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Introduction

These on-going investigations concern the use of anomalous elastic scattering for the detection of oxidation states, in particular but not exclusively of those which have interesting biological consequences, including Zn^{2+} , an important precursor to malignancy in breast due to its focal role within the metalloproteinase (MMP), MMP II. The investigations build upon results obtained in a three year XRF study conducted in conjunction with colleagues from City University (Geraki et al., 2002, 2004a,b), and from association with the atomic physics theory group of R.H. Pratt at the University of Pittsburgh. Using a highly sensitive synchrotron XRF technique at the bending magnet beamline XMaS (ESRF), the City University group were able to characterize normal and benign breast tissue in terms of trace elemental concentrations, allowing distinction from malignant tissues. It is apparent that in diseased tissues there are particular elevations of Zn, as well as other elements such as Fe and Cu. While XRF will detect concentrations of an element such as Zn it is clearly not sensitive to the oxidation state of the element. Recent work by the Exeter group has indicated that pre-edge anomalous Rayleigh scattering can provide such information (Hugtenburg et al., 2002; Hugtenburg and Bradley, 2003).

Few direct measurements of anomalous Rayleigh scattering exist, due to difficulties in for instance correcting for target size, attenuation and source profile. In studies conducted by this group at the XMaS beamline, direct measurement of anomalous scatter cross-sections have been attempted for several elements over a limited photon energy range starting from just below the K-edge. Results from these confirm predictions from the independent atom approximation, in particular the oscillatory nature of below edge structure due to electron bound-bound resonant intermediates. In these studies we have been seeking to examine the influence of atomic and oxidation number on the size and structure of bound-bound resonant peaks. Attenuation effects have been minimised by employing dilute solutions of salt solutions and also thin film depositions of the associated neutral metal. General trends, predicted within the independent particle approximation, have also been confirmed including increase in the size of bound-bound resonances with decreasing Z and with

increased ionization state. Figure 1 demonstrates particular relevance to the low-Z electrolytes of biological systems, the lines being provided as a guide to the eye.

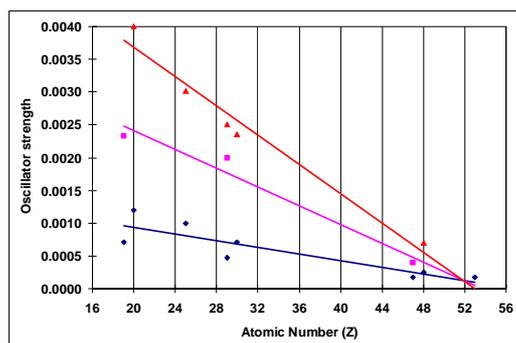


Figure 1. General trend in oscillator strength as a function of Z and charge (blue = neutral, pink = +1, red = +2).

While previous synchrotron studies utilizing fine structure in anomalous diffraction have been greatly successful, the fine structure of interest is above edge and corresponds to interatomic effects. The current work focuses on fine structure entirely generated by an atomic effect and predicted within the confines of the independent atomic model, with electronic configurations defined by the Dirac-Slater exchange potential. Bound-bound resonance occurs with the summing of intermediates associated with the Rayleigh scatter amplitude, being physical when a bound electron has access to an unoccupied orbital. In the case of neutral and chemically ionised systems this involves transition to a higher energy state, resonances occurring for bound electrons at energies above associated below-edge emissions such as resonant Raman scatter (RRS) and fluorescence. Available anomalous scattering factors (ASF) provides a qualitative guide to the energy dependent structure in the vicinity of the atomic orbital binding energies. The construction, based on the Kramer-Kronig relations, is a composite of two resonant effects, that of photoionisation and photo-excitation. Photo-ionisation leads to the familiar broad minima centred on the ionisation threshold; photo-excitation or bound-bound resonance introduces a significant constant contribution to the cross-section as well as rapid fluctuations below edge forming a Rydberg series of maxima and minima approaching the edge.

Findings

We have focused on measurement and evaluation of near edge structure for atoms and ions in the aqueous system, dominated below edge by bound-bound resonance. Preliminary results have concurred with the most common method of measurements of anomalous scattering, determined for thin crystalline samples or vapour-deposited metallic material. Solutions give access to ionic states, several examples of simple molecular systems possessing effectively a neutral coordination in an amorphous arrangement. As an example, and also to validate utility of anomalous scatter in such an arrangement, measurements were first made for a 3.7 mg/ml solution of molecular iodine is shown in figure 2 below. These results were obtained in a pilot study using the ultra-dilute EXAFS beamline 16.5, Daresbury.

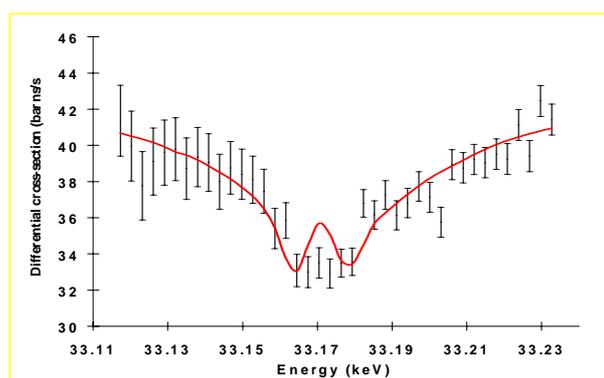


Figure 2. Results for molecular iodine, showing structure below the K-absorption edge at 33.164 keV and concurring with the predictions from existing theory, indicated by the solid line.

