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DOI
10.1016/0301-0104(95)00331-4

Publication date
1995

Published in
Chemical Physics

Citation for published version (APA):
Multiphonon decay of stretch vibrations in zeolites

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Received 17 July 1995

Abstract

The vibrational dynamics of free and hydrogen bonded O–H and O–D groups in zeolites are investigated as a function of temperature with picosecond infrared saturation spectroscopy. From the temperature dependence of the population relaxation rate the order of the multiphonon relaxation process is obtained. It is noted that, in contrast with the conventional theory for vibrational relaxation of an oscillator in a dense medium, the absolute decay rate hardly scales with the number N of accepting modes. This leads us to conclude that, in addition to the order N of the relaxation process, the relaxation rate is also determined by the number of possible relaxation channels. From the temperature dependence of the decay rate of H-bonded oscillators we obtain insight in the role of H-bonding in vibrational relaxation in solids. It is found that the hydrogen bond efficiently accepts part of the oscillator energy in the relaxation process.

1. Introduction

The dynamics of molecular vibrations in the electronic ground state have been explored extensively during the last decades with ultrafast vibrational spectroscopy (see Ref. [1] for an early review). These experiments have induced a great theoretical effort to describe the dynamical processes, which has led to a satisfactory comprehension of many quasi-elastic vibrational interactions (see, e.g., Ref. [2]). In contrast, the inelastic processes are less well understood [3]. In particular, a fundamental understanding of population decay of vibrational excitations in the solid phase is lacking and calculated decay rates disagree with experimentally determined inverse population lifetimes (see, e.g., Ref. [4]).

It is generally assumed that excited high-frequency molecular stretch vibrations (like O–H and C–H vibrations and their deuterated analogues) in the condensed phase dissipate their energy into several low-frequency vibrations of the matrix surrounding the oscillator. The sum of the frequencies of these accepting modes, which are the modes of the low-frequency vibrations over which the vibrational energy is distributed upon deexcitation, should be equal to the oscillator frequency to obey energy conservation in the relaxation process. In the theory for vibrational relaxation of a molecule in a dense medium developed by Nitzan et al. [5–7], it is assumed that one specific combination of accepting modes dominates the relaxation process. This specific combination of accepting modes is called the relaxation channel, and the number of modes in that channel is the order of the relaxation process. With increasing temperature the occupation of the low-frequency phonons raises and consequently the relaxation rate increases. The order of the process can be deduced from the temperature dependence of the relaxation rate [5,6]. The same theory leads to the
so called energy gap law [8], implying that the vibrational relaxation rate should exhibit an exponential, or rather super exponential, dependence on the order of the multiphonon process. Thus, as the number of accepting modes increases by one, the relaxation rate is expected to decrease by (at least) one order of magnitude.

We concentrate on the relaxation dynamics of (diatomic) molecular vibrations in solid matrices, for which the relaxation occurs to several phonons of the solid host. This is somewhat different from the relaxation of polyatomic molecules in liquids, for which the discrete molecular vibrations of solute and solvent molecules govern the relaxation rates [3]. In previous studies, the temperature dependence of the relaxation rate has been investigated with picosecond infrared laser pulses [9-14]. Assuming a single average frequency for the accepting modes, it was inferred that the $v = 1$ excited state of O-H oscillators in fused silica decays into 4 phonons [9], and O-H and O-D groups chemisorbed on silica surfaces were found to relax into 4 and 3 modes respectively [10]. Similarly, for O-H in the zeolite mordenite the number of accepting modes was found to be $N = 4$ [11], and the temperature dependence of relaxation of the S-H stretch vibration in hydrogenated chalcogenide glass could be described adequately with a 7th order process [14]. However, it is noted that all lifetimes of these different molecular vibrations (in the temperature range from 10 to several hundred K) are of the same order of magnitude ($\sim 100$ ps), which is in contrast with the energy gap law (see also Ref. [14]).

From a careful analysis of O-D transient saturation experiments in the zeolite mordenite, it was deduced that vibrational relaxation of the O-D oscillators results in a shift of the O-D absorption band [15]. Deexcitation of excited O-D groups results in a fast heating of the zeolite lattice, which shifts the absorption frequency of the unexcited oscillators. The shift of the absorption band following O-D relaxation was found to occur within the time-resolution of that experiment ($< 10$ ps), which implies that the hydroxyl excess energy is indeed thermalized over low-frequency lattice modes [15].

