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The Theoretical Estimation of the *G*-Values for the Ionization and Excitation of Thirty-eight Gaseous Compounds Irradiated by 100 keV Electrons

Kiyoshi OKAZAKI, Masaki YAMABE, and Shin SATO
Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

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The *G*-values for the ionization and excitation of thirty-eight gaseous compounds irradiated by 100 keV electrons have been calculated by combining the binary-encounter-collision theory with the theory of the degradation spectrum, which is based on the continuous-slowing-down approximation (CSDA). The thirty-eight compounds include C_2—C_6 alkanes, cycloalkanes, C_2—C_4 olefins, acetylene, 1,3-butadiene, benzene, toluene, phenol, pyrrole, furan, several alcohols, ethers, ketones, acetaldehyde, carbon dioxide, and hydrogen cyanide. Most of the calculated *G*-values of the electrons were in fair agreement with the experimental values. In the cases of several hydrocarbons, the dissociation from the superexcited state into the neutral fragments was taken into account, since the data for the fragmentation ratios were available. In the case of acetylene, the discrepancy in the *G*-values of electrons obtained experimentally and theoretically suggests that excited acetylene gives rise to a chemi-ionization reaction. In order to check the CSDA, the Fowler equation for helium has been calculated and the results compared with those obtained under the CSDA. The discrepancy in the *G*-values obtained by the two methods did not exceed 7%.

Three years ago we started the theoretical calculation of the *G*-values for the ionization and excitation of gaseous compounds irradiated by 100 keV electrons. Previously we have reported the results obtained with 5 rare gases (He, Ne, Ar, Kr, and Xe),[1,2] 5 diatomic molecules (H_2, N_2, CO, NO, and O_2),[3] and 3 ten-electron-containing molecules (H_2O, NH_3, and CH_4).[4,5] All of the *G*-values estimated were in fair agreement with the experimental ones. This agreement encouraged us to extend the calculation to other compounds. In this paper, we wish to report the results obtained with 38 gaseous compounds, which include most of the compounds whose *W*-values have been reported in the literature.

Method of Calculation

The details of the method of calculation have been reported in previous papers;[1–5] therefore, we will not repeat them here. In the present calculation, we do not take the double collision into account, since we know that the contribution of this process to the final *G*-values does not exceed 5% if the molecules consist of atoms with low atomic numbers.[5]

In the following calculation, all of the molecules excited to above their ionization potentials are assumed to ionize. Strictly speaking, this is not correct, for some of the superexcited states are known to dissociate into neutral fragments, as was mentioned by Platzman.[6] The correction for this process will be discussed in a later section.

Constants Used for Calculation

In order to perform the calculation, we need the constants belonging to each electron in the molecules; the binding energy (I_i), the average kinetic energy (E_i), and the energies of the lowest excited singlet and triplet states of the molecules (E_s and E_t).

The binding energy of an electron in the outermost shell is the ionization potential of the molecule. This value has been measured accurately by means of photoelectron spectroscopy.[7] For the binding energies

TABLE 1. THE ENERGIES OF THE LOWEST SINGLET AND TRIPLET STATES (eV)

	Compound	E_s	E_t
1.	Ethane	7.7[a]	6.3
2.	Propane	7.6	6.2
3.	Butane	7.5	6.1
4.	Isobutane	7.5	6.1
5.	Pentane	7.5	6.1
6.	Isopentane	7.5	6.1
7.	Neopentane	7.5	6.1
8.	Hexane	7.5	6.1
9.	Cyclopropane	7.8	6.4
10.	Cyclopentane	8.7	7.3
11.	Cyclopentene	6.2	4.2
12.	Cyclopentadiene	4.8[a]	3.4
13.	Cyclohexane	8.7[b]	7.3
14.	Spiro[2.2]pentane	7.8	6.4
15.	Ethylene	5.0[a]	3.6[a]
16.	Propylene	6.5[a]	5.1
17.	1-Butene	6.2	4.8
18.	*cis*-2-Butene	6.2	4.8
19.	*trans*-2-Butene	6.2	4.8
20.	2-Methyl-1-propene	6.2	4.8
21.	Acetylene	5.2[a]	4.0
22.	*s-trans*-1,3-Butadiene	6.0[a]	3.9
23.	Benzene	4.7[a]	3.6[a]
24.	Toluene	4.7	3.6
25.	Phenol	4.6	3.5
26.	Pyrrole	5.7[a]	4.5[a]
27.	Furan	5.9[a]	4.7
28.	Methanol	4.0	3.0
29.	Ethanol	4.0	3.0
30.	1-Propanol	4.0	3.0
31.	2-Propanol	4.0	3.0
32.	Dimethyl ether	3.8	2.8
33.	Diethyl ether	3.8	2.8
34.	Acetone	3.8[a]	2.8
35.	2-Butanone	3.8	2.8
36.	Acetaldehyde	3.6[a]	2.6
37.	Carbon dioxide	5.7[a]	4.5
38.	Hydrogen cyanide	6.5[a]	5.0

a) Ref. 10. b) Ref. 11.

