

Chapter 1

Introduction and Background

Synchrotron-based x-ray absorption spectroscopy (XAS) has proven to be a versatile structural probe for studying the local environments of cations in a variety of materials ranging from crystalline solids, glasses, and high-temperature liquids to aqueous sorption systems which involve metal complexes associated with (or sorbed at) solid/water interfaces. The structural information provided by XAS includes average interatomic distances and the number and chemical identities of neighbors within about 6 Å of a selected atom species. In many cases including short-range ordering of cations in crystalline solids, cation environments in poorly ordered materials such as gels, glasses, melts, radiation damaged materials, and the structure and composition of sorbed species at solid/water interfaces of environmental importance, XAS provides unique structural data not duplicated by other methods.

X-ray absorption spectroscopy is the measurement of the x-ray absorption coefficient of a matter as a function of excitation energy. The x-ray absorption spectrum is typically divided into two energy regions: the X-ray Absorption Near-Edge Structure or XANES region, and the Extended X-ray Absorption Fine Structure or EXAFS region, shown in Figure 1.1. The XANES region is also sometimes referred to as the Near-Edge X-ray Absorption Fine Structure or NEXAFS region. The XANES/NEXAFS and EXAFS spectral regions provide different types of information about an element and its local environment [1,2].

X-ray absorption spectroscopy in the soft x-ray region is an important technique to investigate environmental and biological samples because the x-ray energy range covers core-electron excitation energies of many light atoms which are

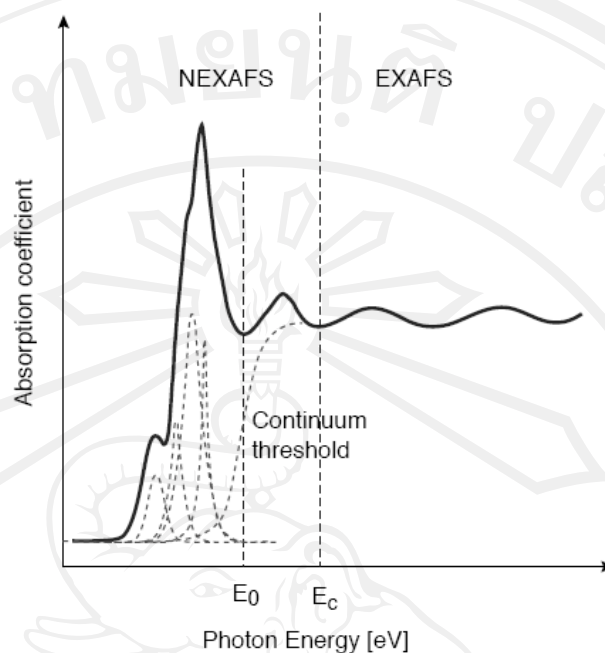


Figure 1.1: In an x-ray absorption edge there are discrete structure from core electron transition (dotted line) superimposed. The photon ionization energy (E_0) is the threshold energy the photoelectron need to have escape into continuum and E_c is the critical energy value for EXAFS [3].

the primary atoms in those kinds of samples. However this x-ray technique is difficult to apply when measuring the structural interfaces at the atomic and molecular level for liquid or wet samples. The problem is that soft-x-ray beamlines must be under vacuum: typically with soft-x-ray spectroscopy systems, the samples also must be in vacuum, which means the sample must be contained or behind a barrier such as a thin window. A liquid or wet sample generally cannot be put in a high-vacuum system because the sample will evaporate and the high vapor pressure will not be compatible with the vacuum of the beamline.

