Evidence of Rotational Fröhlich Coupling in Polaronic Trions

Maxim Trushin,1 Soumya Sarkar,2 Sinu Mathew,2 Sreetosh Goswami,2 Shaffique Adam,1,3,4 and T. Venkatesan2,3,5

1Centre for Advanced 2D Materials, National University of Singapore, Singapore 117546
2NUSNNI NanoCore, National University of Singapore, Singapore 117411
3Department of Physics, National University of Singapore, Singapore 117551
4Yale-NUS College, Singapore 138527
5Department of Electrical and Computer Engineering and Materials Science and Engineering, National University of Singapore, Singapore 117583

(Dated: November 22, 2019)

Electrons commonly couple through Fröhlich interactions with longitudinal optical phonons to form polarons. However, trions possess a finite angular momentum and should therefore couple instead to rotational optical phonons. This creates a polaronic trion whose binding energy would be determined by the crystallographic orientation of the lattice. Here, we demonstrate theoretically within the Fröhlich approach and experimentally by photoluminescence emission that the binding energy of the bare trion (20 meV) is significantly enhanced by the phonons at the interface between two-dimensional semiconductor MoS2 and bulk transition metal oxide SrTiO3. The low-temperature binding energy changes from 60 meV in [001]-oriented substrates to 90 meV for [111] orientation, a result of the counter-intuitive interplay between the rotational axis of the MoS2 trion and that of the SrTiO3 phonon mode.

Introduction — The quasiparticle concept is a powerful tool for understanding physics of many-body phenomena [1]. The concept was invented a few decades ago to describe the Fermi liquid [2], and later on applied to a broad range of phenomena including superconductivity [3, 4], magnetic ordering [5], and fractional quantum Hall effect [6]. The optically excited two-dimensional (2D) semiconductors are a home to tightly-bound excitons and trions — the quasiparticles composed of electrons and holes glued together by Coulomb forces [7]. Recently, yet another exhibit in this quasiparticle zoo — a polaronic trion was reported [8]. In this Letter, we demonstrate that a rotational optical (RO) phonon mode is necessary for the trion to engage in polaronic coupling that explains the underlying mechanism leading to formation of polaronic trions.

In quasiparticle language, the conventional (Fröhlich [3, 10]) polaron is an electron dressed with phonons. The energy needed to undress the polaron (i.e. to release the electron) is the polaron binding energy. Typically, the strongest Fröhlich coupling occurs with longitudinal optical (LO) phonons in polar crystals with large difference between the static dielectric permittivity and its electronic contribution, such as in SrTiO3 [11, 12]. However, the trion-phonon interaction is distinct from coupling of phonons to free electrons. The outer electron in the trion is bound to the excitonic core (see Fig. 1), resulting in a finite angular momentum which enables stronger coupling with RO rather than LO phonon modes. To maximize the effect, the trion’s plane of rotation must match the polarization plane created by the RO mode (see Fig. 1). Hence, we can probe polaronic trions by either changing the Fröhlich coupling itself or the angle between rotational planes of the trion and the RO phonon mode. SrTiO3 hosts RO phonons with very low vibration frequency [13] enabling an ideal environment to investigate the rotational Fröhlich coupling with trions. Notably, by changing the SrTiO3 crystal orientation, one can tilt the rotational axis of the RO phonon mode and hence investigate the angular dependence of this coupling.

PL spectroscopy. — Monolayer MoS2 is grown on single crystal SrTiO3 substrates by chemical vapor deposition [14], and our samples are of comparable quality with those reported previously (sample characterization is elaborated in [15]). We use three different crystallographic orientations of the SrTiO3 substrate to tailor the polaronic effects in 2D MoS2. Fig. 2, shows the differential PL emission spectra of the excitonic (right) and trionic (left) peaks in the MoS2 PL extracted from Lorentz fitting described in [15]. We have confirmed that the low energy peak is indeed a trion and does not arise from defect bound excitons through excitation power dependent measurements (Fig. S4 in [15]). The exciton-trion peak separation is the trion binding energy we are after. At low temperatures, the trionic peak splits further away from the excitonic maximum, and the splitting turns out to be dependent on the crystallographic orientation of the SrTiO3 substrate. We have achieved binding energy enhancement of up to 60 meV that is enormous having in mind that bare trion binding energy is less than 30 meV. Fig. 2b, shows the full width at half maximum (FWHM) for trionic and excitonic PL peaks. The trion FWHM experiences a significant broadening below the soft phonon activation temperature $T_a \sim 132^\circ$
The unperturbed Hamiltonian describing the relative quasiparticle, the polaronic trion [8].

