^{14}N NQR study of proton position and dynamics in some hydrogen bonded organic ferroelectrics

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Outline

- ^{14}N NQR
- ^{1}H-^{14}N NQDR
- Hydrogen bonded organic ferroelectrics

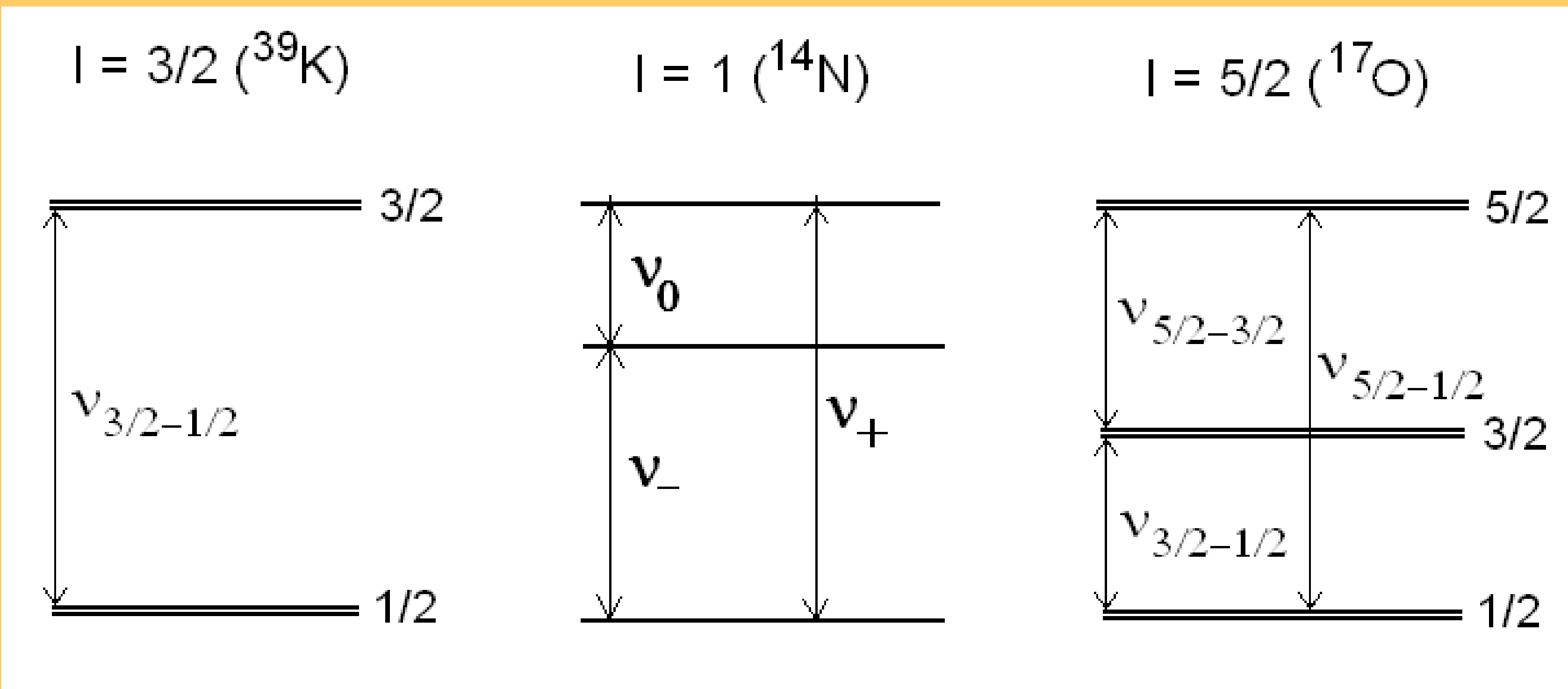
  - phenazine–chloranilic acid (1:1)

  - 1,2-diazine–chloranilic acid (2 : 1)

  - 2,3,5,6-tetra(2'-pyridyl)pyrazine-chloranilic acid (1:2)
- Conclusions

Nuclear quadrupole energy levels

$$H_Q = \frac{e^2 qQ}{4I(2I-1)}\left(3I_z^2 - I(I+1) + \frac{\eta}{2}\left(I_+^2 + I_-^2\right)\right)$$



^{14}N NQR frequencies and spin-lattice relaxation rates

$$\nu_+ = \frac{e^2qQ}{4h}(3+\eta)$$

$$\nu_- = \frac{e^2qQ}{4h}(3-\eta)$$

$$\nu_0 = \nu_+ - \nu_- = \frac{e^2qQ}{2h}\eta$$

$$W_i^{\uparrow} = W_i(1 - h\nu_i / 2k_BT)$$

$$W_i^{\downarrow} = W_i(1 + h\nu_i / 2k_BT)$$

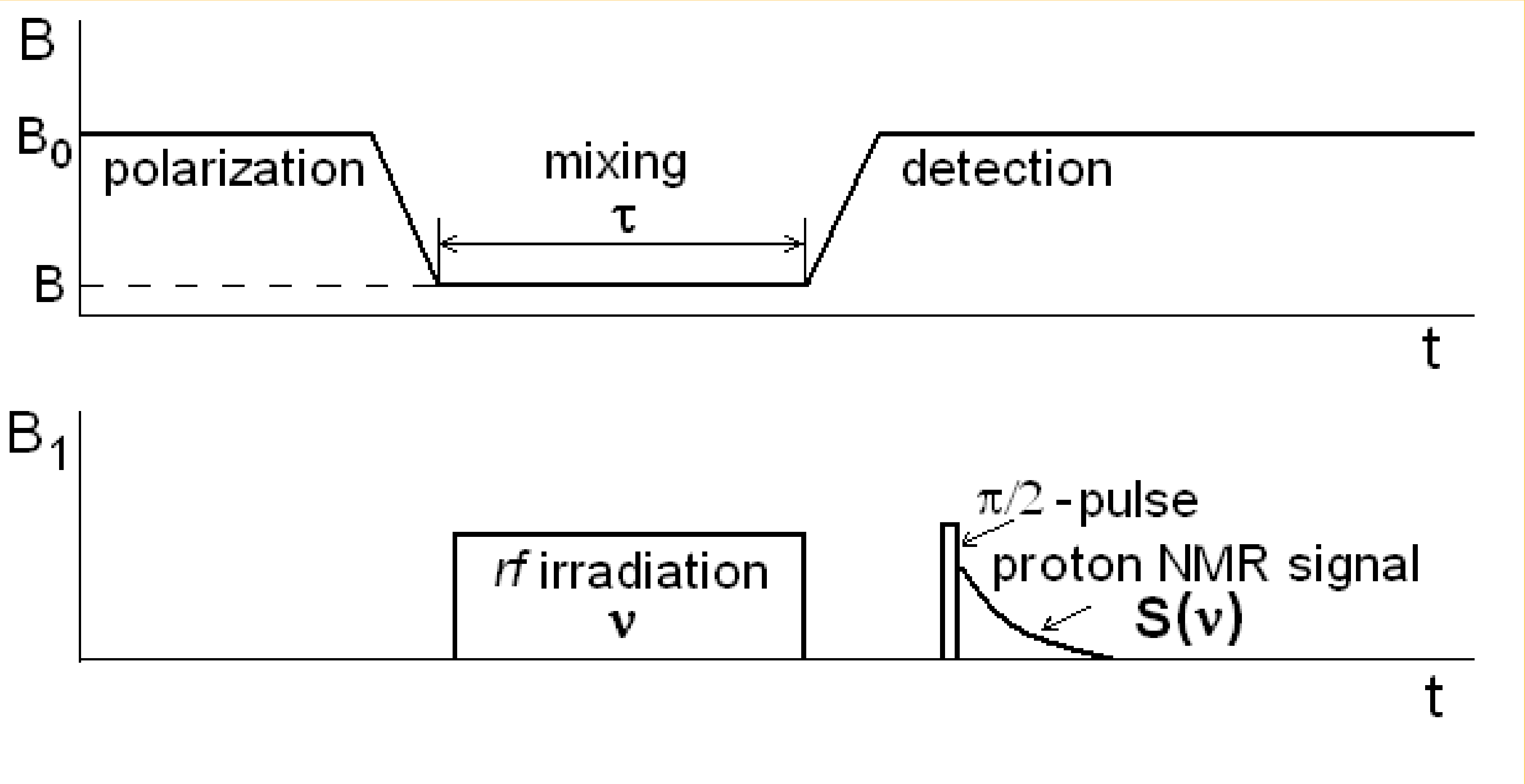
- local origin
- sensitive to small changes in the electron charge distribution

Nuclear quadrupole double resonance (NQDR):
indirect detection of ^{14}N,^{17}O, ...

