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Pure Nuclear Quadrupole Resonance of *Ionic* Halides. I. ^{79}Br-NQR Investigation of the Hydrogen Bonding, the ^{1}H–^{2}D Isotope Effect, and the "Order-Disorder" Transition in the Anilinium Bromides $C_6H_5NH_3^{\oplus}Br^{\ominus}$, $C_6H_5ND_3^{\oplus}Br^{\ominus}$, and $C_6D_5NH_3^{\oplus}Br^{\ominus}$*,†

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The ^{79}Br-NQR spectra of anilinium bromide, $C_6H_5NH_3^{\oplus}Br^{\ominus}$, of anilinium-$d_3$ bromide, $C_6H_5ND_3^{\oplus}Br^{\ominus}$, and of anilinium-$d_5$ bromide, $C_6D_5NH_3^{\oplus}Br^{\ominus}$, have been investigated in the temperature range $77 \leq T/K \leq 350$. The three compounds show an order-disorder phase transition near room temperature. The respective transition temperatures have been determined as 296.9 K ($C_6H_5NH_3^{\oplus}Br^{\ominus}$), 291.5 K ($C_6H_5ND_3^{\oplus}Br^{\ominus}$), and 297.6 K ($C_6D_5NH_3^{\oplus}Br^{\ominus}$). The large value of the ^{79}Br-NQR frequency ($\nu = 17.780$ MHz at 77 K for $C_6H_5NH_3^{\oplus}Br^{\ominus}$) and the large ^{1}H–^{2}D isotopic shift of this frequency ($\approx$400 kHz at 77 K by deuteration of the $NH_3^{\oplus}$-group) have been interpreted in terms of hydrogen bonding N–H···$Br^{\ominus}$. The state of order in the high temperature modification is discussed in the light of the ^{79}Br-NQR spectrum. The ^{79}Br-NQR frequency of the $Br^{\ominus}$ ion in the low temperature modification is related to the change in the monoclinic angle β and to the temperature dependence of the order parameter $s \propto \{(T_c - T)/T_c\}^{1/3}$.

In the course of an X-ray study of anilinium bromide, $C_6H_5NH_3^{\oplus}Br^{\ominus}$, Taguchi[1)] noticed that "Weissenberg photographs prepared at different seasons of the year, using one and the same crystal, showed differences in detail." This remarkable behavior led to the discovery of the phase transition of anilinium bromide. According to him,[1)] $C_6H_5NH_3^{\oplus}Br^{\ominus}$ is orthorhombic (modification **I**, D_{2h}^{10}-Pnaa, $Z=4$) above, and monoclinic (modification **II**, C_{2h}^{5}-$P2_1/a$, $Z=4$) below the transition temperature, given as $T_{II,I}=300.7$ K. The transformation was studied as well by calorimetry, DTA, and dilatometry showing a typical lambda type behavior of the heat capacity and an abnormal thermal expansion below $T_{II,I}=295$ K.[2)] The X-ray diffraction analysis of the high temperature modification **I** by Nitta *et al.*[3)] led to the determination of the positional parameters (hydrogen excluded). The crystal symmetry requires that the principal axis of the anilinium ion (N–$C_1 \cdots C_4$ axis) lies on a twofold symmetry axis. On the other hand, it is reasonable to assume a pyramidal configuration (C_{3v}) of the $-NH_3^{\oplus}$-group. The lack of correspondence between the symmetry of this group (threefold axis) and the point-group symmetry of the anilinium cation (twofold axis) indicates that there must be either a static orientational disorder of the $-NH_3^{\oplus}$-group or a rotation about the C_1–N bond as a "free" rotation or fast reorientation of the ammonium group. In the monoclinic structure of the low temperature modification **II** the requirement of the twofold symmetry imposed on the $C_4 \cdots C_1$–N axis is lost. An infrared study by Cabana and Sandorfy[4)] corroborates the implications of the X-ray work.

We became interested in the phase transition of anilinium bromide in the course of ^{35}Cl-, ^{79}Br-, ^{127}I-NQR studies on chloroanilinium salts[5,6a)] and on other possibly hydrogen bonded iodides and bromides (*e.g.* guanidinium halides[6b,c)]). For $C_6H_5NH_3^{\oplus}Br^{\ominus}$ (**I**) one expects a ^{79}Br-NQR signal, to be observable with a nonpulse technique only if in the time scale of the NQR experiment (some 10^{-7} s) there is the same ordered arrangement of neighbors around each of the crystallographically equivalent $Br^{\ominus}$ ions. The NQR experiment, therefore, may be helpful to decide between a static orientational disorder of the $NH_3^{\oplus}$-group on the one hand, and a "free" rotation or a fast reorientation of this group on the other.

Experimental

Materials. Anilinium bromide, $C_6H_5NH_3^{\oplus}Br^{\ominus}$, and anilinium-$d_5$ bromide, $C_6D_5NH_3^{\oplus}Br^{\ominus}$, were prepared by adding freshly distilled aniline or aniline-d_5 (Merck, 99% D) to an excess of an aqueous solution of hydrobromic acid. The precipitated salts were recrystallized from aqueous HBr and dried over P_2O_5 in a desiccator. The identity of the colorless crystal powders was proven by chemical analyses [Calcd (found) for C_6H_8BrN: C, 41.41 (41.32), H, 4.63 (4.69), N, 8.05% (8.10%); for $C_6H_3D_5BrN$: C, 40.26 (40.14); ^{2,1}H: 4.50 (4.50), N: 7.81% (7.83%)]. The compounds are free of water of crystallization. $C_6H_5NH_3^{\oplus}Br^{\ominus}$ decomposes at 292 °C. The degree of deuteration of $C_6D_5NH_3^{\oplus}Br^{\ominus}$ was checked by high resolution ^{1}H-NMR to be 95% or better. Anilinium-d_3 bromide, $C_6H_5ND_3^{\oplus}Br^{\ominus}$, was prepared by dissolving $C_6H_5NH_3^{\oplus}Br^{\ominus}$ in excess D_2O (98% D) and removing the water with P_2O_5 in a desiccator system. This process was repeated twice. Again the degree of deuteration was checked by ^{1}H-NMR to be 95% or better. This last result has also been strengthened by the NQR spectra of this compound.

NQR Measurements. The ^{79,81}Br-NQR spectra were observed on polycrystalline samples with a Decca-Radar-NQR-spectrometer, using Zeeman modulation and side band suppression. The spectrometer was, in general, operated with a time constant of 10 s. The internal marker system, used for the determination of the resonance frequencies, was checked by frequent comparisons with a Rhode & Schwarz WIK BN 4421 frequency meter and a Rhode & Schwarz FEG 3 frequency counter. Additionally, the marker unit was

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proved to be correct by giving the literature values for the ^{35}Cl-NQR frequency of α-paradichlorobenzene as described earlier.[7] The measured NQR frequencies are considered to be accurate to at least ± 0.005 MHz.

Temperature Measurements. The sample temperature was achieved either by thermostating the sample holder with a Lauda Kryostat TUK 30D (temperature range $245 < T/\mathrm{K} < 350$) or by immersing the sample holder into different slush baths[8] (for $T < 245$ K) or into liquid nitrogen ($T = 77$ K).

The temperature measurement units, each consisting of an iron-constantan thermocouple and a Metrawatt Symmetra D millivoltmeter, were calibrated in the temperature range $280 \leq T/\mathrm{K} \leq 310$ (that is, within the vicinity of the transition points) with a standardized mercury thermometer with 0.1° graduation before and after use. The calibration of the thermocouple was done as well at the liquid nitrogen boiling point. During the NQR measurements the thermocouple was placed inside the sample holder very close to the sample tube. It was checked in separate runs that the temperature measured with this thermocouple and at this position, within the reading accuracy (0.1 K) of the instrument, was identical with the temperature inside the sample measured with the second thermocouple under the conditions of the NQR experiments. This condition was fulfilled, at least in the temperature range $280 \leq T/\mathrm{K} \leq 310$. At $T = 77$ K, the difference between both thermocouples in their respective positions was not larger than 0.5 K, which is rather unimportant for the NQR measurements on the anilinium bromides investigated here, since the temperature coefficient of the ^{79}Br-NQR frequency drops down to $|\Delta\nu/\Delta T| \leq 1$ kHz K^{-1} at 77 K. The temperature measurements are therefore considered to be accurate to ± 0.1 K at $280 \leq T/\mathrm{K} \leq 310$, and to ± 0.5 K, or better, outside this range.

