General and Inorganic Chemistry

Molecular-beam mass spectrometry of van der Waals clusters. Mass spectrum of hydrogen sulfide dimer

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Hydrogen sulfide clusters generated by ultrasonic expansion of an H_2S—Ar mixture into a vacuum were detected by electron impact mass spectrometry. The mass spectrum of the dimer, $(H_2S)_2$, was obtained under conditions of predominant dimerization. A mechanism of the formation of ions that involves intracluster reactions between the fragment ions of the monomer and the monomer molecule has been suggested.

Key words: clusters, intracluster chemical reactions; mass spectrometry, molecular beams.

In the studies of weakly bonded van der Waals complexes particular attention is paid to the formation and dynamics of neutral clusters, while their fragmentation in ionization processes has been studied in only a few experiments. However, the possible fragmentation during the detection of neutral clusters by ionization methods may exert a substantial effect on the ratio between the intensities of neutral and ionic clusters.[1]

To describe the processes that occur during ionization of clusters by electrons (with an energy of 20—100 eV) the following scheme has been suggested.[2] Initially, one of the cluster molecules is rapidly ($\sim 10^{-14}$ s) ionized. The excess energy obtained in this process is liberated through evaporation of monomers or through the occurrence of either monomolecular fragmentation of the cation within the cluster or an intracluster chemical reaction of the cation with one (or several) monomers. This reaction yields a new ion, which can undergo successive reactions with other monomeric molecules within the cluster. In the case of dimers, of interest is the possibility of intricate interaction of fragment ions possessing certain kinetic energies, as the molecular ion decays, with the monomer molecules.

In this work we present the results of a study of the mass spectrum of the positive ions of the hydrogen sulfide dimer obtained using mass spectrometry in combination with time-of-flight separation of the contributions of clusters of various sizes to the intensity of lines in the mass spectrum.

Experimental

The scheme of the experimental unit was described previously.[3] A beam of neutral clusters was generated through supersonic expansion of a mixture of the carrier gas (Ar) with hydrogen sulfide vapor obtained by decomposition of iron(II)

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 839—844, May, 1995.

sulfide by hydrochloric acid. Mass-spectroscopic analysis showed the presence of a minor admixture of carbon dioxide (the intensity of the peak with m/z 44 (CO_2^+) was ~1.5 % of the intensity of the peak corresponding to H_2S^+). Most of the experiments were carried out using a mixture of H_2S (11 %) with argon that was prepared at room temperature in a stainless-steel vessel connected with the admission chamber.

A traditional system for the generation of an supersonic beam, consisting of a nozzle (with a diameter of the hole (d) of 0.12 mm), and a skimmer (with a diameter of the hole of 0.6 mm), was used in the unit. The beam was subjected to ionization by electron impact (the energy of the electrons was 16—100 eV) and was detected using an MS-7303 quadrupole mass spectrometer in the range of 2—200 amu; the flow of ions was detected by a secondary electronic multiplier and an electrometric amplifier. The distance between the hole of the skimmer and the ionization zone was 12.5 cm. The pressure in the admission chamber was 500 Torr. The zones of formation of the beam were pumped by oil diffusion pumps; the analyzer chamber was pumped by a mercury diffusion pump. The steady-state pressure in the nozzle—skimmer chamber was 10^{-5} Torr, that in the analyzer chamber was 10^{-6} Torr.

To decrease the gas flow to the mass spectrometer, pulse inlet was used. A pulse valve (see Ref. 3) opened the hole of the nozzle for ~0.5 ms at regular intervals, with a frequency of 2—4 Hz.

After the electrometric amplification, the signal being detected passed through a KAMAK network of modules connected to an IBM PC/AT computer. The operation of the KAMAK system was synchronized with the operation of the pulse valve. Pulse intensities of mass spectral lines (with tuning to a particular m/z ratio), obtained by integrating the increase in the ionic current over the duration of the pulse, and time profiles of the increase in the ionic current were measured during the experiment. The pulse profiles were recorded using an ADC F4226 instrument, which can store an array of 1024 measurements, the interval between which varies from 10 to 0.4 μs. The most essential frontal part of a pulse that reflects the velocity distribution of particles in a beam was recorded.

