Heating of Liquid Water and Ice Irradiated by Far-infrared Electromagnetic Waves

Theoretical Study by Quantum Mechanical Molecular Dynamics

Motohiko Tanaka (Chubu University, Japan)
H. Kono (Tohoku U.)
K. Maruyama (Osaka City U.)
Y. Zempo (Hosei U.)

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Our Motivation

We are interested in the physics of interactions of matters with electromagnetic waves.

We have clarified the heating mechanism of water (pure, salty) and magnetite by microwaves.

Now we are extending our study to the heating of water (& ice) by far-infrared waves.

Study the heating of water

Water:

Most common dielectric material (liquid and ice)

Related to biophysics processes – effects of EM radiations

Peculiar matter

Structured by hydrogen bonds

Most dense at 4^{o}C; ice (solid) floats on liquid

High electrical conductivity, …

Heating mechanism of water

– Already answered for microwaves (Tanaka & Sato, 2007)

-- How is water heated by far-infrared waves ?

Microwave heating of water

Four different mechanisms !

1. Liquid water is heated through the induction of small-angle rotation of molecules

2. Salty water is better heated than pure water due to addition of Na^+ & Cl^- (ion) acceleration

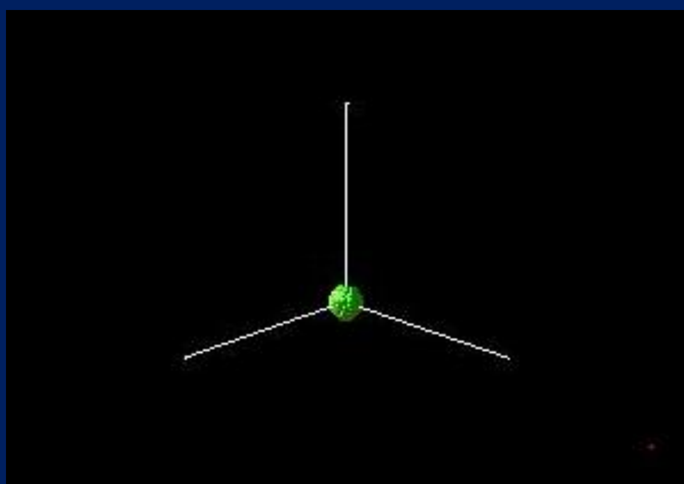
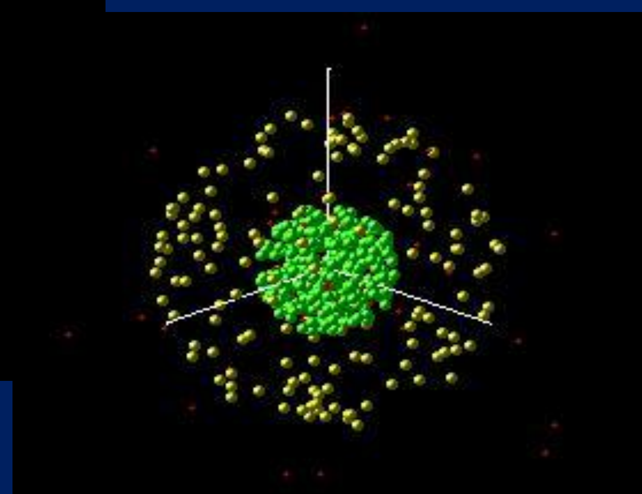
3. (Pure) ice is not heated, because of rigid crystal structure due to hydrogen bonds

4. Salty ice is melted by loosening of hydrogen bonding by salt ions

Tanaka & Sato, J.Chem.Phys. (2007); JMPEE (2008)

Absorption of EM wave energy

1. Laser light - <u>high frequency</u> (infrared, 800nm)
   Electrons first absorb energy, followed by
      Expansion of hot electrons
      Coulomb explosion of non-neutral ions (H+, Li+)

Murakami and Tanaka, Phys.Plasmas (2008)

Absorption of EM wave energy (2)

Microwaves - <u>Low frequency</u> (2GHz)

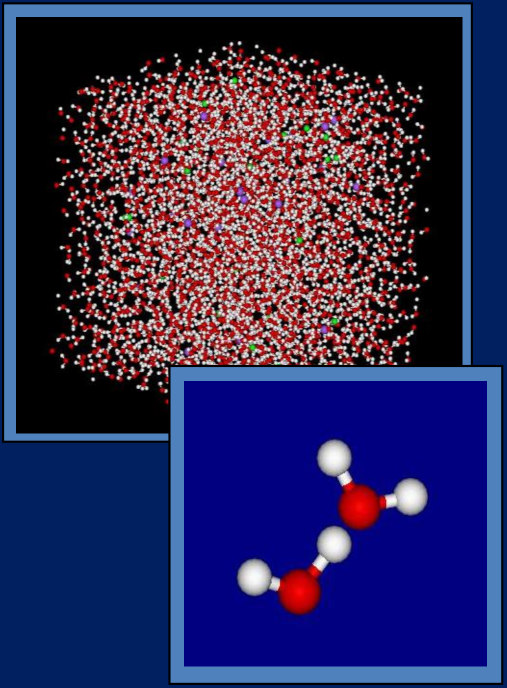
2a. Water (liquid):

small-angle rotation of molecules

-> relax to molecular translation

2b. Ice (solid): *no absorption*

Tanaka and Sato, JCP (2007); JMPEE (2008)



3. Magnetite:

agitation of electron spin in 3d orbital

-> relax to atomic vibrations...

Tanaka, Kono and Maruyama, Phys.Rev. B (2009).

Absorption of EM wave energy (3)

