A cell for combined UV-visible and x-ray absorption spectroscopy studies under low-temperature and air exclusion conditions

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A measuring system that integrates a low-temperature optical cell UV-visible (UV-Vis) for air exclusion experiments with a liquid x-ray absorption spectroscopy (XAS) cell (x-ray absorption near-edge spectroscopy and extended x-ray absorption fine structure) is reported here together with its application in studies of organometallic complexes. UV-Vis measurements are performed in a three-compartment glass vessel, fitted with an external fiber optics probe. This UV-Vis cell is suitable for the measurement of oxygen- and air-sensitive compounds at variable temperatures (RT to −78 °C). The liquid XAS cell is filled with the UV-Vis solution at low temperature and can be used in both fluorescence- or transmission-mode measurements with (frozen) solutions. The complete measuring system is reusable and easy to clean and handle. To test the performance of these cells the oxygenation behavior of a dinuclear organometallic copper(I) complex was studied in acetone by UV-Vis and XAS. It is shown that direct correlation of low-temperature UV-Vis and XAS data is possible in organic solvents. © *2002 American Institute of Physics.*
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I. INTRODUCTION

Low-temperature UV-visible (UV-Vis) spectroscopy is a useful technique to study the oxygenation behavior of synthetic copper oxygenase mimics.[1,2] In addition, x-ray absorption spectroscopy (XAS)[3,4] is a powerful technique that is often used in both biological (proteins and enzymes) and synthetic model systems in order to get a better understanding of the structure of the active metal sites and their surroundings. X-ray absorption near-edge spectroscopy (XANES)[5] can give information about the oxidation state of the metal and extended x-ray absorption fine structure (EXAFS)[6] about the number and type of atoms surrounding the metal center. Dinuclear copper complexes and their oxygenation behavior have been studied extensively by optical and XAS techniques.[7–13]

Recently, we have obtained UV-Vis and XAS data for two synthetic copper oxygenase mimics,[2] but we were not able to reliably correlate these data because of differences in sample preparation. To overcome this, an integrated system is needed, which allows the measurement of both UV-Vis and XAS on the same sample. In the literature, there are many examples of specialized cells that combine more than one experimental technique. Several cells for combining UV-Vis with other techniques have been reported: diffuse reflectance spectroscopy,[14] difference spectroscopy[15] and variable- and low-temperature spectroscopy.[8,9,16,17] In addition, there exist several examples of specialized XAS cells, e.g., for high-temperature measurements,[18–21] *in situ* catalytic studies,[20,22–26] combination with electrochemistry,[27–29] and for corrosive or air-sensitive compounds.[30–32] Furthermore, specialized procedures for sample preparation for both solid[33,34] and liquid samples have been described. All these cells are designed for the combination of various techniques. However, none of these cells allow the combination of UV-Vis and XAS measurements at low temperature. Weber, Ostafin, and Norris have described an EXAFS cell that is suitable for low-temperature fluorescence-mode XAS of air-sensitive compounds.[35] Furenlid, Renner, and Fajer have designed a glass cell that allows electron paramagnetic resonance, optical, and XAS measurements on the same sample,[36] and have used it to carry out oxidation and reduction reactions with a nickel porphyrin complex at room temperature.[37] For our research, however, we needed a different type of XAS cell, which is suitable for study on (frozen) solutions and which can be combined with a low-temperature UV-Vis cell. We have designed therefore, a setup, which allows filling of a specialized XAS cell directly from the UV-Vis solution at low temperature under anaerobic conditions. The design and the performance of this measuring system are reported here. Although we will only discuss XAS measurements on frozen samples, the system is also applicable for study in organic solvents at room temperature.[38]

II. EXPERIMENTAL APPARATUS

A. Low-temperature UV-Vis cell and setup

The UV-Vis spectroscopy setup has to meet certain requirements: it has to be suitable for low-temperature measurement. This implies that a dry atmosphere has to be cre-