Principle of the Method

A beam resulting from adiabatic expansion of a gas mixture contains clusters of various sizes. To obtain information on the fragmentation of neutral clusters during electron impact ionization, one should compare the signals measured for ionic currents with the composition of neutral clusters. This is achieved by using the pulse procedure for recording the profiles of the leading fronts of ionic current pulses for various m/z. Numerous measurements of the time profiles of pulses of the constituents of a molecular beam with experimental conditions varying over wide limits made it possible to conclude that the shapes of pulses for cluster constituents of various masses are essentially different. For the fronts of pulses of heavy particles, "spreading" of shapes appears later and is broadened, due to the effect of "velocity slipping"[4] and the higher translational temperatures for particles of larger masses.

The pulses of ionic currents that contain contributions of various constituents of a beam are superpositions of the ionic currents of the individual components, and, therefore, their shapes quantitatively reflect the compositions of the components. It should be noted that the shape of the leading front of a pulse depends not only on the mass of the cluster component, but also on the pressure and temperature in the bulk of the admission, the diameter of the nozzle hole (d), and the type of carrier gas. The determination of the composition of the cluster components in the ionic current with a particular m/z involves selection of "basic" pulses of individual components for given experimental conditions and the expansion of the pulse measured in terms of these "basic" pulses, *i.e.*, determination of the resolution coefficients. It should be noted that the density pulse of an individual cluster component in the region of the ionizer differs somewhat from the pulse of the ionic current of the same component when it is recorded. However, under the experimental conditions, the change in the shape of the pulse may be neglected. We introduced a correction for the position of the pulse on the time scale, which takes into account the difference between the times of flight of ions with different masses through the region of the quadrupole analyzer. The "basic" shapes of pulses of individual cluster components were determined by gradual dilution of the mixture of the compound under study with an inert gas up to the limiting concentrations at which the shape of the pulse for the two latest measurements was invariable. The selection of ions with particular m/z for the measurement of pulses is an independent task in the investigation of various substances. In the present work, the measurements were carried out using the lines corresponding to parent ions of the monomer, dimer, and trimer; the line with m/z 65 has also been used for the dimer.

Results and Discussion

The effect of the pressure of admission on clusterization. Initially, we studied the variation of the composition of a cluster mixture as a function of experimental conditions. Using these data we chose the conditions under which the mixture consisted of monomers and dimers with only minor admixtures of larger clusters. To determine these conditions, we measured the dependences of the intensities of the parent lines of monomers, dimers, and trimers on the pressure (p_0) in the bulk of admission.

Figure 1 presents the pressure dependences of the ratio between the intensities of the parent line of a cluster and the dominant line of the monomer (m/z 34) for the parent line of the dimer (m/z 68) and the parent line of the trimer (m/z 102). The dependences are plotted on logarithmic coordinates and reflect the power law:[5]

$$\rho_n/\rho_1 = Kp_0^{\alpha(n)},$$

where ρ_n and ρ_1 are densities of the cluster (M_n) and the monomer (M), respectively, resulting from supersonic

