# Terahertz and Water

Winter College on Optics: Terahertz Optics and Photonics
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Dr. Fabio Novelli
Phys. Chem. 2, Ruhr University Bochum, Germany
fabio.novelli@rub.de

# Terahertz and Water: outline

1. Terahertz time-domain spectroscopy
    1. Examples of non-linear responses
    2. Linear and non-linear spectroscopy
    3. Optical rectification (OR) and electro-optical sampling (EOS)
    4. Models to obtain the optical properties (Fresnel equations)

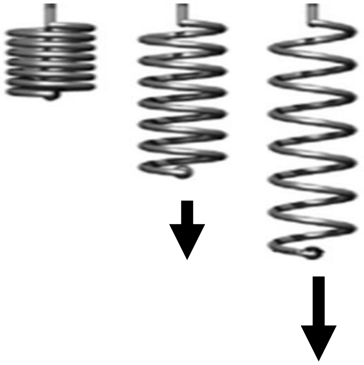
2. Water and solvation
    1. Infrared absorption modes of liquid water
    2. Introduction to solvation science
    3. Study ions in water with THz: rattling, hydration layers
    4. Gold nanoparticles
    5. Long-range protein effects on water
    6. Non-linear terahertz response of water

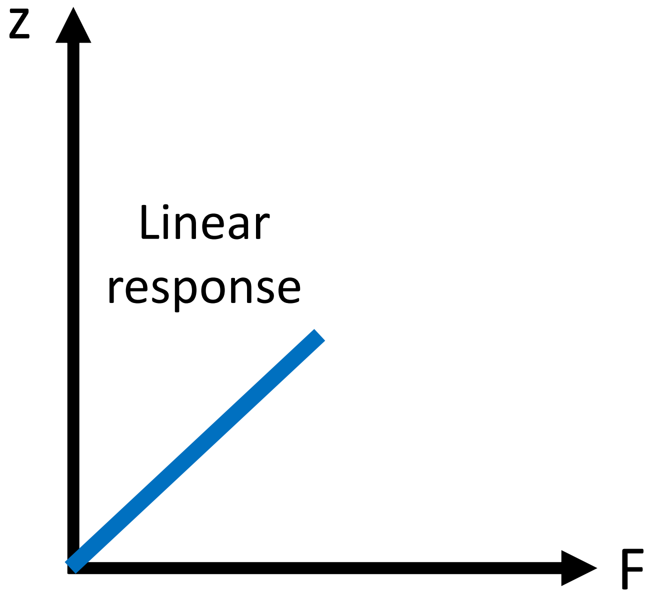
# A non-linear response you can touch

Hooke’s law, linear response

*The elongation,* $x$*, of a rubber band is proportional to the applied force,* $F$

1. $z = k \cdot F$





# A non-linear response you can touch

Hooke's law, linear response

*The elongation,* x, *of a rubber band is proportional to the applied force,* F

1. $z = k \cdot F$

...only up to a certain value of F !

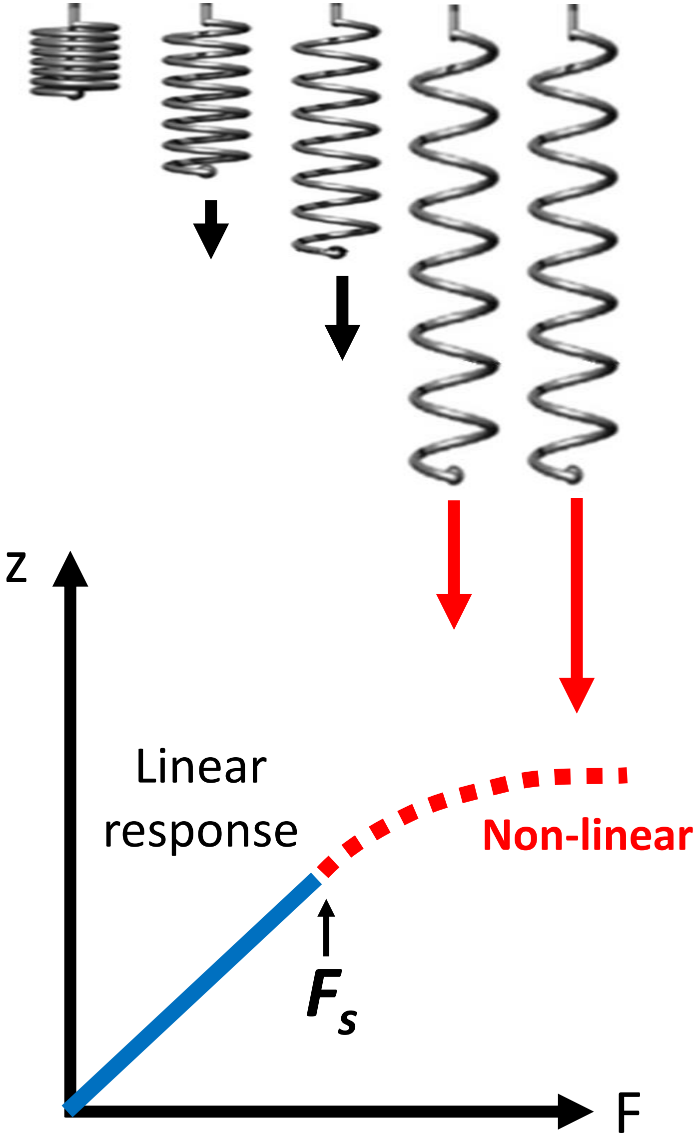
beyond that, we can Taylor-expand k(F)

2. $k = k(F) = k_1 + k_2 \cdot F + k_3 \cdot F^2 + \ldots$

and we have a non-linear response of the elongation w.r.t. the applied force

3. $z = k_1 \cdot F + k_2 \cdot F^2 + k_3 \cdot F^3 + \ldots$

Typically, the non-linear terms are small and important only for large applied force

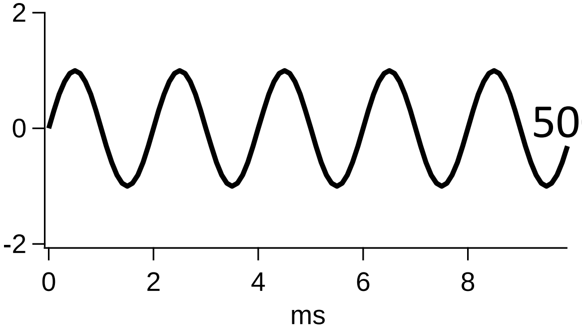


# A non-linear response you can hear

*Loudspeakers*

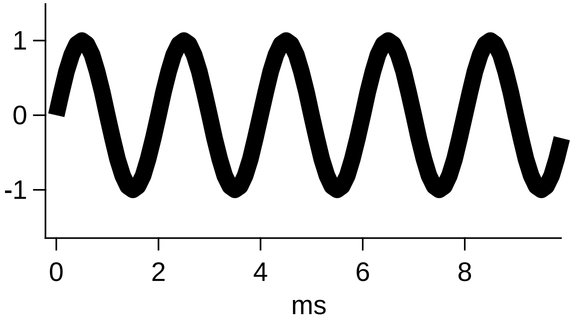
Apply an AC voltage, the membrane deforms accordingly, oscillating. This modulates the air density, which we hear.

Low input voltage



500 Hz

**Membrane deformation**



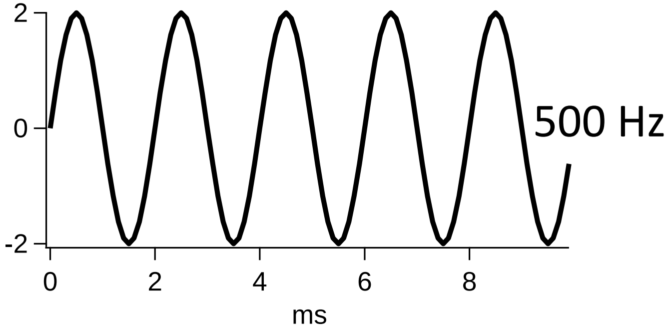
# A non-linear response you can hear

*Loudspeakers*

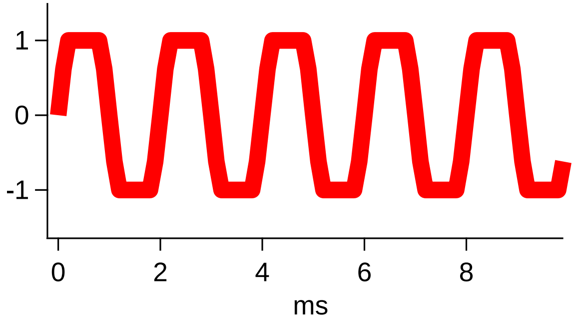
aixfoam.com

If the voltage we apply is too large, the membrane cannot deform proportionally, and the sound you hear is **distorted** !

High input voltage



**Nonlinear deformation**



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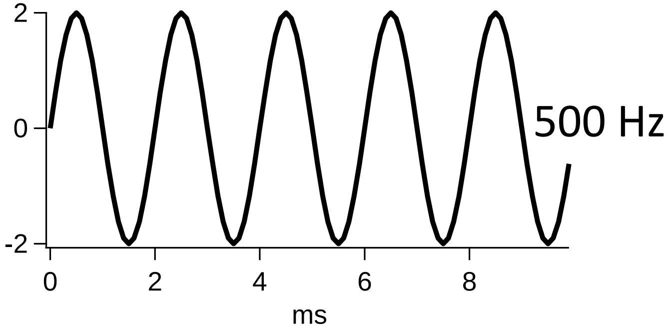
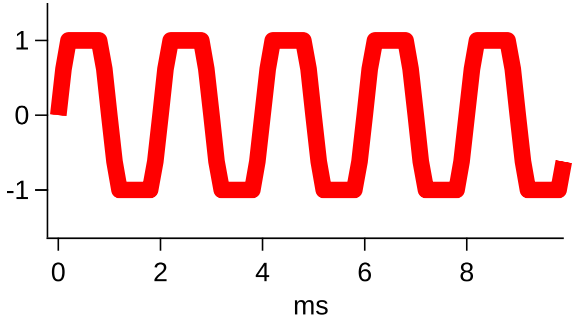
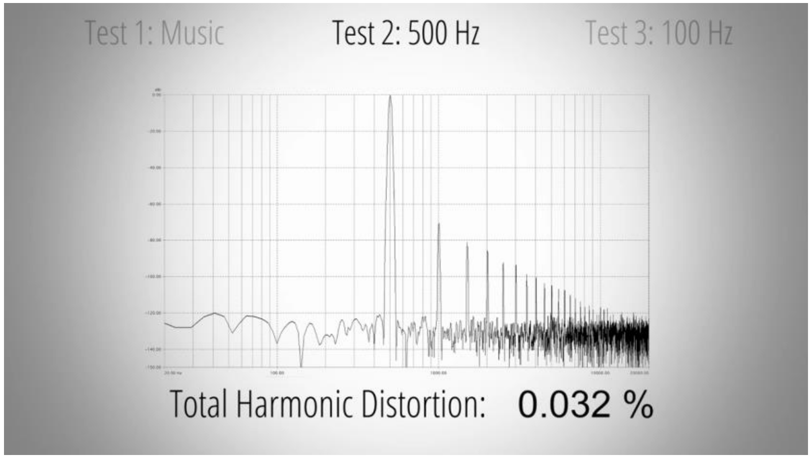


**Nonlinear deformation**

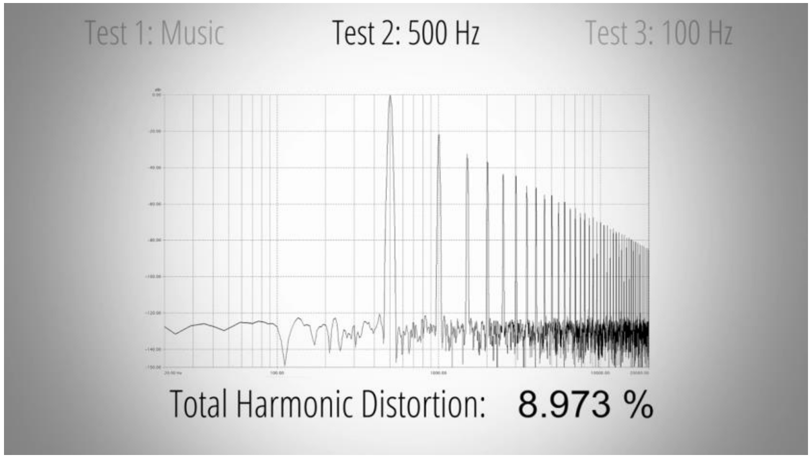


500 Hz, low distortion



Total Harmonic Distortion: 0.032 %

500 Hz, high distortion



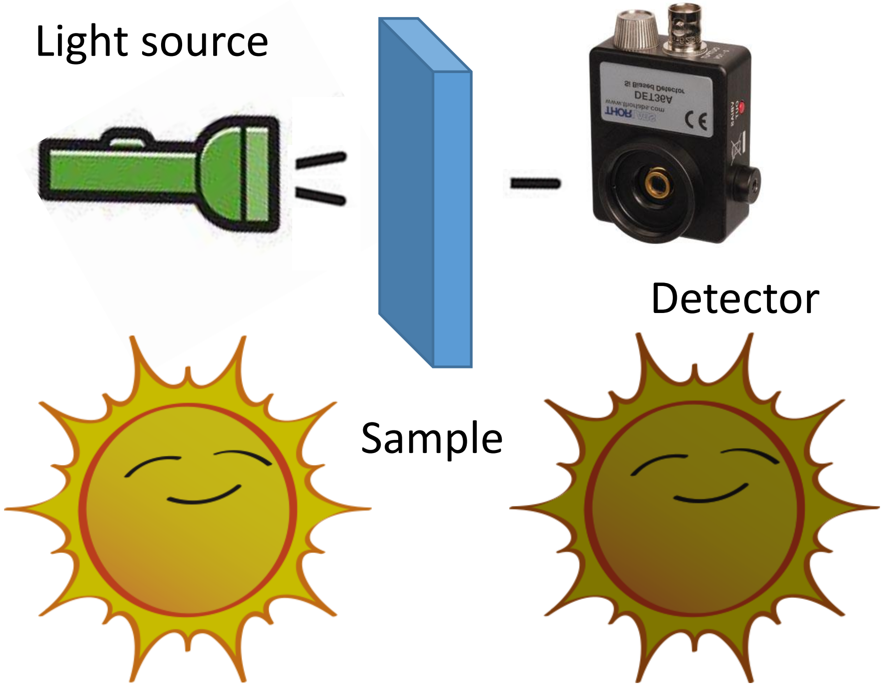
Total Harmonic Distortion: 8.973 %

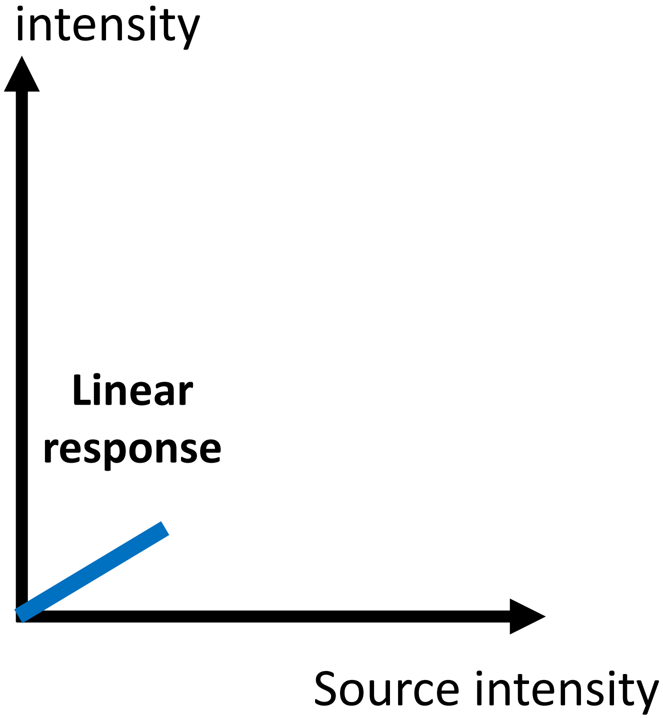
https://www.youtube.com/watch?v=7dLArMd-y64

Julian Krause https://www.youtube.com/@JulianKrause

# A nonlinear response you could see

$$I(x) = I_0 e^{-\alpha x}$$





# A nonlinear response you could see

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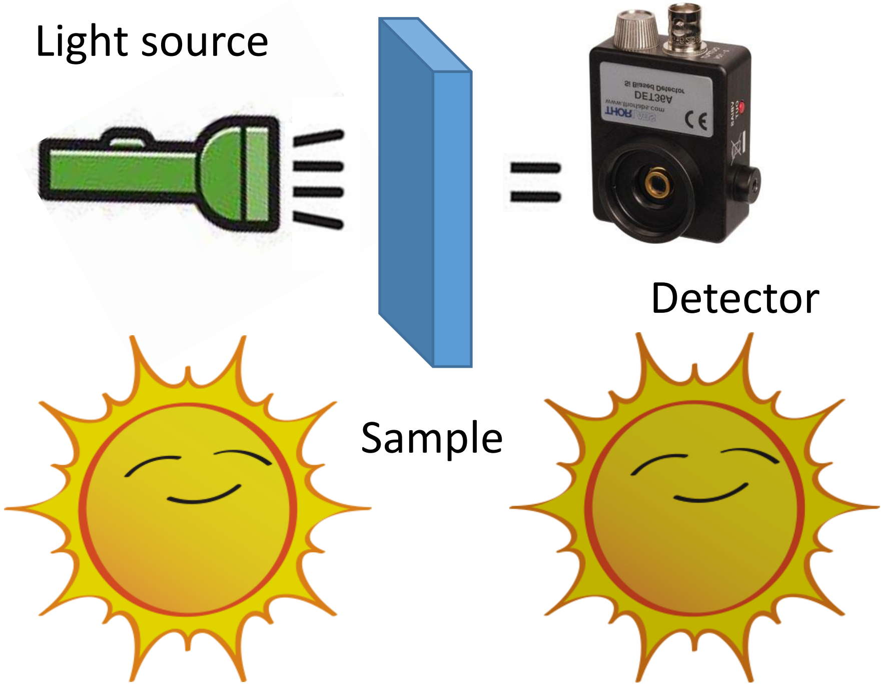
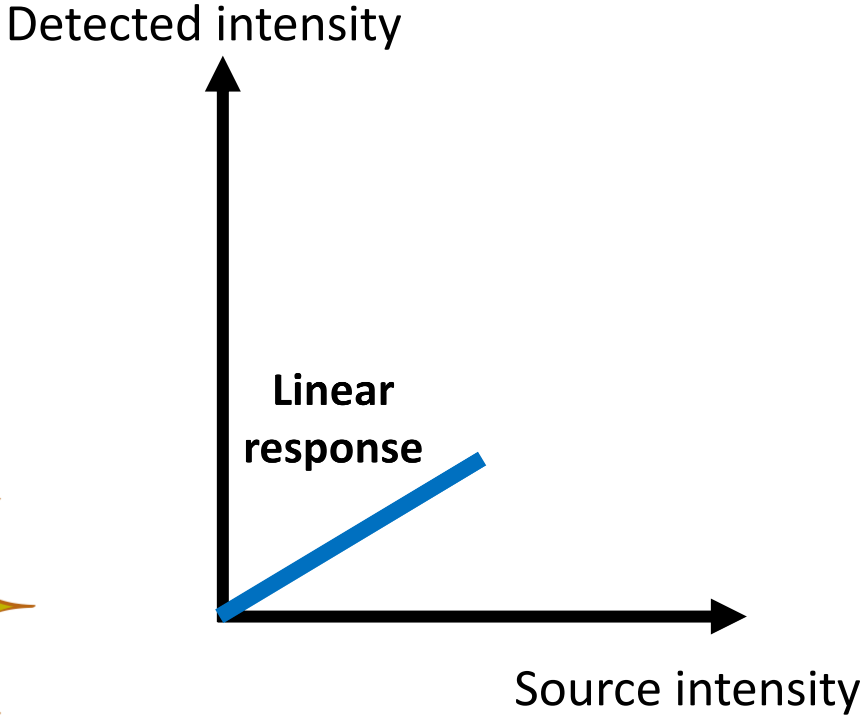
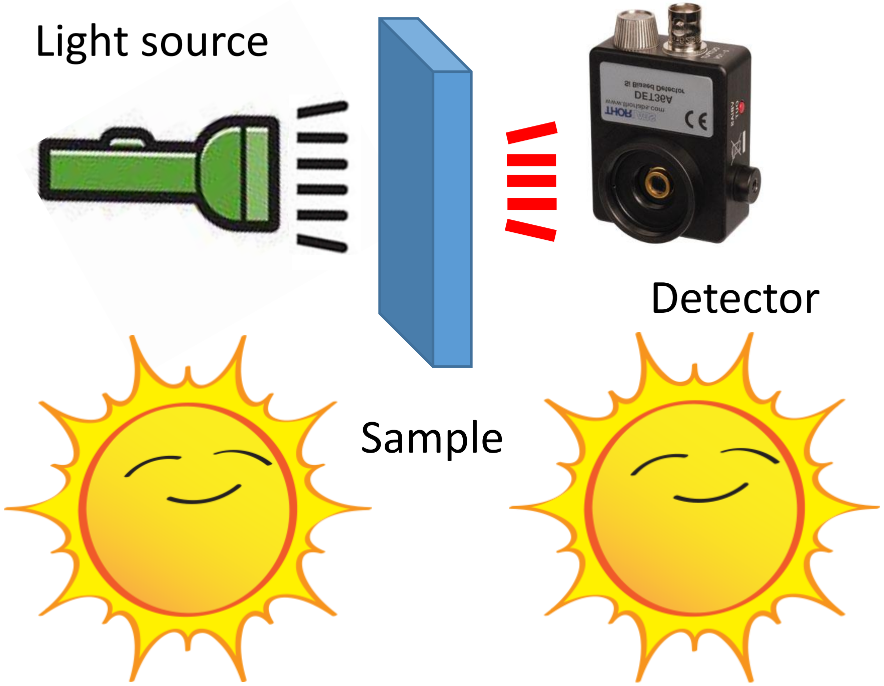
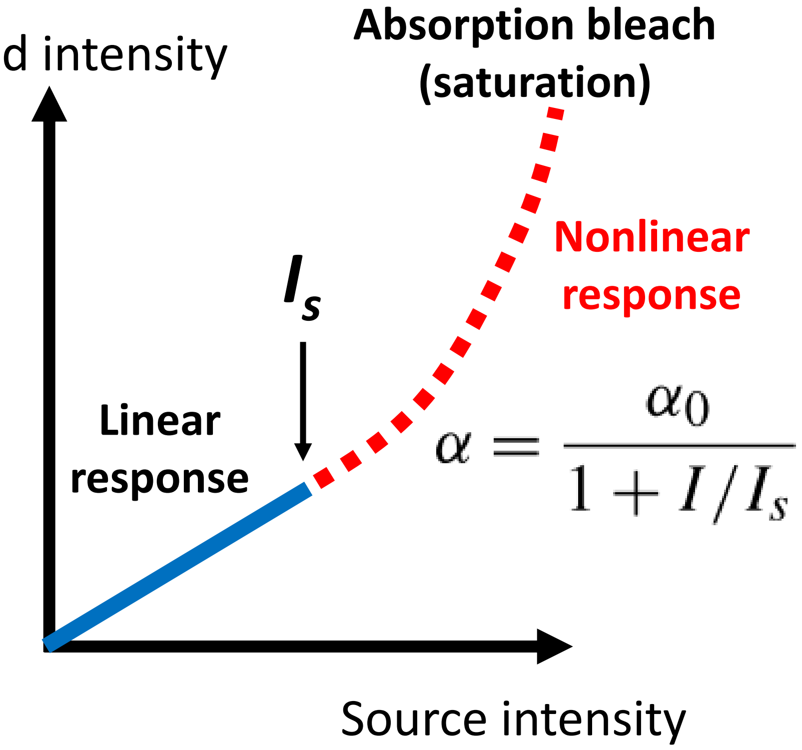




# A nonlinear response you could see

$$I(x) = I_0 e^{-\alpha(I)x}$$

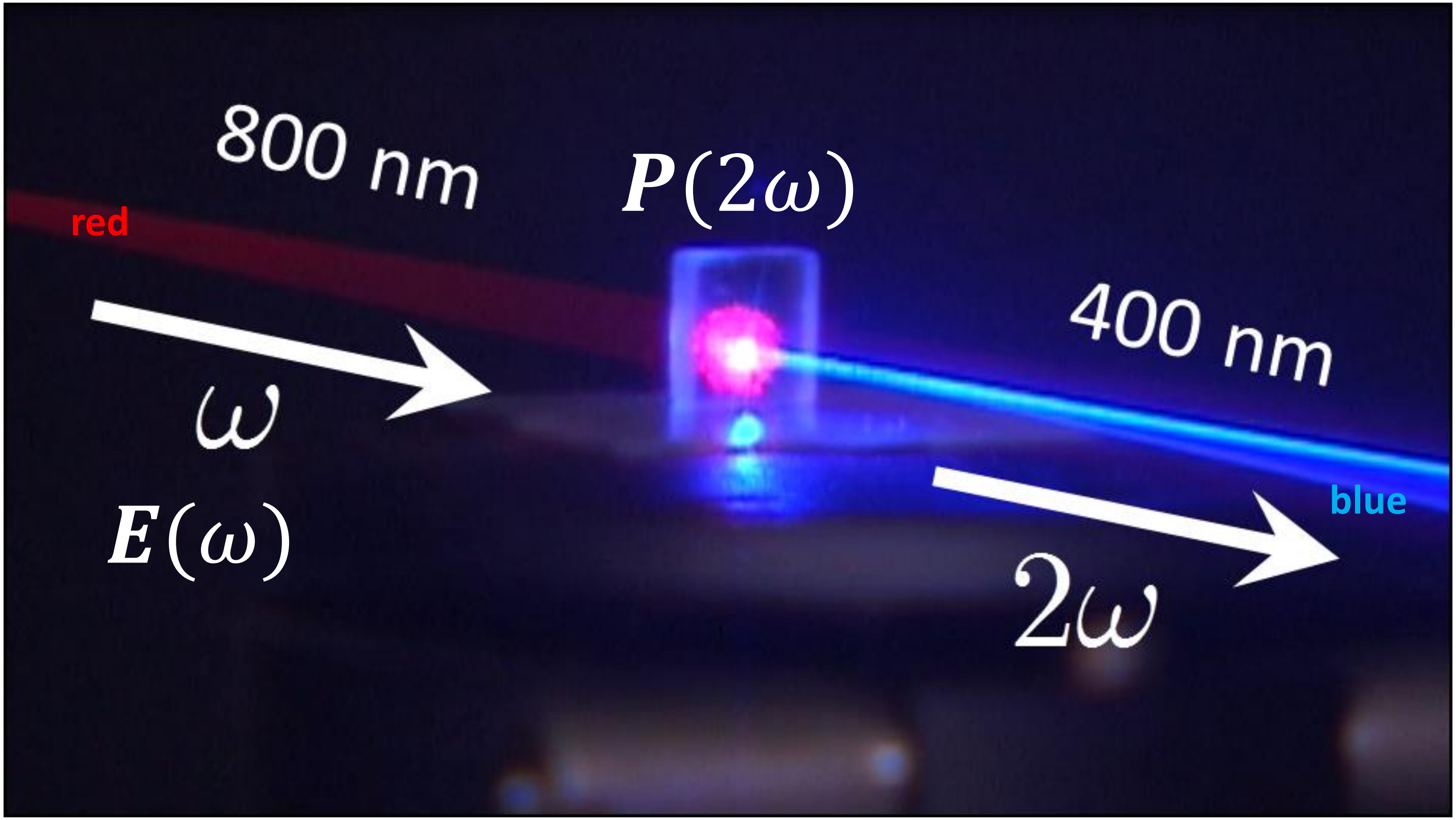




$$\alpha = \frac{\alpha_0}{1 + I/I_s}$$

https://solarsystem.nasa.gov/solar-system/sun/overview/

# Nonlinear optics allows to *make new* colors! Example: SHG



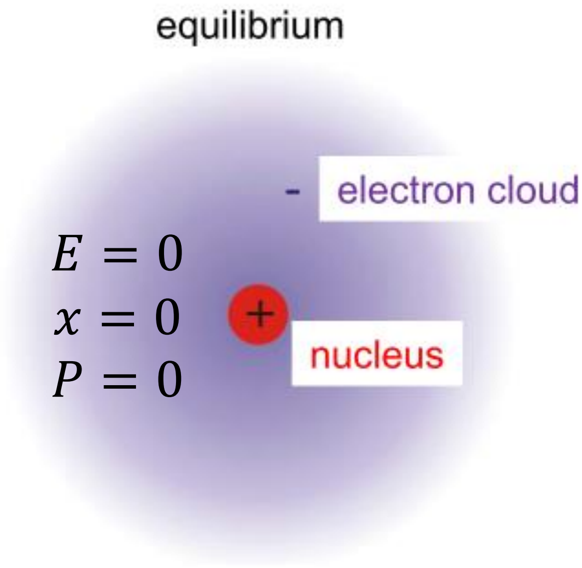
P.A. Franken, et al, Physical Review Letters 7, p. 118 (1961)

http://www.vincentkemlin.website/?page_id=140
https://en.wikipedia.org/wiki/Second-harmonic_generation

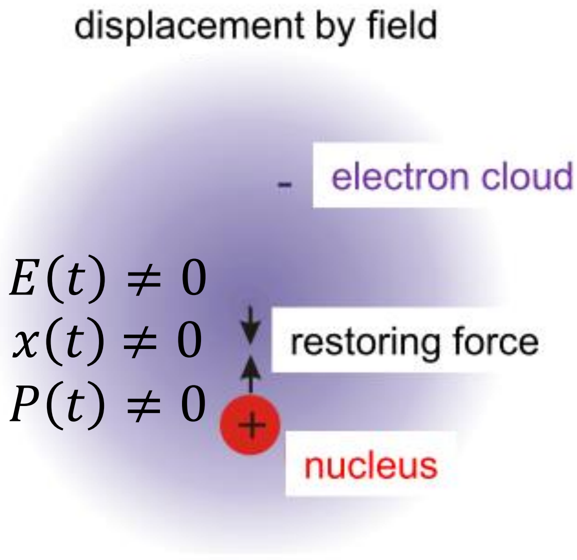
# Linear spectroscopy, elastic response: output frequency = input frequency

$$E \xrightarrow{\chi} P \xrightarrow{\text{wave eq.}} E_{out}$$

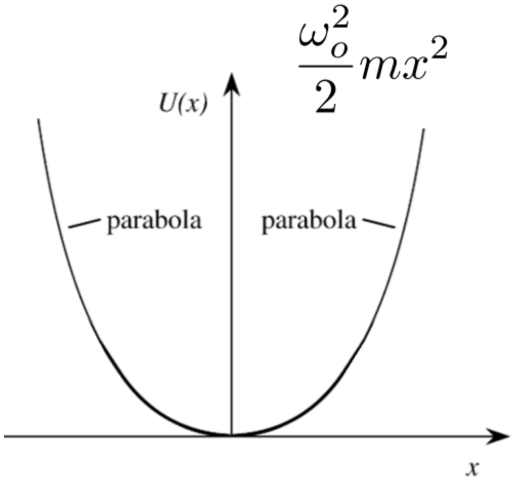
$$P(t) = \varepsilon_0 \chi^{(1)} E(t)$$



$E = 0$
$x = 0$
$P = 0$



$E(t) \neq 0$
$x(t) \neq 0$
$P(t) \neq 0$



$$\frac{\omega_o^2}{2} m x^2$$

Harmonic potential for small displacement, elastic restoring force

$$\frac{F_{res}}{m} = -\frac{1}{m}\frac{\mathrm{d}V}{\mathrm{d}x} = +\omega_o^2 x$$

# Linear optics

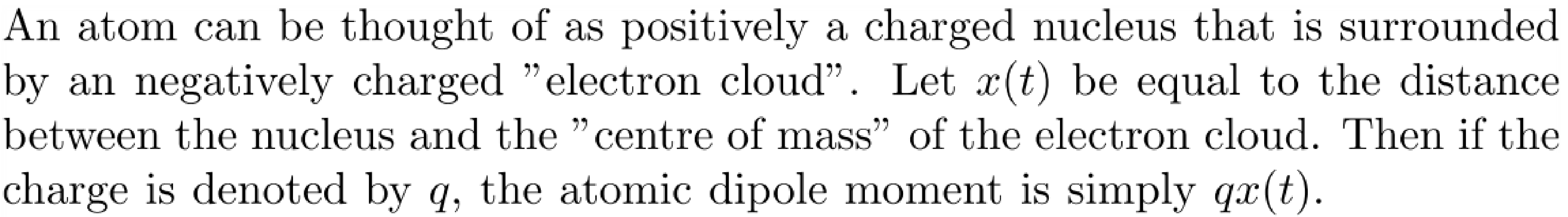
- In general one expects that when an electric field $\boldsymbol{E}$ is applied on a material, it excites dipoles and induces a polarization density $\boldsymbol{P}$, i.e. $\boldsymbol{P} = f(\boldsymbol{E})$
- For linear optics in a material that is <u>dispersionless</u>, <u>lossless</u>, <u>isotropic</u>, and <u>without free charges</u>:

$$\boldsymbol{P}(t) = \varepsilon_0 \chi^{(1)} \boldsymbol{E}(t)$$

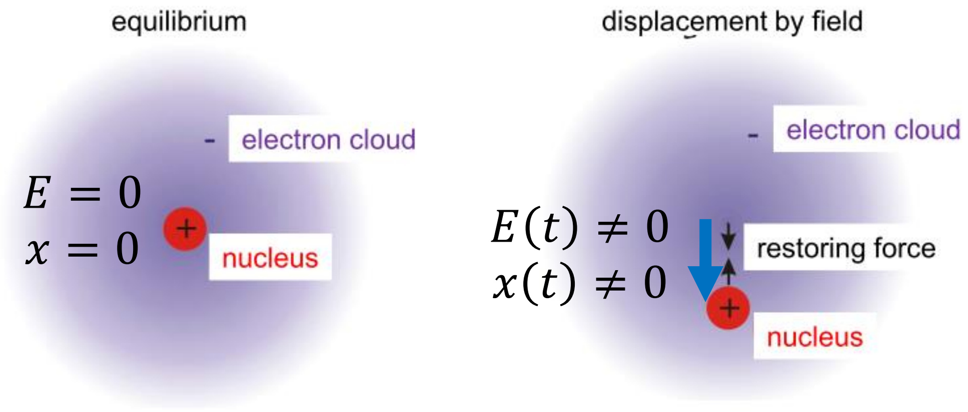
- $\varepsilon_0 \sim 8.854 \cdot 10^{-12} F/m$ vacuum electric permittivity
- $\chi^{(1)}$ is the first-order electric susceptibility (scalar!)

# Linear optics: Lorentz model

- The Lorentz model allows to find an expression for the susceptibility $\chi^{(1)}$



An atom can be thought of as positively a charged nucleus that is surrounded by an negatively charged ”electron cloud”. Let $x(t)$ be equal to the distance between the nucleus and the ”centre of mass” of the electron cloud. Then if the charge is denoted by $q$, the atomic dipole moment is simply $qx(t)$.



$E = 0$
$x = 0$

$E(t) \neq 0$
$x(t) \neq 0$

$\boldsymbol{p(t)} = qx(t)$
*induced dipole*!