Results

Two NQR signals have been observed for anilinium bromide in the frequency range $7 \leq \nu/\mathrm{MHz} \leq 30$ at $T = 273$ K (modification **II**) and at $T = 303$ K (modification **I**) as well. Both resonances have been ascribed to the Br$^\ominus$ ion as the frequency ratio is identical with the ratio of the quadrupole moments of the bromine isotopes $Q(^{79}\mathrm{Br})/Q(^{81}\mathrm{Br}) = 1.1970$. This NQR spectrum gives evidence that there is only one bromide ion in the asymmetric unit of the crystallographical unit cell, in accordance with the results of the X-ray work.[1,3] In Table 1 the ^{79}Br-NQR frequencies of the investigated anilinium bromide samples are listed for $T = 77$ K, for a second temperature just below, and for a third just above the respective transition temperatures of the different species. Well defined NQR signals have been observed in both the low temperature modification **II** and the high temperature modification **I**. No change in the line shapes could be seen in passing through the

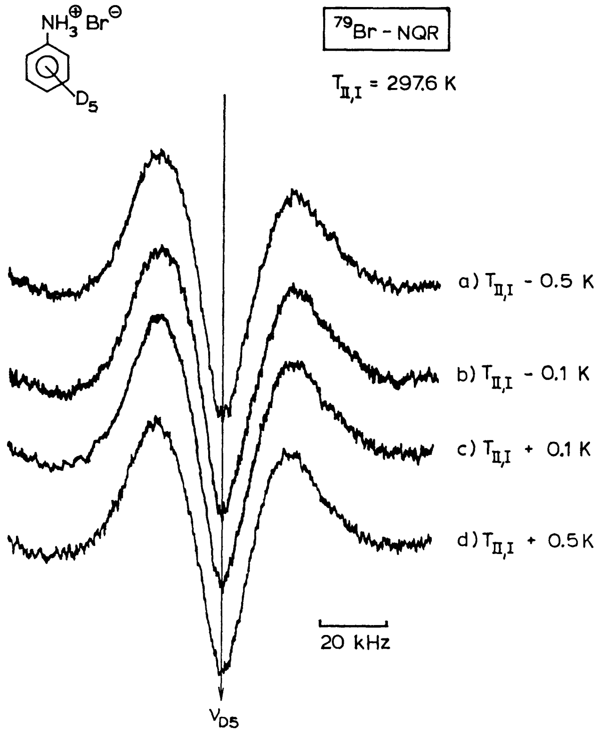

Fig. 1. ^{79}Br-NQR signal of anilinium-d_5 bromide in passing the phase transition point. The signals at four different temperatures near $T_{\mathrm{II,I}}$ are shifted relative to each other in such a way that the center of the signals, ν_{D5}, falls together. The experimental (unshifted) results are: a) $T = 297.1$ K: $\nu_{\mathrm{D5}} = 16.458$ MHz; b) $T = 297.5$ K: $\nu_{\mathrm{D5}} = 16.447$ MHz; c) $T = 297.7$ K: $\nu_{\mathrm{D5}} = 16.443$ MHz; d) $T = 298.1$ K: $\nu_{\mathrm{D5}} = 16.441$ MHz.

Table 1. ^{79}Br-NQR frequencies of anilinium bromides[a)]

Sample	Symbol	Modification II							Modification I			
		$T = 77$K			$T < T_{\mathrm{II,I}}$				$T > T_{\mathrm{I,II}}$			
		ν_{exp}/MHz	S/N	$\Delta\nu_{1/2}$/kHz	T/K	ν_{exp}/MHz	S/N	$\Delta\nu_{1/2}$/kHz	T/K	ν_{exp}/MHz	S/N	$\Delta\nu_{1/2}$/kHz
$C_6H_5NH_3^\oplus Br^\ominus$	ν_{H}	17.780	16	19	294.2	16.557	24	15	298.7	16.471	27	13
$C_6H_5ND_3^\oplus Br^\ominus$	ν_{D3}	17.390	5	17	290.4	16.118	22	17	298.7	16.055	24	16
$C_6D_5NH_3^\oplus Br^\ominus$	ν_{D5}	17.688	20	17	294.2	16.538	22	15	298.8	16.437	22	15
$C_6H_5NH_3^\oplus Br^\ominus / C_6D_5NH_3^\oplus Br^\ominus$ [b)]	ν_{H}	17.780	6.5	17	294.2	16.561	(5.5)	(13)	298.7	16.473	9	14
	ν_{D5}	17.689	6.5	14		16.541	(4)	(9)		16.438	9	13
$(C_6H_5NH_3^\oplus)_{1-x}(C_6D_5NH_3^\oplus)_x Br^\ominus$ [c)] ($x = 0.5$)	ν_{SS}	no ^{79}Br-NQR signal			294.2	16.553	6	18	298.7	16.457	5	19
$C_6H_5NH_{3(1-x)}D_{3x}^\oplus Br^\ominus$ [c)] ($x = 0.5$)	—	no ^{79}Br-NQR signals at $T = 77$ K and at room temperature observed										

a) Estimated error in ν: $< \pm 0.005$ MHz: S/N = signal-to-noise ratio; $\Delta\nu_{1/2}$ = half width. For $T_{\mathrm{II,I}}$ see Table 2.
b) Mechanical mixture. c) Solid solution.

transition point (Fig. 1). Deuteration of the ammonium group has a very pronounced effect on the ^{79}Br-NQR signal of the $Br^{\ominus}$ ion. The frequency is shifted by about 400 kHz or more to lower values for both modifications. In contrast, the shift of the NQR line caused by deuteration of the benzene nucleus is smaller by about an order of magnitude near room temperature, but it is at first sight unexpectedly large (92 kHz) at T=77 K. Again the resonance frequency is lowered. The mechanical mixture of anilinium bromide and anilinium-d_5 bromide exhibits the ^{79}Br-NQR signals of the crystalline components with reduced signal-to-noise ratio. Figure 2 demonstrates the relative frequency shift due to the ring deuteration. In the solid solution $(C_6H_5NH_3^{\oplus})_{1-x}(C_6D_5NH_3^{\oplus})_xBr^{\ominus}$ there is a statistical distribution of fully protonated and ring-deuterated anilinium cations. Therefore the electric field gradient varies statistically at the bromine nucleus. The extreme values of the EFG may be taken to be those of the pure components of the solid solution. For T=294 K and T=299 K the difference between the resonance frequencies of $C_6H_5NH_3^{\oplus}Br^{\ominus}$ and $C_6D_5NH_3^{\oplus}Br^{\ominus}$ is small, some 30 kHz at most. Consequently, one observes a single broadened ^{79}Br-NQR line, for the solid solution with x=0.5 approximately centered in the middle of the lines of the pure components (Figs. 2i and 2ii). At T=77 K the ^{79}Br-NQR signal of the solid solution is spread over ≈90 kHz, and in this case no signal has been found using a conventional superregenerative oscillator (Fig. 2iii). As one may expect from the large separation of the ^{79}Br-NQR signals of $C_6H_5NH_3^{\oplus}Br^{\ominus}$ and $C_6H_5ND_3^{\oplus}Br^{\ominus}$, no signal could be found for the solid solution of the anilinium bromide and anilinium-d_3 bromide, $C_6H_5NH_{3(1-x)}D_{3x}^{\oplus}Br^{\ominus}$ (x=0.5). In addition to the ^{1}H-NMR analysis, this result proves that the degree of deuteration of the anilinium-d_3 bromide sample is fairly high.

