

Supplementary Information: ‘Strong spin-orbit quenching via the product Jahn-Teller effect in neutral group IV qubits in diamond’

Christopher J. Ciccarino,^{1,2,*} Johannes Flick,^{1,3,*} Isaac B. Harris,^{1,4}

Matthew Trusheim,¹ Dirk R. Englund,⁴ and Prineha Narang^{1,†}

¹*John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA*

²*Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, USA*

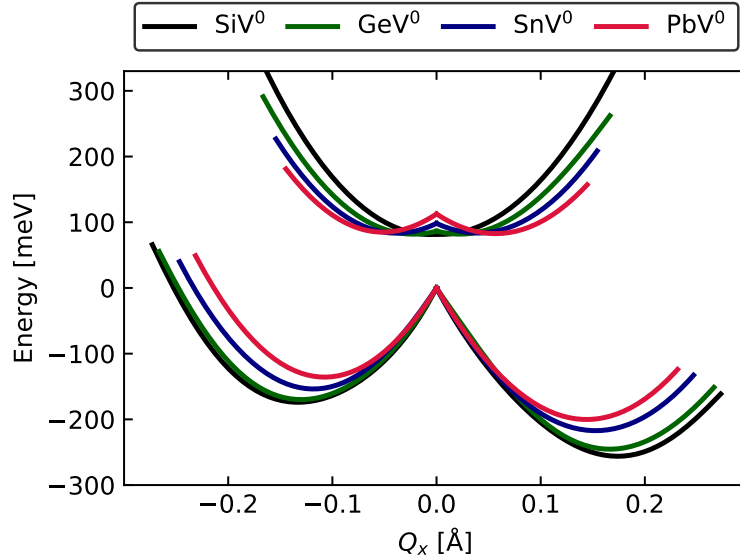
³*Center for Computational Quantum Physics, Flatiron Institute, New York, NY, USA*

⁴*Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA, USA*

(Dated: October 1, 2020)

SUPPLEMENTARY NOTE 1: ADDITIONAL DISCUSSION OF DEFECT CANDIDATES

The calculated potential energy surfaces (PES) for each of the group IV neutral defects are shown in Fig. 1. These serve as a starting point for our treatment of the coupled Jahn-Teller situation, with the extracted parameters listed in Table 1 of the main text.



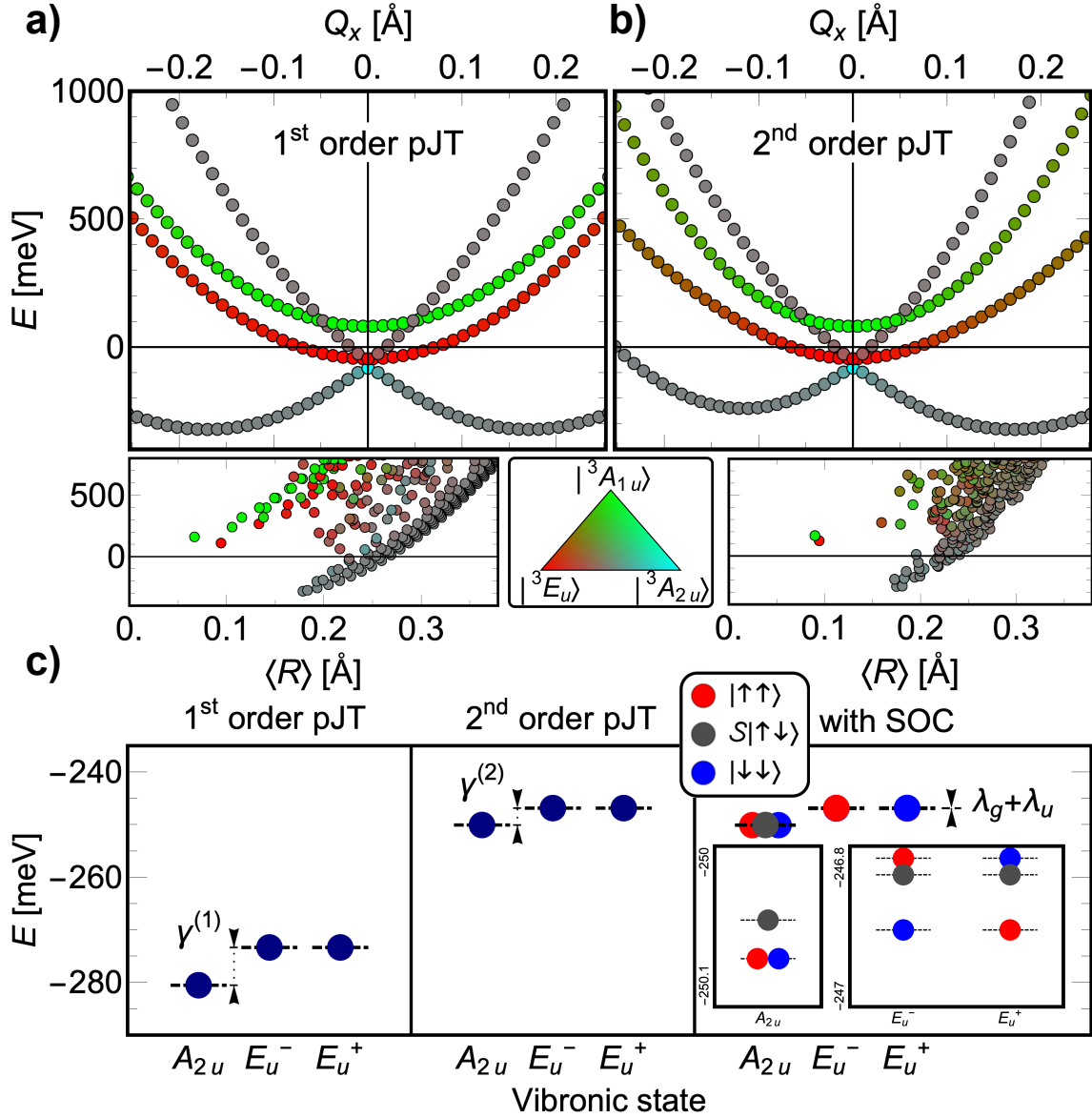
Supplementary Figure 1. Potential energy surfaces calculated using first principles density functional theory for each of the group IV neutral defect centers. The energy is scaled by the energy of the D_{3d} point for the lowest of the two potential energy surfaces for each of the defects studied.

We present the full vibronic solutions to the Jahn-Teller + static correlation interactions to first and second order in electron-phonon coupling for all four of the defect candidates. We also detail the lowest-energy A_{2u} and E_u states to both orders in coupling and additionally with the non-perturbative inclusion of SOC.

In all of the candidates studied, inclusion of second order pJT causes axial asymmetry about $Q_x = 0$ in the adiabatic solutions, as seen in Figs. 2-5(a,b). However, in general the electronic character of the solutions does not change dramatically between first and second order coupling. More noticeable qualitative differences can be seen in the vibronic solutions as a function of the expectation value of the position relative to the D_{3d} minima, $\langle R \rangle$. Here, the higher-lying states of the vibrational spectrum change quite dramatically for all of the defects studied. For instance, many of the higher energy states above $E = 0$ are expected to be found within 0.15 Å of the D_{3d} minima and have electronic characters corresponding to

