Temperature Dependences of NQR Frequencies and Nuclear Quadrupole Relaxation Times of Chlorine in 2,6-Lutidinium Hexachlorotellurate(IV) as Studied by Pulsed NQR Techniques *

Keizo Horiuchi

Department of Chemistry, Division of General Education, University of the Ryukyus, Nishihara, Okinawa 903-01, Japan

Takashige Shimizu, Hitomi Iwafune, Tetsuo Asaji, and Daiyu Nakamura

Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464-01, Japan

Z. Naturforsch. **45a**, 485–489 (1990); received August 25, 1989

The temperature dependences of the ^{35}Cl NQR frequencies ν_Q and the nuclear quadrupole spin-lattice relaxation times T_{1Q} in 2,6-lutidinium hexachlorotellurate(IV) was observed at various temperatures between 80 and 343 K. This crystal undergoes a phase transition at $T_c = 229$ K. A single and three pairs of ^{35}Cl NQR frequencies were observed above and below T_c, respectively. The hysteresis of the phase transition and a discontinuity in the temperature dependence of the resonance frequencies at T_c indicate that this phase transition is of first order. Although the resonance frequencies of the pairs in the low temperature phase are very close to one another, T_{1Q} and ν_Q below T_c could be accurately determined by measuring the Fourier transform spectra of each line. Above ca. 250 K, T_{1Q} showed an exponential decrease which is attributable to the overall reorientational motion of $[TeCl_6]^{2-}$ with an activation energy of 82 kJ mol^{-1}.

Introduction

We have studied the ionic dynamics of molecular ions and structural phase transitions in pyridinium hexachlorometallates(IV) by chlorine NQR and ^{1}H NMR experiments [1–3]. In these complexes, nuclear relaxations of chlorine and hydrogen resulting from the fluctuation of the electric and magnetic interactions due to the motions of cations and anions were investigated by observing the ^{35}Cl nuclear quadrupole spin-lattice relaxation time T_{1Q} and ^{1}H spin-lattice relaxation time T_1. To study these phenomena when hydrogens in the pyridinium ions are substituted by methyl groups, in the present paper the ^{35}Cl NQR technique was applied on 2,6-lutidinium hexachlorotellurate(IV) $[(2,6\text{-lutH})_2TeCl_6]$.

In previous work we have used a pulsed Fourier transform (FT) NQR spectrometer [4–7], this having a higher resolution than the usual superregenerative spectrometer, thus allowing for the observation of the subtle changes of line shapes and line splittings often occurring at phase transitions. Moreover, the frequencies of signals which are closely spaced can be better determined with this spectrometer.

Experimental

The sample was synthesized by dissolving 2,6-lutidine and tellurium(IV) oxide in conc. hydrochloric acid with molar ratio 2:1 and identified by observing the ^{35}Cl NQR frequency at 298 K, which agreed well with the reported one [8].

The temperature of the specimen was controlled within ± 0.5 K, and determined with an accuracy of ± 1 K. Besides the homemade FT-NQR spectrometer [4], a modified Dean-type superregenerative spectrometer was used to observe NQR spectra at room temperature. DTA measurements were done with a homemade apparatus [9].

T_{1Q} above T_c was measured by the 180°-τ-90° pulse sequence. T_{1Q} and ν_Q below T_c were determined by measuring FT-NQR spectra calculated from free induction decay (FID) signals. The 90°-τ-90° pulse sequence was used to measure T_{1Q} by observing the FT

Reprint requests to Prof. D. Nakamura, Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464-01, Japan.

* Presented at the Xth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Takayama, Japan, August 22–26, 1989.

0932-0784 / 90 / 0300-0485 $ 01.30/0. – Please order a reprint rather than making your own copy.

power spectrum which needs no phase corrections. Practically speaking, T_{1Q} was determined by plotting $(F_\infty - F_\tau)/F_\infty$ vs. τ, where F_∞ and F_τ are the peak-heights of the FT spectrum obtained from FID signals after a 90° pulse and the 90°-τ-90° pulse sequence, respectively.

Results

DTA Measurements

DTA curves were recorded in the range 140–430 K. A sharp peak was observed at 228 K with decreasing temperature and at 229 K with increasing temperature. We call the high and low temperature phases HTP and LTP, respectively.

