Stable electronic-nuclear spin systems NV-^{13}C in diamond for quantum technologies

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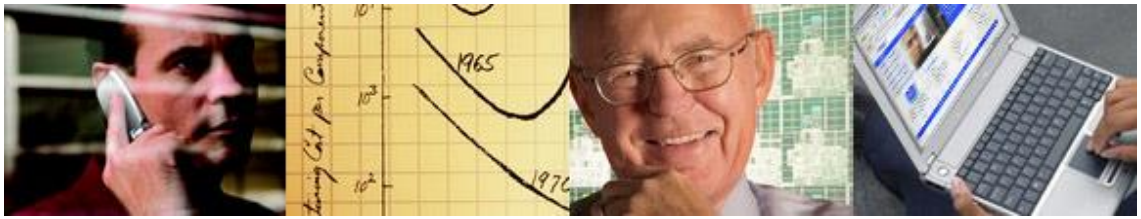
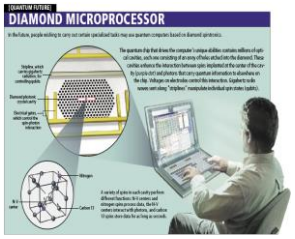
Motivation: NV applications in quantum nanotechnologies

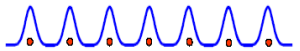


Quantum computers



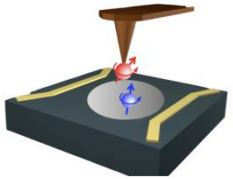
QC on
NV centers

Quantum cryptography



«Photon gun»
on single NV centers

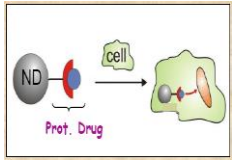
Quantum nanometrology



Single-spin
magnetometer on
NV centers

Decisive advantage – room temperature conditions (!)

Biomedical applications



Delivery of NDNV
into bioobjects

Diamond is an exceptional material

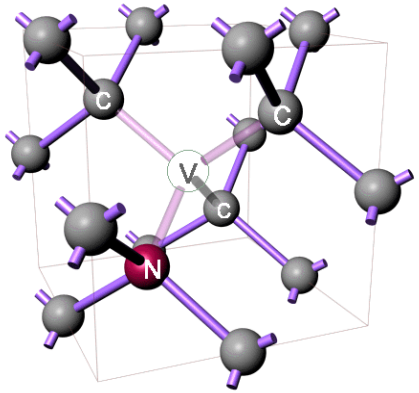
- Hardest material
- High heat conductivity
- Widest optical transparency window
- Chemically inert and biocompatible
- Wide bandgap ~ 5.6 eV
- A wide variety of optically active colour centers
  (> 500 electronic, > 150 vibrational)

(from

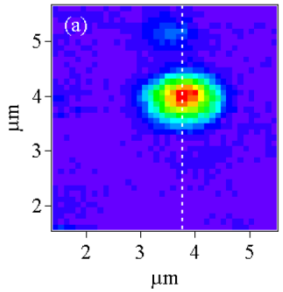
GR1(V^0,741nm)
NV^- (637nm)
Si-V^0 (738nm)
…
Ni (NE8, 800nm)
Xe (812nm)
VH (1358nm)
NVH (1456nm)

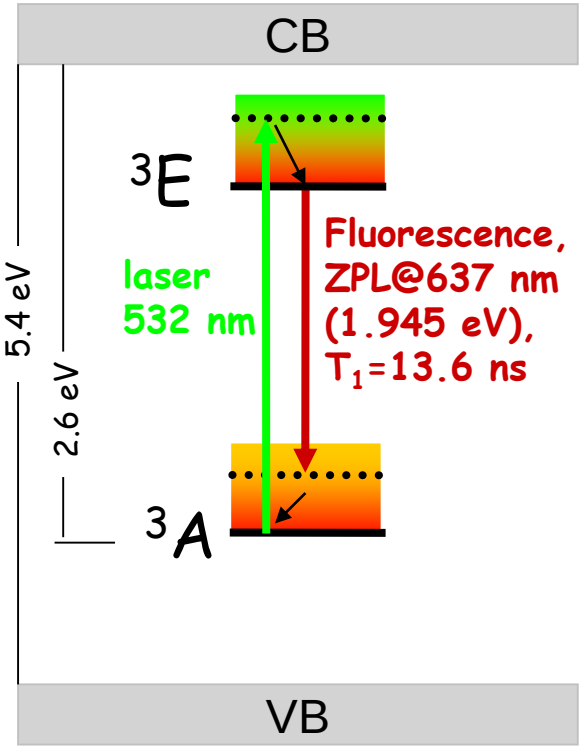
NV ID

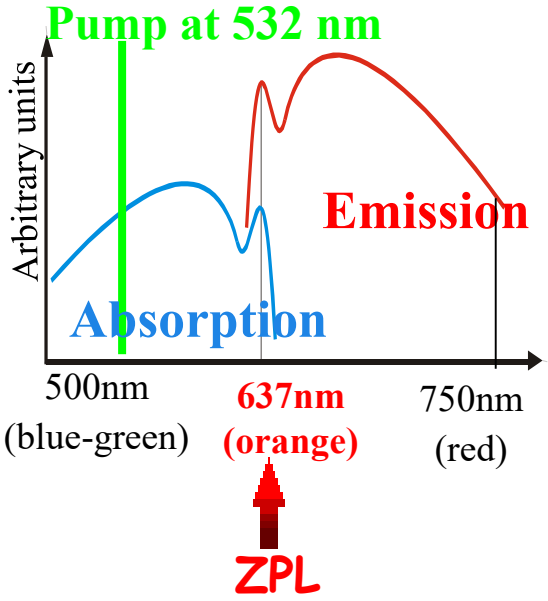
- Structure
- Simple Energy diagram
- Abs./ Em. Spectra



- Single NV

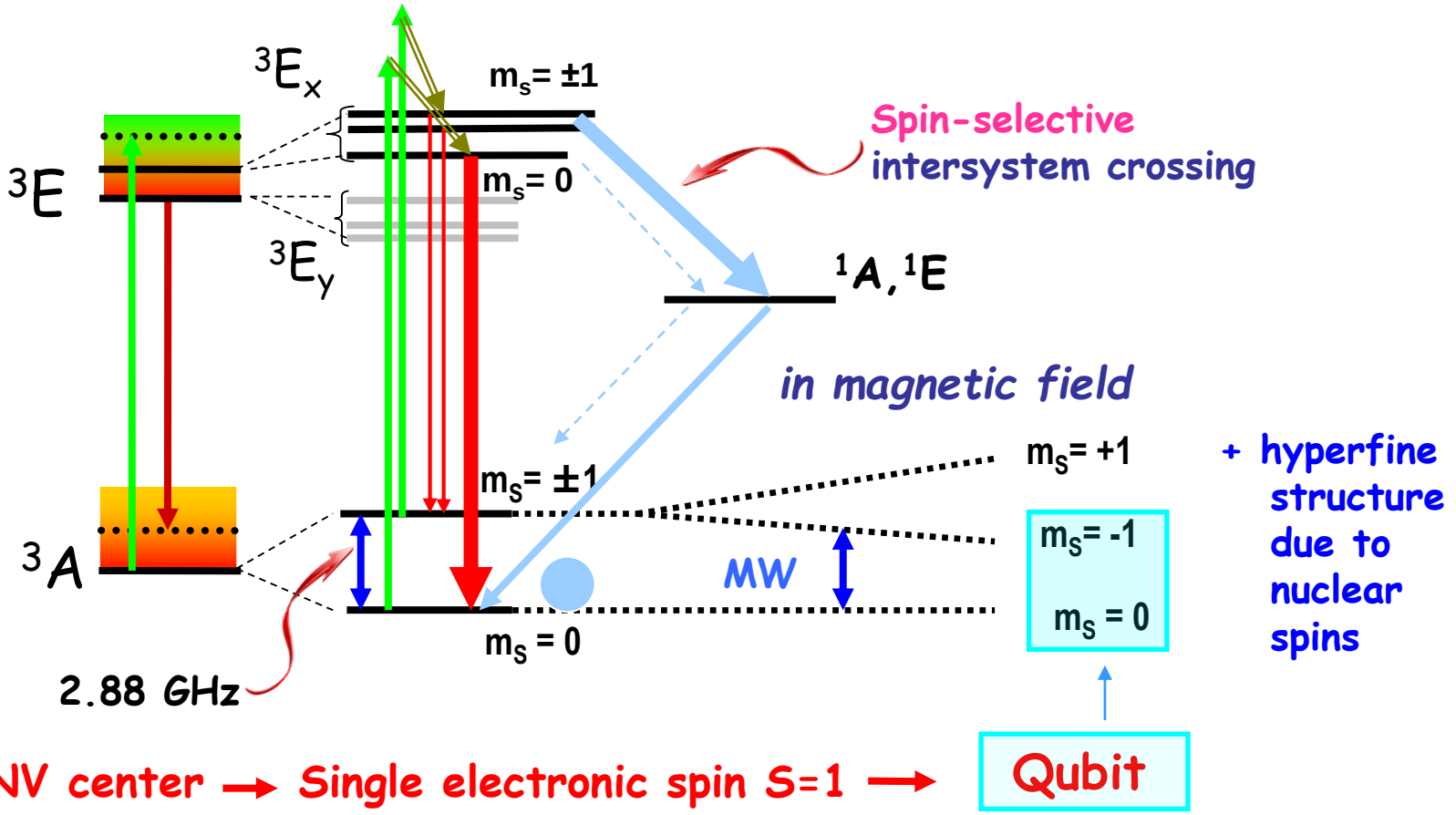






- C_{3v} symmetry, 6 e^- model, paramagnetic ground state (S = 1)
- Perfectly photostable
- Optical detection of single NV centers (Gruber et. al. Science, 1997)

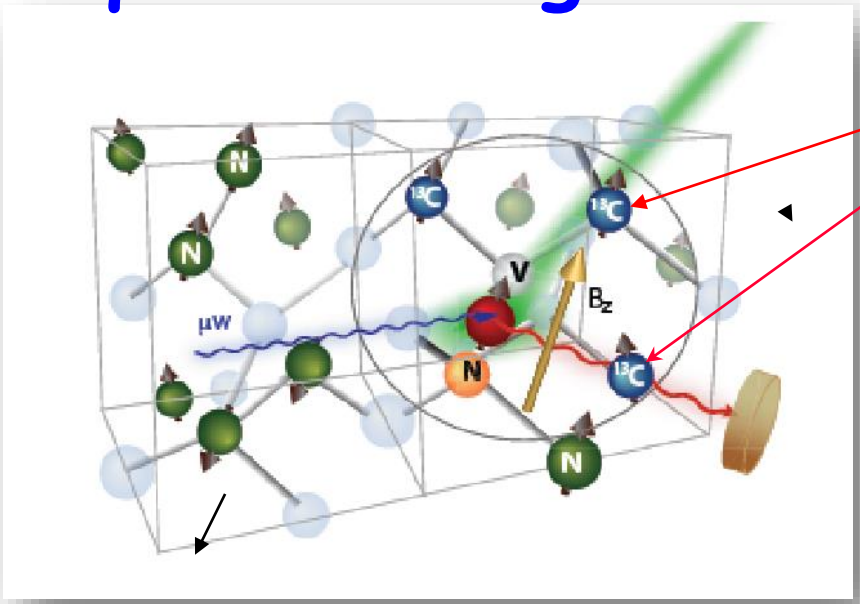
Single NV center = single qubit



Single NV center → Single electronic spin S=1 →

- "Green" pulse aligns the center into the m_S=0 spin state → optical initialization
- The center emits bright fluorescence only in the m_S=0 spin state → optical readout
- MW at 2.88 GHz → coherent manipulation by single e-spin
- Long coherence time (~ few ms in isotopically pure diamond at RT) → many gates

^{13}C spin environment as a resource: quantum registers & quantum memoris

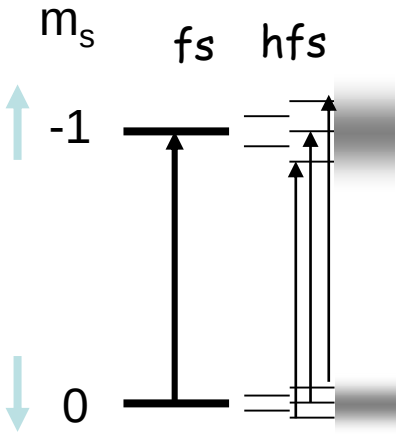


Proximal ^{13}C nuclei (I=1/2)
(~1.1% natural abandence)

They have strong hfi with NV and can be used as a resource for QIP :

The idea was put forward conceptually in 2001 in : **Wrachtrup, Kilin, Nizovtsev, Opt. & Spectrosc. 91 (2001) 429**

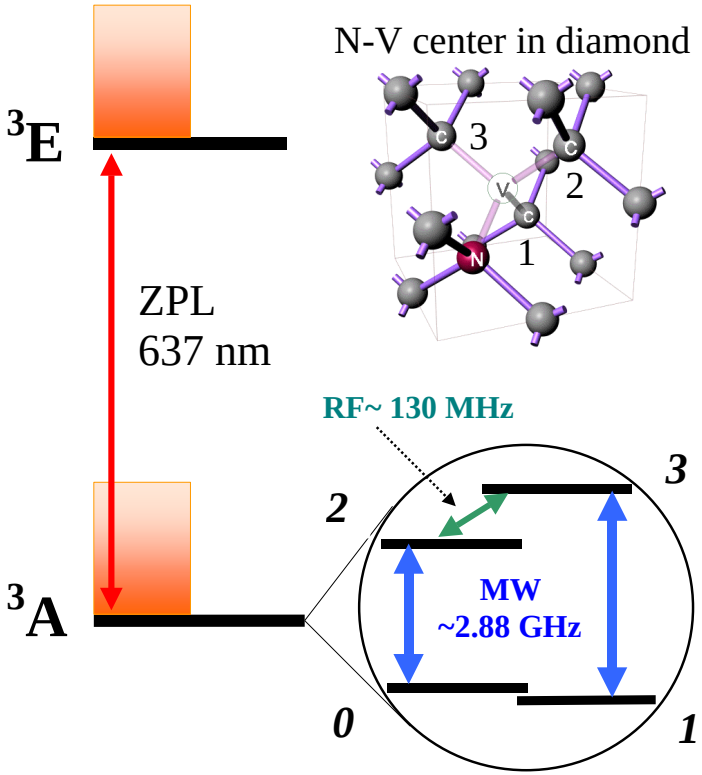
Remote nuclei form spin bath with mutual spin flip-flops resulting in NV e-spin decoherence



Challenge:
- to initialize, manipulate and readout individual nuclear spins,
- to develop techniques to suppress decoherence due to spin bath
- to provide complete understanding of spin properties (energies & eigenstates) of NV+n^{13}C spin system.