* These authors contributed equally

† prineha@seas.harvard.edu

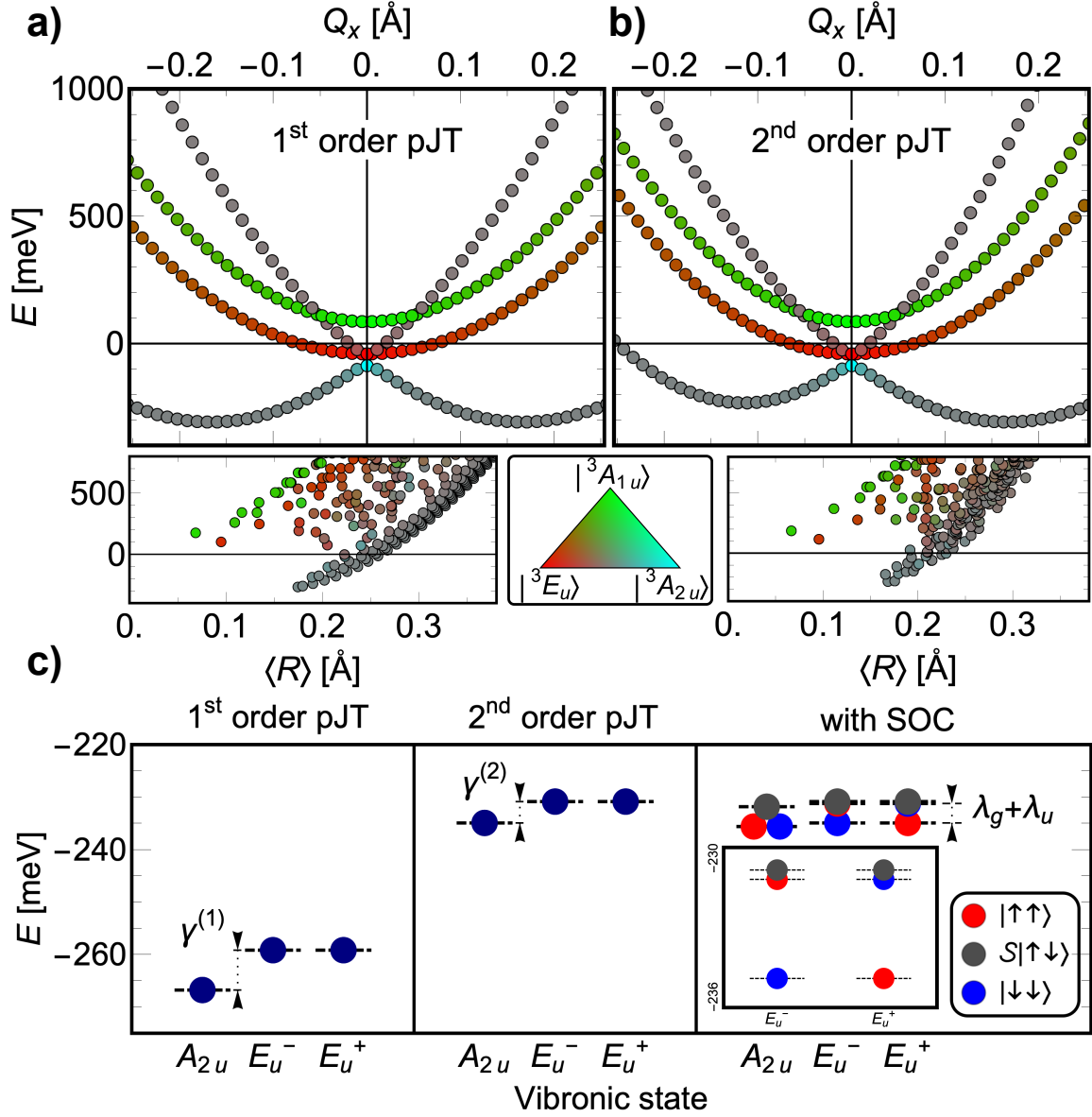


Supplementary Figure 2. (a) Adiabatic solutions to the coupled product Jahn-Teller + static correlation Hamiltonians including up to first order coupling in the pJT for SiV^0 . The undistorted electronic states are projected onto the symmetry-adapted wavefunctions by color, as shown in the triangular color map. Below the adiabatic solutions we show the full vibronic solutions plotted as a function of the nuclear position coordinate $R = \sqrt{Q_x^2 + Q_y^2}$ relative to the D_{3d} minima. (b) Same as (a) except we include up to second order couplings in the pJT. (c) Lowest vibronic solutions for SiV^0 considering (left to right) first order pJT, second order pJT and second order pJT in addition to spin-orbit coupling. The insets are zoomed in panels to reveal the m_s -resolved sublevels.

$|^3A_{1u}\rangle$ and $|^3E_u\rangle$ states. However in second order, many of these states disappear from the spectrum. Such a dramatic shift and deviation from behavior for first order coupling is additional evidence suggesting a first order treatment is not sufficient.

Panel (c) in Figs. 2-5 focus on the lowest energy solutions for our coupled pJT + static correlation situation, which the right-most plots also including the effects of spin-orbit coupling. The general trends for each of the group IV neutral candidates studied are similar when considering first vs. second order pJT. The splitting between the lowest vibronic solutions of symmetry A_{2u} and E_u , denoted by γ , decreases when second order coupling is included, with the γ values presented in Table 1 of the main text.

The more defect-dependent features are found when considering the effects of SOC. The coupling strengths $\lambda_{u/g}^0$ obtained

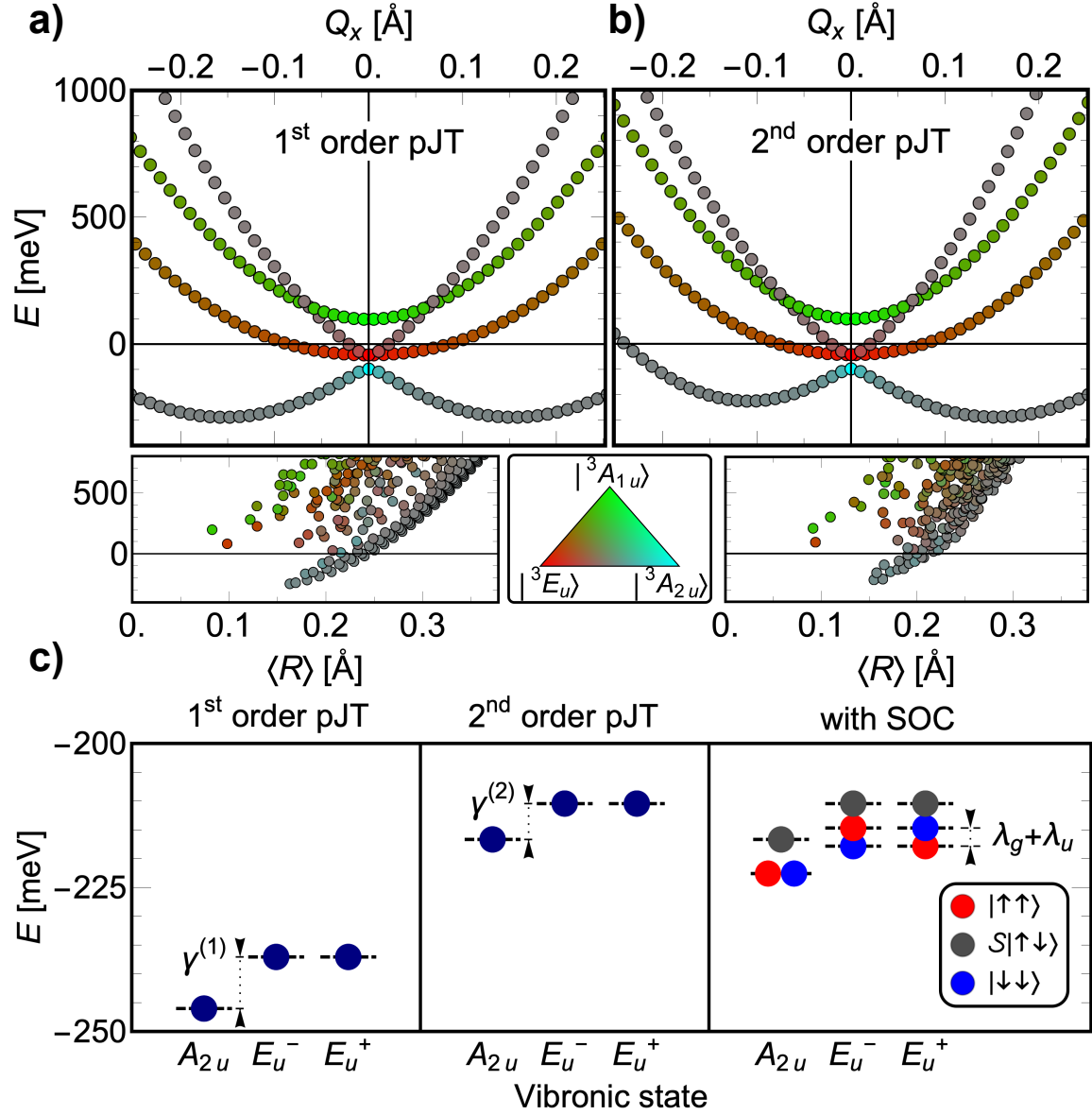


Supplementary Figure 3. Same format as Fig. 2, data for GeV^0 . Adiabatic solutions to the coupled product Jahn-Teller + static correlation Hamiltonians including up to first order coupling in the pJT for GeV^0 . The undistorted electronic states are projected onto the symmetry-adapted wavefunctions by color, as shown in the triangular color map. Below the adiabatic solutions we show the full vibronic solutions plotted as a function of the nuclear position coordinate $R = \sqrt{Q_x^2 + Q_y^2}$ relative to the D_{3d} minima. **(b)** Same as (a) except we include up to second order couplings in the pJT. **(c)** Lowest vibronic solutions for GeV^0 considering (left to right) first order pJT, second order pJT and second order pJT in addition to spin-orbit coupling. The inset is a zoomed in panel to reveal the m_s -resolved sublevels.

from first principles calculations grow with the mass of the defect substituent, with SiV having a total $\lambda_g^0 + \lambda_u^0 < 10$ meV while PbV having a total $\lambda_g^0 + \lambda_u^0 > 250$ meV. These coupling strengths are useful for understanding the observed trends when SOC is included.

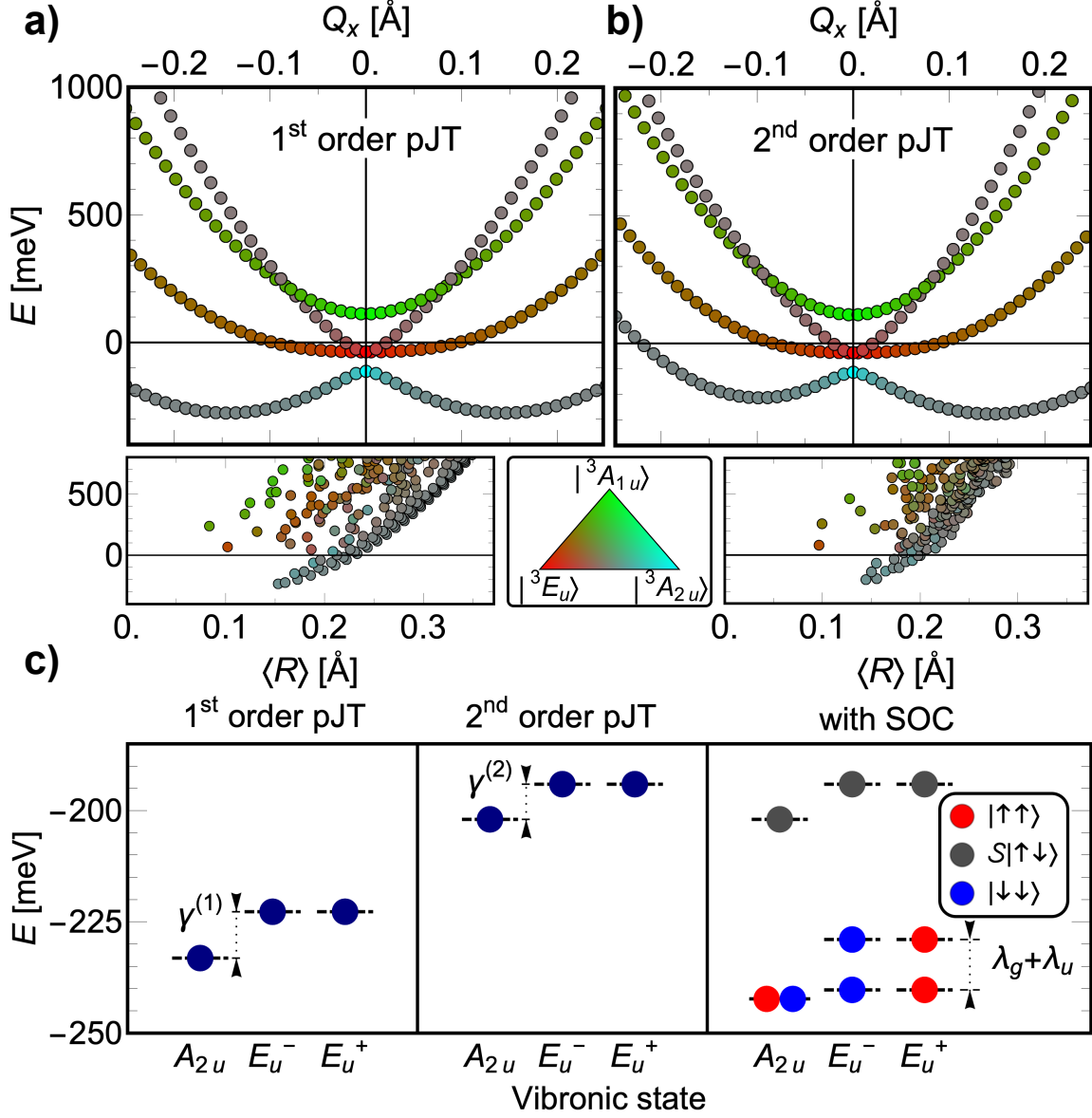
The effects of SOC are two-fold. First, $m_s = \pm 1$ are split oppositely by construction of the SOC Hamiltonian. Second, the absolute energy of the vibronic states shifts due to the non-perturbative treatment used. The first effect can be seen in the splitting between the m_s states of the E_u vibronic solutions. In the case of the absolute energy shift, this is visible in the energy difference between the $m_s = \pm 1$ and $m_s = 0$ A_{2u} states.

