

# Impact dissociation of molecular ions produced by photoionization of various molecules

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The dissociation of accelerated  $\text{H}_2\text{S}^+$ ,  $\text{CS}_2^+$ ,  $\text{CH}_3\text{I}^+$ , and  $\text{CF}_3\text{I}^+$  molecular ions in collisions with Kr atoms has been investigated with a photoionization mass spectrometer. The initial states of the molecular ions could be specified quite definitely by varying the energy of the monochromatic ionizing photons. Increases in the relative impact-dissociation cross section  $\sigma$  in various parts of the spectrum indicate the presence of rather highly excited molecular ions in the beam. The greatest increase in  $\sigma$  (by a factor of about two) was observed for the  $\text{H}_2\text{S}^+$  and  $\text{CF}_3\text{I}^+$  decays in the regions of the spectra in which these ions are produced in the excited electronic states  $^2A_1$  and  $^2E_{1/2}$ , respectively. The part played by autoionization is noted; this process results in more highly excited states of the initial ions than does the direct excitation mechanism.

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## 1. INTRODUCTION

The use of the dissociation of ions in collisions with atoms to investigate the energy and structural characteristics of molecular and fragmented ions was proposed and developed some time ago<sup>[1-5]</sup> and is now being widely employed.<sup>[6-8]</sup> The continuous improvement of the technique has made it possible to employ the double mass spectrometer and the double-focusing mass spectrometers to investigate a broad class of polyatomic ions, both very simple and complex ones (see, e.g., the review article by three of us<sup>[9]</sup>).

In these studies the excitation energy of the initial ions was set by varying the energy of the electrons used to ionize the molecules or by producing the same ions by ionizing different molecules. In all cases, however, the excitation energy of the initial ions remained to a considerable extent undetermined since electron impact produces a large variety of ions having different vibrational and electronic excitations. The logical way to continue these studies would be to use photoionization to investigate the relation between the excitation of the molecular ions and their impact-dissociation cross section.<sup>[10,11]</sup> The use of photoionization makes it possible accurately to fix the vibronic state of the ions by varying the photon energy. This is the great advantage of this method over the use of electron-impact ionization.

In this paper we present the results of the first detailed study of the impact dissociation of various ions produced in collisions of photons of controlled energy with appropriate molecules and accelerated to 2.7 keV, and draw definite conclusions concerning both the effect of the excitation of the ions on their dissociation cross section and on the mechanisms leading to the production of excited ions.

## 2. EXPERIMENTAL TECHNIQUE

The work was done with a type MKh-1311 mass spectrometer<sup>[12]</sup> using the "Aston-band" method.<sup>[9,13]</sup> The molecular ions were dissociated in the fieldfree region

between the ion source and the magnetic field in the drift tube of the mass-spectrometer analyzer where the target gas (krypton) was admitted at a pressure of  $\sim 10^{-4}$  Torr.

The initial ions were produced by photoionization of  $\text{H}_2\text{S}$ ,  $\text{CS}_2$ ,  $\text{CH}_3\text{I}$ , and  $\text{CF}_3\text{I}$  molecules, a hydrogen discharge tube being used as the ultraviolet source. The wavelength  $\lambda$  of the radiation was varied in the interval  $\sim 90$ -130 nm using a vacuum monochromator with a resolution of 0.5 nm. The investigated substances were admitted into the ionization chamber of the mass-spectrometer ion source through a multichannel glass leak valve. The stability of the krypton pressures and of the pressures of the investigated substances was monitored both with magnetoionization vacuum gages and via the molecular ion currents. In all cases the ions experienced only single collisions with the krypton atoms; this was verified by a special study of the effect of the krypton pressure on the relative dissociation cross sections  $\sigma = I^*/I_M$  of the ions ( $I_M$  is the primary molecular-ion current and  $I^*$  is the secondary ion-fragment current) measured at the maximum of the corresponding peaks on varying  $\lambda$  through 0.5-1 nm.

