Optomechanical Switching of Azobenzene

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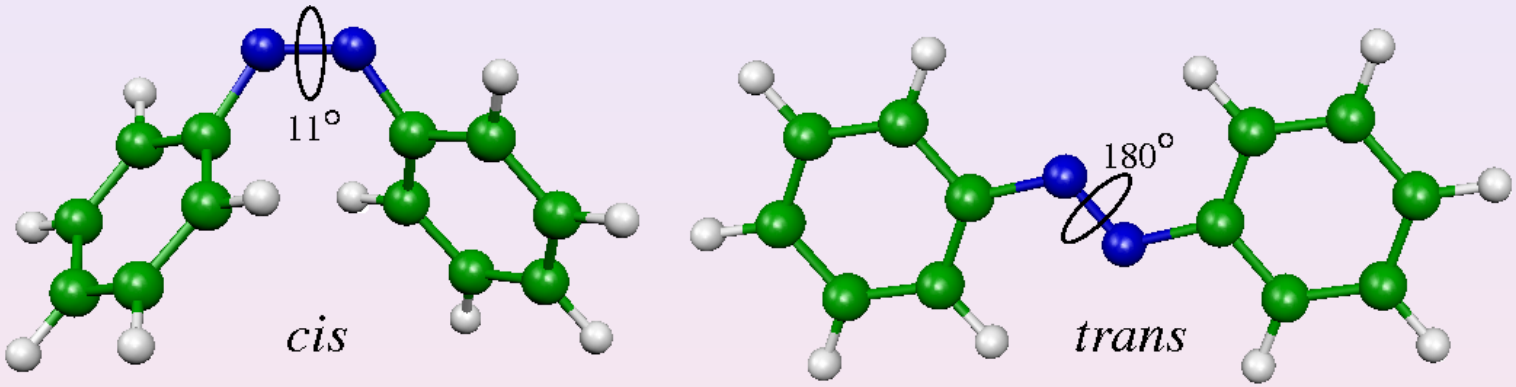
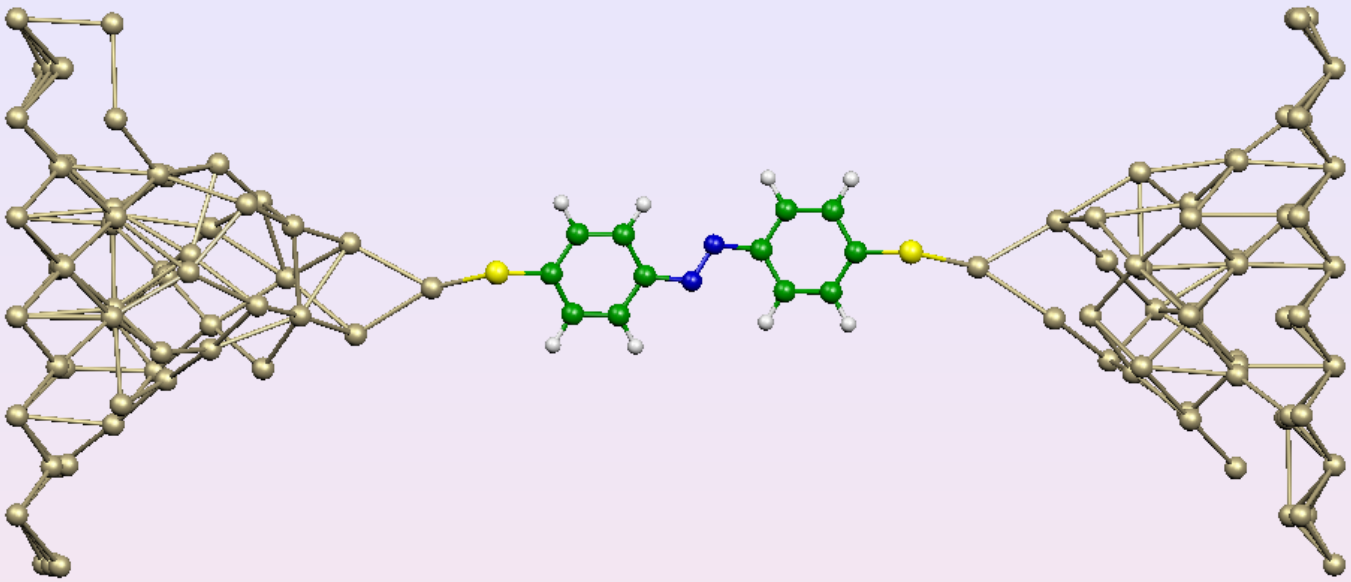
- **azobenzene** (AB) exists in two different isomers:
  - *trans* - lowest energy structure, CNNC dihedral 180°
  - *cis* - about 12 kcal/mol (0.52 eV) higher in energy



- barrier about 35 kcal/mol (1.52 eV) above the *trans*-AB energy
- optical switching possible via excited singlet states, e.g. $S_0 \leftrightarrow S_1$ [n (HOMO) and π^* (LUMO) orbitals in effect]
- most useful applications when AB is embedded

single-molecule optomechanically driven junction



aimed functionality:

- switching between two electric current flows by applied laser pulses
- continuous current variations by applied stretching force
- sensor for the applied stretch/force

