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## Two-photon resonance enhanced MPI-PES above the lowest ionization threshold. Observation of the $[a^1\Delta]5p\pi^2\Phi$ state of the SH (SD) radical

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### Abstract

A  $(2+1)$  resonance enhanced multiphoton ionization photoelectron spectroscopy (REMPI-PES) study of the hitherto unobserved  $[a^1\Delta]5p\pi^2\Phi$  Rydberg state of the SH (SD) radical is reported. Despite the fact that this state has an excitation energy which exceeds the lowest ionization energy, ionization is observed to occur preferentially by the absorption of a third photon after the two-photon excitation step, rather than through autoionization. Photoelectron spectra show a large asymmetry in the rotational branching ratios, which is attributed to the high value of  $A^+$  in the ionic state.

### 1. Introduction

The mercapto radical (SH) plays an important role in the ultraviolet photochemistry of sulphur-containing species released into the atmosphere from natural and anthropogenic sources. Moreover, as the result of the relatively high cosmic abundance of sulphur the molecule is also of interest from an astrophysical point of view. Nevertheless, detailed information of its spectroscopic and photochemical properties is relatively scarce [1–3].

The  $X^2\Pi$  ground state of the SH radical has a  $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(4\sigma)^2(5\sigma)^2(2\pi)^3$  electronic configuration. Spin-orbit interaction ( $A'_0 = -376.835 \text{ cm}^{-1}$ ) leads to an inverted splitting, with the  $^2\Pi_{3/2}$  state below the  $^2\Pi_{1/2}$  state [1]. The highest occupied molecular orbital in the ground

state ( $2\pi$ ) is essentially a nonbonding  $3p_x$  atomic orbital on the sulphur atom. Removal of an electron from this orbital gives rise to three different ionic states,  $X^3\Sigma^-$ ,  $a^1\Delta$ , and  $b^1\Sigma^+$ , which are located at 10.42, 11.65, and 12.76 eV above the ground state of the neutral radical [4,5].

Resonance enhanced multiphoton ionization (REMPI) spectroscopy has proven to be a versatile tool for the study of Rydberg states. Such studies have enabled identification of Rydberg states of a large range of molecular and radical systems, particularly when used in combination with high-resolution photoelectron spectroscopy (REMPI-PES) [6,7]. In the present study we have applied REMPI-PES to characterize a hitherto unobserved Rydberg state of the SH radical with an excited ionic core, viz., the  $^2\Phi$  state derived from the excited core configuration

$[a^1\Delta]5p\pi$ . The results show that this state is unusual in a number of respects. Although its excitation energy exceeds the lowest ionization energy and autoionization processes would therefore be expected to dominate the ionization dynamics, two-photon excitation spectra with well-resolved rotational structure could be obtained. The present work demonstrates that in this particular state autoionization processes play a relatively minor role, i.e. after excitation of the  ${}^2\Phi$  state the molecule is dominantly ionized by absorption of another photon. Finally, we report preliminary partially rotationally resolved photoelectron spectra resulting from  $(2+1)$  REMPI via the  $[a^1\Delta]5p\pi$   ${}^2\Phi$  state. These spectra show significant differences from previously reported rotationally resolved photoelectron spectra in other molecules, and underline the need for a proper quantum mechanical description of the ionization process.

## 2. Experimental

A detailed description of the experimental setup has been reported elsewhere [7]. Ground-state SH (SD) radicals were produced by photolysis of  $H_2S$  ( $D_2S$ ) via excitation to the first dissociative absorption band which spans the wavelength range 180–270 nm. A single excimer-pumped dye laser provided photons both for the photolysis and for the subsequent two-photon resonant MPI spectroscopy of the SH (SD) radicals. For calibration purposes resonances of xenon and of atomic sulphur (which is also produced by the photolysis of  $H_2S$  ( $D_2S$ ) and SH (SD)), in the two-photon energy range of 79500–89800  $cm^{-1}$  were used to provide both wavelength and photoelectron kinetic energy calibration. As a consequence of the space charge effects due to  $H_2S^+$  ( $D_2S^+$ ) and  $S^+$  ions created by the absorption of two photons the energy resolution in the photoelectron spectra obtained on these  $(2+1)$  REMPI transitions of SH (SD) was limited to  $\approx 25$  meV. With the spectrometer operating in the ion-detection mode the peaks corresponding to  $S^+$ ,  $SH^+$  ( $SD^+$ ), and  $H_2S^+$  ( $D_2S^+$ ) could be well separated.

