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The Specific Features of the Interaction of Ionising Radiation with a Molecular Medium and the Role of Tracks in Radiation Chemistry

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The interactions of charged particles with a molecular medium are surveyed and the highly excited molecular states arising under these conditions are discussed. The processes involving the absorption of energy in a condensed phase and the role of collective excitations are considered in detail. The relation between the structure of the track and the characteristics of the radiation-chemical reactions in the tracks of particles of different kinds is analysed.
The bibliography includes 170 references.

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I. INTRODUCTION

When charged particles pass through a substance, their interaction with the atoms and molecules of the medium results in energy transfer to the medium. This energy is consumed mainly in the excitation and ionisation of the medium. The energy of slow, heavy particles is converted into the kinetic energy of the movement of the atoms of the medium. In solids, when the transmitted kinetic energy is sufficiently large, atoms can be dislodged from their equilibrium positions. As a result, regions with a damaged structure are formed in the irradiated medium in which molecular excited states, positive and negative ions, and secondary electrons dislodged from atoms and ions are localised. All these defects are concentrated along the trajectory of the primary particle and form a track in the given substance. Since the effect of hard electromagnetic radiation on matter involves the dislodgement of fast Compton electrons and photoelectrons, the tracks of X-rays and γ-rays reduce to the tracks of fast electrons distributed throughout the specimen.

The tracks of α-particles and the electrons dislodged by X-rays were first observed visually in the Wilson cloud chamber. Subsequently bubble and spark chambers were developed. Detectors based on the determination of the change in the structure of the specimen by treating the latter with appropriate chemical reagents have come to be widely used for the detection of tracks. They include primarily photoemulsions and also different types of solid detectors.[1]

Experimental observations of tracks yield in the first place information about the charged particle itself (mass and charge) and play an important role in the identification

of unknown elementary particles. As regards the characteristics of the track of the particle, they make it possible to measure only the ionisation density in gases along the track and to find specific energy losses. However, such information is quite inadequate to explain the changes which occur in the molecular medium on passage of ionising radiation. The microstructure of the short-lived regions of primary excitations and ionisations along the particle track is of decisive importance for the final chemical reactions. In order to achieve agreement between the theoretical model of the radiolysis of water and experimental data, it was necessary to take into account the non-uniform distribution of the active intermediate species in the electron tracks.[2,3]

The spectrum of the states arising on exposure of the medium to ionising radiation is much more complex than in the case where the medium is irradiated with light. The former includes states in the region of the continuous spectrum corresponding to the ionisation of electrons from the inner shells of the molecules with subsequent cascade of ionisations owing to the "shake-up" and Auger effects, the collective states of the plasmon type, and the so-called "superexcited" states.[4] All these states are short-lived, decomposing after 10^{-16}–10^{-12} s into active intermediates which initiate the chain of radiation-chemical reactions.

Since the instantaneous picture of the primary distribution of excitations on ionisation cannot be measured directly, it is investigated by numerical experiment on a computer. The passage of ionising radiation through matter is modelled with the aid of the statistical test method (the Monte Carlo method). In order to model the passage of radiation, it is necessary to know the excitation and ionisation cross-sections of the molecules.

Computer modelling makes it possible to find the spatial and energy distribution of the dislodged electrons and the densities of the ions and excited states generated at different distances from the axis of the particle track. The spatial-energy structure of the tract is a characteristic of the radiation which contains much more information than the usually employed characteristic—the linear energy loss (LEL). Knowing the structure of the track, it is possible to identify the characteristics of the primary radiation-chemical reactions in the tracks of particles of different kinds.[5] The evolution of ideas about the role of tracks in radiation chemistry can be traced in the relevant reviews.[6,7]

In the present review we have endeavoured to deal with the entire set of questions associated with the primary stage of radiolysis and its influence on the subsequent chemical reactions. The consecutive pattern of the physicochemical processes arising in the medium on irradiation is examined: from the initial physical stage of the radiolysis, in the discussion of which much attention has been devoted to the specific features of the condensed phase which are not usually taken into account, to the subsequent physicochemical stage. Much space has been devoted to the discussion of the relation between the structure of the track and the character of the radiation-chemical reactions occurring in it.

II. INTERACTIONS OF CHARGED PARTICLES WITH ATOMS AND MOLECULES

Since numerous books and reviews (see, for example, Refs. 8–13) have been devoted to the interactions of charged particles with an atomic-molecular medium, we shall confine ourselves in the present review to a brief discussion of the question and shall quote a series of formulae used in calculations of the degradation of the energy of the charged particles in the medium.

Fairly simple analytical expressions for the inelastic scattering cross-sections are valid in the case of fast particles, whose velocity is high compared with the velocities of atomic electrons [the energy of the particle $E \gg (M/m)E_b^a$, where M is the mass of the particle, m the mass of the electron, and E_b^a the binding energy of the electron in the atom]. For a sufficiently high transmitted energy $\varepsilon \gg I_n$ (where I_n is the potential of ionisation from the nth electron shell), the dislodged electron can be regarded as free and the scattering cross-section is defined by the familiar Rutherford formula

$$d\sigma = (2\pi Z^2 e^4/mv^2\varepsilon^2)\,d\varepsilon, \qquad (1)$$

where Z and v are the charge and velocity of the arriving particle. Such collisions have come to be referred to as short-range or knockout collisions. For energy transfers leading to the excitation of an atom or molecule to the nth quantum state from the initial zero-point state with a transition energy $\hbar\omega_{0n}$ (such collisions are referred to as long-range or glancing collisions), the cross-section is estimated from the Bethe formula[9]

$$d\sigma_{0n}(q) = (4\pi Z^2 e^4 f_{0n}(q)/mv^2\hbar\omega_{0n}q)\,dq \qquad (2)$$

where $\hbar q$ is the absolute magnitude of the transmitted momentum and $f_{0n}(q)$ the generalised oscillator strength introduced by Bethe.[9] The generalised oscillator strengths as well as semiempirical formulae for the ionisation cross-sections and total non-elastic scattering cross-sections may be found in a series of publications.[12–17]

For polyatomic molecules, the ionisation cross-section can be represented by an additive quantity. For the H_2O molecule, the experimental ionisation cross-sections in the electron energy range from 0.1 to 20 keV have been expressed[18] in the form $\sigma_i(H_2O) = \sigma_i(H_2) + \frac{1}{2}\sigma_i(O_2)$. The differences between such additive cross-sections and the experimental cross-sections are insignificant over the entire calculated range. It has been shown[19] that the ionisation cross-section of a molecule can be quite accurately represented by the sum of the ionisation cross-sections of the chemical bonds. Having analysed the experimental data for the ionisation cross-sections of 40 hydrocarbon molecules of different kinds, Grosse and Bothe[19] calculated the effective ionisation cross-sections of the C–H, π(C–C), σ(C–C), C–O, and other bonds. The values obtained make it possible to represent approximately the ionisation cross-section of an arbitrary molecule with the given chemical bonds to within 2%. Such additivity had been observed earlier in another study.[20]

In the investigation of the effect of charged particles on matter, it becomes necessary not only to estimate the cross-sections but also to find the probabilities of the excitation or ionisation of a species as a function of its distance from the axis of the track (the impact parameter) ρ. For this purpose, one uses a quasi-classical approach, according to which it is assumed that the charged particle moves along a definite trajectory, is structureless, and can be regarded as merely the source of a variable electromagnetic field. This approach is most legitimate for heavy charged particles.

The trajectory of a heavy charged particle in a substance is to a large extent linear, since, with the exception of the knock out collisions, the interaction with the atoms of the medium hardly causes a curvature in its path. For long-range collisions, one can find in this instance the dependence of the probability of the excitation of the nth quantum state of the atom (molecule) on the impact parameter ρ. The expansion of the Coulombic interaction operator into a multipolar series and the restriction of the latter to the dipolar term lead to the following expression for the probability of the transition of the system to the nth quantum state in terms

of the first-order perturbation theory:[21]

$$W_{0n}(\rho) = (Z^2e^4/\hbar^2)\left|\int_{-\infty}^{\infty}\frac{x_{0n}vt + y_{0n}\rho}{[(vt)^2+\rho^2]^{3/2}}\exp(i\omega_{0n}t)\,dt\right|^2, \quad (3)$$

where

$$x_{0n} = \sum_{i=1}^{N}\langle\psi_n|x_i|\psi_0\rangle; \quad y_{0n} = \sum_{i=1}^{N}\langle\psi_n|y_i|\psi_0\rangle, \quad (4)$$

ψ_n and ψ_0 are the wave functions of the N-electron system, and the x axis is directed along the trajectory of the incoming particle. The integrand decreases in inverse proportion to the cube of the distance from the axis of the tract and the interaction is therefore significant only in the region of distances of closest approach.

It can be shown that the effective collision is $\tau \cong 2\rho/v$. The collision is regarded as adiabatic if the collision time is much greater than the period of the quantum transition $2\pi/\omega_{0n}$, i.e. the inequality

$$\omega_{0n}\rho/\pi v \gg 1 \quad (5)$$

holds. In this case the integrand in Eqn.(3) oscillates repeatedly during the period of the collision and the integral is close to zero. Consequently atoms are not excited in an adiabatic collision.

The condition specified by inequality (5) is too strong: the "much greater than" sign should be replaced by the "greater than" sign, i.e. for excitation it is sufficient that the effective collision time should be less than the quantum transition time. To demonstrate this rigorously, it is necessary to calculate integral (3). After representing the exponential function in the integrand by a cosine and a sine using Euler's formula and integrating by parts, we obtain

$$W_{0n}(\rho) = \frac{4Z^2e^4\omega_{0n}^2}{\hbar^2v^4}[|x_{0n}|^2K_0^2(\eta) + |y_{0n}|^2K_1^2(\eta)] \quad (6)$$

where $\eta = \omega_{0n}\rho/v$ and $K_0(\eta)$ and $K_1(\eta)$ are modified Bessel functions (Macdonald functions[22]). For $\eta = \pi$, the functions $K_0^2(\eta)$ and $K_1^2(\eta)$ are almost zero (see the graph on p.196 of Ref.22). After setting $\eta = \pi$, we find the effective size of the region of direct excitations:

$$b_{\text{eff}} = \pi v/\omega_{0n}. \quad (7)$$

Thus the excitation has an appreciable probability for $\rho \leq b_{\text{eff}}$.

