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*Citation for published version (APA):*
Bonn, M., Brugmans, M. J. P., Kleyn, A. W., & Santen, van, R. A. (1995). Fast energy delocalization upon vibrational relaxation of a deuterated zeolite surface hydroxyl. *Chemical Physics*, *102*(5), 2181-2185. https://doi.org/10.1063/1.468740

*DOI:*
10.1063/1.468740

*Document status and date:*
Published: 01/01/1995

*Document Version:*
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

*Please check the document version of this publication:*

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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# Fast energy delocalization upon vibrational relaxation of a deuterated zeolite surface hydroxyl

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(Received 20 June 1994; accepted 25 October 1994)

In this time-resolved study of vibrational dynamics of deuterated surface hydroxyls at acid sites in the zeolite Mordenite, we investigate the O–D $\mathbf{T_1}$ vibrational lifetime and transient band shifts. It is shown that after infrared excitation of the stretching mode of a surface hydroxyl, the excess energy is rapidly distributed over delocalized low-energy lattice modes upon de-excitation. This is asserted from the observation that nonexcited hydroxyls are perturbed by the relaxation of their excited counterparts immediately after this relaxation. This observation can be made owing to better resolution in transient transmission spectroscopy obtained by deuteration of the surface hydroxyls. This assignment allows for accurate estimates of lattice temperatures after relaxation of the vibration. Further, from the observation that the vibrational lifetime is dependent on frequency (increasing from 25 to 70 ps with increasing frequency), it is concluded that the deuterated acidic protons are hydrogen bonded to lattice oxygen atoms in the zeolite. © *1995 American Institute of Physics.*

## I. INTRODUCTION

Vibrational energy transfer processes have been extensively studied during the past decades. In the gas phase, substantial information has been obtained on the (re)distribution of vibrational energy and energy decay routes.[1] In the condensed phase however, a lot of questions still remain unresolved due to the short time scales involved and the fact that this information in general cannot be obtained from measurements in the frequency domain. Time-resolved (picosecond) infrared spectroscopy has thus been proven a powerful tool in the investigation of the vibrational dynamics of solids in general[2] and the zeolite hydroxyl in particular.[3–6] In these pump–probe experiments the vibration under investigation is saturated 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 $\mathbf{T_1}$ can be obtained.

Zeolites, also known as molecular sieves, are crystalline alumino-silicates with large internal surfaces due to the presence of microscopic channels and pores. They have cation exchange capacity, and when $H^+$ exchanged they are solid acids. These acidic zeolites are widely applied in hydrocarbon conversion reactions in the petrochemical industry. Their acidity is due to Brønsted catalytically active hydroxyl (O–H) groups, located between a silicon and an aluminum atom on the surface, pointing into the zeolite cavity. The relations between reactivity, acidity, infrared absorption frequency, and the local environment of the zeolite hydroxyl in the zeolite lattice have been the subject of ongoing research. For a recent review, see Ref. 7.

Here we present the results of a time resolved study on the deuterated version of the zeolite Mordenite. The vibrational lifetime of the deuterated zeolite hydroxyl cannot be obtained by conventional infrared spectroscopy, since the width of the O–D absorption band is determined by inhomogeneous broadening and/or dephasing. The vibrational lifetimes are on the order of 100 ps, corresponding to a bandwidth of 0.05 $cm^{-1}$, whereas the absorption linewidths are approximately 30 $cm^{-1}$. The zeolite under investigation here is the acidic form of the zeolite Mordenite. The structure of zeolite Mordenite is known to consist of two types of channels, composed of 12-ring cages (6.5×7.0 Å) and 8-ring cages (2.6×5.7 Å), respectively.[8] Recently, the acidity of the zeolite Mordenite has been the subject of much research.[9–14] In order to gain better insight into the dynamics of vibrational relaxation and the properties of this surface hydroxyl, we performed a time-resolved vibrational study of deuterated hydroxyls.

## II. EXPERIMENT

The zeolite samples consist of pressed self-supporting crystalline zeolite discs of 5 $mg/cm^2$. Acid forms of Mordenite were obtained by *in vacuo* heating (1 h at 743 K) of Mordenite in which $Na^+$ cations were exchanged by $NH_4^+$ cations. The Mordenite under investigation was specified by Si/Al and H/T (T=Si or Al) ratios of 6.7 and 0.13, respectively. Deuteration was achieved by exposing the zeolite disc to 500 mbar of $D_2$ gas (Messer Griesheim, 99.7%) at 693 K and allowing exchange for 1 h, resulting in approximately


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70% exchange as observed from the absorption spectra. These spectra were recorded using a Perkin–Elmer 881 double beam IR spectrometer.

