Dynamics of hydroxyl deuterons and bonded water molecules in NaDY(0.8) zeolite as studied by means of deuteron NMR spectroscopy and relaxation

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ABSTRACT

Deuteron spin–lattice relaxation and spectra were measured for NaDY (0.8) zeolite containing some heavy water. Two subsystems of deuterons with different mobility were disclosed at low temperatures with their respective relaxation rates differing by two orders of magnitude. Spectra exhibit different shapes related directly to a specific motional model. Hydroxyl deuterons perform incoherent tunneling along the hydrogen bond, then on increasing temperature jumps to excited states and over the barrier appear. Hydrogen bonded water molecules perform 180° rotational jumps about the twofold symmetry axis. Spectral amplitudes are consistent with the water content of 13 D_2O molecules per unit cell. Above about 240 K translational mobility becomes significant and finally water molecules diffuse across the free space of cages. Diversity in temperature dependence of hydroxyl deuteron dynamics may indicate location of adsorbed molecules.

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1. Introduction

Zeolites are porous inorganic crystals basically with the atomic formula TO_2, where the oxygens are arranged tetrahedrally around the central atom T (T represents silicon or aluminum atoms in the more common zeolites). Zeolite Y of the faujasite type has a well defined pore system. The supercages of 1.16 nm inner diameter are interconnected by 12-oxygen rings of 0.74 nm diameter. Moreover, there are also smaller sodalite cages of inner diameter of 0.66 nm connected to supercages by windows of 0.25 nm diameter formed by 6-oxygen rings. The unit cell of Y zeolite consists of eight supercages and eight sodalite cages and contains 192 T atoms and 384 oxygen atoms [1].

Hydroxyl protons in zeolite HY are attached to oxygens bridging tetrahedrally coordinated silicon and aluminum atoms. These protons compensate the negative framework charges introduced by tetrahedrally coordinated aluminums, alternatively the same role is played by sodium cations. Thus OH groups are named as structural or bridging OH groups (SiOHAl). In real crystals some imperfections can be found in a form of silanol (SiOH) groups or OH groups associated with some extra-framework aluminum species [2].

The unit cell of zeolite Y contains 384 oxygen atoms at four crystallographically inequivalent positions from O1 to O4. One can therefore expect four different types of bridging hydroxyl groups with protons at the positions from H1 to H4. The protons H1 and H4 point into supercages while the protons H2 and H3 are directed towards the 6-oxygen rings. Czjzek et al. [3] used neutron diffraction to determine the following abundances of protons at respective positions in the unit cell: $n(1)=28.6$, $n(2)=9.5$ and $n(3)=15$ in zeolite HY (Si/Al=2.4). No H4 protons were detected. The positions H1 and H3 are occupied preferentially and that confirms the results of quantum mechanical calculations [4,5].

Surface hydroxyl groups were studied extensively by NMR methods in pioneering works in Leipzig already during 1970s [6,7]. More recent reviews by Brunner [8] and Hunger [9] provide a good overview of the state of art in this field with a lot of references. Surface hydroxyl groups can be characterized by various NMR parameters: chemical shift, abundance, dipolar broadening and quadrupole parameters in case of deuterons.

^{1}H MAS NMR spectra of HY zeolite consists of three dominating lines: (i) at 1.9 ppm due to non-acidic hydroxyl groups at framework defects, (ii) at 3.9 ppm from bridging OH groups involving O1 atoms in supercages, and (iii) at 4.9 ppm from protons on O3 atoms pointing into the sodalite cage [10]. The dipolar interaction between the H and Al nuclei contributes to the width of [27]Al spectra and allows the determination of the

corresponding distance, 0.238 nm [11]. The proton chemical shift and the corresponding deuterium quadrupole coupling constant both depend on the structure and chemical bonds. A formula relating them was derived [12] and analyzed in terms of the bond polarization theory [13]. Also an earlier study by means of the quadrupole resonance indicates that the deuteron quadrupole coupling constant is a sensitive probe of slight structure changes in the high pressure ice forms. A dependence of the quadrupole coupling constant on the square of the OD stretching frequency as well as on the OD bond length was derived [14].

It seems obvious that studying hydroxyl groups by ^{2}H MAS NMR would be advantageous. Surprisingly, there are only a few related papers published already some time ago [15]. The quadrupole coupling constant about 236 kHz was obtained for bridging hydroxyl groups from the corresponding doublet in the spectrum indicating static positions of deuterons at room temperature [2,16]. Narrow components were attributed to some defects, such as silanol groups. That means that deuteron spectroscopy does not discriminate between the O1D and O3D bridging hydroxyl groups. MAS NMR studies give evidence for a mobility of acidic protons at temperatures above 500 K [17,18]. Proton mobility in zeolites was extensively studied [19]. A wide range of barriers was obtained for on-site proton jumps depending on the separation of Brønsted sites in zeolites considered, e.g. 61 kJ/mol for HY. The results are consistent with theoretical estimations [20].

Neutron diffraction studies indicate that the deuterium at O3 will be affected first by water molecules at low water content [21]. Moreover, one may expect in sodalite cages clusters of water molecules, hydrogen-bonded with each other as well as with the framework oxygens. Thus it becomes possible that also hydroxonium ions can be formed [22,23].

