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STOPPED-FLOW X-RAY ABSORPTION SPECTROSCOPY IN DISPERSIVE MODE

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A new stopped-flow device particularly suitable for X-ray absorption spectroscopy in dispersive mode has been built. Time-resolved measurements of X-ray absorption spectra have been made for reactions in mixed solutions of (i) iron(III) nitrate and catechol and (ii) iron(III) nitrate and sodium thiosulfate with time resolutions of ~5 ms to a few seconds. Two-step variation of the spectra was observed for the former reaction, while one-step variation for the latter.

Introduction

Using the energy dispersive X-ray absorption spectrometer/1-3/, a whole profile of an absorption spectrum of interest can be recorded simultaneously without any mechanical motion during the measurement. Thus, the method is suitable for time resolved X-ray absorption spectroscopy. Preliminary results of time resolved experiments using dispersive X-ray absorption spectrometers were reported by Matsushita et al./4/, Fontaine et al./5/ and Sayers et al./6/. In these proceedings Tourillon et al./7/ also give more detailed report on the time-resolved in-situ investigation of the inclusion of metallic aggregates within a conducting polymer using the dispersive EXAFS technique.

In the present paper we report the present status of the stopped-flow experiment for kinetic studies of reactions in solutions using the dispersive X-ray absorption spectrometer at the Photon Factory. The stopped-flow method using optical absorption in visible region is an established technique in studying kinetics of reactions in solutions. In the X-ray region, stopped-flow scattering experiments were performed using synchrotron radiation/8-10/. In one/10/ of these works, a new stopped-flow device having a slit type mixer was developed and used, which give uniform mixing over a large window area of the observation cell. In the previous report/4/, we used this type of device for the preliminary stopped-flow
X-ray absorption measurement. Since then, we have made a number of improvements to the design of the device and prepared a new stopped-flow device particularly suitable for EXAFS and XANES studies in dispersive mode. The results of a test experiment were reported recently/11/. The kinetics of reactions in solutions are now being studied using this device on the dispersive spectrometer with time resolutions of \( \approx 5 \) ms to a few seconds.

Stopped-Flow Device

Figure 1 schematically shows the mixer and the observation cell of the new stopped-flow device. Two solutions, A and B, flowing along two different paths are mixed at points P and \( P' \) in the ring shaped mixer. The mixed solutions at P and \( P' \) then meet at point Q resulting in a better mixing of the two solutions A and B. The mixed solution then flows into 11 narrow channels, each 0.4 mm high and 0.3 mm wide and spaced by a period of 0.6 mm, and finally reaches a 1 mm thick sample cell sandwiched by two 100 \( \mu \)m thick Mylar windows. The size of the window is 4 mm wide and 6 mm high. The two Mylar windows of 200 \( \mu \)m total thickness transmit 77\% of X-ray photons of an energy of 7 keV, while two 50\( \mu \)m thick quartz windows previously used/10/ transmit only 17\% of the incident X-ray photons of the same energy. In order to avoid the vibration of the window materials by the rapid variation of the pressure in the cell, the Mylar windows are kept tensioned. This was realized by gluing the Mylar sheets to the periphery of the window at elevated temperature and subsequently cooling them down to room temperature. No appreciable effect of the vibration of the windows was observed in the absorption spectra measured for the mixing of an aqueous solution of iron(III) nitrate\((\text{Fe(NO}_3)_3)\) with water with a time resolution of 5 ms to 0.1 s over the time range of 0 - 0.15 s and 0 - 1.5 s. On the other hand, we observed effects of vibration in the absorption spectrum with

![Fig.1](image1.png)

Mixing chamber and observation cell of a new stopped-flow device for use with the dispersive X-ray absorption spectrometer. The observation cell sandwiched by two 100 \( \mu \)m Mylar windows is 4 mm wide, 6 mm high and 1 mm thick. For more details, refer to the text.

![Fig.2](image2.png)

Fig.2
Block diagram of stopped-flow device for use with the dispersive X-ray absorption spectrometer.
thinner untensioned Mylar windows. The use of the ring shaped mixer improved the mixing efficiency. The uniformity of mixing over the window area of the cell was confirmed by observing the uniformity of color change after mixing 0.1 M NaOH with a pH indicator and 0.105 M HCl. As shown in the figure, the observation cell was located at the focus of the dispersive spectrometer. The absorbance was obtained by measuring transmitted intensity, \( I \), through the reacting solution and that, \( I_0 \), through a reference 1 mm thick water layer. The measurement of \( I \) was made by filling the cell with water which was sent through the path C shown in Fig.1. This function was added to the previous design of the stopped-flow cell in order to make the measurement of \( I_0 \) easier.

