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Journal

Inorganic Chemistry, 63(34)

ISSN

0020-1669

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et al.

Publication Date

2024-08-26

DOI

10.1021/acs.inorgchem.4c01666

Peer reviewed

Analyzing the Intensities of K-Edge Transitions in X₂ Molecules (X = F, Cl, Br) for Use in Ligand K-Edge X-ray Absorption Spectroscopy

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Cite This: *Inorg. Chem.* 2024, 63, 15557–15562



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ABSTRACT: Ligand K-edge X-ray absorption spectroscopy (XAS) is regularly used to determine the ligand contribution to metal–ligand bonds. For quantitative studies, the pre-edge transition intensities must be referenced to an intensity standard, and pre-edge intensities obtained from different ligand atoms cannot be compared without standardization due to different cross sections at each absorption edge. In this work, the intensities of the 1s → σ* transitions in F₂, Cl₂, and Br₂ are analyzed for their use as references for ligand K-edge XAS. We show that the intensities of these transitions are equal to the intensities of the 1s → np transitions in the unbound halogens. This finding is supported by a comparison between the normalized experimental intensities for the molecules and the calculated oscillator strengths for the atoms. These results highlight the potential for these molecules to be used as intensity standards in F, Cl, and Br K-edge XAS experiments.

The ligand orbital contribution to metal–ligand bonds is frequently evaluated by performing X-ray absorption spectroscopy (XAS) at the K-edge for ligand donor atoms: a technique that is collectively referred to as “ligand K-edge XAS”. This technique probes transitions of localized ligand 1s electrons to primarily metal-based molecular orbitals (MOs). The transition intensity is weighted by the amount of ligand *p*-orbital character (λ^2) in the acceptor MO (Ψ^*) and by the intrinsic intensity of a ligand 1s → *np* transition ($I_{1s \rightarrow np}$):^{1,2}

$$I_{1s \rightarrow \Psi^*} = \frac{h}{N} \lambda^2 I_{1s \rightarrow np} \quad (1)$$

where *h* is the number of holes in the acceptor MO, *N* is the number of absorbing atoms, and *n* is the principal quantum number of the valence *p*-orbitals for a given ligand. By combining ligand K-edge XAS measurements with electronic structure calculations, Solomon and co-workers provided the first demonstrations of this approach to probe orbital mixing in transition metal complexes with M–Cl and M–S bonds.^{2–7} Further studies have advanced this methodology for M–Cl^{8–14} and M–S^{15–21} bonds, and expanded the range of ligand chemistries to include systems incorporating M–P,^{13,14,19,22–30} M–O,^{31–37} M–N,^{19,38–41} and M–C bonds.^{42–47}

To interrogate bonding trends, previous ligand K-edge XAS studies varied the metal while holding the ligand constant. The opposite approach (varying the ligand) requires probing multiple ligand K-edges, which can pose technical challenges related to differences in sample preparation, X-ray spectrometer characteristics, and data reduction methods. In addition, intensities from different edges cannot be compared directly unless the value of $I_{1s \rightarrow np}$ is quantified at each edge. One approach to determine $I_{1s \rightarrow np}$ is to measure the ligand K-edge spectra of a compound with known λ^2 and use eq 1 to solve for $I_{1s \rightarrow np}$. For $D_{2d}CuCl_4^{2-}$, λ^2 was determined using electron paramagnetic resonance (EPR) spectroscopy and later refined

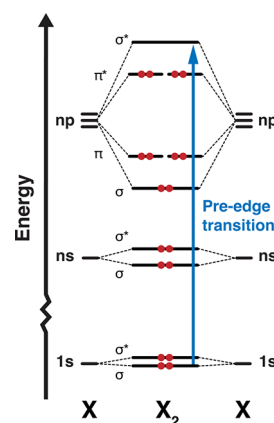


Figure 1. Qualitative MO diagram for dihalogen molecules. Electron occupancy is shown by red circles. The pre-edge transition studied here is represented by a blue arrow.

