Supplementary Information: First principles investigation of defect emission from hBN

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I. EXPERIMENTAL MEASUREMENT

Hexagonal boron nitride (hBN) flakes (Graphene Supermarket Inc.) were drop-casted on silicon substrate, and annealed at 850°C for half an hour in an argon atmosphere of 1 Torr.[1] The sample was mounted on a Helium-flown open-loop cryostat that was operated at 4 K. A continuous-wave (CW) 532 nm diode laser at 300 μW was used as the excitation source for this study. Excitation and collection light were focused through a high numerical aperture (NA) of 0.95, giving the spot size of $\sim$ 500 nm. The collection light was spectrally filtered by a 532 nm dichroic beamsplitter and an additional 568 nm longwave-pass filter to reject reflected excitation pump and render only pure emission signal from the emitter. The signal was collected through a 62.5 μm-core multimode fiber, acting as a pinhole to provide confocality for the photoluminescence setup. A 300g/mm grating equipped in a high-resolution charge coupled device (CCD) camera was used to spectrally resolve the emission signal. The acquisition time of 30 sec was chosen for capturing of the spectrum.

The cryogenic photoluminescence (PL) measurements were performed with a home-built confocal PL setup. A 0.5×0.5 cm^2 silicon substrate was mounted in a liquid Helium flown cryostat equipped with a feedback loop heating system. The temperature was set at 4.0 ± 0.5 K for the PL measurements. A 532 nm continuous-wave laser, set at 300 μW excitation power, was used to generate a confocal map and excite the defect centers through a 0.95 numerical aperture ($\times$150) objective. The emitted light was filtered with a long pass 568 nm and collected through a multimode fiber into a spectrometer equipped with a high resolution charge coupled device (CCD) to resolve the emission spectra from the emitters.

II. THE FIRST PRINCIPLE CALCULATION OF THE HUANG-RHYS FACTOR AND THE PL SPECTRUM

In the following, we describe the theoretical formalism for the calculation of the Huang-Rhys factor S_{HR} and the photoluminescence lineshape $L(\hbar\omega)$. $L(\hbar\omega)$ is calculated according to the formula

$$L(\hbar\omega) = C\omega^3 A(\hbar\omega) \quad , \tag{1}$$

where $A(\hbar\omega)$ is defined as the optical spectral function and C is a normalization constant. We make the following assumptions for the evaluation of $A(\hbar\omega)$: (1) the Born-Oppenheimer approximation whereby the degrees of freedom electrons, $\mathbf{r}_i$ and nuclei, $\mathbf{R}_I$, are separated, (2) the single configurational coordinate model[?] , where we replace the large number of ionic position vectors $\mathbf{R}_I$ by a single configuration coordinate, Q (this approximation justifies the use of the 1D configurational coordinate diagrams) and (3) the Frank-Condon approximation[?] . Then, we derive the relationship between $A(\hbar\omega)$ and the spectral function of electron-phonon coupling $S(\hbar\omega)$ according to the method of moments,[2] as follows. First, we express $A(\hbar\omega)$ in terms of the generating function $G(t)$:

$$A(\hbar\omega) = \int_{-\infty}^{\infty} G(t) e^{i\omega t - \gamma|t|} dt \quad , \tag{2}$$

where $G(t) = e^{S_+(t) + S_-(t) - S_{HR}}$, and $S_\pm(t)$ are give by

$$S_+(t) = \int_0^\infty S(\hbar\omega)e^{i\omega t}n(\hbar\omega)d(\hbar\omega) \tag{3}$$

$$S_-(t) = \int_0^\infty S(\hbar\omega)e^{-i\omega t}(n(\hbar\omega)+1)d(\hbar\omega) \quad , \tag{4}$$

which, at zero temparture, gives $S_+(t) = 0$ and $S_-(t)$ becomes the Fourier transform of $S(\hbar\omega)$. Note that we can express $G(t)$ as $G(t) = e^{S_+(t)+S_-(t)}$, setting the $S(0)$ to zero, because it only becomes a factor in Eq. 2.

Next, we present the derivation of q_k (Eq. 4 in the main text) from the 1D configuration coordinate approximation. In this approximation, the ground state potential energy of the ions, assuming they behave as coupled harmonic oscillators, can then be written as

$$E_g(Q) = \frac{1}{2}m\omega^2(Q - Q_{0g})^2 \quad , \tag{5}$$

where Q_{0g} is the equilibrium normal mode corresponding to ground electronic state. The excited state potential energy of the ions in normal mode k is then

$$E_e^k(Q) = E_{eg} + \frac{1}{2}m\omega^2(Q - Q_{kg})^2 - \frac{1}{2}m\omega^2(Q - Q_{kg})(Q_{ke} - Q_{kg}) \quad , \tag{6}$$

where the dimensionless quantity $S_k = \frac{1}{2}m\omega^2(Q_{ke} - Q_{kg})^2$ characterizes the strength of the electron-phonon coupling for phonon mode k, which is the partial HR factor.

The function $S(\hbar\omega)$ is defined as follows:

$$S(\hbar\omega) = \sum_k S_k\delta(\hbar\omega - \hbar\omega_k) \quad , \tag{7}$$

ω_k is the phonon frequency and S_k is the partial HR factor. The Dirac delta function is approximated here as a gaussian with width σ. S_k is given by

$$S_k = \frac{\omega_k}{2\hbar}q_k^2 \quad , \tag{8}$$

where q_k is given by

$$q_k = \sum_{ai} m_a^{1/2}\left(R_{e,ai} - R_{g,ai}\right)\Delta r_{k,ai} \quad , \tag{9}$$

where a enumerates the atoms, $i = x, y, z$, m_a is the atomic mass of species a, $R_{g/e,ai}$ is the position of atom a in the ground/excited state, and $\Delta r_{k,ai}$ is the atomic displacement in normal coordinates. The total HR factor is then given by

$$S = \sum_k S_k \quad . \tag{10}$$

It is important to note that a multilayer hBN has out-of-plane breathing (flexural) modes, in which the hBN sheets ripple along the z-axis.[3] These phonon modes induce a slight planar strain which does not affect the main features of the electronic structure, and therefore will not be considered in the present analysis.

III. CALCULATION CONVERGENCE

In order to confirm the robustness of these calculated HR factors, we have compared the HR values obtained using SIESTA against the values obtained using VASP for N_BV_N and $2O_{2B}V_N$ on a 7x7 supercell. The VASP results are: 4.62 for N_BV_N and 7.06 for $2O_{2B}V_N$. For N_BV_N, we have also calculated the HR factor in a 5x5 supercell to compare

against the value obtained for the 7x7. The HR factor in the 5x5 supercell is 4.57, which is very close to the value obtained for the 7x7 supercell.

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