

Observation of the Fundamental Bending Vibrations of Hydroxyl Groups in HNa–Y Zeolite by Neutron Inelastic Scattering¹

Since hydroxyl groups are primary Brønsted acidic sites in zeolites, much effort has been spent to determine the location and strength of these sites. Infrared spectroscopy is still the technique used most often and numerous studies have been reported on the stretching vibrations of the O–H bonds (e.g., Ref. (1)). It is now assumed that the band at $\sim 3750\text{ cm}^{-1}$ is due to silanol groups and that the bands at around 3650 and 3550 cm^{-1} correspond to bridged OH groups located respectively in the supercages and in the sodalite cages. The other vibrations of the O–H bonds, namely the in-plane (δ) and out-of-plane (γ) deformations, cannot be measured by transmission infrared because of strong absorption bands due to the framework below 1200 cm^{-1} . In-plane bending vibrations of OH groups have, however, been derived from overtones and combination bands by diffuse reflectance spectroscopy, taking into account anharmonicity (2). These bending modes, which occur in the range $700\text{--}1100\text{ cm}^{-1}$, were found to be more sensitive to the structure and composition of the zeolites than the stretching modes.

The two types of OH group deformations can be measured by neutron inelastic scattering (NIS) because of the high sensitivity of this technique toward hydrogen motions (3). NIS spectra of sodium and decationated Y zeolite are reported here and the $\delta(\text{OH})$ and $\gamma(\text{OH})$ modes are derived from a comparison of the two spectra.

The neutron experiments were performed at the Institut Laue-Langevin using the beryllium-filter detector spectrometer INFB.

¹ The experimental work was performed at the Institut Laue-Langevin, Grenoble, France.

The incident energy was varied stepwise in the range $200\text{--}2000\text{ cm}^{-1}$, using a Cu (220) monochromator. The frequency values given in this paper have been corrected from a systematic shift due to the beryllium filter (4); the estimated precision is $\pm 15\text{ cm}^{-1}$. The instrumental resolution varies with the incident energy E_0 ; it can be approximated by polynomial functions in energy and $\Delta E/E_0$ is of the order of 5%. A better resolution can be obtained with this spectrometer (5) but at a cost of a factor of about 10 in the peak signal intensity. The zeolites were contained in cylindrical aluminum containers and placed in a helium cryostat. Large quantities of zeolite were used because probe molecules were subsequently adsorbed on the two samples (6).

The initial Na–Y zeolite was obtained from the Linde Company (LZ-Y52) and the nominal composition was $\text{Na}_{56}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}$. A first sample was prepared by placing the powder on a series of 20 stainless-steel platelets, in a quartz reactor, the aluminum container being connected to the bottom of the reactor. The zeolite was calcined at 720 K under flowing oxygen (rate of temperature increase: 5 K/min) and evacuated at the same temperature to 10^{-4} Pa with a cryopump. The zeolite was dropped in the aluminum container under vacuum and separated from the reactor with a torch. A large quantity of dehydrated zeolite (49 g) could be prepared in this way.

The starting material was ion exchanged using an aqueous solution of NH_4Cl and carefully washed with distilled water. The degree of exchange was determined by flame spectrometric analysis of the residual sodium. After drying in air at 350 K , the HNa–Y zeolite was calcined at 630 K under

