Tutorial 5

# Let them roll!

## Hands on
## (*ab initio*) Molecular Dynamics

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# Molecular Dynamics: the idea

- “Computer experiment”
  - Prepare the sample: select model system and numerically solve **Newton's equations** of motion.
  - Perform measurement
- Here: Born-Oppenheimer Molecular Dynamics
  - Converge electronic density for each step
  - Calculate *ab initio* forces on atoms [ remember J. Wieferink' s lecture on July 13th ]

# It should be very simple

- Newton's equation:

$$F(x,t) = m\ddot{x}$$

- Naive approach:
  - Use just simple integrator (e.g. the Euler integrator)
  -

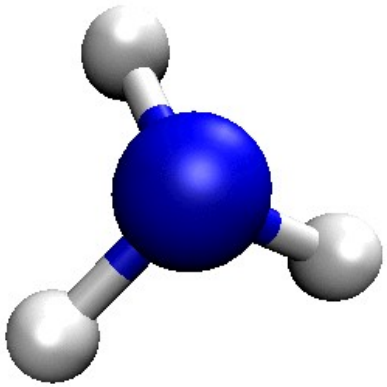
$$x(t_1) = x(t_0) + v(t_0)\Delta t_1 + \frac{F}{2m}\Delta t_1^2$$

$$x(t_2) = x(t_1) + v(t_1)\Delta t_2 + \frac{F}{2m}\Delta t_2^2$$

$$\vdots$$

  - Have fast / not so accurate force evaluation ?
  - Use big time step – fast evolution over time

# Would it work?



$\Delta t = 3fs$

- Not really …
- It is simple, but details and accuracy are important

# Which conditions should we simulate?

- Natural ensemble: microcanonical
  - time-independent Hamiltonian:

    energy is conserved
- Also possible to simulate other ensembles: canonical (discussed further on), NPT, NPH, etc.

# A model MD program

1. Read essential parameters (temperature, # of atoms, time step, etc.)
2. Initialize system – positions and velocities
3. Evaluate forces
4. Integrate equations of motion

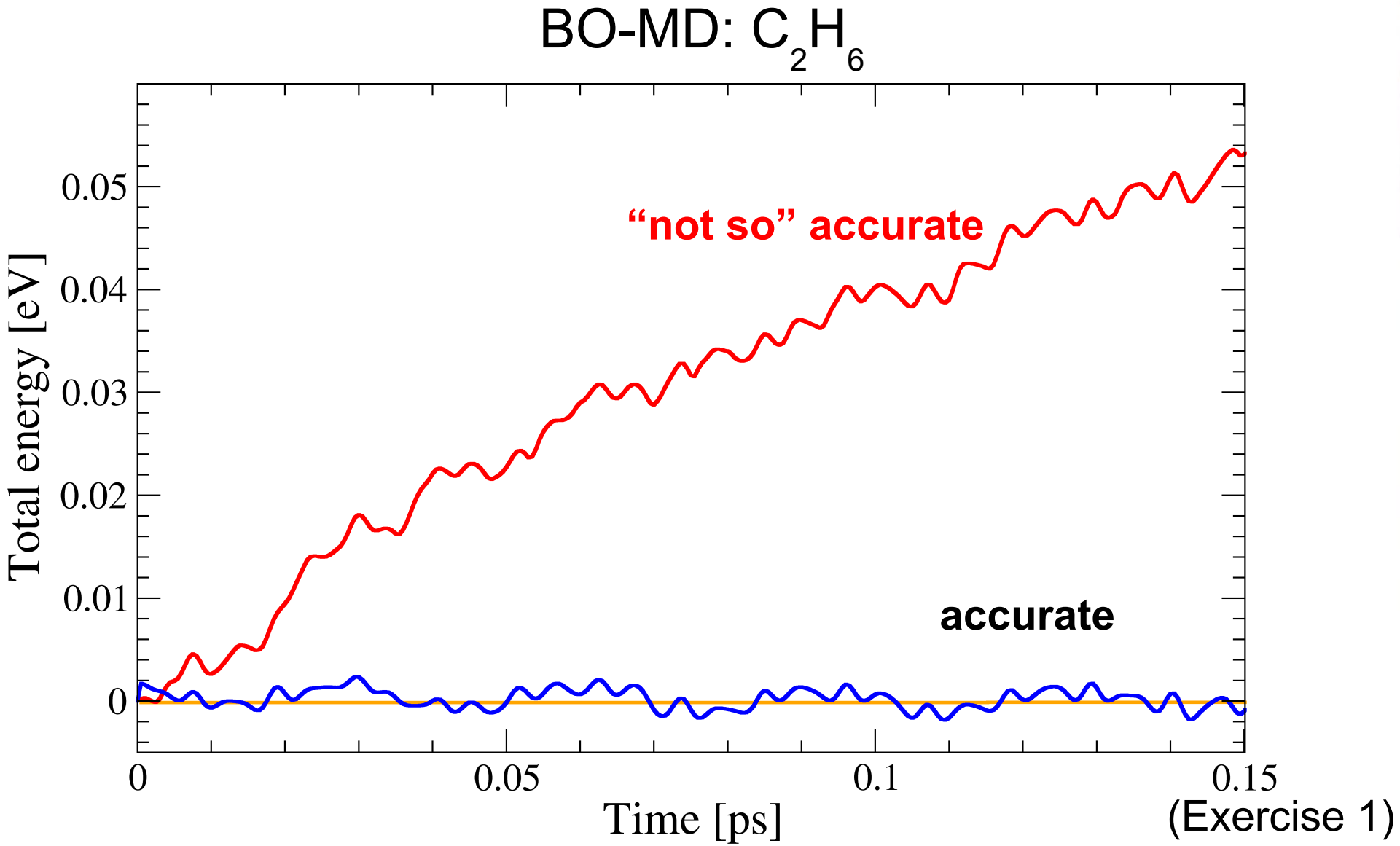
Central loop

5. Stop after a given time – enough statistics for your measurement

# Details of the central loop (Exercise 1 and 2)

- The force evaluation
  - In Born-Oppenheimer Molecular Dynamics (BOMD), forces are evaluated at electronic self consistency.
  - Stability of MD simulations depends critically on the accuracy of the forces.
  - When forces are not accurate enough, there is an undesired systematic deviation from the Born-Oppenheimer surface.

# Need of accurate self-consistency




(Exercise 1)

# Details of the central loop

- Integrating the equations of motion
  - Verlet algorithm:

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{F(t)}{2m}\Delta t^2 + \dddot{r}\frac{\Delta t^3}{3!} + O(\Delta t^4)$$

$$r(t-\Delta t) = r(t) - v(t)\Delta t + \frac{F(t)}{2m}\Delta t^2 - \dddot{r}\frac{\Delta t^3}{3!} + O(\Delta t^4) \quad +$$

$$r(t+\Delta t) + r(t-\Delta t) = 2r(t) + \frac{F(t)}{m}\Delta t^2 + O(\Delta t^4)$$

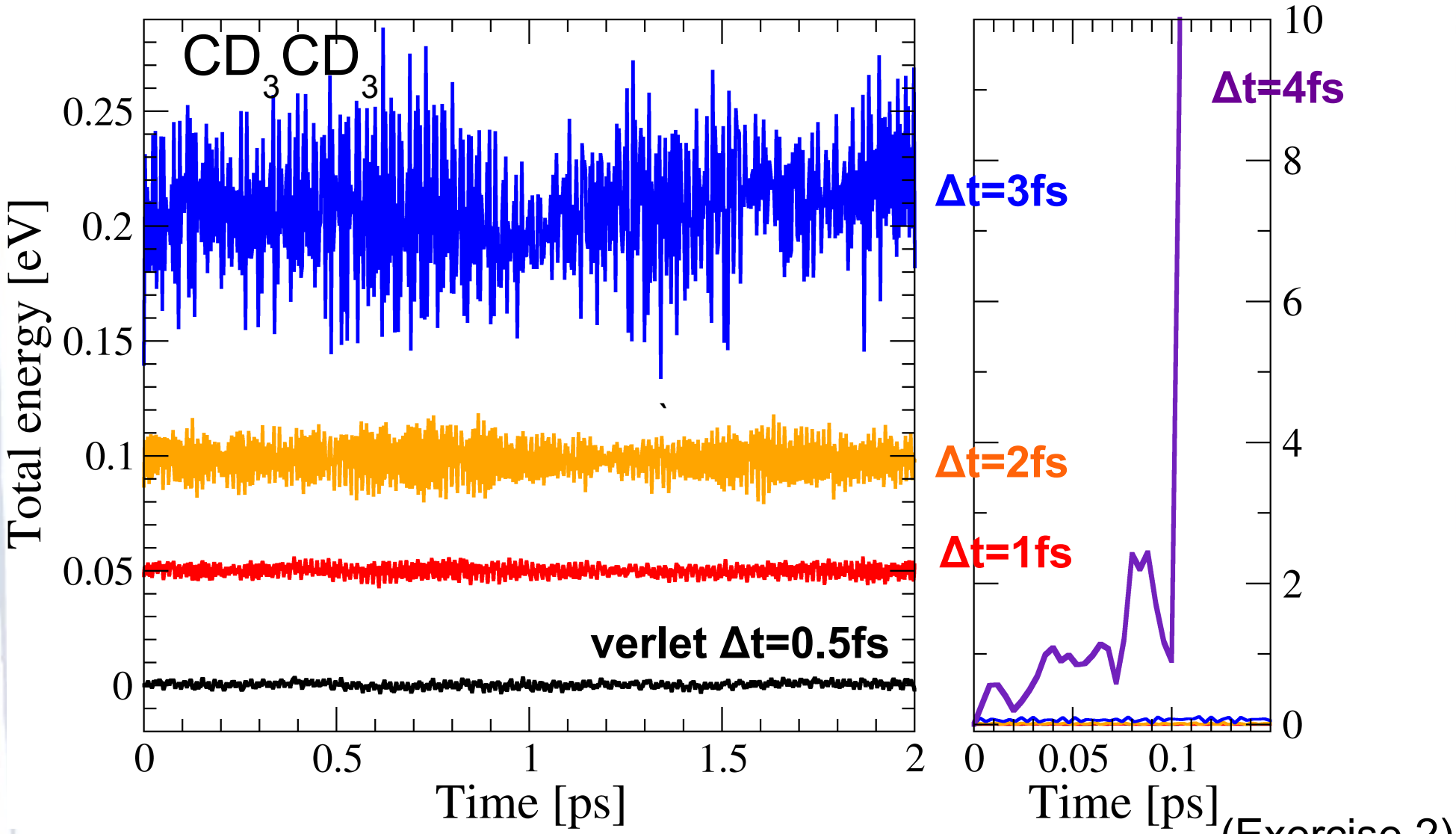
error

$$\Rightarrow r(t+\Delta t) \approx 2r(t) - r(t-\Delta t) + \frac{F(t)}{m}\Delta t^2$$

