Proton Dynamics in One-dimensional Hydrogen-bonding System in Molecular Co-crystals TMP-D_2ca and DMP-H_2ca

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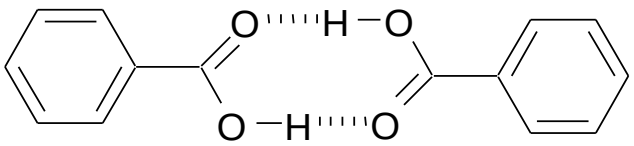
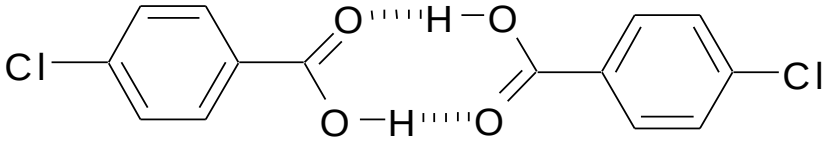
NMR/NQR Studies of Intermolecular Hydrogen Transfer

Hydrogen bonded carboxylic acid dimer



H-transfer with tunneling

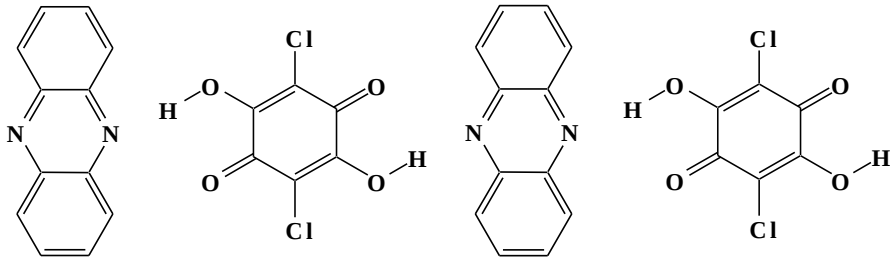
- **^{1}H NMR S. Nagaoka et al., J. Chem. Phys. 79 (1983) 4694.**



NQR of nearby nucleus

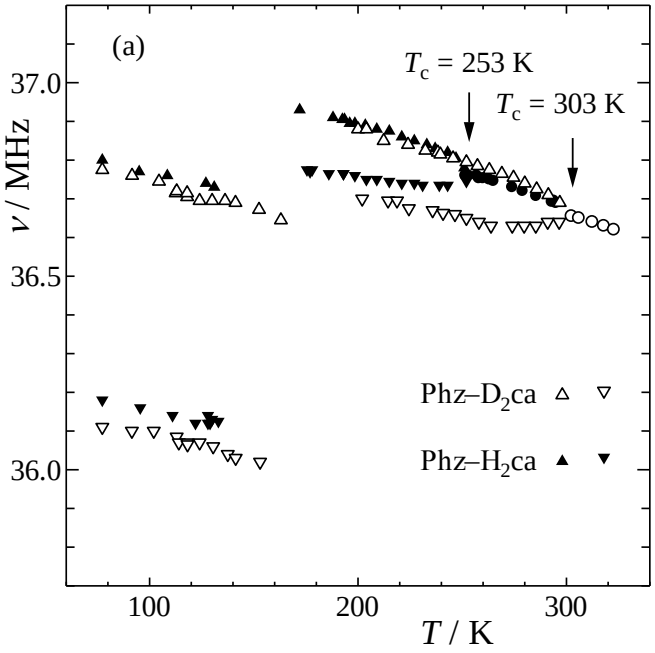
- **^{35}Cl NQR T. Nihei, S. Ishimaru, R. Ikeda, Z. Naturforsch. 55a (2000) 355.**

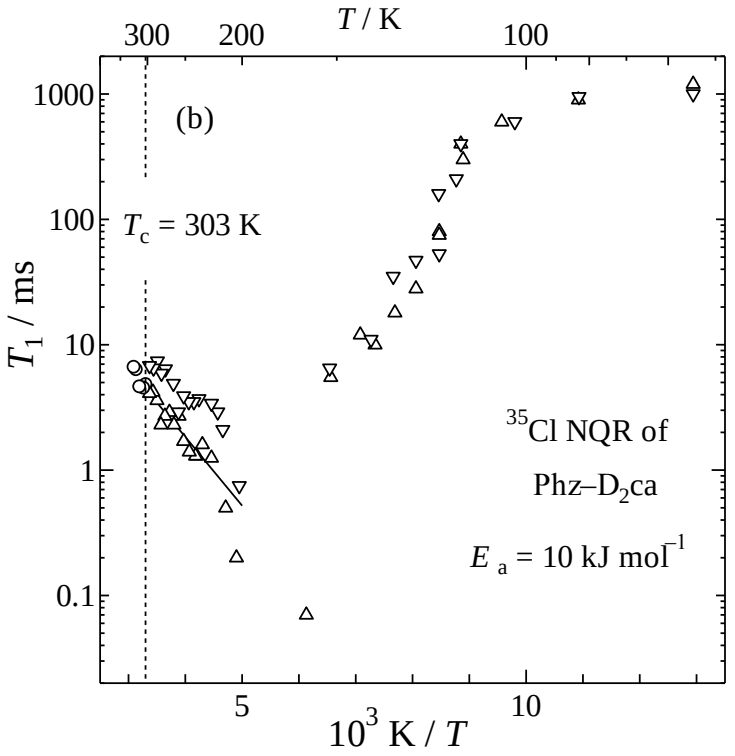
NMR/NQR Studies of Intermolecular Hydrogen Transfer



