

# Infrared spectroscopy with *ab initio* path integral techniques



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# Motivation: general remarks

**Aim:** dynamics of complex molecular systems:  
Infrared (IR) spectroscopy

## Features:

- Size of 10-100 atoms
- Interactions cannot be easily parametrized (no force fields)
- Electrons are necessarily treated explicitly (DFT)
- Thermal fluctuations cannot be neglected (NVT ensemble)
- Nuclear quantum effects are important

## Solutions:

- “classical” *ab initio* molecular dynamics
- Path integral *ab initio* molecular dynamics

# Motivation: path integrals

When does one need quantum effects on nuclei ?

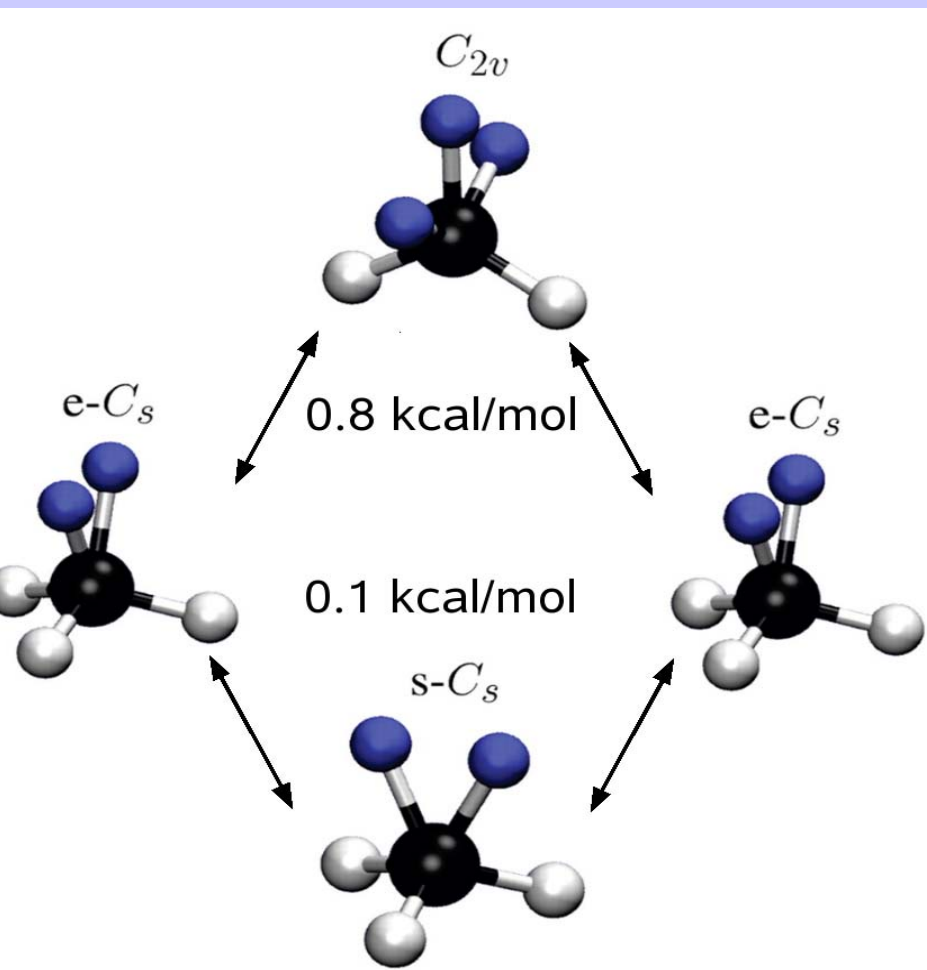
- low energy barriers
- light reduced masses
- isotope substitution
- low temperatures

Requirements on the method - wish list:

- Generality
- Ab initio
- Scalability

# Motivation: example

## Infrared spectra of protonated methane: $\text{CH}_5^+$



### Structure:

- Ground state:  $C_s$  symmetry
- Tripod and moiety
- 3-center-2-electron bond.

### Energetics:

- Internal rotation (nearly free)
- Scrambling ( $\sim 400\text{K}$ )

# Path Integral MD: brief overview

$$Z = \oint Dq e^{-\frac{1}{\hbar} S[q]}$$

Path Integrals exploit *quantum-classical isomorphism*.

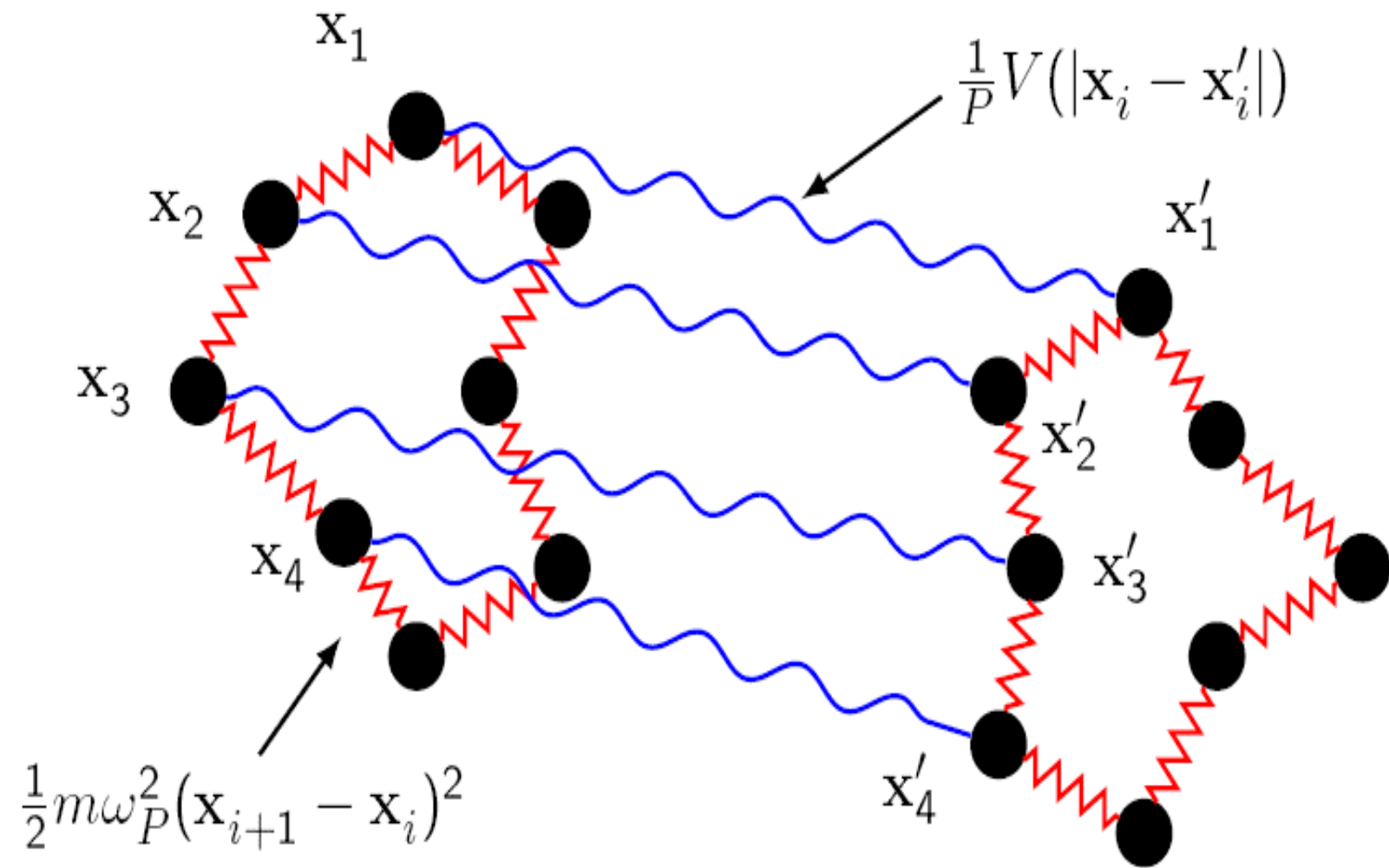
$$\begin{aligned} Z &= \text{Tr} \hat{\rho} = \int dx_1 \langle x_1 | \exp[-\beta \hat{H}] | x_2 \rangle_{x_1=x_2} = \int dx_1 \langle x_1 | \left( \exp\left[-\frac{\beta}{P} \hat{H}\right] \right)^P | x_2 \rangle_{x_1=x_2} \\ &= \lim_{P \rightarrow \infty} \int \prod_{i=1}^P dx_i \langle x_i | \exp\left[-\frac{\beta}{P} \hat{H}\right] | x_{i+1} \rangle_{x_{P+1}=x_1} \cong \int \prod_{i=1}^P dx_i \exp[-\beta V_{\text{eff}}(\{x_i\})] \end{aligned}$$

