Homogeneous Emission Line Broadening in the Organo Lead Halide Perovskite CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$

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A. Derivative of the absorption coefficient

To obtain a value for the spectral width of the absorption edge of vapor-deposited CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ that can be sensibly compared to the spectral with of the observed PL emission, we calculate the derivative of the absorption coefficient and subsequently determine its spectral width as illustrated in **Figure S1.** If the predominant broadening can be described as a convolution of a sharp edge with a characteristic distribution function, this method will allow us to extract the width of this distribution function. We obtain a full width at half maximum (FWHM) of 56 meV.
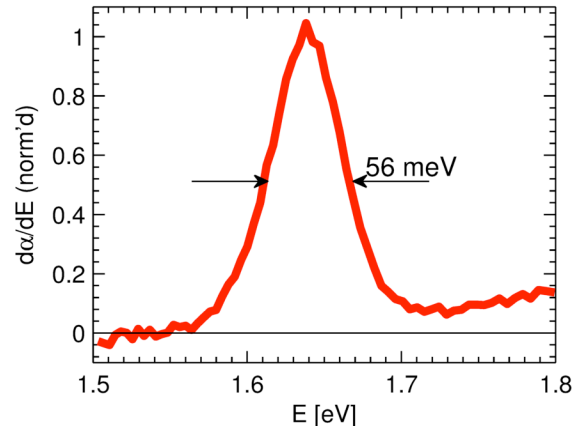
Figure S1: Derivative of the absorption coefficient of vapour deposited $CH_3NH_3PbI_{3-x}Cl_x$ (as originally displayed in Figure 1b of the main article). The arrows illustrate the full width at half-maximum of 56 meV.

B. Normalized plots of PL emission spectra

Figures S2 displays a subset of the PL emission spectra for different excitation energies, originally shown un-normalized in Figure 2a of the main article. Here, the data is plotted in a normalized form to allow accurate, detailed comparison of the shapes of the spectra. It is apparent from the plot that the PL emission spectrum of vapor-deposited $CH_3NH_3PbI_{3-x}Cl_x$ does not undergo any changes under variation of the excitation energy across the investigated range. This confirms the results of the analysis presented in Figure 2c of the main text.

