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On the Continuous Slowing Down Approximation for the Degradation Spectra of Secondary Electrons

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The degradation spectra of secondary electrons produced in helium irradiated with high energy electrons have been calculated by two methods. In the first method, the direct integration of the basic formula was carried out and in the second one, the continuous-slowing-down-approximation (CSDA) was used. When the energy of incident electrons is 1 keV (1 eV$=9.648\times10^4$ J/mol), the second method gave a *G*-value of ionization, 2.17, while the first method gave 2.29. With the decrease in the energy of incident electrons, the CSDA was found to become less reliable. With the incident electrons of 100 eV, the error in the *G*-value of ionization exceeded 15%. The implication of these calculations to the theoretical treatment of the initial process of radiation chemistry is discussed. As an example, the spatial distribution of ion-pairs in γ-irradiated water has been recalculated.

The degradation spectrum of secondary electrons produced in a material irradiated with ionizing radiations is a useful concept for discussing physical and chemical changes induced by these secondary electrons in the material. However, the numerical calculation of the degradation spectrum is not a simple problem, even when all the inelastic collision cross sections of electrons are known. Consequently, the continuous-slowing-down-approximation (CSDA) has often been used for the calculation.

In the previous papers,[1–4] the theoretical estimation of *G*-values of ionization and excitation has been made on many atoms and molecules by using the CSDA. The calculated *G*-values were found to be in fair agreement with those obtained experimentally. However, we were not confident of these calculated *G*-values, partly because of the CSDA.

The accuracy of CSDA has been discussed by many investigators,[5,6] but few numerical checks have been made.[7,8] Klots and Wright carried out Monte Carlo calculations to obtain accurate degradation spectra in some physical model systems and compared them with those calculated under CSDA. Both spectra apparently coincided with each other, but the implication of these calculations to the theoretical treatment of radiation chemistry was not given. The Monte Carlo calculation is very laborious and time-consuming.

The basic formula for the degradation spectrum has been originally proposed by Fano.[9] The numerical calculation of this formula is not a difficult problem, if the energy of incident electrons is not extremely high and if the material consists of simple atoms or molecules.

In the present paper, we will calculate the exact degradation spectra of secondary electrons in helium irradiated with less than 1 keV electrons and estimate the *G*-values of ionization and excitation. These spectra and the *G*-values will be compared with those calculated by using CSDA. Since all the collision cross sections used in the present calculations are obtained by the classical binary-encounter-collision theory, "the exact degradation spectrum" does not mean the true one but the mathematically exact one.

Theory

The basic form of the degradation equation for secondary electrons is expressed as follows:

$$y(T)\int_{E_0}^{T} k(T,E)\,\mathrm{d}E = \int_{E_0}^{\lambda} y(T+E)k(T+E,E)\mathrm{d}E + \int_{2T+I}^{T_0} y(T')k(T',T+I)\,\mathrm{d}T' + S(T). \tag{1}$$

Here, $y(T)$ is the degradation spectrum at the electron energy T, and $k(T, E)$ is the probability per unit path length that an electron of energy T experiences an energy loss between E and $E+\mathrm{d}E$. This probability is the product of the differential cross section by the number density of molecules in the medium. $S(T)$ is the energy distribution of source electrons. In the present calculations, $S(T)=\delta(T_0-T)$. When an electron induces ionization, we cannot distinguish which electron is the incident electron or the electron originally attached to the medium. In the formulation, we define the electron carrying the larger energy after collision to be the incident one; therefore, the upper limit of the integration range of the first term in the right hand side of Eq. 1, λ, is the lesser of T_0-T and $T+I$, where I is the ionization energy, and the lower limit of the second term is $2T+I$. E_0 is the lowest energy loss resulted from the collision.

It is mathematically possible to obtain the degradation spectrum $y(T)$ by numerically solving Eq. 1, if all inelastic collision cross sections are known; however, since the lowest energy loss E_0 is usually much smaller than that of the incident electron T_0, numerous reiterations for integration are necessary and consume a long time for the calculation even by the use of an electronic computer. In the present calculations, the T_0 is limited to 1 keV. If its energy is increased, the calculation time is increased exponentially.

Continuous-slowing-down-approximation. In 1954, Spencer and Fano showed that, if the inelastic collision cross section is proportional to $(\pi e^4/T)(1/E^2)$ and the lowest energy loss E_0 can be assumed to be much smaller than T, the degradation spectrum for the incident particle is expressed as the reciprocal of the stopping power of the medium for that particle.

