Exploring the phonon-assisted excitation mechanism of luminescent centres in hexagonal boron nitride by photoluminescence excitation spectroscopy

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The two-dimensional material hexagonal boron nitride (hBN) hosts single-photon emitters active at room temperature. However, the microscopic origin of these emitters, as well as the mechanism through which they are excited, remain elusive. We address these issues by combining ab initio calculations with low-temperature photoluminescence excitation spectroscopy. By studying 26 defect transitions, we find excellent qualitative agreement of experiments with the emission and absorption line shapes of the carbon trimers \( \text{C}_2\text{C}_N \) and \( \text{C}_2\text{C}_B \), while enabling us to exclude 24 defect transitions for one luminescent centre. Furthermore, we show an enhanced zero-phonon line intensity at two-phonon detuning. This unambiguously demonstrates that luminescent centers in hBN, and by inference single-photon emitters, are excited through a phonon-assisted mechanism. To the best of our knowledge, this study provides the most comprehensive insight into the excitation mechanism and the microscopic origin of luminescent centers in hBN.

Keywords: single-photon emitter, hexagonal boron nitride, photoluminescence excitation, excitation mechanism, ab initio calculations, defect identification, luminescent centre

Luminescent centres in hexagonal boron nitride (hBN) have gained an increased scientific interest due to the demonstration of single photon emission with a brightness comparable to semiconductor quantum dots in bulk [1]. These single-photon emitters (SPE) emit at photon energies around 2 eV and persist even at room temperature [2]. This makes hBN a promising material to realise future optoelectronic technologies such as quantum telecommunication [3] and quantum sensing [4]. However, though the origin of these luminescent centres has been narrowed down to carbon-based defects [5, 6], their exact microscopic composition remains elusive despite tremendous efforts in ab initio calculations [7–11]. Furthermore, it remains unclear what physical processes are involved in the excitation mechanism. For applications of hBN luminescent centres in quantum technologies, it is essential to address both issues.

We address these issues by using inspirational work on color centers in diamond, where photoluminescence excitation (PLE) spectroscopy has provided crucial insight into the excitation mechanism [12–14]. This technique measures the photoluminescence as a function of excitation photon energy, probing off-resonant transitions and therefore the underlying excitation mechanism. PLE has previously been applied to 2 eV luminescent centres in

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group I centres. Room- and low-temperature spectra of several group I centres are shown in Supplementary Information [11,12,13].

The optical excitation of 2 eV luminescent centres in hBN does not involve above-band excitations since the photon energy of the excitation laser (∼2.5 eV) is much smaller than the band gap of ∼6 eV [18]. Supported by charge transfer experiments [19], the excitation mechanism most likely involves only electronic states inside the band gap, so-called deep levels. This makes the excitation laser energy very important since there are only few, discrete electronic states available in contrast to a continuum of states for interband transitions in semiconductors.

We discuss two possible excitation mechanisms for 2 eV luminescent centres in hBN. The first is the empiric scheme illustrated by a Jablonski diagram in Fig. 1. Here, the driving laser excites an electron from a deep level below the Fermi level $E_F$ to another level far below the conduction band. From here, the electron relaxes to the excited state $|e\rangle$ by dissipating energy $\Delta_e$. Then, a photon belonging to the ZPL is emitted by a transition to the ground state $|g\rangle$, followed by another relaxation with energy $\Delta_g$. We highlight that the ZPL energy equals the driving laser energy minus the two relaxation energies $\Delta_e$ and $\Delta_g$. Since 2 eV SPE in hBN show non-zero bunching amplitudes on time scales longer than the antibunching times [20,21], it is necessary to add shelving state(s) represented by $|s\rangle$.

The second potential excitation mechanism is a phonon-assisted process. To illustrate this mechanism, Fig. 1 shows two electronic states coupled strongly to a single phonon mode, with energy $\hbar \Omega$, resulting in discrete vibronic energy levels $|e, n\rangle$ and $|g, m\rangle$. The driving laser excites the defect to a high lying vibronic state which rapidly relaxes to its lowest lying state $|e, 0\rangle$ in the excited electronic manifold. A photon is then emitted through an electronic transition to the ground-state manifold, producing ZPL and PSB emission. By varying the frequency of the driving laser, we can resonantly excite different phonon states in the excited-state manifold. Thus, the ZPL and PSB emissions are enhanced at laser detunings of $\hbar \Omega$ and $2\hbar \Omega$, a fact we leverage in our PLE experiments. Further details on the excitation mechanisms are given in the Methods.

The phonon-assisted excitation scheme, also called the Huang-Rhys model, has been proposed in previous works [15,22,23]. Recent PLE experiments [15,16] observed an enhanced ZPL emission at detunings ranging from 160 to 200 meV. This observation, however, can be assigned to both an empiric scheme with $\Delta_e + \Delta_g = 160 - 200$ meV and a phonon-assisted scheme with $\hbar \Omega = 160 - 200$ meV. To unambiguously demonstrate that the excitation mechanism is phonon-assisted, the observation of higher-order phonon peaks is necessary.

**RESULTS AND DISCUSSION**

Photoluminescence excitation spectroscopy

To generate luminescent centres in hBN we use a process that was developed recently in our group [6]. Briefly, we irradiate high-quality multilayer hBN with oxygen atoms and use subsequent annealing to achieve high densities of luminescent centres. In our previous work, we carried out room-temperature characterisation of group I and group II centres, as defined in Ref. [6]. In this work, we focus our attention on low-temperature characterisation of group I centres. Room- and low-temperature spectra of several group I centres are shown in Supplementary Information [11,12,13].
Fig. 1 shows the experimental PLE data, i.e. the photoluminescence as a function of laser detuning that is defined as the laser energy minus the ZPL energy (for more details see Supplementary Information VI and V). To investigate the absorption characteristic, we study the ZPL intensity which is defined as the area under the ZPL. To efficiently compare the photoluminescence for all 26 defect transitions with the experiment, we calculate the photoluminescence mean and variance of each predicted line shape and plot them in Fig. 2a. Here, different colors correspond to different defects as shown in Supplementary Information VI. The scatter plot shows that the photoluminescence mean and variance for most of the calculated defects differ significantly from the experimental data. We highlight that the scatter plot is independent on the ZPL energy of the defects since their photoluminescence line shapes are matched with the experimental ZPL energy. Fig. 2b shows the region close to the experiments, where the five defects shown here are the most likely candidates for the luminescent centres observed experimentally. From these five defects, we neglect \( V_B \) (where \( \beta \) refers to the minority spin channel) since the predicted ZPL energy of 2.7 eV is too high for the measured spectra (details in Supplementary Information VI). Similarly, the predicted ZPL energy for the \( C_{2B} V_N [S = 3] \) defect is smaller (0.9 eV) than the measured spectrum. For completeness, however, we include its photoluminescence spectrum in Supplementary Information VI.

Therefore, we can exclude 23 defect transitions and consider only three defects for comparison with our experiments: \( C_{2C} N \), \( C_{2B} N \), and the triplet state of \( V_{N_C} \) (called \( V_{N_C} \) in the main text for simplicity). Fig. 2c shows the schematic and the electronic levels of these
FIG. 2. Scatter plot and schematics of defects. (a) Scatter plot comparing the photoluminescence mean and variance of theoretically calculated defect line shapes with the experimental data of Fig. 3. (b) The region around the experimental data, marked by the square in (a), highlighting the most likely candidates. (c) Schematics and electronic levels of C$_2$C$_N$, C$_2$CB and V$_NCB$ where the latter is taken from Ref. [27]. We note that the PBE functional is used for all defects but for C$_2$CN, C$_2$CB and V$_NCB$ where the HSE06 functional is applied.