For the experiments intense ($\approx$100 $\mu$J) picosecond (20 ps) tunable infrared (2200–4500 $cm^{-1}$) pulses are generated by parametric downconversion of 1064 nm Nd–YAG pulses in $LiNbO_3$ crystals (an extensive description of the experimental setup can be found in Ref. 15). 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 O–D oscillators are excited from their $v=0$ to $v=1$ vibrational state by the pump pulse tuned to the O–D absorption frequency and focused onto the sample (beam waist $\approx$0.4 mm diam). Due to large anharmonicity (the O–D $v=1\rightarrow 2$ absorption is shifted by about 100 $cm^{-1}$ from the $v=0\rightarrow 1$ absorption)[4] the excited O–D ($v=1$) cannot absorb the pump light. This results in a bleaching of the O–D absorption on a picosecond time scale, i.e., a temporary increase of transmission of light of this wavelength through the sample. Hence the equilibration of the population distribution can be monitored by measuring the transmission of the weak probe pulse whose time delay with respect to the pump pulse can be varied. The decay of the pump-induced transmission with time is related to the vibrational lifetime of the excitation $\mathbf{T_1}$, as: $\ln[T(t)/T_0]\sim\exp(-t/\mathbf{T_1})$, 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. The pump repetition rate can be regulated from 1 to 10 shots per second. The laser pulse has a bandwidth of 11 $cm^{-1}$ (full width at half-maximum, Gaussian line shape) at O–D absorption frequencies, which is three times smaller than the bandwidth at O–H frequencies. This better frequency resolution, and a reduced scattering of the laser pump light at O–D frequency as opposed to O–H, are the reasons for investigating the deuterated sample.

## III. RESULTS

In Fig. 1 the O–D stretch region of the conventional infrared absorption spectrum for deuterated Mordenite is depicted. A recent paper proposed that—similar to Y-zeolite—the absorption peak of the (deuterated) hydroxyls in Mordenite consists of two contributions: a low-frequency (LF) and a high-frequency (HF) subpeak, resulting from hydroxyls in the small 8-ring cages and in the larger 12-ring cages, respectively.[13] This decomposition was carried out for the absorption spectrum and the result (see Fig. 1) is in agreement with Ref. 13.

Three typical results of room temperature pump–probe experiments for deuterated Mordenite are shown in Fig. 2. With the laser tuned to the top of the absorption band (2662 $cm^{-1}$) the transmission was found to return to equilibrium value $T_0$ with a time constant of 55 ps [Fig. 2(a)]. If the laser frequency is tuned to the low-frequency side of the absorption band (at 2640 $cm^{-1}$), two striking changes occur in the measured decay: a decay with smaller time constant of 36 ps is found and the relative transmission $\ln[T(t)/T_0]$ is found to relax to a negative value [Fig. 2(b)]; after decay of the excited oscillators, the absorbance has increased. Contrary effects are observed on the high-frequency side of the absorption peak (at 2672 $cm^{-1}$); a larger lifetime $\mathbf{T_1}$ is observed and after relaxation an increase in transmission is detected [Fig. 2(c)]. So the experiments present us with the vibrational lifetime $T_1$ as well as an offset (level) of the transmission after vibrational relaxation.

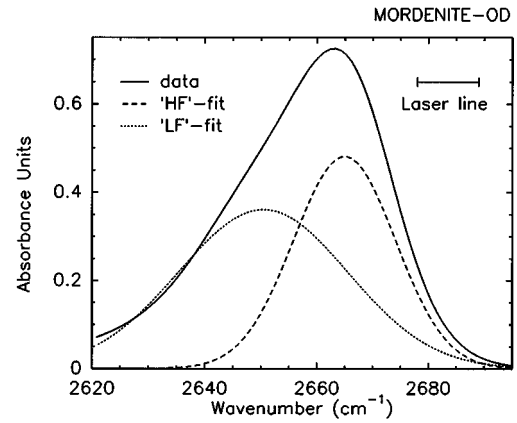


FIG. 1. Absorption spectrum for O–D absorption bands for deuterated zeolite Mordenite and the deconvolution. The LF peak is caused by deuterated hydroxyls situated in the small cages, the HF peak by deuterated hydroxyls sticking into the larger 12-ring cages. Both the LF and HF peak are represented by single Gaussian line shapes. Sum of two peaks coincide with data, except for low-frequency side of the LF peak. Bar shows FWHM of laser line.

