JOURNAL OF CHEMICAL PHYSICS VOLUME 114, NUMBER 7 15 FEBRUARY 2001

Vibrational dynamics of the C–O stretch vibration in alcohols

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(Received 25 July 2000; accepted 15 November 2000)

We present a study on the vibrational dynamics of the C–O stretch vibration of methanol and ethanol in carbon tetrachloride (CCl_4) solution. The relaxation of the excited C–O stretch vibration was observed to occur in two steps. In the first step energy is transferred from the $v=1$ state of the C–O stretch vibration to an intermediate state with a time constant of 3.2±0.2 ps for methanol and 3.2±0.7 ps for ethanol. The intermediate state is most likely formed by the $n=3$ or 4 state of the C–O–H bending mode, which is also known as the torsional mode. In the second step energy is transferred from this intermediate state to low-energy modes, leading to a full equilibration of the energy. In methanol this thermalization occurs with a time constant of 28±1 ps. In ethanol the second step is faster, with a time constant of 12±2 ps.
[DOI: 10.1063/1.1338974]

I. INTRODUCTION

The lifetime of an excited vibration strongly depends on the availability of accepting modes to which energy can be transferred. These accepting modes can be other lower-frequency vibrational modes within the excited molecule, but also low-frequency solvent modes. In the past decades, there has been a large number of studies on C–O stretch vibrations.[1–21] Interestingly, there is a very broad range of lifetimes T_1 of the excited state of the different C–O stretch vibrations, ranging from sub-picosecond to hundreds of picoseconds.

Exceptionally large values for T_1 of several hundreds of picoseconds are found in studies on carbonyl (–CO) complexes of transition metals in liquid solution.[1–6] Apart from the central atom and ligands of these complexes, the relaxation rate was observed to depend strongly on temperature and solvent. The long vibrational lifetime of the excited vibration can be explained by the absence of suitable accepting modes in the form of molecular vibrations. The relaxation mechanism will therefore involve a transfer of energy directly to solvent modes or maybe even to vibrations of solvent molecules. This mechanism explains the strong solvent and temperature dependence in the relaxation. This is illustrated by the observation that for rhodium carbonyl complexes in chloroform $(CHCl_3)$, T_1 varies between 600 and 750 ps for complexes with different numbers of rhodium atoms and CO-ligands, but for the complex $Rh(CO)_2(C_5H_7O_2)$, T_1 is found to be 90 ps.[4] Apparently the more complex organic ligand acetyl acetonate $(C_5H_7O_2)$ provides more accepting modes than the carbonyl ligands, resulting in a faster relaxation of the excited carbonyl C–O stretch vibration.

Another group of compounds with quite long lifetimes for C–O stretch vibrations is formed by complexes of carbon monoxide (CO) bound to hemoglobin, myoglobin and model heme compounds (metalloporphyrin complexes).[7–11] In studies on these vibrations it was found that T_1 does not significantly depend on temperature[8] and solvent,[10] but only on the structure of the heme group and the central metal atom. For the different compounds, T_1 is found to lie between 10.7 and 44.5 ps. The predominant vibrational relaxation process was shown to be transfer of energy from CO to vibrations of the heme group by anharmonic coupling. As a result, there is hardly any solvent or temperature dependence, as energy transfer to solvent modes is not the dominant process.

When CO is chemisorbed to platinum or rhodium particles supported on SiO_2, the relaxation of the excited C–O stretch vibration is faster than that of the CO–heme complexes. For these systems T_1 is observed to be in the range 5–10 ps.[12,13] When CO is chemisorbed on metal surfaces the relaxation rate is even higher:[14–17] T_1 was found to be 2.2 ps for CO on a Pt(111) surface[14,15] and 3 ps for CO on a Cu(100) surface.[17] The relaxation mechanism is thought to be excitation of electron–hole pairs in the metal through dipole–dipole coupling, in agreement with the observation that T_1 does not depend on temperature or the surface coverage.[14]

The fastest relaxation of the C–O stretch vibration is observed when the C–O group is part of an (organic) molecule. Then the mechanism probably involves intramolecular relaxation, where energy is transferred from the excited vibration to one or more other vibrations of the molecule by anharmonic coupling. The C–O stretch vibration of acetic acid in carbon tetrachloride (CCl_4) was observed to have a lifetime of 0.7 ps[18] and the amide I vibration in peptides[19,20] to have a lifetime around 1.2 ps. The amide I vibration of peptides mainly involves the C–O stretching modes of the amide backbone. The C–O stretch vibration of a coumarin dye was observed to have a lifetime of 2 ps.[21]

