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LETTERS

Dynamics of Infrared Photodissociation of Methanol Clusters in Zeolites and in Solution

Mischa Bonn,^{*,†,‡} Huib J. Bakker,[†] Aart W. Kleyn,[†] and Rutger A. van Santen[‡]

*FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands, and
Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513,
5600 MB Eindhoven, The Netherlands*

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We have investigated the dynamics of the O–H stretch vibration of clustered (hydrogen-bonded) methanol molecules in solution and in Na–zeolites with time-resolved (picosecond) pump–probe infrared spectroscopy. It is shown that in both cases, after resonant IR excitation, vibrational relaxation occurs by breaking the hydrogen bond between the methanol molecules. This process occurs much faster in solution ($T_1 \leq 3$ ps) than inside the zeolite ($T_1 = 10 \pm 3$ ps). A second remarkable difference is that whereas in solution a rapid hydrogen-bond reassociation occurs ($\tau_r = 25 \pm 3$ ps), in the zeolite this process takes considerably longer ($\tau_r \gg 2$ ns).

Introduction

Methanol adsorption in zeolites has received substantial attention from both experimental (see, e.g., refs 1–3) and theoretical^{4–8} points of view. This interest is caused by the fact that zeolites are very effective catalysts for methanol synthesis and conversion. A frequently employed tool in these investigations is IR spectroscopy, since the frequencies (and line widths) of molecular vibrations contain information on the interaction of the molecule with its immediate environment. In this letter, we report on conventional (linear) and time-resolved (picosecond) nonlinear infrared spectroscopic experiments performed on methanol in solution and adsorbed to the sodium form of Y-zeolite. It is shown that, although the linear absorption spectra for the two systems are very similar, the vibrational *dynamics* of the methanol molecules are markedly different. We obtain novel information on the dynamic behavior of molecules incorporated in zeolites, which cannot be obtained with conventional linear spectroscopy.

Results and Discussion

In Figure 1 two absorption spectra in the O–H stretching region, measured with a Perkin-Elmer 881 double-beam IR spectrometer, are depicted. The upper panel shows the absorption of a 2 mm thick sample of a solution of 0.25 M methanol in carbon tetrachloride. The spectrum consists of three spectral components at 3645, 3520, and 3350 cm^{-1} . These are known^{9–11} to be due to absorption by (i) isolated methanol molecules and methanol molecules terminating clusters/chains by accepting an H bond (both ~ 3645 cm^{-1}), (ii) methanol molecules terminating chains/clusters by donating an H bond (singly hydrogen-bonded) (3520 cm^{-1}), and (iii) internal doubly hydrogen-bonded methanol molecules inside the cluster (3350 cm^{-1}). Hence, the integrated absorption of the 3520 cm^{-1} peak is a measure for the number of clusters and the integrated absorption of the 3350 cm^{-1} peak is a measure for the size of the methanol clusters.

The lower panel of Figure 1 shows the spectrum of methanol adsorbed to NaY, characterized by a silicon–aluminum ratio of Si/Al = 2.4. The ~ 10 mg zeolite sample was pressed into a self-supporting disk and water was removed by heating to 700 K in vacuo for 1 h. Interestingly, apart from the absence of the 3645 cm^{-1} peak, the absorption spectrum looks very

[†] FOM-Institute for Atomic and Molecular Physics.

[‡] Eindhoven University of Technology.

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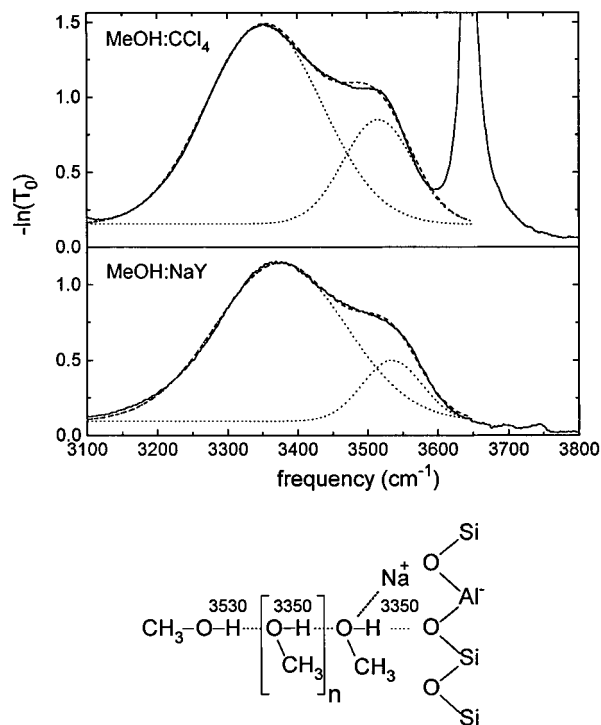


