

**s9.m1.p1** The Effect Of Deuteration On The Crystalline Structure And The Motion Of Methyl Group In Lithium Acetate Dihydrate B. Nicolai<sup>a</sup>, F. Fillaux<sup>b</sup>, A. Cousson<sup>a</sup>,<sup>a</sup> Laboratoire Léon Brillouin, CEA Saclay, France, <sup>b</sup> LADIR-CNRS, Thiais, France

Keywords: molecular interactions, organic materials, molecular solids

Quantum rotational dynamics of methyl groups at low temperature is well known as a very sensitive probe of local potentials in molecular crystals[1]. The methyl-group dynamics is commonly described with the single particle model: the methyl group is considered as a symmetric quantum rotor performing a one-dimensional rigid rotation about its threefold axis in a rigid environment. The energy levels of this quantum rotor can be obtained by solution of the Schrödinger equation. Each triply degenerate energy level are split into 2 sublevels, due to the overlap of the wavefunctions in the adjacent wells. The magnitude of this tunnel splitting depends on the potential shape (barrier height...).

Rotational dynamics of methyl groups give rise to observable tunnelling transitions in many molecular crystals. Above ~1  $\mu\text{eV}$ , tunnelling transitions are best observed by inelastic neutron scattering (INS) techniques.

Rotational tunnelling of methyl groups in lithium acetate dihydrate ( $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ ) has been intensively studied, experimentally and theoretically [2-4]. This compound is particularly interesting because it is one of the rare compounds in which several tunnelling lines have been reported for a single type of methyl group. This has been interpreted in terms of coupled pair rotors, coupling with the centre of mass motion or infinite chain couplings.

Powder [5] and single-crystal neutron diffraction measurements on the protonated, deuterated and partially deuterated compounds reveal a phase transition from Cmmm to Pman due to an ordering of the  $\text{CD}_3$  group at liquid helium temperature and independent of the deuteration of the water molecules. We are not aware that a similar phase transition has ever been reported.

**s9.m1.p2** Variable Temperature Crystal Structure Studies of m-Nitroaniline. G. Wójcik, J. Holband, *Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wyb. Wyspińskiego 27, 50-370 Wrocław, Poland.*

Keywords: thermal expansion, phase transition, rigid body analysis.

Meta-nitroaniline crystal, a well known optically nonlinear material, has been recently investigated in terms of crystal engineering method<sup>1, 2</sup>. The objective of these studies concerned the molecular packing<sup>1</sup> and its variations in potential polymorphic structures<sup>2</sup>. Our recent paper has dealt with molecular dynamics leading to thermodynamic transitions in the m-nitroaniline crystal as studied with relaxation (proton NMR, dielectric) and calorimetric (DSC) methods<sup>3</sup>. The occurrence of the phase transition to a plastic phase at temperature above ambient has been reported<sup>3</sup>. In the low temperature range (about 140 K) an anomaly on the DSC curves, similar to those connected with glass transition has been observed as well<sup>3</sup>.

The actually reported variable temperature X-ray diffraction measurements has provided the m-nitroaniline crystal structures at several temperatures between 90 K and 350 K. The temperature dependences of the unit cell parameters confirm the occurrence of the phase transitions and the contraction of the crystal lattice along the b axis direction as had been previously found by direct dilatometric measurements<sup>4</sup>. The principal axes cross-sections of the thermal expansion tensor at variable temperatures will be shown. The rigid body analysis including the attached non-rigid nitro group<sup>5</sup> performed with the THMA11 Program<sup>6</sup> provides the temperature dependences of the principal elements of the molecular  $T$  and  $L$  tensors and indicates a libration motion which constitutes probably a driving force of the phase transition.

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