Chapter 3
Instrumentation

This chapter is describes the implementation of a novel endstation design built for an x-ray absorption experiment on solid and liquid phase samples at one atmosphere for the beamline 9.3.1 at the ALS.

3.1 The Advanced Light Source (ALS) and Beamline 9.3.1

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 beam stored at energy of 1.9 GeV. Figure 3.1 shows a lay out of the Advance Light Source (ALS). The beamline 9.3.1 is based on a bending magnet which provides high resolution x-ray beams for electron, ion and x-ray spectroscopy measurements in atomic, molecular, and materials science.

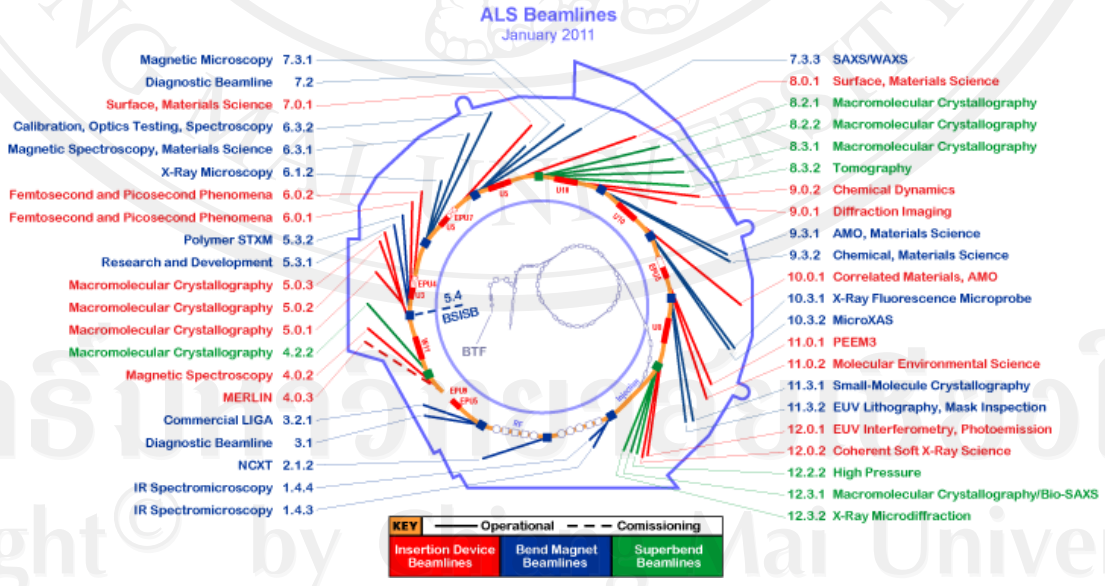

Figure 3.1: A lay out of the Advanced Light Source (ALS) [20].

There are four difference endstations including magnetic mass spectrometer, Polarized-x-ray emission spectrometer, solid-sample X-ray absorption endstation and liquid cell endstation for high vacuum environment. The beamline 9.3.1 operates extremely well in the energy range of chlorine K. NEXAFS has been extensively employed, providing valuable electronic structure information about many compounds; it is especially used on the beamline 9.3.1 to study catalysts and molecules of biological importance.

The schematic diagram of the beamline was shown in Figure 3.2. The beamline is built around a double Si (1,1,1) crystal monochromator with a 2.32 to 5.6 keV energy range. This range includes the K-edges of sulfur and chlorine. The optical design includes two identical, but oppositely defecting, toroidal mirrors positioned symmetrically before and after the monochromator. This approach yields two benefits: high resolution by providing parallel x-rays for diffraction by the Si crystals, and a small beam spot by means of 1:1 focusing of the storage ring source with a minimum of aberrations. The minimum beam size is better than 0.7 x 1.0 mm, and the position stability is less than 0.2 mm. The beamline delivers approximately 10^{10} to 10^{11} photons/s over most of its photon energy range, with a resolving power up to 8000 [21].

