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Oscillatory Variation near the C–K Edge in the Photon *W*-Value of Ethylene

Isao H. Suzuki* and Norio Saito
Electrotechnical Laboratory, Sakura-mura, Niihari-gun, Ibaraki 305

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The dependence of ethylene *W*-value on photon energy has been precisely measured in the region from 269 to 324 eV by using monochromatized synchrotron radiation. The *W*-value showed an oscillatory variation at the $C_{1s} \rightarrow \pi^*$ excited state as well as the C–K edge. A model has been proposed in which the inner-shell excitation gives rise to a change in the energy of the electron ejected from the molecule having absorbed a photon. It has been found that the model can reproduce the oscillatory variation feature of the *W*-value.

The *W* value of ionizing radiation is a fundamental constant regarding interaction between the radiation and a gas; average energy expended by the radiation to produce an ion pair. A variety of measurements have been carried out on the *W*-values of atoms and molecules for different radiation above several keV.[1] It is well known that the *W*-value is constant for that radiation. Recently some group measured the *W*-value of molecules for electrons in the region below 1 keV.[2–6] Those *W*-values increased with decreasing energy. This phenomenon originates from the fact that the fraction of neutral excitations exceeds that of ionizations in electron-molecule collisions as the electron energy decreases. Srdoč and Obelić measured the *W*-values of methane and propane for photons using characteristic X-rays and filtered bremsstrahlung radiation.[5,6] The measured *W*-values showed a slight increase with decreasing energy. By using line spectra in discharge lamps, Samson and Haddad obtained the *W*-value of Xe for photon in the region of 12 to 90 eV.[7] They found distinct increase of the *W*-value at the ionization threshold of the 4d electron. This increase was ascribed to a decrease of the energy of the electron ejected from the 4d orbital in comparison to that of the O-shell.

Studies on the *W*-value of methane and propane for photons were performed in the ultra-soft X-ray region by the present authors.[8–10] A novel variation near the C–K edge was found in the energy dependence of the *W*-value. This variation was interpreted in connection with the transition of the K-shell electron into the Rydberg orbitals and the ionized state. According to the energy loss spectrum using a high energy electron beam, ethylene shows transitions of the K-shell electron into the $1b_{2g}$ orbital (π^*) at 284.7 eV and into the Rydberg orbitals (3s and 3p) at 287.4 and 287.8 eV.[11] Similar results were found by Eberhardt et al., who obtained an electron yield spectrum using monochromatized synchroton radiation.[12] The transitions of the K-shell electron into the Rydberg orbitals and the ionized state in ethylene probably make the *W*-value oscillate in those energies, as well as methane and propane. However, it remains unsolved how the transition into the π^* orbital affect the *W*-value in ethylene, because methane and propane have no π^* orbital. It is interesting to measure the energy dependence of the *W*-value of ethylele in the region near the excited state $(1s)^{-1}\,(1b_{2g})^1$.

In the present study, the *W*-value of ethylene for photon has been measured precisely from 269 to 324 eV by using a proportional counter.

Experimental

Synchrotron radiation from the storage ring at the Electrotechnical Laboratory was monochromatized by a plane grating monochromator (resolving power: about 150).[10,13,14] The monochromatized photons entered a gas-flow proportional counter (Manson-04) with a thin Al window (thickness: 1500 Å). Ethylene (purity: 99.9%) was supplied to the counter at 5.3×10^3 Pa. Signals from the counter were amplified and accumulated in a multichannel analyzer (MCA: Canberra-40). The resultant pulse height distributions of the signals were transferred to a micro-computer. Using this computer, the pulse height distributions were analyzed to obtain average pulse height.

