

## SUPPLEMENTAL INFORMATION

for

### **EPR, ENDOR, and Electronic Structure Studies of the Jahn-Teller Distortion in an Fe<sup>V</sup> Nitride.**

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### Decomposition of $\mathbf{T}_{obs}$ for $^{15}\text{N}$ Nitride

Decompositions have been carried out for the observed  $^{15}\text{N}$  dipolar coupling tensor:

$$\mathbf{T}_{obs} = [+4.9, -6.7, +1.8] \text{ MHz} \quad \text{S1}$$

This tensor contains both non-local contributions from through-space dipolar interactions between the  $^{15}\text{N}$  and electron spin on iron, and local contributions from  $p$ -orbital spin density.

$$\mathbf{T}_{loc} = \mathbf{T}_{loc}^z + \mathbf{T}_{loc}^{x,y} \quad \text{S2}$$

The through-space interaction gives an axial tensor with its primary contribution along the preferred axis,  $T^z$ ,

$$\mathbf{T}_{non-loc} = [+2a, -a, -a]; a = \frac{\rho_{\text{Fe}} g_e \beta_e g_n \beta_n}{r^3} = -2.2 \text{ MHz} \quad \text{S3}$$

Use of the crystallographically determined Fe-nitride distance,  $r = 1.506 \text{ \AA}$ , and the typical value of  $\rho_{\text{Fe}}$ ,  $\sim +0.9$  yields,  $a = -2.2 \text{ MHz}$  ( $g_n < 0$  for  $^{15}\text{N}$ ). With this value, subtraction of  $\mathbf{T}_{non-loc}$  from  $\mathbf{T}_{obs}$  arrives at the local contributions

$$\begin{aligned} \mathbf{T}_{loc} &= \mathbf{T}_{obs} - \mathbf{T}_{non-loc} \\ \mathbf{T}_{loc} &= [+8.5, -9.3, +0.4] \text{ MHz} \end{aligned} \quad \text{S4}$$

The local interaction  $\mathbf{T}_{loc}$  can be further uniquely decomposed into two axial contributions, one with the preferred axis along the Fe-N bond,  $\mathbf{T}_{loc}^z$ , and one with it orthogonal to the bond

$$\begin{aligned} \mathbf{T}_{loc} &= \mathbf{T}_{loc}^z + \mathbf{T}_{loc}^y \\ &= [+6.4, -3.2, -3.2] + [+2.9, -5.8, +2.9] \text{ MHz} \end{aligned} \quad \text{S5}$$

The local dipolar contributions to  $\mathbf{T}_{obs}$  may also be written in terms of contributions spin densities in the three individual 2p orbitals,  $\rho_i$ :

$$\begin{aligned} T_z &= +2T_0\rho_z - T_0\rho_y - T_0\rho_x = +9.3 \text{ MHz} \\ T_y &= -T_0\rho_y + 2T_0\rho_y - T_0\rho_x = -8.9 \text{ MHz} \\ T_x &= -T_0\rho_z - T_0\rho_y + 2T_0\rho_x = -0.4 \text{ MHz} \end{aligned} \quad \text{S6}$$

where  $T_0$  is the uniaxial hyperfine parameter for a unpaired  $p$  electron,  $T_0(^{15}\text{N}) = -78 \text{ MHz}$ .<sup>1</sup> These three equations are linearly dependent and in general cannot be solved for the three individual spin densities, only for differences between spin densities (failure to satisfy Cramer's rule). However, because  $\mathbf{T}_{loc}$  can be uniquely decomposed into only two local dipolar contributions,  $\mathbf{T}_z$  and  $\mathbf{T}_y$ , each proportional to the spin density in the corresponding 2p orbital of nitride, the third contributor must be negligible,  $\mathbf{T}_x$ ,  $\sim 0$ , along with the spin density in the 2px orbital. The resulting 2p spin densities on the  $^{15}\text{N}$  nitride are:  $\rho_x \sim 0$ ,  $\rho_y = -0.04$ ,  $\rho_z = -0.08$ . These local dipolar contributions can be viewed as arising from spin density transferred to an idealized  $\text{N}^{3-}$  via electron donation from filled orbitals on N to partially occupied  $d\delta(xy, x^2-y^2)$  orbitals on  $\text{Fe}^{\text{V}}$  and/or polarization of the filled  $2p$  orbitals on N. The negative signs of the spin densities imply that spin polarization dominates.

