CPMD Tutorial

Car–Parrinello Molecular Dynamics

Introduction

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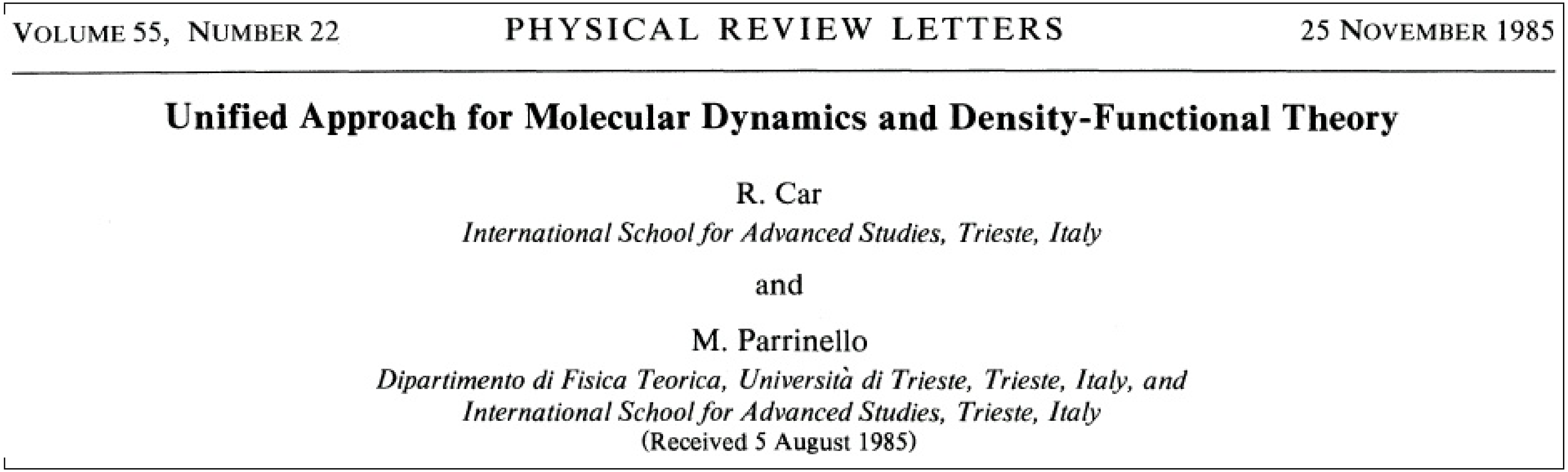
EPF Lausanne

Taiwan, July 2005

Introduction

CPMD — concept 1

- Car-Parrinello Molecular Dynamics – Roberto Car & Michele Parrinello, *Physical Review Letters* **55**, 2471 (1985) — 20 years of Car-Parrinello method!



VOLUME 55, NUMBER 22 PHYSICAL REVIEW LETTERS 25 NOVEMBER 1985

Unified Approach for Molecular Dynamics and Density-Functional Theory

R. Car
International School for Advanced Studies, Trieste, Italy

and

M. Parrinello
Dipartimento di Fisica Teorica, Università di Trieste, Trieste, Italy, and
International School for Advanced Studies, Trieste, Italy

(Received 5 August 1985)

CPMD — concept 2

- `CPMD` code — `http://www.cpmd.org/`; based on the original code of Roberto Car and Michele Parrinello

CPDM

What is it, what is it not?

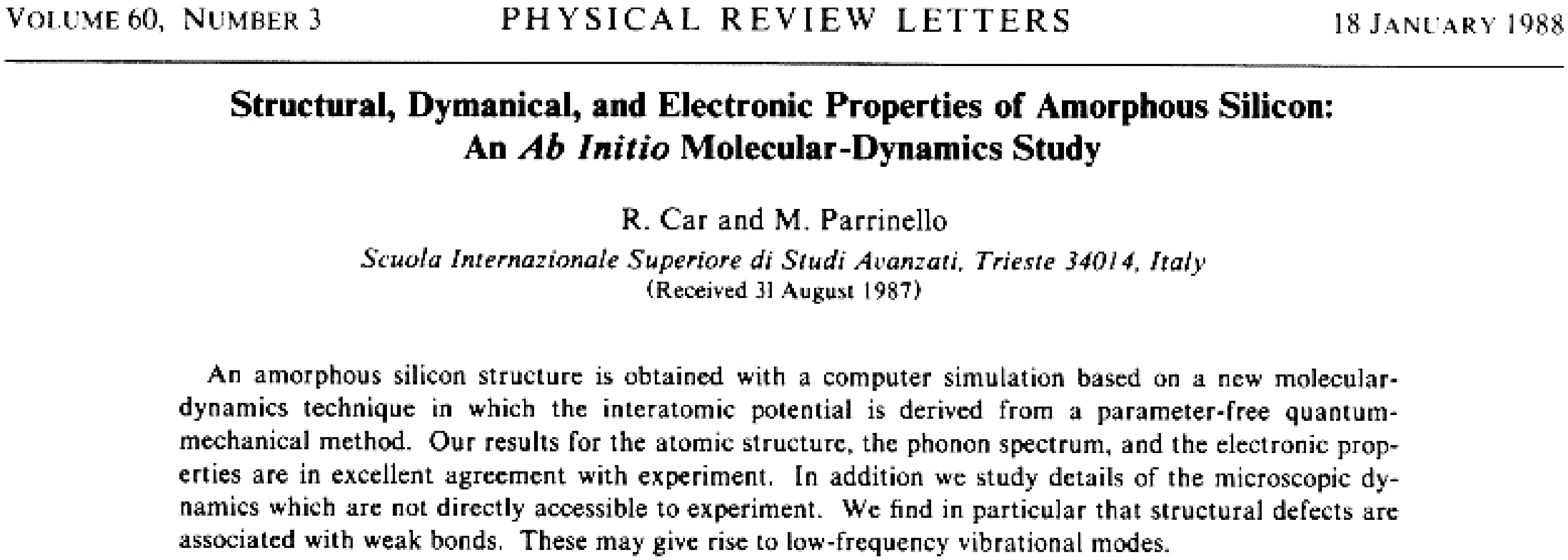
- Computer code for performing static, dynamic simulations and analysis of electronic structure
- About 200'000 lines of code — FORTRAN77 with a flavour towards F90
- (Freely) available via `http://www.cpmd.org/` with source code
- Most suitable for dynamical simulations of condensed systems or large molecules — less for small molecules or bulk properties of small crystals
- Computationally highly optimised for vector and scalar supercomputers, shared and distributed memory machines and combinations thereof (SMP)