In this paper we present a study on the temperature-dependence of the vibrational relaxation rate of different O-H and O-D vibrations in zeolites. From the comparison of the temperature dependences of the relaxation rates of the O-H and O-D oscillators we deduce that for solids which have a broad low-frequency mode density of states, relaxation does not occur via one channel, but results from coupling to several relaxation channels. For these cases, the number of decay channels should explicitly be taken into account in addition to the energy gap law, which leads to a much weaker dependence of the relaxation rate on the number of accepting modes. Furthermore we will show that hydrogen bonding significantly changes the temperature dependence of the hydroxyl relaxation rate. With reference to these results the role of H-bonding on vibrational relaxation in solids will be discussed.

2. Experiment

The excited state population lifetimes of O-H and O-D groups in acid zeolites are investigated with time-resolved infrared saturation spectroscopy [16]. Intense picosecond pulses in the mid-infrared are generated with an optical parametric amplifier (OPA), which consists of a mode-locked Nd:YAG laser that pumps three LiNbO$_3$ non-linear crystals (see Ref. [17] for an extensive description of the setup). From the intense mid-infrared pulse, which is tuned to the absorption band of the oscillators, a weak pulse ($\sim 1\%$) is split off to serve as a probe. The remaining strong part, the pump pulse, is focused onto the sample and excites a significant amount of hydroxyls to the $v = 1$ vibrational excited state. The probe pulse is sent into a variable delay and is focused onto the same spot of the sample as the pump pulse. The transmission of the probe pulse is now measured as a function of delay time with respect to the pump pulse. If the probe pulse arrives before the pump pulse, the probe transmission in thermal equilibrium, $T_0$, is measured. For the temperature ranges in the experiments presented in this study, all vibrational population of the hydroxyl stretch vibration is in the $v = 0$ ground state in thermal equilibrium. The pump pulse saturates (bleaches) the absorption because the excited oscillators cannot absorb the light due to the anharmonicity of the vibration. Hence, if the probe pulse arrives simultaneously with or just after the pump pulse, the probe transmission is increased. By recording the probe transmission as a function of delay with the pump pulse, $T(t)$, the return of the transmission to the
equilibrium value can be monitored. From two-color experiments on zeolites [18,19] it is inferred that the excited $v = 1$ level decays directly to the $v = 0$ ground state, and that no other levels are involved in the relaxation process. Thus the excited population lifetime $T_1$ can be deduced directly from single-color experiments because the probe transmission decays exponentially with the excited $v = 1$ population lifetime: 

$$\ln \left( \frac{T(t)}{T_0} \right) \sim \exp(-t/T_1).$$

The pulse duration of the mid-infrared pulses is 25 ps and the pulse energies range from 100 to 200 $\mu$J typically, depending on the exact frequency. The pulses are far from transform limited and the FWHM (full width half maximum) linewidths range from about 34 cm$^{-1}$ at the O-H absorption frequency (3600 cm$^{-1}$) to about 7 cm$^{-1}$ at the O-D frequency (2650 cm$^{-1}$). The repetition rate of the pulses is 10 Hz, but in some experiments the pump pulse repetition rate was reduced using a synchronized mechanical shutter to reduce the steady-state heating in the laser focus.

The zeolites used in this study are hydrogen-exchanged zeolites Y and mordenite with silicon to aluminum ratios of Si/Al = 2.8 and 6.7 respectively. The acid hydrogenated forms were obtained by in vacuo heating (at least 1 h at 723 K) zeolites in which Na$^+$ cations were exchanged by NH$_4^+$ cations. For the zeolite Y denoted with NaHY/0.07 not all of the Na$^+$ ions were exchanged so that a lower proton concentration was achieved. (The proton concentration is denoted as the ratio H/T in the suffix of the sample identifier, where T denotes the sum of silicon and aluminum concentrations, $T = Si + Al$.) The zeolites HY/0.27 (zeolite Y) and HM/0.13 (mordenite) are fully exchanged and contain the highest proton concentrations. The protons are covalently bonded to bridging oxygen atoms in the zeolite lattice and give rise to O-H stretch absorption bands around 3600 cm$^{-1}$ (see Ref. [20] for the absorption spectra of NaHY/0.07 and HY/0.27; center frequencies and linewidths of the absorption bands are given in Table 1). Zeolite Y has two absorption bands, one at higher frequency (~ 3640 cm$^{-1}$) referred to as the HF band and one at lower frequency (~ 3550 cm$^{-1}$, LF band). The HF band arises from protons which point into the larger supercages of the porous zeolite structure, whereas the LF band comes from hydroxyls which point into the smaller sodalite cages. The LF protons are hydrogen bonded to other oxygen atoms in the structure, whereas the HF protons can be considered as free oscillators. Mordenite has a single absorption band around 3610 cm$^{-1}$ [21,22]. It was shown recently that this band is also composed of an LF and an HF band and that the protons which constitute the low-frequency part of the absorption band are H-bonded as well [15,23].

