A Posteriori Quantization of the Nuclear Motion by Backfill Calculations

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Introduction

- The computations of the IR spectra of the hydrogen bonded systems have some difficulties with anharmonic effects, proton coupling…
- The proton transfer is one of the most common elementary reaction in enzymology and biochemistry.
- One of the possibility is numerical solving the Schrödinger equation for proton motions.
- The analysis of the structural fluctuation along molecular dynamics.

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- The analysis of the structural fluctuation along molecular dynamics.

The idea of combining the molecular dynamics with numerically solving the Schrödinger equation for proton motion.

Computational approach

- Computation of the trajectory:
  - Car–Parrinello molecular dynamics;
  - Born-Oppenheimer molecular dynamics.
- The selection of the snapshots from molecular dynamics trajectory.
- The main analysis e.g. quantization of nuclear motion.

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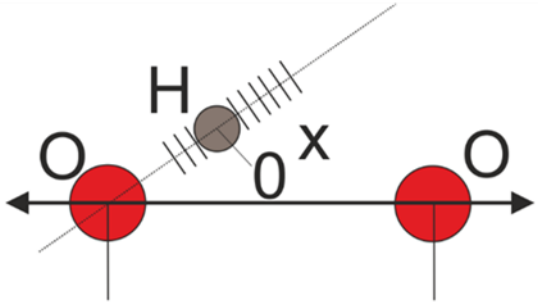

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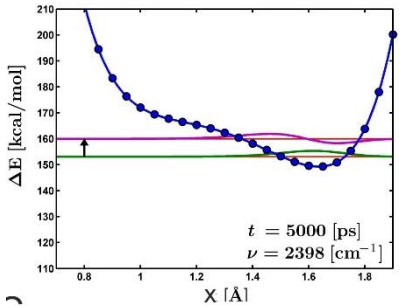
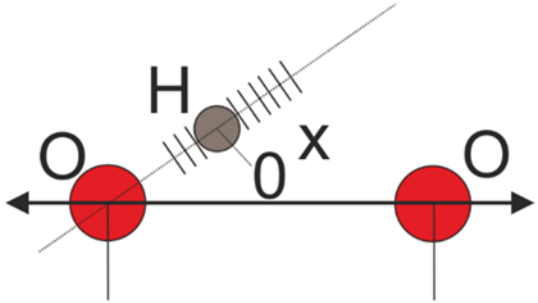




Calculation of the energy for selected proton positions.
Numerical solving the Schrödinger equation.

Computation details

Molecular Dynamics (CP2K, CPMD, Terachem)

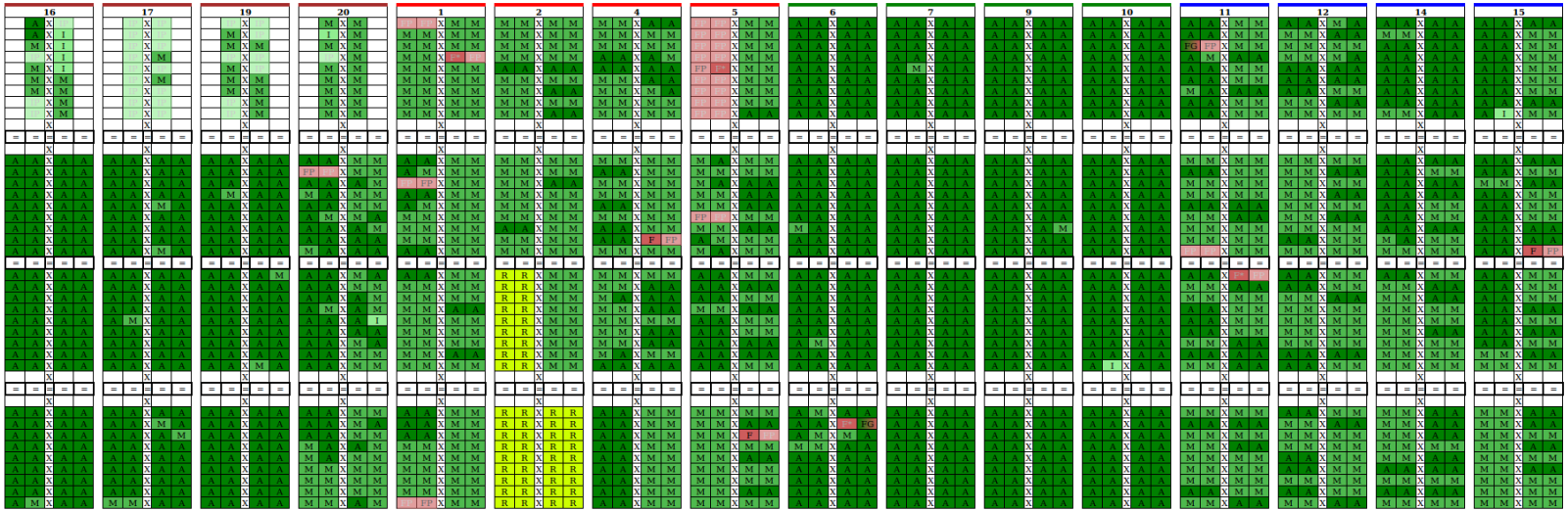
Density Functional Theory (DFT), post-HF methods

The trajectory analysis: the snapshots computations

Analysis of the proton motions (quantum effects)

Analysis the electronic structure fluctuation along MD

Backfill mechanism

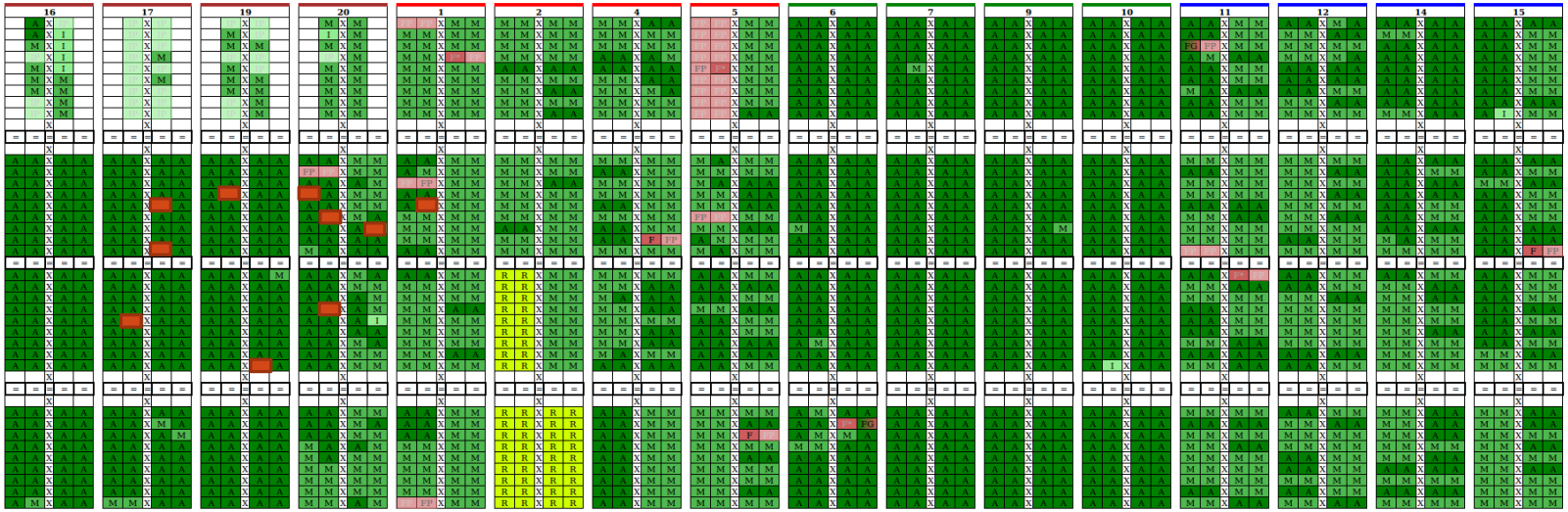


Backfill mechanism

The large number of the small jobs

hundreds of thousands jobs with walltime shorter than few minutes.

- The space between long jobs.



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Scheduler have a lot of work!

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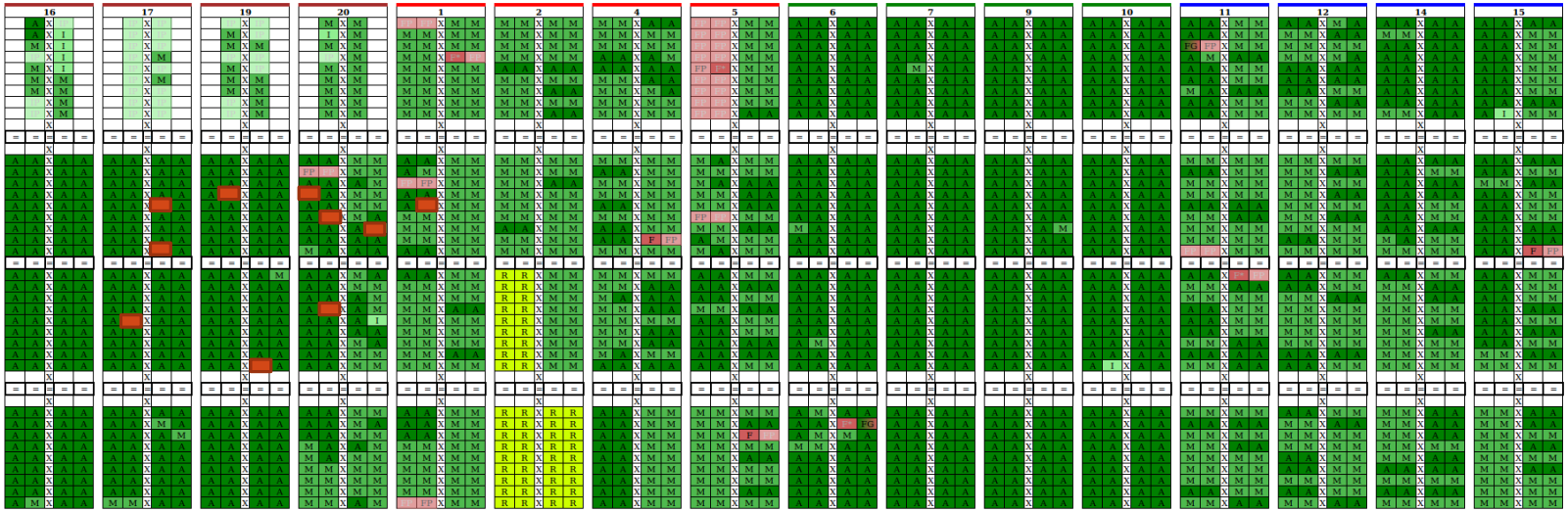
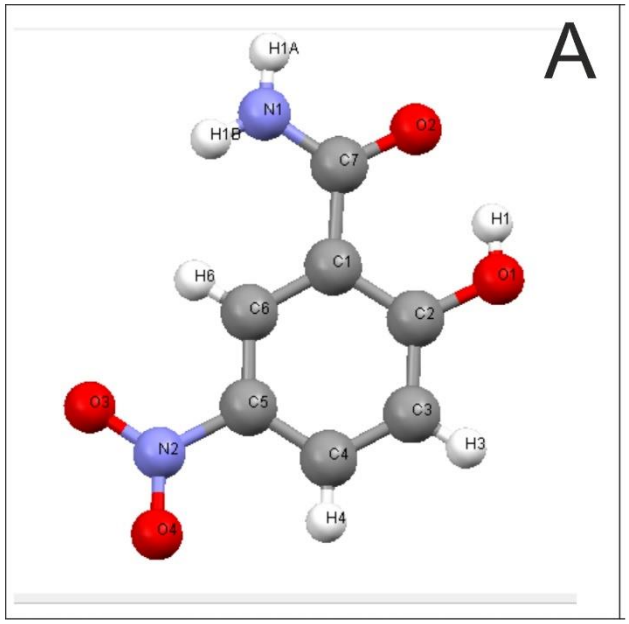


