

## Structure Analysis of the Excited Molecules in the Equilibrium State

Yuji Ohashi, Manabu Hoshino, Akiko Sekine, Hidehiro Uekusa,  
*Department of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8551, Japan. E-mail: yohashi@cms.titech.ac.jp*

When the crystal is irradiated with UV or visible light at low temperatures, the averaged molecule in the crystalline lattice reaches the equilibrium state composed of ground and excited states. The structure of the excited molecule in the equilibrium state can be analyzed by X-rays if the occupancy factor of the produced excited molecules exceeds the limiting value (>5%). This method is called equilibrium analysis of excited molecule. Recently we obtained the excited structure of the diplatinum complex with the equilibrium method[1]. The Pt-Pt and Pt-P distances of the diplatinum complex are shortened at the excited state.

The same method was applied to the other complex crystals and was successful to observe the structures of the excited molecules. The first example is the  $(VO)(acac)_2$  complex. The unit-cell was expanded at the equilibrium state and the molecular structure indicated that one V=O and four V-O bonds around the central vanadium atom were expanded by 0.0043(8) and 0.0045(7)Å. The second example is the  $[Au(PPh_3)_2]Cl$  complex. The unit-cell of the crystal shrank and the Au-P and Au-P distances decreased 0.0055(4) and 0.0057(4)Å in the equilibrium state. The structural changes at the equilibrium state suggest that the excited molecules are produced more than 5% in the crystal and the changes of the bond distances well explain the structures of the excited molecules.

[1] Yasuda N., Uekusa H., Ohashi Y., *Bull. Chem. Soc. Jpn.*, 2004, 77, 933.

**Keywords:** excited structure, photoreaction, equilibrium state