







Optical lineshapes for orbital singlet to doublet transitions in a dynamical Jahn-Teller system: The NiV⁻ center in diamond

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We apply density functional theory to investigate interactions between electronic and vibrational states in crystal defects with multimode dynamical Jahn-Teller (JT) systems. Our focus is on transitions between orbital singlet and degenerate orbital doublet characterized by $E \otimes (e \oplus e \oplus \dots)$ JT coupling, which frequently occurs in crystal defects that are investigated for applications in quantum information science. We utilize a recently developed methodology to model the photoluminescence (PL) spectrum of the negatively charged split nickel-vacancy center (NiV⁻) in diamond, where JT-active modes significantly influence electron-phonon interactions. Our results validate the effectiveness of the methodology in accurately reproducing the observed 1.4 eV PL lineshape. The strong agreement between our theoretical predictions and experimental observations reinforces the identification of the 1.4 eV PL center with the NiV⁻ complex. This study highlights the critical role of JT-active modes in affecting optical lineshapes and demonstrates the power of advanced techniques for modeling optical properties in complex systems with multiple JT-active frequencies.

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I. INTRODUCTION

Electronic degeneracy occurs in molecular structures or point defects in solids with highly symmetric atomic configurations, leading to the intricate coupling between electronic and symmetry-lowering vibrational degrees of freedom known as the Jahn-Teller (JT) effect [1–4]. If the coupling is not too strong, the system exhibits a dynamical aspect, where there is no change in the local symmetry and no splitting of degeneracy, but rather an alteration in the nature of the vibronic states [5]. This phenomenon is known as the dynamical Jahn-Teller (DJT) effect [3].

The dynamic interplay between electronic and ionic degrees of freedom can influence specific, measurable properties of the electronic system [6]. Furthermore, the closely intertwined electronic and vibrational components can generate a distinct array of vibronic states, giving rise to specific features within emission or absorption spectra. The emergence of such spectral attributes was first discussed in the pioneering paper on the DJT effect by Longuet-Higgins *et al.* [3]. This research examined the lineshape of the orbital singlet A to orbital doublet E transition in an $E \otimes e$ DJT system. They used an effective single-degenerate-mode model to depict the motion along a symmetry-breaking direction, which

dynamically couples electronic states. In this fundamental description of the JT effect, they demonstrated that the lineshapes for $A \rightarrow E$ transitions exhibit two intensity peaks, a hallmark of a JT-active system. While this single-mode model correctly describes the general features of simple DJT systems, it raises the question of its precision in characterizing systems with many JT-active modes. In her theoretical work, O’Brien [7] showed that with strong vibronic coupling, the issue of many frequencies can be approximated by an effective model of a single-degenerate mode. She later affirmed that this simplification efficiently describes the optical lineshapes of the two-degenerate-mode system $E \otimes (e \oplus e)$ [8]. However, the effectiveness of the single-effective mode method is not guaranteed in cases of weak coupling; a multimode approach is necessary, as demonstrated by studies simulating the photoemission spectrum of C₆₀⁻ [9,10].

Recent advancements in exploring crystal defects as quantum systems for technological applications have sparked a renewed interest in the DJT effect within color centers [11–16]. A primary challenge in analyzing the DJT effect in such systems is the electron-phonon coupling to a continuum of vibrational frequencies. Therefore, theoretical investigations often employ the single-effective mode model to explore spectral and magnetic properties. In addition, when modeling optical sidebands in DJT systems involving many vibrational modes, the standard Huang-Rhys (HR) theory, developed for adiabatic states, is typically employed to capture contributions from JT-active modes [13,14,16]. A recent study [17]

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highlighted the limitations of both the single-mode model and HR theory in accurately simulating optical lineshapes by examining the absorption lineshape of the $A \rightarrow E$ triplet transition in the negatively charged nitrogen-vacancy (NV) center in diamond. In that work, some of the present authors developed a rigorous methodology based on density functional theory (DFT) calculations to overcome these limitations and accurately model multimode $E \otimes (e \oplus e \oplus \dots)$ DJT systems [17].

In this paper, we apply this recently developed methodology to elucidate the photoluminescence (PL) spectrum of the negatively charged split nickel-vacancy center (NiV^-) in diamond [16]. In the previous application of the method to the absorption spectrum of the negatively charged NV center in diamond [17], the JT coupling was minor relative to the contribution from electron-phonon coupling involving symmetry-preserving a_1 modes. While the theory did allow for obtaining the correct weight distribution in the absorption lineshape, the DJT effect did not yield any sharply visible spectral features from the JT-active modes. In the NiV^- case, however, the influence of JT-active modes with e_g symmetry is more than three times greater than that of symmetry-preserving a_{1g} modes, leading to noticeable JT-specific features in the optical lineshape that we are able to reproduce using our methodology. By comparing optical lineshapes derived from standard HR theory applied to JT-active modes against those obtained through rigorous treatment of DJT multimode systems, we demonstrate that HR theory alone cannot adequately explain the observed spectral features.