Example: 2-hydroxy-5-nitrobenzamide



intramolecular
hydrogen bond

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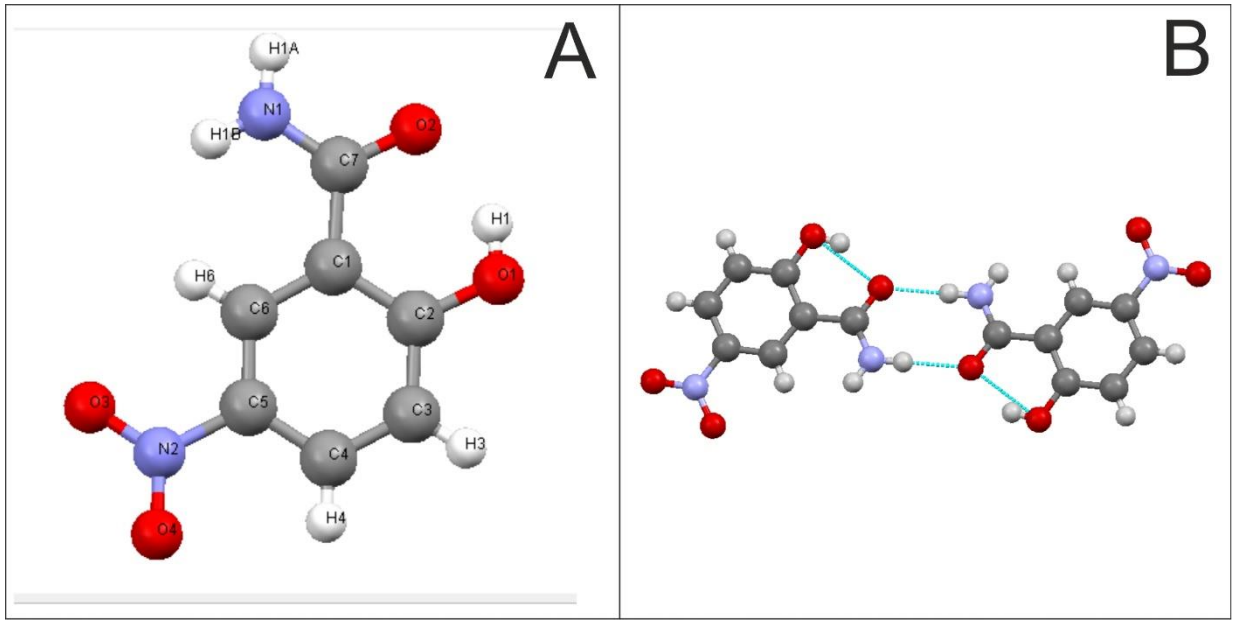

intramolecular hydrogen bond

the cyclic dimer

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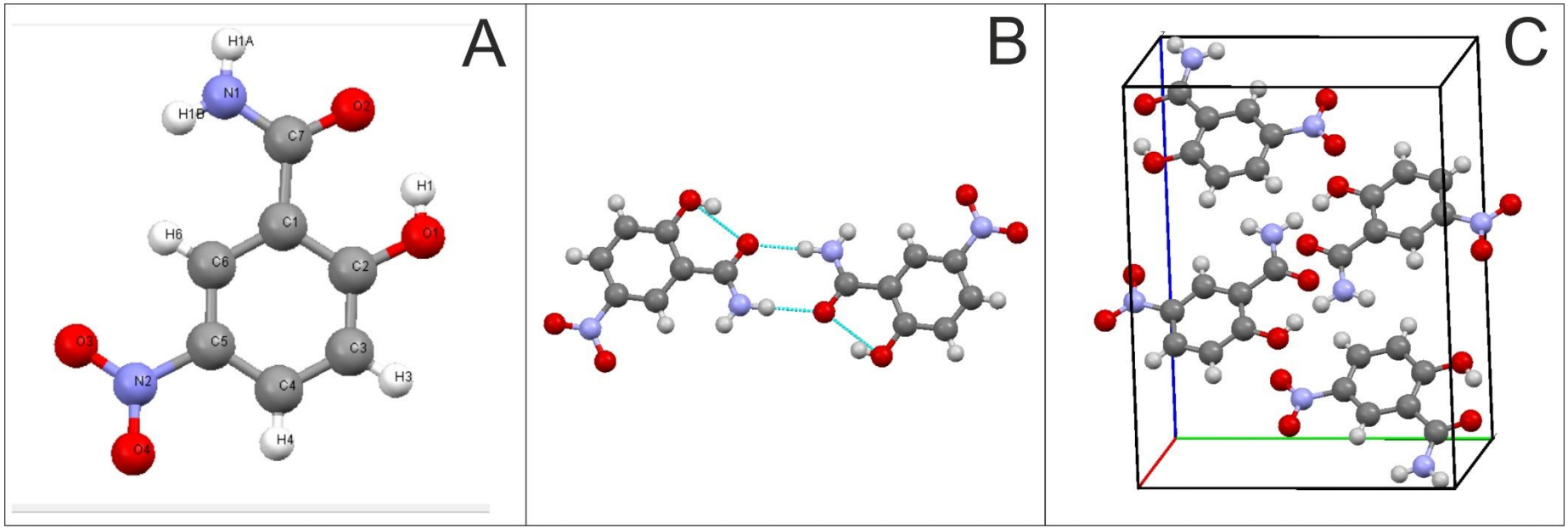

intramolecular hydrogen bond

the cyclic dimer

hydrogen bond in crystal field

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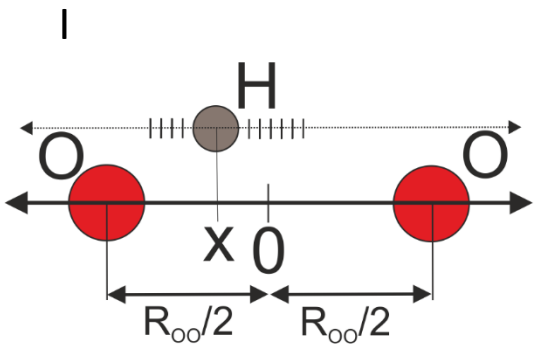