The relaxation mechanism of the C–O stretch vibration of systems where C–O acts as a ligand has been extensively studied and is quite well understood. In contrast, very little is known about the rate and mechanism of vibrational relaxation of excited C–O stretch vibrations when the C–O group is part of an (organic) molecule. Here we present a study on

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the vibrational dynamics of the C–O stretch vibration of methanol and ethanol in solution.

II. EXPERIMENT

Experiments were carried out at the free electron laser FELIX in The Netherlands. This free electron laser (FEL) has been described in detail elsewhere.[22] In short, this source for short infrared pulses is tunable from 5 to 110 μm (2000–90 cm^{-1}) and delivers macropulses of 5–10 μs in duration, which consist of a train of micropulses. In our experiments, the micropulses were spaced by 40 ns, with a typical energy of 10 μJ. The micropulses had a typical length of 1.2 ps [full width at half maximum (FWHM)]. At a wavelength of 9.64 μm the micropulses had a bandwidth of 0.10 μm, which means that the pulses are close to being transform-limited. The macropulses had a repetition rate of 10 Hz.

These mid-infrared pulses are used in one-color pump–probe experiments. In these experiments an intense pump pulse excites a significant number of molecules to an excited vibrational state, which causes a transmission change of the delayed, weaker probe. This transmission change is measured as a function of the delay between pump and probe pulses. The transmission change is defined as T/T_0, where T is the transmission of the probe pulse in the presence of a pump pulse and T_0 the transmission of the probe pulse without a pump pulse present.

Before passing through the sample, the probe pulses are split in two parts of which one is delayed by an extra 20 ns. This part subsequently passes through the sample at a time when the sample is not affected by a pump pulse, contrary to the ‘‘undelayed’’ part of the probe. Since the bias of the mercury–cadmium–telluride (MCT) detector is actively reversed between the detection of the two probe pulses, the signal measured is $T-T_0$. This allows for a significant improvement of the signal-to-noise ratio, as in this way heating effects on the measured transmission changes are reduced, because both pulses are affected in the same way by heating. Separate measurement of T_0 allows the calculation of the relative transmission change T/T_0. The polarization of the probe pulses was rotated 90 degrees, with respect to the polarization of the pump pulses, in order to eliminate coherent artefacts due to thermal gratings.

The reflection of a zinc selenide (ZnSe) plate, placed in the probe beam, was used as a reference to correct for the macropulse to macropulse intensity fluctuations of the FEL. The beams were focused into the sample with barium fluoride (BaF_2) lenses. The experiments were performed on a 0.14 M solution of methanol in CCl_4 in a temperature controlled sample cell with BaF_2 windows and a sample length of 0.5 mm. Experiments were also performed on a 0.34 M solution of ethanol in CCl_4.

The pump–probe experiments on the methanol solution were carried out at different temperatures, ranging from room temperature to 70 °C, and at different wavelengths within the C–O stretch absorption band.

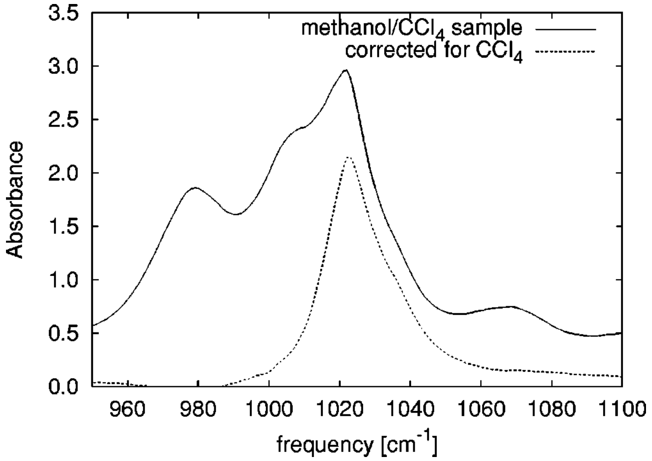

FIG. 1. Linear absorption spectrum of a 0.14 M methanol in CCl_4 sample with a sample length of 0.5 mm (solid line) and corrected for the absorption of CCl_4 (dashed line).

