Study of small benzene clusters by pulse molecular beam mass spectrometry

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A simple method for separating contributions of different-sized clusters formed in a pulse supersonic beam to a mass-spectral signal has been suggested. The method is based on the analysis of time pulse profiles measured for different ions of the beam and makes it possible to calculate mass spectra of small clusters. The electron impact mass spectrum of the benzene dimer has been obtained and analyzed in the framework of the concept of intracluster ion-molecular chemistry.

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

Van der Waals clusters are of interest as models of an intermediate state between the gas and solid states. The study of their properties makes it possible to better understand the mechanism of several phenomena (crystal growth, formation of aerosols, *etc.*). The study of the interaction between molecules inside clusters also can form a missing link connecting gas-phase bimolecular reactions and the chemistry of solutions.[1] Small van der Waals benzene complexes have been studied previously by various methods: deflection of a molecular beam in an electric field,[2] IR[3—5] and UV spectroscopy,[6] electron diffraction,[7] and multiphoton ionization combined with time-of-flight mass spectrometry.[8—12] Homogeneous condensation of benzene vapor in a supersonic molecular beam is usually used for the generation of clusters, and a mass spectrometer is most frequently used as the detector. In these experiments, the condensation results in a set of clusters of different sizes, and it is difficult to separate signals of particles of a certain size by any method of detection. It is difficult to identify particles in the beam due to the possible superposition of residual ions formed by the fragmentation of heavy clusters into molecular ions of lighter clusters. At present, only time-of-flight mass spectrometry with multiphoton dichromatic ionization makes it possible to identify components of a cluster mixture assigned to particular lines of the absorption spectrum. The absorption spectra of the benzene dimer $(C_6H_6)_2$[8] and the excitation spectra of $(C_6H_6)_2$[9a], $(C_6H_6)_3$,[9b] and $(C_6H_6)_n$ (n = 2— 4)[10] have been obtained and the bond energies and ionization potentials of neutral and ionic clusters $(C_6H_6)_n$ (n = 1—5)[12] have been determined by this method. When the traditional method of ionization is used, the data of electron impact mass spectra for clusters of a certain size are necessary to determine the composition of clusters and to select the experimental conditions for studying clusters of a certain size.

The purpose of this work is to develop a method for determining the contributions of different-sized clusters to the intensity of mass-spectral lines and to calculate the mass spectra of small benzene clusters.

Experimental

The installation was described in detail in Ref. 13. Clusters are formed in a supersonic beam when a mixture of benzene vapor and a carrier-gas expands. A gas mixture with benzene vapor saturated at 20 °C was prepared in a glass flask attached to the chamber of the beam source. The traditional system for beam formation, consisting of a nozzle with a hole 0.12 mm in diameter, and a separator with a hole 0.6 mm in diameter was used in the installation. An MS 7303 quadrupole mass spectrometer was used as the detector. The energy of ionizing electrons was usually 70 eV. The separator and the ion source of the mass spectrometer were separated by a diaphragm 3 mm in diameter. The distance between the hole of the separator and the ionization zone was 12.5 cm. The system of differential evacuation consisted of two diffusion oil pumps for evacuation of the zones of beam formation and a diffusion mercury pump for evacuation of the chamber of the analyzer. The stationary pressures in the nozzle—separator and analyzer chambers were 10^{-5} and 10^{-6} Torr, respectively.

A previously described[13] system of pulse input was used to decrease the total gas flow to the mass spectrometer. The time of the open state of the valve was ~500 μs, and the pulse frequency was ~2—4 Hz. The system for registering the ion current included a secondary-electron multiplier, an electrometric amplifier, and a set of KAMAK modules connected with a controlling computation complex based on an IBM PC/AT. The ion current was measured by the system of KAMAK units and synchronized with the work of the pulse valve. Pulse profiles were measured by an F4226 ADC, which stored a total of 1024 measurements at intervals from 10 to 0.4 μs.

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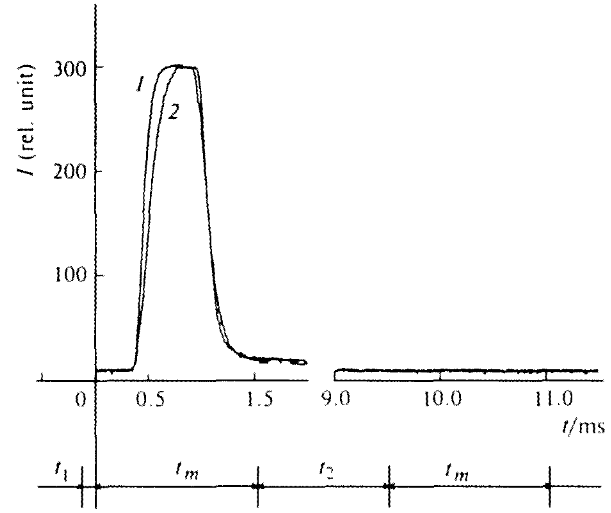

Fig. 1. Pulse profiles for the mass-spectral line of the carrier-gas (argon, m/z 40) at pressures in the chamber of the beam source p = 500 (*1*) and 100 (*2*) Torr for a 7 % mixture of C_6H_6 in argon. Pulses are normalized at the points of the maximum intensity.

