



UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO DI CHIMICA

MolSimEng 2018

**Ab-initio and force field molecular dynamics
applied to vibrational spectroscopy: the case of
Deoxyguanosine and Ac-Phe-Met-NH₂**

Fabio Gabas, Riccardo Conte, Michele Ceotto

Semiclassical Methods

Power spectrum

$$I_{\chi}(E) = \frac{1}{2\pi\hbar} \int dt e^{iEt/\hbar} \langle \chi | \chi(t) \rangle \equiv \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \langle \chi | e^{-i\hat{H}t/\hbar} | \chi \rangle e^{iEt/\hbar} dt$$

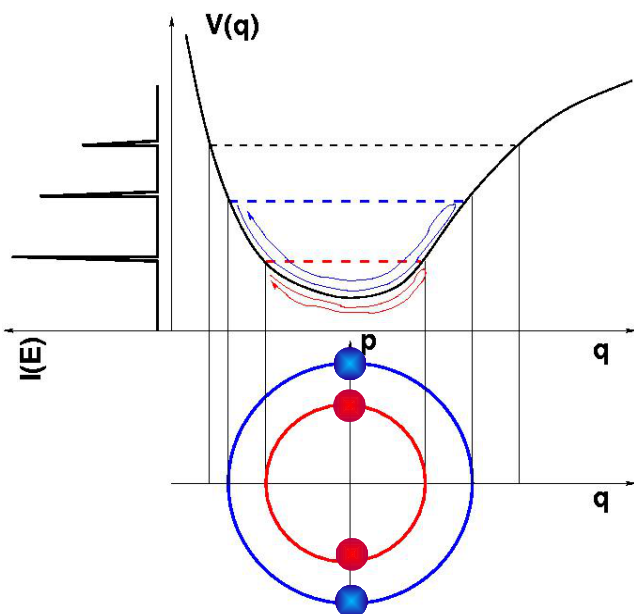
Semiclassical Methods

Power spectrum

$$I_{\chi}(E) = \frac{1}{2\pi\hbar} \int dt e^{iEt/\hbar} \langle \chi | \chi(t) \rangle \equiv \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \langle \chi | e^{-i\hat{H}t/\hbar} | \chi \rangle e^{iEt/\hbar} dt$$

MC-SCIVR

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



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

\mathbf{q}_{eq} at equilibrium geometry

Harmonic sampling for \mathbf{p}_{eq}

- 1) Ceotto, M.; Atahan, S.; Shim, S.; Tantardini, G. F.; Aspuru-Guzik, A., *Phys. Chem. Chem. Phys.* 2009, 11, 3861–3867.
- 2) Ceotto, M.; Atahan, S.; Tantardini, G. F.; Aspuru-Guzik, A., *J. Chem. Phys.*, 2009, 130, 234113.

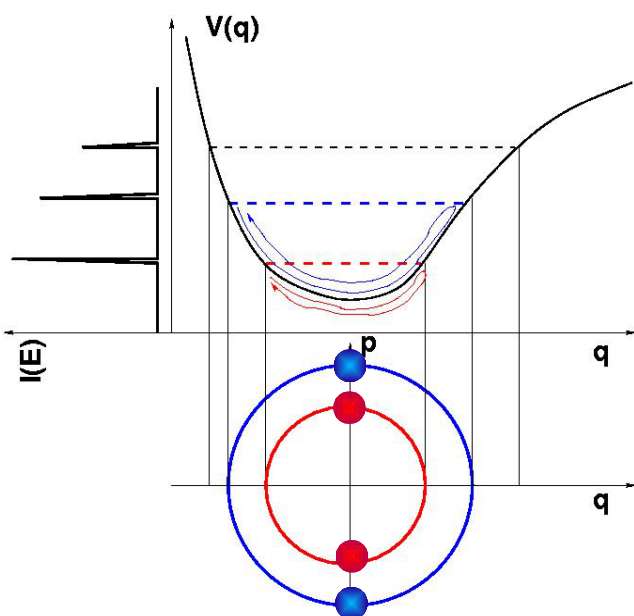
Semiclassical Methods

Power spectrum

$$I_{\chi}(E) = \frac{1}{2\pi\hbar} \int dt e^{iEt/\hbar} \langle \chi | \chi(t) \rangle \equiv \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \langle \chi | e^{-i\hat{H}t/\hbar} | \chi \rangle e^{iEt/\hbar} dt$$

MC-SCIVR

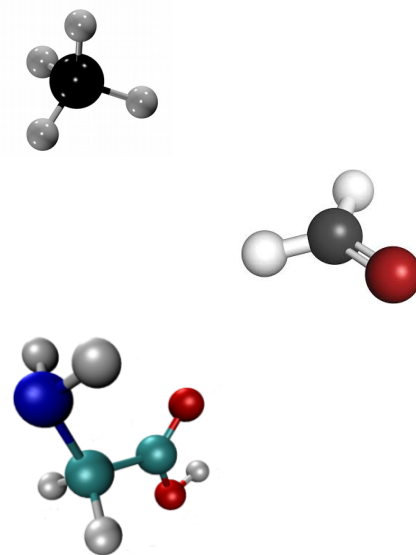
$$I_{\chi}(E) = \left(\frac{1}{2\pi\hbar} \right)^F \sum_{k=1}^{N_{traj}} \frac{1}{2\pi\hbar T} \left| \int_0^T dt \langle \chi | \mathbf{p}_t, \mathbf{q}_t \rangle e^{\left\{ \frac{i}{\hbar} [S_t + Et + \phi_t] \right\}} \right|^2$$



