N_2 positively charged defects in diamond. A Quantum Mechanical investigation of the structural, electronic, EPR and vibrational properties.

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Formation Energy versus supercell size

In Table S1 the defect formation energy, E_f, is reported as a function of the supercell size. E_f is defined as the difference between E_{def}, the total energy of the defective system, and M times E_{diam}, the total energy of pristine diamond per atom (-38.05591 E_h), plus E_{N_2}, the total energy of the isolated N_2 molecule (-109.31265 E_h). On going from S_{64} to S_{1000} E_f changes by only 0.004 E_h, that is about 0.11 eV.

Table S1: Defect formation energy of the N_2^+ system as a function of the supercell size. M is the number of carbon atoms contained in the defective system, E_{def} is the total energy of the defective system, while E_f is the formation energy.

Supercell	M	E_{def} (E_h)	E_f (E_h)
S_{64}	62	-2469.21468	-0.436
S_{216}	214	-8253.70620	-0.429
S_{512}	510	-19518.25479	-0.429
S_{1000}	998	-38089.54174	-0.432

Hyperfine coupling and quadrupolar ($P_{||}$) constants

Table S2 reports the data in Gauss, as required by one of the referees, whereas in the corresponding table of the main text they are in MHz, as in the most recent experimental paper (Ref.[1]).

Site	A_{iso}	B_1	B_2	B_3	$P_{||}$	
^{14}N	+39.35	+17.66	-8.83	-8.83	-0.87	
	+37.86	+17.55	-8.77	-8.77	-0.80	Ref.[1]
	+37.67	+17.53	-8.77	-8.77	-	Ref.[2]
^{15}N	-55.20	-24.77	+12.39	+12.39	-	
$^{13}C_1$ (a)	-4.37	+0.91	-0.62	-0.29	-	
$^{13}C_1$ (a)	-4.39	-	-	-	-	Ref.[1]
$^{13}C_2$ (b)	+3.97	+1.48	-0.80	-0.68	-	
$^{13}C_3$ (c)	+1.32	+0.60	-0.31	-0.29	-	
$^{13}C_4$ (d)	+1.26	+0.47	-0.25	-0.22	-	
$^{13}C_5$ (h)	+0.31	+0.16	-0.10	-0.06	-	
$^{13}C_6$ (e)	-0.15	+0.33	-0.19	-0.15	-	
$^{13}C_7$ (f)	+0.13	+0.34	-0.20	-0.14	-	

Table S2: Hyperfine coupling and quadrupolar ($P_{||}$) constants (Gauss) for the doublet state ($S_z = 1/2$) of the N_2^+ defect based on the 6-31G-J* basis set. $\mathscr{B}$ tensor components are sorted so that $|B_1| > |B_2| > |B_3|$. The constants are in descending $|A_{iso}|$ order for the carbon atoms (from C_1 to C_7). The labels in round brackets are those shown in Fig. 1 of the main text.

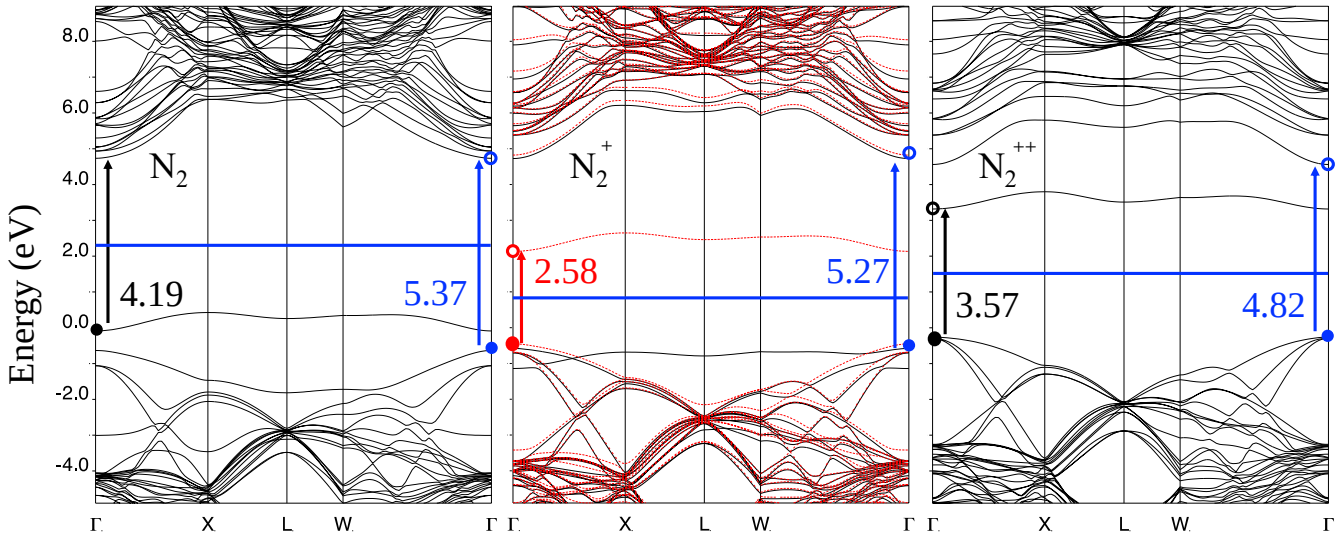

Figure S1: Sketch of the band structures of the N_2, N_2^+ and N_2^{++} defects in diamond. The N_2 and N_2^{++} ground state is a closed shell singlet; it is a doublet for N_2^+. Filled and empty circles (black for N_2 and N_2^{++}, red for N_2^+) indicate occupied and virtual defect levels. In the N_2^+ case the smallest gap corresponds to a transition between beta spin levels, highlighted by a red arrow. Data refer to the S_{64} supercells.

[1] O. Tucker, M. Newton and J. Baker, *Phys. Rev. B*, 1994, **50**, 15586–15596.
[2] J. Van Wyk and J. Loubser, *J. Phys. C: Solid State Phys.*, 1983, **16**, 1501.