

## ULTRAFast OPTICS

## Imaging a chemical reaction

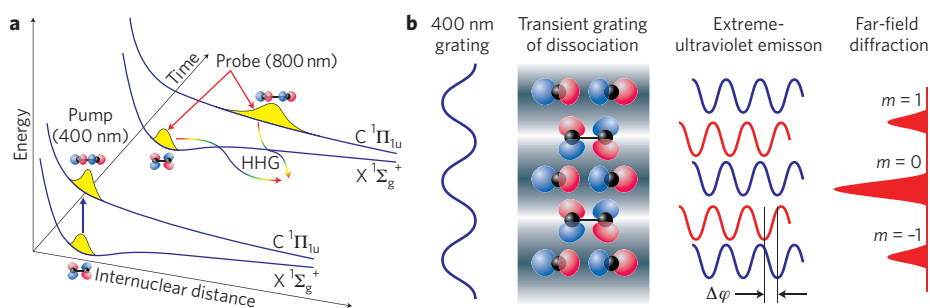
High-harmonic interferometry can be used to measure the amplitude and phase of light emitted from molecules. This method has now been used to reveal the ultrafast dynamics of electrons and nuclear interactions during a chemical reaction.

Anh-Thu Le and Chii-Dong Lin

Gaining complete control over chemical reactions has been the dream of chemists and physicists for decades. To achieve this goal, one must first be able to follow and characterize (or ‘image’) the dynamics of the coupling between electronic and nuclear motion within molecules on a femtosecond timescale. This has been traditionally achieved using the pump–probe scheme, which involves delaying two ultrashort laser pulses with respect to each other. The first pulse — the pump — creates excited states in molecules to initiate a chemical reaction. These molecules are then imaged by a second pulse — the probe — at different points in time following the excitation. Because ultrashort pump pulses can typically excite only a small fraction of molecules at a time, signals from molecules undergoing chemical transformation are much weaker than signals from ground-state molecules, thus making the task technically challenging.

Wörner *et al.* have now overcome this difficulty by introducing a transient grating technique to measure the high-order harmonic generation (HHG) from excited molecular bromines in real-time as they dissociate<sup>1</sup>. At the heart of their experiment is an 800 nm Ti:Sapphire laser that has its output split to generate both the pump and probe pulses. The pump consists of two synchronized second-harmonic (400 nm) pulses of 40 fs duration that cross in a gas jet and interfere to form a transient intensity grating (Fig. 1), which gives rise to a pattern of alternating planes of excited and unexcited molecules. Following excitation, the repulsive dissociative  $C^1\Pi_{1u}$  state of molecular bromine dissociates into two bromine atoms. The fraction of initial molecules excited was close to 10%.

The probe — a time-delayed 30 fs, 800 nm pulse — was used to measure the high harmonics generated from the time-dependent coherent superposition of the two electronic states in this transient grating at different time delays. The grating causes the high-harmonic radiation to diffract into several orders. From the intensities of the zero- ( $m = 0$ )



**Figure 1** | Pump–probe scheme for the high-harmonic transient grating interferometry of dissociating  $\text{Br}_2$ . **a**, Schematic of the potential energy curves of the ground and excited states of  $\text{Br}_2$ . Coupled electronic and nuclear wave functions are prepared by two pump pulses (400 nm) and subsequently interrogated by a delayed probe pulse (800 nm). **b**, Two synchronized pump pulses set up a transient grating of dissociating  $\text{Br}_2$ , from which high harmonics are generated by a probe pulse. Harmonic signals are recorded in the far-field as diffraction patterns.  $\Delta\varphi$  is the phase difference between high harmonics from the excited state and the ground state.

and first-order ( $m = \pm 1$ ) diffraction, the amplitude and phase of the harmonics from the excited state relative to the ground state were extracted as a function of time delay and harmonic order.

Measuring the amplitudes and phases of the harmonics allows the molecular targets to be characterized. Although this has already been accomplished for ground-state molecules<sup>2–4</sup>, the transient grating interferometry approach of Wörner *et al.* enables the structure of the excited molecules to be studied. This approach is analogous to optical holography in many ways, as a hologram is created when the light scattered from an object is allowed to interfere with a coherent reference beam. Instead, in the work of Wörner *et al.*, the coherent nature of HHG allows the unexcited molecules within the transient grating to function as a reference from which the amplitude and phase of HHG from the excited molecules can be obtained.

Pump–probe experiments of bromine have been carried out previously by Leone and others<sup>5</sup>. They chose to measure the photoelectron spectra using the extreme-ultraviolet high harmonics (mostly 17th order) of the 800 nm pump pulse. High-resolution spectra were taken to

distinguish the photoelectrons emitted by  $\text{Br}_2$  from those of the two dissociated Br atoms, but this limited the probe pulse to hundreds of femtoseconds. Based on such measurements, it was concluded that atomic-like electron spectra appear in the range of 40–85 fs.

