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Journal
Nature Physics, 13(2)

ISSN
1745-2473

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Publication Date
2017-02-01

DOI
10.1038/nphys3928

Peer reviewed

Interlayer Electron-Phonon Coupling in WSe_2/hBN Heterostructures

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Engineering layer-layer interaction provides a powerful way to realize novel and designable quantum phenomena in van der Waals heterostructures[1-16]. Interlayer electron-electron interactions, for example, have enabled fascinating physics that is difficult to achieve in a single material, such as Hofstadter’s butterfly in graphene/boron nitride (hBN) heterostructures[5-10]. In addition to electron-electron interactions, interlayer electron-phonon interactions allows for further control of physical properties of van der Waals heterostructures. Here we report extraordinary interlayer electron-phonon interaction in WSe_2/hBN heterostructure, where optically silent hBN phonons emerge in Raman spectra with surprisingly strong intensity through resonant coupling to WSe_2 electronic transitions. Excitation spectroscopy reveals the double-resonance nature of such enhancement, and identifies the two resonant states to be the A-exciton transition of monolayer WSe_2 and a new “hybrid” state present only in WSe_2/hBN heterostructures. Our first observation of the interlayer electron-phonon interaction is important for fundamental understanding of van der Waals heterostructures, and can open up new ways to engineer electrons and phonons for novel device applications.

Van der Waals heterostructure of atomically thin two-dimensional (2D) crystals is a new class of material in which novel quantum phenomena can emerge from layer-layer interactions[1-16]. For example, electron-electron interactions between adjacent 2D layers can give rise to a variety of fascinating physical behavior: The interlayer Moiré potential between graphene and hBN layers leads to mini-Dirac cones and the Hofstadter's butterfly pattern in graphene/hBN heterostructures[5-10]; electronic couplings between MoS_2 and MoS_2 layers lead to a direct- to indirect-bandgap transition in bilayer MoS_2[11,12]; and Coulomb interactions between $MoSe_2$ and WSe_2 layers lead to interlayer exciton states in $MoSe_2/WSe_2$ heterostructures[13,14]. Similar to electron-electron interactions, electron-phonon interactions also play a key role in a wide range of phenomena in condensed matter physics: the electron-phonon coupling sets the intrinsic limit of electron mobility[17], dominates the ultrafast carrier dynamics[18], leads to the Peierls instability[19], and enables the formation of Cooper pairs[20]. Exploiting interactions between electrons in one layered material and phonons in an adjacent material could enable new ways to control electron-phonon coupling and realize novel quantum behavior that is not possible before. For example, it has been recently shown that electrons in monolayer FeSe can couple strongly with phonons in the adjacent $SrTiO_3$ substrate, which may play an important role in the anomalously high superconductivity critical temperature in the system[21,22]. However, the unusual interlayer electron-phonon interactions in the van der Waals heterostructures have been little explored so far, although there have been indications that interlayer interactions between graphene electrons and the substrate phonons is a limiting factor for higher graphene electron mobility at room temperature[23,24].

Here we report, for the first time, an extraordinary interlayer electron-phonon coupling in WSe_2/hBN heterostructures, as illustrated in Fig. 1a. Vibration modes of hBN lattice (labeled with red arrows) can significantly modulate the behavior of electrons and holes in WSe_2 (red and blue clouds), thus enabling efficient interlayer electron-phonon coupling. Experimentally, such interaction manifests as emerging resonant Raman scattering processes that involve both hBN phonon vibrations and WSe_2 electronic resonances: Two prominent new Raman peaks appear in the heterostructure composed of WSe_2 encapsulated in hBN flakes, with the Raman shifts corresponding to the hBN ZO phonon mode and the hBN ZO + WSe_2 A_{1g} combinatorial mode, respectively. These Raman modes are remarkably strong, with intensities three orders of magnitude higher than the Raman signal of phonons in pure hBN. Excitation spectroscopy reveals that the new Raman peaks of hBN ZO phonons are enhanced by WSe_2 electronic transitions in a double-resonance process. This double resonance involves both the well-known A-exciton of monolayer WSe_2, and a rather surprising new electronic transition present only in the WSe_2/hBN heterostructures that originates from the interactions between the adjacent WSe_2 and hBN layers. In addition, we show that the new Raman peaks from the interlayer electron-phonon couplings in the heterostructure can be controlled efficiently through electrostatic gating of the monolayer WSe_2. Our study demonstrates for the first time the presence of remarkable interlayer electron-phonon interactions in van der Waals heterostructures, which will be important for understanding electron behavior from carrier mobility to energy relaxation dynamics in 2D materials, and offers new opportunities to engineer novel quantum phenomena in van der Waals heterostructures.

