The development of ultrafast pulse techniques allows researchers today to monitor chemical dynamics within a molecule, which holds important implications for our understanding of the underlying quantum mechanisms behind chemical reactions. Based at the Hebrew University of Jerusalem, Professor Daniel Strasser and his colleagues are developing a novel approach for time-resolved imaging of structural dynamics at an unprecedented level of detail. "We are trying to use a new type of radiation source. In the high-order harmonic generation (HHG) source, amplified femtosecond laser pulses in the near-infrared (IR) are focused onto an atomic gas target producing ultrafast bursts of EUV light," he explains. This approach generates pulses at a high photon energy as well as a very high bandwidth, opening up new possibilities in research. "You can open up a new window beyond the femtosecond (10⁻¹² of a second) time scale, going into the attosecond (10⁻¹⁸) regime, where we could look then not just at the dynamics of atomic nuclei moving inside a molecule, but even at the dynamics of electrons, which form the chemical bond," says Professor Strasser.

**Reaction dynamics**

This research is built out of a recognition of the difficulty of calculating the properties of complex chemical systems. While quantum mechanics can be applied to describe how atoms, molecules and electrons behave, calculating how a system will behave on the quantum level remains a very challenging task. "This is a difficult computational task to perform exact calculations, so to speed-up computations we use certain approximations. In order to know which approximations can be applicable, we need to first understand the underlying chemical mechanism," outlines Professor Strasser. While state-of-the-art quantum chemistry calculations have been successfully implemented to calculate and predict the molecular ground state, and provide detailed insights into the molecular structure, Professor Strasser says there are limits to our existing knowledge. "Currently, ab-initio theoretical descriptions of chemical reactions have limited predictive power to describe excited state dynamics in which one chemical bond is broken and another is formed. This is essentially what we need to better understand in order to improve the synthesis of new materials, of new chemical compounds," he explains. "Presently, this know-how is still largely the result of trial-and-error experiments, designed based on the professional intuition of very experienced individuals."

A general method for monitoring reaction dynamics over very short timescales would give researchers more information and lead to deeper insights into chemical reaction mechanisms, a goal which lies at the core of Professor Strasser’s work. Researchers in the project aim to develop a new experimental instrument, including an HHG source for ultrafast EUV pulses, so that scientists can visualise chemical reactions during the making and breaking of chemical bonds. "Our experiments can then guide theorists towards making improved approximations and developing better calculation codes that can be tested against the experimental data. This detailed dynamical understanding of how one bond breaks and another is formed could then potentially guide the synthesis of new materials," explains Professor Strasser. For example, "Imagine that you discover that a molecule in a particular shape would be a great drug for treating cancer," continues Professor Strasser. “State-of-the-art quantum chemical calculations could be performed to predict the stability and structure of the potential new drug. However, the ability to synthesise the new molecule would still rely heavily on intuition and a lengthy trial-and-error approach.”

While some quantum chemistry codes have been developed to treat dynamics, even the most sophisticated computers struggle when asked to predict a chemical reaction in which a chemical bond breaks, an issue Professor Strasser and his colleagues are working to address. "My idea is that if we can experimentally visualise bond breaking, and test against state-of-the-art calculation methods, at some point we’ll be able to achieve the same understanding of reaction dynamics as we currently have for ground-state structure,” he outlines. A lot of the existing time-resolved techniques are spectroscopic methods which rely on prior theoretical understanding of the molecular system, but Professor Strasser and his colleagues are developing a different approach. "We are trying, in principle, to minimise the need to rely on prior knowledge. One way to directly visualise the structure of small molecules is called Coulomb explosion imaging,” he says.

**Looking at new exciting photo-chemical processes such as multiple-detachment of molecular anions.**

Professor Daniel Strasser explains: A number of different methods are available to monitor and probe the dynamics of chemical reactions, now researchers are developing a novel approach using ultrafast EUV pulses. This approach could help scientists gain new insights into structural rearrangements and build a deeper understanding of how chemical bonds are made and broken.
**Coulomb explosion imaging**

This method takes advantage of the Coulombic repulsion between nuclei that occurs when the electrons responsible for chemical bonding are removed. The positively charged nuclei are in a repulsive state, which leads to a molecular explosion, offering scientists a window into the structure of the molecule. “The Coulomb force is inversely proportional to the distance square. If you have charges that are close together, they will release more energy, while if charges are further apart, they will release less energy. Using our coincidence fragment imaging method, in which we measure the released energy and the correlations between different fragments of a single molecule, we get a direct glimpse into the structure of the molecule when the electrons were removed,” explains Professor Strasser. Using this method at different stages during a chemical reaction will allow researchers to probe the time evolving molecular structure. “Using the ultrafast bursts of high energy photons produced by HHG will allow us to remove multiple electrons at a controlled time and initiate time-resolved Coulomb explosion,” continues Professor Strasser. “We basically want to produce a movie of the chemical reaction dynamics evolving in real time.”

A good example of such a scenario is double proton transfer, which is known to be an important DNA damage mechanism. While the importance of double proton transfer has been known for many years, debate continues about how it happens, a topic which Professor Strasser says could be investigated in greater depth using the new time resolved imaging method. “A DNA base pair, which is connected by hydrogen bonds, can be excited into a proton transfer state, leading to a sudden change of structure, called tautomerization, where each part gives its proton to the other,” he says. Earlier time-resolved experiments left certain questions around this unanswered, in particular whether the protons are exchanged in concert or sequentially. “Some researchers believe it is a sequential proton transfer, meaning that a first proton is transferred on a time scale of a few hundred femtoseconds, and only a few picoseconds later is the second proton transferred,” explains Professor Strasser. “There’s still some disagreement over this, with different theories to support different hypotheses.”

This is a topic that Professor Strasser plans to revisit once the imaging method has been refined further, while it will also be tested on other simple molecules, such as methanol and methyl iodide. A large amount of work has already been done on methanol, yet Professor Strasser says the project team has opened new interesting questions. “For example – when you remove two electrons from the Methanol system, you can drive dynamics in which a proton migrates from the methyl to the oxygen, forming a water H2O+ cation observed in coincidence with a CH3+: In other events we observe breaking of all three C-H bonds of a single methanol molecule and the formation of two new bonds producing a stable H3+: fragment,” he outlines. Once the method has been tested on these molecules it will then be applied on less well-known systems, in which researchers don’t know what is happening in certain reactions, while Professor Strasser also plans to continue his research into the development of new methods. “My main interest is in performing better experiments,” he stresses. “We’re always expanding our toolbox of methods for looking at new exciting photo-chemical processes such as multiple-detachment of molecular anions. My main goal is to understand how chemical bonds break and how they are made.”