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Effect of Inner-shell Excitations on the *W*-Value of Propane

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The dependence of the propane *W*-value on photon energy has been precisely measured near inner-shell excited states using monochromatized synchrotron radiation. The *W*-value showed an oscillatory variation in this energy region. A model has been proposed in which inner-shell excitation is assumed to give 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. A post-collision interaction is suggested to take place just above the C–K edge of propane.

The *W*-value of ionizing radiation represents the mean energy expended by the radiation to produce an ion pair. A variety of studies were carried out regarding the *W*-values of gases (including propane) in a region higher than several keV.[1] However, a limited number of studies were performed for low energy radiation, although information on the *W*-values in this region is important for calculations regarding the radiation-transport phenomena.[2–7] Recently, Combecher reported on the electron *W*-value for propane in the energy region below 260 eV.[2] The *W*-value showed an increase with decreasing energy. This increase probably originated from the fact that the fraction of neutral excitations exceeded that of ionizations in electron-molecule collisions as the electron energy decreased. Srdoč measured the *W*-value of propane for photons from 90 eV to 280 eV using characteristic X-rays and filtered bremsstrahlung radiation.[3] The obtained data showed a slight increase with decreasing energy.

Samson and Haddad obtained the *W*-value of Xe for photons with energies from 12 eV to 90 eV.[4] Their results showed a distinct variation of the *W*-value over the energy region. This variation was ascribed to a change in the ejected electron energy which was caused by transitions to excited states of the Xe ion. Work on the *W*-value of methane for photons was performed in the ultra-soft X-ray region by the present authors.[5] An oscillatory variation near the C–K edge was found in the energy dependence of the *W*-value. Propane has the K-shell ionization energy of 290.6 eV.[8] Transitions of the K-electrons to unoccupied orbitals are supposed to take place slightly below the ionization threshold although there is no available data on the K-shell excitation spectrum.[9–11] These types of excitations and ionizations probably cause molecules to change into different types of states of the molecular ion. The *W*-value is expected to be affected by these ion states near the K-edge.

The present paper reports precise measurements of the *W*-value of propane for photons from 260 eV to 360 eV. The fine structure of the *W*-value found in this energy region is discussed in connection with the transitions of C-1s electrons.

Experimental and Analysis Method

Synchrotron radiation from the storage ring (electron energy: 400 MeV) at the Electrotechnical Laboratory was monochromatized by a plane grating monochromator.[12,13] The resolving power of the monochromator was about 150. The monochromatized photons entered a gas-flow proportional counter (Manson-04) with a thin film window. The window material was VYNS (thickness: 25 μg/cm^2) or Al (1500 Å). Propane (purity: 99.99%) was introduced into the counter. The gas pressure was set to be 40 Torr for the Al window and 100 Torr for the VYNS window.

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 heights. The pulse height distribution can be approximately expressed by the following,[14,15]

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

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 generated 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.[14] This fitting procedure served to remove any interference due to contamination of the photon beam when the correct pulse height distributions were determined from the experimental data. 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.[3,5,14]

Using Eq. 2, relative *W*-values were obtained for photons with energies from 260 eV to 360 eV. Any nonlinearity of electric circuits (*e.g.*, preamp and MCA) was corrected for. Also, any change in P owing to a drift in the gas pressure was cancelled by performing several measurements at the same photon energy in the course of the experiment. There may be photoabsorption by propane in which only neutral fragments are produced but in which no ion pair are

