Microscopic picture of electron-phonon interaction in two-dimensional halide perovskites

David Feldstein,1 Raúl Perea-Causín,1 Shuli Wang,2 Mateusz Dyksik,2,3 Kenji Watanabe,4 Takashi Taniguchi,4 Paulina Plochocka,2,3 and Ermin Malic1

1Chalmers University of Technology, Department of Physics, 412 96 Gothenburg, Sweden
2Laboratoire National des Champs Magnétiques Intenses, UPR 3228, CNRS-UGA-UPS-INSA, Grenoble and Toulouse, France
3Department of Experimental Physics, Faculty of Fundamental Problems of Technology, Wrocław University of Science and Technology, Wrocław, Poland
4Research Center for Functional Materials, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

Perovskites have attracted much attention due to their remarkable optical properties. While it is well established that excitons dominate their optical response, the impact of higher excitonic states and formation of phonon sidebands in optical spectra still need to be better understood. Here, we perform a theoretical study on excitonic properties of monolayered hybrid organic perovskites—supported by temperature-dependent photoluminescence measurements. Solving the Wannier equation, we obtain microscopic access to the Rydberg-like series of excitonic states including their wavefunctions and binding energies. Exploiting the generalized Elliot formula, we calculate the photoluminescence spectra demonstrating a pronounced contribution of a phonon sideband for temperatures up to 50 K—in agreement with experimental measurements. Finally, we predict temperature-dependent linewidths of the three energetically lowest excitonic transitions and identify the underlying phonon-driven scattering processes.

In the last years, much effort has been devoted to the study of perovskite materials [1–5]. Their broad absorption spectrum [6] combined with impressive light-emitting properties [7] make them a promising material for optoelectronic applications. They have been, in particular, applied as active material in solar devices exhibiting a power conversion efficiency of up to 25.2 % [8, 9]. Beyond photovoltaics there has been a rising interest in perovskite based diodes and lasers [10–13]. Recently, layered perovskites have emerged as a subclass of the bulk material exhibiting enhanced excitonic properties and tunable characteristics [14]. Their optical and electronic properties can be tailored through an external stress [15, 16], an internal chemical pressure [17] or by varying their layer thickness [18]. In addition, a wide variety of compositions can be made thanks to the large amount of organic cations that can be integrated into the structure. These materials are considered as a dimensional reduction of 3D perovskites with the general formula \((A')_m A_{n-1} B_n X_{3n+1}\), where \(A'\) is the cation that intercalates between the inorganic \(A_{n-1} B_n X_{3n+1}\) layers and \(n\) can be understood as the thickness of the inorganic layers. Here, the screening of the Coulomb interaction is weaker compared to 3D perovskites resulting in considerably larger exciton binding energies [19, 20]. As a direct consequence, excitons are stable at room temperature and determine the optical response and the nonequilibrium dynamics of these materials. Recent experimental studies on optical properties of 2D perovskites have focused on exciton binding energies [21], absorption linewidths [22–27], phonon sidebands [28], and high-density effects [29]. However, a microscopic understanding of some of the reported findings, e.g. the formation of phonon sidebands and the microscopic origin of excitonic linewidths, have not been well understood yet.

Here, we present a joint theoretical study on optical properties of monolayered hybrid organic perovskites supported by experimental photoluminescence (PL) measurements. The aim of the work is to provide a micro-
scopic understanding of many-particle processes determining the temperature-dependent PL in these materials. We focus on the monolayered (PEA)$_2$PbI$_4$, which is a particular case of the n-layered (PEA)$_n$MA$_{n-1}$Pb$_n$I$_{n+1}$ perovskite [30, 31], cf. Fig. 1(a). Here, the inorganic layer consists of corner-sharing PbI$_6$ octahedra sandwiched between two organic layers of PEA (phenyl ethyl ammonium). The lower dielectric constant of the organic layer results in a dielectrically confined quantum well.

