Photoionization mass spectrometric studies of the isomeric transient species CH₂SH and CH₃S

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The products of the reaction of F atoms with CH₃SH are studied by photoionization mass spectrometry. Two thresholds, at 7.536 ± 0.003 eV and 9.262 ± 0.005 eV, are observed at mass 47, and identified with the adiabatic ionization potentials of CH₂SH and CH₃S, respectively. These conclusions are confirmed by additional experiments with CD₃SH, where an adiabatic ionization potential of 7.522 ± 0.003 eV is obtained at mass 49 (CD₂SH⁺) and a value of 9.268 ± 0.005 eV is found at mass 50 (CD₃S⁺). From an earlier appearance potential for CH₂S⁺ (CH₃SH) and the present ionization potential of CH₂SH, an upper limit for D₀(H–CH₂SH) = 92.4 ± 2.0 kcal/mol. The corresponding S–H bond energy in CH₂SH derived from a recent kinetics-based value for ΔH°₀(CH₃S) is 86.1 ± 0.6 kcal/mol. A discrepancy in the difference of ΔH°₀(CH₃S⁺) and ΔH°₀(CH₂SH⁺) arising from recent theoretical and experimental determinations is resolved in favor of the ab initio values.

I. INTRODUCTION

Recently, there has been an upsurge of interest in the thermochemistry of organosulfur species, motivated at least in part by the emission of sulfur-containing pollutants from the combustion of sulfur-containing fuels. Ng and collaborators have utilized two techniques: (1) laser photodissociation of a supersonic neutral beam with time-of-flight detection of products and their kinetic energies, and (2) vacuum ultraviolet photoionization mass spectrometry, to produce data on the heats of formation of neutral radical species and their cations. In some experiments, they have combined the two techniques, producing radicals by laser photodissociation, and photoionizing the radicals. Thus, utilizing a pulsed beam of CH₃SCH₂ as the sample and 193 nm laser light, they generate CH₃S (CH₃SH) and then determine the photoion yield curve of CH₃S⁺ (CH₃S). In this way, they obtain a value for the adiabatic ionization potential of CH₃S (1344 ± 2 Å = 9.225 ± 0.014 eV). In previous photofragmentation experiments utilizing CH₃SH, CH₃SCH₂, and CH₃SSCH₂, they deduced ΔH°₀(CH₃S) = 35.0 ± 1.0 kcal/mol. Combining these values, they arrive at ΔH°₀(CH₃S⁺) = 247.7 ± 1.1 kcal/mol.

One might imagine that this quantity could be directly obtained from appearance potential measurements such as

CH₃SH + hv → CH₃S⁺ + H + e.

However, it has been shown by collisional activation experiments, charge transfer, and ab initio calculations that the isomeric form CH₂SH⁺ is significantly more stable, and is the species observed at threshold. This parallels the behavior of the corresponding oxyhydrocarbons—CH₂OH⁺ is significantly more stable than CH₂O⁺.

Nicovich et al. studied the kinetics of bromination of CH₃SH, CH₃SCH₂, and CH₃SSCH₂. One of their findings is that CH₃S, rather than CH₂SH, is formed upon reacting bromine with CH₃SH, and hence CH₃S is more stable than CH₂SH. This behavior is opposite to that of the corresponding oxygen species—CH₂OH is more stable than CH₂O. Furthermore, Nicovich et al. obtain ΔH°₀(CH₂S) = 29.9 ± 0.3/29.4 ± 0.6 kcal/mol (second- and third-law values) or ΔH°₀(CH₂S) = 31.44 ± 0.54 kcal/mol, significantly lower than the value (35.0 ± 1.0 kcal/mol) reported by Nourbakhsh et al.