As noted by an insightful reviewer, in the general case where all three 2p orbitals have non-zero spin densities, one can solve for individual spin densities by introducing an additional semi-empirical equation, which assumes that the isotropic coupling obeys a McConnell relationship:

$$a_{iso} = Q_0(\rho_x + \rho_y + \rho_z) = +7.7 \text{ MHz} \quad \text{S7}$$

where  $Q_0$  is the spin polarization constant  $(-67 \text{ MHz})^2$

### ***<sup>57</sup>Fe Quadrupole Splitting***

The <sup>57</sup>Fe quadrupole splitting parameter ( $\Delta E_q$ ) has been previously determined by Mössbauer spectroscopy<sup>2, 3</sup>. The quadrupole splitting derives from the interaction between the nuclear electric quadrupole moment and the electric field gradient (EFG) that originates from the asymmetric electronic charge distribution due to the ligand field. Thus, the quadrupolar splitting provides important electronic structure information regarding the charge asymmetry about the Fe nucleus. Calculations of the quadrupole splitting were made using ORCA<sup>4</sup> and yield  $\Delta E_q = 4.21$  mm/s (PBE0) or 5.12 mm/s (CASSCF). This is in excellent agreement with the experimental value<sup>3</sup> of 4.78 mm/s, and provides a confirmation of the  $e_a^3$  electronic configuration with Fe valence orbital electron density localized in the  $xy$  plane.

### ***Analysis of $^{11}\text{B}$ Quadrupole Interaction***

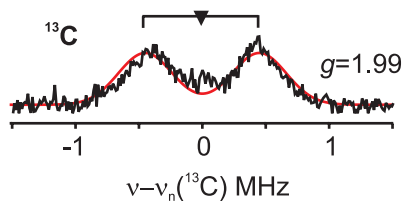
The small value of the experimentally derived quadrupole coupling parameter,  $e^2qQ = 2P_1 \approx 0.5$ , compared to the intrinsic coupling constant for a single  $^{11}\text{B}$  electron in a  $2p$  orbital,  $|e^2qQ_0| \approx -5.3$  MHz,<sup>5</sup> and the axial character of the tensor, can be analyzed in terms of a trigonally symmetric  $sp^3$  hybridized boron equivalently bonded to three nitrogens, as well as to one carbon, an approach similar to that used in discussing the  $^{14}\text{N}$  coupling of trialkyl amines (Eqn. 9).

$$\left| \frac{e^2qQ}{e^2qQ_0} \right| = \left| -\frac{3\cos\alpha}{1-3\cos\alpha} [2-(C+N)] \right| \approx \frac{1}{2} [2-(C+N)] \approx 0.1 \quad \text{S8}$$

Here,  $C$  and  $N_\sigma$  are respectively the occupancies of boron  $sp^3$  orbitals involved in bonding to the carbon and the average of the occupancies of the three nitrogens;  $\alpha = 109.5^\circ$  is the idealized internal angle between the principle directions of  $sp^3$  hybridized orbitals. The small value for the experimental coupling indicate that with  $C + N \sim 2$ , namely that all four of the boron  $sp^3$  orbitals are involved in single bonds, Thus, whereas the small hyperfine coupling to  $^{11}\text{B}$  indicates that it interacts minimally with the  $\text{Fe}^{\text{V}}$  ion, the small and axial quadrupole coupling of  $^{11}\text{B}$  shows effective  $C_{3v}$  symmetry at this atom, in agreement with the crystal structure results