- Invented by Prof. E. L. Hahn, Berkeley, CA, USA

- Further developed in various laboratories:
  - London, UK (Prof. J. A. S. Smith)
  - Oxford, UK (Prof. D. T. Edmonds)
  - Urbana, IL, USA (Prof. T. L. Brown)
  - Kaliningrad, Russia (Prof. V. Grechishkin)
  - Ljubljana, Slovenia (Prof. R. Blinc)

Basic detection procedure: Magnetic field cycling

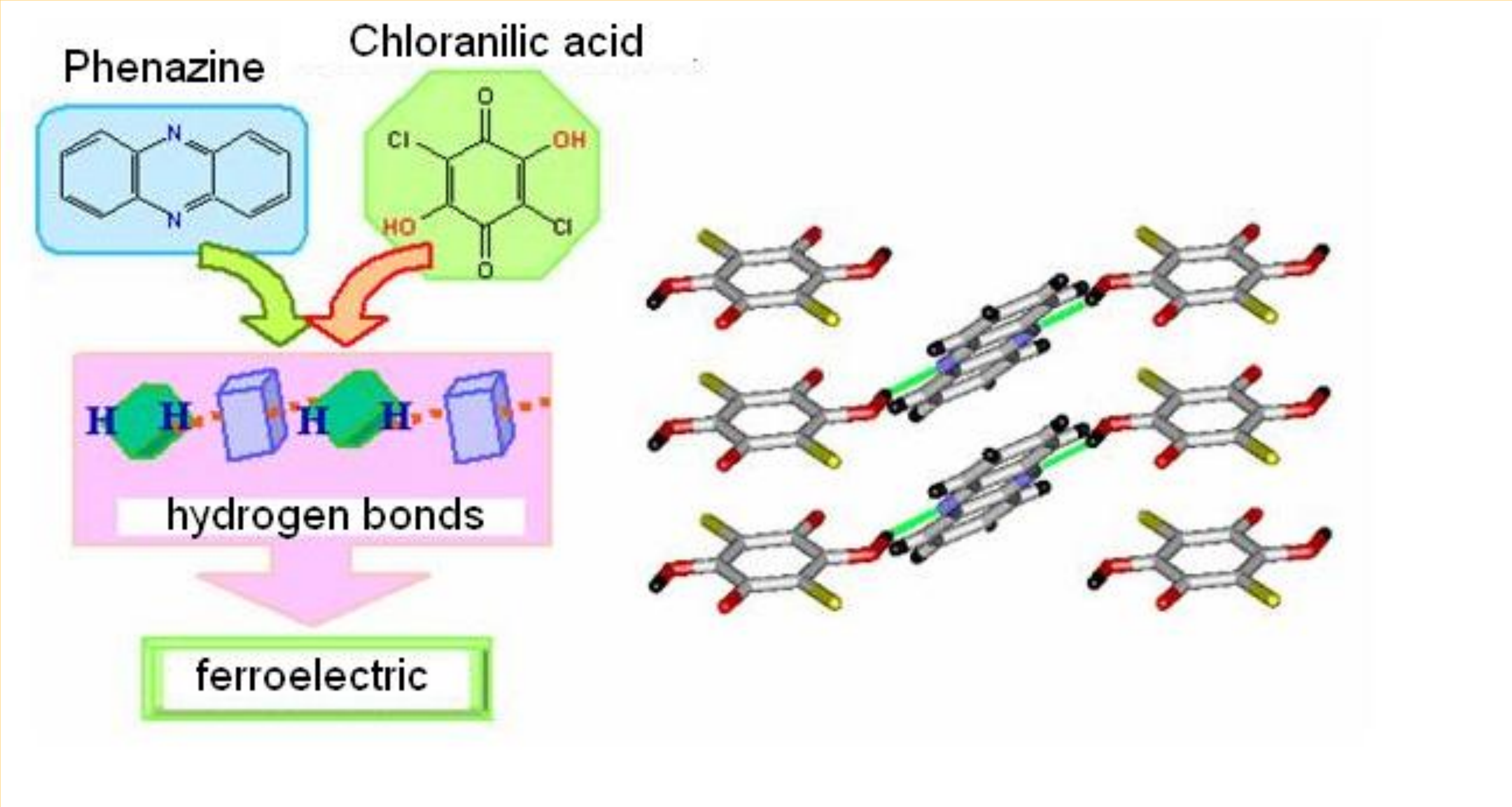


^1H-^{14}N NQDR techniques

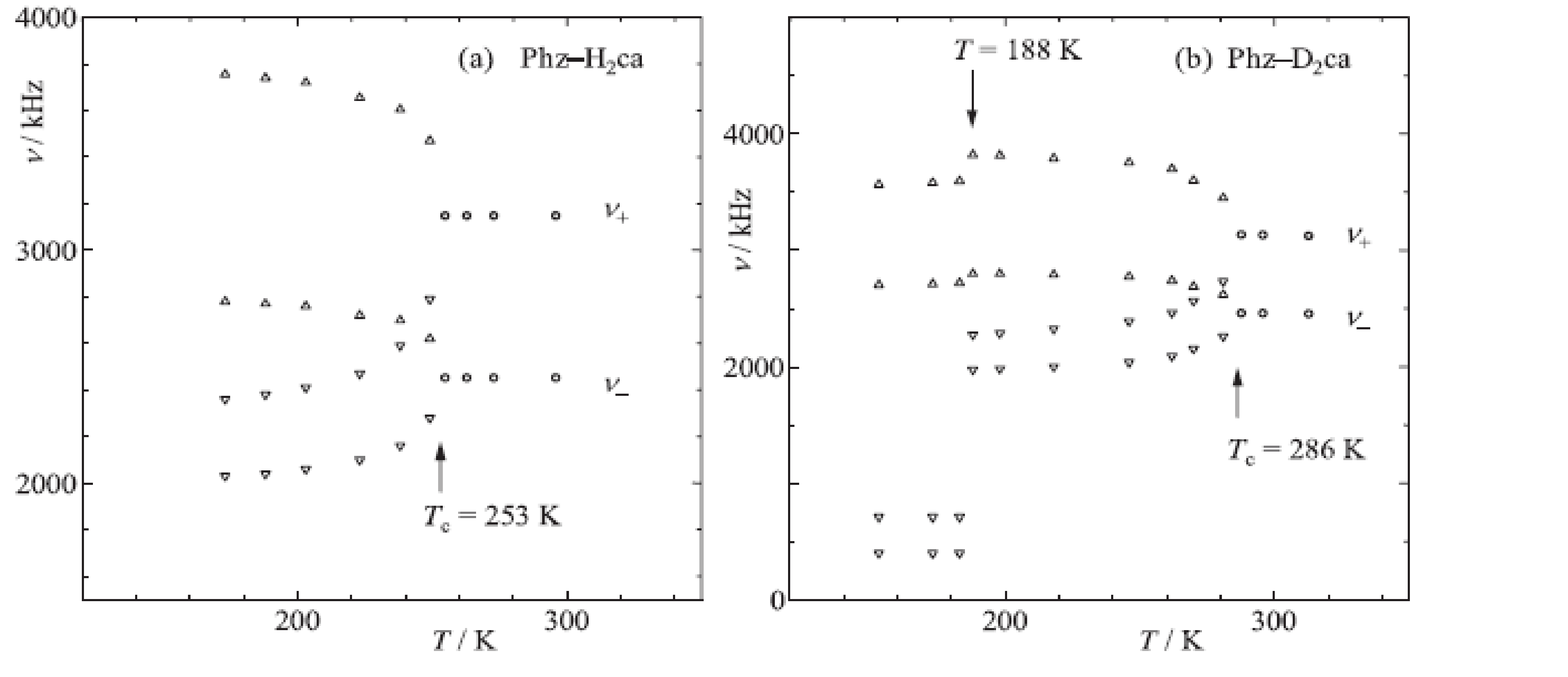
- **Level crossing**
- Blinc et al, *J. Chem. Phys.* 57 (1972) 5087
- Edmonds, *Phys. Rep.* 29 (1977) 234
- **Cross relaxation spectroscopy**
- Seliger et al, J. Chem. Phys. 65 (1976) 2887
- Stephenson, Smith, Proc Roy. Soc. A 416 (1988) 149
- **Solid effect**
- Seliger, Žagar, J. Magn. Reson. 193 (2008) 54
- **Frequency sweeps, 2-frequency irradiation**
- Seliger et al, J. Magn. Reson. A 106 (1994) 214

