Supporting Information: Phonoritons in a monolayer hBN optical cavity

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1. DERIVATION OF THE QED PHONORITONIC HAMILTONIAN

To describe the dressing of excitons by phonons and cavity photons from first principles, we consider the fundamental many-body Hamiltonian in (non-relativistic) quantum electrodynamics (QED). We consider here a single photonic cavity mode corresponding to the lowest momentum mode perpendicular to the cavity mirrors and in-plane electric field polarization. The generalization to multi-modes is not expected to change the conclusions as shown in Ref. [1]. Within the velocity gauge, the QED problem can be written as follows:

$$\hat{H}_{\mathrm{QED}} = \hat{H}_{\mathrm{el}} + \omega \hat{b}^\dagger \hat{b} + \frac{A_0^2}{2}(\hat{b}^\dagger - \hat{b})^2 + A_0 \sum_{rs\mathbf{k}} \left(\langle \phi_{r\mathbf{k}} | \hat{e} \cdot \hat{p} | \phi_{s\mathbf{k}} \rangle \hat{c}^\dagger_{r\mathbf{k}} \hat{c}_{s\mathbf{k}} \hat{b}^\dagger + h.c. \right), \tag{1}$$

where $\hat{b}^\dagger$ and $\hat{b}$ are the photon creation and annihilation operators respectively, $\hat{H}_{\mathrm{el}}$ is the many-body electronic Hamiltonian, $\hat{c}^\dagger_{r\mathbf{k}}, \hat{c}_{s\mathbf{k}}$ are the electronic creation and annihilation operators in the $\{\phi_r\}$ basis (with r band indices and $\mathbf{k}$ wavevectors in the first Brillouin zone), $\hat{p}$ the single particle momentum operator, $\hat{e}$ the photon field polarization and $A_0 = \sqrt{\frac{1}{2\pi c\, a}}$, with a the area of the unit cell, is the amplitude of the vector potential. In order to derive the coupling of this Hamiltonian to lattice degrees of freedom we consider the parametric dependence of the Hamiltonian on the phonon displacements of the atoms $\{\mathbf{R}_{\mathbf{q}\alpha}\}$, corresponding to the phonon mode α with momentum $\mathbf{q}$. To first order in this displacement, the Hamiltonian can be expanded as

$$\hat{H}_{\mathrm{QED}} \simeq \hat{H}_{\mathrm{QED,\ eq}} + \left. \frac{\partial \hat{H}_{\mathrm{QED}}}{\partial \mathbf{R}_{\mathbf{q}\alpha}} \right|_{\mathrm{eq}} \mathbf{R}_{\mathbf{q}\alpha} \tag{2}$$

where the subscript "eq" indicates the $\mathbf{R}_{\mathbf{q}\alpha} = 0$ condition which corresponds to no phonon displacements. The first term in the equation is the usual polaritonic Hamiltonian, while the second term describes its coupling to the lattice. Since the coupling of photons to the electronic structure occurs via the creation/annihilation of neutral excitations (electron-hole pairs), one can approximate the many-body electronic eigenstates of the Hamiltonian by the excitonic ones and therefore diagonalize the electronic component, $\hat{H}_{\mathrm{el}} |\Psi^{\mathrm{exc}}_i\rangle \simeq \epsilon^{\mathrm{exc}}_i |\Psi^{\mathrm{exc}}_i\rangle$ [1]. This gives matrix elements like

$$\langle \Psi^{\mathrm{exc}}_i | \hat{H}_{\mathrm{QED}} | \Psi^{\mathrm{exc}}_j \rangle = \langle \Psi^{\mathrm{exc}}_{i,\mathrm{eq}} | \hat{H}_{\mathrm{QED,\ eq}} | \Psi^{\mathrm{exc}}_{j,\mathrm{eq}} \rangle + \langle \Psi^{\mathrm{exc}}_{i,\mathrm{eq}} | \left. \frac{\partial \hat{H}_{\mathrm{QED}}}{\partial \mathbf{R}_{\mathbf{q}\alpha}} \right|_{\mathrm{eq}} | \Psi^{\mathrm{exc}}_{j,\mathrm{eq}} \rangle \mathbf{R}_{\mathbf{q}\alpha}, \tag{3}$$

