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Excitation from Superexcitation of Hydrocarbons. Estimation of Their Yields by the Optical Approximation

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A simple calculation has been made based on the so-called optical approximation to obtain the yields of excitation from superexcitation of the hydrocarbons, methane, ethane, propane, *n*-butane, *n*-pentane, ethylene, propylene, butene-1, butene-2, 1,3-butadiene, acetylene, and cyclopropane. Their dipole-matrix-elements squared for excitation from superexcitation, M_d^2, have been found to be directly proportional to the number of carbon atoms in the hydrocarbons, and the ratio of M_d^2 to M_i^2, the dipole-matrix-element squared for ionization, is about 0.2. Thus, the yields, per 100 eV energy absorbed, of excitation from superexcitation are nearly equal to 0.8 for all the hydrocarbons described here.

A possible role of neutral fragments in radiation chemistry, which are formed by dissociation of superexcited molecules, was first suggested by Platzman.[1-3] Since then, however, little evidence has been presented for their role in radiation chemistry. On the other hand, reliable evidence has been required for the role of a hot hydrogen atom as a reaction intermediate in radiolysis.[4,5] Recently, however, evidence has been presented for a possible role of hot hydrogen atoms and superexcited states in radiation chemistry.[4-6] Namely, the hydrogen formation in the radiolysis of liquid olefins except ethylene is interpreted[4,5] in terms of the hydrogen-atom abstraction reaction of hot hydrogen atoms formed by direct excitation which must partially involve superexcitation. Moreover, a simple calculation has been made[6] based on the so-called optical approximation to attempt quantitative substantiation of the above viewpoint. In recent years studies have been made by Ausloos and his collaborators[7] of the primary decomposition processes in photolysis of various hydrocarbons at the photon energies a little higher than the ionization potential.

If, according to Platzman's theory, a polyatomic molecule AB receives energy of radiation, this energy may be utilized in direct ionization as

$$\mathrm{AB} \rightarrow \mathrm{AB}^+ + \mathrm{e}^- \tag{1}$$

with a probability δ, or in the formation of a superexcited state

$$\mathrm{AB} \rightarrow \mathrm{AB}' \tag{2}$$

with a probability $(1-\delta)$. This is followed by

$$\mathrm{AB}' \rightarrow \mathrm{AB}^+ + \mathrm{e}^-, \text{ pre-ionization,} \tag{3}$$

$$\searrow \mathrm{A} + \mathrm{B}, \text{ "dissociation".*1} \tag{4}$$

It has been suggested[1] that the probability δ is much less than unity, and that there is, consequently, a real competition between Processes (3) and (4). The optical approximation introduced by Platzman[2,8] is now able to provide at least an approximative quantitative description of these processes. The yield g_d, per 100 eV energy absorbed, of the formation of the superexcited states followed by Process (4) may be estimated by the optical approximation. Namely, the yield g_d is taken as proportional to M_d^2, the dipole-matrix-element squared for excitation from superexcitation.[*2] Thus, the role of the neutral fragments in radiation chemistry may be estimated by the quantity M_d^2. This paper presents the quantity M_d^2 for various hydrocarbons of which the optical spectra have already been known.

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[1] R. L. Platzman, *J. Phys. Radium*, **21**, 853 (1960).

[2] R. L. Platzman, *Vortex*, **23**, 372 (1962).

[3] R. L. Platzman, *Radiation Res.*, **17**, 419 (1962).

[4] Y. Hatano and S. Shida, *J. Chem. Phys.*, **46**, 4784 (1967).

[5] Y. Hatano, S. Shida and S. Sato, This Bulletin, **41**, 1120 (1968).

[6] Y. Hatano, S. Shida and M. Inokuti, *J. Chem. Phys.*, **48**, 940 (1968).

[7] P. Ausloos and S. G. Lias, "Preprints of International Conference on Photochemistry, München (1967)," Part I, p. 211, and the references therein.

[*1] The term "dissociation" means any reorganization of atoms in the molecule which protects it against pre-ionization. The term, therefore, encompasses true dissociation, predissociation, and internal conversion.[2]

[8] R. L. Platzman, "Radiation Research 1966. Proceedings of the Third International Congress of Radiation Research, Cortina d'Ampezzo, Italy, 1966," ed. by G. Silini, North-Holland Publ. Co., Amsterdam (1967), p. 20.