The pulse height distribution can be approximately expressed by the following,[10,15]

$$f(z) = \frac{z^{x-1}\cdot \exp(-z/z_a)}{z_a^x\cdot \Gamma(x)}\,. \tag{1}$$

In the above equation, z indicates the number of electrons amplified by the electric field within the counter, z_a denotes the average gas amplification factor, x is the average number of the electrons initially produced by the radiation effect of a photon, and Γ is the gamma function. The distributions calculated using Eq. 1 were fitted to those obtained by observation.[10] The average pulse height distribution P is given by

$$P(E_p) = \int z\cdot f(z)\cdot dz = z_a\cdot x = \frac{z_a\cdot E_p}{W_p(E_p)}\,, \tag{2}$$

where E_p indicates the energy of a photon and W_p denotes the *W*-value.[5,6,8–10]

Using Eq. 2, relative *W*-values were obtained for photons with energies from 269 to 324 eV. Any change in P owing to a drift in the gas pressure was cancelled by measuring the P several times at the same photon energy in the course of the experiment. There may be photoabsorption by ethylene in which only neutral fragments are produced but in which no ion pair is formed. This process should alter the *W*-value, although the present technique using a proportional counter cannot count up these types of processes. At present,

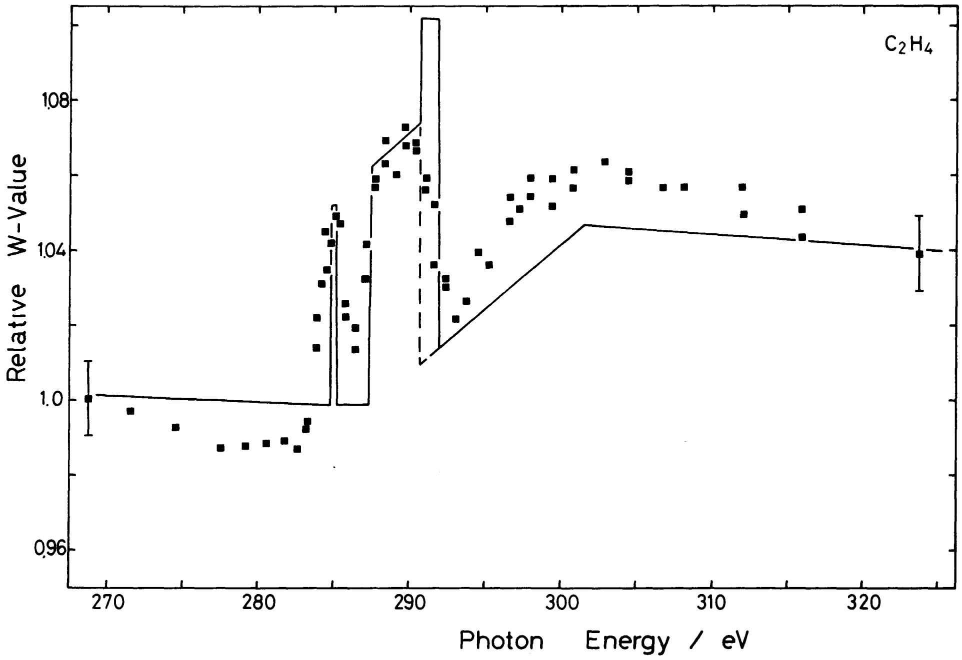

Fig. 1. *W*-Value of ethylene as a function of photon energy near the C-K edge. Solid squares indicate measured data. Solid curve denotes the calculated profile based on the present model. Bars indicate the error sizes of the measured data. Broken line means the profile when a post-collision interaction does not occur (see text).

Table 1. Energy Values Used in the Calculation of the *W*-Value (in Units of eV)

W-Value for sufficiently high energy radiation	(W)	25.8
Average energy of subionization electron for an electron with an energy E	$(U_1$ for $E<30)$	11
	$(U_2$ for $E>200)$	22
First ionization energy	(E_f)	10.5
Average of ionization energy for valence electron	(E_v)	16.1
Ionization energy of the inner-shell	(E_K)	290.6
Average energy of Auger electron	(E_A)	245.8
Average energy of deexcitation electron from the $(1s)^{-1}(\pi^*)^1$ state	$(E_{A\pi})$	255
Average energy of deexcitation electron from the $(1s)^{-1}(R)^1$ state	(E_{AR})	255
Average energy gain of Auger electron in a post-collision interaction	(a)	E_p-288

π^* and R indicate $1b_{2g}$ and Rydberg orbitals, respectively. E_p denotes photon energy.

these processes are assumed to be negligible, by analogy of the results of ionization yield of methane by Backx and Van der Wiel.[16]

Results and Discussion

The energy dependence of the *W*-value is shown with solid squares for photon energies from 269 to 324 eV in Fig. 1. The solid curve indicates a calculated profile based on a model described below. The measured *W*-value gradually decreases from 269 eV to 283 eV as the photon energy increases. The *W*-value rises to a peak at 285 eV, drops to a sharp valley at 287 eV and again goes up to a broad peak at 290 eV. Above a minimum at 293 eV, the experimental data show a near-linear dependence on the photon energy between 293 and 301 eV. Above the latter energy, the *W*-value seems to have a slight decreasing trend.