Heating of water by far-infrared waves

New features

1. Intra-molecular vibrations occur in far-infrared range

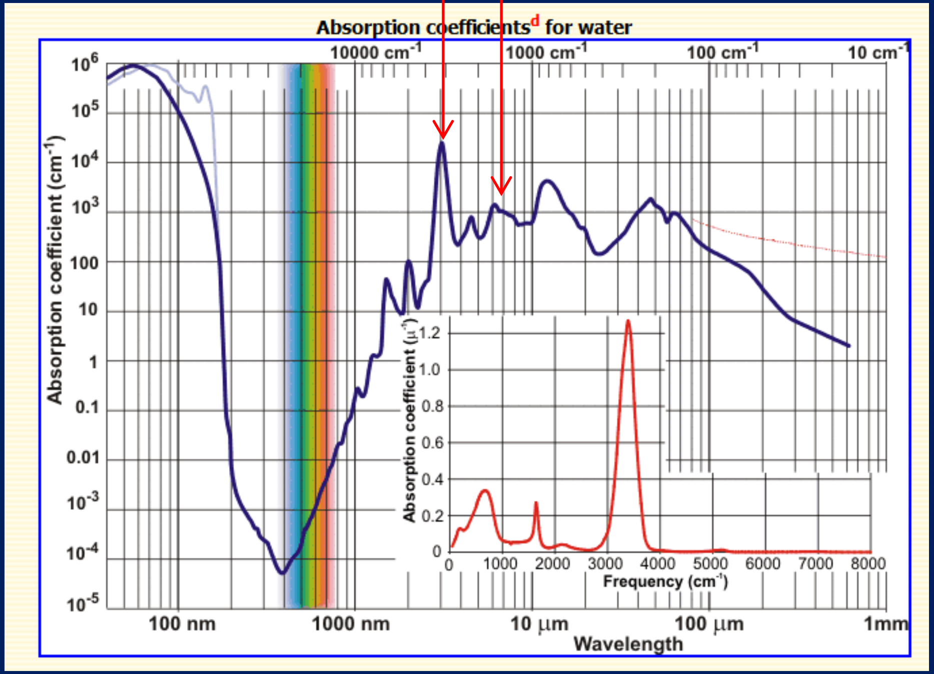
O-H bond stretching : 3490 cm^{-1} (105THz)

H-O-H bending: 1644 cm^{-1} (49THz)

O-H

H-O-H

Absorption coefficient



http://www.lsbu.ac.uk/water/

Absorption of EM wave energy (continued)

1. Intra-molecular vibrations occur in far-infrared range
2. Electric polarization of molecules may play a major role…

-> 1 & 2 are the effects of *quantum mechanics*
We need a tool of QM for many-body problems !

cf: *Classical (Newtonian) dynamics*
– basically for fixed charges under prescribed forces

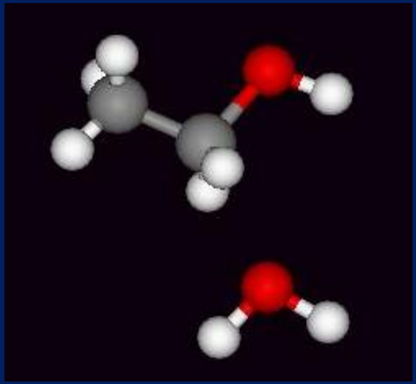
Quantum mechanical molecular dynamics

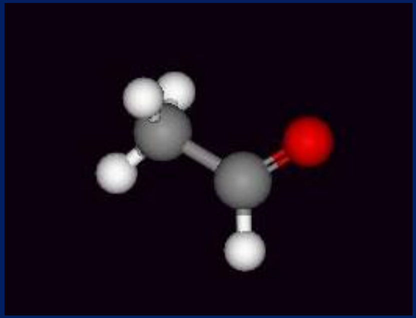
When electron distribution in molecules (charge cloud) is distorted
– by collision, chemical reactions

Electron distribution must be determined by quantum mechanics

✖ *However, Schroedinger eq. can treat only a few-body problem !!*
So, …

ethanol





acetoaldehyde

Quantum mechanics by DFT MD

Three approximations

(1) Separate quantum electrons and classical ions

(2) Assembly of single electrons (via exch-correl)

(3) Ground-state electrons

Schroedinger eq. is reduced to that for electron density

Kohn-Sham equation (Density Functional Theory)

$$\left[-\frac{\hbar^2}{2m}\nabla^2+\upsilon_{KS}(r,t)\right]\varphi_i(r,t)=\varepsilon_i\varphi_i(r,t)$$

electron density $n(r,t)=\sum_i^{occ}\left|\varphi_i(r,t)\right|^2$

$$\upsilon_{KS}(r,t)=\upsilon_{ext}(r,t)+\int d^3r'\frac{e^2n(r,t)}{\left|r-r'\right|}+\upsilon_{xc}(r,t)$$

The DFT molecular dynamics

SIESTA code (Spanish Initiative for Electronic Simulations of Thousand Atoms, J.M.Soler et al., http://www.uam.es/siesta/)

* Atomic-orbital basis set

- *faster than the plane-wave basis codes*

* Exchange-correlation potential:

