Ultrafast vibrational dynamics of water

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Comment on: Vibrational relaxation and spectral evolution following ultrafast OH stretch excitation of water by A. Pakoulev, Z. Wang, D.D. Dlott

In a recent Letter by Pakoulev et al. (Chem. Phys. Lett. 371 (2003) 594), time-resolved anti-Stokes Raman measurements of the spectral evolution and relaxation of the OH stretch vibrations of pure H₂O were presented. These measurements led the authors to reinterpret the results presented in Chapter 4. Here we show that this reinterpretation is incorrect.
6.1 Introduction

In a recently published Letter [69], time-resolved anti-Stokes Raman measurements of the spectral evolution and vibrational relaxation of pure H₂O were presented. It was observed that the spectrum of the OH-stretch excitation undergoes a rapid blue shift with a time constant of ~0.4 picoseconds (ps), and that the vibrational lifetime is ~0.7 ps. These results are quite surprising, since they appear to be contradictory to the results we obtained in Chapter 4 in which the vibrational dynamics of H₂O were probed with femtosecond mid-infrared pump-probe spectroscopy [51]. In the latter study, the vibrational lifetime of H₂O was found to be only 0.26±0.02 ps, and it was observed that the vibrational relaxation was followed by a slower thermalization process with a time constant τₑq of 0.55±0.05 ps.

The authors of Ref. [69] reinterpret the 0.26 ps time constant of Chapter 4 as spectral diffusion, and the 0.55 ps time constant as the true vibrational lifetime of the O·H stretch vibration of water. However, in this reinterpretation they overlooked several essential elements of the mid-infrared pump-probe results that disprove this reinterpretation.

In our femtosecond mid-infrared pump-probe experiments on water, the O·H stretch vibrations (3000-3600 cm⁻¹) of water were excited with an intense infrared pump pulse (pump). This excitation results in a bleaching of the fundamental ν = 0 → 1 transition and in an induced absorption of the ν = 1 → 2 transition. The ν = 1 → 2 transition is red-shifted by ~250 cm⁻¹ with respect to the ν = 0 → 1 transition. The transmission changes were probed with a second, independently tunable femtosecond mid-infrared pulse (probe). The change in absorbance induced by the pump is given by ln[T(τ)/T₀], with T(τ) the transmission of the sample in presence of the pump, and T₀ the transmission of the sample in absence of the pump.

In Fig. 6.1 femtosecond pump-probe data are shown obtained for a sample of pure H₂O using a pump pulse with a central frequency of 3550 cm⁻¹ and four different probe frequencies. The pump pulse had a pulse duration of 220 fs and an energy of ~10 μJ. The probe had a pulse duration of 220 fs and an energy <1 μJ. The results shown in Fig. 6.1 show the presence of two relaxation processes: a first fast process with a time constant of 0.30±0.05 ps, and a second, slower process with a time constant of 0.55±0.05 ps. These results are very similar to the results reported in Chapter 4.

6.2 Spectral diffusion or vibrational relaxation

Pakoulev et al. [69] suggested that the fast decays of the absorption at frequencies <3100 cm⁻¹ and of the bleaching at frequencies >3500 cm⁻¹ we observed, could result from spectral diffusion within the ν = 1 → 2 band.

For our results, spectral diffusion will lead to a shift to higher frequencies, because in this study the pump pulse had a central frequency of 3250 cm⁻¹ (see Fig. 4.2), which is at the red side of the O·H stretch absorption band. A frequency of 3100
Spectral diffusion or vibrational relaxation

Figure 6.1. Femtosecond mid-infrared pump-probe scans of liquid water at 298 K. The central frequency of the pump is 3550 cm\(^{-1}\).

cm\(^{-1}\) corresponds to the high-frequency side of the \(v = 1 \rightarrow 2\) transition. Hence, a shift of the \(v = 1 \rightarrow 2\) response to higher frequencies is expected to lead to a *rise* of absorption with a time constant of \(\sim 0.3\) ps, and not, as is observed, to a *decay* with \(\sim 0.3\) ps. In addition, at 3500 cm\(^{-1}\) the response of the \(1 \rightarrow 2\) transition will be much weaker than the response of the fundamental \(v = 0 \rightarrow 1\) transition. Hence, spectral diffusion to higher frequencies with a time constant of \(\sim 0.3\) ps should result in a *rise* of a bleaching signal at 3500 cm\(^{-1}\), and not, as is observed, in a *decay* with this time constant. Finally, pumping at 3550 cm\(^{-1}\) (Fig. 6.1) is observed to lead to the same results as pumping at 3250 cm\(^{-1}\) [51], which indicates that for H\(_2\)O spectral diffusion within the O-H stretch absorption band is extremely fast with a time constant <100 fs. This notion agrees with the results of a previous study of the depolarization of vibrational excitations in water [104]. In view of the above, the relaxation process with a time constant of \(\sim 0.3\) ps cannot be explained from spectral
diffusion. Instead, the decay of the absorption observed at 3100 cm\(^{-1}\) and of the bleaching at frequencies >3500 cm\(^{-1}\) with time constant 0.30±0.05 ps must represent the population relaxation of the \(v = 1\) state.