As discussed in the main text, the SOC effects are strongly suppressed because of the vibronic nature of the pJT solutions. As a result, the splittings $\lambda_g + \lambda_u$ are found to be smaller than 5% of what would be expected for a purely electronic system.



Supplementary Figure 4. Same format as Fig. 2 data for SnV^0 . Adiabatic solutions to the coupled product Jahn-Teller + static correlation Hamiltonians including up to first order coupling in the pJT for SnV^0 . The undistorted electronic states are projected onto the symmetry-adapted wavefunctions by color, as shown in the triangular color map. Below the adiabatic solutions we show the full vibronic solutions plotted as a function of the nuclear position coordinate $R = \sqrt{Q_x^2 + Q_y^2}$ relative to the D_{3d} minima. **(b)** Same as (a) except we include up to second order couplings in the pJT. **(c)** Lowest vibronic solutions for SnV^0 considering (left to right) first order pJT, second order pJT and second order pJT in addition to spin-orbit coupling.

In the case of SiV^0 , this splitting is therefore only about 0.1 meV. This means that the absolute energy shifts are also quite negligible. For the $E_u^\pm$ states, the ordering is $m_s = [\pm 1, 0, \mp 1]$, which is an ordering one would expect a perturbative treatment, e.g. like in the case of the NV^- [1]. The splittings grow for GeV^0 and the ordering indeed changes such that the $m_s = 0$ sublevel is highest in energy. This trend continues for the heavier defects SnV^0 and PbV^0 . In the case of PbV^0 , we see a roughly 50 meV absolute energy shift when SOC is included, which corresponds to the largest ZPL shift we find as a result of SO interactions, shown in Table 1 of the main text.



Supplementary Figure 5. Same format as Fig. 2, data for PbV^0 . Adiabatic solutions to the coupled product Jahn-Teller + static correlation Hamiltonians including up to first order coupling in the pJT for PbV^0 . The undistorted electronic states are projected onto the symmetry-adapted wavefunctions by color, as shown in the triangular color map. Below the adiabatic solutions we show the full vibronic solutions plotted as a function of the nuclear position coordinate $R = \sqrt{Q_x^2 + Q_y^2}$ relative to the D_{3d} minima. **(b)** Same as (a) except we include up to second order couplings in the pJT. **(c)** Lowest vibronic solutions for PbV^0 considering (left to right) first order pJT, second order pJT and second order pJT in addition to spin-orbit coupling.

SUPPLEMENTARY NOTE 2: DERIVATION OF THE PRODUCT JAHN-TELLER HAMILTONIAN TO SECOND ORDER

In the neutral charge state of the group IV centers in diamond, the excited electronic state exhibits a product Jahn-Teller effect due to simultaneous Jahn-Teller distortions of the e_u and e_g defect orbitals, as outlined in the main text. Here the pJT Hamiltonian is given to first order, in the same form as in Ref. 2:

$$\hat{H}_{\text{pJT}}^{(1)} = F_u (\hat{X} \hat{\sigma}_z \otimes \hat{\sigma}_0 - \hat{Y} \hat{\sigma}_x \otimes \hat{\sigma}_0) + F_g (\hat{X} \hat{\sigma}_0 \otimes \hat{\sigma}_z - \hat{Y} \hat{\sigma}_0 \otimes \hat{\sigma}_x). \quad (1)$$

As described in the main text, F_u and F_g are the coupling constants for the first-order interaction of the e_u and e_g holes, respectively, with the E_g -type phonon mode. The E_g mode spans a 2D vibrational space denoted by bosonic creation and

annihilation operators $\hat{X}, \hat{Y}$ by $\{\hat{X}, \hat{Y}\} = (\hat{a}_{\{x,y\}}^\dagger + \hat{a}_{\{x,y\}})/\sqrt{2}$. The $\hat{\sigma}$ matrices are the standard Pauli matrices, and $\hat{\sigma}_0$ is a 2×2 unit matrix. In this work we extend the product Jahn-Teller Hamiltonian such that it includes electron-phonon coupling to second order in the phonons. This is represented by

$$\begin{aligned} \hat{H}_{\text{pJT}}^{(2)} = & F_u(\hat{X}\hat{\sigma}_z \otimes \hat{\sigma}_0 - \hat{Y}\hat{\sigma}_x \otimes \hat{\sigma}_0) + F_g(\hat{X}\hat{\sigma}_0 \otimes \hat{\sigma}_z - \hat{Y}\hat{\sigma}_0 \otimes \hat{\sigma}_x) \\ & + G_u(\hat{X}^2 - \hat{Y}^2)[\hat{\sigma}_z \otimes \hat{\sigma}_0] + 2G_u\hat{X}\hat{Y}[\hat{\sigma}_x \otimes \hat{\sigma}_0] + G_g(\hat{X}^2 - \hat{Y}^2)[\hat{\sigma}_0 \otimes \hat{\sigma}_z] + 2G_g\hat{X}\hat{Y}[\hat{\sigma}_0 \otimes \hat{\sigma}_x]. \end{aligned} \quad (2)$$

This is a direct extension of the single $E \otimes e$ Jahn-Teller which has been described to second order in coupling [3]. The second-order coupling terms for the e_u and e_g orbitals are denoted by the constants G_u and G_g , respectively. The parameters $\hbar\omega_E$, F_u, F_g , G_u and G_g can be computed using the information provided in the calculated potential energy surface. To derive the relations between these coupling parameters and the potential energy surfaces, we use the same methods used for describing the single $E \otimes e$ Jahn-Teller problem [4]. The potential energy surface can be written in vibrational displacement coordinates (Q_x, Q_y) , i.e., first quantization, by

$$\begin{aligned} \hat{U}_{\text{pJT}}^{(2)} = & \frac{1}{2}K(Q_x^2 + Q_y^2)\hat{\sigma}_0 \otimes \hat{\sigma}_0 + \left[V_u(Q_x\hat{\sigma}_x + Q_y\hat{\sigma}_y) + W_u\left[(Q_x^2 - Q_y^2)\hat{\sigma}_x - 2Q_xQ_y\hat{\sigma}_y\right]\right] \otimes \hat{\sigma}_0 \\ & + \hat{\sigma}_0 \otimes \left[V_g(Q_x\hat{\sigma}_x + Q_y\hat{\sigma}_y) + W_g\left[(Q_x^2 - Q_y^2)\hat{\sigma}_x - 2Q_xQ_y\hat{\sigma}_y\right]\right]. \end{aligned} \quad (3)$$

Here K is the effective spring constant for the E_g phonon mode spanning the 2D (Q_x, Q_y) space. The coupling constants $V_{u/g}$ and $W_{u/g}$ are analogous to $F_{u/g}$ and $G_{u/g}$ in Eq. 2. This expression represents a 4×4 matrix. We can analytically transform Eq. 3 above to a diagonal basis, such that we can read off the eigenvalues. We first transform to a polar-coordinate representation: $(Q_x, Q_y) \rightarrow (\rho, \phi)$. We next introduce the unitary transformation matrix from a single Jahn-Teller to second order in coupling [4], $\hat{S}_{\Omega_{u/g}}$, and adopt it to our product Jahn-Teller situation:

$$\begin{aligned} \hat{S}_{\Omega_{u/g}} = & \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\Omega_{u/g}/2} & e^{-i\Omega_{u/g}/2} \\ e^{i\Omega_{u/g}/2} & -e^{i\Omega_{u/g}/2} \end{pmatrix}, \\ \Rightarrow \hat{S}_{\text{pJT}} = \hat{S}_{\Omega_u} \otimes \hat{S}_{\Omega_g} = & \frac{1}{2} \begin{pmatrix} e^{-i(\Omega_u+\Omega_g)/2} & e^{-i(\Omega_u+\Omega_g)/2} & e^{-i(\Omega_u+\Omega_g)/2} & e^{-i(\Omega_u+\Omega_g)/2} \\ e^{-i(\Omega_u-\Omega_g)/2} & -e^{-i(\Omega_u-\Omega_g)/2} & e^{-i(\Omega_u-\Omega_g)/2} & -e^{-i(\Omega_u-\Omega_g)/2} \\ e^{i(\Omega_u-\Omega_g)/2} & e^{i(\Omega_u-\Omega_g)/2} & -e^{i(\Omega_u-\Omega_g)/2} & -e^{i(\Omega_u-\Omega_g)/2} \\ e^{i(\Omega_u+\Omega_g)/2} & -e^{i(\Omega_u+\Omega_g)/2} & -e^{i(\Omega_u+\Omega_g)/2} & e^{i(\Omega_u+\Omega_g)/2} \end{pmatrix}. \end{aligned} \quad (4)$$

