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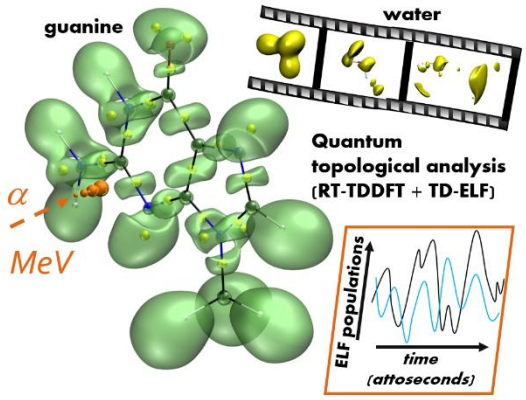
ABSTRACT

We report original analyses of attosecond electron dynamics of molecules subject to collisions by high energy charged particles based on Real-Time Time-Dependent-Density-Functional-Theory simulations coupled to Topological Analyses of the Electron Localization Function (TA-TD-ELF). We investigate irradiation of water and guanine. TA-TD-ELF enables qualitative and

quantitative characterizations of bond breaking and formation, of charge migration within topological basins, or of electron attachment to the colliding particle. Whereas the Lewis-VSEPR structure of gas phase water is blown out within a few attoseconds after collision, that of guanine is far more robust and reconstitutes rapidly after impact even though the molecule remains electronically excited. This difference is accounted by the presence of the electron bath surrounding the impact point which enables energy relaxation within the molecule. Our approach should stimulate future studies to unravel the early steps following irradiation of various types of systems (isolated molecules, biomolecules, nanoclusters, solids…) and is also readily applicable to irradiation by photons of various energies.

TOC GRAPHICS



KEYWORDS quantum chemical topology, attosecond electron dynamics, radiation damages, DNA base, Real-Time TDDFT.

High energy charged particles (electrons, positrons, protons, alphas, hadrons…) interact with matter in turn inducing electronic excitations or ionization of the constituting molecules[1]. A fine understanding of irradiation is essential in various scientific domains. In astrochemistry ionizing radiations (IoR) deeply impact the complex chemistry occurring in gases or on grains[2]. In biology IoR cause deleterious damages to genomes, proteins or signaling pathways that normally regulate cell activity, having harmful consequences like accelerated aging, tumors and cancers[3]. Let us also mention that protection of astronauts from IoR is the major obstacle for planning human interplanetary travels. On the opposite, IoR have beneficial effects in proton- or hadron-therapies or for sterilization purposes in industry. Interaction of IoR with matter and their subsequent ultrafast consequences continues to challenge both experimental and computational approaches. Massive efforts push the development of attosecond sources, which in turn have started to stimulate new developments in computational physical chemistry[4]. In this Letter we are interested in deciphering the attosecond response of molecules' electron clouds submitted to ionizing radiations. We emphasize that collisions with charged particles are very different from absorptions of X-ray or UV/visible photons or from interactions of molecules with strong laser fields. Collision with keV-MeV alpha produces superposition of highly excited electronic states. The energy deposited locally into the electronic cloud is typically of several tens of eV. Although useful, the analysis of electron dynamics based on the occupations of molecular orbitals (MO) is cumbersome for these processes because of the very large number of involved MOs. The Electron Localization Function (ELF)[5-6]and its extension to the time domain[7] are alternative appealing tools. Two-or three dimensional plots of TD-ELF have been reported to describe alterations of molecular density fields when molecular systems interact with ultra-short laser pulses or collide with slow ions[8-10]. TD-ELF actually incorporates a valuable wealth of

information on the time evolution of the chemical structure that is potentially accessible by quantum topological analyses[8, 11]. We extend the analysis of ELF within the framework of gradient field theory which was initially developed for stationary electronic structures[12-13] to non-stationary electronic structures and apply it for the first time to irradiation of molecules by high energy alpha particles. Our approach enables, for instance, to qualitatively and quantitatively characterize formation/breaking of bonds between nuclei, electron flows (charge migration) among topological basins, or the attachment of electron density to the colliding particle. To illustrate the strength of the approach we successively consider collision of water or of a DNA base (guanine) by alpha particles and analyze the evolution of the ELF topological basins in combination with other descriptors of the electron dynamics.

