

# <sup>35</sup>Cl NQR Study of Guest Dynamics in Thiourea-CCl<sub>4</sub> Inclusion Complex \*

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<sup>35</sup>Cl nuclear quadrupole resonance measurements on thiourea-CCl<sub>4</sub> inclusion complex yielded two resonance lines with intensity ratio 1:3. This indicates that the guest CCl<sub>4</sub> molecule occupies the three-fold symmetry site in the channel formed by the thiourea framework. The resonance frequencies closely follow Bayer's equation between 4.2 K and 27 K. At higher temperatures the resonance lines faded out. This is attributed to the onset of reorientation of the CCl<sub>4</sub> molecule. The activation energy for this motion was estimated to be 6 kJ mol<sup>-1</sup>.

Thiourea forms inclusion complexes with various organic molecules [1]. The thiourea molecules link with each other to form a trigonal framework with channels along the unique axis, and the guest molecules are accommodated in the channel [2]. Most of the molecules which can be enclathrated in the thiourea channel are alicyclic and branched aliphatic hydrocarbons; a number of thermodynamic studies have been done on these thiourea adducts aiming at examining the relative stability of the complexes and the host-guest and, in some cases, guest-guest interactions in the complexes [3].

Thiourea also forms stable compounds by enclathrating small molecules such as CCl<sub>4</sub>, CHCl<sub>3</sub>, and C<sub>2</sub>Cl<sub>6</sub>. As small guests can easily be studied by means of various spectroscopic methods, these complexes can be utilized to derive information on the intermolecular interactions in the adducts. To understand the interactions governing the structure and dynamical properties of thiourea adducts, we have started thermodynamic and spectroscopic studies with the thiourea-CCl<sub>4</sub> inclusion complex. First of all, we measured the heat capacity of this compound and found a phase transition of the first order at 41.3 K and another one of the second order at 67.2 K [4].

We now measured <sup>35</sup>Cl NQR frequencies in this material at low temperature to examine the structure and dynamic behavior of the guest CCl<sub>4</sub> molecules as

well as their possible relation to the phase transitions. The present paper describes some experimental results and discusses a model of the thiourea-CCl<sub>4</sub> complex.

## Experimental

The procedure of sample preparation and identification was described in [4]. The specimen has a molar host/guest ratio of 3:1. It was sealed in an ampoule with a small amount of helium gas for heat exchange.

<sup>35</sup>Cl NQR frequencies were measured with a super-regenerative spectrometer above 4.2 K. The temperature was measured with Au/Fe-Constantan and Chromel-P-Constantan thermocouples to within 0.1 K. The uncertainty in the frequency measurements was ±0.4 kHz at 4.2 K and increased gradually up to about 2 kHz at 27 K.

## Results and Discussion

We detected two <sup>35</sup>Cl NQR signals at  $\nu_1 = 41.1300$  MHz and  $\nu_2 = 40.8315$  MHz with an intensity ratio of about 1:3 at 4.2 K. The resonance frequencies lowered to 40.991 and 40.678 MHz at 20.3 K. The weighted average of the resonance frequencies, 40.756 MHz at 20 K, is slightly lower than that (40.92 MHz) in the neat CCl<sub>4</sub> crystal and comparable with those in CCl<sub>4</sub> complexes with various organic molecules [5].

The fact that only two NQR lines with intensity ratio 1:3 were observed indicates unambiguously that all the guest CCl<sub>4</sub> molecules accommodated in the