Cocrystal phenazine-chloranilic acid (1:1)

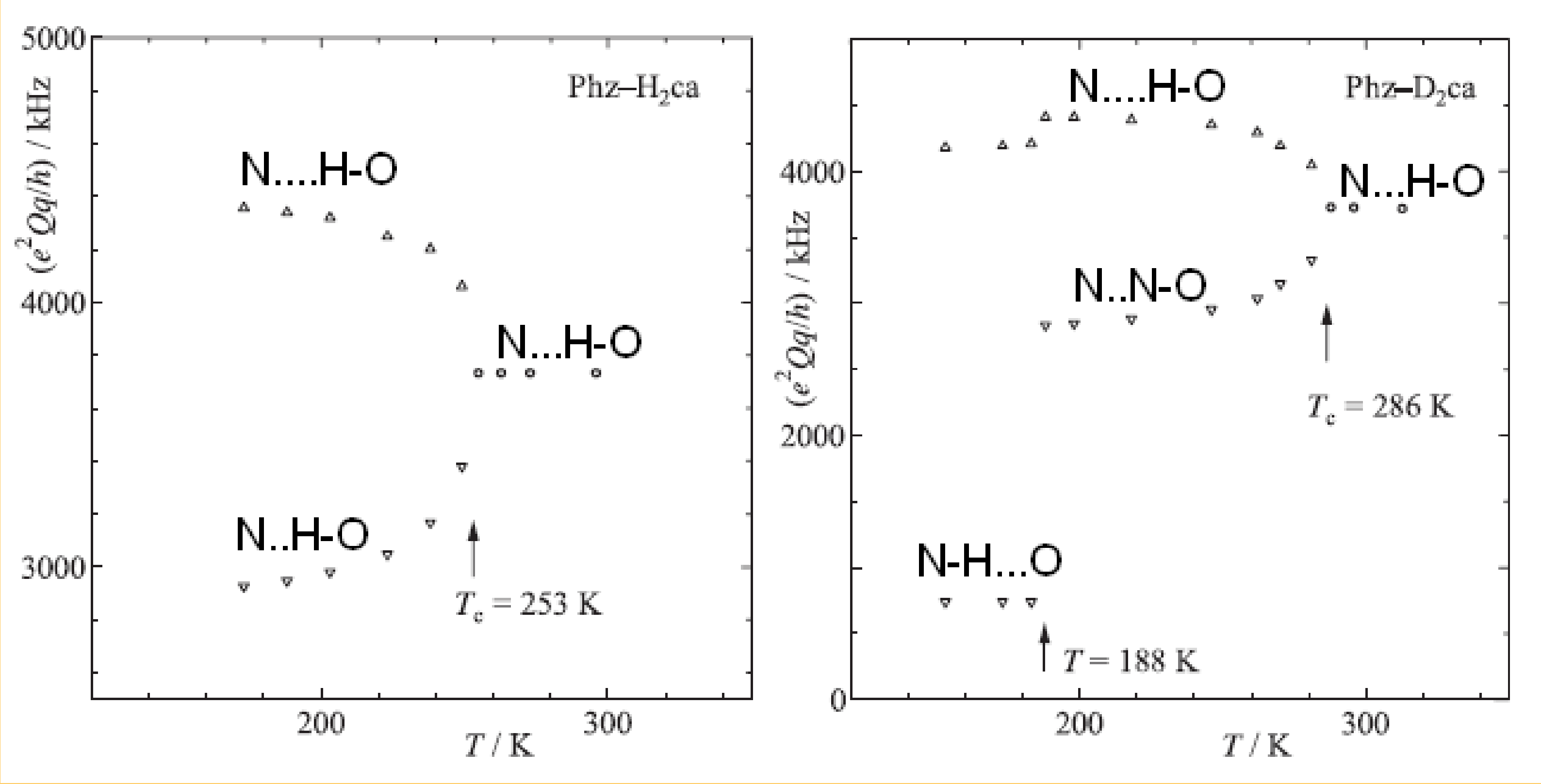
organic ferroelectric



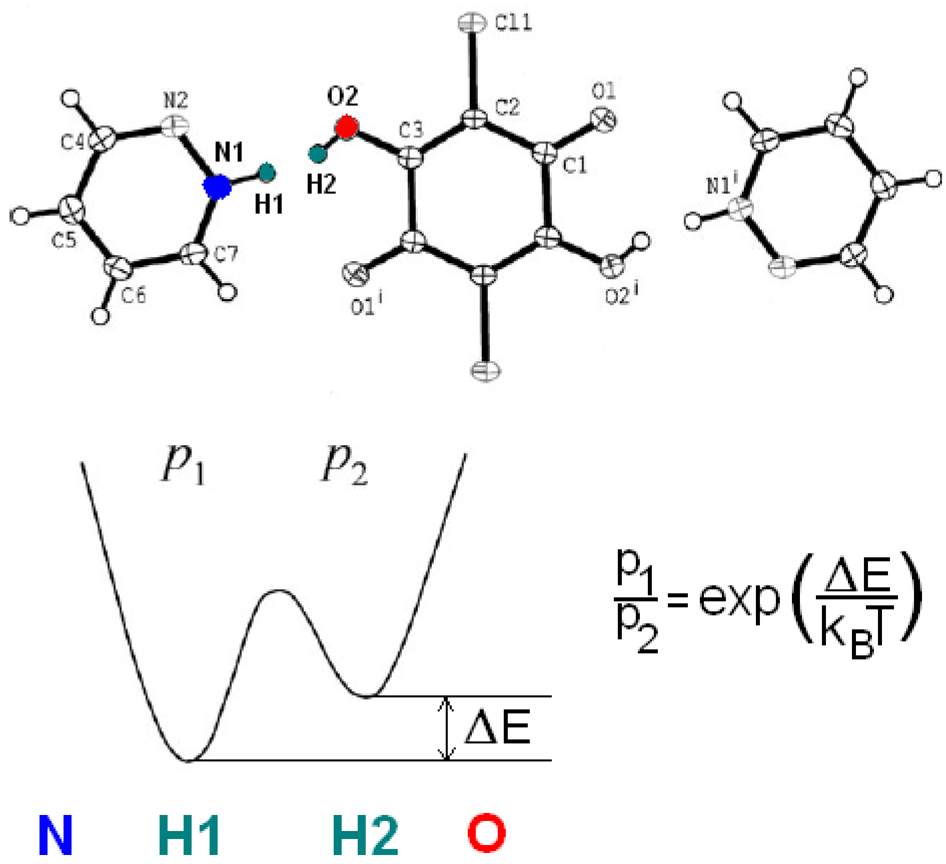
^{14}N NQR results



^{14}N NQR results