Figure 1. Linear absorption spectra of (i) a 2 mm thick solution of 0.25 M methanol in carbon tetrachloride (offset by 1.2 absorbance units) and (ii) methanol adsorbed to $\text{Na}_{0.27}\text{Y}$, both at 298 K. The spectrum is deconvoluted into two Gaussian lines (dotted lines) the sum of which is shown as a dashed line. Note the similarities between the absorption spectra.

similar to that of methanol in solution. This indicates that also in the zeolite clustering of the methanol occurs, presumably around the favored adsorption sites, the Na^+ atoms; it has been established that the heat of adsorption of methanol to these sites is much higher than to the bare zeolite pore walls or silanol groups.¹ Indeed, upon increasing the pressure, both peaks increase in intensity, but at some point the $\sim 3530\text{ cm}^{-1}$ peak stops growing, suggesting that no more clusters can be formed. The 3350 cm^{-1} peak grows continuously with methanol pressure, indicating that the size of the clusters increases. Thus we conclude that both in solution and in the zeolite the methanol is present as hydrogen-bonded clusters. The microscopic picture of the methanol and the associated transition frequencies that emerges^{9–12} is shown in the bottom of Figure 1, where we cannot exclude multiple adsorption to one Na^+ site, the formation of cyclic (sub-)structures, or multiple bonding within the cluster. In the zeolite the chain is terminated on one side by the sodium atom and on the other by a methanol molecule with $\tilde{\nu}_{\text{O-H}} = 3530\text{ cm}^{-1}$. In solution the same picture applies^{9,12} with a methanol molecule taking the place of the sodium atom.

For the time-resolved experiments intense picosecond (18 ps) tunable infrared (2200–4500 cm^{-1}) pulses are generated by down-conversion of 1064 nm Nd:YAG pulses in LiNbO_3 crystals (for details, see ref 13). Our setup generates independently tunable, parallel polarized infrared pump ($\sim 100\text{ }\mu\text{J}$) and probe ($\sim 1\text{ }\mu\text{J}$) pulses, allowing for two-color experiments. For the experiments described in this letter, the 5 Hz pump pulse was tuned to 3350 cm^{-1} , the frequency of the O–H stretch vibration of methanol molecules inside the clusters. The pump pulse (focused onto the sample, focus diameter 0.4 mm) excites a significant fraction (typically 10%) of these molecules to the first vibrationally excited state of the O–H stretch vibration. The subsequent relaxation is followed with the 10 Hz probe pulse (focused onto the same spot as the pump; every other shot is used for reference): With the probe pulse the pump-

