

Impact of Hydrogen Bonding on the Vibrational Relaxation of para-Nitroaniline

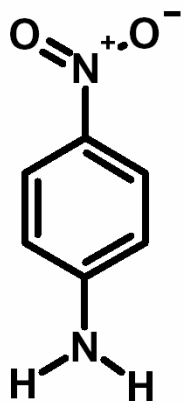


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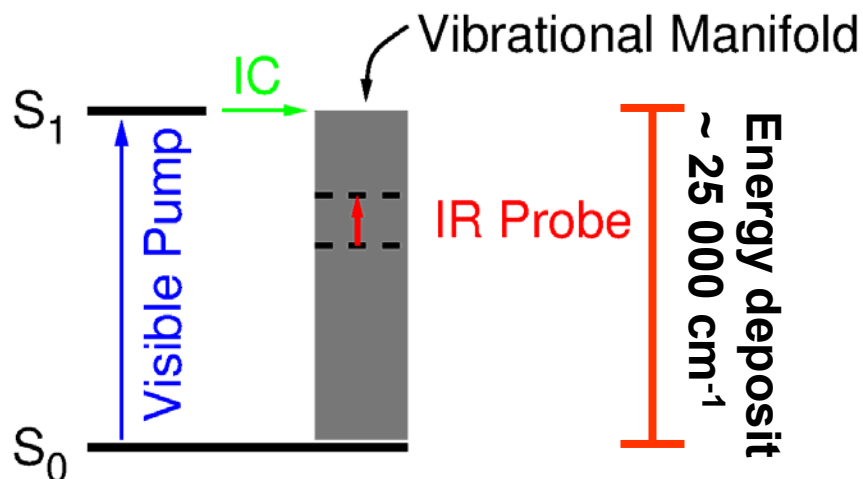
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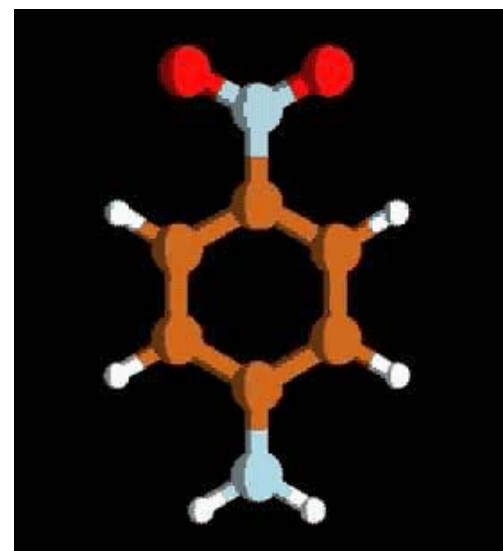
para-Nitroaniline and its symmetrical NO₂ stretch mode as a model system

1. Internal Conversion within 400 fs



Energy deposit similar or even larger as in chemical reactions!

2. Sym. NO₂ stretch mode: excellent IR absorption ($\epsilon_{\text{IR}} = \text{ca. } 3000 \text{ M}^{-1} \text{ cm}^{-1}$ at 1315 cm⁻¹)

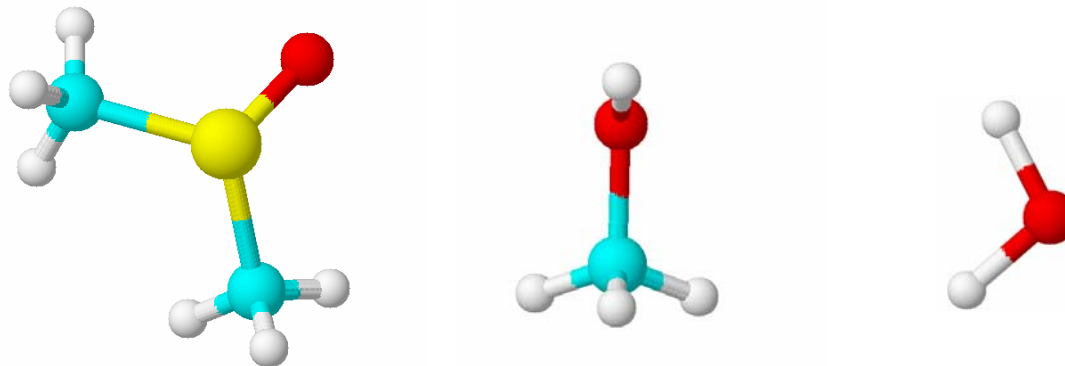


Solvent Effects on para-Nitroaniline (pNA) Observed by Visible Spectroscopy

Solvent	DMSO	MeOH	H ₂ O
Internal Conversion Decay Time	0.36 ps	0.38 ps	0.29 ps
Characteristic Cooling Time	2.8 ps, (9.3 ps)	1.9 ps, (7.3 ps)	1.1 ps, (3.1 ps)