Our electron dynamics simulations are based on Real Time TD-DFT[14] (Time-Dependent Density Functional Theory) which is a powerful theoretical approach to address attosecond dynamics of matter submitted to irradiation by laser field or charged particles[15-23]. We focus on inelastic collisions that are known to be largely dominant for kinetic energies of few tens of keV and higher[1]. The colliding particle is described as a point charge moving in space at constant velocity. The TD Coulomb potential created by the particle is included in the external Kohn-Sham potential. We use an implementation of RT-TDDFT in the deMon2k software[24] (see Reference [25] for details). All calculations have been done with the GGA (Generalized-Gradient-Approximation) CAP-PBE exchange-correlation potential[26-27]. CAP stands for Correct Asymptotic Potential and exhibits a correct $1/r$ asymptotic behavior[26]. The capabilities of various XC functionals to fully capture the physics involved ionization by high energy particles are not yet fully understood. Global hybrids or range-separated hybrids would provide better

description of Rydberg or charge separated states than GGA which constitutes a limitation of the present protocol. More technical details on the simulation protocol can be found in SI.

The quantum chemical topology of ELF relies on the analysis of the gradient field of a scalar function by applying the theory of dynamical systems[28]. The latter provides a partitioning of the molecular space into non-overlapping volumes (basins). The ELF topology displays atomic and non-atomic maxima that can be related to chemical concepts issued from the Lewis theory. The core basins, labeled C(X) are located at nuclear centers, whereas the valence basins are located in the remaining space. These valence basins are characterized by a synaptic order, *i.e.* the number of core basins with which they share a common boundary[13]. Monosynaptic basins, labeled V(X), usually associated to the lone-pair regions of X atoms, while disynaptic basins, labeled V(X, Y), correspond to two-center covalent X-Y bonds. Basins with a synaptic order of zero (termed as asynaptic) are sometimes found in the molecular space. They are labeled as V(A) in this work. The integration of the electron density over the basin volume provides a basin population or intrinsic moments[29]. Topological analyses have been performed with a modified version of the TOPCHEM package[30].

Figure 1 depicts the total ionization cross section for water as a function of the kinetic energy of the colliding particle. Each point results from an average over one hundred trajectories with different initial positions of the alpha particle and impact parameter (see SI for details). RT-TDDFT results are in excellent agreement with the available experimental data[31]. Notably the maximum ionization probability around 0.1 MeV is recovered. RT-TDDFT results are also in good agreement with perturbative approaches such as the first Born Approximation Continuum Distorted Wave (FBA-CDW) or the Continuum Distorted Wave-Eikonal Initial State (CDW-EIS) methods[32-33,31, 34]. At higher energies the slope of the RT-TDDFT curve follows that of

standard models. The apparent capability of our RT-TDDFT implementation based on the CAP-PBE functional to simulate ionization by charged particles is in line with a few previous analogous simulations of collisions of water with fast protons[16]. These are encouraging results for future applications to large molecular systems.

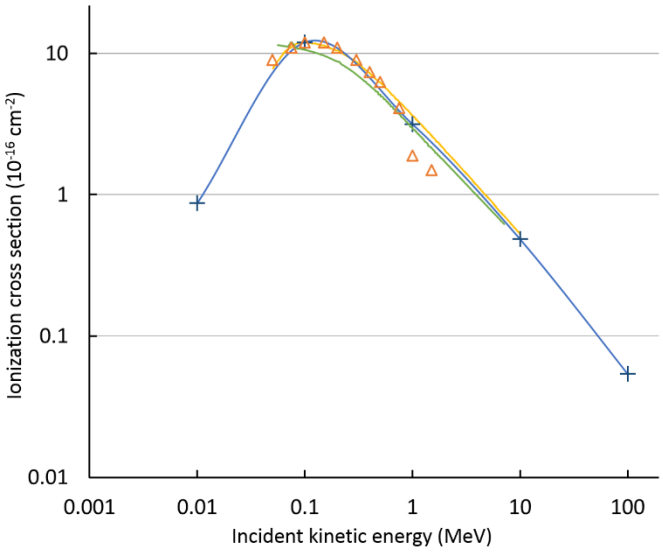


Figure 1: ionization cross-section for gas phase water. Ionization probability is calculated 1fs after collision. RT-TDDFT curve normalized to the experimental value for 0.1MeV. Blue line: RT-TDDFT; yellow: CDW-EIS model[34]; green: FBA-CDW model, orange triangles: experiments from Rudd et al[31].