Deuterons can be used instead of protons to increase the dynamic range accessible by NMR spectroscopy. The deuteron quadrupole coupling constant is two orders of magnitude larger than the dipole-dipole coupling constant for protons. Moreover, the quadrupole interaction is a one-spin interaction which makes it easier to specify the symmetry of reorientational jumps. Since the quadrupole interaction depends on the value of the electric field gradient at the position of deuteron, its value reflects differences in binding [24,25]. The quadrupole coupling constant for D_2O depends on the state of matter and equals 318.6 kHz in gas phase, about 230 kHz in liquid phase, and 216–225 kHz in solids [26, and references therein], and 225 kHz in ice [27]. The quadrupole coupling constant for deuterons on Si–OD–Al sites amounts to 236 kHz [28].

Infrared spectroscopy (IR) [29–31] as well as ^{1}H MAS NMR spectroscopy [8,10] allow to point out differences between hydroxyl groups in supercages and in the 6-oxygen rings. The stretching frequency of hydroxyls in sodalite cages (Si–O2H–Al and Si–O3H–Al) is lower than of those in supercages (Si–O1H–Al) because of hydrogen bonding of OH groups with oxygen atoms in sodalite cages. The concentration of both kinds of hydroxyls in zeolites NaHY at various Na/H exchange degrees was determined by quantitative IR studies of pyridine, piperidine and ammonia adsorption [32,33]. Work by Bielański and Datka revealed [32] that the concentrations of hydroxyls in supercages and sodalite cages depend on the degree of Na/H exchange. Protons introduced at low degrees of Na/H exchange were found to form hydroxyls in supercages, whereas protons introduced at high degrees of Na/H exchange formed hydroxyls in sodalite cages. It may be explained by the fact, that Na$^+$ cations inside hexagonal prisms are stabilized by six oxygens of hexagonal prism. Concentrations of hydroxyls in supercages and sodalite cages were found to be comparable [32] in the zeolite NaHY with the exchange degree of 80%. Here we are going to search for differences in mobility

between these two hydroxyl groups in the presence of a small amount of D_2O using the deuteron NMR spectroscopy.

2. Theoretical background

2.1. Spectra

The quadrupole interaction couples the quadrupole moment eQ of a deuteron to the electric field gradient (efg). The gradient at a position of a deuteron depends on the features of the chemical bond (e.g. its length). Thus, the value of the quadrupole coupling constant $C_Q = e^2qQ/h$ may be different for different substances. Deuteron spectra are particularly useful in studies of molecular mobility due to the high value of C_Q. The spectra are symmetric and composed of doublets at $\pm v_Q$. Assuming a vanishing asymmetry parameter $\eta = 0$, the doublet separation equals $2v_Q = (\frac{3}{4})C_Q|3\cos^2\Theta - 1|$, where Θ defines the angle between the principal axis of efg and the direction of the magnetic field. Such doublets are related to singularities corresponding to the orientations near $\Theta = \pi/2$ in the powder spectrum and their separation equals $(\frac{3}{4})C_Q$. The corresponding spectrum represents motionless deuterons and is commonly called "Pake doublet" (Fig. 1a).

Reorientation of deuterons makes their position time dependent and, if the reorientation frequency $\omega_\tau = 1/\tau$ is higher than C_Q, leads to averaging of the spectrum [34]. The rotation-averaged powder spectra are characterized by an effective quadrupole coupling constant $C_Q^e = (\frac{1}{2})C_Q(3\cos^2\varphi - 1)$, where φ is the angle between the rotation axis and the principal axis of efg [34]. We have calculated some deuteron spectra for such molecules, where the angle between the vectors from the central atom to deuterons equals 109.5°. For $\varphi = 70.5°$ we get $C_Q^e = -(\frac{1}{3})C_Q$ (Fig. 1c). This case refers to the threefold rotation of CD_3, D_3O^+ and ND_4^+, which all have a similar tetrahedral structure [35–37]. The sign of C_Q^e indicates its orientation in the molecular reference
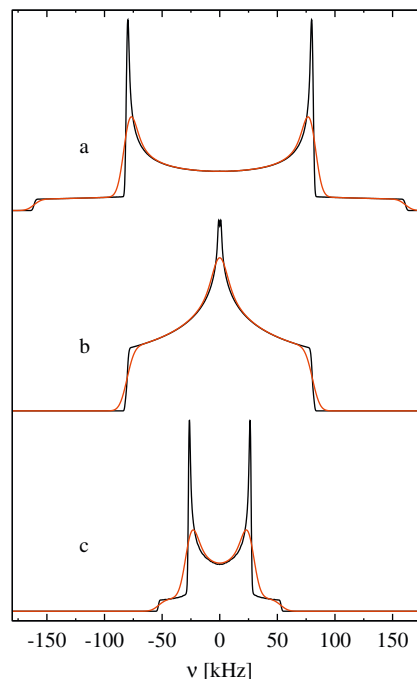

Fig. 1. Simulated deuteron NMR powder spectra in case of: (a) motionless deuteron, (b) π- jumps about the twofold symmetry axis, and (c) $(2\pi/3)$- jumps about the threefold axis. The spectra were calculated with $C_Q = 215$ kHz using the Gaussian broadening 0.5 kHz. The thicker curve shows spectra with the 5 kHz broadening, used when analyzing experimental results.