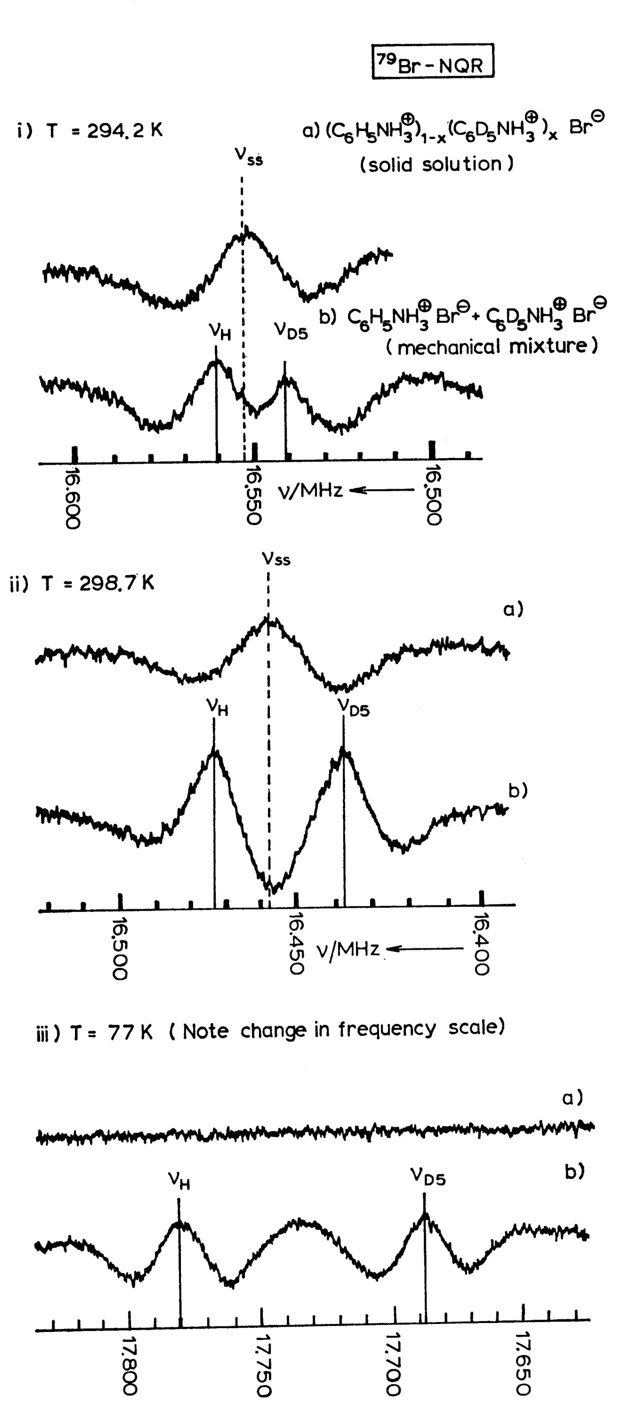

Fig. 2. ^{79}Br-NQR signals of a) the solid solution of anilinium bromide and anilinium-d_3 bromide (x=0.5) and of b) the mechanical mixture of an equal amount of the pure components: i) at a temperature just below the resp. $T_{II,I}$, ii) at a temperature just above the resp. $T_{II,I}$, iii) at T=77 K [frequency scale condensed compared with i) and ii)].

The temperature dependence of the ^{79}Br-NQR frequency of anilinium bromide and its two deuterated derivatives, $C_6H_5ND_3^{\oplus}Br^{\ominus}$ and $C_6D_5NH_3^{\oplus}Br^{\ominus}$, has been investigated in the temperature range $77 \leqq T/K \leqq 350$. (The crystal structure determination[3]) of the high temperature modification was done at T=343 K.) As usual in NQR spectroscopy, the resonance frequency decreases with increasing temperature, but, moreover, the frequency *versus* temperature curves of all three species show the following peculiar behavior. At T= 77 K the absolute value of the temperature coefficient $|\Delta\nu/\Delta T|$ is less than 1 kHz K^{-1}. It increases progres-

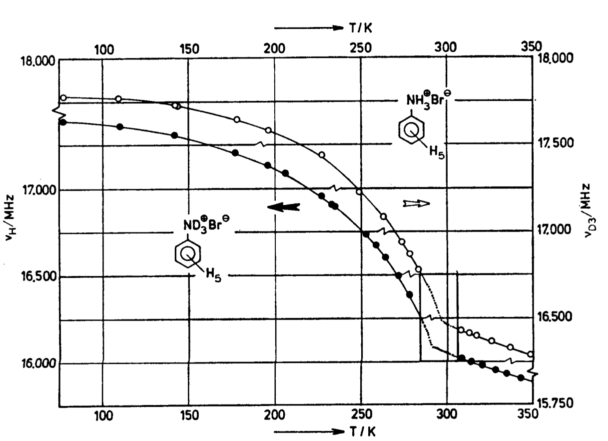

Fig. 3. Temperature dependence of the ^{79}Br-NQR frequencies of anilinium bromide (open circles: ○) and anilinium-d_3 bromide (full circles: ●) in the temperature range $77 \leqq T/K \leqq 350$. The area around the transition point is enlarged in Fig. 4.

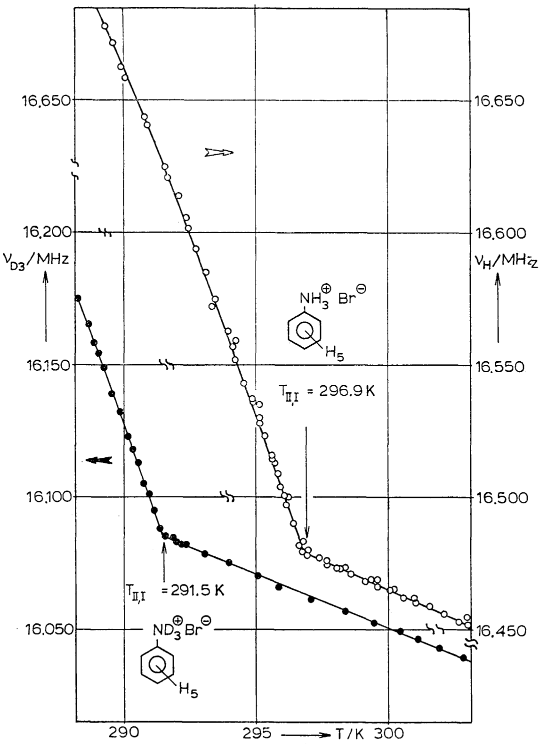

Fig. 4. Temperature dependence of the ^{79}Br-NQR frequencies of anilinium bromide (open circles: ○), and of anilinium-d_3 bromide (full circles: ●) in the close vicinity of the transition points.

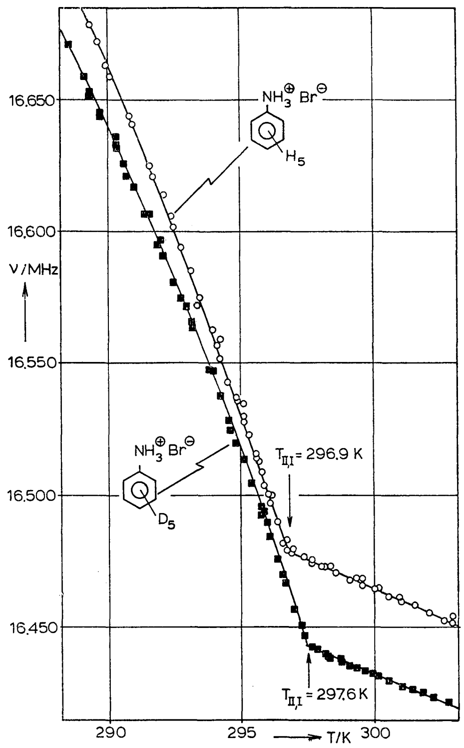

Fig. 5. Temperature dependence of the ^{79}Br-NQR frequencies of anilinium bromide (open circles: ○), and anilinium-d_5 bromide (full squares: ■) in the close in the close vicinity of the transition points.

