Pressure Dependence of the Proton Transfer Equilibrium in Hydrogen Bonded Complexes *

Mariusz Maćkowiak, Piotr Kozioł, and Jan Stankowski
Institute of Molecular Physics, Polish Academy of Sciences, Poznań, Poland

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^{35}Cl NQR measurements were carried out on complexes of pentachlorophenol with nitrogen bases as a function of pressure (up to 300 MPa) and of temperature. It is shown that the sign and magnitude of the pressure coefficient of the ^{35}Cl NQR frequency is related to the degree of proton transfer. An anomaly in the pressure coefficient of ν (^{35}Cl) has been observed near 50% of the proton transfer in the hydrogen bond. This anomaly is discussed assuming that the proton transfer equilibrium is pressure dependent. The fact that the transition from the double-well potential of the hydrogen bond to the single-well potential occurs in the critical manner is also taken into account.

Introduction

The aim of the present work is to find a correlation between the sign and magnitude of the pressure coefficient of the ^{35}Cl NQR frequency and the degree of proton transfer in the hydrogen bond. Complexes of pentachlorophenol with nitrogen bases make a molecular model system for such a study. By an appropriate selection of the base strength it is possible to modify the properties of the hydrogen bond. Variations of the proton localisation in the hydrogen bond are reflected by changes of the electric field gradient (EFG) and therefore by changes of the NQR frequency.

The synthesis of complexes of pentachlorophenol with different bases and the apparatus for the high pressure NQR measurements are described in previous papers [1, 2].

The ^{35}Cl NQR spectra of the complexes investigated consist of five lines corresponding to the five chlorine atoms at the benzene ring. The NQR frequencies at normal pressure of most of the investigated complexes have been registered first by Grech et al. [3]; the frequencies determined by us (Table 1) agree with their results. To eliminate the "crystal field effect" one usually introduces an average value of the NQR frequency ($\bar{\nu}_Q$). Since the electron densities at the five chlorine atoms are modified differently by the possible hydrogen bonds, the interpretation of an average value of the resonance frequencies may rise some doubts.

The linear dependence of the average ^{35}Cl NQR frequencies on the polarity of the hydrogen bond found in these complexes [4] gives evidence of the decisive role of the electric field arising from the dipole moment $\vec{\mu}$ of the hydrogen bond (which polarizes the C–Cl bond as a result of the internal Stark effect). According to the Bloembergen theory [5] the shift of the NQR frequency induced by the electric field is proportional to the magnitude of its z component. Calculations of the z component of the electric field vector produced by a dipole moment equal to $3 \cdot 10^{-29}$ C · m and placed in the middle of the O … N bond were performed by Kalenik [6]. His calculations prove that an increase of the hydrogen bond polarity leads always to a decrease of the resonance frequencies. The contribution of the hydrogen bond dipole moment to the electric field gradient (EFG) at the Cl nuclei is highest for the nucleus which shows the lowest NQR resonance frequency. That is why in analysing the pressure effects we shall concentrate mainly on the interpretation of the pressure coefficients of the lowest frequency resonance lines.

Studies of the influence of pressure on the NQR spectrum of ferroelectric crystals have shown that the hydrogen bond is relatively easy to deform and its compressibility coefficient $\mathrm{d}R_{\mathrm{O}\ldots\mathrm{O}}/\mathrm{d}p \approx 0.003$ nm · GPa^{-1} [7].

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Reprint requests to Prof. J. Stankowski, Institute of Molecular Physics, PAN, ul. Smoluchowskiego 17/19, 60-179 Poznan, Poland.

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Table 1. Complexes of pentachlorophenol with various nitrogen bases, pK_a values of the bases, average resonance ^{35}Cl NQR frequency $\bar{\nu}_Q$, NQR frequencies of the lowest frequency line ν_L and their pressure coefficients $\partial\nu_L/\partial p$ ($T = 77$ K).

