

IR spectral simulations by semi-classical molecular dynamics applied to large gaseous molecules

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Outline

Introduction

- PAHs hypothesis

- Objectives

Tight-Binding Molecular Dynamics

IR absorption spectral simulations

- Classical MD

- Semi-classical MD

Application to naphthalene

- Validation in the harmonic PES region

- Simulating the 0 K anharmonic IR spectrum

- Temperature effects

Comparisons

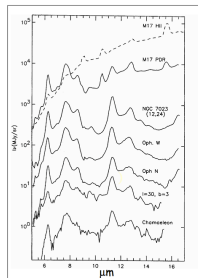
- other theoretical methods

- experiments

Polycyclic Aromatic Hydrocarbon hypothesis in the interstellar medium

- ▶ **Unidentified Infrared (UIR)** bands:
 - First observed by Gillet *et al.*
[Gillett *et al.*, *ApJ* (1973)]
 - High spectral resolution of UIR bands from ISO.
[Van Dienenhoven *et al.*, *ApJ* (2004)]
- ▶ UIR features are generally attributed to **(PAHs)** or **PAH-related molecules**.
[Allamandola *et al.*, *ApJ Supp. Ser.* (1989)], [Puget & Léger, *A&A* (1989)]
- ▶ IR emission of molecules follows from a visible-UV electronic excitation: molecular carriers are thus transitory vibrationally excited.
- ▶ IR emission spectral characteristics: governed by anharmonicities of the ground state PES.

Unidentified Infrared Bands



Objectives

Challenge:

- ▶ **unknown large molecular system** (PAH-based molecules; > 100 atoms of carbon)
- ▶ isolated, **high vibrationally excited** but rotationally cold => difficult to reproduce in experiments
- ▶ IR emission spectral characteristics: governed by **anharmonicities** of the ground state PES

Goal:

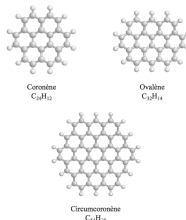
- ▶ Build **an efficient IR spectral simulation code** for PAH or PAH-based molecules.
- ▶ Try to **reproduce** as good as possible **anharmonic, thermal and dynamical effects** on the IR spectral patterns

Methods:

- ▶ **Semi-empirical tight-binding electronic structure representation**
- ▶ **Semi-classical IR spectral simulations** by classical molecular dynamics with corrections

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Polycyclic Aromatic Hydrocarbons



Tight-Binding model

Total energy :

$$E = T_{\text{core}} + E^{\text{rep}} + E_{\text{TB}}$$

Schrödinger equation :

$$H\Psi_{\ell} = \epsilon_{\ell}\Psi_{\ell}$$

Molecular Orbitals Ψ_{ℓ} (LCAO) :

$$\Psi_{\ell} = \sum_{i\alpha} c_{i\alpha}^{\ell} |i\alpha\rangle$$

Secular equation :

$$\mathbf{HC} = \mathbf{SC}\epsilon$$

The hamiltonian matrix elements $\langle i\alpha | H | j\beta \rangle$ of \mathbf{H} are computed analytically in the tight binding framework.

$$E_{\text{TB}} = \sum_{\ell}^{\text{occ}} n_{\ell} \epsilon_{\ell} + U \delta_{n_{\ell}, 2}$$

Pairwise repulsive interaction potential :

$$V_{\text{core}}^{(i,j)}(r_{ij}) = V_{\text{core}}^{(i,j)}(r_0) \left(\frac{r_0}{r_{ij}} \right) \exp \left\{ n_b \left[- \left(\frac{r_{ij}}{r_c} \right)^{n_c} + \left(\frac{r_0}{r_c} \right)^{n_c} \right] \right\}$$

Tight-Binding Potential

$$H = T + V_{\text{eff}} \quad (1)$$

V_{eff} is expressed as a sum of atom-centered contributions:

$$V_{\text{eff}}(\mathbf{r}) = \sum_j v_{\text{eff}}^{(j)}(\mathbf{r} - \mathbf{r}_j) \quad (2)$$

