Thiourea and Thiourea Inclusion Compounds. A ^{14}N NQR Investigation

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Z. Naturforsch. **55a,** 331–334 (2000); received October 13, 1999

Presented at the XVth International Symposium on Nuclear Quadrupole Interactions, Leipzig, Germany, July 25–30, 1999.

A reinvestigation of the nitrogen-14 NQR in thiourea has permitted to record, apparently for the first time, the resonances above 169 K. The first order and second order of the transitions at 169 K and 202 K, respectively, appear clearly from the temperature dependence of the resonance frequencies; the modulated structure, incommensurate or commensurate, is also seen on the ^{14}N NQR spectrum. This study is the first step of a new investigation of thiourea and its inclusion compounds.

Key words: Thiourea; Nitrogen-14 NQR; Phase Transitions; Commensurate; Incommensurate Modulations; Inclusion Compounds.

Introduction

For the physicist, thiourea is a very interesting compound exhibiting remarkable ferroelectric properties and phase transitions. Its ferroelectric behaviour was first reported by Solomon [1] in 1956. It was the first organic compound found to exhibit ferroelectricity. Since then many investigations, using mainly dielectric and thermodynamic methods, have been published about the phase transitions in thiourea. Goldsmith and White in 1959 [2], using the variation of its dielectric properties with temperature, described five phases between 80 and 300 K with the transition-temperatures 169, 176, 180, and 202 K. Other investigations, based on the thermodynamic behaviour were also made, especially by Futama [3]. In 1964, Smith and Cotts [4] published a nitrogen-14 NQR investigation of thiourea together with some data on the proton relaxation time. They observed two discrete resonances below 169 K but none above this temperature and explained this by a special fast relaxation that would broaden the resonances. In 1983 and 1985, Anferova et al. reported [5] a nitrogen resonance in thiourea in the frame of a nitrogen/proton double resonance investigation, but with no details. The ability of thiourea to form, like urea, inclusion compounds makes it also an interesting compound for the chemist.

Structural investigations [6] have shown the occurrence of incommensurate modulation in phases II and IV and a commensurate one between phase I and II, in a rather narrow temperature range.

As NQR is well suited for investigating incommensurate phases via the line shape and the relaxation times, it was challenging to undertake a new NQR investigation of thiourea at temperatures above 169 K using pulse spectrometers with signal processing that are more powerful than the continuous wave models used in the past. Incidentally, it would also be interesting to re-examine some inclusion compounds (I.C.), like TCIC (thiourea cyclohexane I.C.) investigated in 1975 [7].

Experimental Results

Nitrogen-14, with its nuclear spin $I=1$, has an NQR spectrum composed of three lines, ν_+, ν_- and ν_0, obeying the relation $\nu_+ - \nu_- = \nu_0$; the quadrupole coupling constant and asymmetry parameters are given by

$$e^2Qq = \frac{2}{3}(\nu_+ + \nu_-) \quad \text{and} \quad \eta = 3\,\frac{\nu_+ - \nu_-}{\nu_+ + \nu_-}\,.$$

In what follows, we will consider only the ν_+ resonances which may consist of several lines if several sites are present in the sample. The frequencies of these resonances are usually between 2 and 4 megahertz. Due to

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† Deceased on March 8, 1999.