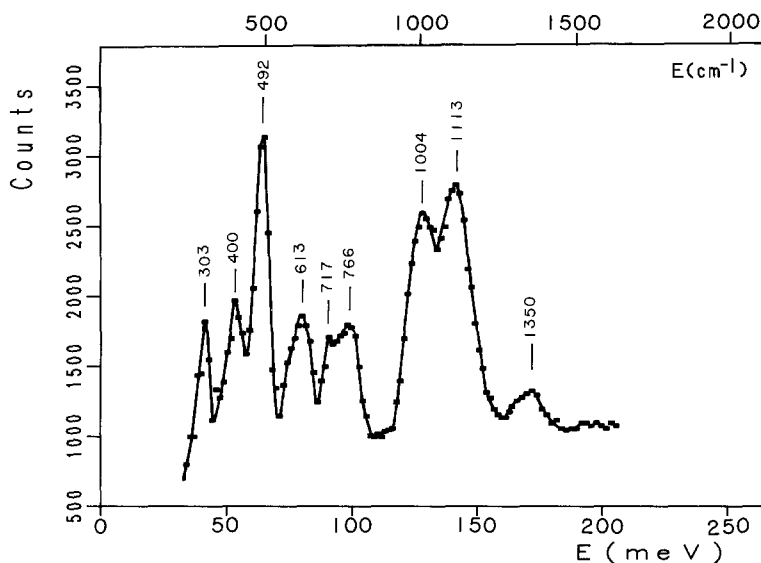


FIG. 1. Neutron inelastic scattering (NIS) spectrum of Na-Y at 20 K. The values within the figure are the peak frequencies in cm^{-1} ; they have been corrected, as have the energy scale for wavenumbers, from the experimental frequency shift.

flowing oxygen (rate of temperature increase: 0.2 K/min) and outgassed at the same temperature. The thickness of a powder layer was ~ 4 mm, to avoid aluminum extraction as much as possible. After the thermal treatment, 33 g of zeolite were transferred to the aluminum container. The composition of the dehydrated zeolite was found to be $\text{H}_{44}\text{Na}_{12}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}$.

The NIS spectra of Na-Y and HNa-Y are shown in Figs. 1 and 2, respectively. The spectrum of an empty container has been subtracted in each case. For Na-Y, however, some coherent Bragg scattering occurs at small energy transfers (longer wavelengths) and this might change slightly the relative intensities of the first peaks in Fig. 1. The spectra were recorded at 20 ± 10 K because they were used as backgrounds to study the vibrational modes of adsorbed molecules. Very low temperatures are needed in this case to reduce the high dynamical disorder which has been measured for molecules chemisorbed in zeolites (7, 8). It has been found in this work that the temperature dependence of the NIS intensi-

ties is much smaller for the zeolite than for adsorbed molecules, because the mean-square amplitude is lower for all atoms, including hydrogen in HNa-Y zeolite.

The NIS and infrared spectra of Na-Y are very similar and contain about 10 peaks (the small peak at 1350 cm^{-1} in Fig. 1 cannot yet be assigned to a fundamental or multiphonon feature). There is, however, an important difference between the two methods: some vibrational modes are inactive in infrared whereas in NIS one measures the vibrational density of states weighted by the scattering cross sections and by the atomic displacements (9, 10). The NIS spectra could therefore be used in future as more stringent tests of the framework frequency calculations. These calculations (11-14) have shown that the early assignment (15) in terms of internal and external vibrations of Al_2SiO_4 tetrahedra is still useful, although most of the modes are delocalized.

The NIS spectrum of HNa-Y zeolite (Fig. 2) has a much higher signal intensity, when compared to Na-Y, because of the large incoherent cross section of hydrogen. The

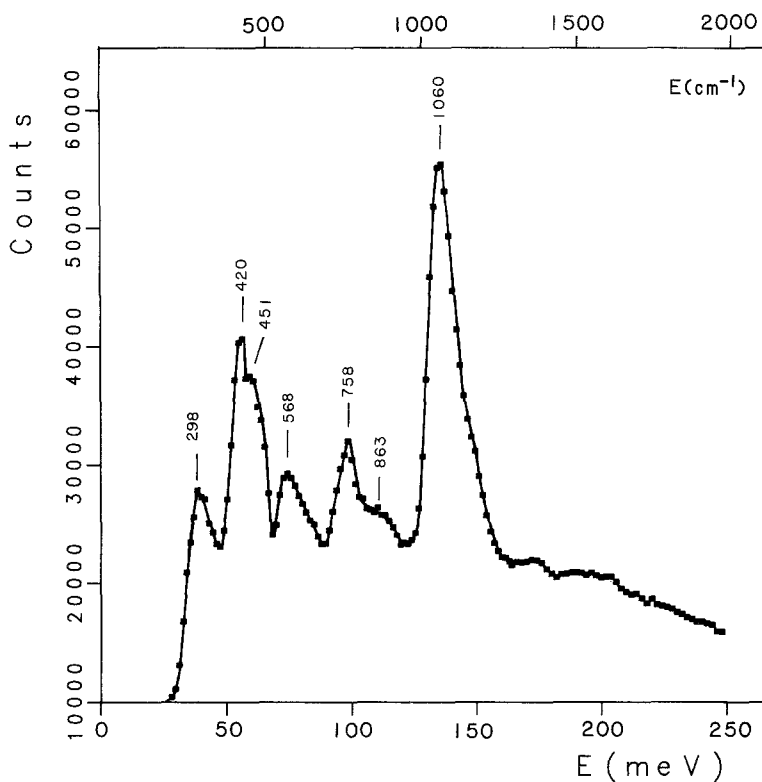


FIG. 2. NIS spectrum of HNa-Y obtained at 20 K. Designations of peaks as in Fig. 1.