Intra-atomic matrix elements ($i = j$):

$$\langle i\alpha | H | i\beta \rangle = \langle i\alpha | T | i\beta \rangle + \langle i\alpha | v_{\text{eff}}^{(i)} | i\beta \rangle + \langle i\alpha | \sum_{j \neq i} v_{\text{eff}}^{(j)} | i\beta \rangle \quad (3)$$

$$= \epsilon_{\alpha}^{(i)} \delta_{\alpha\beta} + \langle i\alpha | \sum_{j \neq i} v_{\text{eff}}^{(j)} | i\beta \rangle \quad (4)$$

with $\epsilon_{\alpha}^{(i)}$ is the energy of the atomic orbital $|i\alpha\rangle$.

Inter-atomic matrix elements ($i \neq j$):

$$\langle i\alpha | H | j\beta \rangle = \langle i\alpha | T | j\beta \rangle + \langle i\alpha | v_{\text{eff}}^{(i)} | j\beta \rangle + \langle i\alpha | v_{\text{eff}}^{(j)} | j\beta \rangle \quad (5)$$

$$= t_{\alpha,\beta}^{(i,j)}(\mathbf{r}_i - \mathbf{r}_j) \quad (6)$$

The three-center integrals are neglected.

Tight-Binding Potential

For C_nH_m in the present work:

- ▶ Minimal Slater atomic basis set :
 - ▶ 2s, 2p for carbon
 - ▶ 1s for hydrogen.
- ▶ Orthogonal basis set :

$$\langle i\alpha | j\beta \rangle = \delta_{ij} \delta_{\alpha\beta} \quad (7)$$

- ▶ Tight-binding matrix size: $N \times N$ with $N = 4n + m$
- ▶ Tight-binding matrix elements:

$$\langle i\alpha | H | i\beta \rangle = \epsilon_{\alpha}^{(i)} \delta_{\alpha\beta} \quad (8)$$

$$\langle i\alpha | H | j\beta \rangle = t_{\alpha,\beta}^{(i,j)}(\mathbf{r}_i - \mathbf{r}_j) \quad (9)$$

[Van-Oanh *et al.* J PC A, 106 (2002) 10144]

[Van-Oanh *et al.* PCCP, 7 (2005) 1779]

Tight-Binding Potential

$$\langle i\alpha | H | j\beta \rangle = t_{\alpha,\beta}^{(i,j)}(\mathbf{r}_i - \mathbf{r}_j) \quad (10)$$

The hopping integrals are evaluated following the work of Slater and Koster.

$$\mathbf{r}_{ij} = (\mathbf{r}_i - \mathbf{r}_j) = r_{ij}(\mathbf{i} \cos \theta_x + \mathbf{j} \cos \theta_y + \mathbf{k} \cos \theta_z) \quad (11)$$

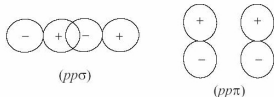
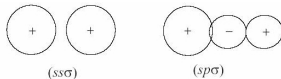
with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$

$$t_{s,s}^{(i,j)}(\mathbf{r}_i - \mathbf{r}_j) = ss\sigma(r_{ij})$$

$$t_{s,p_x}^{(i,j)}(\mathbf{r}_i - \mathbf{r}_j) = sp\sigma(r_{ij}) \cos \theta_x$$

$$t_{p_x,p_x}^{(i,j)}(\mathbf{r}_i - \mathbf{r}_j) = pp\sigma(r_{ij}) \cos^2 \theta_x \\ + pp\pi(r_{ij}) [1 - \cos^2 \theta_x]$$

$$t_{p_x,p_y}^{(i,j)}(\mathbf{r}_i - \mathbf{r}_j) = \cos \theta_x \cos \theta_y [pp\sigma(r_{ij}) - pp\pi(r_{ij})]$$



