has also been used by the Michigan group and their collaborators at IQE Inc. to implement an electrically pumped polariton laser in the GaAs material system emitting at around 650 nm at temperatures up to 155 K (ref. 9).

Impressively, the GaN polariton laser has a threshold current density of 169 A cm^{-2} — two orders of magnitude lower than that (13.9 kA cm^{-2}) of its vertical-cavity surface-emitting laser (VCSEL) counterpart made of the same material[10]. This is mainly because condensation and lasing with exciton polaritons are achieved for carrier densities well below the Mott exciton bleaching density. However, when comparing threshold performances of different semiconductors lasers, it is important to distinguish clearly between the threshold current density of planar device structures and the total threshold power, which is often used for nanolaser devices[2]. It is not straightforward to compare these two distinct types of devices; the only suitable parameter for comparison is the threshold density per device volume. In fact, nanolasers show much lower threshold currents of ~180 nA (ref. 1) than that (4 mA) of the polariton laser reported by Bhattacharya et al. Nevertheless, the extremely small volumes of nanolasers make the threshold carrier densities of these two devices comparable. Furthermore, it may be possible to improve the current device scheme by replacing the bulk GaN active region with multiple quantum wells located at the antinodes of the cavity electric field, potentially reducing the threshold still further.

As Bhattacharya and co-worker's polariton laser is made from the wide-bandgap semiconductor GaN, light emission occurs in the ultraviolet region. Shifting semiconductor laser operation to such short wavelengths had proved very difficult, preventing VCSELs from being used in applications such as high-density optical data storage, displays, high-resolution printing, and chemical and biological sensing. Thus, the realization of ultraviolet emission from the polariton laser represents a significant technological breakthrough, and the approach could be very useful for creating practical devices that operate in this important spectral domain. Furthermore, unlike their population-inversion counterparts, polariton lasers can lase at wavelengths that are not restricted to those near the bandgap edge. In fact, their lasing wavelength can be easily fine tuned by controlling the dispersion properties of polaritons, which can be adjusted on demand by modifying the trap depth through simply selecting the exciton photon detuning condition.

Despite these very important advantages, actual applications of polariton lasers are still unclear. Their biggest drawback is probably their fairly low output powers, which are limited by dissociation of exciton polaritons at high carrier injection densities. Thus, their applicability is likely to be restricted to applications requiring very low laser powers. For example, polariton lasers could be assembled in parallel to form large matrices, each consisting of thousands of devices, but consuming very little electrical power and producing minimal heat. If combined with enhanced polariton–polariton interactions in confined geometries or multiple cavities, such polariton devices could also lead to optoelectronic sources emitting non-classical light[11]. Furthermore, owing to their potential to be modulated at very high speeds, polariton lasers could perhaps form the basis for highly efficient optical interconnects with the aim of replacing wire connections, leading to smaller and more powerful electronics[12].

In summary, the realization of a room-temperature, electrically injected polariton laser represents an important step towards the practical implementation of polaritonic light sources. In many ways, the first report of a semiconductor laser device based on Bose–Einstein condensation that is pumped electrically at room temperature opens a new era in optoelectronics. It may not be long before polaritonic devices start to claim their share of the optoelectronics market, just as double heterostructure devices did 40 years ago.   □

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RAMAN SPECTROSCOPY

Watching a molecule breathe

Marrying the single-molecule detection ability of surface-enhanced Raman scattering with the extreme time resolution of ultrafast coherent spectroscopy enables the vibrations of a single molecule to be observed.

Lukasz Piatkowski, James T. Hugall and Niek F. van Hulst

Chemical reactions and biological processes typically involve the dynamic reorganization of a huge number of molecules. At ambient temperature and in natural biological environments, such events can be extremely complex. One dream of biologists and chemists is to be able to peek into any molecule and follow the movement of any of its atoms in real time.

This is a tantalizing prospect, as it will give researchers the ability to view each molecule individually and investigate its femtosecond dynamics, enabling its function to be scrutinized in greater detail than previously. In this issue of Nature Photonics, Steven Yampolsky and co-workers[1] bring this dream a step closer to reality by tracking atomic vibrations in a single molecule at room temperature, using time-resolved surface-enhanced coherent anti-Stokes Raman scattering (CARS).

It is now 25 years since the first optical detection of individual molecules. After initial endeavours under cryogenic conditions[2,3], individual fluorescent molecules were detected at room temperature[4], and soon after the time-resolved approach was developed[5,6]. These advances rapidly led to a very powerful technique for investigating

processes such as cellular dynamics, protein folding, enzymatic reactions, molecular motors and polymer mobility. The universally observed discrete blinking and bleaching of fluorescent single molecules was initially used to confirm their quantized nature. More recently, this discrete on–off switching has developed as the essential trick behind modern super-resolution microscopy techniques[7]. Despite the widespread adoption of single-molecule methods, the time resolution of acquired information has been limited to millisecond or longer timescales, which are orders of magnitude slower than the actual femtosecond to picosecond dynamics of molecular events. Only with the advent of broadband lasers and advanced pulse shaping in recent years have the first ultrafast responses of individual molecules been captured, revealing femtosecond vibrational wave packets[8].

