High electron mobility, quantum Hall effect and anomalous optical response in atomically thin InSe


Experimental

S1. Graphene-InSe contacts
S2. Electron transport in InSe monolayers
S3. Few-layer InSe in the two-probe geometry
S4. Further examples of electron transport in 2D InSe
S5. Estimating effective g-factor
S6. Stability of InSe flakes at ambient conditions

Theory

S7. DFT modelling of the N-layer InSe band structure

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S1. Graphene-InSe contacts

The gate-tunable work function of graphene enabled us to form ohmic contacts between few-layer graphene and 2D InSe\(^2\). Prior to measurements of the InSe’s electronic properties, we characterized all contacts for each device using the three-terminal measurement geometry (see Fig. S1, inset). The contact resistance, \(R_C\), typically varied between 5 and 30 kΩ·µm. Figure S1 shows examples of such measurements as a function of back gate voltage.

Supplementary Figure 1 | FLG contacts to 2D InSe. The three-terminal resistance was measured using a contact in question (contact 1 for the case shown in the inset) as both current and voltage probe. A finite length of the InSe section next to the FLG interface can contribute to such measurements of \(R_C\) but, using complementary four-probe measurements, we found that this contribution was relatively small and could be ignored. \(V_{tg} = 5\) V, \(I = 10\) nA and \(T = 120\) K.
S2. Electron transport in InSe monolayers

As mentioned in the main text, contacts to 1L InSe had high resistances, and we were able to carry out electrical measurements of the monolayers only in the two-probe geometry. Transport properties were studied by applying a source-drain voltage $V_{sd}$ and measuring the source-drain current $I_{sd}$ as a function of back gate voltage, $V_{bg}$. As shown in Fig. S2a, $I_{sd}$ grows with $V_{bg}$, yielding an on/off ratio of $\sim10^2$ for this 1L device. In the off state, our measurements were limited by leakage currents. In the on state, the 2-terminal resistance decreased to only 1 MΩ at highest carrier concentrations we could reach. The field effect mobility, $\mu \approx 0.02 \text{ cm}^2/\text{Vs}$, was estimated using the relation $\mu = \left(\frac{L}{W C V_{sd}}\right) \frac{dI_{sd}}{dV_{bg}}$ where $L$ and $W$ are the length and width of the InSe channel, and $C$ is the capacitance per unit area of the back-gate dielectric ($\text{SiO}_2$ and hBN layers). Although the measured changes in resistance may be related to the field effect in monolayer InSe, we note that $R_C$ also varies with gate voltage and, therefore, can affect the two-probe measurement analysis. In principle, this contribution may be even dominant if the contact resistance is much larger than that of the InSe channel.

We also studied the photoresponse of monolayer InSe under illumination with a laser beam. Fig. S2b shows the $I_{sd}(V_{sd})$ dependence measured under illumination with different laser powers, $P$. The photocurrent $I_{ph} = I_{sd} - I_{sd-dark}$ follows a power law $I_{ph} \sim P^\gamma$ with $\gamma \sim 0.3$ (Fig. S2c). Figure S2d shows the observed time-dependent response for InSe monolayers, revealing a significant optical modulation of the current.
Supplementary Figure 2 | Characterization of monolayer InSe. a, $I_{sd}$ as a function of gate voltage for one of our monolayer devices. Room T and $V_{sd} = 5$ V. Inset: $I_{sd}(V_{sd})$ curves for different $V_{bg}$. b, $I_{sd}(V_{sd})$ dependence measured at $V_{bg} = 0$ V in the dark and under illumination with a 488 nm laser at different incident powers. c, Photocurrent as a function of laser power at $V_{sd} = 1$ V and $V_{bg} = 0$ V. The solid blue line represents the power law, $I_{ph} \sim P^{0.3}$. d, Time-resolved photo response under excitation at 633 nm ($V_{sd} = 1$ V and $V_{bg} = 0$ V).

