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First experimental observation on different ionic states of the CH_3SS radical: A HeI photoelectron spectrum

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A continuous flowing CH_3SS radical beam is produced *in situ* by pyrolysis of CH_3SSCH_3 at $215(\pm 0.5)\,°C$. An obvious and complete photoelectron (PE) spectrum of the CH_3SS radical is recorded *in situ* for the first time. Five sharp peaks at 8.63, 9.36, 9.94, 10.29, 10.72 eV and one broader band at 11.82 eV are observed in the PE spectrum below 12 eV. The first peak with the lowest ionization energy, 8.63 eV, is attributed to removal of an electron from the highest occupied molecular orbital (HOMO) $5a''$ of the CH_3SS radical, corresponding to the $CH_3SS^+(X\,^1A') \leftarrow CH_3SS(X\,^2A'')$ ionization. The vibrational spacing $600\pm 60\,cm^{-1}$ on the first peak corresponds to the $S-S$ stretch mode excited in the CH_3SS^+ cation upon photoionization process. The sharp peaks at 9.36 and 9.94 eV come from removal of the electron from the $16a'$ orbital, leading to $^3A''$ and $^1A''$ ionic states of the CH_3SS radical, and the sharp peaks at 10.29 and 10.72 eV should be the result of removal of the electron from the $15a'$ orbital of the CH_3SS radical. To assign the photoelectron spectroscopy (PES) bands of the CH_3SS radical, both GAUSSIAN2 (G2) and improved density functional theory (DFT) calculations on different ionic states of the CH_3SS radical are also performed. The PES experimental ionization energies of the CH_3SS radical agree with those calculated with G2 and DFT. [DOI: 10.1063/1.1343081]

INTRODUCTION

It is well-known that dimethyl disulfide CH_3SSCH_3 is an important precursor in the atmospheric sulfur chemistry cycle that could contribute to formation of acid rain.[1–6] Numerous experimental and theoretical studies on CH_3SSCH_3 have been also performed. The laser photofragmentation time-of-flight mass spectroscopic technique investigated the photodissociation process of CH_3SSCH_3. The kinetic energy threshold measurement suggests that the CH_3S_2 radical formed at the threshold of the above-mentioned process has the CH_3SS structure, and gives the first ionization energy $8.67\pm 0.03\,eV$ for the CH_3SS radical.[7] In fact, Butler *et al.*[8] proposed first by threshold photoelectron photoion coincidence (PEPICO) method that the CH_3S_2 species has CH_3SS structure.

Our laboratory has demonstrated the ability to generate a continuous flowing beam of radicals via the pyrolysis of parent species or the microwave discharge of suitable compounds, allowing us to perform HeI photoelectron spectroscopy (PES) studies on reactive open-shell species,[9–14] such as the I (Ref. 9) and Br (Ref. 10) atoms, the NO_3,[11] $R_2N(R=CH_3,C_2H_5)$,[12,13] and CH_3O (Ref. 14) radicals. The CH_3SS radical is produced from pyrolysis of the same precurssor as the CH_3S radical,[14] but at lower temperature:

$$CH_3SSCH_3 \xrightarrow{285(\pm 0.5)\,°C} CH_3S^{\bullet} + CH_3S^{\bullet},$$

$$CH_3SSCH_3 \xrightarrow{215(\pm 0.5)\,°C} CH_3SS^{\bullet} + CH_3^{\bullet}.$$

In this paper, we present a PES study on different ionic states of the CH_3SS radical.

EXPERIMENT

The experiment is performed on a double-chamber UPS machine-II which was built specifically to detect transient species as described elsewhere.[15] A continuous flowing CH_3SS beam is produced *in situ* by pyrolysis of CH_3SSCH_3 at $215(\pm 0.5)\,°C$ in a quartz tube using a double-heater inlet system. That is to say, the new species is produced within 1–2 cm of the photoionization region of the spectrometer, and then it passes through the photoionization point and is quickly pumped out. The purity of CH_3SSCH_3 is 99% and it was bought from the ACROS Company. The PE spectrum of CH_3SSCH_3 in the low temperature is the same as in Ref. 16. The PE spectrum of the CH_3SS radical is measured at a resolution of about 30 meV as indicated by the $Ar^+(^2P_{3/2})$ photoelectron band. Experimental vertical ionization energies (I_v in eV) are calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample.