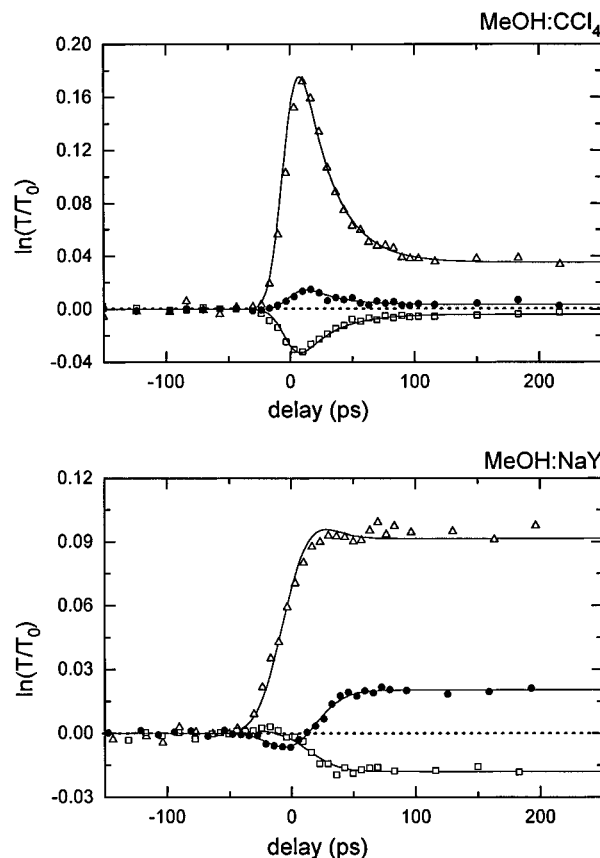


Figure 2. Results of the pump-probe experiments for the two systems: Relative transmission of probe pulses at 3350 (Δ), 3530 (\square) and 3100 (\bullet) cm^{-1} as a function of delay with the pump pulse. The pump pulse is tuned to 3350 cm^{-1} in all the experiments. T and T_0 denote the transmission of the probe pulse in presence and in absence of the pump pulse, respectively. Probing at 3100 cm^{-1} (\bullet), an induced absorption (negative $\ln(T/T_0)$) is observed for the zeolite, not present in solution. Lines are calculations with $T_1 = 2$, $\tau_r = 25$ ps, and τ_i is infinite for MeOH:CCl_4 and $T_1 = 10$ ps and both τ_r and $\tau_i = \infty$ for MeOH:NaY .

induced transmission changes are monitored as a function of delay between pump and probe. Three probe frequencies were employed: 3100 ($\nu = 1 \rightarrow \nu = 2$, see below), 3350 , and 3530 cm^{-1} . The spectral full width at half maximum of the pulses is typically 20 cm^{-1} .

The results of the time-resolved experiments for methanol in solution are shown in Figure 2a. Probing at 3350 cm^{-1} (Δ) a transmission increase is observed, with a subsequent decay with a 25 ps time constant. Probing at 3100 cm^{-1} (\bullet), the same signal (of smaller amplitude) is observed. Probing at 3530 cm^{-1} (\square) an *absorption* increase is observed, decaying with exactly the same time constant as the signal at 3350 cm^{-1} . These results are equivalent to corresponding measurements by Graener et al.⁹ on ethanol dissolved in CCl_4 . It was shown that the observed signals can be accounted for by noting that a very effective way for the methanol molecule to get rid of its excess vibrational energy, is by breaking its hydrogen bond ($E_{\text{H-bond}} \sim 2000\text{ cm}^{-1}$).⁹ Vibrational relaxation occurs by breaking the hydrogen bond, and this process occurs very rapidly (for ethanol $T_1 = 5 \pm 3\text{ ps}$).⁹ In the picture at the bottom of Figure 1 this means that the methanol chain is broken, thus creating new end groups (absorbing at $\tilde{\nu}_{\text{O-H}} = 3530\text{ cm}^{-1}$) at the expense of internal methanol molecules ($\tilde{\nu}_{\text{O-H}} = 3350\text{ cm}^{-1}$). The observed decay time of 25 ps at both frequencies is therefore not the vibrational lifetime T_1 but rather the hydrogen-bond reassociation lifetime τ_r . This value is in good agreement with the $20 \pm 5\text{ ps}$ reassociation time of ethanol.⁹ A similar

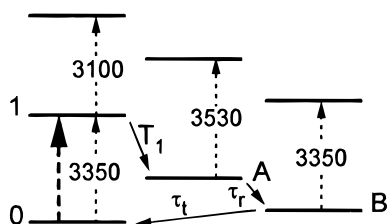


Figure 3. Seven-level system used in the calculations: After excitation with the pump pulse (thick, dashed arrow) from $v = 0$ to $v = 1$ excited state absorption from $v = 1$ to $v = 2$ becomes possible ($\tilde{\nu} \approx 3100 \text{ cm}^{-1}$). Relaxation with time constant T_1 results in a change in absorption frequency due to the breaking of hydrogen bonds. Reassociation of the hydrogen bonds occurs with time constant τ_r resulting in a thermal nonequilibrium state, from which relaxation with time constant τ_t back to the original ground state occurs. τ_t is long ($\tau_t \gg 2 \text{ ns}$) compared to the experimental time scale.

vibrational predissociation process by one IR photon has been observed for gas-phase methanol clusters.¹⁰

For a sufficiently long vibrational (predissociation) lifetime T_1 , one would expect (i) an excited state $v = 1 \rightarrow v = 2$ absorption red-shifted to about 3100 cm^{-1} due to the anharmonicity of the vibration⁹ and (ii) a time delay between the transmission maximum at 3350 cm^{-1} and the absorption maximum at 3530 cm^{-1} , since T_1 is simply the time it takes to break the hydrogen bond resulting in the 3530 cm^{-1} species. The absence of both the pump-induced absorption (negative $\ln(T/T_0)$) at 3100 cm^{-1} and no significant time delay between the other two signal maxima indicates that the vibrational lifetime is very short compared to the duration of our pulses (18 ps). The signal observed at 3100 cm^{-1} is identical—albeit of smaller amplitude—with that at 3350 cm^{-1} due to the spectrally broad induced transmission changes when pumping the $\tilde{\nu}_{\text{O-H}} = 3350 \text{ cm}^{-1}$ transition. This was determined independently from the transient absorption spectrum to be about 170 cm^{-1} full width at half-maximum.