S3. Few-layer InSe in the two-probe geometry

Fig. 3a of the main text showed resistivity measurements for a 6L InSe device using the 4-probe configuration. In this case, the accessible range of gate voltages was limited by the contact resistance between graphene and InSe so that channel resistances of up to only a few kΩ could be examined. To demonstrate that much higher off-state resistances and, therefore, high on/off ratios could be achieved, we also studied this 6L device in the 2-probe geometry (Fig. S3). By varying $V_{tg}$ from 2 to 6 V, the two-terminal resistance changed from 4 GΩ to 40 kΩ, that is, the on/off ratio was $\sim 10^5$ with the off state being limited by electrical leakage. At all gate voltages the field-effect device was in the linear regime up to $V_{sd} \approx 15$ mV.
Supplementary Figure 3 | Field effect in 6L InSe using two-probe measurements. a, $I_{sd}$ as a function of $V_{tg}$ ($V_{sd} = 40$ mV, $V_{bg} = -10$ V). b, $I_{sd}(V_{tg})$ at several $V_{tg}$ and measured for $V_{bg} = -10$ V and $T = 10$ K.

S4. Further examples of electron transport in 2D InSe

Fig. S4 shows the resistivity of 3L and 10L InSe as a function of back gate voltage at different $T$. Independent of thickness, the resistivity grows with $T$ for all values of $V_{bg}$, similar to the case of 6L InSe discussed in the main text. The electron mobility $\mu$ for these devices was also sufficiently high to allow the observation of pronounced SdHO. Examples of $\rho_{xx}(B)$ and $\rho_{xy}(B)$ are shown in Fig. 4c where the oscillations start at around 6 T. One can notice that SdHO in this figure exhibit some additional beatings. Moreover, the carrier concentration determined from the Hall effect, $n = 7.8 \times 10^{12}$ cm$^{-2}$, differs from that estimated from the oscillations period, $n_1 = 5.65 \times 10^{12}$ cm$^{-2}$. To explain these observations, we carried out a Fourier transform analysis of $\rho_{xx}(B)$ and found that the beatings can be attributed to an additional oscillation frequency of $\approx 44$ T. It corresponds to the carrier density $n_2 = 2.12 \times 10^{12}$ cm$^{-2}$. The sum of two $n_1$ and $n_2$ equals the carrier density determined from the Hall effect. This behavior is attributed to the second electrical 2D subband that starts being occupied in 10L
InSe, in contrast to the single subband occupancy in 3L and 6L devices for the same carrier density.

Supplementary Figure 4| Transport properties of few-layer InSe. ρ_{xx} as a function \( V_{bg} \) for 3L (a) and 10L (b) InSe measured at \( V_{tg} = 9.5 \) V and \( V_{tg} = 5 \) V, respectively. c, \( ρ_{xx}(B) \) and \( ρ_{xy}(B) \) for 10L InSe (\( V_{bg} = 80 \) V and \( V_{tg} = 5 \) V; \( T = 5 \) K). d, Fourier transform of the SdHO shown in (c). Arrows indicate two fundamental frequencies that correspond to \( n_1 = 5.65 \times 10^{12} \) cm\(^{-2}\) and \( n_2 = 2.12 \times 10^{12} \) cm\(^{-2}\).

S5. Estimating the effective g-factor

We have measured temperature dependence of \( ρ_{xx} \) in the quantum Hall regime to get an estimate for the effective \( g^* \)-factor\(^2\). Its value is determined by the single-particle Zeeman energy and a many-body contribution arising from exchange splitting of electron spin states in
partially occupied Landau level. Figure S5 shows $\rho_{xx}$ as a function of $V_{bg}$ at $B = 30$ T for our 6L InSe device. We observe a clear activation behavior $\rho_{xx}^{\text{min}} \sim \exp\left(-\frac{\Delta E}{k_B T}\right)$ of the minimum in $\rho_{xx}$ at $n = 3$ which yields $\Delta E/k_B \approx 9$ K where $k_B$ is the Boltzmann constant (Fig. S5 inset). Assuming no Landau level broadening, $\Delta E$ equals half of $g^* \mu_B B$ ($\mu_B$ is the Bohr magneton) and provides a lower bound for $g^* \mu_B B \approx 18$ K, so that $g^* \approx 0.9$. If we take into account Landau level broadening $\Gamma \approx \pi k_B T_D$, where $T_D = 9 \pm 2$ K is the Dingle temperature determined from SdHO (see Fig. 3c of the main text), the effective $g^*$-factor can be determined using relation $\Delta E = \frac{g^* \mu_B B - \Gamma}{2}$ which yields $g^* \mu_B B \approx 40$ K corresponding to $g^* \approx 2.3 \pm 0.3$. Further experiments in tilted magnetic field are required to improve the accuracy of determining the g-factor.