III. RESULTS

The linear absorption spectrum of the methanol solution is shown in Fig. 1. The C–O stretch absorption band of methanol in CCl_4 is centered at 1023 cm^{-1}. The linear absorption spectrum of the ethanol solution is shown in Fig. 2. The C–O stretch absorption band of ethanol in CCl_4 is centered at 1050 cm^{-1}. In these figures the spectra corrected for the absorption of CCl_4 are also shown. The absorbance A was calculated from the measured transmittance of the sample (T_{sample}) and the transmittance of air (T_{air}) by

$$A=-\ln\left(\frac{T_{\mathrm{sample}}}{T_{\mathrm{air}}}\right). \tag{1}$$

For the methanol solution, pump–probe scans at different temperatures and at frequencies between 1020 and 1045 cm^{-1} ($\lambda=9.80$–9.57 μm) all showed bleaching signals very similar to the measurement shown in Fig. 3. The bleaching signal clearly exhibits a biexponential decay. This biexponential decay is observed in all other measurements. The

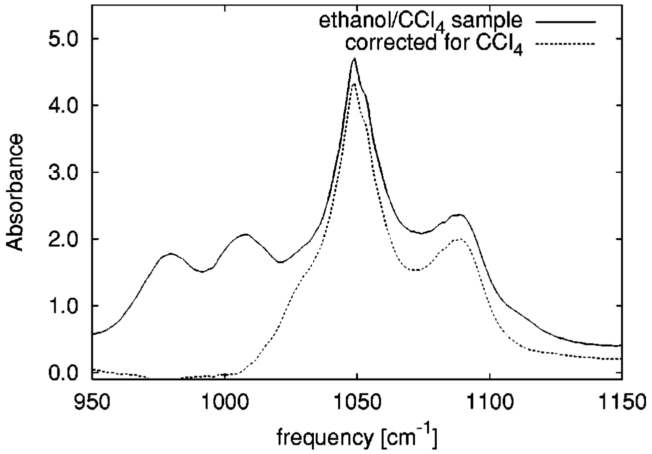

FIG. 2. Linear absorption spectrum of a 0.34 M ethanol in CCl_4 sample with a sample length of 0.5 mm (solid line) and corrected for the absorption of CCl_4 (dashed line).

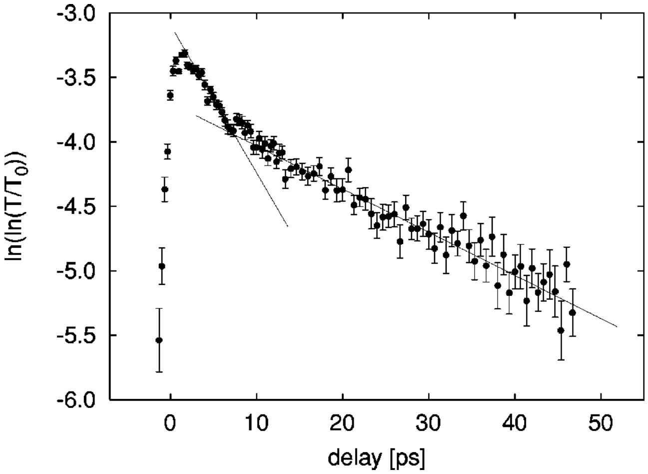

FIG. 3. Pump–probe delay scan of methanol in CCl_4 at a frequency of 1037 cm^{-1} ($\lambda=9.64$ μm), $T=43$ °C. The solid lines are guides to the eye and illustrate that the bleaching signal clearly exhibits a biexponential decay.

amplitude of the bleaching signal strongly decreases when the laser frequency is tuned away from the center of the absorption band.

At the red side of the C–O stretch absorption band of ethanol, at a frequency of 1045 cm^{-1}, an induced absorption was found, which decays at the same rate as the bleaching signal. This induced absorption is attributed to absorption of the $v=1$ state of the C–O stretch vibration. The observed small red shift of the excited-state absorption in ethanol indicates that the anharmonicity of this stretch vibration is quite small. This also explains the rapid decrease in bleaching signal amplitude, when the frequency of pump and probe is tuned away from the center of the absorption band.