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

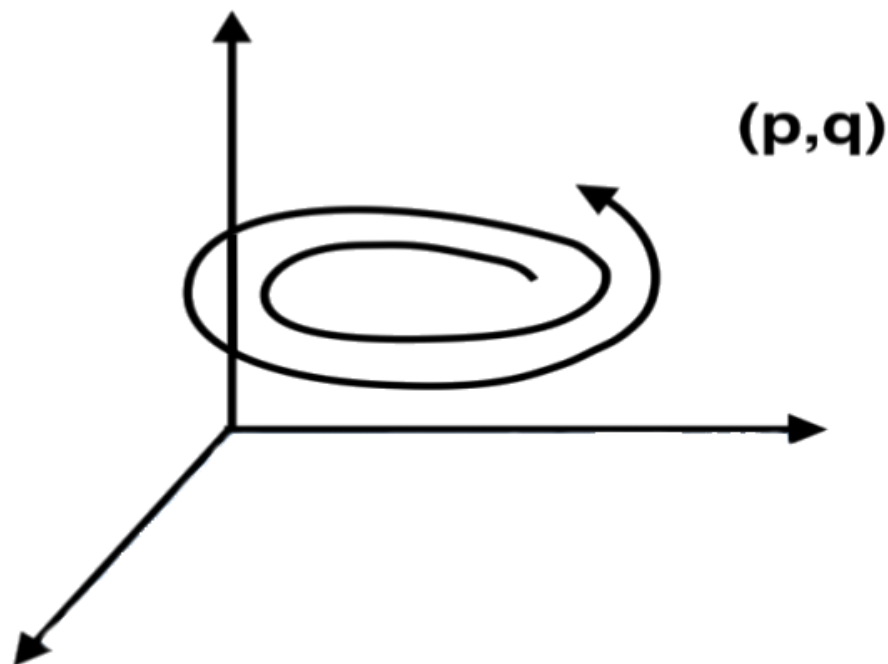
\mathbf{q}_{eq} at equilibrium geometry

Harmonic sampling for \mathbf{p}_{eq}



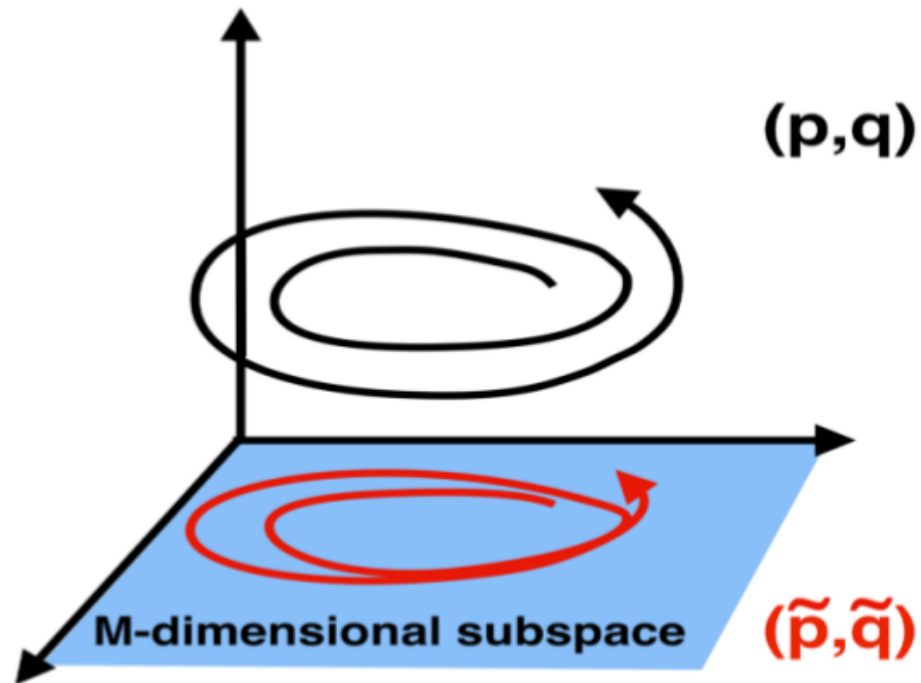
- 1) Ceotto, M.; Atahan, S.; Shim, S.; Tantardini, G. F.; Aspuru-Guzik, A., *Phys. Chem. Chem. Phys.* 2009, 11, 3861–3867.
- 2) Ceotto, M.; Atahan, S.; Tantardini, G. F.; Aspuru-Guzik, A., *J. Chem. Phys.*, 2009, 130, 234113.
- 3) Ceotto M., Tantardini G.F., Aspuru-Guzik A., *J. Chem. Phys.* 135 (21), 214108 (2011)
- 4) Gabas F., Conte R., and Ceotto M., *JCTC*, 2378-2388 (2017)

Semiclassical Methods: the Divide-and-Conquer idea



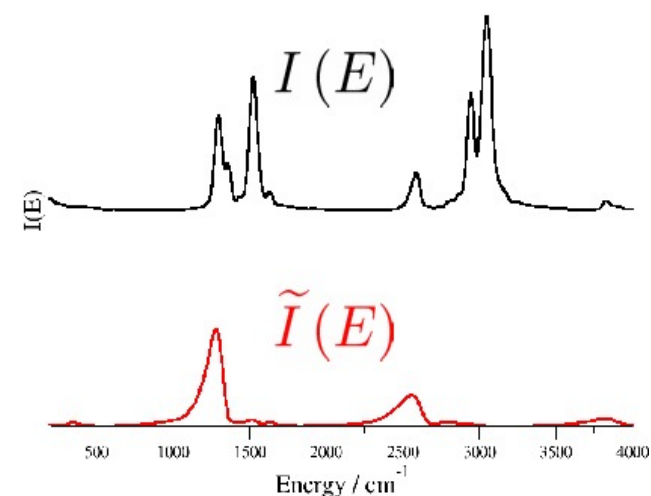
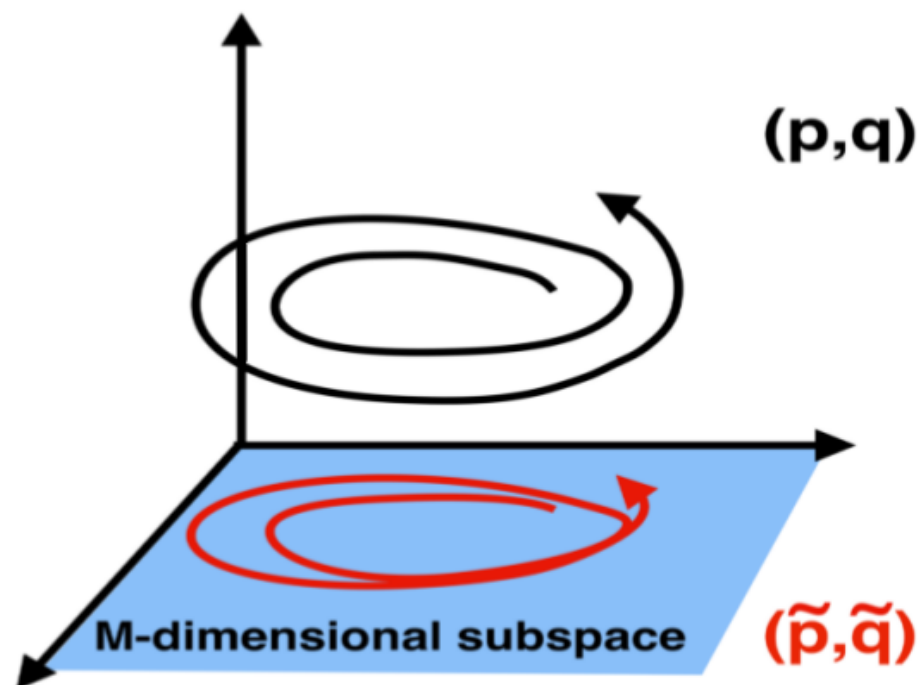
- 5) M. Ceotto, G. Di Liberto, R. Conte, *Physical Review Letters* 119, 010401 (2017)
- 6) Di Liberto, G., Conte, R., Ceotto, M. *The Journal of Chemical Physics*, 148(1), 014307. (2018)

