A study of the dissociation of CH₃CH₂SH⁺ by collisional activation: Evidence of nonstatistical behavior

Y.-J. Chen, S. Stimson, P. T. Fenn, and C. Y. Ng
Ames Laboratory, United States Department of Energy, Ames, Iowa and Department of Chemistry, Iowa State University, Ames, Iowa 50011
Wai-Kee Li
Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong
N. L. Ma
Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Hong Kong

(Received 12 January 1998; accepted 9 February 1998)

The absolute total cross sections for CH₃CH⁺, C₂H₄⁺, C₂H₅⁺, CH₃⁺, CH₂SH⁺(CH₃S⁺), CH₄S⁺(HCSH⁺), CHS⁺(CSH⁺), and H₂S⁺ produced by the collision-induced dissociation (CID) reaction of CH₃CH₂SH⁺+Ar have been measured in the center-of-mass collision energy ($E_{c.m.}$) range of 1–42 eV. Using the charge transfer probing technique, we found that the mass 47 product ions have overwhelmingly the CH₂SH⁺ structure. The onsets for CH₃CH⁺, C₂H₅⁺, C₂H₅⁺, CH₂SH⁺, H₂S⁺, and CH₃⁺ are consistent with their corresponding thermochemical thresholds. The formation of the higher energy channels CH₃CH⁺+SH and CH₃+CH₂SH⁺, which involve the C–S and C–C bond scissions, are found to dominate in the entire $E_{c.m.}$ range. The lower energy channel corresponding to the formation of CH₂CHSH⁺+H is not found. The strong preference observed for the formation of the higher energy channels is in accord with the conclusion obtained in the recent CID study of CH₂SH⁺, providing evidence that the CID of CH₃CH₂SH⁺ is also nonstatistical. The high yields of CH₃CH⁺+SH and CH₂SH⁺+CH₃ are attributed to the more efficient translational to vibrational energy transfer for the low frequencies C–S and C–C stretching modes than for the high frequencies C–H and S–H stretching modes, along with the weak couplings between these low and high frequencies vibrational modes of CH₃CH₂SH⁺. The relative abundances of product ions formed by the single-photon ionization of CH₃CH₂SH were also measured for comparison with the CID results. The CH₂CHSH⁺+H channel is observed in the photoionization of CH₃CH₂SH. Similar to the finding in the photoionization of CH₃SH, the relative abundances of fragment ions formed in the photoionization of CH₃CH₂SH are in qualitative accord with statistical predictions. To rationalize the dissociation mechanisms of CH₃CH₂SH⁺, we have also performed ab initio calculations to locate the possible transition structures for the observed dissociation channels.

I. INTRODUCTION

We have recently examined the collision-induced dissociation (CID) reaction of CH₃SH⁺+Ar. The absolute cross section for CH₃⁺+SH is found to be significantly higher than that for CH₂⁺+H. Since the CH₃⁺–SH bond is considerably stronger than the H–CH₂⁺ bond, this observation suggests that the CID of CH₂SH⁺ is nonstatistical, and is thus bond selective. However, this conclusion is contrary to the results observed in the dissociation of CH₃SH⁺ excited by photoionization (PI) (Ref. 3) and charge exchange. The breakdown diagrams for the unimolecular dissociation of CH₂SH⁺ activated by PI and charge exchange are in qualitatively agreement with the statistical quasiequilibrium theory (QET).

Motivated by the striking differences in the CH₃SH⁺ dissociation product branching ratios observed between the CID experiment and the PI and charge exchange studies, we have further examined the CID of CH₃CH₂SH⁺. The latter ion contains an extra C–C bond compared to CH₂SH⁺. In order to compare the dissociation mechanisms activated by collision and PI, we have also performed a PI mass spectrometric study of CH₃CH₂SH. The structures of the mass 47 (CH₂SH⁺ or CH₃S⁺) product ions formed in the CID reaction of CH₃CH₂SH⁺+Ar and in the PI of CH₃CH₂SH have also been probed by using the charge exchange probing method.

The reactant CH₃CH₂SH⁺ ions in the present CID experiment are prepared by PI of CH₃CH₂SH in the threshold region. By using a sufficiently high photon energy resolution, the CH₂CHSH⁺ ion can be formed in its ground vibrionic state. Since the CH₂CHSH sample is introduced by supersonic expansion into the ion source and PI is known to favor a small change in rotational quantum numbers, the re-
tron nonresonant two-photon pulsed field ionization photoelectro optic VUV light detector. The recent high resolution total cross section measurements have been described in detail for CH$_3$CH$_2$SH.

The first to fifth photoelectron bands for the mass 47 ions were probed by the charge distribution for excitation of the C–S stretching mode ($\nu_6^\prime = 628$ cm$^{-1}$) of CH$_3$CH$_2$SH$^+$. In the present experiment, CH$_3$CH$_2$SH is introduced into the PI source as a free jet formed by supersonic expansion through a nozzle with a diameter of 75 $\mu$m at a stagnation pressure of $\approx 120$ Torr. By setting the PI wavelength at 1333 Å and a wavelength resolution of 5 Å [full-width-at-half-maximum (FWHM)], the CH$_3$CH$_2$SH$^+$ reactant ions were formed in their ground vibrionic states. The rotational temperature of CH$_3$CH$_2$SH$^+$ thus formed is expected to be $< 150$ K, characteristic of the neutral CH$_3$CH$_2$SH jet. We note that finite vibrational excitations of CH$_3$CH$_2$SH$^+$ due to the thermal population of low frequency vibrational modes of CH$_3$CH$_2$SH may not be efficiently relaxed by the mild beam expansion employed in this experiment.

For absolute total cross section measurements, the reactant CH$_3$CH$_2$SH$^+$ ions were extracted and guided by the lower QMS (operated in the RF only mode) and the lower RF octopole ion guide to the middle QMS. The middle QMS, functioning as a mass filter, passed only the desired CH$_3$CH$_2$SH$^+$ ions to the upper RFOIGGC, where collision-activated dissociation occurred with Ar. The pressure of Ar in the upper RFOIGGC was monitored with a MKS Baratron, and maintained at 2 – 3 $\times 10^{-4}$ Torr. In this pressure range, the CID product ion intensity was found to have a linear dependence on the Ar gas cell pressure. The reactant ions and the product ions formed in the upper RFOIGGC were then mass selected by the product QMS and detected with the modified Daly-type scintillation ion detector.

