First Experimental Observation on Different Ionic States of both Methylthio (CH$_3$S') and Methoxy (CH$_3$O) Radicals**

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When combined with ab initio or density-functional theory (DFT) calculations, HeI photoelectron spectroscopy (PES) richly provides information on orbital energies, ionic states, bonding, and vibrational fine structure data that cannot be easily obtained by other experimental techniques. While there have been many PE spectroscopic studies of stable closed-shell molecules over the past 30 years, corresponding studies of open-shell radicals have been fewer.[1-9] Both the methylthio (CH$_3$S)[$^3$-14] and methoxy (CH$_3$O)[$^1$-18] radicals are important intermediates in combustion, photochemical and atmospheric reactions. The competitive effects of the dynamic Jahn–Teller distortion and spin–orbit coupling and their influences on the ground states of both CH$_3$S' and CH$_3$O are the subject of numerous experimental and theoretical studies.[19-24]

Studies on these two radicals have been based on ab initio calculations to determine the energetics and geometry of the CH$_3$S' radical in its ground and excited electronic states,[22-29] but as yet there is no report on the different ionic states for CH$_3$S' or of direct experimental evidence of the ionization energies of different ionic states for CH$_3$O'. Two separate photoionization mass spectrometry (PIMS) studies gave the first ionization energy of the CD$_3$O$_2$ isotopeomer ([10.726 ± 0.008] eV[23]) (10.74 ± 0.02) eV[30]). Slightly different calculated ionization energies of CH$_3$O' have been reported by Curtiss et al.[20] and Dyke et al.[25] (10.78 and (10.72 ± 0.02) eV, respectively). Clearly, experimental measurements of the ionization energies for both radicals are necessary.

In our laboratory, we generate a well characterized source of radicals or atoms by in situ pyrolysis and microwave discharge of precursor molecules.[19-21] In this communication, we would like to report the PES studies on the electronic structures of both methylthio and methoxy radicals. To our knowledge, this is the first experimental observation of different ionic states for both radicals.

The methylthio radical

The thermal, homolitic dissociation of suitable precursors is the most widely used method for generating radicals. Thermal decomposition of disulfides gives alkylthio radicals[25] Calculations on CH$_3$SSCH$_3$ indicate that the S–S bond is the weakest present and therefore pyrolysis of CH$_3$SSCH$_3$ offers a simple route to the CH$_3$S' radical [Eq. (1)].

$$\text{CH}_3\text{SSCH}_3 \xrightarrow[285-295^\circ\text{C}]{\text{2CH}_3\text{S}'}$$

Figure 1a shows the in situ PE spectrum of the species generated by pyrolysis of the CH$_3$SSCH$_3$ molecule at 285 °C and Figure 1b shows the lower ionization energy region (E < 11.00 eV) in greater detail. The three bands at E = 9.26, 9.91, and 10.32 eV are very sharp and correspond to the ionization of nonbonding electrons of the generated radical, because, in this case, the vertical ionization energy $E_v$ is equivalent to the adiabatic ionization energy $E_A$. The first ionization energy of the CH$_3$S' radical[26] (9.26 eV) is in good agreement with both
adiabatic ionization energy values obtained from two PIMS studies\(^{[22,23]}\) and a G2 first ionization energy calculation (9.25 eV)\(^{[26,27]}\). The vibrational fine structure spacing of this band also supports the assignment, as the spacing energy (\(\nu = (1100 \pm 60) \text{cm}^{-1}\)) is in good agreement with the presence of the \(v_{C-S}\) stretching mode of the \(\text{CH}_2\text{SSCH}_3\) ion (\(\nu = (1098 \pm 2) \text{cm}^{-1}\)).\(^{[3,4]}\)