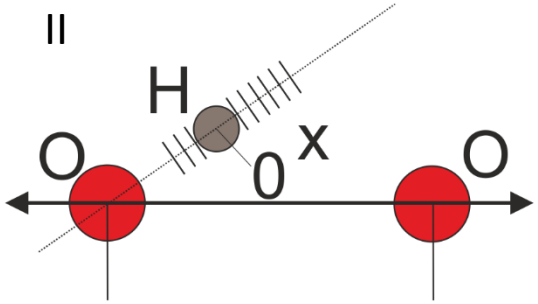

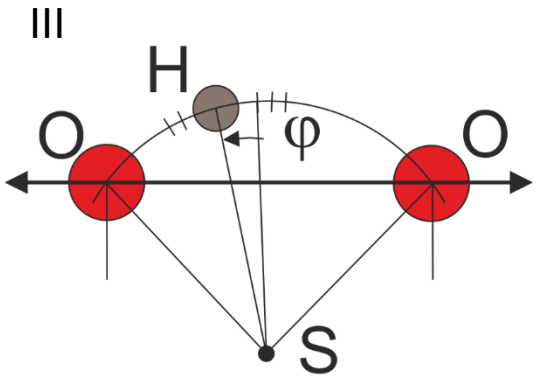

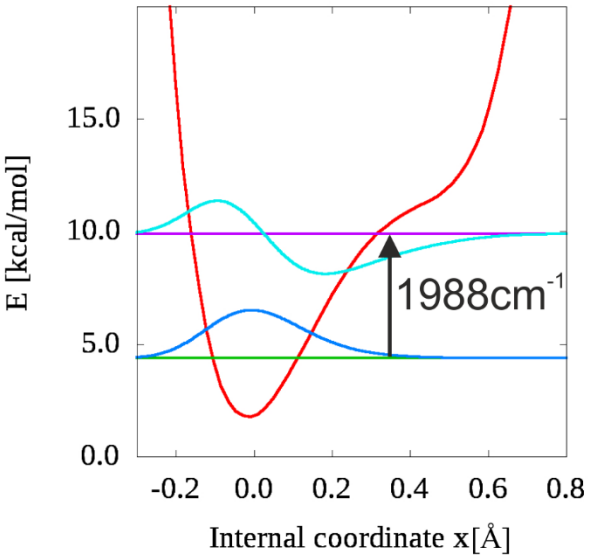

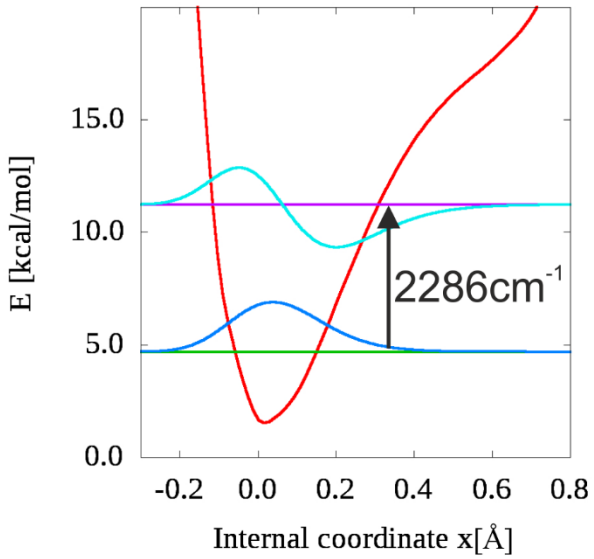

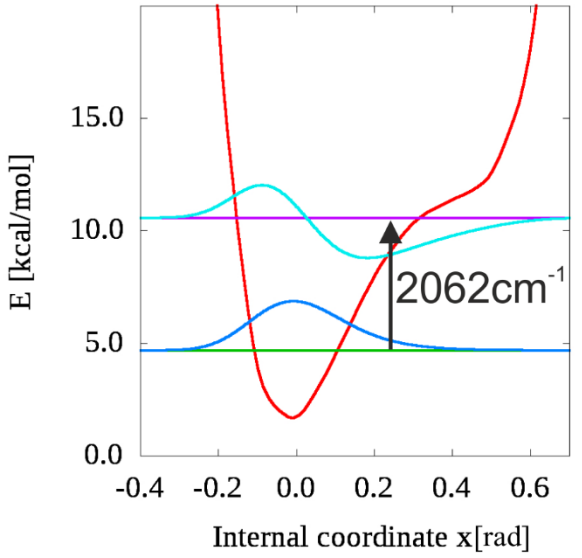

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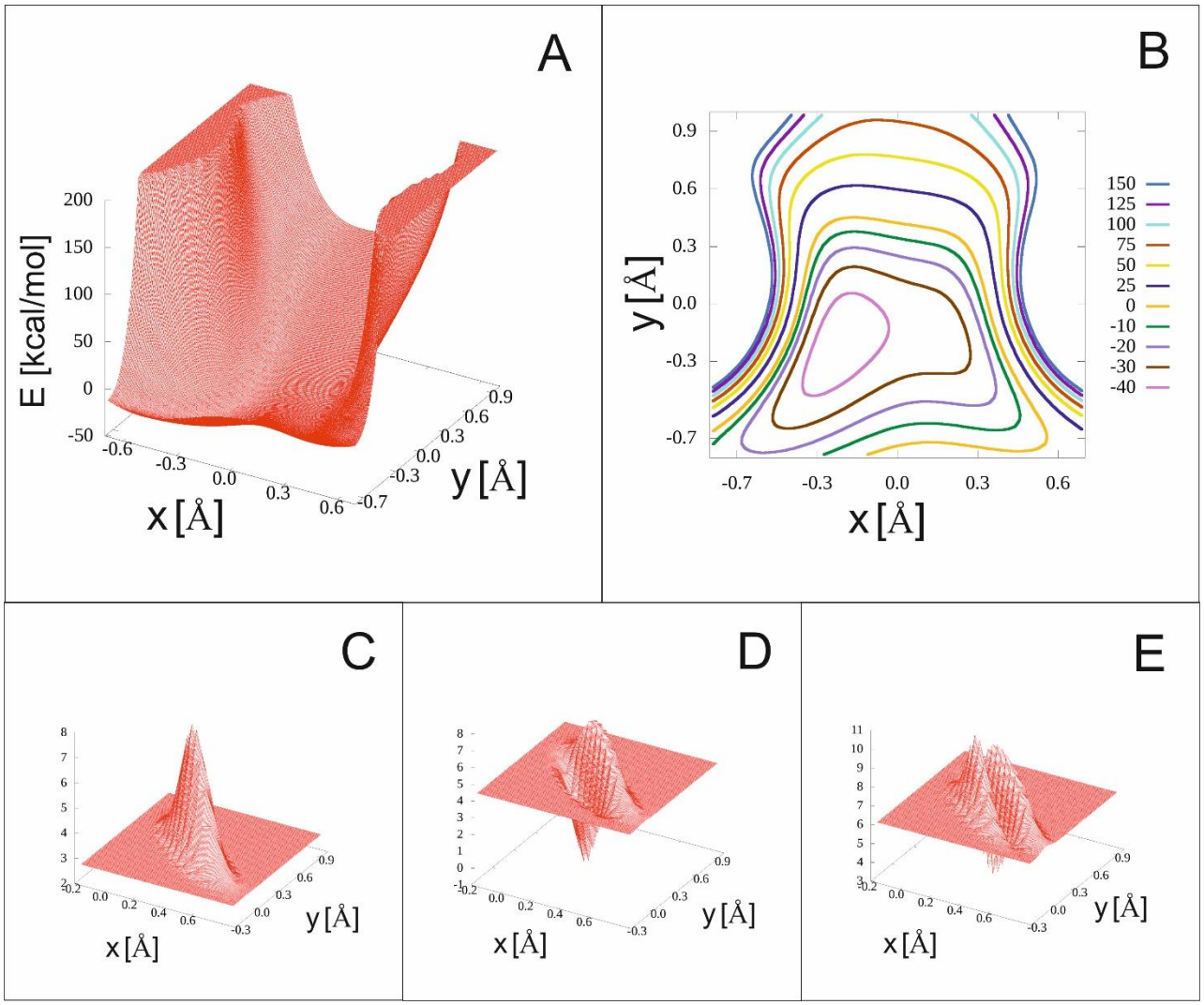

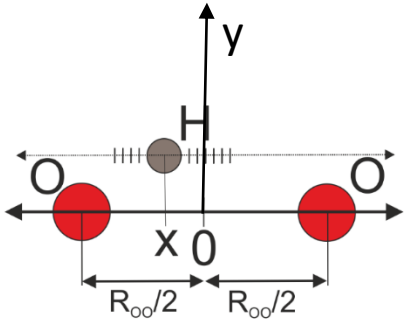

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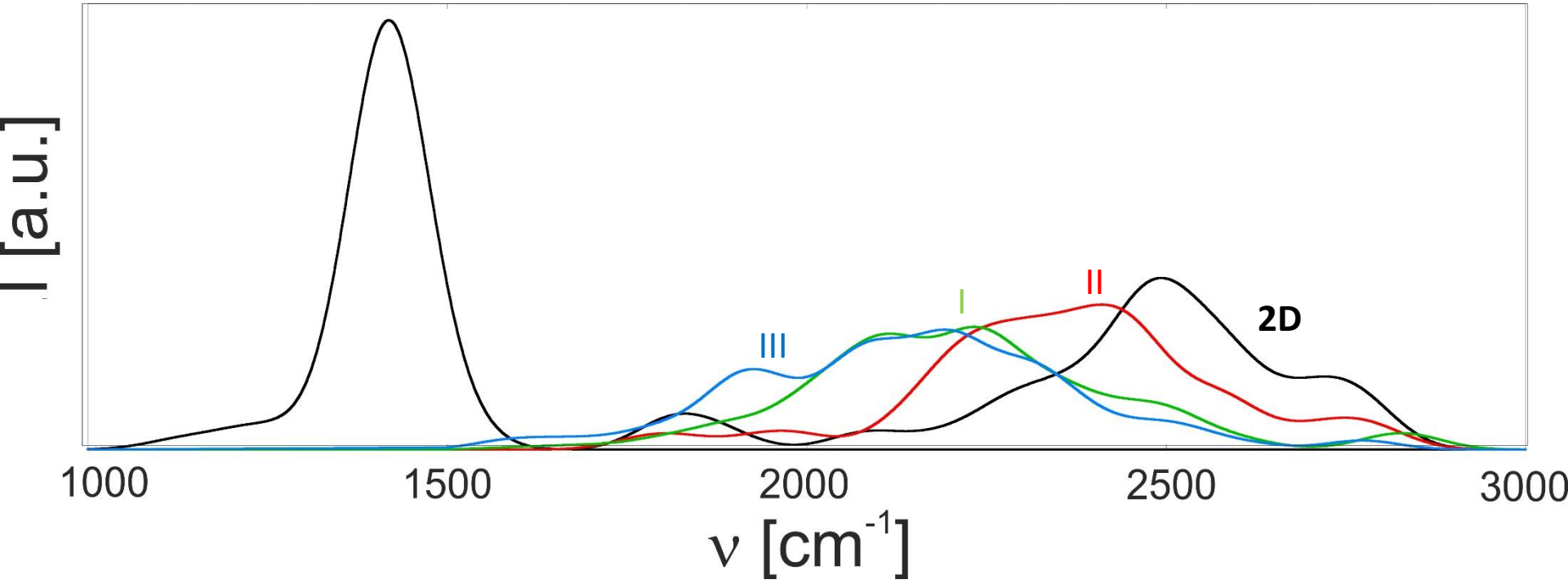
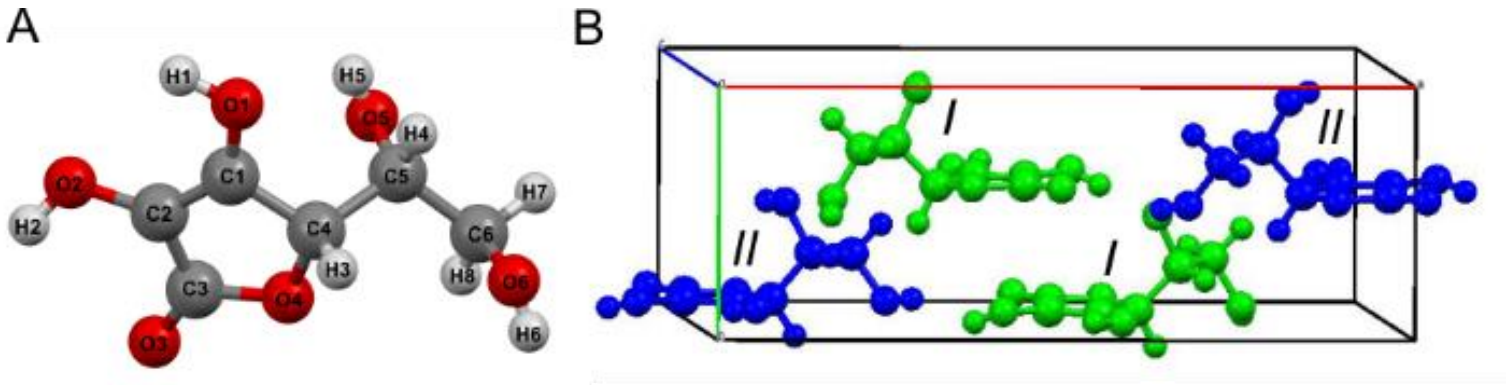


