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Dissociation of Positive Molecular Ions

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The dissociation of accelerated positive molecular ions on collision with atoms and molecules (impact dissociation) is considered. Various experimental methods for the investigation of such dissociation are compared. The mechanisms of the impact dissociation of molecular ions are examined in relation to the simplest diatomic ions. Attention is concentrated on the impact dissociation of polyatomic ions. The scope of this in the determination of the structures and energetics of excited ions is discussed.
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I. INTRODUCTION

The study of the structures and excitation energies of ions yields much information about the structure and state of the initial neutral molecule; furthermore, it has additional interest, since ions arise and are involved in various processes and information about their structures and excitation energies can be used to characterise such processes.

The structures and excitation energies of ions can be studied by mass-spectroscopy using different procedures, in particular it is possible to investigate their spontaneous dissociation or their dissociation under the influence of various agents, i.e. induced or impact dissociation. The spontaneous dissociation of molecular ions is already used in mass-spectrometry to determine the mechanisms of the dissociation of the initial ion, to determine the structure of the ion, to classify the transition states leading to a specific reaction, and to obtain analytical information about mixtures. Impact dissociation reactions of molecular ions can yield more information about the ion and the initial molecule than spontaneous dissociation, particularly because they can occur with any ion and via numerous channels. The impact dissociation of ions can be achieved by the same procedures as the ionisation of molecules, i.e. as a result of the collision of electrons and protons, but with ions and not molecules. This excites the initial ions (they can actually be ionised further) and causes their dissociation, yielding their fragmentation spectra, which can be called the mass spectra of the ions by analogy with the mass spectra of molecules. The mass spectra of both positive and negative ions can be studied in this way. However, the study of the dissociation of ions under the influence of electrons and photons is only just beginning and so far only the first experiments have been carried out with the simplest ions.

This is due to considerable technical difficulties in studies of this kind, although there is no doubt that this procedure will yield more accurate answers to many questions concerning the structures and the energy states of ions and the mechanisms of their dissociation of accelerated ions by collisions with atoms and molecules.

In experiments designed to investigate impact dissociation one measures the total dissociation cross-sections, the relative probabilities of the formation of various fragments (dissociation spectra), and the angular and energy distributions of the dissociation products. Many characteristics of impact dissociation have been observed and investigated; these yield conclusions concerning the structures and excitation energies of the initial ions and also concerning the mechanisms of their decomposition.

The present review is devoted mainly to studies on the dissociation of polyatomic ions and its aim is not to cover the majority of investigations in this field. The fundamental characteristics of impact dissociation were discovered by the present authors on the basis of experiments carried out mainly at the Karpov Physicochemical Institute. The dissociation of diatomic molecular ions is considered only in order to examine the mechanisms of impact dissociation. The entire vast experimental and theoretical data on the dissociation of the simplest molecular ions evidently merit separate consideration.

II. EXPERIMENTAL METHODS FOR THE INVESTIGATION OF THE DISSOCIATION OF IONS

There are several groups of investigators of the dissociation of ions, who are using the usual analytical mass-spectrometers without any significant modification, i.e. in approximately the same way as in the work of Aston[1], who first observed the dissociation of H_2^+ ions on collision with the molecules of the residual gases. However, it is already clear that, by employing the usual mass-spectrometers with a single analyser, it is possible to obtain only very limited information about the dissociation processes of molecular ions. For this reason, in order to study in detail the ion dissociation reactions and hence obtain information about their mechanisms and about the structures and excitation energies of the ions and of the initial molecules, it is necessary to apply a modified mass-spectrometric technique, which involves at least two analysers and a collision chamber.

In a sector mass-spectrometer with a single magnetic analyser dissociation is usually observed in the region where there is no magnetic field between the outlet slit of the ion source and the magnet and it can occur both as a result of collisions with the molecules of residual gases and spontaneously. The fragment ions then give diffuse peaks in the collector, the so called Aston bands or "fractional" peaks, the positions of which on the mass scale are defined by the formula

$$m^* = \frac{m_f^2 q_i}{m_i q_f^2}, \qquad (1)$$

where m^* is the apparent mass of the fragment ion, m_f and q_f are the true mass and charge of the fragment ion, and m_i and q_i are the mass and charge of the initial ion. This formula was obtained on the assumption that the velocity of the ion does not change significantly on decomposition. This is in fact found to be the case in the experiments. If the charge does not change either in the decomposition of the initial singly-charged ion, Eqn. (1) simplifies to

$$m^* = \frac{m_f^2}{m_i}. \qquad (2)$$

On the other hand, if the ion decomposes in the ion source during the acceleration process, the apparent mass of the fragment ion is defined by the formula[2]

$$m^* = \left(\frac{m_f^2 q_i}{m_i q_f^2} \cdot \frac{V_1}{V}\right) + \left(1 - \frac{V_1}{V}\right)\frac{m_f}{q_f}, \qquad (3)$$

where V_1 is the potential difference corresponding to the distance traversed by the metastable ion before the decomposition point and V is the total accelerating potential difference.

The use of a mass-spectrometer with a single magnetic analyser to investigate ion dissociation suffers from the disadvantages that, in the region between the ion source and the magnetic analyser, all the ions emerging from the ion source can dissociate. As a result, the peaks corresponding to different dissociation processes can be superimposed. In particular, this hinders the observation of spontaneous and impact dissociation in the ionisation of polyatomic molecules. The absence of a localised gas target (collision chamber) hinders the determination of the collision cross-sections. The technique for the investigation of the dissociation of the simplest ions in a usual mass-spectrometer has been described[3].

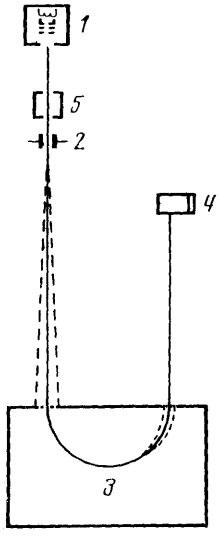


Figure 1. Schematic illustration of a mass-spectrometer: 1) ion source; 2) electrostatic deflector; 3) magnetic analyser; 4) ion detector; 5) collision chamber.

Thus mass-spectrometers with a single magnetic analyser are at present used mainly to investigate the dissociation of the simplest diatomic and triatomic molecular ions. Modified designs of such apparatus have been used by Los[4] and Durup et al.[5] Fig. 1 presents a schematic illustration of Los's apparatus. In contrast to the usual mass-spectrometers, it incorporates a collision

chamber *5*. The presence of narrow collimators at the outlet from the collision chamber makes it possible to achieve a high angular resolution (10^{-3} rad). The analysing magnet has an inhomogeneous field, which results in a high resolving power with respect to energy ($\sim 10^{-4}$).

The disadvantages of single mass-spectrometers are eliminated in apparatus with two magnetic analysers (double mass-spectrometers), which were used for the first time to investigate the impact dissociation of the simplest diatomic and triatomic ions by Ioffe[6-9] at the Leningrad Physicotechnical Institute.

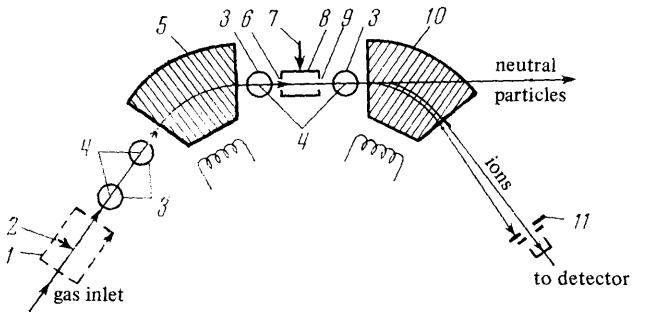


Figure 2. Schematic illustration of a double mass-spectrometer: 1) ion source; 2) electron beam; 3) diffusion pumps; 4) electronic valves of the ionisation manometer; 5) mass-monochromator; 6) inlet slit S_1 of the collision chamber; 7) admission of target gas; 8) collision chamber; 9) outlet slit S_2 of the collision chamber; 10) mass analyser; 11) the slit S_3 before the ion collector.

