On the Order-Disorder Phase Transformation of Anilinium Halides

V. Inelastic Neutron Scattering on Anilinium Bromide, $C_6H_5NH_3^{\oplus}Br^{\ominus}$, and its Partially Deuterated Derivatives $C_6H_5ND_3^{\oplus}Br^{\ominus}$ and $C_6D_5NH_3^{\oplus}Br^{\ominus}$

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The order-disorder phase transition which occurs at $T_c = 296.9$ K in anilinium bromide, $C_6H_5NH_3Br$, is studied by inelastic neutron time-of-flight measurements. Data are taken from hydrogenated and partially deuterated samples ($C_6D_5NH_3Br$ and $C_6H_5ND_3Br$) below and above the transition temperature. From the inelastic scattering data the phonon frequency distribution in the range of the intermolecular vibrations is calculated. The assignment of bands is given and changes in the spectra with temperature are discussed. The analysis of the quasielastic line revealed substantial broadening due to rotational diffusion of the $-NH_3^{\oplus}$ group. These jump diffusion processes were observed in the orthorhombic high temperature and − with markedly diminished rate − in the monoclinic phase below T_c. From the correlation times at different temperatures the activation energies are estimated for both phases. Comparison with calculated elastic incoherent structure factors suggests jumps of 60° for hindered rotation.

Introduction

The reversible solid ⇌ solid phase transformation of anilinium bromide, $C_6H_5NH_3Br$, at $T_c = 296.9$ K has been extensively studied by different, mainly spectroscopic and diffraction methods ([1−4] and literature cited therein). A recent structure determination by neutron and X-ray diffraction of the orthorhombic high temperature phase [1] revealed a disorder of the $-NH_3^{\oplus}$ group which also affects the phenyl ring. Complete order of the whole molecule is found at temperatures well below the transition temperature T_c, where the anilinium ion occupies only one of the two possible orientations of the high temperature phase [2]. Temperature dependent ^{79}Br-NQR studies of $C_6H_5NH_3Br$, $C_6H_5ND_3Br$ ($T_c = 291.5$ K) and $C_6D_5NH_3Br$ ($T_c = 297.6$ K) [3] and ^1H-NMR work on $C_6H_5NH_3Br$ [4] showed a close connection between the mechanism of the phase transition and the hydrogen bonds N−H ⋯ Br. A dynamical model for the disordered orthorhombic

structure is proposed, mainly considering reorientational $-NH_3^{\oplus}$ motions [1]. The phase transition is characterized by a continuous change from the state of disorder (two orientations) to the ordered state [2].

Inelastic incoherent neutron spectroscopy is very sensitive to dynamics of hydrogen atoms due to the high incoherent scattering cross-section (for a general review see e.g. [5] and [6]). Ratcliffe [7] performed incoherent inelastic neutron scattering (INS) measurements on anilinium chloride and bromide at 77 K in the range of $0 - 500$ cm^{-1} ($0 - 60$ meV). By comparison with corresponding IR and Raman spectra he achieved the assignment of torsional bands and calculated the height of the barrier against the $-NH_3^{\oplus}$ rotation from the $-NH_3^{\oplus}$ torsional frequency. The calculation was based on a periodic potential (120° periodicity) in a simple harmonic approximation.

The purpose of the present study is (i) verification of the assignment of various parts of the inelastic neutron pattern by partial deuteration of the anilinium bromide, (ii) determination of the impact of the phase transition on the INS spectra and (iii) estimation of the residence times and activation energies by analysis of the broadening of the quasielastic line. We therefore performed several inelas-

tic time-of-flight measurements above and below the transition temperature.

Experimental

Anilinium bromide was prepared from an aqueous solution of aniline and hydrobromic acid. The deuteration of the $-NH_3^\oplus$ group was achieved by four repeated recrystallizations of the compound from heavy water, which was then removed in a desiccator system [3]. Ring deuterated aniline (Merck, 99% D), and hydrobromic acid gave the ring deuterated sample.

Neutron time-of-flight measurements were performed on the rotating crystal spectrometer TOF2 at the cold source of the FR2 reactor of the Kernforschungszentrum Karlsruhe. The results were recorded as energy gain spectra with an incident energy of 5.06 meV and 20 different angular positions between 80° and 166°. Data were collected on polycrystalline material of the three compounds. The time-of-flight spectra were converted into the double differential scattering cross section. The generalized phonon density of states $G(\hbar\omega)$ was calculated after corrections for multiphonon contribu-tions by an iterative process. $G(\hbar\omega)$ is the sum of the partial densities of the atomic components weighted with their scattering power and vibrational amplitudes. The experimental energy resolution $\Delta E/E$ lies between 5% and 10% for neutron energy gain between 0 meV and 100 meV, respectively. The quasielastic scattering, observed in an energy range up to ± 3 meV, was analysed by Lorentzian-Gaussian convolution fits.

