High Pressure NQR Study of the Phase Transition in Anilinium Iodide*

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Z. Naturforsch. **41 a,** 290–293 (1986); revised version received October 1, 1985

The ^{127}I NQR frequency in anilinium iodide $C_6H_5NH_3^{\oplus}I^{\ominus}$ was studied at pressures up to 300 MPa and within the temperature range 77 K – 290 K. With increasing pressure the order-disorder transition point T_c is shifted to higher temperatures. The pressure coefficient of the phase transition temperature amounts to $dT_c/dp = 4.2 \times 10^{-2}$ deg MPa^{-1}. The pressure coefficient of the NQR frequency is negative. In addition, the ^{127}I nuclear quadrupole coupling constants and the respective asymmetry parameters η were evaluated as a function of pressure. The results confirm the close connection between the mechanism of the phase transition and the dynamics of the $N-H^{\oplus}\dots I^{\ominus}$ hydrogen bonds.

Introduction

Anilinium iodide ($C_6H_5NH_3^{\oplus}I^{\ominus}$) belongs to the anilinium halides family, the properties of which have been extensively studied by Weiss and coworkers [1, 2, 3, 4]. The crystal is composed of anilinium ions $C_6H_5NH_3^{\oplus}$ and $I^{\ominus}$ anions. The NQR study of this compound, carried out by Fecher [4] has shown the anomalous temperature dependence of the ^{127}I NQR frequency. It was also pointed out that the charges on the NH_3 group make a significant contribution to the electric field gradient (EFG) at the ^{127}I nuclei. The charge distribution of a free halide ion is spherically symmetric. Therefore, the EFG at the site of the halide nucleus and the NQR frequency which is proportional to the EFG, are zero. The rather high ^{127}I NQR frequency (a nonzero EFG) suggests that there is a deviation from the spherosymmetric charge distribution around the iodide nuclei, presumably caused by the $N-H^{\oplus}\dots I^{\ominus}$ hydrogen bond. The importance of the hydrogen bond for the EFG at the site of the iodine nucleus is also supported by the significant ^{127}I NQR frequency shift on deuteration of the ammonium group.

The anilinium ion $C_6H_5NH_3^{\oplus}$ contains an uncoupled pair of hindered rotors: the C_6H_5 and the NH_3 groups. The hindering potential for NH_3 is presumably caused by the $N-H^{\oplus}\dots I^{\ominus}$ hydrogen bond. The hindering potential for C_6H_5 probably results from steric repulsion between neighbouring phenyl rings. A proton magnetic resonance study carried out by Ratcliffe and Dunnel [5] has shown reorientations of the $NH_3^{\oplus}$ groups and C_6H_5 phenyl rings with the activation energies of 8.5 kJ · mol^{-1} and 75 kJ · mol, respectively. In addition, an order-disorder process of the NH_3 group is involved in the phase transition which occurs at 240.3 K. Above $T_c = 240.3$ K the anilinium iodide is orthorhombic and the NH_3 groups are orientationally disordered. Below T_c the structure of $C_6H_5NH_3^{\oplus}I^{\ominus}$ is monoclinic.

In anilinium salts one has the possibility to modify the hinderance (predominantly hydrogen bonding) to the rotation of the NH_3 groups by applying high pressure. In the present work we examine the ^{127}I NQR frequency and the low temperature phase transition in anilinium iodide under the effect of hydrostatic pressure. The influence of pressure on the NQR frequency and the order-disorder transition temperature is analyzed in the scope of a microscopic model. The influence of

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* Presented at the VIIIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Darmstadt, July 22–26, 1985.

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the NH_3 group rotation and $N-H^{\oplus}\ldots I^{\ominus}$ hydrogen bond dynamics on the EFG at the site of iodine nucleus is discussed.

Experimental

The NQR measurements were performed with an ISSz-1-12 type pulse spectrometer. The details of our pressure device can to be found in [6]. Polycrystalline $C_6H_5NH_3^{\oplus}I^{\ominus}$ was used. All measurements were carried out at decreasing temperature. The temperature was measured with an accuracy of 0.1 K by means of a thermocouple. The pressure was measured with an accuracy of ± 2 MPa by means of a manganine coil.

Results and Dicussion

The ^{127}I NQR frequency in anilinium iodide $C_6H_5NH_3^{\oplus}I^{\ominus}$ was studied at pressures up to 300 MPa and at temperatures 77 K to 290 K. Figure 1 shows the temperature dependence of the $\nu_{3/2} \leftrightarrows \nu_{5/2}$ NQR line for ^{127}I in $C_6H_5NH_3^{\oplus}I^{\ominus}$ at four selected pressures $p = 0.1$ MPa, 114 MPa, 187 MPa, and 260 MPa in the vicinity of the phase transition point. As the pressure raises the NQR frequency decreases. With increasing pressure the order-disorder transition point T_c is shifted to higher temperatures. The pressure dependence of the transition point is shown in Figure 2. In the pressure range studied, $T_c(p)$ is linear within the accuracy of measurement with a slope $\mathrm{d}T_c/\mathrm{d}p = 4.2 \times 10^{-2}$ deg · MPa^{-1}.