^{35}Cl NQR Frequencies

The temperature dependence of the ^{35}Cl NQR frequencies in $(2,6\text{-lutH})_2TeCl_6$ is shown in Figure 1. Resonance frequencies observed at various temperatures are listed in Table 1. Frequency scanning was made at room temperature in the range 14–19 MHz; only a single signal was observed. However, three pairs of NQR signals were observed at 80 K. Hereafter we call these lines such as indicated in Figure 1. Judging from the peak height of the FT spectra, the intensities of the two component lines of each pair are equal. It is difficult to compare the intensity of three pairs to each other owing to the lines spread over a wide range (ca. 400 kHz at 80 K), but the integrated intensity ratio of the three pairs seems to be nearly 1:1:1.

ν_1 was almost temperature independent, ν_2 decreased most drastically and ν_3 and ν_4 decreased linearly with increasing temperature. The intensity of all six signals except ν_2 decreased gradually with increasing temperature while ν_2 decreased more rapidly. Although the intensity ratio of ν_1 and ν_2 remained nearly the same even at 180 K, only ν_2 could not be observed at 228 K. The intensity of the all lines except ν_2 became very weak at 229 K compared with that at 228 K, and the HTP signal ν_h appeared at the same temperature. When measurements were made at 229 K, in the course of time the intensity of ν_h became strong whereas that of ν_3 and ν_4 became weak. The spectra were recorded after the specimen had been held at 229 K for one hour. The results are shown in Figure 2. At 230 K, the lines ν_3 and ν_4 disappeared completely (see Fig. 2), although ν_1, ν_5, and ν_6 were still observable with very weak intensity. The lines ν_5 and ν_6 disappeared at ca. 231 K, but ν_1 could be observed up to 232 K.

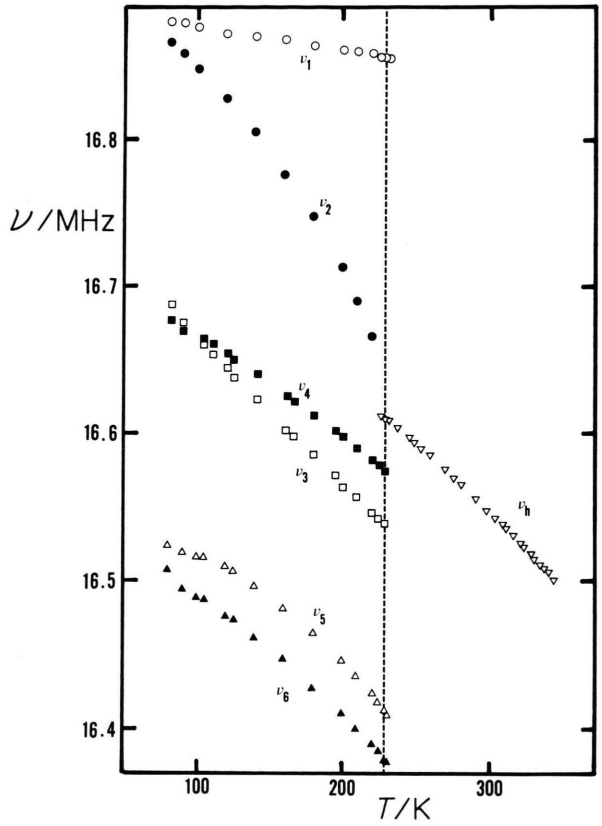

Fig. 1. The temperature dependence of ^{35}Cl NQR frequencies in 2,6-lutidinium hexachlorotellurate(IV). The broken line indicates the phase transition temperature $T_c = 229$ K.

Table 1. ^{35}Cl NQR frequencies ν_Q observed at several temperatures in 2,6-lutidinium hexachlorotellurate(IV) crystals.

T/K	ν_Q/MHz						
	ν_h	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
81		16.880	16.866	16.688	16.677	16.525	16.508
139		16.870	16.805	16.624	16.641	16.497	16.462
200		16.861	16.713	16.564	16.598	16.446	16.411
229	16.610	16.856	–	16.539	16.575	16.413	16.379
298	16.548						
343	16.501						

ν_h decreased monotonously with increasing temperature, and its intensity became gradually weak on heating and disappeared at ca. 350 K. On decreasing the temperature, the HTP was slightly supercooled.