On the stationary electron density of isolated water obtained by a SCF (Self-Consistent-Field) procedure one recognizes on the ELF isosurfaces (Figure 2, Top) the well-known Lewis-VSEPR[35] structure comprised of oxygen core basin (C(O)), of two disynaptic protonaned basins V(O,H) associated to O-H bonds and of two monosynaptic basins V(O) positioned around the HOH plane and associated to the oxygen lone pairs. The electron density integrated within the basins are also in line with the Lewis structure (*e.g.* around 2 electrons in the oxygen core shell, 2.3 in each lone pair…). We now consider five collisional trajectories with incident kinetic energies of 0.01, 0.05, 0.1, 1 and 100 MeV. We selected three snapshots for each trajectories (Figure 3); when the particle is approaching at 2 Å from H_2O (Left), when it is within H_2O

(Middle) and when it has moved 4 Å away from the molecule (Right). These distances refer to the van der Waals envelope of the molecule. Movies of ELF isosurfaces can also be found in SI for each of them.

The fastest particle (100 MeV) traverses the water structure causing only moderate perturbations to the ELF basins. After collision, periodic jiggling of the ELF basins are observed. They reflect Rabi oscillations among the excited electronic states populated by the transient collision. For impact energies of 1 MeV and below, we observe important modifications of the ELF already at the moment of collision. The formation of topological basins discloses probably the emission of electrons in Rydberg states or in the continuum. It is around 0.05-0.1 MeV that the perturbations seem to be the most severe, which corresponds to collision energies for which the amount of energy transferred to the molecule reaches a maximum (Figure S2). Note that the core basin C(O) remains undisturbed whatever the impact energy. On contrary to the stationary topology, the ELF valence regions seems to be scattered within the molecular space because many asynaptic valence basins (V(A)), not clearly associated to atoms, are observed (see Figure 3). These asynaptic basins appear as a typical signature of the intensity of collisions, although they are associated to small topological patches containing little electron densities.

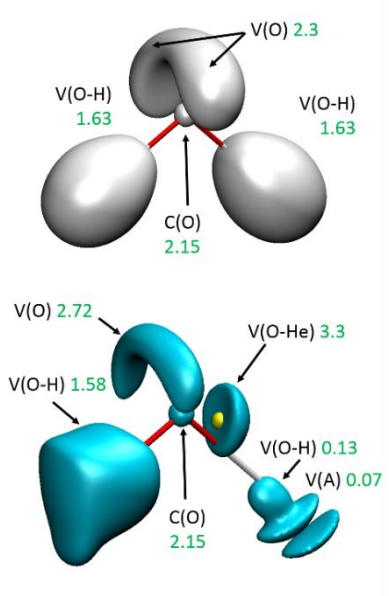


Figure 2: ELF isosurfaces (0.88) on the stationary electron densities of H_2O isolated (Top) and in presence of He nucleus (α particle, in yellow, Bottom). ELF topological basin populations are given in electron numbers.

Interestingly for energies of 1 and 100 MeV no ELF basins encompassing the helium nucleus are formed. We interpret this result as a consequence of the ultrashort timescale of the collision that doesn't enable the electron cloud to attach around the helium nucleus. On the opposite, for incident energies of 0.5 MeV and below, a disynaptic V(O, He) basin is formed when the He^{2+} nucleus is present within the water electron cloud (pictures in the middle). This reflects transient formation of bond between these nuclei. For energies of 0.05 and 0.01 MeV the alpha particle leaves the molecule with a fraction of electron cloud. Large monosynaptic V(He) basins containing respectively 0.49 and 0.79 electrons are identified on Figure 3 for these energies. This feature is a clear signature of the so-called electron attachment channel that topological analyses of TD-ELF are able to capture. All the dynamical features outlined above are to be contrasted with the ELF topological analysis performed on a fictitious stationary electron density with the helium atom situated within the water molecule (Figure 2, bottom). A disynaptic basin V(O, He) is found which holds 3.3 electrons among which 0.48 are attributed to He. The comparison of

stationary (SCF) *vs*. propagated electron densities illustrates the existence of specific ELF topological patterns on the attosecond regime.

