

**Table II.** Energy Components (kcal/mol) for Arene Complexes

complex <sup>a</sup>	form <sup>b</sup>	Coulomb	1/r <sup>12</sup>	1/r <sup>6</sup>	total
BB	T	-0.45	1.76	-3.62	-2.32
	S	1.37	1.96	-5.03	-1.70
BN	T	-0.71	2.57	-5.34	-3.47
	S	0.35	2.74	-6.23	-3.15
BA	T	-0.57	2.08	-4.85	-3.34
	S	0.61	3.61	-8.29	-4.07

<sup>a</sup>B = benzene, N = naphthalene, A = anthracene. <sup>b</sup>T = T-shaped, S = stacked.

reported distances are between the center of the C9-C10 bond and the center of the benzene ring, while for anthracene the distance is between the center of the middle ring and the center of the benzene ring. A distorted T structure still has the lowest interaction energy (-3.5 kcal/mol) for the benzene-naphthalene pair. The lowest energy stacked structure in this case was located with the constraint that the rings lie in parallel planes. The interaction energy is -3.2 kcal/mol for the optimal form, which is displaced to have two benzene hydrogens roughly over the centers of the two naphthalene rings.

Upon increasing the system size further to anthracene, preference for a slightly tipped stacked structure finally emerges (Figure 14). The interaction energy of -4.1 kcal/mol is now 0.7 kcal/mol lower than that for the best T-shaped structure, which had to be located including a constraint that the ring planes be orthogonal. The stacked structure now has a benzene hydrogen near the center of each of the three rings in anthracene. However, the preference for the stacked structure is not electrostatic. As for the benzene dimers, the stacked structures are actually Coulombically repulsive, +0.35 and +0.61 kcal/mol for the complexes with naphthalene and anthracene, respectively. The binding for all of these systems is dominated by the van der Waals (1/r<sup>6</sup>) attraction, as summarized in Table II. This term is favored by more densely packed arrangements, which leads to the preference for stacked structures as the size of the components in-

creases. Some optimizations were also carried out for naphthalene and anthracene dimers; T-shaped and stacked structures are found to be nearly isoenergetic for the naphthalene dimers, while a strong preference for stacked anthracene dimers is obtained.

The key messages for molecular design from these results are that (1) stacked structures become more favorable with increasing size of the arenes and (2) the preferred geometry for stacked structures is offset with hydrogens roughly over ring centers. It may be noted that these notions are combined in the molecular tweezer of Zimmerman and Wu that shows a remarkable affinity for clamping adenine between two anthracene plates.<sup>24</sup>

### Conclusion

In the present paper, new potential function parameters have been reported for benzene that yield results in general accord with experimental data for the gas-phase dimer, pure liquid benzene, benzene in dilute aqueous solution, and the benzene dimer in water. It is recommended that this expanded model be incorporated into the description of aromatic groups in peptide residues.<sup>11a</sup> Furthermore, the present results have provided insights of value in molecular design, including estimates of the energetics of phenyl-phenyl interactions and observations on the disfavoring of face-to-face stacking of benzene in solution and on the enhanced favorability of stacked, shifted structures with increasing arene size. The value of condensed phase simulation work as a complement to experimental studies on molecular recognition and design has also been further demonstrated.<sup>34</sup>

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## Investigation of the Electronic Excited States of C<sub>2</sub>H<sub>3</sub>S<sup>+</sup> and C<sub>2</sub>H<sub>3</sub>O<sup>+</sup> by Means of Collision Spectroscopy

P. Traldi,<sup>†</sup> M. Hamdan,<sup>\*,†</sup> and Cristina Paradisi<sup>‡</sup>

Contribution from the C.N.R., Area di Ricerca di Padova, Corso Stati Uniti 4, 35100 Padova, Italy, and Centro Studio Meccanismi di Reazioni Organiche del C.N.R., Via Marzolo 1, 35131 Padova, Italy. Received September 20, 1989

