1-1-8. Time-Resolved Infrared Spectroscopy

Overview

Time-Resolved Infrared Spectroscopy (TR-IR) is the spectroscopic method that infrared vibrational spectra are measured with very high time resolution from picoseconds to nanoseconds. Infrared vibrational spectroscopy, which is called molecular fingerprint, is the excellent analytical method because not only it gives us the information required for molecule identification but also it can be measured regardless of the kind, shape, or environment of samples. TR-IR having sufficient time resolution enable us to apply the analysis using infrared vibrational spectroscopy to the analysis for photochemical processes. This usefulness of TR-IR has been known for a long time but the application to the field of photochemistry began since 2000s thanks to the developments of universal TR-IR systems.

Current Status and Frontiers

The TR-IR system that is widely used now obtains the mid-infrared (MIR) and UV-visible pulses for its measurements from an output of Ti:sapphire regenerative amplifier using non-linear optical processes. TR-IR spectra are measured using multi-channel MIR detector array equipped with a polychromator. In addition, the usage of a nanosecond laser synchronized with the amplifier enables us to measure TR-IR spectra ranging from sub-picoseconds to milli-seconds. By taking the difference between the data with and without the pump pulse, it is able to detect a signal with absorbance change of $< 10^{-5}$.

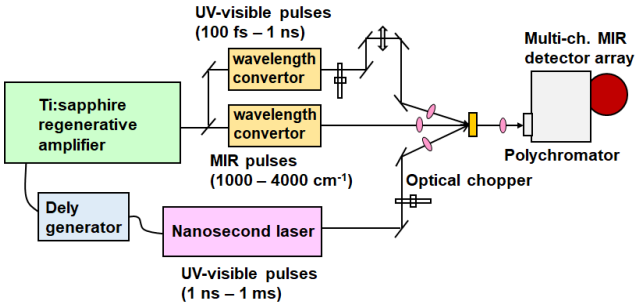

Figure 1. Schematic of time-resolved infrared spectroscopy system.

The vibrational bands that are mostly used are the CO stretching vibrations. This is because the vibrations strongly absorb infrared light and their energies are isolated in an IR spectrum. Particularly, the wavenumbers of CO bands in metal complexes are known as a good maker to know the electron density on the metal because its bond is formed by the charge transfer between the d-orbitals of metal and the π-orbitals of CO. Furthermore, to obtain the sufficient information on a molecule from TR-IR spectra, it is necessary to measure the spectra in the fingerprint region less than 1700 cm^{-1} and assign the measured spectra to the normal vibrational modes. A typical example is the TR-IR study of a solution of $[Ru(bpy)_3]^{2+}$ (bpy = bipyridine) in 2014 (Onda et al). They measured the TR-IR spectra ranging from 1000 to 1700 cm^{-1} in the picosecond range. In addition, they studied the samples with ligand and isotope substitutions and carefully found out which substructure each vibrational peak is originated from. By comparing this experimental

result to the spectral simulations by quantum chemical calculations, they optimized the calculation conditions. This optimized calculation result enables us to have a more reliable discussion on the excited electronic states and structures.

Another feature of infrared spectra is that since the wavelength of light to use is long ~μm, inhomogenous samples having structures less than μm, such as powders and devices, can be measured ignoring the effect of light scattering. TR-IR has the same feature. One example is the measurements of photocarrier dynamics in powdered semiconductor photocatalysts. The photocarriers in conduction band generated by photoexcitation strongly absorb MIR light because of their freedom of motions. The trapped electrons, which have less freedom of motions, absorbs near infrared light. By measuring these temporal variations, the photocarrier dynamics in powered photocatalysts such as TiO_2 and $SrTiO_3$ were measured (Yamakata, et al.). Moreover, the high energy resolution and narrow bandwidth of vibrational peaks in IR measurements enable us to measure photocarrier dynamics in the semiconductor and valence change in the metal complex separately in a hybrid photocatalyst of a powdered semiconductor and a metal complex (Sato, Onda, et al.).

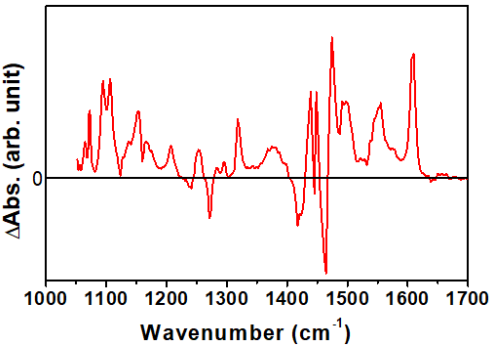

Figure 2. TR-IR spectra of a 1 mM THF solution of $[Ru(bpy)_2]^{2+}$.

References

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Future Perspectives and Directions

More reliable and user-friendly TR-IR systems would become widespread. It would be possible to apply more practical samples such as thin layer films, single crystals, suspension solutions, and electrochemical cells.

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