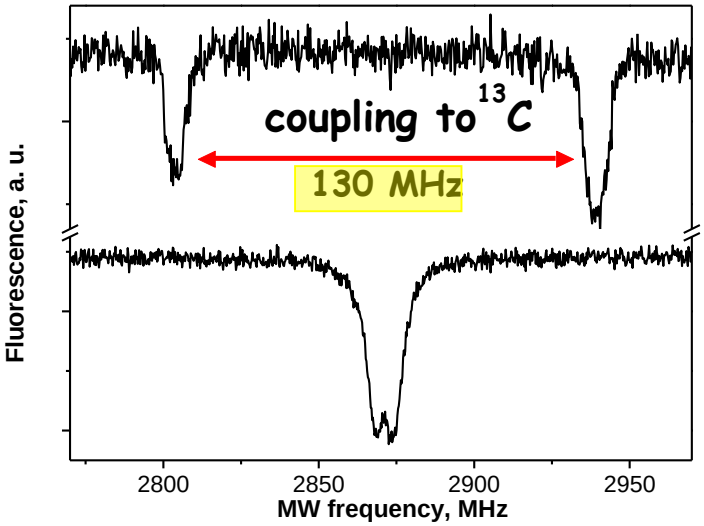
Breakthrough of 2004: first two-qubit CROT operation in NV+^{13}C spin system at RT

Jelezko et al. PRL 93 (**2004**) 130501



FS+HFS in the ^3A state of single NV+ single ^{13}C

Comparative ODMR spectra



NV+^{13}C

NV

Engineered Quantum Information in Nanostructured Diamond

equind

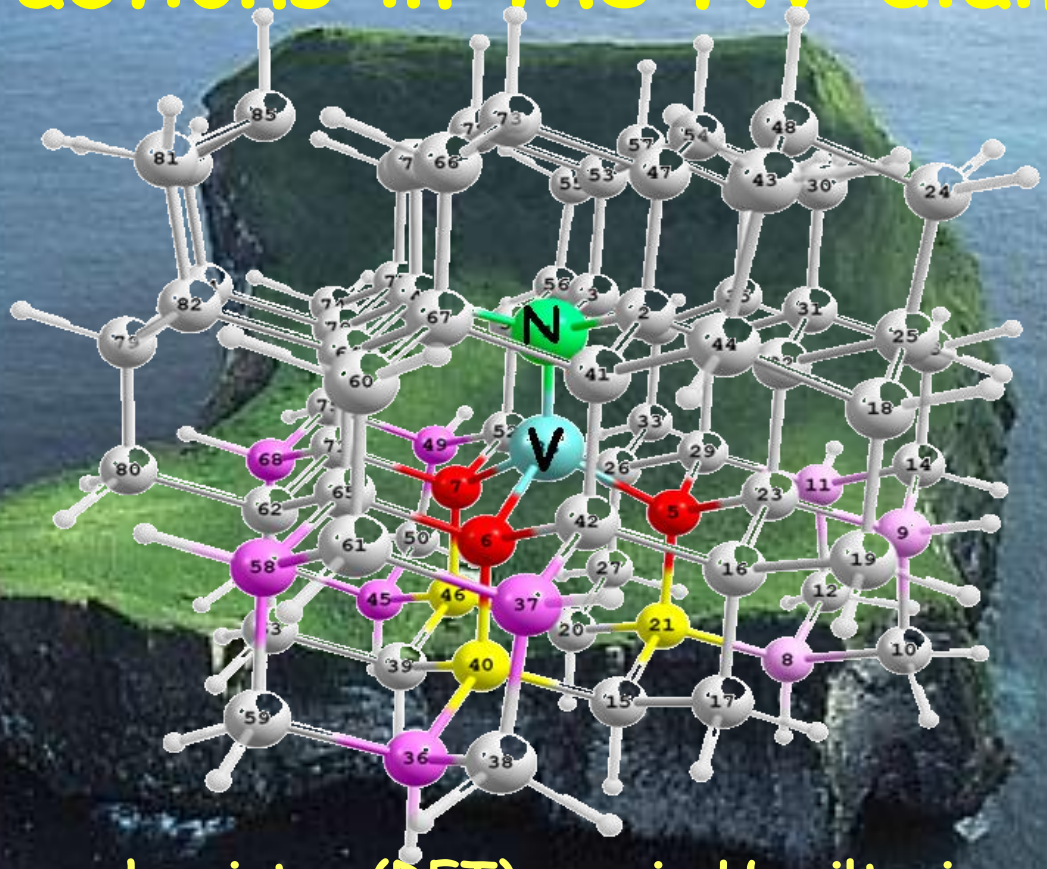
EQUIND consortium (2007-2010)

Materials	Theory	QIPC
Twitchen – Element6 Synthesis, structuring Ultrapure diamond	**Kilin** Quantum chemistry Cavity quantum electro-dynamics	**Prawer / Roch** Single-photon source and QKD
Prawer / Steeds Implantation, structuring	**Newton / Steeds** Bulk characterization	**Rarity / Prawer** Photonics structures
Krüger / Prawer Nanodiamonds and surface functionalisation		**Wrachtrup** Spin-based quantum operations

Recent results on NV diamond:

- reliable, automated manipulation with single NV + few nearby nuclear spins in diamond was achieved;
- fine structure of the excited state was elucidated;
- ODMR in the excited state was observed;
- stains influence was understood both experimentally and theoretically;
- singlet states (quantity, positions, characteristic times…) were studied;
- photochromism of NV (transformations NV^- to NV^0 and back) was studied;
- multipartite systems (NV+few ^{13}C) were implemented and studied;
- entangled Bell states, GHZ states were created and investigated;
- dynamical methods of decoherence suppression was applied;
- specific features of NV in nanodiamonds were studied;
- diamond engeneering (isotopically pure); creation of NV's…
- photon collection (NV in PC) etc…
- **and many others ……**

Our contributions: characterization of hyperfine interactions in the NV diamond



Methods: quantum chemistry (DFT) + spin Hamiltonian.
Basic desired quantities – characteristics of hyperfine interactions between electronic spin of the NV center and nearby ^{13}C nuclear spins.
We have used Gaussian and Orca program packages.

Quantum Chemistry "line" to find $A^{(n)}$ for Spin Hamiltonian

DFT calculates the spin-up and spin-down densities ($\rho_{\uparrow}$, $\rho_{\downarrow}$) distributions over the relaxed carbon clusters with NV

$$A = A_{iso} * I + A_{aniso}$$

$$A_{iso} = \frac{2\mu_0}{3}(g_e\mu_e)(g_n\mu_n)\rho_\sigma(r_n)$$

- Isotropic (Fermi contact) part

Spin density: $\rho_\sigma = \rho_\uparrow - \rho_\downarrow$

$$A_{aniso} = \frac{\mu_0}{4\pi}(g_e\mu_e)(g_n\mu_n)\int T(r)\rho_\sigma(r + r_n)dr$$

- Anisotropic (dipolar) part

$$T(r) = \frac{1}{r^5}\begin{pmatrix} 3x^2 - r^2 & 3xy & 3xz \\ 3xy & 3y^2 - r^2 & 3yz \\ 3xz & 3yz & 3z^2 - r^2 \end{pmatrix}$$

-dipole-dipole interaction tensor (traceless)

Spin Hamiltonian for NV-^{13}C

Spin hamiltonian $H = H_0 + H_{Zeeman} + H_{hfi}^{[n]}$

Hyperfine interaction with n nuclear spins

Zero-field splitting: $H_0 = D_X S_X^2 + D_Y S_Y^2 + D_Z S_Z^2 =$

$= D[S_Z^2 - S(S+1)/3] + E(S_X^2 - S_Y^2)$

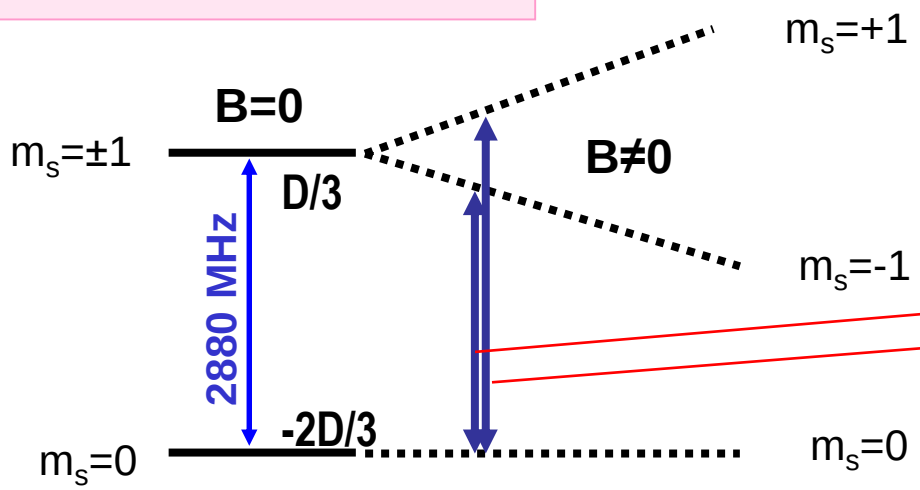
In coordinate system where Z axis is the C_{3V} symmetry axis (NV PACS)

$D = 3D_Z/2,\ E = (D_X - D_Y)/2$

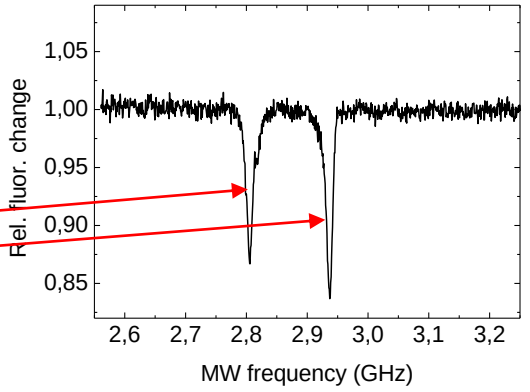
S_X, S_Y, S_Z are standard spin S=1 matrices

D=2880 MHz; E=0 due to C_{3V} symmetry

$H_{Zeeman} = \gamma^{(NV)} B$



Typical ODMR spectrum of single NV center at B≠0



Hyperfine interactions

$$H_{hfi}^{(j)} = \hbar \sum_{KL} A_{KL}^{(j)} S_K \otimes I_L^{(j)}$$

hfi matrices

$$\mathbf{A} = \begin{pmatrix} A_{XX} & A_{XY} & A_{XZ} \\ A_{YX} & A_{YY} & A_{YZ} \\ A_{ZX} & A_{ZY} & A_{ZZ} \end{pmatrix}$$

The main problem is to find matrices A which are different for different ^{13}C atoms

$$H_{hfi}^{[1]} = \sum_{KL} A_{KL}^{(1)} S_K \otimes I_L$$

single nuclear spin I

$$H_{hfi}^{[2]} = H_{hfi}^{[1]} \otimes e + \sum_{KL} A_{KL}^{(2)} S_K \otimes e \otimes I_L$$

two nuclear spins I

. . . . . .

$$H_{hfi}^{[n-1]} = H_{hfi}^{[n-2]} \otimes e + \sum_{KL} A_{KL}^{(n-1)} S_K \otimes \underbrace{e...e}_{N-2} \otimes e \otimes I_L$$

n-1 nuclear spins I

$$H_{hfi}^{[n]} = H_{hfi}^{[n-1]} \otimes e + \sum_{KL} A_{KL}^{(n)} S_K \otimes \underbrace{e...e}_{N-1} \otimes e \otimes I_L$$

n nuclear spins I

Dimensionality of Hilbert space for NV-n^{13}C is $d_H = (2S+1)\prod_{j=1}^{n}(2I^{(j)}+1) = 3 \times 2^n$

Hamiltonian diagonalization gives energy levels E_α and spin wave functions:

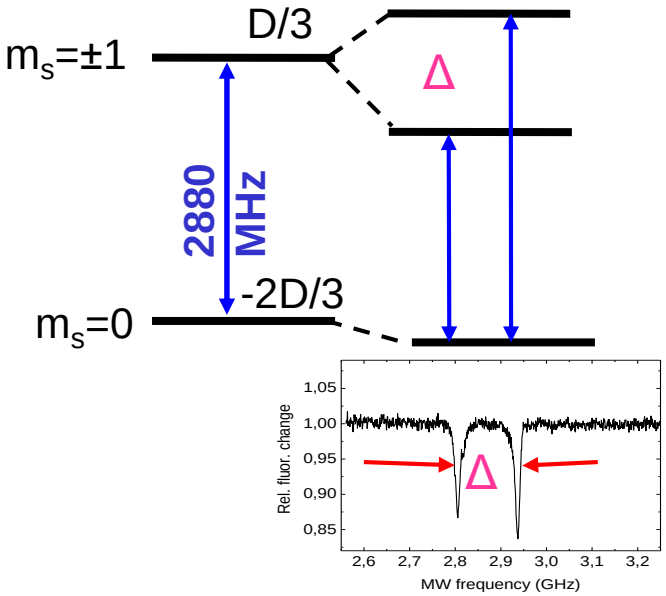
$$|\alpha\rangle = \sum_{m_S=-S}^{S} \sum_{m_I^{(1)}=-I^{(1)}}^{I^{(1)}} \cdots \sum_{m_I^{(n)}=-I^{(n)}}^{I^{(n)}} c^{(\alpha)}_{m_S, m_I^{(1)} \ldots m_I^{(n)}} \left| m_S, m_I^{(1)}, \ldots m_I^{(n)} \right\rangle$$

coeff. to be find

basis vectors

NV center ODMR spectrum: Hyperfine structure

NV without ^{13}C NV with single ^{13}C



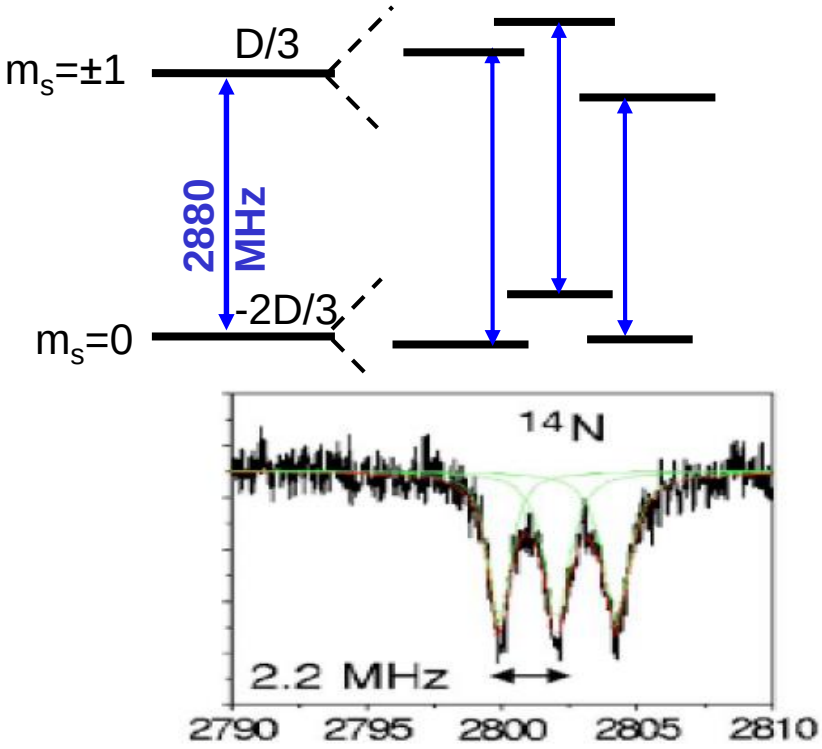
ODMR spectrum of NV+^{13}C spin system at B=0 consists of two lines with characteristic hfi splitting $\Delta \sim A$ (Δ=**130 MHz for NN ^{13}C**).

