Using AS SCIVR to understand Proline vibrational spectrum

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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]

Starting Point: MC SCIVR

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

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

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

The novelty: otf AS SCIVR

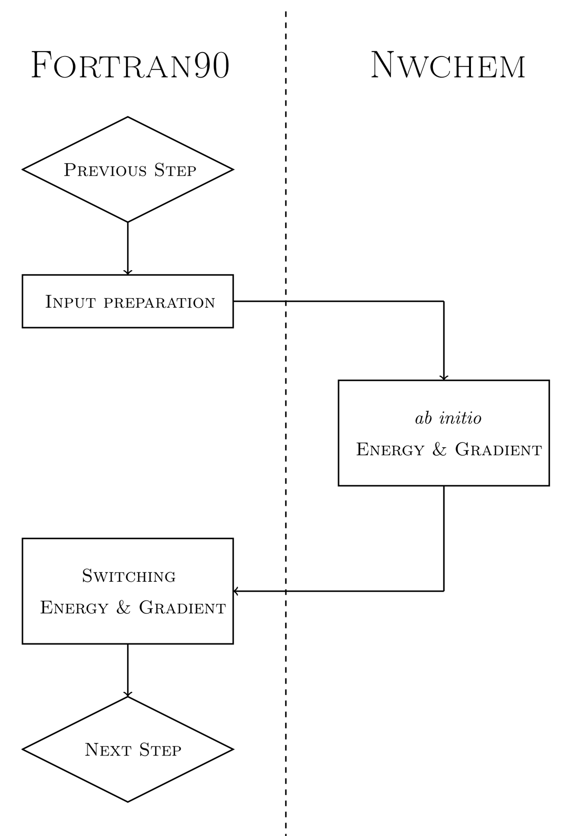


Fig. 1: Flux diagram of a single step of the Adiabatic Switching method

AS dynamics

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

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

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