Example: Vitamin C



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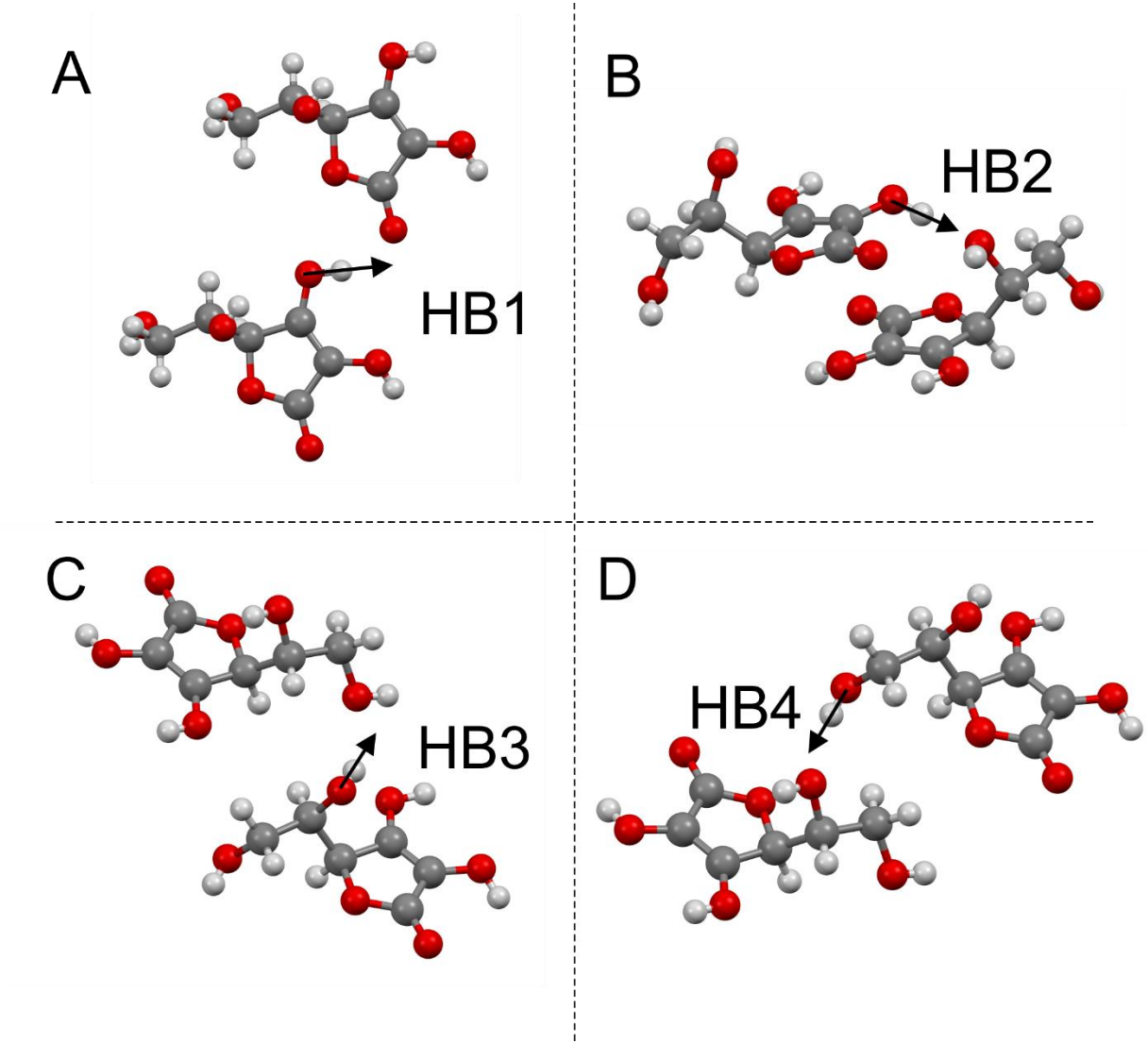
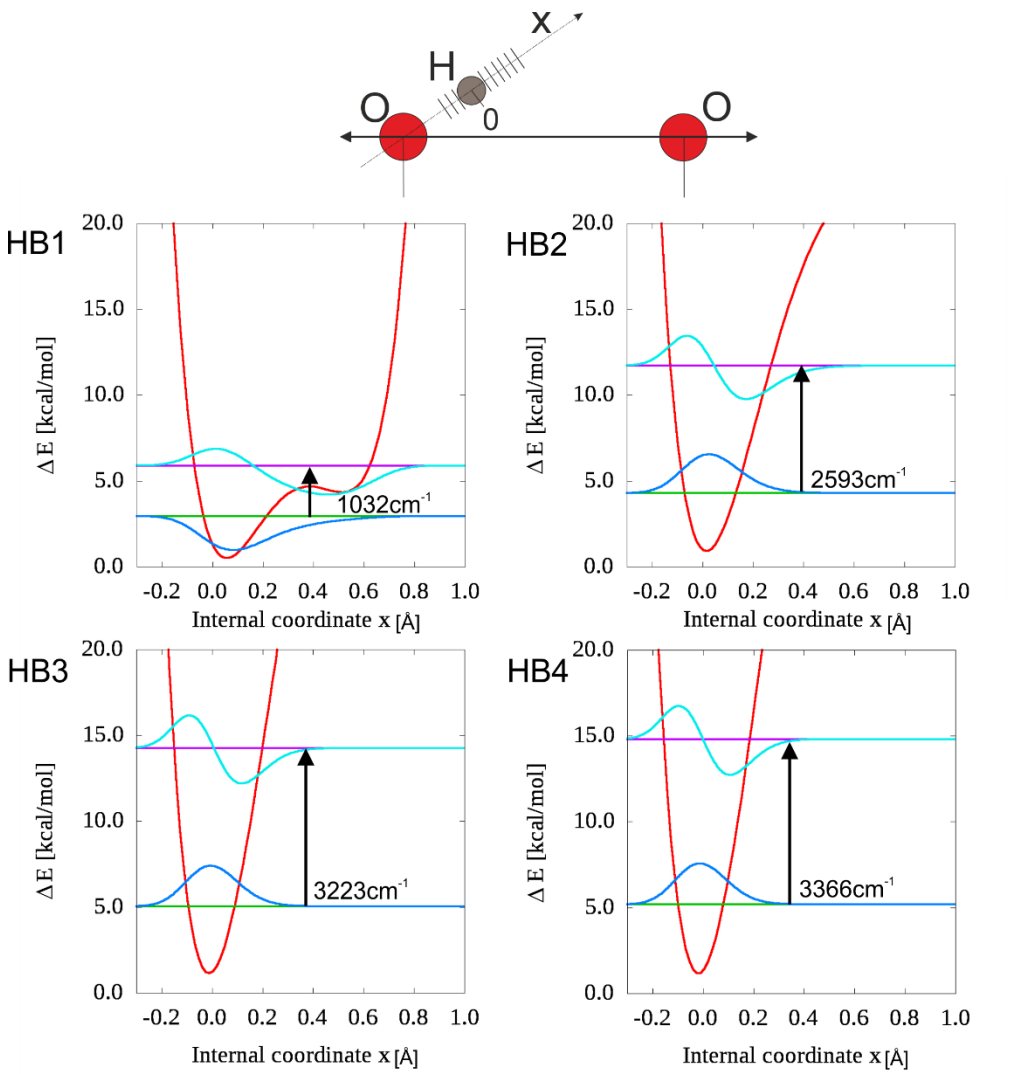


four kinds of hydrogen bonds

Example: Vitamin C



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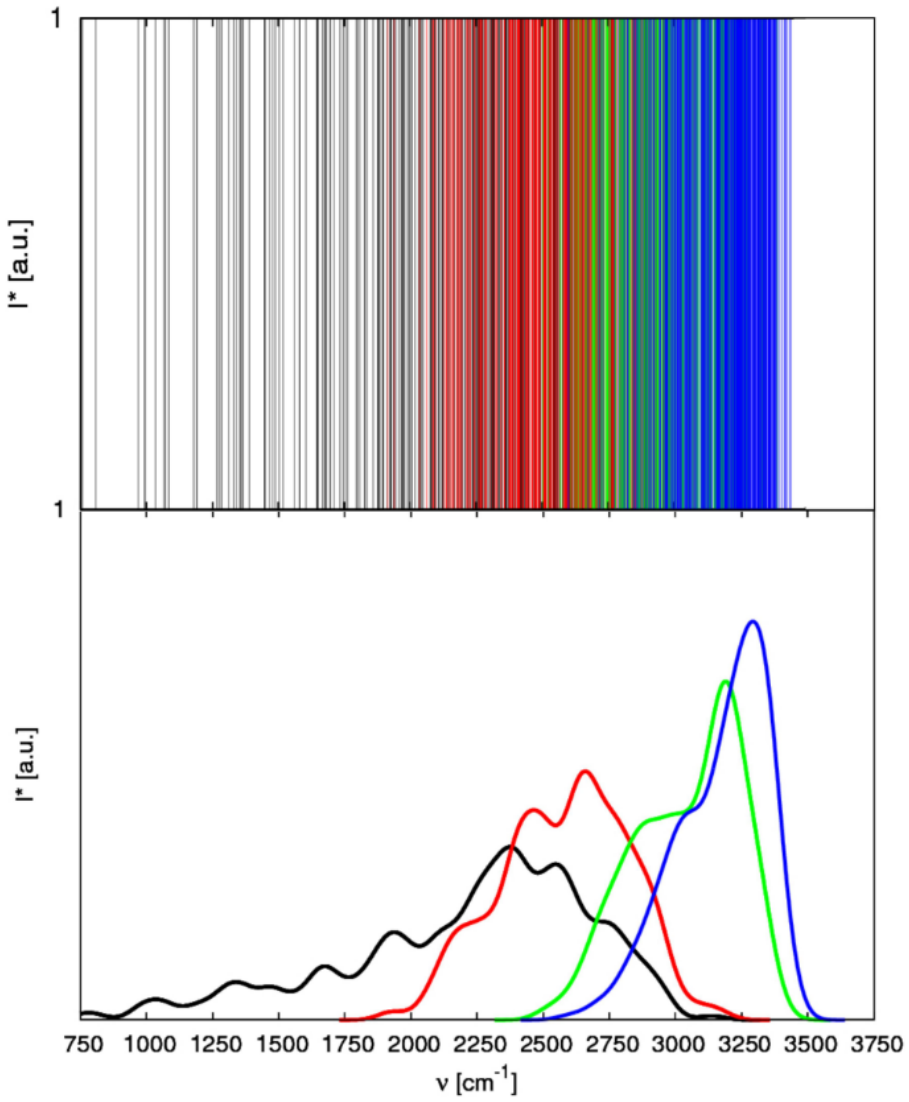
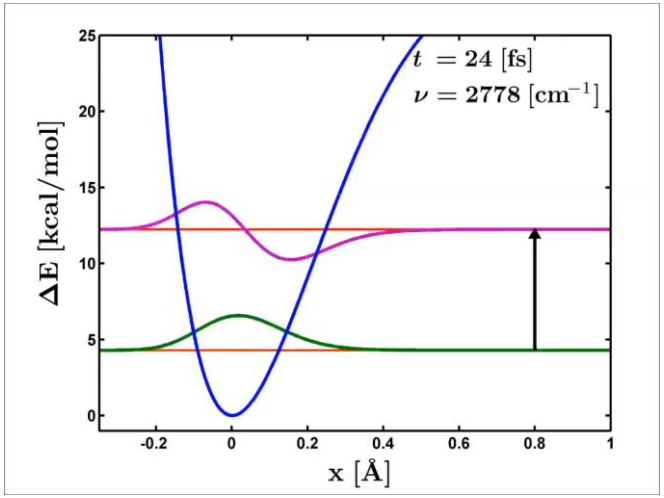
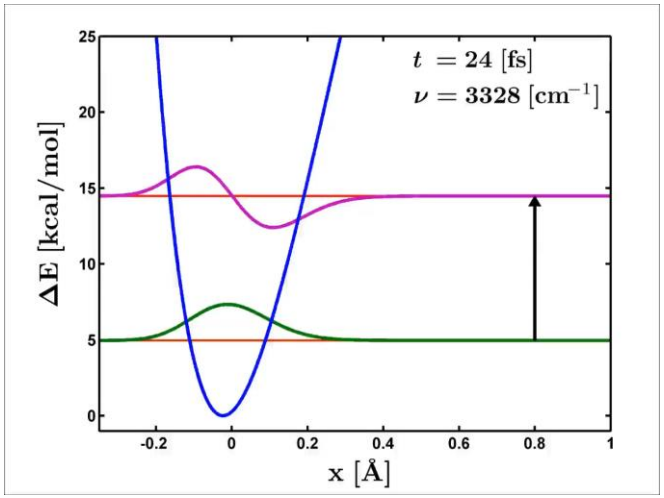
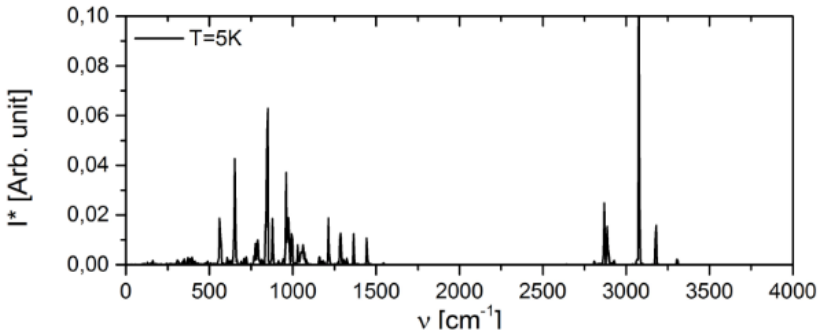




