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Abstract

Full Text

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On the Distribution of the Energy of Ionizing Radiation in Molecular Mixtures

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Chemical changes occurring in a substance under irradiation by ionizing radiation are preceded by primary elementary acts of energy absorption and its transfer, often over quite considerable distances from the place of initial absorption (in liquids up to 100 Å, and in molecular crystals over still greater distances). The phenomenon of energy transfer manifests itself in a violation of the rule of radiation-chemical additivity, when the primary chemical transformation undergone by each component of a mixture becomes nonproportional to the fraction of the energy absorbed by it ([1]). In all practical questions connected with the distribution of the energy of ionizing radiation in a substance, it is customary to assume that the energy absorbed by each component is proportional to its electronic fraction in the mixture. A justification of this rule exists only for fast particles in the Bethe–Bloch stopping-power theory ([2]). From the expression for the Bethe–Bloch stopping power it follows that the molecular stopping power is approximately equal to the sum of the atomic stopping powers (the so-called Bragg rule).

Inokuti ([3]), using the benzene molecule as an example, subjected Bragg's rule to a theoretical test. According to his data, the inelastic-scattering cross sections calculated by the additive scheme proved to be considerably smaller than the π-electron cross sections obtained in the approximation of the "metallic model" of π-electrons. Subsequently, the hypothesis of selective absorption of energy by π-electrons was supported and developed in the works of Lemborn–Swallow ([4]) and Matsuzawa ([5]). According to the authors of these works, numerous examples of radiation protection by aromatic additives can be explained without invoking the concept of energy transfer if one assumes a high probability of energy absorption by π-electrons.

In our work ([6]) we obtained an expression for the excitation cross section of molecular levels by fast electrons, averaged over all orientations of the molecule in space. In the approximation of the "metallic model," the excitation cross sections of the π-electron levels of the benzene molecule were programmed and calculated on the BESM-2 electronic computer. In parallel, a calculation was carried out of the total inelastic-scattering cross section of the benzene molecule according to the additive scheme, in which

$$\sigma_{\text{add}}(C_6H_6) = 6[\sigma(H) + \sigma(C)].$$

The results of the calculation are given in Table 1. From a comparison of the last two columns of Table 1 it follows that the absorption cross section per electron according to the additive scheme is approximately half the absorption cross section per π-electron. This discrepancy, however, lies within the accuracy of the approximate models used.* Moreover, in the cal–

* The transition intensities are very sensitive to the choice of wave functions. Thus, wave functions giving energy terms with an accuracy up to 10%, when used to calculate the transition probability, may lead to an error of up to 100%; see, for example, ([7]).

in the energy region under consideration the contribution of the K-shell electrons of carbon atoms is smaller than the contribution of the valence electrons; therefore, division of σ_{add} by the total number of electrons in the C_6H_6 molecule, equal to 42, gives an underestimated value of the absorption cross section per electron. Consequently, our results do not allow one to draw a conclusion about the selectivity of energy absorption by π-electrons. The conclusions of Inokuti ([3]) were based on clearly underestimated calculated values of atomic cross sections.

Of undoubted interest are experimental data on the passage of charged particles through organic compounds. If, in accordance with the hypothesis of the authors of works ([3–5]), π-electrons had anomalously large absorption cross sections, this would be manifested in measurements of the stopping power of compounds containing π-electrons. A number of experimental data have been published in the literature on measurements of stopping power for protons and helium ions passing through gases and polymer films consisting of molecules with different chemical structures ([8–10]). Calculation of the molecular stopping power as the sum of the atomic stopping powers gives results consistent with experiment at proton energies $E_p > 150$ keV. At energies below 150 keV, discrepancies appear which exceed the experimental error, indicating that Bragg' s rule is not fulfilled in this region. This is clearly seen from the stopping-power curves given in work ([10]) for gases having the same stoichiometric formula, propylene C_3H_6 and cyclopropane $(CH_2)_3$. In the energy region above 150 keV the two curves practically coincide; at energies below 150 keV the curves diverge. Recalculation of the data on the stopping power of a number of chemical compounds given in work ([9]) per one absorbing electron (see Table 2 of work ([6])) shows that at proton energies above 200 keV the chemical bond, within the accuracy of the experiment, does not affect the stopping power. Below 200 keV the discrepancy exceeds the experimental error; in this energy region the chemical nature of the compound is already manifested. It is interesting to note that benzene vapor at $E_p < 200$ keV has a stopping power per electron smaller than that of vapors of compounds having no free π-electrons.

The stopping power of a substance includes losses both to excitation of electronic states of atoms and molecules and to ionization. For different chemical compounds the relative fractions of the energy going into ionization and into excitation may be different. An approximate estimate of the ratio of the number of excitation events N_e to the number of ionization events N_i can be obtained from the energy balance for the absorbed energy E ([15]). Namely:

$$\frac{N_e}{N_i} = \frac{W - \overline{E}_i - \varepsilon}{\overline{E}_e}, \tag{1}$$

where W denotes the average energy going to the formation of an ion pair ($W = E/N_i$), $\overline{E}_i$, $\overline{E}_e$ are the average ionization and excitation energies, respectively, and ε is the average energy of pre-excitation electrons, i.e., electrons whose energy is below the first excitation potential of the molecule ([16]). For gases the values of W have been measured rather accurately; to find the average energy of pre-excitation electrons it is necessary to know their energy distribution function, $f(\varepsilon)$. As $f(\varepsilon)$ we took the distribution function from work ([17]). This gives the following expression for $\overline{\varepsilon}$:

