The mechanism for photofragmentation of H2S revealed by multiphoton ionization photoelectron spectroscopy

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Multiphoton ionization photoelectron measurements for H_2S were carried out at several laser wavelengths in the 422–475 nm region, in order to obtain a direct evidence for the mechanism of ionic fragmentation which takes place by resonantly enhanced multiphoton ionization (REMPI). An ion current spectrum of multiphoton ioniztion was also measured for H_2S in this wavelength region, indicating that the ionization takes place via three-photon resonant Rydberg states. From photoelectron spectra obtained here, it has been found that the main peaks are attributed to the H_2S^+ ion in the ground state with $v = 0$. Other photoelectron bands due to $v = 1$ have also been observed together with some satellite bands. It should be mentioned that no photoelectron bands above 1.3 eV have been found. These experimental evidences directly support the parent ion fragmentation mechanism that the formation of HS^+ and S^+ ions mainly results from the ground state H_2S^+ ion with $v = 0$ and $v = 1$, respectively, by additional photon absorption. This conclusion differs from that recently suggested by Carney and Baer from their mass-resolved REMPI experiments.

I. INTRODUCTION

Ionic fragmentation of molecules occurring by resonantly enhanced multiphoton ionization (REMPI) in laser excitation experiments has recently received much attention from experimental and theoretical points of view.[1] One of the remarkable features found from mass spectrometric studies of REMPI is the extensive fragmentation. Several consecutive photon absorptions are possible by laser pulses with a duration of several nanoseconds.

Three mechanisms have so far been proposed for the REMPI fragmentation. (1) Neutral fragments are initially formed by dissociation or predissociation of an intermediate neutral resonant state, and then ionized by additional photon absorption to give ionic fragments.[2] (2) Parent ions are initially formed, and then absorb additional photons to dissociate into ionic fragments. This mechanism is referred to as the parent ion fragmentation mechanism.[3,4] (3) Ionic fragments are formed by dissociative ionization via an autoionizing state of the original molecule. This mechanism is often called the autoionization "ladder" mechanism.[5]

Several mass-resolved REMPI experiments for relatively large molecules have suggested that the parent ion fragmentation mechanism is favored.[1] On the contrary, concerning H_2S, Carney and Baer[6] have recently suggested from a laser power dependence of the fragmentation that the autoionization ladder mechanism is favored rather than the parent ion fragmentation mechanism.

The purpose of the present work is to clarify the initial state of the ionic fragmentation in REMPI experiments of H_2S by carrying out measurements of photoelectron kinetic energy distribution. Photoelectron spectroscopic measurements in REMPI should provide direct information about the initially ionized states from which we may deduce the possible mechanism of ionic fragmentation. Recently, a few studies have indicated that MPI photoelectron spectroscopy is very powerful for studying such fragmentation mechanisms.[7-10]

II. EXPERIMENTAL

The photoelectron spectrometer used in the present work is described elsewhere in detail.[11] A gaseous sample of H_2S was introduced into an ionization region in a vacuum chamber through a 100 μ nozzle. The stagnation pressure in the sample source was kept at about 100–200 Torr at which essentially no dimer formation takes place.[12]

A Nd–YAG pumped dye laser (Quanta-Ray DCR-1A, PDL-1) was used in the present laser irradiation experiments. Photoelectron kinetic energy measurements were carried out with a time-of-flight (TOF) electron analyzer which is a magnetically shielded 10 cm long field-free drift tube attached with a channeltron on the other end. Measurements of total ion currents were also carried out with a channeltron in order to obtain multiphoton ionization spectra.

Photoelectron signals thus obtained were fed into an ultrafast transient recorder of 500 MHz/channel (Biomation Model 6500). Signal averaging and storage were performed with a microcomputer based data acquisition system.

Calibration for the time scale was carried out by using Xe as a reference sample which shows two sharp photoelectron peaks due to the well-known $^2P_{3/2}$ and $^2P_{1/2}$ states (12.130 and 13.436 eV, respectively). The overall photoelectron energy resolutions were about 50 and 150 meV for photoelectron with kinetic energies of 0.6 and 2.0 eV, respectively.