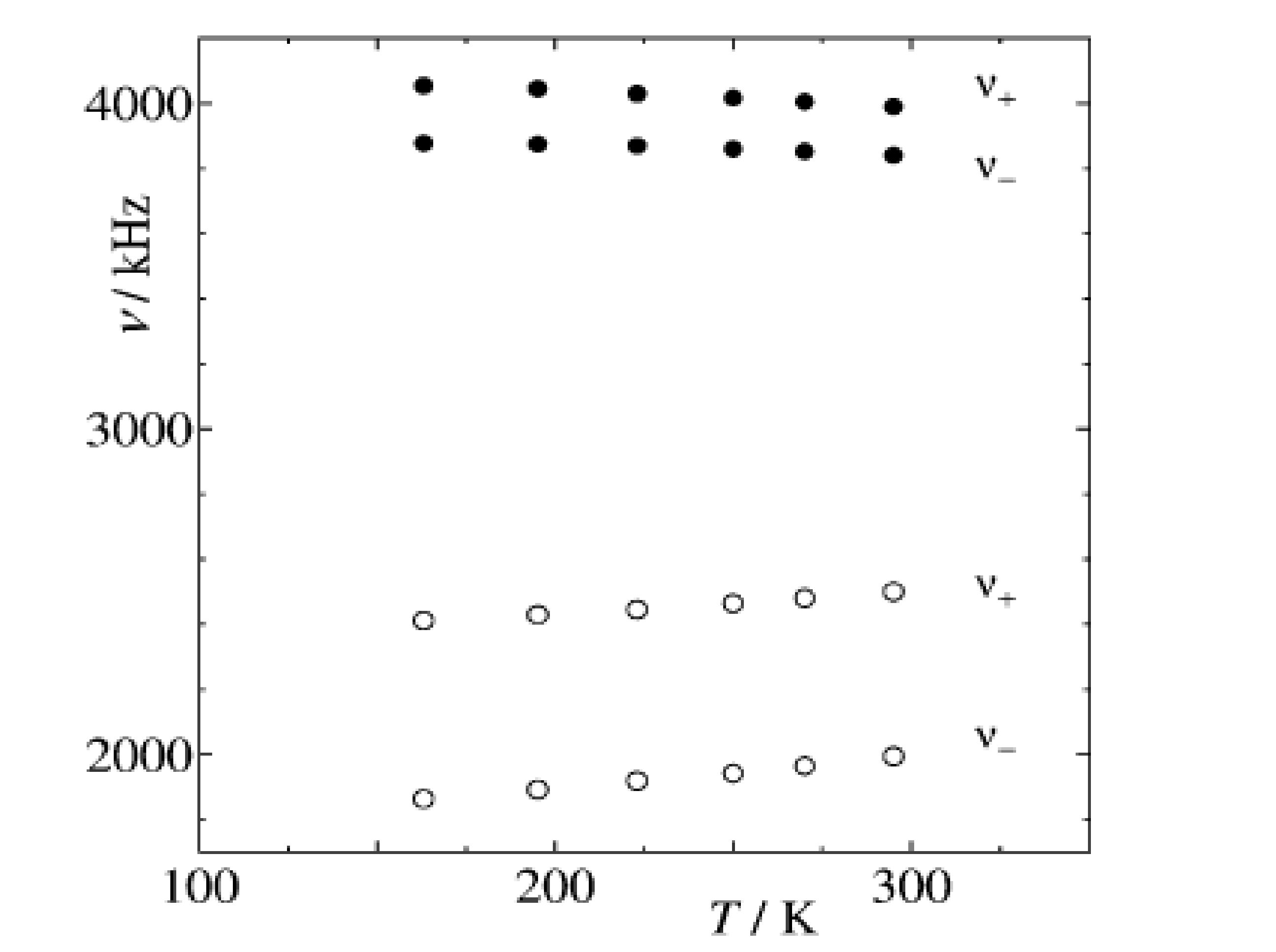
1,2-diazine-chloranilic acid (2:1)



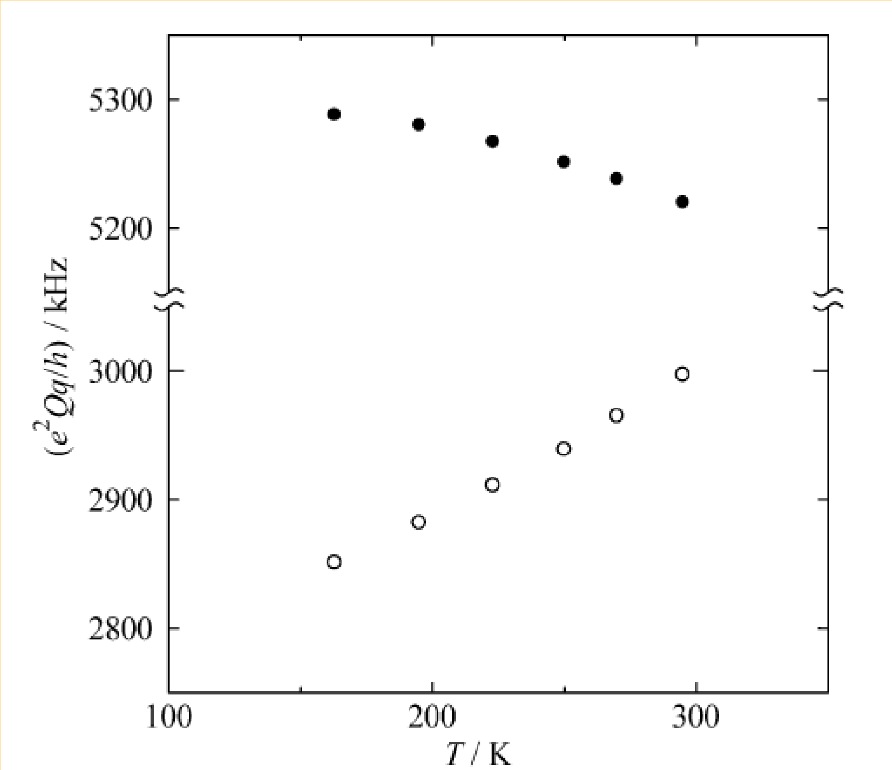
$$\frac{p_1}{p_2} = \exp\left(\frac{\Delta E}{k_B T}\right)$$