Analogously, **Figures S3** displays a normalized subset of the time-resolved PL emission spectra originally shown un-normalized in Figures 3a of the main article. No change of the spectral shape with time-delay can be observed in agreement with the analysis displayed in Figure 3c of the main text.
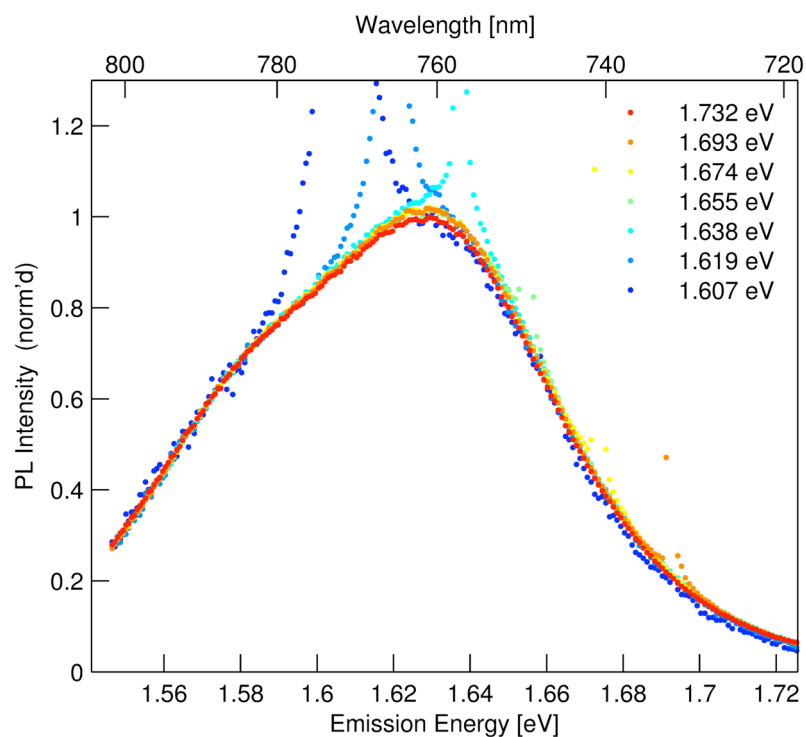
Figure S2: Normalized PL emission spectra of evaporated $CH_3NH_3PbI_{3-x}Cl_x$ films taken at excitation energies close to the absorption edge ranging from 1.607 eV (dark red) to 1.732 eV (dark blue). The excitation intensity was held constant at 5 W cm^{-2}. The narrow peaks originate from scattered excitation light.
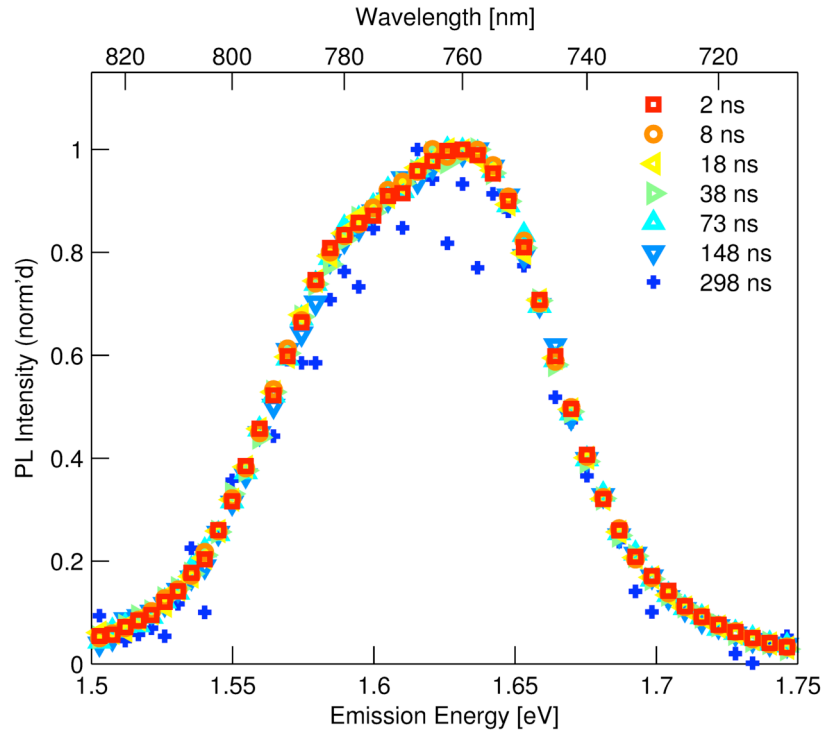
Figure S3: Normalized PL emission spectra of evaporated $CH_3NH_3PbI_{3-x}Cl_x$ films at different time-delays between excitation and detection. The spectra were reconstructed from a set of time-resolved measurements taken over a range of excitation energies by means of time-correlated single photon counting (Excitation energy: 2.43 eV, fluence: 6 µJ/cm², repetition rate: 2 MHz). Data points were extracted by integrating the time-resolved data over a window of ±2 ns centered at the delay time stated in the legend.

C. PL emission spectrum and optical absorption edge at T = 160 K

We acquired basic PL emission and optical absorption data for vapor-deposited $CH_3NH_3PbI_{3-x}Cl_x$ also for temperatures lower than 297 K. The possibilities for investigating the emissive properties of the material by means of low temperature studies are restricted because organometal halides are known to undergo structural phase transitions at temperatures below 297 K. Hence to allow for relevant conclusions to be made on the temperature-dependence of optoelectronic properties, these have to be based on observations made on the same crystal and electronic structure of the material. For lead triiodide perovskite ($CH_3NH_3PbI_3$) a phase transition from the tetragonal to the trigonal crystal system was found to occur around T = 150-160 K.[1,2] In our experiments we were able to observe a transition through a sudden shift of the optical absorption edge and of the position of the PL emission peak between around 140 K. In **Figure S4**, we therefore show PL emission and optical absorption data acquired at T = 160 K, which is close to the lowest possible temperature for which we can be sure not to have entered the phase-transition regime. The data is compared to those from measurements at room temperature (297 K) taken with exactly the same setup under otherwise identical experimental conditions.

With decreasing temperature we observe a shift of the absorption onset and the PL emission peak to lower energy, in agreement with a decrease in bandgap energy and the expected change in thermal occupation of states at the band edges. In addition, the absorption onset develops a more pronounced feature at T = 160 K, which could arise from excitonic enhancement effects.[3] Figure S4 shows that the spectral width of both the absorption onset and the PL decreases roughly proportionally to T. The lower spectral width of the PL emission may be explained by the combination of two effects. First, the tail of the Fermi-distribution of electrons near the conduction band minimum, which is responsible for

fundamental thermal emission broadening in semiconductors, is reduced. Second, because of the lower phonon population present in the material at low temperature, the effect of phonon-induced broadening is diminished. This is expected to primarily affect the high-energy side of the spectrum, as in first order only phonon absorption processes are limited by the available population. The observed spectral changes are therefore in accordance with expectations of phonon-mediated broadening. The high-energy edge of the PL spectrum sharpens with lowered temperature (lower phonon absorption), while the pronounced low-energy shoulder of the PL emission continues to exist when cooling the sample down to $T = 160$ K (largely unaffected phonon emission).