Hydrogen bonded supramolecular co-crystals

- **T. Asaji *et al.*, J. Phys.: Condens. Matter 19 (2007) 226203.**

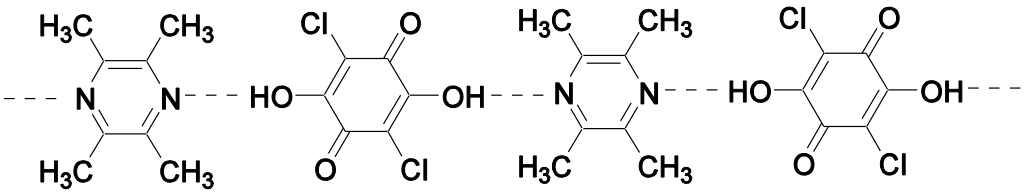




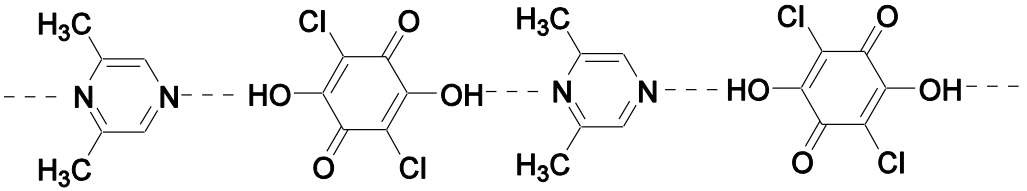
One-dimensional Hydrogen Bond in TMP-H_2ca and DMP-H_2ca

Tetramethylpyrazine(TMP)-Chloranilic acid(H_2ca) (1:1)
and Dimethylpyrazine(DMP)-Chloranilic acid(H_2ca) (1:1)