Theoretical PLE of three defects

To calculate the PLE for the three selected defects, we use the partial Huang-Rhys parameters generated from ab initio calculations to construct the spectral density [28]

$$J_{\text{Sim}}(\omega) = \sum_k s_k \delta(\omega_k - \omega),$$

where $s_k$ is the partial Huang-Rhys parameter associated to a phonon mode of frequency $\omega_k$. Notably, the ab initio calculations do not reproduce the low-energy PSB at detunings from 20 to 50 meV (see Supplementary Information [VII]), although this low-energy PSB has the same excitation mechanism as the ZPL (see Supplementary Information [IX]). This deviation is due to the ab initio calculations being carried out in a perfectly planar system with high symmetry that exhibits vanishing coupling to acoustic phonons, i.e. the corresponding Huang-Rhys factors are zero. This is in contrast to our experiments where the symmetry can be broken by local strain, non-radiative defects close by, non-parallel hBN layers as well as the vicinity of edges, kinks, and grain boundaries. Such a symmetry breaking allows the coupling to acoustic phonons which we observe in our experimental photoluminescence line shape. We highlight that the low-energy PSB observed in our experiments have been reported in almost all works on 2 eV SPE in hBN, independent on the generation process [5, 6, 20, 21, 29].

To account for the symmetry breaking in our experiments, we include acoustic modes by adding a Gaussian contribution to the spectral density, such that the total spectral density is written as $J(\omega) = J_{\text{Sim}}(\omega) + J_{\text{LA}}(\omega)$ with

$$J_{\text{LA}}(\omega) = \alpha \omega_e^2 \omega \exp(-\omega^2/\omega_e^2).$$

Here, $\alpha$ and $\omega_e$ are found by fitting the photoluminescence spectrum. This form of spectral density is commonly used to describe the acoustic phonons resulting from deformation potential coupling observed in semiconductor quantum dots [17]. We refer the reader to the Methods for more details on the theory and fitting procedure used. With the spectral density at hand, we can cal-
calculate the dynamics and optical properties of the system using the polaron method, which enables us to derive a master equation that is non-perturbative in the electron-phonon coupling strength [17, 30]. Crucially, this description allows us to directly simulate the full PLE of defects. More details are provided in the Methods section.

First, we compare the photoluminescence spectrum with the calculated emission line shapes (see Fig. 3a). We note that the experimental data is identical in all three panels. We find good qualitative agreement for C$_2$CN and C$_2$CB, with the position of the first- and second-order PSB closely resembling the experimental data, as well as capturing the sidebands due to acoustic phonons located on both ZPL and phonon replicas. In contrast, the calculated V$_{NCB}$ spectrum shows poor agreement with the experimental photoluminescence, predicting a much broader PSB in comparison to C$_2$CN and C$_2$CB, with notable vibronic activity at energies between 50 and 150 meV that is not present in the experimental data.

To calculate the ZPL intensity as a function of laser detuning, we replicate the experiments in our theoretical model: we introduce a weak driving field to the emitter and vary the laser detuning. For each detuning we then calculate the ZPL intensity, sweeping out the line shapes seen in Fig. 3b. Comparison with the experimental data is done by rescaling the calculated line shapes to match the ZPL intensity around 170 meV. For the luminescent centre in Fig. 3b, we find excellent qualitative agreement for C$_2$CN and C$_2$CB, while V$_{NCB}$ once again shows poor agreement. Experiments on two other luminescent centres also show agreement for C$_2$CN and C$_2$CB as shown in Supplementary Information X. The complete theoretical PLE data for the three studied defects is presented in Supplementary Information VII.

Photoluminescence has been used in various works to try to identify the underlying defect of 2 eV SPE in hBN. Many candidate defects were proposed including vacancies [2, 31], oxygen-based defects [32] and carbon-based defects [5, 6, 10]. Our results highlight that low-temperature PLE is a superior technique for defect identification compared to photoluminescence, allowing us to disregard V$_{NCB}$ for one luminescent centre. However, though this is the case for the current luminescent centre under investigation, we highlight that other luminescent centres, also generated by our process, might show agreements with other defects such as V$_{NCB}$.

In our previous work, we revealed the generation mechanism of our irradiation-based process as an amorphisation during irradiation followed by recrystallisation via thermal annealing [14]. This generation mechanism holds for C$_2$CN and C$_2$CB since these defects can also be formed during recrystallisation in a carbon-enriched environment. Moreover, C$_2$CN has a shelving state that might explain the bunching observed in autocorrelation measurements [21].

**Vibronic spectra of ground and excited state**

To study the excitation mechanism of luminescent centres in more detail, we investigate the vibronic spectra of both ground and excited state. We explore the vibronic spectrum of the ground state by analysing the PSB emission observed in the photoluminescence spectrum. Complementarily, we investigate the vibronic spectrum of the excited state by comparing the PLE intensities of two optical PSB with the ZPL intensity. This provides the emission relation of ZPL and PSB and helps to verify the underlying excitation mechanism.
FIG. 4. Detailed study of ZPL and PSB intensities. (a) The spectral ranges of two optical PSB are shaded in orange and yellow, on top of the photoluminescence spectrum (at 168 meV detuning). The ZPL and background ranges are shown in green and grey, respectively. (b) PSB and ZPL intensities in colors corresponding to (a). (c) ZPL intensity in green and flipped photoluminescence in blue. (d) Advanced phonon-assisted excitation mechanism reflecting two distinct PSB and PLE peaks at first order. The PLE intensities in (b) and (c) as well as the photoluminescence spectrum in (c) are background-corrected and normalised (see Supplementary Information).}

First, we study two first-order optical PSB at detunings of around 160 meV and 190 meV, respectively. The PSB intensities are defined as the area under the PSB, as shown by shaded areas in Fig. 4a. We note that the bandwiths of both PSB intensities are identical to the one used for the ZPL intensity (10 meV). We obtain an almost identical qualitative behaviour of PSB intensities and ZPL intensity as shown in Fig. 4b. This result both demonstrates that the ZPL and the two optical PSB have the same excitation mechanism and indicates that the vibronic lifetime is much faster than the electronic lifetime. To the best of our knowledge, this is the first time that ZPL and PSB intensities of hBN luminescent centres are investigated simultaneously.

Next, we compare the ZPL intensity with the photoluminescence spectrum where we flip the latter for qualitative comparison (see Fig. 4b). We find that both ZPL intensity and photoluminescence show two peaks at detunings of 160 meV and 190 meV. These two peaks have almost identical strength for the ZPL intensity while the photoluminescence has a weaker peak around 190 meV compared to 160 meV detuning. Thus, ground and excited states seem to show different phonon coupling. Fig. 4c shows the most likely phonon-assisted excitation mechanism that is modified compared to Fig. 1a. Here, the first-order states are sketched as two distinct levels with two possible interpretations. Either a coupling to two optical phonon modes at 160 meV and 190 meV or a coupling to one optical phonon mode (either at 160 meV or 190 meV) that is dressed by acoustic phonons. For the excited state, coupling to two optical phonons is more likely because the two peaks at 160 meV and 190 meV show equal strength. The second-order phonon replicas in Fig. 4d are shown as continua since our experimental resolution is too low to assign individual states.

The optical PSB intensities at one-phonon detuning (170 meV) and the ZPL intensity at two-phonon detuning (340 meV) show comparable strengths, as shown in Supplementary Information. These PLE intensities are assigned to two-phonon processes (see Methods) and as expected their intensities are indeed lower compared to one-phonon processes like the ZPL at 170 meV detuning, since the latter involves fewer phonon excitations. This further supports the phonon-assisted excitation mechanisms presented in Fig. 1 and Fig. 4d.

