



Contribution ID: 20

Type: ORAL CONTRIBUTION

Proton Dynamics in One-dimensional Hydrogen-bonding System in Molecular Co-crystals TMP-D2ca and DMP-H2ca

Thursday, 16 September 2010 14:00 (20 minutes)

Recently, hydrogen-bonded supramolecular co-crystals have attracted much interest in aim for functional materials such as ferroelectrics [1]. By use of ^{35}Cl nuclear quadrupole resonance (NQR) we have studied an organic ferroelectric, phenazine(Phz)-chloranilic acid (H2ca) co-crystal, Phz-H2ca, and found an electric field gradient fluctuation probably due to a proton dynamics in hydrogen bond [2]. For the detection of rather slow motion of proton in the hydrogen-bonding system, NQR spin-lattice relaxation of the nearby atom will be quite sensitive. In the co-crystal of tetramethylpyrazine (TMP) with H2ca, TMP-H2ca, the spin-lattice relaxation time (T_1) of ^{35}Cl NQR showed a steep decrease with increasing temperature above ca. 250 K. The decrease could be explained by the Arrhenius law with the activation energy of 35 kJ mol $^{-1}$ [3]. In the present paper we studied a possible proton motion in another compound with a similar one-dimensional hydrogen bond, DMP-H2ca, the co-crystal between 2,6-dimethylpyrazine (DMP) and H2ca. The isotope effect on the hydrogen motion by deuteration of the acid hydrogen in TMP-H2ca was also studied. Fig. 1 shows temperature dependence of ^{35}Cl T_1 of TMP-D2ca compared with that of TMP-H2ca. By the deuteration the activation energy increased to 50 kJ mol $^{-1}$. The deuteron motion was confirmed by ^2H NMR spin-lattice relaxation measurements which resulted in the activation energy of 49 kJ mol $^{-1}$. Fig. 2 shows temperature dependence of ^{35}Cl T_1 of DMP-H2ca. In this compound the relaxation is dominated by lattice vibration suggesting no transfer motion of proton between the acid and base molecules.

References

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Session Classification: BIOLOGY, CHEMISTRY, MEDICINE, ARCHAEOLOGY, MINERALOGY

Track Classification: Biology, Chemistry, Medicine