III. RESULTS AND DISCUSSION

A. MPI ion current spectrum of H_2S

A multiphoton ionization (MPI) spectrum of H_2S obtained here in the 422–475 nm laser wavelength region is shown in Fig. 1. A similar MPI spectrum for H_2S has very recently been reported by Carney and Baer,[6] but its spectral resolution is considerably lower than that shown in Fig. 1.
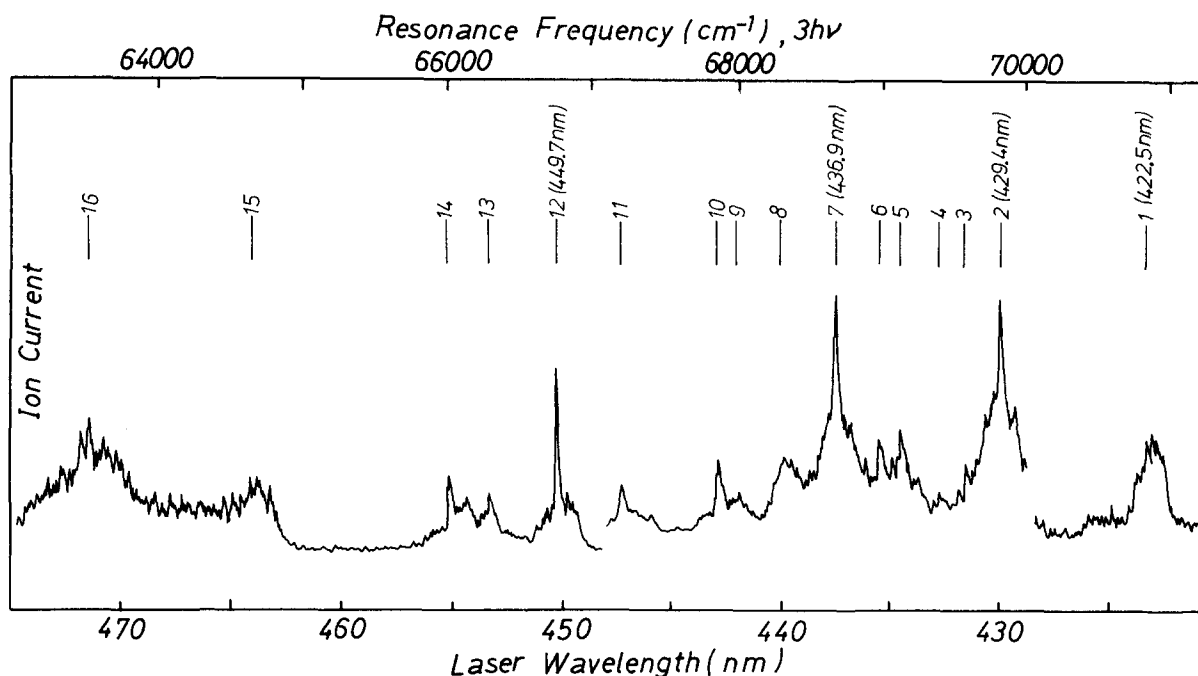
FIG. 1. An MPI ion current spectrum obtained here for H_2S in the laser wavelength region 422–475 nm. The ordinate is the total ion current.

It should be pointed out that all the peaks in the MPI spectrum in Fig. 1 can be assigned on the basis of the vacuum UV absorption spectrum of H_2S recently reported by Masuko et al. [13] in 142–162 nm VUV region. It has been found that three-photon energies for the main MPI peaks are in excellent agreement with the energies of the Rydberg series reported by Masuko et al., [13] as shown in Table I.

From the comparison of wave numbers in Table I, it may be concluded that the MPI peaks appearing at 449.7, 436.9, 429.4, and 422.5 nm correspond to four Rydberg states $4A$-3(0, 0, 0), $4A$-1(1, 0, 0), $3C$(0,0, 0),

TABLE I. Comparison of Rydberg state energies of the MPI spectrum with those of the vacuum UV absorption spectrum.

