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Zero-kinetic-energy pulsed-field ionization spectroscopy of the $a^1\Delta$ state of SH^+ (SD^+)

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The results of a zero-kinetic-energy pulsed-field ionization study on the $a^1\Delta$ ($v^+=0$) excited ionic state of SH^+ (SD^+) obtained via two-photon excitation of the $[a^1\Delta]3d\pi^2\Phi$ ($v'=0$) Rydberg state and subsequent one-photon pulsed-field ionization are reported. Accurate ionization energies as well as rotational constants are obtained. A detailed comparison between the rotational branching ratios resulting from the pulsed-field ionization process and those of a direct ionization process is made. The results elucidate the dynamics of the high- n Rydberg states involved in pulsed-field ionization of SH (SD). © 1996 American Institute of Physics. [S0021-9606(96)01202-8]

I. INTRODUCTION

Zero-kinetic-energy¹ (ZEKE) photoelectron spectroscopy, and especially its more widely used pulsed-field modification, zero-kinetic-energy pulsed-field ionization² (ZEKE-PFI) photoelectron spectroscopy, have in recent years been developed into an extremely powerful tool to perform high-resolution spectroscopy on molecular ions. The majority of the studies reported so far have concentrated on high-resolution spectroscopy of molecular ions in their electronic ground state,¹⁻⁹ although recently a few ZEKE-PFI studies have demonstrated that this kind of spectroscopy can be applied equally successfully to the study of electronically excited states of the molecular ion.¹⁰⁻¹⁵ In these latter studies a single VUV photon was employed to excite a neutral molecule in its electronic ground state to high- n Rydberg states converging upon electronically excited ionic states, which were subsequently ionized by pulsed-field ionization into an electronically excited state of the molecular ion and a free electron.

In this work we have extended this approach to study electronically excited ionic states with ZEKE-PFI spectroscopy by employing a low-lying Rydberg state with an excited ionic core as the "initial" state for one-photon pulsed-field ionization. This low-lying Rydberg state is populated by two-photon resonant excitation from the ground state enabling selective excitation of just one particular vibrational and rotational level. It is clear that this combination of multiphoton excitation and one-photon pulsed-field ionization carries some distinct advantages over VUV ZEKE-PFI studies, which use the electronic ground state as the "initial" state for pulsed-field ionization. First of all, it allows the investigation of the spectroscopic properties of excited ionic states without the need to resort to VUV excitation sources. Secondly, the pulsed-field ionization process can be studied starting from a *single* vibrational and rotational level of the intermediate Rydberg state, thereby reducing considerably the number of resonances in the ZEKE-PFI spectra.

The subject of the present study is the mercapto radical (SH), which plays an important role in the ultraviolet photochemistry of sulphur-containing species released into the at-

mosphere 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 on the spectroscopic and photochemical properties of the SH (SD) radical and, especially, its molecular ion is relatively scarce.^{6,16-26}

The SH (SD) radical has a $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(4\sigma)^2(5\sigma)^2(2\pi)^3$ ($X^2\Pi$) electron ground state configuration. Spin-orbit interaction [$A''_0 = -376.835 \text{ cm}^{-1}(\text{SH})$ (Ref. 23); $-376.75 \text{ cm}^{-1}(\text{SD})$ (Ref. 16)] leads to an inverted splitting with the $^2\Pi_{3/2}$ state below the $^2\Pi_{1/2}$ state. Removal of an electron from the 2π molecular orbital, which is essentially a nonbonding $3p_x$ atomic orbital centered on the sulphur atom, gives rise to three different ionic states: the $X^3\Sigma^-$ ground ionic state, and the $a^1\Delta$ and $b^1\Sigma^+$ excited ionic states. The higher lying $A^3\Pi$ and $B^1\Pi$ excited ionic states derive from the removal of an electron from the 5σ molecular orbital.

Until recently the ionization energies for the aforementioned ionic states were only known with an accuracy of 0.01 eV (80 cm^{-1}) from HeI VUV photoelectron spectroscopy (PES) measurements.¹⁹ A more accurate determination of the ionization energy of the $X^3\Sigma^-$ ground state (10.37 eV) was recently achieved by the rotationally resolved nonresonant two-photon pulsed-field ionization (N2P-PFI) studies of Hsu *et al.*⁶ leading to a value of $84\,057.5 \pm 3 \text{ cm}^{-1}$. Similarly, relatively little is known about the vibrational and rotational constants of the ionic states. Accurate values have only been determined for the $X^3\Sigma^-$ and $A^3\Pi$ ionic states by absorption and emission studies of the $A^3\Pi-X^3\Sigma^-$ band system.^{18,20,21}

Here, we will be concerned with the study of the $a^1\Delta$ excited ionic state of the SH^+ (SD^+) ion. To this purpose we will employ the low-lying $[a^1\Delta]3d\pi^2\Phi$ ($v'=0$) Rydberg state of SH (SD), excited by two-photon excitation from the ground state, as the "initial" state in the approach described above. Recently, we have applied (2+1) resonance enhanced multiphoton ionization photoelectron spectroscopy (REMPI-PES) to characterize this hitherto unobserved Rydberg

state.²⁷ Analysis of its rotationally resolved two-photon excitation spectrum unambiguously showed it to be of ${}^2\Phi$ symmetry and allowed for an accurate determination of its spectroscopic parameters. Nonrotationally resolved photoelectron spectra for ionization *via* low rotational levels of the ${}^2\Phi$ state revealed that the ionic core associated with this particular ${}^2\Phi$ state is the $a\ {}^1\Delta$ ($v^+=0$) excited state of the ion, and that this ionic core is not, within our signal-to-noise ratio, contaminated with contributions from other ionic states.