Supplementary Figure 5 | g-factor from temperature dependence of SdHO in 6L InSe. $\rho_{xx}$ as a function of $V_{bg}$ for $T$ from 1.4 K (black) to 20.5 K (orange). $B = 30$ T, $V_{tg} = 6.5$ V. Inset: Log-scale of $\rho_{xx}^{\text{min}}$ versus $1/T$ at $n = 3$. The best linear fit (solid line) yields $\Delta E/k_B = 9$ K.

S6. Stability of InSe flakes at ambient conditions

Figure S6 shows photoluminescence (PL) from encapsulated (2L) and non-encapsulated (22L) InSe films measured immediately after preparation and a few months later. One can see that
the PL response from the encapsulated sample remained practically unchanged, maybe even slightly improving with time due to annealing at room T. In contrast, the non-encapsulated InSe showed a significant drop of about 80% in the PL intensity already after one month of exposure to the air, despite being much thicker than the encapsulated bilayer. This translates into one layer of InSe being completely destroyed every couple of days, in agreement with the degradation rates reported in ref. 3. No PL signal could be detected from the non-encapsulated sample after two month under ambient conditions.

Supplementary Figure 6 | Stability of InSe thin films at ambient conditions. PL response of encapsulated (2L) and non-encapsulated (22L) InSe films. Laser power 1.35 mW; excitation energy 2.33 eV.

S7. DFT modelling of the N-layer InSe band structure

Modelling of few-layer InSe was performed using semi-local density functional theory (DFT) with van der Waals corrections. We used the optB88 functional as implemented in the VASP code together with a plane-wave basis with a cut-off energy of 600 eV. We sampled the 2D Brillouin zone with a 12×12 grid. Note that the optB88 functional, being rooted in semi-local
DFT, underestimates the band gap. Hence, when analysing the excitation energies, we apply the “scissor” correction, previously employed in studies of other semiconductors\(^6\)\(^7\)\(^8\)\(^9\)\(^10\)\(^11\). A calculation with optB88 gives a bulk InSe band gap \(E_{g}^{DFT} = 0.27\) eV, compared to the bulk experimental value of \(\hbar \omega_{A\infty} = 1.25\) eV, measured at room temperature. Hence, to interpret the room temperature optics in the main text, we subtract

\[
\delta E_{g}^{300K} = \hbar \omega_{\infty} - E_{g}^{DFT} \approx 0.98\text{ eV}
\]  \hspace{1cm} (1)

from the energies of all valence band states while keeping the conduction band energies unchanged. This is equivalent to adding \(\delta E_{g}^{300K}\) to the energies of all the interband transitions identified by analysing selection rules determined by the wave functions in the bands of monolayer and NL InSe. Note that the scissor correction should be temperature-dependent. For example, it has been found\(^12\)\(^13\) that \(\hbar \omega_{A\infty} = 1.4\) eV at low temperatures (\(T = 1.4\) K), hence the scissor correction at low temperature should be 1.13 eV.
**Supplementary Figure 7** | **Band structure of InSe.** The electronic band structure of few-layer InSe, with zero energy set at the lowest (c) conduction band edge. In the monolayer (1L), the structure exhibits $z \rightarrow -z$ mirror symmetry, illustrated in the inset; we plot bands with $z \rightarrow -z$ symmetric wave functions in red and antisymmetric in blue. For two or more layers, this symmetry is no longer present. Principal optical transitions $A$ and $B$, are marked by vertical lines, $A$ in red and $B$ in blue. For $NL$ InSe ($N=2,3,4$) the insets expand the dispersion of overlapping bands in the vicinity of the Γ-point, with the valence subband involved in the $B$-transition identified by a circle.