GAUSSIAN2 (G2) AND IMPROVED DFT CALCULATIONS

In order to assign the PES bands of the CH_3SS radical, G2 calculations have been performed on the $^2A''$ ground state of the CH_3SS radical in C_s symmetry, the ground $^1A'$, and several ionic states of the CH_3SS^+ cation. The G2 theoretical procedure has been described in detail by Curtiss *et al.*[17] Briefly, the G2 method uses MP2(full)/6-31G* to get the structure, subsequent single point calculations [at the MP4/6-311G(d,p), MP4/6-311+G(d,p), MP4/6-

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311G($2df,p$), QCISD(T)/6-311G(d,p), and MP2/6-311+G($3df,p$) levels, respectively] are then carried out to obtain total energies at the QCISD(T)/6-311+G($3df,p$) level, making certain assumptions about additivity. The additivity approximations have been examined in a separate study and have been found to be valid in most cases. Finally, a small semiempirical correction, referred to as the higher level correction (HLC) is applied. This is based on the number of α and β electrons. The computed ionization energies (E in eV) are obtained from the difference of the total energy of the resulting cation / ${}^2A''$ ground state in C_s symmetry.

The density functional theory (DFT) calculations have also been performed for getting the vertical ionization energies on different ionic states of the CH_3SS radical, because the DFT calculation was applied successfully to the assignment of the PES bands for the NO_3,[11] R_2N(R $=CH_3,C_2H_5,C_3H_7$),[12,13,18] CH_3S,[14] and CH_3O (Ref. 14) radicals. The DFT calculation is carried out with the Amsterdam density functional (ADF) program package in which a density fitting procedure is used to obtain the Coulomb potential, and an elaborate 3D numerical integration technique is employed to calculate the Hamilton matrix elements. The Vosko–Wilk–Nusaair parametrization of uniform electron gas data is used for the exchange-correlation energy and potentials, which is usually called the local spin density approximation (LSDA). The gradient correction of exchange energy due to Becke and that of correlation energy developed by Perdew have been performed. The molecular orbitals were expanded in an uncontracted triplet ζ-STO basis set augmented by polarization basis functions.

The vertical ionization energies (E_v in eV) computed using the DFT program are obtained from the total energy difference of the resulting cation/neutral species in this study. The sum method proposed by Ziegler–Rauk–Baerends is used to calculate the total energies of singlet states described by multideterminatal wave functions. The geometries used in the calculation for the neutral radical are taken from optimizational results at the UMP2/6-31G* level of theory.

RESULTS AND DISCUSSION

Figure 1 gives the PE spectrum of the new species pyrolyzed CH_3SSCH_3 at 215(±0.5) °C. An expanded PE spectrum in which a fine vibrational structure on the first peak could be clearly seen in the low ionization energy region (<12.50 eV) is given in Fig. 2.

From Figs. 1 and 2, it is clearly seen that the first peak at 8.63 is a sharp peak with some structures in the higher ionization energy side. This phenomenon shows that the highest occupied molecular orbital (HOMO) of the species pyrolyzed CH_3SSCH_3 should be slightly bonding or slightly antibonding orbitals, because removal of the electron from these orbitals always leads to sharp peak with some structure in the higher ionization energy side.[16]

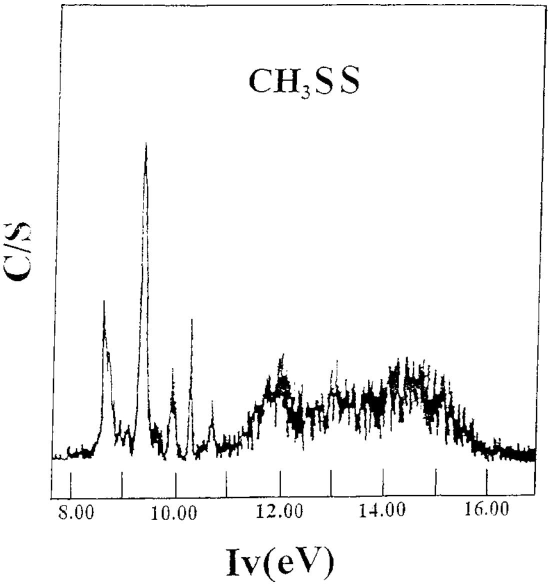

FIG. 1. HeI photoelectron spectrum of CH_3SS radical which is produced by pyrolysis of CH_3SSCH_3 at 215(±0.5) °C.