# Linear optics: Lorentz model

- A classical damped and driven harmonic oscillator

$$\overset{\substack{\text{acceleration}\\ \downarrow}}{\ddot{x}}(t) + 2\gamma \underset{\substack{\uparrow\\ \text{damping}}}{\dot{x}}(t) + \omega_o^2 \overset{\substack{\text{restoring}\\ \text{term}\\ \downarrow}}{x}(t) = \frac{qE(t)}{\underset{\substack{\uparrow\\ \text{driving}\\ \text{term}}}{m}}$$

$$\ddot{x}(t) \equiv \frac{\mathrm{d}^2 x(t)}{\mathrm{d}t^2}$$

$$\dot{x}(t) \equiv \frac{\mathrm{d}x(t)}{\mathrm{d}t}$$

$m \equiv$ mass of electron cloud

$E \equiv$ electric field

$\omega_o \equiv 2\pi \times$ resonant frequency

$\gamma \equiv$ damping coeifficent

Optical Properties of Solids, Wooten, Ch.1, https://doi.org/10.1016/C2013-0-07656-6
https://en.wikipedia.org/wiki/Harmonic_oscillator

# Linear optics: Lorentz model

- If $E(t) = E(\omega)e^{-i\omega t}$ and $x(t) = x(\omega)e^{-i\omega t}$, write $x(\omega)$ as a function of $E(\omega)$

$$\ddot{x}(t) + 2\gamma\dot{x}(t) + \omega_o^2 x(t) = \frac{qE(t)}{m}$$

$$\frac{d^2x}{dt^2} = (-i\omega)^2 x(\omega)e^{-i\omega t} = -\omega^2 x(\omega)e^{-i\omega t}$$

$$-\omega^2 x(\omega)e^{-i\omega t} + 2\gamma(-i\omega)x(\omega)e^{-i\omega t} + \omega_0^2 x(\omega)e^{-i\omega t} = \frac{qE(\omega)e^{-i\omega t}}{m}$$

$$\boxed{x(\omega) = \frac{q}{m}\cdot\frac{E(\omega)}{\omega_0^2 - \omega^2 - i2\gamma\omega}}$$

# Linear optics: Susceptibility

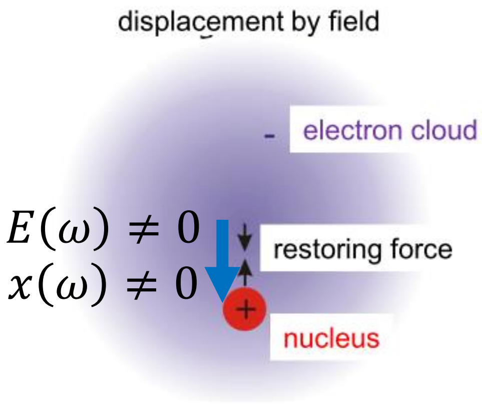
- For $E(t) = E(\omega)e^{-i\omega t}$ and $P(t) = P(\omega)e^{-i\omega t}$, we apply a field and the medium acquires a polarization

$$\boxed{P(\omega) = \varepsilon_0 \chi^{(1)} E(\omega)}$$

- This equals the average dipole moment per unit volume at $\omega$. Assuming $N$ independent oscillators:

$$\boxed{P(\omega) = Np(\omega) = Nqx(\omega)}$$

$$\boxed{\chi^{(1)} = \frac{Nq^2}{\varepsilon_0 m} \frac{1}{\omega_0^2 - \omega^2 - i2\gamma\omega}}$$



$p(\omega) = qx(\omega)$

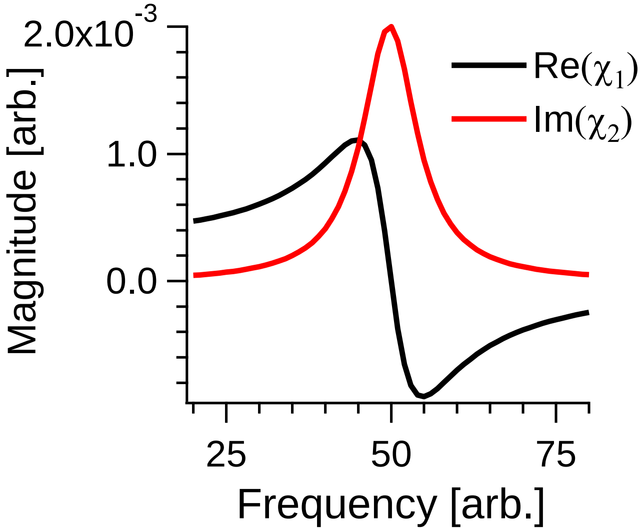
$induced\ dipole!$

# Linear optics: Susceptibility

- $\chi^{(1)}(\omega) = Nqx(\omega) = \frac{Nq^2}{\varepsilon_0 m}\frac{1}{\omega_0^2 - \omega^2 - i2\gamma\omega}$
- Calculate the real and imaginary parts of $\chi^{(1)}(\omega)$ and draw the trends around the resonance $\omega_0$

$$\left(\frac{c}{a+ib}\right) = \left(\frac{c}{a+ib}\right)\left(1 = \frac{a-ib}{a-ib}\right) = \left(\frac{ac}{a^2+b^2}\right) - i\left(\frac{bc}{a^2+b^2}\right)$$

$$\boxed{\begin{aligned} Re\left(\chi^{(1)}\right) &= \frac{Nq^2}{\varepsilon_0 m}\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + (2\gamma\omega)^2} \\ Im\left(\chi^{(1)}\right) &= \frac{Nq^2}{\varepsilon_0 m}\frac{2\gamma\omega}{(\omega_0^2 - \omega^2)^2 + (2\gamma\omega)^2} \end{aligned}}$$



# A lot of optical functions!

- $1 + \chi = \bar{n}^2 = \varepsilon$ (complex functions!)

| | |
|---|---|
| Conductivity | $\sigma = \sigma_1 + i\,\sigma_2$ |
| Dielectric constant | $\varepsilon = \varepsilon_1 + i\,\varepsilon_2$ $\quad \varepsilon = 1 + \frac{4\pi i\sigma}{\omega}$ $\quad \varepsilon_1 = 1 - \frac{4\pi\sigma_2}{\omega}$ $\quad \varepsilon_2 = \frac{4\pi\sigma_1}{\omega}$ |
| Refractive index | $\bar{n} = n + i\,k$ $\quad \varepsilon = \bar{n}^2$ $\quad \varepsilon_1 = n^2 - k^2$ $\quad \varepsilon_2 = 2\,n\,k$ |
| | $n^2 = (\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}\,)/2$ $\quad k^2 = (-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}\,)/2$ |
| Absorption coefficient | $\alpha(\omega) = 2\omega\,k/c \equiv \omega\varepsilon_2/nc$ |
| Classical skin depth | $\delta = c/\omega\,k$ |
| Surface impedance | $Z = 4\pi\ /c\bar{n}$ |
| Reflectivity | $R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$ (at normal incidence) |

- The real parts often (not $\sigma$!) relate to refraction, the imaginary parts to absorption. What about R?

Solid State Physics, G. Grosso and G. Pastori Parravicini, Academic Press (2000), Ch.11

https://doi.org/10.1016/B978-0-12-304460-0.X5000-2

https://doi.org/10.1016/B978-012304460-0/50011-6

**Nonlinear Optics, Boyd, Ch.1**

# Nonlinear spectroscopy: output frequency ≠ input frequency

$$\begin{tikzcd} E \arrow[r, "\chi"] & P \arrow[r, "\text{wave eq.}"] & E_{out} \end{tikzcd}$$

$$\boxed{\chi = \chi(E) = \chi^{(1)} + \chi^{(2)}E + \chi^{(3)}E^2 + \ldots \qquad P = P^{(1)} + P^{(2)} + P^{(3)} + \ldots.}$$

*Linear optics*

$$P^{(1)} \equiv \epsilon_o \chi^{(1)} E^1$$

*Second-order response*

$$P^{(2)} \equiv \epsilon_o \chi^{(2)} E^2$$

*Third-order response*

$$P^{(3)} \equiv \epsilon_o \chi^{(3)} E^3$$

Nonlinear Optics, Boyd, Ch.1

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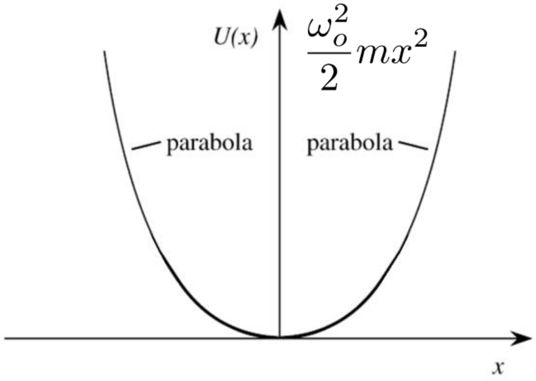
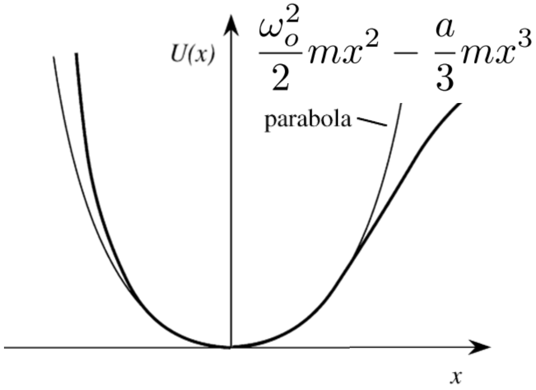


Harmonic, centrosym.
Lorentz model

*Second-order response*

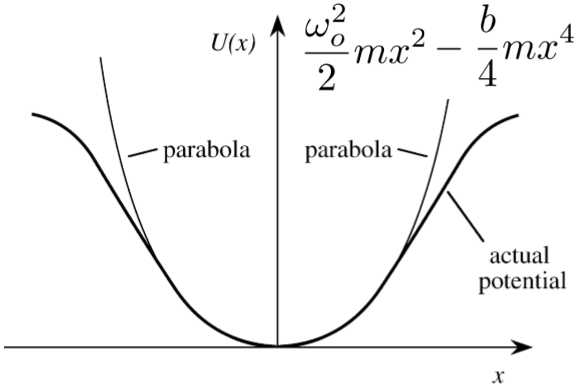
$$P^{(2)} \equiv \epsilon_o \chi^{(2)} E^2$$



Anharmonic, non centrosym.
$\chi^{(2)} \propto a$

*Third-order response*

$$P^{(3)} \equiv \epsilon_o \chi^{(3)} E^3$$



Anharmonic, centrosym.
$\chi^{(3)} \propto b$

**Nonlinear Optics, Boyd, Ch.1**

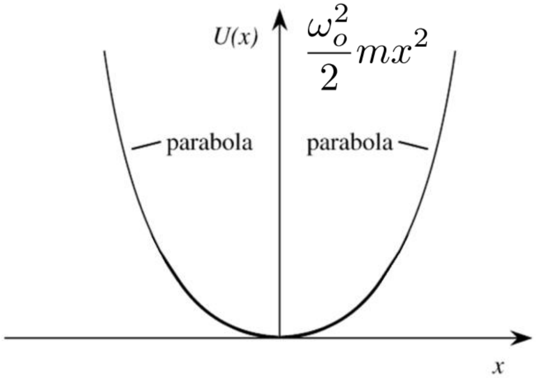
# Nonlinear spectroscopy: output frequency ≠ input frequency

Nonlinear spectroscopy directly measures the anharmonicity!
→ Invaluable tool to study matter

$$\left|\chi^{(1)}(\omega)\right| \approx 1$$

*Linear optics*

$$P^{(1)} \equiv \epsilon_o \chi^{(1)} E^1$$

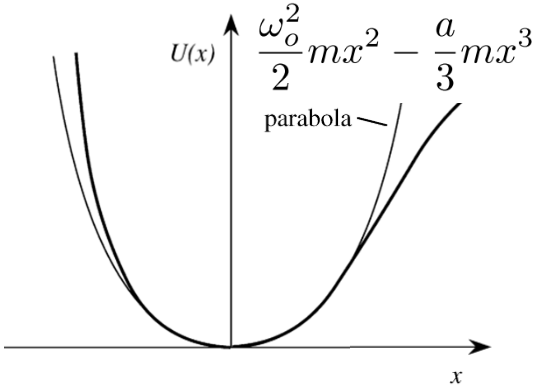


Harmonic, centrosym.
Lorentz model

$$\left|\chi^{(2)}(2\omega)\right| \approx 10^{-12}\,\frac{m}{V}$$

*Second-order response*

$$P^{(2)} \equiv \epsilon_o \chi^{(2)} E^2$$

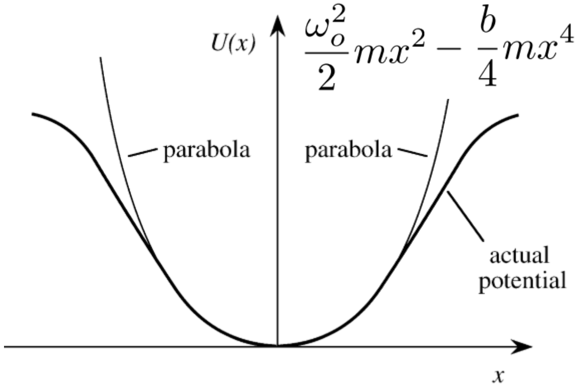


Anharmonic, non centrosym.
$\chi^{(2)} \propto a$

$$\left|\chi^{(3)}(3\omega)\right| \approx 10^{-23}\,\frac{m^2}{V^2}$$

*Third-order response*

$$P^{(3)} \equiv \epsilon_o \chi^{(3)} E^3$$



Anharmonic, centrosym.
$\chi^{(3)} \propto b$

$$P(t) = \varepsilon_0 \chi E(t)$$

$$\chi(E) = \chi^{(1)} + \chi^{(2)} E + \chi^{(3)} E^2 + \ldots$$

$$P = P^{(1)} + P^{(2)} + P^{(3)} + \ldots$$

| *Linear optics* | *Second-order response* | *Third-order response* |
|---|---|---|
| $P^{(1)} \equiv \epsilon_o \chi^{(1)} E^1$ | $P^{(2)} \equiv \epsilon_o \chi^{(2)} E^2$ | $P^{(3)} \equiv \epsilon_o \chi^{(3)} E^3$ |

$$\boxed{\text{If } E(t) = \quad E_o \cos(\omega t) \text{ find } P^{(1)}, P^{(2)}, \text{ and } P^{(3)}.}$$

$$\boxed{\text{Mixing one beam via } \chi^{(1)}, \chi^{(2)}, \text{ and } \chi^{(3)}}$$

"Elastic" response $\omega_{\text{input}} = \omega \rightarrow \omega_{\text{output}} = \omega$

- $P^{(1)} = \varepsilon_0 \chi^{(1)} E_0 cos(\omega t)$

$$P(t) = \varepsilon_0 \chi E(t)$$

$$\chi(E) = \chi^{(1)} + \chi^{(2)} E + \chi^{(3)} E^2 + \ldots$$

$$P = P^{(1)} + P^{(2)} + P^{(3)} + \ldots$$

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If $E(t) = \quad E_o \cos(\omega t)$ find $P^{(1)}, P^{(2)}$, and $P^{(3)}$.

Mixing one beam via $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$

"Elastic" response $\omega_{\text{input}} = \omega \rightarrow \omega_{\text{output}} = \omega$

- $P^{(1)} = \varepsilon_0 \chi^{(1)} E_0 cos(\omega t)$

- $P^{(2)} =$

$$P(t) = \varepsilon_0 \chi E(t)$$

$$\chi(E) = \chi^{(1)} + \chi^{(2)} E + \chi^{(3)} E^2 + \ldots$$

$$P = P^{(1)} + P^{(2)} + P^{(3)} + \ldots$$

*Linear optics*

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"Elastic" response $\omega_{\text{input}} = \omega \rightarrow \omega_{\text{output}} = \omega$

- $P^{(1)} = \varepsilon_0 \chi^{(1)} E_0 cos(\omega t)$

$$\underbrace{\cos^2\theta = \frac{1 + \cos(2\theta)}{2}}$$

- $P^{(2)} = \varepsilon_0 \chi^{(2)} E_0^2 cos^2(\omega t) =$

$$P(t) = \varepsilon_0 \chi E(t)$$

$$\chi(E) = \chi^{(1)} + \chi^{(2)}E + \chi^{(3)}E^2 + \ldots$$

$$P = P^{(1)} + P^{(2)} + P^{(3)} + \ldots$$

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*Third-order response*

$$P^{(3)} \equiv \epsilon_o \chi^{(3)} E^3$$

$$\boxed{\text{If } E(t) = E_o \cos(\omega t) \text{ find } P^{(1)}, P^{(2)}, \text{ and } P^{(3)}.}$$

## Mixing one beam via $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$

"Elastic" response $\omega_{\text{input}} = \omega \rightarrow \omega_{\text{output}} = \omega$

- $P^{(1)} = \varepsilon_0 \chi^{(1)} E_0 cos(\omega t)$

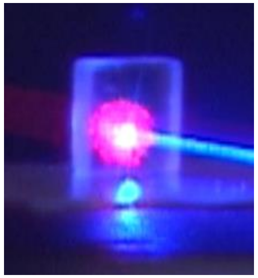
Rectification

$\omega \rightarrow 0$

Second harmonic

$\omega \rightarrow 2\omega$

- $P^{(2)} = \varepsilon_0 \chi^{(2)} E_0^2 co\overbrace{s^2(\omega t) = \varepsilon_0 \chi^{(2)}}^{\cos^2\theta = \frac{1+\cos(2\theta)}{2}} E_0^2 \frac{1+cos(2\omega t)}{2} = \frac{\varepsilon_0 \chi^{(2)} E_0^2}{2} + \frac{\varepsilon_0 \chi^{(2)} E_0^2 cos(2\omega t)}{2}$



$$P(t) = \varepsilon_0 \chi E(t)$$
$$\chi(E) = \chi^{(1)} + \chi^{(2)}E + \chi^{(3)}E^2 + \ldots$$
$$P = P^{(1)} + P^{(2)} + P^{(3)} + \ldots$$

| *Linear optics* | *Second-order response* | *Third-order response* |
|---|---|---|
| $P^{(1)} \equiv \epsilon_o \chi^{(1)} E^1$ | $P^{(2)} \equiv \epsilon_o \chi^{(2)} E^2$ | $P^{(3)} \equiv \epsilon_o \chi^{(3)} E^3$ |

$$\boxed{\text{If } E(t) = \ E_o \cos(\omega t) \text{ find } P^{(1)}, P^{(2)}, \text{ and } P^{(3)}.}$$

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Rectification ω→0 Second harmonic ω→2ω

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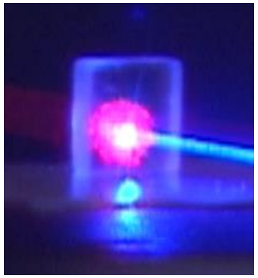
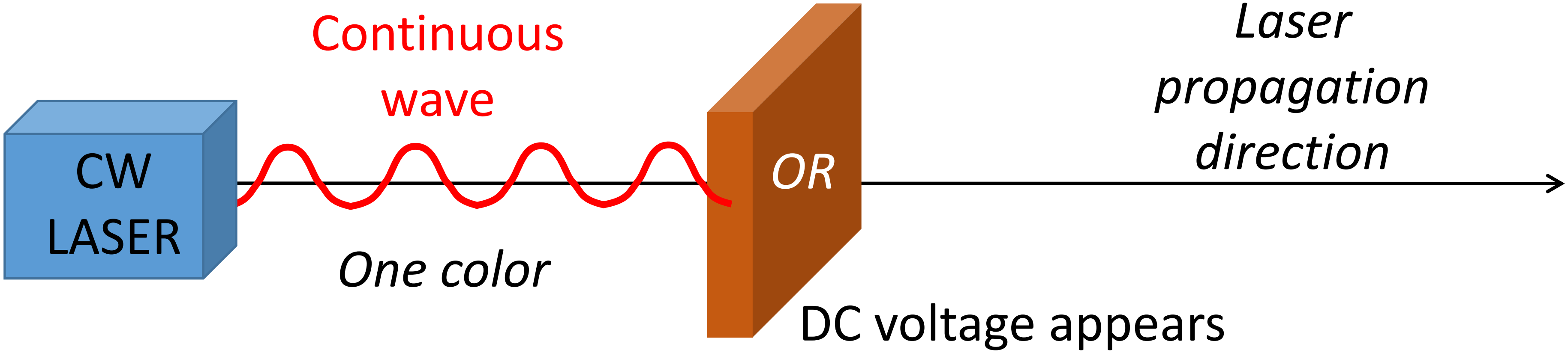


Kerr ω→ω Third harmonic ω→3ω

- $P^{(3)} = \varepsilon_0 \chi^{(3)} E_0^3 \overbrace{cos^3(\omega t) = \varepsilon_0 \chi^{(3)}}^{\cos(3\theta) = 4\cos^3\theta - 3\cos\theta} E_0^3 \frac{3cos(\omega t) + cos(3\omega t)}{4}$

# THz generation: Optical rectification (OR)



$\chi^{(2)}_{bulk} \neq 0$

e.g. ZnTe; GaP

Continuous wave

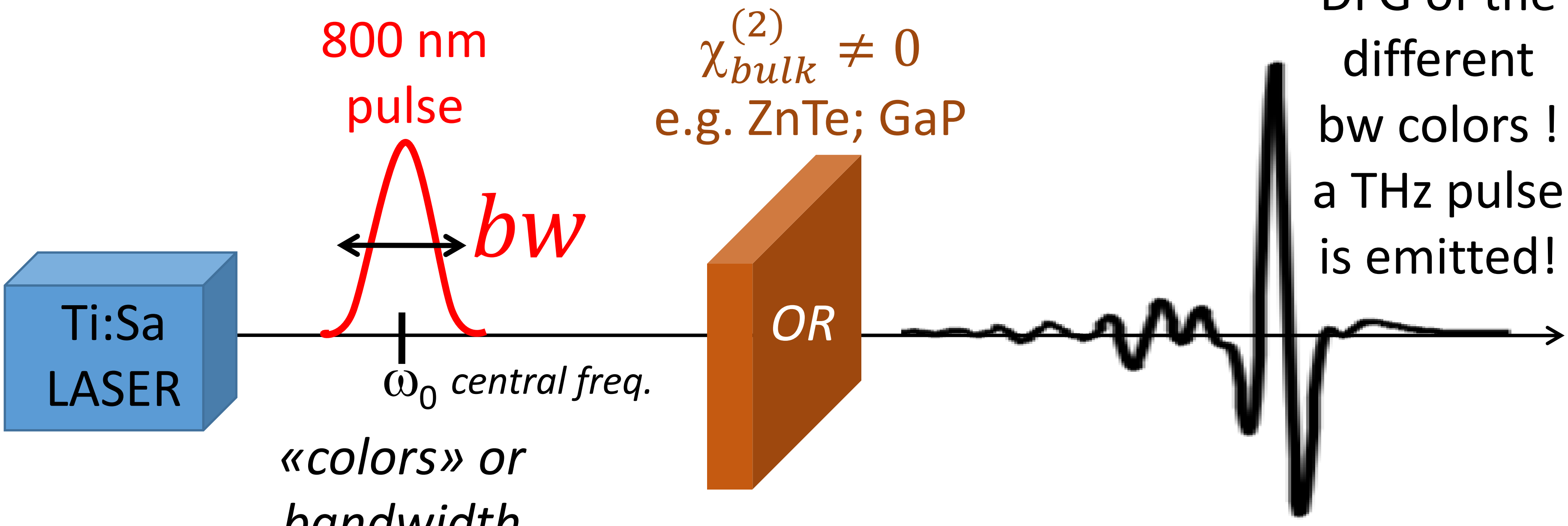
*One color*

*Laser propagation direction*

DC voltage appears across the sample, $\propto \varepsilon_0 \chi^{(2)}$

# THz generation: Optical rectification (OR)

- What changes if a pulsed laser source is used?



800 nm pulse

$bw$

$\chi^{(2)}_{bulk} \neq 0$

e.g. ZnTe; GaP

Ti:Sa LASER

OR

$\omega_0$ *central freq.*

*«colors» or bandwidth*

DFG of the different bw colors ! a THz pulse is emitted!

*THz pulse is made of colors from 0 (DC) to bw (up to ~10 THZ)*

# THz detection: electro-optical sampling (EOS)

- OR can be described as DFG of ‘tails’ (bw): $\omega_0 - \omega_{0-bw} = \omega_{THz} \ll \omega_0$
- EOS: $\chi^{(2)}$effect; $\omega_0 - \omega_{THz} \approx \omega_0$. *“Some sort of inverse OR“*.
- EOS is based on Pockels’ / linear electro-optic effect. Here, a (low frequency) electric field induces birefringence in a medium with $\chi^{(2)}_{bulk} \neq 0$. <u>The amount of ellipticity (polarization rotation) scales with THz field</u>!

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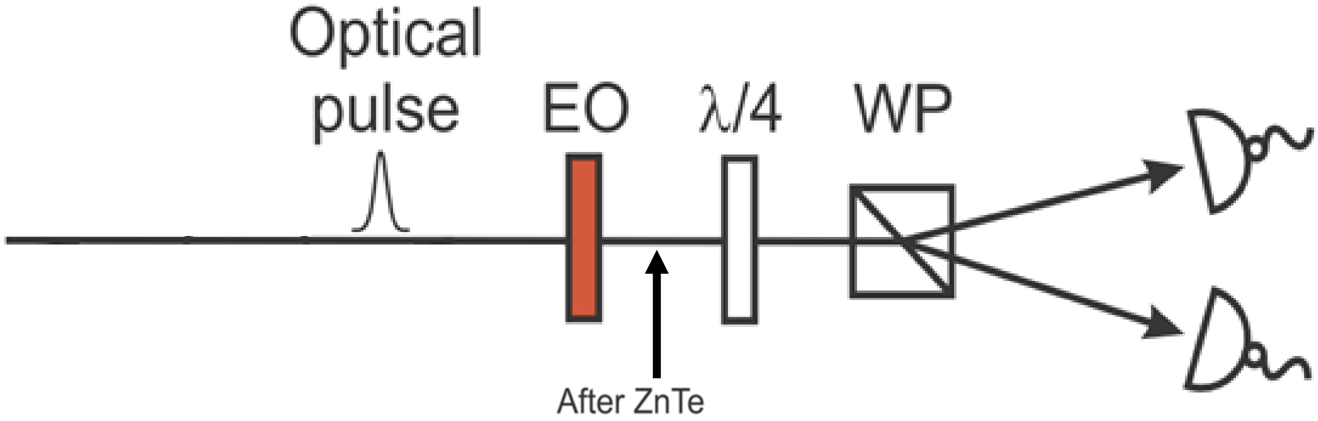

Balanced diodes

Optical pulse polarization without THz ↔

EO: crystal with $\chi^{(2)}_{bulk} \neq 0$
λ/4: quarter wave-plate
WP: Wollaston prism

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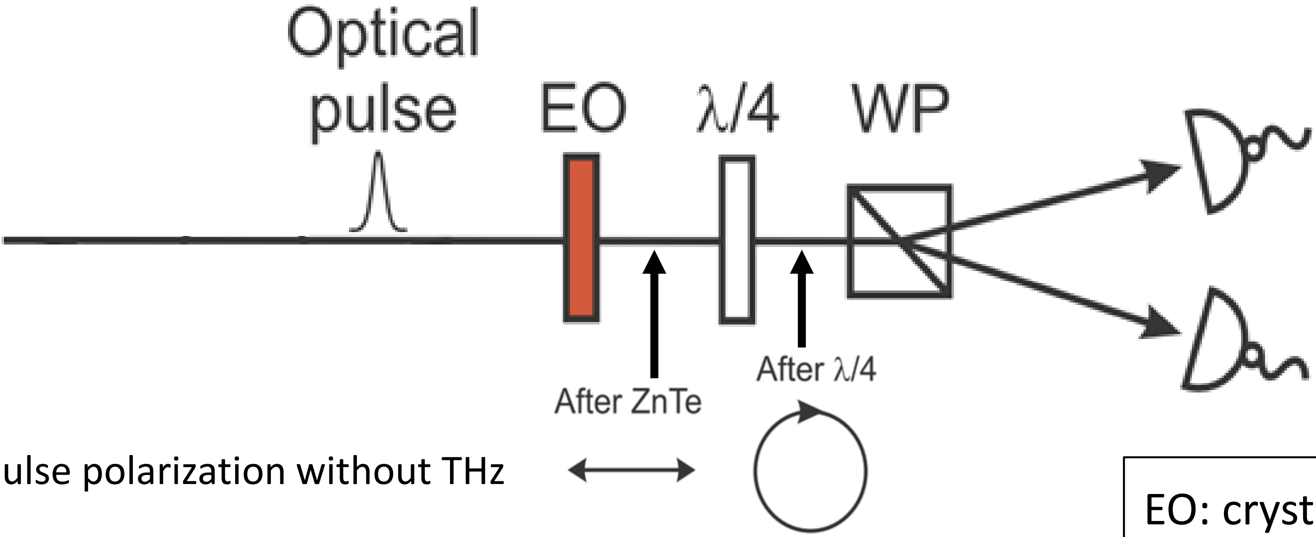

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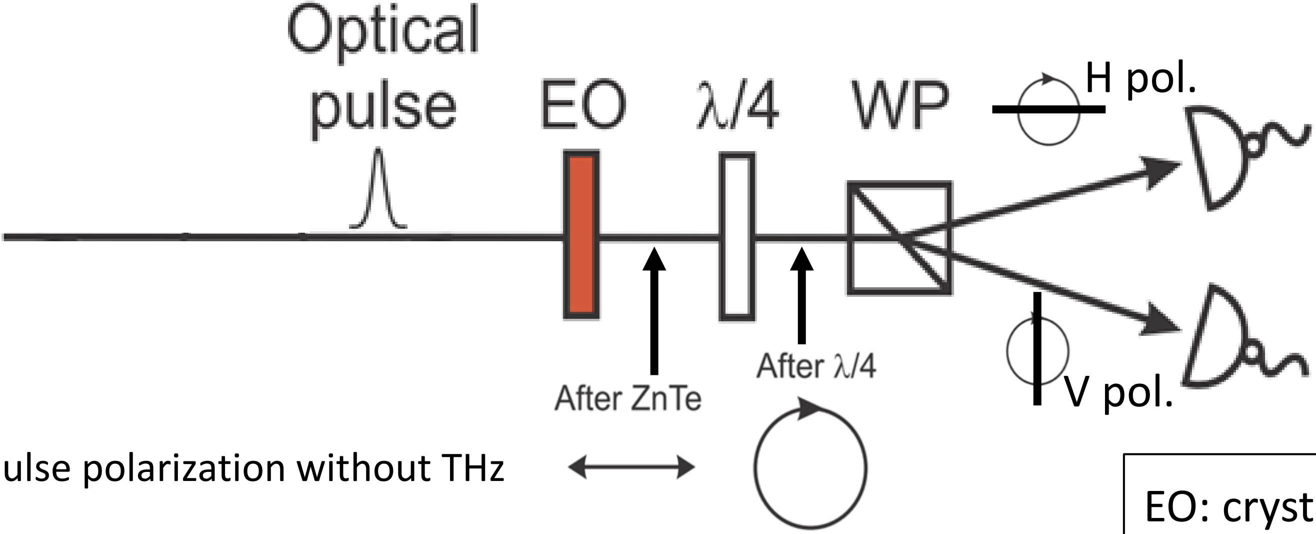

Balanced diodes: the voltage difference is zero

Optical pulse polarization without THz

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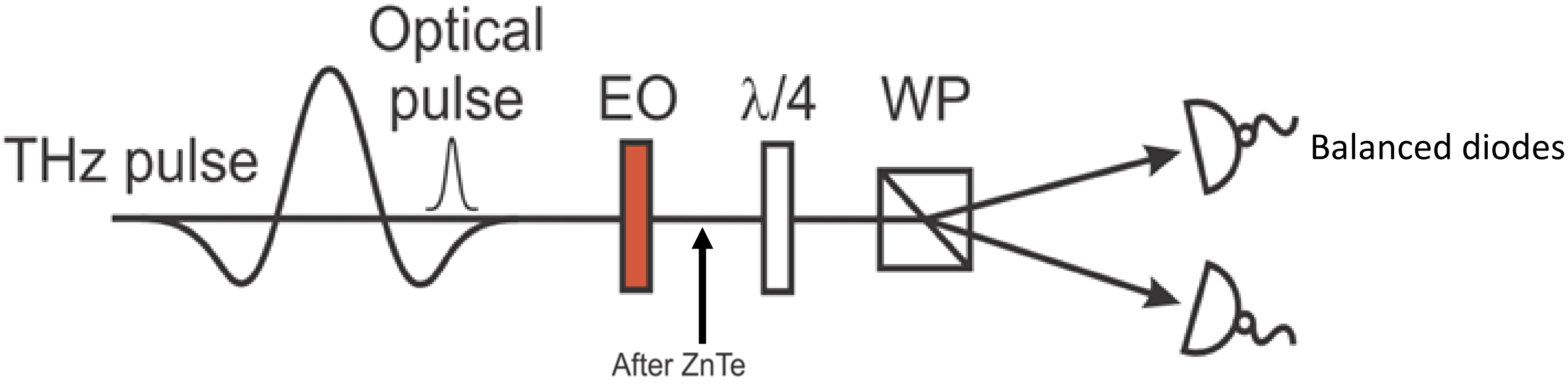

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Optical pulse polarization **with** THz 

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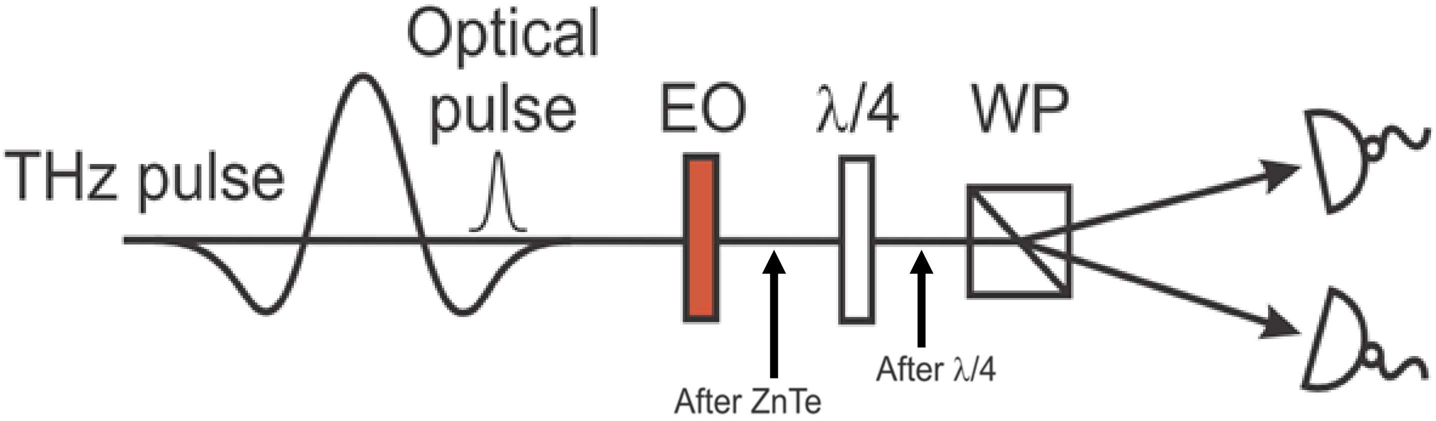

Balanced diodes

Optical pulse polarization **with** THz

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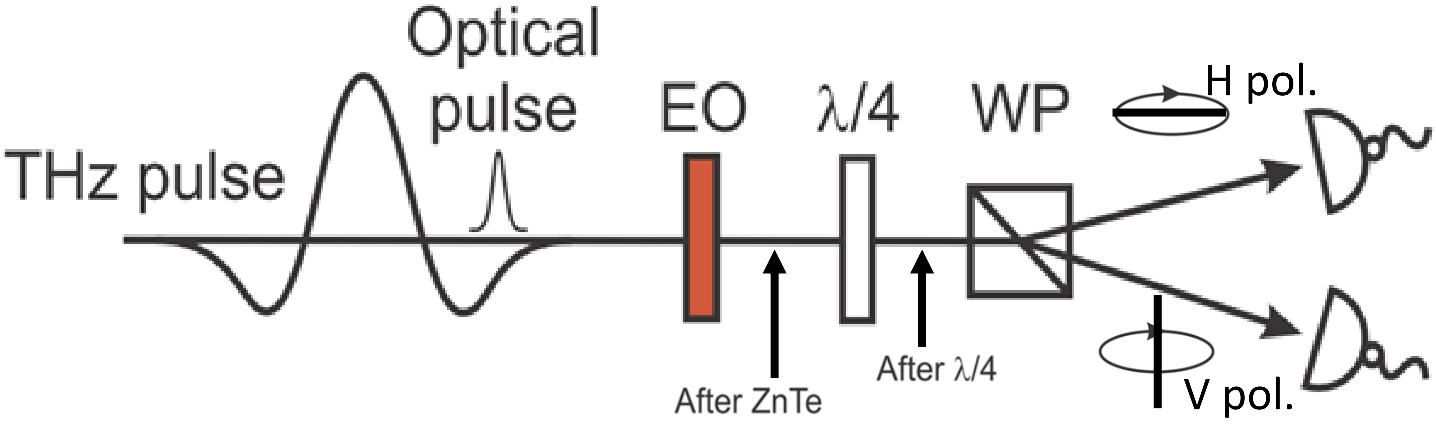

Balanced diodes: **the voltage difference is proportional to the THz field amplitude**

Optical pulse polarization **with** THz

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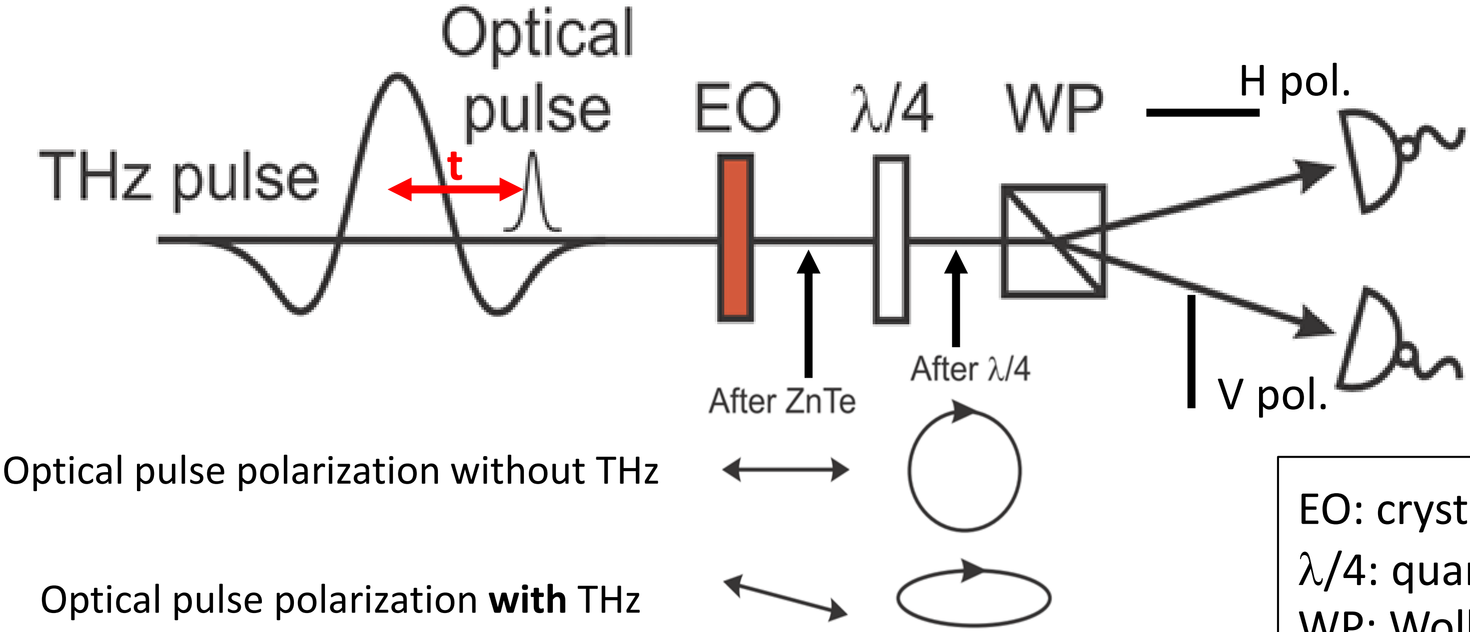

Balanced diodes: the THz field shape in time is collected by varying the time delay **t**

EO: crystal with $\chi^{(2)}_{bulk} \neq 0$
λ/4: quarter wave-plate
WP: Wollaston prism

# THz generation: charge-current methods

- When we apply an electric field $E_{in}$ to a material, it develops a polarization $\boldsymbol{P}$ which can act as the source of the emitted signal, $E_S$.

$$E_{\mathrm{in}} \xrightarrow{\chi} \boldsymbol{P} \xrightarrow{\text{wave eq.}} E_s$$

- This is the **only way** $\boldsymbol{E_s}$ **can be emitted**, **if material** has **no free changes**

Optics Communications 256, 400 (2005)

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➢“*Whenever a free charge is accelerated, it emits radiation*”

- **If the material excited by** $\boldsymbol{E_{\text{in}}}$ **has free charges, the field can create a current,** $\boldsymbol{J}$**, and the current can be the source of the emitted signal**.

$$E_{\text{in}} \xrightarrow[\text{conductivity}]{\sigma} \boldsymbol{J} \xrightarrow{\text{wave eq.}} E_s$$

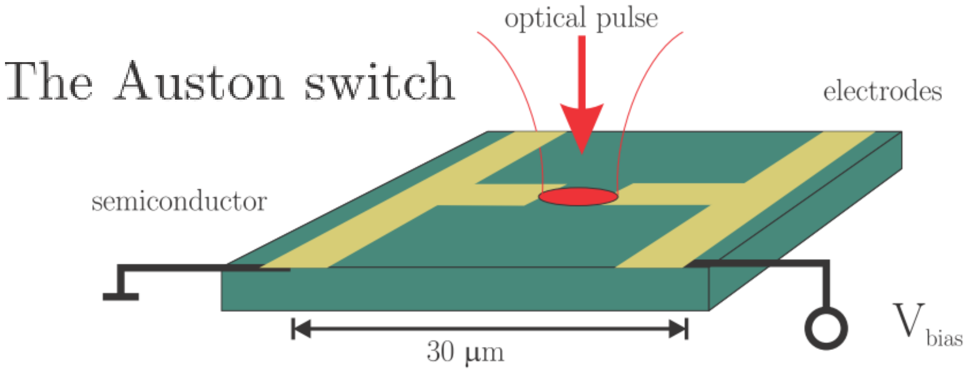
- This is the way an antenna works, and also synchrotron radiation - which is, at simplest, an antenna with relativistic “fast” charges.