- If we know A matrix we can calculate Δ !!!

-In turn, if we have known Δ_i for all possible positions of ^{13}C with respect to NV we can determine the position by measuring Δ_i!!!

FS due to nuclear spin I=1 of ^{14}N:

$A_\perp$=-2.70 MHz, $A_{|||}$=-2.14 MHz, Q=-5.01 MHz,



ODMR spectrum of ^{14}NV center consists of three lines with the characteristic HFI splitting ~ 2.2 MHz.

+ Nuclear Zeeman effect $\gamma_n^{(N)}B$ with

$$\gamma_n^{(N)} = 0.31 \text{ kHz/Gauss}$$

Typical energy levels, eigenstates and allowed transitions between them for the ^{14}NV-1^{13}C spin system with distant ^{13}C

$$A = \begin{pmatrix} A_{XX} & A_{XY} & A_{XZ} \\ A_{YX} & A_{YY} & A_{YZ} \\ A_{ZX} & A_{ZY} & A_{ZZ} \end{pmatrix}$$

Secular approximation (terms ~ S_Z)

$$\Delta^{\pm} = \sqrt{A_{nd}^2 + (A_{ZZ} \mp \gamma_n^{(C)} B)^2}$$

magnetic field ||OZ

B=0

B(||OZ)≠0

D/3

2870 MHz

-2D/3

m_S=+1

m_S=-1

m_S=0

16 15 18 17 14 13 12 11 10 9 8 7 6 5 4 2 3 1

Δ^+ Δ^- δ

m_S=+1 m_S=-1 m_S=0

$\delta=\gamma^{13C}B$ – nuclear Zeeman

$m_I^{(N)} = -1$ $m_I^{(N)} = 0$ $m_I^{(N)} = +1$

Comparison with experimental data of *PRB 85 (2012) 13407 (Cachan, France)*

More them 400 ^{14}NV-1^{13}C centers were systematically studied !!!

PHYSICAL REVIEW B 85, 134107 (2012)

High-resolution spectroscopy of single NV defects coupled with nearby ^{13}C nuclear spins in diamond

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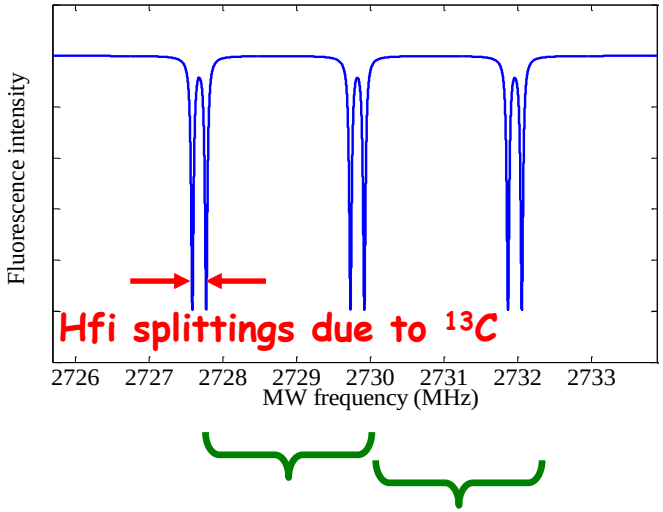
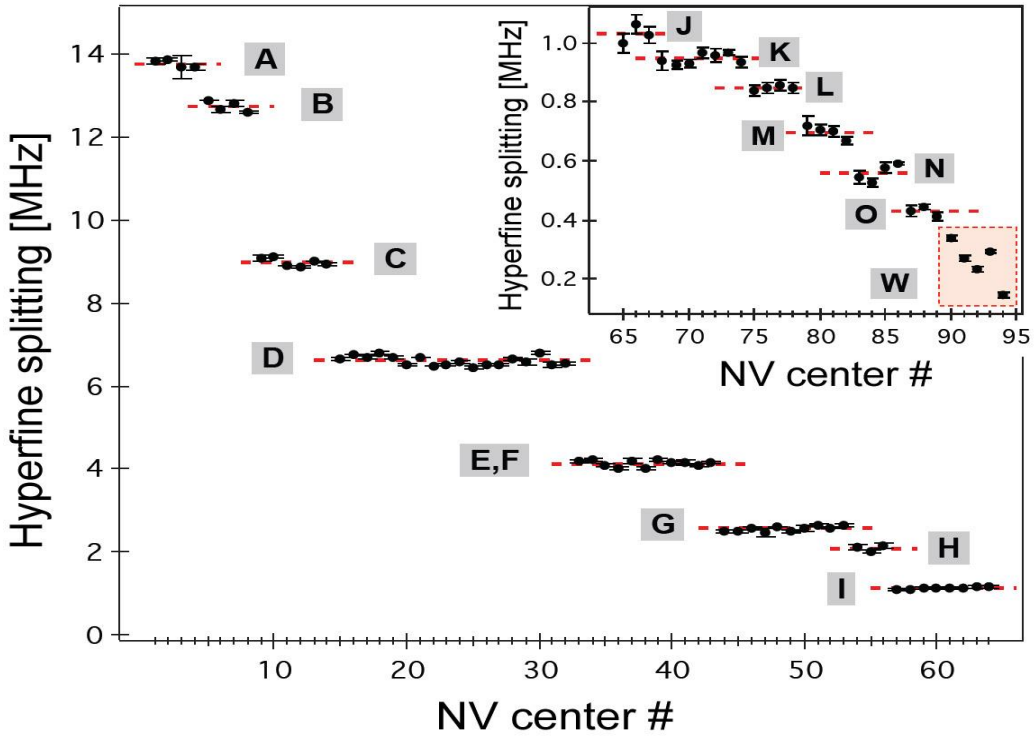




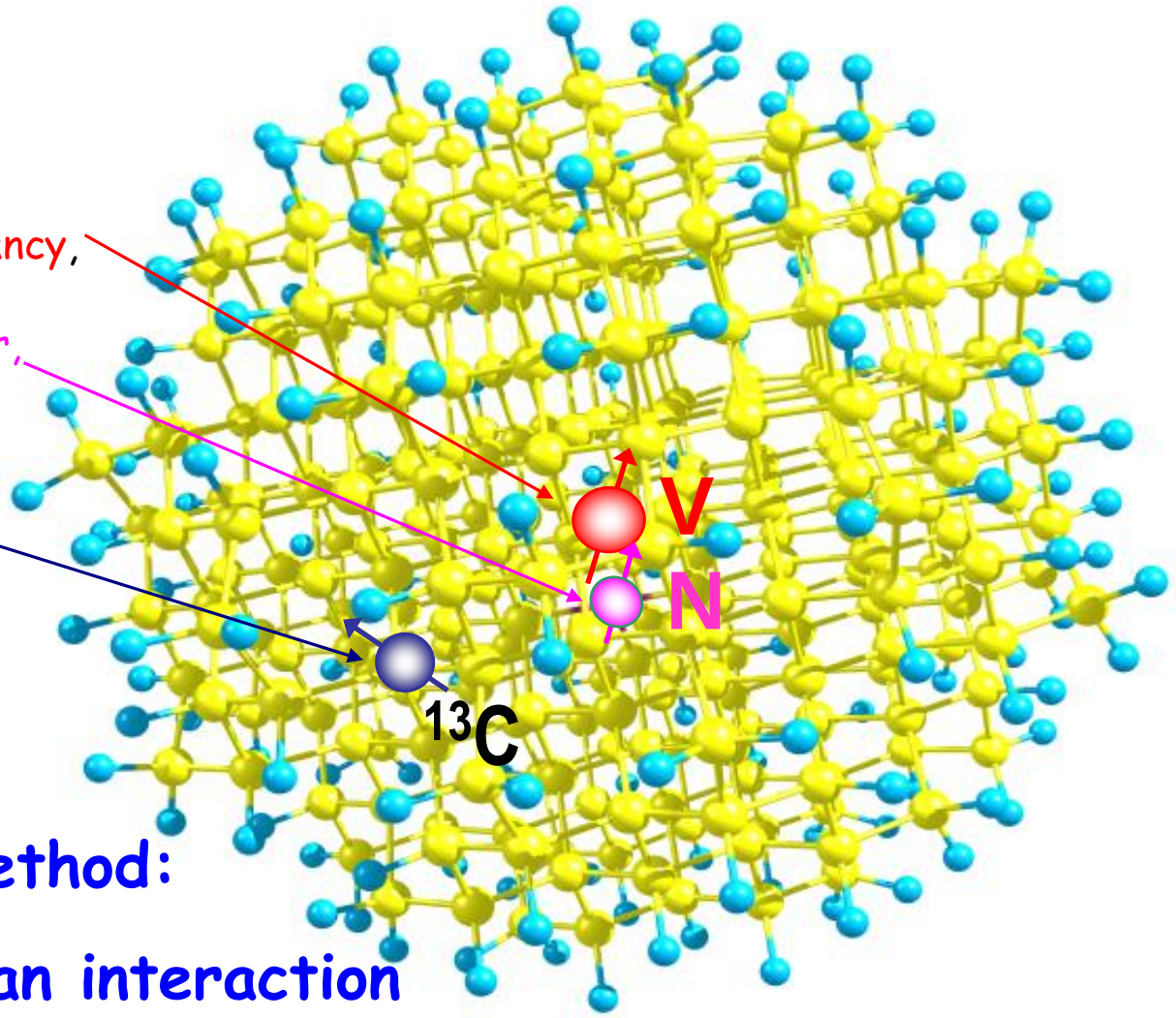
Simulation of 3-spin systems in the H-terminated cluster $C_{291}[NV]^{-}H_{172}$

Three-spin system:

i) electronic spin S=1 of NV center, localized near vacancy,

ii) nuclear spin I=1 of the ^{14}N atom of the center,

iii) nuclear spin I=1/2 of the ^{13}C atom somewhere in cluster



$$A = \begin{pmatrix} A_{XX} & A_{XY} & A_{XZ} \\ A_{YX} & A_{YY} & A_{YZ} \\ A_{ZX} & A_{ZY} & A_{ZZ} \end{pmatrix}$$

Spin hamiltonian method:

NV ZFS+hfi+Zeeman interaction

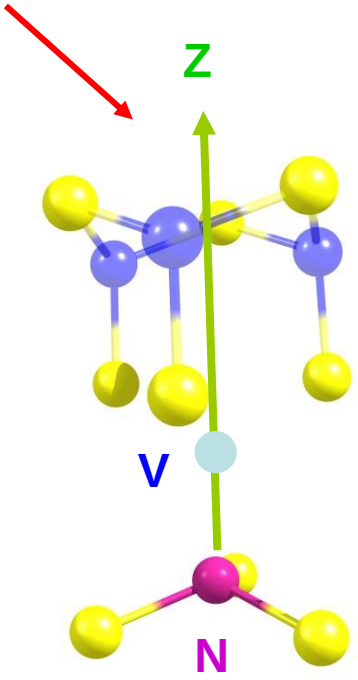
Our recent article New Journal of Physics 16 (2014) 083014

Simulated *hfi* and spatial characteristics for the "families" of equivalent positions of ^{13}C n-spin in the $C_{291}[NV]^{-}H_{172}$ cluster.