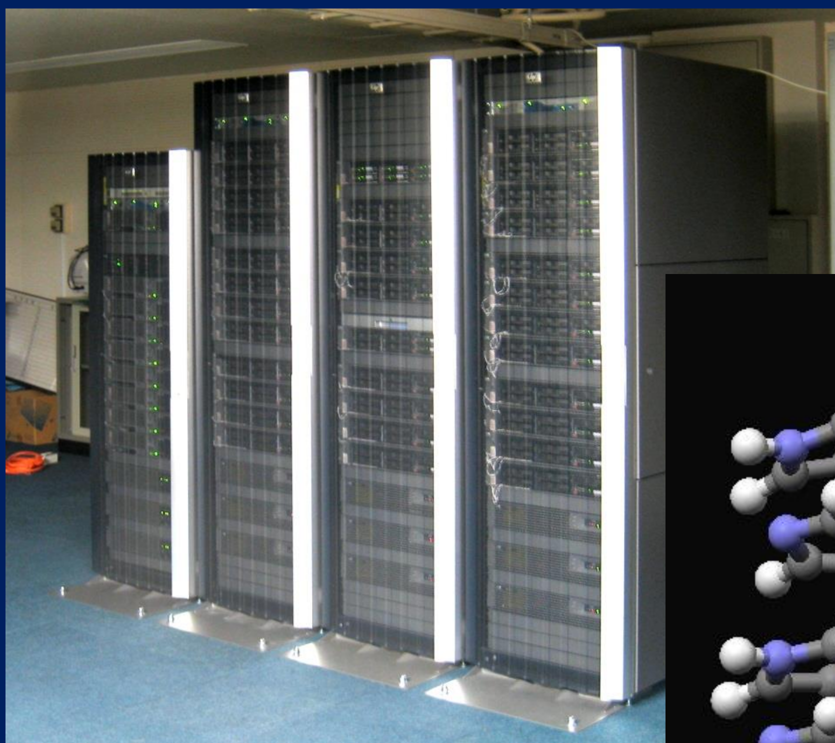
- *choice of PBE functional with GGA*

* Coded for MPI parallel machines

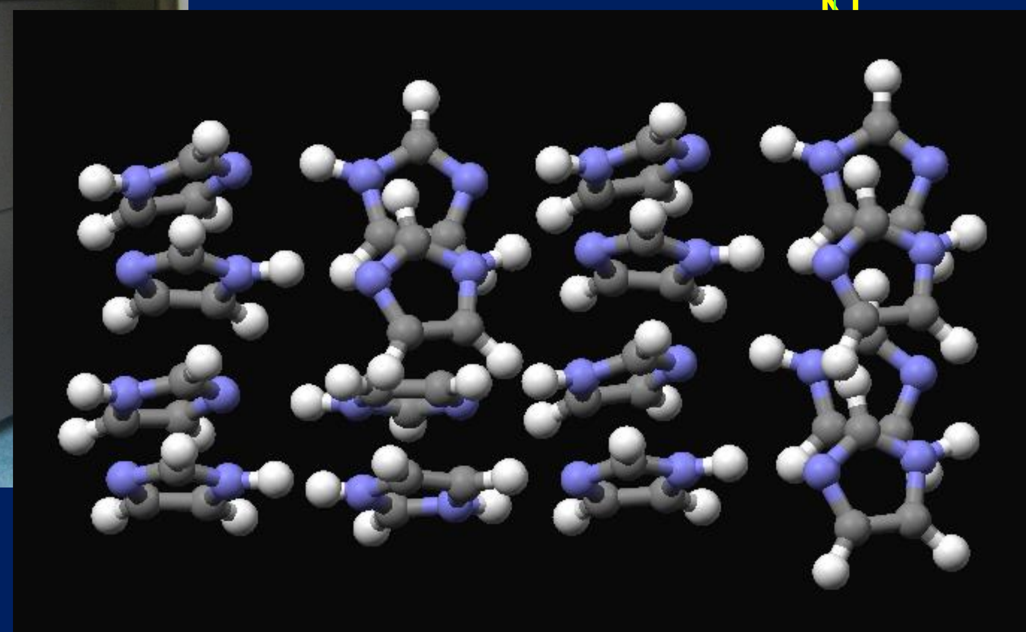
- *optimum # of procs depends on # of atoms*

DFT simulation by cluster computer

Low-latency network is essential



AMD Opteron
64(2.8GHz) + 40cpu(2.6GHz)
+ Infiniband interconnect



Ion liquid imidazole which consists of organic molecules with high electrical conductivity

Geometry of simulation

To obtain an organized structure

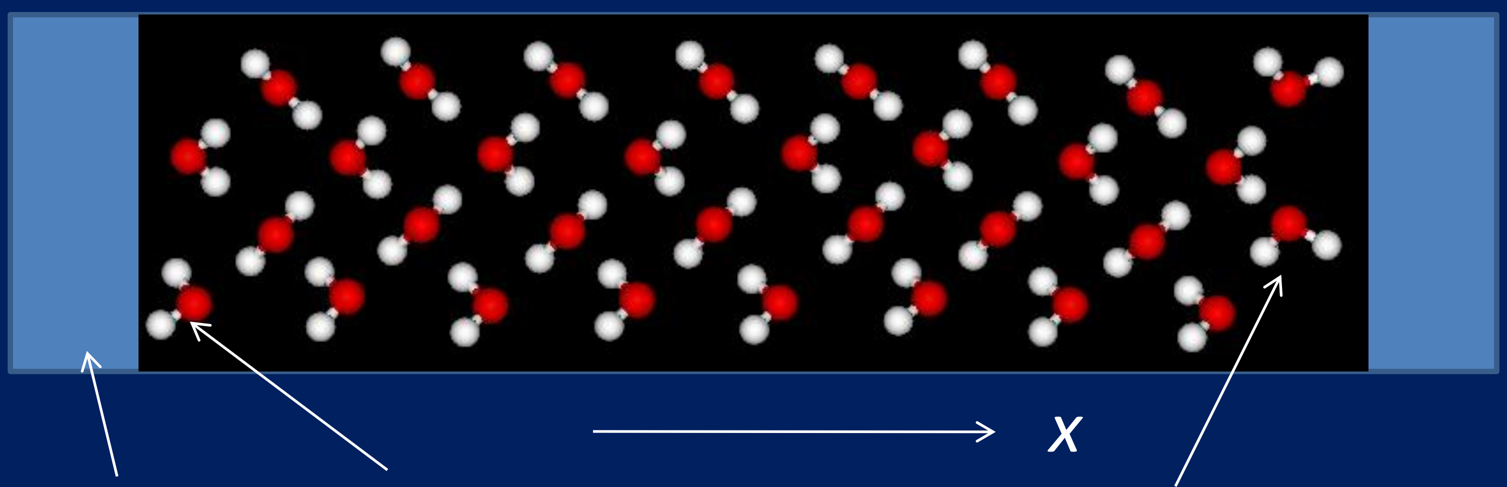
–> Generate ice, randomize it at a finite temperature

Non-periodicity in boundary conditions

- Needed to apply a (uniform) E field in Siesta

- Polarization requires non-periodicity

$$E_x(t) = E_0 \sin \omega t$$

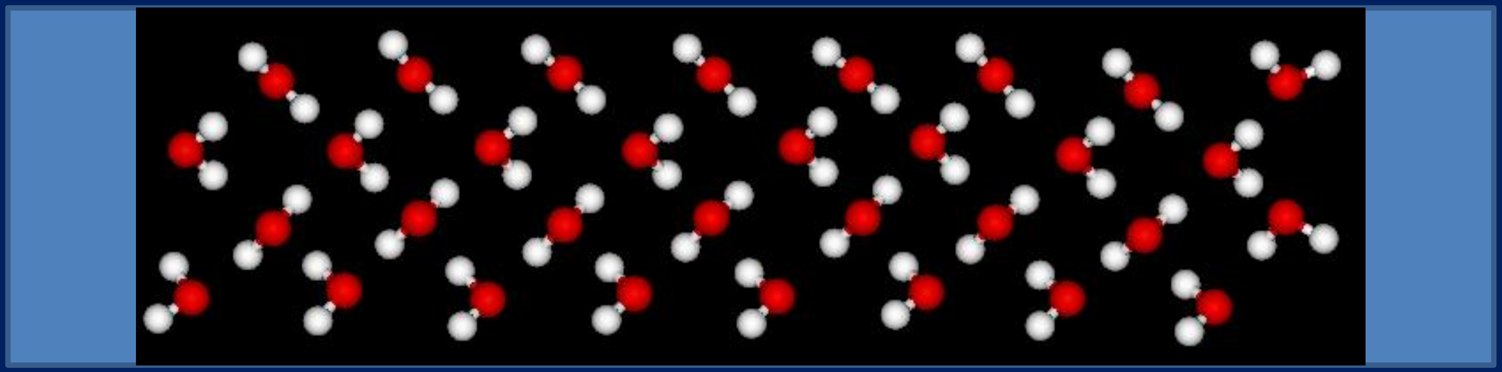


vacuum region

Fix the guiding-center positions of molecules in edge region

Geometry of simulation (2)