Finally, the quantum partition function turns out to be isomorphic to the configurational integral over **closed paths**. Paths can be approximated by **beads**, connected via harmonic **springs**.

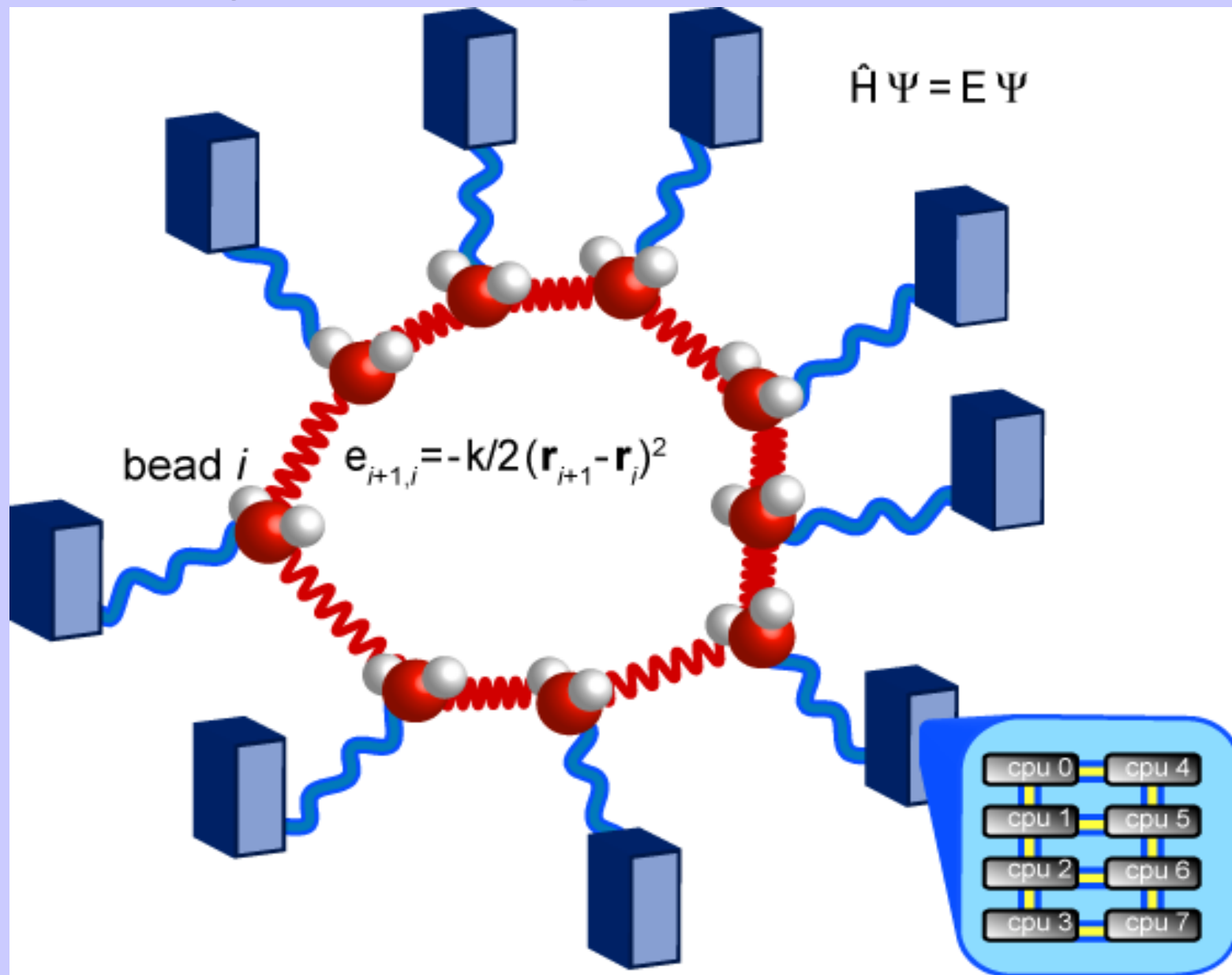
Path Integral formalism is, in principle, exact for static properties.

Path Integrals scale linearly with respect to the number of beads

# Path Integral MD: Illustration



# Path Integrals: intrinsic parallelization scheme



# PIMD: General formalism

One simulates *classical* object with the effective potential:

$$V_{\text{eff}}(\{x_j\}) = \frac{m \omega_P^2}{2} \sum_{j=1}^P (x_j - x_{j+1})^2 + \frac{1}{P} \sum_{j=1}^P \phi(x_j) \quad \omega_P = \frac{\sqrt{P}}{\beta \hbar}$$

Normal mode transform diagonalizes spring terms:

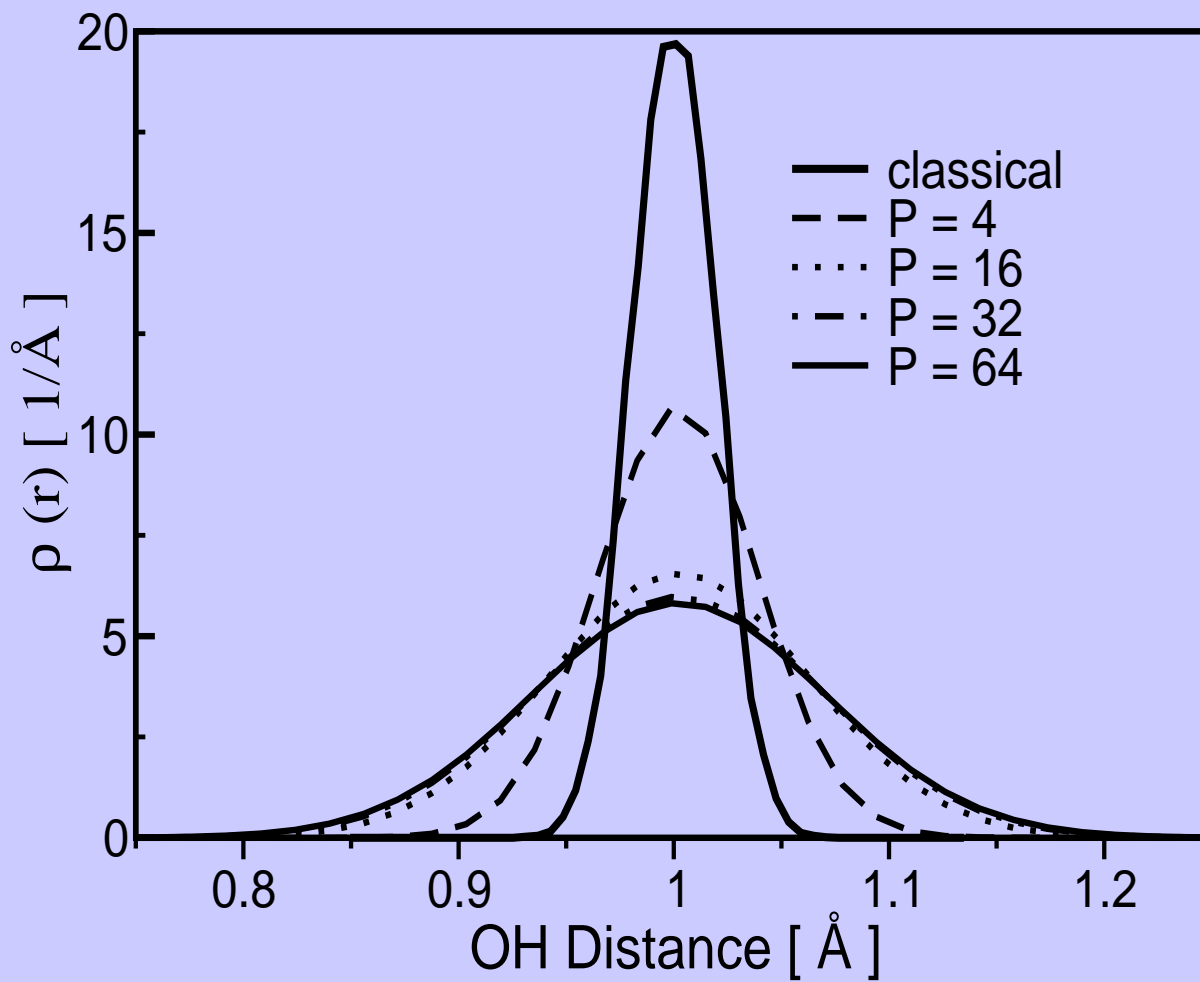
$$\mathbf{q} \equiv \frac{1}{\sqrt{P}} \mathbf{U} \mathbf{x} \quad \mathbf{x} \equiv \sqrt{P} \mathbf{U}^T \mathbf{q}$$

Hamiltonian in normal modes reads:

$$H(\mathbf{q}; \mathbf{p}) = \sum_{j=1}^P \frac{p_j^2}{2 \tilde{m}_j} + \sum_{j=1}^P \frac{m \omega_P^2}{2} \lambda_j q_j^2 + \frac{1}{P} \sum_{j=1}^P \phi[x_j(\mathbf{q})]$$



# Path Integrals: typical convergence scenario



concepts: CMD

centroid:

$$x_c \equiv \frac{1}{P} \sum_{i=1}^P x_i$$

- Statistical mechanics in terms of centroid density
- Centroids follow quasi-classical dynamics
- Equations of motion are purely classical

$$m\ddot{x}_c = - \frac{\partial V_{eff,c}}{\partial x_c}$$

- Normal mode transform is natural for CMD
- Adiabatic CMD
- Timestep should be decreased accordingly
- CMD is exact in the classical limit, free particle and for **purely** harmonic potentials.

choice of fictitious kinetic masses

MD:

No real-time information

Efficient sampling

Massive thermostating scheme

$$\tilde{m}_j = m\lambda_j$$

adiabatic Centroid MD:

Centroids yield quasi-classical dynamics

Dynamics of non-centroid modes is artificial

Non-centroid modes are lightened

Massive thermostating of non-centroid modes

$$\tilde{m}_1 = m$$

$$\tilde{m}_j = m\lambda_j / \gamma$$

ring Polymer MD:

Dynamics of all modes is physical

No thermostats

Observables are computed w.r.t. all beads

$$\tilde{m}_j = m$$

# IR spectra: time correlation functions

Absorption coefficient:  $\alpha(\omega) \propto \frac{\omega}{n(\omega)} (1 - \exp[-\beta \hbar \omega]) \cdot I(\omega)$

Spectral density:  $I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp[-i\omega t] C(t)$

Quantum time correlation function:  $C(t) \equiv \langle \hat{\mathbf{M}}(0) \hat{\mathbf{M}}(t) \rangle$

Detailed balance condition:  $I(-\omega) = \exp[-\beta \hbar \omega] I(\omega)$

Kubo-transformed quantum TCF  
is substituted by classical TCF\*  $I(\omega) = \frac{\beta \hbar \omega}{1 - \exp[-\beta \hbar \omega]} I_K(\omega)$

x spectra: quantum correction factor

Quantum corrected absorption coefficient:

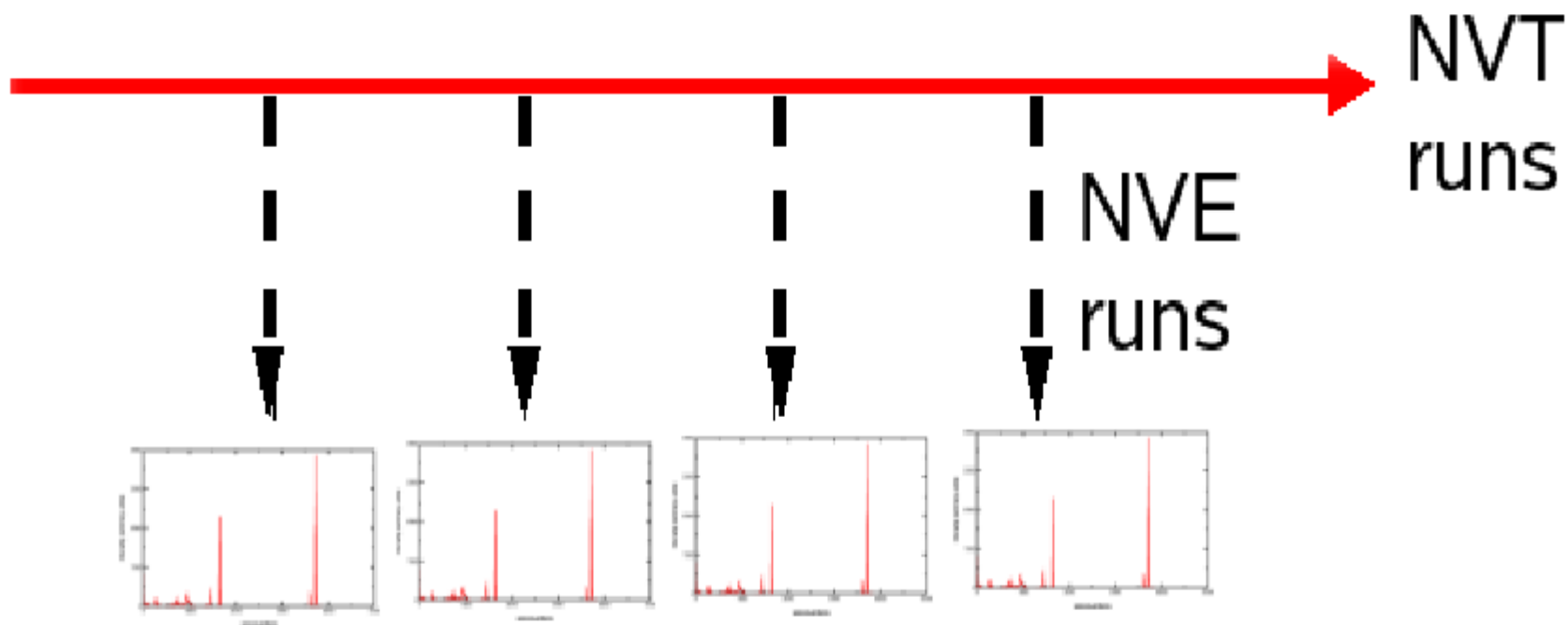
$$\alpha_{\text{QC}}(\omega) \propto \frac{\omega}{n(\omega)} (1 - \exp[-\beta \hbar \omega]) \cdot Q(\omega) \cdot I_{\text{cl}}(\omega)$$

Quantum correction factor:  $Q(\omega) = \frac{\beta \hbar \omega}{1 - \exp(-\beta \hbar \omega)} \equiv Q_{\text{HA}}(\omega)$

Resulting expression:  $\alpha_{\text{HA}}(\omega) \propto \frac{\omega^2}{n(\omega)} \cdot I_{\text{cl}}(\omega)$

One should improve the quality of the classical correlation function and *NOT* the quantum correction factor

# R spectra: computational procedure



- Resulting **canonical** spectrum is an average over **NVE** ones
- Translation-rotation corrections are employed
- Ergodicity is achieved by increasing the number of runs
- Resolution is controlled by a single run length

# Frequency analysis of the PI Hamiltonian

Normal mode eigen values:

$$\lambda_{2j-1,2j-2} = 2P \cdot \left[ 1 - \cos\left(\frac{2\pi(j-1)}{P}\right) \right] = 4P \sin^2\left(\frac{\pi(j-1)}{P}\right)$$

Corresponding frequencies:

$$\omega_k = \omega_P \sqrt{\frac{m}{\tilde{m}_k} \lambda_k}$$

CMD is a trivial case.

RPMD chain frequencies:

$$\omega_{2j-1,2j-2} = \frac{2P}{\beta\hbar} \sin\left(\frac{\pi(j-1)}{P}\right)$$

Chain frequencies **converge** with P:  $\lim_{P \rightarrow \infty} \omega_{2j-1,2j-2} = \frac{2\pi(j-1)}{\beta\hbar}$

Chain frequencies are **linear** in temperature

# PIMD: General formalism

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Chain frequencies are **linear** in temperature

**First chain frequencies are in the low/mid  
TB range for chemical systems**

# Testing RPMD: OH diatomic.

$$V(\{\mathbf{r}_j\}) = \frac{\mu\omega_P^2}{2P} \sum_{j=1}^P (\|\mathbf{r}_j\| - r_0)^2$$

Purely harmonic case ( $r_0=0$ ):

- Normal mode transform preserves the form of the potential.
- Centroid equations of motion are closed

For any finite  $r_0$ : this is **not** the case.