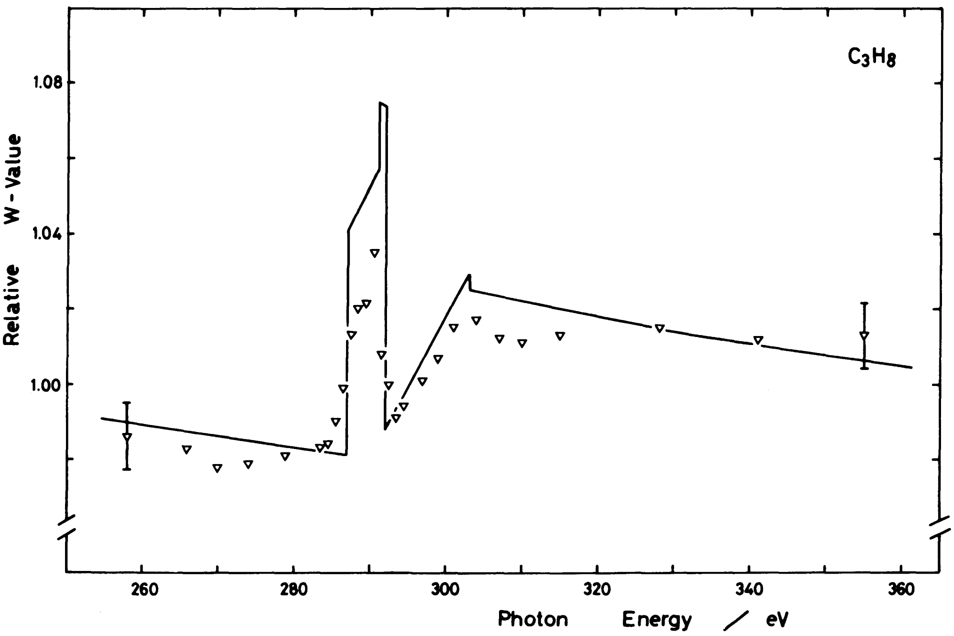

Fig. 1. Dependences of the propane W-value on the photon energy in the region from 260 eV to 360 eV. Open triangles indicate measured results. Solid curve denotes the calculated profile based on the present model. Bars indicate the error sizes of the measured data.

formed. This process should alter the W-value, although the present technique using a proportional counter can not count up these types of processes. At present, these processes are assumed to be negligible, by analogy of the results of ionization yield of methane by Backx and Van der Wiel.[16]

The photoabsorption spectrum was measured using a gas cell (length: 200 mm, inner diameter: 14 mm) with thin VYNS windows (for the entrance and exit of photon beams) and the proportional counter. The counter served to discriminate signals from the noise owing to a contamination of the photon beam, *e.g.*, higher order photons and stray photons with longer wavelengths.

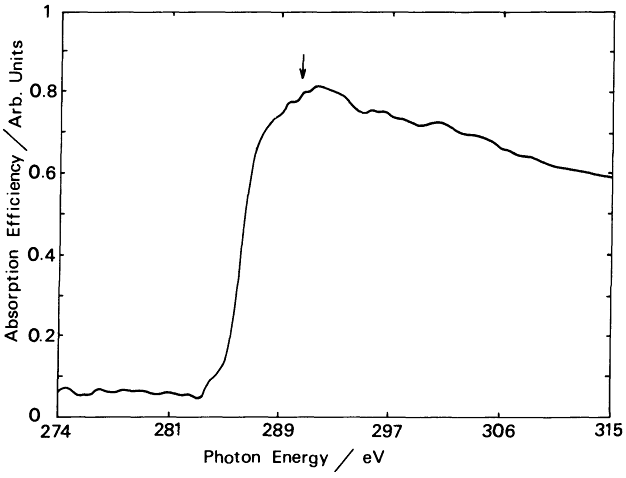

Fig. 2. Photoabsorption spectrum of propane in the region from 274 eV to 315 eV. Arrow indicates the threshold energy of the K-shell ionization (Ref. 8).

Results and Discussion

The relative W-values derived from the measurements are shown with open triangles for photon energies from 260 eV to 360 eV in Fig. 1. The solid curve indicates a calculated profile based on the model described below. The measured W-value slightly decreases with increasing energy from 260 eV to 280 eV. The W-value shows a sharp rise at 286 eV, goes to a maximum at 291 eV and again decreases to a minimum at 294 eV. A linear dependence of the W-value data on the photon energy is seen from 294 eV to 304 eV. The W-value is essentially constant above 304 eV.

In order to clarify the origin of the variation in the W-value shown in Fig. 1, the present authors observed the photoabsorption spectrum of propane around the C-K edge (Fig. 2). Although the inner-shell excited states are not separated from one another (Fig. 2) owing to the low resolving power of the present monochromator, the following items are possibly discernible in the figure. The absorption efficiency is low below 285 eV, becomes high at about 287 eV and has a maximum at around 291 eV. Above 291 eV, this efficiency gradually decreases with increasing photon energy. Judging from the inner-shell excitation spectra of methane and ethane,[9,10] the high efficiency at 287 eV can probably be ascribed to a transition of C-atomic orbitals, 1s→3s. In the cases of methane and ethane, the transition (1s→3s) is low in intensity. This type of transition is supposed to occur with a higher probability because of the poorer symmetry of propane relative to methane and ethane. It is seen in Fig. 2 that this transition is followed by transitions to higher excited states (*e.g.*, 1s→3p) and to the ionized state.