$H_2S$  (99.6%, Messer Griesheim) and  $D_2S$  (98%D, Campro Scientific) were used without further purification. Each was introduced into the spectrometer, in turn, as a continuous effusive ‘leak’.

## 3. Results

Figs. 1a and 2a show the two-photon excitation spectra of the SH and SD radical in the two-photon energy range of 84800–85600  $cm^{-1}$  obtained by monitoring only photoelectrons with a kinetic energy of about 4.2 eV. These photoelectrons derive from a photoionization process in which ground state  $X^2\Pi(v''=0)$  SH (SD) radicals absorb three photons and are ionized into the  $a^1\Delta(v^+=0)$  ionization continuum. Confirmation that the resonances in the excitation spectrum do indeed derive from resonance enhancement at the two-photon level by a bound state of the SH (SD) radical is found by measuring excitation spectra with mass-resolved ion detection. The spectra obtained when monitoring the  $SH^+$  ( $SD^+$ ) channel show all the same features as the above electron-detected spectra. The excitation spectra show two sub-bands whose energy separations correspond well with the spin-orbit splitting of the  $X^2\Pi$  ground state ( $A_0''(SH) = -376.96$   $cm^{-1}$  [1],  $A_0''(SD) = -376.75$   $cm^{-1}$  [8]).

Rotational analysis of these excitation spectra has been performed using combination differences based upon the well-known rotational constants of the  $X^2\Pi$

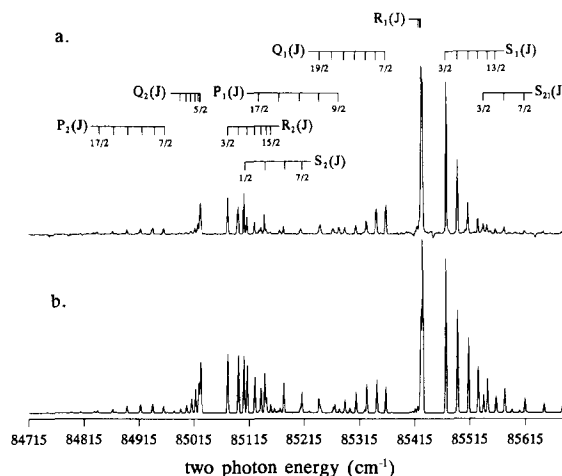


Fig. 1. Two-photon excitation spectrum of the  $[a^1\Delta]5p\pi^2\Phi(v' = 0) \leftarrow X^2\Pi(v'' = 0)$  transition of SH. Individual line assignments are indicated by the combs above the spectrum. (a) Experimental spectrum obtained by collecting photoelectrons deriving from a  $(2+1)$  ionization process to the  $a^1\Delta(v^+ = 0)$  state. (b) Simulated spectrum employing the spectroscopic constants given in Table 1.

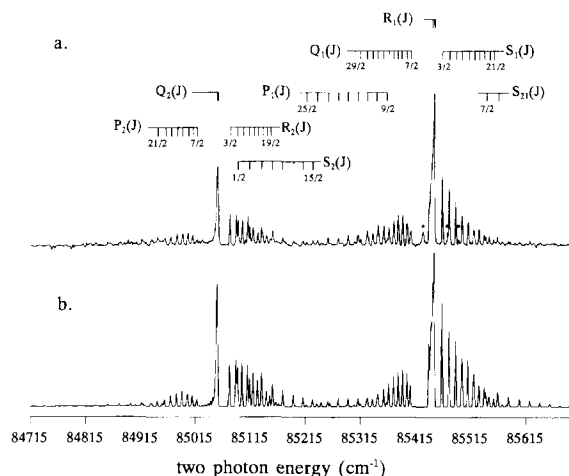


Fig. 2. Two-photon excitation spectrum of the  $[a^1\Delta]5p\pi^2\Phi(v'=0) \leftarrow X^2\Pi(v''=0)$  transition of SD. Individual line assignments are indicated by the combs above the spectrum. (a) Experimental spectrum obtained by collecting photoelectrons deriving from a  $(2+1)$  ionization process to the  $a^1\Delta(v^+=0)$  state. The resonances marked with an asterisk do not derive from SD but from SH impurities. (b) Simulated spectrum employing the spectroscopic constants given in Table 1.