Band	λ_l (cm^{-1})	MPI spectrum this work $3h\nu_l$ (cm^{-1})	Vacuum UV spectrum Masuko et al. [13] $h\nu_{VUV}$ (cm^{-1})	Assignment
1	422.5	71 006	70 972	$3D$(0, 0, 0)
2	429.4	69 861	69 857	$3C$(0, 0, 0)
3	430.9	69 615	69 662	$4A$–4(1, 0, 0)
4	432.2	69 414	69 406	$3A_2$(0, 1, 0)
5	433.9	69 134	69 137	$4A$–3(1, 0, 0)
6	434.9	68 983	68 975	$4A$–2(1, 0, 0)
7	436.9	68 659	68 653	$4A$–1(1, 0, 0)
8	439.4	68 279	68 269	$3A_2$(0, 0, 0)
9	441.4	67 962	67 995	$4A_2'$(2, 0, 0)
10	442.3	67 823	67 824	$4A$–3(0, 1, 0)
11	446.8	67 145	67 137	$4A$–4(0, 0, 0)
12	449.7	66 717	66 716	$4A$–3(0, 0, 0)
13	452.7	66 263	66 273	$4A$–2(0, 0, 0)
14	454.6	65 988	65 980	$4A$–1(0, 0, 0)
15	463.5	64 721	64 733	$4A_1$(0, 0, 0)
16	471.3	63 645	63 327	$4A_2'$(0, 0, 0)

and $3D$(0, 0, 0), respectively, which have been reported in the VUV absorption study of Masuko et al. [13] According to these authors, [13] excitation of an electron from the $2b_1$ nonbonding orbital to the $4pa_1$ Rydberg orbital gives rise to four kinds of Rydberg states with different total electronic angular momenta; $4A_1$ – 1, – 2, – 3, and – 4. The $3C$ and $3D$ Rydberg states are due to excitation of an electron from the $2b_1$ nonbonding orbital to the $3da_1$ and $3da_2$ Rydberg orbitals, respectively.

B. REMPI photoelectron spectra

According to a HeI (58. 4 nm) photoelectron study of H_2S, [14,15] the first ionization band shows a sharp peak which corresponds to an adiabatic ionization energy of 10. 48 eV. The first photoelectron band also shows a weak peak due to the $v = 1$ level of the symmetric stretching vibrational mode of H_2S^*. Its wave number is reported to be $\nu_1 = 2516$ cm^{-1} (0. 31 eV). [15]

The kinetic energy of photoelectrons emitted from a molecule by four-photon absorption K is given by

$$K = 4h\nu_l - I_a - nh\nu_v \tag{1}$$

when only a single vibrational mode is excited. Here, ν_l is the laser frequency, I_a the adiabatic ionization energy, n the vibrational quantum number, and ν_v the vibrational frequency. In Table II, the photoelectron energies (K) calculated from Eq. (1) with $h\nu_1 = 0. 31$ eV are compared with those experimentally obtained.

