Corrigendum: Experimental $^1$H and $^{13}$C Solid-State NMR Signal Assignment of Paramagnetic Copper (II) 2-Pyrazine-Carboxylate Complex using Density Functional Theory Calculations (2021 J. Phys.: Conf. Ser. 1819 012032)

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Page 10: In the References section, the following text appears:

“[9] Glumglomchit P, Rajagukguk J, Kaewkhao J, Kirdsiri K. 2008. Key Engineering Materials766, pp. 246-251”
This should read: Chutia P, Kato S, Kojima T, and Satokawa S 2009 Polyhedron 28 370-380

“[12] Zaman F, Rooh G, Srisittipokakun N, Ahmad T, Khan I, Shoaib M, Rajagukguk J, Kaewkhao J. 2019. Solid State Sciences89:50-56”
This should read: Dong Y B, Smith M D, and Zur Loye H C 2000 Solid State Sciences 2 335-341

“[30] Rajagukguk J, Sinaga B, Kaewkhao J. 2019. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy223:117342.”
This should read: Solomon I, 1995 Phys. Rev. 99 559-565
Experimental $^1$H and $^{13}$C Solid-State NMR Signal Assignment of Paramagnetic Copper (II) 2-Pyrazine-Carboxylate Complex using Density Functional Theory Calculations

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Abstract. We have acquired $^1$H and $^{13}$C solid-state NMR (ssNMR) spectra of the paramagnetic Cu(II)-2-pyrazine-carboxylate (Cu-Py) complex and assigned paramagnetic $^1$H/$^{13}$C signals using density functional theory (DFT) calculations. The unpaired electron in Cu(II) ion exacerbates the $^1$H and $^{13}$C chemical shifts in the Cu-Py complex through hyperfine interactions, making the conventional NMR signal assignment non-feasible. Further, the nuclear fast relaxation in paramagnetic metal-organic system hampers application of routine ssNMR techniques for signal acquisition. In our work we have employed simple DEPTH experiment at 50 kHz magic angle spinning (MAS) for acquiring $^1$H and $^{13}$C 1D ssNMR spectra of the paramagnetic Cu(II)-2-pyrazine-carboxylate (Cu-Py) complex. The paramagnetic augmented (diamagnetic chemical shift + paramagnetic shift) 1D $^1$H and $^{13}$C ssNMR signals (shifts) from Cu-Py complex have major contribution from Fermi contact interaction due to proximity of the organic arm to Cu$^{2+}$ ion (Cu$^{2+}$-C/H atoms 0-5 Å). The unpaired electron spin density distributed over the pyrazine-carboxylate organic arm is crucial in understanding Fermi contact shifts and hence accounts for $^1$H and $^{13}$C ssNMR signal assignment. The theoretical Fermi contact shifts together with diamagnetic shifts, calculated using density functional theory (DFT) at B3LYP level of theory with various basis sets viz. 6-311G, 6-311G+(D) and 6-311G++(D), were compared with the experimental shifts to facilitate the process of signal assignment. Vibrational analysis of Cu-Py complex was performed at B3LYP level of theory with various basis sets in comparison with experimental IR data. This further assisted in double validation of DFT optimized Cu-Py structure used here for extracting Fermi contact shifts. Furthermore molecular orbital analysis on the DFT optimized Cu-Py structure articulates the spin density distribution mechanism, thereby stipulating the location of the unpaired electron in the Cu(II) d$^9$ or d$^8$ orbital in Paramagnetic Cu-Py complex.