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

*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:*

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

Proline: the experiment

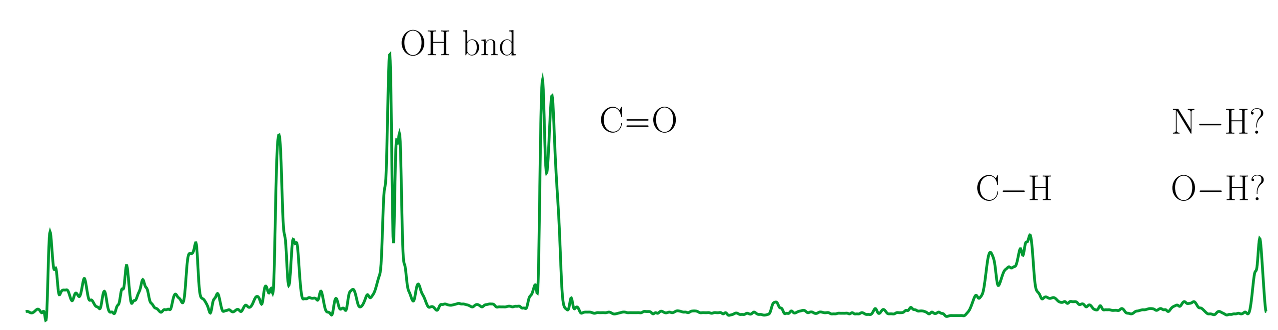


Fig. 2: The experimental spectrum of Proline from [4]: **still an open problem**

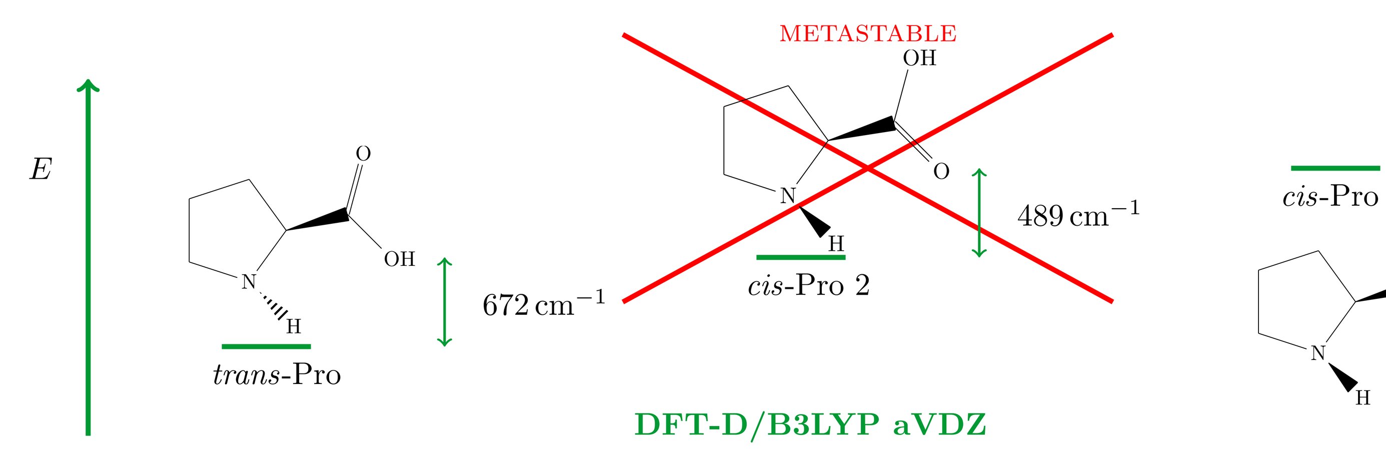
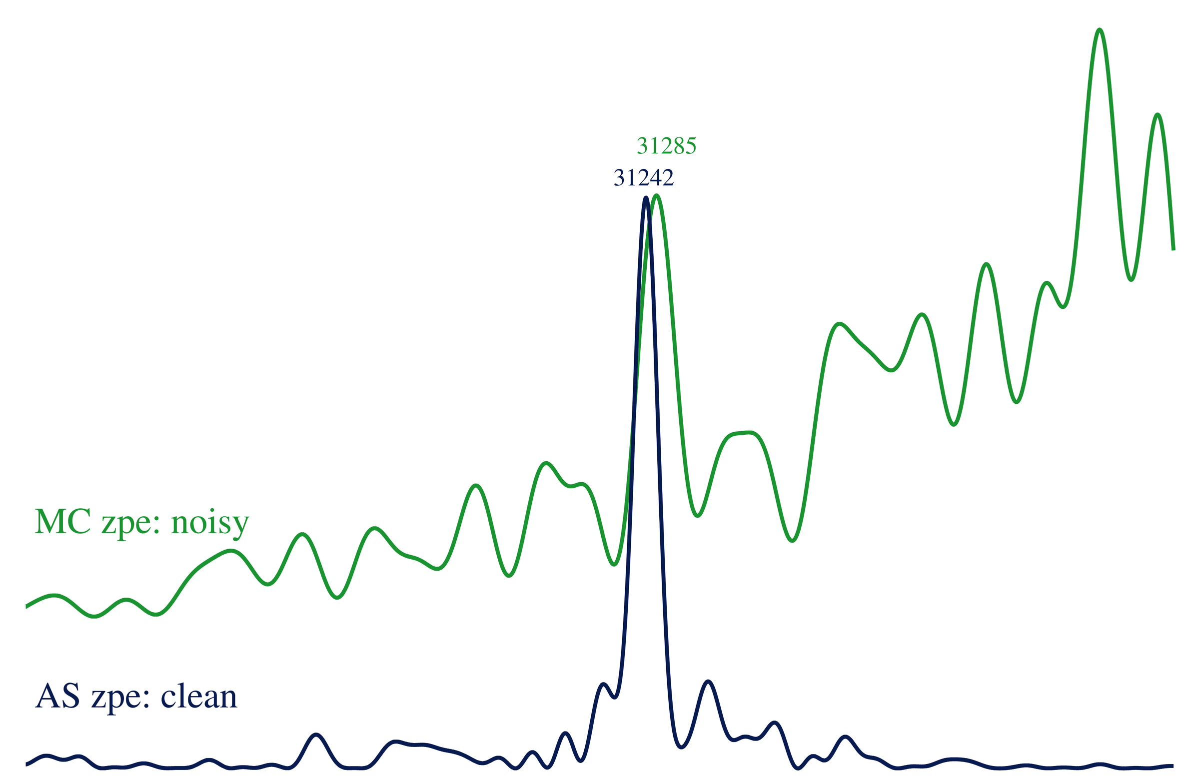


Fig. 3: Proline has a lot of similar conformers: **which ones are in the spectrum?**

The need for AS SCIVR

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



Acknowledgements

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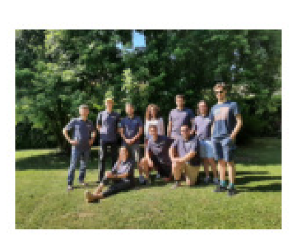

