

s7.m3.o1 **The Study of Light-Induced Transient Species by Crystallographic Methods.** P. Coppens, *Department of Chemistry, SUNY at Buffalo, Buffalo, NY 14260-3000, USA.*

Keywords: instrumentation, excited states.

The study of light-induced metastable and transient species is a frontier field of X-ray Crystallography, that is highly relevant to Chemistry and Materials Science. Among the potential subjects for analysis are identification and geometry determination of excited states, time-resolved studies of electron transfer and study of photochemical reactions. The appropriate choice of experimental technique depends on the lifetime of light-induced species. While for metastable states steady pump and probe sources may be used, pulsed lasers and synchrotron sources become essential for the study of short lived species. Cryogenic techniques range from conventional liquid nitrogen flow systems to helium cryostats and helium flow systems.

We have combined Crystallography with infrared spectroscopy, Differential Scanning Calorimetry and theoretical calculations in the study of oxygen and η^2 bound transition metal nitrosyl complexes [1]. We have found that the photo-induced isomerization is not limited to NO complexes, but occurs also for other diatomic molecules bound to transition metal complexes [2]. Analysis of electronic vs. solid state influence on the process indicates the former to be dominant, though a number of observations indicate that the effect of the crystal matrix can not be fully discounted.

Equipment for the study of time resolved species will be described [3]. It includes fluorescence monitoring of the diffractometer-mounted sample, which is essential for following molecular excitation during the experiment. To minimize the heat dissipated in the crystal, small crystals are used, and the photoactive species being studied are diluted with inactive spacer molecules. The crystal is immersed in a helium gas flow for cooling. Rapid data collection at high brightness sources is essential.

s7.m3.o2 **Electric field driven structural changes in DKDP.** S.J. van Reeuwijk, A. Puig-Molina, H. Graafsma, *European Synchrotron Radiation Facility, 6 rue Jules Horowitz, 38043 Grenoble, France.*

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KDP (KH_2PO_4) and DKDP (KD_2PO_4) are well known and extensively studied ferroelectrics. In the paraelectric phase (spacegroup I-42d) the hydrogen atom is distributed over two equivalent positions in the hydrogen bond linking the PO_4 tetrahedra. Below T_C the hydrogens order gradually into one of the positions (spacegroup Fdd2) and the heavy atoms displace with this ordering [1]. Upon deuteration the phase transition temperature shifts from 122K to 229K. To clarify the process of the phase transition and the role of the H/D atom in the transition, many studies were carried out. Structural studies have mainly been concerned with structural changes (atomic positions, temperature parameters and H/D site occupancy) induced by either temperature [1] or hydrostatic pressure [2]. Here we present a study in which an external electric field was applied to induce the structural changes. The electric field, in contrast to temperature and hydrostatic pressure, is a vector quantity, and, thereby, gives additional insight into the process of the phase transition.

For both KDP and DKDP the piezoelectric constant, d_{36} , shows a Curie-Weiss behaviour with an anomaly at T_C . By applying an electric field parallel to the c axis, and measuring the change in cell parameter using x-ray diffraction, we determined the piezoelectric constant at different values approaching the phase transition temperature.

Subsequently, for DKDP the electric field induced changes in integrated intensity were measured for a number of reflections at room temperature. Refinement of the data yielded the structural changes inside the unit cell, i.e. the ordering of the D atoms and the displacement of the other atoms. The results agree very well with temperature induced structural changes [1] and thermodynamic theory. Finally, the process of the phase transition is discussed.

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