Studies on the dissociation of polyatomic ions using double mass-spectrometers have begun at the Karpov Physicochemical Institute[10-12]; a schematic diagram of one of these instruments is presented in Fig. 2. The first magnetic analyser (mass-monochromator) isolates the beam of the ions being investigated and directs them to the collision chamber which has controllable inlet and outlet slits S_1 and S_2. Beyond the chamber, there is a second magnetic analyser (the mass-analyser) which analyses the spectrum of the fragments arising as a result of impact or spontaneous dissociation. The width of the slit S_3 before the collector varies in the range 0–16 mm. The differential evacuation of the mass-spectrometer is achieved by four diffusion pumps, which give a pumping rate of 100 litre s^{-1}. The ion source consists of a gas source with ionisation of the molecules by an electron beam with a controllable energy. The accelerating potential varies from 2 to 5 kV. Furthermore, there is a possibility of a further acceleration of the ions up to 100 keV. On a double mass-spectrometer, it is possible to investigate both the spontaneous dissociation of the metastable ions and the dissociation resulting from single collisions of the accelerated ions with the molecules of the gas admitted to the collision chamber up to a pressure of 10^{-4} torr, measured with the aid of a calibrated ionisation manometer or a McLeod gauge.

The total dissociation cross-section of the ions σ is calculated from the formula

$$\sigma = \frac{I^* kT}{Ipl}, \qquad (4)$$

where I^* is the current due to the secondary fragment ions, I the current due to the initial ions, p the gas pressure in the collision chamber, l the effective length of the collision chamber†, k the Boltzmann constant, and T the absolute temperature of the gas in the chamber.

For single collisions I^*/I varies linearly with pressure and the dissociation cross-section is characterised by the slope of the linear plot of I^*/I against p. Fig. 3 illustrates relations of this kind for a number of dissociation processes of ions derived from ethylene. Extrapolation of the I^*/I–p straight lines to zero pressure yields intercepts on the ordinate axis, which characterise the contribution of spontaneous decompositions to the given dissociation process.

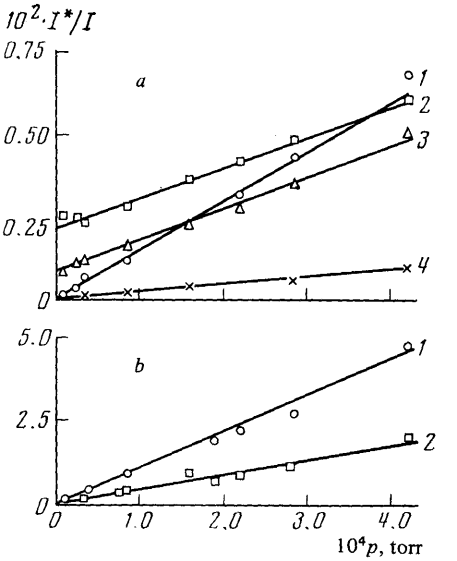


Figure 3. Variation of the relative ionic currents (I^*/I) with gas pressure p (measured using an LM-2 gauge) in the collision chamber. *a*: 1) $C_2H_4^{2+} \rightarrow C_2H_4^+$; 2) $C_2H_4^{2+} \rightarrow C_2H_3^+ + H^+$; 3) $C_2H_4^{2+} \rightarrow C_2H_2^+ + H_2^+$; 4) $C_2H_4^{2+} \rightarrow C_2H^+$; *b*: 1) $CH_2^+ \rightarrow CH^+ + H$; 2) $CH_2^+ \rightarrow C^+$.

To determine the true extent of spontaneous decomposition, it is always necessary to investigate the relation between the ratio I^*/I and the pressure in the region where it occurs, as has been done in studies on a double mass-spectrometer. In certain other investigations the pressure was not measured directly in the region where ions are decomposed but measurements were made of parameters such as the pressure in the system for supplying the ion source with gas[16] or of the current due to the initial ions[17], which is proportional to the gas pressure in the ion source. A situation may arise where the pressure in the region where ions decompose varies only slightly

† It is as a rule greater than the geometrical length of the collision chamber. The methods for its calculation have been described[13,14] and in the study of Menendes et al.[15] the collision region was isolated by an electric field.

when the pressure in the filling system is altered (for example with a high pumping rate in this region and when it is remote from the source) and is close to the background (residual) pressure. Then, when dissociation occurs on collision with the molecules of the background gas, the ratio I^*/I will vary only slightly as a function of the pressure measured in this way, creating the impression that it is apparently independent of pressure. One cannot rule out the possibility that such a situation arose under the conditions used by Wankenne and Momigny[17]. Extrapolation of this relation to zero pressure (in the measurement of p by the above methods) leads to an incorrect determination of the contribution by the spontaneous decomposition of the metastable ions. For this reason, the pressure must be measured directly in the region where decomposition is observed.

For a more complete understanding of the impact dissociation process, it is necessary to carry out investigations for different kinetic energies of the initial ions, particularly in the region of threshold energies, which permits the determination of the dissociation and excitation energies of the ions. A number of instruments have been constructed[18-20] for the investigation of dissociation under the conditions of low energies.

Double-focussing mass-spectrometers have been used recently to study ion dissociation. In such instruments there are three regions in which it is possible to observe the dissociation of metastable ions[21]. The first region is between the inlet slit of the ion source and the inlet to the electrostatic analyser. The second region is between the electrostatic and magnetic analysers and the third region is located in the accelerating section of the ion source. In the study of spontaneous decompositions in the first region the defocussing method is used. The double-focussing mass-spectrometer transmits only ions with a narrow range of kinetic energies. Ions formed on spontaneous decomposition possess only part of the energy of the initial ion. To detect the metastable ion in the reaction $m_0^+ \rightarrow m_1^+$, it is necessary to increase the ratio of the accelerating potential V to the potential on the plates of the electrostatic analyser E by the factor m_0/m_1, i.e. the mass-spectrometer must be defocussed in relation to the initial ion[22]. This can be done by scanning the accelerating potential from its usual value corresponding to a constant potential E using a magnetic field tuned for the transmission of the ion with the mass m_1. The spectrum of all the ions generated on spontaneous decomposition by the ions with the mass m_1 can be obtained in this way.

In another method[23-25] the peaks corresponding to the decomposition of the metastable ions are observed by decreasing the potential applied to the electrostatic analyser by the factor m_1/m_0 and by tuning the magnetic field for the transmission of the "apparent mass" $m^* = m_1^2/m_0$. The advantage of this method over the first procedure is that, in carrying out quantitative measurements, the intensities of different metastable transitions can be more effectively compared under the same conditions in the ion source, in particular at a constant accelerating potential.

The technique for the investigation of spontaneous dissociation in a double-focussing mass-spectrometer having the Nier–Jones geometry, with scanning of the potential applied to the electrostatic condenser, has been described in relation to the decomposition of the ions formed from the toluene molecule[26]. The sensitivity achieved in recording the ions generated on decomposition amounted to $(1 - 2) \times 10^{-6}$ of the intensity of the initial ion, i.e. about 10^{-4}%.

McLafferty and coworkers[27] used a mass-spectrometer with the reverse geometry. Here the ion source in the double-focussing instrument was located in the place of the detector and the detector was in the place of the ion source. Spontaneous decompositions are recorded in the region between the magnetic and electrostatic analysers. This method has certain advantages compared with the other two procedures described above. The scanning of the potential applied to the electrostatic condenser yields the entire spectrum of the fragment ions obtained from the given initial ion. Ion dissociation on collision is now also beginning to be investigated on apparatus with double-focussing having both normal and reverse geometry[28].

In the study of ion dissociation the measurement of the angular and energy distributions of the dissociation products is important. To measure the angular distributions of ions in double mass-spectrometers, it must be possible to move the second analyser relative to the axis passing through the centre of the collision chamber, as for example in the apparatus illustrated in Fig. 2. Another method has been used in studies[4,5] where a deflecting collimator was mounted at the outlet from the collision chamber and was able to scan the ion beam via a narrow collimator.

The energy distribution is measured with the aid of magnetic[4,5] or electrostatic analysers. A method for the energy spectroscopy of ions using a double-focussing mass-spectrometer, which makes it possible to record the changes in the energy of the fragment, equal to 10^{-4} eV in the centre of mass system for a dissociating ion, has been reported[29]. A novel apparatus using a 127° electrostatic analyser and a quadrupole mass-analyser, which were positioned beyond the collision chamber, has been used to measure the angular and energy distributions of the dissociation products of certain diatomic ions[30]. The nature of the energy distribution of the dissociation products is important, since the efficiency of the recording of the fragment ions depends on it. When it is necessary to measure the total dissociation cross-section, all the fragment ions formed in the collision chamber should be recorded in the collector. This is most important also for the comparison of the intensities of different metastable transitions. Incomplete recording of the protons has been the cause of an error in the measurement of the total dissociation cross-section of the H_2^+ ions in certain early investigations, discussed in a number of communications[13,14,31].

