The development of a combined simultaneous XAFS/FTIR facility for the study of matrix species

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The development of an experimental facility that allows for the combined, simultaneous collection of both XAFS and FTIR data is presented. The application of this technique to the study of matrix isolated RbReO₄ is discussed.

1. Introduction

The use of matrix isolation techniques where highly reactive and unstable (vapour phase) species are stabilised in cryogenic hosts at low temperatures is relatively common. However, the vast majority of spectroscopic techniques employed to characterise the matrix isolated species are not able to give either intra- or inter-atomic distances. Therefore, we have set up a research programme (Beattie *et al.*, 1989, 1992, 1994; Young, 1990, 1991, 1996) to use XAFS to obtain bond-length information from such matrix isolated species. As all the samples have to be prepared *in-situ*, it became apparent that it would be highly desirable to be able to use a second spectroscopic technique simultaneously in order to increase the confidence of the interpretation of the XAFS data. In addition, such a facility would also allow for the observation and correlation of the effects of annealing or photolysis of the matrix. The most commonly employed spectroscopic technique for matrix isolation experiments is infrared, and in particular FTIR as this gives very good speciation data, with sharp well resolved features. Previously, we have reported a combined XAFS/FTIR experiment (Young and Spicer, 1990), but this employed sequential collection of the FTIR and XAFS data. Therefore, we decided to develop a combined XAFS/FTIR facility that would allow for the simultaneous collection of data from both techniques. Such a facility is the subject of this paper.

2. Experimental Considerations

The requirements for carrying out simultaneous IR and XAFS measurements are not trivial due to the restricted space and access in many XAFS stations and also there are not many window and substrate materials that are suitable for both techniques. In order to maximise the efficiency of the design it was felt desirable to incorporate the possibility of carrying out either transmission IR or reflectance IR experiments using the same set-up. The design finally adopted, constructed and commissioned is shown in Fig 1 for both transmission and reflectance geometries. The heart of the apparatus was a machined aluminium block (*ca.* 6" x 8") that contained a variety of ports that allowed for the passage of X-rays (Be windows) or IR (CsI windows), as well as the sample furnace and fluorescence window (Be foil mounted in a re-entrant flange). The sample deposition substrate was CsI for the IR transmission experiments and a polished high purity Al (99.999%) sputtering target for the reflectance IR experiments. These were maintained at below 10 K by an APD DE204SL closed cycle helium cryostat. The samples were sublimed from quartz holders within the resistively heated tantalum wound quartz furnace (temperature monitored by a thermocouple) and mixed with the matrix gas prior to condensation, the exact experimental conditions having been determined by off-line experiments in the home laboratory. The growth of the sample was monitored by changes in both the XAFS and FTIR spectra (see Fig. 2 below). In addition to the ports shown there were also ports above and below the left hand sample ports to allow for matrix gas entry (ca. 3 mmole/hr) and also photolysis irradiation. The vacuum chamber was pumped through large bore tubing by a turbo-pump and liquid nitrogen trap, and pressures of *ca.* 1 x 10⁻⁶ mbar were achieved in the chamber prior to turning on the cryostat. The IR experiments were carried out using the external beam facilities of a Bruker IFS66 FTIR spectrometer with either a KBr beamsplitter for the mid-IR (MIR) or Mylar beamsplitters for the far-IR (FIR), and in both cases DTGS detectors were employed with CsI (MIR) or PE (FIR) windows. The IR beam was focused to *ca.* 2-3 mm at the sample using the parabolic mirrors, and the ellipsoidal mirrors then re-focused the beam onto the detectors. We found that it was possible to get 10-20% light throughput, compared to the main sample compartment, but due to the quality of the spectrometer, this was still more than adequate for the experiments. We have noted however, that the positioning and shielding of the electronics is vital, as the Bremsstrahlung radiation from the
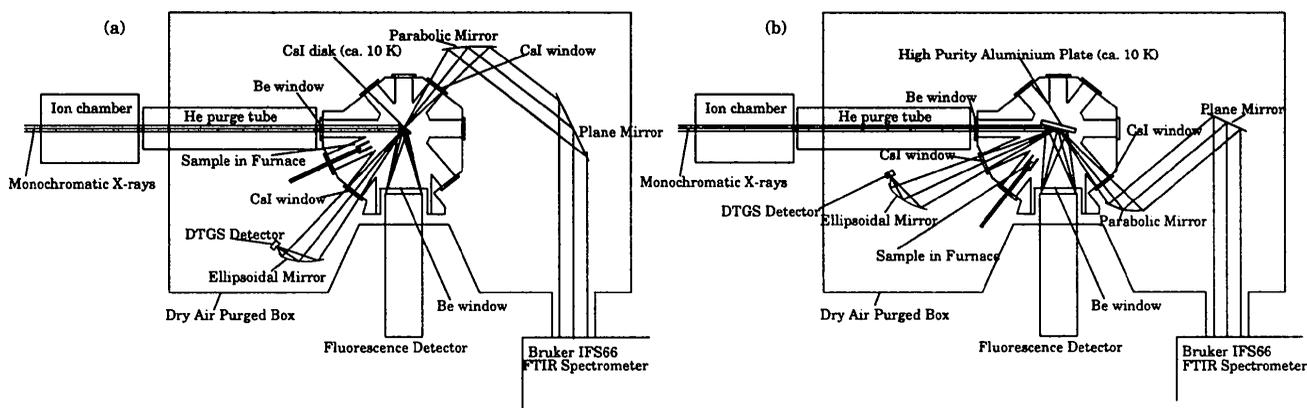