The pressure coefficient of the NQR frequency $\mathrm{d}\nu/\mathrm{d}p$ is negative at all temperatures investigated and for the $\nu_{3/2} \leftrightarrows \nu_{5/2}$ transition equals − 3.38 kHz MPa^{-1}, − 1.53 kHz MPa^{-1}, − 2.29 kHz MPa^{-1}, and − 2.36 kHz MPa^{-1} at $T = 77$ K, 207 K, 255 K, and 295 K, respectively. Figure 3 shows the pressure dependence of the $\nu_{1/2} \leftrightarrows \nu_{3/2}$ and $\nu_{3/2} \leftrightarrows \nu_{5/2}$ NQR lines for ^{127}I in $C_6H_5NH_3^{\oplus}I^{\ominus}$ at 77 K. Iodine has a spin 5/2 and it is therefore possible to evaluate both the nuclear quadrupole coupling constant e^2qQ/h and the asymmetry parameters η from the NQR frequencies. Figure 4 shows the pressure dependence of e^2qQ/h and the respective asymmetry parameter η evaluated at 77 K. With increasing pressure the value of the quadrupole coupling constant decreases whereas the asymmetry parameter increases.

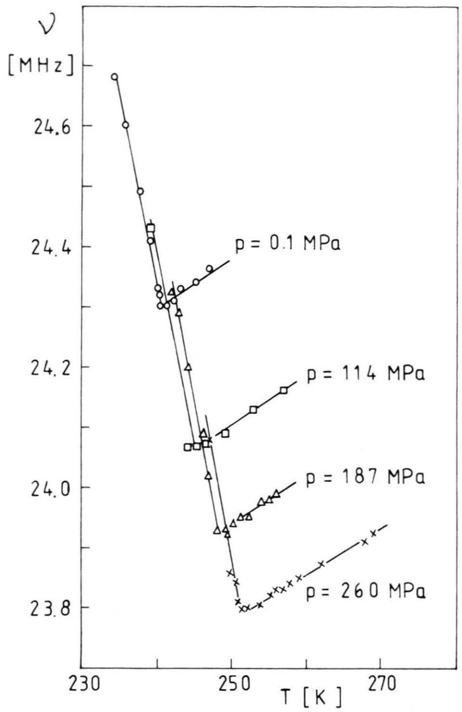

Fig. 1. The temperature dependence of the $\nu_{3/2} \rightleftarrows \nu_{5/2}$ NQR line for ^{127}I in $C_6H_5NH_3^+I^-$ under isobaric conditions.

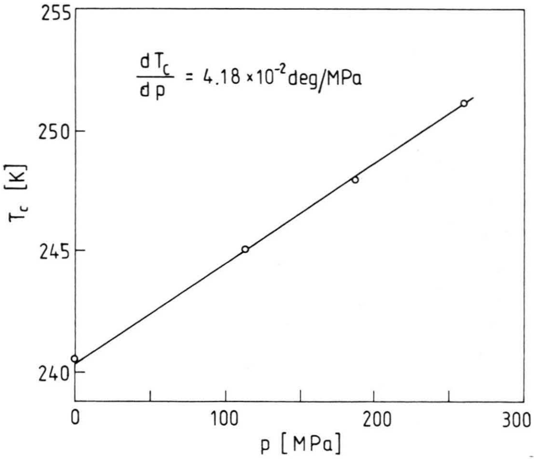

Fig. 2. The pressure dependence of the phase transition point.

Anomalous temperature dependences of ν_Q are often found in crystals with molecular reorientations or disorder; the present case is another example. Typical examples of such salts are NH_4I_3 and α-NH_4HgCl_3 [7, 8].