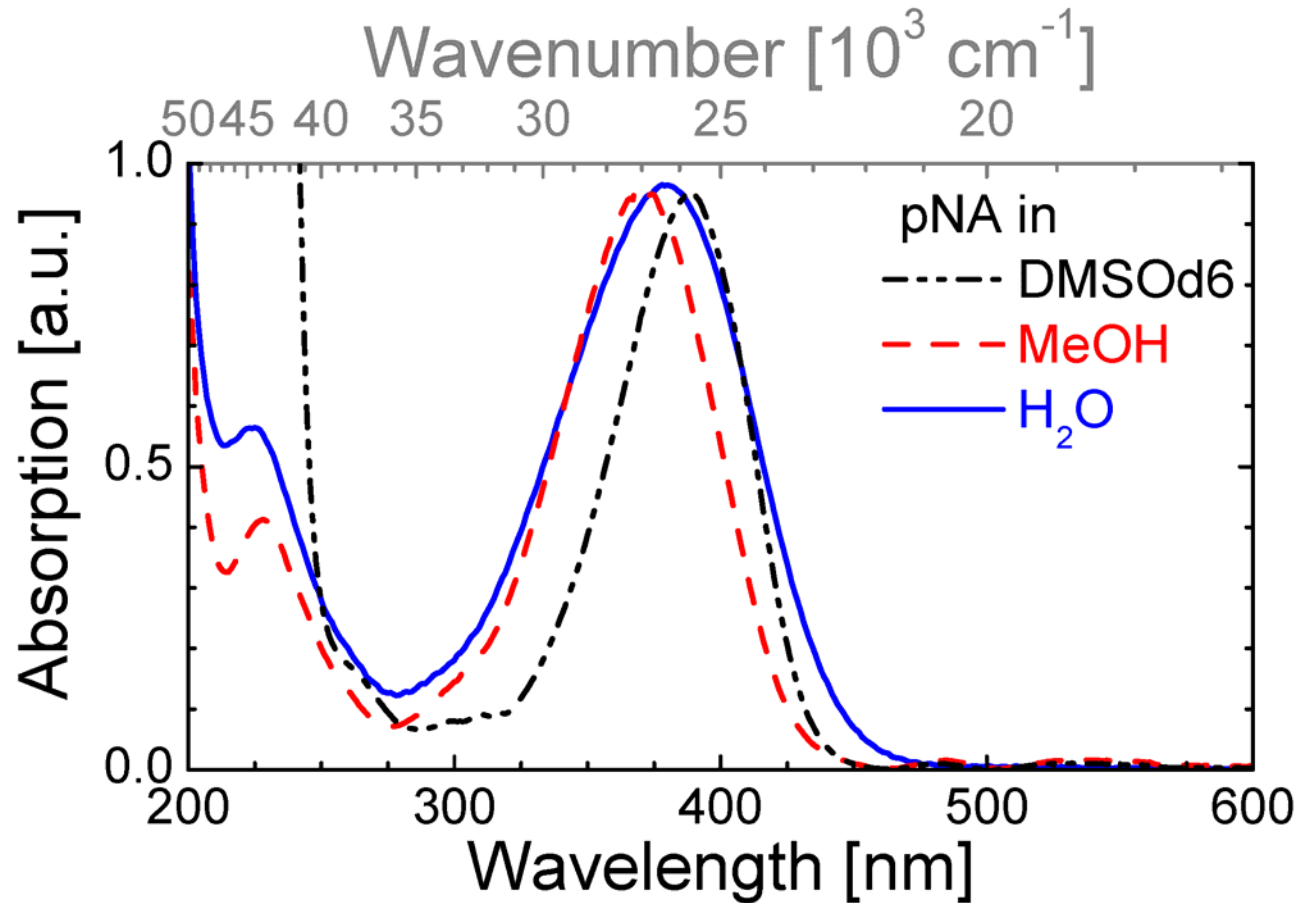
S. A. Kovalenko et. al.: J. Chem. Phys. 115, 3256 (2001)

Solvents: Physical Properties



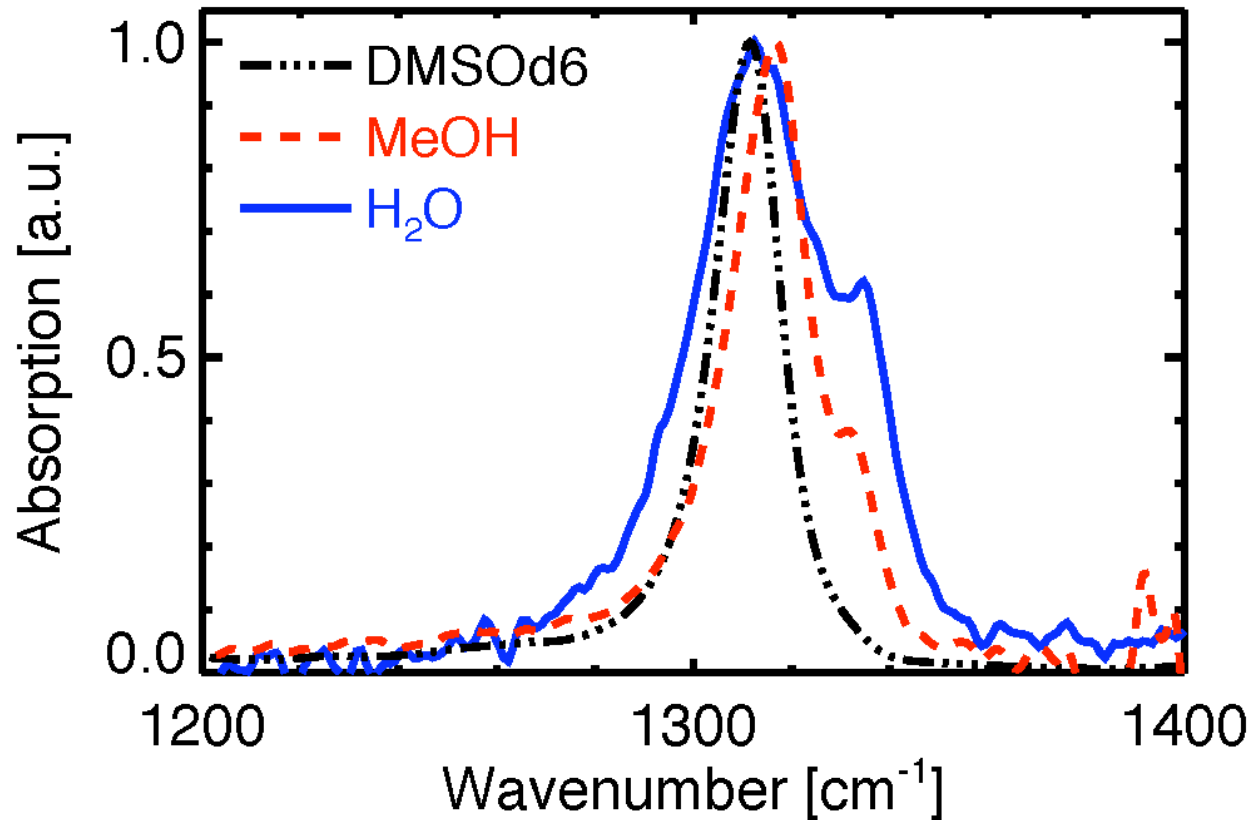
Solvent	DMSO	MeOH	H ₂ O
Hydrogen Bonds	aprotic	protic	protic
Dipole Moment	1.7	1.7	1.9
Dielectric Constant	49	33	78

