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Chemical Shifts of Sulfur KLL Auger Electron Energies in Its Compounds

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The sulfur 1s and 2p photoelectron spectra and $KL_{23}L_{23}$ Auger electron spectra in various sulfur compounds involving solid sulfur were measured by means of irradiation by Al *Kα* and Cr *Kα* X-rays. The chemical shifts of the S1s and S2p photoelectron spectra for compounds referred to the data for solid sulfur differ from each other in magnitude, but all are larger than that for the Auger electron spectra in the corresponding compound. The shift of the Auger electron spectra is different in fashion from those of the photoelectron spectra; the difference is largely attributable to the differences in relaxation energies. The extra-atomic relaxation energies due to core-electron emission were estimated by combining the atomic spectral data and the XPS and AES data of compounds; they were found not necessarily to depend upon the atomic charges. From the calculated sulfur *Kα* X-ray spectra corresponding to the difference in the binding energy between 1s and 2p, the number of electrons on each sulfur atom was obtained by using the method derived from Coulson *et al.*, while the isolation was attempted on the basis of the contribution of polarization energies due to surrounding atoms to the extra-atomic relaxation energies.

Various arguments have been advanced during the last decade concerning the chemical shift of the kinetic energy of the Auger electron accompanied by the photoemission of the inner electrons of atoms in compounds.[1–7] Wagner[4] defined the difference in kinetic energy between an Auger line and a photoelectron line as the Auger parameter for an element. He attributed the difference in the Auger parameter to changes in the polarizabilities of the ligand ions. The first work concerning the chemical shift of the sulfur KLL Auger electron energy has been reported by Fahlman *et al.*[8,9] for two sulfur atoms with different oxidation numbers (+VI and −II respectively) in sodium thiosulfate. Recently Asplund *et al.*[10] and Keski-Rahkonen *et al.*[11] measured the sulfur $KL_{23}L_{23}(^1D)$ Auger energy in the free molecule.

With regard to the theoretical treatment for the Auger electron energy, Shirley[12,13] *et al.* introduced a static relaxation energy into the intermediate-coupling formulas given by Asaad and Burhop[14] in order to calculate the KLL Auger energies. This relaxation energy was derived by extending the concept of the polarization potential introduced by Hedin and Johansson[15] for photoemission to the case of the two-hole final state in the Auger electron emission process.

The present paper will report on the chemical shifts of the 1s and 2p photoelectron spectra and the $KL_{23}L_{23}$ ^1D Auger electron spectra for sulfur with various oxidation states in its compounds. The absolute values of the sums of the extra-atomic and outer relaxation energies are estimated from the total relaxation energies observed experimentally and the inner atomic relaxation energies obtained from the optical data for S^{6+} and S^{7+} ions.

Experimental

The measurements were performed by using an AEI ES-200-type electron spectrometer. Specimens were irradiated either with Cr $K\alpha_{1,2}$ radiation ($K\alpha_1$=5414.7 eV and $K\alpha_2$= 5405.5 eV)[16] in order to obtain the S1s photoelectron line and the SKLL Auger line, or with Al $K\alpha_{1,2}$ radiation for the other photoelectrons. Because of the spin orbit interaction, two paired lines with an energy separation of 9.2 eV between Cr $K\alpha_1$ and Cr $K\alpha_2$ were always observed in the spectra.

For the purpose of the energy calibration of the spectrometer, in the case of alminium irradiation, the photoelectron peaks of four kinds of metals, Cu, Au, Pd, and Ag, which had been evaporated onto a stainless steel sample holder *in vacuo*, were used with the following binding energies,[17] and the spectrometer constant was determined.

$$Cu2p_{3/2} = 932.8,\ Au4f_{7/2} = 83.8,\ Pd4d = 0.0,$$
$$Pd3d_{3/2} = 335.2,\ Ag3d_{5/2} = 368.2.$$