The exciton emission energy exhibits the usual monotonic dependence on the substrate orientation. Finally, the exciton size. This results in the trion binding energy much lower than that of exciton.

Figure 1. (a) A trion consists of a tightly-bound excitonic core and an electron weakly coupled to the core by the electron-dipole interactions. In a polaronic trion, a RO phonon mode is shown by the red arrows. The black and magenta arrows show directions of the trion (LT) and RO phonon (LRO) angular momenta respectively, and θ is the angle between them.

(b) Schematic of MoS2/SrTiO3 heterostructure utilized to create rotational Fröhlich interactions. The RO phonon mode is due to the rotating TiO6 octahedra (see also Fig. 3).

K, and the broadening turns out to be strongly dependent on the substrate orientation. In contrast, the exciton FWHM demonstrates much smaller broadening and weaker dependence on the substrate orientation. Finally, the exciton emission energy exhibits the usual monotonic blue shift given by the Varshni relation [17] whereas the trion emission energy undergoes an unusual red shift below \( T_a \) (see Fig. 2 and Table S1 in [15]). The data presented in Fig 2 all together indicates that the trion is not a conventional trion anymore but is an entirely new quasiparticle, the polaronic trion [3].

**Trion Hamiltonian.** — The trion can be seen as an electron weakly interacting with the excitonic core. The unperturbed Hamiltonian describing the relative electron-exciton motion can be written as

\[
\hat{H}_0 = -\frac{\hbar^2}{2\mu_T} \left[ \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) \right].
\]  

Here, we use polar coordinates \( \{ \varphi, r \} \). The trion reduced mass, \( \mu_T = m_X m_e / m_T \), is defined in terms of the trion \( m_T = m_X + m_e \), exciton \( m_X = m_e + m_h \), electron \( m_e \), and hole \( m_h \) effective masses, respectively. The energy in Eq. (1) is counted from the exciton ground-state level, as shown in Fig. 1b. The first (second) term in the square brackets is the tangential (radial) momentum operator with the eigenvalues \( k_\varphi \) \( (k_r) \) given in units of the Planck constant \( \hbar \). The electron-dipole interaction perturbing \( \hat{H}_0 \) is much weaker than the direct Coulomb potential responsible for the exciton formation and rapidly vanishes at the distances much larger than the exciton size. This results in the trion binding energy much lower than that of exciton.

**Rotational Fröhlich coupling.** — The 2D Fourier transform of the polaronic interaction can be written as \( |V_q|^2 = 8\pi^2 e^2 F^2 / q \), where \( e \) is the elementary charge, \( q \) is the in-plane wave vector, and \( F \) is a proportionality coefficient between the phonon mode amplitude and dielectric polarization created by this mode [18]. To express \( F \) in terms of macroscopic quantities we adopt an argument by Kittel [18] where the phonon perturbation producing dielectric polarization is equivalent to the Coulomb potential screened by the phononic part of the dielectric permittivity, i.e.

\[
\frac{2e^2}{\hbar \omega} \sum_Q \frac{(4\pi F)^2}{Q^2} Q^2 r = \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \sum_q \frac{2\pi e^2}{q} Q r e^{iqr},
\]

where \( \epsilon_0 \) \( (\epsilon_\infty) \) is the static (high-frequency) dielectric permittivity at the MoS2/SrTiO3 interface, \( \hbar \omega \) is the phonon energy quantum, \( r \) is the in-plane coordinate, \( Q \) is the phonon wave vector whose absolute value can be written in terms of in-plane \( (q) \) and axial \( (q_\parallel) \) components as \( Q = \sqrt{q_\parallel^2 + q^2 - 2qq_\parallel \cos(\pi/2 + \theta)} \). The axial component does not contribute to rotational Fröhlich coupling and can be integrated out easily. The resulting polarization turns out to be \( \theta \) dependent, \( F = \sqrt{\hbar \omega \cos \theta (\epsilon^{-1}_\infty - \epsilon^{-1}_0) / (8\pi)} \), and the polaronic potential reads

\[
V_q = -i\hbar \omega \sqrt{\cos \theta} \sqrt{\frac{2\pi \alpha r_\omega}{q}},
\]

where \( r_\omega = \sqrt{\hbar/2\mu_T \omega} \) is the interaction length, and

\[
\alpha = \frac{e^2}{2\hbar \omega r_\omega} \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right)
\]

