Simulation of laser-induced quantum dynamics of the electronic and nuclear motion in the ozone molecule on the attosecond time scale

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- Electron dynamics in molecules in most of the time are strongly coupled to nuclear dynamics. Proper theoretical description of them in polyatomic molecules is a challenge.

- We propose a new scheme for the description of the coupled electron and nuclear motion in the ozone molecule.

- The electron dynamics as well as the nuclear dynamics will be treated separately.
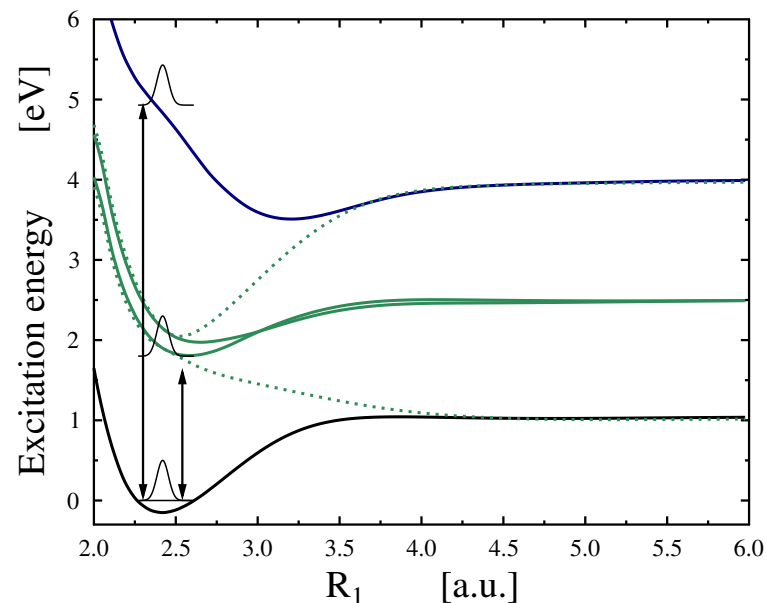
The electronic structure of the molecule
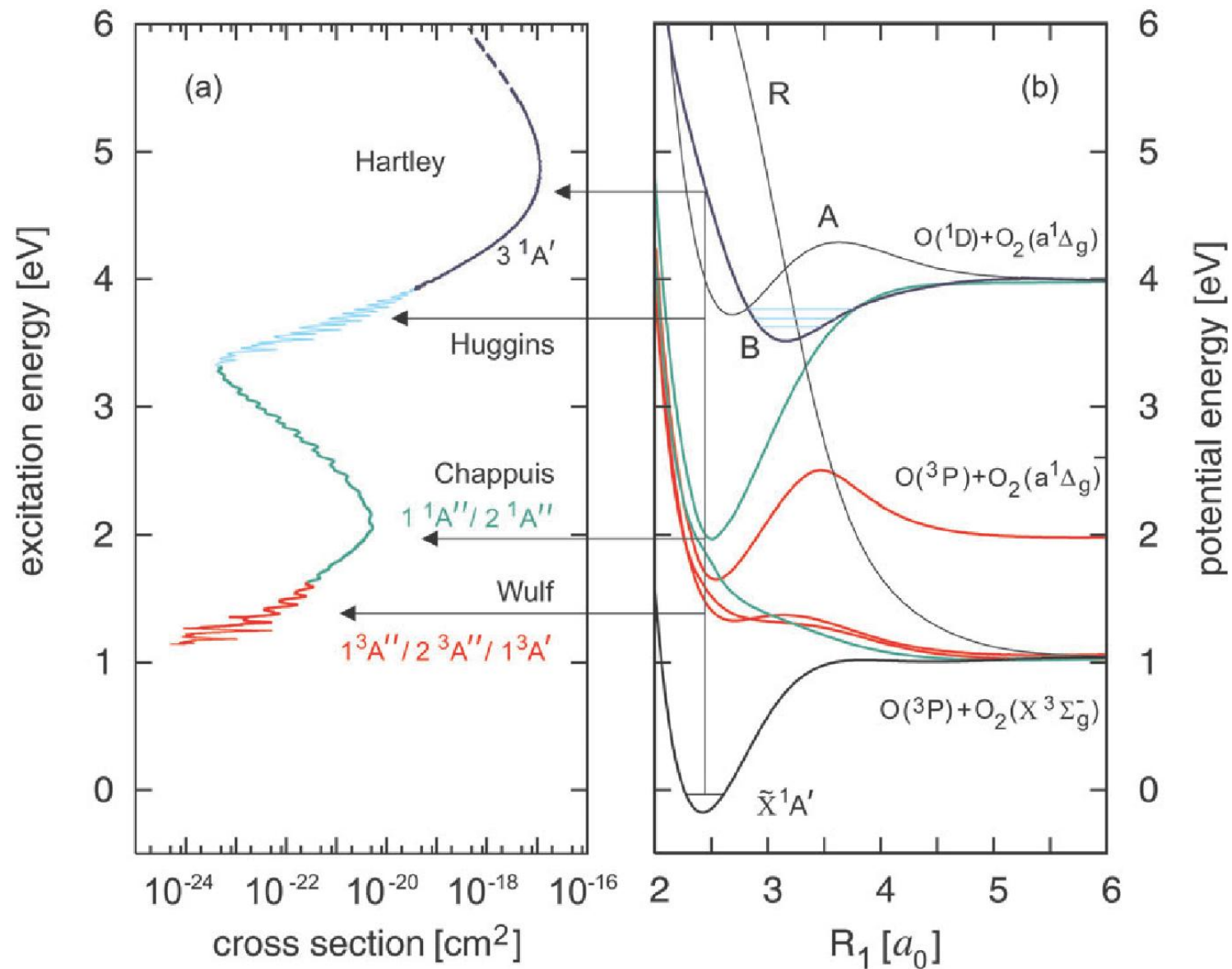
Preparing initial coherent non stationary state by pump pulses;

It is a superposition of different repulsive states in the Chappuis band* (which are populated by NIR radiation) as well as in the Hartley band (which is populated by the 3rd harmonic pulse);

Neither the electrons nor the nuclei are in a stationary state;

*S. Y. Grebenshchikov, Z-W. Qu, H. Zhu and R. Schinke, Phys. Chem. Chem Phys. **9**, 2044 (2007).

Parameters

The center wavelength of the NIR is 750nm, the center wavelength of the UV is 260nm.

The intensities are: NIR: up to $10^{14}W/cm^2$ ($10^{14}W/cm^2$);
UV: up to $10^{13}W/cm^2$ ($2 \times 10^{11}W/cm^2$).

The NIR pulse has a width just below 4fs and for the UV 3fs.

Time-dependent Born–Oppenheimer Separation

The total wave function of the molecular system Ψ_{tot} can be assumed as:

$$\Psi_{tot}(\vec{r}_{el}, \vec{R}, t) = \sum_{k=1}^{n} \Psi_{nuc}^{k}(\vec{R}, t)\psi_{el}^{k}(\vec{r}_{el}; \vec{R})$$

- $\Psi_{nuc}^{k}(\vec{R}, t)$ is the nuclear wave function;

- $\psi_{el}^{k}(\vec{r}; \vec{R})$ is the electronic wave function;

- n is the number of the molecular electronic states (now $n = 4$);

Nuclear Dynamics

$$i\frac{\partial}{\partial t}\Psi_{nuc}^{k}(\vec{R},t) = \sum_{l} H_{k,l}\Psi_{nuc}^{l}(\vec{R},t)$$

where

$$H = T_{nuc} + V + K$$

- T_{nuc} is the nuclear kinetic energy;

- $V_{k,k}$ $(k = 1, ...n)$ is the $k - th$ B-O potential;

- $K_{k,l}$ with $k \neq l$ is the coupling term between the $(k,l) - th$ electronic states (nonadiabatic coupling (NAC) and the light-matter coupling $(\vec{\mu}(k,l) \cdot \vec{E}(t))$;

- The nonadiabatic coupling term is neglected within the Born-Oppenheimer approximation but plays a key mechanistic role at the conical intersections (CI)!

- In the ozone molecule the two states ($^1B_1$ and $^1A_2$, in C_{2v}) of the Chappuis band are strongly coupled through nonadiabatic interaction arising from a symmetry-allowed CI;

- In the actual nuclear quantum dynamical calculations this nonadiabatic electron-nuclear coupling will be fully taken into account;

- Diabatic potential energies have been used for the nuclear dynamical calculations *;

*S. Y. Grebenshchikov, Z-W. Qu, H. Zhu and R. Schinke, Phys. Chem. Chem Phys. **9**, 2044 (2007)

The nuclear Schrödinger equation is solved by using the MCTDH (multi configuration time dependent Hartree) method*.

It is very efficient approach for solving the TD nuclear Schrödinger equation. Molecules with 25-30 modes can be described by using it.