Results

Assignment of Bands and Temperature Dependence

The frequency distribution of the monoclinic $C_6H_5NH_3Br(II)$ at 288 K in the region of the external vibrations, together with that of partially deuterated samples is shown in Fig. 1. The peak at 6 meV, reduced by deuteration of the benzene ring, but unaltered by deuteration of the $-NH_3^\oplus$ group, is attributed predominantly to vibrations of the ring. A frequency shift is observed at the same time which corresponds to the greater mass of the deuterated ring.

The peak at 17 meV is reduced by both kinds of deuteration, phenyl and $-NH_3^\oplus$ groups are involved.
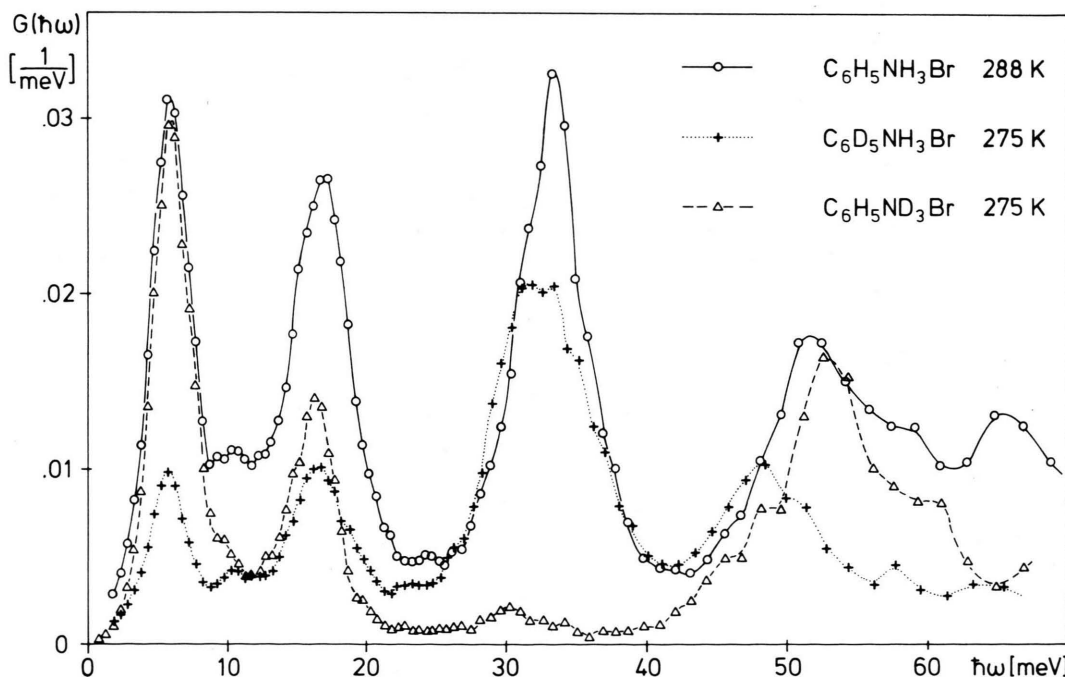

Fig. 1. Comparison of the generalized phonon density of states for anilinium bromide with those for its partially deuterated derivatives (monoclinic phase).

The area of the different peaks is proportional to the number of protons. No frequency shift is observed.

The peak found for $C_6H_5NH_3Br(II)$ at 33 meV almost disappears in $C_6H_5ND_3Br(II)$, indicating that it is strongly related to a motion of the $-NH_3^{\oplus}$ group. Its high intensity is a sign of torsional motion of the $-NH_3^{\oplus}$ group, because the intensity increases with decreasing mass of the scatterer. The whole molecular mass must be considered for a translational motion, a reduced effective mass only for a torsional one.

In the energy range above 50 meV the evaluation becomes increasingly difficult due to the low thermal occupation of the levels involved and high multiphonon contributions to the scattered intensity. Nevertheless, a comparison of the spectra suggests dominant ring modes in the $50 - 70$ meV region. This assignment of bands, derived from scattered intensities, is in agreement with that proposed by Ratcliffe [7]. The coincidence of the phonon density of states peaks (INS) with the zone center frequencies as measured by Raman indicates flat dispersion branches.

Figure 2a compares the spectra of monoclinic (275 K and 294 K) and orthorhombic (333 K) $C_6D_5NH_3Br$. A pronounced intensity loss is observed for the $-NH_3^{\oplus}$ torsional band in the high temperature phase (I) as well as a slight shift to lower frequencies. The latter might be explained by weaker hydrogen bonds in the orthorhombic phase. Weaker bonding, however, is usually connected with higher amplitudes of vibration, and should thereby lead to an increase of the scattered intensity. The observed decrease is therefore somewhat surprising. A possible explanation may be a shorter residence time of the $-NH_3^{\oplus}$ group in one of the two positions at high temperatures, which implies an increase of the jump rate between available orientations. The higher stability in the monoclinic phase is indicated by the striking shift of the $-NH_3^{\oplus}$ torsional band to higher frequencies in the 105 K measurement (Figure 2b). The structure on the low frequency slope of the $-NH_3^{\oplus}$ torsional band was found as a shoulder in the INS work of Ratcliffe [7] at 77 K also and was assigned to ring modes from IR and Raman results.