Visible Spectra of pNA in Various Solvents



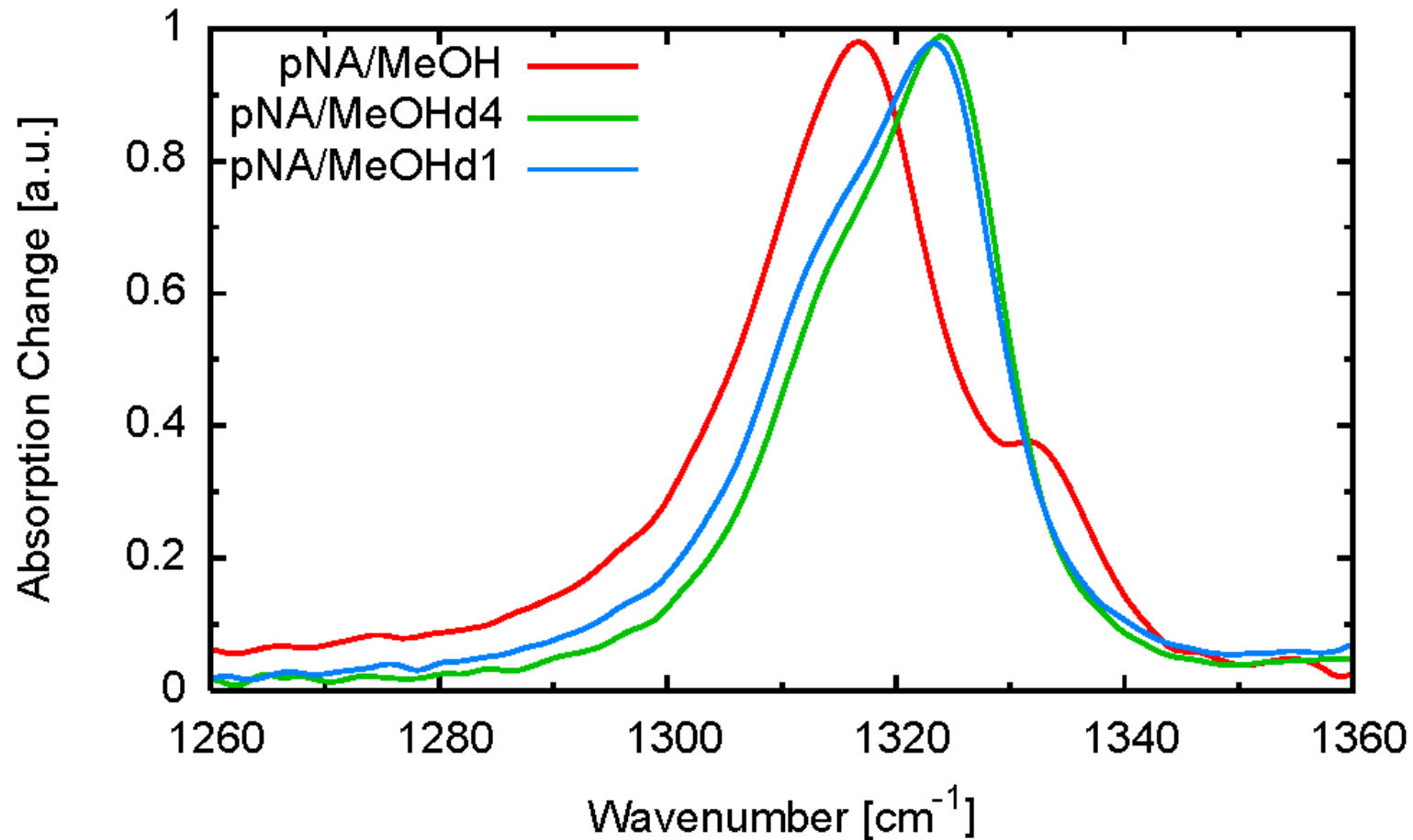
Pronounced Solvatochromic effects observed

