

Supplementary Information: Vibrationally resolved optical excitations of the nitrogen-vacancy center in diamond

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Supplementary Table 1. Convergence of vertical excitation energies (VEEs) with respect to the size of the supercell. VEEs (eV) of many-body excited states relative to the 3A_2 ground state of the NV^- center in diamond computed using TDDFT at the PBE level of theory. Results obtained with the $(2 \times 2 \times 2)$, the $(3 \times 3 \times 3)$ and the $(4 \times 4 \times 4)$ supercells are shown.

Excited state	$(2 \times 2 \times 2)$	$(3 \times 3 \times 3)$	$(4 \times 4 \times 4)$
3E	1.978	2.076	2.095
1A_1	1.283	1.334	1.341
1E	0.504	0.510	0.512

SUPPLEMENTARY NOTE 1: SUPERCELL SIZE CONVERGENCE

To check convergence with respect to the size of the supercell, we performed TDDFT calculations at the PBE level of theory for supercells with up to 512 atomic sites, corresponding to a supercell with $(4 \times 4 \times 4)$ repetitions of the unit cell. Vertical excitation energies (VEEs) of many-body excited states are summarized in Supplementary Table 1. We found that the difference in the VEEs calculated with the $(3 \times 3 \times 3)$ and the $(4 \times 4 \times 4)$ supercells is less than 0.02 eV, indicating that the $(3 \times 3 \times 3)$ supercell already yields relatively well converged results.

SUPPLEMENTARY NOTE 2: ANALYSIS OF VERTICAL EXCITATION ENERGIES

As discussed in the main text, we attribute the overestimate of the VEE of the 1A_1 state to the neglect of the double excitation Slater determinant $|a_1\bar{a}_1\rangle$. Here, we provide a simple estimate of the error based on perturbation theory: the coupling strength between the double excitation Slater determinant and the singlet state, $\langle a_1\bar{a}_1|\hat{H}|^1A_1\rangle$, can be estimated using the coefficient of the configuration $|a_1\bar{a}_1\rangle$, $c_{a_1\bar{a}_1}^{^1A_1}$ predicted by QDET calculations [1], and the energy difference, $E_{^1A_1} - E_{a_1\bar{a}_1}$; the correction to the energy of the singlet state, $E_{^1A_1}^{(2)}$, can then be estimated using the coupling strength and the difference $E_{^1A_1} - E_{a_1\bar{a}_1}$. Here $\hat{H}$ is the many-body electronic Hamiltonian.

QDET results [1] indicate that the weight of the $|e_x\bar{e}_x\rangle$ and $|e_y\bar{e}_y\rangle$ configurations in the 1A_1 state is $\left|c_{e_x\bar{e}_x}^{^1A_1}\right|^2 + \left|c_{e_y\bar{e}_y}^{^1A_1}\right|^2 = 0.938$ (see Supplementary Table 2), while the weight of $|a_1\bar{a}_1\rangle$ and other configurations with higher energies amounts to 0.062 [1]. For simplicity we assume the weight of $|a_1\bar{a}_1\rangle$ configuration is 0.062, corresponding to $\left|c_{a_1\bar{a}_1}^{^1A_1}\right| = 0.25$ [1]. The energy of the $|a_1\bar{a}_1\rangle$ configuration relative to the 3A_2 ground state is 7.33 eV, estimated using Kohn-Sham orbital energies at

Supplementary Table 2. Contribution of Slater determinants to the many-body electronic states of the NV^- center in diamond. Contribution of single and double excitation Slater determinants (%) to the many-body electronic states, as obtained from TDDFT and QDET calculations. Slater determinants are denoted in the hole notation, and the contributions are given in terms of the coefficients defined in equation (1) of the main text.

	Slater det.	TDDFT@PBE			TDDFT@DDH			QDET		
		1E_x	1E_y	1A_1	1E_x	1E_y	1A_1	1E_x	1E_y	1A_1
Single Excitations	$ e_x\bar{e}_x\rangle$	45.1	–	50.0	41.9	–	49.8	44.9	–	46.9
	$ e_x\bar{e}_y\rangle$	–	45.1	–	–	41.9	–	–	44.9	–
	$ e_y\bar{e}_x\rangle$	–	45.1	–	–	41.9	–	–	44.9	–
	$ e_y\bar{e}_y\rangle$	45.1	–	50.0	41.9	–	49.8	44.9	–	46.9
	$ a_1\bar{e}_x\rangle$	4.0	1.1	–	5.9	–	–	3.3	–	–
	$ a_1\bar{e}_y\rangle$	1.1	4.0	–	–	5.9	–	–	3.3	–
Double Excitations	$ e_x\bar{a}_1\rangle$	–	–	–	–	–	–	3.3	–	–
	$ e_y\bar{a}_1\rangle$	–	–	–	–	–	–	–	3.3	–
	$ a_1\bar{a}_1\rangle$	–	–	–	–	–	–	–	–	2.6

the DDH level of theory. It is thus 5.36 eV higher than the 1A_1 state. Within perturbation theory, the coefficient of the $|a_1\bar{a}_1\rangle$ configuration is

$$\left| c_{a_1\bar{a}_1}^{^1A_1} \right| \approx 0.25 \approx \left| \frac{\langle a_1\bar{a}_1 | \hat{H} | ^1A_1 \rangle}{E_{^1A_1} - E_{a_1\bar{a}_1}} \right|. \quad (1)$$

With the estimated $E_{^1A_1} - E_{a_1\bar{a}_1} = -5.36$ eV, we have $|\langle a_1\bar{a}_1 | \hat{H} | ^1A_1 \rangle| \approx 1.34$ eV. Therefore the second order correction to the energy is

$$E_{^1A_1}^{(2)} = \frac{|\langle a_1\bar{a}_1 | \hat{H} | ^1A_1 \rangle|^2}{E_{^1A_1} - E_{a_1\bar{a}_1}} \approx -0.34 \text{ eV}. \quad (2)$$

Using this correction to estimate the energy of the 1A_1 state we obtain 1.64 eV, which is in good agreement with the experimentally inferred zero-phonon absorption energy of $1.51 \sim 1.60$ eV [2] and the QDET VEE value of 1.270 eV [1].

