Electronic Supplementary Information

Towards the evaluation of defects in MoS_2 by cryogenic photoluminescence spectroscopy

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The Electronic Supplementary Material contains additional details on the experimental methods and Raman and PL spectroscopy, mainly decomposition of the Raman and PL spectra, and maps of Raman and PL spectral parameters at 300, 250, 200, 150, 100, 50 and 10 K for the as-grown and transferred CVD MoS_2.

Experimental Methods Details

The MoS_2 monolayers were grown using chemical vapor deposition (CVD) with MoO_2 (Sigma Aldrich #234761) and S (Sigma Aldrich #344621) as the sources at atmospheric pressure: A 3x1 cm^2 piece of Si/SiO_2 (300 nm) substrate was cleaned in acetone and isopropanol with an ultrasonic bath, dried using ultrapure Ar gas, and subsequently placed face down on a quartz crucible containing 30 mg of MoO_2 powder. The crucible was installed at the center of a 0.5-inch quartz tube and a 90 mg S source was placed at its edge, which was inserted into a 1-inch quartz tube. Thus, the MoO_2 was at the center of the oven and the S was just outside the oven. The tube was flushed for 5 min with a 120 sccm Ar flow at room temperature. Thereafter, the MoS_2 growth was initiated with an Ar flow of 120 sccm. The temperature was gradually increased to the growth temperature of 1123 K at 40 K/min and held there for 10 minutes. After the growth, the oven was opened, and the sample was quickly cooled to room temperature in an Ar flow of 120 sccm.

For some experiments, the MoS_2 was transferred to a different Si/SiO_2 (300 nm) substrate using a wet transfer process: a thin layer of Poly(methyl methacrylate) (PMMA) was spin-coated on the CVD-grown MoS_2. A 1 M KOH solution was used to dissolve part of the SiO_2, while the Si wafer sank to the bottom and the PMMA/MoS_2 floated on the KOH solution. The PMMA/MoS_2 was subsequently transferred several times on the surface of deionized water for washing and finally transferred to a new Si/SiO_2 wafer. The PMMA was then removed using acetone vapors.

Ambient Raman and photoluminescence (PL) spectral maps were measured using a WITec Alpha300R spectrometer equipped with a piezo stage and a RayShield Coupler. The maps were measured with a 2.33-eV (532 nm) laser excitation at a laser power of approximately 0.1 mW. Gratings of 600 and 1800 lines/mm were used for the PL and Raman spectra, respectively.

Temperature dependent Raman and photoluminescence (PL) spectral maps were measured using a low temperature confocal Raman microscope insert (attoRAMAN, attocube) that was placed in a Physical Property Measurement System (PPMS, Quantum Design). Before each measurement, the sample space was flushed several times with He gas, and the sample space was evacuated to 5 mbar. The Raman and PL spectra were acquired using a WITec Alpha300 spectrometer with a 2.33 eV (532 nm) laser excitation, a 100x objective (numerical aperture 0.82), and a lateral resolution of 500 nm. At well-defined temperatures, Raman spectral maps of 25×25 μm^2 were acquired with lateral steps of 500 or 1000 nm in both directions. The 1800 lines/mm grating was used for the Raman spectra measurements and the 600 lines/mm grating was used to measure the PL. A laser power of approximately 0.1 mW was used. The intensity response of the CCD detector was calibrated using a tungsten halogen light source (HL-2000-CAL, Ocean Optics).

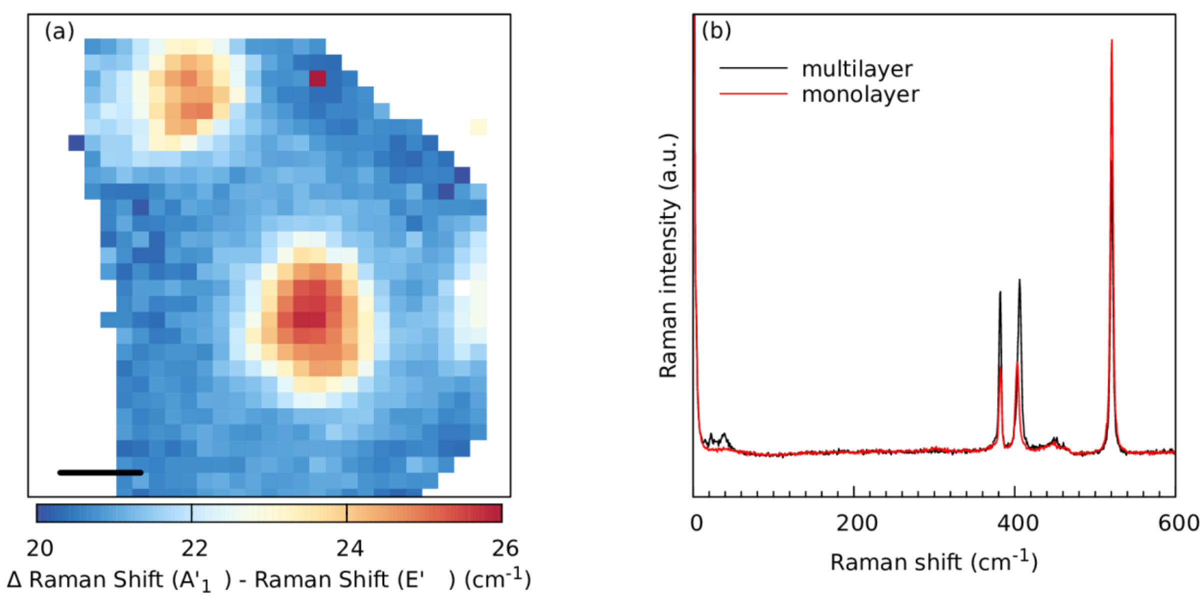

Figure S1. (a) Raman map showing the difference in Raman shift between the A'$_1$ and E' modes at 300 K. The scale bar is 5 μm. (b) The Raman spectra of the monolayer (red line) and the central seed area (black line) at ambient conditions.

300K – CVD grown

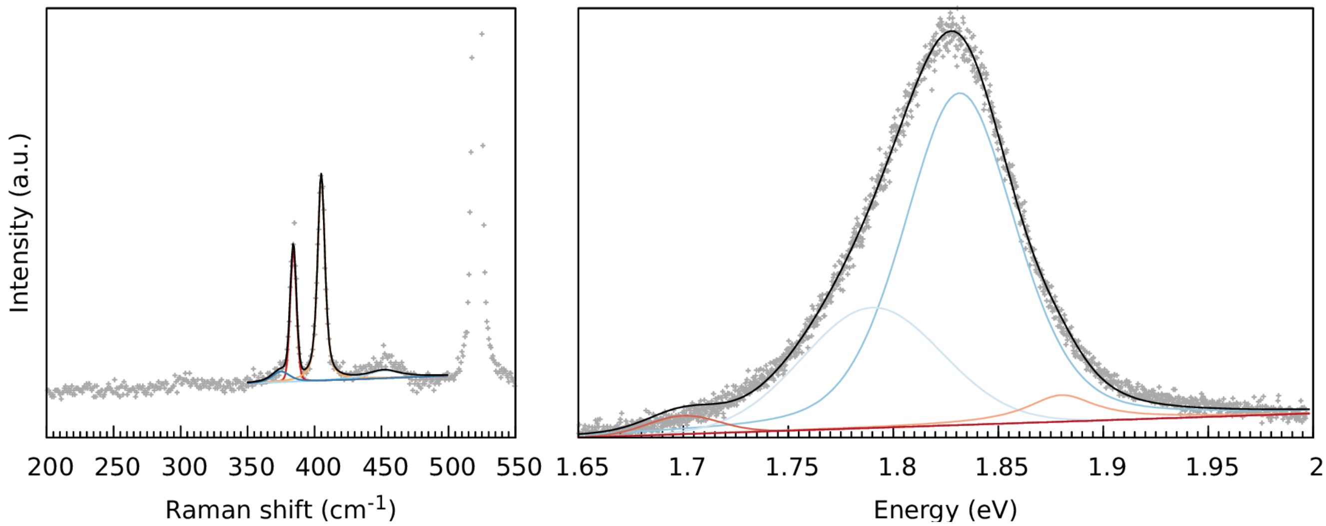

Figure S2. Raman and PL spectrum of MoS_2 at 300 K. The experimental data is marked by gray dots and fits of the individual bands of the MoS_2 monolayer are shown in red for the E', yellow for the A'$_1$, dark blue for the LO(M) and light blue for the 2LA(M) component for the Raman spectra. For the PL spectrum, the individual components are marked by brown for the X^{B1} mode, red for the X^{B2} mode, light blue for the charged exciton (trion, X^-), blue for the neutral A exciton X^0 and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

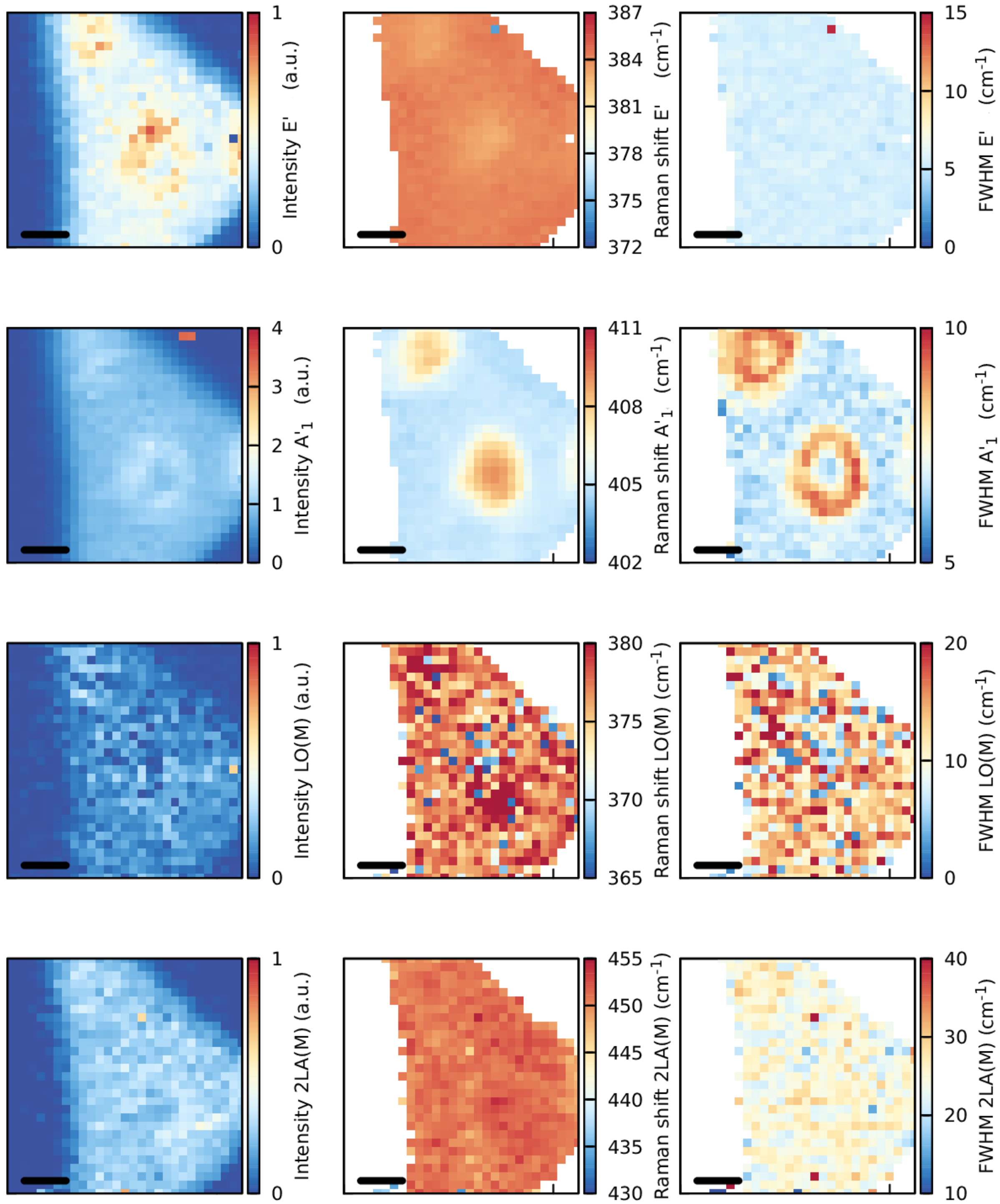

Figure S3. Maps of the fitted intensity, Raman shift and FWHM of the E' and A’$_1$, LO(M) and 2LA(M) modes at 300 K. The scale bar in each panel is 5 μm.