The reactant ion beam energies were determined by the retarding potential method, using the upper octopole ion guide to retard the reactant CH$_3$CH$_2$SH$^+$ ions. The retarding potential curve thus obtained was differentiated to yield the most probable laboratory kinetic energy ($E_{lab}$) of the reactant ions and the FWHM of the kinetic energy distribution. The $E_{lab}$ resolution for CH$_3$CH$_2$SH$^+$ achieved in this experiment was $\pm 0.2$ eV as measured by the FWHM of the $E_{lab}$ distribution. The center-of-mass collision energy ($E_{c.m.}$) resolution was $\pm 0.08$ eV (FWHM). The collection efficiencies for reactant and product ions were maximized at each $E_{c.m.}$ by optimizing the voltage settings applied to the ion lenses, the octopole ion guides, and the QMS's.

To probe the structure of the mass 47 ions formed in the CID reaction of CH$_3$CH$_2$SH$^+$ + Ar, we used both the lower and upper RFOIGGCs. Reactant CH$_3$CH$_2$SH$^+$ ions prepared by PI of CH$_3$CH$_2$SH were first selected by the reactant QMS to enter the lower RFOIGGC, where the CID reaction CH$_3$CH$_2$SH$^+$ + Ar took place. The Ar gas cell pressure used was $5 \times 10^{-4}$ Torr. The mass 47 product ions thus formed in the $E_{c.m.}$ range of 4.5 – 6.5 eV were selected by the middle QMS and guided into the upper RFOIGGC, in which the structure for the mass 47 ions was probed by the charge transfer reaction with benzene (C$_6$H$_6$) at $E_{c.m.} < 0.4$ eV. Charge transfer product C$_6$H$_6^+$ ions, if formed, were detected by the product QMS. The C$_6$H$_6$ pressure used in the upper gas cell was $3 \times 10^{-4}$ Torr. The IE's for CH$_3$, CH$_2$SH, and CH$_3$CH$_2$SH$^+$ are $0.08$ eV for the IE of CH$_3$CH$_2$SH.

The N2P-PFI-PE spectrum also reveals a vibrational progression corresponding to excitation of the C–S stretching mode ($\nu_6^\prime = 628$ cm$^{-1}$) of CH$_3$CH$_2$SH$^+$. In the present experiment, CH$_3$CH$_2$SH is introduced into the PI source as a free jet formed by supersonic expansion through a nozzle with a diameter of 75 $\mu$m at a stagnation pressure of $\approx 120$ Torr. By setting the PI wavelength at 1333 Å and a wavelength resolution of 5 Å [full-width-at-half-maximum (FWHM)], the CH$_3$CH$_2$SH$^+$ reactant ions were formed in their ground vibrionic states. The rotational temperature of CH$_3$CH$_2$SH$^+$ thus formed is expected to be $< 150$ K, characteristic of the neutral CH$_3$CH$_2$SH jet. We note that finite vibrational excitations of CH$_3$CH$_2$SH$^+$ due to the thermal population of low frequency vibrational modes of CH$_3$CH$_2$SH may not be efficiently relaxed by the mild beam expansion employed in this experiment.

For absolute total cross section measurements, the reactant CH$_3$CH$_2$SH$^+$ ions were extracted and guided by the lower QMS (operated in the RF only mode) and the lower RF octopole ion guide to the middle QMS. The middle QMS, functioning as a mass filter, passed only the desired CH$_3$CH$_2$SH$^+$ ions to the upper RFOIGGC, where collision-activated dissociation occurred with Ar. The pressure of Ar in the upper RFOIGGC was monitored with a MKS Baratron, and maintained at 2 – 3 $\times 10^{-4}$ Torr. In this pressure range, the CID product ion intensity was found to have a linear dependence on the Ar gas cell pressure. The reactant ions and the product ions formed in the upper RFOIGGC were then mass selected by the product QMS and detected with the modified Daly-type scintillation ion detector.

The reactant ion beam energies were determined by the retarding potential method, using the upper octopole ion guide to retard the reactant CH$_3$CH$_2$SH$^+$ ions. The retarding potential curve thus obtained was differentiated to yield the most probable laboratory kinetic energy ($E_{lab}$) of the reactant ions and the FWHM of the kinetic energy distribution. The $E_{lab}$ resolution for CH$_3$CH$_2$SH$^+$ achieved in this experiment was $\pm 0.2$ eV as measured by the FWHM of the $E_{lab}$ distribution. The center-of-mass collision energy ($E_{c.m.}$) resolution was $\pm 0.08$ eV (FWHM). The collection efficiencies for reactant and product ions were maximized at each $E_{c.m.}$ by optimizing the voltage settings applied to the ion lenses, the octopole ion guides, and the QMS’s.

To probe the structure of the mass 47 ions formed in the CID reaction of CH$_3$CH$_2$SH$^+$ + Ar, we used both the lower and upper RFOIGGCs. Reactant CH$_3$CH$_2$SH$^+$ ions prepared by PI of CH$_3$CH$_2$SH were first selected by the reactant QMS to enter the lower RFOIGGC, where the CID reaction CH$_3$CH$_2$SH$^+$ + Ar took place. The Ar gas cell pressure used was $5 \times 10^{-4}$ Torr. The mass 47 product ions thus formed in the $E_{c.m.}$ range of 4.5 – 6.5 eV were selected by the middle QMS and guided into the upper RFOIGGC, in which the structure for the mass 47 ions was probed by the charge transfer reaction with benzene (C$_6$H$_6$) at $E_{c.m.} < 0.4$ eV. Charge transfer product C$_6$H$_6^+$ ions, if formed, were detected by the product QMS. The C$_6$H$_6$ pressure used in the upper gas cell was $3 \times 10^{-4}$ Torr. The IE's for CH$_3$, CH$_2$SH, and CH$_3$CH$_2$SH$^+$ are $0.08$ eV for the IE of CH$_3$CH$_2$SH.

The N2P-PFI-PE spectrum also reveals a vibrational progression corresponding to excitation of the C–S stretching mode ($\nu_6^\prime = 628$ cm$^{-1}$) of CH$_3$CH$_2$SH$^+$. In the present experiment, CH$_3$CH$_2$SH is introduced into the PI source as a free jet formed by supersonic expansion through a nozzle with a diameter of 75 $\mu$m at a stagnation pressure of $\approx 120$ Torr. By setting the PI wavelength at 1333 Å and a wavelength resolution of 5 Å [full-width-at-half-maximum (FWHM)], the CH$_3$CH$_2$SH$^+$ reactant ions were formed in their ground vibrionic states. The rotational temperature of CH$_3$CH$_2$SH$^+$ thus formed is expected to be $< 150$ K, characteristic of the neutral CH$_3$CH$_2$SH jet. We note that finite vibrational excitations of CH$_3$CH$_2$SH$^+$ due to the thermal population of low frequency vibrational modes of CH$_3$CH$_2$SH may not be efficiently relaxed by the mild beam expansion employed in this experiment.