Family	N_C	$\bar{A}_{ZZ}$ (MHz)	$\bar{A}_{nd}$ (MHz)	$\bar{A}_k^{(0)}$ (MHz)	$\overline{\lvert\cos(Zz)\rvert}$	$\bar{Z}$ (Å)	$\bar{r}_{XY}$ (Å)	$\bar{r}_{NC}$ (Å)
A	6	12.451	1.166	12.471	0.288	- 0.522	3.937	**4.536**
B	3	11.386	1.434	11.451	0.412	- 2.655	2.972	**5.298**
C	3	-8.379	0.827	8.437	0.907	- 2.109	1.487	**4.118**
D	6	-6.450	0.931	6.521	0.296	- 0.010	2.552	**3.089**
E	3	4.055	0.826	4.136	0.848	-2.643	1.491	4.621
F	6	3.609	0.738	3.682	0.829	1.577	2.562	**2.566**
G	6	2.281	0.240	2.292	0.247	0.008	5.166	**5.446**
H	3	1.884	0.208	1.895	0.956	-4.242	2.976	**6.673**
I	3	-1.386	0.130	1.392	0.167	0.005	4.458	**4.780**
J	6	-1.145	0.328	1.191	0.488	-2.110	3.932	**5.497**
K1	3	-0.886	0.510	1.022	0.555	-2.118	2.985	**4.871**
K2	3	-1.011	0.014	1.012	0.029	-0.002	4.460	4.785
L	3	0.980	0.121	0.986	0.069	-0.535	2.972	**3.737**
M	3	0.602	0.557	0.819	0.865	2.127	1.460	**1.513**
N	6	0.725	0.095	0.731	0.219	-0.541	6.467	**6.855**
O1	3	0.673	0.171	0.694	0.528	-4.712	4.479	**7.847**
O2	3	0.655	0.166	0.676	0.902	3.707	2.983	**3.578**
P	6	0.474	0.190	0.510	0.402	-2.635	5.355	**6.909**
Q	6	0.391	0.273	0.477	0.524	-2.645	3.953	**5.897**
R	3	-0.226	0.393	0.453	0.759	2.115	2.985	**3.009**
S	3	0.412	0.060	0.417	0.119	-0.511	5.942	**6.351**
T	3	0.366	0.149	0.395	0.955	3.709	1.504	**2.485**
U	3	0.286	0.225	0.364	0.624	1.578	4.481	**4.484**
V	6	-0.209	0.232	0.312	0.639	2.105	3.927	**3.945**
W	3	-0.200	0.171	0.266	0.941	-4.220	1.489	**6.135**
X	6	0.211	0.152	0.259	0.899	-4.768	2.573	**6.990**
Y	**6**	**-0.228**	**0.001**	**0.227**	**0.002**	**-0.522**	**5.381**	**5.834**
Z1	3	0.158	0.131	0.205	0.857	4.226	3.001	**3.903**
Z2	3	0.086	0.184	0.203	0.464	1.576	4.447	**4.447**
on-NV-axis	**1**	**0.187**	**0.001**	**0.187**	**1.000**	**-4.734**	**0.009**	6.465

$$A = \begin{pmatrix} A_{XX} & A_{XY} & A_{XZ} \\ A_{YX} & A_{YY} & A_{YZ} \\ A_{ZX} & A_{ZY} & A_{ZZ} \end{pmatrix}$$

$$A_{nd}^2 = A_{ZX}^2 + A_{ZY}^2$$



Comparison of the calculated *hfi* splittings with experimental data of *PRB 85 (2012) 13407*

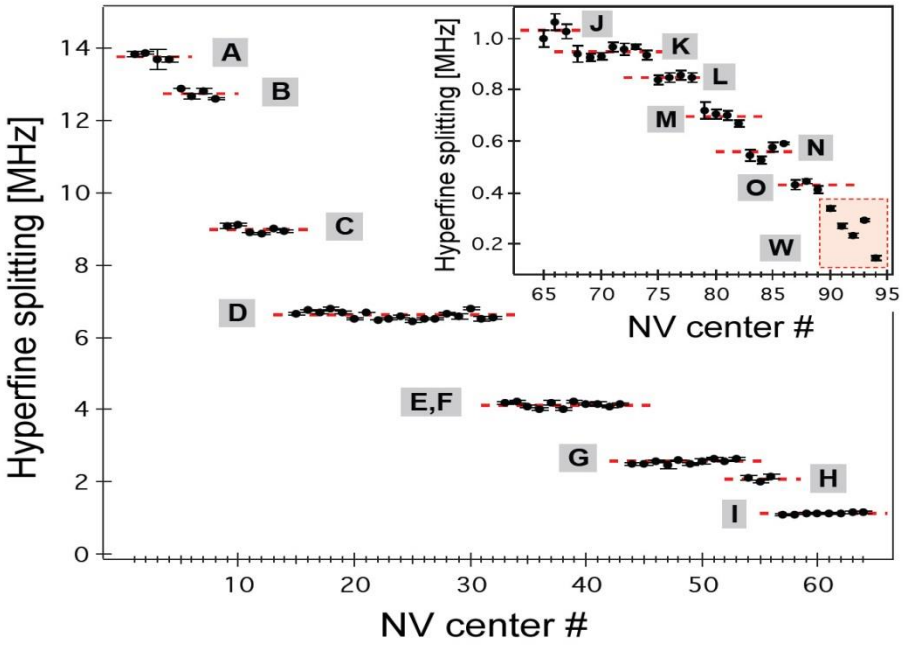
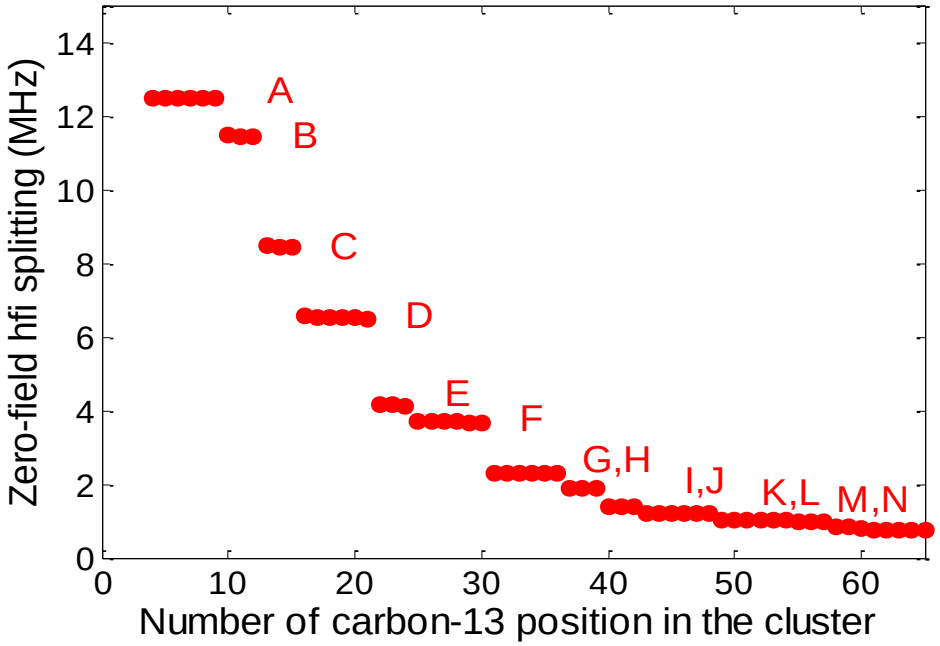
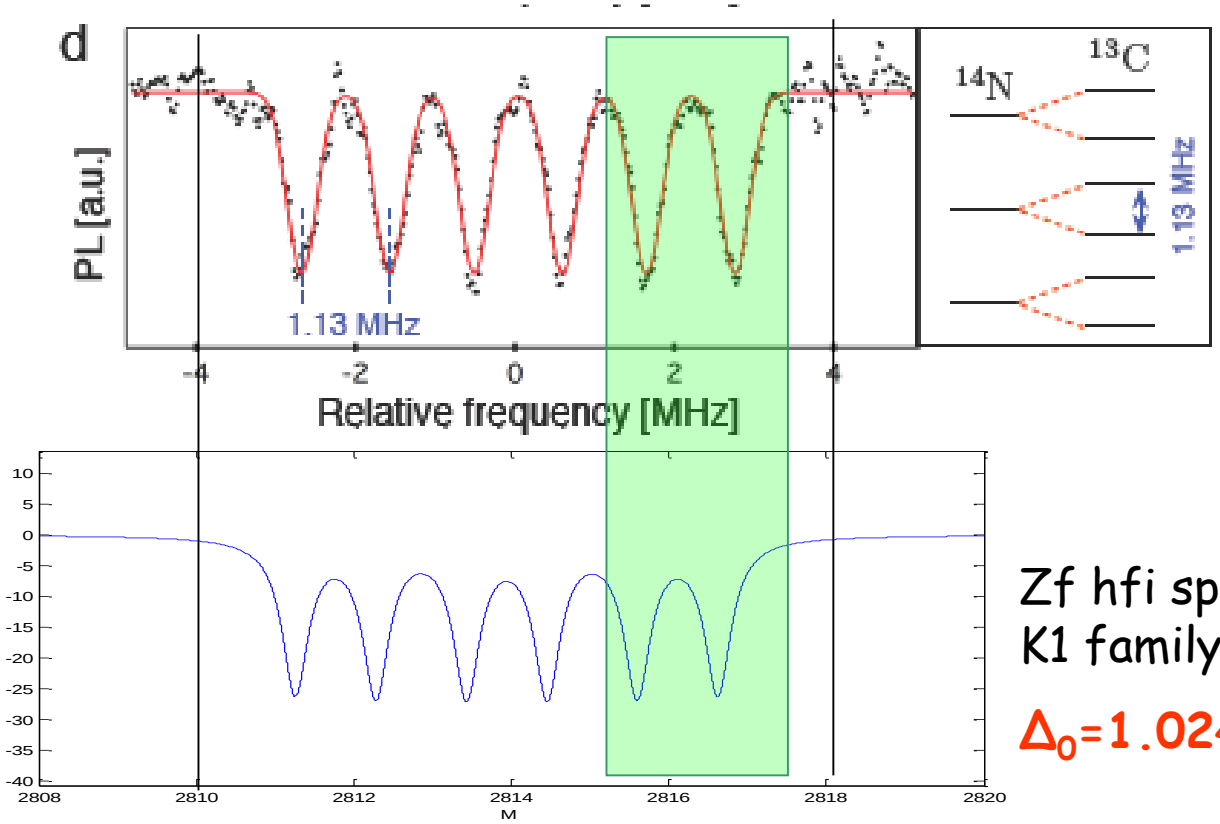


FIG. 2: Distribution of ^{13}C hyperfine splittings observed for a set of roughly 400 single NV defects at low magnetic field ($B \approx 20$ G). The well-documented[20,22] 130 MHz splitting linked to a ^{13}C placed in the nearest neighbour lattice sites of the vacancy is not represented. The capital letters denote the lattice sites corresponding to a given hyperfine splitting. The dash red lines represent the mean value of each ^{13}C family (A to O) and error bars represent estimated errors in ESR spectra fit with a 95 % confidence interval. For a given ^{13}C family, the small dispersion of the hyperfine splittings is attributed to local paramagnetic defects, which could shift the nuclear spin levels.The mean of the hyperfine splitting associated with each ^{13}C family are summarized in table I.



There were NO fitting parameters in our simulation !

Simulated ODMR spectrum of the specific $^{14}NV+^{13}C$ system (hfi splitting=1.024 MHz, K1 family) at B=20 gauss vs experimental spectrum (PRB 85 (2012) 13407)

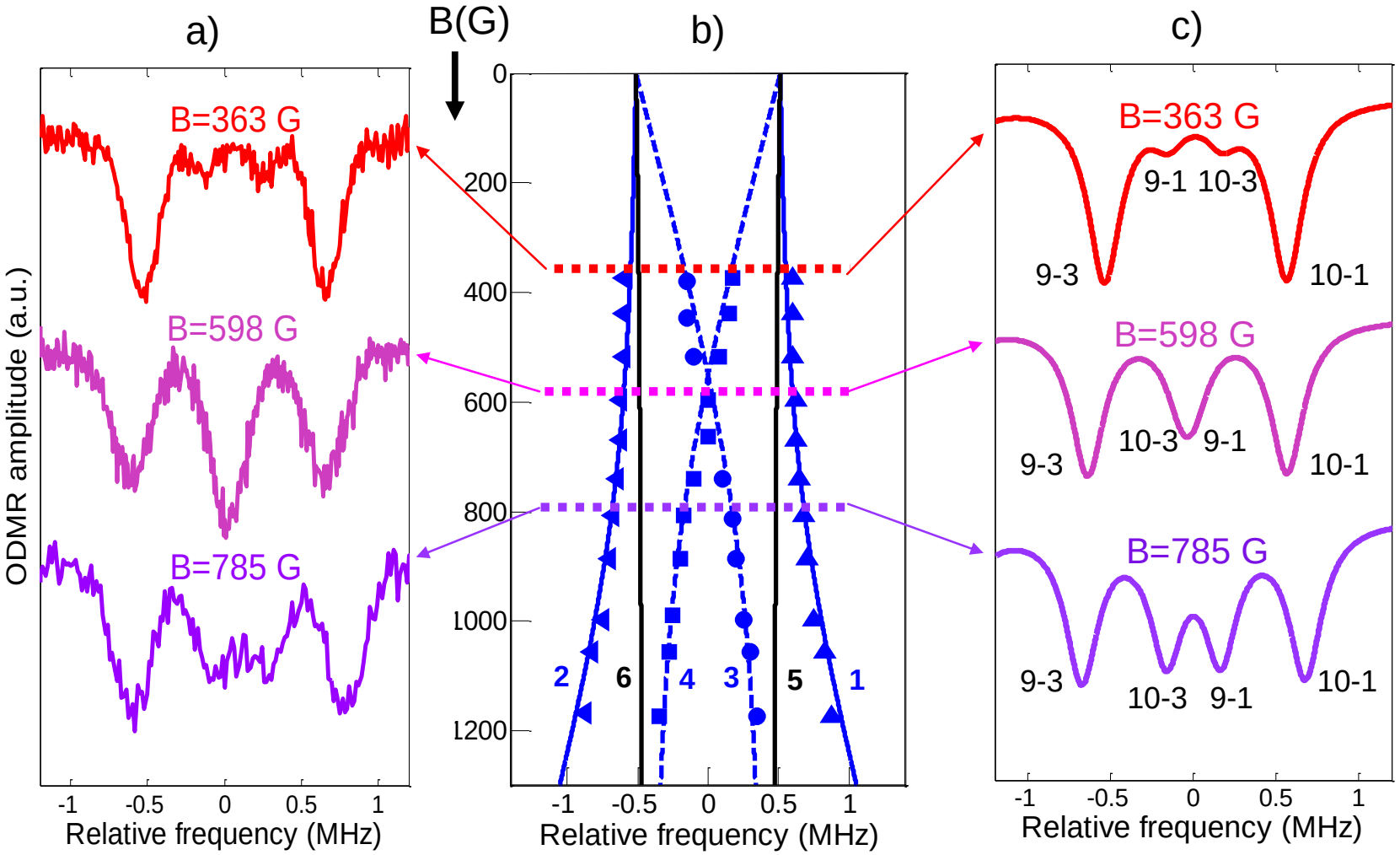


Zf hfi splitting for one K1 family member

Δ_0=1.024 MHz

The only fit parameter was the width of lorentzians which was taken =200 kHz according to the experiment

EPR spectra of K1 family at different magnetic fields: Experiment vs. theory

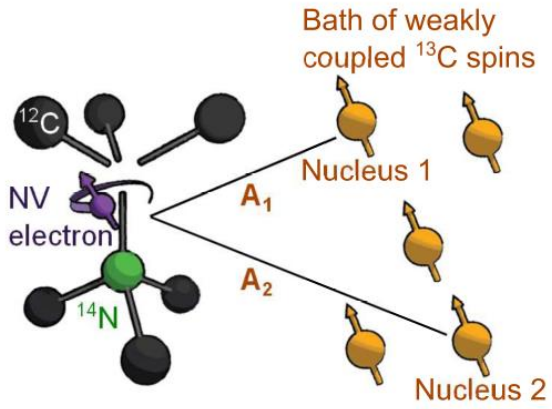


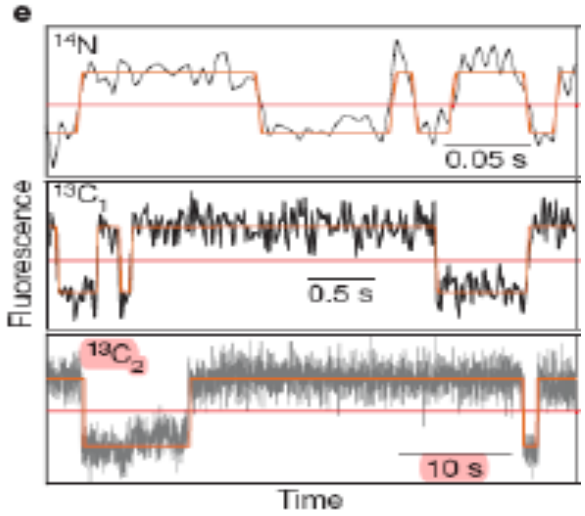
Again, the only fitting parameter was the lorentzians widths !