Fig. S7 shows the calculated band structure for 1L, 2L, 3L, and 4L InSe. For 1L InSe the lowest conduction band is labelled $c$, the highest valence band as $v$, the second and third highest valence band as $v_1$ and $v_2$, respectively. In 2L InSe each of these bands split into two subbands, which are traced by examining the wave functions of the bands at the Γ-point; higher energy conduction subbands and lower energy valence subbands are indicated by the symbols ($c'$, $v'$, $v_1'$, $v_2'$). The highest valence bands are “sombrero-shaped”\(^{14,15,16}\). The conduction band of monolayer InSe splits into several subbands, reducing the principal gap of $NL$ InSe with increasing number of layers, while the electron effective mass changes only slightly. Two electron-hole excitations are highlighted in each panel, corresponding to the hole placed either at the top of the highest valence band which originates from the top valence band $v$ in 1L InSe ($A$-transition), or at the Γ-point in the highest of the bands generated by hybridization of the monolayer $v_1$ band ($B$-transition). We attribute these energies to the observed peaks in the photoluminescence (PL).

The PL intensity is governed by the matrix element for the optical transition ($A$- or $B$-type) and the occupation of photo-excited electron-hole states, both determined by the electron wave function in the bands. In monolayer InSe, the wave functions of any given band can be decomposed into orbitals.
\[ \psi_\pm = \frac{1}{\sqrt{2}} \sum_{\text{orb}} c_{\text{orb,In}} (\varphi_{\text{orb,In1}} \pm \varphi_{\text{orb,In2}}) + c_{\text{orb,Se}} (\varphi_{\text{orb,Se1}} \pm \varphi_{\text{orb,Se2}}), \]  

where \( c_{\text{orb}} \) are complex coefficients, \( \varphi_{\text{orb}} \) are the atomic orbitals (\( s \) or \( p \)) on the respective atoms, the set of orbitals in the decomposition are \( \text{orb} = (s, p_x, p_y, p_z) \), and, in the case of \( p_z \) orbitals, they are defined with opposite signs on the two atoms belonging to the same species in the unit cell: \( \varphi_{p_z,\text{In2}}(\vec{r} - \vec{R}_{\text{ln2}}) = -\varphi_{p_z,\text{In1}}(\vec{r} - \vec{R}_{\text{In1}}) \). In this construction the wave functions exhibit mirror plane symmetry of the crystal: bands are either even (\( \psi_+ \)) or odd (\( \psi_- \)) with respect to \( z \to -z \) reflection. The optical transition for in-plane polarized light is determined by the matrix element \( \langle \psi_v | p_x | \psi_c \rangle, \langle \psi_v | p_y | \psi_c \rangle \) of the in-plane momentum operator, which is zero between even-odd bands.

