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Interatomic contributions to molecular x-ray emission rates

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The K x-ray emission rates in molecules have been calculated by the use of the discrete variational $X\alpha$ (DV-$X\alpha$) method with and without interatomic transitions. The comparison of the obtained results is used to estimate the relative importance of contributions from interatomic transitions. For the CO molecule, it is found that the C K x-ray emission rate increases by about 20% when the interatomic contributions are included. However, the interatomic transitions play a minor role for Cr and Mn K x-ray emission in tetrahedral and octahedral compounds.

I. INTRODUCTION

The chemical effect on x-ray emission spectroscopy has been an important subject since early days of x-ray spectroscopy and extensive studies on transition energies and profiles of x-ray lines have been reported.[1] On the other hand, quantitative investigations for x-ray emission-rates and relative intensities of lines are rather scarce. With recent advances in high-energy-resolution x-ray spectrometers, experimental data for molecular x-ray spectra and relative intensities of x-ray lines in molecules have been obtained. Theoretical calculations of molecular x-ray emission rates become possible by the use of modern high-speed large-memory computers.

In the theoretical calculations of molecular x-ray emission spectra, it is usual to neglect the contributions from interatomic transitions, sometimes called cross over transitions, and to use the single-center approximation.[2] Urch[3,4] estimated the chemical effect on the x-ray emission spectra by the use of a simple molecular-orbital (MO) approach and pointed out that the crossover terms can be ignored for M K x-ray emission rates in tetrahedral MX_4 or octahedral MX_6 molecules. On the other hand, Adachi and Taniguchi[5] calculated $L_{2,3}$ x-ray intensities for SO_4^{2-} by the use of the discrete variational (DV) $X\alpha$ method and found that neglect of contributions from the crossover transitions causes errors in predicting the experimental values for Li_2SO_4.

Using the Slater-type linear combination of atomic orbitals (LCAO) functions and MO coefficients from the complete neglect of differential overlap (CNDO/2) theory, Larkins and Rowlands[6] showed that there are significant interatomic contributions to the C K x-ray transition rates in the CO, HCN, and CO_2 molecules. They also pointed out that the relative intensity ratios are less sensitive for inclusion of the crossover transitions than the absolute transition rates.

Rowlands and Larkins[7] made *ab initio* MO calculations for the absolute transition rates of x-ray emission in CO and examined the importance of the factors influencing the molecular x-ray emission spectra, such as choice of basis set, choice of length and velocity forms, electronic relaxation, and interatomic contributions. According to their results, the contribution of the interatomic terms is more significant to the transition rates for the C K x rays than are those for the O K x rays. In the

TABLE I. Molecular-orbital energies (eV) and orbital populations (%) for CO.

Level	Occupation number	E (eV)	C 1s	 2s	 2p	O 1s	 2s	 2p
6σ	0	17.11		21	50		8	21
2π	0	-0.70			71			29
5σ	2	-8.36		45	39		1	15
1π	4	-10.27			29			71
4σ	2	-12.46		23			23	54
3σ	2	-27.50		12	10		68	10
2σ	2	-269.92	100					
1σ	2	-509.90				100		

TABLE II. K x-ray transition energies E (eV) and emission rates (arbitrary units) for carbon and oxygen atoms in CO.

	C				O			
Level	E	($\mathcal{R}_{\mathrm{I}}$)[a]	($\mathcal{R}_{\mathrm{II}}$)[b]	Δ[c]	E	$\mathcal{R}_{\mathrm{I}}$	$\mathcal{R}_{\mathrm{II}}$	Δ
3σ	265.4	3.218	8.157	153.5	512.2	21.44	25.56	19.2
4σ	281.8	0.4842	0.8336	70.4	528.9	132.9	145.0	9.1
1π	284.1	33.04	40.86	23.6	530.9	390.8	394.5	3.3
5σ	286.8	31.83	38.58	21.2	533.3	43.47	43.14	-0.8
Total		68.57	88.43	29.0		588.6	608.2	3.3

[a] Without contributions from interatomic transitions.