With $\Omega_{u/g}$ defined relative to [4]

$$\tan \Omega_{u/g} = \frac{V_{u/g} \sin \phi - W_{u/g} \rho \sin 2\phi}{V_{u/g} \cos \phi + W_{u/g} \rho \cos 2\phi}. \quad (5)$$

We then apply the unitary transformation and can read off the eigenvalues in the now-diagonal matrix, $\hat{U}_{\text{pJT}}^{(2)}$:

$$\hat{U}_{\text{pJT}}^{(2)} = \hat{S}_{\text{pJT}}^\dagger \hat{U}_{\text{pJT}}^{(2)} \hat{S}_{\text{pJT}} \Rightarrow \begin{aligned} \varepsilon_{++}(\rho, \phi) &= \frac{1}{2}K\rho^2 + \rho [c_u(\rho, \phi) + c_g(\rho, \phi)] \\ \varepsilon_{+-}(\rho, \phi) &= \frac{1}{2}K\rho^2 + \rho [c_u(\rho, \phi) - c_g(\rho, \phi)] \\ \varepsilon_{-+}(\rho, \phi) &= \frac{1}{2}K\rho^2 + \rho [c_g(\rho, \phi) - c_u(\rho, \phi)] \\ \varepsilon_{--}(\rho, \phi) &= \frac{1}{2}K\rho^2 - \rho [c_u(\rho, \phi) + c_g(\rho, \phi)] \end{aligned} \quad (6)$$

with $c_i(\rho, \phi) = \sqrt{V_i^2 + W_i^2\rho^2 + 2V_iW_i\rho \cos 3\phi}$. From this eigenvalue spectrum we can observe up to two surfaces which are unstable. These correspond to cases where $\varepsilon(\rho, \phi) < 0$. If the u and g orbitals couple constructively, we get either ε_{--} or ε_{++} . Convention of $\rho > 0$ means the ε_{--} surface can be unstable. This corresponds to a constructive interference of the two Jahn-Teller interactions, with c_u and c_g having the same sign. We label corresponding coefficients associated with constructive interference with (1) superscripts. Additionally, either the ε_{-+} or ε_{+-} can be unstable. Either of these represent a destructive interference of the Jahn-Teller interactions, with c_u and c_g having opposite signs. We denote corresponding coefficients of destructive Jahn-Teller interference with (2) superscripts.

We now aim to find expressions for the displacement ρ_0 , Jahn-Teller energy E_{JT} and second-order energy barrier δ_{JT} in terms of the coupling constants $V_{u/g}$, $W_{u/g}$ and the vibrational spring constant K . This will enable us to connect the former terms, which are attainable from our first-principles DFT calculations, to the latter terms, which are required for solving the product Jahn-Teller Hamiltonian, Eq. 2.

A. Lower surface

We start first with the surface corresponding to $\varepsilon_{--}(\rho, \phi)$. We hope to find the coordinates (ρ_0, ϕ_0) associated with the energy minimum. To do this we take the derivative with respect to ρ :

$$\frac{\partial}{\partial \rho} \varepsilon_{--}(\rho, \phi) = \rho K - \frac{W_g \rho (W_g \rho + V_g \cos 3\phi)}{c_g(\rho, \phi)} - c_g(\rho, \phi) - \frac{W_u \rho (W_u \rho + V_u \cos 3\phi)}{c_u(\rho, \phi)} - c_u(\rho, \phi). \quad (7)$$

We find the displacement minima ρ_0 can take on multiple values, depending on the value of $\cos 3\phi$. Minima can occur for $\cos 3\phi \rightarrow \pm 1$. We choose here to focus on the case where $\cos 3\phi \rightarrow 1$. This yields the following minima:

$$\rho_0^\pm \Big|_{\cos 3\phi \rightarrow 1} = \frac{|V_g + V_u|}{\pm K - 2|W_g + W_u|}, \quad (8)$$

with the $\pm$ superscript corresponding to the $\pm K$ in the denominator. If we insert these solutions for ρ_0 back into ε_{--} , we find two expressions, one which corresponds to the Jahn-Teller instability energy $E_{\text{JT}}^{(1)}$, i.e., the absolute minima:

$$\varepsilon_{--}(\rho_0^-, \phi) \Big|_{\cos 3\phi \rightarrow 1} = -\frac{1}{2} \frac{(V_g + V_u)^2}{K - 2|W_g + W_u|} \rightarrow E_{\text{JT}}^{(1)} = \frac{1}{2} \frac{(V_g + V_u)^2}{K - 2|W_g + W_u|}, \quad (9)$$

and another which corresponds to a saddle point:

$$\varepsilon_{--}(\rho_0^+, \phi) \Big|_{\cos 3\phi \rightarrow 1} = -\frac{1}{2} \frac{(V_g + V_u)^2}{K + 2|W_g + W_u|}. \quad (10)$$

The difference in these two energies represents the barrier height, $\delta_{\text{JT}}^{(1)}$:

$$\varepsilon_{--}(\rho_0^-, \phi) - \varepsilon_{--}(\rho_0^+, \phi) \Big|_{\cos 3\phi \rightarrow 1} = -\frac{2(V_g + V_u)^2 |W_g + W_u|}{K^2 - 4|W_g + W_u|^2} \Rightarrow \delta_{\text{JT}}^{(1)} = \frac{4E_{\text{JT}}^{(1)} |W_g + W_u|}{K + 2|W_g + W_u|^2}. \quad (11)$$

B. Higher surface

In addition to $\varepsilon_{--}(\rho, \phi)$ being energetically unstable, the pJT solutions can also allow for either $\varepsilon_{-+}(\rho, \phi)$ or $\varepsilon_{+-}(\rho, \phi)$ to be unstable. We consider here $\varepsilon_{+-}(\rho, \phi)$ however we note that the resulting expressions are the same. We carry out a similar procedure as above; that is, we take the first derivative:

$$\frac{\partial}{\partial \rho} \varepsilon_{+-}(\rho, \phi) = \rho K - \frac{W_g \rho (W_g \rho + V_g \cos 3\phi)}{c_g(\rho, \phi)} - c_g(\rho, \phi) + \frac{W_u \rho (W_u \rho + V_u \cos 3\phi)}{c_u(\rho, \phi)} + c_u(\rho, \phi), \quad (12)$$

and look for places where these expressions are equal to zero. Here we find for $\cos 3\phi \rightarrow 1$:

$$\rho_0^\pm \Big|_{\cos 3\phi \rightarrow 1} = \frac{|V_g - V_u|}{-2|W_g - W_u| \pm K}. \quad (13)$$

From these expressions we can obtain the Jahn-Teller energy:

$$E_{\text{pJT}}^{(2)} = -\varepsilon_{-+}(\rho_0^-, \phi) \Big|_{\cos 3\phi \rightarrow 1} = \frac{1}{2} \frac{(V_g - V_u)^2}{K - 2|W_g - W_u|}, \quad (14)$$

and from the difference of the $\pm$ minima we can get the barrier height:

$$\varepsilon_{-+}(\rho_0^-, \phi) - \varepsilon_{-+}(\rho_0^+, \phi) \Big|_{\cos 3\phi \rightarrow 1} = -\frac{2(V_g - V_u)^2 |W_g - W_u|}{K^2 - 4|W_g - W_u|^2} \Rightarrow \delta_{\text{pJT}}^{(2)} = \frac{4E_{\text{pJT}}^{(2)} |W_g - W_u|}{K + 2|W_g - W_u|^2}. \quad (15)$$

Combining now with the constructive surface, we find the following expressions relating ρ , E_{JT} and δ_{JT} to the coupling constants describing the potential energy surface:

$$E_{\text{pJT}}^{(1)} = \frac{1}{2} \frac{(V_g + V_u)^2}{K - 2|W_g + W_u|}, \quad \delta_{\text{pJT}}^{(1)} = \frac{4E_{\text{pJT}}^{(1)} |W_g + W_u|}{K + 2|W_g + W_u|^2}, \quad \rho_0^{(1)} = \frac{|V_g + V_u|}{K - 2|W_g + W_u|}, \quad (16)$$

$$E_{\text{pJT}}^{(2)} = \frac{1}{2} \frac{(V_g - V_u)^2}{K - 2|W_g - W_u|}, \quad \delta_{\text{pJT}}^{(2)} = \frac{4E_{\text{pJT}}^{(2)}|W_g - W_u|}{K + 2|W_g - W_u|}, \quad \rho_0^{(2)} = \frac{|V_g - V_u|}{K - 2|W_g - W_u|}. \quad (17)$$

In each line, we have three expressions and three unknowns, allowing us to solve for $K, V_{u/g}, W_{u/g}$. We now wish to express these quantities in terms of only energies. This amounts to converting the spring constants K and coupling constants V and W to phonon energy $\hbar\omega_E$ and coupling constants F and G . We first use the relation $K = m_C\omega_E^2$ to relate the effective spring constant K to the E_g phonon frequency ω_E , with m_C representing the mass of a carbon atom. For the coupling parameters, we find

$$E_{\text{pJT}}^{(1)} = \frac{1}{2} \frac{(F_g + F_u)^2}{\hbar\omega_E - 2|G_g + G_u|}, \quad \delta_{\text{pJT}}^{(1)} = \frac{4E_{\text{pJT}}^{(1)}|G_g + G_u|}{\hbar\omega_E + 2|G_g + G_u|}, \quad (18)$$

$$E_{\text{pJT}}^{(2)} = \frac{1}{2} \frac{(F_g - F_u)^2}{\hbar\omega_E - 2|G_g - G_u|}, \quad \delta_{\text{pJT}}^{(2)} = \frac{4E_{\text{pJT}}^{(2)}|G_g - G_u|}{\hbar\omega_E + 2|G_g - G_u|}. \quad (19)$$

These are the expressions used in describing the coupling constants in the main manuscript. We note that when evaluating the first-order Jahn-Teller, we augment the expression above by setting $\delta_{\text{JT}} = 0$ (and therefore $G_g, G_u, W_g, W_u = 0$). This correspondingly shifts the coupling parameters and effective phonon energy $\hbar\omega_E$. The resulting values are shown in Table 1.