Deuterated versions of zeolite HY/0.27 were obtained by keeping the samples for some time (a few hours typically) at an elevated temperature (around 650 K) in a background of D$_2$ gas, after the standard heating procedure. The absorption spectrum around the O-D absorption frequency after this exchange procedure displays an LF O-D absorption band around 2684 cm$^{-1}$. From the absorption spectrum it is inferred that both the LF protons and the HF protons are exchanged by deuterons to the same level and that a ratio of D/(D+H) = 0.7 is reached. These deuterated zeolites Y are denoted as HDY/0.19 where the suffix represents the D/T deuteron density.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Vibration</th>
<th>Center (cm$^{-1}$)</th>
<th>FWHM$^a$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHY/0.07</td>
<td>HF O-H</td>
<td>3645</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>LF O-H</td>
<td>3558</td>
<td>81</td>
</tr>
<tr>
<td>HY/0.27</td>
<td>HF O-H</td>
<td>3637</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>LF O-H</td>
<td>3549</td>
<td>53</td>
</tr>
<tr>
<td>HM/0.13</td>
<td>O-H</td>
<td>3610</td>
<td>49</td>
</tr>
<tr>
<td>HDY/0.19</td>
<td>HF O-D</td>
<td>2683</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>LF O-D</td>
<td>2620</td>
<td>36</td>
</tr>
</tbody>
</table>

$^a$ Full width at half maximum.
room temperature) due to the asymmetry of the absorption band.

It is well known that the results obtained with time-resolved saturation spectroscopy can be misinterpreted if heating of the sample in the laser focus is neglected [24,25]. The energy that is dumped in the laser focus for every pump pulse depends on the pump energy and on the spectral overlap of the pulses with the absorption band. In the experiments described in this paper, up to about 150 \( \mu \)J is dumped in a focus of typically 0.3 mm diameter with every pump pulse. Thus even at pulse-repetition rates as low as 10 Hz, a steady-state heating of the sample in the focus can be expected. The steady-state temperature increase in the laser focus reached after many pulses was calculated using the differential equations for heat diffusion out of the focus by conduction [26]. (In the calculations it is shown that the heat loss through radiation is negligible.) At repetition rates of 10 Hz steady-state temperature increases up to 120 K were calculated. By decreasing the repetition rate and comparing the relaxation rates at different temperatures and different repetition frequencies it was verified experimentally that these calculations are good estimates for the temperature increase (see Section 3.1). Unless stated otherwise, all temperatures reported in this study include the calculated steady-state temperature increases due to the multiple laser pulses.

3. Results and discussion

3.1. Isotope and temperature dependence

Two typical results for pump–probe experiments on the HF O–H oscillators in zeolite HY/0.27 at different temperatures are depicted in Fig. 1. The probe transmission change \( \ln(T/T_0) \) is plotted on a semi-logarithmic scale as a function of the delay time with respect to the saturating pump pulse. At exact temporal overlap of pump and probe pulses (delay \( t = 0 \) ps) the probe transmission is increased due to bleaching of the \( \nu_0 \rightarrow \nu_1 \) transition. The decay of the pump-induced transparency is clearly faster at higher temperatures. Exponential decay times for the bleaching of \( \tau = 271 \pm 9 \) ps at 260 ± 30 K and \( \tau = 64 \pm 3 \) ps at 830 ± 30 K are obtained by fitting a single exponential decay to the signal after the pump pulse is over. Fits are made starting at the same signal level to minimize differences in the decay times due to small deviations from exponential decays at large signal amplitudes (this effect is caused by spectral averaging over the excited fractions by the probe pulses and is discussed in Ref. [19]).

Care should be taken to identify the bleaching lifetime \( \tau \) with the \( T_1 \) relaxation time for O–H vibrations in zeolites with a high O–H concentration. It was shown previously that a resonant coupling mechanism decreases the observed bleaching lifetime for the highest oscillator densities [20]. Recently it was found in two-color pump–probe experiments that this is caused by dipole–dipole coupling which leads to spectral diffusion of the vibrational excitations in zeolite.

1 For bleaching signals decaying with a time-constant smaller than 40 ps, we have fitted the whole transient signal using the rate equations equations that describe the pump intensity, excited oscillator density, and probe intensity simultaneously as a function of delay time (see also Ref. [27]) to obtain the proper value for the relaxation time.