by comparison studies to $D_{4h}CuCl_4^{2-}$ using EPR, Cu K-edge XAS, and Cl K-edge XAS.^{48–52} This λ^2 was then used in tandem with the Cl K-edge XAS data to determine a value for $I_{Cl\ 1s \rightarrow Cl\ 3p}$.²

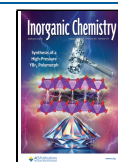
We began examining the dihalogen molecules (F₂, Cl₂, and Br₂) to understand how $I_{1s \rightarrow np}$ changes for F, Cl, and Br. For these homodiatomic molecules, each halogen atom contributes exactly half to the resulting MOs, $\lambda^2 = 0.5$ (Figure 1). The K-edge spectra of gaseous F₂, Cl₂, and Br₂ have been reported

Received: April 23, 2024

Revised: July 21, 2024

Accepted: July 31, 2024

Published: August 7, 2024



and exhibit intense transitions to the antibonding σ^* orbitals.^{53–55} While the K-edge spectrum of I_2 has also been reported, the intensity of the $1s \rightarrow \sigma^*$ transition could not be quantified with high confidence owing to the much larger lifetime broadening.⁵⁵

The results of our normalization and curve fitting for the previously reported^{53–55} K-edge spectra of F_2 , Cl_2 , and Br_2 are shown in Figure 2. The spectrum for F_2 was collected via

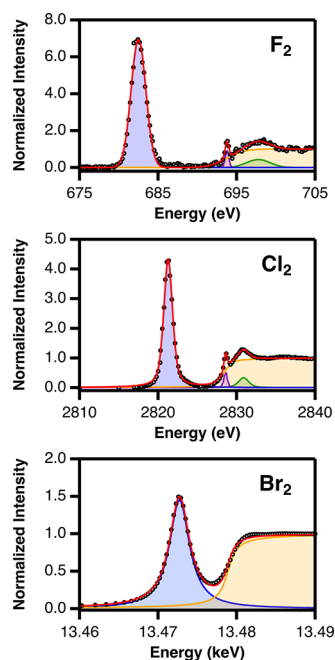


Figure 2. K-edge XAS spectra for F_2 , Cl_2 , and Br_2 . Experimental data points (circles) are fit using pseudo-Voigt functions. The intense, lowest energy feature (blue) is assigned to the $1s \rightarrow \sigma^*$ transition. Higher energy features (purple and green) are associated with Rydberg transitions. The edge-step (orange) corresponds to the rising edge region. Experimental data were digitized from publications for F_2 (ref. 53) and Cl_2 (ref. 54), and obtained from the author of ref. 55 for Br_2 .

electron energy-loss spectroscopy (EELS) while the spectra for Cl_2 and Br_2 were collected with synchrotron XAS in transmission mode. Data reduction and fitting were performed as previously described,^{4,9,32} and the fit parameters for the σ^* pre-edge transitions are presented in Table 1. The Lorentzian component (η) of the pseudo-Voigt functions was increased from 0% for F, to 50% for Cl, and 100% for Br to account for increased core-hole broadening. These η were chosen as values

Table 1. Fit Parameters for the $1s \rightarrow \sigma^*$ Transition in the Normalized K-Edge Spectra of Dihalogens

	peak energy (eV)	η	height ^c	fwhm ^c	intensity ^d
F_2^a	682.5	0	6.97(5)	2.20(2)	16.3(8)
Cl_2^a	2821.3	0.5	4.33(4)	1.33(2)	7.6(4)
Br_2^b	13472.7	1	1.45(1)	3.09(4)	7.1(4)