For methanol in NaY, the results (depicted in Figure 2b) are strikingly different. Although initially the same behavior is observed, i.e., a transmission increase around 3350 cm^{-1} and a transmission decrease around 3530 cm^{-1} , the subsequent relaxation is absent. Apparently, the rapid reassociation does not occur in the zeolite. A second difference is that (i) at 3100 cm^{-1} an induced absorption is observed and (ii) the 3530 cm^{-1} data show a delayed rise of absorption compared to 3350 cm^{-1} , both demonstrating that the vibrational lifetime T_1 is relatively long. At 3100 cm^{-1} the induced transmission subsequent to the induced absorption is again caused by spectral overlap of the 3100 cm^{-1} probe pulse with the 3350 cm^{-1} absorption line. For both systems we established that the transmission changes after relaxation showed no changes for delay times up to 2 ns.

Summarizing our data, it is clear that excitation of the internal O—H stretch for both systems results in the dissociation of hydrogen bonds. This process occurs more rapidly in solution than in the zeolite. Subsequently, in solution a reassociation takes place, equilibrating to a somewhat elevated temperature. In the laser focus, this temperature remains constant on the largest experimental timescale of 2 ns.^{9,12} In the zeolite reassociation does not take place within 2 ns, resulting in a situation where the energy has thermalized within the clusters, but the methanol cluster distribution is nonthermal. Also here, temperature diffusion out of the laser focus is slow.¹⁴

The appropriate level scheme for these systems is shown in Figure 3. After excitation with the pump pulse ($\tilde{\nu} = 3350 \text{ cm}^{-1}$, thick, dashed arrow) from $v = 0$ (N_0) to $v = 1$ (N_1), excited-state absorption from $v = 1$ to $v = 2$ becomes possible ($\tilde{\nu} \approx 3100 \text{ cm}^{-1}$). Vibrational relaxation with time constant T_1

results in a change of the O—H absorption spectrum due to the breaking of hydrogen bonds [e.g., $\tilde{\nu} = 3350 \rightarrow 3530 \text{ cm}^{-1}$ (N_A)]. Reassociation of the hydrogen bonds occurs with time constant τ_r resulting in a new equilibrium state at higher temperature (N_B), from which relaxation with time constant τ_t back to the original ground state occurs (infinite compared to experimental time scales). The associated rate equations for the four populated levels read

$$\frac{\partial N_0(z, t_p)}{\partial t_p} = \frac{-\sigma_{01}}{h\nu} I(z, t_p) [N_0(z, t_p) - N_1(z, t_p)] + (1/\tau_t) N_B(z, t_p) \quad (1)$$

$$\frac{\partial N_1(z, t_p)}{\partial t_p} = \frac{\sigma_{01}}{h\nu} I(z, t_p) [N_0(z, t_p) - N_1(z, t_p)] - (1/T_1) N_1(z, t_p) \quad (2)$$

$$\frac{\partial N_A(z, t_p)}{\partial t_p} = (1/T_1) N_1(z, t_p) - (1/\tau_r) N_A(z, t_p) \quad (3)$$

$$\frac{\partial N_B(z, t_p)}{\partial t_p} = (1/\tau_r) N_A(z, t_p) - (1/\tau_t) N_B(z, t_p) \quad (4)$$

$$\frac{\partial I(z, t_p)}{\partial z} = -\frac{\sigma_{01}}{V} [N_0(z, t_p) - N_1(z, t_p)] I(z, t_p) \quad (5)$$