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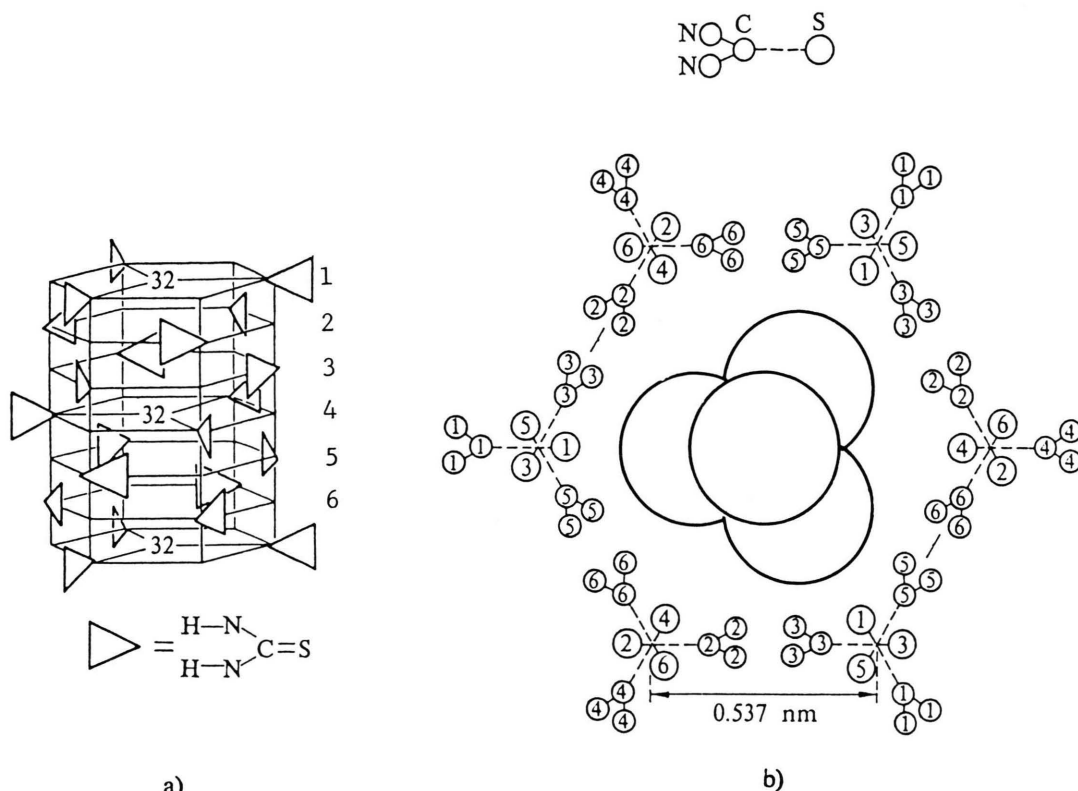


Fig. 1. Host lattice structure of thiourea adduct. a) The stacking arrangement of the layers of thiourea molecules. b) Downward view along the crystallographic *c*-axis. The numbers indicate the order of the stacking layers along the *c*-axis [reproduced from A. F. G. Cope, D. J. Gannon, and N. G. Parsonage, *J. Chem. Thermodynamics* **4**, 829 (1972)].

channel are crystallographically equivalent and occupy a special position with three-fold symmetry. If we assume that the host structure of the CCl<sub>4</sub> adduct is essentially the same as that of the thiourea-cyclohexane adduct [2] as reproduced in Figure 1, the three-fold symmetry axis passes through the center of the channel in the trigonal unit cell. It is therefore obvious that three chlorine atoms in the guest molecule interact with the wall of the channel but the fourth chlorine is located on the three-fold axis and is almost free from any interaction with the atoms on the wall.

The temperature dependence of the resonance frequencies is shown in Figure 2. The temperature coefficients,  $-dv_Q/dT$  at 20 K are 14.0 and 15.6 kHz  $T^{-1}$  for  $\nu_1$  and  $\nu_2$ , respectively, being much larger than those in the CCl<sub>4</sub> crystal [6] (3–5 kHz  $T^{-1}$ ), and also larger than those in the CCl<sub>4</sub>-Dianin's compound and in the CCl<sub>4</sub>-Fe(III) tris(acetylacetonate) clathrates [7]. Both resonance lines broadened and weakened very rapidly on heating, and faded-out above 25.2 K ( $\nu_1$ ) and 27.2 K ( $\nu_2$ ).

A theory for the temperature dependence of the NQR frequency was originally presented by Bayer [8]. His theoretical expression for the NQR frequency at a temperature  $T$ ,  $\nu_Q(T)$ , is given, for a molecule undergoing two-dimensional librational motion, by

$$\nu_Q(T) = \nu_Q(0) - \frac{3h\nu_0}{4\pi^2 I_L \nu_L} \cdot \frac{1}{\exp(h\nu_L/kT) - 1}, \quad (1)$$

where  $\nu_0$  is the NQR frequency in the "static" molecule, and  $I_L$  and  $\nu_L$  are the principal moment of inertia and the librational frequency, respectively, of the molecule.  $\nu_Q(0)$  is the NQR frequency at absolute zero, where only the zero-point libration remains, and is given by

$$\nu_Q(0) = \nu_0 [1 - 3h/8\pi^2 I_L \nu_L]. \quad (2)$$

We fitted (1) to our experimental resonance frequencies (Fig. 2) by use of a damping Gauss-Newton non-linear least squares method and determined  $\nu_Q(0)$ ,  $\nu_L$ , and the ratio  $\nu_0/I_L$ , the values of which were then used to calculate  $\nu_0$  and  $I_L$  by applying (2). The parameters