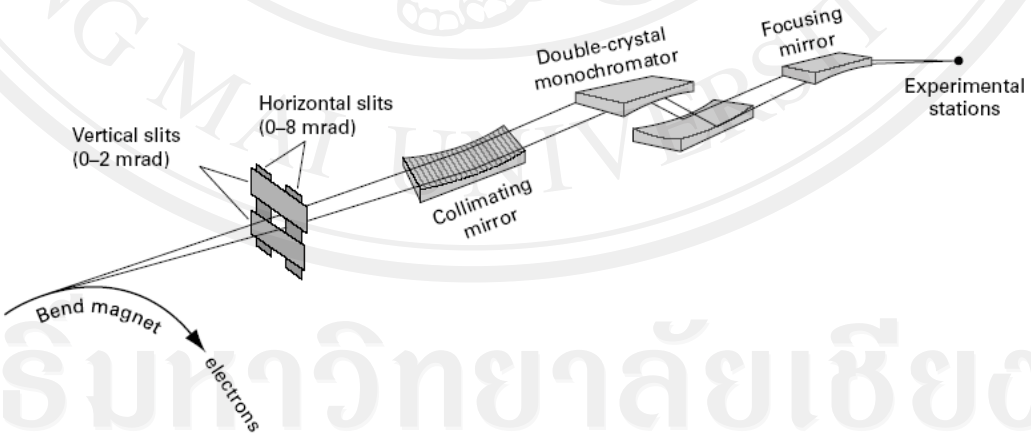

Figure 3.2: Schematic overview of the synchrotron radiation beamline 9.3.1 at ALS [20].

3.2 Endstation

A new endstation was designed and constructed to perform an x-ray absorption experiment on solid and liquid samples at one-atmosphere pressure. The endstation consists of two major parts; beam diagnostics and an experimental station. Figure 3.3 shows a schematic diagram of the endstation and Figure 3.4 shows a photo of the the endstation. The beam diagnostics are in vacuum and integral to the beamline, while the experimental station is at one-atmosphere pressure and located after the Be window where the X-ray beam exits the beam diagnostic section.