Our results of photoluminescence and ZPL intensity indicate that ground and excited states have different phonon couplings. A detailed study of the ZPL intensity suggests that the excited state couples to two distinct optical phonons. The 190 meV peak is at lower detunings for the excited state than for the ground state, corresponding to a redshift of the excited state. This redshift is smaller than 10 meV and in agreement with previous observations in PLE and stimulated emission depletion (STED). However, this redshift is within the spectral PLE resolution for both experiments and therefore lacks significant evidence. To study this small redshift and the excitation mechanism in more detail, PLE measurements with a higher spectral resolution would be needed.

CONCLUSION

In summary, we have studied the emission and absorption properties of luminescent centres in hBN. Combining our experimental results with ab initio calculations, we find excellent qualitative agreement for C2N and C2B, while we could exclude 24 defect transitions for one luminescent centre. We note that low temperatures are necessary to reveal differences between C2N, C2B, and V3V - in particular in their emission line shape. Further methods like pump-probe schemes and nuclear magnetic resonance (NMR) are needed to identify the nature of 2 eV luminescent centres in hBN. To exclude the possibility of multiple defects responsible for luminescent centres, auto-correlation ($g^2$ function) and cross-correlation measurements are required. Nevertheless, our excellent agreement of PLE with ab initio calculations is outstanding compared to previous work. Moreover, the combination of PLE spectroscopy with ab initio calculations presented in this work could be applied to other solid-state materials to narrow down the number...
of possible defects responsible for luminescent centres or SPE.

We use an irradiation-based process [6] that generates luminescent centres showing excellent agreement with the theoretical curves of C\textsubscript{2}C\textsubscript{N} and C\textsubscript{2}C\textsubscript{B} (see Fig. 3 and Supplementary Information X). However, the irradiation-based process also generates different types of luminescent centres with distinct photoluminescence line shapes, as presented in Supplementary Information XI and XII as well as in our previous work [8]. Some of these luminescent centres show poor agreement with C\textsubscript{2}C\textsubscript{N} and C\textsubscript{2}C\textsubscript{B} and instead agree well with the emission line shape of V\textsubscript{N}C\textsubscript{B}. Thus, different luminescent centres may have different microscopic origins that could be inferred by low-temperature PLE spectroscopy combined with \textit{ab initio} calculations.

In our experiments, we observe enhanced ZPL and PSB emission at one-phonon detuning as well as an enhanced ZPL intensity at two-phonon detuning, the latter for the first time to the best of our knowledge. These observations unambiguously demonstrate that the studied luminescent centre has a phonon-assisted excitation mechanism with a phonon energy around 170 meV. Moreover, we find indications that the excited state couples to two distinct optical phonons. All in all, our experiments reveal new insight on 2 eV luminescent centres in hBN that can be inferred on SPE with similar photon energies and line shapes.

The first observation of an enhanced ZPL intensity at two-phonon detuning can have two different explanations. First, our generation process is different to previous studies [15, 16, 24, 36, 39] which might result in a different type of luminescent centre. Secondly, luminescent centres in previous studies may have been bleached before measurements at large laser detunings could be carried out. Bleaching of 2 eV luminescent centres in hBN is an unresolved challenge, since only a few luminescent centres showed stable emission for months [20] while many centres bleached relatively quickly [21, 37]. Moreover, luminescent centres showed blinking [6, 26, 38] and most of the centres were stable only for several minutes [2, 3, 24, 34, 39]. It is essential to solve these stability challenges for any real-world application of 2 eV luminescent centres in hBN.

Besides identifying the microscopic origin of SPE in hBN, clarifying their excitation mechanism is essential for optimum performance in real-world applications. The ubiquitously used 532 nm laser efficiently excites SPE with ZPL around 2.15 eV because the laser energy of 2.33 eV matches the one-phonon detuning of around 170 meV. This fortunate coincidence of an ubiquitously laser with the one-phonon detuning has been a gift for the research field on 2 eV SPE in hBN. Moreover, other SPE might exist in hBN that require excitation energies that differ from the commonly used green lasers.

**METHODS**

**Excitation mechanisms**

In the empiric mechanism, the two relaxation processes \(\Delta_c\) and \(\Delta_g\) are associated with \(|e\rangle\) and \(|g\rangle\), respectively. In the phonon-assisted excitation mechanism (Fig. 11), we do not show the Fermi level for clarity.

**Optical spectroscopy**

The optical characterisation is described in detail in Supplementary Information X. For PLE measurements at low temperature, we used a supercontinuum white light laser in combination with a tunable laser line filter resulting in a PLE resolution of \(\sim 5\) meV.

**One- and two-phonon processes**

To identify one- and two-phonon processes, we use the electronic states \(|e, n\rangle\) and \(|g, m\rangle\) of the phonon-assisted excitation mechanism presented in Fig. 11.

At a laser detuning of \(\sim 170\) meV, we excite the electronic state \(|e, 1\rangle\) that relaxes to \(|e, 0\rangle\) by the emission of one phonon. From \(|e, 0\rangle\), the ZPL emission is realised without any further phonon emission, while the PSB process involves another phonon that is emitted by relaxation from \(|g, 1\rangle\) to \(|g, 0\rangle\). Therefore, the ZPL is a one-phonon process while the PSB is a two-phonon process. The above described two-phonon process is similar for the optical PSB at \(\sim 190\) meV and the acoustic PSB at \(\sim 10\) meV.

At ZPL detunings of \(\sim 340\) meV we excite the state \(|e, 2\rangle\), introduced in the phonon-assisted mechanism in Fig. 11. This state relaxes by the emission of two phonons to \(|e, 0\rangle\) from where a ZPL emission is realised without any further phonon emission. Thus, this process is also a two-phonon process like the optical PSB at \(\sim 170\) meV detuning.

**Ab initio calculations**

All the \textit{ab initio} calculations for the ground states, excited states and normal modes were performed within the GPAW electronic structure code [40] using a plane wave basis set with 800 eV plane wave cut off and a Γ-point sampling of the Brillouin zone. All the defects were represented in a 7x7x1 supercell (monolayer) and allowed to fully relax until the maximum force was below 0.01 eV/Å. A vacuum of 15 Å was used in the vertical direction.

The PBE exchange correlation (xc-)functional [41] was used for all calculations. In addition, for C\textsubscript{2}C\textsubscript{N}, C\textsubscript{2}C\textsubscript{B}, and V\textsubscript{N}C\textsubscript{B} the relatively more accurate HSE06 functional was used for the calculation of the ZPL energies. The excited states were calculated using the direct optimisation-maximum overlap matrix (DO-MOM) method [42] with a maximum step length, \(\rho_{\text{max}}\), for the quasi-Newton search direction of 0.2. Compared to the standard Delta-SCF approach, the DO-MOM method yields improved convergence and avoids variational collapses during the SCF optimisation [42]. For further details on the theory and calculation details we refer to our previous work [33].

In all calculations, we considered in-plane defect structures and verified their dynamical stability by the absence of imaginary frequencies in the Γ-point phonon
spectrum. Only for the excited state of VN, i.e. \((2)^3B_1\), does the carbon atom of the defect relax out of plane. The out-of-plane configuration is stable compared to the planar configuration by 0.23 eV for monolayer hBN. This energy difference is 0.036 eV in a trilayer hBN with a VN defect embedded in the central hBN layer (of the trilayer hBN) [6].