In the case of Cr *Kα* irradiation, however, the inner-shell photoelectron lines of the metals measured are not so strong in intensity because of the low ionization efficiency of such orbital electrons. Therefore, as is shown in Fig. 1, the calibration procedures were adjusted: the sodium 1s photoelectron and the $NaKL_{23}L_{23}$ ^1D Auger electron for freshly evaporated sodium chloride were measured by the irradiation of alminium $K\alpha_{1,2}$ and also by a chromium $K\alpha_1$ X-ray source. As the kinetic energy of the Auger line is independent of the excitation energies, the energy difference in the 1s photoelectron kinetic energies obtained by both methods must be equal to the energy difference between Al and Cr *Kα*

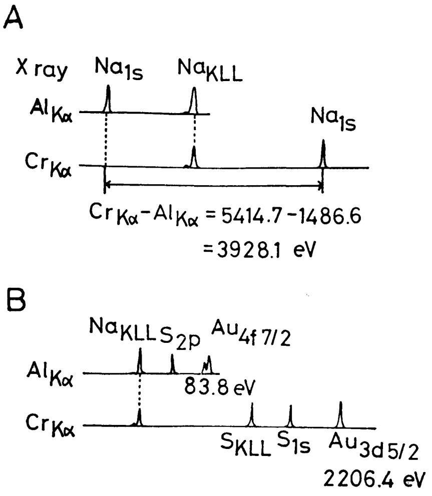

Fig. 1. Energy scale calibration for the case of Cr *Kα* X-ray excitation.
A) i) Charging effect is calibrated by NaKLL Auger electron. ii) The energy difference of Nals peaks obtained by Al *Kα* and Cr *Kα* excitation is calibrated with the energy difference of two X-ray sources.
B) The extent of charging is calibrated by the energy of $Au3d_{5/2}$ photoelectron peak of gold evaporated on the sample.

X-rays. Therefore, the spectrometer constant, the energy calibration for a scale reading, was calculated with the observed photoelectron energies and the energy difference between the two characteristic X-ray lines, 3928.1 eV.

The charging of the sample during each measurement was calibrated by the energy of the $Au4f_{7/2}$ photoelectron peak of the thin gold layer(83.8 eV) evaporated onto the sample from a tungsten filament. On the other hand, for Cr $K\alpha$ X-ray irradiation, not the $Au4f_{7/2}$ peak but the $Au3d_{5/2}$ photoelectron peak(2206.7 eV of the binding energy) was used to determine the extent of charging effects, except for sodium salts. For sodium salts, the Na_{KLL} Auger electron peak, whose energy was calibrated by the Al $K\alpha$-$Au4f_{7/2}$ method, was used for this purpose.

All the samples were powdered and placed onto a backing of double-backed cellophane tape at room temperature. All the chemicals were used without additional purification. Samples of the sodium salts were dried at 100 °C *in vacuo* for a few hours in order to remove any water of crystallization or any water adsorbed on the samples.

Results and Discussion

In Figs. 2a, b, and c, the spectra of the Sls and 2p photoelectrons and the $KL_{23}L_{23}$ ^1D Auger electron for sodium thiosulfate are shown. Sodium thiosulfate is a historic compound for which the chemical shift in the sulfur KLL Auger electron spectrum was first observed by the Uppsala group in 1966.[8,9] This compound has the structural formula of $2Na^+[S\text{-}SO_3]^{2-}$, containing two sulfur atoms in different chemical states, with oxidation numbers of +VI and −II. Three photoelectron peaks were observed for sulfur 1s in Fig. 2a; the central peak is an overlap of the other two peaks. The two kinds of sulfur in thiosulfate exhibit two peaks corresponding to the central and the ligand sulfur, each of which has two peaks due to the two strong energy sources of Cr $K\alpha$ X-rays used for the excitation, with a splitting energy of 9.2 eV. Therefore, there should be a total of four components, and the central one must be an overlapped peak for each of two different sulfur atoms. For the sulfur 2p photoelectron obtained by Al $K\alpha_{1,2}$ excitation and the $KL_{23}L_{23}$ ^1D Auger electron spectra, two peaks were observed corresponding to two kinds of different-oxidation-state sulfur. The magnitude of the chemical shift of the photoelectron line for two kinds of sulfur is different from those of the Auger electrons. That is, the chemical shift in the binding energy is 7.2 eV for the 1s orbital and 6.0 eV for the 2p orbital, while it is only 4.4 eV for the $KL_{23}L_{23}$ ^1D Auger electron.