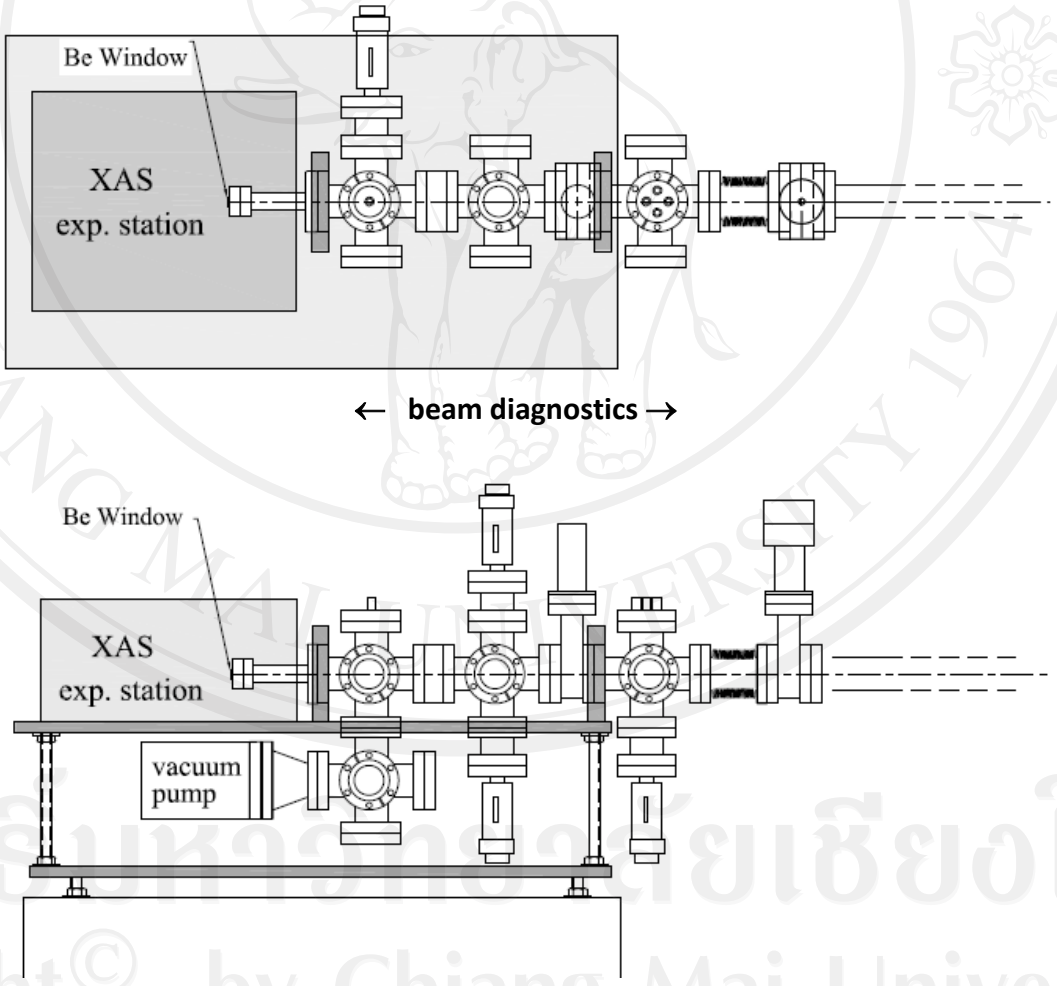

Figure 3.3: Schematic diagram of the endstation consisting of two major parts; beam diagnostics and an experimental station.

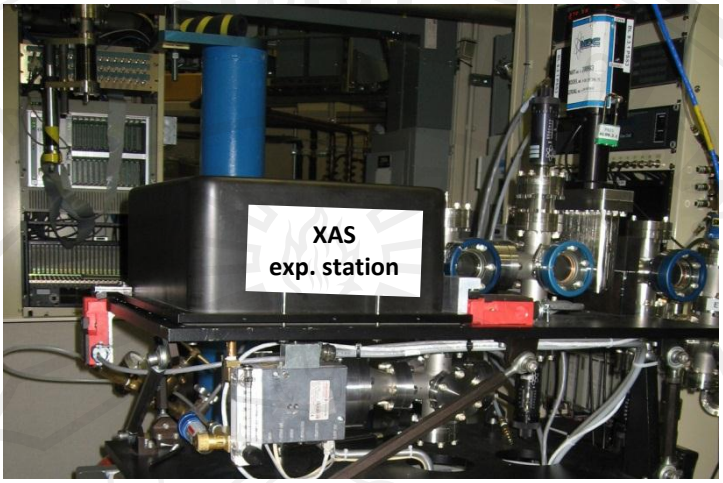

Figure 3.4: The endstation.

3.2.1 Beam Diagnostics Section

The diagram in Figure 3.5 shows the components of the beam diagnostics section. There are a pair of fluorescent screens for endstation and beam alignment, a quadrant beam-position sensor for beam stability control, an ion-gauge and optical shutter for the interlock system, and an aluminum-mylar film for I_0 measurement.

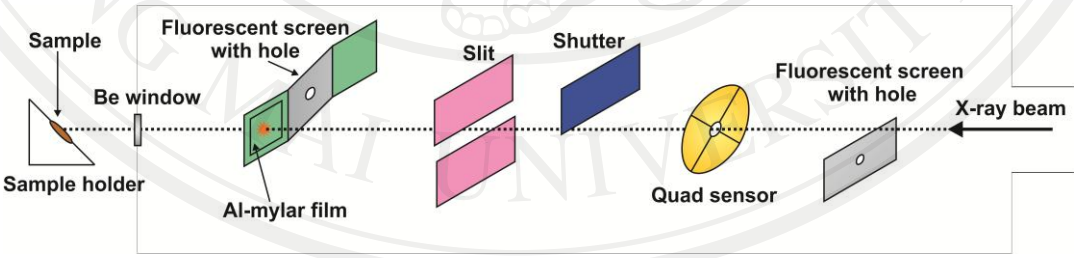

Figure 3.5: The beam diagnostics components.