Fig. 1b shows an optical microscope image of the heterostructure, where monolayer WSe_2 is encapsulated with thin hBN flakes (~10 nm thick) by a dry transfer method using polyethylene terephthalate (PET) stamp (See methods). The contact electrodes are fabricated on the exposed part of WSe_2 outside top hBN, as illustrated in Fig. 1c, which allows us to study the doping-dependent behavior. Fig. 2a shows light emission spectra of the heterostructure with different photoexcitation energies (E_{exc} = 1.849, 1.857, and 1.862 eV). The prominent peaks at 1.71 eV and 1.68 eV are the well-known exciton and trion photoluminescence (PL) in pristine WSe_2[25]. Surprisingly, we observe two additional strong peaks that do not exist in the emission spectra of either pristine WSe_2 or hBN, as labeled by the green and orange arrows. These unique emission peaks in the heterostructures are quite unusual in several aspects. Most notably, their peak energies shift by exactly the same amount as the excitation light, a defining signature of Raman scattering processes. In addition, these new Raman peaks show distinct polarization dependence: the Raman intensities are strongest for parallel incident and outgoing photon polarizations (red curves), and disappear completely in the cross-polarization configuration (black curves). In contrast, WSe_2 exciton and trion PL intensities show negligible linear polarization dependence in these exfoliated WSe_2

encapsulated in hBN. Such distinctive polarization dependence allows us to obtain clean Raman features without the PL background by simply subtracting the cross-polarization spectra from the parallel-polarization spectra. Black curve in Fig. 2b shows the subtracted spectrum for photoexcitation at 1.849 eV. Two prominent Raman peaks with sharp edges located at 820 (mode I) and 1070 cm^{-1} (mode II) are clearly observed.

Raman modes with energy shifts at 820 (mode I) and 1070 cm^{-1} (mode II) do not exist in either isolated WSe_2 or hBN. The Raman-allowed hBN phonon mode is the E_{2g} mode at 1367cm^{-1} (Ref.[26,27]). On the other hand, both A_{1g} and E_{2g} Raman modes of WSe_2 are around 250cm^{-1} (Ref.[28]). Instead, the Raman peak energies in WSe_2/hBN heterostructures match well with the hBN ZO mode (820 cm^{-1}) and hBN ZO + WSe_2 A_{1g} mode (820 cm^{-1} + 250 cm^{-1})[26,27]. Consequently, we attribute the new Raman modes to the hBN ZO phonon and the combinatorial hBN ZO and WSe_2 A_{1g} phonon in WSe_2/hBN heterostructures. These new Raman peaks of the heterostructures exhibit several surprising properties. First, hBN ZO mode (see inset of Figure 2b) is not Raman active, and thus is completely absent in the Raman measurement of pristine hBN[27]. The red curve in Fig. 2b is a Raman spectrum from pristine hBN (measured on the same heterostructure but outside WSe_2), where the only observable hBN Raman peak is the in-plane E_{2g} mode at 1367 cm^{-1} (broad peak at 950 cm^{-1} corresponds to 2nd order Raman mode of Si substrate). Second, and more surprisingly, the observed hBN ZO Raman peak is extraordinary strong: the hBN ZO Raman peak at a photoexcitation of 1.849 eV is more than three orders of magnitude stronger than hBN E_{2g} mode measured at the same experimental condition (Fig. 2b).