The measurement agrees qualitatively with the predicted cross-sections provided by the University of Pittsburgh group. The energy of the minimum at 10 ± 5 eV below the K-edge (33.164 keV) is in reasonable agreement with the ASF prediction (10.2 eV), incorporating a small influence of the below-edge bound-bound resonance structure. Measured Rayleigh scattering differential cross-section for iodine in the vicinity of the K-edge have been compared with relativistic form factors with ASF corrections from an existing database (Hugtenburg et al., 2002). Another example (Fig. 3), demonstrating sensitivity to charge state, concerns measurements of near-edge Rayleigh scatter for a dilute (1 mg/ml) solution of manganese (II) sulphate. The results demonstrate the strong influence of both charge state and Z value on the size of the bound-bound oscillations (further supporting predictions of Figure 1). The line in red represents the neutral atom prediction, while that in blue depicts the Mn^{2+} prediction (Hugtenburg and Bradley, 2004).

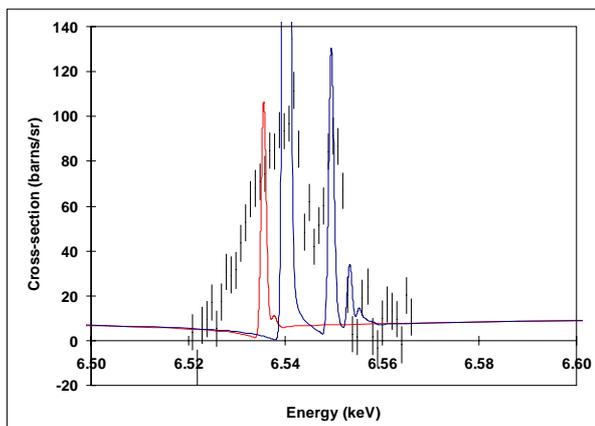


Figure 3. Results for Mn^{2+} , showing below-edge structure (the absorption edge for the neutral species being at 6.537 keV).

Discrepancies with predictions, in particular broadening, are anticipated in the dilute aqueous system, being suggestive of complex effects; our results for Mn show the strongest resonance from 1s to 4p and 5p transitions to be broadened (by around 5 eV), possibly due to the excitation of valence electrons to perturbed states in the aqueous environment. The suppression of resonance involving occupied orbitals may offer information about the availability of certain chemical

pathways. The results suggest a role for the bound-bound contributions, known to be important for atoms and ions with valence configurations that allow transitions from a bound s-orbital to an unoccupied 4p-orbital or below. In the particular circumstance, bound-bound oscillations generate minima several 10's of eV below the real position of the edge. In direct analogy to photo-excitation we anticipate that the bound-bound resonance structure offers a probe of the unoccupied state. Resonance occurs at high resolutions (within several eV of the edge). At XMaS, we have proceeded to obtain results for Cu^{2+} (Fig 4).

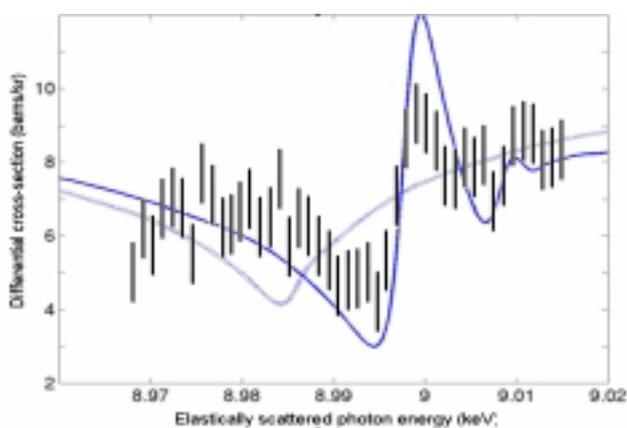


Fig. 4. The darker line represents predicted anomalous scattering cross-sections for Cu^{2+} ; the lighter line provides the same for neutral Cu. The absorption edge for neutral Cu is at 8.98 keV.

Finally, in Fig. 5, preliminary results are shown for a 1 mol ZnCl_2 solution, indicating anomalous scattering for Zn^{2+} . The results, preliminary in nature, encourage further research, in particular towards seeking improvement in measurement sensitivity.

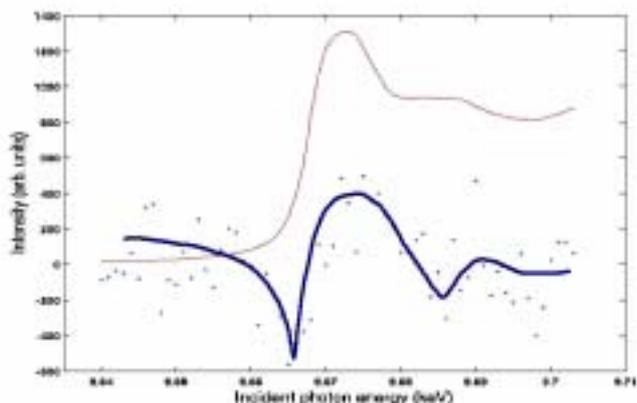


Figure 5. The line in red represents the rising absorption edge for Zn; measured points refer to the anomalous scattering signal for Zn^{2+} . The line in blue is a guide to the eye and should not be construed to be predictions (predictions from the Pittsburgh group are in progress).

References

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