^{15}N-NMR Study on Complexes of Low-Spin Ferritetraphenylporphyrin

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^{15}N-NMR chemical shifts, spin-lattice, and spin-spin relaxation times of the four pyrrole nitrogen nuclei in complexes of low-spin ferritetraphenylporphyrin with pyridine and 1-methylimidazole in chloroform have been studied. Although deviations from an axial symmetry are observed at 4K by EPR and ENDOR spectroscopy, only one ^{15}N-NMR absorption signal can be detected at $T < 200$ K indicating that rhombic distortions are averaged out at temperatures where NMR is observed. From an analysis of the ^{15}N-NMR relaxation behavior it was possible to determine the magnitude of the hyperfine coupling constant A, from which the Fermi contact term to the chemical shift was obtained. For a calculation of the pseudocontact shift, which is of the same size as the contact term, not only the shifts arising from the 'orbital term' but also bonding effects between the pyrrole nitrogen orbitals and the Fe^{3+} orbitals have to be considered.

Introduction

The enzymatic function of heme proteins, which play a vital role in many biological processes, rests largely upon the specific interactions between the central metal ion and the porphyrin nitrogens and the ligands coordinated perpendicular to the porphyrin plane. Nuclear magnetic resonance (NMR) spectroscopy is a well established technique for studying details of electronic and molecular structure of paramagnetic complexes. Analysis of chemical shifts, spin-spin, and spin-lattice relaxation times provides a measure of the distribution of unpaired electrons in the ligand skeleton of the paramagnetic organic complexes. Most of the NMR studies on porphyrins and its derivatives result from ^{1}H and/or ^{13}C resonance measurements [1 – 3]. Only a few ^{15}N-NMR data of pyrrole nitrogen in porphyrins have been reported [4 – 7], which are restricted more or less on diamagnetic species such as metal-free porphyrin or its metallo complexes with Zn and/or Cd.

Here, we report on measurements of ^{15}N chemical shifts, spin-spin, and spin-lattice relaxation times (T_1 and T_2) of the four pyrrole nitrogen atoms in low-spin ($S = 1/2$) ferritetraphenylporphyrin (= Fe(III)TPP) with pyridine (= Py) or 1-methylimidazole (= CH$_3$-Im) complexed in axial position, *i.e.*, perpendicular to the porphyrin ring plane as it is shown in Fig. 1.

Materials and Methods

[Fe(III)TPP]Cl and ZnTPP were synthesized and purified as described in the literature [8, 9]. For the synthesis of H$_2$TPP 95% enriched ^{15}N-pyrrole (Sharp & Dohme) was used. All solvents were distilled before use. The concentration of the chloroform solutions was: 50 mM [Fe(III)TPP]Cl and 1 M pyridine (or 1-methyl-imidazole). Approximately 2 ml of these solutions were taken for the NMR experiments.

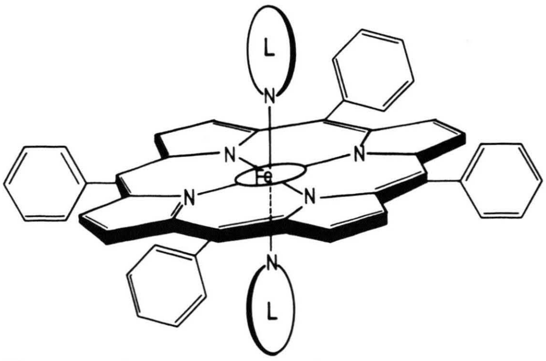

Fig. 1. Ferritetraphenylporphyrin; L = pyridine or 1-methylimidazole.

Abbreviations:

[Fe(III)TPP]Cl,	ferritetraphenylporphyrin
Py,	pyridine;
CH$_3$-Im,	1-methylimidazole.

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Chemical shift and relaxation time measurements were performed on a modified Bruker-B-KR 322 s spectrometer at 2.114 T (9.12 MHz), which was equipped with a B-NC 12 computer and a magnetic disk system. For the measurements of T_1 a $[180^\circ_{+x'} - t - 90^\circ - 5 \cdot T_1 - 180^\circ_{-x'} - 90^\circ -]$ pulse sequence was used in order to minimize the systematic error of T_1 arising in an off-resonance pulse experiment [10, 11]. All T_2 values were obtained from line widths measurements at half height. The shift reported here are taken against the ^{15}N-NMR absorption of diamagnetic ZnTPP dissolved in chloroform at 298 K as external standard. Because of the large chemical shifts observed (≈ 2 ppt) any susceptibility corrections (≈ 0.5 ppm) can be neglected.