Since in this work we focus on the effect of the Γ-phonons ($q = 0$), in the following we drop the sum over momenta. Nevertheless the results can be generalized to finite q, which is necessary when dealing, for example, with exciton coupling with surface acoustic waves or any other finite momentum excitation. The first term of Eq. 3 can be expressed as follows:

$$\langle \Psi^{\mathrm{exc}}_{i,\mathrm{eq}} | \hat{H}_{\mathrm{QED,\ eq}} | \Psi^{\mathrm{exc}}_{j,\mathrm{eq}} \rangle = \left[\epsilon^{\mathrm{exc}}_{j,\mathrm{eq}} + \omega \hat{b}^\dagger \hat{b} + \sum_\alpha \Omega_\alpha \hat{a}^\dagger_\alpha \hat{a}_\alpha + \frac{A_0^2}{2}(\hat{b}^\dagger + \hat{b})^2 \right] \delta_{ij} + A_0 \left(\mathcal{M}^{\mathrm{exc}}_{ij} \hat{b}^\dagger + \mathcal{M}^{\mathrm{exc}*}_{ji} \hat{b} \right) \tag{4}$$

where $\mathcal{M}^{\mathrm{exc}}_{ij} = \langle \Psi^{\mathrm{exc}}_{i,\mathrm{eq}} | \sum_{rs\mathbf{k}} \langle \phi_{r\mathbf{k},\mathrm{eq}} | \hat{e} \cdot \hat{p} | \phi_{s\mathbf{k},\mathrm{eq}} \rangle \hat{c}^\dagger_{r\mathbf{k}} \hat{c}_{s\mathbf{k}} | \Psi^{\mathrm{exc}}_{j,\mathrm{eq}} \rangle$ are excitonic matrix elements of the bilinear electron-photon coupling, the same as the ones introduced in Ref. [1]. For completeness we also introduced the energy term for the phonons with $a^\dagger_\alpha$ and a_α being the creation and annihilating operators for the mode with index α.

The second term in Eq. 3 gives origin to two terms, the standard exciton-phonon coupling and the phonoritonic coupling introduced in the main text. Indeed we can rewrite this term as:

$$\begin{aligned} \langle \Psi^{\mathrm{exc}}_{i,\mathrm{eq}} | \left. \frac{\partial \hat{H}_{\mathrm{QED}}}{\partial \mathbf{R}_\alpha} \right|_{\mathrm{eq}} | \Psi^{\mathrm{exc}}_{j,\mathrm{eq}} \rangle \mathbf{R}_\alpha = & \langle \Psi^{\mathrm{exc}}_{i,\mathrm{eq}} | \left. \frac{\partial \hat{V}}{\partial \mathbf{R}_\alpha} \right|_{\mathrm{eq}} | \Psi^{\mathrm{exc}}_{j,\mathrm{eq}} \rangle \mathbf{R}_\alpha + \\ & + A_0 \langle \Psi^{\mathrm{exc}}_{i,\mathrm{eq}} | \frac{\partial}{\partial \mathbf{R}_\alpha} \left[\sum_{rs\mathbf{k}} \left(\langle \phi_{r\mathbf{k}} | \hat{e} \cdot \hat{p} | \phi_{s\mathbf{k}} \rangle \hat{c}^\dagger_{r\mathbf{k}} \hat{c}_{s\mathbf{k}} \hat{b}^\dagger + h.c. \right) \right] \Bigg|_{\mathrm{eq}} | \Psi^{\mathrm{exc}}_{j,\mathrm{eq}} \rangle \mathbf{R}_\alpha \end{aligned} \tag{5}$$

where $\hat{V}$ is the electrostatic potential generated by the nuclei. We identify the first term on the right hand side as