The values for the vibrational lifetime $\mathbf{T_1}$ are obtained by numerically solving the appropriate set of coupled spatio-temporal rate equations describing the transmission of the pump pulse through the sample.[16] This renders the time-dependent population distribution of the O–D oscillators in the zeolite sample. Subsequently, the transmission of the probe pulse is evaluated numerically. The calculations need as input the pulse parameters of both pump and probe (pulse shape, duration, and intensity) and sample parameters (absorption cross section, oscillator density, and sample length). Fit parameters are the time constant $\mathbf{T_1}$ and the offset of the transmission after vibrational relaxation. To account for this offset, the number of oscillators under the laser band was allowed to change proportional to the number of deexcited oscillators, as this deexcitation is the cause of this offset. The results of the calculations are shown as solid lines in Fig. 2. Clearly, our experiments could very well be described by a simple model with (i) a single time constant accounting for population decay and (ii) the change in oscillator density according to the number of relaxed oscillators.

In Fig. 3, the vibrational lifetime $\mathbf{T_1}$ is plotted versus laser frequency through the absorption band for Mordenite. Note the continuous increase of $\mathbf{T_1}$ with frequency. These experimentally obtained $T_1$ times are essentially convolutions of the actual $T_1$'s within the laser pulse infrared bandwidth, due to the width of the laser band.

The level $L$ to which the transmission was found to relax—normalized to the magnitude of the signal (top)—is plotted versus wave number in Fig. 4. Exciting on the low-frequency side of the absorption band, the absorption is en-


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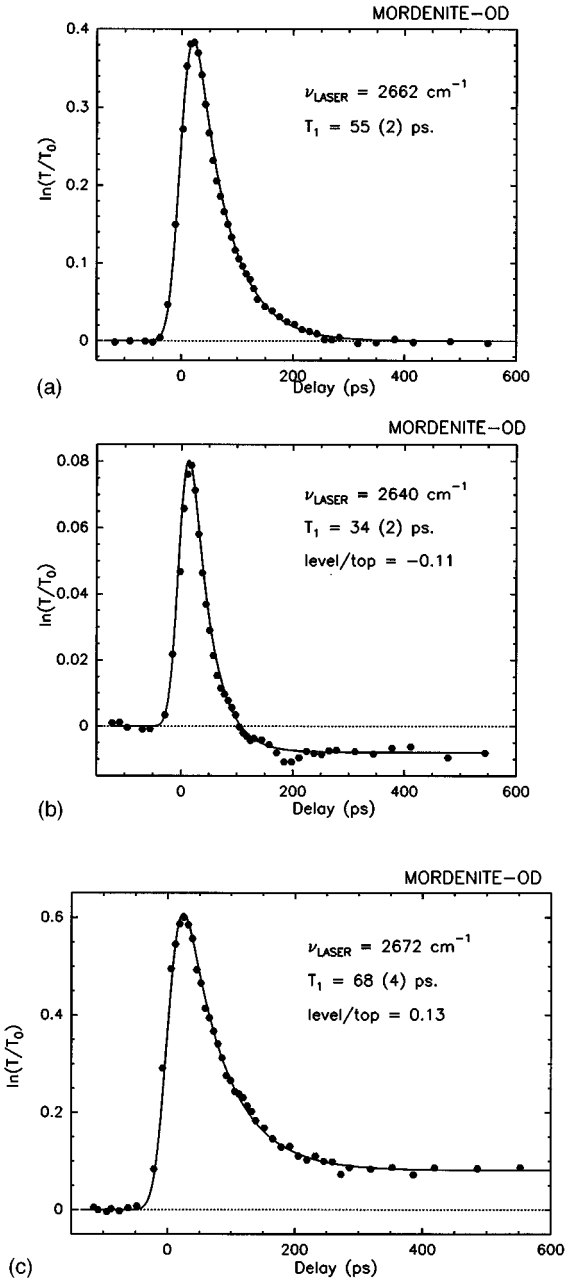