FTIR-Spectra of pNA in different solvents



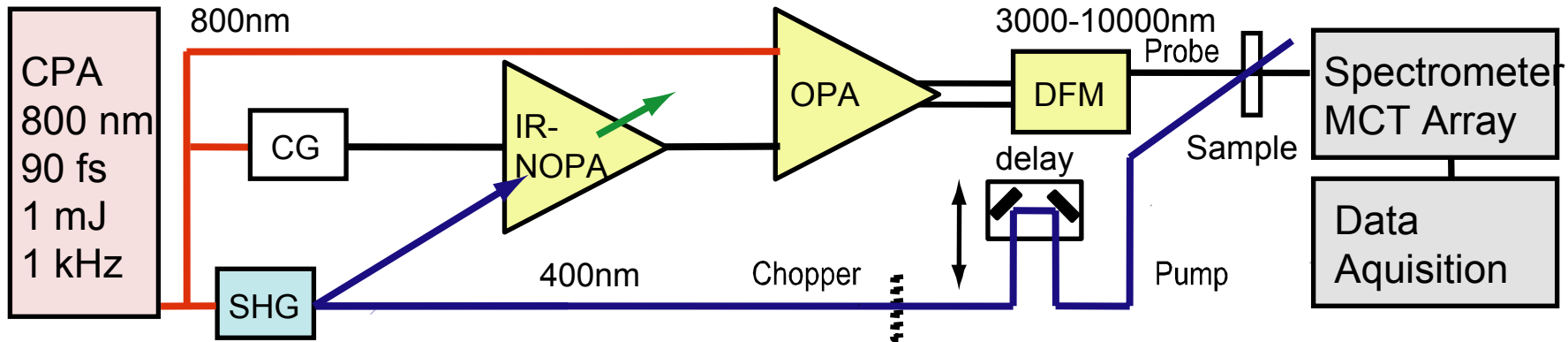
Spectral shape of pNA absorption strongly influenced by solvent properties

FTIR-Spectra of pNA in deuterated solvents



pNA – a good sensor for hydrogen bonds

Set-up of VIS-Pump-IR-Probe Experiment



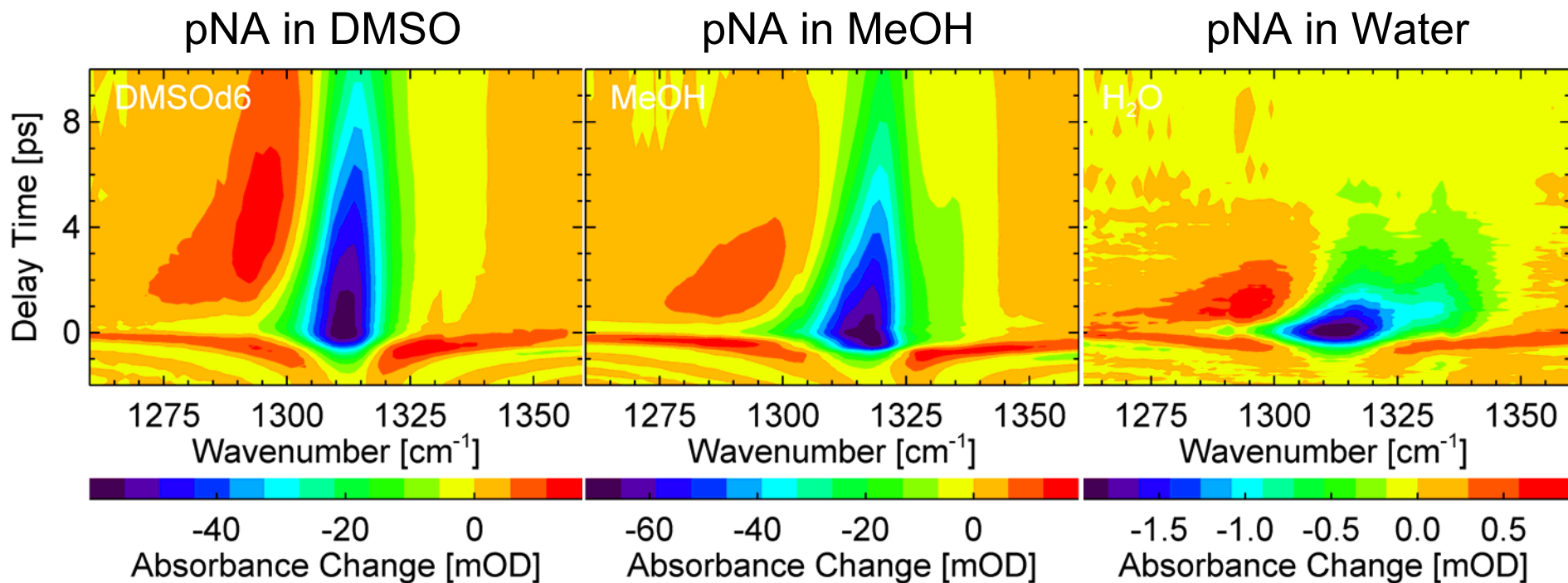
Laser system: TiSa CPA (814 nm, 1 KHz, 90 fs)