^{13}C spin flipping due to hfi with the NV center

At zero magnetic field the hyperfine coupling of the n-spin $\boldsymbol{I}$ to the e-spin $\boldsymbol{S}$ of the NV center (A is the *hfi* matrix with elements A_{KL}) initiates its flip-flops due to the presence in the Hamiltonian $H_{hfi} = \boldsymbol{S}\,\hat{A}\,\boldsymbol{I}$ of the terms $\sim S_Z I_+, \quad S_Z I_-$. **The rate of these flip-flops is proportional to**

$$\gamma_0 = A_{nd}^2 / \left(A_{nd}^2 + A_{ZZ}^2 \right)$$ **where** $A_{nd} = \sqrt{A_{ZX}^2 + A_{ZY}^2}$ **is off-diagonal part of the hfi matrix.**





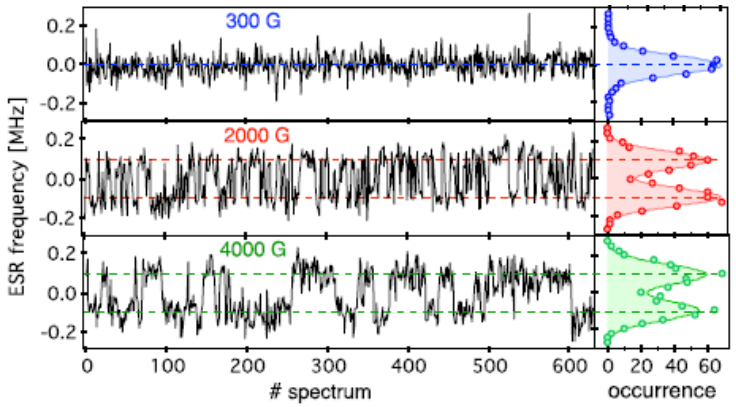
Many applications of the NV-^{13}C spin systems benefit from low flipping rate (long spin lifetime)

Experimental observations of the stable NV-^{13}C spin systems. 1

PRL **113,** 137601 (2014) PHYSICAL REVIEW LETTERS week ending 26 SEPTEMBER 2014

Probing the Dynamics of a Nuclear Spin Bath in Diamond through Time-Resolved Central Spin Magnetometry

A. Dréau,[1,*] P. Jamonneau,[1] O. Gazzano,[2] S. Kosen,[1] J.-F. Roch,[1] J. R. Maze,[3] and V. Jacques[1,†]



Hfi splitting = 201 kHz

FIG. 2 (b) Time evolution of the instantaneous ESR frequency over 630 consecutive individual spectra recorded at different magnetic fields (total acquisition time ~300 s). The right panels show the corresponding histograms. (c) Top panel: Averaged sum of

Experimental observations of the stable NV-^{13}C spin systems. 2

LETTER (august 2016)

doi:10.1038/nature12919

Quantum error correction in a solid-state hybrid spin register

G. Waldherr[1]*, Y. Wang[1]*, S. Zaiser[1], M. Jamali[1], T. Schulte-Herbrüggen[2], H. Abe[3], T. Ohshima[3], J. Isoya[4], J. F. Du[5], P. Neumann[1] & J. Wrachtrup[1,6]

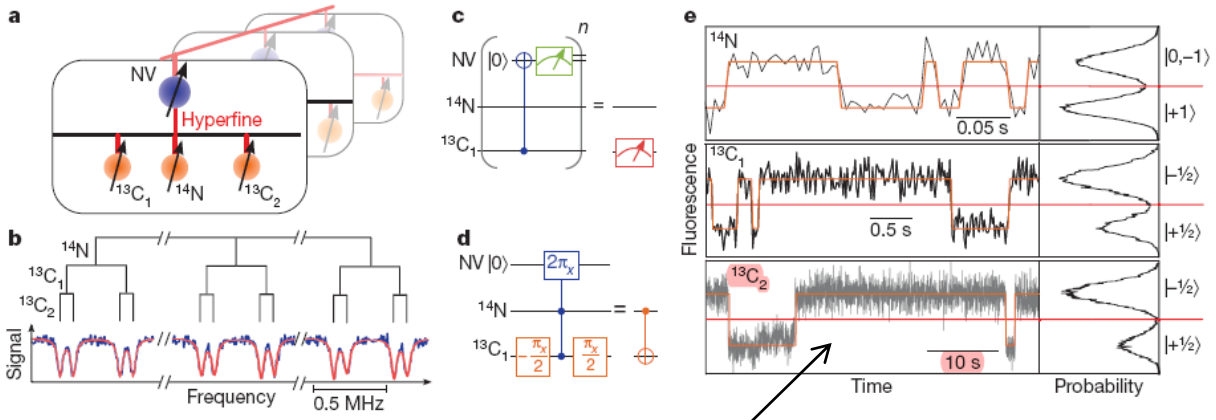


Figure 1 | Single-shot readout and control of a nuclear spin register via the NV. a, Illustration of the quantum register consisting of three nuclear spins (orange circles with black arrows) coupled by hyperfine interaction to the NV electron spin (blue circles with black arrows), forming a prototype single node of a larger register[15,17]. $^{13}C_{1,2}$ refers to ^{13}C nuclei at different lattice positions. b, Hyperfine splitting (^{14}N, 2.16 MHz; $^{13}C_1$, 413 kHz; $^{13}C_2$, 89 kHz) of the $m_S = 0$ to -1 transition into 12 individual lines. c, 'Wire diagram' for projective readout of nuclear spins[10,27]; the diagram here is for a ^{13}C spin. d, Wire diagram of a CNOT gate between two nuclear spins. e, Left side, time trace of NV fluorescence photons during repetitive readout of a particular nuclear spin (see c). The timescales of the dynamics depend on the nuclear spin life times and the C_nNOT_e gate durations. Right side, photon-counting histograms of the time traces. The red line indicates the threshold for nuclear spin state discrimination.

Hfi splitting = 89 kHz

Experimental observations of the stable NV-^{13}C spin systems. 3

PRL 116, 230502 (2016) PHYSICAL REVIEW LETTERS week ending 10 JUNE 2016

Quantum Metrology Enhanced by Repetitive Quantum Error Correction

Thomas Unden,[1] Priya Balasubramanian,[1] Daniel Louzon,[1,3] Yuval Vinkler,[3] Martin B. Plenio,[2,4] Matthew Markham,[5] Daniel Twitchen,[5] Alastair Stacey,[5,†] Igor Lovchinsky,[6] Alexander O. Sushkov,[6,‡] Mikhail D. Lukin,[6] Alex Retzker,[3] Boris Naydenov,[1,2] Liam P. McGuinness,[1] and Fedor Jelezko[1,2,*]

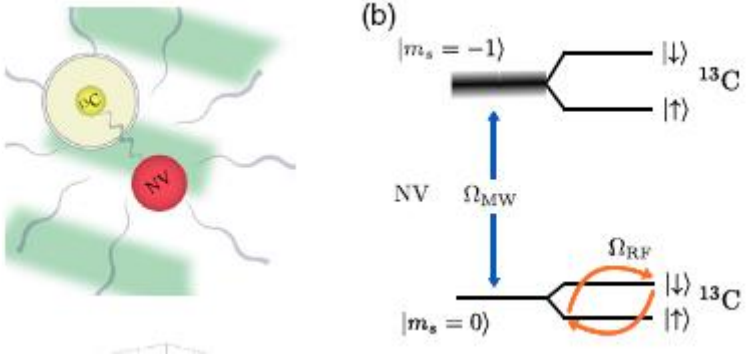
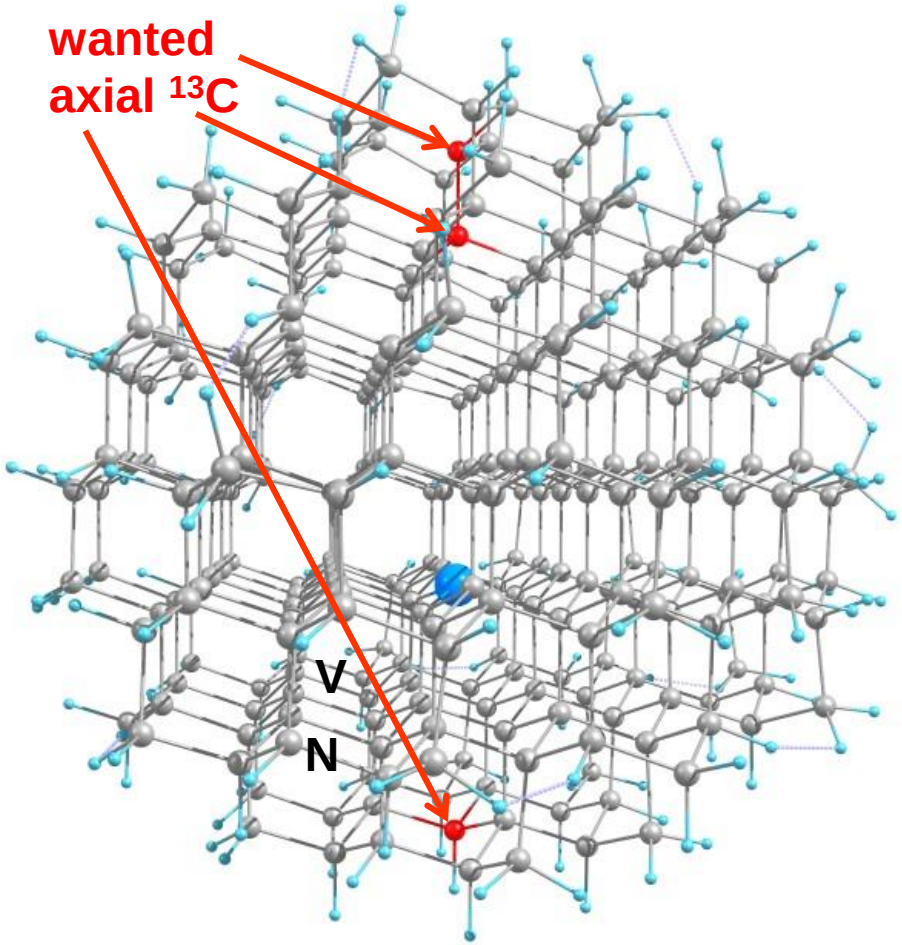


FIG. 1. The quantum system of interest and its fundamental properties. (a) Quantum register formed by a NV and a near-axial ^{13}C nucleus (auxiliary qubit) in the diamond lattice. (b) Energy level structure of the quantum register, showing the ground state spin manifold $|0\rangle$, $|-1\rangle$ of the NV center and the spin manifold $|\uparrow\rangle$, $|\downarrow\rangle$ of the ^{13}C spin. The NV-spin transitions are driven by a resonant microwave signal Ω_{MW}, and the nuclear spin is driven by a radio frequency signal Ω_{rf}. To resolve the energy degeneracy of the NV spin states $|\pm 1\rangle$ and to define the NV qubit corresponding to the states $|0\rangle$ and $|-1\rangle$, an external magnetic field of about 340 G was applied. The magnetic field is aligned to the symmetry axis of the NV center. The coupling between the NV center and nuclear spin is given by the hyperfine interaction, which in our case shows only a parallel component of 50 kHz (note that other

Hfi splitting = 50 kHz

Simulation of the cluster $C_{291}[NV]H_{172}$: Non-flipping ^{13}C nuclear spins



One evident candidate for such stable systems are the **axial systems i.e. those having ^{13}C on the NV axis**.

In the cluster $C_{291}[NV]H_{172}$ there are three such positions.

In this case
$A_{nd}=0$ (!!!) $\rightarrow$ $\gamma_0=0$

Simulated *hfi* and spatial characteristics for the "families" of equivalent positions of ^{13}C n-spin in the $C_{291}[NV]^{-}H_{172}$ cluster.

Family	N_C	$\bar{A}_{ZZ}$ (MHz)	$\bar{A}_{nd}$ (MHz)	$\bar{\Delta}_k^{(0)}$ (MHz)	$\overline{\lvert\cos(Zz)\rvert}$	$\bar{Z}$ (Å)	$\bar{r}_{XY}$ (Å)	$\bar{r}_{NC}$ (Å)
A	**6**	**12.451**	**1.166**	**12.471**	**0.288**	**- 0.522**	**3.937**	**4.536**
B	3	11.386	1.434	11.451	0.412	- 2.655	2.972	**5.298**
C	3	-8.379	0.827	8.437	0.907	- 2.109	1.487	**4.118**
D	6	-6.450	0.931	6.521	0.296	- 0.010	2.552	**3.089**
E	3	4.055	0.826	4.136	0.848	-2.643	1.491	**4.621**
F	6	3.609	0.738	3.682	0.829	1.577	2.562	**2.566**
G	6	2.281	0.240	2.292	0.247	0.008	5.166	**5.446**
H	3	1.884	0.208	1.895	0.956	-4.242	2.976	**6.673**
I	3	-1.386	0.130	1.392	0.167	0.005	4.458	**4.780**
J	6	-1.145	0.328	1.191	0.488	-2.110	3.932	**5.497**
K1	3	-0.886	0.510	1.022	0.555	-2.118	2.985	**4.871**
K2	3	-1.011	0.014	1.012	0.029	-0.002	4.460	4.785
L	3	0.980	0.121	0.986	0.069	-0.535	2.972	**3.737**
M	3	0.602	0.557	0.819	0.865	2.127	1.460	**1.513**
N	6	0.725	0.095	0.731	0.219	-0.541	6.467	**6.855**
O1	3	0.673	0.171	0.694	0.528	-4.712	4.479	**7.847**
O2	3	0.655	0.166	0.676	0.902	3.707	2.983	**3.578**
P	6	0.474	0.190	0.510	0.402	-2.635	5.355	**6.909**
Q	6	0.391	0.273	0.477	0.524	-2.645	3.953	**5.897**
R	3	-0.226	0.393	0.453	0.759	2.115	2.985	**3.009**
S	3	0.412	0.060	0.417	0.119	-0.511	5.942	**6.351**
T	3	0.366	0.149	0.395	0.955	3.709	1.504	**2.485**
U	3	0.286	0.225	0.364	0.624	1.578	4.481	**4.484**
V	6	-0.209	0.232	0.312	0.639	2.105	3.927	**3.945**
W	3	-0.200	0.171	0.266	0.941	-4.220	1.489	**6.135**
X	6	0.211	0.152	0.259	0.899	-4.768	2.573	**6.990**
Y	6	-0.228	0.001	0.227	0.002	-0.522	5.381	5.834
Z1	3	0.158	0.131	0.205	0.857	4.226	3.001	**3.903**
Z2	3	0.086	0.184	0.203	0.464	1.576	4.447	**4.447**
on-NV-axis	**1**	**0.187**	**0.001**	**0.187**	**1.000**	**-4.734**	**0.009**	**6.465**

Hfi splitting = 187 kHz (close to exp. 201 kHz)

For two other axial ^{13}C calculated hfi splittings were 94.7 kHz and 99.3 kHz

Simulated *hfi* and spatial characteristics for the "families" of equivalent positions of ^{13}C n-spin in the $C_{291}[NV]^{-}H_{172}$ cluster.