TABLE 2. THE G-VALUE OF IONIZATION FROM EACH ORBITAL

The binding energy of the electron in the orbital is I_i. The number in parentheses behind the value of I_i is the number of electrons in the orbital. The number in parentheses behind the value of G_i is the number of electrons ejected because of the Auger effect.

Compound		I_i (eV) and G_i
1. Ethane	I_i	11.51(2), 11.92(4), 14.15(4), 20.96(2), 28.84(2), 307(4)
	G_i	0.90, 1.67, 1.22, 0.33, 0.21, 0.020(6)
2. Propane	I_i	11.06(4), 11.35(2), 12.67(2), 12.84(2), 13.91(2), 14.87(2), 19.71(2), 23.95(2), 30.63(2), 307(6)
	G_i	1.28, 0.61, 0.50, 0.49, 0.42, 0.38, 0.24, 0.18, 0.13, 0.021(6)
3. Butane	I_i	10.67(2), 11.25(2), 11.66(2), 11.91(2), 12.04(2), 13.25(2), 13.41(2), 13.58(2), 15.29(2), 19.53(2), 21.25(2), 26.41(2), 31.62(2), 307(8)
	G_i	0.62, 0.55, 0.51, 0.48, 0.47, 0.39, 0.38, 0.37, 0.30, 0.20, 0.18, 0.13, 0.10, 0.022(9)
4. Isobutane	I_i	10.69(4), 11.43(2), 12.27(2), 12.73(4), 13.73(4), 14.85(2), 18.75(2), 24.08(4), 32.05(2), 307(8)
	G_i	1.12, 0.49, 0.43, 0.79, 0.69, 0.30, 0.21, 0.29, 0.096, 0.022(7)
5. Pentane	I_i	10.37(2), 11.21(2), 11.57(2), 11.66(2), 11.79(2), 12.24(2), 12.57(2), 12.96(2), 13.80(2), 13.99(2), 15.54(2), 19.57(2), 19.92(2), 23.42(2), 28.13(2), 32.22(2), 307(10)
	G_i	0.56, 0.50, 0.43, 0.42, 0.41, 0.38, 0.36, 0.33, 0.30, 0.29, 0.24, 0.17, 0.16, 0.13, 0.096, 0.080(2), 0.022(7)
6. Isopentane	I_i	10.32(2), 10.68(2), 11.39(2), 11.80(2), 11.98(2), 12.41(2), 12.71(2), 13.21(2), 13.74(2), 14.25(2), 14.99(2), 18.65(2), 21.14(2), 24.15(2), 26.79(2), 32.83(2), 307(10)
	G_i	0.57, 0.52, 0.44, 0.41, 0.39, 0.37, 0.35, 0.32, 0.30, 0.28, 0.26, 0.18, 0.15, 0.12, 0.10, 0.078(2), 0.022(7)
7. Neopentane	I_i	10.40(6), 12.31(6), 13.11(4), 14.25(6), 17.64(2), 24.22(6), 33.25(2), 307(10)
	G_i	1.40, 1.01, 0.60, 0.78, 0.18, 0.34, 0.073(2), 0.022(7)
8. Hexane	I_i	10.43(2), 11.19(2), 11.20(2), 11.51(2), 11.65(2), 11.85(2), 12.17(2), 12.30(2), 13.03(2), 13.34(2), 13.60(2), 14.23(2), 15.06(2), 20.10(2), 20.43(2), 22.26(2), 24.76(2), 26.95(2), 28.39(2), 307(12)
	G_i	0.46, 0.38, 0.38, 0.36, 0.35, 0.33, 0.31, 0.31, 0.27, 0.26, 0.25, 0.23, 0.21, 0.13, 0.13, 0.11, 0.095, 0.084, 0.078, 0.022(7)
9. Cyclopropane	I_i	10.06(4), 11.95(4), 12.64(2), 15.35(2), 20.17(4), 31.63(2), 307(6)
	G_i	1.73, 1.24, 0.56, 0.40, 0.53, 0.14(2), 0.023(7)
10. Cyclopentane	I_i	10.49(4), 11.04(4), 11.34(4), 13.50(4), 14.21(2), 15.75(2), 18.58(4), 25.52(4), 33.30(2), 307(10)
	G_i	1.09, 0.97, 0.91, 0.65, 0.29, 0.25, 0.38, 0.23, 0.080(2), 0.024(7)
11. Cyclopentene	I_i	9.00(2), 10.57(2), 10.60(2), 10.95(2), 11.33(2), 11.80(2), 12.92(2), 14.54(2), 15.03(2), 17.33(2), 18.60(2), 24.82(2), 25.05(2), 32.99(2), 307(10)
	G_i	0.80, 0.54, 0.54, 0.50, 0.47, 0.43, 0.36, 0.29, 0.28, 0.22, 0.20, 0.13, 0.13, 0.086(2), 0.025(7)
12. Cyclopentadiene	I_i	8.55(2), 10.40(2), 10.45(2), 10.78(2), 10.85(2), 11.59(2), 13.86(2), 14.72(2), 16.97(2), 17.66(2), 24.14(2), 24.51(2), 32.78(2), 307(10)
	G_i	0.84, 0.55, 0.55, 0.51, 0.51, 0.45, 0.33, 0.29, 0.23, 0.22, 0.14, 0.14, 0.090(2), 0.026(7)
13. Cyclohexane	I_i	9.81(4), 11.05(2), 11.43(2), 11.57(4), 12.39(4), 13.89(4), 14.31(2), 14.83(2). 18.67(2), 20.25(4), 26.95(4), 33.98(2), 307(6)
	G_i	1.15, 0.42, 0.39, 0.76, 0.65, 0.52, 0.25, 0.23, 0.16, 0.28, 0.18, 0.066(2), 0.024(7)
14. Spiro[2.2]pentane	I_i	9.45(2), 9.82(4), 11.06(2), 11.82(2), 12.10(2), 12.71(2), 14.54(4), 17.53(2), 20.25(4), 27.44(2), 33.08(2), 307(10)
	G_i	0.76, 1.37, 0.51, 0.44, 0.42, 0.38, 0.60, 0.22, 0.35, 0.11, 0.086(2), 0.025(7)
15. Ethylene	I_i	10.50(2), 11.47(2), 11.65(2), 14.37(2), 19.21(2), 20.01(2), 307(4)
	G_i	1.00, 0.86, 0.84, 0.60, 0.39, 0.23, 0.022(7)
16. Propylene	I_i	9.69(2), 10.73(2), 11.45(2), 12.63(2), 13.30(2), 14.22(2), 18.31(2), 23.57(2),