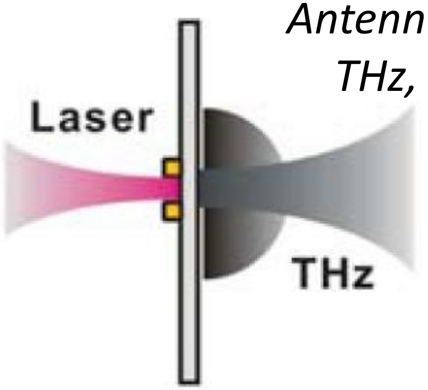
Optics Communications 256, 400 (2005)

https://en.wikipedia.org/wiki/Synchrotron_radiation

# THz generation/detection by current: photoconductive antenna methods

- A photoconductive (PC) antenna consists of two metal electrodes (often gold) that are coated on a semiconductor substrate (GaAs), with a gap in between the electrodes. The "Auston switch" has an H-like structure with a gap in the order of 5 µm. Bias voltage is applied across the electrodes (10s V, 10s KHz AC).
- THz generation is obtained as follows:
  1. We excite the gap with an ultra-short pulse of light (~10-100 fs)
  2. Light generate free carriers and, hence, a current $\boldsymbol{J}$ in the material
  3. The bias field across the gap accelerates the free carriers
  4. The accelerated charges emit THz radiation (polarized || bias)





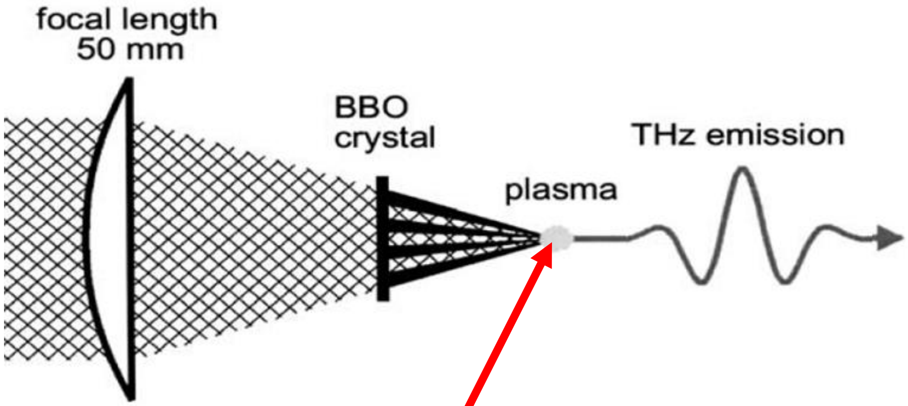
*Antenna generates THz, side view*

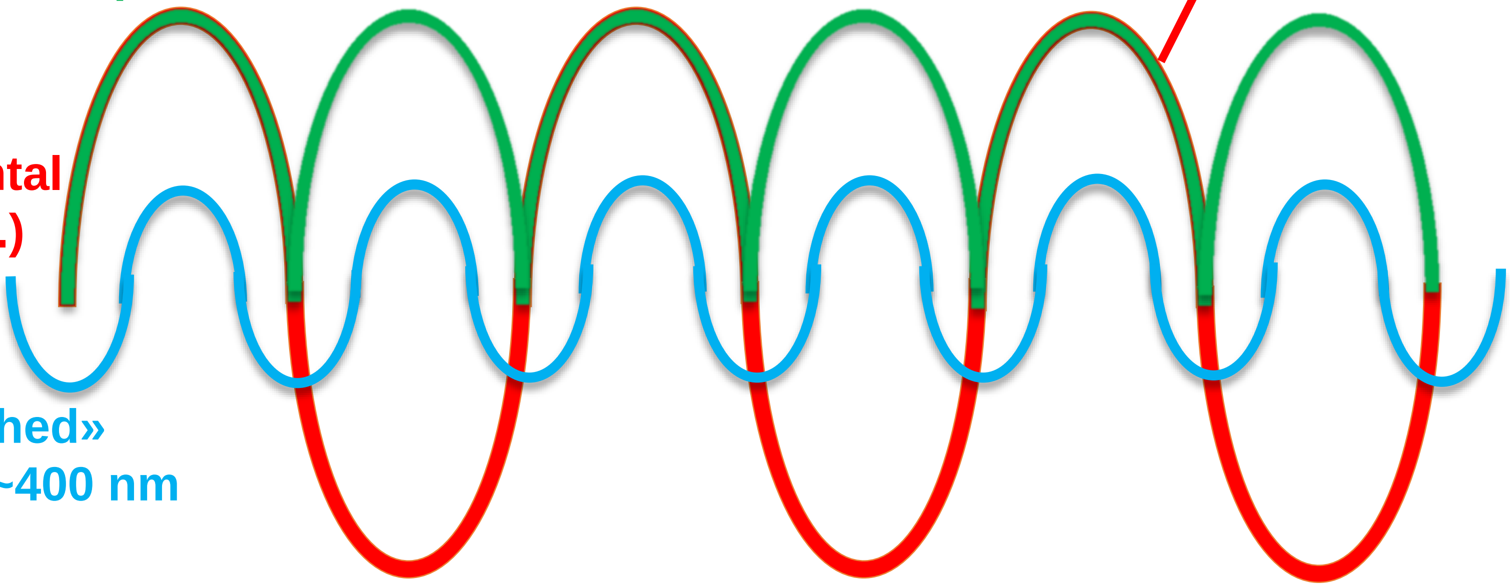
# THz generation by charge-current(?): Plasma

- <u>Focus I+II harmonics in plasma</u>

❖800 nm focused in air/nitrogen

❖carriers excited by phase-matched 400 nm





**Spatial distribution of plasma**

**Laser funsamental (1st harm.) ~800 nm**

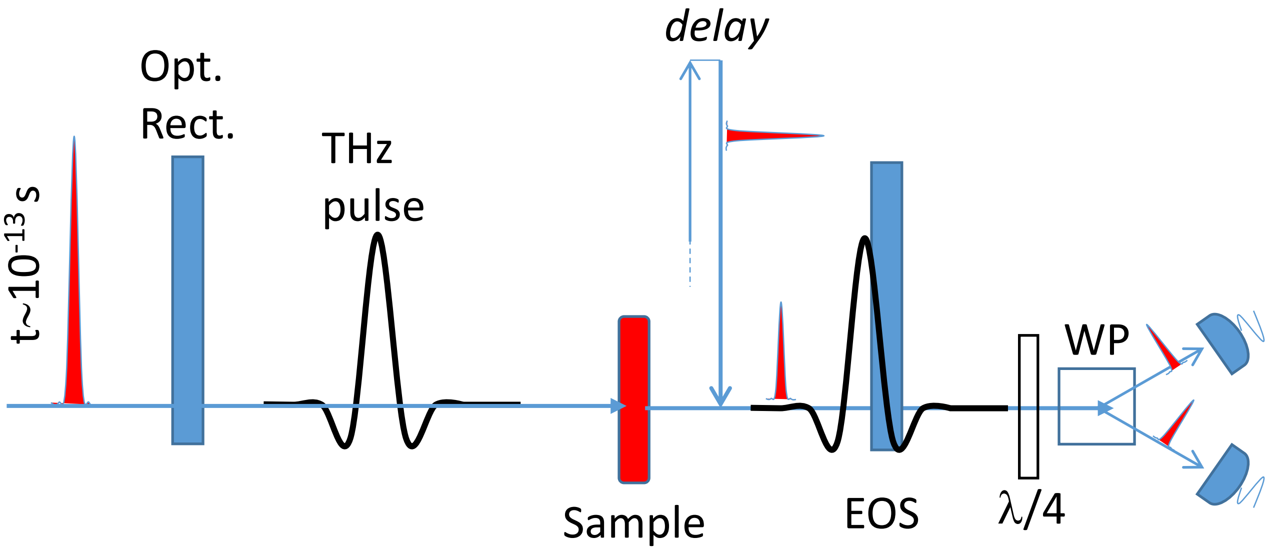
**«matched» SHG, ~400 nm**

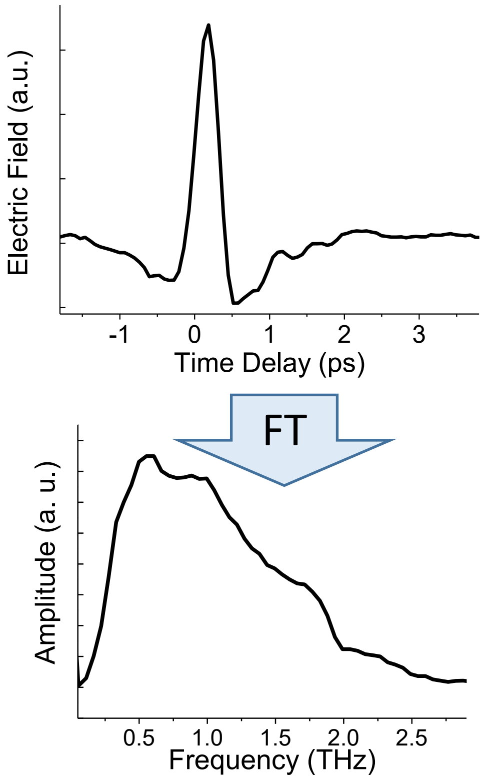
Pro: can generate up to very high THz frequency (>20 THz)
(however, THz is hard to detect with EOS above ~7 THz)

➢ Relevant work on THz plasma: *New J. Phys. 15, 075002 (2013)*

# THz-TDS with OR and EOS

- 1 THz = 33.36 $cm^{-1}$ = 4.14 meV ($\lambda$=300 $\mu$m)
- Covers the 3÷100 $cm^{-1}$ spectral region
- Pulsed lasers → THz time-domain spectroscopy

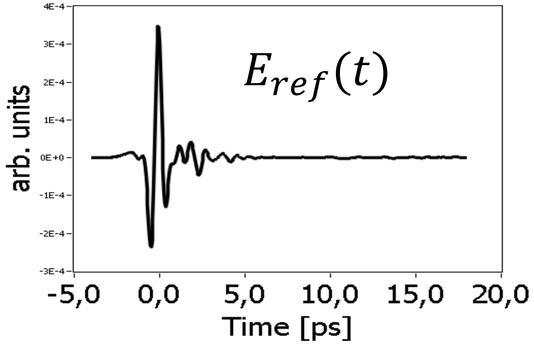




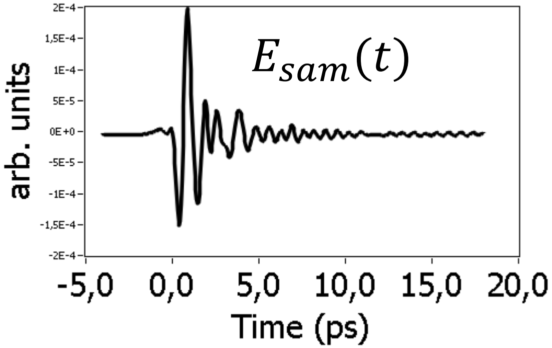
# THz-TDS measures linear response, $\chi^{(1)}$

**1)** Detect THz time-shape with and without the sample

**REF**



**SAMPLE**



*Hoffmann Ph.D. 2006*

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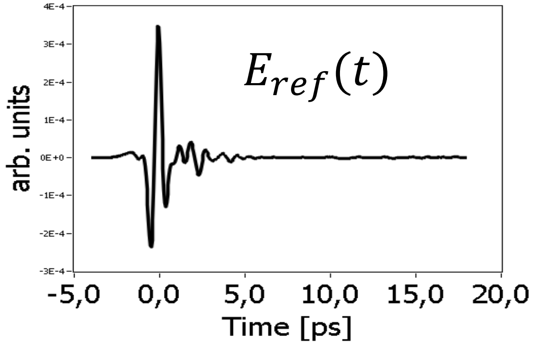

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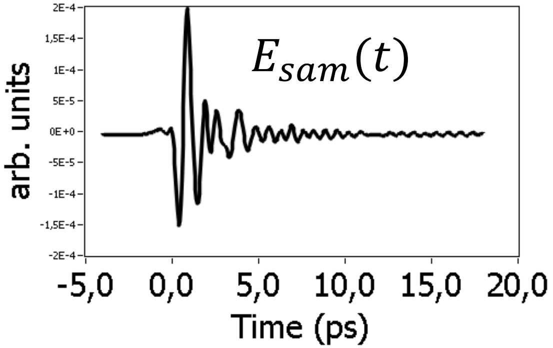
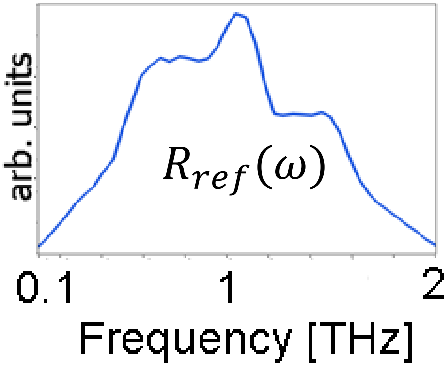


**2)**Fourier transform (magnitude shown)

**REF**



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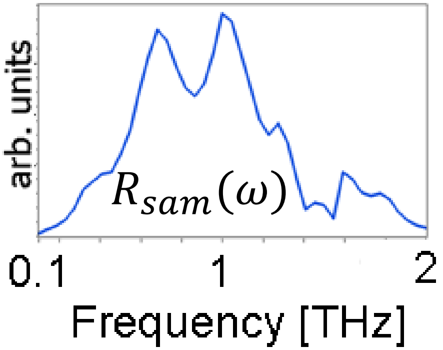

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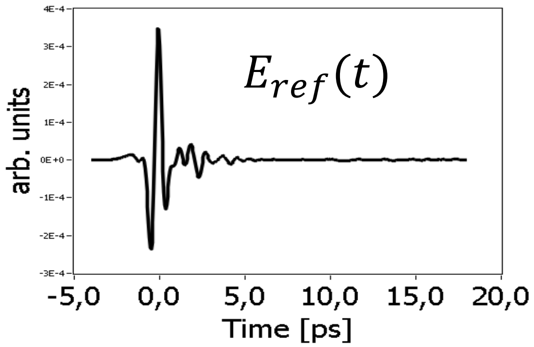

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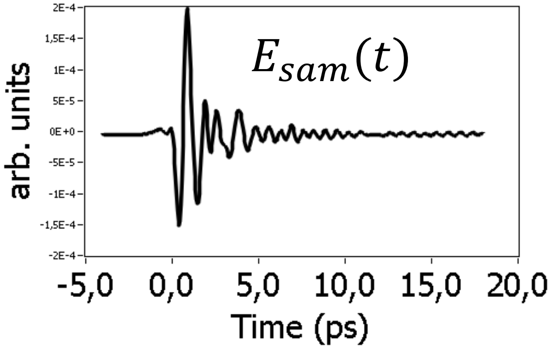

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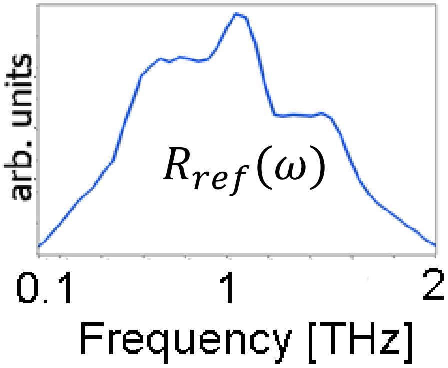

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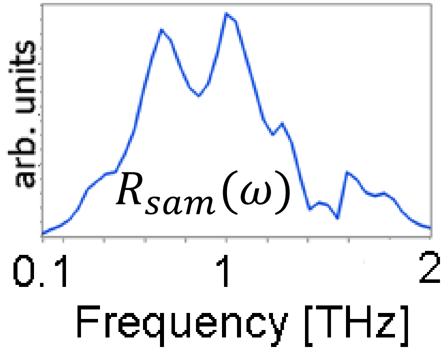


**3)** Model to obtain optical parameters

$$\frac{E_{\rm sam}}{E_{\rm ref}}(\omega) = R(\omega)e^{i\phi(\omega)}$$

$R(\omega)$: amplitude ratio

$\phi(\omega)$: phase difference

Index of refraction

$$n_r(\omega) = 1 + \frac{c}{\omega d}\,\phi$$

Absorption coefficient

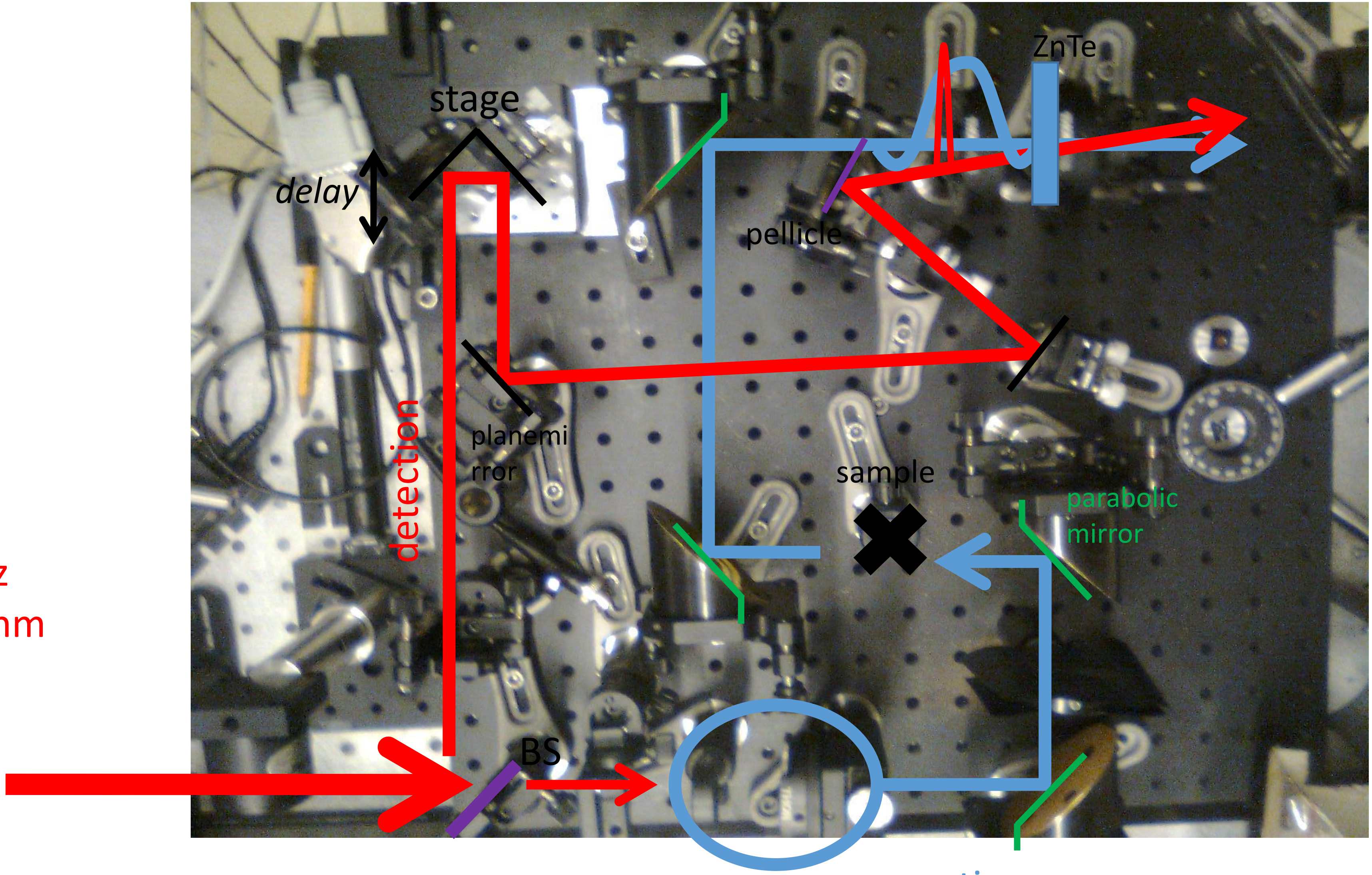
$$\alpha(\omega) = -\frac{2}{d}\ln\left(\frac{(n_r(\omega)+1)^2}{4n_r(\omega)}\,R\right)$$

$c$: speed of light

$d$: sample thickness

*Hoffmann Ph.D. 2006*

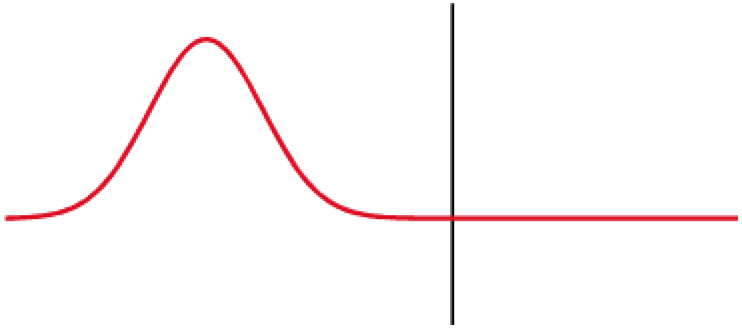
# THz-TDS setup



Ti:Sa
1 kHz
800 nm
50 fs
1 W

# Fresnel equations

The **Fresnel equations** (or **Fresnel coefficients**) describe the **amount of** reflected and transmitted electromagnetic radiation (including light) when incident on an interface between different optical media.



Partial transmission and reflection of a pulse travelling from a low to a high refractive index medium.

https://en.wikipedia.org/wiki/Fresnel_equations

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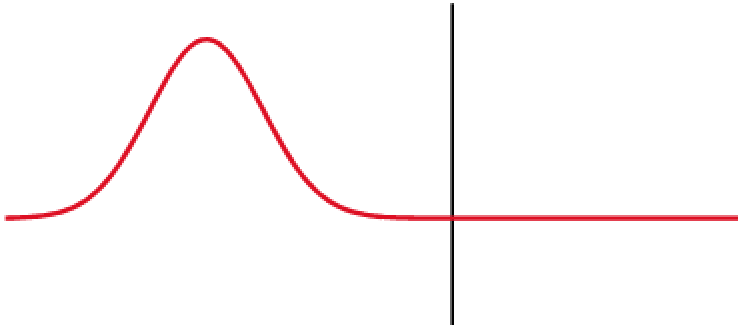
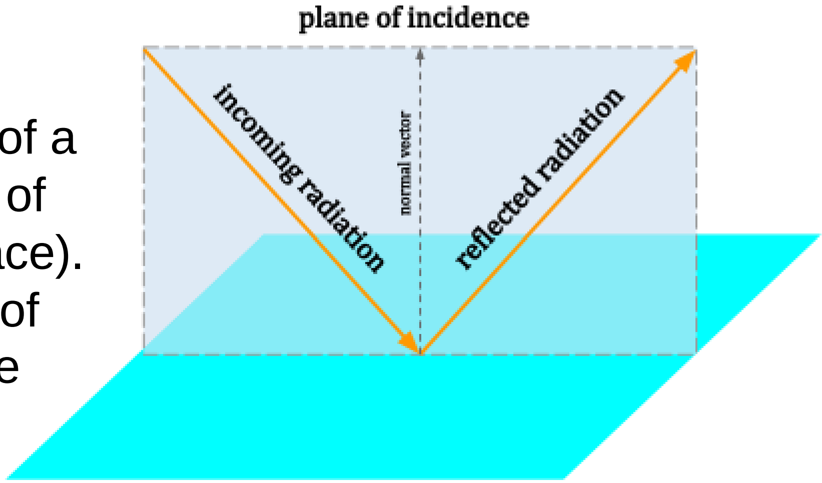


Partial transmission and reflection of a pulse travelling from a low to a high refractive index medium.

The s polarization refers to polarization of a wave's electric field *normal* to the plane of incidence (inside the plane of the interface). The p polarization refers to polarization of the electric field *in* the plane of incidence



https://en.wikipedia.org/wiki/Fresnel_equations

# Fresnel equations

There are two sets of Fresnel coefficients for the two different linear polarization components of the incident wave (s and p).

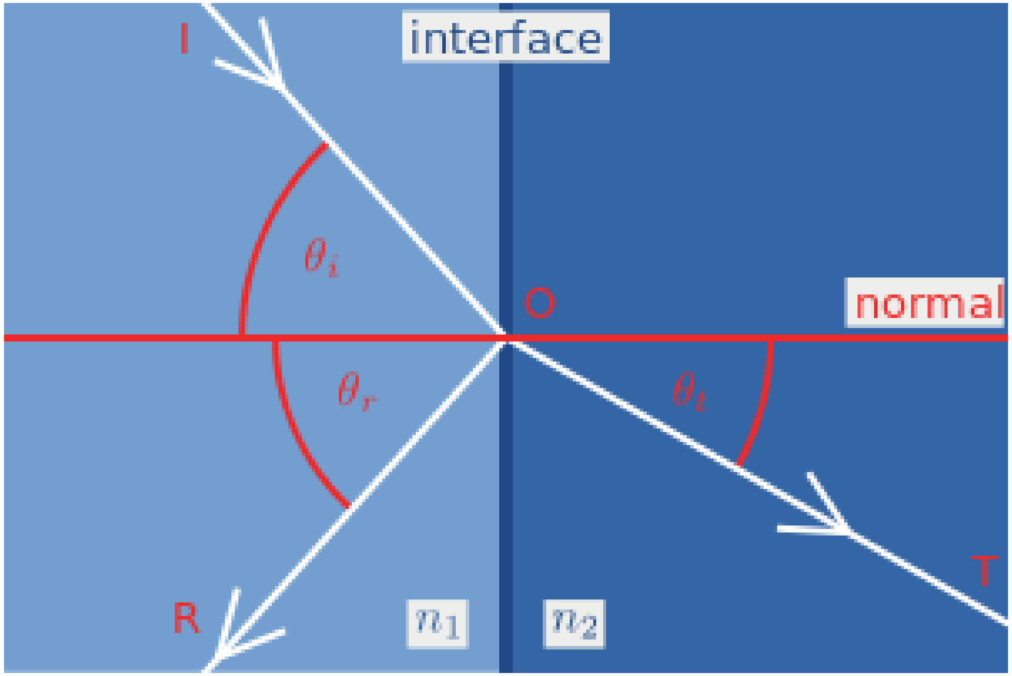
**Please note that these coefficients quantify amplitude and phase, not intensity!**

$$r_\mathrm{s} = \frac{n_1 \cos\theta_\mathrm{i} - n_2 \cos\theta_\mathrm{t}}{n_1 \cos\theta_\mathrm{i} + n_2 \cos\theta_\mathrm{t}},$$

$$t_\mathrm{s} = \frac{2 n_1 \cos\theta_\mathrm{i}}{n_1 \cos\theta_\mathrm{i} + n_2 \cos\theta_\mathrm{t}},$$

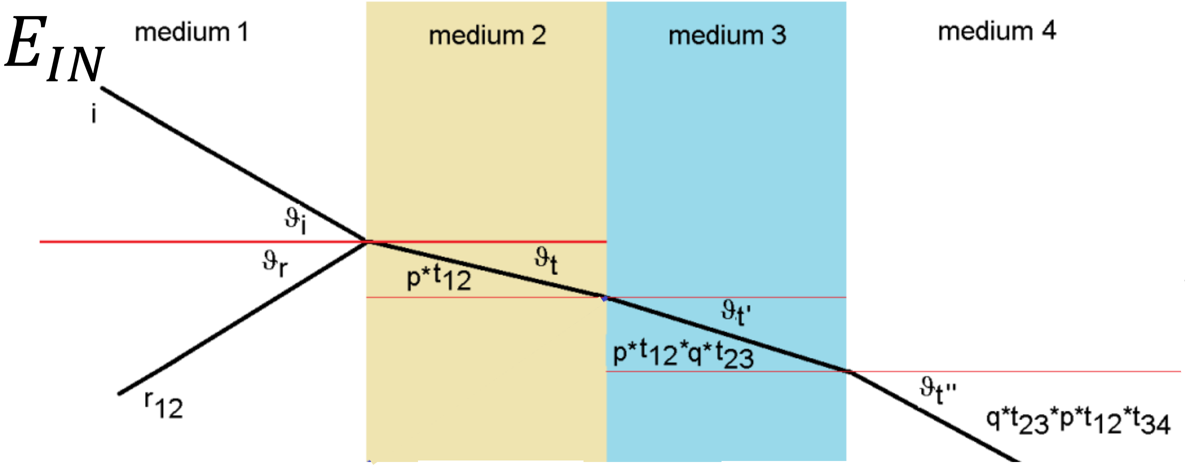
$$r_\mathrm{p} = \frac{n_2 \cos\theta_\mathrm{i} - n_1 \cos\theta_\mathrm{t}}{n_2 \cos\theta_\mathrm{i} + n_1 \cos\theta_\mathrm{t}},$$

$$t_\mathrm{p} = \frac{2 n_1 \cos\theta_\mathrm{i}}{n_2 \cos\theta_\mathrm{i} + n_1 \cos\theta_\mathrm{t}}.$$



https://en.wikipedia.org/wiki/Fresnel_equations

# THz-TDS analysis: thick sample and substrate



$$p = e^{i\frac{\omega d}{c}\widetilde{n}_2(\omega)} \qquad q = e^{i\frac{\omega D}{c}\widetilde{n}_3(\omega)}$$

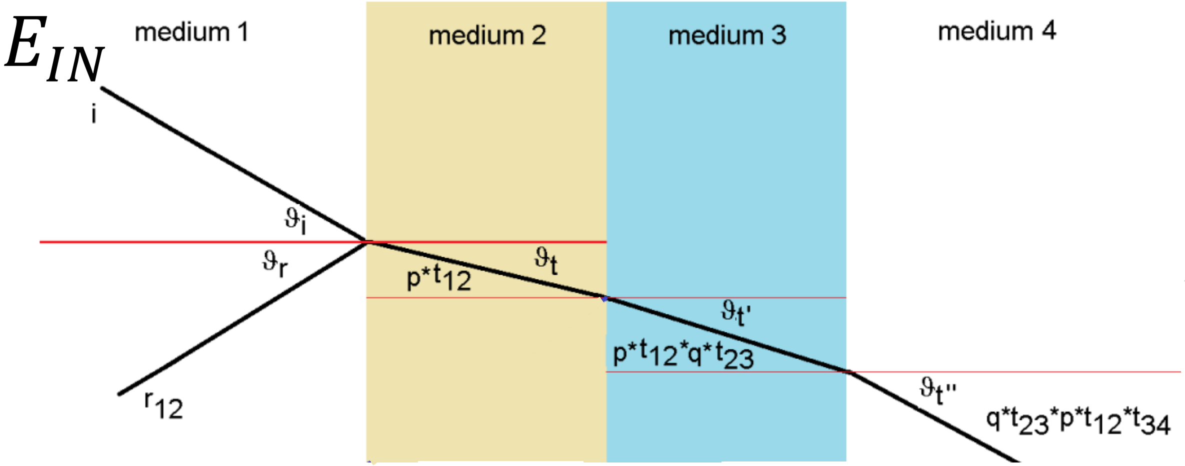
S polarization

$$\widetilde{r}_{ij}(\omega) = \frac{\widetilde{n}_i(\omega)\cos(\vartheta_i) - \widetilde{n}_j(\omega)cos(\vartheta_j)}{\widetilde{n}_i(\omega)\cos(\vartheta_i) + \widetilde{n}_j(\omega)cos(\vartheta_j)}$$

$$\widetilde{t}_{ij}(\omega) = \frac{2\widetilde{n}_i(\omega)cos(\vartheta_i)}{\widetilde{n}_i(\omega)\cos(\vartheta_i) + \widetilde{n}_j(\omega)cos(\vartheta_j)}$$

$$\tilde{n} = n + ik$$

# THz-TDS analysis: thick sample and substrate



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$$\tilde{n} = n + ik$$

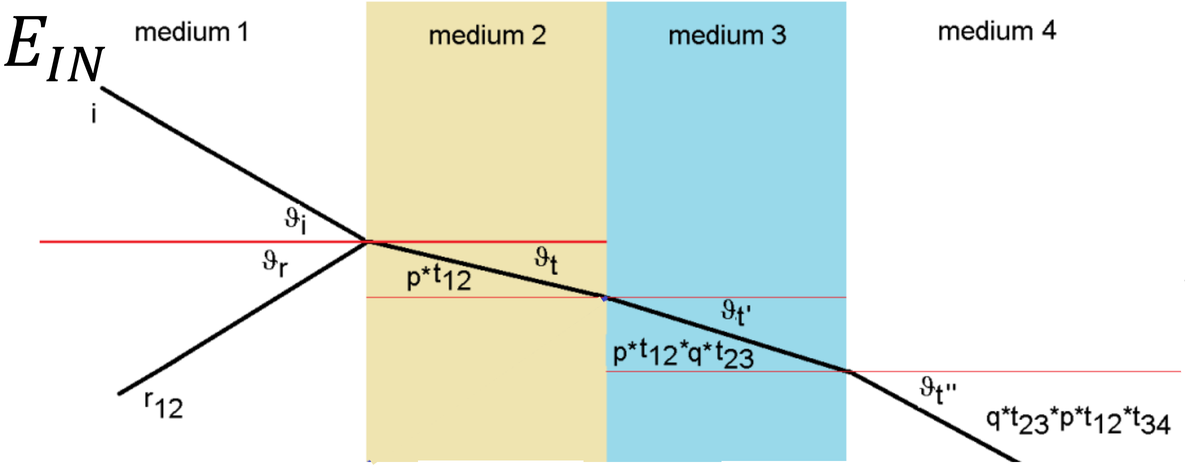
Field transmitted by the sample, for an “optically thick” sample (2) on an “optically thick” substrate (3)

$$\widetilde{E}_S(\omega) = E_{IN}\widetilde{t}_{12}(\omega)\widetilde{t}_{23}(\omega)e^{i\frac{\omega d}{c}\widetilde{n}_2(\omega)}\widetilde{t}_{34}(\omega)e^{i\frac{\omega D}{c}\widetilde{n}_3(\omega)}$$

Get the reference by removing the sample (medium 1 = medium 2)

$$\widetilde{E}_R(\omega) = E_{IN}\widetilde{t}_{13}(\omega)e^{i\frac{\omega d}{c}\widetilde{n}_1(\omega)}\widetilde{t}_{34}(\omega)e^{i\frac{\omega D}{c}\widetilde{n}_3(\omega)}$$

# THz-TDS analysis: thick sample and substrate



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$$\tilde{n} = n + ik$$

$$\frac{\widetilde{E}_S(\omega)}{\widetilde{E}_R(\omega)} = \frac{\widetilde{t}_{12}(\omega)\widetilde{t}_{23}(\omega)}{\widetilde{t}_{13}(\omega)} e^{i\frac{\omega d}{c}(\widetilde{n}_2(\omega)-\widetilde{n}_1(\omega))}$$

For normal incidence and in air: $= \frac{2}{1+\widetilde{n}_2(\omega)}\frac{2\widetilde{n}_2(\omega)}{\widetilde{n}_2(\omega)+\widetilde{n}_3(\omega)}\frac{1+\widetilde{n}_3(\omega)}{2}e^{-\frac{\omega d}{c}k_2(\omega)}e^{i\frac{\omega d}{c}(n_2(\omega)-1)}$

If low absorbing/high refracting: $= \frac{2}{1+n_2(\omega)}\frac{2n_2(\omega)}{n_2(\omega)+n_3(\omega)}\frac{1+n_3(\omega)}{2}e^{-\frac{\omega d}{c}k_2(\omega)}e^{i\frac{\omega d}{c}(n_2(\omega)-1)}$