As a result a comparison between the absorption spectrum and the energy dependence of the *W*-value for propane, a model is here proposed as follows.

i) Below 287 eV: Photons can only excite the valence electrons of propane, which occupy 10 molecular orbitals (composed of C-2s, C-2p, and H-1s orbitals) in the ground state. 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 represented by the following expression.[1-4]

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

W denotes the W-value for radiation with a sufficiently high energy (24.0 eV),[1] U indicates the average energy of sub-ionization electrons, and E is the energy of an electron. Using Eq. 3, the photon W-value is given by

$$W_p(E_p) = \frac{E_p}{1+n_e} = \frac{E_p \cdot W}{E_p + W - E_v - U_2}, \tag{4}$$

where E_v is the average binding energy the valence electrons and n_e denotes the average number of ion pairs produced by the ejected photoelectrons. In the derivation of Eq. 4, the following relation was utilized.

$$n_e(E) = \frac{E}{W_e} = \frac{E_p - E_v - U_2}{W} \tag{5}$$

The term E_v is assumed to be 17.9 eV.[8] The average subionization energy, U_2, is assumed to be 25 eV from data regarding the W-value for low energy electrons.[2] Multiple ionizations of the valence electrons are at present assumed to be negligible because there is no available data for this type of process.

ii) Between 287 eV and 290.6 eV: Photons can excite the inner-shell electrons to the Rydberg orbitals and a hole can be formed in the inner-shell. (Unoccupied orbitals in the ground state are called Rydberg orbitals in the present study.) After this excitation, an Auger transition is supposed to occur since fluorescence yield is extremely low in a light element. Several types of Auger transitions have been reported in propane. The average energy of those Auger electrons has been estimated to be 248 eV from the work by Rye *et al.*[17] The average energy of the Auger electrons in the present case is supposed to be slightly different from 248 eV due to the existence of that electron in the Rydberg orbital. This average energy E_{RA} is assumed to be 255 eV, by analogy from a resonance-type Auger electron spectrum of CO.[18] The W-value is given by

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

In a comparison of Eq. 6 with Eq. 4, E_{RA} (255 eV) is lower than $E_p - E_v$ (*e.g.*, 267.1 eV for the photon with energy of 285 eV). Thus, the W-value at 287 eV becomes higher than that at 285 eV. In the present model, it is assumed that the photoabsorption probability involving the valence electrons can be negligibly low above 287 eV on account of the spectrum shown in Fig. 2.

iii) Between 290.6 eV and 292 eV: The inner-shell electrons can be ejected from the molecule by the photons. The energy of this ejected photoelectron is very low. This electron is supposed to be retrapped through a post-collision interaction by that propane molecular ion when a second high-energy electron is ejected through an Auger transition, as seen in the case of CO.[19] The Auger electron obtains a somewhat higher energy owing to the existence of the slow photoelectron, compared to a normal Auger electron. The energy gain of the Auger electron is equal to the energy which the trapped electron loses. The average energy of the Auger electrons is here assumed to be (248 eV+E_p−288 eV).

iv) Between 292 eV and 302.6 eV: The inner-shell electrons can be ionized and can quickly escape from the molecular field. An Auger transition follows this photoelectron ejection. The photoelectron has an energy of $E_p - E_k$ (E_k: the ionization energy of the inner-shell, 290.6 eV[8]), and the Auger electron has an average energy of 248 eV (E_A). The former electron can not ionize other ambient molecules because the electron energy is lower than the first ionization energy of the valence electron. (The vertical ionization energy 12.0 eV is considered here.[8])

v) Above 302.6 eV: The photoelectron ejected from the inner-shell has an energy higher than the first ionization energy of propane. This electron, as well as the Auger electron formed subsequently, can ionize other molecules. The W-value is expressed by

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

where U_1 indicates the average energy of the subionization electrons for the electron with kinetic energy between 12 eV and 60 eV. The U_1 value is assumed to be 11 eV on account of Combecher's study.[2]

The present model is summarized in Fig. 3. Initial and final configurations in the figure denote the configuration of the relevant electrons just after photoabsorption and that after the Auger transition if it happens, respectively. Based on the present model, the relative W-value has been calculated and drawn with the solid curve in Fig. 1. In this