To understand the extraordinarily strong Raman peak from the hBN ZO phonon, we perform systematic Raman spectroscopy with photoexcitation energy varied from 1.8 to 1.89 eV. Fig. 3a shows 2D color plot of observed Raman spectra where horizontal axis, vertical axis and color scale correspond to emission energy, excitation energy and Raman intensity, respectively. Orange and green dashed lines show that the emission and excitation energies have a strictly linear dependence for both mode I and II, confirming that the emission features correspond to Raman peaks. In addition, we observe that the Raman intensities change dramatically with the excitation laser energy. Specifically, mode I shows strong enhancement with the excitation energy at 1.85 eV and 1.82 eV, and mode II shows strong enhancement with 1.85 eV excitation energy. Such sensitive dependence of Raman intensities on photoexcitation energy is a defining feature of resonant Raman processes, where the Raman signal gets strongly enhanced when the incident or outgoing photons are in resonance with electronic transitions. However, electronic resonances from hBN are at ultraviolet frequencies due to the large bandgap of hBN (at ~ 5.8 eV)[29], and they cannot contribute to the resonant Raman scattering observed in this study. Therefore the electronic resonances observed in the Raman spectra must originate from WSe_2. Indeed, part of the resonant Raman features matches well with the known exciton resonance in WSe_2: both mode I and mode II show Raman enhancement when the outgoing photon energies match with the A exciton transition in WSe_2 at 1.71 eV (white dashed line in Fig. 3a).

The emerging Raman mode I and II in WSe_2/hBN heterostructures therefore are quite unique: the phonon excitation is dominated by hBN vibrations, but the electronic excitation is through the neighboring layer of WSe_2. These peculiar Raman modes thus demonstrate extraordinary interlayer couplings between electronic states in WSe_2 and vibrational modes in hBN (i.e. interlayer electron-phonon coupling between van der Waals layers) that has never been reported before. This interlayer electron–phonon coupling also explains the emergence of hBN ZO phonons in the Raman spectra: the WSe_2/hBN interface has a different symmetry compared with the bulk hBN, and the Raman forbidden hBN ZO phonon becomes allowed at the interface. In addition, the ZO phonons correspond to out-of-plane vibrations in hBN, which couple more strongly to the atoms in WSe_2 compared to the in-plane E_{2g} phonons in hBN. Further examination of the ZO phonon symmetry shows that the Raman signals should exhibit perfect linear polarization dependence as observed in our experiment (Supplementary Information Part 1).

The strong enhancement of Raman mode I at 1.85 eV excitation energy (Fig. 3a), however, cannot be explained by any known resonances in pristine WSe_2, because neither the incident photon energy (1.85 eV) nor the outgoing photon energy (1.75 eV) matches with the A or B exciton transitions in WSe_2. It suggests that new optical resonances may have been created in WSe_2 due to interactions with the adjacent hBN layers. To investigate this possibility, we performed optical reflection spectroscopy of hBN-encapsulated WSe_2. Indeed, the WSe_2-hBN heterostructure (red curve in Fig. 3b) shows distinctively different reflectance contrast spectra from the pristine one (black curve in Fig. 3b): an additional pronounced optical resonance emerges at 1.85 eV (labeled as X peak, see blue arrow in Fig. 3b), which matches exactly with the resonance energy observed in the Raman spectra. The emergence of X peak is further confirmed by photoluminescence excitation (PLE) spectroscopy of the heterostructure (Supplementary Information Part 2). The other prominent peaks at 1.71 and 2.12 eV are present in both pristine WSe_2 and WSe_2/hBN heterostructures and they correspond to the well-known A and B exciton transitions of WSe_2, respectively.