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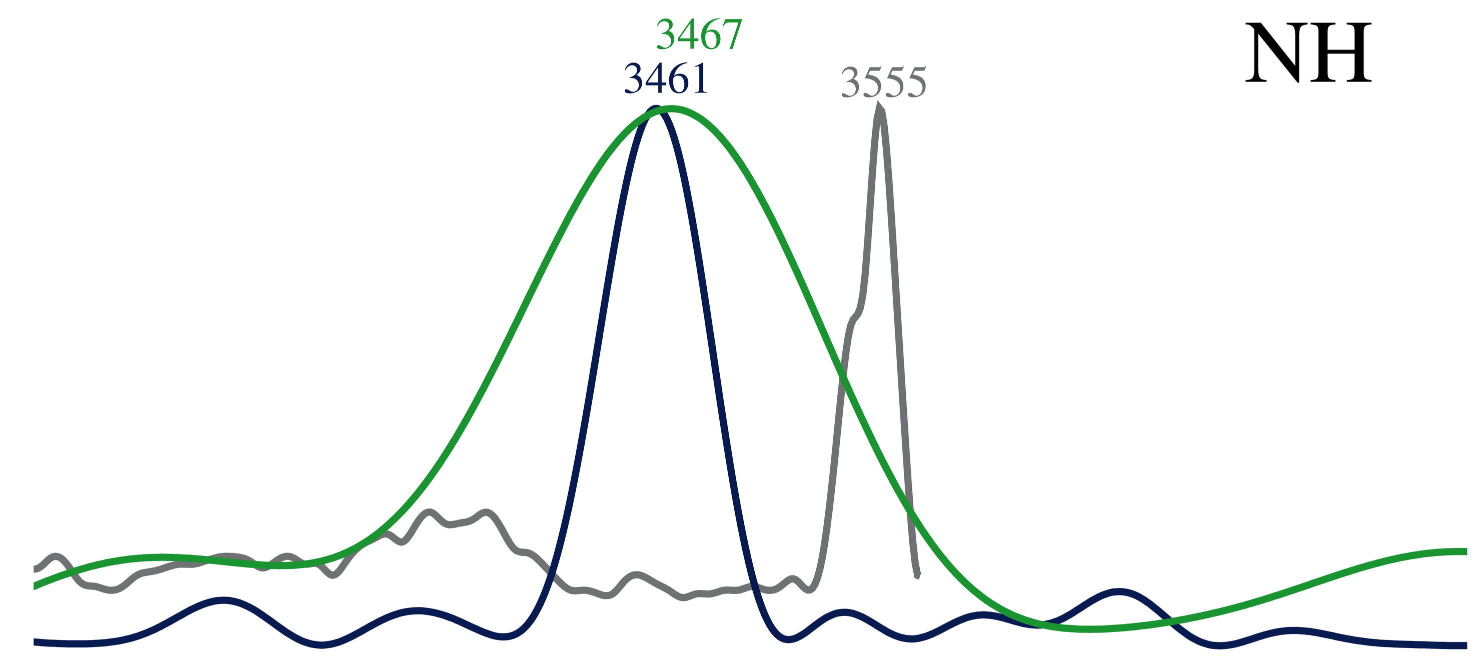
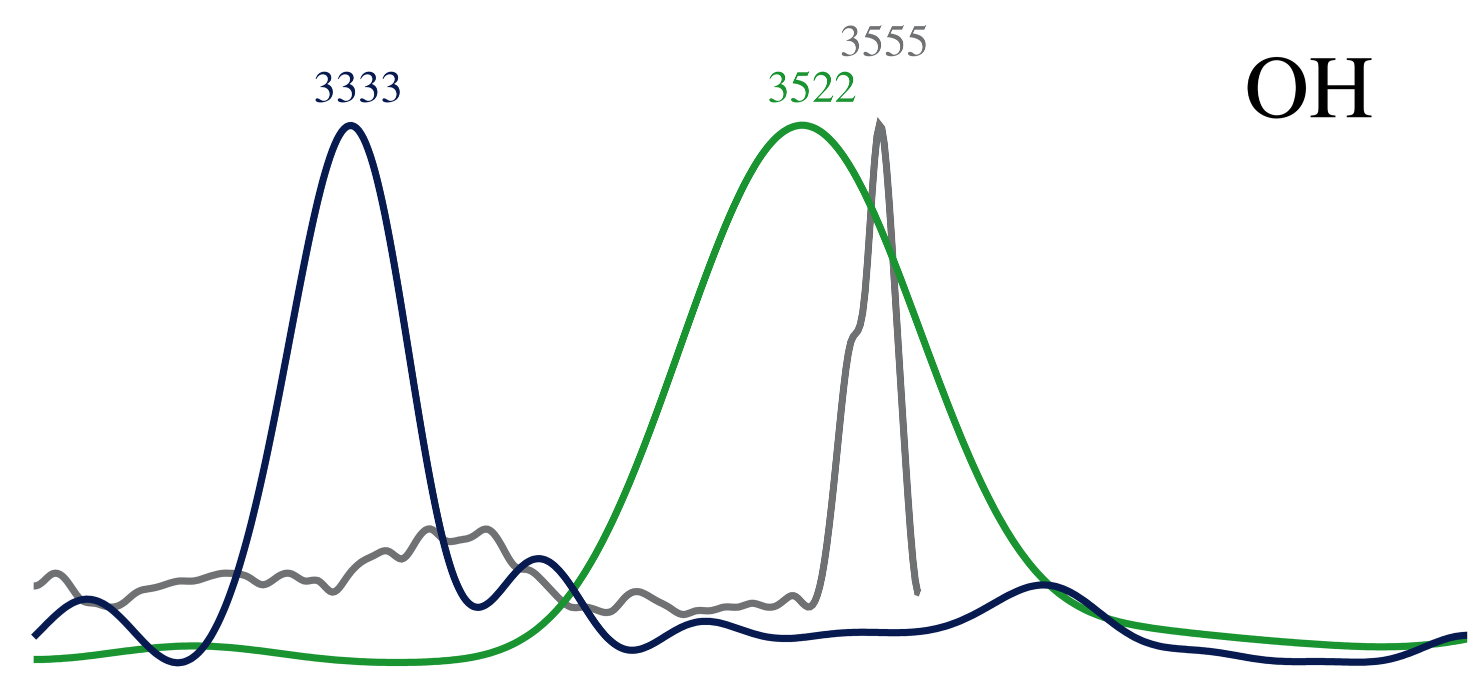