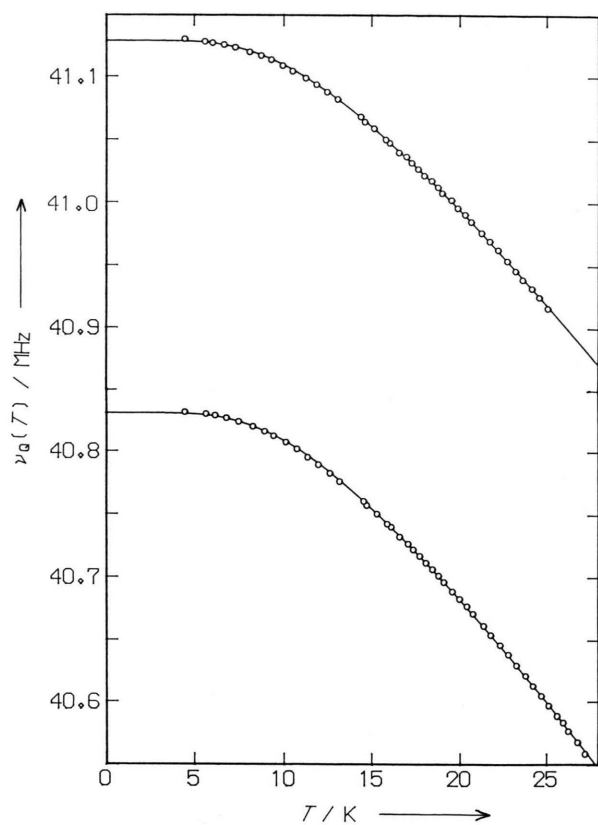


Fig. 2. Temperature dependence of the <sup>35</sup>Cl NQR frequencies,  $\nu_1$  (upper curve) and  $\nu_2$  (lower curve). The solid lines represent the calculated frequencies using (1) with the parameters from Table 1.

thus determined are recorded in Table 1. The error bounds for  $\nu_Q(0)$  and  $\nu_L$  correspond to the ordinary standard deviations whereas those for  $\nu_0$  and  $I_L$  mean the combined errors estimated from the above standard deviations. The solid lines in Fig. 2 represent the theoretical resonance frequencies produced with these parameters. The agreement between the experimental and the theoretical resonance frequencies is excellent for both  $\nu_1$  and  $\nu_2$ . We see also that the librational frequencies as well as the moment of inertia deduced from the two resonance frequencies coincide with each other and, moreover, the value of the theoretical moment of inertia agrees very well with the value,  $4.90 \cdot 10^{-45} \text{ kg m}^2$ , calculated from the molecular geometry of CCl<sub>4</sub> on assuming a C–Cl bond distance of 0.1767 nm.

The analysis of the NQR frequency by the Bayer theory leads in most cases to an unrealistically small moment of inertia, due mainly to the neglect of a

Table 1. Fitting parameters in (1) for two NQR lines. Estimated errors are given in parentheses.

	$\nu_1$	$\nu_2$
$\nu_0/\text{MHz}$	41.464 (10)	41.186 (08)
$\nu_Q(0)/\text{MHz}$	41.1284 (4)	40.8305 (4)
$\nu_L \text{ cm}^{-1}/\text{cm}^{-1}$	24.8 (2)	24.4 (2)
$I_L/10^{-45} \text{ kg m}^2$	4.19 (10)	4.00 (07)
$SS/\text{MHz}^a$	$2.1200 \cdot 10^{-5}$	$2.4856 \cdot 10^{-5}$

<sup>a</sup>  $SS = \sum [\nu_Q(T, \text{obs}) - \nu_Q(T, \text{calc})]^2$ .

highly anharmonic effect of the molecular libration in the theoretical treatment [9]. However, as mentioned above, the present NQR data obeyed almost perfectly the simple Bayer theory and led to the reasonable value of the moment of inertia; this strongly suggests that the CCl<sub>4</sub> molecule accommodated in the thiourea channel behaves as an ideal harmonic oscillator at low temperatures. In other words, the motion of a CCl<sub>4</sub> molecule is not appreciably coupled to the motion of the rest of the crystal. Moreover, it is also suggested that the two librational frequencies  $\nu_L$  coincide with each other because the guest molecule undergoes an isotropic libration in the channel. As a result, the three-dimensional potential surface for the libration is well approximated by a sinusoidal potential function.

We can therefore represent the librational potential by use of three-fold potential functions, such as

$$V(\theta) = V_0[1 - \cos(3\theta)], \quad (3)$$

where  $\theta$  is the librational angle and  $V_0$  represents the potential barrier for the molecular rotation. In the harmonic vibrational approximation,  $V_0$  is related to the librational frequency through

$$V_0 = (1/3^2)(2\pi \nu_L)^2 I_L. \quad (4)$$

With  $\nu_L \text{ cm}^{-1} = 24.6 \text{ cm}^{-1}$  and  $I_L = 4.10 \cdot 10^{-45} \text{ kg m}^2$ ,  $V_0$  was calculated to be  $5.9 \text{ kJ mol}^{-1}$ . This low rotational potential may be overcome easily, and so the exchange between the apical and the basal chlorines as well as the three fold reorientation can occur at considerably low temperatures. The former exchange is accompanied by a large shift of the NQR frequency, resulting in line broadening and then leading to the fade-out of the signals on heating.

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