Calculation of Extra-atomic Relaxation Energy. The $KL_{23}L_{23}$ Auger energy, $E_{KL_{23}L_{23}}$, can be expressed by the following relation;

$$E_{KL_{23}L_{23}} = E_K - E_L - E_L^*, \qquad (1)$$

where E_K and E_L are the observed values of the binding energy for the K and L shells respectively. The E_L^* value is more complicated and does not correspond to the binding energy of the L shell. At the moment of the Auger electron ejection, one hole must have been in the L shell. Shirley *et al.*[12,13,18,19] presented the following formula for E_{KLL} by using the binding energy of E_L instead of E_L^*;

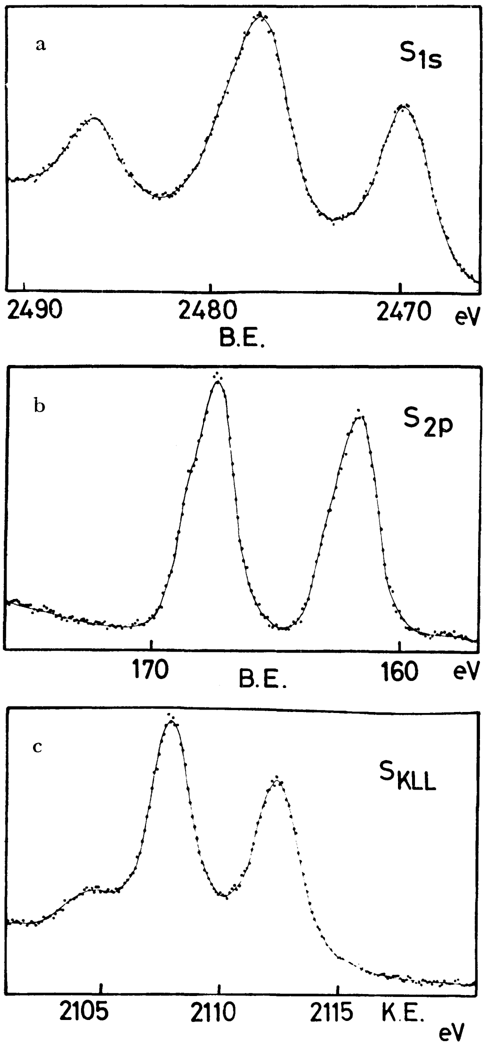

Fig. 2. Sulfur 1s and 2p photoelectron and $KL_{23}L_{23}$ Auger electron spectra in sodium thiosulfate.
a) 1s photoelectron (Cr $K\alpha$ excitation), b) 2p photoelectron (Al $K\alpha$ excitation), c) KLL Auger electron (Cr $K\alpha$ excitation).

$$E_{KL_{23}L_{23}} = E_K - 2E_L - \mathfrak{F} + E_R. \qquad (2)$$

Here, the last two terms are the correction ones which result from substitution of E_L for E_L^*. $\mathfrak{F}$ is a final-state two-electron interaction term provided by the spin-orbit coupling.[14] Each final state interaction term can be evaluated from the values of Slater's integrals, F's and G's. E_R is a static relaxation energy. This term was derived from the work of Hedin and Johansson[15] on polarization energies for electron holes, by extending it to the two-hole final state resulting from the Auger process. The term is approximately twice the dynamic relaxation energy for a photoelectron ejection. Generally, the relaxation energy may be separated into two parts, atomic and extra-atomic relaxation energies.

It is difficult, however, to distinguish between the outer atomic relaxation energy and the extra-atomic relaxation energy, because the outer electrons participate in the bonding orbitals in the compound; that is, these electrons belong to both the central and the surrounding atoms. Here, for the analysis of the sulfur

$KL_{23}L_{23}$ Auger transition, we classified the 3s and 3p orbital electrons as contributing to the extra-atomic relaxation energy, together with the surrounding atoms. The 1s, 2s, and 2p orbital electrons are considered to contribute to the atomic relaxation energy.

