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EXAFS of nebulized solutions

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Abstract. — The first EXAFS results on nebulized solutions are presented. High quality spectra from *in situ* X-ray absorption experiments are performed on micrometer-sized spheres of nickel (II) bromide in 95% alcoholic or in aqueous solution via ultrasonic nebulization. The structural information given by the X-ray absorption complete the data given by other absorption spectroscopies. The strong dissociation of the precursors is shown and the first coordination sphere of the nickel atom is evidenced. It is formed by nickel atoms surrounded by hydrating water molecules.

The optical properties of small particles, which have been reviewed by Campillo and Lin [1], have been the subject of a great number of studies during the past years: absorption (using visible or infrared radiation) and fluorescence are two techniques among the powerful spectroscopies in aerosol analysis. They use radiation with a wavelength larger than the size of the droplets. Aerosol is considered as a stable dispersion of small particles into a gas phase. The first theory concerning the optical behavior of a mist is based on the solution of the Maxwell's equation for scattering and absorption of electromagnetic waves by a dielectric sphere by Mie [2] and more recently by Kerker [3]. The propagation of a high intensity laser beam through an absorbing aerosol cloud has been described by Walsh *et al.* [4]. In spite of an extensive number of available spectroscopic analysis, there remain some unresolved structural problems at the nanometer scale concerning atomized products. Our aim is to develop an *in situ* absorption technique adapted to nebulized solutions by extending the spectroscopic studies of aerosols to the small wavelengths into the X-ray range.

A schematic diagram of our experimental arrangement is described in figure 1. A detailed description of the ultrasonic nebulizer used to produce gels of zirconia particles [5] and further studied by EXAFS can be found elsewhere [6]. Nickel (II) bromide dissolved in a 95% ethanol solution is introduced in the reservoir. The nebulization chamber is then circulated with helium during five minutes. A mist of the solution is thus generated by the atomizer which active part is constituted by a piezoelectric transducer operating at a frequency of 1.6 MHz. The diameter of the droplets is given by the relation $d = [\pi\sigma/4\rho f^2]^{1/3}$ where σ and ρ are respectively the surface tension and the density of the solution and f is the frequency of the transducer, $d = 2 \mu\text{m}$ in our experiments. The micrometer-sized spheres are carried by a circulator toward

Fig. 1. — Outline of the experimental set up used for the X-ray absorption measurements of a mist of micrometer-sized droplets of solutions. The apparatus is composed of an ultrasonic nebulizer producing the mist from a 5 cm high geyser generated from the solution. The spray chamber is designed to promote a good mixing and transport of the aerosol towards the analysis cell where the droplets are irradiated in various situations. A close circuit permits to keep a constant level in the solution and a stable density of particles in front of the X-ray source.

the X-ray irradiation cell for XAS experiments. We note two important advantages of the ultrasonic nebulizer: first the aerosol is practically monodispersed, secondly both aerosol production rate and carrier gas flow rate can be independently varied.

The typical EXAFS measurements, at room temperature, were carried out at LURE (Orsay) on the Ni K-edge (8250-9000 eV energy range). The synchrotron radiation was provided by the 1.85 GeV storage ring of DCI. The X-ray beam of the EXAFS IV station was monochromatized by a double Bragg reflection (111) of Si crystals. The intensity of the positron beam was about 300 mA. We used an air-filled ionization chamber to measure the photon intensity before the target. In order to avoid charging of the droplets under X-ray irradiation, we have used helium at atmospheric pressure as a carrier gas which furthermore has the advantage of a low X-ray absorption cross section. We note a smaller signal/noise ratio for those data obtained with an air filled cell. A fluorescence detector is used for measurement of the absorption coefficient, the escape depth of photons being in the range of a few micrometers. The fluorescence detection consists of a plastic scintillator coupled with a high gain photomultiplier. In order to reduce the photon fraction contributing to the background of the spectra at the Ni K-edge, we used a cobalt filter placed in front of the scintillator that absorbs the scattered photons. The advantage of the fluorescence detection is well recognized for the local structural study of very dilute solutions, it is in addition fair adapted for our geometrical configuration.

Four samples have been examined by EXAFS: two molar solutions prepared by dissolving NiBr_2 in 95% ethanol or in water and two crystallized compounds: Ni and $\text{NiBr}_2 \cdot 2\text{H}_2\text{O}$. These powders have been used as standards for determining the phase shifts and the amplitude factors in the analysis procedure of the EXAFS spectra. NiBr_2 crystallizes in a close-packed cubic structure built from layers of octahedral NiBr_6 coordination groups each sharing an edge common with six others adjacent groups. The Br^- anions are characterized by a pyramidal coordination. Weigel [7] has elucidated the structure of the dihydrate: each nickel ion is surrounded by two water

molecules such that the Ni–O distance is 0.20 nm, the four Br[−] ions are located at 0.26 nm from the Ni atoms. The oxide NiO [8] which has a NaCl structure where Ni and O atoms alternate in a simple cubic packing, each atom being surrounded by six others at the vertices of a regular octahedron.

Fig. 2. — *In situ* experimental EXAFS oscillations $\chi(k)$ above the Ni K-edge of a nebulized molar solution of NiBr₂ in 95% ethanol.

