2D HYBRID PEROVSKITES

Shaky lattices for light–matter interactions

Impulsive Raman spectroscopy reveals how atoms are pushed into action by light absorption. The surprising sensitivity of this behaviour to the polaronic character of 2D perovskites opens up new avenues for tailored light–matter interactions.

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The ever-growing energy demand of society has spurred a frantic search for new optoelectronic materials for energy conversion and utilization. Over the past years, a novel class of 'soft' organic–inorganic hybrid semiconducting materials has emerged that exhibits fascinating optical and mechanical properties, combining flexibility, tunability and low processing cost[1,2]. These materials are composed of a perovskite metal-halide crystal lattice with organic cations, which introduces an inherent 'softness' in the material, leading to profound implications for their optical behaviour. While three-dimensional perovksites are the main focus of activity for photovoltaic applications, low-dimensional perovskites have recently emerged as exciting new candidates for light emitting devices[3,4]. These self-assembled two-dimensional quantum wells form bound electron–hole pairs (excitons) after photoexcitation, but comparatively little is known about their ensuing dynamics. In fact, a complex interplay of electronic, excitonic and phononic effects has been implicated to describe the optical response. For example, strong exciton–phonon couplings[5] in this class of materials controls the emission linewidths and even enables highly efficient white light emission[4]. Writing in *Nature Materials*, Félix Thouin and colleagues[6] now provide evidence for polaronic effects — that is, strong interaction with the structural response — on the excitons generated in low-dimensional perovskites, which may suggest additional strategies to fine-tune the optical properties of these materials.

The researchers investigated a class of two-dimensional lead-iodide perovskite quantum wells (A_2PbI_4, A = organic cation) with the aim to develop an in-depth understanding of the interplay between the different exciton transitions with the lattice/phonon modes of the crystal structure. The relevant phonon modes in this class of materials are typically located in energy below 100 cm^{-1} (12.4 meV) due to the heavy constituents (Pb, I), rendering their spectroscopic detection extremely challenging with standard frequency-based optical spectroscopy techniques. To circumvent this problem, the authors employed resonant impulsive stimulated Raman scattering spectroscopy, a time-domain implementation of resonance Raman spectroscopy, ideally suited to address low-frequency modes in highly polarisable crystals[7–9]. This technique is a variation on standard optical pump–probe measurements, in which a pump pulse photoexcites the sample at a specific excitonic resonance and the response of the sample is probed by a time-delayed broadband probe pulse (Fig. 1a).

