# Deoxyguanosine and Ac-Phe-Met-$NH_2$ vibrational spectra: a comparison between ab-initio and force field molecular dynamics

Fabio Gabas, Riccardo Conte and Michele Ceotto

UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO DI CHIMICA

fabio.gabas@unimi.it, michele.ceotto@unimi.it

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## Abstract

In semiclassical spectroscopy, a Fourier transform of the survival amplitude leads to the vibrational power spectrum of the molecular system, comprehensive of all quantum anharmonicities, overtones, resonances, zero point energy and tunneling effects. Furthermore, semiclassical dynamics may be efficiently associated to ab-initio molecular dynamics (AIMD) when the focus is on high dimensional systems.[1-2] This combination may provide very accurate results, but unfortunately it presents high computational costs.[3] In contrast, empirical Force Fields (FF) are known to be fast and computationally cheap. [4-5] Here we test the performance of the Amber94 force field against DFT-based AIMD, by studying the vibrational power spectra of two biological systems: the 2-Deoxyguanosine and the Ac-Phe-Met-$NH_2$ dipeptide.

## Methods

$$I_\chi(E) = \frac{1}{2\pi\hbar}\int dt\, e^{iEt/\hbar}\,\langle\chi|\chi(t)\rangle = \sum_k |\,\langle\chi|E_k\rangle\,|^2\delta(E-E_k)$$

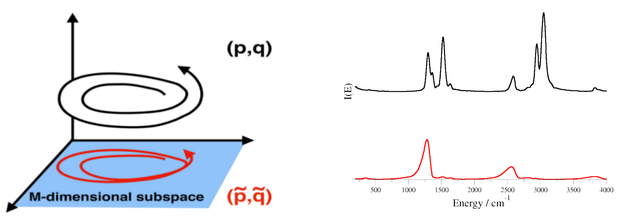
2003

**TA-SCIVR** [6]

$$I_\chi(E) = \left(\frac{1}{2\pi\hbar}\right)^F \int\int d\mathbf{p}_0 d\mathbf{q}_0 \frac{1}{2\pi\hbar T}\left|\int_0^T e^{\frac{i}{\hbar}[S_t(\mathbf{p}_0,\mathbf{q}_0)+Et+\phi_t]}\,\langle\chi\,|\mathbf{p}_t\mathbf{q}_t\rangle\,dt\right|^2$$

2009

**DC-SCIVR** [9]

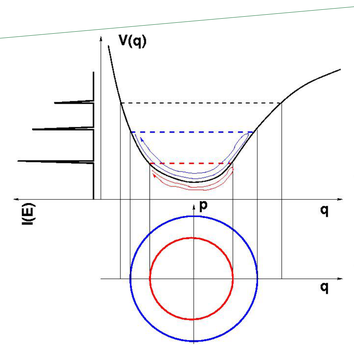



- The projection in subspace helps the trajectory to have a significant overlap with its initial state and hence to give a signal in the spectrum
- The overall spectrum can be recovered as a simple summation over all the subspaces

$$\tilde{I}(E) = \left(\frac{1}{2\pi\hbar}\right)^M \sum_{k=1}^{N_{traj}} \frac{1}{2\pi\hbar T}\left|\int_0^T e^{\frac{i}{\hbar}\left[\tilde{S}_t(\tilde{\mathbf{p}}_0,\tilde{\mathbf{q}}_0)+Et+\tilde{\phi}_t\right]}\,\langle\tilde{\boldsymbol{\chi}}\,|\tilde{\mathbf{p}}_t\tilde{\mathbf{q}}_t\rangle\,dt\right|^2$$

2017

**MC-SCIVR** [7-8]




$$|\chi\rangle = \sum_{k=1}^{N_{states}}\prod_{j=1}^{F}\varepsilon_k(j)\,|p^k_{eq,j}, q^k_{eq,j}\rangle$$

- Frequencies are obtained with a single trajectory with an energy close to the true quantum one.
- The reference state is appropriately chosen, with $\varepsilon_i(j)$ that allows to enforce parity or molecular symmetry.

$$I_\chi(E) = (\frac{1}{2\pi\hbar})^F \sum_{k=1}^{N_{traj}} \frac{1}{2\pi\hbar T}\left|\int_0^T \mathrm{d}t\,\langle\chi|\mathbf{p}_t,\mathbf{q}_t\rangle\, e^{\{\frac{i}{\hbar}[S_t+Et+\phi_t]\}}\right|^2$$

## Results

Different levels of calculation can be employed for the evaluation of the potential energy surface along the trajectory.
Here we compare the DFT B3LYP/6-31G* ab-initio molecular dynamics with the Amber94 empirical Force Field, written specifically for proteins and DNA.

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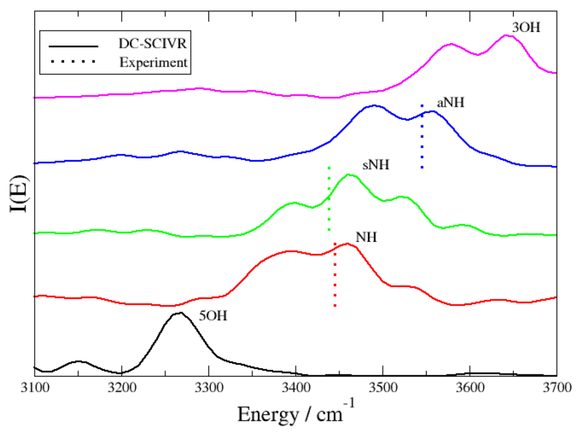
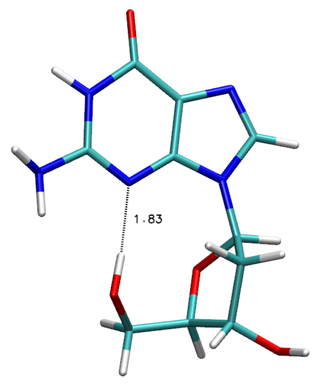
### Ab-initio Molecular Dynamics