Using a fully quantum mechanical approach, we obtain microscopic access to excitonic wavefunctions and binding energies in 2D perovskites. Exploiting the generalized Elliot formula, we model temperature-dependent PL spectra including the emergence of phonon-assisted sidebands. Finally, we determine the spectral linewidth of the energetically lowest excitonic transitions taking into account scattering channels driven by the emission and absorption of acoustic and optical phonons, cf. Fig. 1(b). The theoretical predictions are compared to temperature-dependent measurements of photoluminescence spectra in the investigated 2D perovskites.

As a first step, we determine the excitonic properties of monolayered (PEA)$_2$PbI$_4$ perovskites. To obtain microscopic access to the Rydberg-like series of excitonic states $\nu$, their binding energies $E^\nu_b$ and wavefunctions $\phi^\nu_k$, we solve the Wannier equation [32–34]

$$\frac{\hbar^2 k^2}{2\mu} \phi^\nu_k - \sum_{k'} V_{|k-k'|} \phi^\nu_{k'} = E^\nu_b \phi^\nu_k,$$

where we approximate the Coulomb interaction by the Rytov–Keldysh potential [35, 36] $V_q = \frac{e^2}{2\varepsilon_0 \varepsilon_s q^2 (1 + r_0 q^2)}$ similar to the treatment of atomically thin transition metal dichalcogenides (TMDs) [37]. Here, we used the exciton reduced mass $\mu = 0.108 m_0$ [23] and the average dielectric constant $\varepsilon_s = 3.32$ given by the organic layers [38]. The dielectric constant of the inorganic layer is $\varepsilon_{\text{well}} = 6.1$ and its thickness $L_{\text{well}} = 0.636 \text{ nm}$ [38]. These quantities determine the screening length $r_0 = L_{\text{well}} \frac{\varepsilon_{\text{well}}}{\varepsilon_s}$, which is crucial for the excitonic binding energy $E_b$.

Evaluating the Wannier equation, we find $E^3_b = 228$ meV for the energetically lowest 1s exciton state, while the binding energy decreases to 43 meV and 17 meV in the case of 2s and 3s states, respectively, cf. Fig. 2(a) and Table I. The obtained exciton binding energies are in good agreement with experimentally measured values, cf. the inset of Fig. 2(a). Note that interestingly the 2p state has a larger binding energy than the corresponding 2s state similarly to the case of TMD monolayers [39]. The corresponding eigenfunctions of the three lowest excitonic states are illustrated in Fig. 2(b) and show the typical momentum-dependence well known from the hydrogen problem.

The obtained excitonic binding energies and wavefunctions will be used in the following to calculate the photoluminescence spectrum and the linewidths of excitonic transitions in the investigated 2D perovskite material.

The photoluminescence is calculated applying the density matrix formalism for an interacting system of electrons, phonons and photons [45–47]. Using the Heisenberg equation of motion, we calculate the temporal evolution of the photon number $n_\nu = \langle q \phi^\nu_k \rangle$, which determines the photoluminescence via $I_{\text{PL}}(E) = n_\nu$ [34, 48]. Here, radiative and non-radiative decay channels play the crucial role. The radiative recombination of exciton states within the light cone is given by $\gamma_\nu^\text{r} = \frac{\hbar c^2}{2\varepsilon_0 \varepsilon_s} |M_\nu|^2 \frac{\phi_0^1 (r_{\delta E})^2}{E_0^\nu}$ with $E_0^\nu = E_g + E_b^\nu$ being the excitonic resonance energy and $M_\nu$ being the optical matrix element for interband transitions projected into the polarization $\sigma$ of the emitted light [49, 50]. In the considered low-excitation regime, phonon-driven scattering channels determine the non-radiative dephasing [45, 49]

$$\Gamma^\nu_k = \pi \sum_{j,q,\pm} |G^\nu_{q,j}|^2 \left( n_j^q \pm \frac{1}{2}, \frac{1}{2} \right) \delta(\Delta E^\nu_{k,q})$$

with $E^\nu_{k,q} = E^\nu_j - E^\nu_k \pm \hbar \Omega_q$. The excitonic dispersion $E^\nu_k$ is described in an effective mass approximation with a total exciton mass $M = 0.44 m_0$ [23]. The

| Excitonic state | $E^1_b$ [meV] | $E^2_b$ [meV] | $E^3_b$ [meV] | $E^4_b$ [meV] | $E^5_b$ [meV] |
|----------------|---------------|---------------|---------------|---------------|---------------|
| Binding energy $E_b$ [meV] | 228 | 43 | 17 | 9 | 53 | 19.5 | 20 |

TABLE I. Excitonic binding energies $E_b$ obtained by solving the Wannier equation [cf. Eq. (1)].