Semiclassical Methods: the Divide-and-Conquer idea



- 5) M. Ceotto, G. Di Liberto, R. Conte, *Physical Review Letters* 119, 010401 (2017)
- 6) Di Liberto, G., Conte, R., Ceotto, M. *The Journal of Chemical Physics*, 148(1), 014307. (2018)

Semiclassical Methods: the Divide-and-Conquer idea



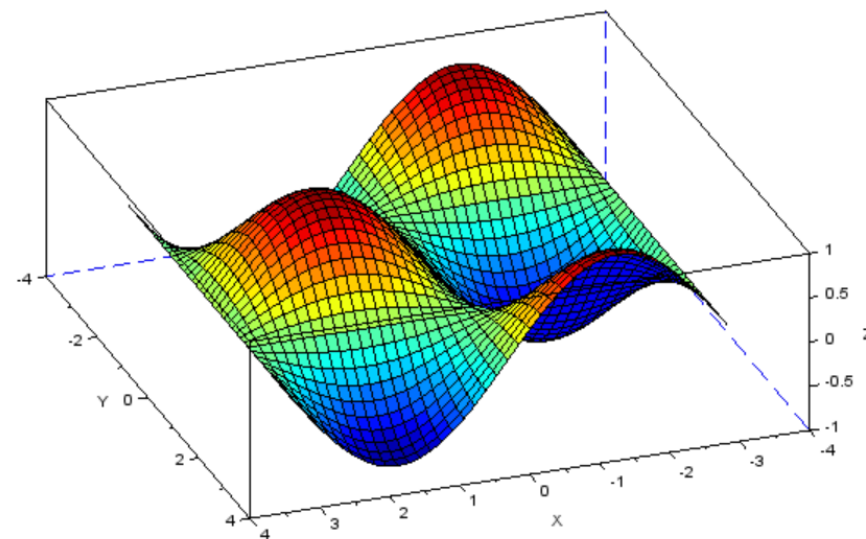
DC-SCIVR

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

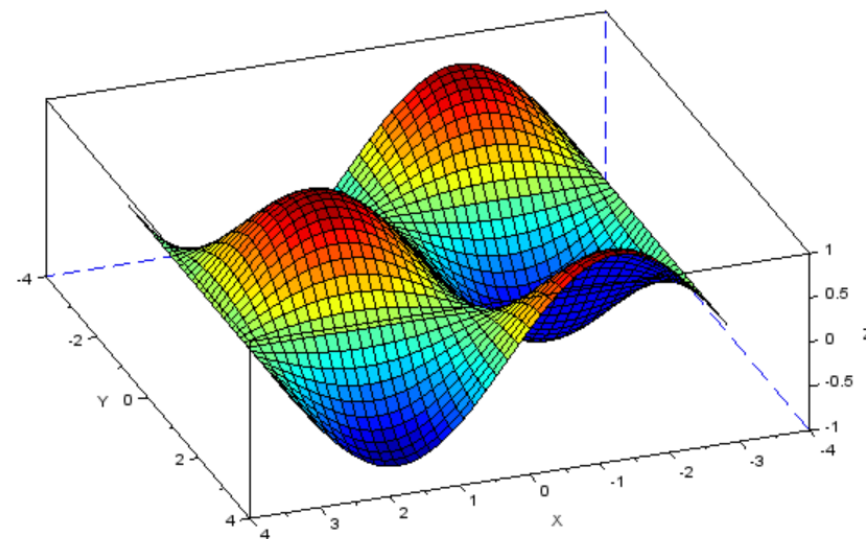
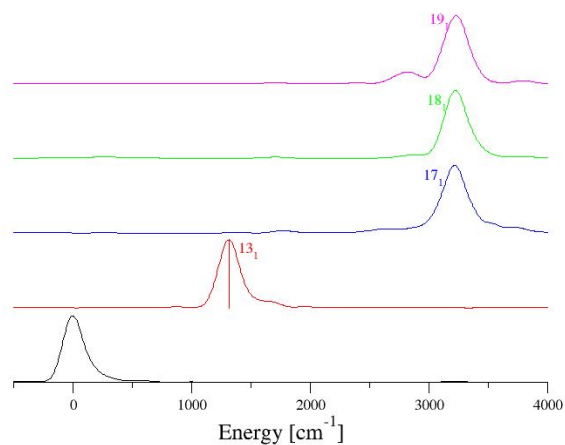
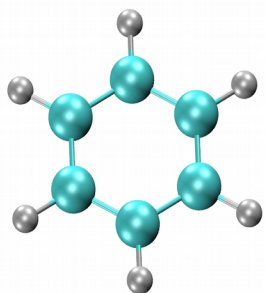
The semiclassical partial spectra are obtained from subspace projected quantities,
while the classical dynamics is **full dimensional**

5) M. Ceotto, G. Di Liberto, R. Conte, *Physical Review Letters* 119, 010401 (2017)

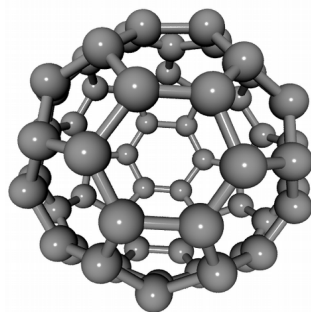
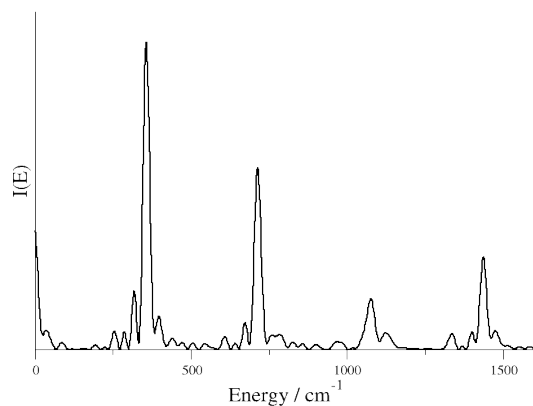
6) Di Liberto, G., Conte, R., Ceotto, M. *The Journal of Chemical Physics*, 148(1), 014307. (2018)



