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

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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 ($T_1 \approx 3$ ps) than inside the zeolite ($T_1 \approx 10 ± 3$ ps). A second remarkable difference is that whereas in solution a rapid hydrogen-bond reassociation occurs ($\tau_r \approx 25 ± 3$ ps), in the zeolite this process takes considerably longer ($\tau_r \approx 2$ ns).

Introduction

Methanol adsorption in zeolites has received substantial attention from both experimental (see, e.g., refs 1–3) and theoretical4–8 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 known9–11 to be due to absorption by (i) isolated methanol molecules and methanol molecules terminating clusters/chains by accepting an H bond (both $\sim3645$ 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 $\sim10$ 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
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 \(3530\) cm\(^{-1}\) peak stops growing, suggesting that no more clusters can be formed. The \(3530\) 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 \(\nu_{O-H} = 3530\) 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 (\(\sim 100\) \(\mu\)J) and probe (\(\sim 1\) \(\mu\)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-induced transmission changes are monitored as a function of delay between pump and probe. Three probe frequencies were employed: \(3100\) (\(\nu = 1\), 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\(^{-1}\) (\(\Delta\)) 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\(^{-1}\) (\(\Xi\)) 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\(_3\). 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 (\(E_{\text{H-bond}} \sim 2000\) cm\(^{-1}\)).\(^9\) Vibrational relaxation occurs by breaking the hydrogen bond, and this process occurs very rapidly (for ethanol \(T_1 = 5 \pm 3\) 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 \(\nu_{O-H} = 3530\) cm\(^{-1}\)) at the expense of internal methanol molecules (\(\nu_{O-H} = 3350\) 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 \(\tau_r\). This value is in good agreement with the 20 ± 5 ps reassociation time of ethanol.\(^9\) A similar
results in a change of the $O-H$ absorption spectrum due to the breaking of hydrogen bonds [e.g., $\nu = 3350 \rightarrow 3530$ cm$^{-1}$ ($N_b$)].

Reassociation of the hydrogen bonds occurs with time constant $\tau_r$, resulting in a new equilibrium state at higher temperature ($N_b$), from which relaxation with time constant $\tau_i$ back to the original ground state occurs (infinite compared to experimental time scales). The associated rate equations for the four populated levels read

$$\frac{\partial N_0(z,t_p)}{\partial t_p} = -\frac{\sigma_0}{h\nu} I(z,t_p)[N_0(z,t_p) - N_1(z,t_p)] + (1/\tau_i)N_0(z,t_p)$$

(1)

$$\frac{\partial N_1(z,t_p)}{\partial t_p} = \frac{\sigma_0}{h\nu} I(z,t_p)[N_0(z,t_p) - N_1(z,t_p)] - (1/\tau_i)N_1(z,t_p)$$

(2)

$$\frac{\partial N_A(z,t_p)}{\partial t_p} = (1/\tau_i)N_A(z,t_p) - (1/\tau_r)N_A(z,t_p)$$

(3)

$$\frac{\partial N_B(z,t_p)}{\partial t_p} = (1/\tau_i)N_B(z,t_p) - (1/\tau_r)N_B(z,t_p)$$

(4)

$$\frac{\partial I(z,t_p)}{\partial z} = -\frac{\sigma_0}{V} [N_0(z,t_p) - N_1(z,t_p)]I(z,t_p)$$

(5)

$N_i$ denotes the population in level $i$, $x, z$ the coordinate perpendicular to the sample surface, $t_p$ the time coordinate in a moving frame, $\sigma_0$ 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, 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 3530 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 $T_1 > 4$ 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 3530 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 ± 3 ps observed for ethanol in CCl$_4$. The reassociation time $\tau_r$ is found to be 25 ± 3 ps. For methanol in the zeolite the data are adequately
described with an infinite reassociation time \( \tau_e \) (implying \( \tau_e \gg 2 \text{ ns} \)) and \( T_1 = 10 \pm 3 \text{ ps} \). 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 \( \tau_e < 100 \text{ ms} \), 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 \( \tau_e \) 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 with other zeolite oxygen lattice atoms. 18 In case the methanol cluster is surrounded by others vicinity; the solvent acts as a cage, keeping the dissociated fragments together sufficiently long to reassociate. 18 In case the methanol cluster is surrounded by the 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, \( T_1 \leq 3 \text{ ps} \) for methanol in solution and \( T_1 = 10 \pm 3 \text{ ps} \) 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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References and Notes