Variation of the transition dipole moment across the OH stretching band of water

Chem. Phys. ***341****, 218 (2007), J. J. Loparo etc.*

발표자 : 전윤남

4th January, 2008

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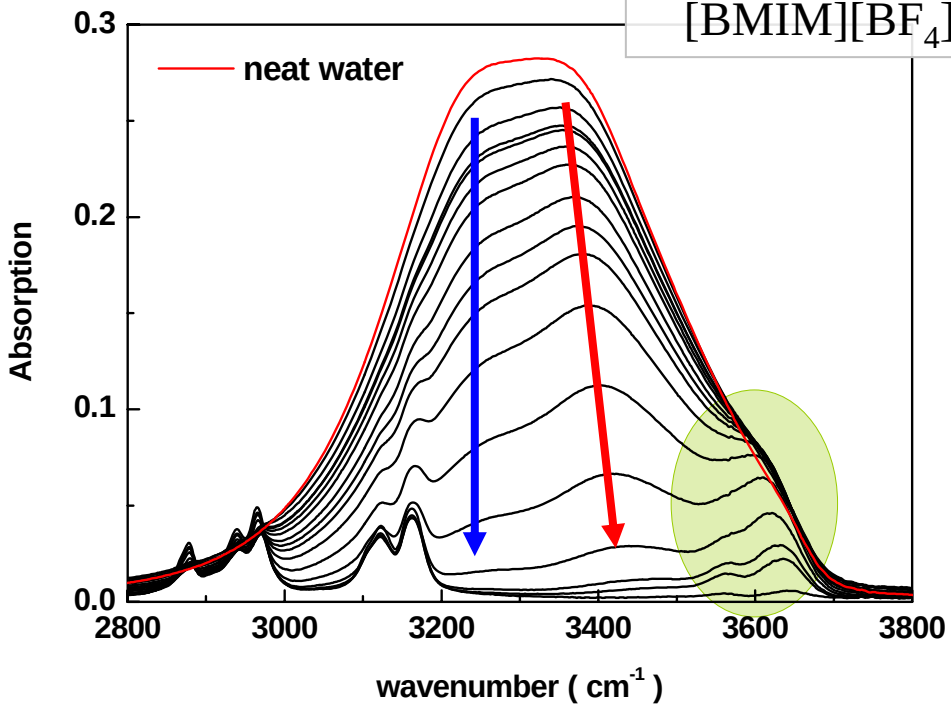
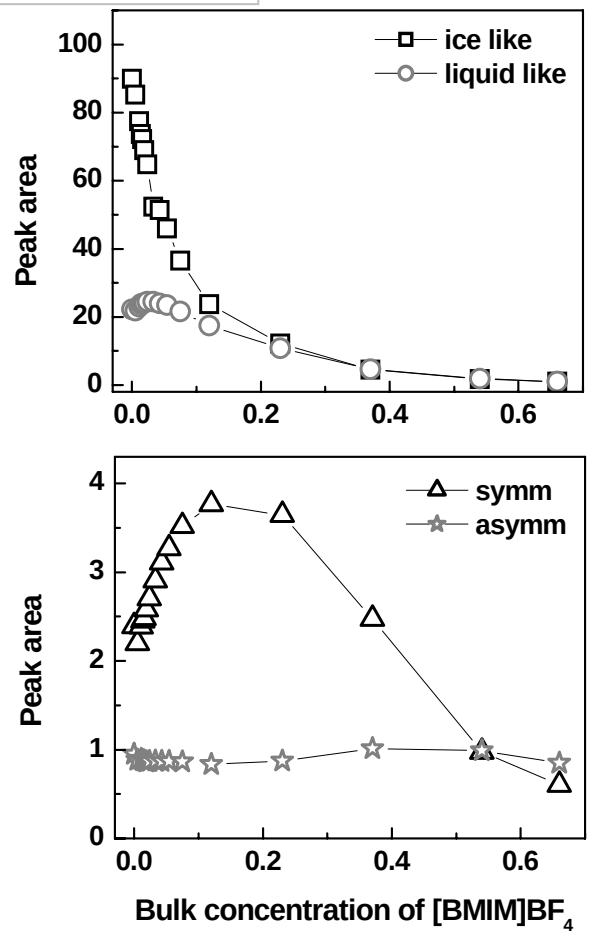
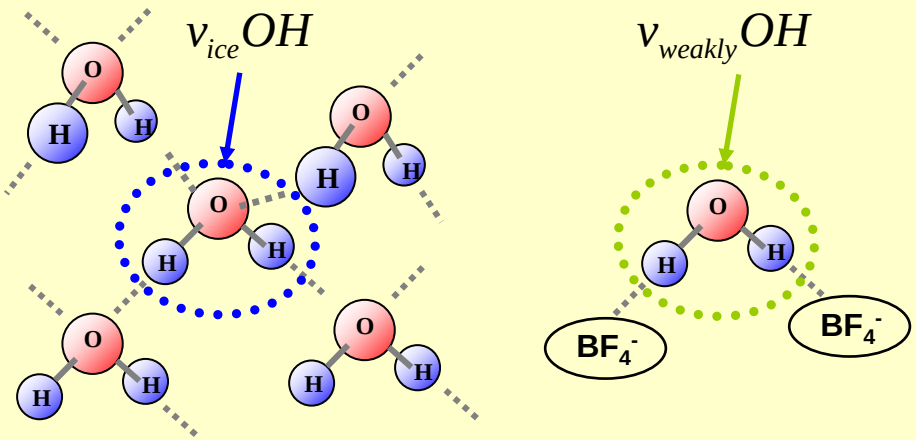
Nonlinear Optics

