

# Nonlinear interactions of dipolar excitons and polaritons in MoS<sub>2</sub> bilayers

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Nonlinear interactions between excitons strongly coupled to light are key for accessing quantum many-body phenomena in polariton systems [1–5]. Atomically-thin two-dimensional semiconductors provide an attractive platform for strong light-matter coupling owing to many controllable excitonic degrees of freedom [6–10]. Among these, the recently emerged exciton hybridization opens access to unexplored excitonic species [11–13, 15, 16], with a promise of enhanced interactions [14]. Here, we employ hybridized interlayer excitons (hIX) in bilayer MoS<sub>2</sub> [11, 12, 15, 16] to achieve highly nonlinear excitonic and polaritonic effects. Such interlayer excitons possess an out-of-plane electric dipole [11] as well as an unusually large oscillator strength [12] allowing observation of dipolar polaritons (dipolaritons [17–19]) in bilayers in optical microcavities. Compared to excitons and polaritons in MoS<sub>2</sub> monolayers, both hIX and dipolaritons exhibit  $\approx 8$  times higher nonlinearity, which is further strongly enhanced

when hIX and intralayer excitons, sharing the same valence band, are excited simultaneously. This gives rise to a highly nonlinear regime which we describe theoretically by introducing a concept of hole crowding. The presented insight into many-body interactions provides new tools for accessing few-polariton quantum correlations [20–22].

Excitons in two-dimensional transition metal dichalcogenides (TMDs) have large oscillator strengths and binding energies [23], making them attractive as a platform for studies of strong light-matter coupling in optical microcavities [6–9]. A variety of polaritonic states have been realised using monolayers of  $\text{MX}_2$  ( $\text{M}=\text{Mo}, \text{W}$ ;  $\text{X}=\text{S}, \text{Se}$ ) embedded in tunable [7, 9, 10, 24] and monolithic microcavities [14, 25–28].

One of the central research themes in polaritonics is the study of nonlinear interactions leading to extremely rich phenomena such as Bose-Einstein condensation [1, 2], polariton lasing [3, 4] or optical parametric amplification [5]. Polaritons formed from tightly bound neutral intralayer excitons in TMDs are not expected to show strong nonlinearity. However, pronounced nonlinear behavior was observed for trion polaritons [24, 29] and Rydberg polaritons [30]. Enhanced nonlinearity can be achieved by employing excitonic states with a physically separated electron and hole, e.g. in adjacent atomic layers [31] or quantum wells [17–19, 32, 33]. Such interlayer excitons have a large out-of-plane electric dipole moment, and thus can strongly mutually interact [34]. Typically, however, interlayer or ‘spatially indirect’ excitons possess low oscillator strength [31, 35]. Thus, in order to strongly couple to cavity photons, hybridization with high-oscillator-strength intralayer excitons is required [14, 17–19, 36].

An attractive approach for realization of dipolar excitons and polaritons is to employ the recently discovered exciton hybridization in  $\text{MoS}_2$  bilayers [12, 37]. This

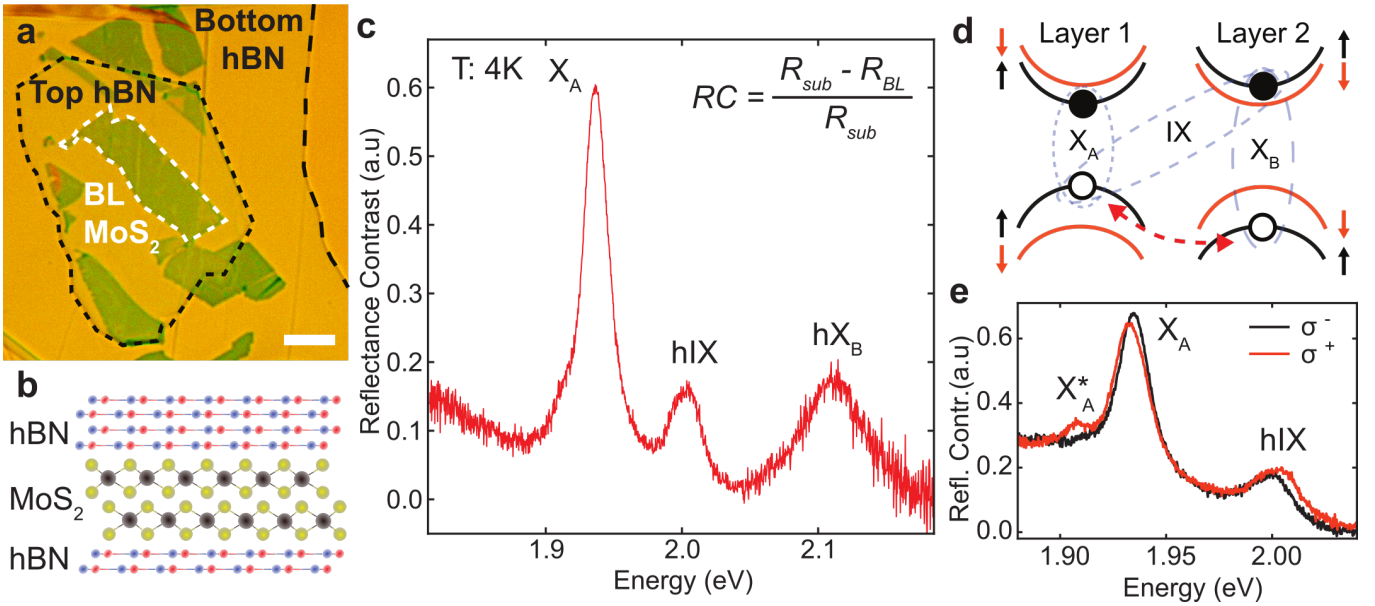


FIG. 1. **Homobilayer MoS<sub>2</sub> and its optical response.** **a**, Bright field microscope image of an encapsulated BL MoS<sub>2</sub> transferred on top of a DBR. Scale bar: 10  $\mu\text{m}$ . **b**, Schematic side-view of the fabricated heterostructure comprising a BL MoS<sub>2</sub> sandwiched between few-layer hBN. **c**, Reflectance contrast (RC) spectrum of the sample measured at low temperature (4 K) showing three distinct absorption features at 1.937 eV, 2.004 eV and 2.113 eV for X<sub>A</sub>, hIX and hX<sub>B</sub>, respectively. The measured linewidths for X<sub>A</sub>, hIX, and hX<sub>B</sub> are 20, 23 and 64 meV, respectively. RC is calculated using the formula in the top-right corner of the graph. **d**, Sketch of the conduction and valence bands in two adjacent layers of MoS<sub>2</sub>, displaying the allowed optical transitions of A and B direct intralayer excitons (X<sub>A</sub> and X<sub>B</sub>) and interlayer excitons (IX) for spin-up states (black lines) at the K point in the bilayer momentum space. IX hybridizes with X<sub>B</sub> through the hole tunnelling between the two layers (red dashed arrow). At the K' point of the bilayer Brillouin zone, the same configuration applies for the states with the opposite spins. **e**, RC spectra of excitons in BL MoS<sub>2</sub> detected in two circular polarizations in an out-of-plane magnetic field of 8 T at  $T=4$  K. Zeeman shifts of opposite signs are observed for X<sub>A</sub> and hIX. The absorption peak of the charged intralayer exciton (X<sub>A</sub><sup>\*</sup>) shows near unity circular polarization.

