The Estimation of the *G*-Values for Ionization and Excitation of Ten-Electron Molecules: Methane, Ammonia, and Water 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, Ibaraki 319-11*

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The binary-encounter collision theory is applied to calculate the *G*-values for the ionization and excitation of methane, ammonia, and water irradiated by 100 keV electrons. Double collision of the incident electron in a molecule is also taken into account. On the assumption of the occurrence of certain reactions in the systems, the *G*-values for electrons, various radicals, and several final products were estimated. Some of the results are as follows: the *G*-values for electrons were 3.60 for methane, 3.56 for ammonia, and 3.00 for water. These values are in fair agreement with the experimental values: 3.6 for methane, 3.8 for ammonia, and 3.3 for water. The calculated *G*-value for hot hydrogen atoms was about 1.0 for all three compounds. The ratios of the *G*-value for excitation to that for electrons are 1.1 for methane, 1.5 for ammonia, and 1.7 for water. An estimation was also made of the *G*-value for the emission of highly-excited hydrogen atoms using reported cross sections. The *G*-values are 0.1 for methane and ammonia, and 0.2 for water.

Methane, ammonia, and water are iso-electronic with neon. The radiolyses of these compounds have been extensively investigated by many radiation chemists.[1–9] They measured the *G*-values of the final products both in the pure state and in systems containing electrons or radical scavengers. On the basis of these results, they constructed reaction sequences consisting of ion-molecule reactions and radical reactions, and estimated the *G*-values for the primary products such as electrons, radicals, and singlet- and triplet-excited states of the parent molecules. On the other hand, radiation physicists are concerned with the *W*-values of these gases (the *W*-value is equal to $100/G$(electrons)) and have measured them accurately.[10–13] They also reported various physical processes occuring during irradiation, such as the emissions of intermediate species and the lifetimes of the highly-excited atoms produced.[14] At present, therefore, we are in a good position to view generally the entire sequence of the radiolyses of methane, ammonia, and water.

Previously, the authors calculated the degradation spectra of electrons in noble gases from He to Xe, and estimated the *G*-values of electrons and singlet- and triplet-excited states.[15,16] Although the method was a classical one, the calculations are in fair agreement with the experimental results. After the calculation on noble gases, they extended the calculation to water irradiated by 10 keV electrons.[17] Since the method of calculation was established, the estimation of the *G*-values for electrons and excited states was straightforward. The main concern in Ref. 17, therefore, was the estimation of the *G*-values of the various products which are of interest to radiation chemists. In order to estimate these values, all of the available spectroscopic, photochemical, and radiation chemical data were considered.

The present paper is an extension of Ref. 17, and treats the radiolyses of methane, ammonia, and water. The water molecule was again chosen as one of the objects of research, since the above three compounds are iso-electronic and it is thought worthwhile to compare them on the same basis.

Method of Calculation

The differential cross section, $\sigma_E(T)$, and the total cross sections for ionization and excitation, $Q_s(T)$, at an electron energy T were estimated using the classical binary-encounter theory, the details of which have been described in previous papers.[15–17] Only the parameters, the binding energy (I_i), the average kinetic energy (E_i), the energy of the first excited singlet state (E_s) and that of the lowest triplet state (E_t) have to be replaced by the values corresponding to those for the molecular orbitals.

The formulation of the stopping power, $S(T)$, is the same as that given in Ref. 17. Once $\sigma_E(T)$ and $S(T)$ are obtained, we can calculate the degradation spectra for electrons, $y(T)$, in the three compounds on the assumption of continuous slowing down. The procedure for the calculation of $y(T)$ is the same as that given in Ref. 15. Since we know that the contribution from double collisions to the *G*-values for electrons cannot be ignored, they were calculated for the three compounds. The cross sections for different types of double collisions have been formulated in Ref. 16. Then, as stated in Ref. 15, we can estimate the *G*-value of any process by integrating $Ty(T)\ Q_s(T)$ over $\ln T$.

Constants Used for Calculation

Tables 1 and 2 summarize all the constants used for the calculations for methane, ammonia, and water. Each value was determined as follows.

