# Restructuring of Molecules with Lasers

## Hydrogen Migration Controlled with Laser Pulses

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Light can conduct the play of atoms and molecules in the microcosm. Humans manage to interfere with this play. Researchers from the Laboratory of Attosecond Physics (LAP) of the Max Planck Institute of Quantum Optics (MPQ) and the Ludwig-Maximilians-Universität (LMU) and from the Department of Chemistry of the LMU have now used light to reconfigure hydrocarbons. Using ultra-short laser pulses they removed an outer hydrogen atom from one side of a hydrocarbon molecule and directed it to the opposite side, where it rebounded. The method could be used in the future to synthesize new substances by controlling chemical reactions.

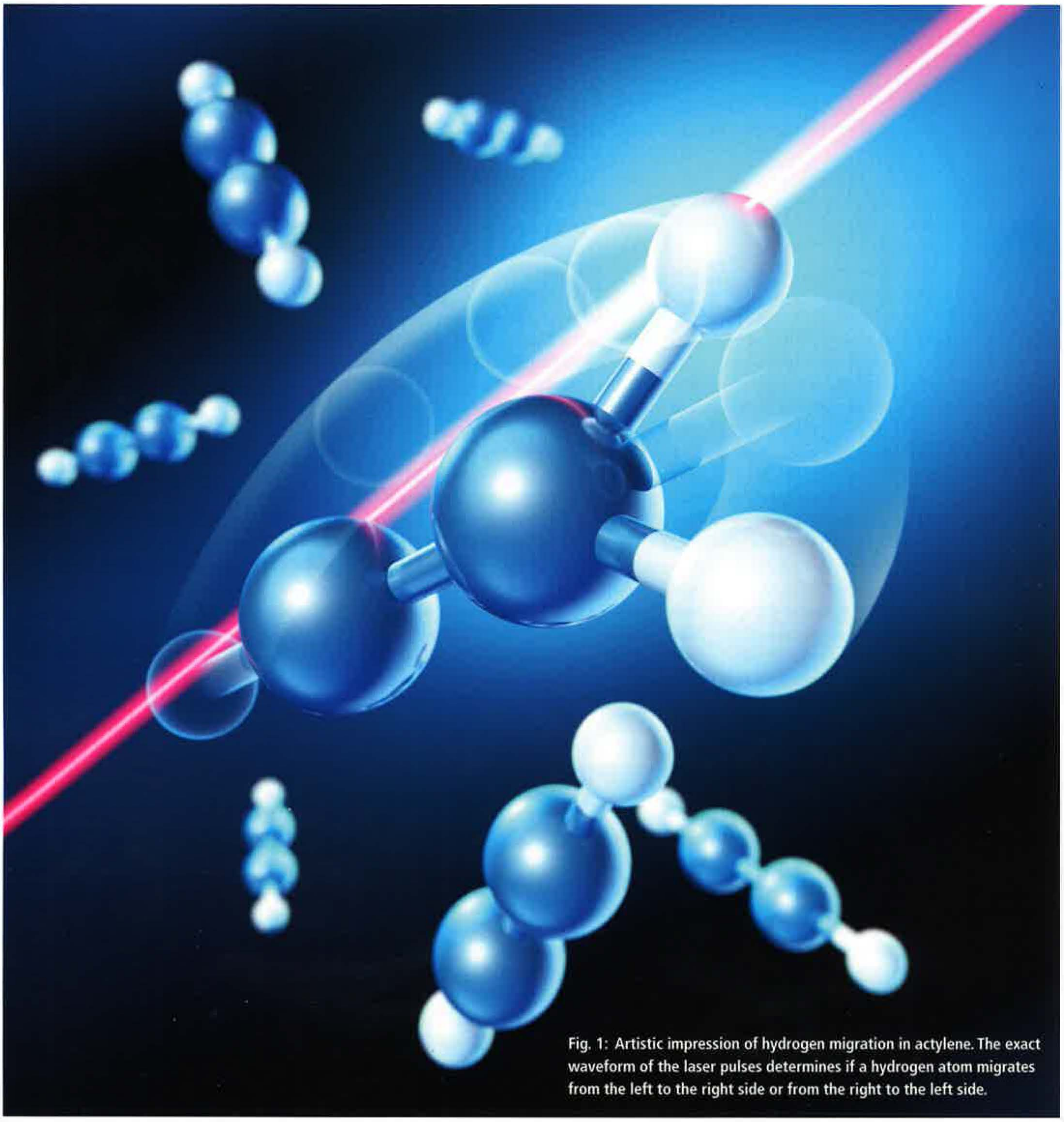

Fig. 1: Artistic impression of hydrogen migration in actylene. The exact waveform of the laser pulses determines if a hydrogen atom migrates from the left to the right side or from the right to the left side.

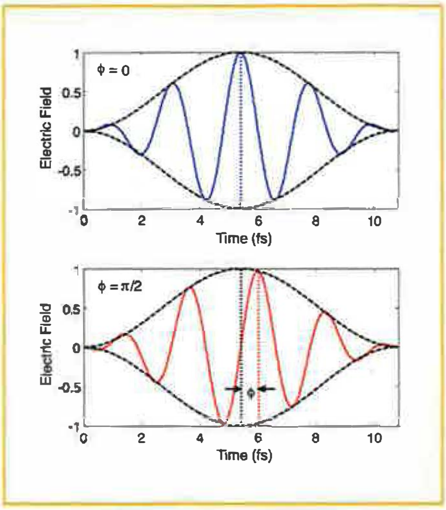


Fig. 2: Evolution of the electric field of a single-cycle laser pulse for two values of the laser phase φ.