51 approach allows realization of uniform samples suitable for the observation of macro-  
 52 scopic many-body phenomena [38]. Interlayer excitons unique to bilayer MoS<sub>2</sub> pos-  
 53 sess a large oscillator strength, comparable to that of the intralayer exciton, arising  
 54 from interlayer hybridization of valence band states, aided by a favourable orbital

55 overlap and a relatively small spin-orbit splitting among semiconducting TMDs [12].  
 56 Such hybridized interlayer excitons (hIX) are highly tunable using out-of-plane elec-  
 57 tric field [11, 15] and their valley degree of freedom persists up to room temperature  
 58 [16].

59 Here we use hIXs in bilayer MoS<sub>2</sub> to realize highly nonlinear excitonic and dipo-  
 60 laritonic effects. We unravel a previously unexplored interaction regime involving  
 61 intra- and interlayer excitons stemming from the fermionic nature of the charge  
 62 carriers in a valence band shared between different excitonic species. This regime,  
 63 accessible using broadband excitation resonant with both hIX and intralayer exciton  
 64 transitions, provides strong (up to 10 times) enhancement of the exciton nonlinear-  
 65 ity, already enhanced by up to 8 times in MoS<sub>2</sub> bilayers compared with monolayers.  
 66 We support our experimental findings with microscopic theory, analysing the exci-  
 67 tonic many-body physics and the cross-interactions and introducing the nonlinear  
 68 mechanisms of the hole crowding.

69 Our heterostructure samples consists of a MoS<sub>2</sub> bilayer (BL) sandwiched between  
 70 hBN and placed on a distributed Bragg reflector (DBR). Fig. 1a shows a bright  
 71 field microscope image of the encapsulated BL MoS<sub>2</sub>. A sketch of the side view  
 72 of the device is displayed in Fig. 1b. The reflectance contrast (RC) spectrum of  
 73 the studied MoS<sub>2</sub> bilayer, displayed in Fig. 1c, shows three peaks: the intralayer  
 74 neutral excitons X<sub>A</sub> at at 1.937 eV (see Fig. 1d), hybridized interlayer exciton hIX  
 75 at 2.004 eV and hybridized B-exciton at 2.113 eV. Due to the quantum tunnelling  
 76 of holes, B-excitons hybridize with an interlayer exciton (IX) (Fig. 1d), which is a  
 77 direct transition in the bilayer momentum space [12]. The ratio of the integrated  
 78 intensities of X<sub>A</sub> and hIX is 4.5. Based on these data, we estimate the electron-  
 79 hole separation  $d = 0.55$  nm (see details in Supplementary Note S1) in agreement

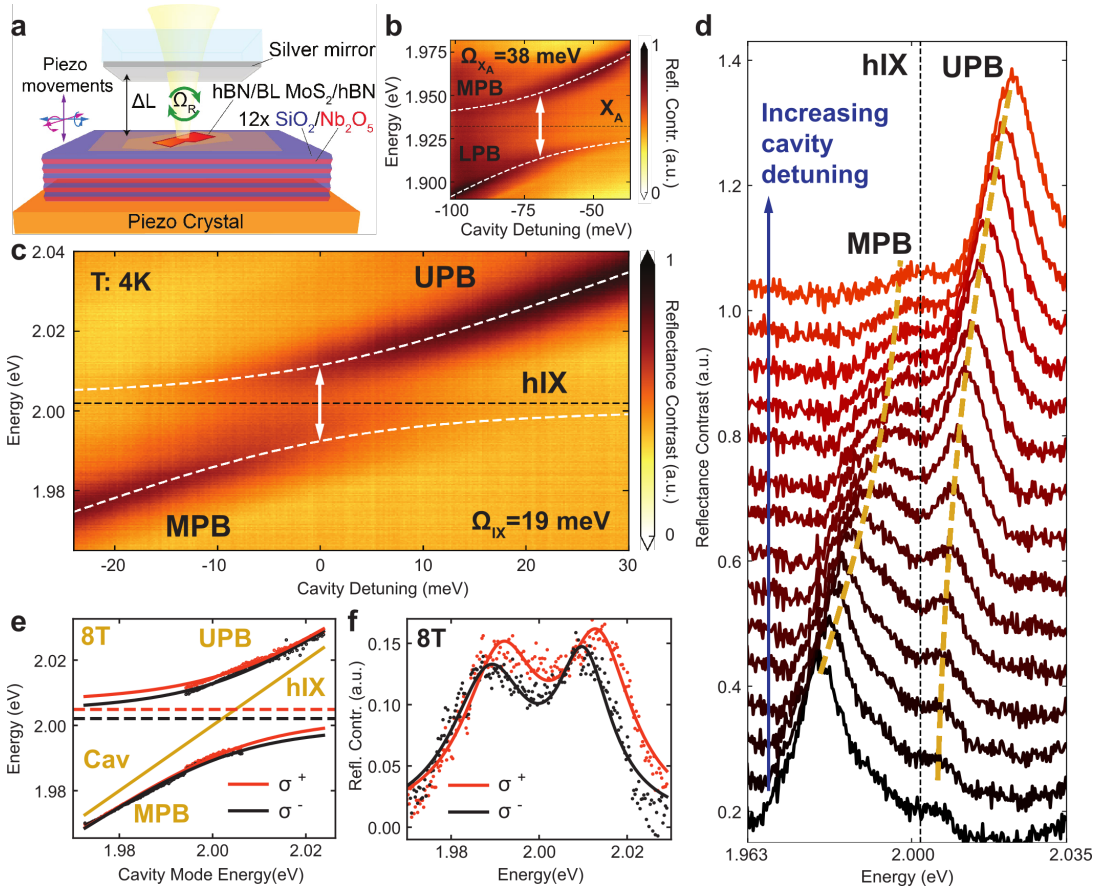


FIG. 2. **Strong exciton-photon coupling in MoS<sub>2</sub> bilayers.** **a**, Schematics of the tunable open microcavity composed of a bottom DBR and a top semi-transparent silver mirror. **b**, **c**, Low temperature (4K) RC spectra measured as a function of the cavity-exciton detuning ( $\Delta = E_{cav} - E_{exc}$ ) for cavity scans across **b** X<sub>A</sub> and **c** hIX energies. White dotted lines show the fitting obtained using the coupled-oscillator model providing the Rabi splittings  $\Omega_{hIX} = 19$  meV and  $\Omega_{X_A} = 38$  meV. **d**, RC spectra measured for the cavity-exciton detunings in the vicinity of the anticrossing between hIX and the cavity mode. **e**, Dipolariton dispersion measured with circularly polarized detection for 8 T magnetic field. The orange and black solid curves are the coupled oscillator model fits for  $\sigma^+$  and  $\sigma^-$  detection, respectively. The positions of the Zeeman-split hIX peaks are shown by dashed lines. **f**,  $\sigma^+$  (orange) and  $\sigma^-$  (black) RC spectra measured at 8 T at the hIX-cavity anticrossing. Fitting with two Lorentzians (solid lines) is shown.