TMP-H_2ca



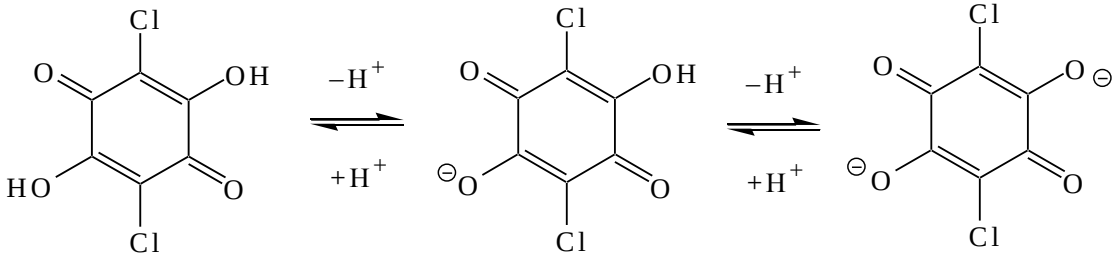
DMP-H_2ca



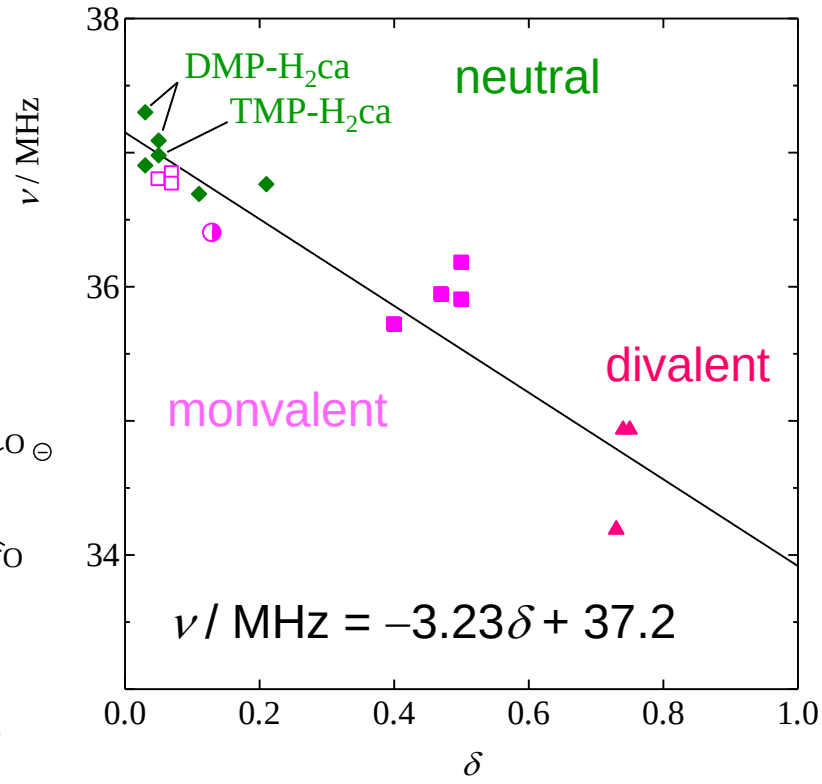
- **H-bonded supramolecule**

^{35}Cl NQR frequency

Sensitive to electronic state of chloranilic acid



neutral monvalent divalent



Measure of proton transfer

TMP-H_2ca: 37.000, 36.961 MHz at 77 K

DMP-H_2ca: 37.301, 37.091 MHz at 77 K

Freq.(77 K) vs proton transfer correlation

- **Neutral molecular co-crystal without proton transfer**

T. Asaji, J. Seliger, V. Žagar, and H. Ishida Magn. Reson. Chem. 48 (2010) 531-536.