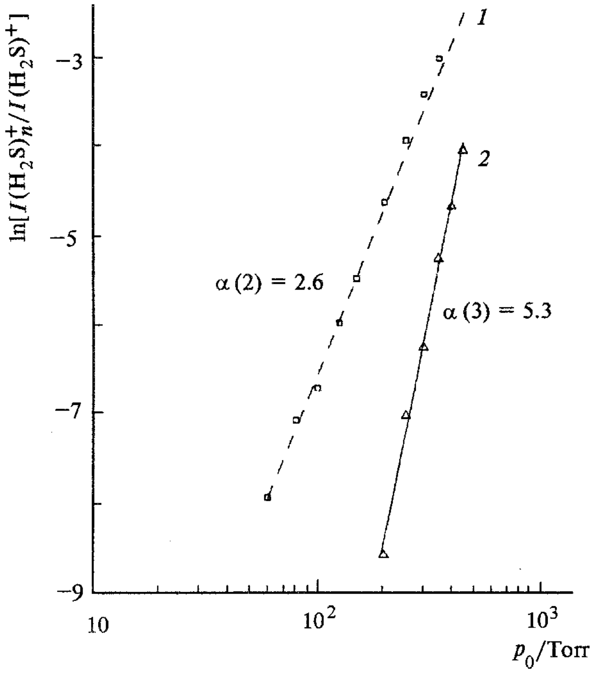

Fig. 1. Dependence of the $\ln[I(H_2S)_n^+/I(H_2S)^+]$ value on the pressure in the bulk of admission for an 11 % H_2S—Ar mixture: *1*, $(H_2S)_2^+$ (*m/z* 68); *2*, $(H_2S)_3^+$ (*m/z* = 102).

expansion; *n* is the number of molecules comprising the cluster; *K* and α(*n*) are constants for a cluster of size *n*. Figure 1 demonstrates that the intensity of the parent line of trimers with *m/z* 102 substantially decreases compared with the intensity of the parent line of the dimers with *m/z* 68 as the pressure decreases, which confirms the view that to obtain a cluster mixture consisting mostly of dimers one should use low pressures. In the region p_0 = 60 to 200 Torr, the exponent of the power dependence for the intensity of the parent line of the dimer was determined as α(2) = 2.6. The α(2) value at low pressures was calculated on the assumption that clusterization in this region is weak and the intensity of the dominant line of the monomer with *m/z* 34 is proportional to the density of the monomer (at least, the most intense "cluster" line with *m/z* 68 is < 1 % of the line with *m/z* 34 at 200 Torr). For the power dependence of the ratio between the intensities of the lines with *m/z* 102 and *m/z* 34 at a pressure of 200 to 450 Torr, the α(3) exponent was found to be 5.3.

A comparison of the α(2) value with the literature data[5] suggests that the line with *m/z* 68 results from ionization of both the dimer and, possibly, the trimer. The α(2) value is close to α_{21} = 2.4 found previously[6] for a mixture of 10 % C_2H_4 with helium. Judging from the general views of nucleation (which is known to initially yield dimers and then higher clusters, all of which appear simultaneously with approximately equal intensities) and based on the experimental fact that at low pressures, lines of heavy clusters are practically missing (the most intense line, *m/z* 102, is < 2 % of the line with *m/z* 68 at 200 Torr), one may conclude that for a mixture of 11 % H_2S with Ar, clusterization occurs at the stage of dimerization at p_0 of 60 to 200 Torr (or, in terms of the p_0d parameter, in the 0.72—2.4 Torr cm region). The intensity of the parent line of the dimer results only from ionization of the dimer itself at 60—200 Torr. In the region of p_0 of 200 to 500 Torr, some increase in the slope of the linear plot for the line with *m/z* 68 is observed, which probably reflects the increase in the contribution of the products of ionization of heavier clusters to this line. However, the deviation of the initial section from the linear extrapolation is small, so that at p_0 < 500 Torr, the greatest contribution to the parent line of the dimer is made by dimers themselves.

The pulse mass spectrum. In the region of *m/z* of 34 to 68 at a pressure of 500 Torr, the pulse mass spectrum, in addition to the argon lines (*m/z* 40 and 36), exhibits intense lines with *m/z* 35 and 64—68. Figure 2 shows the variation of the pulse mass spectrum in the *m/z* 64—68 region with the pressure in the bulk of admission (500 and 250 Torr). The spectrum at p_0 = 250 Torr (the dashed line in Fig. 2) was obtained by normalization of the intensity of the line with *m/z* 65. An analysis of the fronts of pulses of the line with *m/z* 65 for a mixture of 11 % H_2S with Ar and of the line with *m/z* 68 for a mixture highly diluted with inert gas (the signals of the parent lines of trimers with *m/z* 102 and of heavier clusters disappear on dilution) makes it possible to argue that the line with *m/z* 65 is free from contributions of trimers or heavier clusters and is purely a "dimer" line. Figure 3 demonstrates that the shape of the pulse front of the line with *m/z* 65 (curve *1*) corresponds