The exact degradation equation for the incident particle may be written as follows:

$$y_1(T)\int_{E_0}^{T} k(T,E)\mathrm{d}E = \int_{E_0}^{\lambda} y_1(T+E)k(T+E,E)\mathrm{d}E + S(T). \tag{2}$$

This equation is similar to Eq. 1 except for the second term of the right hand side of Eq. 1, the term which corresponds to the generation of new particles. The result of Spencer-Fano's derivation may be expressed as follows:

$$y_1(T) \approx 1/s(T) = \left[\int_{E_0}^{T} k(T,E)E\mathrm{d}E\right]^{-1}, \tag{3}$$

where, $s(T)$ is the stopping power. Now let us consider that the incident particle is an electron, then $y_1(T)$ calculated above corresponds to the degradation spectrum of the incident electron. Once $y_1(T)$ is calculated, the degradation spectrum of the second generation $y_2(T)$ can be calculated as follows:

$$y_2(T) = \frac{N}{s(T)}\int_{T}^{1/2(T_0-T)}\int_{2T_2+I}^{T_0} y_1(T)\sigma(T_1,T_2)\,\mathrm{d}T_1\mathrm{d}T_2. \tag{4}$$

Here, N is the number density of electrons in the medium and $\sigma(T_1,\ T_2)$ is the cross section for the formation of electrons with energy T_2 in the collision of electrons with energy T_1. A similar equation for the degradation spectrum of the third generation can be constructed:

$$y_3(T) = \frac{N}{s(T)}\int_{T}^{1/4(T_0-3I)}\int_{2T_2+I}^{T_0} y_2(T)\sigma(T_1,T_2)\,\mathrm{d}T_1\mathrm{d}T_2. \tag{5}$$

The degradation spectrum of all electrons is thus calculated by summing up those of all generations:

$$y(T) = \sum_{m} y_m(T). \tag{6}$$

Collision-cross-section. All the inelastic collision cross sections used in the present calculations are derived by the classical binary-encounter-collision-theory. These cross sections have been fully discussed in a previous paper.[1)] For example, $\sigma(T_1,\ T_2)$ is expressed as follows:

$$\sigma(T_1,T_2) = \frac{\pi e^4}{T_1+I_1+E_1}\left[\frac{1}{(T_2+I_1)^2} + \frac{4E_1}{3(T_2+I_1)^2} + \frac{1}{(T_1-T_2)^2} + \frac{4E_1}{3(T_1-T_2)^3}\right]. \tag{7}$$

Here I_i and E_i are the binding energy and the average kinetic energy of i-th shell.

G-*Values of Ionization and Excitation.* Once $y(T)$ is obtained, we can calculate the G-values of ionization and excitation.

$$G_\mathrm{n} = \frac{1}{100\ T_0}\int_{E_\mathrm{n}}^{T_0} Ty(T)Q_\mathrm{n}(T)\,\mathrm{d}\ln T. \tag{8}$$

Here Q_n and E_n are the total cross section and the threshold energy for the excitation process n.

Subexcitation Electrons. In order to discuss the behavior of secondary electrons in the medium, the initial energy distribution of subexcitation electrons is indispensable, which can be calculated by using $y(T)$:

$$N(T)_{T<E_0} = \int_{E_0}^{T+I} y(T+E)k(T+E,E)\mathrm{d}E + \int_{2T+I}^{T_0} y(T')k(T',T+I)\mathrm{d}T'. \tag{9}$$

Results and Discussion

The Degradation Spectra near the Energy of Incident Electrons. Figure 1 shows the $y(T)$ near the source energy, 1 keV. The solid line shows the result of the direct integration of Eq. 1 and the dashed line shows the result calculated under the CSDA. Table 1 summarizes necessary in-put data.

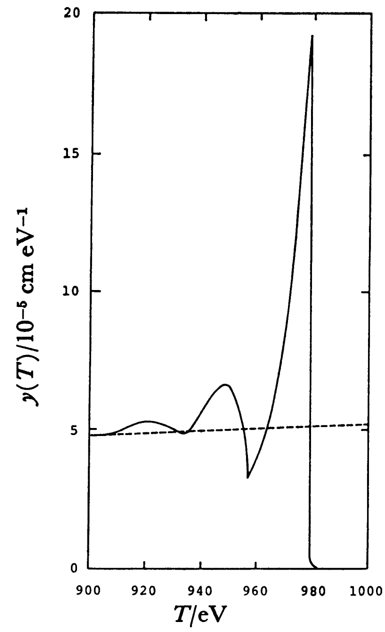

Fig. 1. The degradation spectra of secondary electrons near the energy of incident electrons.
——: Direct integration, ----: CSDA calculation.