ground state and the calculation of rotational line strengths. The latter have been obtained by inserting the wavefunctions for both the ground and excited states, expressed in a parity-conserving Hund's case (a) basis, and matrix elements derived using a conventional linear molecule Hamiltonian [9], into the appropriate expression for the two-photon transition probability [10]. The comparison of experimental with simulated excitation spectra for several possible excited-state symmetries led to the unambiguous conclusion that the transitions observed in Figs. 1a and 2a derive from a two-photon  $^2\Phi \leftarrow \leftarrow ^2\Pi$  transition. This conclusion is buttressed by the fact that in the excitation spectra no transitions to excited state levels with  $J' \leq 3/2$  could be discerned in either spectrum, and by the observation that the relative intensities of the various rotational branches can be reproduced reasonably well by the  $T_{\pm 2}^2$  two-photon transition tensor.

The spectral parameters obtained from a least-squares fit to the observed line positions are given in Table 1, while the simulated spectra based upon these constants are depicted in Figs. 1b and 2b. In simulating these spectra we have taken the distribu-

Table 1

Spectroscopic constants (in  $\text{cm}^{-1}$ ) derived in the present study for the zero point level of the  $[a^1\Delta]5p\pi^2\Phi$  state of SH and SD

	$T_0$	$B_0$	$D_0 \times 10^4$	$A_0$
SH ( $X^2\Pi$ )		9.604	4.8299	-376.835
SH ( $[a^1\Delta]5p\pi^2\Phi$ )	85277.6(3)	8.350(1)	-0.8(1)	-0.42(8)
SD ( $X^2\Pi$ )		4.900	1.35	-376.75
SD ( $[a^1\Delta]4p\pi^2\Phi$ )	73720.2	4.828	1.3	+8.14
SD ( $[a^1\Delta]5p\pi^2\Phi$ )	85271.3(3)	4.573(2)	0.47(9)	-0.30(6)

The values in parentheses represent one standard deviation in the last digit, except in the case of the band origins. Constants for the zero point level of the  $X^2\Pi$  ground state of SH [1] and SD [8] and the  $[a^1\Delta]4p\pi^2\Phi$  state of SD [3] are included for comparison.

tion of the population over the ground state rotational levels as determined in previous studies on the photodissociation of  $\text{H}_2\text{S}$  ( $\text{D}_2\text{S}$ ) [11,12], i.e. the overall population in the  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  spin-orbit states of SH (SD) is in the ratio of 3:2, and the rotational distribution over each of these states is characterized by a Boltzmann temperature of 300 K.

Figs. 3a and 3b depict the photoelectron spectra obtained for  $(2+1)$  ionization via the  $S_1(3/2)$  and

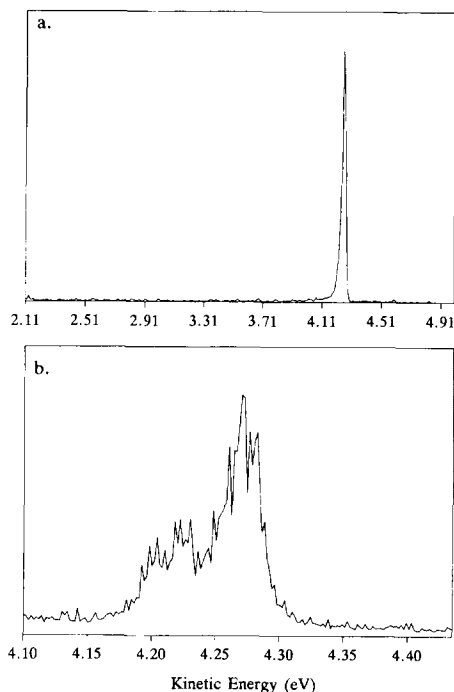


Fig. 3. Photoelectron spectra obtained for  $(2+1)$  ionization via the (a)  $S_1(3/2)$  and (b)  $S_1(13/2) + R_{21}(13/2)$  rotational transitions to the  $[a^1\Delta]5p\pi^2\Phi(v'=0)$  state of SH.