We have n electronic diabatic states ($k = 1$, ground and $k = 2, ..., n$ excited). The MCTDH nuclear wave function for the $k - th$ state is $\Psi_{nuc}^k(\vec{R}, t)$ and contains the relative phases between the electronic states:

$$\Psi_{nuc}^k(\vec{R}, t) = \exp(-i\phi_k(\vec{R}, t))a_k(\vec{R}, t)$$

$\exp(-i\phi_k(\vec{R}, t))$ is the phase of the $k - th$ state, which oscillates very fast. $\Psi_{nuc}^k(\vec{R}, t)$ coefficients are provided by the MCTDH and contain all the information about the phases.

*H.-D. Meyer, U. Manthe, and L. S. Cederbaum, *Chem. Phys. Lett.* **165**, 73 (1990); U. Manthe, H.-D. Meyer, and L. S. Cederbaum, J. Chem. Phys. **97**, 3199 (1992); M. H. Beck, A. Jäckle, G. A. Worth, and H.-D. Meyer, Phys. Rep. **324**, 1 (2000); Worth, G. A.; et al., The MCTDH Package, Version 8.2, (2000), Version 8.3, (2002), Version 8.4 (2007), University of Heidelberg, Germany; See http://mctdh.uni-hd.de/; H.-D. Meyer, F. Gatti, and G. A. Worth, Eds.; Multidimensional Quantum Dynamics: MCTDH Theory and Applications. Wiley-VCH, Weinheim, (2009).

The TD density operator is*:

$$\hat{\rho}(\vec{R}, \vec{R}', t) = \left|\Psi_{tot}(\vec{r}, \vec{R}, t)\right\rangle \left\langle \Psi_{tot}(\vec{r}, \vec{R}', t)\right|,$$

the density matrix can be defined as:

$$\rho_{ii}(\vec{R}, \vec{R}', t) = \left\langle \psi_{el}^i(\vec{r}; \vec{R})\right| \hat{\rho}(\vec{R}, \vec{R}', t) \left|\psi_{el}^i(\vec{r}; \vec{R}')\right\rangle = \Psi_{nuc}^i(\vec{R}, t)\Psi_{nuc}^{i*}(\vec{R}', t).$$

The population on the $i - th$ state is:

$$P_{ii}(t) = \int d\vec{R}\rho_{ii}(\vec{R}, \vec{R}, t).$$

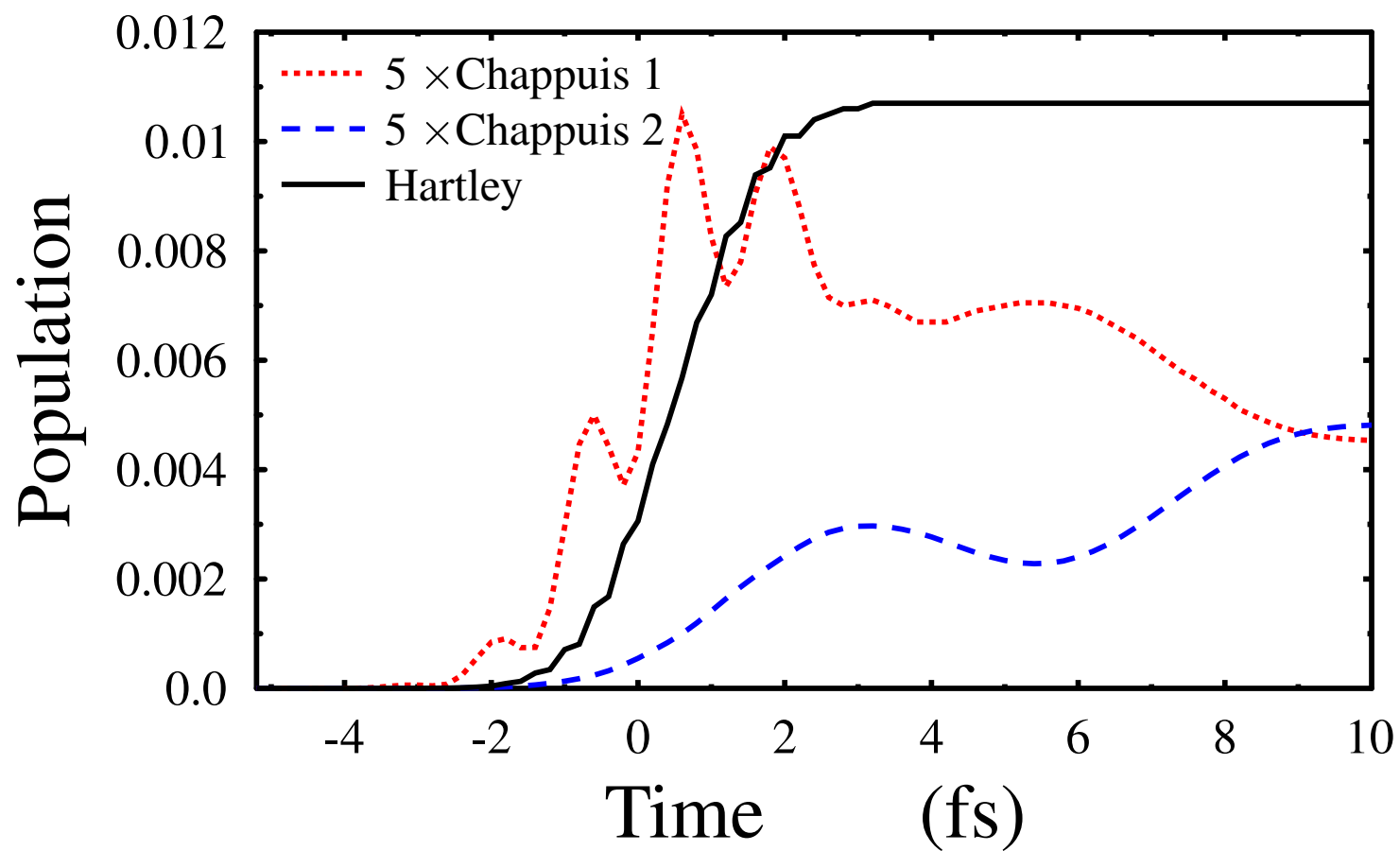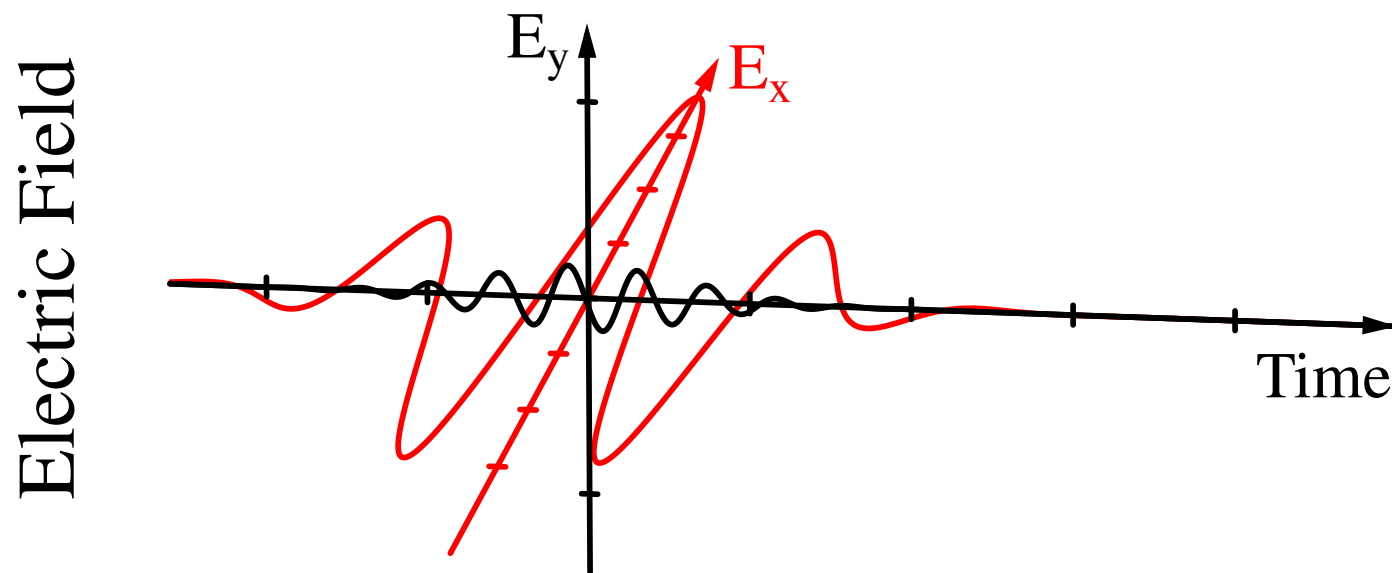*G. J. Halász, A. Perveaux, B. Lasorne, M. A. Robb, F. Gatti and Á. V., *PRA* **86**, 043426 (2012).

