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Non-empirical Calculation of the G-Values for the Ionization and Excitations in Diatomic Molecules Irradiated by 100 keV Electrons

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The binary-encounter collision theory has been applied to the calculation of the G-values for the ionization and excitations of diatomic molecules irradiated by 100 keV electrons. The obtained G-values of electrons are as follows, in the order of H_2, N_2, CO, NO, and O_2: 2.83, 2.55, 2.68, 3.61, and 2.98. These values are in fair agreement with the experimental ones. The present non-empirical method is compared with the semi-empirical ones proposed by other investigators. The G-values of some other products were also calculated: the excited hydrogen atoms in the radiolysis of H_2 (0.9) and the ozone formation in the radiolysis of O_2 (12.6). These G-values are also in fair agreement with the experimental ones.

Many investigators have measured the W-values ($=100/G_e$; G_e is the G-value of electrons) of diatomic molecules by the saturation-ion-current-method.[1-4] In the experiments of the radiolysis of carbon monoxide, nitric oxide, oxygen, and nitrogen, some of the information about the yields of the charged and excited species produced in the primary process has been obtained by measuring the final products and by considering the reaction mechanisms.[5-10] However, scarcely no theoretical treatment of the primary process in the radiolysis of these molecules has been carried out.

Recently, we have developed the non-empirical method for the estimation of the initial G-values by combining the binary-encounter collision theory with the theory of the degradation spectrum.[11,12] We have thus far calculated the cases of noble gases from helium to xenon and of such molecules as methane, ammonia, and water, and have shown that our calculation can provide much information for use in considering the primary processes of the radiolyses of these atoms and molecules.[13,14]

In this paper, we will apply this method to estimating the initial G-values of products from five diatomic molecules: H_2, N_2, CO, NO, and O_2. The most striking aspect of the present results is that the W-values calculated from this comparatively simple method are in reasonable agreement with the experimental values. In the discussion, we will compare the present method with the semi-empirical ones proposed by other investigators.[15-18]

Method of Calculation

The procedure for the present calculation is the same as that shown in the previous paper,[11-14] except for the treatment of the highly excited states of hydrogen to be described below; this treatment was special because the energies of these highly excited states are now available.

When the modes of the excitations of hydrogen are considered in further detail, two channels of the energy loss of electrons have to be introduced at the energy above the ionization potential. These channels are the dissociative excitation and the dissociative ionization. In the present treatment, their threshold energies are denoted by E^* and $E^\dagger$ respectively. When high-energy-electrons lose the energies between E^* and $E^\dagger$, we assume that one half of the energy gives rise to the ordinary ionization ($H_2^+ + e^-$), while the other half of this energy gives rise to the dissociative excitation ($H + H^*$). Therefore, the cross section for the dissociative excitation producing an excited hydrogen atom may be expressed in this form:

$$Q_{de}(T) = \frac{1}{2}\int_{E^*}^{E^\dagger} [\sigma_{E,\mathrm{dir}} + \sigma_{E,\mathrm{exc}}]\mathrm{d}E \tag{1}$$

for $T \geq E^\dagger$. Here $\sigma_{E,\mathrm{dir}}$ and $\sigma_{E,\mathrm{exc}}$ denote, respectively, the differential cross sections for direct and exchange excitations.[11,12] When $E^* \leq T < E^\dagger$, the upper limit of the integral in Eq. (1) has to be replaced by T. When $T < E^*$, $Q_{di}(T)$ is set equal to zero.

Similarly, the total cross section for the dissociative ionization ($H + H^+ + e^-$) may be expressed by:

$$Q_{di}(T) = \frac{1}{4}\int_{E^\dagger}^{E^{**}} [\sigma_{E,\mathrm{dir}} + \sigma_{E,\mathrm{exc}}]\mathrm{d}E \tag{2}$$

for $T \geq E^{**}$. Here E^{**} is the threshold energy for the double excitation ($H^* + H^*$). When $E^\dagger \leq T < E^{**}$, the upper limit of Eq. (2) has to be replaced by T. When $T < E^\dagger$, $Q_{di}(T)$ is set equal to zero. The factor of 1/4 in Eq. (2) has to be introduced because there are two energy-loss-processes (the ordinary ionization and dissociative ionization); also, we cannot distinguish the origin of the scattered electron and so do not know whether it is originally the incident electron or the molecular electron.