Family	N_C	$\bar{A}_{ZZ}$ (MHz)	$\bar{A}_{nd}$ (MHz)	$\bar{\Delta}_k^{(0)}$ (MHz)	$\overline{\lvert\cos(Zz)\rvert}$	$\bar{Z}$ (Å)	$\bar{r}_{XY}$ (Å)	$\bar{r}_{NC}$ (Å)
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R	3	-0.226	0.393	0.453	0.759	2.115	2.985	**3.009**
S	3	0.412	0.060	0.417	0.119	-0.511	5.942	**6.351**
T	3	0.366	0.149	0.395	0.955	3.709	1.504	**2.485**
U	3	0.286	0.225	0.364	0.624	1.578	4.481	**4.484**
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Y	**6**	**-0.228**	**0.001**	**0.227**	**0.002**	**-0.522**	**5.381**	**5.834**
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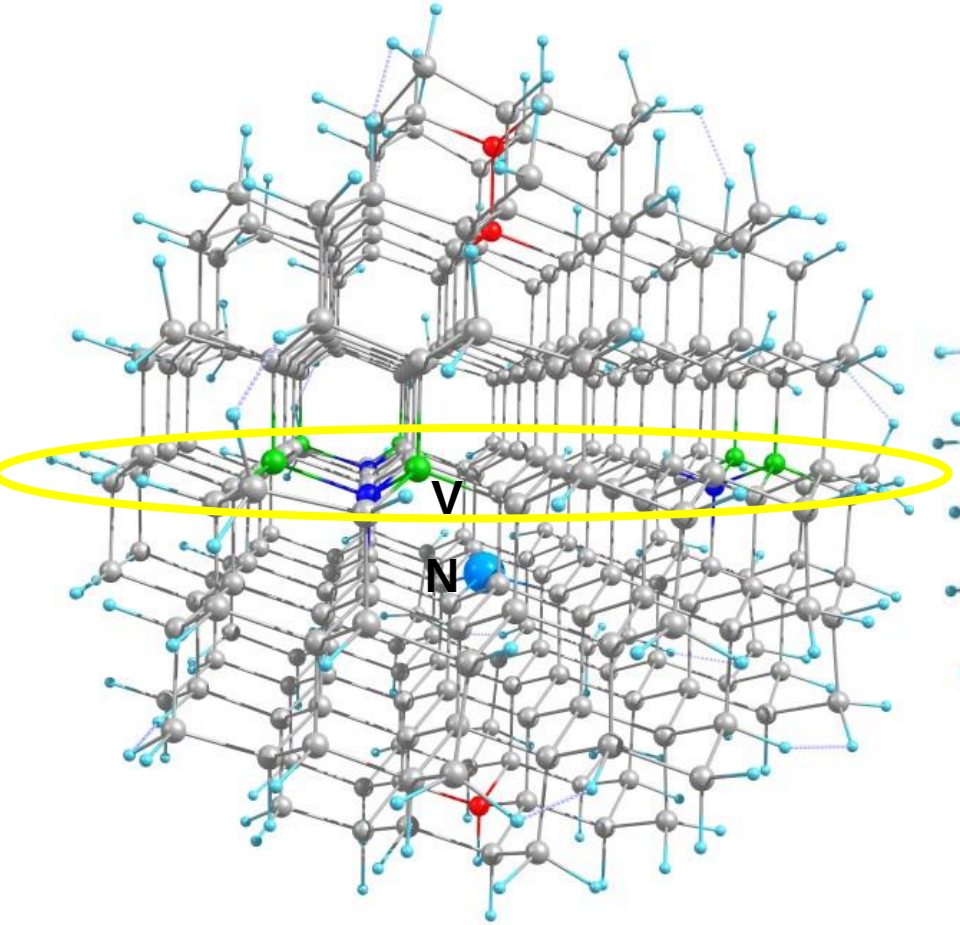
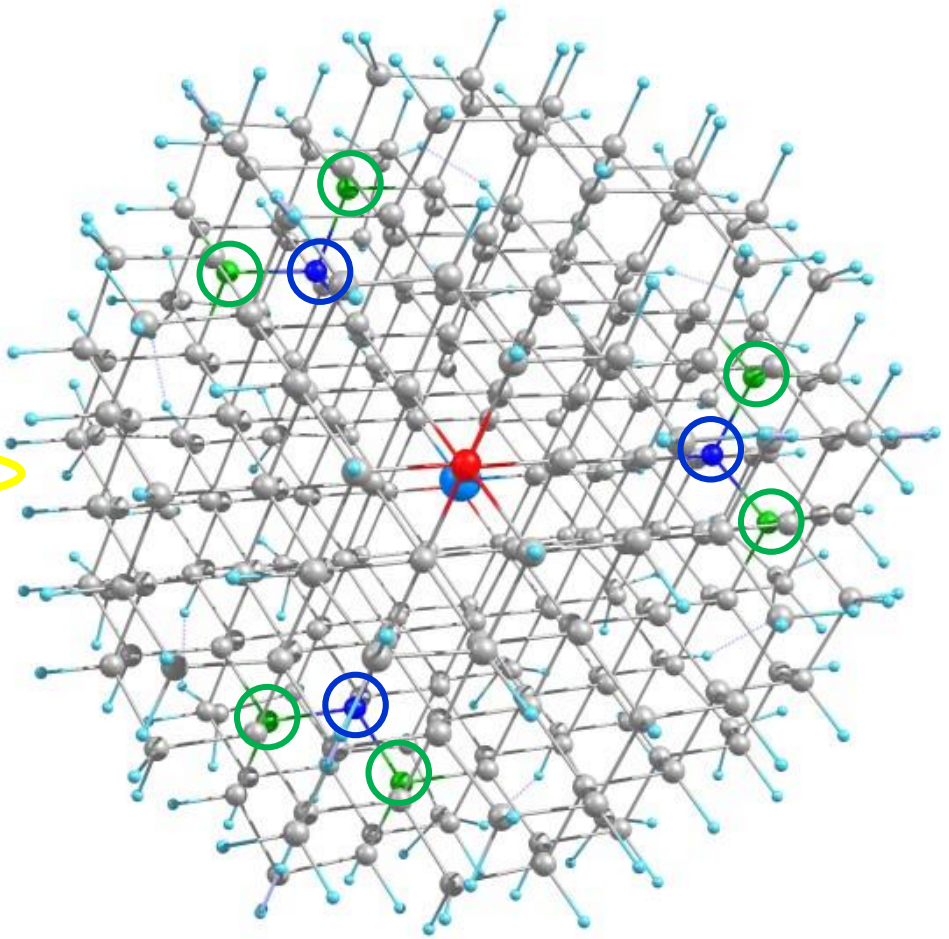
Z2	3	0.086	0.184	0.203	0.464	1.576	4.447	**4.447**
on-NV-axis	**1**	**0.187**	**0.001**	**0.187**	**1.000**	**-4.734**	**0.009**	**6.465**

Non-axial near-non-flipping ^{13}C nuclear spins: Positions (Blue – family K2, green – family Y)

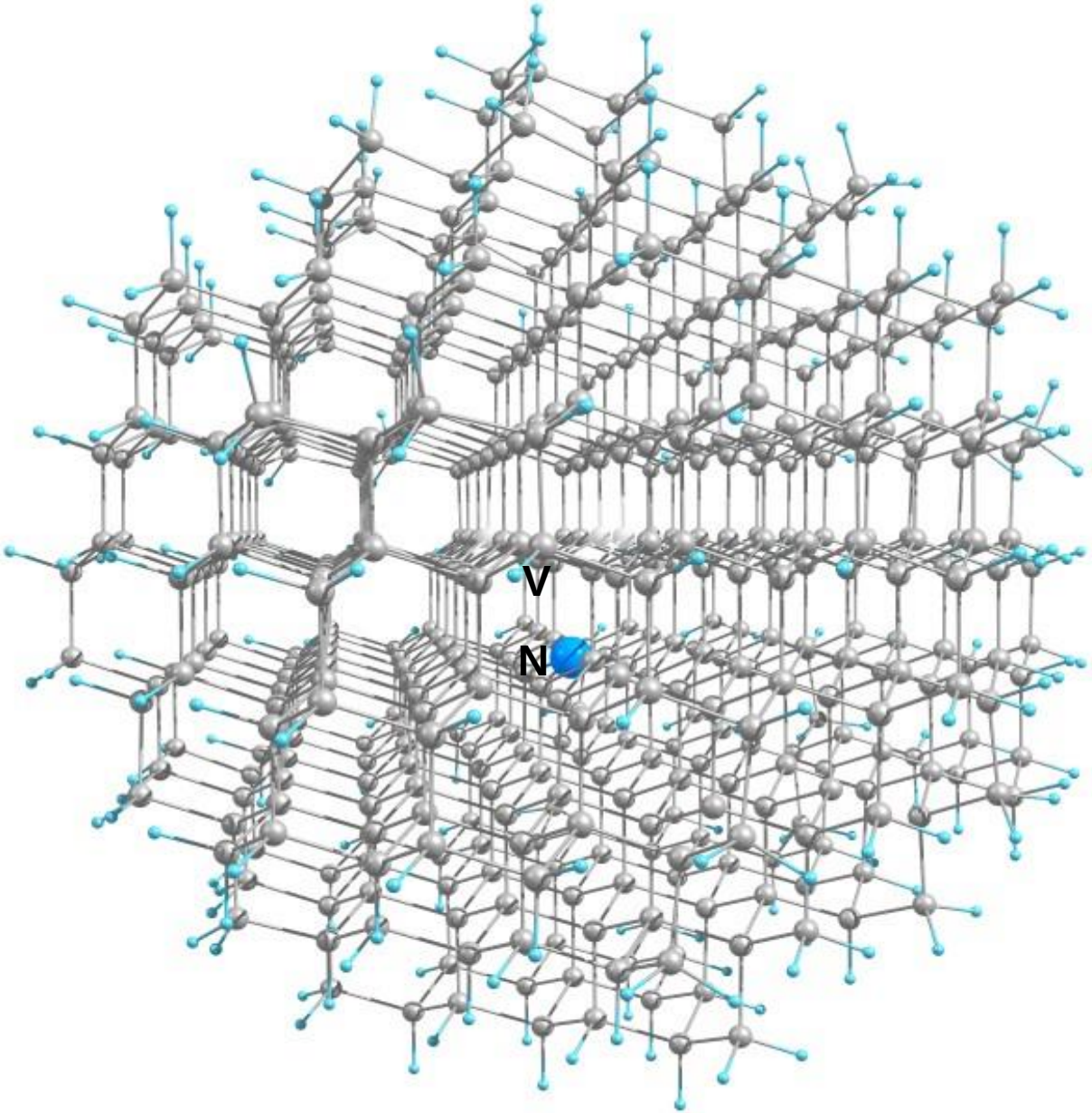
Side view $\perp$(111)



Top view along (111)



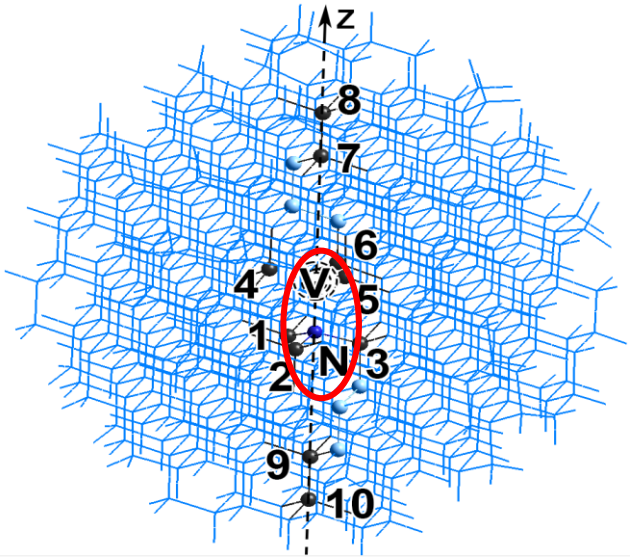
Larger $C_{510}[NV]H_{252}$ cluster

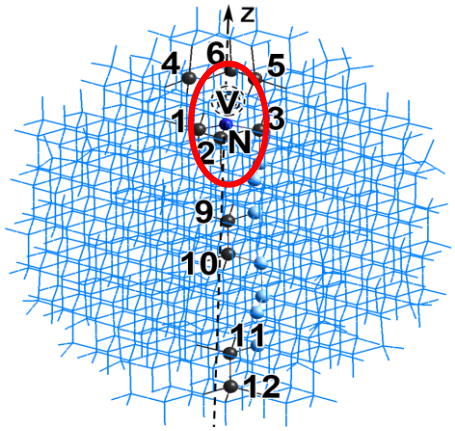


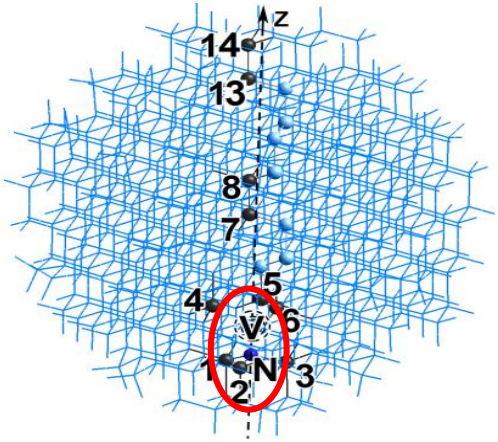
Again we simulated hfi matrices for all possible positions of ^{13}C in the cluster and used them in spin-Hamiltonian of NV-^{13}C spin systems to calculate the observable.
Here we are interested in the search of hfi characteristics and positions for stable (or near-stable) systems NV-^{13}C.