According to Eqn.(2), the excitation cross-section is proportional to the oscillator strength of the quantum transition. The latter is non-zero only for transitions without a change in the total electron spin. Since the ground state of the molecules is of the singlet type [only the O_2 ($S = 1$) and NO ($S = 1/2$) molecules are exceptions], a fast charged particle excites only singlet states on interaction with a molecule. As in irradiation by light, the triplet states are then populated via radiationless intersystem crossing transitions S → T.[23,24] Further, we may note that in the calculations of the cross-sections described above no account was taken of the terms due to electron exchange. When these terms are taken into account, the probability of the excitation of triplet states is not zero. The excitation cross-section for a triplet state has been shown[25] to be proportional to E^{-3}, i.e. it decreases very rapidly with increase of the electron energy (while the excitation cross-section for singlet states is proportional to $E^{-1}\ln E$). The excitation of triplet states is therefore effective only for low electron energies. Ochkur's formula[25] has been modified by Rudge[26] and calculations of the excitation of triplet states by the Ochkur–Rudge formula can be found in two communications.[27,28]

Molecules in triplet states exhibit an enhanced reactivity and are longer-lived and it is therefore important to estimate the relative probability of triplet excitations. One of the authors of this review showed[29] that, when a substance is irradiated by a stream of charged particles, at least two additional mechanisms for the population of triplet states appear compared with irradiation by light. In the first place, there is the generation of triplet states on recombination of a positive ion with a thermalised electron. As a consequence of the high statistical weight of the triplet state, the probability of the formation of a molecule in this state is three times greater than in the singlet state.[30] The second possibility arises because slow electrons with $E < 100$ eV, which effectively excite triplet states, predominate in the spectrum of secondary electrons. In this respect the most favourable conditions are created on irradiation with heavy ions, since, having as a rule low velocities, the latter generate low-energy secondary electrons. As a result, the role of triplet states in radiation-chemical processes should be much greater than in photochemistry.[29] Experimental evidence for this, based on the measurement of the relative phosphorescence and fluorescence yields, has been published.[31]

Any electron whose energy is less than the lowest electronic excitation level of the medium is referred to as a "subexcitation electron". It is not able to transfer its energy for the excitation of electrons, but its energy is sufficient to excite molecular vibrations and rotations. Furthermore, subexcitation electrons can lose energy in elastic collisions and also in processes involving their capture by a molecule or a positive ion. The behaviour of subexcitation electrons therefore depends on the process which predominates in the given medium (see Section VI below).

III. THE NATURE OF THE HIGHLY EXCITED MOLECULAR STATES ARISING ON EXPOSURE TO IONISING RADIATION

In contrast to photochemistry, in radiation chemistry the energy of the radiation is so high that the transfer to molecules of energy greatly exceeding their ionisation potential becomes possible. This results in the formation of both discrete high-energy states in the autoionisation region of the spectrum (the so-called "superexcited" states—see below) and states in the region of continuous spectrum which arise owing to the ionisation of electrons in the inner shells of the molecule and are accompanied by the appearance of the corresponding vacancies ("holes"). An ion with a vacancy in an inner shell must be regarded as in a highly excited state with energy equal to the reorganisation energy of the electron shell of the molecule on formation of the vacancy. This energy can be either transmitted to one or several electrons of the molecule with a subsequent ionisation or transfer to unoccupied orbitals (the Auger effect[32–34]—see Fig.1) or can be radiated in the form of an X-ray quantum.

Repeated ionisation is characteristic of molecules consisting of light atoms on dislodgement of an electron from an inner shell, whereas fluorescence begins to be manifested appreciably only for elements with an atomic number $Z_a > 30$. The ratio of the probabilities of the Auger effect and X-ray fluorescence is $W_a/W_r \cong 10^6/Z_a^4$.[32] Table 1 lists the probabilities W_a and W_r, the width of the levels ΔE, and the yields of the fluorescence associated with the K–LL transition for a series of atoms. For light elements (and also for their chemical compounds), the probability of emission is very low, while for heavy elements the opposite behaviour is observed. Thus the K-fluorescence yield is 0.96 for thallium ($Z_a = 81$).[32]

Although processes involving the dislodgement of an electron from inner shells take place much more rarely than those where an electron is dislodged from outer shells (the degradation spectrum is displaced towards low-energy electrons), their role is very important owing to the high probability of the subsequent repeated ionisation. The yield of ionisation from the K shells of light elements has been estimated[35] as $g_K \cong 10^{-2}$ per 100 eV of the absorbed energy, i.e. the absorption by the medium of an electron having an energy of 1 MeV results in the formation of approximately 10^2 ions with a hole in the K shell. For comparison, we may point out that the average number of ions formed under these conditions is approximately 3×10^4, since approximately 30 eV is consumed in the formation of a pair of ions. However, the abstraction of a K electron causes a cascade of subsequent ionisations.

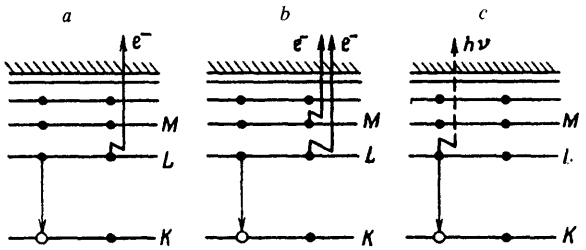


Figure 1. The possible forms of the evolution of the state with a vacancy in the K shell: *a*) KLL–Auger effect; *b*) double $KLIM$–Auger effect; c) emission of the K_α X-ray line. In processes *a* and *b* the electron can pass to an unoccupied orbital instead of undergoing a transition to the continuous spectrum.

Table 1. The probabilities of the radiative and Auger–KLL transitions for different atoms.[32]

Atom	z_a	$10^{-14} W_a$, s^{-1}	$10^{-14} W_r$, s^{-1}	ΔE, eV	$W_r/(W_a+W_r)$
Ne	10	7.40	0.063	0.98	0.0085
Mg	12	8.07	0.130	1.07	0.016
Ar	18	11.29	0.83	1.59	0.068
Ni	28	12.23	4.85	2.24	0.284
Kr	36	13.46	14.39	3.65	0.517

There are two physical mechanisms leading to ionisation on formation of a vacancy in an inner electron shell. One of these is due to the "shake-up" of the electron shell on dislodgement of an inner electron. On dislodgement of an inner electron the sharp change in the electromagnetic field in which the outer electrons move leads to additional ionisation (for a more detailed description of the "shake-up" mechanism, see the review of Matveev and Parilis[33]). The other mechanism is due to the Auger effect,[32] where an electron is transferred from one of the higher orbitals to an unoccupied inner orbital and the energy evolved is transferred to one or several outer electrons (see Figs. 1*a* and 1c). This process can be regarded as internal conversion of the quantum of electromagnetic radiation emitted on transition of an electron from an upper to a lower level. The Auger effect occurs after the formation of a vacancy over a period of 10^{-15}–10^{-11} s (depending on the extent to which the transitions are allowed), while the "shake-up" of the electron shell accompanies the formation of a vacancy and takes place over a period of 10^{-16}–10^{-15} s. Both mechanisms contribute to the formation of multicharged ions.

Table 2. The relative yields of ions with different numbers of charges on irradiation of neon with X-rays.[36]

Ion	Ne^+	Ne^{2+}	Ne^{3+}	Ne^{4+}	Ne^{5+}
Yield, %	6.5±0.7	68.5±2.0	22±2	2.8±0.5	0.3

The probability of repeated ionisation on dislodgement of an electron from the K shell is very high. For example, it is almost 99% for neon ($Z_a = 10$). When an L electron is dislodged, the probability of ionisation diminishes to 13%.[36] Table 2 lists the relative yields of Ne ions with different numbers of charges on irradiation of the gas with X-rays (K_α Al line with $E = 1256$ eV). The overall yield of multicharged ions is 93.5% (its value less than 99% is due to the ionisation from L and higher shells). A similar distribution is to be expected also for light molecules. For heavier elements, the probability of the formation of ions with the number of charges $n \geq 4$ becomes greater than for doubly charged ions.[37]

The repeated ionisation of molecules on dislodgement of electrons from inner shells can lead to their decomposition into several positively charged fragments and can ultimately give rise to a sequence of reactions different from that in photochemistry. According to estimates,[38] this effect should increase in the ultra-relativistic range of energies of the incoming particles. It is also noteworthy that, among states with an internal vacancy, highly excited states of an ion, which are not populated on irradiation with light, are in fact populated (for example, there is a possibility of the formation of N_2^+ in the $C^2\Sigma^+$ state[39]).

The excitation of atoms to discrete states with energies higher than the first ionisation potential I_1 generally leads to autoionisation, which can be explained by the fact that in the case of atoms autoionisation takes place over a period of 10^{-14}–10^{-11} s, while the duration of emission, which is the only competing process, is 10^{-9}–10^{-6} s. Emission from autoionisation states takes place only in rare instances. Thus the autoionisation peaks for the O atom at $\lambda = 878$–879 and 791–793 Å are characterised by an ionisation efficiency $\eta(E) < 1$. Prohibitions owing to selection rules lead to lifespans of these states $\tau = 10^{-8}$ s, which makes possible their radiative decay.[40] For atoms, this is exceptional, but the situation is different for molecules.

Platzman[4] drew attention to the fact that, according to experiments on the irradiation of molecular gases by vacuum ultraviolet light, the probability of the ionisation of certain gases $\eta(E) < 1$ when $E > I_1$ (for E exceeding I_1 by 10 eV and more). These results were confirmed by experiments[41] on mixtures incorporating a noble gas and various molecules. An isotope effect is then observed. The replacement of hydrogen by deuterium led to an increased probability of

ionisation. Hence Platzman concluded that there is an effective competition between autoionisation and predissociation. Platzman used the term "superexcited states" for discrete states with $E > I_1$ in which predissociation takes place (see the relevant reviews[7,42]). Subsequently we shall use the abbreviation SES for such states.

As a consequence of vibronic interactions, there is a possibility of yet another non-ionisation channel leading to the decomposition of SES—radiationless relaxation via the conversion of the electronic energy into the vibrational energy of molecules and, in the case of a condensed phase, into the thermal energy of the medium. For fluorescent molecules, there is a possibility of fluorescence from the lowest excited state (in conformity with Kasha's empirical rule,[43] the molecular fluorescence originates from the lowest excited level regardless of the wavelength of the exciting light).

The SES formation and decomposition reactions can be represented schematically as follows:

$$\mathrm{ABC} \xrightarrow{h\nu > I_1} \begin{cases} \longrightarrow \mathrm{ABC^+} + \mathrm{e^-} & \text{(direct ionisation);} \quad (8a) \\ \longrightarrow \mathrm{ABC^{**}} & \text{(formation of SES);} \quad (8b) \end{cases}$$

$$\mathrm{ABC^{**}} \begin{cases} \longrightarrow \mathrm{ABC^+} + \mathrm{e^-} & \text{(autoionisation);} \quad (9a) \\ \longrightarrow \mathrm{AB^\bullet} + \mathrm{C^\bullet} & \text{(predissociation);} \quad (9b) \\ \longrightarrow \mathrm{ABC} + \Delta E'_{vib} + h\nu_1 & \text{(radiative relaxation);} \quad (9c) \\ \longrightarrow \mathrm{ABC} + \Delta E_{vib} & \text{(radiationless relaxation).} \quad (9d) \end{cases}$$

In the optical approximation for small molecules, the radiation yield of SES is estimated as being within the limits $g_{SES} \cong 0.6$–1.[44] Analogous estimates have been made also by Bednar.[35]

The important role of SES in radiation chemistry consists in the fact that their decomposition involves the formation of highly excited products (radicals). Such "hot" radicals can enter into endothermic reactions. In his first fundamental study, Platzman[4] already pointed out the possibility of a reaction with direct formation of the molecular product:

$$\mathrm{H^\bullet} + \mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{OH}. \quad (10)$$

A series of data indicate that molecular hydrogen is formed by an analogous pathway in the radiolysis of hydrocarbons.[42]

Three possible pathways leading to the formation of SES can be considered: (1) the excitation of an electron in an inner shell to an unoccupied orbital; (2) the formation of a Rydberg state, these are a sequence of hydrogen-like levels converging to the ionisation potential $I \geq I_1$; (3) excitation of two valance electrons.