$CH_4(1a_1)^2(2a_1)^2(1t_2)^6$: The binding energies ($I_i$) were taken from ESCA data.[18,19] The average kinetic energies (E_i) were calculated from the SCF functions proposed by Palke and Lipscomb.[20] Since the absorption spectrum of methane begins at 1455 Å,[21] the energy of the first excited singlet state, $E_{s,1t2}$, was assumed to be 8.5 eV. No experimental data on the energies of the inner-shell excited states (E_s and E_t) are available. Therefore, these values were tentatively estimated as shown in Table 1. The equations used

TABLE 1. BINDING ENERGIES (I_i), AVERAGE KINETIC ENERGIES (E_i), AND ENERGIES TO THE FIRST EXCITED SINGLET STATE (E_s) AND TO THE LOWEST TRIPLET STATE (E_t)

	Orbital	No. of electrons	I_i (eV)[a)]	E_i (eV)	E_s (eV)	E_t (eV)
CH_4	$1t_2$	6	13.0	20.31	8.52[b)]	6.5[c)]
	$2a_1$	2	23.1	30.34	19[d)]	17[c)]
	$1a_1$	2	290.7	437.1	286[d)]	284[c)]
NH_3	$1a_2''$	2	10.85	52.53	6.5[e)]	4.5[c)]
	$1e'$	4	15.8	28.48	11.5[f)]	9.5[c)]
	$2a_1'$	2	21.22	42.60	17[f)]	15[c)]
	$1a_1'$	2	405.6	605.3	401[f)]	339[c)]
H_2O	$1b_1$	2	12.6	70.40	7.42[g)]	5.0[h)]
	$3a_1$	2	14.7	66.46	9.5[i)]	7[j)]
	$1b_2$	2	18.4	28.41	13[k)]	11[j)]
	$2a_1$	2	32.2	74.94	27[k)]	25[j)]
	$1a_1$	2	539.7	799.6	535[k)]	533[j)]

a) Refs. 18, 19. b) Ref. 21. c) $E_t = E_s - (E_s - E_t)_{H_2O, 1b_1} = E_s - 2$. d) $E_s = I_i - (I_i - E_s)_{1t_2} = I_i - 4.5$. e) Ref. 24. f) $E_s = I_i - (I_i - E_s)_{1a_2''} = I_i - 4.4$. g) Ref. 24. h) Ref. 25. i) Ref. 22. j) $E_t = I_i - (I_i - E_t)_{1b_1} = I_i - 7.6$. k) $E_s = I_i - (I_i - E_s)_{1b_1} = I_i - 5.2$.

TABLE 2. THE CONSTANTS USED FOR DOUBLE COLLISIONS

	CH_4	NH_3	H_2O	Ne
No. of electrons	6	6	6	6
Orbitals involved	$1t_2$	$1a_2''$, $1e'$	$1b_1$, $3a_1$, $1b_2$	2p
$\bar{I}_i$ (eV)	13.0	14.2	15.2	21.56
$\bar{E}_s$	8.52	10.0	10.0	16.8
$\bar{E}_t$	6.5	8.0	9.0	16.7
$\bar{E}_i$	20.31	36.5	55.0	112.8
I_{ii}	25.0	27.0	29.0	41.07
E^{**}	25.0	28.0	30.0	45.0
E^{+*}	31.5	35.0	37.0	57.6
$\bar{r}$ (Å)	0.86	0.79	0.75	0.45

for the estimations are summarized in the footnotes of Table 1.

$NH_3(1a_1')^2(2a_1')^2(1e')^4(1a_2'')^2$: The values of I_i were taken from ESCA data, and the E_i values were calculated from the SCF functions proposed by Duncan.[23)] The energy of the first excited singlet state, $E_{s,1a_2''}$, was estimated from the electron-impact spectrum data reported by Lassettre *et al.*[24)] Other values of E_s and E_t were estimated in a manner similar to those of methane.

$H_2O(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$: The values of I_i, $E_{s,1b_1}$ and $E_{t,1b_1}$ are the same as those used in Ref. 17, except for the E_t of the inner shells, which were estimated in a manner similar to that for the values of E_t for methane. The E_i values were calculated from the SCF functions proposed by Ellison and Shull.[26)]