Therefore, the total cross section for the ordinary ionization can be expressed by:

$$Q_i(T) = \frac{1}{2}\int_{I_i}^{T} [\sigma_{E,\mathrm{dir}} + \sigma_{E,\mathrm{exc}}]\mathrm{d}E - \frac{1}{2}Q_{de}(T) - Q_{di}(T) \tag{3}$$

Constants Used for Calculation

The binding energies (I_i), the kinetic energies (E_i), and the lowest energies of the allowed and forbidden excitations (E_s and E_t) used in the present calculation are summarized in Table 1. Here, the I_i values are those obtained by the technique of ESCA[19] and the E_i values are those calculated from the SCF wave functions.[20-23] The E_s and E_t values in the outermost shell were those experimentally obtained,[24] and the values in the inner shells were calculated using the following equations: $E_s(\text{inner shell}) = I_i(\text{inner}) - (I_i - E_s)_{\text{outermost}}$, $E_t(\text{inner shell}) = I_i(\text{inner}) - (I_i - E_t)_{\text{outermost}}$.

Table 2 shows the constants used for the calculation

Table 1. The binding energy (I_i), the kinetic energy (E_i) and the lowest allowed (E_s) and forbidden (E_t) levels of electrons

Molecule	(orbital)		I_i	E_i	E_s	E_t
H_2	$1\sigma_g$	2	16.0	31.96	12.6	8.8
N_2	$3\sigma_g$	2	15.57	52.18	9.2	6.2
	$1\pi_u$	4	16.69	43.87	10.3	7.3
	$2\sigma_u$	2	18.75	65.57	12.4	9.4
	$2\sigma_g$	2	37.3	59.8	31.0	28.0
	$1\sigma_u$	2	409.9	600.0	404.0	401.0
	$1\sigma_g$	2	409.9	600.0	404.0	401.0
CO	5σ	2	14.5	52.52	8.4	6.2
	1π	4	17.2	50.08	11.0	9.0
	4σ	2	20.1	68.41	14.0	12.0
	3σ	2	38.3	70.93	32.0	30.0
	2σ	2	295.9	434.8	290.0	288.0
	1σ	2	542.1	792.0	536.0	534.0
NO	2π	1	9.26	70.20	6.5	3.9
	1π	4	14.0	57.42	11.0	9.0
	5σ	2	16.7	52.85	14.0	11.0
	4σ	2	21.7	73.45	19.0	16.0
	3σ	2	40.6	73.19	38.0	35.0
	2σ	2	410.3	605.7	408.0	405.0
	1σ	2	543.3	799.5	541.0	538.0
O_2	$1\pi_g$	2	13.1	82.14	8.4	1.0
	$1\pi_u$	4	17.0	72.24	12.3	4.9
	$3\sigma_g$	2	18.8	60.08	14.1	6.7
	$2\sigma_u$	2	25.3	90.40	20.6	13.2
	$2\sigma_g$	2	39.6	78.19	34.9	27.5
	$1\sigma_u$	2	543.1	795.1	538.0	531.0
	$1\sigma_g$	2	544.2	794.8	540.0	532.0

Table 2. The constants used for the calculation of the double collision

	H_2	N_2	CO	NO	O_2
n_e	2	6	6	7	8
$\bar{I}_i$ (eV)	16.0	16.3	16.3	14.1	16.5
$\bar{E}_s$	12.6	10.0	10.0	11.0	12.0
$\bar{E}_t$	8.8	7.0	8.0	9.0	4.4
E_i	31.96	46.6	51.0	58.0	72.0
I_{ii}	20.7[a]	32.6	32.6	28.2	33.0
E^{**}	29.9	33.0	33.0	28.0	33.0
E^{+*}	33.3	41.0	41.0	35.0	41.0
$\bar{r}$ (Å)	1.06	1.094	1.128	1.15	1.208

a) Calculated by use of the equation; $I_{ii}=E^{\dagger\dagger}-I_i$.

of the double collision. The procedure used to estimate these constants was the same as that described in a previous paper.[12]

In the case of the hydrogen molecule, the values of E^*, $E^\dagger$, and $E^{\dagger\dagger}$ are 17.0, 23.1, and 36.7 eV respectively. Here, $E^{\dagger\dagger}$ is the threshold energy of the double ionization.

