

# Calculations of X-Ray Emission Spectra for Sulfur Dioxide by the DV- $X\alpha$ Method

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X-ray emission spectra of S  $K\beta$ , S  $L_{2,3}$  and O  $K\alpha$  for sulfur dioxide were calculated by the discrete variational  $X\alpha$  (DV- $X\alpha$ ) method. The absolute energies of the peaks in the theoretical spectra agree with the experimental values within an error of 3%. The relative energies and intensities of peaks in the theoretical spectra are in good agreement with the experimental values. The spectral features of the experimental spectra are assigned to the molecular orbitals. Copyright © 1999 John Wiley & Sons, Ltd.

## INTRODUCTION

The x-ray emission spectra which originate from electronic transition between a valence level and an inner-shell level have been widely used for determining electronic structures of substances.<sup>1</sup> An important characteristic arises from the dipole selection rule on the x-ray emission. On the other hand, there is a problem that not all the features of the x-ray emission spectra correspond to the valence levels because non-diagram lines or satellites sometimes appear in the spectra. Therefore, theoretical investigations are necessary for reliable interpretations of the measured spectra and for a detailed understanding of the electronic structures of substances.

Theoretical investigations of the x-ray emission spectra have been carried out for a variety of free molecules.<sup>2–4</sup> Among them, sulfur dioxide is one of the best experimentally characterized.<sup>5</sup> In order to evaluate the participation of the sulfur 3d orbital in chemical bonds and electronic properties of sulfur dioxide, many theoretical studies<sup>6–15</sup> and experimental analyses<sup>1,16–19</sup> have been performed. However, there are only two experimental papers on the x-ray emission spectra<sup>1,16</sup> in the literature and theoretical calculations of the x-ray emission spectra are also scarce.<sup>2,3</sup> Kondratenkio *et al.*<sup>2</sup> calculated fine structures of the x-ray emission spectra for the  $SO_2$  molecule, using the *ab initio* Hartree–Fock method. Higher energy portions of the spectra were adequately obtained in their calculations, but systematic discrepancies between the theoretical and experimental results were observed for the lower energy part of the

spectra. Timonova *et al.*<sup>3</sup> calculated the S  $K\beta$  and O  $K\alpha$  x-ray emission spectra for  $SO_2$  by the configuration interaction method. The spectra obtained did not reproduce the experimental spectra well.

The discrete variational (DV)  $X\alpha$  molecular orbital (MO) method<sup>20–23</sup> has been found useful for analyzing x-ray spectra. Adachi and Taniguchi<sup>20</sup> performed calculations of the  $L_{2,3}$  and  $K\beta$  x-ray emission spectra for  $XO_4^{n-}$ ,  $XO_3^{n-}$  and  $XO_2^{n-}$  ( $X = P, S$  and  $Cl$ ) anion complexes. The calculated peak energies and intensities were in excellent agreement with the experimental values. Mukoyama *et al.*<sup>21</sup> calculated chemical effects on  $I(K\beta):I(K\alpha)$  x-ray intensity ratios in Cr and Mn compounds by the DV- $X\alpha$  method. The results were in qualitative agreement with the experimental values.

In this work we employed the DV- $X\alpha$  method to obtain the x-ray emission spectra of  $SO_2$ . According to the dipole selection rule, S  $K\beta$ , S  $L_{2,3}$  and O  $K\alpha$  x-ray emission spectra are necessary to clarify the structure of the valence levels of  $SO_2$ . The K emission reflects p components in the valence levels and the  $L_{2,3}$  emission corresponds to s or d components. The theoretical S  $K\beta$ , S  $L_{2,3}$  and O  $K\alpha$  x-ray emission spectra were compared with the experimental spectra<sup>1,16</sup> with respect to both energy and intensity. The features in the experimental spectra are assigned to the molecular orbitals of the valence levels.

## COMPUTATIONAL METHOD

The details of the computational code SCAT used in the present work by the DV- $X\alpha$  MO method were described by Adachi *et al.*<sup>24</sup> Hartree–Fock–Slater atomic calculations were performed to generate numerical atomic wavefunctions as the basis functions. The

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matrix elements in the secular equation were calculated in the DV method<sup>25</sup> and this equation was then solved to obtain energies and molecular orbitals.