	SiV ⁰				
	$\hbar\omega_E$	F_g	F_u	G_g	G_u
First order	78.6	104	97.3	0	0
Second order	87.3	98.4	92.7	11.6	-3.31
	GeV ⁰				
	$\hbar\omega_E$	F_g	F_u	G_g	G_u
First order	78.3	111	84.3	0	0
Second order	86.6	107	79.0	4.71	3.22
	SnV ⁰				
	$\hbar\omega_E$	F_g	F_u	G_g	G_u
First order	79.7	117	68.6	0	0
Second order	87.7	114	63.3	3.93	3.60
	PbV ⁰				
	$\hbar\omega_E$	F_g	F_u	G_g	G_u
First order	81.6	125	55.4	0	0
Second order	90.8	121.8	49.5	5.22	3.50

Supplementary Table 1. Tabulated parameters for the Jahn-Teller couplings shown in Eqs. 1,2 along with the effective phonon energy $\hbar\omega_E$ of the E_g phonon modes in the 2D vibrational coordinate space. We compute these quantities to first and second order in pJT interactions. All quantities are in units of meV.

SUPPLEMENTARY NOTE 3: TWO-HOLE STATES

The DFT calculations performed in this work were restricted to the triplet manifold with $S = 1$. The corresponding excited-state energies and geometries will correspond to one of the four following two-hole states:

$$\mathcal{A}|e_{ux}e_{gx}\rangle, \mathcal{A}|e_{ux}e_{gy}\rangle, \mathcal{A}|e_{uy}e_{gx}\rangle, \mathcal{A}|e_{uy}e_{gy}\rangle.$$

Here $\mathcal{A}$ is the antisymmetrization operator for the two hole occupation states. All of these are accompanied by the same spin component (i.e., $\otimes|\downarrow\downarrow\rangle$) in our spin-polarized calculations. However these states are not irreducible representations of the D_{3d} point group, only their linear combinations are (See Ref. 2 for derivation). The symmetry-adapted states of the

D_{3d} point group in the triplet subspace are expressed as [2]:

$$\left. \begin{aligned} |^3A_{1u}\rangle &= \mathcal{A} \frac{1}{\sqrt{2}} (|e_{ux}e_{gy}\rangle - |e_{uy}e_{gx}\rangle) \\ |^3E_{uy}\rangle &= \mathcal{A} \frac{1}{\sqrt{2}} (|e_{ux}e_{gy}\rangle + |e_{uy}e_{gx}\rangle) \\ |^3E_{ux}\rangle &= \mathcal{A} \frac{1}{\sqrt{2}} (|e_{ux}e_{gx}\rangle - |e_{uy}e_{gy}\rangle) \\ |^3A_{2u}\rangle &= \mathcal{A} \frac{1}{\sqrt{2}} (|e_{ux}e_{gx}\rangle + |e_{uy}e_{gy}\rangle) \end{aligned} \right\} \otimes \left\{ \begin{array}{c} | \uparrow\uparrow \rangle \\ \mathcal{S} | \uparrow\downarrow \rangle \\ | \downarrow\downarrow \rangle \end{array} \right. . \quad (20)$$

We apply these relations to project our solutions found in Fig. 2(b,c) of the main text as well as Figs. 2-5(a,b) onto these two-hole wavefunctions.

SUPPLEMENTARY NOTE 4: ELECTRONIC CORRELATION

Contrary to the case of the single Jahn-Teller, the product Jahn-Teller system includes an electronic correlation term $\hat{W}$. This is necessary to account for the energy difference observed in calculation between the pairs of states $(\mathcal{A}|e_{ux}e_{gx}\rangle, \mathcal{A}|e_{uy}e_{gy}\rangle)$ and $(\mathcal{A}|e_{ux}e_{gy}\rangle, \mathcal{A}|e_{uy}e_{gx}\rangle)$ when constrained at a D_{3d} geometry. An appropriate Hamiltonian model of this system therefore requires a proper account of this energy splitting.

The electronic correlation term has already been discussed in Ref. 2 and so we do not provide a complete description here. In general the static correlation $\hat{W}$ can be described as

$$\hat{W} = \Lambda \left(|^3A_{1u}\rangle \langle ^3A_{1u}| - |^3A_{2u}\rangle \langle ^3A_{2u}| \right) - \Xi \left(|^3E_{ux}\rangle \langle ^3E_{ux}| + |^3E_{uy}\rangle \langle ^3E_{uy}| \right) \quad (21)$$

We are left to find the coupling constants Λ and Ξ . The constant Λ can be directly read off from our DFT calculations. The constant Ξ requires additional mixing of hole wavefunctions. We take the values from Ref. 2. Once these constants are found, we can adapt Eq. 21 to the antisymmetrized basis already used for the pJT interaction. Thus it becomes:

$$\hat{W} = \frac{\Lambda}{2} \begin{bmatrix} -1 & 0 & 0 & -1 \\ 0 & 1 & -1 & 0 \\ 0 & -1 & 1 & 0 \\ -1 & 0 & 0 & -1 \end{bmatrix} - \frac{\Xi}{2} \begin{bmatrix} 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \end{bmatrix}. \quad (22)$$

SUPPLEMENTARY NOTE 5: SPIN-ORBIT COUPLING

We now outline the spin-orbit interaction in the product Jahn-Teller system. Firstly, we note that the two holes are confined to the e_u and e_g orbitals. Both of these orbitals have been well-studied in the case of group IV negative centers [5, 6]. We begin with the general form of the SOC Hamiltonian [1, 5, 7]:

$$\hat{h}_{\text{SOC}}(\mathbf{r}) = \frac{\hbar}{4c^2m^2} \left(\hat{\nabla}V(\mathbf{r}) \times \hat{\mathbf{p}} \right) \cdot \hat{\boldsymbol{\sigma}}. \quad (23)$$

Here $V(\mathbf{r})$ is the potential energy of the electron due to the magnetic field created by the nucleus, m is the electron mass and $\hat{\mathbf{p}}$ is its momentum. The variable $\hat{\boldsymbol{\sigma}}$ is connected to the electron spin $\hat{\mathbf{S}}$, represented here by the Pauli matrices. In the D_{3d} point group, both $V(\mathbf{r})$ and $\hat{\mathbf{p}}$ transform as vectors [5] which allows us to write $(\hat{\nabla}V(\mathbf{r}) \times \hat{\mathbf{p}}) = \hat{\mathbf{L}}$. As a result, we can recover an expression for SOC which is proportional to $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$. In a non-spherical system, the general form $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ is decomposed to an axial and non-axial contribution [1]:

$$\hat{H}_{\text{SOC}} = \sum_k \lambda_{x,y} \left(\hat{L}_x^k \hat{S}_x^k + \hat{L}_y^k \hat{S}_y^k \right) + \lambda_z \left(\hat{L}_z^k \hat{S}_z^k \right). \quad (24)$$

Here the operators $\hat{L}_i^k, \hat{S}_i^k$ operate on the k^{th} electron or hole considered. With such a form we are interested in understanding how each of the two holes occupying either e_u or e_g orbitals behave when acted upon by the $\hat{L}_i$ operators. This has been

worked out previously [5] and we summarize below, beginning with the axial portion. In both the g and u orbital branches, the orbitals each can be transformed from a x/y to a $+/-$ basis: $e_{\pm} = 1/\sqrt{2}(e_x \pm ie_y)$, analogous to the treatment of p orbitals, such that the $\hat{L}_z$ operator acted on the $\pm$ basis returns $\hat{L}_ze_{\pm} = \pm\hbar e_{\pm}$. For the non-axial situation, the operator $\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y$ acts on either the e_u or e_g orbitals such that $\hat{L}_{\pm}e_{\pm} \propto a_{2u}$. Here, a_{2u} would correspond to orbitals outside of the (e_u, e_g) manifold and of lower energy. For all situations we assume these a_{2u} states are fully occupied and therefore do not participate in any excitation. Given this energy difference, the $\hat{L}_x$ and $\hat{L}_y$ operators effectively have zero matrix elements in the (e_g, e_u) manifold [5]. We also note that because of the opposite parity of the e_u and e_g orbitals, $\hat{\mathbf{L}}$ does not couple e_u and e_g orbitals together.