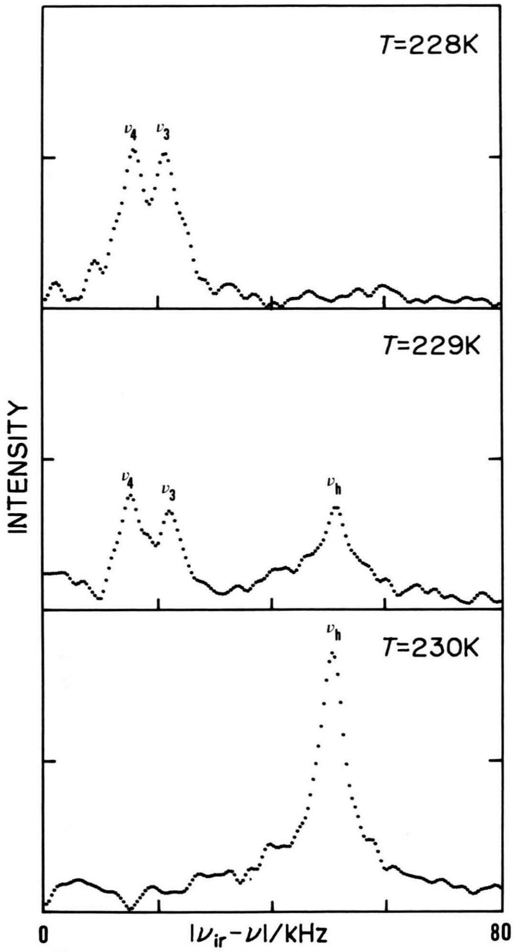

Fig. 2. Temperature variation of ν_3, ν_4, and ν_h peaks around T_c with increasing temperature. These three Fourier transform power spectra are obtained from FID signals which were accumulated by 1024 times. The same irradiated frequency ν_{ir} (16.560 MHz) was employed for the measurements made at three temperatures. Although ν_3 and ν_4 look close owing to fold back of ν_3, ν_3, and ν_4 are separated by ca. 40 kHz.

Table 2. ^{35}Cl nuclear quadrupole spin-lattice relaxation times T_{1Q} determined for 2,6-lutidinium hexachlorotellurate(IV) crystals at several temperatures.

T/K	T_{1Q}/ms						
	ν_h	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
100		900	530	580	580	630	700
140		775	200	310	430	450*	480*
220		315	100	165	145	195	225
230	140						
298	13.6						
343	0.505						

* Values measured at 160 K.

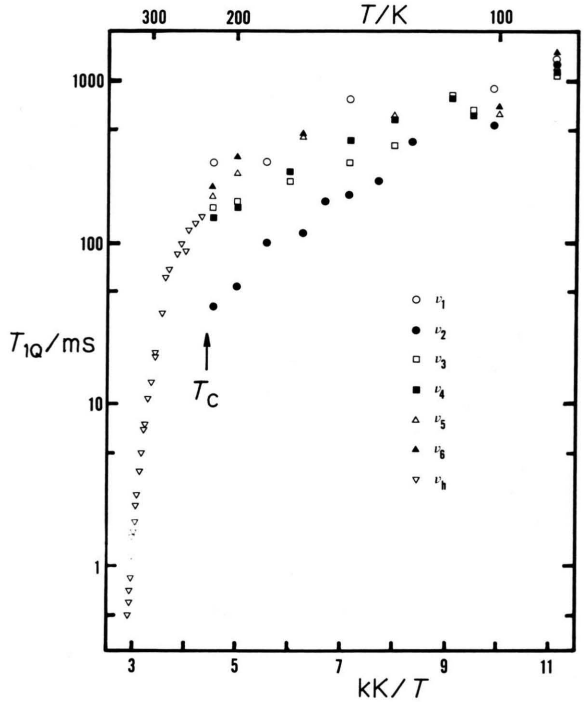

Fig. 3. Temperature dependences of T_{1Q} of ^{35}Cl nuclei in 2,6-lutidinium hexachlorotellurate(IV).

The lines ν_3 and ν_4 appeared at 226 K, and ν_h disappeared completely at 225 K. These results clearly indicate that this phase transition is of first order.