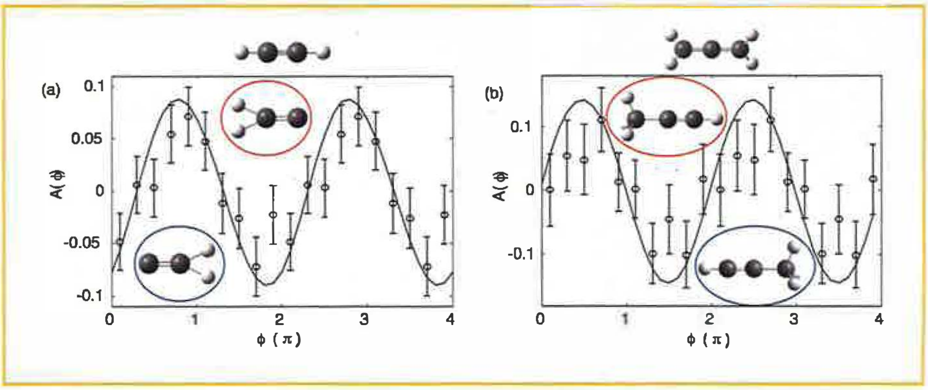


Fig. 3: Control of hydrogen migration in (a) acetylene and (b) allene. Shown is the asymmetry parameter for the hydrogen migration as a function of the laser phase. An asymmetry amplitude of 0.1 corresponds to a migration in one direction that is preferred over the other direction by 10 percent. The solid lines are the results of quantum chemical simulations. The ball-and-stick models (grey for carbon and white for hydrogen atoms) show the corresponding molecular structure after hydrogen migration for positive (red ellipse) and negative (blue ellipse) asymmetry parameters.

## Photo-Isomerization

Everything in these experiments happens unbelievably fast – within just a few millionths of a billionth of a second. An ultrashort laser pulse hits an acetylene molecule. The symmetric, linear hydrocarbon molecule with one hydrogen atom on each outer side starts to wobble, and is ionized. On an extremely short timescale, a hydrogen atom on one side becomes lose and migrates to the other side, where it rebounds. Vinylidene is formed from acetylene.

