Ab-initio Molecular Dynamics in the Nanosciences
(1) Applications

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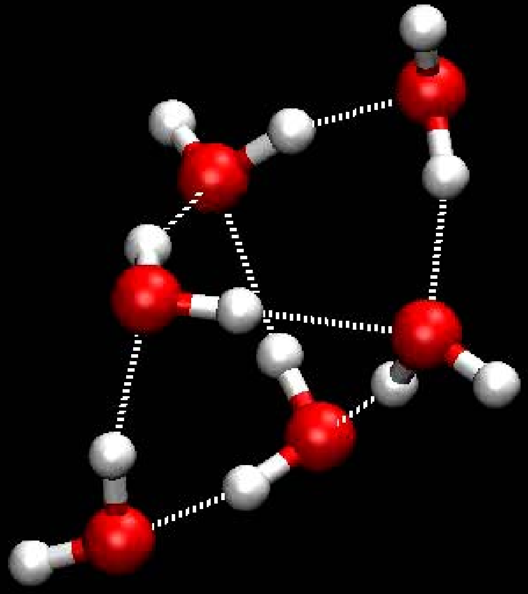


Regional School on Science at the Nanoscale, Hanoi December 2009

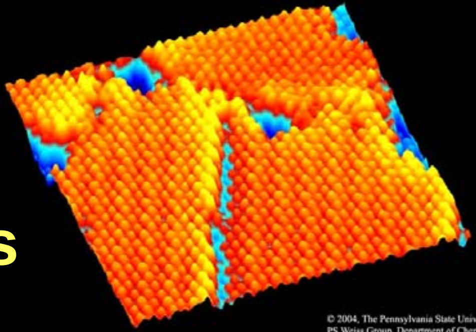
DEMOCRITOS
DEmocritos MOdeling Center for Research In aTOmistic Simulation INFM

Outline:

1. Car-Parrinello Molecular Dynamics

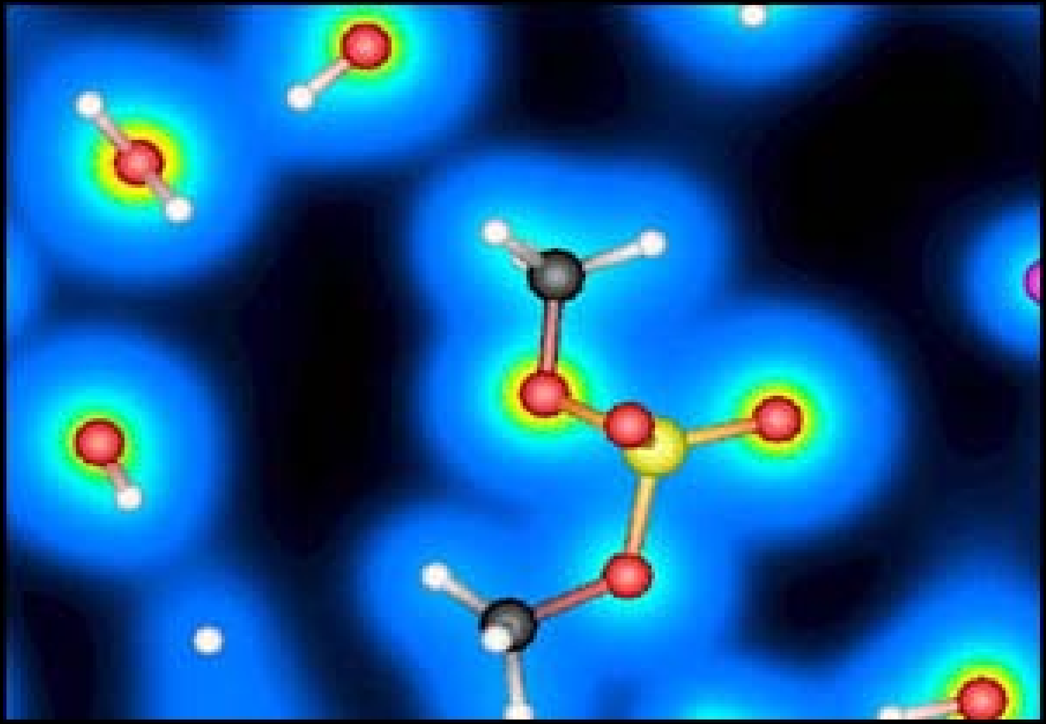
2. Two case studies:

Self-assembled monolayers on Gold surfaces
(understanding metal/organic interfaces)



Infrared absorption of water nanoclusters
(understanding the greenhouse effect)

Ab-initio molecular dynamics



"Molecular dynamics"
for atoms

$Ma = F = -dE/dR$

Schroedinger equation
for electrons

$H\psi = E\psi$

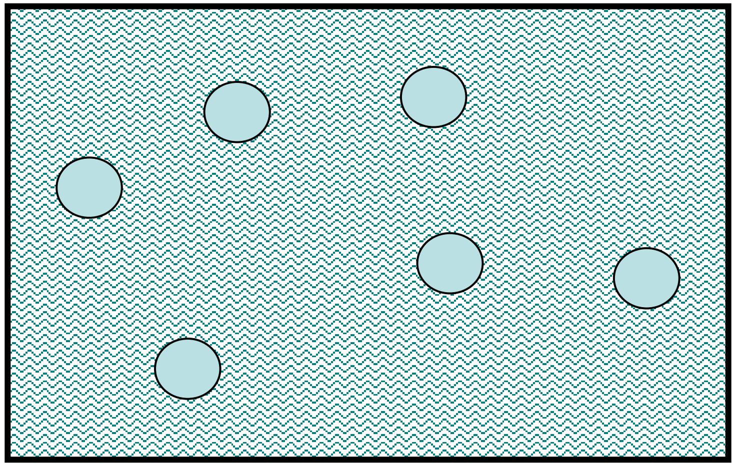
- e^--e^- interactions:
  - Density Functional Theory
- e^--nuclei interactions:
  - Pseudopotentials

"Ab-initio" molecular dynamics = Classical molecular dynamics in the potential energy surface generated by the electrons in their quantum ground state

How to keep electron in the ground state (1)

$$M_I \frac{d^2 R_I}{dt^2} = F_I = -\frac{dE(\{R\})}{dR_I}$$

$$E(\{R\}) = \langle \psi_0 | H_e(\{R\}) | \psi_0 \rangle$$



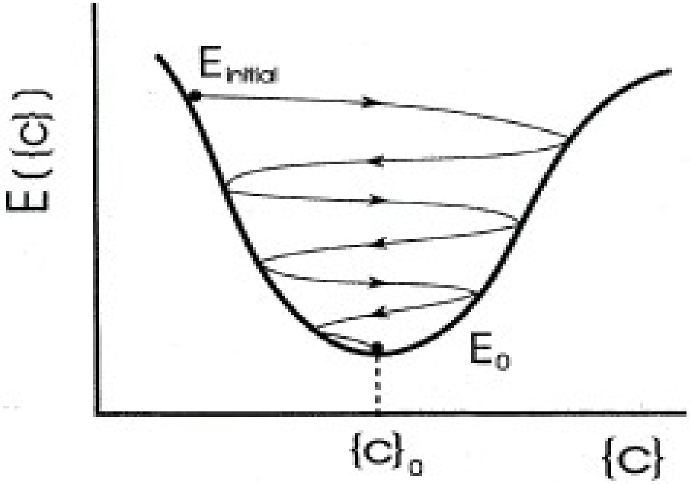
If we expand wavefunctions in a basis set

$$\psi = \sum_i c_i \varphi_i$$

$$\langle \psi | H_e | \psi \rangle = \sum_{i,j} c_i c_j^* \langle \varphi_i | H_e | \varphi_j \rangle$$

finding the ground state is equivalent to minimizing a quadratic form in the {c}'s (variational principle). So, standard minimization schemes can be used, e.g. steepest descent:

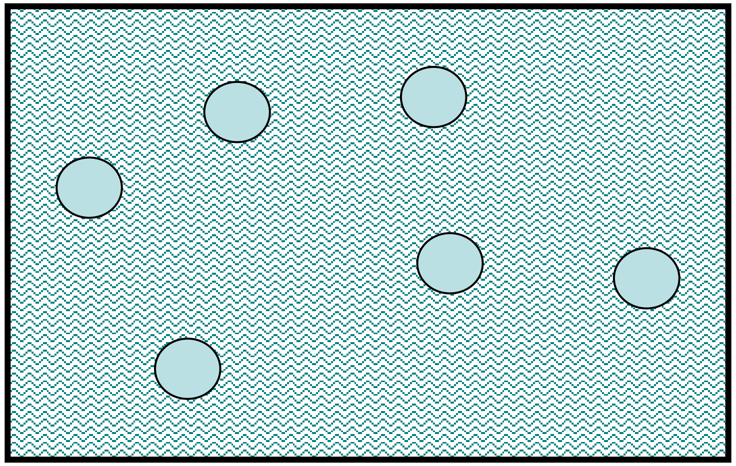
$$\dot{\psi} = -\frac{\delta}{\delta \psi} \langle \psi | H_e | \psi \rangle = -H_e \psi$$