Results

Figure 1 shows the degradation spectra, $y(T)$, of the electrons in H_2, N_2, CO, NO, and O_2. It is noticeable that the $y(T)$ in N_2 nearly agrees with that of CO, probably because the construction of the molecular orbitals in the two molecules are similar. Figures 2, 3, 4, 5, and 6 show the $T\cdot y(T)\cdot Q_s(T)$ values for the

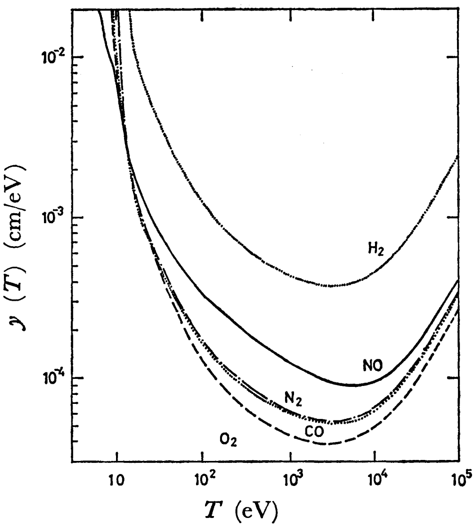

Fig. 1. The electron degradation spectra in H_2 (……), N_2 (·—·—), CO (……), NO (——), and O_2 (----).

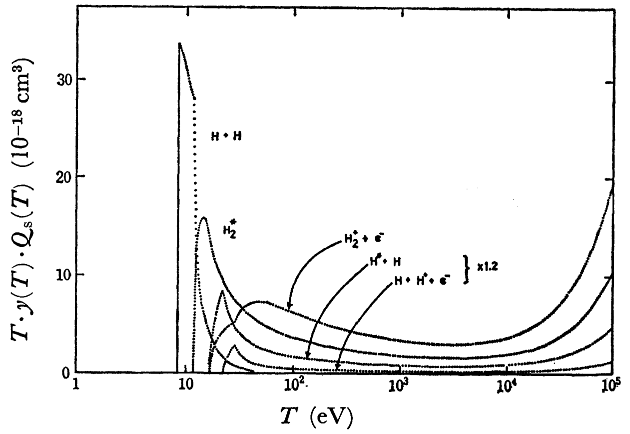

Fig. 2. Contribution of different portion of the electron degradation spectrum to the ionization and excitation in H_2.

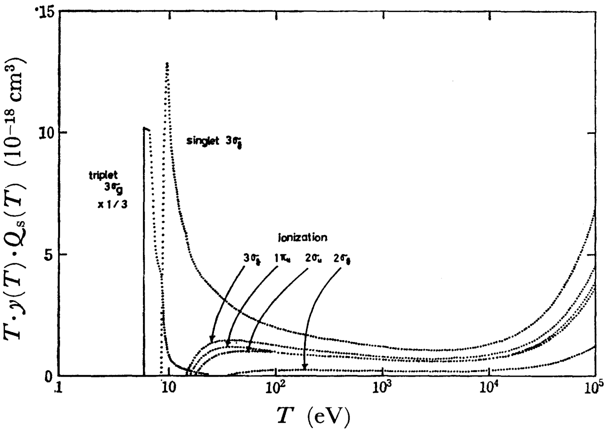

Fig. 3. Contribution of different portion of the electron degradation spectrum to the ionization and excitation in N_2.

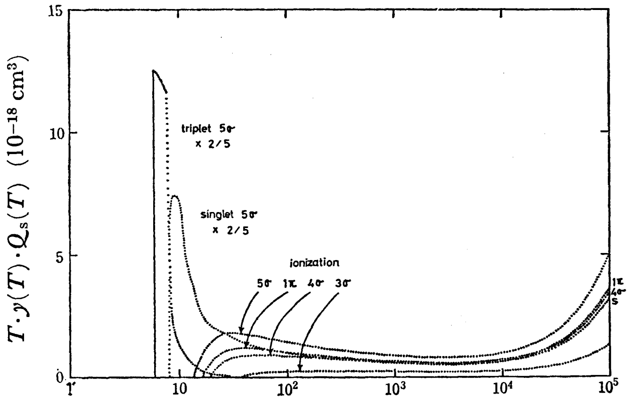

Fig. 4. Contribution of different portion of the electron degradation spectrum to the ionization and excitation in CO.