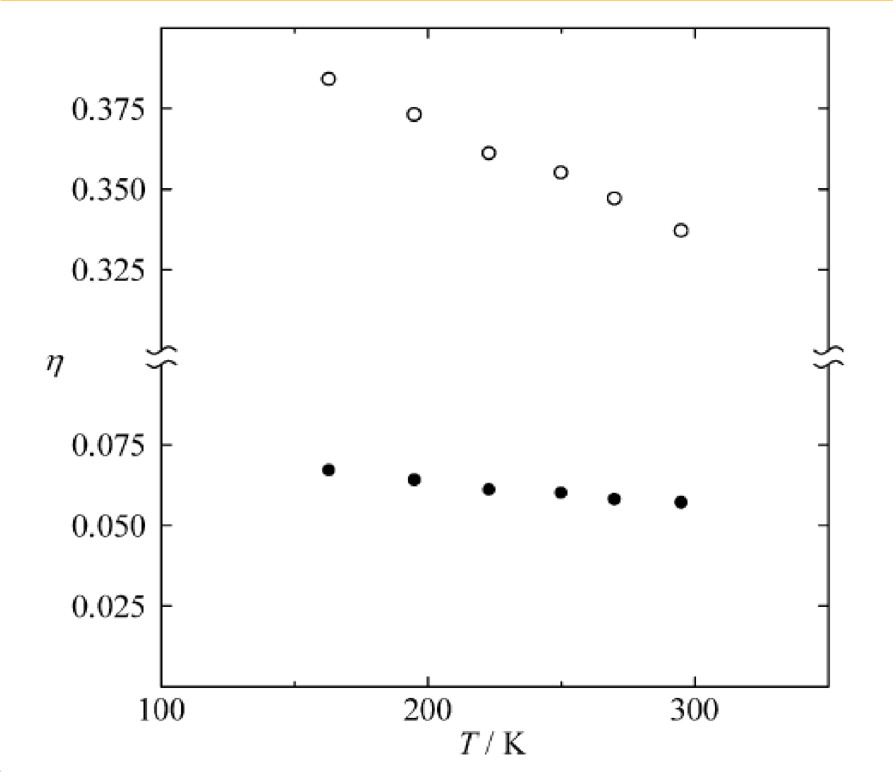
Gotoh, Asaji, Ishida, *Acta Crystallogr.* C64 (2008) o550

^{14}N NQR frequencies

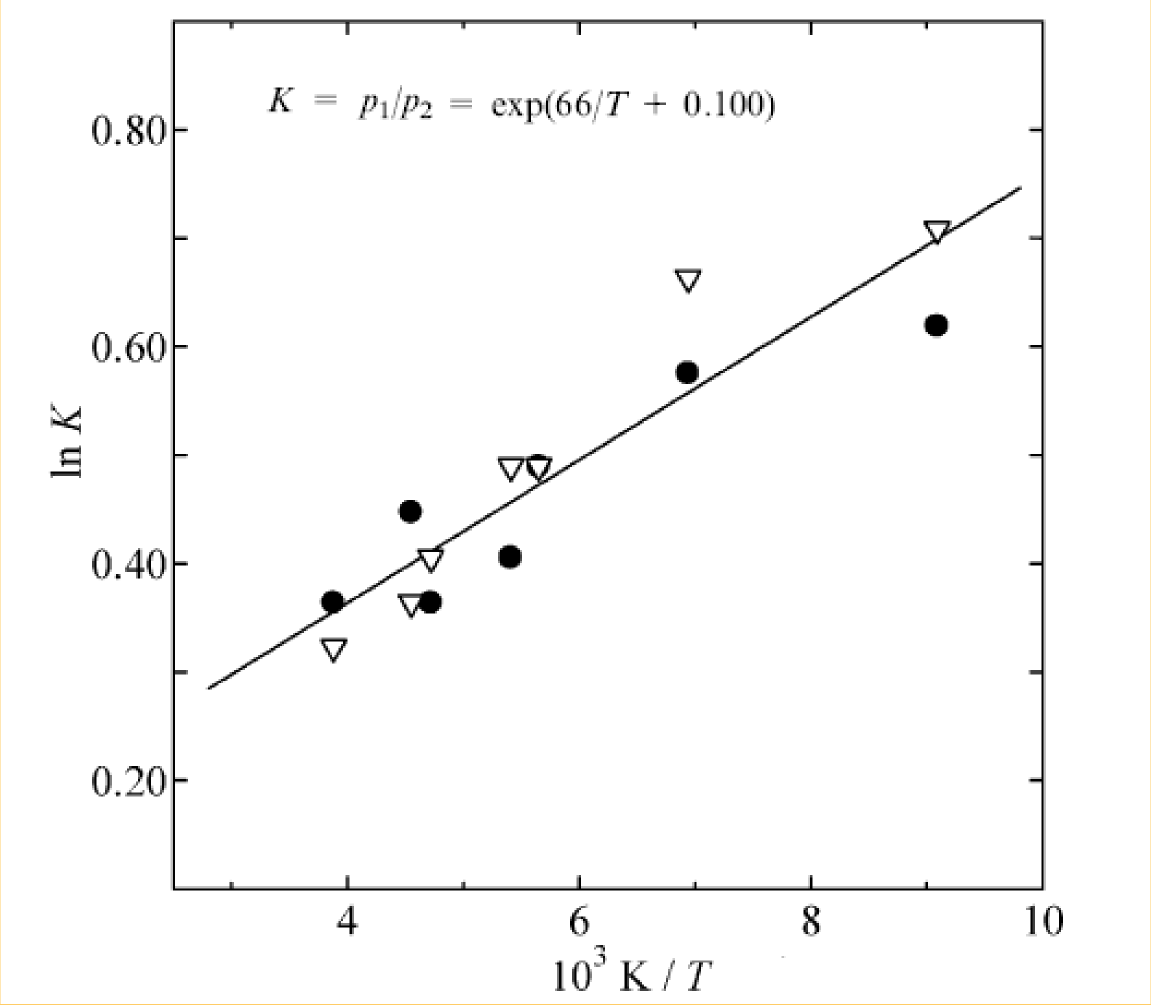


$^{14}N\ e^2qQ/h$ and η





X-ray diffraction data



Principal values of the EFG tensor

T/K	p_1	p_2	$\frac{eQV_{ZZ}/h}{\mathrm{kHz}}$	$\frac{eQV_{YY}/h}{\mathrm{kHz}}$	$\frac{eQV_{XX}/h}{\mathrm{kHz}}$
163	0.624	0.376	−2851	1973	878
195	0.608	0.392	−2882	1978	904
223	0.598	0.402	−2911	1981	930
250	0.590	0.410	−2939	1991	948
270	0.585	0.415	−2965	1997	968
295	0.580	0.420	−2997	2003	994

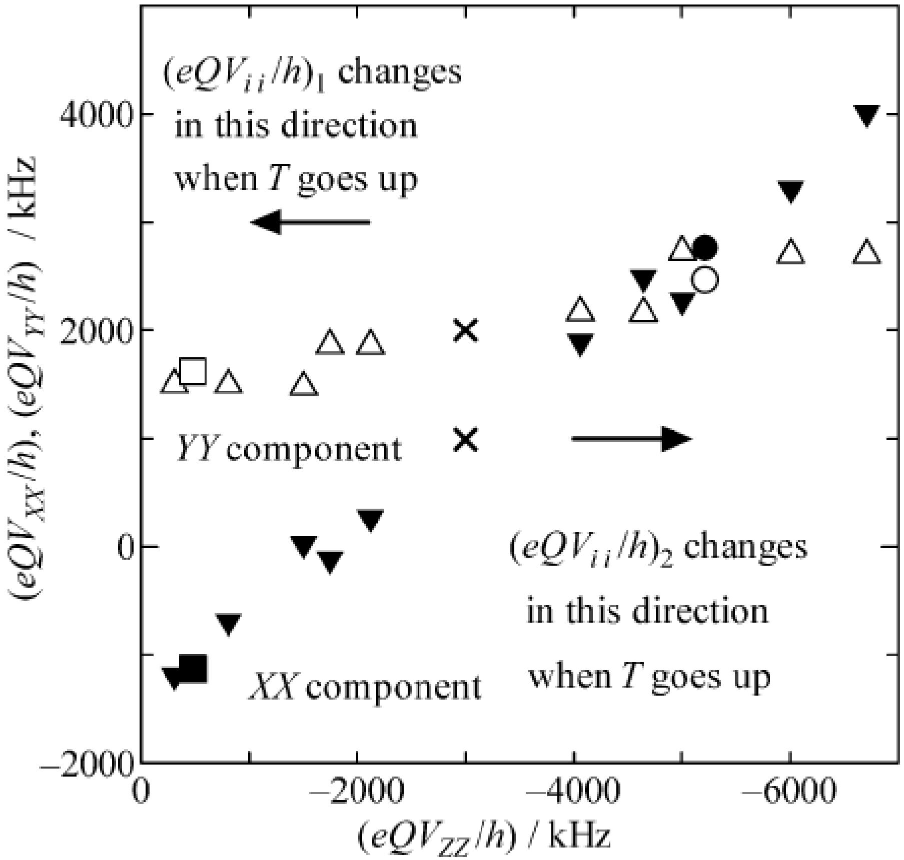
$$eQV_{ii}/h = p_1(eQV_{ii}/h)_1 + p_2(eQV_{ii}/h)_2\ ;\ i = X, Y, Z$$