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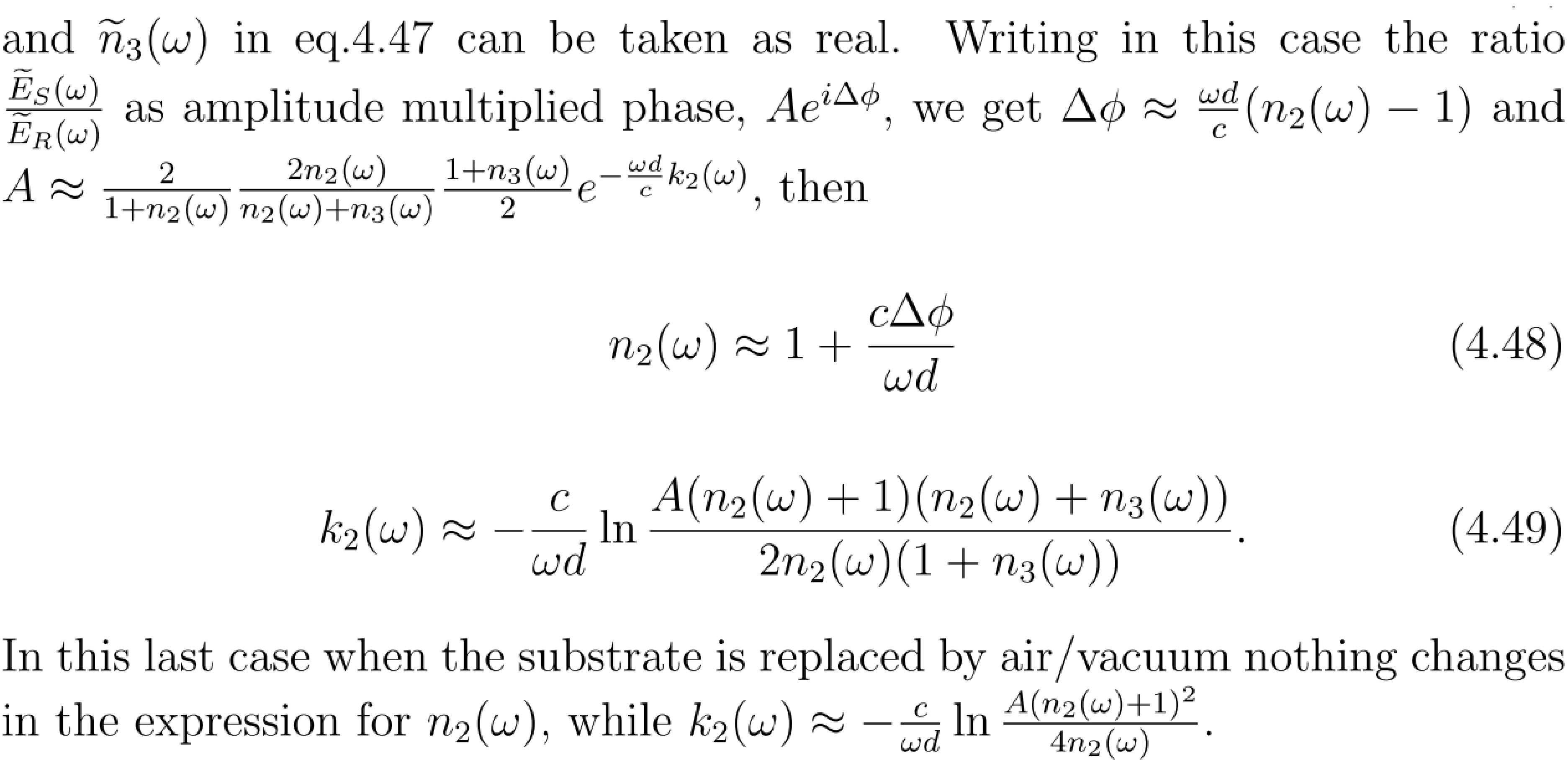


and $\widetilde{n}_3(\omega)$ in eq.4.47 can be taken as real. Writing in this case the ratio $\frac{\widetilde{E}_S(\omega)}{\widetilde{E}_R(\omega)}$ as amplitude multiplied phase, $Ae^{i\Delta\phi}$, we get $\Delta\phi \approx \frac{\omega d}{c}(n_2(\omega)-1)$ and $A \approx \frac{2}{1+n_2(\omega)}\frac{2n_2(\omega)}{n_2(\omega)+n_3(\omega)}\frac{1+n_3(\omega)}{2}e^{-\frac{\omega d}{c}k_2(\omega)}$, then

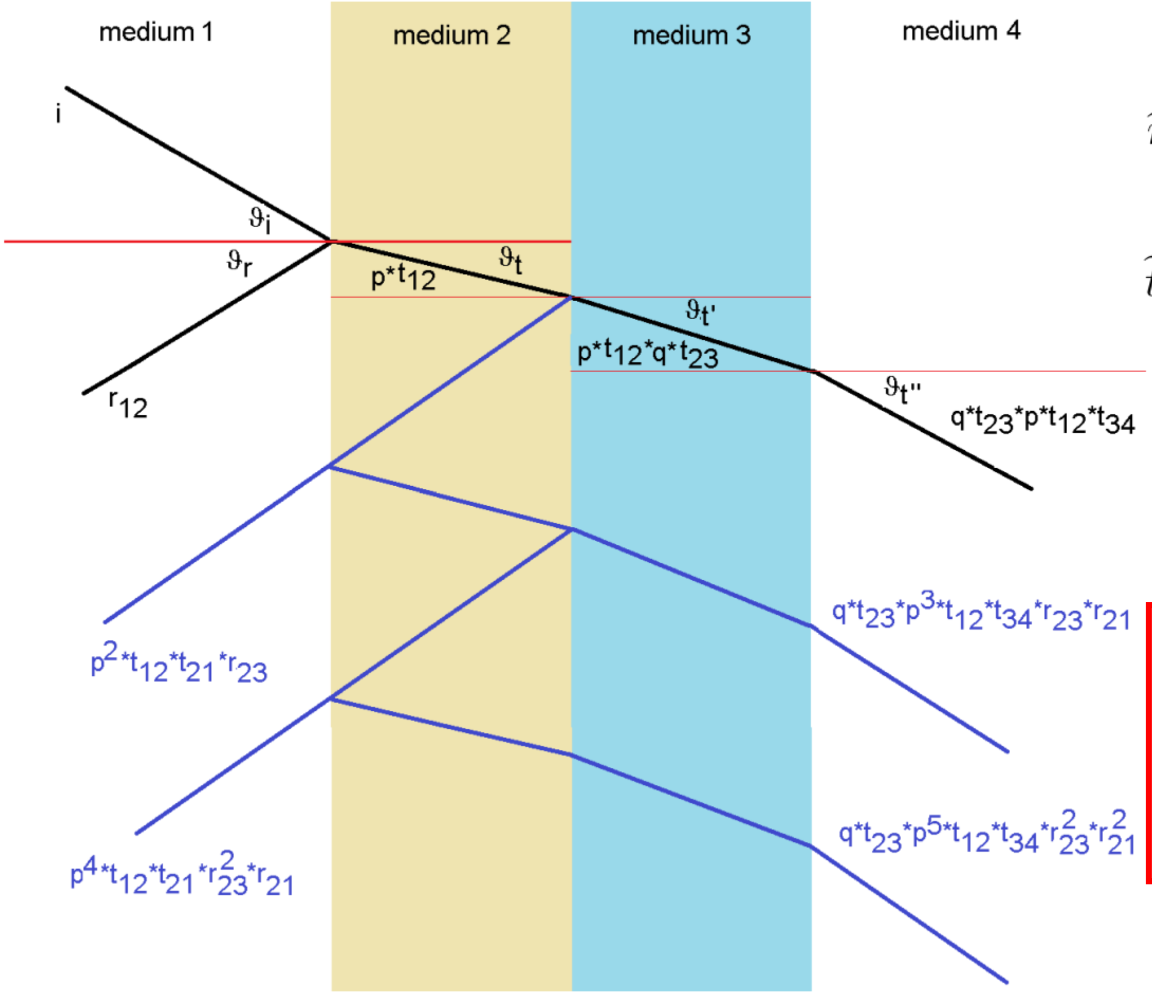
$$n_2(\omega) \approx 1 + \frac{c\Delta\phi}{\omega d} \tag{4.48}$$

$$k_2(\omega) \approx -\frac{c}{\omega d}\ln\frac{A(n_2(\omega)+1)(n_2(\omega)+n_3(\omega))}{2n_2(\omega)(1+n_3(\omega))}. \tag{4.49}$$

In this last case when the substrate is replaced by air/vacuum nothing changes in the expression for $n_2(\omega)$, while $k_2(\omega) \approx -\frac{c}{\omega d}\ln\frac{A(n_2(\omega)+1)^2}{4n_2(\omega)}$.

http://hdl.handle.net/10077/8588

# In general, may consider multiple reflections



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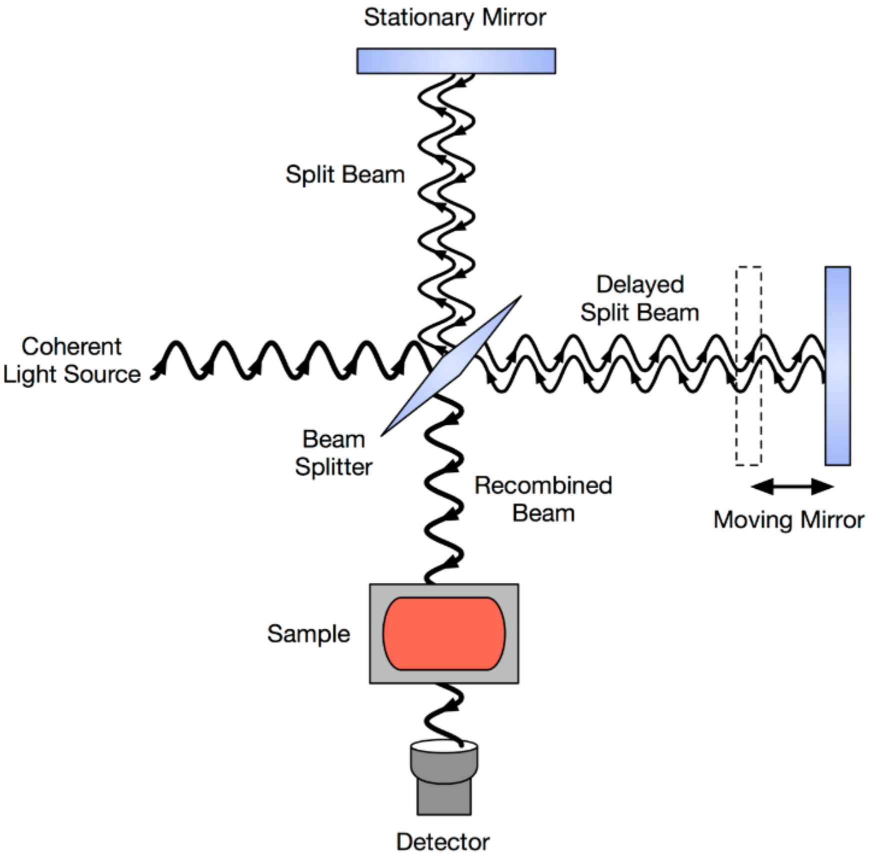
$$\tilde{n} = n + ik$$

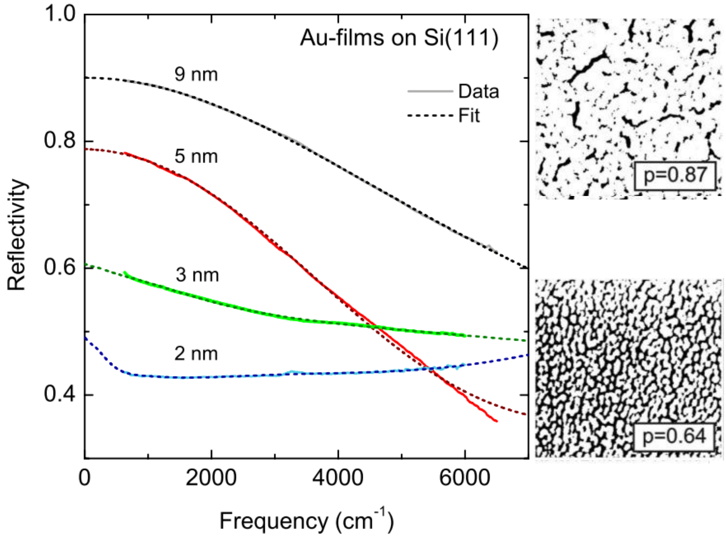
Conductivity of a thin sample (all simultaneous reflections within):

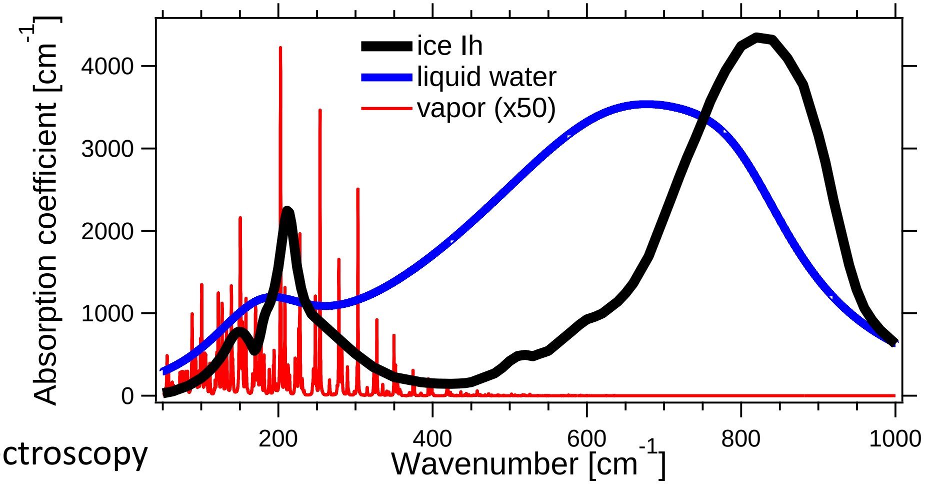
$$\widetilde{\sigma}_2(\omega) \approx \frac{1+\widetilde{n}_3(\omega)}{Z_0 d}\,\frac{\widetilde{E}_R(\omega) - \widetilde{E}_S(\omega)}{\widetilde{E}_S(\omega)}$$

http://hdl.handle.net/10077/8588

# Note: some of the experiments I will show you later have been measured with an FTIR…







10.1103/PhysRevB.78.205409
10.1103/PhysRevB.76.125408
https://en.wikipedia.org/wiki/Fourier-transform_infrared_spectroscopy

# Terahertz and Water: outline

1. Terahertz time-domain spectroscopy
    1. Examples of non-linear responses
    2. Linear and non-linear spectroscopy
    3. Optical rectification (OR) and electro-optical sampling (EOS)
    4. Models to obtain the optical properties (Fresnel equations)

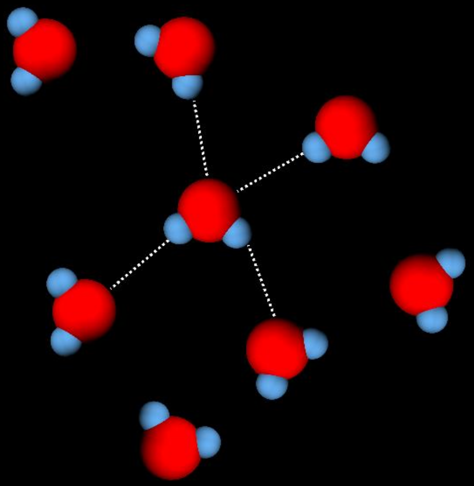
2. Water and solvation
    1. Infrared absorption modes of liquid water
    2. Introduction to solvation science
    3. Study ions in water with THz: rattling, hydration layers
    4. Gold nanoparticles
    5. Long-range protein effects on water

https://en.wikipedia.org/wiki/The_Blue_Marble

Zoom out

https://en.wikipedia.org/wiki/Pale_Blue_Dot
https://en.wikipedia.org/wiki/The_Blue_Marble

Zoom in



Liquid water: network of hydrogen-bonded molecules that fluctuates (~ps)

Zoom out

https://en.wikipedia.org/wiki/Pale_Blue_Dot
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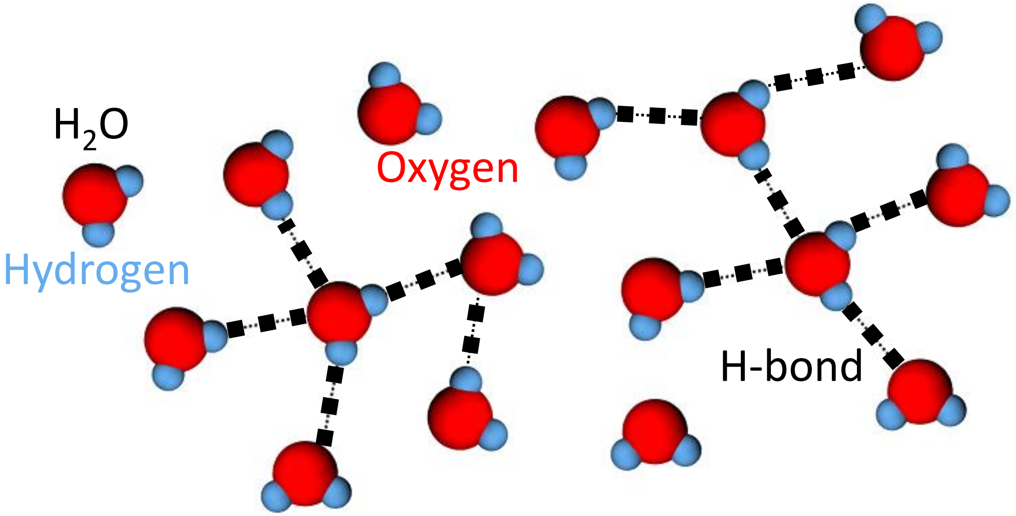
# Water: ubiquitous solvent, *strange liquid*

- **Microscopic**: tetrahedral network of hydrogen-bonded molecules. Each molecule has ~4 H-bonds breaking/forming on the **~ps timescale**



https://water.lsbu.ac.uk/water/index.html
https://doi.org/10.1002/9781119300762.wsts0002

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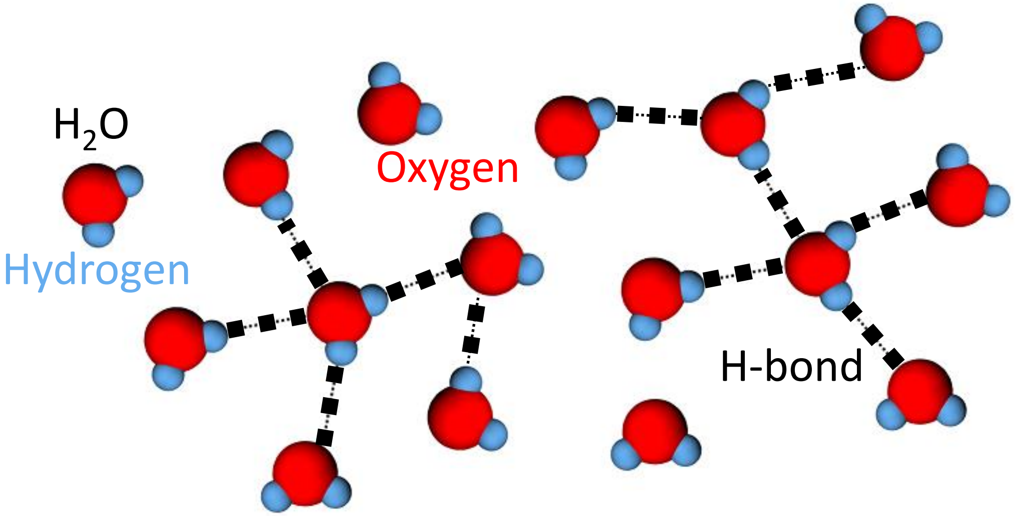

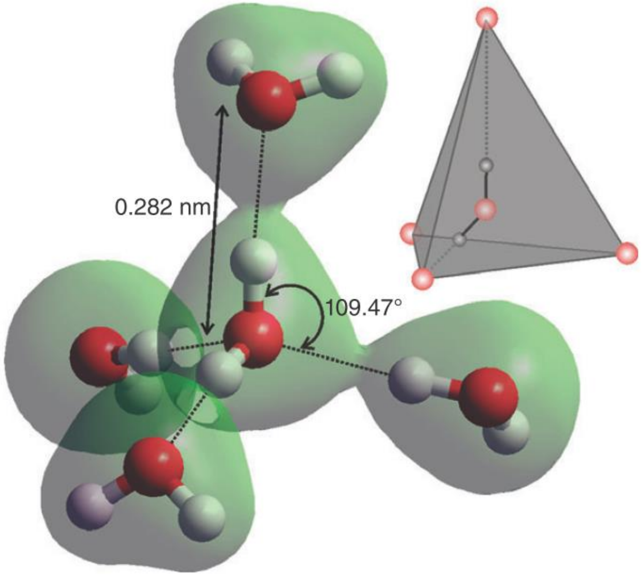

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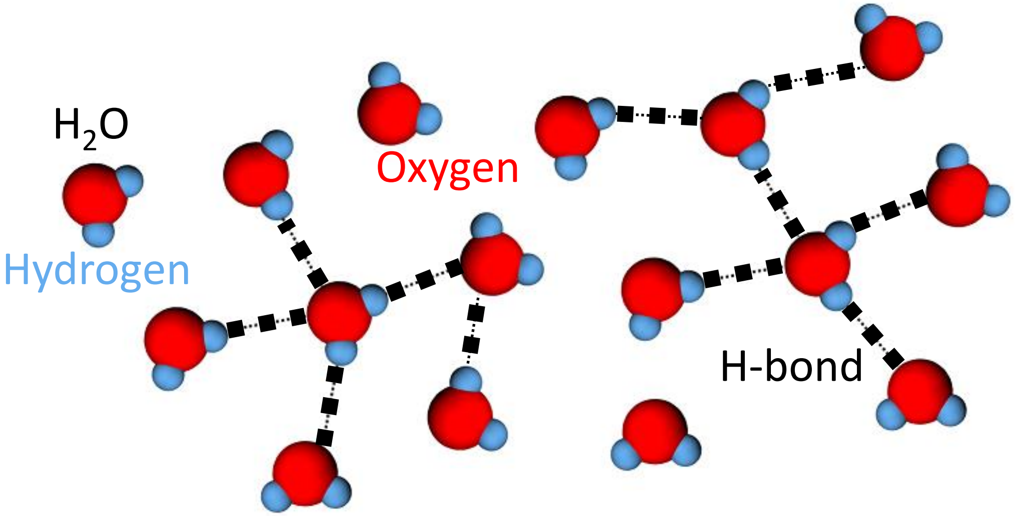

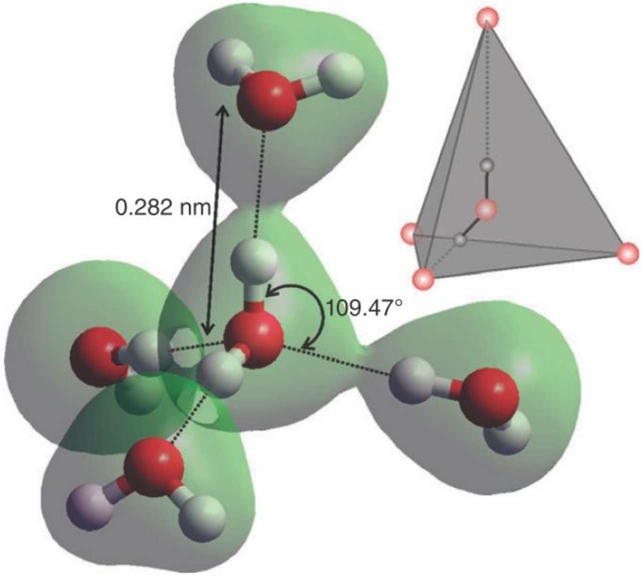

- **Macroscopic anomalies** (expands on freezing, density max at 4 °C, etc.): unclear how molecular interlinking results in bulk behavior.

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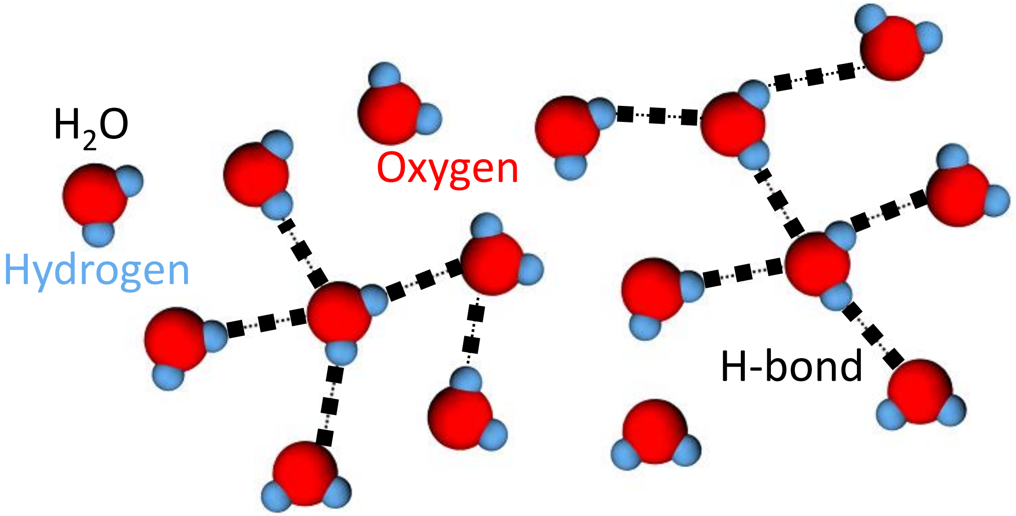

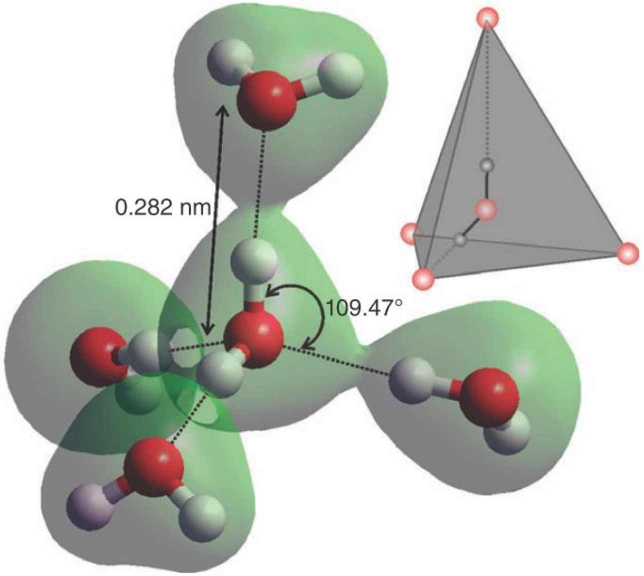

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***"No one really understands water." P. Ball, Nature 452, 291***

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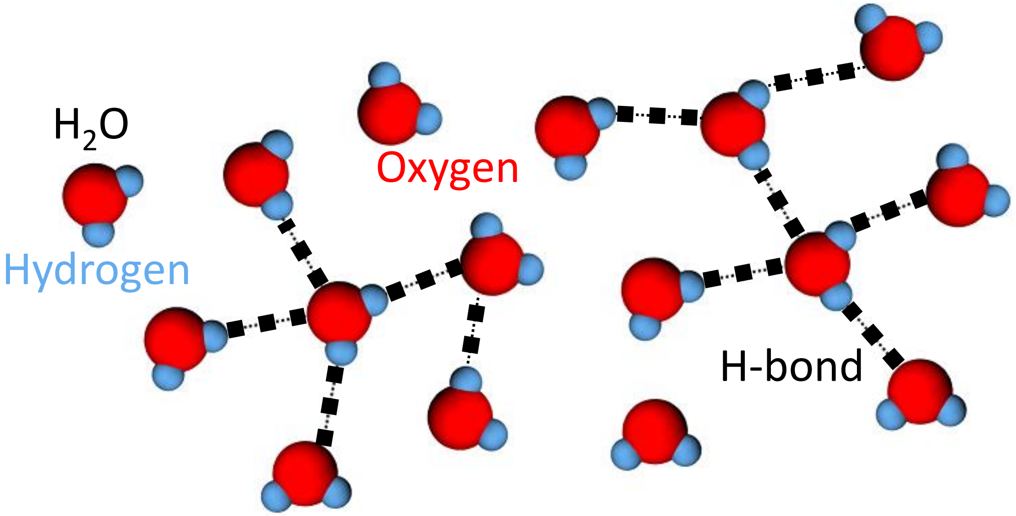

**Good news:**

***THZ (~ps) radiation can probe the collective motion of H-bond network***

- **Macroscopic anomalies** (expands on freezing, density max at 4 °C, etc.): unclear how molecular interlinking results in bulk behavior.

MISSING LINK

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# Water is “black” in the terahertz range

- Hydrogen bond lifetime is ~1 ps
    - ➢1/1ps = 1 THz: <u>THz radiation probes collective, intermolecular water modes</u>
- Water strongly absorbs THz radiation

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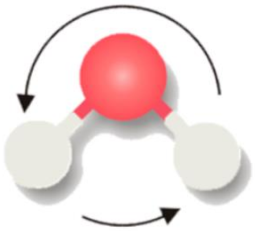
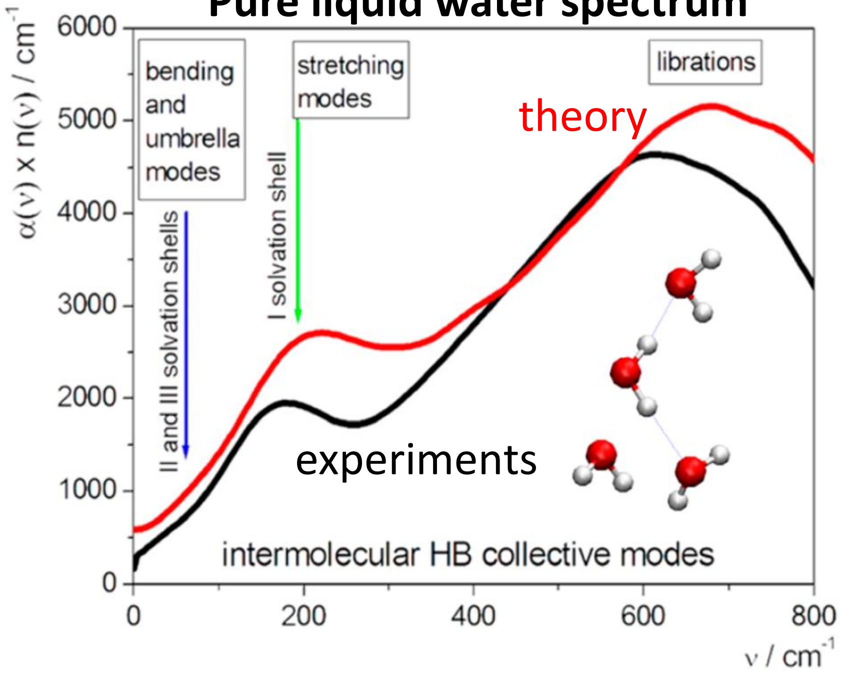
Dielectric Spectroscopy

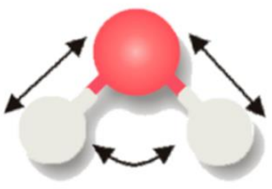


rotational transitions

**Pure liquid water spectrum**



Infrared Spectroscopy

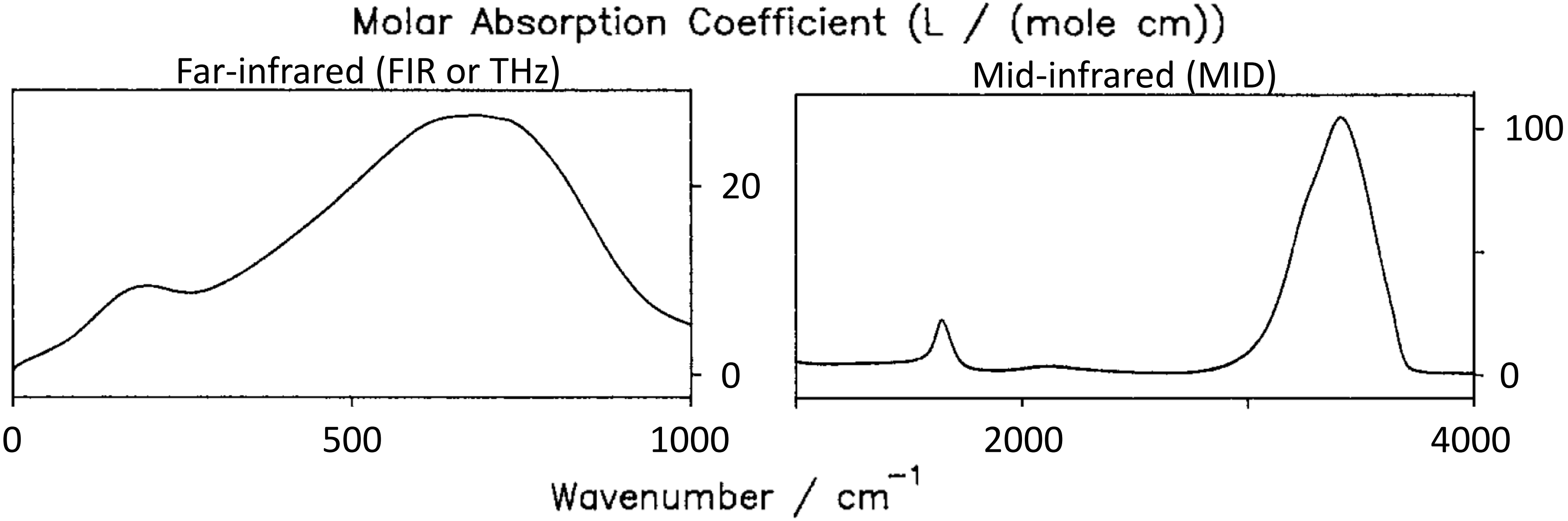


vibrational modes

**3-700 cm$^{-1}$; 0.1-20 THz; 3mm-14 μm**

*J. Am. Chem. Soc.* 2014, 136, 12800−12807

# (again, the full IR absorption of liquid $H_2O$)



J.E. Bertie, Z. Lan, Applied Spectroscopy 50, 1047 (1996)

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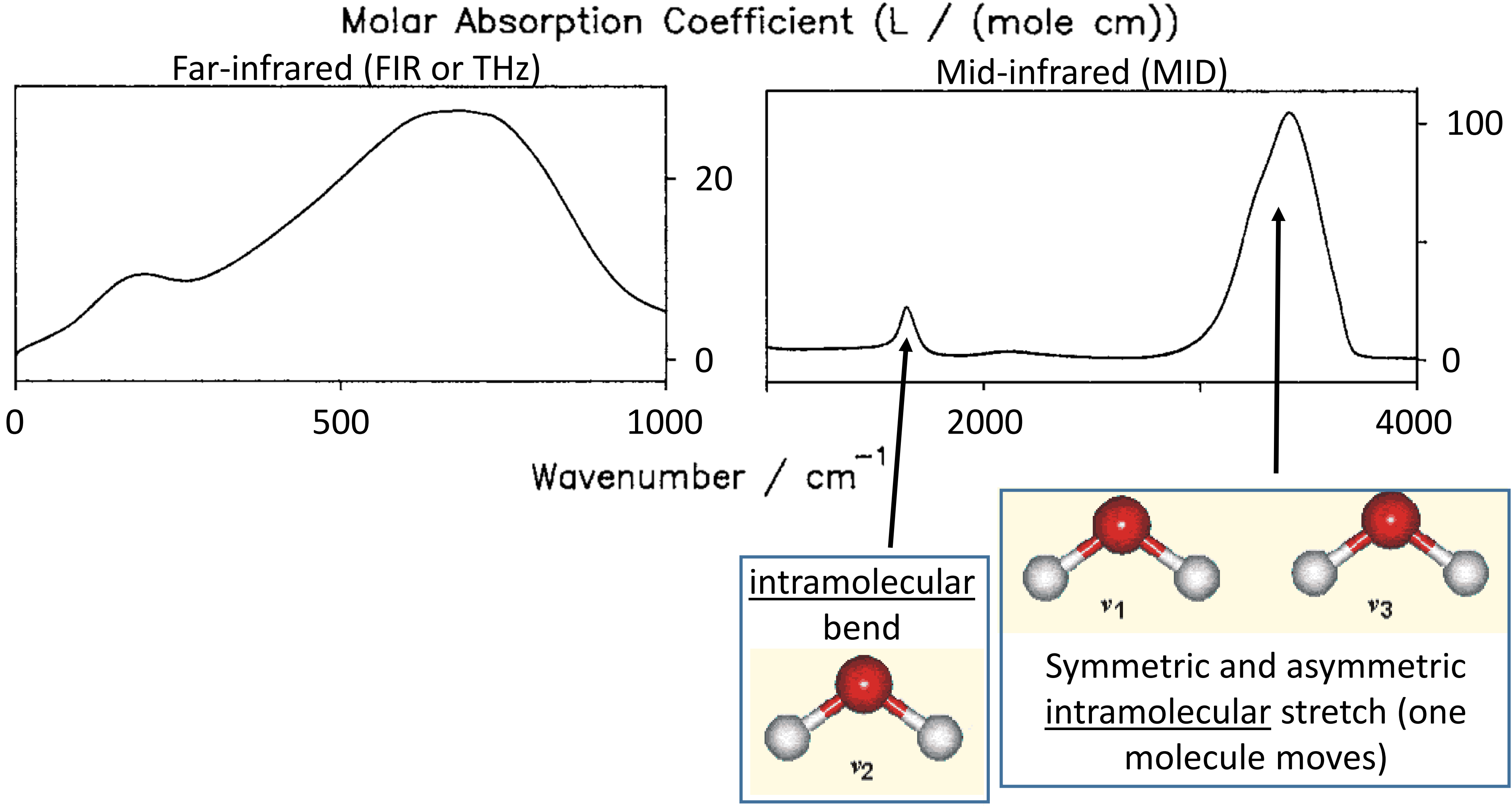


intramolecular bend

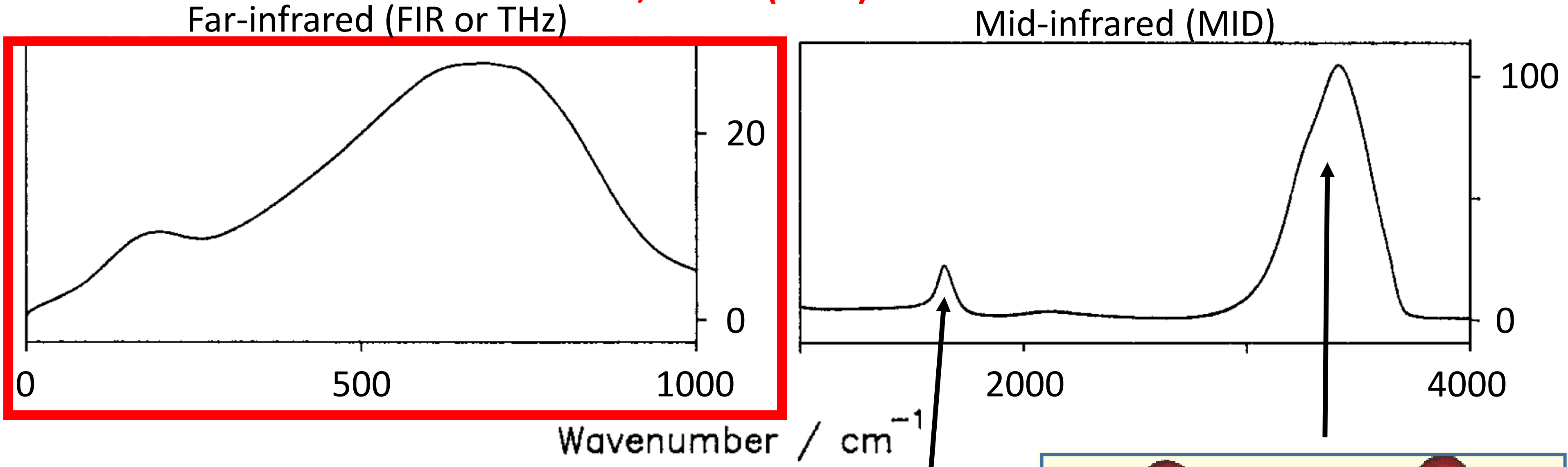
Symmetric and asymmetric intramolecular stretch (one molecule moves)

https://water.lsbu.ac.uk/water/water_vibrational_spectrum.html

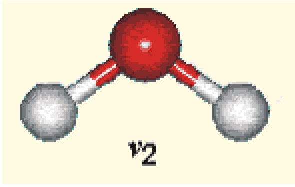
J.E. Bertie, Z. Lan, Applied Spectroscopy 50, 1047 (1996)