Assignment of the sharp bands (Figure 1) to ionic states proceeds as follows: According to the \(C_2\) symmetry of \(\text{CH}_2\text{SS}^+\), as determined by a microwave study\(^{[5]}\) and assuming a \(2\bar{E}\) ground state, as proposed by theoretical studies\(^{[39,40]}\), the valence shell molecular orbitals would be, in the order of increasing energy, \((5a_1)^2(2e)^1(6a_1)^2(7a_1)^2(3e)^2\). The HOMO (3e) is essentially derived from the nonbonding lone-pair orbital of the sulfur atom with a smaller contribution from S–S antibonding. The removal of an electron from the HOMO will generate a \(\text{CH}_2\text{SS}^+\) ion in the \(1A_1, 1\bar{E},\) and \(1A_1\) ionic states (\(J = 1, \frac{3}{2}, 0\), respectively) and the three PES bands corresponding to these three ionic states of \(\text{CH}_2\text{SS}^+\) should be very sharp. The degeneracy of the ionized states is given by \(2J + 1\), so that the ratio of the PES band areas of the ionic states should be \(3:2:1\) for \(1A_1; 1\bar{E}; 2A_1\). Figure 1b reveals an band area ratio of \(3.02\pm 1.95:1.00\) for the bands at \(E = 9.26, 9.91,\) and 10.32 eV, respectively, which is very close to the expected ratio. The measured PE spectrum has provided, for the first time, evidence of different ionic states of the \(\text{CH}_2\text{SS}^+\) radical.

This assignment of the PES bands for \(\text{CH}_2\text{SS}^+\) is also supported by the results of improved DFT calculations on the ground state of the \(\text{CH}_2\text{SS}^+\) radical and of the ground and (several) ionic states of the \(\text{CH}_2\text{SS}^+\) ion. Such a calculation was used to assign PES bands for a number of other radicals.\(^{[35,36]}\) Table 1 includes the ionization energies \(E_i\), as determined by the maxima of the bands in the PE spectra, and the computed ionization energies \(E_i\) for different ionic states of \(\text{CH}_2\text{SS}^+\). According to the Frank–Condon principle, \(E_i\) is obtained from the total energy difference between the ground states of the cation and the neutral radical in \(C_2\) symmetry. According to Table 1 the low energy ionization energies from the PE spectrum for the \(\text{CH}_2\text{SS}^+\) radical (9.26, 9.91, and 10.32 eV) are in good agreement with the computed ionization energies (9.266, 10.024, and 10.421 eV).

The higher energy PES bands for the methylthio radical at \(E = 11.92, 13.60,\) and 14.73 eV (Figure 1a) are very broad, which indicates that the corresponding ionized electrons occupied bonding orbitals or several orbitals of \(\text{CH}_2\text{SS}^+\). The broad PES band at 11.92 eV is assigned to the ionization of the \(7a_1\) orbital to consequently form both triplet \(3\bar{E}\) and singlet \(1\bar{E}\) ionic states. This assignment is supported on the basis of the computed ionization energies of 11.724 (\(\bar{E}\)) and 12.156 eV (\(\bar{E}\)) as the two states are very similar in energy and thereby appear overlapped. Similarly, the broad PES band at 13.60 eV is assigned to the ionization of the \(6a_1\) orbital as the computed ionization energies of the formed triplet and singlet states 12.810 (\(\bar{E}\)) and 13.916 eV (\(\bar{E}\)) are again close and overlap. The very broad band at 14.73 eV is assigned to ionization of the less energetic valence orbitals of \(\text{CH}_2\text{SS}^+\).

**The methoxy radical**

The incomplete combustion of methanol leads to the production of the methoxy radical, which, in the presence of nitrogen oxides, produces the mutagenic methyl nitrite \(\text{CH}_3\text{ONO}^-\).\(^{[32]}\) Methyl nitrite has also attracted considerable attention from atmospheric contamination studies since photodissociation processes cleave the molecule into NO and \(\text{CH}_3\text{O}\) species.\(^{[33,34]}\) That is, methyl nitrite can be used as a
source of methoxy radicals. We generate a CH$_3$O$^+$ source by
pyrolysis of CH$_3$ONO at 275 °C and its PE spectrum was
recorded in situ.