Figure 1
Schematic Layout for Combined XAFS/FTIR experiments, (a) transmission IR, (b) reflectance IR.

Wiggler magnet caused severe noise problems. In order to reduce absorptions due to atmospheric water and carbon dioxide the experiment was placed in a dry air purged box. The XAFS measurements were carried out on station 9.2 of the Daresbury SRS using a Si(220) double crystal monochromator operating at 50% harmonic rejection. Appropriately filled ion chambers and either a NaI/Tl scintillation counter or a multi-element SSD were used for measuring I_0 and I_f, respectively. In general, we found that the scintillator gave very acceptable data. The X-ray air path was reduced as much as possible by the use of He purge tubes.

We have successfully used the apparatus in both the transmission (Young, 1996) and reflectance IR geometries (see below). Initially, transmission IR was employed to reduce the problems of the central deposition window acting as an optical component, but more recently we have found that the data quality from both the IR and XAFS experiments is improved if the reflectance geometry is used. We do find however, that we tend to be working at the extreme detection limits of both techniques, i.e. in order to get sufficient sample for good quality XAFS data, the IR data is nearly saturated at the absorption bands. In the near future we intend to re-locate the experiment to station 16.5 at the Daresbury SRS, where there should be an order of magnitude increase in the X-ray flux at the sample. In addition, there is more space available in order to improve the vacuum characteristics of the chamber.

3. Application to the Study of the Molecular Structure of RbReO₄.

Matrix isolation has found widespread use in the study of high temperature chemistry, where the spectroscopic characterisation of the vapour phase species can be a major obstacle. In a number of cases vapour phase electron diffraction has also been used to determine the structure of the vapour phase species, but this is often fraught with difficulties such as the vapour composition and 'soft' bending modes. One class of compounds that has been well studied are the oxy-anions of general formula A_xMO_y, where $x = 1,2$ and $y = 2-4$. In general, the co-ordination of the cation is bidentate, but rare examples of tridentate co-ordination such as in $CsClO_3$ (Beattie and Parkinson, 1983) are known. The perrhenate anions have been studied by both matrix isolation IR

(Bencivenni *et al.*, 1979, 1984; Arthers *et al.*, 1983) and by vapour phase electron diffraction (Spridonov *et al.*, 1965; Roddatis *et al.*, 1973; Petrov *et al.*, 1980), therefore we decided to use RbReO₄ as a test example for the new apparatus. Whilst the matrix IR spectrum (Bencivenni *et al.*, 1984; Arthers *et al.*, 1983) of this has been reported, the ED data was only available for CsReO₄ (Petrov *et al.*, 1980) and TlReO₄, (Roddatis *et al.*, 1973) and that for KReO₄ (Spridonov *et al.*, 1965) was very poor. The IR and ED data both indicate that the structure of these molecular species have C_{2v} symmetry with bidentate co-ordination of the Rb.