FIG. 2. (a) Exciton binding energy of the energetically lowest s-type excitonic states in 2D perovskites. The inset shows a direct comparison to the measured values denoted by dots (and the corresponding references [28, 38, 40–44]). (b) Momentum-dependent wavefunctions for 1s, 2s, and 3s excitonic states, respectively.
The appearing exciton-phonon matrix element $G_{q}^{\mu \nu}$ is given by the coupling elements for electrons and holes $g_{\nu}^{e,h} \phi_{k}^{\mu} \phi_{k+q}^{\nu}$ with the exciton wavefunctions $\phi_{k}^{\mu}$ of the involved initial and final exciton states. The electron-phonon coupling reads $g_{q}^{j,\alpha} = D_{q}^{j,\alpha} (\frac{\hbar}{2 m_{q}})^{1/2}$ with a constant deformation potential for optical phonons, i.e., $D_{q}^{j,\alpha} = D_{op}^{j,\alpha}$, and with $D_{q}^{j,\alpha} = D_{ac}^{j,\alpha} |q|$ for acoustic phonon modes. First-principle studies are needed to obtain access to the full phonon dispersion and electron-phonon coupling elements. While this is beyond the scope of this work, we extract the values for deformation potentials from the experimentally measured temperature-dependent linewidth of the 1s exciton assuming one dominant optical and acoustic phonon branch, cf. Table II. We find that the linear increase of the PL linewidth at low temperatures can be traced back to the scattering with acoustic phonons characterized by the velocity $c_{AC} = 2100 \text{m/s}$. At high temperatures, there is a deviation from a linear increase and the major contribution stems from scattering with optical phonons exhibiting an energy of 35 meV. Note that there is also a defect-induced linewidth $\Gamma_{0} = 6.7 \text{meV}$ at zero temperature.

Considering a many-particle Hamilton operator including exciton-photon and exciton-phonon interaction and evaluating the Heisenberg equation of motion for the photon number $n_{\nu \sigma}$, we find a coupled set of differential equations including phonon- and photon-assisted polarizations. Then, the cluster expansion scheme [51] is used to factorize the many-particle expectation values disregarding contributions connected to multi-phonon processes [45]. The final analytic expression for the $\sigma$-polarized photon flux emitted in perpendicular direction with respect to the monolayer is given by [45]

$$I_{PL,\sigma}(E) = \frac{2}{\hbar} |M_{\sigma}|^{2} \sum_{\mu} \frac{|\phi_{\mu}(r = 0)|^{2}}{(E_{\nu}^{\sigma} - E)^{2} + (\gamma_{\nu,\sigma}^{\mu} + \Gamma_{0})^{2}} \times \left( \gamma_{\nu,\sigma}^{\mu} N_{0}^{\mu} + \sum_{\nu',q,j,\pm} |G_{q}^{\nu \mu}|^{2} N_{q}^{\nu} \eta_{q}^{\nu,\pm} \left( \frac{\Gamma_{\nu}^{\nu}}{\Omega_{q}^{\nu} - (\gamma_{\nu,\sigma}^{\mu} + \Gamma_{0})} + \left( \frac{\Gamma_{\nu}^{\nu}}{\Omega_{q}^{\nu}} \right)^{2} \right) \right)$$

where $\eta_{q}^{\nu,\pm} = 1/2 \pm 1/2 + n_{q}$ denotes the relevant phonon occupation factor for absorption/emission and $N_{q}^{\nu}$ represents the exciton occupation corresponding to the Boltzmann distribution for the considered stationary PL. The first term describes the direct photoluminescence that is often referred to as zero-phonon contribution. The second term shows the phonon-assisted indirect PL and results in the emergence of phonon sidebands. Evaluating Eq. (3), we obtain a microscopic access to the temperature-dependent PL and find that the linewidth of the exciton transition clearly increases with temperature, while its intensity becomes smaller, cf. Fig. 3(a).