### Empirical Force Field

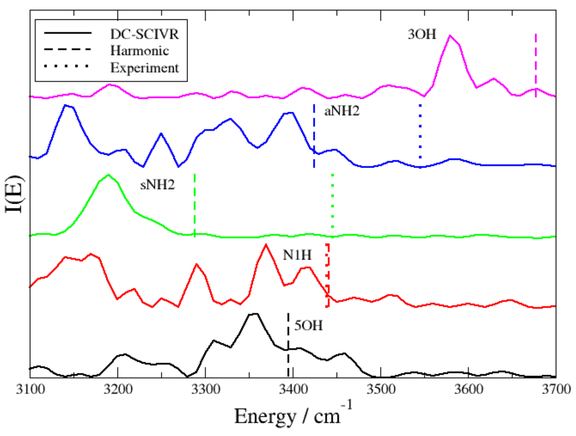
### 2-Deoxyguanosine



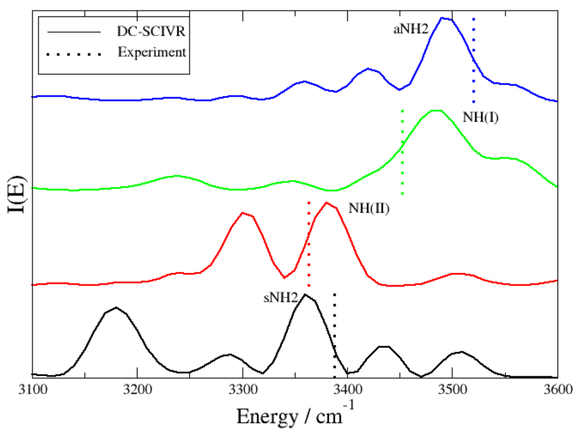

| mode | Exp | DC-SCIVR |
|---|---|---|
| 3OH | | 3640 |
| $aNH_2$ | 3545 | 3560 |
| NH | 3438 | 3460 |
| $sNH_2$ | 3445 | 3460 |
| 5OH | | 3270 |
| | **MAE** | **17** |



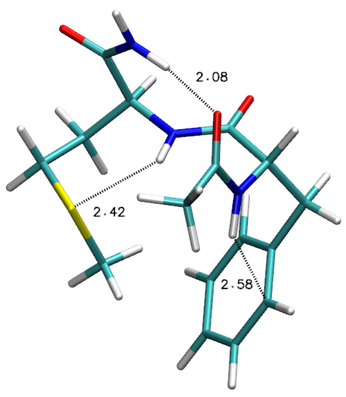

| mode | Exp | DC-SCIVR | Harm. |
|---|---|---|---|
| 3OH | | 3580 | 3678 |
| aNH2 | 3545 | 3400 | 3425 |
| NH | 3438 | 3370 | **3441** |
| sNH2 | 3445 | 3190 | 3288 |
| 5OH | | 3360 | 3395 |
| | **MAE** | **156** | **93** |



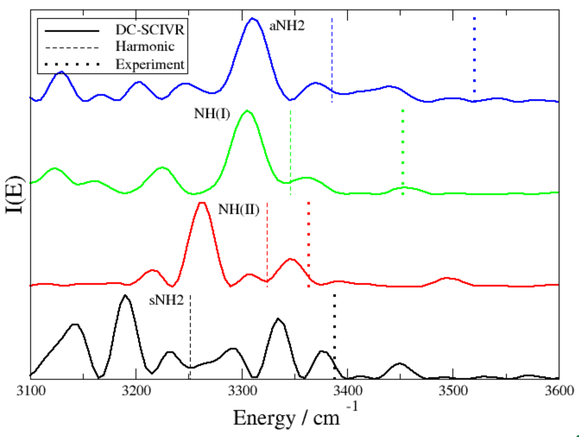

### Ac-Phe-Met-$NH_2$




| mode | Exp | DC-SCIVR |
|---|---|---|
| aNH2 | 3520 | 3490 |
| NH(I) | 3452 | 3480 |
| NH(II) | 3363 | 3380 |
| sNH2 | 3388 | 3360 |
| | **MAE** | **26** |




| mode | Exp | DC-SCIVR | Harm. |
|---|---|---|---|
| aNH2 | 3520 | 3310 | 3385 |
| NH(I) | 3452 | 3305 | 3346 |
| NH(II) | 3363 | 3270 | **3324** |
| sNH2 | 3388 | 3190 | 3251 |
| | **MAE** | **162** | **104** |




## Conclusions

- Semiclassical ab-initio results are in agreement with the experiment with the typical accuracy of the method (20-30 cm-1)
- The best Amber results come from harmonic analysis, while the worst set derives from the semiclassical approach
- Amber seems to perform well only in describing free, uncoupled motion, like for example some simple NH stretchings

## Future Perspective

- Since Amber was implemented to simulate biological systems in condensed phase, it remains an open question if a semiclassical analysis on such kind of system can be valuable.
- Results coming from other more accurate Force Fields still have to be tested upon the semiclassical methodology

## References

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