ESRF

Experiment title: Structural investigation of gas-phase metal halides	Experiment number: CH656
Beamline: BM29	**Date of Experiment:** from: 14-2-1999 to: 19-2-1999
Shifts: 15	**Local contact(s):** M. Borowsky
	Date of Report: 18-3-1999
	Received at ESRF: 23 AVR. 1999

Names and affiliations of applicants (*indicates experimentalists):

P. D'Angelo*
Dipartimento di Chimica,
Università di Roma "La Sapienza"
P.le A. Moro 5, 00185 Rome, Italy

A. Filipponi*

A. Di Cicco*

Report:

The determination of the structure of metal halides has been carried out in the past 50 years by means of electron diffraction (ED) investigations, spectroscopic methods and theoretical calculations. In spite of the large amount of research work which has been performed, the available information on the structure, shape and bond length distribution of even simple metal halides is sometimes ambiguous. The most challenging question about the geometry of metal dihalides is whether they are linear or bent. These molecules generally have very low bending or puckering mode frequencies and undergo large amplitude motions. Electron diffraction provides an average picture of the molecule being distributed on the bending or puckering potential surfaces. Thus, even a linear molecules will appear to be bent and it is impossible to distinguish by electron diffraction alone between truly linear and bent molecules.
In a previous paper [1], based on data collected at BM29, we have shown that third generation synchrotron sources can provide x-ray absorption spectroscopy (XAS) data with visible oscillations often above 20 $Å^{-1}$. This makes it possible to obtain structural information with an accuracy comparable to that of ED investigation. Moreover, a deep insight into the shape of the interatomic potential function can be gained by performing XAS studies as a function of the temperature. The collection of high temperature data is essential as it increases the sensitivity to configurations far from the equilibrium.

In this experiment we have collected XAS spectra of gaseous $CdBr_2$, CdI_2, $HgBr_2$, HgI_2, SnI_2, $SnBr_2$, $SnCl_2$, and ZnI_2 in a temperature range depending on the vapor pressure and stability of the molecule (ranging from 400 to 1200 K). Spectra were collected at least at three different temperatures and they were highly sampled in k space and extended to the highest energy where an oscillation could be observed. All the samples were measures in 30 cm long cylindrical quartz or Pyrex cells and the amount of compound was chosen in order to obtain an optimal jump in the absorption spectra.

The cells were placed in the ESRF-BM29 tubular oven which was mounted on a x-z translator stage which allowed the alignment of the cell windows to the beam.
In the case of of the bromide and iodide molecules the XAS data were collected at both the metal and halide K edges and the combined data analysis of the spectra will allow a higher accuracy in the determination of the structural parameters.
We believe that these are the first measurements of gaseous metal dihalides that have been ever performed by EXAFS technique.

In Fig. 1 we show, as an example, the effect of increasing temperature on measured EXAFS signal for $HgBr_2$ at the Br K-edge. Fig. 2 shows the Fourier Transform of the same spectra. A deep insight into the bond length and bond-angle distribution will be gained from the analysis of the EXAFS data in the framework of the multiple-scattering theory. A detailed analysis of our data is currently in progress and the results will be presented elsewhere [2].

References:

[1] A. Filipponi and P. D' Angelo, "Accurate determination of molecular structures by XAS.", J. Chem. Phys. **109**, 13 (1998)).
[2] P. D' Angelo, A. Filipponi, and A. Di Cicco, *inpreparation.*

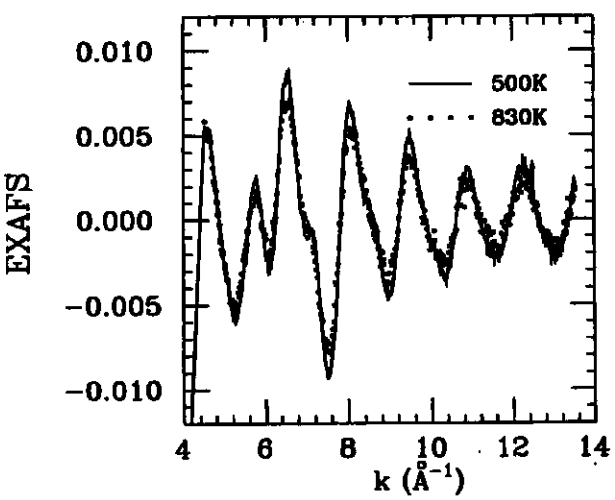

Fig. 1

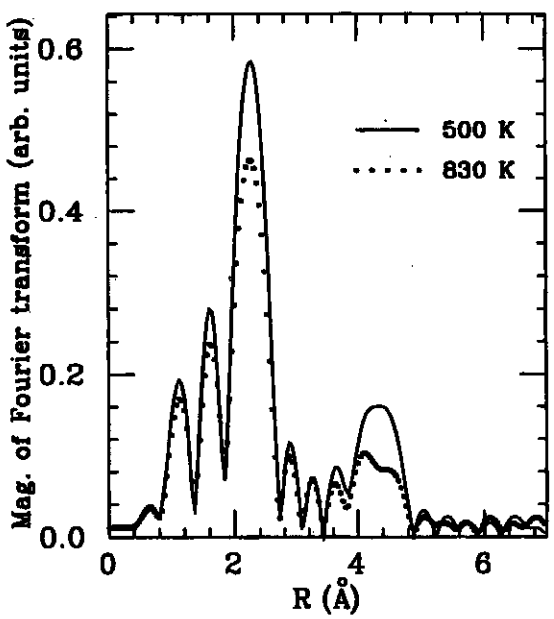

Fig. 2