### <sup>13</sup>C ENDOR Spectroscopy

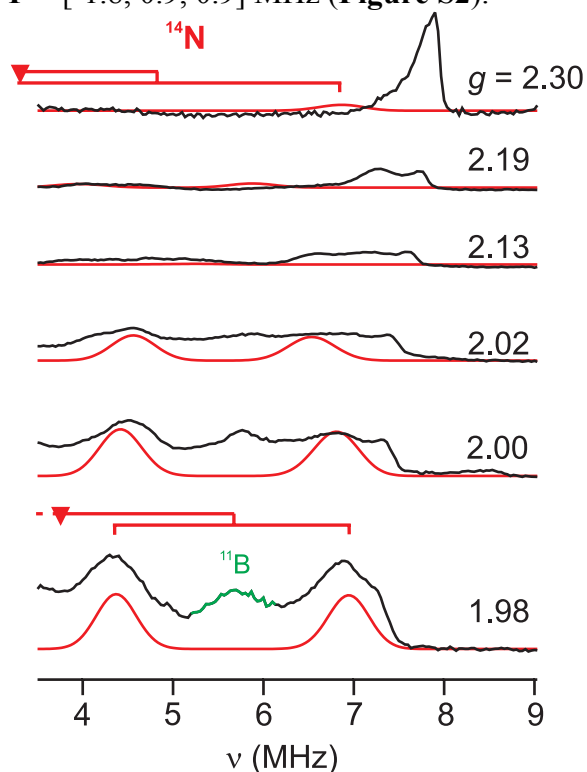
The small coupling suggests that the signal does not come from carbons associated with the Fe-C bonds, as these would be anticipated to have a larger  $A$ ; they presumably have greater linewidths, and thus are not observed in natural abundance.



**Figure S1.** Q-band 2D field-frequency Mims pulse detected <sup>13</sup>C ENDOR. *Simulation parameters:*  $g=[2.30, 1.98, 1.98]$ ;  $A=[0.9,0.9,0.9]$  MHz, coaxial with  $g$ ; ENDOR line width, 0.5 MHz; EPR line width, 500 MHz. *Conditions:* Microwave freq, 35.04 GHz;  $\pi$  pulse length = 50 ns;  $\tau = 500$  ns; repetition rate, 20 ms;  $t_{rf} = 30$   $\mu$ s; RF randomly hopped.

### <sup>14</sup>N ENDOR of Tripodal Ligand

The six nitrogens in the ligand, two in each carbene, can have different coupling tensors and have differing orientations relative to  $\mathbf{g}$ , and the poor resolution resulting from the overlap of these signals makes it impossible to determine the coupling parameters for individual nitrogens. However, a representative average hyperfine coupling has been obtained by treating the six nitrogens as a single nitrogen with resolved features governed both by hyperfine and quadrupole interactions. The 2D pattern of <sup>14</sup>N spectra from the tripodal ligand can be satisfactorily described in this fashion with the following interaction parameters:  $\mathbf{A} = [2.0, 3.3, 3.3]$  MHz and  $\mathbf{P} = [-1.8, 0.9, 0.9]$  MHz (Figure S2).



**Figure S2.** Q-band 2D field-frequency soft Davies pulse detected <sup>14</sup>N ENDOR. *Simulation parameters:*  $\mathbf{g} = [2.30, 1.98, 1.98]$ ;  $\mathbf{A} = [2.0, 3.3, 3.3]$  MHz;  $\mathbf{P} = [-1.8, 0.9, 0.9]$  MHz;  $\mathbf{A}$  and  $\mathbf{P}$  coaxial with  $\mathbf{g}$ ; ENDOR line width 0.5 MHz; EPR line width, 500MHz. *Conditions:* Microwave freq, 34.968 GHz;  $\pi$  pulse length = 200 ns;  $\tau = 600$  ns; repetition rate, 20 ms;  $T_{rf} = 30 \mu\text{s}$ ; RF randomly hopped.

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