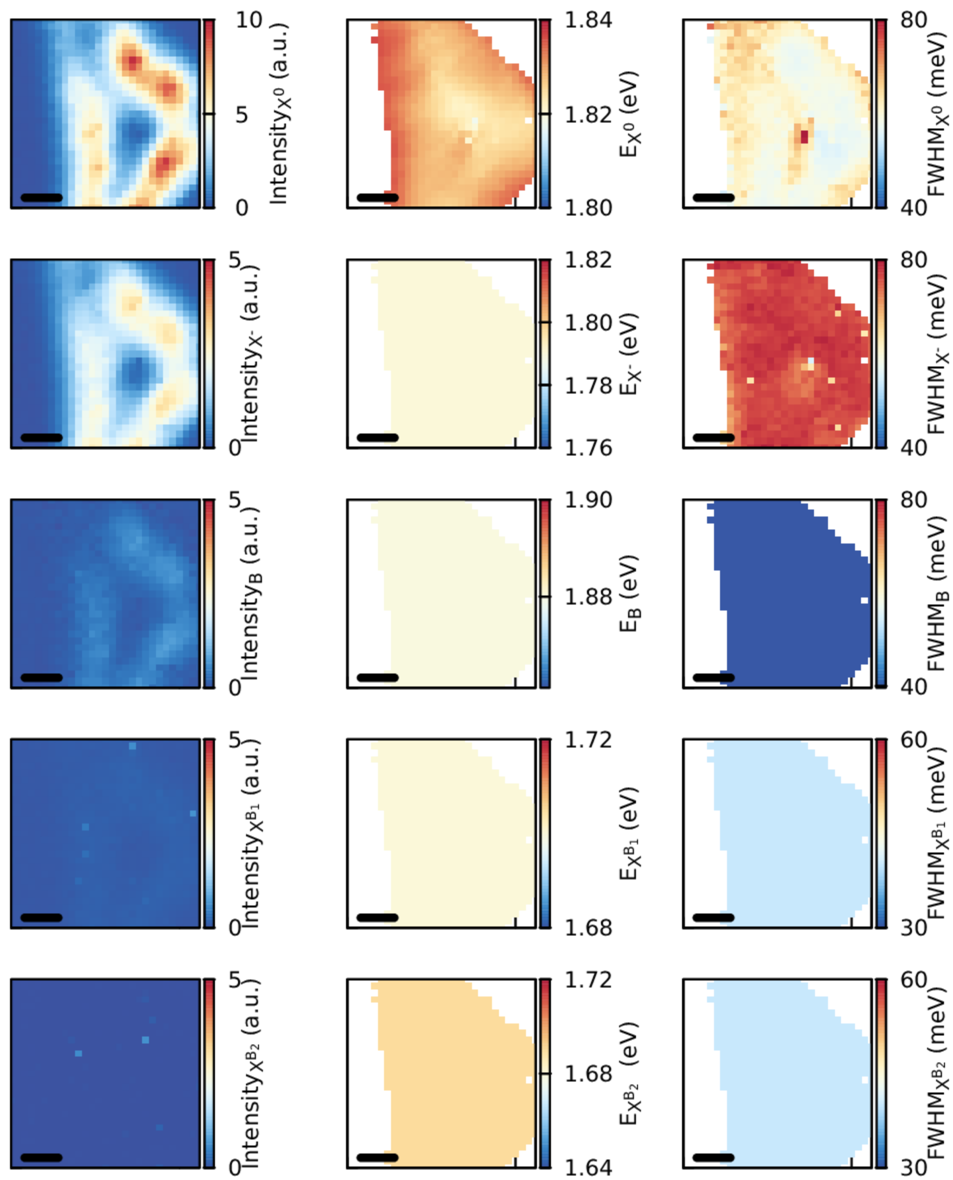

Figure S4. Maps of the fitted intensity, photon energy E and FWHM of the neutral A exciton X^0, the charged exciton (trion, X^-), the B exciton and X^{B1} and X^{B2} at 300 K. The scale bar in each panel is 5 μm.

250 K – CVD grown

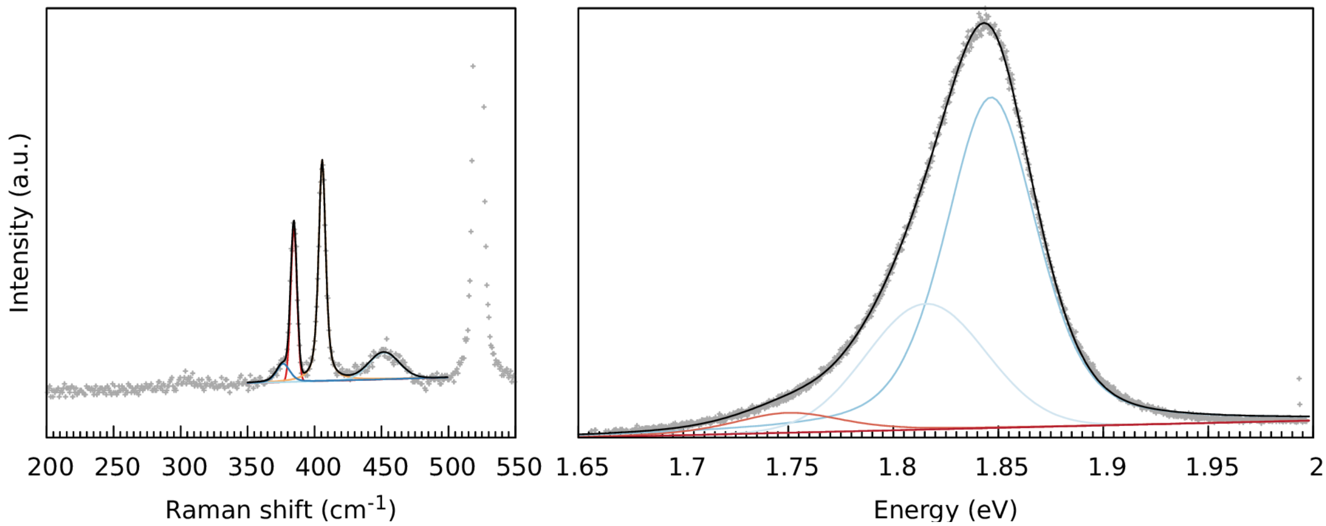

Figure S5. Raman and PL spectrum of MoS_2 at 250 K. The experimental data is marked by gray dots and fits of the individual bands of the MoS_2 monolayer are shown in red for the E', yellow for the A'_1, dark blue for the LO(M) and light blue for the 2LA(M) component for the Raman spectra. For the PL spectrum, the individual components are marked by brown for the X^{B1} mode, red for the X^{B2} mode, light blue for the charged exciton (trion, X^-), blue for the neutral A exciton X^0 and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

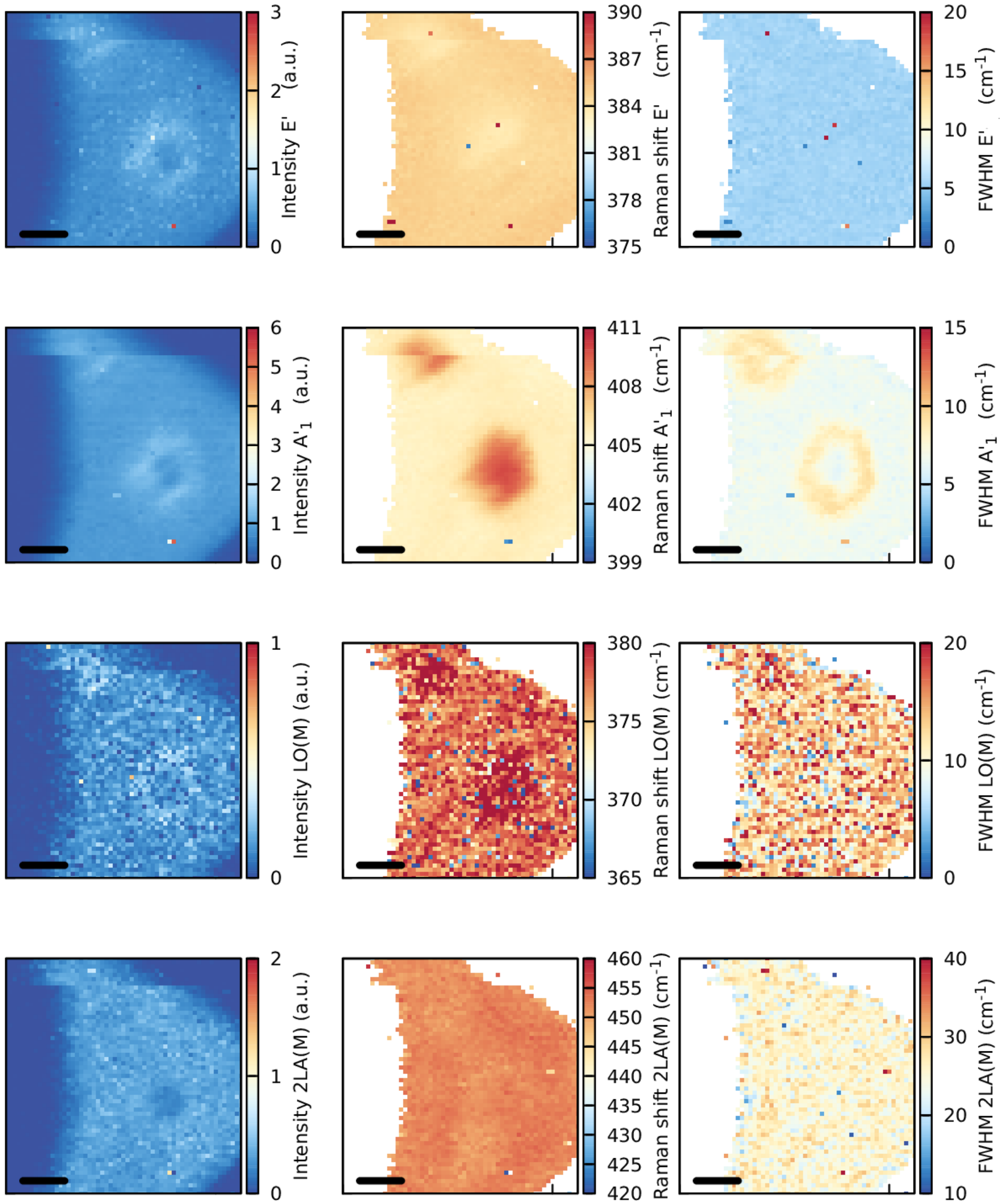

Figure S6. Maps of the fitted intensity, Raman shift and FWHM of the E', A'$_1$, LO(M) and 2LA(M) modes at 250 K. The scale bar in each panel is 5 μm.

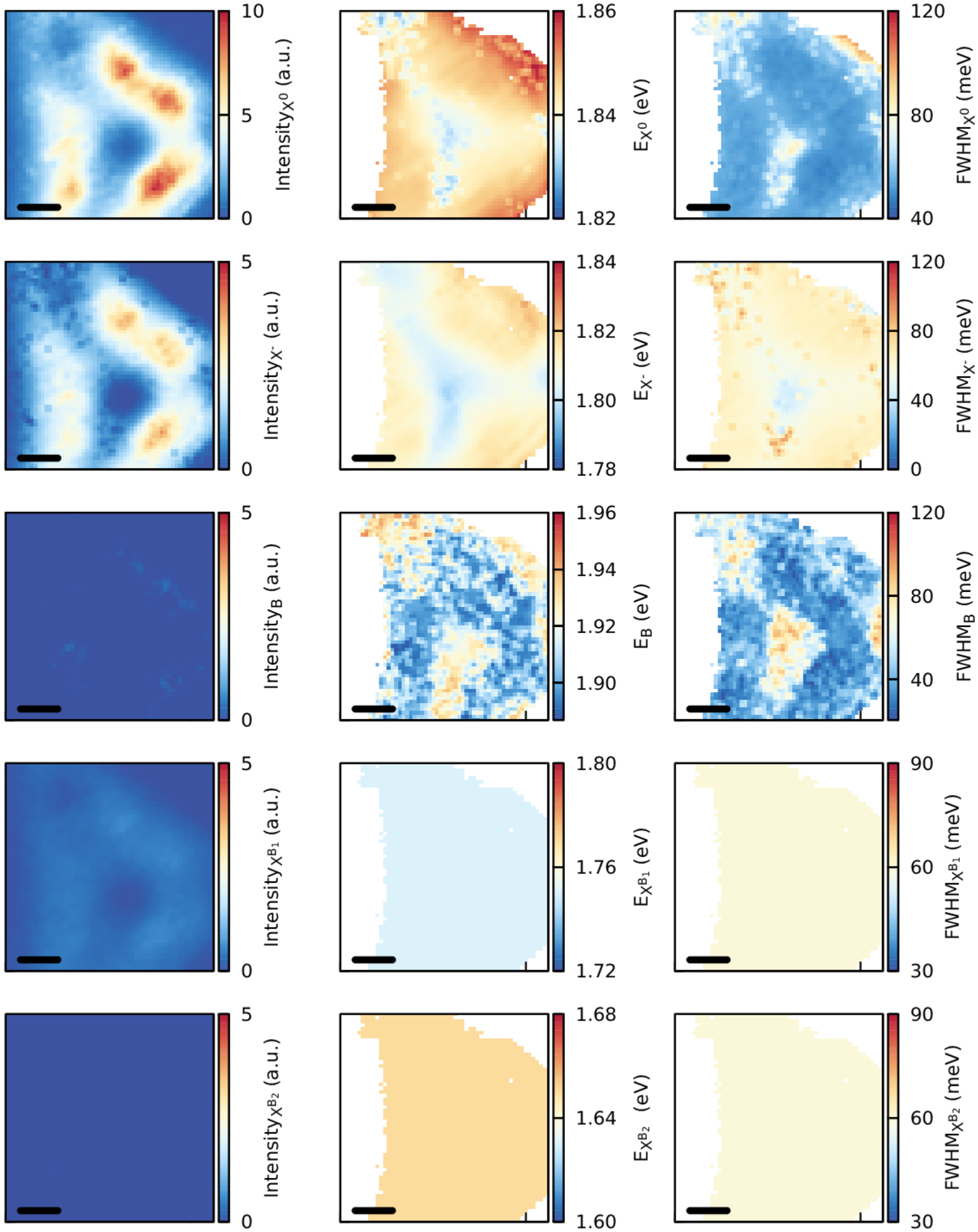

Figure S7. Maps of the fitted intensity, photon energy E and FWHM of the neutral A exciton X^0, the charged exciton (trion, X^-), the B exciton and X^{B1} and X^{B2} at 250 K. The scale bar in each panel is 5 μm.