TABLE 1. THE BINDING ENERGY (I_1) AND THE AVERAGE KINETIC ENERGY(E_1) OF ELECTRONS IN HELIUM, AND THE SINGLET(E_s) AND TRIPLET(E_t) EXCITATION ENERGIES OF HELIUM IN UNITS OF eV

I_1	E_1	E_s	E_t
24.581	38.74	21.2	19.8

Since the lowest energy loss accompanying the inelastic collision in helium is the triplet excitation energy, $E_\mathrm{t}=19.8$ eV, no electrons can be produced having energy in the range 980.2 to 999.9 eV. The solid line correctly expresses this transient effect. The oscillations of $y(T)$ for energies near the source energy, which is known as the Lewis effect,[10)] is also correctly expressed by the solid line. The spacing between maxima is about 30 eV. On the other hand, the $y(T)$ obtained by using the CSDA does not show such effects. If the detailed structure of $y(T)$ near the source energy is to be included, CSDA cannot be used.

The numerical calculation of such oscillations of $y(T)$ has been carried out by Douthat, who used a different approximate method named SF-2 cord.[6)] The general trend of the degradation spectrum he reported is in fair agreement with that obtained here.

The Degradation Spectra and the G-*Values of Ionization and Excitation.* In Fig. 2 two degradation spectra calculated by the two methods are compared: the solid curve is the result of the direct integration and the dashed one is that calculated under CSDA. Both curves are apparently in good agreement. In the range from 900 to 80 eV, the difference is within a few %, but below 80 eV, the difference increases to about

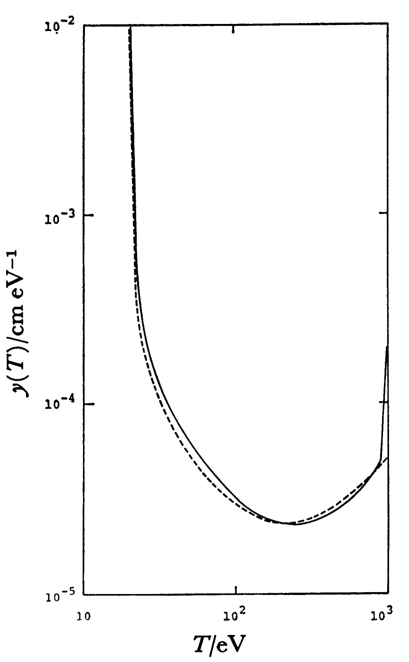

Fig. 2. The degradation spectra of secondary electrons produced in helium irradiated with 1 keV electrons.
——: Direct integration, ----: CSDA calculation.

20%. These calculations depend upon the mesh with which the numerical integration is carried out. For the solid curve, the smallest mesh used was 0.1 eV; with this mesh, the curve obtained was nearly completely converged. For the CSDA calculation, the logarithmic mesh was used; the curve shown in Fig. 2 was obtained with log $(\Delta T/T)=0.01$. With this mesh, the convergion was nearly complete.

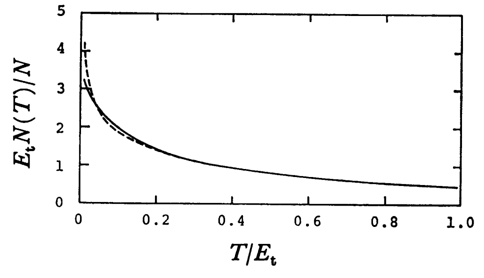

Fig. 3. The initial energy distribution of subexcitation electrons produced in helium irradiated with 1 keV electrons.
——: Direct integration, ----: CSDA calculation.

TABLE 2. THE G-VALUES OF IONIZATION AND SINGLET AND TRIPLET EXCITATIONS CALCULATED BY THE TWO METHODS: DIRECT INTEGRATION (DI) AND THE APPROXIMATE METHOD USING CSDA[a)]

	DI	CSDA
G_{ion}	2.29	2.17
G_{singlet}	0.91	0.82
G_{triplet}	0.17	0.14

a) Comparison of the calculated G_{ion} with experiment has been made in Ref. 2.

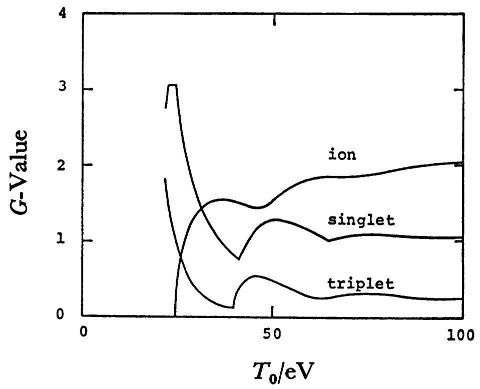

Fig. 4. The source energy dependence of the G-values of ionization and singlet and triplet excitations calculated by the direct integration.