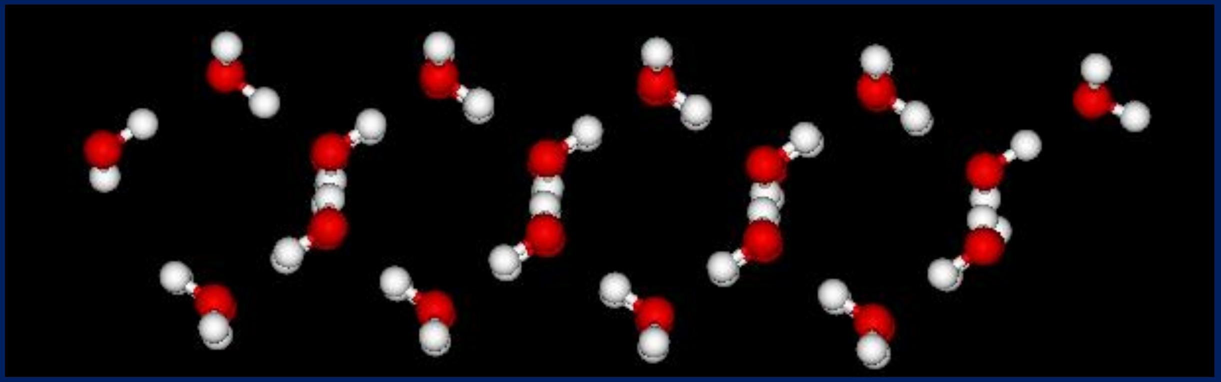
Rectangular box $6.2\,\mathring{A}\times 6.2\,\mathring{A}\times 33\,\mathring{A}$



