TRACING "LOOSE ELECTRONS" BY PICOSECOND TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY WITH NEAR-INFRARED EXCITATION

K. Iwata¹, T. Takaya², K. Yuzaki², Y. Takada², S. Saha², H. Hamaguchi², and H. Kuroda³

¹Research Centre for Spectrochemistry, Shool of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan; E-Mail: iwata@chem.s.u-tokyo.ac.jp

² Department of Chemistry, Shool of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

³ IR EEL Research Center, Research Institute of Science and Technology, The Tokyo University of Science, Yamazaki 2461, Noda, 278-8510, Japan

Keywords: near-infrared, time-resolved Raman, electron transfer, bianthryl

Abstract: We develop a picosecond time-resolved Raman spectrometer with a near-infrared sensitive ICCD. By using near-infrared picosecond time-resolved Raman spectroscopy in combination with femtosecond time-resolved near-infrared absorption spectroscopy, we can study the structure and dynamics of short-lived species associated with "loose electrons".

Time-resolved spectroscopy in the near-infrared region has not been fully utilized. However, many of the photochemical systems that have "loose" electrons, such as intra- or inter-molecular charge transfer states or electronically excited states of large conjugated systems, have absorption in this spectral region. Because electrons have to become loose when a chemical reaction occurs, it is important to trace them directly with time-resolved spectroscopy. We develop a femtosecond time-resolved near-infrared spectrometer with the wavelength coverage of 0.9 to 1.5 μ m. We also develop a picosecond time-resolved Raman spectrometer that can be used with the probe light in the near-infrared. By using both of these spectrometers, we can study the structure and dynamics of short-lived molecular species associated with the "loose electrons". The combination of the two methods is quite effective when studying detailed mechanism of chemical reactions.

Both of the femtosecond time-resolved near-infrared spectrometer and picosecond time-resolved Raman spectrometer use the pump-probe technique. The probe light of the femtosecond time-resolved near-infrared spectrometer is generated by self-phase modulation on a sapphire plate where the amplified output of a mode-locked Ti:sapphire laser is focused. The probe light after the photoexcited sample is dispersed by a spectrograph and is detected by an InGaAs array detector. For the picosecond time-resolved Raman measurement, the probe light is generated at an optical parametric amplifier pumped by the second harmonic of the amplified Ti:sapphire laser output. A near-infrared sensitive ICCD [1] is used as the detector, which enables us to record near-infrared excited picosecond Raman spectra with good SN ratios.

Photoinduced intramolecular electron transfer of 9,9'-bianthryl (BA) in polar solvents has been actively studied as a prototype photochemical reaction. In this reaction, the locally excited (LE) state is the reactant while the charge transfer (CT) state is the product. There remain basic questions, however, concerning the mechanism of this reaction. It is not clear, for example, if there is an intermediate state between the LE state, which is formed immediately after the photoexcitation, and the CT state, which is produced in a few hundreds femtoseconds or in several picoseconds depending on the solvent polarity. We need to know the characters of the LE and CT states, as well as their decay and rise kinetics, for understanding this basic electron transfer reaction.

We first measured the femtosecond time-resolved near-infrared spectra of BA. The decay of the LE state and the rise of the CT state were clearly recorded. The LE state decayed in 0.4 ps while the CT state appeared in 0.4 ps. There was no intermediate observed between the two states. The

LE state was directly converted to the CT state. We also measured the time-resolved near-infrared spectra of anthracene (monomer) and N-(9-anthryl)carbazole (C9A). All the three molecules showed similar transient absorption bands in the near-infrared region (Fig. 1). The LE state of BA should be similar to the first excited singlet (S_1) states of anthracene and C9A.

For studying the reacting state of the electron transfer reaction further, we measured the picosecond time-resolved resonance Raman spectra of the three molecules with the probe light wavelength of 1064 nm. The obtained spectrum for the S_1 state of anthracene is shown in Fig. 2. The spectrum agrees with the reported spectrum of S_1 anthracene obtained by the time-resolved FT Raman method [2], although the use of the ICCD detector enabled us to reduce the exposure time by an order of magnitude. As shown in Fig. 1, the near-infrared absorption of the LE states of BA and C9A were similar to the anthracene's absorption. Their Raman spectra, however, were quite different. It is likely that the character of the reactant LE state of BA is not identical with the S_1 state of anthracene. It is possible that the vibrational dephasing rate in the LE state of BA is much larger than that of the anthracene S_1 state. From the Raman data, it is obvious that the presence of the neighbouring anthracene ring affects the electronic and vibrational states of the LE state of BA substantially.

Both of the two time-resolved spectroscopic methods in the near-infrared region are indispensable for obtaining key information on the electron transfer reaction of 9,9'-bianthryl.



Fig. 1. Transient near-infrared spectra of anthracene (a, 200 ps), 9,9'-bianthryl (BA) (b, 240 fs), and 9-anthrylcarbazole (C9A) (c, 240 fs).



Fig. 2 Picosecond transient Raman spectrum of S_1 anthracene probed at 1064 nm. Exposure time, 17 min.

Acknowledgements:

This work is supported by Grant-in-Aid's for Creative Scientific Research (No.11NP0101) and Scientific Research (B) (No. 15350005) from Japan Society for the Promotion of Science, and Grant-in-Aid for Scientific Research on Priority Areas (Area 417, No. 15033219) from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government.

References:

- S. Kaminaka, T. Ito, H. Yamazaki, E. Kohda and H. Hamaguchi, J. Raman Spectrosc. 33, 498 (2002).
- 2. G.S. Jas, C. Wan, K. Kuczera, and C.K. Johnson, J. Phys. Chem. 100, 11857 (1996).