Quantitative analysis of Raman excitation spectroscopy provides more detailed information on the interlayer coupling between hBN phonon and WSe_2 electronic states. Orange and green circles in Fig. 3c and d show the dependence of Raman intensity on the excitation energy for mode I and II, respectively. As discussed before, two optical resonances (A exciton and X peak states in WSe_2) are involved in the resonant Raman process, and the double-resonance model yields an energy-dependent Raman intensity in the form of

$$I_{XA}{}^{\alpha}(E) \sim \left| \frac{A_{XA}^{\alpha}}{(E_X - E - i\gamma_1)(E_A + E_{ph}^{\alpha} - E - i\gamma_2)} \right|^2 \qquad (1)$$

where E_A = 1.71 eV and E_X = 1.85 eV are the two resonance energies, γ_1 and γ_2 ~ 7 meV is the energy broadening of the resonances, $\alpha = I, II$ labels the two Raman modes, with the phonon energy E_{ph}^{I} = 820 cm^{-1} and E_{ph}^{II} = 1070 cm^{-1}. A_{XA}^{α} are constant fitting parameters, and the values are related to the electronic transition oscillator strengths and the electron-phonon coupling matrix elements [30]. The Raman excitation spectral profile of both modes can be well reproduced by Eq. 1, shown as blue curves in Fig. 3c and 3d. For mode I (Figure 3c), two peaks at 1.847 and 1.818 eV in Raman excitation spectra correspond to the resonance of incident photon to X peak and outgoing photon to A peak, respectively. For mode II (Figure 3d), only one peak appears at 1.848 eV because the resonances for incident and outgoing photon are close in energy. The excellent agreement between the theory and data confirms that the resonant Raman process is dominated by the double resonance channel where both the X peak transition and the A exciton transition are important.

In addition, we find that the unique interlayer coupling between WSe_2 and hBN can be controlled effectively through electrostatic gating of WSe_2 in the heterostructure. Fig. 4a-c show the gate-dependent exciton and trion absorption, X peak absorption and resonant Raman spectra of WSe_2 encapsulated in hBN, respectively. When WSe_2 is gated from charge neutral (Vg = 0 V) to electron doped (Vg = 30 V), the exciton absorption decreases and trion absorption emerges gradually. In contrast, both X peak in absorption (Fig. 4b) and the resonant hBN Raman peak (Fig. 4c) show much more sensitive doping-dependence than exciton and trion absorption: both features decrease strongly with the electron doping, and completely disappear at a relatively low doping level. As a result, the hBN ZO phonon Raman intensity can be varied by more than two orders with a carrier density increase of less than 4×10^{12} cm^{-2} in WSe_2. This strong doping dependence of X peak and Raman intensity is quite surprising, and its origin is not clear. One possibility is that the doped electrons can strongly renormalize the interlayer interactions between WSe_2 and hBN through many-body screening effects, and suppress the optical absorption and Raman features associated with the interlayer couplings[10,31].

In depth theoretical investigations will be required to provide detailed microscopic mechanism that leads to the X peak and the interlayer electron-phonon interactions in WSe_2/hBN heterostructures, which is beyond the present study (Supplementary Information Part 3). Understanding and further control of such interlayer electron-phonon in the van der Waals heterostructure, which in principle should be widely present, will not only advance our fundamental knowledge of this new class of materials, but also enable new ways to dynamically manipulate electrons and phonons for novel device applications.

Methods:

Raman features from interlayer electron-phonon coupling is most prominent in the van der Waals heterostructures of WSe_2 encapsulated in hexagonal hBN, which are prepared with polyethylene terephthalate (PET) stamp by dry transfer method[32]. Monolayer WSe_2 and ~ ten nanometer thick hBN flakes are first exfoliated onto silicon substrate with 90 nm oxide layer. We use PET stamp to pick up the hBN flake and monolayer WSe_2 in sequence with accurate alignment based on optical microscope. The PET stamp with hBN/WSe_2 heterostructure is then stamped onto another hBN flake to form encapsulated WSe_2 monolayer. Polymer and samples are heated up at 60 ℃ for the pick-up and 130 ℃ for the stamp process. Finally we dissolve the PET in dichloromethane for 12 hours at room temperature. For the gate dependence study, we purposely picked up WSe_2 monolayer larger than top hBN flake in order to have an electrical contact on the exposed area outside hBN encapsulation.