framework vibrations also appear in the spectrum of HNa-Y because for these framework modes, the hydrogen atoms will "ride" on the oxygen atoms, receiving an appreciable displacement with respect to the center of mass. The lattice vibrations in HNa-Y are, however, modified in shape and position compared with Na-Y: some peaks are shifted down in frequency (e.g., 568/613 cm^{-1} and 451-492 cm^{-1}) and the spectrum is greatly changed around 750 cm^{-1} . A full interpretation of these modifications requires precise calculations of the vibrational density of states. The downward shift of some modes is in agreement with the computed weakening of the [Si-O-Al] bond upon bonding by a proton (16). Three new features are found in Fig. 2, when compared to Fig. 1, at 1060, 863, and 420 cm^{-1} . The peak at 1060 cm^{-1} is assigned to the $\delta(\text{OH})$ modes of the bridged hydroxyls in the su-

perages and in the small cavities. Since these modes are localized, their frequency can be compared to the data obtained by diffuse reflectance spectroscopy, namely 1015 and 1055 cm^{-1} (2); these two frequencies are not resolved in the NIS spectrum. The NIS frequencies and intensities can often be derived from a normal coordinate analysis (8-10), but such a calculation is not a useful test for the assignment of hydroxyl group frequencies since for any given assignment a set of force constants can always be found. The small peak at 863 cm^{-1} is assigned to the $\delta(\text{OH})$ mode of silanol groups (a frequency of 825 cm^{-1} has been previously measured for this mode in Ref. (2)). The fact that this band at 863 cm^{-1} is not observed with Na-Y indicates that during the thermal treatment of the decationated zeolite some defects or extra-framework phase is produced. This has also been

found by magic-angle-spinning (MAS) nmr in H-Y zeolites (17). One of the advantages of NIS is that the integrated intensities of the bands can yield the relative amount of a given species, as in nmr. The amount of nonacidic O-H groups, relative to the bridged hydroxyl groups, is, however, difficult to evaluate here because the $\delta(\text{OH})$ modes of the bridged hydroxyls overlap with strong peaks of the framework; it can be estimated to $20 \pm 10\%$. This important proportion could be due to the large quantity of zeolite treated, resulting in self-steaming. The peak at 420 cm^{-1} , in Fig. 2, is assigned to the $\gamma(\text{OH})$ modes of the bridged hydroxyls; it is comparable in frequency to what has been measured for the out-of-plane deformation of H in transition metal clusters. This value of 420 cm^{-1} is exactly the same as the one which has been derived from recent quantum chemical calculations (18). It is also found that the quantity of residual NH_4^+ is negligible in our sample since there is no peak in Fig. 2 in the range $1350\text{--}1700 \text{ cm}^{-1}$, where one expects the bending vibrations of NH_4^+ .

In a recent neutron scattering study of zeolite Rho, features similar to those observed here were reported (19), but the assignment was different. Peaks at 1150 and 1060 cm^{-1} were assigned to $\delta(\text{OH})$ and $\gamma(\text{OH})$, respectively, and a large peak at 360 cm^{-1} was not accounted for; it was later suggested that the last peak corresponded to $\gamma(\text{OH})$ (18).

Finally, it is well known that zeolite acidity cannot be defined only from the stretching vibrations of O-H bonds (1, 20-22). Other parameters must be taken into account and one of them is proton mobility which is best measured by nmr (23, 24). Measurement of this mobility was attempted in zeolite Rho by quasi-elastic neutron scattering (19) but no proton diffusion could be measured with the result that only an upper limit could be given for the diffusion coefficient ($4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). We have also previously observed that the mobility of hydrogen is too slow to be measured on

the neutron time scale ($10^{-12}\text{--}10^{-9} \text{ s}$), and using a better instrumental resolution we have found that proton diffusion in different zeolites (e.g., Ref. (25)) was lower than $10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The mobility of adsorbed molecules can, however, be determined by this technique (25, 26) and good agreement has been obtained with pulsed field gradient nmr (27).

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