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of Bernstein[5] and the 694.3 cm^{-1} feature of Hollenberg and Dows,[2] and also in agreement with the neat crystal spectra, provided that the center-of-band is put at 692 cm^{-1} (see below).

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Kinetic Energy Release in the Dissociation of Some Simple Molecular Ions. Water and Hydrogen Sulfide

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The technique of ion kinetic energy spectroscopy has been applied to a study of $S^{+\cdot}$ formation from $H_2S^{+\cdot}$ and $O^{+\cdot}$ formation from $H_2O^{+\cdot}$. Unimolecular formation of $S^{+\cdot}$ occurs by predissociation of the first excited state via the repulsive $^4A_2$ state of $H_2S^{+\cdot}$. Above the classical crossover region this reaction proceeds rapidly on the mass spectrometer time scale but tunneling through the barrier occurs slowly and gives rise to metastable ions which fragment with conversion of all the available potential energy to kinetic energy. Collisional excitation of ground state $H_2S^{+\cdot}$ yields excited ions which rapidly dissociate via the $^4A_2$ repulsive surface to give substantially excited $(v=2)H_2$. This reaction occurs with the partitioning of some 30% of the available energy into translational energy of the products. The heat of formation of $S^{+\cdot}$, determined from the appearance potential, requires only slight correction for the excess energy term arising from the potential energy difference between the crossover region and the ground state of the products because the repulsive surface is unusually flat. Ground state $H_2O^{+\cdot}$ ions undergo collision-induced excitation with loss of 22 ± 4 eV of kinetic energy to give a high energy excited state which fragments directly to give $O^{+\cdot}(^2D$ or $^2P)$ and vibrationally excited H_2. Appearance potential measurements do not provide a reliable assignment of the products because of the excess energy terms. These results are in contrast to earlier conclusions that fragmentation upon electron impact yields two hydrogen atoms.

INTRODUCTION

The kinetic energy (T) acquired by the fragments when a molecular ion dissociates offers a means of probing unimolecular reactions.[1] It is advantageous to study simultaneously the related process of collision-induced fragmentation and to measure both the kinetic energy (T) released upon reaction and the kinetic energy (Q') lost[2] by the reactant ion in these collisional processes. In small molecular ions, where excited states are well separated and where at least some thermochemical data for these states are available, unimolecular[3] and collision-induced[4] dissociation studies can be combined for a better understanding of the nature of fragmentation reactions as well as the thermochemistry of the system. The type of question which can be addressed is as follows: (i) does a particular reaction occur by predissociation? (ii) what is the approximate energy of the reactant state? (iii) is the kinetic energy release consistent with the formation of ground state products?

Reactions (1) and (2) have been chosen for study by this method,

$$H_2S^{+\cdot} \rightarrow S^{+\cdot} + H_2(2H), \qquad (1)$$

$$H_2O^{+\cdot} \rightarrow O^{+\cdot} + H_2(2H), \qquad (2)$$

both because of the intrinsic practical and theoretical

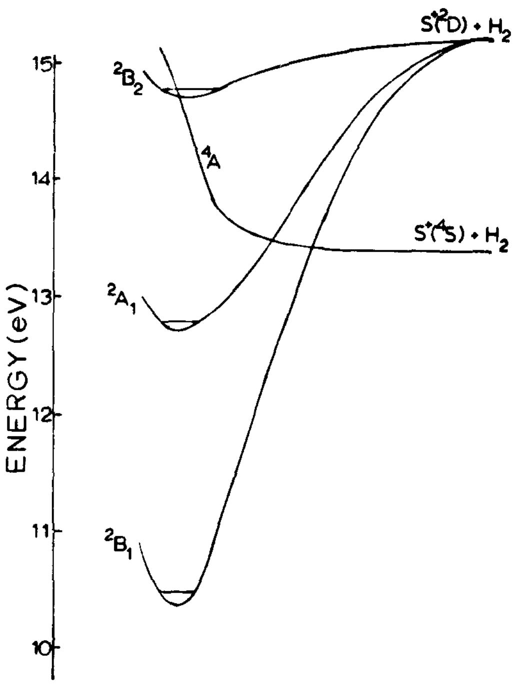

FIG. 1. Electronic states of $H_2S^{+\cdot}$ (after Fiquet-Fayard and Guyon, Ref. 7).