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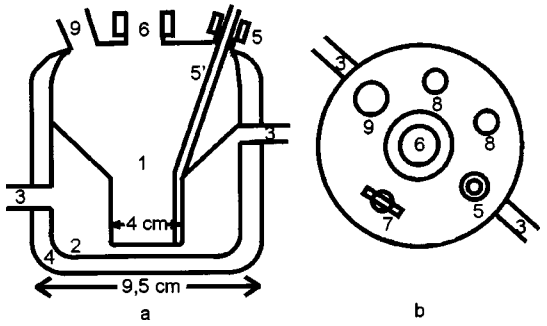

FIG. 1. Scheme of the UV-Vis cell. (a) Cross section from the side, (b) top view. For explanation of numbers, see the text.

ated to avoid condensation on the optical windows. Furthermore, the cell has to be suitable for measurements under inert conditions with the possibility of controlled addition of oxygen and direct transfer of the solution to a XAS cell (*vide infra*) *in situ*. It also has to be possible to stir mechanically and to control the temperature of the sample accurately. Finally, the cell has to be reusable and easy to clean and handle.

All these requirements have been incorporated into the following setup. The UV-Vis spectroscopy setup consists of a glass cell, a closed-circuit cryostat, an external fiber optics probe, a UV-Vis spectrophotometer with probe adapter, a Schlenk line, and an oxygen cylinder. The low-temperature UV-Vis cell (Fig. 1) consists of a three-compartment glass vessel. The inner compartment (1) is the sample chamber; the second compartment is the refrigerant chamber (2), and the third compartment is a vacuum jacket (4) for insulation purposes. The refrigerant chamber (2) has an inlet and outlet (3) (∅ 12 mm) for the refrigerant liquid of the closed-circuit cryostat.[39] Specialized tubing is used for the cryostat at −80 °C; foam insulation[39] insulates this tubing. The tubes are connected to the glass vessel by a tube clamp. The inner compartment protrudes almost to the bottom of the cell to enable the use of a magnetic stirrer inside the sample chamber.

The top view of the cell [Fig. 1(b)] clearly shows the different inlets and outlets. A thin glass tube (5′) (outer ∅ 3 mm) is inserted into the sample chamber through an open GL 14 cap (5) (Schott) with a silicon ring. This tube is fitted with a thermocouple type K (chromel/alumel) for continuous in situ temperature control. For the actual UV-Vis measurements, an external fiber-optics probe[39] is placed in the cell through an open GL 32 cap (6) (Schott) with a silicon ring. The probe is connected to an electronic absorption spectrophotometer[39] via two glass fiber wires (length: 2 m). The cell furthermore contains a stopcock (7) connected to an argon Schlenk line, a B19 inlet (9) for introduction of the sample solution, and two B14 (8) inlets for the introduction of gasses (e.g., oxygen).

B. Liquid XAS cell

In line with earlier work,[13] we initially used a very simple XAS cell that consists of an aluminum body (29 ×24×1 mm) with a rectangular aperture (15×10 mm), which forms the sample chamber (150 μL). Two rectangular

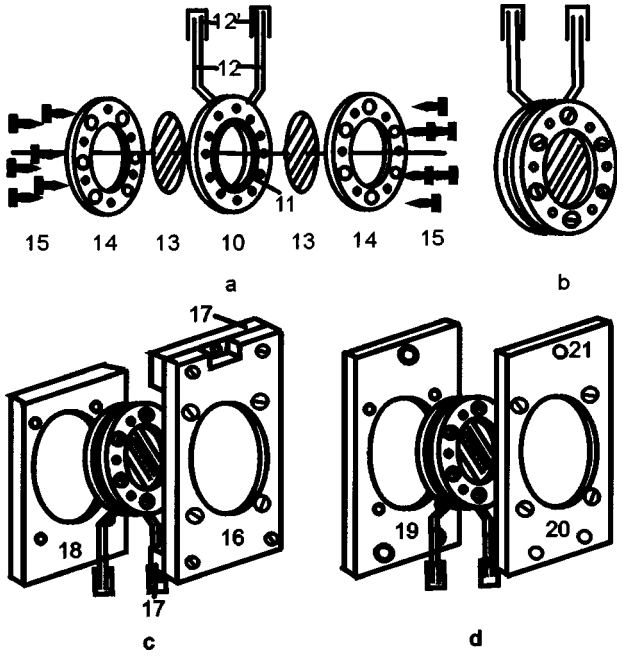

FIG. 2. (a) Scheme of the XAS cell in parts. (b) Scheme of assembled XAS cell. (c) Scheme of XAS cell with cell holders for EMBL-Outstation, Hamburg, Germany. (d) Idem with cell holders for SRS Daresbury, Warrington, UK.

pieces of Kapton (polyimide film) (24×18 mm) are glued on both sides by cyano acrylate glue (Permacol). On one side of the sample chamber, there are two radial perforations through which the cell can be filled, after which they are closed with glue (two-component UHU plus schnellfest).