The mathematical treatment of the spectra is based on the procedure previously described [6]. The data were first calibrated, averaged and normalized. The backgrounds were subtracted and the EXAFS oscillations were Fourier transformed. The k -space used for the Fourier transform was limited by $k_{\min} = 26 \text{ nm}^{-1}$ and $k_{\max} = 120 \text{ nm}^{-1}$. The least squares fitting method for coordination shell determination has been employed with values of phases and amplitudes calculated according to the procedure of McKale *et al.* [9]. The first coordination shell of the nickel ions is formed by bromide ions and oxygen issued from H₂O molecules. The Br[−] are too close to each other to be resolved on the Radial Distribution Function. The free parameters used in the fit procedure were the interatomic distance, the coordination number and the Debye-Waller factor while the K-edge position shift was fixed. The reliability factor of least squares fitting of the data for the four samples were similar. Figure 2 shows the fine structures of the absorption above the Ni K-edge of a nebulized molar solution of NiBr₂ in 95% ethanol. We note that this spectrum exhibits oscillations containing information mainly associated to the Ni–O bonds.

Fig. 3. — Module (full line) and imaginary part (dotted line) of the Fourier transform corresponding to the k^3 -weighted EXAFS spectrum of a nebulized molar solution of NiBr_2 in 95% ethanol. The pseudo radial distribution functions are uncorrected for the phase shift of the Ni–O and Ni–Br pairs.

Two sub-shells are required to fit EXAFS data of both aqueous and alcoholic solutions as well as for that of the $\text{NiBr}_2 \cdot 2\text{H}_2\text{O}$ standard. The Ni–Br contribution is included in a shoulder of the Ni–O peak illustrated in the figure 3 for the nebulized solution of NiBr_2 in ethanol. The major contribution of the peak appears at a distance $R = 0.205$ nm of the nickel cation, it is attributed to the oxygen atoms of the water molecules in accordance with the X-ray diffraction results of Caminiti and Cucca [10] on aqueous Ni–Br solution. The Radial Distribution Function analysis shows a Ni–Br bond at 0.254 nm. This distance is smaller than the distance $R_{\text{Ni-Br}} = 0.262$ nm found by Caminiti and Cucca and higher than the distance $R_{\text{Ni-Br}} = 0.251$ nm found by Ludwig *et al.* [11]. An achievement of this structural investigation concerns the contraction of the bonds in the nebulized solutions with an increase of the Debye-Waller factors.

This study confirms the octahedral coordination of the nickel cation in the alcoholic nebulized solution as well as in the aqueous nebulized solution, similarly as in the dihydrate bromide. In spite of the strong dissociation of the solution, the Br^- anions are replaced by water molecules in the first coordination sphere as seen in table I. Our results are in good agreement with the Differential Anomalous Scattering data of Ludwig *et al.* [11] on 4 M aqueous NiBr_2 solution and EXAFS results of Lagarde *et al.* [12] on the same solution.

We have tested for the first time the applicability of *in situ* X-ray Absorption Spectroscopy to structural characterization of micrometer-sized droplets of a mist. We can safely conclude that this technique is well suitable for giving some detailed local information about atomic distances

Table I. — Ni—O and Ni—Br bond lengths, nickel coordination numbers and Debye-Waller factors obtained by simulation of EXAFS spectra for the following samples: 1) crystallized NiO powder, 2) nebulized molar solution of NiBr₂ in 95% ethanol, 3) nebulized nickel (II) bromide in a normal aqueous solution 4) crystallized NiBr₂·2H₂O powder.

Sample	1	2	3	4
sub - shell 1				
Ni - O Dist., (nm)	0.209	0.205	0.206	0.209
Coord. Num.	6	5.7	5.6	2
σ , (nm)	0.0061	0.0068	0.0071	0.0064
sub - shell 2				
Ni - Br Dist., (nm)		0.254	0.253	0.255
Coord. Num.		0.7	0.8	4
σ , (nm)		0.009	0.0084	0.0062

and coordination numbers in such samples.

Because of the large surface/volume ratio of each droplet, the thermal and chemical exchanges are fast and efficient. Therefore this reactor should be very useful for on line studies such as evolution of the local structure of the precursor during the powder elaboration process.

References

- [1] CAMPILLO A.J. and LIN H.B., Absorption and fluorescence spectroscopy, in Optical effects Associated with Small Particles, S. Ramaseshan Ed. (Word Publishing Co., Singapore, 1988).
- [2] MIE G., *Ann. Phys.* **25** (1908) 377.
- [3] KERKER M., The scattering of light and other electromagnetic radiation (Academic Press, New York, 1969).
- [4] WALSH J.L. and ULRISH P.B., Laser beam propagation in the atmosphere, J.W. Strohbehn Ed. (Springer Verlag, New York, 1978).
- [5] DUBOIS B., RUFFIER D. and ODIER P., *J. Am. Ceram. Soc.* **72** (1989) 713.
- [6] LANDRON C., RUFFIER D., DUBOIS B., ODIER P., BONNIN D. and DEXPERT H., *Phys. Status Solidi* **121** (1990) 360.
- [7] WEIGEL D., *Bull. Soc. Chim. France* **10** (1963) 110.
- [8] WELLS A.F., Structural inorganic chemistry (Oxford University Press, London, 1975).
- [9] MCKALE A.G., VEAL B.W., PAULIKAS A.P., CHAN S.K. and KNAPP G.S., *J. Am. Ceram. Soc.* **110** (1988) 3763.
- [10] CAMINITI R. and CUCCA P., *Chem. Phys. Lett.* **89** (1982) 110.
- [11] LUDWIG K.F., WARBURTON W.K. and FONTAINE A., *J. Chem. Phys.* **87** (1980) 620.
- [12] LAGARDE P., FONTAINE A., RAOUX D., SADO C. and MIGLIARDO P., *J. Chem. Phys.* **72** (1980) 3061.