The dissociation of CH$_3$ONO to produce CH$_3$O$^+$ and NO,
should lead to contamination of the PE spectrum of CH$_3$O$^+$
with bands due to the NO species. Figure 2a shows the PE

![Figure 2. a) An in situ HeI-PE spectrum (given as relative intensities $I_{rel}$) of the products (CH$_3$O$^+$ and NO) from the
pyrolysis of CH$_3$ONO; b) the expanded spectrum in the lower ionization energy region ($E < 14.00$ eV).](image)

description of products generated by pyrolysis of CH$_3$ONO and
Figure 2b shows the lower ionization energy region ($E <
10.70$ eV) can be assigned to NO since the fine structure
energy ($\tilde{v} = 2260$ cm$^{-1}$) and the band at 9.54 eV with the
greatest local intensity match the bands of NO alone. The two
bands in the higher energy region ($E = 16.56$ and 18.32 eV)
are also characteristic of NO species. The remaining bands in
Figure 2 are therefore derived from the ionization of CH$_3$O$^+$.

Assignment of the three sharp bands in Figure 2 for CH$_3$O$^+$
follows the same process used for CH$_3$S$: For $C_3v$ symmetry
and a $\Sigma^+$ ground state, the molecular orbitals would be, in
the order of increasing energy, (3a)$_2$(4a)$_2$(1e)$_2$(5a$_1$)$_2$(2e)$_2$. The
HOMO (2e) of CH$_3$O$^+$ has a dominant contribution from the
lone-pair electrons of the oxygen atom with a small degree of
C–O antibonding character.\[20\]. The removal of an electron
from the HOMO will generate a CH$_3$O$^+$ ion in the 1A$_2$, 1E,
and 1A$_1$ states. The sharp band at 10.78 eV matches the
computed G2 adiabatic ionization energy (10.78 eV)\[20\], and is
in good agreement with the reported first ionization energy of
the CD$_3$O$^+$ isotope from two PIMS studies ((10.72 ±
0.008)\[23\] and (10.74 ± 0.02) eV)\[20\]. This band is therefore
attributed to the A$_2$ ionic state of CH$_3$O$^+$ and the vibrational
fine structure spacing ($\tilde{v}(1950 ± 60$ cm$^{-1}$) is as expected for a
\nu_{C=O} stretching mode. The bands at 12.50 and 13.72 eV are
designated as the 1E and 1A$_1$ ionic states of CH$_3$O$^+$, respecti-
vely, because of the sharpness of the bands and because the expected 3:2:1 band area ratio for 1A$_2$:1E:1A$_1$ is indeed observed
(3.11:2.01:1.00 for the bands at 10.78, 12.50, and 13.72 eV).

This assignment is again supported by the improved DFT
calculations performed in a manner similar to those for the
methyli tho radical. The calculation presumed a $\Sigma^+$ ground
state and the radical and its ionic states were restricted to $C_{3v}$
symmetry. The total energy of the singlet state, described by a
multideterminant wave function, was calculated using the the
sum method of Ziegler et al.\[27\]. Table 2 shows the
good agreement between the ionization energies measured
($E = 10.78(1)$A$_2$, 12.50(1)E, and 13.72(1)A$_1$ eV) and calcu-
lated ($E = 10.791, 12.502, and 13.728$ eV). Also of interest is a
vibrational fine structure at $\tilde{v} = (1950 ± 60$ cm$^{-1}$) present
on the first band but absent on the other two. This phe-
omenon is currently under investigation.

Finally, the broad, higher energy PES band at 15.20 eV
(Figure 2a) can be assigned to ionization of electrons of the
5A$_1$ orbital leading to the 1E and 1E ionic states (calculated
ionization energies are 14.994 (1E) and 15.381 eV (1E)).