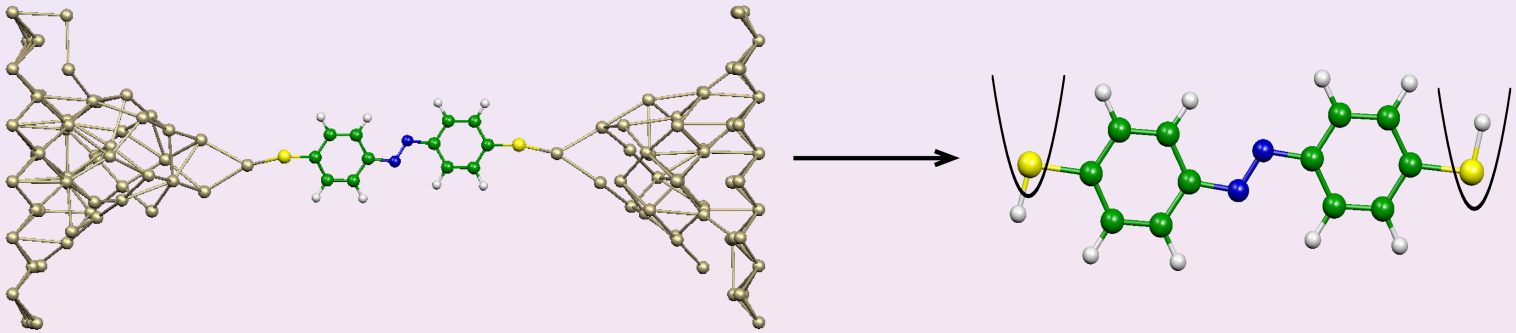
expt. setup: J. Reichert, H. Fuchs (Univ. Muenster)

objectives of the present computational study

- impact of mechanical strain
  - Is the optical switching possible for such an embedded AB?
  - CNNC rotation or NNC inversion or ...?
  - What extensions are favourable for the isomerization?
  - ...
- impact of chemical properties of gold-thiolate environment
  - Does the $n \longrightarrow \pi^*$ electronic structure survive?
  - How much are excitation energies modified?

model

- focus on mechanical impact of the gold-thiolate environment
- effect of the electrodes qualitatively modeled by harmonic restraining potentials:



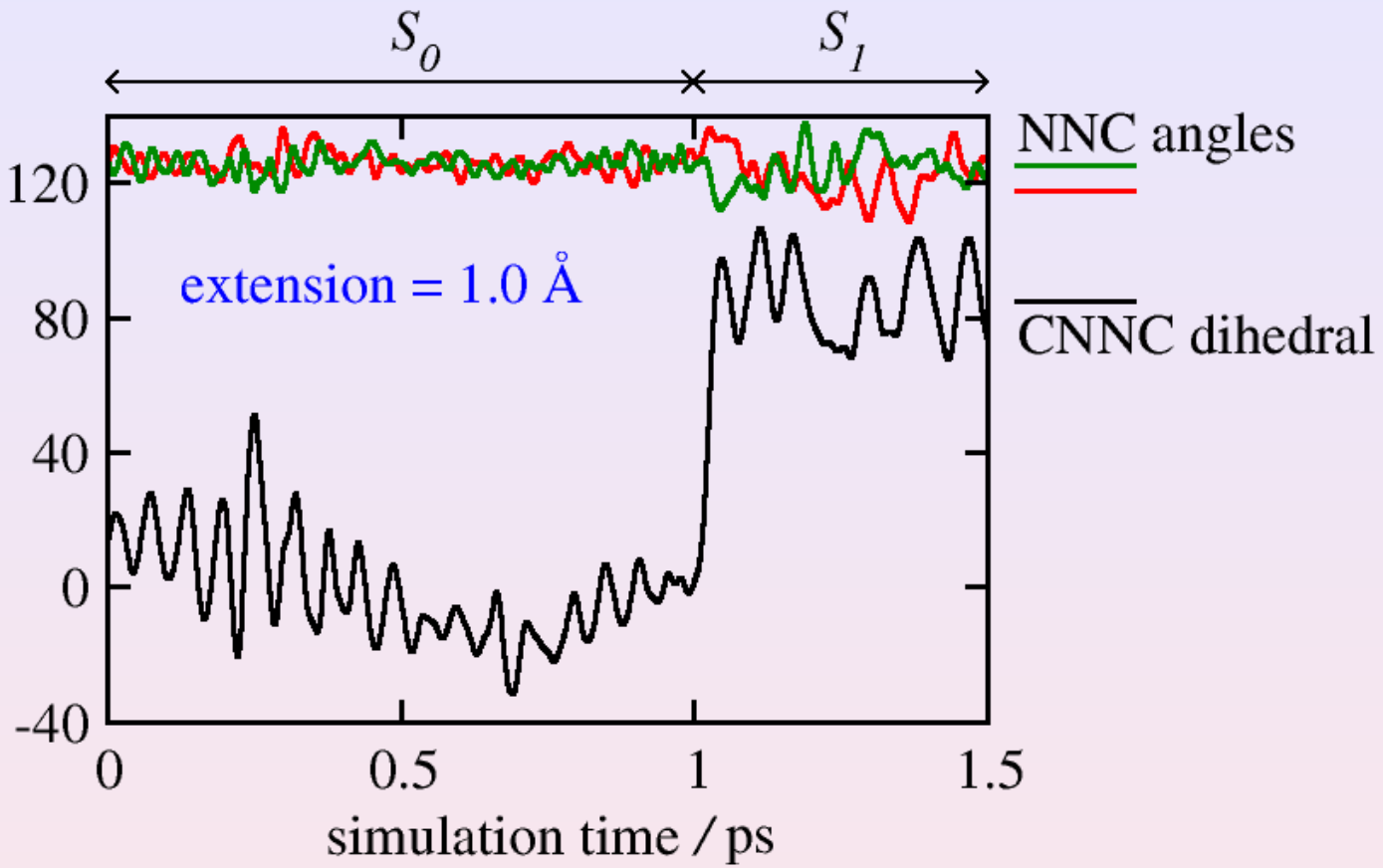
$\Rightarrow$ dithioazobenzene (DAB) with restrained sulfur atoms in dynamical simulations