80 with previous studies [16]. We further confirm the nature of the hIX states by  
 81 placing the BL MoS<sub>2</sub> in magnetic field where the valley degeneracy is lifted (Fig.  
 82 1e). In agreement with recent studies [15, 39], we measure a Zeeman splitting with

83 an opposite sign and larger magnitude in hIX compared with  $X_A$  (-3.5 versus 1.5  
84 meV).

85 We study the strong coupling regime in a tunable planar microcavity (Fig. 2a)  
86 formed by a silver mirror and a planar DBR [7]. RC scans as a function of the cavity  
87 mode detuning  $\Delta = E_{cav} - E_{exc}$ , where  $E_{cav}$  and  $E_{exc}$  are the cavity mode and the  
88 corresponding exciton energy, respectively, are shown in Fig. 2c,d. Characteristic  
89 anticrossings of the cavity mode with  $X_A$  and hIX are observed, resulting in lower,  
90 middle and upper polariton branches (LPB, MPB, and UPB, respectively). The  
91 extracted Rabi splittings are  $\Omega_{X_A} = 38$  meV for  $X_A$  and  $\Omega_{hIX} = 19$  meV for hIX  
92 (Supplementary Note S2). Fig. 2d shows the RC spectra in the vicinity of the  
93 anticrossing with hIX, providing a more detailed view of the formation of the MPB  
94 and UPB. The intensity of the polariton peaks is relatively low for the states with  
95 a high exciton fraction at positive (negative) cavity detunings for the MPB (UPB).  
96 As the Rabi splitting scales as a square root of the oscillator strength, the ratio  
97  $\Omega_{X_A}/\Omega_{hIX} = 2$  is in a good agreement with the RC data for integrated intensities of  
98  $X_A$  and hIX. From the Rabi splitting ratio we can estimate the tunneling constant  $J$   
99 leading to the exciton hybridization. The corresponding coefficient is  $J = 48$  meV  
100 (see Supplementary Note S1 for details), matching the density functional theory  
101 predictions [12]. In polarization-resolved cavity scans in an out-of-plane magnetic  
102 field (Fig. 2e,f), similarly to hIX behaviour, we observe opposite and larger Zeeman  
103 splitting for dipolaritons relative to the intralayer polaritons (see Supplementary  
104 Figure S4). Chiral dipolariton states are observed distinguished by their opposite  
105 circular polarization (Fig. 2f).

106 We investigate the nonlinear response of  $X_A$  and hIX in the bare BL flake as a  
107 function of the laser power using both narrow band (NB, full-width at half maxi-

108 mum, FWHM=28nm) and broad band (BB, FWHM=50 nm) pulsed excitation (see  
 109 Methods). Our resonant pump-probe experiments have confirmed that the lifetimes  
 110 of the hIX and  $X_A$  states are considerably longer than the pulse duration of  $\approx 150$   
 111 fs (Supplementary Note S3). Measured RC spectra are shown in Fig. 3a,b for the  
 112 NB and in Fig. 3c for BB excitation. In the NB case, the excitation was tuned to  
 113 excite either  $X_A$  or hIX independently, while in the BB case, both resonances were  
 114 excited simultaneously.

115 As seen in Figs. 3a,b both  $X_A$  and hIX spectra behave similarly upon increasing  
 116 the power of the NB excitation: a blueshift of several meV is observed, accompanied  
 117 by the peak broadening and bleaching. For the BB excitation, however, a different  
 118 nonlinear behaviour is observed as shown in Fig. 3c: the broadening and complete  
 119 suppression of the hIX peak is observed at much lower powers, accompanied by  
 120 a redshift. This is in contrast to  $X_A$ , whose behaviour is similar under the two  
 121 excitation regimes.

122 The resulting energy shifts, peak linewidths and intensities are shown in Fig. 3d,e  
 123 as a function of the exciton density (see details in Supplementary Note S4 and S6).  
 124 Fig. 3d quantifies the trends observed in Figs. 3a,b showing for the BB excitation an  
 125 abrupt bleaching of the hIX peak above the hIX density  $5 \times 10^3 \mu\text{m}^{-2}$  accompanied  
 126 by a redshift of  $\approx 4$  meV and a 12 meV broadening. For the NB case, a similar  
 127 decrease in peak intensity is observed only around  $4 \times 10^4 \mu\text{m}^{-2}$ , accompanied with a  
 128 peak blueshift of  $\approx 7$  meV and a broadening exceeding 15 meV. In Fig. 3e, however,  
 129 it is apparent that the observed behaviour under the two excitation regimes is similar  
 130 for  $X_A$ . A similar blueshift, broadening and saturation are observed at slightly  
 131 higher densities compared to the hIX under the NB excitation (Supplementary  
 132 Note S5). We also find that due to the increased excitonic Bohr radius, the onset