2 The small transient band shifts which are sometimes observed upon vibrational relaxation due to heating of the lattice occur instantaneously with deexcitation [15] (see also the Introduction). These band shifts, which thus develop with the same time constant \( \tau \), do not affect the exponential decay times if the final transmission level is subtracted from the data. This is done for all measurements reported in this study.

219

At high O-H concentrations the excitations diffuse spectrally out of the probe bandwidth, which manifests itself in the one-color experiments as an enhanced decay rate for the probed excitation. Dipole-dipole coupling strongly depends on oscillator concentration and on the transition dipole moment of the vibrations, thus for low O-H concentrations and for the O-D experiments the spectral diffusion is negligible [19].

For these experiments we assume that the measured inverse bleaching lifetime equals the population relaxation rate:

\[ \frac{1}{\tau(\theta)} = \frac{1}{T_1(\theta)} = k_{10}(\theta), \]

where \( \theta \) is the temperature. For zeolite HY/0.27, which has a high O-H density, the inverse bleaching lifetime is a combination of the relaxation rate and the rate for spectral diffusion. For the two decades of signal measured in our experiments (see Fig. 1), the spectral diffusion process can be approximated by a single exponential decay [19]. The temperature dependence of the spectral diffusion can be neglected compared to the temperature dependence of the relaxation rate for HY/0.27, and accordingly we define:

\[ \frac{1}{\tau(\theta)} = k_{sd} + k_{10}(\theta), \]

where \( k_{sd} \) is the rate constant for spectral diffusion.

The population decay rates of the HF O-H vibrations for the zeolites NaHY/0.07 and HY/0.27 are shown in Fig. 2 as a function of temperature. A constant, temperature independent rate of \( k_{sd} = 1 \times 10^9 \text{ s}^{-1} \) is subtracted from the bleaching decay rates for zeolite HY/0.27 to yield the same population decay rate at low temperatures as for the low-concentration zeolite NaHY/0.07. It is seen in Fig. 2 that this yields the same population decay rates for both zeolites over the whole temperature range studied. This indeed confirms that the contribution of spectral diffusion to the bleaching decay rate is indeed hardly temperature dependent.

We can compare the experimental temperature dependence of the population decay rate to the temperature dependence that follows from the theory of Nitzan et al. [5,6] to determine the order of the multiphonon decay process (see also Refs. [7,9-11,14]). The theoretical expression for the multiphonon relaxation rate (based on Fermi's Golden Rule) is given by [5,6]

\[ k_{10} = \frac{2\pi}{h} \sum_{\{i\}} |G_{\{i\}}|^2 \frac{n_{\{i\}}}{\rho_{\{i\}}}, \]  

where \( \{i\} = 1, 2, ..., N \) denote the phonon sets of the \( N \) accepting modes with frequencies \( \nu_{\{i\}} \), \( G_{\{i\}} \) is the coupling coefficient to the set \( \{i\} \), \( n_{\{i\}} \) is determined by the thermally averaged occupation numbers of the individual phonon modes, and \( \rho_{\{i\}} \) is the compound multiphonon density of states which is given by a convolution of the single phonon density of states for the set \( \{i\} \). Energy conservation is obeyed by the constraint \( \sum_{\{i\}} \nu_{\{i\}} = \nu \), where \( \nu \) is the frequency of the oscillator. It is assumed that the temperature dependence of the relaxation rate \( k_{10} \) in Eq. (1) is completely determined by \( n_{\{i\}} \), which yields [6]
where $h$ and $k_B$ are Planck’s and Boltzmann’s constants. It is assumed that the coupling terms in Eq. (1) strongly depend on the order of the decay process,

$$G_{\{i\}} = A \delta^N,$$

with $A$ and $\delta$ constants for a specific combination of oscillator and surrounding solid, with $\delta \ll 1$ [6,8]. This is the previously mentioned energy gap law for vibrational relaxation from which it follows that it is sufficient to consider only the processes which are of lowest order (smallest $N$) in the decay process. In the theory of Nitzan et al. it is assumed that the accepting modes are in thermal equilibrium during the relaxation process. This is a valid assumption if the depopulation of the excited oscillators is much slower than the thermalization of the deexcited energy within the phonon bath. For the relaxation of hydroxyl groups in porous crystalline zeolites it was indeed experimentally determined that the thermalization occurs (almost) immediately upon relaxation [15].