FIG. 2. Relative transmission of an infrared probe pulse $\ln[T(t)/T_0]$ ($T_0$ is the transmitted probe energy in absence of the pump pulse) as function of the delay between pump and probe pulses for zeolite Mordenite O–D at three laser frequencies; (a) top of the absorption peak (2662 cm$^{-1}$), (b) on the low-frequency side of the absorption peak (2640 cm$^{-1}$), and (c) at 2672 cm$^{-1}$. The values for the fitted energy decay times $\mathbf{T_1}$ (and the corresponding standard deviations) are denoted in the graph. The top of the absorption peak is situated at 2662 cm$^{-1}$. The vibrational relaxation time is found to be dependent on frequency.

hanced after the relaxation of excited oscillators. On the high-frequency side, there is a decrease in absorption after relaxation. This points to a redshift of the absorption peak caused by the vibrational relaxation; the absorption band is shifted towards the laser band (into resonance), with the laser at low frequencies, and shifts away from the laser at high frequencies.[17]

At this point it is important to note that there are *three*

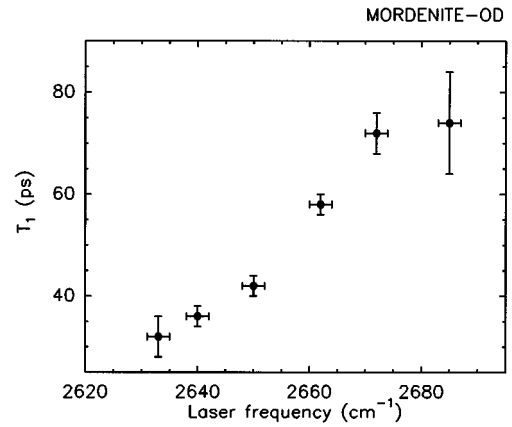


FIG. 3. The vibrational lifetime $\mathbf{T_1}$ as a function of laser frequency for Mordenite O–D. $\mathbf{T_1}$ is found to increase with frequency. Laser bandwidth with Gaussian shape has full width at half-height of 11 cm$^{-1}$. Error bars denote $\pm 2\sigma$ for average results at different experiments.

relevant time scales in the experiment: (i) the vibrational lifetime $\mathbf{T_1}$, (ii) the onset time of the level $L$, i.e., the time between vibrational relaxation and the change in transmission hereby caused [considered instantaneous in our calculations, but not necessarily so (see below)], and (iii) the slow relaxation time of this last effect (the observed offset of the transmission is constant for 1 ns after vibrational relaxation, but has faded when the next pulse pair travels through the sample (after ≈1 s). Similar double relaxation effects have been observed before for fluids,[15,28] but not in vibrational relaxation experiments on surface hydroxyls.

## IV. DISCUSSION

### A. Hydrogen bonding

The observed frequency dependence of the vibrational lifetime $\mathbf{T_1}$ in Mordenite (Fig. 3) could have two probable

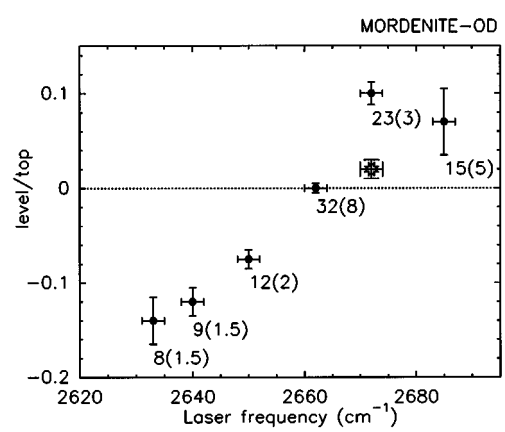


FIG. 4. The observed level to which the logarithm of the normalized transmission ($\ln[T(t)/T_0]$) was found to relax, normalized to the magnitude of the signal, as a function of laser frequency. After relaxation, on the red side of the absorption peak a decrease in transmission is observed, on the blue side an increase. The numbers indicate the lattice temperature increase after deexcitation (see the text). The star denotes a measurement with 90% *lower* pump energy.


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causes. Due to the laser bandwidth of 11 $cm^{-1}$, the two types of deuterated hydroxyls (situated in the 8-ring and 12-ring cavities) are probed simultaneously in the experiment. If the two species have different $\mathbf{T_1}$'s, the *observed* frequency dependence could be caused by two frequency independent contributions. The second possibility is that there is an actual frequency dependence in one or both of the subpeaks. The first possibility however implies a decay with two time constants. Experiments in which both peaks were probed equally could not be modeled with two time constants, assuming these to be the slowest and fastest decay times observed. This implies at least one of the hydroxyl species has a frequency dependent $\mathbf{T_1}$. Extensive argumentation can be found in Ref. 18.