For absolute total cross section measurements, the reactant CH$_3$CH$_2$SH$^+$ ions were extracted and guided by the lower QMS (operated in the RF only mode) and the lower RF octopole ion guide to the middle QMS. The middle QMS, functioning as a mass filter, passed only the desired CH$_3$CH$_2$SH$^+$ ions to the upper RFOIGGC, where collision-activated dissociation occurred with Ar. The pressure of Ar in the upper RFOIGGC was monitored with a MKS Baratron, and maintained at 2 – 3 $\times 10^{-4}$ Torr. In this pressure range, the CID product ion intensity was found to have a linear dependence on the Ar gas cell pressure. The reactant ions and the product ions formed in the upper RFOIGGC were then mass selected by the product QMS and detected with the modified Daly-type scintillation ion detector.

The reactant ion beam energies were determined by the retarding potential method, using the upper octopole ion guide to retard the reactant CH$_3$CH$_2$SH$^+$ ions. The retarding potential curve thus obtained was differentiated to yield the most probable laboratory kinetic energy ($E_{lab}$) of the reactant ions and the FWHM of the kinetic energy distribution. The $E_{lab}$ resolution for CH$_3$CH$_2$SH$^+$ achieved in this experiment was $\pm 0.2$ eV as measured by the FWHM of the $E_{lab}$ distribution. The center-of-mass collision energy ($E_{c.m.}$) resolution was $\pm 0.08$ eV (FWHM). The collection efficiencies for reactant and product ions were maximized at each $E_{c.m.}$ by optimizing the voltage settings applied to the ion lenses, the octopole ion guides, and the QMS’s.
C_{6}H_{6} are known to be 9.2649 ± 0.0010 eV, 11 7.536 ± 0.003 eV, 12 and 9.243842 ± 0.000006 eV, 13 respectively. Using these IE values, we calculated that the charge transfer reaction \(~\rightleftharpoons 1\) for CH_{3}S \rightleftharpoons 1 C_{6}H_{6} is slightly exothermic by 0.0211 eV, whereas the charge transfer reaction \(~\rightleftharpoons 2\) for CH_{2}SH \rightleftharpoons 2 C_{6}H_{6} is endothermic by 1.708 eV. The \(D_{H}^{0}\) values given in reactions (1) and (2) are the corresponding heats of reaction at 0 K,

\[ \text{CH}_{3}\text{S}^{+} + \text{C}_{6}\text{H}_{6} \rightarrow \text{CH}_{3}\text{S} + \text{C}_{6}\text{H}_{6}^{+}, \quad \Delta H_{0}^{0} = -0.0211 \text{ eV}, \]

\[ \text{CH}_{2}\text{SH}^{+} + \text{C}_{6}\text{H}_{6} \rightarrow \text{CH}_{2}\text{SH} + \text{C}_{6}\text{H}_{6}^{+}, \quad \Delta H_{0}^{0} = 1.708 \text{ eV}. \]

Since near-resonant charge transfer reactions usually have large cross sections, we should observe the formation of C_{6}H_{6} if the mass 47 ions have the CH_{3}S^{+} structure, while the charge transfer cross section should be negligibly small if CH_{2}SH^{+} ions are produced in the CID reaction of CH_{3}CH_{2}SH^{+} + Ar.

It is known that CH_{2}SH^{+} ions are produced at the onset by the PI of CH_{3}SH.\(^{3}\) This conclusion is based on the fact that the thermochemical threshold of \(\Delta H_{0}^{0} = 11.541 \text{ eV}\) for process (3) is very close to the appearance energy (AE) of \(\approx 11.55 \text{ eV}\) for the mass 47 ion observed in the dissociative PI of CH_{3}SH,

\[ \text{CH}_{3}\text{SH}^{} + h\nu \rightarrow \text{CH}_{2}\text{SH}^{+} + \text{H} + e^{-}, \quad \Delta H_{0}^{0} = 11.541 \text{ eV}. \]

The formation of CH_{2}SH^{+} by process (3) has been further confirmed by Fenn et al. using benzene as the charge transfer probing reactant.\(^{2}\) The latter experiment can be taken as a validation of the charge transfer probing technique used here for the structural identification of the mass 47 ions (CH_{2}SH^{+} or CH_{3}S^{+}) formed in the PI and CID reactions.

The data acquisition for the TQDO apparatus has recently been upgraded to be controlled by a Pentium PC system.\(^{14}\) This improvement allows computer control of the QMS and monochromator scans, the voltage settings applied to individual components of the ion optics system, the reactant ion kinetic energy determination, and the background corrections in absolute total cross section measurements. The procedures outlined above were conducted mostly in an automatic mode.

The ethanethiol and benzene were obtained from Aldrich Chemical Co. and Fisher Scientific with purities of 99.5%
TABLE I. Appearance energies (AEs) and Δ.PI* values for C₂H₅⁺, C₃H₇⁺, C₄H₇⁺, CH₃SH⁺(CH₃S⁺), CH₃S⁺, CH₄⁺, and H₂S⁺ formed in the CID of CH₃CHS⁺ and PI of CH₃CHSH respectively.

<table>
<thead>
<tr>
<th>Product ions</th>
<th>AE(CID)* (eV)</th>
<th>Δ.PI* (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CHS⁺</td>
<td>1.47±0.06</td>
<td></td>
</tr>
<tr>
<td>CH₃CH⁺</td>
<td>1.9±0.2</td>
<td>2.0±0.06</td>
</tr>
<tr>
<td>C₂H₅⁺</td>
<td>2.0±0.2</td>
<td>2.0±0.06</td>
</tr>
<tr>
<td>C₃H₇⁺</td>
<td>4.2±0.2</td>
<td></td>
</tr>
<tr>
<td>CH₃SH⁺</td>
<td>1.7±0.2</td>
<td>1.73±0.06</td>
</tr>
<tr>
<td>CH₃S⁺</td>
<td>1.5±0.4</td>
<td>1.42±0.06</td>
</tr>
<tr>
<td>CHS⁺</td>
<td>7.2±0.5</td>
<td></td>
</tr>
<tr>
<td>CH₄⁺</td>
<td>3.8±0.3</td>
<td></td>
</tr>
<tr>
<td>H₂S⁺</td>
<td>2.0±0.3</td>
<td>1.93±0.06</td>
</tr>
</tbody>
</table>

*This work. Δ.PI=AE(PI)−IE(CH₃SH), where AE(PI) is the AE determined in the PI of CH₃CHSH.

This work. Appearance energy determined in the CID study of CH₃CHS⁺+Ar. The uncertainties represent the precision of the measurements.

and 99.9%, respectively. The Ar gas is from Air Products and has a purity of 99.998%.