is the standard Fröhlich coupling constant [9]. The striking difference between the standard 2D polaronic interaction [11, 18] and Eq. (3) is the \( \sqrt{\cos \theta} \) pre-factor that
FIG. 2. (a) Pseudocolor map of the differential PL emission intensity ($|dI/dE|$) from 2D MoS$_2$ demonstrates two quasiparticle peaks attributed to excitons and trions. The splitting between them depends on temperature and SrTiO$_3$ substrate orientation with the strongest separation for [111]-oriented SrTiO$_3$ crystals below 50 K. (b) Temperature dependence of FWHM for trionic (upper panel) and excitonic (lower panel) PL quasiparticle peaks for different SrTiO$_3$ substrate orientations indicates much stronger Fröhlich interactions for the former than for the latter. (c) Extracted trionic and excitonic PL energies vs. temperature with the corresponding Varshni fits as dashed lines indicate anomalous behavior of the PL trion peak below 132 K. The error bars are standard error for three samples.

occurs due to the special direction singled out by the angular momentum of a RO phonon mode. Note that the effective mass in $r_w$ is given by $\mu_T$ instead of $m_e$ as in the conventional case \textsuperscript{[11]}.

Polaronic perturbation. — In the non-perturbed limit, when both dipole and polaronic perturbations vanish, the plane-wave solution suggests the kinetic energy $E_k$ of the relative electron-exciton motion be a sum the radial
The following expression for the polaronic energy correction \[18\] coordinates. The perturbation theory suggests the following expression for the polaronic energy correction \[18\] beyond perturbation theory, see e.g. Refs. \[11, 19, 20\])

\[
E_P = -\int \frac{d^2q}{(2\pi)^2} \frac{|V_q|^2}{E_k - E_{k-q} - \hbar \omega}. \tag{5}
\]

We evaluate Eq. \((5)\) for the binding energy correction \((k \to 0)\). Despite the electron-exciton relative motion being 2D, the rotational polaronic coupling is effectively 1D. This is because RO phonon modes produce no radial polarization (hence, no radial electric field, see Fig. \((1b)\)), and, therefore, the energy difference \(E_k - E_{k-q}\) does not contain \(q_r\). The binding energy correction can then be written as

\[
E_P = \frac{2}{\pi} \int_0^\infty dq_r \int_0^\infty dq_\theta \frac{\hbar^2 \omega^2 |\alpha_r\omega| \cos \theta}{\sqrt{q_r^2 + q_\theta^2}} \frac{2\mu_T/\hbar^2}{q_r^2 + q_\theta^2} \\
= \alpha \hbar \omega \cos \theta \ln (2r_\omega/a), \tag{6}
\]

where \(1/a\) is a momentum cut-off. Similar to the conventional expression for the 2D polaron binding energy, \(E_P = \frac{\alpha}{2} \alpha \hbar \omega\), our result is linear in \(\alpha\) (this also holds beyond perturbation theory, see e.g. Refs. \[11, 19, 20\]) and linear in phonon energy \(\hbar \omega\), setting the scale of polaronic interactions. However, Eq. \((6)\) is different in two important ways: since the RO phonon modes are decoupled from both the axial and radial electron motion, this results respectively in the \(\cos \theta\) and \(\ln (2r_\omega/a)\) pre-factors (the latter is a weak function of the order of unity and less important than the former). The logarithmic divergence is a well-known property of the Fröhlich coupling in a 1D limit \[21\]. The length \(\alpha\) is the lattice constant that determines the first Brillouin zone size in MoS\(_2\). If \(q_r\) is retained in the denominator of Eq. \((5)\), and \(\theta\) is set to zero, we recover the conventional result.

**Discussion.** — The dressed trion binding energy is \(E_{PT} = E_P + E_T\), where \(E_T\) is the bare trion binding energy. The latter can also be estimated perturbatively \[22\], but we assume the phenomenological formula \[22\]

\[
E_T(\epsilon_0) = E_T(1)/\epsilon_0^{\beta_T}, \tag{7}
\]

where \(\beta_T = 0.085\) is a constant, \(E_T(1) = 42\) meV is \(E_T\) at \(\epsilon_0 = 1\). To make predictions regarding binding energy in realistic samples the multi-domain structure of the SrTiO\(_3\) substrate must be taken into account. The axis of antiphase rotation of neighboring oxygen TiO\(_6\) octahedra is different in each domain \[24\]. We assume that the domain orientation is perfectly random, so that any of three mutually perpendicular orientations are weighted equally in the binding energy calculation. In the simplest case of the [001]-grown substrate, the rotational axis of RO mode in [001]-oriented domain is normal to the trion plane and the polaronic effect is maximal (see Fig. \((3a)\)). The other two [010]- and [100]-oriented domains do not contribute at all because the phonon mode rotation axis is parallel to the trion plane and \(\theta = \pi/2\) in Eq. \((6)\). Hence, the total \(E_{PT}\) reads

\[
E_{PT}[001] = E_T + \alpha \hbar \omega \ln (2r_\omega/a). \tag{7}
\]