^{35}Cl NQR Frequencies in TMP-H_2ca and TMP-D_2ca

Deuteration Effect

- NQR freq. increases by 20-30 kHz
- T_c increases from 83 K to 86 K

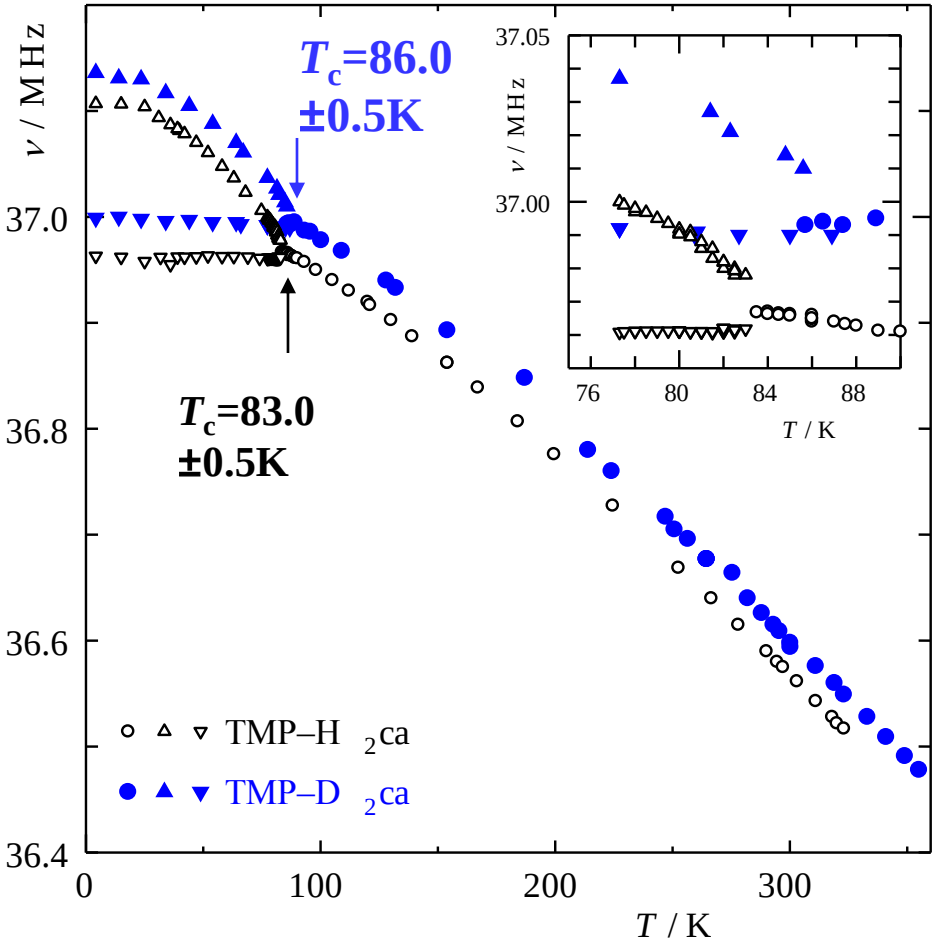
$$\Delta\nu = (T_c - T)^{\beta}$$

$\beta = 0.34 \pm 0.03$ for TMP-H_2ca

$\beta = 0.29 \pm 0.07$ for TMP-D_2ca

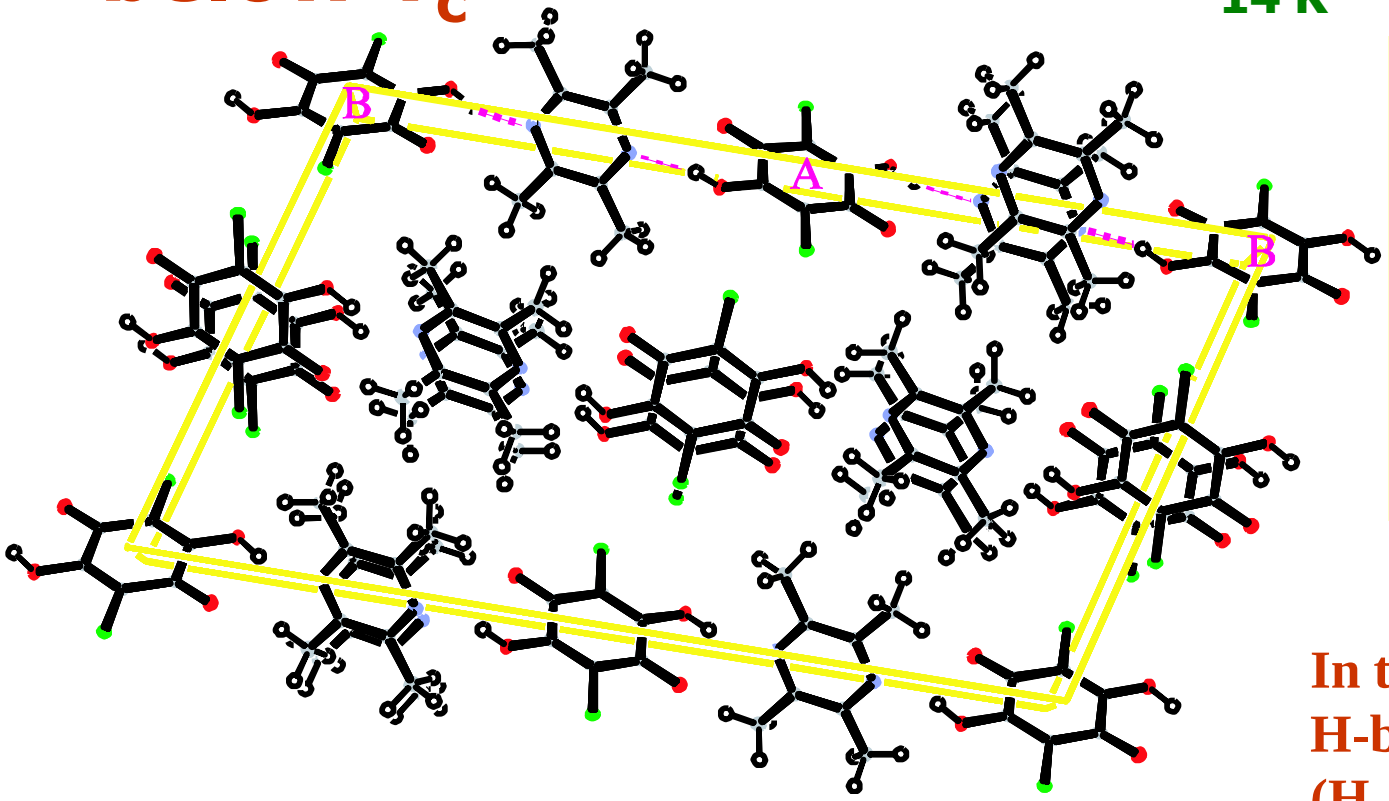
Structural Change

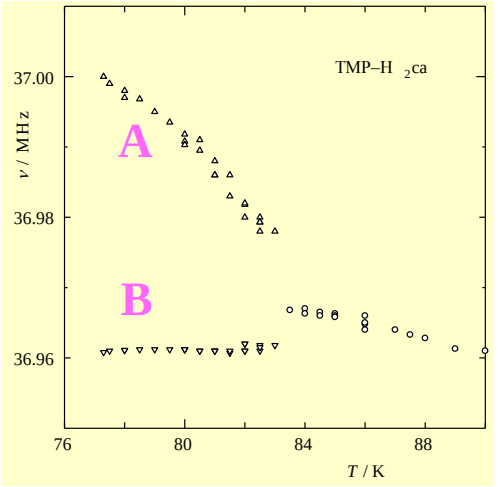
- Two Freqs. in LT phase
- Disappearance of center of inversion on TMP molecular center