With this type of cell, we obtained reasonable data, however, also a number of serious problems was encountered: leakage of the sample through the glue of the windows due to slight solubility of the glue in the used organic solvents, causing contamination of the sample with substituents from the glue. Another experimental problem was observed during oxygenation of the sample: oxygenated samples are prepared by purging oxygen through a filled cell while it is cooled in dry ice; this caused the warming up of the sample (due to the low-sample volume) and, as a consequence, decomposition of the oxy complexes which are only stable at −78 °C.

It was decided therefore, to design a XAS cell that would overcome these problems. The XAS cell should meet the following requirements: (i) no glue should be used; (ii) the maximum cell size should be 24×40×4 mm; (iii) it should be possible to fill the XAS cell inside the UV-Vis cell at low temperature; (iv) leakage of solvents should be prevented; (v) the cell should be reusable; (vi) it should be easily handled and cleaned; and (vii) it should be adjustable to cryostats of XAS beam lines at different synchrotrons.

Taking all these requirements into account, the cell, depicted in Fig. 2, was designed and constructed. The body of the cell (10) consists of a ring, (stainless steel, outer ∅: 20 mm, inner ∅: 9 mm); the thickness of most of the ring is 1 mm, with a rim (11) directly surrounding the sample compartment (width: 0.5 mm, total thickness: 1.15 mm). This rim is polished to ensure optimum contact with the window, thus avoiding leakage while no glue is needed. The body of the

cell (10) is fitted with 12 radial perforations (screw thread, ∅ 1.6 mm). The sample chamber (100 μL) is completed with two filling capillaries (12) (stainless steel, 0.7×0.4 mm, length 20 mm), which are closed with Teflon caps (12′). Two circular Kapton disks (13) (∅ 14 mm) are used as windows, and fastened by two stainless steel rings (14) (outer ∅ 20 mm, inner ∅ 9 mm, thickness 0.5 mm) with 12 radial perforations (∅ 1.6 mm). The sample is assembled with 12 set screws (stainless steel, 1.6×3 mm), six on each side (15). The cell is sealed only by pressure from the screws and no glue or O rings are used, since neither is inert to organic solvents. The rim on the body of the cell is polished to ensure maximum contact with the Kapton windows. Precise closing of the cell with equall tightening of the screws is essential to avoid leakage. The sample only comes into contact with the Kapton and stainless steel. This basic liquid XAS cell [Fig. 2(b)] can be filled inside the UV-Vis cell (*vide infra*) and it can be assembled in liquid nitrogen with the cell holder [Figs. 2(c) and 2(d)]. Described here are cell holders for the cryostat of the D2 EXAFS beam line of the European Molecular Biology Laboratory (EMBL) Outstation at the Deutsches Elektronen Synchrotron (DESY) in Hamburg, Germany [Fig. 2(c)] and for the cryostat of the 8.1 Anglo Dutch EXAFS station, and other EXAFS stations at the SRS of the CLRC-Daresbury Laboratory, Warrington, UK [Fig. 2(d)].

The cell holder for the EMBL-Outstation (Fig. 2c) consists of two stainless steel plates (16) (23×32×1 mm) and (18) (23×38×1 mm). Both have a conical aperture (outer ∅ 21 mm, inner ∅ 19 mm) in the middle for embedding the XAS cell. Part (18) has four radial perforations (screw thread, ∅ 1.6 mm); part (16) has four conical perforations for set screws (stainless steel, 1.6×3 mm) and a rectangular aperture (5×8 mm) on top. Two stainless steel strips (17) (23×6×1 mm) have been attached to (18) as spacers, of which the top strip contains a radial perforation (∅ 2.5 mm) for attachment to the cryostat arm.