Table 2 shows the constants used for the calculations for double collisions. The values for $\bar{I}_i$, $\bar{E}_s$, $\bar{E}_t$, and $\bar{E}_i$ are the averages of the I_i, E_s, E_t, and E_i for the corresponding molecular orbitals.[16,17)] The second ionization potential, I_{ii}, of neon is 1.9 times the first ionization potential, I_i.[16)] It is assumed that the values of I_{ii} for methane, ammonia, and water are 1.9 times the average first ionization potentials ($\bar{I}_i$). The I_{ii} value calculated for methane is in good agreement with those obtained experimentally[27)] and theoretically.[28)] The energy of the doubly-excited state (E^{**}) and that of the excited ion (E^{+*}) were determined in a manner similar to those for the rare gases.[16)] The mean distance between valence electrons ($\bar{r}$) was calculated by placing them uniformly on a sphere whose radius is the bond length. The bond lengths of C–H, N–H, and O–H are reported to be 1.1, 1.0, and 0.96 Å, respectively.[29)]

Results

Figure 1 shows the degradation spectra, $y(T)$, for methane, ammonia, water, and neon. The results for neon were reproduced from a previous paper.[15)] At low electron energies (<100 eV), the $y(T)$ for neon is different from those for the iso-electronic molecules. Figure 2 shows the $Ty(T)$ $Q_s(T)$ for the ionization and

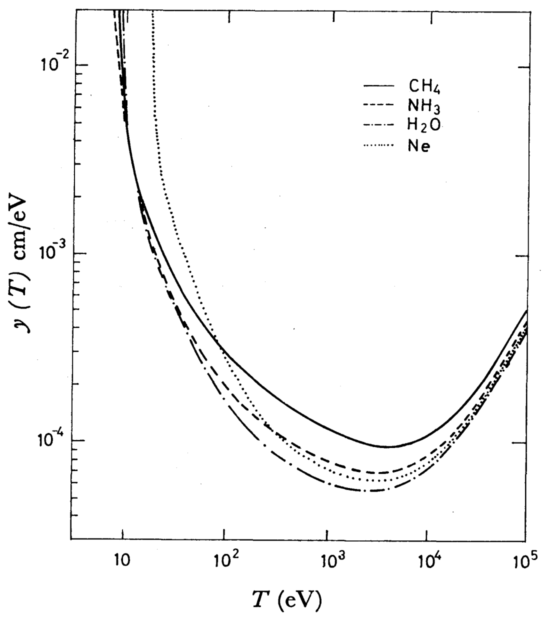

Fig. 1. Degradation spectra in methane, ammonia, water, and neon.

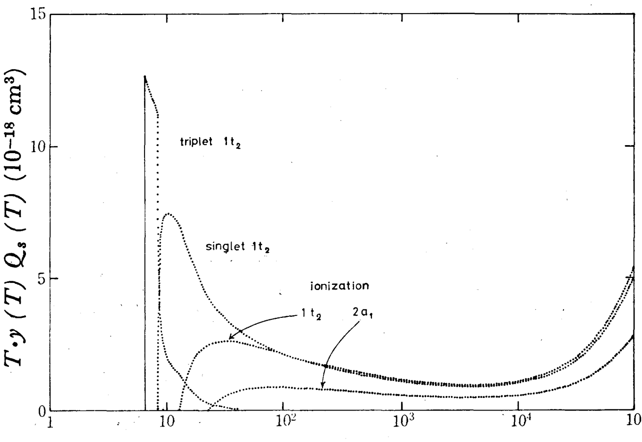

Fig. 2. Contribution of different portions of the electron degradation spectrum to the ionization and excitation in methane.

TABLE 3. THE G-VALUES FOR IONIZATIONS AND SINGLET AND TRIPLET EXCITATION. THE VALUES IN PARENTHESES ARE THOSE OBTAINED IN REF. 17.

	Orbital	G_i	$G_{ex,s}$	$G_{ex,t}$
CH_4	$1t_2$	2.59	3.45	0.78
	$2a_1$	0.36	0.15	0.0070
	$1a_1$	0.018	0.0005	0.000009
NH_3	$1a_2''$	1.55	3.48	1.12
	$1e'$	1.06	0.89	0.052
	$2a_1'$	0.38	0.19	0.0079
	$1a_1'$	0.0098	0.0002	0.000003
H_2O	$1b_1$	1.17 (1.26)	2.67 (2.80)	0.93 (1.00)
	$3a_1$	0.83 (0.68)	1.22 (0.96)	0.081 (0.029)
	$1b_2$	0.34 (0.44)	0.31 (0.39)	0.015 (0.011)
	$2a_1$	0.21 (0.21)	0.076 (0.076)	0.002 (0.0016)
	$1a_1$	0.0062 (0.005)	0.0001 (0.000079)	1×10^{-6} (1.5×10^{-6})

excitation of methane as a function of ln T. Similar figures can be obtained for ammonia and water. Table 3 summarizes the G-values for the ionization and excitation from each molecular orbital. The values for water in parentheses are those reported previously.[17] Although the values (E_t and E_i) used in the present calculation are slightly different from those in Ref. 17, the G-values obtained are in fair agreement with each other. The difference in the energies of the incident electrons, 10 and 100 keV, produces no noticeable change in the calculated G-values. Table 4 shows the G-values for the double collisions. The yields for double collision for the three compounds are approximately the same.