The peak at 8.63 eV is assigned to be the first PES band of the CH_3SS radical, because the measured ionization energy (8.63±0.02 eV) is in excellent agreement with adiabatic ionization energy values obtained from two previous photoionization studies of this species, i.e., 8.67±0.03 eV (Ref. 7) and 8.62±0.05 eV,[19] respectively. This assignment is also supported by an analysis of fine vibrational structure on the first PES peak of this species. The vibrational spacing $600\pm 60\ \mathrm{cm}^{-1}$ on the first PES peak of the species is close to the reported vibrational frequency $610\pm 160\ \mathrm{cm}^{-1}$ of the neutral CH_3SS species,[20] because the vibrational spacing on the PES band caused by electron ionization of a nonbonding orbital should be close to vibrational frequency with the neutral species. The position of the first PES peak compares well

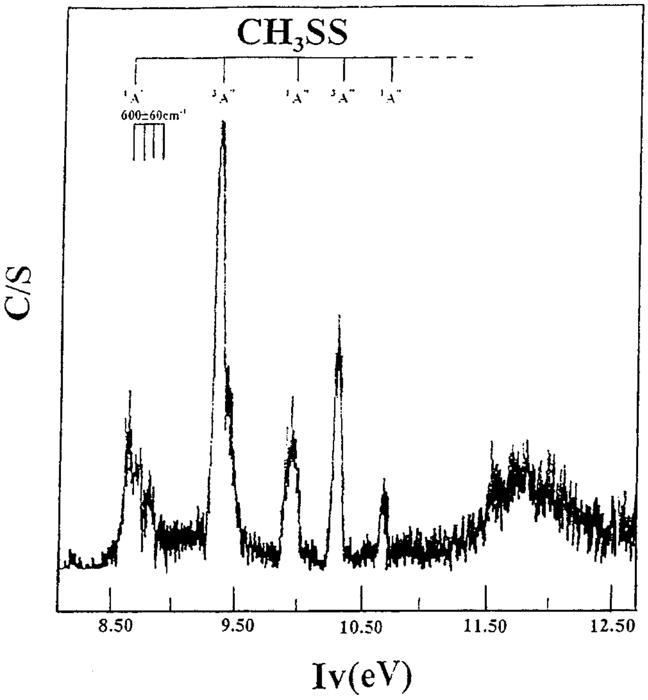

FIG. 2. The expanded PE spectrum of CH_3SS radical in the low ionization energy region (<13.00 eV).

TABLE I. The experimental vertical ionization energies (I_v in eV), calculated ionization energies (E in eV), according to C_s symmetry by using the G2 and DFT methods, and relative intensities of PES signals observed from different ionic states of the CH_3SS radical.

PES experimental I_v(eV)[a]	G2 energies E(eV)	DFT energies E(eV)	Cationic states	Relative intensity	
				This work[b]	Stat. ratio
8.63	8.524	8.702	$^1A'$[c]		
9.36	9.175	9.321	$^3A''$[d]	3.05	3
9.94	10.340	10.125	$^1A''$[d]	1.00	1
10.29	10.558	10.534	$^3A''$[e]	2.97	3
10.72	11.101	11.226	$^1A''$[e]	1.00	1
11.82	12.613	12.708	$^3A'$[f]		

[a] ±0.02 eV.
[b] Corrected for analyzer sensitivity ±0.02.
[c] Ionic state comes from electron ionization of the HOMO $5a''$ for CH_3SS radical.
[d] Ionic state comes from electron ionization of the SHOMO $16a'$ for CH_3SS radical.
[e] Ionic state comes from electron ionization of the $15a'$ orbital for CH_3SS radical.
[f] Ionic state comes from electron ionization of the $4a''$ orbital for CH_3SS radical.

with results of both G2 and DFT calculations, and can be assigned as the $^1A'$ ionic state of the CH_3SS radical (see Table I). Table I gives the PES experimental vertical ionization energies (I_V in eV) and corresponding G2 and DFT computed ionization energies (E in eV) for different ionic states of the CH_3SS radical. According to the Frank–Condon principle, the energies of the ionic states are given using the vertical ionization energy (I_V), chosen as the maxim of the PES bands, and the computed ionization energy (E) should be obtained from the difference of total energy of the resulting cation/neutral radical in C_S symmetry for the CH_3SS radical. That is to say, the previous photoionization experimental studies and both G2 and DFT calculations support that the first PES peak at 8.63 ± 0.02 eV for the species pyrolyzed CH_3SSCH_3 is the first PES peak of the CH_3SS radical, i.e., it represents the generation of the CH_3SS radical.

From Figs. 1 and 2, it is also seen that the four peaks at 9.36, 9.943, 10.29, and 10.72 eV which together appear on the PE spectrum accompanied with the first peak at 8.63 eV are very sharp. These phenomena show that ionizations corresponding with the four sharp peaks come also from removal of the electron from nonbonding orbitals of the species pyrolyzed CH_3SSCH_3, because the vertical ionization energy (I_V in eV) is equivalent to the adiabatic ionization energy (I_A in eV) on the PES bands.