**TABLE II.** Values for the deformation potentials for optical and acoustic phonons are extracted from the performed measurements of temperature-dependent excitonic linewidths in PL spectra assuming one dominant optical and acoustic phonon branch.

| $D_{AC}$  | $c_{AC}$  | $D_{OP}$  | $\hbar \omega_{OP}$ | $\Gamma_{0}$  |
|-----------|-----------|-----------|---------------------|--------------|
| 1.9 eV    | 2100 m/s  | 158 eV/nm | 35 meV             | 6.7 meV      |
The zero-phonon linewidth ranges between \( \sim 5 - 10 \text{ meV} \) at low temperatures and \( \sim 50 \text{ meV} \) at room temperature.

In Figs. 3(b)-(d), we decompose the direct PL stemming from radiative exciton recombination within the light cone (\( Q = 0 \)) from the indirect contribution to the PL arising from phonon-assisted exciton recombination from states with a non-zero center-of-mass momentum. We find a clear separation of the two contributions up to \( 50 \text{ K} \). At higher temperatures, the zero-phonon line becomes so broad that the phonon sideband is only visible as a low-energy shoulder. It becomes evident in an asymmetrically broadened exciton transition toward lower energies. The energetic separation of \( \sim 35 \text{ meV} \) between the zero-phonon line and the phonon sideband is governed by the energy of the involved optical phonons. In contrast, the weak contribution of phonon absorption leads to a negligible indirect photoluminescence on the high energy side of the zero-phonon line.

Optical phonons also govern the broadening of the zero-phonon line for temperatures above \( 100 \text{ K} \), while at lower temperature acoustic phonons dominate the PL linewidth, as will be further discussed later. The overall red-shift toward lower energies with decreasing temperature stems from a shift in the relative position of the conduction and valence bands due to polaronic effects [52] as well as due to the temperature-dependent elongation of the lattice. This phenomenon is known as Varshni shift and can be described with the empiric formula [53]

\[
E_g(T) = E_g(0) - \frac{\alpha_1 T^2}{\gamma_1 T + \gamma_2},
\]

where \( E_g(0) \) is the band gap energy at \( T=0 \text{K} \) and \( \alpha_1, \alpha_2 \) are material-specific constants. The red-shift is treated phenomenologically in this work and the material-specific constants are fitted to experimental data.

To be able to directly compare the theoretical prediction to experiment, we have also performed temperature-dependent PL measurements of the same 2D perovskites. The experimental PL spectra were collected from a monocrystalline (PEA)\(_2\)PbI\(_4\) thin sheet (\( \sim 100 \text{ nm} \)) exfoliated from chemically synthesized crystals. To provide better stability of the exfoliated perovskite layer it was encapsulated by h-BN sheets (for more details see Ref. 23). For temperature-dependent PL measurements, the sample was mounted on the cold finger of a helium flow cryostat with a quartz optical window. PL was excited with the frequency-doubled output of a mode-locked Ti:sapphire laser and tuned to 400 nanometers. The excitation laser beam was focused on the sample using a 50× microscope objective with a numerical aperture of 0.55, giving a spot size of approximately one micrometer diameter. The emitted PL was collected through the same objective and directed to a spectrometer equipped with a liquid nitrogen cooled charge-coupled device camera.