II. NiV^- CENTER IN DIAMOND

Nickel is a common impurity in diamond produced under high-pressure and high-temperature conditions, creating identifiable features that can be detected using optical and electron paramagnetic resonance methods [18–21]. A notable fingerprint of the nickel impurity is the 1.4 eV PL line [18], which is associated with the NiV^- center [16]. The atomic configuration of this system is depicted in Fig. 1(a). The impurity ion resides precisely at the inversion center between two adjacent vacancies, resulting in the point-group symmetry of the defect being D_{3d} , displaying spin-doublet configurations in both the ground and optically excited states [16] [Fig. 1(b)].

The molecular orbital model for this center can be constructed by considering the presence of six carbon dangling bonds surrounding the nickel atom and the contribution of five $3d$ atomic orbitals of Ni [16]. This atomic basis results in a total of 11 molecular orbitals. In the ground state, seven orbitals constitute filled closed shells located deep within the valence band. The highest energy orbital among these is a_{1g} [Fig. 1(c)], which is essential in the considered optical transition. The remaining four orbitals form two degenerate doublets with e_u and e_g symmetry within the band gap. The e_u orbitals are filled with three electrons, forming an orbital doublet with E_u symmetry. This state can be described by a single determinant wave function, as shown in Fig. 1(c). This E_u electronic state constitutes an $E_u \otimes (e_g \oplus e_g \oplus \dots)$ DJT system where e_g symmetry vibrational modes couple the components of degenerate electronic states (E_{ux} and E_{uy}).

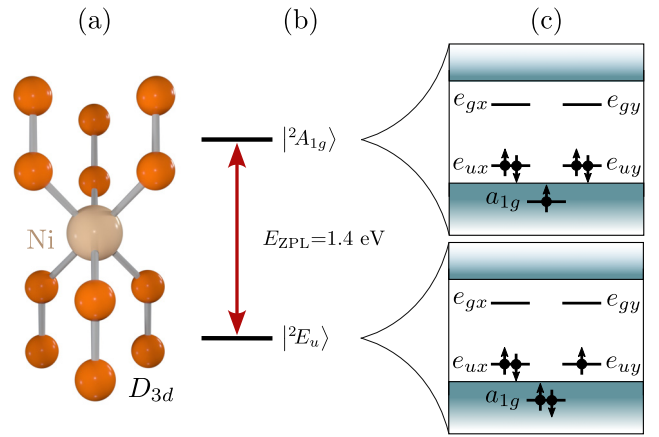


FIG. 1. (a) Atomic structure of the split nickel-vacancy (NiV^-) center in diamond. (b) Electronic level diagram of NiV^- . (c) Electronic configurations in the single-electron picture of $m_s = 1/2$ spin sublevels of the ground $|^2E_u\rangle$ and excited $|^2A_{1g}\rangle$ single-determinant wave functions.

In contrast, the optically excited state is an orbital singlet with A_{1g} symmetry. In this state, one of the spin minority a_{1g} electrons is promoted to the e_u orbital, resulting in a single-determinant wave function depicted in Fig. 1(c).

When considering the electron-phonon interaction during an optical $^2A_{1g} \rightarrow ^2E_u$ transition, the symmetry-breaking JT-active vibrational modes of e_g symmetry and the symmetry-preserving modes of a_{1g} symmetry participate in the transition. The participation of the a_{1g} symmetry modes can be described using the customary adiabatic HR theory [22].

The arrangement of optically active states in NiV^- is formally equivalent to a generalized problem of A -to- $E \otimes (e \oplus e \oplus \dots)$ transition [3,8], often observed in trigonal and octahedral symmetry systems. Therefore, in the subsequent theoretical description, the electronic E_u and A_{1g} , along with the vibrational e_g and a_{1g} symmetries, will be denoted by E , A , e , and a , emphasizing the applicability of theory across systems with similar symmetry.

III. VIBRONIC BROADENING OF OPTICAL EMISSION

The theory for vibronic broadening of optical lineshapes for $A \rightarrow E$ transitions and the analysis of multi-mode $E \otimes (e \oplus e \oplus \dots)$ JT systems is detailed in Refs. [17,23]. Here, we briefly review the formulas describing the PL lineshape of the A -to- E transition; we refer the reader to the original references for a complete derivation.

A. Vibronic states

As the initial state in the emission process (labeled by i) is an excited state characterized as an orbital singlet, we can express its vibronic wave function in an adiabatic form:

$$|\Psi_{i;kl}\rangle = \chi_{i;l}^a(\mathbf{Q}_a)\chi_{i;k}^e(\mathbf{Q}_e)|A\rangle, \quad (1)$$

where $\chi_{i;l}^a(\mathbf{Q}_a)$ and $\chi_{i;k}^e(\mathbf{Q}_e)$ are the harmonic components of the vibrational wave function, corresponding to the a - and e -symmetry modes, with the quantum numbers l and k labeling different harmonic excitations. \mathbf{Q} describes the set of

symmetry-adapted normal coordinates. The term $|A\rangle$ denotes the electronic wave function, which in the static adiabatic approximation depends only on the electronic degrees of freedom.

