Sulfur K-Edge Absorption Spectra of Na_2SO_4, Na_2SO_3, $Na_2S_2O_3$, and $Na_2S_2O_x$ (x=5—8)

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X-Ray absorption spectra of the sulfur K-edges of SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, and $S_2O_x^{2-}$ (x=5—8) were measured with synchrotron radiation. The spectra show similarly strong absorption bands which originate in bound-state transitions to antibonding 3p-type orbitals and in shape resonances related to 3d-type orbitals. The K-edge spectrum for the terminal sulfur atom in $S_2O_3^{2-}$, however, shows only a bound-state transition. Differences in chemical environments and bonding around the X-ray absorbing atoms are discussed to interpret the spectra.

K- and L-shell X-ray absorption spectra for molecules such as SO_4^{2-},[1] SF_6,[1,2] and SiF_4,[3] where electronegative ligand atoms surround a central atom, show resonance-like bands below and above the ionization threshold and quite weak Rydberg series. Nefedov[4] and Dehmer[5] first introduced the concept of effective potential barrier in interpreting X-ray absorption spectra of molecules in which a B, S, or Si atom is bonded with two or more electronegative atoms. When an excited electron is within the cage of electronegative atoms near an electropositive atom, the electron experiences net attraction due to the partially screened nucleus of the central atom; when an excited electron is at a long distance, the electron undergoes only the Coulomb attraction by the molecular ion. At intermediate distances the potential constitutes a barrier due to electronegative atoms located there. The barrier in this case is primarily a pseudopotential barrier rather than the centrifugal barrier which is known in context with high angular momentum states of atoms[6] and molecules.[7] The effective potential barrier separates excited states into outer- and inner-well states. In the inner-well region, there exist bound and quasi-bound states below and above the ionization threshold, respectively. Transitions to inner-well states are of strong tendency to occur because of the large overlap between the wavefunctions of the initial and final states. On the other hand, Rydberg transitions are considerably or completely suppressed because Rydberg orbitals are in the outer-well region.

The effective potential barrier is only a qualitative concept and is not a rigorously physical model. Recently, the orgin of the resonance-like absorption near the inner-shell ionization threshold is interpreted in terms of shape resonance[7] or multiple-scattering resonance[8] within the framework of a rigorous theory of potential scattering. The molecular orbital theory is also powerful for predicting the energy position and transition probability of quasibound-state resonances as well as bound-state resonances.[3,9] In all cases, the chemical environment and bonding around an X-ray absorbing atom contribute dominantly to the origin of resonances.

Ion SO_4^{2-} is a typical cage-like molecule and its inner shell absorption spectra have been studied both experimentally[1] and theoretically.[5,10] There exist various kinds of stable sulfur-containing oxyanions. It is thus interesting to measure X-ray absorption spectra of several derivatives of SO_4^{2-} and to investigate how the deformation of the cage-like structure with T_d symmetry can be reflected on absorption spectra. Relative to SO_4^{2-}, SO_3^{2-} can be regarded as a one-ligand-free ion and $S_2O_3^{2-}$ as a one-ligand-exchange ion.

In the present work, we measured sulfur K-edge absorption spectra for SO_4^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$ as well as their S 2p XPS spectra and interpret the ligand effect on resonance-like bands; i.e., transitions to bound and quasi-bound states. Furthermore, we measured absorption spectra for $S_2O_x^{2-}$ (x=5—8) and analyse them by comparison with spectra for SO_4^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$.

Experimental

All samples for measurements were polycrystalline powders of sodium salts: Na_2SO_3, Na_2SO_4, $Na_2S_2O_3$, $Na_2S_2O_5$, $Na_2S_2O_6 \cdot 2H_2O$, $Na_2S_2O_7$, and $Na_2S_2O_8$. They were obtained from Wako Pure Chemical Industry Co. and were not purified any further. The sample of $Na_2S_2O_7$ contained ≈10% $NaHSO_4$.

Sulfur K-edge absorption spectra were measured with a UHV compatible double crystal monochromator[11] at the Soft X-Ray Station (BL-11B) of the Photon Factory in the National Laboratory for High Energy Physics. Ge(111) was used as a monochromatizing crystal and its energy resolution was about 1 eV around the sulfur K-edge (≈2.5 KeV). Absorption spectra were obtained by collecting total electrons from the samples, which had been coated on oxidized aluminium plates. The photon energy was calibrated with the first intense peak (2469.8 eV) in the sulfur K-edge absorption spectrum of NiS powder.[12]

Sulfur 2p XPS spectra were measured with a laboratory ESCA spectrometer VG ESCALAB. Mg$K\alpha$ line (1253.6 eV) was used as an excitation source. Samples coated on scotch tape were used. Binding energies of spectra were calibrated with the Au $4f_{7/2}$ peak (83.8 eV) from gold evaporated on samples.