**Open system model for PLE**

To model the PLE we use information about the phonon modes extracted from the ab initio calculations to construct an open system model for the defect transition. The emitter is modelled as a two level system with ground and excited states \(|g\rangle\) and \(|e\rangle\) respectively, with transition energy \(\hbar \omega_L = 2.15\) eV. The emitter is driven by a continuous wave laser with frequency \(\omega_L\), and interacts with both vibrational and electromagnetic environments. The form of this interaction is given in the Supplementary Information. To account for strong electron-phonon coupling and resultant PSB observed for luminescence centres, we make use of the polaron method [17, 44]. This approach addresses the system energy levels with modes of the vibrational environment using a unitary transformation, providing an optimised basis in which to do perturbation theory. We then derive a Born-Markov master equation in the transformed frame which is non-perturbative in the original electron phonon interactions. This allows us to describe the dynamics [44] and, crucially, the PSB of the optical transition in question [30, 45]. For further details of the model described above, we refer the reader to the Supplementary Information VII and XII.

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**Author contributions**

M.F. and A.H. carried out all experiments. M.F. and N.S. analysed and interpreted the experimental data. A.S. designed and performed the ab initio calculations. K.S.T. supervised the ab initio calculations. M.F., A.S., J.I.-S., K.S.T., and N.S. discussed the experimental results and compared them with the ab initio calculations. J.I.-S. developed the open quantum systems model, and fitted the theoretical curves to the experimental data. All authors contributed to writing the manuscript.

**Competing interests**

The authors declare that they have no competing interests.

**Note**

During the final stage of the preparation of this manuscript we became aware about a thorough study of defects in hBN, focusing on tailoring the ZPL energy [40].

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SUPPLEMENTARY MATERIALS
EXPLORING THE PHONON-ASSISTED EXCITATION MECHANISM OF LUMINESCENT CENTRES IN HEXAGONAL BORON NITRIDE BY PHOTOLUMINESCEENCE EXCITATION SPECTROSCOPY

I. LOW-TEMPERATURE SPECTROSCOPY

Fig. 5a shows the photoluminescence of the same luminescent centre at room ($T = 300$ K) and low temperature (10 K). Decreasing the temperature leads to a narrower ZPL and a qualitatively different PSB, as shown in Fig. 5b. At room temperature we obtain a broad PSB in contrast to distinct peaks at low temperature that reveal a detailed structure. This is consistent with various group I centers showing a broad PSB at room temperature [6] and several low-temperature line shapes revealing highly structured PSB (see Supplementary Information II). Selected photoluminescence spectra at low temperature are shown in Fig. 5.

Interestingly, among the presented line shapes, we find qualitatively different PSB as shown in Fig. 5b and d. As discussed in the main text, the differences in photoluminescence may be due to different underlying defects among the luminescent centres studied. Additional low-temperature spectra and optical PSB are shown in Supplementary Information II and III. We note that we use the same excitation laser at a photon energy of 2.37 eV for all measurements in Fig. 5.

The highly-resolved PSB presented in Fig. 5b and d show that low-temperature measurements allow precisely studying the vibronic coupling of luminescent centres in hBN. However, the different PSB line shapes correspond to variations in the vibronic coupling among the luminescent centres. Therefore, in order to clarify whether the excitation mechanism is a phonon-assisted process, it is useful to restrict our attention to individual luminescent centres.

FIG. 5. Low-temperature photoluminescence of luminescent centres in hBN. (a) Room- and low-temperature spectra of the same luminescent centre under 2.37 eV excitation. a.u., arbitrary units. (b) Optical PSB at room- and low-temperature of the luminescent centers shown in (a) with corresponding colors. The ZPL detuning is defined as the photon energy minus the ZPL energy. (c) Photoluminescence spectra of several luminescent centres at $T = 10$ K under 2.37 eV excitation. cps, counts per second. (d) Optical PSB of the luminescent centres shown in (c) with corresponding colors, shifted vertically for clarity. The PSB in (b) and (d) are background-corrected for easier comparison, as described in Supplementary Information II.
II. BACKGROUND CORRECTION AND FURTHER LOW-TEMPERATURE PSB

For easy comparison of PSB, we carried out a background correction via a publicly available script [47]. We use this script with the asymmetric Huber function at fourth order and $s = 0$. In Fig. 6a, we show the background correction for one photoluminescence spectrum.

FIG. 6. Background correction and further optical PSB. (a) Background correction of one photoluminescence spectrum. The raw spectrum is shown in blue, the background in yellow and the background-corrected spectrum in red. (b) The PSBs from the luminescent centers shown in Fig. 7.
III. FURTHER LOW-TEMPERATURE PHOTOLUMINESCENCE SPECTRA

FIG. 7. Further photoluminescence spectra of luminescent centres. The centres are photoexcited with a green laser at 2.37 eV. Each panel shows four photoluminescence spectra, giving a total of 16 additional spectra of luminescent centres. The normalised intensity is shown in arbitrary units (a.u.). The temperature is 10 K.
IV. RESCALING OF PLE SPECTRA

The PLE measurements shown in Fig. 1 are done by two laser sweeps: Sweep 1 and Sweep 2. We use two different laser settings to keep the power between 0.75 and 1.93 mW (see Fig. 8a). We first describe the rescaling within one sweep, followed by the rescaling between two sweeps. We finally describe the rescaling to one excitation power.

We measure the excitation power as a function of excitation energy prior to the PLE measurements (Fig. 8a). Within one sweep, the exposure time at power \( P_i \) is set to

\[
t_1 \cdot \frac{P_1}{P_i},
\]

where \( t_1 \) and \( P_1 \) are the exposure time and power at the beginning of the sweep while \( P_i \) is the current power (at a specific laser energy or laser detuning). This adjustment in exposure time is meaningful, since the luminescent centres studied show a linear dependence of the intensity with excitation power in the studied power range, as shown in Fig. 8d. Furthermore, the detector operates in a constant count regime which avoids saturation.

At each laser detuning in Sweep 2, the exposure time is adjusted as described by equation (1). To rescale the spectra of Sweep 2 to Sweep 1, we multiply each spectrum of Sweep 2 (after adjusting the exposure time) by

\[
t_1 \cdot \frac{P_1}{P_i} \cdot \frac{t_1}{t^*_1} \cdot \frac{P_1}{P^{*}_1},
\]

where \( t^*_1 \) and \( P^{*}_1 \) are the exposure time and the excitation power at the beginning of Sweep 2.

We will give an example why this multiplication is meaningful. At the end of Sweep 2, the excitation energy is identical to the beginning of Sweep 1. However, the excitation power at the end of Sweep 2 is \( P^{*}_{\text{end}} \). Now we calculate the exposure time at the end of Sweep 2. Calculating the exposure time of Sweep 2, we multiply equation (1) with equation (2) and get

\[
t^*_1 \cdot \frac{P^{*}_1}{P^{*}_{\text{end}}} \cdot \frac{t^*_1}{t^*_1} \cdot \frac{P^{*}_1}{P^{*}_{\text{end}}} = t_1 \cdot \frac{P_1}{P^{*}_{\text{end}}}
\]

which is identical to the exposure time given by equation (1) where \( P_1 \) is replaced by \( P^{*}_{\text{end}} \).