Similarly, including the $|e_x\bar{a}_1\rangle$ Slater determinant in the expansion of the many-body wavefunction brings the VEE of the 1E_x state closer to the experimental and high-level theoretical results. For the 1E_x state, we have $E_{^1E_x} - E_{e_x\bar{a}_1} = -5.53$ eV, and $\left| c_{e_x\bar{a}_1}^{^1E_x} \right| = 0.18$ from QDET results. Hence we can estimate $\langle e_x\bar{a}_1 | \hat{H} | ^1E_x \rangle \approx 1.00$ eV and an energy correction $E_{^1E_x}^{(2)} \approx -0.18$ eV. Using this energy correction, the energy of the 1E_x state becomes 0.50 eV, in much better agreement with the experimentally inferred zero-phonon absorption energy of $0.34 \sim 0.43$ eV [3, 4] and the QDET

Supplementary Table 3. Geometry relaxation in excited states. Mass-weighted displacement ΔQ ($\text{amu}^{0.5} \text{ \AA}$) between the equilibrium geometries of the 3A_2 ground state (GS) and the excited states (ES), and the Franck-Condon (FC) shift E_{FC} (meV) in the ESs. Equilibrium geometries of the ESs are obtained using TDDFT or constrained occupations DFT (ΔSCF) with PBE and DDH functionals.

State	Method	Configuration ^a	ΔQ^b	E_{FC}^c
3E	TDDFT (PBE)	$\bar{a}_1\bar{e}$	0.583	187
3E	TDDFT (DDH)	$\bar{a}_1\bar{e}$	0.634	255
3E	ΔSCF (PBE)	$\bar{a}_1\bar{e}$	0.625	219
3E	ΔSCF (DDH) ^d	$\bar{a}_1\bar{e}$	0.635	246
1A_1	TDDFT (PBE)	$e\bar{e}$	0.111	17
1A_1	TDDFT (DDH)	$e\bar{e}$	0.094	17
1E	TDDFT (PBE)	$e\bar{e}$	0.415	64
1E	TDDFT (DDH)	$e\bar{e}$	0.413	105

^a Electronic configuration of many-body states in the hole notation.

^b $\Delta Q = \left(\sum_{\alpha=1}^{N_{\text{atoms}}} \sum_{i=x,y,z} M_{\alpha} (\mathbf{R}_{\alpha i, \text{ES}} - \mathbf{R}_{\alpha i, \text{GS}})^2 \right)^{0.5}$, where M_{α} is the mass of the α th atom, $\mathbf{R}_{\alpha i, \text{ES}}$ ($\mathbf{R}_{\alpha i, \text{GS}}$) is the equilibrium atomic structure of the ES (GS).

^c $E_{\text{FC}} = E_{\text{ES@GS}} - E_{\text{ES@ES}}$, where $E_{\text{ES@GS}}$ is the total energy of ES at the equilibrium geometry of the GS, and $E_{\text{ES@ES}}$ is the total energy of ES at the equilibrium geometry of the ES.

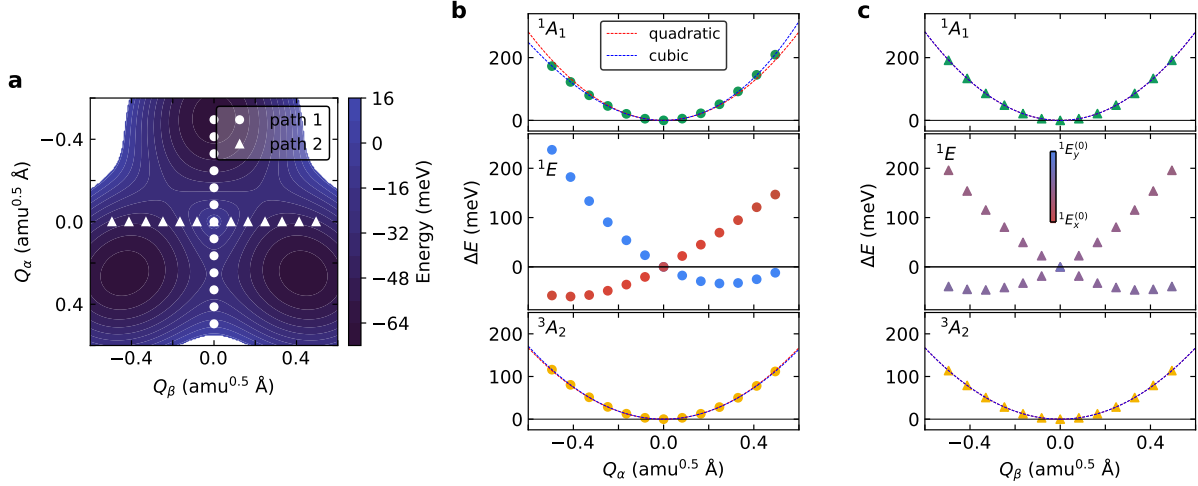
^d The $\bar{a}_1\bar{e}_x^{0.5}\bar{e}_y^{0.5}$ configuration was used to converge the ΔSCF (DDH) calculation.

VEE value of 0.463 eV [1]. For the 1E_y state, including the $|e_y\bar{a}_1\rangle$ configuration brings the value of VEE to 0.50 eV.

For completeness we note that QDET and TDDFT calculations are built on spin-unpolarized and spin-polarized ground state Kohn-Sham orbitals, respectively, and this difference has been neglected in our comparison.

SUPPLEMENTARY NOTE 3: GEOMETRY RELAXATION

To quantify the magnitude of geometry relaxation in excited states, we computed the mass-weighted atomic displacement between geometries of excited states and the 3A_2 ground state, ΔQ , and the Franck-Condon (FC) shift, E_{FC} , for many-body excited states, as shown in Supplementary Table 3. TDDFT results obtained at the PBE level are generally similar with those obtained at the DDH level. For the 3E excited state, TDDFT and constrained-occupations DFT (ΔSCF) yield comparable results. For the 1A_1 singlet state, TDDFT predicts a minor displacement and FC shift,



Supplementary Figure 1. Potential energy curves (PECs) of the NV^- center in diamond.

a Adiabatic potential energy surface (PES) of the lower branch of the 1E state. Q_α , Q_β configuration coordinates represent the collective motion of effective e phonon modes. **b-c** PECs of the 1A_1 state (up panel), the 1E states (middle panel) and the 3A_2 state (bottom panel) along path 1 and path 2 defined in **a**. Relative change in total energy, ΔE , computed at the PBE level of theory as a function of Q_α and Q_β is reported. The color of the 1E states represents the weight of $^1E_x^{(0)}$ and $^1E_y^{(0)}$ configuration. The PECs of the 1A_1 and 3A_2 states are fitted by quadratic functions (red dashed lines) and cubic functions (blue dashed lines).

indicating that the geometry of the 1A_1 state is close to that of the 3A_2 ground state. On the other hand, a more significant displacement and FC shift are found for the 1E state, indicating that its geometry is significantly displaced from that of the 3A_2 ground state.