In a recent thorough investigation[6] of O–H relaxation in Y-zeolites with time-resolved spectroscopy, it was concluded that an increase of $\mathbf{T_1}$ with frequency suggests hydrogen bonding of the hydroxyl hydrogen to neighboring oxygen atoms: a stronger H bond weakens the original O–H bond and consequently decreases the absorption frequency. Simultaneously the hydrogen bond enhances the coupling to accepting modes, resulting in a faster decay. If the laser is tuned to the low-frequency side of the absorption peak, hydroxyls will be probed that are more strongly hydrogen bonded, and consequently exhibit faster decay. This accounts for the decrease of $\mathbf{T_1}$ on lowering the laser frequency. So the observed frequency dependence of $\mathbf{T_1}$ in Mordenite O–D is attributed to hydrogen bonding of at least one of the two deuterated hydroxyl species. The most likely candidate for hydrogen bonding are the hydroxyls in the smaller 8-ring cages, causing the downshifted and broadened LF-absorption peak, by analogy with Y-zeolite.[6,19]

### B. Fast energy delocalization

In a time resolved study of the C–H-stretch vibration in $CHBr_3$ it was found that after excitation of the C–H vibration there are *two* relaxation processes.[15] First the energy is transferred to other vibrations within the molecule. Due to anharmonic coupling these vibrations affect the C–H-stretch frequency, thus changing the transmission at the original frequency. These vibrations can have lifetimes up to nanoseconds. This effect causes the transmission to relax with two time constants: first the pump-induced transmission decays with the vibrational lifetime constant $\mathbf{T_1}$ whereafter a second relaxation process is observed, with a much larger time constant, reflecting the energy flow out of the molecule.

Here, we also find evidence for a second slow relaxation process. After the actual vibrational relaxation, the system is found to relax to a nonequilibrium state which is stationary for at least 2 ns. This is manifested in a transmission after vibrational relaxation different from the transmission before; somehow the absorption frequencies of the oscillators are affected by the vibrational relaxation. In principle, the relaxation of excited oscillators could affect *only* the oscillators that were excited (a ''local'' effect as observed in $CHBr_3$) or the absorption of *all* oscillators (a ''nonlocal'' effect). The ''local hypothesis'' can be visualized as follows, in analogy to $CHBr_3$: decay of the excited O–D oscillator entails the redistribution of the energy into accepting modes, for which the sum of energies is in resonance with the O–D vibrational energy. If the excitation of one of the accepting modes, brought about by deexcitation of the O–D stretching mode, causes the O–D stretch frequency to change, and the lifetime of this excitation is sufficiently large, this would account for the observed offset of transmission after vibrational relaxation.

Opposed to this is the nonlocal possibility which involves a rapid redistribution of the energy in the O–D vibrational quantum over the zeolite lattice, causing *all* the oscillators to shift in frequency. This hypothesis requires that the excess energy released by the relaxing O–D oscillator is equilibrated over the zeolite lattice on a time scale that is short compared to the O–D lifetime. In this case the frequency shift would not be instantaneous, since it would take some time to ''delocalize'' the excess energy.

There are four indications as to whether the effect is local or nonlocal, all in favor of the nonlocal hypothesis: First we found a dependence of the offset of the transmission after relaxation on pump pulse energy. Several experiments with gradually decreasing pump energy, showed the level/top ratio to continually decrease, and go to zero for sufficiently small pump energies (see, e.g., the star in Fig. 4). From the nonlocal point of view, this dependence can easily be explained: there will be a smaller perturbation of all the oscillators and hence a smaller shift of the absorption band when less energy is deposited onto the lattice due to the excitation of less O–D oscillators. The local hypothesis, however, implies that the magnitude of the level/top ratio is independent of the number of excited oscillators and consequently independent of pump pulse energy, because in this hypothesis the top and the transmission offset are both proportional to the number of excited oscillators.

Second, a similar dependence of the transmission offset after vibrational relaxation was found on O–D concentration: for lower O–D concentrations (achieved by allowing less exchange with $D_2$) the offset after relaxation decreased. The preceding argument holds here as well; for lower oscillator densities, less oscillators will be excited and less energy will be dumped onto the zeolite lattice.