Apply electric field $E_x(t) = E_0 \sin \omega t$ $\omega/2\pi = 5$ THz

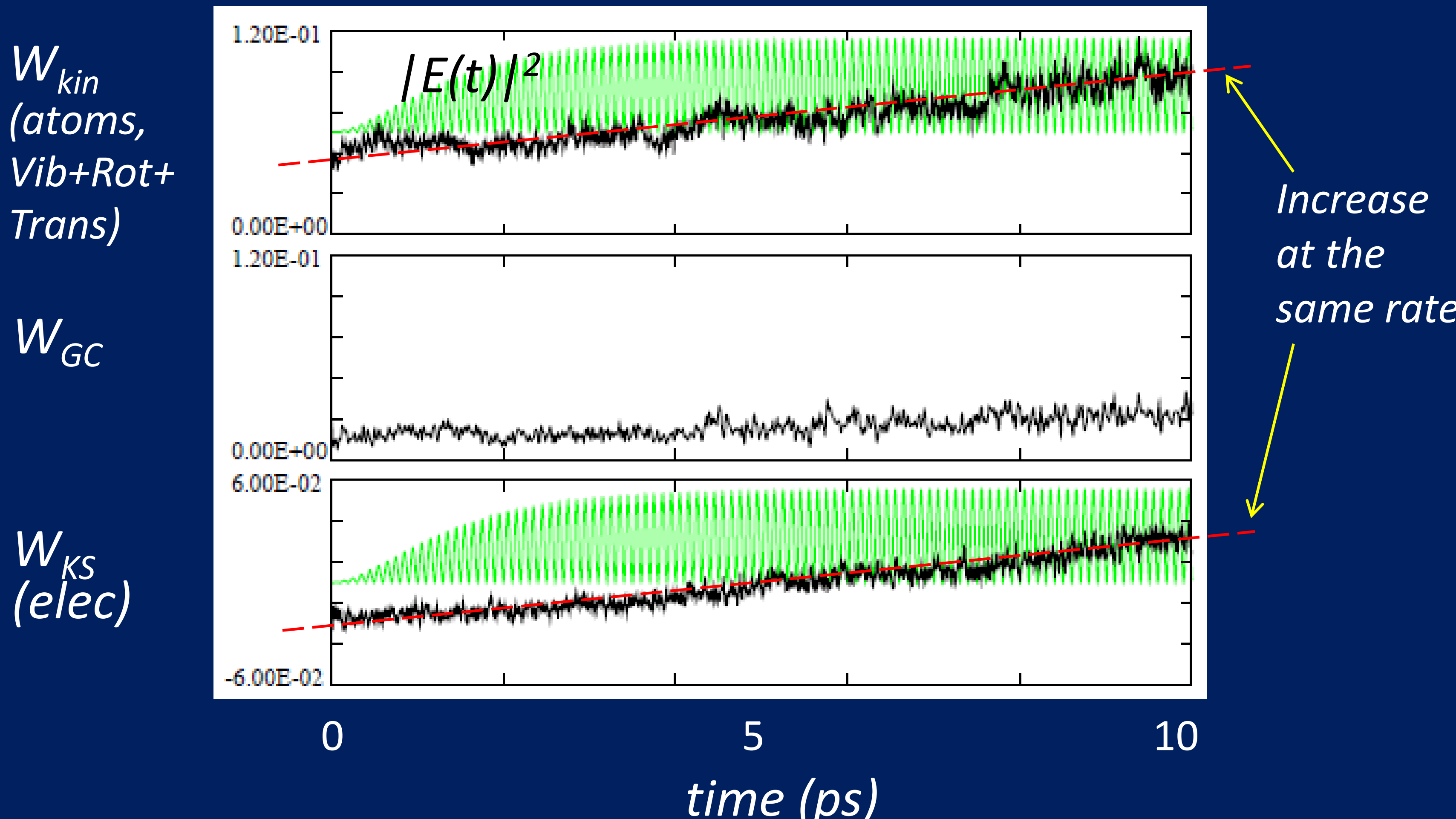
$\Delta t = 1$ fs

view from an oblique direction



Results: Energy history for Liquid water

f = 5THz (period 0.2ps), E = 0.1 V/Angstrom



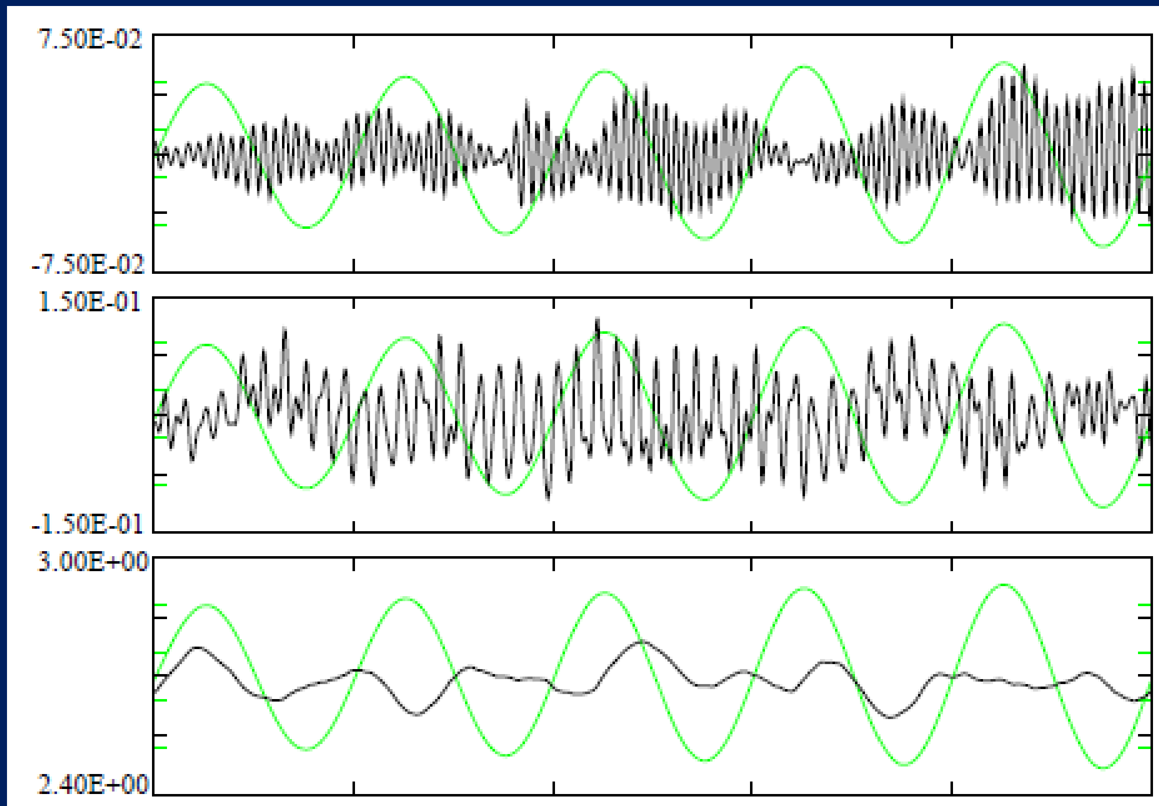
Intra-molecular vibrations (of H_2O)

O-H bond = 0.97 Ang

$\Delta\ell_{O-H}$
(bond stretching)

$\Delta\ell_{H-H}$
(bending)

ℓ_{O-O}
(molecular distance)



1.00 1.50 2.00
time (ps)