Data availability:

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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Acknowledgments:

We thank S. Kahn for technical suggestions on heterostructure preparation and J. Yuk for fruitful discussions on sample characterization. This work was primarily supported by Office of Basic Energy Science, U.S. Department of Energy under Contract No. DE-AC02-05CH11231 (van der Waals heterostructure program). The preparation of WSe2/hBN heterostructures acknowledges the support of the Laboratory Directed Research and Development (LDRD) funding by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. F.W. also acknowledges the support from a David and Lucile Packard fellowship. S.T acknowledges the support from NSF DMR 1552220 NSF CAREER award. Growth of hexagonal boron nitride crystals was supported by the Elemental Strategy Initiative conducted by the MEXT, Japan and a Grant-in-Aid for Scientific Research on Innovative Areas “Science of Atomic Layers” from JSPS.

Author contributions:

F.W. J.K. and C.J. conceived the research. C.J. and J.K. carried out optical measurements. C.J. and F.W. performed theoretical analysis. J.K., C.J., J.S., Z.W. and M.K. fabricated gate-tunable van der Waals heterostructures. B.C., X.F. and S.T. grew WSe2 crystals. K.W. and T.T. grew hBN crystals. All authors discussed the results and wrote the manuscript.

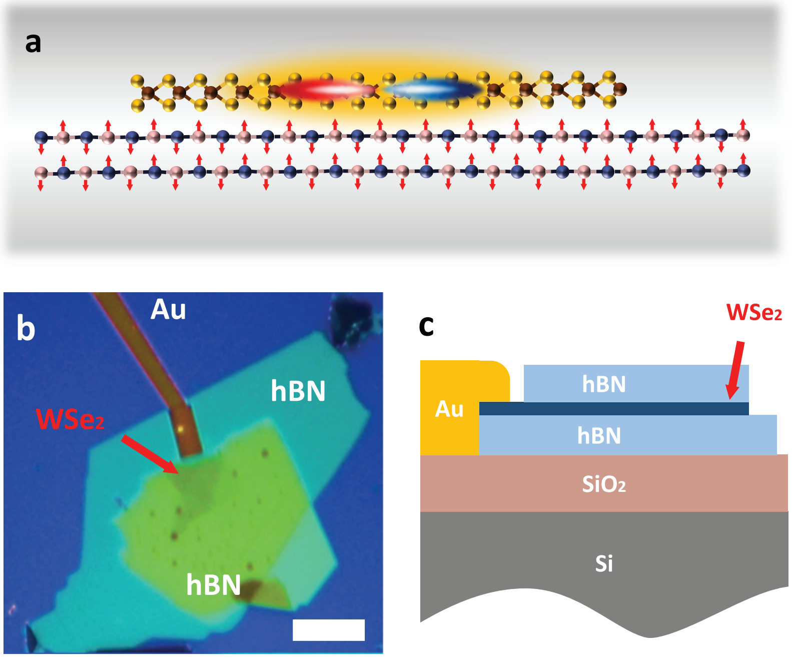
Figures captions

Figure 1: WSe_2/hBN heterostructures. **(a)** Illustration of interlayer electron-phonon coupling. Red arrows in hBN (bottom) and red/blue clouds in WSe_2 (top) shows schematically the phonon vibration in hBN and the electron/hole states in WSe_2, respectively. Such interlayer electron-phonon interactions can lead to novel electronic and optical properties in the van der Waals heterostructure. **(b)** Optical microscope image of WSe_2 encapsulated in hBN layers. The scale bar corresponds to 5 µm. **(c)** Illustration of the gate-tunable device. A contact electrode (Au/Ti) is fabricated on the exposed part of WSe_2 outside top hBN to allow for electrostatic gating.