200 K – CVD grown

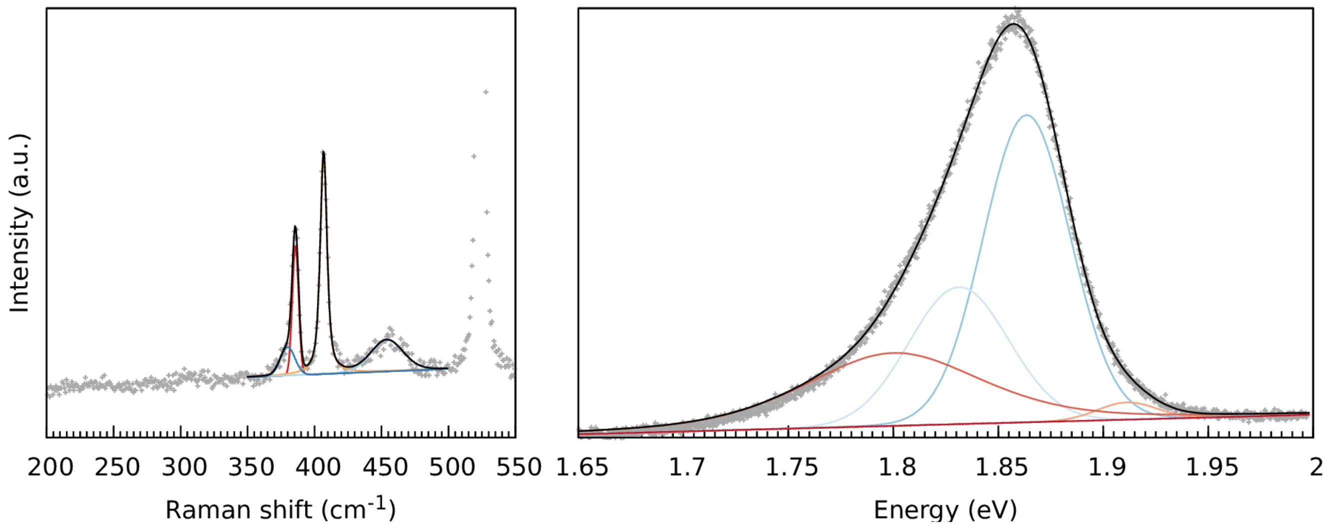

Figure S8. Raman and PL spectrum of MoS_2 at 200 K. The experimental data is marked by gray dots and fits of the individual bands of the MoS_2 monolayer are shown in red for the E', yellow for the A'_1, dark blue for the LO(M) and light blue for the 2LA(M) component for the Raman spectra. For the PL spectrum, the individual components are marked by brown for the X^{B1} mode, red for the X^{B2} mode, light blue for the charged exciton (trion, X^-), blue for the neutral A exciton X^0 and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

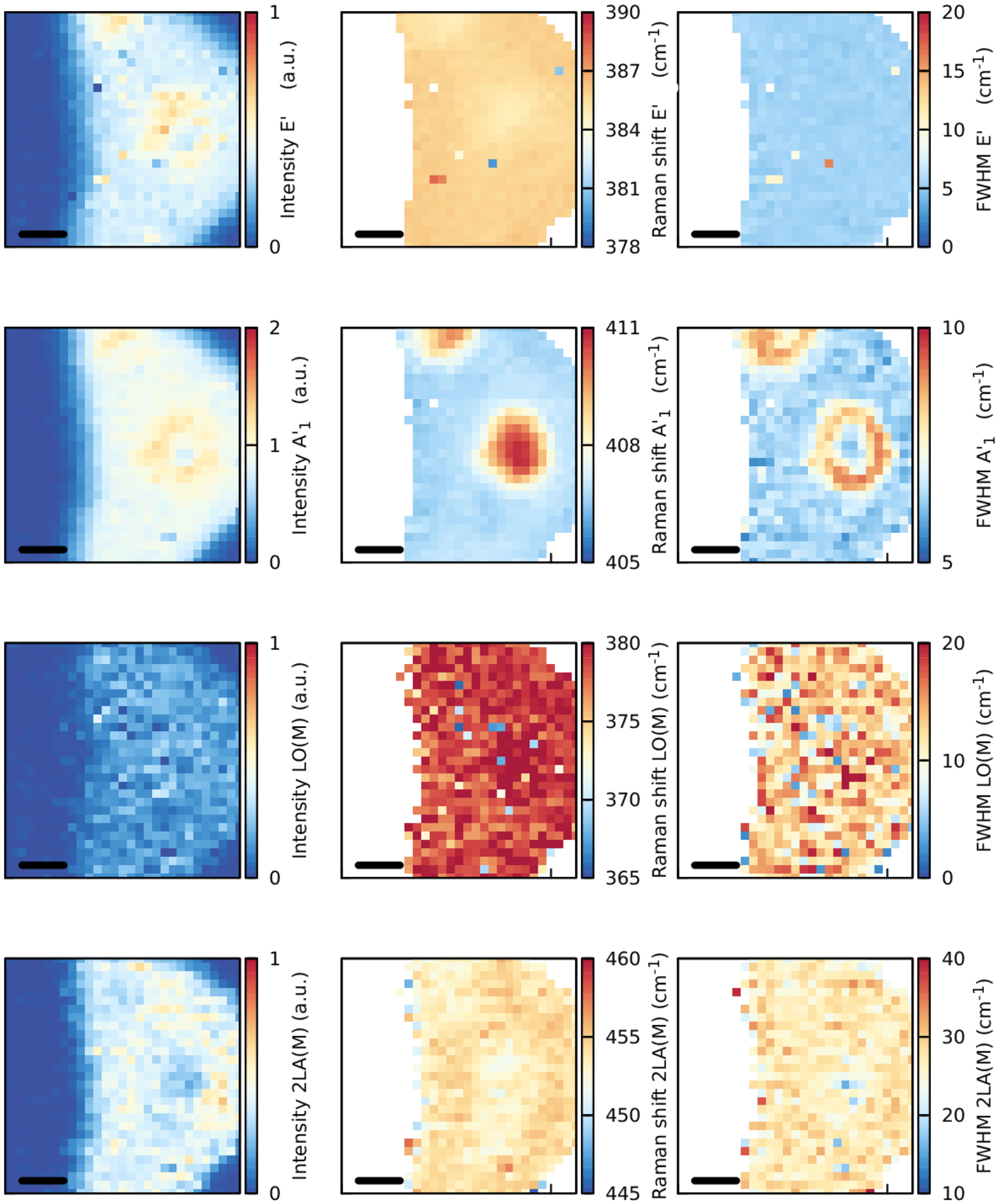

Figure S9. Maps of the fitted intensity, Raman shift and FWHM of the E', A'$_1$, LO(M) and 2LA(M) modes at 200 K. The scale bar in each panel is 5 μm.

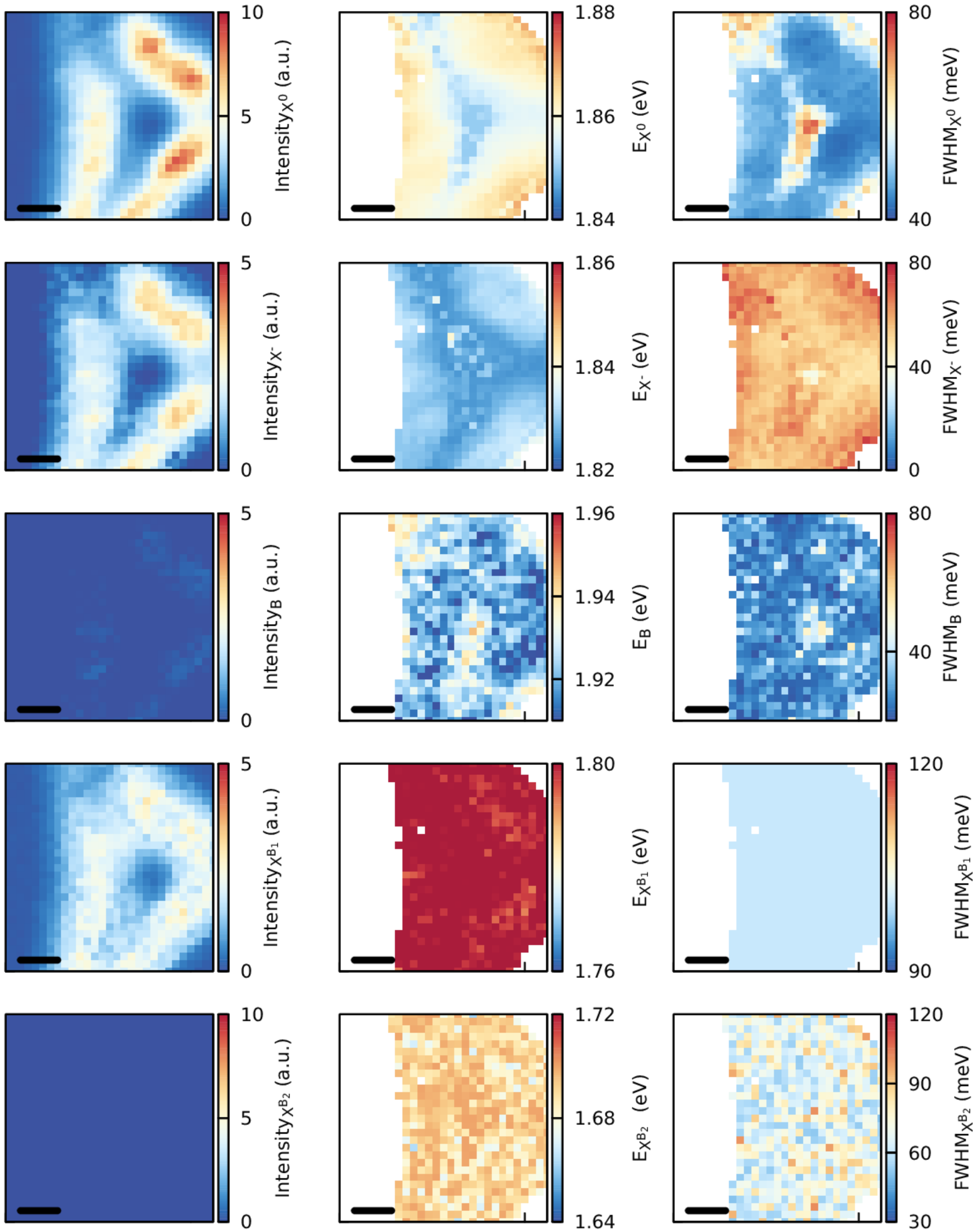

Figure S10. Maps of the fitted intensity, photon energy E and FWHM of the neutral A exciton X^0, the charged exciton (trion, X^-), the B exciton and X^{B1} and X^{B2} at 200 K. The scale bar in each panel is 5 μm.

150 K – CVD grown

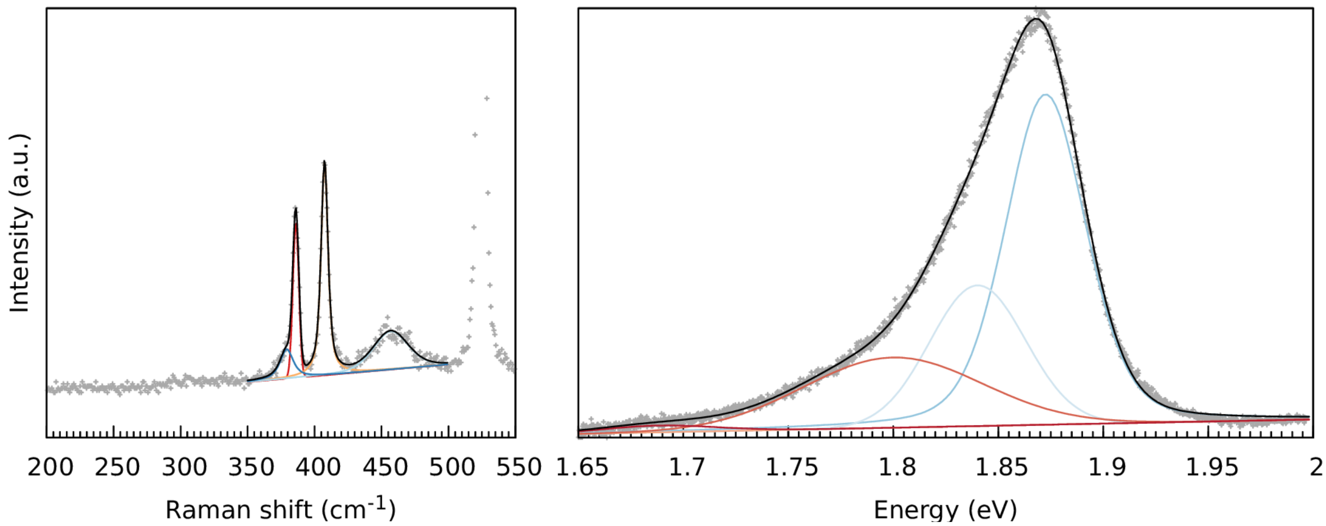

Figure S11. Raman and PL spectrum of MoS_2 at 150 K. The experimental data is marked by gray dots and fits of the individual bands of the MoS_2 monolayer are shown in red for the E', yellow for the A'_1, dark blue for the LO(M) and light blue for the 2LA(M) component for the Raman spectra. For the PL spectrum, the individual components are marked by brown for the X^{B1} mode, red for the X^{B2} mode, light blue for the charged exciton (trion, X^-), blue for the neutral A exciton X^0 and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

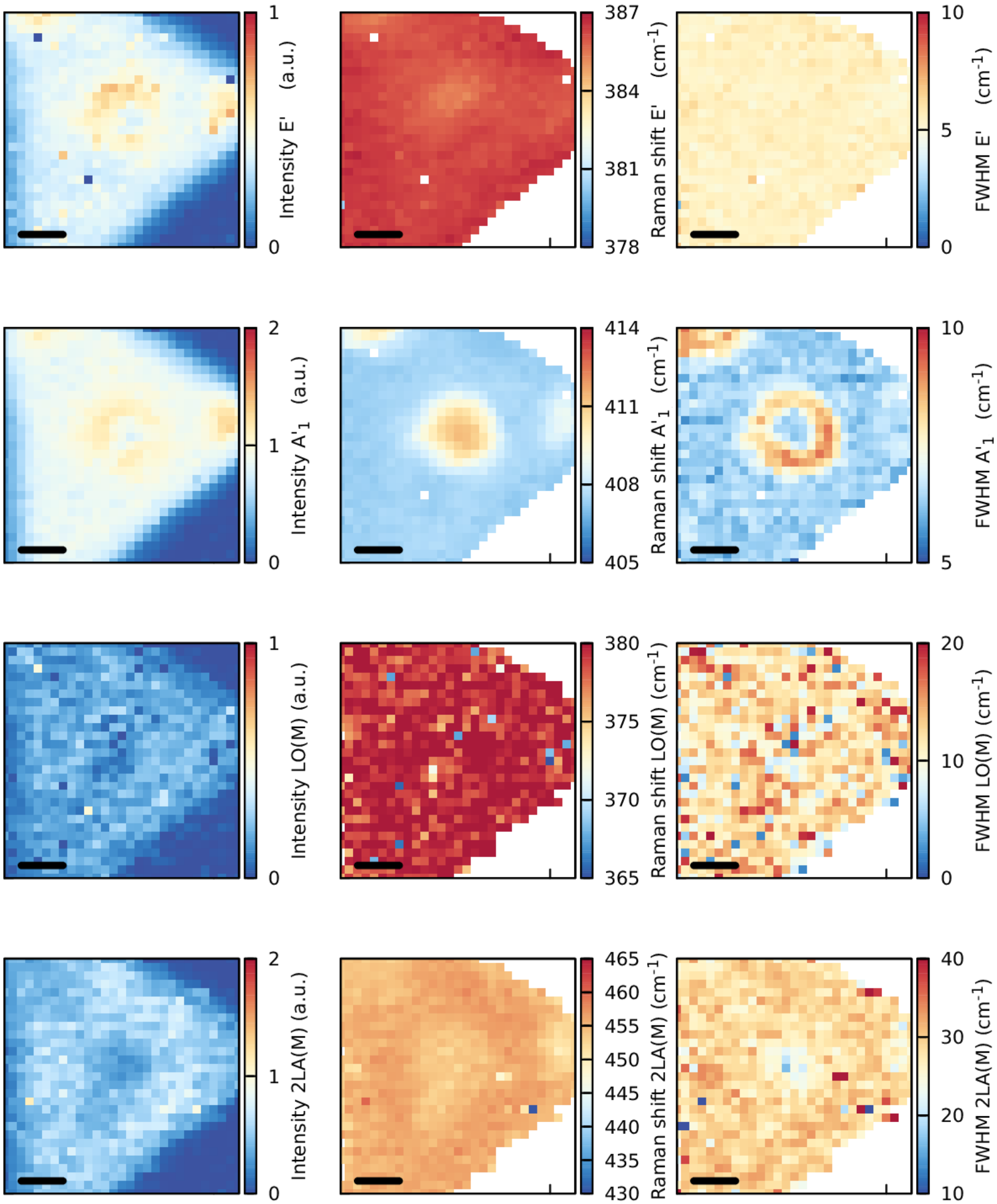

Figure S12. Maps of the fitted intensity, Raman shift and FWHM of the E', A'$_1$, LO(M) and 2LA(M) modes at 150 K. The scale bar in each panel is 5 μm.