Radial dependence of the hopping integrals $t_{\alpha,\beta}^{(i,j)}(r_{ij}) = \{ss\sigma, sp\sigma, pp\sigma, pp\pi\}$

$$t_{\alpha,\beta}^{(i,j)}(r_{ij}) = t_{\alpha,\beta}^{(i,j)}(r_0) \left(\frac{r_0}{r_{ij}} \right) \exp \left\{ n_b \left[- \left(\frac{r_{ij}}{r_c} \right)^{n_c} + \left(\frac{r_0}{r_c} \right)^{n_c} \right] \right\} \quad (12)$$

Tight Binding Molecular Dynamics

Atomic motions are driven by classical law:

$$\mathbf{F}_i = m_i \frac{d^2 \mathbf{r}_i}{dt^2}$$

- ▶ Hellmann-Feynman force:

$$F_{x_i}^{\text{HF}} = -\frac{\partial}{\partial x_i} \sum_{\ell} n_{\ell} \langle \psi_{\ell} | H | \psi_{\ell} \rangle$$

- ▶ Repulsive force:

$$F_{x_i}^{\text{rep}} = -\frac{\partial}{\partial x_i} V_{\text{core}}^{(i,j)}(r_{ij})$$

Forces computed analytically.

Equations of motion are solved numerically using the Verlet velocity integration algorithm.

Dipole moment :

$$\boldsymbol{\mu}(t) = \sum_i q_i \mathbf{r}_i \quad (13)$$

Partial charge :

$$q_i = \sum_{\ell} \sum_{i\alpha} n_{\ell} (c_{i\alpha}^{\ell})^2 \quad (14)$$

IR absorption cross-section

At a finite temperature T :

$$\sigma(\omega, T) = \frac{\pi \omega}{3 \hbar c \epsilon_0} [1 - \exp(-\beta \hbar \omega)] I^Q(\omega, T). \quad (15)$$

$I^Q(\omega, T)$: quantum IR absorption lineshape

- ▶ From quantum mechanics:

$$I^Q(\omega, T) = \sum_i \sum_f \rho_i \langle f | \boldsymbol{\mu} | i \rangle \delta\left(\frac{E_f - E_i}{2} - \omega\right) \quad (16)$$

- ▶ From quantum linear response theory: Fourier transform of the quantum time autocorrelation function of the dipole moment $\boldsymbol{\mu}$

$$I^Q(\omega, T) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle [\hat{\boldsymbol{\mu}}(0), \hat{\boldsymbol{\mu}}(t)] \rangle dt. \quad (17)$$

In the classical limit:

$$\sigma^C(\omega, T) = \lim_{\hbar \rightarrow 0} \sigma(\omega, T) = \frac{\pi \beta \omega^2}{3 c \epsilon_0} I^C(\omega, T). \quad (18)$$

Classical absorption lineshape:

$$I^C(\omega, T) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle dt. \quad (19)$$

it is denoted as **classical** spectrum

Semi-classical MD

In a general semi-classical scheme:

Using the classical correlation function $I^C(\omega, T)$:

$$I^C(\omega, T) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle dt. \quad (20)$$

Introducing a correction factor $D(\omega, T)$ into the IR absorption cross section :

$$\sigma(\omega, T) = \frac{\pi \omega}{3 c \epsilon_0} [1 - \exp(-\beta \hbar \omega)] D(\omega, T) I^C(\omega, T). \quad (21)$$

Usual expressions of $D(\omega, T)$:

1. Symmetrization of time correlation function, leads to:

$$D^S(\omega, T) = \frac{2}{1 + \exp(-\beta \hbar \omega)}, \quad (22)$$

2. Double harmonic approximation:

$$D^H(\omega, T) = \frac{\beta \hbar \omega}{1 - \exp(-\beta \hbar \omega)}. \quad (23)$$

These correction factors allow the detailed balance to be satisfied, *i.e.*

$$I_{\text{corr}}(-\omega, T) = \exp(-\beta \hbar \omega) I_{\text{corr}}(\omega, T).$$

The latter is widely used in the literature.