350K

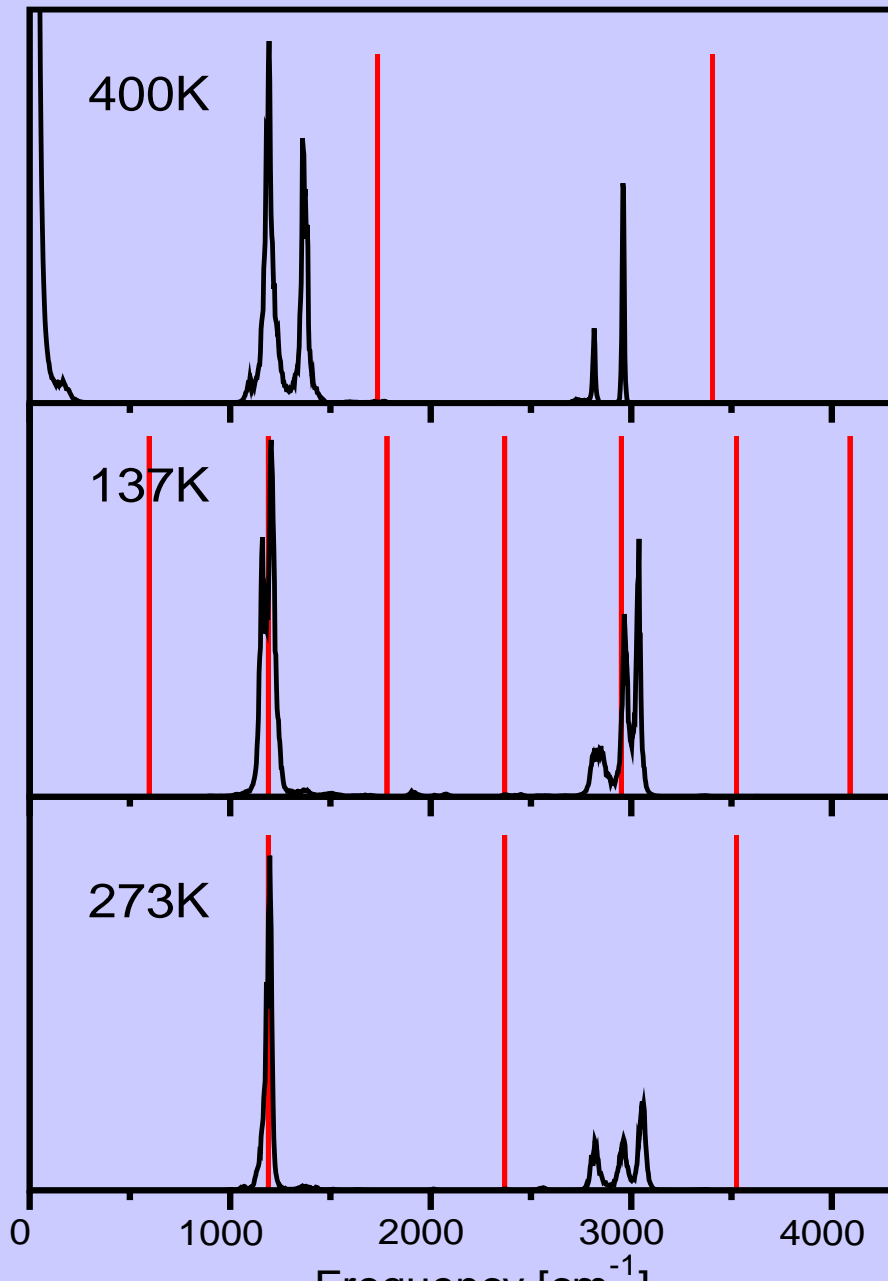
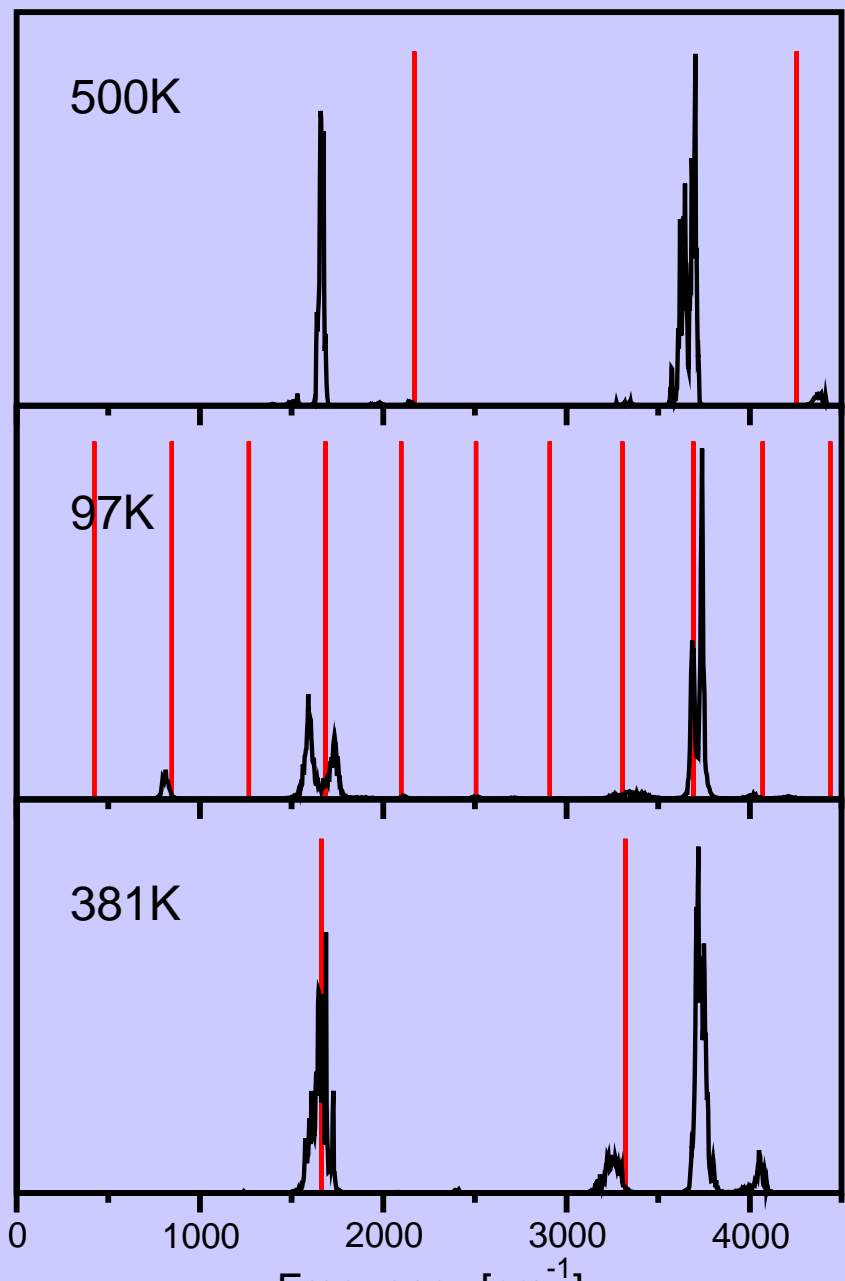
109K

437K

0 1000 2000 3000 4000  
[cm<sup>-1</sup>]

What happens  
if a chain frequency  
“**hits**” the physical one ?