Results and Discussion

SO_4^{2-} and SO_3^{2-}. In the absorption spectrum for Na_2SO_4 shown in Fig. 1, there exist an intense peak (indicated as A) and two broad bands (indicated as B and C). Nefedov and Fomichev[1] also measured the sulfur K- and $L_{2,3}$-edge absorption spectra for Na_2SO_4. But the K-edge spectrum for SO_4^{2-} obtained in the present work shows a much better resolution than that by Nefedov and Fomichev.[1] Ion SO_4^{2-} belongs to the T_d point group, and there are two unoccupied valence (antibonding) orbitals, a_1^* of 3s character and t_2^* of 3p character; the intense peak A is assigned not to S 1s-a_1^* (dipole forbidden) but to S 1s-t_2^* dipole allowed transition. Following previous investigations,[1,2,5] the K- and $L_{2,3}$-shell absorption spectra can be placed on a common relative energy scale referenced to the location of respective inner-shell ionization potentials. Based on Dehmer's interpretation of the $L_{2,3}$ spectrum for ion SO_4^{2-} [5] and on the theoretical interpretation of the Si K-edge absorption spectrum for the isoelectronic molecule SiF_4 (cited in Ref. 3), the peaks B and C in the K spectrum for SO_4^{2-} shown in Fig. 1 are transitions to 3d-like e* and t_2^* orbitals, respectively. In the T_d symmetry, however, the e* orbital does not have a p component and peak B cannot be assigned only to a 1s-e* transition. We should appreciate a contribution from a 1s-t_2^* transition to peak B. Thus, it is necessary to reinterpret the origin of peak C as well as peak B.

The spectrum for Na_2SO_3 is also shown in Fig. 1. Ion SO_3^{2-} has a trigonal-pyramidal C_{3v} structure with a sulfur atom at the apex. There are two valence-type unoccupied orbitals: e* of 3pπ character and a_1^* of 3s and 3pσ character. Transitions from S 1s to these orbitals are both dipole-allowed; the most intense peak indicated as A can be assigned to a transition to the e* valence orbital and the second peak B to a transition to the a_1^* orbital. Furthermore, there are one a_1^* and two e* orbitals of 3d character. The a_1^* orbital of 3d character with a large contribution from 3p is directed toward the region where there is no ligand or no potential barrier; the transition to a_1^* becomes lower in energy and stronger in intensity. The third peak C can be assigned to the transition to the d-like a_1^* orbital. Other d-type (e*) shape resonance are observed in the higher energy region similarly to the case of SO_4^{2-}.

$S_2O_3^{2-}$ and $S_2O_5^{2-}$. In the absorption spectrum for $Na_2S_2O_3$ shown in Fig. 2, several bound-state transitions are observed. Ion $S_2O_3^{2-}$, belonging to the C_{3v} point group, is considered as SO_3^{2-} coordinated with one more sulfur atom. There are inequivalent sulfur atoms (central and terminal); the terminal sulfur atom is negative (formal oxidation number −2) and the central sulfur atom highly positive (formal oxidation number +6). This explains well the S 2p XPS spectrum