**Abstract:** The electronic excited states of the gaseous ions C<sub>2</sub>H<sub>3</sub>S<sup>+</sup> and C<sub>2</sub>H<sub>3</sub>O<sup>+</sup> generated from a variety of precursor molecules by electron impact were investigated by means of translational energy spectroscopy (TES). The spectra of C<sub>2</sub>H<sub>3</sub>S<sup>+</sup> show three electronic transitions that can be assigned to C<sub>2</sub>H<sub>3</sub>S<sup>+</sup> ( $\bar{C} \leftarrow \bar{X}^1A$ ), ( $\bar{D} \leftarrow \bar{X}^1A$ ), and ( $\bar{A}^1A \rightarrow \bar{X}^1A$ ). The observation of the latter transition and its measured energy is the first experimental evidence that this ion has a long-lived (ca. 2 μs) electronic excited state located at 2.7 eV above its ground state. The spectra of C<sub>2</sub>H<sub>3</sub>O<sup>+</sup> offer no evidence of long-lived excited states. However, two collisionally induced electronic transitions involving the  $\bar{X}^1A_1$  ground state and two upper electronic excited states are clearly evident. The relative intensities of both transitions are clearly dependent on the identity of the precursor molecule. This dependence is attributed to the formation of different structures of the incident C<sub>2</sub>H<sub>3</sub>O<sup>+</sup> ion. This deduction is in accord with earlier experimental data and high-level theoretical calculations.

The structure, reactivity, thermochemical properties, and fragmentation pathways of the gaseous ions C<sub>2</sub>H<sub>3</sub>S<sup>+</sup> and C<sub>2</sub>H<sub>3</sub>O<sup>+</sup> continue to attract considerable interest. In recent years a number of techniques have been used to investigate both ions, including

collision spectroscopy,<sup>1-3</sup> ion cyclotron resonance,<sup>4,5</sup> photoionization,<sup>4,6</sup> and ab initio molecular orbital calculations.<sup>7</sup> Despite

<sup>†</sup>C.N.R., Area di Ricerca di Padova.

<sup>‡</sup>Centro Studio Meccanismi di Reazioni Organiche del C.N.R.

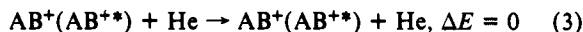
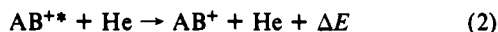
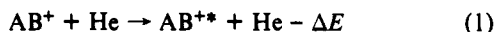
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such numerous activities, information on the energy, stability, and lifetime of the electronic excited states of both ions remains very sparse.<sup>8</sup> Such information is important for the correct interpretation of collision-induced dissociation spectra, which are normally aimed at the structural elucidation of organic ions. In a recent and detailed experimental investigation of  $C_2H_3S^+$  by means of collision spectroscopy, it was suggested by Cooks et al.<sup>2</sup> that observed differences in the fragmentation patterns of  $C_2H_3S^+$  species at low (5–25 eV) and high (keV) collision energies might be due to the involvement of an excited electronic state in the latter case.

In the present paper the electronic states of the gaseous  $C_2H_3S^+$  and  $C_2H_3O^+$  ions are investigated by means of translational energy spectroscopy (TES). In this technique, a monoenergetic mass selected ion beam is focused into a collision cell containing research grade He where the projectile ions experience collisional excitation and/or de-excitation. Such collisional processes are manifested as discrete losses or gains in the translational energy of the projectile ion and can be precisely measured by scanning a post-collision electrostatic energy analyzer. The present investigation is, to the best of our knowledge, the first application of this method to probe the electronic excited states of gaseous organic ions.

The collision processes investigated in this work can be expressed as



where  $AB^+$  and  $AB^{*+}$  are the respective ground and an excited states of the projectile  $C_2H_3S^+$  and  $C_2H_3O^+$  ions, while  $\Delta E$  is the net energy loss (gain) of the scattering process. Equation 1 represents an inelastic scattering process in which part of the translational energy,  $\Delta E$ , is converted into internal excitation energy of either the projectile ions and/or of the He target. The latter possibility is not indicated in eq 1, because the first excited state, He ( $2s\ ^3S$ ) at 19.81 eV above the ground state, is well outside the investigated energy range. Equation 2, on the other hand, represents the opposite process, where internal excitation energy of the projectile ion is converted into translational energy. Equation 3 refers to an elastic scattering process in which interchange between translational and internal excitation energy does not take place. More details regarding processes 1–3 have been given elsewhere.<sup>9</sup>