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

### A. Experiments with $\text{H}_2\text{S}$

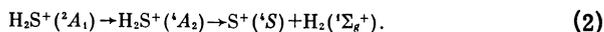
We investigated the following processes for the dissociation of  $\text{H}_2\text{S}^+$  molecular ions:



At photon energies  $E_{ph}$  up to 14 eV the ionization process results in  $\text{H}_2\text{S}^+$  ions in two bound states: the  $^2B_1$  ground state when  $E_{ph} > 10.43$  eV ( $\lambda < 118.9$  nm), and the  $^2A_1$  first excited electronic state when  $E_{ph} > 12.81$  eV ( $\lambda < 98.2$  nm).<sup>[14]</sup> In general, therefore, the  $\text{H}_2\text{S}^+$  ions entering reaction (1) may be excited.

The  $^2A_1$  state can decay spontaneously via two channels: by radiative transitions to the  $^2B_1$  ground state and, at energies above 13.36 eV (reckoned from the

ground state of the molecule), by predissociation via the  ${}^4A_2$  repulsive quartet state according to the scheme<sup>[14]</sup>



Until recently there was considerable difference of opinion regarding the lifetime  $\tau$  of  $\text{H}_2\text{S}^+$  ions in the  ${}^2A_1$  state. According to Dixon *et al.*<sup>[15]</sup> the predissociation times range from  $10^{-6}$  to  $10^{-8}$  sec, depending on the vibrational level. Lifetimes  $\tau$  close to  $5 \times 10^{-6}$  sec have recently been obtained<sup>[16]</sup> for both channels (predissociation and radiation).

Most of our attention in the work was given to process (1a) in which  $\text{S}^+$  ions are produced. The intensity of the  $\text{HS}^+$  ions from process (1b) was measured only in the region  $\lambda \geq 94$  nm since the process



takes place when  $\lambda < 93$  nm and the  $\text{S}^+$  ions produced by this process in the ion source overlap the  $\text{HS}^+$  ions from process (1b), which have the same effective mass.

The results on the  $\lambda$ -dependence of  $\sigma$  for the dissociation of  $\text{H}_2\text{S}^+$  ions via channel (1a) are shown in Fig. 1 (curve a). The behavior of the cross section for production of  $\text{HS}^+$  ions in process (1b) is similar in the indicated wavelength region.

The fact that  $\sigma$  is constant in the initial portion of the spectrum indicates that the  $\text{H}_2\text{S}^+$  ions carry little or no vibrational excitation. In view of the similarity of the equilibrium geometric configurations of the  $\text{H}_2\text{S}^+$  ion ( ${}^2B_1$ ) and the  $\text{H}_2\text{S}$  molecule ( ${}^1A_1$ ),<sup>[15]</sup> the Franck-Condon factors for transitions to higher vibrational levels of the  ${}^2B_1$  state are small and it is mainly the lower levels of the  $\text{H}_2\text{S}^+$  ion that are populated. Hence the peak in  $\sigma$  at  $\lambda \sim 103$  nm (Fig. 1) may be due to an admixture of vibrationally excited  $\text{H}_2\text{S}^+$  ions produced by autoionization of  $\text{H}_2\text{S}$  molecules. Autoionization may also play a definite part in the population of the higher vibrational levels of the  ${}^2B_1$  ground state of the  $\text{H}_2\text{S}^+$  ion in the region  $\lambda < 101.5$  nm, where the sharpest rise of the dissociation cross section is observed. At least this may be the case for the interval  $101.5 < \lambda < 98$  nm. When  $\lambda \leq 98$  nm the  ${}^2A_1$  state (which, as was noted above, has a long lifetime) is excited, and this leads to an increase in  $\sigma$  in that region of the spectrum.

The fact that the radiative lifetime of the  ${}^2A_1$  state is

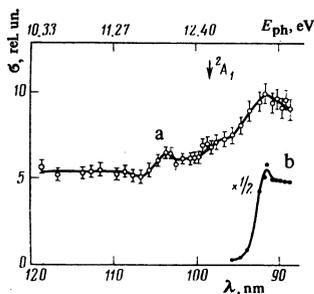


FIG. 1. Relative intensity of  $\text{S}^+$  ions produced in collisions of  $\text{H}_2\text{S}^+$  ions with krypton atoms (curve a) and by spontaneous decay of metastable  $\text{H}_2\text{S}^+$  ions (curve b).