Then, Eq. 2 is rewritten as follows;

$$E_{\rm KLL} = E_{\rm K} - 2E_{\rm L} - \mathfrak{F} + E_{\rm R}^{\rm A} + E_{\rm R}^{\rm ex}, \qquad (3)$$

where $E_{\rm R}^{\rm A}$ and $E_{\rm R}^{\rm ex}$ are the atomic and extra-atomic relaxation energies respectively. Here, it is a reasonable assumption* that the $-\mathfrak{F}+E_{\rm R}^{\rm A}$ term is independent of the oxidation numbers of the element to be investigated. The magnitude of the extra-atomic relaxation energy, $E_{\rm R}^{\rm ex}$, is a useful parameter for characterizing the bonding of ligand atoms in compounds.

The numerical value of $-\mathfrak{F}+E_{\rm R}^{\rm A}$ in Eq. 3 can be derived from the data for the atomic spectroscopy.[21] In the case of the sulfur ion with the oxidation number of +VI, there are no electrons in the 3s and 3p orbitals, so the contribution of the outer-orbital electrons to the relaxation energy for the ionization of the 2p electron is zero. Therefore, E(L) in Eq. 1 is equivalent to the ionization potential of S^{+6}, and E(L*), to that of S^{+7}. $-\mathfrak{F}+E_{\rm R}^{\rm A}$ can be obtained as the difference between these ionization potentials. The relative energy diagram for the total energies of the S^{6+}, S^{7+}, and S^{8+} ions, and also for the 1s hole state of the S^{6+} ion, is given in Fig. 3. In the Auger electron spectrum, the most intensive peak is assigned to the ^1D term, and it is necessary to add the energy difference between the ^3P and ^1D terms in the $2p^4$ configuration because the ^3P state in $2p^4$ is a ground state and the ionization energy of S^{7+} corresponds to the ^3P states in S^{8+}. The values for each state are obtained from the optical data[10] and are listed in Table 1. Consequently, from these data the value of −55.0 eV for $-\mathfrak{F}+2E_{\rm R}^{\rm A}$ is estimated. In Eq. 3, $E_{\rm R}^{\rm ex}$ can be calculated by introducing the value for $-\mathfrak{F}+E_{\rm R}^{\rm A}$ and the measured values for the binding energy of 1s and 2p electrons and the Auger electron energy. In the gaseous state, the energy of the Auger electron is equal to the kinetic energy itself, and the binding energy of photoelectrons referred to the vacuum level can be obtained directly. In solid compounds, however, the energy reference used for photoelectrons is usually the Fermi level of the specimen. In order to evaluate $E_{\rm KLL}$ in Eq. 3, the Auger electron must be normalized with the same reference level as the photoelectron binding energies. When the Fermi level is used for the binding energy reference, the Auger electron kinetic energy should be estimated by referring to it. In this case, the kinetic energy of the electron ejected from the Fermi level is coincident with the X-ray source energy, 5414.7 eV for Cr $K\alpha_1$. This situation is shown schematically in Fig. 4.

TABLE 1. TOTAL ENERGY DIFFERENCES BETWEEN IONIZED STATES

	Change in electron configuration	Energy difference (eV)
S^{6+}	$1s^22s^22p^6$ —— $S^{7+}1s^22s^22p^5$	280.99
S^{7+}	$1s^22s^22p^5$ —— $S^{8+}1s^22s^22p^4(^3P)$	328.80
S^{8+}	$1s^22s^22p^4(^3P)$ —— $S^{8+}1s^22s^22p^4(^1D)$	7.19