From the recorded spectra no distinct effect caused by the phase transition can be directly detected. The analysis of the quasielastic scattering, however, gives a direct indication of the phase transition.

Quasielastic Line Broadening

The quasielastic scattering was analysed for $C_6D_5NH_3Br$ at 363 K, 333 K, 308 K, 300 K, 294 K, and 105 K and on $C_6H_5NH_3Br$ at 333 K, 294 K, and 288 K in the original time-of-flight patterns. For $C_6D_5NH_3Br$ a considerable broadening is observed, which increases with temperature (Figure 3). It is almost absent at 105 K, where the line width corresponds to instrumental resolution. Figure 4 does not present any broadening for $C_6H_5ND_3Br$, indicating that the jump diffusion processes of the $-NH_3^{\oplus}$ groups are the origin of the observed line broadening. As expected, this partially deuterated sample does not show any change in the pattern when passing the transition temperature.

The total line is composed of the elastic part represented by a Gaussian function and the quasielastic contribution which is of Lorentzian shape. The width of the latter depends on the diffusion constant, or in the case of discontinuous diffusion, on the average time between two jumps (residence time τ) and on the geometry of the position which is available for the proton by a jump [8].

The purely elastic scattering is proportional to the so-called Elastic Incoherent Structure Factor (EISF) and gives the time averaged spatial distribution of the diffusing proton and therefore information about the geometry of the motion. Jump diffusion about one rotational axis and one rotational angle leads to a single Lorentzian. Its line width is independent of momentum transfer Q for $Q \gg$ reciprocal jump distance l^{-1}.

Figure 5 represents computer fits to the observed lines for $C_6D_5NH_3Br$ at several temperatures. These continuous lines are composed of the sum of a Gaussian function and a convolution of a Lorentzian with a Gaussian function. This convolution gives the quasielastic part folded with the instrumental resolution [9]. The base lines present the inelastic background arising from vibrational excitations at low energies. The background is estimated by extrapolation between the regions without quasielastic contributions and then adapted in the least squares calculations.

Figure 6 shows the full width at half maximum Γ of the pure Lorentzian as a function of the squared

momentum transfers Q^2. No relevant change of Q^2 is recognizable in the range covered by these experiments. The saturation of the line-width with increasing Q indicates jump diffusion [10].

