Using AS SCIVR to understand Proline vibrational spectrum

Giacomo Botti,Chiara D. Aieta, Michele Ceotto and Riccardo Conte

Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy

Abstract

Semiclassical dynamics is able to reproduce quantum effects from classical dynamics runs, allowing the vibrational study of very large dimensional systems.[1] Adiabatic switching has already proven capable of improving precision and accuracy of semiclassical results of challenging model potentials and small molecular systems.[2] I extended the technique to larger molecular systems, whose semiclassical spectrum is usually collected by means of a single run evolved with ab initio "on-the-fly" calculations. This application has been benchmarked on small molecules and then tested on glycine, improving the pre-existing SC calculations. Finally, this new approach has permitted a preliminary study of the vibrational spectrum of the 17-atom proline, a still open problem in theoretical and experimental chemistry.[3, 4]

Starting Point: MC SCIVR

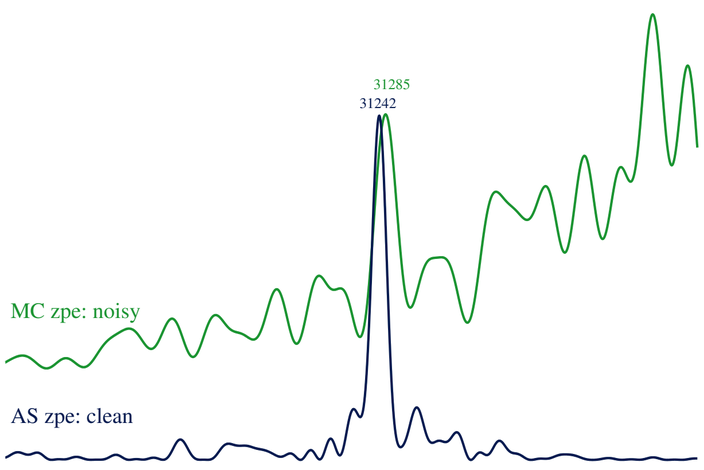
$$I_{\mathrm{qct}}(E) = \frac{1}{2T}\left|\int_0^T dt\, e^{iEt/\hbar} p(t)\right|^2 \tag{1}$$

$$I_{\mathrm{ta}}(E) = \left(\frac{1}{2\pi\hbar}\right)^{N_v} \iint d\mathbf{p}_0 d\mathbf{q}_0 \frac{1}{2\pi\hbar T}\left|\int_0^T dt e^{\frac{i}{\hbar}[S_t(\mathbf{p}_t,\mathbf{q}_t)+Et+\phi_t(\mathbf{p}_t,\mathbf{q}_t)]}\langle\psi|g_t(\mathbf{p}_t,\mathbf{q}_t)\rangle\right|^2 \tag{2}$$

$$I_{\mathrm{mc}}(E;\mathbf{p}_{\mathrm{mc}},\mathbf{q}_{\mathrm{mc}}) = \left(\frac{1}{2\pi\hbar}\right)^{N_v} \frac{1}{2\pi\hbar T}\left|\int_0^T dt e^{\frac{i}{\hbar}[S_t(\mathbf{p}'_t,\mathbf{q}'_t)+Et+\phi_t(\mathbf{p}'_t,\mathbf{q}'_t)]}\langle\psi(\mathbf{p}_{eq},\mathbf{q}_{eq})|g_t(\mathbf{p}'_t,\mathbf{q}'_t)\rangle\right|^2 \tag{3}$$