Table 2. (continued)

Compound		I_i (eV) and G_i
		29.82(2), 307(6)
	G_i	0.98, 0.79, 0.69, 0.57, 0.52, 0.47, 0.31, 0.21, 0.15(2), 0.023(7)
17. 1-Butene	I_i	9.59(2), 10.50(2), 11.39(2), 11.80(2), 11.98(2), 13.16(2), 13.58(2), 14.62(2), 18.34(2), 20.87(2), 26.04(2), 30.96(2), 307(8)
	G_i	0.78, 0.64, 0.54, 0.50, 0.49, 0.41, 0.38, 0.34, 0.23, 0.19, 0.14, 0.11(2), 0.023(7)
18. *cis*-2-Butene	I_i	9.12(2), 10.56(2), 11.76(2), 11.85(2), 12.74(2), 12.99(2), 13.61(2), 14.90(2), 17.10(2), 22.48(2), 25.25(2), 31.16(2), 307(8)
	G_i	0.90, 0.64, 0.51, 0.50, 0.44, 0.42, 0.39, 0.33, 0.26, 0.17, 0.15, 0.11(2), 0.023(7)
19. *trans*-2-Butene	I_i	9.12(2), 10.24(2), 11.42(2), 11.95(2), 13.03(2), 13.36(2), 13.44(2), 13.55(2), 18.16(2), 21.32(2), 26.08(2), 30.77(2), 307(8)
	G_i	0.89, 0.68, 0.54, 0.49, 0.42, 0.40, 0.39, 0.39, 0.24, 0.19, 0.14, 0.11(2), 0.023(7)
20. 2-Methyl-1-propene	I_i	9.17(2), 10.55(2), 10.91(2), 12.12(2), 12.68(2), 13.46(2), 13.90(2), 13.97(2), 17.05(2), 23.48(2), 24.32(2), 31.12(2), 307(8)
	G_i	0.88, 0.64, 0.59, 0.48, 0.44, 0.39, 0.37, 0.37, 0.26, 0.16, 0.15, 0.11(2), 0.023(7)
21. Acetylene	I_i	11.04(4), 17.86(2), 20.44(2), 27.34(2), 307(4)
	G_i	1.74, 0.43, 0.36, 0.24, 0.024(6)
22. *s-trans*-1,3-Butadiene	I_i	9.07(2), 10.30(2), 11.27(2), 11.38(2), 11.68(2), 13.47(2), 13.72(2), 18.00(2), 19.58(2), 25.81(2), 30.36(2), 307(8)
	G_i	0.92, 0.70, 0.58, 0.57, 0.54, 0.42, 0.40, 0.26, 0.23, 0.15, 0.12(2), 0.025(7)
23. Benzene	I_i	9.24(4), 10.07(4), 11.30(2), 12.29(4), 12.49(2), 14.80(2), 15.22(2), 19.24(4), 26.05(4), 32.75(2), 307(12)
	G_i	1.05, 0.90, 0.37, 0.63, 0.31, 0.23, 0.23, 0.32, 0.20, 0.075(2), 0.026(7)
24. Toluene	I_i	8.82(2), 9.58(2), 9.80(2), 10.12(2), 11.06(2), 11.74(2), 12.15(2), 12.29(2), 13.14(2), 13.51(2), 14.37(2), 15.07(2), 18.48(2), 19.42(2), 22.99(2), 26.12(2), 27.86(2), 33.15(2), 307(14)
	G_i	0.60, 0.50, 0.47, 0.44, 0.37, 0.33, 0.31, 0.30, 0.26, 0.25, 0.23, 0.21, 0.15, 0.14, 0.11, 0.090, 0.083(2), 0.064(2), 0.027(7)
25. Phenol	I_i	8.52(2), 9.80(2), 10.09(2), 10.48(2), 10.99(2), 12.03(2), 12.43(2), 12.45(2), 12.53(2), 13.62(2), 14.69(2), 15.17(2), 18.68(2), 19.48(2), 24.79(2), 26.27(2), 31.45(2), 34.55(2), 307(12), 540(2)
	G_i	0.66, 0.48, 0.45, 0.41, 0.37, 0.31, 0.30, 0.29, 0.29, 0.25, 0.22, 0.20, 0.15, 0.14, 0.098, 0.091(2), 0.070(2), 0.062(2), 0.023(8), 0.0019(10)
26. Pyrrole	I_i	8.2(2), 9.2(2), 12.6(2), 13.0(2), 13.7(2), 14.3(2), 14.8(2), 17.5(2), 18.1(2), 18.8(2), 22.3(2), 23.8(2), 29.5(2), 290.3(8), 406.1(2)
	G_i	1.11, 0.84, 0.43, 0.40, 0.37, 0.34, 0.32, 0.24, 0.23, 0.21, 0.16, 0.15, 0.11(2), 0.023(7), 0.0038(9)
27. Furan	I_i	8.9(2), 10.3(2), 13.0(2), 13.8(2), 14.4(2), 15.1(2), 15.6(2), 17.5(2), 18.6(2), 19.2(2), 23.5(2), 25.2(2), 34.1(2), 290.9(8), 539.4(2)
	G_i	0.98, 0.69, 0.42, 0.38, 0.35, 0.32, 0.30, 0.25, 0.22, 0.21, 0.16, 0.14, 0.091(2), 0.023(7), 0.0027(10)
28. Methanol	I_i	10.83(2), 11.98(2), 12.82(2), 13.97(2), 14.49(2), 22.88(2), 33.84(2), 307(2), 540(2)
	G_i	0.80, 0.68, 0.61, 0.53, 0.50, 0.26, 0.15(2), 0.0097(7), 0.0049(9)
29. Ethanol	I_i	10.46(2), 11.47(2), 11.96(2), 12.50(2), 13.00(2), 14.38(2), 14.65(2), 20.07(2), 26.83(2), 34.06(2), 307(4), 540(2)
	G_i	0.65, 0.55, 0.51, 0.48, 0.45, 0.38, 0.37, 0.23, 0.15, 0.11(2), 0.014(7), 0.0035(9)
30. 1-Propanol	I_i	10.25(2), 11.44(2), 11.45(2), 12.02(2), 12.13(2), 13.28(2), 13.68(2), 13.94(2), 15.20(2), 19.60(2), 22.53(2), 29.31(2), 34.17(2), 307(6), 540(2)
	G_i	0.55, 0.45, 0.45, 0.41, 0.40, 0.35, 0.33, 0.32, 0.28, 0.19, 0.15, 0.11, 0.085(2), 0.016(7), 0.0027(9)