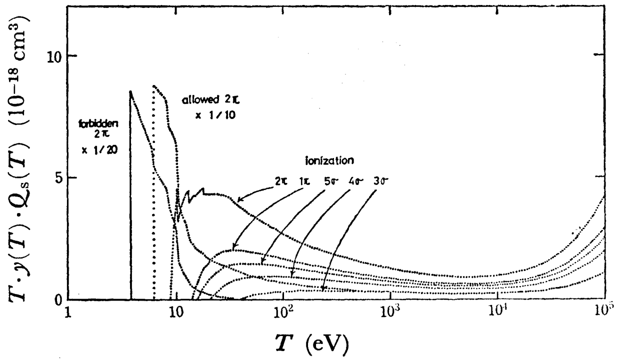

Fig. 5. Contribution of different portion of the electron degradtion spectrum to the ionization and excitation in NO.

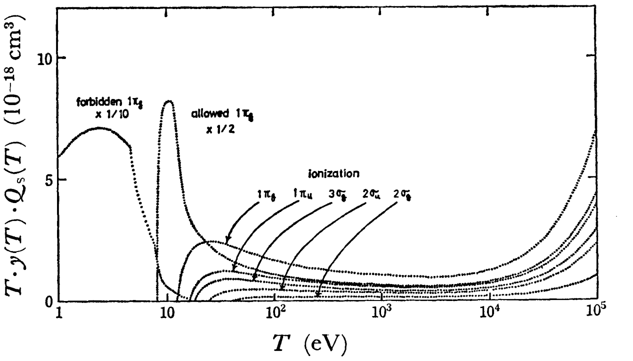

Fig. 6. Contribution of different portion of the electron degradation spectrum to the ionization and excitation in O_2.

excitations in H_2, N_2, CO, NO, and O_2 respectively as functions of In *T*. Figures 7 and 8 show the $T\cdot y(T)\cdot Q_s(T)$ values for the excitations from the inner shell in N_2, CO, NO, and O_2.

Tables 3 and 4 summarize the *G*-values for the ionization and excitations on each molecular orbital of the five diatomic molecules, and also for each double collision. Here, the values in parentheses are the *G*-values for autoionization in N_2 and CO. The M^{ii}, M^{ee}, M^{ie}, and M^{ie} values in Table 5 denote, respectively, double ionization, double excitation, ionization and successive excitation, and excitation and successive ionization.

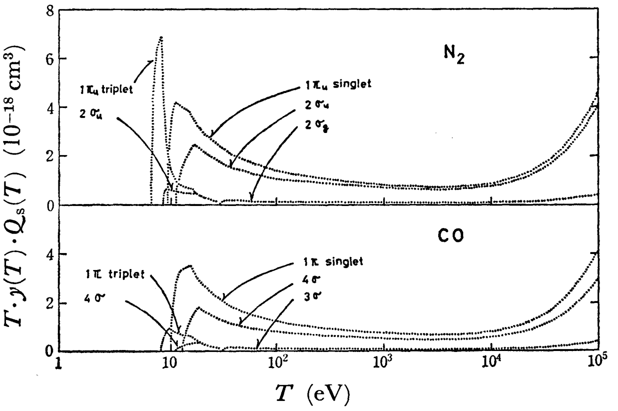

Fig. 7. Contribution of different portion of the electron degradation spectrum to the inner-shell-excitations in N_2 and CO.