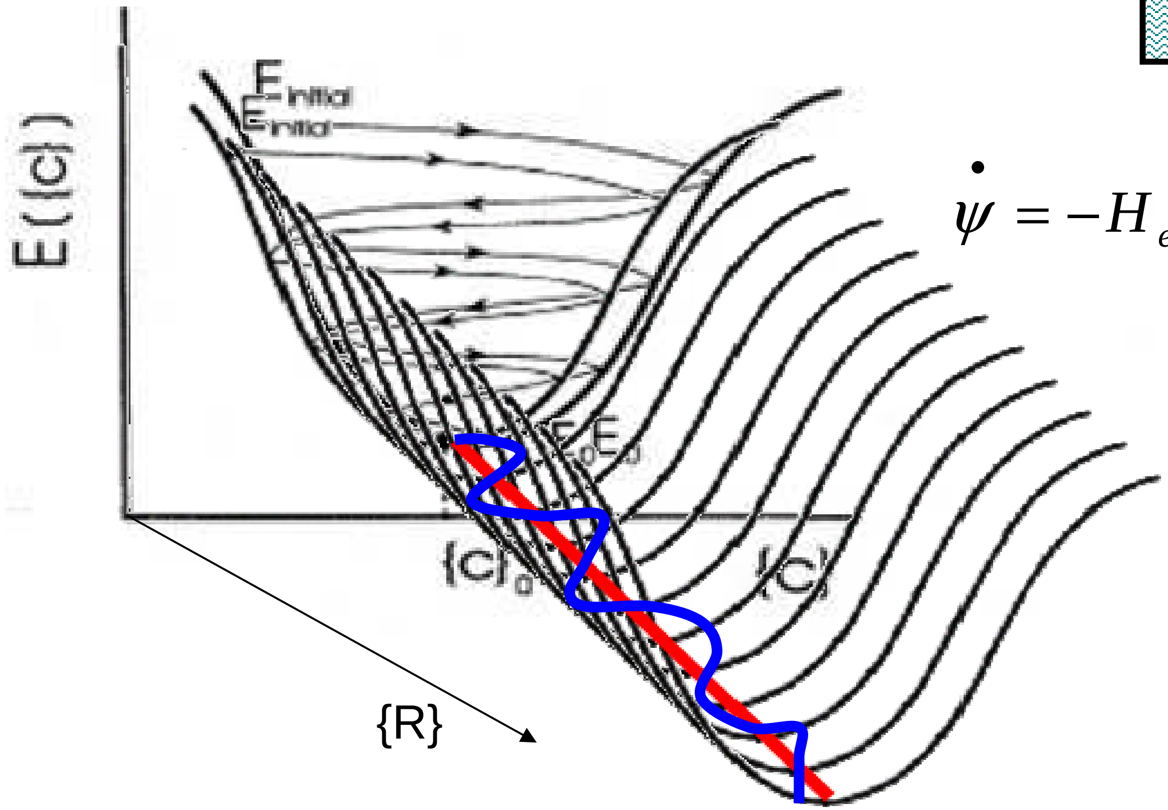


How to keep electron in the ground state (2)

$$M_I \frac{d^2 R_I}{dt^2} = F_I = -\frac{dE(\{R\})}{dR_I}$$

$$E(\{R\}) = \langle \psi_0 | H_e(\{R\}) | \psi_0 \rangle$$





$$\dot{\psi} = -H_e(\{R\})\psi$$ down to the minimum for each {R}

$$\ddot{\psi} = -H_e(\{R\})\psi \quad ???$$

$$M_I \ddot{R}_I = -\frac{dE(\{R\})}{dR_I}$$

The Car-Parrinello algorithm

Born-Oppenheimer -versus- Car-Parrinello AIMD

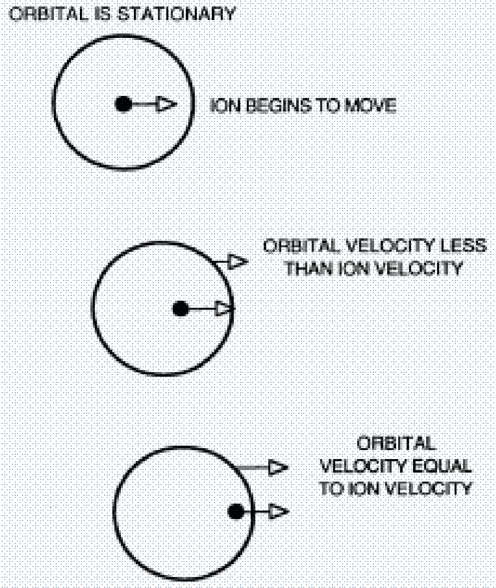


FIG. 24. Schematic illustration of how an orbital will eventually lag behind a moving ion during a simulation with $\mu\dot{\psi} = -[H-\lambda]\psi$, as discussed in the text. Convention the same as in Fig. 23.

Born-Oppenheimer

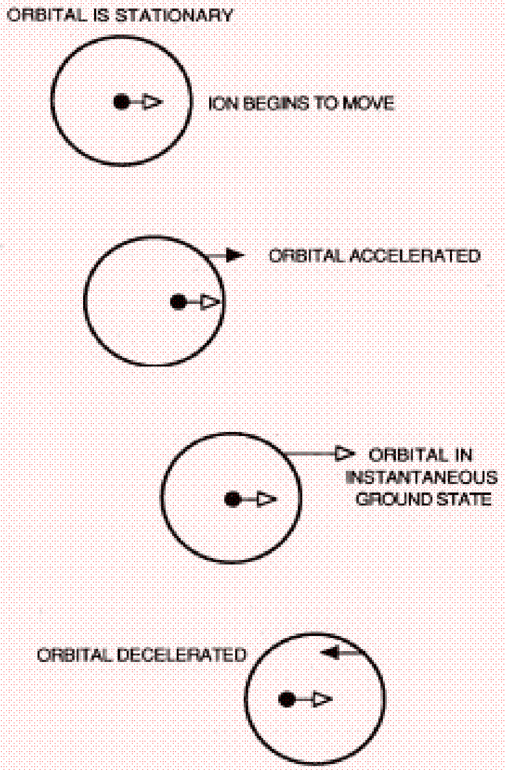


FIG. 23. Schematic illustration of how an orbital will oscillate around a moving ion during a simulation with $\mu\ddot{\psi} = -[H-\lambda]\psi$, as discussed in the text. Velocities and accelerations are designed as open and filled arrows, respectively.