Photoelectron spectra obtained at the laser wavelengths of 449. 7. 436. 9, 429. 4, and 422. 5 nm, at which the sharp MPI peaks appear in Fig. 1, are shown in Fig. 2 as a function of the time of flight in the units of ns or the photoelectron kinetic energy in the units of eV. The four-photon energies for these laser wavelengths
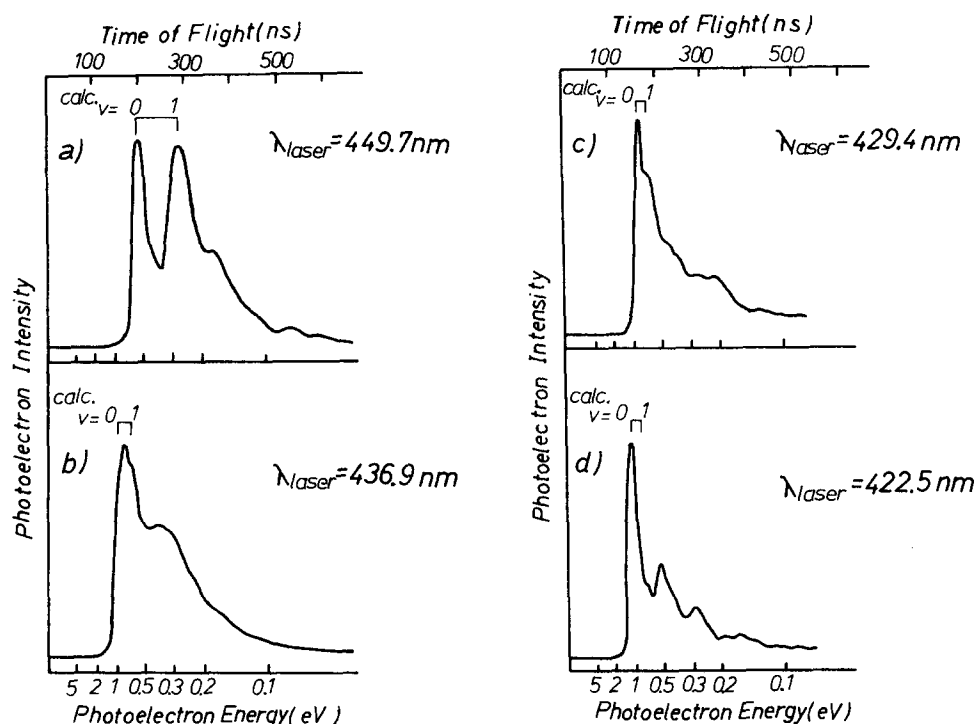
FIG. 2. REMPI TOF photo-electron spectra of H₂S obtained at laser wavelengths of (a) 449.7 nm, (b) 436.9 nm, (c) 429.4 nm, and (d) 422.5 nm.

are 11.03, 11.35, 11.53, and 11.74 eV, which exceed the I_a value (10.48 eV) by 0.55, 0.87, 1.05, and 1.26 eV, respectively. From the main photoelectron peaks shown in Fig. 2, we obtained kinetic energies of 0.53, 0.75, 1.01, and 1.24 eV, which are in good agreement with the above-mentioned estimated values. Thus, it may definitely be concluded from the present work that four-photon ionization of H₂S takes place via the three-photon resonant Rydberg states at the laser wavelengths used.

In each photoelectron spectrum, several satellite bands were also observed at the lower energy side, as shown in Fig. 2. A few satellite bands in each case may be explained in terms of vibrational structure of the lowest ionic state. The 449.7 nm spectrum (a) in Fig. 2 shows that the second peak is clearly separated from the main peak. The energy separation between these two peaks is 0.27 eV, approximately equal to the above-mentioned ν_1 vibrational energy of the ground-state ion (0.31 eV).

In general, vibrational structure of a photoelectron band should be governed by the Franck–Condon factors between the initial and the final state of ionization. Therefore, the intensity distribution of the first two bands in spectrum (a) in Fig. 2 suggests that the molecular structure of the corresponding Rydberg state somewhat differs from that of the ground-state ion. (A HeI photoelectron spectrum for H₂S shows a dominant $v = 0$ peak in the first ionization band, [14,15] suggesting that the molecular structure of the ground-state ion is almost the same as that of the ground-state molecule.) On the other hand, according to the VUV spectroscopic study of Masuko et al., [13] the structure of 4A Rydberg state of H₂S slightly differs from that of the ground-state molecule. Therefore, the above explanation for

the appearance of the two distinct bands in spectrum (a) in Fig. 2 seems to be consistent with the conclusion deduced from the VUV study.

In spectrum (a) in Fig. 2, a few additional, but weak bands appear in the low energy region below 0.2 eV. However, the origin for these weak bands is not clear at the present time. Spectrum (b) obtained at 436.9 nm in Fig. 2 also shows a shoulder attributable to the vibrational structure (ν_1 mode) of the ion.

