The Contribution of the Double Collision Occurring in an Atom to the Yield of the Ionization and Excitations of Noble Gases Irradiated by 100 keV Electrons

Kiyoshi Okazaki, Shin Sato, and Shin-ichi Ohno*

Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

* Japan Atomic Energy Research Institute, Tokai-mura, Ibaragi 319-11

(Received December 24, 1974)

Gryzinski's classical treatment of the double ionization has been used to estimate the contribution of the double-collision process to the G-values of the ionizations and excitations of noble gases irradiated by 100 keV electrons. Except for helium, the double collision accounted for 5—15% of the yield of electrons. The total G-values calculated are ultimately as follows (in the order of He, Ne, Ar, Kr, and Xe): 2.28, 2.53, 3.09, 3.41, 3.67 for G(electrons); 0.84, 1.37, 1.78, 1.54, 1.41 for G(excited singlet states); 0.17, 0.07, 0.13, 0.23, 0.39 for G(triplet states).

The cross sections for the formation of multiplycharged ions of atoms and diatomic molecules in collision with high-energy electrons have been measured by many investigators over the past forty years. 1-6) Recently more reliable values of the cross sections in a wide energy range of the incident electrons have been reported.⁷⁻¹⁰⁾ On the other hand, the theoretical treatment of the formation of the multiply-charged ions has not been developed remarkably since Gryzinski proposed the classical treatment of double ionization.¹¹⁾ Although a quantum mechanical estimation of the double ionization has been proposed by Mittleman, 12) his method is at present limited in its field of application. Gryzinski's classical method has recently been modified and used by Tripathi and Rai¹³⁾ to estimate the cross section for the double ionization of He and Li+. Their results agreed reasonably well with the experimental ones.

In a previous paper, 14) we ourselves have calculated the G-values of the ionizations and excitations of noble gases irradiated by 100 keV electron, using the classical binary encounter collision theory. Although the Gvalues calculated were roughly consistent with those expected from the experiment, there were a few defects in the results. One of the most serious was that the calculated W-value of Ne was larger than that of He. It is experimentally known that these values are reversed in magnitude. This discrepancy might result from the assumption on the basis of which the calculation was carried out. In the previous calculation, we ignored the contributions of the double ionization and the excitation from the inner shells. This might have affected the W-values obtained. In the present paper, we calculated the amount of the double ionization by using Gryzinski's classical method and also estimated the contributions of the double excitation and the excitations from the inner shells.

Method of Calculation

Approximations. Since the probability of the double collision of high-energy electrons in an atom is much smaller than that of the single collision, we used the following three approximations: 1) When the stopping power, S(T), of a gas and the degradation spectrum, y(T), of electron are calculated, the contributions of the

double collision and the excitations from the inner shells are ignored; that is, the S(T) and y(T) previously obtained are used as they were. 2) The cross section of the double collision is formulated by Gryzinski's method.¹¹⁾ The differential cross sections involved in the formulation of the double collision are, however, evaluated by the method previously used.¹⁴⁾ The details of the formulation will be shown later. 3) The double collision is calculated only on the electrons in the outermost shell of the atom. In order to calculate the double collision in which the electrons in the inner shells are involved, we need more parameters than are available at present. According to the estimation of Roy et al., 15) the contribution of the inner shells to the double collision is much smaller than that of the outermost shell.

Formulation. Even within the treatment of the single collision we had to consider various types of collisions, such as the ionizations from all of the shells, the ionization accompanied by the exchange of electrons, and the singlet and triplet excitations. Moreover, the energy range of the incident electrons, higher or lower than the ionization potential or the energies of the excited states, had to be taken into account. In the treatment of the double collision, we have to consider all of the combinations of these collisions.