TABLE 2. (continued)

Compound		I_i (eV) and G_i
31. 2-Propanol	I_i	10.18(2), 11.23(2), 11.78(2), 12.31(2), 12.69(2), 12.85(2), 13.66(2), 13.95(2), 14.93(2), 18.87(2), 24.21(2), 28.02(2), 34.53(2), 307(6), 540(2)
	G_i	0.57, 0.47, 0.43, 0.40, 0.38, 0.37, 0.33, 0.32, 0.29, 0.20, 0.14, 0.11, 0.084(2), 0.016(7), 0.0027(9)
32. Dimethyl ether	I_i	9.94(2), 11.73(2), 11.98(2), 12.89(2), 13.33(2), 14.27(2), 14.58(2), 22.37(2), 23.53(2), 34.83(2), 307(4), 540(2)
	G_i	0.71, 0.53, 0.51, 0.45, 0.43, 0.38, 0.37, 0.20, 0.18, 0.11(2), 0.014(7), 0.0035(9)
33. Diethyl ether	I_i	9.51(2), 11.02(2), 11.42(2), 11.79(2), 12.03(2), 12.40(2), 12.58(2), 13.27(2), 14.01(2), 14.28(2), 14.84(2), 19.88(2), 20.29(2), 26.07(2), 27.74(2), 35.17(2), 307(8), 540(2)
	G_i	0.55, 0.41, 0.38, 0.36, 0.34, 0.33, 0.32, 0.29, 0.26, 0.26, 0.24, 0.15, 0.15, 0.10, 0.093, 0.067(2), 0.018(7), 0.0022(10)
34. Acetone	I_i	9.68(2), 11.79(2), 12.12(2), 12.49(2), 13.28(2), 13.96(2), 14.05(2), 14.67(2), 17.46(2), 24.91(2), 27.53(2), 34.47(2), 307(6), 540(2)
	G_i	0.67, 0.46, 0.44, 0.42, 0.37, 0.34, 0.34, 0.32, 0.24, 0.14, 0.12, 0.091(2), 0.017(7), 0.0029(10)
35. 2-Butanone	I_i	9.51(2), 11.47(2), 11.86(2), 12.24(2), 12.51(2), 12.96(2), 13.21(2), 13.96(2), 14.59(2), 14.95(2), 17.37(2), 21.89(2), 25.90(2), 29.43(2), 34.64(2), 307(8), 540(2)
	G_i	0.59, 0.40, 0.38, 0.36, 0.34, 0.32, 0.31, 0.28, 0.26, 0.25, 0.20, 0.14, 0.11, 0.092(2), 0.074(2), 0.019(7), 0.0023(10)
36. Acetaldehyde	I_i	10.20(2), 12.23(2), 12.38(2), 13.17(2), 14.21(2), 14.58(2), 19.27(2), 26.66(2), 34.14(2), 307(4), 540(2)
	G_i	0.72, 0.53, 0.52, 0.47, 0.42, 0.40, 0.26, 0.17, 0.12(2), 0.015(7), 0.0038(9)
37. Carbon dioxide	I_i	13.79(4), 17.59(4), 18.07(2), 19.36(2), 33.73(2), 34.67(2), 307(2), 540(4)
	G_i	0.95, 0.66, 0.31, 0.28, 0.13, 0.13, 0.0082(6), 0.0082(8)
38. Hydrogen cyanide	I_i	13.0(2), 14.4(2), 21.1(2), 33.1(2), 308(2), 426(2)
	G_i	1.10, 0.93, 0.52, 0.27, 0.016(6), 0.011(7)