Seeing an individual molecule is interesting, but identifying it and probing its properties are even more important. Molecular vibrations provide a primary fingerprint for such identification. Therefore, vibrational spectroscopy, especially Raman scattering, is important as it provides access to the spectral signals of molecular species, allowing chemical recognition. However, the Raman response of molecules is about ten orders of magnitude weaker than the response of the widely used fluorescence process, making the detection of Raman photons from a single molecule insurmountably difficult.

Fortunately, plasmonic enhancement has come to the rescue: Raman scattering can be hugely enhanced in the locality of resonant metallic nanoparticles. Indeed, in 1997, the first surface-enhanced Raman signal from a single molecule was reported with thousands of photons per second — comparable to the fluorescence emission of a single molecule[9,10].

The Raman response does not show the characteristic quantized blinking and bleaching present in fluorescence; observed fluctuations are generally due to variations in the plasmonic enhancement relative to the molecule position. Thus, how can you be sure that you are measuring an individual molecule? This unease has been haunting Raman spectroscopists for some time, until the use of isotopes with distinct spectra could confirm the detection of one species at a time[11].

Being able to identify a single molecule by Raman spectroscopy is one thing, but being able to track the femtosecond to picosecond time evolution of a single molecule would seem like an impossible challenge. CARS is the ultrafast coherent version of spontaneous Raman, yet despite
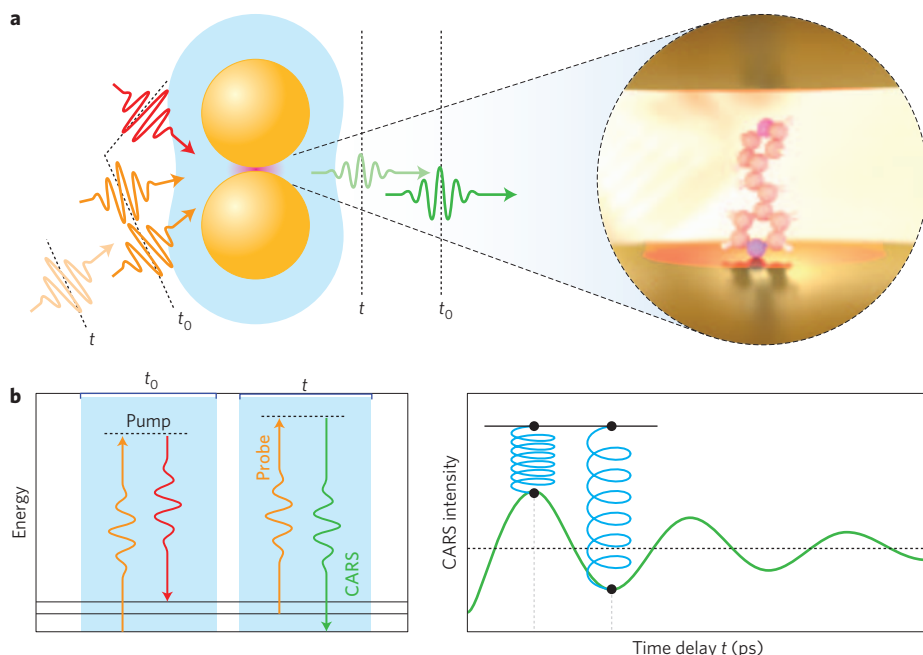

Figure 1 | TR-SECARS. a, A single molecule squashed inside the nanogap of a gold dumbbell experiences locally enhanced pump and probe pulses. **b**, The CARS pump and probe pulses drive a vibrational wave packet in the electronic ground state. Molecular vibrations are visualized through the oscillatory character of the CARS signal.

strenuous effort, the single-molecule limit had not been reached by CARS[12].

Now, the group of Eric Potma and Vartkess Apkarian at the University of California in Irvine, USA, has reported the observation of the ground-state vibration of single molecules by combining plasmonic enhancement of the Raman response and ultrafast lasers to achieve time-resolved surface-enhanced CARS (TR-SECARS)[1].

In an experiment, they use an ultrafast pump–probe scheme in which a pump-induced change in the molecule (in this case, an excited vibrational state) is monitored over time using a probe beam by varying the time delay between the pump and probe pulses (Fig. 1). During operation, the broadband pump–Stokes pulse pair (the pump) excites a specific set of vibrations in the molecule, forming a vibrational wave packet. This wave packet, being a coherent superposition of several vibrational states, evolves in time as the molecule vibrates. The probe pulse generates the measured CARS signal, which is used to monitor the time evolution of the wave packet. While the molecule vibrates, the interaction between the wave packet and the probe beam is modulated with a frequency corresponding to the beating between the excited vibrational modes. The oscillatory character of the TR-CARS traces thus contains information about the dynamics of vibrating atoms within the molecule (Fig. 1b).

To obtain sufficient sensitivity, they positioned the molecules of interest (an analogue of stilbene) within the enhanced electric field of a plasmonic antenna, for which they chose a gold dumbbell structure enclosed in silica (Fig. 1a). Such plasmonic structures confine the electric field to nanometric volumes and thus provide extremely strong field enhancement. That, in combination with the intrinsic enhancement of the SECARS technique (which scales with the eighth power of the electric field), allowed them to capture the CARS signal of a single molecule.