Keywords: Paramagnetic Solid-state NMR, Cu(II) 2-pyrazine-carboxylate, Density Functional Theory (DFT) calculations, Fermi-contact shifts, Metal-organic complex
1. Introduction
Organometallic and metal-organic complexes are extensively found in nature and have wide range of applications as catalysts in chemical reactions, reactive sites in drug delivery systems and functionalizing agents in smart materials. Nuclear magnetic resonance (NMR) is a robust and well established spectroscopic characterization technique to probe such systems. The NMR chemical shift, a distinctive chemical signature of C/H (1H − 0-14 ppm, 13C − 0-220 ppm) chemical group present, provides a thorough information of the structure of the metal-organic systems through advanced (2D-correlation NMR) experiments. On the contrary if the metal ion in the metal-organic complex is paramagnetic, then the valuable chemical shift information is hampered by hyperfine interaction between nucleus (13C/1H) and unpaired electron(s). In the case of solution-state NMR of paramagnetic molecules, metal-organic complexes and metallobiomolecules, there is well established methodology developed over 3-4 decades to circumvent the problems in NMR interactions augmented by paramagnetic one, thereby accounting for structural resolution.[1] Similarly, Solid-state nuclear magnetic resonance (ssNMR) studies on paramagnetic metal-organic complexes using very fast magic angle spinning (VFMAS) technique that was successfully first applied on metal-organic complex,[2-3] has grown drastically and ventured into various experimental ideas viz. Cu distances measurement using paramagnetic augmented 13C nuclear relaxation rates[4] and methodology in probing hyperfine interactions in paramagnetic metal-organic solids.[5,6]

In the work presented in this article we have focused on assignment of 1D 1H and 13C ssNMR signals of paramagnetic Cu(II) 2-pyrazinecarboxylate (Cu-Py) complex, acquired using the ssNMR methods developed for paramagnetic systems,[1-7] in combination with density functional theory (DFT) calculations. Paramagnetic metal-organic complexes such as Cu(II) 2-pyrazinecarboxylate complex have far reaching applications in pharmaceutical industry as anti-tumour agent,[8] chemical industry as catalytic agent by functionalizing zeolite super-cage,[9] smart materials as nano-channels,[10] ensemble of metal-organic frameworks[11] and synthesis of mixed-metal molecular magnets.[12] The 1H and 13C ssNMR signals acquired on paramagnetic Cu-Py complex using VFMAS technique at 50 kHz speed manifests paramagnetic augmented shifts, a sum of diamagnetic chemical shift and Fermi-contact shift. The short distances of <10 Å between nuclei (C/H) in the organic arm to the paramagnetic center (Cu2+) consequently manifest in terms of contact shifts[13-15], while unpaired electron – nuclei dipolar interaction evident out as line broadening[13-15] due to relaxation in the 1H/13C ssNMR spectrum of paramagnetic Cu-Py complex.

Under established methodology, the paramagnetic metal ion to nuclei distance is crucial in estimating, whether the paramagnetic metal-organic complex renders interpretable 1D NMR spectrum. [4] The distances to the ligating Oxygen and Nitrogen atoms to the central copper ion in Cu-Py complex is 1.93 Å and 1.98 Å respectively as reported by Klein et al. for CuL2 (Cu-Py complex) in ref. [16]. The ligand atoms’ distance to Copper ion affects the magnitude of unpaired electron density spread over the organic arm through spin-delocalization and spin-polarization mechanisms.[17] Here in paramagnetic complexes, unpaired electron spin density over entire molecule due to Cu2+ (S=1/2) remains a major bottle neck for 1H and 13C NMR signal assignment. In this article we report the investigation of paramagnetic Cu(II) 2-Pyrazine-Carboxylate (Cu-Py) complex and assignment of 1H and 13C ssNMR signals aided by DFT calculations.

2. Experimental Section
2.1. Sample
The paramagnetic metal-organic complex copper (II) 2-pyrazinecarboxylate (2-pyrazinecarboxylic acid copper (II) salt Cu-Py) of 97% quality level assay, bearing CAS number 304656-23-3 was purchased from Merck Sigma-Aldrich, France. The blue to grey powder of Cu-Py complex with empirical formula (hill-notation) C16H6CuN3O4 has a molecular weight of 309.73 kg/mol.
2.2. Solid-state NMR spectroscopy

One dimensional solid-state NMR spectra of $^1$H and $^{13}$C in paramagnetic Cu(II) 2-pyrazinecarboxylate complex were acquired on Bruker Avance III 300 MHz spectrometer equipped with double resonance 1.3 mm VTN probe. Both $^1$H and $^{13}$C 1D experiments were acquired with 50 kHz MAS frequency at room temperature. The temperature at the site of sample (MAS rotor) was 58°C due to friction owing to the MAS speed. The spectra were reference to tetramethylsilane (TMS). A DEPTH\(^1\) pulse sequence was used to acquire both $^1$H and $^{13}$C 1D ssNMR spectrum to suppress the background signal from the probe-head. The 90° hard pulse of nutation frequencies 132 kHz for $^1$H and 76 kHz for $^{13}$C (pulse duration 1.90 μs for $^1$H and 3.3 μs for $^{13}$C) was used. Fast relaxation in paramagnetic systems facilitated to employ fast repetition technique\(^2\) to improve SNR,\(^3\) therefore the inter-scan delay was set to 100 ms for $^1$H and 70 ms for $^{13}$C. Number of scans (repetition) was set to 512 for $^1$H and 128k for $^{13}$C. Spectrum was processed using an exponential apodization of 100 Hz ($^1$H) and 250 Hz ($^{13}$C).