TABLE 3. CALCULATED G-VALUES (G_s: singlet excitation, G_t: triplet excitation, G_e: electrons, G_e': electrons corrected for the neutral fragmentation of the superexcited state) AND OBSERVED G-VALUES OF ELECTRONS ($G_\mathrm{e}^\mathrm{exp}$)

Compound	G_s	G_t	G_e	G_e'	$G_\mathrm{e}^\mathrm{exp}$	
1. Ethane	1.94	0.93	4.45	3.88	4.24	a)
2. Propane	2.20	0.94	4.37	3.68	4.27	a)
3. Butane	1.50	1.07	4.84	4.27	4.22	b)
4. Isobutane	1.97	1.01	4.56		4.35	a)
5. Pentane	1.35	1.08	5.03	4.26	4.26	b)
6. Isopentane	1.33	1.08	5.06		4.18	a)
7. Neopentane	2.05	1.01	4.61		4.31	c)
8. Hexane	1.25	1.06	4.88		4.27	b)
9. Cyclopropane	1.75	0.92	4.91	4.11	4.22	c)
10. Cyclopentane	0.94	0.73	5.08		3.94	d)
11. Cyclopentene	2.04	1.67	5.25			
12. Cyclopentadiene	3.87	2.44	5.11			
13. Cyclohexane	0.68	0.74	5.28		4.41	b)
14. Spiro[2.2]pentane	0.87	0.95	5.52			
15. Ethylene	5.07	1.68	4.06	3.22	3.92	c)
16. Propylene	2.29	1.36	5.00	4.17	4.03	a)
17. 1-Butene	2.37	1.51	5.02	4.27	4.20	c)
18. *cis*-2-Butene	2.26	1.55	5.10	4.39	4.24	c)
19. *trans*-2-Butene	2.24	1.55	5.14	4.38	4.24	c)
20. 2-Methyl-1-propene	2.26	1.54	5.12		4.20	c)
21. Acetylene	6.52	0.91	2.92		3.95	a)
22. *s-trans*-1,3-Butadiene	2.41	2.66	5.17	4.13	4.00	c)
23. Benzene	4.91	1.61	4.57		4.29	c)
24. Toluene	3.87	2.03	5.22			
25. Phenol	4.04	2.05	5.28			
26. Pyrrole	2.54	1.60	5.22			
27. Furan	2.67	1.52	4.78			
28. Methanol	7.38	1.37	3.78		4.24	c)
29. Ethanol	6.74	1.60	4.12		3.98	b)
30. 1-Propanol	6.32	1.75	4.29		4.08	b)
31. 2-Propanol	6.38	1.77	4.30		4.13	b)
32. Dimethyl ether	7.23	1.73	4.11		4.18	c)
33. Diethyl ether	6.56	2.08	4.50		4.24	b)
34. Acetone	6.96	1.85	4.20		3.88	c)
35. 2-Butanone	6.68	2.00	4.45			
36. Acetaldehyde	8.05	1.73	3.85		3.79	a)
37. Carbon dioxide	5.55	0.77	2.58		2.99	a)
38. Hydrogen cyanide	4.19	0.94	2.99			

a) G. G. Meisels, *J. Chem. Phys.*, **41**, 51 (1964). b) P. Adler and H. K. Bothe, *Z. Naturforschg.*, **20**a, 1700 (1965). c) R. M. Leblanc and J. A. Herman, *J. Chim. Phys.*, **63**, 1055 (1966). d) L. M. Hunter and R. H. Johnsen, *J. Phys. Chem.*, **71**, 3228 (1967).

of the other electrons in several molecules, the experimental data obtained by ESCA are available;[8] however, most of the binding energies of electrons in large molecules are not known. In this case, we use the values calculated by Dewar and Worley.[9] They obtained these values by using the MINDO approximation.

