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Negative-ion photoelectron spectroscopy of CH_3S^-

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Abstract

A 364-nm negative-ion photoelectron spectrum of CH_3S^- has been recorded. The electron affinity is 1.867 ± 0.004 eV. Well-resolved vibrational structure has been observed such that the C–S symmetric stretch and the C–H symmetric stretch have been measured at 725 ± 15 cm^{-1} and 1260 ± 30 cm^{-1} , respectively. The spin–orbit splitting is reported at 265 ± 15 cm^{-1} . The large spin–orbit splitting quenches the Jahn–Teller modes seen in the analogous radicals, CH_3O and CF_3S . © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many experimental [1–4] and theoretical [5] studies have focussed on the methoxy anion and radical because of its importance in atmospheric reactions. In addition, a great deal of attention has been given to CH_3O due to its C_{3v} geometry and the concomitant ^2E ground electronic state, allowing for both Jahn–Teller and spin–orbit effects. These effects make understanding the radical challenging through both experimental and theoretical techniques.

Recently, CH_3O and several other alkoxy radicals (RO), where $\text{R} = \text{CH}_3\text{CH}_2$, $(\text{CH}_3)_2\text{CH}$ and $(\text{CH}_3)_3\text{C}$, have been studied in this laboratory by performing photoelectron spectroscopy on the corresponding anions (RO^-) [4]. The spectra show more vibrational

structure, in comparison to the early spectra [6,7], due to an increase in instrument resolution. New values for the electron affinities and vibrational frequencies have been measured. The photoelectron spectrum of CH_3O^- is dominated by Jahn–Teller activity. In fact, only transitions that involve a Jahn–Teller active vibrational mode are observed in the ground state of the spectrum.

Given the information obtained from the photoelectron spectrum of CH_3O^- , we have chosen to turn our attention to the sulfur analog, CH_3S , which could also have Jahn–Teller and/or spin–orbit effects given its ^2E ground electronic state. This species is important as an intermediate in the oxidation of naturally occurring sulfur species in the atmosphere. There have been several previous studies on CH_3S using different techniques including electron detachment [8], laser-induced fluorescence (LIF) [9,10], microwave spectroscopy [11], and photodissociation [12]. All of these studies report a significant spin–orbit splitting of the ^2E state into $^2\text{E}_{3/2}$ and $^2\text{E}_{1/2}$

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states but no obvious Jahn–Teller activity has been observed.

Janousek and Brauman [8] performed electron photodetachment experiments on CH_3S^- using an ion cyclotron resonance spectrometer. From this experiment, they were able to determine the electron affinity (EA), vibrational frequencies, and spin–orbit splitting. Similar measurements were obtained by Moran and Ellison [7] in a previous negative-ion photoelectron spectroscopy study of CH_3S^- . This is in contrast to the first PES experiment in 1978 by Engelking et al. [6], which could not resolve the spin–orbit splitting. Laser-induced fluorescence studies also accurately measured the spin–orbit splitting in CH_3S as well as some vibrational frequencies. More recently, Neumark et al. looked at the photodissociation spectroscopy and dynamics of CH_3S [12]. They obtained the photofragment translational energy and angular distributions, and elucidated the mechanism for predissociation via a repulsive state.

An EA of CH_3S has been determined from the photoelectron spectrum presented in this paper and it agrees well with previous measurements [7,8]. The spin–orbit splitting has been measured and is consistent with the 255.463 cm^{-1} determined by Miller et al. [10]. Improved resolution allows for a better understanding of the vibrational modes active in the spectrum and a more complete assignment of the features has been made. In addition, polarization studies have provided evidence that there are no Jahn–Teller interactions. Lastly, the results in this study are compared with previous CH_3S studies as well as CH_3O [3,4] and CF_3S [13–15].