sively with increasing temperature, reaching a maximum value of $|\Delta\nu/\Delta T| \approx 30$ kHz K^{-1}. At a certain critical temperature, which is considered to be the transition temperature $T_{II,I}$ of the respective species, each frequency *versus* temperature curve changes abruptly in slope. Above this critical temperature $|\Delta\nu/\Delta T|$ has a much lower value, approximately 4 kHz K^{-1}. The temperature dependence of the ^{79}Br-NQR frequencies of $C_6H_5NH_3^{\oplus}Br^{\ominus}$ and $C_6H_5ND_3^{\oplus}Br^{\ominus}$ is graphically displayed in Fig. 3 for the whole temperature range investigated. $\nu(T)$ of the ring-deuterated compound $C_6D_5NH_3^{\oplus}Br^{\ominus}$ has been omitted, since its respective frequencies have only been measured at $T=77$ K and at $247 \leqq T/K \leqq 345$; they would be nearly indistinguishable from those of the fully protonated anilinium bromide in the scale used in Fig. 3. The close similarity of the ν–T-curves is clearly seen. For $T < T_{II,I}$ the curvature is quite similar to that of the monoclinic angle β *versus* temperature in the special case of anilinium bromide.[1] More generally, $\nu(^{79}Br) = f(T)$ resembles a function "order parameter$=f(T)$" near the critical temperature. Figures 4 and 5 show sections of the $\nu(T)$-graphs in close vicinity of the transition points of the three species. Regarding the frequency scale and the strongly expanded temperature scale, the scatter of the points on these curves is rather small. For anilinium bromide and anilinium-d_5 bromide, the $\nu(^{79}Br) = f(T)$ data were collected from at least two different samples of each compound in several $\nu = f(T)$ runs. $C_6H_5ND_3^{\oplus}Br^{\ominus}$ has been studied in only one sample in a single temperature run.

In addition to the large frequency shift due to the ammonium deuteration, also the transition tempera-

TABLE 2. TEMPERATURE DEPENDENCE OF ^{79}Br-NQR FREQUENCIES OF ANILINIUM BROMIDE, ANILINIUM-d_3 BROMIDE, AND ANILINIUM-d_5 BROMIDE IN THE VICINITY OF THE TRANSITION TEMPERATURES $T_{II,I}$: $\nu_{calcd}\,(^{79}Br) \pm \sigma = a_0 + a_1T + a_2T^2$

Compound	σ/MHz	a_0/MHz	10^2a_1/MHz K^{-1}	10^5a_2/MHz K^{-2}	Z[a]	Temperature range	$T_{II,I}$/K[b]
$C_6H_5NH_3^{\oplus}Br^{\ominus}$	0.0023	−26.6195	+32.0881	−59.1864	40	$288 \leqq T/K \leqq 296.5$	296.9±0.1
	0.0009	+18.6045	−1.0152	+1.0073	27	$297.5 \leqq T/K \leqq 348.5$	
$C_6H_5ND_3^{\oplus}Br^{\ominus}$	0.0008	−32.7306	+36.5000	−67.7667	19	$286 \leqq T/K \leqq 291$	291.5±0.1
	0.0007	+18.2308	−1.0578	+1.1031	21	$292 \leqq T/K \leqq 343$	
$C_6D_5NH_3^{\oplus}Br^{\ominus}$ [c]	0.0015	−28.2405	+33.0538	−60.6156	46	$288.5 \leqq T/K \leqq 297.5$	297.6±0.1
	0.0006	+18.4613	−0.9737	+0.9920	35	$298 \leqq T/K \leqq 345$	

a) σ=standard deviation; Z=Number of experimental points in the least-squares fit. b) Determined as intersection of the respective polynomials in the temperature range $290 \leqq T/K \leqq 300$K. c) For $246.5 \leqq T/K \leqq 297.5$: $\nu_{D5} = -265.1364 + 428.9561 \cdot 10^{-2}T - 2441.3889 \cdot 10^{-5}T^2 + 618.3218 \cdot 10^{-7}T^3 - 589.6038 \cdot 10^{-10}T^4$, where ν is in MHz and T in K. σ=0.0016 MHz; Z=76.

ture $T_{\mathrm{II,I}}$ is affected strongly by the isotopic exchange in being lowered by as much as 5.4 K (see Fig. 4). However, the critical temperature of $C_6D_5NH_3^\oplus Br^\ominus$ is only slightly elevated (by 0.7 K) as compared with that of $C_6H_5NH_3^\oplus Br^\ominus$ (see Fig. 5). The transition temperatures $T_{\mathrm{II,I}}$ of the three anilinium species have been determined as the intersection of the respective ν-T-curves of the ^{79}Br-resonances. For this reason, the function $\nu(^{79}\mathrm{Br})=f(T)$ have been described in a polynomial form for both modifications **I** and **II** of the three species. Table 2 gives the coefficients a_i of the polynomials

$$\nu = \sum a_i \cdot T^i \qquad (1)$$

for each of the three anilinium bromide species. Three coefficients (parabolic approximation: a_0, a_1, a_2) were found to describe $\nu(T)$ reasonably well in the given temperature range. Additionally, the standard deviation σ, the number of experimental points used in the least squares fit and the transition temperatures determined are listed. It was not possible to describe the ^{79}Br-NQR frequencies of the low temperature modification **II** analytically for the whole temperature range from 77 K to $T_{\mathrm{II,I}}$ by either a simple Bayer-type function[9]

$$\nu = a - \frac{b}{e^{c/T}-1} \qquad (2)$$

or in a polynomial form with a reasonable number of parameters.

Discussion

In the first section we discuss the significance of the value of the ^{79}Br-NQR frequency of anilinium bromide with regard to the question of hydrogen bonding in this compound. In the second part this question will be dealt with in the light of the hydrogen-deuterium isotope effect. Then the state of order of the high temperature modification is discussed and the fourth section treats the temperature dependence of the ^{79}Br-NQR frequencies and its relation to the order parameter of the low temperature modification.

The Origin of the Finite Electric Field Gradient at the Site of the Ion $Br^\ominus$ *in* $C_6H_5NH_3^\oplus Br^\ominus$. The detection of a Br-NQR signal in anilinium bromide is interesting in itself. The charge distribution of a free bromide ion is spherically symmetric, therefore, the electric field gradient (EFG) vanishes, whereby e^2qQ/h and ν are zero. A non-zero EFG at the site of the bromine nucleus in $Br^\ominus$ can be created by its incorporation into a crystal lattice at a site with non-cubic point symmetry, it is considered to be small in purely ionic crystals. Additional interactions such as covalent bonding and hydrogen bonding may enlarge the EFG and thereby the resonance frequency.

The question arises, whether the rather high value of the ^{79}Br-NQR frequency in anilinium bromide is in itself a proof for $N{-}H^\oplus\cdots Br^\ominus$ hydrogen bonding in this solid. For comparison we shall discuss briefly the ^{79}Br-frequencies of other bromides (Table 3). Having $Na^\oplus$ ions as next nearest neighbors of $Br^\ominus$ substitutionally incorporated into KBr, Andersson[10] found for $^{79}Br^\ominus$ $e^2qQ/h=14.03$ MHz. This shows that $\nu(^{79}\mathrm{Br})$-values of up to 7 MHz can be caused by a non-cubic point symmetry. Larger ^{79}Br-NQR frequencies are found for $BaBr_2$, $PbBr_2$, and $PBr_4^\oplus Br^\ominus$, compounds in which some interatomic distances metal-to-bromine and bromine-to-bromine, respectively, are smaller than the commonly accepted ionic radii sum.[11,12] Interpreting this as a sign for a small covalent bond character the high $^{79}Br^\ominus$-NQR frequencies of these three compounds are understandable.