2.3. DFT calculation

The quantum chemical calculations on the Cu-Py complex were performed with density functional theory (DFT) using generalized gradient approximation (GGA) applying the hybrid potential implemented in the G16\(^4\) program. The Bewoulf type (Configuration: 2.3 GHz processor, 16GB RAM) computational facility at IMMM, Le Mans, France composed of 8 nodes, out of which 4 nodes was used for Gaussian 16 (G16) calculation. Input and output structures, DFT data and calculated spectra (IR, UV & NMR) were formulated and analysed using GaussView 6 (GV6, version 6.0.16).

The input structure of Cu-Py was obtained from XRD parameters of CuL\(_2\) system in the ref. \([16]\) for DFT calculations. The XRD lattice parameters and positions were manually inserted via Diamond 3.0c (Crystal Impact Inc.) software, thereby a .mol2 file was generated. This .mol2 file served as input molecular structure for the DFT calculations. A full geometry optimization was performed on this unrelaxed XRD structure with unrestricted Hartree-Fock (UHF) at B3LYP\(^{[21,22]}\) level of theory with the 6-311G, 6-311G+(d) and 6-311G+++(d) basis sets. The self-consistent field (SCF) convergence was upto 10\(^{-6}\) Hartree or up to 64 iterations. Frequency calculation showed no imaginary vibrations (negative frequencies). Further, the vibrational analysis of the DFT data was performed, using the experimental IR data on Cu-Py complex from the refs. \([9,23]\). Further, unpaired electron spin density at respective C/H nuclei were extracted from the output file, under section the “Fermi-contact coupling”, of geometry optimization job.

Molecular orbital analysis of the paramagnetic Cu-Py complex was done by performing population analysis (POP=FULL) on G16. The formatted checkpoint file was analyzed using CHEMCRAFT (version 1.8) - a graphical visualization program, and unpaired electron spin density mapping facilitating to comprehend shape of unpaired electron orbital was performed.

3. Results and Discussion

3.1. One dimensional $^1$H and $^{13}$C solid-state NMR spectrum of paramagnetic Cu(II) 2-pyrazine-carboxylate complex.

Very-Fast Magic Angle Spinning (VFMAS) technique i.e. spinning the sample faster than 30 kHz (here in this work 50 kHz) rendered well resolved $^1$H and $^{13}$C signals in Cu(II) 2-pyrazine-carboxylate complex (Cu-Py) as observed for very first time by Wickramasinghe \(et al.\)\(^[3]\) in Cu(II)-D-Alanine. The hyperfine shifts in $^1$H and $^{13}$C spectrum provides high spectral resolution by dispersing the signals and also facilitates to decouple partially the weaker proton-proton dipolar network.\(^[2,3,19,25]\) On the contrary, the valuable shifts containing chemical signature information of C/H ($^1$H – 0 -14 ppm, $^{13}$C – 0 – 220 ppm) is exacerbated in the $^1$H and $^{13}$C spectrum, leading to unassignable signals, and thereby hampers structure elucidation. Figure 1 shows the (A) Cu-Py complex along with (B) $^1$H and (C) $^{13}$C spectrum. A DEPTH\(^1\) pulse sequence with a short recycling inter-scan delay of 100 ms for both $^1$H and $^{13}$C rendered the spectra shown in the Figure 1 (B&C). The 1D $^1$H spectrum of Cu-Py
shows strong features of paramagnetic perturbation with 3 peaks $H_a$, $H_b$, and $H_c$ at 118.8 ppm, 66.7 ppm, and 49.3 ppm, corresponding to three sites of hydrogen in the Cu-Py molecule. All the three hydrogen signals are out of the normal chemical shift range (0-14 ppm) except a peak $H_d$. This broad peak $H_d$ appears to be a conjunction of more than two signals, arising from the non-chelated pyrazine-carboxylates with copper. In the $^{13}$C spectrum there are 4 peaks $C_1$, $C_2$, $C_3$, and $C_4$ distributed between -400 ppm to +600 ppm dictating the features of hyperfine shifts (contact). The peaks $C_3$ at 230.6 ppm and $C_3$ at 147.3 ppm are in normal $^{13}$C chemical shift range (0-220 ppm), though it is a cumulative shift due to hyperfine shift confirmed from DFT calculation. The peaks $C_1$ at 509.2 ppm and $C_4$ at -265.8 ppm are broadest due to fast paramagnetic relaxation and are the consequence of close proximity of the carbon site to the Cu$^{2+}$ ion. Four carbon peaks corresponding to five carbon symmetric sites leads to the conclusion that one of expected signals is absent.