III. RESULTS AND DISCUSSION

A. Absolute total cross section and identification of CID product channels

Figure 2 depicts the mass spectrum observed for the CID reaction of CH₃CHS⁺+Ar at E_c.m. = 5.3 eV by scanning the product quadrupole mass spectrometer, showing that C₂H₅⁺ and CH₂SH⁺(CH₃S⁺) are the major product ions. The product ions observed in the CID reaction of C₂H₅SH⁺+Ar are C₂H₅⁺, C₃H₇⁺, C₄H₇⁺, CH₃CH⁺, CH₃S⁺, CH₄⁺, CHS⁺, and CH₂⁺. We note that the mass peaks for CH₂⁺ and CH₃⁺ are not shown in Fig. 2.

The absolute total cross section for the dominant product ions C₂H₅⁺ and CH₂SH⁺(CH₃S⁺) in the E_c.m. range of 1–37 eV are plotted in Fig. 3(a). The cross sections of C₂H₅⁺ and CH₂SH⁺(CH₃S⁺) exhibit a maximum at E_c.m. = 3–7 eV. The maximum cross section for C₂H₅⁺ is about 5 Å², which is more than three times higher than the maximum cross section of 1.8 Å² for CH₂SH⁺(CH₃S⁺). The cross section curves for the minor product ions are depicted in Fig. 3(b) for C₂H₅⁺, C₃H₇⁺, and CH₃⁺ and in Fig. 3(c) for CH₄⁺, CHS⁺, and H₂S⁺. The onsets for these minor product ions are found to rise very gradually as E_c.m. is increased. The cross section of C₂H₅⁺ increases rapidly at E_c.m. > 8 eV and reaches ≈2 Å² at E_c.m. ≈ 30 eV, a value similar to the cross sections for C₂H₅⁺ and CH₂SH⁺ (and/or CH₃S⁺). The cross sections for other minor product ions are <1 Å² in the entire E_c.m. range.

One of the most important pieces of information obtained in a low energy CID study is the AE of the product ions, from which upper limits of the bond dissociation energies at 0 K (D_b) involved can be calculated. The AE(CID) values for C₂H₅⁺, C₃H₇⁺, C₄H₇⁺, CH₃⁺, CH₂SH⁺, CH₃S⁺, CHS⁺, and H₂S⁺ determined by the cross-section curves are listed in Table I. At E_c.m., below these AE(CID) values, the intensities for the corresponding product ions are at the background level. These AE(CID) values represent upper limits for the true thermochemical thresholds of the processes involved. Using the current recommended thermochemical data listed in Table II, we have calculated the ΔH_b values for the reactions possibly responsible for the observed CID product ions. All atomic and molecular species in the following reactions are assumed to be in their ground states:

CH₃CHS⁺+Ar→CH₃CHŞ⁺+H+Ar,

ΔH_b = 1.47 eV,

(4)

→CH₃CH⁺+SH+Ar, ΔH_b = 1.96 eV,

(5)

→CH₂H⁺+H₂+Ar, ΔH_b = 1.97 eV,

(6a)

→CH₂CH⁺+H₂S+Ar, ΔH_b = 4.28 eV,

(7a)

→C₂H₅⁺+H₂S+Ar, ΔH_b = 5.87 eV,

(6b)

→C₂H⁺+H₂+Ar, ΔH_b = 4.87 eV,

(7b)

→C₂H⁺+CH₃S+Ar, ΔH_b = 4.03 eV,

(8a)

→C₂H⁺+CH₃S+Ar, ΔH_b = 5.50 eV,

(8b)

→CH₃⁺+CH₃+SH+Ar,

ΔH_b = 7.91 eV,

(8c)

→CH₂S⁺+CH₃+Ar, ΔH_b = 1.73 eV,

(9a)

→CH₂S⁺+CH₃+Ar, ΔH_b = 3.18 eV,

(9b)

→CH₂⁺+C₂H₄+Ar, ΔH_b = 0.92 eV,

(10a)

→HCS⁺+CH₄+Ar, ΔH_b = 1.10 eV,

(10b)

→CH₂⁺+CH₃+H+Ar,

ΔH_b = 5.40 eV,

(10c)

→CH₂⁺+CH₃+H₂+Ar,

ΔH_b = 3.0 eV,

(11a)

→CHS⁺+CH₃+2H₂, Ar, ΔH_b = 7.59 eV,

(11b)

→CHS⁺+CH₃+H+Ar,

ΔH_b = 4.57 eV,

(11c)
By comparison of the observed AE(CID) value for a product ion with the thermochemical thresholds of possible reaction channels, information about the structure of the product ion can be obtained.

The formation of \( \text{CH}_3\text{CH}_2^+ + \text{SH} \) is supported by the excellent agreement observed between the AE(CID) value of \( 1.9 \pm 0.2 \text{ eV} \) for \( \text{CH}_3\text{CH}_2^+ \) and the thermochemical threshold of \( \Delta H_0^\circ = 1.96 \text{ eV} \) for reaction (5). In the previous CID study of \( \text{CH}_3\text{SH}^+ + \text{Ar} \), the formation of \( \text{CH}_3^+ + \text{SH} \), which results from the cleavage of the \( \text{CH}_3^+ - \text{SH} \) bond, has a sharp onset. As shown in Fig. 3(a), the experimental onset for \( \text{CH}_3\text{CH}_2^+ \) from the CID reaction of \( \text{CH}_3\text{CH}_2\text{SH}^+ + \text{Ar} \) is also sharp. These observations are consistent with the interpretation that the formation of \( \text{CH}_3^+ + \text{CH}_3\text{CH}_2^+ \) from \( \text{CH}_2\text{SH}^+ + \text{CH}_3\text{CH}_2^+ \), respectively, involves a direct \( C - S \) bond breakage process via a loose transition complex. Since the charge in \( \text{CH}_3\text{CH}_2\text{SH}^+ \) is mainly located at the S atom, the formation of \( \text{CH}_3\text{CH}_2^+ + \text{SH} \) from \( \text{CH}_3\text{CH}_2\text{SH}^+ \) must involve the charge transfer from the \( \text{SH}^+ \) moiety to the \( \text{CH}_3\text{CH}_2 \) component during the \( C - S \) bond cleavage process. Such a charge transfer process corresponds to a curve crossing between the potential surfaces formed by \( \text{CH}_3\text{CH}_2^+ + \text{SH} \) and \( \text{CH}_3\text{CH}_2^+ + \text{SH} \). Considering that the IE (\( \text{SH} \)) = 10.4219 \pm 0.0004 eV (Ref. 17) is significantly higher than the IE(\( \text{CH}_3\text{CH}_2\) ) = 8.13 eV,\(^15\) the charge transfer from \( \text{SH}^+ \) to \( \text{CH}_3\text{CH}_2 \) should be an energetically favored process. This may account for the fact that \( \text{SH}^+ \) is not observed as a CID product.