Introduction

[BMIM][BF_4]+H_2O mixtures







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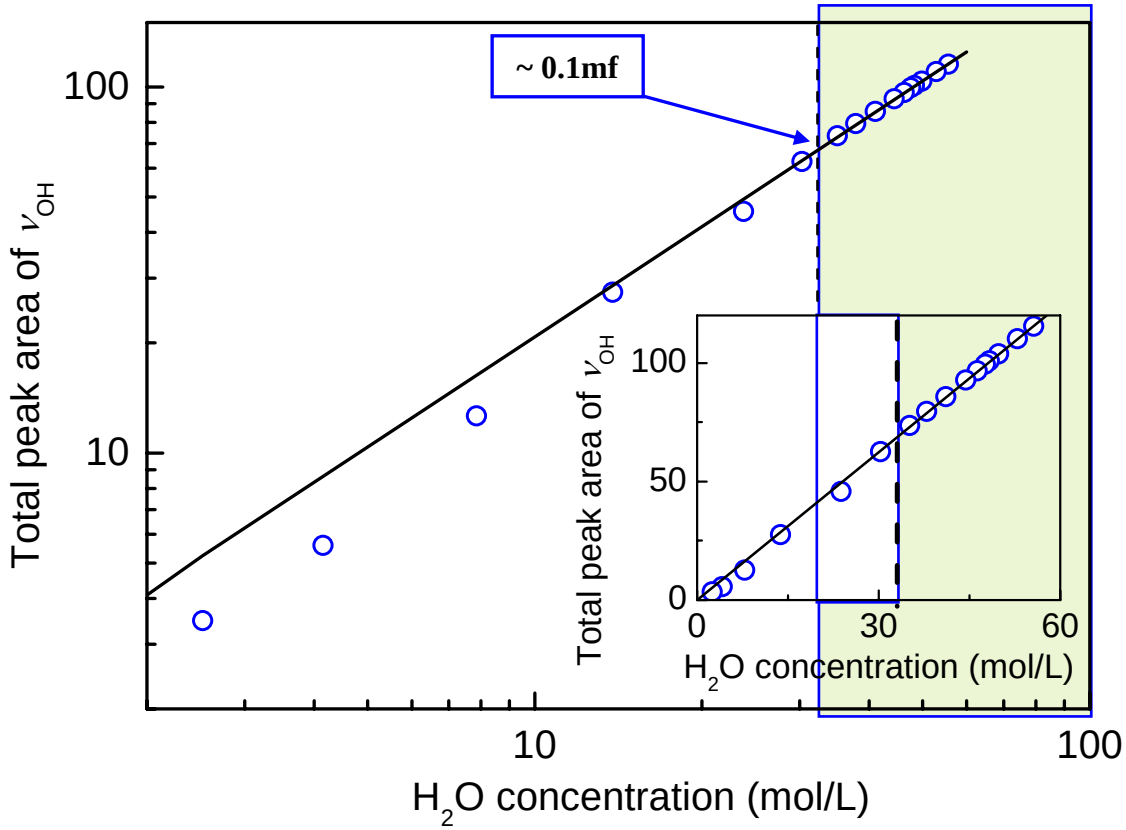

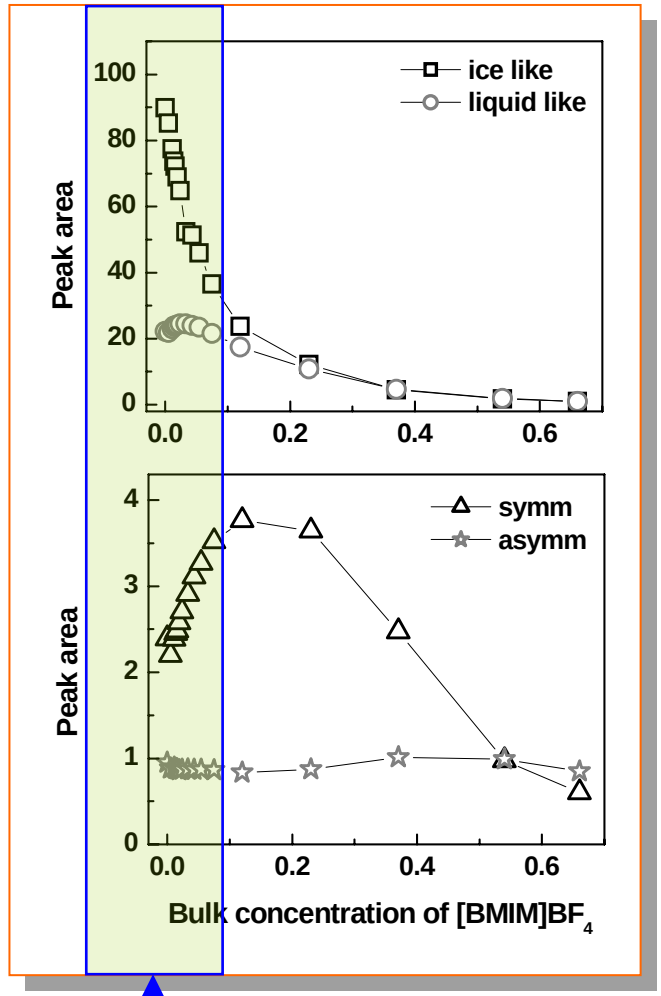

strength of $\nu_{ice}OH \geq$ strength of $\nu_{weakly}OH$??