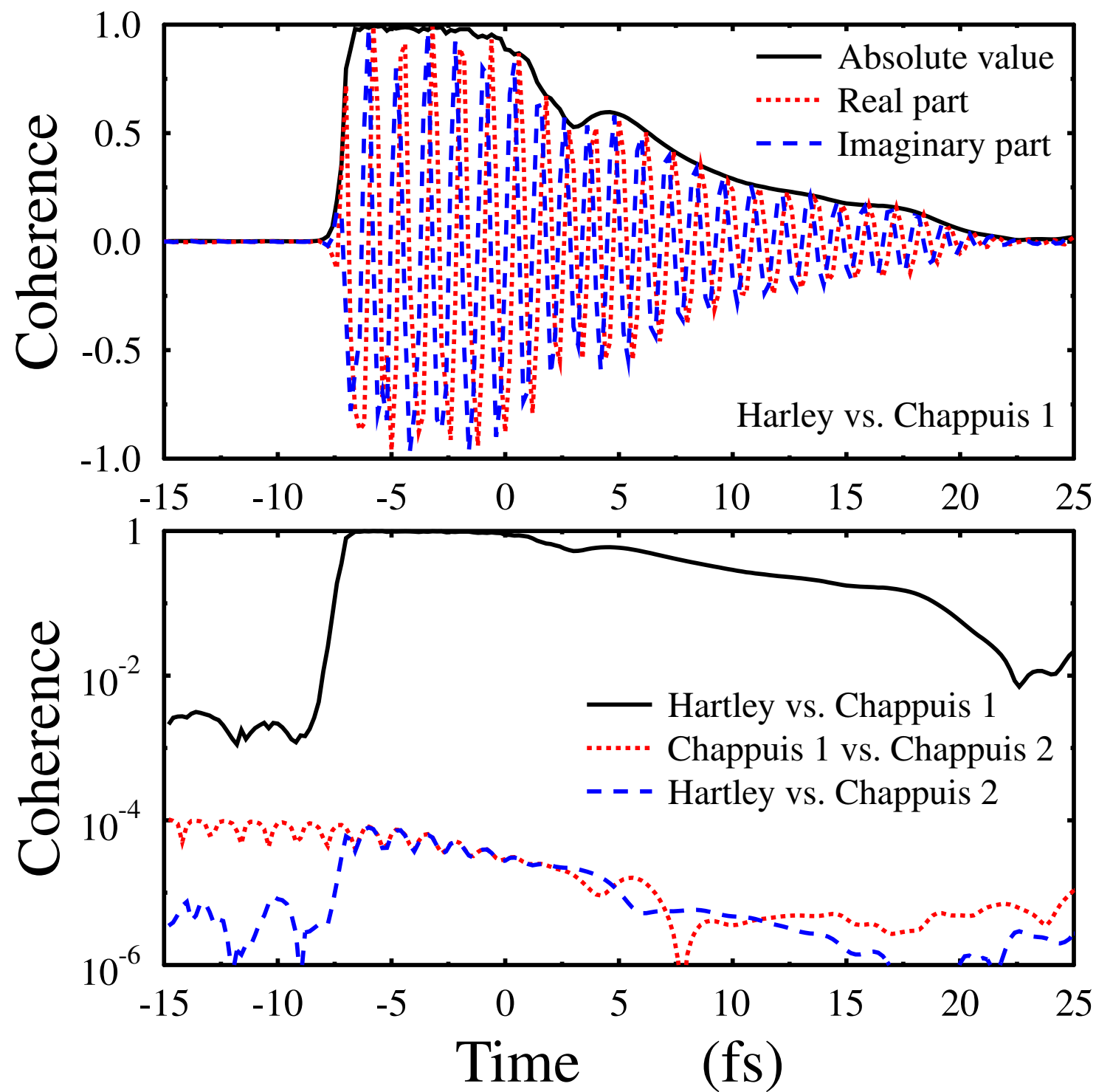The density matrix element over the $i - th$ and $i' - th$ molecular electronic states is:

$$\rho_{ii'}(\vec{R}, \vec{R}', t) = \left\langle \psi_{el}^i(\vec{r}; \vec{R}) \middle| \hat{\rho}(\vec{R}, \vec{R}', t) \middle| \psi_{el}^{i'}(\vec{r}; \vec{R}') \right\rangle = \Psi_{nuc}^i(\vec{R}, t) \Psi_{nuc}^{i'*}(\vec{R}', t),$$

The relative electronic coherence between the $i - th$ and $i' - th$ states is *:

$$C_{ii'}(t) = \int d\vec{R} \rho_{ii'}(\vec{R}, \vec{R}, t) / \sqrt{P_i(t) P_{i'}(t)}.$$
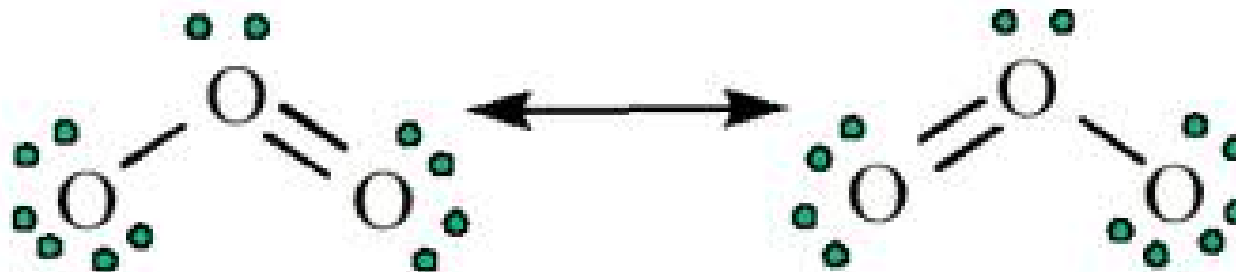
*G. J. Halász, A. Perveaux, B. Lasorne, M. A. Robb, F. Gatti and Á. V., *PRA* **86**, 043426 (2012).
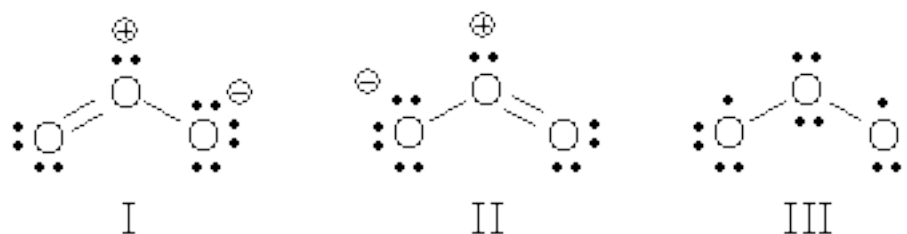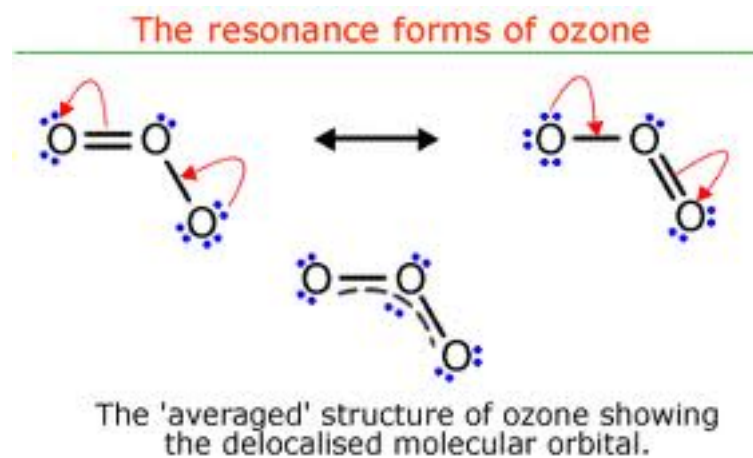
Electronic structure part

The resonance structure, or resonance forms of the ozone

The molecule can be described by an average of the two resonance forms

The resonance forms of ozone

The 'averaged' structure of ozone showing the delocalised molecular orbital.

I   II   III

The molecular orbital diagram of ozone

Within the hybrid orbital approximation each oxygen atom combines its $2s$, $2p_z$ and $2p_y$ orbitals to make three $2sp^2$ hybrid orbitals.