$$\overline{\varepsilon} = \frac{2I\,(I + E_1)}{2I + E_1} - I_1, \tag{2}$$

where E_1 is the first excitation potential, and I is the first ionization potential. For molecules, the energy of the lower triplet level must be taken as E_1. Since for saturated compounds the position of the triplet level is uncertain, for them E_1 was determined from the long-wavelength

to the absorption edge. Table 2 gives the ratios N_e/N_i for several classes of compounds. The values of $\bar{E}_e$ were determined from the maximum in the optical absorption spectrum; data on the spectra of inelastic scattering of electrons with an initial energy of 390 eV were also used ([18]). The values of $\bar{E}_i$ were taken from the work of Stevenson ([19]), in which the mean energy going into ionization is determined from mass-spectrometric data and includes the energy falling on excited states of ions. Allowance for multiple ionization, as well as for "superexcited" states ([20,21])

Table 1*

Excitation cross sections of the benzene molecule

E, eV	σ_π	σ_{add}	$^1/_6\sigma_\pi$	$^1/_{42}\sigma_{\text{add}}$
700	2.28	7.98	0.38	0.19
1000	1.68	6.06	0.28	0.15
1500	1.18	4.32	0.20	0.10

* In units of $\pi a_0^2 = 0.88 \cdot 10^{-16}$ cm^2.

should somewhat lower the ratios N_e/N_i given in the last column of Table 2, since it leads to an increase in $\bar{E}_i$ and $\bar{E}_e$. As is seen from the data of Table 2, for all compounds the ratio N_e/N_i is of order unity; at the same time, the relative fraction of excitations in the case of substances containing π-electrons is somewhat greater than in the case of saturated compounds.

Table 2

Ratio of the number of excitation acts to ionization acts

Substance	W_β, eV ([15])	$\bar{E}_i$, eV ([19])	$\bar{E}_e$, eV	$\bar{\varepsilon}$, eV	N_e/N_i
CH_4	27.3	15.0	11	2.6	0.9
C_2H_6	24.5	14.8	10.5	2.5	0.7
C_3H_8	24.3	14.2	10	2.5	0.8
C_2H_2	25.7	15.2	8.5	1.7	1.0
C_2H_4	26.1	13.9	7.5	1.3	1.4
C_6H_6	25.5	15.5	7	1.5	1.2

The totality of the theoretical and experimental data presented in this communication argues against the hypothesis of selective absorption of energy by π-electrons. Apparently, up to velocities of the incident particle not greatly exceeding the velocities of molecular electrons, the additivity rule is fulfilled. However, it is not yet possible to indicate precisely what error is made in taking the absorbed energy to be proportional to the electronic fraction of the component, since the contribution of slow secondary electrons is unknown.

In considering the mechanism of radiation-chemical processes, it is customary to suppose that the chemical changes caused by ionizing radiation are mainly the result of the action of secondary electrons, most of which have energies below 100 eV ([22,23]). This idea is based on the circumstance that a primary fast electron with an energy of 1 MeV produces $\sim 3 \cdot 10^4$ secondary electrons, the spectrum of which is shifted into the region of low energies. In this, however, it is not taken into account that ionization and excitation induced by the primary fast particle also lead to chemical transformations. The fraction of elementary acts attributable to interaction with fast electrons is by no means negligibly small. This follows from the circumstance-

that the most probable process of degradation of the energy of a fast particle is its loss in small portions ([24]). The spectrum of the ejected electrons is shifted toward low energies, and the relative number of tertiary, quaternary, etc. electrons is small. According to measurements by Decher and Kulenkampff ([25]), upon irradiation of air with 4.9 MeV electrons, the ratio of the number of all ionizations to the number of primary ionizations is 2.5, i.e., each ejected electron on average produces an additional 1.5 ionization events. Since part of the secondary ionizations is produced by fast secondary electrons, it may be roughly

assumed that the ratio of the number of ionizations by fast and slow electrons is 1 : 1. An analogous ratio is apparently also valid for excitation events, since $N_e \approx N_i$ (see Table 2), while, as follows from Bethe' s calculations for hydrogen atoms, the relative probability of excitation is greater for fast electrons than for slow ones ([26]). Thus, we arrive at the conclusion: of the total number of primary elementary events upon irradiation of the system by fast electrons or by γ-rays of Co^{60}, fast electrons account for approximately 50%. In other words, if by $dN(E)$ we denote the number of elementary events produced by electrons whose energy lies in the interval from E to $E + dE$, then after a stationary distribution has been established the following equality is approximately satisfied:

$$\int_0^{E=100\text{ eV}} dN(E) \approx \int_{E=100\text{ eV}}^{E_0} dN(E), \tag{3}$$

where E_0 denotes the maximum energy of the electron beam*. The estimates made are qualitative in character; the true value of the contribution of fast electrons to the overall balance of elementary events may differ from 50%, but it will always constitute a significant part of the total number of elementary events.

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* It should be noted that electrons of all energies from E_0 down to zero are present in the case of complete degradation of the energy of the fast particle. In thin films, where multiple scattering is unlikely, electrons in the energy region intermediate between $E_0 - \varepsilon$ and ε ($\varepsilon \sim 100$ eV) are practically absent.

Note: Figure translations are in progress. See original paper for figures.