The magnitude of ΔH°₀(CH₂SH) is still in doubt. However, ΔH°₀(CH₃S⁺) has been determined by several groups. Nourbakhsh et al. state that the literature value for ΔH°₀(CH₂SH⁺) is in the range 206–209 kcal/mol. Their own values, included in this literature, are at the lower end of this range. In fact, they give ΔH°₀(CH₂S⁺) = 204.5 ± 1.2 kcal/mol from appearance energy measurements on CH₃SCH₂, and ΔH°₀(CH₂S⁺) = 206.2 ± 1 kcal/mol from appearance energy measurements on CH₂SCH₂. If we restrict ourselves for the moment to the recent values of Nourbakhsh et al. for ΔH°₀(CH₃S⁻) and ΔH°₀(CH₂S⁻), we arrive at a difference of (41.5–43.2) ± 1.6 kcal/mol.

Nobes and Radom, allowing for the 206–209 kcal/mol flexibility in ΔH°₀(CH₃S⁺), choose an experimental difference in the heats of formation of the isomeric cations from Nourbakhsh et al. to be somewhat lower, 39.0–41.1 kcal/mol. Nevertheless, their ab initio calculated difference at the Gaussian 2 (G2) level of theory, <33.0 kcal/mol, is significantly lower than that of Nourbakhsh et al. Upon more detailed analysis, they find that their calculated value of ΔH°₀(CH₂S⁺) is lower by about 5 kcal/mol, while their calculated value of ΔH°₀(CH₂S⁺) is higher by about 5 kcal/mol, than the values obtained by Nourbakhsh et al. Hence, they question not only the difference in heats of formation, but each value separately.

We recently prepared CH₂O and CH₂OH by the reac-
tion of F atoms with CH$_3$OH, and studied these isomeric species by photoionization mass spectrometry. Several prior studies indicated that the reaction of F atoms with CH$_3$SH should proceed analogously, generating both CH$_3$S and CH$_3$S. Using selectively deuterated species, we hoped to measure the previously undetermined ionization energy of CH$_3$SH, and to check the ionization potential of CH$_3$S. With these measurements, and a critical examination of existing literature values, we hoped to resolve the discrepancy between ab initio theory and experiment for CH$_3$SH+.

II. EXPERIMENTAL ARRANGEMENT

Experiments were performed with both CH$_3$SH and CD$_3$SH. The transient species CH$_3$S (CD$_3$S) and CH$_3$S (CD$_3$S) were prepared in situ by reactions of F atoms with CH$_3$SH (CD$_3$SH). The fluorine atoms were generated in a microwave discharge through pure F$_2$. The description of the flow tube and reaction cup has been given previously, as has the photoionization mass spectrometric method.

The measurements were performed utilizing the peak light intensities in the many-line emission spectrum of a discharge in molecular hydrogen. The nominal wavelength resolution was kept at 0.84 Å (full width at half maximum). The sample of CH$_3$SH was from Aldrich (99.5 + % purity), while CD$_3$SH was obtained from MSD Isotopes, and had a stated D atom purity of 99%.

III. EXPERIMENTAL RESULTS

A. Experiments with CH$_3$SH

The anticipated products from reaction with F atoms, CH$_3$S and CH$_3$S, would both appear at mass 47 upon photoionization. In the analogous study of CH$_3$OH and CH$_3$O, it was found that CH$_3$O$^+$ could not be observed, although CD$_3$O$^+$ was detected. The CH$_3$O$^+$ was inferred to decompose on a time scale of several μs. Hence, it was not clear a priori if CH$_3$S$^+$ could be observed.

Figure 1 is a display of the photoion yield curve at mass 47, subsequent to the F + CH$_3$SH reaction. The wavelength range shown (1300–1600 Å) corresponds to a photon energy (9.5–7.5 eV) much less than is required (~11.5 eV) for dissociative ionization of CH$_3$SH to produce mass-47 ions.