<table>
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<th>Degeneracy</th>
<th>( c ) (odd)</th>
<th>( v ) (even)</th>
<th>( v_1 ) (odd)</th>
<th>( v_2 ) (even)</th>
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<td>( E^{\text{DFT}} ) (eV)</td>
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<td>0.002s 0.349p_z</td>
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<td>0.207p_x 0.207p_y</td>
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<td>( E^{\text{DFT}} - \delta E_g^{300K} ) (eV)</td>
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<td>0.034p_x 0.034p_y</td>
<td>0.043p_x 0.043p_y</td>
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<td>( E^{\text{DFT}} - \delta E_g^{300K} ) (eV)</td>
<td>0.229s 0.014p_z</td>
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<td>0.207p_x 0.207p_y</td>
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**Supplementary Table S1** | Orbital composition of wave functions in 1L-InSe. Orbital decomposition of the wave functions at the \( \Gamma \)-point of conduction band (\( c \)), valence band (\( v \)), and doubly degenerate bands \( v_1 \) and \( v_2 \) (modulus square of the overlap integral between the DFT wave function and the spherical harmonics centered on each atom, \( |c_{\text{orb}}|^2 \) from Eq. 2) into \( s \) and \( p \) orbitals of In and Se atoms in monolayer InSe. The \( z \to -z \) symmetry classification of the bands is noted in brackets. Atoms are listed from bottom to top for the 2L crystal. The \( \Gamma \)-point band energies are provided relative to the conduction band edge, where \( E^{\text{DFT}} \) is the band energy from DFT and \( E^{\text{DFT}} - \delta E_g^{300K} \) is the value obtained after applying scissor correction \( \delta E_g^{300K} \). The energies corresponding to \( \hbar \omega_A \) and \( \hbar \omega_B \) are marked in bold.
The decomposition of the valence and conduction band states in 1L InSe to atomic orbitals, shown in Table S1, reveals that both states are dominated by $s$ and $p_z$ orbitals, but in different combinations: $c$ is dominated by $s$ of In and $p_z$ of Se atoms, while $v$ is dominated by $p_z$ orbitals of both In and Se atoms. Moreover, the valence band wave function is symmetric, and the conduction band wave function is antisymmetric to $z \rightarrow -z$ transformation; thus the optical matrix element vanishes. In $NL$ InSe (e.g. bilayer, $N=2$), the stacking order is such that In atoms in the second layer are directly above Se atoms in the first layer, while Se atoms in the second layer are located above the centre of the hexagons in the first layer. This stacking order removes the $z \rightarrow -z$ mirror symmetry, which is reflected by the orbital decomposition of the band edge states. For example, in Table S2, the contribution of orbitals centred on atom In1 differs from that of orbitals centred on In2. This lower symmetry of few-layer InSe crystals allows the optical matrix element to be finite, which is reflected in Fig. S7 by marked $A$-transitions from the highest valence band to the lowest conduction band. We attribute this transition to the lowest energy PL line in $NL$ InSe, discussed in the main text.

Also, in 1L InSe, there are two pairs of deeper valence bands, $v_1$ and $v_2$. Each pair is double-degenerate at the $\Gamma$-point and both are composed dominantly of $p_x$ and $p_y$ orbitals of Se, but $v_1$ is odd while $v_2$ is even with respect to $z \rightarrow -z$ reflection. Therefore, the mirror symmetry argument allows transition between $c$ and $v_1$ bands, which we attribute to the $B$ line observed in the PL experiments (see main text). In the bilayer, $v_1$ and $v_2$ are mixed, giving rise to four bands, all doubly degenerate at the $\Gamma$-point: $v_1$, $v_1'$, $v_2$, and $v_2'$. In $v_1$ and $v_1'$, the wave function is concentrated on the Se atoms on the inside of the bilayer, while in $v_2$ and $v_2'$, it is concentrated on the Se atoms on the outside. Among all these bands, we find (see below) that the strongest transition couples the band $v_1$ with the lowest conduction band, hence, we attribute this
transition to the experimentally observed B line in PL. In Fig. S8, we gather the DFT-calculated values of the energies of A- and B-type electron-hole excitations, with the scissor-corrected values given by the energy scale on the right hand side axis.

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<th>c</th>
<th>v</th>
<th>v_1</th>
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**Supplementary Table 2 | Orbital composition of wave functions in 2L-InSe.** Relative weights on the valence s and p orbitals of In and Se atoms in 2-layer InSe at the Γ-point (|c_{orb}|^2 from Eq. 2), for the bands labelled in Fig. S7. Atoms are listed from bottom to top for the 2L crystal. Band energies are provided relative to the lowest conduction band edge (c). E^{DFT} is the Γ-point energy value obtained using DFT and E^{DFT} - \delta E_{300K}^{300K} is the value obtained after subtracting the scissor correction \delta E_{300K}^{300K} for room temperature. The energies corresponding to transitions \hbar \omega_A and \hbar \omega_B are marked in bold.