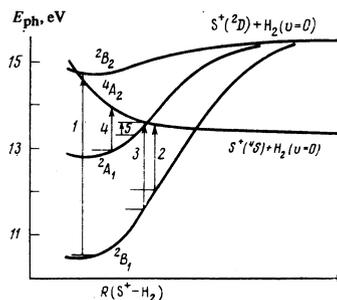
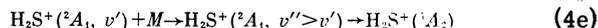
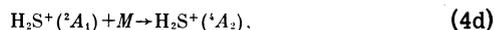
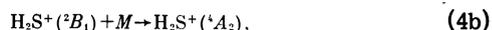


FIG. 2. Dissociative transitions in  $\text{H}_2\text{S}^+$  in collisions with atoms: 1—process (4a), 2—(4b), 3—(4c), 4—(4d), 5—(4e). The potential energy curves were taken from Ref. 17.

close to the characteristic time for collision of an  $\text{H}_2\text{S}^+$  ion with an atom makes it possible to suggest another interpretation of the rise of  $\sigma$  at  $\lambda < 98$  nm, namely, that transitions take place from the  ${}^2A_1$  state to the ground state of the  $\text{H}_2\text{S}^+$  ions ( ${}^2B_1$ ), and indeed to the highest vibrational levels (because of the considerable difference between the geometric configurations). Experiments, which we hope to perform in the future, in which the kinetic-energy distribution of the  $\text{S}^+$  ions from process (1a) is measured, might shed some light on this matter. The region  $\lambda \lesssim 91.5$  nm, where  $\sigma$  is maximal and has some tendency to fall, is of interest. In this region metastable  $\text{H}_2\text{S}^+$  ions are decaying via channel (2) (Fig. 1, curve b) with an intensity that, in our experiments, is comparable with the intensity observed for impact dissociation via channel (1a). The cross section  $\sigma$  for impact dissociation was therefore determined by subtracting the spontaneous component from the relative yield of secondary  $\text{S}^+$  ions.

The following can be said about the mechanism of impact dissociation of  $\text{H}_2\text{S}^+$  ions. It is clear that the increase in  $\sigma$  with increasing energy of the ionizing radiation is associated with the appearance of excited  $\text{H}_2\text{S}^+$  ions in the beam. These, as was indicated above, may be vibrationally excited ions, both in the  ${}^2B_1$  electronic ground state and, when the photon energy exceeds 12.62 eV, in the  ${}^2A_1$  state. From the potential energy curves presented in Fig. 2 we may conclude that the dissociation takes place through the  ${}^4A_2$  repulsive state as the lowest dissociative state for Franck-Condon transitions in excited  $\text{H}_2\text{S}^+$  ions. The following processes leading to population of the  ${}^4A_2$  dissociative state of  $\text{H}_2\text{S}^+$  ions in collisions with target atoms or molecules  $M$  are possible:



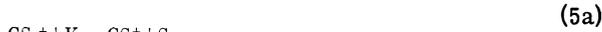
On the basis of data obtained via the ionization of  $\text{H}_2\text{S}$  molecules by electron impact, Jones *et al.*<sup>[18]</sup> conclude that impact dissociation of  $\text{H}_2\text{S}^+$  ions in the  ${}^2B_1$  ground state occurs as a result of an electronic transition to the  ${}^2B_2$  second excited bound state and subsequent predissociation via the  ${}^4A_2$  state, i. e., according to the scheme (4a). However, the  ${}^4A_2$  state can also be reached by direct electronic transitions in process (4b), and also as a result of transitions to the  ${}^2A_1$  first ex-

cited electronic state of the  $\text{H}_2\text{S}^+$  ion at vibrational levels close to the point at which the potential energy curve crosses the curve for the  ${}^4\text{A}_2$  state followed by predissociation, i. e., according to scheme (4c).

Similar processes for the population of the  ${}^4\text{A}_2$  state in collisions with atoms are also available for electronically excited  $\text{H}_2\text{S}^+$  ions in the  ${}^2\text{A}_1$  state (schemes (4d) and (4e)), collision-induced predissociation via scheme (4e) involving vibrational overexcitation of the  $\text{H}_2\text{S}^+$  ion. It is difficult at present to assess the parts played by the several collisional dissociation mechanisms, but to give preference in the case of excited ions to mechanism (4a), which involves an appreciably greater expenditure of energy, would be unfounded.