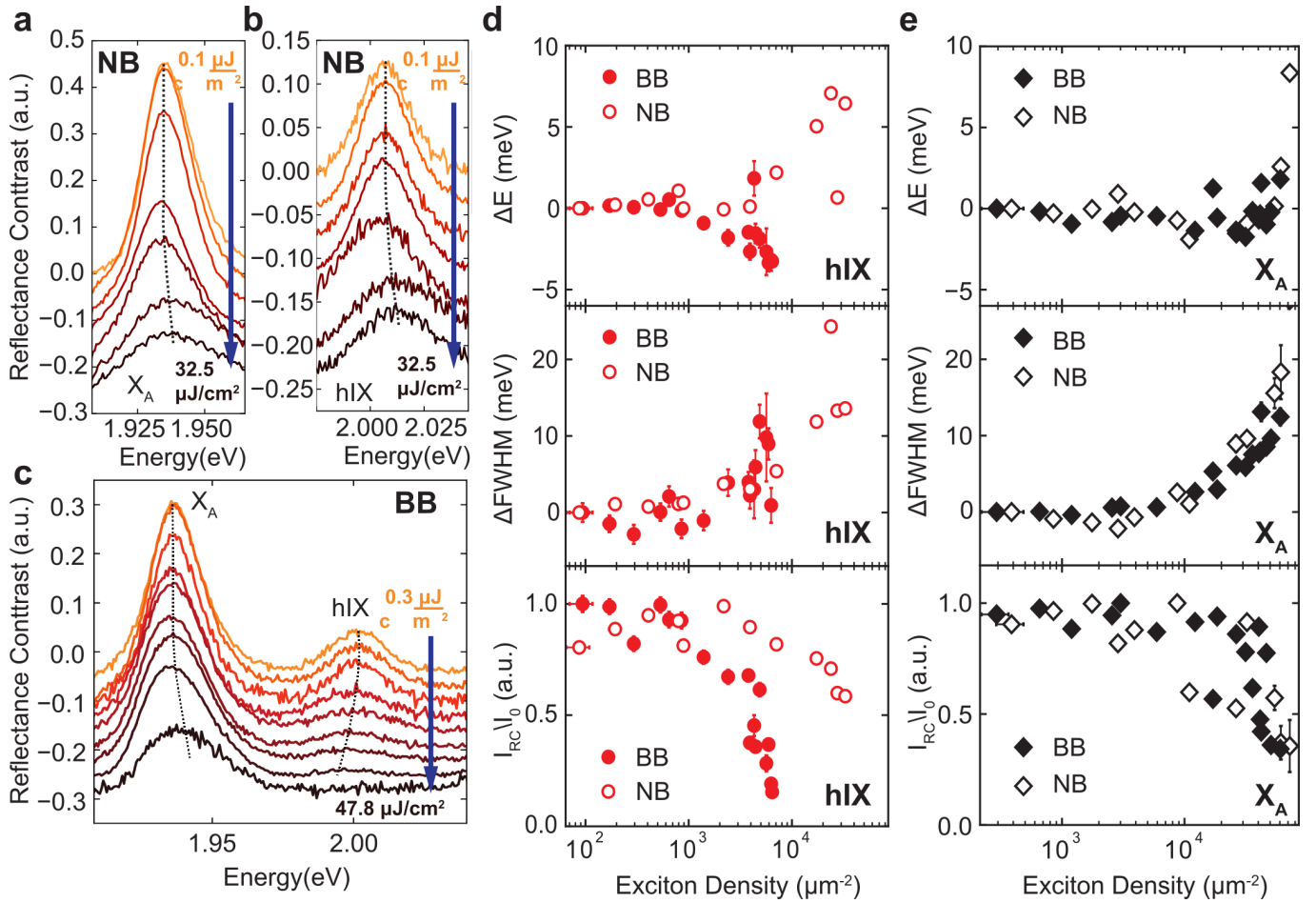


FIG. 3. **Exciton nonlinearity in MoS<sub>2</sub> bilayers.** **a, b, c**, RC spectra measured with the NB (FWHM=28nm) excitation for the X<sub>A</sub> (**a**) and hIX (**b**), and with the BB (FWHM=50nm) excitation (**c**) at different fluences. The dashed curves are guide for the eye. **d, e**, The energy shift  $\Delta E$  (top), linewidth variation  $\Delta FWHM$  (middle) and normalized integrated intensity (bottom) as a function of the exciton density for the hIX (**d**) and X<sub>A</sub> (**e**). Solid (open) symbols show the results for the BB (NB) excitation. For the normalized intensity we divide the intergrated intensity at each laser power by that at the maximum intensity.

133 of the nonlinear behaviour for X<sub>A</sub> in bilayers occurs at a lower exciton density than  
 134 for X<sub>A</sub> in monolayers (Supplementary Note S7).

135 We develop a microscopic model to describe the contrasting phenomena under  
 136 the NB and BB excitation. Under the NB excitation, either X<sub>A</sub> or hIX excitons  
 137 are created as sketched in Fig. 4a. In this case, nonlinearity arises from Coulomb



138 exciton-exciton interactions causing the blueshift and dephasing [40]. For simplic-  
 139 ity, in the main text we will use a Coulomb potential  $V_{Coul}$  combining the exchange  
 140 and direct terms further detailed in Supplementary Note S8. We confirm (see Sup-  
 141 plementary Note S8) that for the intralayer exciton-exciton interaction ( $X_A$ - $X_A$ )  
 142 the dominant nonlinear contribution comes from the Coulomb exchange processes,  
 143 as in the monolayer case [40, 41], while for the hIX-hIX scattering the dominant  
 144 contribution is from the direct Coulomb (dipole-dipole) interaction terms [19]. For  
 145 both  $X_A$  and hIX, the Coulomb interaction is repulsive, and thus leads to the exper-  
 146 imentally observed blueshifts. We find that for the modest electron-hole separation  
 147  $d = 0.55$  nm in the bilayer,  $V_{Coul}$  is overall 2.3 times stronger for hIX compared  
 148 with  $X_A$ .

149 Analysing the shapes of the reflectance spectra in the NB case, we note that they  
 150 depend on the rates of radiative ( $\Gamma_R$ ) and non-radiative ( $\Gamma_{NR}$ ) processes. The area  
 151 under RC curves is described by the ratio  $\Gamma_R/(\Gamma_R + \Gamma_{NR})$ . This ratio changes under  
 152 the increased excitation if the rates depend on the exciton densities. Specifically,  
 153 we account for the scattering-induced non-radiative processes that microscopically  
 154 scale as  $\Gamma_{NR} \propto |V_{Coul}|^2 n$ , i.e. depend on the absolute value of the combined matrix  
 155 elements for the Coulomb interactions and the exciton density  $n$  [40]. This process  
 156 allows reproducing the RC behaviour and bleaching at increasing pump intensity.  
 157 Moreover, it explains stronger nonlinearity for  $X_A$  in bilayers compared to monolay-  
 158 ers. Namely, the scattering scales with the exciton Bohr radius,  $V_{Coul} \propto \alpha$ , which is  
 159 larger in the bilayers due to the enhanced screening (Supplementary Note S8).

160 In the BB case, both  $X_A$  and hIX excitons are generated simultaneously, and  
 161 together with intraspecies scattering ( $X_A$ - $X_A$  and hIX-hIX), interspecies scatter-  
 162 ing ( $X_A$ -hIX) occurs, similarly to the direct-indirect exciton Coulomb scattering in

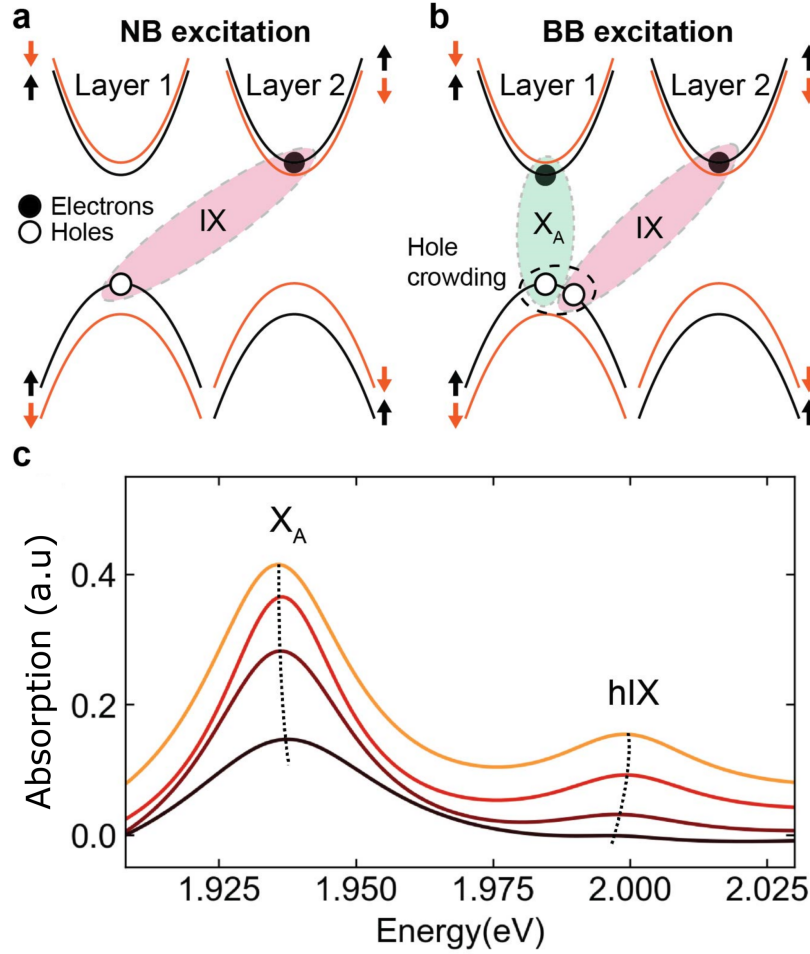


FIG. 4. **Theoretical model for nonlinear optical response in MoS<sub>2</sub> bilayers.** **a, b,** Schematic diagram showing exciton generation under the NB (**a**) and BB (**b**) excitation. In (**a**) only generation of hIX is shown. In (**b**), the holes of the two excitonic species share the same valence band. **c,** Theoretically calculated absorption spectra for the BB excitation case (see Supplementary Note S8), providing qualitative agreement with the experiment. The dashed black curves are guides for the eye.

