

Controlling the Electrons Provides Means for Controlling Chemistry

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Chemistry is by and large considered to be the science of making and breaking bonds between atoms, forming chemical entities with fascinating material properties for nature and technology. Chemists consider themselves as architects using the periodic table of elements as building blocks. Of course everyone is aware that electrons are responsible for the chemical bond and in fact the chemical reactivity. Still classical chemical approaches are changing pressure and temperature which primarily affect the nuclei.

Ever since the beginning of photochemistry did physicochemists expect that chemistry is governed by the quantum mechanical state of the electrons. On the other hand the concept of molecular orbitals seems to imply that electrons cannot be steered. It is only now that scientists are able to show that this is indeed not true and that controlling the electrons ultimately provides means for controlling chemistry. Very recently a research team led by scientists at the FOM Institute for Atomic and Molecular Physics (AMOLF)^[1] has shown that it is possible to control the relative product yields of competing reaction channels by optical excitation of a molecule with ultrashort laser pulses specifically shaped for steering the direction of a chemical process. As a model system the authors have chosen the D₂ molecule. These D₂ molecules are ionized and dissociated by photons from a single femtosecond laser pulse around 760 nm. By controlling the absolute phase of the laser field the re-

maining electron can now be either localized on one or the other D atom, leaving the other nucleus bare, that is, detectable as a D⁺ ion. Now, normally one cannot distinguish from which D atom of the original D₂ molecule the D⁺ ion is coming from. If, however, the D–D molecules are oriented, for example, vertically in space, and the dissociation is anisotropic, it becomes feasible to distinguish the two D nuclei.

To understand and appreciate the fascinating development in this field it is helpful to recall a few technical and scientific prerequisites. Already since the development of the first laser by Maiman^[2] scientists have searched for shorter and shorter laser pulses in an attempt to push the limits of time resolution. Here, the last five years have brought us a real breakthrough with laser pulses as short as a few hundred attoseconds (1 as = 10⁻¹⁸ s)^[3]. Depending on the laser wavelength (respectively frequency) these ultrashort pulses may consist of only a few optical cycles. However, the temporal behavior of a laser pulse is not only defined by the duration but also by the phase. Typically the electric laser field $E(t)$ is expressed as shown in Equation (1):

$$E(t) = a(t) \cdot \cos(\omega t + \varphi) \quad (1)$$

where $a(t)$ is the envelope, ω the laser frequency, t the time and φ the carrier envelope phase (CEP). Pivotal to the current discussion is the CEP φ , which is illustrated in Figure 1 for a typical few cycle laser pulse as used by Kling et al.^[1] The difference between the two CEP's illustrated is obviously the sign of the electric field.

Not too long ago most scientists believed that the phase of a laser field did not matter in terms of photochemical

processes. In fact, it was only a few years ago that Corkum and co-workers reported the first experiment capable of determining the absolute CEP of a laser pulse.^[4] Consequently the stabilization of the CEP became feasible.^[5] Employing these ingredients Kling et al. now investigated the effect of the phase of a laser field on photochemical processes in the D₂ molecule.

The particular photochemical process under investigation by Kling et al.^[1] is the dissociative ionization of D₂. These D₂ molecules were optically excited by laser pulses around 760 nm with duration of about 5 fs leading to the formation of D⁺ and D. By only looking at those molecules lying on a preference axis defined by the laser field combined with the anisotropy of the dissociation process the authors are able to distinguish an "upper" and a "lower" D nucleus, which is detected as a D⁺ ion, if it does not carry the electron. Since the electron must reside with the other nucleus (thus constituting a D atom), this implies electron localization. If the CEP of the laser pulse is random, equal amounts of D⁺ ions are emitted into cones pointing upwards and downwards (relative to the laser polarization axis). If

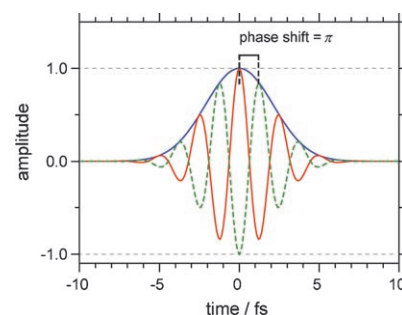


Figure 1. Illustration of two typical laser fields $E(t)$ at $\lambda = 760$ nm, duration: about 5 fs; red line $\varphi = 0$, green line: $\varphi = \pi$, blue line: envelope $a(t)$.

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the CEP is locked to $\varphi=0$ 60% of D^+ appear in the upper cone ($P_{\text{up}}=0.6$) and 40% in the lower cone ($P_{\text{down}}=0.4$). For $\varphi=\pi$ 60% of D^+ appear in the lower cone and 40% in the upper cone. This leads to an asymmetry parameter $A(\varphi)$ given in Equation (2) as defined by Kling et al.^[1]

$$A(\varphi) = \frac{P_{\text{up}} - P_{\text{down}}}{P_{\text{up}} + P_{\text{down}}} \quad (2)$$

The periodicity in CEP is $2\pi=360^\circ$ (see Figure 2).

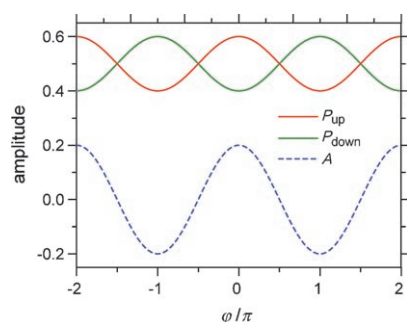


Figure 2. Schematic CEP dependence of the probabilities P_{up} and P_{down} and the asymmetry parameter A . Reconstructed from ref. [1].

