remain unreacted following photoirradiation (Fig. 1g). This is due to the relative positioning of the barrel-shaped molecules in the precursor crystal; one unreacted barrel then acts as a template around which other barrels are organized and react to form the polymerized crystals. Such levels of structural detail would be extremely challenging to obtain without single-crystal X-ray studies.

Both studies report that the polymerized crystals can be exfoliated into two-dimensional sheets by dispersing polymerized crystals in 1-methyl-2pyrrolidone for a number of days at 50 °C. Analysis of the resulting materials using atomic force microscopy and scanning electron microscopy showed that aggregates of sheets were the major products; however, in some instances individual monolayer sheets could be found. Schlüter and co-workers go on to demonstrate that the sheets are

sufficiently robust to support their own weight by suspending aggregates of sheets — made up of around three layers of two-dimensional polymers - across micrometre-scale holes. This remarkable demonstration reveals properties that are unlikely ever to be achieved using molecular or supramolecular materials and the advantage of exploiting covalent bonding in the formation of such large two-dimensional structures.

The reports by King and Schlüter illustrate great potential for the preparation of two-dimensional materials. The ability to tailor the structure of the materials at the molecular level, to characterize the systems using single-crystal X-ray diffraction and to subsequently isolate individual sheets is a tantalizing vision for chemists and materials scientists alike9. However, the vision undoubtedly spreads far beyond to physics communities, particularly those interested in unusual electronic and optical

properties, and to biological communities, for whom sheets with tailored pores have great potential as membranes. The future of these materials is undoubtedly bright, and I have no doubt that this is a field that will grow and grow.

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OUANTUM CONTROL May the electric force be with you

Intense laser fields can apply strong forces to molecules, distorting molecular potentials. Now, these effects have been used to precisely control the branching ratios of a polyatomic photodissociation reaction.

Albert Stolow

lectric forces underlie all of chemistry. Ultimately, it is the rearrangement of charges and their associated electric fields that governs chemical reactivity. The actions of catalysts and enzymes may be understood in this way: they interact - through electric fields - with specific bonds or moieties within a reagent, which affects both structure and energetics. By applying electric forces with very high spatial precision, catalysts and enzymes can 'stabilize' a transition state relative to reagents or products, thereby exponentially enhancing reaction rates. There is, however, another way to apply electric forces to molecules, namely through laser fields a method known as 'quantum control'¹. Modern short-pulse lasers can apply precisely timed electric forces that are of strengths comparable to the forces that bind matter itself, and the implications of this are just starting to be worked out. Now, writing in Nature Chemistry, Solá, Bañares and colleagues describe² a laser-based method for controlling branching ratios and product kinetic energy distributions in the photodissociation of CH₃I.

Light, an oscillating electromagnetic field, interacts strongly with charged particles such as electrons, predominantly through electric forces. One usually thinks of laser light as inducing spectroscopic transitions in molecules, provided that the associated transition is optically allowed and that the light is resonant (non-resonant light has no effect). This picture, however, really only applies when the laser field is very weak. It may surprise readers that, as lasers get stronger, even non-resonant fields can have effects on molecules and solids. This is because molecules in electric fields experience energy-level shifts - a wellknown phenomenon called the Stark effect. This effect can not only shift energy levels, but, because it is coordinate-dependent, it can also even distort potential energy surfaces. Usually, these effects are tiny; however, a strong non-resonant laser field allows the application of electric fields orders of magnitude stronger than can be conventionally applied by, for example, high-voltage power supplies. Strong electric forces can indeed be applied to molecules, with great control.

What is the nature of this laser 'electric field' control? The wavelength of light is much longer than the size of a molecule, so the entire molecule feels the same electric field. This is quite different from catalysts or enzymes, which apply electric fields at very specific locations within a molecule. However, laser electric fields can be applied with great precision in their timing, leading to an alternative approach to enhancing or controlling chemical reactivity. In its most general implementation, strong non-resonant (for example, near-infrared) laser fields lead to a dynamic Stark control effect that distorts molecular potentials, but without any net absorption of light, as illustrated in Fig. 1. Here, a given chemical reaction, starting as reagents at the red arrow, may proceed towards the set of products B via its minimum energy pathway, the reaction coordinate. The idea of dynamic Stark control is that applying a laser electric field at a specific time — as the reaction is transiting the transition-state region leads to a distortion in the potential energy surface and re-directs the reaction towards





the set of products **A**. Since there is no net consumption of photons, the laser field acts as a catalyst rather than as a reagent. This type of control is exerted through the timing and strength of the laser field and was previously demonstrated for the photodissociation of a diatomic molecule³. It is more challenging to apply dynamic Stark control to polyatomic molecules because their typically smaller electronic level spacings lead to multiphoton absorption and, therefore, higher-excitedstate chemical reactions. Other approaches must be considered. Rather than avoiding all resonances, an attractive method of strong laser-field control over molecular dynamics is to make use of a specific resonance, but in the strong-field regime. This is the domain of light-induced conical intersections (LICIs)⁴. In a strong field, a resonance can be thought of as 'lifting' the ground state up by the photon energy whereby it intersects the excited state. In general, the crossings of excited states of polyatomics form conical intersections. In this case, the conical intersection exists only while the laser field is on, hence the term LICI. Solá,

Bañares and colleagues provide the first demonstration² of light-induced conical intersection control over photodissociation dynamics in a polyatomic molecule. Using a laser pulse longer than the reaction timescale, the authors demonstrate that a LICI can be induced and that branching between ground- and excitedstate photochemistry may be controlled. They studied the photodissociation of CH₃I, which photofragments through a major product channel that gives CH₃ and an excited iodine atom, I*. However, by varying the strength, duration and timing of a laser control field, they show that they can open up another product channel — through the creation of a LICI - which gives CH_3 and a ground-state iodine atom as products. The authors go further with even stronger laser fields. They show that by using a laser pulse shorter than the reaction timescale, the states that form the LICI become themselves distorted due to the dynamic Stark effect, forming light-induced potentials. In CH₃I photodissociation, the precise timing of the light-induced potential manifests itself as a modification of the kinetic energy released by the CH₃ product.

Solá, Bañares and colleagues have described an important step in the use of stronger laser fields to control neutral chemical reactions in larger molecules. Importantly, this is achieved without the use of multiphoton transitions, which invariably lead to higher-excited-state chemistry. The challenge for this field will be to control total reaction yields more generally, such as in solution, but in such cases the strong field polarization response of the solvent must be taken into account. This will introduce both challenges and opportunities. Nevertheless, there are many knobs to turn, including laser frequency, intensity, pulse shape and polarization. Whether by non-resonant means or by judicious use of resonance as in the case here, strong laser fields open new avenues to applying timed electric forces to reacting molecules.

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