  - Implemented: Velocity-Verlet

$$v(t+\Delta t) = v(t) + \frac{F(t+\Delta t) + F(t)}{2m}\Delta t$$

# How do energy fluctuations look like?




(Exercise 2)

# Simulating the canonical ensemble

- The idea: couple the system to a thermostat
- Why is it interesting:
  - Experiments are usually done at constant temperature
  - If system suffers a conformational change, energy difference becomes kinetic energy, and temperature in the simulation would change

# Simulating the canonical ensemble

- Simulating the real coupling:
  - Stochastic thermostat, e.g. Andersen
    - Particle randomly selected, with probability $\upsilon\Delta t$, has its velocity replaced by one drawn from a Maxwell-Boltzmann distribution at the target temperature (the heat bath).
    - Drawback: since it is stochastic, it destroys the trajectory of the system – **not to be used** for time dependent properties.

# Simulating the canonical ensemble

- Simulate the effect of coupling:
  - Velocity rescaling, e.g. Berendsen
    - **It does not sample the canonical ensemble**
    - Scales velocity with factor λ

$$\lambda = \left[1 + \frac{\Delta t}{\tau}\left(\frac{T_0}{T} - 1\right)\right]^{1/2}$$

# Simulating the canonical ensemble

- Extended Lagrangian, e.g. Nosé-Hoover
  - Inclusion of the heat bath in the Lagrangian as continuous degrees of freedom

$$\mathscr{L}_{\text{nose}} = \sum_i \frac{\mathbf{m}_i}{2} s^2 \dot{\mathbf{r}}_i - U\left(\mathbf{r}^N\right) + \frac{Q}{2}\dot{s}^2 + (3N+1)\frac{\ln s}{\beta}$$

  - Energy of the system is not conserved anymore, but the energy of the extended system (subsystem + heat bath) is.
  - Equations of motion:

$$\mathscr{H}_{\text{nose-hoover}}(\mathbf{p_i}, \mathbf{r_i}, \pi, \eta) = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + U\left(\mathbf{r}^N\right) + \frac{1}{2Q}\pi^2 + 3N\frac{\eta}{\beta}$$

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i};\ \ \dot{\mathbf{p}}_i = -\frac{\partial U}{\partial \mathbf{r_i}} - \frac{\mathbf{p}_i \pi}{Q};\ \ \dot{\eta} = \frac{\pi}{Q};\ \dot{\pi} = \left(\sum_i \frac{\mathbf{p}_i^2}{m_i} - \frac{3N}{\beta}\right)$$

# Other famous extended Lagrangian

- Car-Parrinello MD
- Wave function extrapolation: Kühne-Parrinello, Niklasson.
- NPT ensemble: Andersen, Parrinello-Rahman-Nosé

# Simulating the canonical ensemble

- Stochastic velocity rescaling (Bussi-Donadio-Parrinello)
  - Conserved (pseudo-)hamiltonian

$$\tilde{H}(t) = H(t) - \int_0^t \left(\overline{K} - K(t')\right) \frac{dt'}{\tau} - 2\int_0^t \sqrt{\frac{K(t')\overline{K}}{N_f}} \frac{dW(t')}{\sqrt{\tau}}$$

  - In practice, after every velocity verlet step, new velocities are calculated. These velocities are rescaled by a factor $\alpha$, such that:

$$\begin{aligned} \alpha^2 &= e^{-\Delta t/\tau} + \frac{\overline{K}}{N_f K}\left(1 - e^{-\Delta t/\tau}\right)\left(R_1^2 + \sum_{i=2}^{N_f} R_i^2\right) \\ &+ 2e^{-\Delta t/2\tau}\sqrt{\frac{\overline{K}}{N_f K}\left(1 - e^{-\Delta t/\tau}\right)} R_1 \end{aligned}$$

# Thermostats comparison (Ex. 3)

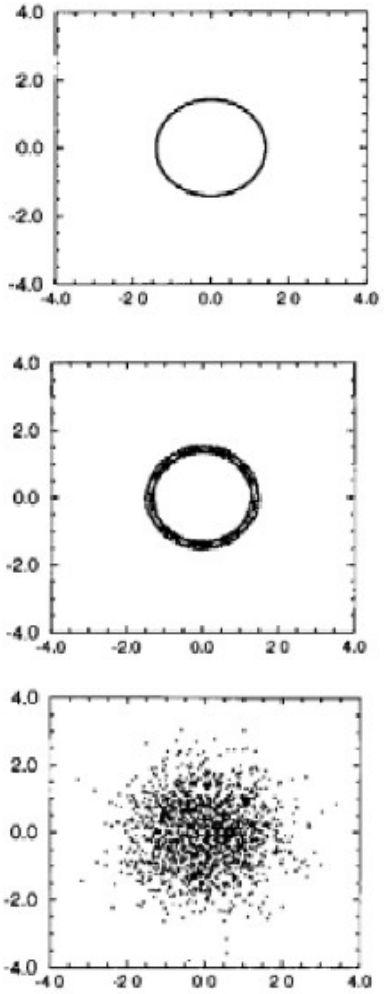
Andersen

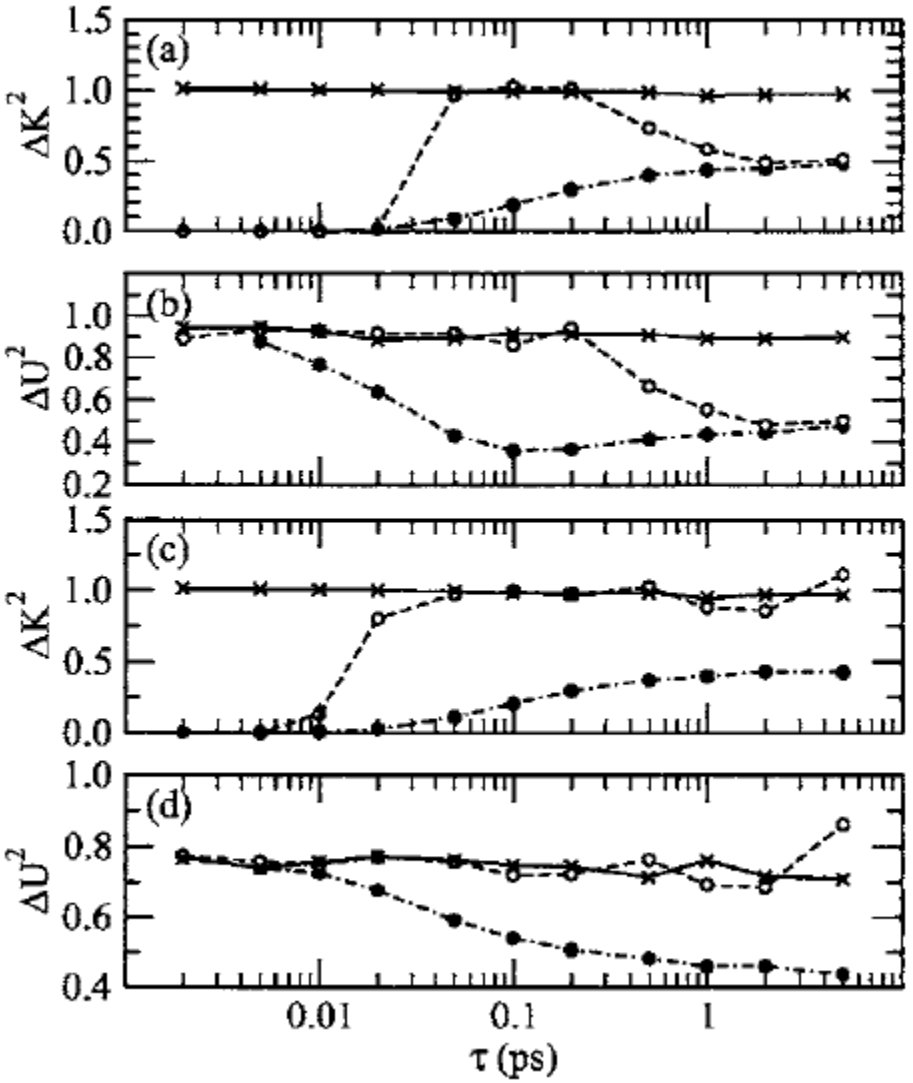
- *Static* averages in the canonical ensemble, but *dynamical* quantities are meaningless
- Good for equilibration: excites "equipartition-wise" all the modes.