water rich region

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Introduction

Condon approximation :

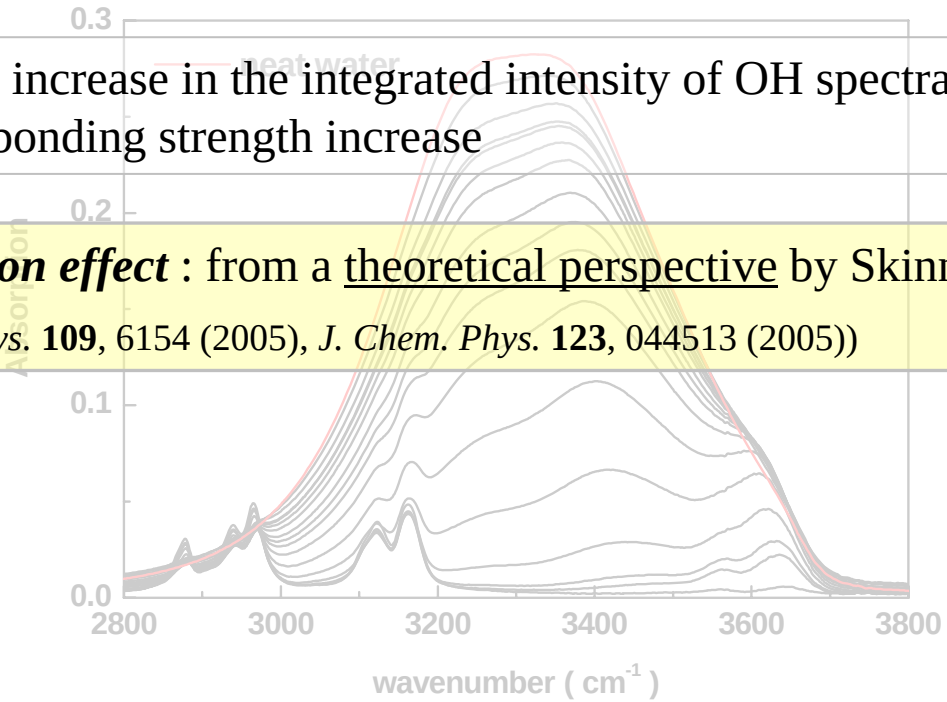
assume the OH transition dipole is independent of the solvent degrees of freedom

(S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*, Oxford Univ. Press, New York, 1995)

Question : increase in the integrated intensity of OH spectral line shape as hydrogen bonding strength increase

non-Condon effect : from a theoretical perspective by Skinner and coworkers

(*J. Chem. Phys.* **109**, 6154 (2005), *J. Chem. Phys.* **123**, 044513 (2005))



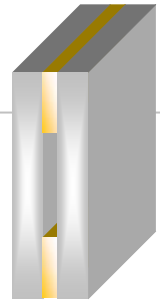
Experiments & Sample & Detector

experiments & sample for the IR and Raman

IR : collected on a Thermo Electron spectrometer (2 cm^{-1} resolution)

Raman : 514.5 nm line of an Ar^+ ion laser (by Saykally and cowokers)

sample cell : 1 mm CaF_2 window with 50 μm spacer



sample & detector for the echo signal

HOD in D_2O : **flowed as a 50 μm jet**

- to avoid the generation of any non-resonant signal from the sample cell

2% H_2O in D_2O

- OD of υOH ~ 0.4

Theory & Simulation

$$\mu = \mu(q_0) + \left.\frac{\partial \mu}{\partial q}\right|_{q=q_0} q + \left.\frac{\partial^2 \mu}{\partial q \partial Q}\right|_{q=q_0, Q=Q_0} qQ + \cdots$$

q : intramolecular OH coordinate

Q : refers to the bath coordinates

$\frac{\partial \mu}{\partial q}$: transition dipole moment independent on the bath coordinates

$\frac{\partial^2 \mu}{\partial q \partial Q}$: transition dipole moment dependent on the bath coordinates

For the **OH stretch** of HOD, it is now well established that the dominant interaction of the OH coordinate with the intermolecular degrees of freedom is expressed through the electric field E that the surroundings exert on q.

Therefore, **we equate Q with E**.

*$(E \propto \omega_{OH})$

Theory & Simulation

$$\mu = \mu(q_0) + \left.\frac{\partial \mu}{\partial q}\right|_{q=q_0} q + \left.\frac{\partial^2 \mu}{\partial q \partial Q}\right|_{q=q_0, Q=Q_0} qQ + \cdots$$

??

$$\mu_{10}(\omega) = \mu_1 + \mu_2 \cdot (\omega - \omega_g)$$

gas phase frequency

$$\gamma \equiv \left(|\mu_2| / |\mu_1|\right) \cdot \Delta\omega$$

⇒ $\gamma << 1$: Non-Condon Effect (NCE) is negligible

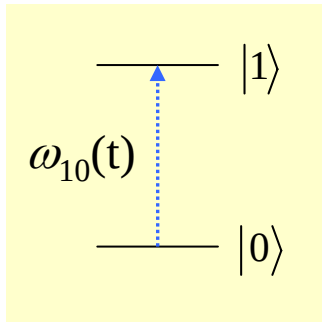
Theory & Simulation

Absorption line shape (from the linear response function)