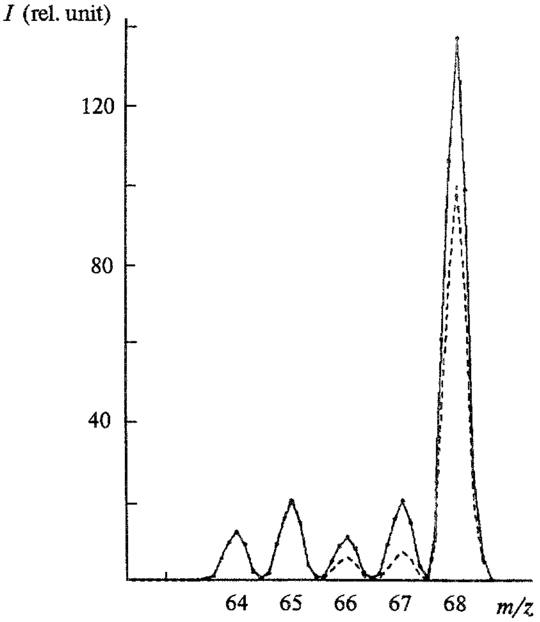

Fig. 2. Variation of the pulse mass spectrum of the dominant lines of the hydrogen sulfide dimer with decreasing pressure in the bulk of admission from 500 Torr (solid line) to 250 Torr (dashed line).

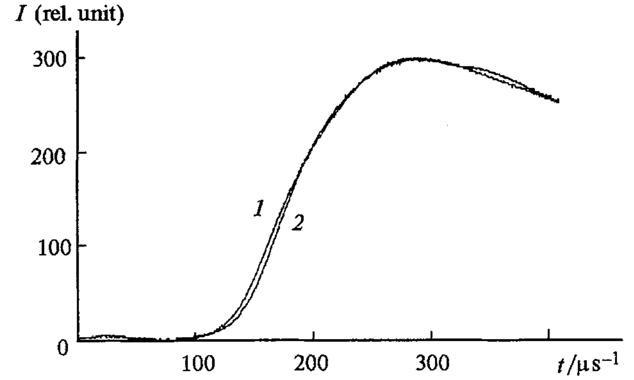

Fig. 3. Profiles of the pulses of mass spectral lines measured in an H_2S/Ar beam (p_0 = 300 Torr): *1*, *m/z* 65 (HS_2^+) for an 11 % H_2S—Ar mixture; *2*, *m/z* 68 ($(H_2S)_2^+$) for 2 % H_2S—Ar.

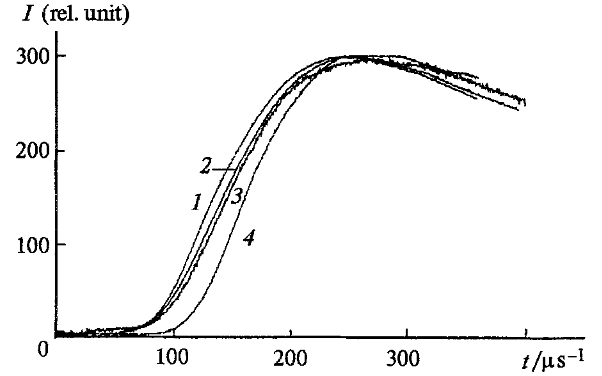

Fig. 4. Profiles of the pulses of some dominant mass spectral lines of hydrogen sulfide dimer $(H_2S)_2^+$ (*1—3*), measured in an H_2S/Ar beam, for an 11 % H_2S—Ar mixture and of the parent line of the trimer $(H_2S)_3^+$ (*4*) for a dilute H_2S—Ar mixture (p_0 = 300 Torr): *1*, *m/z* 65; *2*, *m/z* 66; *3*, *m/z* 67; *4* — *m/z* 102.

to the shape of the front of the line with *m/z* 68 for a very dilute mixture (curve *2*). The slight displacement of the curves is due to the difference between the times of flight of the ions through the mass analyzer. A comparative analysis of the spectra (see Fig. 2) makes it possible to conclude, first, that the lines with *m/z* 68, 67, and 66 at p_0 = 500 Torr are due not only to ionization of the dimer but also to the fragment ions derived from heavier clusters and, second, that the line with *m/z* 64, like the line with *m/z* 65, contains practically no contribution from clusters with greater masses than the dimer.