SUPPLEMENTARY NOTE 4: NON-ADIABATIC COUPLING BETWEEN SINGLET STATES

The electron-phonon coupling entering the effective Hamiltonian discussed in the main text reads

$$\hat{H}_{e-ph} = \sum_{ij} \sum_{\lambda=\alpha,\beta} g_{ij,\lambda} \hat{c}_i^\dagger \hat{c}_j \left(\hat{b}_\lambda^\dagger + \hat{b}_\lambda \right), \quad (3)$$

where $g_{ij,\lambda}$ is the linear electron-phonon coupling strength between electronic state i , j and phonon mode λ . Considering C_{3v} symmetry and using e_x and e_y vibrational modes as collective variables

(CVs, which we call Q_α , Q_β), the electron-phonon coupling strength can be simplified as

$$g_{ij,\alpha} = \begin{pmatrix} 0 & \tilde{G} & 0 \\ \tilde{G} & G & 0 \\ 0 & 0 & -G \end{pmatrix}, \quad g_{ij,\beta} = \begin{pmatrix} 0 & 0 & \tilde{G} \\ 0 & 0 & -G \\ \tilde{G} & -G & 0 \end{pmatrix}. \quad (4)$$

$\tilde{G}$ is the coupling strength between the 1A_1 and the 1E states,

$$\tilde{G} = \sqrt{\frac{\hbar}{2\omega_e}} \left\langle ^1A_1 \left| \frac{\partial V}{\partial Q_\alpha} \right| ^1E_x \right\rangle = \sqrt{\frac{\hbar}{2\omega_e}} \left\langle ^1A_1 \left| \frac{\partial V}{\partial Q_\beta} \right| ^1E_y \right\rangle, \quad (5)$$

and G is the coupling strength between the 1E_x and 1E_y states,

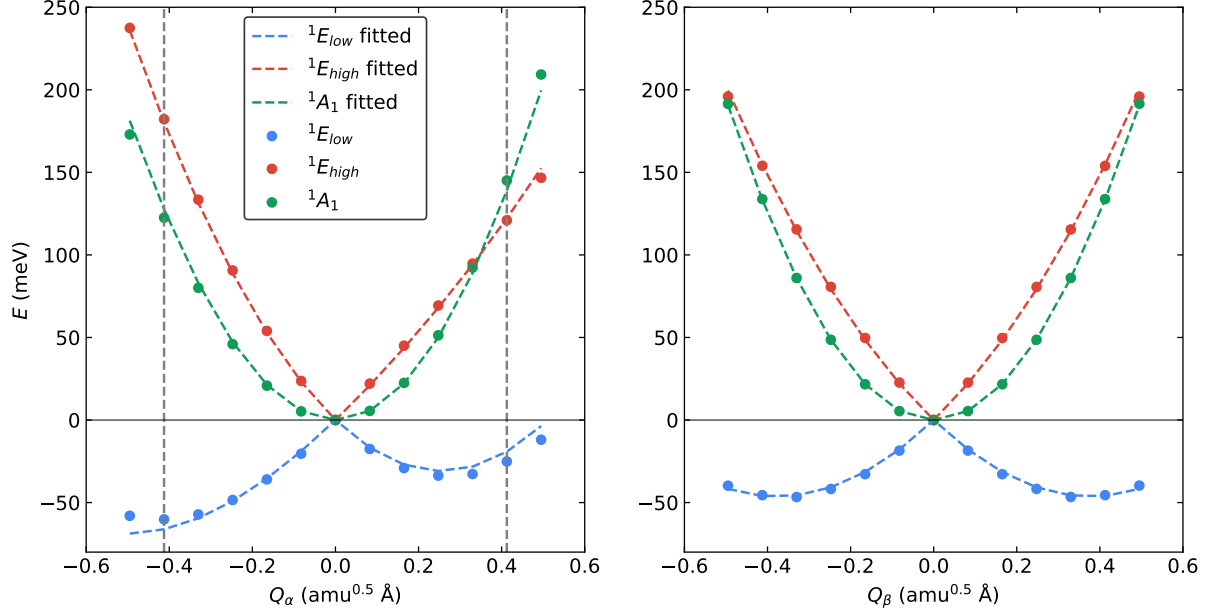
$$G = \sqrt{\frac{\hbar}{2\omega_e}} \left\langle ^1E_x \left| \frac{\partial V}{\partial Q_\alpha} \right| ^1E_x \right\rangle = -\sqrt{\frac{\hbar}{2\omega_e}} \left\langle ^1E_y \left| \frac{\partial V}{\partial Q_\alpha} \right| ^1E_y \right\rangle = -\sqrt{\frac{\hbar}{2\omega_e}} \left\langle ^1E_x \left| \frac{\partial V}{\partial Q_\beta} \right| ^1E_y \right\rangle. \quad (6)$$

Here V is the potential energy of the many-body system. The dependence of $\tilde{G}$ and G on Q_α and Q_β is neglected.

We computed the potential energy curves (PECs) of many-body electronic states along path 1 ($Q_\beta = 0$) and path 2 ($Q_\alpha = 0$) using TDDFT with the PBE functional, as shown in Supplementary Figure 1. Along path 1, we observe a local minimum for $Q_\alpha < 0$, a cusp at $Q_\alpha = 0$ and 60 meV higher than the minimum, and a saddle point for $Q_\alpha > 0$ with a barrier height of 26 meV. The PEC of the 1A_1 state has a curvature that corresponds to an effective phonon energy of 81 meV, which is 19 meV higher than that of the 3A_2 ground state. The PEC of the 1A_1 state is also slightly anharmonic as shown by the quality of a cubic function fit (blue dashed line) compared to a quadratic one (red dashed line).

By fitting the adiabatic PECs along path 1 and path 2 obtained by solving the effective Hamiltonian, to the PECs from first-principles calculations, we obtained the parameters for the effective Hamiltonian, i.e. $\hbar\omega_e = 63.0$ meV, $\tilde{G} = 133.2$ meV, and $G = 62.4$ meV, as shown in Supplementary Figure 2.