It is not known to which modes the hydroxyl stretch vibration couples. The highest modes of the zeolite Y lattice are the asymmetric T-O stretching modes around 1100 cm\(^{-1}\), so that at least four accepting modes are required for relaxation of the O-H stretch vibrations around 3600 cm\(^{-1}\). In Table 2 the zeolite framework modes with frequencies above 300 cm\(^{-1}\) are listed as well as the hydroxyl bending modes, which can also act as accepting modes. We have calculated the temperature dependence of the relaxation rate according to Eq. (2) using the modes of Table 2 for $N = 4, 5,$ and $6$ mode processes. Because of the intrinsic spectral widths of the modes, the anharmonicities, and the uncertainties in the experimentally determined mode frequencies, all combinations are considered for which the sum of the frequencies falls within $\pm 200$ cm\(^{-1}\) of the O-H oscillator frequency. For all these combinations the two most extreme temperature dependences of the relaxation rate are plotted for $N = 4, N = 5,$ and $N = 6$ in Fig. 2. A zero-temperature relaxation rate of $k_{10}(0) = 7.5 \times 10^9$ s\(^{-1}\) indicates that the $\nu = 1$ excited state of the HF O-H vibration in zeolite Y decays into 5 accepting modes.

To study the effect of isotope exchange, the temperature dependence of the bleaching lifetime for the O-D vibration in zeolite Y is measured. In Fig. 3 the decay rate for the HF vibration of zeolite HDY/0.19 is plotted as a function of temperature. Because the zeolite framework modes are basically unchanged upon hydrogen/deuteron exchange [29], the zeolite framework modes and the O-D bending modes given in Table 2 are used to calculate the temperature depen-
dence of the decay rate. At least three accepting modes are required to distribute the HF O–D vibrational energy of 2683 cm⁻¹ and for \( N = 3 \) and \( N = 4 \) the extremes for the temperature dependences are plotted in Fig. 3 with a zero-temperature decay rate of \( k_{10}(0) = 7.5 \times 10^9 \text{ s}^{-1} \). The experimental data fall within the extremes of the \( N = 3 \) processes, but at higher temperatures the data increase stronger with temperature than expected for a 3rd order process. This suggests that at low temperatures the HF O–D vibration decays into 3 accepting modes, but that at high temperatures 4th order relaxation processes start to dominate.

By comparing the results from HF O–H and O–D vibrations in zeolite Y it is clear that, although the temperature dependences imply that the number of accepting modes in the relaxation processes differ by two, or maybe one at higher temperatures, the absolute (zero-temperature) relaxation rate only differs by a factor 3.3. This is in contrast with the energy gap law which predicts that a change in \( N \) by one implies a change in the absolute vibrational lifetime with (at least) one order of magnitude, but is analogous to the effect of isotope exchange in other systems \[ 10 \]. Also the observation that the temperature dependence of the HF O–D vibration suggests a smooth cross-over from \( N = 3 \) to \( N = 4 \) at higher temperatures contradicts the energy gap law.

It is striking that the order of the process hardly seems to matter for the experimentally determined relaxation rates. Even for the relaxation of the S–H vibration in As₂S₃ glass, which is found to be of 7th order, the vibrational lifetime is between 60 and 350 ps \[ 14 \]. We think that the energy gap law as stated in Eq. (3) cannot be applied straightforwardly to vibrational relaxation in solids which have a broad density of low-frequency accepting modes. For these systems, the underlying assumption that only one relaxation channel dominates in the population decay is too large a simplification. With increasing order of the decay process, the coupling coefficient to one specific set of accepting modes decreases strongly according to the dependence in Eq. (3), but on the other hand for higher \( N \) many more sets are available for which the sum of the mode frequencies equals the oscillator frequency. Thus with increasing order the number of possible decay channels increases and this compensates roughly the decrease in the coupling strength to each of these decay channels separately. From the temperature dependence of the HF O–H relaxation rate (Fig. 2) it is inferred that the decay is dominated by 5-mode processes. Simply counting the number of all possible combinations of the modes of Table 2 for which the sum of the frequencies lies within \( \pm 200 \text{ cm}^{-1} \) of the O–H frequency, we find 73 combinations for \( N = 4 \), 250 combinations for \( N = 5 \), and 385 combinations for \( N = 6 \). Apparently the relaxation process is dominated by many of the 250 5-mode processes, but one cannot exclude \( N = 4 \) processes from contributing to the relaxation. The corresponding calculation of possible combinations within 150 cm⁻¹ of the HF O–D frequency yields 20 \( N = 3 \) combinations and 91 \( N = 4 \) combinations. Thus indeed, going from an \( N = 5 \) process for O–H to an \( N = 3 \) process for O–D, the total number of possible combinations strongly decreases (from 250 to 20) which might roughly balance the increase in coupling coefficients going from \( N = 5 \) to \( N = 3 \) processes.