In the case of either [011] or [101] domain orientation we have \(\cos \theta = 1/\sqrt{2}\) (see Fig. \((3b)\)). The [110]-oriented domains do not contribute here, and \(E_{PT}\) reads

\[
E_{PT}[011] = E_T + \sqrt{2} \alpha \hbar \omega \ln (2r_\omega/a). \tag{8}
\]

The [111] orientation suggests \(\cos \theta = 1/\sqrt{3}\) (see Fig. \((3c)\)), and all three possible mutually perpendicular domain ori-
orientations do contribute equally. Hence, we have

\[ E_{PT[111]} = E_T + \sqrt{3} \alpha \hbar \omega \ln (2\tau \omega / a). \]  

(9)

Combining Eqs. (7,8,9) we are able to fit the polaronic trion binding energy measured for all crystallographic orientations of the substrate.

The MoS$_2$/SrTiO$_3$ interface static dielectric constant \( \epsilon_0 \) is by far dominated by SrTiO$_3$ (STO), especially at low temperature, when \( \epsilon_{\text{STO}} \) exceeds \( 10^4 \) \[25\]. Since the upper side of MoS$_2$ is exposed to air, we take \( \epsilon_a = \epsilon_{\text{STO}} / 2 \). and \( \epsilon_{\text{STO}} \) depends on temperature \( (T) \) according to the Curie-Weiss law modified by Barrett as

\[ \epsilon_{\text{STO}} = T_2 / a \left( \frac{1}{T} \coth \left( \frac{T}{T_1} \right) - T_C \right), \]

where \( T_2 = 9.10^4 \) K, \( T_1 = 84 \) K, and Curie temperature \( T_C = 38 \) K. The RO phonon frequency is dominated by the \( A_{1g} \) mode with the temperature dependence given by \[\frac{13}{16} \omega = \omega_0 \left( 1 - T / T_a \right)^{1/4}, \]

\( T < T_a \), where \( \hbar \omega_0 = 7 \) meV, and the mode activation temperature \( T_a = 132 \) K. The effective masses are \( m_e = 0.342 m_0 \), \( m_h = 0.455 m_0 \) \[27\] (\( m_0 \) is the free electron mass), the lattice constant \( a = 3.15 \) Å, and, finally, \( \epsilon_\infty = 12.5 \) — the average value between high-frequency permittivities for MoS$_2$ \[29\] and SrTiO$_3$ \[30\].

The binding energy is shown in Fig. 4 as a function of temperature for different substrate orientations. The highest binding energy (\( \sim 90 \) meV) is achieved for [111]-grown substrate despite the smallest \( \cos \theta = 1 / \sqrt{3} \) (hence, the weakest coupling) for [111]-domain orientation. This is almost twice larger than the highest trion binding energy reported so far in n-doped MoS$_2$ (\( \sim 40 \) meV \[29\], \( \sim 50 \) meV \[31\]). Moreover, the polaronic trion binding energy allows for 200% tunability (from \( \sim 30 \) meV to \( \sim 90 \) meV), which far exceeds that possible by conventional electrostatic gating \[31\].

**Outlook.** — The polaronic trion discussed here is a complex three-component quasiparticle comprising the exciton core, an electron, and an RO phonon mode coupled together by both Coulomb and Fröhlich interactions, resulting in a large enhancement of the binding energy. Remembering that the exciton itself is a composite quasiparticle, one can imagine creating a hierarchy of energy-rich quasiparticles optically excited in more complicated materials with the required interactions. It is therefore plausible that the rotational Fröhlich coupling described here could be used to tune the binding energy to be comparable to the electronic bandgap in an appropriate 2D semiconductor. In this case, the ground state will be re-constructed leading to exotic phases such as the excitonic insulator \[32, 33\].

