	Experiment title: Sulfur speciation of heavy oil fractions by X-ray absorption spectroscopy	**Experiment number**: CH2425
Beamline:	**Date of experiment**: from: 25th April 2007 to: 1st May 2007	**Date of report**:
Shifts:	**Local contact(s)**: Jean Susini, Murielle Salomé	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Ana Mijovilovich*
Frank de Groot
Bert Weckhuysen

Report:

It is known that the sulfur content of crude oils is increasing due to the use of more heavy and ultra-heavy crudes. At the same time, the regulations for sulfur content in transportation fuels are getting stricter. Together, this implies that in the refinement the desulfurization has to be drastically improved to keep acceptable levels of product quality. Knowledge of the composition of crude oils at the molecular level will allow identifying the desulfurization steps that need to be improved.

Sulfur K-edge XANES may assist in obtaining this improved sulfur speciation [1-3]. The sulfur XANES speciation capacity will be exploited to understand the basic features of the XANES spectra and their relation to the structure at the molecular level. So far the XANES has been used as fingerprinting, used for principal component analysis, based on a few reference compounds, targeting for the real composition at the molecular level of very complex oil samples. However, it has been shown that compounds showing the same coordination may have different XANES spectra when the chemical nature of the compounds is different, for example peptide vs. inorganic compounds [4]. The understanding of the relation between the chemical properties (aromatic vs. thiophenes, the influence of the number of rings in aromatic compounds) and edge features (edge position, height and shape of white line, and the additional resonances at the edge, small shoulders) is lacking for the sulfur compounds present in oils and its derivatives. Recent advances in XANES computer codes have provided a theoretical base for the experimental results in molecular biology for example [5], and a similar approach is attempted in this work.

Experimental method

Sulfur K-edge XANES was measured in ID21 at ESRF, for a number of thiophenic and aliphatic sulfur compounds. Samples of crude oil fractions were also measured. All samples were measured in fluorescence mode, in order to minimize self-absorption effects. The solid samples were measured as solid powders and also diluted in toluene and also diluted in 1-methyl naphthalene.

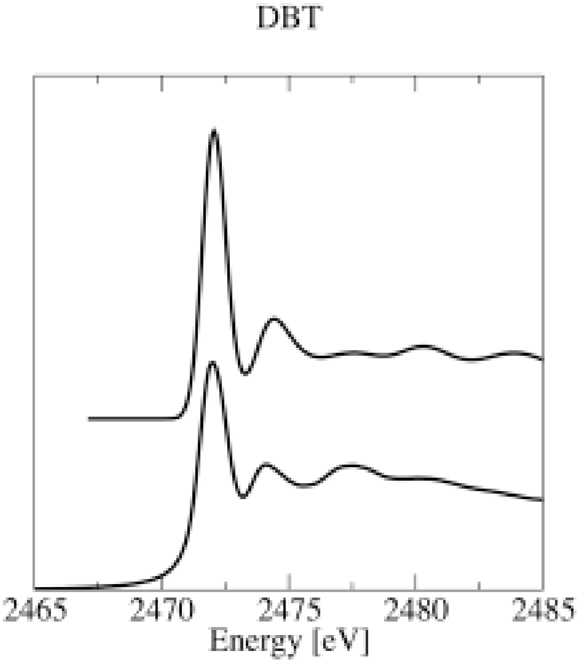
DFT simulations of the XANES spectra were performed using StoBe [6]. The calculated transitions were broadened using Gaussians with a linearly increased broadening up to 4 eV in the first 20 eV after the edge.

Results

In [7] we simulated the sulfur K-edge XANES for three model compounds containing thiophenic (dibenzothiophene and dibenzothiophene sulfone) and aliphatic (DL-methionine) sulfur. While thiophenes constitute the most abundant fraction of sulfur compounds in crude oil after desulfurization, methionines are very important in enzymatic redox processes. Thus, these compounds provide a good starting point to understand the influence on the spectrum profile of the molecular orbitals of these selected functional groups.

The simulations reproduce well the spectra and the position of the edge (within 0.3 eV) (Fig1). Analysis of the molecular levels of the first unoccupied orbitals ("LUMOs") (Fig 2) shows the similarities and dissimilarities of the compounds. For example, the similar edge position and shape of the white line for DBT and DLM makes it difficult to differentiate between the two compounds. However, when looking at the energy distribution of the LUMOS, the difference in the broadening of the white line can be explained by the different spreading in energy of the first transitions.

Identical groups can lead to very different XANES. In [7] we have shown that similar XANES may stem from different functional groups, posing a problem for speciation. However we have shown that the small differences in the shapes of their white lines and frequency of the higher oscillations stem from the different electronic structure of the groups, setting a theoretical basis to use them for speciation. The same analysis is being done on dibenzyl and diphenyl sulfur compounds, and the results will be published elsewhere.



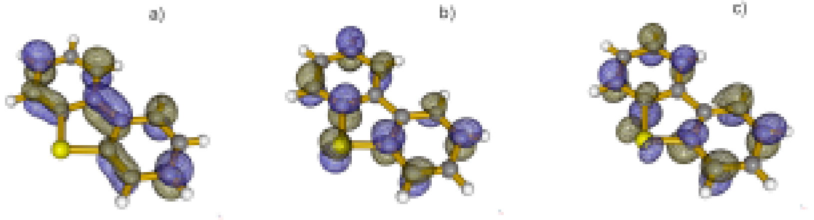


Fig. 1 (left). Experiment and simulations fo Dibenzothiophene: a) experiment, b) relaxed with no orthogonal transition moments.

Fig. 2 (top right). Lowest Unoccupied Molecular Orbital contributing to the white line of DBT: a) LUMO, LUMO+1, c) LUMO+2.

References

[1] G.S. Waldo, O.C. Mullins, J.E. Cramer, S.P. Cramer. Fuel 1992, 71, 53-57.

[2] E. Wiltfong, S.Mitra-Kirtley, O.C. Mullins, B. Andrews, G. Fujisawa, J.W. Larsen. Sulfur speciation in different kerogens by XANES spectroscopy. Energy & Fuels, 2005, 19, 1971-1976.

[3] G. Sarret, J. Connan, A. Kasrai, M. Bancroft, A. Charrie-Duhaut, S. Lemoine, P. Adam, P. Albrecht, L. Eybert-Bérard. Chemical forms of sulfur in geological and archeological asphaltenes from Middle East, France, and Spain determined by sulfur K- and L-edge X-ray absorption near-edge structure spectroscopy. Geochimica et Cosmochimica Acta, 1999, 63, 22, 3767–3779

[4] K. Clark-Baldwin, D.L. Tierney, N. Govindaswamy, E.S. Gruff, C. Kim, J. Berg, S. A. Koch, J.E. Penner-Hahn. The Limitations of X-ray Absorption Spectroscopy for Determining the Structure of Zinc Sites in Proteins. When Is a Tetrathiolate Not a Tetrathiolate?. J. Am. Chem. Soc. 1998, 120, 8401-8409.

[5] A. Mijovilovich, W. Meyer-Klaucke. Simulating the XANES of metalloenzymes- a case study. J. Synchrotron Rad. 2003, 10, 64-68.

[6] StoBe-deMon code. K. Hermann, L.G.M. Pettersson, et al. 2001

[7] A. Mijovilovich, L.G.M. Pettersson, S. Mangold, M.J. Janousch, J. Susini, M. Salomé, F.M.F. de Groot, and B.M. Weckhuysen. On the interpretation od Sulfur K-edge XANES spectra: a case study on thiophenic and aliphatic sulfur compounds. J. Phys. Chem. A 2008, submitted for publication.