Figure 2 shows a block diagram of the system for the stopped-flow experiment. Two cylinders pressurized by nitrogen-gas drive two syringes which send solutions stored in two reservoirs into the mixing chamber described in Fig.1. The motion of the syringes is detected by a limit-switch, which sends a signal to a computer to initiate data collection. The mixing of solutions and data collection can automatically be repeated many times with a control of a microprocessor in order to obtain good statistics of the data.

**Experimentals**

The experiment was performed on Beamline 4A at the Photon Factory in Tsukuba, Japan. The electron storage ring was operated at 2.5 GeV and 260 - 100 mA. The dispersive spectrometer had silicon 111 dispersing crystal and a RETICON RL1024-SF photodiode array with Gd,0.5:Tb phosphor screen optically coupled to the diode array with an optical fiber faceplate. The higher harmonics from the dispersing crystal was rejected using a platinum-coated flat mirror placed between the sample and the detector. Sixteen spectra were successively recorded with a time resolution of 5 ms to a few seconds. Details of the detector and the data collection system are reported by Oyanagi et al./12/ in these proceedings.

The stopped-flow cell was placed at the focal position of the spectrometer. We studied the reaction of Fe³⁺ aqua ions with a number of ligands. In this paper we show two examples: the reaction between iron(III) nitrate(Fe(NO₃)₃) and catechol (C₆H₄(OH)₂), and that between iron(III) nitrate and sodium thiosulfate(Na₂S₂O₃). In these reactions, the color of the mixed solutions changes in two steps after mixing. On the other hand, two-step variation of X-ray absorption spectra was observed for the former reaction, while one step-variation for the latter.

**Reaction between iron(III) nitrate and catechol**

A 0.3 M aqueous solution of iron(III) nitrate was mixed with a 0.3 M methanolic solution of catechol. In the iron(III) nitrate solution, an Fe³⁺ ion is surrounded by 6 water molecules forming an aqua complex. By mixing it with catechol, two of the water molecules are replaced by a catechol molecule. This formation of complex causes an absorption in the visible region resulting in the change of the color of the solution into blue-black. The color of the solution then changes into blue in several tens seconds. Figures 3(a), (b) and (c) show the variation of XANES above Fe K-absorption edge with the time after mixing the two solutions.

Fig.3(a) gives the variation of the spectra in the time range from 0 to 155 msec with a time resolution of 5 ms. Immediately after the mixing, the shift of the absorption edge took place toward the lower energy side from the edge of the spectrum for the aqueous solution of iron(III) nitrate. After this fast edge-shift, no appreciable change in the spectrum was observed in this time scale. We also found that this edge shift was retarded by adding an excess of H⁺ ions in the solution and that such an edge shift was not observed for the complex formation between Fe³⁺ aqua ion and disodium 4,5-dihydroxybenzene 1,3-disulfate((H₂O),C₆H₂(SO₃Na)₂) which has a similar main structure to that of catechol. The fast shift of the absorption edges would be due to the charge transfer from the ligand to the metal ion immediately
after the formation of the complex. The spectra for the mixed solution shown in Fig. 3(a) are noisy because the signal level was far below the saturation level of photodiodes of the detector with such a short exposure time. It should be noted here that a low signal-to-noise ratio causes a continuous background in the absorbance curve, because $I_0$ and $I_0$ are not negligible in $I_0/I = (I_0 + I_d)/(I_0 + I_d)$, where $I_0$ and $I_0$ are signals for $I_0$ and $I_0$, and $I_0$ and $I_d$ are contributions of dark currents of photodiodes to $I_0$ and $I$. The higher absorbance above the edge of the curves 1 to 16 in Fig. 3(a) than those in Figs. 3(b) and (c) are due to this effect.

In Figs. 3(b) and (c), the variation of the spectra in time ranges of 0 to 1.2 s and 0 to 45 s are respectively shown with time resolutions of 50 ms and 3 s. A slower variation in the XANES region was clearly observed. The absorption spectrum more than 10 minutes after the mixing agreed well with that for the Fe$^{2+}$ aqua complex. Therefore the second variation of the spectrum corresponds to the decomposition of the complex and the formation of the Fe$^{2+}$ aqua complex.