- just 1 degree of freedom : OH stretching vibration

(ignoring population relaxation and reorientation)

- including the Non-Condon effects (NCE)



Raman polarizability : largely **independent of hydrogen bonding strength**

(- S. A. Corcelli, J. L. Skinner, *J. Chem. Phys.* **109**, 6154 (2005))

$$I_{IR}(\omega) = \mathrm{Re}\left[\int_{-\infty}^{+\infty} dt\, e^{i\omega t}\left\langle \mu_{10}(t)\mu_{10}(0)\cdot\exp\left[-i\int_0^t d\tau\, \omega_{10}(\tau)\tau\right]\right\rangle\right]$$

$$I_{R}(\omega) = \mathrm{Re}\left[\int_{-\infty}^{+\infty} dt\, e^{i\omega t}\left\langle \alpha_{10}(t)\alpha_{10}(0)\cdot\exp\left[-i\int_0^t d\tau\, \omega_{10}(\tau)\tau\right]\right\rangle\right]$$

Theory & Simulation

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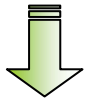


experimentally observed frequency- and temperature-dependent absorption coefficient

$$\sigma_{IR}(\omega) \propto \omega(1-e^{-\beta\hbar\omega})I_{IR}(\omega)$$

(R. Zwanzig, *Nonequilibrium Statistical Mechanics*, Oxford Univ. Press, Oxford, 2001)

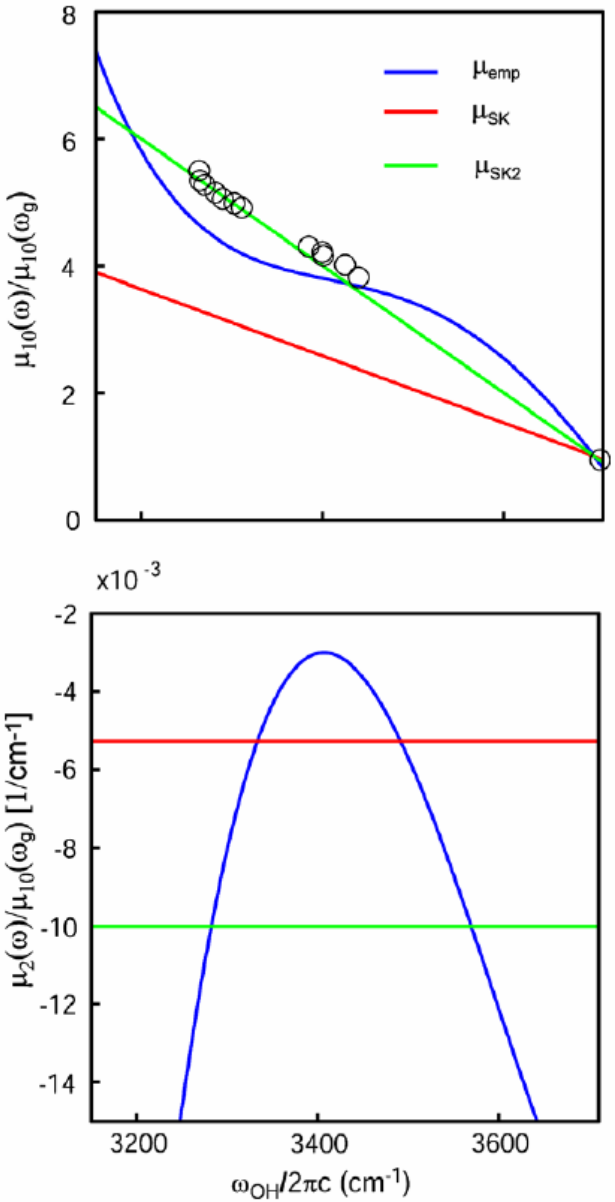
observed Raman scattering intensity for incoherent Stokes scattering

$$\sigma_{R}(\omega) \propto (\omega_L-\omega)^4(1-e^{-\beta\hbar\omega})^{-1}I_{R}(\omega)$$

(D. A. McQuarrie, *Statistical Mechanics*, Harper and Row, New York, 1976,

G. E. Walrafen, M. R. Fischer, M. S. Hokmabadi, W. –H. Yang, *J. Chem. Phys.* **85**, 6970 (1986))

Theory & Simulation



μ_{SK} : frequency-dependent transition dipole

-(calculated by Skinner and coworkers)

μ_{emp} : frequency-dependent transition dipole

-(determined from the ratio of the IR and Raman)

