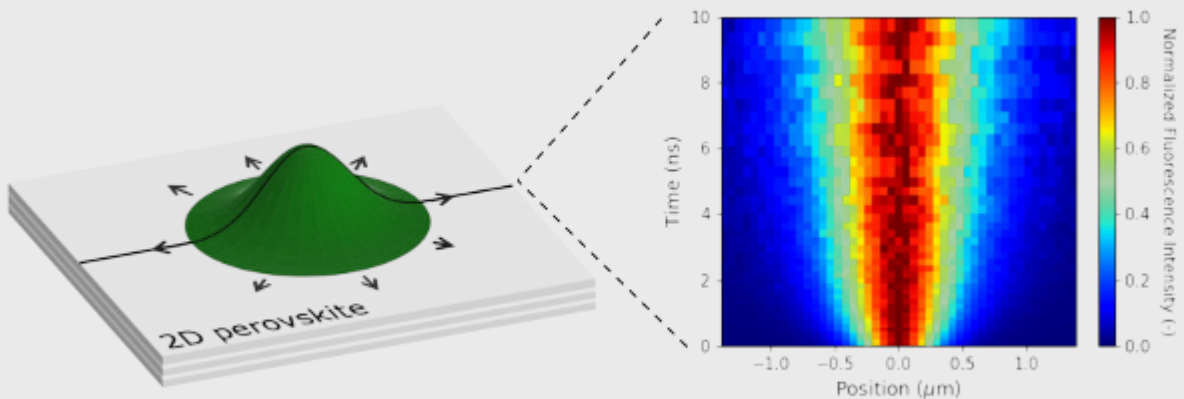


Exciton Transport in 2D Perovskites: Visualising the Flow of Energy in a Soft Semiconductor

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by

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Researchers from the Universidad Autonoma de Madrid have for the first time visualised the unique physics of the transport of optical excitations (or excitons) in two-dimensional perovskites. Using transient fluorescence microscopy, they show how small changes in the softness of these materials can result in dramatic differences in their excitonic energy transport characteristics. This discovery is crucial in the development of high efficiency solution-processed photovoltaic and light emitting technologies – a field in which metal-halide perovskites are playing an increasingly central role.

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ithin a decade after their first reports, solar cells based on metal-halide perovskites have advanced to the top of the list of most efficient single cell junctions, rivalling even crystalline silicon. However, one key missing ingredient in perovskites is chemical stability, posing a challenge for commercialisation. A promising route to tackle the stability issue is the use of lower dimensional perovskites, such as two-dimensional (2D) perovskites, which show a better resistance towards degradation than the conventional 3D phases. Indeed, recent solar cells based using 2D perovskite show dramatically improved stability while maintaining high performance. Reduced dimensionality, however, significantly alters the photophysical properties of the perovskites. Importantly, rather than acting as free carriers, electrons and holes are bound to each other and travel through the material as neutral pairs called excitons. The exciton-binding energy of these materials is in some cases so high that excitons can only be split up into electrons and holes at charge separation sites. To guarantee

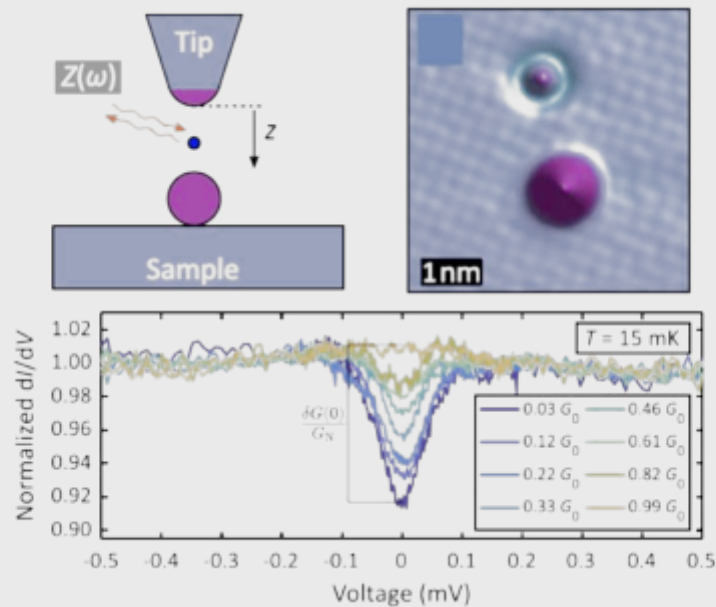
that every absorbed photon can also contribute to the energy generation in a solar cell, excitons need to diffuse far enough to reach such sites. This makes charge separation and energy extraction much more challenging and it is somewhat of a surprise that 2D perovskite based solar cells work as well as they do.