In the measurement of the total dissociation cross-sections of simple diatomic and triatomic ions, where there is no need for a high resolution, the slit before the ion collector must be as wide as possible. Sometimes it must also be made wide in the study of the dissociation of polyatomic ions[32]. This is difficult to achieve in analytical mass-spectrometers. For a narrow slit, it is necessary to measure the distribution of the peak intensity by scanning the magnetic field and the total current must be found by integrating this distribution. In double-focussing apparatus this procedure is more complicated, since it is necessary to scan the electric and magnetic fields[33]. Quantitative analysis of metastable transitions involving polyatomic ions may be experimentally difficult, requiring the use of a computer, as was done by Coutant and McLafferty[34].

In concluding this section, we shall consider briefly a method for the investigation of ion dissociation under the influence of electron and photon impact. The dissociation in collisions with electrons is studied by the method of ion and electron beams intersecting at right angles. To

reduce the signal arising due to the impact dissociation of the initial ions in collisions with the molecules of the background gas, the pressure in the region of the intersection of the beams is less than 10^{-9} torr. Furthermore, a technique involving modulation of the peaks is employed to isolate the required signal. Measurements have been made of the dissociation cross-sections of H_2^+, O_2^+, N_2^+, and D_2^+ for electron energies in the range 10–1500 eV.[35]

Using the emission from a ruby laser to investigate the photodissociation of H_2^+ ions[36], the energy spectrum of the protons was found to depend on the plane of the polarisation of the light and vibrational structure was observed, reflecting the populations of the vibrational levels of the initial H_2^+ ions. Thus the study of the photodissociation of molecular ions by means of laser light with simultaneous analysis of the dissociation products with respect to kinetic energies may prove to be promising in the sense of creating a desirable method for determining the excitation energies of molecular ions obtained in different processes. Still greater possibilities arise when tunable lasers are used.

III. DISSOCIATIVE COLLISIONS OF DIATOMIC IONS

The studies on the impact dissociation of diatomic ions carried out up to 1970 have been reviewed in a book[37] and two articles[38,39]. The aim of this section is to describe the fundamental mechanisms of the impact dissociation of accelerated ions with illustrations by examples taken mainly from the recent studies in this field.

The impact dissociation of a diatomic ion proceeds via the mechanism

$$AB^+ + M \begin{cases} \longrightarrow A^+ + B + M \\ \longrightarrow B^+ + A + M \end{cases}, \qquad (5)$$

where all the species on the right-hand side can also be formed in excited states and, for high kinetic energies, in ionised states.

The dissociation mechanisms have been classified by Durup[38], the classification having been somewhat modified by Los[4]. Four mechanisms can be put forward for the impact dissociation of molecular ions: (1) electronic transitions to unbound states of the molecular ion or to bound states above the dissociation limit; (2) vibrational-rotational transitions to a continuum without a change in the electronic state of the ion AB^+ (adiabatic mechanism); (3) dissociation via the formation of an intermediate complex (AB^+M), which decompose into $A^+ + B + M$ or into $B^+ + A + M$, which occurs when the energies of the relative motion are of the order of magnitude of the bond energy of the AB^+ ion; (4) predissociation caused by the collision.

The contribution of each mechanism to the total dissociation cross-section depends to a large extent on the kinetic energy E_0 of the AB^+ ion and also on its excitation. Since ion dissociation has been studied over an extremely wide range of values of E_0 (from several electron-volts to tens of MeV for H_2^+ ions), it is possible to estimate the approximate limits of the region of E_0 within which a particular mechanism predominates. Electronic transitions predominate over a wide range of energies from hundreds of electron-volts to the maximum values achieved experimentally. Vibrational transitions are probably important for energies in the range 10–100 eV. Finally, induced predissociation has been observed for energies in the range $\sim 10^3$–10^4 eV.

There is an unambiguous relation between the distribution of the dissociation products in the centre of mass coordinates based on the AB^+ ion and the form of the distribution in terms of the laboratory coordinate system, or, using the mass-spectrometric terminology, the shape of the peak in the ion collector. We may note that, in order to obtain the true energy distribution in the centre of mass coordinates on transformation from the distribution in terms of the laboratory coordinate system, account must be taken of the apparatus function of the instrument[5,40]. The relation between the shape of the peak and the energy distribution of the dissociation products for double-focussing mass-spectrometers has been considered[41,42]. There is a simple relation between the energy in the centre of mass system and the energy E_A of the fragment ion in terms of the laboratory system. For convenience we shall assume that the masses of the species A and B involved in reaction (5) are $m_A = m_B = m$. If the velocity of the fragment in the centre of mass system is u, then

$$E_A = \frac{m(v_0 + u)^2}{2} = \frac{mv_0^2}{2} + mv_0 u\cos\varphi + \frac{mu^2}{2} = \frac{E_0}{2} + \frac{W}{2} + mv_0 u\cos\varphi, \qquad (6)$$

where v_0 is the velocity of the AB^+ ion, φ the angle at which the A^+ ion is ejected in the (A, B) centre of mass system, W the kinetic energy of the dissociation products in the (A, B) centre of mass system, and E_0 the kinetic energy of the initial AB^+ ion. The quantity $\frac{1}{2}W + mv_0 u\cos\varphi = \Delta E$ is the additional kinetic energy acquired by the A^+ ion in the laboratory system of coordinates.

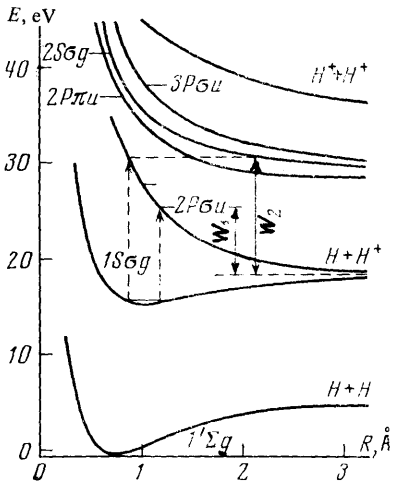


Figure 4. Potential energy curves for H_2^+ ions.

We shall consider this in relation to the dissociation of H_2^+ ions, the potential energy curves for which are shown in Fig. 4. In the electronic transition from a particular vibrational level in the ground state $1s\sigma_g$ to the nearest unbound state $2p\sigma_u$ in the centre of mass system a kinetic energy in the range from W_1 to W_2 is liberated, since for $E_0 \simeq 10^3$ eV and above the collision time is much shorter than the vibration period of the nuclei and the Franck–Condon principle is maintained in the electronic transition.

The limits W_1 and W_2 are determined by the initial vibrational level of the H_2^+ ion. In the measurement of the energy distributions use is made of narrow outlet collimators, which isolate the fragment ions emerging in the centre of mass system at angles close to $\varphi = 0°$ and 180°. Then, in accordance with Eqn. (6), two energies are observed in terms of the laboratory system for each energy of the fragment in the $\frac{1}{2}W$ centre of mass system (and the corresponding velocity u):

$$E_1 = \frac{E_0}{2} + mv_0u + \frac{1}{2}W;$$

$$E_1' = \frac{E_0}{2} - mv_0u + \frac{1}{2}W.$$

Thus in the laboratory coordinate system an energy distribution with two symmetrical maxima will be observed. The maxima will be diffuse owing to the contributions of different W acquired by the dissociation products of the AB^+ ions in a particular initial vibrational state and in consequence of a distribution with respect to vibrational states in the beam of the initial H_2^+ ions. Since in reality the outlet slits of the instruments have a finite width and transmit a proportion of the ions with a transverse velocity component u, the form of the distribution changes, since the number of ions detected increases for $\Delta E \simeq 0$ [the values of W in Eqn. (6) can be neglected, since $W \ll E_0$].

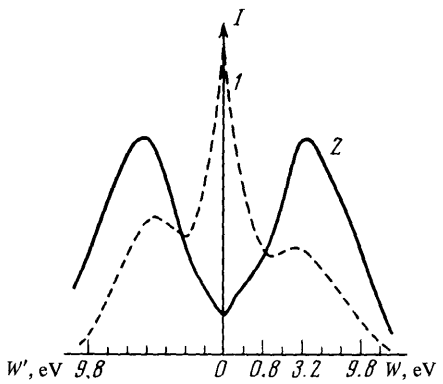


Figure 5. The energy spectrum of H^+ ions in the centre of mass system on impact dissociation of H_2^+: 1) without allowance for the apparatus function; 2) with allowance for the apparatus function.