* O1 uses one $2sp^2$ orbital to combine with one $2sp^2$ orbital of O2, making a sigma bonding and sigma antibonding orbital

* O3 uses one $2sp^2$ orbital to combine with a second $2sp^2$ orbital of O2, making another sigma bonding and sigma antibonding orbital

* Two $2sp^2$ orbitals on O1, one $2sp^2$ orbital on O2, and two $2sp^2$ orbitals on O3 are non-bonding.
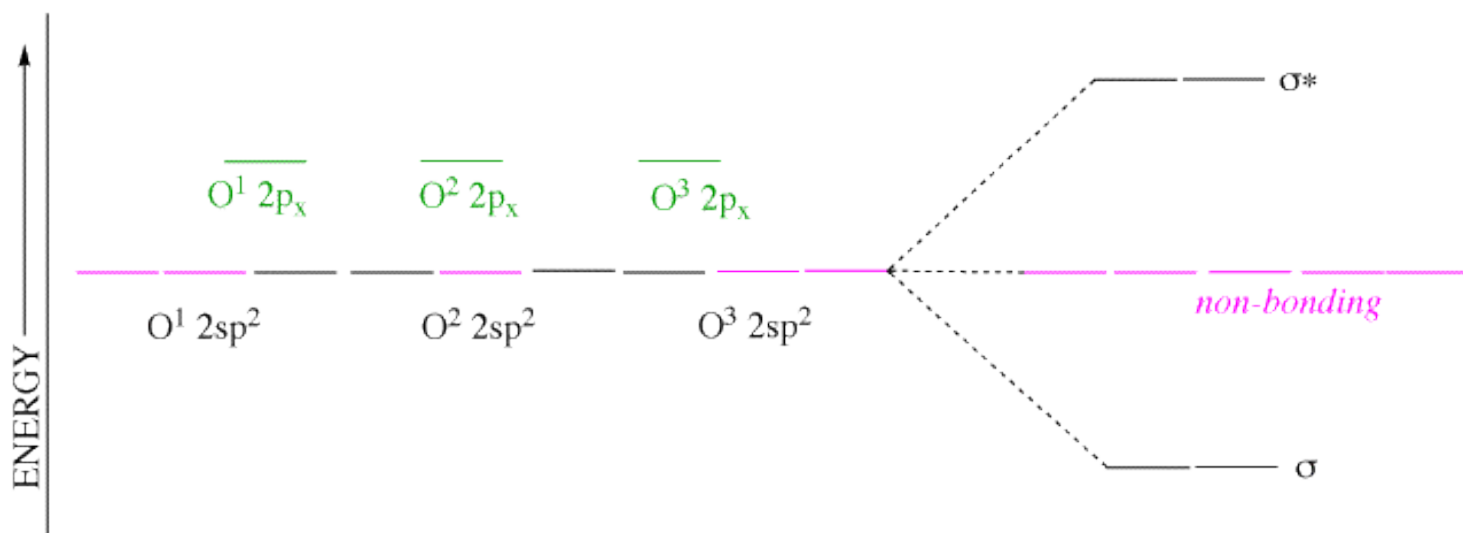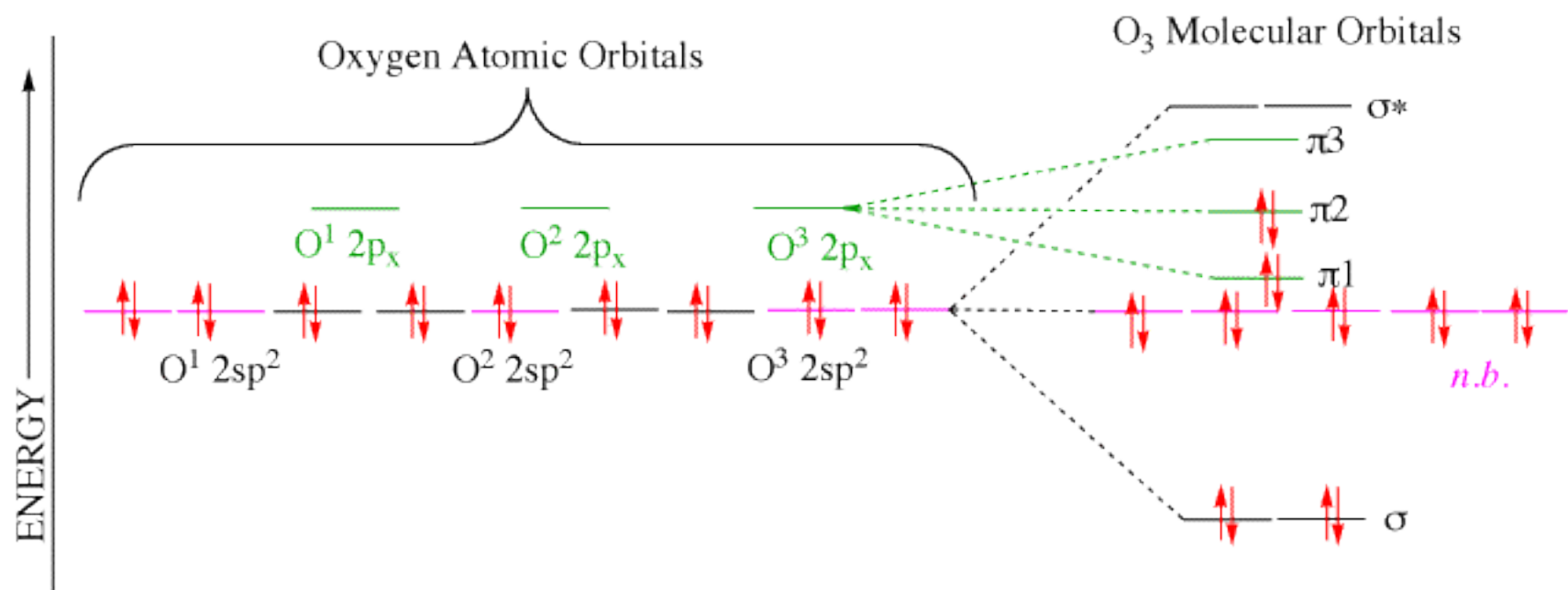
The $2p_x$ orbital on O1, the $2p_x$ orbital on O2, and $2p_x$ orbital on O3 combine to form three π symmetry orbitals.
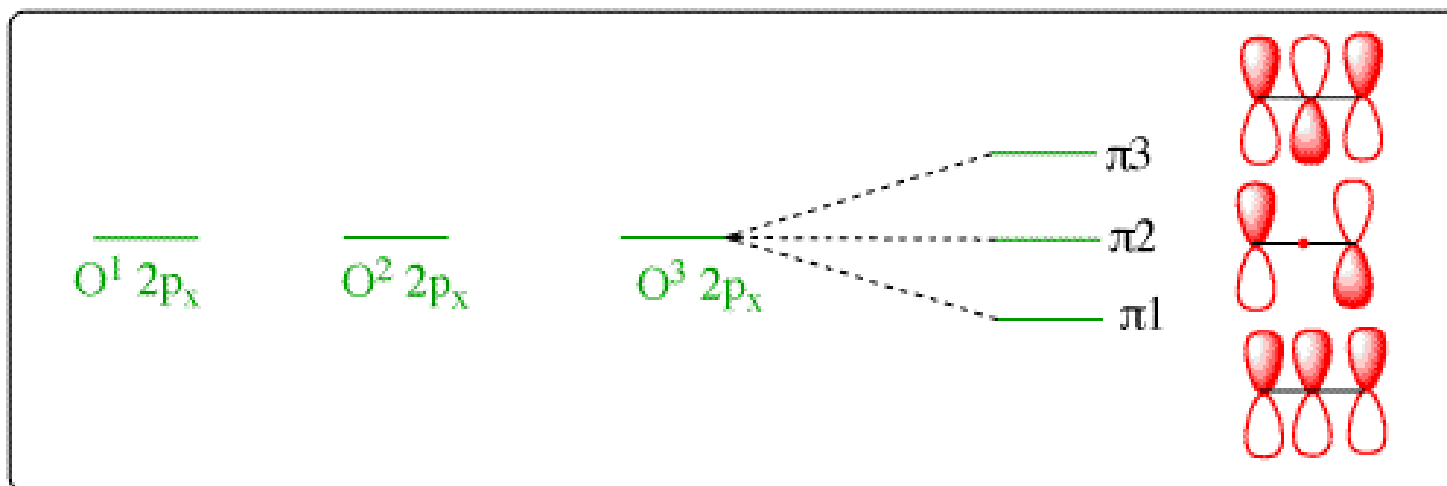
The p orbitals in the picture above indicate electron density in those orbitals.