The additional broadening in $C_6H_5NH_3Br$ compared to that in $C_6D_5NH_3Br$ (by about 10%) is certainly not produced by reorientation of the phenyl ring around the C—N-axis. A proton magnetic relaxation study [4] had demonstrated that the respective mechanism sets in at much higher temperatures. A reorientation of the phenyl ring around an axis vertical to the C—N direction has to be taken into consideration. The structure determination [1] of the orthorhombic phase revealed a reorientation
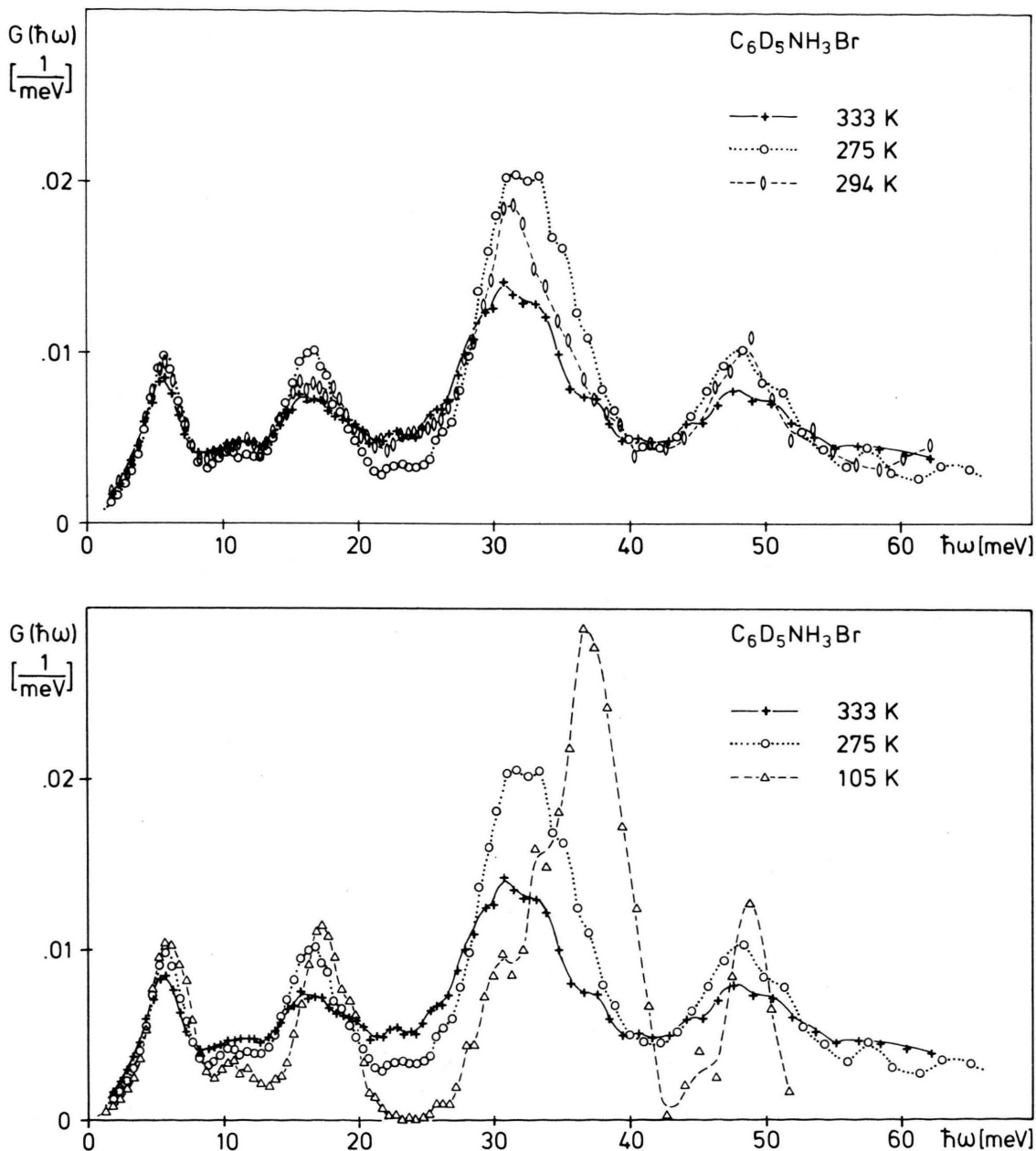

Fig. 2 a, b. Phonon frequency distribution for $C_6D_5NH_3Br$ at different temperatures.
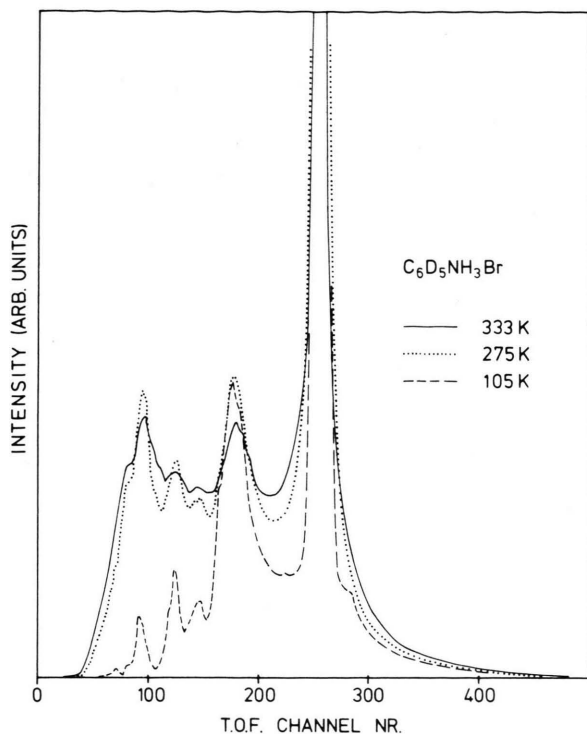
Fig. 3. Time-of-flight spectra of $C_6D_5NH_3Br$ showing increasing quasielastic line broadening with rising temperature.
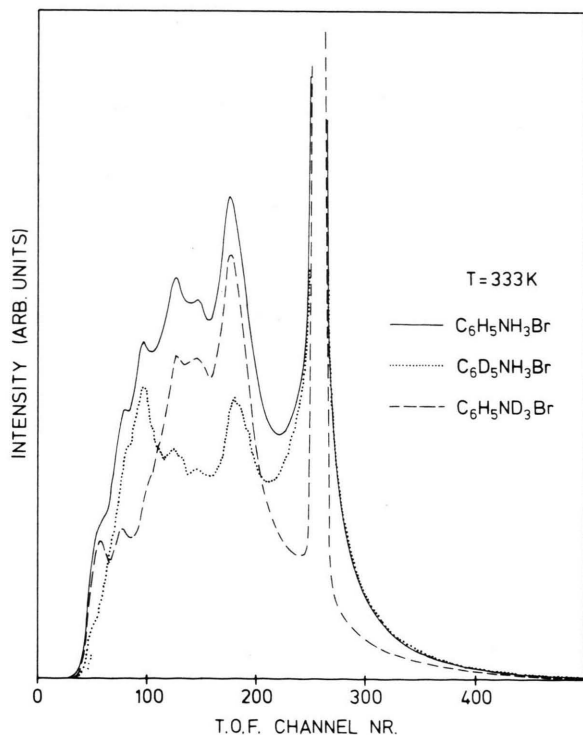

