Temperature Dependence of ^{2}H Nuclear Quadrupole Interaction in Very Short Hydrogen Bonds in Some Organic Acidic Salt Crystals

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The ^{2}H nuclear quadrupole interaction parameters, e^2Qq/h and η, are closely related to the shape of the potential energy surface at hydrogen bonds and depend sensitively on their geometry. We measured the temperature dependence of the ^{2}H NMR spectra of the crystalline acidic salts $KDCO_3$, KD acetylenedicarboxylate, RbD acetylenedicarboxylate, and KD maleate, which contain very short O-D$\cdots$O type hydrogen bonds. The temperature coefficient decreases with increase in the O$\cdots$O distance in the hydrogen bond. *Ab inito* molecular orbital calculations of the electric field gradient tensor based on the temperature dependent structure of each crystal indicate that thermal expansion of the hydrogen bond geometry is not responsible for this tendency. *Ab initio* calculations also predict that a fictitious off center shift of the hydrogen position in a symmetric hydrogen bond causes very high e^2Qq/h values. This suggests that low energy vibrational excitation may be responsible for large positive d(e^2Qq/h)/dT values in symmetric hydrogen bonds.

Key words: Hydrogen Bond; Quadrupole Coupling Constant; ^{2}H NMR.