importance of the water molecular ion and also because many aspects of these decompositions have been investigated by a variety of other experimental methods.[5]

Hydrogen sulfide molecular ions undergo unimolecular fragmentation to give $S^{+\cdot}$.[6] Potential energy surface correlations of Fiquet-Fayard and Guyon[7] indicate that all three bonding states of $H_2S^{+\cdot}$ ($^2B_1$, $^2A_1$, and $^2B_2$) might undergo predissociation via the repulsive $^4A_2$ state to form ground state products, $S^{+\cdot}(^4S_u)$ and $H_2(^1\Sigma_g^+)$ (Fig. 1). Alternatively, direct excitation to the repulsive $^4A_2$ state could lead to ground state $S^{+\cdot}$ formation. (No consideration need be given the formation of other than ground electronic state products since the energies of such states are much greater than the appearance potential of $S^{+\cdot}$ formation.[6]) In addition to an abundant fragment ion, there is also an abundant unimolecular metastable process leading to $S^{+\cdot}$ formation.[6] This requires a relatively long lifetime ($>10^{-6}$ sec) for the precursor ions, which could be achieved by a predissociation mechanism if there were a relatively low probability for curve crossing. Direct excitation to a repulsive state is not expected to allow the observation of a unimolecular metastable fragmentation. The photoionization results[6] indicate that the appearance potential of the normal daughter $S^{+\cdot}$ ions is 13.40 eV and that of the metastable ions is 13.36 eV. Also, the excitation functions for these two processes are different.

The photoelectron spectrum of H_2S^{8-11} indicates a very low probability for formation of ions in other than the $^2A_1$ state in the vicinity of the appearance potential of $S^{+\cdot}$. Loss of vibrational structure in the $^2A_1$ band at energies above the $S^{+\cdot}$ appearance potential has been reported and attributed to the onset of a rapid predissociation.[8,9] Other recent photoelectron spectra[10,11] and an optical spectrum[12] indicate a change in structure in this region but no significant broadening. Furthermore, this change in vibronic structure occurs at approximately the energy required to straighten the molecule.[12] Although the predissociation may be slow relative to the vibrational periods of the ion, this does not rule out the possibility of a fast predissociation on the mass spectrometer time scale. Hence, predissociation of the $^2A_1$ state [Reaction (3)] is probably the main mechanism of normal $S^{+\cdot}$ ion formation in hydrogen sulfide:

$$H_2S^{+\cdot}(^2A_1)\rightarrow H_2S^{+\cdot}(^4A_2)\rightarrow S^{+\cdot}(^4S_u)+H_2(^1\Sigma_g^+). \qquad (3)$$

Because of the low Franck–Condon factors for forming $H_2S^{+\cdot}$ ions in the ground electronic state with energy in the vicinity of the onset of $S^{+\cdot}$, this can be neglected as a significant contributor to normal $S^{+\cdot}$ ion formation.[7] However, direct excitation to the repulsive surface and predissociation of the $^2B_2$ state, Reaction (4), will also make a contribution at energies well above the threshold,

$$H_2S^{+\cdot}(^2B_2)\rightarrow H_2S^{+\cdot}(^4A_2)\rightarrow S^{+\cdot}(^4S_u)+H_2(^1\Sigma_g^+). \qquad (4)$$

The behavior of water is remarkably different from that of hydrogen sulfide. First, no unimolecular metastable has been observed[13] in the mass spectrum. Second, the ionization efficiency curve for $O^{+\cdot}$ indicates a very low probability for the formation of products in the ground state (onset at ~18.8 eV) and a much higher probability for formation of excited products (onset at ~28.13 V).[14] Furthermore, beam studies[15] have shown that over 90% of the $O^{+\cdot}$ ions formed by electron impact are in an excited state, tentatively assigned as the ^2D state.