Figures 3(e) and (f) present a comparison of theoretically predicted and experimentally measured temperature- and energy-dependent PL spectra. We find a good qualitative agreement in terms of the appearance of the phonon-sideband at the lower energy side of the zero-phonon line (cf. the rectangular boxes). Both in experiment and theory, we find a pronounced phonon sideband appearing at \( 2.33 \text{ eV} \) and staying clearly visible and distinguishable from the zero-phonon line for temperatures up to \( 50 \text{ K} \). Above this temperature the phonon sideband visible in experiment seems to merge/vanish with the main peak in contrast to theoretical predictions where this occurs around \( 100 \text{ K} \). We expect that this discrepancy can be related to h-BN encapsulation which might modify the motion of the inorganic layer and the related phonon mode with respect to the bulk case [28]. Indeed in case of the bulk (PEA)\(_2\)PbI\(_4\) crystals the phonon side-band can be resolved up to around \( 100 \text{ K} \) [22]. This observation may indicate that the electron-phonon interaction can be substantially modified in thin layers of 2D perovskites due to possible residual strain induced by the organic cation interacting with the encapsulating layer [54]. It is also worth to note that in encapsulated layers the LO phonon energy is slightly lower than in bulk samples [22, 28, 43] which also points to the non-negligible impact of encapsulation.

The spectral broadening of excitonic resonances with temperature plays an important role for the visibility of phonon sidebands. Thus, we study the exciton-phonon scattering channels determining the temperature-dependent spectral linewidth of the three energetically lowest excitonic transitions. The linewidth is determined on a microscopic footing within the second-order Born-Markov approximation resulting in the momentum-dependent scattering rates given in Eq. (2). The appearing sum over all phonon modes and momenta includes all scattering processes that fulfill the energy conservation, i.e.

\[
E_{k+q}^\mu - E_k^\nu \pm \hbar \Omega_q = 0,
\]

where \( \Omega_q \) is the energy of the phonon with the mode \( j \) and momentum \( q \), while \( E_{k+q}^\mu \) and \( E_k^\nu \) are the energies of the initial and final excitonic states. We include absorption (-) and emission (+) processes with optical and acoustic phonons. Since only the states within the light cone (i.e. \( k \approx 0 \)) contribute to the direct PL, the linewidth of the zero-phonon line is determined by the scattering rate \( \Gamma_{k=0}^\nu \). The resulting linewidths and their underlying microscopic scattering channels are displayed in Fig. 4. We find spectral linewidths of approximately \( 50 \text{ meV} \), \( 25 \text{ meV} \) and \( 15 \text{ meV} \) for 1s, 2s and 3s transitions at room temperature, respectively. In the case of 1s, we show that the scattering with acoustic phonons dominates the linewidth up to temperatures of approximately \( 150 \text{ K} \), cf. the orange shaded region in Fig. 4(a). We find a linear dependence on temperature reflecting the behaviour of the phonon occupations that are described by the Bose-Einstein distribution. Optical phonons start to be important for temperatures above \( 100 \text{ K} \) (red region) and become the main channel governing the linewidth of 1s from approximately \( 150 \text{ K} \). Optical phonons are important only at higher temperatures, since their energy is \( 35 \text{ meV} \) and thus the phonon occupation is negligibly

\[
\sim \frac{E}{kT} \ll 1,
\]

where this occurs around \( 100 \text{ K} \). We expect that this

\[
\sim 50 \text{ meV}
\]

\[
\sim 5 - 10 \text{ meV}
\]

\[
\sim 50 \text{ meV}
\]

\[
\sim 35 \text{ meV}
\]
FIG. 4. (a)-(c) Temperature-dependent exciton linewidth of the three energetically lowest excitonic transitions (1s, 2s and 3s) resolving the contribution of optical and acoustic phonons. (d)-(f) Microscopic scattering channels driven by optical phonons for the considered excitonic transitions.

small at low temperatures. There is also a temperature-independent contribution stemming from radiative recombination (grey region, 2.66 meV) that also limits the lifetime of 1s excitons in the light cone. The oscillator strength considerably decreases for higher transitions due to more spatially extended wavefunctions. Hence, the radiative recombination has only a marginal contribution to their linewidths with $1.9 \cdot 10^{-1}$ meV for 2s and $4.9 \cdot 10^{-2}$ meV for 3s, cf. Figs. 4(b)-(c). Note that we assume an ideal defect-free sample by disregarding the constant broadening $\Gamma_0$ that arises from scattering with defects and does not have any impact on the investigated temperature dependence.