We previously calculated the average kinetic energies by using the SCF functions reported in the literature. In the present paper, we use the following relation to estimate them, since the SCF functions are not available for most of the molecules:

$$E_\mathrm{i} = 2.34 I_\mathrm{i}^{0.93}. \tag{1}$$

Equation 1 roughly satisfies the relation between the I_i and E_i values for rare gases, diatomic molecules, and ten-electron-containing molecules.

For the E_s and E_t values, we use the values reported by Herzberg[10] and Lassettre and Francis.[11] When no data are available, these values are tentatively assumed from those of similar compounds. The E_s and E_t values used in the present calculation are summarized in Table 1.

Results

The calculated results are summarized in Tables 2 and 3. Table 2 shows the *G*-values of ionization from each orbital in the molecules. This table can be used when discussing the initial process of energy absorption from high-energy electrons and also the properties of the ions initially produced. So far, such a discussion has been made for an only limited number of molecules.[3-5]

In Table 3, the total *G*-values of ionization and excitations are summarized; the experimental values are listed in the last column. Except for a few compounds, the calculated *G*-values of electrons are roughly equal to, or a little larger than, the observed ones.

Discussion

Neutral Fragmentation of the Superexcited State. In the present calculation, all compounds excited to above their ionization potentials are assumed to ionize; therefore, if the neutral fragmentation of the superexcited state is an important process, the *G*-values of the electrons listed in Table 3 may be overestimated. Since the amount of the neutral fragmentation is dependent upon the form and energy of the superexcited state, the estimation is not easy. However, we have a procedure to estimate them, although it is very rough—the optical approximation proposed by Platzman.[12]

According to the Bethe theory, the total cross section for ionization may be expressed as follows:

$$Q_\mathrm{i}(T) = \frac{4\pi a_0{}^2 R}{T} M_\mathrm{i}{}^2 \ln \frac{4c_\mathrm{i} T}{R} \tag{2}$$

Here, a_0 is the Bohr radius, R is the Rydberg energy, c_i is a constant, and $M_\mathrm{i}{}^2$ is the dipole matrix-element squared for ionization:

$$M_\mathrm{i}{}^2 = \int_I^\infty \eta(E) \frac{R}{E} \frac{\mathrm{d}f}{\mathrm{d}E} \mathrm{d}E \tag{4}$$

where E is the excitation energy, I is the ionization potential, $\mathrm{d}f/\mathrm{d}E$ is the differential oscillator strength, and $\eta(E)$ is the probability of ionization upon excitation at E. On the other hand, the total cross section of dissociation into the neutral fragments may be expressed as follows:

$$Q_\mathrm{d}(T) = \frac{4\pi a_0{}^2 R}{T} M_\mathrm{d}{}^2 \ln \frac{4c_\mathrm{i} T}{R}. \tag{4}$$

Here, $M_\mathrm{d}{}^2$ is the dipole matrix-element squared for dissociation:

$$M_\mathrm{d}{}^2 = \int_I^\infty [1-\eta(E)] \frac{R}{E} \frac{\mathrm{d}f}{\mathrm{d}E} \mathrm{d}E. \tag{5}$$

Therefore, if we can assume that these two total cross sections are applicable throughout the energy range of the incident electron, the ratio of neutral fragmentation/ionization may be expressed in this form:

$$F = M_\mathrm{d}{}^2/M_\mathrm{i}{}^2 = G_\mathrm{d}'/G_\mathrm{e}'. \tag{6}$$

Here, G_d' and G_e' are the *G*-values of neutral fragmentation and of ionization from the superexcited state respectively. In the present calculation, the sum of G_d' and G_e' should be equal to G_e.

Using the oscillator strengths reported in the literature,[13-15] Hatano estimated the F ratios for several hydrocarbons.[16] We can use these values for the calculation of G_d' and G_e'. The calculated results are included in Table 3. Except for a few compounds, the corrected *G*-values of the electrons, G_e', are in good agreement with those obtained experimentally. Most of the differences between calculation and experiment in the *G*-value of electrons, G_e and $G_\mathrm{e}{}^\mathrm{exp}$, seem to be explainable in terms of this fragmentation of the superexcited state. If this is true, Table 3 suggests that the neutral fragmentation from the superexcited state of oxygen-containing compounds is small compared with that of hydrocarbons.

Chemi-ionization. In the cases of a few compounds (C_2H_2, CH_3OH, and CO_2), the calculated *G*-values of electrons are smaller than the observed ones. In the case of acetylene especially, the difference in *G*-value amounts to 1.0.

It is well known that some of the excited states of rare gases give rise to the Hornbeck-Molnar process, which induces an extra ionization:[17)

$$M^* + M \longrightarrow M_2{}^+ + \mathrm{e}^-$$

If a similar reaction should occur in acetylene, the difference in the *G*-value of electrons may be explainable. According to the mass-spectrometric study by Koyano *et al.*, acetylene excited by ultraviolet light at 121.6 nm gives rise to the following chemi-ionization:[18]

$$\begin{aligned} \mathrm{C_2H_2^* + C_2H_2} &\longrightarrow \mathrm{C_4H_3^+ + H + e^-} \\ &\searrow \mathrm{C_4H_2^+ + H_2 + e^-} \end{aligned}$$

This process might be the cause of the difference in the *G*-value of electrons between calculation and experiment. Such processes, however, have not been reported with methanol and carbon dioxide.