Capabilities

- Solution of electronic and ionic structure
- XC-functional: LDA, GGA, meta-GGA, hybrid
- Molecular dynamics with NVE, NVT, NPT ensembles
- General constraints (MD and geometry optimisation)
- Metadynamics
- Free energy functional
- Path integrals
- QM/MM
- Wannier functions
- Response properties: TDDFT, NMR, Raman, IR, . . .
- Norm conserving and ultra-soft pseudo potentials

CPMD: Examples

Amorphous Si



VOLUME 60, NUMBER 3 PHYSICAL REVIEW LETTERS 18 JANUARY 1988

Structural, Dymanical, and Electronic Properties of Amorphous Silicon: An *Ab Initio* Molecular-Dynamics Study

R. Car and M. Parrinello

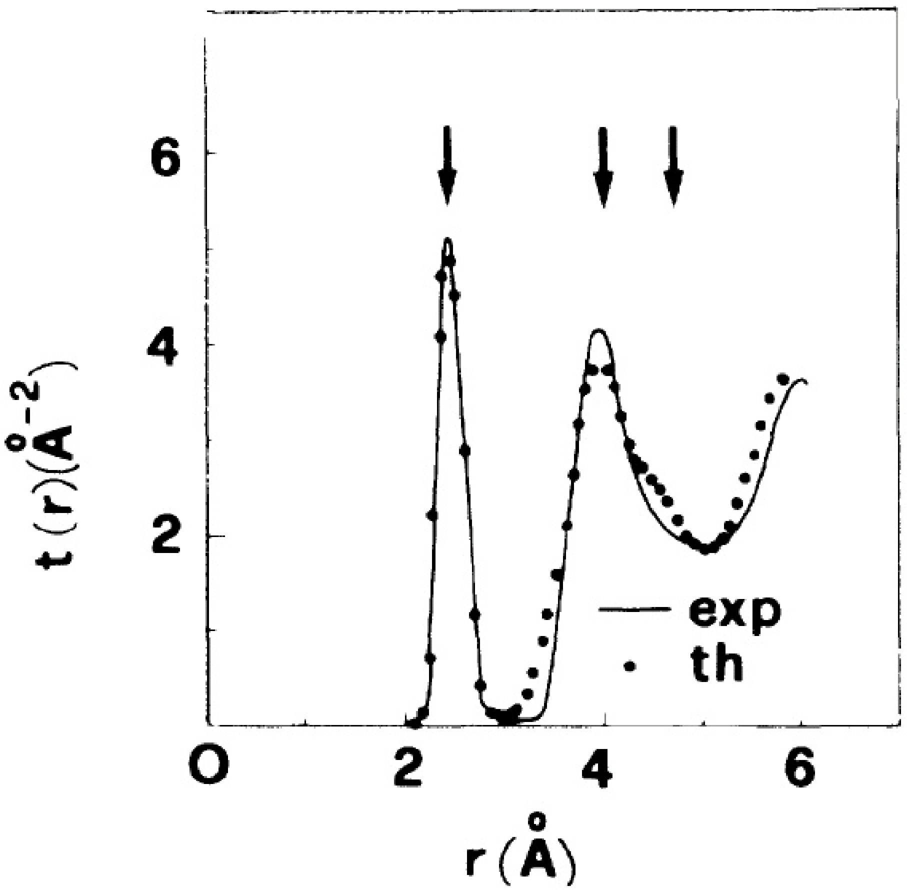
Scuola Internazionale Superiore di Studi Avanzati, Trieste 34014, Italy

(Received 31 August 1987)

An amorphous silicon structure is obtained with a computer simulation based on a new molecular-dynamics technique in which the interatomic potential is derived from a parameter-free quantum-mechanical method. Our results for the atomic structure, the phonon spectrum, and the electronic properties are in excellent agreement with experiment. In addition we study details of the microscopic dynamics which are not directly accessible to experiment. We find in particular that structural defects are associated with weak bonds. These may give rise to low-frequency vibrational modes.

