

# Theoretical Study of Mössbauer Hyperfine Parameters of Fe Bound to Ammonia

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## Abstract

The first-principles Discrete Variational method was employed to study the species formed by the interaction of an Fe atom and ammonia. Total energy calculations were performed for several configurations. The hyperfine parameters isomer shift, quadrupole splitting and magnetic hyperfine field were calculated for the ground state found ( ${}^5E$ ), and compared to reported experimental values obtained by Mössbauer spectroscopy in frozen ammonia. Key-words: FeNH<sub>3</sub>; Hyperfine interaction; Electronic structure; Discrete variational method; Density functional theory.

# 1 Introduction

There have been many theoretical investigations about the nature of bonding of the lone pair ligands, such as the  $\text{NH}_3$  molecule, to transition metals [1]. The latter may absorb ammonia strongly on their surfaces. The main interest is related to the fact that important chemical reactions involving ammonia are catalyzed by transition metals. On the other hand, the technique of isolation of atoms and small molecules in frozen gases allows the use of Mössbauer spectroscopy to probe charge and spin distributions. In this context an investigation of Fe isolated in solid ammonia has been reported; the reaction product  $\text{FeNH}_3$  was identified, and Mössbauer hyperfine parameters were measured [2].

In the present work, we report a theoretical study for the species  $\text{FeNH}_3$  by using the Discrete Variational method (DVM) [3] developed in the framework of the local spin-density approximation (LSDA) of density-functional theory [4]. We have performed total energy calculations in order to determine the ground state. Finally, the Mössbauer hyperfine parameters isomer shift ( $\delta$ ), quadrupole splitting ( $\Delta EQ$ ) and components of the magnetic hyperfine field ( $H_F$ ) are calculated and compared to experiment.

## 2 Theoretical Method

In this section we describe briefly the DVM method. The full details have been discussed elsewhere [3]. The essence of the DVM scheme is to solve the set of Kohn-Sham equations, which for the spin-polarized case [4] is written in Hartree atomic units as:

$$\left[-\frac{1}{2}\nabla^2 + V_c(\vec{r}) + V_{xc}^\sigma(\vec{r})\right]\phi_{i\sigma}(\vec{r}) = \varepsilon_{i\sigma}\phi_{i\sigma}(\vec{r}) \quad (1)$$

where the Coulomb potential  $V_c$  includes electron-nucleus and electron-electron interactions and  $V_{xc}^\sigma$  is the spin-dependent exchange-correlation potential of spin  $\sigma$  derived by von Barth and Hedin [5]. Both potentials are functionals of the electron density  $\rho_\sigma$  of spin  $\sigma$

$$\rho_\sigma(\vec{r}) = \sum_i^N n_{i\sigma} |\phi_{i\sigma}(\vec{r})|^2 \quad (2)$$

where the summation in Eq. (2) runs over the lowest  $n$  molecular spin orbitals  $\phi_{i\sigma}$  with occupation  $n_{i\sigma}$ , which are expanded on a basis of atomic numerical orbitals-LCAO approximation-centered at the symmetrically equivalent atoms.  $\rho_\sigma$  has the freedom to be different for the two spin orientations.

The Discrete Variational scheme leads to a set of secular equations to be solved self-consistently,

$$([H] - [E][S])[C] = 0 \quad (3)$$

where  $[H]$ ,  $[S]$  and  $[C]$  are respectively the hamiltonian, the overlap and the eigenvector matrices. All the matrix elements are obtained by 3-dimension numerical integrations. The integration scheme used here is the pseudo-random Diophantine method [3], except for the core region of the atoms, where a precise polynomial integration is performed [6]: this is necessary for an accurate evaluation of the hyperfine parameters on Fe, as well as for the total energy.

The functional dependence of the  $V_c$  potential on  $\rho(\vec{r})$  leads to the so-called three-center integrals, which have a large computational cost. In order to calculate it by one-dimensional integrations, the exact molecular charge density is fitted to a multicenter-multipolar expansion (SCM) [7].

$$\rho(\vec{r}) \cong \rho_{SCM} = \sum_j d_j \sum_{\nu}^I \sum_m C_{\ell m}^{\nu \lambda} R_N(r_{\nu}) Y_{\ell}^m(\hat{r}_{\nu}). \quad (4)$$

Here  $r_{\nu}$  is the local coordinate relative to site  $\nu$ , the summation is over a set  $I$  of atoms equivalent by symmetry,  $R_N$  are piecewise parabolic radial functions centered at atoms  $\nu$  and  $\lambda$  denotes different basis functions of a given  $\ell$  ( $j = I, \ell, \lambda, N$ ). Theoretically  $\rho_{SCM}$  allows calculations of the Coulomb and exchange-correlation potentials as precise as one wishes; in the present calculations, partial waves up to  $\ell = 2$  were employed for Fe and  $N$ , and  $\ell = 1$  for  $H$ ; the least square error of the fit of  $\rho$  was  $\sim 0.04$ .