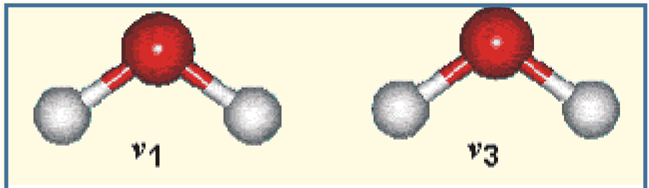
# (again, the full IR absorption of liquid $H_2O$)

**Terahertz absorption: <u>collective modes</u> of the hydrogen bonded water molecules PNAS 107, 12068 (2010)**



<u>intramolecular</u> bend





Symmetric and asymmetric <u>intramolecular</u> stretch (one molecule moves)

https://water.lsbu.ac.uk/water/water_vibrational_spectrum.html

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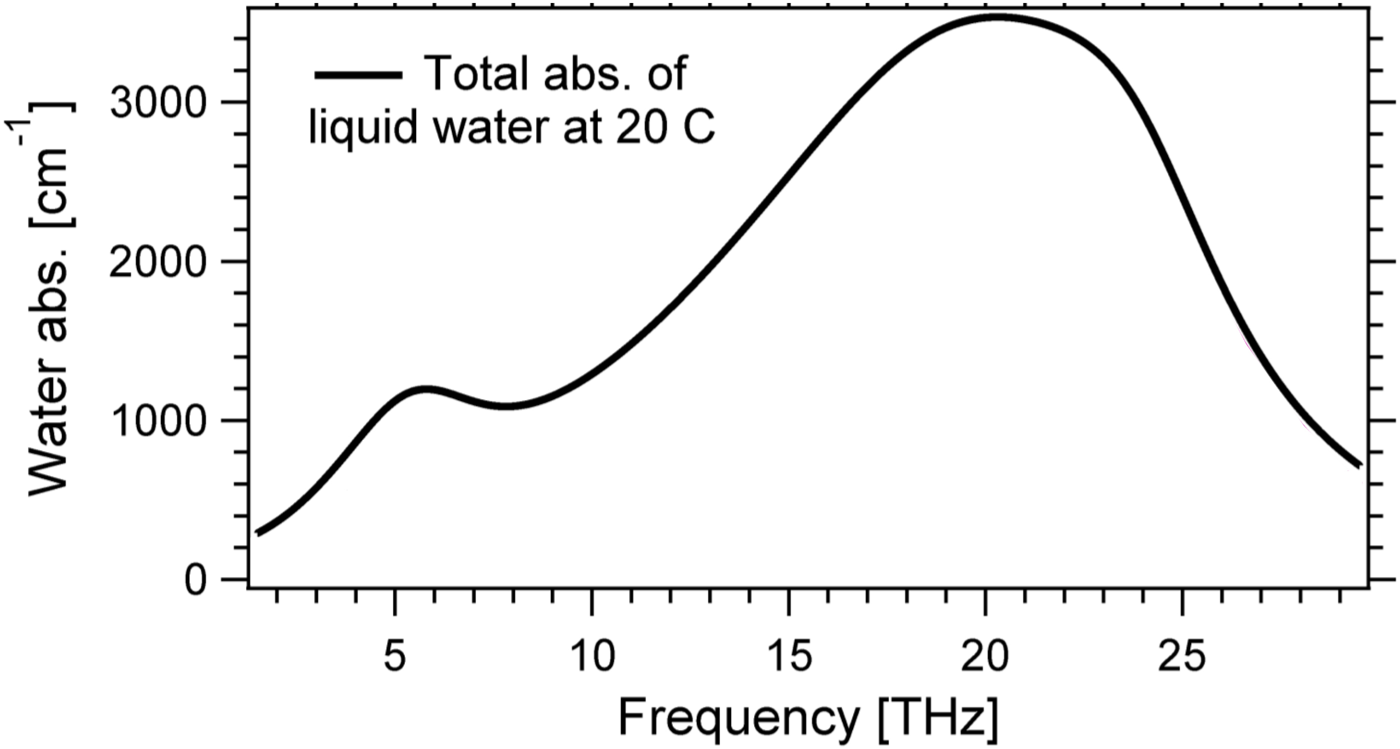
# THz spectroscopy on liquid water

- THz radiation probes *intermolecular* water modes
- Water strongly absorbs THz: sensitive spectroscopic probe



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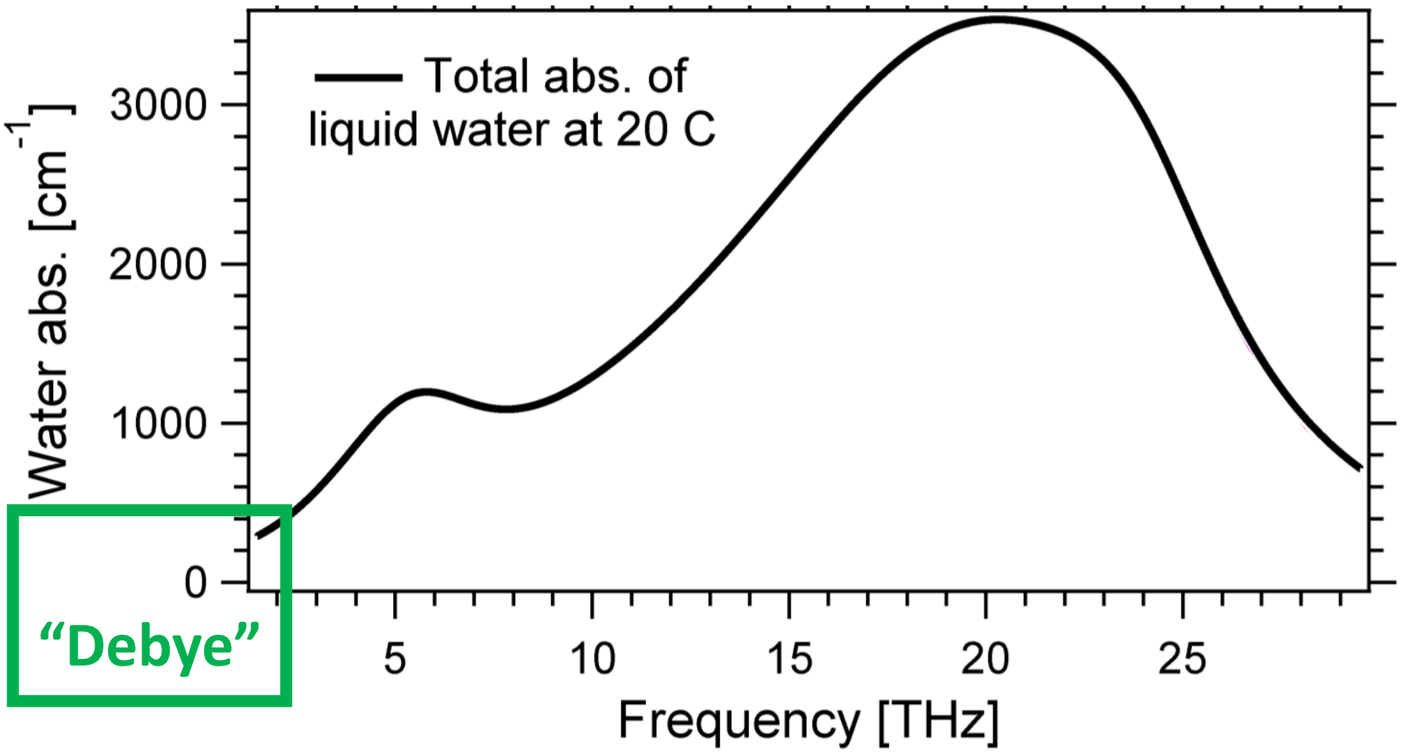
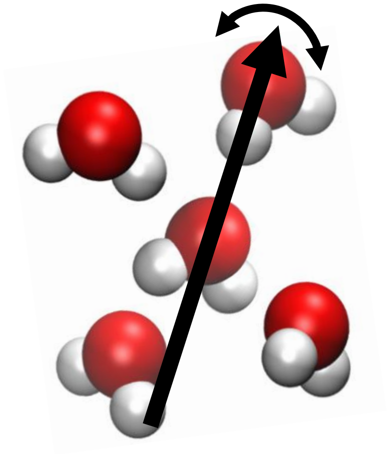


**Below 1 THz:**



**Debated**, see, e.g., Hölzl *et al*., Phys. Chem. Chem. Phys. 23, 20875, 2021

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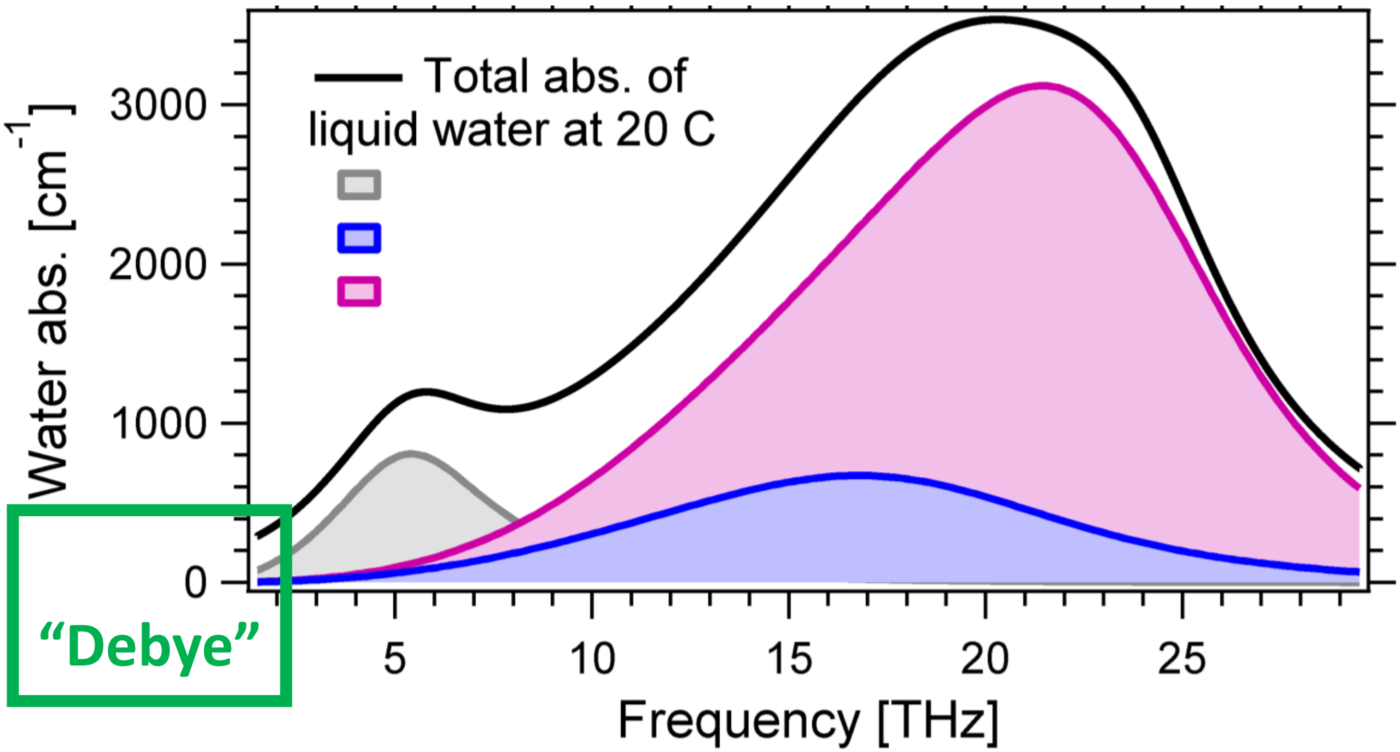

Minimal fit **between 2 and 25 THz**: at least **three bands**

J. Phys. Chem. Lett 8, 2373, 2017

Materials 13, 1311, 2020

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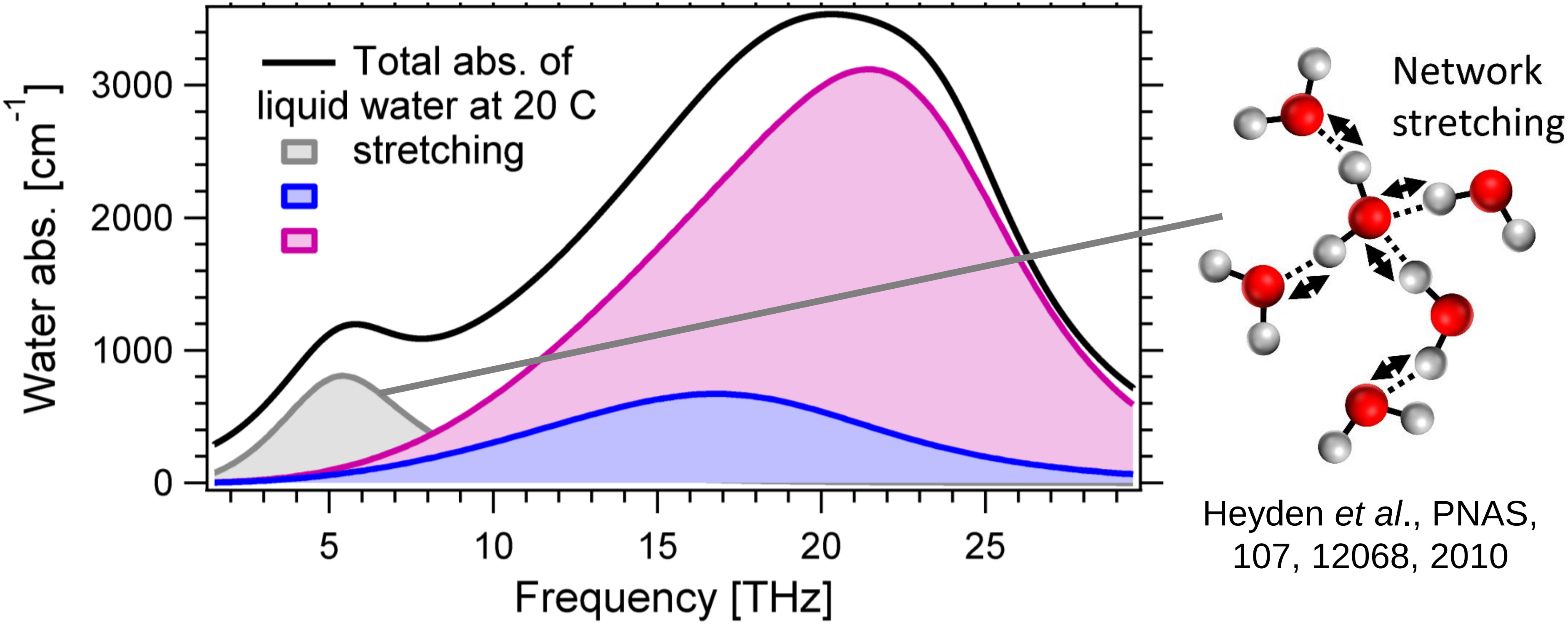

Heyden *et al*., PNAS, 107, 12068, 2010

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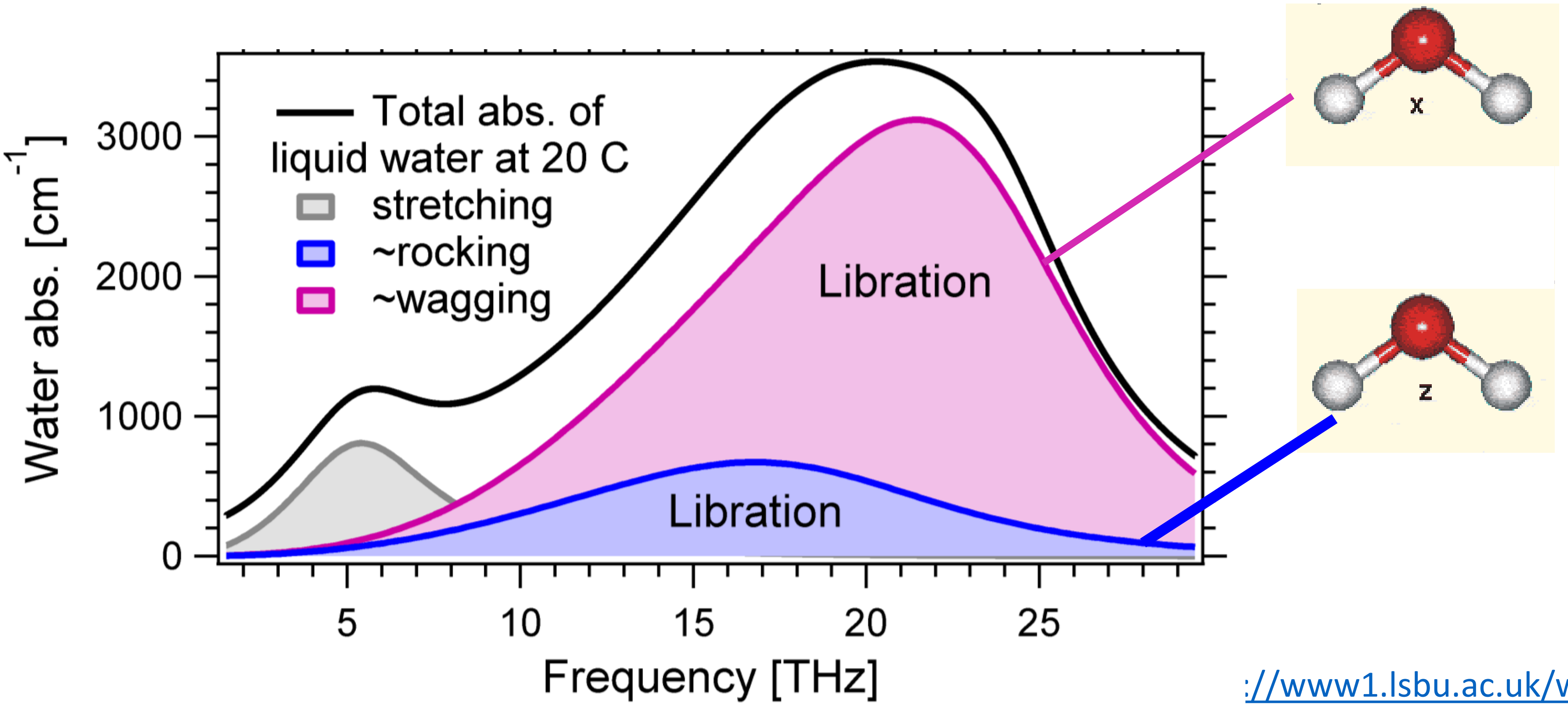

://www1.lsbu.ac.uk/water/

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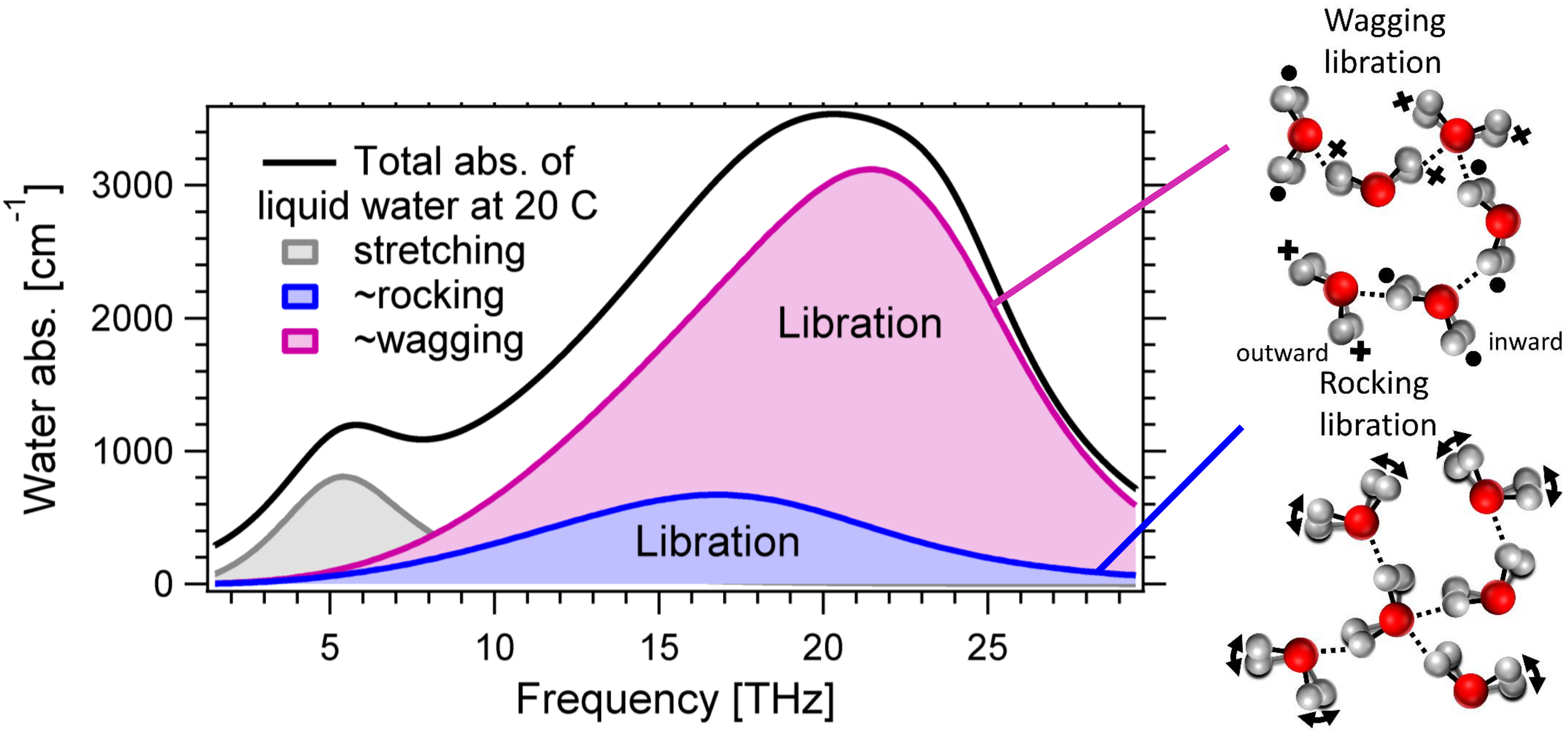
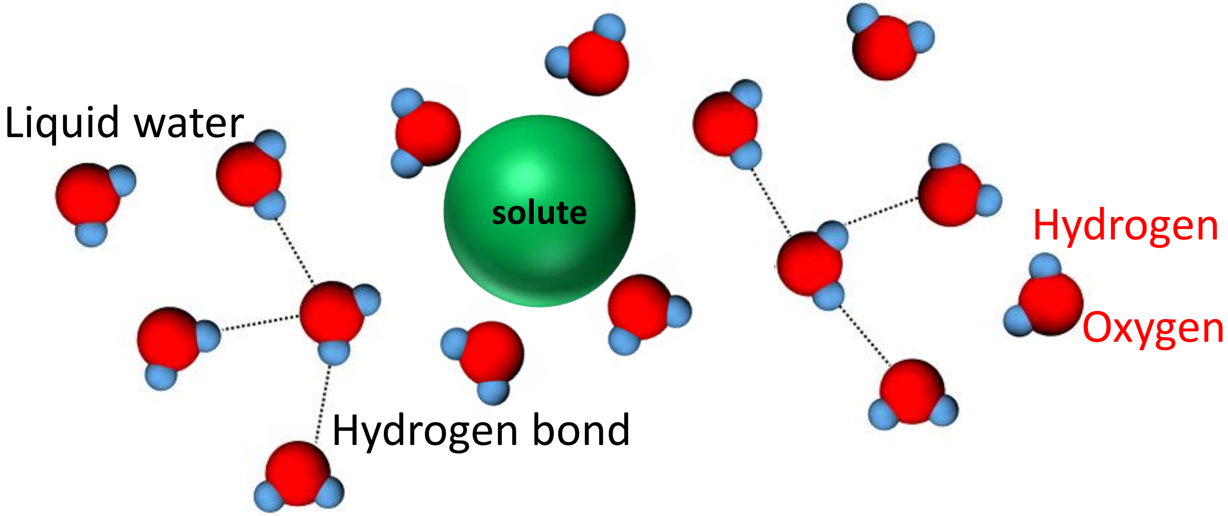


# What happens when we add a solute?

- When a solute is added to water, the fluctuating hydrogen-bonded network rearranges, and both the solvent-solvent and solvent-solute entropy end enthalpy change non-trivially



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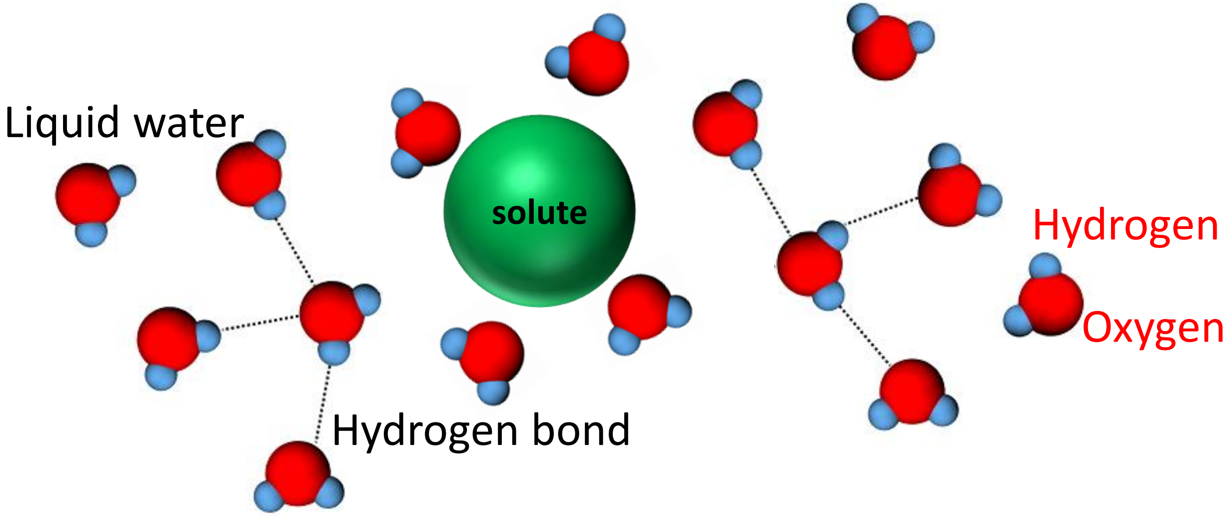

- “**The difficulty in understanding all reactions in aqueous media begins with the media.**” Chem. Rev. 105 335 2005
- The structures of proteins, nucleic acids, and cell membranes, as well as many other biological molecules, strictly depend upon water being the solvent.

# Solvation

- Solvation science studies “how the solvent is involved in the control, mediation and regulation of chemical reactions”

  *RESOLV cluster of excellence, https://www.solvation.de/*

# The *simplest* take on… Solvation

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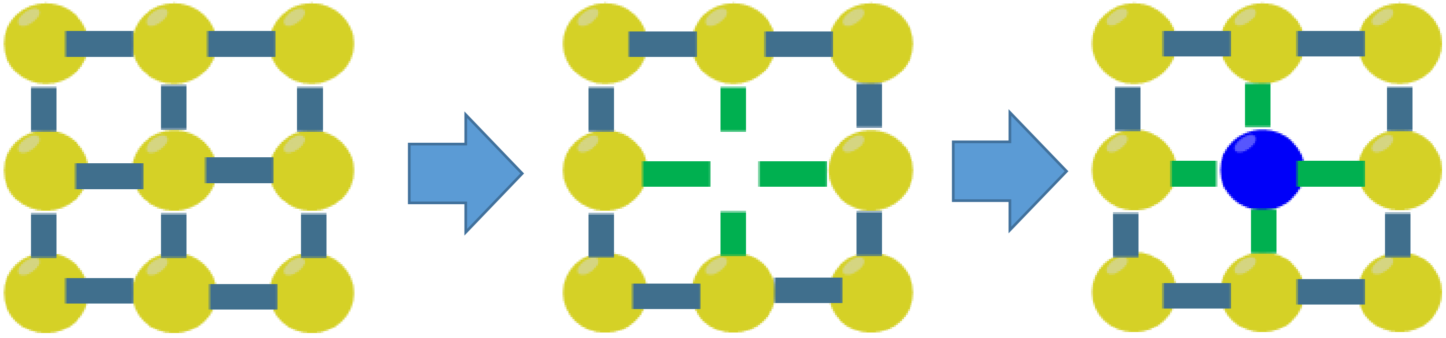
- A solvation process involves many steps (not necessarily in this order)



1. Pure liquid solvent 2. Creation of cavity 3. Insertion of solute

https://en.wikipedia.org/wiki/Solvation

Chapter 3 of Anslyn and Dougherty, Modern Physical Organic Chemistry (2006)

# The *simplest* take on… Solvation

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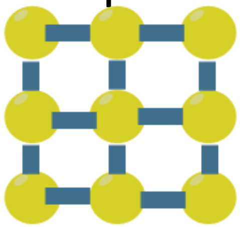

- Liquids have rapidly changing molecular order with high cohesive interactions between molecules. Enthalpy (binding interactions between molecules) and entropy (large because molecules can move) determine the free energy and hence the system's structure.

Chapter 3 of Anslyn and Dougherty, Modern Physical Organic Chemistry (2006)

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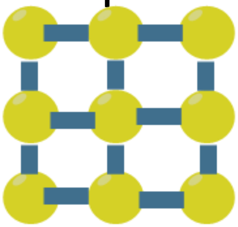
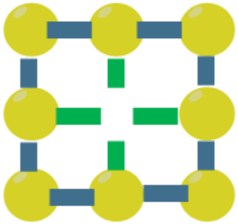


2. Creation of cavity



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- For solvation to happen, the solvent must make space for a solute. This is both entropically (less configurations) and enthalpically (less bonds) unfavorable for the solvent.

Chapter 3 of Anslyn and Dougherty, Modern Physical Organic Chemistry (2006)

# The *simplest* take on… Solvation

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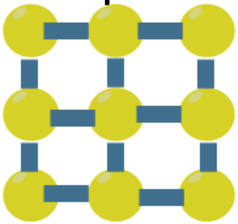
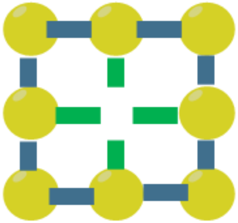
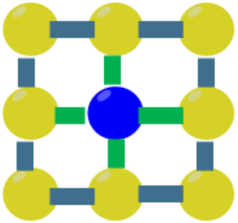


2. Creation of cavity



3. Insertion of solute



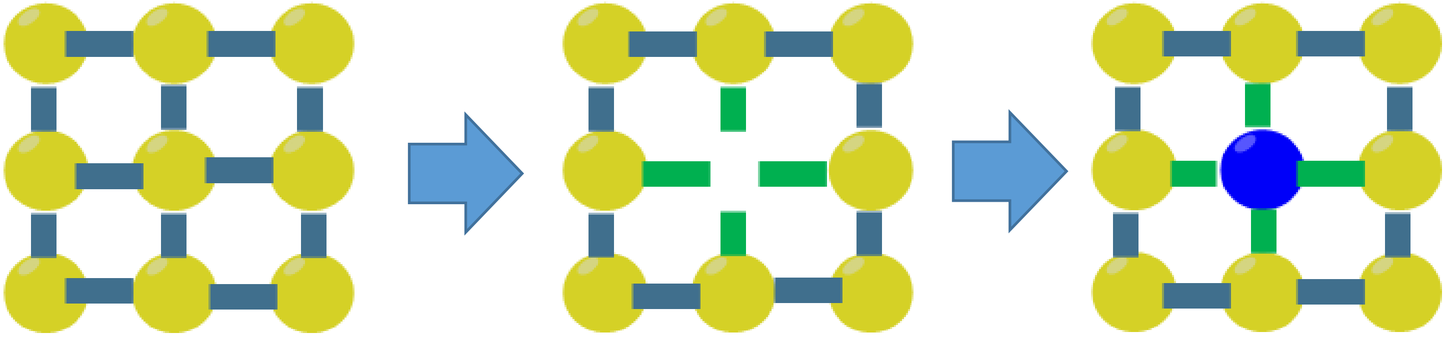
- Liquids have rapidly changing molecular order with high cohesive interactions between molecules. Enthalpy (binding interactions between molecules) and entropy (large because molecules can move) determine the free energy and hence the system's structure.
- For solvation to happen, the solvent must make space for a solute. This is both entropically (less configurations) and enthalpically (less bonds) unfavorable for the solvent.
- Enthalpy cost for the solute: it has to dissolve, leading to fewer solute-solute interactions. When the solute occupies the cavity: enthalpically favorable solvent-solute interactions; favorable entropy of mixing (solute crystal and pure solvent taken separately are more ordered than the co-mixture of solvent and solute).

Chapter 3 of Anslyn and Dougherty, Modern Physical Organic Chemistry (2006)

# The *simplest* take on… Solvation

- The enthalpy and entropy of solvent-solute interactions give the energy gained upon solvation. All these contributors taken together constitute the **solvation energy**.

- A solvation process involves many steps (not necessarily in this order)



1. Pure liquid solvent 2. Creation of cavity 3. Insertion of solute

https://en.wikipedia.org/wiki/Solvation

Chapter 3 of Anslyn and Dougherty, Modern Physical Organic Chemistry (2006)

Angew. Chem. Int. Ed. **2019**, 58, 3000–3013

# FTIR measurements on aqueous salt solutions: ions have short-range effects on water

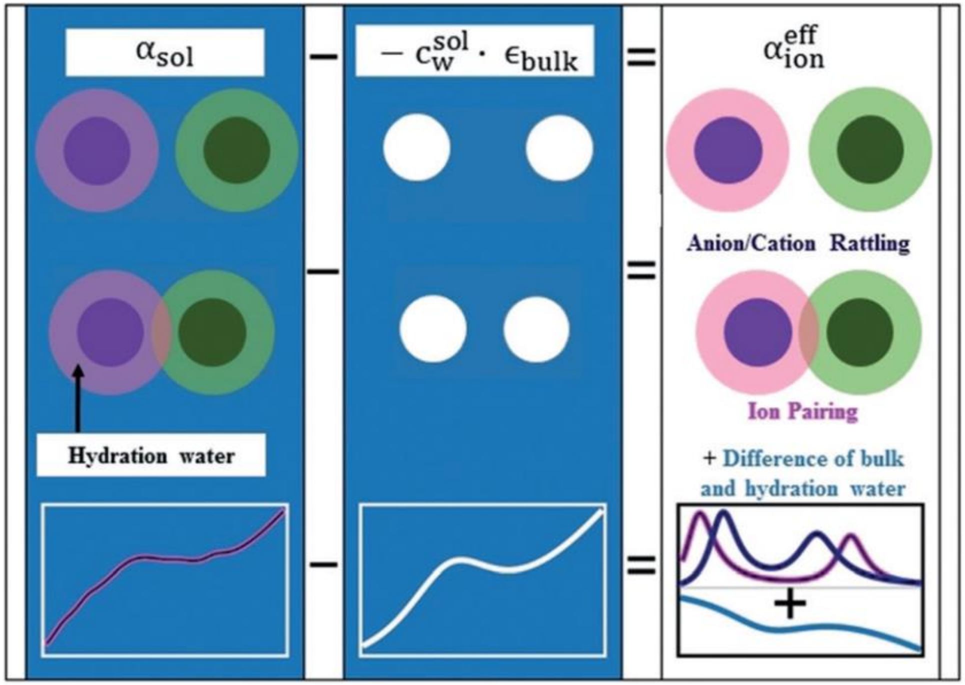


***Figure 2.*** Schematic representation of ion hydration. Left: bulk-like water (blue), water in the vicinity of ions (purple and dark green), and hydration water (pink and light green) contribute to the total absorption of the solution. Subtraction of a concentration-weighted bulk-water spectrum (middle) yields the effective absorption of the solvated ion or ion pair (right). The resulting spectrum is a superposition of a negative part arising from the difference in the absorption between hydration and bulk water and the (positive) absorption arising from the hydrated anion/cation or hydrated ion pair.