163 double quantum wells [42]. Since  $X_A$  and hIX are formed by the holes from the  
 164 same valence band (Fig. 4a), an additional contribution arises from the phase space  
 165 filling, i.e. the commutation relations for the excitons (composite bosons) start to  
 166 deviate from the ideal weak-density limit once more particles are created [43]. For  
 167 particles of the same flavour, the phase space filling enables nonlinear saturation ef-  
 168 fects in the strong coupling regime, similar to polariton saturation observed in [29].

169 However, in the presence of several exciton species, we reveal a distinct phase space  
 170 filling mechanism which we term the *hole crowding*. Crucially, we observe that the  
 171 commutator of the  $X_A$  annihilation operator ( $\hat{X}$ ) and hIX creation operator ( $\hat{I}^\dagger$ )  
 172 is non-zero,  $[\hat{X}(\mathbf{p}), \hat{I}^\dagger(\mathbf{q})] = -\hat{B}_{\mathbf{p},\mathbf{q}}$ . Here  $\mathbf{p}$ ,  $\mathbf{q}$  are exciton momenta and  $\hat{B}_{\mathbf{p},\mathbf{q}}$  is  
 173 an operator denoting the deviation from the ideal commuting case ( $\hat{B}_{\mathbf{p},\mathbf{q}} = 0$ ) of  
 174 distinct bosons where holes do not compete for the valence band space.

175 This statistical property of modes that share a hole has profound consequences  
 176 for the nonlinear response. Namely, the total energy is evaluated as an expecta-  
 177 tion value over a many-body state with both  $X_A$  and hIX excitons,  $|N_X, N_{\text{hIX}}\rangle :=$   
 178  $(\prod_{\mathbf{p}}^{N_X} \hat{X}^\dagger)(\prod_{\mathbf{q}}^{N_{\text{hIX}}} \hat{I}^\dagger)|\Omega_{max}\rangle$ , where  $N_X$  and  $N_{\text{hIX}}$  particles are created from the ground  
 179 state  $|\Omega_{max}\rangle$ . If the excitonic modes are independent, the contributions from  $X_A$   
 180 and hIX simply add up. However, the hole coexistence in the valence band induces  
 181 the excitonic interspecies scattering. The phase space filling combined with the  
 182 Coulomb energy correction leads to a negative nonlinear energy contribution. This  
 183 nonlinear term scales as  $\Delta E_{\text{hIX}} = -\eta\sqrt{n_X n_{\text{hIX}}}$ , where  $\eta > 0$  is a coefficient defined  
 184 by the Coulomb energy and Bohr radii and  $n_{X,\text{hIX}}$  are the exciton densities (see Sup-  
 185 plementary Note S9). This nonlinearity also modifies the non-radiative processes  
 186 leading to substantial broadening for the hIX states.

187 According to this analysis, the effect of the BB excitation should be most pro-  
 188 nounced for hIX. In addition to the possible hIX-hIX scattering (similar to that  
 189 occurring under the NB excitation), much stronger  $X_A$  absorption leads to the  
 190 phase space filling in the valence band. Such hole crowding introduces additional  
 191 scattering channels for hIX and leads to its RC spectra bleaching at lower hIX ex-  
 192 citon densities. On the other hand, as only relatively small hIX densities can be  
 193 generated, both the NB and BB excitation cases should produce similar results for

194  $X_A$ . Using the estimated nonlinear coefficients caused by the hole crowding, we  
 195 model the RC in the BB regime and qualitatively reproduce the strong bleaching  
 196 and redshift for hIX at the increased density.