Therefore a sharp peak appears at the centre of the distribution (Fig. 5). Transitions for which $W \simeq 0$ make a definite contribution to this maximum; these are vibrational transitions to the continuum of the $1s\sigma_g$ state adjoining the dissociation limit. The contribution of the vibrational transitions increases with increase of the atomic number of the target[38,40]. Some workers believe that electronic transitions to the $2p\sigma_u$ state from high vibrational levels of the ground state make a significant contribution to the formation of the central peak[43]. The possibility of dissociation via the excited state $2p\pi_u$, which has a low-slope potential curve, is also assumed. A shift of the central peak towards lower energies has been observed in experiments with different targets, particularly when the excitation energy of the target is small[38,44]. The position of the central peak is determined by the quantity $E_0/2 - E^*/2$, where E^* is the energy consumed in the dissociation process (the excitation energy of the particles involved in the collision).

The angular distributions of the protons in the dissociation of accelerated H_2^+ ions have been studied both theoretically and experimentally. A calculation carried out for different internuclear distances R (i.e. for different vibrational levels) has shown that, for low values of R, protons move apart preferentially parallel to the axis of the beam. For large values of R, dissociation with the orientation of the internuclear axis at right angles to the axis of the beam is more likely. The simultaneous excitation of the target can markedly alter the distribution and can lead to various anomalies[43,45-48].

The cross-section for the dissociation of H_2^+ ions due to electronic transitions has been estimated theoretically by various investigators in terms of the Born approximation[49-56]. Despite the fact that this is a high-energy approximation, it has been used successfully for energies in the range 1–100 keV. The contribution of the vibrational mechanism to the total dissociation cross-section has also been estimated[57]. For this purpose, the classical momentum approximation was employed[58]. For an energy of H_2^+ ions of 3 keV and collisions with hydrogen atoms, the cross-section for the vibrational dissociation is approximately 10% of the experimental value. Calculations have been made for vibrational transitions due to polarisation forces in terms of a modified Born approximation[59].

Table 1. The dissociation cross-sections Σ of H_2^+ ions obtained from different molecules.

Initial molecule	H_2	CH_4	C_2H_4	C_4H_{10}	$C_{12}H_{24}$	GeH_4	SiH_4
$10^{16} \cdot \Sigma$, cm^2	1.06[65]	2.5[66]	1.4[65]	1.7[65]	1.4[65]	2.1[67]	1.7[67]

The dissociation cross-section of H_2^+ ions depends on vibrational excitation. Experiments confirming this fact have been carried out by different groups of investigators[60-64]. H_2^+ ions were obtained not only by the ionisation of H_2 molecules by electrons of different energies but also in the dissociative ionisation of various hydrogen-containing molecules[65-67]. Table 1 lists the experimental dissociation cross-sections of H_2^+ ions obtained from different molecules. The energy of the H_2^+ ions was 3.8 keV and the target was neon. Evidently the most excited H_2^+ ions are formed in the dissociative ionisation of methane molecules by electrons (E_e = 120 eV).

The interpretation of experiments on the dissociation of N_2^+ is less unambiguous than in the case of H_2^+ owing to the more complicated electronic structure[69-72]. A marked dependence of the impact dissociation cross-section of N_2^+ ions on the energy of the electrons ionising the nitrogen molecules has been observed in a number of studies[73-75]. This result suggests an appreciable proportion of excited N_2^+ ions in the beam. Among these may be not only vibrationally excited but also electronically excited ions. The N_2^+ ions formed by the ionisation of HN_3 molecules are appreciably excited[76]. The most probable process in the dissociation of N_2^+ ions for energies in the region of about

10^3 eV is an electronic transition to a section of the $D^2\Pi_g$ potential curve above the dissociation limit and predissociation in the $C^2\Sigma_u^+$ state[77,78].

Heteronuclear ions dissociate via the same mechanisms as homonuclear ions. However, there are certain characteristic features owing to the presence of a permanent dipole moment in heteronuclear ions[59]. The dissociation of the heteronuclear ions HeH^+,[79-81] HD^+,[82,83] CO^+, and NO^+ [72] has been studied.

IV. METASTABLE IONS

In mass-spectrometry metastable ions are excited ions whose lifetime with respect to decomposition and emission is of the order of 10^{-6}–10^{-5} s. This is determined by the residence time of the ions in the ion source after their formation as a result of the ionisation of the molecules by electrons and by the time taken to traverse the path from the field-free region of the mass-spectrometer to the point where the metastable ion decomposes. The observed slow decompositions of the ions may be due to different causes. Firstly, as a result of the ionisation of the molecule, the ion can be formed in excited electronic states, which have longer lifetimes with respect to emission and emit with transition to an unbound state or to a section of a bound state above the dissociation limit. Secondly, the ion may be in an excited state which has a barrier; in this case the dissociation proceeds via the tunnel effect. Calculations of the permeability of the barrier carried out by the usual equations have shown that, for example, for a barrier height of 1 eV and widths of 0.15 and 0.25 Å, the lifetimes of N_2^{2+} and NO^{2+} are found to be respectively $\sim 10^{-7}$ and 10^{-6} s.[16] Calculations for the spontaneous decomposition of $C_2H_4^{2+}$ and CO^{2+} ions have shown that their lifetimes are of the order of $\sim 10^{-5}$ and 10^{-4} s respectively.

The third possible mechanism involves slow predissociation in the excited state of the ion. Predissociation usually takes place during a period which is much shorter than the lifetime with respect to emission. When not all the selection rules are obeyed, predissociation is then slow[84]. Thus the metastable ion will be observed when the predissociation time is of the order of magnitude of the lifetime with respect to emission, which in turn should be $>10^{-7}$ s.

The rate of predissociation in the mass-spectra of polyatomic molecules, is calculated using the quasiequilibrium theory of mass-spectra, the latest review of which has been written by one of its originators[85]. This theory presupposes that the processes leading to the formation of the mass-spectra consist of a series of consecutive and competing reactions, the rates of which can be calculated on the basis of the theory of absolute reaction rates.

The general expression for the rate constant for a unimolecular reaction is[85]:

$$k(E) = \frac{S}{h}[N^*(E-\varepsilon_0)/\rho(E)],$$

where S is the symmetry factor equal to the number of identical reaction paths (with the same activation energy and activated complex), h Planck constant, $N^*(E-\epsilon_0)$ the number of states of the activated complex with energy $\leq E-\epsilon_0$, $\rho(E)$ the density of the states of the initial ion with a total energy E, and ϵ_0 the activation energy.

The quasiequilibrium theory predicts that the rate constant should be a monotonically increasing function of the internal energy. Considering the molecular ion as an assembly of N harmonic oscillators (N is the number of internal degrees of freedom of the molecular ions) and assuming for simplicity that the frequencies of all the oscillators are identical, we obtain a simple expression for the decomposition rate constant:

$$k(E) = \nu\left(1-\frac{\varepsilon_0}{E}\right)^{N-1},$$

where ν is the frequency factor.

Table 2. C–H bond dissociation energies E_{C-H}.

Ion	$C_3H_8^+$	$C_3H_7^+$	$C_3H_6^+$	$C_3H_5^+$	$C_3H_4^+$	$C_3H_3^+$
E_{C-H}, kcal mole^{-1}	8	92	49	102	44	150

Ions with a large excitation energy E have large decomposition rate constants and decompose in the ion source. Weakly excited ions have $k \simeq 10^6$ s^{-1} and decompose after emerging from the ion source into the field-free region of the analyser, forming "metastable peaks". Since metastable ions are weakly excited, the energy of the process should play a significant role in their dissociation. In particular, one may expect appreciable differences in the spontaneous decomposition of alkane ions with even and odd numbers of hydrogen atoms. Table 2 presents the dissociation energies of the C–H bonds for ions with three carbon atoms[85] and Table 3 lists the intensities of the spontaneous decompositions for the corresponding ions obtained from propane molecules.

Table 3. The intensities of the spontaneous decompositions (% relative to the intensity of the initial ions).

