Halogen NQR and the Phase Transition in CH_3Hg-Halide Family

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The temperature dependence of the ^{35}Cl NQR line and its relaxation has been measured from 77 K to room temperature. The known displacive phase transition near 162 K is reflected in the change of the slope of the temperature dependence of the quadrupole line, but not so in the chlorine or proton relaxation. The results are discussed in view of the proposed structural changes and thermal vibrations.

Key words: Methylmercury Chloride; NQR; Crystal Structure; Phase Transition; Thermal Vibrations.

Introduction

CH_3HgCl (methylmercury(II) chloride, MMC) is a toxic compound, representing also one of the initial steps in the metabolic chain for Hg poisoning. It belongs to the methylmercury(II) halide family with relatively uncomplicated molecular composition which has a simple scheme of molecular vibrations with a single torsional mode. These compounds are known to exhibit different structural phase transitions [1, 2] in the solid state and are a good example for studying and modelling this type of phase transitions. The aim of this research is to use Cl NQR to examine the hypothesis of analogous sequence of isostructural phases at ambient pressure in the methylmercury(II) chloride, bromide and iodide [2]. This hypothesis has been made mainly on the basis of Raman measurements, available structural data and space group analysis.

The room temperature structure of MMC shown on Fig. 1 is tetragonal, space group P4/nmm [2, 3]. It is supposed that below 162 K a displacement phase transition, driven by the softening of a phonon at the Brillouin zone boundary, occurs. The linear molecules CH_3HgCl move out of the mirror planes and the unit cell doubles. The low temperature structure of MMC is presumably isostructural to the room temperature orthorombic structure of CH_3HgI [2], space group Pmab, Fig. 2 (in standard notation Pbcm). It may be represented with a displacement modulation wave (the wavelength having double the length of the high temperature unit cell), superimposed onto the high temperature structure.

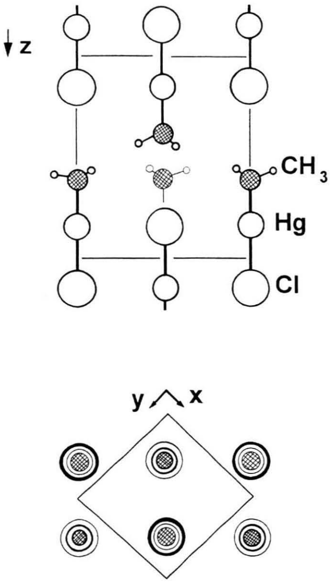

Fig. 1. Room temperature crystal structure of CH_3HgCl.

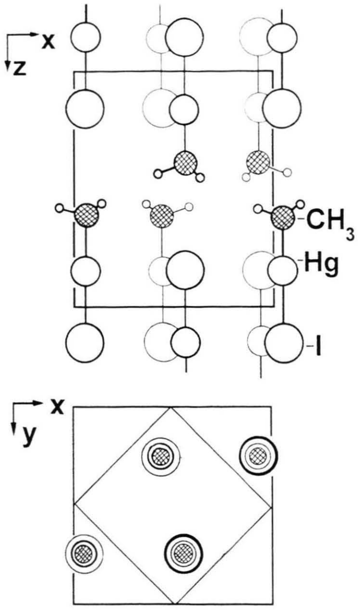

Fig. 2. Room temperature crystal structure of CH_3HgI, presumably isostructural to the low temperature structure of CH_3HgCl.

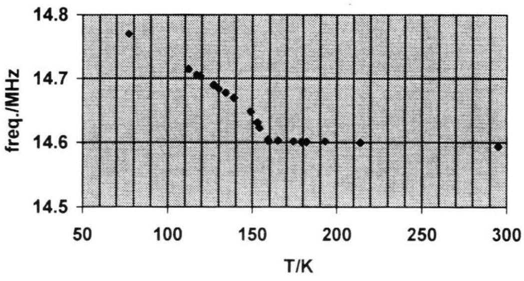

Fig. 3. Temperature dependence of the ^{35}Cl NQR line in CH_3HgCl.

The published structural data for CH_3HgBr roughly fit into this picture.

Measurements

According to our knowledge, the ^{35}Cl NQR frequency in MMC at 77 K is published [4] as well as the halogen NQR frequencies in MM bromide and MM iodide [4]. Microwave determinations of the chlorine [5], bromine and iodine quadrupole coupling constants (QCC) in the gas phase [6] are known, too.