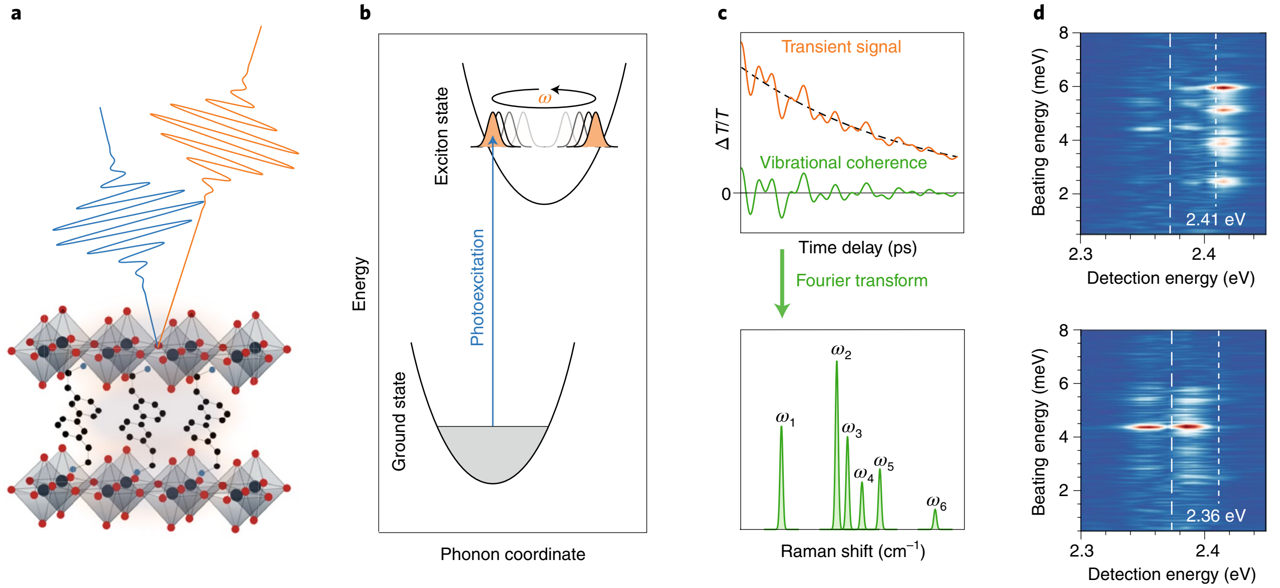

Fig. 1 | Resonant impulsive stimulated Raman scattering spectroscopy on hybrid perovskite materials. a, Pump–probe schematic to investigate layered two-dimensional hybrid perovskites. **b**, Vibrational wavepacket generation (orange) on the exciton state after photoexcitation. The wavepacket evolves in time according to the underlying potential with a frequency, ω. **c**, Transient signal response before (orange) and after (green) subtraction of the underlying electronic dynamics reveals vibrational coherences (top), which upon Fourier transformation provide a Raman spectrum of the sample (bottom). **d**, Comparison of the impulsive response from Thouin and colleagues for energetically slightly different pump wavelengths. Panel **d** reproduced from ref. [6], Springer Nature Ltd.

Importantly, the pump pulse is chosen to be broad in frequency and temporally compressed such that it covers multiple vibrational energy levels of the material. As a consequence, it generates vibrational wavepackets (Fig. 1b), which evolve in time according to the underlying potential energy surface and modulate the pump–probe signal. The frequency content of these coherent vibrational oscillations can be retrieved by Fourier transformation resulting in the Raman spectrum of the material (Fig. 1c). Importantly, since the vibrations are detected in the time domain, temporally invariant signals such as Rayleigh scattering or photoluminescence do not deteriorate the Raman spectrum as in frequency-domain resonance Raman spectroscopy.

Making use of this powerful spectroscopic technique at varying temperatures ranging from room temperature to 5 K, the researchers conducted pump-dependent studies by exciting the continuum (above the bandgap) or either of the two prominent excitonic transitions found in this material. Intriguingly, the retrieved Raman spectrum for one of the excitonic transitions varied considerably from the other spectra. This result was complemented with state-of-the-art computational modelling based on density functional theory to understand the character of each of the observed modes. Equipped with this knowledge, the authors concluded that the difference in Raman spectra is due to polaronic contributions to the excitonic transition — that is to say that the photoexcited charges result in a lattice polarization/deformation.

One of the key advantages of vibrational spectroscopy is its extreme structural sensitivity, in principle providing detailed information on atomic structure and dynamics. This relationship, however, only strictly holds if one can confidently assign the observed vibrational dynamics to actual atomic displacements, which ultimately relies on the level of agreement between experiment and theory. Here, the work by Thouin and colleagues is unique in that it accurately predicts not only the number but also the relative and absolute energies of the associated phonons. As a result, we can be very confident that the theoretically predicted atomic motions, coupled with the experimentally observed spectral amplitudes, provide a detailed picture of the structural dynamics resulting from photoexcitation. It is particularly remarkable how different these amplitudes and thus atomic motions are for a tiny change in excitation energy (Fig. 1d). What this ultimately means is that the material responds completely differently to two photons whose energies differ by as little as 50 meV (to compare, the thermal energy at room temperature is 25.7 meV).

The presence of polaronic effects has been widely discussed in three-dimensional bulk hybrid perovskite structures but can also clearly play a key role in two-dimensional perovskites, as evidenced by studies on the luminance linewidths of these materials[4,5]. The findings in this study thus provide important insight into the fascinating optical properties of these materials. More generally, the ability to characterize, rationalize and eventually tune the immediate material response, which in turn has critical implications on any downstream consequences of photoexcitation, is particularly exciting in the context of the history of condensed-phase light–matter interactions. In molecular systems, the ability to tune how a system responds to the absorption of a photon is extremely limited, because the associated molecular orbitals and vibrational modes are inextricably linked[10]. With hybrid perovskites, however, experimentalists are blessed with being in charge of a number of parameters that have tremendous impact on the vibronic structure of the material and thereby the nature and consequences of light–matter interactions. The challenge for the community will now be to build on these results and move towards the rational design of two-dimensional perovskites devices with controlled exciton–phonon coupling and hence controlled luminance and polaronic properties. ❐

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