

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-workers¹ 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 fission⁴, and in chemistry it forms the basis for the celebrated Rice–Ramsperger–Kassel–Marcus theory of unimolecular reactions⁵. 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 wins⁶; 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 systems⁷, and understanding and controlling the mechanism of intramolecular rearrangements may help the design of new non-linear optical devices. □

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Published online: 5 February 2012

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^{2–5}. 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^{6–8}, 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 context⁹.

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

forces acting on refractive elements. But electrostriction directly produces a strain at the field location within the material, whereas the usual description of radiation pressure is that it only acts on the boundary between refractive domains. As a result, electrostriction naturally couples optical fields and (acoustic) density waves in solids, and plays an important role in phonon-assisted Brillouin scattering processes. The local density change produced by electrostriction has its origin in the mechanism of photoelastic coupling — in other words, the dependence of a substance's optical susceptibility on its density; a concept encapsulated at a basic level by the nineteenth-century Clausius–Mossotti relation. In practice, the sign and amplitude of electrostrictive effects vary for different materials depending on their microscopic structure and symmetry.

Gaurav Bahl and colleagues, reporting in *Nature Physics*¹⁰, now help to bridge the gap between electrostrictive effects in dielectrics and the principles of optomechanics. They carried out experiments on silica microspheres about 150 μm in diameter. On the optical side, these microsphere resonators support whispering-gallery cavity modes with a high quality factor. On the mechanical side, they possess a rich set of motional modes: from breathing (contour) modes associated with a global displacement of the resonator boundary, to density-wave modes that are closer to the usual picture of a phonon in a solid. The authors demonstrate optically cooling 'acoustic' motion of such a density-wave mode using electrostrictive effects assisted by the cavity modes. In analogy to the phenomenon of spontaneous Brillouin scattering (well-known, for example, in optical fibres), they name this novel effect 'spontaneous Brillouin cooling'.

In phonon-assisted light scattering experiments, the Stokes (anti-Stokes) process corresponds to an incident photon that emits (absorbs) a phonon and is consequently scattered with a red-shifted (blue-shifted) frequency. To reach the regime of Brillouin cooling, Bahl and co-workers select two distinct optical modes of the sphere that are exactly separated by the energy of the target phonon, and optically pump the lower-energy mode. In this situation, the anti-Stokes process becomes resonant and assisted by the two optical resonances (Fig. 1). The resulting large imbalance between Stokes and anti-Stokes processes leads to a net absorption of phonons by photons. The acoustic

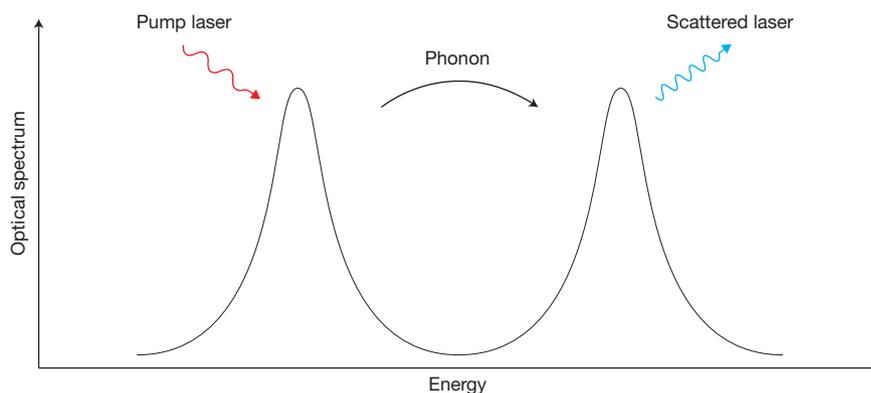


Figure 1 | The double-optical-resonance-assisted anti-Stokes process. The optical cavity spectrum of a system comprises two peaks separated by the energy of a single phonon. Incoming pump-laser light at the wavelength of the lower-energy peak is Brillouin scattered and blue-shifted. In this way energy is removed from the system's vibrational mode.

motion is consequently cooled and the scattered photons carry away the excess energy in the form of additional fluctuations. This is the exact principle of optomechanical cavity cooling, but with an acoustic phonon mode driven by optical electrostriction.

The present experiments achieved a net cooling from ambient temperature down to 19 K. This still leaves the acoustic mode far from the mechanical quantum regime, which is expected well below the millikelvin range for the 95-MHz mode under consideration. To some degree, the moderate cooling stems from the comparatively weak level of optical–mechanical coupling provided by electrostriction. The authors evaluate a vacuum optomechanical-coupling rate in the few tens of Hertz range, about four orders of magnitude smaller than in current nanophotonics-based optomechanical systems^{11–14}. However, the approach has several other interesting features. First, the dual optical mode configuration opens the possibility of amplifying the anti-Stokes cooling process by optical stimulation of the second resonance. Second, because the acoustic mode is well localized in the sphere, it is protected from clamping losses that usually affect the flexural or breathing modes of mechanical structures. The authors show that the mechanical dissipation of the acoustic mode already approaches the bulk dissipation expected for silica. This is important because this anti-Stokes cooling process mixes three waves (two optical and one acoustic) and scales with the product of the three related quality factors. Silica may not be the best material in terms of mechanical dissipation, but the same arrangement would become very appealing

in high-quality crystals. Last, and maybe most importantly, such electrostrictive coupling is almost ubiquitous, which means that the principles demonstrated by Bahl *et al.* can be exported to a broad range of experimental platforms. Semiconductors such as germanium or gallium arsenide exhibit a larger photoelastic coupling than silica, and even the sign of the effective optomechanical coupling can be tailored by an appropriate choice of material and geometry. For all of these reasons, there are probably many more surprises to come from future research that merges quantum-optical-control techniques with phonon propagation and storage in amorphous and crystalline solids. □

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Published online: 22 January 2012