The characteristic pulses for the carrier-gas Ar at the pressures in the beam source p = 100 and 500 Torr are presented in Fig. 1. The delay between opening of the valve and the beginning of measurements t_1 was 100 μs, and time resolution was 10 μs. The same conditions were used for measuring the mass spectra of the pulse beam. The intensity of the pulse beam was calculated as the difference between the sum of the measurements of ADC during the whole period (t_m) of the open state of the valve and the sum of the measurements of ADC during the same time period t_m after the delay (t_2 = 8 ms) following closing of the valve when the signal achieved a stationary background level. The detailed shapes of the pulse profiles were measured with a time resolution of 0.4 μs at t_1 = 350—500 μs. When pulse profiles measured for different masses of ions were compared, a correction to the flight time of ions in the zone of the quadrupole analyzer was introduced.

Results and Discussion

Electron impact mass spectra of the cluster beam. Electron impact mass spectra of the supersonic beam of a 5 % C_6H_6/argon mixture were recorded at pressures from 100 to 600 Torr in the chamber of the beam source. In the latter case, ions with masses up to the five times the mass of benzene were detected.

The mass spectrum obtained using rough measurements, at p = 600 Torr in the range of weights from 24 to 230 a.m.u. is presented in Fig. 2. The results of more detailed measurements in the range of the most intense lines is shown in Fig. 3.

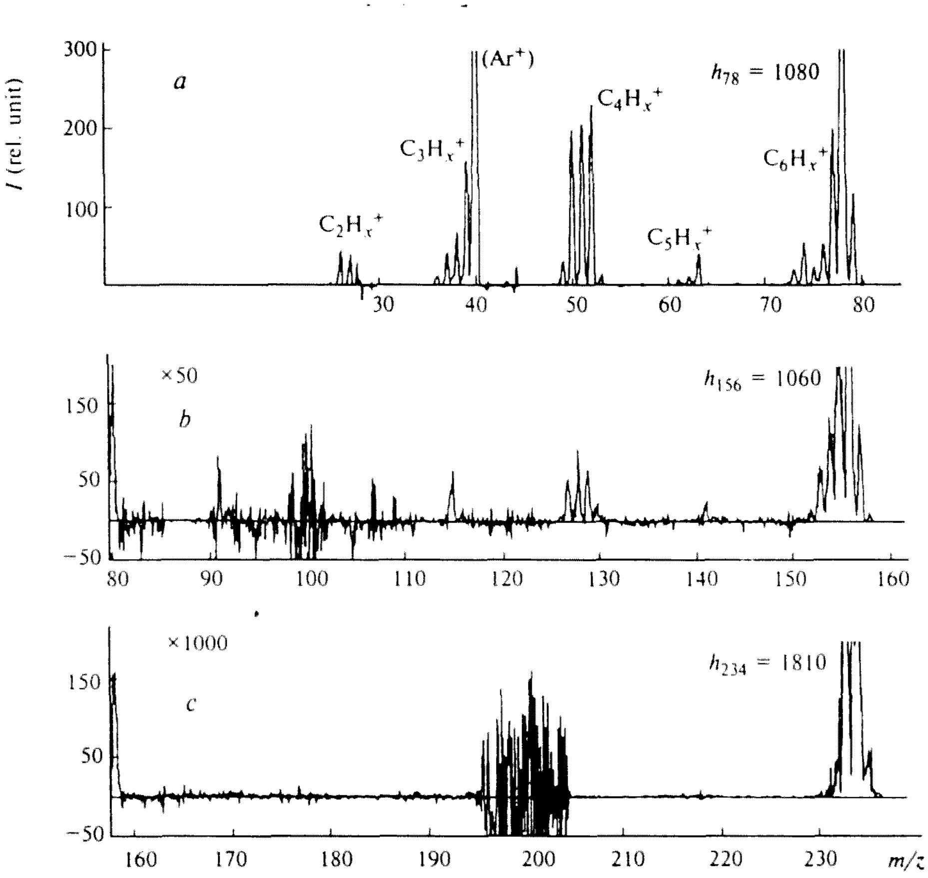

Fig. 2. Electron impact mass spectrum of the pulse beam for a 5 % mixture of C_6H_6 in argon at p = 600 Torr in ranges of m/z from 24 to 80 (*a*), 80 to 158 (*b*), and 158 to 236 (*c*).