Decomposition process	I^*/I, %	Decomposition process	I^*/I, %
$C_3H_8^+ \rightarrow C_3H_7^+ + H$	1.5	$C_3H_6^+ \rightarrow C_3H_5^+ + H$	0.1
$C_3H_7^+ \rightarrow C_3H_5^+ + H_2$	0.1	$C_3H_5^+ \rightarrow C_3H_3^+ + H_2$	2.0

The last Table shows that the spontaneous decomposition of ions with an even number of hydrogen atoms proceeds with loss of one hydrogen atom in accordance with the low activation energies for this process listed in Table 2. The spontaneous decomposition of ions with an odd number of hydrogen atoms involves the loss of two hydrogen atoms in the form of a molecule, since the activation energy for this process is reduced owing to the formation of a bond between the two hydrogen atoms abstracted.

The significant influence of the energy relations on the dissociation process frequently leads to the decomposition of the metastable ions via pathways other than simple bond dissociation. In particular, many rearranged ions are formed, since the decomposition reactions with the rearrangement of these atoms have small activation energies. This process has been discussed in detail in a monograph[88]. The decomposition of the molecular ion derived from benzoic acid labelled with deuterium in the

carboxy-group may be quoted as an example of the interchange of the positions of the atoms involved in the decomposition of metastable ions. In this case the loss of the OH group is twice as likely as the loss of OD, while for the decomposition in the ionisation chamber during periods comparable to the time required for the rotation of the carboxy-group the loss of OD groups predominates greatly over the loss of OH groups[89].

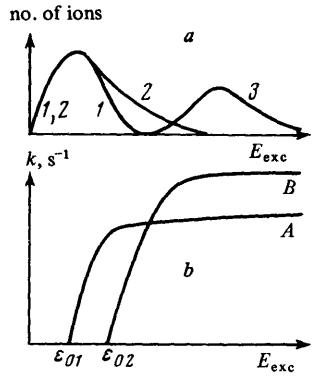


Figure 6. Impact activation of the direct bond dissociation reaction[91].

The contribution of decomposition reactions with rearrangement is greater by 2–3 orders of magnitude compared with simple bond dissociation reactions for metastable ions than for the ions decomposing in the ionisation chamber[90]. The rearrangement reactions hinder the determination of the structure of the metastable ions and their contribution may be reduced by the impact activation of the direct bond dissociation reactions. This idea is illustrated schematically in Fig. 6. Fig. 6*a* shows the distribution of ions with respect to the excitation energy E_{exc} in the ion source at the instant of their formation (curve *2*). Curve *1* describes the distribution with respect to excitation energy of the metastable ions which do not have sufficient time to dissociate in the ion source and decompose in the field-free region. Curve *A* in Fig. 6*b* represents the hypothetical dependence of the decompositon rate constant for rearrangement reactions on the excitation energy E_{exc}. Curve *B* illustrates the analogous relation for the simple bond dissociation rate constant. Curve *A* is below curve *B* for high values of E_{exc}, because the rearrangement reactions have lower frequency factors than the direct bond dissociation reactions. On the other hand, the activation energy $\epsilon_{01} < \epsilon_{02}$. The Figure shows that metastable ions, which have low excitation energies, decompose mainly via rearrangement reactions. In order to reduce their contribution, it is necessary to increase the excitation energy of the metastable ion, i.e. to shift the distribution defined by curve *1* to the position characterised by curve *3*. This is achieved by the collision of the metastable ion with a neutral particle in the region of ion drift. It has been shown[91] for the molecular ions $C_6H_5CD_3^+$ and $C_6D_5CH_3^+$, which decompose with abstraction of H or D atoms, that the contribution of the decomposition with a rearrangement of H and D atoms in impact activation is smaller by a factor of 5 compared with the spontaneous decomposition of the ions.

In the mass-spectra of polyatomic molecules the fraction of metastable ions can be fairly high. It has been shown[32] that in the mass-spectrum of n-octane, 26% of the molecular ions $C_8H_{18}^+$ undergo a metastable transition leading to the formation of the ions $C_6H_{13}^+$. Many instances of the spontaneous decomposition of molecular and fragment ions in the mass-spectra of n-octane, n-hexane, benzene, n-butane, isobutane, and other compounds have been investigated[32,57] with the aid of a double mass-spectrometer. Certain aspects of the spontaneous decomposition of polyatomic ions have been elucidated in a review[92].

We shall also consider the spontaneous decompositions of doubly-charged ions and certain simple singly-charged ions. As in the study of the decomposition of other metastable ions, valuable information is obtained here by studying the energy spectra of the dissociation products.

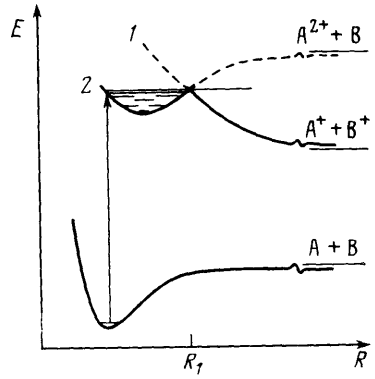


Figure 7. Hypothetical potential energy curves for a doubly-charged ion.

In the decomposition of doubly-charged ions the kinetic energy of the fragments in the centre of mass system is high (several electron-volts) and the peak has a characteristic shape with two vertices and an intervening minimum[93]. The depth of the minimum depends on the width of the collimating slits and the distance between the vertices defines the most probable kinetic energy of the fragments in the centre of mass system. The distance between the charged fragments in the doubly-charged ion can be inferred from this kinetic energy. Fig. 7 presents schematic potential curves for a neutral diatomic molecule and its doubly-charged ion. For large interatomic distances R, the potential energy of the system of ions A^+ and B^+ varies in accordance with the Coulomb law: namely as e^2/R. The overall energy of A^{2+} and B tends to a limit, which lies above the sum of the ionisation potentials of A and B, since the double-ionisation potential of A is greater than the sum of the ionisation potentials of A and B. For a certain value of R_1, the total energies of states *1* and *2* are equal. At this point the states leading to the formation of $A^+ + B^+$ and to $A^{2+} + B$ intersect, provided that they have different symmetries[84]. For the same symmetry and spin, the levels do not intersect, which leads to the formation of a barrier in one of the states. If the AB^{2+} ion is formed in a vibrationally excited state

close to the top of the barrier, then rapid predissociation takes place since the corresponding selection rules are fulfilled[84]. When the AB^{2+} ion is formed in the lower vibrational levels, it is almost stable, since the probability of passing through the barrier decreases sharply with increase of its width and height. The lifetimes characteristic of metastable ions ($\lesssim 10^{-5}$ s) will be observed in a small region of excitation energies of the AB^{2+} ion, located several tens of electron-volts below the top of the barrier. The energy of the A^+ and B^+ fragments in the centre of mass system will thus characterise the position of the top of the barrier.

For the doubly-charged ions N_2^{2+}, O_2^{2+}, I_2^{2+}, Br_2^{2+}, IBr^{2+}, and ICl^2, the kinetic energies of the fragments and the position of the top of the barrier have been determined[94]. The kinetic energy of the fragments from CO^{2+} has been found to be [57,95,96] 5.5– 6 eV, which corresponds to R = 2.6 Å. Metastable decompositions have been observed also for the CO_2^{2+} and N_2O^{2+} ions[96], the $C_2H_4^{2+}$, $C_2H_3^{2+}$, and $C_2H_2^{2+}$ ions[57,97], and for the doubly-charged ions derived from aromatic hydrocarbons (benzene, naphthalene, and biphenyl derivatives)[98]. The ion decomposition reaction $C_6H_6^{2+} \rightarrow CH_3^+ + C_5H_3^+$ results in the liberation of 2.8 eV of energy, which corresponds to a charge separation in the ion of 5.14 Å.[99]

Metastable ions were observed recently for the diatomic single-charged ions N_2^+ and NO^+ [16,17,100,101] and HS^+ ions[102]. The predissociated states were not identified exactly and much work is still required here.

V. IMPACT DISSOCIATION OF POLYATOMIC IONS

Systematic studies have been made on a double mass-spectrometer (Fig. 2) of the dissociation of a series of polyatomic ions on collision with various targets[57]. The total cross-sections for dissociation via different channels (reaching values of about 4×10^{-15} cm^2 for certain ions), their dependence on the excitation energy of the initial ion and its origin, and the dependence of the cross-sections on the kinetic energy of the ions and the type of target have been determined. Such data have been obtained for the ions[10–14,32,57] CH_4^+, CD_4^+, CH_5^+, CD_5^+, $C_2H_4^+$, $C_2H_4^{2+}$, $C_3H_8^+$, $C_4H_{10}^+$, $C_6H_6^+$, $C_7H_{16}^+$, $C_8H_{18}^+$, and many others[57]. Comparison of the mass-spectra of molecules in dissociative ionisation by electrons with the dissociation spectra of the corresponding ions obtained on collision between the accelerated molecular ions and neutral particles is also of interest.