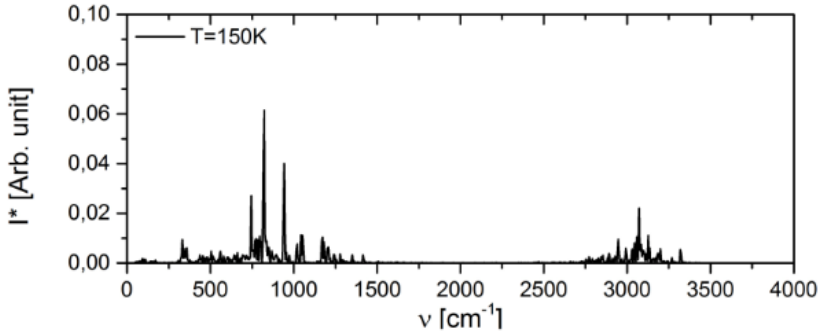


Example: Vitamin C

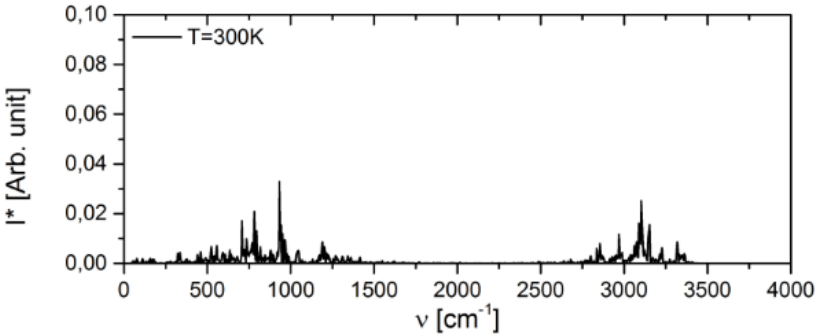
5K



150K



300K



Example: Vitamin C

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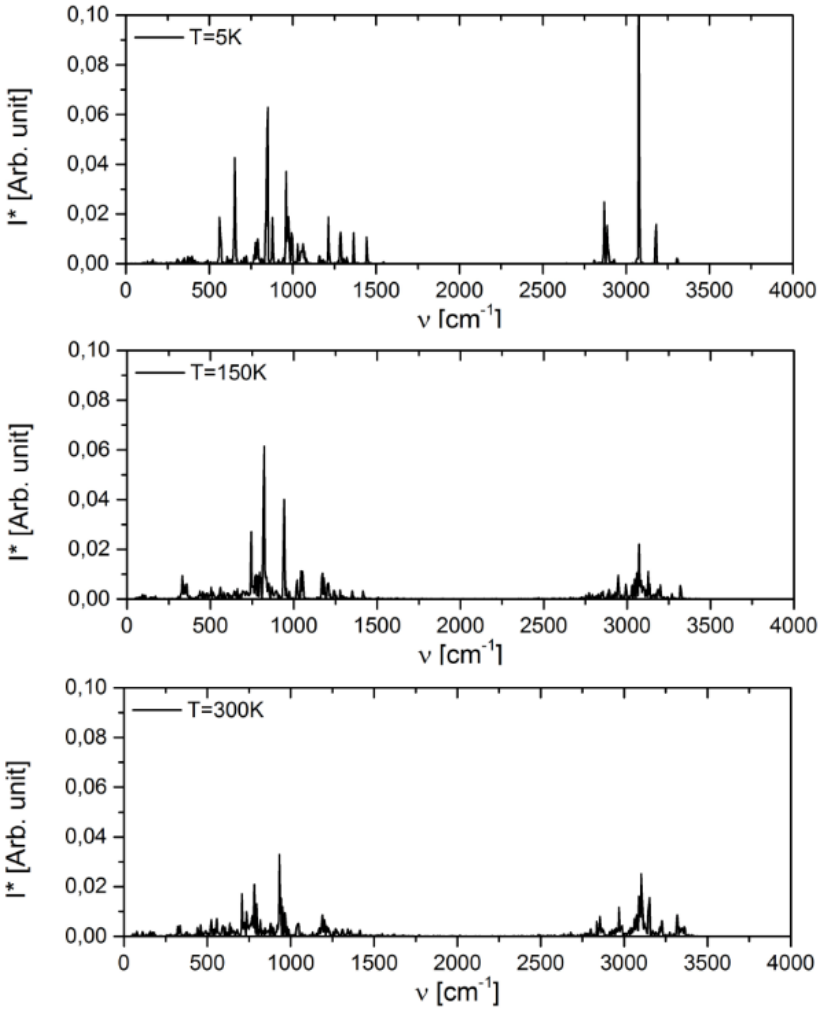
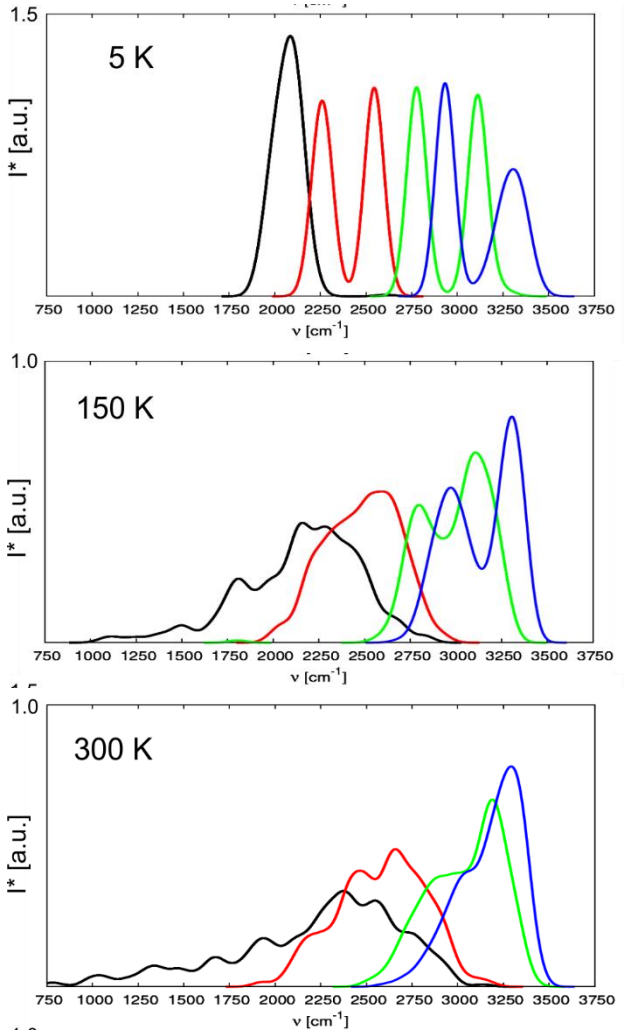
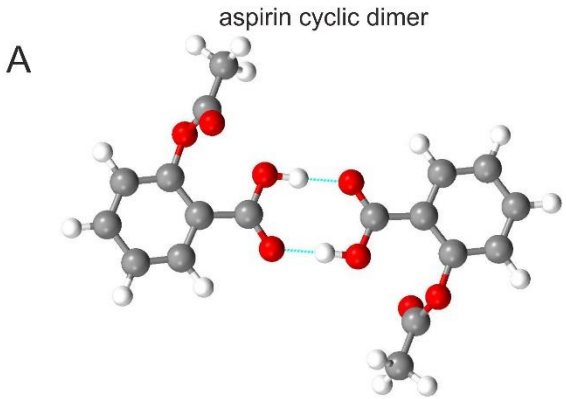
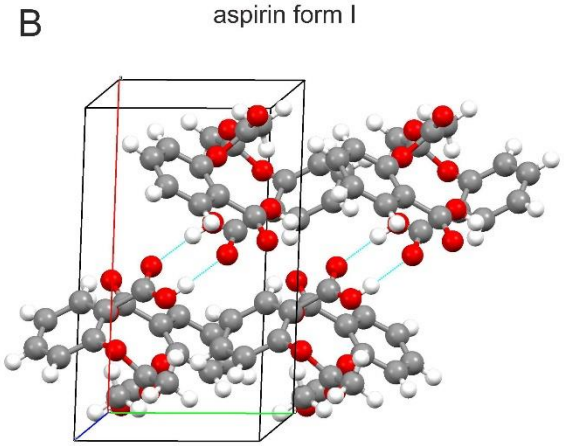
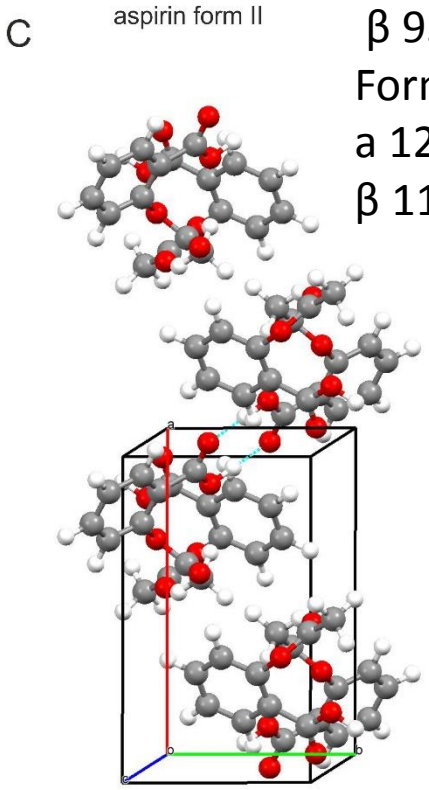