- Berendsen
  - Does not sample any known ensemble.
  - If $\tau$ small (strong coupling), yields completely unreliable trajectories, at *seemingly* the right temperature.
- Nosé-Hoover
  - Rigorously samples the canonical ensemble
  - Dynamical quantities (e.g. autocorrelations) are *typically seen* to be reliable
  - But: has ergodicity issues (fixable via Nose-Hoover chains)
- Bussi-Donadio-Parrinello
  - Rigorously samples the canonical ensemble
  - Dynamical quantities are reliable
  - No ergodicity issues

# On Ergodicity

Harmonic oscillator




×BDP
o NH
•Berendsen

Lennard-Jones solid @20K

Lennard-Jones liquid @120K

# What can we use MD for, anyway?

- Measures of:
  - Diffusion coefficients in liquids
  - Rotational-vibrational spectra with anharmonic contributions
  - Evaluating the excess free energy via thermodynamic integration
  - (Fast) rates and phenomenology of reactions
  - Out-of-equilibrium quantities, e.g. heat diffusion
- Furthermore:
  - Together with **enhanced sampling techniques**,

    e.g. replica exchange, constrained dynamics (Blue-Moon ensemble), transition path sampling, transition interface sampling, forward flux sampling...

    measures of free energy **differences**

    -> phase diagrams, reaction rates`

# Calculating vibrations via MD (Ex. 4)

- Time autocorrelation functions can give information about vibrations
  - From Fermi's golden rule, the dipole time auto correlation function gives the intensities of IR active frequencies

$$I(\omega) = \int_{-\infty}^{\infty} dt\, \mathrm{e}^{i\omega t} \langle \vec{M}(t) \cdot \vec{M}(0) \rangle_t$$

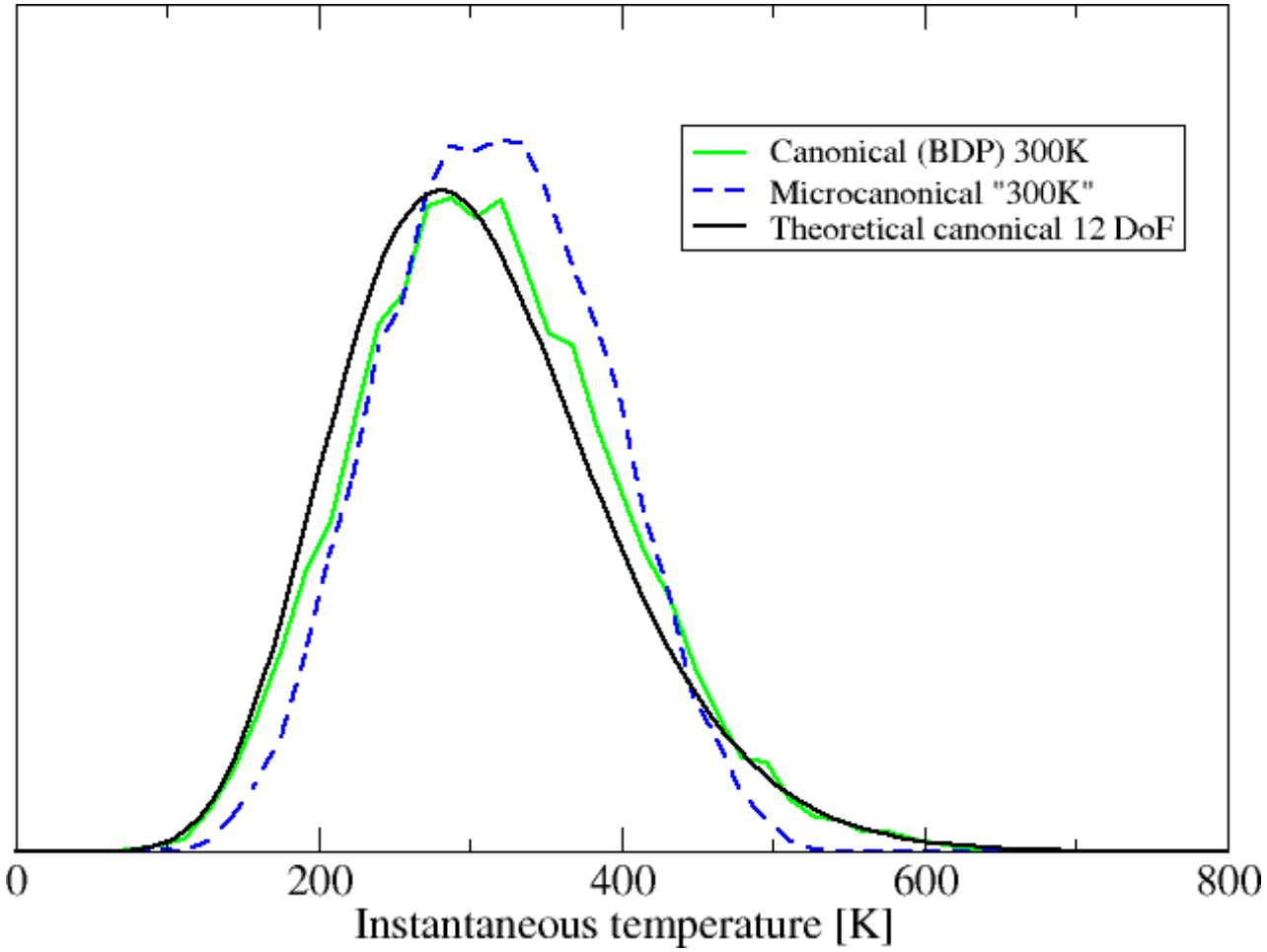
  - Velocity time autocorrelation gives all frequencies of vibration.

$$\mathrm{VDOS}(\omega) = \sum_{i=1}^{N} \int_{-\infty}^{\infty} dt\, \mathrm{e}^{i\omega t} \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle_t$$

  - Possible to assign to individual atoms displacements and project on eigenmodes.

# Calculating vibrations via MD (Ex. 4)

- Canonical versus microcanonical sampling



# Calculating vibrations via MD (Ex. 4)

- Advantages:
  - It doesn't rely on the harmonic approximation
  - Take into account anharmonic effects present in experiments
  - Simulate at different temperatures
- Challenges:
  - Needs a lot of statistics – difficult for big systems, especially if *ab initio*
  - Nuclei are classical, but in reality quantum effects for light nuclei are needed – ongoing work in the community

# Excess free energy (Ex. 5)

- Thermodynamic-path integration.

  The absolute free energy cannot be calculated in a finite time MD.

  But, the difference in free energy from a reference system, or condition of the system (e.g. very low *T*) can be often evaluated.

  For example, by integrating: $\frac{\partial(\beta\mathcal{F})}{\partial\beta} = \langle\mathcal{U}\rangle_{NVT}$

- Pay attention to possible hysteresis along the integration path!

# Exercises overview

- Exercise 1- NVE ensemble
  - Investigate 2 different self consistency accuracy settings

⇨ 14:30 - 14:50 (20 min)

- Exercise 2 – NVE ensemble
  - Velocity verlet with 1fs and 3fs time step
  - Ethane vs. Heavy Ethane

⇨ 14:50 - 15:10 (20 min)

- Exercise 3 – NVT ensemble
  - Investigate 4 thermostats: Berendsen, Andersen and Nosé-Hoover, Bussi-Donadio-Parrinello

⇨ 15:10 - 15:40 (30 min)

- Exercise 4 – Application: $CD_3CD_3$
  - Harmonic vibrations
  - Anharmonic vibrations: dipole and velocity autocorrelations
  - Temperatures: 600K first 2 rows, 450K next 2 rows, 300K last 2 rows.

⇨ 15:40 - 17:00 (80 min)

# Exercises overview

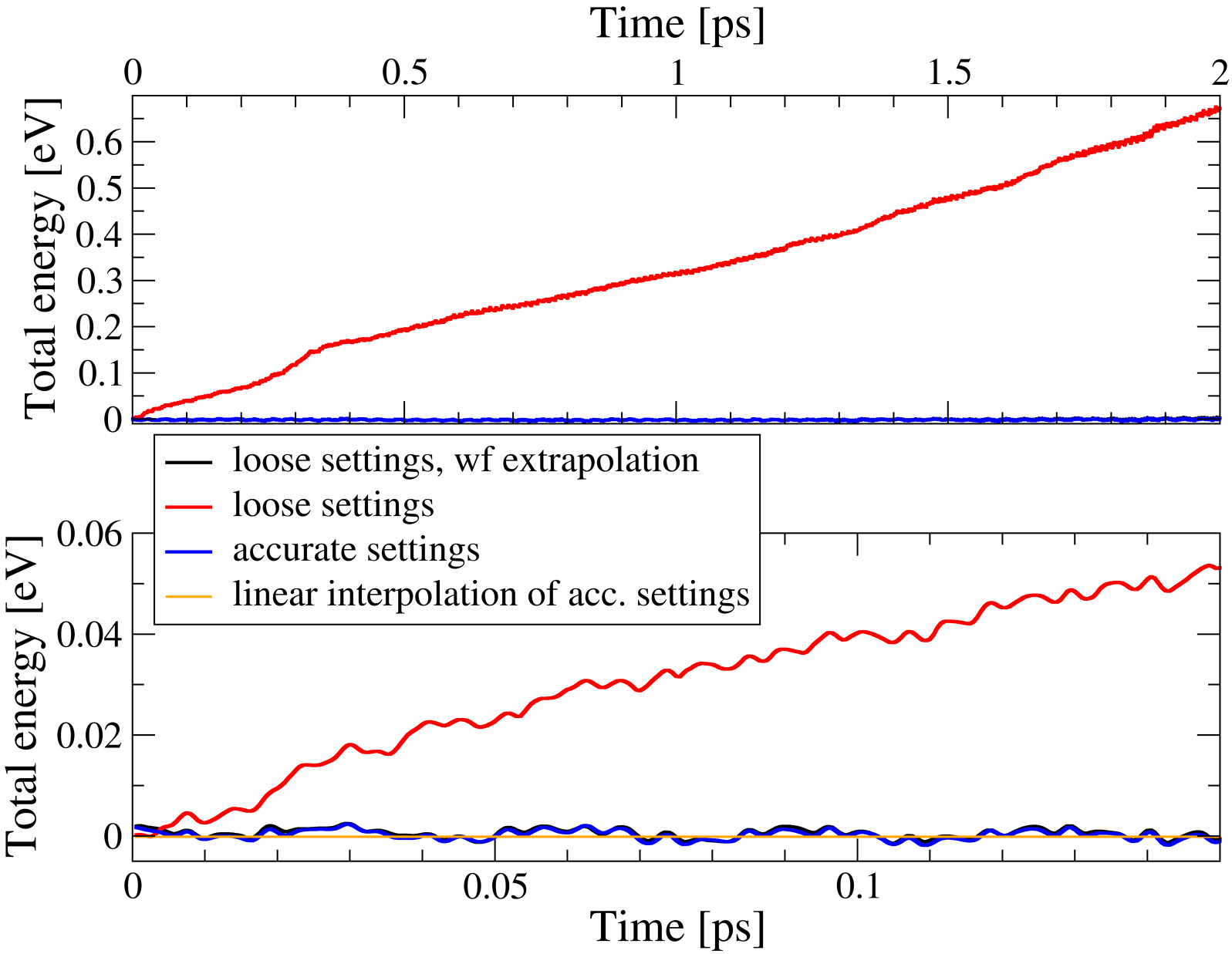
- Exercise 5 – Evaluating (excess) free energy.
  - Parallelizing over groups, each group calculates the average energy at a given temperature
  - Postprocessing done by one of us (possibly on the real data calculated by the participants ... and on-air)