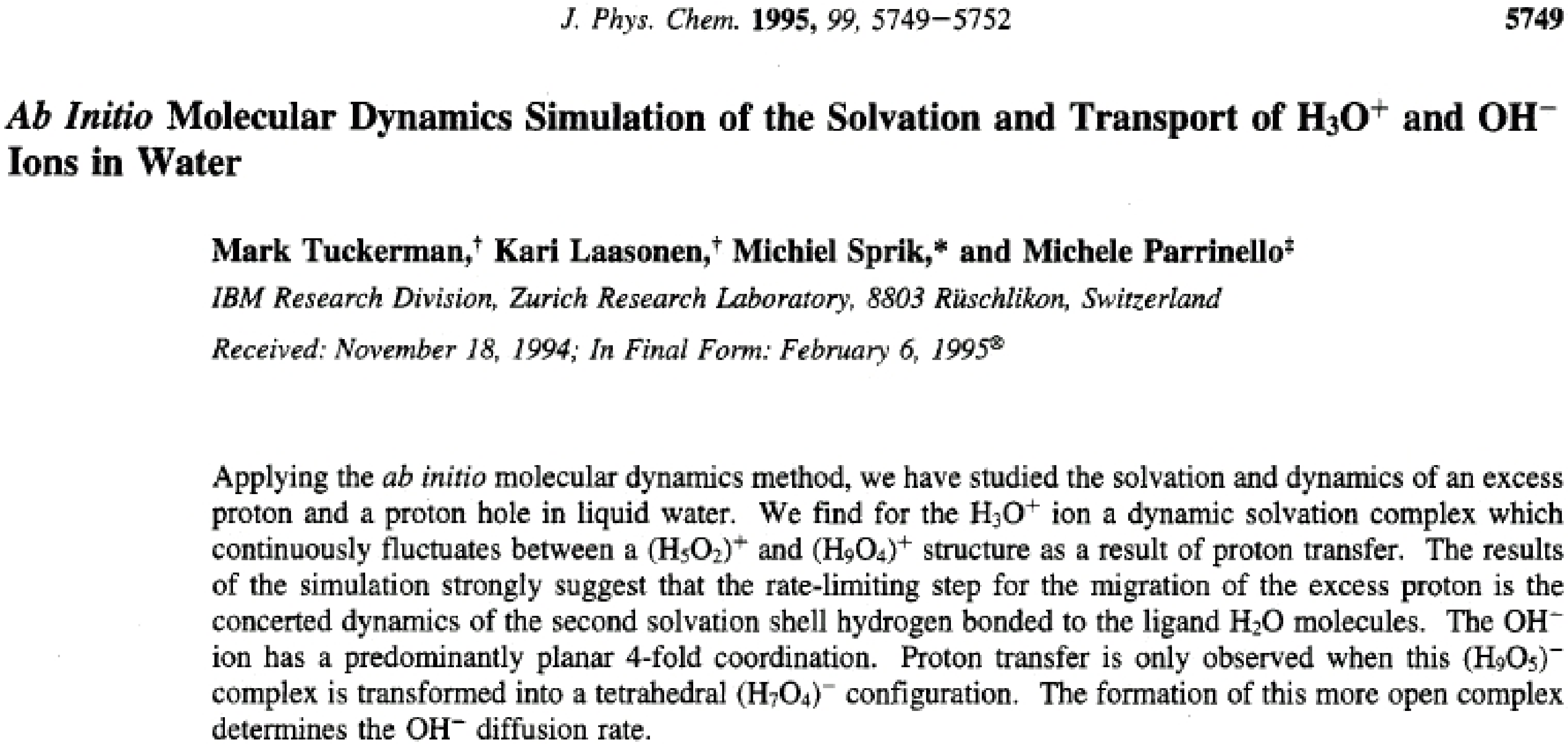
CPMD: Examples

Amorphous Si



CPMD: Examples

Liquid water: Solvation and transport of ions



J. Phys. Chem. **1995,** *99,* 5749−5752 **5749**

Ab Initio Molecular Dynamics Simulation of the Solvation and Transport of H_3O^+ and OH^- Ions in Water

Mark Tuckerman,[†] Kari Laasonen,[†] Michiel Sprik,* and Michele Parrinello[‡]

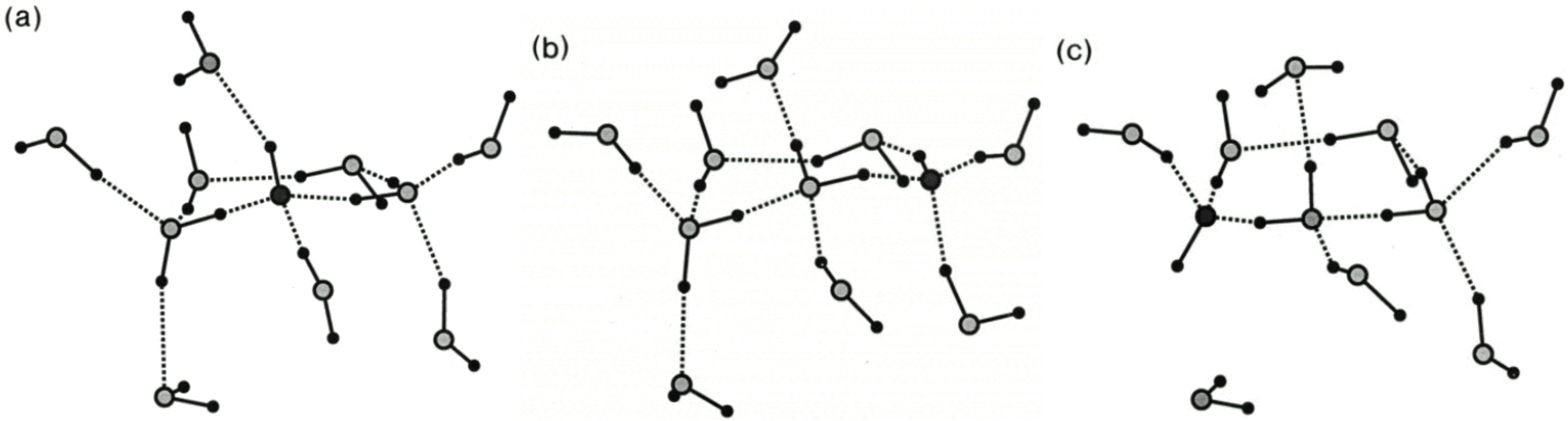
IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

Received: November 18, 1994; In Final Form: February 6, 1995[®]

Applying the *ab initio* molecular dynamics method, we have studied the solvation and dynamics of an excess proton and a proton hole in liquid water. We find for the H_3O^+ ion a dynamic solvation complex which continuously fluctuates between a $(H_5O_2)^+$ and $(H_9O_4)^+$ structure as a result of proton transfer. The results of the simulation strongly suggest that the rate-limiting step for the migration of the excess proton is the concerted dynamics of the second solvation shell hydrogen bonded to the ligand H_2O molecules. The OH^- ion has a predominantly planar 4-fold coordination. Proton transfer is only observed when this $(H_9O_5)^-$ complex is transformed into a tetrahedral $(H_7O_4)^-$ configuration. The formation of this more open complex determines the OH^- diffusion rate.