[*2] The term "excitation from superexcitation" means formation of the superexcited states followed by the processes except for ionization, namely by the "dissociation" processes.[2]

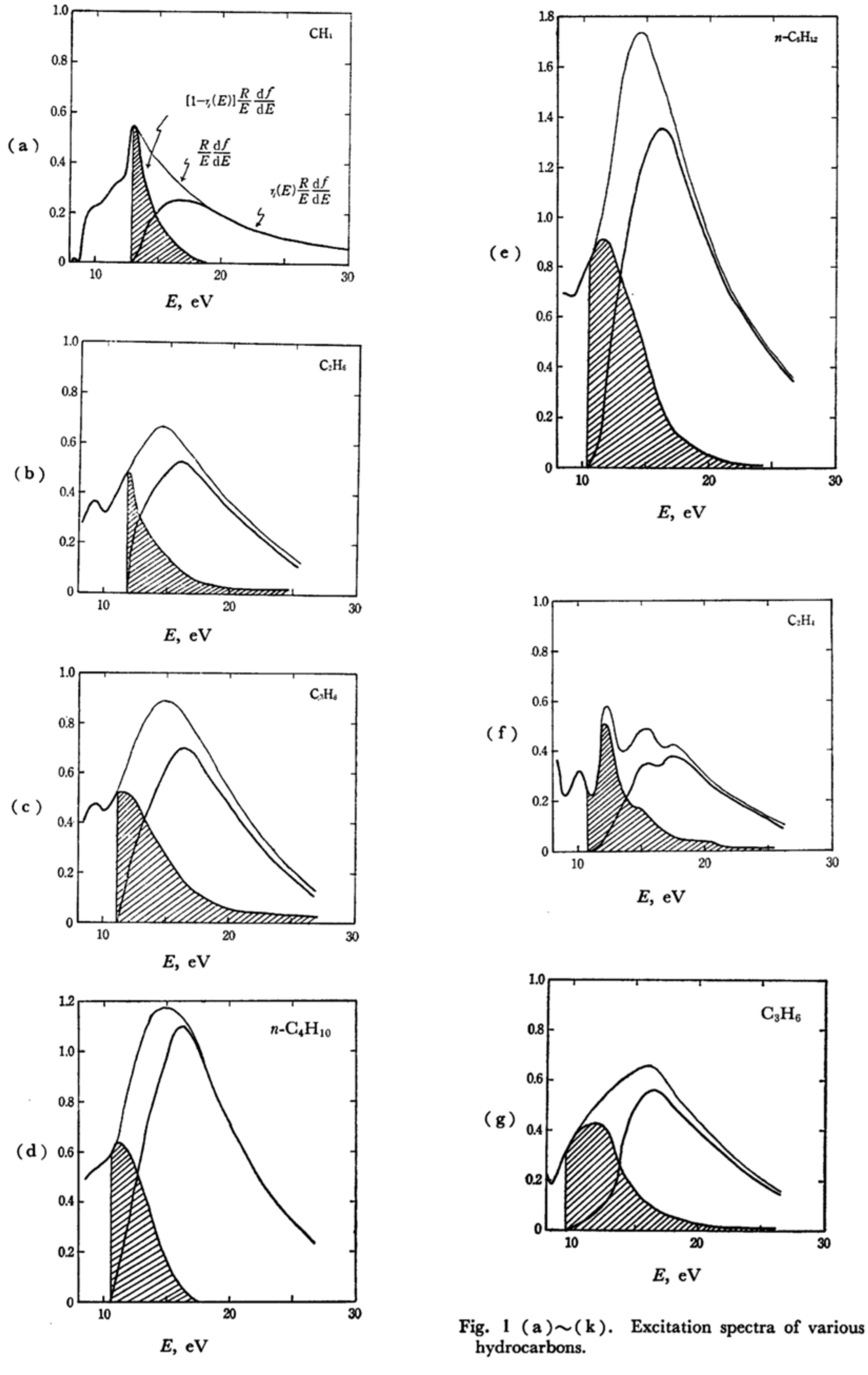
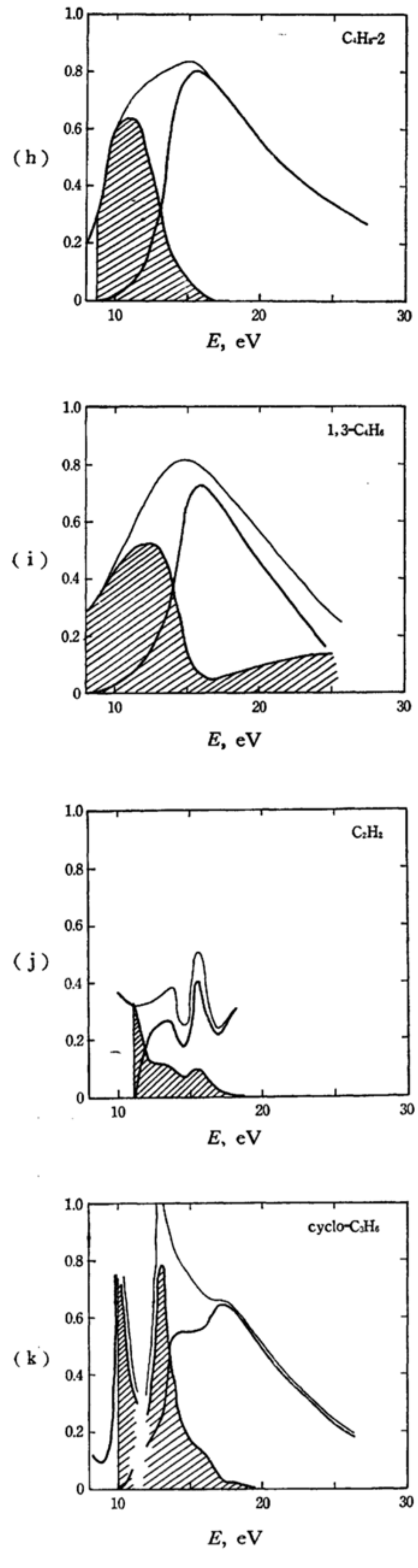