In the tetragonal phase NH_4Br(**III**), where hydrogen bonding is undoubtedly present, the ^{79}Br quadrupole coupling constant does not exceed 6 MHz[13] because the hydrogen bonds are arranged in a nearly regular tetrahedron around $Br^\ominus$ resulting in a charge distribution which is close to spherosymmetry. This is lost if one or more of the hydrogens in the $NH_4^\oplus$ group are substituted by alkyl groups. For seven alkylammonium bromides Frausto da Silva and Vilas Boas[14] found ^{79}Br-NQR signals in the frequency range of $12<\nu/\mathrm{MHz}<19$ at $T=306$ K. They claim that the distortion of the symmetry of the electron cloud of the halide ions "is so pronounced that it cannot be originated only by second order lattice effects in a 100% ionic structure" but by the formation of $N{-}H^\oplus\cdots X^\ominus$ hydrogen bonds. These bonds had been postulated before from X-ray and IR studies.[15] Hydrogen bonding has been proposed to be present in anilinium bromide as well.[1-4] The rather high ^{79}Br-NQR frequency of anilinium bromide

TABLE 3. ^{79}Br NUCLEAR QUADRUPOLE COUPLING DATA OF BROMIDE IONS $Br^\ominus$ IN DIFFERENT INORGANIC AND ORGANIC SOLIDS

Compound	Method[a]	T/K	$\nu(^{79}\mathrm{Br})$/MHz	Remarks	Reference
$C_6H_5NH_3^\oplus Br^\ominus$	PQR	77	17.780	Modification **II**	This work
$K_{1-x}Na_xBr$ ($x\ll 1$)	NMR	RT	7.015	$Na^\oplus$ in shell {1,0,0}	10
$BaBr_2$	PQR	77	26.01	—	29
			14.59		
$PbBr_2$	PQR	77	33.305	Orthorhombic modification	36, 37
			24.741		
$PBr_4^\oplus Br^\ominus$	PQR	77	22.25[b]	Assigned to $Br^\ominus$	38
$NH_4^\oplus Br^\ominus$	NMR	$\approx$80	2.83	Tetragonal modification	13
		$\approx$230	$\approx$0.5		
$CH_3NH_3^\oplus Br^\ominus$	PQR	306	12.88	—	14

a) NMR=quadrupole splitting of wide line Br-NMR; PQR=pure Br-NQR.

b) Four NQR frequencies near 240 MHz are ascribed to the ^{79}Br in $PBr_4^\oplus$[38,39].

TABLE 4. HYDROGEN-DEUTERIUM ISOTOPE EFFECT ON THE ^{35}Cl, ^{79}Br, AND ^{127}I-NQR FREQUENCIES OF SIMPLE AND COMPLEX HALIDES[a)]

Compound	Nucleus	T/K	ν_H/MHz	$\frac{\nu_H-\nu_D}{\text{kHz}}$	$10^2\frac{\nu_H-\nu_D}{\nu_H}$	Comments	Reference
Anilinium bromide	^{79}Br	77	17.780	+390	+2.19	$T<T_{II,I}$	This work
$C_6H_5NH_3^{\oplus}Br^{\ominus}$		289.8	16.664	+533	+3.20		
$C_6H_5ND_3^{\oplus}Br_{\ominus}$		298.7	16.471	+416	+2.53	$T>T_{II,I}$	
Anilinium bromide	^{79}Br	77	17.780	+92	+0.52	$T<T_{II,I}$	This work
$C_6H_5NH_3^{\oplus}Br^{\ominus}$		294.2	16.557	+19	+0.11		
$C_6D_5NH_3^{\oplus}Br^{\ominus}$		298.7	16.471	+34	+0.21	$T>T_{II,I}$	
3-Chloroanilinium iodide	^{127}I	77	24.359	+817	+3.35	$\nu(5/2\rightleftharpoons3/2)$ $I^{\ominus}$	6a
3-Cl$C_6H_4NH_3^{\oplus}I^{\ominus}$			24.620	+598	+2.43	$\nu(3/2\rightleftharpoons1/2)$	
3-Cl$C_6H_4ND_3^{\oplus}I^{\ominus}$		298	26.544	+832	+3.13	$\nu(5/2\rightleftharpoons3/2)$	
			24.934	+728	+2.92	$\nu(3/2\rightleftharpoons2/2)$	
	^{35}Cl	77	34.995	−11	−0.03	Cl at benzene ring	
		298	34.738	−10	−0.03		
Guanidinium iodide	^{127}I	300	27.235	+449	+1.65	$\nu(5/2\rightleftharpoons3/2)$ site A; $\eta_A=0$	6b
$[C(NH_2)_3]^{\oplus}I^{\ominus}$			13.614	+221	+1.63	$\nu(3/2\rightleftharpoons1/2)$	
$[C(ND_2)_3]^{\oplus}I^{\ominus}$			25.018	+499	+1.99	$\nu(5/2\rightleftharpoons3/2)$ site B; $\eta_B=0$	
			12.510	+251	+2.01	$\nu(3/2\rightleftharpoons1/2)$	
4-Chloropyridinium hexa-chlorostannate(IV)	^{35}Cl	298	17.521	+8	+0.05	Cl in $SnCl_6^{2\ominus}$	This work
$(4\text{-ClC}_5H_4NH^{\oplus})_2SnCl_6^{2\ominus}$			17.322	+11	+0.06		
$(4\text{-ClC}_5H_4ND^{\oplus})_2SnCl_6^{2\ominus}$			14.982	−35	−0.23		
			35.928	−4	−0.01	Cl at pyridine ring	
Tris(sarcosine)calcium chloride	^{35}Cl	292	2.160	+40	+1.85	paraelectric phase: "N–H···Cl$^{\ominus}$"-bonding	22
$(CH_3N^{\oplus}H\cdots CH_2COO^{\ominus})_3\cdot CaCl_2$							
$(CH_3N^{\oplus}D\cdots CH_2COO^{\ominus})_3\cdot CaCl_2$							
Barium dibromide dihydrate	^{79}Br	77	4.57	−40	−0.88	—	29
$BaBr_2\cdot 2H_2O$							
$BaBr_2\cdot 2D_2O$							
Sodium tetrachloro-	^{35}Cl	273	28.83±1	0	0		
aurate(III) dihydrate $NaAuCl_4\cdot 2H_2O$			28.44±1	≈+10 ±10	(≈+0.04 ±0.04)		
$NaAuCl_4\cdot 2D_2O$			27.46±1	0	0		30
			25.67±1	≈+30 ±10	≈+0.12 ±0.04	"O–H···Cl–Au"-bonding	
2,2-Dichloropropane	^{35}Cl	77	34.883	+23	+0.07	No H-bonding	40
$CH_3CCl_2CH_3$							
$CD_3CCl_2CD_3$							

a) The subscripts H and D mark the value for the protonated and the deuterated form respectively. The error in ν is ±0.005 MHz or less for the first five compounds. The error in $\nu_H-\nu_D$ is ±0.002 MHz or less for the ^{35}Cl-NQR frequencies of 3-chloroanilinium iodide and 4-chloropyridinium hexachlorostannate(IV) and for the ^{79}Br-NQR frequencies of anilinium bromide/anilinium-d_5 bromide around room temperature (see Fig. 2).

found (17.780 MHz at $T=77$ K) supports the assumption of a hydrogen-bridged bromide ion. However, the frequency value alone may not be sufficient as a reliable proof of N–H$^{\oplus}$···Br$^{\ominus}$ hydrogen bonding.

^{1}H–^{2}D Isotope Effect. The substitution of D for H in the ammonium group of anilinium bromide was undertaken to gain some more definite NQR evidence about the hydrogen bridge N–H$^{\oplus}$···Br$^{\ominus}$ in this compound. In case there is no hydrogen bonding N–H$^{\oplus}$···Br$^{\ominus}$, the ion Br$^{\ominus}$ is isolated and therefore not affected by this isotopic exchange in the first approximation. If at all, only a slight shift of the resonance frequency to higher values is expected because of the reduced torsional amplitudes of the N–D modes.