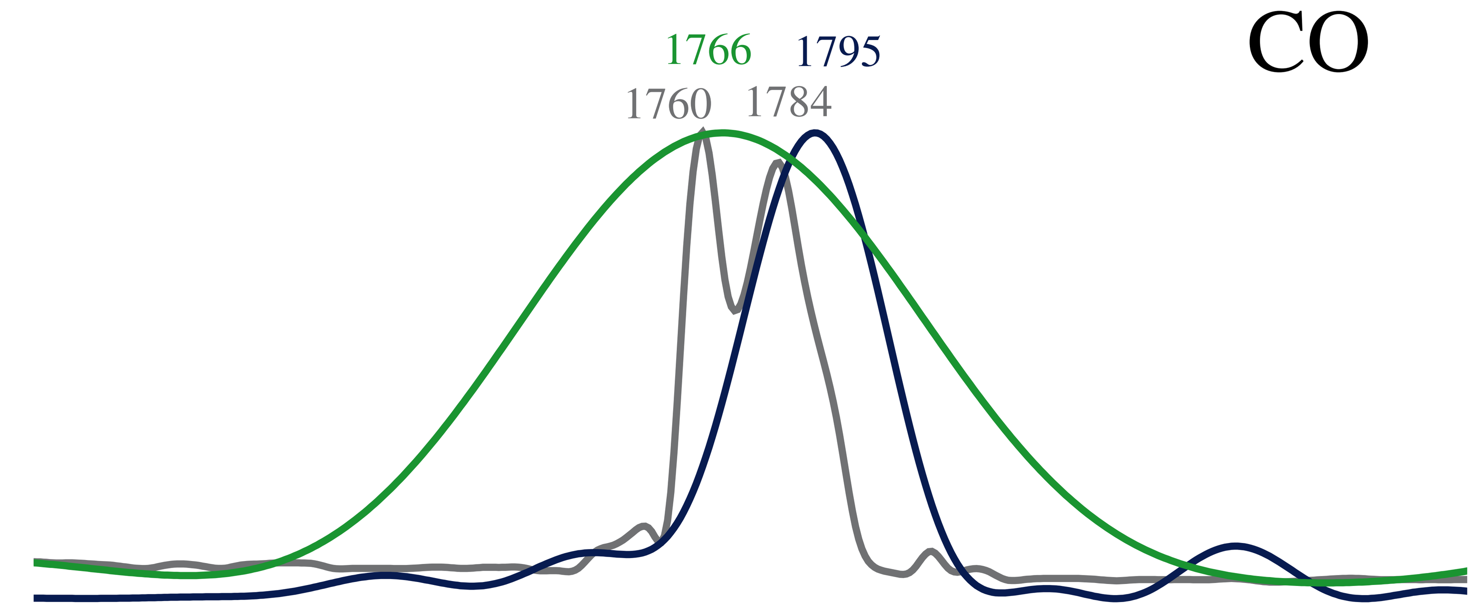
The spectra

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







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