^{35}*Cl Nuclear Quadrupole Spin-Lattice Relaxation Time*

The temperature dependence of ^{35}Cl T_{1Q} is shown in Fig. 3 and the values at some temperatures are given in Table 2. In the LTP, T_{1Q} of all lines decreased with increasing temperature, but that of ν_2 decreased more rapidly than the others.

In the HTP, T_{1Q} of ν_h decreased markedly with increasing temperature. log T_{1Q} of ν_h was proportional to T^{-1} above ca. 300 K.

Discussion

The Measurements of T_{1Q} by Use of the FT Spectra

When many lines exist in a narrow frequency range, it is difficult to measure ν_Q and/or T_{1Q} of each line precisely. The frequencies of ν_3 and ν_4 were closely spaced in the range 80 and 229 K, and the frequency difference of these lines was at most ca. 40 kHz. The same is true for the ν_5 and ν_6 lines. In such cases, the FT-NQR spectra of each line make it possible to determine ν_Q and/or T_{1Q} exactly.

Preliminary measurements of T_{1Q} for the same spectrum with the FT method and the usual method show that the linearity of $(F_\infty - F_\tau)/F_\infty$ vs. τ plots obtained with the FT method is poor as compared with that derived with the usual method. As can be seen from the results of this study (Fig. 3), the error of the experimental values seems to be somewhat large. Thus, T_{1Q} measured by use of FT-NQR spectra seems to be less accurate than that evaluated by the usual method.

ν_Q *and* T_{1Q} *in the Low Temperature Phase*

The ^{35}Cl NQR lines observed in the LTP are probably assignable to the six chlorines in one octahedral complex anion by considering the intensity ratio of the two lines belonging to each pair mentioned above. The temperature dependences of ν_1 and ν_2 are different from that of the other signals. This can be explained by the effect of H-bonding between chlorines of the complex anion and hydrogens in the 2,6-lutidinium ion as follows. In the present complex crystal, the temperature dependence of ν_1 and ν_2 may involve two terms, i.e., the usual Bayer term [10] and the term relating to H-bonding. It is well known that, when a hydrogen atom approaches the resonant chlorine from the direction perpendicular and parallel to the principal z axis of the EFG produced at the resonant nucleus, the NQR frequency of the nucleus decreases and increases, respectively [11]. H-bonding is usually weakened due to the activation of thermal vibrations. In view of the foregoing discussion, it is reasonable that ν_1 is nearly temperature independent, because of the cancellation of the Bayer term by the term responsible for H-bonding, which has a positive temperature coefficient. The steep temperature coefficient of ν_2 is thought as due to the fact that the H-bonding term contributes additively to that of the usual Bayer term. As already mentioned above, ν_2 faded out near T_c. Because T_{1Q} of ν_2 is in the order of 10 ms near T_c, this fade-out phenomenon can be attributed to a static effect. Atoms and/or ions which create a partial EFG at the chlorine nuclei in question are responsible for the fade-out of the signal. Hydrogens in the 2,6-lutidinium ions which form H-bonds with the chlorines meet the above requirements if these hydrogens (or the cations as a whole) are slightly disordered, and the disorder is expected to be excited with increasing temperature.

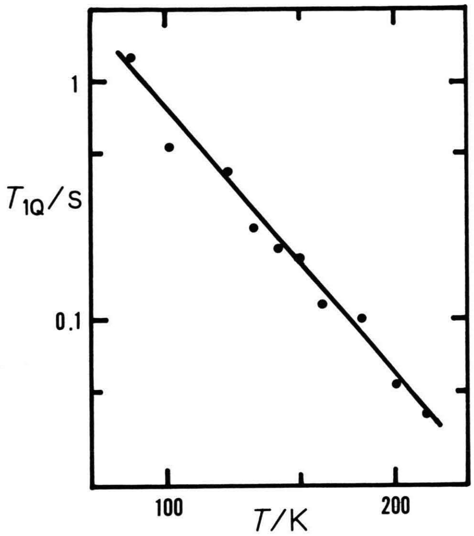

Fig. 4. The ^{35}Cl T_{1Q} of ν_2 versus log T. The straight line, obtained by least-squares fitting, yields $d\log(T_{1Q}/s)/d\log(T/K) = -3.7$.