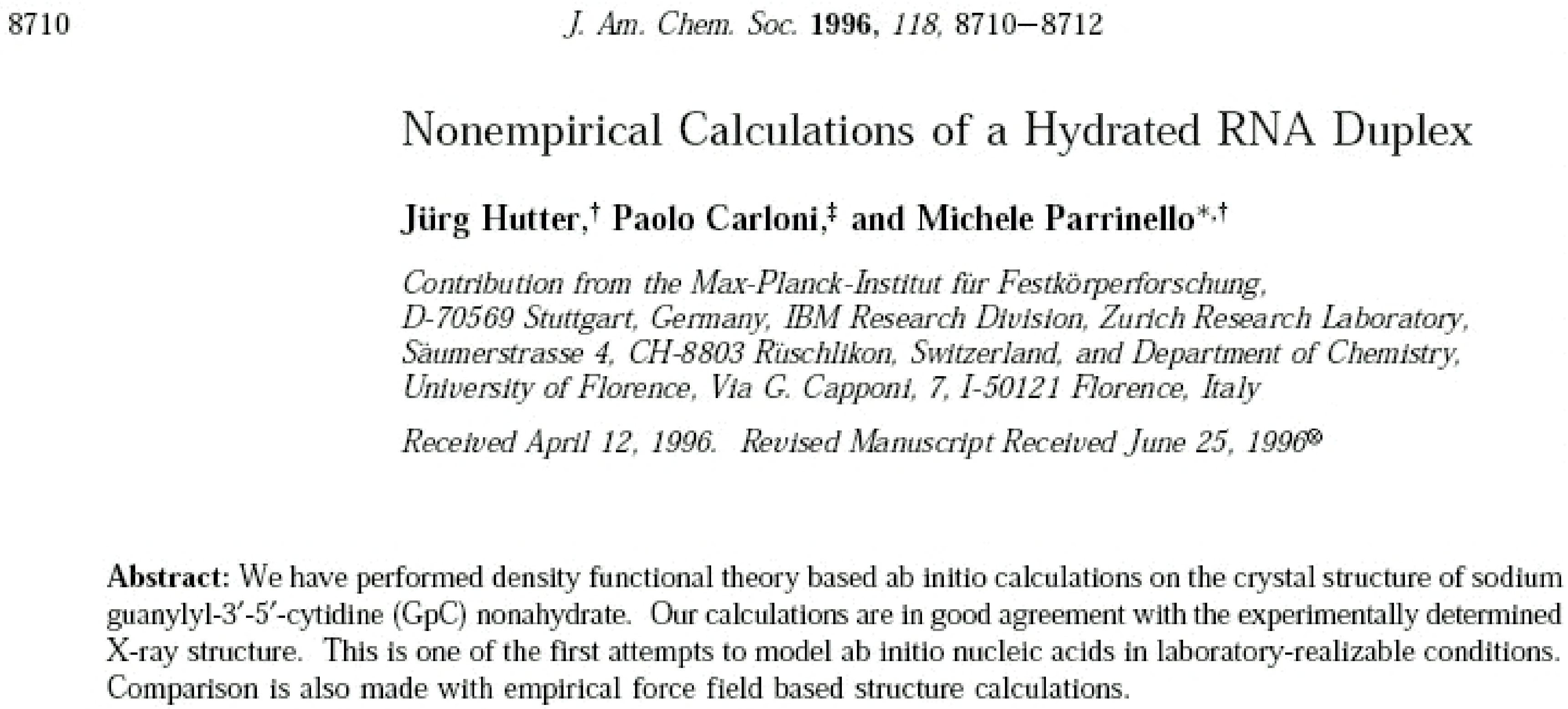
CPMD: Examples

Liquid water: Solvation and transport of ions



CPMD: Examples

RNA duplex



J. Am. Chem. Soc. **1996,** *118,* 8710–8712

Nonempirical Calculations of a Hydrated RNA Duplex

Jürg Hutter,[†] **Paolo Carloni,**[‡] **and Michele Parrinello**[*,†]

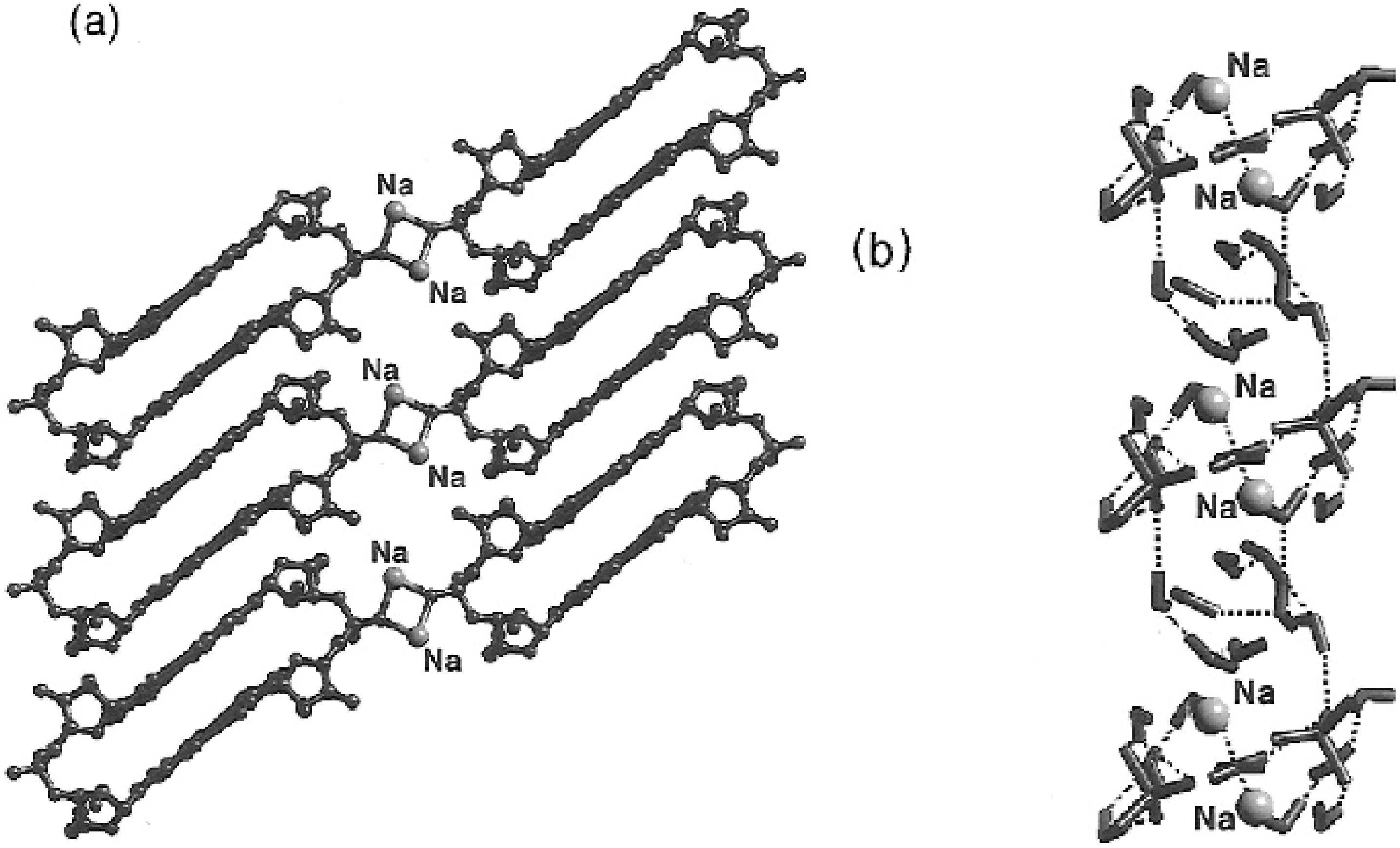
Contribution from the Max-Planck-Institut für Festkörperforschung,
D-70569 Stuttgart, Germany, IBM Research Division, Zurich Research Laboratory,
Säumerstrasse 4, CH-8803 Rüschlikon, Switzerland, and Department of Chemistry,
University of Florence, Via G. Capponi, 7, I-50121 Florence, Italy

Received April 12, 1996. Revised Manuscript Received June 25, 1996[⊗]

Abstract: We have performed density functional theory based ab initio calculations on the crystal structure of sodium guanylyl-3′-5′-cytidine (GpC) nonahydrate. Our calculations are in good agreement with the experimentally determined X-ray structure. This is one of the first attempts to model ab initio nucleic acids in laboratory-realizable conditions. Comparison is also made with empirical force field based structure calculations.