Fig. 2 shows the Re L₃-edge XANES and FTIR spectra recorded simultaneously during deposition of RbReO₄ into a solid N₂ matrix at 10 K. The IR spectra are shown for the Re-O stretching region, and are in very good agreement with those published previously (Bencivenni, 1984). The only other significant features in the IR spectra were from the ubiquitous matrix isolated H_2O, CO_2 and CO that are always present in such experiments. On the basis of previous ^{18}O enrichment studies (Arthers, 1983; Bencivenni, 1984) the bands are assigned as: 970.0 cm⁻¹ (v_{A_1} terminal), 941.1 cm⁻¹ (v_{B_2} terminal), 914.6 cm⁻¹ (v_{A_1} bridging), 893.6 cm⁻¹ (v_{B_1} bridging). The other very low intensity bands are probably due to small traces of dimeric species also trapped in the matrix, thus indicating the usefulness of combined *in-situ* FTIR monitoring in identifying the species under investigation.

Fig. 3 shows the Re L₃-edge XAFS and FT (average of 10 spectra) measured at the end of the deposition. The first peak in the FT contains the Re-O interactions, and this refined (using EXCURV98 (Binsted, 1998)) to a single shell of oxygen atoms at 1.74(2) Å with a Debye-Waller factor of 0.004 Å². When two shells were used, and the Debye-Waller factors constrained to the same value, the Re-O distances refined to the same value. Therefore, we believe that there is no evidence for anything but a regular tetrahedral geometry at the Re metal. In the case of the ED data on CsReO₄ (Petrov *et al.*, 1980) and TlReO₄ (Roddatis *et al.* 1973) carried out at *ca.* 570 °C the Re-O distances were 1.737(5) and 1.72(1) Å, respectively, and there was also no
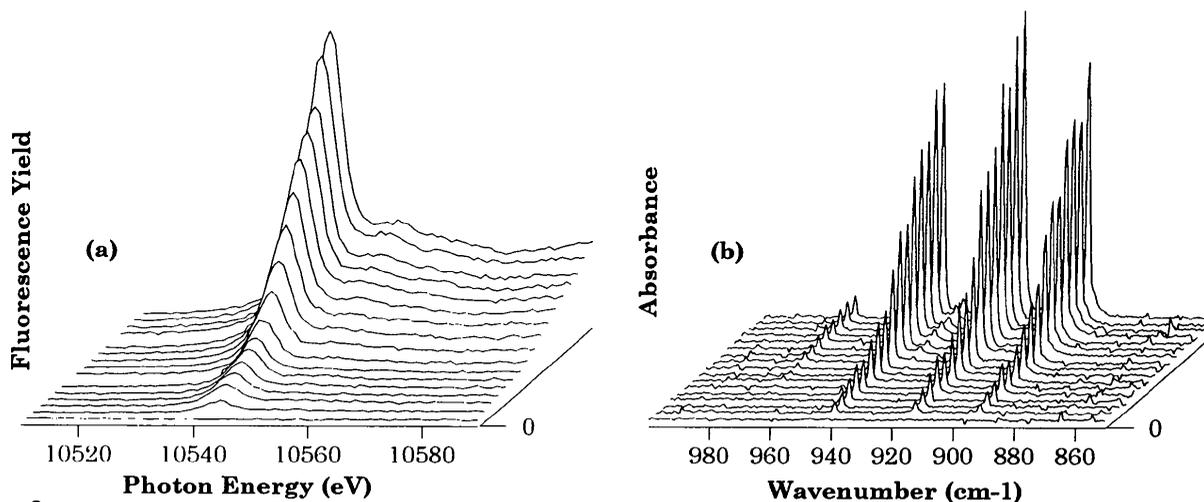