Semi-classical MD

The **semi-classical** expression used in the present work:

$$\sigma(\omega, T) = \frac{\pi \omega}{3 c \epsilon_0} [1 - \exp(-\beta \hbar \omega)] D(\omega, T) I^C(\omega, T). \quad (24)$$

with

$$I^C(\omega, T) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle dt. \quad (25)$$

Two corrections:

1. Symmetrization of time correlation function:

$$D^S(\omega, T) = \frac{2}{1 + \exp(-\beta \hbar \omega)} \quad (26)$$

2. Initial condition preparation following the semi-classical quantization theory in order to bring the system into its corresponding quantum energy level :

$$Q_i = \left[\frac{(2 \langle n_i \rangle + 1) \hbar}{\omega_j} \right]^{1/2} \sin \varphi_i \quad (27)$$

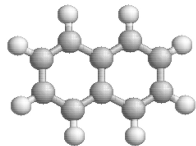
$$P_i = [(2 \langle n_i \rangle + 1) \hbar \omega_j]^{1/2} \cos \varphi_i \quad (28)$$

with

$$\langle n_i \rangle = \frac{1}{\exp(\beta \hbar \omega_j) - 1}$$

Simulation Details

- ▶ Naphthalene $C_{10}H_8$
- ▶ 48 vibrational modes ($170 - 3000 \text{ cm}^{-1}$)
- ▶ 22 IR active modes
- ▶ 8 very closed frequency C-H stretching modes
- ▶ Degenerated modes at $1150, 1664, 3125$ and 3136 cm^{-1}
- ▶ MD simulations performed in microcanonical ensemble
- ▶ Data collected from 100 samplings (*i.e.* 100 initial conditions)
- ▶ MD simulation duration for each sampling = 300 ps



Double Harmonic Approximation

Within the uncoupled harmonic approximation framework, the exact quantum correlation function is known:

$$I^Q(\omega, T) = \sum_i^{3N-6} \frac{\hbar}{2\omega [1 - \exp(-\beta\hbar\omega)]} \left| \frac{\partial \boldsymbol{\mu}}{\partial Q_i} \right|^2 \delta(\omega - \omega_{0,i}) \quad (29)$$

It is referred to as **static** spectrum:

$$\sigma(\omega) = \frac{\pi}{6 c \epsilon_0} \sum_i^{3N-6} \left| \frac{\partial \boldsymbol{\mu}}{\partial Q_i} \right|^2 \delta(\omega - \omega_{0,i}) \quad (30)$$

The $3N - 6$ harmonic frequencies ω_0 can be obtained by diagonalizing the mass-weighted Hessian matrix at the equilibrium \mathbf{R}_0 *i.e.*:

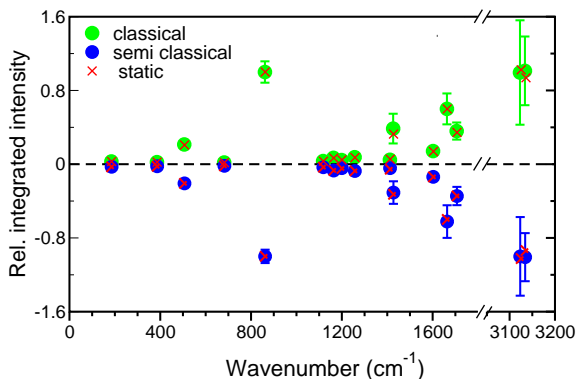
$$\frac{\partial^2 V}{\partial \xi_i \partial \xi_j}$$

- ▶ *Hessian matrix computed analytically*
- ▶ $\frac{\partial \boldsymbol{\mu}}{\partial Q_i}$ *computed analytically*

Semi-classical MD: validation in the harmonic PES region

Imposing a set of "empirical" quantum numbers so that the KE of each mode is proportional to its frequency and the mean KE is equal to 10 K