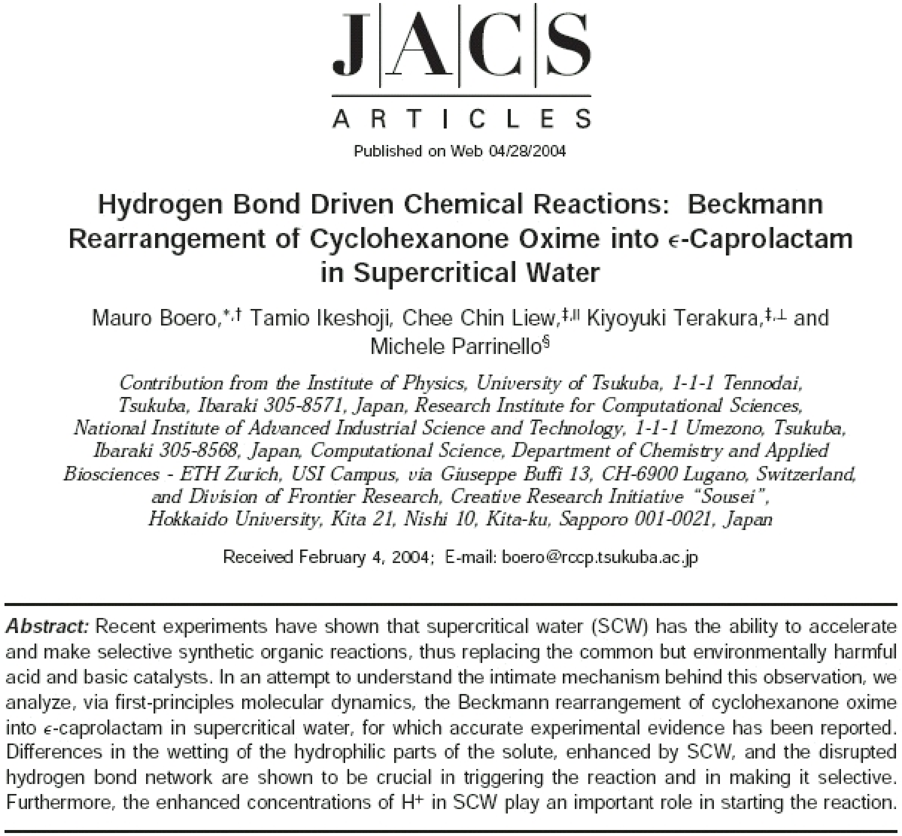
CPMD: Examples

RNA duplex



CPMD: Examples

Reactions in supercritical water



JACS
ARTICLES
Published on Web 04/28/2004

Hydrogen Bond Driven Chemical Reactions: Beckmann Rearrangement of Cyclohexanone Oxime into ϵ-Caprolactam in Supercritical Water

Mauro Boero,[*,†] Tamio Ikeshoji, Chee Chin Liew,[‡,∥] Kiyoyuki Terakura,[‡,⊥] and Michele Parrinello[§]

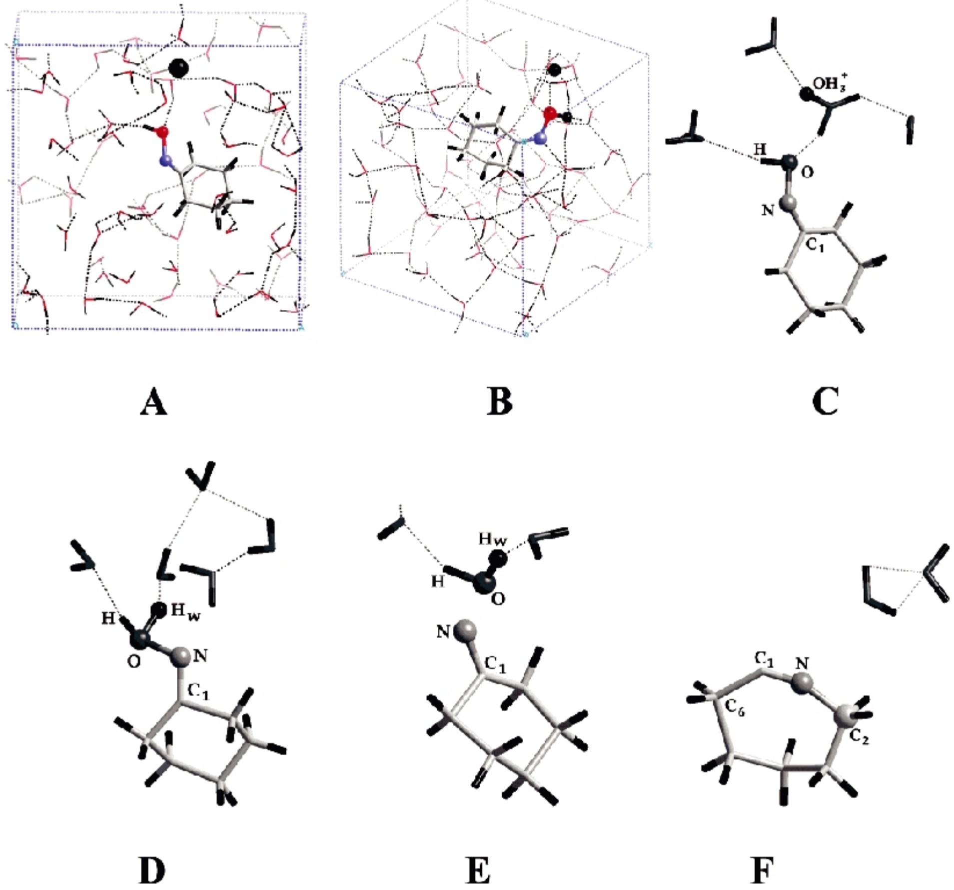
Contribution from the Institute of Physics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan, Research Institute for Computational Sciences, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan, Computational Science, Department of Chemistry and Applied Biosciences - ETH Zurich, USI Campus, via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland, and Division of Frontier Research, Creative Research Initiative "Sousei", Hokkaido University, Kita 21, Nishi 10, Kita-ku, Sapporo 001-0021, Japan

Received February 4, 2004; E-mail: boero@rccp.tsukuba.ac.jp

Abstract: Recent experiments have shown that supercritical water (SCW) has the ability to accelerate and make selective synthetic organic reactions, thus replacing the common but environmentally harmful acid and basic catalysts. In an attempt to understand the intimate mechanism behind this observation, we analyze, via first-principles molecular dynamics, the Beckmann rearrangement of cyclohexanone oxime into ϵ-caprolactam in supercritical water, for which accurate experimental evidence has been reported. Differences in the wetting of the hydrophilic parts of the solute, enhanced by SCW, and the disrupted hydrogen bond network are shown to be crucial in triggering the reaction and in making it selective. Furthermore, the enhanced concentrations of H^+ in SCW play an important role in starting the reaction.