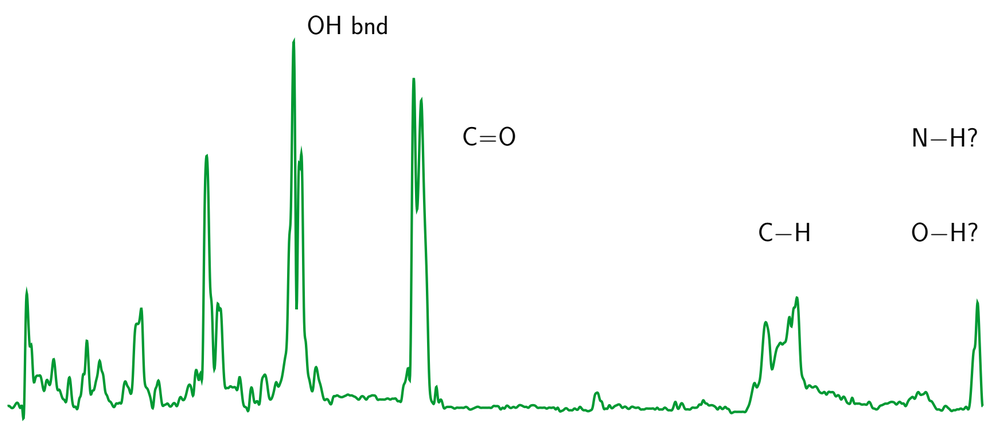
The need for AS SCIVR

AS trajectory collects more signal than the **MC** one

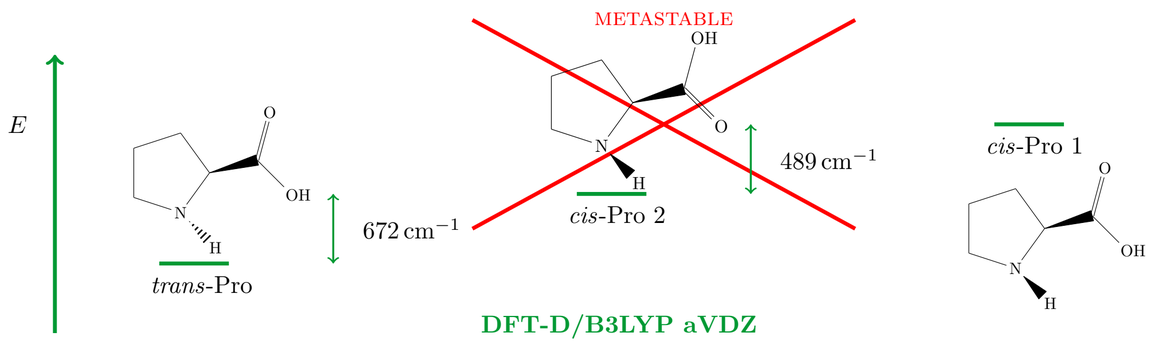


Proline: the experiment

The experimental spectrum of Proline from [5]: **still an open problem**



Proline has a lot of similar conformers: **which ones are in the spectrum?**



The novelty: otf AS SCIVR

AS dynamics

- Velocity Verlet integrator
- Harmonic potential in normal modes
- *ab initio* energy and gradient at each step
- the smoother, the better

$$H_{\mathrm{as}} = [1-\lambda(t)]\, H_{\mathrm{harm}} + \lambda(t) H_{\mathrm{anh}} \tag{4}$$

$$\dot{\mathbf{p}} = (\lambda-1)\mathbf{g}_{\mathrm{harm}} - \lambda\mathbb{C}^T\mathbf{g}_{ai} \tag{5}$$