Such a restructuring of atoms in a molecule, induced by light, is generally called photo-isomerization. Photo-isomerization plays a large role in nature, for example in the visual process in human eyes and other vertebras, as well as in vitamin-D synthesis in human skin. The restructuring of atoms often results in clearly different chemical and physical properties of a molecule. The possibility to control photo-isomerization can therefore open up new perspectives in the catalysis and synthesis of new compounds.

## Hydrogen Migration with Tailored Laser Pulses

In experiments it was now achieved to control the direction of hydrogen migration with tailored laser pulses [1], where a bound hydrogen atom is steered from one side of the molecule to the other. Quantum chemical simulations show that this process is enabled by controlled laser-coupling of various vibrational states of the molecule.

Besides acetylene (ethyne), also the larger molecule allene (propyne) was studied. In both cases the hydrogen migration in the ionized state of the molecule was initiated and controlled via phase-stable laser pulses, which consist of about one oscillation of the electrical field (fig. 2). The phase stability results in an exactly reproducible electric field waveform for each of the pulses. A certain waveform corresponds to a laser phase φ, with a value that can be freely chosen. A change in the laser phase then results in a modification of the electric field waveform. The influence of the laser phase on the hydrogen migration process was studied with a so-called reaction microscope. This instrument measures the movement of charged particles and allows determining if a hydrogen atom migrated from the right to the left or from the left to the right side.

The vinylidene molecular ion, which is formed upon hydrogen migration from acetylene, is unstable and decays asymmetrically: one of the two carbon atoms has two hydrogen atoms bound to it, whereas the other carbon atom has no hydrogen attached anymore. This asymmetric decay is visualized with the reaction microscope and the direction of hydrogen migration is determined for each molecule. The number of registered hydrogen migrations for each side is recorded and analyzed as a function of the laser phase, and then brought into relation. The result is shown in fig. 3(a), which demonstrates the control of hydrogen migration with the laser phase.

In the case of allene, hydrogen migration leads to the formation of a propyne ion, which has three hydrogen atoms on one side, and only one on the other. The formation of the propine ion results with high probability in the split off of a tri-hydrogen ion, which informs about the direction of the preceding hydrogen migration. As depicted in fig. 3(b), the hydrogen migration in the larger allene can be controlled analogously to acetylene. This shows that the method also works for longer-chain hydrocarbon molecules.

## Underlying Mechanism

The experimental observations and the underlying mechanism were explained with quantum mechanical simulations. These compute the motions of atoms in the respective molecule during and after the interaction with the intense laser field. To cope with the computational effort in view of the many possible motions, the theoretical chemists used a trick: first, the influence of the laser field and its phase were computed. After the interaction of the molecule with an ultrashort laser pulse, the description of the molecule is switched to a carefully chosen coordinate system, in which the hydrogen migration can be described. The motion of migrating hydrogen atoms can then be depicted as a path on a potential surface, as shown in fig. 4. This way, the relation between the laser phase and the directional motion of the hydrogen atoms can be evaluated. The simulations reveal that the steering of the hydrogen migration becomes possible since the phase of the laser pulses is transferred to certain molecular vibrations. In combination with the ionization process, vibrational wave packets can be created, where an initial kick (to the left or right) is given to the migrating hydrogen. The kick depends on the laser phase and leads to directional hydrogen migration.