The extreme values $(eQV_{ii}/h)_1$ and $(eQV_{ii}/h)_2$ (i = X, Y, Z)

Temp. range	$\left(\frac{eQV_{ZZ}/h}{\text{kHz}}\right)_1$	$\left(\frac{eQV_{YY}/h}{\text{kHz}}\right)_1$	$\left(\frac{eQV_{XX}/h}{\text{kHz}}\right)_1$
163–195 K	−2123	1856	267
195–223 K	−1745	1860	−115
223–250 K	−1504	1478	25
250–270 K	−807	1499	−692
270–295 K	−309	1499	−1190

Temp. range	$\left(\frac{eQV_{ZZ}/h}{\text{kHz}}\right)_2$	$\left(\frac{eQV_{YY}/h}{\text{kHz}}\right)_2$	$\left(\frac{eQV_{XX}/h}{\text{kHz}}\right)_2$
163–195 K	−4060	2168	1892
195–223 K	−4645	2160	2485
223–250 K	−5004	2729	2276
250–270 K	−6007	2699	3308
270–295 K	−6709	2699	4010

Correlation diagram



- × $T = 295$ K ($p_1 \approx p_2$)
- □ ■ 1,2-diazinium perchlorate (NH)
- △ ▼ extreme values
- ○ ● H-bond free nitrogen

X-ray diffraction + ^{14}N NQR

- The weight of the state O-H...N increases with increasing temperature.
- The weight of the state O^{-}...$H-N^{+}$ decreases with increasing temperature.

(a) The ionic character of the state O^{-}...$H-N^{+}$ increases with increasing temperature.

(b) The double-well potential displaces in the direction N→O with increasing temperature.

Solely ^{14}N NQR (adjustable ΔE)

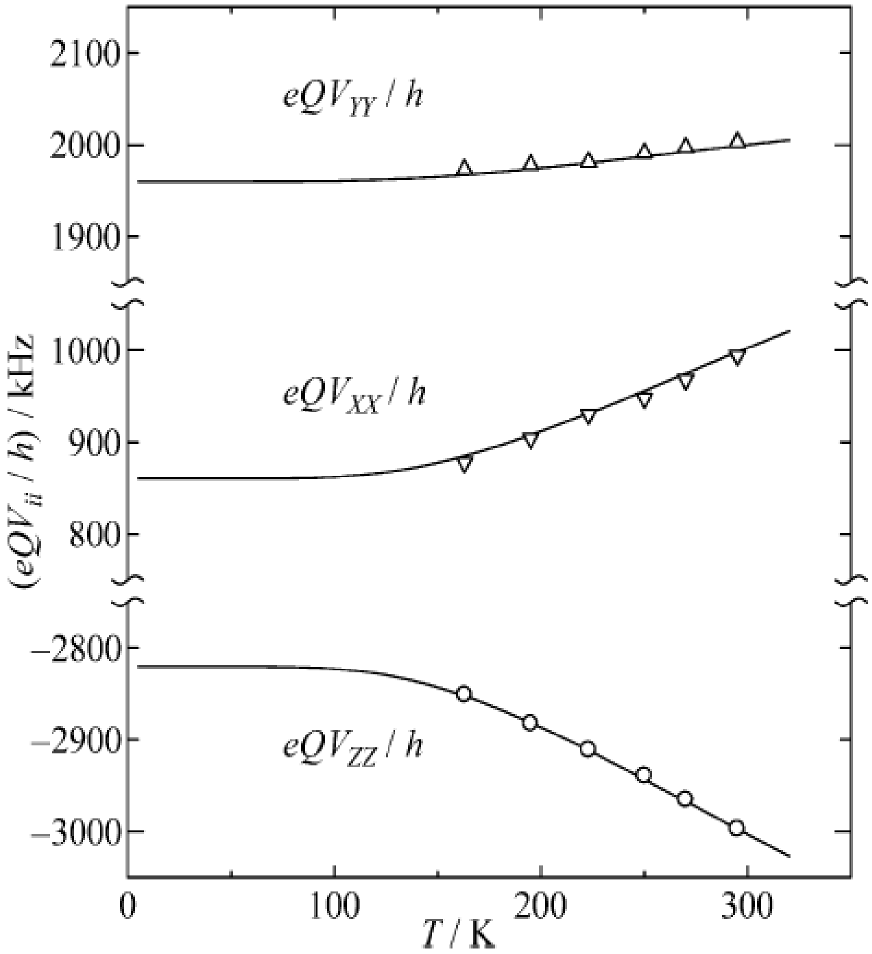
$eQV_{ii}/h = p_1(eQV_{ii}/h)_1 + p_2(eQV_{ii}/h)_2$

$p_1/p_2 = \exp(\Delta E/k_BT)$

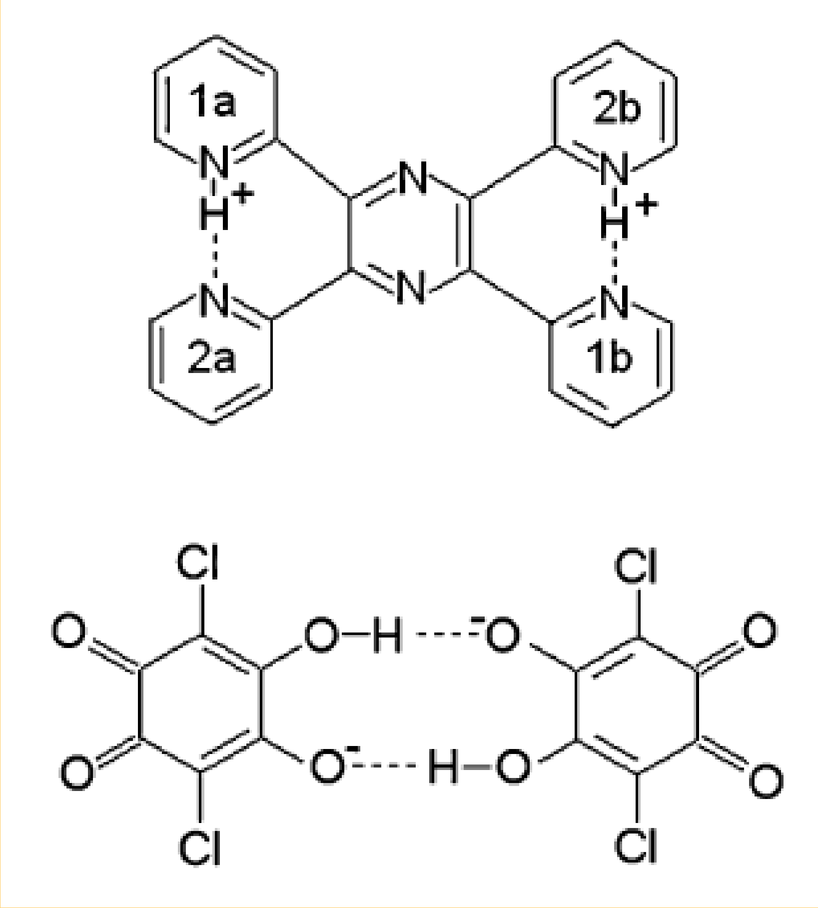
$\Delta E/k_B = (650 \pm 50)$ K

$(eQV_{ZZ}/h)_1 = -2820$ kHz
$(eQV_{YY}/h)_1 = 1960$ kHz
$(eQV_{XX}/h)_1 = 860$ kHz

