

## QUANTUM CHEMISTRY

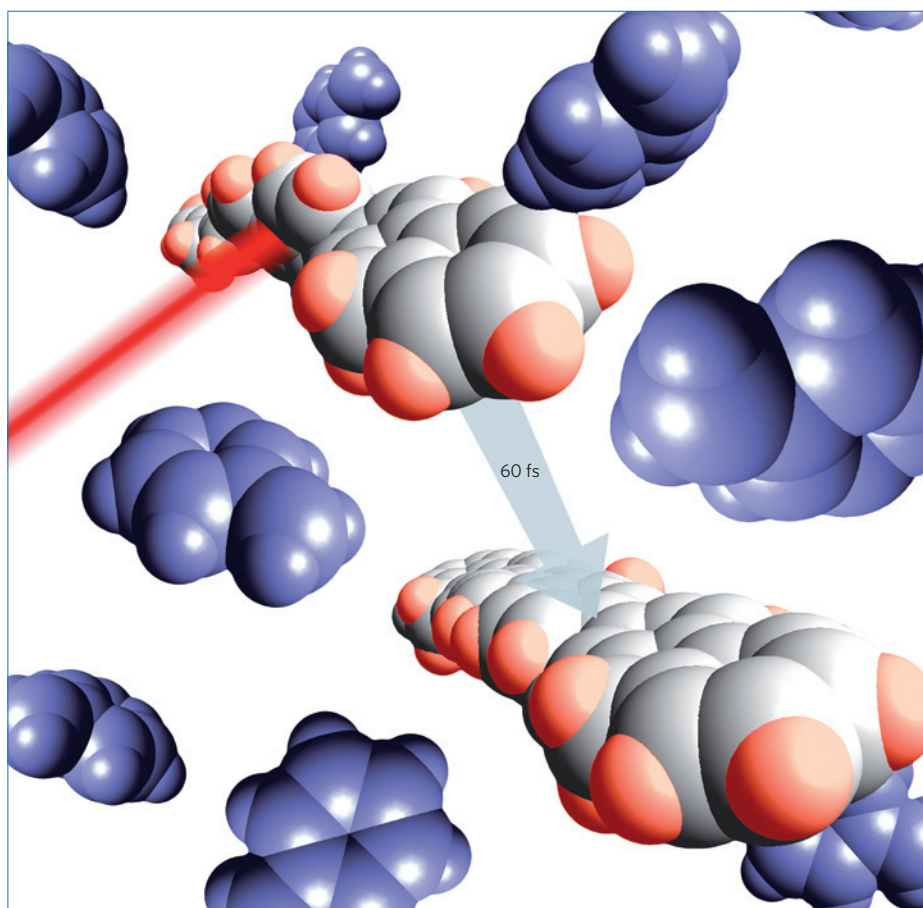
# A lightning-fast change

A single photon can alter the shape of a molecule. It is now shown that quantum effects can play an important role in this change leading to conformation relaxation rates hundreds of times faster than previously expected.

Shaul Mukamel

Conformational relaxation is one of the most common photophysical processes that occur in large conjugated molecules upon photoexcitation; bond angles and lengths adjust to a new excited-state geometry in a motion that is typically overdamped by friction. Jenny Clark and her colleagues, reporting in *Nature Physics*<sup>1</sup>, have now discovered that, under the right circumstances, such torsional reorganization can be ultrafast, occurring in less than a vibrational period — two orders of magnitude faster than is typical for such motion. The authors used a pump–probe technique: an oligofluorene molecule in solution was pumped by a femtosecond laser into a specific electronic state. The changes in absorption for a second probe pulse sent at a variable delay were then used to monitor the flattening dynamics of the molecular structure. The torsional mode responsible for these dynamics was pumped by electronic relaxation following the optical excitation and acquires high energy in a short time scale (100 fs), which induces an inertial, frictionless motion that results in a large configurational change.

Ultrafast torsional relaxation following photon absorption can drive reactions such as the *cis*–*trans* isomerization that is the primary step of vision. Torsional motions have low frequencies compared with typical intramolecular vibrations. Moreover, coupling to the surrounding solvent and to other vibrations causes friction. Thus, the motion is strongly overdamped, which leads to slow (tens of picoseconds) relaxation. It is well known, however, that friction does not occur instantaneously<sup>2</sup>; the effect of friction cannot be felt at timescales shorter than those of the intermolecular collisions. In this short-time regime, nuclear motions are inertial, frictionless and fast. Technically this shows up as ‘memory effects’ in the equations of motion: the



Conformational change. Laser light can bring fluorene molecules into a flat geometry much more quickly than was previously thought possible.

damping rate associated with friction should be replaced by a memory term that vanishes at short times, and friction only sets in for times longer than the collision time. Another manifestation of this memory is that the velocity correlation function of a Brownian particle in solution has a Gaussian short-time dependence that eventually becomes exponential. This is well established experimentally and by computer simulations.