3.2. Assignment of $^1$H and $^{13}$C shifts in Cu(II) 2-pyrazine-carboxylate complex using spin densities calculated through DFT calculations

The problem of assigning $^1$H and $^{13}$C ssNMR signals in paramagnetic Cu-Py complex lead to systematic DFT studies and extraction of theoretical hyperfine shifts. The contact shifts ($\delta_{EC}$), a major contributing hyperfine factor in moderate sized paramagnetic metal-organic complexes to the hyperfine shifts, are characteristics of unpaired electron spin densities $\rho(\vec{r})$ at the site position of the nucleus ($\vec{r}$) expressed in Equation (1):

$$\delta_{EC} = (S_e + 1) \frac{g_e^2 \mu_e^2 \mu_0}{g_B} \rho(\vec{r}) \tag{1}$$

where $\delta_{EC}$ is the contact shift (relative frequency scale in ppm), $S_e$ is total electronic spin [$= \frac{1}{2}$ for Cu(II)], $g_e$ is the g-factor of the electron, with the others having the usual meaning. For the metal-organic complexes of moderate size, where the hyperfine shift and contact shifts are simplified as in Equation (2):

$$\delta_{hf} \approx \delta_{EC} = m \frac{(S_e + 1)}{T} \rho(\vec{r}) \tag{2}$$

where $m$ is collection of physical constants:

$$m = \frac{g_e^2 \mu_e^2 \mu_0}{g_B} = 2.35 \times 10^6 \text{ ppm K au}^{-1}$$
From Equation (1) evidently asserts that the theoretical hyperfine shifts (=contact shifts) for both hydrogen ($^1$H) and carbon ($^{13}$C) nuclei can be calculated for Cu-Py complex system with $S_e = \frac{1}{2}$ (unpaired electron number =1) for known experimental temperature $T$ (here, $T=58°C$, temperature rise, friction due to 50 kHz MAS) except spin densities ($\rho_{\alpha\beta}$) at desired nuclear position is extracted. These spin densities are obtained by DFT calculations performed as shown in the next subsection.

3.2.1. Geometry optimization and Vibrational analysis: Validating the DFT optimized structure

The crystal structure data for paramagnetic Copper (II) 2-pyrazine-carboxylate complex (Cu-Py) was obtained from a reference, Klien et al.,[16] serving as an accurate input structure for DFT calculations on the Cu-Py complex. The structures reported in ref. [16] are CuL$_2$ (Cu-Py complex) and CuL$_2$[H$_2$O]$_2$. Among the two, the magnetic measurement details and other structural parameters confirmed CuL$_2$ as a reliable input structure for the DFT calculations that are performed on Cu-Py complex.

Cu(II) 2-pyrazine carboxylate complex is formed by ligation of pyrazine-carboxylate ligand. Pyrazine, a bridging ligand with nitrogen as active ligand atom and Carboxylate, another ligating entity with oxygen as active ligand atom together form an excellent charge transfer complex with transition metal ions viz. Cu(II),[16] Ni(II),[28] Mn(II),[28] Co(II)[27] etc. The complex bond distance of Cu-O and Cu-N of 1.93 Å and 1.98 Å reported by Klien et al.,[16] is crucial to understand the effect of spin density distribution and mechanism over the C and H atoms over the entire molecule. The CuL$_2$ reported in the ref. [16] is equivalent to the system (Cu-Py) discussed here. The Cu-Py complex is a six-coordinated ligand, with nitrogen and oxygen as ligating atoms to Cu with no counter ions, though a weak coordination exists with neighboring carboxylate group. Each molecular units of CuL$_2$ are separated by an intermolecular distance of 2.72 Å, thus evading the intermolecular magnetic exchange.[16] A full DFT optimization on geometry was performed on the structure and bond distances and angles was compared to ensure reliability of the structure for further calculations.