$S_1(13/2) + R_{21}(13/2)$  rotational lines of the  $SH^2\Phi \leftarrow \leftarrow X^2\Pi$  two-photon transition. The first photoelectron spectrum shows that ionization only occurs to the  $a^1\Delta(v^+ = 0)$  level; no photoelectron peaks corresponding to ionization to higher vibrational levels of the  $a^1\Delta$  state, nor to the energetically allowed  $b^1\Sigma^+$  ionic state are observed. Apart from this photoelectron peak the spectra also show a peak of similar magnitude corresponding to the production of slower photoelectrons (not shown in Fig. 3). These photoelectrons might in principle arise from direct two-photon ionization of  $H_2S$  and atomic sulphur, but also from autoionization of the  $^2\Phi$  state of  $SH$  into the  $X^3\Sigma^-$  ionic ground state continua. The present study cannot differentiate between these processes, since the differences between the lowest ionization energies of  $H_2S$  (10.468 eV) [13],  $SH$  (10.421 eV) [4] and  $S$  (10.357 eV) [14] are too small to enable a separation of electrons according to the species from which they originated. However, when excitation spectra are recorded monitoring only the slow photoelectrons, the resonances present in Fig. 1a cannot be observed. This, and the resolution of the observed excitation spectra, would seem to indicate that autoionization of the  $^2\Phi$  state, if present at all, is not a particularly efficient process.

#### 4. Discussion

The rotational analysis of the excitation spectra in Figs. 1 and 2 shows unambiguously that the state responsible for the resonance enhancement is of  $^2\Phi$  symmetry. From the small isotope shift of  $T_0$  in going from  $SH$  to  $SD$  it can be concluded that the  $v^+ = 0$  level is excited. The photoelectron spectra obtained for ionization via  $^2\Phi(v^+ = 0)$  rotational levels allow two further conclusions. First, the ionic core associated with this Rydberg state is the excited  $a^1\Delta(v^+ = 0)$  state of the  $SH^+$  ion. Secondly, the potential energy curves of the  $^2\Phi$  and  $a^1\Delta$  states must be reasonably similar, since only the  $v^+ = 0$  vibrational level of the  $a^1\Delta$  state is observed in the photoelectron spectra.

The results of an *ab initio* study by Bruna and Hirsch [15] suggest that the only  $^2\Phi$  Rydberg states with an  $a^1\Delta$  ionic core and an excitation energy just

above the  $X^3\Sigma^-$  ionic ground state must arise from the  $[a^1\Delta]5p\pi$  and  $[a^1\Delta]4d\pi$  configurations. On the basis of the quantum defects derived from the energies calculated for the  $[a^1\Delta]4p\pi^2\Phi$  and  $[a^1\Delta]3d\pi^2\Phi$  states [15], the former Rydberg states are predicted at excitation energies of 10.43 and 10.67 eV, respectively. The quantum defect derived from the excitation energy of the  $^2\Phi$  state observed in the present study ( $T_0 \approx 10.57$  eV) is either 1.45 or 0.45, depending upon the choice of principal quantum number  $n$ . This value falls between the theoretical limits, and thus offers no unambiguous guide as to whether the observed resonance should be attributed to the  $[a^1\Delta]5p\pi$  or  $[a^1\Delta]4d\pi$  configuration. The results of previous one-photon VUV absorption [2] and (2 + 1) REMPI [3] studies, however, indicate that the highest occupied  $2\pi$  molecular orbital in the ground state is to a major extent composed of the  $3p_x$  orbital on the sulphur atom. The atomic Laporte selection rules for two-photon excitation ( $\Delta l = 0, \pm 2$ ) then would suggest that the observed resonance enhancement at 10.57 eV should be associated with the  $[a^1\Delta]5p\pi$  configuration.