As those of methane and propane, it is important to consider the oscillatory variation of the *W*-value of ethylene in connection with the excitation transitions of the 1s electron. Hitchcock and Brion observed electron energy loss spectra of ethylene for the 1s electron excitation in the energy resolution of 0.2—0.5 eV.[11] The observed spectra show strongly resonant transitions of the 1s electron to the $1b_{2g}$ orbital at 284.68, 285.04, and 285.50 eV. The transitions into the 3s orbital and the 3p orbital were found to occur at 287.4 and 287.8 eV, respectively. Those to higher Rydberg orbitals and that to the ionized state appeared above 288.3 and 290.6 eV, respectively. They further found shake-up states at 292.6 and 295.2 eV. Eberhardt and coworkers observed an electron yield spectrum of ethylene in the same energy region by use of monochromatized synchrotron radiation.[12] The same transitions were identified although the resolution was lower and the observed energy values deviated slightly (0.3—0.7 eV).

A comparison between the inner-shell excited states and the energy dependence of the *W*-value gives us a model for interpretation as follows. Table 1 lists energy values necessary for calculation of the W-value on the basis of the present model. These energies have been estimated from available data in the literature, e.g. Auger electron spectra and photoelectron spectra.

i) Below 284.7 eV: Only a valence electron is ejected by photoabsorption, because the photon cannot excite an inner-shell electron. The average energy of this ejected electron is E_p-E_v, where E_v is the average binding energy of the valence electrons. Ethylene has 6 orbitals for valence electrons, which are $1b_{1u}$, $1b_{1g}$, $1b_{2u}$, $2b_{3u}$, and $2a_g$.[17,18] The value of E_v is assumed to be 16.1 eV. (Adoption of vertical ionization energy is supposed to be appropriate in the present study.) The ejected photoelectrons ionize ambient molecules and produce a number of ion pairs. On the other hand, the W-value of low energy electrons (W_e) can be approximately given by the following equation.[1,19]

$$W_e(E)=\frac{E\cdot W}{E-U} \tag{3}$$

The term W denotes the W-value for radiation with a sufficiently high energy (25.8 eV),[1] U indicates the average energy of sub-ionization electrons, and E is the energy of a primary electron. The sub-ionization electrons mean the electrons which do not contribute to ionization in a system receiving irradiation. In this case, the average number of ion pairs, N_e, is given by

$$N_e=\frac{E}{W_e}=\frac{E-U}{W}. \tag{4}$$

Using Eqs. 3 and 4, the photon W-value is expressed by the following.

$$W_p(E_p)=\frac{E_p}{1+N_e}=\frac{E_p\cdot W}{E_p+W-E_V-U_2}. \tag{5}$$

Where U_2 is assumed to be 22 eV from the data regarding the W-value for low energy electrons.[3] Multiple photoionization of the valence electrons is assumed to occur only at negligibly low probability at present.

ii) Between 284.7 and 285.1 eV: The 1s electrons can be excited to the π^* orbital ($1b_{2g}$) and a hole is formed in the inner-shell. After this excitation, an Auger transition is supposed to occur because fluorescence yield is extremely low in a light element. A variety of Auger transitions have been observed in ethylene.[20,21] The average energy of Auger electrons, E_A, has been estimated to be 245.8 eV, according to the spectrum by Rye et al.[20] However, the average Auger electron energy in the present case is supposed to be somewhat higher than 245.8 eV owing to the existence of that electron in the π^* orbital. This average energy $E_{A\pi}$ is assumed to be 255 eV, by analogy from a resonance-type Auger electron spectrum of CO.[22,23] The W-value is expressed by

$$W_p(E_p)=\frac{E_p}{1+N_e}=\frac{E_p\cdot W}{E_{A\pi}+W-U_2}. \tag{6}$$

When Eq. 6 is compared with Eq. 5, $E_{A\pi}$ (255 eV) is lower than E_p-E_v (e.g., 270.9 eV for the photon with energy of 287 eV). This fact means that the W-value at 287.4 eV becomes higher than that at 287 eV. In the present model, it is assumed that the photoabsorption probability involving the valence electrons can be negligibly low in this photon energy region on account of the spectra of the inner-shell excitation.[11,12] This assumption is also applied for the energy region above 287.4 eV (cases iv) to vii)).

