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LNF-84/63(P)
22 Ottobre 1984

C.R. Natoli: DISTANCE DEPENDENCE OF CONTINUUM
AND BOUND STATE OR EXCITONIC RESONANCES IN
X-RAY ANSORPTION NEAR EDGE STRUCTURE (XANES)

Invited Talk at the
"Third International EXAFS Conference",
Stanford, Ca. (USA),
July 16-20, 1984.

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The rising interest in XANES is due to the experimental evidence that information on coordination geometry and bonding angles, not given by EXAFS, can indeed be extracted from XANES^(1,2). In this paper I would like to point out that certain features of XANES, being sensitive to interatomic distances, can also be exploited to determine first coordination bond lengths to a few percent accuracy (5% or less)⁽³⁾. This aspect of XANES is particularly useful whenever EXAFS modulations are too weak to be measured, as in the case of low Z backscatterers. For the sake of concreteness, I shall limit myself to K-edge absorption spectra of simple molecules containing C-C, C-N, C-O type of bonds and of two series of Mn and V oxides (see Tables I and II). These cases are general enough to serve as an illustration of other cases.

In ref.(4), I suggested that the following relation

$$(E_r - \bar{V})R^2 = C_r = \text{const} \quad (1)$$

should correlate the energy position $\bar{E}_r = E_r - \bar{V}$ of a continuum resonance (measured from an average interstitial potential \bar{V} in the material under consideration) and the bond length R between the absorbing atom and its nearest neighbor(s), responsible for the resonance through a "caging" effect.

Eq.(1) was obtained by imposing the condition $\text{Det } M = 0$ at the resonant energy, where M is the multiple scattering matrix⁽⁴⁾. Here I observe

that the same relation can be obtained in m.s. theory on the basis of a simple scaling argument in case the maximum in the spectrum is not a resonant maximum, but is still due to neighbors at distance R from the photoabsorber.

In general, application of Eq.(1) is impaired by the fact that \bar{V} is not an experimentally accessible quantity and may be different in the systems under comparison. To circumvent this difficulty, I suggest here the use of a relation similar to Eq.(1) for bound or excitonic resonances, i.e.

$$(E_b - \bar{V})R^2 = C_b. \quad (2)$$

Subtraction of Eq.(1) and Eq.(2) then yields

$$(E_r - E_b)R^2 = C_r - C_b \quad (3)$$

a relation containing only measurable quantities and of immediate application. By the term "bound or excitonic resonances" I mean those spectral pre-edge features due to transition to truly bound states in molecules (e.g., the π^* transition in diatomic molecules⁽⁵⁾) or to antibonding states of 3d character in metal oxides⁽⁶⁾. Both have in common the feature that they fall in an energy region where atomic resonances of the constituent atoms occur and, so to speak, are driven by them.

However, use of Eq.(2) needs some discussion, since the quantity C_b would in general depend itself on R, due to the nonnegligible energy dependence of the atomic phase shifts in the resonant region⁽⁴⁾. A simple model of an excitonic resonance between two like atoms at distance R apart, driven by an atomic resonance in s state, located at energy E_a and with half width Γ , will illustrate the point. In such a case the condition for the two atom cluster resonance is

$$\cotg \delta(E) = \frac{\cos(\kappa R)}{\kappa R} \quad (4)$$

where $\kappa = (E - \bar{V})^{1/2} = \bar{E}^{1/2}$. Putting $\varrho_a = \kappa_a R = (E_a - \bar{V})^{1/2} R$, $\varepsilon = \bar{E}_a / \Gamma$, $\cotg \delta(E) \approx (\bar{E} - \bar{E}_a) / \Gamma$ and, to within 10% accuracy, $\arccos(x) \approx \pi/2(1-x)^{1/2}$, Eq.(4) can be solved analytically to give the wanted relation between the cluster resonance E_b and the bond length R. The result is

$$(E_b - \bar{V})^{1/2} R \approx \kappa_b R = \pi/2 \left[\varepsilon + (2/\pi + 2\varepsilon/\varrho_a + \varepsilon^2)^{1/2} \right] (1 + \pi\varepsilon/\varrho_a)^{-1}. \quad (5)$$

It is interesting to consider the two limiting cases, $\Gamma \rightarrow 0$ ($\epsilon \rightarrow \infty$) and $\Gamma \rightarrow \infty$ ($\epsilon \rightarrow 0$). For $\Gamma \rightarrow 0$, limit of infinitely sharp atomic resonance, $\kappa_b R = \theta_a = \kappa_a R$, implying that, whatever the bond length, the molecular resonance E_b is pinned down at the atomic value \bar{E}_a and C_b in Eq.(2) is $\bar{E}_a R^2$.

For $\Gamma \rightarrow \infty$, limit of very weak dependence of atomic phase shifts on energy $\kappa_b R = (\pi/2)^{1/2}$, recovering Eq.(1), since in this case the resonance is a continuum resonance. The true state of affairs for a bound-excitonic resonance lies in between. For typical values of $E_a \lesssim 5$ eV, $1.2 \lesssim \theta_a \lesssim 2.5$, $\Gamma \sim 10$ eV, one finds $\pi\epsilon/\theta_a \sim 1$, so that one is in the range of small deviation ($\sim 10\%$) of the r.h.s. of Eq.(3) from constancy, considering that usually $C_r \sim 5C_b$ and $\Delta R/R \sim 30\%$. Although oversimplified, the model contains all of the relevant features of real systems and one can expect the above estimates to apply to them. One can then assume constancy of the r.h.s. of Eq.(3) and read off the consequences. When applied to free molecules, Eq.(3) states that the energy difference between the σ^* and the π^* resonance depends only on the bond length, provided initial state differences, like more or less covalency or polarity of the bond, have the same effect on the two excited states. For chemisorbed molecules one is led to the same conclusions, provided the two resonances are affected by the metal substrate shielding in the same way. Under these assumptions, the constant should be transferable from one phase to another.