Remarkably, Potma and colleagues observed that the TR-SECARS signal oscillates for durations of up to 10 ps. As the vibrational beating period was about 1 ps, this implies that they could see the molecule vibrate approximately ten times before the signal died out. It is important to note that a single time trace is not obtained instantly, but is a result of averaging the CARS signal for many minutes (up to 1 h). The researchers acknowledge that they were able to realize such a long averaging time for a single molecule as a result of the static and stable nature of the environment they created. Interestingly, because of the interaction between the vibrating atoms and their direct neighbours, the TR-SECARS signal develops a characteristic noise, rather than decaying to zero. Yampolsky *et al.*

elegantly showed that the time-averaged noise scales with $1/(N \cdot V)$, where N is the number of molecules and V is the number of vibrational states excited. Thus, knowing the number of vibrational states involved, they showed by statistical analysis that it is possible to distinguish whether one addresses a single molecule or multiple molecules. For a single molecule and two vibrational states involved, the averaged signal tends to half of its initial value.

It should be noted that the single-molecule nature of the signal is determined without *a priori* knowledge of the coverage or location of the molecules, but from the post-experiment statistical analysis of the SECARS traces. Although being very specific to the time-resolved wave packet interference experiments, statistical analysis of the phase noise, as shown by Yampolsky *et al.*, can also be used to distinguish the signal from one, two or many molecules with a reasonably high reliability, thus adding a further technique to the toolbox for distinguishing single-molecule detection from few-molecule detection. That being said, the use of isotopes[11] is still the only definitive test for a single-molecule Raman response.

The first realization of TR-SECARS on a single molecule at room temperature is exciting and an important experimental achievement, which places this technique head-to-head with time-resolved, fluorescence-based, single-molecule detection[8]. TR-SECARS has an important advantage over fluorescence schemes in

that a CARS signal can be generated from virtually any molecule — it is not limited to photoactive molecules. If geometry concerns can be overcome, this will open up the possibility of directly investigating the local dynamics of biologically relevant, complex single molecules without using fluorescent labelling.

A key drawback of the TR-SECARS technique is that the data had to be acquired for approximately an hour to obtain a sufficiently high signal-to-noise ratio to discern a single molecule. This is exceptionally long compared to more routine single-molecule fluorescence detection. The sample thus requires a remarkable stability and the risk of photodamaging the molecule and/or the plasmonic structure has to be cautiously considered. The system was made stable by attaching the molecule to the plasmonic structure and encapsulating it in silica. It is thus unclear how applicable this technique will be to less restrictive geometries and more complex molecules.

The immense power of plasmonics to tailor and enhance the interaction of light with single molecules is indisputable and has stimulated a new branch of science. The ability to extract ever-more-detailed information about the behaviour of a single molecule is truly remarkable. To obtain this information, however, one has to sculpt the environment in the vicinity of the molecule to such a large extent that it differs considerably from natural systems.

This artificial landscape doubtlessly alters the response of the molecule from its free natural response. If we want to measure the intrinsic natural behaviour of molecules to understand how they behave as part of more complex systems, is it viable to study them in such contrived situations? Conversely, without such engineered systems, would it even be imaginable to measure such detailed dynamics of a single molecule? The achievement of performing enhanced, ultrafast Raman scattering on a single molecule is a true landmark, yet the challenge of tracking a single vibration under real-life conditions remains. ❑

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INTEGRATED OPTICS

Flexible chalcogenide photonics

Embedding a thin layer of chalcogenide glass inside a polymer paves the way for a new form of flexible optical waveguides and integrated optical circuits.

Barry Luther-Davies

The development of flexible photonics is still in its infancy, but it is spurring researchers to develop techniques for transferring complex optical circuits onto flexible substrates. Many applications have been proposed for this technology; some of the most widely touted are board-to-board optical interconnects, biosensors, 'wearable' photonics and flexible displays[1,2]. Many of these applications demand inexpensive devices. Hence, cost-effective, large-scale manufacturing processes are required that can produce devices whose optical responses do not change on bending.

Writing in *Nature Photonics*, Li and co-workers[3] now show that high-quality optical waveguides and associated devices can be fabricated by embedding a soft-glass photonic layer within a structured polymer membrane.

To date, much research into flexible photonics has focused on devices made entirely from polymers, as they naturally impart the required flexibility[4]. However, this all-polymer approach necessitates that all the layers constituting an optical waveguide be deposited and processed at low temperatures using techniques such as spin coating, doctor blading

and even inkjet printing. Structuring to create waveguide cores is then based on simple processes, such as moulding or exposing a photosensitive core material through a mask. Unfortunately, polymer-based systems generally have rather small refractive index differences between their cores and claddings. This means that light confinement is weak, making it impractical to realize small photonic structures with sharp bends such as microring resonators. Furthermore, bending the whole device can easily cause light to spill out of the waveguide. As a result, there has been a growing interest in finding a way to