Molecular energy transfer in liquid water

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Motivation

- **Liquid water** is the matrix of life.

  *‘Be water my friend’*

  Bruce Lee

- Water molecules in **nonequilibrium energy states** can be found all around, also capital in technology.
How do excited states of a water molecule relax back to equilibrium?

- These are **ultrafast processes**: picoseconds ($10^{-12}$ s) down to femtoseconds ($10^{-15}$ s)

- Ultrafast **spectroscopy** is currently able to probe the fundamental aspects: controlled vibrational/rotational excitations are produced and followed in time.

- And **computers** allow us to calculate and understand these processes.
Molecular structure in a nutshell

Let’s consider a **diatomic** molecule:

a bunch of electrons plus two nucleae

**Born-Oppenheimer approximation:**
Electrons are 2,000 times lighter, so we might consider that the nucleae move in the potential energy surface defined by the electrons ...
...what will result in a series of associated vibrational levels
Don’t forget rotations!
Water: vibrations and rotations

Vibrational modes

- Symmetric Stretch: 3657 cm\(^{-1}\)
- Bend: 1595 cm\(^{-1}\)
- Asymmetric Stretch: 3756 cm\(^{-1}\)

Rotations

And we stay on the ground electronic surface
H$_2$O/D$_2$O spectrum gas phase

Ground

H$_2$O

Bend fundamental

Stretch fundamental

D$_2$O

(001) ASYMMETRIC STRETCH
(100) SYMMETRIC STRETCH
(020) BEND OVERTONE
(010) BEND FUNDAMENTAL
(000) GROUND STATE
When we come to the liquid

A bunch of frequencies are now possible, mostly for the stretch

(Rey et al. 2002)
$\text{H}_2\text{O}/\text{D}_2\text{O}$ spectrum liquid phase

- **Librations**
- **Bend**
- **Stretch**

$\text{H}_2\text{O}$

$\text{D}_2\text{O}$
Pump-probe spectroscopy

FIG. 2. Transient infrared probe spectra of HDO:D$_2$O (}
How do vibrational and rotational relaxation take place?

Of course we want to know in liquid water!

MOLECULAR DYNAMICS:

- Integration of the classical equations of motion, ...

- Equilibrium averages over a ‘trajectory’

- Or non-equilibrium averages over several initially perturbed trajectories
More convenient for HOD in D$_2$O

$\tilde{\nu}_1 = 2530 \text{ cm}^{-1}$

O-D stretch

$\tilde{\nu}_2 = 1450 \text{ cm}^{-1}$

Bend

$\tilde{\nu}_3 = 3430 \text{ cm}^{-1}$

O-H stretch

[Graph showing vibrational modes and spectral data]
The semiclassical Landau-Teller approach

Relaxation rate of deuterated water (HOD)

\[ H = H_{\text{HOD}} + H_{\text{coupling}} + H_{\text{Bath}} \]

\[ H_{\text{coupling}} = H_{V-B} + H_{\text{Cor}} + H_{\text{Cen}} \]

\[ H_{V-B} = -\sum_{i=1}^{3} q_i F_i \]

Transition rate constant (bath contribution)

\[ k_{if} = \gamma_{if} \int_{-\infty}^{\infty} dt e^{i\omega_{if}t} \sum_{s,s'} \langle i|q_s|f\rangle \langle f|q_{s'}|i\rangle \langle F_s F_s'(t) \rangle \]
One HOD molecule is kept rigid and the forces exerted by its D$_2$O neighbors are computed during a long equilibrium trajectory.
Available pathways for the OH mode
The way down the vibrational ladder

Recent experimental access to bend and librations in pure water

- Elsaesser et al., JPC A ’07
- Bend relaxation
  - 170 fs
- Librations
  - < 100 fs

- We will initially focus on BEND RELAXATION
What is going on the final step?

- Relaxation time $\sim$ Fourier transform of force-force time correlation function at transition frequency of the bend.

What does this really mean?
Reasons for a more convenient approach

- Experiments seem to rule out VV transfer.
- Small anharmonicity of the bend.
- Reasonable good classical harmonic behavior for times up to ~ 0.2 ps.
- Equivalence of quantum and classical relaxation rates for harmonic models.
- A classical simulation (one flexible molecule with harmonic bend) might be a reasonable thing to do ...
Not that bad

Relaxation time $270 \text{ fs}$
(expt. $170 \text{ fs}$)

Ingrosso, Rey, Elsaesser, Hynes
JPC A 113, 6657 (2009)

**Figure 3.** Simulations of the average $\text{H}_2\text{O}$ bend energy relaxation after excitation of one water molecule, immersed in rigid, SPC/E water. a:
Trying to follow excess energies…