Example: Aspirin





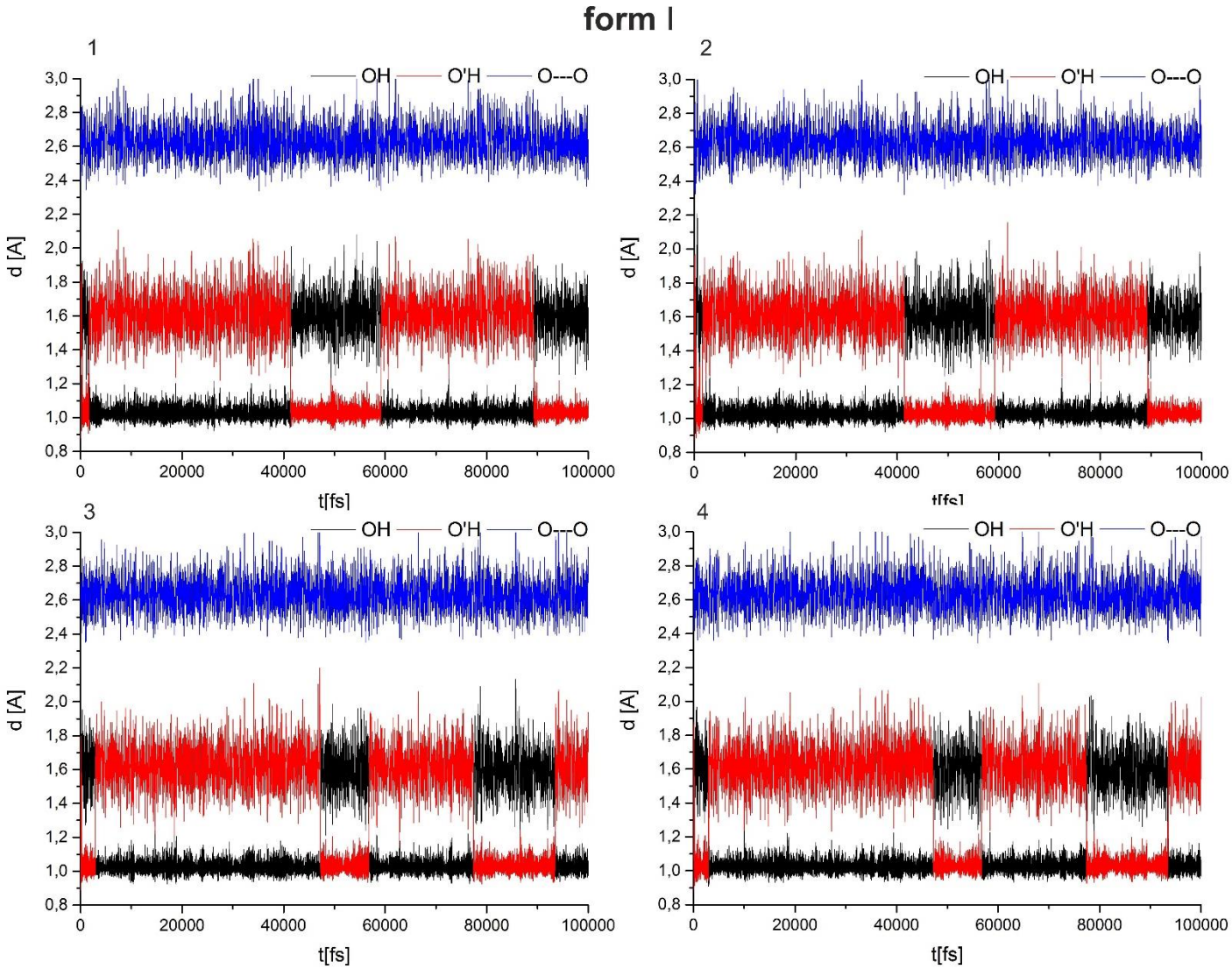


Form I:
a 11.233(3) Å, b 6.544(1) Å, c 11.231(3)Å,
β 95.89(2)°, V 821.218Å^3;
Form II:
a 12.095(7)Å, b 6.491(4) Å, c 11.323(6) Å,
β 111.509(9)°, V 827.1(8)Å^3.

Space group:

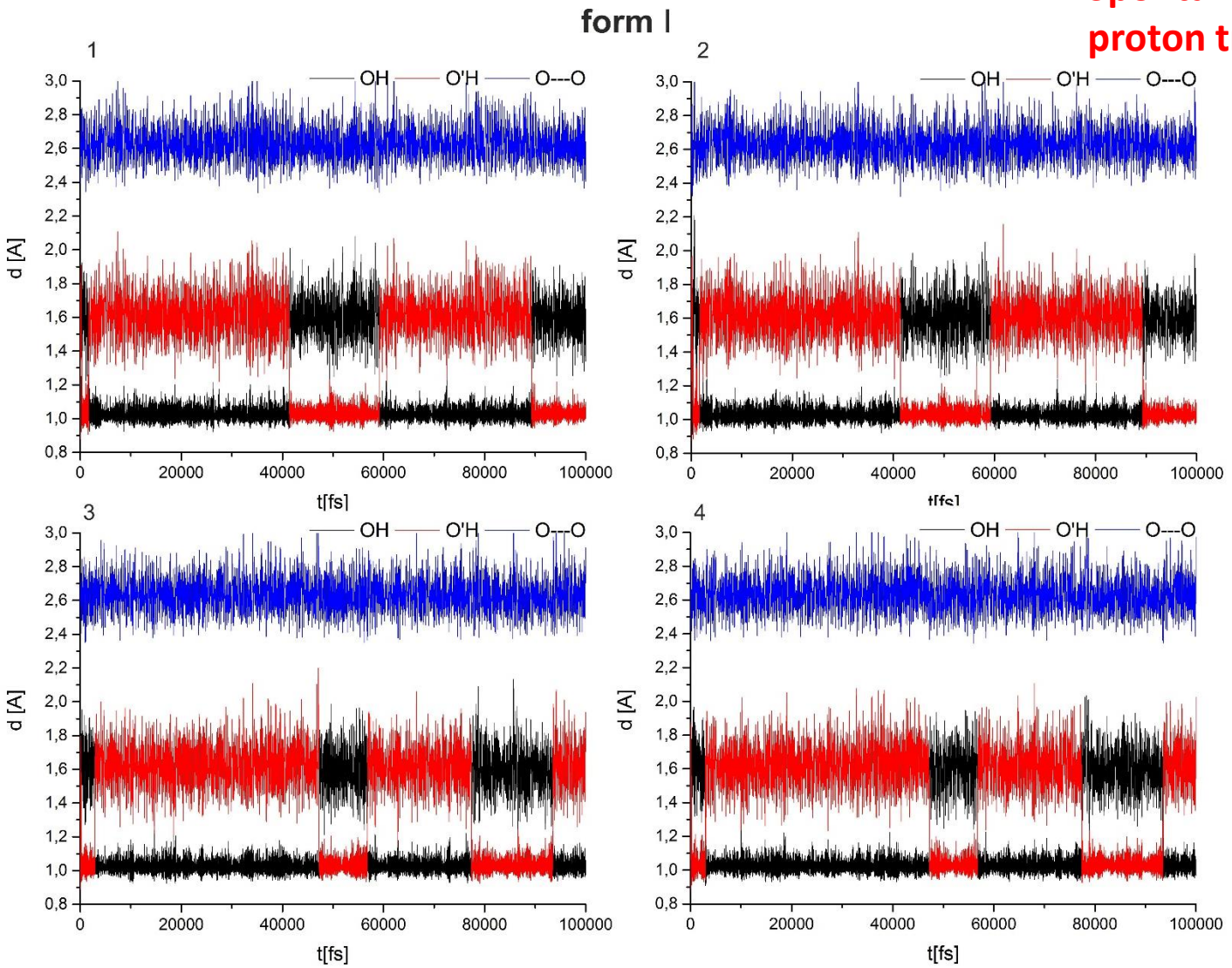
$P2_1/c$

Example: Aspirin



Example: Aspirin

Spontaneous and synchronous proton transfer.



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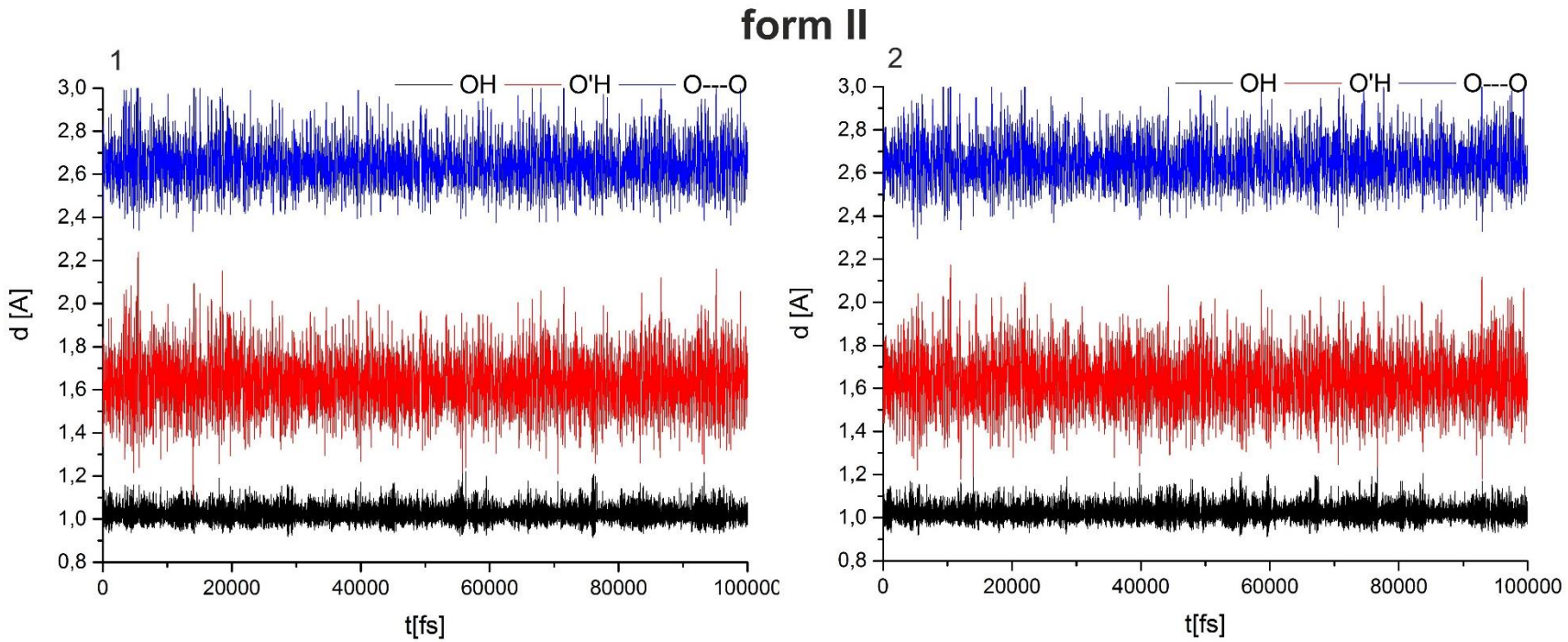