## B. Experiments with $\text{CS}_2$

The following decays were observed in the impact dissociation spectrum of  $\text{CS}_2^+$



The channel leading to the production of  $\text{CS}^+$  ions is the most intense and was investigated in the experiment. The yield of  $\text{S}^+$  ions was lower by about a factor of two, and the lowest intensity was observed for the  $\text{S}_2^+$  ions.

At photon energies up to 14 eV the  $\text{CS}_2^+$  ion can be produced in the  ${}^2\Pi_g$  ground state, which has two components— ${}^2\Pi_{g1/2}$  (10.07 eV) and  ${}^2\Pi_{g3/2}$  (10.13 eV)—and in the  ${}^2\Pi_u$  excited state (12.58 eV).<sup>[19]</sup> The long-wave part of the spectrum has not been investigated in sufficient detail. We gave most attention to the  $\lambda < 100$  nm ( $E_{\text{ph}} > 12.4$  eV) region (Fig. 3), where intense autoionization processes populate both the  ${}^2\Pi_g$  electronic ground state and the  ${}^2\Pi_u$  excited state.<sup>[20]</sup> The  $\sigma$  vs  $\lambda$  curve has two maxima, whose positions correspond to the two autoionization peaks on the photoionization efficiency curve. The ratio of the partial cross sections for excitation of the  ${}^2\Pi_g$  and  ${}^2\Pi_u$  states of the  $\text{CS}_2^+$  ion is about two (Fig. 3, curve b).<sup>[20]</sup> Despite the fact that the present technique did not enable us to determine the relative part played by vibrational excitation in the  ${}^2\Pi_g$  ground state and the  ${}^2\Pi_u$  vibronic state, high vibrational levels of all electronic states are populated with higher probability, as a rule, in autoionization than in direct ionization; hence the appearance of these maxima seems reasonable. The conclusion drawn by Kim *et al.*<sup>[21]</sup> from their study of collisional dissociation of  $\text{CS}_2^+$  ions produced by electron impact does not seem very convincing. These

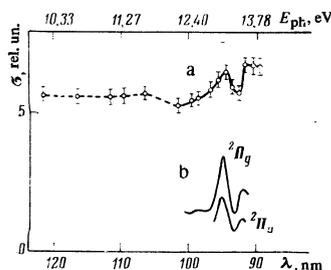


FIG. 3. Cross section for impact dissociation of  $\text{CS}_2^+$  ions vs ionizing photon energy: a— $\sigma$  vs  $\lambda$  for the  $\text{CS}_2^+ + \text{Kr} \rightarrow \text{CS}^+ + \text{S}$  process, b—partial cross sections for excitation of the  ${}^2\Pi_g$  and  ${}^2\Pi_u$  ionic states.

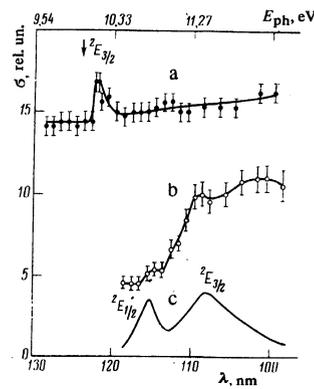


FIG. 4. Impact dissociation cross section of  $\text{CH}_3\text{I}^+$  and  $\text{CF}_3\text{I}^+$  ions vs ionizing photon energy: a— $\sigma$  vs  $\lambda$  for the  $\text{CH}_3\text{I}^+ + \text{Kr} \rightarrow \text{I}^+ + \text{CH}_3$  process, b— $\sigma$  vs  $\lambda$  for the  $\text{CF}_3\text{I}^+ + \text{Kr} \rightarrow \text{CF}_3\text{I}^+ + \text{I}$  process, c—photoelectron spectrum of  $\text{CF}_3\text{I}$  taken at the  $\lambda = 58.4$  nm line.<sup>[24]</sup>

authors based their assumption that the  $\text{CS}_2^+$  ions were not excited on the corresponding photoelectron spectrum taken at the HeI line,<sup>[22]</sup> although it is well known that autoionization, which is capable of yielding highly excited ions, is excluded in that case.