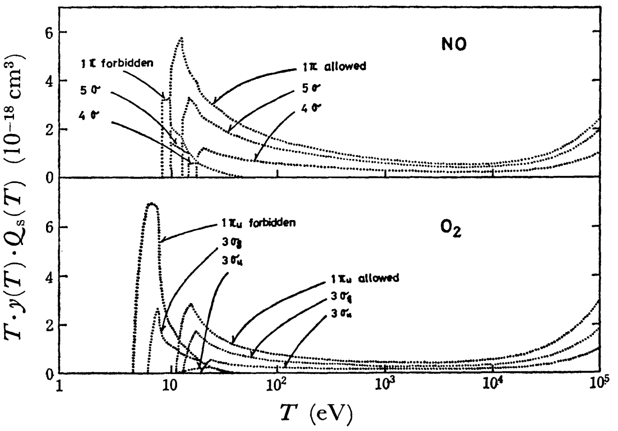

Fig. 8. Contribution of different portion of the electron degradation spectrum to the inner-shell-excitations in NO and O_2.

Table 3. The *G*-value of ionizations and excitations in hydrogen molecule

Mode	*G*-value
$H_2{}^* \to H + H$	0.82
$H_2{}^* \to H_2{}^*$	1.98
$H_2{}^* \to H + H^*$	0.68
$H_2{}^+ \to H_2{}^+$	2.62
$H_2{}^+ \to H + H^+$	0.18
$H_2{}^{ii} \to H^+ + H^+$	0.015
$H_2{}^{ee} \to H^* + H^*$	0.031
$H_2{}^{ie} \to H^+ + H^*$	0.17
$H_2{}^{ei} \to H^* + H^+$	0.026

Discussion

W-Value. The calculated *G*-values of electrons and *W*-values are summarized in Table 6, along with the *W*-values obtained both experimentally[1-4] and theoretically.[15-18] Obviously, our *W*-values are in fair agreement with the experimental ones. Similar

TABLE 4. THE G-VALUES FOR THE IONIZATIONS AND EXCITATIONS ON EACH MOLECULAR ORBITAL

		G_i	$G_{ex,s}$	$G_{ex,t}$
N_2	$3\sigma_g$	0.59	1.24	0.58
	$1\pi_u$	0.93	1.55	0.26
	$2\sigma_u$	0.47	0.59(0.20)	0.027(0.005)
	$2\sigma_g$	0.13	0.049	0.0017
	$1\sigma_u$	0.0072	0.00018	0.0000031
CO	5σ	0.67	1.69	0.65
	1π	0.93	1.37	0.070
	4σ	0.41	0.43(0.37)	0.014(0.008)
	3σ	0.13	0.048	0.0014
	2σ	0.010	0.00034	0.0000054
	1σ	0.0051	0.000093	0.0000014
NO	2π	0.54	2.72	2.12
	1π	1.16	1.41	0.18
	5σ	0.46	0.49	0.049
	4σ	0.32	0.22	0.022
	3σ	0.14	0.040	0.0055
	2σ	0.0085	0.00017	0.00014
	1σ	0.0061	0.000093	0.000097
O_2	$1\pi_g$	0.87	1.65	7.05
	$1\pi_u$	0.94	0.92	0.50
	$3\sigma_g$	0.34	0.27	0.076
	$2\sigma_u$	0.25	0.12	0.010
	$2\sigma_g$	0.099	0.025	0.0017
	$1\sigma_u$	0.0040	0.000061	0.0000015
	$1\sigma_g$	0.0040	0.000050	0.0000015

TABLE 5. THE G-VALUES FOR EACH DOUBLE COLLISION

	N_2	CO	NO	O_2
M^{ii}	0.025	0.009	0.133	0.039
M^{ee}	0.039	0.008	0.148	0.054
M^{ie}	0.081	0.065	0.388	0.143
M^{ei}	0.031	0.006	0.097	0.041

TABLE 6. THE G-VALUES OF ELECTRONS AND W-VALUES

	H_2	N_2	CO	NO	O_2
G_e	2.83	2.55	2.68	3.61	2.98
W-value					
present	35.3	39.2	37.3	27.7	33.5
experiment	35.9[a]	34.1[a]	33.2[a]	27.5[a]	31.0[a]
		34.9[b]	33.3[c]		30.9[b]
					30.4[d]
calculation	34.9[e]	35.7[f]	35.8[g]		32.0[f]

a) Ref. 1. b) Ref. 2. c) Ref. 3. d) Ref. 4. e) Ref. 16. f) Ref. 15. g) Ref. 17.

results have been obtained previously with noble gases from He to Xe, methane, ammonia, and water.[11–14] Therefore, it may be concluded that our method is useful for estimating the G-values of the electrons for all atoms and molecules.