Owing to their short lifespan, the states of the first type decompose via the Auger mechanism and cannot be classified as SES, since the latter are neutral. Hydrogen-like excited states, referred to as the Rydberg states, are much longer-lived. At any rate, this is the case when I is not very large, i.e. a hole is formed in the valence shell (although deeper valence levels can also be involved). The interaction of the electronic and vibrational movements leads to predissociation. In the Rydberg state the electron is sufficiently remote from the positive ion and moves more slowly, which ensures the exchange of the electronic and vibrational energies.

A special case of SES consists of highly excited vibrational Rydberg states converging to I_1. The vibrational quanta added to the electronic energy (which is less than the ionisation potential) cause the transition of the electron to the state with $E > I_1$. Most of the autoionisation thresholds for E which exceed I_1 by several electron-volts, have a vibronic, Rydberg origin.[40] In these states predissociation competes with autoionisation as a result of which $\eta(E)$ becomes less than unity. Such a possibility of the appearance of SES was first pointed out in a review by one of the present authors[7] and also by Nishikawa and Watanabe.[45] The role of Rydberg states in radiation chemistry has been discussed in two communications.[46,47]

The energy levels of the Rydberg states are described by the "hydrogen-like" formula

$$E_n = e^2/2a_0(n-\delta_R)^2, \quad (11)$$

where n is the principal quantum number, δ_R the Rydberg shift of the level, and a_0 the Bohr radius. Eqn.(11) is valid for molecules for low values of n, when the distance between the electronic levels greatly exceeds the distance between the rotational and vibrational levels. With increase of n, the adiabatic approximation ceases to be valid. The interaction of the Rydberg electronic states with the rotational-vibrational movement leads to a marked broadening of the lines and the Rydberg spectrum becomes almost continuous. As a result, the lifespans of the molecular Rydberg states are smaller by many orders of magnitude than those of the atomic states. Thus the width of the Rydberg level in the H_2 molecule is 1–5 cm^{-1} for autoionisation, where $n = 8$–11,[48] which corresponds to $\tau = \hbar/\Delta E \cong 10^{-12}$ s, i.e. is of the order of magnitude of the vibrational period.

The lifespan of the Rydberg states increases significantly when they are characterised by a large angular momentum l. Fano[49] showed that, when the energy of the incoming electron exceeds by several electron-volts the ionisation potential, then the formation and subsequent decomposition of the intermediate negative complex can result in the appearance of Rydberg states with a high orbital momentum l.[50] Owing to the appearance of a centrifugal barrier, the lifespan of such states increases greatly both relative to the autoionisation and predissociation states and relative to the radiative transition times. Evidently the nature of the Rydberg states where $\tau = 10^{-5}$–10^{-4} s, which had been observed[51,52] for N_2, O_2, CO_2, NH_3, etc., is apparently the same. It must be emphasised that these long lifetimes have been recorded in a rarefied gas, while in a condensed phase the situation may be different.

The interaction of Rydberg levels with the vibrational-rotation motion in diatomic molecules has been investigated by Golubkov and Ivanov.[53] Rydberg states with a hole in an inner shell have not so far been considered theoretically. The behaviour of Rydberg states in a condensed phase likewise still remains virtually uninvestigated. In this case the demoninator in Eqn.(11) for the energy should include the dielectric constant of the medium $\varepsilon(\omega)$, since the radius of the Rydberg state can reach hundreds of Ångstroms and for this reason there may be numerous molecules between the positive ionic residue and the electron. It is still not clear to what extent the lifespan of the Rydberg states would decrease under these conditions.

The measurement of the intensity of the luminescence of the decomposition products as a function of the energy of the ionising radiation is an effective method for the identification of SES. A series of such measurements have been made.[54,55] Thus, after irradiating hydrocarbons with electrons, it has been shown that, when $E > I_1$, lines of the Balmer series for the H atoms appear, i.e. H* is formed. For CH_4, the threshold corresponding to the appearance of the Balmer lines is 21.8 eV, which greatly exceeds the ionisation potential $I_1 = 12.51$ eV. The intensity of the lines then diminishes consistently with increasing number of the lines n, which indicates the Rydberg nature of the SES formed on excitation of the inner valence electrons from non-bonding orbitals.

Experimental data demonstrating unambiguously the formation of SES on two-electron excitation have been published.[55] Measurements of the probabilities of the absorption of energy and ionisation showed that $\eta(E) < 1$ is observed for CH_4 in the range of energies from 27 to 80 eV. Since the highest ionisation potential of the valence electrons is 21.3 eV and the next potential corresponds to the ionisation of the K shell and is in the region of 290 eV, the formation of SES in the given instance corresponds to the excitation of two or more electrons.

Thus, among the three possible pathways dealing with the formation of SES the last two are actually realised.

IV. ENERGY LOSSES OF A CHARGED PARTICLES IN A CONDENSED MEDIUM. COLLECTIVE STATES.

1. Ionisation Energy Losses by a Charged Species

Over most of the path traversed by fast charged species, the energy losses in the excitation and ionisation of the electrons of the medium make the main contribution to the retardation of such a species; these energy losses have come to be referred to as ionisation losses. Numerous publications have been devoted to the determination of the ionisation losses (see, for example, the relevant monographs[8-10, 56-58]). Among the various methods for the calculation of ionisation losses, the commonest is the Bethe–Bloch method, according to which the medium is considered to be an *ensemble* of independent atoms (molecules). The average ionisation losses per unit length of the path traversed were formulated thus:

$$S_e = -(\mathrm{d}E/\mathrm{d}x)_e = n_0 \sum_n \hbar\omega_{0n}\sigma_{0n}, \qquad (12)$$

where n_0 is the density of the species constituting the medium and the summation includes integration with respect to continuous states. Using for σ_{0n} the formulae obtained within the framework of the Bethe theory for S_e, it is possible to obtain the following expression ($v/c \ll 1$) [10]

$$S_e = (4\pi Z^2 e^4 n_0 Z_a/mv^2) \ln (2mv^2/\bar{I}_a), \qquad (13)$$

where $\bar{I}_a$ denotes the average excitation potential of the atoms of the medium, introduced in accordance with the relation

$$Z_a \ln \bar{I}_a = \sum_n f_{0n} \ln (\hbar\omega_{0n}). \qquad (14)$$

The quantity $\bar{I}_a$ is best determined experimentally, although methods have been developed for its calculation (see the relevant review[59]). Formulae for S_e taking into account the relativistic effects have been published.[8,56]

For molecular media and high energies of the charged species, the values of S_e can be calculated according to the Bragg rule by means of an additive scheme. Z_a and $\bar{I}_a$ in Eqns.(13) and (14) are then replaced by N_m and $\bar{I}_m$ in conformity with the expressions

$$N_m = \sum_a n_a Z_a; \quad N_m \ln \bar{I}_m = \sum_a n_a \ln \bar{I}_a, \qquad (15)$$

where n_a is the number of atoms of type a in the molecule.

For velocities of the charged particles slightly exceeding the velocities of the valence electrons, the Bragg rule does not hold. For protons, appreciable discrepancies appear already for energies below 150 keV.[60] In calculations of S_e in such cases, it is essential to introduce corrections for the effect of the binding of electrons (for details, see Starodubtsev[56] and Ahlen[59]).

In a condensed medium, for high velocities of the charged particles, the excitation condition (7) is fulfilled when the impact parameter ρ has values significantly exceeding the average distance between the molecules. As a consequence of the polarisation of the medium by the moving charged particle, the interaction of the latter with distant molecules is weakened. As a result, the real energy losses become smaller than the values calculated by Eqn.(13) as the simple sum of the energy losses in individual collision steps.

One way of taking into account the influence of the macroscopic properties of the medium on the retardation of the charged particles is to introduce the dielectric constant of the medium $\varepsilon(\omega)$ into the differential cross-section for the inelastic interaction.[14,61] In the general case the linear response of the system to the electric field of the charge is defined in terms of the dielectric constant, which depends on the frequency and the wave vector $\varepsilon(\mathbf{q}, \omega)$. The quantity $\varepsilon(\mathbf{q}, \omega)$ is an extension (to fields which vary in space) of the dynamic dielectric constant $\varepsilon(\omega)$. The probability, referred to unit time, of the transfer of the momentum $\mathbf{q}$ and the energy $\hbar\omega$ (in terms of the Born approximation) from the charged particle to the electrons of the system is defined by the imaginary component of the reciprocal of the dielectric constant:[62]

$$W(q, \omega) = \frac{8\pi Z^2 e^2}{\hbar q^2} \operatorname{Im}\left[\frac{1}{\varepsilon(q, \omega)}\right] = \frac{8\pi Z^2 e^2}{\hbar q^2} \cdot \frac{\varepsilon_2(q, \omega)}{\varepsilon_1^2(q, \omega) + \varepsilon_2^2(q, \omega)}, \qquad (16)$$

where $\varepsilon_1(\mathbf{q}, \omega)$ and $\varepsilon_2(\mathbf{q}, \omega)$ are the real and imaginary components of the dielectric constant.

Eqn.(16) is used as the initial expression in the macroscopic consideration of the energy losses by the particle in its interaction with the electron gas. In recent years this expression has come to be used also for the calculation of the energy losses in molecular liquids (particularly in water[63]). However, the calculation of the energy losses by Eqn.(16) is extremely difficult because the explicit form of the function $\varepsilon(\mathbf{q}, \omega)$ is as a rule unknown (the electron gas is an exception).

2. Excitation of Collective States of the Plasmon Type in a Molecular Medium

In the condensed phase, broad, intense maxima in the range 15–25 eV appear in the energy loss spectra of fast electrons apart from the absorption maxima and energies close to the electronic transition energies in isolated molecules (Fig.2). These maxima have come to be referred to as the excitation of collective states of the plasmon type. The plasmon states are delocalised, i.e. they characterise the states of the entire assembly and not of individual molecules and their lifespan is short.

A theory of plasmon states has been devised by Bohm and Pines for free electrons in metals[64] and is fully consistent with experimental data for inelastic energy losses by fast electrons in metallic films. Although the possibility of collective excitations of the plasmon type in molecular media was pointed out by Fano as early as 1960,[65] this question remained controversial for a long time (see the relevant discussion in a number of communications[7,47,66]). In 1974 Brandt and Ritchie (quoted by Kutcher and Green[66]) formulated the criteria which must be satisfied by the dielectric function of the medium in the vicinity of the plasmon absorption point, while Heller et al.[67] showed that the criteria of Brandt and Ritchie are satisfied for a broad absorption peak in water with a maximum at 21.4 eV. Subsequently absorptions of the plasmon type were observed also in other molecular liquids[68] and in solid films.[83]

We shall deal briefly with the nature of the plasmon vibrations. Plasmons are defined as the quanta associated with the vibrations of the electron density of plasma. They can be regarded as coherent periodic deviations of the electron density at each point from its average value:

$$\Delta n(\mathbf{r}, t) = n(\mathbf{r}, t) - \bar{n} = \Delta n_{max} \exp[i(\omega t - \mathbf{qr})].$$

These vibrations are longitudinal, i.e. the direction of their propagation **q** coincides with the electric field strength vector **E**.