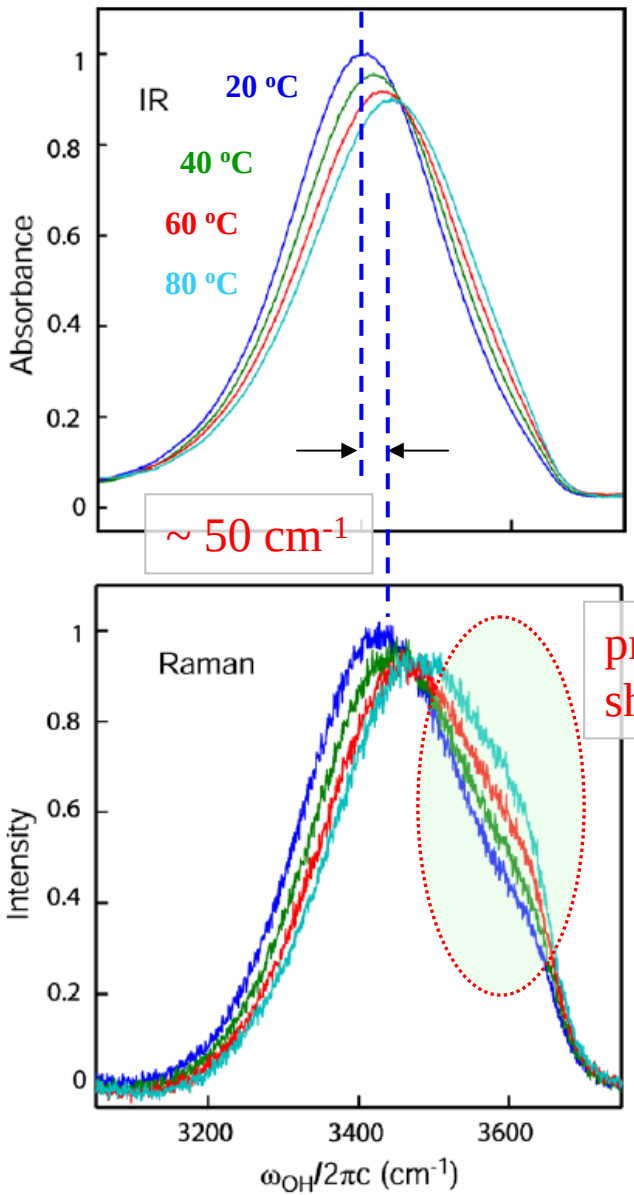
$$\left|\mu_{emp}(\omega)\right| \propto \sqrt{\frac{I_{IR}(\omega)}{I_{Raman}(\omega)}} \propto \sqrt{\frac{\sigma_{IR}(\omega)}{\sigma_{Raman}(\omega)} \cdot \frac{\omega}{(\omega_L - \omega)}(1-e^{-\beta h\omega})^2}$$

μ_{SK2} : frequency-dependent transition dipole

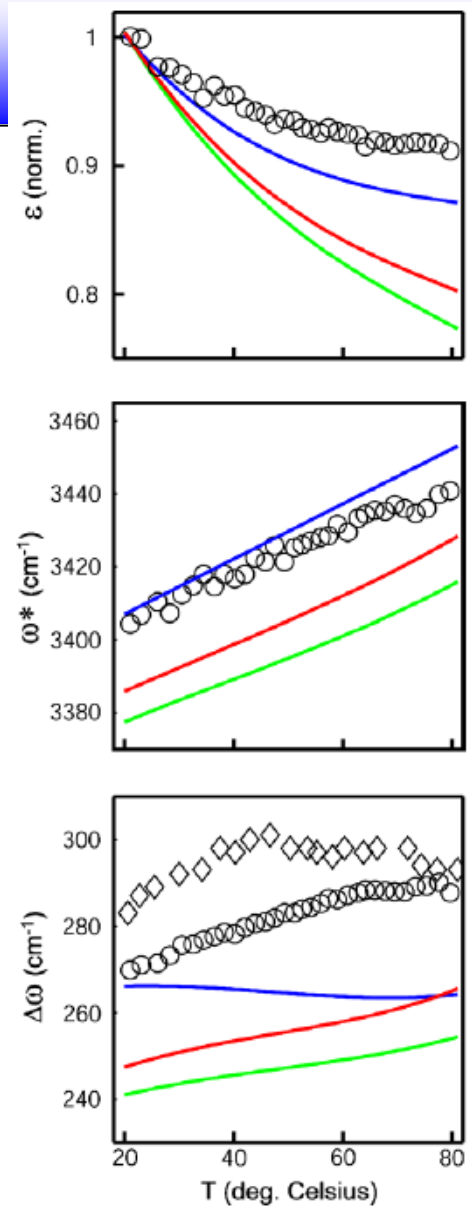
-(calculated by Skinner and coworkers, twice the slope)

* data : A. V. Iogansen, *Spectrochim. Acta A* **55**, 1585 (1999)