2. Experiment

The details of the negative-ion photoelectron spectroscopy experiment have been described elsewhere [16]; therefore, only a brief description will be given here. O^- ions are produced by flowing O_2 and helium through a microwave discharge. Methane is injected into the flow tube and reacts with the O^- ions to make OH^- ions. Downstream from the primary $\text{O}^- + \text{CH}_4 \rightarrow \text{OH}^- + \text{CH}_3$ reaction in the flow tube, methyl sulfide, CH_3SCH_3 , is introduced in order to react with the OH^- ions forming CH_3S^- .

The ions are differentially pumped, accelerated to 735 eV, and mass selected with a Wien filter before entering the interaction chamber. The 364-nm ($h\nu = 3.408\text{ eV}$) line from an Argon ion laser enters the interaction region at a right angle to the ion beam. Photodetached electrons are collected orthogonal to both the laser and ion beam axes. The electron energies are analyzed using a hemispherical analyzer and detected with a position-sensitive detector. The spectra are collected as number of electrons vs. electron kinetic energy (eKE). The spectra presented in this paper are plotted vs. electron binding energy (eBE), $h\nu - \text{eKE}$.

The polarization of the laser with respect to the electron collection axis can be changed by rotating a wave plate that is positioned in the laser beam path before the interaction chamber. Spectra were collected at 0° (parallel), 54.7° (magic angle), and 90° (perpendicular). In addition, the ions can be cooled from room temperature (300 K) to 200 K by flowing liquid nitrogen through a sleeve that encompasses the flow tube. Both of these variations to the experiment aid in the assignment to the features in the photoelectron spectra by analyzing the dependence of the spectra on the laser polarization and temperature.

Because they have similar masses, the photoelectron spectrum of NO_2 (mass 46) contaminates the photoelectron spectrum of CH_3S^- which has a mass of 47 amu. A majority of the NO_2 features lie at higher energies than the CH_3S features; however, there is some overlap between the two spectra. It is difficult to filter out the NO_2^- ions completely with the Wien filter and therefore some signal attributed to NO_2 is present in the photoelectron spectrum. As a result, the NO_2^- spectrum was recorded separately and subtracted from the CH_3S^- spectrum. All spectra displayed in this paper reflect this subtraction unless otherwise noted.

3. Results and discussion

3.1. Photoelectron spectra

The 364-nm photoelectron spectrum of CH_3S recorded under cooled conditions at the magic angle is displayed in Fig. 1. Each feature in the spectrum has been fit to a Gaussian function in order to obtain