Double Ionization: After the occurrence of the first ionizing collision with an incident electron, there are two types of second ionizations; one is Case A, in which the second ionization is induced by the incident electron, while the other is Case B, in which the second ionization is induced by the electron which recoiled in the first collision. According to the treatment of Gryzinski, ¹¹⁾ the total ionization cross section in Case A is expressed in this form:

$$\begin{split} Q_{\rm ii}^{\ A}(T) &= \frac{1}{2} \int_{I_{\rm i}}^{T-I_{\rm ii}} [\sigma_{E, \rm dir} + \sigma_{E, \rm exc}] \frac{n_{\rm e}(n_{\rm e}-1)}{4\pi \bar{r}^2} \\ &\times \int_{I_{\rm ii}}^{T-E} [\sigma_{E', \rm dir}(T-E) + \sigma_{E', \rm exc}(T-E)] \mathrm{d}E' \mathrm{d}E \end{split} \tag{1}$$

for $T \ge I_i + I_{ii}$. Here, n_e is the number of electrons in the outermost shell of the target atom; \bar{r} , the mean distance between atomic electrons; T, the initial energy of the incident electron; E, the energy loss of the incident electron in the first collision—therefore, T - E is the energy of the scattered electron and $E - I_i$ is the energy

of the electron ejected from the atom in the first collision; $I_{\rm i}$, the ionization potential of the target atom; $I_{\rm ii}$, the second ionization potential of the atom; E', the energy loss in the second collision—therefore, T-E-E' is the energy of the doubly scattered electron and $E'-I_{\rm ii}$ is the energy of the electron ejected from the atom in the second collision.

As has been stated above, the differential cross sections, $\sigma_{E,\text{dir}}$ and $\sigma_{E,\text{exc}}$, are the same as those used in the previous paper:¹⁴⁾

$$\sigma_{E,\text{dir}} = \frac{\pi e^4}{T + L + E_1} \left(\frac{1}{E^2} + \frac{4E_1}{3E^3} \right) \tag{2}$$

$$\sigma_{E,\text{exc}} = \frac{\pi e^4}{T + I_i + E_i} \left\{ \frac{1}{(T + I_i - E)^2} + \frac{4E_i}{3(T + I_i - E)^3} \right\} (3)^{16}$$

In a similar manner, the differential cross sections for the second ionizations are expressed as follows:

$$\sigma_{E',\text{dir}}(T-E) = \frac{\pi e^4}{T - E + E_i + I_{ii}} \left(\frac{1}{E'^2} + \frac{4E_i}{3E'^3} \right)$$
(4)

$$\sigma_{E',\text{exc}}(T-E) = \frac{\pi e^4}{T - E + E_1 + I_{11}} \left\{ \frac{1}{(T - E + I_{11} - E')^2} + \frac{4E_1}{3(T - E + I_{11} - E')^3} \right\}$$
(5)

When $T < I_i + I_{ii}$, $Q_{ii}^A(T)$ is set equal to zero.

Similarly, the total double-ionization cross section in Case B may be expressed by:

$$Q_{ii}^{B}(T) = \frac{1}{2} \int_{I_{i}+I_{ii}}^{T} [\sigma_{E,dir} + \sigma_{E,exc}] \frac{n_{e}(n_{e}-1)}{4\pi \tilde{r}^{2}} \times \int_{I_{e}}^{E-I_{i}} [\sigma_{E',dir}(E-I_{i}) + \sigma_{E',exc}(E-I_{i})] dE' dE \quad (6)$$

for $T \ge I_i + I_{ii}$. When $T < I_i + I_{ii}$, $Q_{ii}{}^B(T)$ is set equal to zero. A simple calculation can show that $Q_{ii}{}^A(T) = Q_{ii}{}^B(T)$.