![Figure 2](image.png)

**Figure 2.** Crucial XRD parameters of Cu-O/ Cu-N bond distances and O-Cu-N bond angle in paramagnetic Cu-Py complex. (Input structure from Klien et al.,[16] for DFT calculations)

The calculations on the Cu-Py complex were performed with no symmetric constrains on Gaussian 16 with gas phase conditions (isolated gaseous state approximations). The structure of CuL$_2$ in Klien et al., as initial structure (see Figure 2) was subjected to DFT optimization of geometry under Hartree-Fock theory using B3LYP functional in combination with 6-311G, 6-311G+(d) and 6-311G++(d) basis sets. A comparative details the crucial distances and angles in Cu-Py complex is shown in Table 1. The Cu-N and Cu-O distances for the DFT optimized structure using 6311G basis set are 1.925 Å and 1.970 Å respectively, while with 6311G+(d) and 6-311G++(d) are 1.928 Å and 2.002 Å with a
difference of 0.008 Å – 0.018 Å. Further the crucial angle O-Cu-N was 83.6° after optimization with 6-311G, 6-311G+(d) and 6-311G++(d), with an error of 1.06% as to experimental (XRD) data. This DFT result supported as reliability factor on the DFT optimized structure for further calculations.

**Table 1.** Comparison of DFT (B3LYP) optimized Cu-O and Cu-N distances and O-Cu-N angles with experimental (XRD)[16] in paramagnetic Cu-Py complex.

| Parameters | Basis set | Cu-O bond distance (Å) | Cu-N bond distance (Å) | O-Cu-N bond angle (°) |
|------------|-----------|------------------------|------------------------|-----------------------|
| Cu-O (1.933 Å) | 6-311G | 1.925 | 1.970 | 83.6 |
| Cu-N (1.983 Å) | 6-311G+(d) | 1.929 | 2.002 | 83.6 |
| O-Cu-N (84.4°) | 6-311G++(d) | 1.929 | 2.002 | 83.6 |

References [16]

Frequency calculation on these DFT optimized structures with basis set viz., 6311G, 6-311G(d), 6311G+(d) and 6-311G++(d) confirmed the absence of imaginary vibrations (negative frequency components) indicating the global minima of energy minimization of the optimized structure. Further frequency calculations also served for vibrational analysis of the Cu-Py complex. The prominent modes of vibrations in Cu-Py complex viz. stretching modes ν(CH)arom at 3077 cm⁻¹, νas(COO) at 1653 cm⁻¹, ν(CC)arom at 1588 cm⁻¹ and ν(CN)arom at 1167 cm⁻¹, in-plane bending β(CH)arom at 1293 cm⁻¹, βs(COO) at 860 cm⁻¹ and βas(COO) at 551 cm⁻¹, and weak aromatic ring deformation at 462 cm⁻¹ in experiment IR[9,23] are fairly in agreement with the DFT calculated data (especially structure optimized with 6-311G++(d) basis set) presented in this work. **Table 2** details out comparison between experimental IR and DFT calculated vibrational peaks (with appropriate scaling factors for respective basis sets) using various basis sets in Cu-Py complex. The experimental IR data used here in this work is from the ‘neat’ complex of Cu(II) 2-pyrazinecarboxylate mentioned in ref. [23]. The experimental IR frequencies are in accordance with the theoretical frequency calculations using B3LYP theory with various basis sets.

