

2014. 02. 14 Journal Club

**Recent Progress in theoretical analysis of
vibrational sum frequency generation
spectroscopy**

Akihiro Morita, and Tatsuya Ishiyama,
Phys. Chem. Chem. Phys. **2008**, 10, 5801.

Presenter – Woongmo Sung

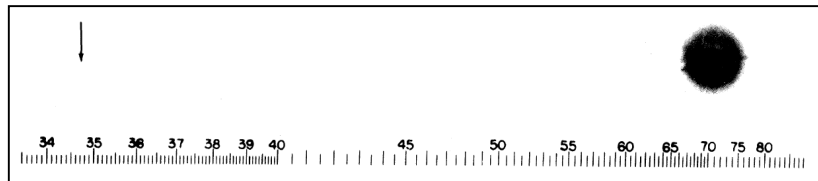
Nonlinear Optics

“Nonlinear Optical phenomena are ‘nonlinear’ in the sense that they occur when the response of a material system to applied optical field depends in a nonlinear manner upon a strength of the optical field.”

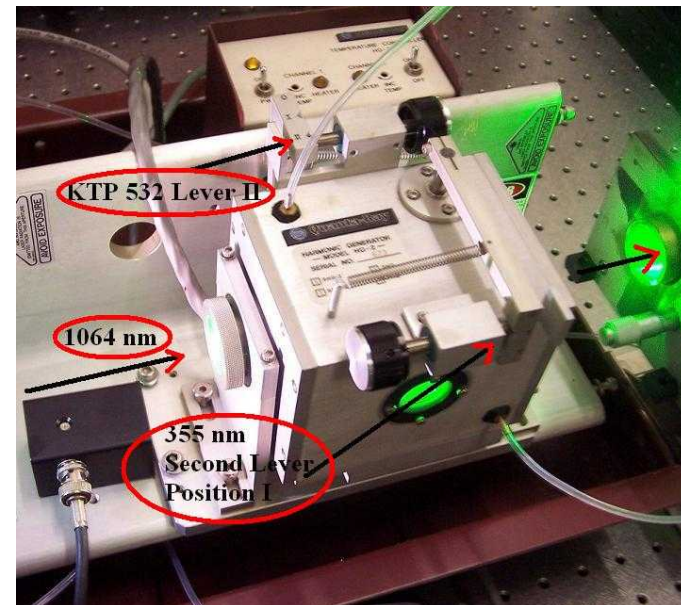
(From chapter 1 of Nonlinear Optics written by Robert. W. Boyd.)

$$\vec{P} = \vec{P}^{(1)} + \vec{P}^{(2)} + \vec{P}^{(3)} + \dots = \chi^{(1)} \vec{E} + \chi^{(2)} : \vec{E}\vec{E} + \chi^{(3)} : \vec{E}\vec{E}\vec{E} + \dots$$

Ex) Second Harmonic Generation



Franken et al. Phys. Rev. Lett. **1961**, 7, 118.



<http://www.pchemlabs.com/>

$\chi^{(1)}$ and $\chi^{(2)}$ in magnitude

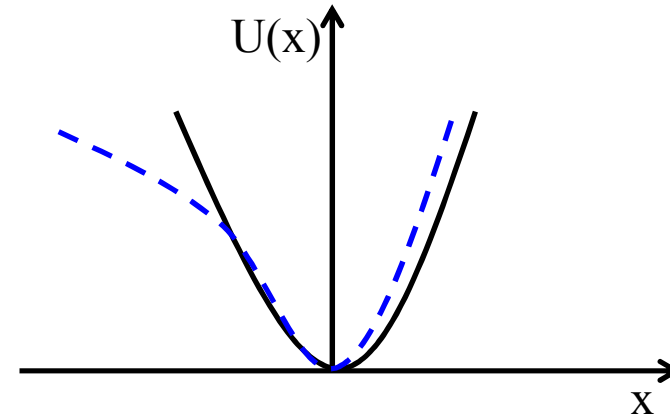
*Description of higher order polarization response

- Classical model : Anharmonic oscillator

→ Ex) Noncentrosymmetric media

$$\ddot{\vec{x}} + 2\gamma \dot{\vec{x}} + \omega_0^2 \vec{x} + a\vec{x}^2 = -e\vec{E}(t) / m$$

$$U = -\int \tilde{F} d\tilde{x} = \frac{1}{2} m\omega_0^2 \tilde{x}^2 + \frac{1}{3} m\omega_0^2 \tilde{x}^3$$



(*See chapter 1.3 in Shen or chapter 1.4 in Boyd.)

$$x = \lambda x^{(1)} + \lambda^2 x^{(2)} + \lambda^3 x^{(3)} + \dots$$

$$\rightarrow x^{(1)} = -\frac{e}{m} \frac{E}{D(\omega)}, \quad x^{(2)} = -a \left(\frac{e}{m}\right)^2 \frac{E^2}{D(2\omega)[D(\omega)]^2}$$

Corresponding susceptibility is, $P(\omega) = -Nex(\omega) = \chi E$,

$$\rightarrow \chi^{(1)} = \frac{N\left(\frac{e^2}{m}\right)}{D(\omega)}, \quad \chi^{(2)} = \frac{N\left(\frac{e^3}{m^2}\right)a}{D(2\omega)[D(\omega)]^2}, \quad D(\omega) = \omega_0^2 - \omega^2 - 2i\omega\gamma$$

$\chi^{(1)}$ and $\chi^{(2)}$ in magnitude

For non-resonant condition , $\omega_o \gg \omega$

$$\chi^{(1)} \sim \frac{N(\frac{e^2}{m})}{\omega_o^2}, \chi^{(2)} \sim \frac{N(\frac{e^3}{m^2})a}{\omega_o^6}, D(\omega) \sim \omega_o^2$$

For condensed matters, $N \sim 10^{23}$. And by assuming $mad^2 \sim m\omega_o^2 d^2$ when electron is located at distance of d (lattice constant) from its equilibrium position,

$$\begin{aligned} \rightarrow \left| \frac{P^{(2)}}{P^{(1)}} \right| &= \left| \frac{\chi^{(2)} E}{\chi^{(1)}} \right| = \frac{e E}{m \omega_o^4 d} = \frac{1.6 \cdot 10^{-19} C}{9.1 \cdot 10^{-31} kg} \frac{E}{(10^{16} rad / s)^4 \cdot 3 \cdot 10^{-10} m} \\ &\sim \frac{E}{10^{11} V / m} = \left| \frac{E}{E_{at}} \right| \end{aligned}$$

\rightarrow Magnitude of light's electric field should be large.

Then, how much?