TABLE 4. THE G-VALUES FOR DOUBLY-CHARGED IONS, DOUBLY-EXCITED MOLECULES, AND EXCITED IONS

	CH_4	NH_3	H_2O	Ne
M^{++}	0.11	0.10	0.10	0.15
M^{**}	0.16	0.11	0.13	0.11
M^{+*}	0.54	0.43	0.49	0.26

Reaction Sequences and the Product Yields

The calculated G-values which are shown in Tables 3 and 4 cannot be compared directly with the observed values, because most of the ions and excited states initially produced are too short-lived to be measured experimentally. We, therefore, have to consider the reaction sequences for each compound. Since fragmental reports on these reaction mechanisms are abundant,[1-9,17,21,30-57] they were collected and the reaction sequences were reconstructed. The most perplexing problem arises when the branching ratios have to be taken into consideration. Such a case is often encountered in reconstructing the reaction sequence of methane. Therefore, the relative abundances based on the branching ratios are somewhat tentative.

CH_4: The fragmentation modes assumed for the ions and excited states produced are summarized as follows:

$$\begin{array}{lll}
\text{orbital} & & \text{relative abundance}^{3,30-34)} \\
\text{Ionization from } (1t_2) \longrightarrow & CH_4^+ + e^- & 0.6 \\
\qquad\qquad\qquad\quad \searrow & CH_3^+ + H + e^- & 0.4 \\
(2a_1) \longrightarrow & CH_4^+ + e^- & 0.6 \\
\qquad \searrow & CH_3^+ + H' + e^- & 0.4 \\
(1a_1) \longrightarrow & CH_4^{6+} + 6e^- &
\end{array}$$

where H′ denotes a hot hydrogen atom. When an electron in the $(1a_1)$ orbital is ejected, the Auger effect is expected to occur and fragmentation of the ion will take place, however, since there is no available information for the mode of this fragmentation and the G-value of this process is very small, it was assumed that only ionization occurs and the ions produced react as follows:

$$CH_4^{6+} + 11CH_4 \longrightarrow 6CH_5^+ + 6CH_3$$

The number of electrons ejected in the Auger effect was estimated by the method described in Ref. 15.

$$\begin{array}{lll}
\text{Excitation from } (1t_2) \text{ triplet} \longrightarrow & CH_3 + H & \\
\text{singlet} \longrightarrow & CH_3 + H & 0.4^{\;1,21,35-44)} \\
\qquad\quad \longrightarrow & CH_2 + H_2 & 0.4 \\
\qquad\quad \longrightarrow & CH + H_2 + H & 0.15 \\
\qquad\quad \longrightarrow & C + 2H_2 & 0.05 \\
(2a_1) \longrightarrow & CH_4^+ + e^- & 0.6^{\;3,32-34)} \\
\qquad \searrow & CH_3^+ + H' + e^- & 0.4 \\
(1a_1) \longrightarrow & CH_4^{6+} + 6e^- & \text{(Auger effect)}
\end{array}$$

Double collisions:

$$\begin{array}{lll}
CH_4^{2+} \longrightarrow & CH_3^+ + H^+ & 0.5^{\;16,32-34)} \\
\qquad \searrow & CH_2^+ + H^+ + H' & 0.5 \\
CH_4^{**} \longrightarrow & CH_4^+ + e^- & 0.6 \\
\qquad \searrow & CH_3^+ + H' + e^- & 0.4 \\
CH_4^{+*} \longrightarrow & CH_3^+ + H' & 0.5 \\
\qquad \searrow & CH_2^+ + H_2 & 0.5
\end{array}$$

The successive reactions of these fragment ions have been investigated by many researchers.