Molecular orbitals of the ozone

- $\pi 1$, bonding all the way across the 3 atoms;

- $\pi 2$, non-bonding, zero pi electron density on the second atom;

- $\pi 3$, antibonding, the mathematical sign of the wavefunction changes with every atom, repulsive interaction between atoms;

Details of the QC calculations

- Gaussian and Molpro packages were used;

- SA-4-CASSCF(18,12)/STO-3G;

- Various schemes of state-averaging were used depending on the number of coupled states;

- Here we state-averaged over X, Chap1, Chap2, and B;

- Larger basis set were also tried (aug-cc-pVTZ and perhaps even larger). Results do not change when looking at the electronic wavepacket;

- MRCI calculations were also performed to check that the CASSCF calculations where correct in terms of electronic wavefunctions;

Electron dynamics

The electronic charge density at the Franck-Condon (FC) geometry is:

$$\rho_{el}^{i}(\vec{r}; \vec{R}_{FC}) = N \int_{N(spin)} d\sigma_1 d\sigma_2 \ldots d\sigma_N \int_{N-1(space)} d\tau_2 \ldots d\tau_N$$
$$\left| \psi_{el}^{i}(\vec{r}_1 = \vec{r}, \sigma_1, \vec{r}_2, \sigma_2, ..., \vec{r}_N, \sigma_N; \vec{R}_{FC}) \right|^2$$

The transition density between the $i - th$ and $i' - th$ molecular electronic states is:

$$\gamma_{el}^{ii'}(\vec{r}; \vec{R}_{FC}) = N \int_{N(spin)} d\sigma_1 d\sigma_2 \ldots d\sigma_N \int_{N-1(space)} d\tau_2 \ldots d\tau_N$$
$$\psi_{el}^{i*}(\vec{r}_1 = \vec{r}, \sigma_1, \vec{r}_2, \sigma_2, ..., \vec{r}_N, \sigma_N; \vec{R}_{FC})$$
$$\psi_{el}^{i'}(\vec{r}_1 = \vec{r}, \sigma_1, \vec{r}_2, \sigma_2, ..., \vec{r}_N, \sigma_N; \vec{R}_{FC})$$

It is a measure of the interference between states i and i'.

The differential electronic charge density (difference of the electronic charge density between an excited state (B or Chap1) and the ground state) at the FC geometry:
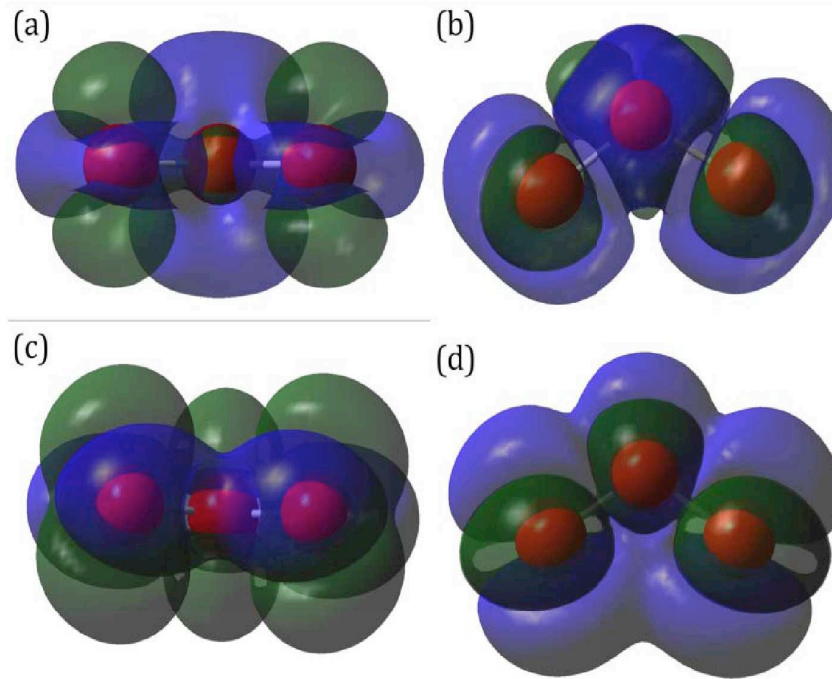
For B(top) state, (a) side view, (b) top view, this state comes from one $n_\pi \to \pi*$ and two $n_\sigma \to \sigma*$ electron excitations;

For Chap1(bottom) state, (c) side view, (d) top view, this state comes from one $n_\sigma \to \pi*$ electron excitation;

Blue: hole; green: electron.

The total molecular wavepacket at the FC geometry is:

$$\Psi_{mol}(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2, ..., \vec{r}_N, \sigma_N; \vec{R}_{FC}, t) =$$
$$\sum_i \Psi_{nuc}^i(\vec{R}_{FC}, t)\psi_{el}^i(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2, ..., \vec{r}_N, \sigma_N; \vec{R}_{FC})$$

(here the TD coefficients are the nuclear wave functions at FC)

The total charge density at FC is:

$$\rho^{tot}(\vec{r}, t; \vec{R}_{FC}) = \sum_i |\Psi_{nuc}^i(\vec{R}_{FC}, t)|^2 \rho^i(\vec{r}; \vec{R}_{FC})$$
$$+ \ 2Re \sum_{i<i'} \Psi_{nuc}^{i*}(\vec{R}_{FC}, t)\Psi_{nuc}^{i'}(\vec{R}_{FC}, t)\gamma_{el}^{ii'}(\vec{r}; \vec{R}_{FC}).$$

The excited-state differential charge density at the FC point (the difference of the total charge density between an excited state (B or C1) and the ground state:

$$\Delta\rho^{exc}(\vec{r}, t; \vec{R}_{FC}) = |\Psi_{nuc}^{B}(\vec{R}_{FC}, t)|^2 [\rho^{B}(\vec{r}; \vec{R}_{FC}) - \rho^{GS}(\vec{r}; \vec{R}_{FC})]$$

$$+ \ |\Psi_{nuc}^{C1}(\vec{R}_{FC}, t)|^2 [\rho^{C1}(\vec{r}; \vec{R}_{FC}) - \rho^{GS}(\vec{r}; \vec{R}_{FC})]$$

$$+ \ 2Re \sum_{i<i'} \Psi_{nuc}^{B*}(\vec{R}_{FC}, t)\Psi_{nuc}^{C1}(\vec{R}_{FC}, t)\gamma_{el}^{B,C1}(\vec{r}; \vec{R}_{FC}).$$

Snapshots of the time evolution of the excited differential electronic charge density at the FC geometry. Side view (blue: hole; green: electron)*.
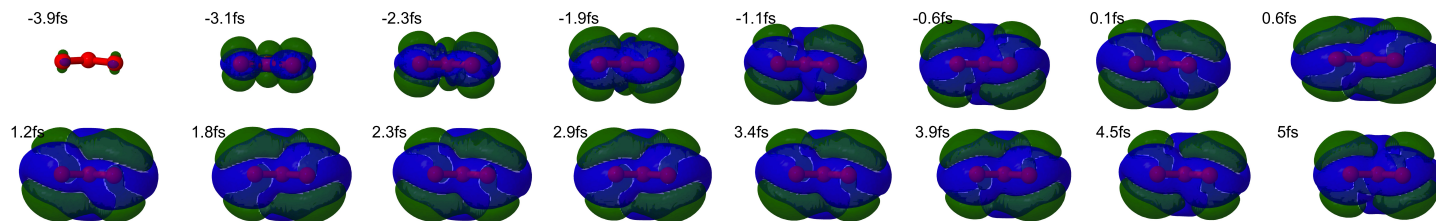
A "periodic twisting" motion of the differential electronic charge density has been induced by exciting a coherent superposition of $C1$ and B states. The period of this motion is about $1.2 - 1.3\,fs$.
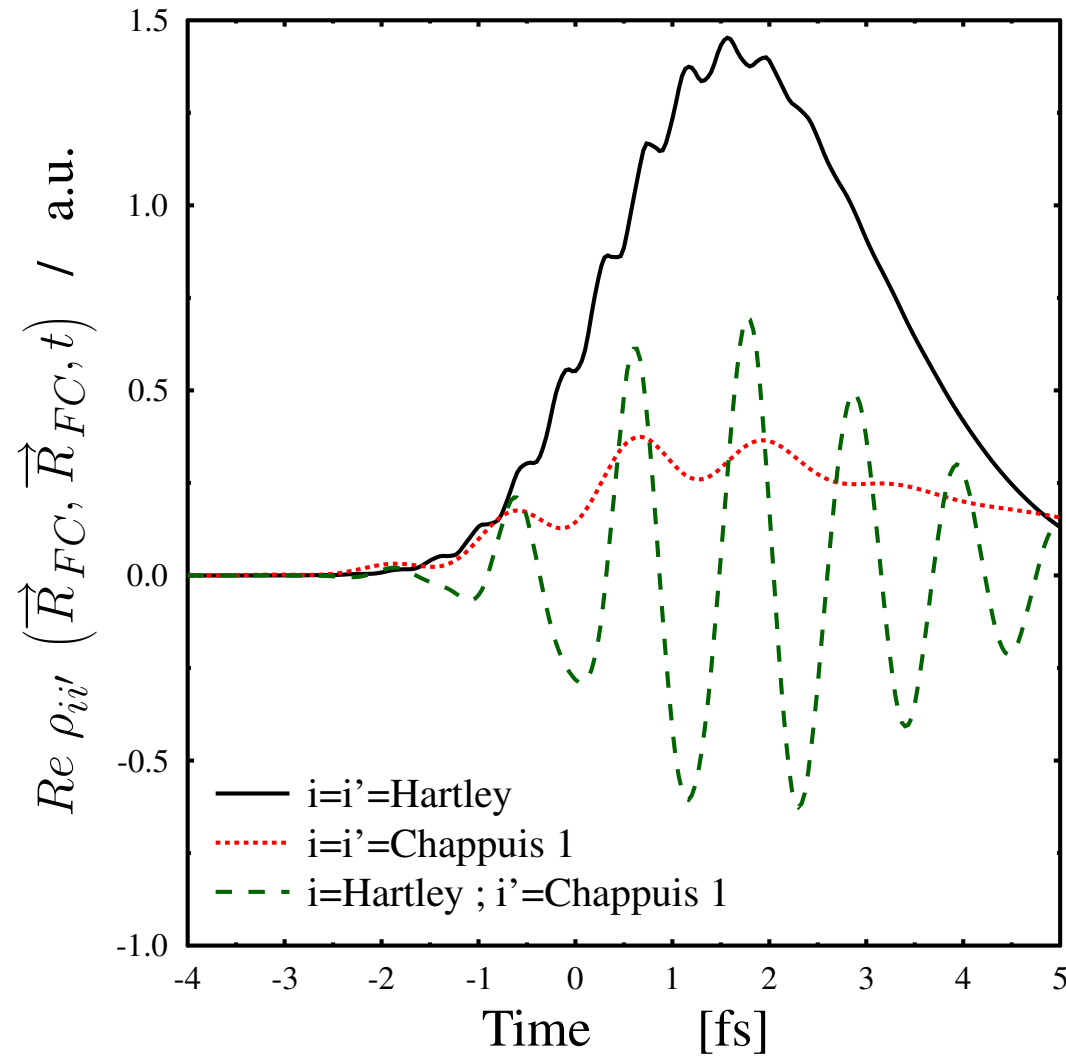
Local population densities for the $C1$ (blue) and B (red) states and the real part of the interference term (green) at the FC point as functions of time.