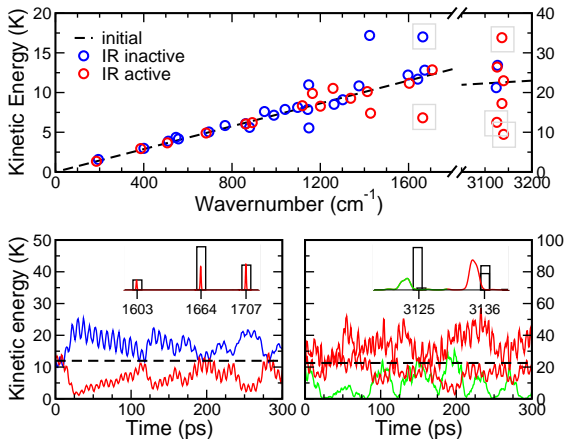
Spectrum of 100 semi-classical MD samplings will be compared to the static and to the classical spectra. A very good agreement is observed for the semi-classical method.



Semi-classical MD: validation in the harmonic PES region

Imposing a set of "empirical" quantum numbers so that the KE of each mode is proportional to its frequency and the mean KE is equal to 10 K

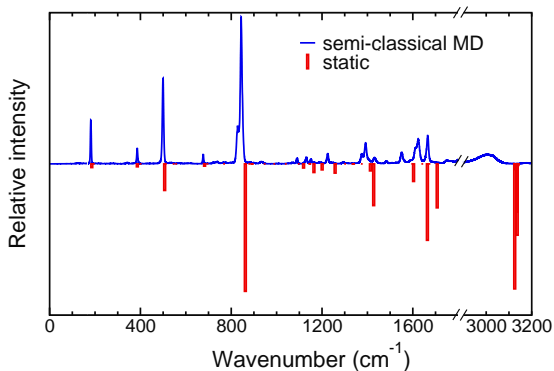
The system is indeed in the harmonic potential energy surface region and in the nearly absence of mode couplings.



For the degenerated modes, small couplings will cause significant energy transfers

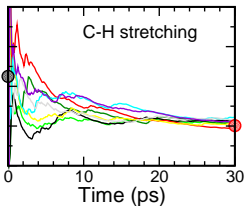
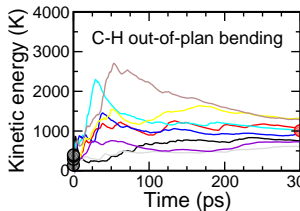
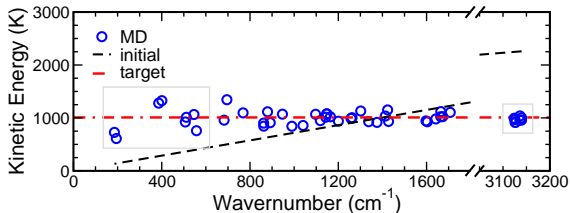
OK anharmonic IR spectrum

The system is initially localized in the vibrational ground state $E_i = \hbar\omega_{i,0}/2$
The IR spectrum is shifted towards smaller wavenumbers due to the anharmonicity.
The band intensities change too much compared to the harmonic spectrum.



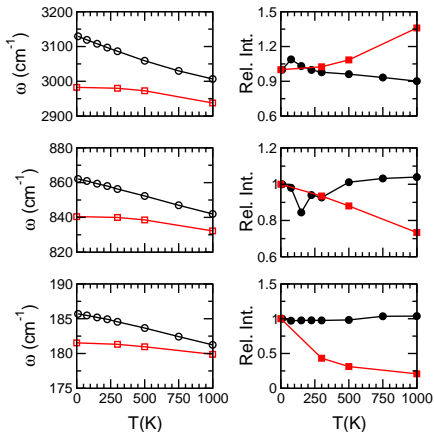
Intramolecular Vibrational Energy Redistribution (IVR)

The system is initially localized in the vibrational ground state $E_i = \hbar\omega_{i,0}/2$
Strong mode couplings \Rightarrow IVR \Rightarrow energy equipartition $\Rightarrow E = \langle E_i \rangle \forall i$



Temperature effects on the IR spectrum

Classical and semi-classical MDs don't lead to the same results both for the frequencies and for the intensities of the bands
Intensities behave quite differently in the **semi-classical** MD depending on the frequency region.