- varying the distance between the two restraining centres mimics variations of a distance between electrodes of an STM/AFM apparatus

methods

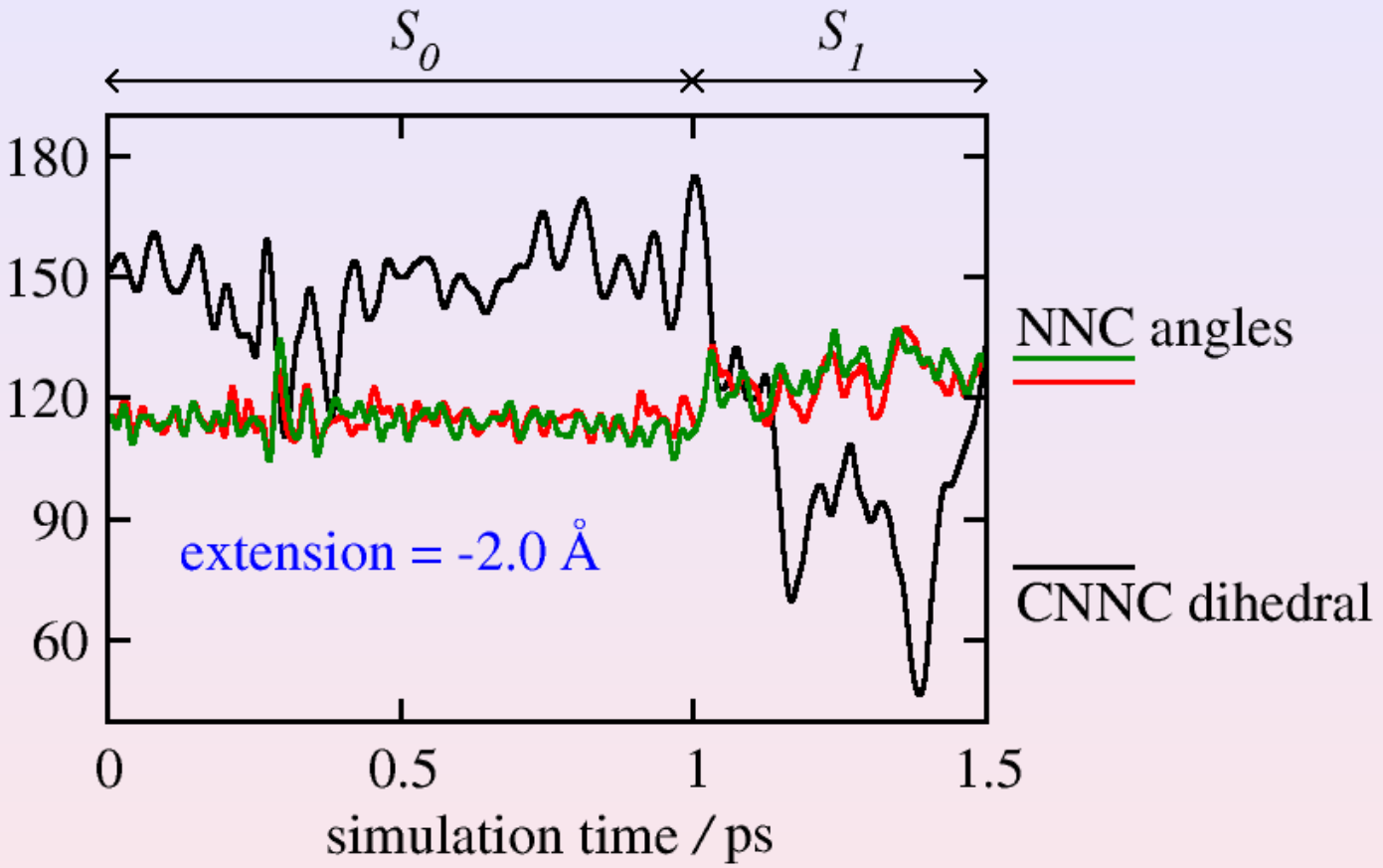
- S_0 state by Density Functional Theory (DFT) with PBE functional [1, 2], Goedecker pseudopotentials [3] and plane waves
- S_1 state by generalized [7] ROKS [6] extension to DFT
- atomar structure by either molecular dynamics simulations or static geometry optimization
- computer code: CPMD [4, 5]