Results & Discussion



prominent shoulder



peak intensity

peak position

peak width

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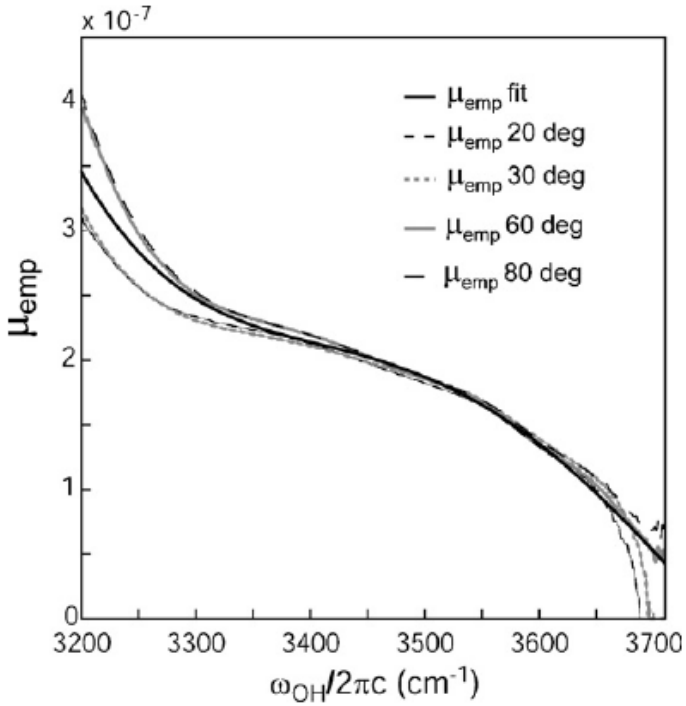
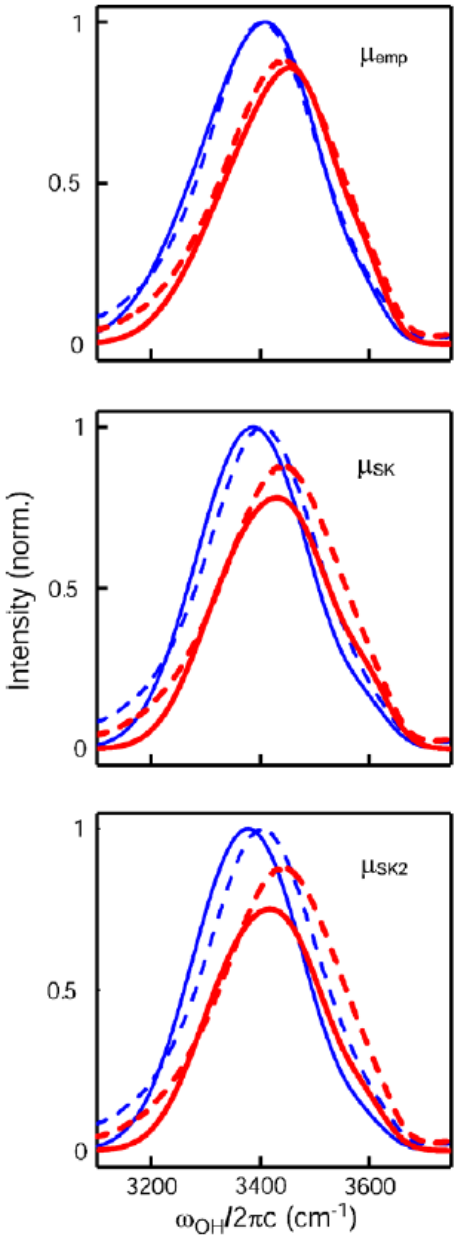
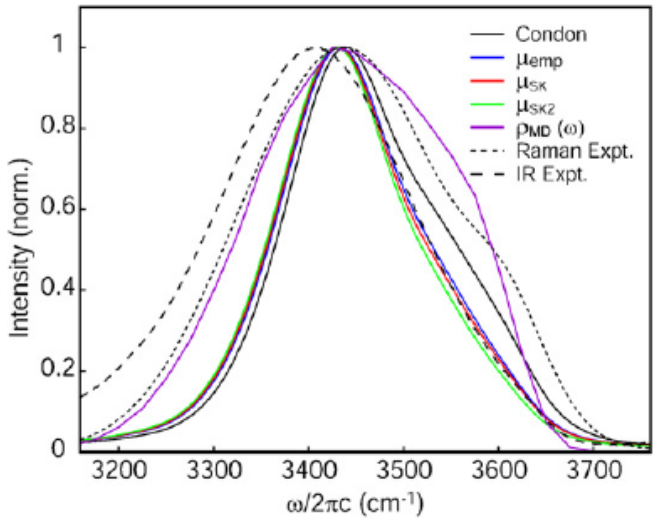


Results & Discussion





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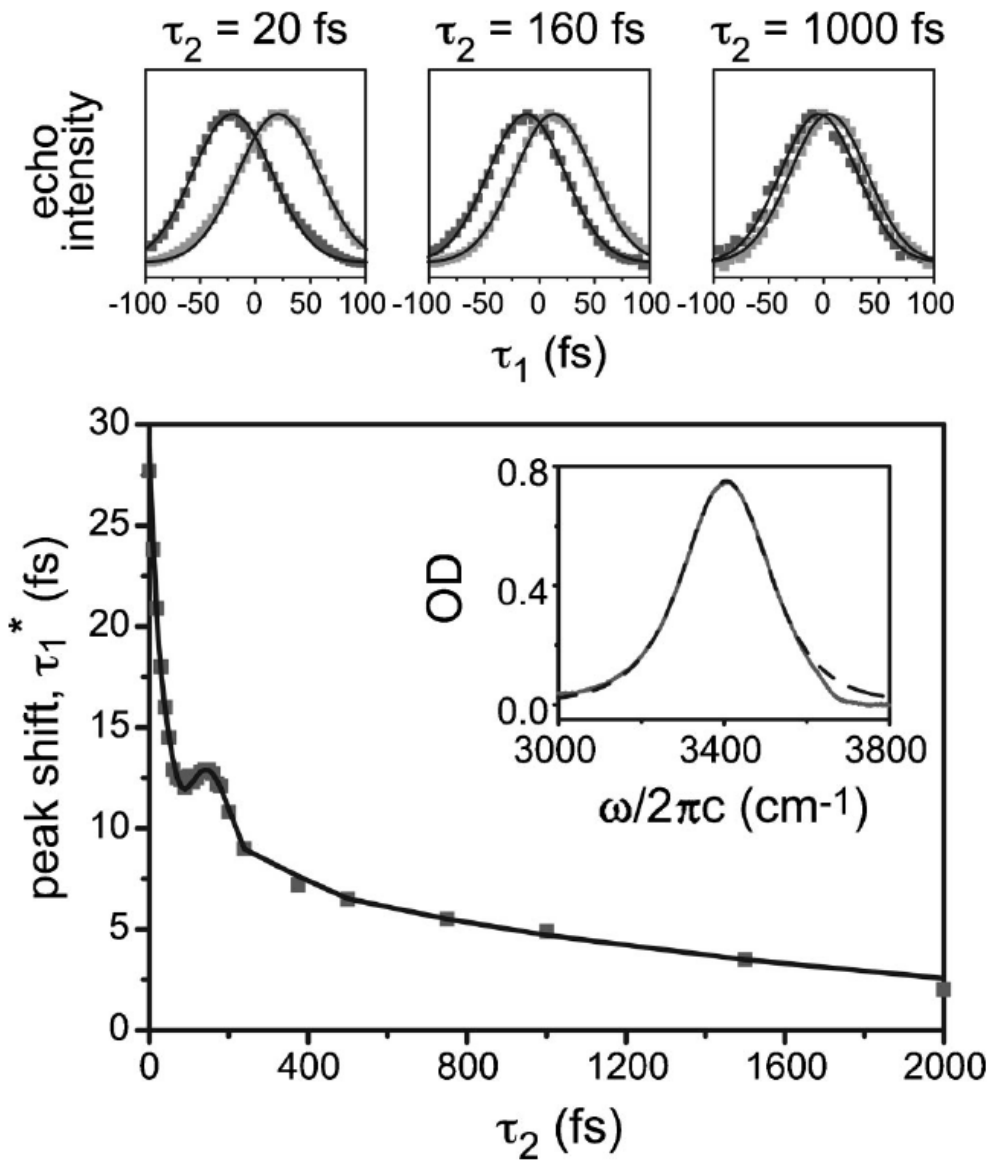
Introduction – echo signal