Researchers from the Condensed Matter Physics Centre (IFIMAC) at the Universidad Autonoma de Madrid have now directly visualised exciton transport in 2D perovskites using transient photoluminescence microscopy (TPLM). By detecting the photoluminescent signal from a population of excitons as a function of time and position, TPLM can create little movies of the broadening of this population with a spatial resolution of just a few tens of nanometers and at a sub-nanosecond frame duration. The results show that excitons undergo an initial fast diffusion through the crystalline plane, followed by a slower subdiffusive regime as excitons get trapped. Interestingly, the regime of slow trap state-limited transport disappears at higher illumination intensities. Using theoretical modelling, the authors find that this can be explained by a trap filling behaviour. This suggests that under typical illumination by the sun in a photovoltaic device, the role of traps in these materials may actually be minimal. The most important finding of this study though, is that the early intrinsic diffusivity depends sensitively on the choice of organic spacer that is used to separate the inorganic sheets in 2D perovskites. Between commonly used organic spacers (phenethylammonium and butylammonium), diffusivities and diffusion lengths differ by as much as an order of magnitude. Across a wide range of different spacers, it is shown that these changes are closely correlated with variations in the softness of the lattice, suggesting a dominant role for exciton-phonon coupling and exciton-polaron formation in the spatial dynamics of excitons in these materials. Crucially, long exciton diffusion lengths in light emitting applications such as LEDs can reduce device performance, as it increases the possibility of encountering a trapping site. Meanwhile, for light harvesting applications, long diffusion lengths are essential for the successful extraction of excitons. The insights from this study therefore provide a clear design strategy to further improve the performance of 2D perovskite solar cells and light emitting devices.

[\[Full article\]](#)

References

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lomb blockade revealed by an STM.

Article: published in *Physical Review Letters* by [Alfredo Levy Yeyati](#) and [Juan Carlos Cuevas](#), IFIMAC researchers and members of the Theoretical Condensed Matter Physics Department.

As the dimensions of a conductor are reduced, quantum mechanics starts to play a significant role in its electronic transport properties. Atomic-size contacts, as those produced using STM techniques, constitute the ultimate limit in the miniaturization of electronic devices. In this extreme limit, electrical conduction is mainly determined by the quantum mechanical transmission probability of electrons through the junction. However, deviations from this simple picture can occur at very low temperatures due to the effect of quantum fluctuations in the applied voltage, leading to a phenomenon called dynamical Coulomb blockade.

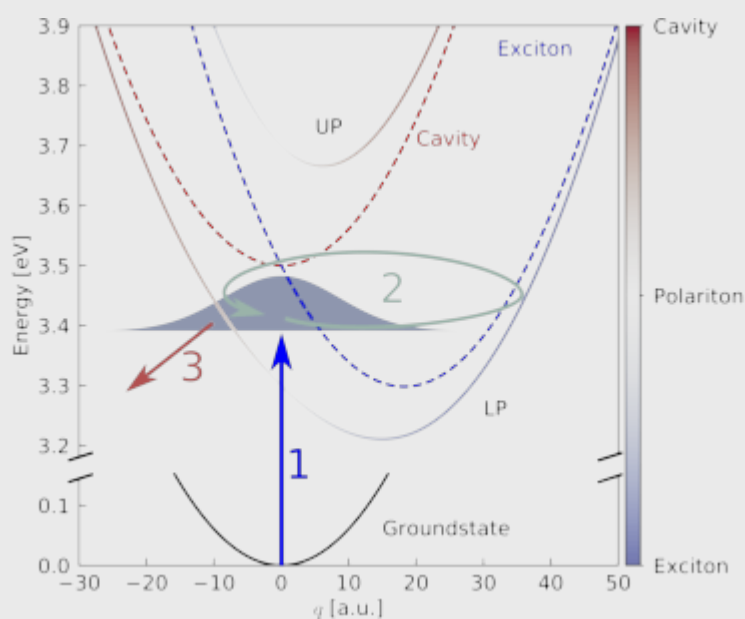
Now, a novel insight into dynamical Coulomb blockade (DCB) at the atomic scale has been reported in a work published in *Physical Review Letters* by a collaboration between groups of the [Max Planck Institute for Solid State Research](#) (Stuttgart), the [Okinawa Institute of Science and Technology](#), the [University of Ulm](#), the [University of Konstanz](#), and the IFIMAC researchers [Alfredo Levy Yeyati](#) and [Juan Carlos Cuevas](#). In this work, these researchers used an ultra-low temperature STM to form few-atom junctions with an exquisite control and they revealed the influence of DCB in measurements of the electrical current. More importantly, they demonstrated that these measurements can be used to determine the transmission coefficients of these atomic-scale junctions. Such a determination was possible thanks to an excellent agreement with a microscopic theory of DCB and the nature of the conduction channels was elucidated with the help of *ab initio* DFT transport calculations. Thus, they concluded that probing the DCB by STM provides a complementary technique for locally