results for *cis*: ultrafast CNNC rotation



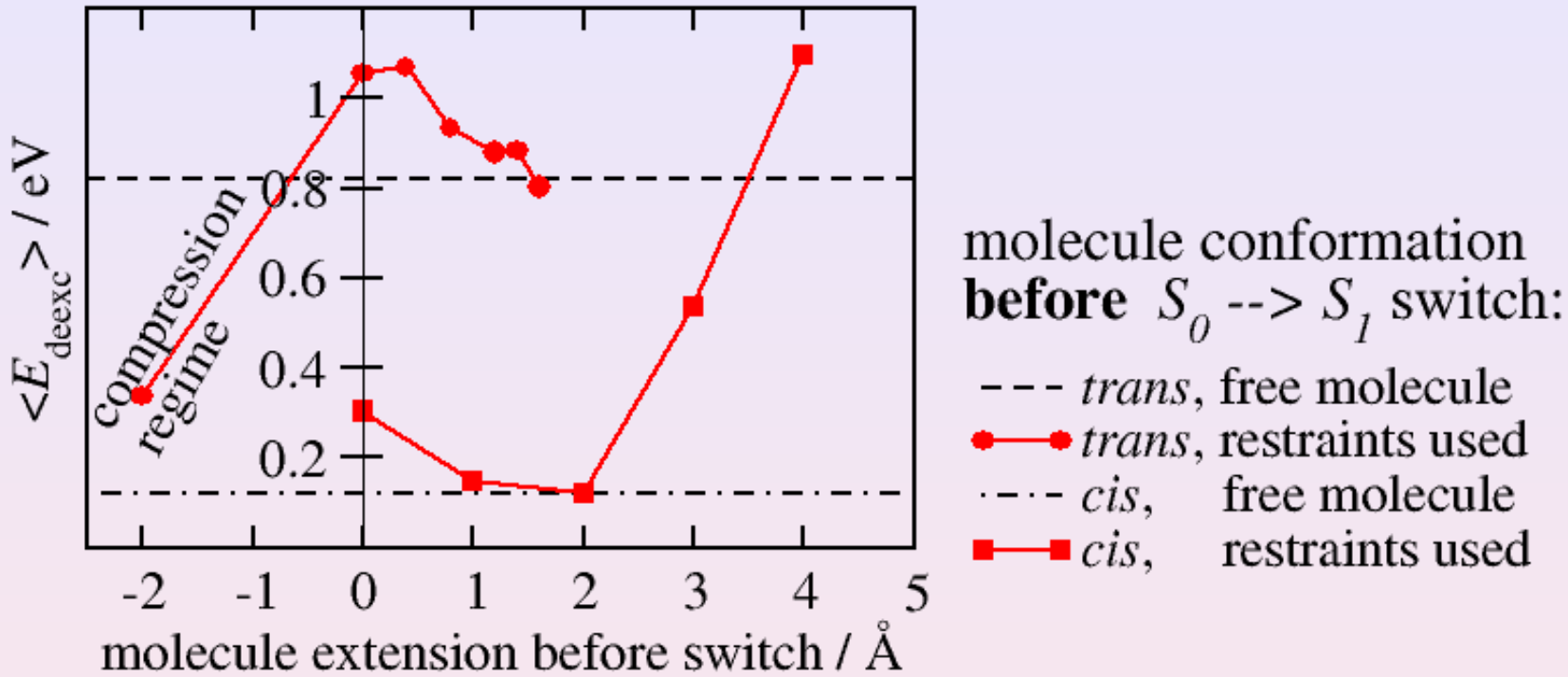
- the ultrafast rotation upon $S_0 \rightarrow S_1$ switch present regardless the value of the pulling force applied

results for *trans*: compression regime important



results: tuning dexcitation gap (1)

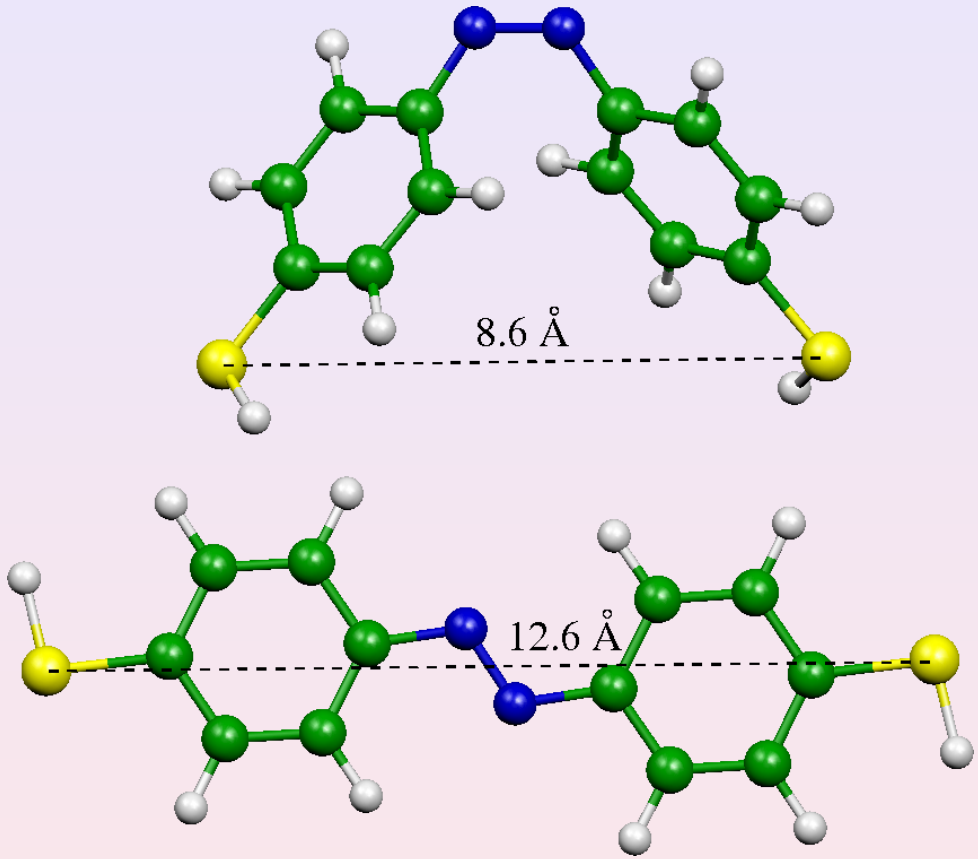
average deexcitation gaps over 0.5 ps trajectory



- absolute energy gap significantly red-shifted by mROKS
- gap changes vs. applied stretch captured more reliably
- average gaps for unrestrained (free) DAB important as a reference (related to most experimental data)
- tuning deexcitation gap