The observation of a rotationally resolved resonance-enhanced excitation spectrum involving a Rydberg state lying at energies above the lowest ionization threshold is highly unusual [16,17]. More generally, autoionization will dominate the overall ionization process and, as a consequence, lead to an extensive broadening of the excitation spectra and limit the role of resonance enhancement. In the present study excitation spectra of the  $[a^1\Delta]5p\pi^2\Phi$  state have been obtained by monitoring only those electrons that specifically derive from a resonance-enhanced ionization process. Apparently the influence of autoionization is reduced to such an extent that its lifetime becomes long enough to allow significant resonance enhancement. In principle a discrete state built upon the  $a^1\Delta$  ionic core is coupled to the ionization continua of the lower-lying  $X^3\Sigma^-$  ground state of the ion via off-diagonal matrix elements which originate from the electrostatic part ( $e^2/r_{ij}$ ) of the electronic Hamiltonian, i.e. such discrete states should be subject to electrostatic autoionization processes leading to an ion in its  $X^3\Sigma^-$  ground state and a free electron [18]. The electrostatic interaction between the  $[a^1\Delta]5p\pi^2\Phi$  Rydberg state and the  $^2\Phi$  final-state continuum is, using Slater determinants,

proportional to the integral  $\langle 2\pi^+(1)5\pi^+(2) | e^2 / r_{12} | \epsilon\phi^+(1)2\pi^-(2) \rangle$ , in which  $\epsilon\phi^+$  denotes the continuum orbital of the leaving electron. Our observation that electrostatic autoionization is not dominant consequently indicates that this integral must be relatively small.

The lowest member of the  $[a^1\Delta]n\pi\pi^2\Phi$  series,  $n = 4$ , has recently been identified in a two-photon resonance-enhanced excitation study with mass-resolved ion detection on SD [3]. For SH only fragmentary rotational structure in the wavelength region of the  ${}^2\Phi \leftarrow \leftarrow {}^2\Pi$  transition could be seen. In this study it was observed that the lower- and higher-frequency rotational branches appeared in the experimental spectrum with, respectively, larger and smaller intensities than predicted by two-photon rotational linestrength calculations. These differences were attributed to the effects of  $l$ -uncoupling within the  $[a^1\Delta]4p$  Rydberg complex. Similar differences are observed in our study of the  $n = 5$  member of this series in both SH and SD. Most probably they also arise from  $l$ -uncoupling phenomena, although we do not wish to rule out completely the influence of heterogeneous predissociation. The measurement of the linewidth of individual rotational transitions should give an indication as to whether such a predissociation is important. However, for the majority of the rotational transitions the linewidths were clearly determined by saturation effects. Saturation was virtually unavoidable as both the production of SH (SD) radicals and the  ${}^2\Phi \leftarrow \leftarrow {}^2\Pi$  transition probability are reduced by lowering the laser power. The overall transition probability is therefore expected to be proportional to the fourth power of the laser intensity. The narrowest rotational line is observed for the strong  $S_1(3/2)$  transition of SH (SD) with a linewidth of  $0.65 \text{ cm}^{-1}$ , which is close to the sum of the effective two-photon laser bandwidth ( $0.35 \text{ cm}^{-1}$ ) and a Doppler-broadening of  $0.2 \text{ cm}^{-1}$ .

When the parameters derived from the rotational analysis of the excitation spectra are considered we notice that the differences with the parameters obtained previously for the  $[a^1\Delta]4p\pi^2\Phi$  Rydberg state of SD are rather larger than might have been expected. First, for the latter state a quantum defect  $\delta$  of 1.66 was found, which is close to the value predicted by the ab initio calculations of Bruna and Hirsch [15]. Our deduced quantum defect of the