**Table 2.** Comparison of DFT (B3LYP) calculated modes of vibrations at various basis sets with experimental IR[23] in paramagnetic Cu-Py complex.

| IR Assign. (expt[23] cm⁻¹) | 6-311G | 6-311G(d) | 6-311G+(d) | 6-311G++(d) |
|----------------------------|--------|-----------|------------|-------------|
| ν(CH)arom (3077)           | 3111   | 3103      | 3105       | 3127        |
| ν(COO)as (1653)            | 1606   | 1715      | 1690       | 1702        |
| ν(C-C)arom (1588)          | 1547   | 1575      | 1570       | 1582        |
| β(CH)arom (1293)           | 1282   | 1278      | 1277       | 1287        |
| ν(CN)arom (1167)           | 1126   | 1156      | 1146       | 1154        |
| βs(COO) (860)              | 808    | 829       | 823        | 829         |
| βas(COO) (551)             | 531    | 534       | 529        | 533         |
| φ(C-C)arom (462)           | 477    | 456       | 450        | 460         |

* ν- stretching, β- in-plane bending&φ- Ring deformation ref. [23]

Among the DFT vibrational data obtained using various basis sets, 6-311G++(d) was in close proximity to the experimental IR. The DFT vibrational analysis on Cu-Py complex suggests that the structure optimized using 6-311G++(d) can be used further for more accurate DFT calculations.
Further the structure optimized using 6-311G++(d) was used for extraction of hyperfine shifts and comprehension of unpaired electron distribution using Population analysis.

3.2.2. $^1$H & $^{13}$C signal assignment of Cu-Py complex using DFT calculated spin densities

The lack of understanding of unpaired electron spin density spread over the nuclei (C/H in particular) in the pyrazine-carboxylate molecule remained a major bottleneck for assignment of $^1$H and $^{13}$C hyperfine shifted signals. With full geometry optimization using DFT of Cu-Py complex in hand, the next step of calculating hyperfine shifts in $^1$H/$^{13}$C in Cu-Py complex, was performed. At the end of the geometry optimization, involving less than 100 atoms in a molecule under unrestricted mode, generates unpaired electron spin densities on nuclei (C/H). The unpaired electron spin density distribution in the Cu-Py complex is depicted in the Figure 3 as a molecular orbital plot from POP population analysis job in G16. The spin density ($\rho$) range from +0.00014 au (positive spin density in blue mesh) to-0.00014 au (negative spin density in red mesh). The mechanism of spin density distribution and few other molecular orbital analysis details are discussed in next section. These spin densities $\rho$(in au) were plugged into Eq. 2 to obtain $^1$H/$^{13}$C hyperfine shifts (contact shifts) in Cu-Py complex. The diamagnetic part of the total shift in Cu-Py complex calculated using NMR=GIAO (Gauge-Independent Atomic Orbital) under B3LYP theory with 6-311G+(2d,p) basis set was added to the hyperfine shifts to obtain total shifts in the Cu-Py complex. Table 3 details out comparison of experimental total shifts ($\delta_{expt}$) with theoretical total shifts ($\delta_{calc}$) calculated using DFT in $^1$H and $^{13}$C and thereby signal assignment in paramagnetic Cu-Py complex.

Table 3. Assignment of $^{13}$C and $^1$H hyperfine shifted signals using unpaired electron spin density at Carbon and Hydrogen nuclei calculated by DFT [B3LYP/6-311G++(d)] in paramagnetic Cu-Py complex.

| Nuclei | Site No. (Fig. 2) | Spin density $\rho$ [au] | Hyperfine shift (theoretical) $\delta_{NMR}$ [ppm] | Diamagnetic shift (theoretical)$\delta_0$ [ppm] | Total shift (theoretical) $\delta_{calc}$ [ppm] | Expt. shift $\delta_{expt}$ [ppm] | <Signal assign.>(Fig. 1 B & C) |
|--------|------------------|------------------------|--------------------------------|---------------------------------|---------------------------------|--------------------------------|-----------------------------|
| $^{13}$C | C4, C12         | 0.00341                | 364                          | 148                             | 512                             | 509 <C₄>                      |
|         | C6, C14         | 0.00088                | 94                           | 145                             | 239                             | 231 <C₆>                      |
|         | C2, C10         | -0.00014               | -15                          | 146                             | 131                             | 147 <C₂>                      |
|         | C1, C9          | -0.00395               | -422                         | 144                             | -278                            | -266 <C₁>                     |
|         | C8, C16         | -0.00482               | -514                         | 166                             | -350                            | *NO <C₈>                      |
| $^1$H   | H5, H13         | 0.00040                | 43                           | 8.8                             | 52                              | 49 <H₅>                       |
|         | H3, H11         | 0.00063                | 67                           | 9                               | 76                              | 66 <H₃>                       |
|         | H7, H15         | 0.00119                | 127                          | 9.2                             | 146                             | 118 <H₇>                      |