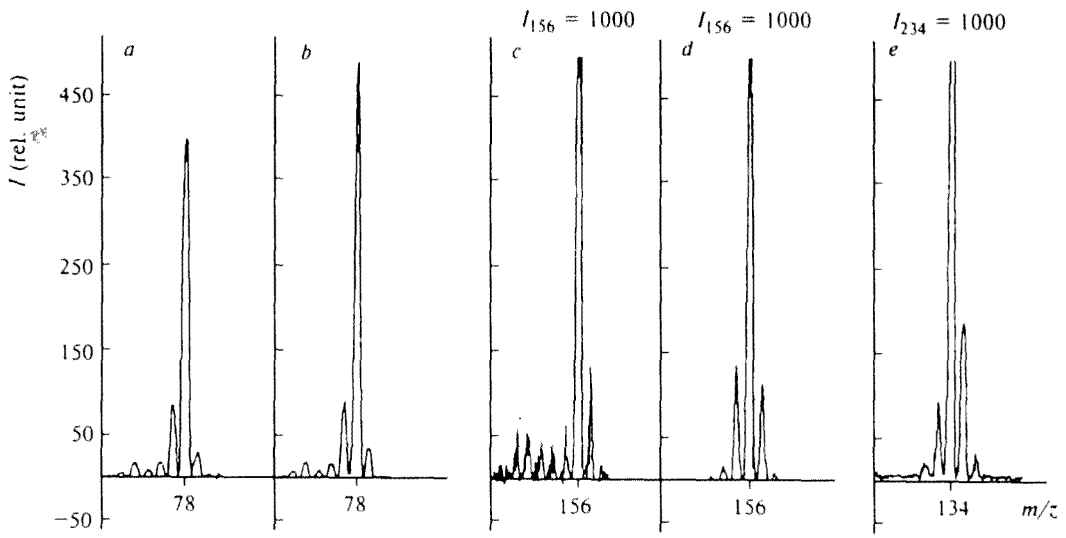

Fig. 3. Groups of peaks located near peaks of main cluster ions $(C_6H_6)_n{}^+ = (C_6H_6)_n{}^+$ (n = 1, 2, 3). p, Torr: 100 (*a*, *c*); 500 (*b*, *d*, *e*).

Figure 2 shows the spectra of three regions located by the shift in the value corresponding to the molecular weight of benzene M = 78. The spectrum in the upper part of Fig. 2 is similar to that of the monomer and contains groups of peaks assigned to ions of the composition $C_6H_x{}^+$, $C_5H_x{}^+$, $C_4H_x{}^+$, $C_3H_x{}^+$, and $C_2H_x{}^+$. In the range of higher mass numbers, peaks of $(C_6H_6)_2{}^+$ (m/z 156), $(C_6H_6)_3{}^+$ (m/z 234), $(C_6H_6)_4{}^+$ (m/z 312), and $(C_6H_6)_5{}^+$ (m/z 390) are observed as well as the adjacent peaks corresponding to the loss of hydrogen atoms from these ions. The ratio of the heights of the peaks of the main lines is the following: $h_{78} : h_{156} : h_{234} : h_{312} : h_{390}$ = 1000 : 20 : 1.8 : 1.5 : 1.0.

The presence of the intense background lines in the m/z 100 and m/z 200 range (groups of isotopic peaks of Hg^{++} and Hg^+) prevents the detection of cluster ions. The area of maximum noise (M = 198—204) creates a blank for measuring fragmentary ions of the composition $(C_6H_6)_2C_3H_6{}^+$—$(C_6H_6)_2C_4{}^+$; however, the appearance of ions of this type is highly improbable.

The change in the intensity of the peaks as the pressure decreases to p = 100 Torr, at which it can be assumed the main components of the beam are monomers and dimers, is evidence for considerable fragmentation of the heavy clusters (Fig. 3).

The peaks with m/z 91, 115, 127—130, and 141 cannot be assigned to residual ions of the dimer due to the possible fragmentation of the heavier clusters. To determine the contribution of the dimers, the contributions of different clusters to the signals of the residual ions must be determined.

Pulse profiles. Numerous measurements of time profiles of the pulses of components of the molecular beam under various experimental conditions show that the shape of the pulse depends substantially on both the size of the cluster and the type of carrier-gas as well as on the pressure in the beam source and the diameter of the nozzle. These dependences can be explained in terms of the Kantrovits—Gray rate distribution for supersonic beams.[14] The frontal regions of the normalized pulses for the lines with m/z 40 (Ar^+), m/z 78, 156, 234, 312, and 390 at the time resolution of 0.4 μs are presented in Fig. 4. The pressure in the beam source was 300 Torr, and the temperature in the source was insignificantly increased, which made it possible to obtain a gas mixture with a concentration of ~30 %. Each curve was obtained by averaging 20 to 100 pulses, depending on the absolute value of the signal. The progressively higher temperature and the effect of rate slipping typical of heavy particles in a supersonic beam[14] result in an increase in the time for achieving an ionization zone and greater blurring of the pulse density for heavier particles. Only the pulse for m/z 40 (Fig. 4) reflects the rate distribution of argon atoms, while the other pulses are complex curves reflecting along with the rest of the fragmentation of clusters the fact that their behavior shows only a general tendency to change shape at various masses.