G-value of Excitation. The calculated *G*-values for singlet and triplet excitations are summarized in Table 3; however, there are no available experimental data which they can be directly compared with. In Fig. 1,

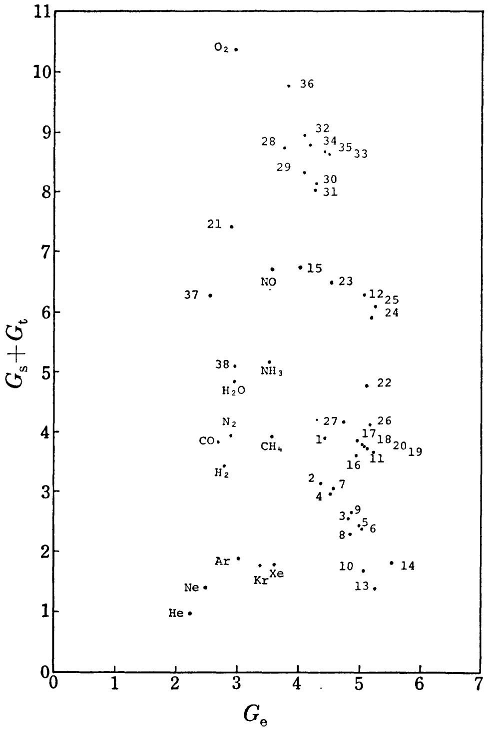

Fig. 1. Correlation between the Calculated G-values of Electrons (G_e) and Excited States (G_t+G_s). The number corresponds to the compounds listed in Table 3.

we plot all of the calculated G-values, including the results obtained in the previous papers.[1–5] The G-values of the electrons range from 2 to 6, while those of the excitations range from 1 to 11. Although the plots are widely scattered, there are some tendencies: the ratios of $G(\text{excitation})/G_e$ are smaller than unity for rare gases and saturated hydrocarbons, while those for oxygen-containing compounds and unsaturated hydrocarbons range from 1 to 4. This figure may provide useful information when the details of the radiolysis are discussed.

Appendix

In order to calculate the degradation spectrum, we have thus far used the CSDA. However, this approximation has not been justified quantitatively.[19] Before the concept of the degradation spectrum was developed, the W-values ($W=100/G_e$) had been calculated by using a more direct method.[20,21] The equation used for such calculations is called the Fowler equation. The actual calculation using the Fowler equation, however, is very tedious, even if an electronic computer is used. Consequently, only a few compounds have been subjected to the calculation.[22,23]

In the following, we will show the calculation for helium using the Fowler equation and compare its result with that obtained under the CSDA. Since both calculations use exactly the same cross sections for various inelastic collisions, the results may clarify the limits of the applicability of the CSDA in the calculation of the W-value.

The Fowler equation to be calculated may be written as follows:

$$N_m(T) = \sum_k \{N_m(T-E_k)+\delta_{km}\}p_k(T) + \sum_i \int_{I_i}^{T} \{N_m(T-E)+N_m(E-I_i)+\delta_{im}\}\frac{dp_i(T)}{dE}dE \quad (7)$$

Here, $N_m(T)$ is the number of atoms in the excited or ionized state, m, produced by the impinging of an electron with the energy, T, into a helium gas; I_i is the binding energy; E_k is the energy of the k-th excited state, and E is the energy loss. The suffixes i and k indicate the ionized and excited states respectively. $p_k(T)$ is the probability that an electron with the energy, T, loses its energy, E_k, in the first collision with the medium and excites the atom to the k-th state. When the medium absorbs the residual energy, $T-E_k$, of the electron, the number of the m-th excited state produced is $N_m(T-E_k)$. The $\{dp_i(T)/dE\}dE$ is the probability that an electron with the energy, T, loses its energy, $E \approx E+dE$, in collision with an atom and ionizes the atom to the i-th state. As a result of this collision, the energies of the scattered and ejected electrons are $T-E$ and $E-I_i$ respectively. Therefore, the numbers of the m-th excited states produced by absorbing the energies of $T-E$ and $E-I_i$ are $N_m(T-E)$ and $N_m(E-I_i)$. The δ_{km} and δ_{im} are Kronecker deltas. When m is equal to k, $\delta_{km}=1$; *i.e.*, an atom is excited to the m=k state in the first collision with the electron of energy, T. The formulation of $p_k(T)$ and $\{dp_i(T)/dE\}dE$ can easily be made as the ratios of the total cross section for ionization and excitations previously formulated.[1]

Equation 1 is a Volterra second-kind integral equation. In order actually to solve this equation, we must first calculate $N_m(T)$ numerically at an energy near the threshold energy. Then, using the obtained $N_m(T)$, we calculate $N_m(T)$ at a higher energy. This calculating method is opposite to that used in the calculation of the degradation spectrum under CSDA, where the calculation is carried out from the higher energy to the lower energy.