^aExperimental spectra were digitized from published data sets for F_2 (ref 53) and Cl_2 (ref 54). ^bThe spectrum of Br_2 (ref 55) was provided by the original author. ^cThe error in the peak height and width are their standard deviations from the curve fit. ^dThe estimated error in the integrated intensity (5%) accounts for the error introduced from data reduction, based on previous work.⁴

that well model experimental data and were constrained to reduce the number of free parameters in the fit. Based on previous work, the error in integrated intensities from background subtraction, normalization, and fitting is estimated to be 5%.⁴

The intensity of the $1s \rightarrow \sigma^*$ transition is described in terms of the dipole strength, D_0 :

$$I_{1s \rightarrow \sigma^*} = kD_0 = \frac{k}{3|G|} \sum_{\alpha\beta\gamma} |\langle G_\alpha | \hat{r}_\beta | E_\gamma \rangle|^2 \quad (2)$$

where G and E are the many-electron ground and excited states, $|G|$ is the degeneracy of the ground state, \hat{r} is the dipole operator, and k is a constant scaling the dipole strength to experimental intensity. The indices α , β , and γ sum over the components of the ground state, dipole operator, and excited state. The constant $1/3$ derives from transforming D_0 from a space-fixed coordinate system into orientationally averaged, molecule-fixed operators.⁵⁶ The following derivation is similar to that of Shadle et al.,² omitting the reliance on bond length in accordance with a study by Neese et al. showing that the transition dipoles for K-edge excitations are localized on the absorbing atoms.¹

For the $1s \rightarrow \sigma^*$ transition in a $D_{\infty h}$ - X_2 molecule, the ground state, dipole operator, and excited state transform as Σ_g^+ , Σ_u^+ , and Σ_u^+ , respectively. Because these irreducible representations are singly degenerate, the summation over their components may be omitted and $|G| = 1$, simplifying eq 2 to

$$I_{1s \rightarrow \sigma^*} = \frac{k}{3} |\langle \Sigma_g^+ | \Sigma_u^+ | \Sigma_u^+ \rangle|^2 \quad (3)$$

Equation 3 contains many-electron states and must be related to one-electron states to define the intensity in terms of MO coefficients. This transformation begins by using eq 20.2.10 in Piepho and Schatz,⁵⁶ resulting in

$$I_{1s \rightarrow \sigma^*} = \frac{2k}{3} \langle \sigma_g^+ | \sigma_u^+ | \sigma_u^+ \rangle^2 \quad (4)$$

where the magnitude of the many-electron matrix element has been replaced by a reduced matrix element.

To relate eq 4 to MO coefficients, a one-electron transition dipole matrix element between the donor (σ_g^+) and acceptor (σ_u^+) orbitals must be defined. Then, using Piepho and Schatz eq 10.2.2,⁵⁶ it is equated to a reduced matrix element.

$$\langle \sigma_g^+ | \hat{r} | \sigma_u^+ \rangle = \langle \sigma_g^+ | \sigma_u^+ | \sigma_u^+ \rangle \quad (5)$$

This one-electron matrix element is equated to MO coefficients by substituting wave functions for the donor and acceptor orbitals from the linear combination of atomic orbitals approximation:

$$\langle \sigma_g^+ | \hat{r} | \sigma_u^+ \rangle = \left\langle \frac{1}{\sqrt{2}} (1s_1 + 1s_2) | \hat{r}_z | \frac{1}{\sqrt{2}} (np_{z,1} + np_{z,2}) \right\rangle \quad (6)$$

where the subscripts on the atomic orbitals are atomic indices. Only the z component of the dipole operator is considered because the acceptor p -orbitals lie only along that axis. Instead of the local coordinate system often used to define MOs, the acceptor σ^* orbital is given in terms of a global coordinate system, in which the antibonding wave function is the additive combination of atomic orbitals (Figure 3). Furthermore, we have neglected overlap (S_{12}) in normalizing the acceptor wave function since ligand K-edge XAS measures the acceptor