The AE(CID) value of \( 2.0 \pm 0.2 \text{ eV} \) for \( \text{C}_2\text{H}_4^+ \) is consistent with the thermochemical threshold \( \Delta H_0^\circ = 1.97 \text{ eV} \) for reaction (6a), but significantly lower than that of \( \Delta H_0^\circ = 5.87 \text{ eV} \) for reaction (6b). So we may conclude that the formation of \( \text{C}_2\text{H}_4^+ \) is accompanied by \( \text{H}_2\text{S} \) at the threshold. At higher \( E_{c.m.} \)'s, the H-elimination from internally excited \( \text{C}_2\text{H}_3^+ \) may also contribute to the production of \( \text{C}_2\text{H}_4^+ \). Thus, reaction (6b) is a possible source of \( \text{C}_2\text{H}_4^+ \) at \( E_{c.m.} > 5.9 \text{ eV} \).

The AE(CID) value determined for the formation of \( \text{C}_2\text{H}_5^+ \) is \( 4.2 \pm 0.2 \text{ eV} \) and is in accord with the thermochemical threshold of \( \Delta H_0^\circ = 4.28 \text{ eV} \) for reaction (7a). The thermochemical threshold of \( \Delta H_0^\circ = 4.87 \text{ eV} \) for the dissociation channel \( \text{C}_2\text{H}_5^+ + \text{H}_2\text{S} + \text{H} \) [reaction (7b)] is slightly higher than the AE(CID) for \( \text{C}_2\text{H}_5^+ \). At sufficiently high \( E_{c.m.} \)'s, excited \( \text{C}_2\text{H}_5^+ \) and \( \text{C}_2\text{H}_5^+ \) formed in reactions (5) and (6a) might undergo H and H elimination, respectively, to produce \( \text{C}_2\text{H}_5^+ \). As shown in Fig. 3(b), the rapid growth of the cross section for \( \text{C}_2\text{H}_5^+ \), beginning at \( E_{c.m.} \approx 7 \text{ eV} \), is accompanied by the corresponding drop in the cross section for \( \text{C}_2\text{H}_5^+ \) as \( E_{c.m.} \) is increased. This observation suggests that the increase in the \( \text{C}_2\text{H}_5^+ \) intensity is mostly resulted from the secondary decomposition of excited \( \text{C}_2\text{H}_5^+ \) at \( E_{c.m.} > 7 \text{ eV} \).

The AE(CID) value of \( 1.7 \pm 0.2 \text{ eV} \) for the mass 47 ion is in excellent agreement with the thermochemical threshold of \( \Delta H_0^\circ = 1.73 \text{ eV} \) for reaction (9a), indicating that \( \text{CH}_3\text{SH}^+ \) is formed near the CID onset for the mass 47 ion. To confirm this structure for the mass 47 ion, we have performed the charge transfer probing experiment using the double RFOIGGC scheme described in the Experiment. On the basis of the energetics for reactions (1) and (2), we expect to observe \( \text{C}_4\text{H}_6^+ \) if the mass 47 ion has the \( \text{CH}_3\text{S}^+ \) structure, whereas no \( \text{C}_4\text{H}_6^+ \) ions should be produced if the mass 47 ion possesses the \( \text{CH}_2\text{SH}^+ \) structure. Since no charge transfer product \( \text{C}_4\text{H}_6^+ \) ions were observed, we conclude that the mass 47 ions formed in the CID reaction of \( \text{CH}_3\text{CH}_2\text{SH}^+ + \text{Ar} \) at \( E_{c.m.} = 1.7 – 5.0 \text{ eV} \) have indeed predominantly \( \text{CH}_2\text{SH}^+ \) structure. The thermochemical threshold of 3.18 eV for the
formation of CH₃S⁺+CH₃ [reaction (9b)] is considerably higher than that of reaction (9a).

A very weak onset is observed at AE(CID)=1.5±0.4 eV for the CH₂S⁺ ion. Although this value is higher than the thermochemical threshold of ΔH₀=0.92 eV for reaction (10a), we conclude that CH₂S⁺+CH₃ is formed at the AE(CID) for CH₂S⁺. The thermochemical threshold for the formation of CH₂S⁺+CH₃+H [reaction (10c)] is ΔH₀=5.40 eV, suggesting that excited CH₂SH⁺ may be the precursor of CH₂S⁺ at Eᵥ=5.4 eV. The formation of cis-HCS⁺ (and/or trans-HCS⁺) (Ref. 22) together with CH₁ [reaction (10b)], which has a thermochemical threshold of ≈1.1 eV, is also a viable process.

The onset for HCS⁺ is very gradual, indicating that this ion may be produced by a stepwise dissociation mechanism or via a tight transition complex. The upper limit of the AE(CID) for HCS⁺ is estimated to be 7.2±0.5 eV, which is significantly higher than the ΔH₀ values of 3.1 and 4.57 eV for reactions (11a) and (11c), respectively. The formation of HCS⁺ may involve the further dissociation of excited CH₂SH⁺ and/or CH₂S⁺. We note that the ΔH₀ for CSH⁺ is 3.1 eV higher than that for HCS⁺ (see Table II). The formation of CSH⁺ at higher Eᵥ’s cannot be excluded.

The cross section for CH₃⁺ is on average the lowest in the Eᵥ range of interest here. The cross section curve for CH₃⁺ has a weak onset at 3.8±0.3 eV and exhibits a plateau in the Eᵥ range of 4–8 eV. At Eᵥ=8 eV, the cross section for CH₃⁺ begins to rise gradually as Eᵥ is increased. Since the AE(CID) for CH₃⁺ is in good agreement with the thermochemical threshold of ΔH₀=4.03 eV for reaction (8a), we conclude that the breakage of the CH₃⁻→CH₂SH bond to form CH₃⁻ and CH₂SH does not have a potential barrier. Although the charge of CH₂CH₂⁺⁻ is originally located at the S atom, the charge may hop from CH₂SH⁻ to CH₃ during the cleavage of the C=C bond in CH₂CH₂⁺⁻. Since the IE of CH₂SH (7.536±0.003 eV) (Ref. 22) is substantially lower than the IE of CH₃ (9.8380±0.0004 eV),¹⁸ we expect that the formation of CH₃⁻+CH₂SH is not favorable. We note that the thermochemical threshold for the formation of CH₃⁻+CH₂SH [reaction (8c)] is ΔH₀=7.91 eV, which appears to coincide with the further increase in cross section for CH₃⁻ at Eᵥ=8 eV. A finite contribution to the formation of CH₃⁻ at Eᵥ>8 eV may arise from the further dissociation of CH₂CH₂⁻⁻.