Structural Change below T_c

$P2_1/n$ a = 13.34 b = 4.69 c = 24.62 Å β=105.4° at 14 K



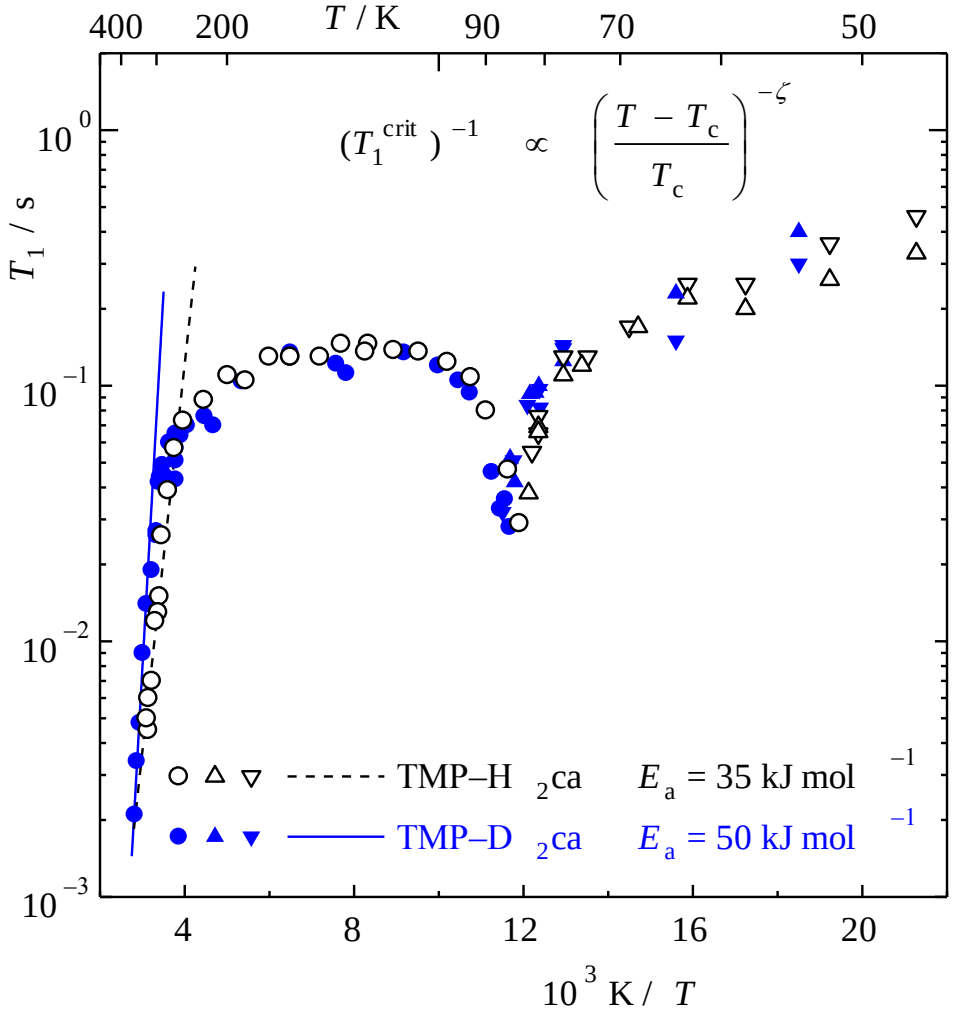


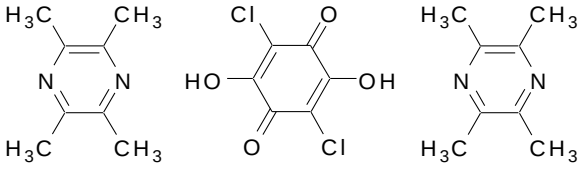
1d H-bonding network along [0,0,1]

In the LT phase the H-bonds between $(H_2ca)_A$ and TMP become weaker than that between $(H_2ca)_B$ and TMP