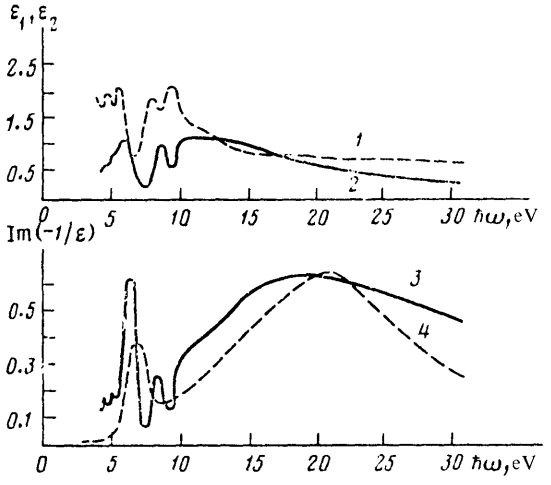


Figure 2. The form of the dielectric constant functions $\varepsilon_1(\omega)$ (curve *1*) and $\varepsilon_2(\omega)$ (curve *2*) and the energy loss function $\mathrm{Im}[-1/\varepsilon(\omega)]$ (curves *3* and *4*) in polystyrene; curve *3*—calculation based on ε_1 and ε_2 (Voltz[61]); curve *4*—experimental spectrum of the energy losses by electrons.[82]

According to Maxwell's equations, in the medium we have[61]

$$\mathrm{rot}\,\mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t} + \frac{4\pi}{c}\mathbf{j} = i\omega\varepsilon(\omega)\mathbf{E} = 0. \qquad (17)$$

The magnetic field **H** = 0, since fields arising from the time variation of the electric induction vector **D** and the current **j** cancel out. An equation for the intrinsic frequencies of the plasmon vibrations follows from Eqn.(17):

$$\varepsilon(\omega) = 0. \qquad (18)$$

In the case of bound electrons, for example, in a molecular medium, the collective vibrations are not manifested in a pure form, being always combined with intramolecular transitions. The electron density vibrations can be represented in this case as a longitudinal polarisation wave, which leads to the vibrations of the dipole moment of the molecule. Such a wave is illustrated schematically in Fig.3 for non-polar molecules.

The passage of a fast particle with a velocity v and a charge e through the medium is equivalent to the current $\mathbf{j} = e\mathbf{v}\delta(x - vt)$. This entails the polarisation of the medium. The electric field $\mathbf{E}_{pol}$ arising as a result of this polarisation interacts with the moving particle, as a consequence of which the latter loses energy. By solving the Maxwell equations in the given medium, it is possible to find $\mathbf{E}_{pol}$ and to obtain an expression for the probability of the energy loss $\hbar\omega$ along the path of length l for a single scattering of the particle in the solid angle $d^2\Omega$ owing to a deviation by an angle θ:[69]

$$\frac{\partial^2 W}{\partial(\hbar\omega)\partial^2\Omega} = \frac{l}{(e\pi a_0 q)^2}\,\mathrm{Im}\left[-\frac{1}{\varepsilon(\mathbf{q}, \omega)}\right] \qquad (19)$$

where the momentum q transmitted to the medium depends on the scattering angle and can be found from the laws of the conservation of the energy and momentum of the particle.

As in Eqn.(16), the principal dependence on the transmitted energy in Eqn.(19) consists in the factor $\mathrm{Im}[-1/\varepsilon(\mathbf{q}, \omega)]$. The maxima in the losses occur both in the region of the maxima in $\varepsilon_2(\mathbf{q}, \omega)$, which corresponds to allowed transitions in isolated molecules, and in the region of the zero values of the denominator, i.e. in the region corresponding to the solutions of Eqn.(18), which denotes the excitation of collective states; in order to find the frequencies, it is necessary to know the explicit form of the function $\varepsilon(\omega)$.

The medium with bound electrons can be represented by a set of oscillators, each of which is characterised by three parameters: the intrinsic frequency of the oscillator ω_i, the oscillator strength f_i, and the decay constant γ_i (a quantity which is equal to the reciprocal of the lifespan of the state). The following expression is valid for the dielectric constant of the medium in terms of the approximation $q \to 0$:[61,70]

$$\varepsilon(\omega) = 1 + \sum_i f_i\omega_p^2(\omega_i^2 - \omega^2 - i\gamma_i\omega)^{-1} \qquad (20)$$

where ω_p is the frequency of the plasma vibrations in the free electron system, which depends on the electron density n_e:

$$\omega_p = (4\pi n_e e^2/m)^{1/2}. \qquad (21)$$

Since the region $\hbar\omega < 30$ eV is important for the collective vibrations, the electrons in the inner atomic shells can be disregarded. The quantity n_e is therefore determined by the density of the valence electrons and in the summation with respect to i in Eqn.(20) it is necessary to consider oscillators corresponding to the transitions of valence electrons alone. An approximate expression for the frequency ω_p in molecular liquids has been published:[68]

$$\hbar\omega_p,\ \mathrm{eV} = 28.8\,(N_v\rho/M)^{1/2} \qquad (22)$$

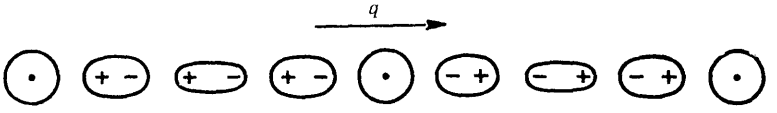


Figure 3. Schematic representation of the longitudinal polarisation wave in a condensed medium consisting of non-polar molecules.

where N_v is the number of valence electrons per molecule, M the molecular weight, and ρ the density of the medium (g cm^{-3}); for water, $\hbar\omega_p \cong 19.2$ eV.

The intrinsic frequencies of the vibrations of the medium must satisfy Eqn.(18). It is very difficult to calculate these frequencies from Eqn.(20). We shall consider several special cases.

For free electrons in a metal, $f_0 = 1$, $\omega_0 = 0$, and all the $f_i = 0$ $(i \neq 0)$;

$$\varepsilon(\omega) = 1 - \omega_p^2(\omega^2 - i\gamma_0\omega)^{-1}. \quad (23)$$

If the decay is slight, resonance is manifested at $\omega_2 = \omega_p$, i.e. free plasmons are excited.

In many molecules the maximum oscillator strength corresponds to one of the transitions. Suppose that it is f_1; in this case, one can put approximately

$$\varepsilon(\omega) = 1 + f_1\omega_p^2(\omega_1^2 - \omega^2 - i\gamma_1\omega)^{-1}. \quad (24)$$

For a weak decay, the energy loss function has only one maximum corresponding to $\varepsilon(\omega) = 0$:

$$\omega_r = (f_1\omega_p^2 + \omega_1^2)^{1/2}. \quad (25)$$

For low densities (gas phase), $\omega_p = 0$ and the maximum of the absorption function corresponds to $\omega_r = \omega_1$, i.e. as for an isolated molecule. In the opposite case, at very high densities, subject to the condition

$$f_1\omega_p^2 \gg \omega_1^2, \quad (26)$$

the quantity $\mathrm{Im}[-1/\varepsilon(\omega)]$ is a maximum for $\omega_r = f_1^{1/2}\omega_p$, i.e. corresponds to the longitudinal collective vibrations of free electrons. Peaks of the energy loss function between these two limiting cases cannot be fully assigned either to collective vibrations or to one-electron transitions. The latter situation is typical for molecular liquids.

The value of $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$, and the function $\mathrm{Im}[-1/\varepsilon(\omega)]$ in liquid water are presented in Fig.4. The $\varepsilon_2(\omega)$ peaks on the graph correspond to intramolecular transitions. The $\hbar\omega_1 = 13.5$ eV transition has the maximum oscillator strength $f_1 = 0.43$. The peak of the energy loss function $\mathrm{Im}[-1/\varepsilon(\omega)]$ at 21 eV is of plasmon origin, i.e. it corresponds to the longitudinal vibrations of the assembly of molecules. However, these are not the plasma vibrations of free electrons, since condition (26) is not explicitly fulfilled in this instance. Indeed, according to Eqn.(22), $\hbar\omega_p \cong 19.2$ eV for water. For the $\hbar\omega_1 = 13.5$ eV peak with $f_1 = 0.43$, we obtain $f_1(\hbar\omega_p)^2 = 159$ eV^2, while $(\hbar\omega_1)^2 = 182$ eV^2. Nevertheless, an appreciable change in the positions of the maximum indicates a relatively high contribution of the collective effects.

The theoretical determination of the energy loss function $\mathrm{Im}[-1/\varepsilon(\mathbf{q}, \omega)]$ is very difficult. In the region $q \to 0$ one can use optical data. For the electron gas, the expression for the dielectric constant has been obtained by Lindhard.[64] A semiempirical expression defining $\varepsilon(q, \omega)$ for water has been proposed.[71]

There are several ways in which collective excitations can break down. In the electron gas the breakdown takes place as a consequence of the interaction of the electrons with one another. The Coulombic interaction of electrons is strongly shielded by the electron cloud and is manifested only over short distances. As a result of such short-range interaction, the vibration energy of the plasmon is converted into the kinetic energy of the movement of individual electrons, i.e. it is distributed over the entire electron gas.[72]

In atomic-molecular media, the decay of plasmon states is due to the interaction of plasmons with electrons and also with the lattice vibrations or with impurities. The electron–plasmon interaction is of the long-range type. When a plasmon is absorbed, the momentum $\mathbf{q}$ is transferred to the electron; as a result, the collective excitation is converted into a one-particle excitation. This process is identical with the absorption of a photon having the same energy. Wölff[73] (see also Nazierea and Pines[74]) showed that the lifespan of the plasmon can be expressed in this case in terms of optical constants: the absorption coefficient κ and the refractive index n:

$$1/\tau = n\kappa\omega. \quad (27)$$

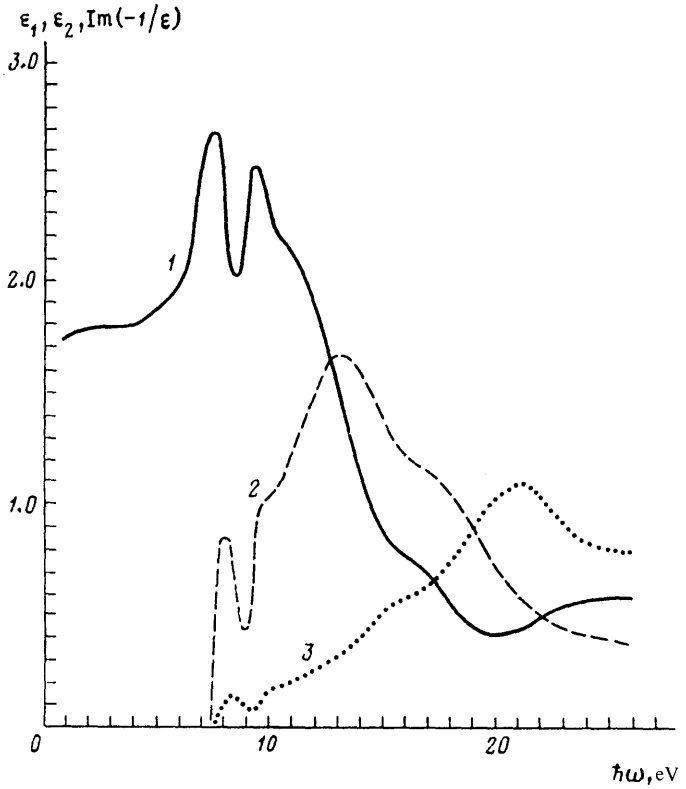


Figure 4. The form of the dielectric constant functions $\varepsilon_1(\omega)$ (curve *1*) and $\varepsilon_2(\omega)$ (curve *2*) and the energy loss function $\mathrm{Im}[-1/\varepsilon(\omega)]$ (curve *3*) in liquid water.[67]