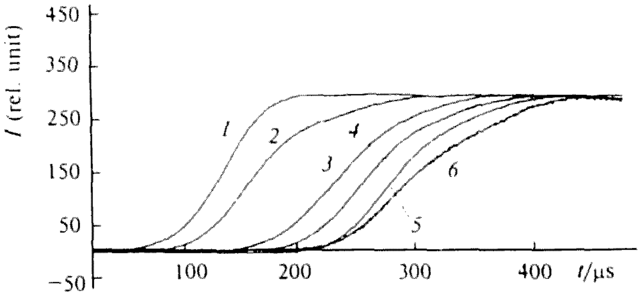

Fig. 4. Pulse profiles for the main mass-spectral lines for a beam of C_6H_6 in argon (30 % C_6H_6 in argon; p = 300 Torr). m/z: 40 [Ar^+] (*1*); 78 [$(C_6H_6)^+$] (*2*); 156 [$(C_6H_6)_2{}^+$] (*3*); 234 [$(C_6H_6)_3{}^+$] (*4*); 312 [$(C_6H_6)_4{}^+$] (*5*); and 390 [$(C_6H_6)_5{}^+$] (*6*).

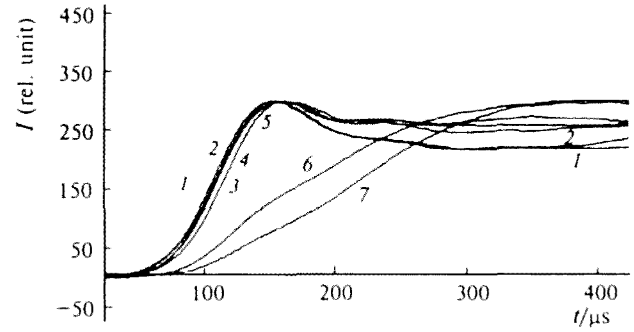

Fig. 5. Pulse profiles for lines of the group of ions $C_6H_x^+$ for a beam of C_6H_6 in argon (5 % mixture of C_6H_6 in argon; p = 300 Torr). 73 (*1*); 74 (*2*); 75 (*3*); 76 (*4*); 77 (*5*); 78 (*6*); and 79 (*7*).

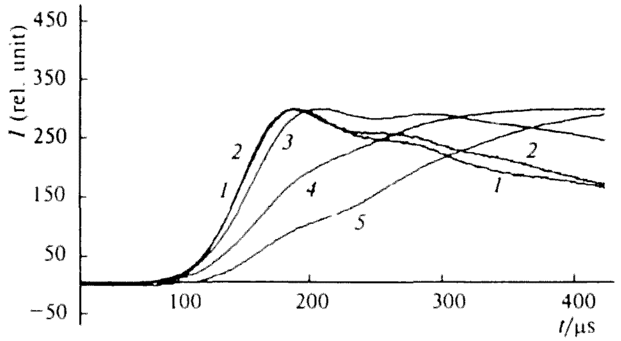

Fig. 6. Pulse profiles for lines with m/z 49 for a 5 % mixture of C_6H_6 in argon (*1*) and m/z 78 ($C_6H_6^+$) (*2—5*) at various concentrations of the gas mixture of C_6H_6 in argon in the chamber of the beam source (%): 0.2 (*2*); 0.5 (*3*); 3.5 (*4*); and 7 (*5*).

The analysis of the shapes of the pulses measured for the mass-spectral peaks of the $C_6H_x^+$ ions in the 5 % mixture of C_6H_6 in argon at p = 300 Torr (Fig. 5) shows that fragmentary ions of heavy clusters also make a considerable contribution to the signals of the molecular (m/z 78) and isotopic (m/z 79) ions. At the same time, the lines of the ions with m/z 75—77 are mainly caused by monomers, with a small contribution due to the fragmentation of clusters.

For quantitative analysis, it is necessary to determine the "basic" pulse profiles for monomers, dimers, and larger clusters under certain conditions of the formation of the molecular beam and then to use them for modeling the constituent (due to fragmentation processes) profiles. To obtain the "basic" pulse, C_6H_6/argon mixtures strongly diluted with argon, which should produce beams with a low degree of condensation, were used. The profiles for m/z 78 ($C_6H_6^+$) at various concentrations of benzene in argon in a range from 0.2 to 7 % are shown in Fig. 6 (p = 300 Torr). Decreasing the concentration made it possible to obtain profiles with a decrease in the "cluster" effect. The profile for the peak with m/z 78 (*2*) measured at a benzene concentration of 0.2 % is close to the profile for the peak with m/z 49 (*1*) at a concentration of 7 % (Fig. 6), which indicates the possibility of measuring the "basic" profile of the monomer pulse on the line with m/z 49. Testing all fairly intense lines in the range of m/z from 24 to 79 (see the first column in Table 1) made it possible to establish that