The transition energy for the x-ray emission can be obtained using the relationship

$$\Delta E = E(V^0C^1) - E(V^1C^0) \quad (1)$$

where  $E(V^1C^0)$  is the total energy of a molecule in the initial state with a hole in the inner-shell level  $C$  and  $E(V^0C^1)$  is the total energy of the molecule after the electron transition from the valence level  $V$  to the inner-shell  $C$ .

In the  $X\alpha$  method, it is well known that the transition energy of the x-ray emission can be calculated more precisely with Slater's transition state method,<sup>20</sup> where half an electron was removed from the initial level of the transition and added into the final level. Using this method, the transition energy in Eqn (1) is well approximated as

$$\Delta E = \varepsilon_v(V^{0.5}C^{0.5}) - \varepsilon_c(V^{0.5}C^{0.5}) \quad (2)$$

where  $\varepsilon_v$  and  $\varepsilon_c$  are the energy eigenvalues of the valence level  $V$  and the inner-shell  $C$ , respectively.

In the present calculations, in order to improve the precision of the calculation, the relative energies between the transition energies from the valence levels  $V_1$  and  $V_2$  were calculated:

$$\begin{aligned} \Delta E_2 - \Delta E_1 &= [E(V_1^1V_2^0C^1) - E(V_1^1V_2^1C^0)] \\ &\quad - [E(V_1^0V_2^1C^1) - E(V_1^1V_2^1C^0)] \\ &= E(V_1^1V_2^0C^1) - E(V_1^0V_2^1C^1) \end{aligned} \quad (3)$$

When the transition state method is used, Eqn (3) becomes

$$\Delta E_2 - \Delta E_1 = \varepsilon_{v_2}(V_1^{0.5}V_2^{0.5}C^1) - \varepsilon_{v_1}(V_1^{0.5}V_2^{0.5}C^1) \quad (4)$$

The x-ray emission intensity in the dipole approximation is written as<sup>26</sup>

$$I_n \propto E_n^3 D_n^2 \quad (5)$$

where  $E_n$  is the transition energy of an electron from the  $n$ th valence level and  $D_n$  is the dipole matrix element:

$$D_n = \langle \psi_c | \mathbf{r} | \psi_n \rangle \quad (6)$$

where  $\psi_c$  is a core level wavefunction,  $\mathbf{r}$  the position vector and  $\psi_n$  the wavefunction of the  $n$ th valence level.  $D_n$  was evaluated with the software SXS,<sup>20</sup> where the integration in Eqn (6) was carried out by the DV integration scheme,<sup>25</sup> i.e. evaluated as the weighted sums of integrand values at sampling points. To improve the precision of integration by one digit, the sampling points were scattered suitably for the spatial distribution of the core wavefunction in question. The wavefunctions in the ground state were used in the present work. To generate the theoretical spectra, a Lorentzian curve was placed at each eigenenergy. Its height was proportional to the intensity and its width was taken to correspond to the experimental value.

Atomic orbitals of oxygen 1s–2p and sulfur 1s–3d were used as the basis functions. The internuclear distance between the sulfur and oxygen atoms was taken to be 1.43 Å and the O–S–O angle was taken to be

119.5°.<sup>27</sup> The value  $\alpha$  was chosen to be 0.7 in all the calculations.<sup>24</sup>

## RESULTS AND DISCUSSION

For analyzing the S  $K\beta$ , S  $L_{2,3}$  and O  $K\alpha$  x-ray emission spectra of SO<sub>2</sub>, the valence level structure was first investigated. Atomic orbital components for the valence levels calculated for the ground state are shown in Table 1. It can be seen that the SO<sub>2</sub> molecule has nine occupied valence levels. The lower lying 5a<sub>1</sub>, 3b<sub>2</sub> and 6a<sub>1</sub> levels include mainly the oxygen 2s and sulfur 3s, 3p components, while the levels in the higher valence region, that is, 7a<sub>1</sub>, 2b<sub>1</sub>, 4b<sub>2</sub>, 1a<sub>2</sub>, 5b<sub>2</sub> and 8a<sub>1</sub>, are constructed largely from the oxygen 2p and the sulfur 3p components. The sulfur 3d component is considerably involved in all the valence levels.