### Experimental Section

The measurements were performed on a reversed-geometry double-focusing mass spectrometer (VG ZAB-2F).<sup>10</sup> Briefly,  $C_2H_3S^+$  and  $C_2H_3O^+$  ions were formed from a variety of precursors (ethyl disulfide, tetrahydrothiophene, 2-methylthioethanol, propylene sulfide, 1,2-ethanedithiol, and thioacetanilide were used to form  $C_2H_3S^+$ , while  $C_2H_3O^+$  ions were generated from acetone, propylene oxide, *n*-butanol, diethyl ether, tetrahydrofuran, 1,3-propylene glycol, ethylene glycol, and 2-methoxyethanol) in an electron impact ion source maintained at a pressure of ca.  $10^{-5}$  Torr and a temperature of 200 °C, using a nominal ionizing electron energy of 100 eV. Ions were extracted at 8 kV, mass

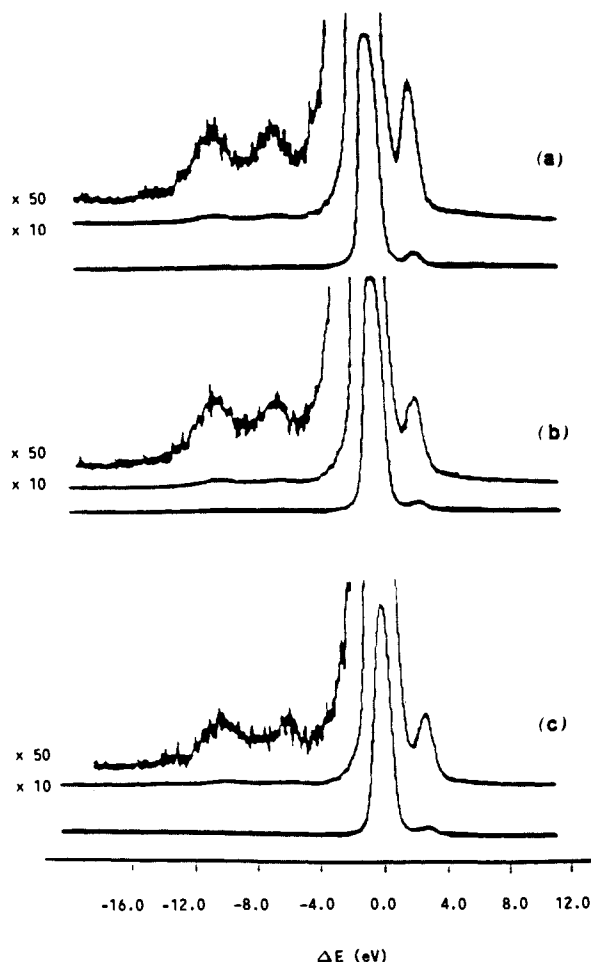


Figure 1. Translational energy spectra of 8 keV  $C_2H_3S^+$  ions scattered off He target. The ions were generated from (a) 1,2-ethanedithiol, (b) tetrahydrothiophene, and (c) ethyl disulfide.

analyzed by a magnetic sector, and focused into a collision cell situated at the focal point between the magnetic sector and an electrostatic energy analyzer. Excitation and de-excitation of the projectile ions were effected in the collision cell, using research grade He maintained at a pressure of ca.  $10^{-4}$  Torr. The TES of the scattered ions were acquired by scanning the postcollision electrostatic energy analyzer.

### Results and Discussion

The translational energy spectra of 8 keV  $C_2H_3S^+$  ions scattered off He taken at an energy resolution of 0.7 eV (fwhm) are shown in Figure 1a–c. A superelastic peak centered at an energy gain of  $2.7 \pm 0.2$  eV is observed in the three spectra. This peak can be assigned to the collisional de-excitation process,  $C_2H_3S^+(\tilde{A}^1A \rightarrow \tilde{X}^1A)$ . The observation of this transition also indicates that the  $\tilde{A}^1A$  excited state has a minimum lifetime of ca. 2  $\mu s$  (the transit time of the ions between the source and the collision cell). This transition can be easily compared to the emission transition ( $\tilde{A}^1A \rightarrow \tilde{X}^1A$ ), observed in the IR spectrum<sup>11</sup> of the isoelectronic neutral  $C_2H_2O_2$ . This peak may also include a small contribution from the transition ( $\tilde{a}^3A \rightarrow \tilde{X}^1A$ ). However, this contribution is expected to be insignificant, because earlier TES investigations<sup>12</sup> have clearly demonstrated that spin-nonconserving transitions are generally very weak.