$$A = \begin{pmatrix} A_{XX} & A_{XY} & A_{XZ} \\ A_{YX} & A_{YY} & A_{YZ} \\ A_{ZX} & A_{ZY} & A_{ZZ} \end{pmatrix}$$

Prediction 2: Non-flipping axial ^{13}C nuclear spins in the $C_{510}[NV]H_{252}$ cluster







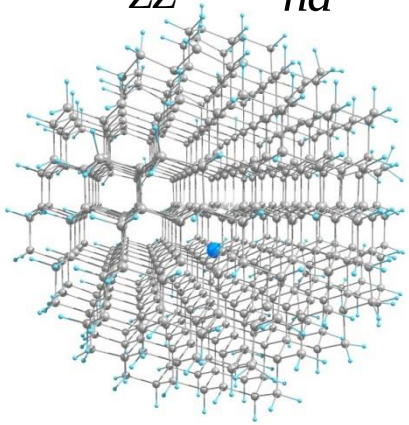
Position	A_{XX}(κHz)	A_{YY}(κHz)	A_{ZZ}(κHz)	R_{NC}(Å)
7	-268.6 (-273.2)	-268.7 (-274.7)	183.1 (177.2)	6.47 (6.51)
8	-128.0 (-126.0)	-127.9 (-126.3)	85.1 (88.8)	8.05 (8.08)
9	-59.0 (-57.8)	-58.9 (-58.0)	99.9 (98.4)	4.58 (4.61)
10	-30.6 (-30.3)	-30.6 (-30.3)	58.7 (57.7)	6.15 (6.17)
11	-15.6	-15.6	31.4	12.80
12	-10.6	-10.6	21.0	14.37
13	-8.3	-8.3	16.6	10.89
14	-6.0	-6.0	12.0	12.46

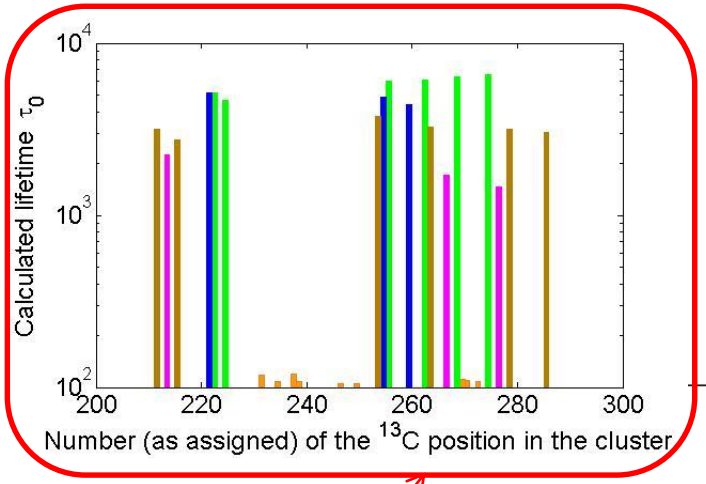
Simulated "lifetimes" of all possible ^{13}C nuclear spins in the $C_{510}[NV]H_{252}$ cluster

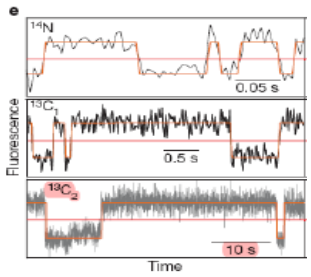
^{13}C spin "lifetime"

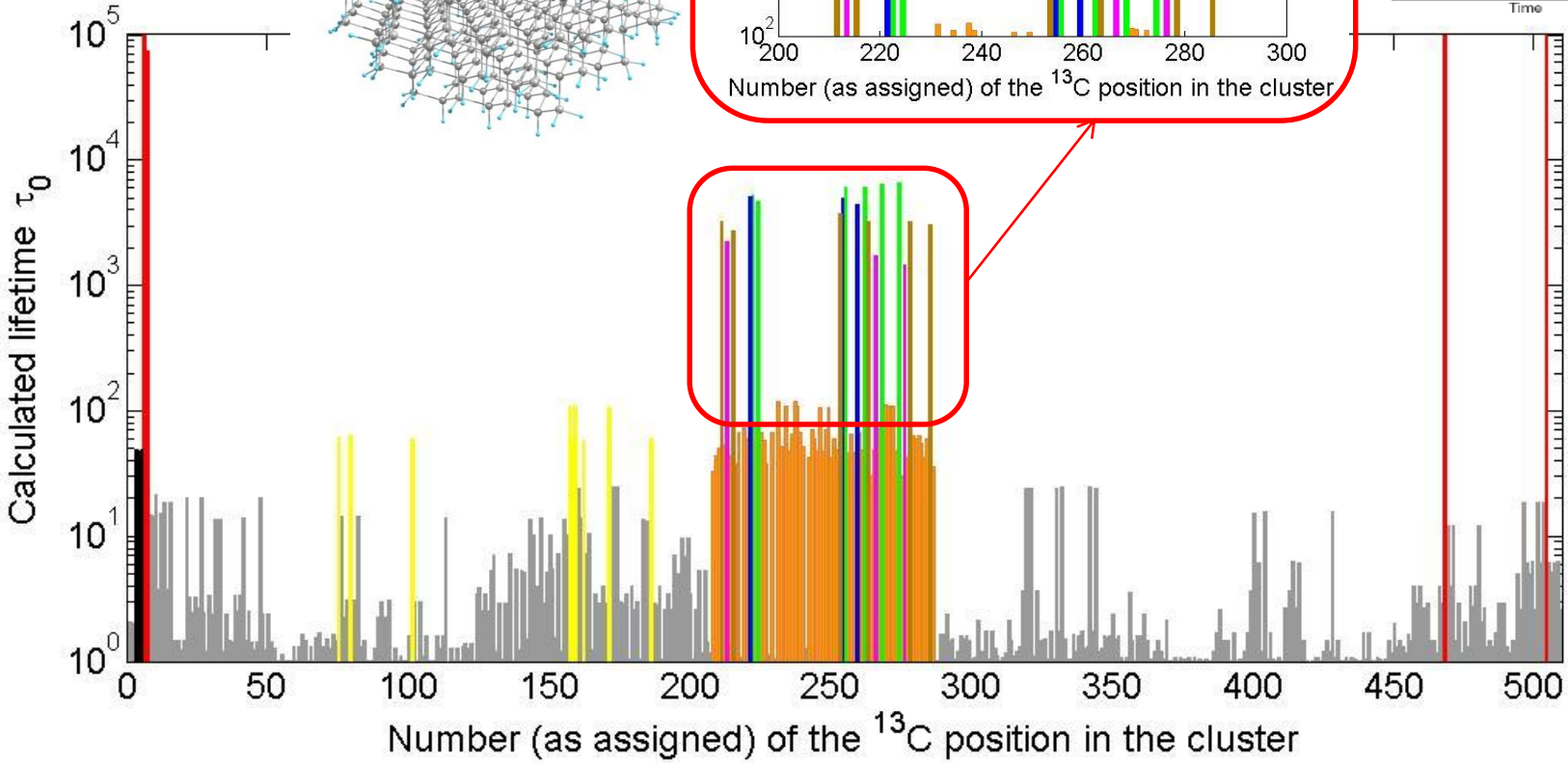
$$\tau_0 = 1/\gamma_0 = 1 + A_{zz}^2 / A_{nd}^2$$

Keep in mind the log scale !!!!

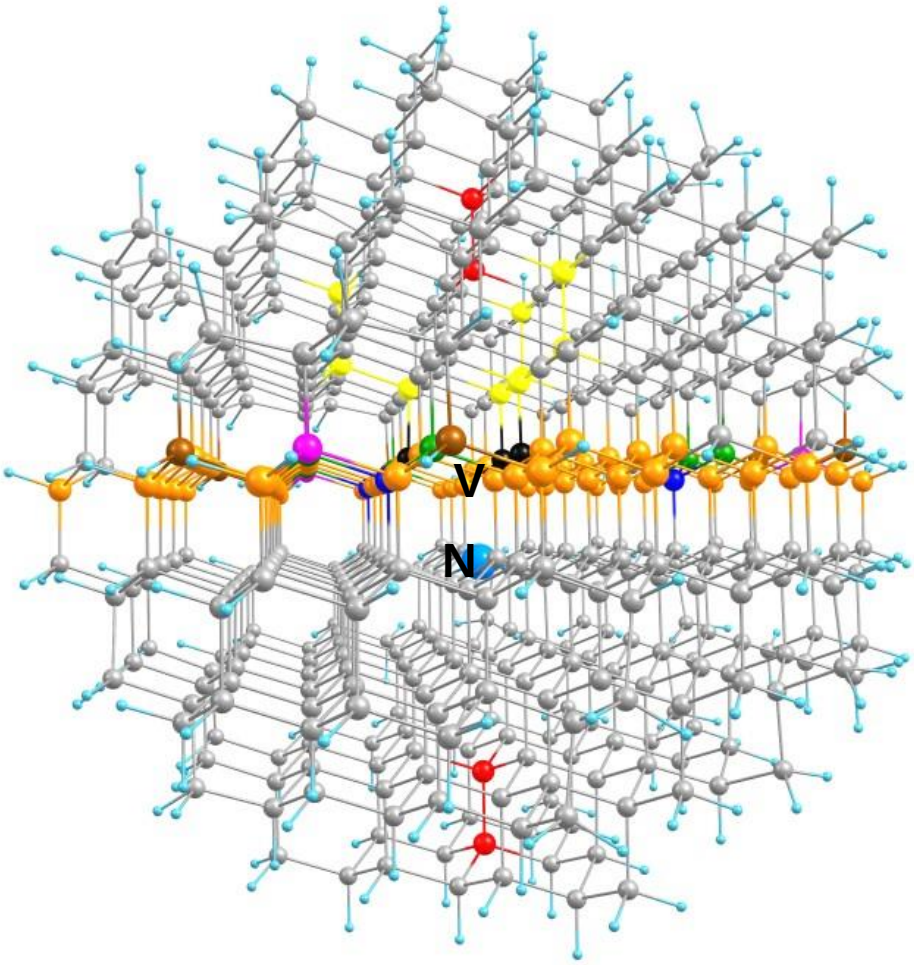


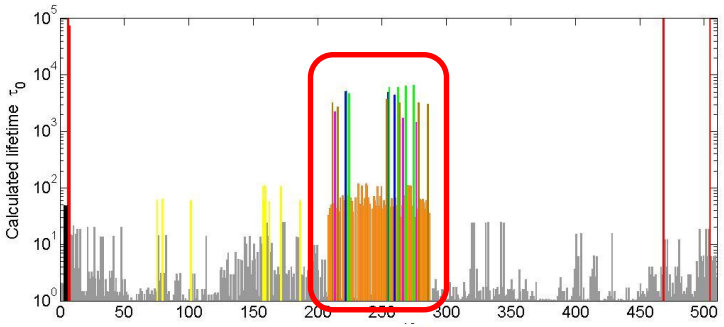


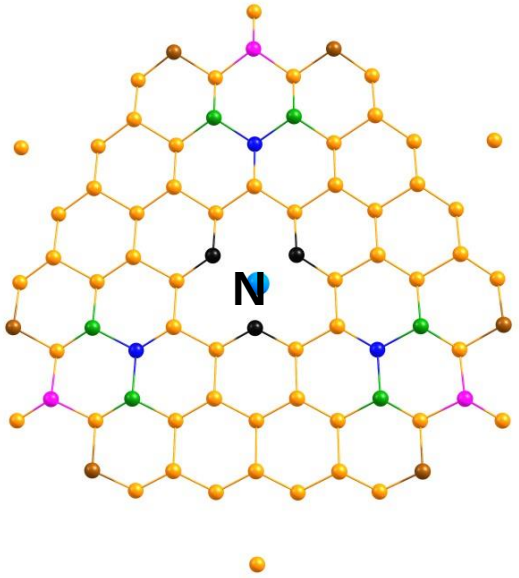




Spatial locations of near-stable NON-axial systems NV-^{13}C in the cluster







Comparison with experiments

Position/family	A_{zz} (kHz)	A_{nd} (kHz)	Γ_0 ($\times 10^{-3}$)	Δ_0 (kHz)	cosZz	R_{CN} (Å)	R_{CZ} (Å)	R_{CXY} (Å)
axial C7	183.1	0.3	0.0030	183.1	1.00	6.47	6.47	0
axial C8	85.1	0.3	0.0138	85.1	1.00	8.05	8.05	0.004
axial C469	99.9	0.1	0.0020	99.9	1.00	4.58	-4.58	0.003
axial C505	58.7	0	0	58.7	1.00	6.15	-6.16	0.004
St1 (average)	-1001.6	14.5	0.2096	1001.8	-0.01	4.78	1.73	4.45
St2(average)	-204.9	2.7	0.1747	204.9	0.001	5.82	2.25	5.36
St3(average)	-53.0	1.3	0.5734	53.0	-0.01	7.78	2.21	7.46
St4(average)	-51.9	0.9	0.3269	51.9	-0.001	8.15	2.24	7.83

Hfi splitting = 201 kHz

Hfi splitting = 89 kHz

Hfi splitting = 50 kHz

So, we predicted many new stable non-axial positions for ^{13}C nuclear spin !

Interpretation: QChemistry for stable ^{13}C

Stable (or near-stable) NV-^{13}C spin systems have small off-diagonal elements A_{ZX} and A_{ZY} in their hfi matrices A_{KL}, resulted from anisotropic (dipole-dipole) part of hfi. They are expressed in terms of spin density

$$\rho_\sigma = \rho_\uparrow - \rho_\downarrow$$

$$A_{aniso} = \frac{\mu_0}{4\pi}(g_e\mu_e)(g_n\mu_n)\int T(r)\,\rho_\sigma(r+r_n)\,dr$$

- Anisotropic (dipolar) part

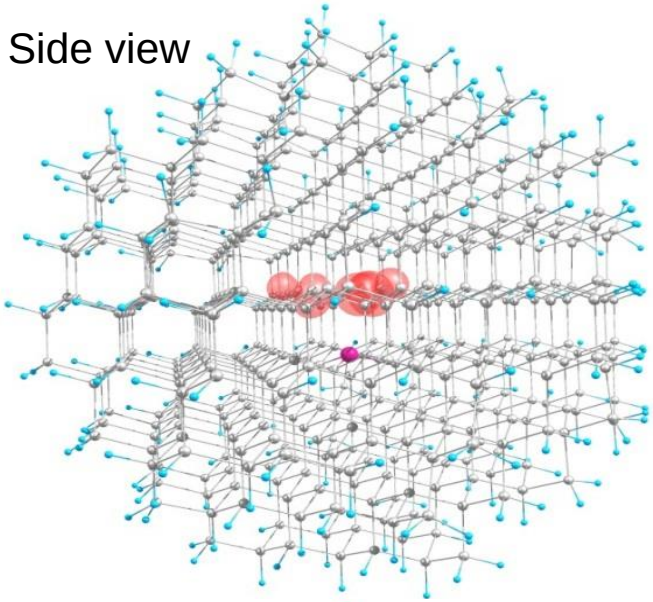
$$T(r) = \frac{1}{r^5}\begin{pmatrix} 3x^2-r^2 & 3xy & 3xz \\ 3xy & 3y^2-r^2 & 3yz \\ 3xz & 3yz & 3z^2-r^2 \end{pmatrix}$$

-dipole-dipole interaction tensor (traceless)

If the local spin density distribution in the location of certain ^{13}C is symmetric with respect to the sign change of x and y then the integrals will be zero !!! So, we need just to visualize the spin density….