The fluorescent screens function to facilitate alignment of the beam onto the sample, each screen has a hole of about 1.6 mm diameter at the center. We align the center of the screen and the sample holder during alignment before the Be-window was installed. Figure 3.6 shows schematic diagram of the alignment set up. A small laser pointer was used to establish the optical axis of the diagnostic section through the sample holder. The screens and the sample holder are moved to the position in

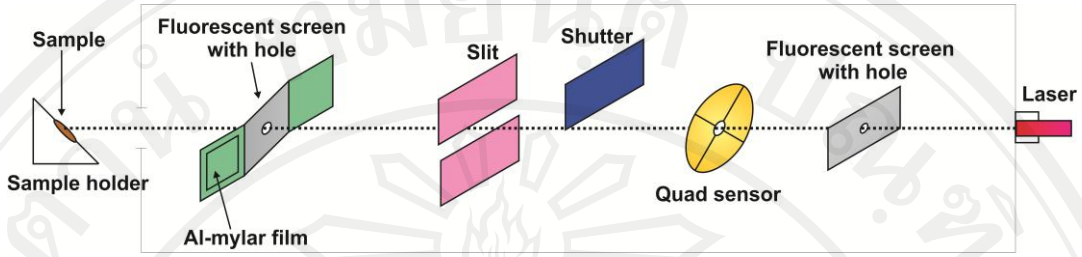

Figure 3.6: The alignment using laser beam.

which laser beam goes through the holes and hit the center of the sample holder, and then their positions were marked. The positions we have marked ensure that users have a tool for adjustment of the endstation when we connect the endstation to the soft x-ray beamline. The screens are coated with phosphorescent material sensitive to x-ray radiation which is useful to see the positions of the x-ray beam and also useful to view the beam shape for adjustment of the beam focus.

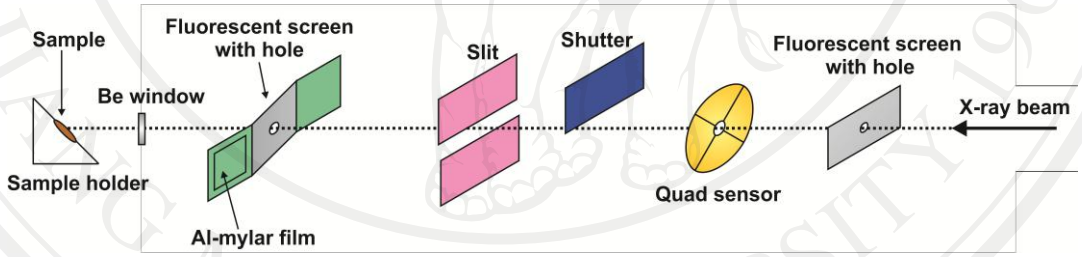

Figure 3.7: The alignment using x-ray beam.

To connect the endstation to the beamline, the final alignment (shown in Figure 3.7) is done after the pressure of the endstation is in the same order of the pressure of the beamline; the gate valve is then opened. Both screens must be set at the position previously marked. It is necessary to adjust the position of the endstation platform until the x-ray beam hitting the flourencent screens is visible and to continue adjustment until the beam goes all the way through the holes of both screens. In this way the user is sure that the x-ray beam is directed to the center of the Be-window. Then the screens are no longer needed and are moved out of the beam path.

The endstation has interlock systems both in the diagnostic section and the enclosure. An ion gauge was installed in the diagnostic section close to the Be-window. Gate valves in the beamline were interlocked to the ion-gauge readings to avoid venting the beamline if the Be-window were to break. The enclosure is interlocked with the optical shutter of the endstation: whenever the enclosure is opened, the optical shutter automatically closed to avoids x-ray radiation to user.