In case of a hydrogen bond N–H$^{\oplus}$···Br$^{\ominus}$, the effect of deuteration can be followed along the lines given by Coulson[16)] for the isotope effect on an asymmetric O–H···O bond. In a normal isolated O–H bond, replacement of hydrogen by deuterium leads to a small shortening of the interatomic distance due to the anharmonicity of the O–H vibration. In an O–H···O hydrogen bonding system a decrease of the distance r_{O-H} causes an increase of the distance R_{O-O}[17,18,19a)]. Therefore, if $r_{O-D}<r_{O-H}$, as in the isolated bond, the O–O distance is enlarged by deuteration, $(R_{O-O})_D>(R_{O-O})_H$ (the subscripts H and D stand for the hydrogen and deuterium bond respectively). This indeed has been found experimentally for short and intermediate asymmetric O–H···O hydrogen bonds (Ubbelohde effect)[20,18b,21)]. By analogy, for the bond N–H$^{\oplus}$···Br$^{\ominus}$ in anilinium bromide, $r_{N-D} < r_{N-H}$ and $(R_{N-Br})_D > (R_{N-Br})_H$ is expected. Deuteration moves the bromide ion farther away from the nitrogen and the hydrogen atoms and $Br^{\ominus}$ approaches somewhat more the state of an isolated, non-hydrogen bonded ion. The ^{79}Br-NQR frequency should decrease upon deuteration and the frequency shift should be positive:

$$\Delta\nu_{H-D} = \nu_H(^{79}Br) - \nu_D(^{79}Br) > 0. \qquad (3)$$

This has been found here for the anilinium bromides $C_6H_5NH_3{}^{\oplus}Br^{\ominus}$ and $C_6H_5ND_3{}^{\oplus}Br^{\ominus}$ (Tables 1 and 4). Also the magnitude of the H–D isotope effect support the assumption of hydrogen bonding in anilinium bromide. For $X^{\ominus} = I^{\ominus}$, $Cl^{\ominus}$, an analogous ^{1}H–^{2}D effect on the halogen NQR frequencies of the halide ions has been found in 3-chloroanilinium iodide,[6a] guanidinium iodide,[6b] and tris(sarcosine)calcium chloride[22] as well. Table 4 shows that the NQR frequency shifts due to deuteration, $\Delta\nu_{H-D}$, range from $+1.5\%$ to $+3.5\%$.

The ability of complex ions like $SnCl_6{}^{2-}$ to form hydrogen bonds is strongly reduced compared with that of $X^{\ominus} = Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$. This is seen on the infrared spectra of the corresponding guanidinium salts,[23] pyrimidinium salts,[24,25] and pyridinium salts.[26] Hydrogen bonding in 4-chloropyridinium hexachlorostannate(IV) is proposed in ^{35}Cl-NQR and X-ray work[27,28] and should be rather weak. Deuteration, therefore, has only a small influence on the ^{35}Cl frequencies of the complex ion. A frequency shift toward a more isolated $SnCl_6{}^{2-}$ ion is expected. Accordingly, the lowest ^{35}Cl-NQR signal attributed to the hydrogen-bonded-chlorines should move to higher frequencies and the two other signals to lower frequencies. This view is supported by experimental results.

Examples for deuteration shifts presumably caused by other effects than hydrogen bonding are also found in Table 4: the isotope effects on the NQR frequencies of the meta-Cl in 3-chloroanilinium iodide, of the *para*-Cl in 4-chloropyridinium hexachlorostannate(IV), and, as a reference, of the chlorine atoms in 2,2-dichloropropane. All these chlorines show small but definite positive or negative isotopic shifts.

The ^{1}H–^{2}D isotope effect on the ^{79}Br-NQR signal in $BaBr_2 \cdot 2H_2O$[29] and on the ^{35}Cl-NQR signals of $NaAuCl_4 \cdot 2H_2O$[30] does not follow the lines developed above for hydrogen bonded halides. This is not surprising in the case of the barium salt, since its bromine frequency is well within the limits of a purely ionic $Br^{\ominus}$, and the $Br^{\ominus}$ may not be hydrogen bonded at all in $BaBr_2 \cdot 2H_2O$. In $NaAuCl_4 \cdot 2H_2O$ the O–H$\cdots$Cl bond[30–32] is a rather debatable one, the shortest O–Cl distance (3.42 Å[33]) is appreciably longer than the sum of the usually accepted van der Waals radii (3.20 Å[19b]). Here Gallagher's[20] proposal may be followed that deuteration strengthens very weak hydrogen bonds. Fryer and Smith[30] explained in this way the isotopic shift of the lowest ^{35}Cl-NQR signal, but stressed the fact that other solid state effects may also be responsible for the small H–D effect in $NaAuCl_4 \cdot 2H_2O$.

The shift of the ^{79}Br-NQR frequency of the $Br^{\ominus}$ by deuteration of the benzene ring of anilinium bromide remains to be discussed. It is in the order of an effect of lattice dynamics at room temperature and above it, but quite large at liquid nitrogen temperature. The reason for this is not clear to us yet. It might be that this strong shift is due to hindered oscillations of the anilinium ion around its longest axis. Indications of such oscillations have been found by Nitta *et al.*[3] for the high temperature phase and the close similarity of the structures may allow such a behavior in the low temperature phase as well. An investigation of partially deuterated anilinium bromides, as $4\text{-}DC_6H_4NH_3{}^{\oplus}Br^{\ominus}$ and $2,3,5,6\text{-}D_4C_6HNH_3{}^{\oplus}Br^{\ominus}$, could probably be helpful in finding an explanation for this large isotope effect.

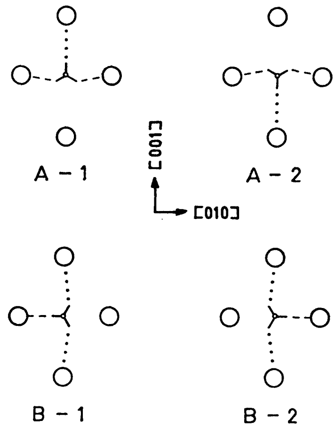

Fig. 6. Energetically favored orientations of the $-NH_3{}^{\oplus}$ group with respect to neighboring bromide ions $Br^{\ominus}$ according to Ref. 3. Short hydrogen bonds ($R_{N-Br} =$ 3.30 Å) are hyphenated, long hydrogen bonds ($R_{N-Br} =$ 3.48 Å) are dotted. ○=Br; ⅄ =NH_3.

State of Order in the High Temperature Modification. The apparent discrepancy between the symmetry of the anilinium ion in the crystal (diagonal axis through N–$C_1 \cdots C_4$) and the symmetry of the $-NH_3{}^{\oplus}$ group (threefold axis) disappears, when the three hydrogen atoms bound to the nitrogen atom "occupy statistical positions by some means."[1,3] There are two limiting cases shown by Taguchi[1] and Nitta *et al.*:[3] a static statistical distribution (model **a**) and a dynamic statistical distribution (model **b**). In both models an orientationl disorder of the $NH_3{}^{\oplus}$ group with respect to the four neighboring bromide ions is assumed. Four orientations of the $NH_3{}^{\oplus}$ group are energetically favored as shown in Fig. 6 (taken from Ref. 3). In the orientations A-1 and A-2 there are two strong and one weak hydrogen bond between the nitrogen atoms and the bromide ions. Both, A-1 and A-2, are equally probable in the high temperature modification, whereas in the monoclinic low temperature phase one of these orientations would be stabilized. Additionally, there may be a further arrangement B characterized by one strong and two weak hydrogen bonds, also with two equally probable orientations B-1 and B-2. "Static statistically distributed" means that the ammonium hydrogens occupy the positions given by A-1 and A-2 (or by A-1, A-2, B-1, and B-2) randomly in space. They remain in these position for a time, long compared to the time scale of the respective technique (here the NQR spectroscopy, that is the residence time is longer than about 10^{-7} s). Model **b** (dynamic statistical distribution) assumes randomness in time, that is a short correlation time (less than 10^{-8} s). The $-NH_3^{\oplus}$ group is "flipping among different orientations"1) or even rotating freely (as incorporated into the X-ray structure factor calculations by Nitta *et al.*3)). Model **a** fulfills the demand of the space group for a twofold symmetry along the principal axis of the anilinium ion by averaging in space, model **b** by averaging in time.

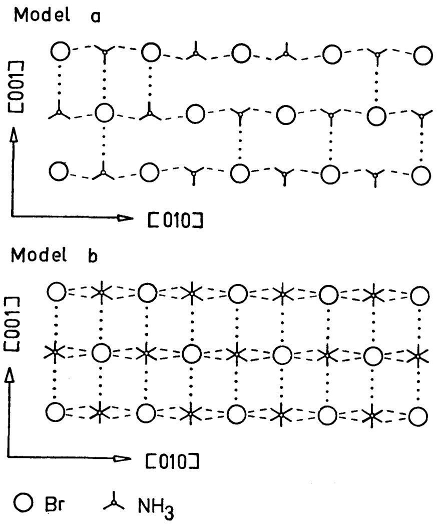

Fig. 7. Schematic representation of a static statistical distribution (random in space: model **a**) and dynamical statistic distribution (random in time: model **b**) of the hydrogen atoms of the $-NH_3^{\oplus}$ group. Only the orientations A-1 and A-2 are considered. Short hydrogen bonds are hyphenated, long hydrogen bonds are dotted. The local symmetry at the bromide ions is different in model **a**, whereas it is identical at each $Br^{\ominus}$ in model **b**.

