

Controlling molecular reactivity with atto and few femtoseconds pulses

The availability of short atto and few fs XUV, UV and NIR pulses[1,2] has shed new insights on the dynamics of ultrafast structural molecular rearrangements. Because of their inherent width in energy, ultrashort laser pulses access a coherent set of excited electronic states of molecules, thereby entangling inherently the electronic and nuclear motions.

In the very well-known Born Oppenheimer approximation the force on the nuclei is local. But the Born Oppenheimer approximation fails critically when several electronic states are near in their energies. We demonstrate that even in the presence of strong non-adiabatic coupling the exact force remains local on a grid. We show that the total force exerted by the vibronic wave packet on the nuclei at every molecular geometry is made of two terms: A potential gradient term, $\mathbf{F}_V$, driven by the local population in each electronic state and a non-classical, non-adiabatic term, $\mathbf{F}_{NAC}$, driven by the local electronic coherences.[3-5] In the case of ultrafast non adiabatic dynamics in the three lowest states of the methane cation, we show that it is the local NAC term of the force on the non adiabatic seams that drives the structural rearrangement.[3-4] We further show that the control on the force by electronic coherence is robust in an ensemble of molecules initially randomly oriented with respect to the pulse polarization.[5,6] As a final example of tuning vibronic dynamics with the short pulse parameters, we will discuss preliminary results that show that it is possible to imprint the chirality of a short femto second pulse on the multi electronic state vibronic density after the pulse is over for a vibrating diatomic molecule.[7]

References

- [1] M. Nisoli *et al.*, Chem. Rev. **117**, 10760 (2017).
- [2] O. Alexander *et al.*, Appl. Phys. Lett. **126**, 170501 (2025).
- [3] G. Pandey, M. Cardosa-Gutierrez, R. D. Levine, and F. Remacle, Ultrafast Science, **6**, 0167(2026).
- [4] M. Cardosa-Gutierrez, R. D. Levine, and F. Remacle, J. Phys. B At. Mol. Opt. Phys. **57**, 133501 (2024).
- [5] M. Cardosa-Gutierrez, G. Pandey, R. D. Levine, and F. Remacle, J. Phys. Chem. Lett., 7642 (2025).
- [6] M. Cardosa-Gutierrez, R. D. Levine, and F. Remacle, J. Phys. Chem. A **128**, 2937 (2024).
- [7] A. Smeers, S. Ghose, R.D. Levine, F. Remacle, submitted (2026).

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