⇨ 17:00 - 17:30 (30 min)

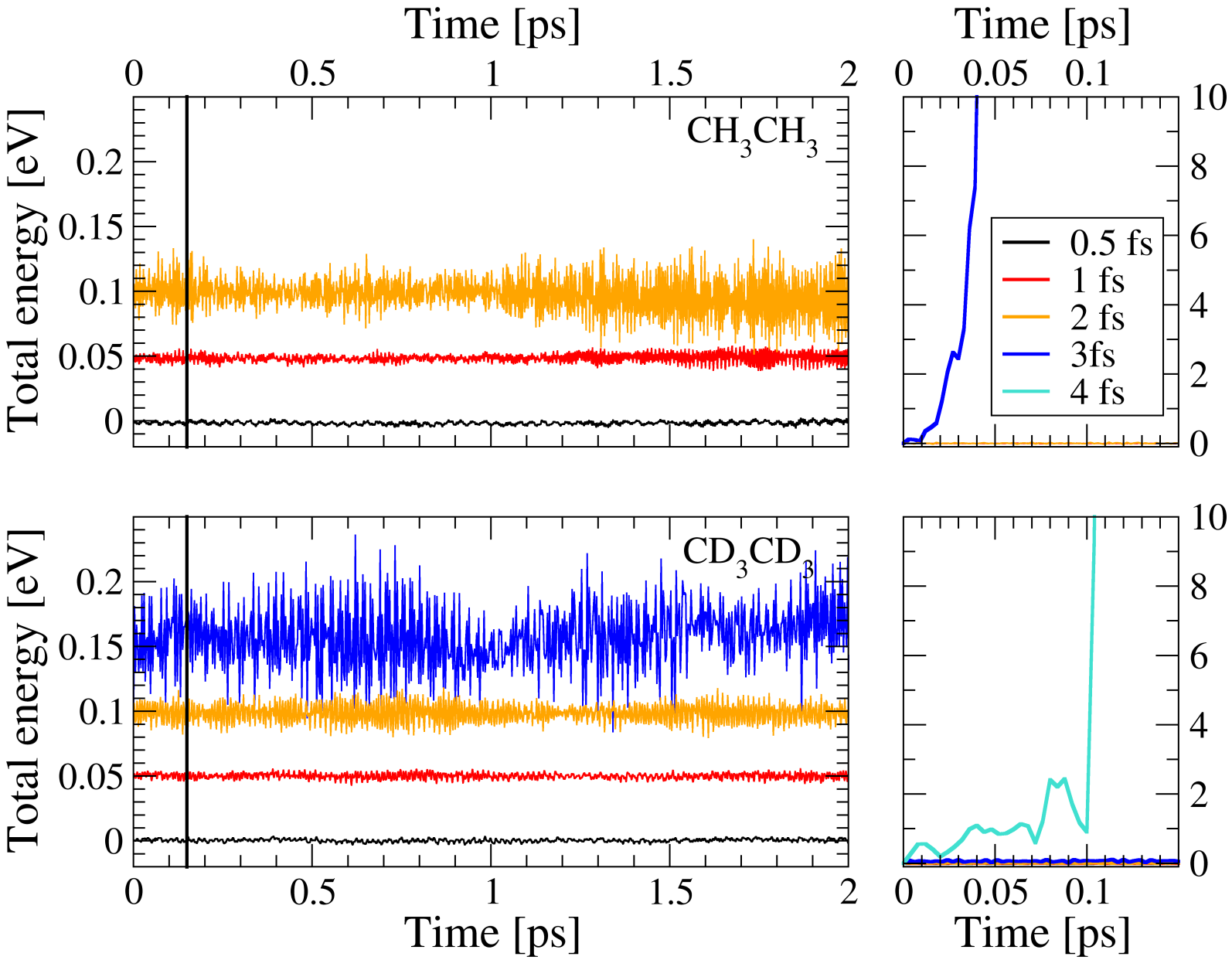
- Small project –Estimation of Heat flux
  - Mimicking the “Laser-Flash Measurements”: ab initio heat conduction of a 1D (infinite) -($CD_2$)- chain
  - Introduction on phonons (provided)
  - Generation of non equilibrium conditions

⇨ **Setting**
17:30 – 18:00
**Calculations**
over night
**Discussion**
tomorrow at ...