At the red side of the C–O stretch absorption band of methanol (1015 cm^{-1} and lower), no signal was observed, which can be explained by the fact that the red side of the C–O stretch absorption band of methanol overlaps with an absorption band of CCl_4.

IV. DISCUSSION

Transfer of energy from an excited C–O stretch vibration to one or more other vibrations within the excited molecule is much faster and much less temperature dependent than transfer to low-energy solvent modes.[1–6] Hence, the observation that the vibrational relaxation of the C–O stretch vibration of methanol and ethanol in CCl_4 is fast and not temperature dependent strongly suggests that the relaxation mechanism is an intramolecular process.

The CH_3-rock vibration is quite close in energy to the C–O stretch vibration, especially in ethanol. However, the coupling between these modes is very small[23] and it is, therefore, not very likely that the CH_3-rock mode is the accepting mode in the relaxation of the excited C–O stretch vibration. In addition, the energy difference between the C–O stretch mode and the CH_3-rock mode is quite different for methanol and ethanol. This difference in the ''energy gap'' would lead to different relaxation rates of the excited C–O stretch vibration of the two different alcohols if the CH_3-rock mode were the accepting mode. However, we observe identical lifetimes in both alcohols.

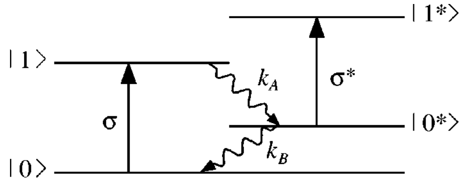

FIG. 4. States and decay scheme used to describe the relaxation of the excited C–O stretch vibration. The cross sections for a radiative transition are indicated by σ and σ^*. The rate of the 1→0* relaxation is given by k_A and the rate of the 0*→0 relaxation is given by k_B.

In studies on gas-phase spectra of methanol, a strong coupling was found to exist between the $v=1$ state of the C–O stretch vibration and the states with 3 or 4 quanta in the C–O–H bending mode (or torsional mode as it is also denoted).[24,25] This suggests that the C–O–H bending mode might very well be the accepting mode in the relaxation of the excited C–O stretch vibration in methanol and ethanol. This relaxation is followed by equilibration of the energy over all other degrees of freedom. In this way, the C–O–H bending mode would act as an intermediate state in the relaxation, thereby explaining the observed biexponential decay.

In order to determine the decay-time constants of the two relaxation processes, we use a simple model which is described in detail elsewhere.[26,27] In this model, the relaxation of the excited vibration $|1\rangle$ occurs via an intermediate state $|0^*\rangle$, rather than directly back to the ground-state $|0\rangle$. The rate of relaxation from the first excited state $|1\rangle$ to the intermediate state $|0^*\rangle$ is given by k_A and the relaxation rate of the second step in the relaxation $|0^*\rangle \rightarrow |0\rangle$ is given by k_B. The cross section of the 0→1 transition is denoted by σ and the cross section of the 0*→1* transition by σ^*. The solid line in Fig. 5 is calculated with this model, which is illustrated in Fig. 4.

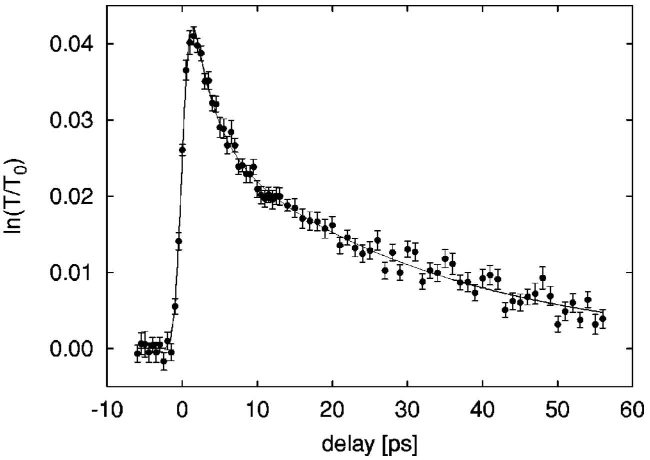

FIG. 5. Pump–probe delay scan of methanol in CCl_4 at a frequency of 1025 cm^{-1} ($\lambda=9.76$ μm), $T=31$ °C. The solid line is calculated using the model described in Sec. IV.