As a result of this, we can effectively treat SOC as only having $\hat{L}_z\hat{S}_z$ terms, as has been done for the group IV negatives [5, 8]. Also since e_u and e_g orbitals cannot be mixed by SOC, we can treat SOC as acting separately on the hole in the e_g and e_u orbitals. We therefore can begin with the product of the SOC interactions for each of the individual holes:

$$\hat{H}_{\text{SOC}} = \hat{H}_{\text{SOC}}^{(u)} \otimes \hat{\sigma}_0 + \hat{\sigma}_0 \otimes \hat{H}_{\text{SOC}}^{(g)} = \frac{\lambda_u^0}{2}(\hat{\sigma}_y \otimes \hat{\sigma}_0) + \frac{\lambda_g^0}{2}(\hat{\sigma}_0 \otimes \hat{\sigma}_y) = \frac{i}{2} \begin{pmatrix} 0 & -\lambda_u^0 & -\lambda_g^0 & 0 \\ \lambda_u^0 & 0 & 0 & -\lambda_g^0 \\ \lambda_g^0 & 0 & 0 & -\lambda_u^0 \\ 0 & \lambda_g^0 & \lambda_u^0 & 0 \end{pmatrix}. \quad (25)$$

Here λ_u^0 and λ_g^0 are the spin-orbit splittings for the e_u and e_g orbitals, respectively, which have been obtained from DFT calculations previously [8]. This form involves the single-hole SOC Hamiltonians which are the same as the group IV negatives, $\hat{H}_{\text{SOC}} = \lambda_{u/g}^0 \hat{\sigma}_y / 2$. The use of $\hat{\sigma}_y$ is useful as it allows us to evaluate the SOC effect on the x/y orbitals by effectively transforming to the $\pm$ basis.

Despite the lack of effective non-axial coupling, we note that the axial SOC can still potentially couple the $m_s = 0$ triplet and singlet states for the singly-excited hole configuration we consider here. These singlet states are expected to be higher in energy due to Coulomb repulsion [1]. Because of this, we do not explicitly consider these singlet state couplings in our treatment of SOC. We next use Eq. 25 as a starting point for both a perturbative and non-perturbative treatment of SOC.

C. Perturbation Theory

In the hopes of defining a basis suitable for direct diagonalization of the Jahn-Teller and spin-orbit interactions, we also define antisymmetrized product states written in terms of a $\pm$ basis in the same manner as the single-hole case. The basis set is:

$$\mathcal{A}|e_{u+}e_{g+}\rangle = \frac{1}{2} \begin{pmatrix} 1 \\ i \\ i \\ -1 \end{pmatrix}, \quad \mathcal{A}|e_{u-}e_{g+}\rangle = \frac{1}{2} \begin{pmatrix} 1 \\ -i \\ i \\ 1 \end{pmatrix}, \quad \mathcal{A}|e_{u+}e_{g-}\rangle = \frac{1}{2} \begin{pmatrix} 1 \\ i \\ -i \\ 1 \end{pmatrix}, \quad \mathcal{A}|e_{u-}e_{g-}\rangle = \frac{1}{2} \begin{pmatrix} 1 \\ -i \\ -i \\ -1 \end{pmatrix}, \quad (26)$$

Here the coefficients are written in the basis of the $e_{ux/y}$ and $e_{gx/y}$ states as:

$$\left(\mathcal{A}|e_{ux}e_{gx}\rangle \quad \mathcal{A}|e_{uy}e_{gx}\rangle \quad \mathcal{A}|e_{ux}e_{gy}\rangle \quad \mathcal{A}|e_{uy}e_{gy}\rangle \right)^{\top}.$$

These orbital definitions allow us to write a basis for the combined Jahn-Teller and spin-orbit interactions. By treating spin-orbit coupling as a perturbation to the vibronic system, we can write this as:

$$|\tilde{\Psi}_{\pm\pm}\rangle = \sum_{n,m} \left[a_{nm} \mathcal{A}|e_{u\pm}e_{g\pm}\rangle |n, m\rangle + b_{nm} \mathcal{A}|e_{u\mp}e_{g\pm}\rangle |n, m\rangle + c_{nm} \mathcal{A}|e_{u\pm}e_{g\mp}\rangle |n, m\rangle + d_{nm} \mathcal{A}|e_{u\mp}e_{g\mp}\rangle |n, m\rangle \right]. \quad (27)$$

The summation is performed over (n, m) phonon modes in the 2D $(\hat{X}, \hat{Y})$ E_g -phonon space. The indices $\pm\pm$ separately addresses the $u\pm$ and $g\pm$ orbitals. We can then define the Ham reduction factors in the following manner:

$$\lambda_u + \lambda_g = p_u \lambda_u^0 + p_g \lambda_g^0 = 2|\langle \tilde{\Psi}_{\pm\pm} | \hat{H}_{\text{SOC}} | \tilde{\Psi}_{\pm\pm} \rangle|. \quad (28)$$

We then expand this expression, using the basis defined in Eq. 27:

$$\lambda_u + \lambda_g = 2 \sum_{n,m,k,\ell} \left[a_{nm} \langle e_{u\pm}e_{g\pm} | \mathcal{A}(k, \ell) + b_{nm} \langle e_{u\mp}e_{g\pm} | \mathcal{A}(k, \ell) + c_{nm} \langle e_{u\pm}e_{g\mp} | \mathcal{A}(k, \ell) + d_{nm} \langle e_{u\mp}e_{g\mp} | \mathcal{A}(k, \ell) \right] \hat{H}_{\text{SOC}} \\ \left[a_{nm} \mathcal{A}|e_{u\pm}e_{g\pm}\rangle |n, m\rangle + b_{nm} \mathcal{A}|e_{u\mp}e_{g\pm}\rangle |n, m\rangle + c_{nm} \mathcal{A}|e_{u\pm}e_{g\mp}\rangle |n, m\rangle + d_{nm} \mathcal{A}|e_{u\mp}e_{g\mp}\rangle |n, m\rangle \right]. \quad (29)$$

Since the electronic states are orthogonal (as are the vibrational states), this expression greatly simplifies, and we have:

$$\begin{aligned}
&= \sum_{n,m} 2a_{nm}^2 \overbrace{\langle e_{u\pm} e_{g\pm} | \mathcal{A} \rangle \hat{H}_{\text{SOC}} [\mathcal{A} | e_{u\pm} e_{g\pm} \rangle]}^{\frac{1}{2}(\lambda_g^0 + \lambda_u^0)} + 2b_{nm}^2 \overbrace{\langle e_{u\mp} e_{g\pm} | \mathcal{A} \rangle \hat{H}_{\text{SOC}} [\mathcal{A} | e_{u\mp} e_{g\pm} \rangle]}^{\frac{1}{2}(\lambda_g^0 - \lambda_u^0)} \\
&\quad + 2c_{nm}^2 \overbrace{\langle e_{u\pm} e_{g\mp} | \mathcal{A} \rangle \hat{H}_{\text{SOC}} [\mathcal{A} | e_{u\pm} e_{g\mp} \rangle]}^{\frac{1}{2}(\lambda_u^0 - \lambda_g^0)} + 2d_{nm}^2 \overbrace{\langle e_{u\mp} e_{g\mp} | \mathcal{A} \rangle \hat{H}_{\text{SOC}} [\mathcal{A} | e_{u\mp} e_{g\mp} \rangle]}^{\frac{1}{2}(-\lambda_g^0 - \lambda_u^0)} \\
&= \lambda_g^0 \sum_{n,m} (a_{nm}^2 + b_{nm}^2 - c_{nm}^2 - d_{nm}^2) + \lambda_u^0 \sum_{n,m} (a_{nm}^2 - b_{nm}^2 + c_{nm}^2 - d_{nm}^2). \quad (30)
\end{aligned}$$

This lets us extract the relevant Ham reduction factors

$$\begin{aligned}
p_u &= \sum_{n,m} (a_{nm}^2 + b_{nm}^2 - c_{nm}^2 - d_{nm}^2), \\
p_g &= \sum_{n,m} (a_{nm}^2 - b_{nm}^2 + c_{nm}^2 - d_{nm}^2). \quad (31)
\end{aligned}$$

We note that while a perturbative treatment of SOC is not sufficient for the group IV^0 defects studied, we find that the derived Ham reduction factors computed using the perturbative expressions above and the Ham reduction factors found using the nonperturbative approach (outlined below) are in rather good agreement (see Table 2). This is consistent with Ref. 8, where a similar framework was applied to the group IV^- emitters.

D. Simultaneous inclusion of spin-orbit coupling

We now describe how we find the solution to the coupled spin-orbit and Jahn-Teller problems. This would amount to solving the following Hamiltonian:

$$\hat{H} = \hat{H}_{\text{osc}} + \hat{H}_{\text{pJT}}^{(2)} + \hat{W} + \hat{H}_{\text{SOC}}. \quad (32)$$

which is the same as Eq. 2 in the main text except for the additional spin-orbit coupling contribution. To do this we must first describe this spin-orbit Hamiltonian. The spin-state, which we denote as $|\chi\rangle$, can take on one of three values for an $S = 1$ system:

$$|\chi\rangle = \begin{pmatrix} | \uparrow \uparrow \rangle \\ \mathcal{S} | \uparrow \downarrow \rangle \\ | \downarrow \downarrow \rangle \end{pmatrix} = \overbrace{\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}}^{m_s}. \quad (33)$$

The expansion of spin-orbit basis states as defined above (Eq. 27) is combined with spin index:

$$|\tilde{\Psi}_\Gamma\rangle = \sum_{n,m} [a_{nm}^\chi \mathcal{A} | e_{u\pm} e_{g\pm} \rangle | n, m \rangle |\chi\rangle + b_{nm}^\chi \mathcal{A} | e_{u\mp} e_{g\pm} \rangle | n, m \rangle |\chi\rangle + c_{nm}^\chi \mathcal{A} | e_{u\pm} e_{g\mp} \rangle | n, m \rangle |\chi\rangle + d_{nm}^\chi \mathcal{A} | e_{u\mp} e_{g\mp} \rangle | n, m \rangle |\chi\rangle]. \quad (34)$$

Here Γ can refer to the angular momentum state of the two-particle system. The coefficients are all spin-dependent (denoted by χ) and so there are really twelve electronic states. We note the expansion presented in Eq. 34 directly couples spins and phonons with the hole orbitals. With a twelve state basis, we need to augment our Jahn-Teller, spin-orbit and electronic correlation Hamiltonians appropriately. For the case of Jahn-Teller and electronic correlation, we assume these effects are spin-independent. This lets us write them in the twelve-state basis as:

$$\begin{aligned}
\hat{H}_{\text{pJT}}^{(2),\chi} &= \hat{H}_{\text{pJT}}^{(2)} \otimes \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \\
\hat{W}^\chi &= \hat{W} \otimes \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (35)
\end{aligned}$$

For the case of spin-orbit coupling, this interaction is not independent of spin. The spin-orbit interaction affects the $m_s = \pm 1$ oppositely but does not affect the $m_s = 0$ levels. From this, our spin-dependence becomes:

$$\hat{H}_{\text{SOC}} = \left(\frac{\lambda_u^0}{2} (\hat{\sigma}_y \otimes \hat{\sigma}_0) + \frac{\lambda_g^0}{2} (\hat{\sigma}_0 \otimes \hat{\sigma}_y) \right) \otimes \overbrace{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}}^{m_s}. \quad (36)$$

This equation represents an expansion of the spin-orbit interaction to each of the m_s states in the $S = 1$ triplet two-hole basis. In defining our basis states, we are explicitly accounting for the angular momenta of the system.

