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Published in:
Chemical Physics Letters

DOI:
10.1016/0009-2614(93)E1334-D

Citation for published version (APA):
DOI: 10.1016/0009-2614(93)E1334-D

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Hydrogen bonding in acidic zeolites observed by time-resolved vibrational spectroscopy

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Received 9 July 1993; in final form 8 November 1993

With time-resolved vibrational spectroscopy new information is obtained about the structural environment and vibrational dynamics of acidic hydroxyls in proton loaded zeolites. From O-H vibrational population lifetimes of zeolite Y we conclude that part of the protons are hydrogen bonded. Furthermore we find that the vibrational dynamics of the O-H oscillators are influenced by a resonant coupling mechanism.

1. Introduction

Solid acids, like hydrogen exchanged zeolites, are widely applied as hydrocarbon conversion catalysts in the petrochemical industry [1]. The protons that are covalently bonded to bridging oxygen atoms in the structure form acidic Bronsted sites. The dynamical physical and chemical interactions of the protons with the zeolitic lattice are of interest in understanding the catalytic properties of these sites. We have studied the relaxation of vibrationally excited O-H groups in several zeolites with picosecond infrared saturation spectroscopy [2,3].

Previously, Casassa et al. [4] reported a vibrational relaxation experiment on O–H in zeolite ZSM-5. In that experiment the zeolite was saturated with CCl₄ which might have influenced the vibrational dynamics. Excited population lifetimes of O–H in a zeolite Y and in a mordenite were presented recently [5]. We show that from an extensive study on vibrational population lifetimes of O–H in different zeolites new information can be obtained about the interactions of the hydroxyls with the proton loaded zeolitic framework.

With conventional infrared spectroscopy two O–H stretch absorption bands are observed for zeolite Y. We present the first conclusive evidence that the protons in the low-frequency (LF) band are hydrogen bonded to other lattice oxygen atoms, while those in the high-frequency (HF) band are not. Furthermore we find that the vibrational lifetimes decrease with increasing proton concentration, and that this is caused by a (nearly) resonant deactivation mechanism like dipole–dipole coupling.

2. Zeolite Y

The highly symmetric structure of zeolite Y is depicted schematically in fig. 1 (see also ref. [6]). When silicon is substituted by aluminum, charge compensation is needed, and this is provided by Na⁺ cations in the interstices of the structure. Proton loaded zeolites were obtained by heating in vacuo (at least 1 h at 723 K) zeolites in which (part of) the Na⁺ cations were exchanged by NH₄⁺ cations. All T sites (T=Si or Al) in zeolite Y are crystallographically equivalent, so there are at most four different oxygen atoms around an aluminum atom to which in principle a proton can be covalently bonded, as is indicated in the smaller pictures in fig. 1. We have studied proton loaded zeolites Y with silicon to
Fig. 1. Schematic representation of the faujasite structure of zeolite Y. The corners denote the positions of the T atoms (T = Si or Al), and the lines represent the bridging oxygen atoms. For clarity the hidden lines are not shown (see ref. \[61\] for a more extensive picture). The small pictures show the 4 different positions of the protons that are covalently bonded to the oxygen atoms around an aluminum atom (\(O\)). The Na\(^+\) cations (if present) are located in the cavities of the structure.

Fig. 2. Conventional room temperature infrared absorption spectra of three zeolites Y, \((\cdots)\) HY/0.27, \((\cdots)\) (Na) HY/0.22, \((\cdots\cdots)\) NaHY/0.07. Two distinct peaks arising from acidic hydroxyl groups at high frequency (HF) and at low frequency (LF) are observed.

aluminum ratios of Si/Al = 2.4 and 2.8 and various degrees of Na\(^+\)/H\(^+\) exchange. The samples used in the experiments presented in this Letter were self-supported discs of 3.5 to 6 mg/cm\(^2\) \[7,8\].