After carrying out all the rescaling mentioned above, we rescale the data to 1 mW at an excitation energy of 2.431 eV. This is the reason why we have absolute values in the photoluminescence (i.e. constant dose) shown in Fig. 1.
FIG. 8. **Power dependence of excitation source and photoluminescence.** (a) Photoluminescence spectra at several excitation powers, given by the legend. (b) The excitation power as a function of excitation energy. We performed two laser sweeps with different laser settings to obtain a similar power for all laser detunings. (c) Power-dependent photoluminescence. cps, counts per second. (d) Integrated zero-phonon line (ZPL) as a function of excitation power (not background corrected). The integrated spectral range (2.155 to 2.170 eV) is shown by vertical dashed lines in (c). We observe a linear dependence of the ZPL intensity as a function of excitation power.
V. DETAILED EXPERIMENTAL PLE DATA

Fig. 9b shows the photoluminescence spectra for several laser detunings. We obtain strong variations with laser detuning that are investigated in detail under continuous laser detuning, as shown in Fig. 9d. To investigate the absorption characteristic, we study the ZPL intensity which is defined as the area under the ZPL with a bandwidth of 10 meV (Fig. 9c). We observe a strong ZPL intensity at a detuning of 168 meV while an intermediate ZPL intensity is obtained at a detuning of 341 meV. These two important detunings are highlighted by horizontal lines in Fig. 9d and the corresponding photoluminescence spectra are shown in Fig. 9b. Another important detuning is exactly between the two aforementioned, i.e. at 255 meV, which yields a small ZPL intensity because it lies between the two states $|e, 1\rangle$ and $|e, 2\rangle$.

![Diagram](image)

**FIG. 9.** PLE of a luminescent centre in hBN at 10 K. (a) Empiric and phonon-assisted excitation mechanism. The zero-phonon line (ZPL), the first-order phonon sideband (1st PSB), and shelving state(s) $|s\rangle$ are shown. The empiric mechanism has relaxation processes with energies $\Delta_e$ and $\Delta_g$ (associated with $|e\rangle$ and $|g\rangle$, respectively) while the phonon-assisted mechanism shows relaxation via phonons with energy $\hbar \Omega$. The excited states are labelled with $|e,n\rangle$ corresponding to the electron in the excited state and its environment occupied by $n$ phonons. Similarly, $|g,m\rangle$ describes the electron in the ground state with $m$ phonon in its environment. The band gap is given by $E_g \sim 6$ eV [18] and more details are presented in the Methods of the main text. (b) Photoluminescence spectra of the luminescent centre at several laser detunings, given by the legend. (c) ZPL intensity as a function of laser detuning. The spectral range for the ZPL intensity is shown by the vertical lines in (d). (d) PLE map of a luminescent centre in hBN. The horizontal lines correspond to the spectra shown in (b) and the dim upward line in the bottom right corner corresponds to the silicon Raman $\sim 520$ cm$^{-1}$. 
### VI. DETAILS ON \textit{AB INITIO} CALCULATIONS

| Defect          | Charge and spin state | ZPL (eV) | $\Delta Q$ | HR | ZPL (eV) | $\Delta Q$ | HR |
|-----------------|-----------------------|----------|------------|----|----------|------------|----|
| $C_2CN - VN$   | $C_2CN - VN$ (S=3) (E=2.15 eV) | 0.2 | 1.3 | 7.45 | 0.96 | 1.76 | 19.7 |
| $C_2CN - VN$   | $C_2CN - VN$ (S=0) (E=0.0 eV) | 1.96 | 0.8 | 5.72 | 0.72 | 1.42 | 15.7 |
| $C_2CN - V_{N+1}^*$ | $C_2CN - V_{N+1}^*$ (S=2) | - | - | - | - | - | - |
| $C_2CN - V_{N-1}^*$ | $C_2CN - V_{N-1}^*$ (S=2) | - | - | - | 1.96 | 1.3 | 9.1 |
| $C_{2N}VN$     | $C_{2N}VN$ (S=2) | 2.08 | 1.083 | 7.16 | - | - | - |
| $C_{2N}VN$     | $C_{2N}VN$ (S=0) (E=0.0 eV) | 2.2 | 0.83 | 4.14 | - | - | - |
| $C_{2N}VN^1$   | $C_{2N}VN^1$ (S=3) (E=1.43 eV) | 1.7 | 0.72 | 3.82 | 1.07 | 0.41 | 1.29 |
| $C_{2N}VN$     | $C_{2N}VN$ (S=0) (E=0.0 eV) | 1.47 | 1.31 | 9.05 | - | - | - |
| $C_{2N}VN^1$   | $C_{2N}VN^1$ (S=3) (E=0.0 eV) | 0.9 | 0.29 | 0.635 | 1.17 | 0.8 | 4.99 |
| $C_{2B}VN$     | $C_{2B}VN$ (S=2) | 1.41 | 1.08 | 5.67 | 1.1 | 0.8 | 5.07 |
| $C_{2B}VN^1$   | $C_{2B}VN^1$ (S=0) | 0.77 | 0.61 | 3.2 | - | - | - |
| $C_{2B}VN$     | $C_{2B}VN$ (S=3) (E=0.64 eV) | 0.9 | 0.29 | 0.635 | 1.17 | 0.8 | 4.99 |
| $C_{2B}VN^1$   | $C_{2B}VN^1$ (S=0) (E=0.0 eV) | 0.7 | 0.9 | 5.56 | - | - | - |
| $C_{2B}VN$     | $C_{2B}VN$ (S=3) (E=0.64 eV) | 1.12 | 1.39 | 9.91 | 0.74 | 1.19 | 10.8 |
| $C_{2B}VN$     | $C_{2B}VN$ (S=3) (E=0.0 eV) | 1.39 | 3.05 | 45 | - | - | - |
| $C_{2B}VN^1$   | $C_{2B}VN^1$ (S=2) | 0.74 | 13.52 | 36.8 | - | - | - |
| $V_{BN}CN$     | $V_{BN}CN$ (S=3) | - | 2.7 | 0.41 | 0.3 | - | - |
| $C_{B}C_{N}VN$| $C_{B}C_{N}VN$ (S=3) (E=3.92 eV) | 1.37 | 0.92 | 10.5 | - | - | - |
| $C_{B}C_{N}VN^1$ | $C_{B}C_{N}VN^1$ (S=0) (E=0.0 eV) | 2.95 | 1.19 | 7.45 | - | - | - |
| $C_{B}C_{N}$   | $C_{B}C_{N}$ (S=2) | 1.67 | 0.26 | 1.26 | - | - | - |
| $C_{B}C_{B}$   | $C_{B}C_{B}$ (S=2) | 1.36 | 0.26 | 1.2 | - | - | - |
| $V_{NB}CB$     | $V_{NB}CB$ (S=3) | 1.75 | 0.53 | 1.50 | - | - | - |

**TABLE I.** Zero-phonon lines (ZPL), momentum displacements ($\Delta Q$) and Huang-Rhys factors (HR) of all studied defects. Here, $\alpha$ refers to the majority spin channel and $\beta$ to the minority spin channel. The energy $E$ in the second column gives the energy difference between the singlet and triplet state. It is only given for defects that show both a singlet and a triplet state. The ZPL energies for $V_{BN}CB$, $V_{2CN}$ and $V_{2CB}$ defects are calculated with the HSE06 functional, while we used the PBE functional for all other defect transitions.

**FIG. 10.** \textit{Detailed scatter plot for all studied defects.} The color of the symbols correspond to one defect, given by the legend. Within each color, we use different symbols for different defect transitions.
VII. FITTING AND COMPARISON WITH EXPERIMENT

In this section we outline the fitting procedure used to compare the polaron model to experiment. The fitting is done in two parts, in the first we extract the width of ZPL, the second fits the inhomogeneous broadening about the ZPL associated to acoustic phonons. To do both of these fits, we consider the emission lineshape driven by an excitation laser with detuning $\Delta = 168$ meV. We also assume that the phonons decay on a much faster timescale than emission occurs, which allows us to ignore the excitation effects during the fitting procedure. This allows us to disregard the coherent driving term $\Omega_R \sigma_x / 2$ and the phonon dissipator $\mathcal{K}_{\text{PH}}$ in Eq. 5 and assume that the emitter is initially in its excited state.