We note that we can equivalently write the full SOC interaction in second-quantized notation in terms of the holes. This would take the form

$$\hat{H}_{\text{SOC}} = \sum_{ab\sigma\sigma'} \langle a\sigma | \hat{h}_{\text{SOC}} | b\sigma' \rangle \hat{c}_{a\sigma}^\dagger \hat{c}_{b\sigma'}. \quad (37)$$

with a, b representing defect orbitals ($a, b \in [e_{ux}, e_{uy}, e_{gx}, e_{gy}]$), σ representing spin ($\sigma, \sigma' \in [\uparrow, \downarrow]$) and $\hat{c}^\dagger$ ($\hat{c}$) representing the fermionic creation (annihilation) operators for our defect system. We have already discussed the nature of these matrix elements at the beginning of this section. We find the matrix elements for $\hat{h}_{\text{SOC}}$ are nonzero only in the case of $\langle e_{ux}\sigma | \hat{h}_{\text{SOC}} | e_{uy}\sigma \rangle$ and $\langle e_{gx}\sigma | \hat{h}_{\text{SOC}} | e_{gy}\sigma \rangle$ and their complex conjugates. There is no coupling between u and g orbitals. Altogether this results in the following Hamiltonian:

$$\hat{H}_{\text{SOC}} = \sum_{\sigma=\uparrow,\downarrow} \mp \frac{i}{2} \left(\lambda_u^0 (\hat{c}_{uy\sigma}^\dagger \hat{c}_{ux\sigma} - \hat{c}_{ux\sigma}^\dagger \hat{c}_{uy\sigma}) + \lambda_g^0 (\hat{c}_{gy\sigma}^\dagger \hat{c}_{gx\sigma} - \hat{c}_{gx\sigma}^\dagger \hat{c}_{gy\sigma}) \right). \quad (38)$$

Where the $\mp$ is used, as opposed to $\pm$, because we are dealing with holes instead of electrons. More compactly, this becomes

$$\hat{H}_{\text{SOC}} = \sum_{\alpha=u,g} \sum_{\sigma=\uparrow,\downarrow} \mp \frac{i\lambda_\alpha^0}{2} (\hat{c}_{\alpha y\sigma}^\dagger \hat{c}_{\alpha x\sigma} - \hat{c}_{\alpha x\sigma}^\dagger \hat{c}_{\alpha y\sigma}). \quad (39)$$

Here the notation means there is an overall minus sign for $\uparrow$ and plus sign for $\downarrow$ in the innermost summation. We note that this Hamiltonian is equivalent to Eq. 25 and Eq. 36 in the single excitation manifold.

In the case of group IV neutrals, both the e -type orbitals act with $\hat{L}_z$ as $\hat{L}_z e_\pm = \pm \hbar e_\pm$. Thus the orbital angular momenta m_ℓ for the single holes are ± 1 . This suggests the orbital angular momenta of the two-particle system can take on the values $m_\ell \in [2, 0, -2]$. As noted earlier, the spin sublevels can take on $m_s \in [1, 0, -1]$, and so from these we see that there are indeed 12 states of the triplet subspace for this system.

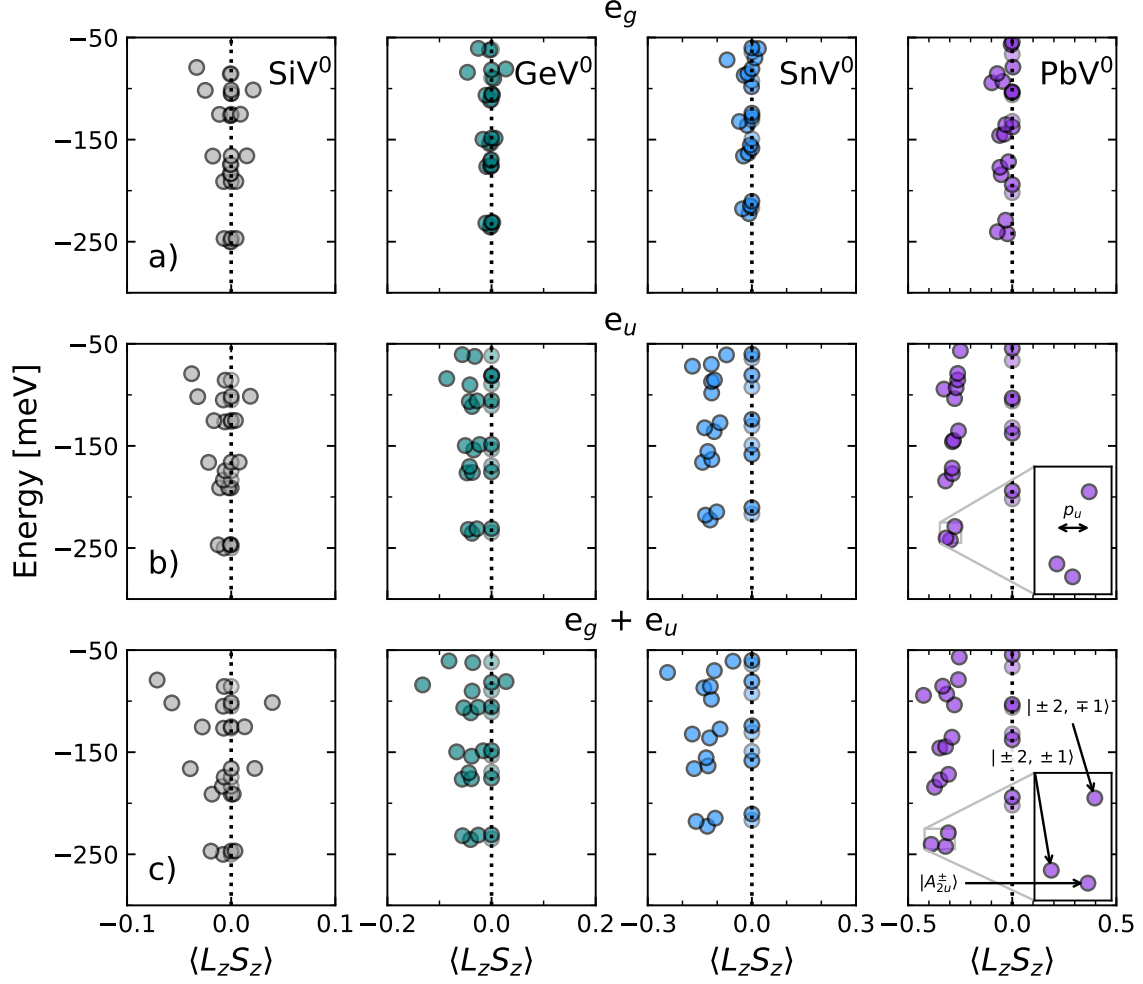
However we note some aspects of these possible states that are of relevance. First, states with $m_s = 0$ should not be affected by spin-orbit interactions. We also note that the combinations $m_\ell = 2, m_s = 1$ and $m_\ell = -2, m_s = -1$ are equivalent, as are $m_\ell = 2, m_s = -1$ and $m_\ell = -2, m_s = 1$. These pairs are both Kramer's degenerate, similar to the case of the group IV negatives. Such degeneracy could be broken with either magnetic fields or crystal strain. There can also exist states with $m_\ell = 0$. Such states are split by $\pm(\lambda_g - \lambda_u)/2$. While these $m_\ell = 0$ states exist, they do not appear in the lowest-energy E_u orbitals and instead are of higher energy. Thus we do not consider these for the remaining discussion, and only consider $m_\ell = \pm 2$ states. For this we have three distinct eigenvalue scenarios:

1. $m_\ell = \pm 2, m_s = \pm 1$ (i.e., $m_j = \pm 3$)
2. $m_\ell = \pm 2, m_s = \mp 1$
3. $m_\ell = 2$ or $m_s = 0$

For this reason we only expect to see up to three nondegenerate eigenvalues from solving the combined pJT + SOC Hamiltonian. We also note that m_j is not a sufficient index in evaluating the effects of spin-orbit interactions, even though this was the case for the group IV negatives. However anytime $m_j = \pm 3$ we are confined to option (1). The three distinct eigenvalue situations can be described in $|m_\ell, m_s\rangle$ notation as $|\pm 2, \pm 1\rangle$, $|\pm 2, \mp 1\rangle$ and $|\pm 2, 0\rangle$. States within this final classification are not affected by spin-orbit interactions and we thus focus on the first two labels.