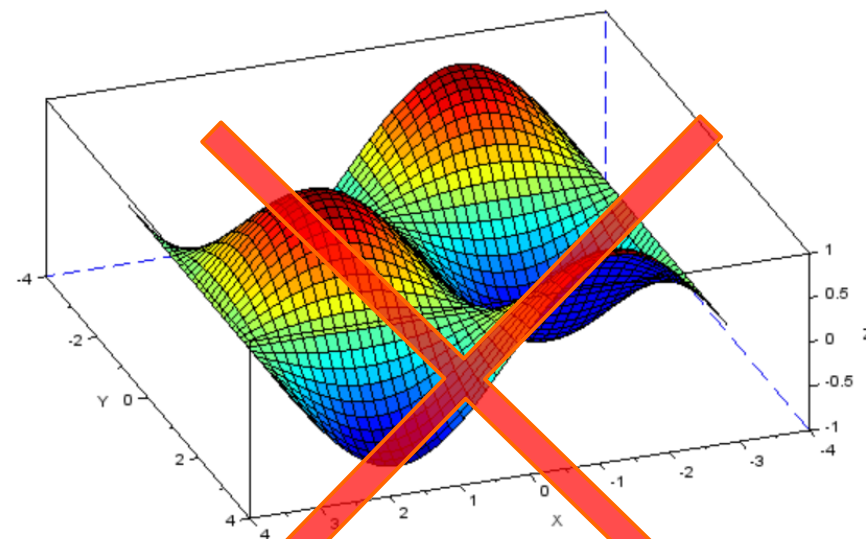
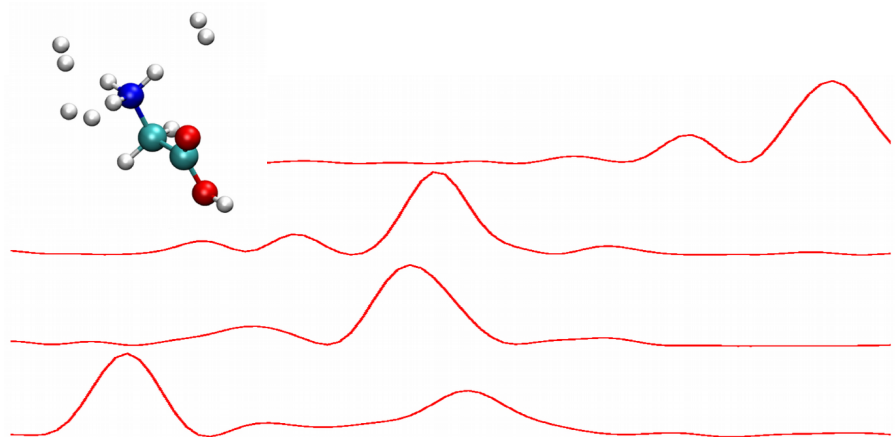
Potential Energy Surface



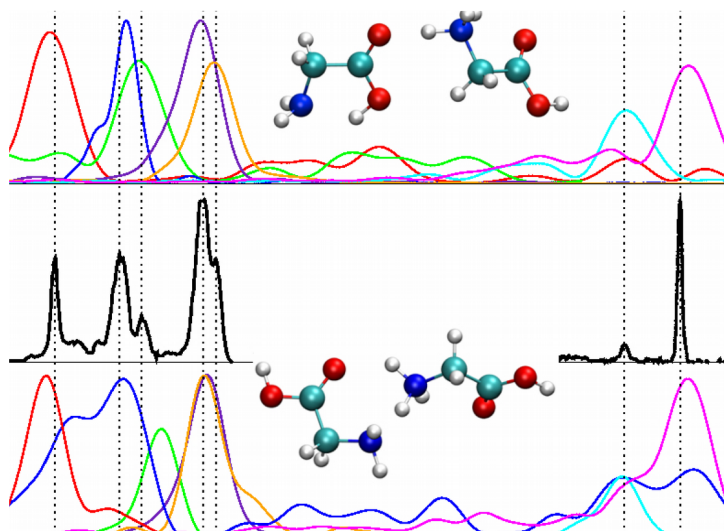
Potential Energy Surface



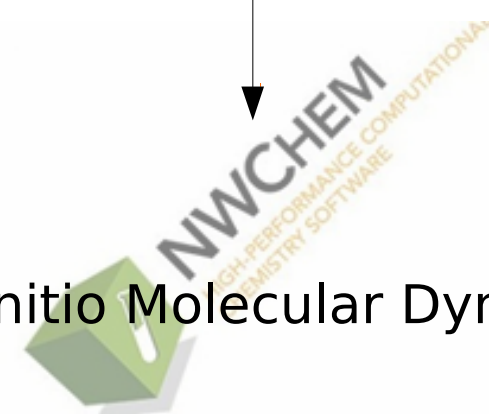
- 5) M. Ceotto, G. Di Liberto, R. Conte, *Physical Review Letters* **119**, 010401 (2017)
6) Di Liberto, G., Conte, R., Ceotto, M. *The Journal of Chemical Physics*, 148(1), 014307. (2018)

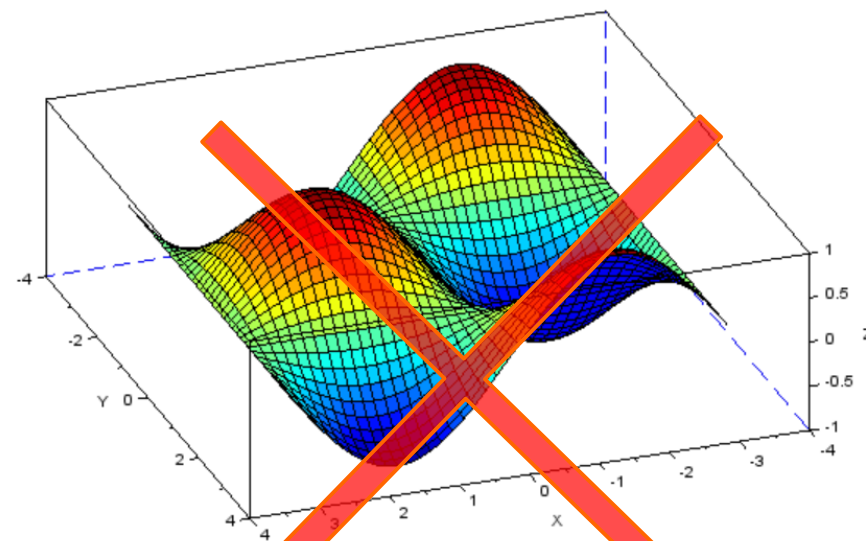
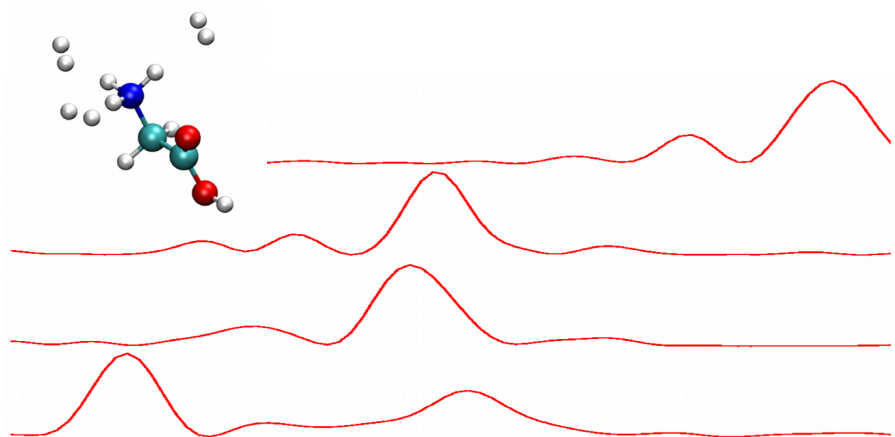