The AE(CID) for H₂S⁺ is determined to be 2.0 ±0.3 eV, indicating that reaction (12) is responsible for the formation of H₂S⁺ at the onset. The ab initio calculations suggest that C₂H₅⁻ and H₂S⁺ are formed via a CH₂CH₂SH⁻⁻ intermediate (see Sec. III C below). Due to the similar IE for H₂S (10.4682±0.0002 eV) (Ref. 16) and CH₂CH₂ (10.507 ±0.004 eV),¹⁵ the intensities for product H₂S⁺ and CH₂CH₂⁻⁻ are expected to be similar. This expectation is consistent with the similar cross sections observed for H₂S⁺ and C₂H₅⁻⁻.

Figure 4(a) shows the relative abundances in percentage for the observed CID product ions C₂H₅⁻⁻, C₂H₅⁺⁺, C₂H₅⁻⁺, CH₃⁻⁻, CH₃⁺⁺, CH₃⁻⁺, CH₂SH⁺⁺, CH₃S⁺⁺, CHS⁺⁺, and H₂S⁺⁺ in the Eᵥ range of 2–42 eV. Here, the sum of the abundances for all product ions at a specific Eᵥ is normalized to 100%. Due to the poor signal to noise ratios for the cross section data at Eᵥ<2 eV, the relative abundance data at this Eᵥ range are not included in Fig. 4(a).

The relatively abundance of C₂H₅⁻⁻ reaches a plateau at 3–6 eV and decreases monotonically from 63% to 20% as Eᵥ is increased from 6 eV to 42 eV. The decrease of the relative abundance for C₂H₅⁻⁻ appears to coincide with the increase in the relative abundance for C₂H₅⁺⁺, suggesting that a fraction of excited C₂H₅⁺⁺ ions initially formed at Eᵥ>7 eV further decomposes by H₂-elimination to produce C₂H₅⁻⁻. Over the Eᵥ range of 2–42 eV, the relative abundance of CH₂SH⁺⁺ remains constant at ≈25%. The relative abundances for C₂H₅⁻⁻, CH₃⁻⁻, and CH₂SH⁺⁺ become nearly the same at Eᵥ=25–42 eV. The relative abundance for CH₂S⁺⁻ decreases from 15% to 5% as Eᵥ is increased from 2 eV to 14 eV, and gradually increases again from 5% to 10% as Eᵥ is further increased to 42 eV. The relative abundances for other minor product ions are found to be <10% over the entire Eᵥ range. We expect that the relative abundances for all product ions become similar at high Eᵥ’s (>30 eV) that
are significantly higher than the endothermicities of the dissociation reactions (3)–(12).

B. Photoionization efficiency spectra for fragment ions from CH$_3$CH$_2$SH

We have measured the PIE spectra (not shown here) for ions from CH$_3$CH$_2$SH in the wavelength range of 1350–950 Å using a wavelength resolution of 5 Å (FWHM). The photoions observed are CH$_3$CH$_2$SH$^+$, C$_2$H$_4$S$^+$, C$_2$H$_5^+$, C$_2$H$_4^+$, CH$_2$SH$^+$ (CH$_3$S$^+$), CH$_3$S$^+$, and H$_2$S$^+$.

In the PI experiment, fragment ions can be considered as produced by the unimolecular dissociation of excited CH$_3$CH$_2$SH$^+$ ions initially formed by the PI of CH$_3$CH$_2$SH. The maximum excitation energy ($E_{ex}$) acquired by CH$_3$CH$_2$SH$^+$ thus formed can be calculated as $E_{ex} = h \nu - IE(\text{CH}_3\text{CH}_2\text{SH})$. The AE(CID) value can be compared directly to $\Delta(PI) = AE(PI) - IE(\text{CH}_3\text{CH}_2\text{SH})$, where AE(PI) is the AE for a fragment ion observed in PI. The $\Delta(PI)$ values for the photoions C$_2$H$_4$S$^+$, C$_2$H$_5^+$, C$_2$H$_4^+$, CH$_2$SH$^+$ (CH$_3$S$^+$), CH$_3$S$^+$, and H$_2$S$^+$ are in good agreement with the corresponding AE(CID) values (see Table I). It is known that C$_2$H$_4$S$^+$ can exist in several isomeric structures. On the basis of the $\Delta(PI)$ value of 1.47±0.06 eV for C$_2$H$_4$S$^+$, we conclude that CH$_3$CHSH$^+$ is formed at the PI threshold for C$_2$H$_4$S$^+$. We have also probed the structure for the mass 47 ion formed in the PI of CH$_3$CH$_2$SH by examining its charge transfer reaction with benzene. The fact that no charge transfer product C$_6$H$_5^+$ ions were observed indicates that the mass 47 ions formed in the PI of CH$_3$CH$_2$SH have predominantly the CH$_2$S$^+$ structure.

Figure 4(b) shows the relative abundances of the fragment ions CH$_3$CHSH$^+$, C$_2$H$_4^+$, C$_2$H$_5^+$, CH$_2$SH$^+$, CH$_3$S$^+$, and H$_2$S$^+$ observed in the PI of CH$_3$CH$_2$SH in the $E_{ex}$ range of 1.5–3.8 eV. Here, the sum of the abundances for all photoions except for that for CH$_3$CH$_3$S$^+$ is normalized to 100%. The high abundances for CH$_2$S$^+$ and CH$_3$CHSH$^+$ at $E_{ex}$<1.7 eV are consistent with the fact that CH$_2$S$^+$+CH$_4$ and CH$_3$CHSH$^+$+H are the only two energetically allowed dissociation channels in this $E_{ex}$ range. The formation of CH$_2$S$^+$+CH$_4$ necessarily involves a tight transition complex. Thus, we expect that the intensities for CH$_3^+$ and CH$_3$S$_2^+$, which are formed by a simple bond cleavage process, overtake that for CH$_3$S$^+$ at higher $E_{ex}$s. This expectation is confirmed by the relative abundance data of Fig. 4(b), showing that CH$_3$S$^+$ is the dominant product ion at $E_{ex}$>1.8–2.8 eV, while C$_2$H$_5^+$ becomes the major product ion at $E_{ex}$>2.8 eV. Although the relative abundance curves obtained by the PI of CH$_3$CH$_2$SH are not energy-selected data, it is interesting to note that the $E_{ex}$ dependencies of these relative abundance curves are in qualitative accord with the statistical QET predictions.