The snapshots belong to those time values for which the green curve has maxima or minima.

- The population densities at the FC point are totally symmetric (A_1);

- The interference term is $A_2(B_1 \oplus B_2)$;

- Therefore the electronic charge density is not totally symmetric;

- Time-dependent anisotropy of the electronic cloud which could be detected in time resolved photoelectron spectra experiments using attosecond XUV probe pulse, which is in progress.

Electron dynamics beyond the FC region?

$$\triangle \rho^{exc}(\vec{r}, t) = \int \{ |\Psi_{nuc}^{B}(\vec{R}, t)|^2 [\rho^{B}(\vec{r}; \vec{R}) - \rho^{GS}(\vec{r}; \vec{R})]$$

$$+ \; |\Psi_{nuc}^{C1}(\vec{R}, t)|^2 [\rho^{C1}(\vec{r}; \vec{R}) - \rho^{GS}(\vec{r}; \vec{R})]$$

$$+ \; |\Psi_{nuc}^{C2}(\vec{R}, t)|^2 [\rho^{C2}(\vec{r}; \vec{R}) - \rho^{GS}(\vec{r}; \vec{R})]$$

$$+ \; 2Re \sum_{i < i'} \Psi_{nuc}^{B*}(\vec{R}, t) \Psi_{nuc}^{C1}(\vec{R}, t) \gamma_{el}^{B,C1}(\vec{r}; \vec{R}) + ... \} d\vec{R};$$

We excite only the B state of the Hartley band with a much larger intensity pump pulse ($10^{14}W/cm^2$) than previously. (The center wavelength and the FWHM are 260 nm and 3 fs, respectively.) The population obtained is more pronounced. The non-stationary state is a coherent superposition of the ground and the B Hartley states*.
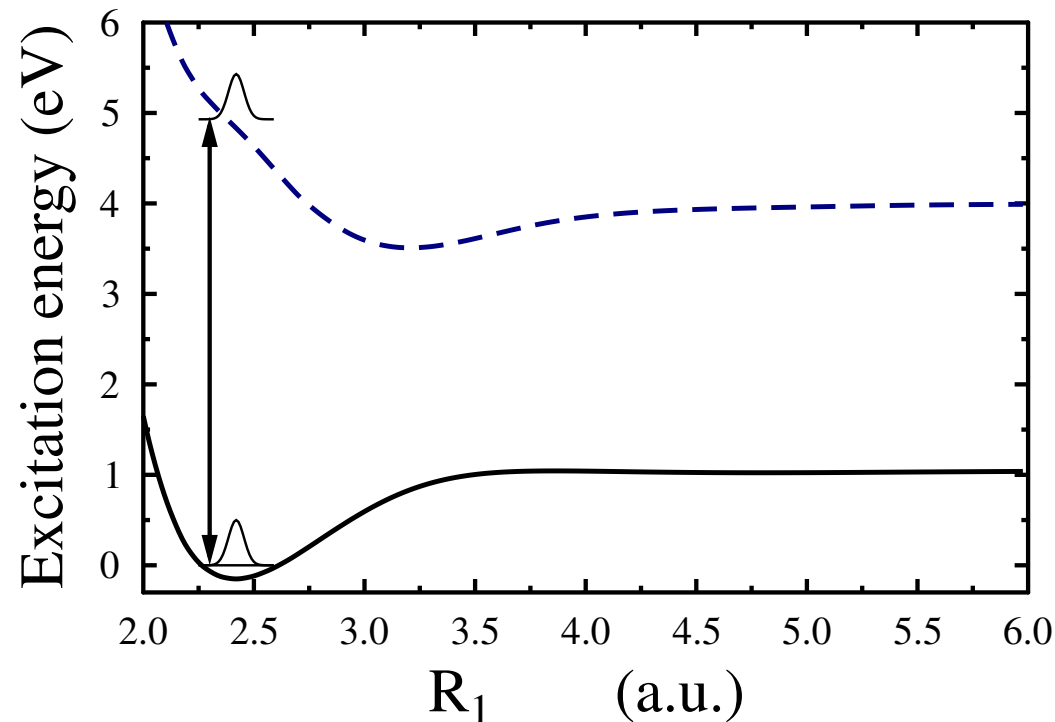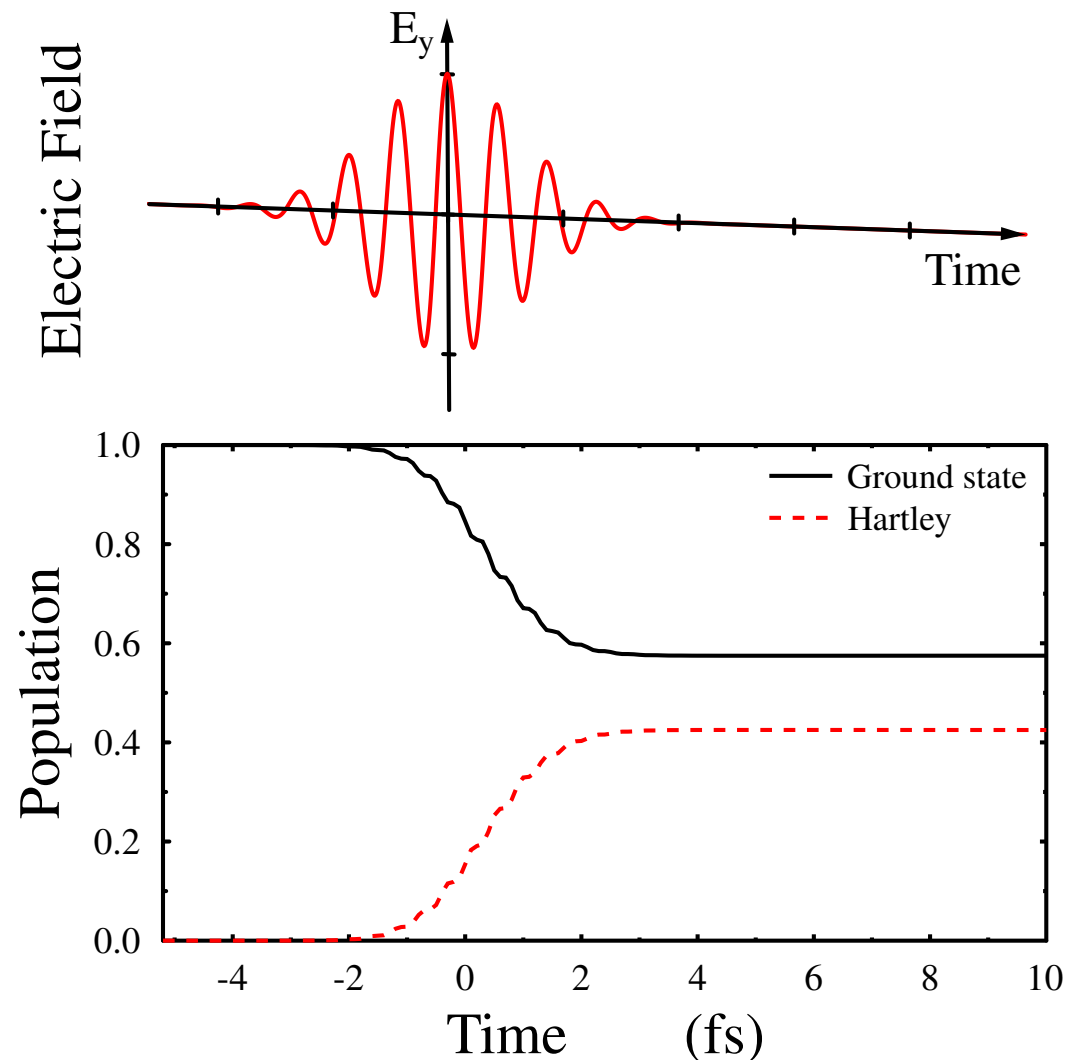
*G. J. Halász, A. Perveaux, B. Lasorne, M. A. Robb, F. Gatti and Á. V., Coherence revival during the attosec-ond electronic and nuclear quantum photodynamics of the ozone molecule.(arXiv 1305.5038v1) *in press. PRA.*