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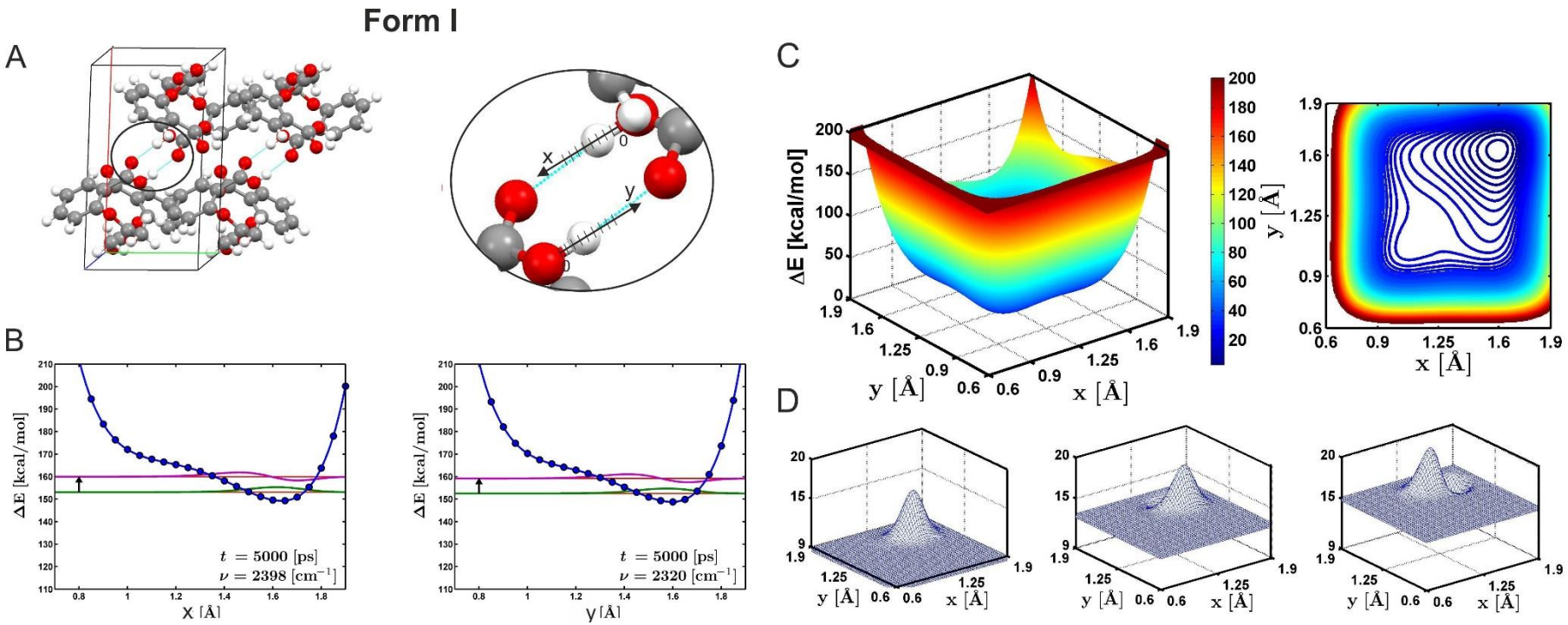

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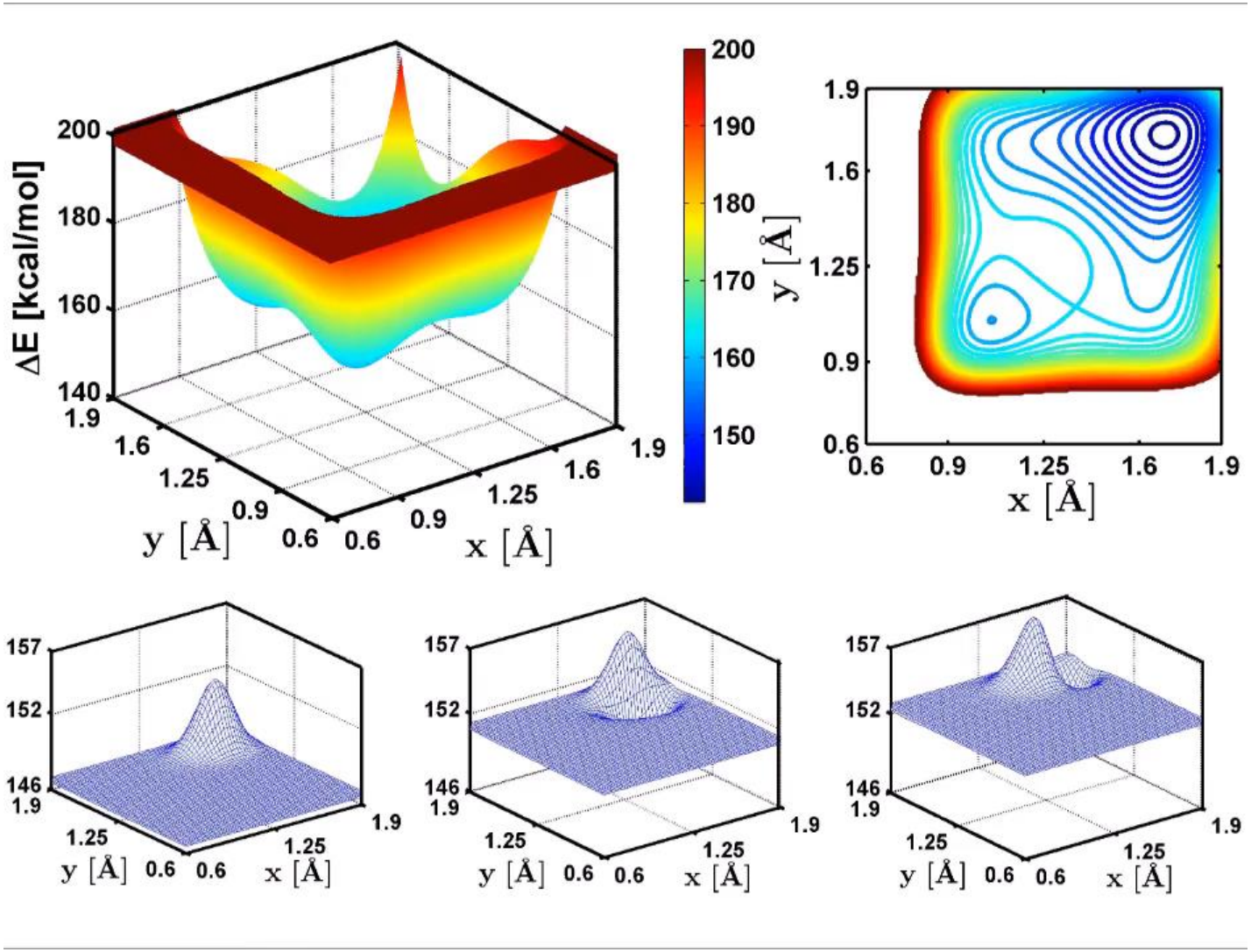

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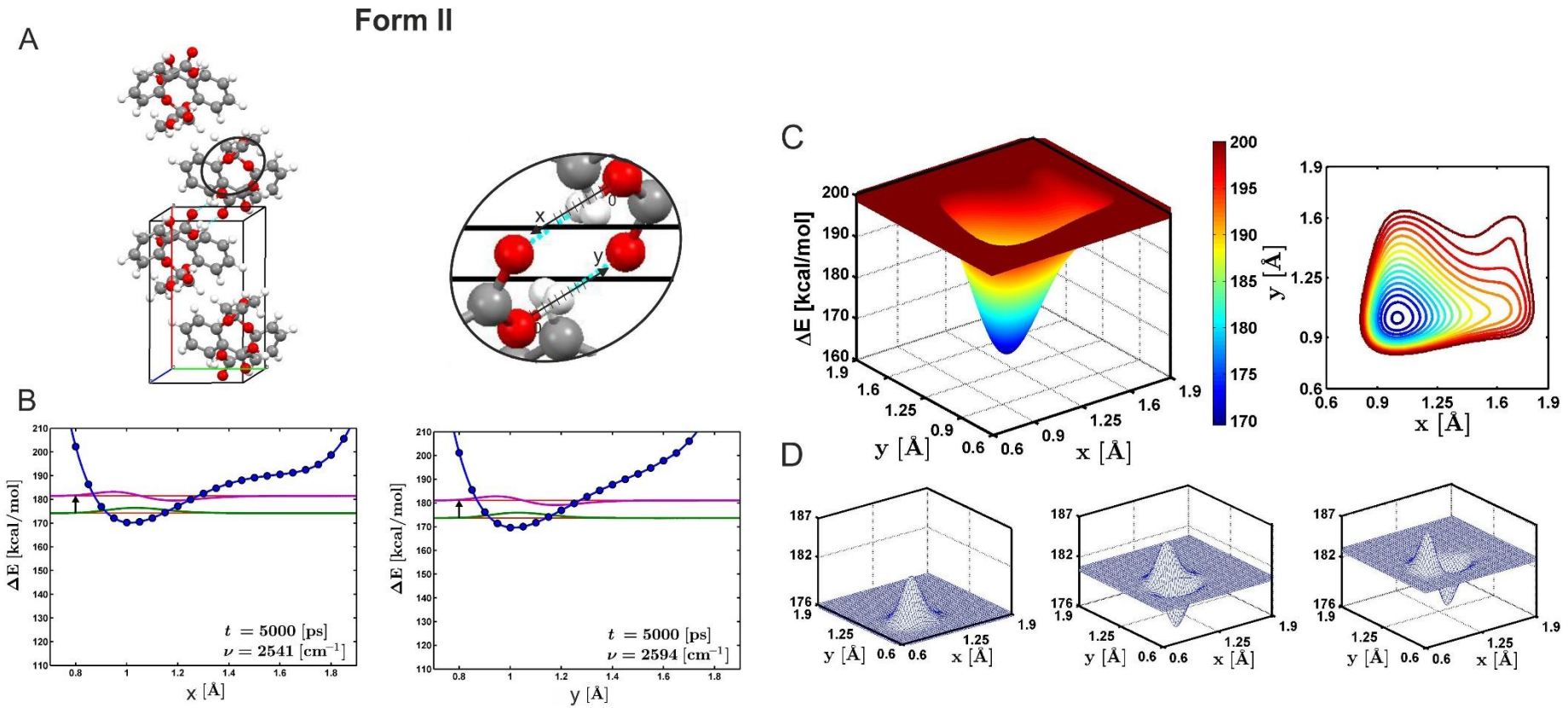