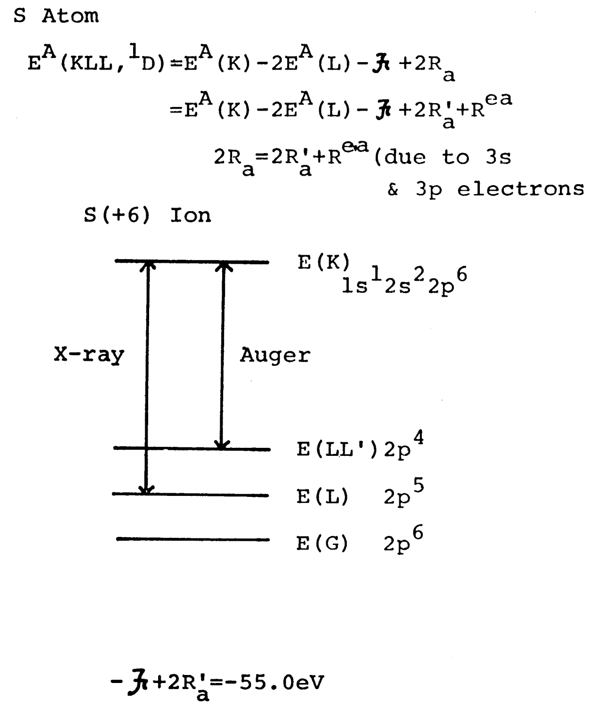

Fig. 3. Total energy level diagram of sulfur ions in various ionized states.
E(G): S^{6+} ground state, E(L): one 2p electron ionized state (S^{7+}), E(LL′): two 2p electrons ionized state (S^{8+}), E(k): one 1s electron ionized state.

In Table 2, the sulfur $KL_{23}L_{23}$ ^1D Auger electron

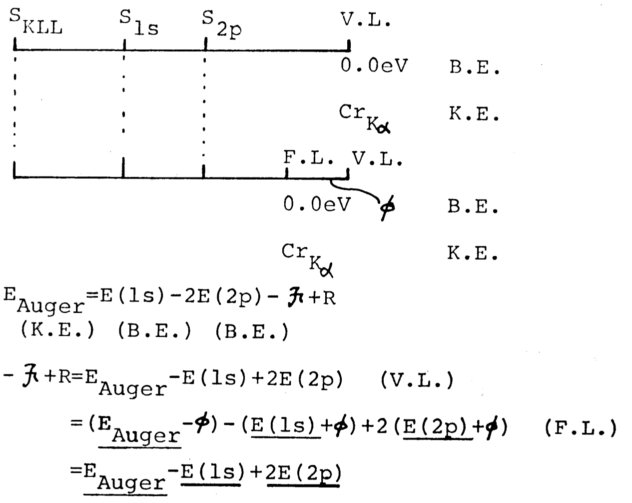

Fig. 4. The Auger electron energy referred to the Fermi level.
V. L.: vacuum level, F. L.: Fermi level,
$\underline{E(1s)}$, $\underline{E(2p)}$: binding energy referred to F. L.,
$E_{\rm Auger}$: Auger electron energy referred to V. L.,
$\underline{E_{\rm Auger}}$: Auger electron energy referred to F. L.,
ϕ: work function.

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* This assumption is supported by an atomic orbital calculation of the $-\mathfrak{F}$ term and of the relaxation energies of free atoms.[20]

TABLE 2. CHEMICAL SHIFTS OF PHOTOELECTRON ($E_{\rm b}$) AND AUGER ELECTRON ($E_{\rm Auger}$) AND EXTRA-ATOMIC RELAXATION ENERGY ($R^{\rm ea}$)

Sample	$E_{\rm b}$(S1s)	$\Delta E_{\rm b}$(S1s)	$E_{\rm b}$(S2p)	$\Delta E_{\rm b}$(S2p)	$E_{\rm Auger}$(SKLL)	$\Delta E_{\rm Auger}$	$R^{\rm ea}$
S	2470.8	(0.0)	162.9	(0.0)	2114.2	(0.0)	24.2
ZnS	2469.4	−1.4	161.7	−0.8	2114.4	0.2	23.2
NaSCN	2470.1	−0.7	162.5	−0.4	2111.4	−2.8	21.3
NH_2CSNH_2	2469.4	−1.4	161.8	−1.1	2109.6	−4.6	18.8
Na_2SO	2475.9	5.1	167.9	4.3	2107.6	−6.6	21.1
Na_2SO_4	2478.2	7.4	169.1	6.2	2105.9	−8.3	21.1
$Na_2S_2O_3$(C)	2477.0	6.2	167.8	4.9	2107.9	−6.3	21.5
$Na_2S_2O_3$(L)	2469.8	−1.0	161.8	−1.1	2112.3	−1.9	21.1
BaS_2O_3(C)	2477.3	6.5	168.4	5.5	2108.2	−6.0	22.7
BaS_2O_3(L)	2470.1	−0.7	162.5	−0.4	2112.6	−1.6	22.5
44′-Dithio-bis(morpholine)	2470.7	−0.1	163.0	0.1	2114.0	−0.2	24.3