The quasi-linear dependence of the linewidth for higher states (2s and 3s) is caused by the fact that scattering with acoustic phonons is the main mechanism limiting the lifetime of 2s and 3s states at all temperatures. To explain the overall low importance of optical phonons for higher excitonic states, we investigate the wavefunction overlap $\sum_{k,\alpha} \phi_k \phi^\alpha_{k+\omega}$ of the involved initial and final scattering states that enters in the exciton-phonon coupling elements. In particular, it is important to consider the specific momenta where energy conservation is fulfilled, cf. circular and triangular markers in Fig. 5 denoting these momenta for optical and acoustic phonons respectively. We find that the only possible scattering channel fulfilling the energy conservation for the 1s exciton is the intraband 1s$\rightarrow$1s scattering with optical and acoustic phonons, as shown in Fig. 4(d).

For the higher 2s and 3s states, multiple scattering channels are possible, cf. Figs. 5(b)-(c). Nevertheless, in all three cases it is the intraband scattering with acoustic phonons that shows the maximum wavefunction overlap due to the small momentum transfer of this transition. To be able to explain which specific scattering channel and phonon mode dominates the linewidth, it is not always sufficient to only consider the wavefunction overlap. The exciton-phonon coupling element is determined by the wavefunction overlap weighted by the corresponding deformation potential that is constant for optical phonons and linear in $q$ for acoustic phonons. Furthermore, the temperature- and energy-dependent occupation of the involved phonon modes also needs to be considered since it directly enters the scattering rate, cf. Eq. (2). The combination of a strong electron-phonon coupling, large wavefunction overlap, and a moderate phonon number results in a very efficient intraband scattering with acoustic phonons that dominates the linewidth. The efficiency of scattering with optical phonons decreases for higher states despite the enhanced number of possible scattering channels—as already seen in transition metal dichalcogenides [50]. This can be traced back to lower excitonic binding energies and thus more spatially extended excitonic wavefunctions.

While acoustic phonons predominantly induce scattering within an excitonic band, optical phonons can also bridge larger energy distances between different bands. To better understand these processes, we further decompose the most important scattering channels with opti-
cal phonons in Figs. 4(d)-(f). Since for optical phonons the coupling strength and phonon number do not depend on momentum, the efficiency of a particular scattering channel is only determined by the wavefunction overlap. We find that the most important contribution caused by optical phonons corresponds to emission processes to the energetically lower 1s state (blue areas in Figs 4(e)-(f)). Note that spontaneous emission is much more likely than stimulated emission at low temperatures, where the phonon number is very small. Moreover, the fact that spontaneous emission does not depend on the phonon number results in the constant linewidth at low temperatures. For 2s excitons, the wavefunction overlap for the optical phonon absorption processes $2s \rightarrow 3s$ and $2s \rightarrow 3d$ stands out (cf. Fig. 5(b)), which is directly reflected in their important contributions to the optical phonon portion of the linewidth in Fig. 4(e).

The 3s exciton state is close to the continuum allowing multiple scattering channels driven by emission and absorption of phonons. The scattering with optical phonons at the 3s state is dominated by the $3s \rightarrow 1s$ transition induced by spontaneous emission (cf. Fig. 4(f)). Furthermore, due to the energetic proximity of other states, significant wavefunction overlap exists for interband acoustic phonon scattering processes (cf. Fig. 5(c)). However, the small phonon number at the large momenta involved in these scattering processes drastically reduces the efficiency of these channels resulting in an even smaller linewidth at room temperature compared to the 1s exciton exhibiting much fewer scattering channels.

In summary, we have presented a theoretical study supported by experimental measurements shining light on excitonic properties of monolayered halide perovskites. Based on a quantum mechanical approach, we have determined the eigenfunctions and binding energies of the entire Rydberg-like series of excitonic states. Furthermore, we have calculated and measured temperature-dependent photoluminescence spectra with a particular focus on the emergence of low-energy phonon sidebands. Finally, we have provided microscopic insights into the exciton-phonon scattering channels governing the temperature-dependent spectral linewidth of the three energetically lowest excitonic transitions. Overall, our work contributes to a better understanding of optical properties of 2D perovskites and can guide future studies in this growing field of research.

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Corresponding author: causin@chalmers.se

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