Potential Energy Surface

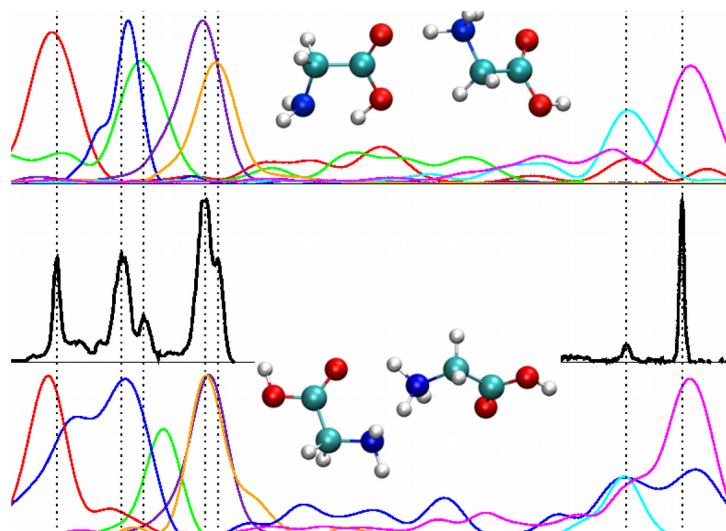


Ab-initio Molecular Dynamics





Potential Energy Surface



Molecular mechanics
Force Fields

AIMD vs Force Field



Ab-initio Molecular Dynamics

Computationally demanding

Accurate electronic potential
energy calculations



Molecular Mechanics / Force Field

Computationally cheap

AIMD vs Force Field



Ab-initio Molecular Dynamics

Computationally demanding

Accurate electronic potential
energy calculations

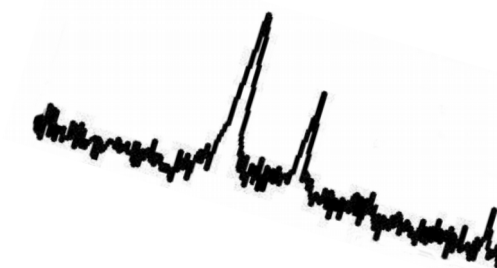
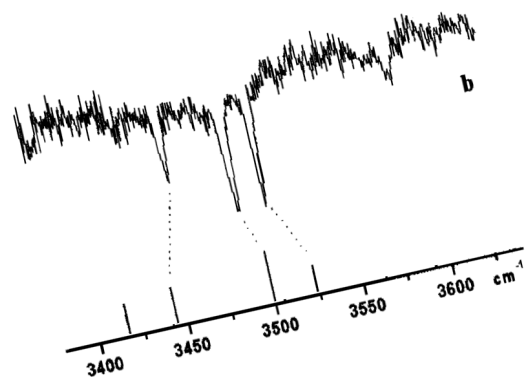


Molecular Mechanics / Force Field

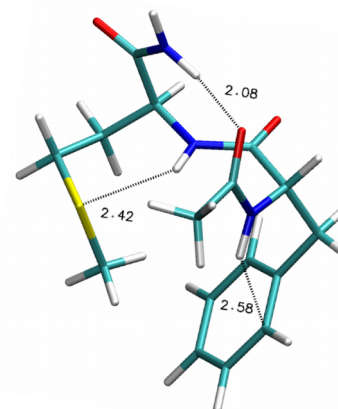
Computationally cheap

**How accurate is it
in the semiclassical
framework?**

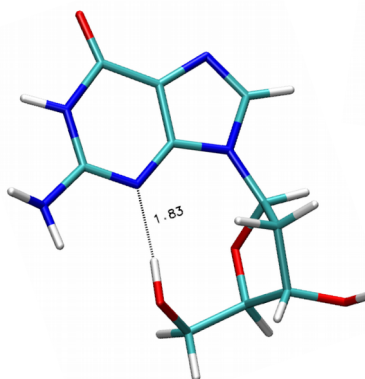
AIMD vs Force Field



Ac-Phe-Met-NH₂



Deoxyguanosine



Molecular Mechanics / Force Field



Ab-initio Molecular Dynamics

Computationally demanding

Accurate electronic potential energy calculations

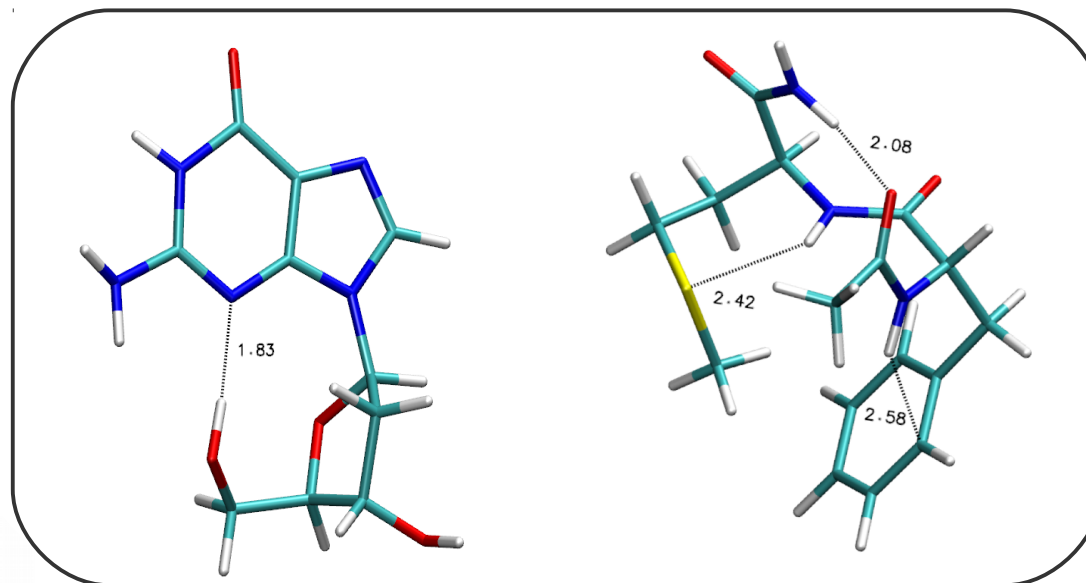
Computationally cheap

How accurate is it in the semiclassical framework?

8) Choi, M. Y., & Miller, R. E. (2006), *Journal of the American Chemical Society*, 128(22), 7320-7328.