Fig. 1 (a)∼(k). Excitation spectra of various hydrocarbons.



Calculation and Discussion

The yield g_d is proportional to the quantity M_d^2 (in atomic units):

$$M_d^2 = \int_I^\infty [1 - \eta(E)] \frac{\mathbf{R}}{E} \frac{\mathrm{d}f}{\mathrm{d}E} \mathrm{d}E, \qquad (5)$$

where E is the excitation energy, $\mathbf{R}$ the Rydberg energy, I the ionization energy, $\mathrm{d}f/\mathrm{d}E$ the differential oscillator strength, $\eta(E)$ the probability of ionization upon excitation at E. Now, attention has to be paid to a slight difference between the quantity M_d^2 in Eq. (5) and the quantity M_s^2 in the previous paper.[5,6] The latter is determined by the decomposition mode s, namely the threshold excitation energy J_s for s. Since, however, a reasonable assumption, $\phi_s(E)=1-\eta(E)$ at $I<E$ and $\phi_s(E)=0$ at $J_s<E<I$ where $\phi_s(E)$ is the probability of decomposition s upon excitation at E, was introduced in the previous paper,[5,6] the value of the above two quantities have eventually been identical. Utilizing data on ionization, namely the W value and M_i^2, the dipole-matrix-element squared for ionization,[1] we may write $g_d=(100/W)(M_d^2/M_i^2)$.

In calculating M_d^2 by numerical integration in Eq. (5), we have utilized the following sources of information. The differential oscillator strength $\mathrm{d}f/\mathrm{d}E$ and the probability $\eta(E)$ are deduced from photoabsorption data[2,9,10] and are shown in Fig. 1

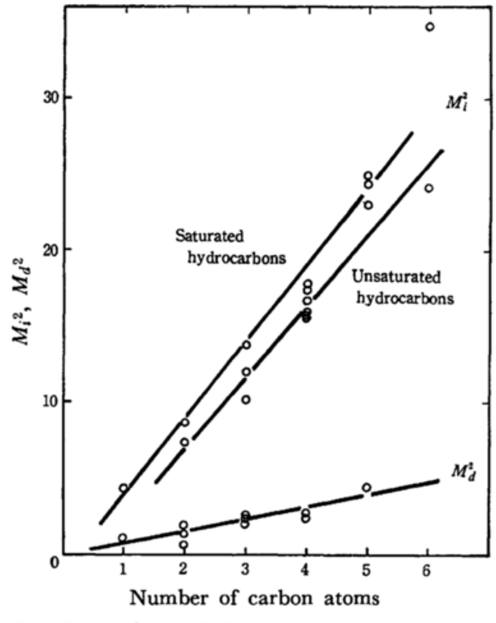


Fig. 2. Values of M_d^2 and M_i^2 for various hydrocarbons against the number of carbon atoms. The values of M_i^2 are quoted from the data by Schram *et al.*[11] Each circle corresponds to a particular hydrocarbon. Refer to Table 1.