$[a^1\Delta]5p\pi^2\Phi$  state, on the other hand, is only 1.45. Secondly, the spin-orbit interaction parameter  $A$  for the  $[a^1\Delta]4p\pi^2\Phi$  state was determined as  $+8.1 \text{ cm}^{-1}$ , a value whose sign at least is in good agreement with a priori expectations since the dominant contribution to this term should arise from the spin-orbit coupling of the single  $4p\pi$  electron. The magnitude of  $A$  seems, however, somewhat large for a Rydberg state with an ionic core which does not contribute to the spin-orbit coupling. On the basis of the value found for the  $[a^1\Delta]4p\pi^2\Phi$  state a value of about  $+3 \text{ cm}^{-1}$  would be predicted for the  $[a^1\Delta]5p\pi^2\Phi$  state. In contrast, a small negative value is found for both SH and SD. Finally, the rotational constant  $B$  of the  $[a^1\Delta]5p\pi^2\Phi$  state in SD is significantly smaller than that of the  $[a^1\Delta]4p\pi^2\Phi$  state. Since both states have the same ionic core, similar values would have been anticipated in an unperturbed Rydberg description. The origin of these differences is not clear, but might be due to  $l$ -uncoupling. In this respect it is interesting to note that an analysis of the angular momentum composition of the  $4p\pi$  and  $5p\pi$  orbitals at the equilibrium distance reveals that the  $5p\pi$  orbital contains a significantly larger amount of  $d$  character than the  $4p\pi$  orbital [19], thereby explaining at least in part the lower value of its quantum defect. Similarly,  $l$ -uncoupling might be at the origin of the negative value of  $D$  found for the  $[a^1\Delta]5p\pi^2\Phi$  state in SH.

The photoelectron spectra obtained for ionization via the  $S_1(3/2)$  and  $S_1(13/2) + R_{21}(13/2)$  rotational transitions indicate two more interesting aspects of the  $[a^1\Delta]5p\pi^2\Phi$  state. Although direct ionization of  $\text{H}_2\text{S}$  ( $\text{D}_2\text{S}$ ) and S prohibits an accurate determination of the extent to which the  $[a^1\Delta]5p\pi^2\Phi$  state of SH (SD) may ionize directly into the  $X^3\Sigma^-$  ionic ground state, the photoelectron spectrum shown in Fig. 3a and the fact that no resonances could be observed in this ionization channel (vide supra) demonstrate that the  $[a^1\Delta]5p\pi^2\Phi$  state possesses a relatively 'pure' ionic core. This conclusion offers valuable opportunities for state-selective chemistry inasmuch as the  $\text{SH}^+$  ( $\text{SD}^+$ ) ions generated in the photoionization process, resonance enhanced by this state, occur almost exclusively in the excited  $a^1\Delta$  state.

The second observation concerns the photoionization dynamics which are highlighted in the partially

rotationally resolved photoelectron spectrum of Fig. 3b. This photoelectron spectrum shows that ionization of the  $[a^1\Delta]5p\pi^2\Phi$  state gives rise to an intuitively unexpected markedly asymmetric distribution over the rotational levels of the ionic state. Previous rotationally resolved photoelectron spectroscopic studies have shown more or less symmetric distributions for positive and negative  $\Delta N$  transitions with a large intensity of the  $\Delta N = 0$  transition [20–22]. Such behaviour would be expected on the basis of a classical description of rotation where gaining or losing angular momentum would be equally probable. While a detailed quantitative analysis of the photoionization dynamics is only possible on the basis of high-quality ab initio calculations, which will be presented in a forthcoming publication [23], it is easily shown that the observed asymmetry derives from the fact that ionization involves a state with a high value of  $\Lambda^+$ . The intensity distribution for an ionizing transition can be written as a sum of products of a generalized rotational line strength factor, which is dependent on  $N$  and  $N^+$ , and the square of a reduced multipole moment matrix, which is independent of  $N$  and  $N^+$  [24]. When  $\Lambda^+$  is not considerably smaller than  $N^+$ , the line strength factors indeed predict asymmetric distributions.

In the present study we used REMPI-PES to investigate the rather unusual aspects of excitation and ionization of the  $[a^1\Delta]5p\pi^2\Phi$  state of the SH (SD) radical. In a future paper [25] we shall extend our observations of the excited states of the SH and SD in the energy range between 77900 and 95000  $\text{cm}^{-1}$ . In this region we have seen at least five new Rydberg states which are either built upon the  $a^1\Delta$  or  $b^1\Sigma^+$  excited ionic cores.

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