Mobility of acetone confined in zeolite nanocages revealed by means of deuteron NMR spectroscopy

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Studies of molecular mobility are among classical applications of NMR spectroscopy. The molecular motion shapes the NMR spectra, making the nuclear spin interactions time dependent, and introducing different degrees of spectral averaging within the constraints imposed by the transformation properties of the respective nuclear spin Hamiltonians. The choice of deuterons as spin probes, characterized by a much stronger quadrupole interaction with suitable one-particle transformation properties, guarantees more success, when compared to protons.

The doublet with the separation \( \delta = (3/4)C_Q \), where \( C_Q \) is the quadrupole coupling constant, and asymmetry parameter \( \eta = 0 \), is observed for immobile deuterons. Uniaxial rotation of molecular groups e.g. methyl groups or ammonium ions, provides characteristic spectra under condition \( \delta \tau_c < 1 \), thus for correlation times \( \tau_c < 10^{-6} \) s. Threefold rotation provides the doublet with \( \delta = (1/4)C_Q \). Exchange (π-jumps) about the twofold symmetry axis of e.g. ammonium ion or water molecule, yields spectrum characterized by \( \eta = 1 \) [1]. Thus jumps of deuterons with axially symmetric quadrupole interaction may yield a spectrum with \( \eta \neq 0 \). This observation guides our study, as such spectra were obtained for \((\text{CD}_3)_2\text{CO}\) and ND₃ confined in cages of zeolites at low temperature.

As a model system we take two methyl groups (immobile or rotating), performing jumps with an amplitude \( \phi \) on a cone with the opening angle \( \Theta \) between threefold axes. Spectra were calculated using WEBLAB package conveniently available via internet [2]. Spectra in a wide range of angles provide a basis for fits to experimentally obtained ones. The angle \( \Theta \) equals 58° for \((\text{CD}_3)_2\text{CO}\), and with jump amplitude \( \phi = 42° \) we get a good fit to the spectrum at 20 K for 86 molecules per unit cell in NaX zeolite with rotating methyl groups. Except of such torsional jumps about the twofold axis of acetone, also oscillations by 66.7° of the molecular plane appear on increasing temperature. Further on also oscillations by 79.5° about the axis perpendicular to the molecular plane are evidenced.

Stepwise appearance of respective spectral components and their relative contributions observed for NaX and NaY zeolites allow to point out differences in acetone bonding and local structures. Acetone appears on Lewis acid sites, where the carboxyl oxygen of acetone interacts with the Al atom of the zeolite framework, and a coordination adsorption complex is created. Such geometry dominates in the case of NaX and NaY. Molecular reorientations and their activation energy as well as temperature \( T_S \) (below \( T_S \) all molecules become localized) indicate on stronger interaction of acetone with Lewis sites in the case of NaY.

Keywords: zeolite; deuteron NMR; molecular dynamics; acetone

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References