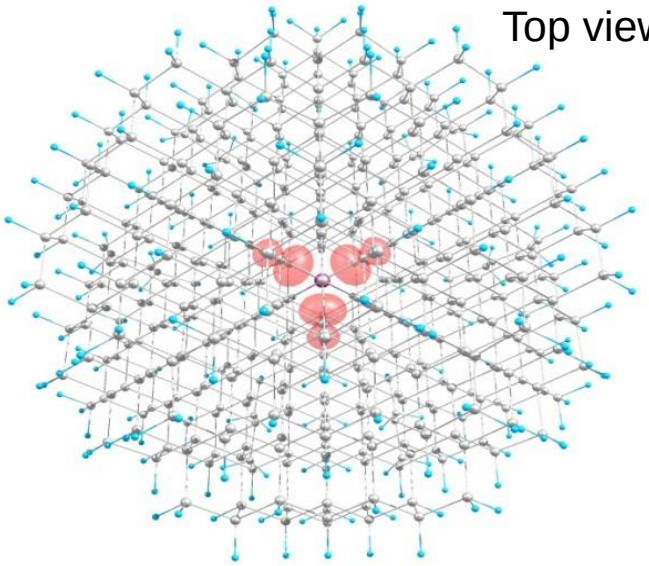
Spin density distribution over the cluster

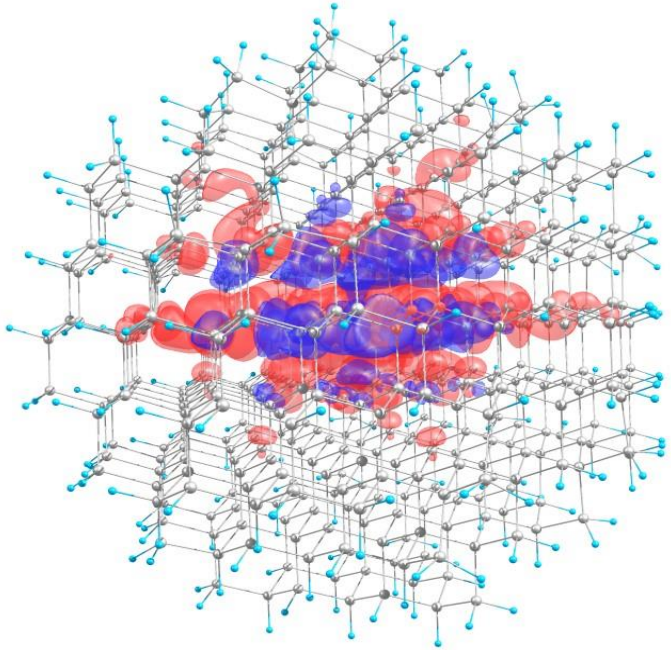
Side view



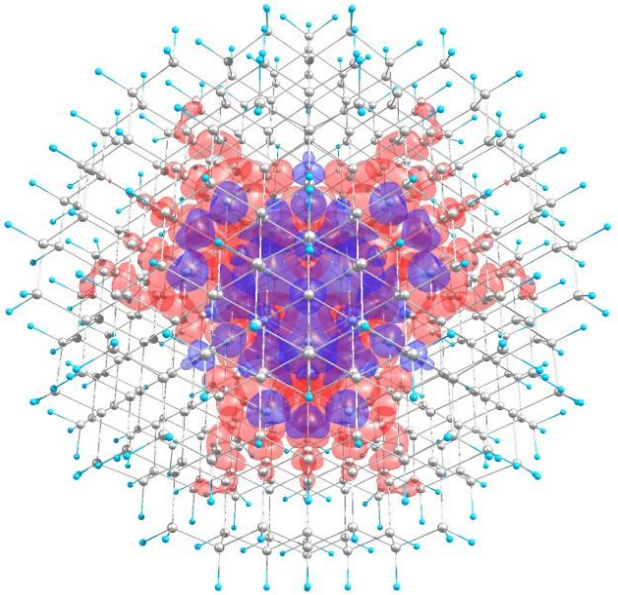
contour at
0.01

Top view



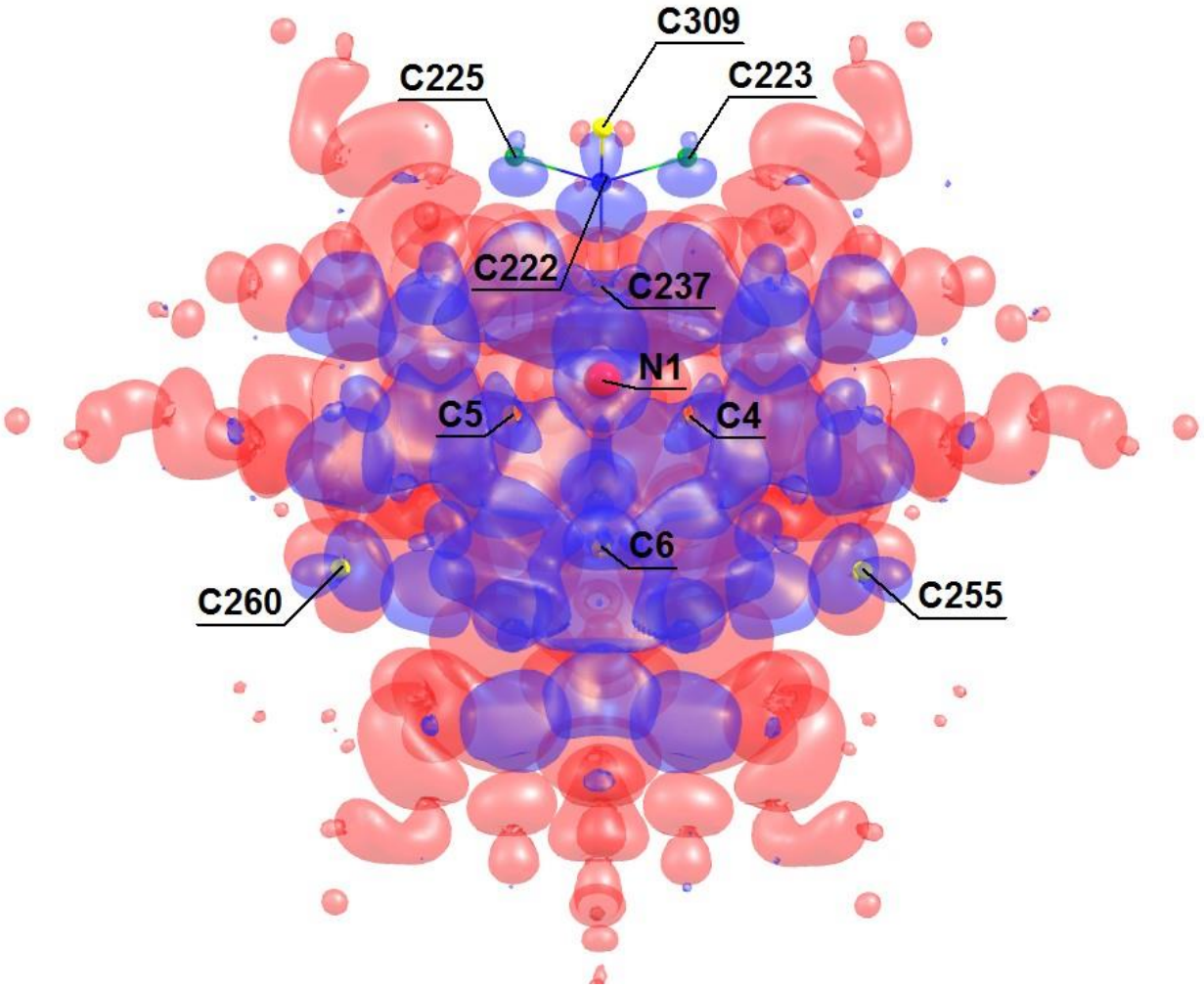


contour at
0.0001



Spin density distribution near stable positions is symmetric!

Top view



Red – positive spin density distribution contour with small value (~0.0001) over the cluster.
Blue – negative spin density.

View is chosen so to visualize symmetric negative spin density distributions **at stable positions C222, C225 and C223.**

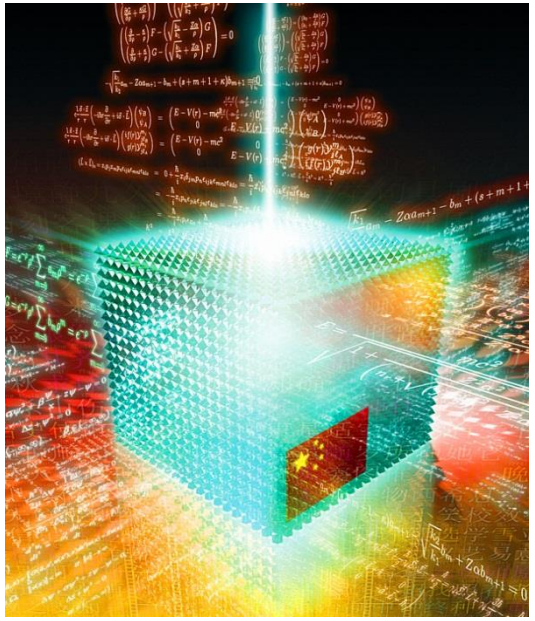
Positions C222, C255 and C260 belongs to the St1(K2) family, positions C225, C223 – to the St2(Y) family.

Conclusion:

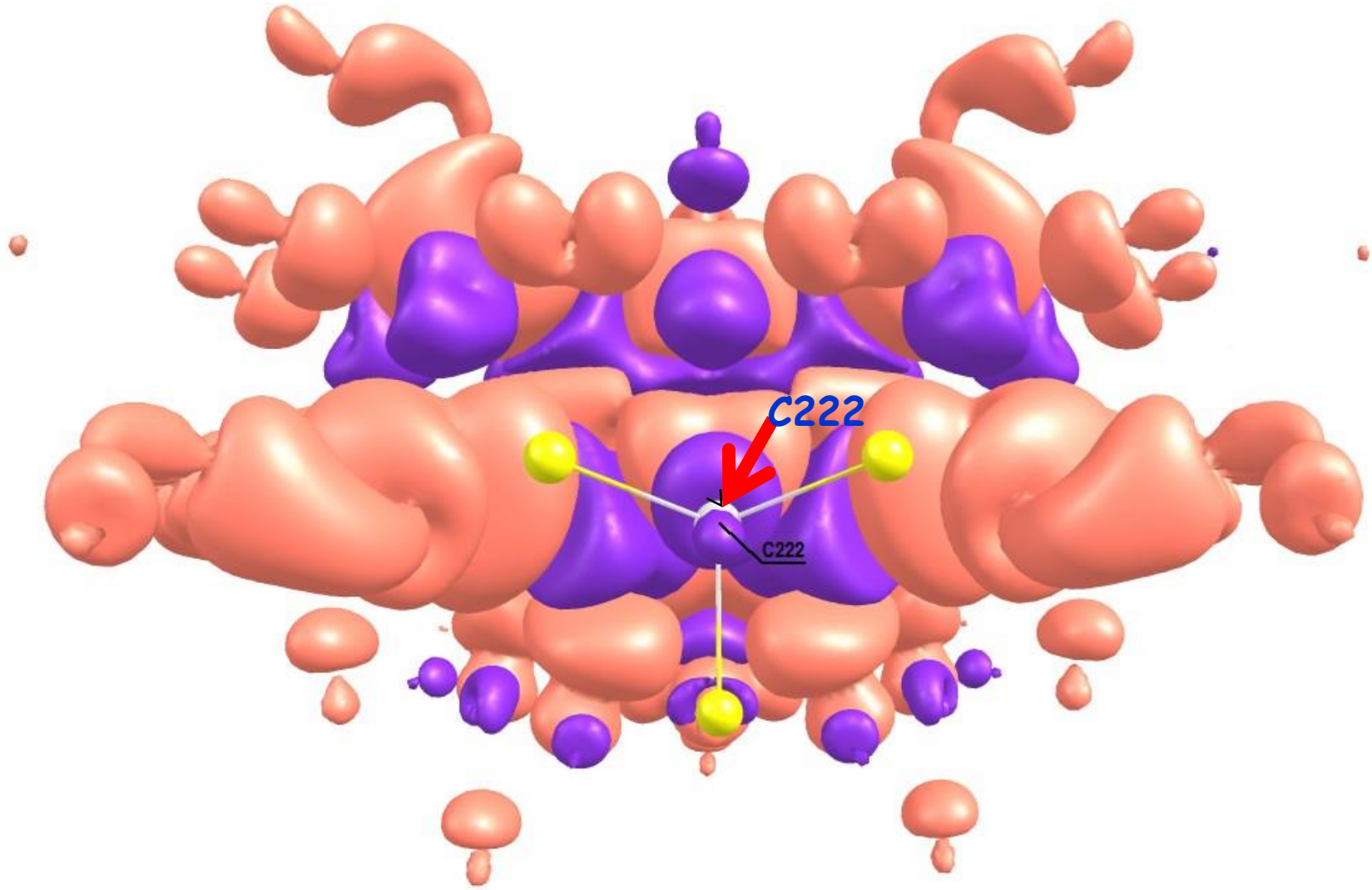
We have demonstrated that modern quantum chemistry is not alchemy but the powerful instrument for simulation of various quantum systems, in particular – of hyperfine interactions in diamond.

We hope that our results will help experimentalist to find wanted stable NV-^{13}C for various applications in emerging quantum technologies.

Supercomputers are in action



Spin density distribution near one specific stable position C222



Thank you for attention