It was also recognized that the assignment of the PES bands for a new species can be also supported by theoretical analysis on the new species proposed. According to C_s symmetry, the molecular orbitals of valence shell of the CH_3SS radical would be in the following order of increasing energy:

$$\sim 13a'^2 14a'^2 4a''^2 15a'^2 16a'^2 5a''^1.$$

The removal of an electron from the HOMO will leave the ion in the singlet state $^1A'$, whereas removal of an electron in turn from each of the other valence shell orbitals can leave both triplet and singlet states of the ion.

The HOMO ($5a''$) of the CH_3SS radical is an essentially lone-pair orbital on the end sulfur atom with some $S-S$ antibonding character. This means that removal of an electron from the HOMO ($5a''$) of the CH_3SS radical, leading to the ion in singlet state $^1A'$, should give a sharp PES peak with fine structure. The vibrational spacing $600\pm60\,\mathrm{cm}^{-1}$ on the first peak at 8.63 eV is close to the reported vibrational frequency $610\pm160\,\mathrm{cm}^{-1}$ of the $S-S$ stretch mode for the neutral CH_3SS radical.[20]

An analysis for orbital character of the CH_3SS radical finds that both $16a'$ and $15a'$ orbitals of the CH_3SS radical are sulfur lone-pair orbitals with contributions from the two sulfur atoms. This means that the removal of the electrons of both $16a'$ and $15a'$ orbitals for the CH_3SS radical should lead to four sharp peaks on the PE spectrum, because each of both $16a'$ and $15a'$ orbitals will lead to both triplet and singlet states of the ion. The intensity of the PES band, corresponding to the triplet state $^3A''$ should be three times that of the singlet state $^1A''$, because the intensity of the PES band is the representation of relative ionic statistical weights.

A careful analysis for the intensities of the four sharp peaks at 9.36, 9.94, 10.29, and 10.72 eV finds that the intensity of the peak at 9.36 eV is about 3.05 times that of the peak at 9.94 eV, and the intensity of the peak at 10.29 eV is 2.97 times that of the peak at 10.72 eV. That is to say, the intensity ratio of the four sharp peaks for species pyrolyzed CH_3SSCH_3 are also in good agreement with relative ionic statistical weight led by ionization of both $16a'$ and $15a'$ orbitals of the CH_3SS radical. The PES band centered near 11.82 eV could be attributed to removal of the electron from the $4a''$ orbital or maybe comes from removal of the electrons from more orbitals in the deep valence shell of the CH_3SS radical, because the band is very broad.

The above assignment for the PES bands of the CH_3SS radical is supported by the results of both G2 and DFT calculations. As indicated in Table I, experimental and theoretical results agree reasonably well.

In a word, from the previous other experimental studies,[7,8,19,21] and from the analysis on the intensities of the PES peaks for the species pyrolyzed CH_3SSCH_3 and both G2 and DFT calculations on different ionic states of the CH_3SS radical, it is concluded that the PE spectrum presented for the species pyrolyzed CH_3SSCH_3 is the PE spectrum of the CH_3SS radical, i.e., the pyrolysis of CH_3SSCH_3 at $215(\pm0.5)$ °C generates the CH_3SS radical.

An interesting phenomenon is also attended that the first PES band at 9.84 eV for the methyl CH_3 radical[22,23] is not seen on the PE spectrum of the species pyrolyzed CH_3SSCH_3. A reasonable explanation may be that the CH_3 radical generated by pyrolysis of CH_3SSCH_3 transforms fastly into the ethane,

$$CH_3^* + CH_3^* \rightarrow CH_3CH_3,$$

because the lifetime of the alkyl radical is shorter than that of alkylthio radical.[24] The first PES band[16] with the highest intensity for the ethane generated buries below the PES band centered near 11.82 eV of the CH_3SS radical.

CONCLUSIONS

A continuous flowing CH_3SS radical beam is produced *in situ* by pyrolysis of CH_3SSCH_3 at 215(±0.5) °C. An obvious and complete PE spectrum of the CH_3SS radical is *in situ* recorded. Five sharp peaks at 8.63, 9.36, 9.94, 10.29, and 10.72 eV, led by removal of the electrons from the HOMO $5a''$, second highest occupied molecular orbital (SHOMO) $16a'$ and $15a'$ orbitals of the CH_3SS radical, respectively, in the low ionization energy region (<12.00 eV), appear clearly on the PE spectrum of the CH_3SS radical. The broad band at 11.82 eV is observed and assigned. Both G2 and DFT calculations on different ionic states of the CH_3SS radical are also performed for assigning the PES bands of the CH_3SS radical. The PE spectrum of the CH_3SS radical provides another example in which the G2 calculation can predict correctly the ionization energies of different ionic states for the species studied. And the improved DFT calculation can also give good results for both the lowest and higher ionic states of the radicals that are not too large.

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