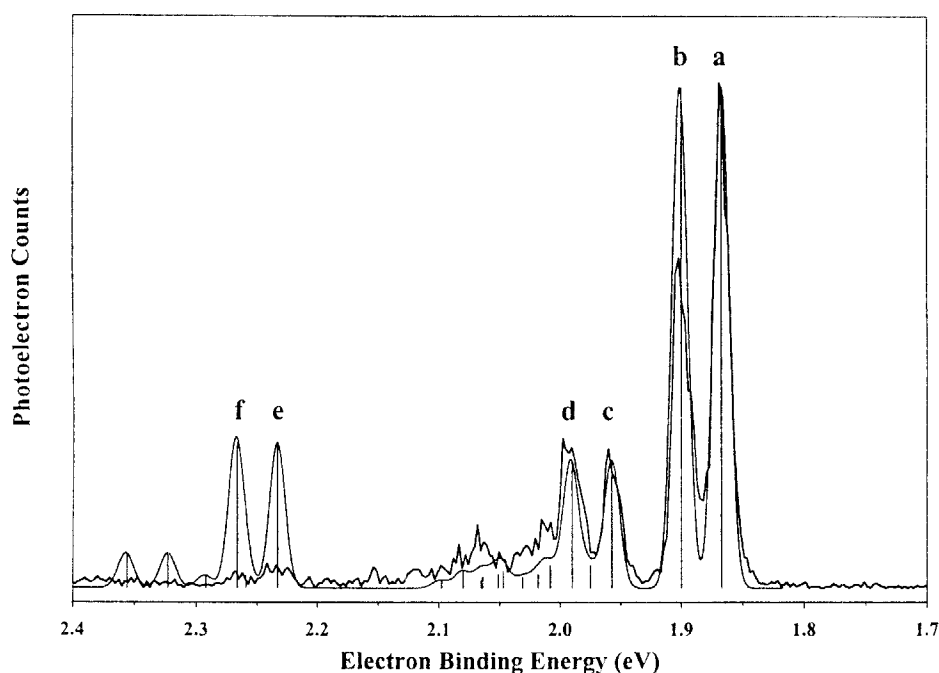


Fig. 1. The 364-nm negative-ion photoelectron spectrum of CH_3S^- recorded at the magic angle at 200 K (thick line). A simulation of the spectrum, based on calculated and experimental measurements, is shown with a thin line. Also shown is a stick spectrum, identifying the position of each individual transition in the simulation.

the energy positions. Peak a is identified as the 0_0^0 transition yielding an electron affinity (EA) equal to 1.867 ± 0.004 eV. This is in good agreement with previous values by Janousek and Brauman [8] (1.861 ± 0.004 eV) and Moran and Ellison [7] (1.871 ± 0.012 eV). From the energy positions of each peak, the spin-orbit splitting and some vibrational frequencies have been determined. The spin-orbit splitting is measured at 265 ± 15 cm^{-1} between peaks a and b. Peak c is assigned as one quantum of C–S stretch, 3_0^1 , with a frequency of 725 ± 15 cm^{-1} and a spin-orbit excited state lying ~ 275 cm^{-1} higher in energy (peak d). The C–H symmetric stretching frequency is measured to be 2960 ± 30 cm^{-1} at peak e, 1_0^1 , and has a spin-orbit splitting of ~ 275 cm^{-1} identified at peak f. It is difficult to directly measure other vibrational frequencies and assign the features between 2 and 2.2 eV; however, an explanation of these features can be found in the following section. Energy positions, frequencies and assignments of some features are listed in Table 1.

The spin-orbit splitting and C–S stretching frequency agrees well with previous measurements. The study by Janousek and Brauman measured the spin-orbit splitting of the ^2E state to be 280 ± 50 cm^{-1} and

Table 1
 CH_3S^- peak positions, frequencies and assignments

Peak ^a	Energy (eV)	Frequency ^b (cm^{-1})	Assignment ^c
	1.780 ± 0.008	700 ± 30	$\overline{3}_0^{11}$
	1.816 ± 0.008	410 ± 30	3_0^{11}
a	1.867 ± 0.004	0	0_0^0
b	1.900 ± 0.004	265 ± 15	$\overline{0}_0^0$
c	1.957 ± 0.004	725 ± 15	3_0^1
d	1.991 ± 0.004	1000 ± 15	$\overline{3}_0^1$
e	2.234 ± 0.008	2960 ± 30	1_0^1
f	2.267 ± 0.008	3225 ± 30	$\overline{1}_0^1$

^a Unlabelled peaks are hot bands.

^b Frequencies are with respect to the 0_0^0 transition at 1.867 eV.

^c A bar, X, denotes a spin-orbit excited state.

the C–S stretching frequency was $770 \pm 50 \text{ cm}^{-1}$ [8]. Similarly, Moran and Ellison reported a spin–orbit splitting between peaks a and b of $260 \pm 80 \text{ cm}^{-1}$ and a C–S stretching frequency of $750 \pm 100 \text{ cm}^{-1}$ with a spin–orbit splitting equal to $280 \pm 130 \text{ cm}^{-1}$ [7]. Neither of these studies provided a direct measurement of the C–H stretching frequency, however both reported a value of 1360 cm^{-1} for the umbrella motion, which was not easily observed in the present photoelectron spectrum. Laser-induced fluorescence experiments by Akimoto et al. [9] and Miller et al. [10] have reported spin–orbit splittings of $280 \pm 20 \text{ cm}^{-1}$ and 255.5 cm^{-1} , respectively. In all, the value of the spin–orbit splitting is consistent amongst different measurement techniques.