1. Dependence of the Total Dissociation Cross-Sections and the Dissociation Spectra on the Dissociation Energy of the Ions and the Type of Target

Table 4 presents the dissociation spectra of ions from methane obtained when they collide with different atoms and molecules[10,12,57]. The kinetic energy of the ions was 2530 eV and the energy of the electrons in the ion source was 70 eV.

The Table shows that the dissociation spectra depend only slightly on the mass and the structure of the neutral target particle‡. However, the absolute values of the cross-sections differ markedly. For example, the cross-section for the process $CH_4^+ \rightarrow CH_3^+ + H$ on collision of CH_4^+ ions with air molecules is 7×10^{-16} cm^2, while on collision with hydrogen it amounts to only 2.5×10^{-16} cm^2. Similar results were obtained for the dissociation of ions from ethylene in collisions with air molecules and neon atoms[103].

‡Only collision with helium leads to more extensive dissociation.

Table 4. The relative intensities of the products of the dissociation of methane ions on collision with the target atoms and molecules.

Process	Target						
	He	Ne	Ar	H_2	n-C_4H_{10}	n-C_5H_{12}	CH_4
$CH_4^+ \rightarrow CH_3^+$	100	100	100	100	100	100	100
$CH_4^+ \rightarrow CH_2^+$	53	44	49	50	34	35	39
$CH_4^+ \rightarrow CH^+$	17	9	11	11	9	10	9
$CH_4^+ \rightarrow C^+$	6	3	4	4	3	3	3

The cross-sections for the individual processes depend to a large extent on the energy consumed in the process. Table 4 shows that the cross-sections decrease appreciably with increase of the number of hydrogen atoms lost, which also requires greater energy expenditure. However, for high energies of the ions, the cross-sections for the individual processes approach one another[13]. This may be associated with the increase of the excitation energy received by the ion in the collision and also with the increase of the contribution to the dissociation cross-section by processes involving the loss ("abstraction") of an electron, which results in the simultaneous dissociation of several bonds in the case of methane.

Table 5. The dissociation cross-sections ($10^{16}\sigma$, cm^2) of CD_5^+ ions on collision with air molecules and neon atoms.

Decompositon process	ϵ_0, eV	Neon	Air
$CD_5^+ \rightarrow CD_4^+ + D$	4.4	0.13	0.28
$CD_5^+ \rightarrow CD_3^+ + D_2$	1.3	1.1	2.0
$CD_5^+ \rightarrow CD_2^+ + D_2 + D$	6.5	0.3	0.56
$CD_5^+ \rightarrow CD^+ + 2D_2$	5.5	0.08	0.18
$CD_5^+ \rightarrow C^+ + 2D_2 + D$	9.3	0.03	0.06
Total cross-section Σ		1.64	3.06

A dependence of the cross-section on the energy ϵ_0 consumed in the given dissociation process has been observed for all the processes studied with the kinetic energies of the initial ions in the region of several keV. Table 5 illustrates this fact for the CD_5^+ ions obtained in the ion source by an ion–molecule reaction.

It is interesting to note[57] that the total dissociation cross-section of CD_5^+ ions is smaller almost by a factor of two than for CD_4^+ ions. On the basis of the relation between the dissociation cross-section and the process energetics, this can be accounted for by the greater stability of the CD_5^+ ion compared with the CD_4^+ ion. The greater stability of CD_5^+ may be due to the structure of its electron shell, which is isoelectronic with that of the neon

atom, and the low internal excitation energy, which, as will be seen from the description below, greatly influences the total dissociation cross-section. Other examples of this kind can be found in studies on the dissociation of ions produced from propane as a result of collision with neon atoms. Table 6 lists the cross-section for the formation of dissociation products with three, two, and one carbon atoms and the total dissociation cross-sections Σ of certain ions from propane with a kinetic energy of 2.8 keV.[57,105]

Table 6. The overall dissociation cross-sections of the ions formed from propane ($10^{16}\sigma$, cm^2).

Dissociation products	Initial ions							
	$C_3H_8^+$	$C_3H_7^+$	$C_3H_6^+$	$C_3H_5^+$	$C_3H_4^+$	$C_3H_3^+$	$C_3H_2^+$	C_3H^+
$C_3H_n^+$	6.2	5.3	7.6	5.7	7.5	4.2	3.9	2.1
$C_2H_m^+$	13.6	3.1	1.8	0.7	0.4	0.3	0.4	0.4
CH_k^+	0.5	0.4	0.3	—	—	—	—	0.6
Σ	20.3	8.8	9.7	6.4	7.9	4.5	4.3	3.1

Evidently, with decrease of the number of hydrogen atoms in the initial ion, the cross-section for dissociation with rupture of the C–C bond decreases rapidly, becoming constant starting with the $C_3H_4^+$ ion. This behaviour reflects the fact that, with decrease of the number of hydrogen atoms in the ions, the C–C bond is stabilised up to the formation of a double bond in the $C_3H_4^+$ ion. The structure of the $C_3H_8^+$ ion is particularly unstable owing to the greatly weakened C–C bond. The abstraction of a single hydrogen atom leads to a sharp alteration of the structure and the formation of the protonated cyclopropane ring in the $C_3H_7^+$ ion, which is stable. Ions with a smaller number of hydrogen atoms probably retain this carbon skeleton with a gradual increase in the strength of the C–C bonds in the ring. The variation of the total dissociation cross-sections of these ions reflects the variation of the overall cross-sections for the abstraction of hydrogen atoms, which are somewhat greater for ions with an even number of hydrogen atoms (an odd number of electrons), Such variation of the cross-sections with abstraction of hydrogen atoms is characteristic of the ions in the mass-spectra of saturated hydrocarbons and implies that the strength of the C–H bonds varies depending on whether the number of hydrogen atoms in the ion is even or odd.

Spontaneous decomposition processes, superimposed on impact dissociation, have been observed for polyatomic ions[32,106]. As a rule, a high cross-section for dissociation on collision corresponds to an intense spontaneous decomposition of the ions, which is related to the influence of the initial excitation energy of the dissociation cross-section. Many characteristics of the impact dissociation of the ions in the mass-spectrum of n-butane and other molecules have been examined[57,107].

The total cross-sections for the dissociation, with the rupture of C–C bonds, of the molecular ions from saturated hydrocarbons are additive, i.e. the cross-section is proportional to the number of CH_2 groups in the initial ion[32,57]; the data in Table 7 illustrates this finding.

2. Comparison of the Impact Dissociation Spectra of Ions with the Mass Spectra of Molecules Obtained on Electron Impact

Comparison of the dissociation spectra of ions with their mass spectra obtained on electron impact is of great interest. Such a comparison is presented in Tables 8 and 9 for the $C_3H_8^+$ and $C_3H_3N^+$ ions and the corresponding molecules[57,103].

Table 7*. Total dissociation cross-sections Σ (Kupriyanov[57]).

Initial ion	$C_3H_{10}^+$	$C_3H_{14}^+$	$C_3H_{10}^+$	$C_3H_8^+$
$10^{15}\cdot\Sigma$ (calc.), cm^2	4.0	3.0	2.0	1.5
$10^{15}\cdot\Sigma$ (expt.), cm^2	$4.3^{\pm 3}$	$3.0^{\pm 3}$	$2.3^{\pm 6}$	$1.4^{\pm 7}$

*In the calculation of Σ it was assumed that the contribution to the total decomposition cross-section by one CH_2 group in the molecular ion is 5×10^{-16} cm^2.

The mass-spectra of the molecules were obtained for an electron energy of 70 eV. The energy of the accelerated ions was 3.5 keV and the dissociation occurred on collision with air molecules.

Table 8. Comparison of the mass-spectrum ($I_{m.s.}$) of propane and the impact dissociation spectrum (I_{im}) of the propane ion (the relative intensities of the fragment ions are quoted).