Spectra (c) and (d) obtained at 429.4 and 422.5 nm, respectively, indicate that the main peak due to $v = 0$ is dominant, although several satellite bands also appear. The appearance of the dominant peaks in these spectra in Fig. 2 suggests that the molecular structures of the 3C and 3D Rydberg states quite resemble that of the ground-state ion.

TABLE II. Experimental and calculated photo-electron energies.

		K (eV)	
λ_l (nm)	$4h\nu_l$ (eV)	Exptl.	Calcd.[b]
449.7	11.03	0.53	0.55 ($v = 0$)
		0.26	0.24 ($v = 1$)
436.9	11.35	0.75	0.87 ($v = 0$)
		(0.6)[a]	0.56 ($v = 1$)
429.4	11.53	1.01	1.05 ($v = 0$)
		(0.8)[a]	0.74 ($v = 1$)
422.5	11.74	1.24	1.26 ($v = 0$)
		(0.9)[a]	0.95 ($v = 1$)

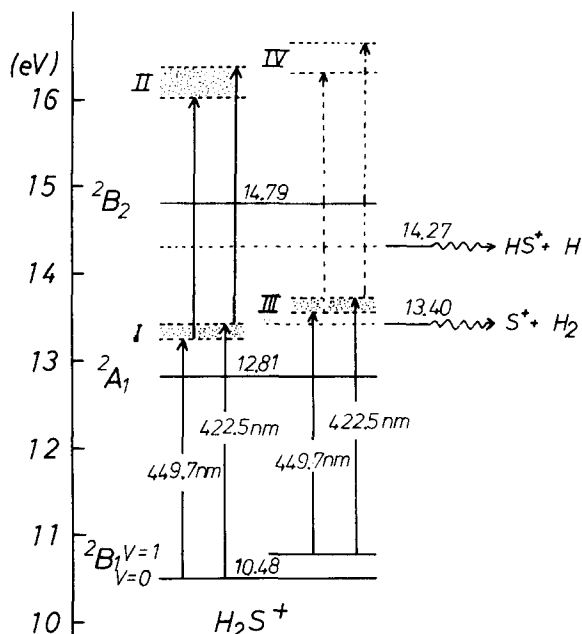[a]Shoulder.
[b]Calculated from Eq. (1).

FIG. 3. An energy diagram of H_2S^+. Predissociation thresholds producing SH^+ and S^+ fragments are also shown. I and II indicate the 13.18–13.36 eV region and the 15.94–16.30 eV region, respectively, corresponding to the one-photon and the two-photon excitation of the $v = 0$ ground-state parent ion. III and IV indicate the 13.50–13.67 eV region and the 16.25–16.61 eV region, respectively, corresponding to the one-photon and the two-photon excitation of the $v = 1$ ground state parent ion.

C. Mechanism for ionic fragmentation

Since the threshold energies of producing S^+ and SH^+ ions are reported to be 13.40 and 14.27 eV, respectively,[16] the formation of these fragment ions needs at least five or six photons under the present laser excitation conditions. From the mass-resolved REMPI study of H_2S, Carney and Baer[6] have indicated that the S^+ and SH^+ fragments formed by laser excitation at 430.0, 437.0, and 449.7 nm, are originated from five- or six-photon resonant autoionizing states. (The laser wavelengths of 430.0 and 437.0 nm used by Carney and Baer[6] are slightly different from the corresponding wavelengths used here. However, there seems to be no essential difference in the results of ionic fragmentation between the two experiments.) They[6] have concluded that the autoionization ladder mechanism is favored, although the possibility of the parent ion fragmentation mechanism is not ruled out. According to the autoionization ladder mechanism, the fragment ions are formed by dissociative ionization from the super-excited states of the H_2S molecule, while the parent ion fragmentation mechanism means that the fragmentation takes place following subsequent photon absorption by the ground-state parent ion (H_2S^+).