CW laser



Coherent DIAMOND™ C-70L : 70W

for 0.1mm of beam diameter,

$$I = \frac{P}{A} = \frac{70W}{\pi(0.5 \cdot 10^{-4} m)^2} \sim 10^{10} W / m^2$$

$$|E| = \sqrt{\frac{2Z_o I}{n}} = \sqrt{\frac{2 \cdot 377 \Omega \cdot 10^{10} W / m^2}{2}} \sim 10^6 V / m \ll 0.00001 \cdot E_{at}$$

Pulse laser



Ekspla PL2251 : 30ps, 30mJ/pulse , 10Hz – 0.3W

$$I_{peak} = \frac{(P \cdot T / \Delta T)}{A} = \frac{(0.3W \cdot 1s / 30 \cdot 10^{-12} s)}{\pi(0.5 \cdot 10^{-4} m)^2} \sim 10^{18} W / m^2$$

$$|E| = \sqrt{\frac{2Z_o I}{n}} = \sqrt{\frac{2 \cdot 377 \Omega \cdot 10^{18} W / m^2}{2}} \sim 2 \cdot 10^{10} V / m \sim 0.2 E_{at}$$

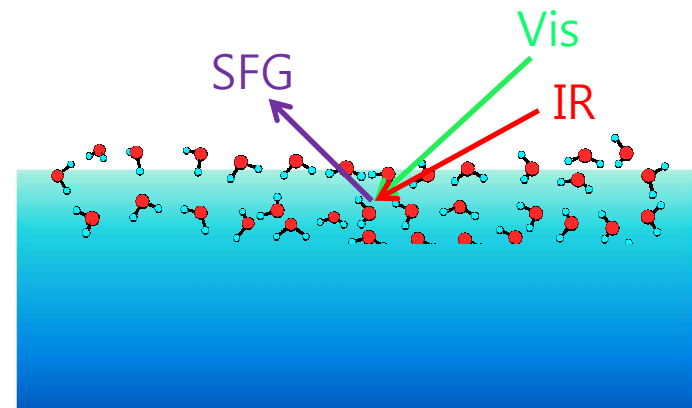
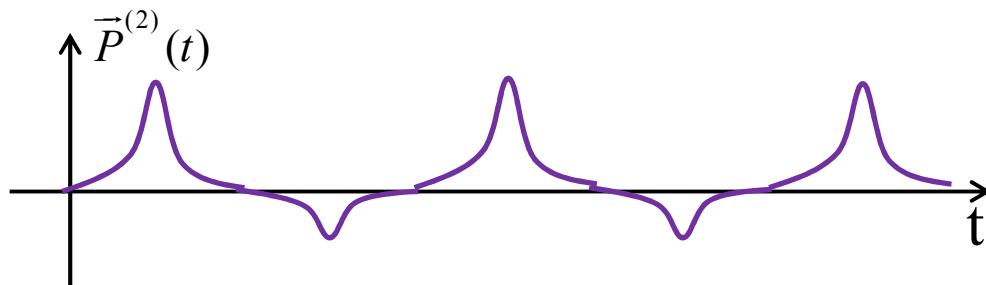
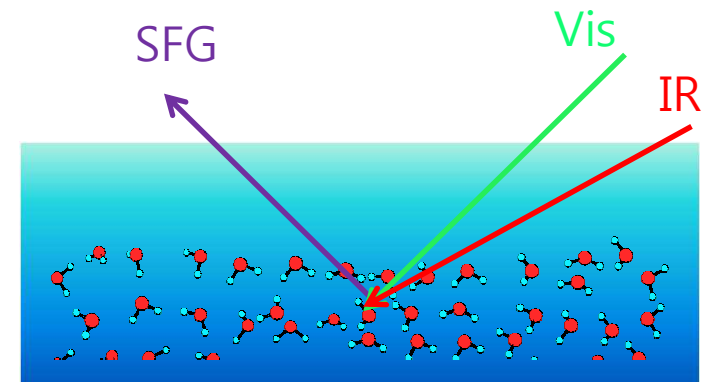
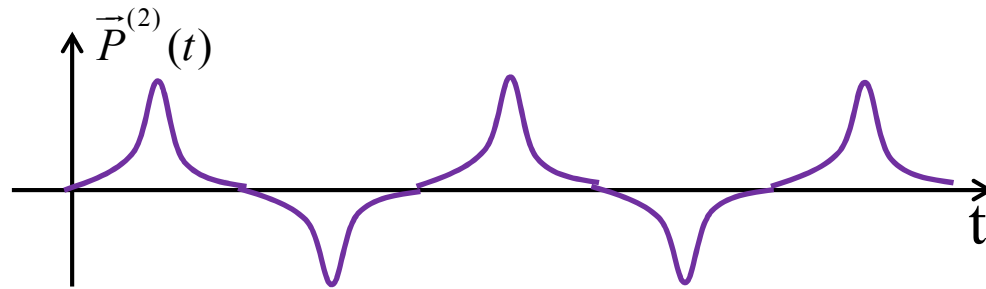
Second order nonlinear optical response

$$P = P^{(1)} + P^{(2)} + P^{(3)} + \dots = \chi^{(1)} E + \chi^{(2)} EE + \chi^{(3)} EEE + \dots$$