The surrounding of the bromide ions (all $Br^{\ominus}$ are crystallographically equivalent) is shown in Fig. 7 for model **a**, representing a part of the projection of the structure of $C_6H_5NH_3^{\oplus}Br^{\ominus}$ on the plane (100). Dashed lines symbolize the strong hydrogen bonds ($R_{N-Br}=3.30$ Å) and dotted lines the weak ones ($R_{N-Br}=3.48$ Å). The $-NH_3^{\oplus}$ groups are oriented randomly in space (only the arrangements A-1 and A-2 are considered). This distribution results in different surroundings for the $Br^{\ominus}$ which average in space to the twofold axis of symmetry for the $Br^{\ominus}$ and the ammonium nitrogen, as observed by X-ray diffraction. However, in a microscopic observation such as NQR, which observes mainly the immediate surroundings of an atom, the different arrangements around each $Br^{\ominus}$ cause different electric field gradients at each bromine nucleus due to divergent contributions of the crystal field. A broadening of the ^{79}Br-NQR line, if not separate bromine signals, should be observed, most likely suppressing the signal beyond the noise level in observing with a non-pulse technique. Since a clear, definite ^{79}Br-NQR signal has been found in the high temperature modification of anilinium bromide and since no broadening of the line could be observed within the limits of the superregenerative detection in passing through the transition point (Fig. 1), it is concluded that a static statistical distribution is incompatible with the results of ^{79}Br-NQR spectroscopy. This conclusion is emphasized by the fact that no bromine signal could be found in the solid solution $C_6H_5NH_{3(1-x)}D_{3x}^{\oplus}Br^{\ominus}$ ($x=0.5$), where the hydrogen and deuterium atoms are distributed "static statistically" among the ammonium nitrogens and where the surroundings of the bromide ions are random with regard to the hydrogen isotope.

The second limiting case, dynamic statistical distribution (model **b**), is also represented in Fig. 7. Here an identical surrounding is given for each $Br^{\ominus}$ also in the microscopic picture by averaging in time. This is in accord with a single, unbroadened ^{79}Br-NQR line in the high temperature phase. The dynamic disorder can be produced by i) a free rotation of the $-NH_3^{\oplus}$ group or ii) by a rapid reorientation of this group. Hydrogen bonding between $NH_3^{\oplus}$ and $Br^{\ominus}$ implies that there is no free rotation of the $-NH_3^{\oplus}$ group. X-Ray diffraction (the distance N–Br is shorter than the van der Waals distance3)), infrared spectroscopy (low frequency of the stretching vibration and enlarged line width4)), and ^{79}Br-NQR spectroscopy (high frequency of the NQR signal and large isotope effect $^1H\leftrightarrow{}^2D$, see preceding discussion) all indicate a hydrogen bond between the anilinium nitrogen and the bromide ion. Free rotation is therefore ruled out. The only model for the disorder in the high temperature modification of anilinium bromide compatible with all experimental results is that of a $-NH_3^{\oplus}$ group which reorients rapidly in a multiple well potential with equilibrium positions given by the hydrogen bonding to the bromide ions.

Temperature Dependence and Order Parameter. In most cases the temperature dependence of NQR frequencies is adequately described in its salient features by the Bayer theory:9a) the average internal EFG at the nucleus decreases with increasing temperature because of the increase in the amplitude of the thermal vibrations. This theory describes only the isochorus part of the temperature dependence, $(\partial\nu/\partial T)_V$. It fails in describing $\nu=f(T)$ at constant pressure if the last term in Eq. 4,

$$\left(\frac{\partial\nu}{\partial T}\right)_P=\left(\frac{\partial\nu}{\partial T}\right)_V-\frac{\alpha}{\chi}\left(\frac{\partial\nu}{\partial T}\right)_T \qquad (4)$$

(α=thermal expansion coefficient, χ=compressibility) is not negligible compared with the Bayer term $(\partial\nu/\partial T)_V$. Kushida *et al.*9b) have shown that the volume expansion affects the temperature dependence of the EFG in ionic or nearly ionic crystals appreciably.

For the high temperature modification of anilinium bromide the temperature dependence of the $\nu(^{79}Br)$ is weak. ν decreases with increasing temperature as predicted by the Bayer theory, $\nu(T)$ being practically linear. The order of magnitude found for $(\partial\nu/\partial T)_P$ of $Br^{\ominus}$ in $C_6H_5NH_3^{\oplus}Br^{\ominus}$ (**I**) is expected from a normal increase of the thermal vibrations and a "normal" volume expansion.

The temperature variation of the ^{79}Br-NQR frequency is by far more pronounced in the low temperature modifications, especially in approaching the transition point (Figs. 3—5). In this temperature region (235≦

T/K$\leqq$303), Suga[2] found an anomalous expansion coefficient. Therefore, it is not surprising that in the low temperature modification $\nu(T)$ cannot be described with a Bayer type function (Eq. 2). At least one additional temperature dependent term has to be considered, which takes the anomalous volume expansion into account. The curvature of $\nu(T)$ reminds of the temperature dependence of an order parameter $s(T)$ near T_c (*e.g.* Ref. 34). The continuous character of the phase transition in $C_6H_5NH_3Br$ and the temperature dependence of the monoclinic deformation β strengthens this analogy. Taguchi[1] considers the monoclinic deformation as a shear, which displaces with respect to the Br$^\ominus$ site the nearest neighbors of the bromide ion (the nitrogen and the hydrogen atoms) in the direction of the c-axis. This displacement is proportional to tan $\Delta\beta$, where $\Delta\beta=\beta-90°$, with $\beta=90°$ at $T=T_{\mathrm{II,I}}$. Since $\Delta\beta<2°$ (at $T=163$ K: $\Delta\beta=1°22'$[1]), tan $\Delta\beta\approx\Delta\beta$, and the change of the N–Br distance with the monoclinic deformation is proportional to the square of $\Delta\beta$:

$$\Delta R_{\mathrm{N-Br}} \propto (\Delta\beta)^2. \qquad (5)$$

The same proportionality holds for the $\Delta R_{\mathrm{H\cdots Br}}$. The maximum component of the electric field gradient, eq, depends on r^{-3}. Assuming that the change in eq is mainly caused by the change in the distance of the nearest neighbors to the ion Br$^\ominus$, one can show that e^2qQ/h of Br$^\ominus$ in the monoclinic phase depends on $(\Delta\beta)^2$. Neglecting the change in the asymmetry parameter, which for $I=3/2$ affects the resonance frequency only weakly, one finds

$$\Delta\nu(^{79}\mathrm{Br}) \propto (\Delta\beta)^2 \qquad (6)$$

in the region just below the transition point, where the monoclinic deformation governs the structural changes with temperature. Figure 8 shows that the expected proportionality (Eq. 6) is well fulfilled in the temperature range 288 K$<T<T_{\mathrm{II,I}}$. It is not expected that Eq. 6 holds outside a small temperature range just below the transition point.