Car-Parrinello

Born-Oppenheimer -versus- Car-Parrinello forces

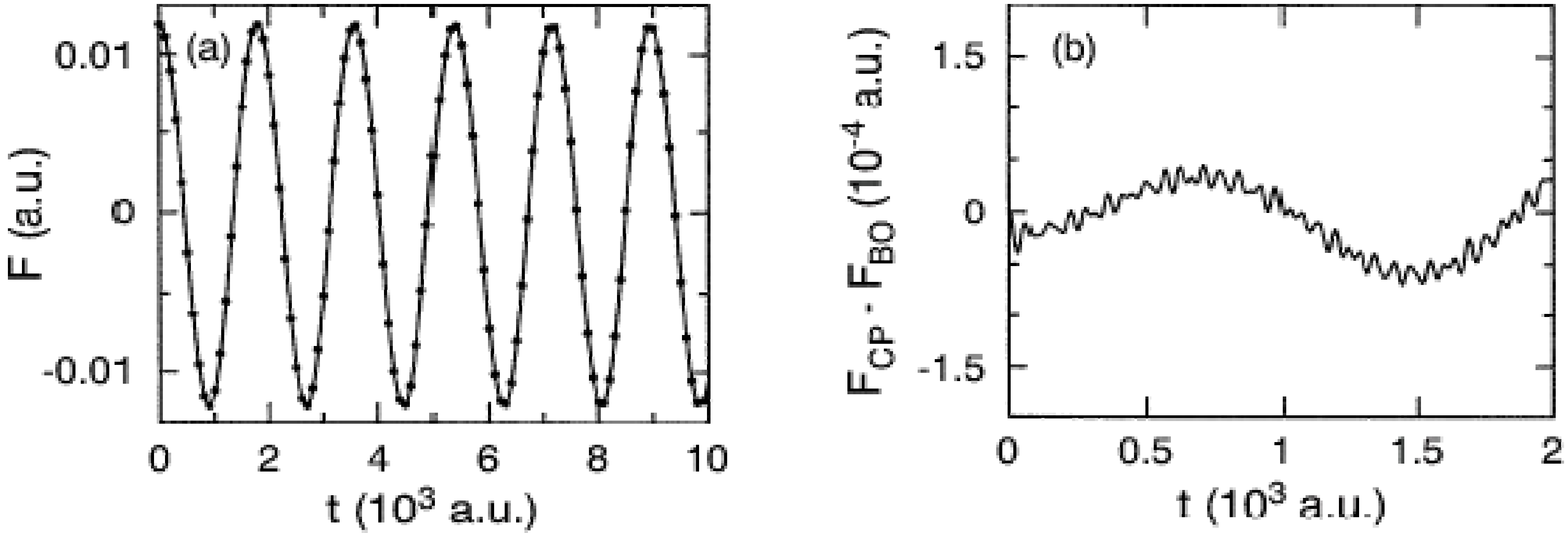


Figure 4. (a) Comparison of the x–component of the force acting on one atom of a model system obtained from Car–Parrinello (solid line) and well–converged Born–Oppenheimer (dots) molecular dynamics. (b) Enlarged view of the difference between Car–Parrinello and Born–Oppenheimer forces; for further details see text. Adapted from Ref. [467].

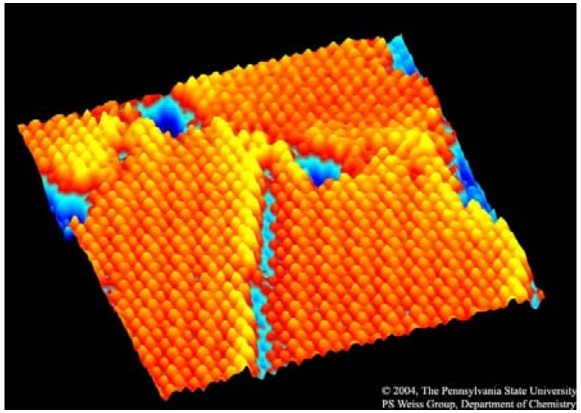
Two case studies:

Structure of thiols $S-(CH_2)_n-CH_3$ on Gold surfaces
(understanding metal/organic interfaces)

Infrared absorption by water nanoclusters
(understanding the greenhouse effect)

SAMs on gold

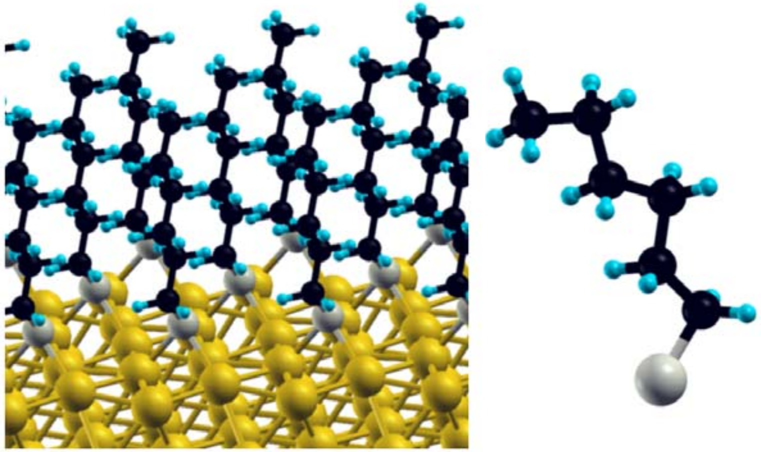
Self Assembled Monolayers (SAMs) of thiols on gold are prototypical metal-organic junctions of ubiquitous application in nanoscience



Weiss Group Pennsylvania State Univ.

Why are they attractive?

- ease of preparation
- tunability of surface properties via modification of molecular structure and functions
- use of SAMs as building blocks, e.g., for ``docking'‘ additional layers to a surface



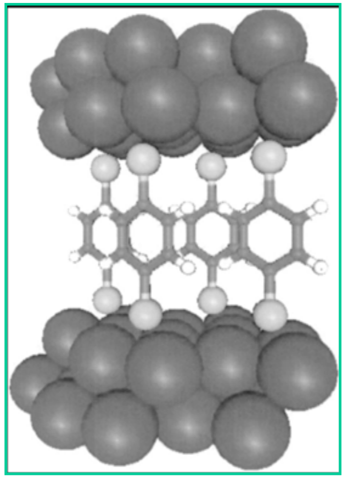
SAMs on gold

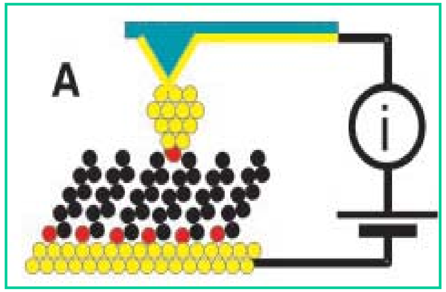
Applications of SAMs in
- molecular electronic devices
- biosensors
- nanolithography
- functionalized surface coatings

(Ulman, Chem. Rev. **96**, 1533 (1996), Schreiber, Prog. Surf. Sci. **65**, 151 (2000)).

Example: molecular devices

- single molecules as basic units of devices
- conductance depends on HOMO-LUMO gap
- thiols widely used because sulfurs bind strongly to the gold electrodes
- however, conductance depends strongly on exp. conditions

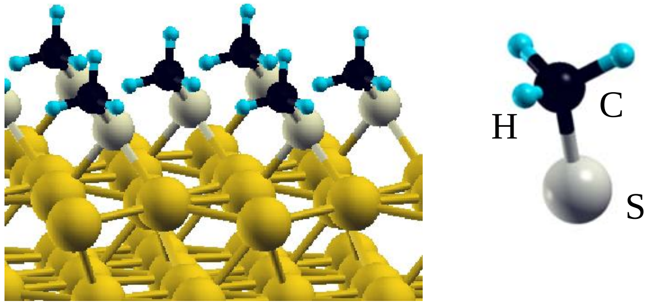




Cui et al., Science **294**, 571 (2001)

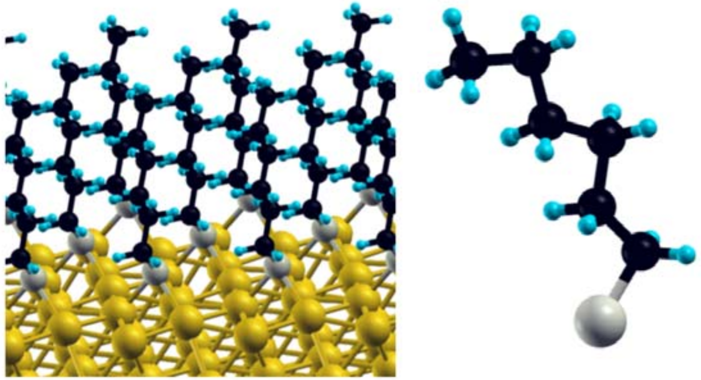
Theory of SAMs on gold

SAMs are challenging from a theoretical point of view due to competition of interactions with different energy / length scales



Structure of SAMs of thiols on Au(111) are controlled by:

- Au-S chemical bond
- van der Waals interaction between chains



What is the structure of the Au/Thiolate interface?

Discrepancy between DFT theory and experiments. Is this discrepancy due to a failure of DFT or something else?