For water in the region of the energy of the plasmon state, $\hbar\omega_r = 21.4$ eV, $n = 0.76$, and $\kappa = 0.36$.[67] Calculation by Eqn.(27) leads to $\tau \cong 1.1 \times 10^{-16}$ s. The lifespan of the plasmon state can be estimated also from the uncertainty relation. It follows from the spectrum of the energy losses in water that the half-width of the excited level with the energy $\hbar\omega_r = 21.4$ eV is $\Delta\hbar\omega_r/2 \cong 3.4$ eV. We therefore obtain $\tau = 1/\Delta\omega_r \cong 10^{-16}$ s, which agrees well with the calculation by Eqn.(27).

V. THE LOCALISATION AND DELOCALISATION OF ENERGY LOSSES

The question of the degree of localisation of the absorbed energy arises from the study of the processes involving the absorption of the energy of the ionising radiation. There

are two possible causes of the delocalisation of its energy. The first is associated with the quantum-mechanical nature of the microparticle and the second with the possibility of collective excitations. We shall consider both causes in greater detail.

The quantum-mechanical nature of micro-objects is reflected by the uncertainty principle. The limitations imposed by the uncertainty principle were not previously taken into account in the study of the interaction of a stream of particles with matter. This was justified[75] by the fact that, during a period of 10^{-16} s, there is sufficient time for the localisation of the excitation as regards the molecules. However, this justification cannot be regarded as correct. It has been emphasised[47] that, since the subsequent localisation is stochastic, the initial delocalisation precludes in principle the determination of the site of the absorption of energy more precisely than is allowed by the uncertainty principle.

If a microparticle with the energy E transmits the energy ΔE to the medium, then at the instant of the transfer the energy of the particle is defined to within ΔE. This uncertainty ΔE in the energy is associated with the uncertainty Δx in the position of the particle during the energy transfer process. This type of relation has been found for ultrarelativistic[75] and non-relativistic[47] particles. It has been shown[76] that in the general case the uncertainty as regards the coordinates of the particle during the transfer of its energy ΔE satisfies the inequality

$$\Delta x \geqslant \hbar v_x/\Delta E. \qquad (28)$$

The uncertainty in the site of the absorption of energy is the same.

The greater the energy transferred, the lower the degree of delocalisation. When inner 1s electrons are dislodged, the energy losses are in fact localised. Indeed, even for ultrarelativistic particles ($v = c$), $\Delta x = 0.66$ nm for the transfer of the energy $\Delta E = 300$ eV (i.e. an energy greater than the ionisation potential of the K shell of the carbon atom) according to Eqn.(28), while in the transfer of $\Delta E = 500$ eV (an energy of the order of magnitude of the ionisation potential of the K shell of the oxygen atom) we obtain $\Delta x = 0.40$ nm.

Table 3. The degrees of delocalisation in the transfer to the medium of the energy $\Delta E = 15$ eV by an electron having an energy E_e.[76]

E_e, eV	10^3	10^4	10^5	10^6	10^7	10^8
$10^{-8}v$, cm s^{-1}	5.93	18.7	58.5	164	282	300	300
Δx, nm	0.26	0.82	2.56	7.2	12.3	13.1	13.1

However, for small losses, which accompany the majority of inelastic scattering steps, the degree of delocalisation can be very considerable. In ionisation most of the dislodged electrons have low energies. The quantity $\Delta E = 15$ eV can be adopted as the most probable energy loss. The results of the calculation of Δx for $\Delta E = 15$ eV and different energies of the incoming electron are presented in Table 3. Evidently, for relativistic electrons, the degree of delocalisation of the ionisation step is not less than 13.1 nm, i.e. is very considerable. In the excitation of an electronic state with an energy of 7.5 eV, the degrees of delocalisation are greater by a factor of 2 than those quoted in Table 3.

Thus the delocalisation region can embrace several tens of molecules of average size. Although subsequently the energy is localised at one of the molecules, it is random and the coordinates of the ionisation or excitation points cannot therefore be determined with an accuracy greater than to within Δx.

According to inequality (28), the degree of delocalisation depends on the velocity of the particle. For this reason, the values of Δx quoted in Table 3 for heavy particles correspond to correspondingly large energies, amounting to $E = (M/m)E_e$. Thus the proton has the velocity $v = c$ for $E \geq 2$ GeV.

The second cause of the delocalisation of energy losses is the collective character of the excited states, which can obtain even in the excitation of the electronic states of a single molecule. The simplest example is the excitation of π-electronic states, which are delocalised along the molecule. A fast electron, exciting such a molecule, transmits energy to the entire assembly of π electrons. As a result, the site of the excitation energy transfer is delocalised along the molecule, which can be fairly long, for example, in the case of a polymer.

The excited electronic states in molecular crystals are also collective owing to periodic symmetry. These are the thoroughly investigated exciton states.[77] The energy of the exciton state is close to the energy of the discrete electronic states of isolated molecules (4–8 eV), but in these states the excitation embraces a greater number of molecules. Under these conditions, the excitation migrates effectively in the crystal over distances up to 100 nm.[77,78] Thus owing to effective migration the excitation of one of the units of the polymer chain spread rapidly along the chain.[79] The high efficiency of such energy migration has been confirmed experimentally:[80] the saturation of the phosphorescence of luminescent additives in polystyrene on β-irradiation has been observed for a 1 : 1 ratio of the concentration of phosphor species and macromolecules, i.e. in the presence of one phosphor species per macromolecule.

Thus the excitations of discrete electronic states ($\Delta E_n < I_1$) in polymer molecules and molecular crystals are known to be delocalised. Collective excited states occur not only in crystals but also in liquids and polymer films when fast charged particles pass through them (see Section IV). The energy of such states as a rule exceeds the first ionisation potential and amounts to 15–25 eV.

It has been shown[76] that the linear size of the collective excitation region is determined by the expression

$$b_{pl} = \pi v/\omega_r = \pi\hbar v/\Delta E_r, \qquad (29)$$

where ω_r is the resonance frequency calculated by Eqn.(25). The maximum size of the region corresponds to $v = c$ and is $b_{pl}^{max} = \pi\hbar c/\Delta E_r$. For water, $\Delta E_r = \hbar\omega_r = 21.4$ eV,[66] which yields $b_{pl}^{max}(H_2O) = 29$ nm.

Thus, in the initial period of approximately 10^{-16} s, the energy transferred by the fast charged particle is delocalised both as a consequence of the quantum-mechanical uncertainty principle and as a consequence of cooperative effects.

As a result of the delocalisation along the direction of motion, caused by the uncertainty principle, the coordinates of the excitation and ionisation points can be determined with an accuracy to within a quantity not exceeding Δx, specified by Eqn.(28). For relativistic electrons, Δx is fairly large and includes several tens of molecules. Thus $\Delta x = 26$ nm for the excitation of the $\Delta E = 7.5$ eV level. This factor is especially important for biological systems characterised by a marked non-uniformity as regards their sensitivity to radiation. The size of the target in radiobiology should not be

less than 10–25 nm (the spread being determined by the value of ΔE leading to the biological effect).

As shown above, the linear size of the collective excitation region of the plasmon type can reach 30 nm. Since the oscillator strengths are concentrated in the region of the peak maximum in the presence of collective peaks, the plasmon absorption is fairly considerable. It follows from the form of the energy loss function in water[66] that the plasmon absorption leads to a decrease of the fraction of the oscillator strength corresponding to transition to discrete excited states compared with their distribution in water vapour. Since the collective excitation of the plasmon type is dissipated mainly via energy transfer to a single molecule with subsequent ionisation, the "pumping" of energy from discrete excitation levels to collective excitation levels should entail an increase of the contribution of ionisation in the liquid phase compared with the gas phase. At the same time the dissipation of collective excitations can serve, as emphasised by Voltz,[81] as an additional source of superexcited states (see Section III). In the case of SES there is competition between predissociation and autoionisation. For the excitation of the SES in the course of the dissipation of the collective excitation, it is essential that the energy liberated in this process should be located in the region of the formation of the SES for the given type of molecules.

In conclusion we shall consider the consequences of the delocalisation of the excited electronic states in long molecules and of the effective migration of the electronic excitation along a polymer chain.[79] This should result in the preferential rupture of the weaker chemical bonds and also chemical bonds in the vicinity of an impurity or chain defects, since the excitation energy is localised at precisely these sites. Track effects arising from the energy transmitted to the electrons of the medium should not be manifested in such a polymer matrix, because the energy absorbed is rapidly dissipated throughout the electronic subsystem. Here there is a clear analogy with metals, where the electron gas dissipates the absorbed energy throughout the bulk of the metal without the formation of linearly extended tracks.

VI. THE STRUCTURE OF THE TRACKS OF CHARGED PARTICLES

1. Tracks of Fast Electrons

Owing to its interaction with atoms and molecules on passing through the medium, a fast electron loses energy not continuously but in individual portions. The probability of such an energy loss step depends on the type of the excited state and energy of the electron (see Section II). It follows from the spectra of the energy losses arising when fast electrons pass through thin films that the most probable energy loss is 15–30 eV.[6] The transferred energy is used in the formation of ions and secondary electrons and also in the excitation of the molecules of the medium. The ions and excited molecules formed are localised in the vicinity of the trajectory of the primary electron and constitute its track.

The distance traversed by the primary electron between the energy transfer steps is referred to as the free path l. The mean $\bar{l} = (n\sigma_{tot})^{-1}$, where σ_{tot} is the overall inelastic scattering cross-section and n the density of the molecules of the medium. For a fast electron, up to $E > 10$ keV, $\bar{l}$ greatly exceeds the size of the region where the energy transmitted to the medium is localised. For example, for a relativistic electron in water, we have $\bar{l} = 200$–300 nm. Consequently a fast electron forms a series of non-overlapping microregions along its path, consisting of excited and ionised molecules.