9) Biswal, H. S., Gloaguen, E., Loquais, Y., Tardivel, B., & Mons, M. (2012). *JPLCL*, 3(6), 755-759.

Computational details



Ab-initio Molecular Dynamics

DFT B3LYP/ 6-31g*

t = **25000** a.u. (**0.6** ps)

dt = **10** a.u (**0.24** fs)

- **DC-SCIVR**



Molecular Mechanics / Force Field

Amber94 FF

t = **1** ps

dt = **0.2** fs

- **DC-SCIVR**
- **Harmonic calculation**

Results: Geometry Optimization



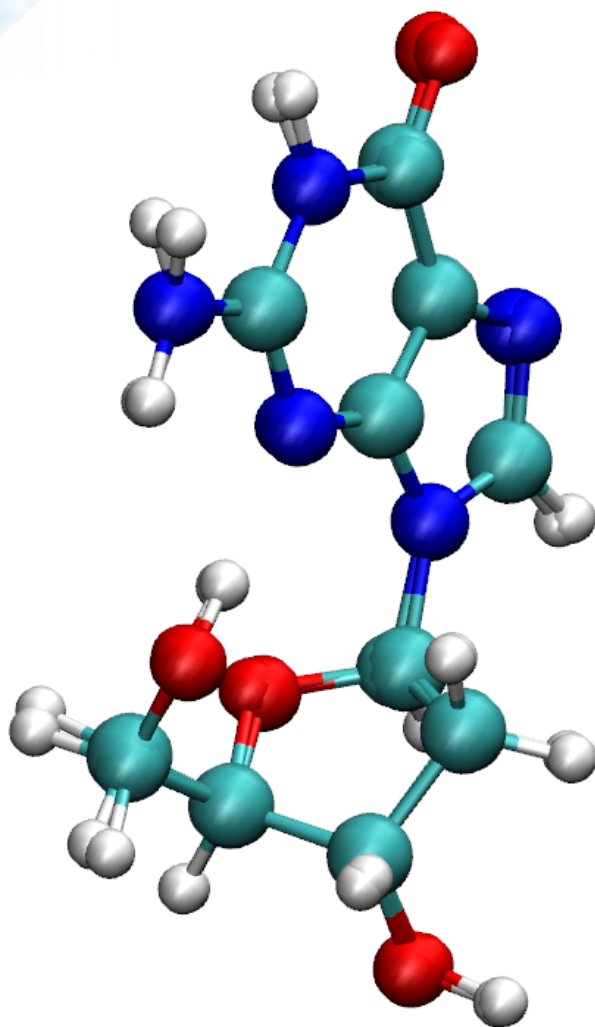
Deoxyguanosine

Ac-Phe-Met-NH₂



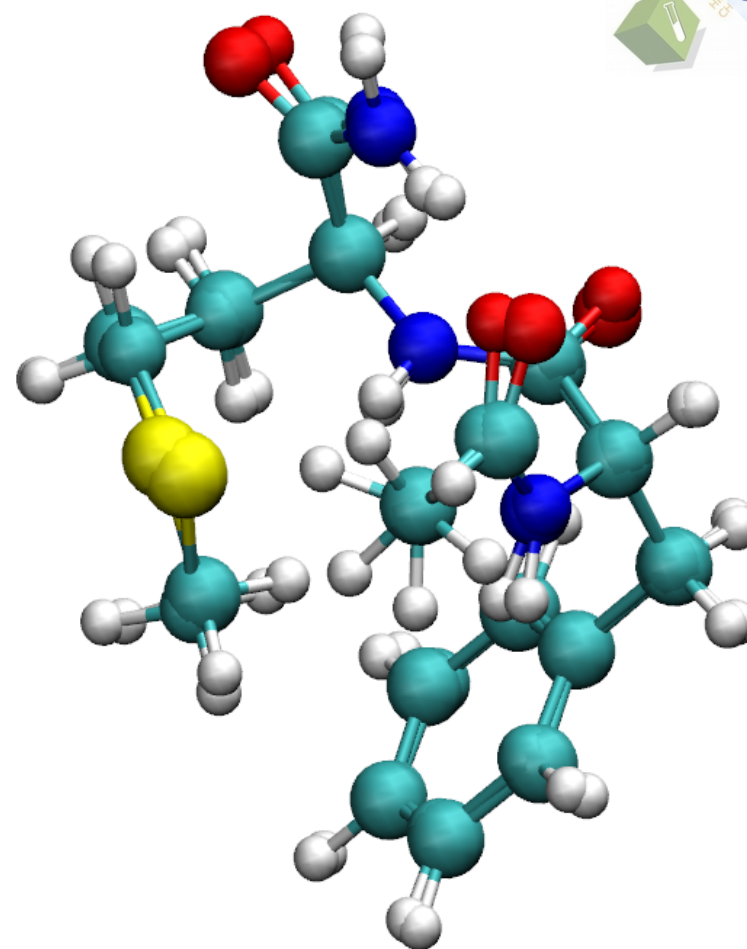
Results: Geometry Optimization