The absence of an equivalent inelastic peak at an energy loss of 2.7 eV can be due to poor population of the  $\tilde{A}^1A$  excited state via heavy particle collisions compared to its population via electron impact dissociative ionization. Differences between the cross sections of the two mechanisms have been reported elsewhere.<sup>13,14</sup>

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**Table I.** Calculated Electronic States of  $C_2H_3O^+$  and Energy Values of the Experimentally Observed Excitation Transitions

state <sup>a</sup>	calcd energy, eV	$R, \text{\AA}^{a,b}$	exptl energy, eV	possible transition
$^1A_1$	0	1.13	$7.0 \pm 0.4$	$\left\{ \begin{array}{l} ^1A_1 \leftarrow ^1A_2 \\ ^1A_1 \leftarrow ^1E \end{array} \right.$
$^3A_1$	4.65	1.35	$9.8 \pm 0.4$	
$^3E$	5.14	1.35		$^1A_1 \leftarrow ^1A_1$
$^3A_2$	5.63	1.35		
$^1A_2$	5.64	1.35		
$^1E$	5.89	1.35		
$^3E$	8.42	1.26		
$^1A_1$	12.31	1.35		

<sup>a</sup>Reference 8. <sup>b</sup>The calculated energies assume fixed internuclear distance,  $R$ , between C and O. <sup>c</sup>Present investigation.

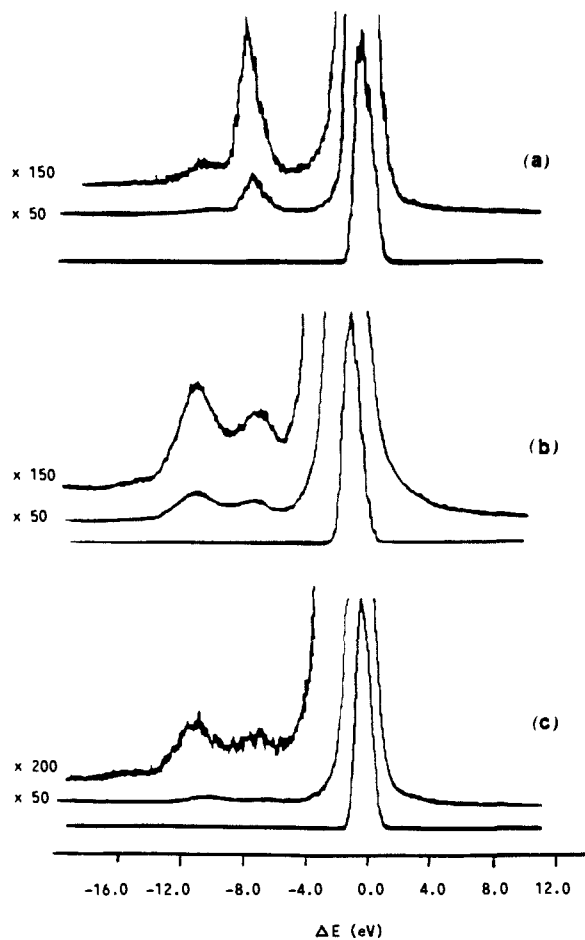
In a crossed beam investigation of  $OH^+$ , the emission transition ( $\bar{A}^3\pi \rightarrow \bar{X}^3\Sigma^-$ ) was observed in collisions between  $H_2O$  and  $He^+$ . However, when the  $He^+$  beam was replaced by an energetic electron beam the same transition was not evident.<sup>13</sup>

Two weak inelastic peaks centered at the energy losses of  $6.7 \pm 0.3$  and  $9.7 \pm 0.3$  eV are also observed in Figure 1a–c. The two peaks can be assigned to the excitation transitions,  $C_2H_3S^+$  ( $\bar{C} \leftarrow \bar{X}^1A$ ) and ( $\bar{E} \leftarrow \bar{X}^1A$ ), respectively. Transitions of similar energies have been observed in the IR spectrum of the isoelectronic neutral  $C_2H_2O_2$ <sup>11</sup> and have been attributed to absorption (excitation) transitions between the  $\bar{X}^1A_g$  ground and the  $\bar{C}$  and  $\bar{E}$  excited states.

Structural differences between  $C_2H_3S^+$  and the isoelectronic neutral  $C_2H_2O_2$  will result in energy differences and/or different state designations for the two species. However, in the light of the complete absence of theoretical and spectroscopic data on the excited states of  $C_2H_3S^+$ , the analogies drawn between the isoelectronic species are useful.