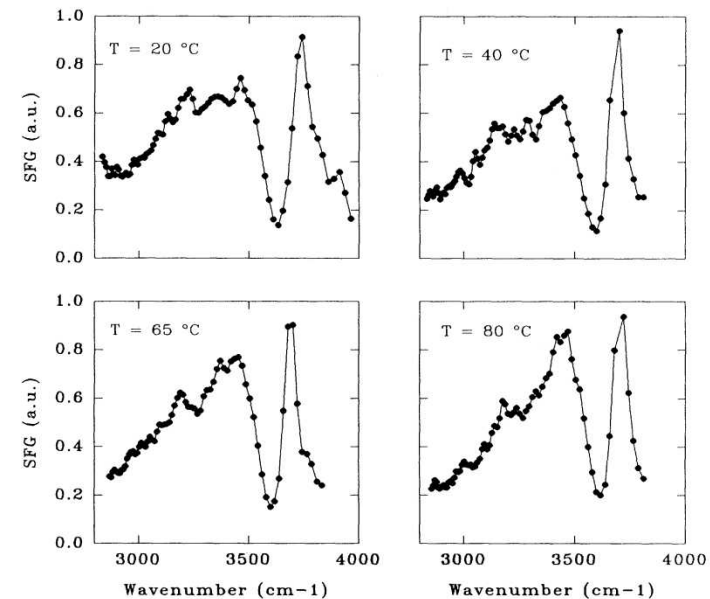
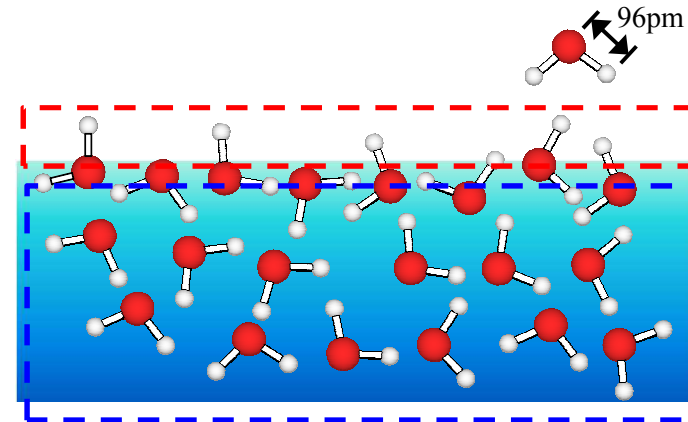
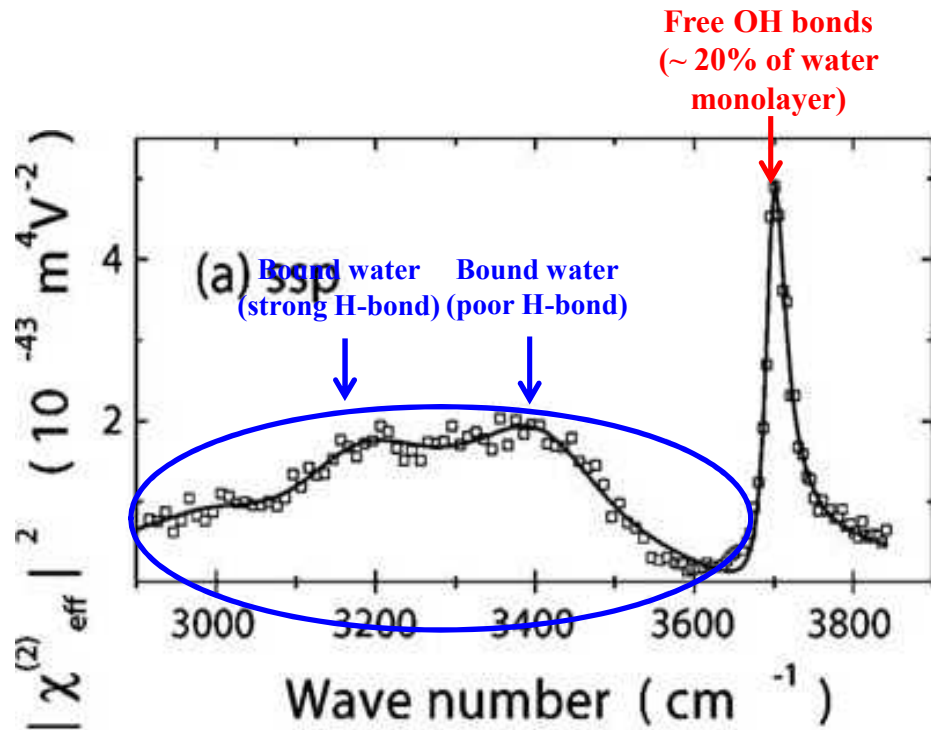
→ $-P = -P^{(1)} - P^{(2)} - P^{(3)} + \dots = -\chi^{(1)} E - \chi^{(2)} EE - \chi^{(3)} EEE - \dots$

$= \chi^{(1)} (-E) + \chi^{(2)} (-E)(-E) + \chi^{(3)} (-E)(-E)(-E) + \dots$ For centrosymmetric materials (ex – liquids.)

$\neq \chi^{(1)} (-E) + \chi^{(2)} (-E)(-E) + \chi^{(3)} (-E)(-E)(-E) + \dots$ For noncentrosymmetric materials (ex – crystals depending on system.)



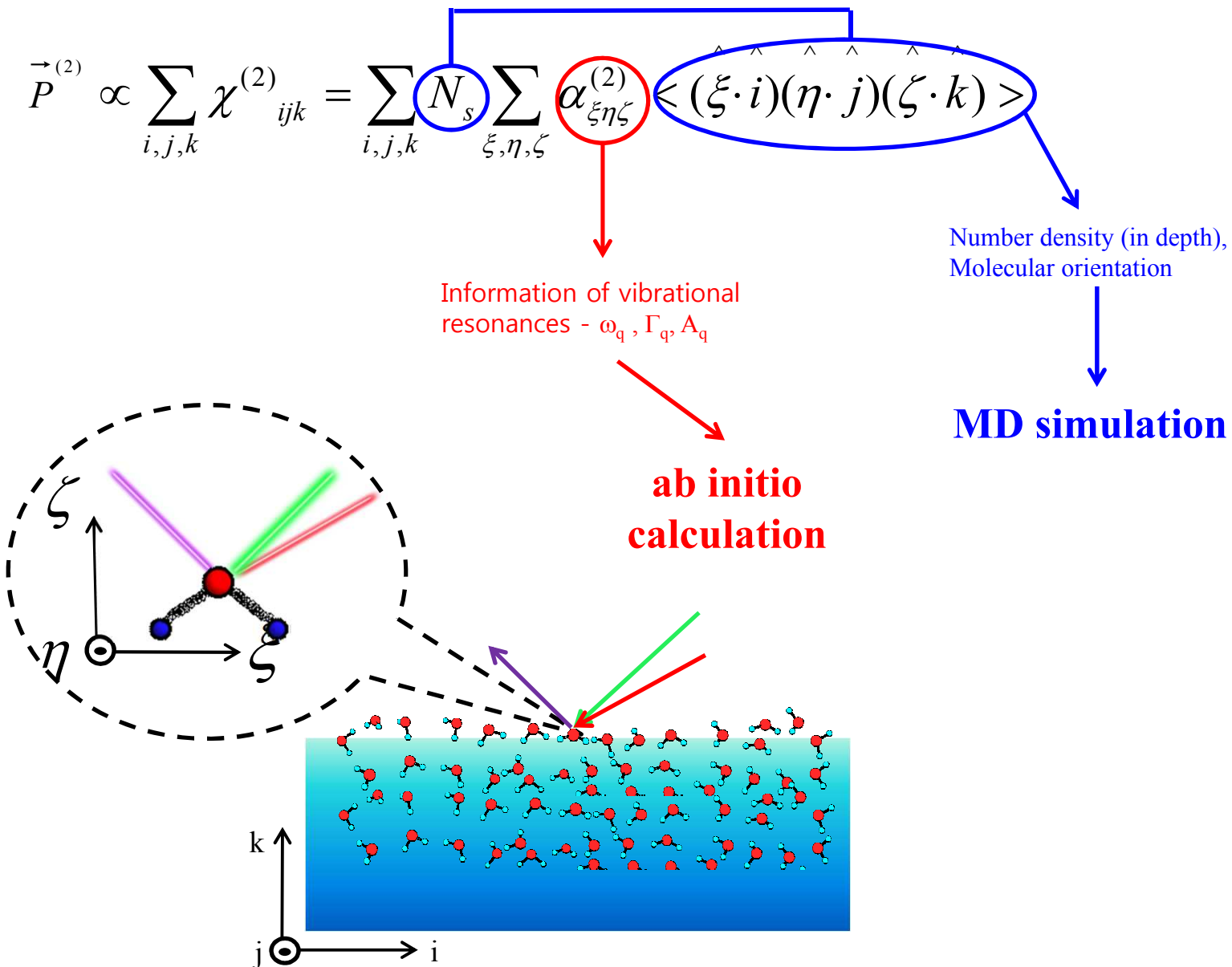
Air / Water interface ? – several water layers may contribute



- What is the depth of bound water layers contributing to SF spectra ? (Help from MD simulation)

- From MD simulation, can SF spectra be reconstructed?

