ESRF	**Experiment title:** X- RAY ABSORPTION STUDIES OF INCLUSION COMPLEXES OF ARGON IN ORGANIC SOLVENTS	**Experiment number:** CH - 221
Beamline: BL - ID12A	**Date of experiment:** from: November 23th 1996 to: November 24th 1996	**Date of report:** April lrst 1997
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l.Motivations

Rare gases have been shown to bind to proteins (e.g. haemoglobin or myoglobin) with some site selectivity : Kr or Xe are even used as probes for phase determination in X-ray protein crystallography. Specific interactions also exist with a variety of organic "cage" molecules (crown ethers, cyclodextrines, etc...) and it is the aim of this project to study the nature of the "host-guest" interaction. For Xenon complexes, valuable information can be extracted from ^{129}Xe NMR spectra. Such information is lacking for Argon which may have a wider range of potential applications. This prompted us to check whether XAFS spectra recorded at the Ar K-edge would be sensitive to "host-guest" interaction in solution.

2. Experiments

Argon trapping : A variety of cage molecules were synthesized in Dijon. The only criteria to prefer one system over another one were : (i) a slightly enhanced solubility of Ar in a given solvent ; (ii) the proved existence of interactions with Xe using ^{129}Xe NMR. Given the different size and polarisability of Xe and Ar, it is not clear how far the latter argument is relevant. Finally, we agreed to start our tests with the following solutions : (1) Argon / pentane *without any sequestering ligand* was proposed as a reference ; (2) Argon / [Kryptofix (222) : MeOH] ; (3) Argon /[cryptophane A : dioxanne]. The concentration of argon ranged from 50 **to** 200 ppm for all solutions which were studied at room temperature.

X-ray Absorption Spectroscopy : XANES spectra have been recorded at the argon K-edge in the fluorescence mode. These experiments were challenging due to : (i) the high dilution of the absorbing element ; (ii) the poor fluorescence yield (5%) of argon ; (iii) the strong reabsorption by the solvent ; (iv) the lack of filters to discriminate fluorescence against scattering. Since BL-ID12A is a windowless high vacuum beamline, the first difficulty was to design a vacuum tight liquid cell with a 12μm thin Kapton window and a large solid angle for fluorescence detection. The latter cell was also used to scan the spectra of Ar gas for energy calibration.

3. Results

As illustrated by Fig.1, spectra of unprecedented quality have been recorded on Ar gas. There is a rich pattern of well resolved multielectron excitations in a 15-30 eV range above the energy threshold : the observed signatures agree nicely with theoretical predictions by Deslattes et al. [1] using Hartree-Fock atomic calculations. With energy sampling steps as small as 10 meV and good statistics, numerical deconvolution against a Voigt lineshape became meaningful and allowed us to assign unambiguously the 1s4p, 1s5p, 1s6p atomic resonances and to set the energy threshold at 3.206.35 eV, *i.e. 0.8* eV above the 1s6p resonance as predicted by theory [2]. With an energy resolution of the monochromator close to the theoretical limit of 0.46 eV, the measured fwhm of the 1s4p resonance yielded a core hole lifetime broadening of 0.68 ±0.01 eV, in full agreement with theory.

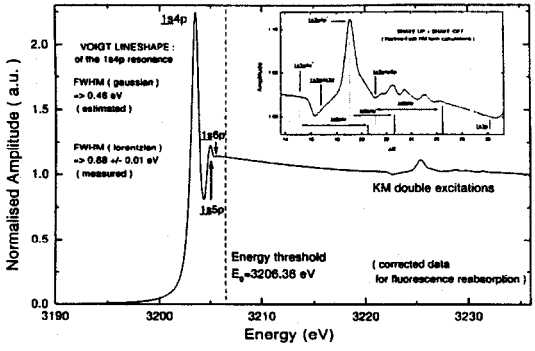

Fig. 1 XANES spectrum of Ar gas with KM multielectron excitations

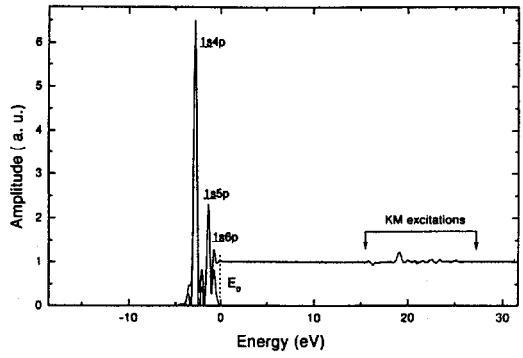

Fig. 2 Deconvolved XANES spectrum of Ar gas with enhanced energy resolution.

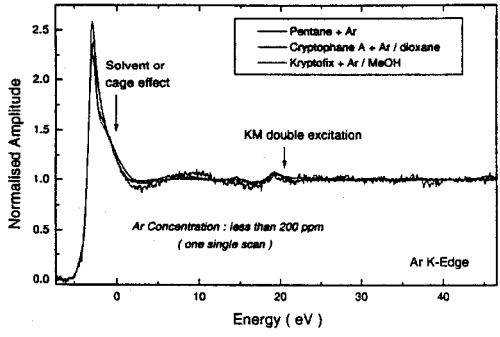

Fig. 3 XANES of Ar solutions (1), (2) and (3). Ar concentration : 50-200 ppm

The XANES spectra of solutions (l)-(3) are displayed in Fig. 3. There is an additional broad resonance above the 1s4p peak that is definitely to be assigned to matrix induced polarisability. Since it appears already in the spectrum of the Ar / pentane solution, we cannot use it to discriminate host-guest interactions against solvent effects. EXAFS oscillations, if any, are weaker than the KM multielectron excitations. Such a strong damping of EXAFS signatures may indicate that argon is not trapped inside the macrocyclic cage of Kryptofix and cryptophane A : the life-time of the complexed species is too short and low frequency vibrational modes are easily excited. ^{129}Xe NMR spectra recorded with the same solvents and comparable conditions also confirm that a large fraction of Xe is "free" or interacting with the solvent.

[1] R.D. Deslattes, R.E. LaVilla, P.L. Cowan, A. Henins, Phys. Rev. A 27, (1983), 923-33
[2] CM. Teodorescu, R.C. Karnatak, J.M. Esteva, A. El Afif, J.P. Connerade, J. Phys. B: At. Mol. Opt. Phys. 26, (1993), 4019-39