

# Attosecond electronic and nuclear quantum photodynamics of the ozone molecule: Probing the time-dependent electron density

A. Perveaux<sup>1,2</sup>, D. Lauvergnat<sup>1</sup>, F. Gatti<sup>2</sup>, G. J. Halász<sup>3</sup>,  
Á. Vibók<sup>4\*</sup>, B. Lasorne<sup>2</sup>

<sup>1</sup>Laboratoire de Chimie Physique, Batiment 349, CNRS, UMR8000, Orsay, F-91405; Univ. Paris-Sud, Orsay, F-91405; France

<sup>2</sup>CTMM, Institut Charles Gerhardt Montpellier, Université Montpellier 2, F-34095 Montpellier, France

<sup>3</sup>Department of Information Technology, University of Debrecen, H-4010 Debrecen, PO Box 12, Hungary

<sup>4</sup>Department of Theoretical Physics, University of Debrecen, H-40410 Debrecen, PO Box 5, Hungary

\*e-mail: vibok@phys.unideb.hu

## Abstract

The coupled electron-nuclear dynamics of ozone is investigated on the attosecond time scale. The time-dependent Dyson orbitals, dipole, and photoelectron spectrum were calculated to characterise the coherent time evolution of the electronic wavepacket.

Recently, we proposed a nonadiabatic scheme for the description of the coupled electronic and nuclear motion in ozone [1, 2]. An initial coherent nonstationary state was prepared as a superposition of the ground and the Hartley B states. In this situation neither the electrons nor the nuclei are in stationary state. The multiconfiguration time-dependent Hartree (MCTDH) method [3, 4] was used to solve the coupled nuclear quantum dynamics in the framework of the adiabatic separation of the time-dependent (TD) Schrödinger equation. The resulting electronic wavepacket shows an oscillation between the two chemical bonds. In addition, a revival of the electronic coherence occurs after the pump pulse is off, which induces a second transfer of population between both states. To characterise the oscillation of the electron density we calculated the TD Dyson orbitals, molecular dipole [5, 6], and photoelectron spectrum [7, 8]. We limited our description of the electronic motion to the Franck-Condon (FC) region only because the nuclear wavepackets in both states stay localized around this point during the first 5–6 fs. The details and the analysis of the quantum dynamics calculations were discussed in our previous works [1, 2].

The objective of the present work is to show realistic measurable quantities that will characterise the coherent evolution of the electronic wavepacket. We start with the TD dipole (see Fig. 1), as an observable that can be measured experimentally [5].

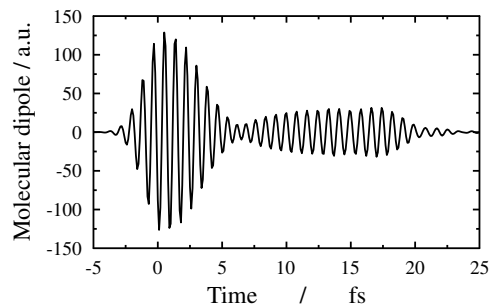


Figure 1: Time-dependent molecular dipole along the y-axis.

The oscillatory time evolution of this dipole directly reflects the electronic coherence in the system. The first time period of this picture denotes the excitation by the pump and the second part reflects the revival of the coherence after the pump is off. As discussed in our previous work [2] this is due to some trapping of the wavepacket in the B state. The oscillation of the dipole corresponds to a transfer of electron between the chemical bonds. This can be further characterized by TD Dyson orbitals that represent the exciton migration [6] (see Fig. 2).

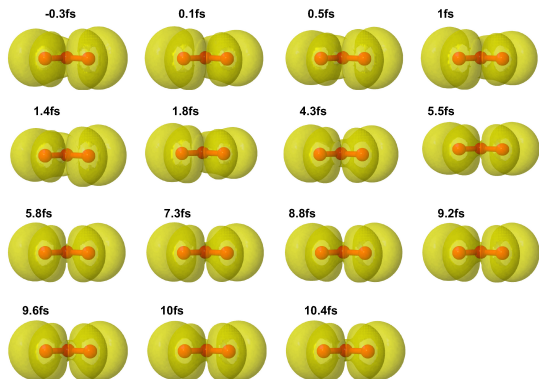


Figure 2: Time-dependent densities of the Dyson orbitals belonging to  ${}^2B_2$  cation channel.

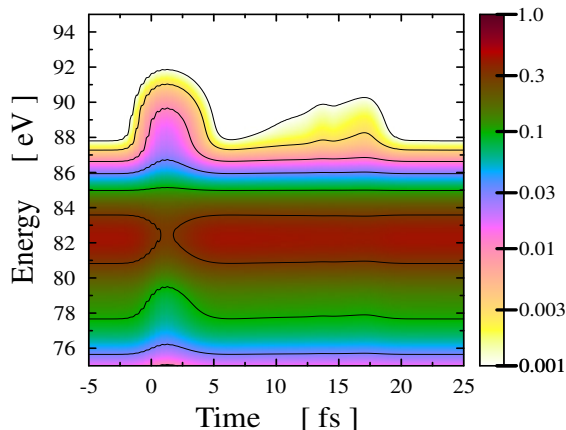


Figure 3: Approximate photoelectron spectrum as a function of the time delay and kinetic energy release.

Although these orbitals are not directly observable, they are key to compute the photoelectron spectrum that can be measured experimentally (see Fig. 3) as a function of the time delay between the probe and the pump.

A revival of coherence can be observed directly if the dipole can be monitored experimentally. It can also be observed indirectly in the time-resolved photoelectron spectrum through the revival of the B band.

## References

- [1] G. J. Halász, A. Perveaux, B. Lasorne, M. A. Robb, F. Gatti, and Á. Vibók, Phys. Rev. A. 86, 043426, (2012).
- [2] G. J. Halász, A. Perveaux, B. Lasorne, M. A. Robb, F. Gatti, and Á. Vibók, Phys. Rev. A. 88, 023425, (2013).
- [3] G. A. Worth, M. H. Beck, A. Jackle, and H.-D. Meyer. The MCTDH Package, see <http://mctdh.uni-hd.de>.
- [4] H.-D. Meyer, F. Gatti, and G. A. Worth, ed. Multidimensional Quantum Dynamics: MCTDH Theory and Applications; Wiley-VCH,(2009),Weinheim ISBN: 978-3-527-32018-9.
- [5] Ch. Neidel, et al...Phys. Rev. Lett. 111, 033001 (2013).
- [6] A. Perveaux, D. Lauvergnat, B. Lasorne, G. Gatti, M. A. Robb, G. J.Halász, and Á. Vibók, Submitted to J. Phys. B.
- [7] F. Remacle, and R. D. Levine, Phys. Rev. A. 83, 013411 (2011).
- [8] B. Mignolet, R. D. Levine and F. Remacle, Phys. Rev. A. 86, 053429 (2012).