I_0 is an electric current proportional to the intensity of the x-ray beam before hitting the sample; it was measured by electrons leaving the film due to the photoelectric effect. When x-rays penetrate the film, electron are ejected from the aluminum surface and cause a current flow through a circuit connected to the film. The current measured from the film was monitored by a Kiethley (model 6517A) electrometer. The film is very thin, so soft x rays can penetrate the film with a minimal attenuation.

Beam-position stability is ensured by adding a quadrant position sensor into the diagnostic section. This is a four-element photodiode sensor with a 1.6 mm central opening. The elements equally share a piece of their center-corner to the opening. Each photodiode section produces a current that is proportional to the light falling on it. These currents are converted to voltages and amplified. The resulting voltages are then fed to the feedback system of the beamline for control of the beam position. The quadrant sensor has been set at the position where the beam goes through the center of the opening, so there is the same or zero voltage reading on all four quadrant photodiodes. If the beam moves out of the center of the opening and falls on one of the quadrant photodiodes, the feedback system receives the voltage from the quadrant photodiode and steers the beam back to the center of the opening.

At the exit end of the beam diagnostic, there is a window made of 0.05 mm thick Beryllium (Be). The window is glued on a surface of a 33.8 mm vacuum flange with a 6.35 mm diameter aperture, resulting in a x-ray transmission ranging from about 0.6 at 2200 eV to 0.97 at 5500 eV [22, 23].

3.2.2 XAS Experimental Section

The XAS experimental station consists of a sample holder and fluorescent detector as shown in Figure 3.8. Both sample holder and detector were installed on a movable stage. The sample stage position can be adjusted to position the sample as close as possible to the Be-window to reduce the attenuation of the x-ray beam in a gas atmosphere (typically helium was used). The sample holder is inclining at an angle of 45° relative to the beam path. At the center of the inclined plane there is a 5-mm-diameter indentation on its surface to support the liquid drop of sample, so only a drop of sample is required for an experiment. A drop of sample spreads as a thin layer over an area of about 1-cm diameter in and around the indentation. Typical distance from the window to the sample is about 1.5 cm. The sample holder was made of aluminum and contacted with a cooling bath which allowed users to cool the sample with dry ice or liquid nitrogen and to freeze the samples to solid. The sample holder together with cooling bath was not permanently attached to the sample stage, because it is necessary to move it into the glove box for sample preparation.

A large-area silicon photodiode is used to measure total fluorescence from the sample. When a fluorescence photon is absorbed in the photodiode an electron-hole pair is formed and photocurrent results when photon-generated electron-pairs are separated. Photodiode current is a relative measure of total fluorescent radiated from the sample after it is hit by x-ray radiation.

The experimental station was covered with a 6-mm thick aluminum enclosure which has three functions. First, to prevents the detector from seeing other light except fluorescent light from the sample. Second, to protect users from x-ray radiation. To ensure the user safety a tungsten sheet about 0.2 mm thick and 9 x14 cm in size was glued on the inside wall of the enclosure behind the sample. Third, an enclosure allows users to flow other gases instead of air during the experiment. For example, helium gas is commonly used in order to reduce absorption of the x-ray beam from the Be-window to the sample.