Ions	$C_3H_7^+$	$C_3H_6^+$	$C_3H_5^+$	$C_3H_4^+$	$C_3H_3^+$	$C_3H_2^+$	C_3H^+
$I_{m.s.}$	8.7	3.9	7.4	1.5	23.0	23.5	13.5
I_{im}	17.4	2.8	5.4	1.2	22.8	23.5	16.7

Table 9. Comparison of the mass-spectrum of C_3H_2N molecules ($I_{m.s.}$) and the impact dissociation spectrum (I_{im}) of $C_3H_2N^+$ ions (the relative intensities of the initial and fragment ions are quoted).

Ions	$C_3H_2N^+$	C_3HN^+	C_3N^+	C_3N^+ $C_3H_3^+$	C_3H^+	$C_3H_3^+$ CNH+	$C_3H_2^+$ CN+	C_3H^+
$I_{m.s.}$	29.5	12.6	3.2	2.6	1.7	7.1	39.4	3.9
I_{im}	36.0	12.2	1.3	3.4	1.4	6.3	36.2	3.2

A comparison of the impact dissociation spectra with the electron impact mass-spectra has also been made for a whole series of other molecular ions (derived from methane, ammonia, water, ethylene, n-octane, n-hexane, benzene, etc.). A significant similarity between the impact dissociation spectra of the ions with an energy of about 3–4 keV and the mass-spectra of the corresponding molecules follows from the data in Tables 8–10 and the

results published by Kupriyanov[57]. A similar phenomenon was noted also by other investigators[28]. Table 10 presents a section of the dissociation spectrum of benzene ions $C_6H_6^+$ and the corresponding section of the mass-spectrum of benzene itself[108]. The mass-spectrum was recorded for an electron energy of 70 eV. The kinetic energy of the $C_6H_6^+$ ions was 8 keV.

Table 10. Comparison of the mass-spectrum ($I_{m.s.}$) of benzene and the impact dissociation spectrum (I_{im}) of benzene ions (the relative intensities of the fragment ions are quoted).

m/e	68	67	66	65	64	63	62	61	55	54	50	40	39
$I_{m.s.}$	43	100	67	46	51	45	25	13	11	18	57	90	92
I_{im}	44	100	57	45	46	36	21	8	11	20	67	117	86

The similarity of the dissociation spectra and the mass-spectra has been noted in the literature for a whole series of other aromatic compounds. It has been shown[57] that the impact dissociation spectra of the $C_3H_6^+$ and $C_4H_8^+$ ions obtained by the ionisation of various molecules are not only close to one another, as can be seen from the data in Table 11, but they also resemble the mass-spectra of the corresponding C_3H_6 and C_4H_8 molecules.

Table 11*. Comparison of the mass-spectra of molecules and the impact dissociation spectra of ions obtained from different compounds.

Process	Dissociation spectra: Initial molecule			Mass-spectra		
	C_3H_6	C_4H_{10}	C_4H_{10}	*a*	C_3H_6	*b*
$C_3H_6^+ \rightarrow C_2H_m^+$	85	83	78	81		76
$C_3H_6^+ \rightarrow CH_k^+$	15	17	22	19		24
Process	**Initial molecule**					
	C_4H_{10}	C_5H_{12}	C_5H_{10}	*c*	C_4H_8	*d*
$C_4H_8^+ \rightarrow C_3H_n^+$	69	54	50	60		58
$C_4H_8^+ \rightarrow C_2H_m^+$	29	43	46	38		40
$C_4H_8^+ \rightarrow CH_k^+$	2	3	4	2		2

* The overall intensities were assumed to be 100.
a) Propene; *b*) cyclopropane; *c*) *cis*-but-2-ene; *d*) *trans*-but-2-ene; energy of the ions 3 keV; target—neon.

Such similarity of the mass-spectra of the ions suggests that in both cases, i.e. in impact dissociation of the ion and in the ionisation of the corresponding molecule by electrons, approximately identical excited ions are produced[109]; the mechanism of their dissociation is also the same.

The similarity of the mass-spectra has likewise been noted in other ion-formation processes, particularly in charge-transfer processes[110,111]. This problem has been examined in detail[112]. In all these instances the energy of the ions does not exceed several keV. For higher kinetic energies of the ions (about 20 keV and above), an appreciable difference is observed between the dissociation spectra of the ions and the mass-spectra of the corresponding molecules. This has been demonstrated for the dissociation of CH_4^+ ions[13,57,103], $C_2H_4^+$ ions,[103] and a number of other ions[13,57]. In these cases, the collisions of the ions with atoms and molecules lead to strong excitation of the ions, as a result of which they dissociate with abstraction of many hydrogen atoms (in the case of CH_4^+ ions) with the same probability as the dissociation involving the abstraction of a single hydrogen atom[13,57,103]. Therefore one should note that an increase of electron energy up to 12 keV does not lead to an intense decomposition of CH_4 molecules under electron impact of the kind observed for the dissociation of CH_4^+ ions on collision with heavy particles in the range of energies of the order of tens of kiloelectron-volts[114].

3. Characteristics of the Ion Dissociation Spectra

Table 12 shows that for each energy there are identical regions in the dissociation spectra of the initial ions containing different numbers of hydrogen atoms. This phenomenon, which we called the "inclusion" of the dissociation spectra of ions[114,115], occurs also for NH_3^+ and NH_2^+ ions[13] as well as certain other ions[57].

Table 12. Parameters of the dissociation spectra of various ions derived from methane for several (four) collision energies (the cross-section for the formation of the C^+ ion was assumed to be 1.0).

Dissociation products	Initial ions: CH_4^+	CH_3^+	CH_2^+	CH_4^+	CH_3^+	CH_2^+
	E_0=1350 eV (Ref.12)			E_0=3000 eV (Ref.12)		
CH_2^+	21	20	—	11	12	—
CH^+	4	5	4	3	4	3
C^+	1.0	1.0	1.0	1.0	1.0	1.0
	E_0=30 keV (Ref.13)			E_0=90 keV (Ref.13)		
CH_2^+	1.9	2.0	—	1.2	1.3	—
CH^+	1.3	1.3	1.3	1.0	1.0	1.0
C^+	1.0	1.0	1.0	1.0	1.0	1.0

Table 13 shows that the phenomenon of "inclusion" of the dissociation spectra is observed for the majority of processes. Thus the situation arises in which the dissociation spectra of ions containing a larger number of hydrogen atoms include the dissociation spectra of ions with a smaller number of hydrogen atoms.

The "inclusion" of spectra makes it possible to infer from the known mass-spectra of molecules obtained on electron impact the mass-spectra of radicals, which are as a rule unknown. In fact, since the spectra for dissociation on collision with molecules and the mass-spectra of molecules under electron impact are similar, presumably the phenomenon of "inclusion" will be observed also for neutral molecules. Table 14 presents the mass-spectra of methane and the radicals CH_3, CH_2, and CH calculated[57,115] from the methane mass-spectrum (b) and

determined experimentally[116] (a). Column c presents the parameters of the mass-spectra calculated from the mass-spectrum for CH_3 radicals.

Table 13. Parameters of the dissociation spectra of the ions obtained from propane (the cross-section for the formation of the CH_3^+ ion was taken to be 1.0).

Dissociation products	Initial ions					
	$C_3H_8^+$	$C_3H_7^+$	$C_3H_6^+$	$C_3H_5^+$	$C_3H_4^+$	$C_3H_3^+$
$C_3H_6^+$	5.2	5.9	—	—	—	—
$C_3H_5^+$	12.8	22.0	10.6	—	—	—
$C_3H_4^+$	2.4	2.3	3.9	0.7	—	—
$C_3H_3^+$	10.5	11.1	10.6	10.5	7.1	—
$C_3H_2^+$	1.9	1.8	2.0	1.9	2.0	1.3
C_3H^+	1.0	1.0	1.0	1.0	1.0	1.0

Table 14 shows that the mass-spectra of CH_3 radicals determined experimentally[116] and calculated[57,115] from the methane mass-spectrum agree satisfactorily. There are no experimental data for the mass-spectra of CH_2 and CH radicals. However, their calculated mass-spectra also agree with the dissociation spectra of CH_3^+ and CH_2^+ ions as well as the dissociation spectra of CH_4^+ and CH_3^+ ions. Therefore one may suppose that the experimental mass-spectra of the radicals are close to those whose parameters are listed in Table 14. Further experimental studies are necessary in order to extend this rule to the mass-spectra of other radicals.