resolving quantum transport characteristics. [Full article]

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Polaritonic Molecular Clock: Listening to Molecules



Article: published in [Nature Communications](#) by R. E. F. Silva, [Francisco J. García-Vidal](#) and [Johannes Feist](#), IFIMAC researchers and members of the Theoretical Condensed Matter Physics Department.

The motion of atoms in a molecule typically occurs on the femtosecond timescale (10^{-15} s). The standard technique used to study chemical reactions at these timescales is pump-probe spectroscopy, where first an ultrashort pump laser pulse initiates the dynamics in the molecule and, some time later, an ultrashort probe laser pulse is used to obtain information about the current state of the molecule. However, the information obtained in these approaches is always somewhat indirect. If you imagine the molecule as a musical instrument and the laser pulses as short sound pulses, these approaches correspond to monitoring the change in the sound frequencies that the instrument responds to when it has been struck by a first sound already (this is known as transient absorption spectroscopy), or even to using such a strong second pulse that it blows apart the instrument, and trying to understand its motion before falling apart by

measuring the pieces that fly away. These experiments are then repeated many times with different time delays between the pulses, to construct something akin to a movie of the molecular motion after it has been excited. One important reason that these approaches are used is that simply “listening” to the molecule, i.e., measuring the light that it emits after the first pulse, normally does not provide the required information. The fundamental reason for this is that a molecule only couples quite weakly to light, which has two main consequences: First, the amount of light that is emitted is typically quite low (making it hard to “hear” the molecule), and second, it takes a long time for the light to be emitted so that even if you can measure it, it is produced at times long after the interesting motion has taken place.

A theoretical proposal by a group of researchers from the Departamento de Física Teórica de la Materia Condensada and the Condensed Matter Physics Center (IFIMAC) at the Universidad Autónoma de Madrid now provides a way to resolve both of these problems at the same time and make it possible to listen to the molecule directly in those first few crucial tens of femtoseconds. The basic idea of this work is to place a molecule in a nanoplasmonic cavity, where the strong coupling between the molecule and the electromagnetic modes of the cavity transforms the molecule into a “loudspeaker”. The nanoplasmonic cavity in this case acts both as a resonator that changes the “sound” of the molecule and as an amplifier that makes it possible to “hear” the molecule. In the article, the authors show that ultrafast molecular dynamics can be traced with femtosecond resolution by looking at the photon emission by the cavity, which only happens when the molecular vibrational wavepacket is close to a position where the molecule and the cavity are in resonance with each other. In this way, the setup acts like a clock that measures how long the molecule takes to reach a given position. In particular, the authors show that this idea works in the regime of strong light-matter coupling, where the molecule and the cavity interact so strongly that their excitations become hybrid light-matter states known as polaritons. In this regime, this novel technique could provide direct insight into the modification of molecular motion induced by polariton formation. This approach could open the window for experimental and theoretical advances in the way we explore ultrafast chemical dynamics, paving a new way to combine femtochemistry and molecular polaritonics using plasmonic nanocavities. [[Full article](#)]