At the long-wavelength end of the spectrum, at least two broad, steplike features appear, which may be attributable to a Franck–Condon vibrational progression in the cation. Their separation corresponds to a vibrational frequency of ~1020 ± 40 cm$^{-1}$. There is a bulge above experimental scatter at ~1629 Å, and perhaps another at ~1603 Å, giving a hint of another progression of ~600 ± 50 cm. The steps display curvature, which we attribute to rotational broadening. The half-rise in the first step, which would approximate the top of the peak in a photoelectron spectrum, occurs at 1643.3 ± 0.7 Å ≈ 7.536 ± 0.003 eV. We attribute this onset, and the ensuing photoion yield curve down to ~1340 Å, to the process

\[ \text{CH}_3\text{SH} + h\nu \rightarrow \text{CH}_3\text{SH}^+ + e. \]

This conclusion is based partly on the analogous behavior of the oxygenated species (CH$_3$OH has a much lower ionization potential than CH$_3$O), and to the fact that Nourbakhsh et al. obtained a much higher value (9.225 eV) for the ionization of the isomeric CH$_3$S. In fact, there is an increase in the photoion yield at about the energy observed by Nourbakhsh et al., which we tentatively attribute to the process

\[ \text{CH}_3\text{S} + h\nu \rightarrow \text{CH}_3\text{S}^+ + e. \]

Hence, unlike the CH$_3$O$^+$ case, the CH$_3$S$^+$ ion appears to be (meta)stable.

At shorter wavelength, there is a broad maximum centered at ~1535 Å, and perhaps a second broad band at ~1365 Å. These could be vibrationally broadened members of a Rydberg series converging to the first excited state of CH$_3$S$^+$.

At about 1340 Å, a new series of steps appears, which we have tentatively assigned to the onset of ionization from the isomeric CH$_3$S, pending a confirmatory study of CD$_3$SH. The spacing of the steps, attributed to a vibrational progression in CH$_3$S$^+$, is about 700 ± 60 cm$^{-1}$. The first step displays a weak bump at the threshold and a rather sharp (rather than rounded) character at the top of the step, which may result from weak autoionization. We choose the half-rise point, as before, which occurs at 1338.6 ± 0.7 Å ≈ 9.262 ± 0.005 eV, as the adiabatic ionization potential of CH$_3$S.

B. Experiments with CD$_3$SH

1. Mass 50, CD$_3$S$^+$

If both isomeric species are formed by the F + CD$_3$SH reaction, then CD$_3$S$^+$ would appear at mass 50, CD$_3$S$^+$ at mass 49. The photoion yield curve at mass 50 during these experiments appears in Fig. 2(a). It is immediately apparent that the structure in the photoion yield curve of Fig. 1 above ~1345 Å [repeated as Fig. 2(b)] is much weaker in Fig. 7(a). In fact, the residual “tail” above ~1345 Å in Fig. 2(a) can be followed all the way to ~1650 Å and closely resem-
FIG. 2. (a) The photoion yield curve at mass 50, monitored during the reaction of F atoms with CD$_3$SH. This photoion yield curve is attributed to the process CD$_3$S + hv → CD$_3$S$^+$ + e. (b) An expanded portion of the photoion yield curve from Fig. 1, attributed to CH$_3$S + hv → CH$_3$S$^+$ + e. Note the similarity in structure between curves (a) and (b), and the much lower "background" above 1340 Å in curve (a).

FIG. 3. The photoion yield curve at mass 49, monitored during the reaction of F atoms with CD$_3$SH. This photoion yield curve is attributed to the process CD$_3$S + hv → CD$_3$S$^+$ + e.

CD$_3$SH is redshifted from that of CH$_3$SH by about 0.014 eV.

At shorter wavelengths, a broad band is evident, with a maximum at ~1535 Å, and then two weaker broad bands with maxima at ~1365 and ~1340 Å. The two first broad bands match those observed in CH$_3$SH$^+$ (CH$_3$SH). Very roughly, these bands could be identified with Rydberg members forming a series converging to a second ionization potential (I.P.), with a vertical I.P. of ~10.2 eV.

The adiabatic ionization potentials of CH$_3$SH, CH$_3$S, and their deuterated variants are summarized in Table I.