Table 14. Parameters of the mass-spectra of methane and certain radicals (the relative cross-sections are expressed in arbitrary units).

Ions formed	Species ionised						
	CH_4	CH_3		CH_2		CH	
		a	*b*	*b*	*c*	*b*	*c*
CH_3^+	31	28	31	—	—	—	—
CH_2^+	6	9	6	6	9	—	—
CH^+	3	3	3	3	3	3	3
C^+	1	1	1	1	1	1	1

4. Dependence of the Ion Dissociation Cross-sections and Spectra on the Electron Energy and the Origin of the Ions

The impact dissociation cross-sections of polyatomic ions as well as those of diatomic ions increase with increase of the electron energy until the attainment of constant values. Fig. 8 illustrates the variation of the dissociation cross-section with electron energy in the ion source for $C_2H_3^+$ ions, which decompose via different channels[114]. The ion energy was 2.8 keV. The corresponding relations for other ions derived from ethylene and methane have also been examined[57,117].

Markedly different impact dissociation cross-sections were obtained for the dissociation of diatomic ions of different origins[65,76], which suggests an appreciable difference between the distributions with respect to excited states for identical ions from different molecules (see Section III). For polyatomic ions, the dissociation cross-sections of identical ions of different origins differ from one another to a lesser extent[10,118]. For example the dissociation cross-sections of the CH_3^+ ions obtained from CH_4 and n-butane are similar[10] and this is also true of the $C_2H_4^+$ ions obtained from C_2H_4, C_3H_8, and n-C_4H_{10}.[118] It is noteworthy that the internal excitation energy in a polyatomic ion can affect not only the total dissociation cross-section, as in a diatomic ion, but also the dissociation spectrum. It is seen from Fig. 8 that the total dissociation cross-section varies mainly as a result of the increase of the cross-section for dissociation processes with a low activation energy. The internal excitation energy has only a slight influence on the cross-sections for dissociation processes with a high activation energy. In order to achieve such processes, the initial ion must be strongly excited on collision and, in conformity with the considerations put forward in Section IV and the discussion of Fig. 6, such a highly excited ion will decompose mainly as a result of simple bond dissociation.

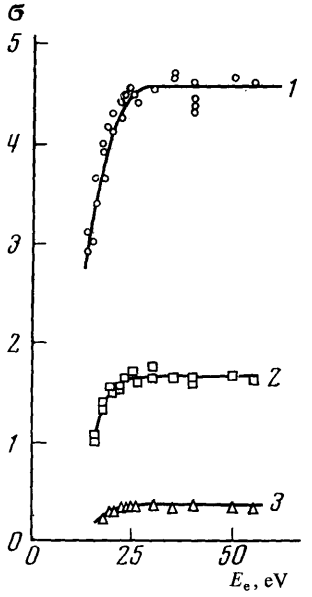


Figure 8. Effect of the electron energy E_e on the relative impact dissociation cross-sections of $C_2H_3^+$ ions: 1) $C_2H_3^+ \rightarrow C_2H_2^+$; 2) $C_2H_3^+ \rightarrow C_2H^+$; 3) $C_2H_3^+ \rightarrow C_2^+$.

Thus the relative yield of the fragments whose formation requires high energies will not depend markedly on the initial excitation energy but will be determined mainly by the structure of the initial ion. The differences between the dissociation spectra in the region of such fragments for identical ions of different origins indicate differences between the structures of these ions. This conclusion has been reached[119] on the basis of an analysis of the dissociation spectra of the $C_6H_7^+$ ions from cyclohexa-1,4-diene and methylcyclohexa-1,4-diene.

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Much less can be said about the specific mechanisms of the impact dissociation of accelerated polyatomic ions than about the dissociation of diatomic ions owing to the insufficiency of detailed information about the decomposition of polyatomic ions, which can be obtained from the angular and energy distributions of the fragments. In the general case the dissociation process can be divided into two stages. Initially, at the instant of collision between the accelerated ion and the target particle, the electronic and vibrational degrees of freedom of the ion are excited. The order of magnitude of the collision time τ is defined by the relation $\tau = \sqrt{\Sigma}/v_0$, where Σ is the total dissociation cross-section.

For the energies of the initial ions $E_0 \simeq 10^3$ eV, τ is approximately 10^{-15}–10^{-16} s. On the other hand, the time of the most rapid dissociation is 10^{-13} s. Therefore in the second stage the isolated molecular ion excited by collision decomposes in accordance with the quasiequilibrium theory of mass-spectra.

The principal experimental characteristics of the impact dissociation of polyatomic ions can be briefly generalised by the following postulates:

1. The dissociation spectra of polyatomic ions depends only slightly on the nature of the neutral target. They are determined by the structure and energy of the excited ions and also by their kinetic energy.
2. The dissociation spectrum is independent of the electron energy in the ion source for $E_e \geqslant 30$ eV. The excitation of the initial molecular ion greatly affects dissociation processes with a low activation energy and only weakly influences dissociation processes with a high activation energy.
3. The total dissociation cross-section depends on the ion dissociation energy. The more stable the given structure the smaller the total dissociation cross-section of the given ion, other conditions being equal.
4. For many ions derived from saturated hydrocarbons, the total cross-section is an additive function of the number of CH_2 groups in the ion.
5. The impact dissociation spectra of the ions and the mass-spectra of the corresponding molecules under electron impact are similar under certain conditions.
6. Similar dissociation spectra have been obtained for many ions differing from one another only in the number of hydrogen atoms (the "inclusion" of the spectra).
7. The decomposition of ions via different channels proceeds with similar probabilities for higher kinetic energies of the ions.

On the basis of these empirical characteristics, it is possible to reach conclusions, admittedly so far qualitative, about the differences or similarities between the structures of ions of identical composition obtained in different ionisation processes. Examples of this kind for the $C_3H_6^+$ ions from cyclopropane and propene and the $C_4H_{10}^+$ ions from n-butane and isobutane can be found in Kupriyanov's thesis[57] and those for the $C_3H_7^+$ ions from different compounds are quoted by Haddon and McLafferty[120]. Table 15 compares the dissociation spectra of the molecular ions from n-butane and isobutane[57].

Evidently these spectra differ markedly for both spontaneous and impact dissociation. This suggests that the structures and excitation energies of the $C_4H_{10}^+$ ions obtained by the ionisation of n-butane and isobutane molecules are different. It is noteworthy that further investigation and accumulation of experimental data are necessary to refine the characteristics of the impact and spontaneous dissociation of polyatomic ions. In particular, the problem of the individual influence of the excitation energy and structure of the ions on their total dissociation cross-section and dissociation spectrum is of interest. The results available at present suggest that the excitation energy probably affects the total dissociation cross-section to a greater extent, while the structure has a greater influence on the dissociation spectrum of the ions. Under real experimental conditions, the beam of the initial ions may contain ions with different structures and excitation energies and the observed differences in the impact dissociation pattern of such ions reflect the differences in the distribution of the initial ions with respect to structure and excitation energy. More careful experiments with allowance for the above factor are needed to solve this problem. In this sense mass-spectrometric study of the photodissociation of ions formed by the photoionisation of molecules with simultaneous analysis of the dissociation products with respect to the angle at which they are ejected and the kinetic energies is promising.

Table 15*. Parameters of the dissociation spectra of the ions obtained from n-butane and isobutane (relative cross-sections).

Decomposition process	n-Butane		Isobutane	
	a	*b*	*a*	*b*
$C_4H_{10}^+ \rightarrow C_3H_7^+$	0.9	9.5	0.1	6.3
$C_4H_{10}^+ \rightarrow C_3H_6^+$	0.9	2.4	0.9	7.5
$C_4H_{10}^+ \rightarrow C_3H_5^+$	0	1.3	0	2.0

* *a*) Spontaneous decomposition spectrum; *b*) impact dissociation spectrum for an ion energy of 3.0 keV; target—air.

The study of spontaneous, induced, and impact dissociation of ions may be called, by analogy with the mass-spectrometry of molecules, the mass-spectrometry of ions if one understands by this the employment of mass-spectrometric techniques for the measurement of the masses and intensities of the ions formed and for the analysis of the structures and excitation energies of the ions obtained in different processes and from different compounds. Thus mass-spectrometry of ions is a new method for the analysis of their structures and excitation energies. It can be used to measure the mass-spectra of ions (by a procedure similar to the measurement of the mass-spectra of molecules), the ionisation potentials and dissociation energies of ions, and other characteristics.

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