Before studying the theoretical spectra, the peak intensity is examined on the basis of the dipole selection rule and the atomic orbital components. The peaks in the S  $K\beta$  spectrum are attributed to a transition between the sulfur 1s level and the valence levels with the sulfur 3p component. Therefore, the transitions from 2b<sub>1</sub>, 7a<sub>1</sub> and 3b<sub>2</sub> have large transition probabilities in the S  $K\beta$  spectrum. Likewise, the transitions from all the valence levels in Table 1 have probabilities in the O  $K\alpha$  spectrum. For the S  $L_{2,3}$  spectrum, intense peaks are expected for the transition from 8a<sub>1</sub>, 6a<sub>1</sub> and 5a<sub>1</sub>, which have the large sulfur 3s component, in addition to those from 8a<sub>1</sub> and 1a<sub>2</sub> with the sulfur 3d component.

The calculated S  $K\beta$ , O  $K\alpha$  and S  $L_{2,3}$  x-ray emission spectra are shown in Figs 1, 2 and 3, respectively, and compared with the corresponding experimental spectra.<sup>1,16</sup> The x-ray energies were calculated using Eqn (2) by the transition state method. The peaks in these spectra are assigned to the valence MOs indicated in the figures. In Fig. 1, good agreement between the theoretical and experimental spectra is obtained for S  $K\beta$ . This agreement provides a substantial assignment of the experimental S  $K\beta$  x-ray emission spectrum. It is found that the features F, K, L, N and P in the spectrum arise from the electron transition from the 5a<sub>1</sub>, 3b<sub>2</sub>, 6a<sub>1</sub>, (7a<sub>1</sub>, 2b<sub>1</sub>, 4b<sub>2</sub>) and 8a<sub>1</sub> valence levels to the sulfur 1s orbital, respectively, where the MOs in par-

Table 1. Orbital components (%) of valence levels for sulfur dioxide

Level	Energy (eV)	S			O	
		3s	3p	3d	2s	2p
8a <sub>1</sub>	-5.96	7	12	12	1	68
5b <sub>2</sub>	-7.09		1	6	1	92
1a <sub>2</sub>	-7.19			15		85
4b <sub>2</sub>	-10.14		14	3	18	65
2b <sub>1</sub>	-10.75		52	1		47
7a <sub>1</sub>	-10.95		31	6	11	53
6a <sub>1</sub>	-15.32	34	17	2	37	11
3b <sub>2</sub>	-24.76		23	3	68	6
5a <sub>1</sub>	-28.95	44	4	2	40	11

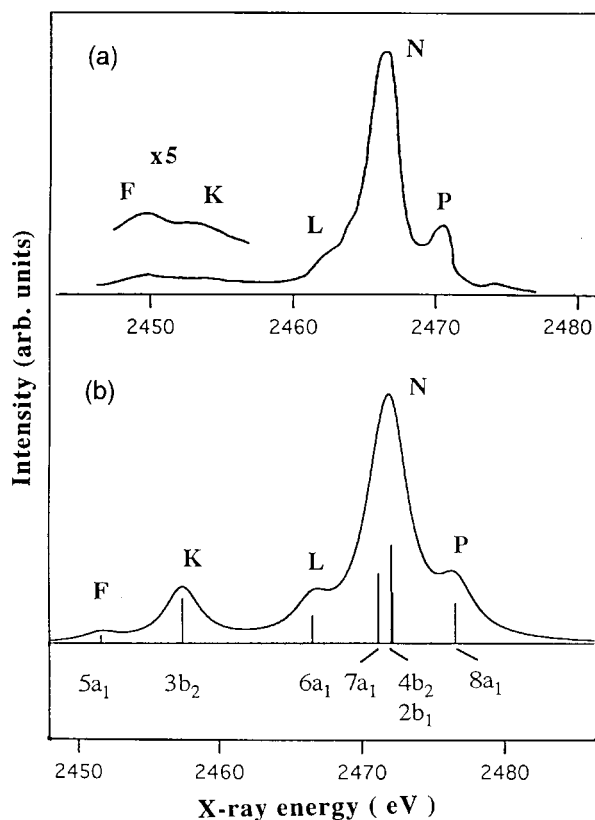


Figure 1. S  $K\beta$  x-ray emission spectra for sulfur dioxide. (a) Experimental<sup>16</sup> and (b) theoretical spectra.

entheses contribute to an identical peak. The highest intensities come from the  $7a_1$ ,  $2b_1$  and  $4b_2$  MOs, which contain the larger sulfur 3p component.