Deoxyguanosine



RMSD = 0.147 Å

Ac-Phe-Met-NH₂



RMSD = 0.318 Å



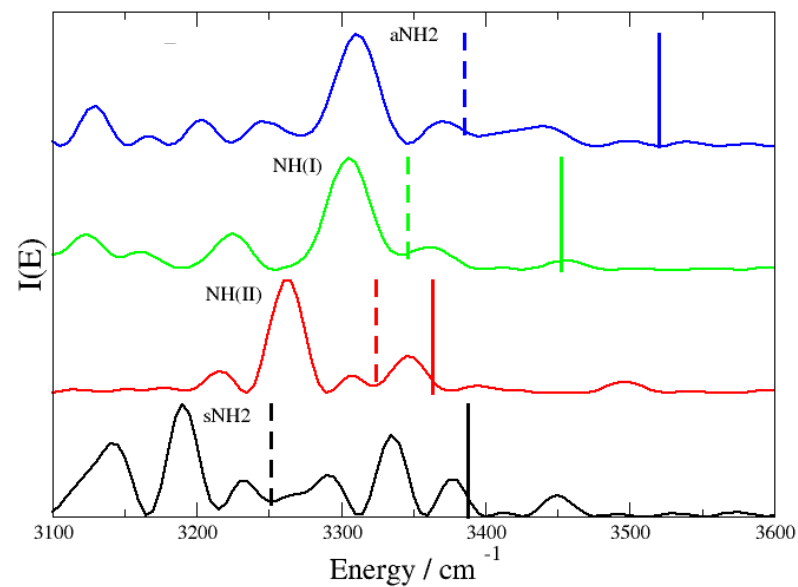
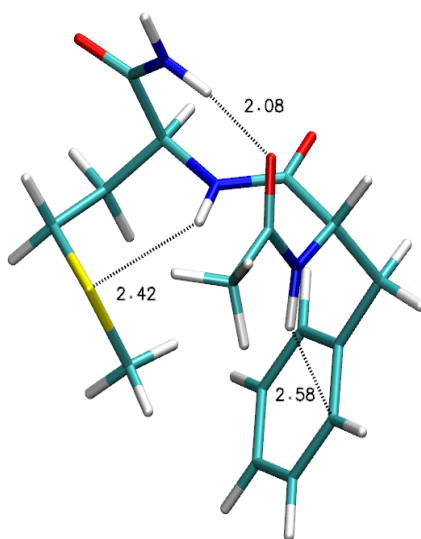
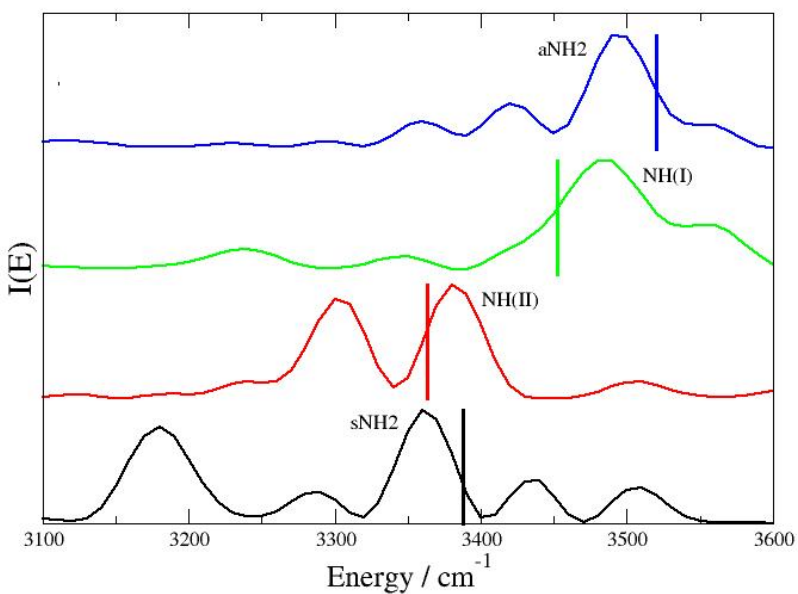
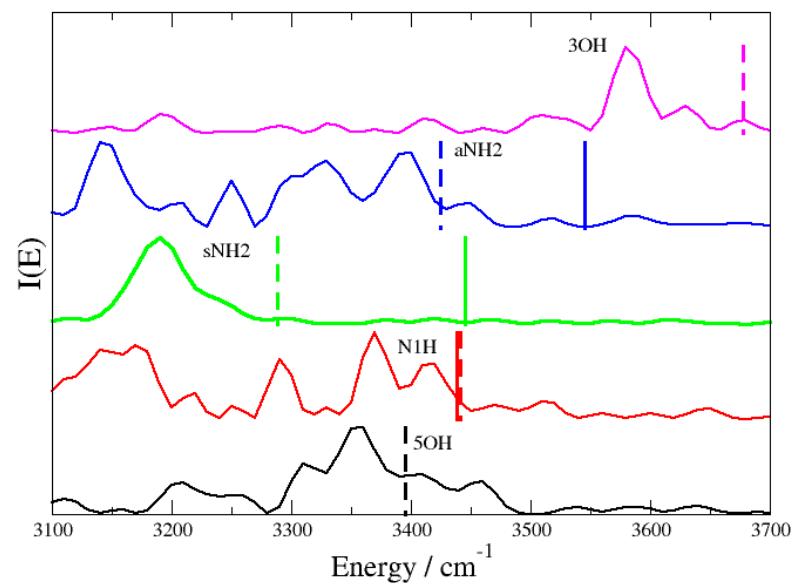
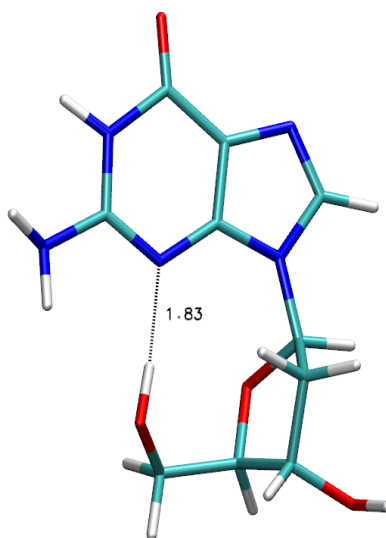
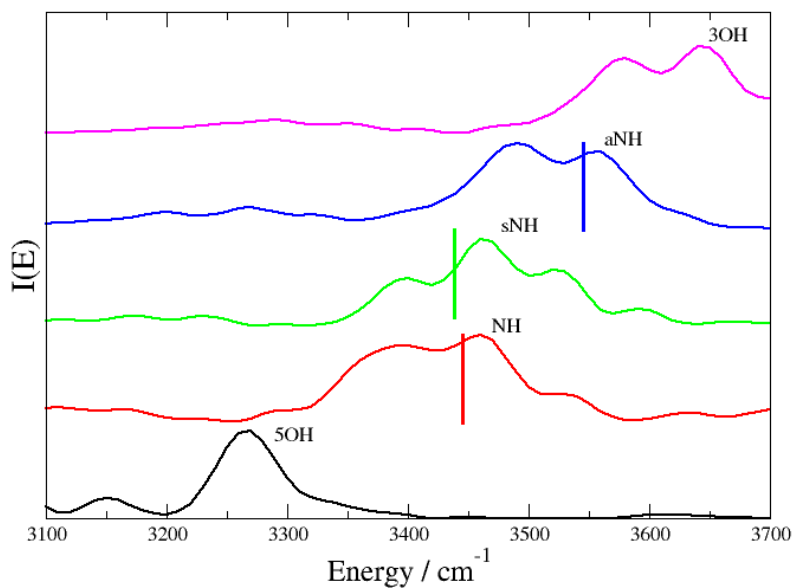
Results: Spectra



Experiment



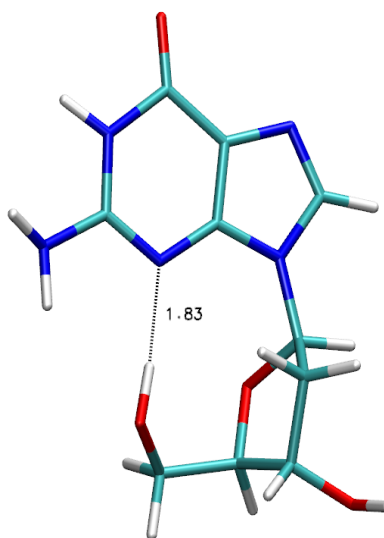
Harmonic



Results: Frequencies

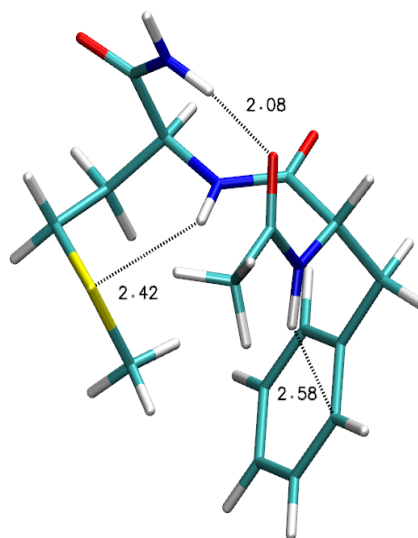


mode	Exp	DC-SCIVR
3OH		3640
aNH ₂	3545	3560
NH	3438	3460
sNH ₂	3445	3460
5OH		3270
	MAE	17