The cell holder for the Daresbury Laboratory [Fig. 2(d)] contains two stainless steel parts (19) and (20) (29×42 ×1 mm). Both parts have several apertures: (a) a conical window (outer ∅ 21 mm, inner ∅ 19.8 mm) located 12 mm from the top edge for embedding the XAS cell; (b) four radial perforations surrounding the central window for set screws (stainless steel, 1.6×3 mm); and (c) three perforations (∅ 3 mm), one of which is located 2 mm from the top edge for mounting to the cryostat arm (21) and two which are located 2 mm from the bottom edge. Around the latter three perforations on part (19) rims have been applied (width: 1 mm, total thickness: 2 mm) to function as spacers between parts (19) and (20).

The assembly of these cell is quick and easy and requires only a screw driver. After the cells have been used for XAS measurements, they can be easily disassembled by removing all the screws. After cleaning of the parts by rinsing with organic solvents, the cell can be reassembled and only new Kapton windows are needed. Thus, the cell is easy to handle and it is reusable.

C. Low-temperature UV-Vis measurement and preparation of XAS samples

The UV-Vis setup was assembled as described above. Subsequently, the cell was deoxygenated by repeated argon/vacuum cycles. All used solvents were distilled, and transferred to the cell (9) under argon together with a magnetic stirrer bar. Scans were collected between 900 and 290 nm (scan speed 4800 nm/min). After recording a spectrum at room temperature the solution was cooled to −78 °C (over a time of 1.5 h).

For a standard measurement, 20 mL of sample solution was prepared in a Schlenk tube. It was introduced into the cell under argon, and a room-temperature scan of the deoxy complex was recorded. The fiber-optics probe was removed and a XAS cell [Fig. 2(b)] was introduced through inlet (6) with a Hamilton syringe of 100 μL [attached to one of the filling inlets (12) of the cell through a Teflon connector]. The plunger of the syringe was slowly lifted, which created a vacuum inside the XAS cell and allowed filling through the second filling inlet (12). After the cell was completely filled, it was closed with Teflon caps (12′) and frozen in liquid nitrogen. The fiber-optics probe was replaced in the cell and the solution was cooled to −78 °C while stirring. Oxygen was introduced through a septum (8), and with cycle mode UV-Vis (30 scans, interval 1 min) the oxygen uptake was followed to completion, after which the oxygen flow was stopped. A second XAS cell was filled and frozen using the same procedure as described above, after which the remaining solution in the UV-Vis cell was allowed to warm up to room temperature during which a second cycle of UV-Vis spectra was recorded. After the solution has reached room temperature, a third XAS cell was filled. Subsequently, the XAS cells were assembled with the cell holders in liquid nitrogen as depicted in Figs. 2(c) and 2(d), and transported in a Dewar vessel for XAS measurements. The UV-Vis cell can be easily cleaned by rinsing with organic solvents and drying, and is completely reusable.

D. XAS measurements

The XAS cell can be employed for measurements in the transmission or fluorescence mode, which require different setups. When Kapton windows are used, the cell cannot be applied in the soft x-ray range. For transmission-mode measurements, the cell is simply inserted between the radiation source and the detector which are aligned. For fluorescence-mode measurements the detector is placed at an angle of 90° in the horizontal plane with respect to the radiation source. The cell must be placed under an angle of 45° to allow fluorescence radiation to be collected onto the detector. In the present work, however, only fluorescence EXAFS was used since it is the preferred method of data collection for dilute samples. The data reported in this article have been acquired at the EMBL Outstation in Hamburg, Germany.