CPMD: Examples

Reactions in supercritical water



CPMD: Examples

Alkane thiols and gold clusters

JOURNAL OF CHEMICAL PHYSICS VOLUME 115, NUMBER 10 8 SEPTEMBER 2001

Interaction of short-chain alkane thiols and thiolates with small gold clusters: Adsorption structures and energetics

Daniel Krüger and Harald Fuchs
Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm Klemm-Str. 10, 48149 Münster, Germany

Roger Rousseau
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Dominik Marx
Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany

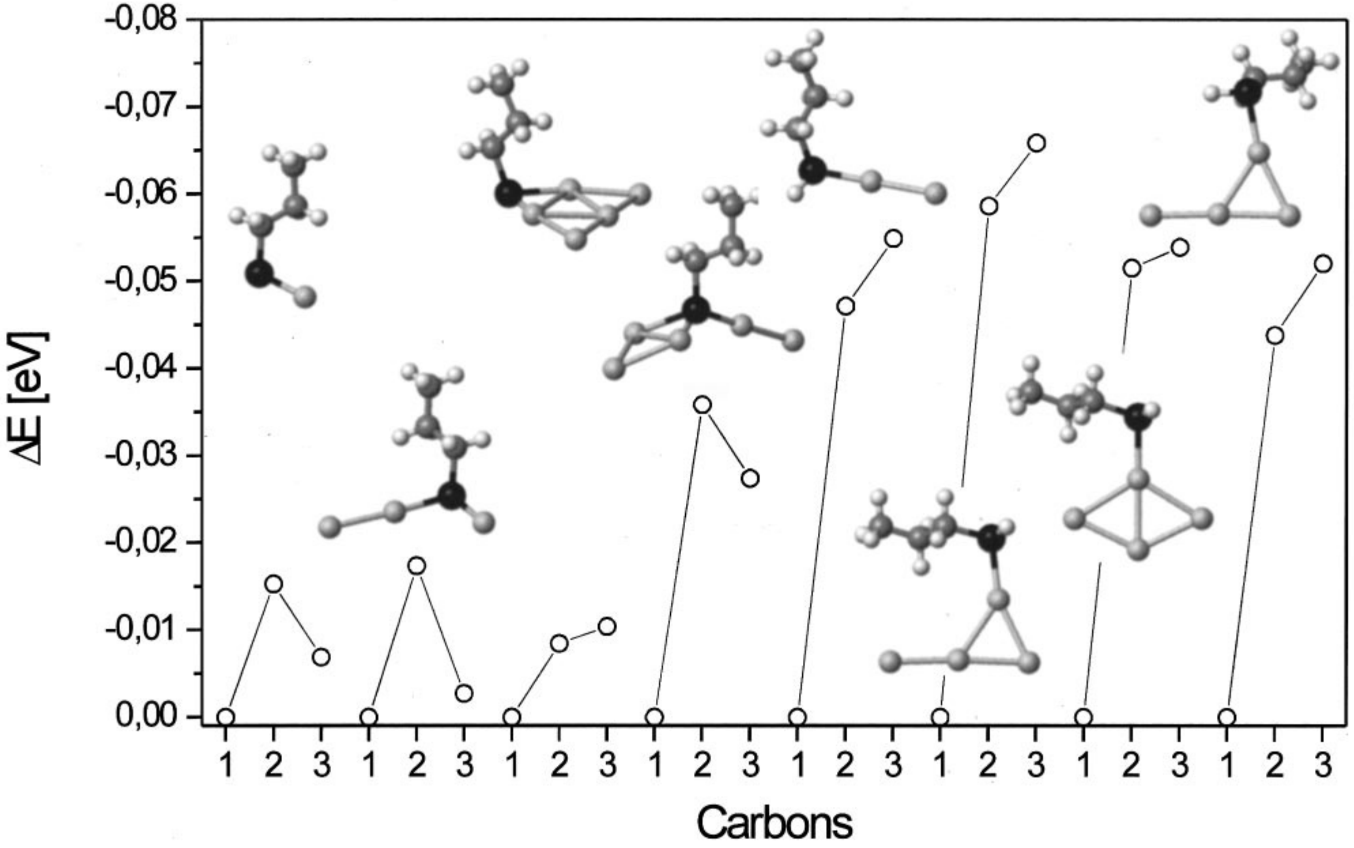
Michele Parrinello
Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany

(Received 7 March 2001; accepted 29 May 2001)

Gold–sulfur bonding is investigated theoretically using a variety of electronic structure methods, including the Becke–Perdew semilocal density functional, the B3LYP hybrid approach, the Hartree–Fock method, and the post Hartree–Fock approaches MP2 and QCISD(T). Particular emphasis is given to adsorption structure and energetics in the case of weak and strong interactions of this general type, using up to five gold atoms and up to three carbon atoms in the aliphatic chain. It is found that all methods which take into account electron correlation, including the density functional methods, lead to quite similar structures. Concerning the energetics, the Becke–Perdew functional is found to overbind typically by about 5–15%. Quasiglobal structural relaxation based on *ab initio* simulated annealing clearly shows that the adsorption of thiolates onto gold clusters results in a dramatic distortion of the cluster framework. From a structural point of view the thiolate sulfur–gold bond has a distinctive directional (covalent) character which results in a clear preference for Au–S–C bond angles in the range of 103.5° and 108.7°. In general, dissociation into open-shell species is preferred against the formation of the ionic closed-shell counterparts if the sulfur–gold bond is forced to break. However, neutral closed-shell products can be favored if fragmentation of the gold cluster is allowed for as a dissociation channel. Finally, it is demonstrated that using ethyl or *n*-propyl chains instead of the methyl group leads to only small changes of the binding energies. [DOI: 10.1063/1.1386806]