Using this $[a\ {}^1\Delta]3d\pi\ {}^2\Phi$ ($v^+=0$) state as the “initial” state in our ZEKE-PFI experiments, we have been able to obtain accurate rotational thresholds for the $a\ {}^1\Delta$ excited state of the SH⁺ (SD⁺) ion, from which its ionization energy and rotational parameters have been derived. Moreover, comparison of the rotational branching ratios obtained from ZEKE-PFI measurements with those of REMPI-PES studies and concurrent theoretical calculations^{26–28} have allowed for a fundamental insight into the dynamical properties of the high- n Rydberg states involved in our ZEKE-PFI studies. It will be shown that these states are relatively insensitive to autoionization processes, which have been investigated separately in non-ZEKE experiments.

II. EXPERIMENT

A detailed description of our setup for laser photoelectron spectroscopy has been given elsewhere.²⁹ In the present experiments counterpropagating beams from two dye lasers, both pumped by the same excimer laser, were employed. One frequency-doubled dye laser, operating on Coumarin 500, provided photons for the photolysis of H₂S (D₂S) *via* excitation to the first dissociative absorption band which spans the wavelength range 180–270 nm, leading to SH (SD) radicals in their $X\ {}^2\Pi$ ground state.²⁴ The same photons were subsequently used for the two-photon resonant excitation of SH (SD) to the $[a\ {}^1\Delta]3d\pi\ {}^2\Phi$ ($v^+=0$) Rydberg state. The second dye laser, operating on DCM, was used to scan the rotational ionization thresholds of the excited $a\ {}^1\Delta$ ($v^+=0$) ionic state.

Resonances of xenon and atomic sulphur [which is also produced by the photolysis of H₂S (D₂S) and SH (SD)] in the two-photon energy range of 79 500–89 800 cm⁻¹ were used to calibrate the pump laser.^{30,31} The probe laser was calibrated using optogalvanic lines of Ne excited in a hollow-cathode discharge.³²

The experiments were performed using a “magnetic bottle” electron spectrometer. On the pole faces of the 1 T electromagnet a pair of grids is mounted which allow for the application of dc and pulsed electric fields. In the present ZEKE-PFI experiments, a fixed dc electric field of 4 V/cm was applied to sweep out the prompt electrons. After an appropriate delay of ~60 ns, a fast electric field pulse of 20 V/cm was used to ionize the high- n Rydberg states. Although it is common practice to use considerably larger delay times,² such delay times did not turn out to be possible in the present experiments. As the result of the relatively fast decay of the high- n Rydberg states on a time scale in the order of 40 ns, the delay time had to be chosen such that a compromise

could be reached between distinguishing prompt and PFI electrons, while still retaining enough PFI electrons to obtain ZEKE-PFI spectra with a reasonable signal-to-noise ratio.

In a second type of experiment, electrons were monitored that derived from various other ionization channels, i.e., near-zero-kinetic-energy electrons resulting from direct ionization and/or rotational autoionization into the $a\ {}^1\Delta$ ionic continua, as well as electrons with a kinetic energy of ~1.2 eV resulting from electrostatic autoionization and/or direct ionization into the ground $X\ {}^3\Sigma^-$ ionic continua. These experiments were performed under considerably reduced power of the probe laser to avoid saturation of the one-photon transition from the $[a\ {}^1\Delta]3d\pi\ {}^2\Phi$ Rydberg state to the high- n Rydberg states converging upon the rotational limits of the excited $a\ {}^1\Delta$ ionic state, and with only a small dc electric field (1 V/cm) which merely served to extract the near-zero-kinetic-energy electrons. H₂S (99.6%, Messer Griesheim) and D₂S (98% D, Campro Scientific) were used without further purification. Each was introduced into the spectrometer, in turn, as a continuous effusive leak.

III. RESULTS

A series of ZEKE-PFI spectra obtained by two-photon excitation of various rotational levels of the $[a\ {}^1\Delta]3d\pi\ {}^2\Phi$ ($v^+=0$) state *via* the $S_1(3/2)$ to $S_1(13/2)$ rotational transitions, and probing the excited $a\ {}^1\Delta$ rotational ionization thresholds by one-photon pulsed-field ionization is shown in Figs. 1(a)–1(f). A similar series could not be obtained for the SD radical because of a considerably lower signal-to-noise ratio in these experiments: here only excitation of the $[a\ {}^1\Delta]3d\pi\ {}^2\Phi$ ($v^+=0$) state *via* the $S_1(3/2)$ rotational transition permitted ZEKE-PFI experiments. This spectrum is depicted in Fig. 2.

