

^2H NMR Studies of Dynamics of Channel-Type Solids

Qiaoying Li

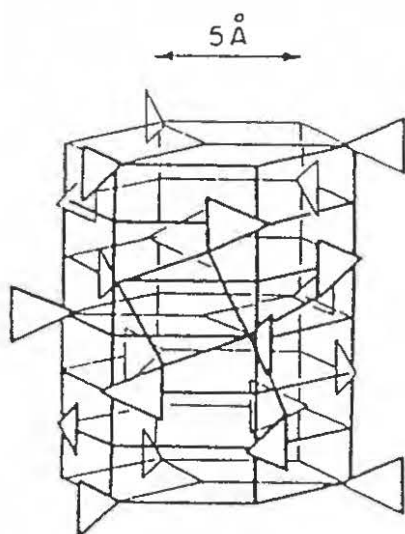
Literature Seminar

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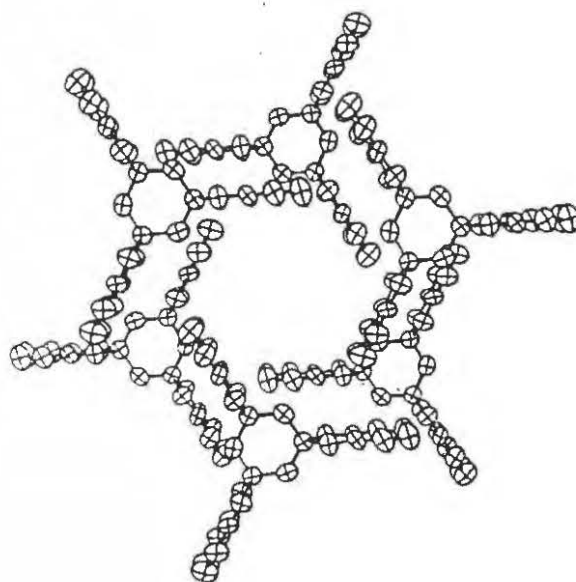
Compared to the NMR spectroscopy of the more common nucleus ^1H , ^2H has the drawbacks of low abundance, low gyromagnetic ratio, and a quadrupolar spin 1. For many years it was a "much maligned magneton"; a landmark article by Diehlor and Leipert in 1964 [1] showed however that ^2H NMR spectroscopy can be very useful in the study of structure and dynamics. With the advent and availability of high-sensitivity FT-NMR spectrometer, the number of ^2H NMR studies of solids have grown rapidly with applications in chemistry, biology and physics [2].

The deuterium nucleus possesses a quadrupole moment as a result of having a spin of 1. The quadrupolar interaction perturbs Zeeman levels, giving two NMR transitions. In the solid state this quadrupolar interaction strongly influences the line shape and relaxation properties of ^2H resonance since the intrinsic anisotropic motions in the solid states prevent complete averaging. Usually these motions occur at rates of $1-10^6$ Hz, just of the right range to affect the ^2H NMR spectra. Thus both the type and rate of motion can be deduced by line shape analysis of the ^2H NMR signal [3].

One class of dynamic solid state materials are inclusion compounds [4], where guest molecules are trapped within cavities or channels. Also of interest are zeolites [5] in which small organic molecules can be sorbed by a three-dimension network of channels. Within the channels the guest molecules exhibit



Channel Formed
Thiourea



Channel Formed by
Cyclophosphazene

various motions as temperature is varied. ^2H NMR spectra have provided detailed information about the nature of motions, the conformations of guest molecules, and geometric features of both guest molecules and host lattice [6]. These effects can be evidenced in the following three examples.

The first is that ^2H NMR spectra of powder sample of thiourea-cyclohexane inclusion compound (TC1C) [6a] changes dramatically in the range 129-345 K. The spectra are interpreted in terms of cyclohexane becoming engaged gradually in various uncoupled dynamic modes and undergoing several conformational alternations. At the lowest temperatures, chair-form conformers prevail; the cyclohexane rings are in an upright position within the channels; with the triad axis z' parallel to the channel axis d , about which they spin rapidly. At 137 K the cyclohexane molecules tip over suddenly so that z' becomes tilted at an averaged angle δ relative to d with onset of nonuniform reorientation about d . Over the next 125 K the reorientation of cyclohexane changes gradually with δ determined to an accuracy of $\pm 1.5^\circ$. It is also found that at 159 K the motion about d becomes uniform and an increase of about 2° in the angle between the axial and equatorial C-D bonds. At about 240 K, rapid ring inversion is observed. The second case is cyclophosphazene (CPZ)-*o*-xylene- d_{12} inclusion compound [6c], ^2H NMR study showed that the rate of motion of *o*-xylene remains rapid throughout the temperature range of 175-380 K, but its averaged symmetry decreases from C_{3v} to C_{2v} at about 308 K. Considerable wobbling of the molecular C_2 symmetry axis about d and a distortion of the benzene ring from a perfect hexagon occur at low temperature. The third example is the small organic molecules (*p*-xylene- d_6 , toluene- d_3 , and benzene- d_6) sorbed by zeolite ZSM-5 [6g], ^2H NMR spectra showed that intracrystalline molecular motions are less restricted with the smaller guest molecules at the order of benzene < toluene < *p*-xylene. These results can be used to characterize the molecular sieve effect. For example, a preferred *p*-xylene in the straight channels has been observed, which tends to support the theory of molecular traffic control.

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