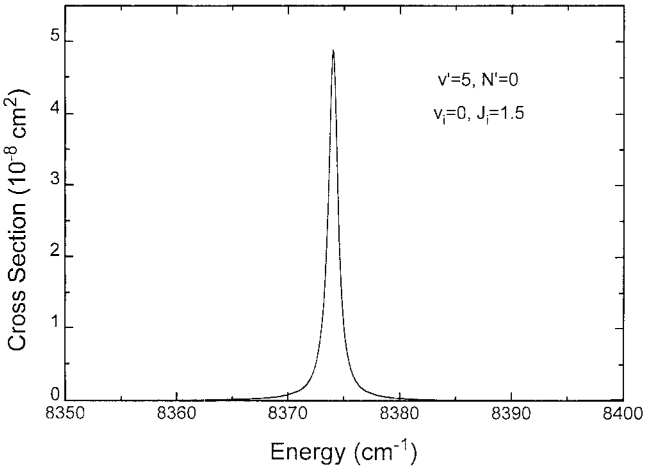

Figure 2. The isolated resonance corresponding to the v' = 5 and N' = 0 level of the A$^2\Sigma^+$ state accessed from the ground X$^2\Pi^-_{3/2}$ state with v_i = 0, J_i = 1.5.

Table 1 gives the widths and energy shifts of the resonances corresponding to the N' = 0 level of the A$^2\Sigma^+$ state for v' = 0-6. Several interesting features are found for these resonances. First, the widths for the resonances for low v' are very small, indicating that the lifetimes of these resonances are rather large. This is due to the fact that the lower levels are far from the crossing points. Second, the widths show quite complicated behavior: they increase up to v' = 4, reach minimum at v' = 5 and increase to v' = 6. Third, the magnitudes of the shifts of the resonances from the unperturbed positions reach maximum for v' = 3, and they change sign from v' = 3 (negative) to v' = 4 (positive).

These interesting patterns may be understood by examining the mathematical expressions[12] for the width Γ_j and the shift ΔE_j of the resonance j,

$$\Gamma_j = 2\pi\langle\varphi_j|H_{so}|\psi_E\rangle^2, \tag{1}$$

and

$$\Delta E_j = P\int dE'\frac{\langle\varphi_j|H_{so}|\psi_{E'}\rangle^2}{(E_j - E')}. \tag{2}$$

In these expressions, $|\varphi_j\rangle$ and $|\psi_E\rangle$ are the wave functions of the unperturbed bound state (unperturturbed eigenstate of the A$^2\Sigma^+$ state here) and the continuum state (eigenstate of

Table 1. Widths (cm^{-1}) and shifts (cm^{-1}) of the resonances corresponding to $N' = 0$ levels of the $A^2\Sigma^+$ state ($v' = 0$-6)

v'	Widths	Unperturbed positions	Shifts
0	8.4×10^{-4}	1526.34	−0.17
1	0.502	3310.82	−1.09
2	2.3	4896.23	−1.18
3	5.6	6275.73	−4.33
4	22.2	7438.47	+0.93
5	0.90	8367.30	+6.27
6	5.58	9032.63	+7.47

the coupled repulsive $^4\Sigma^-$, $^2\Sigma^-$ and $^4\Pi$ states), respectively, H_{50} is the spin-orbit coupling, and P denotes the principal part of the integral. As can be seen in Eq. (1), the width is proportional to the square of the overlap integral. Since most of the overlap occurs between the parts of the bound and continuum wave functions near the classical turning points, maximum overlap will be realized when the classical turning points of the two wave functions at the given energy coincide. This situation is obtained at energies near the crossing point, indicating that repulsive state crossing the bound electronic state nearest to the energy of the vibrational level mostly accounts for the predissociation of that level. This explains the very large width of the $v' = 4$ resonance in Table 1 very well. The $v' = 4$ level of the $A^2\Sigma^+$ state is very close to the crossing point between the $A^2\Sigma^+$ and the $^4\Pi$ state. This effect is reinforced by the large spin-orbit coupling (-150 cm^{-1}) between these two states near the crossing point. On the other hand, the $v' = 0$ to $v' = 2$ resonances are far from any of the crossing points, and their widths are rather small. It is intriguing to see that the width for the $v' = 6$ resonance is larger than that for the $v' = 5$ resonance despite the fact that the latter is farther from the crossing points. The general rule as given above doesn't apply in this case. It seems that the vibrational wave function for the $v' = 6$ level is such that the overlap with the continuum wave function is accidentally larger than for the $v' = 5$ level.

Similarly, the change of the signs of the shifts of the resonance positions from $v' = 3$ to $v' = 4$ can be easily understood by examining Eq. (2): The sign of the quantity ΔE_j is determined by the sign of $(E_j - E')$. Thus, if the bound level is below (above) the continuum wave functions, that is, below (above) the crossing points, ΔE_j will be negative (positive). Since the $v' = 0$ to $v' = 3$ levels are below the crossing points, these resonances are shifted negatively from their unperturbed positions, while the $v' = 5$-6 resonances are shifted to higher energies. The $v' = 4$ resonance lies between the two lowest crossing points, and the shift would be determined by the compromise of the two opposing effects. It turns out that the effect from the lower crossing dominates, giving small positive value (0.93 cm^{-1}) for the shift. The magnitudes of the shifts as function of v' is also easily understandable by invoking Eq. (2): The magnitude of ΔE_j will increase when $(E_j - E')$ is small, that is, when the resonance is near the crossing point. Therefore, the magnitude of ΔE_j increases with v' for $v' \le 3$ as the resonance gets closer to the crossing points.

Although the widths and positions are the most commonly measured properties of the resonances, there are other properties that may also be very important in the dynamical sense, such as the branching ratios, angular distributions of the atomic fragments produced in the predissociation of SH. More analysis will be reported in subsequent publications.

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