$96 \pm 5\,THz$

$50\,THz$

O-H bond stretching: 105 THz, H-O-H bending: 49 THz

Water: Intra-molecular vibrations

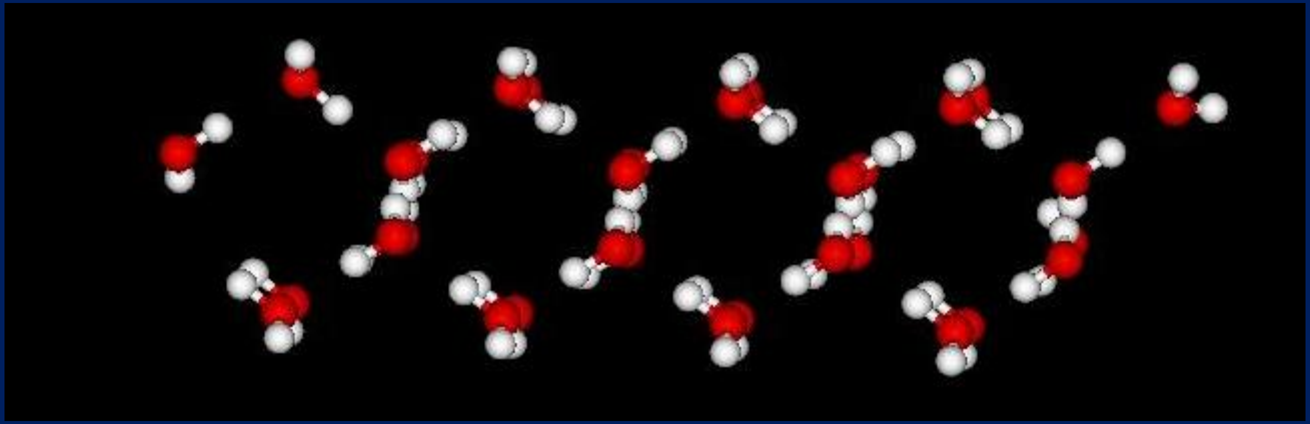
At room temperature

-> molecules are constrained by hydrogen bond

- make intra-molecular vibrations: H-O, H-O-H

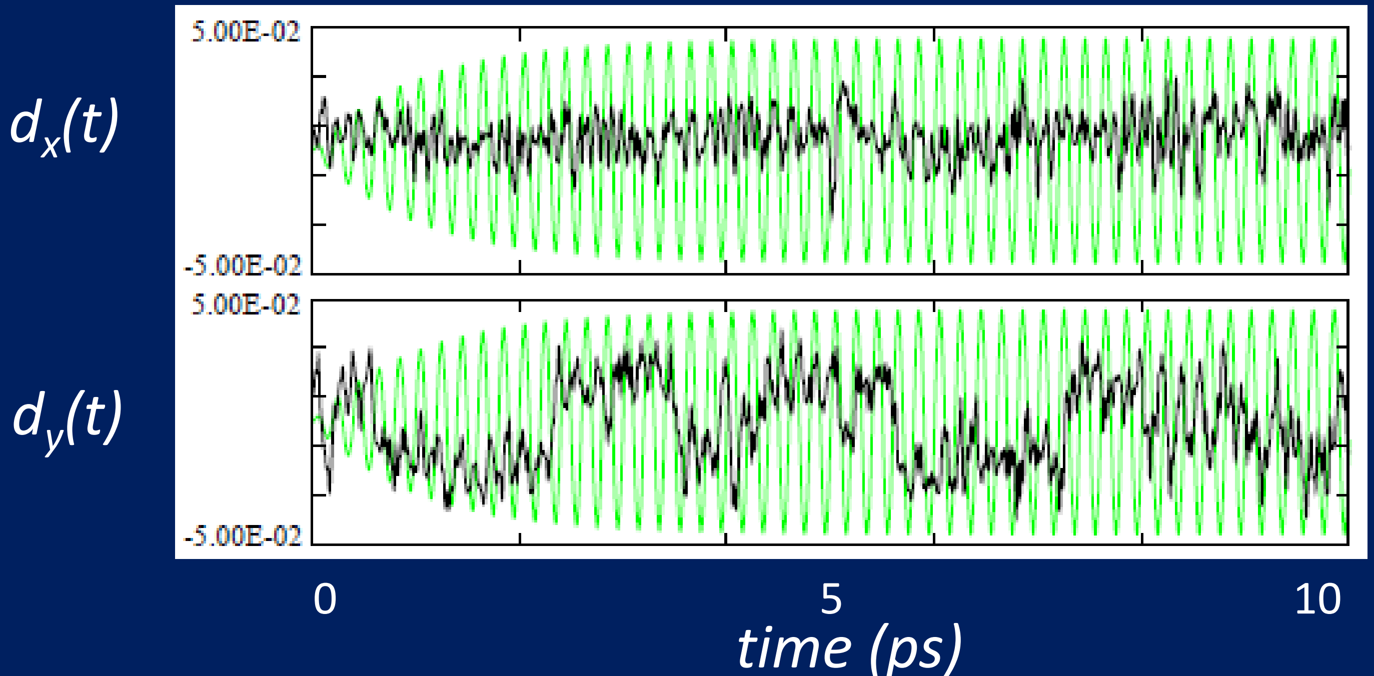
- relax to intermolecular motions

(i.e., rotation + translation)



animation

Time history of dipole moment



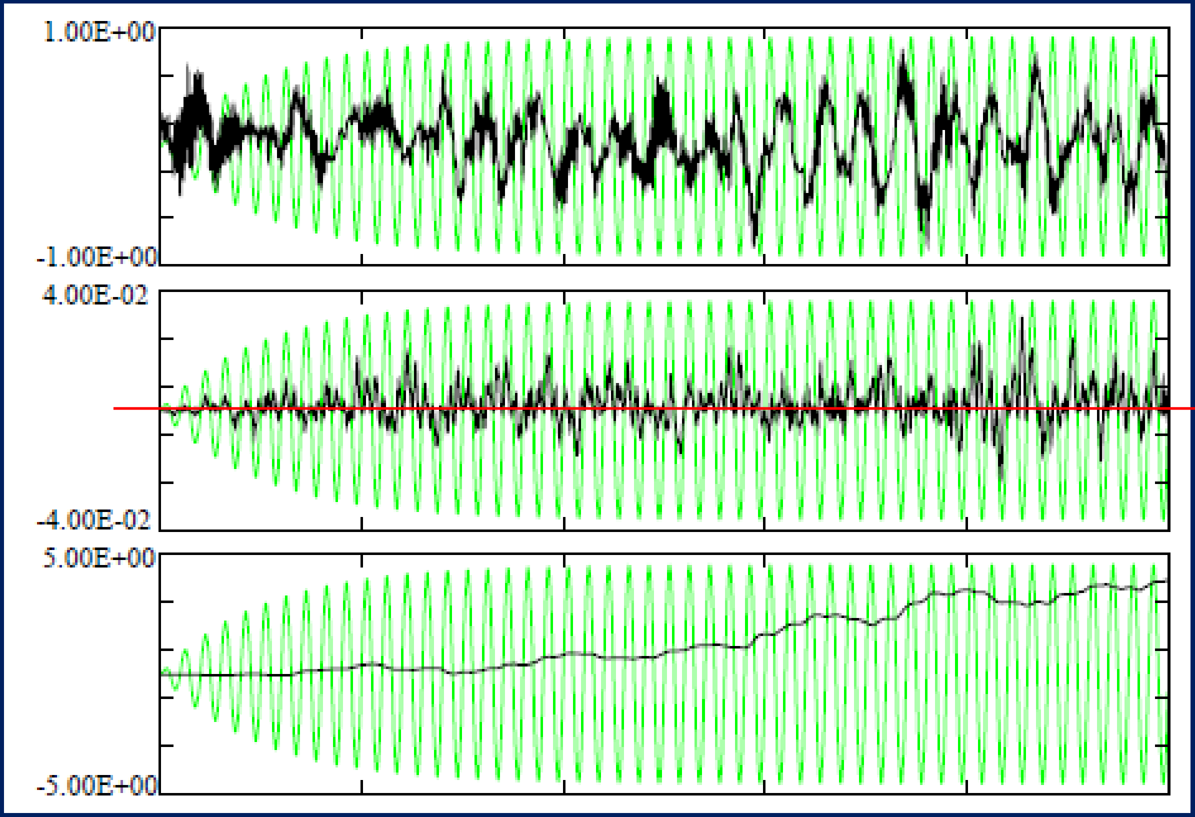
>> Dipole (rotation) itself and E-field
– do not have correlation