IV. INTERPRETATION OF RESULTS

A. CH$_3$SH (CD$_3$SH)

The adiabatic ionization potential of CH$_3$SH obtained in this work is 7.536 ± 0.003 eV. We are unaware of any prior measurement of this quantity. This value for CH$_3$SH is very close to that obtained previously for CH$_3$OH, 7.549 ± 0.006 eV. The implication is that ionization occurs from an unpaired electron localized near the carbon atom. The adiabatic ionization potential of CD$_3$SH determined here is 7.522 ± 0.003 eV, lower than that of the protonated form by ~0.014 eV. Curtiss and co-workers' calculated vibrational frequencies for CH$_3$SH, CD$_3$SH, and the respective cations. From the differences in zero-point energies, one obtains I.P.(CH$_3$SH) - I.P.(CD$_3$SH) = 0.014 eV, in excellent agreement with the experimental observation.

A primary vibrational progression of about 1020 ± 40 cm$^{-1}$ is inferred for CH$_3$SH$^+$. In the photoelectron spectrum of CH$_3$OH, Dyke and co-workers' observed a pri-

<table>
<thead>
<tr>
<th>Species</th>
<th>I.P. (eV)</th>
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<tbody>
<tr>
<td>CH$_3$SH</td>
<td>7.536 ± 0.003*</td>
</tr>
<tr>
<td>CD$_3$SH</td>
<td>7.522 ± 0.003*</td>
</tr>
<tr>
<td>CH$_3$S</td>
<td>9.262 ± 0.005*, 9.225 ± 0.014b</td>
</tr>
<tr>
<td>CD$_3$S</td>
<td>9.268 ± 0.005*</td>
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</table>

*Present results.

bReference 2.
primary vibrational progression of \(1650 \pm 30 \text{ cm}^{-1}\), which they attributed to the C-O stretch, increased from the value (1183 cm\(^{-1}\)) in the neutral species. A similar behavior is inferred here, i.e., the C-S stretch in CH\(_2\)SH \(^+\) is taken to be \(\sim 1020 \text{ cm}^{-1}\), increased from its value in the neutral species.\(^{13}\) The primary vibrational progression in CD\(_2\)SH \(^+\) (900 \pm 40 cm\(^{-1}\)) is slightly smaller than that in CH\(_2\)SH \(^+\), implying the involvement of some hydrogen motion in the normal coordinate associated with this frequency. Recent \textit{ab initio} calculations\(^{13}\) indicate that the major change upon ionization is the reduction of the C-S bond length by \(-0.1 \text{ Å}\). This is expected to result in an increase in the C-S stretching frequency, as observed.

### B. CH\(_2\)S (CD\(_3\)S)

The adiabatic ionization potential of CH\(_2\)S (CD\(_3\)S) obtained in this work is 9.262 \(\pm 0.005 \text{ eV}\) (9.268 \(\pm 0.005 \text{ eV}\)), i.e., there is a small blueshift in the deuterated species. As in the analogous case of CH\(_3\)O, there is believed to be very little change in geometrical structure upon ionization, according to \textit{ab initio} calculations.\(^{13}\) Therefore, the 0→0 Franck–Condon band should be strong. The value of the adiabatic I.P. given by Nourbakhsh \textit{et al.} (1344 \(\pm 2 \text{ Å} = 9.225 \pm 0.014 \text{ eV}\)) lies at the very bottom of the tail in our spectrum, even below the bump. The vibrational interval of \(\sim 700\)–730 cm\(^{-1}\) could be a C-S stretch, not greatly different from that (707 cm\(^{-1}\))\(^{15}\) in the neutral species. The apparent increase in this frequency upon deuteration, though surprising, is consistent with the observed blueshift in the ionization potential. From photodetachment studies of CH\(_3\)S and CD\(_3\)S, Janousek and Braunman\(^{16}\) assign vibrational frequencies of 770 \(+ 50 \text{ cm}^{-1}\) and 660 \(+ 60 \text{ cm}^{-1}\) to the C-S stretch in the protonated and deuterated samples, respectively. Engelking, Ellison, and Lineberger,\(^{17}\) from similar experiments on CH\(_3\)S\(^+\), assign 680 \(+ 40 \text{ cm}^{-1}\) to the C-S stretch.