Pump pulse: 407 nm, $\sim 4 \mu\text{J}$, focal diameter 80 μm

Probe pulse: 7,5 μm , 0,7 μJ , focal diameter $\sim 80 \mu\text{m}$

Spectral resolution: 1,5 cm^{-1} , time resolution: 450 fs

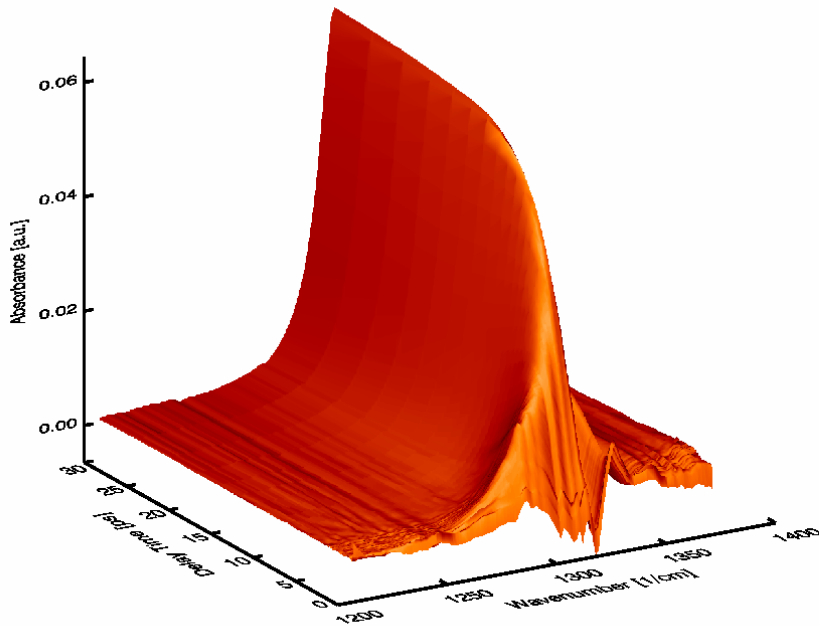
Time Resolved IR Absorption Changes of pNA



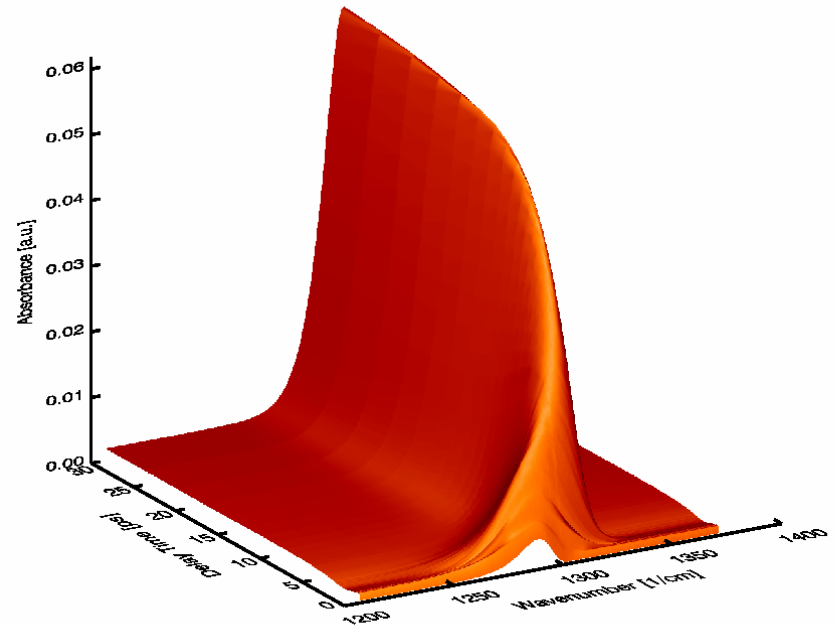
Strong influence of solvent on vibrational relaxation

IR Spectroscopy: Bleach Correction and Fit

- IR-Signal = "bleached" ground state(-) + induced Absorption(+)
- Adding bleached ground state = removal of bleach contribution
- Fitting each transient spectrum with a skewed Gaussian fit