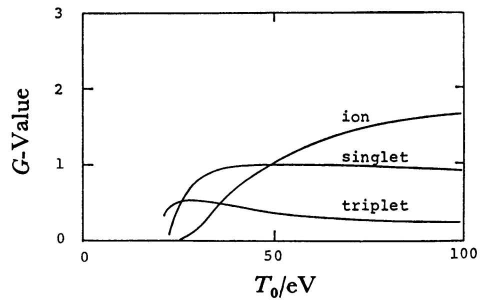

Fig. 5. The source energy dependence of the G-values of ionization and singlet and triplet excitations calculated under the CSDA.

Using these two degradation spectra, we calculated the initial energy distribution of subexcitation electrons and the G-values of ionization and singlet and triplet excitations. The results are shown in Fig. 3 and Table 2. The discrepancy between the CSDA calculation and the direct integration was found in the G-values. The CSDA calculation gave G-values smaller than the direct integration of Eq. 1. This is probably due to the underestimation by the CSDA calculation of $y(T)$ near the threshold energy E_t.

In order to clarify this discrepancy, we calculated the dependence of the G-values of ionization and excitation on the source energy T_0 in the range of 20—100 eV. Figures 4 and 5 show the results. A comparison of these two figures clearly shows that the CSDA calculation underestimates the G-values and that, with the decrease in the source energy, the discrepancy increases. At $T_0=1$ keV, the discrepancy is 6%, while at 100 eV, it increases to 15%.

In a previous paper,[2)] the source energy dependence of the G-values of ionization and excitations of helium was calculated by using the Fowler equation, and curves similar to those in Fig. 4 were obtained. In fact, these two sets of curves coincide exactly with each other. In the actual calculations, the Fowler equation is solved from lower energies, while Eq. 1 is solved from higher energies. The agreement of these sets of curves probably means that the mesh used in these calculations is small enough for the numerical integrations. Incidentally,

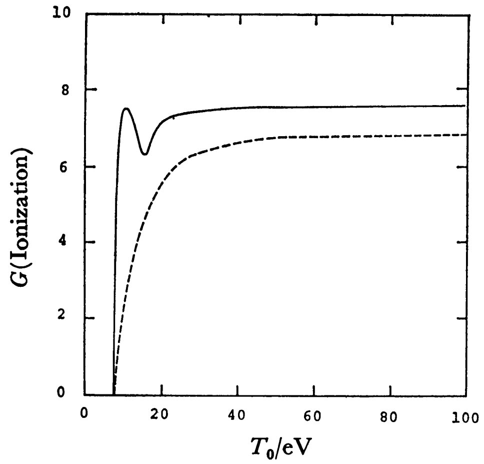

Fig. 6. The source energy dependence of the G-value of ionization in water.
——: Direct integration, ----: CSDA calculation.

it has been proved that the Fowler equation is mathematically equivalent to the Spencer-Fano equation, Eq. 1.[11)]

In summary of the above calculations, it may be said that, if the energy of incident electrons is higher than 1 keV, CSDA is accurate enough to estimate the G-value of ionization and excitation; the error limit caused by the use of CSDA is within 6%.

Relative Numbers of Ion-pairs in Different Spurs Generated in the γ-Irradiated Water. In a previous paper,[4)] we calculated the spatial distribution of ion-pairs produced in water irradiated with ^{60}Co-γ rays. About 27% of ion-pairs were found to be produced in isolated spurs and another 27% were found in the condensed spurs consisting of more than 100 ion-pairs. In that estimation, we used the source energy dependence of the G-value of ionization calculated under CSDA. As has been discussed above, when the source energy is small, the G-value of ionization is underestimated by the CSDA calculation. We calculated the source energy dependence of the G-value of ionization in water by the direct integration of the Spencer-Fano equation. The result is shown in Fig. 6. By using this result, we recalculated the relative frequencies of spurs in water and the relative numbers of ion-pairs in different spurs. The results are shown in Tables 3 and 4, together with those previously reported. It is noticeable that the agreement between calculation and experiment has been improved.

Table 3. Calculated relative frequencies of spurs in water and relative frequencies of clusters observed in a cloud chamber

Ion-pairs per spur	1	2	3	4	>4
Relative frequency/%	65.7	18.6	6.0	3.1	6.6
(Previously reported)	(73.6)	(11.7)	(5.0)	(3.1)	(6.6)
Ion-pairs per cluster	1	2	3	4	>4
Relative frequency/%					
Source: 25 keV[12)]	42.6	22.5	12.4	10.1	12.4
150 keV[13)]	60	23	8	4	5
320 keV[13)]	62	20	9	4	5

Table 4. Relative numbers of ion-pairs in different spurs

Ion-pairs per spur	Relative number/%	
	(CSDA)	(Corrected)
1	26.8	23.1
2	8.5	13.1
3	5.4	6.3
4	4.5	4.4
5—10	10.9	10.6
11—100	16.5	16.0
>100	27.4	26.5

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