The vibronic wave function within the degenerate electronic manifold of the final (ground) state, labeled by f , corresponding to the JT-active state, is expressed as

$$|\Psi_{f;nm}\rangle = \chi_{f;n}^a(\mathbf{Q}_a)|\Phi_{f;m}\rangle, \quad (2)$$

where $\chi_{f;n}^a(\mathbf{Q}_a)$ represents the harmonic states of the modes with a symmetry. The JT component of the problem is captured by

$$|\Phi_{f;m}\rangle = \chi_{f;m}^{e,x}(\mathbf{Q}_e)|E_x\rangle + \chi_{f;m}^{e,y}(\mathbf{Q}_e)|E_y\rangle, \quad (3)$$

where $|E_x\rangle$ and $|E_y\rangle$ represent a basis that transforms as Cartesian irreducible representations of the degenerate doublet of electronic states, and $\chi_{f;m}^{e,\alpha}(\mathbf{Q}_e)$ are corresponding ionic prefactors that must be determined by solving the JT problem [17]. The quantum numbers n and m , respectively, label the harmonic and vibronic excitations of the system.

B. Emission lineshape

Within the zero-temperature limit ($T = 0$ K) of the Franck-Condon approximation, the normalized luminescence intensity $L(\hbar\omega)$ is expressed as [17]

$$L(\hbar\omega) = C\omega^3 A(\hbar\omega), \quad (4)$$

where C is a normalization constant, and $A(\hbar\omega)$ is the spectral function that holds the information about the shape of the phonon sideband.

In the case of $A \rightarrow E$ transition, the spectral function is described by a specific mathematical expression [17]:

$$A(\hbar\omega) = \int A_a(\hbar\omega - \hbar\omega')A_e(\hbar\omega')d(\hbar\omega'). \quad (5)$$

This equation represents a convolution of two spectral functions corresponding to a - and e -symmetry modes:

$$\begin{aligned} A_a(\hbar\omega) &= \sum_n |\langle \chi_{f;n}^a | \chi_{i;0}^a \rangle|^2 \delta(E_{ZPL} + \varepsilon_{f0}^a - \varepsilon_{fn}^a - \hbar\omega), \\ A_e(\hbar\omega) &= \sum_m [|\langle \chi_{f;m}^{e,x} | \chi_{i;0}^e \rangle|^2 + |\langle \chi_{f;m}^{e,y} | \chi_{i;0}^e \rangle|^2] \\ &\quad \times \delta(\varepsilon_{f0}^e - \varepsilon_{fm}^e - \hbar\omega). \end{aligned} \quad (6)$$

In this formulation, the terms $\varepsilon_{\alpha n}^\gamma$ represent the energy eigenvalues of the vibrational/vibronic quantum mechanical level n within the electronic state α , corresponding to the symmetry γ of the vibrational degrees of freedom. E_{ZPL} denotes the zero-phonon line (ZPL) energy.

C. Coupling to a modes

To simplify the estimation of overlap integrals $\langle \chi_{f;n}^a | \chi_{i;0}^a \rangle$ entering $A_a(\hbar\omega)$, we employ the equal-mode approximation [17,24]. This approach assumes that the vibrational modes of the initial state are identical to those of the final state, thereby reducing the problem of calculating the vibrational structure of the ground state alone. Within this approximation,

the evaluation of the spectral function $A_a(\hbar\omega)$ can be achieved using the generating function approach [17,22,25]:

$$\begin{aligned} A_a(\hbar\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} G(t) e^{-\gamma|t|} dt, \\ G(t) &= \exp \left[-\frac{iE_{ZPL}t}{\hbar} - S_a + \int e^{i\omega t} S_a(\hbar\omega) d(\hbar\omega) \right]. \end{aligned} \quad (7)$$

The function $G(t)$ is the generating function for luminescence, and parameter γ accounts for additional broadening effects not captured by the theory. The variable $S(\hbar\omega) = \sum_k S_k \delta(\hbar\omega - \hbar\omega_k)$ is the spectral density of the electron-phonon coupling, where $S_k = \omega_k \Delta Q_k^2 / (2\hbar)$ is the partial HR factor [26] of a -symmetry mode k , and ΔQ_k signifies the alteration of the equilibrium geometry upon optical transition along the direction of vibrational mode $\eta_{k,\alpha}$ (in mass-weighted form) of frequency ω_k . We calculate ΔQ_k by employing the force \mathbf{F}_α exerted on atom α of mass M_α as induced by the electronic transition [17]:

$$\Delta Q_k = \frac{1}{\omega_k^2} \sum_\alpha \frac{\mathbf{F}_\alpha}{\sqrt{M_\alpha}} \eta_{k,\alpha}. \quad (8)$$