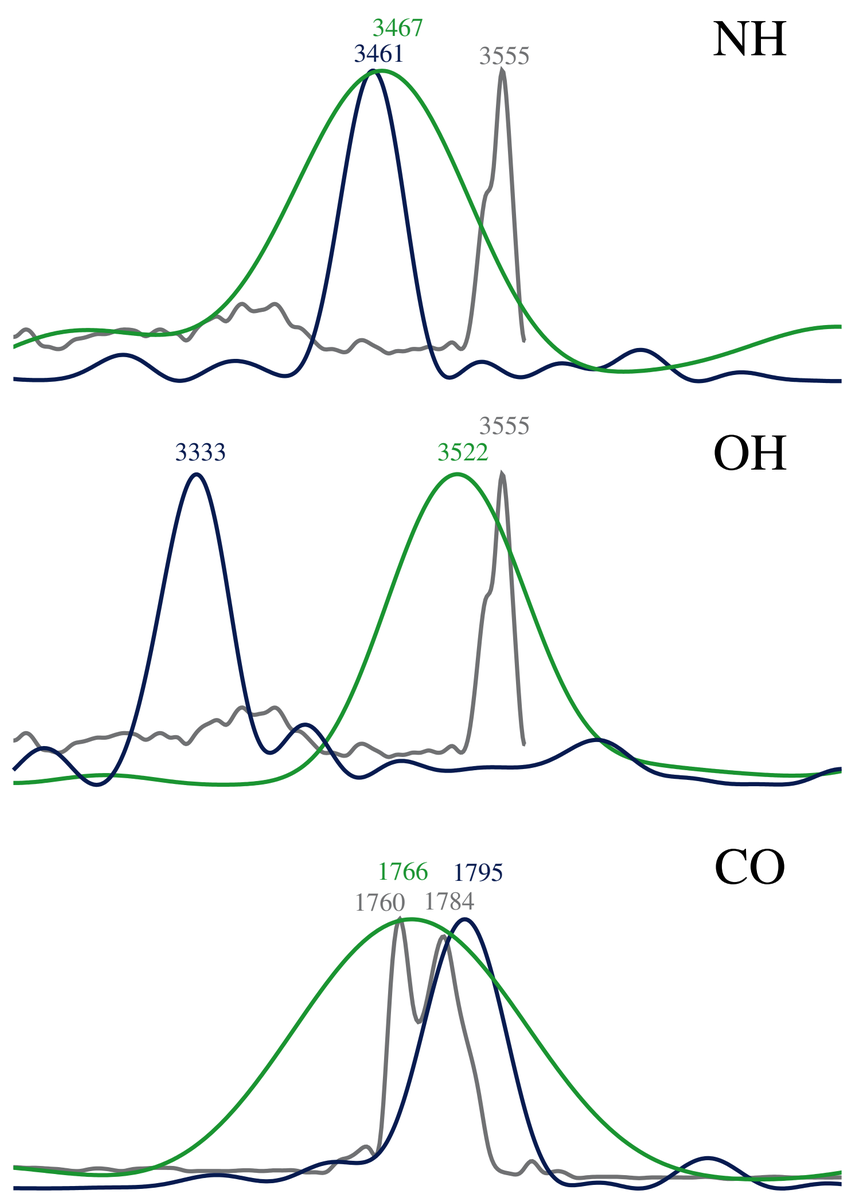
$$\lambda(t) = \frac{t}{T_{\mathrm{AS}}} - \frac{1}{2\pi}\sin\left(\frac{2\pi t}{T_{\mathrm{AS}}}\right) \tag{6}$$

*The new trajectory, starting from "**switching conditions**" $(\mathbf{p}_{as},\mathbf{q}_{as})$ is more stable and descriptive, allowing a better sampling of the phase space:*

$$I_{\mathrm{as-ta}}(E;\mathbf{p}_{as},\mathbf{q}_{as}) = \left(\frac{1}{2\pi\hbar}\right)^{N_v} \frac{1}{2\pi\hbar T}\left|\int_0^T dt e^{\frac{i}{\hbar}[S_t(\mathbf{p}'_t,\mathbf{q}'_t)+Et+\phi_t(\mathbf{p}'_t,\mathbf{q}'_t)]}\langle\psi(\mathbf{p}_{eq},\mathbf{q}_{eq})|g_t(\mathbf{p}'_t,\mathbf{q}'_t)\rangle\right|^2 \tag{7}$$

The spectra

trans-Pro and **cis-Pro** are in the **experimental** spectrum



Acknowledgements

The authors acknowledge financial support from the European Research Council [Grant Agreement No. (647107)—SEMICOMPLEX—ERC-2014-CoG] under the European Union's Horizon 2020 research and innovation program, and from the Italian Ministry of Education, University, and Research (MIUR) (FARE Program No. R16KN7XBRB-project QURE). G.B. thanks INPS for funding his Ph.D. scholarship.

References

(1) Conte, R.; Ceotto, M. *Quantum Chemistry and Dynamics of Excited States: Methods and Applications* **2020**, 595–628.
(2) Conte, R.; Parma, L.; Aieta, C.; Rognoni, A.; Ceotto, M. *J. Chem. Phys.* **2019**, *151*, 214107.
(3) Botti, G.; Ceotto, M.; Conte, R. *J. Chem. Phys.* **2021**, *155*, 234102.
(4) Botti, G.; Aieta, C.; Conte, R. *J. Chem. Phys.* **2022**, *156*, 164303.
(5) Stepanian, S. G.; Reva, I. D.; Radchenko, E. D.; Adamowicz, L. *J. Phys. Chem. A* **2001**, *105*, 10664–10672.

CEOTTO GROUP