No.	Nitrogen base	pK_a base	$\bar{\nu}_Q$ [MHz]	ν_L [MHz]	$\partial\nu_L/\partial p$ [kHz · MPa^{-1}]
1	4-cyano-pyridine	1.9	37.673	36.871	−0.036
2	3-bromo-pyridine	2.9	37.693	36.803	−0.151
3	quinoline	4.9	37.669	36.861	−0.069
4	pyridine	5.25	37.595	37.107	−0.237
5	isoquinolina	5.4	37.508	37.144	−0.035
6	2-methyl-pyridine	5.94	37.509	36.634	−0.374
7	4-ethyl-pyridine	6.02	37.225	36.272	−0.433
8	4-methyl-pyridine	6.05	37.199	36.293	−0.216
9	2,4-dimethyl-pyridine	6.7	36.673	35.807	−0.097
10	imidazole	6.99	36.932	36.003	+0.050
11	morpholine	8.4	36.728	35.808	+0.057
12	triethylamine	10.75	36.755	35.845	+0.161
13	piperidine	11.2	36.886	36.065	+0.162

The proton position in the hydrogen bond is strictly related to the bond length. For this reason, by changing the O ... N distance we are also changing the proton position. The relations between the distance of the electronegative atoms $R_{O...X}$ and the oxygen-proton distance R_{O-H} as well as the proton tunneling effect have been explained by Matsushita and Matsubara [8]. According to their theory the transition from a long hydrogen bond with a double minimum potential to a short bond with a single minimum potential is very sharp and has a critical character.

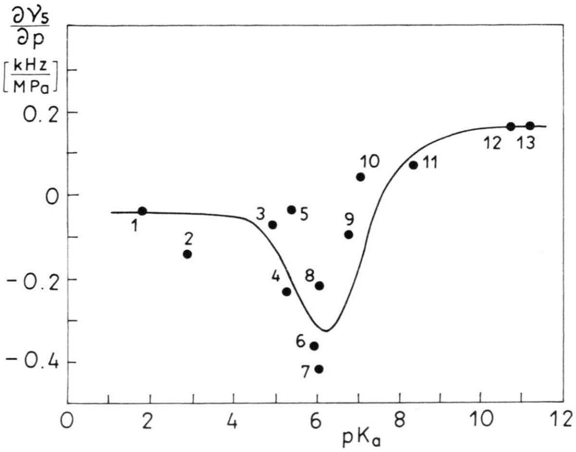

Fig. 1. Pressure coefficient of the ^{35}Cl NQR frequency of the lowest resonance ν_L vs. basicity. The notation is as given in Table 1 ($T = 77$ K).

Results

The dependence of the pressure coefficient of the ^{35}Cl NQR frequency $(d\nu_L/dp)_{T=77\,K}$ (determined for the lowest resonance ν_L) on the pK_a of the base is shown in Figure 1. The dependence of the NQR frequency of the same resonance line plotted vs. the basicity of the nitrogen bases is shown in Figure 2.

The pressure coefficient of the NQR frequency (Table 1) is negative for weak hydrogen bonds and changes insignificantly with increasing pK_a. At $pK_a \approx 6$ a critical increase of the absolute value of $d\nu/dp$ by one order of magnitude is observed, reaching extreme values for complexes in which the degree of the proton transfer amounts to about 50%. Further increase of the pK_a gives an increase of the pressure coefficient from large negative to positive values. For complexes of type $A^- \ldots H-B^+$ the pressure coefficient is positive.