A. Fitting the zero phonon line

To fit the ZPL, we restrict the experimental data to a frequency window $\pm 0.008$ eV around the measured ZPL. This allows us to ignore the phonon sideband contribution, fitting only the ZPL with only function $S_{\text{opt}}(\omega)$. For an emitter initially in its excited state, the ZPL spectrum reduces to a simple Lorentzian lineshape:

$$S_{\text{opt}}(\Delta \omega) \approx \frac{B^2}{2 \Gamma (\Gamma + \gamma)^2 + \Delta \omega^2}, \quad \text{(4)}$$

where $\Delta \omega$ is the detuning from the emitter frequency. After first normalising the data and the above expression to the peak of the ZPL, we do a least min-squared fit. Note that we can fit only a single rate, since $\Gamma$ and $\gamma$ combine to give a single width of the Lorentzian, thus we set $\gamma = 0$ without loss of generality. We find an optimal $\Gamma = 3.15$ meV with residual of $r = 0.098$.

B. Describing electron-phonon sidebands in PL

As discussed in the manuscript, we divide the phonon spectral density into two components $J_{\text{Ph}}(\omega) = J_{\text{FP}}(\omega) + J_A(\omega)$. The first contribution, $J_{\text{FP}}(\omega) = \sum_k S_k \delta(\omega - \omega_k)$, captures the phonons calculated from first principles, where $S_k$ is the partial Huang-Rhys factor associated with a phonon with frequency $\omega_k$. To move to a continuum limit version, we account for the natural lifetime of phonons in a material by approximating the $\delta$-functions in the definition of $J_{\text{Ph}}(\nu)$ with a Gaussian function $\delta(\omega) \approx \sqrt{\frac{\sigma}{2\pi}} \exp\left[-(\omega / \sqrt{2\sigma})^2\right]$, where $\sigma$ is the phonon broadening parameter. We choose the broadening parameter as $\sigma = 5$ meV, such that it phenomenologically reproduces features in the emission spectrum.

The second contribution to the phonon spectral density, $J_A(\omega)$, is associated to acoustic phonons, and leads to the inhomogeneous broadening around the ZPL, which is not captured by the first principle calculations. We assume this spectral density takes the form $J_A(\omega) = \alpha \omega c^{-2} \omega e^{-\omega^2 / \omega_c^2}$, where $\alpha$ and $\omega_c$ are left as fitting parameters. This form of spectral density is commonly used in the semiconductor quantum dot literature, where it describes bulk acoustic phonons. Similarly to the ZPL fits we restrict ourselves to a frequency window of $-0.06$ eV $< \Delta \omega < 0.01$ eV. In contrast to the ZPL fits, however, we use the full expression for the emission spectrum, including the full phonon sideband given in Section XII.C. The value of the optimal phonon parameters extracted from these fits changes depending on the defect. For C$_2$B we find $\alpha \omega_c^{-2} = 1214$ eV$^{-2}$ and $\omega_c = 0.0235$ eV, while for C$_2$B we find $\alpha \omega_c^{-2} = 1295$ eV$^{-2}$ and $\omega_c = 0.0202$ eV. It was not possible to obtain a fit for the acoustic phonon sideband for N$_C$B due to the discrepancy between the sideband produced by first principles calculations and the measured PL. For illustrative reasons, we use the acoustic phonon parameters associated to C$_2$N when plotting the theoretical N$_C$B PL.

Fig. 11 shows the fitted PL lineshapes for the three defects considered in the manuscript. We compare the cases where acoustic phonons are neglected (dashed) and included (solid). For the C$_2$N and C$_2$B defect complexes, we see improved agreement about the ZPL when acoustic phonons are included. N$_C$B remains are poor fit, with and without acoustic phonons. Notably, when acoustic phonons are included, we observe additional acoustic sidebands on the phonon replicas found from DFT calculations.

C. Theoretical photoluminescence emission spectroscopy

The model presented above, and the resulting fits, allow us to calculate the PLE directly from the full phonon model. We do this by varying the detuning of the continuous wave driving laser, $\Delta$, and calculating the emission
spectrum for each detuning. For the driven case, we consider the steady state emission spectrum, defined as:

$$S(\omega) = \text{Re} \left[ \lim_{t \to \infty} \int_0^{\infty} d\tau G(\tau) g^{(1)}_{\text{opt}}(t, \tau) \right], \quad (5)$$

where the integral over $t$ has been reduced to the steady state limit.

Fig. 12 shows the PLE for the three defects considered in the main manuscript.
Fig. 13 shows the photoluminescence for $C_{2B}V_{N}^{-1}[S = 3]$ which does not conform nicely with the experiment.

FIG. 13. Comparison of the experimental photoluminescence (blue) with the theoretical spectrum of $C_{2B}V_{N}^{-1}[S = 3]$ (red). The theoretical spectrum is calculated without acoustic phonons. The spectra in (a) and (b) are identical but plotted over different ranges.
VIII. EXTENDED LEVEL MECHANISM OF $\text{V}_{\text{N}}\text{C}_\text{B}$

![Diagram showing energy levels and transitions for singlet and triplet states of $\text{V}_{\text{N}}\text{C}_\text{B}$](image)

**FIG. 14.** Extended level mechanism of $\text{V}_{\text{N}}\text{C}_\text{B}$. The singlet system is shown on the left and the triplet system on the right. Emission from the triplet state is not possible by direct excitation because the ground state of the triplet state is not populated in equilibrium. However, optical excitation of the singlet system followed by an intersystem crossing (ISC) is possible. This requires laser detunings that are higher than $2.46 - 1.75 \text{ eV} = 0.71 \text{ eV}$. This is much larger than our experimental laser detunings from $\sim 150$ to $400 \text{ meV}$. 
Fig. 15 shows how background-corrected PLE intensities are obtained, by using the ZPL intensity as an example. We use an unrelated photoluminescence range with the same width as the ZPL to define a background intensity (grey curve in the central panel). To obtain the background-corrected ZPL intensity, we subtract this background intensity. The resulting background-corrected ZPL intensity is shown in the right panel of Fig. 15a. Similarly, we obtain the background-corrected intensities for several PSB, as shown in Fig. 15b and in the main text.

Fig. 15b shows the optical PSB intensities. In particular, the optical PSB intensities at one-phonon detuning (170 meV) and the ZPL intensity at two-phonon detuning (340 meV) show comparable strength. All these processes are two-phonon processes (see Methods of the main text).

Fig. 15c shows the acoustic PSB at detunings around 10 meV. The acoustic PSB intensity is lower than for the ZPL, since it is a two-phonon process (see Methods and discussion in the main text). For the background-corrected intensities, we observe an almost identical qualitative behaviour of the acoustic PSB and ZPL intensity.

FIG. 15. Background-correction of PLE intensities and acoustic PSB. (a) Background-correction of the ZPL intensity. The spectral ranges of ZPL and background are shown in the left panel, on top of the photoluminescence spectrum. The resulting PLE intensities are shown in the central panel and the background-corrected ZPL intensity in the right panel. The latter one is defined as the green ZPL intensity minus the grey background intensity. The photoluminescence spectrum in (a) is taken at a detuning of 168 meV. (b) Optical PSB intensities, labelled as in (a). In the right panel, the flipped photoluminescence spectrum is shown in blue. (c) Acoustic PSB intensity, labelling as in (a).
FIG. 16. **Comparison of ab initio calculations with further luminescent centres.** (a) Emitter B. Comparison of emission line shapes and photoluminescence (left column) and theoretical curves with ZPL intensity (right column). The Huang-Rhys factors for emission are shown as black bars in both columns. (b) Emitter C, labelling as in (b). The theoretical curves in the right columns of (b) and (c) are rescaled to match the ZPL intensity around 170 and 340 meV, respectively. Both photoluminescence and ZPL intensity are background-corrected as outlined in Supplementary Information II and IX, respectively.
XI. OPTICAL CHARACTERISATION

For optical characterisation, we use an objective (details below) to focus a laser onto the sample. For photoluminescence (PL), we use a continuous-wave (CW) laser with a photon energy of 2.37 eV. A helium flow cryostat is used for the low temperature measurements.