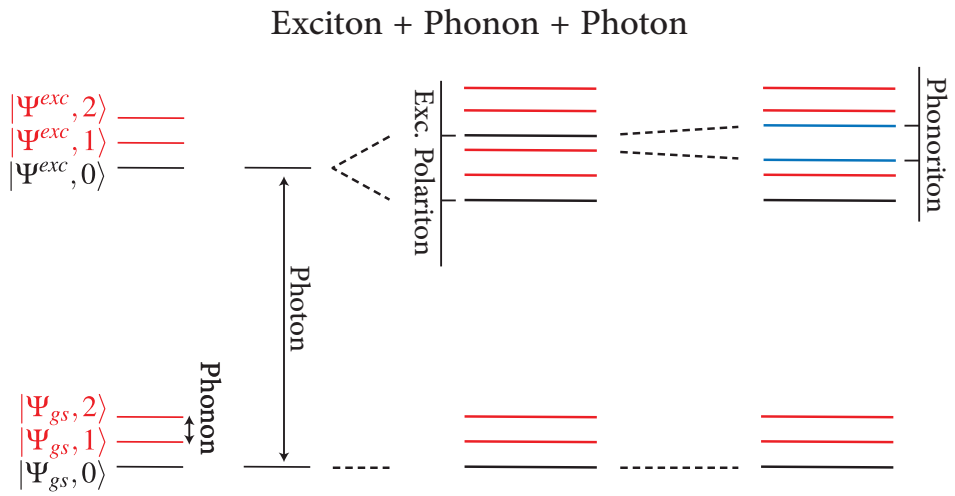

FIG. S1. **Three-particle-hybridization in a Phonoriton.** Energy level representation of the hybridization of exciton, phonon and photons involves mutual dressing of the modes: the cavity photon (left panel), coupling directly to the exciton, creates exciton-polariton states (black line, middle panel), which through the phonoritonic coupling are further mixed with phonons to yield the phonoritonic states (blue line, right panel).

the exciton-phonon coupling:

$$\mathcal{G}^{\rm exc}_{ij,\alpha} \equiv \left\langle \Psi^{\rm exc}_{i,\rm eq} \right| \frac{\partial \hat{V}}{\partial \mathbf{R}_\alpha}\bigg|_{\rm eq} \left| \Psi^{\rm exc}_{j,\rm eq} \right\rangle = \langle \Psi^{\rm exc}_{i,\rm eq}| \sum_{rs\mathbf{k}} g^{\alpha}_{rs\mathbf{k}} \hat{c}^\dagger_{r\mathbf{k}} \hat{c}_{s\mathbf{k}} |\Psi^{\rm exc}_{j,\rm eq}\rangle, \tag{6}$$

with $g_{rs\mathbf{k}}$ the standard single-particle electron-phonon matrix elements [2]. The second term on the right hand side of Eq. 5 contains instead the phonoritonic matrix elements which essentially arise from the variation of the momentum matrix element with respect to the lattice vibration:

$$\mathcal{Z}^{\rm exc}_{ij,\alpha} = \sqrt{\frac{1}{2M_\alpha \Omega_\alpha}} \langle \Psi^{\rm exc}_{i,\rm eq}| \sum_{rs\mathbf{k}} \frac{\partial}{\partial \mathbf{R}_\alpha} \langle \phi_{r\mathbf{k}}|\hat{e}\cdot\hat{p}|\phi_{s\mathbf{k}}\rangle \hat{c}^\dagger_{r\mathbf{k}} \hat{c}_{s\mathbf{k}} \bigg|_{\rm eq} |\Psi^{\rm exc}_{j,\rm eq}\rangle, \tag{7}$$

where we have included the prefactor coming from the canonical transformation of the phononic displacement into creation and annihilation operators, i.e. $\mathbf{R}_\alpha = \sqrt{\frac{1}{2M_\alpha\Omega_\alpha}}(\hat{a}^\dagger_\alpha + \hat{a}_\alpha)$. Finally we can rewrite the full QED Hamiltonian coupled linearly to lattice degrees of freedom as