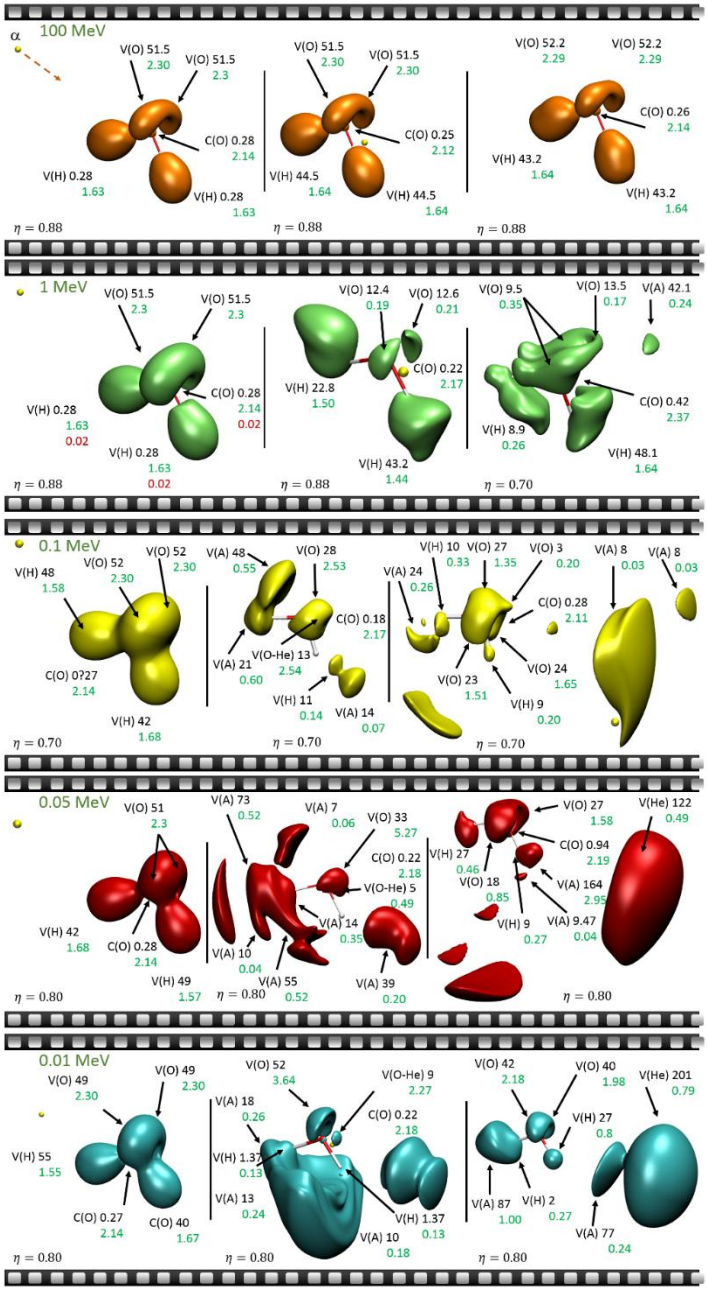


Figure 3: TD-ELF for water molecule impacted by alpha particles of various kinetic energies. For each topological basin we indicate, in order, the volume ($Å^3$) and the electronic population (in green). Some asynaptic basins are not labeled because they hold very little electron density and are thus not meaningful. Values of ELF isosurfaces are given for each picture.

As a second example, we report the collision of a guanine molecule impacted by an alpha particle travelling along a line perpendicular to the aromatic cycles. The kinetic energy of the particle is chosen to be 0.1 or 1MeV, the former being close to the maximum ionization probability as predicted by CDW-EIS models[34]. We also consider two impact points for guanine, either close to the central C=C bond (case *i*) or to the N-H group of the 6-member aromatic cycle (case *ii*). By convention the collision time corresponds to snapshot *a*. We focus first on case *i*) with a 1MeV particle and on the very moment of collision (snapshot *a*-*b*). We also encourage the reader to visualize the movies in SI. The ELF basins around the region of impact are drained by the +2 charge of the alpha particle. The V(C, C) basin is split into two monosynaptic V(C) basins, one located well above the aromatic plane in the direction of the helium atom, the other situated in opposite direction, *i.e.* below the plane. Together these two basins hold 3.5 electrons, which is close to the electronic population of the V(C, C) basins before collision (3.23, snapshot *a*). The intrinsic dipole moments within the monosynaptic V(C) basins are large, indicating strong polarization of the electron cloud caused by the collision. We also note the splitting of the unique V(C, O) basin associated on snapshot *a*) to the C=O bond into two basins comprising each, in average, 1.21 electrons. This is characteristic of a non-conjugated double C=O bond suggesting a weakening of electron delocalization among the aromatic cycle of guanine. As seen from a close examination of the central C-C region (see movies and Figure 4), the original bonding between central C-C atoms progressively reforms within a few hundreds of attoseconds after collision. The V(N) basins are also insightful. Those of nitrogens pertaining to the C=N-C groups belong to the σ system as reflected by ELF attractors lying within the aromatic plane. These basins are strongly affected by collision as seen from the large fluctuations of their electronic populations after disruption of the central C=C bond (Figure S11).