J. Chem. Phys. **122**, 054506 (2005)

Top: Examples of normalized vibrational echoes in the k_+ and k_- wave vector geometries for the indicated waiting times. For each τ_2, the value of τ_1* is obtained by fitting both echoes with Gaussian functions (black lines) to determine the time interval between peak positions.

Bottom: The PS decay (squares) is plotted along with the best fit (black line).

In the inset, the absorption spectrum calculated from the extracted dynamical quantities (dashed line) is superimposed on the experimental spectrum.

$k_+ : -k_\alpha + k_\beta + k_\gamma$

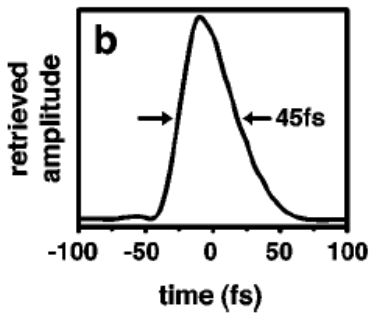
$k_- : k_\alpha - k_\beta + k_\gamma$

Experiment – input for the echo signal

J. Chem. Phys. **125**, 194521 (2006)

Ti:sapphire multipass amplifier

(homebuilt : 30 fs, 1 kHz, 800 nm)



E ~ 5 μJ

λ ~ 3 μm

Δτ ~ 45 fs

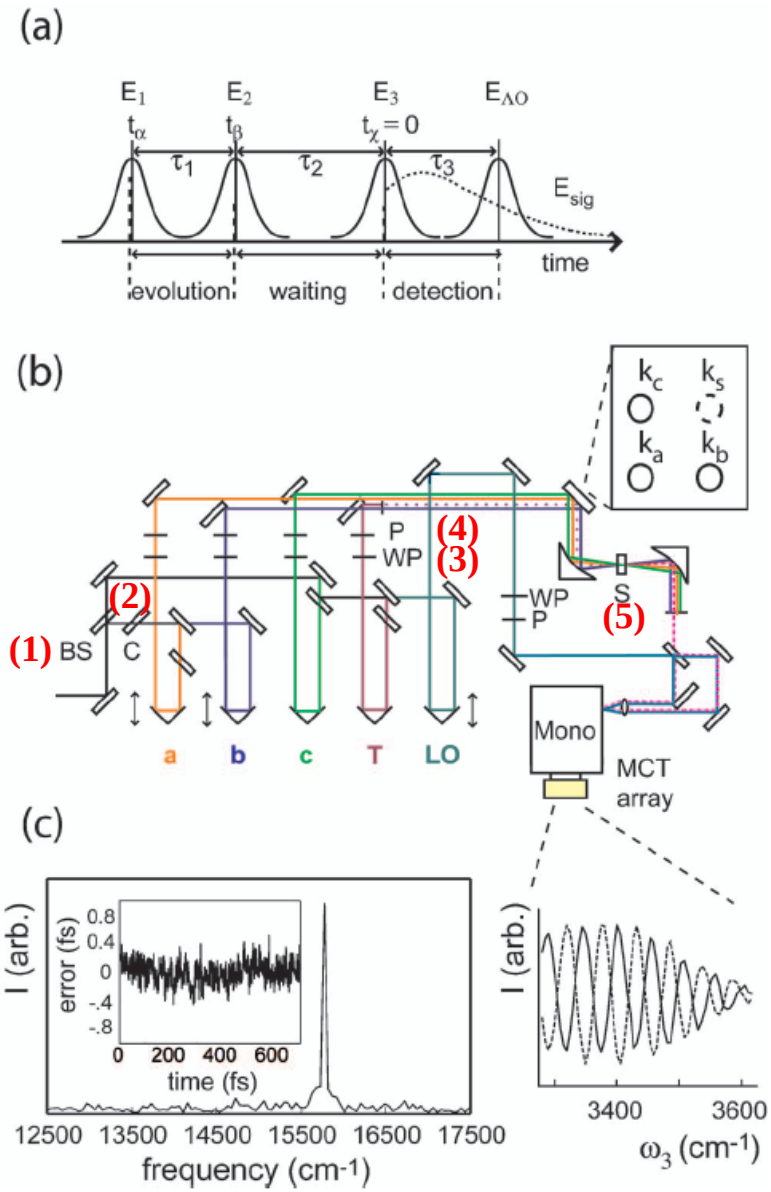
OPA (optical parametric amplifier)