The conventional room-temperature infrared absorption spectra around the O–H stretch frequency were obtained with Fourier-transform infrared spectroscopy \[7,8\]. Absorption spectra for three of the zeolites Y we studied are shown in fig. 2. The spectra show three distinct peaks near 3550, 3640 and 3745 cm\(^{-1}\), respectively (the exact absorption peak positions and widths are denoted in table 1). The absorption band at 3745 cm\(^{-1}\) is assigned to a silanol group (\(=\text{Si–OH}\)) at the external surface of the zeolite particle, the other bands arise from the internal acidic hydroxyl groups (\(=\text{Si–OH}–\text{Al}\)) \[9\]. The low-frequency band is attributed to protons on O\(_{3}\) and O\(_{2}\), whereas the HF band arises from protons on O\(_{1}\) \[9,10\]. The NH\(^+_2\) ions are more easily introduced into the supercages which leads to different relative intensities of LF and HF absorption bands for zeolites with different degrees of exchange.

3. Time-resolved experiments

We have measured O–H vibrational population relaxation times \(T_1\) for both LF and HF absorption bands of zeolites Y (samples at room temperature), using intense picosecond tunable infrared pulses \[11,12\]. A 20 ps infrared pulse, typically 220 \(\mu\)J and wavelength tunable in the O–H absorption region, is split into a strong (99%) pump pulse and a weak (1%) probe pulse that are both focused onto the same spot on the sample (the experimental setup was described previously \[12\]). The pump pulse excites a significant fraction (\(\approx 10\%\)) of the O–H oscillators to the first excited vibrational level (\(v=1\)) thereby bleaching the sample for the laser frequency because less oscillators are available for absorption. The decay of the pump-induced transparency, which reflects the decay of the excited population difference between \(v=1\) and \(v=0\), is probed by monitoring the transmitted probe intensity as a function of time delay with respect to the pump pulse. The energy relaxation time \(T_1\) can be deduced from this decay: \(\ln (T(t)/T_0) \approx \exp (-t/T_1)\), where \(T(t)\) is the transmitted energy of the probe pulse at delay \(t\) and \(T_0\) is the transmitted probe energy in absence of the pump pulse. In fig. 3 the results of typical pump-probe experiments are shown for the LF and HF absorption bands of zeolites NaHY/0.07 and HY/0.27 (the number in the sample identifiers indicates the ratio of hydrogen to T atoms). Note that the LF population lifetimes are significantly smaller than the HF lifetimes and that in zeolite HY/0.27 the O–H stretch vibrations relax faster than in NaHY/0.07.

From the results of an extensive study on both zeolites, summarized in table 1, it is inferred that the
Table 1
Maxima and linewidths of O–H absorption bands and corresponding vibrational lifetimes (samples at room temperature) 

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al</th>
<th>Band</th>
<th>$v_{\text{max}}$ (cm$^{-1}$)</th>
<th>$\Delta v$ (cm$^{-1}$)</th>
<th>$T_1$ (ps)</th>
<th>$T_1/T_1^\text{RF}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHY/0.07</td>
<td>2.8</td>
<td>LF</td>
<td>3558</td>
<td>37</td>
<td>105±18</td>
<td>2.58±0.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HF</td>
<td>3645</td>
<td>19</td>
<td>296±13</td>
<td>1.29±0.06</td>
</tr>
<tr>
<td>(Na)HY/0.22</td>
<td>2.4</td>
<td>LF</td>
<td>3548</td>
<td>57</td>
<td>42±8</td>
<td>1.16±0.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HF</td>
<td>3646</td>
<td>16</td>
<td>223±23</td>
<td>1.03±0.11</td>
</tr>
<tr>
<td>HY/0.27</td>
<td>2.8</td>
<td>LF</td>
<td>3549</td>
<td>53</td>
<td>35±4</td>
<td>1.00±0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HF</td>
<td>3637</td>
<td>24</td>
<td>198±16</td>
<td>0.97±0.08</td>
</tr>
</tbody>
</table>

a) Kubota et al. reported lifetimes of $T_1^\text{LF} = 63 ± 14$ ps and $T_1^\text{HF} = 180 ± 12$ ps for a proton loaded zeolite Y with Si/Al = 5.6 [5].

b) Full width at half maximum of the absorption bands (fig. 2).

c) The errors in $T_1$ represent sample to sample variations obtained from several experiments.

population lifetimes $T_1$ are much longer than expected from the absorption linewidths. A lifetime of 100 ps corresponds to a bandwidth of 0.05 cm$^{-1}$, so the much larger absorption linewidths observed in fig. 2 (see also table 1) are not determined by $T_1$, but rather by dephasing and/or inhomogeneous broadening. Therefore vibrational lifetimes of zeolites cannot be measured in the frequency domain but must be determined by time-resolved measurements.

Scanning the laser frequency through the LF absorption band we found that $T_1^\text{LF}$ increases with frequency, as shown in fig. 4. Although the large laser bandwidth (34 cm$^{-1}$ full width at half maximum at 3600 cm$^{-1}$) means that the observed relaxation times are convolutions of $T_1$ times at frequencies within the laser bandwidth, a strong dependence is observed. No frequency dependence was found for $T_1^\text{HF}$.

4. Hydrogen bonding

The shorter vibrational lifetimes of the LF protons with respect to the HF protons (table 1) cannot be explained by relaxation to different vibrational modes. Vibrational relaxation of an O–H oscillator in a dense medium occurs by coupling to accepting modes for which the sum of the energies is in resonance with the O–H vibration. The process with the smallest number of accepting modes dominates the relaxation rate [13,14]. All oxygen atoms bridge the T atoms in zeolite Y in a very similar way (they can only be distinguished by looking at the larger cavity structures, see fig. 1), so the nearby bonding structure is almost identical for all O atoms. In addition, the frequency difference between LF and HF absorption peaks ($\approx 100$ cm$^{-1}$) is small compared to both the frequencies of the accepting modes ($\approx 1000$ cm$^{-1}$ [7,15,16]) and the width of the compound density of states at the O–H frequency that arises from the broad accepting modes. Hence the LF and HF vibrations couple to very similar accepting modes and nearly identical $T_1$ lifetimes would be expected.

We propose that the difference between $T_1^\text{LF}$ and $T_1^\text{HF}$ must be explained by hydrogen bonding of the LF protons in zeolite Y. Hydrogen bonding of the O–H oscillator, which decreases the O–H frequency [17], increases the coupling to the accepting modes and thus decreases the vibrational lifetime [13,14]. In crystalline micas a similar decrease in O–H vibrational lifetimes was found for absorption bands that were shifted to lower frequency (equivalent to our LF peak) due to hydrogen bonding [18]. For zeolites the coupling strengths are not known, so our experiments call for a theory to make a quantitative comparison of vibrational lifetimes possible.

In addition to $T_1^\text{LF}$ being shorter than $T_1^\text{HF}$, the shorter lifetimes are found at the lower frequencies within the LF absorption band (fig. 4). This is what one expects for the more strongly H-bonded O–H oscillators and is analogous to a similar observation in fused silica [19]. A stronger H bond weakens the original O–H bond more and as a consequence the frequency of that bond will be shifted to a lower frequency, while at the same time $T_1$ will be shorter due to a larger coupling. Thus by scanning the laser fre-
Fig. 3. Relative transmission of an infrared probe pulse \( \ln(T/T_0) \) (\( T_0 \) is the transmitted probe energy in absence of the pump pulse) as function of the delay between pump and probe pulses for zeolite NaHY/0.07 (upper panel) and HY/0.27 (lower panel), for the laser frequency tuned to the maxima of the LF and the HF absorption bands. The values for the fitted energy decay times \( T_1 \) (and the corresponding standard deviations) and \( \nu_{\text{laser}} \) are for the upper panel: (●) \( \nu_{\text{laser}} = 3643 \text{ cm}^{-1} \), \( T_1 = 289(6) \text{ ps} \); (○) \( \nu_{\text{laser}} = 3560 \text{ cm}^{-1} \), \( T_1 = 124(9) \text{ ps} \); for the lower panel, (●) \( \nu_{\text{laser}} = 3637 \text{ cm}^{-1} \), \( T_1 = 201(2) \text{ ps} \); (○) \( \nu_{\text{laser}} = 3549 \text{ cm}^{-1} \), \( T_1 = 36(1) \text{ ps} \).

Fig. 4. Frequency dependence of \( T_1 \) when the laser is scanned over the LF absorption bands (fig. 2) for the three zeolites (×) NaHY/0.07, (□) (Na)HY/0.22, (●) HY/0.27. The x-axis denotes the detuning of the top of the laser band from the maximum of the LF absorption band. The error bars represent sample to sample variations.

plains why, while having a smaller O–H stretch frequency, the LF protons are less acid than the HF protons [20,22]. It is also in agreement with the larger O–H distances for the LF hydroxyls [9] and with the presence of two close oxygen neighbours at 2.6 Å for the LF protons [9,23]. For the zeolite mordenite (Si/Al=7), which has a single absorption band around 3610 cm\(^{-1}\) [24,25], we found a similar frequency dependent \( T_1 \) around 110 ps, which suggests hydrogen bonding in this zeolite as well.

5. Resonant coupling

The (absolute) \( T_1 \) lifetimes in table 1 suggest a dependence on the proton concentration, but might be due to differences in absorbed energy densities. Experiments with varying exciting laser powers and repetition rates (normally 10 Hz) showed that considerable heating in the laser focus due to many laser pulses affects the vibrational lifetimes. Increases in temperature up to 250 K in the laser focus were estimated [26]. To be able to compare vibrational lifetimes at different proton concentrations, we measured both \( T_1^\text{HF} \) and \( T_1^\text{HF} \) for zeolite HY/0.27 as function of absorbed pulse energy density. These dependences now provide a reference lifetime \( T_1^\text{HF} \) at every absorbed energy density. The lifetimes in table
Table 2
Absolute and relative O-H vibrational lifetimes for deuterated versions of zeolite HY/0.27)

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>D/H + D b)</th>
<th>Band</th>
<th>$T_1$ (ps)</th>
<th>$T_1/T_1^\text{ref}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HY/0.27</td>
<td>0</td>
<td>LF</td>
<td>35 ± 4</td>
<td>1.00 ± 0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HF</td>
<td>198 ± 16</td>
<td>0.97 ± 0.08</td>
</tr>
<tr>
<td>DHY/0.15</td>
<td>0.45 ± 0.05</td>
<td>LF</td>
<td>45 ± 8</td>
<td>1.25 ± 0.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HF</td>
<td>273 ± 27</td>
<td>1.24 ± 0.12</td>
</tr>
<tr>
<td>DHY/0.05</td>
<td>0.81 ± 0.05</td>
<td>LF</td>
<td>59 ± 9</td>
<td>1.53 ± 0.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HF</td>
<td>358 ± 32</td>
<td>1.42 ± 0.13</td>
</tr>
</tbody>
</table>

a) The protons were exchanged by deuterons by keeping the proton loaded zeolite samples for several hours at 700 K in D₂ gas.
b) Relative concentration of deuterons as obtained from O-H and O-D stretch absorption intensities.

The $T_1$ lifetimes are scaled by these reference lifetimes, so that the resulting values $T_1/T_1^\text{ref}$ do not depend on laser-induced temperature increases and can be compared directly.

After correction for laser heating, the $T_1$ lifetimes of NaHY/0.07, which has the lowest proton concentration, are still significantly longer than the $T_1$ of HY/0.27 (table 1). To check whether this is caused either by changes in chemical bonds or by a (nearly) resonant coupling mechanism between O-H oscillators, we decreased the proton concentration in zeolite HY/0.27 by partial deuteration. To correct for laser heating effects, the $T_1$ lifetimes again are scaled by lifetimes of the undeuterated zeolite at the same absorbed energy density ($T_1^\text{ref}$). As can be seen in table 2 the O-H vibrational lifetimes increase upon the introduction of O-D stretch absorptions.

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Acknowledgement

We would like to thank J.H.M.C. van Wolput, A. Bot, and M.P. van Albada for fruitful discussions, and E.J. Kossen for technical assistance. The work described in this paper is part of the research program of the Stichting Fundamenteel Onderzoek van de Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Research).

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