In the present study we focus attention on the kinetic energy (T) released during the fragmentations (1) and (2) occurring in the first field-free region of a double-focusing mass spectrometer. The decomposition (1) occurs spontaneously; (2) was induced by allowing ions formed upon electron impact (70 eV) and then accelerated to high energy (5–10 keV), to collide with neutral molecules. Some of the electronic excitations resulting from these collisions are sufficient to permit (2) to occur in the field-free region.[4] This collisional excitation procedure was also used to study Reaction (1). Reactions (5) and (6) are the subject of a companion study,[16]

$$H_2S^{+\cdot}\rightarrow HS^{+}+H\cdot, \qquad (5)$$

$$H_2O^{+\cdot}\rightarrow HO^{+}+H\cdot. \qquad (6)$$

EXPERIMENTAL

All experiments were performed on a Hitachi RMH-2 mass spectrometer[17] modified as previously described.[18] Metastable peak profiles were measured by scanning the accelerating voltage. Narrow β slitwidths were used, and the mean kinetic energy release was calculated[19] from the metastable peak width taken as the full width at half-height, corrected for the width of the main beam.[20] The shape of the peak provides a measure of the distribution of kinetic energies involved[21]; the width at the base line represents the maximum energy release.

Standard operating conditions were, electron energy, 70 eV; electron (trap) current, 1 mA; ion source pressure, 1×10^{-5} torr; source temperature, 160°C; ion accelerating voltage, 8 kV; background pressure in collision region, 2×10^{-7} torr.

The fragmentations following collisional excitation were studied in the same manner as the unimolecular reactions. In addition, the kinetic energy, Q', lost by the reacting ions was calculated from the shift of the position of the collision-induced[22] metastable peak on the energy scale from that calculated for the unimolecular transition. For the cases where both unimolecular and collision-induced metastable peaks were observed simultaneously, a Dupont curve resolver was employed.

Hydrogen sulfide, obtained from Matheson, and doubly distilled water were used without further purification. Deuteration of hydrogen sulfide was carried out by passing the gas through a chromatographic column treated with deuterium oxide (Columbia Organic Chemicals 99.5%).

RESULTS AND DISCUSSION

Hydrogen Sulfide

The measured kinetic energies released in $S^{+\cdot}$ formation from hydrogen sulfide and its deuterated analogs are summarized in Table I. The observed metastable in H_2S is shown in Fig. 2(a); the average value of T calculated from the full width at half-height is 0.037 ± 0.005 eV and the maximum, 0.13 ± 0.01 eV, determined from the base width obtained by extrapolation of the almost linear sides of the metastable peak. In these reactions there is a narrow range of translational energy of the products arising from the following contributions. First, as the system traverses the potential surface from the transition state towards products, the potential energy can be distributed between internal and translational modes.[23] In the case of purely repulsive surfaces of polyatomic molecules it is theoretically possible to have all of the available energy appear as translation of the products, although there is a partitioning (not expected to be statistical) due to the structure of the surface. The second, and in this case perhaps the major contributor to the observed distribution, is the range of internal energy of the fragmenting ions, which may be distributed statistically with some portion appearing as translational energy of the products. In metastable reactions involving ions of long lifetimes (3–6 μsec in our experiments)[24] the range of internal energy has been shown to be quite small.[25]