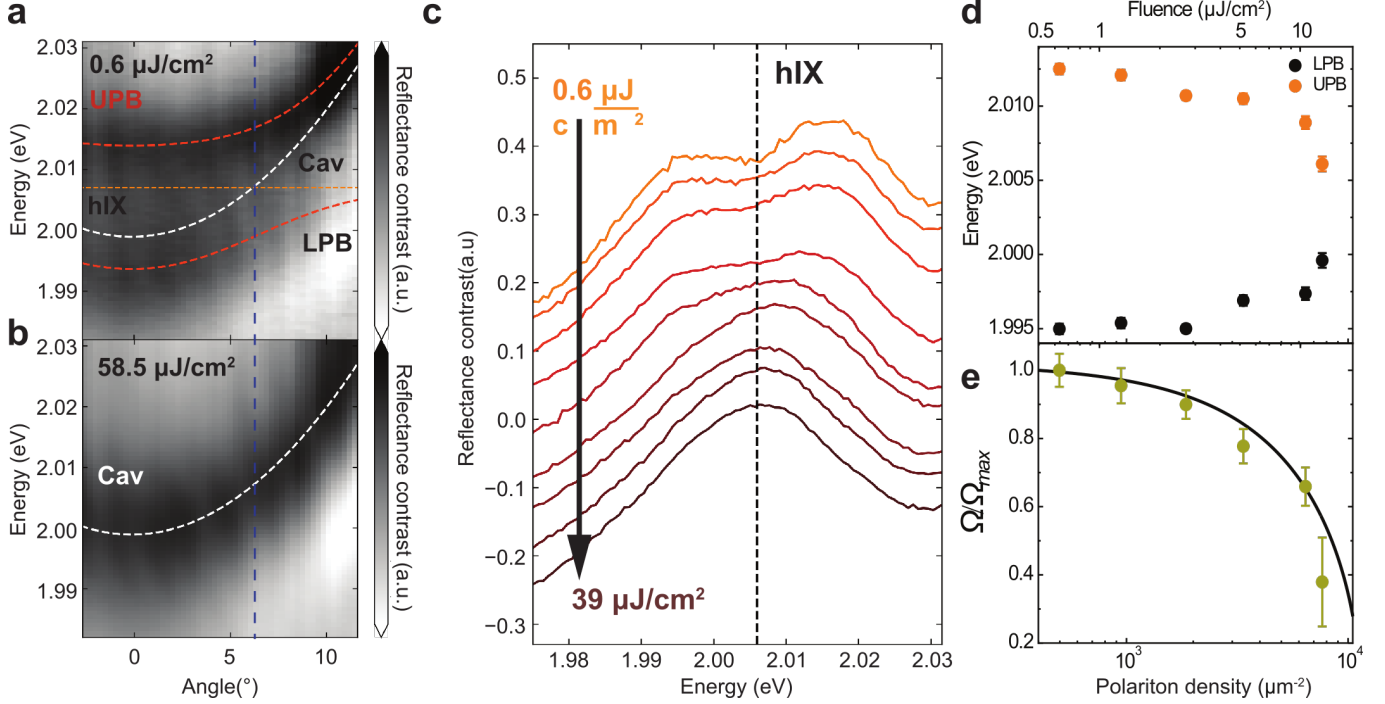


FIG. 5. **Nonlinear behaviour of dipolaritons.** **a, b,** Reflectance contrast spectra measured at different laser fluences for the MoS<sub>2</sub> bilayer placed in a monolithic cavity. (a) The low fluence case ( $0.6 \mu\text{J cm}^{-2}$ ). A clear anticrossing at  $6.5^\circ$  is observed. Dashed red lines show the results of the fitting using a coupled oscillator model, with two polariton branches LPB and UPB formed. White and orange lines show the energies of the uncoupled cavity mode and hIX state, respectively. The vertical line marks the anticrossing angle. (b) The high fluence case ( $58.5 \mu\text{J cm}^{-2}$ ). A complete collapse of the strong coupling regime is observed, with the disappearance of the anticrossing and transition into the weak coupling regime. **c,** RC spectra measured at the anticrossing at  $6.5^\circ$  as a function of the laser fluence. **d,** Measured UPB and LPB peak energies at  $6.5^\circ$  as a function of the laser fluence (see top axis) and the corresponding polariton density (bottom axis). **e,** Symbols show the Rabi splittings normalized by the Rabi splitting measured at the lowest power ( $\Omega/\Omega_{max}$ ) as deduced from **d**. The line shows the fitting using our theoretical model (Supplementary Note S8).

197 We investigate nonlinear properties of dipolar polaritons in a monolithic (fixed-  
 198 length) cavity created by a silver mirror on top of a PMMA spacer (245 nm thick)  
 199 covering the hBN-encapsulated MoS<sub>2</sub> homobilayer placed on the DBR. The cavity  
 200 mode energy can be tuned by varying the angle of observation (0 degrees corresponds  
 201 to normal incidence). We use a microscopy setup optimized for Fourier-plane imag-

ing, thus allowing simultaneous detection of reflectivity spectra in a range of angles as shown in Fig.5(a) displaying the measured polariton dispersion. In this experiment, the cavity mode is tuned around hIX and only two polariton branches LPB and UPB are observed at low fluence of  $0.6 \mu\text{J cm}^{-2}$  with a characteristic Rabi splitting of 17.5 meV. In Fig.5(b), at an increased fluence of  $58.5 \mu\text{J cm}^{-2}$ , only a weakly coupled cavity mode is visible.

Fig.5(c) shows RC spectra taken at  $\sim 6.5^\circ$  around the anticrossing at different laser fluences. The collapse of the two polariton peaks into one peak signifying the transition to the weak coupling regime is observed above  $25 \mu\text{J cm}^{-2}$ . The LPB and UPB energies extracted using the coupled oscillator model (Supplementary Figure S5) are shown in Fig.5(d). As the polariton density is increased, the LPB and UPB approach each other almost symmetrically, converging to the exciton energy. The corresponding normalized Rabi splitting ( $\Omega/\Omega_{max}$ , where  $\Omega_{max}$  is measured at low fluence) are shown in Fig.5(d,e) as a function of the total polariton density.

In this experiment, the cavity mode is considerably above the  $X_A$  energy, which therefore is not coupled to the cavity. Hence, the extracted Rabi splittings are fitted with a theoretically predicted trend of  $\Omega$  for the NB excitation regime (Supplementary Note S8). A nonlinear polariton coefficient  $\beta = 0.86 \mu\text{eV}\mu\text{m}^2$  is extracted by differentiating the fitted function with respect to the polariton density. Comparing our results to  $X_A$  intralayer-exciton-polaritons in monolayers in similar cavities [14], we observe that the nonlinearity coefficient for dipolar interlayer polaritons is about an order of magnitude larger. This is in a good agreement with the theoretically predicted intrinsic nonlinearity of hybridized interlayer polaritons (Supplementary Note S8), and with our experimental data comparing hIX and monolayer  $X_A$  outside the cavity (Supplementary Note S7).

227 In summary, we report the nonlinear exciton and exciton-polariton behaviour in  
228 MoS<sub>2</sub> homobilayers, a unique system where hybridized interlayer exciton states can  
229 be realized having a large oscillator strength. We find that nonlinearity in MoS<sub>2</sub>  
230 bilayers can be enhanced when both the intralayer and interlayer states are excited  
231 simultaneously, the regime that qualitatively changes the exciton-exciton interaction  
232 through the hole crowding effect introduced theoretically in our work. In this  
233 broad-band excitation regime, the bleaching of the hIX absorption occurs at 8 times  
234 lower hIX densities compared to the case when the interlayer excitons are generated  
235 on their own. In addition to this, we find that the dipolar nature of hIX states  
236 in MoS<sub>2</sub> homobilayers already results in 10 times stronger nonlinearity compared  
237 with the intralayer excitons in MoS<sub>2</sub> monolayers. Thus, we report on an overall  
238 enhancement of the nonlinearity by nearly two orders of magnitude. Thanks to the  
239 large oscillator strength, hIX can enter the strong coupling regime in MoS<sub>2</sub> bilayers  
240 placed in microcavities, as realized in our work. Similarly to hIX states themselves,  
241 dipolar polaritons also show 10 times stronger nonlinearity compared with exciton-  
242 polaritons in MoS<sub>2</sub> monolayers. We expect that in microcavities where the cavity  
243 mode is coupled to both hIX and X<sub>A</sub> in MoS<sub>2</sub> bilayers, and the excitation similar  
244 to the broad-band regime can thus be realized, the nonlinear polariton coefficient  
245 will be dramatically enhanced owing to the hole crowding effect, allowing highly  
246 nonlinear polariton system to be realized. We thus predict that MoS<sub>2</sub> bilayers  
247 will be an attractive platform for realization of quantum-correlated polaritons with  
248 applications in polariton logic networks [20] and polariton blockade [21, 22].

## METHODS

249  
250 The hBN/MoS<sub>2</sub>/hBN heterostructures were assembled using a PDMS polymer  
251 stamp method. The PMMA spacer for the monolithic cavity was deposited using a  
252 spin-coating technique, while a silver mirror of 45 nm was thermally evaporated on  
253 top of it.

254 Broad-band excitation was used to measure the reflectance contrast (RC) spectra  
255 of the devices at cryogenic temperatures (4K), defined as  $RC = (R_{\text{sub}} - R_{\text{BL}})/R_{\text{sub}}$ ,  
256 where  $R_{\text{sub}}$  and  $R_{\text{BL}}$  are the substrate and MoS<sub>2</sub> bilayer reflectivity, respectively.  
257 For the magnetic field studies the same RC measurements were performed using  
258 unpolarized light in excitation with polarizers,  $\lambda/4$  polarizers and  $\lambda/2$  waveplates in  
259 collection, to resolve  $\sigma^+$  and  $\sigma^-$  polarization. The low temperature measurements  
260 using the tunable cavity were carried out in a liquid helium bath cryostat (T=4.2K)  
261 equipped with a superconducting magnet and free beam optical access. We used  
262 a white light LED as a source. RC spectra were measured at each  $\Delta L$  and are  
263 integrated over the angles within 5 degrees from normal incidence. The RC spectra  
264 measured in the cavity are fitted using Lorenzians. The peak positions are then used  
265 to fit to a coupled oscillator model, producing the Rabi splitting and the exciton  
266 and cavity mode energies.