Fig. 4. Time-of-flight spectra, showing the jump diffusion broadening of the elastic line for protonated $-NH_3^{\oplus}$ groups.
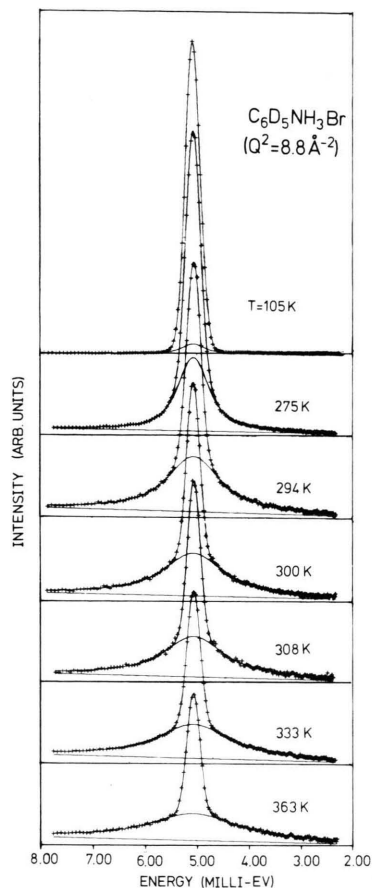

Fig. 5. Temperature dependence of the quasielastic line broadening of $C_6D_5NH_3Br$. The continuous lines are computer fits, representing phonon background, Lorentzian-Gaussian convolution describing the quasielastic scattering, and sum of purely elastic Gaussian line and Lorentzian-Gaussian convolution.

of the whole $C_6H_5NH_3^{\oplus}$ ion simultaneously with the jumps of the $-NH_3^{\oplus}$ group: the axis $N-C(1) \cdots C(4)-H(4)$ has two orientations inclined by $\pm 3°$ with respect to the crystallographic twofold axis [1]. The total tilt of the anilinium ion, caused by the reorientation of the $-NH_3^{\oplus}$ group, is therefore six degrees. This motion should produce additional Lorentzian contributions to the quasielastic scattering.

A rough estimation based on model calculations for different jump diffusion processes [6] was done. The quasielastic form factor for a ring proton with a jump distance $l \approx 0.15$ Å has a first maximum at $Q \approx 30$ Å^{-1} starting at zero for $Q = 0$.

The additional broadening and the increase of the line-width above $Q^2 = 8.5$ Å^{-2} in $C_6H_5NH_3Br$ are therefore not explained by a reorientation of the ring. An extension of the experimental Q-range and further model calculations seem desirable. They