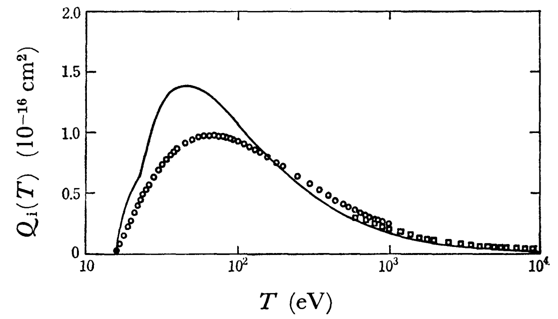

Fig. 9. The total cross section of ionization in H_2. ——, Calculated; ○, Ref. 25; □, Ref. 26.

Recently, Green and his associates have calculated the W-values for N_2.[15] O_2,[15] H_2,[16] and CO[17] out of aeronomic interest. In order to perform the calculation, they accumulated experimental data concerning the total cross section, the energy distribution of the secondary electrons, and the stopping power. They then determined the parameters of one equation to fit the experimental data, and finally they calculated the W-values under the assumption of a continuous slowing down. They did not use the concept of the degradation spectrum. On the other hand, Jones calculated the W-value and the yield of excitations in a hydrogen molecule out of radiation-chemical interest.[18] He did not use the assumption of a continuous slowing down either, but calculated the Fowler equation; the parameters were obtained semi-empirically. These two semi-empirical methods used to estimate the W-value both have the demerits that the method of calculation is very complex and that, if a complete set of the experimental data is not available, the estimation of any value is impossible.

On the other hand, the treatment of our non-empirical calculation is much simpler, and no experimental data on the cross sections are needed. Moreover, once the degradation spectrum of the electrons is constructed, we can estimate the G-values of any process by combining the degradation spectrum with the cross sections if they are available either theoretically or experimentally. However, since the cross sections used in our calculation are formulated only from the Coulomb interaction between two encountering species, the theoretical total cross section does not agree exactly with the experimental one. Nevertheless, the G-values calculated by our non-empirical method are in good agreement with the experimental values.

Figure 9 shows the total cross section for ionization in a hydrogen molecule as a function of ln T. The calculated cross sections at the electron energies from 10^2 to 10^4 eV are in good accordance with the experimental ones, but between the threshold energy and 10^2 eV the calculated ones are about 1.4 times the experimental ones.[25,26] Similarly, the calculated cross sections for N_2, CO, NO, and O_2 under the electron energy of 10^3 eV are much larger than the experimental ones.[25–27]

Since the calculated cross sections in N_2 is about three times the experimental one at its maximum, we tried to calculate the G-values by assuming that the differential and total cross sections were one-third of the cross sections used above; *i.e.*, the stopping power, $S(T)$, is one-third of that used above. However, the G-values thus obtained were the same as those obtained above. This is because, when the degradation spectrum, $y(T)$, is calculated, the stopping power comes to the denominator. That is, the factor of three is cancelled during the course of the calculation. Consequently, we may conclude that, in order to estimate the G-values, it is not necessary to use the absolute cross sections, but only the relative values at each electron energy.

The Ratio of the G-Values of Excited Species to Those of Ionic Ones. We calculated the G-values for the total excitations, G_{ex}, the total loss of molecules, $G(-\mathrm{M})$, and the ratios of the G_{ex} to G_e. The results are shown in Table 7. Since the G_{ex}/G_e ratios of diatomic molecules are much larger than those of noble gases (0.4—0.6)[12)], the excited species may play a more important role in the successive reaction than those in noble gases. This is similar to the finding in the molecules consisting of ten electrons.[14)] Therefore, when we analyze the radiolyses of molecules, we must consider not only the charged species but also the excited ones. Especially, the G_{ex}/G_e of the oxygen molecule is very large because the energy of the lowest excited state ($^1\Delta$) is small.