Although, in the above treatment, Cases A and B have been formulated separately, the final states obtained through the two processes cannot be distinguished. Since we cannot specify the origin of the electron inducing the second ionization—cannot determine whether it is an incident electron or the atomic one, the total cross section of the double ionization should be a half of the sum of $Q_{ii}^{A}(T)$ and $Q_{ii}^{B}(T)$:

$$Q_{ii}(T) = \frac{1}{2} [Q_{ii}^{A}(T) + Q_{ii}^{B}(T)] = Q_{ii}^{A}(T)$$
 (7)

Double Excitation: The above treatment of double ionization can be extended to the double excitation. In the case of excitation, we have two types; one is accompanied by a change in the spin state (SC), while the other is not accompanied by such a change (SNC). In the formulation of the double excitation, therefore, we have to consider the combination of these two types of excitations.

By referring to the formulation of the excitation shown in the previous paper, the total cross sections of all kinds of double excitations can easily be formulated. Here, only the formulation for the case of SNC-SNC will be shown. This case leads to the formation of an excited singlet state. The total cross section for this process may be described as follows:

$$Q_{\text{ee}}(\text{SNC-SNC}) = \int_{E_{\text{a}}}^{I_{1}} [\sigma_{E,\text{dir}} + \frac{1}{2} \sigma_{E,\text{exc}}] \frac{n_{\text{e}}(n_{\text{e}} - 1)}{4\pi\bar{r}^{2}} \times \int_{\pi}^{I_{1i}} [\sigma_{E',\text{dir}}(T - E) + \frac{1}{2} \sigma_{E',\text{exc}}(T - E)] dE' dE \quad (8)$$

for $T \ge I_i + I_{ii}$. Here, E_s is the energy of the lowest excited singlet state and E_{s2} is the energy necessary for the excitation in the second collision; that is, $E_{s2} = E^{**} - E_s$, where E^{**} is the energy of the double excitation state. When $E_s + I_{ii} \le T < I_i + I_{ii}$,

$$Q_{\text{ee}}(\text{SNC-SNC}) = \int_{T-I_{11}}^{I_{1}} [\sigma_{E,\text{dir}} + \frac{1}{2} \sigma_{E,\text{exc}}] \frac{n_{\text{e}}(n_{\text{e}} - 1)}{4\pi\bar{r}^{2}} \\ \times \int_{E_{\text{et}}}^{T-E} [\sigma_{E',\text{dir}}(T-E) + \frac{1}{2} \sigma_{E',\text{exc}}(T-E)] dE' dE \\ + \int_{E_{\text{s}}}^{T-I_{11}} [\sigma_{E,\text{dir}} + \frac{1}{2} \sigma_{E,\text{exc}}] \frac{n_{\text{e}}(n_{\text{e}} - 1)}{4\pi\bar{r}^{2}} \\ \times \int_{E_{\text{e}}}^{I_{11}} [\sigma_{E',\text{dir}}(T-E) + \frac{1}{2} \sigma_{E',\text{exc}}(T-E)] dE' dE$$
 (9)

When $I_i + E_{s2} \le T < E_s + I_{ii}$, the upper limit of the second integral of Eq. (8) should be replaced by T-E. When $E_s + E_{s2} \le T < I_i + E_{s2}$, the upper limit of the first integral of Eq. (8) has to be replaced by $T-E_s$, in addition to the replacement of the upper limit of the second integral by T-E. When $T < E_s + E_{s2}$, $Q_{ee}(SNC-SNC)$ is set equal to zero.

Other combinations, SC-SC, SNC-SC, and SC-SNC, of the double excitation can be formulated in a similar manner by using the energies of the first triplet state (E_t) and the energy necessary for the excitation from the first excited-triplet state to the double-excitation state (E_{t2}) . In the case of SC-SC, we obtain a singlet or a quintet state as the final state. However, the G-value for this process is so small that we assume that the obtained state is always a singlet state.

Ionization and Successive Excitation: This process leads to the formation of a hot ion. As in the case of the double ionization, the second collisions in this case are of two types; one is induced by the electrons scattered in the first collision, while the other is induced by the recoiled electron. The total cross sections of these two processes have the same value. Again, as in the case of the double ionization, we cannot distinguish these two processes. The total cross section, therefore, is equal to that of either of the two processes.