Table 3. The power index n of T in (1) for the low temperature phase resonance lines

Lines	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
n	1.6	3.7	1.7	2.2	1.9	1.7

Theoretically, T_{1Q} is proportional to T^{-2} when the relaxation mechanism is mainly attributable to lattice vibrations [12, 13]. Our results, however, could be approximated by

$$T_{1Q} \propto T^{-n}, \tag{1}$$

where n is a parameter to be fitted. The most probable values of n are given in Table 3.

The values of n for all lines except ν_2 are nearly equal to 2. The value of 3.7 obtained for ν_2 seems to be somewhat larger than the usual experimental ones [7]. It may be possible to fit the observed values to other functions, but the log T_{1Q} vs. log T plot yield a good linear relation within the experimental errors (Figure 4). Large values, such as that of ν_2, have been reported for s-triazine (3.44 and 3.64), which undergoes a second order phase transition from hexagonal to monoclinic at 198.9 K [14].

In pyridinium hexachlorometallates(IV), it has been proposed [3] that the relaxation of the chlorine nuclei is attributable to the fluctuation of the EFG modulated by 60° jumps of the cation around its pseudo C_6 axis. As described above, the chlorines responsible for ν_2 are thought to form H-bonds with the cations. Therefore it is expected that the motions of the $(2,6\text{-lutH})^+$ ion modulate the EFG at the chlorine nuclei in question. The motions should not be 60° jumps of the cation. From the fade-out phenomenon of ν_2, a slight disorder of the cations is inferred. Small angle reorientations among the disordered sites could produce the fluctuation of the EFG.

ν_Q *and* T_{1Q} *in the High Temperature Phase*

In the HTP, T_{1Q} of ν_h decreased rather steeply with increasing temperature. The linear portion of log T_{1Q} vs. T^{-1} plots with a steep inclination is solely attributable to the overall reorientational motion of $[TeCl_6]^{2-}$ anions [15]. The activation energy of this motion is about 82 kJ mol^{-1}. The same type of the octahedral complex anionic motion has been observed for pyridinium hexachlorotellurate(IV) [3]. The ^{35}Cl NQR line of this crystal disappeared at ca. 320 K, and the activation energy is estimated to be 55 kJ mol^{-1}. The activation energy for the motion of the complex anion in the present crystal is much larger than that for the anion in pyridinium hexachlorotellurate(IV). This may be due to the steric hindrance of the substituted methyl groups of the present complex.

[1] Y. Tai, A. Ishikawa, K. Horiuchi, T. Asaji, D. Nakamura, and R. Ikeda, Z. Naturforsch. **43a,** 1002 (1988).
[2] Y. Tai, T. Asaji, R. Ikeda, and D. Nakamura, Z. Naturforsch. **44a,** 300 (1989).
[3] Y. Tai, T. Asaji, D. Nakamura, and R. Ikeda, Z. Naturforsch. **45a,** 435 (1990).
[4] K. Horiuchi, R. Ikeda, and D. Nakamura, Ber. Bunsenges. Phys. Chem. **91,** 1351 (1987).
[5] A. Ishikawa, K. Horiuchi, R. Ikeda, and D. Nakamura, J. Mol. Struct. **192,** 237 (1989).
[6] Y. Furukawa and D. Nakamura, Ber. Bunsenges. Phys. Chem. **93,** 13 (1989).
[7] K. Horiuchi and D. Nakamura, Ber. Bunsenges. Phys. Chem. **93,** 909 (1989).
[8] T. B. Brill and W. A. Welsh, J. Chem. Soc. Dalton Trans. 357 (1973).
[9] Y. Kume, R. Ikeda, and D. Nakamura, J. Magn. Reson. **33,** 331 (1979).
[10] H. Bayer, Z. Phys. **130,** 227 (1951).
[11] D. Nakamura, R. Ikeda, and M. Kubo, Coord. Chem. Rev. **17,** 281 (1975).
[12] J. Van Kranendonk, Physica, **20,** 781 (1954).
[13] J. Van Kranendonk and M. B. Walker, Can. J. Phys. **46,** 2442 (1968).
[14] A. Zussman and M. Oron, J. Chem. Phys. **66,** 743 (1977).
[15] S. Alexander and A. Tzalmona, Phys. Rev. **138,** A845 (1965).