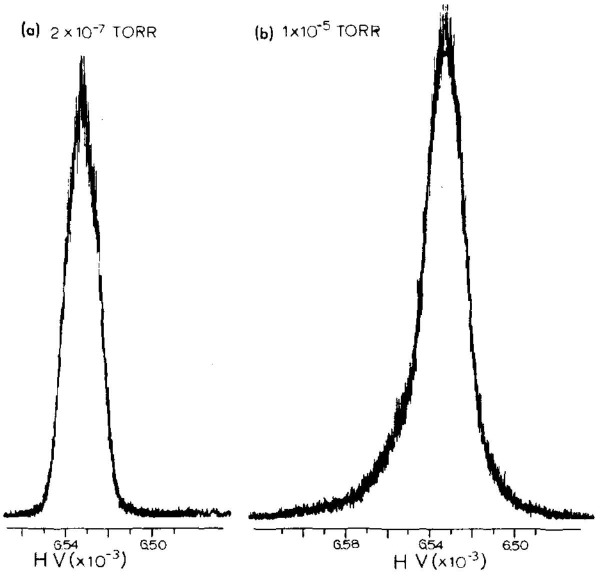

FIG. 2. Metastable transition for $H_2S^{+\cdot}\rightarrow S^{+\cdot}+H_2$ (a) unimolecular reaction, (b) unimolecular plus collision-inducated reaction.

TABLE I. $S^{+\cdot}$ formation: kinetic energy release.

System	Products	Kinetic energy release T (eV) Half-height	Maximum
H_2S	$S^{+\cdot}+H_2$	(0.037)[a]±0.005	$(0.13)\pm0.01$
HDS	$S^{+\cdot}+HD$	$0.075\pm0.005(0.038)$	$0.17\pm0.01(0.14)$
D_2S	$S^{+\cdot}+D_2$	$0.15\pm0.01(0.072)$	$0.22\pm0.02(0.14)$

[a] Figures shown in parentheses have been corrected relative to the value for H_2 for the different zero point energies of HD and D_2, respectively.

The potential energy available for distribution is slightly different for the three systems because of the different zero point energies and vibrational frequencies of H_2, HD, and D_2.[26] The small range of translational energies observed indicates that only a single vibrational quantum level can be populated. For hydrogen formation in the zeroth vibrational level the total translational energies measured using H_2S, HDS, and D_2S will differ by the differences in the values of the zero point energies of H_2, HD, and D_2, respectively. Using H_2 as a reference the corrected translational energies are given in parenthesis in Table I. With one exception, which will be discussed later, these values are all the same. There is no constancy for the values obtained after corrections based on formation of H_2, HD, and D_2 with $v \geq 1$, indicating that these products are formed exclusively in the ground vibrational level. Because of the symmetry of reaction, rotational energy of the products is not expected to have a significant effect.

It is also apparent from Table I that the distribution of kinetic energy released becomes narrower as the number of deuterium atoms in the fragmenting ion increases. (Compare, for example, the ratio of the half-height to the maximum T in H_2S, HDS, and D_2S which is 0.28, 0.44, and 0.68, respectively.) The metastable peaks for the latter two cases have flat tops and steeper sides than that for H_2S shown in Fig. 2(a). We interpret metastable ion reaction leading to $S^{+\cdot}$ as occurring by a tunneling mechanism by which the maximum kinetic energy released corresponds to the difference between the potential energy at the position of the crossover from the $^2A_1$ to $^4A_2$ surfaces compared to that of the separated products. It is expected that any ions having energy above the activation barrier will have decomposed before reaching the field-free region; these comprise most of the normal daughter ions formed at low energy and correspond to the photoionization onset of 13.40 eV.[6] Ions with internal energy below the classical activation barrier may, however, be long lived, predissociating via a tunneling mechanism.[27] The reaction probability for this mechanism would be expected to decrease with deuterium substitution as has been observed for the metastable abundances.[13] In addition, this probability will decrease more rapidly with the internal energy of D_2S^+ than for H_2S^+. This is substantiated by the narrowing of the distribution of kinetic energy release with deuterium substitution and accounts for the unusually large half-height value obtained with D_2S.