For the O  $K\alpha$  x-ray emission spectra in Fig. 2, it is clear that peak D corresponds to the electronic tran-

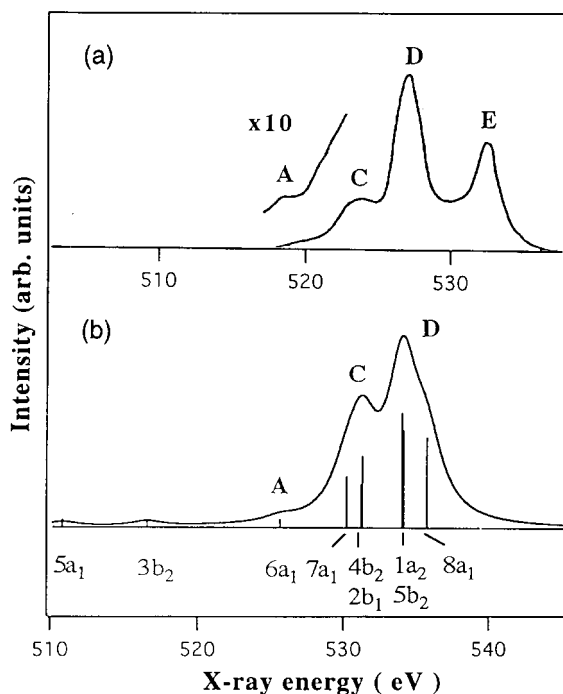


Figure 2. O  $K\alpha$  x-ray emission spectra for sulfur dioxide. (a) Experimental<sup>16</sup> and (b) theoretical spectra.

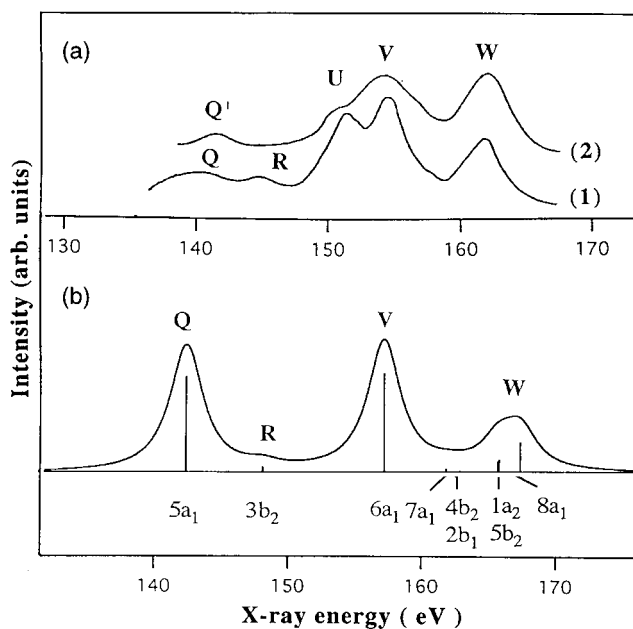


Figure 3. S L x-ray emission spectra for sulfur dioxide. (a) Experimental (1) 1 and (2) 16 and (b) theoretical spectra.

sition from  $8a_1$ ,  $1a_2$  and  $5b_2$  levels to the oxygen 1s level and peaks C and A arise from the transition from the ( $4b_2$ ,  $2b_1$ ,  $7a_1$ ) and  $6a_1$  levels to the oxygen 1s level, respectively. The theoretical relative energies between peaks A, C and D are in agreement with the experimental values. Peak E is not due to an one-electron transition. It was mentioned in the original paper<sup>28</sup> that anomalous scattering from the KAP crystal generated the satellite peak at 532 eV.<sup>28</sup>

In Fig. 3, two experimental S  $L_{2,3}$  spectra labelled (1) and (2) are compared with the theoretical S L spectrum of  $SO_2$ . The experimental spectra differ from each other in several respects. On the lower energy side, spectrum (1) has two peaks (Q and R), whereas spectrum (2) has a single peak (Q'). On the high-energy side, spectrum (2) has two peaks (V and W) with similar heights, whereas the corresponding peaks in spectrum (1) have a different intensity ratio. From the results of the present calculations, peak W is ascribed to the electron transition from  $8a_1$ ,  $1a_2$  and  $5b_2$  levels, which contain the sulfur 3d components. Peaks V and Q arise from the electron transition from  $6a_1$  and  $5a_1$ , which contain mainly the sulfur 3s component. This proves that the 3s atomic orbital in the valence levels of the  $SO_2$  molecule plays a major role in the spectrum.