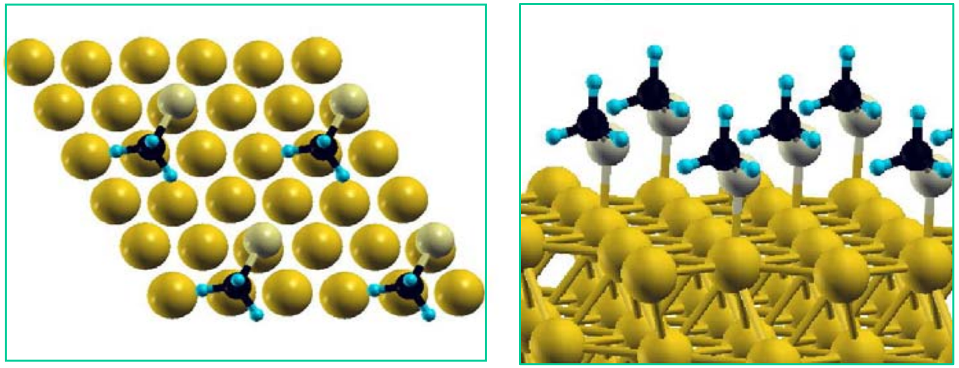
Methanethiols (-SCH_3) on Au(111)

The metal-organic interaction is not well understood and even the structure of this very simple SAM is under dispute.

Exps: Photoelectron diffraction
(Kondoh, PRL,2003),
X-Ray Standing Wave
(Roper, Chem.Phys.Lett.,2004)

⇒ **on-top site**

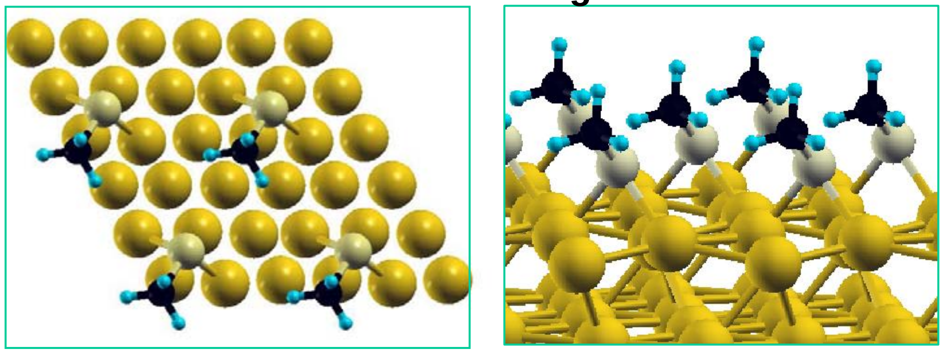
on-top



Theory: DFT structural optimization,
static structures

⇒ **bridge site**
(on-top: +0.3 eV higher)

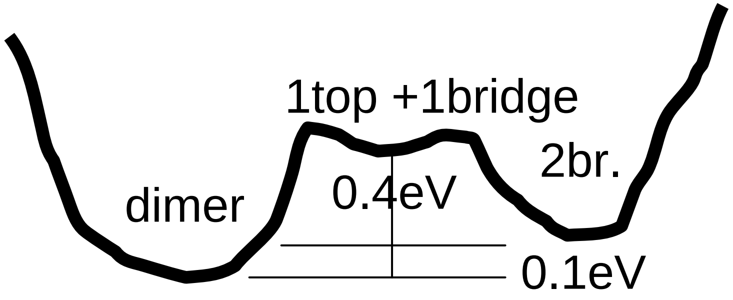
bridge

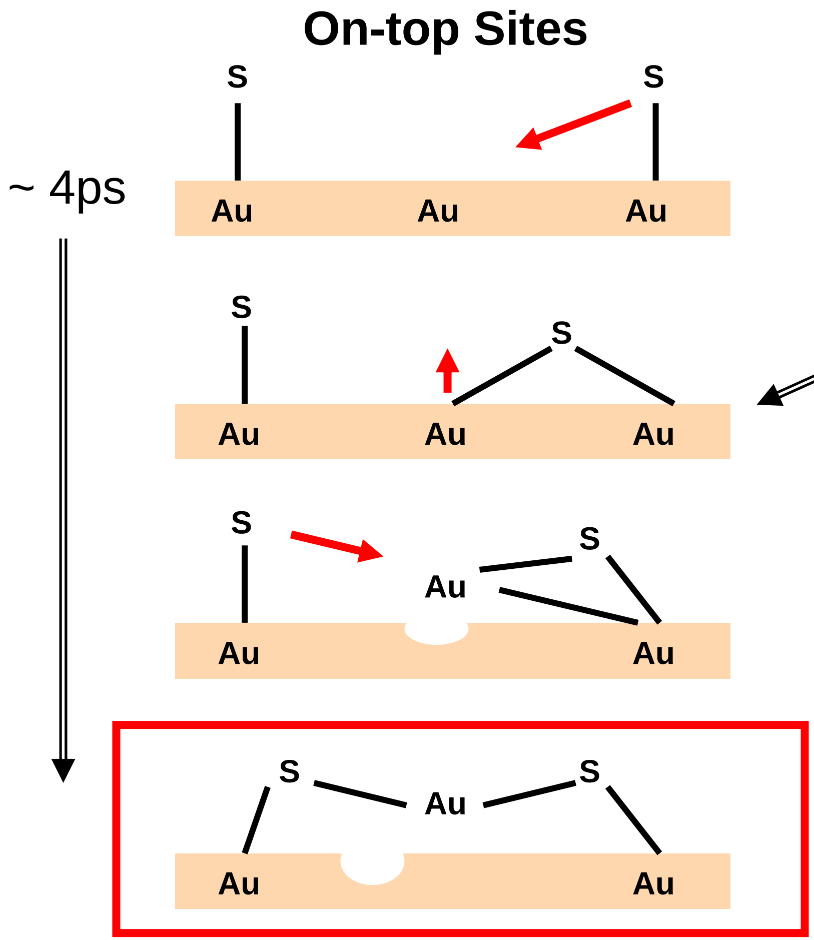


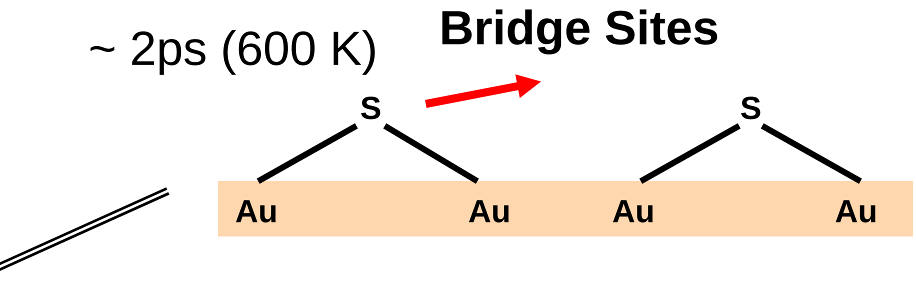
We have studied these systems by means of ab-initio molecular dynamics to explore the configuration space and investigate disorder at the interface

Ab-initio MD of Methanethiols ($-SCH_3$) on Au(111)