## Outlook

The work shows that it is possible to utilize intense laser pulses to not only control

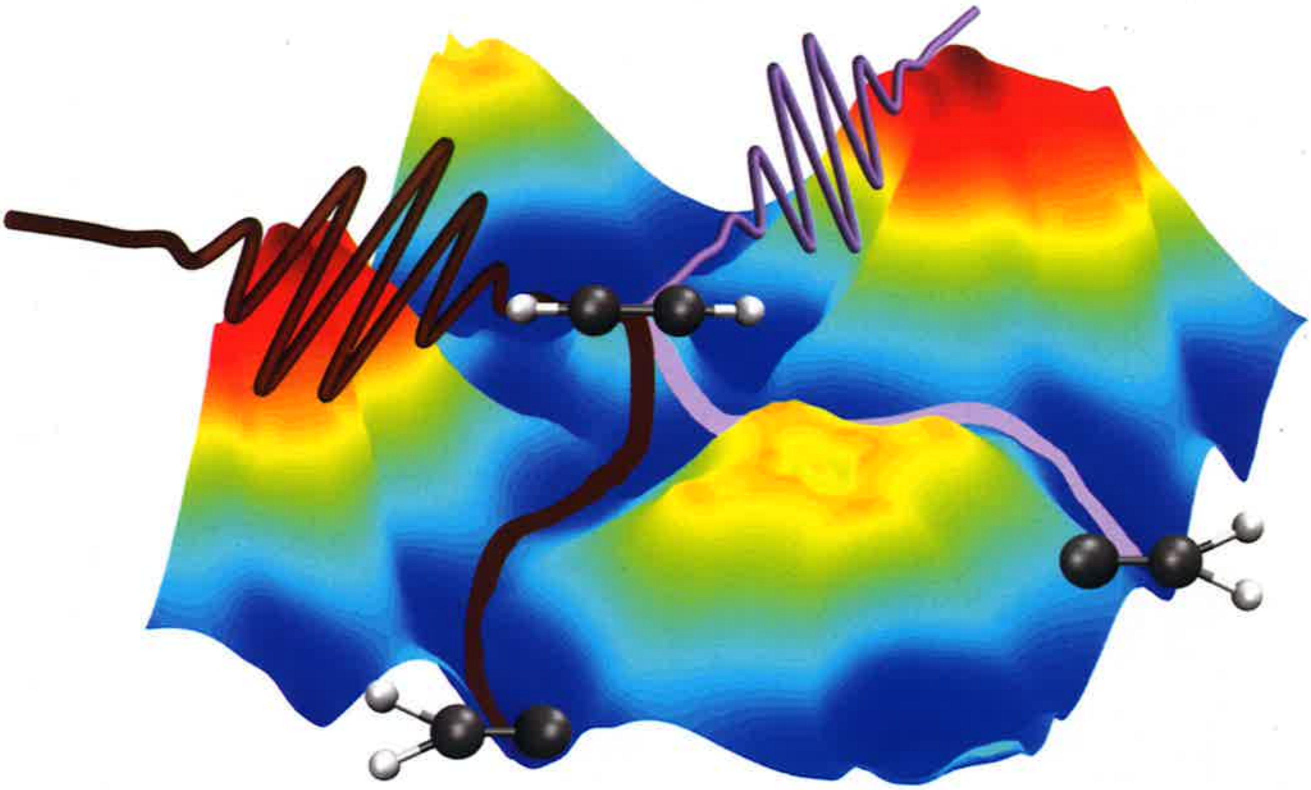

Fig. 4: Potential energy surface used in the simulations of hydrogen migration in acetylene. Each point on the surface corresponds to a certain configuration of the molecule: the initial, linear configuration of acetylene is the middle, while the valleys at the lower edge correspond to the vinylidene configuration. At the bottom valley both hydrogen atoms are on the left side and at the right valley they are found on the right side.

electrons in the microcosm, but also the about 2000-times heavier hydrogen atoms. Since the method is based on the excitation and manipulation of molecular vibrations, it can be used with all kinds of molecules consisting of many atoms. In the future is may thus be feasible to restructure complex molecules and synthesize new compounds. In particular in medicine and for the design of new pharmaceutics this perspective is very appealing.

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More about photoisomerization:
http://bit.ly/photoiso

Visual process in human eyes:
http://bit.ly/vis-proc

[1] All references:
http://bit.ly/GLJ-Kling