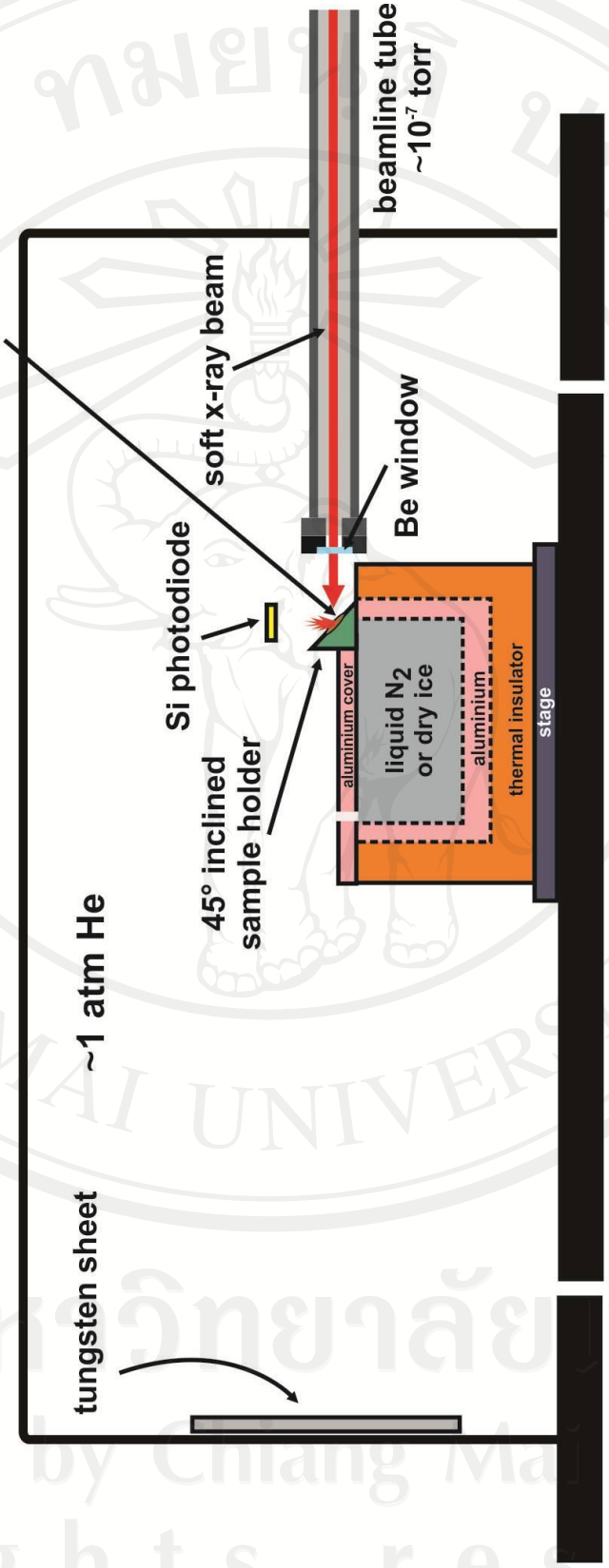

Figure 3.8: The XAS experimental station.

3.3 Gas Cell

Samples in gas phase are measured by a gas absorption cell built in the beamline, which is separated from the beamline by the Kapton window. The Kapton window is used to maintain the pressure in a gas cell in order of hundreds of millitorr while allowing the vacuum part of the beamline to be at 10^{-7} torr or less. The Kapton window was also checked to ensure that it did not contain sulfur or chlorine based molecules which would cause background structure. When the x-ray beam goes into the gas cell and was absorbed by a gas molecule in the chamber some molecular ions and electrons were generated. The molecular ions and electrons were collected by electrodes installed inside the gas cell chamber and connected to a current measurement circuit outside the chamber. The amounts of measured currents are proportional to the amount of absorption events in the chamber. Measuring the currents generated from the sample while scanning energy of the incident photon provides information for the spectrum of x-ray absorption of the gas sample. The spectra shown for gas phase were measured at 0.30 Torr of gas pressure, and an applied voltage difference between the electrodes of the gas cell was 400 V. Data were collected between energy range 2800 and 2900 eV, at intervals of 0.5 eV

between 2800 and 2815 eV, at intervals of 0.1 eV between 2815 and 2835 eV, at intervals of 0.5 eV between 2835 and 2860 eV and at intervals of 1 eV between 2860 and 2900 eV.

3.4 Sample Preparation

For samples with their melting points lower than room temperature, we used liquid nitrogen (-196°C) or dry-ice (solid carbon dioxide, -78.5°C) to freeze the sample to solid phase. Preparation of samples on the sample holder was conducted in a glove box under an atmosphere of nitrogen gas to prevented condensation of water moisture. After the cooling bath was filled with dry-ice or liquid nitrogen in the glove box, the sample is placed on the inclined surface of the sample holder then quickly moved to the sample stage. Dry-ice is also used to cool some samples when being measured in liquid phase to reduce the evaporation rates. The end-station cover is then closed and filled with helium gas.