“Pull-out” mechanism: sulfur atoms pull gold atoms out of the surface







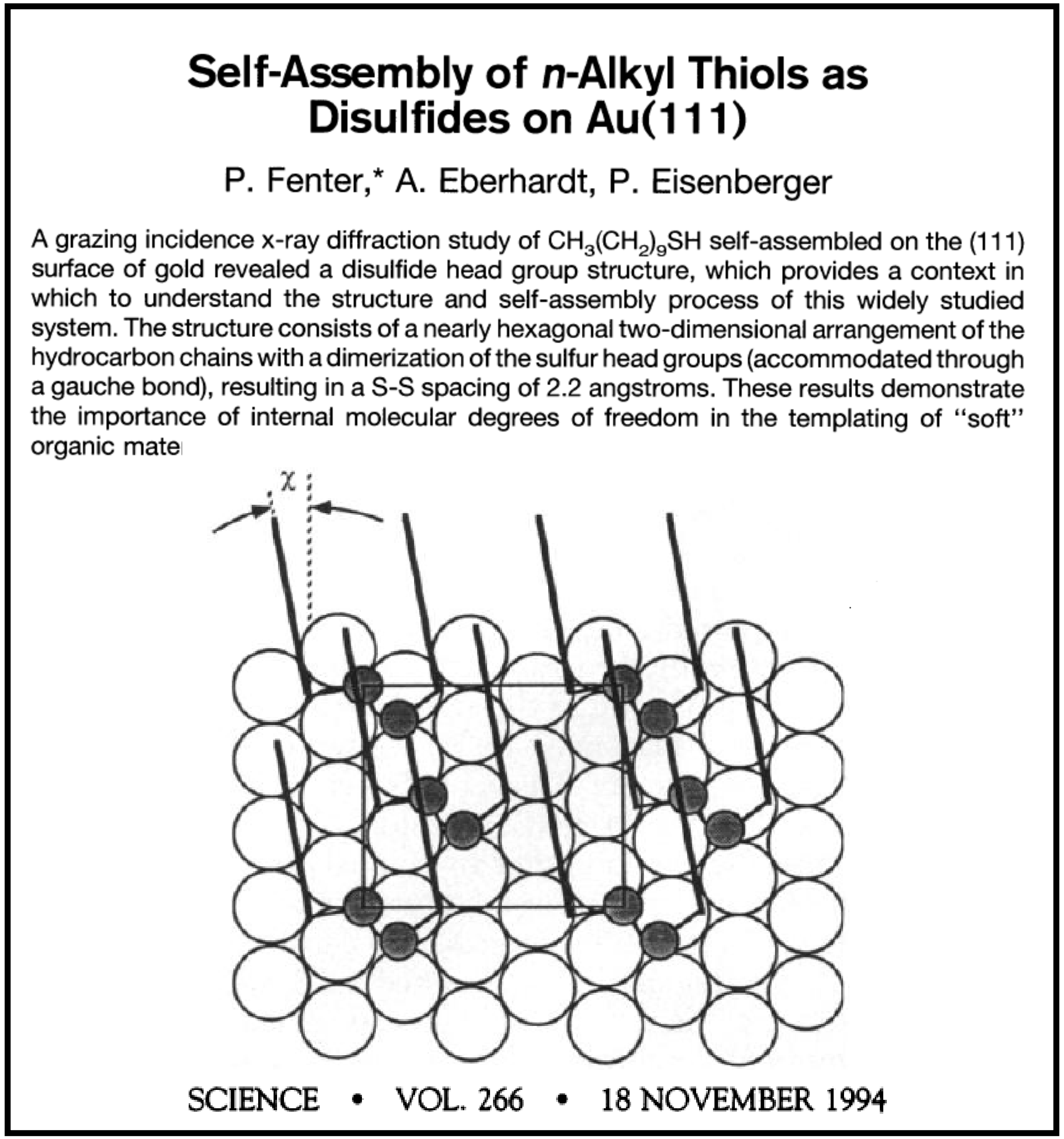
> Vacancies and adatoms are created

> Gold adatoms form bonds with two sulfurs

> Photoelectron diffraction exps confirm this picture

R. Mazzarello et al., PRL **98**, 016102 (2007)

Longer thiols on Au(111)



Self-Assembly of *n*-Alkyl Thiols as Disulfides on Au(111)

P. Fenter,* A. Eberhardt, P. Eisenberger

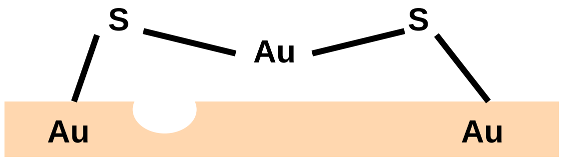
A grazing incidence x-ray diffraction study of $CH_3(CH_2)_9SH$ self-assembled on the (111) surface of gold revealed a disulfide head group structure, which provides a context in which to understand the structure and self-assembly process of this widely studied system. The structure consists of a nearly hexagonal two-dimensional arrangement of the hydrocarbon chains with a dimerization of the sulfur head groups (accommodated through a gauche bond), resulting in a S-S spacing of 2.2 angstroms. These results demonstrate the importance of internal molecular degrees of freedom in the templating of "soft" organic mate

SCIENCE • VOL. 266 • 18 NOVEMBER 1994

Fenter's model after 14 years:

- Doubling of unit cell confirmed
- No evidence for sulfur dimerization

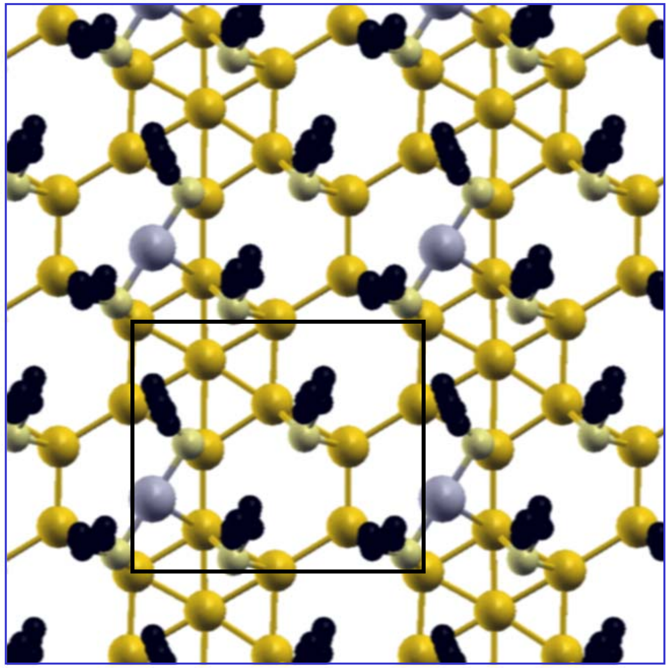
Is dimerization mediated by Au adatoms, as in -SCH_3?



The approach:

+ Ab-initio (DFT) molecular dynamics
+ Grazing incidence X-ray diffraction

Longer thiols on Au(111): ab-initio MD



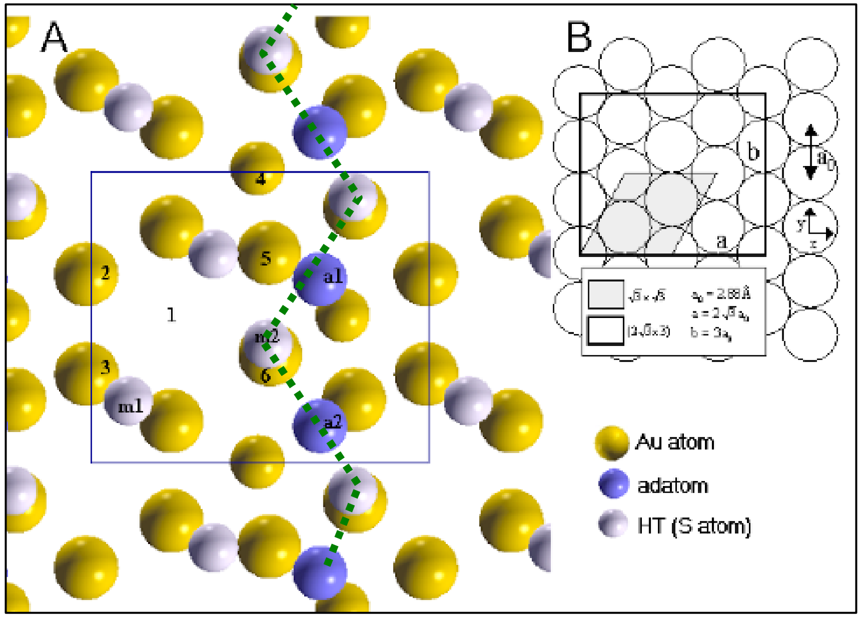
Results from ab-initio MD:

1) Adatoms and vacancies should be present at the surface in similar concentrations, as found for short thiols
2) Chains are more localized because of the hindered S-Au motion imposed by the longer chains
3) Sulfur atoms should be located in either the bridge or S-Au-S (adatom) configurations in roughly equal proportions

Ab-initio results are used to construct tentative models that are then refined by best fit to GIXRD data