Table 1. Mass spectrum of the benzene dimer (n = 2)

Mass	Ion	Neutral fragment	Intensity (%)			Mass	Ion	Intensity
			$n = 1$[15]	$n = 1$*	$n = 2$*			
26	$C_2H_2^+$	C_4H_4	3.4	2.8	0.7	104	$C_8H_8^+$	No pulse
37	C_3H^+	C_3H_5	4.1	3.0	0.2	115	$C_9H_7^+$	2.5
38	$C_3H_2^+$	C_3H_4	5.8	11.0	0.9	116	$C_9H_8^+$	No pulse
49	C_4H^+	C_2H_5	2.5	2.6	<0.1	127	$C_{10}H_7^+$	1.1
50	$C_4H_2^+$	C_2H_4	15.7	16.0	3.0	128	$C_{10}H_8^+$	1.8
51	$C_4H_3^+$	C_2H_3	18.6	17.0	7.7	129	$C_{10}H_9^+$	0.8
52	$C_4H_4^+$	C_2H_2	19.4	18.0	6.8	130	$C_{10}H_{10}^+$	0.3
63	$C_5H_3^+$	CH_3	2.8	2.7	1.5	141	$C_{11}H_9^+$	0.3
73	C_6H^+	5 H	1.5	—	<0.1	151	$C_{12}H_7^+$	1.2
74	$C_6H_2^+$	4 H	4.6	5.0	<0.1	152	$C_{12}H_8^+$	4.2
75	$C_6H_3^+$	3 H	1.6	1.5	0.1	153	$C_{12}H_9^+$	3.6
76	$C_6H_4^+$	2 H	6.0	5.7	1.2	154	$C_{12}H_{10}^+$	3.1
77	$C_6H_5^+$	H	14.4	19.0	7.8	155	$C_{12}H_{11}^+$	11.4
78	$C_6H_6^+$		100.0	100.0	100.0	156	$C_{12}H_{12}^+$	100.0
79	${}^{i}C_6H_7^+$		6.4	6.5	6.4**	157	${}^{i}C_{12}H_{12}^+$	12.9
79	$C_6H_7^+$				4.4**	158	${}^{2i}C_{12}H_{12}^+$	1.6

Note. Each row of Table 1 corresponds to a neutral fragment of a certain mass. The left part of Table 1 contains the data for ions with masses lower than 79, intensities are normalized to the line with m/z 78; for lines with m/z > 79, intensities are normalized to the line with m/z 156. *i* means components containing the isotope ^{13}C.

* The data are the average values of three to seven experimental series, in which mixtures of C_6H_6 in argon with concentrations from 0.2 to 30 % were used at p = 300 Torr.

** The values were estimated from the total value I_{79} = 10.8 %.

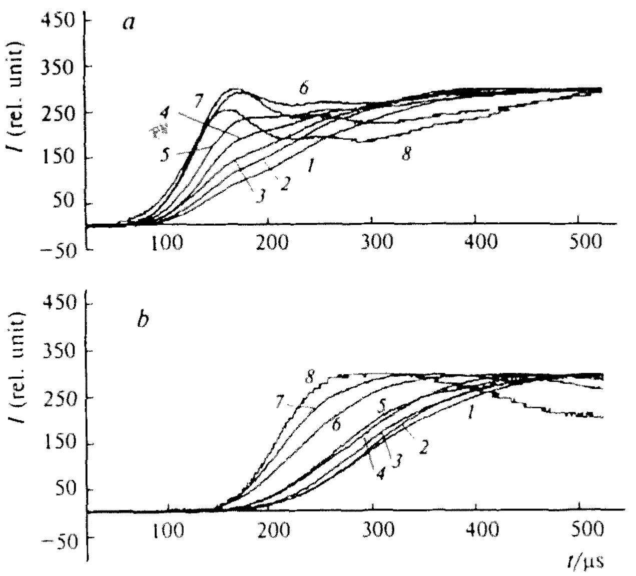

Fig. 7. Dependences of the pulse shape on the energy of ionizing electrons (E_e) for lines of ions with m/z 78 ($C_6H_6^+$) (*a*) (5 % mixture of C_6H_6 in argon; p = 500 Torr) and m/z 156 [$(C_6H_6)_2^+$] (*b*) (3 % mixture of C_6H_6 in argon; p = 500 Torr). E_e/eV: 70 (*1*); 55 (*2*); 45 (*3*); 35 (*4*); 30 (*5*); 25 (*6*); 20 (*7*); and 15 (*8*).