The following shows the case of the ionization and successive excitation without any spin change (I–SNC). A similar formulation can easily be made for the case of I–SC, which is not shown here.

$$Q_{ie}(I-SNC) = \int_{I_{i}}^{T-I_{i1}} [\sigma_{E,dir} + \sigma_{E,exc}] \frac{n_{e}(n_{e}-1)}{4\pi\bar{r}^{2}}$$

$$\times \int_{E_{ss}}^{I_{1i}} [\sigma_{E',dir}(T-E) + \frac{1}{2}\sigma_{E',exc}(T-E)] dE' dE$$

$$+ \int_{T-I_{i1}}^{T-E_{ss}} [\sigma_{E,dir} + \sigma_{E,exc}] \frac{n_{e}(n_{e}-1)}{4\pi\bar{r}^{2}}$$

$$\times \int_{E_{ss}}^{T-E} [\sigma_{E',dir}(T-E) + \frac{1}{2}\sigma_{E',exc}(T-E)] dE' dE$$
 (10)

for $T \ge I_i + I_{ii}$. When $I_i + E_{s2} \le T < I_i + I_{ii}$,

$$Q_{ie}(I-SNC) = \int_{I_{1}}^{T-E_{s}} [\sigma_{E,dir} + \sigma_{E,exc}] \frac{n_{e}(n_{e}-1)}{4\pi\bar{r}^{2}} \times \int_{E}^{T-E} [\sigma_{E',dir}(T-E) + \frac{1}{2}\sigma_{E',exc}(T-E)] dE'dE \quad (11)$$

When $T < I_i + E_{s2}$, $Q_{ie}(I-SNC)$ is set equal to zero.

Excitation and Successive Ionization: This process also leads to the formation of a hot ion. The formulations of $Q_{\rm ei}(SNC-I)$ and $Q_{\rm ei}(SC-I)$ can easily be made by referring to the treatments described above. Only the latter case is shown here:

$$Q_{ei}(SC-I) = \frac{1}{2} \int_{E_{t}}^{I_{t}} \left[\frac{1}{2} \sigma_{E,exc} \right] \frac{n_{e}(n_{e}-1)}{4\pi \bar{\tau}^{2}} \times \int_{E_{t1}}^{T-E} \left[\sigma_{E',dir}(T-E) + \sigma_{E',exc}(T-E) \right] dE' dE$$
 (12)

for $T \ge I_i + E_{ti}$, where E_{ti} is the energy necessary for the ionization from the lowest excited-triplet state to the lowest excited ion. When $E_t + E_{ti} \le T < I_i + E_{ti}$, the I_i in the first integral should be replaced by $T - E_{ti}$. When $T < E_t + E_{ti}$, $Q_{ei}(SC-I)$ is set equal to zero.

Inner-shell Excitation: The formulation is exactly the same as that of the single excitation described in a previous paper, ¹⁴⁾ except that the parameters, I_i , E_i , E_s , and E_t , have to be replaced by the values corresponding to those of the inner shells. In the present calculation, the contributions of the shells more inner than 3s in Ar, 3d in Kr, and 4p in Xe are ignored.

Constants Used for Calculation

The values of E_s , E_t , I_i , and E_i are the same as those used in the previous paper.¹⁴ Table 1 summarizes the I_i , E_s , and E_t values of the inner shells, where the last two values are assumed to be the same. Table 2 shows the mean distance between electrons in the outermost shell of each atom and the second ionization potential (I_{ii}) . The mean distance was calculated by placing the electrons uniformly on a sphere the radius of which had been estimated by Slater.¹⁷)

Table 3 shows the double-excitation energy (E^{**}) and the energy of the lowest excited state of the singly charged ion (E^{+*}) . Some of these values have been experimentally obtained; $^{18-24}$) from them we can calculate $E_{\rm s2}$ and $E_{\rm t2}$. In the case of the double excitation, we can assume that $E_{\rm s2}=E^{**}-E_{\rm s}$ and $E_{\rm t2}=E^{**}-E_{\rm t}$.