Third, the homogeneous linewidth of H on Si(111) was found to be 1 $cm^{-1}$.[20] If the homogeneous linewidth of the zeolite hydroxyl is of the same order of magnitude, this is ten times more narrow than our laser bandwidth. (The deuterated zeolite absorption bands are very similar to the nondeuterated ones). This implies we can only excite the deuterated hydroxyls whose narrow homogeneous absorption bands are situated under the 11 $cm^{-1}$ laser band. In the local hypothesis, only these homogeneous bands could shift upon deexcitation. This could only result in a decrease of the number of oscillators absorbing at frequencies under the laser band; an increase in absorption could never be accounted for. The nonlocal hypothesis, however, predicts a perturbation of all oscillators and, consequently, a shift of the whole absorption band.

Fourth, previous studies of O–H and O–D relaxation in micas and on silica surfaces deduced that the initial relaxation process for an O–H/O–D quantum was to decay into four accepting modes.[21,22] One would expect that the accept-


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ing modes excited on deexcitation of the O–D oscillator would decay fast relative to the O–D oscillator itself, rather than slow. This would be due to the fact that the energy gap between the O–D accepting modes and *their* subsequent accepting modes is a lot smaller than the energy gap between the O–D oscillator and its accepting modes: possible accepting modes for the O–D vibration relaxation process, e.g., O–D bending modes or Si/Al–O stretching modes, all have frequencies ranging from 400 to 1000 $cm^{-1}$.[19,23–25] A smaller energy gap implies that less accepting modes are necessary for deexcitation of these modes. Theory predicts that the vibrational energy transfer possibility increases by at least one order of magnitude when one less accepting mode is needed for deexcitation.[26] Hence, it seems unlikely that the accepting mode excitations have lifetimes exceeding nanoseconds. Since the energy in the O–D oscillator will eventually be degraded to low frequency lattice modes, which are not restricted to the immediate vicinity of the relaxed O–D oscillator, fast relaxation of the *accepting* modes supports the nonlocal hypothesis.

It is thus concluded that the observed effect is nonlocal; we experimentally observe a very rapid redistribution of the energy of the excited oscillator into delocalized modes. The absorption band of neighboring nonexcited oscillators is almost instantaneously redshifted due to the vibrational relaxation of excited oscillators. From our calculations it is concluded that the time it takes for a nonexcited oscillator to be perturbed after deexcitation of an excited neighbor (about 5–10 Å away), i.e., the onset time of the offset of the transmission, is smaller than 10 ps.

### C. Lattice temperature

The observation of very rapid dispersion of the excess energy after deexcitation of the oscillators, indicates that the offset of the transmission is due to an elevated lattice temperature immediately after vibrational relaxation. Indeed, the O–D stretch absorption band was found to shift to lower wave numbers on raising the temperature as can be observed in Fig. 5. Vibrational relaxation causes an almost immediate increase of lattice temperature, which, in turn, causes the absorption band to shift. The result is an increased absorption at the low-frequency side of the peak and decreased absorption at the high-frequency side after relaxation of the excitation as was observed in the experiments (Fig. 4).

The dependence of the absorption band on temperature can qualitatively be understood as follows: an increase in the temperature promotes population of low-frequency vibrations or phonons. This increase in ground state population affects the O–D stretch frequency through modes that are coupled to this stretching mode; an increase in temperature causes a redshift and broadening of the absorption band (see, e.g., Ref. 20).

Since we know the change in transmission induced by the vibrational relaxation (Fig. 4), we can make an estimate of the increase in lattice temperature causing this change in transmission. The expression for the transmission $T$ as a function of temperature $\Theta$ of a laser probe pulse with intensity $L(\tilde{\nu})$ through a sample with temperature dependent absorption band $A(\tilde{\nu},\Theta)$ reads: $T(\Theta)=\int_0^\infty d\tilde{\nu}L(\tilde{\nu})\times\exp[-A(\tilde{\nu},\Theta)]$.