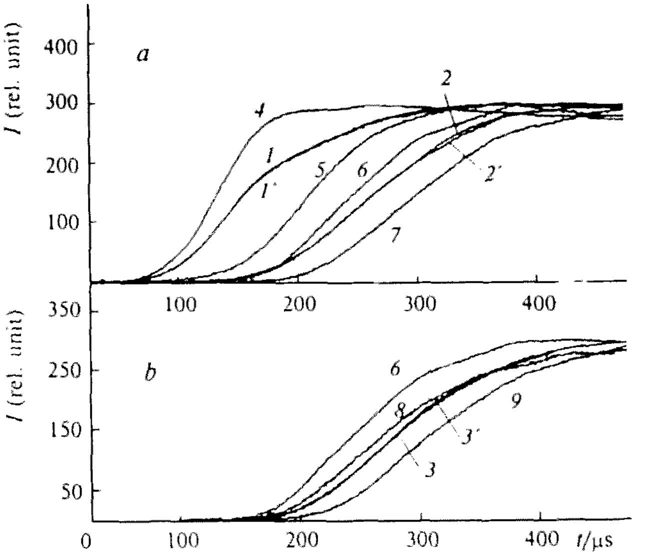

Fig. 8. Monomeric and individual cluster components of complex profiles for lines with m/z 78 (curve *1*), 156 (curve *2*) (*a*), and 234 (curve *3*) (*b*). Basic profiles, m/z: 49 (*4*); 156 (*5*); 234 (*6*); 312 (*7*, *8*); and 390 (*9*). E_e = 70 eV (*1—4*, *7*, and *9*), 15 eV (*5*, *6*, and *8*). Mixture of 5 % C_6H_6 in argon; p = 300 Torr. Curves *1'*, *2'*, and *3'* show profiles obtained by calculation, which are linear combinations of basic profiles with coefficients presented in Table 2.

the minimum contribution from the fragmentation of clusters is observed for the lines with m/z 49, 73, and 74. At low concentrations of benzene (0.2 to 0.5 %), sufficiently exact profiles can be obtained only for the monomer and dimer. In addition, decreasing the pressure is not an efficient method for obtaining "basic" pulse profiles, because due to a decrease in condensation along with a decrease in contributions from the fragmentation of clusters to the shapes of the pulses "blurring" of the shape of the front occurs, which decreases the accuracy of the subsequent quantitative analysis.

The dependence of the pulse shape on the energy of the ionizing electrons can be used to determine the "basic" pulses. The normalized profiles for m/z 78 (*a*) and m/z 156 (*b*) obtained when the energy of the electrons was gradually decreased from 70 to 15 eV are presented in Fig. 7. The change in the shapes of the profiles in Fig. 7, *a* corresponds to a decrease in the intensity of the signal at times t > 200 μs, after which clusters achieve the ionization zone, from its intensity at the times of the transport of monomers t = 100—170 μs. The observed behavior for the line of the dimer with m/z 156 (Fig. 7, *b*) shows that considerable fragmentation of clusters with n > 2 occurs to form a dimer ion. At the same time, the strong dependence of the character of fragmentation on the energy of the electrons in the range of E = 15—40 eV is significant, if it is taken into account that the dissociation energies of ionic clusters of benzene with n = 1—5 are equal to 0.2 to 0.7 eV and the ionization potentials of the clusters range from 9.24 to 8.5 eV.[12] The shapes of the pulses for the lines with m/z 49, 73, and 74 are independent of the energy of the ionizing electrons. This confirms the conclusion that no noticeable amounts of C_4H^+, C_6H^+, and $C_6H_2^+$ ions are formed in the fragmentation of the clusters. The shapes of the pulses for the lines with m/z > 80 substantially depend on the energy of the ionizing electrons for a 5 % C_6H_6/argon mixture at p > 300 Torr. Therefore, the "basic" dimeric, trimeric, and tetrameric pulse profiles were measured for mixtures with low concentrations of C_6H_6 in argon (0.5—1.7 %) using an electron energy of 15 eV.

Mass spectra of small benzene clusters. The partial contributions from each cluster and from the monomer to the intensity of the pulse of a given line were calculated on the basis of measurements of the "basic" pulses using fitting by the least-squares method by the formula: $I_m(t) = \Sigma\alpha_{m,n} \cdot i_n(t)$, where I_m is the intensity (in rel. units) of the complex pulse for the mass-spectral line of the ion with the mass m; i_n are the intensities of normalized "basic" pulses of $(C_6H_6)_n$ components; and $\alpha_{m,n}$ are the partial coefficients determined by fitting; the sum was taken over all components with n = 1—5.

The result of fitting is illustrated in Fig. 8 using the separation of the contributions to the pulses for the lines with m/z 78 (*a*), 156 (*a*) and 234 (*b*) as an example (input of a 5 % mixture of C_6H_6 in argon at p = 300 Torr). The normalized pulses for the lines with m/z 49 (E = 70 eV)

Table 2. Coefficients $\alpha_{m,n}$ reflecting contributions of $(C_6H_6)_n$ clusters to the intensity of the pulse of the ionic current for the mass-spectral line of the ion with mass *m* for mixtures of 0.5 and 5 % C_6H_6 in argon (p = 300 Torr)

m	0.5 %			5 %				
	$n = 1$	$n = 2$	$n \geq 3$	$n = 1$	$n = 2$	$n \geq 3$	$n \geq 4$	$n \geq 5$
51	0.93	0.07		0.89	0.03	0.08		
52	0.88	0.12		0.81	0.03	0.16		
77	0.93	0.07		0.78	0.09	0.13		
78	0.80	0.20		0.58	0.28	0.06*	0.08	
79	0.74	0.26		0.49	0.35	0.16		
156		0.97	0.03		0.12	0.41*	0.46	
234						0.32*	0.11**	0.57
312							0.32**	0.68

* Data for n = 3. ** Data for n = 4.