If applied to metal oxides, Eq.(3) implies that the energy separation between the pre-edge excitonic feature and the first strong absorption maximum after the rising edge is a function of the bond length. Since the inflection point of the rising edge tends to follow this maximum, care should be exercised not to attribute its energy shift to an initial state effect, i.e., different valence state of the metal ion. Any initial state effect should therefore be assessed after correcting for this "bond length effect". Analysis of the edge shifts in the Mn and V oxide series along these lines reveals that initial state effects due to the different chemical states of the metal ion amount to less than 1 eV as opposed to 5-8 eV shifts caused by bond length variation. This result is in keeping with the conclusions of ligand field theory, whereby back-bonding effects tend to neutralize charge transfer from the metal to the ligands so that the net charge on the metal ion remains roughly constant along the series.

Table I summarizes the experimental data for the energy position (eV)

of the π^* and σ^* resonances, the bond length (\AA) and the ionization potential of several molecules in their gas phase. The last column gives the product $\Delta_{\pi\sigma} R^2$ ($\text{eV}\text{\AA}^2$). In keeping with theory one finds that this quantity depends on the atom forming the pair and it is roughly constant within the sa

TABLE I

Molecule	Ref	1s Hole State	$E(\pi^*)$	I.P.	$E(\sigma^*)$	$\Delta_{\pi\sigma}$ (eV)	$R(\text{\AA})$	$\Delta_{\pi\sigma} R^2$ ($\text{eV}\text{\AA}^2$)
C_2H_2	(7)	C	285.6	291.1	310	24.4	1.204	35.4
C_2H_2	(7)	C	284.7	290.8	306	21.3	1.337	38.0
HCN	(9)	C	286.4	293.4	307.9	21.5	1.156	28.7
		N	399.7	406.8	420.8	21.1		28.2
C_2N_2	(9)	C	286.3	294.5	306.3	20.0	1.16	26.9
		N	398.9	407.4	419.3	20.4		27.4
N_2	(8)	N	400.9	409.9	418.9	18	1.095	21.6
CO	(8)	C	287.3	296.2	303.9	16.5	1.128	21.0
		O	534.1	542.6	550.9	16.8		21.4
H_2CO	(8)	C	286.0	294.5	300.9	14.9	1.21	21.8
		O	530.8	539.4	544.0	13.2		19.3
CH_3COH	(8)	C	286.3	294.0	301.0	14.7	1.22	21.9
		O	531.1	538.0	544.5	13.4		19.9
$(CH_3)_2CO$	(8)	C	286.8	293.8	301.0	14.2	1.22	21.1
		O	531.3	537.9	545.0	13.7		20.4

TABLE II

Oxide	Ref	$E_A(3d)$ (eV)	$E_C(4p)$ (eV)	$\bar{R}(\text{\AA})$	$\Delta_{AC} R^2$ ($\text{eV}\text{\AA}^2$)	Coordination
MnO	(6)	0.3	16.0	2.22	77.4	6
Mn_2O_3	(6)	0.5	20.0	2.01	78.8	6
MnO_2	(6)	0.7	22.0	1.90	76.9	6
$KMnO_2$	(6)	1.3	28.0	1.6	68.3	4
VO	(10)	3.0	20.4	2.05	73.1	6
V_2O_3	(10)	3.4	23.5	2.01	81.1	6
V_4O_7	(10)	4.1	25.1	1.98	82.3	6
V_2O_4	(10)	4.5	26.2	1.93	80.8	6
V_2O_5	(10)	5.6	30.1	1.83	82.0	5
NH_4VO_3	(10)	4.8	26.6	1.73	65.2	4
$CrVO_4$	(10)	4.8	24.4	1.76	60.1	4
Vanadinite	(10)	4.5	25.1	1.75	63.1	4
VP_c	(10)	3.9	27.3	1.58	58.4	1
VTPP	(10)	4.1	25.7	1.62	56.7	1

me pair (According to the Z+1 rule, at Carbon and Nitrogen K-edge CO and N₂ have the same final state, so they are listed together).

Similarly Table II summarizes, for the series of Mn and V oxides, the energy position $E_A(3d)$ of the transition to an antibonding state of 3d character on the metal ion (feature A in ref.(6)), the position $E_C(4p)$ of the first strong maximum after the rising edge (feature C in ref.(6)), the length of the metal to ligands bond \bar{R} (or the average value if they are not all equal) and the product $\Delta_{AC}\bar{R}^2$ (eVÅ²).

ACKNOWLEDGMENTS

Illuminating discussions with Dr. F.Sette on the subject of molecular resonances are gratefully acknowledged. Thanks are due to him and Dr.J.Wong for making preprints of their papers available to me prior to publication.

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