[b] With contributions from interatomic transitions.

[c] $\Delta=[(\mathcal{R}_{\mathrm{II}}-\mathcal{R}_{\mathrm{I}})/\mathcal{R}_{\mathrm{I}}]\times 100$.

C K spectrum, the single-center contribution to the total transition probability is only 65% in the length form, while it is 91% in the O K spectrum. Phillips and Larkins extended their calculations to other simple molecules: HCN and CO_2,[8] and HCl.[9]

Recently we have calculated the chemical effect on the $I(K\beta)$:$I(K\alpha)$ x-ray intensity ratios in Cr and Mn compounds by use of the DV-$X\alpha$ MO method.[10,11] The x-ray emission rates were evaluated in the dipole approximation using the MO wave functions. In this model the multicenter integration in the transition matrix element was performed by the DV integration method and the contributions from the interatomic transitions were included. The calculated results are qualitatively in agreement with the measured values.

According to the prediction of Urch,[4] the interatomic contributions in K x ray emission rates for molecules with tetrahedral (T_d) and octahedral (O_h) point-group symmetry are small. However, no numerical estimation for the importance of interatomic transitions in these molecules has been reported. In the present work we present the results of the DV-$X\alpha$ calculations for molecular x-ray emission rates with and without interatomic transitions. First, we calculate the C and O K x-ray emission rates in the CO molecule and compare the relative intensities with those of *ab initio* calculations as well as the experimental data. Then the contributions of interatomic transitions to relative $I(K\beta)$ x-ray satellite intensities and $I(K\beta)$:$I(K\alpha)$ ratios are estimated for the T_d and O_h chemical compounds of Cr and Mn.

II. COMPUTATIONAL METHOD

The MO calculations were made with the DV-$X\alpha$ method, which has been described in detail elsewhere.[12] The Hartree-Fock-Slater calculations are made for each atom and the atomic wave functions obtained in the numerical form are used as the basis functions for the MO calculations. The wave function for the λth MO is expressed as

$$\psi_\lambda=\sum_i C_{i\lambda}\varphi_i \ , \tag{1}$$

where φ_i is the numerical basis function and $C_{i\lambda}$ is the eigenvector determined variationally from the MO calculation.

The K x-ray emission probability in the dipole approximation can be written as[13]

$$I_\lambda \propto E_\lambda^3 D_\lambda^2 \ . \tag{2}$$

Here E_λ is the transition energy of x rays between the K shell and the λth MO and D_λ is the dipole matrix element

$$D_\lambda=\sum_i C_{i\lambda}\langle \varphi_K|\mathbf{r}|\varphi_i\rangle \ , \tag{3}$$

where φ_K is the K-shell wave function and $\mathbf{r}$ is the position vector. In the present model the integration in Eq. (3) is carried out by the DV integration method,[14] i.e., evaluated as the weighted sum of the integrand values at

TABLE III. Comparison of relative K x-ray intensity ratios for carbon and oxygen atoms in CO.

	C				O			
Level	Present	FR[a]	RX[b]	Expt.[c]	Present	FR	RX	Expt.
3σ	0.1996	0.34	0.13		0.0648	0.05	0.04	
4σ	0.0204	0.10	0.0		0.3676	0.42	0.20	0.38
1π	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
5σ	0.944	1.11	0.91	0.59	0.1093	0.11	0.06	0.28

[a] Frozen-orbital approximation (Ref. 8).

[b] Relaxed-orbital approximation (Ref. 8).

[c] Experimental results, including satellite contributions (Ref. 16).

the discrete points distributed randomly according to a certain sampling function. The validity of this integration method to calculate the x-ray emission rates has been already tested.[15]

For the calculations without the interatomic transitions, the summation over i in Eq. (3) is restricted only for the basis functions that belong to the same atom as the initial K-shell vacancy. It should be noted that when the MO wave function consists of two or more basis functions in the same atom, this approximation may be different from the frequently used single-center model

$$D_\lambda^2=\sum_j C_{j\lambda}^2 |\langle \varphi_K|\mathbf{r}|\varphi_j\rangle|^2 , \qquad (4)$$

where j denotes the atomic basis function in the same atom as φ_K.