The G-Value of Emissions. From the present calculations using the $y(T)$, the G-values for the emission of the light from highly excited species can be estimated by the use of the experimental cross sections described in the previous paper.[14)] These cross sections in the hydrogen molecule and the nitrogen molecule have been reported by Vroom and de Heer[28)] and by Aarts and de Heer[29)] respectively. The results are shown in Tables 9 and 10. Especially, the G-value of the emission from excited hydrogen atoms (0.81) accords fairly well with the $G(\mathrm{H^*})$ in Table 8 (0.94). These G-values of the products of the charged and excited species in Table 8 are calculated from Table 3. The G-value of the excited nitrogen atoms in N_2 is the same amount as that of the excited hydrogen atoms in methane, ammonia, and water. However, since the G-value of the excited hydrogen atoms in H_2 is very large, the G-value of the hot hydrogen atoms in H_2 may be produced in a large amount. The G-value of the hot hydrogen atoms was estimated to be about 2.

TABLE 7. THE RATIO OF THE G-VALUE FOR TOTAL EXCITATION TO THAT OF ELECTRONS

	H_2	N_2	CO	NO	O_2
G_{ex}	3.45	3.97	3.85	6.73	10.38
G (−M)	6.27	6.49	6.52	10.21	13.32
G_{ex}/G_e	1.22	1.56	1.44	1.86	3.48

TABLE 8. THE G-VALUE FOR THE PRODUCTS IN HYDROGEN MOLECULE

	G
H_2^*	1.92
H^*	0.94
H	2.49
H^+	0.40
H_2^+	2.43
e^-	2.83

TABLE 9. THE G-VALUES OF EMISSIONS IN HYDROGEN MOLECULE

	G
Lyman α	0.52
H (2s)	0.25
Balmer α	0.03
β	0.006
γ	0.002
δ	0.0008
Total	0.81

TABLE 10. THE G-VALUES OF EMISSIONS IN NITROGEN MOLECULE

	Transition	λ (A)	G
NI	3s ^{4}P$-$2p^3 ^{4}S°	1200	0.028
	3s ^{2}P$-$2p^3 ^{2}D°	1494	0.011
	3s′ ^{2}P$-$2p^3 ^{2}D°	1243	0.0098
	3p ^{4}D°$-$3s ^{4}P	8680	0.012
	2p^4 ^{4}P$-$2p^3 ^{4}S°	1134	0.0064
	3d ^{2}D$-$2p^3 ^{2}D°	1164	0.0026
			0.069
NII	2p^3 ^{3}D°$-$2p^2 ^{3}P	1084	0.018
	2p^3 ^{3}P°$-$2p^2 ^{3}P	916	0.0035
	2p^3 ^{1}D°$-$2p^2 ^{1}D	776	0.0008
	3s ^{1}P°$-$2p^2 ^{1}D	747	0.0010
	3d ^{3}F°$-$3p ^{3}D	5003	0.0015
			0.024
	a $^1\Pi_g-$X $^1\Sigma_g^+(2-0)$	1384	0.0033
	p′ $^1\Sigma_u^+-$X $^1\Sigma_g^+(0-1)$	981	0.0056
	p′ $^1\Sigma_u-$a $^1\Pi_g(0-0)$	2825	0.00016

The Radiolysis of Nitric Oxide. Hochanadel *et al.* proposed the following reaction mechanism and estimated the G-values of the products in the radiolysis at 25°C of NO irradiated by a 2 MeV electron beam:[6)]

$$24.8\,\mathrm{NO} \rightarrow 5.3\,\mathrm{N_2} + 7.0\,\mathrm{NO_2} + 3.6\,\mathrm{N_2O_3}$$

$$\begin{array}{lll} \mathrm{NO} & \rightsquigarrow & \mathrm{NO^+ + e^-} \\ & \rightsquigarrow & \mathrm{NO^* \rightarrow N + O} \end{array}$$

$$\mathrm{NO^+ + e^- \rightarrow NO^* \rightarrow N + O}$$

$$\mathrm{NO + e^- \rightarrow NO^-}$$

$$\mathrm{NO^+ + NO^- \rightarrow N + O + NO}$$

$$\mathrm{N + NO \rightarrow N_2 + O}$$

$$\mathrm{O + NO \rightleftarrows NO_2^{\neq}}$$

$$\mathrm{NO_2^{\neq} + M \rightarrow NO_2 + M}$$

$$\mathrm{NO_2 + NO \rightleftarrows N_2O_3}$$

If the excited state of the outermost shell in our calculation cannot dissociate into nitrogen and oxygen atoms, the G-values of the nitrogen and oxygen atoms can be estimated to be 5.50. Therefore, the G-values of these atoms are in fair accordance with the experimental values (5.3).