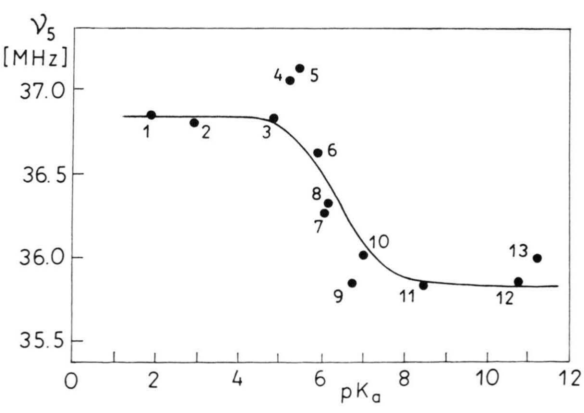

Fig. 2. ^{35}Cl NQR frequency of the lowest resonance ν_L vs. basicity. For notations see Table 1 ($T = 77$ K).

Discussion

The lowest frequency resonance plotted in Fig. 2 vs. pK_a is fitted by a simple proton transfer equilibrium model which assumes the NQR frequency to be a linear combination of frequencies of covalent ν_{HB} and ionic ν_{PT} forms [9, 10]:

$$\nu_L = X_{HB}\,\nu_{HB} + X_{PT}\,\nu_{PT}\,; \quad X_{HB} + X_{PT} = 1\,, \qquad (1)$$

where X_{HB}, X_{PT} are the fractions of the covalent (HB) and ionic (PT) forms of the hydrogen bond, respectively. The equilibrium constant of proton transfer $K_{PT} = X_{PT}/X_{HB}$, is connected with $\Delta pK_a = pK_a(BH^+) - pK_a(AH)$ by the relation [10]

$$\log K_{PT} = \zeta \cdot \Delta pK_a + C\,, \qquad (2)$$

where ζ and C are constants. The value of C is defined by a ΔpK_a at which the population of both states, i.e. HB and PT is the same. Calculations based on the results presented in Table 1 yield $C = -0.89$, $\zeta = 0.77$, $\nu_{HB} = 36.85$ MHz, and $\nu_{PT} = 35.82$ MHz. From (2) the proton transfer equilibrium constant results to be

$$K_{PT} = 10^{(\zeta \Delta pK_a + C)}\,, \qquad (3)$$

and thus

$$\frac{\partial \ln K_{PT}}{\partial p} = \ln 10\,\frac{\partial C}{\partial p}\,. \qquad (4)$$

Using (1), (2), and (4) as well as the thermodynamical relation

$$\frac{\partial \ln K_{PT}}{\partial p} = -\frac{\Delta V}{RT}\,, \qquad (5)$$

where ΔV is the activation volume, the pressure coefficient of the NQR frequency is found to be

$$\frac{\partial \nu_L}{\partial p} = (\nu_{PT} - \nu_{HB})\,X_{PT}\,X_{HB}\left(-\frac{\Delta V}{RT}\right) + X_{PT}\frac{\partial \nu_{PT}}{\partial p} + X_{HB}\frac{\partial \nu_{HB}}{\partial p}\,. \qquad (6)$$

Using the values collected in Table 1 one can estimate the parameters of (6). The values of $\partial\nu_{HB}/\partial p$ and $\partial\nu_{PT}/\partial p$ are -0.04 kHz · MPa^{-1} and 0.16 kHz · MPa^{-1}, respectively, while $\Delta V = -0.9$ cm^3/mol. The results of the above calculations are plotted in Figure 1. They show good agreement with the experimental points for the low and high pK_a values. In the vicinity of $pK_a = 6$, however, the experiment shows much more rapid changes than the theoretical curve suggests. This is in agreement with the model of Matsushita and Matsubara, which predicts nonlinearity of the changes and critical behaviour of the hydrogen bonds going on from double minimum potential bonds to single minimum potential bonds. In our experiments we can expect to observe this effect close to 50% of the proton transfer ($pK_a \approx 6$).

To include the critical behaviour in our calculations we added in (6) an experimental function term

$$F_{exp} = \frac{A}{(\Delta pK_a - 0.775)^n}\,,$$

where A and n are constants. In Fig. 3 the dotted line shows the pressure coefficient of the NQR frequency calculated in this way with the parameters $A = 3.8$ and $n = 0.27$.