$$\begin{aligned} \langle \Psi^{\rm exc}_i|\hat{H}|\Psi^{\rm exc}_j\rangle = &\left[\epsilon^{\rm exc}_j + \omega \hat{b}^\dagger\hat{b} + \sum_\alpha \Omega_\alpha \hat{a}^\dagger_\alpha \hat{a}_\alpha + \frac{A_0^2}{2}(\hat{b}^\dagger + \hat{b})^2\right]\delta_{ij} + \sum_\alpha \left(\mathcal{G}^{\rm exc}_{ij,\alpha}\hat{a}^\dagger_\alpha + \mathcal{G}^{\rm exc*}_{ji,\alpha}\hat{a}_\alpha\right) \\ &+ A_0\left(\mathcal{M}^{\rm exc}_{ij}\hat{b}^\dagger + \mathcal{M}^{\rm exc*}_{ji}\hat{b}\right) + A_0\sum_\alpha \left(\mathcal{Z}^{\rm exc}_{ij,\alpha}\hat{b}^\dagger + \mathcal{Z}^{\rm exc*}_{ji,\alpha}\hat{b}\right)(\hat{a}^\dagger_\alpha + \hat{a}_\alpha) \end{aligned} \tag{8}$$

This is the central equation of the main text and we refer to the eigenstates of such Hamiltonian as the phonoriton quasiparticle states. As sketched in Fig. S1, the photon acts by creating replicas of the purely electronic and phononic states resulting in an optical Stark effect or Rabi splitting where the originally uncoupled states hybridize to yield phonoriton states that have simultaneously electronic, phononic and photonic character.

In this work we consider hBN and in particular the non-dispersive (momentum independent) excitonic states localized around the K-points of the Brillouin zone. These excitonic states occur in a non-hydrogenic series, which is accurately described by a two-band BSE, where only a single valence and a single conduction band are taken into

account [3]. With this simplification the matrix elements appearing in Eq. (8) have one of the two following structures:

$$\mathcal{M}^{\rm exc}_{0j} = \sum_{\mathbf{k}} A^j_{\mathbf{k}} \langle \phi_{v\mathbf{k}} | \hat{e}\cdot\hat{p} | \phi_{c\mathbf{k}} \rangle, \tag{9}$$

$$\mathcal{M}^{\rm exc}_{ij} = \sum_{\mathbf{k}} A^{i*}_{\mathbf{k}} A^j_{\mathbf{k}} \left[\langle \phi_{c\mathbf{k}} | \hat{e}\cdot\hat{p} | \phi_{c\mathbf{k}} \rangle - \langle \phi_{v\mathbf{k}} | \hat{e}\cdot\hat{p} | \phi_{v\mathbf{k}} \rangle \right]. \tag{10}$$

In the equations above we have expressed the excitonic states as a linear combination of singly excited electronic determinants, where the coefficients of the linear combination are given by the solution of the BSE [4–6], $|\Psi^{\rm exc}_j\rangle = \sum_{cv\mathbf{k}} A^j_{cv\mathbf{k}} \hat{c}^\dagger_{c\mathbf{k}} \hat{c}_{v\mathbf{k}} |\Psi_0\rangle$ with $A^n_{cv\mathbf{k}}$ the BSE coefficients, or envelope functions and c and v indices running over conduction and valence bands respectively. The electronic groundstate $|\Psi_0\rangle \equiv |\Psi^{\rm exc}_{\rm j=0}\rangle$ can instead be written as a single determinant of only valence states. Similar expressions as in Eq. 9 and 10 can be readily obtained for the exciton-phonon matrix elements:

$$\mathcal{G}^{\rm exc}_{0j} = \sum_{\mathbf{k}} A^j_{\mathbf{k}} g_{vc\mathbf{k}}, \tag{11}$$

$$\mathcal{G}^{\rm exc}_{ij} = \sum_{\mathbf{k}} A^{i*}_{\mathbf{k}} A^j_{\mathbf{k}} \left[g_{cc\mathbf{k}} - g_{vv\mathbf{k}} \right]. \tag{12}$$

2. ELECTRON-PHONON COUPLING AND EXCITONIC PROBLEM

The ab-initio quantities entering the Hamiltonian in Eq. 2 solved in the main paper require two main calculations: electron-phonon matrix elements and exciton energies and wavefunctions.

The electron-phonon matrix elements have been calculated from using the octopus code [7], by displacing the lattice according to the phonon eigenmodes and subsequently projecting the variation of the electronic potential into the unperturbed Kohn-Sham basis.