Using this model, the measurements on the methanol solution at all the different frequencies and temperatures could be described with one set of k_A and k_B. The cross-section ratios σ^*/σ at the different frequencies increase with increasing frequency from 0.10 ± 0.02 at 1025 cm^{-1} to 0.3 ±0.1 at 1045 cm^{-1}. The lifetime of the excited C–O stretch vibration in methanol ($T_1=1/k_A$) was determined to be 3.2 ±0.2 ps. The lifetime of the intermediate state $|0^*\rangle$ ($=1/k_B$) was determined to be 28 ± 1 ps.

Using the same model we found for the excited C–O stretch vibration in ethanol a lifetime $T_1=1/k_A=3.2\pm0.7$ ps. For ethanol, the lifetime of the intermediate state $1/k_B=12\pm2$ ps, which is about twice as small as for methanol. The decay of the intermediate state is significantly faster in ethanol probably because there are more low-frequency modes in the molecule to which this state can couple.

The increase in the ratio σ^*/σ when tuning the frequency from the red side to the blue side of the absorption band indicates that population of the intermediate state leads to a transient blue shift of the C–O stretch absorption band. Indeed, population of the C–O–H bending mode has been observed to cause a small blue shift of the C–O stretch frequency.[24]

The frequency of the C–O stretch vibration could also be influenced by ''local heating,'' because a lot of energy is dumped into a small volume around the excited molecule right after the relaxation. This might cause the surroundings to resemble the gas-phase more closely and, therefore, cause the frequency of the C–O stretch vibration to shift to its gas-phase value, i.e., to the blue.

Whether the occupation of the C–O–H bending mode or the ''local heating'' is the main cause for the observed blueshift cannot be concluded from our experiments.

In a study on the relaxation of the O–H stretch vibration of ethanol clusters in CCl_4 also a transient blueshift of the initially excited vibration was observed. For this vibration, the relaxation mechanism is believed to involve energy transfer to the hydrogen bond, which even causes the hydrogen bond to predissociate.[28] This in its turn causes a blueshift of the O–H stretch vibration. However, in the case of the C–O stretch vibration, the blueshift cannot be caused by an energy transfer to the hydrogen bond, because a decrease in cluster size (and breaking of a hydrogen bond) causes a redshift of the C–O stretch frequency, instead of the observed blueshift.[29] In addition, judging by the relative intensities of the narrow O–H stretch absorption band due to monomers and the broad O–H stretch absorption band due to clusters in the linear spectrum, it is clear that at the concentration used in our experiments, there are mainly monomers present.

As the experiments were carried out with perpendicular polarizations for pump and probe, the transient signals due to population relaxation could be influenced by orientational relaxation.[30] From dielectric relaxation measurements the Debye relaxation time τ_D was determined to lie in the ranges 47–56 ps for methanol and 138–170 ps for ethanol.[31–34] These relaxation times must be divided by a factor of 3 to get the rotational correlation time.[35] In a perpendicular configuration of the pump and probe polarizations, the reorientation could thus lead to a small and slow increase of the measured signal. This means that the lifetimes, especially those of the intermediate state, could in reality be slightly smaller than we found in our measurements.

V. CONCLUSIONS

We studied the vibrational dynamics of the C–O stretch vibration of methanol and ethanol in CCl_4. The relaxation of the excited C–O stretch vibration was observed to occur in two steps. In the first step energy is transferred from the $v=1$ state of the C–O stretch vibration to an intermediate state with a time constant of 3.2 ± 0.2 ps for methanol and 3.2 ± 0.7 ps for ethanol. This intermediate state is most likely formed by the $n=3$ or 4 state of the C–O–H bending mode.

In the second step energy is transferred from the intermediate state to low-energy modes. In methanol this thermalization occurs with a time constant of 28 ± 1 ps. In ethanol the second step is faster, with a time constant of 12 ± 2 ps, because of the higher number of available accepting modes.

ACKNOWLEDGMENTS

We gratefully acknowledge the skillful assistance by the FELIX staff, in particular Dr. A.F.G. van der Meer. The research presented in this paper is part of the research program of the ''Stichting Fundamenteel Onderzoek der Materie (FOM),'' which is financially supported by the ''Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).''

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