

Study of Urea and Thiourea Inclusion Compounds by NQR and NMR

RENÉ CLÉMENT

Laboratoire de Physicochimie Minérale, Bât. 420,

AND

MICHEL GOURDJI AND LUCIEN GUIBÉ

*Laboratoire d'Electronique Fondamentale (associé au CNRS), Bât. 220 Université Paris XI,
Centre d'Orsay, 91405 Orsay, France*

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Nitrogen-14 NQR was observed in several urea and thiourea inclusion compounds; the study of the temperature dependence of the NQR spectrum in thiourea-cyclohexane revealed several changes which are discussed in view of the results of DTA, X-ray diffraction, and NMR measurements. A similar study of urea-trioxane inclusion compound is also reported.

Pure urea and thiourea crystallize in compact structures (tetragonal and orthorhombic) and when crystallized in presence of some organic molecules such as long-chain hydrocarbons or small rings like cyclohexane, form a hollow hexagonal system of channels in which guest molecules are accommodated (1, 2). It was interesting to observe nitrogen-14 NQR in these inclusion compounds (IC) to obtain information about their structure and about the interaction between host and guest molecules.

OBSERVATION OF NITROGEN-14 NQR IN IC

In urea crystallized with *n*-heptane (3) the ¹⁴N NQR of the urea nitrogen atoms was not found, which is due to the disordered lattice formed by the guest molecules relative to the lattice of host molecules. This disorder is due to the length of the guest molecule not being exactly equal to the height of the unit cell of the host lattice, nor to a multiple or a submultiple of the unit cell height. The compound is not stoichiometric in the sense that the ratio *r* of the number of host molecules to the number of guest molecules is not a small integer. Consequently, the intermolecular environment of each urea nitrogen atom of the host lattice is not the same, and the NQR frequencies are spread over a large band and remain far below thermal noise and cannot be detected with conventional spectrometers.

In a stoichiometric IC, thiourea-cyclohexane IC (TCIC) for which the ratio *r* is exactly 3, several nitrogen-14 NQR lines were found at 77 K (4). Resonances were also found in thiourea-dioxane (4) and in urea-trioxane compounds (5). No line was found in urea-hexadecane, nor in compounds of thiourea with carbon tetrachloride, chloroform, methylcyclohexane, cyclohexene, cyclohexanone, chlorocyclohexane, cyclooctane, and tetrahydropyran. The search was made at only one temperature and it is

quite possible that resonances may be observable at other temperatures in some of the compounds; further research is necessary to investigate this point.

EXISTENCE OF PHASE TRANSITIONS IN IC

The nitrogen-14 NQR in TCIC, from 4.2 K up to room temperature, shows three regions in the NQR spectrum (Fig. 1). To help interpret this behavior, studies using differential thermal analysis (DTA), X-ray diffraction, and NMR were undertaken. NMR was used to study the temperature dependence of the proton linewidth and relaxation time T_1 in partially deuterated samples (thiourea, d_4 -cyclohexane and thiourea-cyclohexane, d_{12}).

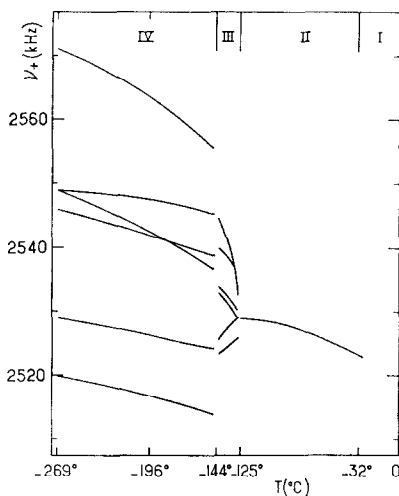


FIG. 1. Diagram of the evolution of the NQR spectrum (ν_+ lines) of nitrogen-14 in TCIC showing the different regions described in the text.

DTA in TCIC shows one endothermal peak under heating at -144°C (4), in urea-trioxane (UTIC) shows three peaks (5) and in the compounds of thiourea with cycloheptane, cyclooctane, and tetrahydropyran, cycloheptane shows no peak (6). The variations of enthalpy are rather small, of the order of 0.3 kcal/mole per guest molecule.