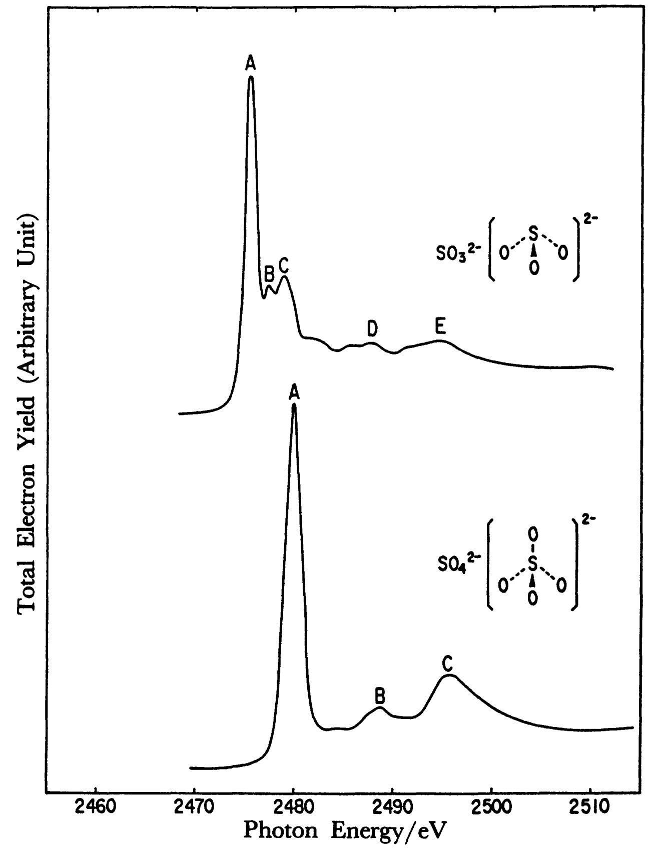

Fig. 1. Sulfur K-edge absorption spectra of Na_2SO_4 and Na_2SO_3.

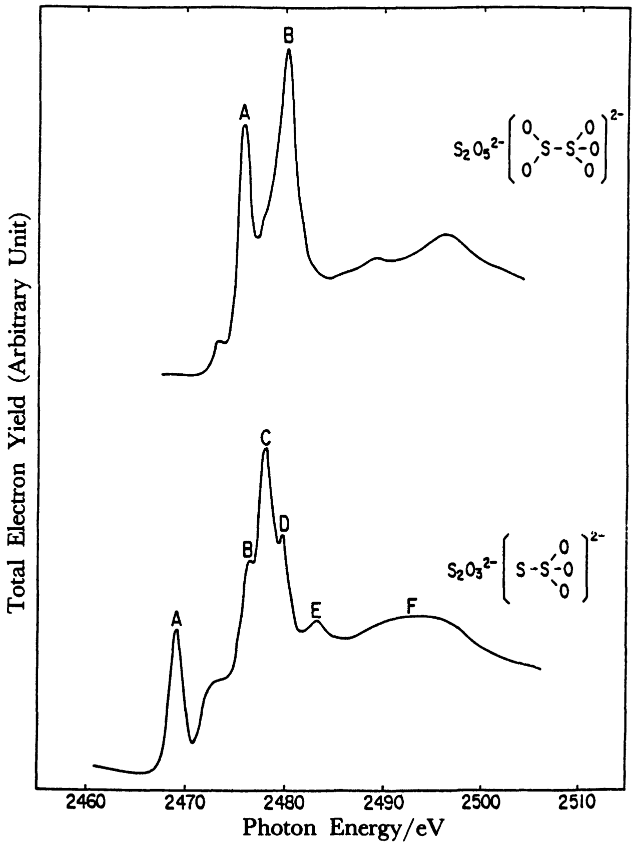

Fig. 2. Sulfur K-edge absorption spectra of $Na_2S_2O_3$ and $Na_2S_2O_5$.

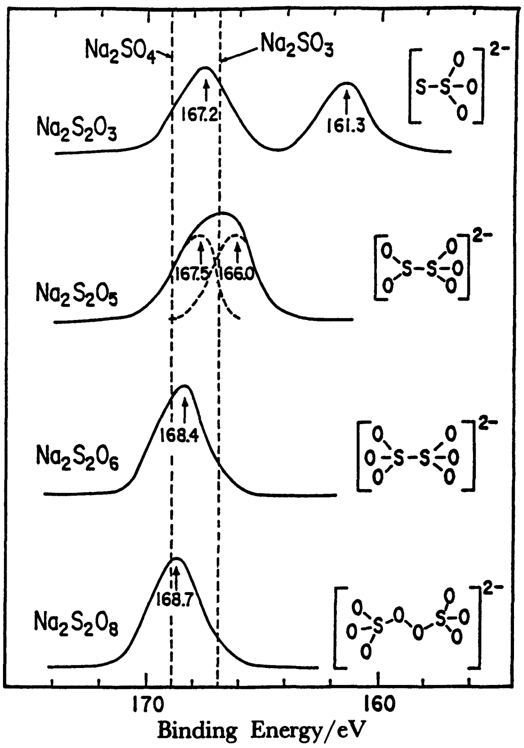

Fig. 3. Sulfur 2p XPS spectra of Na_2SO_4, Na_2SO_3, $Na_2S_2O_3$, and $Na_2S_2O_x$ (x=5—8).