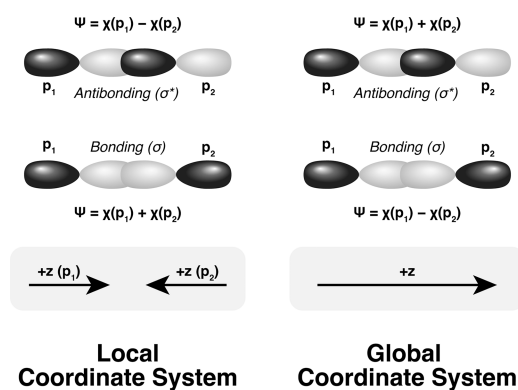


Figure 3. Visualization of transforming from a local coordinate system to a global coordinate system.

orbital population (which accounts for the overlap region) rather than orbital mixing coefficient.

This matrix element is evaluated by expansion into multiple matrix elements while neglecting two-center integrals.

$$\langle \sigma_g^+ | \hat{r} | \sigma_u^+ \rangle = \frac{1}{2} [\langle 1s_1 | \hat{r}_z | 1np_{z,1} \rangle + \langle 1s_2 | \hat{r}_z | 1np_{z,2} \rangle] \quad (7)$$

Because the terms on the right-hand side are equal matrix elements of \hat{r}_z , they are summed and the atomic indices dropped.

$$\langle \sigma_g^+ | \hat{r} | \sigma_u^+ \rangle = \langle 1s | \hat{r}_z | 1np_z \rangle \quad (8)$$

When eqs 5 and 8 are combined, the reduced matrix element is equal to the atomic one-electron matrix element.

$$\langle \sigma_g^+ | \hat{r} | \sigma_u^+ \rangle = \langle 1s | \hat{r}_z | 1np_z \rangle \quad (9)$$

Then, when eqs 4 and 9 are combined and recalling that $|\langle 1s | \hat{r}_x | 1np_x \rangle|^2 = |\langle 1s | \hat{r}_y | 1np_y \rangle|^2 = |\langle 1s | \hat{r}_z | 1np_z \rangle|^2 = |\langle 1s | \hat{r} | 1np \rangle|^2$ for an atom, the ligand K-edge XAS intensity in terms of atomic orbitals is

$$I_{1s \rightarrow \sigma^*} = \frac{2k}{3} |\langle 1s | \hat{r} | 1np \rangle|^2 \quad (10)$$

To account for the per-atom normalization of the experimental data, the right side of eq 10 must be divided by N (2 for X_2), producing the equation for the normalized intensity of the $1s \rightarrow \sigma^*$ transition in X_2 .

$$I_{1s \rightarrow \sigma^*} = \frac{k}{3} |\langle 1s | \hat{r} | 1np \rangle|^2 \quad (11)$$

Finally, to directly relate this equation to the intrinsic intensity of the absorbing atoms, eq 2 is applied to the $1s \rightarrow np$ transition of an unbound halogen atom.

$$\begin{aligned} I_{1s \rightarrow np} &= kD_0 = \frac{k}{3|P|} \sum_i |\langle 1s | \hat{r}_i | 1np_i \rangle|^2 \\ &= \frac{k}{9} \sum_i |\langle 1s | \hat{r}_i | 1np_i \rangle|^2 = \frac{k}{3} |\langle 1s | \hat{r} | 1np \rangle|^2 \end{aligned} \quad (12)$$

where $i = x, y,$ and z Cartesian components. When eqs 11 and 12 are combined, the final relationship between dihalogen $I_{1s \rightarrow \sigma^*}$ and halogen $I_{1s \rightarrow np}$ is simply,

$$I_{1s \rightarrow \sigma^*} = I_{1s \rightarrow np} \quad (13)$$

Thus, the $1s \rightarrow np$ transition intensities for F, Cl, and Br are equal to the corresponding $1s \rightarrow \sigma^*$ transition intensities in F_2 , Cl_2 , and Br_2 .