X-ray diffraction patterns were recorded at different temperatures with a Debye-Scherrer camera and changes in the crystal structure and parameters were detected in the compounds studied (4-6).

STUDY OF TCIC

In TCIC, several regions were characterized from the temperature dependence of the NQR spectrum (Fig. 1); DTA revealed one peak at -144°C which was confirmed by the specific heat measurements of Cope *et al.* (7); from X-ray diffraction, changes of the crystal symmetry were found at -125°C (4) and at -147°C (6). Wide-line NMR showed that motional narrowing occurs at -145°C for the protons of cyclohexane molecules and begins at about -30°C for those of thiourea molecules. From these results the following interpretation of the observed behavior was developed.

In Region II, the X-ray diagram obtained is consistent with the results of Lenné (8) who determined the space group $R\bar{3}2/c$ at room temperature; the 12 nitrogen atoms in the unit cell are equivalent and only one set of resonances is observed. Above -32°C in Region I, the hindered rotation of the molecules of thiourea around the $\text{S}=\text{C}$ direction prevents the observation of the resonance. Regions I and II correspond to the same crystallographic phase. At -125°C a change in crystal symmetry occurs which affects the X-ray diffraction pattern and changes the NQR spectrum. The absence of any DTA peak at this temperature suggests that the transition is of second order. The irregularity of the position of the multiple NQR lines previously observed

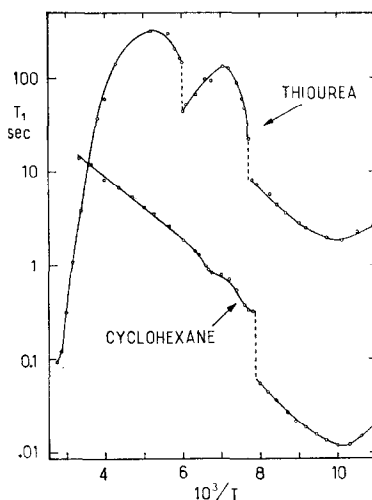


FIG. 2. Temperature dependence of relaxation time T_1 for protons of both thiourea and cyclohexane molecules in TCIC; logarithm of T_1 is plotted as a function of $10^3/T$.

in Phase III just below -125°C (4) should be attributed to their weakness and to insufficient stability of temperature during the experiment. Recent measurements with temperature control indicate that it is possible to follow six lines in this phase (Fig. 1). At -144°C , a DTA peak indicates a phase transition which can be related to the deformation of the crystal observed by X-ray diffraction (6). This is also consistent with the change of the linewidth of the NMR of the cyclohexane protons. Below -144°C , six NQR lines are also seen in Fig. 1 instead of the five previously reported due to the fact that two lines, crossing at -269 and -196°C , remained unresolved.

A study of the temperature dependence of the proton relaxation time T_1 led to the curves shown in Fig. 2. The transition at -144°C appears as a change of the proton T_1 for both host and guest molecules. The transition temperature is not exactly the same for both compounds, a known effect of deuteration which changes transition temperatures significantly. Below the transition, both curves are "parallel" and probably the same motion relaxes both sorts of protons. The existence of a minimum suggests that the motion is activated thermally and the experimental points may be fitted by a curve constructed with a single correlation time. Above the transition, no

major change is seen on the curve corresponding to the cyclohexane protons; a small dip appears at -125°C .

On the other hand, there is a discontinuity in the curve corresponding to thiourea protons at -106°C . At this temperature, a peak in the specific heat curve has been reported (7). The origin of the discontinuity in the proton T_1 is not clear because no effect is seen in the temperature dependence of the NQR frequencies of the nitrogen atom to which protons are bound.

STUDY OF UTIC

The nitrogen-14 NQR spectrum in UTIC was studied from -140 to $+10^{\circ}\text{C}$ where the lines disappear (Fig. 3). There are two ν_+ lines, unlike TCIC between -125 and -32°C , where only one ν_+ line is seen, which is puzzling because the crystal structure of both compounds seems to belong to the same space group $R\bar{3}2/c$ (8, 9). However,