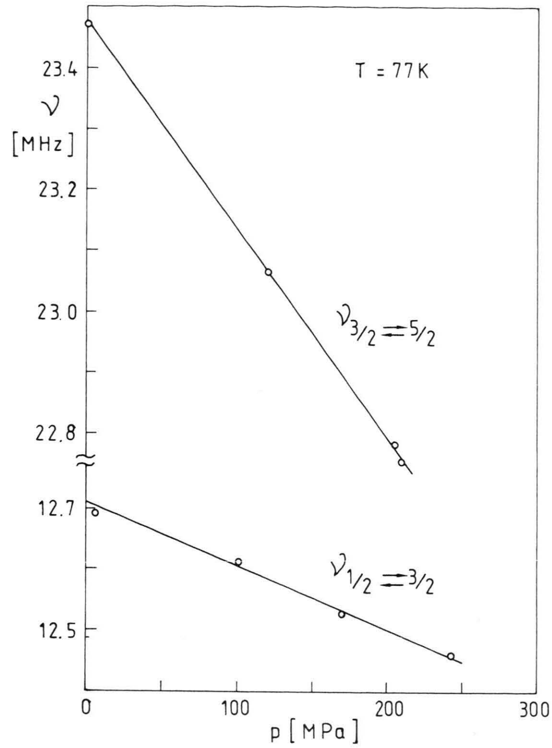

Fig. 3. The pressure dependence of the $\nu_{1/2} \rightleftarrows \nu_{3/2}$ and $\nu_{3/2} \rightleftarrows \nu_{5/2}$ NQR lines for ^{127}I in $C_6H_5NH_3^+I^-$ at 77 K.

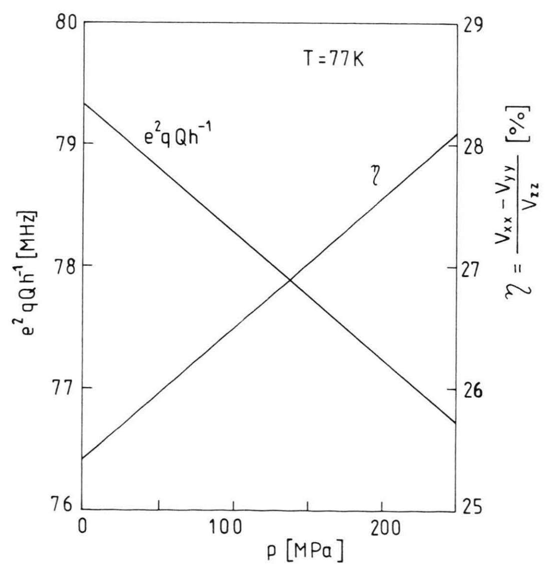

Fig. 4. The pressure dependences of e^2qQ/h and the asymmetry parameter η at 77 K.

The temperature dependences of NQR frequencies in these ammonium salts have successfully been interpreted in terms of a model which assumes that the reorientational motion of the NH_4^+ ion modifies the NQR frequency in the vicinity of the nucleous [9]. An extend of this modification is determined by the length of the jumping or transient time τ_t for the reorientation of NH_4^+ relative to the residence time τ_r in one of its equilibrium orientations. If $2\pi\nu_Q\tau_t \ll 1$ and $2\pi\nu_Q\tau_r \ll 1$ we can observe a time-averaged NQR frequency $\bar{\nu}_Q$ which is given by

$$\bar{\nu}_Q(T) = \nu_0(T) + (\nu_r\tau_r + \nu_t\tau_t)/(\tau_r + \tau_t), \quad (1)$$

where $\nu_0(T)$ corresponds to the NQR frequency in the limit that there is no contribution from NH_4^+ ions to the resonance frequency. $\nu_0(T)$ contains Bayer's effect and decreases monotonously with increasing temperature. Here, τ_r can be assumed to vary with temperature as

$$\tau_r = \tau_0 \exp(E_a/RT), \quad (2)$$

where E_a is the activation energy for the reorientation. τ_r should be the same as the autocorrelation time τ_c usually obtained in T_1 measurements of proton NMR. τ_t depends very weakly on temperature but no theoretical expression for temperature dependence is known. We assume for simplicity that τ_t is constant over the temperature range considered.

According to the above model, when the temperature is raised, the reorientation of NH_3^+ in $C_6H_5NH_3^+I^-$ becomes more excited and the iodine anion is in good contact with the ammonium group. This leads to a nonzero EFG at the iodine nuclei which is created by the $N-H^+...I^-$ hydrogen bond.

The externally applied high pressure causes a change in intermolecular distances leading to an increase of the activation energy and the correlation time τ_c for the reorientational motion of the ammonium group. In effect, pressure shifts the phase transition temperature T_c with a positive pressure coefficient dT_c/dp (Figure 2).

The high pressure acts in a way to destroy the contact between NH_3^+ and I^- because the elongation of the correlation time. Slow rotational motion can contribute to the weakening of the $N-H^+...I^-$ hydrogen bond. The weakness of the $N-H^+...I^-$ hydrogen bond is responsible for the decrease of the EFG at the ^{127}I and the NQR frequency for this nucleus under high pressure.

Conclusion

The phase transition which occurs in anilinium iodide at 240.3 K, apparent by a change in NQR frequency, is related to hindered rotation of the ammonium group. This is the predominant mechanism. Thus the simple activation process formulation applied in this paper is adequate for the description of the pressure effects observed near the phase transition. A closer qualitative analysis requires knowledge of the pressure and temperature dependences of the correlation times. To achieve this, data from proton relaxation time measurements as a function of temperature and pressure are needed.

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