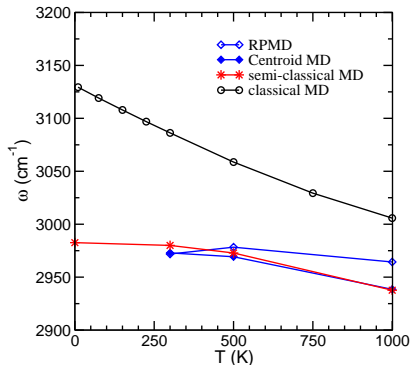


Comparison to Path-Integral MD

Ring-Polymer MD and Centroid MD account for quantum effects on nuclear motion, based on the path integral representation of quantum statistical mechanics.

[Calvo et al. JCP, 132 (2010) 124308; 133 (2010), 074303]

semi-classical results are in good agreement with the centroid MD



Comparison to second order perturbation method

[Basire *et al.*, JCP (2008), JPCA (2009) and (2010)]

Energy level computed by second order perturbation theory through third and fourth derivatives of the potential function (Dunham expansion):

$$E(\{n\}) = \sum_{i=1}^{3N-6} \hbar\omega_{0,i} \left(n_i + \frac{1}{2}\right) + \sum_{ij} \chi_{ij} \left(n_i + \frac{1}{2}\right) \left(n_j + \frac{1}{2}\right)$$

ΔE_k calculated randomly in quanta space $\{n\}$ driven by Metropolis rule at a fixed density of states $\Omega(E)$:

$$\Delta E_k = [\hbar\omega_{0,k} + 2\chi_{kk} + \frac{1}{2} \sum_{i \neq k} \chi_{ik}] + [2\chi_{kk} n_k + \sum_{i \neq k} \chi_{ik} n_i]$$

Absorption cross-sections: harmonic approximation

$$\sigma_{n_k \rightarrow n_k+1}^{(k)} = (n_k + 1) \sigma_{0 \rightarrow 1}^{(k)}$$

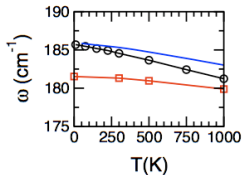
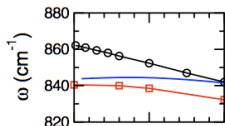
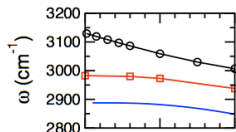
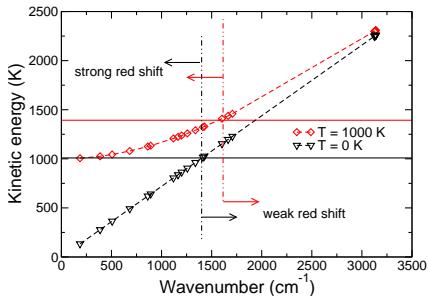
Energy resolved spectrum $\sigma(\omega, E)$ obtained by accumulating intensity $\sigma_{n_k \rightarrow n_k \pm 1}^{(k)}$ at transition energy ΔE_k .

Canonical absorption spectrum obtained through Laplace transformation from $\sigma(\omega, E)$.