M. Prager *et al.*, J. Chem. Phys. 125, 194525 (2006).

^{35}Cl NQR Spin-lattice Relaxation Time in TMP-H_2ca and TMP-D_2ca

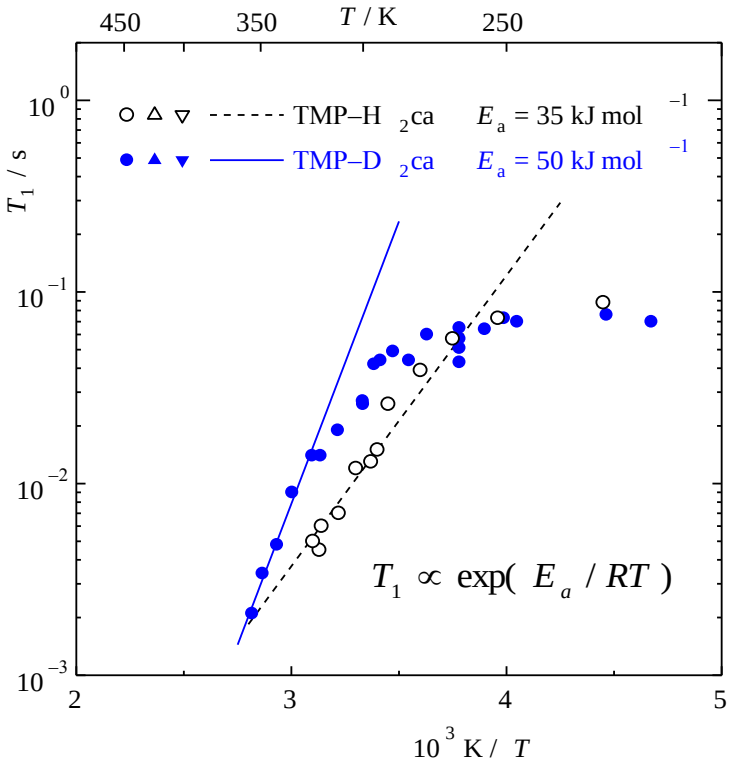


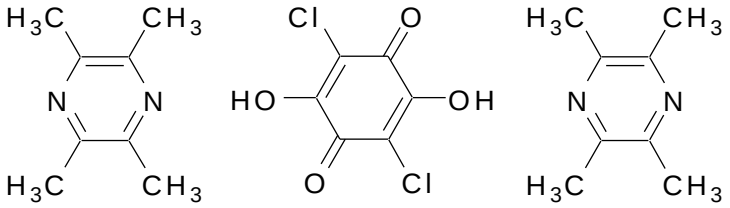


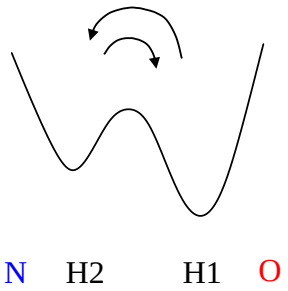
- T_1 dip due to Structural Phase Transition
  - $\zeta = 0.7 \pm 0.1$ for TMP-H_2ca
  - $\zeta = 0.54 \pm 0.07$ for TMP-D_2ca
- A steep T_1 decrease with increasing temperature above 300 K

This result suggests an excitation of a motion which is responsible to EFG fluctuation at the Cl atoms.

^{35}Cl NQR Spin-lattice Relaxation Time in TMP-H_2ca and TMP-D_2ca







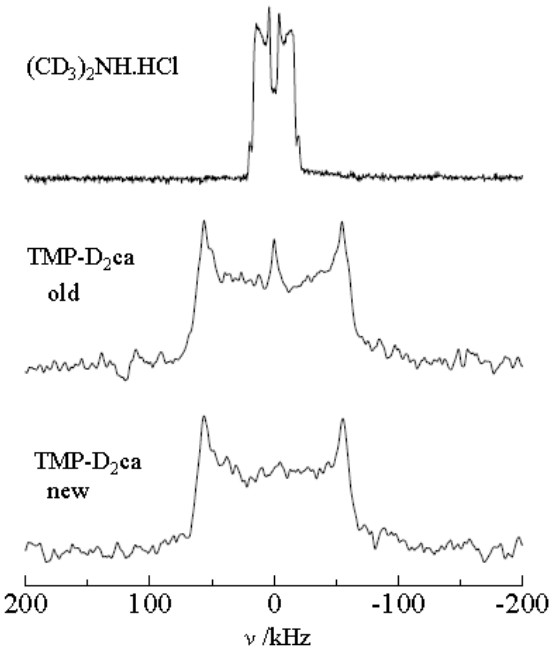
The proton jump between the two potential minima in the N…H-O hydrogen bond is expected

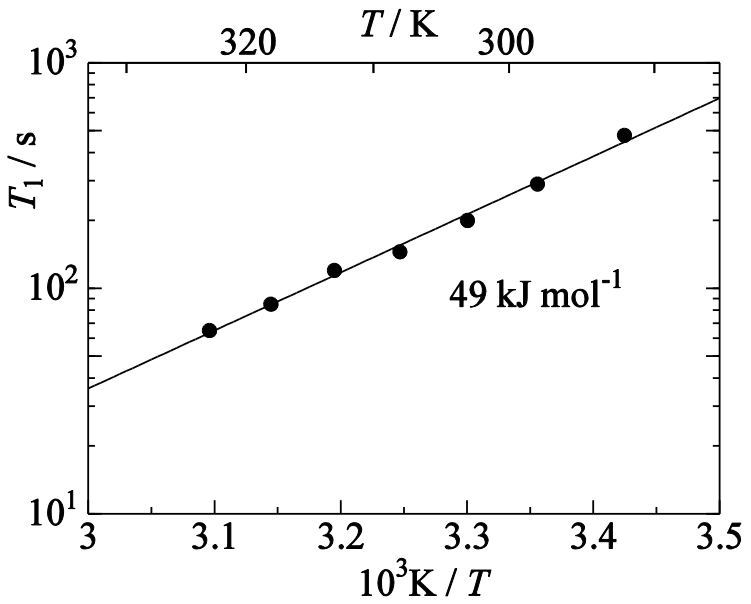
Large deuteration effect suggest the motion which is responsible for the EFG fluctuation is strongly related to the protonic motion