(curve *4*), *m/z* 156 (15 eV) (curve *5*), *m/z* 234 (15 eV) (curve *6*), and *m/z* 312 (70 eV) (curve *7*), which present the "basic" pulses of the monomer, dimer, trimer, and clusters with $n > 3$, respectively, and the complex pulses for the lines with *m/z* 78 (70 eV) (curve *1*), *m/z* 156 (70 eV) (curve *2*) are shown in the upper part of Fig. 8. The partial coefficients $\alpha_{78,n}$ (n = 1—4) and $\alpha_{156,n}$ (n = 2—4) obtained by fitting, which reflect the structure of the complex pulses (curves *1* and *2*), are presented in Table 2.

The resulting profiles of the pulses (curves *1'* and *2'*), which were calculated using the coefficients $\alpha_{78,n}$ and $\alpha_{156,n}$, are shown in Fig. 8, *a*. Three "basic" pulses (curves *6*, *8*, and *9*), which were used for fitting the pulse of the line with *m/z* 234 (70 eV) (curve *3*), and the resulting profile (curve *3'*) are presented in Fig. 8 *b*. The $\alpha_{234,n}$ coefficients (n = 3—5) were used for the calculation of the profile (*3'*). The coefficients obtained by fitting the complex pulses for the lines with *m/z* 51, 52, 79, 156, 234, and 312 and the data for a tenfold diluted mixture are also presented in Table 2. All mentioned coefficients $\alpha_{m,n}$ are related to the normalized profiles. It is not necessary to use normalized pulses, because the ratio of real intensities of pulses for different lines and the partial coefficients related to these pulses must be known for obtaining the mass spectrum of a cluster of *n* size.

The calculated relative intensities of the lines in the mass spectrum of $(C_6H_6)_2$ are presented in Table 1. The presence of the dimeric component was checked for all lines of the mass spectrum of the monomer,[15] whose intensities exceed 1 % of the intensity of the line with *m/z* 78, except the lines with *m/z* 39 and 29 due to the very high value of the pulse for the line with argon *m/z* 40 and the considerable background line with *m/z* 28. The ratio of the intensities of the lines with m_1/z and m_2/z for n = 1 and 2 were calculated from the equation: $(I_{m1} : I_{m2}) = \alpha_{m1,n}/s_1 : \alpha_{m2,n}/s_2$, where s_1 and s_2 are the sensitivities of the apparatus at which the pulses for m_1/z and m_2/z were measured. The agreement of the obtained spectrum for monomer with the published data can be considered as a measure of the reliability of the experimental data for the dimer. The ratio of the intensities of the lines with *m/z* 78 and *m/z* 156 in the spectrum of the dimer turned out to be equal to 89 : 11, and somewhat was different from the value of 93 : 7 obtained in Ref. 2 in the study of the electrical focusing of a molecular beam. It was also determined in Ref. 2 that $(C_6H_6)_2$ is a polar combination. This made it possible to distinguish the signal of the dimer from those of the nonpolar monomer and trimer. The disagreement between our data and the published data may be associated with the geometry of $(C_6H_6)_2$: the fact that dimers are polar[2] means that C_6H_6 molecules are oriented perpendicularly, although only equivalent C_6H_6 molecules were found in the dimer in the spectroscopic study,[8] which means their orientation was parallel. It is assumed[5,8] that both structures can exist, and each can predominate under different experimental conditions of the formation of the beam. Both of the structures are detected in our experiment, while only the polar structure is observed in Ref. 2; therefore, the difference in the

Table 3. Ion-molecular gas-phase reactions related to intracluster chemistry of the benzene dimer