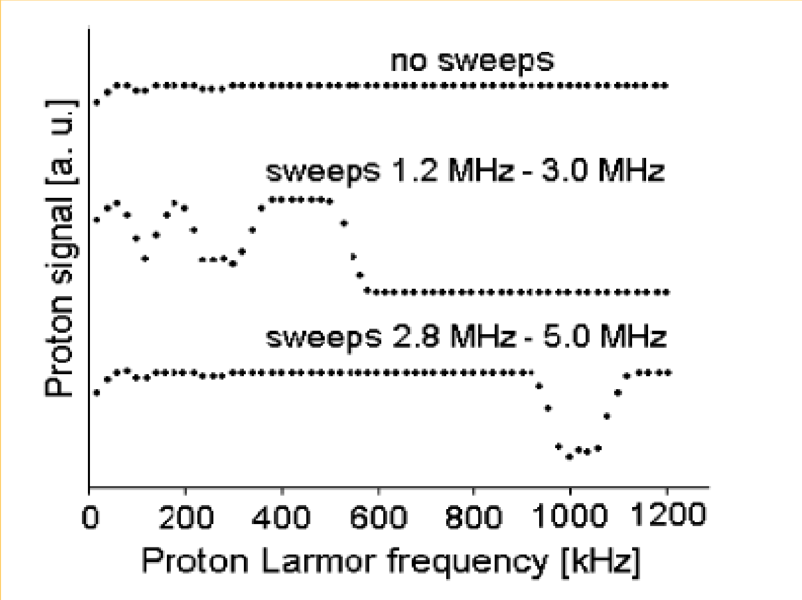
$(eQV_{ZZ}/h)_2 = -4600$ kHz
$(eQV_{YY}/h)_2 = 2350$ kHz
$(eQV_{XX}/h)_2 = 2250$ kHz

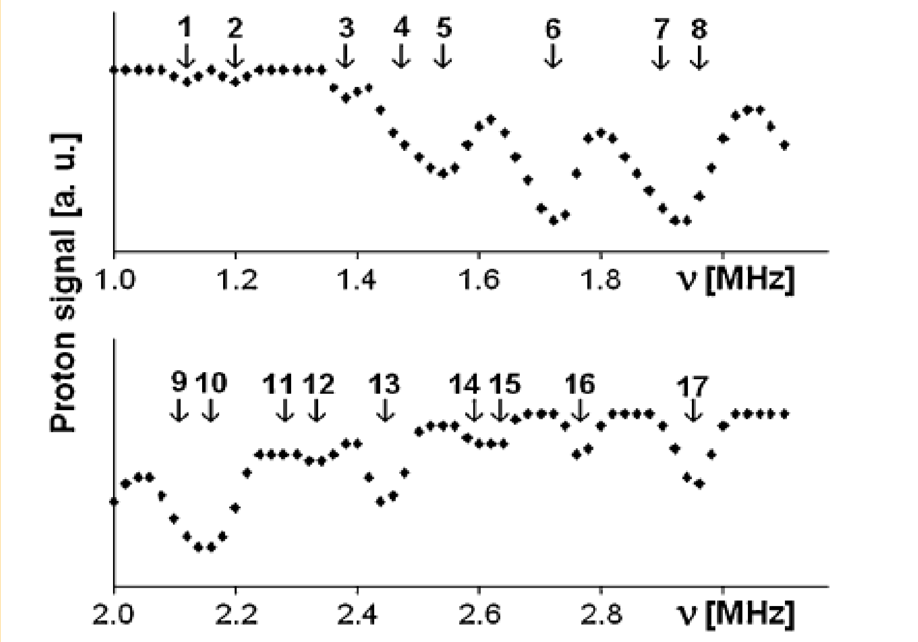


2,3,5,6-tetra(2'-pyridyl)pyrazine (TPPZ) - chloranilic acid (1:2) (ferroelectric)