**Acknowledgements.** — M.T. is supported by the Director’s Senior Research Fellowship at CA2DM (Singapore NRF Medium-Sized Centre Programme R-723-000-001-281, NUS Young Investigator Award R-607-000-236-133). S.S. and T.V. acknowledge support from the National Research Foundation under Competitive Research Program (NRF2015NRF-CRP001-015). S.M. acknowledges support from SinBeRiSE project fund, NUSNNI general purpose account grant IN-398-000-006-001 and international atomic energy agency (IAEA) CRP (F11020).

**Author contributions.** — M.T. and S.S have contributed equally. M.T. devised the model. S.S. grew the MoS$_2$ samples on SrTiO$_3$ with the help of S.M. and performed the PL spectroscopy. All the authors discussed and analysed the data, and wrote the paper. T.V. supervised the entire project.

[1] L. Venema, B. Verberck, I. Georgescu, G. Prando, E. Couderc, S. Milana, M. Maragkou, L. Pereschini, G. Pacchioni, and L. Fleet, Nature Physics 12, 1085 (2016).
[2] L. D. Landau, Sov. Phys. JETP 3, 920925 (1957).
[3] N. N. Bogoljubov, Il Nuovo Cimento (1955-1965) 7, 794 (1958).
[4] J. G. Valatin, Il Nuovo Cimento (1955-1965) 7, 843 (1958).
[5] A. V. Chumak, V. I. Vasyuchka, A. A. Serga, and B. Hillebrands, Nature Physics 11, 453 (2015).
[6] R. B. Laughlin, Rev. Mod. Phys. 71, 863 (1999).
[7] K. F. Mak and J. Shan, Nature Photonics 10, 216 (2016).
[8] S. Sarkar, S. Goswami, M. Trushin, S. Saha, M. Panahandeh-Fard, S. Prakash, S. J. R. Tan, M. Scott, K. P. Loh, S. Adam, S. Mathew, and T. Venkatesan, Advanced Materials, 1903569 (2019).
[9] H. Fröhlich, Advances in Physics 3, 325 (1954).
[10] R. P. Feynman, Phys. Rev. 97, 660 (1955).
[11] J. T. Devreese, Encycl. Appl. Phys. 14, 383 (1996).
[12] H. Takashima, R. Wang, B. Prijamboedi, A. Shoij, and M. Itoh, Ferroelectrics 335, 45 (2006).
[13] J. Petzelt, T. Ostapchuk, T. Gregora, I. Rychetský, S. Hoffmann-Eifert, A. V. Pronin, Y. Yuzuyk, B. P. Gorshunov, S. Kamba, V. Bovtun, J. Pokorný, M. Savi...
[10] G. H. Wannier, Phys. Rev. 59, 1495 (1941).
[11] F. E. M. Povolny, J. L. Lebowitz, and S. R. Benioff, Phys. Rev. B 7, 1192 (1973).
[12] D. K. Efimkin and A. H. MacDonald, Phys. Rev. B 95, 035417 (2017).
[13] Y. Lin, X. Ling, L. Yu, S. Huang, A. L. Hsu, Y.-H. Lee, J. Kong, M. S. Dresselhaus, and T. Palacios, Nano Letters 14, 5569 (2014).
[14] Y.-Y. Pai, A. Tylan-Tyler, P. Irvin, and J. Levy, Reports on Progress in Physics 81, 036503 (2018).
[15] E. Sawaguchi, A. Kikuchi, and Y. Kodera, Journal of the Physical Society of Japan 17, 1666 (1962).
[16] J. H. Barrett, Phys. Rev. 86, 118 (1952).
[17] T. Cheiwchanchamnan and W. R. L. Lambrecht, Phys. Rev. B 85, 205302 (2012).
[18] N. Wakabayashi, H. G. Smith, and R. M. Nicklow, Phys. Rev. B 12, 659 (1975).
[19] A. Laturnus, M. J. van de Put, and W. G. Vandenbergh, npj 2D Materials and Applications 2, 6 (2018).
[20] C. Lasota, C.-Z. Wang, R. Yu, and H. Krakauer, Ferroelectrics 194, 109 (1997).
[21] K. F. Mak, K. He, C. Lee, G. H. Lee, J. Hone, T. F. Heinz, and J. Shan, Nature Materials 12, 207 (2013).
[22] L. Du, X. Li, W. Lou, G. Sullivan, K. Chang, J. Kono, and R.-R. Du, Nature Comm. 8, 1971 (2017).
[23] Y. F. Lu, H. Kono, T. I. Larkin, A. W. Rost, T. Takayama, A. V. Boris, B. Keimer, and H. Takagi, Nature Comm. 8, 14408 (2017).