## C. Experiments with $\text{CH}_3\text{I}$

For  $\text{CH}_3\text{I}$  we investigated the most intense decay channel



The  $\sigma$  vs  $\lambda$  curve (Fig. 4, curve a) has only one feature in a narrow region ( $\lambda \sim 122$  nm) somewhat above the second ionization potential (124 nm—the  ${}^2E_{1/2}$  state), where  $\sigma$  has a small sharp peak. There is also a peak on the photoionization efficiency curve at this energy.<sup>[23]</sup> It is reasonable to suppose that the excitation of the  $\text{CH}_3\text{I}^+$  ions that leads to an increase in  $\sigma$  in this case is due to an autoionization process. In general, autoionization is fairly intense on the entire region  $\lambda > 1.22$  nm, but the vibrational excitation communicated in this process to the ion is inconsiderable, and is not enough to appear on the  $\sigma$  vs  $\lambda$  curve. But the production of  $\text{CH}_3\text{I}^+$  ions in the  ${}^2E_{1/2}$  excited state may be responsible for the peak observed on the  $\sigma$  curve.

## D. Experiments with $\text{CF}_3\text{I}$

In the experiment with  $\text{CF}_3\text{I}$  we investigated the decay



The  $\sigma$  vs  $\lambda$  curve was recorded from the ionization potential of  $\text{CF}_3\text{I}$  to  $\lambda \sim 98$  nm (Fig. 4, curve b). A considerable and rapid rise of  $\sigma$  is observed when the energy of the ionizing photons exceeds 11 eV ( $\lambda \sim 113$  nm) and is sufficient for the formation of  $\text{CF}_3\text{I}^+$  in the  ${}^2E_{1/2}$  excited state.

The maximum of  $\sigma$  is reached when  $E_{\text{ph}}$  is roughly equal to the vertical potential for ionization of  $\text{CF}_3\text{I}$  to the  ${}^2E_{1/2}$  state (11.37 eV<sup>[24]</sup>). The observed increase in  $\sigma$  is probably due to the presence of electronically excited  $\text{CF}_3\text{I}^+$  ions in the beam, and this, in turn, depends on the lifetime of the ions in the  ${}^2E_{1/2}$  state, which can be deactivated either by radiative transition to the  ${}^2E_{1/2}$  ground state or by predissociation with

production of the ion fragment  $CF_3^+$ . The latter process becomes energetically possible when the energy of the ionizing photons exceeds the potential for the appearance of  $CF_3^+$  ions in the  $CF_3I$  mass spectrum—10.89 eV ( $\lambda \sim 113.8$  nm).<sup>[25]</sup> The yield of  $CF_3^+$  ions produced in the ion source begins to increase rapidly when  $\lambda \lesssim 111.5$  nm; this has been attributed by Noutary<sup>[25]</sup> to a new dissociation channel. No repulsive state populated by vertical ionization transitions has been observed in this part of the spectrum, so what takes place here is obviously "fast" predissociation of the  $CF_3I^+$  ions from the  ${}^2E_{1/2}$  state. Some of the ions in the  ${}^2E_{1/2}$  state do not manage to decay within the ion source, i. e., they "survive" longer than  $10^{-6}$  sec. This conclusion is confirmed by the results of an experiment that we undertook with the MAT 731 electron-impact mass spectrometer, in which, by extrapolating to zero pressure, we detected the spontaneous decay of metastable  $CF_3I^+$  ions. It is very probable that the metastable state is the  ${}^2E_{1/2}$  state. From this it follows that electronic excitation of the  $CF_3I^+$  ion may contribute to the observed increase in the impact dissociation cross section.

## CONCLUSION

In all the investigated compounds, the increase in the impact dissociation cross section is connected with the population of the first excited electronic state in the initial molecular ions. This connection may be indirect if high vibrational levels of the ground state of the ion are populated in the deactivation of the excited state. The greatest effect was found for  $H_2S^+$  and  $CF_3I^+$  ions and in parts of the spectrum where the energy of the ionizing radiation approaches the dissociative ionization potential of the corresponding molecules. At lower photon energies there are regions in which the  $\sigma$  vs  $\lambda$  curve is not monotonic, owing to the enhanced internal energy of the initial ions. Comparison with the photoionization efficiency curves suggests that such excitation arises in the autoionization process. Since the spectral dependence of the impact dissociation cross section of ions produced by the direct mechanism is monotonic, virtually all of the clearly evident peaks on the  $\sigma$  vs  $\lambda$  curve may be attributed to excitation resulting from autoionization.

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