Ion-molecule reactions: [3,45]

$$\begin{array}{lll}
CH_4^+ + CH_4 \longrightarrow & CH_5^+ + CH_3 & \\
CH_3^+ + CH_4 \longrightarrow & C_2H_5^+ + H_2 & \\
\qquad\qquad\quad \nearrow & C_2H_5^+ + H & 1/3 \\
CH_2^+ + CH_4 \longrightarrow & C_2H_4^+ + H_2 & 1/3 \\
\qquad\qquad\quad \searrow & C_2H_3^+ + H_2 + H & 1/3 \\
C_2H_3^+ + CH_4 \longrightarrow & C_3H_5^+ + H_2 & \\
C_3H_5^+ + CH_4 \xrightarrow{+M} & C_4H_9^+ & \\
H^+ + CH_4 \xrightarrow{+M} & CH_5^+ &
\end{array}$$

Neutralization reaction: [1-3]

$$CH_5^+ + e^- \longrightarrow CH_4 + H$$

$$C_2H_5^+ + e^- \longrightarrow C_2H_4^* + H$$

$$\begin{aligned} C_2H_4^+ + e^- &\xrightarrow{+M} C_2H_4^* \\ C_4H_9^+ + e^- &\longrightarrow C_3H_6 + CH_3 \end{aligned}$$

A part of the excited ethylene produced will decompose into acetylene and a hydrogen molecule.[1)]

$$\left.\begin{array}{lll} C_2H_4^* & \longrightarrow C_2H_4 & 2/3 \\ & \searrow C_2H_2 + H_2 & 1/3 \end{array}\right\}$$

Radical reactions: The hot hydrogen atoms produced will react with the substrate, methane.[46)]

$$H' + CH_4 \longrightarrow H_2 + CH_3$$

The radicals, CH_2, CH, and C will undergo the following reactions.[1,2)] Here, it is assumed that the ratio of the amount of singlet methylene ($^1CH_2$) to that of the triplet methylene ($^3CH_2$) is unity and C is in ^1S or ^1D state.

$$\begin{aligned} &^1CH_2 + CH_4 \longrightarrow C_2H_6^* \\ &C_2H_6^* \longrightarrow C_2H_6 \\ &^3CH_2 + CH_3 \longrightarrow C_2H_5^* \\ &C_2H_5^* \longrightarrow C_2H_4 + H \\ &CH + CH_4 \longrightarrow C_2H_4 + H \\ &C + CH_4 \longrightarrow C_2H_2 + H_2 \end{aligned}$$

Since hydrogen atoms are not reactive with methane at room temperature, they will remain as one of the most abundant radicals in the system together with methyl radicals.

$$\begin{array}{ll} 2CH_3 \longrightarrow C_2H_6 & k_1{}^{9)} \\ CH_3 + H \longrightarrow CH_4 & k_2 \\ 2H \longrightarrow H_2 & k_3 \end{array}$$

The relative rate constants were assumed to be in the ratio 5: 57: 1 for k_1: k_2: k_3. This ratio is for the reactions of OH radicals and H atoms.[9)] Thus, we can calculate the *G*-values of the intermediate species and final products using the *G*-values of the initial processes shown in Tables 3 and 4. The results are summarized in Table 5 together with the reactions that produced them.

NH_3: A reaction sequence similar to that for methane was constructed as is shown below. This mechanism is much simpler than that for methane because branching is much less common in the case of ammonia.

$$\begin{array}{rlr} \text{Ionization from } (1a_2'') & \longrightarrow NH_3^+ + e^- & ^{47-50)} \\ (1e') & \longrightarrow NH_2^+ + H + e^- & \\ (2a_1') & \longrightarrow NH_2^+ + H' + e^- & \\ (1a_1') & \longrightarrow NH_3^{8+} + 8e^- \ \text{(Auger effect)} & \\ \text{Excitation from } (1a_2'') & \longrightarrow NH_2 + H & ^{51-54)} \\ (1e') & \longrightarrow NH + 2H & \left.\begin{array}{l}0.85\\0.15\end{array}\right\} \\ & \searrow NH + H' + H & \\ (2a_1') & \longrightarrow NH_3^+ + e^- \ \text{(Autoionization)} & \\ (1a_1') & \longrightarrow NH_3^{8+} + 8e^- \ \text{(Auger effect)} & \end{array}$$

Double collisions:

$$\begin{array}{llr} NH_3^{2+} & \longrightarrow NH_2^+ + H^+ & ^{16,49)} \\ NH_3^{**} & \longrightarrow NH_3^+ + e^- \ \text{(Autoionization)} & \\ NH_3^{+*} & \longrightarrow NH_2^+ + H' & \end{array}$$

