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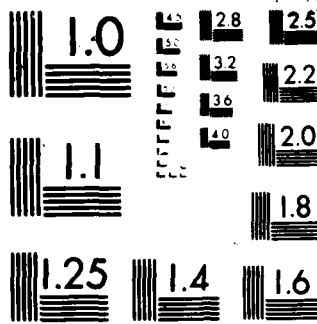
XAS (X-RAY ABSORPTION SPECTROSCOPY) OF GAS PHASE  
METAL-CONTAINING CHEMICAL SYSTEMS(U) BOEING AEROSPACE  
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Technical Report No. 4

XAS OF GAS PHASE METAL-CONTAINING CHEMICAL SYSTEMS



by

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## XAS OF GAS PHASE METAL-CONTAINING CHEMICAL SYSTEMS

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Our experimental program utilizes x-ray absorption spectroscopy (XAS) to study metal-containing chemical systems, such as metal electrolyte solutions, metal complexes and metal cluster systems. Objectives include the direct experimental measurement of chemical structure in dynamic transient phases and in non-condensed phases. In 1986, emphasis was placed on development of capabilities for detecting metal-containing gas phase XAS. This report describes our progress.

A new gas-phase x-ray absorption detector, illustrated in figure 1, was developed. It combines two distinct elements: a long-path x-ray detection chamber (similar to ionization type) and a high temperature vacuum evaporation cell. Both components can be evacuated to  $10^{-5}$  Torr base pressure. A uniform electric field was maintained between two opposing plate electrodes, mounted parallel to the x-ray beam path, for total electron-yield detection. The source aperture for the metal vaporization cell was oriented at an oblique angle close to the x-ray path.

Experimental time on SSRL beam line IV-1 was utilized for tests of the apparatus during high temperature vaporization of Cu metal (source temperatures at approximately 2300 C). Estimates of a Cu vapor density of  $10^{13}$ - $10^{14}$ /cm<sup>3</sup> were based on vaporization rate, source emission profile, and mean thermal velocity. Sensitivity of electron yield detection measurements to this level for some non-metal gas phase systems has been established by Lytle.<sup>1</sup> His results suggested that detectability of x-ray absorption in metal vapors like Cu effluent should be adequate.

Our preliminary data were quite noisy but useful because they revealed a requirement for a more practical scheme of electrical isolation in the detection circuit near a noisy thermal source. The noise was understood to arise from both a thermionic background component (source temperature dependent) background in the vapor and leakage current (time dependent) due to evaporant condensation on electrical insulating components in the chamber. The latter effect was mitigated by installation of a complex baffled insulator system, resulting in a much reduced total noise level. It was then possible to observe a Cu gas absorption edge feature, shown in figure 2. High quality XAS data for a number of volatile metal complexes were measured in the gas chamber detector. For these data there was no thermionic component, suggesting that good quality data can be obtained for high temperature metal vapors, with improved thermionic shielding.

We plan to extend this XAS measurement technique to study structure in metal gas phase reaction species. This will be accomplished by introducing a small partial pressure of reaction gas (CO, Cl<sub>2</sub>, NH<sub>3</sub>, etc.) diluted by an inert carrier gas. Mixing occurs in the vaporization cell so that in the vicinity of the detection electrodes the reaction will be approaching equilibrium. In the long term, our plans include investigation of gas phase species discrimination in XAS detection using more sensitive and trapping schemes such as cyclotron resonance.

Work supported by the Office of Naval Research

## References

1. F. W. Lytle and R. B. Gregor, "GAS PHASE X-RAY ABSORPTION SPECTROSCOPY WITH AN ELECTRON YIELD DETECTOR", presented at 11th Int. EXAFS Conf., Fontevraud, FP, July 1986.

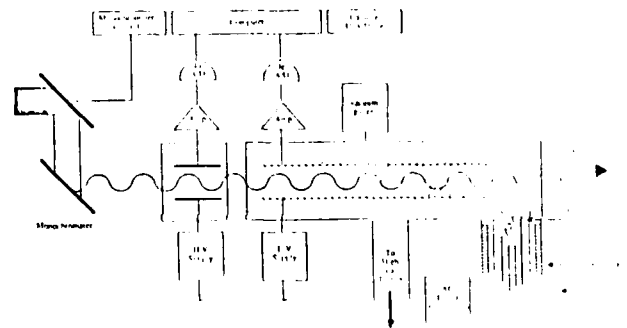


Fig. 1 Gas Phase XAS Detector - Evaporation Cell Concept

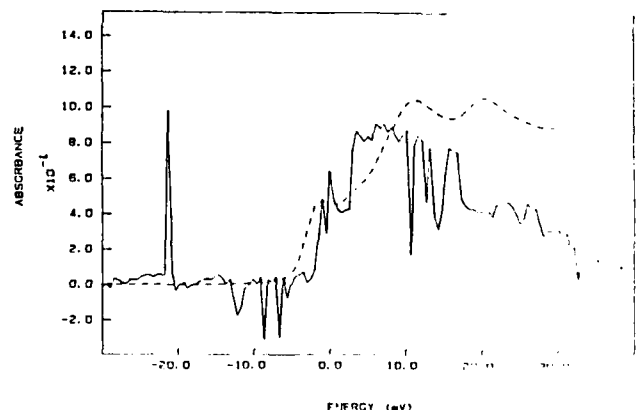


Fig. 2 Cu XAS K-edge spectra, with energy scale referenced to 8.979 eV, for vaporized Cu metal (solid line). Note - large thermionic noise (spikes) and Cu foil calibration (dotted line).

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