

Time-Resolved XAFS Measurements for Laser-Induced Excited State of Tris(2,2'-bipyridine)ruthenium(II) Complex

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Introduction

The electronic states of ruthenium(II) complexes with diimine ligands are widely investigated in relation to their good performance as the light sensitizer for the reductive catalysis system and the tris(2,2'-bipyridine)ruthenium(II) complex ($[\text{Ru}(\text{bpy})_3]^{2+}$) has been a recent subject of the time-resolved X-ray absorption spectroscopy [1]. In this study, the time-resolved XAFS measurements in the order of ns have been carried out using a single-bunch property of PF-AR to investigate not only the electronic state but also the local structure around the Ru center.

Experiments

The time-resolved XAFS spectra were measured at NW2A by using the X-ray pulse selector, by which the X-ray pulse frequency was reduced to 946 Hz. The excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ was generated by a pulse YAG laser (2 ns pulse width, 532 nm). Because all X-ray pulses are synchronized with the YAG laser pulses, the X-ray detector does not need to have the time resolution. The time delay of an X-ray pulse after the YAG laser pulse was varied from 5 ns to 100 μs . A conventional XAFS scan was performed at a constant time delay and repeated by changing it. The incident and transmitted X-ray intensities were measured using the ionization chambers.

Results and Discussion

As seen in Figure 1, in which the normalized XANES spectra are shown at 5, 200, and 500 ns after the excitation, the absorption edge is slightly shifted to lower energy. The time-course plot of X-ray absorbance at 22.130 keV given in Figure 1 indicates that the energy shift is completed within 5 ns and that the shifted edge is recovered to the original energy in the order of a few 100 ns. This time scale is almost consistent with the life time of ca. 300 ns for the triplet MLCT state of $[\text{Ru}(\text{bpy})_3]^{2+}$. It should be however noted that the shift direction of the absorption edge may not be correct because the spectra are numerically normalized so as the absorbance jump to become 1.

The Fourier transform (FT) magnitudes of the EXAFS data are depicted in Figure 2. The local structure around the Ru center at 500 ns after the laser irradiation is almost comparable to that of the ground state. For the triplet MLCT state, it is found that the peak position observed at ca. 1.6 Å (phase-shift uncorrected) assigned to the Ru–N interaction is slightly shifted to the lower distance together with the decrease in intensity.

The changes observed in Figures 1 and 2 are very small and thus a great attention should be paid for the structure

analyses. In this study, the size of excitation laser was about 5 mm ϕ at the sample position while that of X-ray beam was ca. 0.5 \times 0.3 mm². It is very important to focus the laser light to increase the content of the excited state, leading to an increased reliability of the structure analysis.

Acknowledgment

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References

[1] M. Saes, C. Bressler, R. Abela, D. Grolimund, S. L. Johnson, P. A. Heimann, M. Chergui, Phys. Rev. Lett. 90, 047403 (2003).

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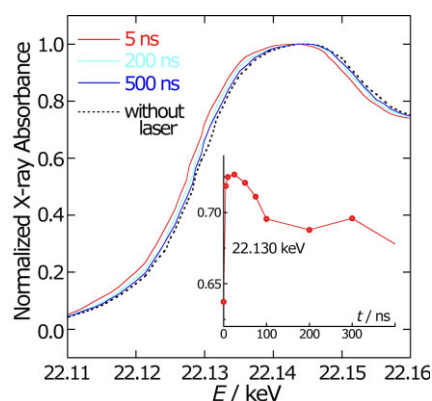


Figure 1: Normalized XANES spectra of laser-excited $[\text{Ru}(\text{bpy})_3]^{2+}$ at 5 (red), 200 (sky blue), and 500 (blue) ns after the 532 nm YAG laser pulse. The change in X-ray absorbance at 22.130 keV is given in the inset.

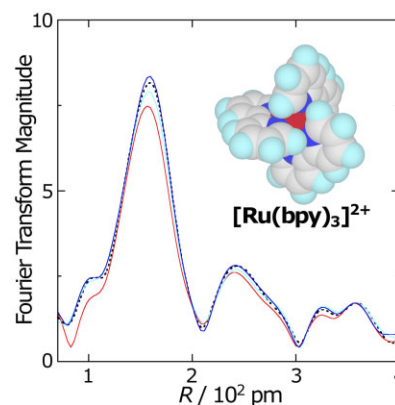


Figure 2: Fourier transform magnitudes of the time-resolved EXAFS data for $[\text{Ru}(\text{bpy})_3]^{2+}$. The meanings of the line indication are the same with Figure 1.