The different signs of the pressure coefficients of the NQR frequency for both forms of hydrogen bonds, covalent bonds and ionic bonds with proton transfer, may be explained by the theory of Matsushita and Matsubara [8]. According to their model the applied pressure shortens the bonds, shifts the position of the proton toward the center of the bond, and therefore causes a change in dipole moment $\vec{\mu}$ and in the EFG. The pressure induced change of the gradient is proportional to $\partial R_{O-H}/$

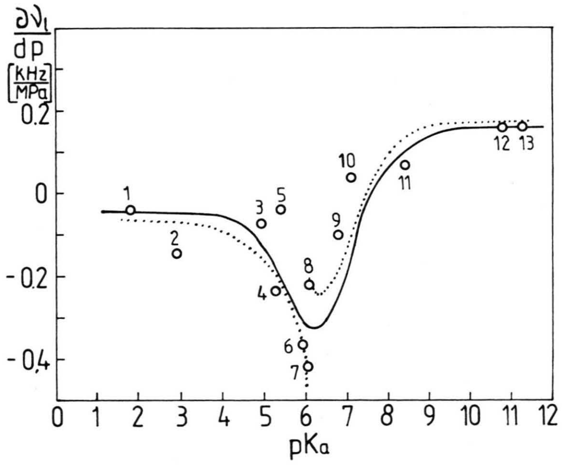

Fig. 3. Pressure coefficient of the ^{35}Cl NQR frequency of the lowest resonance ν_L vs. basicity (——: dependence calculated by use of the simple proton transfer equilibrium model; ·····: dependence calculated with regard to the critical behaviour of the hydrogen bond).

$\partial R_{\mathrm{O...N}}$. Thus one can expect a change in the sign of $\partial \nu/\partial p$ going from covalent O–H...N (negative value of $\partial R_{\mathrm{O-H}}/\partial R_{\mathrm{O...N}}$; the proton moves away from the oxygen nucleus) to ionic $\mathrm{O^-...H-N^+}$ bonds (positive value of $\partial R_{\mathrm{O...H}}/\partial R_{\mathrm{O...N}}$; the proton moves towards the oxygen nucleus).

Taking into account two different tautomeric forms of the hydrogen bond, normal A–H...B and polar $\mathrm{A^-...H-B^+}$, the difference of the free energy ΔG between these two states is [11]

$$\exp\left(-\frac{\Delta G}{RT}\right)=\frac{n_2}{n_1}; \quad n_1+n_2=1\,, \tag{7}$$

where n_1 and n_2 represent the populations of these two states. Using (7) and the relation

$$\nu_L = n_1 \nu_1 + n_2 \nu_2 \tag{8}$$

one gets

$$\frac{\Delta G}{RT}=\ln\left(\frac{\nu_2-\nu_L}{\nu_L-\nu_1}\right). \tag{9}$$

Figure 4 shows the calculated dependence of the NQR frequency ν_L on $\Delta G/RT$ with $\nu_1 = 36.89$ MHz and $\nu_2 = 35.79$ MHz. Using the thermodynamical relation

$$\frac{\partial}{\partial p}\left(\frac{\Delta G}{RT}\right)=\frac{\Delta V}{RT}, \tag{10}$$

(7) and (8) one gets the pressure coefficient of the NQR frequency

$$\frac{\partial \nu_L}{\partial p}=(\nu_2-\nu_1)\, n_2 n_1\left(-\frac{\Delta V}{RT}\right) + n_2\frac{\partial \nu_2}{\partial p}+n_1\frac{\partial \nu_1}{\partial p}. \tag{11}$$

The calculated pressure coefficient of the NQR frequency (ν_L line) using the parameters $\partial\nu_1/\partial p = -0.04\ \mathrm{kHz\cdot MPa^{-1}}$, $\partial\nu_2/\partial p = 0.16\ \mathrm{kHz\cdot MPa^{-1}}$, and $\Delta V = -0.9\ \mathrm{cm^3/mol}$, is shown on Figure 5.