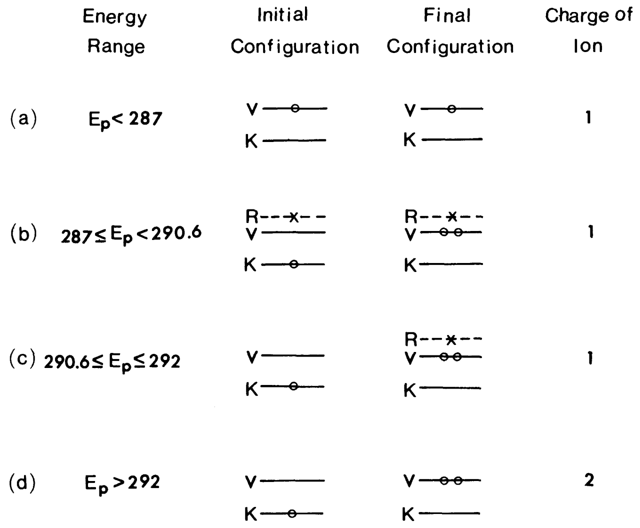

Fig. 3. Illustration of change in the electron configuration. Initial and final configurations indicate the electron configuration just after photoabsorption and that after the Auger transition if it happens, respectively. *Charge of ion denotes the final charge state* of the residual propane ion. E_p is the photon energy. V, K, and R mean the valence orbitals, the inner-shells and Rydberg orbitals, respectively. ○ and × represent a hole and an occupation by an electron, respectively.

calculation, the resolving power of the monochromator was not considered. The calculated curve reproduces the characteristics of the experimental results. Therefore, the present model is essentially correct.

There is a slight discrepancy between the experimental data and the calculated result around 290 eV. This discrepancy is probably caused by the low resolving power of the monochromator. However, the following can not be ruled out with respect to the reason for the discrepancy. Between 287 eV and 290.6 eV, the final configuration of the related electrons is not only one. One part of the final configuration may be the final configuration shown in Fig. 3(a); the configuration with one hole in the valence orbital, which is generated through the ejection of the electron promoted into the Rydberg orbital. From 290.6 eV to 292 eV, there is a possibility that some fractions of the slow photoelectrons are not retrapped by that molecular ion, although the energy of the electron may be lowered through a post-collision interaction. If this is the case, the final configuration is as shown in Fig. 3(d), with two holes in the valence orbitals. The two additional final states mentioned above should make the *W*-value lower than in a model neglecting these states. The calculated result derived from the above consideration is expected to be closer to the experimental data than that in Fig. 1.

If a post-collision interaction does not occur in the region from 290.6 eV to 292 eV, the minimum at 294 eV in the experimental results, shown in Fig. 1, should approach the threshold energy of the K-shell, 290.6 eV. The difference of about 3.5 eV can not be explained by the low resolving power of the monochromator. Thus, it is reasonably expected that the post-collision interaction takes place just above the C–K edge, as well as for CO and methane.14,19) In methane, a minimum has appeared at 295 eV regarding the energy dependence of the *W*-value derived from measurements similar to those in the present work.14) The inner-shell ionization energy of methane is 290.8 eV.8) This type of post-collision interaction is limited to a narrower energy range in propane than in methane. This fact suggests the following. The more electrons exist in molecular orbitals, the more effectively the field of a doubly charged ion is shielded. This may result in there being no occurrence of a post-collision interaction of the photoelectron in propane at an electron energy lower than that in methane by about 1 eV.

The gap at 303 eV in the calculated curve originates from the adoption of the present values on U_1 and the vertical ionization energy. This gap could probably be removed if we could obtain a more reliable U_1 value and could utilize the adiabatic first ionization energy.

Summary

The energy dependence of the photon *W*-value for propane has been precisely determined in the region from 260 eV to 360 eV. An oscillatory structure has been found in the *W*-value near the C–K edge. This structure can essentially be explained by a plain model. In this model, transitions from the ground state to the inner-shell excited states and inner-shell ionization give rise to a change in the energy distribution of the ejected electrons. The Auger transitions are considered to represent the only processes for the re-occupation of the resultant hole in the inner-shell. This change in the energy distribution brings about the oscillatory structure regarding the *W*-value near the K-edge. The following, however, is necessary for a rigorous confirmation of the present model. The energy distribution of ejected electrons and the charge state of residual ions must be accurately determined as a function of photon energy. This type of information will be obtained soon since studies using synchrotron radiation are being vigorously advanced.

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