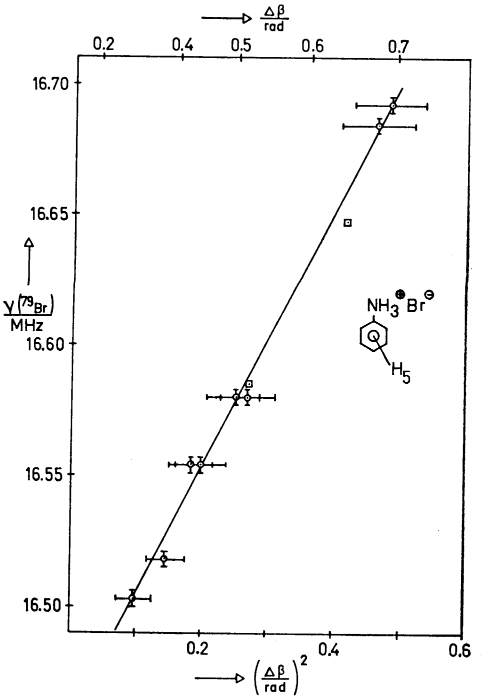

Fig. 8. ^{79}Br-NQR frequency of the low temperature modification of anilinium bromide as a function of $(\Delta\beta)^2=(\beta-90°)^2$. β=monoclinic angle of the low temperature modification **II**. Circles (⊙): the value of $\Delta\beta$ including the limits of error as taken from Fig. 3 in Ref. 1. Squares (▣): $\Delta\beta$ as taken from Fig. 2 in Ref. 1, no limits of error are given in this case.

Suga[2] showed that an order-disorder theory analogous to that of Bragg and Williams describes fairly well main features of the phase transition of anilinium bromide such as transition entropy, anomalous thermal expansion, and the function $\Delta\beta=f(T)$. According to Suga, $\Delta\beta$ is proportional to the order parameter s.

$$\Delta\beta \propto s \qquad (7)$$

It has been shown that the order parameter s is described by a power law

$$s \propto \varepsilon^n \qquad (8)$$

($\varepsilon=(T_c-T)/T_c$; T_c=critical temperature, n=critical exponent). Far from T_C the critical exponent is 1/2 (Landau theory), while it changes (*e.g.* for perovskite-type crystals) down to 1/3 for $\varepsilon<0.1$ in analogy with magnetic and fluid systems[34,35]. Combining the proportionalities (6), (7), and (8), it follows

$$\Delta\nu(^{79}\mathrm{Br}) \propto \varepsilon^{2n}, \qquad (9)$$

and close to the transition point, assuming $n=1/3$,

$$\Delta\nu(^{79}\mathrm{Br}) \propto (T_c-T)^{2/3}. \qquad (10)$$

Although the once-hoped-for universality of the values for the critical exponent n had to be abandoned,[34] it is rather satisfying that the ^{79}Br-NQR frequency in $C_6H_5NH_3^\oplus Br^\ominus$ follows this proportionality (Eq. 10) in the temperature range 295$\leqq T$/K$\leqq$260 with T_C=

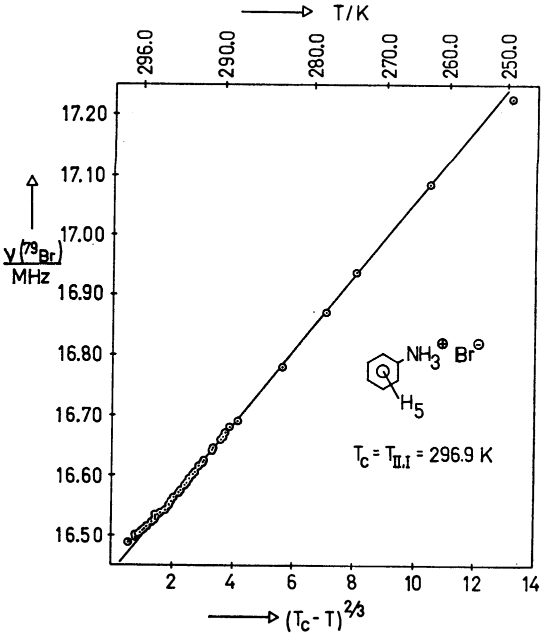

Fig. 9. ^{79}Br-NQR frequency of the low temperature modification of anilinium bromide as a function of the deviation of the temperature from the critical temperature T_c. The power of (T_c-T) indicates a non-classical critical exponent of $n=1/3$ (see text).

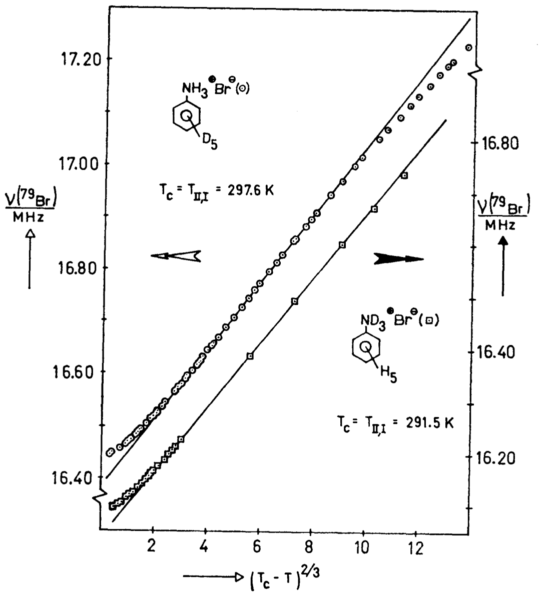

Fig. 10. ^{79}Br-NQR frequencies of the low temperature modification of anilinium-d_3 bromide and anilinium-d_5 bromide as a function of $(T_c - T)^{2/3}$. The power of $(T_c - T)$ indicates a non-classical critical exponent of $n = 1/3$ (see text).

$T_{II,I} = 296.9$ K (Fig. 9). In this region the formation of the ordered monoclinic low temperature phase, expressed by the structural displacement parameter $\Delta\beta$ acting as an order parameter, governs the temperature dependence of the ^{79}Br-NQR frequency. There may be a second region, $225 < T/\mathrm{K} < 260$, where $\nu(^{79}Br)$ is proportional to $(T_c - T)$, that is, $n = 1/2$, but the experimental data are too scarce to be definite in this case. Relation 10 holds also for both deuterated anilinium bromides, $C_6H_5ND_3^{\oplus}Br^{\ominus}$ and $C_6D_5NH_3^{\oplus}Br^{\ominus}$ within a range of some 30 K below $T_{II,I}$ (Fig. 10).

From this it is clear that a simple Bayer-type function (Eq. 2) or a polynomial with a small number of coefficients a_i (Eq. 1) must fail in the description of $\nu(T)$ of anilinium bromide **II**. The temperature dependence of the resonance frequency is in this case a superposition of at least three effects: i) the normal volume independent temperature dependency caused by the increase of the amplitudes of thermal vibrations with increasing temperature (Bayer-term), ii) a strong volume dependent term (second term in Eq. 4), which comes into play through the anomalous thermal expansion below $T_{II,I}$, and iii) a strong variation of the asymmetry parameter η with temperatures just below $T_{II,I}$ not allowing to disregard the η-dependency of the resonance frequency. Such a strong variation of η with temperature has been observed in the (probably isotypic) anilinium iodide below its critical temperature ($T_{II,I} = 241$ K).[6a)] The description of contribution ii) is additionally complicated by the fact that a change from a Landau-type behavior (critical exponent $n = 1/2$) to a non-classical behavior ($n \neq 1/2$) may occur for $\varepsilon = (T_c - T)/T_c < 0.1$.

Résumé

The investigation of the ^{79}Br-NQR spectra of anilinium bromide and its partially deuterated derivatives has lead to the following conclusions:

1. The rather large ^{79}Br-NQR frequency of the $Br^{\ominus}$ ion can be explained by assuming $N\text{–}H^{\oplus}\cdots Br^{\ominus}$ hydrogen bonds and, vice versa, $\nu(^{79}Br)$ of this order of magnitude can serve as an argument for hydrogen bonding in the respective solid.
2. The large frequency shift on deuteration corroborates the model of a hydrogen bonded ion $Br^{\ominus}$. The direction of the $^1H\text{–}^2D$ shift can be explained by assuming that deuteration enlarges the hydrogen bond length in asymmetric hydrogen bonds (Ubbelohde effect).
3. The high temperature modification of anilinium bromide can be described by a model which considers a rapid (faster than $\approx 10^{-8}$ s) reorientating $NH_3^{\oplus}$ group.
4. The strong temperature dependence of the ^{79}Br-NQR frequency found immediately below the transition point can be rationalized by a model which interprets a structural displacement parameter (in this case: $\Delta\beta$) as an order parameter. The non-classical critical exponent is 1/3 in this region for the temperature dependence of the order parameter.

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