There are several reasons why probing the excited molecules using high-harmonic interferometry combined with the transient grating technique is more advantageous than femtosecond photoelectron spectroscopy. HHG is highly selective to the binding energy of each molecular state, therefore making the valence and excited electrons more ‘visible’ than the inner shell electrons. Perhaps more importantly, the amplitudes and phases of many harmonics are simultaneously determined in a single measurement that it is equivalent to probing the excited molecules using light of many different wavelengths. In fact, this technique is better than simply using many different wavelengths as the phases are useful for revealing the structure of the excited molecule at each time delay.

As in any pump–probe experiment, theoretical models are used to extract structural information from the probe signals. Under simple assumptions, harmonic amplitudes and phases can

be used to infer interatomic separations as well as the orbital symmetry of the molecule. The extraction procedure used by Wörner *et al.* is strictly valid only for relatively large time delays, when the nuclear wavepackets from excited and ground states do not overlap. From such data they concluded that the excited Br<sub>2</sub> molecule is atomic-like at around 300 fs after the pump pulse, which is significantly longer than the 40–85 fs extracted from the photoelectron spectra. In principle, HHG signals of different harmonic orders all contain the same information about the molecular structure of the target. This fact can probably be exploited in the future with the help of more advanced theoretical modelling<sup>6</sup> to obtain more accurate structural information of the target.

With today's ultrafast lasers and the emergence of extreme-ultraviolet to X-ray free-electron lasers, scientists now have

access to an array of light pulses with durations ranging from femtoseconds down to attoseconds over a broad spectral region. Imaging a chemical reaction requires various tools to be exploited. Although ultrafast electron diffraction or ultrafast X-ray diffraction may emerge as general tools for characterizing the conformational change of a chemical reaction<sup>7</sup>, understanding the change of chemical bonding in a reaction requires probes that interact strongly with valence and excited electrons. In this regard, probing the dynamic structural change with harmonics emitted in a transient grating may become a powerful tool, although the method may have to be tailored to specific dynamic systems. It will be exciting to see how this method applies to more complicated polyatomic systems, particularly the fast electronic structural changes near the conical intersection,

where two potential energy surfaces of the same symmetry are degenerate. To extract structural information from such complex measurements, however, will require significant advances in theoretical simulations. □

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#### VIEW FROM... SPIE OPTICS AND PHOTONICS 2010

# Optics and chemistry meet

Research into photochemical reactions is now yielding promising ways of converting solar energy into convenient forms of chemical energy that can be easily stored.

David Pile

Photochemistry — the use of light in a chemical reaction — is now becoming a mainstream research area of photonics thanks to the growing interest in energy-rich sustainable fuels such as hydrogen. This was the clear message at the recent SPIE Optics and Photonics meeting this August, which took place in San Diego, USA, and attracted 4,250 registrants.

Topics covered at the conference ranged from metamaterials and photovoltaics to a particularly popular 'Life in the Cosmos' session, which was moderated by laser pioneer Charles Townes and organized by Richard Hoover, astrobiologist group leader at NASA Marshall Space Flight Center. Photochemistry was one topic in particular that, although certainly not the most popular topic discussed, stood out as gaining significant momentum. Talks focused on photocatalysts — materials that enhance light-induced chemical reactions — and their role in generating hydrogen or splitting water for use as solar fuels.

Andrew Bocarsly from Princeton University in the USA discussed the catalytic conversion of CO<sub>2</sub> into methanol, and explained that a major motivation for



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The SPIE Optics and Photonics conference hosted presentations on a broad range of topics, with a particular emphasis on photonics.

studying photochemistry is the generation of fuels and organic compounds from non-petroleum-based sources, as well as the need to find ways of reducing CO<sub>2</sub> emissions. The systems developed by his team, although currently only at the laboratory level, are designed to take a high CO<sub>2</sub> content gaseous waste stream from a power plant or cement factory and, using sunlight, convert it into alcohols and related species that have high energy

densities. The team currently uses high-intensity LEDs with illuminated electrode areas of ~0.1 cm<sup>2</sup> as excitation sources, but aim to develop a larger-area system spanning many square metres that operates under standard sunlight conditions.

"We have demonstrated that a photoelectrochemical cell based on a p-type III–V semiconductor photocathode such as GaP, GaAs or GaInP<sub>2</sub>, together with an aqueous electrolyte containing pyridine as a catalyst, efficiently reduces CO<sub>2</sub> to methanol when the bandgap is illuminated," Bocarsly told *Nature Photonics*.

"Although the optical conversion efficiency was only a few percent at a wavelength of 465 nm owing to the indirect bandgap, irradiation at 365 nm, which excites the p-GaP direct bandgap, achieved an optical conversion efficiency of ~10%. More recently we have been investigating a p-GaAs-based system, as the p-GaAs direct bandgap of ~900 nm is well-matched to the solar spectrum, thus allowing good optical conversion efficiencies to be achieved."

The use of light to generate hydrogen is also a topic of intense research.