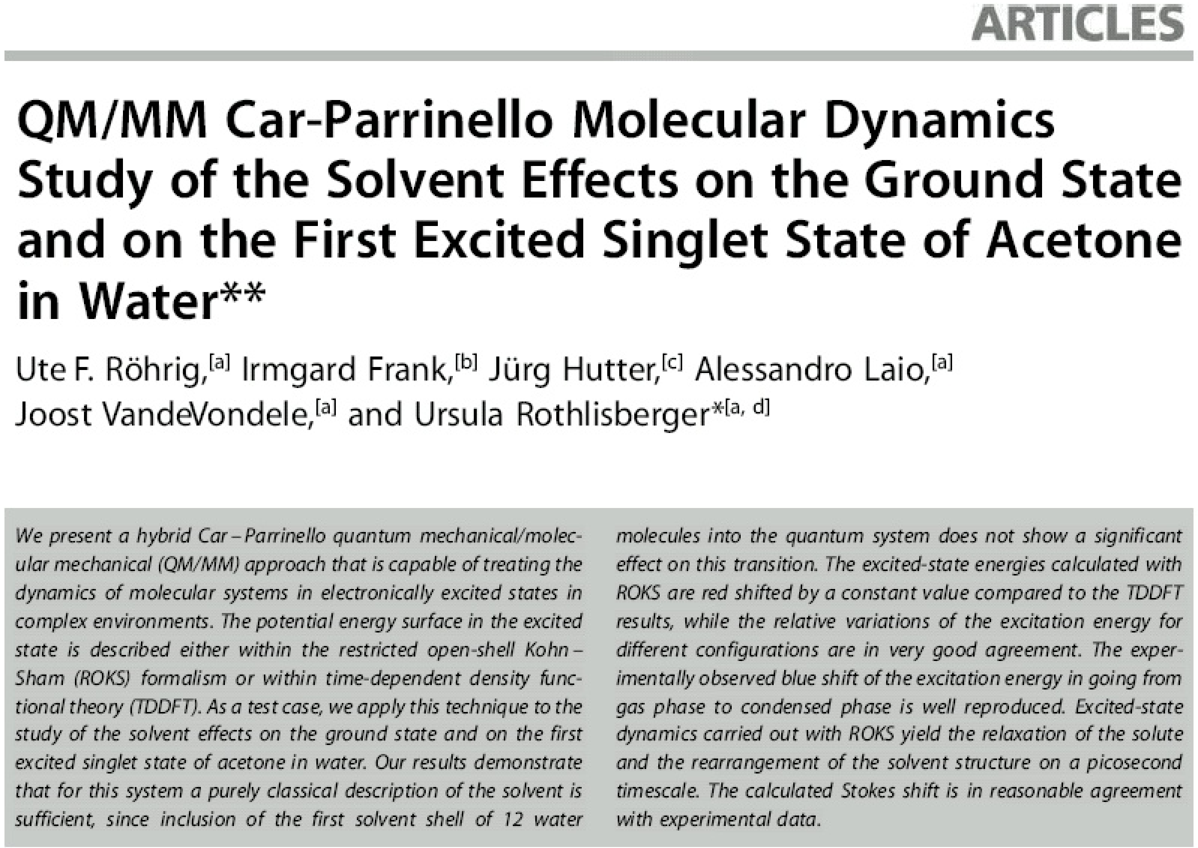
CPMD: Examples

Alkane thiols and gold clusters



CPMD: Examples

QM/MM & electronic excitations



ARTICLES

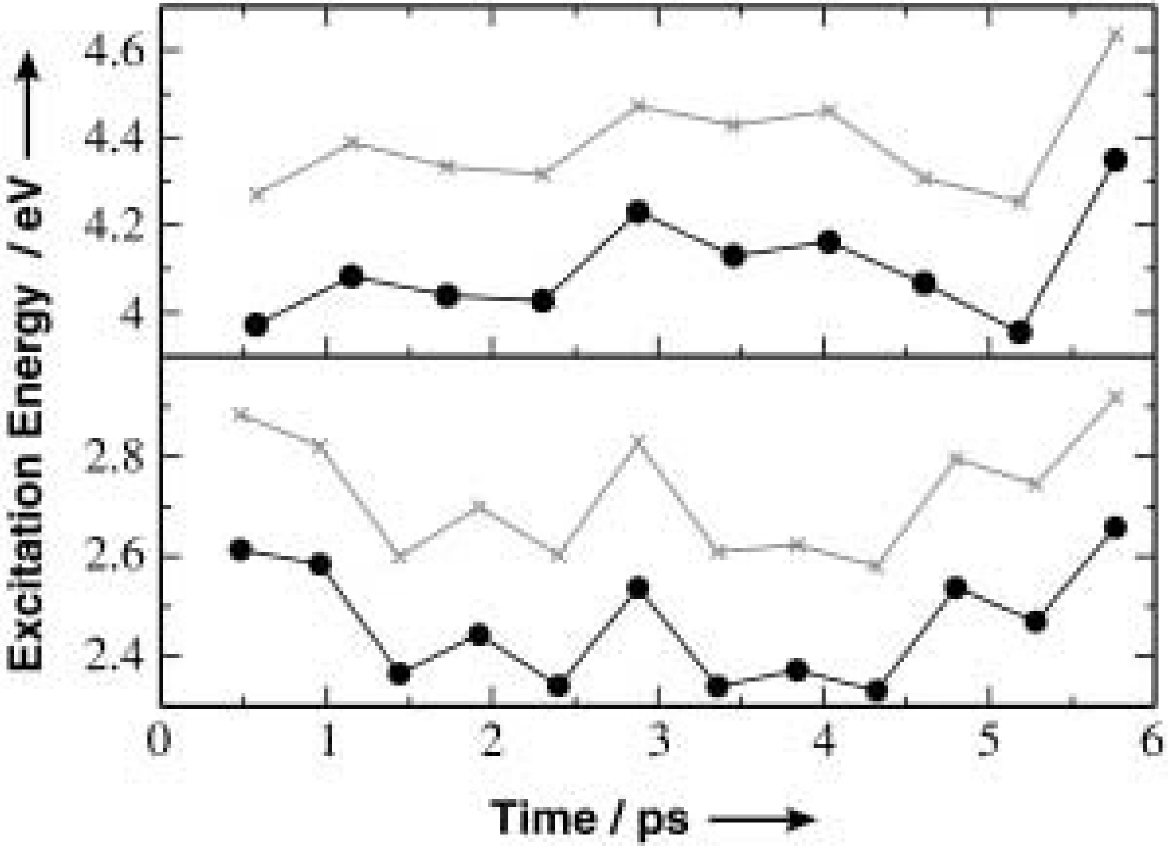
QM/MM Car-Parrinello Molecular Dynamics Study of the Solvent Effects on the Ground State and on the First Excited Singlet State of Acetone in Water**

