Photochemistry of Metal Complexes Studied by Time-resolved Infrared Spectroscopy

(PRESTO-JST, 2Tokyo Tech.) Ken Onda1,2, Sei'ichi Tanaka2, Tatsuhiko Mukuta2, Masataka Funaki2, Kyohei Tannno2

I. Introduction

Transition metal complexes are widely used in various photo-functional materials, for example, a photosensitizer for organic solar cells and artificial photosynthetic systems, a photoredox reagent for organic synthesis, and biological applications such as a fluorescence probe of protein and a photo-anticancer drug. In spite of this wide application, the fundamental photoexcited processes in metal complexes have not been well understood yet because of their complicated structures and excited states. Time-resolved infrared vibrational spectroscopy is one of the best tools for studying such excited state dynamics because vibrational peaks are sensitive to local charge and structure even in complex molecular systems. However, the application of TR-IR to metal complexes was limited to those including a CO group, which has strong infrared absorption. Using this method, we previously studied various organic crystals consisting of hetero-cyclic conjugated molecules and showed that stretching vibrations of double bonds in these molecules are a good probe for ultrafast variations of charge and structure in the crystals [1-4]. Since similar molecules are often used in metal complexes as a ligand, we have applied the same way to studies on photoexcited dynamics in metal complexes by developing a suitable time-resolved infrared spectroscopy system.

II. Experimental

Time-resolved infrared (TR-IR) vibrational spectra were acquired using the pump-probe method using a femtosecond Ti:sapphire chirped pulse amplifier (CPA; 800 nm, 120 fs, 1 kHz). A tunable mid-infrared pulse (1000 - 4000 cm\(^{-1}\)) was generated by optical parametric amplification (OPA) and difference frequency generation (DFG) from the output of the CPA. The bandwidth of the IR pulse was 150 cm\(^{-1}\). A tunable pump pulse (266, 400, 480 - 800 nm) was obtained by nonlinear optical processes from the outputs of CPA and/or OPA. To acquire the transient IR absorption spectrum, the probe pulse was dispersed by a 19 cm\(^{-1}\) polychromator and data were acquired using a 64-channel MCT (mercury cadmium telluride) infrared detector array.

III. Results and discussion

We first studied a prototypical ruthenium complexes, [Ru(bpy)\(_3\)]\(^{2+}\) and [Ru(bpy)\(_2\)(bpm)]\(^{2+}\) (bpy = 2,2'-bipyridine, bpm = 2,2'-bipyrimidine) [5]. Figure 1 shows the vibrational spectra of these complexes at 500 ps after photoexcitation with a 400 nm pulse. By comparing these
complexes and isotope substituted complexes and by using quantum chemical calculations, we assigned all the observed peaks at 1000 - 1700 cm\(^{-1}\) in the triplet metal to ligand charge transfer state (\(^3\)MLCT). In addition, from a careful analysis of temporal variations of all these peaks, we found that only a peak at 1600 cm\(^{-1}\) shows a blue shift over 15 ps as shown in Fig. 2 (magnified the oval area in Fig. 1). We revealed that this peak is assigned to the metal centered state (\(^3\)MC) from dependence of the temporal behavior of the peak on various parameters such as solvent, ligand, and excitation wavelength. Figure 2 compares the temporal variations of the peak under (a) non-reactive and (b) reactive conditions. Because it is considered that the photoreaction occurs via \(^3\)MC, disappearance of the peak at 1600 cm\(^{-1}\) strongly indicates that this peak is assigned to the \(^3\)MC state.

We learned from the result that temporal variations of vibrational peaks of ligands are a good probe for photochemical process in metal complexes, so that we applied the same way to more practical metal complexes. One example is the study on internal rotation of a phenyl group via \(\pi-\pi\) interaction in [Re(dmb)(CO)\(_2\){P(p-FPh)\(_3\)}\(_2\)]\(^+\), which is one of CO\(_2\) reduction photocatalysts. Figure 3 shows the temporal variations of this complex. Because only the peak assigned to phenyl group (indicated by the red arrow) gradually increases over 20 ps, we concluded that it takes 20 ps for the phenyl groups to rotate via a \(\pi-\pi\) interaction after charge transfer to the dmb ligand. We are now studying photoexcited dynamics in more practical metal complexes, for example, characterization of excited states in water oxidation complexes, [Ru(tpy)(pynp)]\(^2+\), in aqueous solution [6] and even multi-reagent and multi-step chemical reactions in supramolecular systems.

References