The two-dimensional nuclear density function (depending on R_1 and R_2, the two bond lengths, and integrated over θ, the bond angle) is:

$$\left|\Psi_{nuc}^i(R_1, R_2, t)\right|^2 = \int \Psi_{nuc}^i(R_1, R_2, \theta, t)\Psi_{nuc}^{i*}(R_1, R_2, \theta, t) \sin\theta d\theta$$

The applied electric field and the time evolution of the diabatic populations on the ground (X) and diabatic excited (B) states[*]
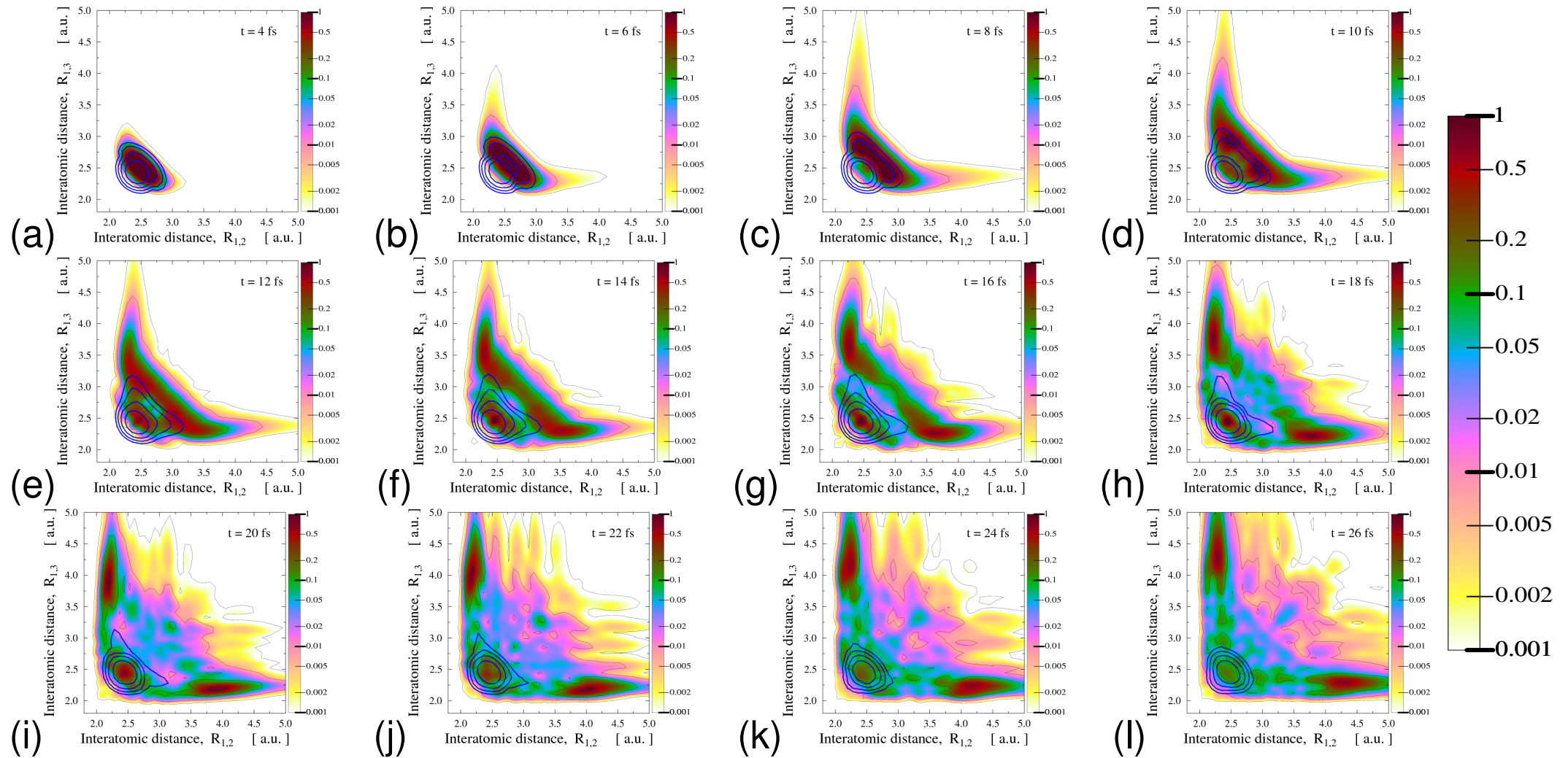

[*]G. J. Halász, A. Perveaux, B. Lasorne, M. A. Robb, F. Gatti and Á. V., Coherence revival during the attosecond electronic and nuclear quantum photodynamics of the ozone molecule.(arXiv 1305.5038v1) *in press. PRA*.

The real, the imaginary parts and the absolute value of the relative electronic coherence between the ground (X) and Hartley (B) states
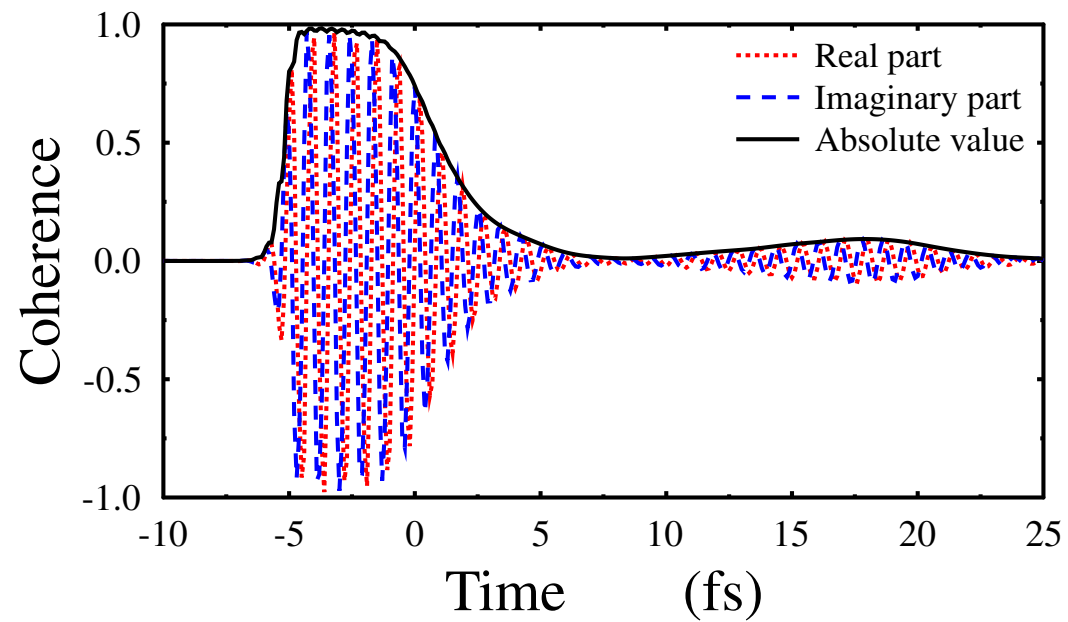
- In the first time period the coherence increases very fast and reaches its maximum;

- It retains this value for 3 - 4 fs, which is approximately equivalent to the duration of the laser pulse;

- A few femtoseconds later ($\sim$ 5 fs), the coherence reappears in contrast with what was observed in previously;

- This phenomenon could be enhanced experimentally by optimizing the parameters of the laser pulse;

Snapshots of the time evolution of the nuclear wave packet density along both O - O bonds*


*G. J. Halász, A. Perveaux, B. Lasorne, M. A. Robb, F. Gatti and Á. V., Coherence revival during the attosecond electronic and nuclear quantum photodynamics of the ozone molecule.(arXiv 1305.5038v1) *in press. PRA.*

- This revival of electronic coherence is interesting because the pump pulse is already off;

- The wave packet oscillates in the B state and then goes back to the FC region where it is still coherent with the part left in the ground state;

- A part of the nuclear wave packet stays trapped on the symmetric ridge of the B potential energy surface, where both O - O bonds increase synchronously;

- A valley-ridge inflection point occurs, where the nuclear wave packet splits into three components;

