Photoionization studies of sulfur radicals and products of their reactions

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A discharge flow–photoionization mass spectrometric system coupled to a synchrotron is employed to study intermediates and products of sulfur radical reactions related to atmospheric chemistry. Sulfur radicals are generated from reactions of oxygen or chlorine atoms with sulfur compounds in a flow tube. The gaseous reaction products are sampled into the ionization region *via* a three-stage differential pumping scheme. Photoionization spectra and ionization energies are measured by dispersing synchrotron radiation to ionize the samples. Using this technique, photoionization spectra and ionization energies of HSO, CH_3SO, C_2H_5SO, HSCl, and some secondary reaction products, SSCl, HSSCl, HSSSH, CH_3SOH and $CH_3SS(O)CH_3$, were measured for the first time.

1. Introduction

Anthropogenic and natural sulfur are emitted into the atmosphere in various chemical forms: SO_2, H_2S, CS_2, OCS, CH_3SH, CH_3SCH_3 and CH_3SSCH_3, to name a few. Roughly, on a global basis, sulfur from natural origins and that from anthropogenic origins contribute equally to the atmosphere. Most of this sulfur returns to the oceans (90%) and the land (10%) as a sulfate in precipitation. The oxidation of anthropogenic SO_2 to H_2SO_4 is the major cause of acid rain. Also, the oxidation of naturally occurring sulfur compounds leads to sulfuric acid particles, which act as condensation nuclei for water to generate clouds and thus change the albedo of the Earth. Therefore, atmospheric sulfur chemistry has immense significance to the biosphere in general and man in particular. Substantial efforts have been directed towards the study of the atmospheric chemistry of these sulfur species (Tyndall & Ravishankara, 1991).

Photoionization mass spectrometry is currently used to study the kinetics and mechanisms of atmospheric reactions of sulfur species (Dominé *et al.*, 1990, 1992). However, photoionization spectra are lacking for most sulfur radicals and their reaction intermediates. Thus, it is important to measure photoionization spectra of sulfur radicals and their reaction products. From such measurements, an optimal wavelength for the ionization of sulfur species in kinetic experiments can be established. Ionization

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Table 1
Sulfur radicals produced from various reactions in this work.

Radicals	Reactions
HS	$O + H_2S \rightarrow HS + OH$
	$Cl + H_2S \rightarrow HS + HCl$
SO	$O + CS_2 \rightarrow SO + CS$
	$O + OCS \rightarrow SO + CO$
HSO	$O + C_2H_5SH \rightarrow HSO + C_2H_5$
	$O + 2\text{-}C_3H_7SH \rightarrow HSO + 2\text{-}C_3H_7$
	$O + HSC_2H_4SH \rightarrow HSO + HSC_2H_4$
CH_3SO	$O + CH_3SSCH_3 \rightarrow CH_3SO + CH_3S$
	$O + C_2H_5SCH_3 \rightarrow CH_3SO + C_2H_5$
C_2H_5SO	$O + C_2H_5SC_2H_5 \rightarrow C_2H_5SO + C_2H_5$
	$O + C_2H_5SSC_2H_5 \rightarrow C_2H_5SO + C_2H_5S$

energies (IEs) of these sulfur compounds can also be derived from the thresholds of their photoionization spectra. We can expect to learn about their thermochemistry from the IE data obtained.

2. Experimental and results

We use a discharge flow–photoionization mass spectrometer (DF–PIMS) to measure the photoionization spectra of sulfur radicals and their reaction products (Cheng & Hung, 1996). Sulfur radicals are generated from reactions of oxygen or chlorine atoms with sulfur compounds (see Table 1), in a flow tube by using a discharge flow technique. The flow reactor is a Pyrex tube (with inner diameter 24 mm and length 600 mm) fitted with a movable injector (outer diameter 8 mm). The gas effluents of the reaction system are sampled into an ionization chamber *via* a three-stage differential pumping scheme. Then, photoionization spectra and ionization energies of mass-selected ions are measured by using a synchrotron as the photoionization source. The detection system is a standard PIMS system with a quadrupole mass filter operated in the pulse-counting mode.

We measured the photoionization spectra of various sulfur compounds. Ionization energies of these compounds were determined from the thresholds of their photoionization spectra near the onset. Three methods were employed to determine the threshold of ionization; the choice of method depends on the characteristics of each spectrum. When the photoion yield curve shows an abrupt rise near the onset, the maximum of its first derivative is well defined and is therefore taken as the threshold. When the spectrum appears as a distinct step but rises less rapidly than in the former case, the midrise point of the onset is taken as the threshold. The thresholds obtained by these two methods typically agree with each other. In some cases, the photoion yield curve has a gradually rising edge, presumably due to poor Franck–Condon overlap between the neutral and the ionic species. In these cases, the threshold is derived from the intersection of the background baseline with the rising edge fitted to a line by a least-squares method. The IEs obtained for various sulfur compounds are listed in Table 2; the results are in agreement with literature values. Thus, it demonstrates that our DF–PIMS system operates properly.