Theoretical modeling



$\alpha^{(2)}$ (or $\beta^{(2)}$ in the article)

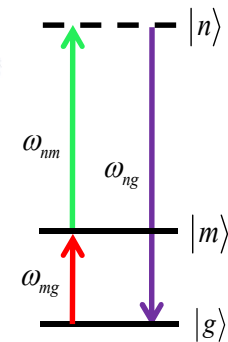
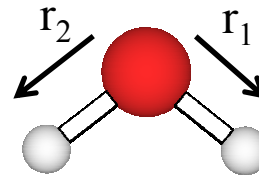
$$\chi_{ijk}^{(2,\text{res})}(\omega_{\text{SFG}}, \omega_{\text{vis}}, \omega_{\text{IR}})$$

$$= \frac{1}{\hbar^2} \sum_{g,n,m} \rho_g^{(0)} \left[\frac{\langle g|\mu_i|n\rangle \langle n|\mu_j|m\rangle \langle m|\mu_k|g\rangle}{(\omega_{\text{SFG}} - \omega_{ng} + i\Gamma_{ng})(\omega_{\text{IR}} - \omega_{mg} + i\Gamma_{mg})} \right. \\ + \frac{\langle g|\mu_k|m\rangle \langle m|\mu_j|n\rangle \langle n|\mu_i|g\rangle}{(\omega_{\text{SFG}} + \omega_{ng} + i\Gamma_{ng})(\omega_{\text{IR}} + \omega_{mg} + i\Gamma_{mg})} \\ - \frac{\langle g|\mu_k|m\rangle \langle m|\mu_i|n\rangle \langle n|\mu_j|g\rangle}{(\omega_{\text{SFG}} - \omega_{nm} + i\Gamma_{nm})(\omega_{\text{IR}} + \omega_{mg} + i\Gamma_{mg})} \\ \left. - \frac{\langle g|\mu_j|m\rangle \langle m|\mu_i|n\rangle \langle n|\mu_k|g\rangle}{(\omega_{\text{SFG}} - \omega_{nm} + i\Gamma_{nm})(\omega_{\text{IR}} - \omega_{ng} + i\Gamma_{ng})} \right] \\ = -\frac{1}{\hbar} \sum_{g,m} (\rho_g^{(0)} - \rho_m^{(0)}) \langle g|\alpha_{ij}(\omega_{\text{SFG}})|m\rangle \frac{\langle m|\mu_k|g\rangle}{\omega_{\text{IR}} - \omega_{mg} + i\Gamma_{mg}}$$

$$\langle g|\alpha_{ij}(\omega)|m\rangle = -\frac{1}{\hbar} \sum_n \left[\frac{\langle g|\mu_i|n\rangle \langle n|\mu_j|m\rangle}{\omega - \omega_{ng} + i\Gamma_{ng}} - \frac{\langle g|\mu_j|n\rangle \langle n|\mu_i|m\rangle}{\omega + \omega_{nm} + i\Gamma_{nm}} \right]$$

$$\beta_{pqr} \approx \frac{1}{2m\omega} \left(\frac{\partial \alpha_{pq}}{\partial Q} \right) \left(\frac{\partial \mu_r}{\partial Q} \right) \left[\frac{\omega - \omega_{\text{IR}}}{(\omega - \omega_{\text{IR}})^2 + \gamma^2} + \frac{i\gamma}{(\omega - \omega_{\text{IR}})^2 + \gamma^2} \right]$$

$$\frac{\partial A}{\partial Q} = C_1 \frac{\partial A}{\partial r_1} + C_2 \frac{\partial A}{\partial r_2}, \quad A = \alpha_{pq} \text{ or } \mu_r$$



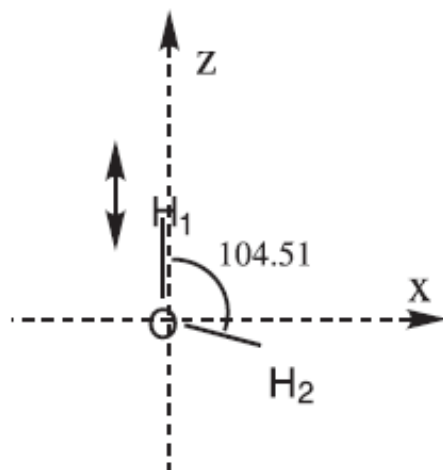
(* Chapter 3 of *Nonlinear Optics* written by Robert. W. Boyd.)

Morita and Hynes, *Chem. Phys.* **2000**, 258, 371.

About a water molecule (in *Chem. Phys.* 2000)

In water molecule, two local OH stretch mode exist.

$$\frac{\partial A}{\partial Q} = C_1 \frac{\partial A}{\partial r_1} + C_2 \frac{\partial A}{\partial r_2}, \quad A = \alpha_{pq} \text{ or } \mu_r$$



$$\begin{bmatrix} \omega_1 - \omega & V_{12} \\ V_{12} & \omega_2 - \omega \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} = 0.$$

symmetric stretching ($C_1/C_2 = +1$)

antisymmetric stretching ($C_1/C_2 = -1$)

Table 1
Selected ab initio properties of a water molecule at the B3LYP/
d-aug-cc-pVTZ level ($k_0 = 0.548$; $l = -1.991$)^a

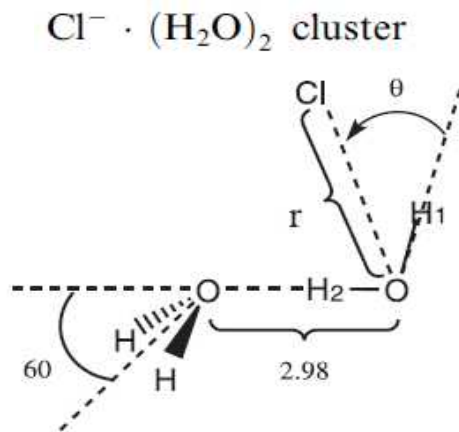
$\partial\mu_r/\partial r_1$	$r = x$	$r = y$	$r = z$
	-0.058	0.000	0.157
$\partial\alpha_{pq}/\partial r_1$	$q = x$	$q = y$	$q = z$
$p = x$	1.539		
$p = y$	0.000	1.656	
$p = z$	-0.163	0.000	7.200

^a Force constant k_0 along a local OH bond, its derivative l with respect to the OH distance r_1 , dipole moment derivative $\partial\mu_r/\partial r_1$, and polarizability derivative $\partial\alpha_{pq}/\partial r_1$. See Fig. 1(a) for the definition of the body-fixed coordinates (units: a.u.).