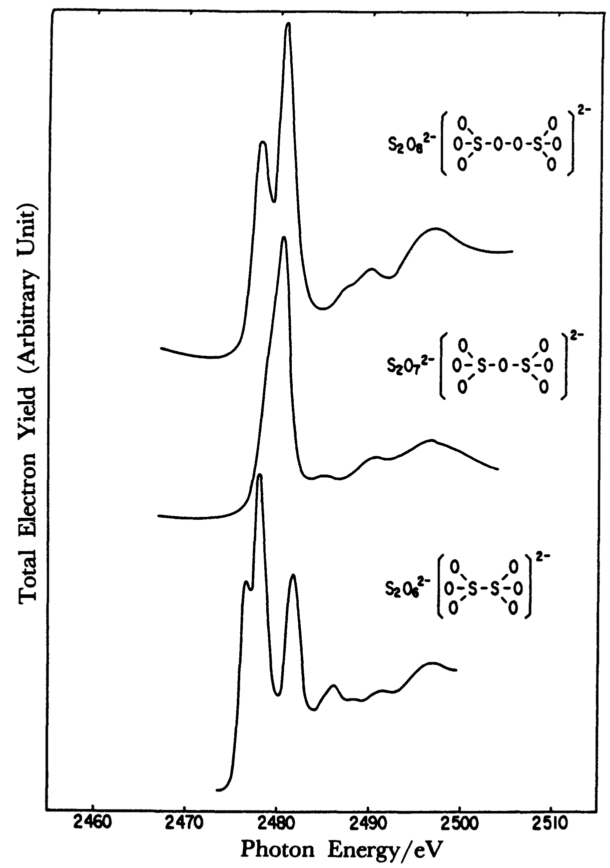

Fig. 4. Sulfur K-edge absorption spectra of $Na_2S_2O_6$, $Na_2S_2O_7$, and $Na_2S_2O_8$.

shown in Fig. 3, where the lower energy peak at 161.3 eV corresponds to the terminal S 2p peak and the peak at 167.2 eV to the central S 2p. Siegbahn et al.[13] reported the S 1s XPS spectrum for $Na_2S_2O_3$, where the difference between the binding energies of the two sulfur atoms is 7.0 eV, larger than the S 2p chemical shift (5.9 eV). The energy difference between peaks A and B in the S K-edge absorption spectrum is 7.2 eV as shown in Fig. 2; therefore, peaks A and B correspond to the transitions to the same lowest unoccupied orbital from the terminal and the central S 1s orbitals, respectively. Based on a simple molecular orbital calculation, there are three antibonding orbitals, $13a_1^*$ (terminal $3p\sigma$ and central $3p\sigma$), $9e^*$ (central $3p\pi$), and $14a_1^*$ (central 3s and $3p\sigma$); the peaks A and B are associated with the transitions to the $13a_1^*$ orbital. The broad band at about 2475 eV between A and B is considered as an onset of the terminal S 1s ionization. It should be noted that the spectrum of the terminal S K-edge shows no shape resonances because the terminal sulfur atom is not affected by the potential barrier. Peaks C and D are assigned to the transitions from central S 1s to $9e^*$ and $14a_1^*$, respectively. They may correspond to the peaks A and B observed in the spectrum for Na_2SO_3 (Fig. 1); the energy separation of C and D for $S_2O_3^{2-}$ is the same as that of A and B for SO_3^{2-}. But C and D for $S_2O_3^{2-}$ shift to the higher energy by about 2.5 eV than A and B for SO_3^{2-}, probably due to the electrostatic effect by the terminal sulfur. Peak E observed for $S_2O_3^{2-}$ is attributed to a d-type shape resonance, which may correspond to peak C for SO_3^{2-}; it is noted that the resonance E of $S_2O_3^{2-}$ is weaker in intensity and higher in energy than the resonance C of SO_3^{2-}, probably due to the chemical bonding with the negative sulfur atom. These results indicate that the peak position and intensity of the d-type shape resonances are very sensitive to the surroundings of the X-ray absorbing atom.

The S K-edge spectrum for $Na_2S_2O_5$ is also shown in Fig. 2. In the XPS spectrum shown in Fig. 3, a broad 2p band is observed. This band has two components associated with $-SO_2$ and $-SO_3$ as indicated by the broken lines, as was previously investigated by Siegbahn et al.[13] In the S K-edge spectrum, the two intense peaks A and B correspond to transitions associated with $-SO_2$ species and $-SO_3$ species, respectively. The energy separation between peaks A and B is 4.4 eV and is larger than the S 1s chemical shift, ≈2 eV, which is estimated from the formal oxidation numbers of $-S(III)O_2$ and $-S(V)O_3$.[13] These two peaks may be attributed to transitions to different final orbitals.