In the DVM scheme, the total energy  $E$  is calculated by a point by point numerical integration of the difference-energy density [8]

$$E = \langle e(\vec{r}, \{\vec{R}_{\nu}\}) - e^{NI}(\vec{r}, \{\vec{R}_{\nu}\}) \rangle + E^{NI} \quad (5)$$

in which a reference system of non-interacting ( $NI$ ) atoms centered at nuclear sites  $\vec{R}_{\nu}$  is introduced in order to suppress numerical noise arising from the energy density  $e(\vec{r}, \{\vec{R}_{\nu}\})$ . The basis set is adopted as the standard reference.

### 3 Results and Discussion

The purpose of the present work is to calculate the Mössbauer hyperfine parameters for the species  $\text{FeNH}_3$ . We performed self-consistent calculations for seven configurations. For each one, the total energy curve covering a wide range of Fe-N distances was obtained

in order to determine the ground state.  $\text{FeNH}_3$  has  $C_{3v}$  structure with the metal atom constrained to lie on the main symmetry axis (the  $z$  axis) of the ligand. The ammonia in the  $\text{FeNH}_3$  molecule was treated using the experimental equilibrium geometry [9]:  $\text{N-H}=1.00\text{\AA}$  with an angle  $\text{H-N-H}=107.2^\circ$ . By this procedure, the ground state of  $\text{FeNH}_3$  was determined to be a  ${}^5E$  with configuration:

$$\begin{aligned} &(\uparrow)9a_1^1 10a_1^1 4e^2 5e^2 \\ &(\downarrow)9a_1^1 4e^1 \end{aligned}$$

where the degenerate  $4e^1\downarrow$  orbital is predominantly of Fe ( $3d_{xy}, 3d_{x^2-y^2}$ ) character. The Fe populations in all configurations are near  $3d^7 4s^1$ , more precisely  $3d^{6.63} 4s^{1.12} 4p^{0.04}$  for the ground state. This means that dissociation would lead to Fe  $3d^7 4s^1$  ( ${}^5F$ ) instead of the Fe ground state  $3d^6 4s^2$  ( ${}^5D$ ) [10]. The Fe-N equilibrium distance found for the  ${}^5E$  ground state is  $1.98\text{\AA}$ .

The isomer shift ( $\delta$ ) is defined as [11]

$$\delta = \frac{2\pi}{3} Z e^2 S'(Z) \Delta \langle r^2 \rangle [\rho_A(0) - \rho_S(0)] \quad (6)$$

where  $A$  and  $S$  refer to absorber and source respectively,  $\Delta \langle r^2 \rangle$  is the difference in the mean-square nuclear radius in the excited and ground states of the Mössbauer nuclear transition and  $S'(Z)$  is a factor to correct for relativistic effects. Only orbitals belonging to the totally symmetric representation of the point group of the molecule ( $C_{3v}$ ) make contributions to  $\rho(0)$  in a non-relativistic approach.

For the  $\text{FeNH}_3$  molecule which is symmetrical around the  $z$  axis, the quadrupole splitting ( $\Delta EQ$ ) of the nuclear level of spin  $I = 3/2$  of  ${}^{57}\text{Fe}$  produced by the interaction between the nuclear quadrupole moment  $Q$  and the electric field gradient of exterior charges  $q$  is given by

$$\Delta EQ = 1/2 e^2 q Q. \quad (7)$$

where

$$q = - \int \rho(\vec{r})(3z^2 - r^2)/r^5 d\vec{r} + \sum_q Z_q(3z_q^2 - r_q^2)/r_q^5. \quad (8)$$

The first term in Eq. (8) is the electronic contribution, which is calculated as a sum over the 3-dimensional grid, while the second one is the point-charge contribution of the neighbor N and H nuclei.

The hyperfine contact field ( $H_c$ ) computed at the Fe nucleus is given by

$$H_c = (8\pi/3) g_e \mu_B \frac{1}{2} [\rho_\uparrow(0) - \rho_\downarrow(0)] \quad (9)$$

where  $g_e$  is the electronic  $g$ -factor,  $\mu_\beta$  the Bohr magneton and  $\rho$  is calculated according to Eq. (2). The dipolar field  $H_D$  is defined as [12]:

$$H_D = \frac{1}{2}g_e\mu_\beta \int [\rho_\uparrow(\vec{r}) - \rho_\downarrow(\vec{r})](3z^2 - r^2)/r^5 d\vec{r} \quad (10)$$

where the densities are computed according to Eq. (2) and the integral is a sum over the 3-dimensional grid. Therefore, the total hyperfine field  $H_F$  is given by the sum of the two components:

$$H_F \cong H_C + H_D.$$

The orbital component of the hyperfine field was not considered here.