These conclusions are consistent with both the photoionization and optical spectra. The energy difference of 0.04 eV between the onset for normal metastable $S^{+\cdot}$ formation determined by photoionization is of the same order as the difference between the half-height and the maximum kinetic energy released. Dixon *et al.*[12] concluded that between 13.36 and 13.40 eV the predissociation lifetimes of the $^2A_1$ state are greater than 10^{-6} sec in agreement with our observations on metastable ions. Ions with lifetimes of the order of 10^{-8}–10^{-6} sec and energies between 13.40 and 13.55 eV as determined by Dixon *et al.* would not make a significant contribution to the unimolecular metastable signal.

The decomposition of stable $H_2S^{+\cdot}$ ions by collision with helium, air, and krypton was also studied. The resultant metastable peak obtained with a pressure of 1.0×10^{-5} torr of air in the first field-free region is shown in Fig. 2(b). The unimolecular peak is unaffected (no enhancement or attenuation) by the presence of the collision gas; however, a second component is evident, shifted to somewhat higher scanning (ion acceleration) voltages. This effect, observed in many systems,[2] arises from the transfer of kinetic energy into electronic excitation of the impacting ion on collision. From the resolution of these two components we have determined half-height and maximum values of 0.40±0.02 and 0.64±0.02 eV, respectively, for the kinetic energy release accompanying the collision-induced reaction. The corresponding energy loss, Q', is 4.4±0.5 eV. These values are found to be independent of the pressure or nature of the collision gas. For the kinetic energies employed the above facts suggest that the collision involves a vertical electronic excitation of $H_2S^{+\cdot}$ leading to fragmentation.[28]

The largest fraction of the impacting ions reaching the collision region (lifetime >3 μsec) are in the lowest vibration levels of the ground state.[29] A vertical excitation of ~4.4 eV can provide the $H_2S^{+\cdot}$ ions with approximately 14.9±0.5 eV relative to the neutral species. This places them in the vicinity of the second excited state ($^2B_2$) which has an adiabatic ionization potential of 14.78 eV.[9] The subsequent decomposition is consistent with mechanism (4) involving the $^4A_2$ repulsive surface. The intermediacy of the $^2B_2$ state cannot be verified; nevertheless, predissociation of this state appears to be a reasonable mechanism.[31]

In this fragmentation there is about 1.5±0.5 eV of energy available for partitioning; of this 0.4 eV on the average appears as translational energy. Hence, the most probable process involves the transfer of 1.1±0.5 eV into internal energy in excess of the zero point energy of hydrogen. The center of this distribution corresponds to the formation of $H_2(v \sim 2)$. The variation between the average and maximum translational energy of the products is quite small indicating that predominantly one vibrational level is populated. In Fig. 2(b) there is evidence for breaks at about 6.49_5 and 6.57_5 keV in the collisional component. These appear in all of the collisional spectra. We interpret this structure as arising from lower probability transitions forming $H_2(v=0, 1)$ accompanied by a correspondingly larger release of kinetic energy. The energy partitioning occurring in the collisional process can be contrasted with the unimolecular fragmentation in which all of the available energy appears as translation. This is not surprising because there is insufficient potential energy available in the spontaneous reaction to allow any vibrational excitation of the products.[32]

Dibeler and Liston's value[6] of $\Delta H_{f0}°(S^+) = 303.9 \pm 0.5$ kcal mole^{-1} calculated from their measured appearance potential (13.36±0.01 eV) for $S^{+\cdot}$ formation in the metastable reaction should be corrected for the excess kinetic energy of the products. Independent of the mechanism of decomposition, the correction appropriate to this threshold measurement is the minimum kinetic energy release. Since this is less than 1 kcal mole^{-1} (see above), corrections to the thermochemical data derived by Dibeler and Liston are not warranted. Simply enlarging the uncertainty limits to ±1 kcal mole^{-1} for the calculated heats of formation suffices. In considering thermochemical data based on appearance potential measurements the assumption of zero kinetic energy release may result in serious errors,[25,34] although this is not the case here.