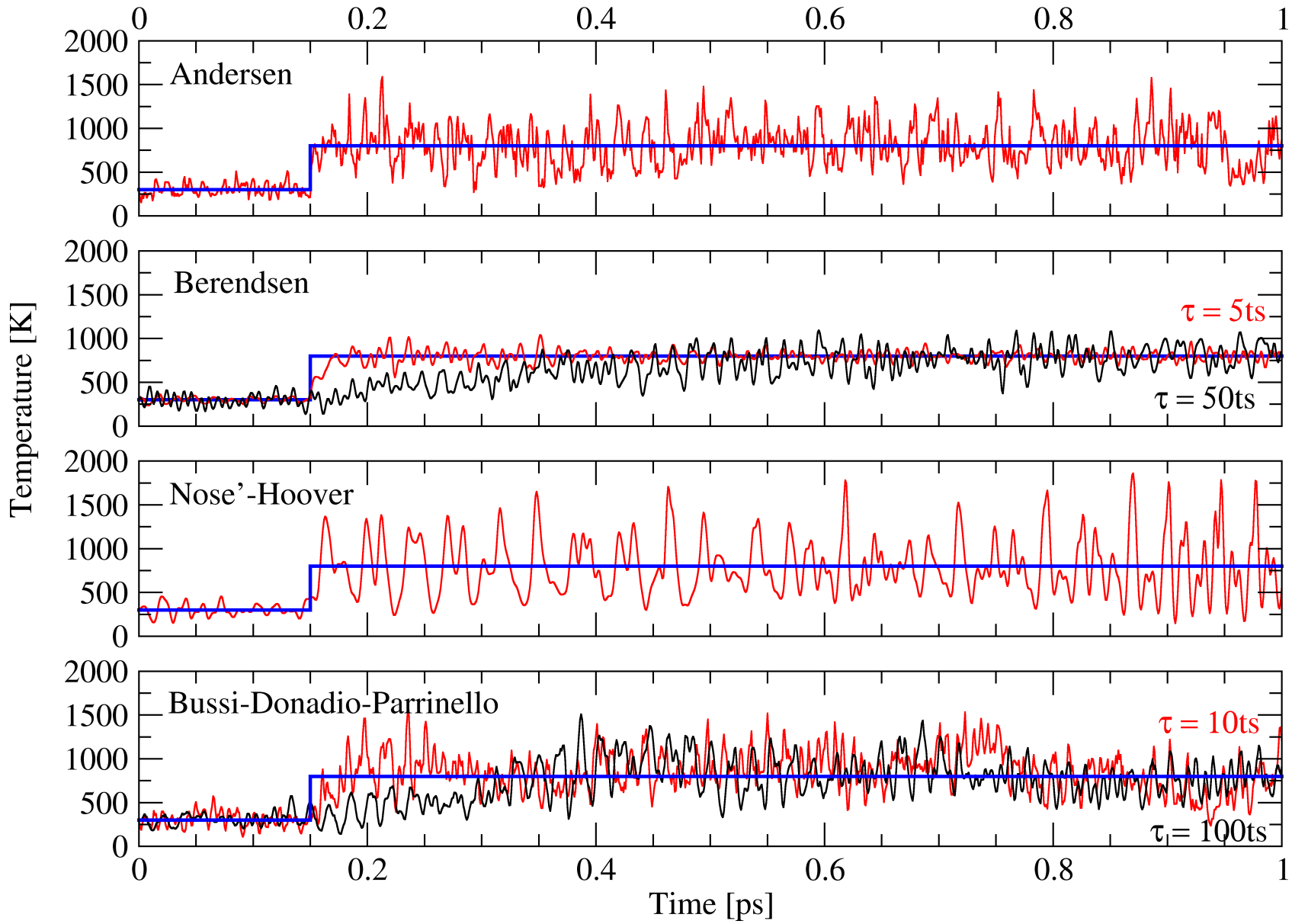
# Comments on exercise 1



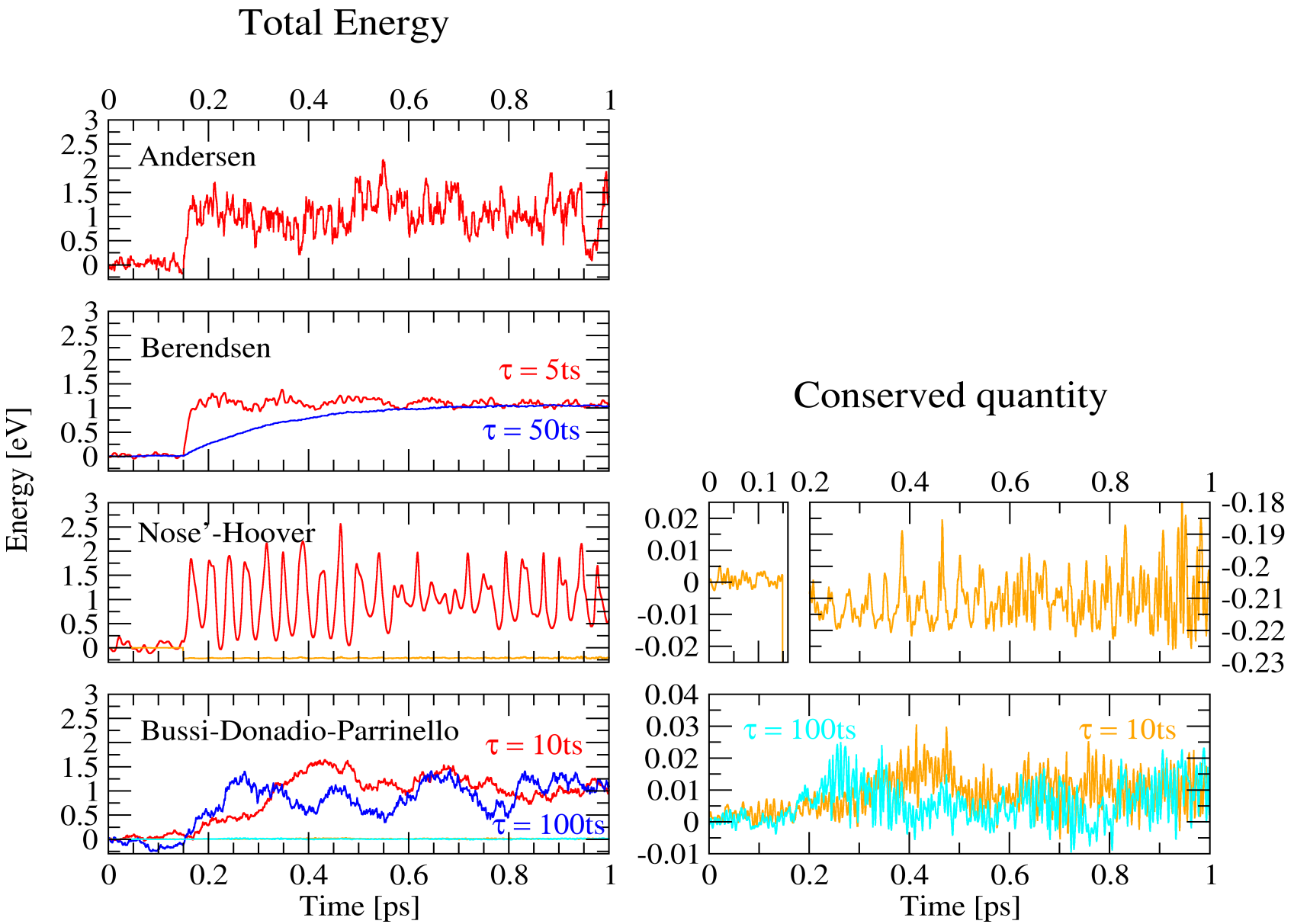
# Comments on exercise 2



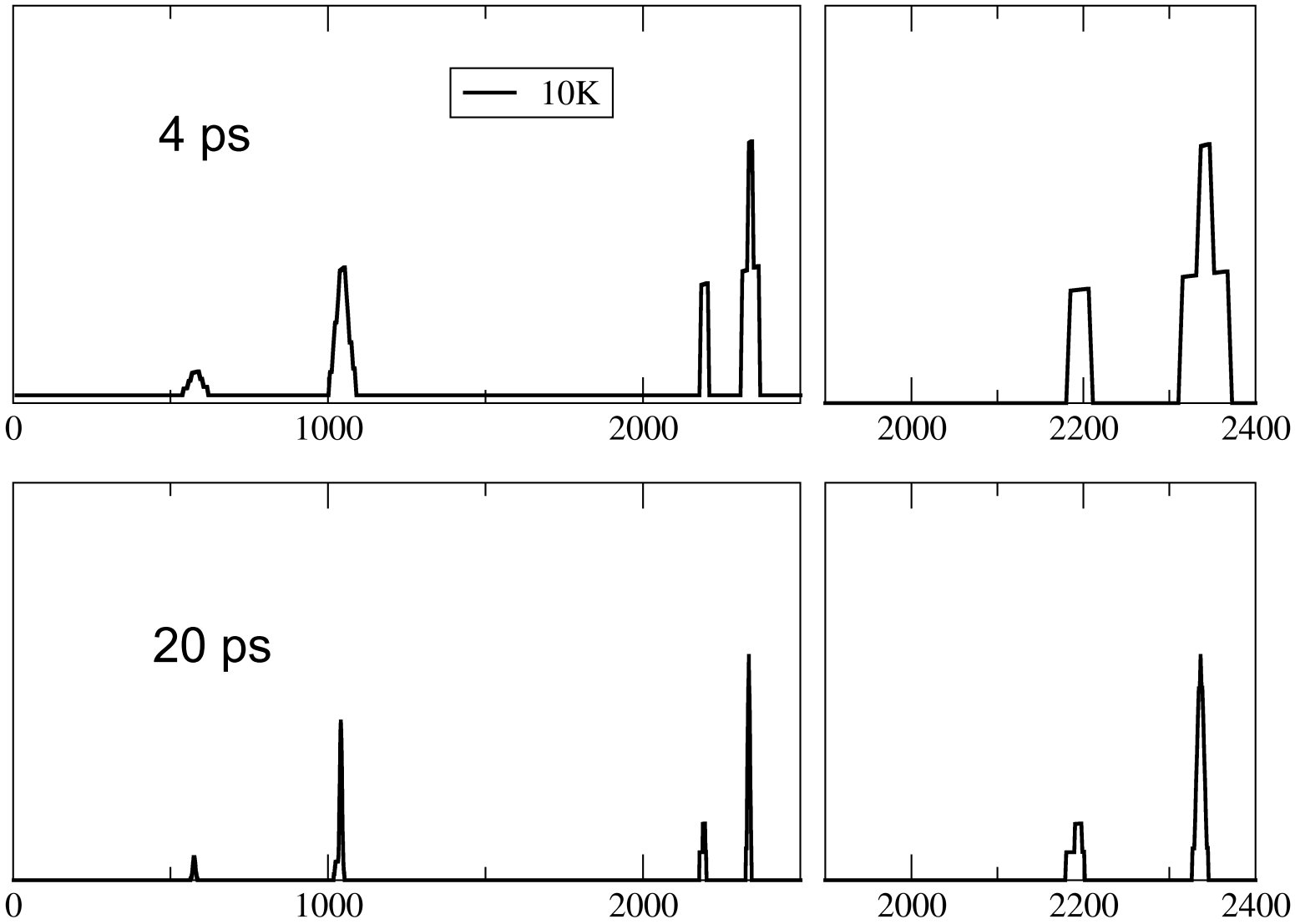
# Comments on exercise 3



# Comments on exercise 3 (ctd.)



# Comments on exercise 4



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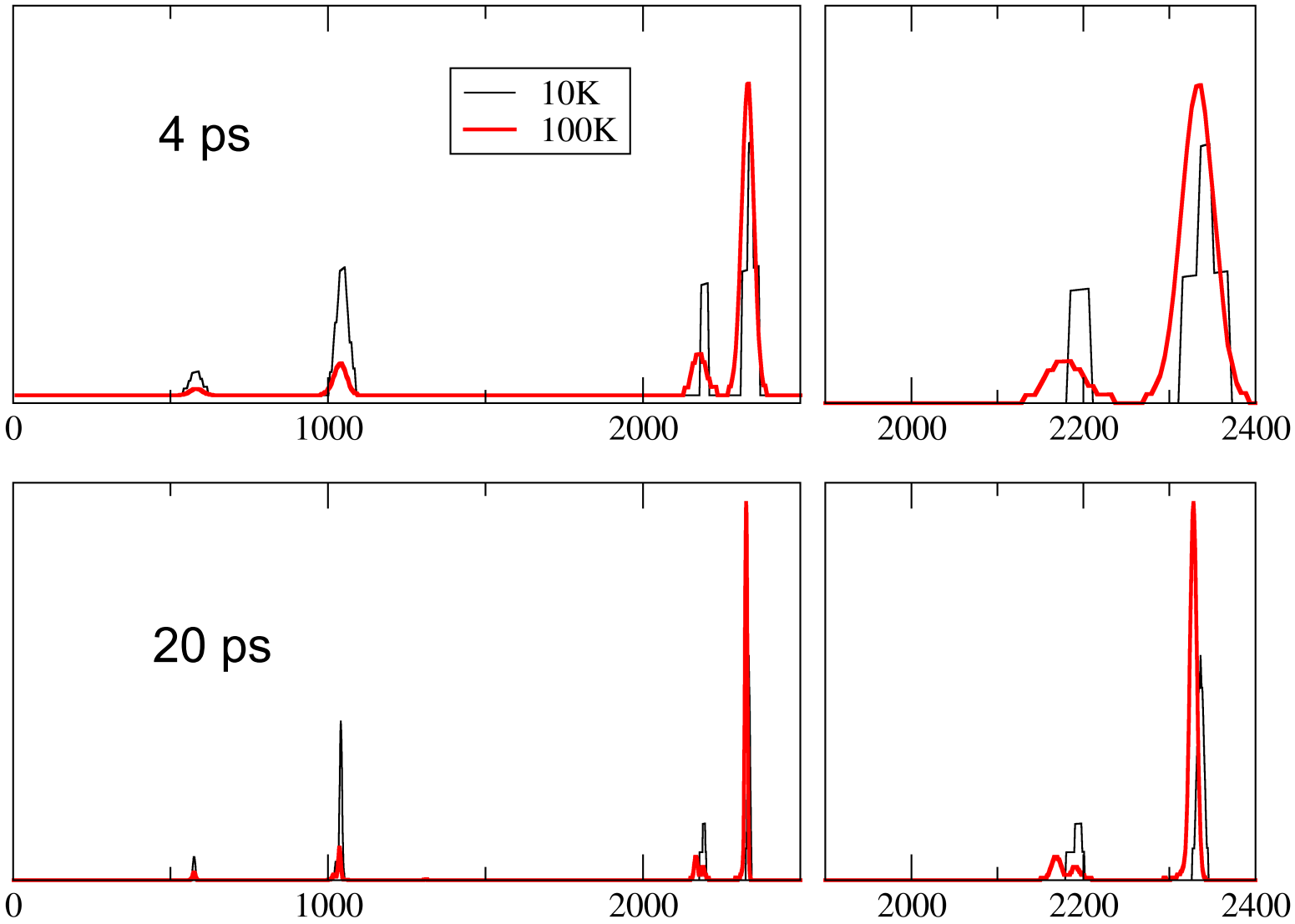