Comparing the relative abundance data plotted in Figs. 4(a) and 4(b), we note two major differences. First, the CH$_3$CHSH$^+$ ion observed in the PI of CH$_3$CH$_2$SH is not found in the CID study. The other difference is that the relative abundance curves for C$_2$H$_5^+$, CH$_2$SH$^+$, and CH$_3$S$^+$ observed in PI exhibit a stronger $E_{ex}$ dependence than that measured in the CID of CH$_3$CH$_3$S$^+$. At $E_{ex}$≈2–2.8 eV, C$_2$H$_5^+$ formed in the PI of CH$_3$CH$_2$SH is not the dominant ion, contrary to the CID results.

C. Theoretical potential-energy profile for the unimolecular reactions of CH$_3$CH$_2$SH$^+$

In order to rationalize the dissociation pathways observed in this study, we have also investigated the transition structures and their energetics involved in the unimolecular reactions of CH$_3$CH$_2$SH$^+$ using the ab initio Gaussian-2 (G2) theoretical procedures. The calculated potential-energy profiles for possible rearrangement and dissociation pathways leading to the formation of CH$_3$CHSH$^+$, CH$_3$CH$_2^+$, C$_2$H$_5^+$, CH$_2$SH$^+$, CH$_3$S$^+$, H$_2$S$^+$, and CH$_4$ are depicted in Fig. 5.

The dissociation reactions of CH$_3$CH$_2$SH$^+$ to form CH$_3$CHSH$^+$+H, CH$_3$CH$_2^+$+SH, CH$_2$SH$^+$+CH$_3$, and CH$_3^+$+CH$_2$SH, which involve the respective cleavage of a single C–H, C–S, and C–C bond, are predicted to have no potential barriers. These theoretical predictions are consistent with the experimental observation that the AE(CID) and $\Delta(PI)$ for these product channels agree with their corresponding thermochemical thresholds. If the elimination of CH$_3$ from CH$_3$CH$_2$SH$^+$ proceeds via a one-step process, it is predicted to involve a four-center cyclic transition structure lying 2.31 eV above the energy for CH$_3$CH$_2$S$^+$ as shown in Fig. 5. We note that the AE(CID) value of 1.5±0.4 eV for CH$_2$S$^+$ is higher than the thermochemical threshold of $\Delta H^0 = 0.92$ eV for the formation of CH$_3$S$^+$+CH$_4$ from reaction (10a). The $\Delta(PI)$ value 1.42±0.06 eV for CH$_3$S$^+$ observed in the PI experiment is close to the AE(CID) value. These observations suggest a potential energy barrier of ≈0.6 eV above the energy of the CH$_3$S$^+$+CH$_4$ channel. However, the theoretical barrier is ≈0.8 eV higher than the experimental barrier.

By a 1,2-H shift, the CH$_3$CH$_2$S$^+$ ion may rearrange to form the CH$_3$CHSH$^+$ (CH$_3$CH$_2$H$_2$) isomeric structure. The CH$_3$CH$_2^+$ and CH$_3$CH$_2$S$^+$ isomers are predicted to be stable with energies lying 0.55 and 0.54 eV, respectively.
respectively, above the parent CH3CH2SH+. The transition structure that interconverts CH3CH2SH+ and CH3CHSH+ by the 1,2-H shift is located to be 1.5 eV higher in energy with respect to that for CH3CH2SH−, whereas the transition structure that allows the interconversion of CH3CH2SH+ and CH3CH2SH2+ by a 1,3-H shift lies 2.71 eV above the parent CH3CH2SH−. The dissociation of CH3CH2SH2+ to yield CH3CH2+ + H2S and H2S+ + CH2CH3 is predicted to have no reaction barriers. Thus, the overall potential barrier for the dissociation from CH3CH2SH+ to form CH3CH2+ + H2S and H2S+ + CH2CH3 is governed by the barrier for the conversion between CH3CH2SH+ and CH3CH2SH2+. The fact that the AE(CID) and Δ(Pt) values for CH3 and H2S+ agree with the thermochemical thresholds for the formation of CH3CH2+ + H2S and H2S+ + CH2CH3 indicates that the potential barrier for the arrangement of CH3CH2SH+ to CH3CH2SH2+ is ≅ 2.0 eV. The latter value is lower than the theoretical barrier by ≅ 0.7 eV.

The formation of CH3CH2SH+ from CH3CH2SH− can be achieved by two 1,2-H shifts, i.e., CH3CHSH2+ → CH3CHSH2− → CH3CH2SH2+. If the second 1,2-H shift, which converts CH3CHSH2+ into CH3CH2SH2−, has a similar potential barrier as that (1.5 eV) for the arrangement from CH3CH2SH+ to CH3CHSH2+, we expect an overall potential barrier of ≅ 2.05 eV with respect to the energy of CH3CH2SH+. Such a value would be closer to the experimental barrier. With this expectation in mind, we have located the transition structure for the second 1,2-H shift between the terminal and middle C atoms. The G2 energy for this transition structure yields an effective barrier of 2.26 eV above the energy of CH3CH2SH+. This calculated barrier is still slightly higher than the experimental value of 2.0 ± 0.2 eV. Taking into account the experimental uncertainties, we consider the theoretical barrier of 2.26 eV associated with the stepwise 1,2-H shift mechanism to be in reasonable accord with the experimental results.

The formation of CHS+ can be accomplished by the further elimination of H2 and H from CH2SH2+ and CH2S+, respectively. These stepwise pathways (not shown in Fig. 5), which result in the formation of CHS+ + H2 + CH3 and CHS+ + H + CH4, are predicted to proceed without a potential barrier.

**D. Dissociation mechanisms for collision-activated CH3CH2SH+**

The two basic assumptions of the statistical QET are that a critical configuration or transition state controls the reaction rate, and that the internal energy is randomly distributed in the molecule’s active degrees of freedom. These assumptions lead to the conclusion that the most favorable product corresponds to the most stable product channel provided that a tight transition structure is not involved. As pointed out above, the formation of CH3S+ + CH4 [reaction (10a), ΔH0 = 0.92 eV] from CH3CH2SH+ involves a tight transition complex. The formation of the other major product channels CH3CHSH2+ + H [reaction (4), ΔH0 = 1.47 eV], CH3CH2+ + SH [reaction (5), ΔH0 = 1.96 eV], and CH3SH2+ + CH3 [reaction (9a), ΔH0 = 1.73 eV], which involve the breakage of the C–H, C–S, and C–C bonds, respectively, in CH3CH2SH+, is expected to proceed via a loose transition structure and to have no potential energy barriers. Since the endothermicities for reactions (4) and (9a) are lower than reaction (5), we expect that CH3SH+ and CH3CHSH2+ are among the major product ions. The observation that CH3CH2+ [reaction (5)] is the dominant product channel for the CID reaction of CH3CH2SH+ + Ar over the Ecm range of 2–30 eV is most interesting. This, together with the fact that CH3CHSH2+ is not observed as a CID product ion, suggests that the CID reaction of CH3CH2SH+ + Ar is not compatible with the statistical QET predictions.