D. Coupling to e modes

In the case of e symmetry modes, the spectral function $A_e(\hbar\omega)$ must be calculated by explicitly solving the vibronic problem $\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_{JT}$ for states described by Eq. (3), where [4]

$$\hat{\mathcal{H}}_0 = C_z \sum_{k;\gamma \in \{x,y\}} \left(-\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_{k\gamma}^2} + \frac{1}{2} \omega_k^2 Q_{k\gamma}^2 \right) \quad (9)$$

describes the motion within the harmonic potential and

$$\hat{\mathcal{H}}_{JT} = \sum_{k;\gamma \in \{x,y\}} C_\gamma \sqrt{2\hbar\omega_k^3} K_k Q_{k\gamma} \quad (10)$$

characterizes the linear JT interaction. Here, ω_k represents the angular frequencies of vibrations, derived as eigensolutions of the zero-order Hamiltonian [Eq. (9)], and K_k denotes the dimensionless vibronic coupling constants [8]. The index $k = 1, \dots, N$ encompasses all pairs of degenerate e -symmetry vibrations. The matrices C_γ act on orbital states, and in the Cartesian representation of degenerate orbitals have the following form [27]:

$$C_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad C_y = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad C_z = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

Following symmetry arguments from Refs. [3,8,17], we represent the JT Hamiltonian $\hat{\mathcal{H}}_{JT}$ in the basis of states of $\hat{\mathcal{H}}_0$, which are also eigenstates of the quasi-angular momentum $\hat{J} = \hat{J}_{el} + \hat{J}_{ph}$. Here, $\hat{J}_{el} = \frac{\hbar}{2} \hat{\sigma}_y$ acts on the orbital component of the wave function, whereas in the Cartesian representation $\hat{\sigma}_y$ is the Pauli matrix. $\hat{J}_{ph} = C_z \sum_k \mathcal{L}_k$ quantifies the total angular momentum of e symmetry harmonic modes, where $\mathcal{L}_k = \hbar(\hat{n}_{k+} - \hat{n}_{k-})$ represents the angular momentum operator for a k vibrational doublet. Here, $\hat{n}_{k\pm} = a_{k\pm}^\dagger a_{k\pm}$ defines the number operator for right- and left-hand phonons, expressed through second quantization operators

$a_{k\pm} = \frac{1}{\sqrt{2}}(a_{kx} \mp ia_{ky})$, with a_{kx} and a_{ky} directly linked to normal modes Q_{kx} and Q_{ky} . In this basis, the eigenstates of $\hat{\mathcal{H}}_0$ are denoted by $|n_1 l_1 \dots n_N l_N; E_{\pm}\rangle$, with orbital wave functions $|E_{\pm}\rangle = \frac{1}{\sqrt{2}}(|E_x\rangle \pm i|E_y\rangle)$ having quantum numbers $j_{\text{el}} = \pm \frac{1}{2}$. Here, $n_k = n_{k+} + n_{k-}$ represents the total number of phonons, and l_k is the angular momentum quantum number for each k vibrational doublet. The matrix elements of $\hat{\mathcal{H}}_0$ and $\hat{\mathcal{H}}_{\text{JT}}$ are then formulated as follows [17]:

$$\begin{aligned} &\langle n_1 l_1, \dots, n_N l_N; E_{\pm} | \hat{\mathcal{H}}_0 | n_1 l_1, \dots, n_N l_N; E_{\pm} \rangle \\ &= \sum_k \hbar \omega_k (n_k + 1), \end{aligned} \quad (11)$$

$$\begin{aligned} &\langle n'_1 l'_1, \dots, n'_N l'_N; E_- | \hat{\mathcal{H}}_{\text{JT}} | n_1 l_1, \dots, n_N l_N; E_+ \rangle \\ &= \sqrt{2} \sum_k K_k \hbar \omega_k \delta_{l'_k l_k + 1} \left[\prod_{j \neq k} \delta_{n'_j n_j} \delta_{l'_j l_j} \right] \\ &\quad \times \left[\sqrt{\frac{n_k - l_k}{2}} \delta_{n'_k n_k - 1} + \sqrt{\frac{n_k + l_k + 2}{2}} \delta_{n'_k n_k + 1} \right]. \end{aligned} \quad (12)$$

Since \hat{J} commutes with $\hat{\mathcal{H}}_{\text{JT}}$, the solution for $\hat{\mathcal{H}}$ can be found separately for each total quantum number $j = j_{\text{el}} + \sum_k l_k$, taking the following form:

$$\begin{aligned} |\Phi_{f;m}\rangle &= \chi_{f;m}^{e,+}(\mathbf{Q}_e) |E_+\rangle + \chi_{f;m}^{e,-}(\mathbf{Q}_e) |E_-\rangle \\ &= \sum_{s=\{+,-\}} \sum_{\mathbf{nl}} C_{f;m;\mathbf{nl}}^s |n_1 l_1 \dots n_N l_N; E_s\rangle, \end{aligned} \quad (13)$$

where $C_{f;m;\mathbf{nl}}^{\pm}$ are coefficients obtained through diagonalization.