For PLE measurements at 10 K, we use a supercontinuum white light laser (78 MHz repetition rate) which is filtered down to a bandwidth of ~ 1 nm with a tunable laser line filter. In order to compensate for intensity changes at different excitation wavelengths, we adjust the integration time of the spectrometer (see Supplementary Information IV). For both photoluminescence (PL) and PLE measurements, the collected light is filtered by a longpass dichroic mirror (550 nm) and a 550 nm longpass filter. The filtered light is focused on the input slit of a spectrometer where the spectrum is obtained. The grating and detector information are given below.

For room temperature PL measurements, a 50X objective (NA = 0.6), a 150 lines/mm grating, and an EMCCD are used. The low-temperature PL and PLE experiments are performed in a home-made confocal microscope with a 50X objective (NA = 0.42), a 500 lines/mm grating, and a CCD detector. Furthermore, a spatial filter is used in front of the spectrometer for low-temperature measurements.
XII. MODELLING PHONON EFFECTS IN PHOTOLUMINESCENCE EMISSION FROM LUMINESCENCE CENTERS

A. The model Hamiltonian

We model the studied defect complex as a two level system (TLS) with ground state \( |g\rangle \) and excited state \( |e\rangle \), with splitting \( \omega_c \) (\( \hbar = 1 \)). The TLS is driven by a continuous wave laser with a frequency \( \omega_L \) and Rabi coupling \( \Omega \). The emitter couples to both a vibrational and optical environment, characterised by the Hamiltonian \[17\]:

\[
H(t) = \omega_c |e\rangle \langle e| + \Omega \cos(\omega_L t) \sigma_x + |e\rangle \langle e| \sum_k g_k (b_k^\dagger + b_{-k}^\dagger) + \sigma_z \sum_i \left( h_i^\dagger a_i^\dagger + h_i a_i \right) + \sum_i \omega_i a_i^\dagger a_i + \sum_k \nu_k b_k^\dagger b_k,
\]

(6)

where we have defined \( a_i^\dagger \) as the creation operator for a photon with energy \( \omega_i \), and \( b_k^\dagger \) as the creation operator for a phonon with energy \( \nu_k \) and wavevector \( k \). We have also introduced the system operators \( \sigma_x = \sigma^y + \sigma^z \) and \( \sigma = |g\rangle \langle e| \). The coupling to the vibrational and electromagnetic environments are characterised by their respective spectral densities: for the optical environment we make the standard quantum optics approximation that the coupling constants \( h_i \) are frequency independent, such that \( J_{EM}(\omega) \approx \frac{\Gamma}{2\pi} \), where \( \Gamma \) is the emission rate of the optical transition; the phonon spectral density takes the form \( J_{ph}(\nu) = \sum_k S_k \delta(\nu - \nu_k) \) where \( S_k = \omega_k^2 |g_k|^2 \) are the partial Huang-Rhys parameters, and contain contributions from phonons calculated through \textit{ab initio} methods and those fitted to the emission as detailed below.

We can simplify the above equation by making the rotating-wave approximation and moving to a frame rotating with respect to the laser frequency \( \omega_L \), yielding the Hamiltonian:

\[
H = \Delta |e\rangle \langle e| + \frac{\Omega}{2} \sigma_x + |e\rangle \langle e| \sum_k g_k (b_k^\dagger + b_k) + \sum_i \left( h_i^\dagger \sigma_i^\dagger e^{i\omega_L t} + h_i \sigma_i (e^{-i\omega_L t}) \right) + \sum_k \omega_k a_k^\dagger a_k + \sum_k \nu_k b_k^\dagger b_k,
\]

(7)

where \( \Delta = \omega_c - \omega_L \) is the detuning between the driving field and the exciton transition. This Hamiltonian forms the starting point of our analysis of the dynamical and optical properties of the defect.

B. Polaron theory for a driven emitter

In order to account for the strong coupling to the vibrational environment, we apply a polaron transformation to the global Hamiltonian, i.e. the unitary transformation \( U_P = |e\rangle \langle e| \otimes B_+ + |g\rangle \langle g| \), where \( B_\pm = \exp \left( \pm \sum_k \nu_k^{-1} g_k (b_k^\dagger - b_{-k}^\dagger) \right) \) are displacement operators of the phonon environment \[17\ [44 [45]. This transformation dresses the excitonic states with vibrational modes of the phonon environment. In the polaron frame, the Hamiltonian may be written as \( H_P = H_0 + H_1^{PH} + H_1^{EM} \), where

\[
H_0 = \tilde{\Delta} |e\rangle \langle e| + \frac{\Omega_R}{2} \sigma_x + \sum_i \omega_i a_i^\dagger a_i + \sum_k \nu_k b_k^\dagger b_k,
\]

\[
H_1^{PH} = \frac{\Omega}{2} (\sigma_x B_x + \sigma_y B_y), \quad \text{and} \quad H_1^{EM} = \sum_i h_i^\dagger \sigma B_+ a_i^\dagger e^{i\omega_L t} + \text{h.c.},
\]

(8)

where we have introduced the phonon operators \( B_x = (B_+ + B_- - 2B)/2 \), \( B_y = i(B_+ - B_-)/2 \), and the Frank-Condon factor of the phonon environment \( B = \text{tr}_B(B_\pm \rho_B) = \exp((-1/2) \sum_k \nu_k^{-2} |g_k|^2 \coth(\nu_k/k_BT)) \), with the Gibbs state of the phonon environment in the polaron frame given by \( \rho_B = \exp(-\sum_k \nu_k b_k^\dagger b_k/k_BT)/\text{tr} \left( \exp(-\sum_k \nu_k b_k^\dagger b_k/k_BT) \right) \).

Notice that the polaron transformation has dressed the operators in the light-matter coupling Hamiltonian, and renormalised the system parameters, such that \( \Omega_R = \Omega B \) and \( \tilde{\Delta} = \Delta - \sum_k \nu_k^{-1} g_k^2 \).

The dynamics of the electronic states of the emitter are described by a 2\textsuperscript{nd}-order Born Markov master equation \[48], where both the electromagnetic field and the transformed vibrational environment are perturbatively eliminated. The polaron transformation means that the vibrational interaction is included non-perturbatively in the interaction strength \[17]. We can use the fact that only terms quadratic in field operators are non-zero when traced with a Gibbs state, so that there will be no cross-terms between the vibrational and electromagnetic dissipators, such that the master equation can be written in two parts:

\[
\frac{\partial \rho(t)}{\partial t} = -i \left[ \tilde{\Delta} |e\rangle \langle e| + \frac{\Omega}{2} \sigma_x, \rho(t) \right] + \mathcal{K_{PH}}[\rho(t)] + \frac{\Gamma}{2} L_\sigma [\rho(t)] + \frac{\gamma}{2} L_{\sigma^*},
\]

(9)
where \( \rho(t) \) is the reduced state of the emitter, \( \hat{L}_\sigma[\rho] = 2\sigma\rho\sigma^\dagger - \{\sigma^\dagger\sigma, \rho\} \) is the Lindblad form dissipator for the electromagnetic environment, and similarly \( \hat{K}_{PH} \) describes the dissipation due to the vibrational environment. Note that we have also included a source of homogeneous broadening given by rate \( \gamma \), to account for experimental imperfections and other dephasing mechanisms such as charge noise. For the optical dissipator, we refer the reader to standard texts in quantum optics for the derivation of the optical component \([18]\), in the following section we outline the derivation of the phonon dissipator.