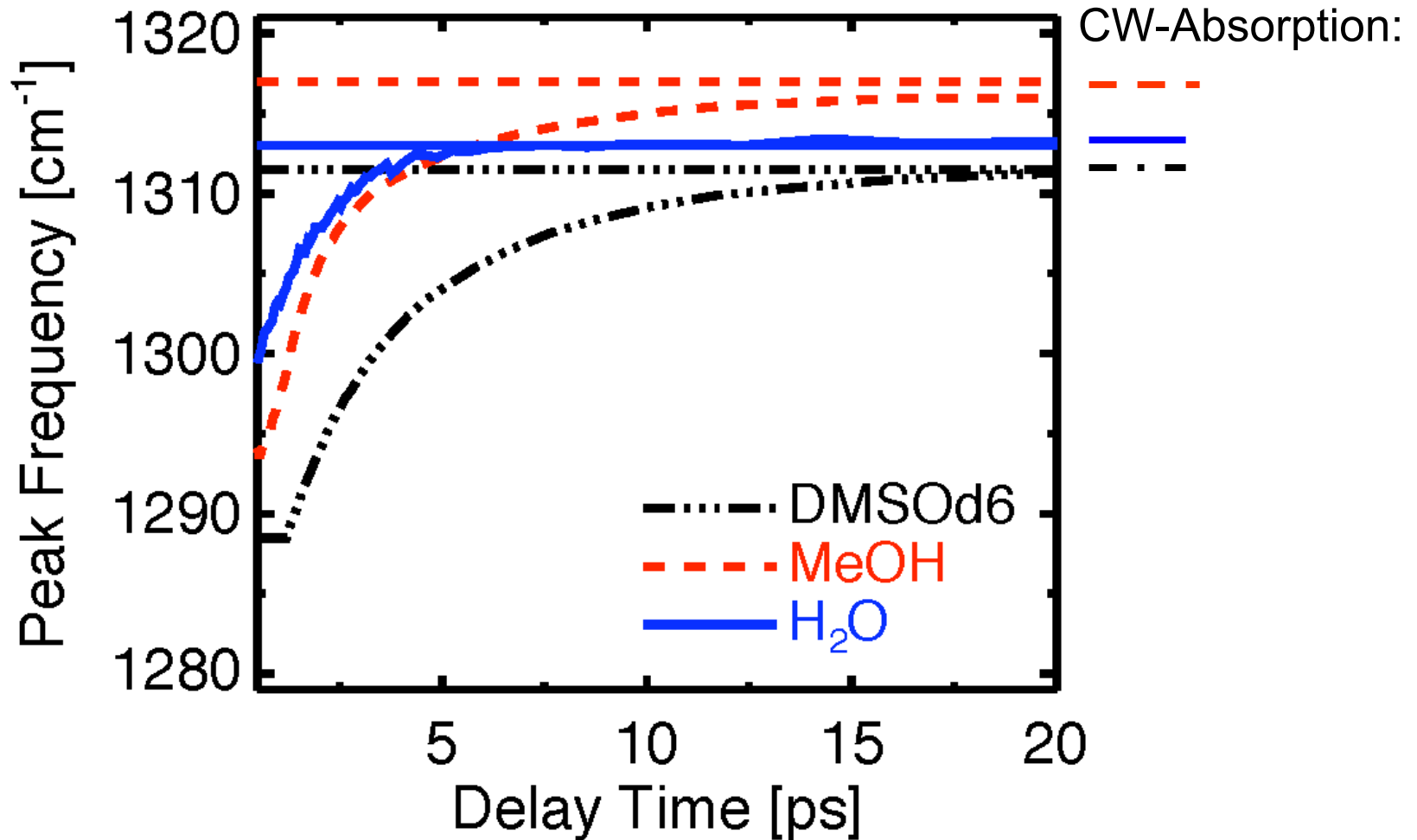


Data after bleach correction



Skewed Gaussian fit

Results of Spectral Fitting Procedure



→ Extracting characteristic cooling time constants by mono-exponential fits

Identification of Trends

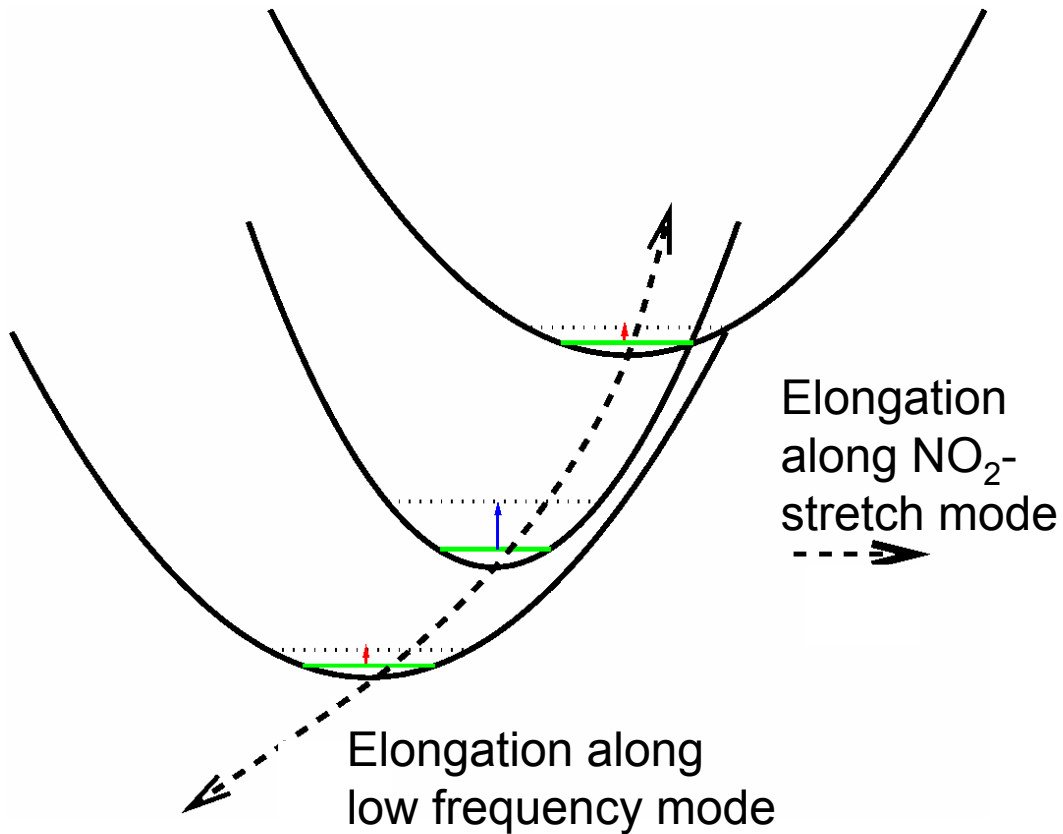
	DMSO(-d6)	MeOH	H ₂ O
Amplitude of peak shift	-29 cm ⁻¹	-25 cm ⁻¹	-15 cm ⁻¹
Time constant of peak shift	3.1 ps	2.1 ps	1.6 ps
Kovalenko's visible data	2.8 ps	1.9 ps	1.1 ps

The larger the hydrogen-bonding capabilities, the shorter the decay times and the smaller the observed peak shift.