The non-adiabatic coupling can be analyzed in terms of the pseudo Jahn-Teller (PJT) interaction between the 1A_1 and the 1E states with strength $\tilde{G}$, together with the dynamic Jahn-Teller (DJT) interaction between two 1E states with strength G [5, 6]. Here we investigate the contribution of the PJT and DJT effect separately by setting either G or $\tilde{G}$ to zero along path 1 (Supplementary Figure 3) and path 2 (Supplementary Figure 4), respectively. The DJT effect only couples two 1E states. Along path 1 (path 2), the DJT effect shifts the local minima of the 1E states away from the $Q_\alpha = 0$ ($Q_\beta = 0$) point and results in the presence of a cusp. On the other hand, the PJT effect couples 1A_1 and 1E states. It increases the curvature of the 1A_1 PES; it also decreases

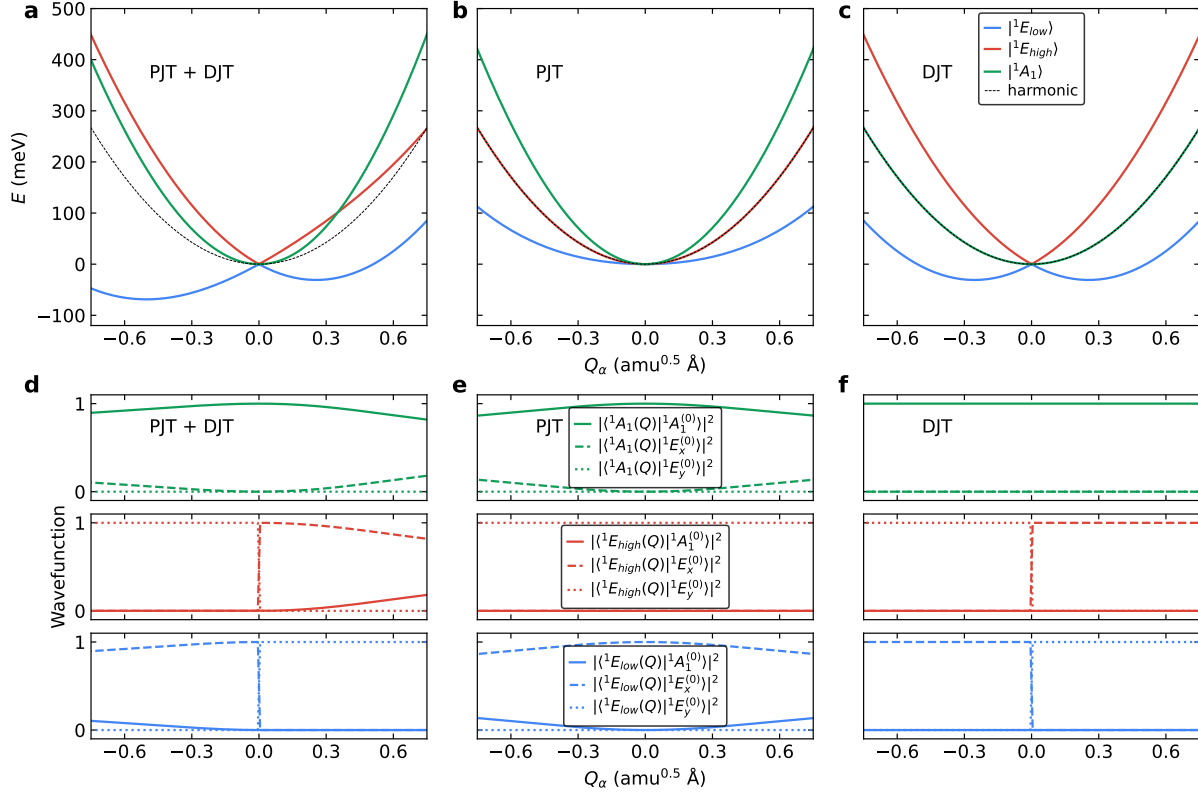


Supplementary Figure 2. Fitting of the potential energy curves (PECs) of the NV^- center in diamond. Potential energy curves (PECs) are obtained from first-principles calculations (dots) and by solving the effective Hamiltonian (dashed lines) along path 1 and path 2, as defined in Supplementary Figure 1. Minima of the 1A_1 state are arbitrarily shifted to 0 meV. The parameters of the effective Hamiltonian (see equation (2) of the main text) are obtained by best fitting the first-principles results.

the curvature of the lower branch of the 1E PESs that can be characterized as 1E_x (1E_y) state along path 1 (path 2), and is accompanied by the mixing of 1E_x (1E_y) wavefunctions with the 1A_1 wavefunction. Either the PJT or the DJT effect taken separately can preserve the axial symmetry of the PESs; Preservation of the axial symmetry is the typical result when electron-phonon coupling is considered only at the linear order. When the PJT and the DJT effects are considered at the same time, the axial symmetry of the PESs is reduced to C_{3v} symmetry.

SUPPLEMENTARY NOTE 5: HUANG-RHYS FACTORS AND SPECTRAL DENSITIES

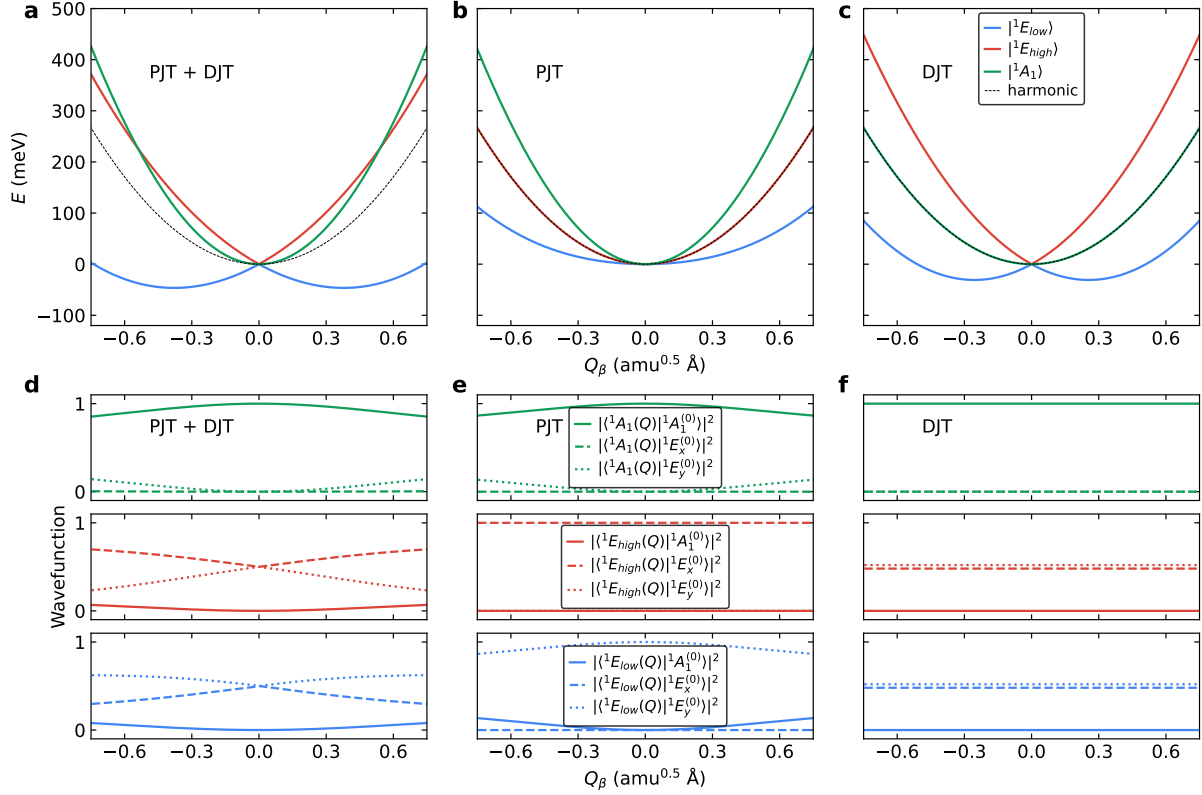
We compared the Huang-Rhys factors (HRFs) and Debye-Waller factors (DWFs) obtained using TDDFT at the PBE and the DDH level, as shown in Supplementary Table 4. Due to the unaffordable cost of computing phonon modes at the DDH level of theory, we approximated the DDH phonons as PBE phonons whose phonon energies are multiplied by a constant factor [8]. For both the $^3E \rightarrow ^3A_2$ transition and the $^1E \rightarrow ^1A_1$ transition, the best agreement with experiment