Frequency shift (in *Chem. Phys.* 2000)

Frequency shift due to force (F: local solvation environment)

- ➔ Cl⁻(H₂O) cluster in ab initio MO calculations as a model system of hydrogen bonding (because shift of OH bond frequency appears similar to bulk water data, ~ 560cm⁻¹)



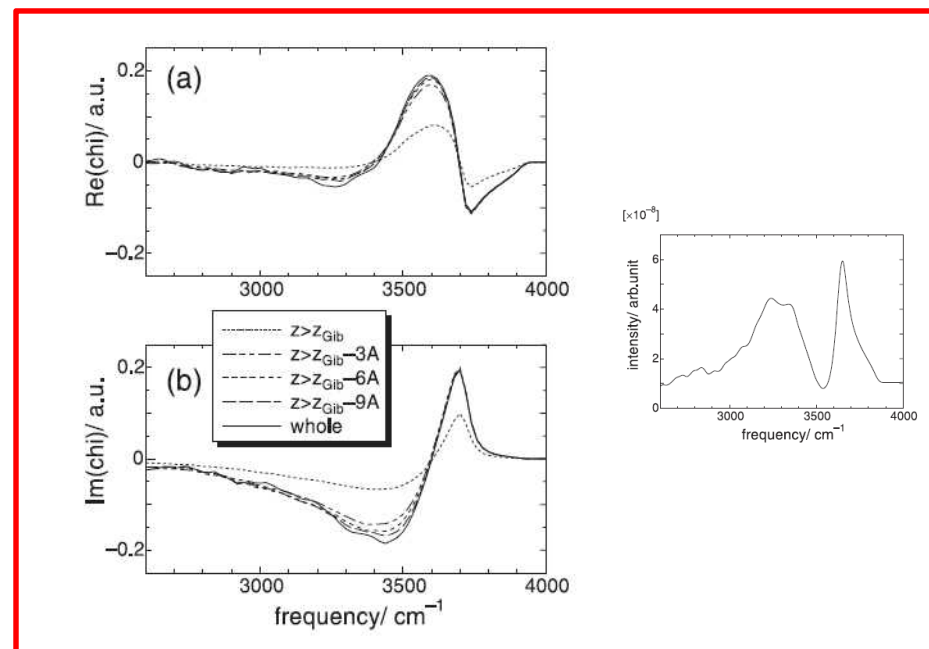
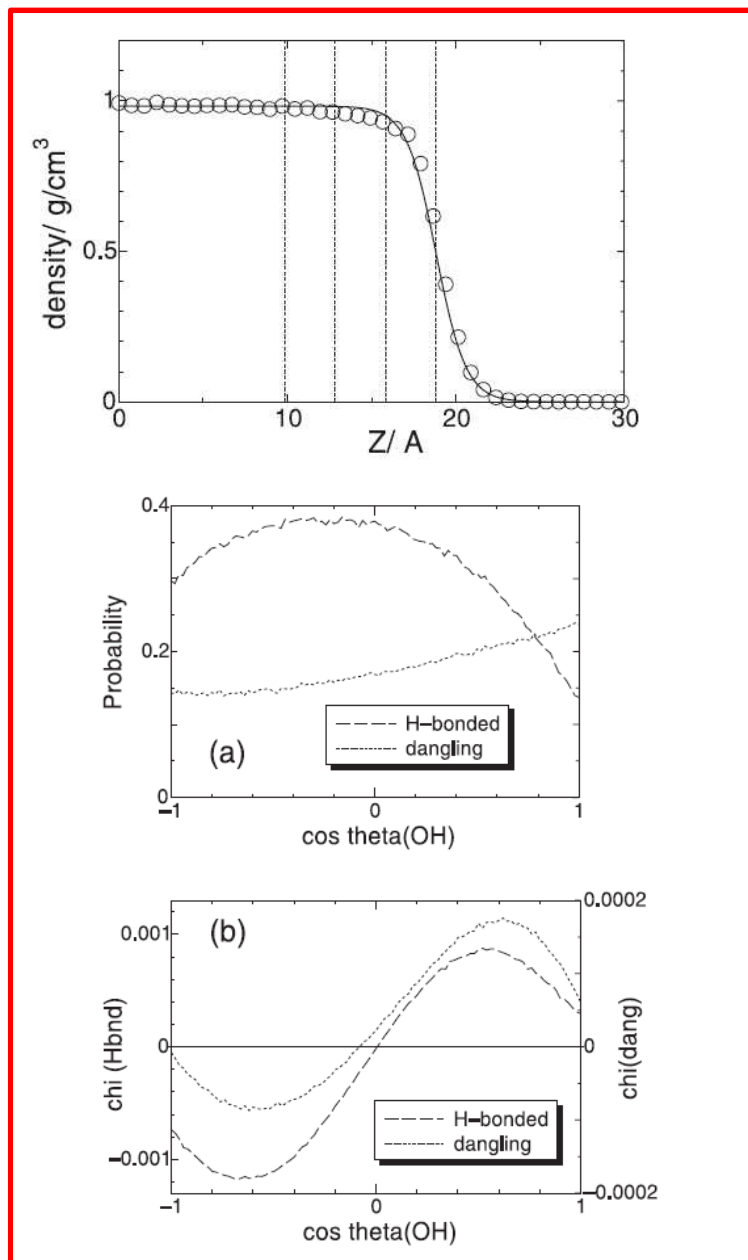
$$\Delta\omega = \sqrt{\frac{k_0 + l\Delta r + G}{m}} - \sqrt{\frac{k_0}{m}}$$

$$\Delta\omega \approx \sqrt{\frac{k_0}{m}} \left(\frac{lF}{2k_0^2} + \frac{G}{2k_0} \right),$$

