

Supplementary Material

Predicted strong spin-phonon interactions in Li-doped diamond

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In this Section, we describe first, how the vibrational frequencies are computed and the IR and Raman spectra are produced in the CRYSTAL code and second, how the energy difference between the two spin states and the position of the peaks in the IR spectra change with the adopted hybrid functional, or when altering the percentage of exact exchange (EX).

I. COMPUTATIONAL DETAILS ON THE IR AND RAMAN SPECTRA

This part is very standard, and has been presented in many previous papers regarding defects in diamond. [1–3]

Frequencies at the Γ point are obtained within the harmonic approximation by diagonalising the mass-weighted Hessian matrix, W , whose elements are defined as [4–8]

$$W_{\alpha i, \beta j}^{\Gamma} = \frac{H_{\alpha i, \beta j}^0}{\sqrt{M_{\alpha} M_{\beta}}} \quad \text{with} \quad H_{\alpha i, \beta j}^0 = \left(\frac{\partial^2 E}{\partial u_{\alpha i}^0 \partial u_{\beta j}^0} \right), \quad (\text{S1})$$

where M_{α} and M_{β} are the masses of atoms associated with the i and j atomic coordinates. Once the Hessian matrix, $\mathcal{H}_{\alpha i, \beta j}$, has been calculated, frequency shifts due to isotopic substitutions can be calculated readily, at no computational cost, by changing masses in Equation S1.

Energy first derivatives with respect to the atomic positions, $v_{\alpha, j} = \partial E / \partial u_{\alpha, j}$, are calculated analytically for all the $u_{\alpha, j}$ coordinates (E is the total energy, $u_{\alpha, j}$ is the displacement coordinate with respect to the equilibrium, α labels each atom), whereas second derivatives at $\vec{u} = 0$ are calculated numerically using a single displacement along each coordinate ($N=2$, the central point and a point on the right side of the parabola):

$$\left[\frac{\partial v_{\alpha j}}{\partial u_{\beta i}} \right] \approx \frac{v_{\alpha j}(0, \dots, u_{\beta i}, \dots)}{u_{\beta i}} \quad (\text{S2})$$

or averaging two displacements ($N=3$):

$$\left[\frac{\partial v_{\alpha j}}{\partial u_{\beta i}} \right] \approx \frac{v_{\alpha j}(0, \dots, u_{\beta i}, \dots) - v_{\alpha j}(0, \dots, -u_{\beta i}, \dots)}{2u_{\beta i}} \quad (\text{S3})$$

Previous calculations[4, 9] have shown that in bulk systems the influence of both u and N is very small (less than 1 cm^{-1}) when H atoms are not present.

Integrated intensities for IR absorption \mathcal{I}_p are computed for each mode p by means of the mass-weighted effective-mode Born-charge vector \mathbf{Z}_p [10, 11] evaluated through a CPHF/KS approach:[12, 13]

$$\mathcal{I}_p \propto |\mathbf{Z}_p|^2. \quad (\text{S4})$$

The relative Raman intensities of the peaks are computed analytically by exploiting a scheme illustrated in refs. 14, 15. Both schemes are based on the solutions of first- and second-order Coupled-Perturbed-Hartree-Fock/Kohn-Sham (CPHF/KS) equations.[16, 17]

II. THE EFFECT OF HAMILTON ON THE ENERGETIC AND VIBRATIONAL PROPERTIES

A long experience shows that the dominant contribution to the energy difference between the spin states is given by the exact exchange percentage, EX. The influence of the other ingredients of the functional is negligible, or much smaller, as documented in previous papers [18–20]. EX percentages between 20 and 30 seem to provide quite reasonable results. B3LYP performs better, or at least not worse, than other hybrid functionals, in general.

functional	EX (%)	ΔE (eV)
B3LYP	20	-0.0067
PBE0	25	-0.0048
PBE0 (50)	50	-0.0024
PBE0 (100)	100	-0.0019

Table S1: Energy difference between low and high spin states. The EX column indicates the percentage of exact exchange. All difference are in eV.

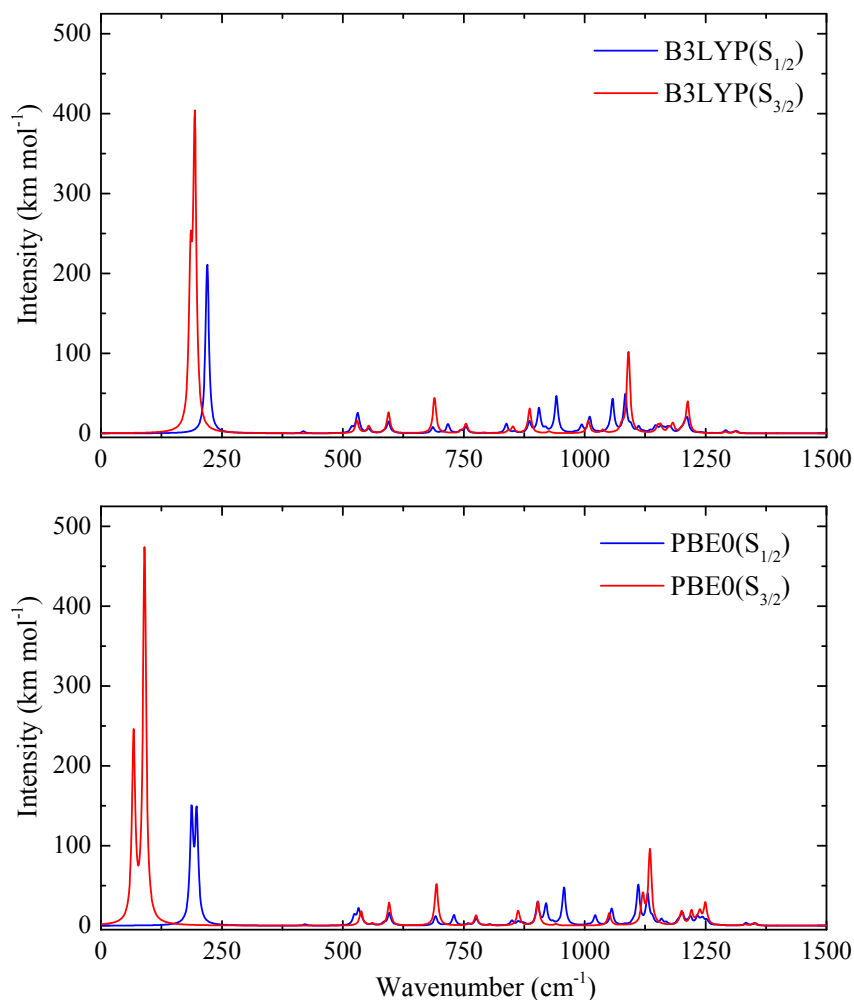


Figure S1: Four computed IR spectra are reported: top B3LYP, bottom PBE0, blue doublet, red quartet.

Table S1 compares B3LYP (20% EX) and PBE0 (25% EX). Also the cases in which in PBE0 the EX percentage is increased to 50 and 100 are reported. The energy difference reduces by a factor larger than 3 between the two extreme cases. What is important to underline, however, is that the relative stability of the two states remains unaltered.

In Figure S1 the B3LYP (top) and PBE0 (bottom) IR spectra are reported for the doublet and quartet spin states. There are important differences between the spectra obtained with the two functionals: the peaks shift, and the difference between $S_z = 3/2$ and $S_z = 1/2$ increases with the exchange percentage. In all the EX % range, higher probably than a few percent, the two spectra show well separated peaks. For pure DFT functionals (LDA, PBE), the difference would most probably disappear.

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