Vibrational energy

Rotational energy of excited water

Rotational energy of 4 closest neighbors

Translational energy of excited water

Translational energy of 4 closest neighbors.
Ultra-ultra-fast rotational and translational energy relaxation
An approach we can ‘see’

Solvent spatial distribution of work done on the CH$_3$Cl vibration during a vibrational period

Whitnell, Wilson, Hynes (1991)
Plan

- A classical computation seems to be good enough.
- During the relaxation process we compute not only the energies but also the *work done by the neighbors of interest*.
- Hopefully we will “see” where the energy goes.
Our case: bend relaxation

\[ \frac{dE_v}{dt} = \sum_i F_{i, ext} \cdot \dot{v}_i - \frac{m_H R^2 \sin \theta}{2M} (m_O \omega_x^2 - M \omega_y^2 - 2m_H \omega_Z^2) \dot{\theta} \]

\[ \Delta E_v(t) = \int_0^t P_{vib}^{ext} dt + \int_0^t P_{vib}^{VR} \equiv W_{ext}(t) + W_{VR}(t) \]

\[ W_{ext} = W_{12}^{V(C)} + W_{34}^{V(C)} + W_{bulk}^{V(C)} \]
So ... who are the culprits?

Rey, Ingrosso, Elsaesser, Hynes JPC A 113, 8949 (2009)
An inside job: Fermi resonance

- **Centrifugal coupling**

\[
H_{Cen} = -\frac{\hbar^2}{2} \sum_{\alpha, \beta} \sum_s \frac{L_\alpha L_\beta}{I_\alpha I_\beta} a_s^{(\alpha, \beta)} \frac{1}{\omega_s^2} q_s
\]

- **2:1 Coupling → 1 bend quantum to 2 rotational quanta**

\[
\frac{dE_v}{dt} = \sum_i \overline{F}^\text{ext}_i \cdot \overline{v}_i - \frac{m_H R^2 \sin \theta}{2M} (m_O \omega_x^2 - M \omega_y^2 - 2m_H \omega_Z^2) \dot{\theta}
\]

- And x axis is taking up most of it
And who is *directly* involved outside?
We know who is taking energy from the excited molecule, but …

- What is it used for?
  - ... does it go to rotation? translation? potential energy?

- The formulas need to be turned inside out:
  - From: who does work on the central molecule? to ...
  - To which motion the central molecule is transferring energy?
Not so messy as it may seem

$$\Delta E^i_v(t) = - \sum_{j \neq i} \Delta U_{ij} - \Delta K^i_{CM} - \Delta K^i_R - \sum_{j \neq i} W^T_{ij} + \sum_{j \neq i} W^R_{ij}$$

They will tend to zero! and silently leave the stage to

- Vibrational energy increment
- Sum of increments for potential energy between i and neighbors
- Variation of center of mass kinetic energy for excited molecule
- Same for rotational energy
- Sum of works of excited molecule on translation of each molecule j
- Same for rotation
New angle on the case

\[ \Delta E_v(t) = W_{\text{ext}} + W_{V-R} = -\Delta E_T - \Delta E_R - \Delta E_P - \sum_i W_T - \sum_i W_R \]
And the winner is …

Excess vibrational energy

Excess potential energy variation (of excited molecule)

Excess rotational energy variation (idem)

Excess translational energy variation (idem)

Rey, Hynes PCCP 14, 6332 (2012)
Who gets the largest cut?
So this might be what’s going on

WATER BEND EXCITATION

3/5

SELF ROTATION

- 50% to 1st shell (preferentially to 3 and 4)
- 50% to waters out of 1st shell

2/5

NEIGHBORS

- 50% of this to 1 and 2 (15% to 3 and 4)
- 35% (only 10% of total initial energy) to outer waters

When all is said and done for the central molecule

~ 95% goes into rotations

60% of it to 4 closest molecules
Almost ALL to 1st+2nd shells

~ 5% into translations
Finally, the simplest case: pure rotational relaxation.

Equilibrium energy time correlation function shows it actually is <100 fs, and that linear responds holds.
But again, what is going on?

Rotational excitation at $t=0$ around different principal axis (colors)

- Total energy transfer
- Transfer to rotations
How rotations relax

Petersen, Moller, Rey, Hynes JPC B (2013)
Here is what might be going on

- **OH stretch relaxes into bend overtone**, with a small chunk of energy taken up by neighbors.

- **Bend overtone relaxes into bend fundamental**, with again some help from friends.

- **Bend fundamental relaxes into rotations**:  
  - 60 % gets channeled through self rotation.  
  - ~95 % ends up as rotations of immediate neighbors.

- **Rotations relax into rotations**: about 85% into rotations and 15% into translations.