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9) R. I. Schoen, *J. Chem. Phys.*, **37**, 2032 (1962).

10) P. H. Metzger and G. R. Cook, *ibid.*, **41**, 642 (1964).

11) B. L. Schram, M. J. van der Wiel, F. J. de Heer and H. R. Moustafa, *ibid.*, **44**, 49 (1966).

TABLE 1. THE VALUES OF M_d^2 AND g_d FOR VARIOUS HYDROCARBONS.

	M_d^2	M_i^2 a)	W, eV b)	g_d
CH_4	1.0	4.28	26.7	0.9
C_2H_6	1.3	8.63	23.6	0.6
C_3H_8	2.6	13.8	23.4	0.8
n-C_4H_{10}	2.4	17.8	22.9	0.6
i-C_4H_{10}	—	17.4	23.0	—
n-C_5H_{12}	4.4	24.4	23.5 f)	0.8
i-C_5H_{12}	—	25.0	23.9	—
neo-C_5H_{12}	—	23.0	—	—
n-C_6H_{14}	—	34.8	23.4 f)	—
cyclo-C_3H_6	2	10.2	—	(0.9 if $W=23$)
C_6H_6	—	24.2	—	—
C_2H_4	1.9	7.32	25.9	1.0
C_3H_6	2.4	12.0	24.8	0.8
C_4H_8-1	2.7 c)	15.3	24.4	0.7
C_4H_8-2	2.7 d)	16.7 d), 15.5 e)	23.9 e)	0.7
C_4H_6-1, 3	>4	15.9	—	(>1 if $W=23$)
C_2H_2	0.6	—	25.3	(0.4 if $M_i^2=6$)

a) Ref. 11 b) Ref. 12 c) See Ref. 5 d) *cis*-Butene-2 e) *trans*-Butene-2 f) Ref. 13

(a)—(k), all of which are drawn on the same scale. Thus, in the first instance, it has been found in these figures that the quantities M_d^2 increase with increasing the number of carbon atoms in the hydrocarbons, while that the oscillator-strength spectra of the hydrocarbons are almost in infinite variety. In the spectra of ethylene, acetylene, and cryclopropane, for example, the marked structures stand in contrast to the smoothness in the spectra of alkanes. The quantities M_d^2 estimated are listed in the first column of Table 1, and are plotted in Fig. 2 against the number of carbon atoms in the hydrocarbons. The data show that the quantities M_d^2 are directly proportional, still very roughly owing to the lack of more reliable basic data, to the number of carbon atoms in the hydrocarbons.*3 There has been, to the author's knowledge, no report with any result such as that shown in Fig. 2, although such result may be easily expected. The quantities M_i^2 taken from ionization cross sections for fast electrons measured by Schram *et al.*[11] are also plotted in Fig. 2. Although the quantities M_i^2 may also be determined by graphical integration in Fig. 1, it forces us to make a rough extrapolation of Schoen's data[9] to higher excitation energies. Figure 2 shows that the values of M_d^2/M_i^2 are nearly equal to 0.2 for all the hydrocarbons described here. Assuming that the W values of the hydrocarbons are equal to 25 eV, we get the values of g_d to be about 0.8. Namely, no peculiarity has been able to be found in the values g_d or M_d^2 at least for all the hydrocarbons under consideration. Going into details and using the W values quoted from the existing paper,[12,13] on the other hand, we get each one of the values g_d to be listed in the last column of Table 1.

Finally, we may add that more reliable and more accurate basic data such as d*f*/d*E*, *W*, and $\eta(E)$ are greatly desirable.

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12) G. G. Meisels, *ibid.*, **41**, 51 (1964).

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

*3 If M_d^2 and M_i^2 are plotted against the number of valence electrons in the hydrocarbons, better-fit lines are obtained for both the quantities.