$$\Delta\omega \approx \sqrt{\frac{k_0}{m}} \left(\frac{lF}{2k_0^2} \right).$$

$$\Delta r = F/k_0$$

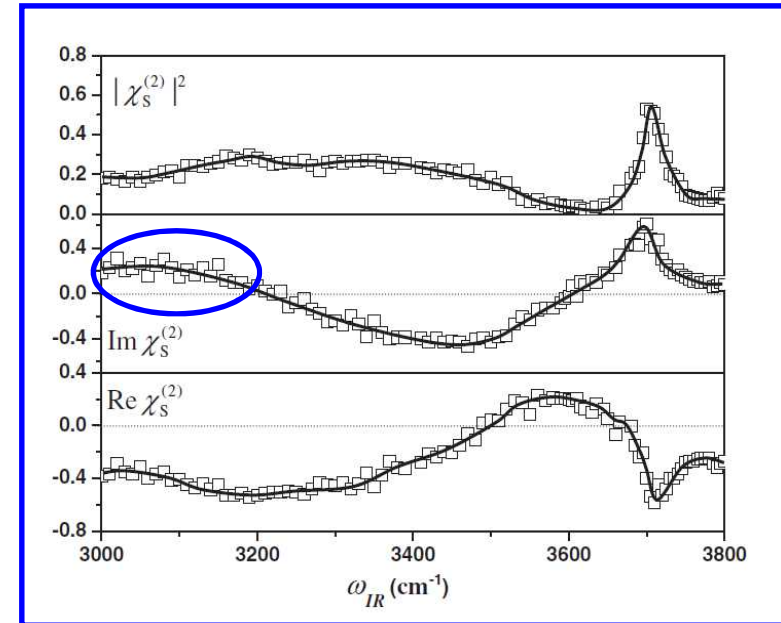
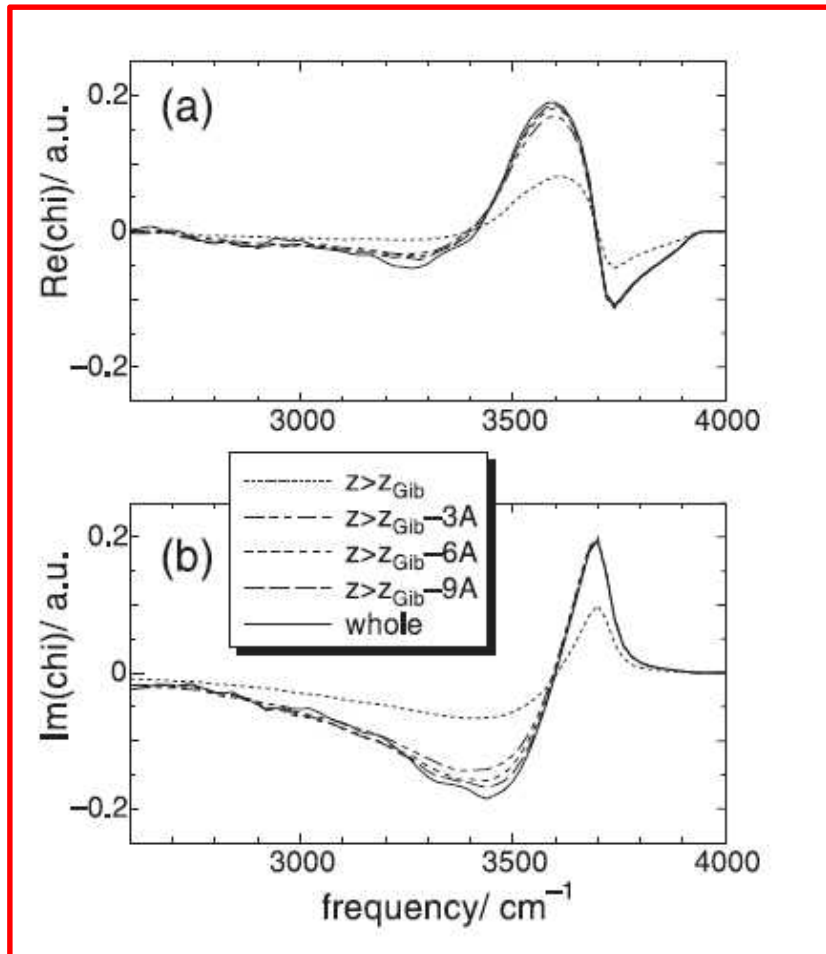
Simulation result (in *Chem. Phys.* 2000)



→ SF signal contribution comes mainly from water molecules with in $\sim -10\text{\AA}$ from GDS.

→ Bound OH – negative $\text{Im}\chi^{(2)}$
 Free OH – positive $\text{Im}\chi^{(2)}$

Inconsistency in complex spectra



Ji et al. Phys. Rev. Lett. **2008**, 100, 096102.

➔ Bound OH – positive $\text{Im}\chi^{(2)}$ in low frequency band shows up

Improvement 1) – Local field correction

- ➔ In the presence of external field E^0 , p-th water molecule feel additional field created by dipoles from surrounding other water molecules.

$$\mu_i(p) = \mu_i^0(p) + \sum_j \alpha_{ij}(p) E_j(p),$$

$$E_i(p) = E_i^0(p) - \sum_{q(\neq p)} \sum_j T_{ij}(pq) \mu_j(q).$$

$$(i, j = x \sim z, p, q = 1 \sim N)$$

$$T_{ij}(pq) = \frac{\delta_{ij} - 3r_i(pq)r_j(pq)}{|\mathbf{r}(pq)|^3}$$

$$U(\mathbf{E}^0) - U(\mathbf{E}^0 = 0) = - \int_0^{\mathbf{E}^0} \boldsymbol{\mu} \cdot \frac{\partial \mathbf{E}}{\partial \mathbf{E}^0} d\mathbf{E}^0.$$

$$\mathbf{M} = - \frac{\partial U}{\partial \mathbf{E}^0} = \mathbf{g}^T \boldsymbol{\mu},$$

$$\mathbf{A} = - \frac{\partial^2 U}{\partial \mathbf{E}^0 \partial \mathbf{E}^0} = \mathbf{g}^T \frac{\partial \boldsymbol{\mu}}{\partial \mathbf{E}^0} = \mathbf{g}^T \boldsymbol{\alpha} \mathbf{g},$$

$$\mathbf{g} = (1 + \mathbf{T} \cdot \boldsymbol{\alpha})^{-1}, \mathbf{g}^T = (1 + \boldsymbol{\alpha} \cdot \mathbf{T})^{-1}$$

Improvement 2) – Time dependent representation

➔ Previously suggested model (energy representation) statistically averaged over instantaneous MD trajectories. And Raman and IR derivatives are given from modeling (ab initio) and fixed during MD.