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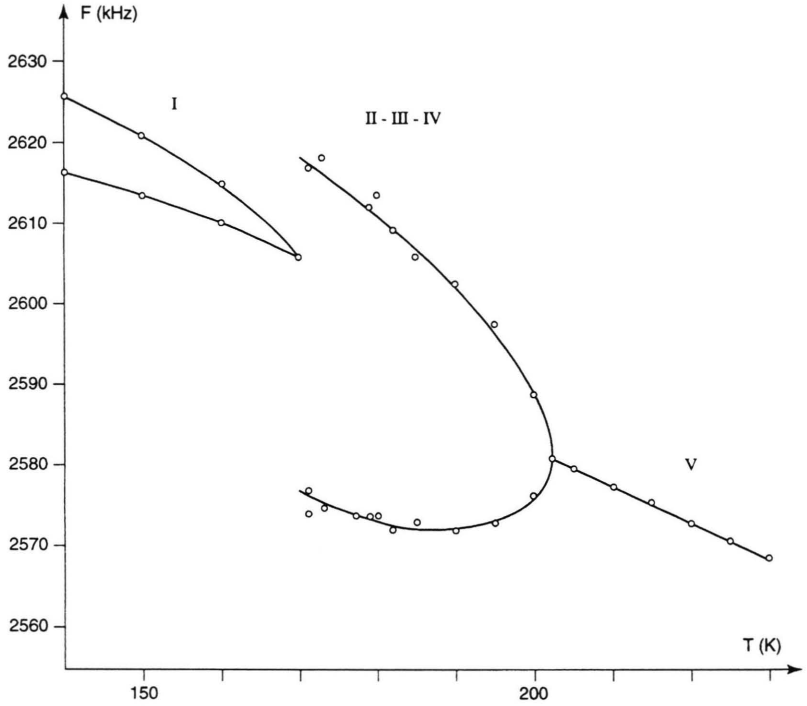

Fig. 1. Temperature dependence of the ^{14}N ν_+ resonance frequency F in pure thiourea. The two curves between 169 and 202 K indicate the upper and lower limits of the spectrum.

the correspondingly low Boltzmann factor, the nitrogen-14 NQR signals are, in most cases, very weak and the experiments time consuming.

Pulse spectrometers with signal accumulation and Fourier transform (FT) are very convenient for studying complex and broad NQR spectra. In practice the analysis is not always straightforward when the spectral features are altered by the spectral response of the spectrometer and if the latter has only one phase detection leading to a folding of the calculated FT spectra, which is true in the present case.

In the determination of relaxation times it is supposed that they are well defined. This is not the case if several mechanisms contribute to the relaxation, so that it cannot be described by a single exponential. However, one can get an idea of the relaxation rate if the amplitude of the echo signal is studied as a function of the sequence separation for T_1 or the pulse separation for T_2, and the time for which the amplitude is $1/e$ of the maximum is retained. If the echo is not observable, it is an alternative method, assuming the distribution is Gaussian, to consider the intersection of the free induction decay inflexional tangent with the abscissa (time axis).

Pure Thiourea

In pure thiourea, the nitrogen-14 resonance could be recorded from 169 to 230 K. The temperature dependence of the spectrum is shown in Figure 1. Just above 202 K, a single narrow line (≈ 1.4 kHz) is recorded (Figure 2). Its width increases with temperature to 2 kHz at 220 K, 3 kHz at 225 K and almost 5 kHz at 230 K. The 230 K temperature corresponds to the beginning of a smearing out of the signal probably due to the onset of molecular reorientations around the $C=S$ bond direction. Upon lowering the temperature, the second order phase transition is found near 202 K; below this transition, the resonance broadens rapidly and almost symmetrically with respect to the extension of the high temperature $\nu(T)$ curve. In Fig. 1, the two lines in this region correspond to the low and high frequency sides of the broad resonance, the width of which reaches 40 kHz in the vicinity of 169 K. Below 169 K, two discrete lines as reported by Smith and Cotts [4] are recorded. A detailed investigation of the temperature range between 169 K and 185 K has been started, especially at 171 K where a commensurate phase is expected to be present [7]. The Fourier transforms of the echoes recorded at every kilohertz between 2570 and 2630 kHz, reveal several conspicuous and rather

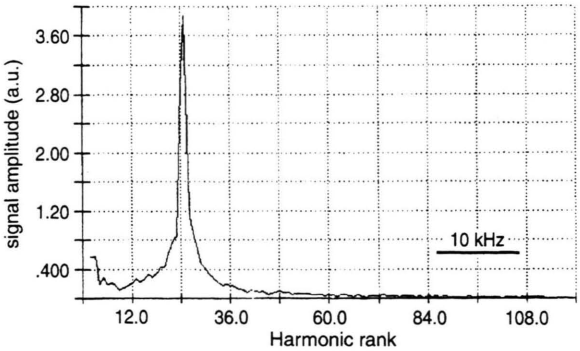

Fig. 2. At 202 K and 2 581 kHz, the resonance appears as a single line with a 1.4 kHz linewidth. In abscissa the rank of the harmonics is shown, the separation between two harmonics being 0.488 kHz. Ordinates are in arbitrary units (a.u.).

narrow lines (about 1.5 kHz, less than 2 kHz) at frequencies:

2 581.15 2 577.20 2 600.55
2 608.44 2 612.73 2 617.60 kHz.