Ion-molecule reactions:[47,55)]

$$\begin{aligned} &NH_3^+ + NH_3 \longrightarrow NH_4^+ + NH_2 \\ &NH_2^+ + NH_3 \longrightarrow NH_3^+ + NH_2 \\ &H^+ + NH_3 \longrightarrow NH_4^+ \end{aligned}$$

TABLE 5. THE *G*-VALUES FOR INTERMEDIATE AND FINAL PRODUCTS FROM METHANE

	Ionization	Excitation	Ion-molecule reaction	Neutralization	Hot-atom reaction	Total intermediate	Radical reaction		Final products
e^-	3.60			0					
CH_4^+	1.63		0						
CH_3^+	1.42		0						
CH_2^+	0.32		0						
H^+	0.11		0						
CH_4^{6+}	0.02		0						
CH_5^+			1.86	0					
$C_2H_5^+$			1.52	0					
$C_2H_4^+$			0.12	0					
$C_4H_9^+$			0.10	0					
H	0.82	2.05	0.20	3.38		6.45	1.11	0	
H′	0.59	0.48			0				
CH_3		2.05	1.75	0.10	1.07	4.97		0	
CH_2		1.27				1.27	0		
CH		0.48				0.48	0		
C		0.16				0.16	0		
H_2	0.27	2.07	1.74	0.55	1.07	5.70	0.16	1.32	7.18
C_2H_2				0.55		0.55	0.16		0.71
C_2H_4				1.09		1.09	1.11		2.20
C_2H_6							0.64	0.03	0.67
C_3H_6				0.10		0.10			0.10
$-CH_4$	3.39	3.96	3.90	—1.86	1.07	10.46	1.91	−4.91	7.46

TABLE 6. THE *G*-VALUES FOR INTERMEDIATE AND FINAL PRODUCTS FROM AMMONIA

	Ionization	Excitation	Ion-molecule reaction	Neutralization	Hot-atom reaction	Total intermediate	Radical reaction	Final products
e^-	3.56			0				
NH_3^+	1.59		0					
NH_2^+	1.79		0					
H^+	0.10		0					
NH_3^{8+}	0.01		0					
NH_4^+			3.56	0				
H	0.88	6.12		3.56		10.56	0	
H′	0.81	0.14			0			
NH_2		4.44	5.25		0.95	10.64	0	
NH		0.91				0.91	0	
H_2					0.95	0.95	2.84	3.79
N_2							1.18	1.18
N_2H_4							0.24	0.24
$-NH_3$	3.39	5.35	5.42	−3.56	0.95	11.55	−8.70	2.85

$$NH_3^{8+} + 15NH_3 \longrightarrow 8NH_4^+ + 8NH_2$$

Neutralization reactions:[5,6,56]

$$e^- + NH_4^+ \longrightarrow NH_3 + H$$

Hot-atom reaction:[46]

$$H' + NH_3 \longrightarrow H_2 + NH_2$$

Radical reactions:[6]

$$\begin{array}{ll} 2NH_2 \longrightarrow N_2H_4 & \\ \quad\quad\searrow NH + NH_3 & \\ NH_2 + H \longrightarrow NH_3 & \\ \quad\quad\quad\searrow NH + H_2 & \\ 2H \longrightarrow H_2 & \\ 2NH \longrightarrow N_2 + H_2 & \end{array}$$

The rate constants of these radical reactions have been summarized by Willis *et al.*[6] The *G*-values thus estimated are listed in Table 6.

H_2O: The reaction mechanism for water has already been discussed in detail in a previous paper.[17] Here, it is summarized.

$$\begin{array}{lll} \text{Ionization from } (1b_1) \longrightarrow H_2O^+ + e^- & & \\ (3a_1) \longrightarrow H_2O^+ + e^- & & \\ (1b_2) \longrightarrow H^+ + OH + e^- & 0.5 & \rceil \\ \quad\quad \times & & \} \\ (2a_1) \longrightarrow H' + OH^+ + e^- & 0.5 & \rfloor \\ (1a_1) \longrightarrow H_2O^{8+} + 8e^- & \text{(Auger effect)} & \end{array}$$

$$\begin{array}{lll} \text{Excitation from } (1b_1) \longrightarrow H + OH & & \\ (3a_1) \longrightarrow H + OH & 0.75 & \rceil \\ \quad\quad \searrow H_2 + O & 0.25 & \rfloor \\ (1b_2) \longrightarrow H' + OH & 0.75 & \rceil \\ \quad\quad \searrow H_2 + O & 0.25 & \rfloor \\ (2a_1) \longrightarrow H^+ + OH + e^- & 0.5 & \rceil \\ \quad\quad \searrow H' + OH^+ + e^- & 0.5 & \rfloor \\ (1a_1) \longrightarrow H_2O^{8+} + 8e^- & \text{(Auger effect)} & \end{array}$$