# Testing RPMD. $\text{H}_2\text{O}$ , $\text{CH}_4$ molecules

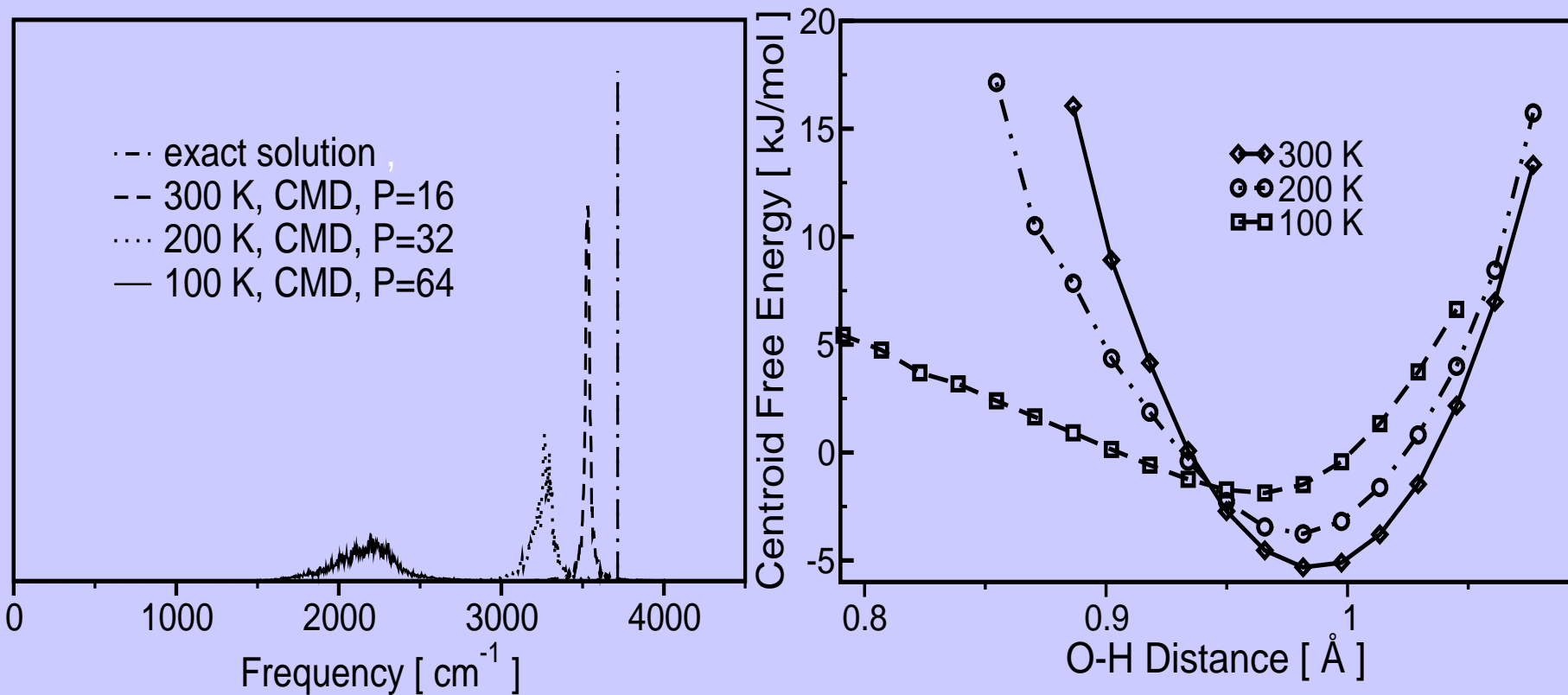


## RPMD: conclusions

- RPMD is *exact* for **purely** harmonic systems
- **No** chemical system is **truly** harmonic
- Even-numbered chain frequencies are observed in IR spectra
- Those spurious peaks vanish with temperature increase
- Resonances between chain and physical frequencies lead to, in principle, unpredictable consequences
- The number of chain frequencies in low/mid IR range **grows** with reciprocal temperature

**One should be extremely cautious about possible resonances**

# Testing CMD: OH diatomic.



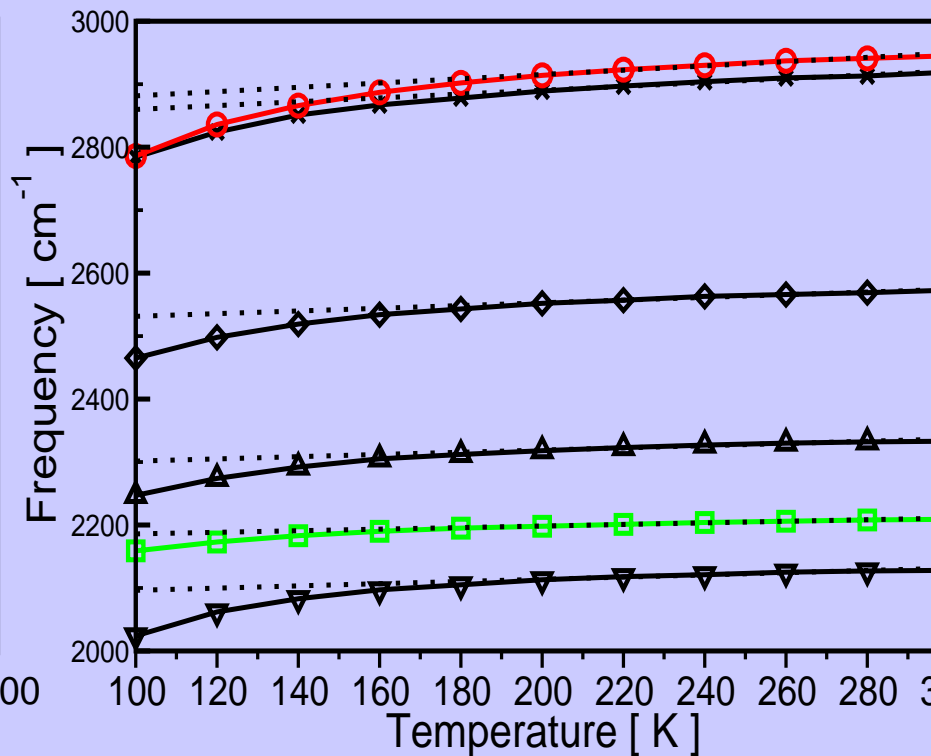
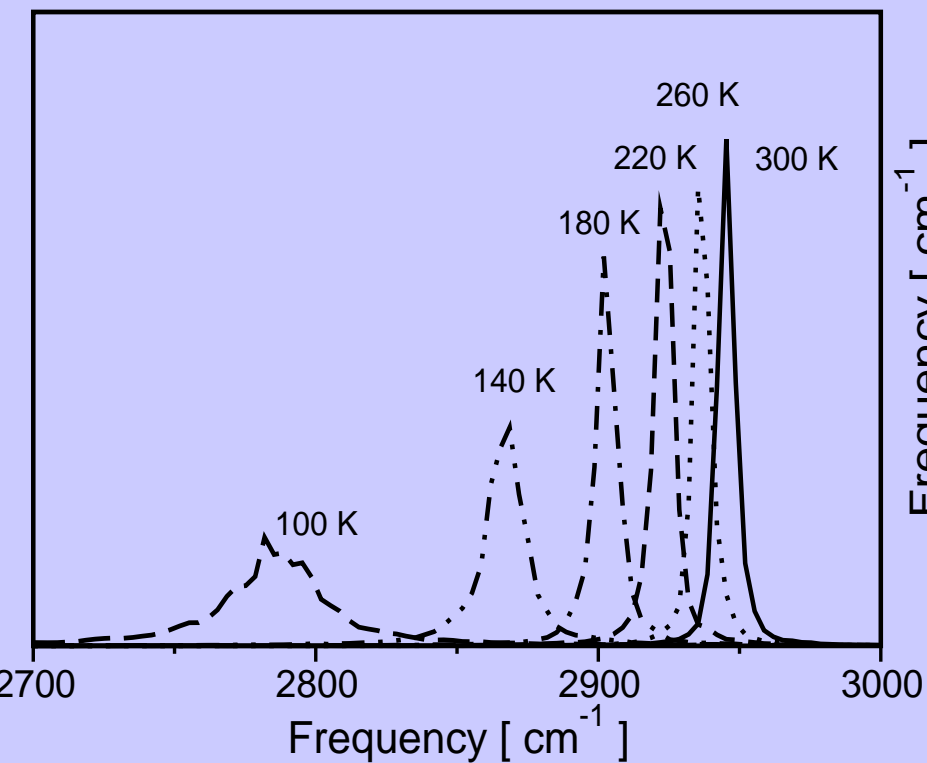
Peak positions are red-shifted and broaden with temperature decrease

At 100K the peak nearly vanishes

These effects are clearly explained by the form of the corresponding free energy profiles

The strength of the effect can be quantified by the body angle of the ring polymer spread: “**curvature**” problem

# Testing CMD: $\text{CH}_4$ , $\text{CD}_4$ , toy methane



A change of normal mode's mass renormalizes temperature  
Angle potential causes a **steric** effect in the **entropic** fashion  
All peaks in toy methane evolve similarly

# Methodical conclusions and outlook

One should be extremely cautious about possible resonances in RPMD

CMD unexpectedly breaks down below certain temperature (“curvature” problem)