# FTIR measurements on aqueous salt solutions: ions have short-range effects on water

- Over a century ago Hofmeister observed that salts can precipitate (salt out) or dissolve/denature (salt in) egg white and serum proteins depending on the constituent ions. It was assumed that the Hofmeister series reflects the long-range structuring of water by specific ions (“structure makers vs. breakers”).

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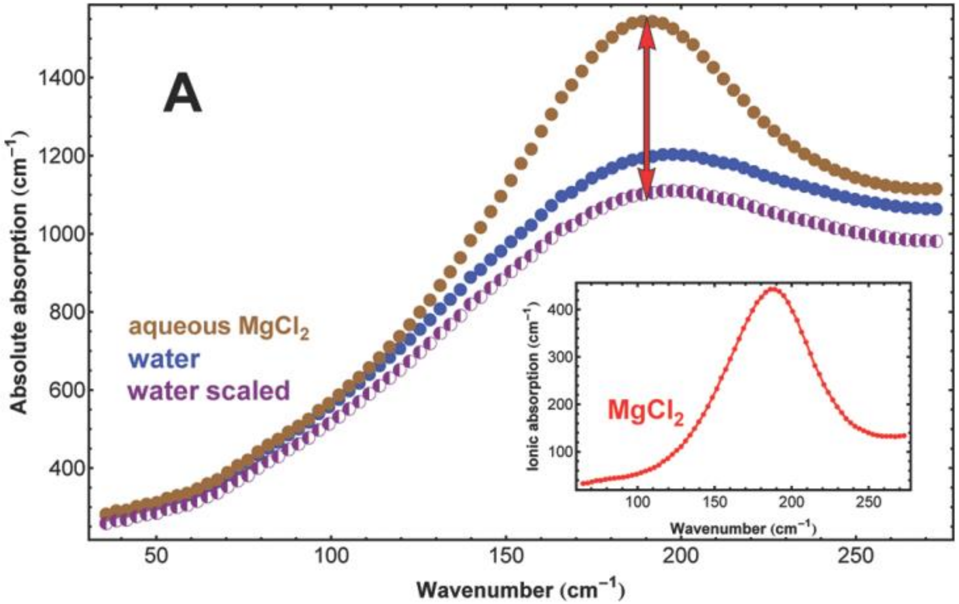
- FTIR shows that anions and cations have specific absorption modes



*J. Am. Chem.Soc.* 2012, 134, 1030–1035

# FTIR measurements on aqueous salt solutions: ions have short-range effects on water

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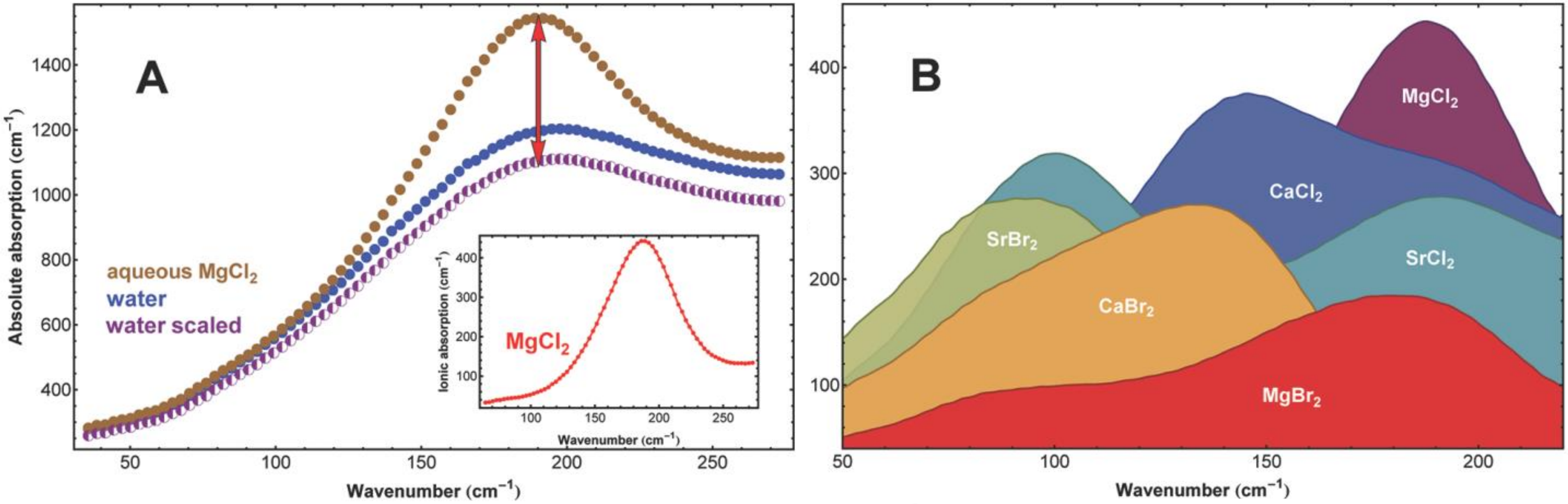

*J. Am. Chem.Soc.* 2012, 134, 1030–1035

# FTIR measurements on aqueous salt solutions: ions have short-range effects on water

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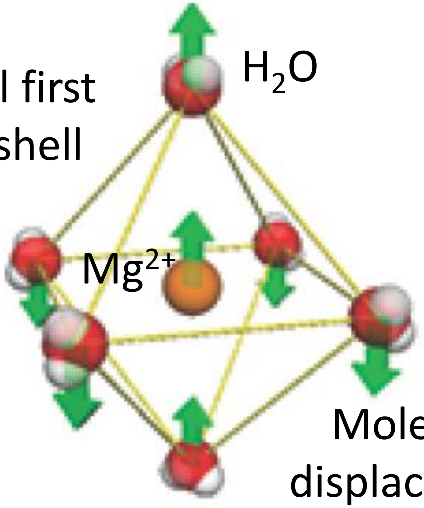
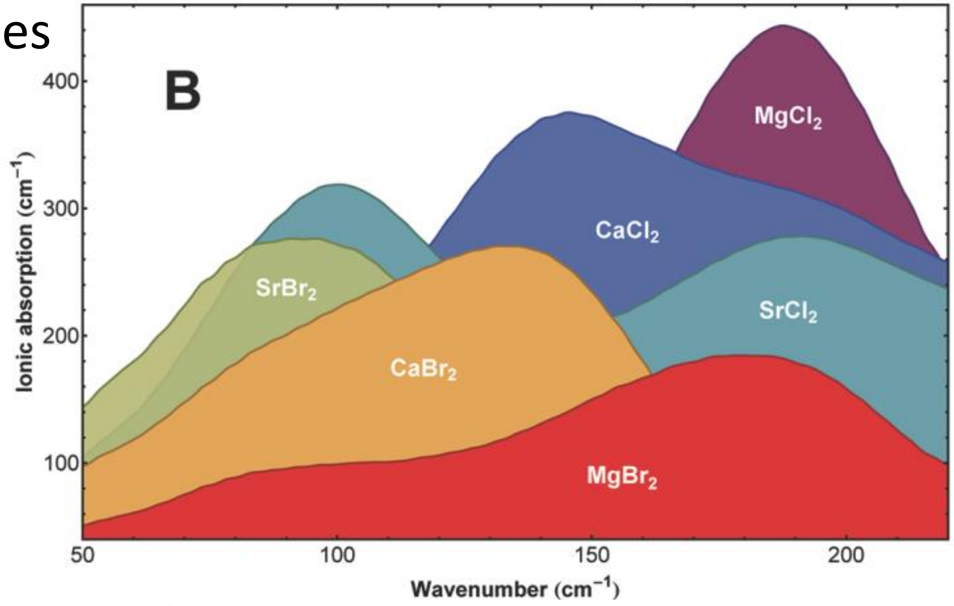
- FTIR shows that anions and cations have specific absorption modes, and MD calculations explain them as the “rattling” of the ions in the hydration “cage” of water molecules

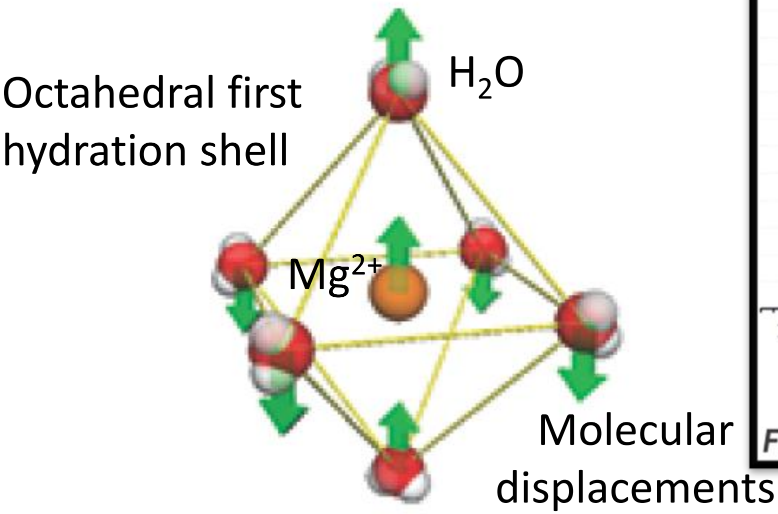




*J. Am. Chem.Soc.* 2012, 134, 1030−1035

# FTIR measurements on aqueous salt solutions: ions have short-range effects on water

- Over a century ago Hofmeister observed that salts can precipitate (salt out) or dissolve/denature (salt in) egg white and serum proteins depending on the constituent ions. It was assumed that the Hofmeister series reflects the long-range structuring of water by specific ions (“structure makers vs. breakers”).
- **Also possible to quantify the “size” of the hydration layers for different ions (how many water molecules are affected)**



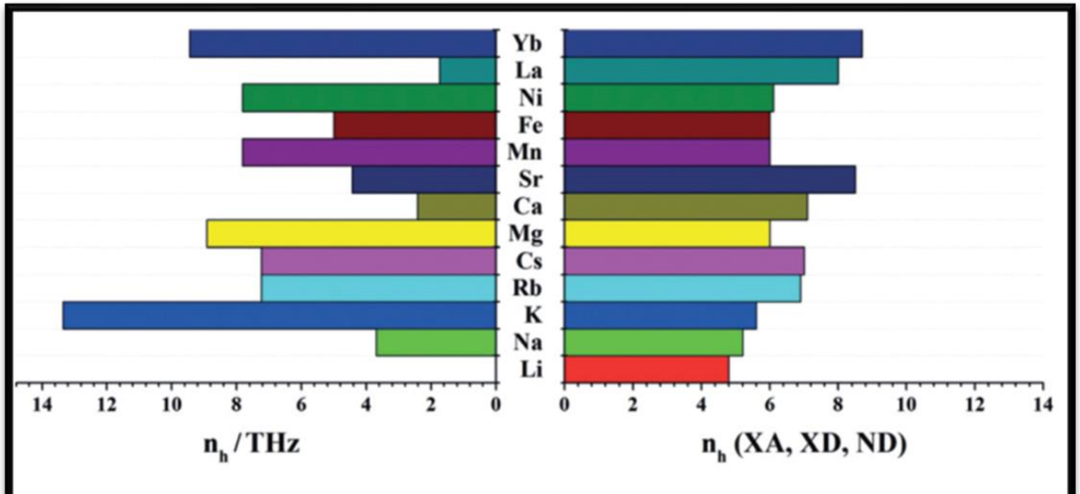
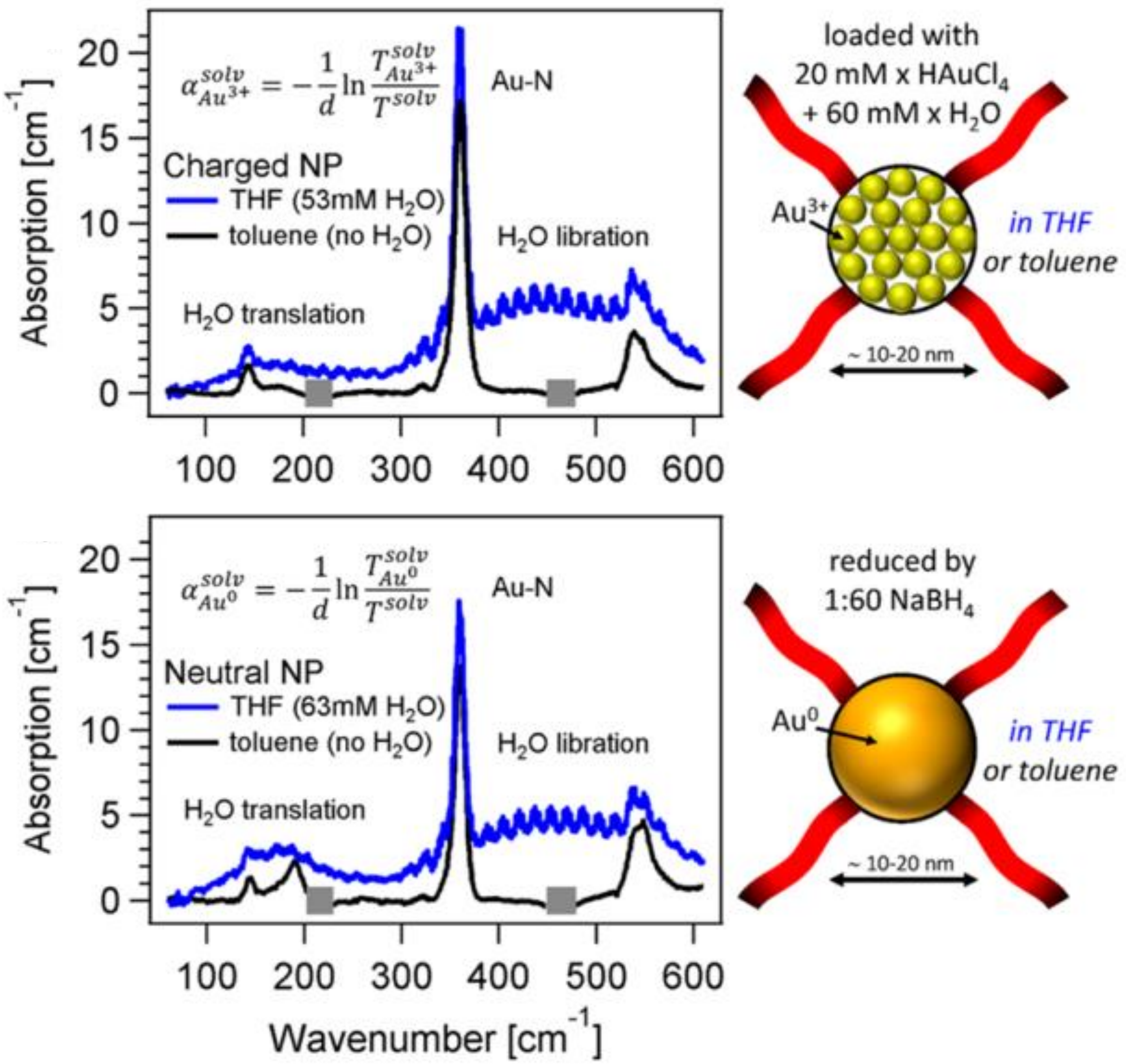


*Figure 9.* Hydration water numbers for different chloride salts as

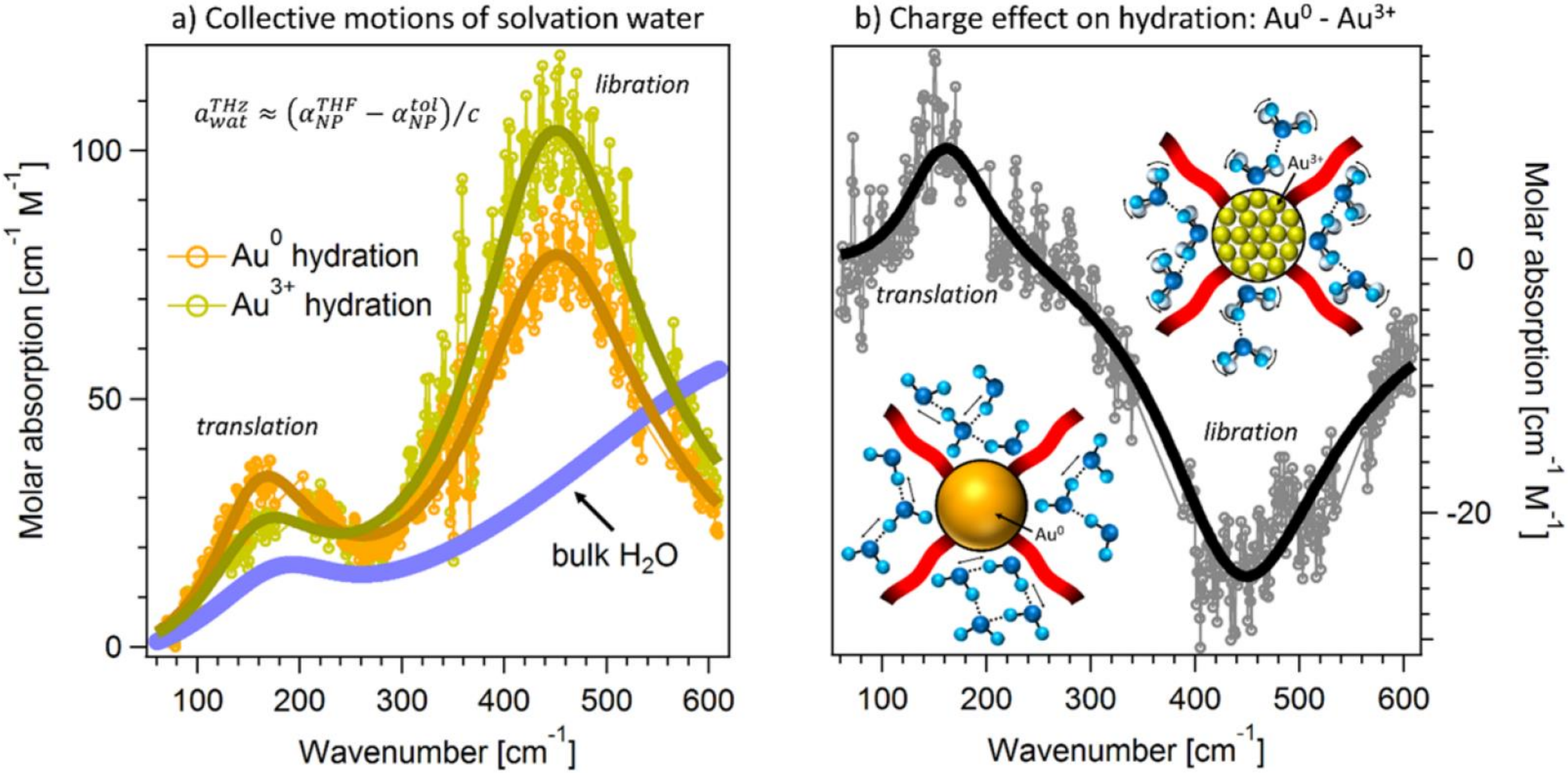
*Angew. Chem. Int. Ed.* **2019**, 58, 3000 – 3013

# FTIR measurements on gold nanoparticles



*J. Phys. Chem. B* 2019, 123, 6521−6528

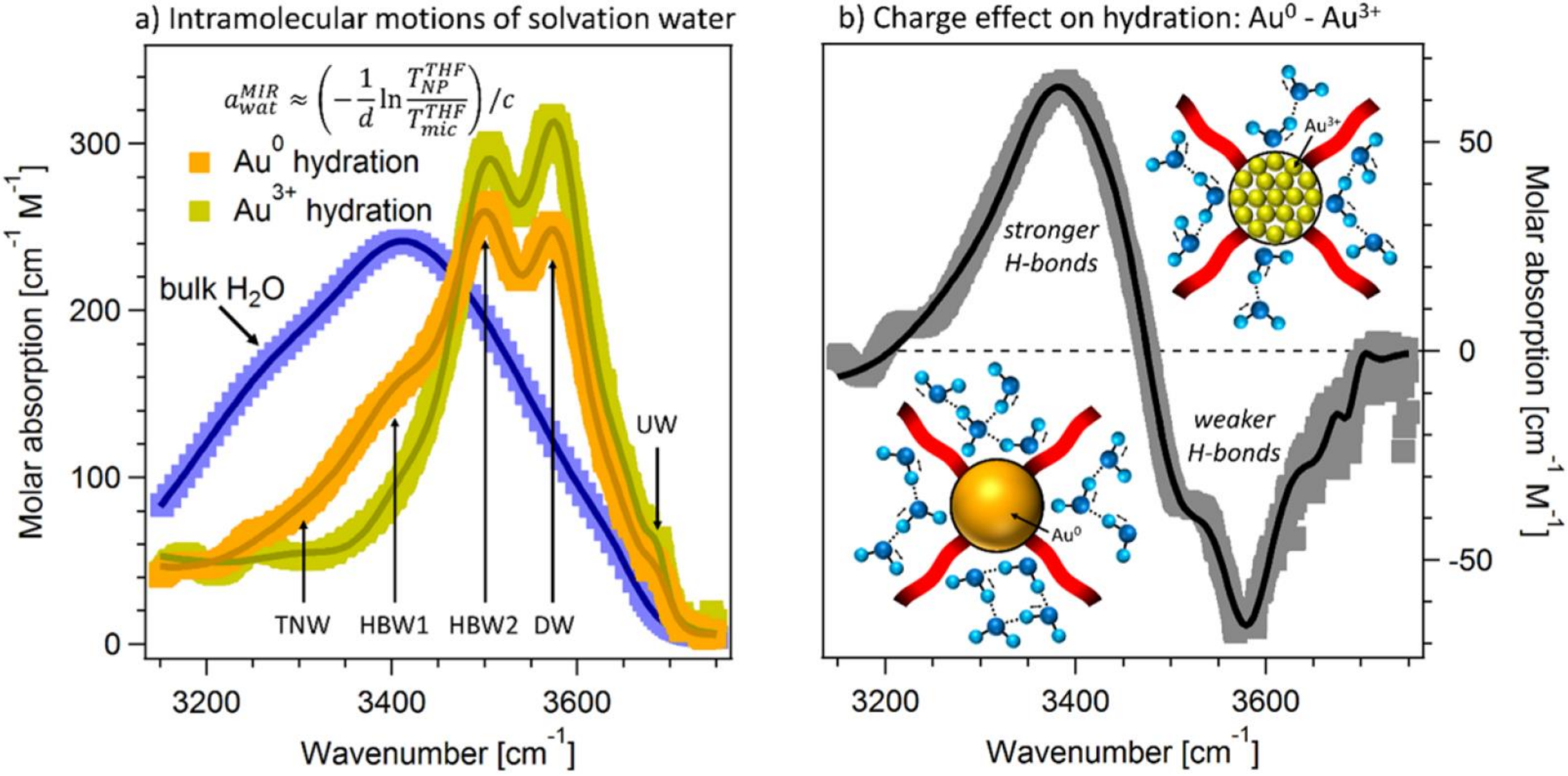
# FTIR measurements on gold nanoparticles



- The libration is enhanced by positive Au NP (suppressed by negative charge)
- The stretch is suppressed by positive Au NP (enhanced by negative charge)

*J. Phys. Chem. B* 2019, 123, 6521–6528

# FTIR measurements on gold nanoparticles



- The OH stretch blue-shifts with positive Au NP / weaker H-bonds
- (The OH stretch red-shifts with negative Au NP / stronger H-bonds)

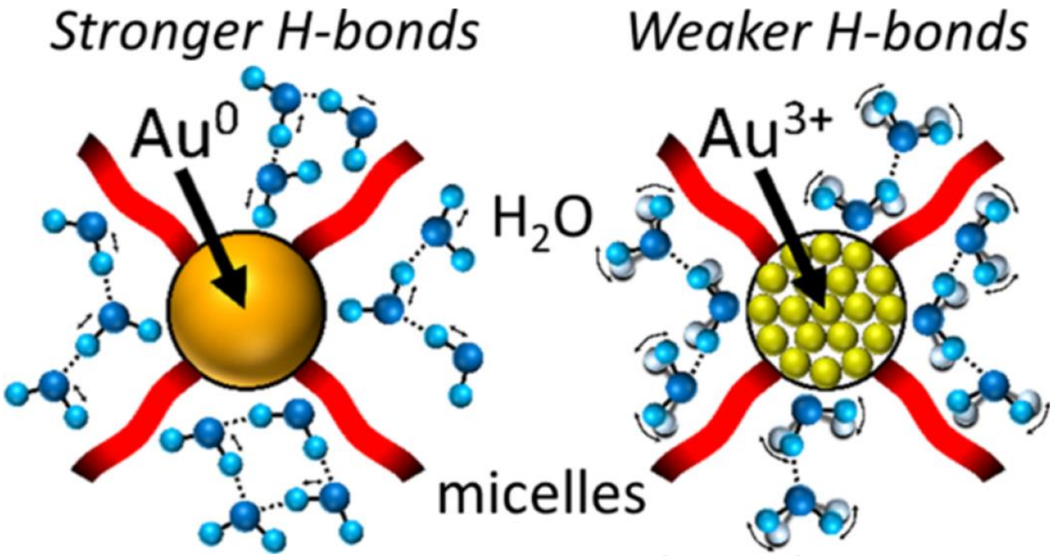
*J. Phys. Chem. B* 2019, 123, 6521–6528

# FTIR measurements on gold nanoparticles

When we add a positive charge, e.g., $Au^{3+}$ vs. $Au^0$:

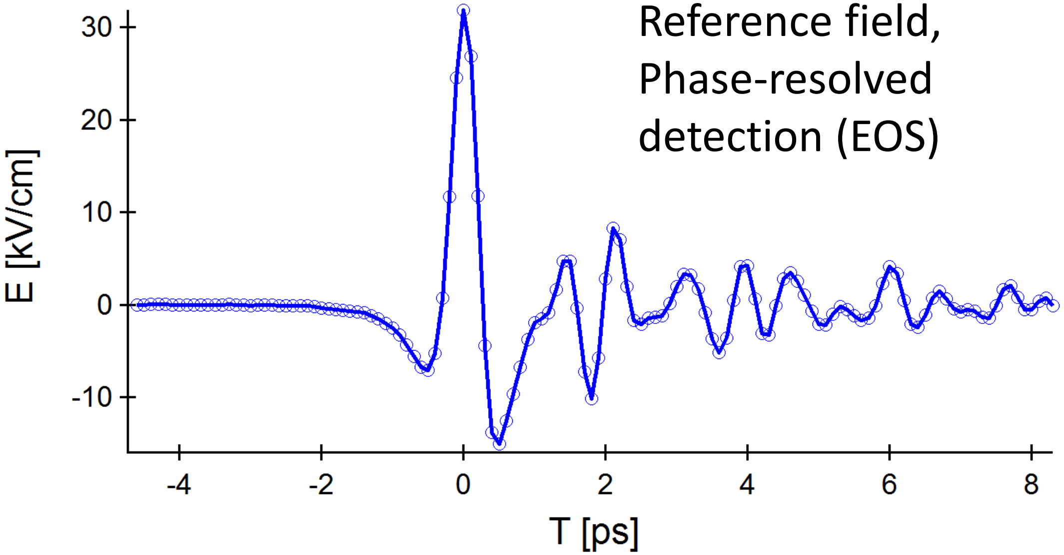
- In the O−H stretch (MIR) region, we observed an overall blue shift for the hydration water around NPs.
- Both intermolecular modes in the THz range are found to be red-shifted.

➢These observations indicate that the intermolecular hydrogen bond is weakened for all gold NPs (more so in Au3+) when compared to bulk water

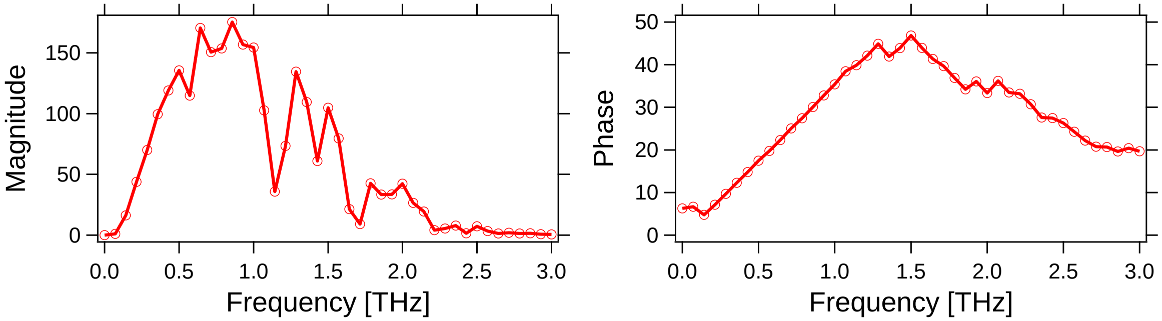


*J. Phys. Chem. B* 2019, 123, 6521−6528

# How good is THz-TDS to measure liquid water?



Reference field,
Phase-resolved
detection (EOS)



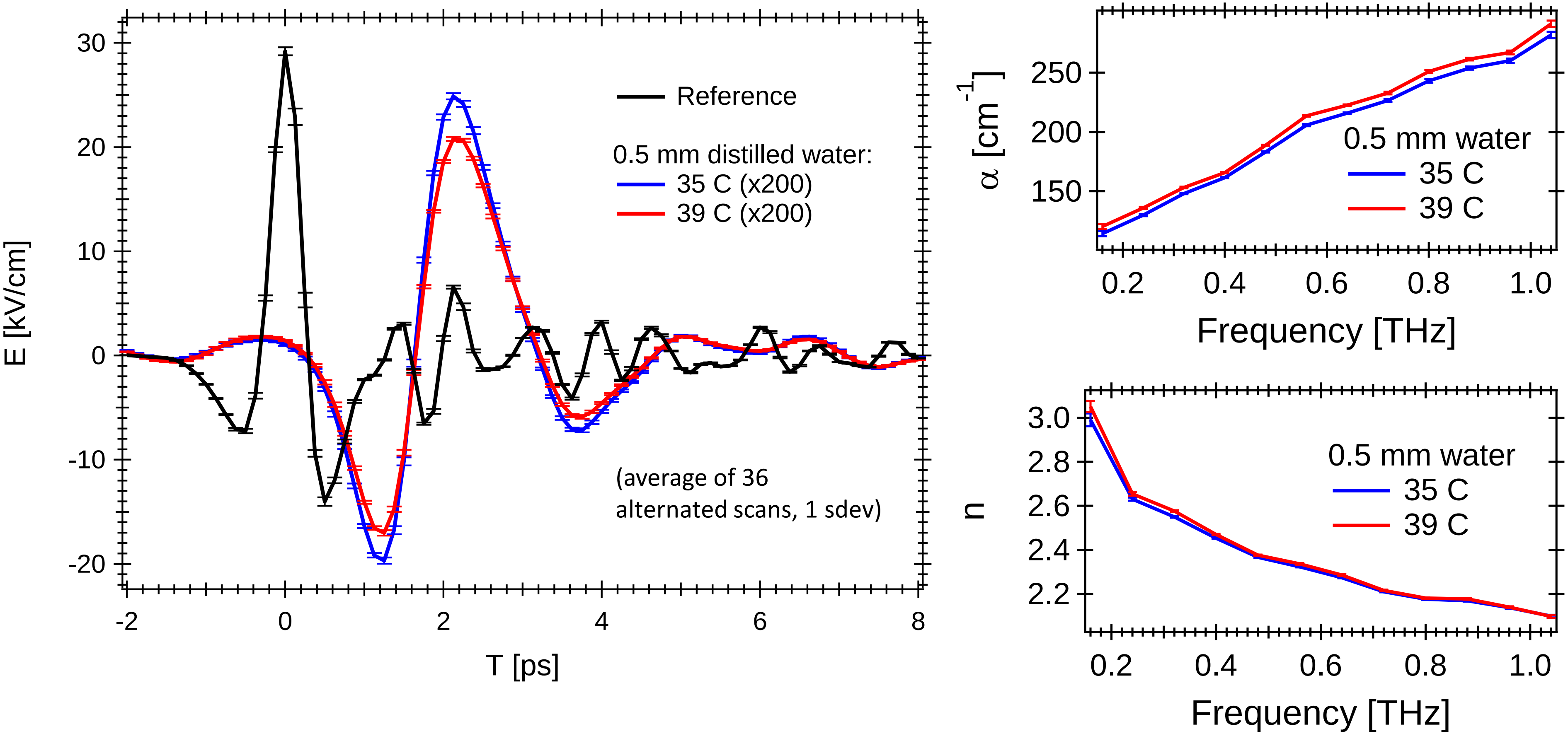
- Source: amplified Ti:Sa, 0.4 mJ/pulse, 790 nm, 1 kHz, 100 fs
- “tilted-front” OR generation: 12x12x12 mm MgO:sLN 62deg
- EOS detection: 0.5 mm thick ZnTe <001> (Eksma)
- Energy conversion eff. $\eta \sim 2 \cdot 10^{-4}$; resulting in a peak electric field of ~30 kV/cm

- **Measurements are performed by detecting the field transmitted by a reference and by the sample, then FT:**
  - **The magnitude ratio ~ $\alpha$**
  - **The phase difference ~ n**

**Optics Letters 41, 5801 (2016)**

# How good is THz-TDS to measure liquid water?

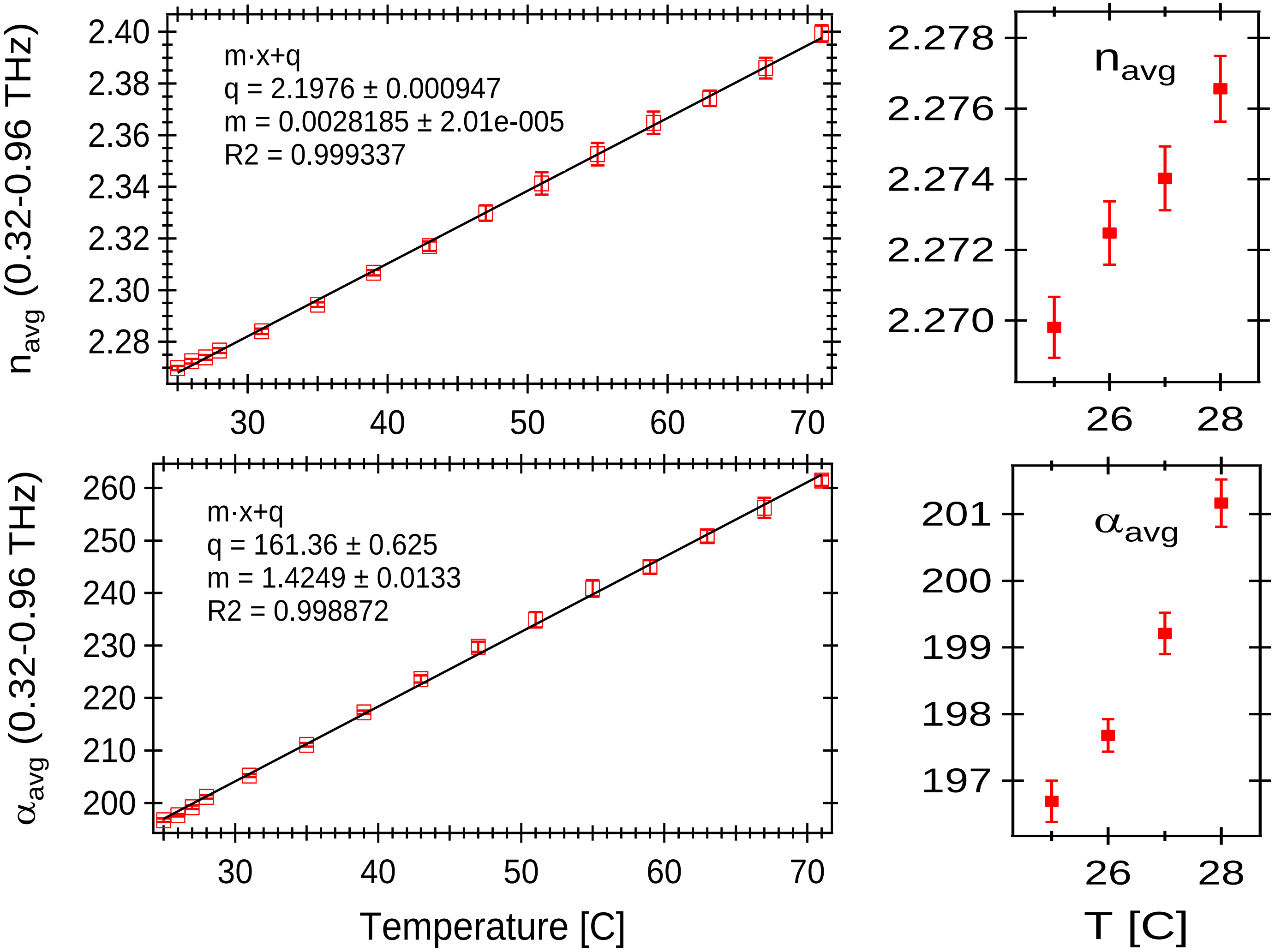
**Transmission of 0.5 mm thick water (10x penetration depth!) vs. temperature**



(average of 36 alternated scans, 1 sdev)

**Optics Letters 41, 5801 (2016)**

# How good is THz-TDS to measure liquid water?



THz-TDS can measure $\chi^{(1)}$ from water with high resolution:

$\Delta n \sim 0.001$

$\Delta\alpha \sim 0.2\ \mathrm{cm}^{-1}$

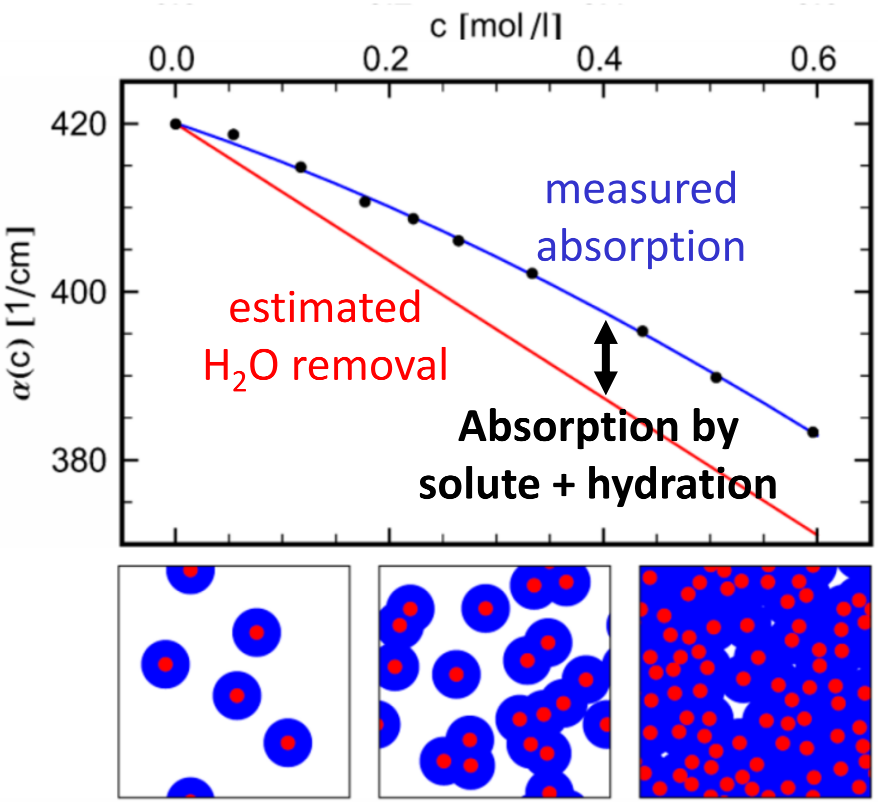
THz-thermometer:

- Non-contact
- Time-resolved
- ≤0.5 C resolution

**Optics Letters 41, 5801 (2016)**

# THz-TDS of water solution with biomolecules

- Average absorption coefficient of an aqueous solution with an added concentration **c** of biomolecules



- Water strongly absorbs THz
- Typically, any solute will absorb less
- When the concentration of the solute increases, the THz absorption decreases
- The "water removal effect" is calculated by assuming that an amount of water equal to the amount of solute is removed from the solution (red line)
- The difference between the measurement (blue) and the water removal (red) is the **absorption by solute + hydration layer**.