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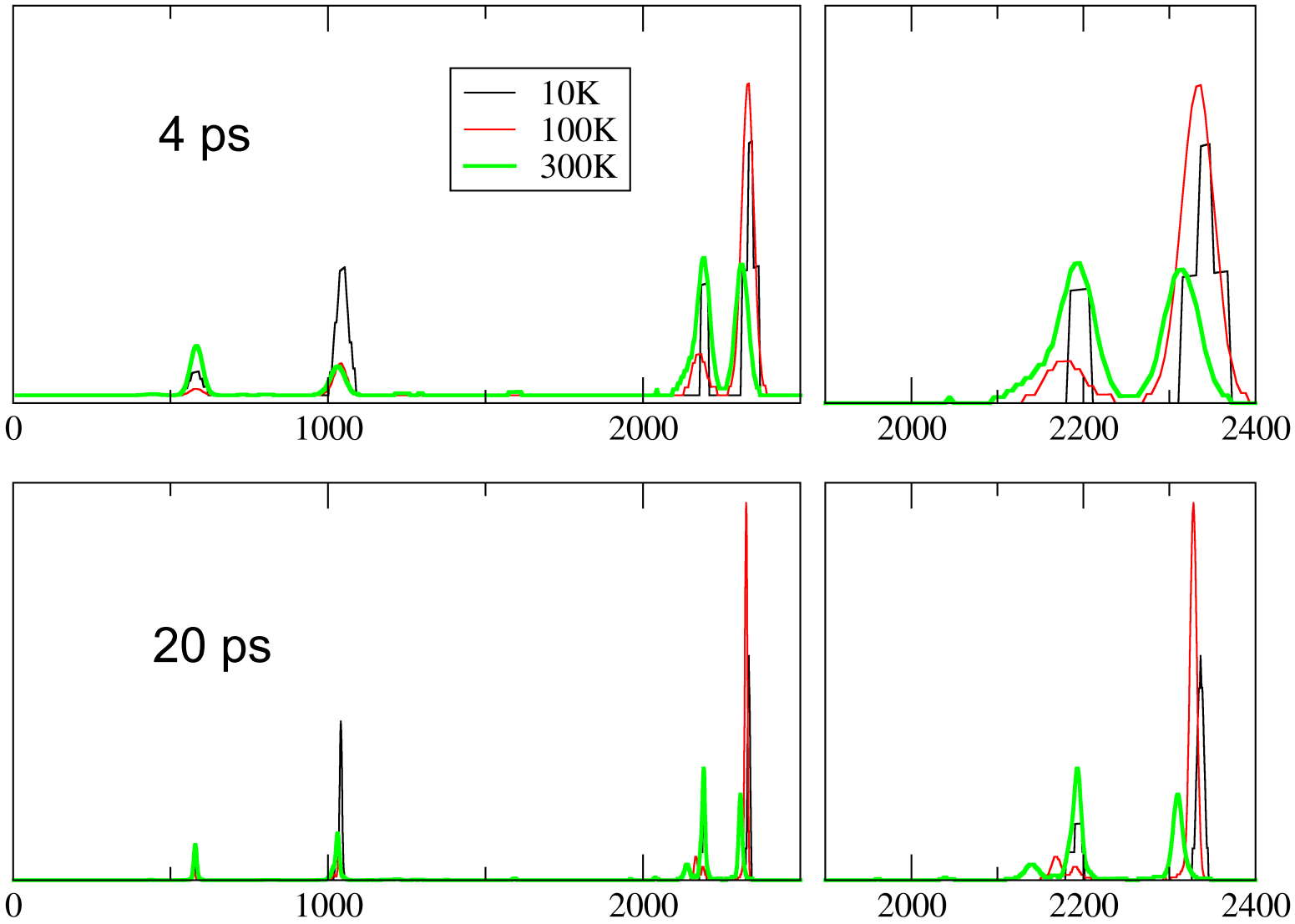

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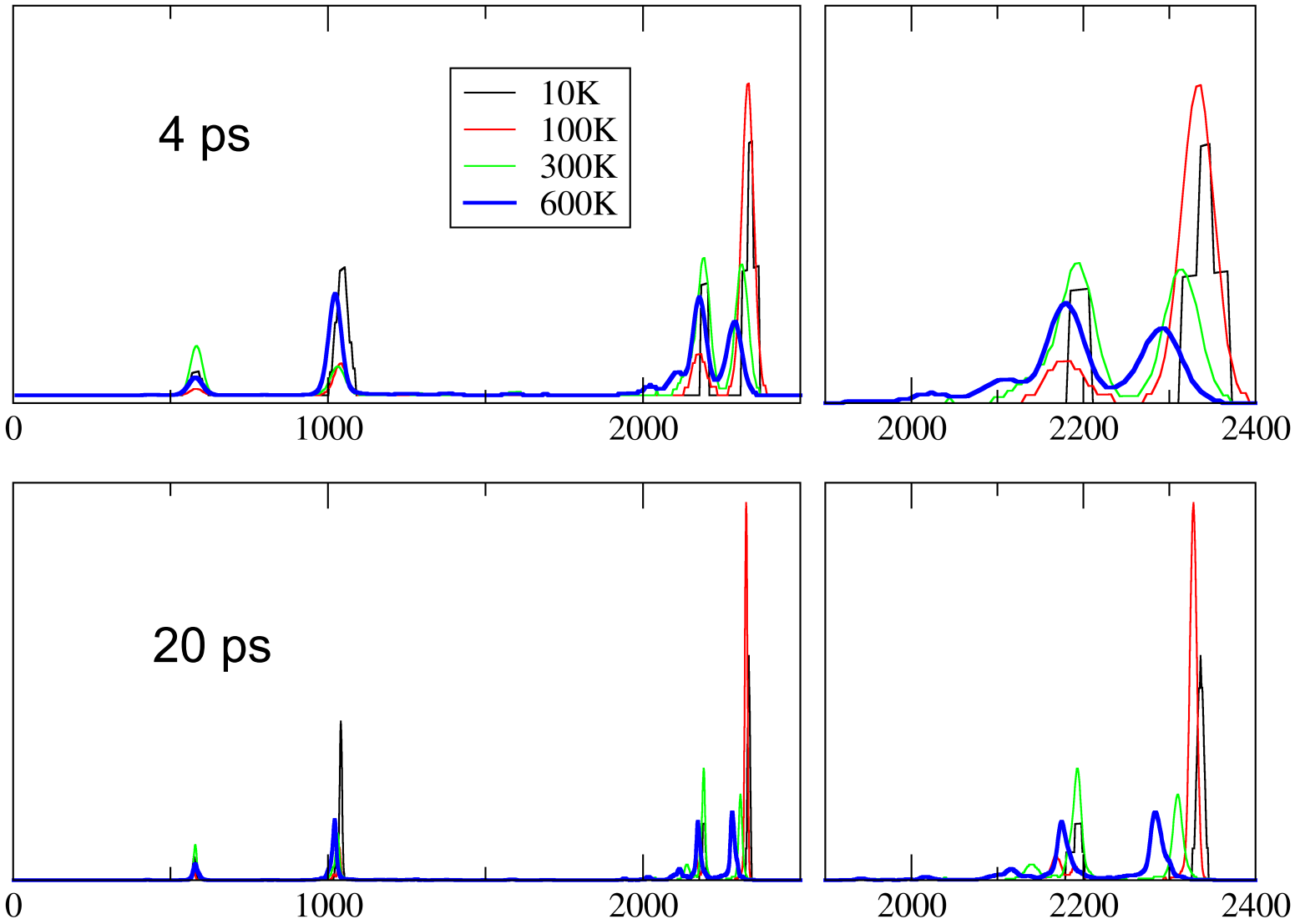