In contrast to the conclusion of Carney and Baer,[6] an evidence supporting the parent ion fragmentation mechanism has been obtained from the present REMPI photoelectron measurements. In other words, the photoelectron spectra obtained here clearly indicate that only the

ground-state parent ions are initially formed as a result of four-photon absorption under the present laser excitation conditions.

From mass-resolved photoionization efficiency curves, Dibeler and Liston[16] have indicated that a significant amount of parent ions are formed from autoionization states up to 20 eV. In VUV photoelectron spectroscopy, it is well known that the parent ions in the ground state as well as in several excited states are initially formed by ionization of H_2S with resonance radiation. As mentioned before, in the present work, no photoelectrons above 1.3 eV have been detected. This fact indicates that the minimum numbers of photons (four photons) are absorbed in the present REMPI experiments. If five photons were absorbed in the ionization step of H_2S, the ground state parent ion should accompany photoelectrons of 3.3–4.2 eV.

In general, molecular autoionization states are expected to have a lifetime as long as or shorter than 10^{-13} s.[17] The present experiments were carried out at the laser intensities at which one photon absorption can compete with dissociation from the predissociation states (such as NH_3 $A - v$ states) with a lifetime of about 1×10^{-13} s.[18] If the H_2S molecule in the Rydberg state is resonantly excited to an autoionization state following absorption of the fourth photon, further up-pumping can be possible and thus the system could climb the autoionization ladder, resulting in ionization as well as fragment ion formation. Such a situation may be easily attained in a two- or three-color experiment, but may not be probable in one-color experiments except the cases of accidental coincidence of the resonance frequencies in two or three excitation processes. Therefore, it would be reasonable to conclude that at the laser wavelengths used in the present REMPI photoelectron experiments only the direct ionization from the Rydberg state takes place following the absorption of the fourth photon.

In the following discussion, we want to point out that the fragmentation depends on the vibrational levels of the ground-state parent ion. An energy diagram for H_2S^+ is shown in Fig. 3, indicating that the excited $^2A_1$ and $^2B_2$ states are located at 12.81 and 14.79 eV, respectively,[15] and the dissociation thresholds of S^+ and SH^+ ions are at 13.40 and 14.27 eV, respectively.[16] According to a photoelectron–photoion coincidence study by Eland[19] and an electron impact ionization mass spectrometric study by Fiquet–Fayard and Guyon,[20] it has been indicated that only S^+ is formed from the excited $^2A_1$ state above 13.40 eV, while SH^+ is from the excited $^2B_2$ state.

By one-photon excitation, it is energetically possible to excite the parent ion at the $v = 1$ level in the ground electronic state $^2B_1$ to the 13.40 eV dissociation region, but not from the $v = 0$ level. In other words, dissociation of H_2S^+ into $S^+ + H_2$ is only possible by one-photon excitation from the $v \geq 1$ levels.

On the other hand, the parent ion in the $v = 0$ ground state may be effectively excited by two-photon absorption to the upper dissociation region to form $HS^+ + H$, as il-

lustrated in Fig. 3. In other words, HS^+ is mainly formed by two-photon excitation from the $v = 0$ level of the ground state via the vibrationally excited levels of the $^2A_1$ state which are lower than the 13.40 eV threshold of the S^+ ion.

According to Eland[19] and Dixon et al.,[21] the excited $^2A_1$ state below 13.56 eV has a lifetime of $(2-5) \times 10^{-6}$ s, that is long enough to absorb an additional photon. In the region between 13.40 and 13.56 eV, the lifetime for the predissociation is reported to be $10^{-8}-10^{-6}$ s by Dixon et al.[21] Above 13.56 eV, since no emission spectrum is reported, the lifetime should be much shorter due to rapid dissociation. From these life-time considerations, it is expected that the above-mentioned two-photon excitation of the parent ion from the $v = 0$ ground state effectively occurs via the long-lived $^2A_1$ state and consequently the formation of HS^+ takes place mainly from the excited $^2B_2$ state.