The excitonic energies and wavefunctions are instead obtained by solving the Bethe-Salpeter Equation (BSE [6]) on a LDA basis using the GPAW code [8, 9]. The BSE is an equation that can be derived within many-body perturbation theory and takes into account the many-body screened interaction between the electron and the hole forming the excitons. In practice, such an equation can be cast in a two-particle Hamiltonian represented in the space of valence and conduction bands. Given the strongly localized nature of the 1s exciton in hBN (the one considered in the manuscript), it is enough to include the last valence and the first conduction band [10–12]. The screened interaction is then calculated at the RPA level by including all the bands up to $100eV$. The BSE is then solved by exact diagonalization on a 60×60 k-points grid and the excitonic energies and the corresponding wavefunctions $A^i_{\mathbf{k}}$ are obtained. In order to properly describe the electronic gap of 7.12 eV as reported in Ref. [13], we have corrected the LDA bandgap by applying a scissor operator.

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[1] S. Latini, E. Ronca, U. De Giovannini, H. Hübener, and A. Rubio, Nano Letters **19**, 3473 (2019).
[2] F. Giustino, Reviews Of Modern Physics **89**, 015003 (2017).
[3] S. Latini, T. Olsen, and K. S. Thygesen, Phys. Rev. B **92**, 245123 (2015).
[4] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. **81**, 2312 (1998).
[5] M. Rohlfing and S. G. Louie, Phys. Rev. B **62**, 4927 (2000).
[6] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).
[7] N. Tancogne-Dejean, M. J. T. Oliveira, X. Andrade, H. Appel, C. H. Borca, G. Le Breton, F. Buchholz, A. Castro, S. Corni, A. A. Correa, U. De Giovannini, A. Delgado, F. G. Eich, J. Flick, G. Gil, A. Gomez, N. Helbig, H. Hübener, R. Jestädt, J. Jornet-Somoza, A. H. Larsen, I. V. Lebedeva, M. Lüders, M. A. L. Marques, S. T. Ohlmann, S. Pipolo, M. Rampp, C. A. Rozzi, D. A. Strubbe, S. A. Sato, C. Schäfer, I. Theophilou, A. Welden, and A. Rubio, The Journal of Chemical Physics **152**, 124119 (2020).
[8] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, Phys. Rev. B **71**, 035109 (2005).
[9] J. Enkovaara, C. Rostgaard, J. J. Mortensen, J. Chen, M. Dułak, L. Ferrighi, J. Gavnholt, C. Glinsvad, V. Haikola, H. A. Hansen, H. H. Kristoffersen, M. Kuisma, A. H. Larsen, L. Lehtovaara, M. Ljungberg, O. Lopez-Acevedo, P. G. Moses, J. Ojanen, T. Olsen, V. Petzold, N. A. Romero, J. Stausholm-Møller, M. Strange, G. A. Tritsaris, M. Vanin, M. Walter,

B. Hammer, H. Häkkinen, G. K. H. Madsen, R. M. Nieminen, J. K. Nørskov, M. Puska, T. T. Rantala, J. Schiøtz, K. S. Thygesen, and K. W. Jacobsen, J. Phys.: Cond. Mat. **22**, 253202 (2010).
[10] L. Wirtz, A. Marini, M. Grüning, C. Attaccalite, G. Kresse, and A. Rubio, Physical review letters **100**, 189701 (2008).
[11] X. Blase, A. Rubio, S. G. Louie, and M. L. Cohen, Physical review B **51**, 6868 (1995).
[12] S. Galambosi, L. Wirtz, J. Soininen, J. Serrano, A. Marini, K. Watanabe, T. Taniguchi, S. Huotari, A. Rubio, and K. Hämäläinen, Physical Review B **83**, 081413 (2011).
[13] S. Haastrup, M. Strange, M. Pandey, T. Deilmann, P. S. Schmidt, N. F. Hinsche, M. N. Gjerding, D. Torelli, P. M. Larsen, A. C. Riis-Jensen, J. Gath, K. W. Jacobsen, J. J. Mortensen, T. Olsen, and K. S. Thygesen, 2D Mater. **5**, 042002 (2018).