The mechanism for pumping high energy into the torsional mode is quite intriguing: it consists of a series of non-adiabatic transitions involving motions of both the electrons and the nuclei. Theoretical simulations demonstrate that non-adiabatic transitions and conical intersections<sup>3</sup> during internal conversion can efficiently convert electronic potential energy into torsional kinetic energy, causing the inertial sub-100 fs torsional

reorganization. Inertial intermolecular solvent motion was investigated in the 1990s by time-dependent fluorescence Stokes-shift experiments of solutes. The study by Clark and co-workers<sup>1</sup> represents the first demonstration of this effect for intramolecular torsional motions.

This study has broader implications in other important areas of chemical dynamics. Intramolecular vibrational relaxation (IVR) is an important mechanism for fast energy exchange between vibrational modes in molecules and is caused by anharmonicities. As a result of this process, energy usually rapidly equilibrates before chemical reactions can occur. The good news is that this makes it possible to predict reaction rates over many orders of magnitude using statistical arguments by comparing the entropy of reactants, products and the transition state. This is done by simply counting volumes in phase space. The idea dates back to Niels Bohr and John Wheeler, who applied it to nuclear fission<sup>4</sup>, and in chemistry it forms the basis for the celebrated Rice–Ramsperger–Kassel–Marcus theory of unimolecular reactions<sup>5</sup>. The bad news is that IVR makes it hard to control and manipulate the rates and outcomes of chemical

reactions. Chemists have long sought ways to beat the statistics and achieve ‘laser-selective chemistry’, where energy pumped into a specific mode can induce a reaction before equilibration with other modes. This could lead to new reaction products and may offer a degree of control not possible by conventional thermal excitation. Early attempts in the 1970s to use strong infrared lasers to perform multiphoton dissociation by pumping energy into a selected bond eventually showed that IVR wins<sup>6</sup>; the laser turned out to be an expensive heating device. Since then there has been much progress in designing selective excitation schemes that beat IVR by making use of coherent control techniques. Although Clark *et al.* did not study a reaction, their investigation demonstrates a selective laser-pumped non-thermal photophysical process that can be controlled. Not all excited states show this fast relaxation. By selecting the excited state, the molecule either slowly planarizes or suddenly locks into a flat geometry.

Apart from the fundamental interest in the study of competing intramolecular energy channels, the work by Clark and co-workers also has possible implications for the design of artificial devices. Organic materials offer a much broader

dynamical range of parameters and are easier to process compared with inorganic semiconductors; however, they are more fragile and photochemistry may complicate or hinder the device operation. Furthermore, selectively pumped torsions may be exploited for fast optical switching between bistable states in artificial photochromic systems<sup>7</sup>, and understanding and controlling the mechanism of intramolecular rearrangements may help the design of new non-linear optical devices. □

Shaul Mukamel is in the Department of Chemistry, University of California, Irvine, California 92697-2025, USA.  
e-mail: smukamel@uci.edu

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## OPTOMECHANICS

# The stress of light cools vibration

Brillouin scattering of light is now shown to attenuate the Brownian motion of microscopic acoustic resonators. This electrostrictive phenomenon could be a useful complement to the ponderomotive and photothermal effects that can optically control optomechanical systems.

Ivan Favero

Optomechanics studies the coupling of light to the motion of mechanical systems. After a pioneering exploration of the basic concepts in the 1970s (ref. 1), it has recently become a burgeoning field of research at the interface of optics and condensed-matter and mesoscopic physics<sup>2–5</sup>. A stunning manifestation of optomechanical phenomena is using the mechanical effects of light to cool the motion of a system to ultra-low temperatures and reveal its quantum behaviour. Such experiments have now started to test the tangible quantumness of mesoscopic mechanical systems<sup>6–8</sup>, with the aim of better understanding the classical–quantum

boundary and the quantum limits of mechanical sensing.

Mechanical effects induced by light on solid-state systems take many forms: radiation pressure ‘pushes’ on a reflecting wall; optical tweezers use ponderomotive effects to manipulate dielectric objects; photothermal effects distort optically absorbing structures. All of these phenomena have been extensively used in recent research in optomechanics to optically control, excite and cool the motion of various micro- and nanomechanical devices. Electrostrictive effects, however, had until recently remained little explored in this context<sup>9</sup>.

Electrostriction is a well-known phenomenon that occurs in fluids of polarizable molecules or in dielectric materials: under an applied electric field the material elastically contracts (or expands) in proportion to the field energy density (that is, the square of the electric field); this is not to be confused with a piezoelectric displacement, which is linearly proportional to the electric field. In an optical-frequency field, electrostriction can be thought of as a contraction (expansion) of the material under a light-induced pressure. This pressure is proportional to the optical energy density, just like the common radiation-pressure and optical-gradient