Ute F. Röhrig,[a] Irmgard Frank,[b] Jürg Hutter,[c] Alessandro Laio,[a]
Joost VandeVondele,[a] and Ursula Rothlisberger*[a, d]

We present a hybrid Car–Parrinello quantum mechanical/molecular mechanical (QM/MM) approach that is capable of treating the dynamics of molecular systems in electronically excited states in complex environments. The potential energy surface in the excited state is described either within the restricted open-shell Kohn–Sham (ROKS) formalism or within time-dependent density functional theory (TDDFT). As a test case, we apply this technique to the study of the solvent effects on the ground state and on the first excited singlet state of acetone in water. Our results demonstrate that for this system a purely classical description of the solvent is sufficient, since inclusion of the first solvent shell of 12 water molecules into the quantum system does not show a significant effect on this transition. The excited-state energies calculated with ROKS are red shifted by a constant value compared to the TDDFT results, while the relative variations of the excitation energy for different configurations are in very good agreement. The experimentally observed blue shift of the excitation energy in going from gas phase to condensed phase is well reproduced. Excited-state dynamics carried out with ROKS yield the relaxation of the solute and the rearrangement of the solvent structure on a picosecond timescale. The calculated Stokes shift is in reasonable agreement with experimental data.

CPMD: Examples

QM/MM & electronic excitations



(Similar) Alternatives

To be fair; for solid-state/dense systems

- `abinit`
- ν-`espresso` (PWSCF, CP, FPMD)
- NWChem
- CP-PAW
- PINY_MD
- Commercial:
  - Wien2k (FLAPW)
  - VASP
  - CASTEP

Out-line

- Monday: Molecular dynamics + density functional theory
- Tuesday: Car-Parrinello molecular dynamics + terminal session
- Wednesday: Pseudo potentials, solid + terminal session
- Thursday: Basic properties, TDDFT + terminal session
- Friday: Further properties + terminal session

apsi & Anatole

. . . and the Swiss Alps

Ari Paavo Seitsonen, *apsi*

- M.Sc.: Teknillinen Korkeakoulu (TKK, Helsinki University of Technology, HUT), Finland
  - supervisors: Martti Puska, Risto Nieminen
  - science: defects in semiconductors, especially InP; clusters; positrons in solids
  - codes: *“pre-CPMD”*, `DMol`
  - computers: Cray X-MP/EA

- PhD: Technische Universität Berlin (TUB), Germany; Fritz-Haber-Institut der Max-Planck-Gesellschaft (FHI der MPG), Berlin, Germany
  - supervisors: Matthias Scheffler, in practise Herbert Over @ Gerhard Ertl's
  - science: surfaces of metals; oxides
  - codes: *Faust* (*pre-CPMD*), `fhi93cp`, `fhi94md`, PVM parallellisation (1994!), MPI
  - computers: IBM workstations, SP2, Cray T3E

- Post-doc: Universitá La Sapienza, Rome, Italy
  - boss: Giovanni B Bachelet
  - science: small fullerenes (C_{36})
- Post-doc: Rechenzentrum Garching der Max-Planck-Gesellschaft (RZG; Computing Centre of Max-Planck-Society), Garching bei München, Germany
  - bosses: Hermann Lederer, Stefan Heinzel
  - task: user support, benchmarking, “grid computing”
  - codes: `CPMD`, `torb`
  - computers: IBM SP4, NEC sX-5

- Post-doc: Max-Planck-Institut für Festkörperforschung (MPI-FKF; Max-Planck-Institute for Solid State Research), Stuttgart, Germany
  - boss: Michele Parrinello
  - science: vibrational properties of water
  - codes: `CPMD`, `Gaussian98`
  - computers: IBM SP3, Cray T3E, Hitachi SR8000-F1
- Post-doc: Centro Svizzero di Calcolo Scientifico (CSCS; Swiss Computational Centre for Scientific Computing), Switzerland
  - boss: Michele Parrinello
  - science: vibrational properties of water, vibrational properties of thiols
  - codes: `CPMD`, `Gaussian98`
  - computers: IBM SP4, NEC sX-5, Hitachi SR8000-F1

- Post-doc: Physikalisch Chemisches Institut, Universität Zürich, Switzerland
  - boss: Jürg Hutter
  - science: electronic excitations in molecules, liquids and solids
  - codes: `CPMD`, `VASP`, `Gaussian03`
  - computers: IBM SP2, SP3, SP4, AMD opteron clusters, Hitachi SR8000-F1

- Ingénieur de Recherche: CNRS & Université Pierre et Marie Curie
  - bosses: Bernard Capelle, Francesco Mauri
  - science: NMR, . . .
  - codes: `CPMD`, `VASP`, `paratec`, `PWSCF`, . . .
  - computers: AMD opteron cluster, IBM SP4, DEISA/grid computing, . . .
- Contact

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  email: `apsi@iki.fi, Ari.P.Seitsonen@iki.fi`

  SkyPE: `ari.p.seitsonen`

  messenger: `aps@iki.fi`

Otto Anatole von Lilienfeld-Toal

- Dipl. Chem. ETHZ, Zürich, Switzerland
  - supervisors: Martin Quack, Nicholas Handy (Cambridge, UK)
  - science: density functional calculations of the vibrational states of CCl_3F
  - codes: CADPAC

- PhD: Laboratory of Computational Chemistry and Biochemistry, EPFL, Lausanne, Switzerland
  - supervisors: Ursula Röthlisberger
  - science: atom centred potentials for properties and design
  - codes: CPMD
  - computers: Opteron/Myrinet cluster

- Prospective Postdoc: from September 2005 at New York University with Mark Tuckerman
  - science: *ab Initio* compound design
  - codes: CPMD, PINE
- Contact

  URL: `http://lcbcpc21.epfl.ch/Group_members/anatole/`

  email: `vonLilienfeld@gmail.com`

Acknowledgements

… for the material!

- Jürg Hutter
- Daniel Sebastiani
- Barbara Kirchner
- Ivano Tavernelli
- Marcella Iannuzzi
- Axel Kohlmeyer
- Rodolphe Vuilleumier
- Michiel Sprik

Questions?