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Derivation of Relation between a parameter of Inverse correlation and effective Charge of X-ray absorbing K-Edge of Copper atom in it's different Compounds

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Abstract

The article gives an overview of the XANES technique contribution to the analysis of multi-component catalysts. The theoretical basis of the technique, the interpretation of the energy position and intensity of XANES features, and the numerical methods developed to interpret XANES data on catalytic systems are described and discussed. XANES in the K-edge of copper in the systems. CuO, Cu(NO₃)₂, La₂CuO₄, CuCl₂, and CuBr have been investigated and transitions have been assigned to the observed structures. The measurements have been used for calculating the first coordination bond distance in the above systems. It is observed that the values so determined agree fairly well with crystallographic values.

Key words : X-ray absorption spectroscopy, XANES, Methods of XANES data analysis, Copper atom.

In the early studies, X-ray absorption spectra of an element were considered independent of its chemical combinations. The idea changed when Bergengren¹ demonstrated the chemical combination affect the position of X-ray absorption edge. Although the core electrons are not directly involved in the formation of chemical bond, the energies of inner electronic-levels are shifted when the chemical-state or the crystallographic environment of an atom changes and it gets reflected into absorption edge-shift. These shifts are primarily due to two main factors:

- (i) the tighter binding of the core level electrons due to change in the effective-charge (or screening) of the X-ray absorbing atom, and
- (ii) the appearance of the energy gap, E_g between the valence band and conduction band when the

metal is transformed into a compound (semiconductor or insulator).

In fact, the electrostatic potential is lowered as soon as the electronic charge on a given atom is reduced. This leads to an increase in the binding energy of core electrons of the atom so the absorption-edge shifts to higher energy. The local potential set up around the X-ray absorbing atom by the differences in charge distribution among atoms in a molecule is due to superposition of the atomic and molecular potentials. The exact nature of this potential is very complicated², particularly in solids, and so the interpretation of the results is not straight forward. Sometimes even the Madelung potential from other atoms of the system is substantial and may affect the chemical shift. Probably due to this complication, studies on chemical shift have been mostly empirical during the last eight decades and to the best of our knowledge, no simple theoretical model has yet been proposed. Only recently, an attempt has been made by Karlsson *et al*³⁻⁴, using Anderson impurity model to calculate theoretically Cu chemical shifts in CuO, Cu(NO₃)₂, La₂CuO₄, CuCl₂, and CuBr and by Bhattacharya *et al*⁵ to calculate double vacancy in heavy ion collisions. However, these methods are complicated need good computational facilities and have not been generalized and extended to K-edge. In the present investigation, we have attempted to develop a simple theoretical potential model for evaluating chemical shift.

Sample Preparation and Experimental

The energy of the primary beam is scanned over the desired absorption edge. The position of the absorption edge of the absorbing atom changes due to the change in the chemical environment around the absorbing atom. This change in the position of the absorption edge due to the chemical environment (around the absorbing atom) is called the chemical shift.

The exact binding energy of an electron depends not only upon the level from which photoemission is occurring, but also upon :

1. The formal oxidation state of the atom.
2. The local chemical and physical environment.

Changes in either (1) or (2) give rise to small shifts in the peak positions in the spectrum, the so-called chemical shifts.

An element forming a compound in a chemical combination suffers through a change in the energy of the absorption edge of the metal. It is due to the change in the potential causing a change in the binding energy of the electron (to be ejected as photon) of the photo-absorbing atom. This shift in the energy of the X-ray absorption edge is known as chemical shift. It is equal to the difference of energy of the absorption edge of the metal in compound (E_c) and in pure elemental state (E_m), i.e., chemical shift ΔE , (in eV) is given by,

$$E = E_c - E_m \quad (1)$$

The extensive studies made by Cauchois⁶, Meisel⁷, Azaroff and Pease⁸, Nagel and Baun⁹, Srivastava and Nigam¹⁰, Mande¹¹ suggested that the chemical shift is governed by the several physico-chemical parameters such as effective charge, valence, ionicity, co-ordination number, number of electrons taking part in the bond formation *etc.* The observed high energy shifts of the X-ray absorption edges are attributed by the following two factors :

- (i) The participation of the valence electrons in the chemical bond formation causes the tighter binding of the core level because of the change of effective charge (or screening) of the nucleus.
- (ii) Appearance of energy gap due to transition from a metal (or element) to a compound.