In Table 1 can be seen the results obtained for the Mössbauer parameters described above for the seven configurations examined, being the second of them the ground state configuration. To determine  $\delta$ , we first performed calculations for free Fe atoms and ions, for which  $\delta$  was measured in frozen gas matrices [13], by using the atomic Density Functional self-consistent method, in order to obtain

$$\alpha = \frac{2}{3}\pi e^2 Z S'(Z) \Delta \langle r^2 \rangle = -0.228 \text{ mm/s} \cdot a_0^{-3}$$

and thus calculate the isomer shifts in Table 1, using this value of  $\alpha$  and the molecular values of  $\rho(0)$ .

In Table 1 we also give the values of  $\Delta EQ$ . Since the sign of the experimental value was determined [2], this constitutes a reliable test for the  ${}^5E$  ground state found. We used here  $Q = 0.20b$  [11]. It may be seen in the table that the ground state configuration (2) is indeed the only one for which the computed value of  $\Delta EQ$  is near the experimental value in both sign and magnitude, all the other configurations giving values very far from experiment.

The hyperfine field  $H_F$  shown in Table 1 is the sum  $H_C + H_D$ . Since it was not possible to measure the sign of  $H_F$ , from the experimental point of view two values are equally possible: +800 or -900 kOe [2]. We can observe that positive fields  $H_C$  are related to configurations where the  $10a_1\uparrow$  (Fe 4s) is occupied.

## 4 Conclusions

We have performed self-consistent local spin-density calculations for seven different configurations of the FeNH<sub>3</sub> molecule. Total energy calculations indicated that the ground state is a  ${}^5E$  corresponding to configuration (2) in Table 1. For this configuration the

computed values of the Mössbauer hyperfine parameters  $\delta$  and  $\Delta EQ$  agree well with the measured values. The calculated value of the magnetic hyperfine field found for the ground state is large and positive, due to the occupation of the  $10a_1^1$  ( $4s\uparrow$ ) orbital. The magnitude of  $H_F$  is somewhat smaller than experiment.

Configuration	$\delta$ (mm/s)	$\Delta EQ$ (mm/s)	$H_C$ (kOe)	$H_D$ (kOe)	$H_F^{(c)}$ (kOe)
(1) ( $\uparrow$ ) $9a_1^1 10a_1^1 4e^2 5e^2$ ( $\downarrow$ ) $4e^1 5e^1$	+0.74	+0.16	+1224	+94	+1318
(2) ( $\uparrow$ ) $9a_1^1 10a_1^1 4e^2 5e^2$ ( $\downarrow$ ) $9a_1^1 4e^1(xy, x^2-y^2)$	+0.42	-1.66	+539	+29	+568
(3) ( $\uparrow$ ) $9a_1^1 10a_1^1 4e^2 5e^2$ ( $\downarrow$ ) $9a_1^1 5e^1(xy, x^2-y^2)$	+0.43	-0.59	+552	+66	+618
(3') ( $\uparrow$ ) $9a_1^1 10a_1^1 4e^2 5e^2$ ( $\downarrow$ ) $9a_1^1 5e^1(yz, xz)$	+0.32	-7.27	+438	-167	+217
(4) ( $\uparrow$ ) $9a_1^1 4e^2 5e^2$ ( $\downarrow$ ) $9a_1^1 4e^1 5e^1$	+0.62	+1.06	-1030	+11	-1019
(5) ( $\uparrow$ ) $9a_1^1 4e^2 5e^2$ ( $\downarrow$ ) $9a_1^1 5e^2(xy, x^2-y^2)$	+0.78	+6.95	-1282	+265	-1017
(6) ( $\uparrow$ ) $9a_1^1 10a_1^1 4e^2 5e^2$ ( $\downarrow$ ) $5e^2(xy, x^2-y^2)$	+0.77	+6.81	+1193	+333	+1526
Experimental	+0.67 <sup>(a)</sup>	-2.0 <sup>(a)</sup>			+ 800 or -900 <sup>(a)</sup>
	+0.60(5) <sup>b</sup>	1.90(5)  <sup>(b)</sup>			

Table 1: Calculated and experimental Mössbauer hyperfine parameters of  $\text{FeNH}_3$ , for calculations at the equilibrium distances.

a) From Ref. 2;  $\delta$  relative to Fe metal at room temperature;

b) From Ref. 14;  $\delta$  relative to Fe metal;

c) Theoretical values of  $H_F = H_C + H_D$ .

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