$$\begin{aligned}
 \chi_{ijk}^{(2,\text{res})}(\omega_{\text{SFG}}, \omega_{\text{vis}}, \omega_{\text{IR}}) &= -\frac{1}{\hbar} \sum_{g,m} (\rho_g^{(0)} - \rho_m^{(0)}) \langle g | \alpha_{ij}(\omega_{\text{SFG}}) | m \rangle \frac{\langle m | \mu_k | g \rangle}{\omega_{\text{IR}} - \omega_{mg} + i\Gamma_{mg}} \\
 &= \frac{2i}{\hbar} \tanh\left(\frac{\hbar\omega_{\text{IR}}}{2k_{\text{B}}T}\right) \int_0^\infty dt \exp(i\omega_{\text{IR}}t) g_+(t)
 \end{aligned}
 \tag{10}$$

$$\chi_{ijk}^{(2,\text{res})}(\omega_{\text{SFG}}, \omega_{\text{vis}}, \omega_{\text{IR}}) = \frac{i\omega_{\text{IR}}}{k_{\text{B}}T} \int_0^\infty dt \exp(i\omega_{\text{IR}}t) \langle \delta\mathcal{A}_{ij}(t) \delta\mathcal{M}_k \rangle$$

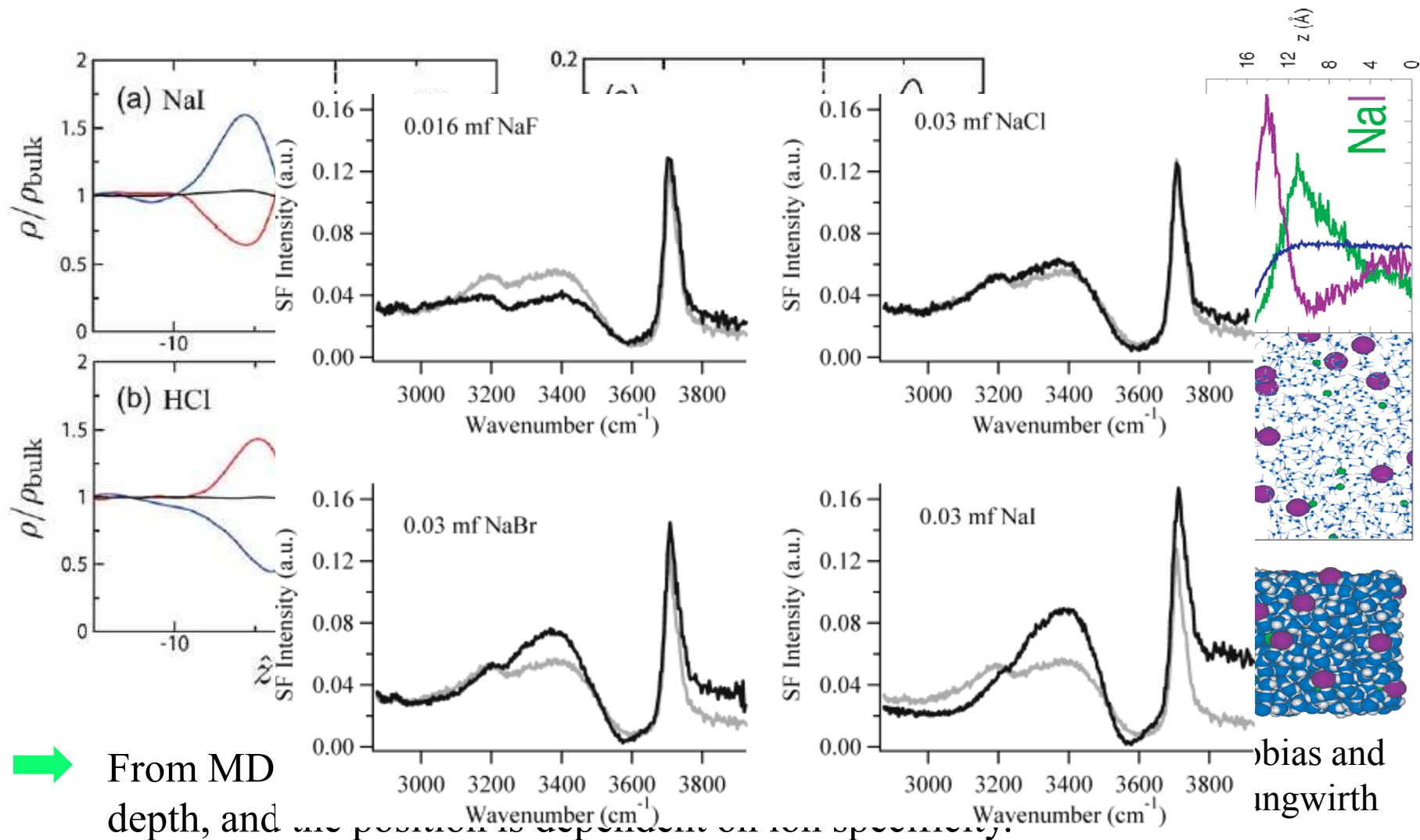
where $g_+(t)$ is the symmetrized time correlation function,

$$g_+(t) = \left\langle \frac{\delta\alpha_{ij}(t)\delta\mu_k + \delta\mu_k\delta\alpha_{ij}(t)}{2} \right\rangle, \tag{11}$$