For peak Q, the intensity in the theoretical spectrum looks much higher than that in the experimental spectra. Taniguchi and Henke<sup>1</sup> examined the intensity of the S  $L_{2,3}$  emission spectrum as shown in Fig. 4. It is clear that peak Q has a high intensity, although peak Q is very broad. The present theoretical spectrum bears a resemblance to the experimental spectrum (1) because all of the spectral peaks appeared in the theoretical spectrum except peak U, which is regarded as a radiative Auger transition.<sup>29</sup>

Table 2 makes a comparison of the calculated and experimental peak energies in the S  $K\beta$ , S  $L_{2,3}$  and O  $K\alpha$  spectra for  $SO_2$ . The theoretical energies were evaluated by the transition state method. In addition,

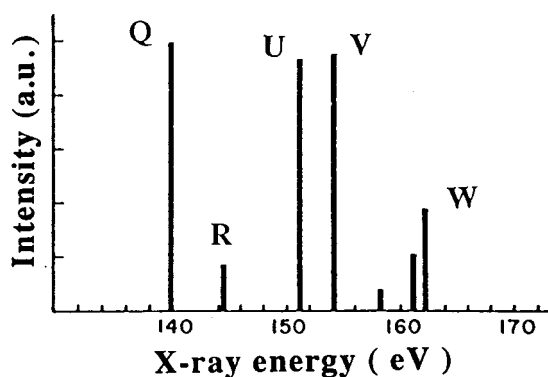


Figure 4. Experimental intensity for SO<sub>2</sub> taken from Taniguchi and Henke.<sup>1</sup>

we also estimated the peak energies using the level energies in the ground state for comparison. The discrepancy between the peak energies in the ground state and in the experimental spectra is large, not less than 7 eV for S L<sub>2,3</sub>, 23 eV for O K $\alpha$  and 78 eV for S K $\beta$ . On the other hand, when the transition state method is used for

the emission energy, the differences from the experimental values are < 7 eV for sulfur x-rays and < 8 eV for oxygen.

## CONCLUSION

We have performed molecular orbital calculations for SO<sub>2</sub> using the discrete variational X $\alpha$  method. The theoretical spectra of the S K $\beta$ , S L<sub>2,3</sub> and O K $\alpha$  x-ray emission have been obtained. In the present calculations, we obtained the relative x-ray emission energies based on the transition state method. The relative energies are in good agreement with the experimental values. The absolute peak energies agree with the experimental values within an error of 3%. The theoretical peak intensities are also in good agreement with the experimental values. The peaks in the S K $\beta$ , S L<sub>2,3</sub> and O K $\alpha$  x-ray emission spectra have been assigned to the valence molecular orbitals.

Table 2. Peak energies (eV) of S K $\beta$ , S L and O K $\alpha$  spectra for SO<sub>2</sub>

Level	S K $\beta$		S L		O K $\alpha$	
	Theoretical	Experimental <sup>a</sup>	Theoretical	Experimental <sup>a</sup>	Theoretical	Experimental <sup>a</sup>
8a <sub>1</sub>	2476.4	2470.7	167.3	161.6	535.8	527.1
1a <sub>2</sub>	2474.8	2466.4	165.7			
5b <sub>2</sub>	2474.7		165.6			
4b <sub>2</sub>	2472.0		162.9			
2b <sub>1</sub>	2471.9	162.8	155.4	155.4	531.4	523.4
7a <sub>1</sub>	2471.0	161.8			531.3	
6a <sub>1</sub>	2466.4	2462.2	157.2	155.4	525.7	518.6
3b <sub>2</sub>	2457.3	2453.0	148.1	144.6	516.6	
5a <sub>1</sub>	2451.5	2449.0	142.4	140.0	510.9	

<sup>a</sup> Read from the figures of the spectra.<sup>1,16</sup>

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