The bump, which appears in both the CH\(_2\)S and CD\(_3\)S experiments, appears lower than the chosen I.P.’s by 240 \(\pm 50 \text{ cm}^{-1}\) and 210 \(\pm 50 \text{ cm}^{-1}\), respectively, and the intensity is \(\sim 1/3\) as large as the first major step. Hsu, Liu, and Miller\(^{18}\) have extracted \(-255.5 \text{ cm}^{-1}\) as the effective spin–orbit splitting in CH\(_2\)S from their spectrum, somewhat higher than the microwave value,\(^{19}\) \(-221.0 \pm 2.0 \text{ cm}^{-1}\). In previous abstraction reactions in our apparatus, the temperature of the transient species was found to be near 298 K. The spin–orbit splitting of Hsu, Iii, and Miller corresponds to \(\sim 29\%\) abundance of the excited spin–orbit component, assuming Boltzmann conditions at 298 K. Hence, it is quite likely that the bump corresponds to photoionization of this excited spin–orbit component. This observation provides additional support for our choice of the adiabatic I.P.

It is conceivable that the photoionization experiment of Nourbakhsh \textit{et al.},\(^{2}\) which involved laser photodissociation of CH\(_3\)SCH\(_3\), produced primarily the excited spin–orbit component, thereby accounting for their lower value. However, their sample of CH\(_2\)S was cooled by supersonic expansion, which should have depopulated the excited state. A more likely explanation is that their lower resolution (1.5 Å), larger spacing between points, and their actual choice of threshold at the very onset of ionization accounts for their lower value.

### V. DISCUSSION OF RESULTS

#### A. ΔH\(_{\text{li}}^0\)(CH\(_2\)SH \(^+\)) and ΔH\(_{\text{li}}^0\)(CH\(_2\)SH)

In Table II, we list some recent literature values for ΔH\(_{\text{li}}^0\)(CH\(_2\)SH \(^+\)). The values of Nourbakhsh \textit{et al.}\(^{2}\) are distinctly lower than the other values. Their experimental value of 204.5 kcal/mol is based on the appearance potential of CH\(_2\)SH \(^+\) from CH\(_3\)SH, essentially the same experiment as performed previously by Kutina \textit{et al.}\(^{20}\) The latter authors select the intersection of a rapidly rising linear portion of the photoion yield curve to the background level, and arrive at 1073.5 \(\pm 0.5 \text{ Å} = 11.550 \pm 0.005 \text{ eV}\), modified to 11.611 \(\pm 0.005 \text{ eV}\) at 0 K. Furthermore, Kutina \textit{et al.}\(^{20}\) explicitly mention that they investigated the pressure dependence of the very weak tail extending below the threshold and concluded that it originates in higher-order collisional processes. Nourbakhsh \textit{et al.}\(^{1}\) select 1104 \(\pm 5 \text{ Å} = 11.23 \pm 0.05 \text{ eV}\) as their threshold. In their Fig. 8(b), this choice is well below the intersection of the linearly rising portion and the background level. Nourbakhsh \textit{et al.}\(^{1}\) attribute the rapid linear increase in CH\(_2\)SH \(^+\) to the onset of the second photoelectron band of CH\(_3\)SH, at \(\sim 11.5 \text{ eV}\). Perhaps the clearest He I photoelectron spectrum of CH\(_3\)SH is that of Cradock and Whiteford.\(^{21}\) The second photoelectron band does indeed have an adiabatic threshold near \(\sim 11.5 \text{ eV}\). However, a careful reading shows that it extends significantly below 11.5 eV, and at 11.611 eV (the value chosen by Kutina \textit{et al.}\(^{20}\) one is well inside the band. Furthermore, photoionization is (in first approximation) an integral over a photoelectron spectrum, and hence the tailing region of the photoelectron band will be steeper in photoionization. If the rapid linear increase in CH\(_2\)SH \(^+\) is due entirely to this band, its onset should occur at a lower value than observed.