We have successfully studied photoionization spectra of several sulfur radicals using this DF–PIMS technique. Up to now, we have focused on some interesting radicals: HS, HSO, CH_3S, CH_3SO and C_2H_5SO. The IE of the HS radical was determined to be 10.45 (4) eV, consistent with the value of 10.4219 (4) eV measured with a nonresonant two-photon pulsed field ionization technique (Hsu *et al.*, 1994). The IE of CH_3S was determined to
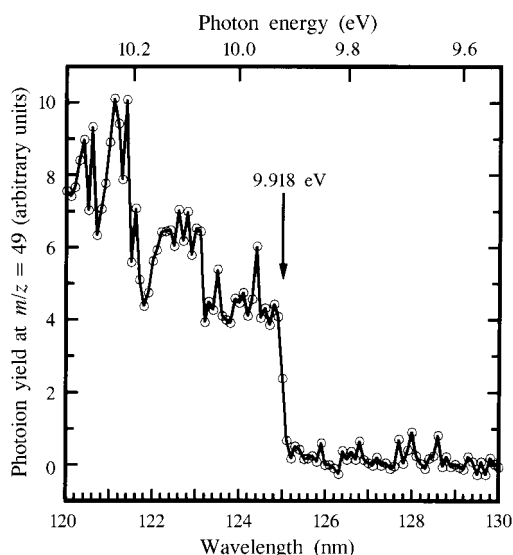
Table 2
Ionization energies (eV) of various sulfur compounds determined in this work.

Species	This work	Previous work
CS_2	10.078 (7)	10.0782 (6)[a]
H_2S	10.460 (11)	10.4682 (2)[b]
OCS	11.171 (7)	11.1736 (15)[c]
CH_3SH	9.46 (2)	9.455 (5)[d]
C_2H_5SH	9.280 (7)	9.285 (5)[e]
$2\text{-}C_3H_7SH$	9.143 (7)	9.14[f]
HSC_2H_4SH	9.280 (14)	–
CH_3SCH_3	8.69 (2)	8.710 (5)[g]
$C_2H_5SCH_3$	8.55 (2)	8.54 (1)[h]
$C_2H_5SC_2H_5$	8.40 (1)	8.41 (1)[i]
CH_3SSCH_3	8.34 (3)	8.18 (3)[j]
$C_2H_5SSC_2H_5$	8.05 (1)	<8.27 (3)[h]

References: (a) Fischer *et al.* (1993a); (b) Fischer *et al.* (1993b); (c) Ono *et al.* (1981); (d) Morgan, Puyuelo *et al.* (1995); (e) Watanabe *et al.* (1962); (f) Ogata *et al.* (1973); (g) Morgan, Orr-Ewing *et al.* (1995); (h) Lias *et al.* (1988); (i) Ma *et al.* (1993); (j) Li *et al.* (1993).

Table 3
Ionization energies (eV) of sulfur species produced from reactions in this work.

Species	This work	Previous work
HS	10.45 (4)	10.4219 (4)[a]
SO	10.34 (4)	10.294 (4)[b]
S_2	9.350 (14)	9.356 (2)[c]
HSO	9.918 (16)	–
HSCl	9.887 (16)	–
SCl_2	9.57 (3)	9.45 (3)[d]
S_2O	10.60 (4)	10.584 (5)[b]
SSCl	9.04 (3)	–
S_3	9.63 (3)	9.68 (3)[e]
HSSH	9.06 (2)	9.41[f]
HSSCl	9.266 (14)	–
HSSSH	≤9.09	–
CH_3S	9.27 (3)	9.2647 (10)[g]
CH_3SS	8.62 (5)	8.67 (2)[h]
CH_3SO	8.99 (2)	–
CH_3SOH	8.67 (3)	–
C_2H_5SO	8.71 (2)	–
$CH_3SS(O)CH_3$	8.82 (5)	–

References: (a) Hsu *et al.* (1994); (b) Norwood & Ng (1989); (c) Liao & Ng (1986); (d) Kaufel *et al.* (1981); (e) Berkowitz & Lifshitz (1968); (f) Frost *et al.* (1977); (g) Hsu & Ng (1994); (h) Ma *et al.* (1994).

be 9.27 (3) eV, in good agreement with the value of 9.2647 (10) eV measured with a nonresonant two-photon pulsed field ionization technique (Hsu & Ng, 1994). For HSO, CH_3SO and C_2H_5SO radicals, photoionization spectra were measured for the first time by our group and their IEs were obtained as 9.918 (16) (Cheng, Eberhard *et al.*, 1997a), 8.99 (2) (Hung *et al.*, 1996) and 8.71 (2) eV (Cheng, Hung *et al.*, 1997), respectively. Fig. 1 shows the photoionization spectrum near the threshold region of HSO; the IE was derived from the distinct step shown at the onset, either from the midrise point or the first derivative of the onset, as indicated by the arrow.

In our studies of sulfur radicals, sometimes secondary reactions could not be avoided. For example, in the case of the CH_3SO radical, we also obtained photoionization spectra of CH_3SOH, CH_3SS and $CH_3SS(O)CH_3$; the IEs determined were 8.67 (3), 8.62 (5) and 8.82 (5) eV, respectively. In the reaction system $Cl/$ Cl_2/H_2S, photoionization spectra of products HSCl, HSSH, HSSSH, SSCl and HSSCl were measured for the first time; the IEs were 9.887 (16), 9.06 (2) (Cheng, Eberhard *et al.*, 1997b), ≤9.01, 9.01 (3) and 9.266 (14) eV, respectively (Eberhard *et al.*,

1997). Other products observed in this reaction system include S_2, S_3 and SCl_2; their photoionization spectra and IEs were also measured (see Table 3).

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Figure 1
The photoionization threshold region of HSO at a nominal resolution of 0.2 nm and with 0.1 nm steps. The arrow indicates the ionization energy of HSO.

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