Water

Formation of $O^{+\cdot}$ ions occurred in our experiments only when induced by collision. The photoelectron spectrum of water[9,35] indicates that the structure of the ground electronic state, which is the predominant component of the ion beam reaching the collision region, is almost identical to that of the water molecule. Furthermore, the intense $(0, 0, 0) \leftarrow (0, 0, 0)$ transition indicates that the lowest vibrational states of $H_2O^{+\cdot}(^2B_1)$ are the most highly populated.[30] Hence, the electronic excitations involved on collision of $H_2O^{+\cdot}$ may closely approximate those for electron or photon impact on water.

The translational energy of the products as determined from the half-height metastable width is 1.3_3 and 1.2_3 eV for water and water-d_2 (Table II). There is a wide range of product kinetic energies as indicated by the maximum value (estimated by linear extrapolation) of 5.0±0.5 eV. These values are found to be independent of the nature and pressure of the collision gas; however, Q' showed a wide variation (22±4 eV) suggesting that it should be taken only as an upper limit to the magnitude of the electronic excitation. Most conclusions concerning the reaction mechanism based on appearance potential measurements have emphasized the formation of $O^{+\cdot}$ in an excited electronic state along with two hydrogen atoms.[14,15,36] Whereas there is little doubt concerning the former conclusion,[15] the validity of the latter (formation of $2H\cdot$), is questionable. The possibility of formation of hydrogen in highly excited vibrational levels cannot be discounted. Our experiments suggest that even at the threshold for $O^{+\cdot}$ formation the considerable translational energy of the fragments and the possible internal energy of hydrogen obviate a simple assignment of products based on appearance potential measurements. Because of the magnitude of the meassured translational energy and the occurrence of the analogous fragmentation in hydrogen sulfide, we suggest that Reaction (7),

$$H_2O^{+\cdot} \rightarrow O^{+\cdot}(^2D \text{ or } ^2P) + H_2(\nu), \qquad (7)$$

in which H_2 is highly vibrationally excited, more closely represents the threshold process.

TABLE II. $O^{+\cdot}$ formation: kinetic energy release.

System	Products	Collision gas	Half-height value of kinetic energy release T (eV)
H_2O	$O^{+\cdot}+H_2$	air, He	1.3_3
D_2O	$O^{+\cdot}+D_2$	air, Ne, He	1.2_3

CONCLUSIONS

The results are consistent with the following picture for hydrogen sulfide. The normal daughter ions, $S^{+\cdot}$, in the mass spectrum arise predominantly from predissociation of the first $(^2A_1)$ and second $(^2B_2)$ excited states of the molecular ion via the repulsive $^4A_2$ state. Ions with a range of energy below the classical crossover region of the $^2A_1$–$^4A_2$ surfaces may predissociate via a slower tunneling mechanism thus giving rise to the unimolecular metastable fragmentations occurring 10^{-6}–10^{-5} sec after the initial ionization. The effective range of internal energy of the ions sampled is about 0.1 eV in agreement with the different photoionization thresholds for normal daughter and metastable $S^{+\cdot}$ ions. On collision a stable beam of $H_2S^{+\cdot}$ ions is excited to the $^2B_2$ bond state and undergoes a rapid predissociation or is excited directly to the repulsive $^4A_2$ surface leading to products $S^{+\cdot}$ and molecular hydrogen in the same electronic configurations is in the spontaneous decomposition.

The spontaneous reaction leads to the formation of $S^{+\cdot}(^4S)$ and $H_2(^1\Sigma)$ in the ground vibrational state, whereas in the collision-induced reaction H_2 is formed predominantly in the $v=2$ vibrational level. In the spontaneous and collision-induced process, 100% and ~30%, respectively, of the available potential energy is converted into translational energy of the products. Such information on the partitioning of energy is required for the better understanding of the nature of the potential surfaces of polyatomic ions. In addition valuable insight into low energy ion–molecule reactions is obtained. For example, thermal velocity collisions of ground state $S^{+\cdot}$ ions with hydrogen could not be reactive. If the relative kinetic energy of approach of the two species were sufficient to allow reaction on thermochemical grounds, once again this would not be expected to occur without prior vibrational excitation of the hydrogen. That is, in order to achieve intimate distances which may allow the formation of an intermediate $H_2S^{+\cdot}$ complex the correct combination of the relative energy of approach and internal energy of hydrogen is required. Such a complex in the form of one of the bound states may dissociate via another unimolecular path to form, for example, HS^+ and $H\cdot$. One would predict a large temperature dependence for such a reaction on the basis of our results.