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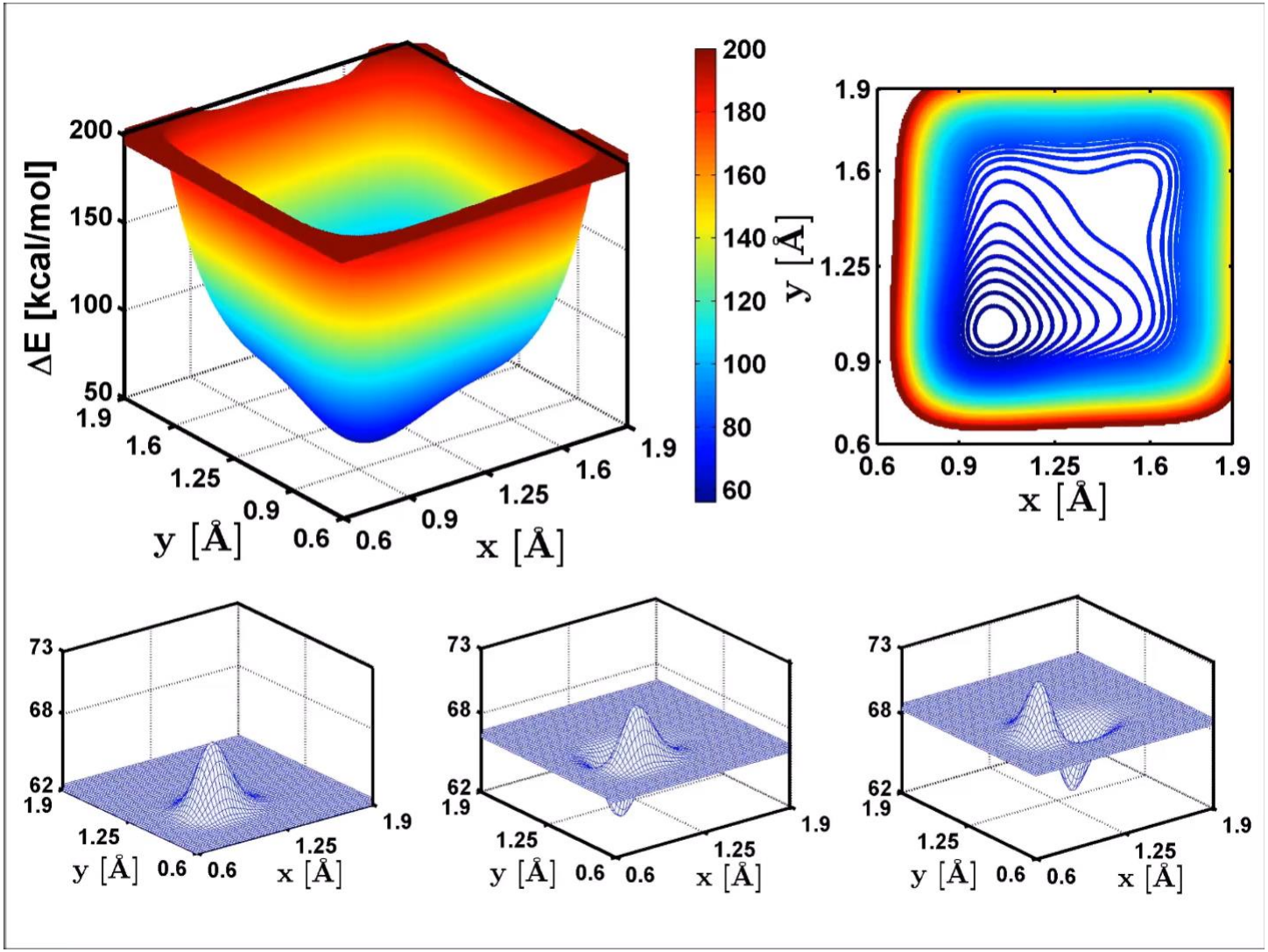

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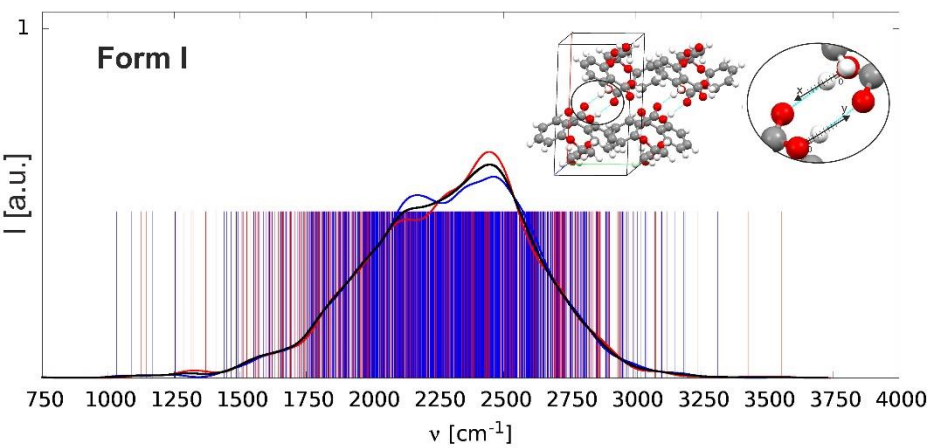

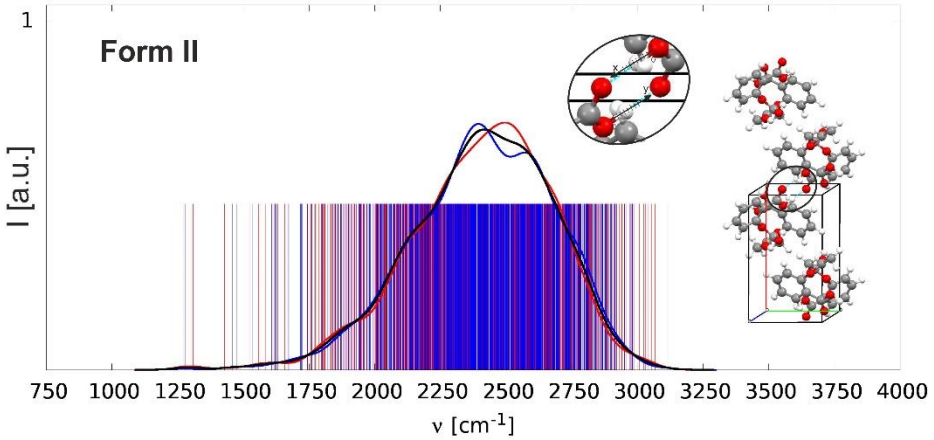

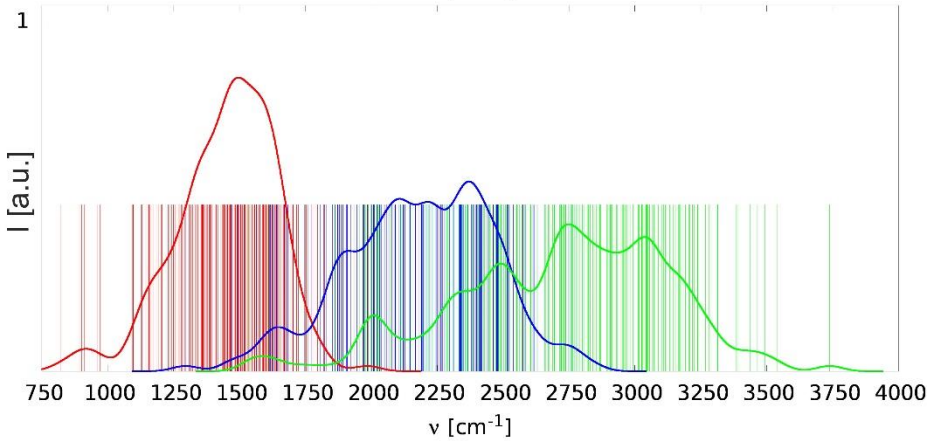

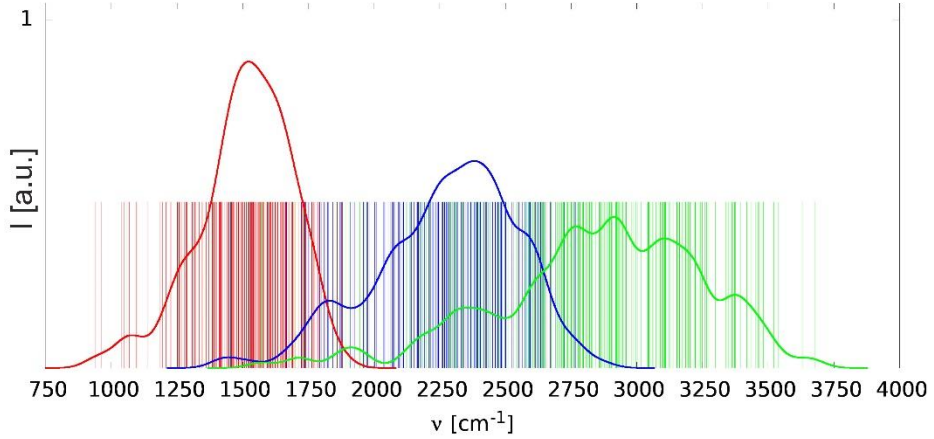

Example: Aspirin

- The spontaneous and synchronous proton transfers were observed in form I of aspirin.
- The two minima in PES were detected for form I of aspirin.
- The hydrogen bond interaction is stronger in the form I of aspirin than in form II.
- The theoretical results were confirmed by the IR spectroscopy experiment.

Conclusions:

- Calculations were performer by using the molecular dynamics with consideration of the quantum effects of proton motions.

- The base for molecular dynamics simulation was the crystal structure of considered systems. The Schrödinger equation was numerically solved for many snapshots from MD trajectory.

- This methodology gave possibility to rationalize the IR spectra of studied systems.

- The proton transfer reaction was described with consideration of the quantum effects.

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Perspective: Kinetic Isotope Effect

Perspectives:

- Comparison with the *a priori* quantization methods*,*

  QWAIM (Quantum wavepackets for atom in molecules).

- Multidimensional quantization of nuclear motions.

Acknowledgment

Obliczenia kwantowo-chemiczne zostały wykonane
przy wykorzystaniu Infrastruktury PL-Grid,
w akademickim centrum komputerowym CYFRONET AGH.

Bibliography:

The series of publications:

M. Brela, J. Stare, G. Pirc, M. Sollner-Dolenc, M. Boczar, M. J. Wójcik, J. Mavri; *J. Phys. Chem. B*, 2012.

M. Z. Brela, M. J. Wójcik, M. Boczar, R. Hashim; *Chem. Phys. Lett*. 2013,558, 8.

M. Z. Brela, M. J. Wójcik, M. Boczar, Ł. Witek, M. Yasuda, Y. Ozaki; *J. Phys. Chem. B*, 2015, 119, 7922-7930.

M. Z. Brela, M. J. Wójcik, Ł. Witek, M. Boczar, E. Wrona, R. Hashim, Y. Ozaki; *J. Phys. Chem. B*, 2016, 120, 3854-93862.

Dziękuję za uwagę