Figure 2: Emission spectra of a WSe_2/hBN heterostructure. **(a)** Light emission spectra of the heterostructure with photoexcitation energies at 1.849, 1.857 and 1.862 eV. In addition to PL from the exciton and trion states in pristine WSe_2 at 1.71 eV and 1.68 eV, two extra Raman peaks (Green and Orange arrows) are observed, whose peak positions shift linearly with the excitation laser energy. Red and black curves are spectra for parallel and perpendicular excitation and emission polarizations, respectively. Both Raman peaks show strong polarization dependence and completely disappear in the cross-polarization configuration. **(b)** Raman spectrum of the heterostructure with 1.849 eV laser excitation (black curve). Two asymmetric Raman peaks are observed with sharp edges located at 820 and 1070 cm^{-1} (orange and green dashed lines), corresponding to hBN ZO mode (820 cm^{-1}) and hBN ZO + WSe_2 A_{1g} mode (820 cm^{-1} + 250 cm^{-1}), respectively. In contrast, Raman spectrum of a pure hBN flake with 1.849 eV laser excitation (red curve) only shows one peak at 1367 cm-1 (blue dashed line), which is over three orders of magnitude weaker than the emerging Raman peaks in the heterostructures. Inset illustrates atom vibration of hBN ZO mode.

Figure 3: Resonant Raman process in WSe_2/hBN heterostructure. (a) Raman excitation spectroscopy of the heterostructure. Horizontal axis, vertical axis and color scale correspond to emission energy, excitation energy and Raman intensity, respectively. Orange and green dashed lines show the linear dependence between excitation and emission energies for both Raman modes. The Raman intensity of both modes are strongly enhanced when emission energy match with WSe_2 A exciton energy at $E_A = 1.71$ eV (white dashed line). On the other hand, mode I also shows enhancement with excitation energy at 1.85 eV, which does not match with known optical resonance in pristine WSe_2. **(b)** Reflection spectroscopy of heterostructures (red) and pristine WSe_2 (black). Both spectra show prominent optical resonances at 1.71 and 2.12 eV, corresponding to A and B exciton transitions in WSe_2, respectively. However, new optical resonance emerges in the heterostructure at $E_X = 1.85$ eV (blue arrow) due to interlayer interaction, which matches exactly with the resonance energy observed in the Raman spectra. **(c and d)** Resonant Raman profile of mode I **(c)** and mode II **(d)**. Blue curves are the theoretically predicted Raman intensity dependence on excitation energy from a double resonance model. The excellent agreement with experimental results (orange and green circles) confirms that the resonant Raman process is dominated by the double resonance channel involving both the X peak and the A-exciton transition.