To get an impression of the number of possible relaxation channels for different values of \( N \), the one-mode spectrum of Table 2 is convoluted \( N \) times. This leads to a broad-band compound mode spectrum for which the top is around 2100 cm⁻¹ for \( N = 3 \), around 2900 cm⁻¹ for \( N = 4 \), and around 3700 cm⁻¹ for \( N = 5 \). From these compound spectra it is indeed confirmed that \( N = 5 \) should be expected for the O–H oscillators around 3600 cm⁻¹ if the number of possible mode combinations governs the relaxation process. Furthermore it is observed that the HF O–D oscillator frequency around 2683 cm⁻¹ is somewhat closer to the top of the \( N = 4 \) compound mode spectrum than to the top of the \( N = 3 \) spectrum. This might explain the apparent cross-over from \( N = 3 \) to \( N = 4 \) at higher temperatures, see Fig. 3. At low temperatures relaxation occurs mainly to 3 modes, because the coupling coefficient is largest for these processes, but at higher temperatures the \( N = 4 \) processes become more important because their coupling coefficients increase more strongly with temperature.

The order of the relaxation process as found for the HF O–H vibration, \( N = 5 \), is different from the results of temperature-dependent studies on O–H groups inside fused silica \[ 9 \] and on O–H on silica surfaces \[ 10 \], which yielded \( N = 4 \). The hydroxyl groups in acidic zeolites differ from those in the latter two systems in that they are bridging silicon and aluminum tetrahedra, whereas in fused silica and on silica sur-
faces the O–H oscillators are only singly bonded to silicon atoms. This structural difference is reflected in the different vibrational frequencies of the accepting modes listed in Table 2 as compared to the frequencies listed in Ref. [27] for SiO3OH groups. From these differences it should not be too surprising that the number of accepting modes in zeolites is different from that in fused silica and on silica surfaces.

Summarizing, we found evidence that the relaxation rate is determined by the coupling coefficients to a certain set of accepting modes given by the energy gap law (Eq. (3)) together with the number of possible relaxation channels, which increases with increasing N. This is in contrast with the main conclusion of Happek et al. [14] that the magnitude of the coupling coefficient itself determines the decay rate, which fails to explain the similar lifetimes for different isotopes. In our interpretation, which is based on both the temperature and isotope dependences, the increase in the number of available channels for relaxation with increasing order roughly balances the decrease of the coupling coefficients.

3.2. Hydrogen bonding

So far we have only considered the \( \cdot \cdot \cdot F \) hydroxyl vibrations in zeolite Y, which can be viewed as free oscillators in the crystalline structure. Zeolite Y also contains LF hydroxyls, which have a slightly smaller absorption frequency due to the fact that the protons (deuterons) are hydrogen-bonded to other oxygen atoms in the lattice [20]. This hydrogen bond shortens the vibrational lifetime of the LF oscillators, which is also reflected in the decrease of the lifetime with decreasing frequency within the inhomogeneous LF absorption band caused by increasing H-bond strengths [20].

This H-bond strength dependence of the lifetime reveals that the difference in HF and LF relaxation rates is not due to the different crystallographic positions of O–H groups in the zeolitic framework, but to the H-bond itself (see also Ref. [30]). To learn more about the effect of H-bonding on the relaxation rate we have studied the temperature dependence of the relaxation rate for hydrogen bonded oscillators in zeolites.

In Fig. 4, the normalized inverse bleaching lifetime is plotted as a function of the temperature for HF and LF O–H oscillators in zeolite HY/0.27 and for O–H in mordenite HM/0.13. The LF hydroxyls in zeolite Y and those in mordenite exhibit the same temperature dependence, which is weaker than that for the HF O–H groups. As stated in the experimental section, for mordenite the center laser frequency is in the low-frequency shoulder of the absorption band, which means that in these experiments mainly H-bonded oscillators are probed (see also Refs. [23,15]). Apparently hydrogen bonding of the O–H oscillators not only leads to an increase of the relaxation rate, but also yields a different temperature dependence. With the same procedure as described in the previous section, the relaxation rate of the H-bonded oscillators can be fitted best with an \( N = 4 \) process, as opposed to the \( N = 5 \) relaxation of the free O–H groups. This is remarkable, because the frequency differences between HF, LF, and mordenite oscillators is negligible with respect to the average accepting mode frequency (see Tables 1 and 2), so that the same order for the relaxation process is expected for all O–H oscillators. For the deuterated hydroxyls the situation is different. In Fig. 5 the temperature dependence of the normalized relaxation rate for the LF deuterons in zeolite HYD/0.19 is compared to that of the HF O–D oscillators.
Fig. 5. Normalized relaxation rate for the HF (•, data from Fig. 3) and LF (○) O–D vibration of zeolite HDY/0.19. The zero-temperature relaxation rate used for the HF data is \( k_{10}(0) = 7.5 \times 10^9 \) s\(^{-1}\) and for the LF data it is \( k_{10}(0) = 23 \times 10^9 \) s\(^{-1}\).