The mass spectrum of the dimer; resolution of the fronts of pulses of individual lines. The pulse mass spectrum obtained at 250 Torr (*i.e.*, at the pressure that corresponds to the beginning of the formation of clusters heavier than dimers) in the *m/z* 64—68 range was compared with the mass spectrum of the $(H_2S)_2$ dimer obtained by resolution of the curves of the fronts of individual lines measured at 300 Torr using the shapes of the fronts of the dimer and trimer. The $I(m/z\ 68) : I(m/z\ 67) : I(m/z\ 66) : I(m/z\ 65) : I(m/z\ 64)$ ratios between the intensities of the lines are 100 : 7.3 : 6 : 21 : 13, and good correlation with the mass spectrum of the dimer is observed for the *m/z* 65 and *m/z* 64 lines: $I_d(m/z\ 68) : I_d(m/z\ 67) : I_d(m/z\ 66) : I_d(m/z\ 65) : I_d(m/z\ 64)$ = 100 : 6 : 5.1 : 21 : 13. The comparison indicates that at p_0 = 250 Torr, clusters heavier than dimers make no contribution to the line with *m/z* 68 but contribute to the lines with *m/z* 67 and 66. Examples of the fronts of pulses of lines with *m/z* 67 and 66 for which resolution was carried out, together with the fronts of the "basic" dimer and trimer pulses, are presented in Fig. 4. The difference between times of flight of ions through the analyzer has been taken into account.

At p_0 = 500 Torr, resolution of the fronts of pulses of the mass spectral lines corresponding to the dominant lines of the monomer, *m/z* 34 (H_2S^+), 33 (HS^+), 32 (S^+), and 35 ($H^{34}S^+$, $H_2{}^{33}S^+$), was carried out. No contributions from the dimer fragments were detected for the lines with *m/z* 34, 33, and 32, whereas the line with *m/z* 35 is caused to a large extent by fragmentation of the dimer, which clearly indicates that the H_3S^+ ion (*m/z* 35) is manifested in the spectrum of the dimer.

The shape of the front of the line with *m/z* 35 and also the "basic" fronts of the monomer, dimer, and trimer lines (*m/z* 34, 68, and 102, respectively) used for the resolution at p_0 = 300 Torr are presented in Fig. 5. The intensity of the fragment ion with *m/z* 35 obtained from the coefficients of resolution of the pulse shape is maximum in the spectrum of the dimer.

Table 1 presents the mass spectrum of the hydrogen sulfide dimer and the contributions of the dimer to the intensities of lines at p_0 = 300 Torr obtained by the resolution of fronts. The absence of dimer fragments with *m/z* 34, 33, and 32 indicates that the complex process of ionization involves no evaporation of neutral monomeric units from the cluster ions, which has been observed in electron impact ionization of benzene[7] and ammonia dimers.[1] An analysis of the spectrum of the

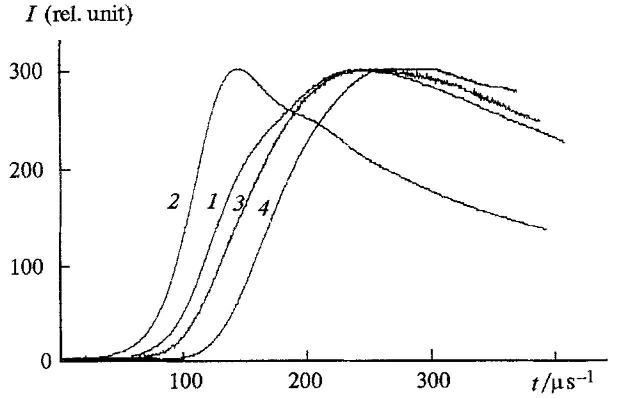

Fig. 5. Profiles of the pulse of the line of the hydrogen sulfide dimer (*1*) for an 11 % H_2S—Ar mixture and of the parent lines of the monomer (*2*), dimer (*3*), and trimer (*4*) for dilute H_2S—Ar mixtures (p_0 = 300 Torr): *1*, *m/z* 35 (H_3S^+); *2*, *m/z* 34 (H_2S^+); *3*, *m/z* 68 ($(H_2S)_2^+$); *4*, *m/z* 102 ($(H_2S)_3^+$).