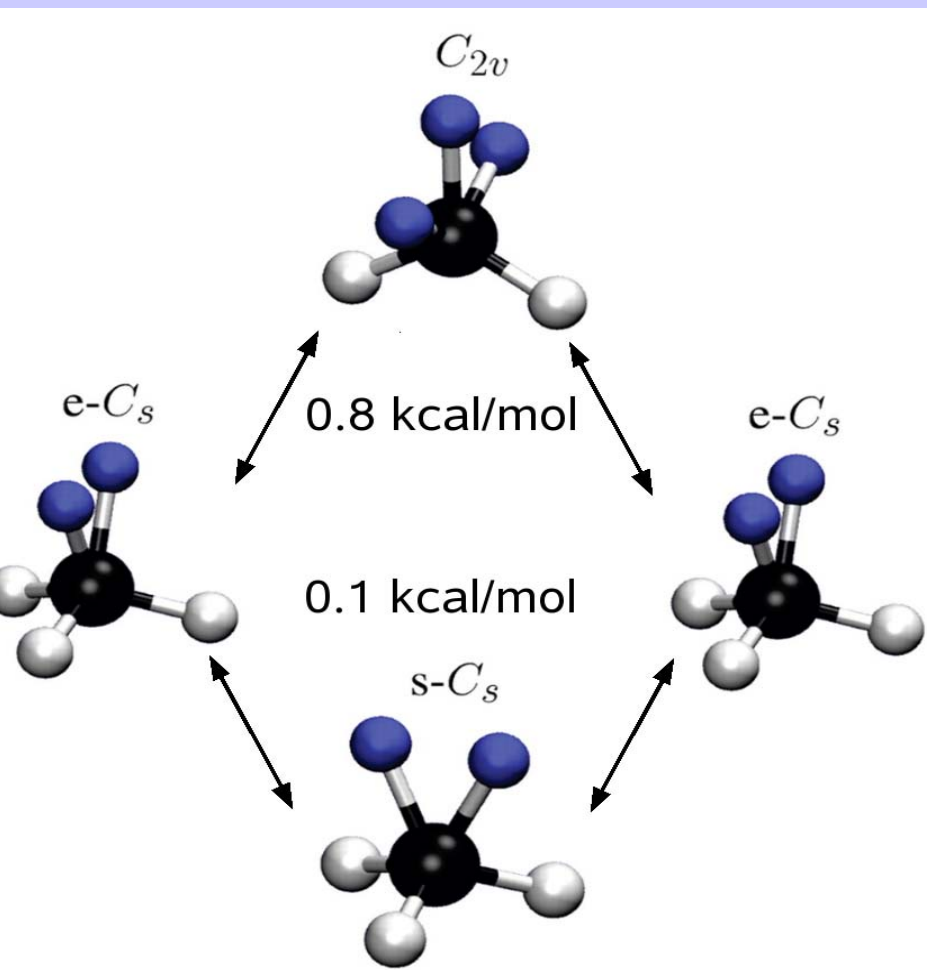
At higher temperatures stretching peaks evolve linearly  
Bending bands remain mainly unaffected

Angular potentials “confine” the spread of the bead cloud

The obtained results provide the grounds to study complex molecular systems by means of CMD

# Motivation: example

## Infrared spectra of protonated methane: $\text{CH}_5^+$



### Structure:

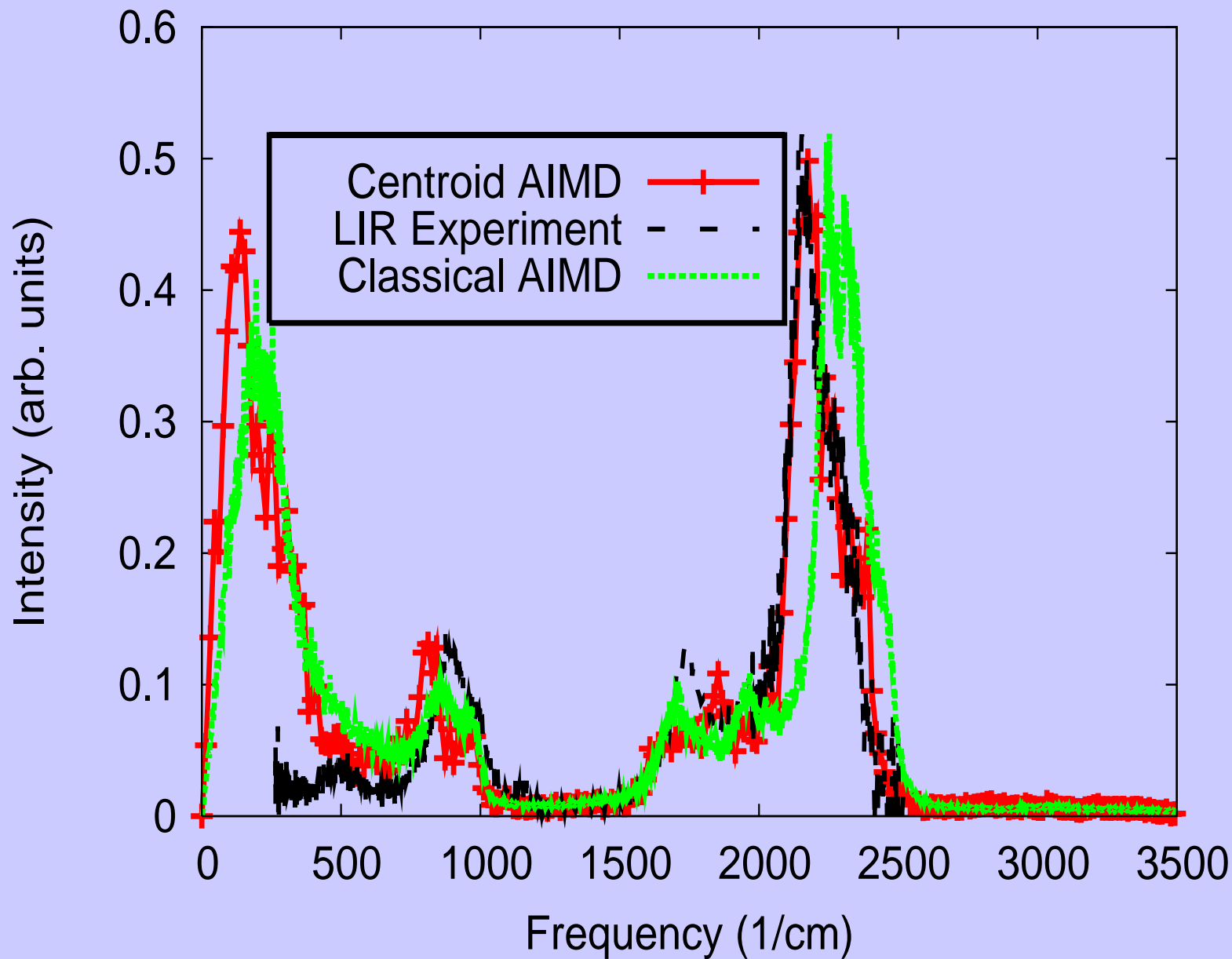
- Ground state:  $C_s$  symmetry
- Tripod and moiety
- 3-center-2-electron bond.