BBO

$KNbO_3$

OPA + experimental area : purged with **dry air**

Experiment – signal setup for the echo signal



J. Chem. Phys. **125**, 194521 (2006)

excitation pulses : **a**, **b** and **c**

tracer : T

local oscillator field : LO
(heterodyne detection)

(1) **BS** (50-50) : 3 mm CaF_2

(2) **C**ompensation plate : 3 mm CaF_2

(3) **WP** : $\lambda/2$ tunable wave plate

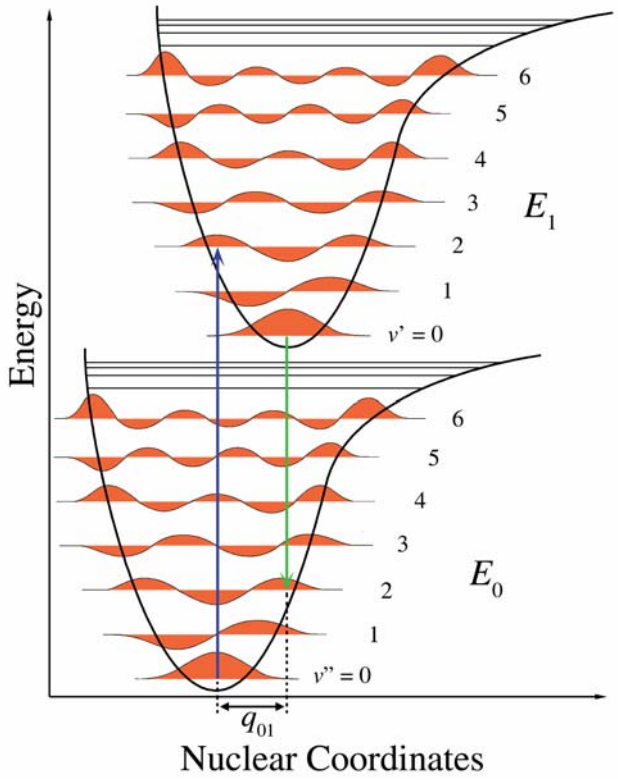
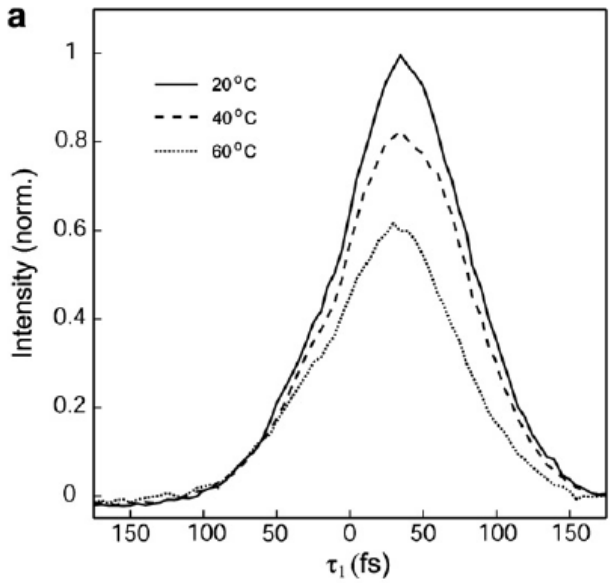
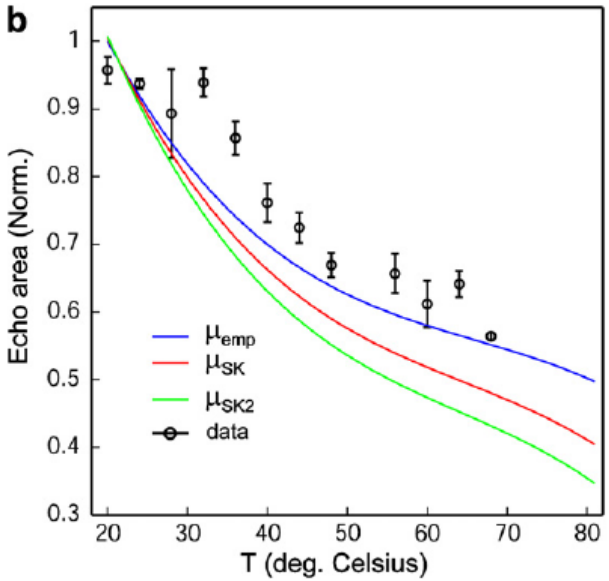
(4) **P** : wire grid CaF_2 polarizer

(5) **S**ample : 50 μm CaF_2 cell
($\tau_2 > 2$ ps)

Introduction – Frank-Condon principle

http://en.wikipedia.org/wiki/Franck-Condon_principle

The **Franck-Condon principle** is a rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy. The principle states that during an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly.



Results & Discussion