The spectrum has also been recorded at two other laser polarization angles, 0° and 90° . Since there is no signal from NO_3 at perpendicular polarization, no subtraction was necessary. From the room-temperature spectra, values for the asymmetry parameter, β , can be determined for each peak using the expression [17]:

$$\beta = \frac{I_0 - I_{90}}{\frac{1}{2}I_0 + I_{90}}$$

where I_0 is the intensity of a specific peak in the 0° spectrum and I_{90} is the intensity of the same peak in the 90° spectrum. Analysis reveals that β is the same, -0.6 , for each peak throughout the spectrum. A value of $\beta < 0$ suggests that the detached electron originates from a π -type orbital in the anion.

The result that all peaks in the spectrum have the same β value is in contrast to what was observed in the CH_3O^- study [4]. Different β parameters were observed for different peaks, providing evidence of Jahn–Teller interactions. There is no indication of any Jahn–Teller interactions in the CH_3S^- photoelectron spectrum, in agreement with previous studies [8–11]. Instead, the peaks are assigned as the two spin–orbit components in the ground state.

Hot bands have been observed in the room temperature spectra at both 54.7° and 90° polarization. These peaks are identified as those that disappear upon cooling the flow tube to 200 K. The measured frequencies are $410 \pm 30 \text{ cm}^{-1}$ and $700 \pm 30 \text{ cm}^{-1}$. They arise from transitions originating from the anion with one quantum of vibration in

the C–S stretch to the ground and spin–orbit excited states of the ground vibrational level in the neutral, $3_1''$ and $\bar{3}_1''$, respectively. The 700 cm^{-1} frequency is in agreement with our calculated value, 710 cm^{-1} , of the C–S stretching vibration in the anion. The splitting is $290 \pm 60 \text{ cm}^{-1}$, larger than that measured between peaks a and b but within error margins, given the decrease in the accuracy in the fitting of the weak hot bands. The positions, frequencies and assignments are also found in Table 1.

3.2. Calculations

In order to better understand the photoelectron spectra, calculations using the Gaussian 94 suite of programs at the MP2(FULL)/aug-cc-pVDZ level have been performed on the anion and neutral species [18]. Both geometry optimizations and frequency calculations were performed. The anion has C_{3v} symmetry and is a 1A_1 state and the neutral is a 2A_1 state with C_s symmetry. The neutral geometry is optimized at C_s symmetry instead of C_{3v} , which has one imaginary frequency, due to Jahn–Teller effects. The difference in energies between the two geometries is approximately 90 cm^{-1} , a bit higher than the Jahn–Teller stabilization energy calculated using a better theoretical method [5].

The CDECK suite of programs has been used to simulate the experimental spectrum and to aid in the interpretation of the spectrum [19]. It has been a successful tool in simulating more complicated spectra in the past [20]. The CDECK programs assume a harmonic oscillator approximation and utilize the normal modes, force constants, and geometries from the Gaussian 94 output files. The normal mode displacements and Franck–Condon factors for transitions from the ground state of the anion to the neutral states are calculated and a stick spectrum is generated. Each stick is broadened with a Gaussian function to best fit the experimental spectrum. In this case, a 15 meV full width at half maximum was used to generate the simulation of the photoelectron spectrum.

The simulation of the CH_3S^- photoelectron spectrum was generated using the frequencies from the MP2 calculations except in the case of the C–S and C–H symmetric stretching vibrations where the experimentally measured frequencies were used. The

C–S stretch was changed from 733 cm^{-1} to 725 cm^{-1} while the C–H stretching frequency was changed from 3060 cm^{-1} to 2960 cm^{-1} . In addition, the calculated frequency of 1465 cm^{-1} was changed to 1600 cm^{-1} in order to better reproduce the experimental spectrum. Lastly, to take into account the spin–orbit excited transitions, the simulated spectrum was shifted by 275 cm^{-1} and then added to the unshifted simulated spectrum. The total simulation is displayed in Fig. 1 as a thin line along with a stick spectrum identifying each transition. The intensities of the peaks at high electron binding energy (involving the C–H stretching vibration) are overestimated, suggesting that the geometry change between the anion and the neutral is actually smaller than that calculated along this coordinate. Calculations using the QCISD method were also performed to optimize the geometries yielding essentially the same results.