Surprisingly, for the D-bonded LF O–D oscillators the temperature dependence is now identical to the HF temperature dependence.

We can think of three possible mechanisms by which an H-bond enhances the relaxation rate: (i) the H-bond increases the anharmonicity of the vibration and thereby it enhances the anharmonic coupling to the accepting modes, (ii) the H-bond itself provides a separate, additional channel for vibrational relaxation which accepts all O–H energy, or (iii) the H-bond is an additional accepting vibration in which part of the oscillator energy can be disposed of upon relaxation. Below, we will discuss the three possible mechanisms with reference to the experimentally observed temperature dependences.

(i) For free O–H groups the temperature dependence indicates a 5th order process, whereas an apparent 4th order process is found for H-bonded oscillators. If the anharmonic coupling is increased by H-bonding, this implies that the increased coupling by the H-bond decreases with temperature. We can rule out this possibility by comparing Figs. 4 and 5: If the anharmonic coupling is affected by a change in the anharmonic potential of the oscillator itself, the decrease of the relaxation enhancement with increasing temperature is expected to be identical for both isotopes. In other words, the difference in the temperature dependences for the free and H-bonded O–H oscillators should also be found for the O–D groups, while the contrary is observed (Fig. 5).

(ii) In liquids, H-bonds are found to provide new relaxation channels [31–34] in which the excess oscillator energy can be dissipated leading to dissociation of the H-bond and releasing the energy surplus as kinetic energy of the dissociated fragments. In rigid solid structures like zeolites, however, dissociation of H-bonds cannot occur. Thus the broad H-bond vibrational potential may be viewed as a wide potential well with very steep walls. The impossibility of H-bond dissociation is confirmed by two-color experiments [19], in which no induced absorption is found at the free oscillator frequency after excitation of H-bonded hydroxyls, unlike the situation for H-bonded liquids [31,32]. Due to the steep-wall H-bond potential, the spatial extent of the wavefunction hardly increases with increasing temperature and thus the H-bond contribution in the relaxation process is hardly temperature dependent. In the conception that the H-bond provides an additional, temperature independent, relaxation channel, the total relaxation rate is written as \( k_{10}(\theta) = k_{H-lattice}(\theta) + k_{H-bond}\). The different temperature dependent relaxation rates for the free and the H-bonded O–H oscillators (Fig. 4) then imply that \( k_{H-bond} > k_{H-lattice}(0) \). This is in contradiction, however, with the results of the O–D experiments (Fig. 5): The identical temperature dependences for free and bonded O–D groups require \( k_{D-bond} \ll k_{D-lattice}(0) \). This would mean that the lifetimes of the LF and HF O–D vibration should be the same, in contrast to our observation. In addition, the D-bond is somewhat weaker than the H-bond, but certainly of the same order of magnitude, so \( k_{H-bond} \sim k_{D-bond} \). Also, from the free (HF) O–H and O–D oscillators we know that \( k_{D-lattice} \) is about 3 times \( k_{H-lattice} \). Hence it is extremely unlikely that \( k_{H-bond} > k_{H-lattice}(0) \) while \( k_{D-bond} < k_{D-lattice}(0) \), so that we can conclude that H-bonds in solid matrices like zeolites do not provide separate relaxation channels.

(iii) We think that our experimental results support the interpretation that the H-bond is an additional accepting vibration to which part of the excess energy is transferred. The H-bond becomes highly excited in this process and due to the small spacing of its vibrational levels, the energy that can be transferred to this vibration is variable. The coupling coefficient to relaxation channels in which the H-bond is highly excited is strong, which means that \( A \) in Eq. (3) to these channels is very large. On the other hand, the total number
of quanta released in the energy decay, or the order $N$ of the process, increases strongly with the energy stored in the H-bond mode due to the closely spaced energy levels. The total amount of energy accepted by the H-bond will therefore be determined by a balance between maximizing the energy transferred into the H-bond, and minimizing the total number of quanta released in the relaxation process. The stronger the H-bond, the larger the energy which can be accepted in the H-bond for the same total number of quanta. This leads to a larger number of possible relaxation channels and thus the relaxation rate increases with increasing H-bond strength.