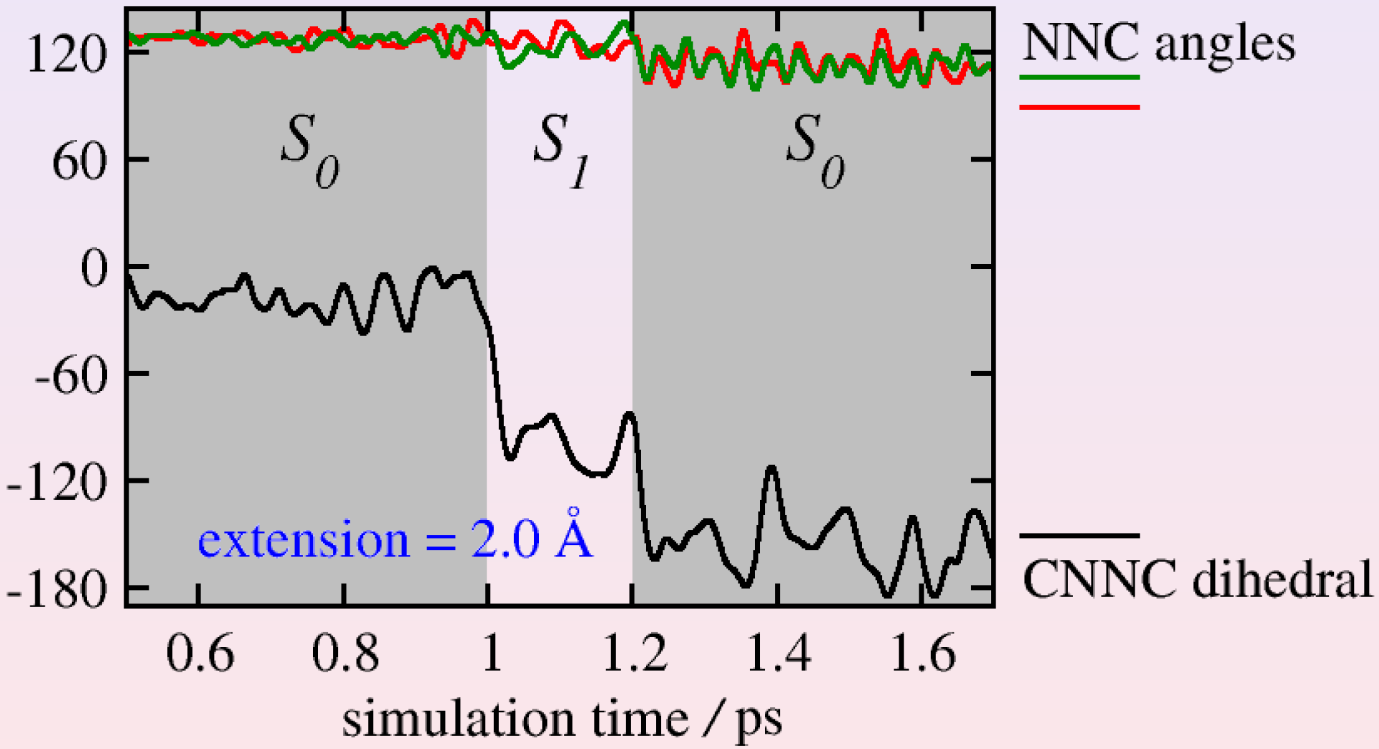
results: isomerization ?

the problem of different lengths ⇒ mechanical hindrance



- *cis*⟶*trans*: more probable for stretched *cis* structure
- *trans*⟶*cis*: more probable in compression regime

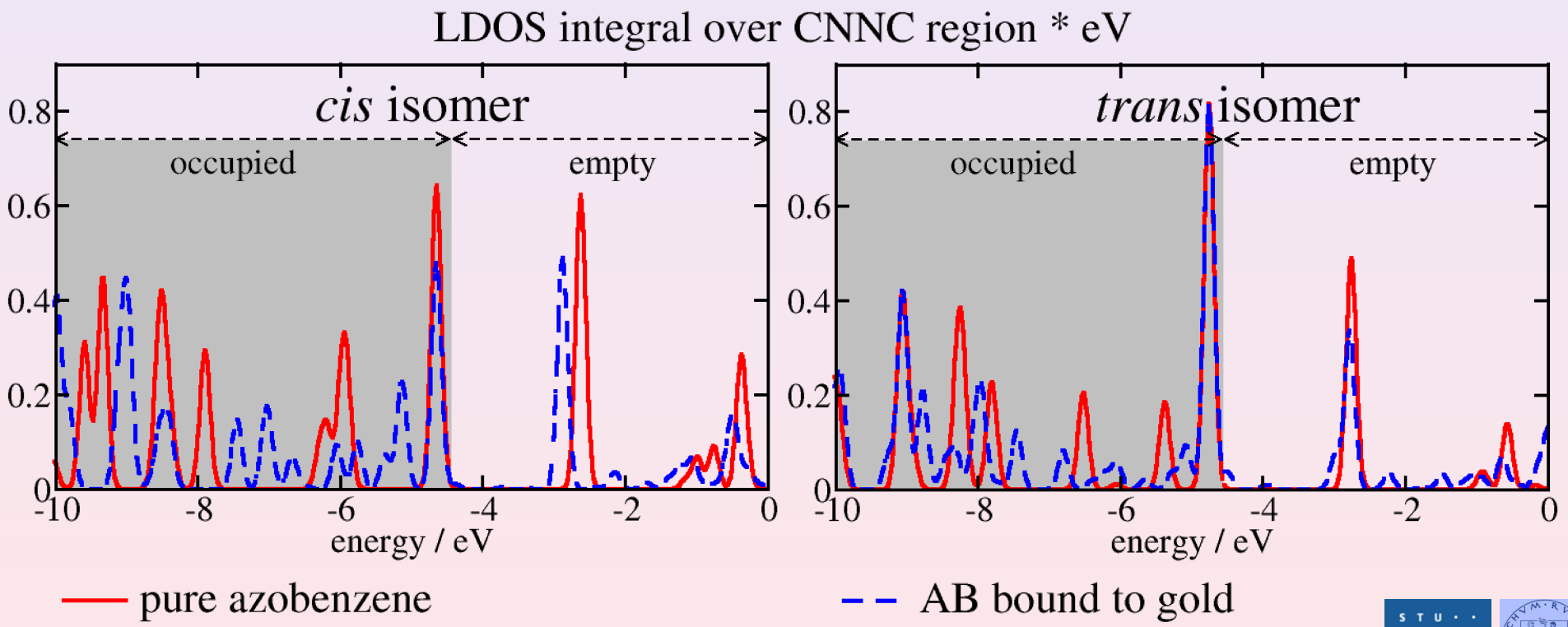
results: *cis*⟶*trans* isomerization



results: chemical effect of gold electrodes (1)

local density of states (LDOS) used as a tool:

$$\rho(E, \vec{r}) = \sum_i |\psi_i(\vec{r})|^2 \delta(E - E_i)$$



results: chemical effect of gold electrodes (2)