Table 1. Ionization potential $(I_{\rm i})$ and the excitation energies to the fierst excited singlet $(E_{\rm s})$ and the lowest triplet $(E_{\rm t})$ states with respect to the inner shells

Atom (shell)	I_{i}	$E_{ m s},E_{ m t}$	Reference
Ne (2s)	48.42	43.65	23)
(1s)	867	865ª)	,
Ar(3s)	29.3	25.22	24)
Kr (4s)	27.4	23.73	19)
(3d)	93.7	91.24	18, 24)
$\dot{\mathbf{Xe}(5s)}$	23.3	20.95	19)
(4d)	67.5	65.2	18)
(4p)	145.5	142	22, 24)

a) Assumed.

Table 2. The mean distance between electrons (\vec{r}) and the second ionization potential (I_{11})

Atom (shell)	\bar{r} (A)	$I_{\rm ii}({ m eV})$
He (1s)	0.60	54.40
Ne (2p)	0.45	41.07
Ar (3p)	0.95	27.62
Kr (4p)	1.22	24.56
Xe (5p)	1.41	21.20

Table 3. The double excitation energy (E^{**}) and the energy of the excited state of the singly charged ion (E^{+*})

Atom	E** (eV)	E+* (eV)
He	57.82 (¹S)	65.4
110	58.34 (³ P)	00.1
Ne	45.0	57.6a)
Ar	30 ^{b)}	36 ^{c)}
Kr	27 ^{b)}	33°)
Xe	23 ^{b)}	28°)

a) Assumed. b) Calculated on the assumption that $E^{**}=I_1+I_{11}/2$. c) Calculated on the assumption that $E^{+*}=I_1+3I_{11}/4$.

In the case of the ionization and successive excitation, we assumed $E_{\rm s2}{=}E_{\rm t2}{=}E^{+*}{-}I_{\rm i}$.

Results

Figure 1 shows the $T \cdot y(T) \cdot Q_s(T)$ for the double collision in Ne as a function of ln T. Similar curves were also obtained in other cases —He, Ar, Kr, and Xe. All the curves for the double ionization have maxima at about twice the threshold energy of each atom and rise again as the T increases over $10^4 \, \mathrm{eV}$. A similar tendency was observed for the cases of the ionization and successive excitation. On the other hand, the cases of the double excitation and the excitation and successive ionization have maxima near the threshould energies and decrease rapidly as the T increases.

Tables 4 and 5 summarize, respectively, the G-values obtained for all of the double collisions and for the inner-shell excitations.

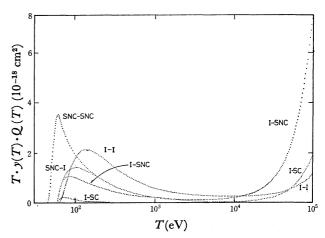


Fig. 1. Contribution of different portions of the electron degradation spectrum to the double collision in Ne.

Table 4. The G-values for each double collision

Process	He	Ne	Ar	Kr	Xe
Double ionization	0.0076	0.146	0.079	0.053	0.057
Double excitation	0.0031	0.112	0.081	0.059	0.060
\overline{SNC} - \overline{SNC}	0.0028	0.105	0.075	0.054	0.055
SC-SC	0.0000050	0.000097	0.00011	0.000099	0.00013
SNC-SC	0.00022	0.0062	0.0049	0.0041	0.0041
SC-SNC	0.000037	0.00081	0.00086	0.00075	0.00095
Ionization excitation	0.017	0.192	0.231	0.097	0.120
I-SNC	0.015	0.160	0.202	0.085	0.105
I– SC	0.0022	0.032	0.029	0.012	0.015
Excitation ionization	0.0029	0.068	0.060	0.038	0.037
SNC-I	0.0029	0.068	0.060	0.038	0.037
SC-I	0.000021	0.00018	0.00032	0.00026	0.00034