energies and binding energies for the sulfur 1s and 2p photoelectrons for various compounds are listed, together with their shifts from those of solid sulfur. A slight deviation in the magnitude of the chemical shifts between 1s and 2p photoelectron peaks is observed for each compound. Wagner's Auger parameter, which describes the energy difference between the kinetic energies of the photoelectron and the Auger electron, corresponds to the change in the extra-atomic relaxation energy, provided that the chemical shifts of two subshells associated with the Auger process are the same. This is not the case for the sulfur KLL Auger transition, however, and so the definition of the Auger parameter becomes ambiguous for these compounds. Ignoring the magnitude of the shifts, a similar tendency is observed in the energy gradation of the 1s and 2p photoelectrons for different samples. On the contrary, the Auger electron energy changes in a different fashion. It is necessary to note that, as photoelectron peaks are expressed with the binding energy scale, while Auger peaks are expressed in the kinetic energy scale, the signs of the chemical shifts are opposite to each other. The chemical shifts in the photoelectron binding energies increase with the increase in the formal charge of the corresponding sulfur atom in a compound. In the case of the $S_{\rm KLL}$ Auger electrons, though, the shift is not necessarily in the same direction as the photoelectron. That is, the chemical shift in photoelectron is largely the function of a charge distribution in the initial state, whereas the final state of electron ejection is largely responsible for the chemical shift of the Auger electron energy. Especially for a sulfur atom with a formal charge such as 0 or −2, the chemical shift is the reverse of that for photoelectrons. In thiourea, the $S_{\rm KLL}$ Auger electron shift is 4.6 eV in the opposite direction of the photoelectron shifts obtained by referring to the value for solid sulfur.

In the last column in Table 2, the extra-atomic relaxation energy, $E_{\rm R}^{\rm ex}$, derived from the method mentioned above is shown. The extra-atomic relaxation energy does not alter as much as the chemical shift in photoelectrons. These results predict that the chemical shift in the photoelectron for sulfur compound will follow a straight line against the calculated charge performed by ignoring the relaxation energy. The difference in the extra-atomic relaxation energy between two kinds of sulfur in thiosulfate is only 0.4 eV, while the chemical shift in the 1s photoelectron is 7.2 eV. It is apparent that less correlation was found between the extra-atomic relaxation energy and the charge density on the atom in these compounds. The fact that the extra-atomic relaxation energy of sulfur in thiourea is the least for the compounds investigated, while that in the sulfur molecule is the most, agrees with the results mentioned above, though the binding energies in the two compounds are not so different (only 1.4 eV).

Charge Density on the Sulfur Atom. As the difference in binding energies between the 1s and 2p orbitals corresponds to the energy of the $K\alpha$ X-ray, a difference in chemical shifts between the 1s and 2p binding energies would bring about a chemical shift in the $K\alpha$ X-ray. Sato *et al.*[22] have measured the $K\alpha$ X-ray energy shift for sulfur in various compounds in solid and liquid states, thus revealing the relationship between the formal oxidation number and the chemical shift from the sulfur molecule. The mean number of the valence electrons associated with the sulfur atom in compounds was calculated from the photoelectron energy shifts according to a theoretical correlation presented by Coulson *et al.*[23,24] According to Gianturco and Coulson,[24] the valence-electron density is calculated by using the self-consistent-field technique and by taking into account both parent and daughter systems for sulfur on the basis of Koopman's theorem model and the adiabatic model. In Fig. 5, the findings on the shifts of 1s and 2p photoelectrons for various oxidation numbers are shown. The two curves in Fig. 3 are adequately represented by