Good agreement with cooling times observed in visible spectroscopy

Off-Diagonal Anharmonicity as reason for peak shift

From a comparison with time resolved raman probing¹ we know the reason for the peak shift: **Off-diagonal Anharmonicity**

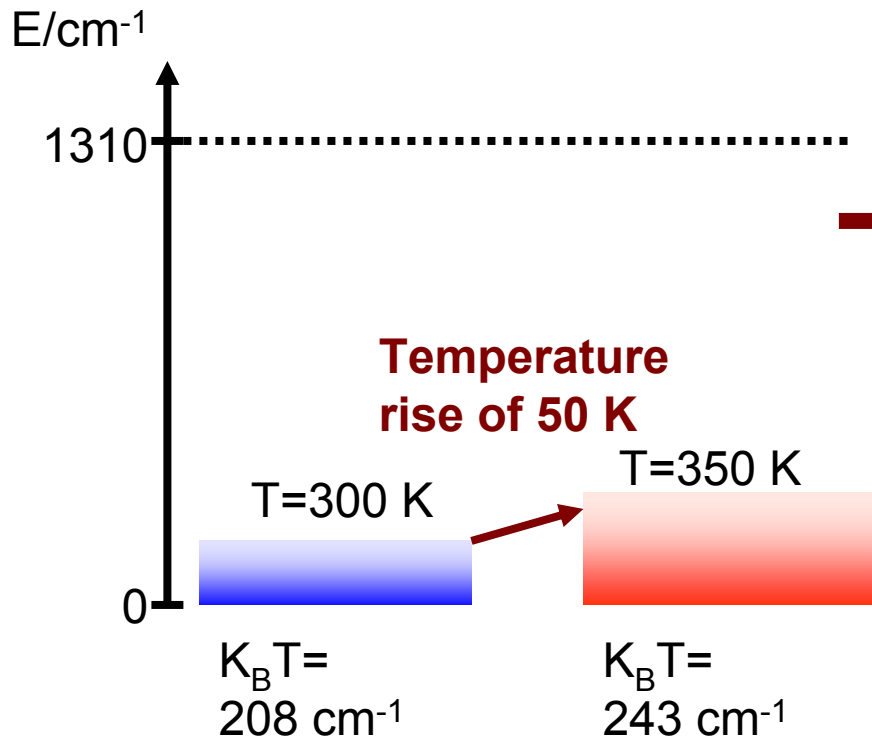


Off-Diagonal Anharmonicity:
Frequency shift of **NO₂-stretch node** is due to excitation of low frequency modes

- Sensor for population of low frequency modes
- IR spectral dynamics shows the same signature as Raman peak shift

¹ T. E. Schrader et al., CPL, 392 (2004) 358-364

Complementary Observation of the Influence of the Low Frequency Modes



Thermally excited modes

Temperature rise of 50 K:

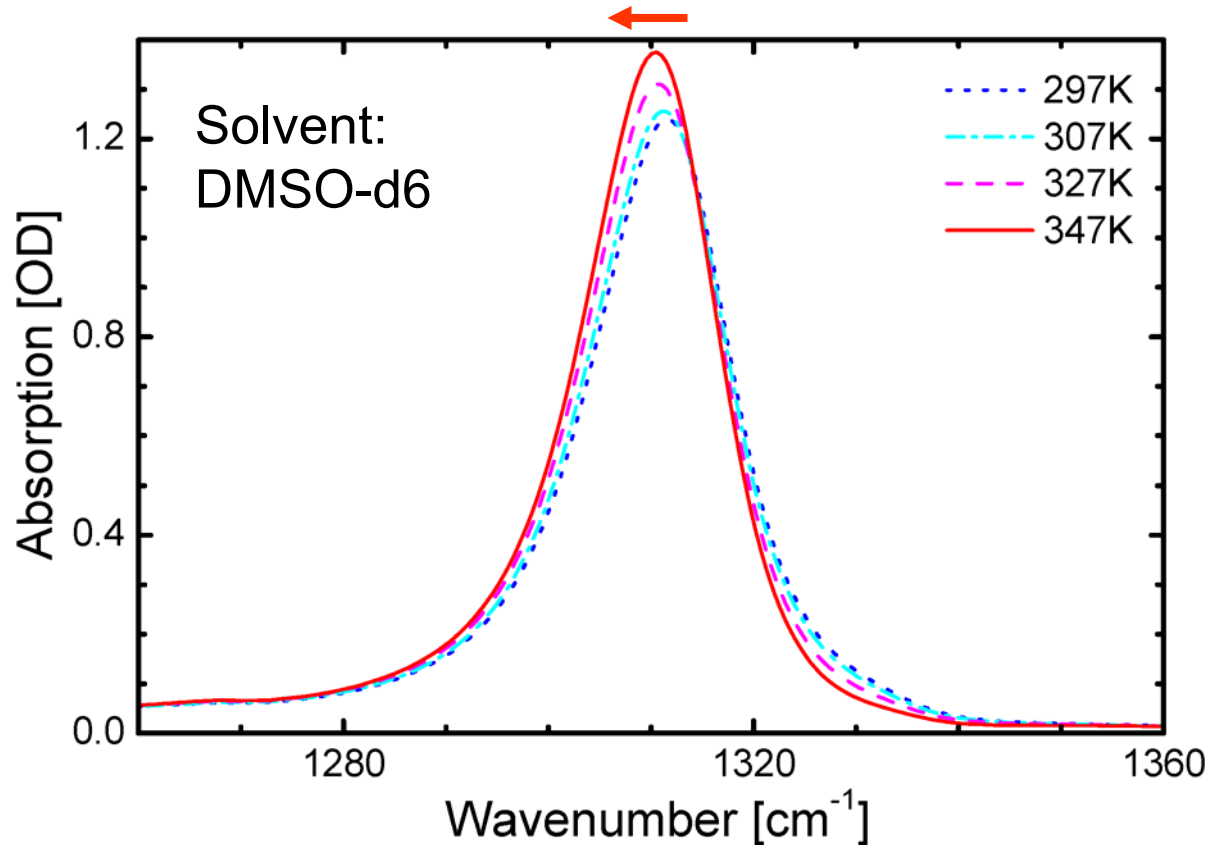
No direct excitation of NO₂ stretch mode at 1310 cm⁻¹