The translational energy spectra of 8 keV  $C_2H_3O^+$  ions scattered off He taken at an energy resolution of 0.8 eV (fwhm) are shown in Figure 2a–c. No superelastic peaks are observed in any of the spectra, indicating that the projectile  $C_2H_3O^+$  ions arriving at the collision cell are predominantly in the ground electronic state. Since no experimental data on the transitions among the electronic states of  $C_2H_3O^+$  are available, our interpretation of the observed transitions is solely based on the ab initio self-consistent-field (SCF) calculations of Yarkony and Schaefer<sup>8</sup> (see Table I). The table shows that within the energy range 0–13 eV there are at least eight predicted bound electronic states. This high-state density makes unambiguous assignment of the observed transitions a difficult task. However, several reasonable assumptions can be made that simplify the picture. First, since no superelastic transitions are observed, the excitation transitions observed in Figure 1 must originate in the ground state. Second, spin-changing transitions are generally weak<sup>12</sup> in TES, therefore only transitions within a given spin manifold (singlet or triplet) can be considered. Third, the observed excitation transitions are within the energy range 5.5–12.5 eV, and therefore the electronic states involved in these transitions are likely to be above the lower energy limit of 5.5 eV. Energies measured at the centers of the two peaks observed in Figure 1 and tentative assignments of the electronic states involved are given in Table I.

The three spectra of Figure 2 clearly show that the relative intensity of the two observed inelastic peaks is dependent on the identity of the precursor molecule. The absence of any superelastic peaks in the same spectra infers that both transitions originate from the ground state of the  $C_2H_3O^+$  incident ion. Differences in the relative intensity of the observed transitions can be attributed to either of the following possibilities. First, the incident  $C_2H_3O^+$  ion beam formed from different molecular precursors may contain different isomeric structures, each of which has its own unique contribution to the observed TES. It has been clearly demonstrated that various  $C_2H_3O^+$  isomers do exist<sup>4,3b,7a</sup> and can be produced under experimental conditions similar to those used in



**Figure 2.** Translational energy spectra of 8 keV  $C_2H_3O^+$  scattered off He target. The ions were generated from (a) tetrahydrofuran, (b) acetone, and (c) diethyl ether.

the present investigation. The experimental work<sup>4,3a</sup> provides evidence for at least three different structures while ab initio molecular orbital calculations<sup>7a</sup> indicate that there should be four observable structures. Second, the observed transitions may originate from different vibrational levels of the ground electronic state which have varying Frank–Condon overlap with the vibrational levels of the upper state(s). Earlier TES investigations<sup>9b,15</sup> have demonstrated that the relative populations of vibrational energy levels of electronic states that have been reached by positive ion–molecule collisions are as predicted by the Frank–Condon factors. However, the latter suggestion has to be treated as a mere possibility that has to be confirmed or rejected through further experiments. Such experiments require a high-pressure ion source to cool down vibrationally excited ions and/or selective generation of ground-state vibrational levels by means of light sources that can provide the appropriate energy for such selection. The authors of this paper do not possess either facility and therefore cannot advance this argument any further.

It is pertinent to point out that the present assignments of the inelastic peaks in both TES spectra are less certain than the assignment of the superelastic peak observed in Figure 1. This uncertainty can be attributed to either of the following arguments. First, no superelastic peaks are observed in the energy range 6–10 eV, which means that the observed inelastic transitions are caused by the excitation of either the projectile ion or the target (including the background). Second, although the background pressure prior to the introduction of He was ca.  $10^{-8}$  Torr, excitation transitions involving background and/or impurity gases cannot be fully ruled out. The presence of  $O_2$  in particular may partially contribute to both transitions. This assumption is based on the well-known absorption spectrum of  $O_2$ ,<sup>16,17</sup> which shows the transition  $O_2(B^3\Sigma_u^-$