$$\Delta E = v(v+3)/11 \text{ for Koopman's theorem model, and} \quad (4)$$

$$\Delta E = v(v+4)/8 \text{ for adiabatic model,} \quad (5)$$

where ΔE is the chemical shift of the S$K\alpha$ X-ray fluorescence line at various oxidation numbers or degrees of ionization, v, from that for neutral sulfur. The energy shift in the $K\alpha$ fluorescence line of sulfur is attributed only to the electronic charge on the sulfur atom; therefore, the number of electrons, n, in the 3s and 3p orbitals of sulfur in a compound can be calculated by using Eq. 5, as $n=6-v$. This assumption seems reasonable, because the term which contributes

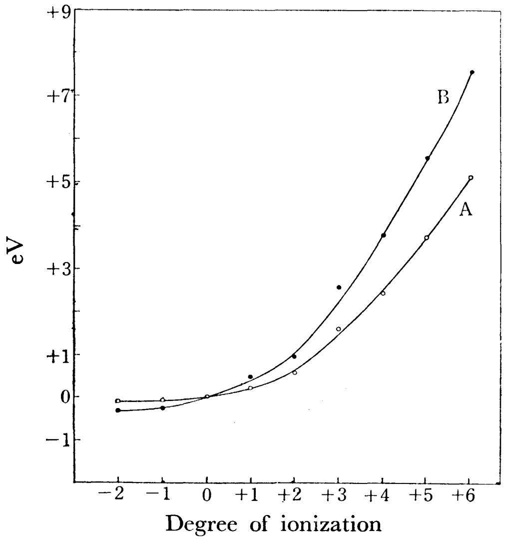

Fig. 5. Shifts in sulfur $K\alpha$ energy due to various degress of ionization.[24]
A) Koopmans' theorem model, B) Adiabatic model.

Table 3. Atomic charge and polarization energy for sulfur atoms

Sample	1s-2p (eV)	$\Delta K\alpha$ a) (calcd)	n b)	$R^{ea'}$ c)	E_{pol} c)
S	2307.9	(0.0)	6.0	13.2	11.0
ZnS	2307.7	−0.2	6.7	14.7	8.5
NaSCN	2307.6	−0.3	7.5	16.5	8.3
NH_2CSNH_2	2307.6	−0.3	7.5	16.6	2.3
Na_2SO_3	2308.7	0.8	4.6	10.1	11.0
Na_2SO_4	2309.1	1.2	4.0	8.8	12.1
$Na_2S_2O_3$(C)	2309.2	1.3	3.8	8.4	13.1
$Na_2S_2O_3$(L)	2308.0	0.1	5.8	12.8	8.3
BaS_2O_3(C)	2308.9	1.0	4.3	9.5	13.2
BaS_2O_3(L)	2307.6	−0.3	7.5	16.5	6.0
4,4′-Dithiobis(morpholine)	2307.7	−0.2	6.7	14.7	9.6

a) Energy shift in sulfur $K\alpha$ X-ray (calcd) from the sulfur molecule. The energy of $K\alpha$ X-ray (calcd) is equal to the difference between the 1s binding energy and 2p. b) Number of electrons on the sulfur 3s and 3p orbitals. c) Relaxation energy due to electrons on the 3s and 3p orbitals proportional to number of electrons(n). d) Polarization energy corresponding to the relaxation energy due to surrounding atoms.