But: Anharmonic coupling to thermally excited low frequency modes should shift the absorption maximum of the NO₂ stretch vibration

Will this be observed?

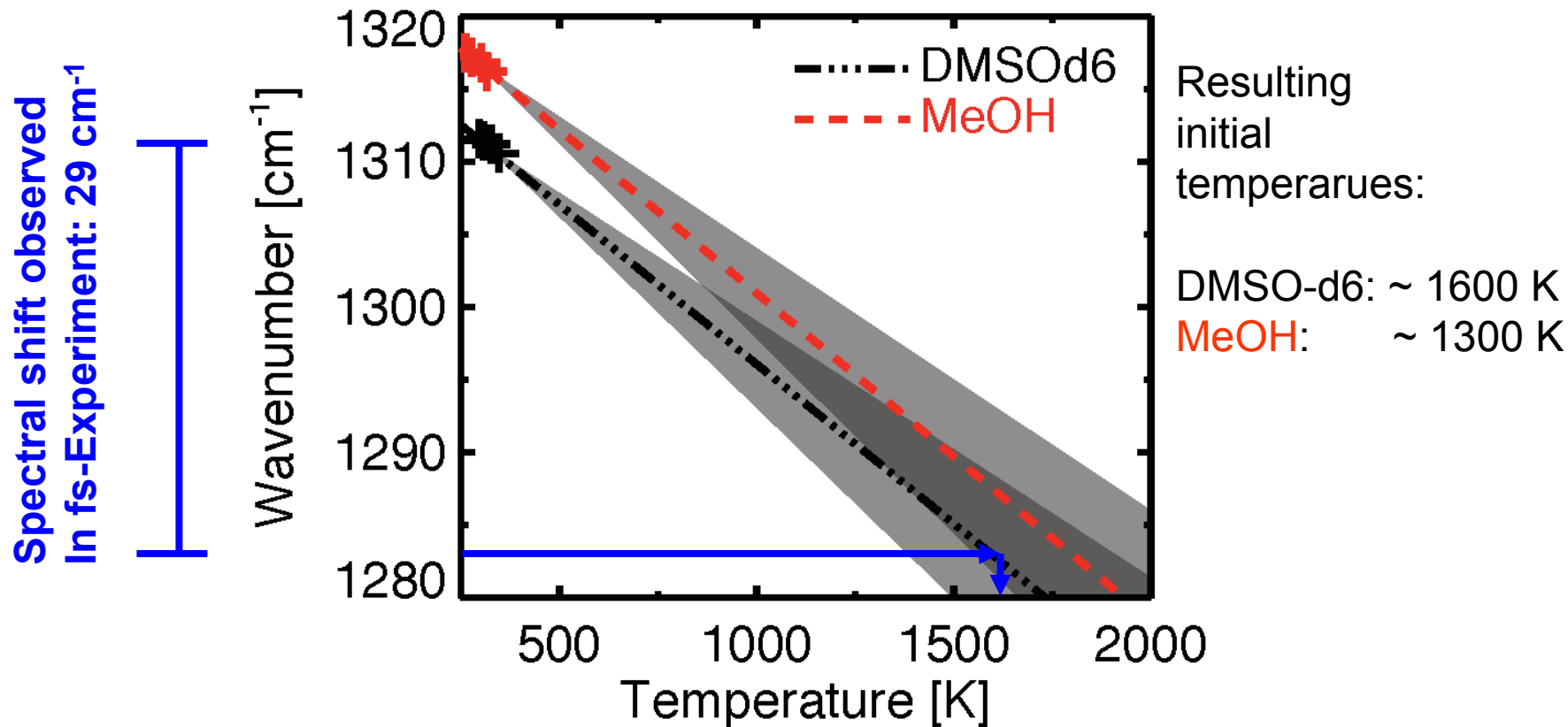
Temperature Dependent Infrared Absorption of pNA

Shift of peak frequency due to heating



Anharmonic coupling to low frequency modes well observed in thermal equilibrium temperature jump experiments

Extrapolation to Observed Spectral Peak Shift



By this extrapolation reasonable initial temperatures are obtained.

Conclusions

- **Visible and infrared absorption spectrum of pNA strongly solvent dependent**
- **Even deuteration state of solvent important**
- **Due to anharmonic coupling NO₂-stretch vibration good sensor for decay of the excitation of low frequency modes**
- **Relaxation processes of pNA determined by hydrogen-bonding capabilities of solvent**
- **The larger the hydrogen-bonding capabilities of the solvent, the shorter the decay times and the smaller the observed peak shift**
- **Data on solvent dependent energy relaxation processes collected, molecular model still under construction**