For the estimation of the yields of ionization and excitations, we have to set up a Fowler equation for each process, one for ionization and two for the excitations, singlet and triplet. Since $N_m(T)$ at lower energies ($T<100$ eV) depends strongly upon T, the mesh of the calculation must be taken to be as small as possible. In the present calculations, we took 0.2 eV for the mesh. Consequently, the calculation time for the Fowler equation was about sixty times that of the method of the degradation spectrum under CSDA. These calculations were carried out by means of two computers, HITAC 8700 at the Tokyo Institute of Technology and HITAC 8800 at the University of Tokyo.

The $N_m(T)$ values for the ionization and singlet and triplet excitations in helium are shown in Fig. 2 as functions of the

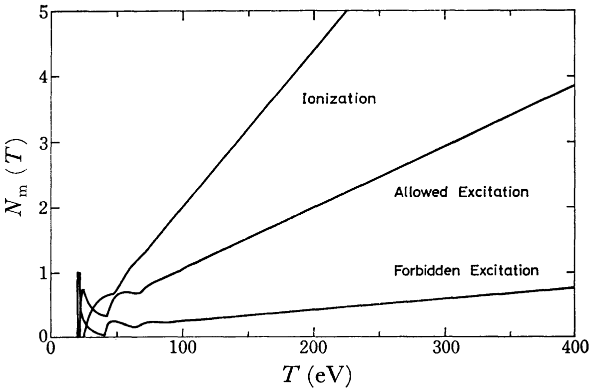

Fig. 2. The yields of ionization and excitations in helium as functions of the incident electron energy.

Table 4. Comparison of the G-values estimated by using the Fowler equation with those obtained by the method of the degradation spectrum under CSDA

Method of calculation	Incident electron energy (keV)	G_e	G_s	G_t
Fowler equation	1	2.35	0.94	0.18
	100	2.38	0.91	0.17
Degradation spectrum	1	2.23	0.88	0.17
	100	2.27	0.85	0.17

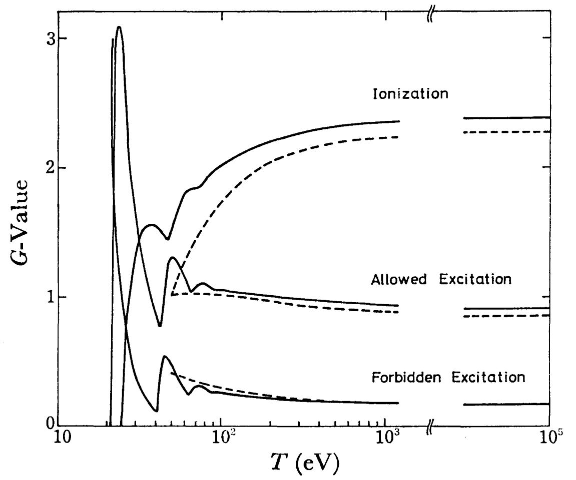

Fig. 3. The G-values for ionization and excitations as functions of ln T.
——: Estimated by using the Fowler equation,
----: estimated by the method of the degradation spectrum under CSDA.

Table 5. Comparison of the W-values obtained experimentally and theoretically

Theoretical:		
Method of calculation		W
Fowler equation	Present	42.0
	Miller[21)]	46.5
	Alkhazov[22)]	46.45±1.0
Degradation spectrum Douthat[24)]		47.9
Degradation spectrum under CSDA		44.05
Experimental:		
Exciting source		W
Po-α		42.7 a)
Po-α		46.0 b)
Tritium-β		42.3 c)
Proton (3.6 MeV)		45.2 d)

a) W.P. Jesse and J. Sadauskis, *Phys. Rev.*, **90**, 1120 (1953). b) J. C. Bortner and G. S. Hurst, *Phys. Rev.*, **93**, 1236 (1954). c) W. P. Jesse and J. Sadauskis, *Phys. Rev.*, **107**, 766 (1957). d) J. E. Parks, G. S. Hurst, T. E. Stewart, and H. L. Weidner, *J. Chem. Phys.*, **57**, 5467 (1972).

electron energy, T. All the yields at the lower energies ($T<500$ eV) are strongly dependent on the energy of the incident electron. However, the yields at the higher energies ($T>1000$ eV) are nearly linear with T. Actually we have calculated the $N_m(T)$ from the threshold energy to 1200 eV, and then extrapolated it to 100 keV by using the linear relation between $N_m(T)$ and T.

Table 4 shows the G-values for ionization and two excitations estimated by the Fowler equation, together with those estimated by the degradation spectrum under CSDA. The values estimated by the two methods agree with each other within 7%. Figure 3 shows the incident electron-energy dependence of the G-values.

For comparison, the experimental and other theoretical W-values of helium are listed in Table 5. The W-value obtained in the present calculation (42.0 eV) seems to coincide with the experimental value (42.3 eV) reported by Jesse and Sadauskis, who used β-rays as the exciting source, while other experiments used heavier particles. This coincidence, however, should be taken as accidental, because the cross sections of ionization and excitations used in the present calculation cannot be more accurate than those used by Miller[21)] and Alkhazov.[22)] This point has already been discussed.[1)]

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