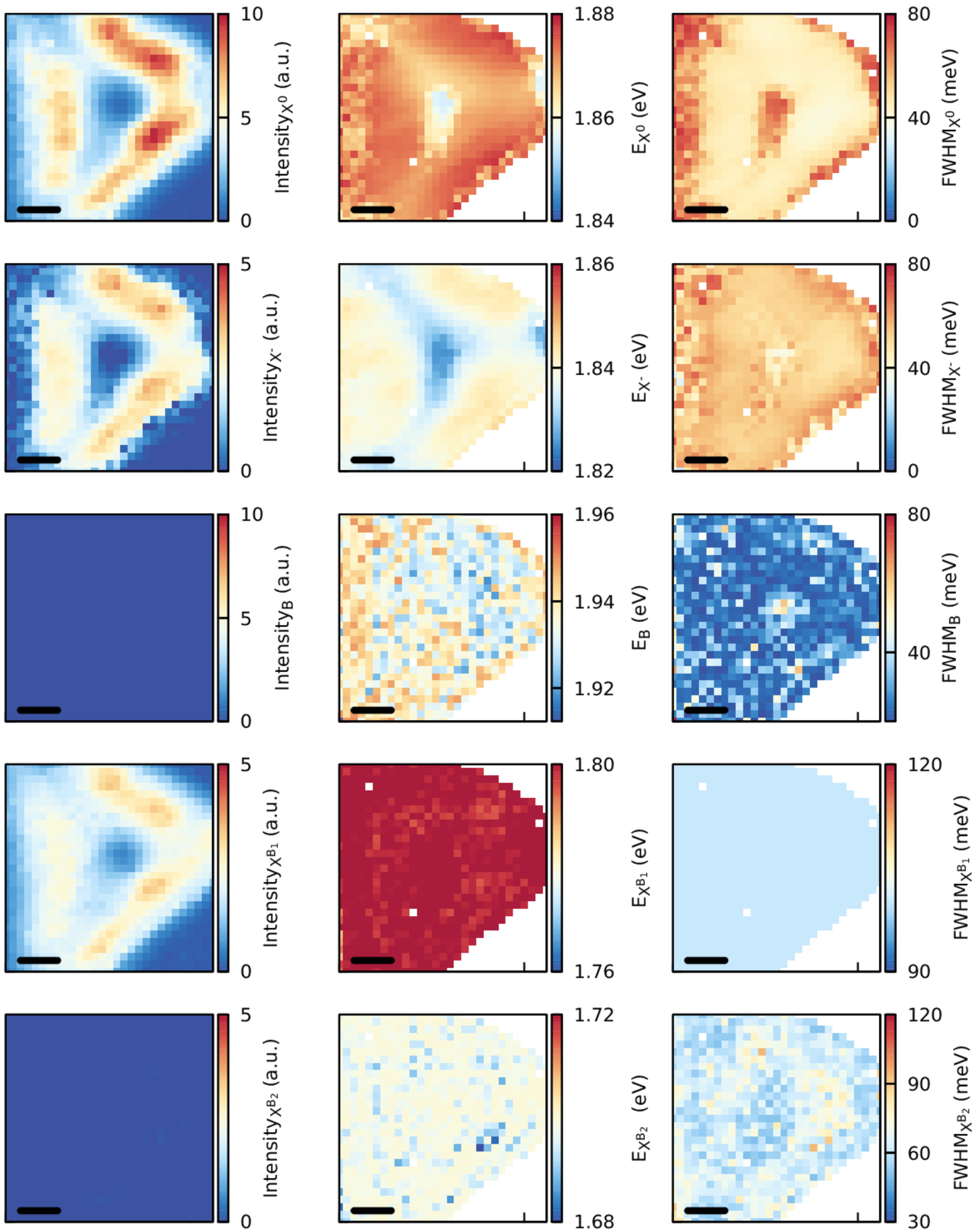

Figure S13. Maps of the fitted intensity, photon energy E and FWHM of the neutral A exciton X^0, the charged exciton (trion, X^-), the B exciton and X^{B1} and X^{B2} at 150 K. The scale bar in each panel is 5 μm.

100 K – CVD grown

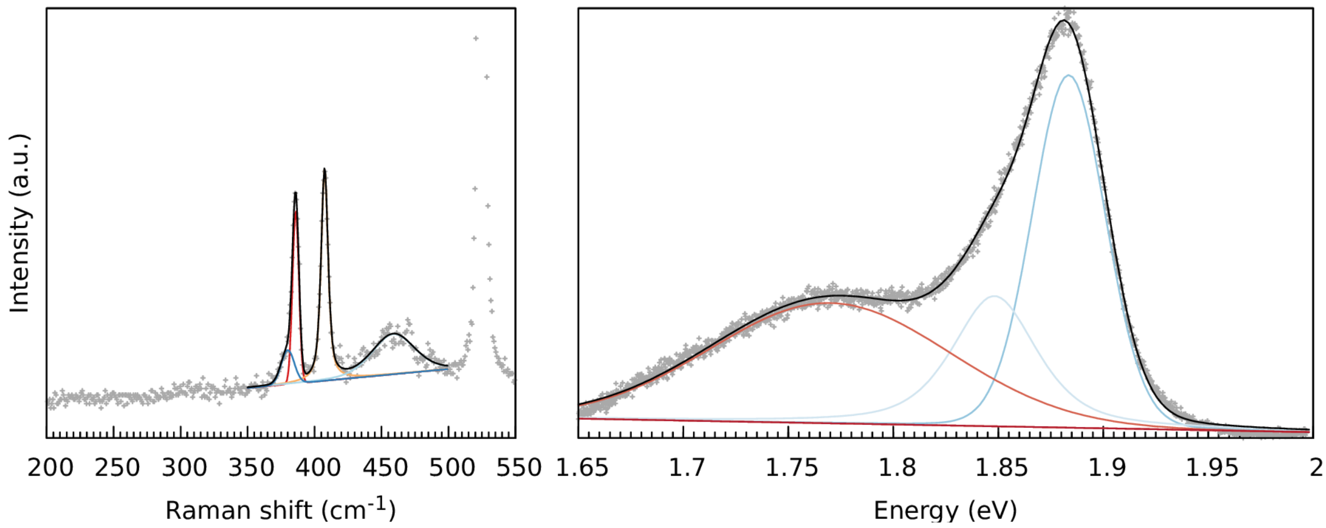

Figure S14. Raman and PL spectrum of MoS_2 at 100 K. The experimental data is marked by gray dots and fits of the individual bands of the MoS_2 monolayer are shown in red for the E', yellow for the A'_1, dark blue for the LO(M) and light blue for the 2LA(M) component for the Raman spectra. For the PL spectrum, the individual components are marked by brown for the X^{B1} mode, red for the X^{B2} mode, light blue for the charged exciton (trion, X^-), blue for the neutral A exciton X^0 and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

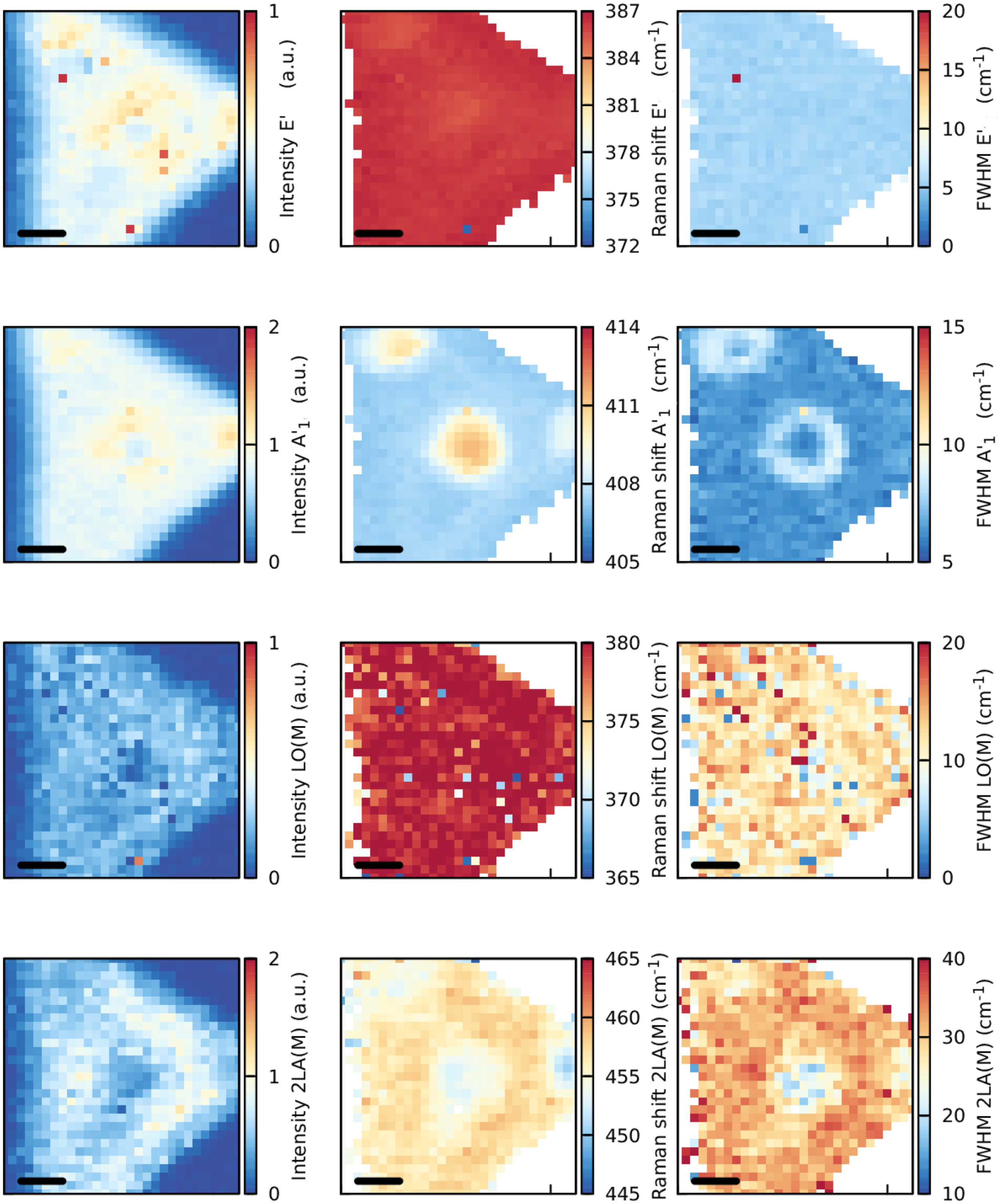

Figure S15. Maps of the fitted intensity, Raman shift and FWHM of the E', A'$_1$, LO(M) and 2LA(M) modes at 100 K. The scale bar in each panel is 5 μm.