The evolution of ideas about the structure of the fast electron track has been considered in a review[6] and in another publication.[7] Mozumder and Magee [84,85] introduced a classification of the energy structures of the track. According to this publication, the energy of the fast electron is consumed in the formation of "spurs" with energies of 6–100 eV, the so-called "blobs" with energies in the range 100–500 eV,† and "short tracks" with energies in the range 500–5000 eV.

The probability that an energy of 20 eV is localised in the spurs is highest.[85] Such spurs contain, as a rule, one ion pair (with a probability of approximately 0.5).[87] The average number of ion pairs in the spur is approximately 1.78 according to Magee and Chatterjee[87] for an average energy in the spur of approximately 30 eV. The maximum energy of the short track (5 keV) is determined from the condition for the overlap of the spurs. Short tracks consist of cylindrical regions with an enhanced concentration of excitations and ionisations and an energy distribution which can be found from the Rutherford formula [Eqn.(1)].

A numerical computer experiment with the aid of the Monte Carlo method is used to find the degradation spectrum and the energy structure of the fast electron track.[88–90] The degradation spectrum and a series of other energy characteristics of the track of a monochromatic electron beam with $E = 10$ keV in water have been found.[89,90] The authors used quantities employed for the gas phase as the interaction cross-sections, i.e. the specific features of the condensed phase were disregarded.

In a condensed phase it is difficult to separate the interaction of an electron with an isolated molecule. For this reason, instead of the molecular excitation cross-section $\sigma_k(E)$, one usually employs in this case the reciprocal of the free path $l^{-1} = n\sigma_k(E)$ in relation to the excitation in the kth state and the cross-section itself is expressed as a function of the energy losses $\mathrm{Im}[-1/\varepsilon(\mathbf{q}, \omega)]$ (see Section IV).

The tracks of an electron with $E_0 = 1$ and 10 keV in water have been modelled.[71,91,92] However, since the dependence of the dielectric constant function $\varepsilon(\mathbf{q}, \omega)$ on $\mathbf{q}$ is unknown, it was modelled using data for the gas phase. The role of the phase state in primary radiolytic processes has been investigated in a study[91] where the overall radiation ionisation and excitation yields and the degradation spectrum of the electrons in water and water vapour were found.# The evolution of the track of a fast electron in water for times up to 10^{-7} s has been investigated[92] by the computer modelling method.

For a more detailed investigation of the influence of the structure of the track on radiation-chemical reactions, it is necessary to know not only the energy characteristics of the track but also the spatial distribution of the secondary electrons and the excitation and ionisation steps throughout the bulk of the track. The Monte Carlo method is also

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† The upper limit to the energy of the blob is extremely arbitrary. In a recent study by Magee and Chatterjee[86] the upper limit was assumed to be 1600 eV.

In a communication by the authors of this review and V.Ya.Sukhonosov, a comparative study of the primary stage of the radiolysis of water in the gas and liquid phases is described: for a brief description of the results, see Ref. 170.

convenient for the determination of this distribution. Studies of this kind have been carried out.[91–95]

The so-called "stochastic" approach, in which an instantaneous picture of the spatial distribution of the excitation and ionisation steps is fixed, has been used in investigations[93,94] of electron tracks. In this case the tracks constitute a set of points in space where inelastic scattering steps have taken place. Having at one's disposal sets of such tracks, it is possible to calculate the spectrum of the absorbed energy in the sensitive regions of the irradiated medium[93] and to calculate their line shapes and the decay of the electronic spin echo signals.[94,95]

When the velocity of the electron exceeds the velocity of light in the medium, an additional source of energy losses, namely the Vavilov–Cherenkov radiation, appears. The contribution of this radiation to radioluminescence has been fairly clearly identified in a series of investigations[96–99] and its role in photoradiation processes has been analysed.[100,101] It has been shown that the number of quanta of such radiation generated on irradiation in the accelerators employed in radiation chemistry is comparable to the light flux from the lamps employed in photochemical experiments. Thus, when photosensitive media are irradiated in accelerators, internal photoradiation processes are inevitable. Since the yield of the Vavilov–Cherenkov radiation is much lower on irradiation with a ^{60}Co source, the irradiation of photosensitive media in an accelerator should be more effective for the same dose.

2. Energy Losses by Pre-excitation Electrons

Since the energy of these electrons is insufficient for the excitation of the electronic states, their energy is consumed in the excitation of vibrational and rotational states and also in inelastic collisions. In polar liquids there is an additional energy loss in dipole relaxation. In the condensed phase the energy losses are determined by the dependence of the dielectric constant of the medium on the frequency and are expressed in terms of the energy loss function $\mathrm{Im}[-1/\varepsilon(\omega)]$ [see Eqn.(16)].

In the range of energies from 5 to 0.5 eV, the resonance process involving the formation of negative molecular ions by the capture of an electron with subsequent ionisation or dissociative ionisation has large cross-sections.[102,103] According to Schulz,[104] such resonances or short-lived states of the negative ion can be divided into two groups. These are in the first place potential shape resonances which arise following the capture of an electron by the potential well formed in the electronic ground state of the molecule as a result of the centrifugal or polarisation forces. The lifespan of such states is 10^{-15}–10^{-10} s. The Feshbach resonances, whose appearance is associated with the excitation of one of the electrons of the molecule, belong to the second group. This results in the formation of a state which is energetically more favourable for the addition of an excess electron. A Rydberg state may be frequently an excited state of this kind.[105] The decomposition of the negative ion formed is as a rule accompanied by the excitation of the molecular vibration. The characteristic energy loss peaks for electrons with energies in the range 0.5–3 eV when they pass through thin films have been interpreted in terms of a resonance energy loss mechanism which involves the formation of an intermediate negative ion.[106–108]

An important characteristic in the study of the pre-excitation electron retardation processes is the thermalisation distance l_{th}. It is essential to know this quantity in determining the size of the spur and the yield of the free ions. The first estimates of the thermalisation distance and time (t_{th}) for slow electrons were made by Samuel and Magee[109] who used for this purpose the classical method based on the random movement of the electron in the Coulombic field of the parent ion. Assuming that the electron traverses identical distances l between collisions in the course of the retardation process and that it loses the same energy $\Delta\varepsilon$ in each collision, the authors obtained $t_{th} \cong 2.83 \times 10^{-14}$ s and $l_{th} = 1.2$–1.8 nm for an electron with an energy of 15 eV. Since the electron cannot overcome the attraction of the parent ion for such a low value of l_{th}, it is captured by the ion after approximately 10^{-13} s, which results in the formation of a neutral molecule in an excited state which is capable of dissociation. However, the experimental yield of the free ions showed that some of the electrons are removed to considerable distances from the ion in the thermalisation process and do not recombine.

The retardation of slow electrons in a condensed medium has been studied theoretically by Frohlich and Platzman[110] taking into account the dielectric properties of the medium. Within the framework of classical electrodynamics, they obtained an expression for the rate of energy loss by an electron moving along a linear trajectory at a velocity v. This expression in fact represents the non-relativistic analogue of the Fermi formula:[111]

$$-\frac{dE}{dt} = \frac{2e^2}{\pi v}\int_0^\infty \omega\,\mathrm{Im}\left[-\frac{1}{\varepsilon(\omega)}\right] xK_0(x)K_1(x)\,d\omega, \qquad (30)$$

where $x = \omega b_{\min}/v$ and $b_{\min}$ is the minimum impact parameter, which is assumed equal to either the intermolecular distance d or to the de Broglie wavelength of the electron λ when $\lambda < d$. Since the form of the function $\mathrm{Im}[-1/\varepsilon(\omega)]$ was not known over a wide range of ω, the authors[110] confined themselves to the calculation by Eqn.(30) of the energy losses only in dipole relaxation and obtained $-dE/dt \cong 10^{13}$ eV s^{-1} for water, which is independent of the electron energy in the experimental range from 1 to 10 eV. This value of energy losses was shown by the authors to be comparable to the energy losses in the excitation of vibrations.

The contributions of various mechanisms to the energy losses have been analysed.[112,113] According to the results of Magee and Helman,[112] the main contribution to the overall energy losses comes from the energy consumed in dipole relaxation (provided that such losses occur). They amount to approximately 1.5×10^{13} eV s^{-1} for water, while the energy lost in vibrations in the infrared range amounts to only approximately 10^{12} eV s^{-1}. The opposite result was obtained by Byakov and Grishkin,[114] who showed that the main contribution to the retardation of the pre-excitation electron comes from the resonance losses in the excitation of retarded longitudinal vibrations of the water molecules. An approximate analytical formulation of the function $\mathrm{Im}[-1/\varepsilon(\omega)]$ was used[114] in the calculation of the energy losses by Eqn.(30). A more accurate calculation by Eqn.(30), carried out by Garin and Byakov[115] using the experimental optical properties of water, confirmed the general conclusion drawn in the previous study.[114]

According to the results of Garin and Byakov,[115] the resonance losses resulting from intramolecular vibration in the infrared range make the main contribution to the retardation of the excitation electrons in polar liquids. The contribution of the losses in dipole relaxation proved to be smaller by an order of magnitude. This conclusion is more valid for non-polar liquids, where the main channel for these losses is not the relaxation of permanent dipole moments (the latter are zero) but the dipole moments induced in the molecules of the medium by the passing electron. As a result, the electron retardation time in the majority of liquids is

determined by the resonance absorption in the infrared range. Liquids made up of molecules with a high symmetry, which have no active vibrations in the infrared range, for example the molecules of methane or neopentane, may constitute exceptions.

According to Garin and Byakov,[115] the rate of energy loss by an electron having $E = 7.5$ eV in Debye relaxation is $(-dE/dt)_D \cong 10^{12}$ eV s^{-1} and the overall rate of resonance losses is $(-dE/dt)_r \cong 4 \times 10^{13}$ eV s^{-1}. The maxima in the region of molecular librations ($\bar{\nu} \cong 700$ cm^{-1}) and the intramolecular stretching vibations ($\bar{\nu} \cong 3400$ cm^{-1}) make the main contribution to the resonance losses. As a consequence of the increase by a factor of approximately 2 of the reduced masses in stretching vibrations in D_2O, the rate of energy loss should be lower by a factor of 2 and the retardation time and the path traversed should therefore be greater by a factor of 2. This conclusion agrees with the results of recent measurements.[116]

The energy barriers had been calculated earlier[117] by Eqn.(30) taking into account the experimental values of $\mathrm{Im}[-1/\varepsilon(\omega)]$. The data obtained in the above studies[115,117] for the overall energy losses by slow electrons agree. However, Raitsimring et al.[117] failed to analyse the contribution of the individual mechanisms to the retardation of slow electrons. On the other hand, they calculated the total thermalisation distances for water, ice, and benzene.

Calculation by Eqn.(30) makes it possible to estimate the energy losses in the course of the linear movement of an electron. The curvature of the trajectory has been taken into account with the aid of the Monte Carlo method[112,113] and analytically.[118] Mention should also be made of the fact that Eqn.(30) does not allow for the energy losses in close collisions of an electron with molecules, including the formation of an intermediate negative ion. The contribution of close collision processes to the energy losses has been estimated by Magee.[113] For water, the contribution of these processes to the rate of energy loss by an electron with $E = 1$ eV amounted to approximately 5×10^{13} eV s^{-1}, while in paraffinic hydrocarbons it amounted to approximately 7×10^{13} eV s^{-1}. Consequently, among all the mechanisms responsible for the retardation of slow electrons, it is difficult to isolate one which would be of decisive importance over the entire thermalisation distance.