Supplementary Figure 3. Dynamic Jahn-Teller (DJT) and pseudo Jahn-Teller (PJT) effect. Potential energy curves (PECs) of the 1A_1 and 1E states along the path with $Q_\beta = 0$ obtained by solving the effective Hamiltonian for non-adiabatic coupling, considering (a) both the PJT and the DJT effect, (b) only the PJT effect, and (c) only the DJT effect. Minima of the 1A_1 curve are arbitrarily shifted to 0 meV for a better comparison. Decomposition of the wavefunctions of the 1A and 1E states onto the wavefunctions at $Q_\alpha = 0$ are displayed in the bottom panel, considering (d) both the PJT and the DJT effect, (e) only the PJT effect, and (f) only the DJT effect.

is obtained when the displacement computed at the DDH level of theory (DDH- ΔQ) was used. Using phonons computed at the PBE level of theory (PBE- ph) or DDH level of theory (DDH- ph) only results in minor changes.

Spectral density of electron-phonon coupling, $S(\hbar\omega)$, computed at different levels of theory are shown in Supplementary Figure 5. Peak positions of the spectral densities computed with DDH- ph are generally right shifted relative to those obtained with PBE. For the $^3E \rightarrow ^3A_2$ transition, all spectral densities have a similar shape, while the one computed with DDH- ΔQ has higher intensities than the one computed with PBE- ΔQ . The opposite is found for the $^1E \rightarrow ^1A_1$ transition, where the spectral densities computed with DDH- ΔQ have smaller intensities than the one computed with PBE- ΔQ . The spectral density for the $^1E \rightarrow ^1A_1$ transition is dominated



Supplementary Figure 4. Dynamic Jahn-Teller (DJT) and pseudo Jahn-Teller (PJT) effect.

Potential energy curves (PECs) of the 1A_1 and 1E states along the path with $Q_\alpha = 0$ considering (a) both the PJT and the DJT effect, (b) only the PJT effect, and (c) only the DJT effect. Minima of the 1A_1 curve are arbitrarily shifted to 0 meV for a better comparison. Decomposition of the wavefunctions of the 1A_1 and 1E states onto the wavefunctions at $Q_\beta = 0$ are displayed in the bottom panel, considering (d) both the PJT and the DJT effect, (e) only the PJT effect, and (f) only the DJT effect.

by the coupling with e type phonons, while the one of the ${}^3E \rightarrow {}^3A_2$ transition is dominated by the coupling with the a_1 type phonons. When using PBE phonons, we find that the spectral density for the ${}^1E \rightarrow {}^1A_1$ transition has a broad (sharp) peak at 73 meV (170 meV), resulting from the coupling with a quasi-local (local) e type phonon mode. Instead, the spectral density for the ${}^3E \rightarrow {}^3A_2$ transition mainly couples with the quasi-local a_1 type phonon mode, resulting in a broad peak at 60 meV. The 162 meV a_1 type local phonon mode is present in both the 1A_1 and 3A_2 states, but it does not contribute to the spectral density for the ${}^1E \rightarrow {}^1A_1$ transition. However, the 170 meV e type local phonon mode is only present in the 1A_1 state. The 170 meV e mode has an energy higher than optical phonons of diamond and couples weakly to the vibrations of the diamond lattice. The spectral density of the ${}^1E \rightarrow {}^1A_1$ transition generally shifts to higher energy direction compared to that of the ${}^3E \rightarrow {}^3A_2$ transition, implying an increase of phonon

Supplementary Table 4. Computed Huang-Rhys factors (HRFs) and Debye-Waller factors (DWFs). Total HRFs and DWFs (%) for ${}^3E \rightarrow {}^3A_2$ and ${}^1E \rightarrow {}^1A_1$ transitions computed at different levels of theory are compared with experiments [7]. Here DDH- ΔQ , PBE- ph denotes results based on the Huang-Rhys theory, evaluated using ΔQ computed at the DDH level and the phonon modes computed at the PBE level of theory. The DWF is calculated as $DWF = e^{-HRF}$. These results are obtained in the dilute limit, approximated by a $(12 \times 12 \times 12)$ supercell with 13824 atomic sites.