^{2}H NMR Spin-lattice Relaxation Time in TMP-D_2ca

Definite evidence of the acid hydrogen motion

The extent of the deuteration was estimated to be 75 % from ^{2}H NMR spectra





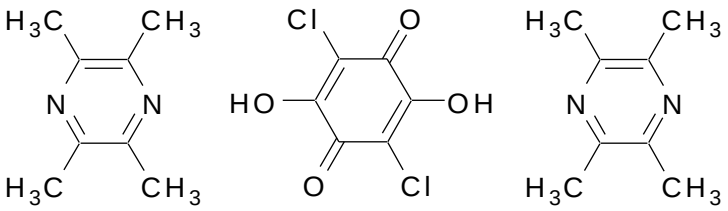
The activation energy of the deuteron motion was determined as 49 kJ mol^{-1}

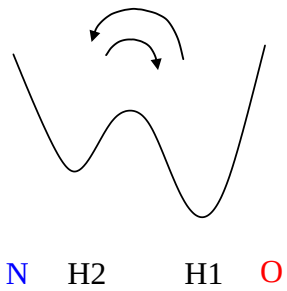
This value shows a very good agreement with that (50 kJ mol^{-1}) obtained from NQR T_1

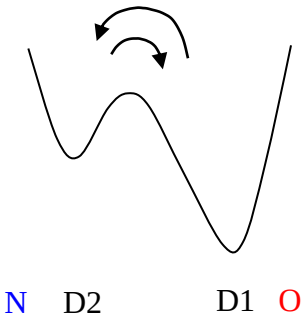
This is a strong evidence for the EFG fluctuation due to the acid hydrogen motion

Deuteration and N…H-O Hydrogen Bond

Why E_a is increased by the deuteration?







By the deuteration, the H-O bond distance decreases (H-O, 0.938(8) Å; D-O, 0.879(4) Å), while the N···H and N···O distances increase (N…H, 1.824(9) Å; N…D, 1.894(5) Å; N…O, 2.7079(8) and 2.7295(6) Å, respectively, for the normal and deuterated hydrogen bond)

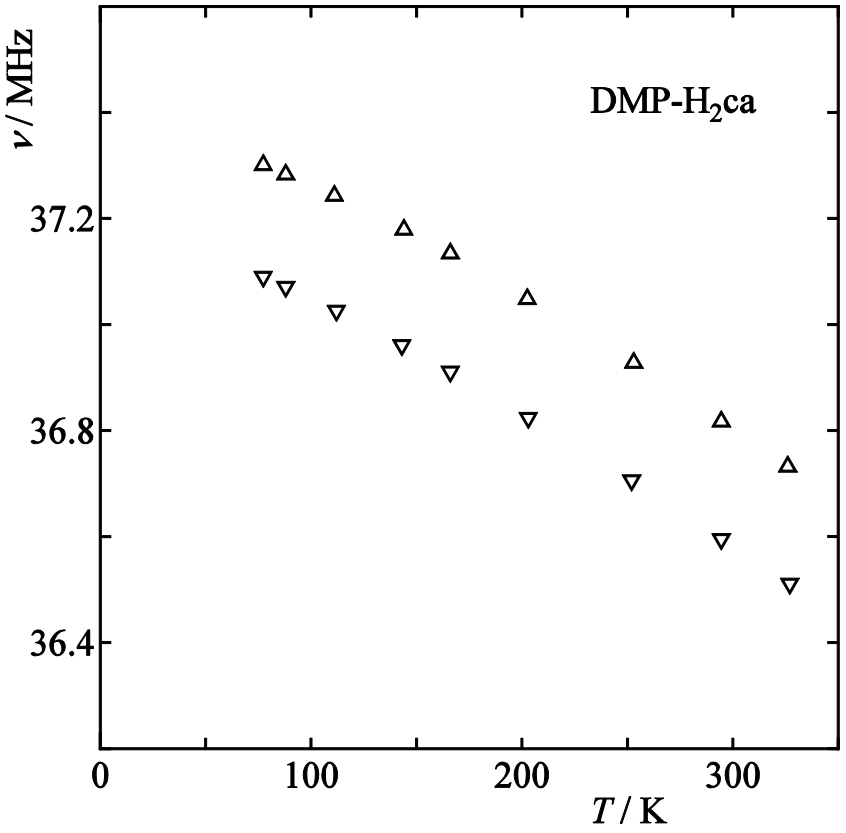
- **Proton shift toward oxygen atom**
- **Weakening of the H-bonding**