ZEKE-PFI spectra obtained by pumping the intermediate rotational levels $N'=3$ and 4 *via* the Q_1 and R_2 rotational branches (not shown here) are barely different from those obtained by pumping *via* the corresponding S_1 rotational branches [see Figs. 1(a) and 1(b)]. Similarly, the ZEKE-PFI spectrum obtained by pumping the $N'=6$ rotational level *via* the $Q_1(13/2)$ rotational transition (not shown here) hardly differs from that obtained *via* $S_1(9/2)$ [see Fig. 1(d)]. Due to the proximity of the $S_1(9/2)$ and ${}^1S_{21}(3/2)$, and of the $S_1(13/2)$ and ${}^1S_{21}(5/2)$ rotational transitions, Figs. 1(d) and 1(f) show additional lines corresponding to ionization from $N'=4$ and $N'=5$, respectively. These lines are marked with asterisks in Figs. 1(d) and 1(f). The rotational branching ratios observed for these transitions are almost identical to those seen in the spectra of Figs. 1(b) ($N'=4$) and 1(c) ($N'=5$), respectively. It can therefore be concluded that alignment effects play a relatively minor role in the present experiments.

Field-free ionization thresholds can be extracted from ZEKE-PFI experiments if one can correct for the Stark shift of the ionization threshold caused by the various electric fields present in the experiments. In our study these fields concern the dc field of 4 V/cm, which is used to sweep out the prompt electrons, the pulsed-field of 20 V/cm, which is

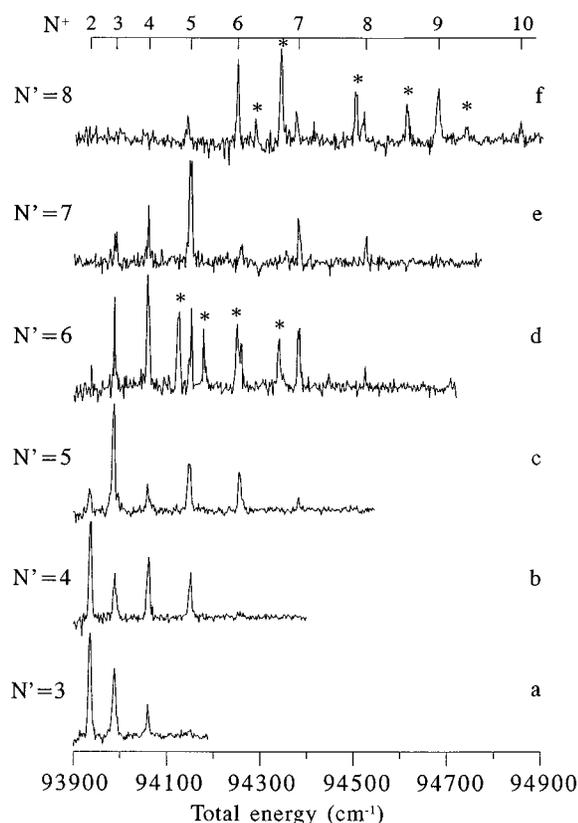


FIG. 1. ZEKE-PFI spectra of the $a^1\Delta$ excited ionic state of SH⁺ obtained after two-photon excitation of the $[a^1\Delta]3d\pi^2\Phi$ ($v'=0$) via the (a) $S_1(3/2)$; (b) $S_1(5/2)$; (c) $S_1(7/2)$; (d) $S_1(9/2)+^1S_{21}(3/2)$; (e) $S_1(11/2)$; and (f) $S_1(13/2)+^1S_{21}(5/2)$ rotational transitions. Individual line assignments are indicated by the comb above the spectrum. For the transitions marked with an asterisk, see text.

used to ionize the high- n Rydberg states, the stray electric fields inherent in the “magnetic bottle” spectrometer, and the motional Stark field induced in molecules moving in the 1 T magnetic field. One could, in principle, account for the first

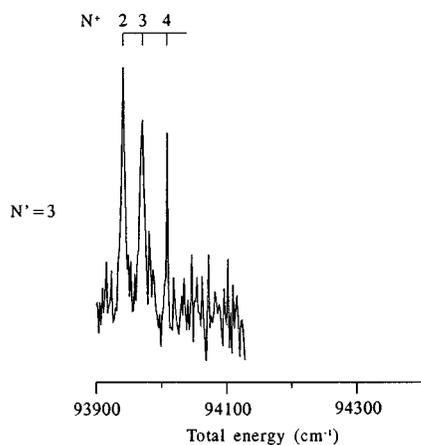


FIG. 2. ZEKE-PFI spectrum of the $a^1\Delta$ excited ionic state of SD⁺ obtained after two-photon excitation of the $[a^1\Delta]3d\pi^2\Phi$ ($v'=0$) via the $S_1(3/2)$ rotational transition. Individual line assignments are indicated by the comb above the spectrum.