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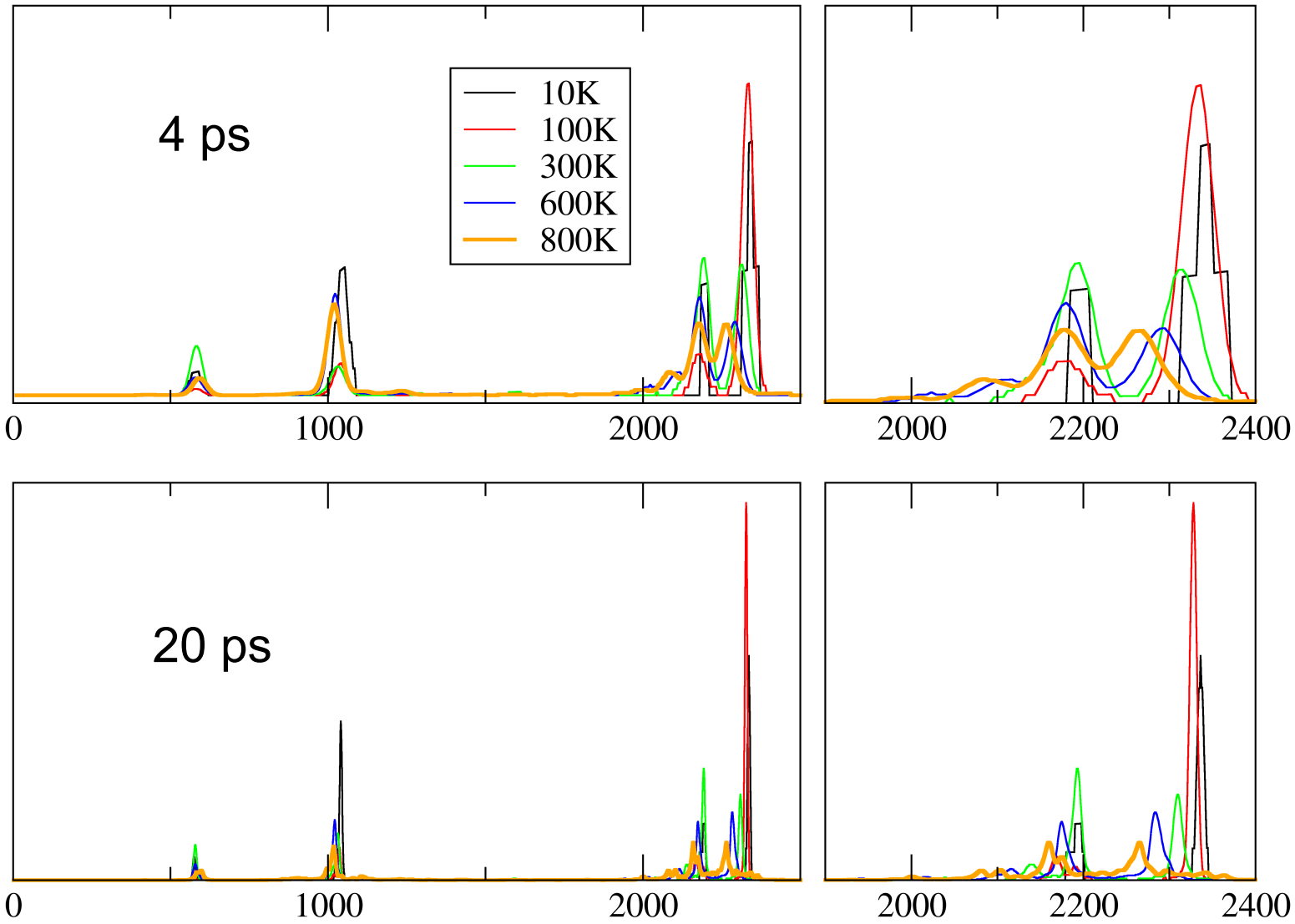

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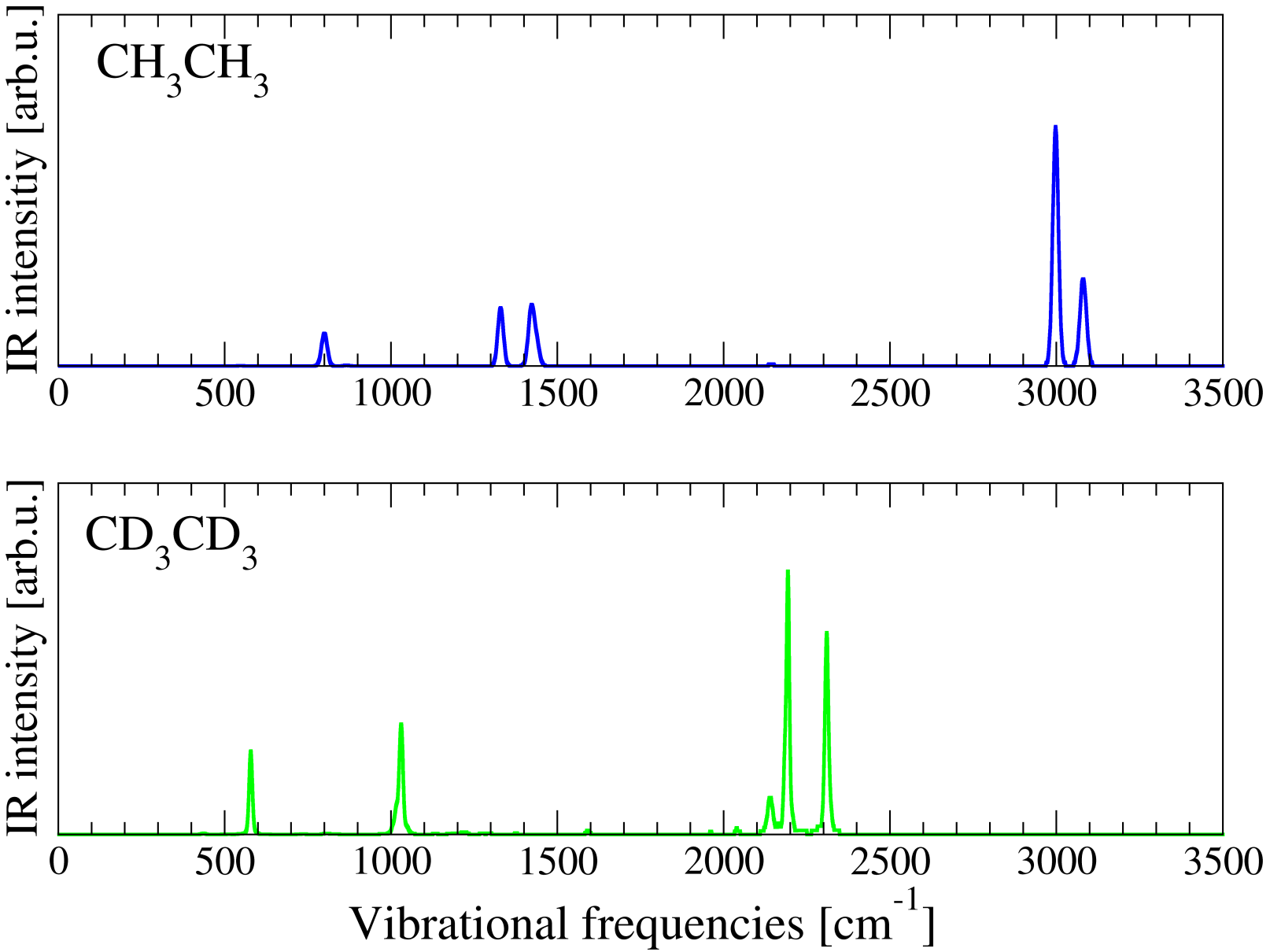

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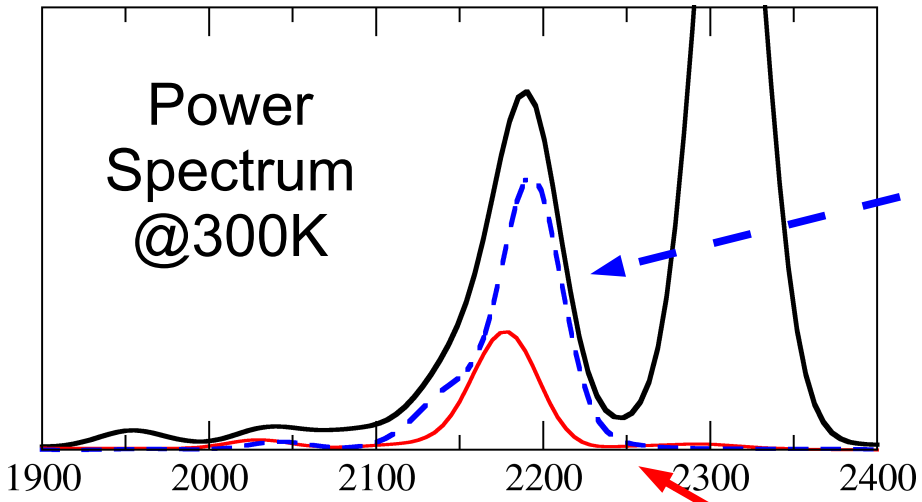
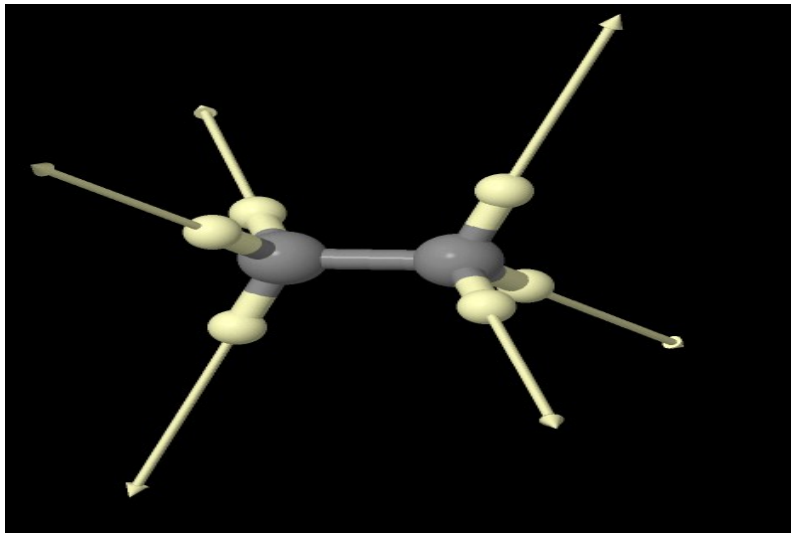
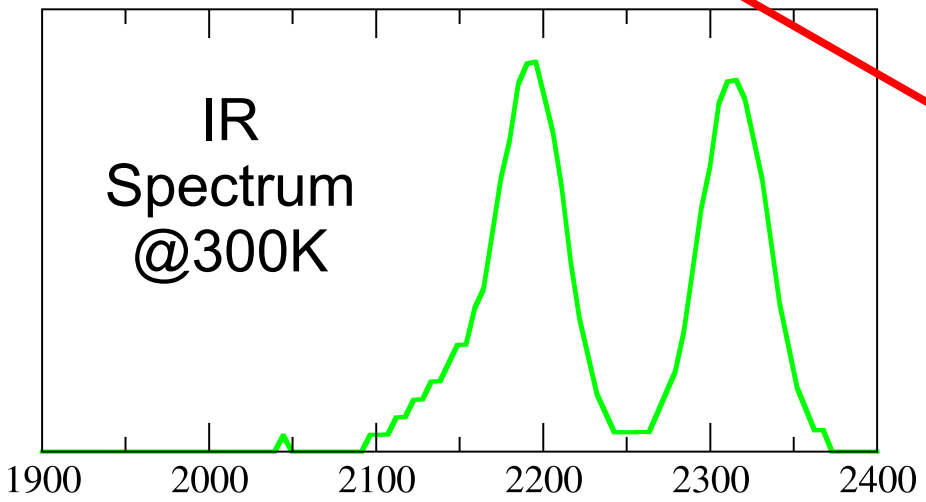
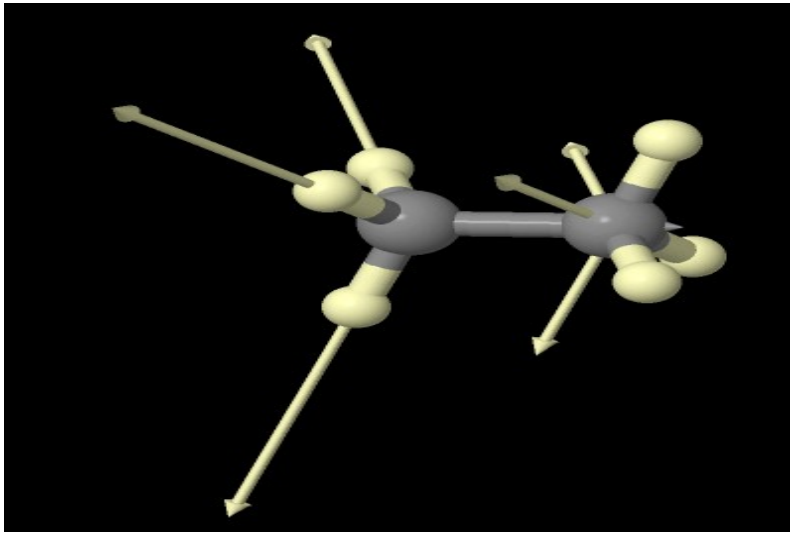