N_x denotes the population in level x , z the coordinate perpendicular to the sample surface, t_p the time coordinate in a moving frame,¹⁵ σ_{01} the cross section for the $0 \rightarrow 1$ transition, $h\nu$ the IR photon energy, $I(z, t_p)$ the space- and time-dependent pump intensity, and V the irradiated volume. The radial profile of the laser pulse was not considered, since this results in only very minor changes in the transients. These equations were solved numerically, after which the transmission of the probe at the three frequencies was evaluated. The amount of transmitted probe is determined by the population difference between the two levels associated with the appropriate transition. These calculations require as input laser pulse parameters (duration, energy, and frequency) and sample parameters (cross sections,⁹ density, sample length, and relaxation times). Apart from the relaxation times all these parameters can be determined independently. Care has to be taken to consider the spectral overlap between the probe pulse and the different contributions to the overall (transient) absorption spectrum, e.g., part of the observed signal at 3530 cm^{-1} is due to changes in the absorption peak centered around 3350 cm^{-1} . The results are shown as lines in Figure 2. It should be stressed that for each system the three kinetic fits result from one single calculation. The results of the calculations were scaled vertically to coincide with experimental signal amplitude (with scaling factors varying only from 0.6 to 1.4, confirming the good agreement between data and calculations). For methanol in solution, the calculations yield an upper limit for the vibrational lifetime of 3 ps. This is concluded not only from the absence of induced absorption around 3100 cm^{-1} (which the calculations predict to be significant for $T_1 > 4 \text{ ps}$) but, more convincingly, from the observation that experimentally there is no detectable delay between the maximum in transmission around 3350 cm^{-1} and the maximum absorption around 3530 cm^{-1} . This implies that the excited 3350 cm^{-1} groups are almost instantaneously converted into 3530 cm^{-1} groups. A T_1 lifetime of 0.5 ps was used in the calculations, adequately describing the data. This value is somewhat smaller than the lifetime of $5 \pm 3 \text{ ps}$ observed for ethanol in CCl_4 .⁹ The reassociation time τ_r is found to be $25 \pm 3 \text{ ps}$. For methanol in the zeolite the data are adequately

described with an infinite reassociation time τ_r (implying $\tau_r \gg 2$ ns) and $T_1 = 10 \pm 3$ ps. For larger T_1 lifetimes one would expect to observe transient bleaching of the 3350 cm^{-1} transition decaying with T_1 and shorter lifetimes defy the observation of the induced absorption around 3100 cm^{-1} and the delay in rise between the 3350 and 3530 cm^{-1} signals. The methanol has reassociated when the next probe pulse hits the sample (implying $\tau_r < 100$ ms, since the repetition rate of our laser system is 10 Hz).

It was shown by Graener et al. that for ethanol in solution, the hydrogen-bond reassociation lifetime τ_r does not depend on the ethanol concentration.⁹ This implies that in solution the sequential hydrogen-bond dissociation and reassociation occurs between the same O–H groups. It is most likely that the solvent plays a crucial role in keeping the dissociated fragments in each others vicinity; the solvent acts as a cage, keeping the dissociated fragments together sufficiently long to reassociate. In the zeolite such a caging effect is not very likely to occur, since in the zeolite experiments the methanol dosage was kept well below complete saturation of the zeolite, implying the pores and cages were not completely filled. This means that after dissociation, the fragments are free to move away from each other, and stabilization of the fragments can occur through association of the methanol fragments with other zeolite oxygen lattice atoms. This association leads to a persistent increase of absorption of the terminal O–H groups absorbing at 3530 cm^{-1} and a persistent decrease of the absorption at 3350 cm^{-1} , and explains the absence of any spectral changes around 3645 cm^{-1} (data not shown here¹⁶). Hence the reassociation rate will be determined by diffusion, indeed slow on our experimental time scales.¹⁷ Additional data corroborating this picture will be published soon.¹⁶

The observation that vibrational relaxation is at least twice as fast for the methanol in solution ($T_1 \leq 3$ ps) compared to inside the zeolite ($T_1 = 10 \pm 3$ ps) is most likely due to the energy mismatch compensation provided by the solvent CCl_4 , a mechanism absent in the zeolite. In the zeolite, the excess energy ($E_{\text{excitation}} - E_{\text{H-bond}}$) can be converted only into excitations of low-frequency vibrations and kinetic energy of the fragments.¹⁸ In case the methanol cluster is surrounded by a solvent, part of the excess energy can also be transferred to the solvent, allowing for a more rapid vibrational relaxation.

Conclusion

We have investigated the vibrational dynamics of methanol in solution and in zeolites. From the linear absorption spectra, we deduce that in both cases clustering of the methanol molecules occurs through hydrogen bonding. As a result, the linear absorption spectra for the two systems are very similar. With nonlinear spectroscopy, we find that for both systems

excitation with resonant infrared pulses leads to breaking of the H bonds and fragmentation of the clusters. However, the vibrational dynamics subsequent to the IR excitation differ greatly in two respects. First, the vibrational population relaxation times (i.e., the vibrational predissociation time) are markedly different, $T_1 \leq 3$ ps for methanol in solution and $T_1 = 10 \pm 3$ ps for methanol inside the zeolite. Second, the reassociation of methanol molecules, after dissociation due to vibrational relaxation, occurring in the liquid phase with a time-constant of 25 ps, is absent on our experimental time scales for the methanol clusters in the zeolite.

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