two electric fields by extrapolation to zero-field conditions,³³ but accounting for the latter fields is considerably more problematic since their strengths are almost impossible to determine. We have therefore adopted another approach to correct for the combined Stark shifts resulting from all fields by seeding the sample with xenon and performing a ZEKE-PFI experiment on xenon *via* the two-photon excited $6p[1/2]_0$ resonance at $80\,119.5\text{ cm}^{-1}$ (Ref. 30) under the same experimental conditions as in the ZEKE-PFI experiments on SH (SD), albeit with considerably reduced laser power to avoid ac Stark shifts. Since the ionization energy of Xe⁺($^2P_{3/2}$) is accurately known, these measurements allow us to determine the total Stark shift as 14.6 cm^{-1} . The motional Stark field is velocity and consequently, mass dependent. Since the mass of xenon is about 4 times larger than that of SH (SD), one would expect that in SH (SD) the motional Stark field would be twice as large, thereby putting into question whether we can use the correction factor found for xenon also for the SH (SD) radical. In this respect it is worthwhile to consider the results of a recent ZEKE-PFI study on HBr (Ref. 9) in the “magnetic bottle” spectrometer, in which we have investigated the influence of the electric fields in more detail. These experiments demonstrated that the combined stray and motional Stark fields amounted to about 0.1 V/cm . Nevertheless, if we use this number for a worst case estimate we conclude that the error introduced by the motional Stark field in SH (SD) is at most 2 cm^{-1} . We will therefore apply the correction of 14.6 cm^{-1} found for xenon to SH (SD), incorporating the uncertainty in the motional Stark field in the final uncertainty in the ionization thresholds.

The energy scale in the spectra presented in Figs. 1 and 2 has been corrected for this Stark shift and is given with respect to the energy of the lowest rotational level of the $X^2\Pi_{3/2}$ ground state of the neutral molecule. Field-free ionization energies of the transition $X^2\Pi_{3/2}(v''=0, J''=\frac{3}{2}) \rightarrow a^1\Delta_2(v'+0, J'+2)$ for SH⁺ and SD⁺ can now easily be extracted from Figs. 1 and 2 as $93\,925 \pm 3\text{ cm}^{-1}$ ($11.6453 \pm 0.0004\text{ eV}$) and $93\,944 \pm 3\text{ cm}^{-1}$ ($11.6476 \pm 0.0004\text{ eV}$), respectively. The accuracy of these numbers is determined by the uncertainties in the wavelength calibration of the two dye lasers, and the determination of the peak positions in the ZEKE-PFI spectra and the Stark shift.

Rotational analysis of the ZEKE-PFI spectra of the SH⁺ radical (Fig. 1) has been performed using the Hund's case (b) expression for the rotational energy levels of the $a^1\Delta$ state:

$$E(N^+) = B_0 N^+(N^+ + 1) - D_0 [N^+(N^+ + 1)]^2,$$

where B_0 is the rotational constant and D_0 the centrifugal distortion correction. The spectral parameters obtained from a least-squares fit of the measured energies to the expression given above are given in Table I. Rotational analysis of the SD⁺ radical ZEKE-PFI spectrum (Fig. 2) allowed only for the determination of the rotational constant B_0 , albeit with less accuracy (see Table I).

Figure 3 shows the results of a non-ZEKE (2+1') REMPI experiment, in which a number of competing (auto)ionization processes have been monitored. These spectra have been obtained by two-photon excitation

TABLE I. Spectroscopic constants (in cm⁻¹) derived for the vibrationless level of the $a^1\Delta$ excited ionic state of SH⁺ and SD⁺. The values in parentheses represent one standard deviation in the last digit. Constants for the vibrationless level of the $X^3\Sigma^-$ ground ionic state of SH⁺ and SD⁺ (Refs. 6 and 20) are included for comparison.

	Ionization thresholds	B_0	$D_0(10^4)$
SH ⁺ $X^3\Sigma^-$	84 057.5	9.134	4.9
SH ⁺ $a^1\Delta$	93 925 ± 3	9.186(8)	9.0(9)
SD ⁺ $X^3\Sigma^-$		4.733	1.29
SD ⁺ $a^1\Delta$	93 944 ± 3	4.85(8)	

of the $[a^1\Delta]3d\pi^2\Phi$ ($v'=0$) Rydberg state of SH *via* the $S_1(11/2)$ rotational transition and subsequent one-photon ionization. The top spectrum displays the ionization yield as a function of the total ($2+1'$) photon energy when only near-zero-kinetic-energy electrons are monitored. The bottom spectrum is obtained when electrons with a kinetic energy of ~ 1.2 eV are selectively monitored.

IV. DISCUSSION

The experiments described earlier, have led to an accurate determination of the field-free ionization energy of the excited $a^1\Delta$ ionic state of SH⁺ as $93\,925 \pm 3$ cm⁻¹, which is in excellent agreement with the previously obtained value of 11.65 ± 0.01 eV.¹⁹ For the excited $a^1\Delta$ ionic state of SD⁺, a slightly higher value of $93\,944 \pm 3$ cm⁻¹ is obtained, in line with the expectation of a small positive isotope shift resulting from the decrease in vibrational frequency in going from the $X^2\Pi$ ground state of the neutral to the $a^1\Delta$ excited state of the ion.^{19,34}

The least-squares fit to the line positions observed in our rotationally resolved ZEKE-PFI spectra has led to the first determination of the rotational parameters of the $a^1\Delta$ ex-

cited ionic state of SH⁺ (see Table I). Our value for the rotational constant B_0 of 9.186 cm⁻¹ is very similar to that of 9.01 cm⁻¹ obtained by Park *et al.* from *ab initio* calculations.³⁴ However, it is significantly larger than that of 8.85 cm⁻¹ calculated from the estimated equilibrium bondlength r_e (Ref. 19) for the $a^1\Delta$ ionic state and the α_e value (Ref. 34).