267 The measurements on the monolithic cavity were performed in a closed loop helium  
268 flow cryostat (T=6K). For the power-dependent RC experiments, we used super-  
269 continuum radiation produced by 100 fs Ti:Sapphire laser pulses at 2 kHz repetition  
270 rate at 1.55 eV propagating through a thin sapphire crystal. The supercontinuum  
271 radiation was then filtered to produce the desired narrow-band excitation.

272 All the exciton and polariton densities were calculated following the procedure

introduced by L. Zhang et al. [14], taking into account the spectral overlap of the spectrum of the excitation laser and the investigated exciton peak (see further details in Supplementary Note S4).

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#### AUTHOR CONTRIBUTIONS

CL and SR fabricated and characterized hBN-encapsulated MoS<sub>2</sub> samples. KW and TT synthesized the high quality hBN. CL and AG designed the microcavity samples. PC, RJ, DGL fabricated the microcavity samples. CL, AG, CT, TL and SDC carried out optical spectroscopy experiments. SC and OK developed theory. AG calculated polariton densities. CL and AG analyzed the data with contribution from AIT, TL, SC, OK, CT, SDC and GC. CL, AG, SC, OK and AIT wrote the manuscript with contribution from all other co-authors. AIT, OK, DGL, GC managed various aspects of the project. AIT supervised the project.



## DATA AVAILABILITY

295

296 The data that support the findings of this study are available from the correspond-  
 297 ing author upon request.

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- 301 [1] H. Deng, H. Haug, and Y. Yamamoto, Exciton-polariton Bose-Einstein condensation, *Reviews of Modern Physics* **82**, 1489  
 302 (2010).
- 303 [2] J. Kasprzak *et al.*, Bose-Einstein condensation of exciton polaritons, *Nature* **443**, 409 (2006).
- 304 [3] S. Christopoulos *et al.*, Room-temperature polariton lasing in semiconductor microcavities, *Physical Review Letters* **98**,  
 305 126405 (2007).
- 306 [4] P. Bhattacharya *et al.*, Room temperature electrically injected polariton laser, *Physical Review Letters* **112**, 236802 (2014).
- 307 [5] A. Amo *et al.*, Collective fluid dynamics of a polariton condensate in a semiconductor microcavity, *Nature* **457**, 291 (2009).
- 308 [6] X. Liu, T. Galfsky, Z. Sun, F. Xia, E. C. Lin, Y. H. Lee, S. Kéna-Cohen, and V. M. Menon, Strong light-matter coupling  
 309 in two-dimensional atomic crystals, *Nature Photonics* **9**, 30 (2014).
- 310 [7] S. Dufferwiel, S. Schwarz, F. Withers, A. A. Trichet, F. Li, M. Sich, O. Del Pozo-Zamudio, C. Clark, A. Nalitov, D. D.  
 311 Solnyshkov, G. Malpuech, K. S. Novoselov, J. M. Smith, M. S. Skolnick, D. N. Krizhanovskii, and A. I. Tartakovskii,  
 312 Exciton-polaritons in van der Waals heterostructures embedded in tunable microcavities, *Nature Communications* **6**, 1  
 313 (2015).
- 314 [8] N. Lundt, A. Maryński, E. Cherotchenko, A. Pant, X. Fan, S. Tongay, G. Sek, A. V. Kavokin, S. Höfling, and C. Schneider,  
 315 Monolayered MoSe<sub>2</sub>: A candidate for room temperature polaritonics, *2D Materials* **4** (2017).
- 316 [9] M. Sidler, P. Back, O. Cotlet, A. Srivastava, T. Fink, M. Kroner, E. Demler, and A. Imamoglu, Fermi polaron-polaritons  
 317 in charge-tunable atomically thin semiconductors, *Nature Physics* **13**, 255 (2017).
- 318 [10] S. Dufferwiel, T. P. Lyons, D. D. Solnyshkov, A. A. Trichet, F. Withers, S. Schwarz, G. Malpuech, J. M. Smith, K. S.  
 319 Novoselov, M. S. Skolnick, D. N. Krizhanovskii, and A. I. Tartakovskii, Valley-addressable polaritons in atomically thin  
 320 semiconductors, *Nature Photonics* **11**, 497 (2017).
- 321 [11] N. Leisgang, S. Shree, I. Paradisanos, L. Sponfeldner, C. Robert, D. Lagarde, A. Balocchi, K. Watanabe, T. Taniguchi,  
 322 X. Marie, *et al.*, Giant stark splitting of an exciton in bilayer mos<sub>2</sub>, *Nature Nanotechnology* **15**, 901 (2020).
- 323 [12] I. C. Gerber, E. Courtade, S. Shree, C. Robert, T. Taniguchi, K. Watanabe, A. Balocchi, P. Renucci, D. Lagarde, X. Marie,  
 324 and B. Urbaszek, Interlayer excitons in bilayer MoS<sub>2</sub> with strong oscillator strength up to room temperature, *Physical*  
 325 *Review B* **99**, 1 (2019).
- 326 [13] N. P. Wilson, W. Yao, J. Shan, X. Xu Excitons and emergent quantum phenomena in stacked 2D semiconductors *Nature*  
 327 **599**, 383-392 (2021).
- 328 [14] L. Zhang, F. Wu, S. Hou, Z. Zhang, Y.-H. Chou, K. Watanabe, T. Taniguchi, S. R. Forrest, and H. Deng, Van der waals  
 329 heterostructure polaritons with moiré-induced nonlinearity, *Nature* **591**, 61 (2021).
- 330 [15] E. Lorchat, M. Selig, F. Katsch, K. Yumigeta, S. Tongay, A. Knorr, C. Schneider, and S. Höfling, Excitons in bilayer mos  
 331 2 displaying a colossal electric field splitting and tunable magnetic response, *Physical Review Letters* **126**, 037401 (2021).