^{1}H-^{14}N NQDR $T<T_c$

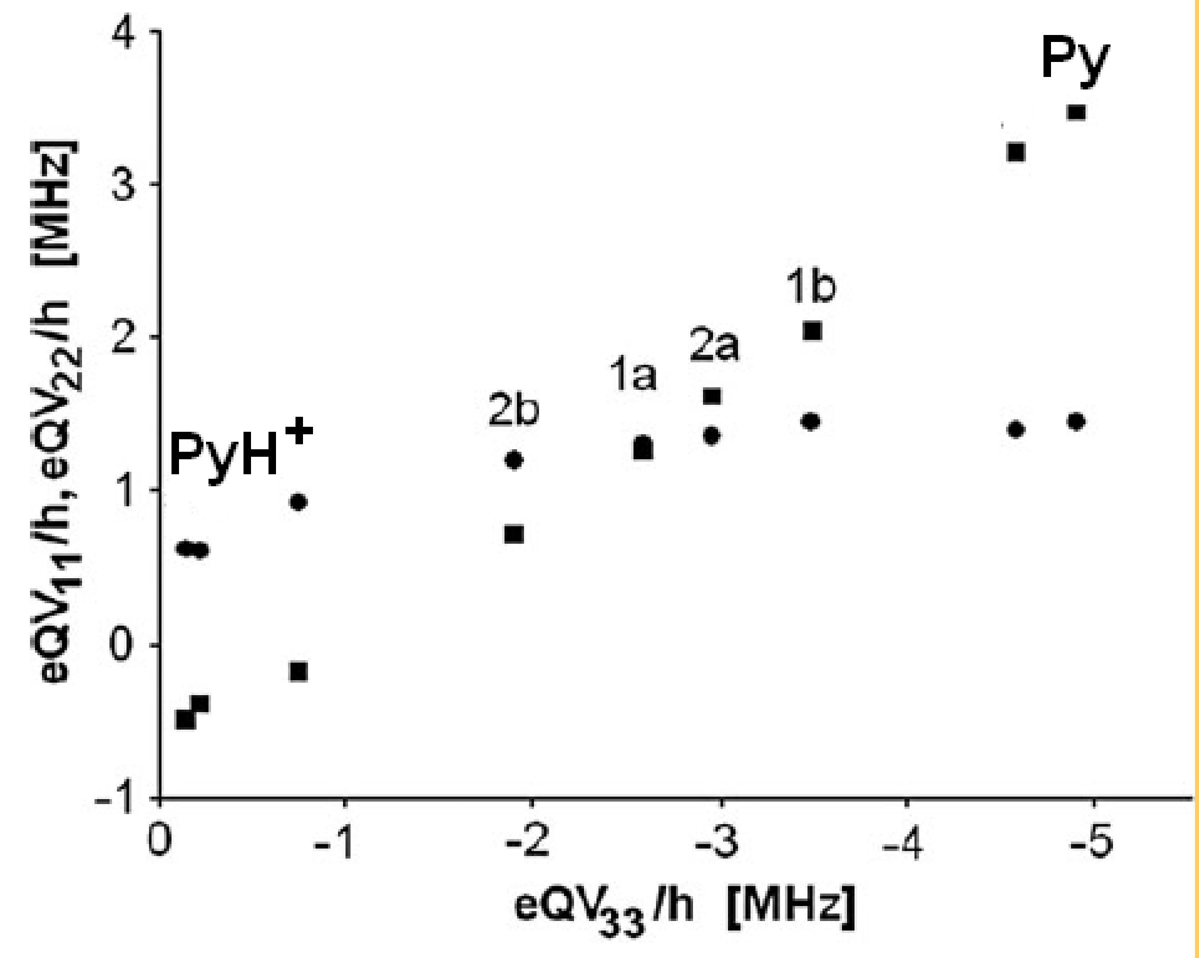




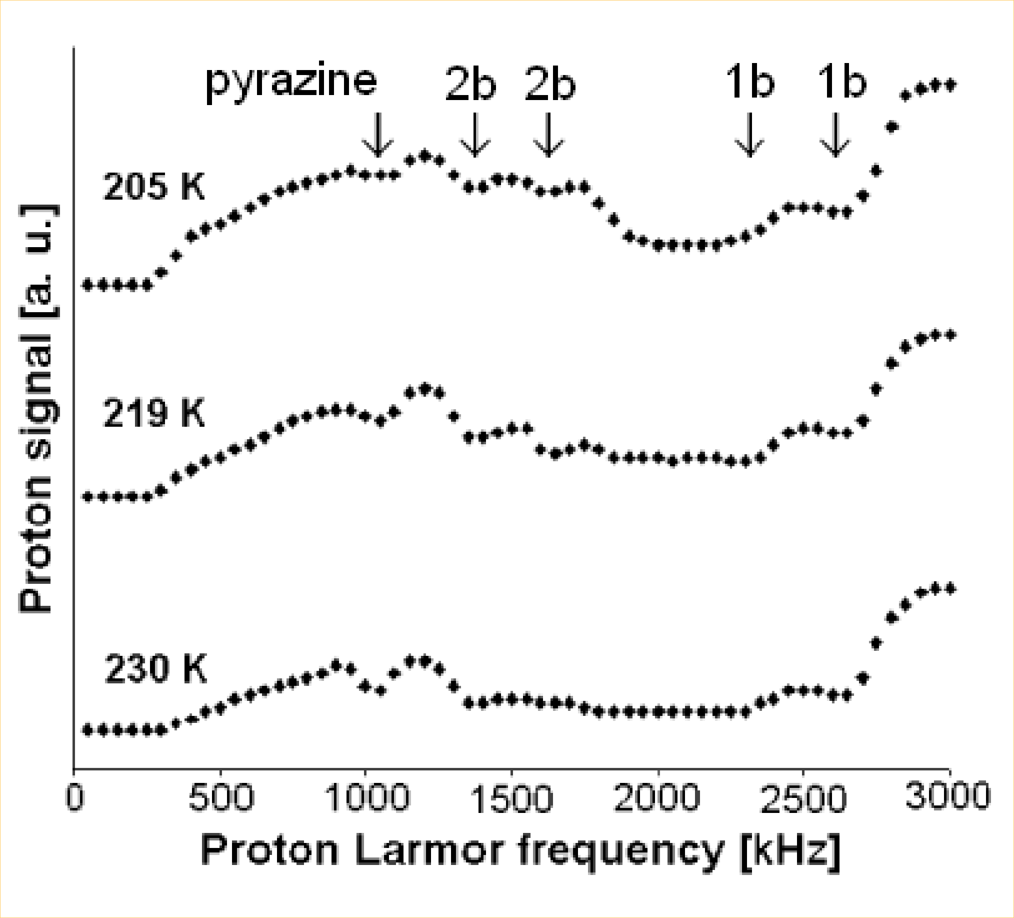
^{14}N NQR results T = 145 K < T_c

Nitrogen position	ν_+, ν_-, ν_0/kHz	e^2qQ/h/kHz	η
Pyrazine	4445, 3398, 1047	5229	0.400
Pyrazine	4373, 3373, 1000	5164	0.387
1b	2770, 2465, 305	3490	0.175
2a	2280, 2155, 125	2955	0.085
1a	1980, 1980, 0	2640	<0.01
2b	1545, 1295, 250	1895	0.264

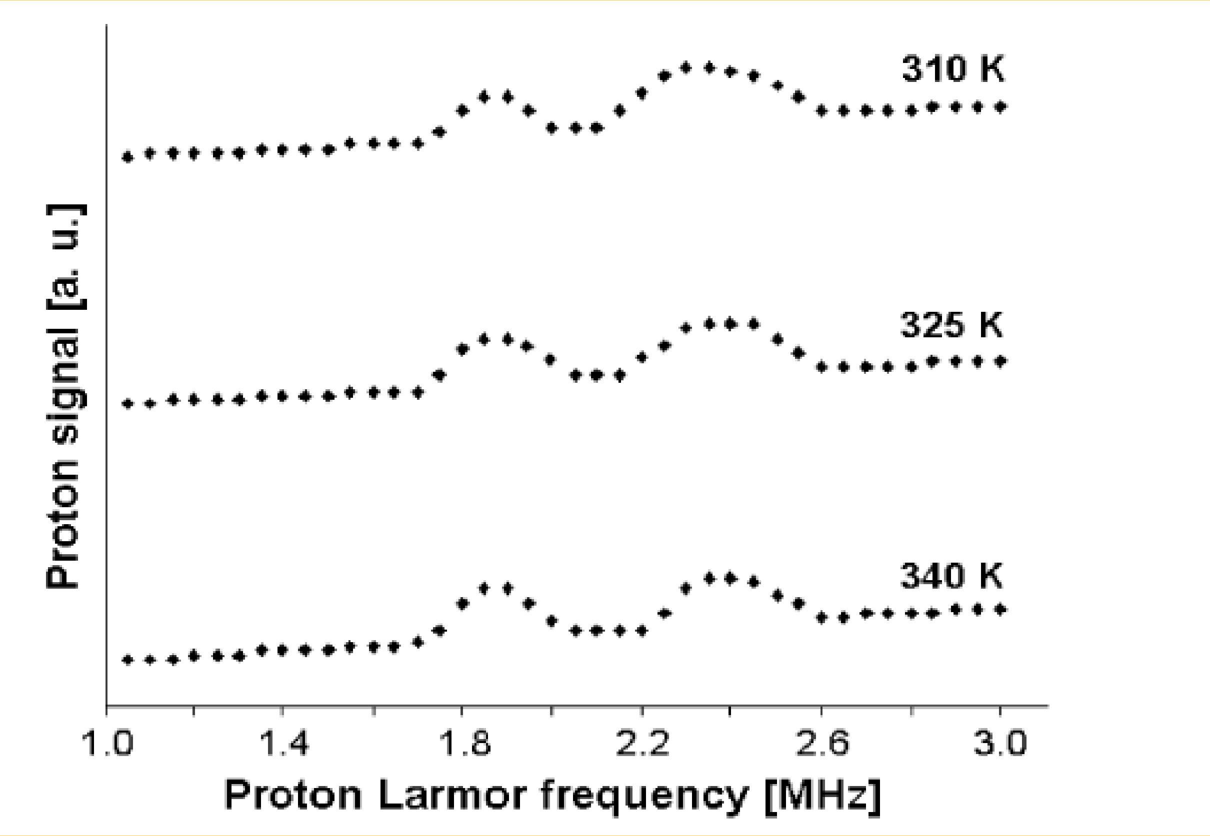
Correlation of the principal values of the quadrupole coupling tensor for pyridine



^{1}H-^{14}N cross-relaxation spectra at $T > T_c = 172$ K



^{1}H-^{14}N cross-polarization spectra T > Tc



Exchange ($T > T_c$):

$N(1a)\text{-}H^{+}...N(2a) \leftrightarrow N(1b)...H^{+}\text{-}N(2b)$

τ(room temperature) ≈ 1 μs

$E_a = k_B.4200$ K

Conclusions

- ^{14}N NQR reflects hydrogen position, displacements and exchange in hydrogen bonds.
- It can be used to study local structure and dynamics of ferroelectrics and other hydrogen bonded solids, where nitrogen participates as either the hydrogen bond acceptor or the hydrogen bond donor.