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

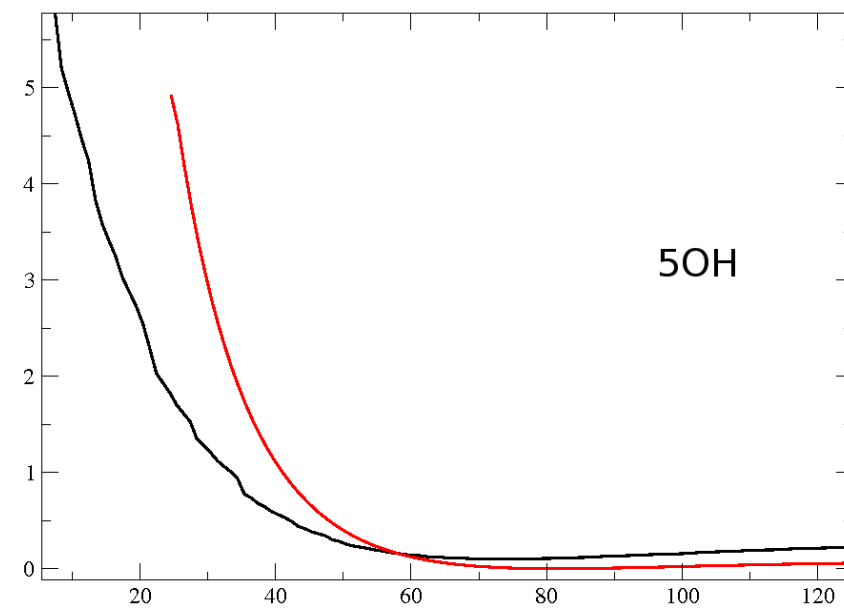
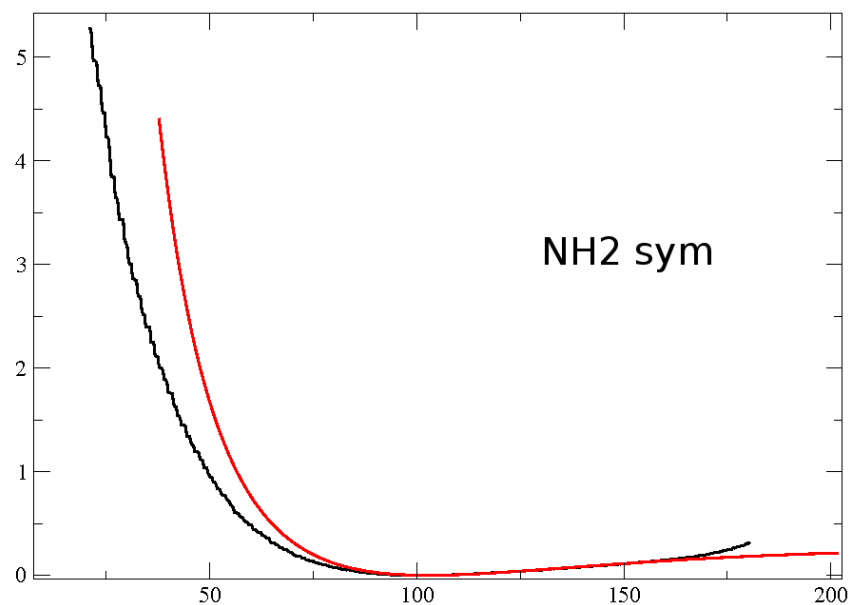
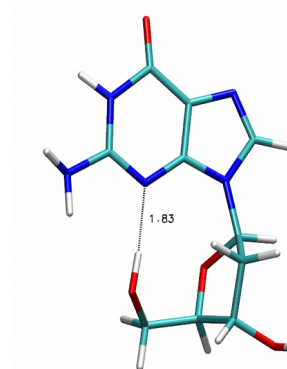
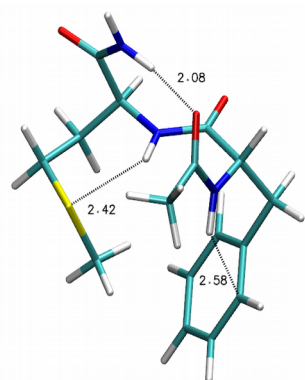
mode	Exp	DC-SCIVR
aNH2	3520	3490
NH(I)	3452	3480
NH(II)	3363	3380
sNH2	3388	3360
	MAE	26



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

PES Considerations

DFT ————
FORCE FIELD ————



Amber94 PES presents **broader** wells

Conclusions



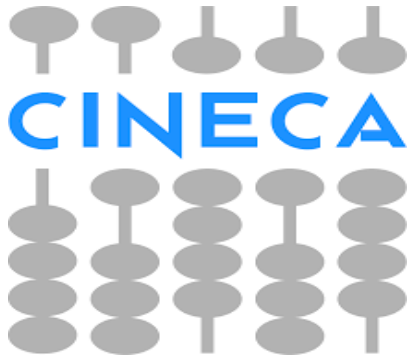
- Semiclassical ab-initio results are in agreement with the experiment with the typical accuracy of the method (20-30 cm⁻¹)
- Amber94 is able to accurately predict minimum geometries
- The best Amber94 results come from harmonic analysis, while the worst set derives from the semiclassical approach
- Amber seems to perform well only in describing free, uncoupled motion, like for example some simple NH stretchings

Future Developments

- Amber94 semiclassical analysis in condensed phase systems
 - Other more accurate Force Fields

Acknowledgments

Computational Support

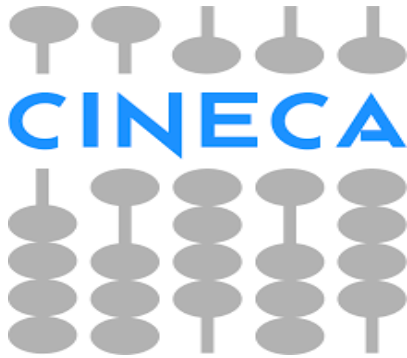


Funding



Acknowledgments

Computational Support



Funding



Thank you for your kind attention