iii) Between 285.1 and 287.4 eV: Photons can excite only valence electrons, because there is no inner-shell excited state in this energy region. Ejected photoelectrons ionize ambient molecules and produce a number of ion pairs. The W_p is expressed by Eq. 5.

iv) Between 287.4 and 290.6 eV: Photons can excite the inner-shell electrons to the Rydberg orbitals and then the formed inner-hole is filled with a valence electron through the subsequent Auger transition. There exists no available report on this type of Auger transition, in which the upper state is a $(1s)^{-1}$ (molecular Rydberg)^1. However, this type of the Auger process is presumed to be very similar to that of the case ii) described above. The average energy of the Auger electrons E_{AR} is assumed to be 255 eV.

v) Between 290.6 and 291.5 eV: The inner-shell electrons can be ejected from the molecule by the photons, but this ejected photoelectron leaves slowly. In the case of CO, the K-shell photoelectron with low energy is retrapped by the molecular ion when a second electron with higher energy is ejected by an Auger transition (post-collision interaction).[24] Since there has been no detailed study in other molecules, the slow photoelectron in the present case is assumed to be retrapped at the instance of the Auger transition. The Auger electron obtains a slightly higher energy owing to the existence of the slow photoelectron than the normal Auger electron. This energy gain of the Auger electron is equal to the energy loss of the trapped electron. The average energy of the Auger electron is here assumed to be 245.8+a eV ($a=E_p-288$ eV), because of no available data in molecules. This post-collision interaction is tentatively assumed to occur between 290.6 and 291.5 eV, in consideration of the energy giving a minimum W-value (293 eV) and of the photon energy resolution.

vi) Between 291.5 and 301.1 eV: The inner-shell electrons can be ionized and can promptly escape from the molecular field. This photoelectron ejection is followed by a normal Auger transition. The photoelectron has an energy of E_p −290.6 eV. However, this electron can not ionize other ambient molecules because the electron energy is lower than the first ionization energy of the valence electron (E_f=10.5 eV). The Auger electron (E_A) has an average energy of 245.8 eV.

vii) Above 301.1 eV: The photoelectron released from the inner-shell has an energy higher than the first ionization energy of ethylene. This electron and the

Auger electron produced subsequently can ionize ambient molecules. The W-value is expressed by the following equation.

$$W_p(E_p) = \frac{E_p}{2+N_{e1}+N_{e2}} = \frac{E_p \cdot W}{E_p+E_A+2W-E_K-U_1-U_2}, \tag{7}$$

where U_1 denotes the average energy of the subionization electrons for the electron with kinetic energy between 11 and 33 eV. The U_1 is assumed to be 11 eV on account of the study by Combecher.[3]

By using the present model, the relative W-value has been calculated and shown with the solid curve in Fig. 1. The resolving power of the monochromator was not included in this calculation. The energy dependence of the calculated W-value is in agreement with the experimental results. Therefore, the present model is essentially correct.

There is a slight discrepancy between the experimental data and the calculated result at a few energies. That at 286 eV is ascribed to the low resolving power of the present monochromator. That between 291 and 293 eV is presumed to originate from the two reasons, except the low resolving power. First, although the energy of the electron may be lowered through a post-collision interaction below 291.5 eV, there is a possibility that some fractions of slow photoelectrons are not retrapped by the molecular ion. If this is the case, the final configuration is that having two holes in the valence orbital. The calculated W-value becomes lower than that shown in Fig. 1 between 290.6 and 291.5 eV. Second, there have been observed slightly distorted pulse height distributions in the proportional counter around 291 eV. The width of the distribution was broader than those in other energies. This phenomenon is supposed to be brought about by a contamination of the used grating, which gave a decrease of output photon intensity near the C-K edge. This should make the effective resolving power lower. From the minimum at 293 eV (not at 290.6 eV), it can be said that the post-collision interaction takes place just above the C-K edge, as well as for methane. However, it is impossible at present to estimate the size of energy region where it occurs. (The broken line between 290.6 eV and 291.5 eV in Fig.1 shows the calculated result in the case of no occurrence of the post-collision interaction.)