Even when account is taken of the energy losses in close collisions, Eqn.(30) does not allow an adequate determination of the thermalisation distance. Electrons with an energy below the vibration excitation threshold are subjected to fairly effective elastic scattering. In the calculation of energy losses via elastic scattering one can as a rule neglect the energy transferred to effect the collision in view of its low value. On the other hand, the contribution of the elastic scattering to the thermalisation distance is comparable and perhaps even greater than the contribution of the inelastic collisions.

Thus it proved difficult to obtain direct information about the thermalisation distance by direct procedures. In a number of studies, for example those in Refs.119–121, the effective thermalisation distances were therefore determined from the distribution functions for electron pairs with respect to distances. These functions were found from the yields of the free ions either in the absence of a field or for low electron field strengths. However, the values obtained in this way are unreliable because the yield of the free ions is only weakly sensitive to the changes in the thermalisation distances.

After the development of a method for the investigation of photoemission phenomena at the metal–solution boundary,[122–124] the direct experimental determination of the thermalisation distances of free electrons became possible (see the studies quoted above and also Refs.116 and 125–127). The path traversed by an electron with $E \cong 3$ eV proved to be approximately 5 nm in H_2O and approximately 10 nm in D_2O.[116] For comparison, we may note that the ionisation path of an electron with $E = 100$ eV in water is approximately 1.5 nm, i.e. is much shorter than the thermalisation distance). In a review by one of the present authors[47] it was stated in the discussion of the form of the function $l(E)$ obtained by Raitsimring et al.[125] that it was essential to explain the absence of the dependence of l on E for $E < 2$ eV. In a recently published study[116] a monotonic decrease of $l(E)$ as the electron was retarded was obtained for D_2O, while for H_2O there is a plateau in the energy range $E = 1$–2 eV. However, it has been correctly stated[116] that, owing to the lack of data for the energy distribution of photoelectrons on excitation of the cathode, it is premature to carry out a detailed interpretation of the results.

After the electron has been thermalised, it can either recombine with a positive ion (not necessarily the parent ion) or it can be captured by a trap. The traps can be not only molecules with a positive electron affinity but also structural defects in the medium or polarisation wells formed when an electron interacts with the surrounding molecules. Such a captured electron has come to be referred to as solvated (hydrated in water). Since very numerous monographs and reviews have been devoted to the solvated electron,[128–130] we shall not deal with these questions. We may note that the theory of the solvated electron is still far from complete.[131]

Numerous studies have also been devoted to the behaviour of the excess electrons induced by irradiation in non-polar solutions and solid matrices (see the relevant reviews[132–134]). It has been established that the excess electrons exist in the medium in two states: localised and quasi-free. Their ratio depends on the nature of the molecules, especially on their symmetry: the higher the symmetry (for example, in neopentane) the greater the fraction of electrons in the quasi-free state.[135]

3. The Structure of the Tracks of Heavy Ions

Among the entire multiplicity of interactions of heavy ions in a medium, the most effective over a large part of the path traversed are, as in the case of fast electrons, the inelastic interactions with the electrons of the medium (electron retardation). Only at the end of the path does the role of elastic interactions with the atoms of the medium and the electron capture and loss processes (charge transfer) increase. The role of the latter processes becomes more pronounced with increasing mass of the ions.

The process in which the energy of the ion is transferred to the electrons of the medium is independent of the mass of the ion and its probability is proportional to the ratio Z^2/v^2. The size (Δx, b_{eff}) of the region where the energy transferred to the medium in glancing collisions is localised is fully determined by the velocity of the charged particle. Hence it follows that a heavy ion generally speaking generates the same track structures as a fast electron having the same velocity v. The specific features of the transfer of the energy of the ion and of its distribution in the medium are manifested by the following factors.

A heavy ion is capable of dislodging an electron with a maximum energy $\varepsilon_{\max} \cong 2mv^2$ on ionisation, while in the case of a fast electron having the same velocity $\varepsilon_{\max} = \frac{1}{2}mv^2$. Consequently in head-on collisions, where the energy transferred $\Delta E \cong \varepsilon_{\max}$, this fraction of the energy is distributed

over larger distances from the site of the primary ionisation than in the collision of electrons having the same velocity.

Since the energy losses and the change in the momentum of the primary heavy ion in individual collisions with electrons of the medium constitute small fractions of the energy and moment of the ion ($\Delta E_{max}/E_0 \cong 4m/M < 2 \times 10^{-3}$), the electron retardation has only a weak influence on the curvature of the trajectory of the ion. For this reason, in the part of the track where ionisation losses predominate, the trajectory of the heavy ion can be regarded as linear.

The strength of the interaction of the ion with the medium is proportional to the square of its charge Z^2. The increase of the charge leads to an increase in the energy transferred to the medium in individual energy loss steps and also in the average energy loss per unit length of the path and of the number of electrons. On the other hand, an increase in Z entails a diminution of the mean free path (because $\sigma_i \propto Z^2$). For this reason, the overlap of the track structures as the ion is retarded occurs earlier for ions with higher values of Z.

The proton and α-particle have the constant charge Z, equal to the nuclear charge Z_a, over most of their path so long as their velocity is sufficiently high. In multicharged ions (for example, in fission fragments) Z is as a rule smaller than the nuclear charge. As a consequence of the charge transfer processes, when a beam of ions has passed through a sufficiently thick layer of the given substance, the ions show a distribution of charges. This distribution is characterised by an average quantity—the effective charge Z_{eff}, which is adopted as Z in the calculations of ionisation energy losses. When the velocity of the ion $v \ll Z_a^{3/4} v_0$, the expression

$$Z_{eff} = \eta Z_a^{1/4} v/v_0,$$

where $v_0 = e^2/\hbar$ is the velocity of the electron in the first Bohr orbital and η a constant which depends on Z_a and the properties of the medium,[136] is valid for Z_{eff}. If Z is now replaced by Z_{eff} in Eqn.(13), then the dependence on the velocity of the ion in the multiplier of the logarithm disappears and it remains only in the logarithmic term. As a result, as the multicharged ion is retarded, its ionisation losses diminish in accordance with a logarithmic law. It will be shown below that this feature is manifested in the specific characteristics of the structure of the track of a multicharged ion.

At high velocities the track of a heavy ion can be regarded as consisting of individual track structures resembling the track structures of a fast electron. However, in radiation chemistry one deals with ions whose initial velocity does not as a rule exceed 10 MeV per nucleon. For initial energies of this kind, the velocity of the ions is less than 4×10^9 cm s^{-1}; the spurs overlap over most of the lengths of the track giving rise to a region of continuous ionisation along the paths traversed. The inner part of this region, which is characterised by an increase in the density of ionisations and excitations, has come to be referred to as the core. For low velocities of the ion, the radius of the core has been assumed[137] to be 1 nm. This value was chosen on the basis of the condition for the retardation of secondary electrons with an energy of 100 eV.

Part of the energy of the secondary electron is absorbed in the core of the track. Only high-energy δ electrons are capable of moving outside the limits of the core and of forming individual track structures. When the tracks of electrons overlap, a continuous shell surrounding the core, narrowing towards the end of the track, is produced.[138]

The distribution of ionisation excitation steps effected by secondary electrons has been studied in many investigations. The Monte Carlo method proved to be the most effective for detailed study.[139–141] The spatial distribution of the ionisation steps and the change of the energy distribution of the δ electrons as a function of the distance from the axis of the track and along the track have been investigated.[140] The data obtained can be used to compare the structures of the tracks of ions of different kinds with specific energies ranging from 82 to 420 keV per nucleon. Table 4 presents the results for the tracks of the α-particle and the multicharged ^{127}I ion in water. Evidently the geometrical dimensions of the tracks of ions having identical velocities are equal. However, the qualitative structure of the core and the dependence of the characteristics of the track of a multicharged ion on the linear energy transfer (LET) are different from those in the track of the α-particle (or the proton).

Table 4. Characteristics of the tracks of α-particles and the multicharged ^{127}I ion in water*.

Characteristic of track	$10^{-8}v$, cm s^{-1}				
	9	7	6	5	4
E, MeV	1.7	1.0	0.75	0.5	0.3
	53	32	24	16.5	10
S_e, eV nm^{-1}	168	212	230	240	252
	6000	5540	5240	3600	3210
Z_{eff}, e	1.85	1.68	1.58	1.47	1.38
	11.0	8.6	7.4	6.0	5.0
N_δ, nm^{-1}	3.3	4.5	5.0	5.7	6.7
	118	118	117	87	84.5
N_i, nm^{-1}	5.2	6.8	7.4	7.9	8.4
	190	177	168.5	118	107
$10^{-21}\bar{n}_i^c$, cm^{-3}	1.46	2.0	2.18	2.4	2.66
	52.6	52.3	51	36.6	33.7
$10^{-19}\bar{n}_i$, cm^{-3}	0.27	0.54	1.0	3.8	7.4
	9.7	14.0	23.8	58.7	94
r_{max}, nm	25.0	20.0	15.0	8.0	6.0

*The values of each parameter for the α-particle and the multicharged ion are given in the upper and lower rows respectively; N_i and N_δ are the number of ions and δ electrons formed by the particle over 1 nm of the length of the track respectively, $\bar{n}_i^c$ is the average concentration of ions in the core of the track, $\bar{n}_i$ the average concentration of ions in the track, r_{max} the maximum radius of the track, and v_i the velocity of the ion.

As already mentioned above, owing to the effective neutralisation of the charge as the multicharged ion is retarded, its LET falls in the range of energies where ionisation losses predominate. Nevertheless, in view of the fact that the radius of the track contracts faster than the rate at which LET diminishes on retardation of a multicharged ion, the average concentration and yield of the primary ions in the track of such an ion behave in the same way as in the track of the α-particle, i.e. they increase with decrease in the energy of the ion. This increase continues up to energies at which the losses in elastic collisions become comparable to ionisation losses (i.e. up to $v \cong 4 \times 10^6$ m s^{-1}).