Table 5. The G-values for the inner shell excitations

Shell	Ne	Ar	Kr	Xe
1s singlet	0.000014	ŀ		
triplet	0.000000	15		
2s singlet	0.0164			
triplet	0.00062			
3s singlet		0.0540		
triplet		0.0025		
3d singlet			0.0176	
triplet			0.00039	
4s singlet			0.0418	
triplet			0.0028	
4p singlet				0.0016
triplet				0.000062
4d singlet				0.0244
triplet				0.00079
5s singlet				0.0365
triplet				0.0027
Total	0.0170	0.0565	0.0626	0.0661
singlet	0.0164	0.0540	0.0594	0.0625
triplet	0.00062	0.0025	0.0032	0.0036

Discussion

Experimentally, the formation of the doubly charged ions is due not only to the double ionization, which we have just calculated, but also to the Auger effect. Therefore, the comparison of the calculated values with the experimental values is somewhat complicated. In the case of He, however, there is no Auger effect, so a direct comparison is possible.

Figure 2 compares the experimentally obtained total cross sections of the double ionization⁶⁻¹⁰⁾ with those calculated by the method described above. A serious discrepancy appears near its maximum value and at very high energies of the incident electrons. Figure 3 summarizes the He+/He2+ ratios obtained both experimentally^{4,6-10)} and theoretically. The a curve is the present calculation, while the b and c curves are the results obtained by means of Mittleman's procedure¹²⁾ and a modification of it²⁵⁾ respectively. d curve is the result obtained by Roy and Rai.26) Their treatment seems to be very similar to ours except for a Judging from modification which is not clear for us. the semi-quantitative agreement of the present calculation with the observed data, it may be concluded that

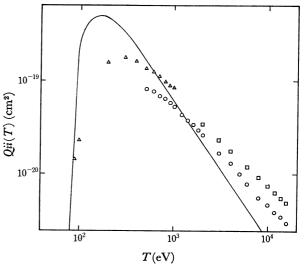


Fig. 2. The total cross section of the double ionization in He. —, calculated; ○, Ref. 7; □, Ref. 9; △, Ref. 6.

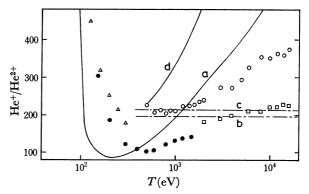


Fig. 3. The He⁺/He²⁺ ratios as a function of $\ln T$. \bigcirc , Ref. 7; \square , Ref. 9; \blacksquare , Ref. 4; \triangle , Ref. 6.

Gryzinski's treatment of the double ionization is generally correct when the yield of the doubly charged ions formed through the double collision is estimated.

Figures 4 and 5 show the ratios of M⁺/M²⁺ as a function of the energy of the incident electron, where M stands for Ne, Ar, Kr, or Xe.¹⁻¹⁰ In the case of Ne, only the double-ionization process seems to explain the experimental data. Probably the Auger effect does not play an important role in the formation of doubly charged ions in Ne. In the cases of Ar, Kr, and Xe, on

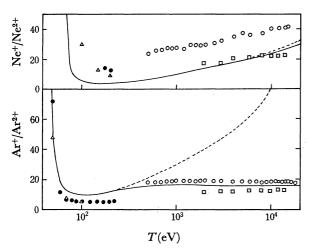


Fig. 4. The Ne⁺/Ne²⁺ and Ar⁺/Ar²⁺ ratios as a function of ln *T*. —, calculated only on the double ionization; —, calculated by including the Auger effect; ○, Ref. 7, 8; □, Ref. 9; ♠, Ref. 1; △, Ref. 3.