The reason why the experimental data are slightly lower than the calculated curve near 280 eV is not clear at present. The photoabsorption cross section near 280 eV is very low owing to no excitation transition of the inner-shell electrons. The electron cloud induced by photoabsorption is distributed more homogeneously in the proportional counter near 280 eV than other energies. This fact may make a small effect on the average pulse height distribution through a possible change in gas amplification factor.

The shake-up states were reported to exist at 292.6 and 295.2 eV.[11] In contrast to the transition to the π^* orbital, the transition probability to those states was considerably lower than that to the normal continuum state. Thus that transition was not expected to make an appreciable effect on the W-value. The experimental W-value does not show a change at those energies in Fig. 1 within experimental accuracy.

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References

1) H. O. Wyckoff, "Average Energy Required to Produce an Ion Pair," *ICRU-Report*, **31**, (1979).

2) E. Weibel and B. Grosswendt, *Nucl. Instr. Meth.*, **211**, 487 (1983).

3) D. Combecher, *Radiat. Res.*, **84**, 189 (1980).

4) B. G. R. Smith and J. Booz, "Proceedings of Sixth Symposium on Microdosimetry," Commission of the European Communities, London (1978) p. 759.

5) D. Srdoč and B. Obelić, "Proceedings of Fifth Symposium on Microdosimetry," Commission of the European Communities, Luxembourg (1976) p. 1007.

6) D.Srdoč, *Nucl. Instr. Meth.*, **108**, 327 (1973).

7) J. A. R. Samson and G. N. Haddad, *Radiat. Res.*, **66**, 1 (1976).

8) I. H. Suzuki and N. Saito, *Radiat. Phys. Chem.*, **26**, 305 (1985).

9) I. H. Suzuki and N. Saito, *Bull. Chem. Soc. Jpn.*, **58**, 3210 (1985).

10) N. Saito and I. H. Suzuki, *Chem. Phys.*, **108**, 327 (1986).

11) A. P. Hitchcock and C. E. Brion, *J. Elect. Spectrosc. Relat. Phenom.*, **10**, 317 (1977).

12) W. Eberhardt, R. P. Haelbach, M. Iwan, E. E. Koch, and C. Kunz, *Chem. Phys. Lett.*, **40**, 180 (1976).

13) T. Tomimasu, T. Noguchi, S. Sugiyama, T. Yamazaki, T. Mikado, and M. Chiwaki, *IEEE Trans. Nucl. Sci.*, NS-**30**, 3133 (1983).

14) N. Saito and I. H. Suzuki, *Bull. Electrotechnical Laboratory*, **49**, 689 (1985).

15) B. Breyer, *Nucl. Instr. Meth.*, **112**, 91 (1973).

16) C. Backx and M. J. Van der Wiel, *J. Phys.*, **B8**, 3020 (1975).

17) K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, "Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules," (Jpn. Scient. Soc. Press, Tokyo, 1981).

18) A. J. Dixon, S. T. Hood, and E. Weigold, *J. Elect. Spectrosc. Relat. Phenom.*, **14**, 267 (1978).

19) M. Inokuti, *Radiat. Res.*, **64**, 6 (1975).

20) R. R. Rye, T. E. Madey, J. E. Houston, and P. H. Holloway, *J. Chem. Phys.*, **69**, 1504 (1978).

21) C. M. Liegener, *Chem. Phys.*, **92**, 97 (1985).

22) L. Ungier and T. D. Thomas, *Phys. Rev. Lett.*, **53**, 435 (1984).

23) C. T. Chen, R. A. DiDio, W. K. Ford, E. W. Plummer, and W. Eberhardt, *Phys. Rev.*, **B32**, 8434 (1985).

24) R. B. Key, Ph. E. Van der Leeuw, and M. J. Van der Wiel, *J. Phys.*, **B10**, 2521 (1977).