

Determination of bond lengths in some compounds of rhenium from the x-ray L_{III} absorption discontinuity

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Abstract. The shapes and the fine structure of the x-ray L_{III} absorption discontinuity of rhenium have been studied in seven octahedral (K_2ReCl_6 , K_2ReBr_6 , $(pyH)_2ReCl_6$, $(dipyH)_2ReCl_6$, $Re(dipy)Cl_4$, $K_2ReO_2(CN)_4$ and ReO_3) and three tetrahedral ($KReO_4$, NH_4ReO_4 and $NaReO_4$) compounds. The bond lengths in these compounds have been determined by applying Levy's theory to the data on the fine structure associated with the edge beyond the molecular orbital region.

Keywords. X-ray L_{III} absorption; bond length; Levy's theory.

1. Introduction

Making use of Kozlenkov's theory (Kozlenkov 1961) of the fine structure of x-ray absorption edges, Levy (1965) and Levy *et al* (1966) have demonstrated the possibility of determining the average radius of the first coordination shell, i.e. the bond length in a compound or complex, from x-ray absorption spectra. Following Levy's method, Mande and Chetal (1966) have determined the bond lengths in some cobalt complexes from the fine structure of the K discontinuities. In a similar way, Bhat (1968) and Srivastava and Nigam (1972) have determined respectively the bond lengths in some yttrium compounds and in some copper complexes. It appears that no attempt has been made so far to obtain bond lengths from the L absorption discontinuities. We have studied in this laboratory the shapes and the fine structure associated with the L_{III} absorption edge of rhenium in some octahedral and tetrahedral compounds (Mande *et al* 1972, Pendharkar 1972). In this paper we show how the bond lengths in the compounds can be determined from the fine structure associated with this discontinuity.

2. Experimental

The absorption spectra were recorded on a Cauchois type 40 cm bent crystal x-ray spectrograph. The details of the experimental set-up for obtaining the absorption spectra have been described earlier (Mande *et al* 1972, Pendharkar 1972, Pendharkar and Mande 1973). Microphotometer records of the spectra were obtained with 100 magnification on a Spectroline Scanner made by Applied Research Laboratory, California. The shapes of the discontinuities in the different compounds were obtained

from a number of microphotometer traces obtained in turn from several spectra of each compound, scanning the discontinuity at different heights.

The compounds studied are K_2ReCl_6 , K_2ReBr_6 , $(pyH)_2ReCl_6$, $(dipyH)_2ReCl_6$, $Re(dipy)Cl_4$, $K_3ReO_2(CN)_4$, ReO_3 , $KReO_4$, NH_4ReO_4 and $NaReO_4$. Pure rhenium metal (99.9%) obtained from British Drug House Ltd., England and $KReO_4$ manufactured by Kochlight Laboratories, England (>99.9%) were used for the preparation of the first seven compounds. The formation of these compounds were confirmed from their chemical analysis. $NaReO_4$ (99%) and NH_4ReO_4 (99%) were obtained from Kochlight Laboratories, England.

3. Results

We have reported the shapes of the main L_{III} edge and the near edge structures corresponding to the molecular orbital (MO) region for two compounds, namely $K_2[ReCl_6]$ (octahedral) and $KReO_4$ (tetrahedral) in an earlier paper (Mande *et al* 1972). The extended fine structure beyond the MO region for these discontinuities is shown in figures 1 and 2 along with the main discontinuities. These curves represent the transmitted intensity in the region of L_{III} absorption. The maxima and minima in the curves, therefore, correspond to the minima and maxima respectively in the absorption coefficient. The shapes of the edge and the fine structure for the octahedral compounds K_2ReBr_6 , $(pyH)_2ReCl_6$, $(dipyH)_2ReCl_6$, $Re(dipy)Cl_4$ and ReO_3 are more

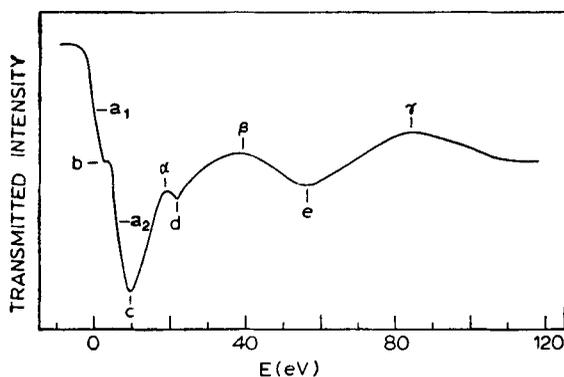


Figure 1. The shape and the fine structure of the Re L_{III} absorption discontinuity in K_2ReCl_6 .