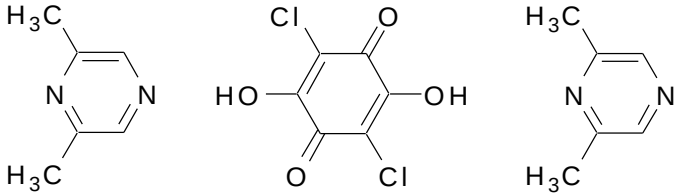
NQR freq.-increase by the deuteration also suggests a weakening of the H-bonding

It may be reasonable to assume that the proton transfer motion from the oxygen site to the nitrogen site requires much more energy when the N…H distance increases.

If so, the deuteration will increase the E_a since it elongate the N…H distance.

^{35}Cl NQR Frequencies in DMP-H_2ca

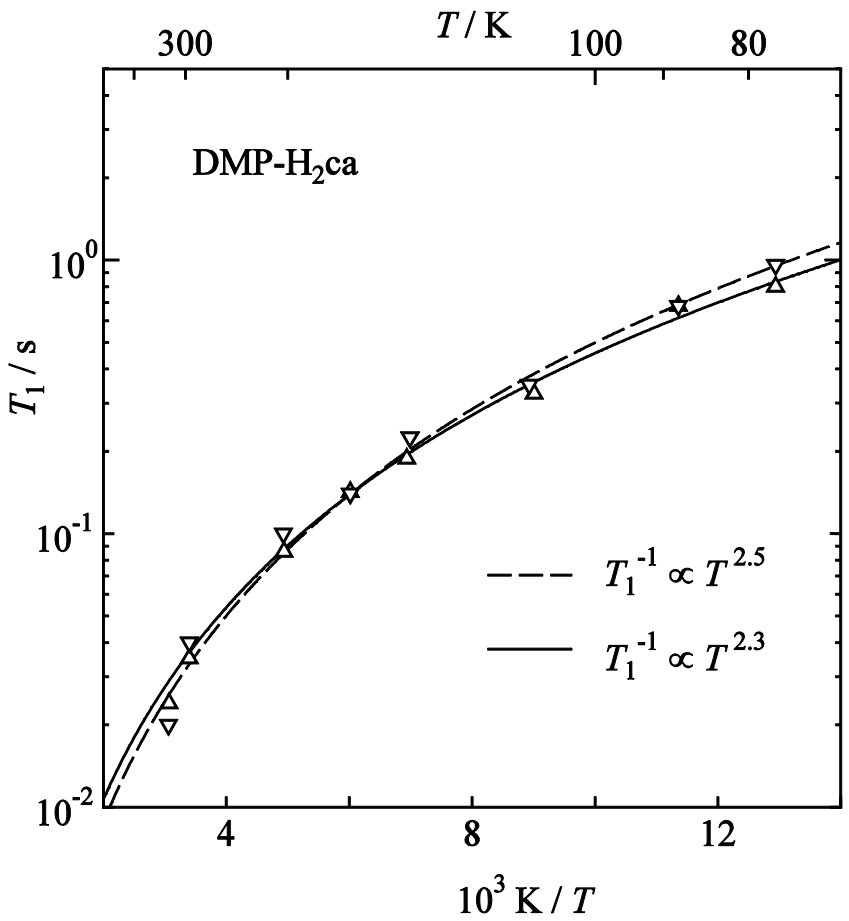




Two frequencies were observed at each temperature studied; 37.301 MHz and 37.090 MHz at 77 K.

- **Neutral molecular co-crystal without proton transfer**

^{35}Cl NQR Spin-lattice Relaxation Time in DMP-H_2ca



The T_1 values of the both NQR lines were almost same and could be explained by the power-law of the temperature: $T_1^{-1} \propto T^{2.3}$ and $T_1^{-1} \propto T^{2.5}$ for the high- and low-frequency lines, respectively. In DMP-H_2ca, the relaxation is dominated by lattice vibration suggesting no transfer motion of proton between the acid and base molecules.

Conclusion

- **Proton transfer motion in one-dimensional hydrogen-bonded supramolecular compound, tetramethylpyrazine-chloranilic acid (TMP-H_2ca), was revealed by ^{35}Cl NQR and ^{2}H NMR relaxation measurements.**
- **The activation energy for the motion increases from 35 kJ mol^{-1} to 50 kJ mol^{-1} by the deuteration.**
- **On the other hand, no transfer motion of proton in the one-dimensional hydrogen bond is expected in 2,6-dimethylpyrazine-chloranilic acid co-crystal (DMP-H_2ca).**