In Fig. 3 a, the Fourier transform of the echo recorded at 2 575 kHz and 171 K, in the low temperature region of phase II, shows the lines at 2 581.15, 2 577.20 and 2 600.55 kHz In Fig. 3 b, recorded at 2 583 kHz, inside the spectrum, it is clear that the recorded lines are well separated and that is a strong support for the commensurate nature of the modulation in this phase.

There are also smaller and broader lines that could not be clearly characterized and they constitute a background that complicate the study of the three high frequency lines. They seem to be mainly in the high frequency part of the spectrum. In Fig. 4, the background is visible on the Fourier transform of the echo, recorded at 2 602 kHz.

These results agree with a commensurate structure though the number of lines (six) is not simply related to the modulation period of 9 cited in the literature [6]. In these conditions, the presence of a background of lines of intensity smaller by a factor of five or more may be explained by the simultaneous presence of another structure; a slight shift in the temperature of the sample is not completely excluded and further experiments are required to precise this point.

In Fig. 5, the FT of an echo recorded at 190 K where the spectrum is broad, shows no sign of a structure in the spectrum.

Below the transition at 169 K, the sample is in phase I [2] and the two lines shown in Fig. 1 are from Smith and Cotts [4].

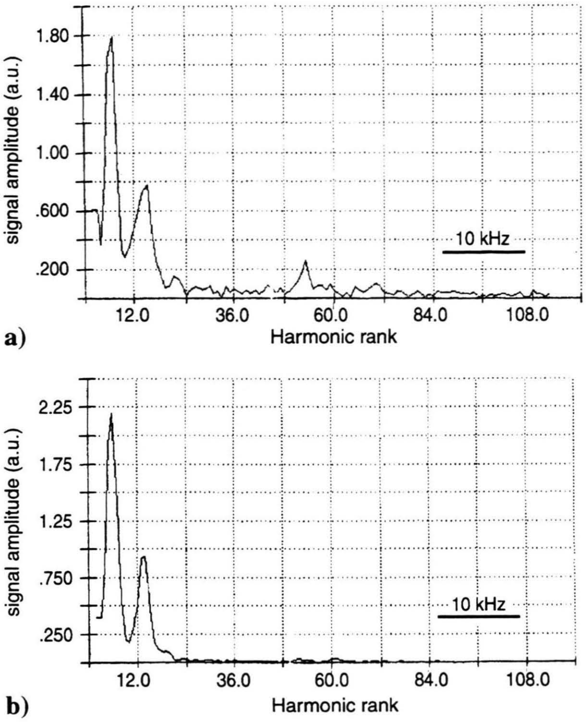

Fig. 3. a) On the Fourier transform of the echo recorded at 171 K and 2 575 kHz, the lines at 2 577.20, 2 580.40 and 2 600.55 kHz can be seen from left to right, respectively. b) The FT of the echo at 2 583 kHz shows the lines at 2 580.40 and 2 577.20; due to the relatively high intensity of these signals, the line at 2 600.55 remains hidden in the noise.

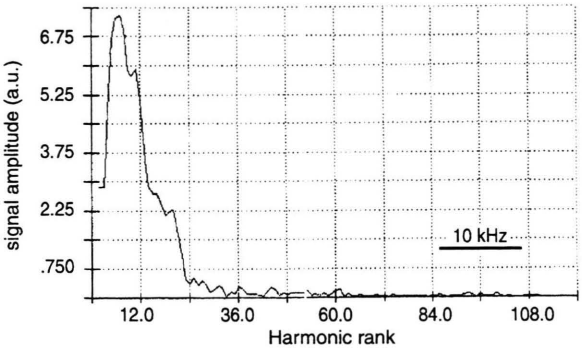

Fig. 4. The FT of the echo recorded at 171 K and 2 602 kHz illustrates the background present in the high frequency part of the spectrum.