**Fig. 3**
Variation of X-ray absorption spectra near Fe K-absorption edge with time elapsed after mixing 0.3 M aqueous solution of iron(III) nitrate (Fe$_3$(NO$_3$)$_3$) and 0.3 M methanolic solution of catechol(C$_6$H$_4$(OH)$_2$). In each of (a), (b) and (c), the absorption spectrum for an aqueous solution of iron(III) nitrate is shown by a solid line as a reference.

(a) Variation of absorption spectra over the time range of 0 - 155 ms. Spectra numbered 1, 2, 4, 8, and 16 were respectively obtained by integrating signals of the diode array over the periods of 0 - 5, 10 - 15, 30 - 35, 70 - 75, and 150 - 155 ms.

(b) Variation of absorption spectra in the time range of 0 - 1175 ms. Spectra numbered 1, 2, 4, 8 and 16 were respectively obtained by integrating signals over the periods of 0 - 50, 75 - 125, 225 - 275, 525 - 575 and 1125 - 1175 ms. Small arrows indicate directions of variation of spectra from 1 to 16.

(c) Variation of absorption spectra over the time range of 0 - 45.5 s. Spectra numbered 1, 2, 4, 8 and 16 were respectively obtained by integrating signals over the periods of 0 - 3, 3.5 - 6.5, 10.5 - 13.5, 24.5 - 27.5 and 42.5 - 45.5 s. Small arrows have the same meaning as in (b).
It is clear that the reaction between iron(III) nitrate and catechol took place in two steps. More detailed discussion will be given elsewhere.

**Reaction of iron(III) nitrate with sodium thiosulfate.**

A 0.6 M aqueous solution of sodium thiosulfate was mixed with a 0.6 M aqueous solution of iron(III) nitrate. This reaction has been known to occur in two steps/13/:

\[
\begin{align*}
\text{Fe}^{3+} + 2\text{S}_2\text{O}_3^{2-} & \rightarrow \text{Fe(S}_2\text{O}_3)^{2-} \quad (1) \\
\text{Fe(S}_2\text{O}_3)^{2-} + \text{Fe}^{3+} & \rightarrow 2\text{Fe}^{2+} + \text{S}_4\text{O}_6^{2-} \quad (2)
\end{align*}
\]

The first reaction takes place in less than a few milliseconds. The color of the solution changes into purple by this reaction. The formed complex is then decomposed as represented by (2) in a few to several tens seconds, where the color of the solution returns transparent again. Fig. 4 shows the variation of the spectrum in XANES region in the time scale of 0 to 18.9 s with a time resolution of 0.1 s. A further variation of the spectrum was observed outside of this time scale. The first spectrum which was obtained by integrating signals over 0 to 0.1 s after mixing exactly agreed with the spectrum for the aqueous solution of iron(III) nitrate. This suggests either that only a small portion of Fe ions are converted into the complex shown by (1) or that the absorption spectrum for the formed complex does not change much compared with that of iron(III) nitrate. The observed variation of the absorption spectrum corresponds to the reaction represented by (2). Figure 5 shows the variation of the EXAFS oscillation with time. Figure 6 shows the Fourier transform of the spectrum shown in Fig. 5. The magnitude of the peak in Fig. 6 decreases as a function of time. A more detailed analysis is now under way.

**Fig. 4**
Variation of X-ray absorption spectra near Fe K-absorption edge with time after mixing 0.6 M aqueous solution of iron(III) nitrate (Fe(NO₃)₃) with 0.6 M aqueous solution of sodium thiosulfate (Na₂S₂O₃) in the time range of 0 - 18.9 s with a time resolution of 0.1 s.

**Fig. 5**
EXAFS oscillations 0.1, 5.1 and 17.6 s after mixing 0.6 M aqueous solution of iron(III) nitrate with 0.6 M aqueous solution of sodium thiosulfate.
Concluding remarks

The new stopped-flow device for use with the energy dispersive X-ray absorption spectrometer has opened up a possibility of studying kinetics of various kinds of reactions in solutions. Several improvements of the system will further enhance the utility of the method. Especially it is desirable to obtain better signal-to-noise ratio for curves obtained with at very short exposure times. This will be realized by using a more sensitive detector with lower noise and a more intense radiation source. The direct-type photodiode array such as the one used by Dartyge et al./14/ looks promising. A multipole wiggler can increase the incident photon flux by one to two orders of magnitudes. With these improvements, it will also be possible to study reaction kinetics in more dilute (a few millimolar concentration) solutions. Ascone et al./15/ already studied pH-dependence of absorption spectra of 5 mM hemoglobin using the dispersive spectrometer.

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