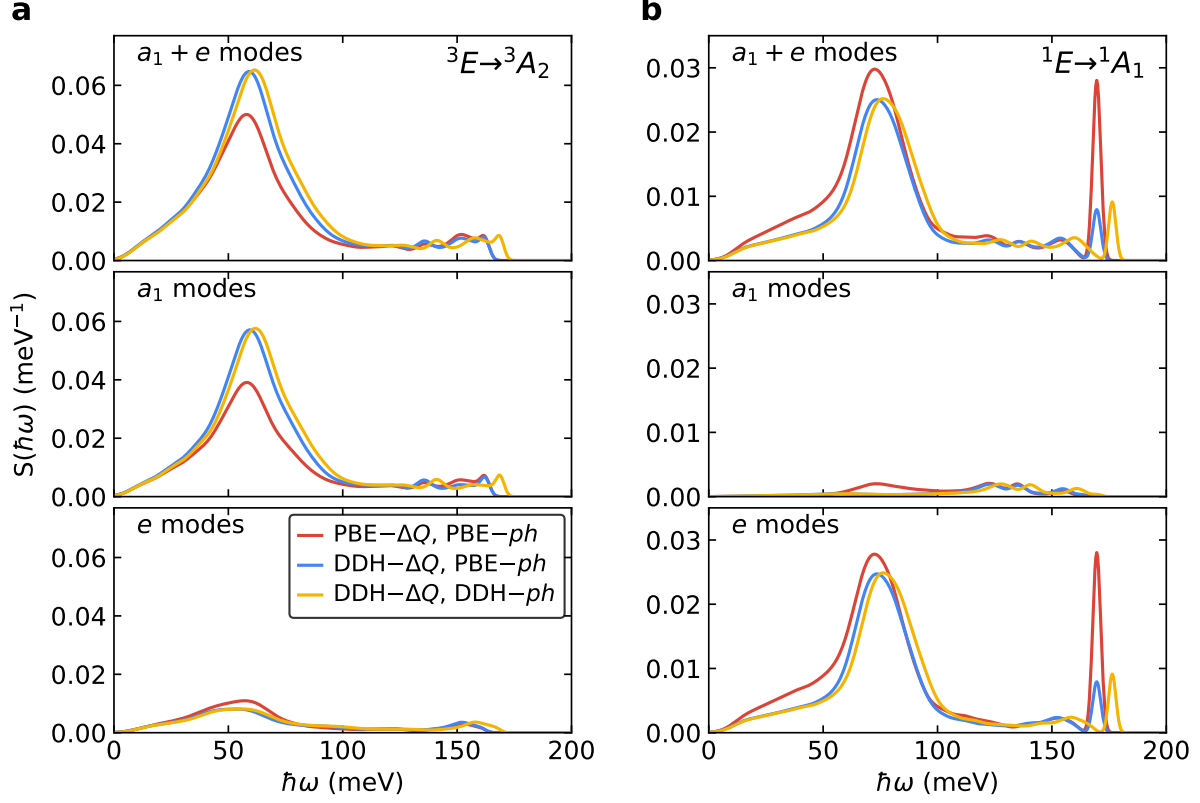
	${}^3E \rightarrow {}^3A_2$		${}^1E \rightarrow {}^1A_1$	
	HRF	DWF(%)	HRF	DWF(%)
PBE- ΔQ , PBE- ph	2.44	8.7	1.42	24
DDH- ΔQ , PBE- ph	2.97	5.1	1.08	34
DDH- ΔQ , DDH- ph	3.08	4.6	1.13	32
Expt. [7]	3.49	3.2	~ 0.9	~ 40

energies in the 1A_1 state compared with those of the 3A_2 state.

The photoluminescence (PL) spectrum of the ${}^3E \rightarrow {}^3A_2$ transition and the absorption spectrum of the ${}^1E \rightarrow {}^1A_1$ transition computed at different levels of theory are shown in Supplementary Figure 6. For both computed spectra, we obtained a better agreement with experiments when DDH- ΔQ was used. For the PL of the ${}^3E \rightarrow {}^3A_2$ transition, we obtained the best agreement with experiments when DDH- ph was used, while for the absorption of the ${}^1E \rightarrow {}^1A_1$ transition, the best agreement was obtained when PBE- ph was used. However, the difference caused by the choice of level of theory used for phonons and overall negligible.

SUPPLEMENTARY NOTE 6: PHONONS OF THE 3A_2 AND 1A_1 STATES

To quantify the differences between the phonons of the 3A_2 ground state and the phonons of the 1A_1 singlet state, we computed the atomic displacements between equilibrium geometries obtained for the ${}^3E \rightarrow {}^3A_2$ and for the ${}^1E \rightarrow {}^1A_1$ transitions. We then project the displacements onto the phonon modes of the 3A_2 state and the 1A_1 state and computed spectral densities of electron-phonon coupling $S(\hbar\omega)$, as shown in Supplementary Figure 7. For both the ${}^3E \rightarrow {}^3A_2$ and the ${}^1E \rightarrow {}^1A_1$ transition, the contributions of the e type phonon modes shift to higher energies when the phonon modes of the 1A_1 state are used, while the contributions of the a_1 type phonon modes remain almost unchanged. This finding implies that the a_1 type mode of the 1A_1 and the 3A_2 state are quite similar, which is consistent with the fact that the two states have similar geometries. The e -type mode of the 1A_1 state has energies apparently higher than those of the 3A_2 state, consistent

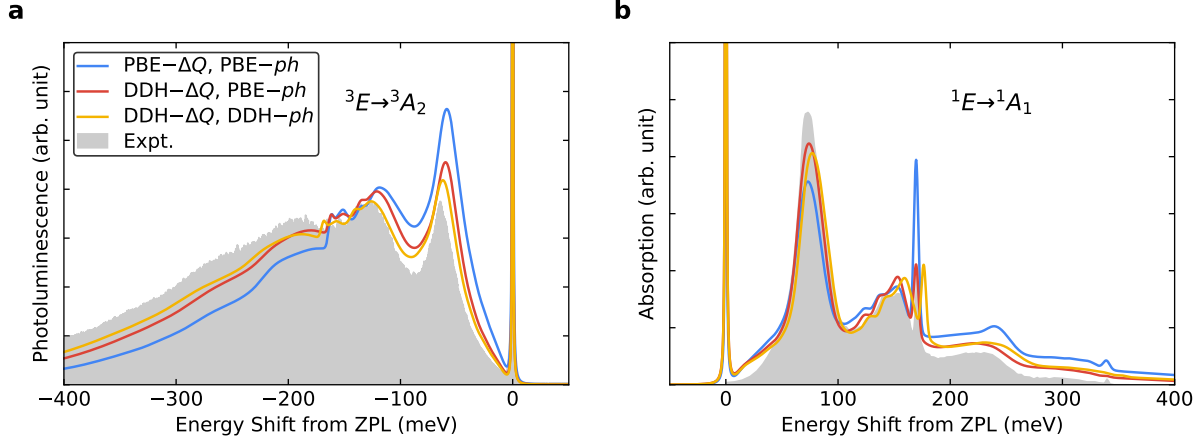


Supplementary Figure 5. Spectral densities of electron-phonon coupling. Spectral densities of electron-phonon coupling $S(\hbar\omega)$ for the ${}^3E \rightarrow {}^3A_2$ transition (a) and the ${}^1E \rightarrow {}^1A_1$ transition (b). Contributions of the a_1 type and e type phonon modes are shown in the middle and the bottom panels, respectively. Here DDH- ΔQ , PBE- ph denotes results based on the Huang-Rhys theory, evaluated using ΔQ computed at the DDH level and the phonon modes computed at the PBE level of theory. These results are obtained in the dilute limit, approximated by a $(12 \times 12 \times 12)$ supercell with 13824 atomic sites.

with the analysis based on non-adiabatic coupling between singlet states.