In the Ecm range of this CID experiment, the collisions are most efficient for the promotion of translation-vibration and translation-rotation energy exchanges. However, electronic excitation by low energy collisions is highly inefficient. In the previous CID study of the CH3SH+ + Ar system, the observation that the formation of CH3+ + SH dominates the more stable product channel CH2SH2+ + H is contrary to the QET prediction. The highest vibrational frequencies of CH3SH+ correspond to the C–H and SH stretching vibrational modes with harmonic frequencies of ≅ 3000 cm−1, while the C–S stretching frequency of 687 cm−1 is the second lowest.2,11 Fenn et al. argue that the internal vibrational excitation of CH3CH2SH+ resulting from the low energy collision with Ar is predominantly deposited in the C–S stretching mode instead of the C–H or S–H stretching modes of CH2SH2+.2 Owing to the large difference in vibrational frequencies between the C–S and C–H (S–H) stretching modes of CH2SH2+, the C–S and C–H (or S–H) vibrational modes of CH3SH+ inefficient. As a consequence, the product CH3+ ion, which results from the C–S bond cleavage, is favored over the product CH2SH+ ion associated with the cleavage of the H–CH2SH+ bond.

This CID study of CH3CH2SH+ + Ar can be considered a test for the physical picture gained in the CID experiment CH3SH+ + Ar. Based on the recent experimental and ab initio calculations,10 the stretching frequencies associated with the C–H, S–H, and C–S bonds of CH3CH2SH+ are similar to those of CH3SH+.26 The C–C stretching mode of CH3CH2SH+ has a frequency of ≅ 1000 cm−1,2,10 although higher than the C–S stretching frequency of 617 cm−1, but significantly lower than the C–H (S–H) stretching frequencies. In addition to the more efficient collision excitations of the C–S and C–C stretching modes, the coupling between the C–S and C–C vibrational modes of CH3CH2SH+ should also be more efficient. Owing to the large frequency difference between the C–S (C–C) and C–H (S–H) stretching modes, the coupling or energy flow between the C–S (C–C) and C–H (S–H) stretching modes is also expected to be small within the time scale of the dissociation. As a consequence, product channels arising from the cleavage of the C–S and C–C bonds may dominate in the collisionally activated dissociation of CH3CH2SH+ This expectation is confirmed by the dominant abundances of the CH3CH2+ and CH2SH+ ions observed in the present CID experiment. The failure to observe the formation of CH2CHSH+; which cor-
responds to a more stable product channel, can be attributed to the inefficient energy flow between the C–H and C–Si(C–C) stretching modes. These results suggest that the CID reaction of CH$_3$CH$_2$SH$^+$ + Ar is not consistent with the QET predictions.

A strong bond is usually associated with a high stretching vibrational frequency. Although the C–H stretching frequency for CH$_3$SH$^+$ and CH$_3$CH$_2$SH$^+$ are typical of a C–H bond, the $D_0$ values for the H–CH$_2$SH$^+$ and H–CH(CH$_3$)SH$^+$ bonds are significantly lower than that of a normal C–H bond. This is due to the energy gained in the formation of the CH$_3$CH$_2$SH$^+$ double bond as the H-atom is departing from the middle C atom of CH$_3$CH$_2$SH$^+$. As pointed out previously by Chen et al.,$^1$ the high frequency and weak bond dissociation energy scenario is a key feature for the observed bond selective collisional-activated dissociation of CH$_3$SH$^+$ and CH$_3$CH$_2$SH$^+$.

The nature of fragment ions and their relative abundances observed in previous PI (Ref. 3) and charge exchange$^4$ studies of CH$_3$SH are in qualitative agreement with predictions of the statistical QET. Similar to this observation, we also find that the nature of fragment ions and their relative abundances measured in the PI of CH$_3$SH$_2$ are in qualitative accord with the QET predictions, indicating that the energy randomization assumption is mostly valid when the internal energy of CH$_3$CH$_2$SH$^+$ is deposited by electronic excitation. As argued in the previous CID study of CH$_3$SH$^+$,$^2$ due to the delocalized nature of electronic wave functions, an ionization process is capable of inducing finite excitation of the vibrational modes involving the C–S (C–C) as well as the C–H (S–H) bond, and thus will promote better couplings or energy flow between all the vibrational modes. As a result, the dissociation of CH$_3$SH$^+$ and CH$_3$CH$_2$SH$^+$ behaves statistically.

IV. CONCLUSION

We have examined the relative abundances for CH$_3$CH$_2$C$^+$, C$_2$H$_4$$^+$, C$_2$H$_5$$^+$, CH$_3$SH$^+$, CH$_3$H$_2$S$^+$, CH$_2$S$^+$, CHS$^+$, and H$_2$S$^+$ formed in the CID reaction of CH$_3$CH$_2$SH$^+$ + Ar in the $E_{c.m.}$ range of 1–42 eV. The CH$_3$CH$_2$S$^+$ channel is found to dominate over this entire $E_{c.m.}$ range. Furthermore, CH$_3$CHSH$^+$ was not observed as a CID product ion. Stemming from the fact that the $D_0$ value for the CH$_3$CH$_2$S$^+$–H bond is greater than that of the H–CH(CH$_3$)S$^+$ bond, this observation suggests nonstatistical behavior in the CID of CH$_3$CH$_2$S$^+$ + Ar. In effect, this system, together with the CID reaction of CH$_3$SH$^+$ + Ar, is an example of bond selective dissociation via collisional activation. Similar to the observation of previous PI studies of CH$_3$SH, the results of this dissociative PI study of CH$_3$CH$_2$SH$^+$ also agree qualitatively with the statistical QET predictions.

The present CID results support the physical picture gained in the previous study of CH$_3$SH$^+$ + Ar. The dominant production of CH$_3$CH$_2^+$ + HS and CH$_3^+$ + CH$_2$SH$^+$ is attributed to the more efficient excitation of the C–S and C–C stretching modes compared to the C–H and S–H stretching modes in the collisional activation of CH$_3$CH$_2$SH$^+$. The failure to observe product ions resulting from C–H bond cleavage is rationalized by the inefficient intramolecular energy flow due to weak couplings between the C–S (C–C) and CH$_3$ (SH) stretching modes of CH$_3$CH$_2$SH$^+$.

ACKNOWLEDGMENTS

W.K.L. acknowledges the support of a Research Grants Council (Hong Kong) Earmarked Grant for Research (Account No. 22160080) and a direct grant (Account No. 220600880) from the Chinese University of Hong Kong. Y.J.C. acknowledges the 1997 research Award of Iowa State University. S.S. was the recipient of the GAANN Fellowship for 1994–1995 and 1996–1997. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This article was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences.