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# Enhancement of the vibrational relaxation rate of surface hydroxyls through hydrogen bonds with adsorbates

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## Abstract

With time-resolved (picosecond) infrared saturation spectroscopy new information is obtained about the interaction of zeolite surface hydroxyls with small adsorbed molecules. It is found that the presence of the adsorbate, which is weakly hydrogen bonded to the zeolite hydroxyl, causes the vibrational lifetime of the zeolite hydroxyl to decrease. Remarkably, this enhancement of the de-excitation is neither due to energy transfer to internal degrees of freedom of the adsorbed species nor into a one-photon desorption process. Rather, it is due to an increased coupling of the hydroxyl stretching mode to its accepting modes.

## 1. Introduction

Zeolites, also known as molecular sieves, are crystalline aluminosilicates with large internal surfaces due to the presence of microscopic channels and pores. They have cation exchange capacity, and when H<sup>+</sup>-exchanged they are solid acids. These acidic zeolites are widely applied in hydrocarbon conversion reactions in the petrochemical industry [1]. Their acidity is due to Brønsted catalytically active hydroxyl (O–H) groups, located between a silicon and an aluminum atom, pointing into the zeolite cavity.

Knowledge of the interaction between the Brønsted catalytic sites in the zeolite and adsorbed species is essential for a fundamental understanding of zeolite catalysis. Time-resolved (picosecond) infrared spectroscopy has been proven to be a powerful tool in the investigation of the vibrational dynamics of the condensed phase in general [2] and the zeolite hydroxyl in particular [3–7]. In these pump–probe experiments, the O–H stretch vibration under investigation is satu-

rated by an intense picosecond infrared laser (pump) pulse. The return to equilibrium is then monitored by the transmission of a weaker pulse, the probe pulse. From these experiments the vibrational lifetime  $T_1$  can be obtained. This lifetime cannot be obtained through conventional infrared spectroscopy, since the width of the absorption band is determined by inhomogeneous broadening and/or dephasing. Here, we present new measurements on the lifetime of the zeolite hydroxyl stretching mode with small molecules adsorbed.

## 2. Experimental

We investigated the vibrational lifetimes of hydroxyls in two zeolites: Y and mordenite. The zeolite samples consist of pressed self-supporting crystalline zeolite discs of 5 mg/cm<sup>2</sup>. Acid forms of zeolites were obtained by in vacuo heating (1 h at 743 K) of mordenite in which Na<sup>+</sup> cations were exchanged by NH<sub>4</sub><sup>+</sup> cations. The mordenite under investigation was spec-

ified by Si/Al and H/T (T=Si or Al) atomic ratios of 6.7 and 0.13, respectively. For the partially exchanged zeolite Y, Si/Al= 2.8 and H/T= 0.07. In some of the experiments the zeolite hydroxyls were deuterated by exposing the zeolite disc to 500 mbar of D<sub>2</sub> gas (Messer Griesheim, 99.7%) at 693 K and allowing exchange for 1 h, resulting in approximately 70% exchange as observed from the absorption spectra. Spectra were recorded using a Perkin-Elmer 881 double beam IR spectrometer. Adsorption of argon, oxygen, nitrogen and methane was performed at 100 K at pressures ranging from 200 mbar to 2 bar.

For the experiments intense ( $\approx 100 \mu\text{J}$ ) picosecond (27 ps) tunable infrared (2200–4500  $\text{cm}^{-1}$ ) pulses are generated by parametric downconversion of 1064 nm Nd:YAG pulses in LiNbO<sub>3</sub> crystals (an extensive description of the experimental setup can be found in Ref. [8]). The spectral width of the infrared pulses is 10  $\text{cm}^{-1}$  at O–D stretch frequencies and 30  $\text{cm}^{-1}$  at O–H frequencies. A pulse is split into a pump pulse (99%) and a weak probe pulse (1%). In the pump-probe experiment a considerable fraction ( $\approx 10\%$ – $20\%$ ) of the hydroxyl oscillators are excited from their  $\nu = 0$  to  $\nu = 1$  vibrational state by the pump pulse tuned to the hydroxyl absorption frequency. Due to a large anharmonicity (the O–H  $\nu = 1 \rightarrow 2$  absorption is shifted by about 100  $\text{cm}^{-1}$  from the  $\nu = 0 \rightarrow 1$  absorption [5,9]) the excited O–H ( $\nu = 1$ ) cannot absorb the pump light. This results in a bleaching of the hydroxyl absorption on a picosecond time scale, i.e. the transmission for light at this frequency through the sample is increased temporarily. Hence the equilibration of the excited population can be monitored by measuring the transmission of a weak probe pulse whose time delay with respect to the pump-pulse can be varied. The decay of the pump-induced transparency is related to the vibrational lifetime of the excitation  $T_1$ :  $\ln[T(t)/T_0] \sim \exp(-t/T_1)$ , 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 principle, only a two-colour experiment directly yields the population lifetime of the excited vibrational mode. In these experiments, the  $\nu = 1 \rightarrow 2$  transient absorption is monitored after excitation of  $\nu = 0 \rightarrow 1$ . With two-colour infrared pump-probe experiments, it has been shown for a zeolite hydroxyl that the lifetimes thus obtained are equal to those obtained from

the one-colour experiment [5]. Furthermore, it has recently been found that the decay of the so-called ‘accepting modes’, which are excited upon de-excitation of the O–H stretching mode, is relatively very fast, confirming the idea that the decay from  $\nu = 1$  to  $\nu = 0$  is effectively direct [10].

### 3. Results

A downshift of the O–D absorption frequency occurs upon adsorption of argon, nitrogen, oxygen and methane on D-mordenite at 100 K (Fig. 1a). This is caused by a weakening of the original O–D bond due

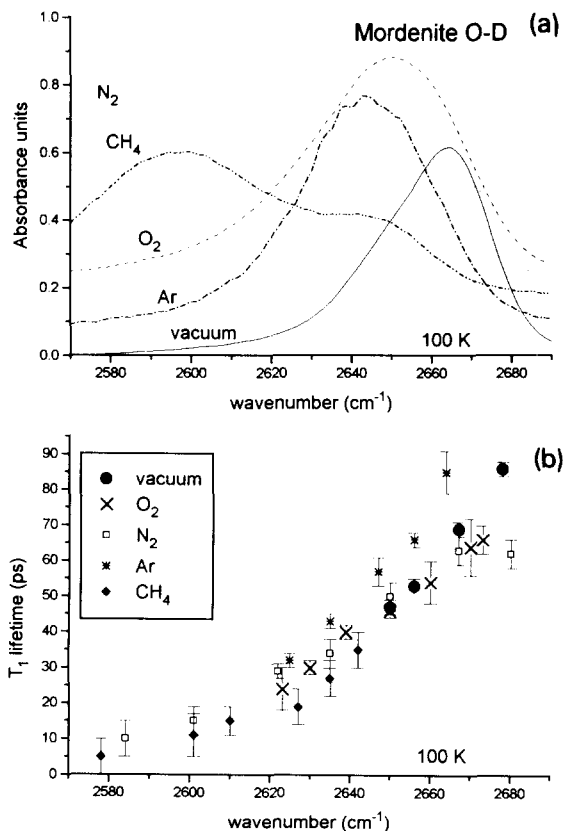


Fig. 1. (a) Absorption spectra in the O–D stretch region of mordenite O–D in vacuum and with several molecules adsorbed. All spectra were recorded at 100 K. Note the shift to lower frequencies on adsorption. (b) The vibrational lifetime  $T_1$  as a function of laser frequency for mordenite O–D with and without adsorption.  $T_1$  is found to increase with frequency. The laser bandwidth with Gaussian shape has a full width at half maximum of 10  $\text{cm}^{-1}$ . Error bars denote  $\pm 2\sigma$ .

to the presence of the hydrogen bond between the hydroxyl deuteron and the adsorbed species [11]. Note that upon  $N_2$  and  $CH_4$  adsorption two distinctive peaks appear: a low-frequency peak due to the perturbed species, i.e. hydroxyls at which adsorption is occurring, and the residue of the non-perturbed species, on which no adsorption takes place, at higher frequencies.

Two typical results of pump-probe experiments for the case of  $N_2$  adsorption are depicted in Fig. 2. For the unperturbed O–D groups ( $\tilde{\nu} = 2667 \text{ cm}^{-1}$ ),  $T_1$  times are equal to those found for the O–D in vacuum ( $T_1 = 60(4) \text{ ps}$ ). The hydrogen bonded species ( $\tilde{\nu} = 2592 \text{ cm}^{-1}$ ), are found to relax faster ( $T_1 = 10(6) \text{ ps}$ ), and an *increased* transmission after vibrational relaxation is observed. In Fig. 1b the results of the pump-probe experiments are summarized: the vibrational lifetime decreases continuously with decreasing frequency, and the lifetime is hardly dependent on the species adsorbed. The lifetimes were obtained by numerically solving the appropriate differential equations [12], that simultaneously account for population excitation and relaxation (multiple absorption steps are allowed). For lifetimes shorter than the pulse duration, an accurate estimate of the lifetime can be ob-

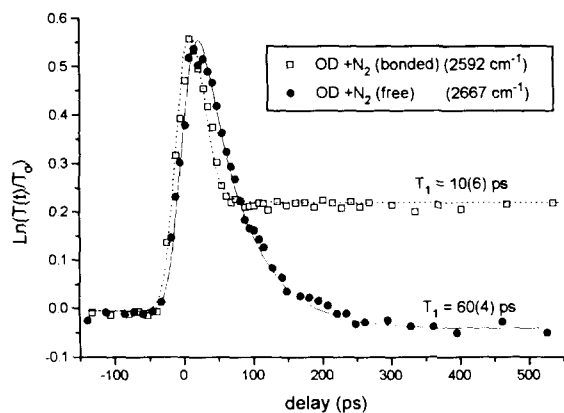


Fig. 2. Results of pump-probe experiments at two different laser frequencies of a mordenite sample with  $N_2$  adsorbed (dashed line in Fig. 1a). Relative transmission of an infrared probe pulse  $\ln|T(t)/T_0|$  ( $T_0$  is the transmitted probe energy in absence of the pump pulse) as a function of the delay between pump and probe pulses. The values for the fitted energy decay times  $T_1$  (and the corresponding standard deviations) were obtained by numerically solving the appropriate differential rate equations (see Ref. [12], the results of which are shown as lines in the figure). The vibrational relaxation time is found to drop dramatically upon hydrogen-bonding and for the hydrogen-bonded species an increased transmission is observed after relaxation.

tained from the width and magnitude of the signal.

Also, we adsorbed  $N_2$  on the so-called HF (high-frequency) hydroxyls in zeolite Na/HY. In zeolite Y there are two types of hydroxyls, with distinctly separated absorption bands (Fig. 3a). The low-frequency (LF) hydroxyls are situated in the small cages, whereas the HF sites are situated in the large super cages [13]. In the partially exchanged sample used here, mostly HF oscillators are present (Fig. 3a). Coincidentally, adsorption of  $N_2$  on the HF hydroxyls shifts the HF oscillator frequency to that of the LF hydroxyls [6]. The absorption spectra and results of time-resolved measurements for the vacuum sample

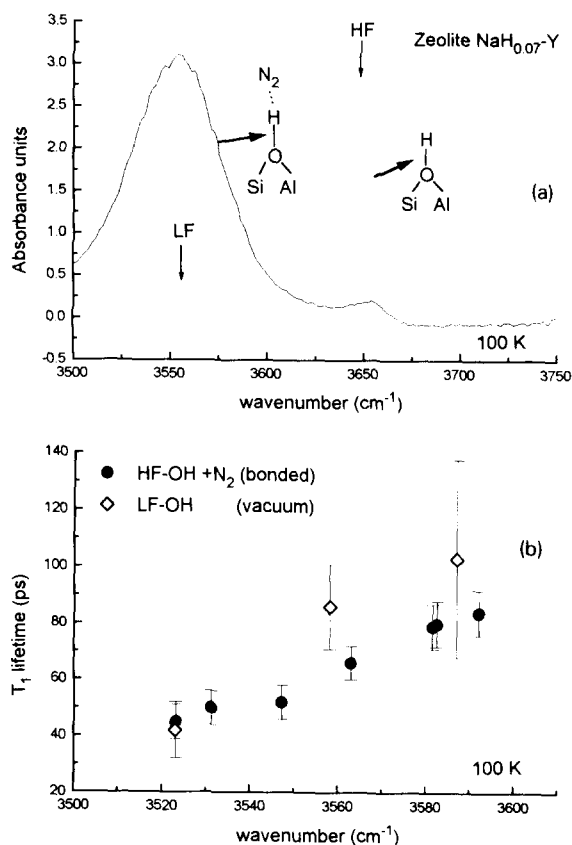


Fig. 3. (a) Absorption spectrum for the O–H region of zeolite  $NaH_{0.07}Y$  (dotted line). Due to the low level of exchange, mainly HF hydroxyls are present. Upon adsorption of  $N_2$  the absorption band shifts to lower frequencies, coinciding with the LF absorption band (solid line). (b) Vibrational lifetimes for the vacuum LF species and the hydrogen-bonded HF species, both absorbing at the same frequency. The lifetimes and the dependence thereof on frequency are very similar. Note the different frequency axes in the two figures.

and the sample with  $N_2$  adsorbed are shown in Figs. 3a and 3b, respectively. Upon adsorption of  $N_2$ , the lifetimes of the HF hydroxyls decrease by over a factor of three and perfectly coincide with the lifetime of the vacuum LF hydroxyls.

#### 4. Energy transfer mechanisms

From picosecond transmission measurements on ethanol dissolved in  $CCl_4$ , it was found that the breaking of hydrogen bonds is an effective relaxation channel for the vibrationally excited ethanol hydroxyl [14]. Whereas the monomeric O–H stretching mode exhibited a  $T_1$  lifetime of 70 ps, the hydrogen-bonded ethanol showed a lifetime of 5 ps. Also, a fast re-association of the hydrogen bond was observed with a time constant of 20 ps. This is possible in liquid ethanol, due to the high density of molecules. In the zeolite, however, one would expect re-association to take longer, due to the lower density of the adsorbates. In our experiments, an increased transmission after complete vibrational relaxation as shown in Fig. 2 was observed for all hydroxyls to which a molecule was adsorbed. In principle, this could be due to desorption of the adsorbed species upon vibrational relaxation of the hydroxyl, i.e. a breaking of the hydrogen bond as observed for ethanol (for nitrogen, the heat of adsorption on the zeolite hydroxyl is  $1000 \text{ cm}^{-1}/\text{bond}$ , i.e. about one third of the vibrational quantum [15]). If desorption were to take place upon vibrational relaxation, the oscillator frequency would shift back to its unperturbed value. Hence, the hydroxyl would no longer absorb light at the laser frequency, since the oscillator frequency would be shifted out of the laser band. This could account for the observed increase in transmission after relaxation (Fig. 2). On the other hand, it has been shown recently that upon vibrational relaxation of zeolite hydroxyls, the excess O–D stretch energy becomes delocalized very rapidly (within 10 ps), culminating in an effective heating of the zeolite lattice [10]. As hydrogen bonds are very sensitive to temperature changes, this could also be the cause of the increased transmission after vibrational relaxation. To check whether the transmission offset is due to a *direct* one-photon desorption process or *indirect* desorption due to ultrafast heating, we performed the experiment with decreasing pump energy. Whereas

the  $T_1$  times are independent of the pump energy, with decreasing pump energy, and consequently less heating of the zeolite, relaxation of the transmission to the original equilibrium transmission occurs as shown in Fig. 4. This rules out the possibility of one-photon desorption: the magnitude of the signal is proportional to the number of excited oscillators and the offset proportional to the number of shifted oscillators. In case of one-photon desorption one would expect the ratio of the two to be independent of the pump energy. The desorption we observe is thermal and indirect, due to rapid delocalization of the excess energy [10]. Thus we conclude that, in contrast to liquid ethanol, dissociation of the hydrogen bond does not occur upon relaxation of the vibrationally excited oscillator.

In principle the internal low-frequency modes of the adsorbed molecule could act as accepting modes. In this case the relaxation rate would depend critically on the exact internal low-frequency mode distribution of the adsorbed species. We observe, however, that the lifetime is hardly dependent on the adsorbed species (Fig. 1b, only for Ar the lifetimes seem somewhat larger). This leads us to conclude that there is no direct energy flow from the excited hydroxyl into internal degrees of freedom of the adsorbed molecule: If specific modes of the adsorbed molecules would act as accepting modes, one would expect different lifetimes for different adsorbates, contrary to what is observed. So, only the *magnitude* of the perturbation of the oscillator by the hydrogen bond determines the relax-

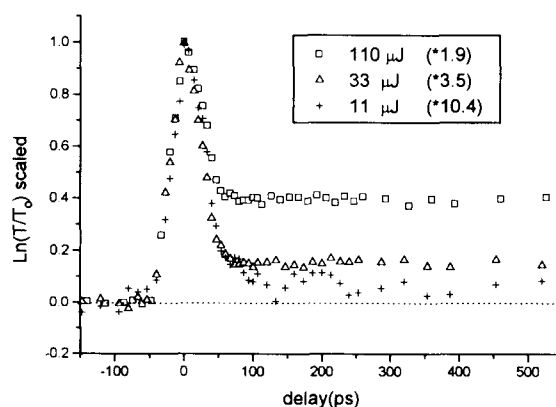


Fig. 4. Three pump-probe experiments for  $N_2$ -perturbed oscillators in D-mordenite with different pump energies. The signals are scaled to 1, with scaling factors indicated in graph. With decreasing pump energy, relaxation to original transmission occurs.

ation rate, and not the specific characteristics of the adsorbed species. This is corroborated by the finding that the N<sub>2</sub>-perturbed HF oscillators in the Y zeolite show the same lifetimes as the vacuum LF species absorbing at the same frequency: In Ref. [7] it was shown that in vacuum the LF hydroxyls are already hydrogen bonded to oxygen lattice atoms. So also here, the vibrational relaxation rate is determined by the magnitude of the perturbation, independent of whether the perturbation is due to zeolite lattice oxygen or molecular nitrogen.

From the above, it is clear that the presence of the adsorbate does not create any new pathways for the vibrational energy to flow into. Therefore, we conclude that the faster vibrational relaxation must be due to an increased coupling between the zeolite hydroxyl and its accepting modes. This enhanced coupling can, on the one hand, be interpreted as an energy mismatch compensation by *minor* energy flow into the hydrogen bond. Upon vibrational relaxation, the vibrational energy is redistributed over the accepting modes. If the sum of energies of these accepting modes is not in resonance with the vibrational quantum, vibrational relaxation will take longer. The possible energy mismatch could be compensated by minor energy flow into the hydrogen bond, into which a wider range of energies can be dissipated with increasing hydrogen bond strength. This interpretation was used to explain and model the solvent-dependent vibrational relaxation rate of the C–H stretching mode of small organic molecules [16].

On the other hand, this enhanced coupling can also be viewed as an increase of the anharmonic interaction between the hydroxyl stretch vibration and the accepting modes, increasing with increasing hydrogen bond strength [7]. In a recent thorough investigation of O–H relaxation in Y zeolites in vacuum with time-resolved spectroscopy, it was concluded that hydrogen bonding of the zeolite hydroxyl to lattice oxygen atoms enhances the coupling to accepting modes, resulting in a faster decay [7]. The experiments described here corroborate this finding. We observe a large increase in the vibrational relaxation rate upon adsorption, and find that the effect of the adsorbate on the vibrational relaxation process is to increase the coupling: despite the presence of the adsorbate, the bulk of the energy is still dissipated over the lattice, albeit faster. The presence of the adsorbate does not

create any new relaxation channels; the hydrogen bond remains intact and no energy is transferred to the adsorbate itself.

## 5. Conclusion

We have succeeded in measuring the lifetimes of surface hydroxyls in zeolites perturbed by small adsorbates. The decay is more rapid for the hydrogen-bonded hydroxyls, but independent of adsorbate. We find no evidence for energy transfer processes between the zeolite hydroxyl and the adsorbate, or energy flow into the hydrogen bond. We therefore conclude that the enhancement of the vibrational relaxation rate is due to an increase in the coupling between the hydroxyl and the zeolite lattice.

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