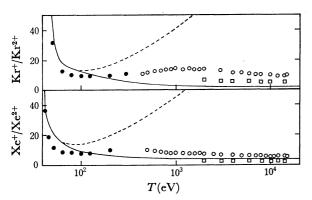


Fig. 5. The Kr⁺/Kr²⁺ and Xe⁺/Xe²⁺ ratios as a function of ln T. ----, calculated only on the double ionization; —, calculated by including the Auger effect; ○, Ref. 8; □, Ref. 10; ●, Ref. 6.

the other hand, the Auger effect seems to play a principal role in the formation of the doubly charged ions at the higher energies of the incident electrons. Since the distribution of the multiply charged ions produced through the Auger effect has been reported for all of the rare gases,²⁷⁾ and since the fluorescence yields have also been reported in the literature,²⁸⁾ we can estimate the relative amounts of the doubly charged ions formed through the Auger effect by using the cross sections of ionizations from the inner shells.¹⁴⁾ Tables 6 and 7 show, respectively, the values used of the relative yields of the doubly charged ions and the fluorescence yields. The corrected M+/M²⁺ ratios obtained by using these values are also shown in Figs. 4 and 5. The agreement with the experimental plots is satisfactory.

Table 6. The fluorescence yield of \mathbf{M}^+ ion with a vacancy in the inner shell

Shell	He	Ne	Ar	Kr	Xe
K		0	0.1	0.6	0.87
L			0	0.04	0.15
\mathbf{M}				0	0
N					0

Table 7. The fraction of M^{2+} ion produced through the auger effect

Shell	He	Ne	Ar	Kr	Xe
1s		0.736	0.105	0.015	0.003
2s			0.02	0.001	0.01
$2\mathbf{p}$			0.74	0.01	0.02
3s				0.13	0.02
3p				0.09	0.04
3 d				0.60	0.03
4s				,	}
4p					0.4
4p 4d					

Table 8. The G-values of electrons and W-values

	He	Ne	Ar	Kr	Xe
G-value	2.28	2.53	3.09	3.41	3.67
single collision	2.27	2.19	2.81	3.20	3.45
double collision	0.014	0.326	0.220	0.150	0.154
inner shell excita	tion	0.017	0.057	0.063	0.066
W-value					
present	43.9	39.5	32.4	29.3	27.2
experimental	42.3	36.3	26.4	24.2	22.0

Table 9. The ratio of the G-value for excitation to that of electrons

	He	Ne	Ar	Kr	Xe
$G_{ m exc}$	1.01	1.44	1.91	1.77	1.80
singlet	0.84	1.37	1.78	1.54	1.41
triplet	0.17	0.07	0.13	0.23	0.39
$G_{ m exc}/G_{ m e}$	0.44	0.57	0.62	0.52	0.49

The Calculation of the G-values. When the G-values of electrons are calculated, the contribution of the double ionization, $G_{\rm ii}$, should be added to the total, because the first ionization in the double ionization has already been counted as a single ionization. In the case of the ionization and successive excitation, the G-value of this process does not contribute to the increase in the G-value of the electrons, while in the case of the excitation and successive ionization, its G-value should be added to the G-value of the electrons and the same amount has to be subtracted from the G-value of the excitations.

The sum of the G-value of the double excitation and the inner-shell excitation corresponds to the G-value of the autoionization state of each atom. Some species in this state may autoionize into multiply charged ions; however, in the present calculation, we assumed that all of the autoionization states produce only singly charged ions.

Table 8 summarizes the G-values of electrons and the W-values both calculated and observed.²⁹⁾ The results appear to be better than those reported in the previous paper,¹⁴⁾ where the double collision and the inner-shell excitation were ignored. Table 9 shows the G-values of the excitations and the ratios of the excitation and ionization. There are no remarkable differences between the values calculated here and those obtained previously.

The authors are indebted to Professor Kazuo Hisatake for estimating the fluorescence yields.

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