To verify this relationship, the oscillator strengths ($f_{1s,np}$) of the $1s \rightarrow np$ transitions in the F, Cl, and Br atoms were calculated using Cowan's atomic structure codes⁵⁷ within the *Missing 1.11* user interface.⁵⁸ The default value for Slater integral rescaling was used, 0.8, and the spin-orbit coupling was not rescaled. Table 2 compares the resulting $f_{1s,np}$ values to

Table 2. Comparison between Calculated Oscillator Strengths for the Halogen $1s \rightarrow np$ Transition and the X_2 Pre-edge Intensities Normalized to the K-Edge Absorption Cross Section

	K-edge absorption cross section ($\times 10^4 \text{ cm}^2 \text{ mol}^{-1}$) ⁵⁹	normalized pre-edge intensity ($\times 10^4 \text{ eV cm}^2 \text{ mol}^{-1}$) ^a	$f_{1s,np} \times 1000$
F_2	23.02	376(19)	261.49
Cl_2	5.42	41(2)	33.69
Br_2	1.04	7.3(4)	17.8

^aObtained by multiplication of the transition intensities in Table 1 by the K-edge absorption cross sections.

the experimental intensities, which were normalized to the K-edge absorption cross section of the absorbing atom. The calculations show that $f_{1s,np}$ decreases by a factor of ~ 10 on moving from F to Cl, followed by an additional decrease by a factor of ~ 2 on moving from Cl to Br. A comparable decrease is observed experimentally, beginning with a 10-fold decrease in intensity moving from F_2 to Cl_2 , followed by a ~ 6 -fold decrease moving from Cl_2 to Br_2 . This agreement between the calculated $f_{1s,np}$ and normalized intensities supports using this methodology for determining atomic parameters from molecular units.

With these $I_{1s \rightarrow np}$ supported by atomic structure calculations, we will consider their use in quantitative ligand K-edge XAS. When comparing these rigorously covalent molecules with metal-halide bonds, it is important to consider that the intrinsic intensity is dependent on the charge of the absorbing atom. Thus, some error is introduced when analyzing metal-halide complexes (which contain anionic halogens) using these covalent standards. However, the change in intensity as a function of charge density has been calculated to be very low ($< 5\%$).² Additionally, there is statistical equivalence between the $I_{Cl \ 1s \rightarrow Cl \ 3p}$ value reported here, 7.6(4), from Cl_2 and that determined from $D_{2d}CuCl_4^{2-}$, 7.0(2).^{2,7} Further factors which can effect data quantification include differences in sample preparation, data acquisition, and data reduction.^{4,31,34,37} Hence, while the agreement between the $I_{Cl \ 1s \rightarrow Cl \ 3p}$ values for Cl_2 and $D_{2d}CuCl_4^{2-}$ is encouraging for the use of Cl_2 and as an intensity standard, additional work is needed to provide experimental validation for the use of F_2 and Br_2 .

This work shows that the $1s \rightarrow \sigma^*$ transition in the K-edge spectra of F_2 , Cl_2 , and Br_2 may be used to calibrate pre-edge intensities in ligand K-edge XAS. These findings are supported by comparison between the experimental intensities and the calculated oscillator strengths for the unbound atoms. Furthermore, the use of these $I_{1s \rightarrow np}$ in ligand K-edge XAS analysis is supported by the agreement between the $I_{1s \rightarrow 3p}$ for Cl determined here and in previous studies. Additional work to validate these findings with other spectroscopic probes of metal-ligand orbital mixing is ongoing.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful to Adriano Filipponi for providing the raw data file for the Br K-edge spectrum of Br₂. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences Heavy Element Chemistry Program of the U.S. Department of Energy (DOE) at LBNL under Contract DE-AC02-05CH11231. J.A.B. received funding from the U.S. DOE through the Office of Nuclear Energy, Integrated University Program Graduate Fellowship.

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