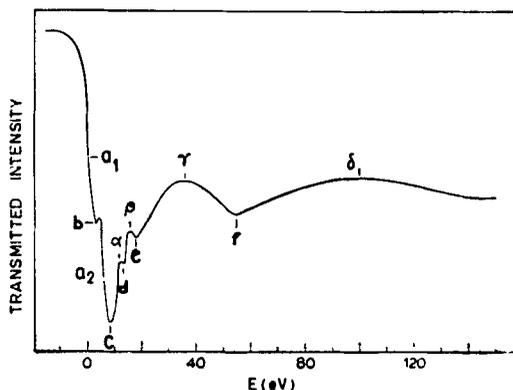


Figure 2. The shape and the fine structure of the Re L_{III} absorption discontinuity in $KReO_4$.

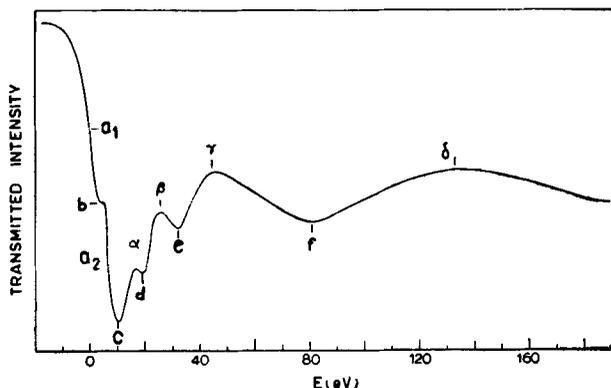


Figure 3. The shape and the fine structure of the Re L_{III} absorption discontinuity in $K_3ReO_2(CN)_4$.

or less similar to those of K_2ReCl_6 , although the positions of the maxima and minima vary from compound to compound. Similarly the shape of the L_{III} edge for the tetrahedral compounds $NaReO_4$ and NH_4ReO_4 resembles that of $KReO_4$. We have observed an extra absorption maximum in the absorption curve for the octahedral compound $K_3ReO_2(CN)_4$, not found for the other octahedral compounds. The shape of the L_{III} discontinuity in this compound is given in figure 3.

The measurements of the energy separation, ΔE , between the absorption maximum e and the subsequent minimum γ for the octahedral compounds (except $K_3ReO_2(CN)_4$), and the absorption maximum f and the subsequent minimum δ for the tetrahedral compounds are given in table 1. The energy difference between the absorption maximum f and the subsequent minimum δ for $K_3ReO_2(CN)_4$ is also included in table 1.

4. Discussion

Mande *et al* (1972) and Pendharkar (1972) have shown that in all the octahedral compounds except $K_3ReO_2(CN)_4$ the absorption maxima b , c and d (figure 1)

Table 1. Bond lengths (r_1) in Angstrom Units obtained from the fine structure of the L_{III} absorption discontinuity.

Compound	ΔE	r_1 Å (This paper)	r_1 Å (x-ray diffraction data)
K_2ReCl_6	27.6 (e- γ)	2.34	2.37 (Aminoff 1936)
K_2ReBr_6	23.2 (e- γ)	2.55	2.50 (Templeton and Dauben 1951)
$(pyH)_2ReCl_6$	29 (e- γ)	2.28	—
$(dipyH)_2ReCl_6$	28.9 (e- γ)	2.29	—
$Re(dipy)Cl_4$	33.9 (e- γ)	2.11*	—
$K_3ReO_2(CN)_4$	44.8 (f- δ)	1.84*	—
ReO_3	44.5 (e- γ)	1.84	1.867 (Meisel 1932)
$KReO_4$	52.2 (f- δ)	1.70	1.77 (Morrow 1960)
NH_4ReO_4	43.7 (f- δ)	1.86	1.84 (Wyckoff 1948)**
$NaReO_4$	50.4 (f- δ)	1.73	1.68 (Wyckoff 1948)**

*These bond lengths are average values, because the octahedral surrounding of rhenium in these compounds is not uniform.

**The bond lengths in the compounds NH_4ReO_4 and $NaReO_4$ are calculated from the coordinates of Re and O atoms, given in the diffraction data.

lie in the MO region, whereas in the tetrahedral compounds and in $\text{K}_3\text{ReO}_2(\text{CN})_4$ the maximum e also lies in the MO region besides the maxima b, c, and d (figures 2 and 3).