Our starting measurement of Cl NQR in MMC powder was performed with a superregenerative NQR spectrometer to get a first information on the temperature dependence. The results of the subsequent pulse FFT measurements of ^{35}Cl NQR between 77 and 300 K are shown on Figure 3. A sharp change of the slope in the temperature dependence of the Cl NQR frequency is seen at 159 K, confirming the suggested [2] displacive phase transition. The temperature dependences of the longitudinal and transverse relaxation times of Cl (Figs. 4 and 5) exhibit no discontinuity at T_c. Figure 6 shows test proton NMR T_1 measurements at 0.75 T and at zero external field (rf excitation and detection at 0.75 T, relaxing outside the magnet). No critical behaviour is noticed there as well.

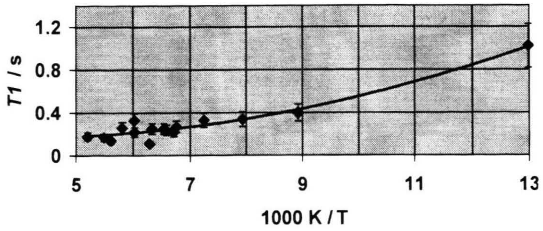

Fig. 4. Temperature dependence of the ^{35}Cl longitudinal relaxation time T_1.

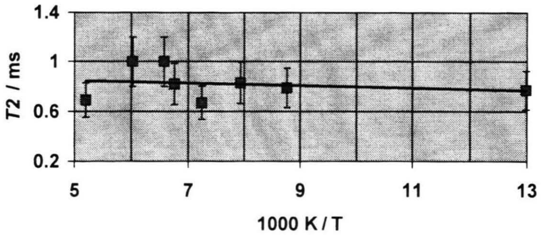

Fig. 5. Temperature dependence of the ^{35}Cl transverse relaxation time T_2.

Discussion

In general, chlorine NQR in MMC does not exhibit large frequency variations. This is true particularly for the high temperature phase, where the temperature coefficient is unusually small. The average QCC ~29 MHz (assuming asymmetry parameter $\eta = 0$) lies relatively low compared to the usual QCC of covalently bonded chlorine (50 - 80 MHz) [7], and is also low compared to the gas molecule QCC (42 MHz) determined by microwave measurements [5]. The first fact indicates the mostly ionic character of the bond ($i \sim 62\%$ [5]), and the second an unusually strong influence of the "crystal field" (30% lowering from gas to solid, instead of the usual < 5% [7]). This means

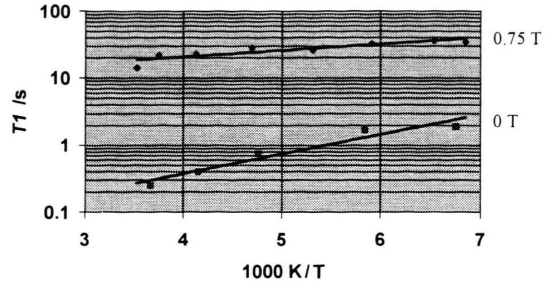

Fig. 6. Spin-lattice relaxation T_1 of the CH_3 protons in external magnetic fields of 0 and 0.75 T.

strong intermolecular interactions, which follows also from Raman data [2], especially when we consider the structure with the planes of closely spaced antiparallel dipoles Cl^--Hg^+ (Figure 1).

In the *high temperature phase* above 159 K a single NQR line is observed for each Cl isotope, as expected from the structure. The temperature dependence seems nearly linear with the already mentioned very small temperature coefficient (74 Hz/K), about 50 times smaller than in a different lattice of otherwise similar linear molecules $HgCl_2$ [8]. The first possible explanation of the weak temperature dependence suggests that those thermal vibrations, which would drastically change the values of the electric field gradient (EFG) at Cl sites are not enough excited. If one assumes that the EFG is determined mainly by the intramolecular bond Cl-Hg, such weakly excited motions should be rotations around the two transversal axes of the linear molecule. In our case one would actually expect such rotational vibrations of the elongated linear molecules, closely packed and all oriented in one direction, to have relatively a high activation energy. On the other hand it is unlikely that other vibrations and all kinds of molecular translations would leave the EFG relatively unchanged since we have evidence of strong intermolecular interactions. Thus, one is rather inclined to explain the small temperature coefficient by two almost compensating contributions to the temperature dependence, like for instance a decrease of the principal value of the EFG in the Bayer sense [9] and proper increase of the asymmetry parameter with increasing temperature. In order to prove this kind of assumptions, accurate structural data at different temperatures should be available to enable quantitative EFG calculations.