The Formation of Ozone. The radiolysis of an oxygen molecule at a high dose rate has been experimented with by Willis *et al.*[7,8] They reported that the *G*-value of ozone is 12.8; this value is used as a chemical dosimeter. If we assume as follows, we can estimate the *G*-value of ozone from the present results: all the nuetralization reactions give two oxygen atoms per ion pair, and all the excited oxygen molecules, except for the lowest excited one ($^1\Delta$), dissociate into two oxygen atoms. That is, one oxygen atom produces one ozone. Then, the calculated *G*-value of ozone is 12.6. This value is in reasonable agreement with the experimental one.

References

1) G. G. Meisels, *J. Chem. Phys.*, **41**, 51 (1964).

2) P. Adler and H. K. Bothe, *Z. Naturforsch.*, **20a**, 1700 (1965).

3) R. M. Leblanc and J. A. Herman, *J. Chim. Phys.*, **63**, 1055 (1966).

4) R. Cooper and R. M. Mooring, *Australian J. Chem.*, **21**, 2417 (1968).

5) C. Willis and O. A. Miller, *Can. J. Chem.*, **48**, 3029 (1970).

6) C. J. Hochanadel, J. A. Ghormley, and P. J. Ogren, *J. Chem. Phys.*, **50**, 3075 (1969).

7) A. W. Boyd, C. Willis, R. Cyr, and D. A. Armstrong, *Can. J. Chem.*, **47**, 4715 (1969).

8) C. Willis, A. W. Boyd, M. J. Young, and D. A. Armstrong, *ibid.*, **48**, 1505 (1970).

9) T. Oka, R. Kato, S. Sato, and S. Shida, This Bulletin, **41**, 2192 (1968).

10) G. M. Meaburn, D. Perner, J. LeCalve, and M. Bourene *J. Phys. Chem.*, **72**, 3920 (1968).

11) S. Sato, K. Okazaki, and S. Ohno, This Bulletin, **47**, 2174 (1974).

12) K. Okazaki, S. Sato, and S. Ohno, *ibid.*, **48**, 1411 (1975).

13) S. Ohno, H. Nagayama, K. Okazaki, and S. Sato, *ibid.*, **48**, 2153 (1975).

14) K. Okazaki, S. Sato, and S. Ohno, submitted for publication.

15) L. R. Peterson and A. E. S. Green, *J. Phys. B*, **1**, 1131 (1968).

16) W. T. Miles, R. Thompson, and A. E. S. Green, *J. Appl. Phys.*, **43**, 678 (1972).

17) T. Sawada, D. L. Sellin, and A. E. S. Green, *J. Geophys. Res.*, **77**, 4819 (1972).

18) W. M. Jones, *J. Chem. Phys.*, **59**, 5688 (1973).

19) K. Siegbahn *et al.*, "ESCA Applied to Free Molecules," North-Holland, Amsterdam (1969).

20) W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 219 (1960).

21) B. J. Ransil, *ibid.*, **32**, 239 (1960).

22) H. Brion, *J. Chem. Phys.*, **30**, 673 (1959).

23) Y. K. Kim, *Radiat. Res.*, **61**, 21 (1975).

24) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J. (1963).

25) D. Rapp and P. Englander-Golden, *J. Chem. Phys.*, **43**, 1464 (1965).

26) B. L. Schram, F. J. de Heer, M. J. van der Wiel, and J. Kistemaker, *Physica*, **31**, 94 (1965).

27) L. J. Kieffer and G. H. Dunn, *Rev. Mod. Phys.*, **38**, 1 (1966).

28) D. A. Vroom and F. J. de Heer, *J. Chem. Phys.*, **50**, 580 (1969).

29) J. F. M. Aarts and F. J. de Heer, *Physica*, **51**, 425 (1970); **52**, 45 (1971); **52**, 609 (1971).