Based on the simulation, the group of features that lies between 2 and 2.2 eV are attributed to overlapping transitions from the ground state of the anion to the ground and spin–orbit excited states of several different vibrations in the neutral (see stick spectrum in Fig. 1). These vibrations involve some combination of the C–S stretch, the umbrella motion, and different quanta of vibrations with frequencies of 610 cm^{-1} , 870 cm^{-1} and 1600 cm^{-1} . As mentioned above, it is difficult to clearly identify and measure the umbrella frequency and the other frequencies due to low intensities and spectral overlap in the experimental spectrum. In the study by Moran and Ellison, the peak assigned as one quantum of the umbrella motion may indeed be composed of the group of transitions that are better resolved and assigned in the present photoelectron study [7].

3.3. Comparison with CH_3O and CF_3S

It is clear from the above results that the features in the photoelectron spectrum of CH_3S^- arise from different types of transitions than those in the photoelectron spectrum of CH_3O^- . Each feature in the spectrum can be assigned as a Franck–Condon allowed transition to either the spin–orbit ground or excited state of different vibrations in the neutral. There is no evidence of Jahn–Teller effects in the

spectrum. They could be quenched by the large spin–orbit effect that is prominent in the spectrum.

Calculations by Janousek and Brauman [8] and, more recently, by Barckholtz and Miller [5] support the lack of Jahn–Teller activity observed in the photodetachment spectrum. The calculations show that the predicted Jahn–Teller stabilization energy, $\sim 40\text{ cm}^{-1}$, is much smaller than the measured spin–orbit splitting of CH_3S , 265 cm^{-1} . Since the spin–orbit splitting is much larger than the Jahn–Teller energy, the spin–orbit interaction quenches the Jahn–Teller interaction such that the ${}^3\text{E}$ electronic state splits into the ${}^2\text{E}_{3/2}$ and ${}^2\text{E}_{1/2}$ states, which have potential energy minima in the symmetric conformation. As a result, no obvious Jahn–Teller activity is observed. In addition, the LIF experiments also only observe transitions to totally symmetric modes [9,10].

In contrast, the CH_3O Jahn–Teller stabilization energy is large, in excess of 200 cm^{-1} [5,21], compared to the spin–orbit splitting 61.5 cm^{-1} , measured by Engelking et al. [22] through emission experiments. When the Jahn–Teller energy is much greater than the spin–orbit splitting, transitions to totally symmetric modes are weak and transitions involving non-totally symmetric modes dominate. This has been seen in the photoelectron spectrum of CH_3O^- [3,4].

Lastly, the results on CH_3S can be compared to those for CF_3S . In fluorescence studies, transitions to both totally symmetric and non-totally symmetric modes have been observed [13,14]. The spin–orbit splitting is reported as 160 cm^{-1} [15], twice the Jahn–Teller stabilization energy, $\sim 80\text{ cm}^{-1}$ [5]. It appears that CF_3S is an intermediate case. The magnitude of the spin–orbit interaction is large such that it reduces the magnitude of the Jahn–Teller interaction; however, it does not completely quench it. As a result both types of modes are observed in the spectrum.

4. Conclusion

The 364-nm negative-ion photoelectron spectrum of CH_3S^- has been recorded with improved instrument resolution. Only transitions to totally symmetric

ric modes in the radical are observed in the spectrum. The spin–orbit splitting is $265 \pm 15 \text{ cm}^{-1}$. The C–S and C–H symmetric stretching frequencies have been measured at $725 \pm 15 \text{ cm}^{-1}$ and $2960 \pm 30 \text{ cm}^{-1}$, respectively. A simulation, based on calculations of the anion and neutral species, has been generated and agrees well with the experimental spectrum. Unlike CH_3O and CF_3S , no Jahn–Teller active modes are observed in CH_3S due to the large spin–orbit interaction relative to the Jahn–Teller interaction.

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