- 332 [16] N. Peimyoo, T. Deilmann, F. Withers, J. Escolar, D. Nutting, T. Taniguchi, K. Watanabe, A. Taghizadeh, M. F. Craciun,  
333 K. S. Thygesen, and S. Russo, Electrical tuning of optically active interlayer excitons in bilayer MoS<sub>2</sub>, *Nature Nanotech-*  
334 *nology* **16**, 888 (2021).
- 335 [17] P. Cristofolini, G. Christmann, S. I. Tsintzos, G. Deligeorgis, G. Konstantinidis, Z. Hatzopoulos, P. G. Savvidis, and J. J.  
336 Baumberg, Coupling quantum tunneling with cavity photons *Science* **336**, 704-707 (2012).
- 337 [18] E. Togan, H.-T. Lim, S. Faelt, W. Wegscheider, and A. Imamoglu, Enhanced interactions between dipolar polaritons, *Phys.*  
338 *Rev. Lett.* **121**, 227402 (2018).
- 339 [19] O. Kyriienko, E. B. Magnusson, and I. A. Shelykh, Spin dynamics of cold exciton condensates, *Phys. Rev. B* **86**, 115324  
340 (2012).
- 341 [20] N. G. Berloff, M. Silva, K. Kalinin, A. Askitopoulos, J. D. Töpfer, P. Cilibrizzi, W. Langbein, and P. G. Lagoudakis,  
342 Realizing the classical xy hamiltonian in polariton simulators, *Nature Materials* **16**, 1120 (2017).
- 343 [21] A. Delteil, T. Fink, A. Schade, S. Höfling, C. Schneider, and A. Imamoglu, Towards polariton blockade of confined exciton-  
344 polaritons, *Nature Materials* **18**, 219 (2019).
- 345 [22] O. Kyriienko, D. Krizhanovskii, and I. Shelykh, Nonlinear quantum optics with trion polaritons in 2d monolayers: con-  
346 ventional and unconventional photon blockade, *Physical Review Letters* **125**, 197402 (2020).
- 347 [23] G. Wang, A. Chernikov, M. M. Glazov, T. F. Heinz, X. Marie, T. Amand, and B. Urbaszek, Colloquium: Excitons in  
348 atomically thin transition metal dichalcogenides, *Reviews of Modern Physics* **90**, 21001 (2018).
- 349 [24] T. P. Lyons, D. J. Gillard, C. Leblanc, J. Puebla, D. D. Solnyshkov, L. Klompmaker, I. A. Akimov, C. Louca, P. Muduli,  
350 A. Genco, M. Bayer, Y. Otani, G. Malpuech, and A. I. Tartakovskii, Giant effective Zeeman splitting in a monolayer  
351 semiconductor realized by spin-selective strong light-matter coupling, (2021).
- 352 [25] D. J. Gillard, A. Genco, S. Ahn, T. P. Lyons, K. Yeol Ma, A. R. Jang, T. Severs Millard, A. A. Trichet, R. Jayaprakash,  
353 K. Georgiou, D. G. Lidzey, J. M. Smith, H. Suk Shin, and A. I. Tartakovskii, Strong exciton-photon coupling in large  
354 area MoSe<sub>2</sub> and WSe<sub>2</sub> heterostructures fabricated from two-dimensional materials grown by chemical vapor deposition,  
355 *2D Materials* **8** (2021).
- 356 [26] J. Gu, B. Chakraborty, M. Khatoniar, and V. M. Menon, A room-temperature polariton light-emitting diode based on  
357 monolayer WS<sub>2</sub>, *Nature Nanotechnology* **14**, 1024 (2019).
- 358 [27] N. Lundt, L. Dusanowski, E. Sedov, P. Stepanov, M. M. Glazov, S. Klembt, M. Klaas, J. Beierlein, Y. Qin, S. Tongay,  
359 *et al.*, Optical valley hall effect for highly valley-coherent exciton-polaritons in an atomically thin semiconductor, *Nature*  
360 *Nanotechnology* **14**, 770 (2019).
- 361 [28] L. B. Tan, O. Cotlet, A. Bergschneider, R. Schmidt, P. Back, Y. Shimazaki, M. Kroner, and A. Imamoglu, Interacting  
362 polaron-polaritons, *Physical Review X* **10**, 021011 (2020).
- 363 [29] R. P. A. Emmanuele *et al.*, Highly nonlinear trion-polaritons in a monolayer semiconductor, *Nature Communications* **11**,  
364 3589 (2020).
- 365 [30] J. Gu, V. Walther, L. Waldecker, D. Rhodes, A. Raja, J. C. Hone, T. F. Heinz, S. Kéna-Cohen, T. Pohl, and V. M. Menon,  
366 Enhanced nonlinear interaction of polaritons via excitonic Rydberg states in monolayer WSe<sub>2</sub>, *Nature Communications*  
367 **12** (2021).
- 368 [31] P. Rivera, H. Yu, K. L. Seyler, N. P. Wilson, W. Yao, and X. Xu, Interlayer valley excitons in heterobilayers of transition  
369 metal dichalcogenides, *Nature Nanotechnology* **13**, 1004 (2018).
- 370 [32] L. V. Butov, Condensation and pattern formation in cold exciton gases in coupled quantum wells, *Journal of Physics:*  
371 *Condensed Matter* **16**, R1577 (2004).
- 372 [33] C. Hubert, Y. Baruchi, Y. Mazuz-Harpaz, K. Cohen, K. Biermann, M. Lemeshko, K. West, L. Pfeiffer, R. Rapaport, and  
373 P. Santos, Attractive dipolar coupling between stacked exciton fluids, *Phys. Rev. X* **9**, 021026 (2019).
- 374 [34] L. Butov, A. Gossard, and D. Chemla, Macroscopically ordered state in an exciton system, *Nature* **418**, 751 (2002).

- 375 [35] A. Fox, D. Miller, G. Livescu, J. Cunningham, and W. Jan, Excitonic effects in coupled quantum wells, *Physical Review*  
376 *B* **44**, 6231 (1991).
- 377 [36] E. M. Alexeev, D. A. Ruiz-Tijerina, M. Danovich, M. J. Hamer, D. J. Terry, P. K. Nayak, S. Ahn, S. Pak, J. Lee, J. I. Sohn,  
378 *et al.*, Resonantly hybridized excitons in moiré superlattices in van der waals heterostructures, *Nature* **567**, 81 (2019).
- 379 [37] I. Paradisanos, S. Shree, A. George, N. Leisgang, C. Robert, K. Watanabe, T. Taniguchi, R. J. Warburton, A. Turchanin,  
380 X. Marie, *et al.*, Controlling interlayer excitons in mos2 layers grown by chemical vapor deposition, *Nature Communications*  
381 **11**, 1 (2020).
- 382 [38] A. Amo, D. Sanvitto, F. Laussy, D. Ballarini, E. d. Valle, M. Martin, A. Lemaitre, J. Bloch, D. Krizhanovskii, M. Skolnick,  
383 *et al.*, Collective fluid dynamics of a polariton condensate in a semiconductor microcavity, *Nature* **457**, 291 (2009).
- 384 [39] Z. Gong, G. B. Liu, H. Yu, D. Xiao, X. Cui, X. Xu, and W. Yao, Magnetoelectric effects and valley-controlled spin quantum  
385 gates in transition metal dichalcogenide bilayers, *Nature Communications* **4**, 1 (2013).
- 386 [40] D. Erkensten, S. Brem, and E. Malic, Exciton-exciton interaction in transition metal dichalcogenide monolayers and van  
387 der waals heterostructures, *Phys. Rev. B* **103**, 045426 (2021).
- 388 [41] V. Shahnazaryan, I. Iorsh, I. A. Shelykh, and O. Kyriienko, Exciton-exciton interaction in transition-metal dichalcogenide  
389 monolayers, *Phys. Rev. B* **96**, 115409 (2017).
- 390 [42] K. Kristinsson, O. Kyriienko, T. C. H. Liew, and I. A. Shelykh, Continuous terahertz emission from dipolaritons, *Phys.*  
391 *Rev. B* **88**, 245303 (2013).
- 392 [43] M. Combescot, O. Betbeder-Matibet, and F. Dubin, The many-body physics of composite bosons, *Physics Reports* **463**,  
393 215 (2008).