$S_2O_6^{2-}$, $S_2O_7^{2-}$, and $S_2O_8^{2-}$. The absorption spectra of S K-edge of $Na_2S_2O_6$, $Na_2S_2O_7$ and $Na_2S_2O_8$ are shown in Fig. 4. Ions $S_2O_x^{2-}$ (x=6—8) have equivalent sulfur atoms.

The chemical environment of the sulfur atoms in $S_2O_6^{2-}$ is similar to that of the central sulfur atom in

Table 1. Assignments of the Absorption Spectra of S K-Edge of Na_2SO_4, Na_2SO_3, and $Na_2S_2O_3$

SO_4^{2-} energy/eV		Transition
2479.9	A	S 1s→t_2*
2488.7	B	d-type shape resonance
2495.6	C	d-type shape resonance

SO_3^{2-} energy/eV		Transition
2475.5	A	S 1s→e*
2477.5	B	→a_1*
2478.9	C	d-type shape resonance
2487.6	D	d-type shape resonance
2494.6	E	d-type shape resonance

$S_2O_3^{2-}$ energy/eV		Transition
2469.2	A	Terminal S 1s→a_1* (Terminal, central S 3pσ)
2476.4	B	Central S 1s→a_1* (Terminal, central S 3pσ)
2478.0	C	→e_1* (Central S 3pπ)
2479.8	D	→a_1* (Central S 3s and 3pσ)
2483.2	E	d-type shape resonance
2493.2	F	d-type shape resonance

Table 2. Assignments of the Absorption Spectra of S K-Edge of $Na_2S_2O_5$, $Na_2S_2O_6$, $Na_2S_2O_7$, and $Na_2S_2O_8$

$S_2O_5^{2-}$ energy/eV		Transition
2475.8	A	S1s→3p (−SO_2)
2480.2	B	→3p (−SO_3)
2489.2		d-type shape resonance
2495.9		d-type shape resonance

$S_2O_6^{2-}$ energy/eV	Transition
2476.5	S 1s→3pσ (S-S)
2477.8	→3pπ (S-O)
2481.7	→3pσ (S-O)
2486.0	d-type shape resonance
2491.2	d-type shape resonance
2496.7	d-type shape resonance

$S_2O_7^{2-}$ energy/eV	Transition
2480.5	S 1s→3p
2490.5	d-type shape resonance
2496.5	d-type shape resonance

$S_2O_8^{2-}$ energy/eV	Transition
2478.2	S 1s→3pσ
2480.7	→3pπ
2486.9	d-type shape resonance
2489.8	d-type shape resonance
2496.7	d-type shape resonance

$S_2O_3^{2-}$. Therefore, in the spectrum for $S_2O_6^{2-}$ shown in Fig. 4, three intense peaks arising from 1s→3p bound-state transitions can be interpreted as corresponding to peaks B, C, and D of the spectrum for $S_2O_3^{2-}$ shown in Fig. 2.

The spectrum for $S_2O_7^{2-}$ closely resembles that for SO_4^{2-}, because each sulfur atom in $S_2O_7^{2-}$ is surrounded by four oxygen atoms. The most intense peak can be considered as a transition from S 1s to t_2*-like (local symmetry) orbital of S 3p character. However, the peak has a shoulder structure at the lower energy side, which may come from ≈10% impurity of $NaHSO_4$ or from a nearly forbidden transition to a_1*-like (local symmetry) orbital of 3s character.

It is expected that the spectrum for $S_2O_8^{2-}$ should resemble that for SO_4^{2-} because of similar chemical environment and bonding to each other. However, two intense peaks are observed, which should be 1s→3p bound-state transitions. It may be reasonable to understand that the higher energy peak is a transition to a t_2*-like (local symmetry) orbital and that the lower one is a transition to an a_1*-like (local symmetry) orbital with a large mixing with t_2* (local symmetry) due to considerable symmetry-lowering in comparison with SO_4^{2-} and $S_2O_7^{2-}$.

Conclusion

Tables 1 and 2 summarize the present results of absorption spectra of S K-edge of Na_2SO_4, Na_2SO_3, $Na_2S_2O_3$, and $Na_2S_2O_x$ (x=5—8) together with the present interpretations. In the spectra for SO_4^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$, there are remarkable differences in 1s→3p bound-state transitions and d-type shape resonances. Especially, the peak position and intensity of the d-type shape resonances are very sensitive to the surroundings of the X-ray absorbing atom. The spectra for $S_2O_x^{2-}$ (x=5—8) can be interpreted on the analogy of those for SO_4^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$.

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