![Table 2. PES ionization energies $E_i$, computed (DFT) ionization energies $E_{i(DFT)}$, and relative intensities $I_{rel}$ of signals
observed from different ionic states for the methoxy radical.

<table>
<thead>
<tr>
<th>$E_i$ (PES) [eV]</th>
<th>$E_{i(DFT)}$ [eV]</th>
<th>Cationic State</th>
<th>Relative intensity measured$^b$ or expected</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.78</td>
<td>10.791</td>
<td>1A$_2$</td>
<td>3.11</td>
</tr>
<tr>
<td>12.50</td>
<td>12.502</td>
<td>1E</td>
<td>2.01</td>
</tr>
<tr>
<td>13.72</td>
<td>13.728</td>
<td>1A$_1$</td>
<td>1.00</td>
</tr>
<tr>
<td>15.20</td>
<td>14.994</td>
<td>1E</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.381</td>
<td>1E</td>
<td></td>
</tr>
</tbody>
</table>

[a] Values are ±0.02 eV and derived from the maxima of the PES bands.
[b] Corrected for analyzer sensitivity ±0.02.

In summary, the PE spectra of both CH$_3$S$^+$ and CH$_3$O$^+$
radicals provide direct experimental evidence for the exis-
tence of different ionic states. The $C_{3v}$ symmetry of both
radicals could be deduced from their respective PE spectra.
The PE spectrum is therefore able to provide both the orbital
energy levels and also molecular symmetry.

Experimental Section

Experiments were performed on a double-chamber ultraviolet-photo-
electron spectrometer (UPS), which was built specifically to detect
transient species.\[19\]. The continuous CH$_3$S and CH$_3$O radicals were
produced in situ by pyrolysis of gas-phase CH$_3$SSCH$_3$ at (285 ± 0.5)$^\circ$C
and CH$_3$ONO at (275 ± 0.5)$^\circ$C, respectively, in a quartz tube. The heating
system employed a double-heater inlet device. The purity of CH$_3$SSCH$_3$
was compared to a reference PE spectrum.\[19\]. The CH$_3$ONO was prepared by
standard methods\[19\] and its purity was confirmed by mass spectrom-

etry and by a reference PE spectrum[40]. The UPS delivered an operational resolution of about 30 meV for the $^{3}P_{2,3}$ band of Ar$. Experimental ionization energies were calibrated by the simultaneous addition of small amounts of Ar and CH$_4$ with the sample.

Received: November 23, December 16, 1999 [Z14310/14409] Revised: February 21, 2000


The Kinetic Order of an Interfacial Diels– Alder Reaction Depends on the Environment of the Immobilized Dinophile**

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Substituent effects are used widely in physical organic chemistry to elucidate the relationships between the structures, reactivities, and properties of molecules. This mechanistic tool finds routine use in many areas, including the determination of reaction mechanisms,[1] the development of catalysts,[2] and the design of selective inhibitors of proteins.[3] We have a program to extend the principles of physical organic chemistry to the reactions of molecules confined at the solid–liquid interface in order to elucidate the factors that uniquely affect these reactions. Here we show one such effect wherein the reactivity of an immobilized molecule is influenced by a substituent effect arising from the surrounding microenvironment. We use the Diels–Alder reaction of soluble cyclopentadiene with quinone immobilized to a self-assembled monolayer (SAM) on gold as a model system.

This work uses monolayers prepared from an alkanethiol terminated in a hydroquinone group and a second alkanethiol terminated in either a methyl or hydroxy group (Figure 1). The reversible two-electron electrochemical oxidation of this hydroquinone to the quinone is well known.[4] In previous work we showed that this quinone undergoes a Diels–Alder reaction with cyclopentadiene (CP) dissolved in the electrolyte to give the cyclodaddition adduct.[5] Since this adduct is not

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[**] We are grateful for the support provided by the MRSEC (National Science Foundation, DMR-9808595) and DARPA.