On the contrary, two-photon absorption of the parent ion from the $v = 1$ ground state giving rise to HS^+ ion production should compete with the fast predissociation following one-photon absorption. Therefore, at a low laser intensity the HS^+ ion formation may not be expected by excitation from the $v = 1$ ground state, while it may become important at a higher intensity.

According to Carney and Baer,[6] the relative amount of HS^+ against S^+ is larger in the 449.7 nm excitation than in the 430.0 nm excitation. This may be explained using the scheme shown in Fig. 3 as follows; further up-pumping from the intermediate $^2A_1$ state above the predissociation threshold is more plausible for the 449.7 nm laser than for the 422.5 nm laser, since the rate of predissociation increases with increasing ex-cess energy above the threshold.

The mechanism of the formation of ionic fragments originating from neutral fragments may be ruled out for the following reasons. If the neutral fragments (SH or S) formed by the present laser excitation are the precursors of the ionic fragments, MPI ion current peaks due to the neutral fragments should appear in the MPI ion current spectrum as were observed in those of NO_2[22] and NH_3.[23] All the bands of the MPI ion current spectrum in Fig. 1, however, well correspond to those of the available VUV absorption spectrum of H_2S and the photoelectron spectra shown in Fig. 2 are obtained by the laser excitation at the main peaks of the MPI ion current spectrum of H_2S. Therefore, at the peak fre-quencies of the MPI ion current spectrum, even if neu-tral fragments are produced, they would not be ionized by the subsequent absorption of four nonresonant photons.

IV. CONCLUSION

From the present measurements of ion currents and photoelectron energies with a Nd-YAG pumped dye laser, it has been found that under the present laser excitation conditions the H_2S molecule is ionized by four-photon ab-sorption via three-photon resonant Rydberg states to produce the ground state parent ion with $v = 0$ as well as $v = 1$ to some extent. Therefore, the laser-induced

ionic fragmentation of HS^+ and S^+ reported by Carney and Baer[6] should be explained in terms of the parent ion fragmentation mechanism that the initially formed ground-state parent ions are further excited by addi-tional photon absorption to produce the fragment ions through the predissociation pathways.

For the ionic fragmentation of H_2S, Carney and Baer[6] have proposed the autoionization ladder mechanism rather than the parent ion fragmentation mechanism, on the basis of their laser power and wavelength de-pendences and their model calculations of rate equations In their rate equation calculations, it has been assumed that at wavelengths longer than 434.4 nm, four photons produce only H_2S^+, five photons produce only S^+, and six photons produce only HS^+. However, as already mentioned in the present paper, five photons cannot pro-duce S^+ from the $v = 0$ ground state H_2S^+. This fact should be taken into account in setting up the rate equa-tions for simulating the laser power dependence of the fragment ion intensities.

One of the most important conclusions obtained here is the fact that the parent ion is formed by the four-photon excitation. From the present work, it may be mentioned that the S^+ fragment is formed by one-photon excitation of the $v = 1$ ground state parent ion, while the HS^+ fragment is formed by two-photon excitation of the $v = 0$ ground state parent ion.

Note added in proof: After this paper had been ac-cepted, a paper of photoelectron spectrum of H_2S by Miller et al. [J. C. Miller, R. N. Compton, T. E. Carney, and T. Baer, J. Chem. Phys. 76, 5648 (1982)] was brought to our attention. From the results of their photoelectron kinetic energy measurements they have concluded that the fragment ions in the multiphoton ion-ization of H_2S at 437 nm are formed as a result of addi-tional photon absorption by parent ions which are them-selves formed with the minimum number of photon ab-sorption steps. This is in agreement with the conclusion reached in the present paper.

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[18] In the MPI experiment of NH_3, we observed the ion current signal via $A-v$ ($v = 0-3$) states of NH_3. The predissociation lifetime for $v = 1$ state determined from the MPI band width is about 1×10^{-13} s. For the MPI study of NH_3, see also Ref. 23.

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