A. Cossaro et al., Science 321, 943 (2008)

Longer thiols on Au(111): XRD results

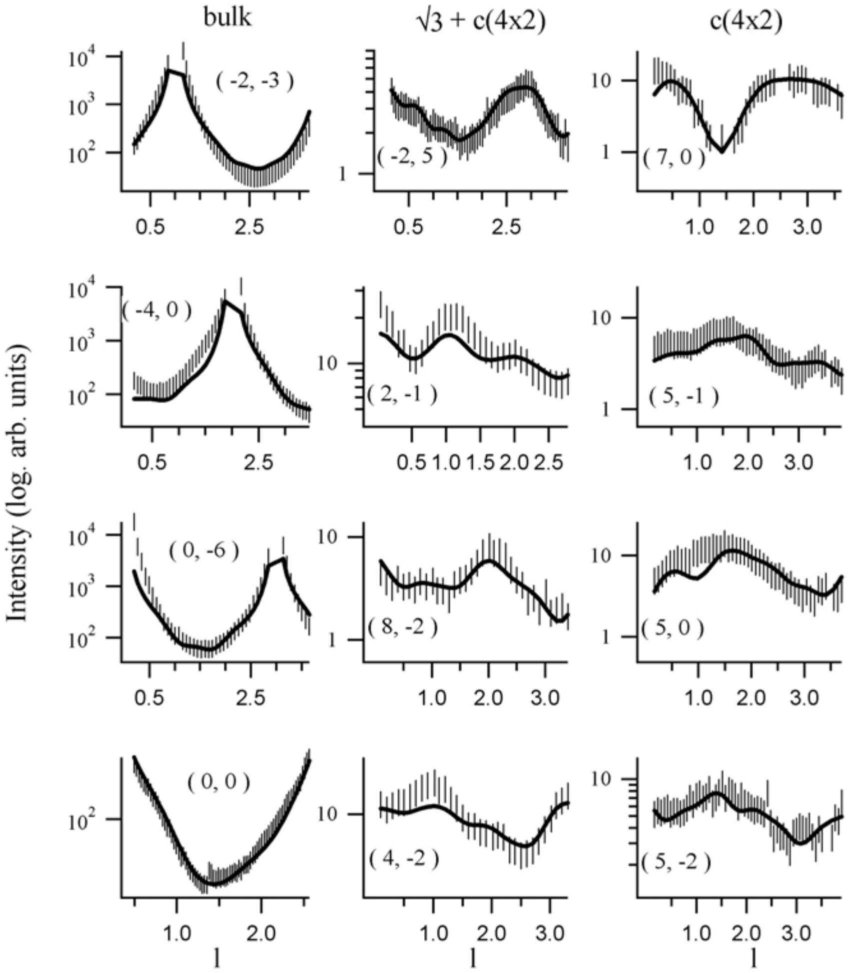


Results of best fit to GIXRD:

Surface is not planar
  1.3 adatoms per c(4x2) cell
  2.8 vacancies per c(4x2) cell

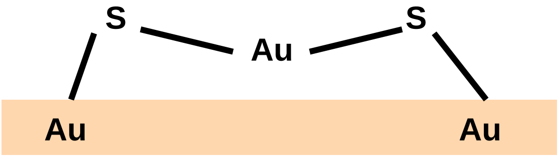
Average structure consists of …-Au-S-Au-… zig-zag chains aligned along the cell short axis

Surface diffraction rods



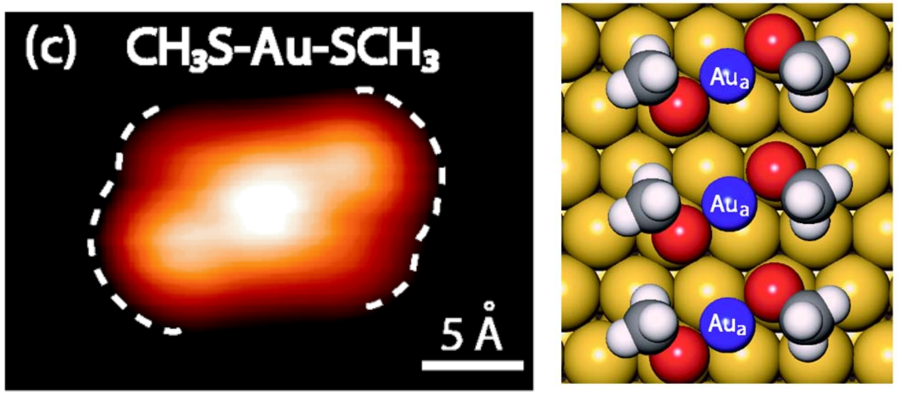
A. Cossaro et al., Science 321, 943 (2008)

RS–Au–RS: a universal motif on gold?



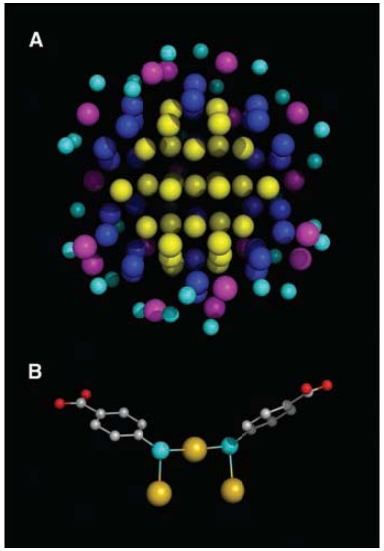
Low-coverage methane-thiol SAMs on Au(111) show similar behaviour: formation of S-Au-S motifs

P. Maksymovich et al., PRL 97, 146103 (2006)



p-mercaptobenzoic molecules on gold nanoparticles form similar staple motifs, as recently found by X-ray diffraction

P. D. Jadzinsky et al., Science 318, 430 (2007)



Two case studies:

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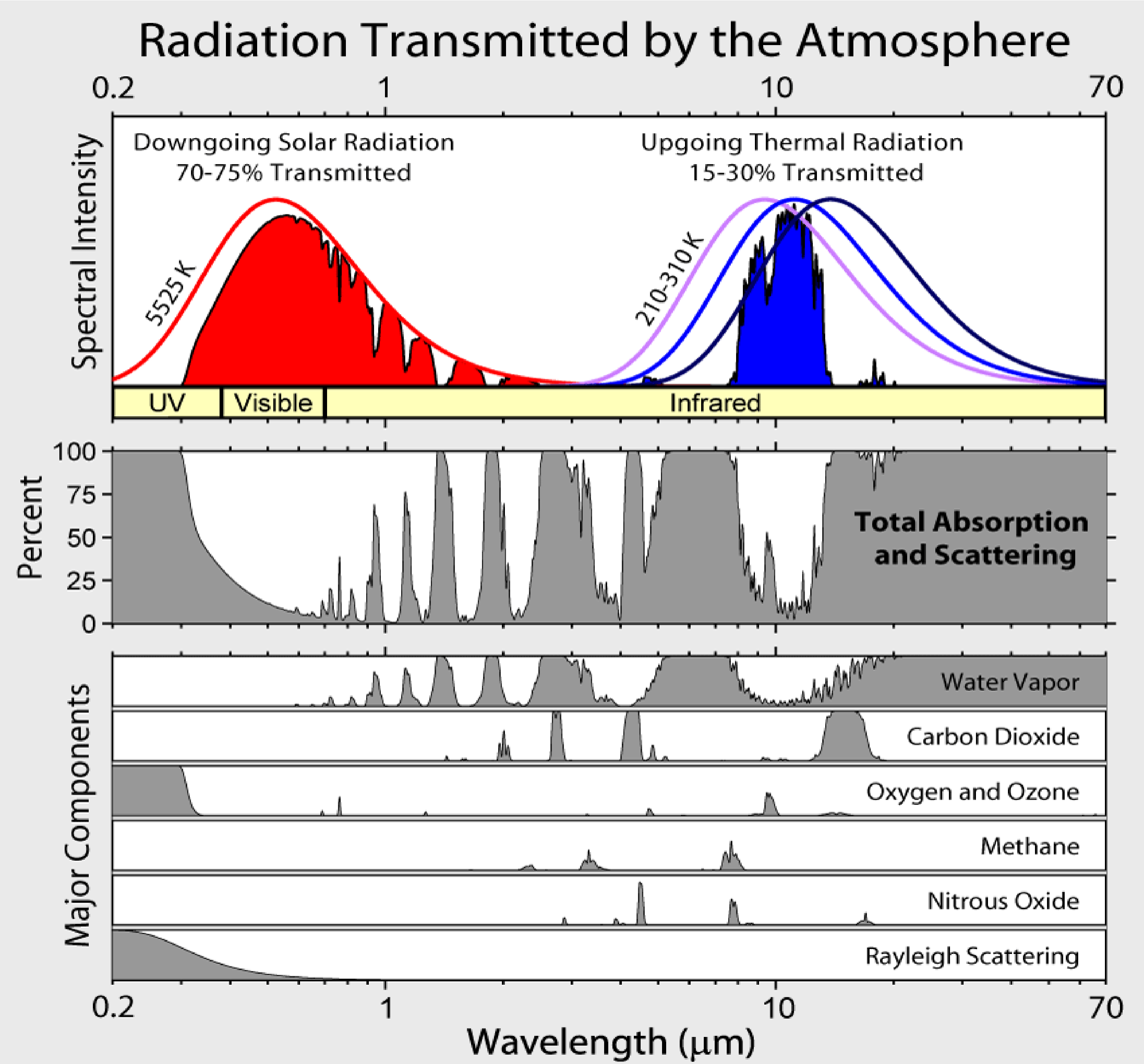
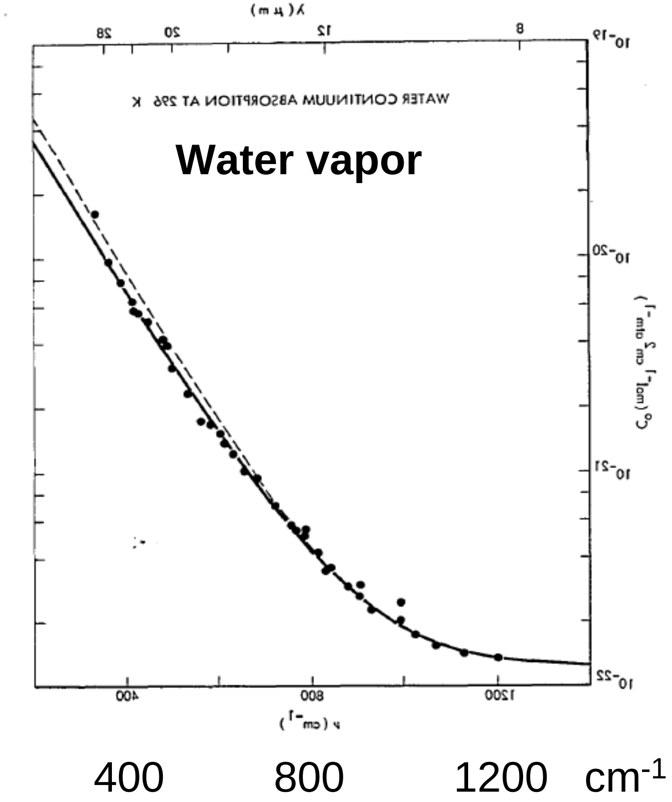
Infrared absorption by water nanoclusters
(understanding the greenhouse effect)