In the discussion of Ref. [69] it is stated that we would claim the region between 3200 and 3400 cm\(^{-1}\) to be insensitive to the \(T_1\) process. This is an incorrect citation: in Chapters 4 and 5 it was stated that in this frequency region the effect of the thermalization is so large that the measured signals are dominated by the thermalization process. In fact, the region between 3200 and 3400 cm\(^{-1}\) is about as sensitive to the \(T_1\) process as the regions <3100 cm\(^{-1}\) and >3400 cm\(^{-1}\). At 3300 cm\(^{-1}\) the signal due to the direct bleaching of the \(v = 0 \rightarrow 1\) transition is observed as a weak shoulder on the very strong thermalization signal (see Fig. 6.1b, note also the differences in magnitude of the overall signals in Fig. 6.1). The signal level of this shoulder is about the same as that of the bleaching at 3500 cm\(^{-1}\) and that of the induced absorption at 3100 cm\(^{-1}\).

6.3 Population relaxation or equilibration

In Ref. [69] the second, slower process with a time constant of 0.55 ps is interpreted as the population relaxation of the O–H stretch vibrations. This interpretation is mainly based on the magnitude of the time constant of the slower process, that is quite similar to the decay time constant of ~0.7 ps of the anti-Stokes Raman scattering signal. However, if the 0.55 ps process would indeed be the vibrational relaxation, a decay of a bleaching with this time constant should be observed in the frequency region 3200-3400 cm\(^{-1}\). Instead, a rise of a bleaching signal with 0.55 ps is observed in this frequency region. Hence, the 0.55 ps process does not represent the vibrational relaxation, but rather the relaxation of an intermediate state (likely the overtone of the bending vibration of H\(_2\)O) that gets populated by the relaxation of the O–H stretch vibration. As a result of this second relaxation process with \(\tau_{eq} = 0.55±0.05\) ps, the H\(_2\)O sample gets heated by ~30 K, which results in a decrease and a blue shift of the O–H stretch vibrational absorption band. Hence, the 0.55 ps process induces a rise of a bleaching at frequencies <3500 cm\(^{-1}\), and an induced absorption at frequencies >3500 cm\(^{-1}\), as is observed in Fig. 6.1 and in Chapters 4 and 5.

Pakoulev et al. claim that their anti-Stokes Raman measurements would be totally insensitive to the thermalization process. In our opinion this claim is not correct. Liquid H\(_2\)O possesses an extremely high density of O–H oscillators, which implies that the relaxation of an O–H oscillator will immediately affect the response of nearby O–H oscillators. In the experiments of Ref. [69], there will indeed be a strong effect of relaxing O–H vibrations on the dynamics of other excited O–H vibrations, because the infrared pulses used in these experiments are long (1.4 ps) compared to the time scales of vibrational relaxation and thermalization. Hence, a large part of the signal observed in Ref. [69] will be formed by water molecules for which the O–H spectrum
has been shifted to the blue as a result of the relaxation of molecules that were excited by the front part of the pulse. This also means that the rapid spectral blue shift observed by Pakoulev et al. likely does not represent a single spectral diffusion process, but forms the result of the consecutive action of the vibrational relaxation of room temperature water and the thermalization. Here it should also be noted that the cross-correlation of 1.8 ps of the pulses used in the experiments of Pakoulev et al. is too long to distinguish the two relaxation processes.

Following this interpretation, the rate limiting step of the blue shift is formed by the thermalization process. Indeed, the value of $\tau_{\text{eq}}$ of 0.55±0.05 ps of this process is quite similar to the time constant of the blue shift of ~0.4 ps reported in Ref. [69]. The blueshift probably also affects the rate of vibrational relaxation of the O–H stretch vibration, which could explain why the anti-Stokes Raman signals measured in Ref. [69] show a relatively slow decay, especially at the blue side of the spectrum.

### 6.4 Conclusion

In conclusion, we demonstrated that the reinterpretation given in Ref. [69] of the results of previous femtosecond mid-infrared pump-probe studies is incorrect. In addition, we argued that, in view of the pulse durations used, the fast spectral blue shift with ~0.4 ps observed in Ref. [69] likely results from the subsequent action of the vibrational relaxation of room temperature water ($T_1 = 0.3\pm0.05$ ps) and a thermalization process ($\tau_{\text{eq}} = 0.55\pm0.05$ ps).