Figure 4: Varying the interlayer electron-phonon coupling with electrostatic doping. The evolution of exciton and trion peaks in the reflection spectra **(a)**, the X peak resonance in the reflection spectra **(b)**, and the resonant hBN Raman peak **(c)** as a function of gate voltages. As gate voltage changes from 0 V to 30 V, WSe_2 gets electron doped, and the trion absorption around 1.68 eV becomes more obvious (a). At the same time, the X peak (b) and resonant hBN Raman peak (c) become weaker and disappear completely at a relatively low doping level.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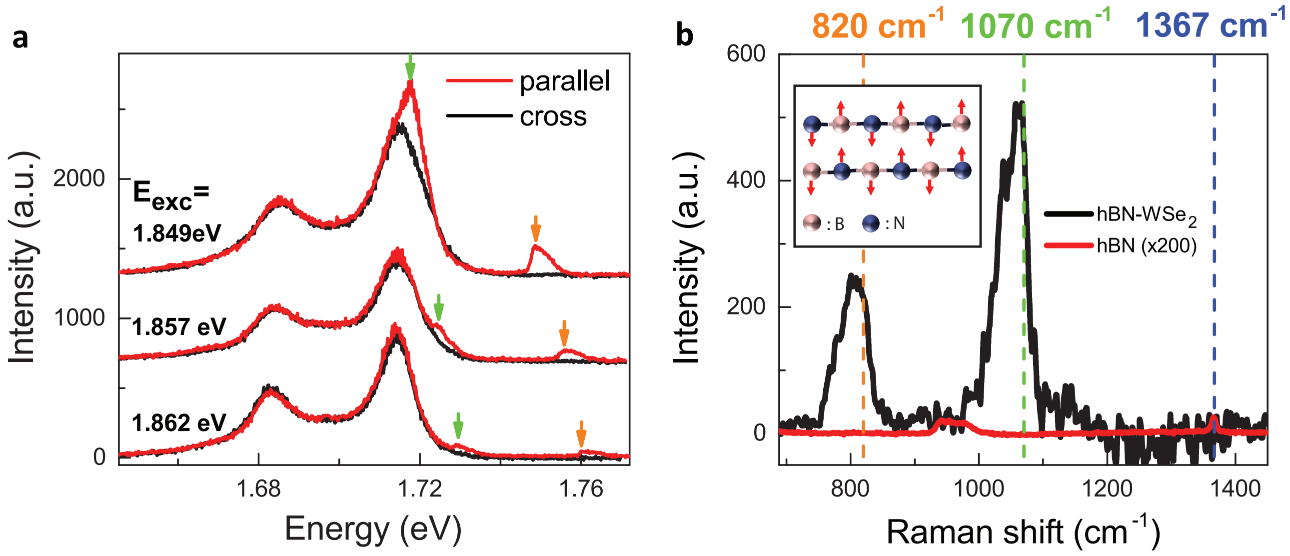
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1.862 eV
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1000
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1.76
Energy (eV)
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1070 cm^{-1}
1367 cm^{-1}
: B
: N
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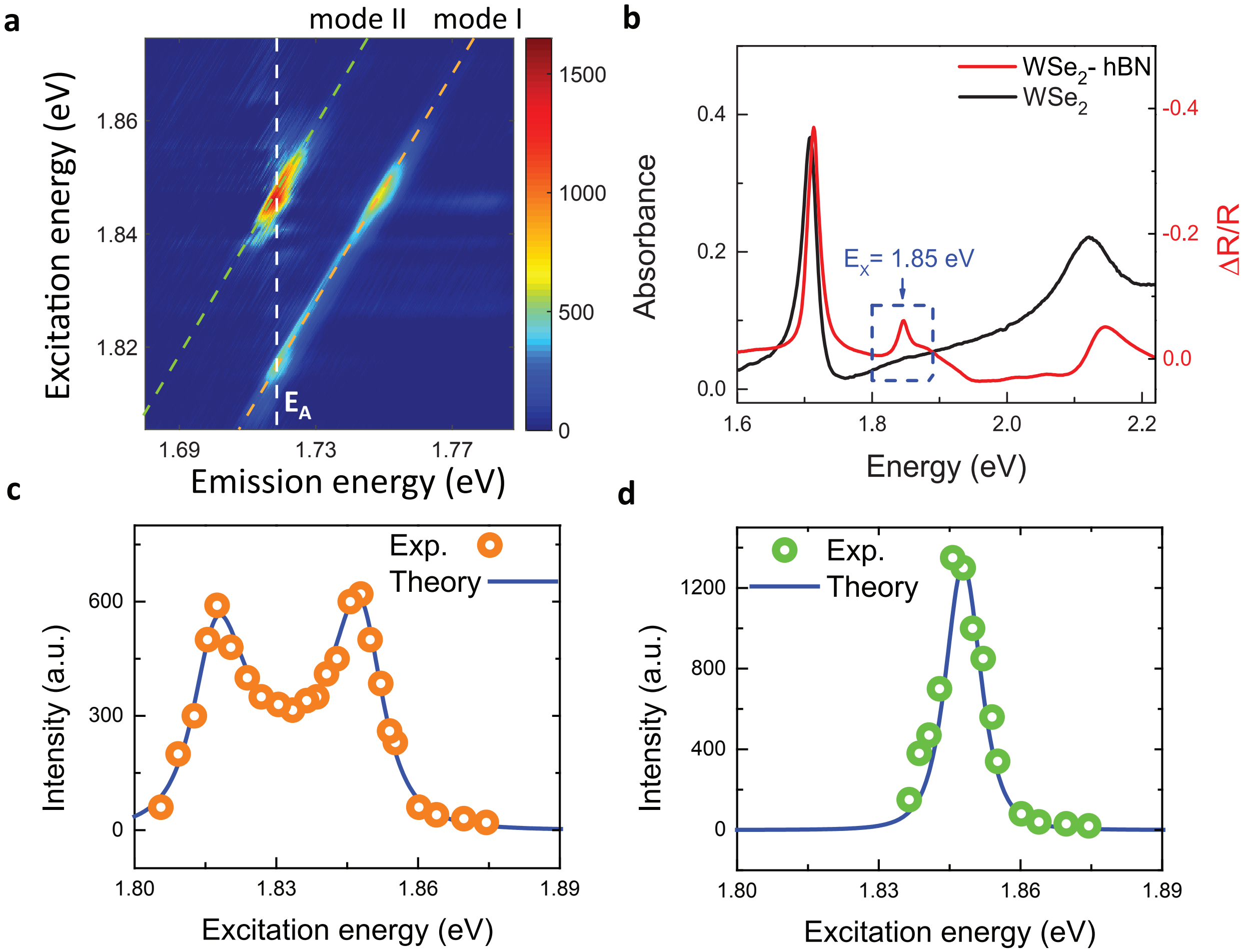
Raman shift (cm^{-1})