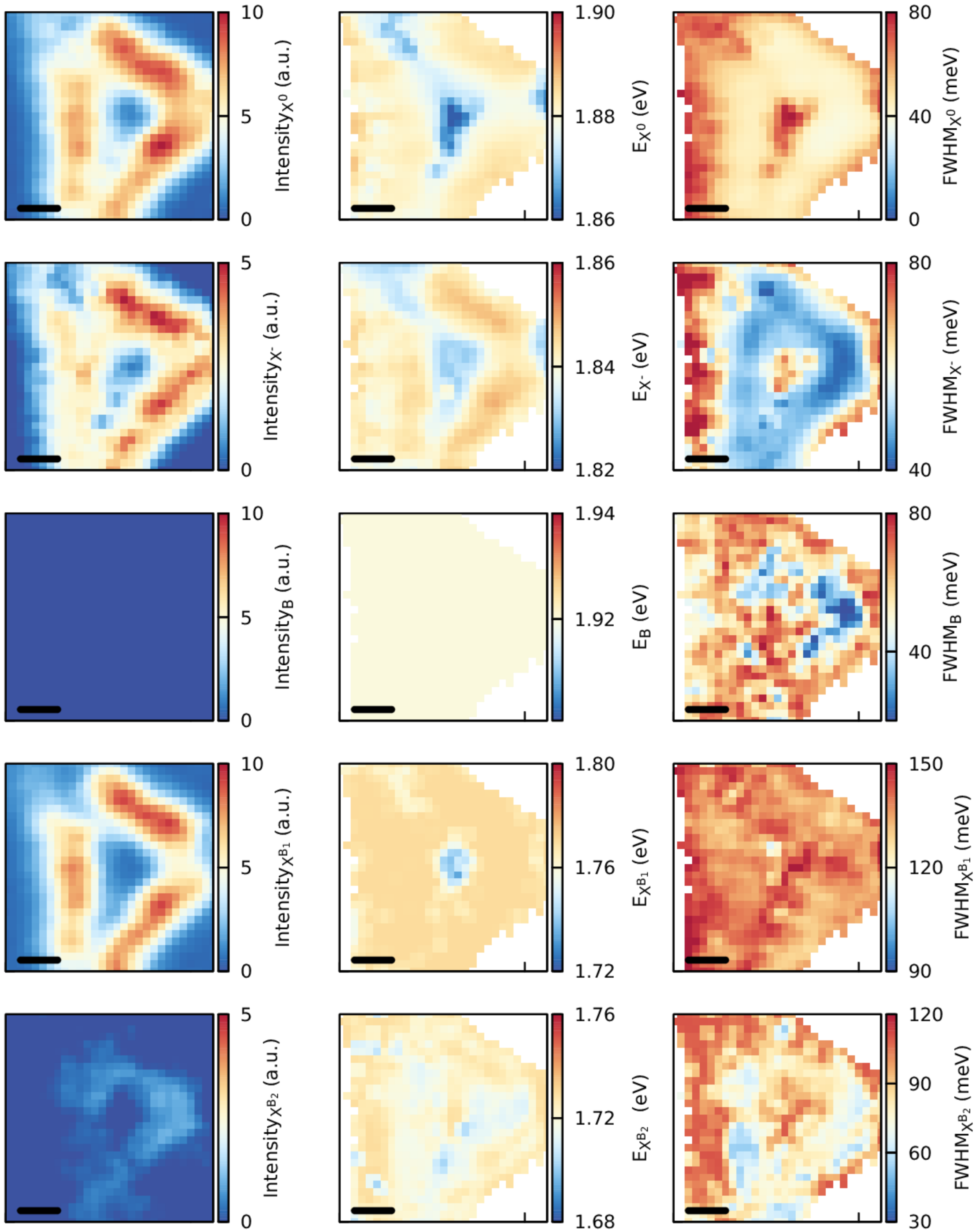

Figure S16. Maps of the fitted intensity, photon energy E and FWHM of the neutral A exciton X^0, the charged exciton (trion, X^-), the B exciton and X^{B1} and X^{B2} at 100 K. The scale bar in each panel is 5 µm.

50 K – CVD grown

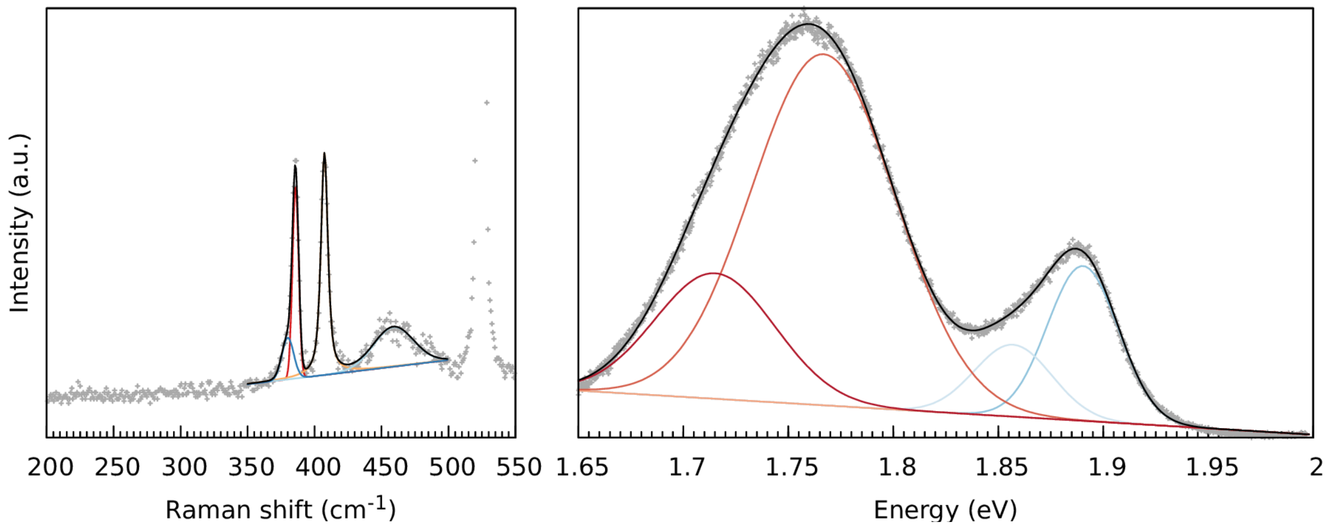

Figure S17. Raman and PL spectrum of MoS_2 at 50 K. The experimental data is marked by gray dots and fits of the individual bands of the MoS_2 monolayer are shown in red for the E', yellow for the A'_1, dark blue for the LO(M) and light blue for the 2LA(M) component for the Raman spectra. For the PL spectrum, the individual components are marked by brown for the X^{B1} mode, red for the X^{B2} mode, light blue for the charged exciton (trion, X^-), blue for the neutral A exciton X^0 and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

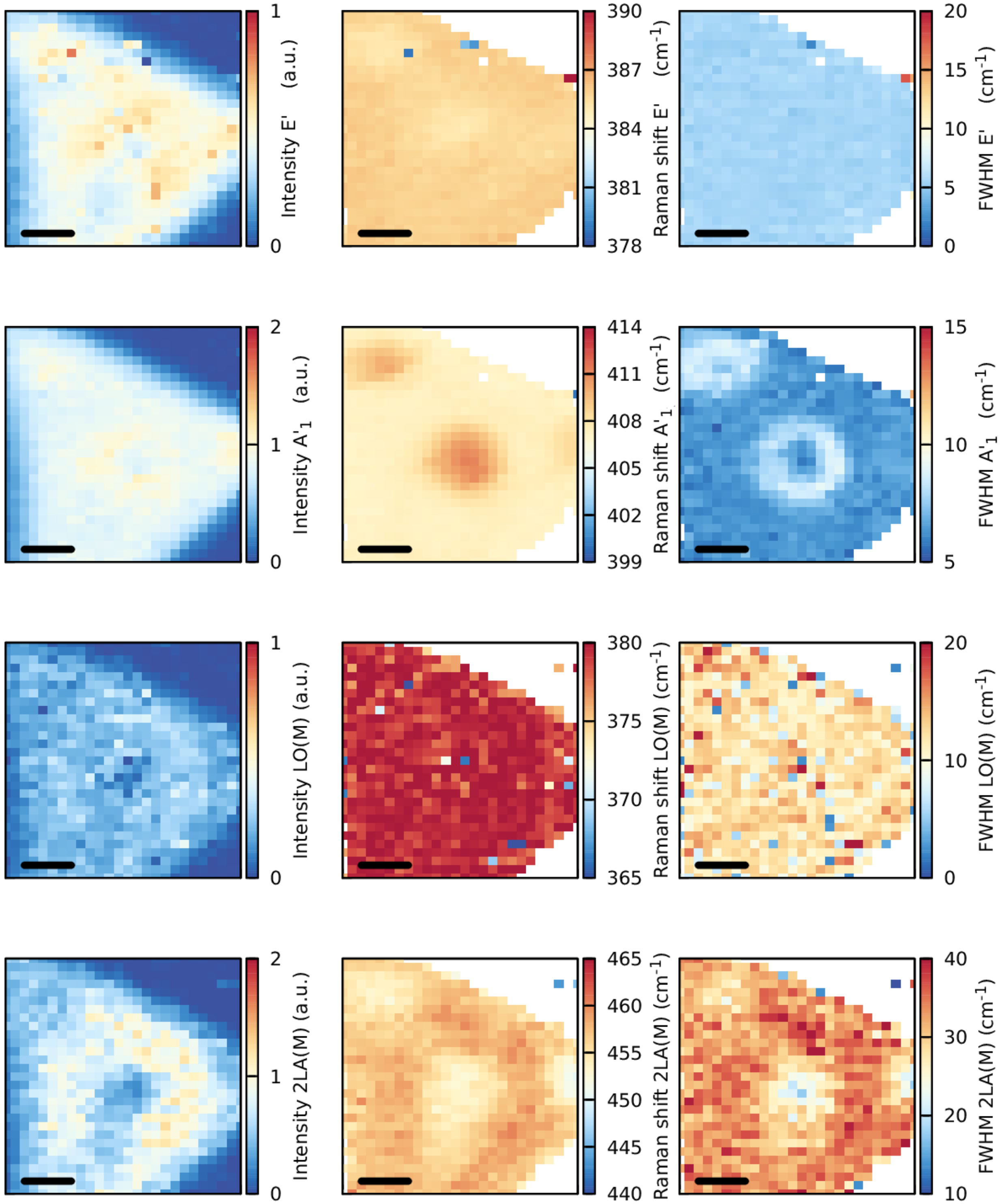

Figure S18. Maps of the fitted intensity, Raman shift and FWHM of the E', A'$_1$, LO(M) and 2LA(M) modes at 50 K. The scale bar in each panel is 5 µm.

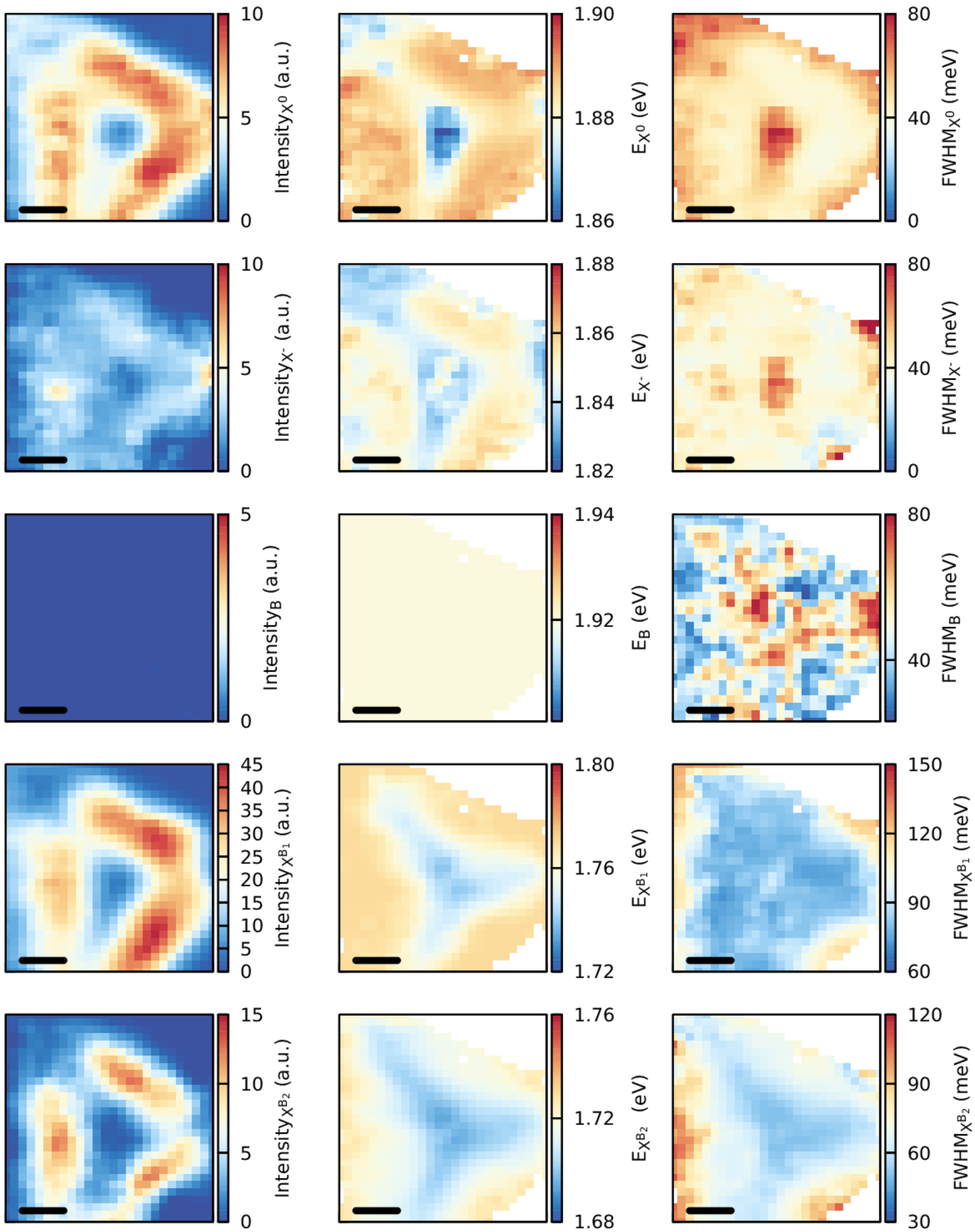

Figure S19. Maps of the fitted intensity, photon energy E and FWHM of the neutral A exciton X^0, the charged exciton (trion, X^-), the B exciton and X^{B1} and X^{B2} at 50 K. The scale bar in each panel is 5 μm.

