Solving Self-Absorption in Fluorescence: Stereochemical Analysis of mM solutions

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Introduction

95% of research uses measurement of a secondary fluorescence photon, which suffers from uncalibrated detector efficiencies and a dominant systematic of self-absorption of the fluorescence photon, which compromises accuracy, analysis and insight. We have developed, coded and implemented a novel self-consistent method to correct for self-absorption seen in high-energy fluorescence X-ray measurements *(1)*. The results herein demonstrate an enormous improvement over any previous attempt to correct for this systematic in the literature and are based on the best theoretical foundation. This method and the resulting software package can be applied to any fluorescence data set, leading to a general solution applicable to a wide-range of experimental investigations. In this way, accurate experimental uncertainties are obtained and implemented in an IFEFFIT-like stereochemical analysis of two mM nickel (II) complexes.

Experimental Methods

Fluorescence and transmission XAS measurements were simultaneously taken of two closely-related organometallics: bis(N -n-propyl-salicyladiminato) nickel(II) (n-pro) and bis(N -i-propyl-salicyladiminato) nickel (II) (i-pro) at the Australian National Beamline Facility, Tsukuba, Japan. The detector used to collect the fluorescence data considered here was a 36-element Ge monolithic planar detector (EURISYS EPIX 35-64-7-ER) produced by Canberra-Eurisys.

Results and Discussion

The complexes considered in this work, n-pro and i-pro, have been shown to have local metal environments with approximate tetrahedral and square planar coordination geometries. A previous publication by this group has confirmed these structures using 'transmission mode' XAFS *(2)*. This provides an excellent test of fluorescent multi pixel data, and further demonstrates the merit of using complimentary techniques to confirm molecular geometries *(3,4)*.

A dramatic discrepancy is seen between the spectra from the two measurements. There is a large dispersion between the individual fluorescence spectra, and the spectral shape has been distorted, preventing high-accuracy analysis. This is due to the self-absorption systematic and also to uncalibrated detector efficiencies in the fluorescence measurement. While the detector

efficiency can be corrected for, there is currently no self-consistent method for removing the effect of self-absorption from the spectra. Previous attempts to remove this systematic have been unable to reduce the variance between spectra significantly and have not produced a physically significant trend with energy. In this work, we predict to high-accuracy the magnitude of dispersion and energy functional due to self-absorption, using the best theory in the literature (*5*). We have developed, coded and implemented a software package entitled SeAFFluX (Self-Absorption Fitting of Fluorescent X-rays) to correct for this systematic in a self-consistent and robust manner. As a result, the dispersion is greatly reduced, and the spectral shape follows the classic XAS trend. The results presented here demonstrate a dramatic improvement over any previous work in the literature. The talk will also discuss insight gained by determining uncertainty from evaluated variance.

Conclusions

The demonstrated success of our self-absorption correction method is an incredibly significant achievement. Prior to the development of our self-absorption correction, the high-accuracy analysis of thousands of critically-important data sets on chemistry, bonding, biological dynamics and disease was impossible and led to countless data sets left only partially analysed and unpublished or abandoned entirely. Our modern theory is of the best quality, allowing our self-absorption correction to be applied to any fluorescence XAS data set and opening up an entire class of experimental investigation.

References
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