Table 1. Dominant lines of the mass spectrum of the hydrogen sulfide dimer and contribution of the dimer to their intensities at p = 300 Torr (E = 70 eV)

Ion	H_3S^+	$(H_2S)_2^+$	HS_2^+	S_2^+	$H_3S_2^+$	$H_2S_2^+$
m/z	35	68	65	64	67	66
I_{rel} (%)	100	85	18	11	5.1	4.3
Contribution of the dimer (%)	66*	97	~100	~100	66	75

* A 28 % contribution to the line with m/z 35 is made by the isotope-containing ions $H^{34}S^+$ and $H_2{}^{33}S$, derived from the monomer.

dimer (see Table 1) indicates that the proportion of fragmentation (*i.e.*, processes involving cleavage of chemical bonds) in the ionized dimer is lower than that in the ionized monomer (the ratio between the intensities of ions, $I[H_2S^+ \cdot H_2S]$: $I[S^+ \cdot H_2S]$: $I[HS^+ \cdot H_2S]$ = 100 : 4.3 : 5.1, differs substantially from the $I[H_2S^+]$: $I[S^+]$: $I[HS^+]$ ratio, equal to 100 : 44 : 42, in the spectrum of the monomer[8]). Fragmentation of the $[(H_2S)_2{}^+]$ cluster ion with excessive internal energy probably does not result in the final stabilization, as $[HS^+ \cdot (H_2S)]$ and $[S^+ \cdot (H_2S)]$ ions are formed. This is indirectly indicated by the contribution of the clusters heavier than dimers to the intensity of lines with m/z 67 and 66 (see Table 1), since these ions, $[HS^+ \cdot (H_2S)_{n-1}]$ and $[S^+ \cdot (H_2S)_{n-1}]$ (Fig. 6), are also not entirely stabilized and undergo evaporation of monomers, thus contributing significantly to the formation of the ions with m/z 67 and 66. The absence of final stabilization may promote the occurrence of intracluster reactions in the $[HS^+ \cdot (H_2S)]$ and $[S^+ \cdot (H_2S)]$ systems.

Analysis of the pulse spectrum in the regions of the dominant lines of the dimer, tetramer, and pentamer (see Fig. 6) suggests that the schemes of intracluster transformations of tetramers and pentamers are similar to that of dimers. This is indicated by the presence of lines corresponding to $[H_3S^+ \cdot (H_2S)_{n-2}]$ ions (not shown in Fig. 5), whose intensity is comparable to that of lines with m/z corresponding to the formula $[HS_2{}^+ \cdot (H_2S)_{n-2}]$ and is only lower than the intensity of the lines of parent ions.

The following main ion-molecular reactions occurring between the H_2S^+, HS^+, and S^+ ions and the H_2S molecule have been reported[9] and studied for low (<0.1 eV) energies of the primary ions (the channels with sections of the processes with σ > 0.2 Å^2 are shown).

$$H_2S^+ + H_2S \longrightarrow H_3S^+ + HS, \quad m/z\ 35,\ \sigma = 5.8\ \text{Å}^2 \tag{1}$$

$$HS^+ + H_2S \;\begin{cases} \longrightarrow H_3S^+ + S, & m/z\ 35,\ \sigma = 2.7\ \text{Å}^2 \\ \longrightarrow HS_2{}^+ + H_2, & m/z\ 65,\ \sigma = 0.6\ \text{Å}^2 \end{cases} \tag{2}$$

$$S^+ + H_2S \;\begin{cases} \longrightarrow S_2{}^+ + H_2, & m/z\ 64,\ \sigma = 2.4\ \text{Å}^2 \\ \longrightarrow HS_2{}^+ + H, & m/z\ 65,\ \sigma = 0.6\ \text{Å}^2 \end{cases} \tag{3}$$

By analogy with the ion-molecular reactions, one may assume that intracluster reactions occur in the $[HS^+ \cdot (H_2S)_{n-1}]$ and $[S^+ \cdot (H_2S)_{n-1}]$ systems formed after the first act of fragmentation of the molecular ion. Reactions like (2) and (3) yield $[HS_2{}^+ \cdot (H_2S)_{n-2-k}]$ and $[S_2{}^+ \cdot (H_2S)_{n-2-k}]$ ions, where k is the number of H_2S molecules evaporated.