The EXAFS scans were acquired around the Cu *K* edge (8980 eV) between 8700 and 9700 eV (plotted 8960 to 9035 eV). The storage ring was operating at 4.5 GeV with maximum currents of 150 mA. The station is equipped with a Si(111) double-crystal monochromator (set to 50% of peak

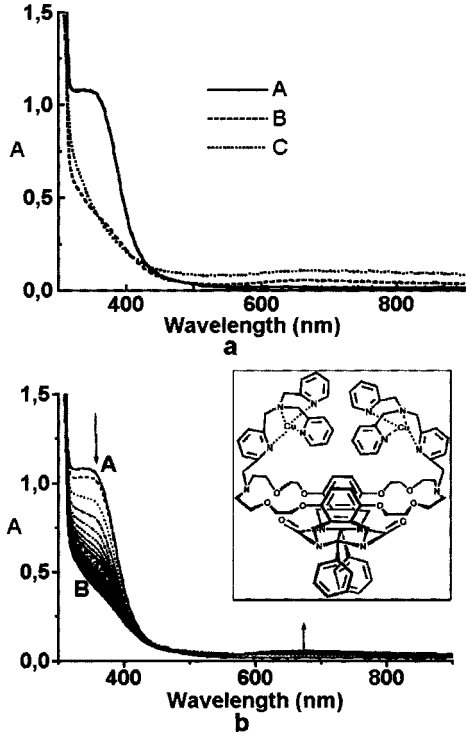

FIG. 3. (a) UV-Vis spectra of copper TMPA basket in acetone. A: deoxy form (−78 °C). B: oxy form (−78 °C). C: warming up of sample to room temperature; (b) oxygenation of the complex followed in time. Inset: copper TMPA basket.

intensity to suppress harmonics),[40] a focusing mirror, a CANBERRA 13 element solid-state fluorescence detector, and an absolute energy calibrator.[41] It was necessary to decrease the opening of the lateral slit to reduce contamination of the signal with Cu contribution, which most likely arises from contaminants in the stainless steel of the cell. Because of the small slit opening and the low concentration, typically 25 to 40 scans per sample were taken (60 to 90 min per scan). During the measurements, the samples were kept at 20 K in the He exchange gas atmosphere of a closed cycle cryostat.

Data reduction was carried out with the EMBL Outstation data reduction package.[42] In this article, we will only present the XANES data of different oxidation states of the so-called (tris[(2-pyridyl)-methyl]amine) (TMPA) basket [Fig. 3(b) inset].[2] More detailed data on this and other systems will be presented in a forthcoming paper.

III. RESULTS AND DISCUSSION

In order to test the performance of the system, a dinuclear Cu(I) complex [Fig. 3(b) inset][2] was studied in acetone. The UV-Vis spectra of the deoxy, oxy, and warmed-up species are depicted in Fig. 3(a). The deoxy complex (A) showed a Cu(I) band at about 350 nm. Upon oxygenation a decrease of this band over time [Fig. 3(b)] was observed, indicated an oxidation to Cu(II), which is a frequently observed phenomenon in Cu_2O_2 systems.[8] After 15 min, the oxygenation seemed to be completed [Fig. 3(a), B]. After warming up of the sample to room temperature, hardly any change was observed in the UV-Vis spectra with respect to the oxygenated sample [Fig. 3(a), C], which pointed to the oxidation state Cu(II). XANES was used to determine the oxidation states of the different samples. The x-ray absorption *K* edges from the different samples are depicted in Fig. 4, which clearly show that the above-mentioned assignments are correct: line A shows a characteristic Cu(I) edge[43] at relatively low energy, with a shoulder. Lines B and C, which are almost identical, are shifted to higher energy; both show a characteristic Cu(II) edge. This result is in excellent agreement with the data obtained from the low-temperature optical measurements. It can be concluded that with this system, direct correlation between UV-Vis and XAS data in organic solvents has been achieved.

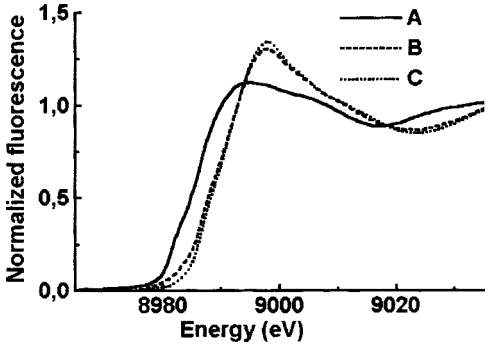

FIG. 4. XANES *K*-edge spectra in acetone. A: deoxy form of the copper complex (−78 °C). B: oxy form (−78 °C). C: warming up of sample to room temperature.

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