10 K – CVD grown

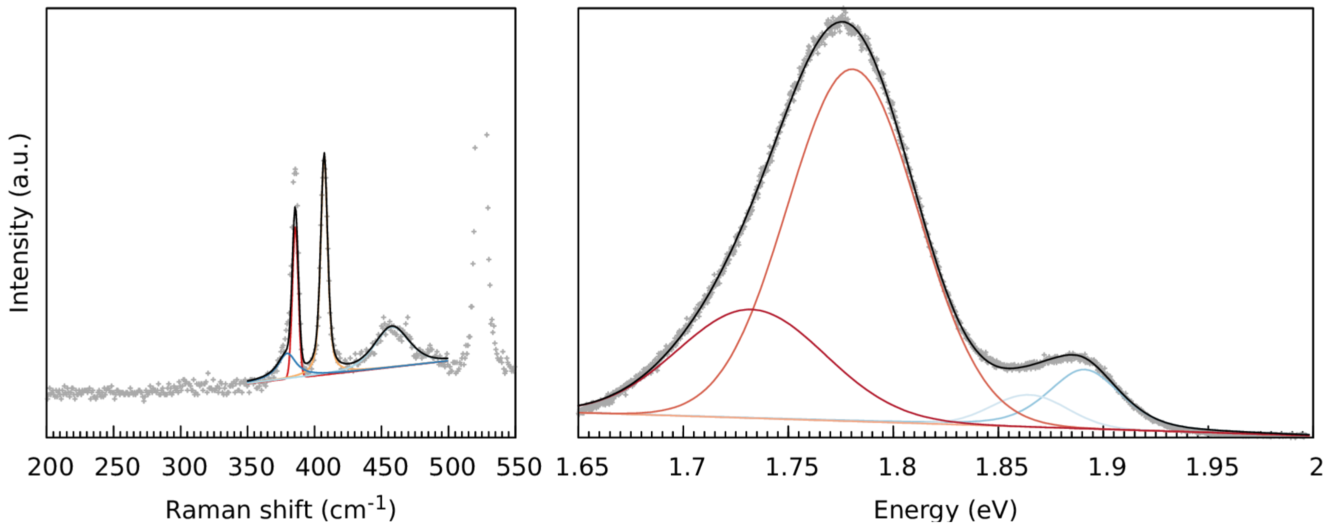

Figure S20. Raman and PL spectrum of MoS_2 at 10 K. The experimental data is marked by gray dots and fits of the individual bands of the MoS_2 monolayer are shown in red for the E', yellow for the A'_1, dark blue for the LO(M) and light blue for the 2LA(M) component for the Raman spectra. For the PL spectrum, the individual components are marked by brown for the X^{B1} mode, red for the X^{B2} mode, light blue for the charged exciton (trion, X^-), blue for the neutral A exciton X^0 and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

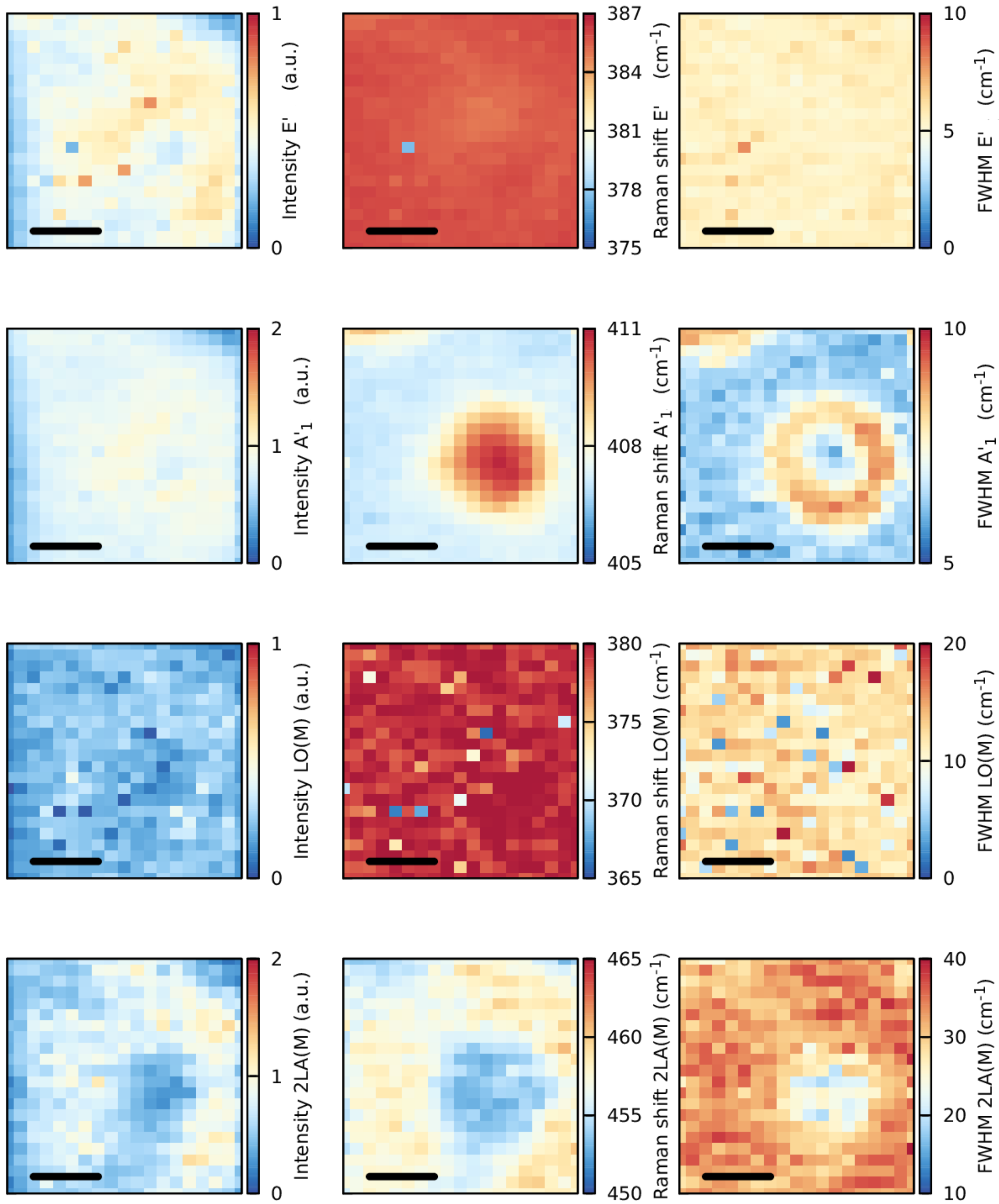

Figure S21. Maps of the fitted intensity, Raman shift and FWHM of the E', A'$_1$, LO(M) and 2LA(M) modes at 10 K. The scale bar in each panel is 5 µm.

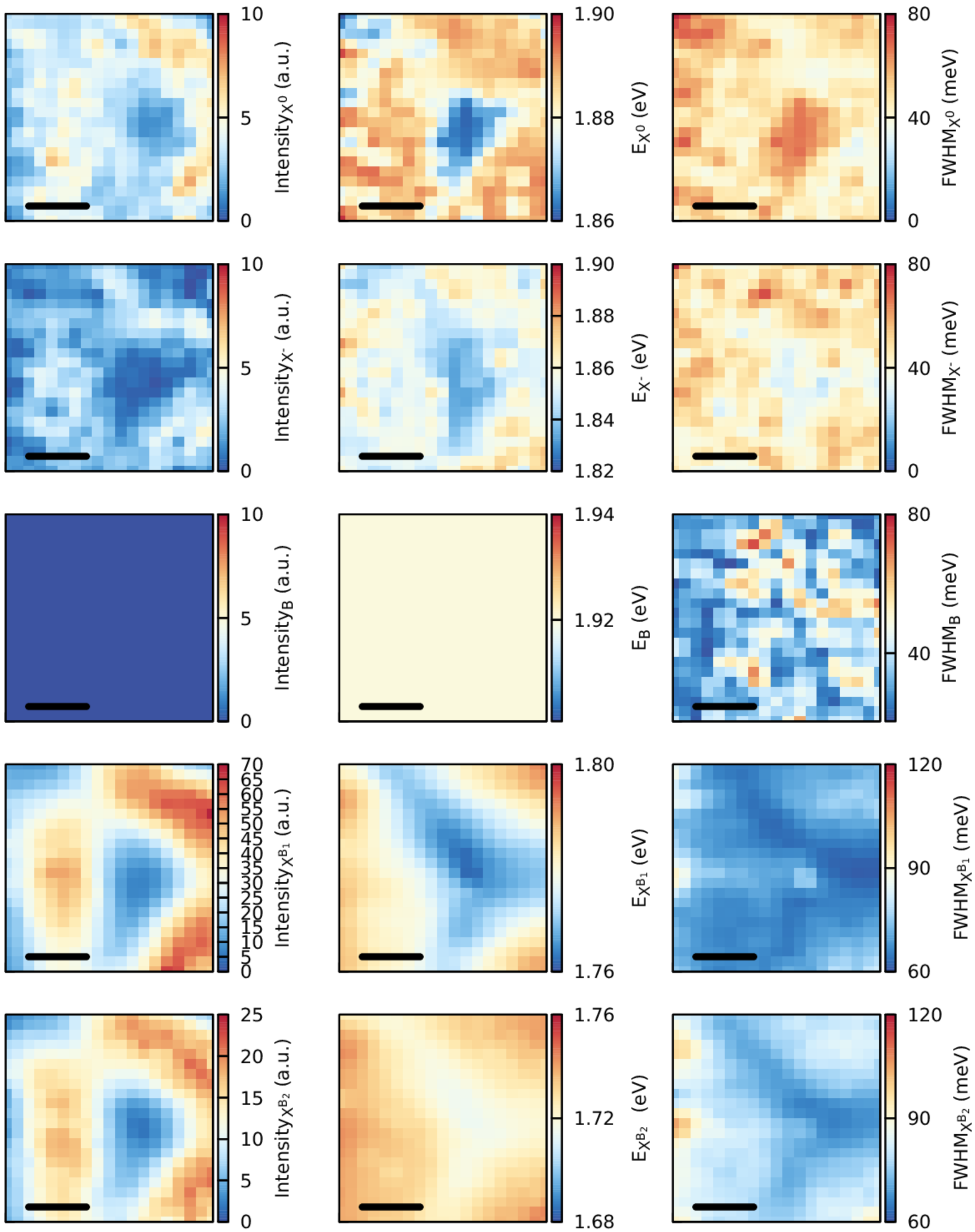

Figure S22. Maps of the fitted intensity, photon energy E and FWHM of the neutral A exciton X^0, the charged exciton (trion, X^-), the B exciton and X^{B1} and X^{B2} at 10 K. The scale bar in each panel is 5 μm.

300 K – transferred

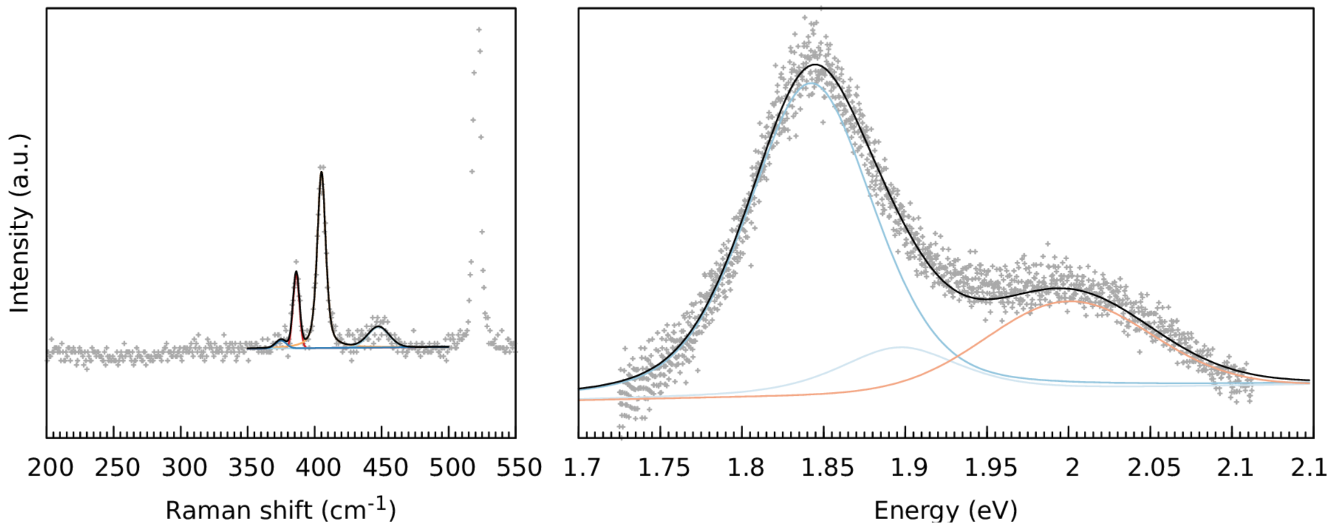

Figure S23. Raman and PL spectrum of MoS_2 at 300 K. The experimental data is marked by gray dots and fits of the individual bands of the MoS_2 monolayer are shown in red for the E', yellow for the A'$_1$, dark blue for the LO(M) and light blue for the 2LA(M) component for the Raman spectra. For the PL spectrum, the individual components are shown in blue for the neutral A exciton X^0, light blue for the charged exciton (trion, X^-) and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

200 K – transferred

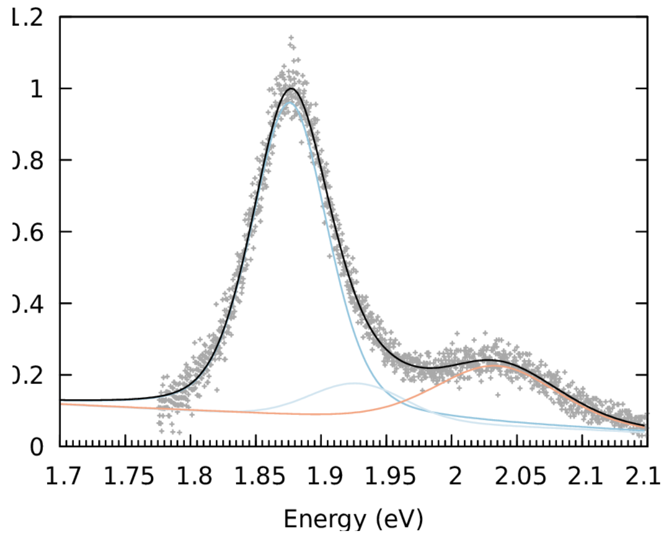

Figure S24. PL spectrum of MoS_2 at 200 K. The experimental data is marked by gray dots and fits of the individual bands of the MoS_2 monolayer are shown in blue for the neutral A exciton X^0, light blue for the charged exciton (trion, X^-) and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