In the *low temperature phase* below T_c = 159 K the Cl NQR temperature dependence becomes rather strong. NQR has been measured down to 77 K, Raman measurements were performed down to 10 K [2]. None of them indicate any further phase transition. At some very slow temperature sweeps we have noticed an indication of a small frequency jump of ~10 kHz at T_c that would indicate a first order phase transition in accordance with Raman measurements [1]. 20 K lower the slope becomes constant and keeps the value 1.61 kHz/K down to 77 K. The single Cl NQR line is not in contradiction with the assumed low temperature structure (Figure 2).

For the mathematical description of the displacement modulation wave, forming the low temperature orthorhombic structure out of the more symmetrical high temperature (tetragonal) one, we assume that the basic set of axes coincides with the low temperature crystal axes. In this coordinate system the wave vector of the modulation wave has the direction (±1,±1,0) with the molecular displacements in the direction (±1,0,0).

In this phase (below T_c = 159 K), the NQR frequency shift from the value just above the transition can be described for the two temperature regions above 140 K and below 140 K. It is proportional to:

$$\text{above 140 K: } \nu_Q - \nu_{Q0} \propto (T_c - T)^{2\beta}, \quad 2\beta = 0.74 \pm 0.04, \ \nu_{Q0} = \nu_Q(T_c); \tag{1}$$

$$\text{below 140 K: } \nu_Q - \nu'_{Q0} \sim \nu_Q - \nu_{Q0} \propto (T'_c - T), \quad T'_c \sim 180\,\text{K}, \ \nu'_{Q0} = \nu_Q(T'_c). \tag{2}$$

Owing to the mirror symmetry of the high temperature structure we can expand the instant Cl NQR frequency in the translational molecular displacement u in the direction x:

$$\nu_Q = \nu_{Q0} + au^2 + o(u^4); \ \nu_{Q0} = \nu_Q(T_c). \tag{3}$$

The equations (1 - 3) allow us to estimate the temperature dependence of the molecular displacements in the low temperature phase from the former mirror plane, assuming the proposed low temperature crystal structure:

$$\text{above 140 K: } u \propto (T_c - T)^{\beta}, \ \beta = 0.37 \pm 0.02; \tag{4}$$

$$\text{below 140 K:} u \propto (T'_c - T)^{\beta'}, \beta' = \frac{1}{2}, \ T'_c = 180\,\text{K}. \tag{5}$$

As already mentioned, the *relaxation measurements,* chlorine T_1 and T_2 and proton T_1 show no discontinuity at the phase transition. The chlorine T_1 below the temperature of its supposed minimum near 180 K (Fig. 4) and the proton T_1 (Fig. 6) show a similar activation energy of 0.02 eV (1.9 kJ/mol), which probably indicates that the dominant relaxation mechanism in both processes are the motion of the CH_3 groups with a rather low activation energy. In the crystal structure, CH_3 groups are enclosed between the layers of Hg-Cl groups (Figs. 1, 2) and their motion is possibly not very sensitive to the fine rearrangements in the enclosing Hg-Cl layers. This would explain the insensitivity of the relaxation to the phase transition. The correlation time of the mechanism, responsible for the Cl relaxation at 180 K where its T_1 approaches its minimum is estimated as $\tau \sim 1/(2\pi\nu_Q) \sim 1 \cdot 10^{-8}$ s. The measurements of proton T_1 should be extended to a wider interval especially to higher temperatures to reveal a possible minimum.

In conclusion, the present measurements are our first step in the research of methylmercury halide compounds. So far only temperature dependence of the Cl NQR frequency seems to reflect the displacement phase transition in MMC. The mechanisms responsible for chlorine quadrupole and proton NMR relaxation do not change appreciably at T_c. We expect a clearer picture after the comparison with similar measurements in other methylmercury(II) halides.

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