Comparison to second order perturbation method

semi-classical red shifts are overestimated/underestimated for low/high frequencies compared to Dunham perturbation method due to energy relaxation

- ▶ Strong red shift: $\hbar\omega < \langle E \rangle_T$
- ▶ Weak red shift : $\hbar\omega > \langle E \rangle_T$



0K anharmonic C-H stretching frequency

Vibrational energy relaxation time of the mode Q_i initially localized in a particular state n_i can be measured by:

$$\tau(n_i) = \int_0^{\infty} \langle \dot{Q}_i(0) \cdot \dot{Q}_i(t) \rangle dt$$

Spectral information at a specific quantum energy level (before relaxation) can also be obtained in a very short time simulation

$$\tau_{\text{char}}(Q_i) \ll T_{\text{sim}} \ll \tau(n_i)$$

Example:

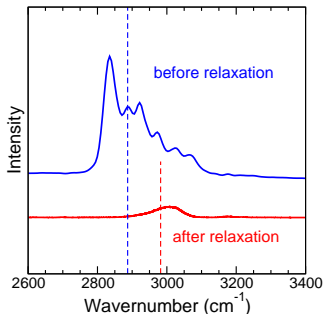
$$n(\text{CHstretchings}) = 1$$

Energy relaxation induces a blue shift to the C-H stretching modes.

Comparison:

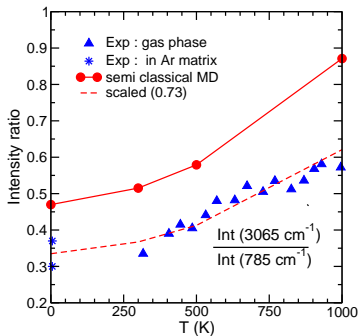
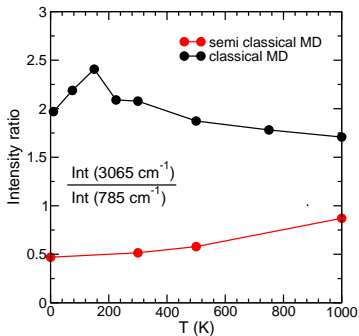
- Dunham perturbation value at 0 K
- semi-classical MD value at 0 K

As a consequence, red shifts are observed for low frequency modes (data not shown)



Comparison to experimental data

semi-classical temperature-dependent intensity ratio matches well the **experimental** trend but **classical** cannot.

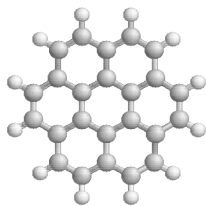


Exp in Ar matrix: [Hudgins *et al.* (1994), Szczepanski *et al.* (1992)]

Exp in gas phase: [Robinson *et al.* (1995)]

Application to coronene

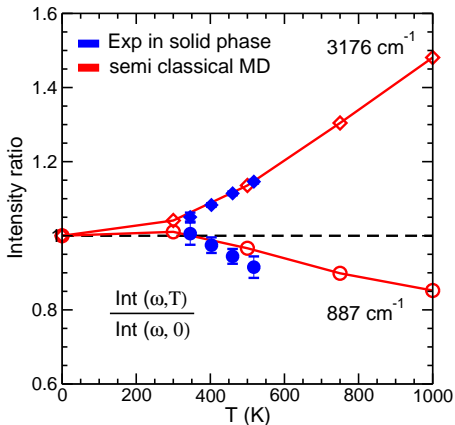
semi-classical MD reproduce also well the experimental temperature-dependent intensity trend of the individual vibrational mode.



$C_{24}H_{12}$

Exp in solid phase:

[Colangeli *et al.* (1992)]



Summary and Outlook

Summary:

- ▶ semi-classical MD is capable to describe the well-known **non linear red shift trend** on the frequencies with temperature due to anharmonicities of the potential energy surface.
- ▶ semi-classical MD provokes an extra **blue shift** to **high frequencies** and **red shift** to **low frequencies** due to energy relaxation. This effect is expected to be less important at high temperature.
- ▶ semi-classical MD provides a very good description of the intensity band evolution as a function of temperature observed by experiments: **Intensity increases for high frequencies** and **decreases for low frequencies**.

Presently:

- ▶ Article in preparation :-)

Outlook:

- ▶ Inclusion of the mechanical and electrical anharmonic intensities and the IVR effects to the second order perturbation method
- ▶ Examining the transferability of the tight-binding potential using ab initio electronic structure information