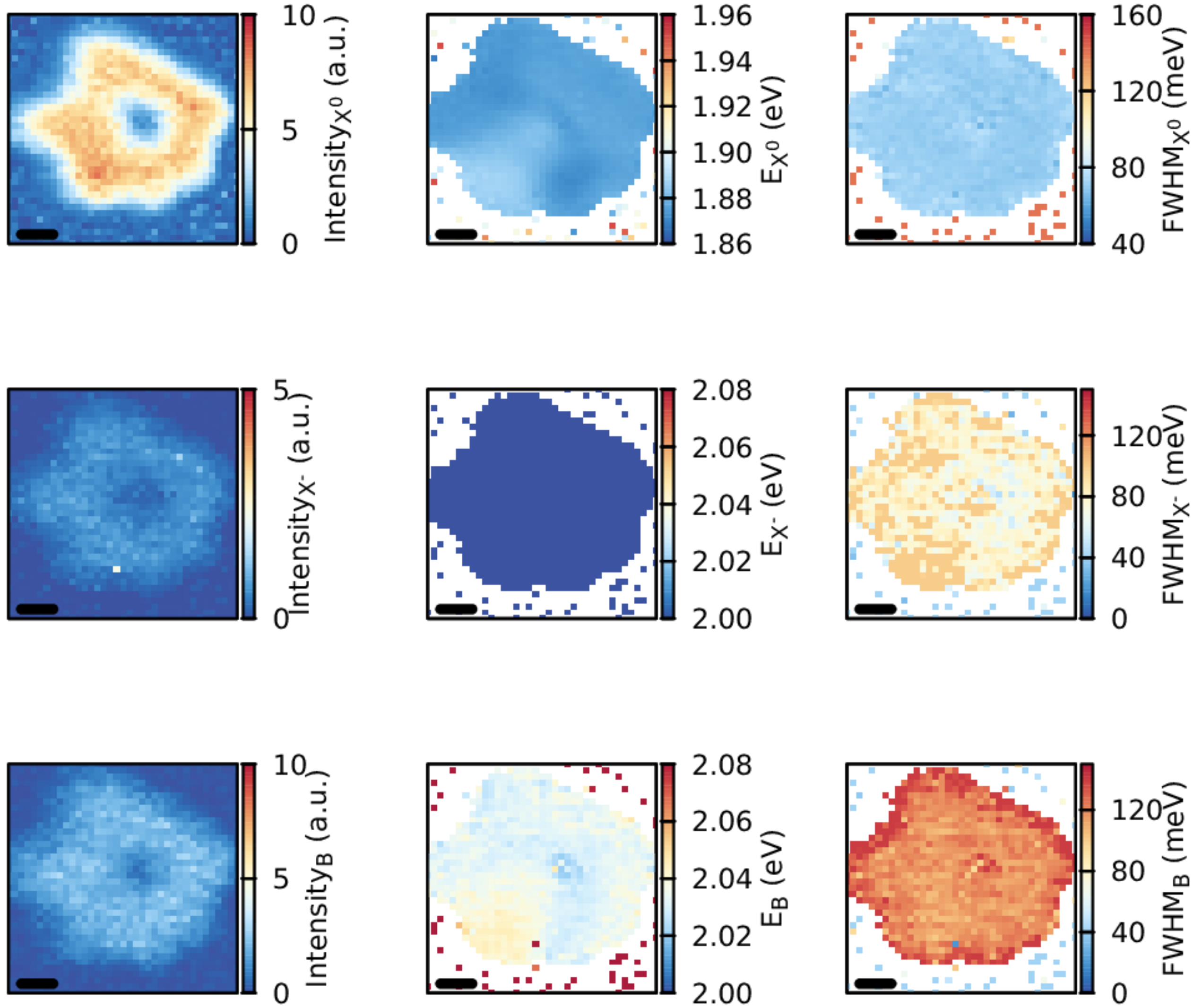

Figure S25. Maps of the fitted intensity, photon energy E and FWHM of the neutral A exciton X^0, the charged exciton (trion, X^-) and the B exciton at 200 K. The scale bar in each panel is 5 µm.

150K – transferred

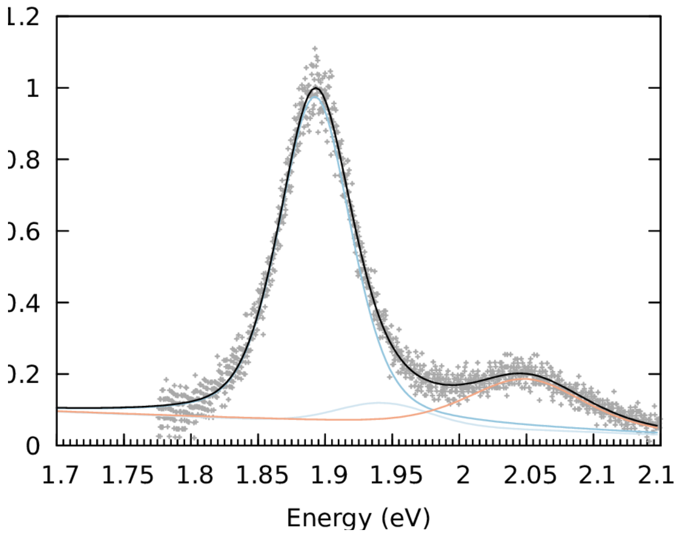

Figure S26. PL spectrum of MoS_2 at 150 K. The experimental data is marked by gray dots and fits of the individual bands of the MoS_2 monolayer are shown in blue for the neutral A exciton X^0, light blue for the charged exciton (trion, X^-) and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

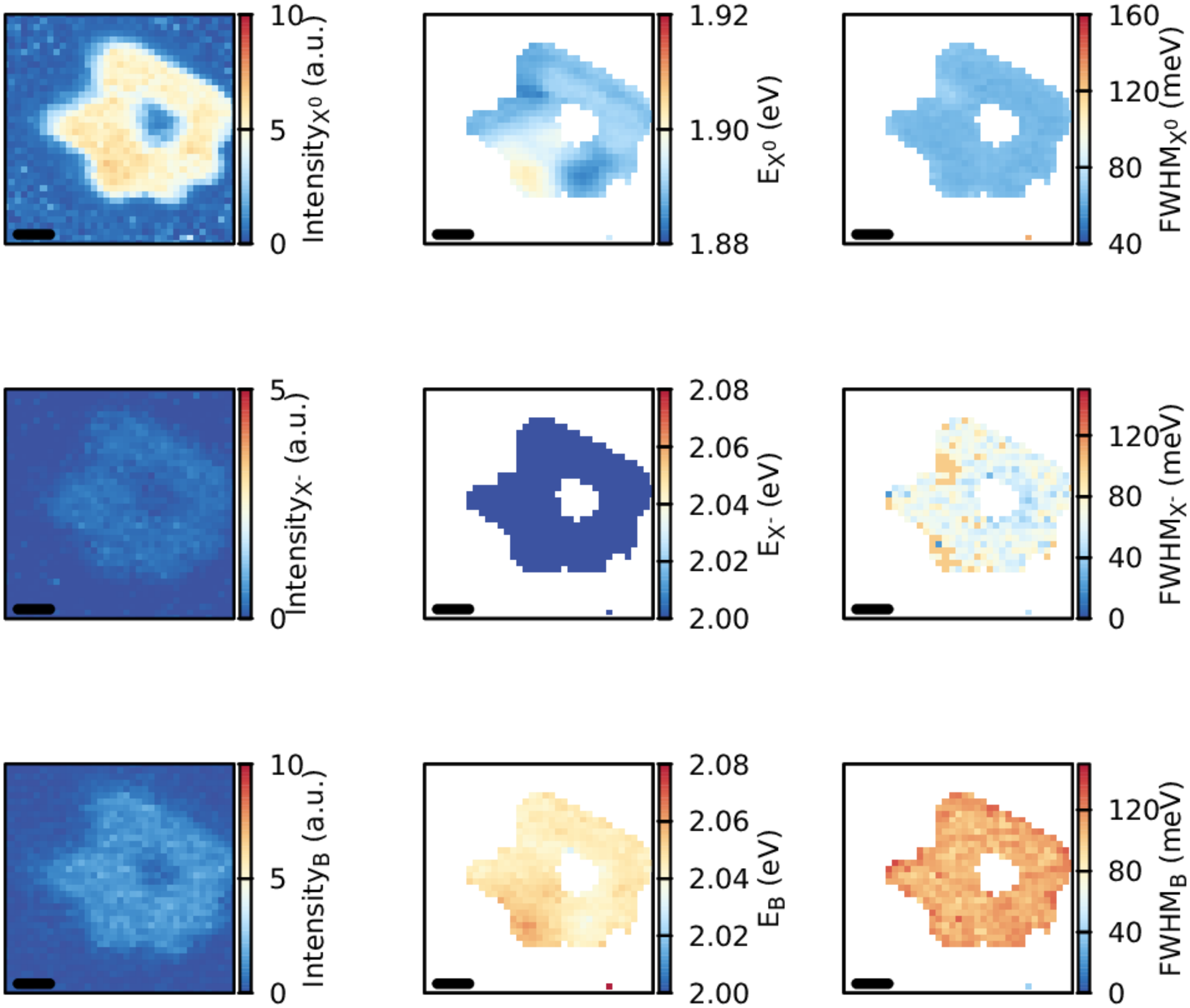

Figure S27. Maps of the fitted intensity, photon energy E and FWHM of the neutral A exciton X^0, the charged exciton (trion, X^-) and the B exciton at 150 K. The scale bar in each panel is 5 μm.

100 K – transferred

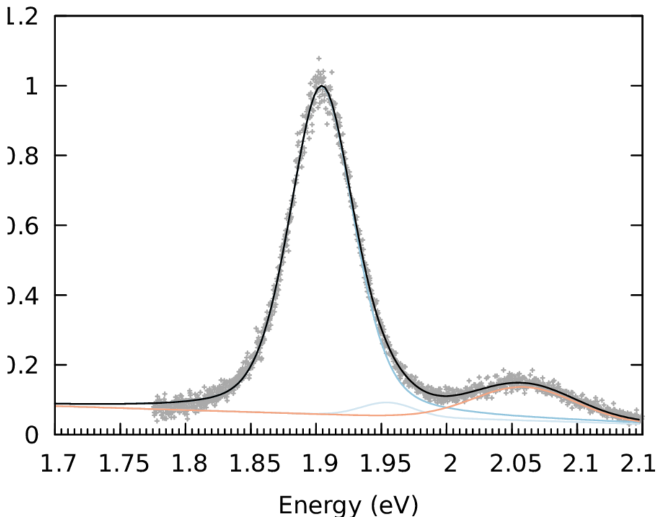

Figure S28. PL spectrum of MoS_2 at 100 K. The experimental data is marked by grey dots and fits of the individual bands of the MoS_2 monolayer are shown in blue for the neutral A exciton X^0, light blue for the charged exciton (trion, X^-) and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

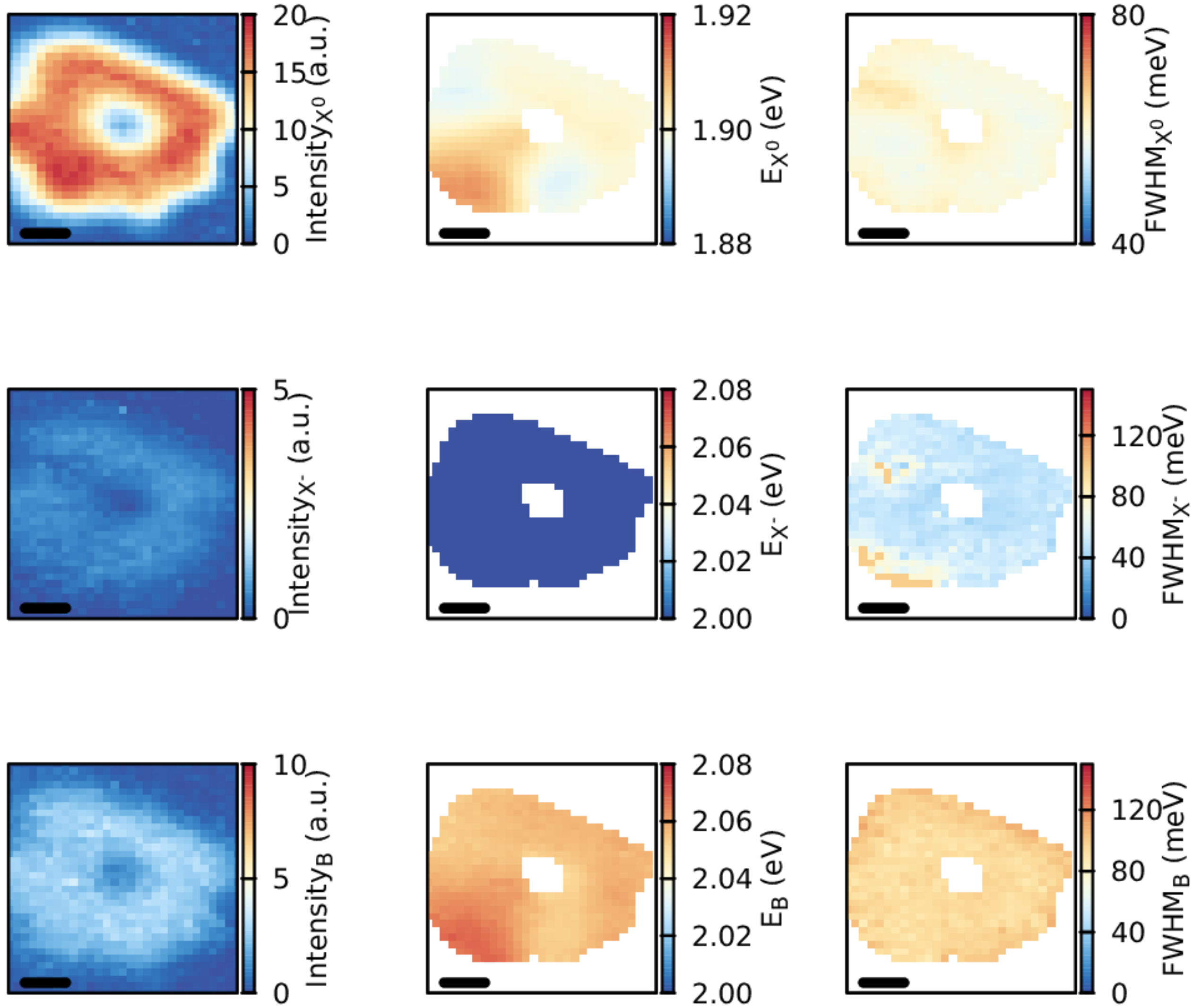

Figure S29. Maps of the fitted intensity, photon energy E and FWHM of the neutral A exciton X^0, the charged exciton (trion, X^-) and the B exciton at 100 K. The scale bar in each panel is 5 μm.