Thiourea-Cyclohexane Inclusion Compound (TCIC)

The thiourea-cyclohexane inclusion compound, TCIC, has been investigated in this laboratory about twenty years ago. Using nitrogen-14 NQR, proton NMR,

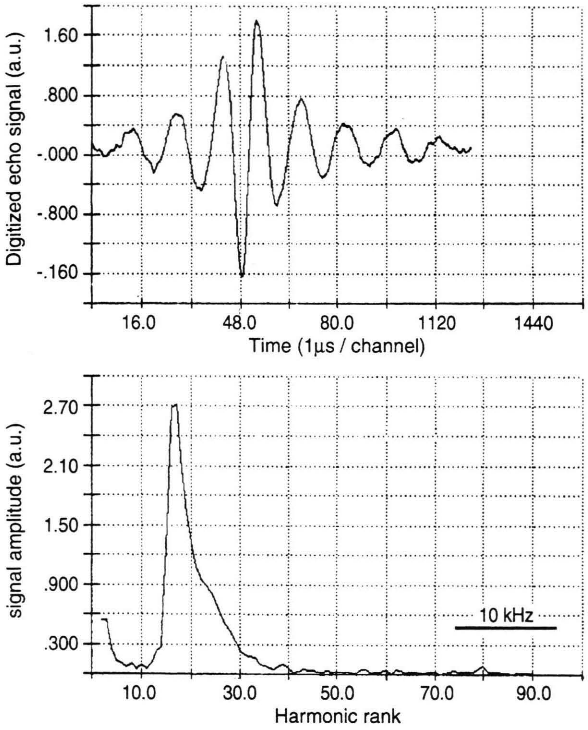

Fig. 5. On the FT (bottom) of an echo (top) recorded at 190 K and 2 610 kHz, where the spectrum is broad, no sign of structure is seen.

thermal differential analysis and X-ray diffraction, had been possible to give a description of the three different phases appearing between 4.2 K and 243 K, the phase transitions occuring at 129 K and 149 K [7]. Using the pulse spectrometer, with signal accumulation and Fourier transform, instead of a continuous wave (cw) spectrometer, we could confirm the former results especially the well resolved structure of the multiline spectra observed below 149 K. In addition, a few relaxation time measurements were made. In all phases T_2 is typically 0.6 ms corresponding to a line width of 0.7 kHz, except in the high temperature part of phase 1, above 210 K, when it begins to decrease from 0.7 ms down to 0.31 ms at 248 K, where the line becomes difficult to observe. A 0.7 kHz line width is usual for nitrogen resonances with $\eta \neq 0$ as there is no first order magnetic dipolar broadening.

T_1 in the high temperature region of phase I is about 15 ms; it increases to 100 ms at 175 K to decrease when approaching the 129 K transition: 27 ms at 153 K. From the top to the bottom of phase II, T_1 increases from 60 ms to 125 ms and, in phase III, below 129 K, it is much higher, 2.6 s. The increase of T_1 upon cooling is due to the slowing down of the hindered reorientational motion of the thiourea molecules responsible for the relaxation [7]. This motion is completely blocked in phase III and relaxation in then only due to dipolar mechanisms and lattice vibrations. The decrease of T_1 when approaching the 129 K transition in phase I is probably due to pretransitional effects.

Conclusion

We could observe the ^{14}N NQR in thiourea above 169 K and visualize the transitions at 169 K and 202 K, respectively, of first and second order. Between the transitions, the spectrum is broad with sharp edges, a shape typical of a incommensurately modulated structure. At 171 K, close to the first order transition, the spectrum consists of narrow and discrete lines thus confirming the presence of a commensurate structure. Such results invite to further investigation for completing the description of the phase system of thiourea in connection with results obtained with other methods.

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