Electric polarization

$D_{ind}(t)$

$D_{ind} \bullet E$

$\int D_{ind} \bullet E \, dt$



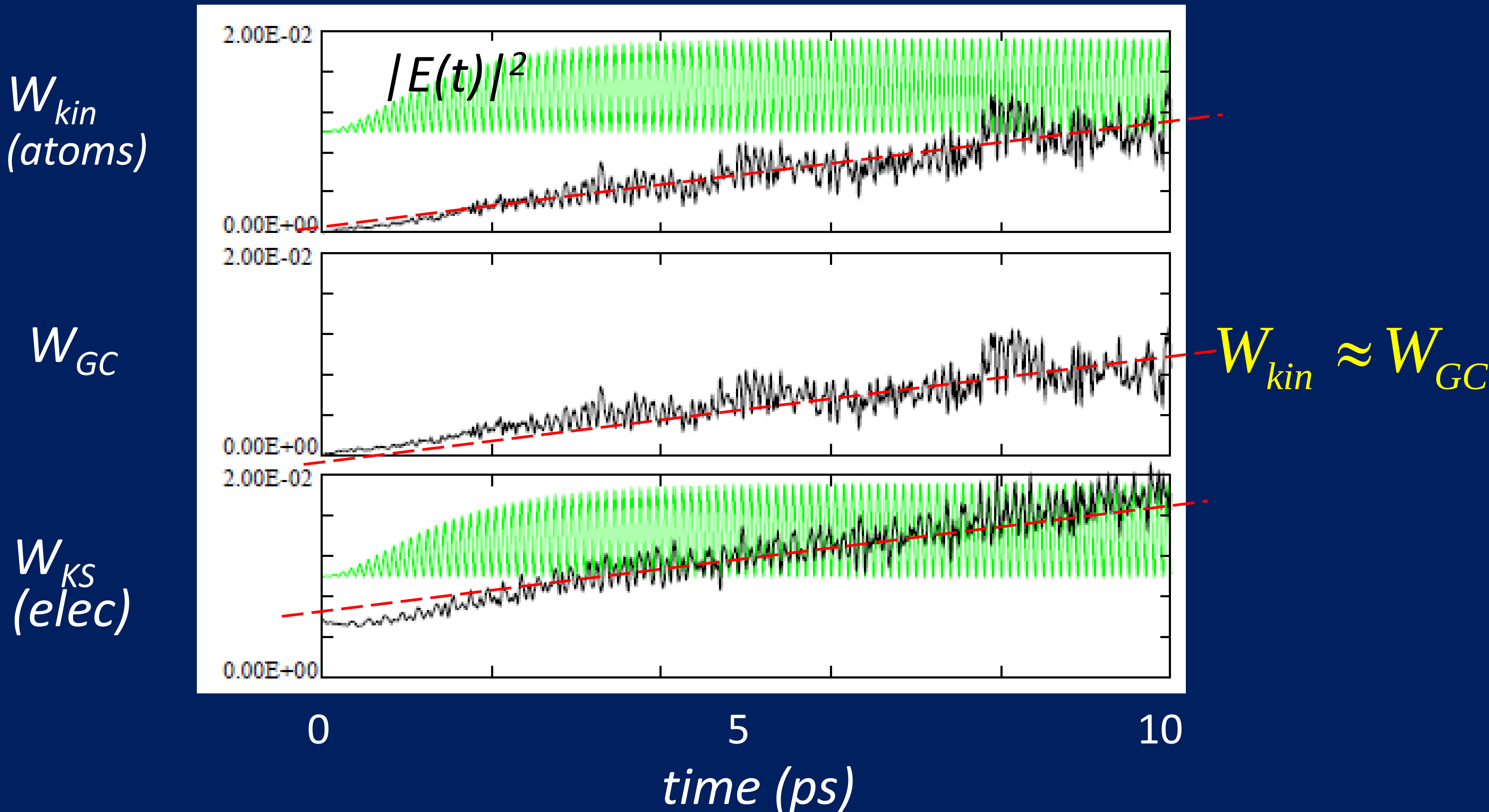
0 5 10

time (ps)

>> Wave E-field -> induce electric polarization
-> excite intra-molecular vibrations
-> relax to translation

Energy history: for Solid ice

f = 5THz (period 0.2ps), E = 0.1 V/Angstrom



>> Heating rate for ice = 1/5 that of liquid – not tiny !!