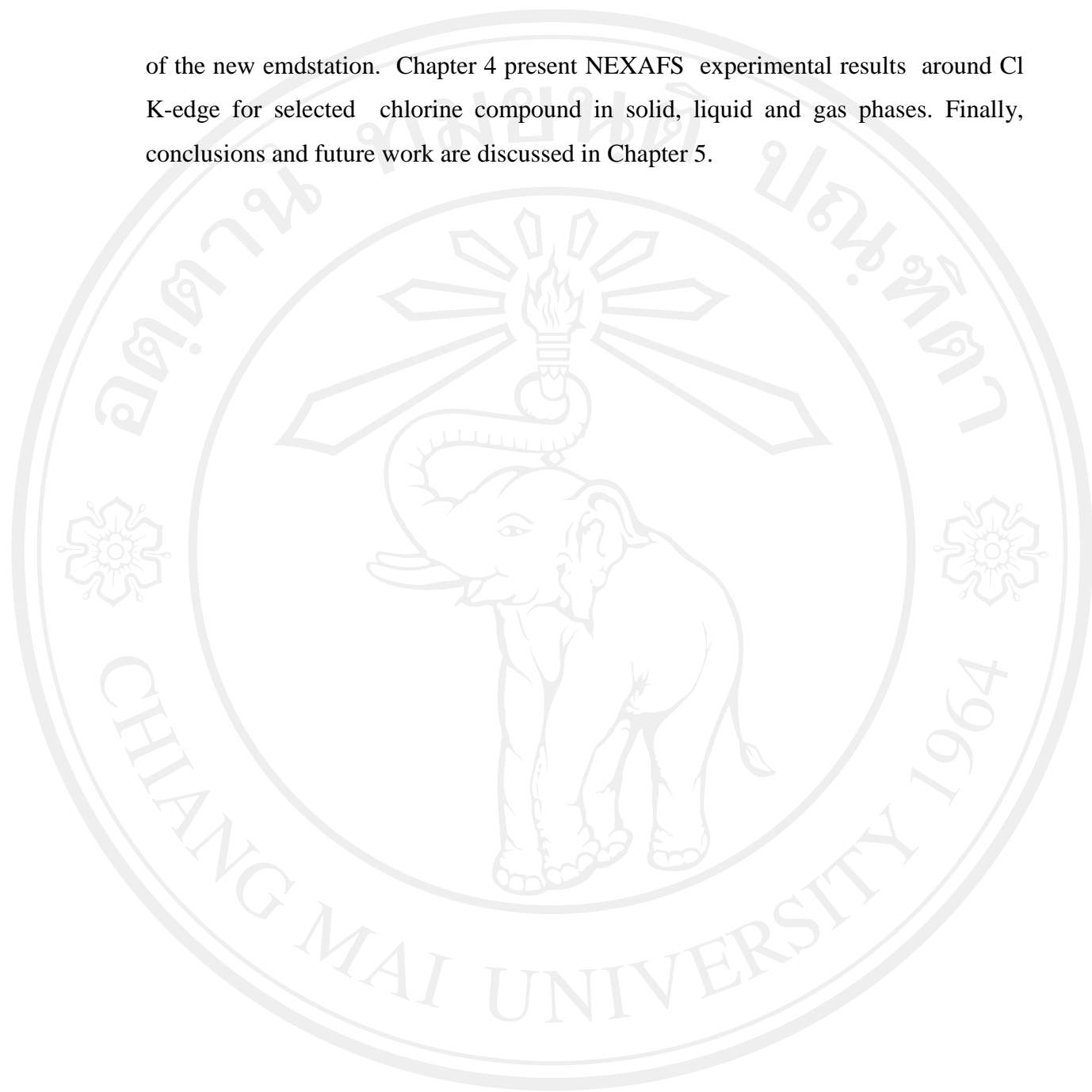
Several techniques to handle liquid samples for XAS experiments have been developed at various levels of complexity. At the beamline 8 of SLRI, Thailand, a rectangular liquid sample cell made of superlens with Kapton tape window is employed in an ambient pressure chamber [4]. M. Freiwald, et al., reported sample cell in which a liquid sample can be circulated through a U-shape tube insert in UHV chamber, soft x-ray are coupled in and out of the sample volume by a silicon nitride membrane window on the tube wall [5]. Kevin Wilson, et al., have developed

sophisticated technique to inject microjet of water into the experimental chamber [6]. P. Nachimuthu, et al., placed a plastic straw filled with liquid samples outside a UHV of beamline port which was separated by a thin window made of Si_3N_4 membrane [7].

The purpose of this work is to design, construct and implement a novel endstation for an x-ray absorption experiment on solid and liquid phase samples at one atmosphere. Such the endstation will be useful for study phase-effects on chlorine by the NEXAFS technique to investigate changes in binding of inner-shell electrons for molecules in different phases: gas or vapor, liquid, and solid chlorine. Chlorine was chosen as our primary samples of interest because it is one of the most abundant naturally occurring chemical elements. It also plays an important and significant role in everyday life ranging from drinking water, plants, food, soils to the manufacture of thousands of products we depend on every day. However the behavior and the ultimate fate of chlorine compounds in the environment are not well understood. The study of “formation of stable chlorinated hydrocarbons in weathering plant material” in [8] shows very interested result reflecting the success of XAS technique on biological and environmental samples. By being able to probe for changes in binding energies for the *same molecule* in gas, liquid, and solid phases at ambient pressure might shed light on the variation of electronic transition with phases of the molecules. The experiment was performed by using synchrotron radiation from the 9.3.1 beamline at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, Berkeley, CA. The ALS provides high brightness synchrotron radiation from accelerated relativistic electron with energy 1.9 GeV. This beamline is based on a bending magnet and includes a Si(111) double-crystal monochromator which provides X-rays photons in the 2.2-5.5 keV energy range with a resolution of approximately 0.4 eV. The selected small molecules of chlorine compound such as dichloromethane (CH_2Cl_2), trichloromethane(CHCl_3), tetrachloromethane(CCl_4) and trichlorofluoromethane (CCl_3F) were studied. X-ray absorption was measured around Cl K-edge for all of those samples in solid, liquid and gas phases.

Theoretical framework for the Near-Edge X-ray Absorption Fine Structure or NEXAFS is provided in Chapter 2. First, we describe about X-ray sources and interactions of X-rays with matter. Thereafter, we describe the X-ray absorption Spectroscopy (XAS), as well as NEXAFS interpretation. Chapter 3 contains the setup

of the new emdstation. Chapter 4 present NEXAFS experimental results around Cl K-edge for selected chlorine compound in solid, liquid and gas phases. Finally, conclusions and future work are discussed in Chapter 5.



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