The experiments with water (and water-d_2) indicate that on collision $H_2O^{+\cdot}$ is electronically excited to a high energy state leading directly to formation of $O^{+\cdot}(^2D$ or $^2p)$ and a vibrationally excited hydrogen molecule. There appear to be two reasons for the absence of a unimolecular reaction in water analogous to that in hydrogen sulfide. First, the bond angle of $H_2O^{+\cdot}$ in the $^2A_1$ state has been estimated[9] as $\sim 180°$. Hence, considerable changes from the most stable geometry would be required for predissociation via the $^4A_2$ state which requires bonded H atoms. Such a transition may be expected to have a low probability. Second, the turning point for HO^+ formation from the $^2A_1$ state lies below the corresponding region for $O^{+\cdot}(^4S)$ formation. Provided the former predissociation is rapid on the metastable time scale ($>10^6$ sec^{-1}) the latter could not compete effectively and no metastable for $O^{+\cdot}(^4S)$ formation would be observed. This also accounts for the predominance of the higher excited states of $O^{+\cdot}$ and the over-all small relative intensity of $O^{+\cdot}$ ions in the mass spectrum of water compared to $S^{+\cdot}$ ions in hydrogen sulfide. The $O^{+\cdot}$ ion comprises 0.7% total ionization in H_2O while $S^{+\cdot}$ constitutes 17% in H_2S.[37]

In summary, we have attempted to show that in small molecules where decomposition via repulsive surfaces can occur, consideration of the kinetic energy released to the fragments can be important. We have also shown how collision-induced dissociation can aid in the interpretation of the unimolecular transitions. Through kinetic energy measurements, information concerning the potential energy surfaces of ions has been obtained.[38]

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[21] See also J. H. Beynon, A. E. Fontaine, and G. R. Lester, Intern. J. Mass. Spectrom. Ion Phys. **8**, 341 (1972).

[22] The term collision-induced metastable is used because the collision occurs in the first field-free region and hence, produces a peak analogous to a unimolecular metastable process. The term used in this connection does not presuppose long lifetimes for the decomposing species.

[23] See, for example, R. G. Cooks, D. W. Setser, K. Jennings, and S. Jones, Intern. J. Mass. Spectrom. Ion Phys. **7**, 493 (1971), and references therein.

[24] This is obtained using 8 keV ions with m/e 34 and an ion-source residence time of 2.5-μsec.[17]

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[27] See G. Herzberg, *Molecular Spectra and Molecular Structure III* (Van Nostrand, Princeton, N.J., 1966), p. 472.

[28] Vibrational excitation to the continuum of the ground state is not considered to make a significant contribution.

[29] This is based on the large Franck–Condon factors for formation of $H_2S^+(^2B_1)$ in the lower vibrational states[8–11] and the value of 10.5 eV [30] for the recombination energy of H_2S^+ (compare ionization potential 10.47 eV).

[30] E. Lindholm, Advan. Chem. Ser. **58**, 1 (1966).

[31] It is possible that some of the kinetic energy Q' lost by the reactant H_2S^+ ion might be transferred to the collision gas. The value of 4.4 eV therefore represents an upper limit to the excitation experienced by the ion but the fact that the same value of Q' was observed for different collision gases suggests that the approximation made here is valid.

[32] The potential surface is quite flat in this region as suggested by the close agreement (~ 1 kcal mole^{-1}) between the value of $\Delta H_f°(S^+)$ obtained from the photoionization of hydrogen sulfide[6] and from other completely independent methods.[33]

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[38] We have also considered these effects in larger molecules in an article to be published.