*NO- Not observed in 1D $^{13}$C ssNMR DEPTH experiment (due to loss of coherence)

The theoretical shifts from DFT calculations performed on Cu-Py complex with various basis sets viz. 6-311G, 6-311G+(d) and 6-311G++(d) were compared with the ssNMR experimental shifts. In the case of structure optimized with 6-311G++(d), the calculated DFT shifts are in closest agreement (error of ±20 ppm) with the experimental shifts. Nonetheless the $^1$H and $^{13}$C shifts have error bars of ±30 ppm for 6-311G and 6-311G+(d). This is quite acceptable for paramagnetic systems, where shifts exacerbate from 100-1000 ppm in both directions, up-and down-field.

The three $^{13}$C ssNMR signals shifted to downfield, assigned as C₁ (509 ppm), C₄ (231 ppm) and C₃ (147 ppm) shows a good accordance with the theoretical shifts arising from the symmetric carbon site
pairs C4/C12 (512 ppm), C6/C14 (239 ppm) and C2/C10 (131 ppm) respectively. One of the two upfield shifted 13C ssNMR signal C4 observed at -266 ppm corresponds to theoretical shifts from carbon site pairs C1/C9 at -278 ppm. The other carbon site pair C8/C16 with a theoretical shift of -350 ppm is extremely shifted, and also was not observed in the ssNMR experiment due to extreme broadening. The fact that the Cu-C distance, a crucial factor to observe NMR signal following Solomon’s rate equation\cite{30, 31} \((R_1, 2\pi r^6\text{Cu-C})\), is reflected in the case of C8/C16 carbon site pair as missing signal due to loss of coherence. From XRD data of Kliten et al.,\cite{15} the carbon site pairs CX/CY distances to Cu are as follows: C4/C12 at 4.26 Å, C2/C10 at 4.09 Å, C6/C14 at 3.02 Å and 13C ssNMR signals arising from the same are downfield shifted at C1 (509 ppm), C2 (231 ppm) and C3 (147 ppm). Further the carbon site pairs closest to Cu, C1/C9 at 2.76 Å manifests a broad 13C signal C6 at -278 ppm, while C8/C16 with a closest carbon-metal proximity in complex of 2.73 Å is not observed in the experiment due to the loss of coherence. The close proximity of these carbon sites makes them vulnerable for fast nuclear relaxation due to unpaired electron in Cu, making ssNMR signal unobservable following Solomon’s rate equation\cite{36, 31} \((R_1, 2\pi r^6\text{Cu-C})\). Nevertheless, with the aid of DFT calculations we see that the expected signal from C8/C16 should be around 350-400 ppm.

The 1H ssNMR spectra clearly shows all the three signals in the down-field region 49 ppm (H1a), 66 ppm (H1b) and 118 ppm (H1c). The theoretical shifts from DFT calculations as well manifest three downfield shifts arising from hydrogens, H5/H13 (attached to carbon site pair C4/C12) at 52 ppm, H3/H11 (attached to carbon site pair C2/C10) at 76 ppm and H7/H15 (attached to carbon site pair C8/C16) at 146 ppm.

With this, the assignment of signals in 1H and 13C ssNMR spectra of paramagnetic Cu-Py complex is completed except the C4 signal arising from the carbon site pair C8/C16 with a theoretical shift (total) of -350 ppm which is not observed in ssNMR experiment due to carbon’s closest proximity (2.73 Å).

### 3.2.3 Molecular orbital analysis of Cu-Py complex: Spin density mechanism and location of unpaired electron

The unpaired electron spin density distribution of Cu2+ ion over the entire organic arm of pyrazine-carboxylate ligand was comprehended by performing full population analysis \((POP=FULL)\) in G16.