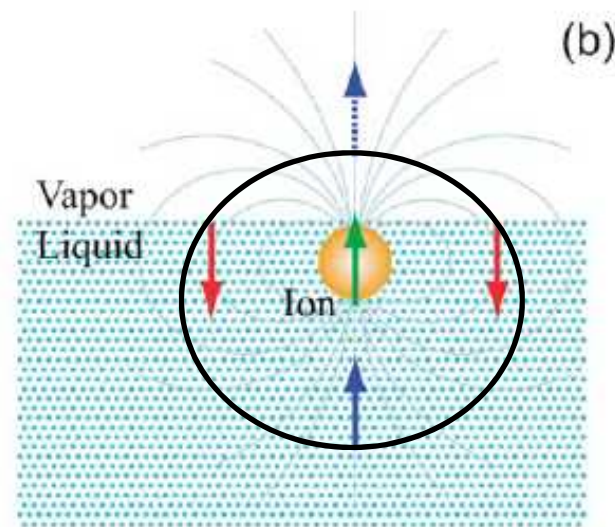
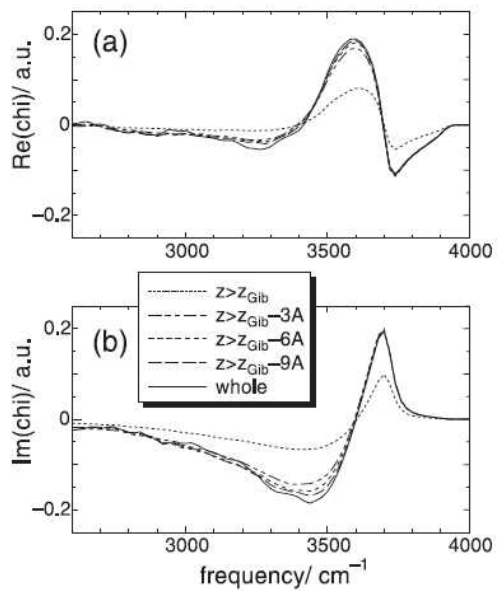
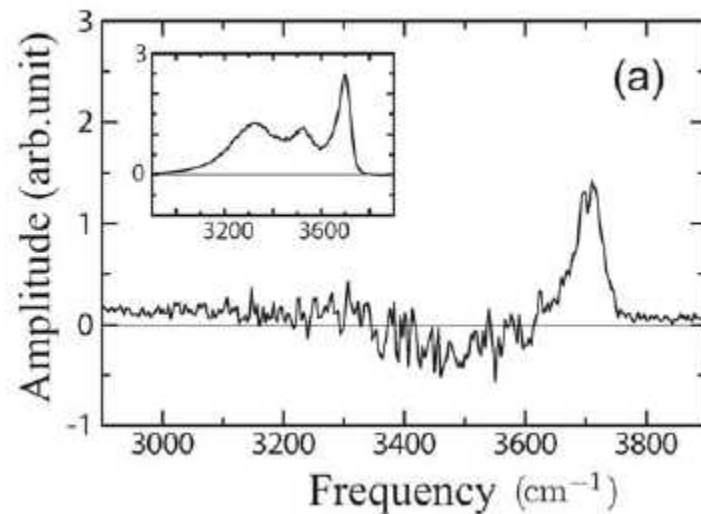
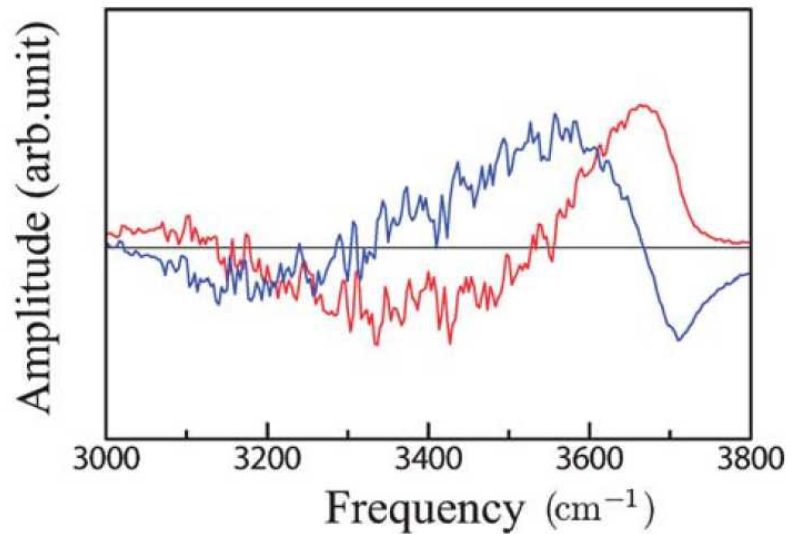
$$g(t) = \langle \delta\alpha_{ij}(t)\delta\mu_k \rangle = \sum_{g,m(\neq g)} \rho_g^{(0)} \langle g | \alpha_{ij}(t) | m \rangle \langle m | \mu_k | g \rangle$$

$$\langle g | \alpha(t) | m \rangle = \exp[i(-\omega_{mg} + i\Gamma_{mg})t] \langle g | \alpha | m \rangle$$

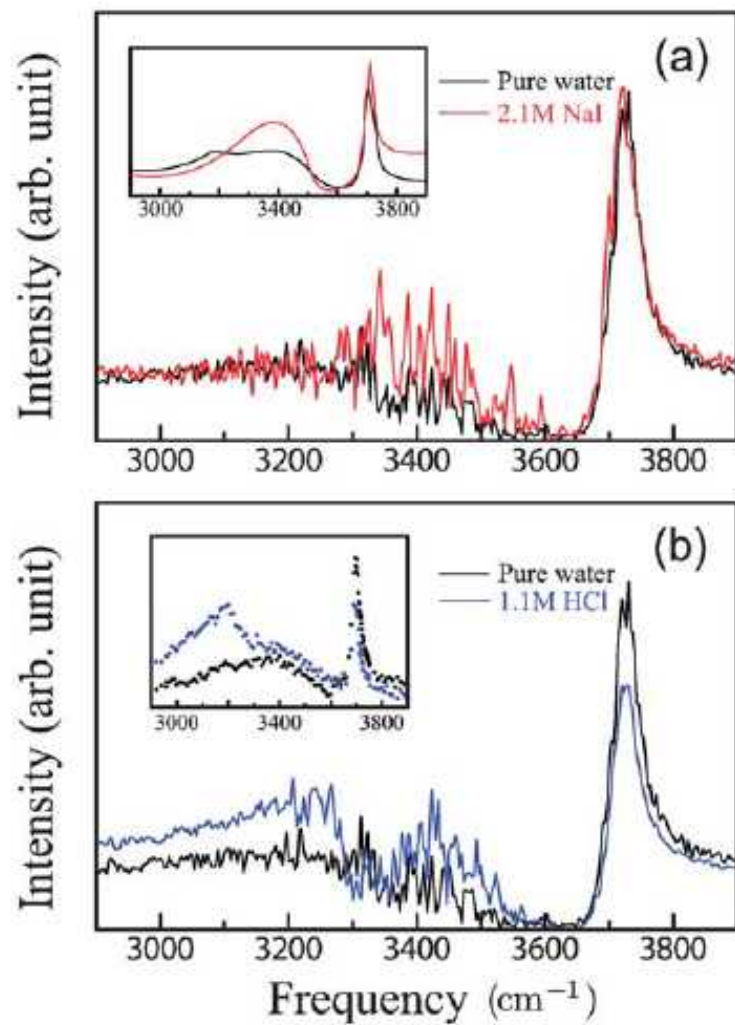
For ions in water – creation of double layer



Local field correction gives different result



Another simulated spectra (acidic solution)



Summary

- More quantitative analysis on SF spectra of air / water interface is accessible via MD , modeling from ab initio.
- Experimental $\text{Im}\chi^{(2)}$ spectra of air / water showing clear deviation from previously simulated spectra by energy representation can be explained by modified model including local field correction running with time dependent representation.
- The authors suggest that positive tail observed in low frequency bound OH band is originated from many body interaction of water molecules.
- Including and excluding local field correction in air / NaI solution, spectra demonstrates big difference in bound OH band. About this, cancellation of transition dipoles of water by opposite local fields was proposed.