- qualitative impact:
  - the n and π^* orbitals no more HOMO and LUMO
- quantitative impacts:
  - noticeable red-shift of the excitation energy especially for *cis* conformation
  - modified weigths of particular orbitals
- conclusions from LDOS:
  - electronic structure of CNNC qualitatively unchanged

  $\Rightarrow$ optical $n \leftrightarrow \pi^*$ switching should remain possible for AB bound to gold

  $\Rightarrow$ the restraint model qualitatively appropriate

conclusions

- rotational isomerization path possible for azobenzene used as a single-molecule junction
- efficient isomerization only within a matching-length interval
- compression of *trans*-AB should increase *trans*$\longrightarrow$*cis* photoisomerisation yield
- tuning the isomerization yield by applied mechanical force should be possible

Acknowledgments

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Atomar structure files for visualization of the gold-azobenzene system provided by Robert Turanský.

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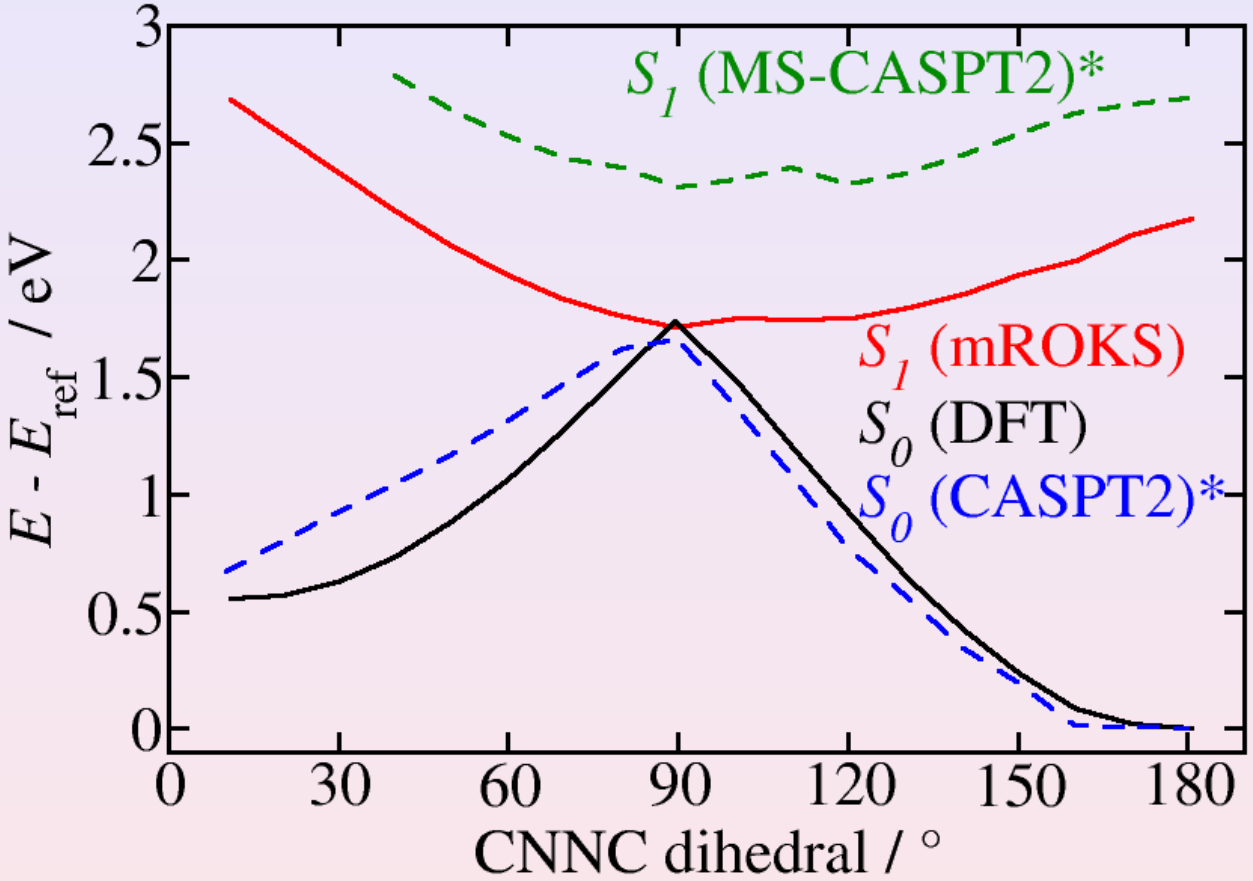
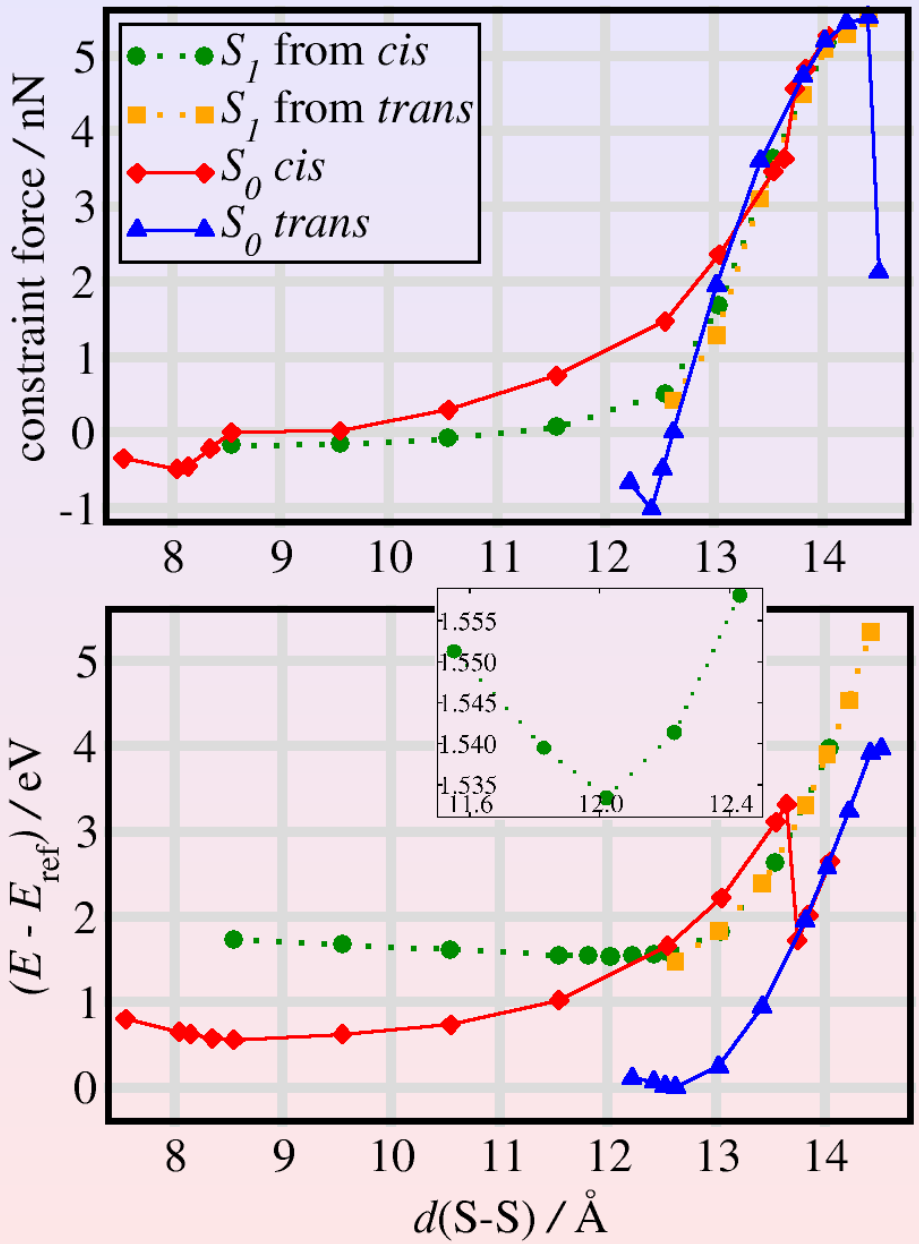
potential-energy surfaces (DFT-based vs. CASPT2)