In the CO molecule we use the 1s, 2s, and 2p atomic orbitals for C and O as the basis functions and the internuclear distance is taken to be 2.132 a.u. For Cr and Mn compounds, CrO_3 (T_d), $KMnO_4$ (T_d), $CrCl_3$ (O_h), and $MnCl_2$ (O_h) are considered. The clusters and bond lengths used for these compounds are given in Ref. 10. In all calculations Slater's statistical exchange parameter was taken to be $\alpha=0.7$.

III. RESULTS AND DISCUSSION

All the numerical computations in the present work have been performed on the FACOM-M-360AP computer in the Information Science Center of Osaka Electro-Communication University.

In Table I, MO energies and orbital populations for the CO molecule are listed. The K x-ray transition energies and emission rates for C and O atoms in the molecule are shown in Table II. The emission rates were calculated with and without the interatomic transitions and the relative change in the rates by inclusion of the interatomic transitions is also listed in the table. It is clear that the absolute emission rates increase by taking into account the interatomic contributions, except for the case of the $5\sigma \rightarrow 1\sigma$ transition. The decrease in the emission rate for this transition in the two-center calculation has also been found by Rowlands and Larkins.[7]

The increase in the emission rates with the interatomic transitions is significant for C K x rays and the single-center approximation gives only 77% of the total emission rate. On the other hand, the interatomic transitions play a less important role in O K x rays. The reason for this difference in the importance of the interatomic transitions between C and O K x-ray emission rates can be explained from the fact that, as can be seen from Table I, the orbital populations of the O atomic orbitals are larger in the 3σ, 4σ, and 1π MO's than those of the C atomic orbitals.

In Table III the present MO results of the relative K x-ray intensities for C and O atoms in the CO molecules are compared with the calculated values of Philips and Larkins[8] and with the experimental data of Ågren and Nordgren.[16] Relative intensities were expressed as the ratio to the transition rate from 1π MO. From the results of Phillips and Larkins,[8] only the values in the length form are shown in the table because they are in excellent

TABLE IV. Relative $K\beta$ x-ray satellite intensities (per $K\beta_{1,3}$ intensity) and $I(K\beta):I(K\alpha)$ ratios in Cr and Mn compounds with and without contributions from interatomic transitions.

		T_d						O_h					
		CrO_3			$KMnO_4$				$CrCl_3$			$MnCl_2$	
Level	$(\mathcal{R}_{\rm I})^{\rm a}$	$(\mathcal{R}_{\rm II})^{\rm b}$	$\Delta^{\rm c}$	$\mathcal{R}_{\rm I}$	$\mathcal{R}_{\rm II}$	Δ	Level	$\mathcal{R}_{\rm I}$	$\mathcal{R}_{\rm II}$	Δ	$\mathcal{R}_{\rm I}$	$\mathcal{R}_{\rm II}$	Δ
$4t_2$	0.016 65	0.017 26	3.7	0.031 26	0.034 27	9.6	$7t_{1u}$	0.000 887	0.000 890	0.3	0.000 343	0.000 346	0.9
$5t_2$	0.002 15	0.002 42	12.6	0.000 06	0.000 08	27.9	$8t_{1u}$	0.006 61	0.006 69	1.2	0.003 67	0.003 71	1.0
$6t_2$	0.020 40	0.021 32	4.5	0.032 19	0.033 90	5.3							
$I(K\beta):I(K\alpha)$	0.1200	0.1203	0.3	0.1237	0.1240	0.2		0.1162	0.1162	0	0.1156	0.1156	0

[a] Without contributions from interatomic transitions.

[b] With contributions from interatomic transitions.