Furthermore theses basins are occasionally split into sub-basins. The V(N) basins belonging to the π system (C**N**CCH$_3$ and C**N**HC) are situated above and below the aromatic plane. They are similarly impacted by collision since they transiently disappear and later reform. Altogether, these topological patterns indicate that both σ and π systems surrounding the impact point are contributing to the redistribution of the delivered energy through the entire molecule (around 67eV, Figure S3). To analyze more in depth the relaxation mechanism we computed the MO occupation numbers and the electronic kinetic energy integrated over atoms (Figures S4 and S9). Collision induces partial depopulation of all initially doubly occupied MOs, except those corresponding to core electrons. The latter point is corroborated by the ELF analysis on core basins (Figure S12). Meanwhile a wide manifold of initially unoccupied MOs acquire electronic populations, typically around 0.05 e^-. We observe continuous fluctuations of occupation numbers in the rest of the simulation, indicating that the molecule remains in a highly excited state. Actually only a moderate fraction of the energy initially deposited by the collision is dissipated by ionization (Figure S3). The electronic kinetic energy integrated over atoms brings further insights into the relaxation mechanism. As expected, it is the atoms closest to the impact point that are the first ones to have their electronic kinetic energy increased, followed by fast (ca 100 as) energy damping and ultimately persistent oscillations on longer times. The other atoms respond with a delay depending on the distance from the impact point, the closer the atom to the impact the faster the local increase of electronic kinetic energy. The aforementioned features are signatures of intense dynamics taking place within the electron cloud even several hundreds of attoseconds after collision. This is also apparent in the movies showing the fluctuating TD-ELF isosurfaces. Somewhat surprisingly the Lewis structure of the molecule appears to be overall robust (see Figure 4 *f*). Simulations corresponding to case *ii*) (impact at the level of 6-members

ring NH group) with 1MeV particles lead to qualitatively similar conclusions. The main difference is that we observe initial disruption of the Lewis-VSEPR structure around the nitrogen atom, before relaxation. With 0.1 MeV alpha particles the energy delivered to the system is much higher (by a factor of almost two, Figure S3) and the electron cloud is clearly more affected. For instance the number of electron loss 2fs after collision, goes from ca 0.3 e- (1MeV) to 1.2 e- (0.1 MeV). Here again the ELF topological structure remains qualitatively robust (Figure S13).