PESs along S_0 optimized CNNC-constrained geometries (pure AB)



*adapted from Gagliardi *et al.* [Theor.Chem.Acc. **111**, 363 (2004)]

dithioazobenzene static pulling/compression

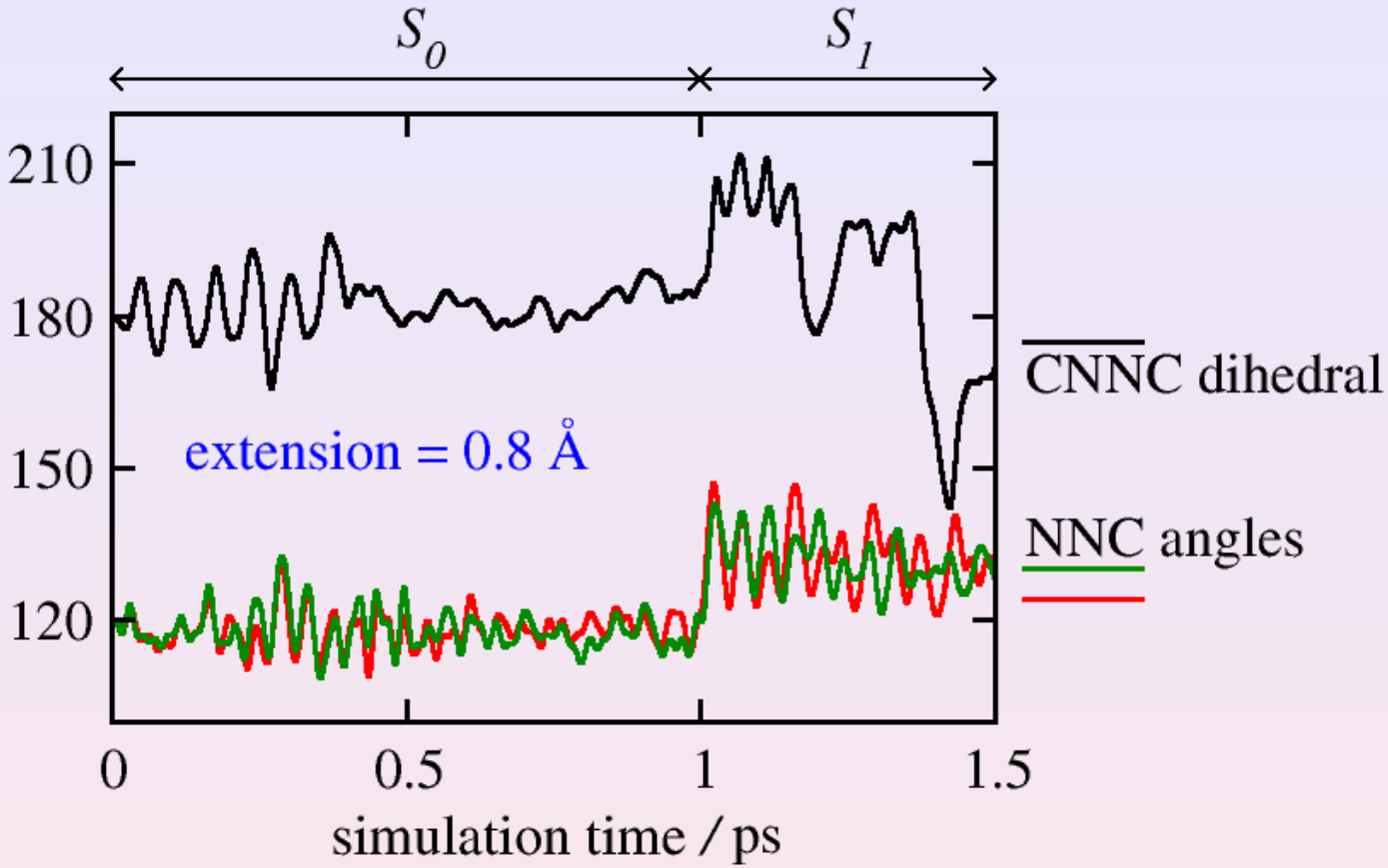


red: *cis* (turns into *trans* when stretched above 5.1 A)

blue: *trans* (S–C bond broken at the end)

S_1: only one isomer
==> the curves overlap

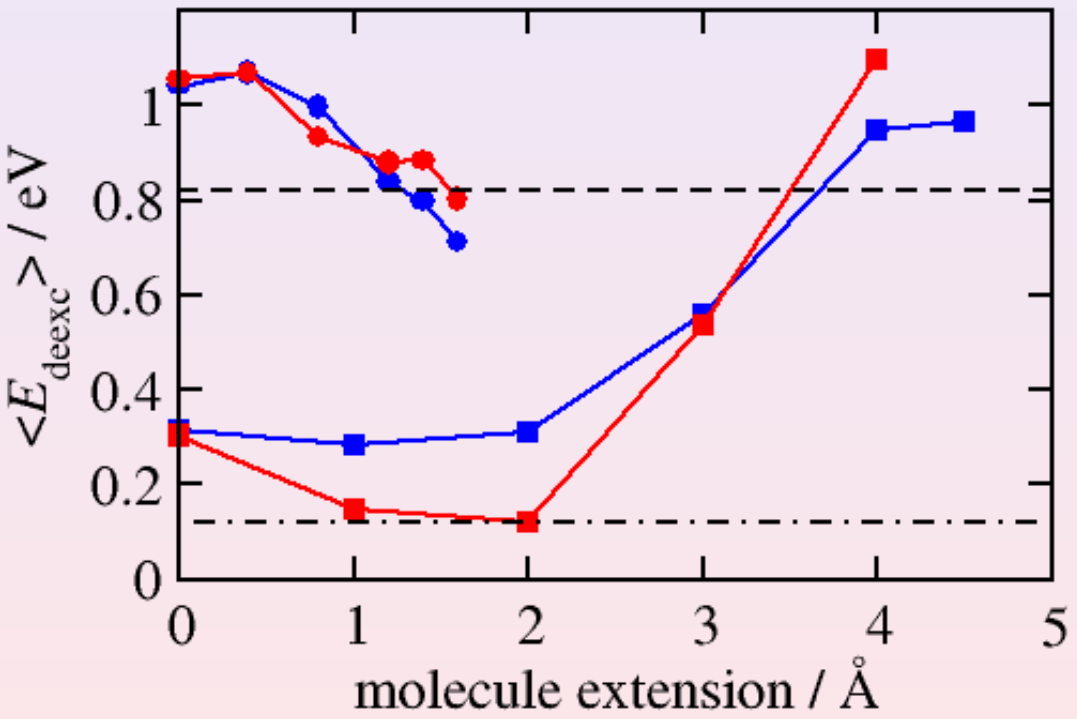
results for *trans*: also NNC variation



- the ultrafast rotation present especially at smaller stretches
- very fast partial opening of NNC angles at larger stretches

average dexcitation gap for two different junction strengths

average deexcitation gaps over 0.5 ps trajectory



blue: harder restraint
red: softer restraint
black: no restraint

molecule conformation **before** S_0 --> S_1 switch:

- *trans*
- *trans*
- *cis*
- *cis*
- *trans*
- *cis*

tuning dexcitation gap (comments)

- significant dependence of the gap on the extension

$\Rightarrow$ tuning the isomerization yield through the controll of the gap by applied mechanical force possible

- effect of restraint stiffness noticeable
- maximum applicable extensions limited by unavoidable effects:
  - *cis* isomer: max. extension ≈ 4.5 Å; beyond this the molecule turns into *trans*-DAB (in ground state!)
  - *trans* isomer: S–C or N–C bond breaks at stretches above 1.6 Å
  - breaking of the junctions or electrodes

computational side - comparisons

number of processors	4	8	16
IBM-SP Power2	3495.00	1482.80	681.33
Opteron244 Intel ATLAS	1708.22	754.46	341.82
HP-XC Itanium2 2proc 1.5 GHz nodes	668.82	321.51	135.90
HP-XC Itanium2 16proc 1.6 GHz node	839.51	450.26	NA
IBM-SMP Power5 ATLAS	719.37	383.81	203.93

Table: total execution times in seconds

- $135.90/321.51 \approx 0.423$ reduction of comput. time by switching from 8 to 16 proc.
- reduction of comput. time to 20% by switching from 4 to 16 proc.