### Energetics:

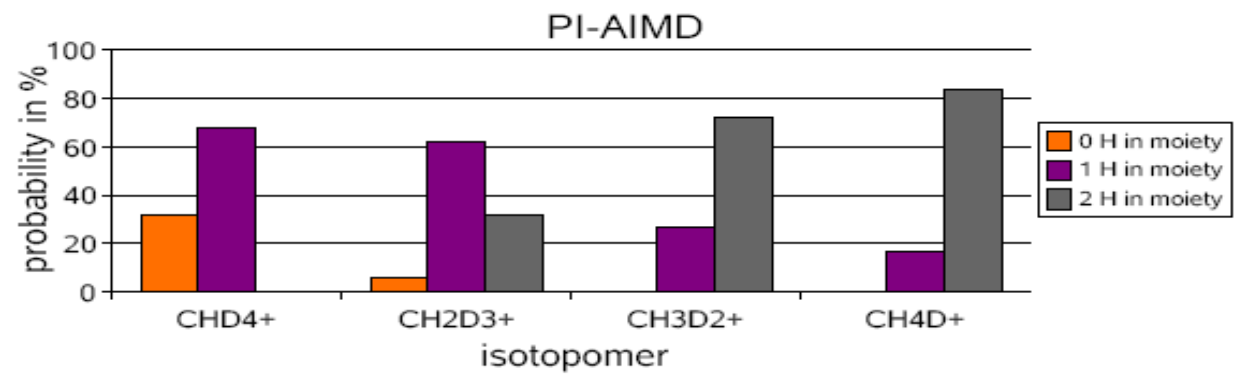
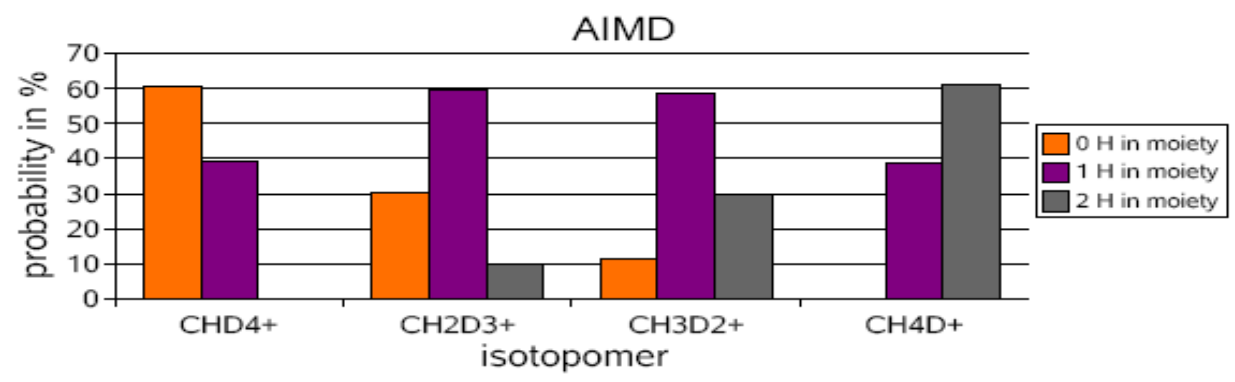
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- Scrambling ( $\sim 400\text{K}$ )



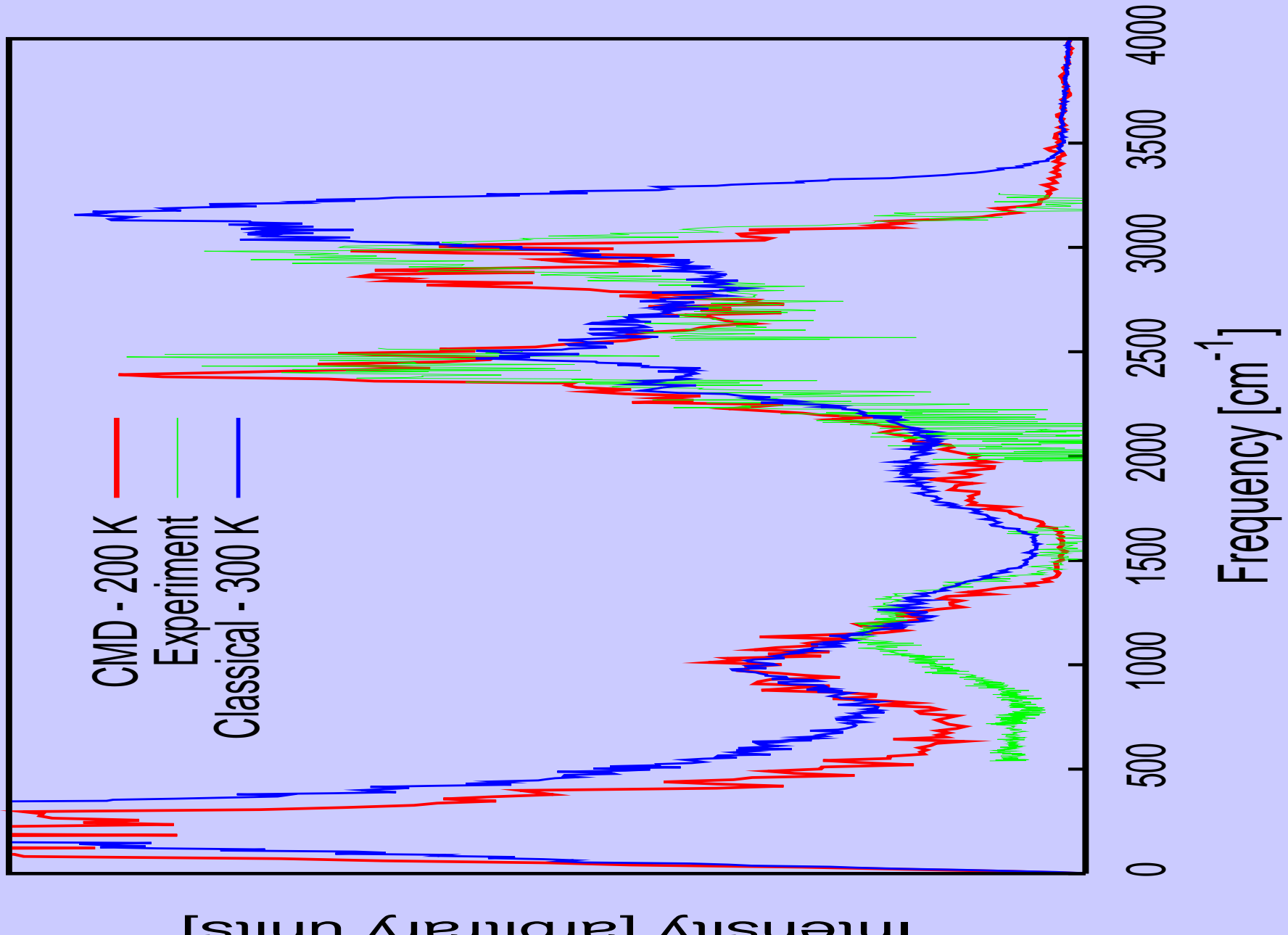
Applications:  $\text{CD}_5^+$ .



# Applications: isotopomers probabilities.



Applications:  $\text{CH}_3\text{D}_2$ .



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