- One part is bound to come back to the FC region, while the rest dissociates along either of both equivalent channels;

Local population density for state B (black) and real part of the interference term (dashed green) at the FC point as functions of time
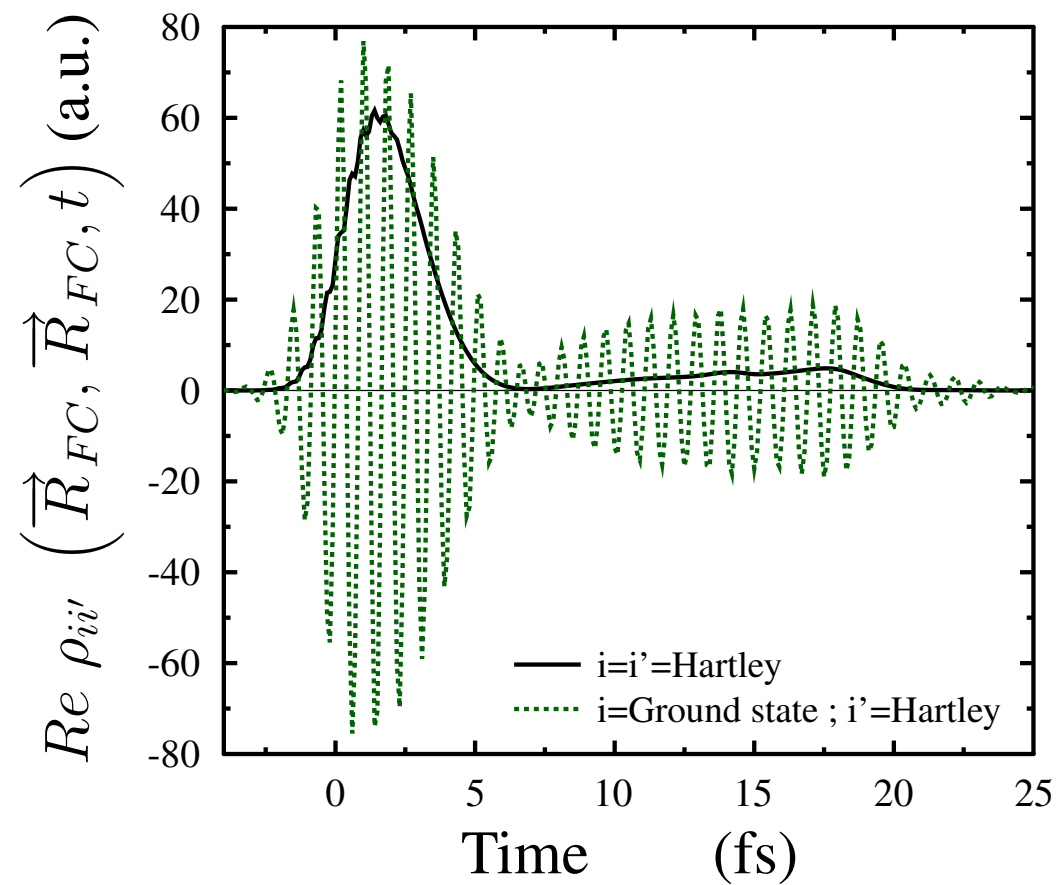
The excited state differential electronic charge density at the FC geometry (difference of the total charge density between the excited state B and the ground state):

$$\triangle\rho^B(\vec{r},t;\vec{R}_{FC}) = \rho^{tot}(\vec{r},t;\vec{R}_{FC}) - [|\Psi^X_{nuc}(\vec{R}_{FC},t)|^2 + |\Psi^B_{nuc}(\vec{R}_{FC},t)|^2]\rho^X(\vec{r};\vec{R}_{FC})$$

$$= |\Psi^B_{nuc}(\vec{R}_{FC},t)|^2[\rho^B(\vec{r};\vec{R}_{FC}) - \rho^X(\vec{r};\vec{R}_{FC})] + 2Re\Psi^{X*}_{nuc}(\vec{R}_{FC},t)\Psi^B_{nuc}(\vec{R}_{FC},t)\gamma^{XB}(\vec{r};\vec{R}_{FC})$$

$$= |\Psi^B_{nuc}(\vec{R}_{FC},t)|^2\triangle\rho^B(\vec{r};\vec{R}_{FC}) + 2Re\Psi^{X*}_{nuc}(\vec{R}_{FC},t)\Psi^B_{nuc}(\vec{R}_{FC},t)\gamma^{XB}(\vec{r};\vec{R}_{FC}),$$

where $\triangle\rho^B(\vec{r};\vec{R}_{FC}) = \rho^B(\vec{r};\vec{R}_{FC}) - \rho^X(\vec{r};\vec{R}_{FC})$.

Time evolution of the excited differential electronic charge density at the FC geometry*
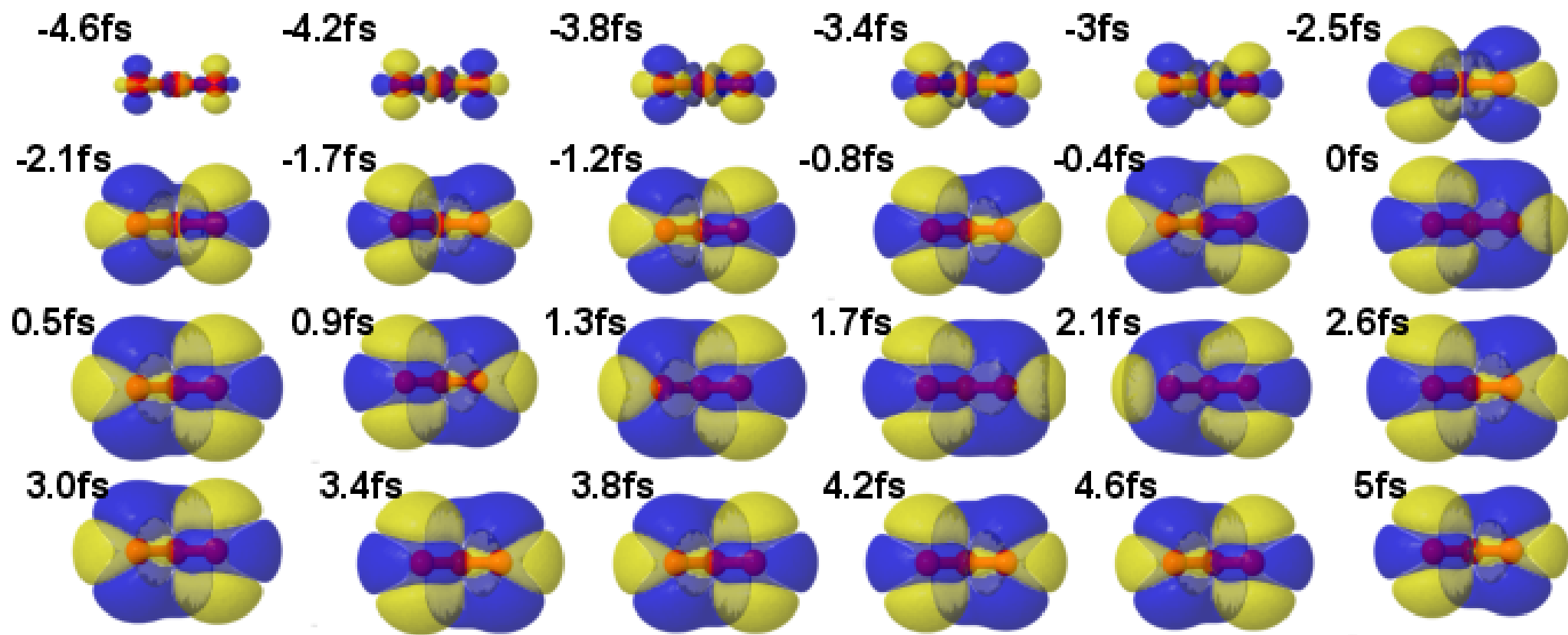
*G. J. Halász, A. Perveaux, B. Lasorne, M. A. Robb, F. Gatti and Á. V., Coherence revival during the attosecond electronic and nuclear quantum photodynamics of the ozone molecule.(arXiv 1305.5038v1) *in press. PRA.*

- The electronic charge density oscillates from one bond to another with a period of 0.8 fs;

- The resulting electronic wave packet is thus a coherent superposition of two chemical structures, $O \cdots O_2$ and $O_2 \cdots O$;

- The subfemtosecond oscillation between both structures at the FC geometry prefigures that the dissociation of ozone could be controlled by modulating the electron density on the attosecond time scale;

Collaborators

Theory

- Gábor Halász (Debreceni Egyetem);

- Fabien Gatti, Benjamin Lasorne, Aurelie Perveaux (University of Montpelier, France);

- Michael A Robb (Imperial College London);

Experiment

- Reinhard Kienberger, Michael Jobst, Ferenc Krausz (Max Planck Institute, Garsching, Germany);

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Thank you for your attention!