The $a^1\Delta$ excited state of the SH⁺ (SD⁺) ion is just one of the three states derived from the electron configuration $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(4\sigma)^2(5\sigma)^2(2\pi)^2$. The potential energy curves of the $X^3\Sigma^-$, $a^1\Delta$, and $b^1\Sigma^+$ ionic states are expected to be quite similar. Verification for this is found in the comparison between the well-known spectroscopic parameters of the $X^3\Sigma^-$ ground ionic state of SH⁺ and SD⁺ and our constants (see Table I).

The ZEKE-PFI spectra obtained in the present study show dramatic differences between the intensities of the various $\Delta N = N^+ - N'$ transitions. In order to put these differences and the number of observed ΔN transitions into proper perspective it is instructive to consider the results of our previous ($2+1$) REMPI-PES experiments and concurrent theoretical calculations on the rotationally resolved ionization dynamics of the $[a^1\Delta]3d\pi^2\Phi$ ($v'=0$) state.²⁶⁻²⁸ First, it is important to note that the REMPI-PES experiments²⁷ demonstrated unambiguously that the $[a^1\Delta]3d\pi^2\Phi$ ($v'=0$) state is a Rydberg state with a very pure ionic core: photoelectron spectra obtained for ionization *via* this state only showed ionization to the $a^1\Delta$ excited ionic state and, within the experimental signal-to-noise ratio, no ionization to the $X^3\Sigma^-$ ground ionic state. This core-preserving photoionization process was thoroughly examined in rotationally resolved one-color ($2+1$) REMPI-PES experiments, in which ionization was established *via* several high rotational levels of the $[a^1\Delta]3d\pi^2\Phi$ ($v'=0$) Rydberg state of the SH radical, in combination with the results of *ab initio* calculations. Most gratifying, it was found that the agreement between the calculated and the measured rotationally resolved photoelectron spectra was excellent. From these studies it could be concluded that the photoionization dynamics *via* this state are peculiar in two respects. First, only transitions up to $\Delta N = \pm 2$ were observed, whereas transitions up to ± 4 were expected. Secondly, strong asymmetries were observed in the ionic rotational branching ratios.

Conservation of angular momentum for one-photon ionization in a diatomic Hund's case (b) limit requires that the selection rule $\Delta N = N^+ - N' = l + 1, l - 1, \dots, -l - 1$ (Ref. 35) is obeyed, where l is the orbital angular momentum associated with the outgoing electron wave. In an atomiclike picture one would expect that on removal of a $3d\pi$ Rydberg electron the p and f partial waves would dominate, from which a rotational ion distribution with transitions up to $\Delta N = \pm 2$ and $\Delta N = \pm 4$, respectively, would be expected. Consequently, the appearance of a maximum value of ΔN in the rotationally resolved photoionization spectrum from a single rotational level should indicate the highest value of l . Since *ab initio* calculations showed that the f wave continua make the dominant contribution to the total photoionization cross section of the $3d\pi$ Rydberg electron, we would expect tran-

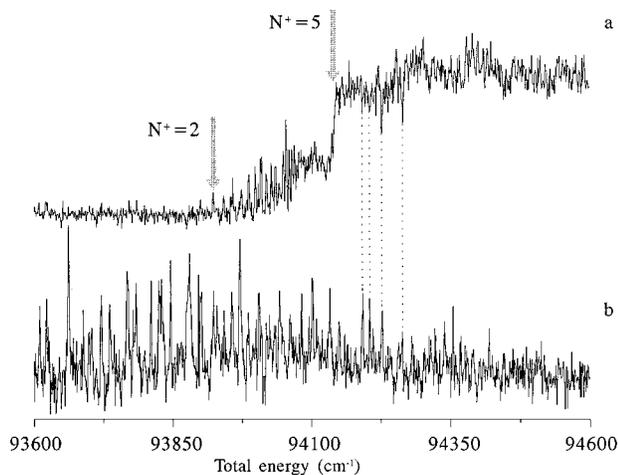


FIG. 3. Ionization spectrum of SH obtained for ($2+1'$) ionization *via* the $S_1(11/2)$ rotational transition of the $[a^1\Delta]3d\pi^2\Phi$ state: (a) ionization into the $a^1\Delta$ excited ionic continua obtained by monitoring near-zero-kinetic-energy electrons; (b) ionization into the $X^3\Sigma^-$ ground ionic continua obtained by monitoring photoelectrons with a kinetic energy of ~ 1.2 eV.

sitions up to $\Delta N = \pm 4$. The fact that only transitions up to $\Delta N = \pm 2$ were observed was attributed to interference effects between the $k\sigma$, $k\pi$, and $k\delta$ photoelectron continua of the $l=3$ outgoing partial wave.