For the temperature-dependent experiment an *Oxford Instruments Microstat* liquid-Helium microscope cryostat was used in conjunction with the tunable fs-pulsed laser based PL spectroscopy setup described in the main manuscript. Therein, the sample is mounted in a chamber under high vacuum ($p < 10^{-5}$ mbar) on a temperature-controlled cold finger. The experimental setup was extended to allow acquisition of optical absorption spectra in addition to photoluminescence measurements. For this purpose, light from a 100 W incandescent lamp was collimated and guided onto the rear surface of the sample such that the transmitted part was collected by the existing optics of the setup and spectrally resolved and detected by a combination of a grating monochromator and a liquid-nitrogen cooled CCD. Absorption spectra were then obtained by comparison of the acquired spectrum of the transmitted light to a reference acquired with the sample removed from the cryostat.
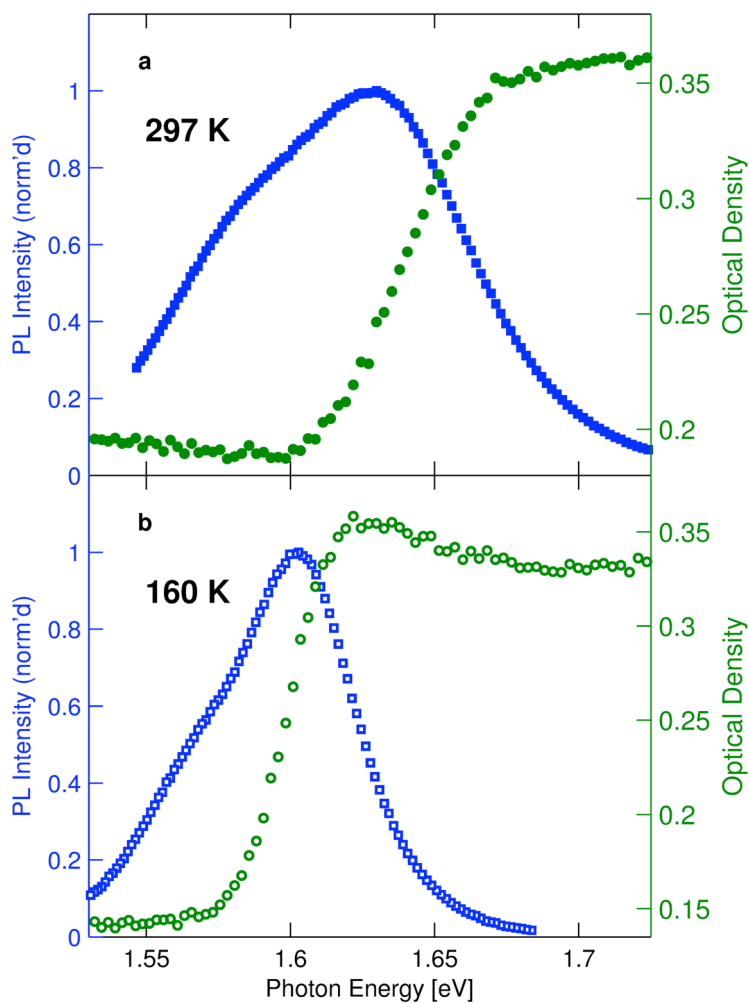
Figure S4: PL emission spectra (blue squares) and optical densities (green circles) of vapor-deposited $CH_3NH_3PbI_{3-x}Cl_x$ films taken at (a) room temperature and (b) $T = 160$ K. The samples were excited at photon energies of 1.732 eV (297 K) and 1.693 eV (160 K) at 80 MHz repetition rate and an intensity of 5 W cm^{-2}. The optical density data shown was obtained from measurements in a simple transmission setup as described in the text, using $OD = -\log_{10}(T)$.

References

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(3) Sturge, M. D. Optical Absorption of Gallium Arsenide between 0.6 and 2.75 eV. *Phys. Rev.* **1962,** *127,* 768-773.