SUPPLEMENTARY NOTE 7: TREATMENT OF ANHARMONIC EFFECTS

As discussed in the main text, the non-adiabatic interaction between singlet states results in a noticeable anharmonicity of the PES of the 1A_1 state, which needs to be carefully taken into account in the calculations of the absorption line shape of the ${}^1E \rightarrow {}^1A_1$ transition. The formalism used to describe the optical process relies on the HR theory, which assumes that the harmonic approximation holds. Since the anharmonic effect is small, we can still use the HR theory and introduce anharmonicity perturbatively. Following Ref. [10], the spectral function for optical



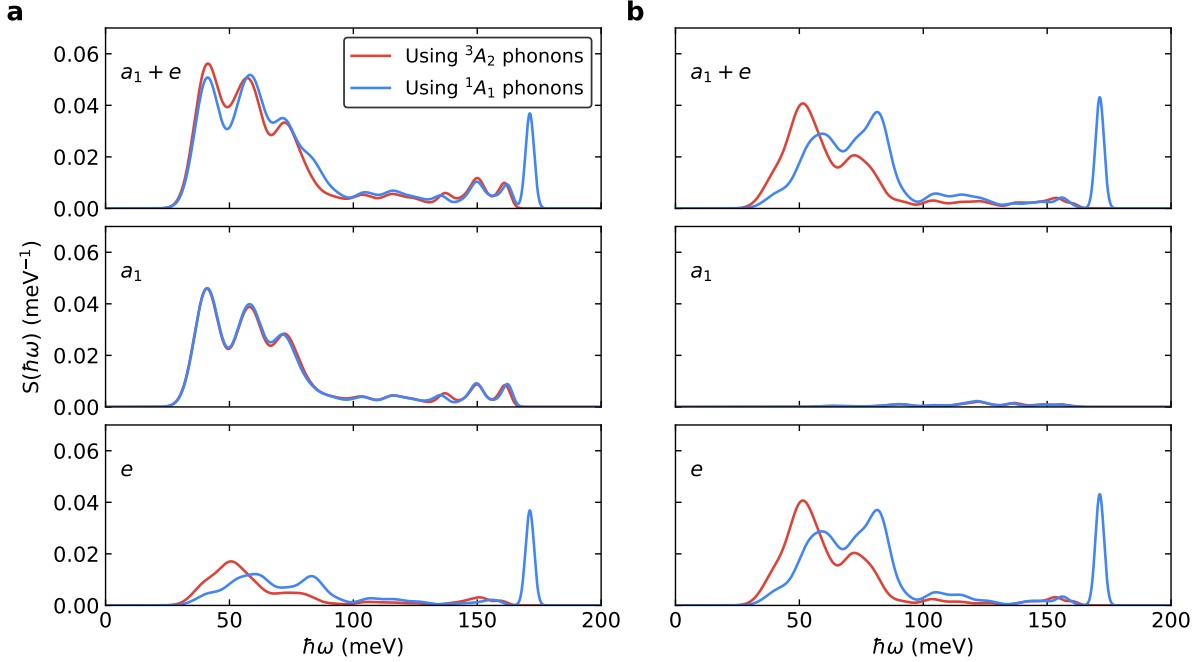
Supplementary Figure 6. Optical spectra. Photoluminescence (PL) spectra of the ${}^3E \rightarrow {}^3A_2$ transition (a) and absorption spectra of the ${}^1E \rightarrow {}^1A_1$ transition (b). Theoretical results are shown as solid lines while experimental results [7, 9] are shown as shaded areas. Here DDH- ΔQ , PBE- ph denotes the line shapes based on the Huang-Rhys theory, evaluated using ΔQ computed at the DDH level and the phonon modes computed at the PBE level of theory. These results are obtained in the dilute limit, approximated by a $(12 \times 12 \times 12)$ supercell with 13824 atomic sites.

Supplementary Table 5. Comparison of Huang-Rhys factors (HRFs) computed using forces and actual displacements. Total HRFs of the ${}^1E \rightarrow {}^1A_1$ transition computed using either $\Delta Q_{k,F}$ ($\sum_k S_{k,F}$) or ΔQ_k ($\sum_k S_k$) for the $(3 \times 3 \times 3)$ supercell. The ratio $r = \frac{a_3 \Delta Q}{a_2}$ reported here is computed based on fitting the results of the one dimensional configurational coordinate diagrams (see Supplementary Figure 8). Here DDH- ΔQ , PBE- ph denotes the line shapes based on the Huang-Rhys theory, evaluated using ΔQ computed at the DDH level and the phonon modes computed at the PBE level of theory.

	PBE- ΔQ , PBE- ph	DDH- ΔQ , PBE- ph
$\sum_k S_{k,F}$	1.33	1.03
$\sum_k S_k$	1.63	1.59
$\frac{\sum_k S_{k,F}}{\sum_k S_k}$	0.816	0.648
r	-0.065	-0.120
$(1 + 3r)$	0.805	0.640

absorption including the lowest order of anharmonic effects reads:

$$A_{\text{abs, an}}(\hbar\omega, T) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{i\omega t} G_{\text{abs, an}}(t, T) e^{-\frac{\lambda|t|}{\hbar}} dt, \quad (7)$$



Supplementary Figure 7. Spectral densities of electron-phonon coupling computed using different sets of phonon modes. Spectral densities $S(\hbar\omega)$ of the ${}^3E \rightarrow {}^3A_2$ transition (a) and the ${}^1E \rightarrow {}^1A_1$ transition (b). Red and blue lines are the spectral densities computed using the phonon modes of the 3A_2 state and the 1A_1 state, respectively. The entire spectral densities, contributions of the a_1 type phonons, and contributions of the e type phonons are shown in the upper, middle and the bottom panels, respectively. The partial Huang-Rhys factors used to evaluate the spectral densities are computed using atomic displacements between different states, which are obtained at the PBE level of theory with the $(3 \times 3 \times 3)$ supercell with 216 atomic sites.

where $G_{\text{abs, an}}(\hbar\omega, T)$ is the generating function including the lowest order of anharmonic effects