The second and most striking feature was found in the strong asymmetry in the rotational branching ratios. Although minor asymmetries are not exceptional,^{36,37} both the measured and calculated rotationally resolved photoelectron spectra showed large differences in intensities between rotational transitions that only differ in the sign of ΔN . This asymmetrical behavior was attributed to large deviations from the classical description of rotational motion where gaining or losing angular momentum would be equally probable, and clearly originated from the high value of electronic orbital angular momentum of the resonant ${}^2\Phi$ state.

The *ab initio* calculations do not predict a considerable photoelectron kinetic energy dependence in the radial dipole matrix elements.²⁸ We would therefore expect the present ZEKE-PFI results and the previous REMPI-PES results to be reasonably similar, provided that the long-lived Rydberg states populated in our ZEKE-PFI experiments are not heavily perturbed by Rydberg–Rydberg and/or Rydberg–continuum interactions. Indeed, our ZEKE-PFI spectra show the same features: most of the intensity lies in rotational transitions with $|\Delta N| \leq 2$, although a few lines with $\Delta N = -3$ and $\Delta N = -4$ can also be seen, and the asymmetries between the $\Delta N = +1$ and -1 and the $\Delta N = +2$ and -2 rotational transitions are apparent (see Figs. 1 and 2).

It appears that our ZEKE-PFI spectra show the same unusual features as observed in the REMPI-PES direct photoionization measurements and in the *ab initio* calculations. Before rushing to conclusions, however, we have to examine the ZEKE-PFI spectra in somewhat more detail. The limited resolution, inherent in the REMPI-PES spectra, prohibits the measurement of rotationally well-resolved photoelectron spectra *via* intermediate levels with $N' < 5$. A direct comparison between the ZEKE-PFI and the REMPI-PES results is consequently difficult for the low intermediate levels with $N' = 3$ and 4. However, the *ab initio* calculations indicate that the observed rotational branching ratios of Figs. 1(a) and 1(b) are quite similar to the calculated ones.²⁸ For $N' = 5$, a comparison between the two experimental techniques is possible and leads to the conclusion that their results show a reasonably good agreement. This is demonstrated in Fig. 4, where the previously obtained rotationally resolved REMPI-PES spectrum *via* the $S_1(7/2)$ rotational transition of the $[a\ ^1\Delta]3d\pi\ ^2\Phi$ Rydberg state²⁸ is displayed, which can be compared directly to the ZEKE-PFI spectrum shown in Fig. 1(c). The $\Delta N = -2$ transition is the most intense in both spectra, while the $\Delta N = 0$ and $+1$ transitions are the next prominent ones. Despite these similarities some discrepancies remain. First, in the ZEKE-PFI spectrum [Fig. 1(c)] the lowest rotational level of the $a\ ^1\Delta$ excited ionic state ($N^+ = 2$) is seen, which corresponds to a $\Delta N = -3$ rotational transition, whereas in the REMPI-PES spectrum for $N' = 5$, only transitions up to $\Delta N = \pm 2$ are observed. Secondly, the asymmetry between $\Delta N = +2$ and $\Delta N = -2$ transitions, obvious in both spectra, is slightly more

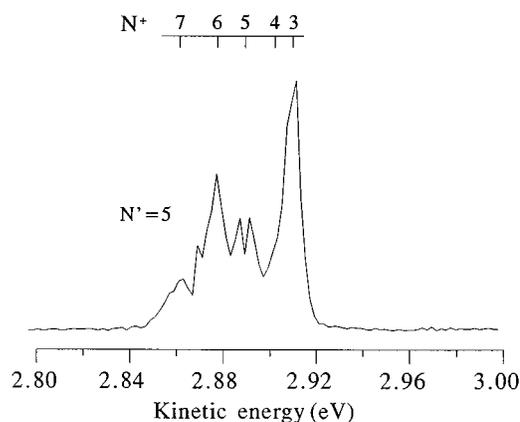


FIG. 4. REMPI-PES spectrum obtained for (2+1) ionization *via* the $S_1(7/2)$ rotational transition of the $[a\ ^1\Delta]3d\pi\ ^2\Phi$ state of SH (Ref. 28). Individual line assignments are indicated by the comb above the spectrum.

enhanced in the ZEKE-PFI spectra: the $\Delta N = -2$ transition has gained intensity with respect to $\Delta N = +2$. Similar considerations for the $\Delta N = +1$ and $\Delta N = -1$ transitions are difficult because of the unresolved $\Delta N = -1$ line in the REMPI-PES spectrum. However, the theoretical calculations reveal that the transition probability $\Delta N = -1$ for photoionization *via* the intermediate rotational level $N' = 5$ is quite small.²⁸ The $\Delta N = -1$ rotational transition, clearly present in Fig. 1(c), consequently has too large an intensity. From the comparison between the ZEKE-PFI spectra of Figs. 1(d)–1(f) with the measured and calculated results for direct photoionization²⁸ a similar agreement is concluded, despite the problem of overlapping S_1 and ${}^1S_{21}$ rotational lines, which leads in both the REMPI-PES and ZEKE-PFI experiments to signals from two instead of one intermediate N' rotational level. A peculiar observation in the ZEKE-PFI spectra of Fig. 1 is the narrowness of some $\Delta N = -3$ and -4 rotational transitions (*vide infra*).