![Figure 3](image-url). Spin density (SD) distribution in paramagnetic Cu-Py complex calculated by DFT (SD value range: +0.00014 au to -0.00014 au, blue mesh: positive SD, red mesh: negative SD)

The output of POP job from G16 was analysed using CHEMCRAFT visualization program. Figure 3 shows a molecular orbital plot with positive/negative spin densities depicted in blue/red mesh with value range of +0.00014 au to -0.00014 au. MO analysis aided in verifying the location of unpaired electron in Cu atom. Though, it is clear on a first glance that normally in square-planar and octahedral complexes involving Cu2+ ion the unpaired electron resides in \(d_{x^2-y^2}\) orbital excluding Jan-Teller effect.
due to counter ion (ligating Oxygen atom from neighbouring pyrazine-carboxylate ligand) to the Cu atom. However, the MO analysis confirmed this estimation through the appearance of blue mesh cloverleaf shape of $d_{x^2}^Z$ on Cu indicating the location of unpaired electron. Further the MO analysis assisted to understand spin density mechanism in paramagnetic Cu-Py complex. The extreme downfield shifted $^{13}$C signal 509 ppm assigned as C$_4$ arising from carbon site pair C4/C12 ($\delta_{\text{calc}}$: 512 ppm) shows intense positive spin density (blue mesh in Fig. 3) distributed on it through spin polarization mechanism. Similarly, downfield shifted $^{13}$C signal 231 ppm assigned as C$_2$ arising from carbon site pair C6/C14 ($\delta_{\text{calc}}$: 239 ppm) shows a small negative spin density (red mesh in Fig. 3) due to spin-polarization mechanism, though leading to positive spin density value of 0.00088 au. This is due the fact that the carbon site pair are engulfed by high positive spin density (blue mesh in Fig. 3) delocalized from the ligating nitrogen atoms (N17 and N19). This is compensated and leads to small positive spin density on both C6/C14 carbon site pairs. Correspondingly the same spin density mechanism is seen in carbon site pair C4/C12 ($\delta_{\text{calc}}$: 131 ppm) giving rise to $^{13}$C signal at 147 ppm assigned as C$_3$. The upfield shifted signal C$_4$ at -266 ppm observed experimentally, arises from carbon site pair C1/C9 ($\delta_{\text{calc}}$: -274 ppm) has higher negative spin density with less compensative positive density from neighbouring atoms leading to intense negative spin density of -0.00395 au. Finally the extreme shifted $^{13}$C signal assigned to C$_5$, experimentally unobserved has highest value of negative spin density of -0.00482 au. This theoretical shift value of -350 ppm for carbon site pair C8/C16 results through spin density due to strong spin-polarization mechanism. Further for the hydrogens H5/H13 stemming from C4/C12 and H3/H11 site pairs stemming from C2/C10 shows a positive spin density through delocalization from their respective carbon atoms. However, the hydrogen site pair H7/H15 stemming from C8/C16 has an intense positive spin density among all hydrogens due to spin-polarisation mechanism from its carbon pair which has highest negative spin density.

4. Conclusion
We have perspicuously shown here the nearly complete assignment of $^1$H and $^{13}$C ssNMR spectra of paramagnetic Cu(II) 2-pyrazine-carboxylate complex with the strong theoretical aid of density functional theory calculations without the need for advanced 2D NMR experiments. The assignment of these paramagnetic signals by the method discussed here strictly depends on the extraction of unpaired electron spin density from DFT calculations. Though straightforward, the need for valid DFT structure, is a crucial criteria and hence a thorough DFT investigation using various basis sets viz. 6-311G, 6-311G+(d) and 6-311G++(d) was performed. Vibrational analysis of the frequency calculations indicates that B3LYP using 6-311G++(d) basis set is favored method for Cu-Py complex which have two different types of ligating atoms (oxygen and nitrogen). Further unpaired electron spin density over the complex and extraction of the same from DFT calculated valid structure remains crucial for $^1$H/$^{13}$C signal assignment. However, the extreme upfield shifted $^{13}$C signal unobserved in ssNMR was tentatively assigned using theoretical shift of -350 ppm calculated using DFT. This facilitates the experimental ssNMR method to search for missing signal’s probable position. Along with DFT calculations and methods previously applied for ssNMR of paramagnetic system the task of assigning $^1$H and $^{13}$C signals in paramagnetic Cu-Py complex is accomplished. Further we have discussed in detail the spin density mechanism on each carbon and hydrogen site in the complex using Molecular Orbital (MO) analysis. Also MO analysis confirms the location of the unpaired electron as Cu’s $d_{x^2-y^2}$ orbital.

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