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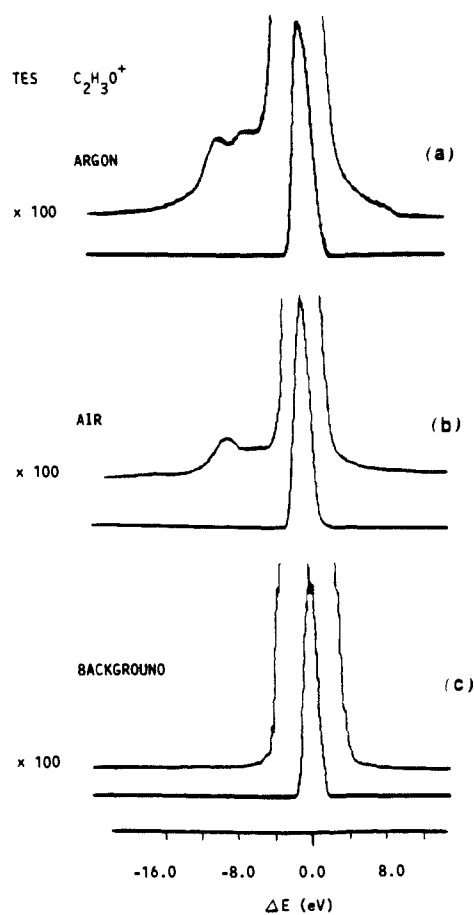


Figure 3. Translational energy spectra of 8 keV  $C_2H_3O^+$  ions generated from acetone and scattered off (a) Ar, (b) air, and (c) background.

$\rightarrow X^3\Sigma_u^-$ ) usually assumed to be associated with the Shumann range, 7.9–9.5 eV, with its maximum reported by various authors to be between 8.47 and 8.73 eV.<sup>18</sup> Although the above two arguments have to be seriously considered when excitation transitions are assigned, there are a number of observations that indicate that in the present work interference by background and impurity gases is insignificant. (i) The TES of  $C_2H_3O^+$  taken at background pressure is shown in Figure 3c. Although this spectrum was acquired under the same experimental conditions (including the intensity of the projectile ion beam) used in Figure 1c, the absence of any excitation/de-excitation transitions in Figure

3c is a strong indication that contribution of background excitation is minimal. (ii) To ensure that the observed transitions are not due to target excitation, a number of target gases, including Ar and air, were used, but as Figure 3a,b clearly shows, no significant differences exist between these spectra and the spectra obtained with He as target. (iii) Dependence of the relative intensity of the transitions observed in Figure 2a–c on the identity of the precursor molecule, strongly suggests that these transitions are associated with the excitation of the projectile ion.

#### Summary and Conclusions

Translational energy spectroscopy has been used to investigate electronic transitions between the low-lying non-dissociative electronic states of the two gaseous ions  $C_2H_3S^+$  and  $C_2H_3O^+$ . The singly charged ion  $C_2H_3S^+$  generated from a number of precursor molecules has a long-lived electronic excited state lying at 2.7 eV above  $X^1A$  ground state. Two collisionally induced excitation transitions between the ground and the two excited states  $\bar{C}$  and  $\bar{D}$  have also been observed. The relative intensities and energies of these states showed no dependence on the identity of the precursor. Also in the case of  $C_2H_3O^+$  two collisionally induced transitions between the ground state and two excited states, at 7.0 and 9.8 eV, respectively, have been observed. However, in contrast with the behavior of  $C_2H_3S^+$  ions, the relative intensities of observed collisionally induced transitions depend on the nature of the precursor molecule. Moreover, no long-lived excited electronic states have been detected for the oxygen-containing ions.

The presented data regarding the energies, stability, and lifetimes of a number of electronic excited states may contribute to a more reliable interpretation of earlier collision-induced dissociation spectra. Thus, the observation of low-lying electronic states of  $C_2H_3S^+$ , well below the threshold for the major fragmentation reactions (e.g. 4.6 eV for CS loss), provides some support to the hypothesis that fragmentation of this ion at high collision energy involves an excited state.<sup>2</sup> In the case of  $C_2H_3O^+$  ions the dependence of the intensity of the observed excitation transitions on the identity of the precursor suggests the involvement of more than one isomeric structure of the incident  $C_2H_3O^+$  ion each of which may have its own unique contribution to the observed TES. This deduction is supported by earlier reports regarding the observation of more than one isomer of  $C_2H_3O^+$  in high-energy-collision experiments.<sup>3</sup> In contrast, only one structural isomer has been observed for the  $C_2H_3S^+$  ionic species both in high- and low-energy-collision experiment. Accordingly, a unique TES spectrum has been obtained in this study for  $C_2H_3S^+$  ions generated from different precursors.

The results of the present investigation indicate that translational energy spectroscopy has a considerable potential in the characterization of small organic cations and their reactivity.

Registry No. 1,2-Ethanedithiol, 540-63-6; tetrahydrothiophene, 110-01-0; ethyl disulfide, 110-81-6; tetrahydrofuran, 109-99-9; acetone, 67-64-1; diethyl ether, 60-29-7.

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