a
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mode I
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Emission energy (eV)
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WSe_2- hBN
WSe_2
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0.2
0.0
-0.4
-0.2
0.0
E_X= 1.85 eV
1.6
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2.2
Energy (eV)
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0
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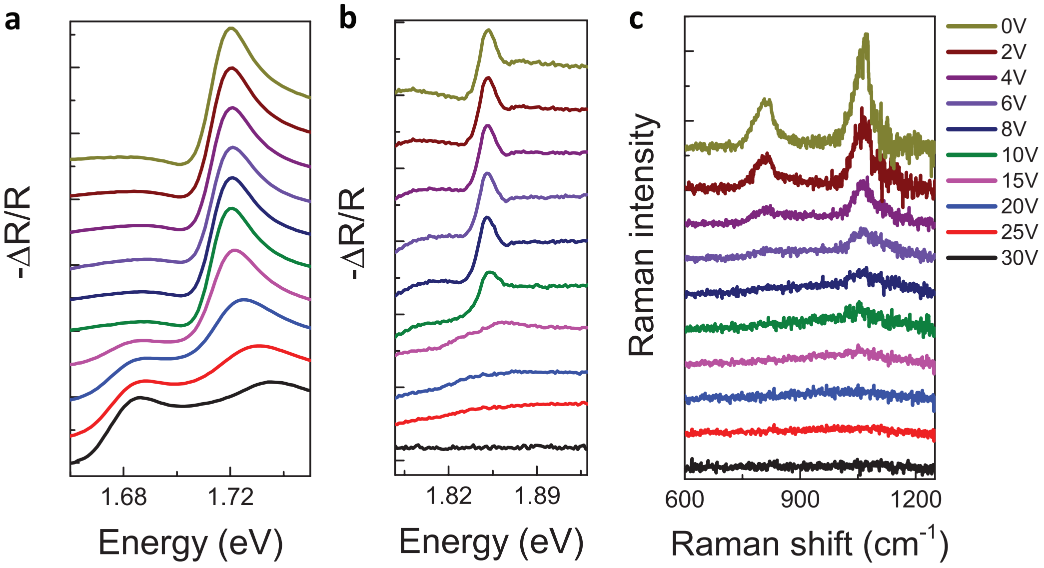
Excitation energy (eV)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Energy (eV)
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-ΔR/R
1.82
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Energy (eV)
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Raman intensity
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1200
Raman shift (cm-1)
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4V
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8V
10V
15V
20V
25V
30V