1. **Deriving the phonon dissipator**

Considering only the coupling to the vibrational modes, we move into the interaction picture with respect to the Hamiltonian \( \hat{H}_0 \), the interaction term becomes:

\[
\hat{H}_1^{PH}(t) = \frac{\Omega}{2}(\sigma_x(t)\hat{B}_x(t) + \sigma_y(t)\hat{B}_y(t)),
\]

where the interaction picture system operators are given by:

\[
\sigma_x(t) = \eta^{-2}\left[\hat{\Delta}\Omega_R(1 - \cos(\eta t))\sigma_z + (\Omega_R^2 + \hat{\Delta}^2\cos(\eta t))\sigma_x + \hat{\Delta}\eta\sin(\eta t)\sigma_y\right],
\]
\[
\sigma_y(t) = \eta^{-1}\left(\hat{\Omega}_R\sin(\eta t)\sigma_z + \eta\cos(\eta t)\sigma_y - \hat{\Delta}\sin(\eta t)\sigma_x\right),
\]

and we have defined the generalised Rabi frequency \( \eta = \sqrt{\hat{\Delta}^2 + \Omega_R^2} \). The interaction picture bath operators are found as \( \hat{B}_{x/y}(t) = e^{i\hat{H}_0 t}\hat{B}_{x/y}e^{-i\hat{H}_0 t} \), with \( \hat{B}_{x/y} \) defined above. In the Schrödinger picture and making the Born-Markov approximation in the polaron frame \([18]\), the dissipator describing the electron-phonon interaction is given by:

\[
\hat{K}_{PH}[\rho(t)] = -\frac{\Omega^2}{4}\int_0^\infty \left( [\sigma_x, \sigma_x(-\tau)\rho(t)]\Lambda_{xx}(\tau) + [\sigma_y, \sigma_y(-\tau)\rho(t)]\Lambda_{yy}(\tau) + \text{h.c.} \right) d\tau,
\]

where we have and introduced the phonon bath correlation functions as \( \Lambda_{xx}(\tau) = \langle \hat{B}_{x}(\tau)\hat{B}_{x}\rangle = B^2(e^{\varphi(\tau)} + e^{-\varphi(\tau)} - 2) \), \( \Lambda_{yy}(\tau) = \langle \hat{B}_{y}(\tau)\hat{B}_{y}\rangle = B^2(e^{\varphi(\tau)} - e^{-\varphi(\tau)}) \) which quantify the response of the phonon environment to the exciton dynamics. Taking the continuum limit over the phonon modes, these correlation functions can be described in terms of the polaron frame propagator \( \varphi(\tau) = \int_0^\infty d\nu \nu^{-2}J(\nu)[\coth(\nu/2k_B T)\cos(\nu\tau) - i\sin(\nu\tau)] \). We can simplify the form of the master equation by evaluating the integrals over \( \tau \), leading to:

\[
\hat{K}_{PH}[\rho_s(t)] = -\frac{\Omega^2}{4}\left( [\sigma_x, \chi_x\rho_s(t)] + [\sigma_y, \chi_y\rho_s(t)] + \text{h.c.} \right),
\]

where we have introduced the rate operators:

\[
\chi_x = \int_0^\infty \sigma_x(-\tau)\Lambda_{xx}(\tau)d\tau = \frac{1}{\eta^2}\left[\Delta \Omega_R (\Gamma^x_0 - \Gamma^y_0)\sigma_z + (\Omega_R^2 \Gamma^x_0 + \hat{\Delta}^2\Gamma^y_0)\sigma_x + \hat{\Delta}\eta\Gamma^x_0\sigma_y\right],
\]
\[
\chi_y = \int_0^\infty \sigma_y(-\tau)\Lambda_{yy}(\tau)d\tau = \frac{1}{\eta^2}\left[\Omega_R \Gamma^y_0\sigma_z - \hat{\Delta}\Gamma^y_0\sigma_x + \eta\Gamma^y_0\sigma_y\right],
\]

and defined the terms \( \Gamma^x_0 = \int_0^\infty \Lambda_{aa}(\tau)d\tau, \Gamma^y_0 = \int_0^\infty \Lambda_{aa}(\tau)\cos(\eta\tau)d\tau, \Gamma^a = \int_0^\infty \Lambda_{aa}(\tau)\sin(\eta\tau)d\tau \), with \( a \in \{x, y\} \). We may understand these terms as the rates at which transitions occur between the eigenstates of the system (i.e. the dressed states) induced by phonons. Qualitatively, \( \Gamma^a_0 \) and \( \Gamma^a \) describe processes where a polaron is formed during excitation of the emitter, resulting in an exchange of energy with the environment. In contrast, \( \Gamma^a \) leads to no net exchange of energy, inducing a pure dephasing type process.

Since we are operating in the polaron frame, the above master equation is non-perturbative in the electron-phonon coupling strength, capturing strong-coupling and non-Markovian influences in the lab frame, despite having made a Born Markov approximation. This provides us with a simple, intuitive, and computationally straightforward method for describing exciton dynamics in a regime where a standard weak coupling master equation would break down \([17]\).
C. Correlation functions and spectra for a driven emitter

We are interested in understanding the impact that phonon coupling has on the PLE spectrum, which can be calculated from the first-order correlation function $g^{(1)}(t, \tau)$. As shown in Ref. [30], the first-order correlation function in the polaron frame for the emitter is written in terms of the polaronic dipole operator $\sigma \equiv \sigma_B + B_\pm$, that is, the correlation function is $g^{(1)}_0(t, \tau) = \langle B_{-}(t + \tau) \sigma^\dagger(t + \tau) B_+(t) \sigma(t) \rangle$. In general, $B_{\pm}$ are many-body displacement operators that do not commute with system operators. However, in the regime that the polaron master equation is valid at second-order, we can factor this correlation function in the Born approximation, such that $g^{(1)}_0(t, \tau) \approx G(\tau) g^{(1)}_{\text{opt}}(t, \tau)$. There are two terms in this expression, the correlation function for the scattered field $g^{(1)}_{\text{opt}}(t, \tau) = \langle \sigma^\dagger(t + \tau) \sigma(t) \rangle$ describing the purely electronic transitions, and the phonon correlation function $G(\tau) = \langle B_{-}(\tau) B_+ \rangle = B^2 \exp(\varphi(\tau))$ which accounts for the relaxation of the phonon environment. This factorisation allows us to split the emission spectrum into two components $S(\omega) = S_{\text{opt}}(\omega) + S_{\text{SB}}(\omega)$, where $S_{\text{opt}}(\omega) = \text{Re}[B^2 \int_{0}^{\infty} dt \int_{0}^{\infty} g^{(1)}_{\text{opt}}(t, \tau) e^{i\omega \tau} d\tau]$ corresponds to purely optical transitions, and $S_{\text{SB}}(\omega) = \text{Re}[\int_{0}^{\infty} dt \int_{0}^{\infty} (G(\tau) - B^2) g^{(1)}_{\text{opt}}(t, \tau) e^{i\omega \tau} d\tau]$ is attributed to non-Markovian phonon relaxation during the emission process, and leads to the emergence of a phonon sideband [49].