In this new basis, the bracketed term in Eq. (6) can be expressed as $|\langle \chi_{f;m}^{e,+} | \chi_{i;0}^e \rangle|^2 + |\langle \chi_{f;m}^{e,-} | \chi_{i;0}^e \rangle|^2$. To calculate these overlap integrals for e -symmetry vibrational modes, similarly to a modes, we use the equal-mode approximation, which assumes that the vibrational shapes and frequencies of the A orbital manifold are well-represented by the zero-order Hamiltonian of the ground state [Eq. (9)]. Furthermore, in the zero-temperature limit, these overlaps are calculated between the zero-phonon state of the excited manifold, denoted as $\chi_{i;0}^e = |00 \dots 0\rangle$, and all vibronic states of the E manifold. Given that $\sum_k l_k$ is conserved, only vibronic solutions where $j = \pm 1/2$ (with $j_{\text{el}} = \pm 1/2$ and $\sum_k l_k = 0$) are relevant for this analysis.

IV. FIRST-PRINCIPLES METHODS

The electronic structure and optical excitation energies of the NiV⁻ center in diamond were investigated through spin-polarized DFT. To calculate the excited state energy and geometry within the framework of Kohn-Sham (KS) DFT, we employed the delta-self-consistent-field (Δ SCF) method [28–30]. In this approach, an a_{1g} electron from the lower-lying occupied KS orbital was excited to an empty e_u orbital, as illustrated in Fig. 1(c). We utilized the r²SCAN functional [31], which combines the numerical efficiency of rSCAN [32] with the transferable accuracy of SCAN [33]. Notably, this functional has demonstrated excellent performance in capturing the structural and electronic characteristics of other deep-level defects in diamond [34]. Our calculations were conducted

within $4 \times 4 \times 4$ supercells, encompassing 512 atomic sites, with the Brillouin-zone sampling centered at the Γ point. The projector-augmented wave method was employed, utilizing a plane-wave energy cutoff of 600 eV. These calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) [35].

A. Zero-order vibrational modes

Determining vibrational modes within the E_u state, specifically pertaining to both a and e irreducible representations, requires an approach that excludes the influence of first-order ($\hat{\mathcal{H}}_{\text{JT}} = 0$) and higher-order JT couplings. To achieve this separation of contributions, we employ an *ab initio* methodology, as discussed in detail in Ref. [23].

In this approach, we consider an electronic configuration characterized by fractional KS orbital occupation, namely $a_{1g}^2 e_{ux}^{1.5} e_{uy}^{1.5}$. This electronic configuration approximates an ensemble state of two degenerate configurations ($a_{1g}^2 e_{ux}^1 e_{uy}^2$ and $a_{1g}^2 e_{ux}^2 e_{uy}^1$), effectively suppressing all JT interactions while preserving the inherent geometry associated with D_{3d} symmetry. Within this configuration, we employ the finite-difference method, as implemented in the Phonopy software package [36,37], to compute the vibrational structure, ensuring that the vibrational modes are well defined with respect to their irreducible representations.

B. Vibrational structure and relaxation profile in the dilute limit

Moderately sized supercells, which are computationally amenable to explicit DFT calculations, pose challenges in accurately capturing the vibrational structure of defects due to periodic boundary conditions and a limited number of vibrational degrees of freedom. To overcome these limitations and achieve high-accuracy and high-resolution lineshapes, we adopt an embedding methodology [17,22]. This approach relies on the short-range character of interatomic interactions and allows for the computation of vibrational structures within significantly larger supercells. More details about the embedding methodology are provided in Sec. 1 of the Supplemental Material [38].

To accurately capture the relaxation profile in the dilute limit, we assess the relaxation component ΔQ_k for each vibrational mode. This is achieved by employing Eq. (8), which utilizes forces that are already converged within the explicitly accessible supercell. These forces are then projected onto the vibrational modes of a system encompassing tens of thousands of atoms. This methodology captures the participation of low-frequency modes and provides a detailed description of the vibrational characteristics in these extensive systems.

C. Vibronic coupling parameters

In the linear JT theory, the adiabatic potential energy surface of the JT-active manifold takes the form of a *sombrero* hat [4]. This surface can be effectively investigated using DFT [17]. Allowing the relaxation along an e -symmetry direction from the high-symmetry configuration (obtained using the fractional occupation), one can monitor the geometry change $\Delta \mathbf{Q}_{\text{JT}}$ that quantifies vibronic coupling in the case of the linear JT coupling. By projecting $\Delta \mathbf{Q}_{\text{JT}}$ onto a pair

k of e -symmetry normal modes, one can estimate vibronic coupling pertaining to the k vibrational doublet:

$$K_k^2 = \frac{\omega_k \Delta Q_k^2}{2\hbar}, \quad (14)$$

where $\Delta Q_k^2 = \Delta Q_{kx}^2 + \Delta Q_{ky}^2$ describes the projection of k -doublet normal coordinates along the relaxation $\Delta \mathbf{Q}_{\text{JT}}$ and can be estimated by directly measuring displacements along each pair of normal coordinates or through the application of Eq. (8), which utilizes force-based calculations. This method allows the estimation of vibronic coupling constants using *ab initio* means.

D. Effective modes and diagonalization

Diagonalizing the Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{JT}}$, which includes many vibrational modes, presents a significant computational challenge due to the large size of the matrices. To address this complexity, we employ a strategy that utilizes a limited set of effective modes [17]. Initially, we define the density of the JT coupling as $K^2(\hbar\omega) = \sum_k K_k^2 \delta(\hbar\omega - \hbar\omega_k)$. We then approximate this density with $K_{\text{eff}}^2(\hbar\omega) = \sum_{n=1}^{N_{\text{eff}}} \bar{K}_n^2 g_\sigma(\hbar\bar{\omega}_n - \hbar\omega)$, where g_σ represents a Gaussian function characterized by a width σ . This approximation incorporates N_{eff} effective vibrations, each parameterized by a frequency $\bar{\omega}_n$ and a corresponding vibronic coupling strength \bar{K}_n^2 . The parameters \bar{K}_n^2 , $\bar{\omega}_n$, and σ are optimized to ensure that $K_{\text{eff}}^2(\hbar\omega)$ closely matches $K^2(\hbar\omega)$. This approach enables using fewer effective modes $N_{\text{eff}} \ll N$, making diagonalization more tractable. To ensure the reliability of the computed spectral functions, we monitor their convergence as a function of the number of effective modes. Additionally, when constructing the basis for \mathcal{H} , we limit the total number of excited phonons, $n_{\text{tot}} = \sum_k n_k$, to a predefined threshold and also track the convergence of our results as this limit increases.

V. RESULTS AND COMPARISON WITH EXPERIMENT

We calculated the optical excitation energy as the energy difference between the adiabatic potential energy surface minima of the 2E_u and ${}^2A_{1g}$ states. The obtained value of 1.36 eV aligns closely with the experimental ZPL energy of 1.40 eV and is consistent with previous theoretical results using the HSE functional, which yielded 1.37 eV [16].

A. Coupling parameters

To obtain the vibrational structure of the ground state and relaxation profiles required to compute electron-phonon coupling parameters for both HR and JT couplings, we employ the embedding methodology described in Sec. IV B. Details and parameters of this methodology, along with convergence tests, are provided in Sec. 1 of the Supplemental Material [38]. This approach enabled the modeling of a large $18 \times 18 \times 18$ supercell, which comprises 46 655 atoms. We calculated the spectral densities for two distinct types of interactions: the coupling for a -symmetry modes, represented by $S(\hbar\omega)$, and the JT coupling for e -symmetry modes, denoted by $K^2(\hbar\omega)$. To achieve a smooth description of the

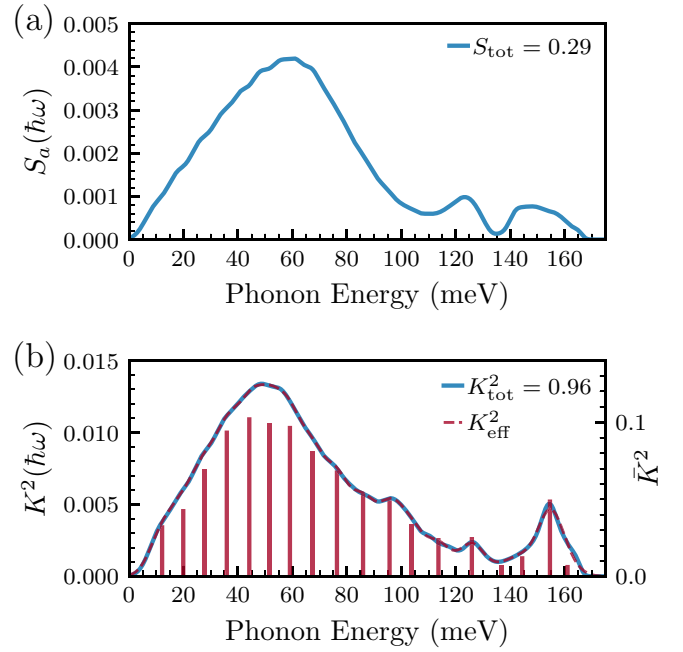


FIG. 2. Spectral densities for (a) HR electron-phonon coupling $S(\hbar\omega)$ in units of $1/\text{meV}$, associated with a_{1g} -symmetry phonons, and (b) JT linear coupling $K^2(\hbar\omega)$. In (b), red stems represent the effective modes with their respective frequencies ω_n and coupling strengths \bar{K}_n^2 . The red dashed line illustrates the spectral density obtained using the effective mode approximation $K_{\text{eff}}^2(\hbar\omega) = \sum_{n=1}^{N_{\text{eff}}} \bar{K}_n^2 g_\sigma(\hbar\bar{\omega}_n - \hbar\omega)$. Both panels also include the total parameters S_{tot} and K_{tot}^2 .

electron-phonon interaction, the delta functions were approximated using Gaussian functions with a variable width, σ , which linearly decreases from 3.6 meV at $\omega = 0$ to 1.5 meV at the highest energy phonon. Our results are illustrated in Fig. 2. Figure 2(a) shows the spectral density $S(\hbar\omega)$ for the HR electron-phonon coupling in units of $1/\text{meV}$, specifically linked to a_{1g} -symmetry vibrational modes. Figure 2(b) depicts the spectral density for the JT linear coupling $K^2(\hbar\omega)$. Figures 2(a) and 2(b) also include values for cumulative metrics: the total HR parameter $S_{\text{tot}} = \sum_k S_k$ and the total JT coupling $K_{\text{tot}}^2 = \sum_k K_k^2$.

Both S_k and K_k^2 define changes in the adiabatic potential energy surface and are directly linked to relaxation energies. The expression $\Delta E_a = \sum_k \hbar\omega_k S_k$ represents the relaxation energy along the symmetry-preserving direction consequent to the vertical transition $A \rightarrow E$. Conversely, $\Delta E_{\text{JT}} = \sum_k \hbar\omega_k K_k^2$ accounts for the JT relaxation, which describes the system's progression along the e -symmetry direction from a high-symmetry to a low-symmetry lowest-energy configuration. Our calculations yield $\Delta E_a = 18.8$ meV and $\Delta E_{\text{JT}} = 63.5$ meV, indicative of a highly pronounced JT contribution to the overall electron-phonon interaction.

B. Spectral functions

The spectral function $A_a(\hbar\omega)$ for a -symmetry modes, shown in Fig. 3(a), was calculated using the generating function approach [Eq. (7)]. The γ parameter was set to 0.35 meV to match the linewidth of the experimental ZPL. Notably,

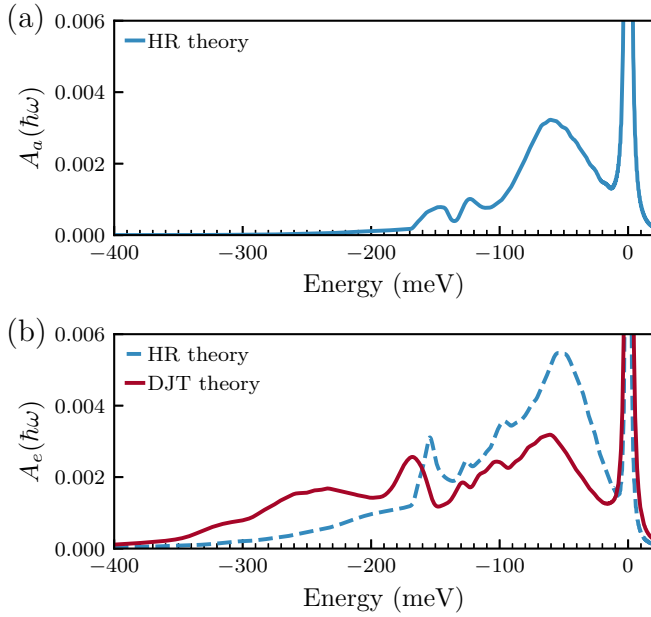


FIG. 3. (a) The spectral function $A_a(\hbar\omega)$ for a -symmetry modes; (b) the spectral function $A_e(\hbar\omega)$ for e -symmetry modes. In (b), we compare spectral functions derived from the dynamical Jahn-Teller theory (solid red line) and the Huang-Rhys theory (dashed blue line).

$A_a(\hbar\omega)$ exhibits a rapid decay to lower energies, becoming negligible for spectral features more than 170 meV below the ZPL. This result contrasts with the experimental lineshape extending to 300 meV below the ZPL [18] (see Fig. 4), indicating that symmetry-preserving modes alone cannot explain these experimental features.

We calculated the spectral function $A_e(\hbar\omega)$ for e -symmetry modes using two distinct methodologies, as depicted in Fig. 3(b). In the HR approach, e modes were treated analogously to symmetric a modes. This involves interpreting $\Delta\mathbf{Q}_{\text{JT}}$ as a displacement between two harmonic potentials, a method previously employed for NiV^- [16]. In contrast, the DJT treatment begins with the diagonalization of the vibronic Hamiltonian $\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_{\text{JT}}$ [refer to Eqs. (11) and (12)] using a selected set of effective modes. For the NiV^- case, it was determined that a count of $N_{\text{eff}} = 18$ effective modes,

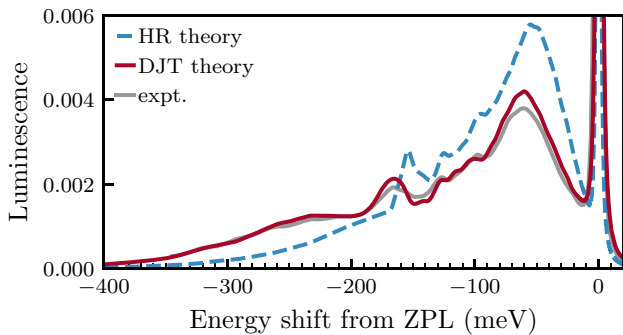


FIG. 4. Theoretical normalized luminescence lineshapes (in units of $1/\text{meV}$) calculated using Huang-Rhys theory (dashed blue line) and dynamical Jahn-Teller theory (solid red line), juxtaposed with the experimental spectrum from Ref. [18], recorded at 77 K.

indicated by red vertical lines in Fig. 2(b), suffices to achieve a spectral resolution of $\sigma = 5$ meV. Further convergence details are provided in Sec. 2 of the Supplemental Material [38]. Following the calculation of the vibronic states [Eq. (13)], we estimate the overlap integrals contributing to $A_e(\hbar\omega)$ [Eq. (6)] and approximate delta functions with Gaussian functions having a width of 5 meV.

Figure 3(b) clearly shows that the JT treatment yields substantially different results compared to the HR function. The DJT spectral function extends more than 300 meV below the ZPL, whereas HR theory produces pronounced features up to 170 meV below the ZPL but decays below this energy. It is evident that DJT theory is crucial for accurately describing the overall extent of the experimental lineshape.

C. Luminescence lineshapes

The final luminescence lineshapes, derived from $A_a(\hbar\omega)$ and $A_e(\hbar\omega)$ using Eqs. (4), are showcased in Fig. 4 alongside the experimental curve from Ref. [18], recorded at 77 K. Although the lineshape derived from HR theory is consistent with the findings of Ref. [16], it fails to capture the experimental trend, underscoring the limitations of the HR approach in describing optical features associated with dominant JT interactions. In contrast, the lineshape obtained from the multimode DJT method (solid red curve in Fig. 4) shows excellent agreement with the experimental spectrum, accurately capturing all spectral features as well as the intensity redistribution. By integrating the ZPL region (above -15 meV), the Debye-Waller factor is estimated to be 35% for the HR theory and 41% for the DJT theory. The DJT approach thus predicts a higher ZPL intensity, with a sideband that is more extended compared to that predicted by HR theory.

As an extension to our investigation of phonon sidebands, we employed the multimode vibronic solution detailed in Eq. (13) to calculate the Ham factor p [6] for the lowest vibronic state, which influences spin-orbit interaction in DJT systems. This factor quantifies the reduction in purely electronic spin-orbit splitting, λ_0 . Under the assumption of stationary ions, the intrinsic splitting λ_0 is estimated for electronic orbitals. In contrast, the experimentally observed coupling derived from vibronic states is represented by $\lambda = p\lambda_0$. The formula for p is given by $p = \sum_{\mathbf{nl}} |C_{f,m\mathbf{nl}}^+|^2 - \sum_{\mathbf{nl}} |C_{f,m\mathbf{nl}}^-|^2$ [14]. We compute a value $p = 0.157$. The result obtained with the single-mode approximation [16] was $p = 0.124$. The similarity in these values indicates that, at least for the case of the NiV^- center in diamond, a multimode analysis may not be crucial for effectively capturing the spin-orbit quenching.

VI. CONCLUSIONS

In this study, we addressed the challenge of accurately modeling systems where Jahn-Teller (JT) interactions play a dominant role. Utilizing a multimode dynamical JT (DJT) approach, we were able to capture the complex optical lineshapes observed in systems characterized by strong JT interactions, specifically in the negatively charged nickel-vacancy center (NiV^-) in diamond.

The methodology developed in Ref. [17], which was initially applied to a case where JT effects were relatively weak, has now been rigorously tested and validated in a scenario where these interactions have a pronounced impact on spectral features. The findings confirm that a multimode approach is crucial for reproducing accurate optical lineshapes and matching experimental observations.

Looking ahead, the implications of this refined JT methodology extend beyond merely reproducing spectral lineshapes. Future research should apply the methodology to *predicting* spectra, and explore how the approach can describe other electron-phonon related processes, such as nonradiative rates and temperature broadening of the zero-phonon line (ZPL). These directions promise to further our understanding of JT effects, potentially leading to enhanced control and manipulation of electronic and optical properties of defects and impurities in semiconductors as well as emitters and qubits applied in quantum technologies.

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