It has been assumed in Ref. 17 that the Auger effect accompanied with the ejection of an electron from the ($1a_1$) orbital results in the formation of only one H_2O^+ ion. Energetically the reaction assumed above is more probable.

Double collisions:

$$\begin{array}{lll} H_2O^{2+} \longrightarrow H^+ + OH^+ & & \\ H_2O^{**} \longrightarrow H_2O^+ + e^- & & \\ H_2O^{+*} \longrightarrow H^+ + OH & 0.5 & \rceil \\ \quad\quad \searrow H' + OH^+ & 0.5 & \rfloor \end{array}$$

Ion-molecule reactions:

$$\begin{array}{l} H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \\ OH^+ + H_2O \longrightarrow H_3O^+ + O \\ H^+ + H_2O \longrightarrow H_3O^+ \\ H_2O^{8+} + 15H_2O \longrightarrow 8H_3O^+ + 8OH \end{array}$$

Neutralization reaction:

$$H_3O^+ + e^- \longrightarrow H_2O + H$$

Hot-atom reaction:

$$H' + H_2O \longrightarrow H_2 + OH$$

The radicals accumulated in the present system through the foregoing reactions are H, OH, and O atoms. The rate constants of the reactions involving these radicals are not all available, so that we cannot write explicitly the reactions of these radicals.

Table 7 summarizes the *G*-values of several intermediate species calculated on the basis of the reactions assumed above.

Discussion

Comparison of Calculation with Experiment. Table 8 summarizes the *G*-values of the final products from methane. Since methane is one of the most stable hydrocarbons, the results obtained at low dose rates cannot be used for comparison, because the secondary reactions of the products play an important role. The experimental results quoted in Table 8 were obtained using a Febetron at a high dose rate[2,4] and a mass spectrometer.[3] The *G*-values estimated in the present calculation agree fairly well with the experimental values. The calculated *G*-values for hydrogen, ethylene,

Table 7. The *G*-values for intermediate roducts from water

	Ionization	Excitation	Ion-molecule reaction	Neutralization	Hot-atom reaction	Total Intermediate
e^-	3.00			0		
H_2O^+	1.71		0			
OH^+	0.62		0			
H^+	0.62		0			
H_2O^{8+}	0.006		0			
H_3O^+			3.00	0		
H		4.37		3.00		7.37
H′	0.52	0.24			0	
OH	0.52	4.61	1.76		0.76	7.65
O		0.39	0.62			1.01
H_2		0.39			0.76	1.15
$-H_2O$	2.96	4.86	3.04	−3.00	0.76	8.62

Table 8. The *G*-values for final products from methane

	Present estimation	Experimental		
		(a)	(b)	(c)
H_2	7.18	5.44	6.9	
C_2H_2	0.71	0.76—0.81	0.7	0.85
C_2H_4	2.20	0.71—1.60	1.6	1.05
C_2H_6	0.67	0.75—1.05	0.6	1.93
C_3H_6	0.10	0.06—0.11	0.2	
C_3H_8		0.03—0.09	0.2	
$-CH_4$	7.46	6.92	7.8	

(a) Ref. 2. (b) Ref. 3. (c) Ref. 4.

and propylene, however, are a little larger than those obtained experimentally. This may be due to the secondary reactions of olefins with hydrogen atoms. Even at the high dose rates obtained using the Febetron, the occurrence of some of the fast secondary reactions cannot be avoided.

Tables 9 and 10 compare the *G*-values of various products obtained in the radiolysis of ammonia.[5,7,8,56,57] The agreement between calculation and experiment is again good. The calculated *G*-values of the intermediate products from water are listed in Table 7. These values may be compared with those reported in Ref. 17. Most of the *G*-values are in good agreement with each other. The *G*-value for hydrogen atoms listed here should be compared with the $G(H)+G(H_3O^+)-G(H')$ in Table 5 of Ref. 17.