The interband transition coupling to light can be found using the DFT wave functions, by calculating the momentum matrix element,
\[
\langle \psi_v | \hat{p} | \psi_c \rangle = \hbar \sum_i C_{i,v}^* C_{i,c} \tilde{g}_i ,
\]

where \(c_i\) are the plane-wave coefficients and \(\tilde{g}_i\) are the reciprocal lattice vectors evaluated using VASP. First, by calculating these matrix elements, we establish that all \(c \rightarrow \nu_1\) transitions from the lowest conduction \(c\)-subband to the highest subband formed by interlayer coupling of monolayer \(\nu_1\)-bands are allowed in the in-plane polarization of light. The magnitude of the matrix element of such \(B\)-type transitions, \(\beta = \sqrt{\left| \langle \psi_{\nu 1} | p_x | \psi_c \rangle \right|^2 + \left| \langle \psi_{\nu 1} | p_y | \psi_c \rangle \right|^2}\), is finite at the \(\Gamma\)-point and does not significantly depend on the number of layers. The calculated values of \(\beta\) are given in Table S3 for 1L, 2L, and 3L InSe.

The calculated optical matrix element of the \(A\)-transition (for up to 5 layers) is presented in Fig. S9, which shows that both \(\langle \psi_v | p_x | \psi_c \rangle\) and \(\langle \psi_v | p_y | \psi_c \rangle\) vanish at the \(\Gamma\)-point, as expected for non-degenerate bands in crystals with a hexagonal Bravais lattice. In the vicinity of the \(\Gamma\)-point, the matrix element is found to be linear in the electron wave vector, \(\vec{k}\), in the band. This allows us to write down the Hamiltonian describing electrons near the edges of the band gap in NL InSe as

\[
\hat{H}_N \approx \begin{pmatrix}
\frac{(\hbar k)^2}{2m_cN} & \frac{\hbar^2\alpha N e}{cm_e} \vec{k} \cdot \vec{A} + eE_z d_z \\
\frac{\hbar^2\alpha N e}{cm_e} \vec{k} \cdot \vec{A} + eE_z d_z & -E_{gN}
\end{pmatrix},
\]

where \(\vec{A}\) and \(E_z\) incorporate the coupling to the vector potential and out-of-plane electric field of a photon, respectively, \(m_e\) is electron mass in vacuum, and \(d_z = \langle \psi_v | z | \psi_c \rangle\). The \(N\)-dependence of the coefficient \(\alpha\) and \(d_z\) are shown in Table S3 and Fig. S9, respectively.
Finally, we note that the strong difference between wave functions in valence bands \( v \) and \( v_1 \) leads to a slow interband relaxation, which is likely to be the reason for the experimentally observed hot luminescence in 1L, 2L, and 3L InSe; this requires the presence of long-living strongly non-equilibrium carriers in the optically pumped system.

**Supplementary Figure 8** | **Transition energies of InSe.** Energies of A- and B-transitions between the lowest conduction band \( c \) and the valence bands \( v \) and \( v_1 \), as marked in Fig. S7. The axis on the left shows the energy gaps obtained from DFT; the axis on the right shows the energies \( \hbar \omega_{A/B} \) obtained after applying the scissor correction. The trend in the A-line energy dependence on the number of layers \( N \) agrees with the earlier theories\(^{14,16,17}\).

**Supplementary Table S3** | **N-layer InSe parameters:** DFT-calculated energy gap \( E_{A/B}^{DFT} \) and transition energy \( \hbar \omega_{A/B} \) obtained using scissor correction; the conduction band effective mass \( m_c \) (in units of free electron mass); coefficients \( \alpha \) and \( \beta \) for the A- and B-transition.
Supplementary Figure 9 | Optical matrix elements of InSe. 

**a.** The optical transition matrix element for vertical transitions between the valence and conduction band in NL InSe, as a function of the modulus of the wave vector. 

**b.** The matrix element $d_z$ as a function of the number of layers $N$. Note that $d_z$ saturates at $N > 40$ to approximately $\frac{d_z}{e} (N = \infty) \approx 15 \, \text{Å}$.
References