[c] $\Delta=[(\mathcal{R}_{\rm II}-\mathcal{R}_{\rm I})/\mathcal{R}_{\rm I}]\times 100$.

agreement with those in the velocity form. They calculated the emission rates in two approaches, the frozen-orbital approach and the relaxed-orbital approach. In the former, the same atomic potential is used both for the initial and final states. In the latter approach, the atomic configuration in the initial state is different from that of the final state, and the exchange and overlap terms due to nonorthogonality of the wave functions are taken into consideration. The present results, based on the frozen-orbital approximation, lie between two values of Phillips and Larkins[8] and are in qualitative agreement with the experimental data of Ågren and Nordgren.[16] However, it should be noted that their experimental values include the contributions from the satellite lines.

In Table IV, the relative intensities of $I(K\beta)$ x-ray satellite lines and $I(K\beta)$:$I(K\alpha)$ intensity ratios for Cr and Mn compounds in T_d and O_h symmetry are shown with and without the interatomic transitions. The relative $I(K\beta)$ satellite intensities are expressed as the ratio to the intensity of the $I(K\beta_{1,3})$ line, which corresponds to the transition from the $3t_2$ orbital in the T_d symmetry and that from the $6t_{1u}$ orbital in the O_h symmetry. The contributions of the interatomic transitions to the intensity of the $I(K\alpha)$ and $I(K\beta_{1,3})$ lines are negligible and their intensities are omitted from the table. The values with interatomic transitions are same as in the previous work.[10]

It is clear from the table for the chemical compounds with the O_h symmetry the interatomic contributions are small. In the T_d symmetry, the contributions from the interatomic transitions are large for the transition from the $5t_2$ orbital, but this line is very weak and could not be observed in our experimental spectra.[10] The transitions from the $4t_2$ orbital [$I(K\beta'')$ line] and from the $6t_2$ orbital [$I(K\beta_{2,5})$ line] increase by 3–10% when the interatomic transitions are taken into account. However, the influence of the interatomic transitions in the $I(K\beta)$:$I(K\alpha)$ ratio is less than 1% because the intensity of the $I(K\beta_{1,3})$ line does not change.

IV. CONCLUSION

We have studied the interatomic contributions to the K x-ray emission rates in molecules using the DV-$X\alpha$ method. The comparison of the emission rates with and without the interatomic transitions has been made for the CO molecule and for the Cr and Mn compounds in the T_d and O_h symmetry. In the case of the CO molecule, it is found that the C K x-ray intensity increases by about 20% by including the interatomic contributions, while the increase in the O K x-ray intensity is a few percent. This fact indicates that in this molecule the interatomic transitions are important in calculations of K x-ray emission rates. These results are in agreement with the *ab initio* Hartree-Fock calculations of Larkins *et al.*[7,8]

For the Cr and Mn compounds in the O_h symmetry, the interatomic contributions to the K x-ray intensity are small. On the other hand, in the T_d symmetry the $I(K\beta'')$ and $I(K\beta_{2,5})$ satellite intensities increase by 3~10% with inclusion of the interatomic transitions. However, the effect on the $I(K\beta)$:$I(K\alpha)$ intensity ratio is small because of negligibly small change in the $I(K\beta_{1,3})$ line intensity. This fact indicates that in the calculations of the $I(K\beta)$:$I(K\alpha)$ intensity ratio for the Cr and Mn compounds in the T_d and O_h symmetry, the single-center approximation gives reasonably accurate results. On the other hand, when we are interested in the intensity of each satellite line, the interatomic contributions play an important role.

As has been shown in previous work,[10] the $I(K\beta)$:$I(K\alpha)$ ratios for these molecules are in qualitative agreement with the experimental data, but quantitatively there is a discrepancy mainly due to neglect of the exchange and overlap effects. It is hoped that more elaborate calculations with both effects would be performed to investigate the importance of interatomic contributions for these molecules, though such calculations become more complicated with increasing the number of atoms and electrons in the molecules.

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