50 K – transferred

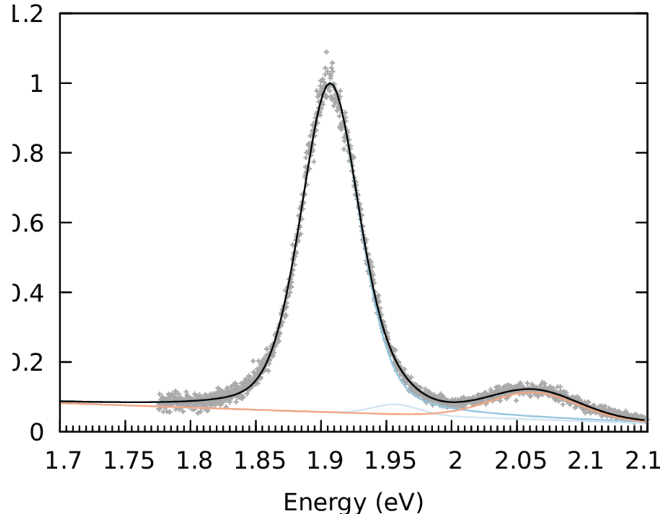

Figure S30. PL spectrum of MoS_2 at 50 K. The experimental data is marked by grey dots and fits of the individual bands of the MoS_2 monolayer are shown in blue for the neutral A exciton X^0, light blue for the charged exciton (trion, X^-) and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

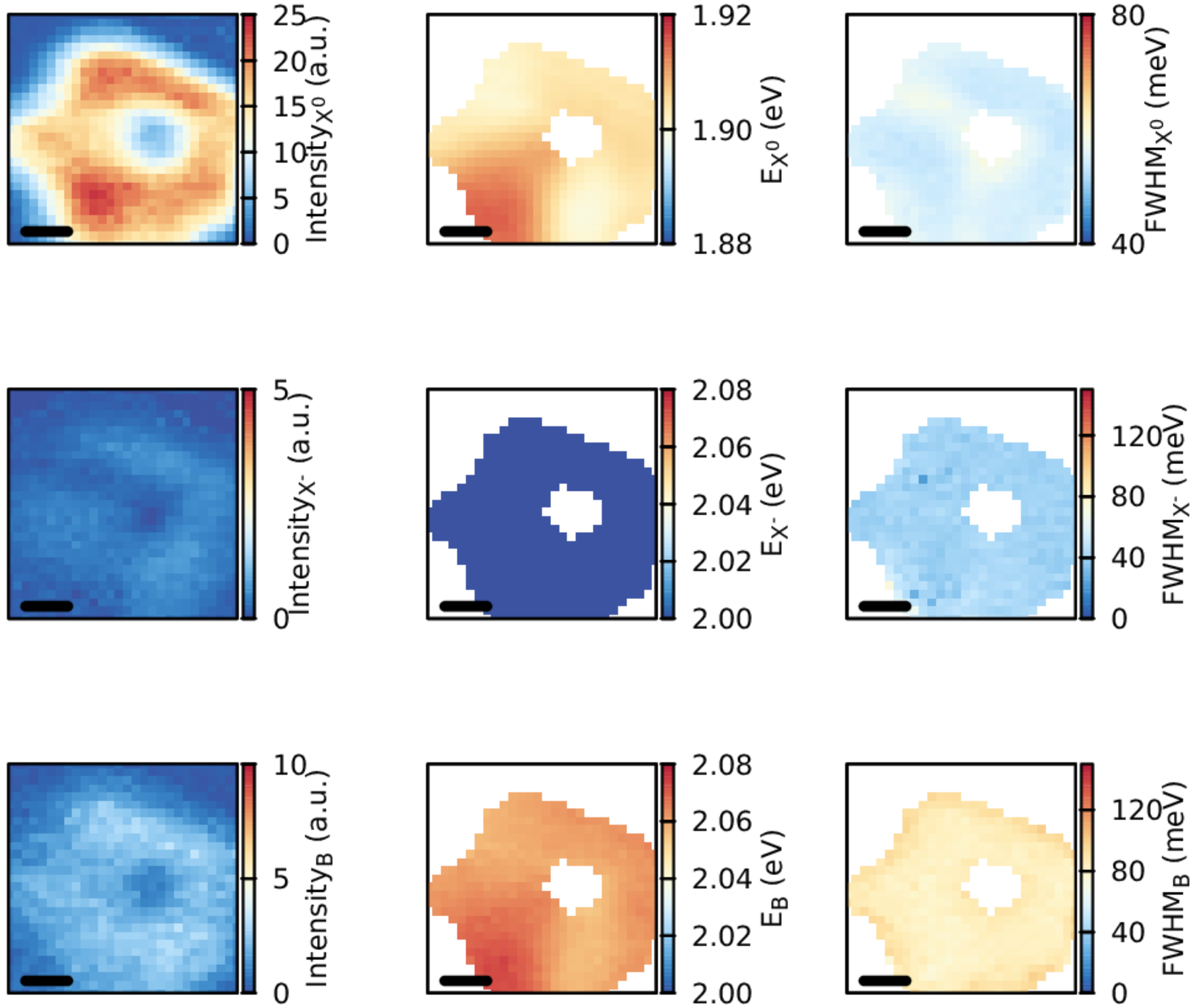

Figure S31. Maps of the fitted intensity, photon energy E and FWHM of the neutral A exciton X^0, the charged exciton (trion, X^-) and the B exciton at 50 K. The scale bar in each panel is 5 μm.

10 K – transferred

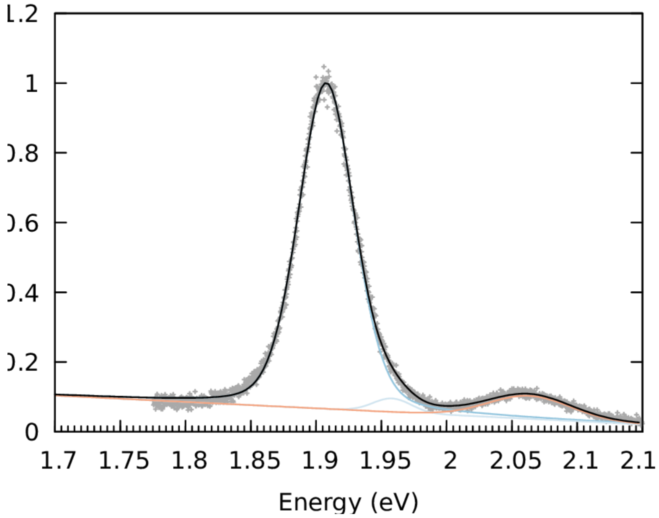

Figure S32. PL spectrum of MoS_2 at 10 K. The experimental data is marked by grey dots and fits of the individual bands of the MoS_2 monolayer are shown in blue for the neutral A exciton X^0, light blue for the charged exciton (trion, X^-) and orange for the B exciton. The resulting curve (sum of the individual components) is represented by a solid black line.

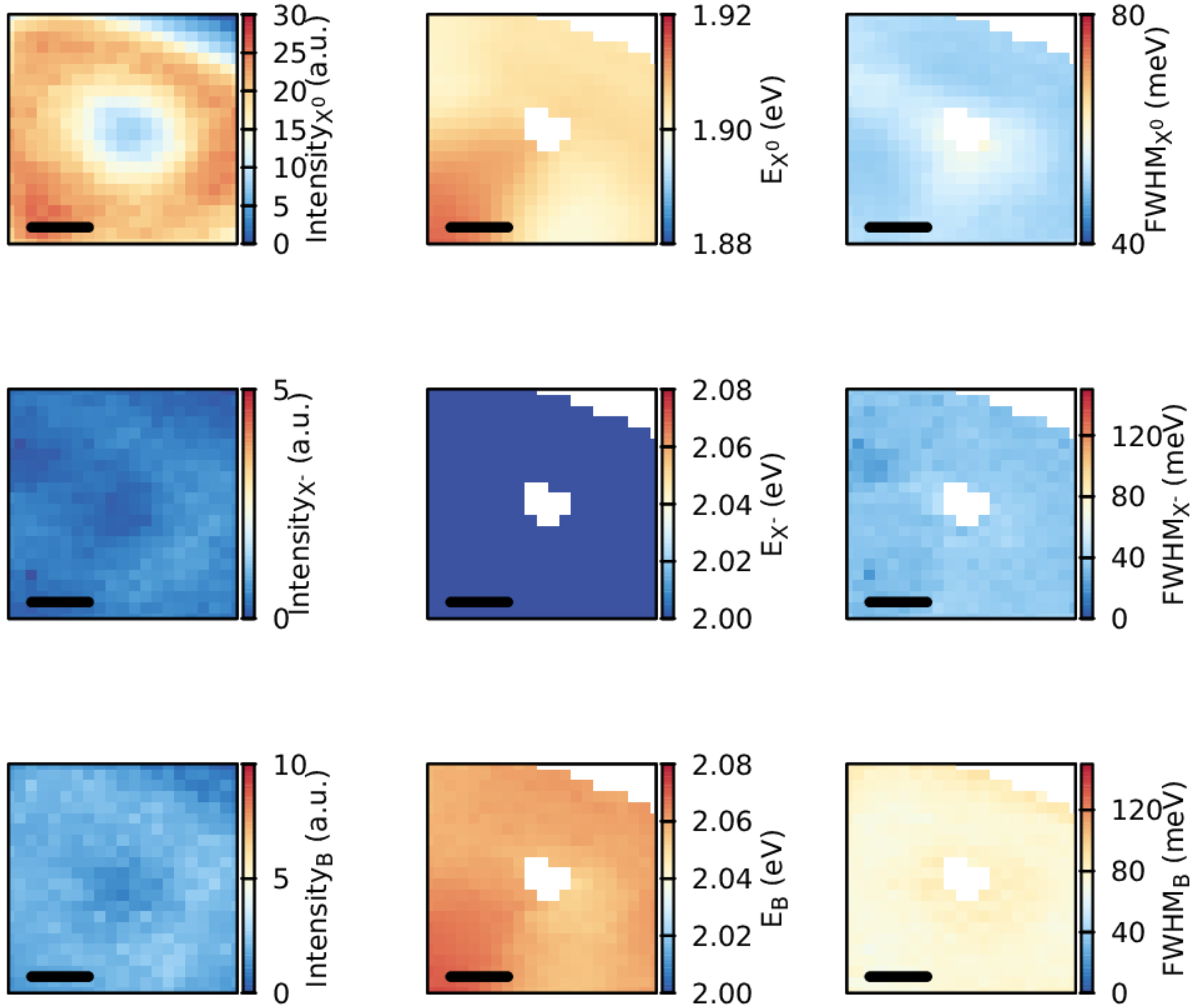

Figure S33. Maps of the fitted intensity, photon energy E and FWHM of the neutral A exciton X^0, the charged exciton (trion, X^-) and the B exciton at 10 K. The scale bar in each panel is 5 μm.

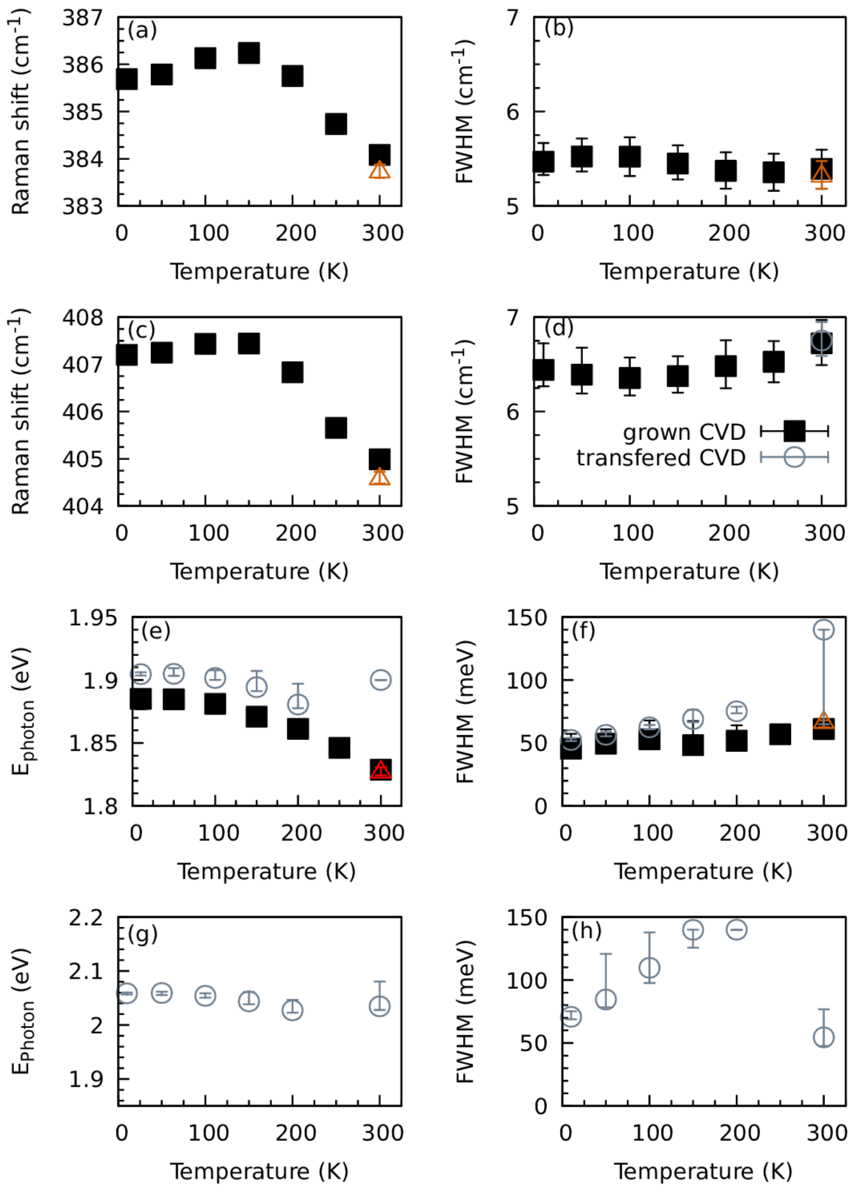

Figure S34. The temperature dependence of the Raman shift and FWHM of the A'₁ (a, b) and E' (c, d) modes and the photon energy E and FWHM of the neutral A exciton X^0 (e, f), and the B exciton (g, h)) The data points are the median values and the 'error' bars represent the first and third quartiles of each data set, respectively, and the red triangle represent the measured data after the sample was cooled to 10 K and subsequently heated back to 300 K.