*J. Am. Chem. Soc.* 2014, 136, 12800–12807

# Proteins can have long-range effects on water

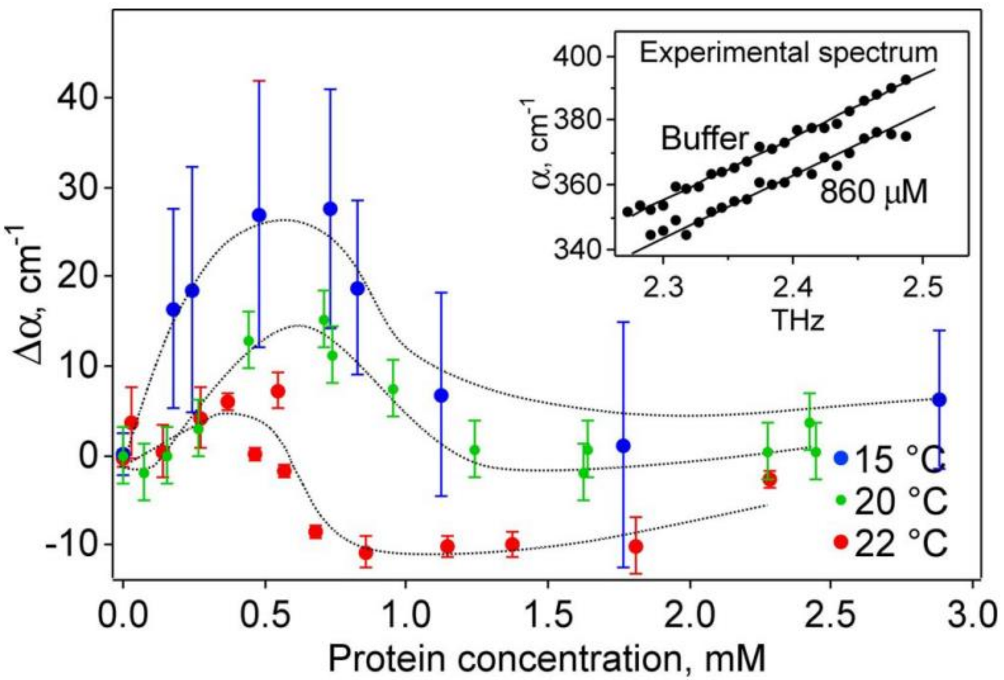


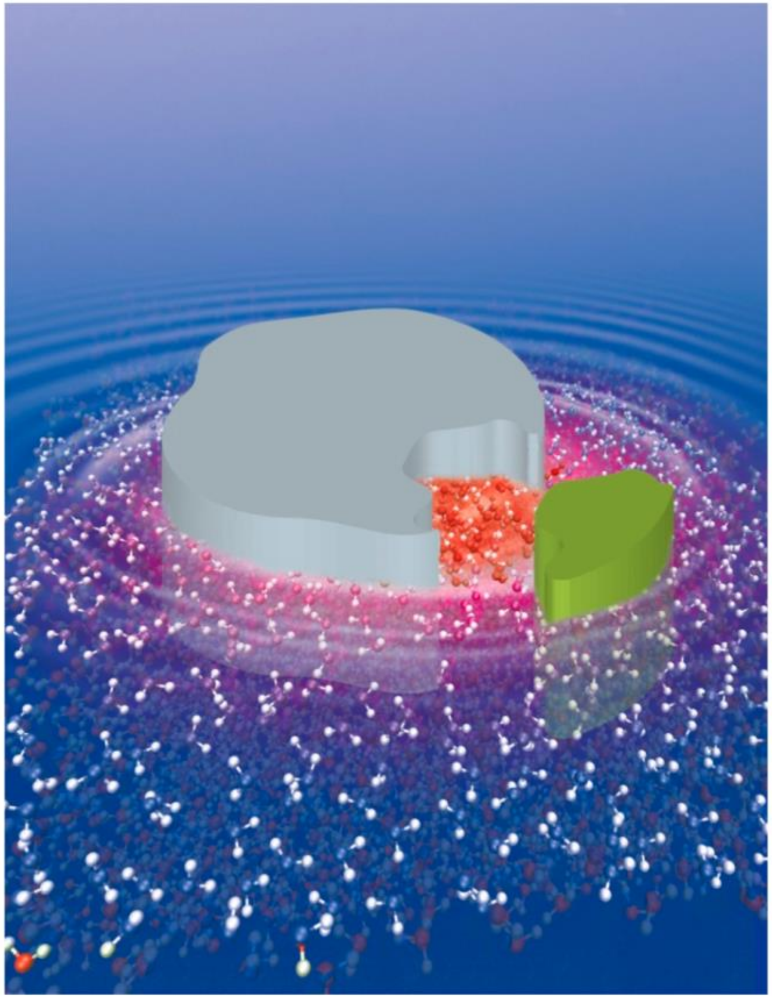
**Fig. 1.** Difference in the THz absorption coefficient at 2.25 THz relative to bulk water plotted against concentration to 3 mM at 15°C, 20°C, and 22°C (more extensive averaging was done at 22°C because of the slightly smaller effect). The absorbance depends nonlinearly on concentration in this region.

- *"We observe an unexpected trend in the measured terahertz absorbance of the five helix bundle protein* $\lambda^*_{6-85}$ *as a function of the protein-to-water molar ratio."*
- *"The trend can be explained by overlapping solvation layers around the proteins."* Theory and experiment suggest an influence on the correlated water network motion beyond 20 Å, greater than the pure structural correlation length usually observed (compare with the diameter of 1x $H_2O$, ~3 Å).

PNAS | **December 26, 2007** | vol. 104 | no. 52 | **20749–20752**

# Protein hydration and molecular recognition

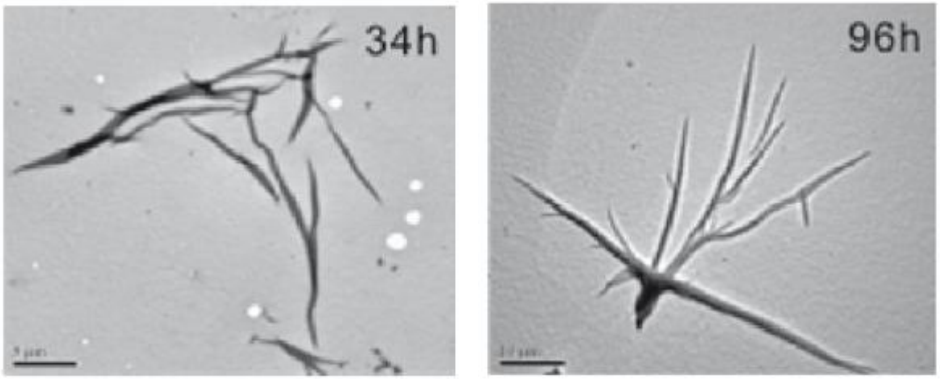
- Example of the correlation between protein function and hydration dynamics: antifreeze proteins (AFPs).
- AFPs enable the survival of organisms in sub-freezing environments by binding to nano-sized ice crystals and preventing the growth: tough recognition problems
- By combined THz spectroscopy and MD simulations, long-range hydration (20 A) dynamics seems to contribute to the recognition
- Hydration dynamics in AFPs have a gradient of retardation toward the "ice binding plane"
- This gradient, which we will call a " hydration funnel ", seems to assist molecular recognition: an entropically favorable docking of a nano-sized ice



*J. Am. Chem. Soc.* 2014, 136, 12800−12807

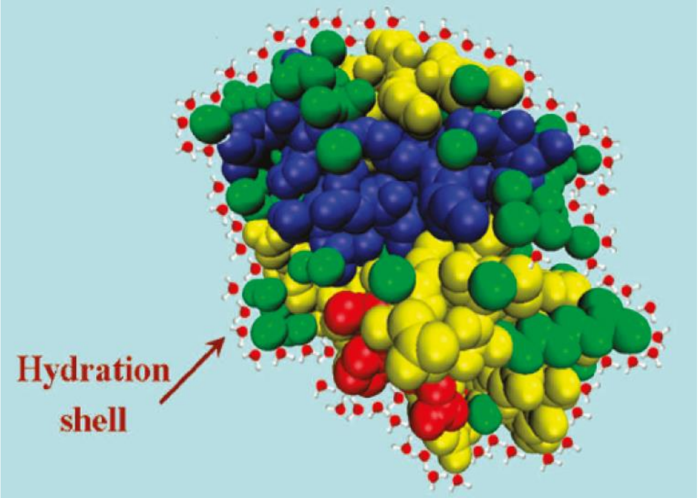
# THz-TDS can distinguish aggregation

- We studied homogeneous aqueous solutions of native human lysozyme and lysozyme fibrils in water



TEM of insulin fibrils, 5 $\mu$m scale

*R. Liu et al./ Biochemical and Biophysical Research Communications* 391 (2010) 862–867



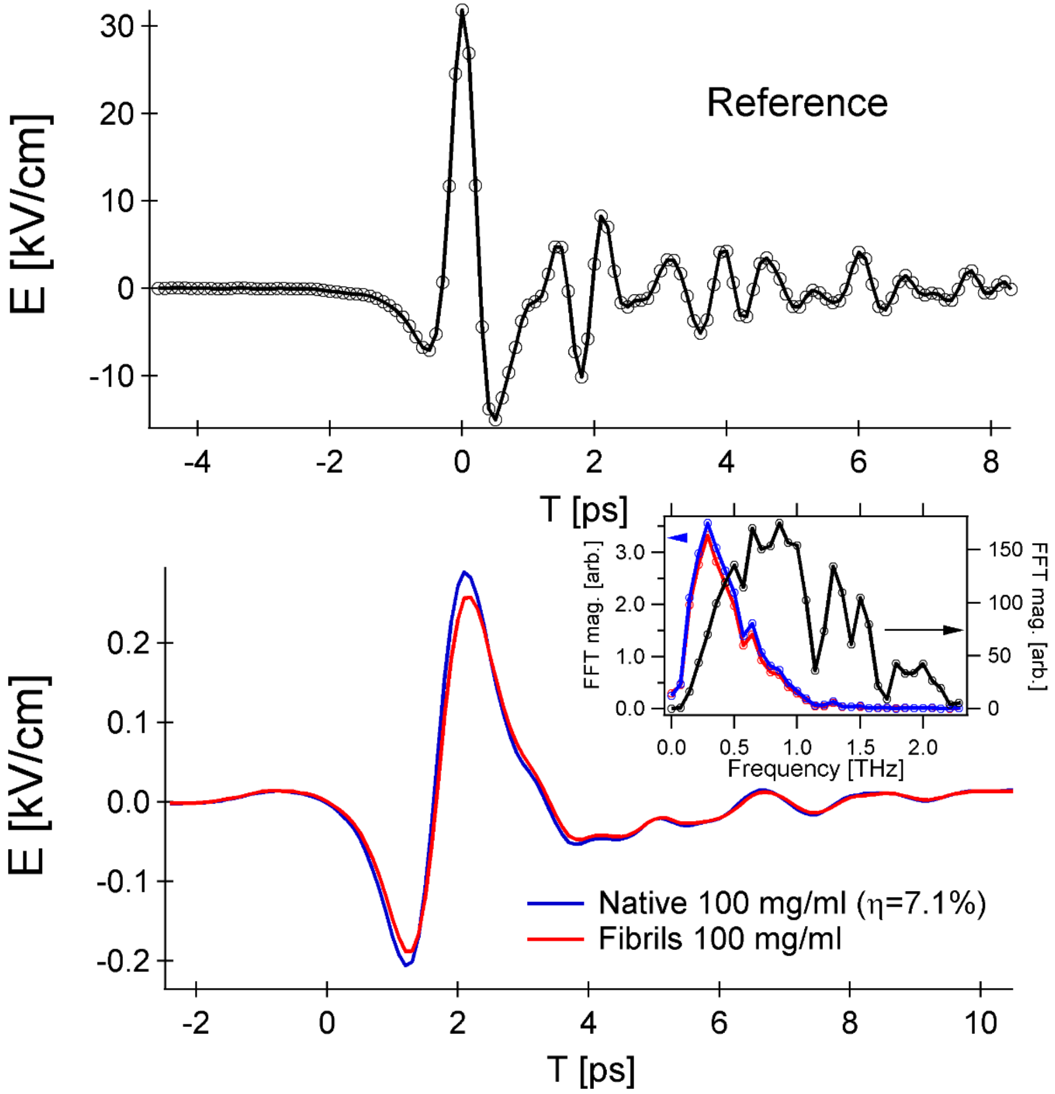
HEW lysozyme, size ~2 nm

*J. Am. Chem. Soc.* 2011, 133, 8942–8947

- Protein aggregation related to some diseases (Alzheimer, Type-II diabetes, …)

*J. Phys. Chem. B* **121**, 4810 (2017)

# Probing native and fibrils of human lysozyme

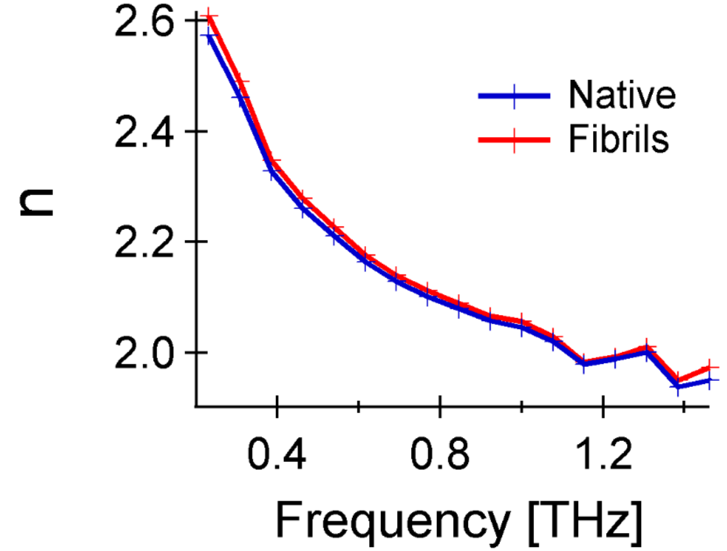


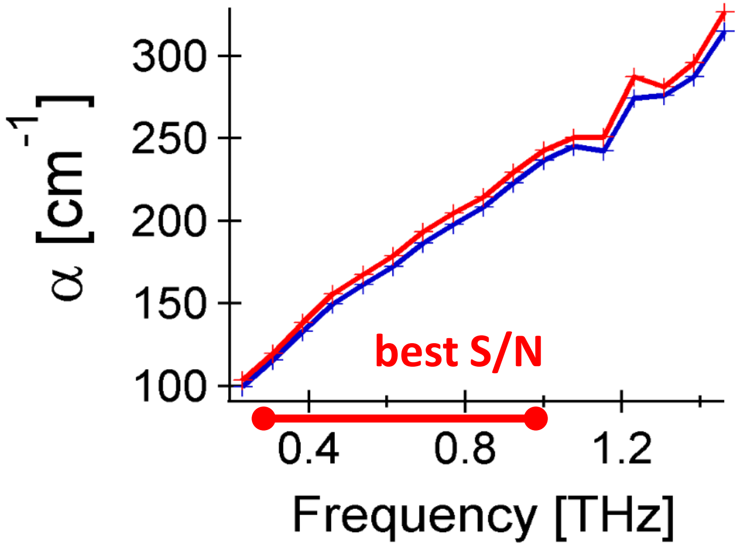
- First time > 10 kV/cm peak THz used to study bio-macromolecules in water

- Can measure >0.5 mm thick water-based samples:
  - sensitive to low concentrations
  - obtain full dielectric response

*J. Phys. Chem. B* **121**, 4810 (2017)

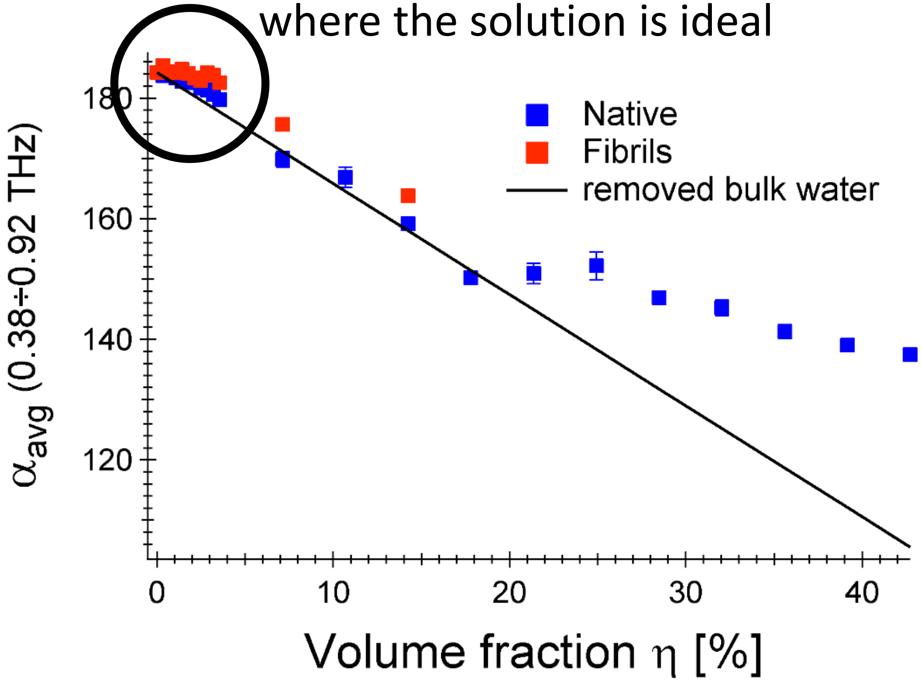
# Probing native and fibrils of human lysozyme





**best S/N**

Low concentrations (<50 mg/ml) where the solution is ideal



$0.356\%\ \eta = 5\ \mathrm{mg/ml}$

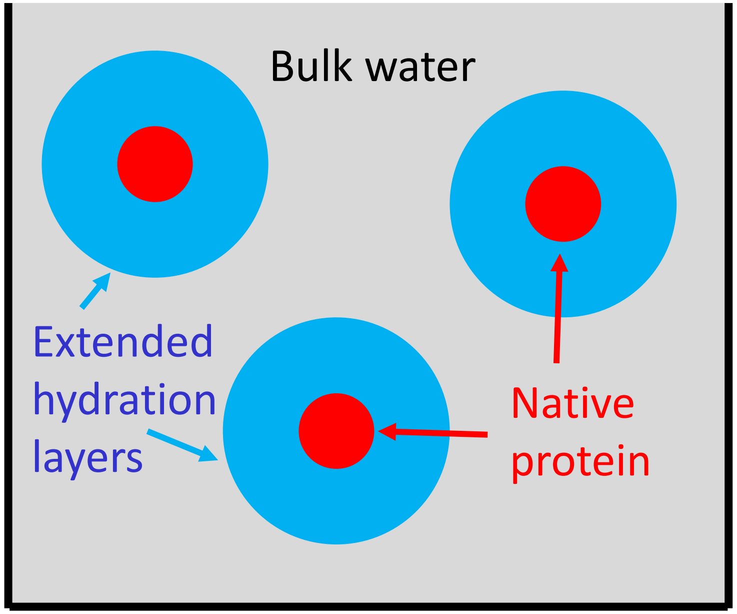
*W.J. Fredericks et al. / Journal of Crystal Growth 141 (1994) 183–192*

*J. Phys. Chem. B* **121**, 4810 (2017)

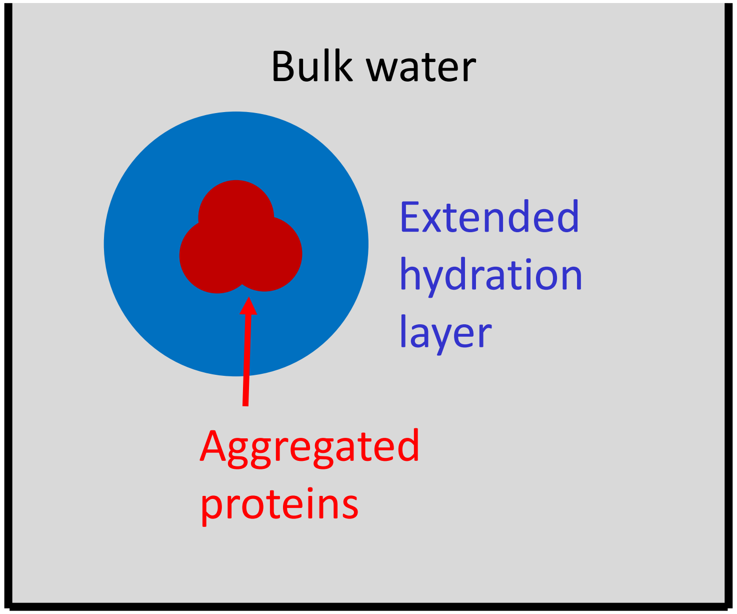
# What happens with fibrils?

Take two solutions containing the same amount of proteins, the first in native form, the latter with the same amount of proteins in aggregated fibrils

## Native



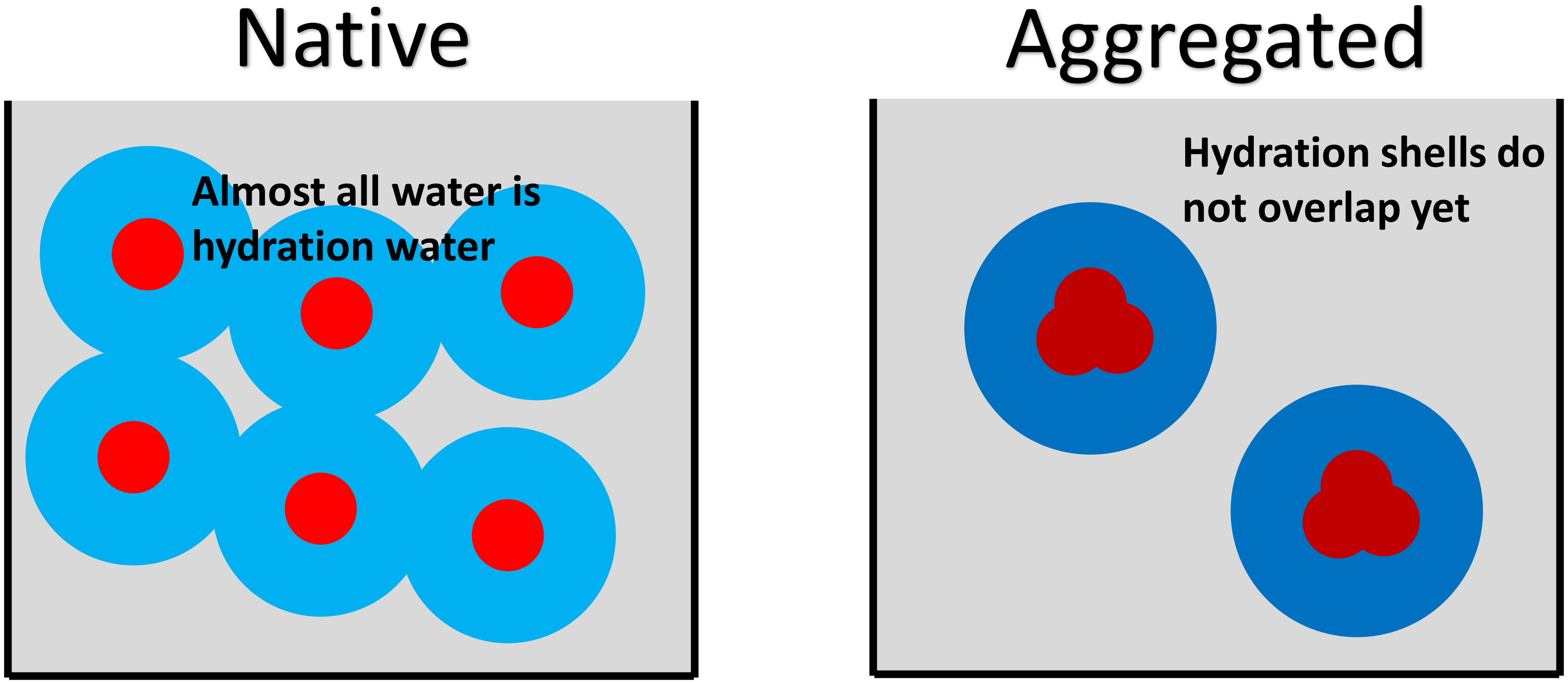
## Aggregated



*J. Phys. Chem. B* **121**, 4810 (2017)

# What happens with fibrils?

Take two solutions containing the same amount of proteins, the first in native form, the latter with the same amount of proteins in aggregated fibrils: **double the concentration**

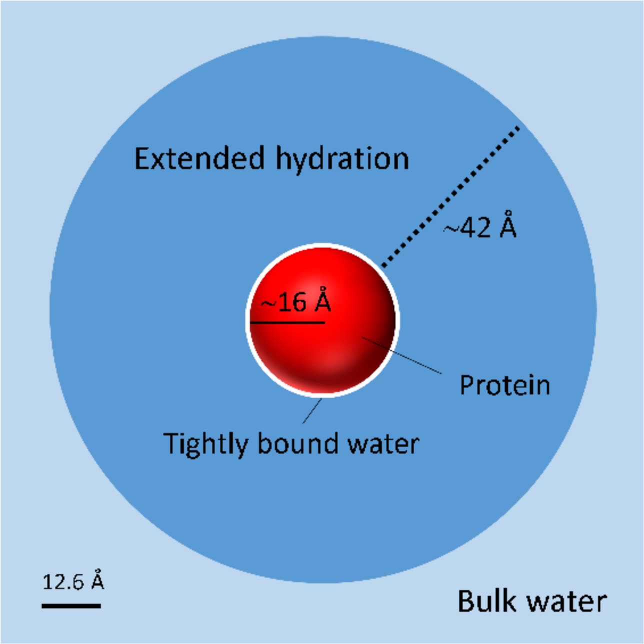


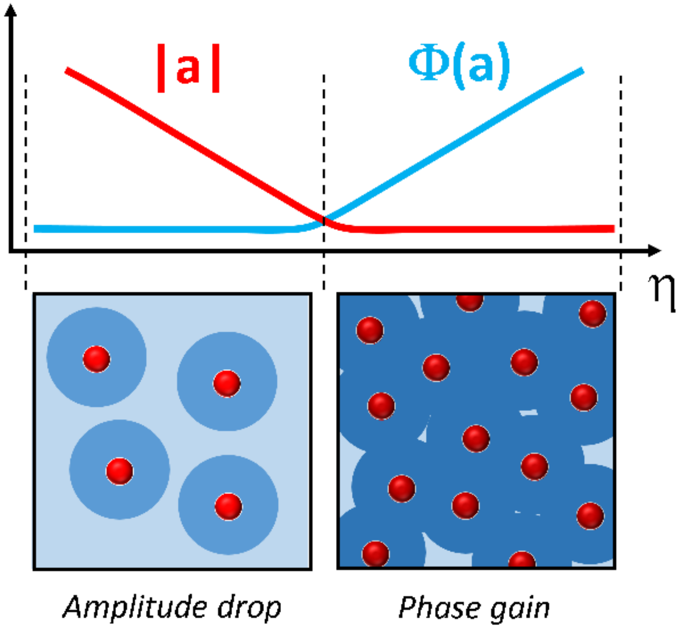
*J. Phys. Chem. B* **121**, 4810 (2017)

# Probing native and fibrils of human lysozyme

THz-TDS is able to look at the bulk-averaged dipole of a solute+hydration unit and:

1. Detect perturbations in the water network induced by proteins up to large distances from the protein surface (for native human lysozyme, up to ~42 Å away for a THz probe with frequency <1 THz)
2. Distinguish between solutions of proteins in different aggregation states





*J. Phys. Chem. B* **121**, 4810 (2017)

# Liquid-liquid phase separation

## The key role of solvent in condensation: Mapping water in liquid-liquid phase-separated FUS

Jonas Ahlers,[1] Ellen M. Adams,[1] Verian Bader,[2] Simone Pezzotti,[1] Konstanze F. Winklhofer,[2] Jörg Tatzelt,[3] and Martina Havenith[1,*]
[1]Department Physical Chemistry, Ruhr-University Bochum, Bochum, Germany; [2]Department Molecular Cell Biology and [3]Department Biochemistry of Neurodegenerative Diseases, Institute of Biochemistry and Pathobiochemistry, Ruhr-University Bochum, Bochum, Germany

“Membrane-less compartmentalization via phase separation in living cells has been linked to the formation of pathological protein aggregates found in neurodegenerative diseases”

“Two thermodynamic driving forces have been proposed: protein-protein and protein-water interactions (mostly enthalpic), as well as the release of preorganized hydration water into the bulk (mostly entropic)”

Biophysical Journal *120*, 1266–1275, April 6, 2021

# Liquid-liquid phase separation

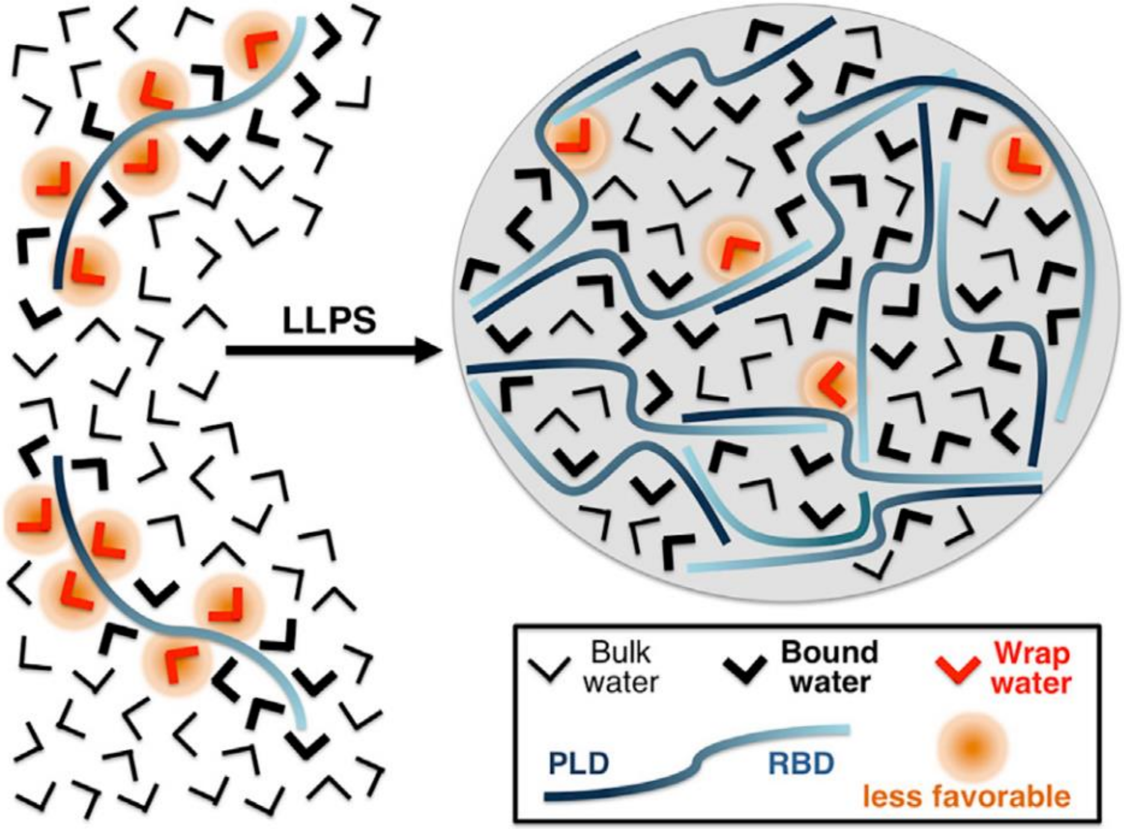


FIGURE 4 Scheme showing the proposed water-mediated contribution of FUS to LLPS. Formation of phase-separated droplets is supported by an increase in tetrahedral coordination of water molecules (bound water; *thick black*) and minimization of less favorable water interactions (wrap water; *red*). To see this figure in color, go online.