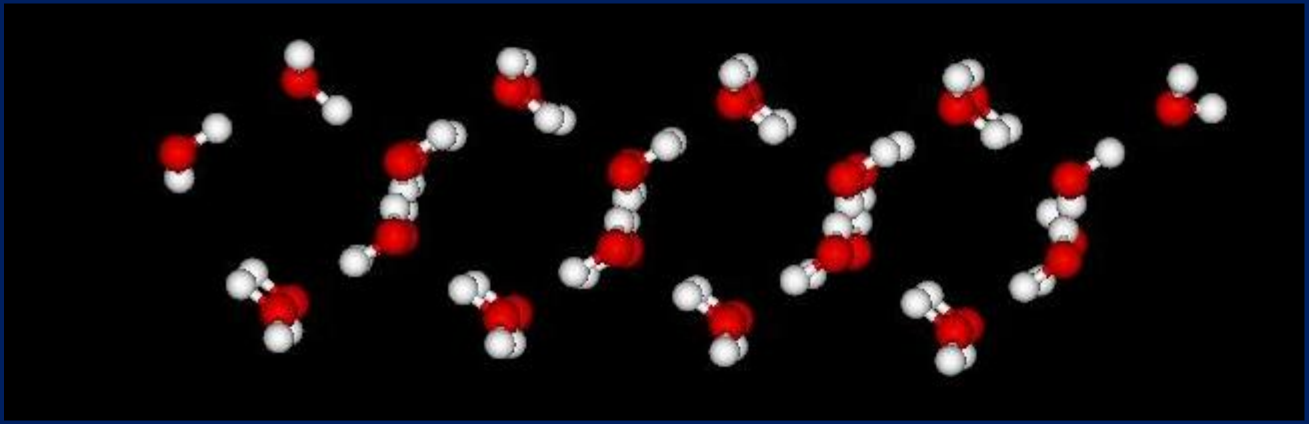
Ice: Inter-molecular vibrations

At very low temperatures

-> molecules are constrained, nearly frozen

- no intra-molecular or rotational vibrations,

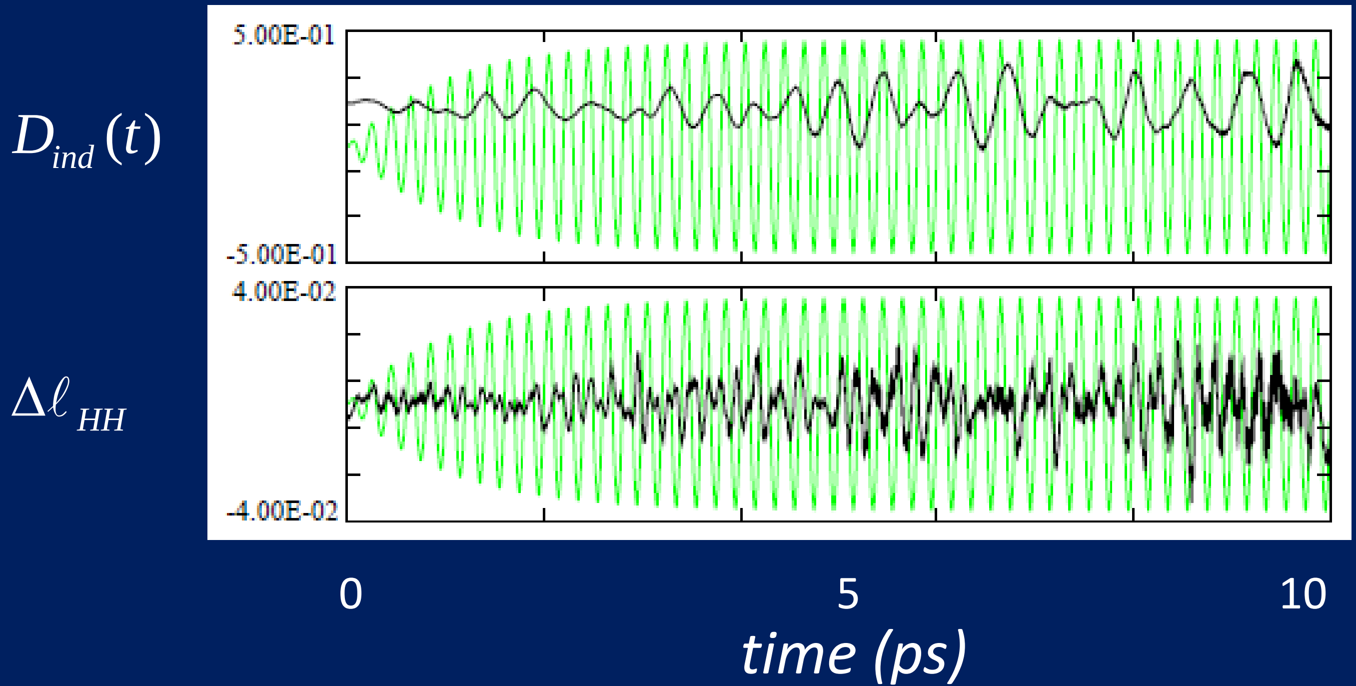
but inter-molecular vibrations



animation

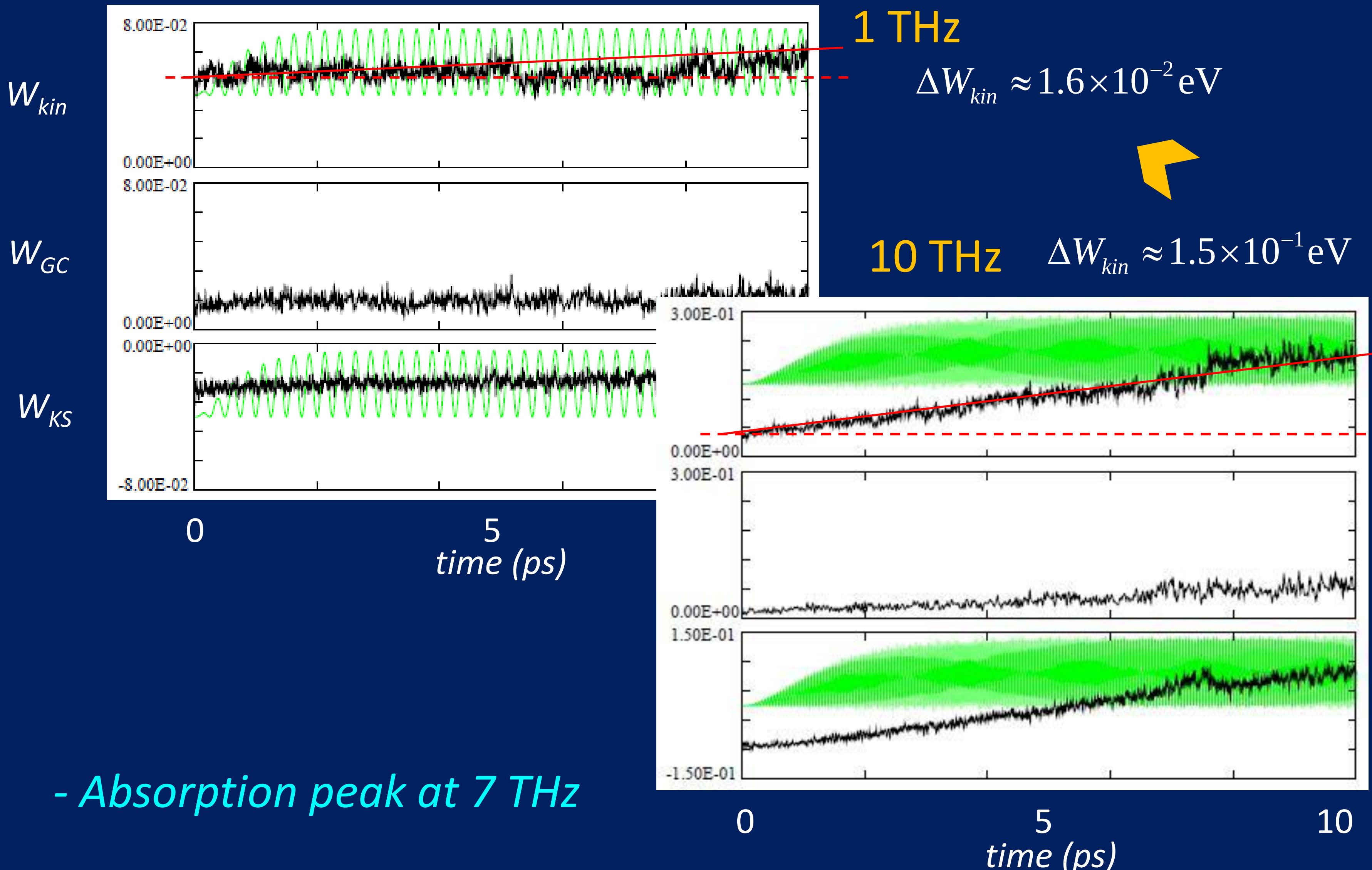
>> Electric polarization -> inter-molecular vibrations

Time history of polarization, for ice



$$We\ have: \int D_{ind} \bullet E\ dt > 0\ !$$

Frequency dependence



- Absorption peak at 7 THz

Summary

- Far-infrared (THz) waves heat water (both in liquid and ice phases) due to induced electric polarization

- Energy paths

  For liquid:

  wave -> intra-molecular vibrations: fast

  -> relax to translation: slow

  For ice: wave -> directly to translation: slow

- Frequency dependence of heating

  ..... For 1THz < for 5THz < for 10THz

Planned Studies

- *Resonance case (in progress)*
  - *around 50 THz*

** Water heating in gas phase (in progress)*
  - *small effect of hydrogen bonds ?*

** Interactions of water with organic molecules*
  - *structuring effects on heating and….*

  - *ionic species*
    possible if non-periodic ?

Our Theoretical Studies of Heating

1. Fe_3O_4 (magnetite) +GHz waves:
   - *Response of electron spins to H-field*

   Phys.Rev.B (2009)

2. H_2O + GHz waves (microwave):
   - *Response of molecular rotation and acceleration of salt by E-field*

   J.Chem.Phys.(2007)

   JMPEE (2008)

3. H_2O + THz waves (far-infrared wave):
   - *Induced electric polarization by E-field*

   Ampere (2011), GCMEA-2

Mechanism of Heating by GHz-THz Waves

"Depending on materials and frequency of electromagnetic waves, different energy absorber (either electron spin, molecular rotation, polarization) responds to these waves."

There is always a counter-process (collision) that hinders synchronization. Hence, the occurrence of finite phase-lag -> non-zero tan δ.
cf: The Lenz law of electromagnetism

Then, EM wave energy is irreversibly transferred to material.

Kamikochi, Japan Photo by M.Tanaka (2004)