to the chemical shift in the binding energy is the same for each subshell except for the charge density on an atom. That is, the chemical shift in the $K\alpha$ X-ray energy is equal to the difference in the chemical. shift between the binding energies of the two subshells. The chemical shifts for the binding energies of core electrons can be considered generally by dividing them into two parts——the inner atomic and the outer atomic parts. The inner atomic part is attributed to the charge density of the host atom and the relaxation energy due to the outer orbital electrons, while the outer atomic part is attributed to the potential energy and polarization energy due to the surrounding atoms which are bonding with the host atoms. The outer atomic part will contribute to the energy shift of orbital electrons homogeneously. Therefore, in the case of the chemical shift of the characteristic X-ray energy of inner orbitals, only the inner atomic part must be taken into account. In Table 3, the energy difference between the 1s and $2p_{3/2}$ photoelectron binding energies, which correspond to the calculated $K\alpha$ X-ray energy, are listed for various compounds. The shifts of these values from that for solid sulfur and the effective numbers of the electrons, n, in the 3s and 3p orbitals of the sulfur atom obtained from Eq. 5 for each compound are also listed in Table 3. Considering the core hole formation in the process of $K\alpha$ X-ray emission, Eq. 5 was adopted for the estimation of the relative atomic charge for sulfur in various compounds by referring to that in solid sulfur. It can easily be predicted that the relaxation energy due to outer-orbital electrons of sulfur atom is a function of the charge density on the outer orbital.

Extra-atomic Relaxation Energy Due to Ligand Atoms. Snyder[25] has recently shown that the relaxation from each shell is proportional to the population of each shell in the isolated atom. According to his investigation, the contribution of 3s and 3p electrons to the relaxation of the 2p core hole state in the sulfur atom is 1.09 eV per electron. For the Auger process, the static relaxation energy is approximately equivalent to twice that in the photoelectron process. Therefore, the static relaxation energy for the 2p hole state in the sulfur atom can be estimated as 2.2 eV per electron in the 3s and 3p orbitals. The static outer atomic relaxation energies for the S_{KLL} Auger electron calculated for various compounds are listed in the fourth column in Table 3. The static relaxation energy for a host atom due to only the surrounding atoms in a compound can be obtained by subtracting the static outer atomic relaxation energy from the static extra-atomic relaxation energy. The values for sulfur in various compounds are also listed in the fifth column in Table 3. The extra-atomic relaxation energy obtained above could be regarded as the polarization energy of surrounding atoms. The data in Table 3 indicate that these extra-atomic relaxation energies do not correlate with the chemical shift in the binding energy of the 1s and 2p photoelectrons. In sulfate, sulfite, and thiosulfate, the energy differences of the 2p photoelectron for the central sulfur atom from that in solid sulfur are appreciably large on the positive side, despite the large polarization energies for a core-hole formation, which generally decrease the binding energies. In these compounds, the largest polarization energy is found in the central sulfur of thiosulfate; the energies decrease from sulfate to sulfite. The central atom in thiosulfate bonds to three oxygen atoms and a sulfur atom, while the sulfur in the sulfate ion is surrounded by four oxygen atoms. Therefore, a sulfur atom bonded to a host atom may give a larger polarization energy than an oxygen atom. A slight difference in the polarization energies for the sulfur atom between sulfate and sulfite may be attributed to the decrease in the coordination number of the host atom. Therefore, the polarization energy is strongly correlated to the nature of the atoms surrounding the sulfur, *e.g.*, the polarizability, the ionic radius, and the number of atoms. The terminal sulfur in thiosulfate, for which the photoelectron chemical shift of S2p is very small on the negative side, gets a little polarization energy. In this compound, the terminal sulfur atom adjoins only a sulfur atom and the distance from the nearest oxygen atom is twice that from a sulfur atom. It may be predicted that the polarization energy is mainly correlated to the nature of the nearest-neighboring atoms. Sulfur in zinc sulfide and sodium thiocyanate has small polarization energies, though the chemical shifts referred to the S2p energy for solid sulfur are negative. The polarizability of the bonding atoms also affect the polarization energy shifts of the host atom. For sodium thiocyanate, the sulfur atom is attached to the carbon atom, making only a little contribution to the polarization energy. This observation is further supported by the facts that the polarization energy of sulfur for 4,4′-dithio-bis(morpholine) is also very small and that no chemical shifts from the sulfur molecule are observable. In this case, considering the molecular structure of the morpholine group, the largest polarization energy can be expected for the core-hole formation of the sulfur atom. However, the results disagree with this prediction, presumably because of the small polarizability of the bonding carbon atoms.

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