Nourbakhsh \textit{et al.}\(^{1}\) choose to disregard their own coincidence experiments, which display an onset for CH\(_2\)SH \(^+\)

<table>
<thead>
<tr>
<th>ΔH(_{\text{li}}^0) (CH(_2)SH (^+))</th>
<th>ΔH(_{\text{li}}^0) (CH(_2)SH)</th>
<th>Method and citation</th>
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<tr>
<td>206 (\pm 2)</td>
<td>208 (\pm 2)</td>
<td>Photoionization (Ref. 22)</td>
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<td>208 (\pm 1)</td>
<td>210 (\pm 1)</td>
<td>Electron impact (Ref. 23)</td>
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<td>(\lesssim 213.1)</td>
<td></td>
<td>Photoionization (Ref. 20)</td>
</tr>
<tr>
<td>208 (\pm 1)</td>
<td>210 (\pm 1)</td>
<td>Charge-transfer ladder (Refs. 4 and 8)</td>
</tr>
<tr>
<td>204.5 (\pm 1.2)</td>
<td></td>
<td>Photoionization, CH(_3)SH (Ref. 1)</td>
</tr>
<tr>
<td>206.2 (\pm 1)</td>
<td></td>
<td>Photoionization, CH(_3)SCH(_3) (Ref. 1)</td>
</tr>
</tbody>
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\(^{a}\)We have applied a correction of 2 kcal/mol to the ΔH\(_{\text{li}}^0\) values given in this citation, in order to convert to ΔH\(_{\text{li}}^0\) and thereby have a uniform basis of comparison. Our calculated correction is 1.82 kcal/mol.

\(^{b}\)The relative proton affinity of CH\(_3\)S (Ref. 4) was combined with the calculated ΔH\(_{\text{li}}^0\)(CH\(_2\)S) from Ref. 8 to arrive at ΔH\(_{\text{li}}^0\)(CH\(_2\)SH \(^+\)).
(CH$_3$SH) at $\sim 1077$ Å = 11.51 eV. They presumably believe that the true onset is too weak to be observed, due to the Franck–Condon gap. However, there is evidence in their coincidence spectrum that parent ion is still being observed until $\sim 1077$ Å, below which it declines and CH$_3$SH$^+$ increases, as expected for the onset of fragmentation.

There is still a more convincing argument against the choice of Nourbakhsh et al. The CH$_3$S$^+$ (CH$_3$SH) fragment appears at a lower energy than CH$_3$SH$^+$ (CH$_3$SH). Therefore, its intensity suffers more from the Franck–Condon gap, yet it is clearly seen in the experiments of Kutina et al.$^{20}$ and Nourbakhsh et al.$^1$ In both experiments, the photoion yield curve of CH$_3$S$^+$ manifests a rapid linear increase at the onset of the second photoelectron band of CH$_3$SH, and then a cusp at $\sim 11.6$ eV. There is nothing in the photoelectron spectrum that suggests such a cusp. However, the cusp matches the observed onset of CH$_3$SH$^-$. The obvious interpretation is that the CH$_3$S$^+$ channel begins to suffer competition from the new channel (CH$_3$SH$^+$) at just the energy corresponding to the cusp. This is the expected behavior when a simple bond rupturing process competes with a more constrained fragmentation having a lower threshold, and was already mentioned by Kutina et al.$^{20}$