We conclude that in this particular ZEKE-PFI study, the rotational branching ratios resulting from the pulsed-field ionization process, in general, resemble, to a large extent, those of the direct ionization process. The minor differences can all be explained when one considers the influence of rotational interactions. High- n Rydberg states, initially populated in our ZEKE-PFI experiments, may autoionize into the various ionization continua of lower-lying rotational levels of the $a\ ^1\Delta$ excited ionic state, resulting in a decrease of the ZEKE-PFI signal. Apart from the depletion of ZEKE-PFI states, this rotational autoionization is also responsible for other effects. A common phenomenon in many ZEKE-PFI studies is the enhancement of $\Delta N < 0$ transitions with respect to the corresponding $\Delta N > 0$ ones. This can be explained by adopting a model in which low- n Rydberg states, which cannot be field ionized directly since they lie too far below their own ionization threshold, can autoionize into the continua of high- n Rydberg states when these decay channels become available upon application of the pulsed field.³ Similarly, these low- n Rydberg states can give rise to “forbidden” transitions in ZEKE-PFI spectra if they autoionize into forbidden

ionization continua under the influence of the pulsed field. A recent study on NO₂ (Ref. 7) has shown that these rotational interactions can give rise to sharp substructure on ZEKE-PFI peaks. The width of such structures is no longer determined by the magnitude of the electric field pulse, but by the principal quantum numbers of the autoionizing low-*n* Rydberg states. The narrowness of some “forbidden” $\Delta N = -3$ and -4 rotational transitions seen in our experiment, whose widths are considerably smaller than the widths of the other lines in the spectra, could be explained with a similar mechanism.^{7,8}

We thus see that rotational interaction, either of discrete-continuum or discrete-discrete nature, is not of dominant importance in our experiments, since the intensity perturbations in our ZEKE-PFI spectra do not prevail to such an extent that the major characteristics of the ionization process observed in the REMPI-PES spectra are eliminated. An example of a situation where the latter does occur is found in the ZEKE-PFI spectra of HCl and HBr.^{5,9} In these molecules rotational interactions dominate the rotational branching ratios and, as a result, REMPI-PES and ZEKE-PFI spectra hardly show any resemblance.

Another kind of core-to-electron energy transfer process that needs to be considered concerns electrostatic autoionization. The ionic core associated with the accessible ZEKE-PFI states is the excited $a^1\Delta$ ($v^+ = 0$) state of the SH⁺ (SD⁺) ion. Hence, accessible discrete states could be subject to autoionization into the continua of the lower-lying $X^3\Sigma^-$ ground state of the ion. The photoelectrons with a kinetic energy of ~ 1.2 eV derived from such an electrostatic autoionization process are, however, quite distinct from the near-zero-kinetic-energy ZEKE-PFI electrons. Electrostatic autoionization may therefore result in an overall depletion of the ZEKE-Rydberg states, but it cannot influence the rotational branching ratios in our ZEKE-PFI experiments. It is clear that the electrostatic coupling between the ZEKE-Rydberg states and the continua of the $X^3\Sigma^-$ ionic ground state is small: the lifetime of these high-*n* Rydberg states is large enough to survive the delay of ~ 60 ns before the pulsed electric field is applied. On the other hand, the delay times possible in the present experiments are significantly shorter than those used in similar ZEKE-PFI experiments on HCl and HBr in the “magnetic bottle” spectrometer.^{5,9} This indicates that electronic autoionization and/or predissociation processes (*vide infra*) do influence the overall lifetime of the high-*n* Rydberg states employed for ZEKE-PFI.

The minor role of electrostatic autoionization for SH (SD) Rydberg states with an $a^1\Delta$ core has also been concluded from other experiments in which we could observe rotationally well-resolved resonance-enhanced excitation spectra of SH (SD) Rydberg states with excitation energies above the lowest ionization threshold.^{25,27} First, if electrostatic autoionization would proceed on a short timescale, these excitation spectra would have exhibited an extensive lifetime broadening. Secondly, (2+1) REMPI-PES spectra obtained for ionization *via* the $[a^1\Delta]5p\pi^2\Phi$ Rydberg state of the SH (SD) radical, which has an excitation energy exceeding the lowest ionization threshold, show that ionization

occurs preferentially by absorption of a third photon after the two-photon excitation step, rather than through electrostatic autoionization.²⁵

The role of high-*n* Rydberg depleting processes has been investigated as well in another type of experiment. In a non-ZEKE experiment we have compared the contribution of the various autoionization processes to that of direct ionization. To this purpose, the intermediate rotational level $N' = 7$ was selected *via* the $S_1(11/2)$ rotational transition. While the probe laser scanned the various ionization thresholds, the photoelectrons deriving from competing ionization processes were selectively monitored. Below and above the first rotational level of the excited $a^1\Delta$ ionic state, the initially populated Rydberg states may couple to the ionization continua of the lower-lying $X^3\Sigma^-$ ground state of the ion leading to an ion in its $X^3\Sigma^-$ ground state and a free electron with a kinetic energy of ~ 1.2 eV. The other possibility of generating photoelectrons with a kinetic energy of ~ 1.2 eV, *viz.*, direct ionization *via* the $[a^1\Delta]3d\pi^2\Phi$ ($v' = 0$) Rydberg state into the continua of the $X^3\Sigma^-$ ground ionic state, is not considered here since our previous REMPI-PES study showed no indication of such a photoionization process.²⁷