In this model the "crystal effect" is responsible for substantial uncertainties in the calculated ΔG values. To avoid too large errors, for that reason some experimental points were omitted.

As one can see, this "energy based model" leads to an equation for the pressure coefficient of the NQR frequency which is identical with (6) evaluated from the proton transfer equilibrium model.

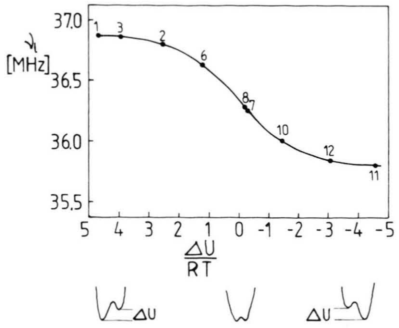

Fig. 4. Dependence of ν_L (^{35}Cl) on $\Delta U/RT$.

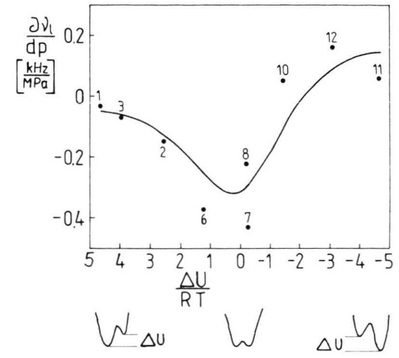

Fig. 5. Pressure coefficient of ν_L (^{35}Cl) as a function of $\Delta U/RT$.

However, the "energy based model" is much more sensitive to the crystal field effect, which may be responsible for substantial uncertainties in the calculated ΔG values.

Detailed studies of the temperature dependence of all NQR lines have also been made. The results show that there is no correlation between the temperature dependence of the NQR frequency and the degree of the proton transfer. Thus, dynamical effects are not responsible for the observed pK_a dependences of $\nu(^{35}\mathrm{Cl}) = f(\mathrm{P})$.

Conclusions

A correlation of the sign and magnitude of the pressure coefficient of the NQR frequency and the degree of proton transfer in the hydrogen bond has been found. It is shown that in the vicinity of 50% proton transfer, the hydrogen bond behaves in a critical manner. The observed phenomena may be explained using the model of Matsushita and Matsubara and assuming a pressure dependence of the proton transfer equilibrium.

Three different mechanisms contribute to the function reflecting the dependence of the pressure coefficient of the NQR frequency on pK_a:

1. The pressure dependence of the proton transfer equilibrium constant which is described by the activation volume $\Delta V = -0.9\ \mathrm{cm^3/mol}$ results in a curve of the shape shown in Figure 6a.

2. Additionally, deformation of the hydrogen bond potential by the pressure (which shifts the proton towards the center of the bond) results in changing of the signs of the pressure coefficient when going from covalent to ionic hydrogen bonds (Figure 6b).

3. Finally, the nonlinearity and critical behaviour of the hydrogen bond when going from a long hydrogen bond with a double minimum potential to a short hydrogen bond with a single minimum potential, as predicted by Matsushita and Matsubara, leads to the shape of the curve as shown on Figure 6c.

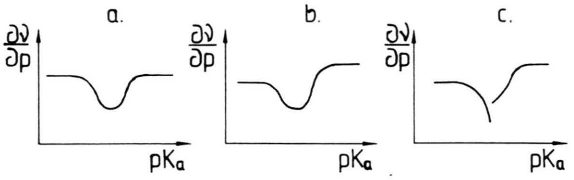

Fig. 6. Schematic drawings showing the influence of the three different mechanisms on the shape of the curve reflecting the dependence of pressure coefficient of the NQR frequency on the pK_a of the base: a) the pressure dependence of the proton transfer equilibrium constant; b) deformation of the hydrogen bond potential by the pressure; c) critical effects.

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