To understand the temperature dependences in this picture the following should be noted. For relaxation of the free HF O–H vibration, the main contribution to the relaxation comes from 5-mode processes, from which an average accepting mode frequency of $\approx 730 \text{ cm}^{-1}$ follows. If an average energy of $\approx 700 \text{ cm}^{-1}$ can be stored in the H-bond, only four zeolite framework modes are required in the decay process. Due to the weak temperature dependence of the coupling to the H-bond, caused by the very steep walls of the the H-bond potential in zeolites [see explanation (ii)], the temperature dependence of the relaxation rate reveals only the number of framework modes active in the relaxation process. Therefore a typical $N = 4$ type behavior is found in Fig. 4 for the H-bonded oscillators. For the HF O–D the average accepting mode energy is $\approx 890 \text{ cm}^{-1}$ for $N = 3$ at lower temperatures. The D-bond, which is somewhat weaker and has a smaller vibrational spacing than the H-bond, should have to accept $\geq 900 \text{ cm}^{-1}$ to reduce the number of zeolite framework modes from 3 to 2. Hence, it is likely that the coupling coefficients to relaxation channels in which 2 zeolite framework modes are involved and the D-bond is very highly excited are smaller than the coupling to 3 framework modes with a much lower excited D-bond. Thus the D-bond does not affect the temperature dependence for O–D relaxation because the number of framework modes involved in the relaxation remains the same. By increasing the number of possible accepting mode combinations however, it does enhance the total number of decay channels and speeds up the relaxation.

4. Conclusions

With ultrafast infrared saturation spectroscopy we have investigated the temperature dependence of vibrational relaxation of O–H and O–D vibrations in zeolites. Two different kinds of oscillators are investigated: free hydroxyls and hydroxyls which are hydrogen bonded to other oxygen atoms in the zeolitic lattice.

We have found that the free O–H oscillators decay mainly via a 5th order multiphonon decay process. The free O–D groups are found to relax into 3 accepting modes at lower temperatures, but above ~ 500 K the temperature dependence of the relaxation rate suggests a cross-over to $N = 4$. Although the number of modes involved in the relaxation process differs, the free O–D excited state lifetime is only about a factor of 3 smaller. The observation that the vibrational lifetimes do not strongly depend on the number of accepting modes is analogous to other experimental findings in similar systems, but disagrees with the assumption that one single channel dominates the vibrational relaxation in a dense medium. Our results lead us to conclude that in solids which have a broad phonon density of states, relaxation occurs to a set of different accepting mode combinations. The relaxation rate is determined by a sum of relaxation rates to these different channels. According to the energy gap law, the coupling coefficient decreases exponentially with the number of modes involved, but the higher the number of modes, the larger the number of possible relaxation channels. These two effects roughly compensate each other for the molecular vibrations in several solids studied so far, and this explains that similar absolute vibrational lifetimes are found for $N = 3$ to $N = 7$ processes.

Hydrogen bonding increases the relaxation rate of the LF oscillators as compared to the free HF oscillators for both the isotopes. The apparent number of accepting modes as determined from the temperature dependence for the H-bonded oscillators is one less than that found for the free O–H oscillators, whereas the same number is found for the LF and HF O–D groups. We interpret this as evidence that H-bonds in these rigid structures do not form new relaxation channels by themselves, but merely act as additional accepting vibrations to which energy can be transferred. This H-bond can be highly excited due to the strong cou-
pling to the hydroxyl vibrat... The actual order of the relaxation process increases strongly with increasing energy stored in the H-bond due to the small H-bond mode spacing. The energy transferred to the H-bond and the number of accepting framework modes are determined by this balance. Due to the rigid structure of the zeolite, the coupling to the H-bond is independent of temperature, so that for H-bonded O–H oscillators in zeolites the temperature dependence suggests \( N = 4 \) (see also Ref. [11]), but this observation should be interpreted as a relaxation process in which 4 framework modes and a high-level H-bond excitation are involved.

Acknowledgement

We would like to thank Erik-Jan Kossen for technical assistance and Natasja Weijtens for the numerical calculations of the laser heating. Aart Kleyn and Rutger van Santen are kindly acknowledged for fruitful discussions. 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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