As a result of the primary effects, the multicharged ion ionises virtually all the molecules contained in a cylinder 0.7 nm in diameter (see the relevant estimates[138]). Most of

the energy of the secondary electrons is also localised in the core of the track. As a consequence of this, the number of ionisation steps in the core of the track of a multicharged ion exceeds the number of molecules. Thus almost every molecule in the core undergoes repeated ionisation and excitation processes and hence dissociates into fragments. For this reason, the region adjoining the axis of the track of a multicharged ion (with a radius of 1 nm) consists of a cylindrical ion core filled mainly by fragment ions. It has been shown[142] that at the end of the physical stage of the inhibition process the core of the track of the multicharged ion consists of a low-temperature, non-isothermal, spatially unlimited non-ideal plasma (an analogous conclusion was reached later by Ritchie and Claussen[143]). The individual components of such a plasma chain exist in local quasi-equilibrium states (for further details, see Miterev[142]). The processes in such tracks proceed under significantly non-equilibrium conditions where it is impossible to introduce a single temperature for all the degrees of freedom of this molecule. As a result, the usual ideas concerning the reaction rate constant lose their significance. In describing the processes in the track of multicharged ions, one must employ the methods of plasma chemistry.[144]

VII. CHARACTERISTICS OF THE RADIATION-CHEMICAL REACTIONS IN THE TRACKS OF PARTICLES OF DIFFERENT KINDS

1. The Influence of the Phase States and the Role of the LET in Radiolysis

In a gas the track structures contain as a rule a small number of active species which are separated by large distances from one another. As a consequence of diffusion, the initial non-uniformity in the distribution of active species rapidly smoothes out and at the beginning of chemical reactions the intermediate species are distributed almost homogeneously throughout the volume. For this reason, the role of tracks in the gas phase is negligible. Only when the gas is acted upon by multicharged ions such as fission fragments can spatial non-uniformity influence the chemical reactions.[145,146]

The spatial non-uniformity in the distribution of the reactions in a liquid is more marked owing to the greater density of this medium. On the other hand, diffusion processes in liquids are slower. Furthermore, the phase state of the medium has an effect on the redistribution of the primary active species (increasing the number of ionised states in the liquid—see Section V) and also on the subsequent relaxation processes and the decomposition of the excited and ionised states.[147] The role of the reverse processes involving the recombination of electrons with the parent ion becomes more pronounced on passing from a gas to a liquid and the degree of decomposition of molecules into radicals as a consequence of the so-called cage effect diminishes.[148]

The differences between the kinetics of the gas- and liquid-phase reactions, which depend on many factors, preclude the differentiation in a pure form of the role of tracks by altering the density of the medium. The most fruitful procedure apparently involves the study of the dependence of the radiation effect on the structure of the track for constant physical and chemical properties of the medium.

One of the characteristics of radiation (and its ionising capacity) is the linear energy transfer. Quantitatively LET is equal to the average energy transferred to the medium when the ionised particle traverses a unit length of its path. For fast particles, the LET is virtually equal to the ionisation losses. It has come to be assumed that the higher the LET the higher the density of the chemically active species in the track and the greater the probability of the reactions of the active species with one another rather than with the molecules of the solute.[149-151] Thus the increase in the yield of molecular hydrogen and the decreased yield of electrons stabilised in the free radicals with increase of the LET in the radiolysis of water are well known.[152,153] The study of the radiolysis of some organic substances also produced data indicating an increase with increasing LET of the yield of molecular products, whose formation can be explained by the recombination of chemically active species, for example, radicals in the tracks.[154]

Calculations for the radiolysis of liquids are carried out by solving the equations of the diffusion-dependent kinetics of radiation-chemical reactions in tracks.[155-158] The use of ideas about the track structures with spherical or cylindrical formations and the application of the equations for diffusion-dependent kinetics explained many experimental facts observed in the radiolysis of aqueous solutions,[156,159,160] in particular, the dependence of the yield of products on the LET. As a result of this factor, LET came to be regarded as a universal characteristic of the quality of the radiation on the assumption that the concentration of the active species in the track depends directly on the LET without taking into account the type of the charged particle.

However, many experimental results obtained in the study of the dependence of the yields of the radiolysis products of organic liquids on the LET failed to find a new theoretical justification within the framework of the existing ideas about the relation between the structure of the track and the LET. Among such experimental facts, one may specify the following: a sharp increase in the yield of low-molecular-weight radiolysis products for high values of LET;[161,162] an increase in the yield of a series of products of the radiolysis of methanol (for example, ethylene glycol[163]), whose formation is attributed to the recombination of radicals in the tracks, with decrease in the LET; the difference between the yields of hydrogen $G(H_2)$ in the radiolysis of benzene by protons and α-particles having identical values of the LET.[164]

In order to explain all these experimental results, it was necessary to resort to the concept of the detailed structure of the track and its dependence on the type of the charged particle.[5]

2. The Influence of the Structure of the Track on Radiation-Chemical Processes in Liquids

The role of the structure of the track has been traced most clearly in relation to the radiolysis of liquids by heavy ions. Precisely in this case it is possible to vary within wide limits the geometrical dimensions of the tracks and the concentrations of the active species in them. The influence of the structure of the tracks of ions has been investigated by Burns[164,165] and also by Kaplan and Miterev.[5]

Using detailed ideas about the structure of the tracks of ions, it is possible to account for the dependence of the yields of products on the LET in the following way.[5] Low values of LET are characteristic of the radiolysis of liquids on irradiation by high-energy protons. The track of the proton consists in this case of a core and branches—the tracks of δ electrons, and the higher the energy of the proton the greater the proportion of its energy removed outside the limits of the core by δ electrons. The core itself is ultimately transformed into individual non-overlapping spurs, i.e. the track of the proton resembles that of

the electron with the exception of certain features (see Section VI). As a result, the character of the radiolysis approaches that of the radiolysis by fast electrons.

As the proton is retarded, its LET and the number of δ electrons increase, while the size of the track actually diminishes, because the maximum energy of δ electrons falls. This results in a sharp increase of both the local and average concentrations in the vicinity of the axis of the track. This tends to increase the yields of the products of the recombination of the active species with increasing LET, i.e. there is a direct correspondence between the density of the active species in the track and the LET. An analogous picture has been observed in the tract of the α-particle.

High values of LET (in excess of 1 keV min^{-1}) are observed when a liquid is acted upon by multicharged ions, such as fission fragments. As already mentioned in the previous Section, the structure of the tracks of such ions has a number of characteristic features. The first of these is associated with the fact that the average concentration of active species increases with increasing LET. For this reason, the yields of many radiolysis products initially increase with decrease in the LET of the fragment, reach a maximum, and then (when in the course of further retardation of the fragment the energy losses in elastic collisions become significant) they dimish. The experimental results for the radiolysis of methanol by fission fragments having different energies can be accounted for in precisely this way.[163]

The second characteristic feature of the structure of the track of a multicharged ion is a high concentration of fragment ions in the core of the track manifested by the fact that mainly low-molecular-weight radiolysis products are formed in the core of the track, while the yields of products with a more complex structure diminish. The high yields of H_2, CO, and CH_4 in the radiolysis of liquid hydrocarbons by multicharged ions are associated with this fact.[161,163,164]

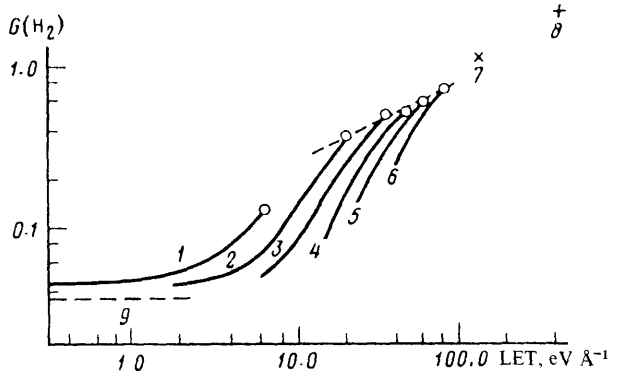


Figure 5. Dependence of the differential yield of molecular hydrogen $G(H_2)$ on the LET in benzene for different ions: 1) ^1H; 2) ^4He; 3) ^7Li; 4) ^9Be; 5) ^{11}B; 6) ^{12}C; 7) ^{20}Ne; 8) fission fragments; 9) fast electrons.[166]

The intermediate values of the LET correspond to the radiolysis of liquids irradiated by different ions. As a result, it has been found that two and more ions can have the same values of the LET (see, for example, La Verne and Schluer[166]). With the exception of the range of low energies, the LET is determined by the ionisation losses S_e [see Eqn. (13)]. If the ionic charges Z are different, then the equality of the S_e (up to the Bragg peak) holds for different velocities of these ions. An ion with a high value of Z has a high velocity v and for this reason the core of its track ($r_c \propto v$) and the region adjoining the core (formed by the tracks of δ electrons) have large dimensions. As a result, the local and average concentrations of the active species in the track of such an ion are reduced.

Thus the higher the charge on the ion the greater the volume of its track in which the linear losses are distributed, i.e. the lower the local concentrations of the active species. As a consequence of this, the radiolysis seen in the track of an ion with a high Z corresponds in essence to a process which is observed for lower LET in the tracks of ions with a lower charge. This behaviour is in fact observed in the measurement of the yield of H_2 in the radiolysis of benzene by various ions[164,166] (Fig. 5).

Thus an important conclusion follows from the analysis of the influence of the structure of the tracks on radiation-chemical processes: there is no direct correspondence between the LET and the local and average concentrations of the active species in the tracks. For this reason, the LET cannot serve as a universal characteristic of the quality of the radiation regardless of the particular species involved.

Attempts have been made to introduce instead of the LET another characteristic of the quality of the radiation, for example, the ratio Z^2/v^2.[167,168] However, a complete description in terms of Z^2/v^2 could not be achieved,[169] which can be readily explained. The factor Z^2/v^2 is an approximation to the LET and all the remarks referring to the use of the LET as a universal characteristic of radiation fully apply also to this parameter.

The dependences of the differential yield $G(H_2)$ on the average density of the absorbed energy in the core of the track have been compared for different ions[166] and it was found that, for the same density, the values of $G(H_2)$ depend significantly on the type of ion and hence also on the distribution of the energy (and the primary species) outside the limits of the core, i.e. they depend on the complete structure of the track.

Apparently the attempts to introduce a universal parameter characterising the radiation-chemical effect of radiation have been unsuccessful. Such a characteristic may be only the spatial distribution of active species in the track. The form of the latter throughout most of the paths of the particles is determined both by the charge Z and by the velocity v of the particles and not solely by their ratio. These two parameters must in fact be used as the characteristics of charged particles. For a comparative estimate of the radiation effects of various types of radiation, certain characteristics averaged over the volume of the track, such as the average energy density in the track, the average concentration of active species in the track, etc., are also useful.

The foregoing has a direct bearing on the dosimetry of the ionising radiation using liquid systems. Since the radiation effect in such systems generally speaking depends on the structure of the track of the charged particles, the determination of the dependence of the readings of liquid type dosimeters on the LET is meaningful only when a single type of radiation is used. Furthermore, the application of a dosimeter calibrated against one type of radiation in the measurement of absorbed doses of other types of radiation requires the introduction of corrections for the specific features of the track effects.

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In conclusion we may note that, in view of the multiplicity and complexity of the active primary species and intermediates formed in the radiolysis of even a thoroughly investigated

medium such as water, there is as yet no firmly established mechanism of the radiolysis in both the primary and subsequent stages. In the first place, the lack of reliable data on the cross-sections of the interactions of slow electrons with molecular media precludes the determination of a detailed spatial distribution of the primary active species in the electron tracks. The types of reactions of the primary active species in the condensed medium, namely ions, superexcited molecular states (for example, Rydberg states), and also plasmon excitations in non-metallic media, have not as yet been firmly established. The solution of these problems would make it possible to carry out calculations for the radiolytic process up to the evaluation of the radiation yields of the final products.

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