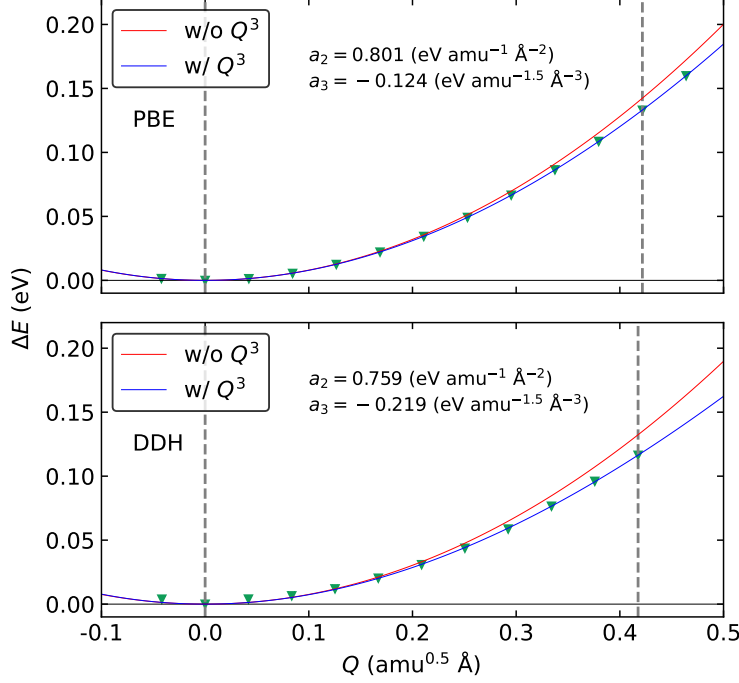
$$G_{\text{abs, an}}(t, T) = \exp \left[it \left(2 \sum_k S_k \omega_k r_k \right) \right] \exp \left[(1 + 3r_k) \left(\int_{-\infty}^{\infty} S(\hbar\omega) e^{-i\omega t} d(\hbar\omega) - \sum_k S_k \right) + \int_{-\infty}^{\infty} C(\hbar\omega, T) e^{-i\omega t} d(\hbar\omega) + \int_{-\infty}^{\infty} C(\hbar\omega, T) e^{i\omega t} d(\hbar\omega) - 2 \sum_k \bar{n}_k(T) S_k \right] \quad (8)$$

Here we have expanded the potential energy to third order with respect to the k th phonon mode

$$V_k(Q_k) = a_{k2} Q_k^2 + a_{k3} Q_k^3. \quad (9)$$

and we have defined r_k as the unitless ratio between the third and the second order coefficients of the expansion

$$r_k = \frac{a_{k3}}{a_{k2}} \Delta Q_k. \quad (10)$$



Supplementary Figure 8. Anharmonic effects of the potential energy curves (PECs). The PECs of the 1A_1 state along the linear path connecting the equilibrium geometries of the 1A_1 state and the 1E state computed using TDDFT with PBE (top panel) and DDH (bottom panel) functional. The energy difference relative to the local minimum, ΔE , is fitted as a function of Q as $\Delta E = a_2 Q^2 + a_3 Q^3$. Blue lines are obtained with the fitted function, while the red lines are obtained neglecting the $a_3 Q^3$ term.

It is evident that the anharmonicity affects the line shape in two ways. Firstly, it shifts the position of the zero-phonon line and also the phonon side bands from E_{ZPL} to $E_{ZPL} - 2 \sum_k S_k (\hbar \omega_k) r_k$. Further, it scales the HRFs. The anharmonic HR factor can be defined as

$$S_{k,\text{an}} = (1 + 3r_k) S_k. \quad (11)$$

The latter effect is responsible for changing the line shape of the transition.

In the following we show an efficient method to compute the anharmonic HR factor. We first compute, at the equilibrium atomic geometry of the 1E state, the force $\mathbf{F}_\alpha$ associated to the 1A_1 PES and exerted on atom α . We then compute the effective displacement associated to the k th phonon, $\Delta Q_{k,F}$, as

$$\Delta Q_{k,F} = \frac{1}{\omega_k^2} \sum_{\alpha=1}^N \frac{\mathbf{F}_\alpha \cdot \mathbf{e}_{k,\alpha}}{\sqrt{M_\alpha}} = \frac{1}{\omega_k^2} \langle \tilde{\mathbf{F}} | \mathbf{e}_k \rangle = \frac{\tilde{\mathbf{F}}_k}{\omega_k^2}, \quad (12)$$

where M_α is the mass of the α th atom, and ω_k and $\mathbf{e}_{k,\alpha}$ are the energy and eigenvector of the k th phonon mode, respectively. $\tilde{\mathbf{F}}_\alpha = \mathbf{F}_\alpha / \sqrt{M_\alpha}$. If we use the definition of $\tilde{\mathbf{F}}_k$ in terms of a derivative

of the potential, and we express the potential as in equations (9), we obtain:

$$\tilde{\mathbf{F}}_k = -\frac{\partial V_k(Q_k)}{\partial Q_k} \Big|_{Q_k=\Delta Q_k} = -2a_{k2}\Delta Q_k - 3a_{k3}\Delta Q_k^2 = -\omega_k^2\Delta Q_k \left(1 + \frac{3a_{k3}}{2a_{k2}}\Delta Q_k\right), \quad (13)$$

where we used the fact that $a_{k2} = \frac{1}{2}\omega_k^2$. Here, ΔQ_k is the actual displacement directly evaluated using the atomic displacements between the equilibrium geometry of the 1A_1 and the 1E states. Then the HRF can be evaluated as

$$\begin{aligned} S_{k,F} &= \frac{\omega_k \Delta Q_{k,F}^2}{2\hbar} \\ &= \frac{\omega_k}{2\hbar} \left(\frac{\tilde{\mathbf{F}}_k}{\omega_k^2} \right)^2 \\ &= \frac{\omega_k \Delta Q_k^2}{2\hbar} \left(1 + \frac{3a_{k3}}{2a_{k2}}\Delta Q_k \right)^2 \\ &= S_k \left(1 + 3\frac{a_{k3}}{a_{k2}}\Delta Q_k + O(a_{k3}^2) \right) \\ &\approx S_k(1 + 3r_k), \end{aligned} \quad (14)$$

which is exactly the anharmonic HR factor $S_{k,\text{an}}$ (equation (11)). In the last step we neglected the term containing a_{k3}^2 . Therefore, by evaluating the HRFs using $\Delta Q_{k,F}$ computed using equation (12), we automatically include anharmonic effects to the lowest order. We also note that if anharmonic effects are negligible, then by definition $S_{k,F} = S_k$.

Supplementary Table 5 reports the total HRFs computed using either forces or displacements. We also report the unitless ratio r of equation (10) evaluated based on the cubic fitting of the PECs of the 1A_1 along the one dimensional configurational coordinate diagram connecting the equilibrium geometries of the 1A_1 and 1E states. By comparing $\frac{\sum_k S_{k,F}}{\sum_k S_k}$ with $(1 + 3r)$, we can conclude that anharmonic effects are included when calculating HRFs using $\Delta Q_{k,F}$.

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