Figure 2

Simultaneous Re L₃-edge XANES (a) and FTIR spectra (b) collected during the deposition of RbReO₄ into a nitrogen matrix at *ca.* 10 K.
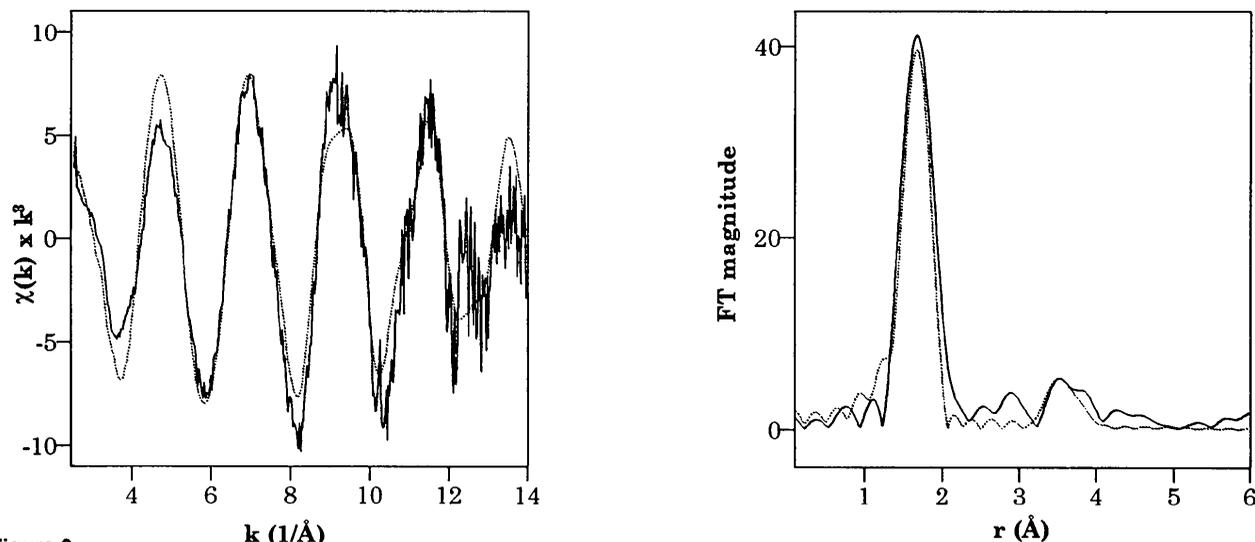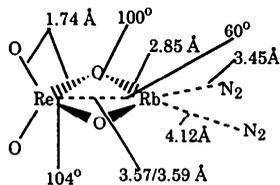
Figure 3

Re L_3-edge XAFS and FT for $RbReO_4$ isolated in a nitrogen matrix at ca. 10 K. (Solid line, experiment, dotted line, theory)

evidence of two Re-O distances. Whilst this might be expected due to the high temperature at which the experiment was carried out, the matrix IR data at ca. 15 K also indicated that the cation has very little effect on the ReO_4 tetrahedron with OReO bond angles of 109° and 102° for the terminal and bridging modes respectively in $CsReO_4$. The Re L_3-edge XAFS data also gave a Re...Rb distance of 3.57 Å, which compares very favourably with the Re...Cs distances of 3.58 Å in $CsReO_4$. Whilst the Rb K-edge data set was very noisy (even though about 15 data sets were averaged together), we were able to extract some structural data. In addition to Rb-O and Rb...Re distances of 2.85 and 3.59 Å, respectively, the data also contained significant contributions from Rb...N distances at 3.45 and 4.12 Å, indicating the nature of the host-guest interaction.

4. Conclusions

We have demonstrated the usefulness of a combined XAFS/FTIR facility for the study of matrix isolated species, and shown using $RbReO_4$ as an example how it can be used to determine intra- and inter-molecular bond lengths in matrix isolated species. The inter- and intra-atomic distances obtained in this study are only consistent with a bidentate co-ordination (as shown pictorially) in good agreement with the matrix IR data and previous ED data. We are currently using the facility for the study of the interaction of 3d transition metal halides with inert and reactive pro-ligands.

1.74 Å   100°
O   60°
      2.85 Å
        O   3.45Å
Re   Rb   N₂
      O
           4.12Å   N₂
O
104°   3.57/3.59 Å

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