If the fluctuations in the absorption coefficient in the vicinity of the x-ray discontinuity are small compared to the mean level of absorption, then according to Kozlenkov (1961), the absorption coefficient $\tau(\mathbf{k})$ is given, considering the first coordination sphere only, as

$$\tau(\mathbf{k}) = A(\mathbf{k}) \sin(2kr_1 + 2\eta) \quad (1)$$

where $A(\mathbf{k})$ is some function of the wave vector \mathbf{k} , r_1 is the distance between the absorbing atom and the first coordination sphere of ligands and η is the atomic phase shift. For the K edge, $A(\mathbf{k})$ becomes a slowly varying function of the wave vector \mathbf{k} . Then the expression (1) takes the form

$$\tau(\mathbf{k}) = \frac{B \sin(2kr_1 + 2\eta)}{2kr_1} \quad (2)$$

where B is a constant. For the K edges, Levy (1965) has shown with some approximations that the fluctuations in $\tau(\mathbf{k})$ exhibit first order Bessel function periodicity. The maximum at $k=0$ is shown to correspond to a kind of ionization or escape peak for the 1s electron. For the electrons with $k>0$, scattering is caused by a discrete charge at $r=r_1$. The subsequent minimum is therefore at $k=\pi/r_1$, which is the well known Bragg condition for diffraction. According to Levy the energy separation, ΔE in electron volts, between the escape maximum of the electron from the molecule and the subsequent minimum gives the mean radius in angstroms of the first coordination sphere through the Bragg relation

$$r_1 = \sqrt{151/\Delta E} \quad (3)$$

This equation is obtained using the expression $k=\pi/r_1$ and the relationship between wavelength in angstroms and energy in electron volts, namely $\lambda = \sqrt{151/E}$, both of which are independent of the symmetry of the initial state of the electron. Thus, assuming that the fluctuations of the absorption coefficient are sinusoidal in nature in the region of the escape peak, one can extend the use of equation (3) for the determination of bond lengths in compounds for L_{III} and other x-ray discontinuities as well.

The absorption maximum e in the curves for the octahedral compounds (except $\text{K}_3\text{ReO}_2(\text{CN})_4$) corresponds to the escape of a $2p_{3/2}$ electron from the molecule, because the peaks lying at lower energies to it belong to the MO region. In the compound $\text{K}_3\text{ReO}_2(\text{CN})_4$ the absorption maximum f corresponds to the escape of the inner electron because in this molecule e also lies in the MO region. The bond lengths (r_1) for the octahedral compounds calculated from the values of the energy separation $\Delta E[(e-\gamma)$ or $(f-\delta)]$ according to Levy's method are given in table 1.

The absorption maximum f in the curves for the tetrahedral compounds represents the escape peak, because the peaks lying at lower energies to it belong to the MO region. The observed energy differences between the maximum f and the minimum δ in the fine structure have been used to calculate the bond lengths in the tetrahedral compounds. The standard error, obtained statistically, in the values of ΔE is found to be within ± 2 eV and, therefore, the errors in the determination of the bond lengths lie within $\pm 0.07 \text{ \AA}$.

The crystal structure of K_2ReCl_6 and K_2ReBr_6 have been reported by Aminoff (1936) and Templeton and Dauben (1951) respectively. The octahedral units in

both these compounds are regular. The crystal structures for $(\text{pyH})_2 \text{ReCl}_6$, $(\text{dipyH})_2 \text{ReCl}_6$ and $\text{Re}(\text{dipy})\text{Cl}_4$ have not been reported so far. It can be assumed that the octahedral units in $(\text{pyH})_2 \text{ReCl}_6$ and $(\text{dipyH})_2 \text{ReCl}_6$ are regular. In the compound $\text{Re}(\text{dipy})\text{Cl}_4$, the Re ion is surrounded octahedrally by four chlorine and two nitrogen atoms of the (dipy) ligand. The compound $\text{K}_3\text{ReO}_2(\text{CN})_4$ which has a *trans* form (Cotton and Wilkinson 1967) contains two oxygen atoms and four cyanogen groups in octahedral sites. Meisel (1932) has reported the crystal structure of ReO_3 . In this compound, the Re ion is surrounded octahedrally by six oxygen atoms forming a regular unit. Wyckoff (1948) and Morrow (1960) have shown that in the compounds KReO_4 , NH_4ReO_4 and NaReO_4 , the rhenium ions have tetrahedral coordination.

The bond lengths obtained from the available x-ray diffraction data are given in the last column of table 1 for comparison. The agreement between our values and those obtained from x-ray diffraction work is satisfactory. The x-ray diffraction data for the compounds $(\text{pyH})_2 \text{ReCl}_6$, $(\text{dipyH})_2 \text{ReCl}_6$, $\text{Re}(\text{dipy})\text{Cl}_4$ and $\text{K}_3\text{ReO}_2(\text{CN})_4$ are not available. It seems reasonable to expect that our values for these compounds are fairly reliable, on account of the satisfactory agreement between the bond lengths determined by the absorption edge fine structure method and the x-ray diffraction data in the other compounds.

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