The photo-electron spectroscopy provides the direct evidence of the first factor. The second factor is believed to be related to various parameters such as covalence, effective charge, coordination number, crystal structure *etc.*

Various attempts have been made by the several workers to correlate the chemical shift with valency, ionicity and coordination number, Sapre *et.al.*¹² and with the effective charge^{13,14,15} Siegbahn *et.al.*¹⁶ have shown using photoelectron spectroscopy that the chemical-shifts are due to change in local potential set up by the differences in charge distribution among atoms in molecule. The first potential is assumed to be approximately proportional to the charge on the atom. It is generally dominant. The second potential is called the molecular potential. This is set up by the charge distribution in the rest of the molecule. The nature of this local potential is very complicated as it is anisotropic and having a three dimensional character. The shape of the local potential depends upon different molecular parameters such as coordination number, bond length, valence of the absorbing atom, electronegativity of the atoms in the molecule, molecular geometry etc. and the core hole depth. The photoelectron eventually tunnels^{17,18} the potential barrier where it is resonantly trapped.

A satisfactory and general theory of chemical shift connecting the other physico-chemical parameters is very difficult to propose due to the complex and anisotropic nature of the molecular potential and perhaps this is the reason why most of the relationship between chemical shift and other physico-chemical parameters proposed by various workers have been empirical in nature. The effective charge on the absorbing atom develops due to different factors such as coordination number, valency, bond length, nature of bonding (covalency), electronegativity etc. The effective charge on the absorbing atom is a measure of the charge transfer from the absorber to the neighbouring atom. Therefore in most of the studies on chemical shift attempts have been made to correlate the chemical-shift with the effective charge.

According to the empirical formula of Agarwal and Verma¹⁹ and the recent years by Louat *et al.*²⁰ and Ali H. *et al.*^{21,22}, the chemical shift is towards the high energy side of the metal edge shown in Table-1. It increases progressively with the increase of the valence of the cation, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of metal-metal bonding.

Table-1 Correlation between SR_2 and q
Values of $(S \times R_2)$ calculated for some Copper K-edge system at different energy modes.

Name of the Absorber	E_A in eV*	Effective Charge q el.per atom	Crystallographicvalue of R in $\text{\AA}$	ΔE_A in eV
CuBr	8.26	1.51	2.4	0.43
Cu ₂ O	10.25	1.60	1.849	1.56
Cu (Acetate) ₂	16.52	1.71	1.947	7.83
CuCl ₂	16.95	1.95	2.30+0.01	8.26
CuF ₂	16.95	1.66	1.93	8.26
CuSO ₄	17.39	1.58	2.10+0.02	8.7
Cu(NO ₃) ₂	17.82	1.60	1.969	9.13
La ₂ CuO ₄	13.47	1.65	1.86	4.78
CuO	16.52	1.45	1.96	7.83
Cu	8.69	Metal		—

3. Method of Calculation and Discussion

In terms of XANES features as the XANES features are affected by the physico-chemical environment of the system, We have tried to correlate the shift of the main peak ΔS of XANES with effective change, q calculated using Pauling's method. Instead of calculating the chemical shift of the edge, we have calculated the

shift of main peak in a compound with respect to the position of the corresponding position in the metal, i.e for a given system,

$$E_{\text{compound}} (\text{main - peak}) - E_{\text{metal}} (\text{main - peak}) = \Delta E \quad (2)$$

Of the different correlations tried we have found that the correlation

$$q = a \Delta E^3 + b \Delta E^2 + c \Delta E + d \quad (3)$$

given the best result.

The result for the system has been shown in Graphs in Fig. 1.

Fig. 1: Exponential curve fit showing correlation between (SR^2) and (q) of Copper System.

Equation of graph : $SR^2 = a + bq$

Coefficients Value

$a = -285.4$, $b = 1812$

$c = -3644$, $d = 2383$

Correlation Coefficient

$R^2 = 0.836$

The high degree of correlation coefficient (r) ~ 91.55% between SR^2 and q suggests that C_r , C_b or C depends upon the chemical environment around the X-ray absorbing atom defined by effective charge on the atom. The high degree of correlation coefficient (r) ~ 91.55% between SR^2 and q suggests that C_r , C_b or C depends upon the chemical environment around the X-ray absorbing atom defined by effective charge on the atom.

Conclusion

The high degree of correlation obtained in the present work suggests that the Energy Moments criterion for the determination of the edge – energy good can be safely suggested as a suitable method for the analysis of XANES features. Here it may be noted that this method also removes the thickness effect of the absorber on the absorption spectra. This approach seems to be a better method for the analysis of XANES features.

New Direction :

Several unresolved problems are being addressed through new directions in XAS that are being pursued in different laboratories. The combination of XAS with X-ray microscopy has shown great promise in studying very small localized domains of larger biological systems, and the possibility for combining imaging with spectroscopy. Another powerful approach has been the combined in situ use of XAS along with other methods, such as X-ray diffraction, electrochemistry, UV/Vis or FTIR/Raman spectroscopy. This methodology has allowed for monitoring of changes in the system and also the integrity of the sample. These methodologies are being applied to substrate binding studies and for following the course of catalytic reactions.

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