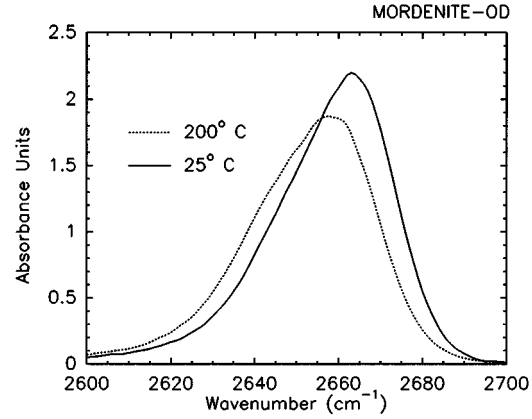


FIG. 5. Absorption spectrum in the O–D stretch region for deuterated Mordenite at two different temperatures. On increasing the temperature, the absorption band is seen to shift to lower wave numbers and decrease in intensity.

From the experiments we obtain the transmission of the probe pulse after vibrational relaxation relative to room temperature transmission. By measuring the absorption spectrum $A(\tilde{\nu})$ as a function of temperature $\Theta$ we can subsequently determine the magnitude of the temperature increase corresponding to the observed offset of the transmission. The momentary increase in temperature causing the offset in transmission was found to vary from 10 °C pumping the flanks of the absorption peak to 30 °C at absorption maximum and could be determined accurately. The lattice temperature increases as calculated from the offset in transmission after relaxation, are indicated for each measurement in Fig. 4. From the calculations it was found that at the top of the absorption peak about 60 of the 150 $\mu$J pump energy is absorbed. If this energy is evenly distributed over the laser focus, this would result in a temperature increase of approximately 10 °C, in good agreement with the experimentally observed values. Previous ultrafast heating experiments in liquids with a molecular thermometer, showed similar temperature increases with somewhat lower pump energies.[27]

A potential danger in the experiments is the steady-state heating of the sample due to the relatively large amounts of energy absorbed in the sample. Vibrational lifetimes are intrinsically dependent on temperature; at higher temperatures decay is more rapid.[26] We checked for steady-state heating effects by measuring $\mathbf{T_1}$ as a function of pump repetition rate; no heating was detected for repetition rates of 5 Hz and lower. All aforementioned experiments were performed at this repetition rate. For pump repetition rates larger than 5 Hz steady-state heating occurs due to the cumulative temperature effect of the pump pulses; the time between pump pulses does not allow for thermal equilibration of the sample. Experimentally, for repetition rates higher than 5 Hz not only a smaller $\mathbf{T_1}$ is observed, but also a change in the offset of the transmission after vibrational relaxation compared to the offset at lower repetition rates (in absence of steady-state heating). This can be understood by noting that, at different


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initial steady-state temperatures the effect of the same temperature increase (due to a single pulse) on transmission will be different. Since we know the single pulse temperature increase at room temperature (Fig. 4), we can now make an estimate of the steady-state temperature increase for repetition rates exceeding 5 Hz, from the change in transmission offset. At pump repetition rates of 10 shots per second, a steady-state temperature increase of $100\pm10$ °C could be detected with the laser tuned to the top of the absorption band.

It is important to note that the conclusions drawn in this study also hold for the nondeuterated zeolite surface hydroxyls as well as for (deuterated) surface hydroxyls on colloidal silica. The long-time signal offsets can also be observed for these systems, albeit less clearly. The temperature effects are even more important for O–H experiments owing to the larger possible pump energies and absorption cross sections.[6]

## V. CONCLUSIONS

We studied the vibrational dynamics of deuterated surface hydroxyls in the zeolite Mordenite. The O–D vibrational lifetime was found to be frequency dependent. It is concluded that this dependence is due to hydrogen bonding of at least one of the two deuterated hydroxyl species in Mordenite. Further, after infrared excitation of surface hydroxyls in the zeolite Mordenite, we observe relaxation of the transmission (reflecting the population relaxation) to nonequilibrium. A satisfactory explanation is presented in terms of a fast redistribution of the energy in the excited oscillators after vibrational relaxation, which affects the absorption frequency of all hydroxyls in the zeolite; it is found that on relaxation of the O–D oscillator, energy is not stored in local modes (e.g., O–D bending), but is dispersed over the zeolite lattice within 10 ps. The induced change in lattice temperature is manifested as relaxation of the transmission to elevated and decreased levels. This allows for accurate determination of the lattice temperature in the laser focus immediately after vibrational relaxation as well as steady-state temperature increases.

## ACKNOWLEDGMENTS

We would like to thank Erik Kossen and Richard Schaafsma for technical assistance and the referee for constructive remarks which improved this paper. 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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