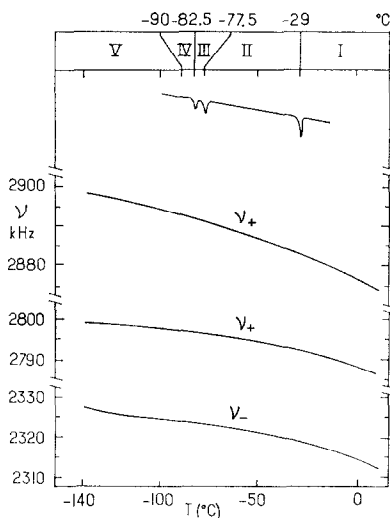


FIG. 3. Behavior of UTIC under variation of temperature: the different regions observed; temperature dependence of the observed NQR spectrum in UTIC; and DTA curve for urea, d_4 -trioxane.

the existence of an inversion center is not demonstrated in the case of UTIC (9). The frequencies in UTIC vary smoothly. The disappearance of the lines at $+10^{\circ}\text{C}$ is probably due to the hindered rotation of the urea molecules about the $\text{C}=\text{O}$ direction. DTA shows three endothermic peaks under heating at -84.5 , -72 , and -30°C (Fig. 3). By deuteration of urea these temperatures are changed and become -82.5 , -77.5 , and -29°C . Examination of X-ray patterns of urea, d_4 -trioxane, recorded at different temperatures shows that above -29°C diffraction spots given by a crystal rotated around its c -axis are consistent with the rhombohedral structure described by Lenné (9). Below this temperature, new diffraction spots are observed and the pattern may be indexed with a monoclinic cell, the dimensions of which are very close to those derived from the rhombohedral cell. No change is observed at the temperature of the two DTA peaks occurring at -77.5 and -82.5°C . At still lower temperatures a modification

is found in which the crystal contracts along the *b* direction and expands along the *a* direction, while parameter *c* remains unchanged.

The proton NMR of the trioxane molecules, between -196°C and room temperature, shows a motional narrowing of the resonance line occurring in three steps (Fig. 4). The first step begins at -150°C , where no DTA peak was recorded, the second at -77°C and the third at -29°C . Considering the temperature dependence of the proton relaxation time T_1 , changes in the relaxation time or in the slope of the curve are seen at the temperature of two DTA peaks, at -29 and -77.5°C , and at the temperature of the transition found by X-ray diffraction at -90°C . Discussion of the values of the second moment of the NMR line of the trioxane protons leads to a model (10) in which

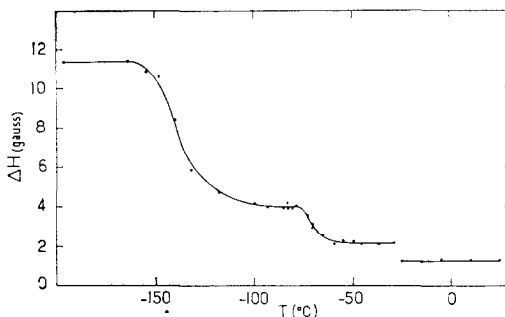


FIG. 4. Variation with temperature of the linewidth of trioxane protons in urea- d_4 -trioxane.

trioxane molecules are at rest below -150°C ; more precisely, the value of the second moment above -150°C is consistent with a reorientation of the trioxane molecules about the axis of the channel, provided the plane of the molecules makes an angle of ca. 25° with the plane perpendicular to the axis of the channel. Such an inclination of the plane of the molecule was already suggested by Cope *et al.* (7) in the case of TCIC and is quite consistent with the "volume" occupied by the molecule as defined from the Van der Waals radii of the constituting atoms. As the NQR spectrum does not change significantly between -140°C and $+10^{\circ}\text{C}$, DTA peaks are thought to be due to modifications of the lattice formed by guest molecules.

CONCLUDING COMMENTS

Study of IC by different methods is a very rich field of investigation and the presence of two sorts of molecules, rather loosely bound to each other in a system in which the host lattice itself cannot be formed without any guest molecule inside its channel, leads to various modifications of the molecular arrangement as the temperature is varied. Plain crystallographic phase transitions of first or second order, as characterized by changes in the X-ray diffraction patterns, are observed as well as the onset of molecular motions which are detected by their effect on NMR and NQR spectra. An extensive study has been made of UTIC and TCIC for which general description and interpretation of the behavior observed are given.

It also may be said that during the course of this work a new IC was prepared, namely the thiourea-ferrocene IC (11).

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