Butler, Baer, and Evans$^{22}$ and Holmes et al.$^{23}$ also base their values on appearance potentials, the first by photoionization and the latter by electron impact. The value inferred from Roy and McMahon$^4$ ($210 \pm 1$ kcal/mol at 0 K) is based on the proton affinity ladder and a calculated $\Delta H^0_{p}$ (CH$_3$S) from Nobes and Radom$^5$ and consequently is independent of the problems associated with the interpretation of thresholds. The $ab$ initio calculated value$^{13}$ (211.7 kcal/mol) is between that of Roy and McMahon$^4$ and also that of Holmes et al.$^{23}$) and the upper limit of 213.1 $\pm 0.2$ kcal/mol obtained from the Kutina et al.$^{20}$ threshold. Although the upper limit remains rigorous, we choose here an average value for $\Delta H^0_{p}$ (CH$_3$SH$^+$) of 211.5 $\pm 2$ kcal/mol. With this value, and our adiabatic ionization potential for CH$_3$SH, we deduce $\Delta H^0_{i}$ (CH$_3$S) = 37.7 $\pm 2$ kcal/mol.

B. $\Delta H^0_{p}$ (CH$_3$S) and $\Delta H^0_{i}$ (CH$_3$S$^+$)

As discussed in the Introduction, Nourbakhsh et al.$^2$ give $35.0 \pm 1$ kcal/mol for $\Delta H^0_{p}$ (CH$_3$S), while the second- and third-law kinetics-based value of Nicovich et al.$^7$ is $31.44 \pm 0.54$ kcal/mol. From the highest vibrational and rotational levels of HF observed in the F + CH$_3$SH reaction, Dill and Heydtmann$^9$ conclude that $\Delta H^0_{p}$ (CH$_3$S) $< 30.6$ kcal/mol. Another less-precise value can be extracted from the gas-phase acidity of CH$_3$SH (359.0 $\pm 2$ kcal/mol) given by Bartmess, Scott, and McIver,$^{24}$ the electron affinity of CH$_3$S (1.861 $\pm 0.004$ eV) obtained by Janousek and Braunman,$^{16}$ and auxiliary data. Thus, $\Delta H^0_{p}$ (CH$_3$S$^-$) = $-10.5 \pm 2$ kcal/mol and $\Delta H^0_{i}$ (CH$_3$S) = $32.5 \pm 2$ kcal/mol. If we combine the value of Nicovich et al.$^7$ with the adiabatic ionization potential of CH$_3$S obtained in the present work, we deduce $\Delta H^0_{i}$ (CH$_3$S$^+$) = 245.0 $\pm 0.5$ kcal/mol. Using various cycles, Nobes and Radom$^8$ calculated $243.1, 242.3,$ and $241.4$ kcal/mol for this quantity, settling upon $242.4 \pm 2.5$ kcal/mol. Subsequently, Curtiss and co-workers$^{13}$ modified this calculated value to 243.8 kcal/mol. Since these calculations on similar molecules have achieved accuracies of $\pm 2$ kcal/mol, the agreement between experiment and theory in the present case is quite satisfactory. If the value of $\Delta H^0_{p}$ (CH$_3$S) given by Nourbakhsh et al.$^2$ were used, there would be a discrepancy of 4–5 kcal/mol between theory and experiment.

C. Difference in stabilities of CH$_2$SH, CH$_2$S, and their cations

From the experimentally based values of $\Delta H^0_{p}$ (CH$_2$SH$^+$) = 245.0 $\pm 0.5$ kcal/mol and $\Delta H^0_{i}$ (CH$_2$S) = 211.5 $\pm 2$ and $< 213.2$ kcal/mol, we obtain a difference of $33.5 \pm 2$ kcal/mol. Nobes and Radom$^8$ obtain $< 33.0$ kcal/mol for this difference, while the value of Nourbakhsh et al.$^2$ is about $40 \pm 2$ kcal/mol. Hence, based on the data and arguments given above, the discrepancy between experiment and $ab$ initio calculation would appear to be resolved in favor of the $ab$ initio value.