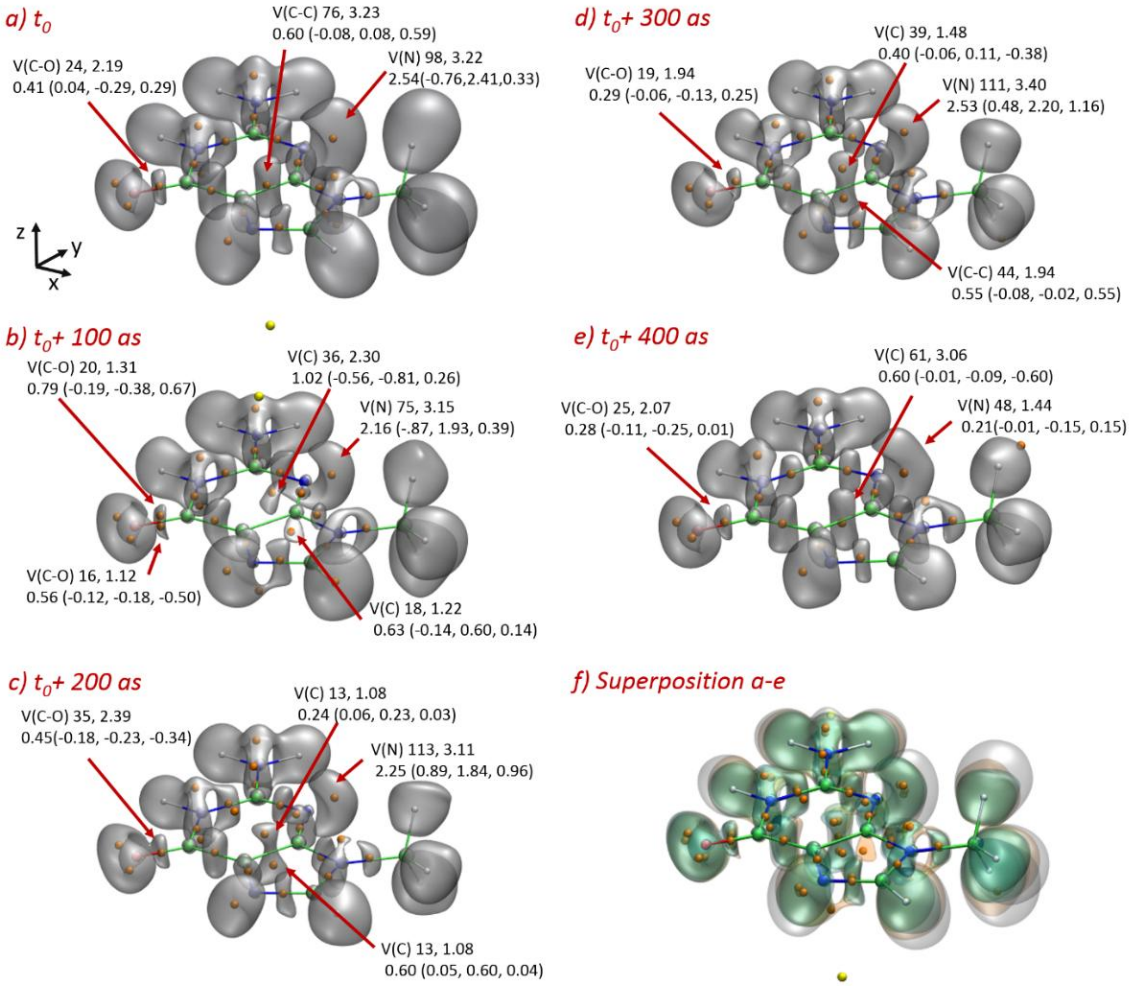


Figure 4: Topological analyses of TD-ELF after collision of guanine by a 1MeV α particle travelling along the z direction. a-e: for each TD-ELF topological basins we indicate, in order, the volume (Å^3), the electronic population and the intrinsic dipole moment (D, components in brackets). f: superposition of ELF isosurfaces (η=0.8) of snapshots a-d. Color code: green: carbons, white: hydrogens, blue: nitrogen, red: oxygen, yellow: helium (α particle) and orange: off nuclei ELF attractors. See also SI for movies.

To conclude, the extension in this Letter of topological analyses of ELF in the context of collision of molecules by high energy charged particles has enabled a fine characterization of the induced attosecond electron dynamics. Other topological descriptors such as the delocalization index δ_{AB}[36] could also be examined in the future. For irradiated guanine the ELF topology is surprisingly robust on the attosecond time scale despite the huge amount of energy deposited on the molecule upon collision. This overall stability of TD-ELF basins should however not mask the intense electron dynamics taking place within the electron cloud. Contrary to water, and presumably to other few atoms molecules, where ionization is the main relaxation pathway, guanine holds has a large enough electron cloud to relax energy, spreading out the deposited energy over the entire molecule. This may explain why the Lewis like structure is globally preserved even for 0.1MeV colliding particles. Nuclear motion should be included in future studies to account for energy dissipation into nuclear modes and possibly to fragmentations. Future studies will have to thoughtfully investigate the influence of environment on the very early steps following interaction of matter by IoR for example to characterize charge migrations or other ultrafast phenomena[37]. Recent implementations of RT-TDDFT within hybrid QM/MM schemes[25, 38-39] should find natural applications in that context. The herein presented analyzing tools should find a prominent place in such future investigations. We finally note that the herein developed approaches are readily application to other types of irradiations for example by photons.

ASSOCIATED CONTENT

Computational details on RT-TDDFT simulations. Movies showing ELF isosurfaces for selected trajectories of water and guanine molecules (mpeg format). The following files are available free of charge.

AUTHOR INFORMATION

The authors declare no competing financial interests.

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