Biophysical Journal *120*, 1266–1275, April 6, 2021

# Terahertz and Water: outline

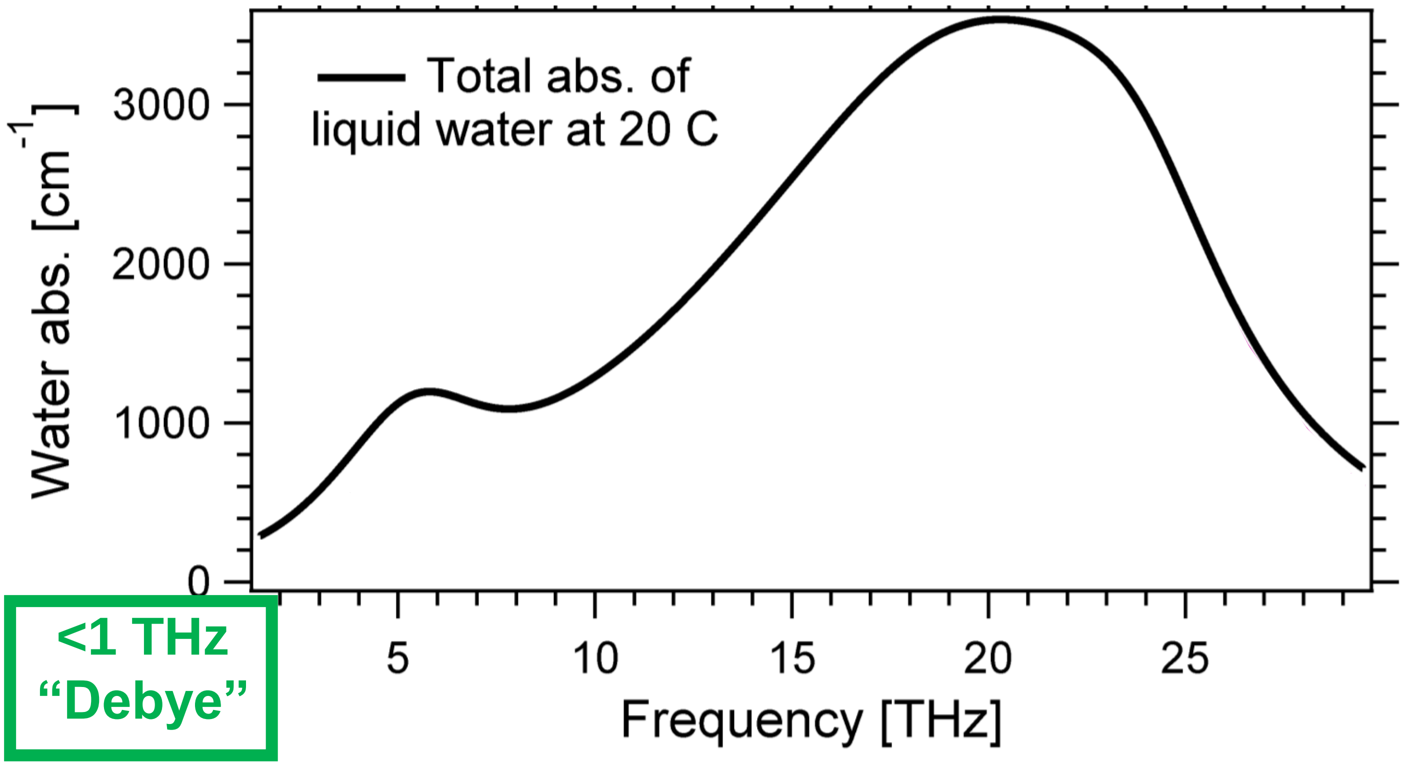
1. Terahertz time-domain spectroscopy
    1. Examples of non-linear responses
    2. Linear and non-linear spectroscopy
    3. Optical rectification (OR) and electro-optical sampling (EOS)
    4. Models to obtain the optical properties (Fresnel equations)

2. Water and solvation
    1. Infrared absorption modes of liquid water
    2. Introduction to solvation science
    3. Study ions in water with THz: rattling, hydration layers
    4. Gold nanoparticles
    5. Long-range protein effects on water
    6. **Non-linear terahertz response of water**

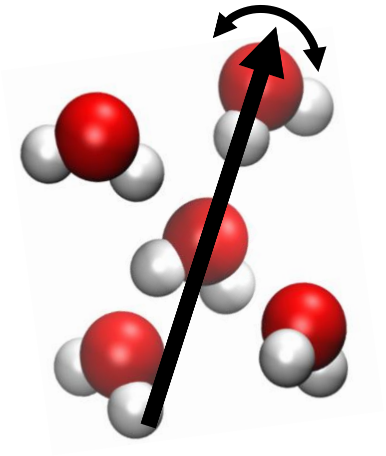
# Liquid water is “black” in the THz range

- THz radiation probes *intermolecular* water modes
- Water strongly absorbs THz: sensitive spectroscopic probe

➢ **How do microwaves heat water?**

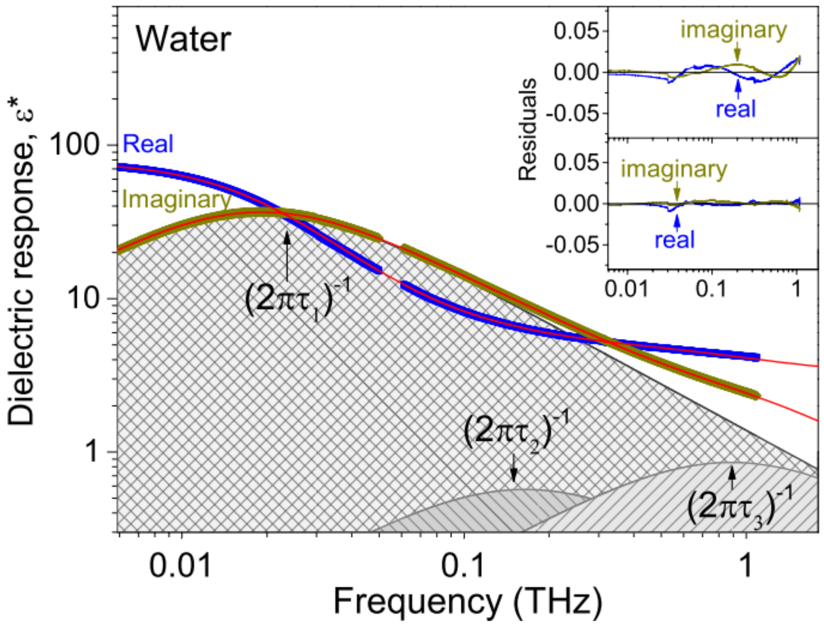


**<1 THz**
**“Debye”**



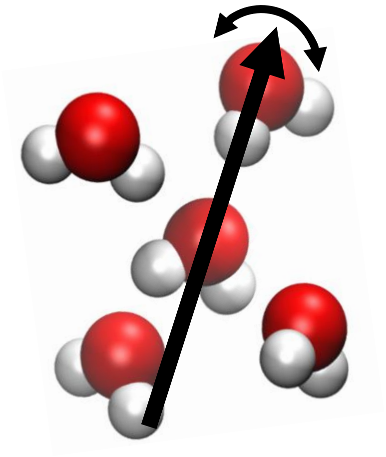
**Debated**, see, e.g., Hölzl *et al.*, Phys. Chem. Chem. Phys. 23, 20875, 2021

# How do microwaves heat water?

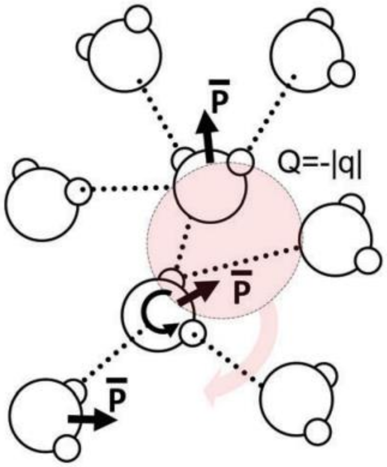


Vinh *et al*., J. Chem. Phys. 142, 164502, 2015

Novelli *et al*., Materials 13, 1311, 2020



Popov *et al*., Phys. Chem. Chem. Phys. 18, 13941, 2016

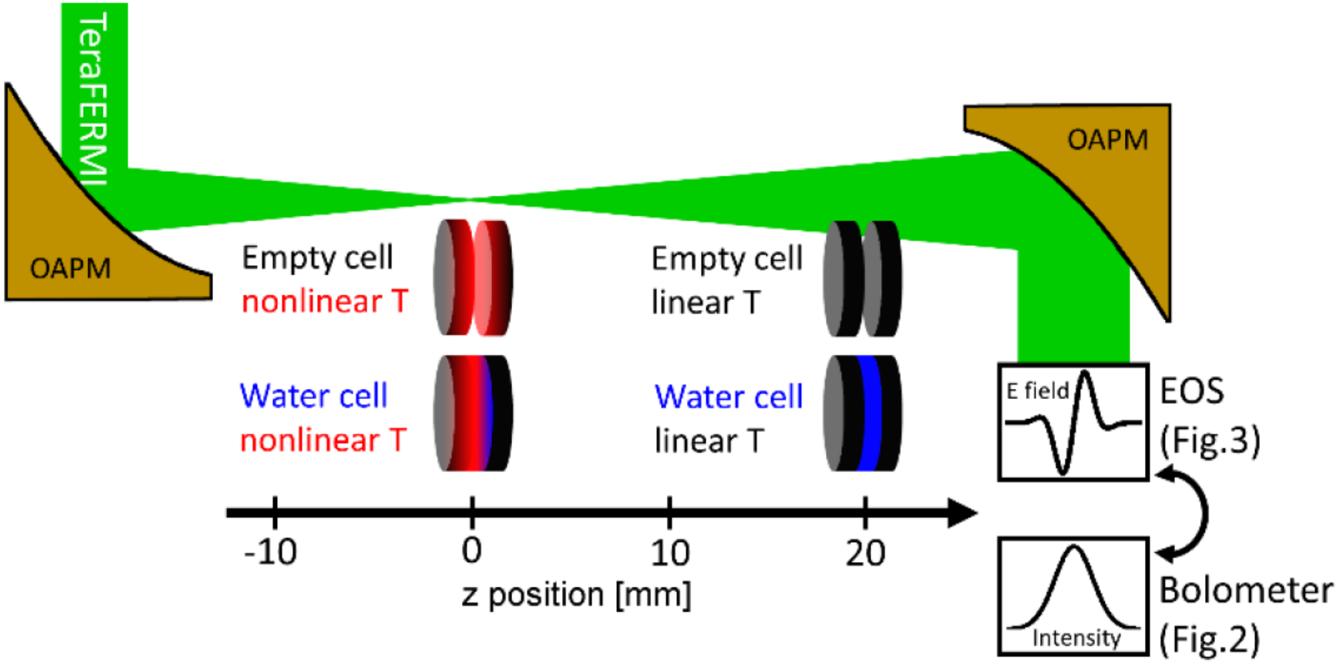


“no evidence for a major impact of cage dynamics or local-diffusive motion”

Hölzl *et al*., Phys. Chem. Chem. Phys. 23, 20875, 2021

# The simplest nonlinear experiment

- At 1 THz we have intense THz sources
- Measure transmission vs. position w.r.t. focus: Z-scan

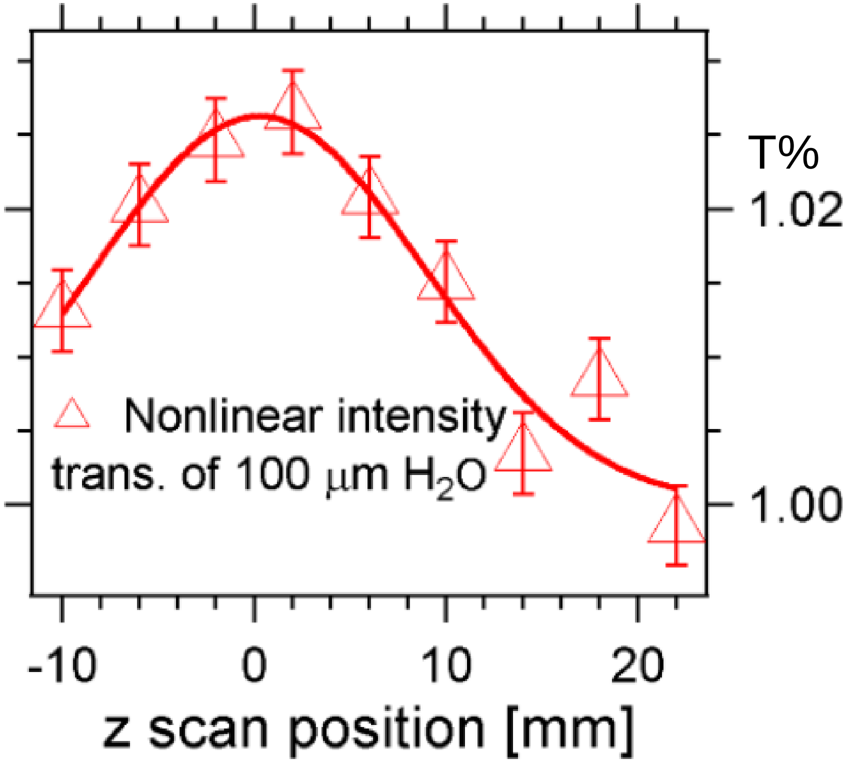


Away from focus:
Low peak power,
Linear optical
functions ($\alpha$, $n$)

Close to focus:
High peak power,
Nonlinear optical
effects ($\alpha^{NL}$, $n^{NL}$)

M. Sheik-Bahae *et al*., IEEE Journal of Quantum Electronics 26, 760, 1990

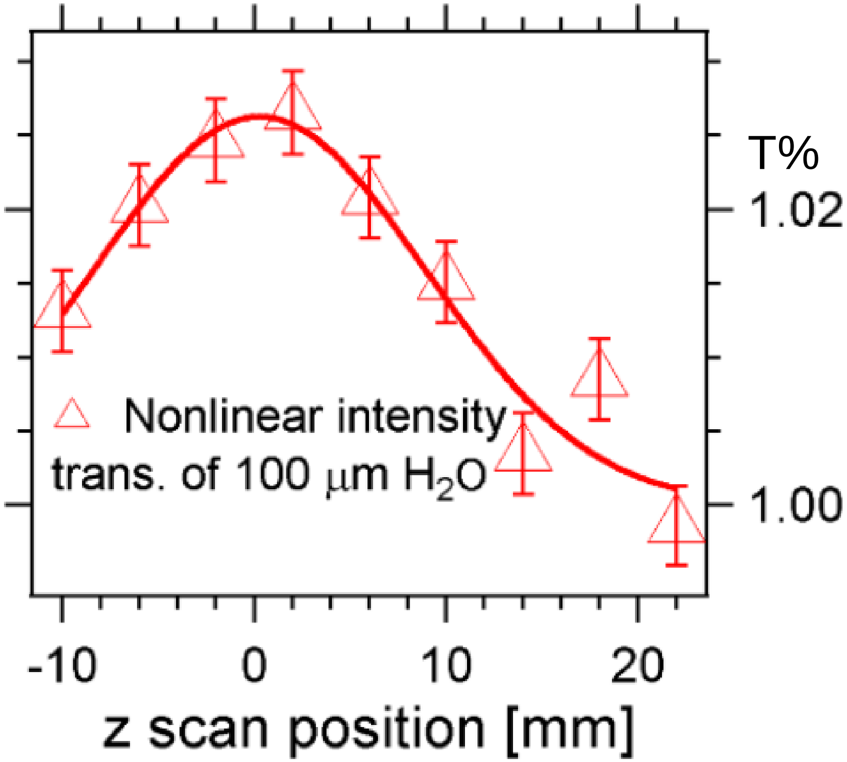
# Intensity detector



$$\alpha(\mathrm{P}) = \alpha + \alpha^{\mathrm{NL}} \times \mathrm{P}$$

$$\alpha^{\mathrm{NL}}_{\mathrm{wat}} = -87 \pm 27\ \mathrm{cm/GW}$$

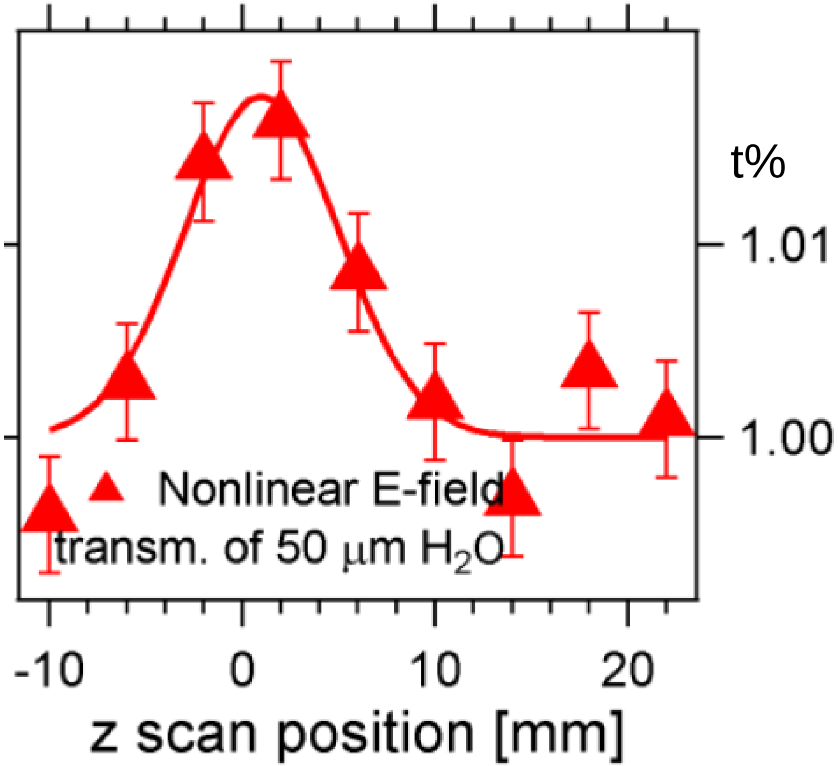
## Intensity detector



$$\alpha(P) = \alpha + \alpha^{NL} \times P$$

$$\alpha_{wat}^{NL} = -87 \pm 27\ \mathrm{cm/GW}$$

## Field detector



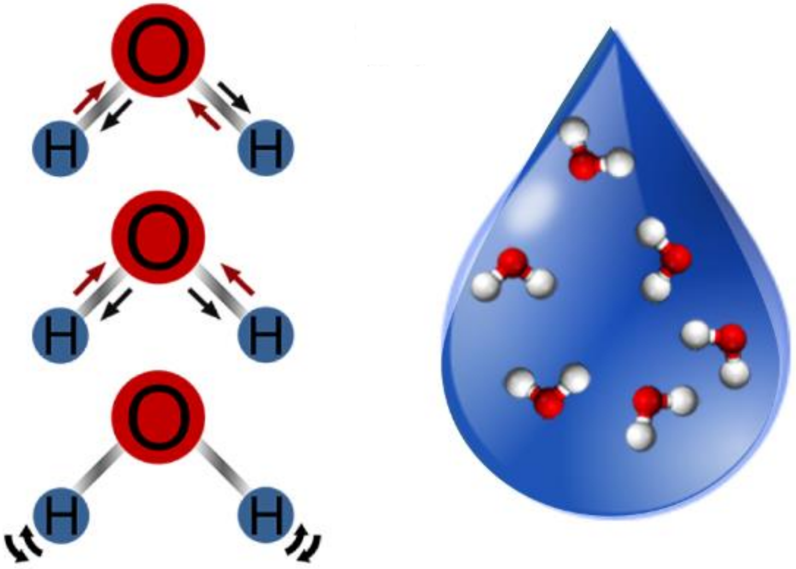
$$n(P) = n + n^{NL} \times P$$

$$n_{wat}^{NL} = (6.5 \pm 2.6) \times 10^{-10} \mathrm{cm}^2/\mathrm{W}$$

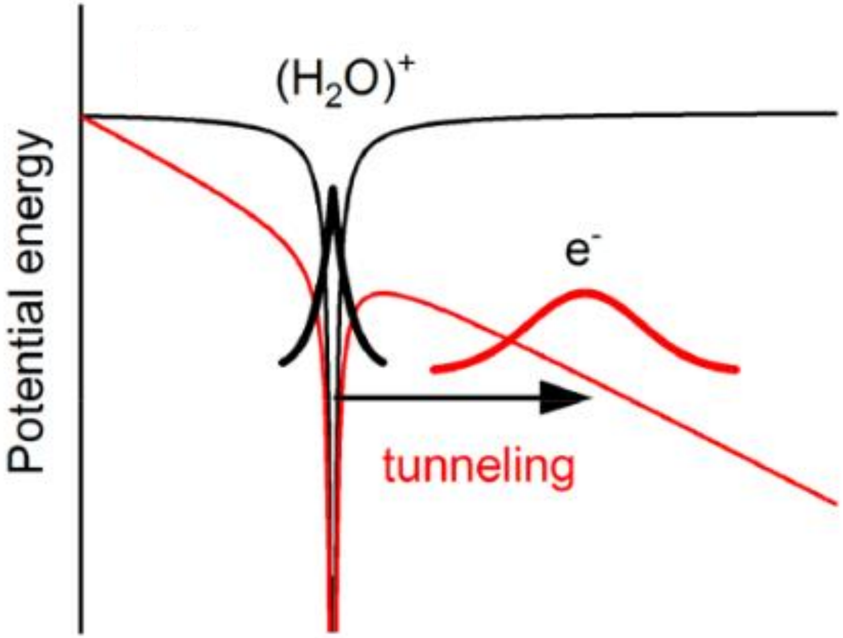
Tcypkin *et al*., Opt. Express 27, 10419, 2019
Novelli *et al*., Appl. Sci. 10, 5290, 2020

# A few groups found similar transient signals ~1 THz… different explanations

Cascaded second-order intramolecular O-H stretch



Irreversible ionization

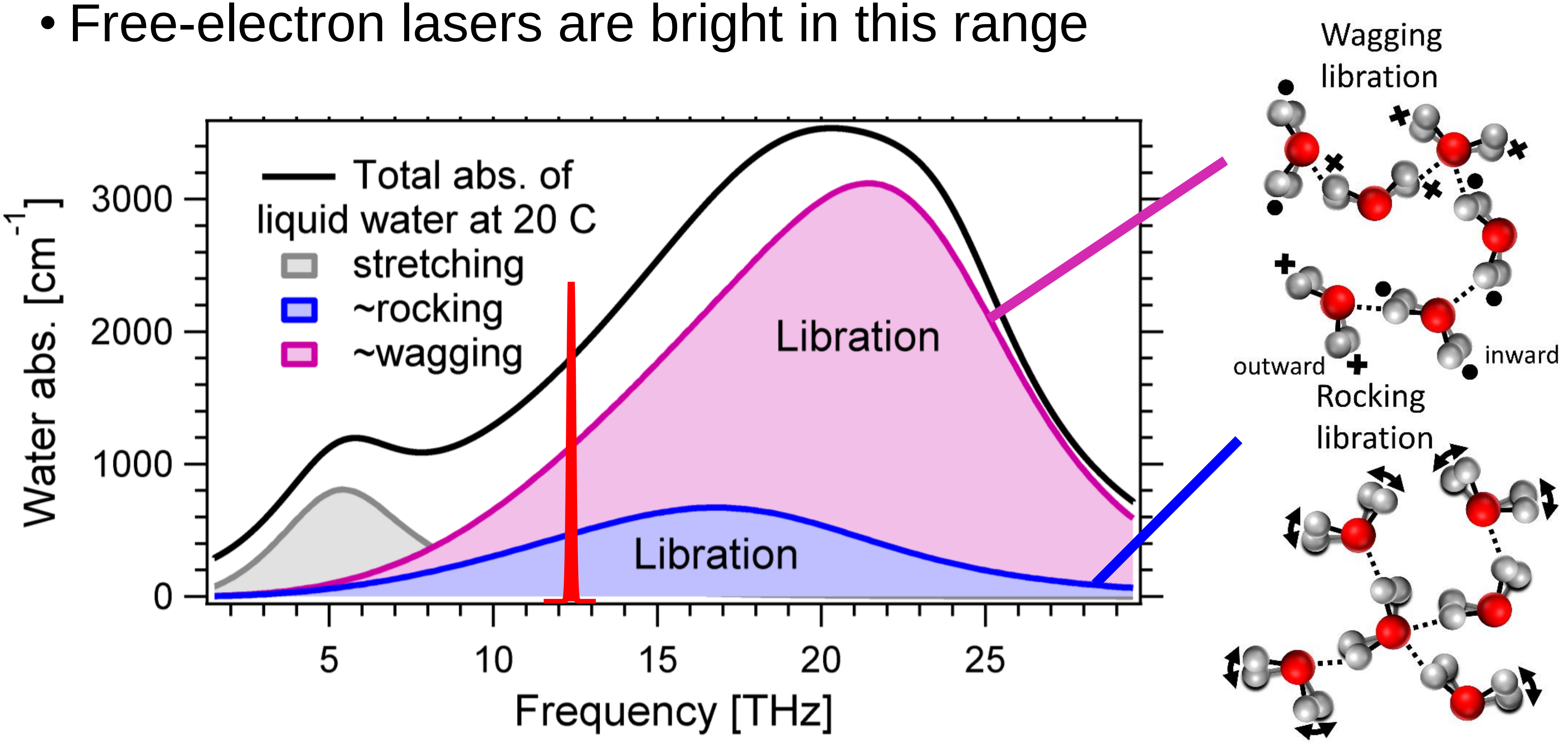


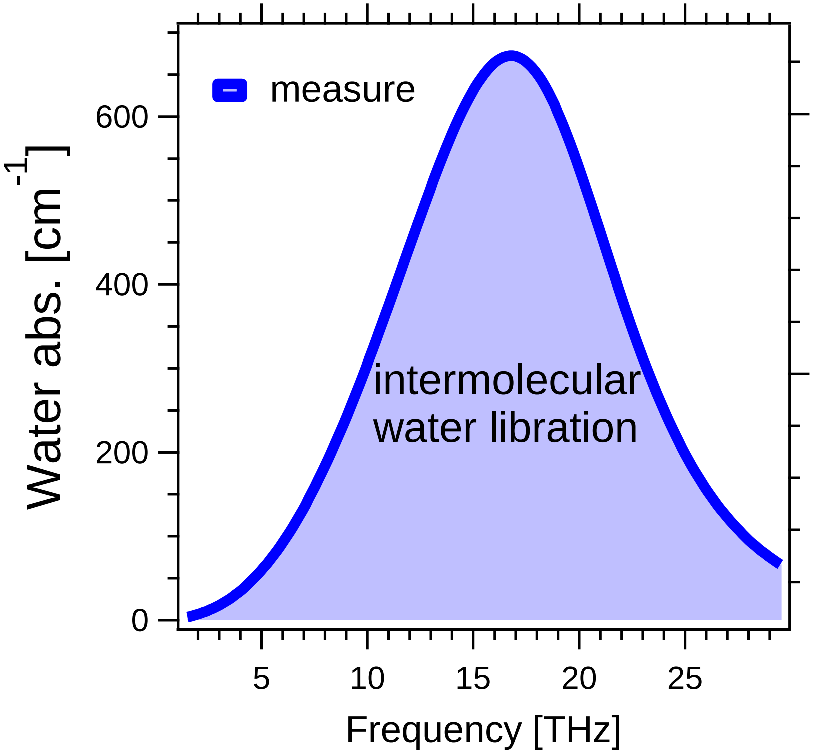
Tcypkin *et al*., Opt. Express 27, 10419, 2019
Tcypkin *et al*., Phys. Rev. Appl. 15, 054009, 2021

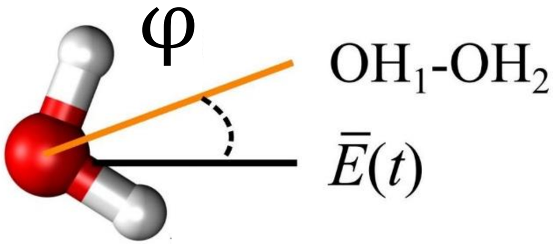
Ghalgaoui *et al*., J. Phys. Chem. Lett. 11, 7717, 2020; Phys. Rev. Lett. 126, 097401, 2021

# Pump-probe on liquid water at 12.3 THz

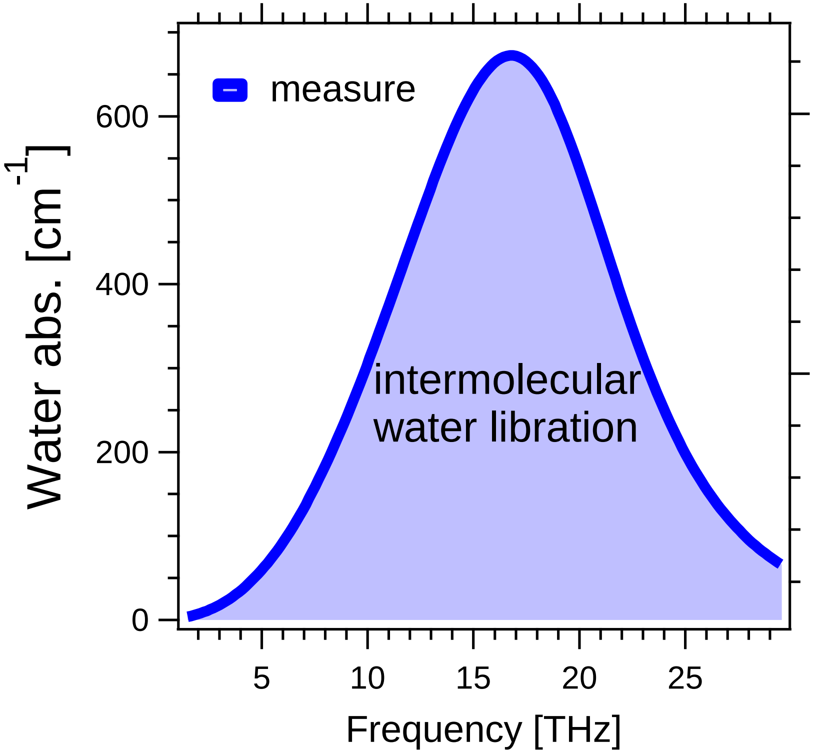
- The microscopic motion associated to the absorption between about 10 and 20 THz is better understood
- Free-electron lasers are bright in this range

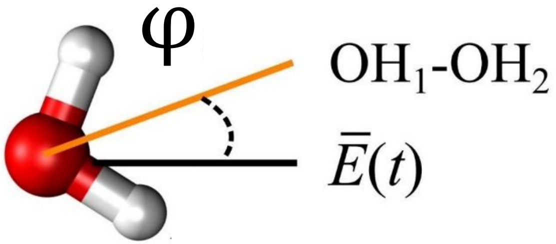



measure
intermolecular
water libration
Water abs. [cm$^{-1}$]
0
200
400
600
5
10
15
20
25
Frequency [THz]

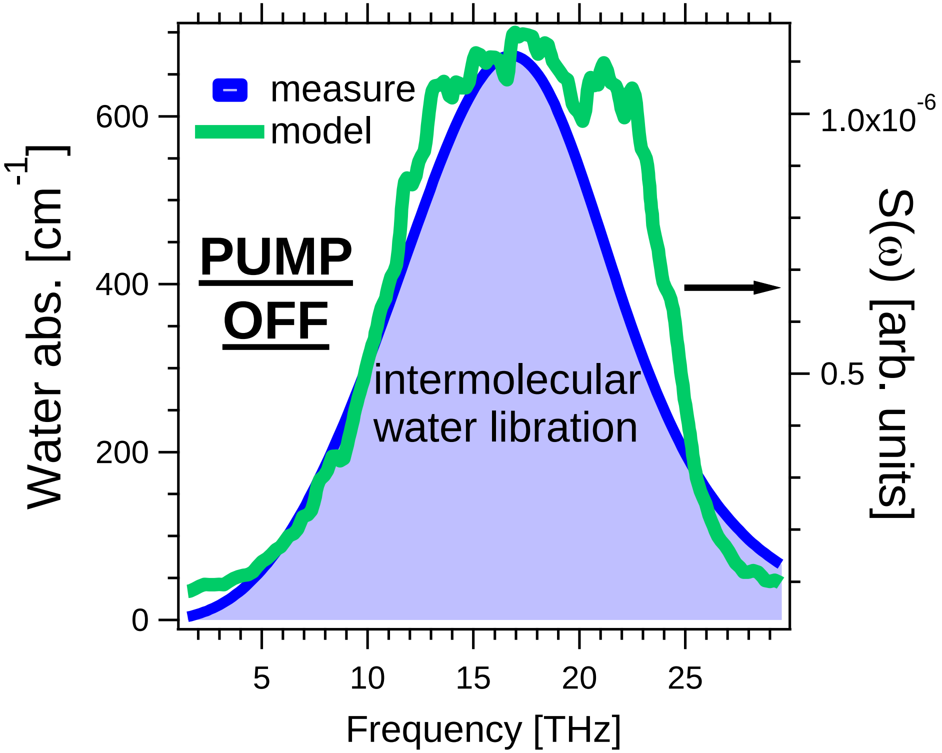


$$S(\omega) \approx FT\left[\langle \frac{d}{dt}[cos\varphi(t)]\rangle\right]$$

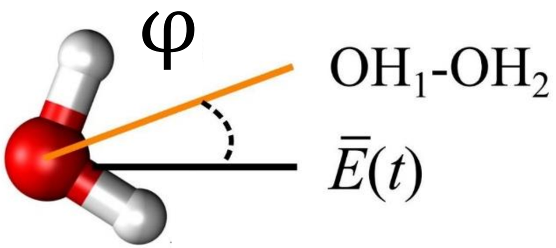




$$S(\omega) \approx FT\left[\langle\frac{d}{dt}[cos\varphi(t)]\rangle\right]$$



Natural dynamics of the damped dipole reorientations: 30-120 fs



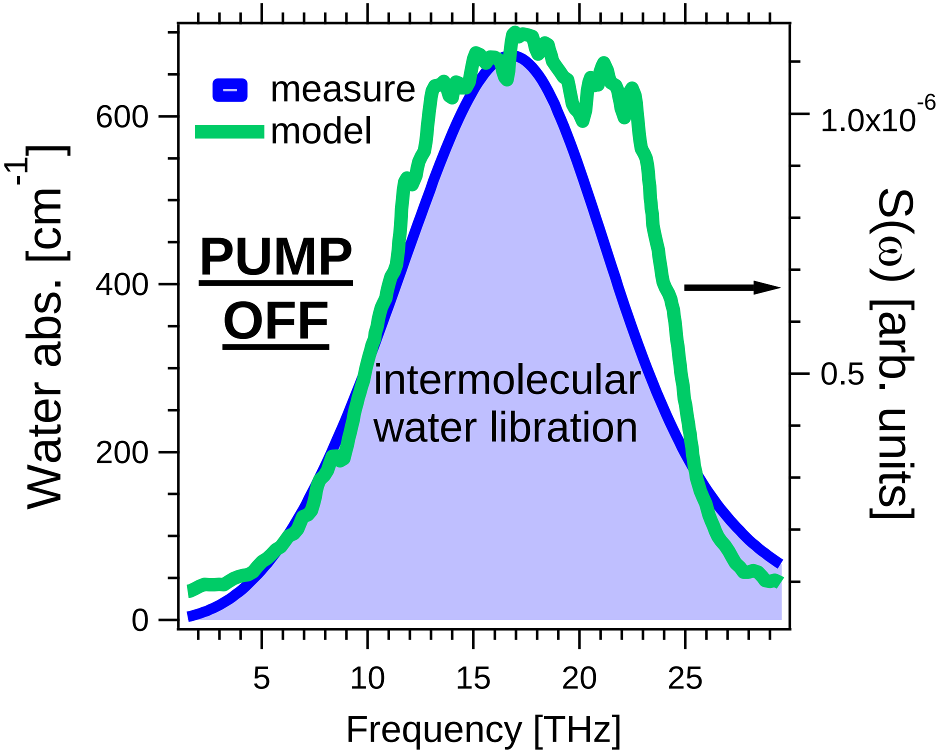
# Pump-probe experiments on water at 12.3 THz:

Novelli *et al*., J. Phys. Chem. B 124, 4989, 2020

Novelli *et al*., Phys. Chem. Chem. Phys. 24, 653, 2022

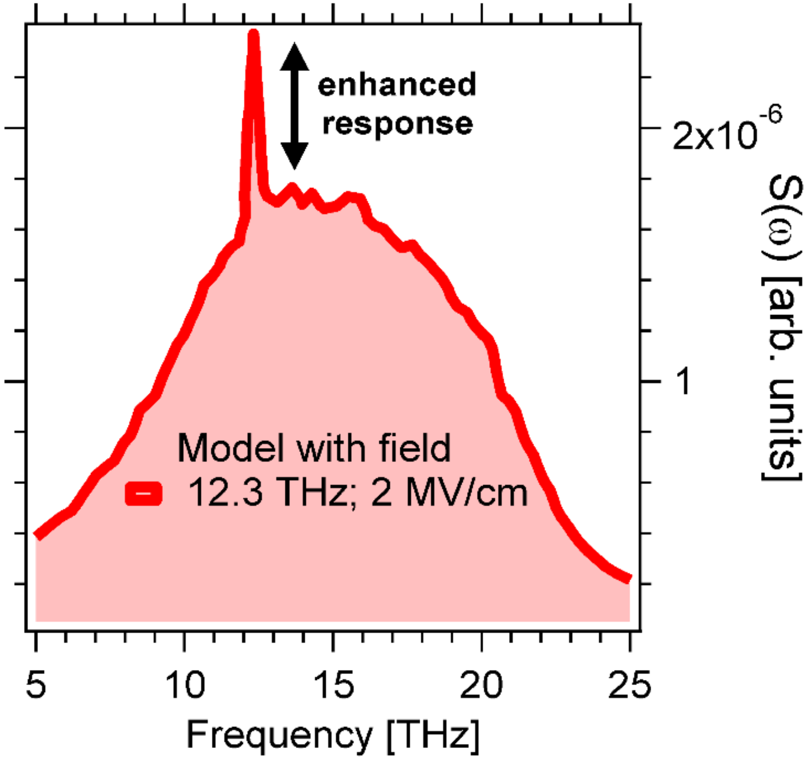
Novelli *et al*., in preparation

$$S(\omega) \approx FT\left[\langle \frac{d}{dt}[cos\varphi(t)]\rangle\right]$$



Natural dynamics of the damped dipole reorientations: 30-120 fs

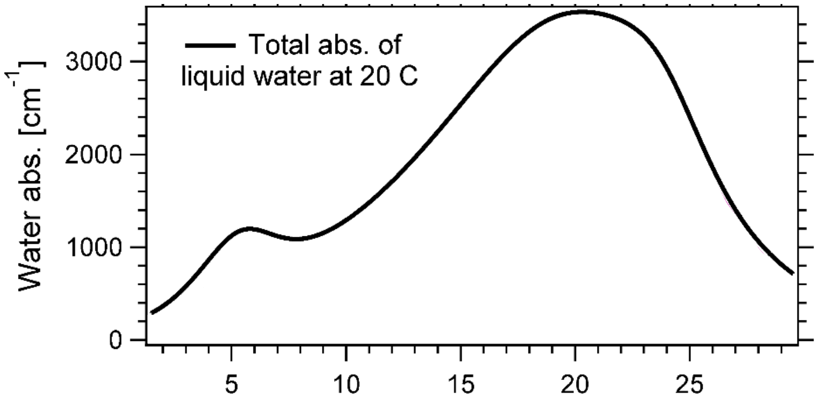
## THz PUMP ON



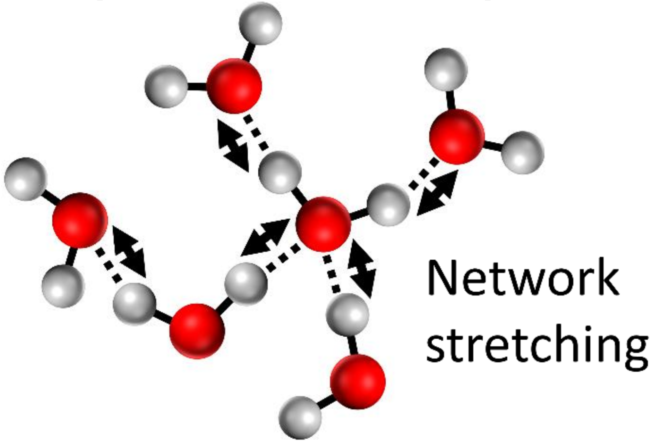
Resonant field: driven water dipole reorientations, transient anisotropy

# Summary: NL THz and pure water

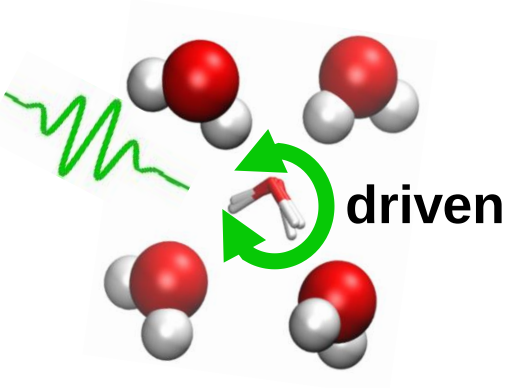
1) Water is “black”
($\alpha \sim 10^3$ cm$^{-1}$; d~10 μm)



2) THz probes water phonons



3) Dynamics ~12 THz:
resonant reorientation
(**structure**)



Novelli *et al*., Materials 13, 1311, 2020; Novelli *et al*., J. Phys. Chem. B 124, 4989, 2020;
Novelli *et al*., Appl. Sci. 10, 5290, 2020; Novelli *et al*., Phys. Chem. Chem. Phys. 24, 653, 2022;
…, Novelli, AIP Advances 12, 115319, 2022; Novelli *et al*., in preparation

# *IT IS VERY IMPORTANT TO LOOK AT THE RIGHT FREQUENCY (**for the intermolecular modes of the water network, this is terahertz range!**)*

https://www.thepoke.co.uk/2017/07/20/gif-frames-per-second-match-leg-speed/

# *IT IS VERY IMPORTANT TO LOOK AT THE RIGHT FREQUENCY (**for the intermolecular modes of the water network, this is terahertz range!**)*

**THANK YOU !!!**

**Fabio.novelli@rub.de**

https://www.thepoke.co.uk/2017/07/20/gif-frames-per-second-match-leg-speed/