Taking $\Delta H^0_{p}$ (CH$_3$S) = 31.44 $\pm 0.5$ kcal/mol from Nicovich et al.$^7$ and 37.7 $\pm 2$ kcal/mol for $\Delta H^0_{i}$ (CH$_3$SH), we find that CH$_3$S is more stable by 6.3 $\pm 2$ kcal/mol.

Shum and Benson$^{25}$ noted that the C–H bond strength in organic sulfur compounds had never been measured. From kinetic studies of the I$_2$ + CH$_3$SCH$_3$ reaction, they cited a preliminary value of 96 $\pm 1$ kcal/mol for the C–H bond strength. Applying this value to the C–H bond strength in CH$_3$SH, one obtains $\Delta H^0_{p}$ (CH$_3$SH) = 38.4 $\pm 1$ kcal/mol, 7.4 kcal/mol higher than their adopted value for $\Delta H^0_{p}$ (CH$_3$S) = 31.0 $\pm 1$ kcal/mol. Nicovich et al.$^7$ noting Dill and Heydtmann$^9$ and Shum and Benson$^{25}$ state that "the C–H bond in CH$_3$SH is thought to be about 6 kcal/mol stronger that the S–H bond." The difference in stabilities of CH$_3$S and CH$_3$SH implied by these measurements is consistent with our deduced value, 6.3 $\pm 2$ kcal/mol.

From measurements of the appearance potential A.P. (CH$_3$S$^+$)/CH$_3$S$< 11.611 \pm 0.005$ eV and I.P. (CH$_3$SH) = 7.536 $\pm 0.003$ eV made in our laboratory, we can arrive by simple subtraction at an upper limit to the C–H bond strength in CH$_3$SH, $D_0$ (H–CH$_3$SH) < 4.075 $\pm 0.006$ eV $\approx$ 93.97 $\pm 0.13$ kcal/mol. If we use the probable value for $\Delta H^0_{p}$ (CH$_3$SH) = 37.7 $\pm 2$ kcal/mol deduced in Sec. V B, the C–H bond energy becomes 92.4 $\pm 2$ kcal/mol. The S–H bond energy recently obtained by Nicovich et al.$^7$ is $D_0$ (H–CH$_3$S) = 86.0 $\pm 0.7$ kcal/mol [or, with our value for $\Delta H^0_{p}$ (CH$_3$SH) $< 30.0 \pm 1$ kcal/mol, $D_0$ (H–CH$_3$S–H) = 86.1 $\pm 0.6$ kcal/mol]. However, if one were to take A.P. (CH$_3$S$^+$)/CH$_3$S$< 11.23 \pm 0.05$ eV from Nourbakhsh et al.$^1$ and combine it with the present I.P. of CH$_3$SH, one would infer $D_0$ (H–CH$_3$SH) = 85 $\pm 1$ kcal/mol, i.e., a C–H bond energy which is less than, or at best equal to the S–H bond energy in CH$_3$SH. This is unlikely, in view of other known S–H and C–H bond energies.
ACKNOWLEDGMENT

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13 L. A. Curtiss (private communication).
15 The vibrational frequencies of CH$_2$SH have not been measured, to our knowledge. However, the C–S stretching frequency in CH$_3$SH has been determined to be 704–710 cm$^{-1}$ [see I. W. May and E. L. Pace, Spectrochim. Acta Part A 24, 1605 (1968)], while that of CH$_3$S is 707 cm$^{-1}$ [see S.-Y. Chiang and Y.-P. Lee, J. Chem. Phys. 95, 66 (1991)]. We assume that it is not very different in CH$_3$SH.
20 R. E. Kutina, A. K. Edwards, G. L. Goodman, and J. Berkowitz, J. Chem. Phys. 77, 5508 (1982). Although it was not clear at that time whether CH$_3$SH$^+$ or CH$_3$S$^+$ was more stable, the experimental threshold for mass 47 from CH$_3$SH was determined accurately, and is currently to be interpreted as CH$_3$SH$^+$.