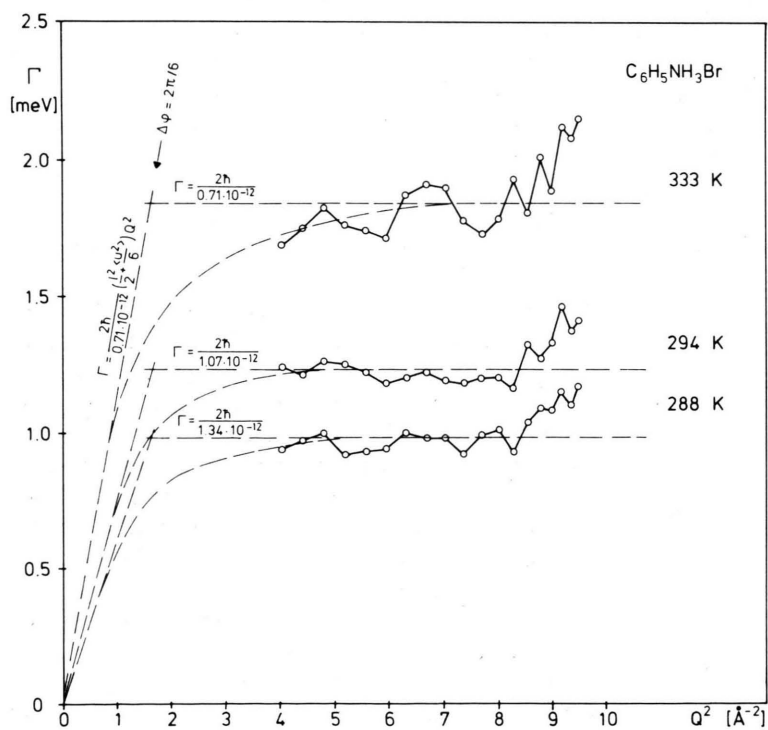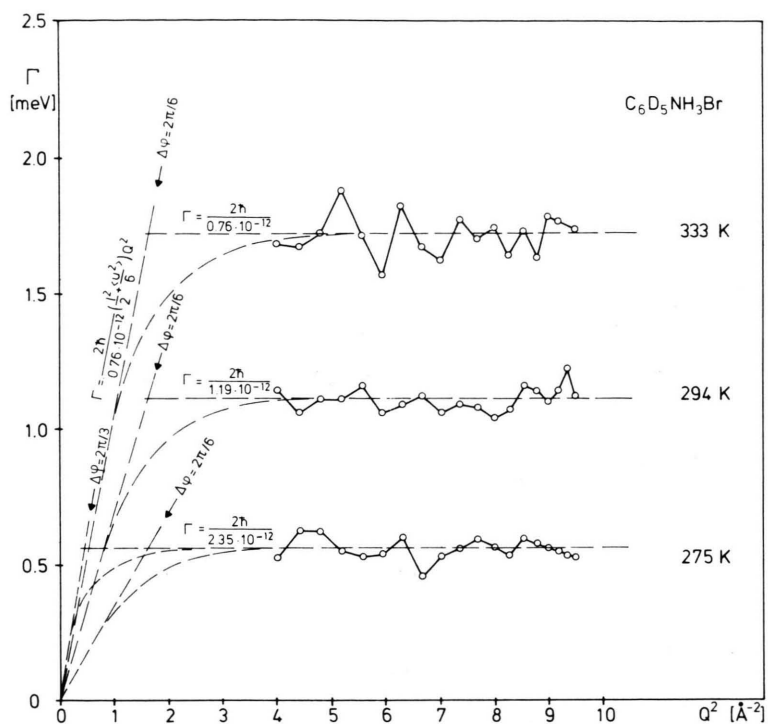Fig. 6. Pure Lorentzian full widths at half maximum Γ as a function of the squared momentum transfer Q^2 for three different temperatures. Dotted lines are calculated from limiting case formulas [10]: a) $C_6D_5NH_3Br$; b) $C_6H_5NH_3Br$.

should consider all possible geometries for jumps and the influence of the jump time. The absence of any quasielastic broadening in $C_6H_5ND_3Br$ (Fig. 4) is in agreement with these model calculations.

Residence Times and Activation Energies

From the mean Lorentzian width (horizontal dotted line in Fig. 6) the residence times of the $-NH_3^{\oplus}$ group within one position were derived according to the relation $\tau = 2\,\hbar/\Gamma$ [10]. The results are listed in Table 1. The reliability of the values is about 4%, becoming less accurate for shorter measuring times. A reasonable evaluation of the 105 K data was not possible. A quasielastic broadening, if present, lies below the experimental resolution of about 0.30 meV, implying a residence time of $\tau > 4 \cdot 10^{-12}$ s.

The shorter residence times in $C_6H_5NH_3Br$ agree with the slightly higher torsional frequency (see Figure 1). The residence time falls from 2.35×10^{-12} s at 275 K in the monoclinic phase − about 20 periods of torsional oscillations − to 0.68×10^{-12} s at 363 K in the orthorhombic phase, corresponding to about 5 vibration periods. The $\ln \tau$ versus $1/T$ plot (Fig. 7) has a bend at the transition point T_c. A similar effect has been observed for the rotational jumps of the $NH_4^{\oplus}$ ion around its fourfold axes in NH_4Cl at 242 K, where an order-disorder phase transition occurs [11].

The residence times of hindered rotator groups in solids are generally described by an Arrhenius dependence on the temperature T, the activation energy V and the correlation time constant τ_0, that is $\tau = \tau_0 \exp(V/RT)$. Activation energies of (5.5 ± 0.6) kJ/mol and (24 ± 5) kJ/mol were derived from the different slopes of the $\ln \tau$ versus $1/T$ curve (Fig. 7) for the two phases. The height of the potential
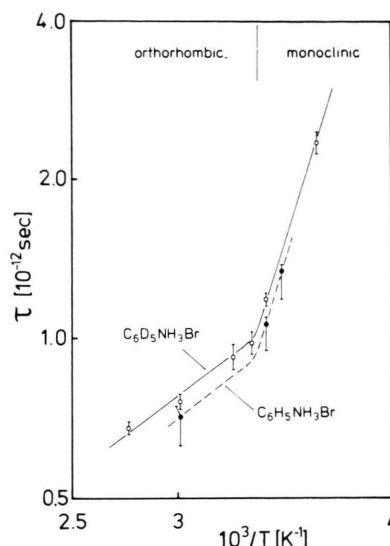

Fig. 7. Arrhenius plot of the residence times giving activation energies of 24 and 5.5 kJ/mol for the monoclinic and orthorhombic phase respectively.

barrier was determined in a similar way for $(CH_3)_3NHCl$ (INS results) [12], for $-NH_3^{\oplus}$ groups in anilinium salts (^{1}H-NMR) [4] and for $NH_4^{\oplus}$ ions in NH_4Cl [11] and $(NH_4)_2SnCl_6$ [13] (both INS).