The explanation given by the authors is based on a two-step mechanism, that is, the assumption that a D_2^+ ion is intermediately formed. Some of the outgoing electrons are turned around and recollide with the ionic core^[6] giving rise to a variety of fascinating effects (e.g. emission of attosecond X-ray pulses). One of these effects is the electronic excitation (recollision excitation) of the D_2^+ ion to the $2p\sigma_u^+$ state which is repulsive and leads to the formation of $D^+ + D$ with characteristic kinetic energy.

Several interesting questions appear immediately. On one hand the authors argue that coupling of the bonding ($1s\sigma_g^+$) and the antibonding ($2p\sigma_u^+$) electronic states of D_2^+ is crucial for the experiment. This coupling could also be connected to sequential excitation. On the other hand Kling et al. give evidence that switching from linear to circular polarization switches off those D^+ ions under investigation. This indicates that sequential excitation is not operative.

Additional experiments and theoretical calculations are required to resolve this issue.

It is by now well-known, that exciting several closely spaced vibrational states of a molecule with a short laser pulse, whose bandwidth covers all these vibrational states, will create a superposition of vibrational states. This is automatically equivalent to a coherent movement of the nuclei in space and time, often called a wave packet. This concept of localizing atoms in space (more precisely: at internuclear distance) and time^[7] is here extended to electrons, that is, the authors create an electronic wave packet by coupling two molecular valence states.

The concept of electronic wave packets is well-established in atomic physics, where it was first introduced to describe Rydberg state properties^[8] and more recently extended to the localization of electronic wave packets.^[9] It is worthwhile to mention that the application of Rydberg state spectroscopy to ion chemistry reveals evidence of what we call “inverse Born–Oppenheimer” situations, where the electronic dynamics is dominated by nuclear dynamics.^[10] A similar situation may in fact apply to the current experiment, where an electronic wave packet is coupled to a dissociation process. This raises the question to what extend the Born–Oppenheimer approximation is still an appropriate assumption for certain ultrafast chemical processes.

According to the picture presented by Kling et al. a superposition of the $1s\sigma_g^+$ (bonding) and $2p\sigma_u^+$ (antibonding) electronic states of the D_2^+ ion leads to an electronic wave packet oscillating between the two cores. Depending on the point in time, where dissociation effectively takes place, the electron will be localized on one or the other core; hence the other core is bare and will be detected as a D^+ ion. Ultimately, the explanation is based on two wave packets, one nuclear and one electronic. One interesting question pertains to the relation between these two wave packets. Can one of these wave packets be steered independently from the other, or are they inherently connected, perhaps even phase-locked? If so, we may ask: which is the master wave packet whose control

we are talking about? From the experimental point of view future experiments on the isotopomers H_2 and HD will be most rewarding, since only the nuclear wave packet should be affected by isotopic substitution.

A theoretical prediction of CEP control in the photodissociation of HD^+ ions has been reported by Roudnev et al.^[11] Their work explicitly goes beyond the Born–Oppenheimer approximation invoking that electronic and nuclear dynamics are strongly coupled. A complementary two pulse concept where creation of a nuclear and an electronic wave packet is steered by one and bond breaking by another laser pulse has been reported for HD^+ by Gronager et al.^[12]

The general effect of phase on photochemical processes was discussed by Korolkov et al.,^[13] Levesque et al.^[14] and more recently by Korolkov and Weitzel.^[15] Even more recent studies in our group revealed dramatic effects of the carrier envelope phase on the product branching ratio in the dissociation of DCI^+ ions.^[16] All these studies, however, only looked at the time evolution of nuclear wave functions without invoking electronic wave functions explicitly. Again, one key question for the future is connected to the relation between a nuclear and an electronic wave packet and to what extend this interplay can be described within the framework of the Born–Oppenheimer approximation.

Would the approach described by Kling et al. also work for a considerably longer pulse? From one point of view the answer is: no. The effect of absolute phase is most likely restricted to a few cycle pulses, probably less than about 15 cycles. In this context it is further important to consider the time dependence of the laser frequency ω . How many cycles are required for ω to be a meaningful quantity? It may also be interesting to look for CEP effects in the infrared (IR) where the field oscillations are much slower.^[15] We are used to thinking about IR experiments in terms of nuclear wave packets, but there is obviously also an electronic impact. In the other extreme limit of continuous-wave (cw) laser radiation, phase effects (although these are effects of relative phase) have also been shown to provide

access to controlling photochemical processes.^[17]

Is the concept transferable to other areas of chemistry? The next step will have to look at small heteroatomic molecules before possibly extending to very large molecules. Most likely it will not be the size of the molecule but the critical frequency of the reaction coordinate, which ultimately limits the applicability. We note, that one can control the branching ratio of product ions in the dissociative ionization of, for example, DCI even without phase-stabilized pulses.^[18] My personal feeling is that beyond the area of control of photochemistry and attosecond generation the current development in the field will most likely find application in optoelectronics, ultrafast diffraction and in chemical analytics.

At this point there are still many open questions in this fascinating area of ultrafast processes in molecules. We have

only started to understand, how electrons can be controlled by ultrafast laser pulses and what impact this will have on chemistry. But the time is ready for exciting new results, which are just waiting to be unraveled in the very near future.

Keywords: carrier envelope phase · control · electron localization · femtochemistry · laser chemistry

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