Radiation Transmitted by the Atmosphere
0.2
1
10
70
Spectral Intensity
Downgoing Solar Radiation
70-75% Transmitted
Upgoing Thermal Radiation
15-30% Transmitted
5525 K
210-310 K
UV
Visible
Infrared
Percent
100
75
50
25
0
Total Absorption
and Scattering
Major Components
Water Vapor
Carbon Dioxide
Oxygen and Ozone
Methane
Nitrous Oxide
Rayleigh Scattering
0.2
1
10
70
Wavelength (μm)

Far-IR water vapor absorption

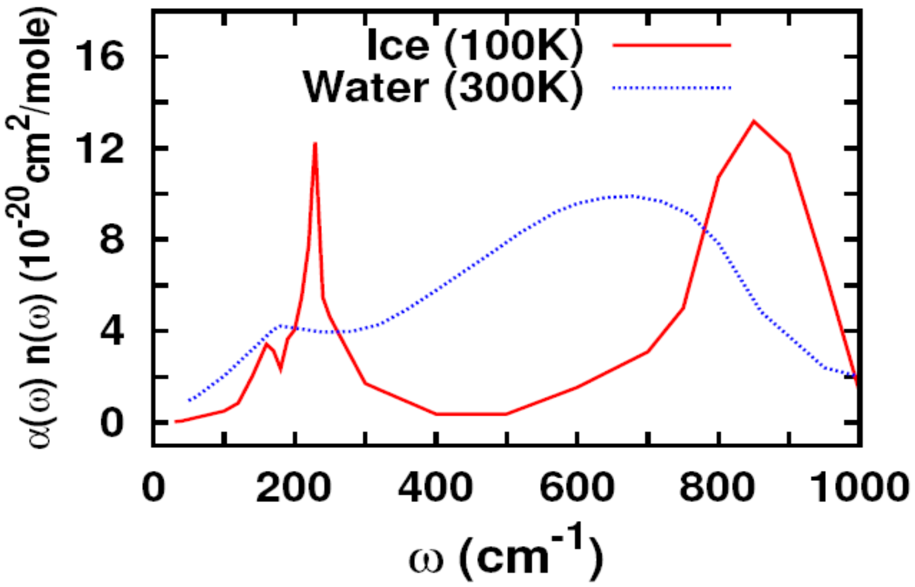


NB: Isolated water molecule does not absorb in the far-IR

Vapor absorption must be due to
1) **collisional broadening or**
2) **water nanodroplets (mostly dimers)**

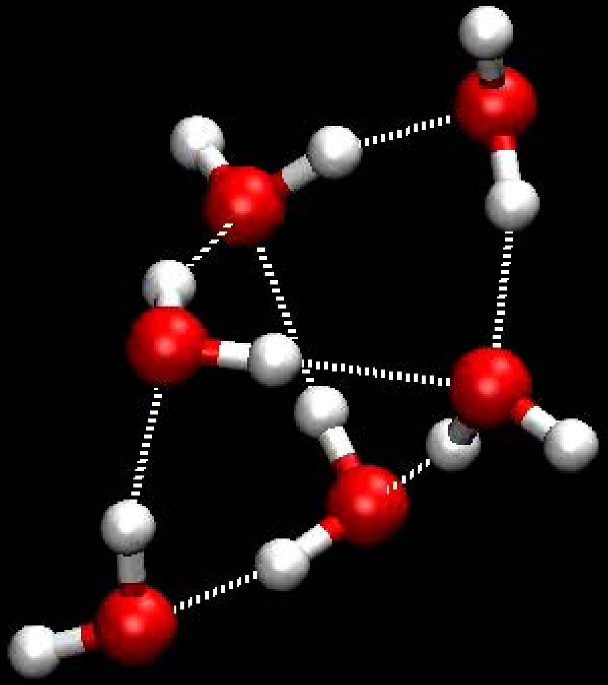
Collisional broadening does not have the correct temperature dependence

Absorption shape of water nanodroplets would have to be different than bulk forms



Water vapor absorption is different from ice and liquid water

Ab-initio molecular dynamics at 200 K



"Fluid" dynamics even at 200 K [J. Rodriguez et al., JCP 110, 9039 (1999)]

Jumps between different locally stable conformations (ring, book, cage)