The activation energy of 5.5 kJ/mol seems to be very reliable as its temperature dependence is negligible in the high temperature phase. In the monoclinic phase, however, the value of V increases with decreasing temperature and has its highest value when the state of order is reached. All conceptions of the phase transition in anilinium bromide postulate a continuous change of the activation energy at the transition point [2, 14]. The final value of the monoclinic angle which increases gradually is 91.37° at $T \approx 160$ K [15].

The activation energy of 24 kJ/mol should only be considered as an estimation for the temperature range just below T_c (275 − 295 K). The barrier height increases when the symmetries of rotator and environment are similar. The environment changes from nearly C_4 symmetry in the orthorhombic phase towards a disturbed C_3 symmetry in the monoclinic phase [1, 2] without ever reaching exact correspondence with the symmetry of the rotator. This correspondence leads to higher barriers, as observed in anilinium chloride [4, 7]. Additional measurements at lower temperatures should give higher barriers. The higher frequency observed in the 105 K result gives some indication. The instru-

Table 1. Mean values for the pure Lorentzian full widths at half maximum Γ and residence times $\tau = 2\hbar/\Gamma$.

Temperature T/K	$C_6D_5NH_3Br$		$C_6H_5NH_3Br$	
	Γ/meV	$\tau \cdot 10^{12}/s$	Γ/meV	$\tau \cdot 10^{12}/s$
105	< 0.30	> 4		
275	0.56	2.35		
288			0.98	1.34
294	1.11	1.19	1.23	1.07
300	1.34	0.98		
308	1.42	0.93		
333	1.72	0.76	1.84	0.71
363	1.93	0.68		

mental resolution did, however, not allow an analysis of the quasielastic scattering at 105 K.

In accordance with Ratcliffe [4, 7] we suppose that the barrier against the $-NH_3^{\oplus}$ group motion is essentially of external origin (via hydrogen bonds), and the internal hindrance is low. Still the interaction between ring and $-NH_3^{\oplus}$ group seems to be strong enough to arrange the ring in an eclipsed position to one of the H atoms of the $-NH_3^{\oplus}$ group [1]. It is concluded from the absence of neutron scattering intensity on the $-ND_3^{\oplus}$ torsion that the motion of $-NH_3^{\oplus}$ group and phenyl ring are decoupled. A frequency of about $33/\sqrt{2}$ meV = 23 meV should be observed for $C_6H_5ND_3Br$ in the case of coupling.

Analysis of the line width gives also information on the jump distance. From the crystal symmetry, angles for an individual jump of 60° or 120° seem reasonable. The Lorentz widths for these two angles at low Q-values were calculated and drawn in Fig. 6 for the 275 K experiment. The calculation was based on a limiting case formula [10] with l = jump distance and $\langle u^2 \rangle/6$ = Debye-Waller coefficient. As no experimental points are available in that Q-range, an evaluation based on elastic incoherent structure factors (EISF) was attempted. The EISF reflects the geometry of the moving proton directly. The quasielastic form factor 1-EISF was in fact

used, as the elastic incoherent scattering is influenced by Bragg reflections.

The integrated Lorentz intensities are plotted in Fig. 8 as a function of $Q \cdot r$ for several temperatures (r = distance of the proton from the rotational axis). They were corrected for the partial Debye-Waller factor of the $-NH_3^{\oplus}$ group and normalized to the incoherent part of the total scattering. The theoretical curves for the 60° and 120° jumps calculated from formulae of [6] reveal marked differences for high Q values. The experimental points show a distinct tendency to a 60° reorientation in both phases for temperatures not so far from the transition point. The 105 K data unfortunately do not allow a corresponding evaluation.