We can evaluate the expectation values $\langle (\hat{L}_z \hat{S}_z)_{u/g} \rangle$ for the hole in each of the g/u orbital branches. Here $(\hat{L}_z \hat{S}_z)_{u/g}$ are defined by $(\hat{L}_z \hat{S}_z)_u = \frac{1}{2} (\hat{\sigma}_y \otimes \hat{\sigma}_0)$ and $(\hat{L}_z \hat{S}_z)_g = \frac{1}{2} (\hat{\sigma}_0 \otimes \hat{\sigma}_y)$. Each of these branches will have their own p factors, analogous to the group IV negatives [8]:

$$\begin{aligned} p_g^{|\pm 2, \pm 1\rangle} &= -2 \langle \pm 2, \pm 1 | (\hat{L}_z \hat{S}_z)_g | \pm 2, \pm 1 \rangle & p_u^{|\pm 2, \pm 1\rangle} &= -2 \langle \pm 2, \pm 1 | (\hat{L}_z \hat{S}_z)_u | \pm 2, \pm 1 \rangle \\ p_g^{|\pm 2, \mp 1\rangle} &= 2 \langle \pm 2, \mp 1 | (\hat{L}_z \hat{S}_z)_g | \pm 2, \mp 1 \rangle & p_u^{|\pm 2, \mp 1\rangle} &= 2 \langle \pm 2, \mp 1 | (\hat{L}_z \hat{S}_z)_u | \pm 2, \mp 1 \rangle \end{aligned} \quad (40)$$



Supplementary Figure 6. (a) Matrix elements $\langle \hat{L}_z \hat{S}_z \rangle$ for e_g orbitals of each of the group IV⁰ defects. (b) and (c) are the same except for the e_u and combined $e_g + e_u$ orbitals. The lowest optically active states are of E_u symmetry and are labeled in $|m_\ell, m_s\rangle$ form in the inset of panel (b), right. The difference in $\langle \hat{L}_z \hat{S}_z \rangle$ for the $|\pm 2, \pm 1\rangle$ and $|\pm 2, \mp 1\rangle$ states is defined as the p factor for a given u/g orbital.

The average of these can be taken to find the total effective quenching factor $p_{u/g}$:

$$p_g = \frac{1}{2} \left(p_g^{|\pm 2, \pm 1\rangle} + p_g^{|\pm 2, \mp 1\rangle} \right) \quad p_u = \frac{1}{2} \left(p_u^{|\pm 2, \pm 1\rangle} + p_u^{|\pm 2, \mp 1\rangle} \right) \quad (41)$$

and we can define corresponding difference $\delta p_{u/g}$ as

$$\delta p_g = \frac{1}{2} \left(p_g^{|\pm 2, \pm 1\rangle} - p_g^{|\pm 2, \mp 1\rangle} \right) \quad \delta p_u = \frac{1}{2} \left(p_u^{|\pm 2, \pm 1\rangle} - p_u^{|\pm 2, \mp 1\rangle} \right) \quad (42)$$

We evaluate each of these $\hat{L}_z \hat{S}_z$ matrix elements on the vibronic solutions to the coupled spin-orbit Jahn-Teller Hamiltonian. The results for the lowest-energy states are visualized in Fig. 6. In almost all cases, outside of SiV⁰, the $\langle L_z S_z \rangle$ expectation values are not symmetrical about zero, as a result of the strong electron-phonon coupling. The reduction factors p_u and p_g can be read off of the plot and are all less than 0.05, signifying a strong quenching due to the product Jahn-Teller effect, as discussed in the main text.

Finally analogous to the group IV negative case, we introduce the term K which is the result of zero-point energy differences for the vibronic $|\pm 2, \pm 1\rangle$ and $|\pm 2, \mp 1\rangle$ wavefunctions, given by

$$K = \langle \pm 2, \pm 1 | \hat{H}_{\text{osc}} + \hat{H}_{\text{JT}}^{(2)} + \hat{W} | \pm 2, \pm 1 \rangle - \langle \pm 2, \mp 1 | \hat{H}_{\text{osc}} + \hat{H}_{\text{JT}}^{(2)} + \hat{W} | \pm 2, \mp 1 \rangle. \quad (43)$$

	SiV ⁰	GeV ⁰	SnV ⁰	PbV ⁰
$p_u^{ \pm 2, \pm 1\rangle}$	0.0250	0.0894	0.2674	0.6356
$p_u^{ \pm 2, \mp 1\rangle}$	-0.0021	0.0563	-0.2026	-0.5503
$p_g^{ \pm 2, \pm 1\rangle}$	0.01374	0.0220	0.0539	0.1427
$p_g^{ \pm 2, \mp 1\rangle}$	0.00934	0.0049	-0.0088	-0.0637
K [meV]	0.0000	0.0074	0.1758	0.5101
p_u	0.0115	0.0165	0.0324	0.0427
p_g	0.0115	0.0122	0.0226	0.0395
δp_u	0.0136	0.0729	0.2350	0.5930
δp_g	0.0022	0.0098	0.0314	0.1032
$\lambda_u + \lambda_g$ [meV]	0.089	0.622	3.15	11.31
(p) p_u	0.011	0.016	0.030	0.040
(p) p_g	0.012	0.013	0.021	0.023
(p) $\lambda_u + \lambda_g$ [meV]	0.089	0.618	3.06	10.6
$\gamma \left(A_{2u}^{\pm} - A_{2u}^0 \right)$ [meV]	0.0241	0.6805	5.922	40.34

Supplementary Table 2. Spin-orbit coupling parameters for the group IV neutral defects calculated using both direct diagonalization and perturbation theory. Quantities obtained via perturbation theory are denoted by (p). We also note the splitting between the $m_s = \pm 1$ and $m_s = 0$ states of the optically-dark A_{2u} state.

With this, we can recover the full effects of spin-orbit splitting by

$$\lambda_g + \lambda_u = p_g \lambda_g^0 + p_u \lambda_u^0 - K. \quad (44)$$

All of these values are tabulated in Table 2. The inclusion of K only becomes energetically significant for the case of PbV⁰.

We finally list the energy difference between the $m_s = \pm 1$ and $m_s = 0$ levels of the optically-dark A_{2u} state, given by $\gamma \left(A_{2u}^{\pm} - A_{2u}^0 \right)$. This energy shift represents the absolute energy shift as a result of including the SOC Hamiltonian directly in solving Eq. 32.

SUPPLEMENTARY NOTE 6: ZERO PHONON LINE ENERGY

The zero-phonon line (ZPL) energy can then be found, as described previously [2], by

$$\text{ZPL} = E_{\text{tot}}^{\text{DFT}}(\mathcal{A}|e_{uy}e_{gy}\rangle \otimes |\downarrow\downarrow\rangle) - E_{\text{tot}}^{\text{DFT}}(|^3A_{2u}\rangle) + \frac{1}{2}(\Lambda + \Xi) - \hbar\omega_E + \langle ^3E_u | \hat{H} | ^3E_u \rangle \quad (45)$$

Here $E_{\text{tot}}^{\text{DFT}}(\mathcal{A}|e_{uy}e_{gy}\rangle \otimes |\downarrow\downarrow\rangle)$ represents the DFT energy obtained for the lowest surface at the D_{3d} geometry, $E_{\text{tot}}^{\text{DFT}}(|^3A_{2u}\rangle)$ is similarly the DFT energy associated with the ground state of the defect, and $\langle ^3E_u | \hat{H} | ^3E_u \rangle$ is the absolute energy after solving the combined Hamiltonian $\hat{H}$ for the system, which in the absence of spin-orbit coupling is given by Eq. 2 of the main text, otherwise it is given by Eq. 32.

SUPPLEMENTARY NOTE 7: STRAIN EFFECTS

We now briefly mention how crystal strain may affect our results. A more complete analysis of strain effects for the group IV⁰ can be found in Ref. 9, where stress was applied to SiV⁰-containing diamond along different directions and resulting optical spectra were analyzed. From this and group theory analysis, one can understand the potential effects of strain.

One important qualitative effect is that while the vibronic state we label with symmetry A_{2u} is optically dark in unstrained diamond, applied uniaxial strain causes this level to couple with the ground A_{2g} state, meaning the transition can be observed [9]. Additionally, quantitative properties of the systems can change. For instance, strain can affect the energy position of the A_{2u} and E_u states to different extents, which can impact the measured splitting γ between them. In the experiments done in Ref. 9, stresses of up to 2 GPa were applied, and the observed energy shifts were up to ~ 10 meV

in magnitude. Thus, strain may have an important quantitative impact on the splittings between the E and A states. These energy shifts would also contribute to differences in the zero phonon line energies.

Additional calculations in which strain and Jahn-Teller effects are treated simultaneously to track the evolution of vibronic states with strain may be possible, as this has been done for the group IV⁻ defects [8]. Since strain is a static effect, it is not expected to directly influence the spin-orbit quenching we discuss throughout the text. However this is outside the scope of the work we present here.

-
- [1] J. R. Maze, A. Gali, E. Togan, Y. Chu, A. Trifonov, E. Kaxiras, and M. D. Lukin, *New J. Phys.* **13**, 025025 (2011).
 - [2] G. Thiering and A. Gali, *npj Comput. Mater.* **5**, 18 (2019).
 - [3] G. Thiering and A. Gali, *Phys. Rev.* **96**, 081115 (2017).
 - [4] I. Bersuker and V. Polinger, *Vibronic Interactions in Molecules and Crystals*, Vol. 49 (Springer Series in Chemical Physics, Springer-Verlag Berlin, Heidelberg, 1990).
 - [5] C. Hepp, *Electronic Structure of the Silicon Vacancy Color Center in Diamond*, Ph.D. thesis, Saarland University (2014).
 - [6] C. Hepp, T. Müller, V. Waselowski, J. N. Becker, B. Pingault, H. Sternschulte, D. Steinmüller-Nethl, A. Gali, J. R. Maze, M. Atatüre, and C. Becher, *Phys. Rev. Lett.* **112**, 036405 (2014).
 - [7] P. Yu and M. Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties*, 4th ed., Graduate Texts in Physics (Springer-Verlag, Berlin Heidelberg, 2010).
 - [8] G. Thiering and A. Gali, *Phys. Rev. X* **8**, 021063 (2018).
 - [9] B. L. Green, M. W. Doherty, E. Nako, N. B. Manson, U. F. S. D’Haenens-Johansson, S. D. Williams, D. J. Twitchen, and M. E. Newton, *Phys. Rev. B* **99**, 161112 (2019).