

LIMITATIONS IN EXAFS AMPLITUDE TRANSFERABILITY FOR LOW-Z SCATTERERS

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Abstract. We have studied the transferability of EXAFS amplitudes between carbon and oxygen as backscattering atoms. EXAFS data were collected on model compounds of known structure. The empirical phase and amplitude functions derived from an oxygen coordination shell were used as references to analyze a carbon coordination shell, and vice versa. It was found that the coordination numbers obtained from EXAFS analysis differ significantly from the real coordination numbers, showing that the backscattering amplitudes are not transferable for low-Z elements e.g. oxygen and carbon.

Introduction. The accuracy of the structural parameters obtained from the EXAFS technique strongly rely upon the transferability of the reference phaseshift and backscattering amplitude functions. These functions can either be extracted from the model compounds of known structure, or be calculated from the available tables^{1,2}. It is generally found that the phase shift functions are less sensitive to the chemical nature of the sample, and are transferable among nearest and next-nearest neighbouring elements in the periodic table³. However, this is not the case with the amplitude functions of low-Z elements⁴. As a result, the coordination numbers determined from EXAFS analysis are not reliable when amplitude transferability is assumed between nearest and next-nearest neighboring low-Z elements: e.g. C, O and N. Despite this fact, the amplitude functions derived from an oxygen coordination shell are frequently used to analyze a carbon coordination shell, and vice versa.

In this note, we demonstrate the serious limitations of EXAFS amplitude transferability between carbon and oxygen scatterers. The model compounds used in this study are:

- i $\text{Fe}(\text{C}_5\text{H}_5)_2$ and $\text{Fe}(\text{III})(\text{H}_2\text{O})_6$ ($\text{Fe}(\text{NO}_3)_3$ 50mM solution in .1N HNO_3)
- ii Na_2MoO_4 and $\text{Mo}(\text{CO})_6$
- iii $\text{Os}_3(\text{CO})_{12}$, $\text{Na}_2\text{Pt}(\text{OH})_6$ and NH_4ReO_4

Crystallographic data for these compounds are listed in Table I. The Fe EXAFS data were collected at room temperature on station X-11A of NSLS, Brookhaven National Laboratory. The Re, Pt and Mo EXAFS data were collected at 77K, on station 9.2 of SRS, Daresbury Laboratory. In all cases, the monochromator was detuned by 50% to reject the higher harmonics, and the data quality was excellent.

Table I. Crystallographic data for the model compounds and Fourier transformation parameters used to isolate the contribution of a shell.

Sample	Shell	N_{crst}	R_{crst}	$\Delta k(\text{\AA}^{-1})$	$\Delta R(\text{\AA})$
$\text{Fe}(\text{C}_5\text{H}_5)_2^5$	Fe-C	10	2.05	2.66-14.91	0.74-2.50
$\text{Fe}(\text{III})(\text{H}_2\text{O})_6^6$	Fe-O	6	1.99	2.69-9.67	0.42-2.12
$\text{Na}_2\text{MoO}_4^7$	Mo-O	4	1.77	3.00-12.00	0.00-2.10
$\text{Mo}(\text{CO})_6^8$	Mo-C	6	2.07	3.06-14.00	0.96-2.10
$\text{Os}_3(\text{CO})_{12}^9$	Os-C	4	1.95	2.70-18.34	0.90-2.10
$\text{Na}_2\text{Pt}(\text{OH})_6^{10}$	Pt-O	6	2.05	2.80-15.30	0.80-2.52
$\text{NH}_4\text{ReO}_4^{11}$	Re-O	4	1.74	2.84-13.83	0.80-2.50

Data Analysis and Results. The EXAFS functions, $\chi(k)$, were obtained from the x-ray absorption data by subtracting a quadratic polynomial, followed by a cubic spline background removal, and normalizing by dividing through the edge jump. The fourier transformation parameters used to isolate a particular shell are listed in Table I. The Fe-O and Mo-C first shell EXAFS functions were analyzed using the phase and amplitude functions derived from the Fe-C and Mo-O shell, respectively. The Os-C shell EXAFS function was analyzed using both the Pt-O and Re-O as references. The EXAFS function of an isolated shell was analyzed using a recently developed $k^1 - k^3$ analysis procedure¹². Briefly, this analysis procedure involves least-square fit in k space with $n=1,3$ weight factors, followed by a comparison of the corresponding k^1 and k^3 weighted fourier transforms in r -space. The fit results are listed in Table II. The experimental and fitted EXAFS spectra for the Fe-O shell are compared in figure 1, which are in good agreement.

Table II EXAFS fit results

Unknown Shell	Ref. Shell	N	$R(\text{\AA})$	$\Delta\sigma^2(\text{\AA}^2)$	$E_0(\text{eV})$	$\Delta N \%$
Fe-O	Fe-C	19.25	1.99	0.0053	14.36	226
Mo-C	Mo-O	2.50	2.05	-0.003	-11.02	-58
Os-C	Re-O	1.5	1.91	-0.0001	-2.5	-50
	Pt-O	1.75	1.94	-0.0004	-2.5	-42

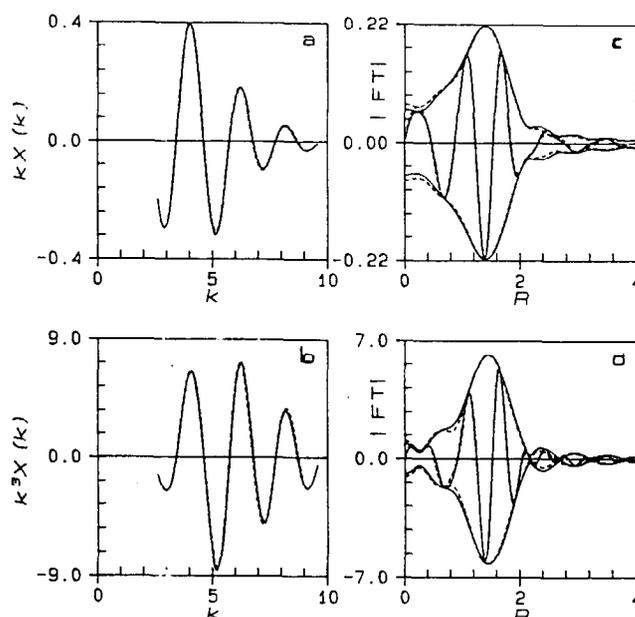


Figure 1. (a) k^1 - weighted and (b) k^3 - weighted EXAFS for the Fe-O shell. Corresponding (c) k^1 - weighted and (d) k^3 - weighted Fourier transforms of the experimental data (solid line) and fitted EXAFS functions (dotted line).

Discussion. The results of this study show that the amplitude functions derived from an oxygen coordination shell can not be used to analyze a carbon shell, and vice versa. This is especially important when coordination numbers are used for detailed modelling of a particular system. The large error in the coordination numbers are due to lack of amplitude transferability among low-Z scatterers. The nearest and next-nearest neighboring low-Z elements have a large difference in chemically sensitive electrons. As a result, the backscattering amplitude $F(k)$ itself is not transferable, which results in serious errors in EXAFS analysis.

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