The lower panel in Fig. 3 displays the spectrum obtained by monitoring these photoelectrons deriving from electrostatic autoionization. There is ample evidence for a high density of discrete resonances, which are known to cause anomalies in ZEKE-PFI spectroscopy,⁷ even though these resonances do not seem to converge upon specific ionization thresholds. In these experiments our initial state is the $[a^1\Delta]3d\pi^2\Phi$ state. It seems highly improbable that one-photon excitation from this state would be able to access Rydberg states with a $b^1\Sigma^+$ excited ionic core, since this would in general involve a two-electron transition. Moreover, in such a picture the density of resonances observed is too high when we bear in mind that we start from a single rotational level in the $^2\Phi$ state. We therefore conclude that the resonances should be assigned to Rydberg states converging upon the $a^1\Delta$ excited ionic core.

If the photon energy of the probe laser exceeds the lowest ionization threshold of the $a^1\Delta$ excited ionic state, rotational autoionization becomes possible, because the discrete states can now couple to the various ionization continua of the lower-lying rotational levels associated with the $a^1\Delta$ excited ionic state. This process is clearly demonstrated in the top spectrum of Fig. 3, where electrons are monitored with near-zero kinetic energy. It is observed that rotational autoionization starts as soon as the lowest rotational level of the $a^1\Delta$ state, $N^+ = 2$, is reached. The prevailing photoionization selection rule $|\Delta N| \leq 2$ would imply that the Rydberg states observed above the $N^+ = 2$ rotational threshold converge upon rotational thresholds with $N^+ \geq 5$. Indeed, the resonances observed between the $N^+ = 2$ and $N^+ = 5$ thresholds seem to converge by and large to the $N^+ = 5$ threshold. The same selection rule makes direct ionization into the continua of rotational levels associated with the $a^1\Delta$ excited ionic state only allowed when the rotational threshold of $N^+ = 5$ is reached. Accordingly, it is observed that at the $N^+ = 5$ threshold, the production of slow electrons is in

creased dramatically. This sharp rise in ionization yield might be attributed to two different scenarios. In the first one rotational autoionization is very inefficient below the $N^+ = 5$ threshold, making the direct ionization channel dominate the ionization characteristics above $N^+ = 5$. In that case we would expect the electronic autoionization channel to show an equivalent drop. What we observe in this channel, however, is that the intensity of the resonances decreases slightly between the $N^+ = 2$ and $N^+ = 5$ thresholds, and gradually dies away above the $N^+ = 5$ threshold without the expected sharp drop. In the second scenario, Rydberg states in the present energy region may be subject to predissociation, a decay channel which will become unimportant for energies where direct ionization is possible. This would similarly lead to a sharp rise in the ionization yield at $N^+ = 5$, but without an accompanying sharp drop in the electronic autoionization channel.

An interesting observation, marked by the broken vertical lines in Fig. 3, concerns the appearance of so-called "window resonances,"³⁸ which originate from the interference between the resonant Rydberg states and the continua of the $X^3\Sigma^-$ ground ionic state and the $a^1\Delta$ excited ionic state. As is observed, these interferences lead to an increase in the electrostatic autoionization channel and a decrease in the direct ionization channel.

In the present study detailed information on the spectroscopy of the excited $a^1\Delta$ ionic state of SH⁺ (SD⁺) and on the underlying dynamics of high- n Rydberg states could be obtained. It is interesting to note that the combined insight obtained from the present ZEKE-PFI study and our previous REMPI-PES work allows for strategies to produce SH⁺ and SD⁺ ions in specific, well-defined rovibronic levels associated with the $a^1\Delta$ excited ionic state. Such strategies are clearly important in the context of state-selective chemistry.

V. CONCLUSIONS

The application of ZEKE-PFI spectroscopy on the [$a^1\Delta$] $3d\pi^2\Phi$ ($v' = 0$) Rydberg state of the mercapto radical, excited by two-photon absorption from the ground state, has enabled us to investigate with high resolution the spectroscopic properties of the $a^1\Delta$ excited ionic state of SH⁺ and SD⁺. The ionization energy of this state has been determined with a considerably improved accuracy, while the state selectivity and high energy resolution inherent in the method have been exploited to obtain its rotational parameters. Apart from the spectroscopic parameters, these ZEKE-PFI experiments in conjunction with experiments probing the various possible ionization pathways have elucidated the intrinsic details of the dynamical properties of the high- n Rydberg states involved in the ZEKE-PFI experiments. We find that these Rydberg state are relatively insensitive to electrostatic and rotational autoionization processes. As a result, we observe that the rotational branching ratios for the pulsed-field ionization process show the same unusual characteristics as the rotational branching ratios resulting from direct ionization.

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