Table 9. Comparison of the *G*-values obtained experimentally with the *G*-values calculated for the radiolysis of ammonia

	Present estimation	Experimental			
		(a)	(b)	(c)	(d)
H_2	0.95	0.75	0.70	0.80	0.74
H	7.0		7.0	7.2	
e^-+H	10.56	12.5	10.4		
NH_2+2NH	12.46		11.9		
e^-	3.56	3.77	3.4	3.9	
$-NH_3$	11.55	14.0			

(a) Ref. 7. (b) Ref. 8. (c) Ref. 56. (d) Ref. 5.

G-values for Ionization and Excitation. Table 11 compares the *W*-values obtained theoretically and experimentally.[10-13] The agreement is again satisfactory, although the values calculated here are a little higher than those obtained experimentally. Consider-

Table 10. The *G*-values for final products from ammonia

	Present estimation	Experimental				
		High dose rate		Low dose rate		
		(a)	(b)	(c)	(d)	(e)
H_2	3.79	3.58	2.9	5.4	4.4	5.5
N_2	1.18	1.0	0.9	1.8	1.45	1.0
N_2H_4	0.24	0.58	0.1			0.4

(a) Ref. 5. (b) Ref. 57. (c) Ref. 7. (d) Ref. 8. (e) Ref. 56.

Table 11. *W*-values obtained theorecially and experimentally

	Present estimation	Experimental		
CH_4	27.8	26.7[a]	27.5[b]	27.6[c]
NH_3	28.1	26.5[a]	26.5[c]	
H_2O	33.3	30.2[d]	29.9[b]	
Ne	38.9[f]	36.3[e]		

a) Ref. 10. b) Ref. 11. c) Ref. 13. d) Ref. 12. e) Ref. 58. f) This value is slightly smaller than that reported in Ref. 16 ($W=39.5$). In the present calculation, inner-shell excitation has been included in the estimation of the stopping power.

Table 12. The ratio between the *G*-value for excitation and that for electrons, and the *G*-value for total loss of the substrate

	Present estimation		Santar and Bednar[59]	
	G_{ex}/G_e	$G(-M)$	G_{ex}/G_e	$G(-M)$
CH_4	1.10	7.36	0.8—0.9	6.4— 6.9
NH_3	1.50	8.74	1.2—1.6	7.4—10.0
H_2O	1.67	7.86	0.7—1.3	5.5— 7.6
Ne	0.57	3.77	0.4	3.7

ing the number of rough approximations involved in the present calculation, the agreement is surprisingly good.

Table 12 shows the ratios of the *G*-values for excitation to those for electrons and the *G*-values for the total loss of the substrate. The same values were calculated by Santar and Bednar[59] using the "optical approximation" proposed by Platzman.[58] Both methods seem to be consistent.

TABLE 13. THE CALCULATED *G*-VALUES FOR EMISSION FROM EXCITED HYDROGEN ATOMS AND OTHER SPECIES

		CH_4	NH_3	H_2O
H Lyman	α	$0.06^{a)}$	$0.05^{b)}$	$0.04^{b)}$
		$0.006^{b)}$		$0.16^{d)}$
	β	$0.001^{a)}$		$0.005^{d)}$
Balmer	α	$0.01^{a)}$		$0.03^{d)}$
	β	$0.003^{a)}$		$0.005^{d)}$
	γ	$0.001^{a)}$		$0.002^{d)}$
	δ	$0.0008^{a)}$		$0.0008^{d)}$
2s→1s		$0.006^{a)}$		
CH		$0.008^{c)}$		
C		$0.0007^{b)}$		
N			$0.008^{b)}$	

The cross section used for the calculation was quoted from Ref. 14 for a), Ref. 39 for b), Ref. 38 for c), and Ref. 60 for d).

The G-value for Emission. Recently, the emission from the excited species produced by electron impact have been measured by several investigators.[14,38,39,60–62] They reported the cross sections for these processes as a function of the energy of incident electrons. Using these cross sections and the degradation spectra obtained here, it is possible to calculate the *G*-values of various emissions for the substrate excited by 100 keV electrons. Table 13 summarizes the calculated results. The total *G*-values for emission from excited hydrogen atoms produced by 100-keV-electron radiolysis are about 0.1 for methane and ammonia, and 0.2 for water.

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