Ring conformation predominant due to entropic effects

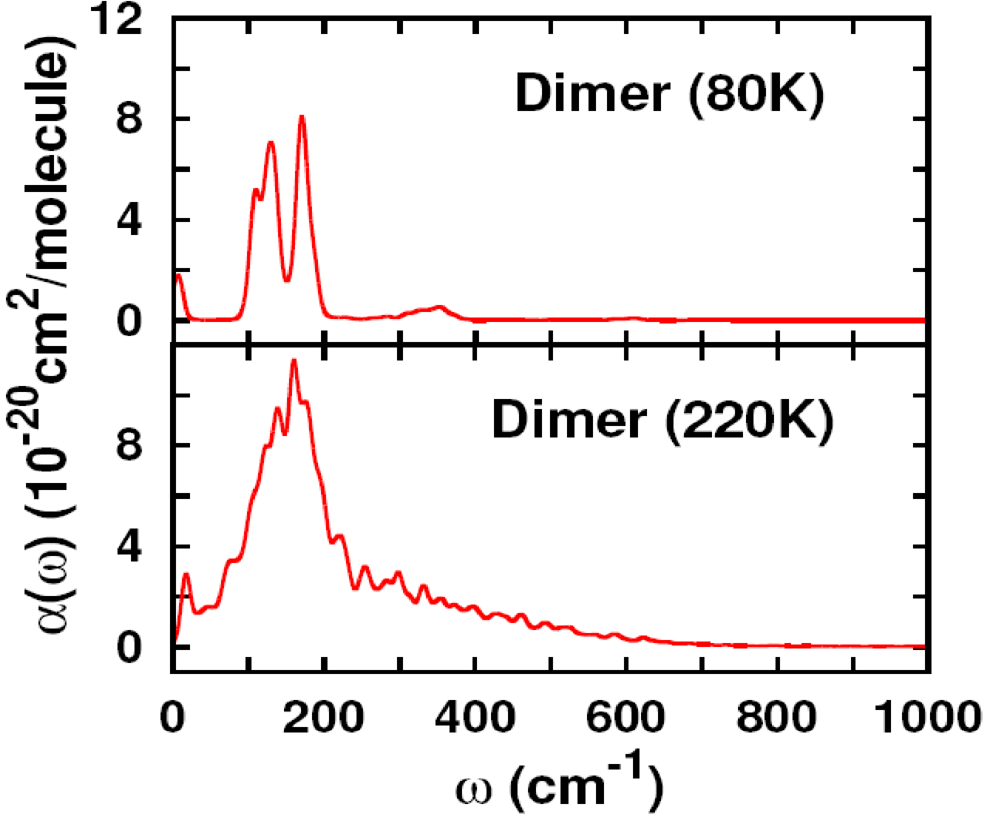
Total dipole moment

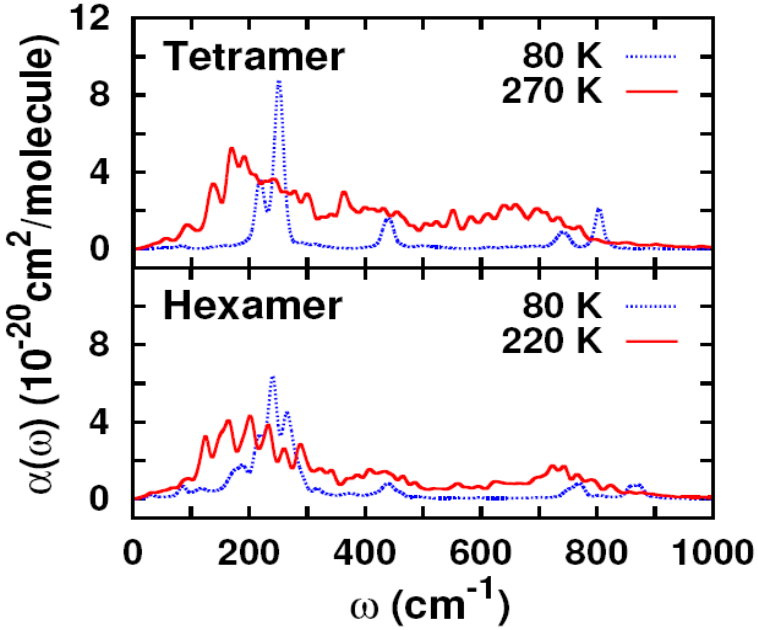
Absorption coefficient from MD trajectory

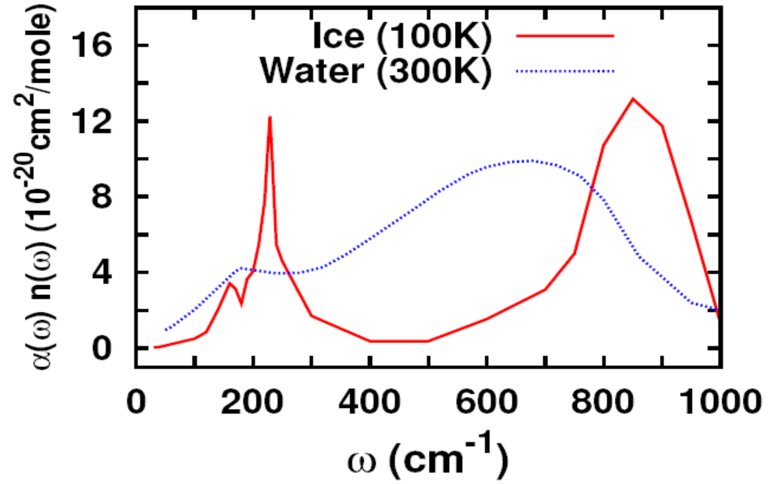
$$\alpha(\omega) = \frac{4\pi\omega \tanh(\beta\hbar\omega/2)}{3\hbar\, n(\omega)\, c\, N} \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle$$

Far-IR absorption by water nanoclusters

M.-S. Lee et al, J. Chem. Phys. 2008



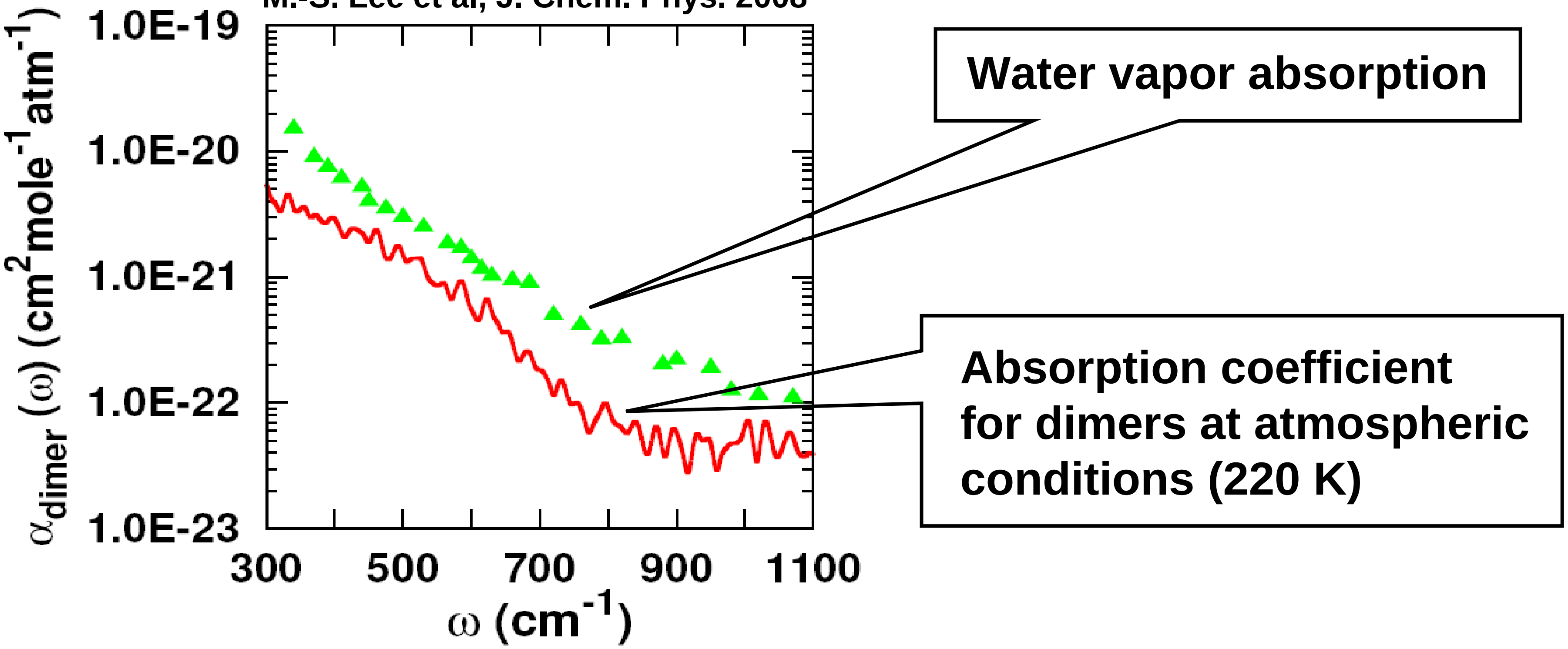




Water dimer absorption is indeed different from ice and liquid water

***"Atmospheric"* nanoscience (?)**

Comparison with water vapor



M.-S. Lee et al, J. Chem. Phys. 2008

Water vapor absorption

Absorption coefficient for dimers at atmospheric conditions (220 K)

Water dimer absorption agrees qualitatively with vapor

Water dimers could be responsible for vapor absorption if their concentration was higher than currently estimated

Conclusions

Can I simulate everything I want?

NO:

The system must be no bigger than one-two hundred atoms

Events must happen in a few picoseconds

You're interested in ground state properties

Van der Waals (dispersion) forces are not important

You have a decent computational facility (say, a few PC processors)

College on Computational Nanoscience
ICTP, 17-28 May 2010

Electronic properties (fundamentals of electronic-structure, many-body effects, magnetism, and nanomaterials)
Richard Martin, Risto Nieminen, Stefano Baroni, Stefan Bluegel, Giulia Galli
Chemistry (catalysis and electrochemistry, how catalytic properties are affected by size)
Matthias Scheffler, Gianfranco Pacchioni, Hannu Hakkinen
Optical properties (solar energy and photovoltaics, plasmonics and photonics)
Elisa Molinari, Ralph Gebauer, Steven Johnson
Mechanical properties (multi-scale modelling, mesoscopic models, nanotribology and friction)
Erio Tosatti, Peter Gumbsch
Electronic and thermal transport (nanoelectronics and thermoelectric materials)
Francesco Mauri, Antti-Pekka Jauho
Control and assembly (self-assembly, models for growth, nano-architectures)
David Tomanek, Sharon Glotzer
Biological and biomimetic materials, and inorganic/organic interfaces
Michele Vendruscolo, Klaus Schuelten

2 “hands-on” tutorials (SIESTA and Quantum-Espresso)

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D. Kanhere (Puna Univ., India)

R. Mazzarello
R. Rousseau (now at PNL)

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V. Derenzi R. Biagi D. Marchetto U. Del Pennino	U. Modena