The occurrence of intracluster protonation to give $[H_3S^+ \cdot (H_2S)_{n-2-k}]$ ions according to a type (1) reaction was confirmed by an experiment carried out at a reduced (to 16 eV) energy of the ionizing electrons and at p_0 = 500 Torr of the admission bulk. In the pulse

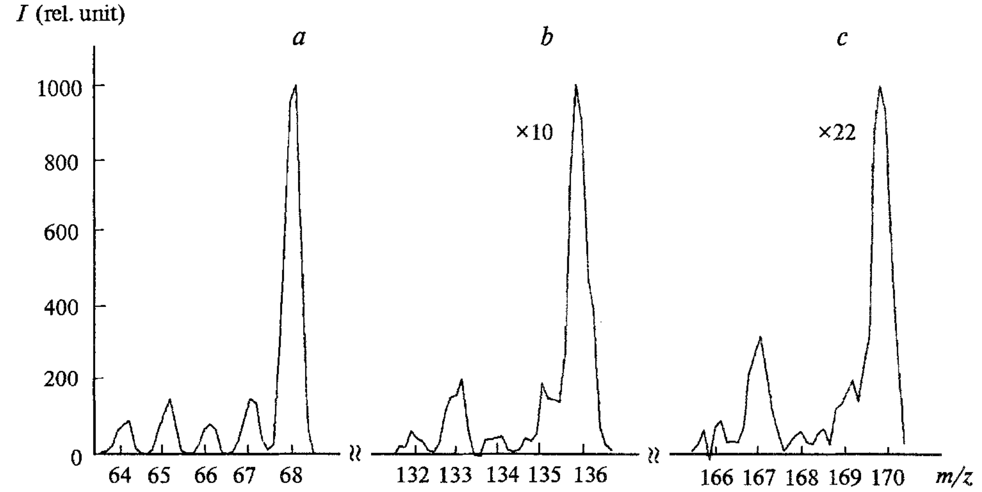

Fig. 6. Pulse mass spectrum of the dominant lines of the dimer (a), tetramer (b), and pentamer (c) in the regions of mass numbers of the parent ions for an 11 % H_2S—Ar mixture at p_0 = 500 Torr in the admission bulk.

mass spectrum, the lines with *m/z* 68 and 35 were the dominant lines (the ratio between their intensities was 100 : 17). The greatest contribution to these lines is probably made by dimers, since at E = 16 eV, the smaller amount of excess energy should result in less pronounced fragmentation of clusters. The lines with *m/z* 67 and 66, corresponding to the primary ionic fragments $[HS^+ \cdot H_2S]$ and $[S^+ \cdot H_2S]$, whose intracluster transformations occur according to pathways (2) and (3) (see the above-presented scheme), are practically missing. Thus, the appearance of the H_3S^+ ion (*m/z* 35) corresponds to the occurrence of a type (1) intracluster reaction. It should be noted that stabilization of the $[H_2S^+ \cdot H_2S]$ ion produced by electron impact (E = 16 eV) is much more probable than its intracluster transformations.

To sum up the foregoing, we can assume the following mechanism of the ionization of the hydrogen sulfide dimer. The excess energy obtained in the primary ionization of an H_2S molecule with a cation is probably released due to two main processes: monomolecular fragmentation of the cation within the dimer without evaporation of the monomer and chemical reactions of the cation with the monomer and of the fragment ions with the monomer within the cluster.

The work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 93-03-4933). The authors are also grateful to the European Environmental Research Organisation (EERO) for support.

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Received October 25, 1994