Discussion

Activation energies for hindered rotation of $-NH_3^{\oplus}$ groups which are involved in hydrogen bonds are listed in Table 2. The values derived from quasielastic scattering are in general agreement with values observed by other methods. The considerable difference in the activation energy between the two phases (approximately a factor of 4) was stated for the two phases of ethylenediammonium chloride, too [19], though the two phase transitions are of different type. Ratcliffe and Dunell [4, 5] derived
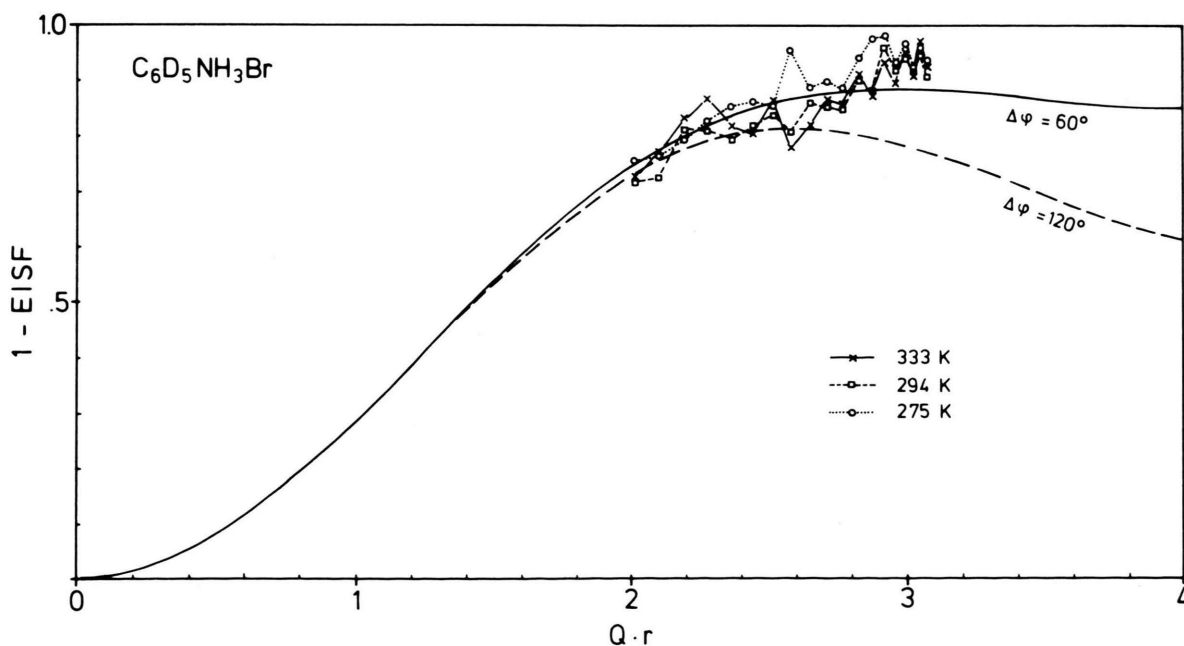

Fig. 8. Comparison of the quasielastic form factor, calculated for jump angles of 60° and 120° with the experimental values.

Table 2. Comparison of activation energies for reorientational motions of $-NH_3^{\oplus}$ groups embedded in hydrogen bond systems.

Substance	Activation energy V/kJ/mol^{-1}	Temperature (range) T/K		Method	Ref.
$(CH_3)_3CNH_3Br$	33.2 ± 0.8	330		NMR	[16]
N_2H_5Cl	31.4 ± 0.3	$220-300$		NMR	[17]
	40	77		INS	
N_2H_5Br	32.3 ± 0.2	$200-280$		NMR	[17]
	37	77		INS	
$N_2H_6Br_2$	35	296		INS	[18]
$BrNH_3CH_2CH_2NH_3Br$	12.3 ± 0.2	$80-300$		NMR	[19]
$ClNH_3CH_2CH_2NH_3Cl$	41.3 ± 0.2	$250-410$	(phase I)	NMR	[19]
	8.6 ± 0.5	$320-550$	(phase II)	NMR	
$C_6H_5NH_3Cl$	37.1 ± 0.6	$295-450$		NMR	[4]
	47.6	77		INS	
$C_6H_5NH_3Br$	11.2 ± 0.1	$77-230$	(phase II)	NMR	[4]
	21.7	77	(phase II)	INS	
	24 ± 5	~ 275	(phase II)	quasiel. INS	this paper
	5.5 ± 0.6	$300-360$	(phase I)	quasiel. INS	
$C_6H_5NH_3I$	8.5 ± 0.1	$77-180$	(phase II)	NMR	[4]

11.2 KJ/mol^{-1} from spin lattice relaxation time measurements and 21.7 KJ/mol^{-1} from the INS torsional frequency of the $-NH_3^{\oplus}$ group. The discrepancy between the two values is considerable. The NMR result might be strongly influenced by the assumptions made about the intramolecular geometry [4]. A recalculation based on the latest neutron diffraction data [2] seems worthwhile. The agreement between the INS value and the result of the quasielastic line broadening is rather good despite the unrealistic assumption of a regular threefold environment of the $-NH_3^{\oplus}$ group in the evaluation of the INS data.

During the preparation of the present manuscript a comprehensive paper of the Durham group was published [20] dealing with their inelastic neutron studies on anilinium halides. The spectra on partial deuterated samples agree with our figures and the activation energies are the same as those given in previous papers. A new value of 13.2 kJ/mol is reported for anilinium iodide from INS. No analysis of quasielastic scattering is given.

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