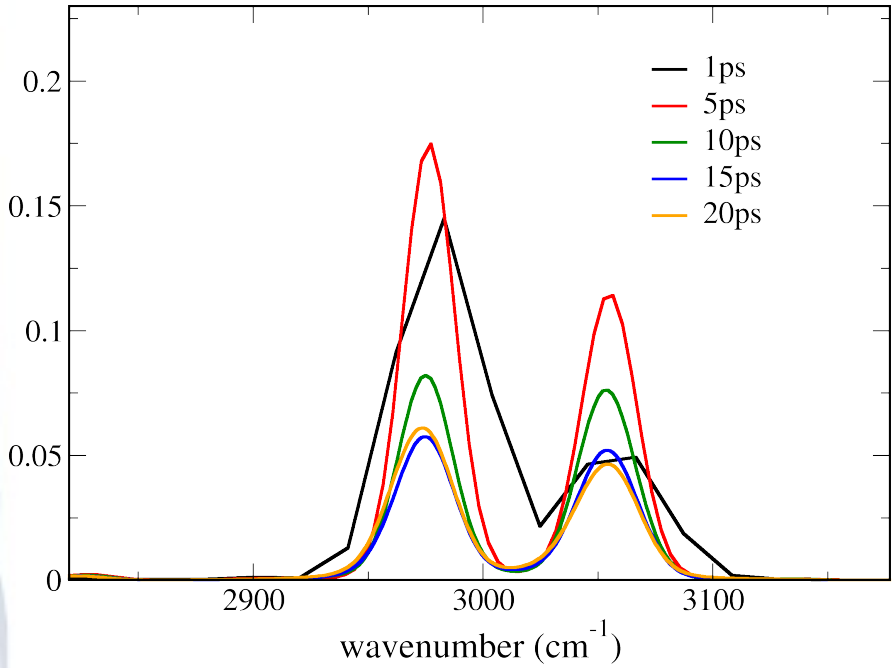


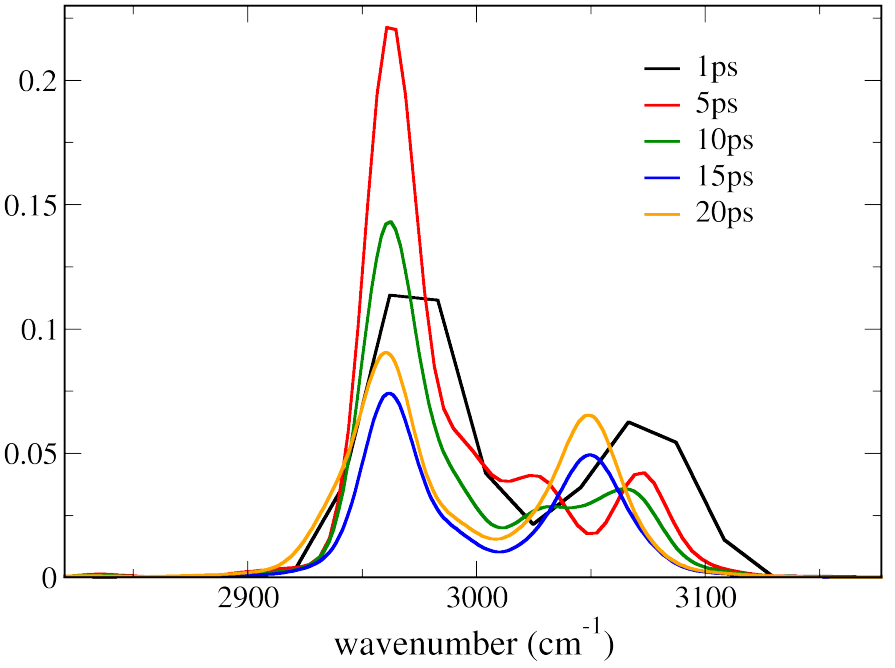
# Comments on exercise 4

Comparison of accurate-force settings vs loose-force settings with wfe (see Ex.1), in the microcanonical ensemble.

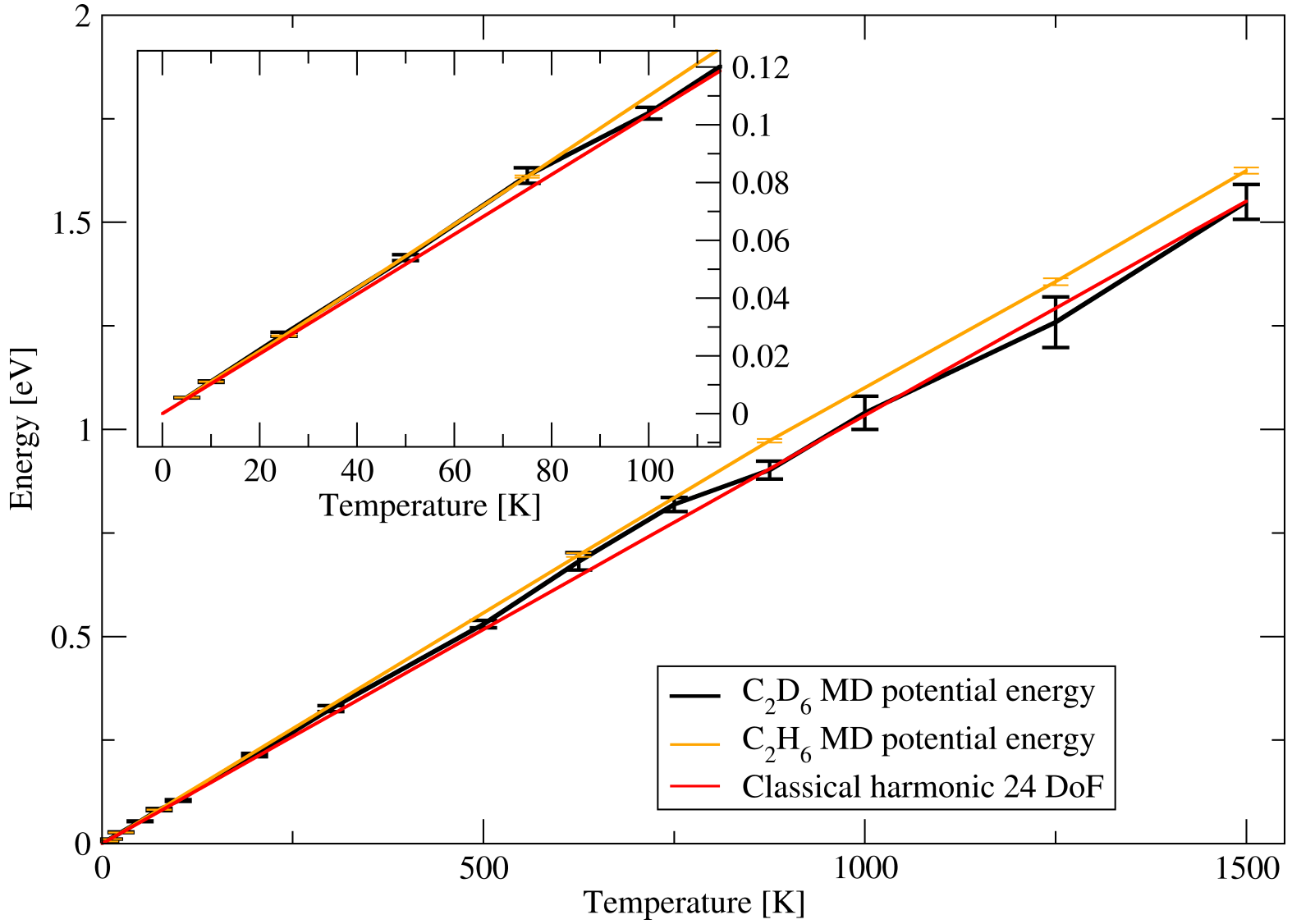
Accurate force




Loose force + wfe



# Comments on exercise 5



# Comments on exercise 5