Reaction				Ion mass
$C_6H_6^+ + C_6H_6$	$\rightarrow C_{12}H_{12}^+$		(1)	156[16]
$C_6H_5^+ + C_6H_6$	$\rightarrow C_{12}H_{11}^+$		(2)	155[16]
	$\rightarrow C_{12}H_{11}^+$	$\rightarrow C_{12}H_9^+ + H_2$	(3)	153[16]
	$\rightarrow C_{12}H_{11}^+$	$\rightarrow C_{10}H_9^+ + C_2H_2^+$	(4)	129[16]
$C_6H_4^+ + C_6H_6$	$\rightarrow C_{12}H_{10}^+$		(5)	154[16]
	$\rightarrow C_{12}H_{10}^+$	$\rightarrow C_{12}H_8^+ + H_2$	(6)	152[16]
$C_4H_4^+ + C_6H_6$	$\rightarrow C_9H_7^+ + CH_3$		(7)	115[17]
$C_4H_3^+ + C_6H_6$	$\rightarrow C_{10}H_9^+$		(8)	129[18]
	$\rightarrow C_{10}H_8^+ + H$		(9)	128[17,18]
	$\rightarrow C_{10}H_7^+ + H_2$		(10)	127[18]
	$\rightarrow C_9H_7^+ + CH_2$		(11)	115[19]
$C_4H_2^+ + C_6H_6$	$\rightarrow C_{10}H_7^+ + H$		(12)	127[17]
$C_3H_3^+ + C_6H_6$	$\rightarrow C_7H_7^+ + C_2H_2$		(13)	91[18]
	$\rightarrow C_9H_7^+ + H_2$		(14)	115[18]

ratios of intensities $I_{78} : I_{156}$ may be related to the different cross sections of the output of $C_6H_6^+$ from the perpendicular and parallel dimeric structures.

The difference in the shapes of the pulses for clusters of size n and $n+1$ decreases as n increases, which decreases the accuracy of the calculations; therefore, only the average data on the ratios of intensities can be given for clusters with $n > 2$: $I_{50} : I_{51} : I_{52} : I_{63} : I_{77} : I_{78} : I_{79} = 1 : 1 : 2.3 : 0.3 : 1.7 : 100 : 11$. These data are related to the 5 % C_6H_6/argon mixture at $p = 300$ Torr.

For the lines with $m/z > 78$, the mass spectra of the trimer and tetramer were determined by fitting three parameters: $I_{78} : I_{79} : I_{115} : I_{128} : I_{129} : I_{141} : I_{156} : I_{233} : I_{234} : I_{235} = 1000 : 100 : 3.7 : 2.7 : 2.9 : 2.0 : 72 : 0.2 : 4.9 : 1.1$ ($n = 3$) and $I_{78} : I_{79} : I_{115} : I_{128} : I_{129} : I_{141} : I_{156} : I_{234} : I_{312} = 1000 : 71 : 6.8 : 5.0 : 4.8 : 0.1 : 39 : 1.7 : 3.1$ ($n = 4$).

As can be seen from Table 1, the "monomeric" and "dimeric" regions of the spectrum of the dimer do not correlate. The presence of intense lines with m/z 130, 116, and 117 corresponding to ions with masses 52, 38, and 39 linked to a benzene molecule is expected, but instead, ions with m/z 115, 128, and 127 are observed. To explain the spectrum of the ions, we used the approach described in Ref. 1, where the analogy between the state of an ionized cluster and a system in which reagents exist during ion-molecular reactions was suggested. In the framework of this concept, it can be assumed that ionization of one of the $(C_6H_6)_2$ molecules is accompanied by fast dissociation of this molecule according to the character of the fragmentation of the monomer, so the $C_6H_6^+$, $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, $C_4H_3^+$, $C_4H_2^+$, $C_3H_3^+$ ions, each of which is one of the reagents of the intracluster reaction, are most probable, and a neutral benzene molecule acts as the second reagent. The well studied ion-molecular reactions[14—16] of benzene with the mentioned ion fragments are listed in Table 3. It can be seen that the same ions were observed in the mass spectrum of the dimer. The only exception is the $C_6H_7^+$ ion, which was determined by subtracting the value of the intensity of the isotopic peak of $C_6H_6^+$ (6.4 %) from the measured intensity of the line with m/z 79 (10.8 %). This ion ($C_6H_7^+$) was not a product of bimolecular reactions and can be considered to be a specific cluster formation.

The relative intensity of the line with m/z 130 ($C_{10}H_{10}^+$) can be used for the estimation of the probability of internal stabilization, because none of the chemical reactions results in the formation of the $C_{10}H_{10}^+$ ion. The excited $C_{10}H_{10}^+$ ion formed in the detachment of C_2H_2 from the dimer can be further stabilized in several ways: (a) by evaporation of the monomer to form $C_4H_4^+ + C_6H_6$; (b) by decomposition in reaction (7) to form $C_9H_7^+ + CH_3$; and (c) by internal stabilization. If it is assumed that the $C_9H_7^+$ ion is mainly formed in reaction (7), the ratio of the intensities of the lines with m/z 52, 115, and 130 gives an estimation of the cross sections of channels (a), (b), and (c) as 100 : 4.4 : 0.5.

Summarizing the aforementioned data, one can conclude that the suggested mechanism of the ionization of the benzene dimer includes two stages. The first is the ionization of a benzene molecule followed by the fragmentation of the radical cation formed. The second stage includes two processes: evaporation of the monomer to give ions forming the "monomeric" region of the mass spectrum and the ion-molecular reactions of the cation with the adjacent molecule, which form ions in the mass range between the monomer and the dimer. The first process is predominant.

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