Excitonic landscape in 2D perovskites

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Two-dimensional (2D) perovskites, specifically those belonging to the Rudlesden–Popper (RP) phase form a subclass of van der Waals semiconductors alongside materials such as transition metal dichalcogenides black phosphorus and emerging layered magnetic semiconductors. Their high environmental stability and surprisingly high efficiency of solar cells based on them have renewed interest in these materials. These natural quantum wells consist of planes of metal-halide octahedra, separated by organic spacers. The unique synergy of soft lattice and opto-electronic properties are often invoked to explain superior characteristic of perovskites materials in applications. At the same time such unique synergy creates fascinating playground for exciton physics which challenges our understanding of this elementary excitation. I will demonstrate that even after decade of intense investigation the notation" unique" so often used in case of perovskites deserves serious scrutiny.

In 2D perovskites combined effects of quantum and dielectric confinement lead to unusually large exciton binding energies, reaching several hundreds of meV for the thinnest quantum wells. As a result, excitonic resonances characterized by exceptionally large oscillator strength remain stable even at room temperature and dominate the optical response near the band edge. Consequently, strongly bound quasi 2D excitons can be investigated both in ultra-thin exfoliated flakes and in bulk-like crystals. However, the thickness of the studied structure can itself exert a pronounced influence on the optical response. Photonic effects associated with finite thickness and high refractive index add further complexity to the spectra, complementing the strong coupling between electronic excitations and lattice vibrations -another" trademark" of metal halide perovskites. Together, these factors give rise to remarkably complex absorption and emission spectra (as shown in Fi 1(a),(b)), complicating the understanding of fundamental optoelectronic properties.

In this presentation I will discuss the optical response of 2D layered perovskites and demonstrate, step by step, how their intrinsic electronic, vibrational, and photonic properties collectively shape the observed spectra. Although more than two decades of research have produced a wealth of studies addressing structural, optoelectronic and polaronic properties, the particularly complex optical response remains a subject of ongoing debate, and a comprehensive understanding is still lacking.

The optical response of a semiconductor near its fundamental bandgap is shaped by three principal factors: (i) the underlying electronic structure, (ii) the coupling between electronic states and lattice vibrations, and (iii) the photonic properties of the structure itself, as schematically shown in Fig1 (c). In presentation, I will revisit how each of these factors contributes to the observed optical response and discuss their interplay in shaping the experimentally measured absorption spectra. In particular, I will outline the often-overlooked importance of photonic effects in linear absorption spectra. Crucially, as summarized in Fig.1 (c), the characteristic energy scales associated with these different contributions partially overlap in 2D perovskites. As a result, disentangling their individual impact on the optical spectra is challenging, and straightforward attribution of specific spectral features to a single underlying mechanism should therefore be approached with caution.

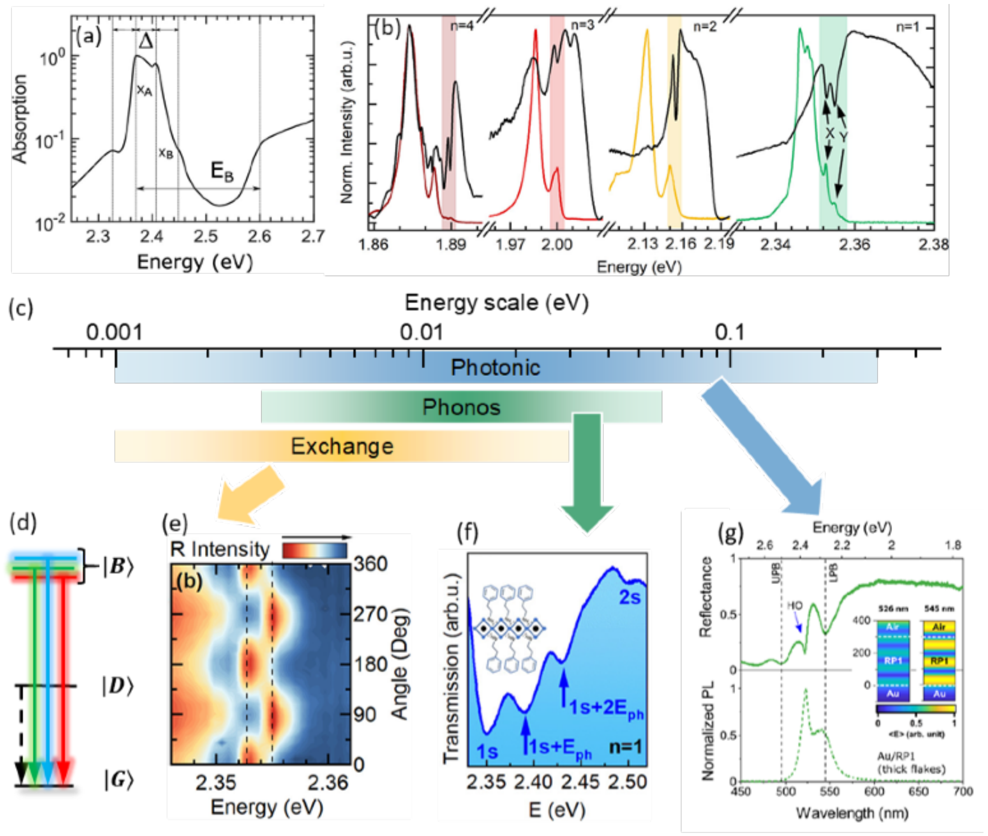

Fig1. (a) Absorption spectrum of (PEA)2PbI4 measured at T = 5 K. The spacing Δ ≈ 35 meV indicates the characteristic separation of spectral features commonly observed in absorption, reflectance, and transmission spectra (adapted from The Journal of Physical Chemistry Letters 2020, 11, 3173–3184.) (b) Photoluminescence (coloured lines) and reflectance (black lines) spectra of PEA2MAn−1PbnI3n+1. Broad multi-peak structures are evident in the reflectance spectra for n = 2, 3, 4. (c) Illustration of characteristic energy scales associated with exchange interaction, exciton–phonon coupling, and photonic effects. (d) Schematic representation of the bright exciton triplet and dark singlet states expected for 2D perovskites. (e) Evolution of the reflectance spectrum as a function of the angle between the incident light polarisation and the in-plane crystal axis. (f) Transmission spectra of (PEA)2PbI4 at T = 4 K showing characteristic equally spaced minima.(g) Reflectance and photoluminescence spectra of a ~ 300 nm thick (BA)2PbI4 flake deposited on a gold substrate. The formation of lower and upper polariton branches is visible in both reflectance and photoluminescence (Nano Letters 2021, 21, 6245–6252.)