In order to supress the "accoustic ringing", which is an extremely troublesome effect in pulsed NMR at low frequencies in addition with high static magnetic field strengths [12], a special NMR sample probe was constructed. Instead of aluminium, which is used extensively for NMR probes, the probe was built from brass with coated metal surfaces in combination with a copper wire shield between the NMR coil and the solid metal surfaces [13, 14]. With an aluminium probe the spurious ringing completely obscured all weak and short free induction decay (FID) signals. Despite the mentioned preventive acoustic measures ringing was still observable if longer signal averaging was necessary, especially at lower temperatures where the FIDs are relatively short (broad lines). For these cases difference spectra from ^{15}N enriched porphyrins and corresponding samples with their natural isotopic nitrogen concentration have been recorded. The disadvantage of this technique is the increase of the data acquisition time by more than a factor of two in order to obtain comparable signal-to-noise ratios.

Results and Discussion

Fig. 2 shows the ^{15}N chemical shift data of [Fe(III)TPP(Py)$_2$]Cl and [Fe(III)TPP(CH$_3$-Im)$_2$]Cl, the bis-pyridine and bis-1-methylimidazole complexes of ferritetraphenylporphyrin plotted *vs.* reciprocal temperature. All values are referred to the ^{15}N absorption of diamagnetic ZnTPP in chloroform as external standard. The shifts are upfield in comparison to the reference. The deviations from linearity observed for the pyridine complex at $T \gtrsim 250$ K are caused by an accelerated ligand exchange between the pyridine complex and the bulk solvent phase. The kinetics of this ligand exchange reaction and the parallel occuring spin transition from the low- to the high-spin electron configuration has been described in a previous investigation [15].

Although the solutions of [Fe(III)TPP(Py)$_2$]Cl in pyridine/chloroform are frozen at $T \lesssim 200$ K, a ^{15}N-NMR absorption still is detectable below this freezing point. Whereas in the liquid state at $T > 200$ K the appearance of only one single Lorentzian line for the four pyrrole nitrogen nuclei in both low-spin complexes reflects an axial magnetic symmetry (see below), a weakly resolved and broad shoulder for

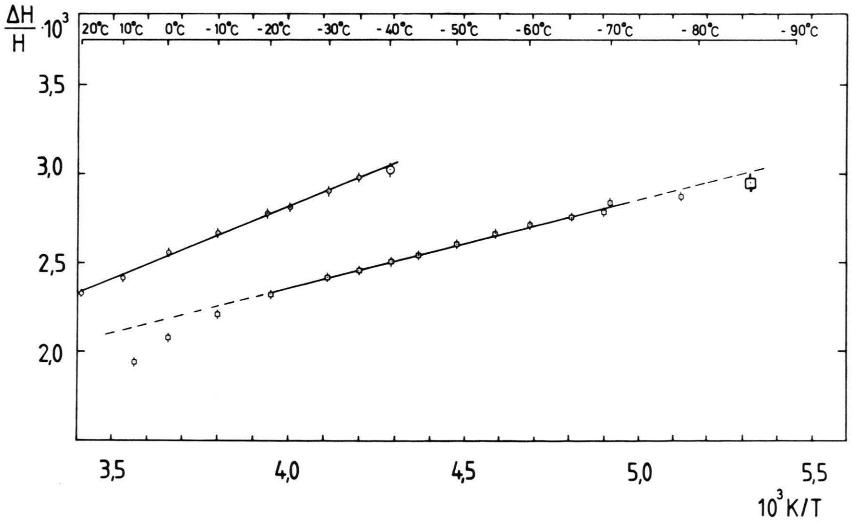

Fig. 2. ^{15}N chemical shifts of the pyrrole nitrogen in low-spin ferritetraphenylporphyrin axially complex with pyridine (□) or 1-methylimidazole (○). All shifts are referred to Zn-tetraphenylporphyrine in chloroform.

the frozen solutions of [Fe(III)TPP(Py)$_2$]Cl at $T \lesssim 200$ K indicates some distortions from the axial magnetic symmetry in this particular temperature range*. At $T \approx 187$ K the ^{15}N absorption suddenly disappears which possibly is caused by an additional phase transition at this temperature *.

Studies of the ^{15}N absorption of [Fe(III)TPP-(CH$_3$-Im)$_2$]Cl at lower temperatures are strongly hampered by the relatively broad signals compared with the pyridine complexes, so that no useful information could be gained at $T \lesssim 230$ K. Because of its higher stability [15], however, the NMR absorption of this low-spin compound can be studied at $T > 300$ K (see also footnote). Fig. 2 clearly demonstrates that a linear relationship exists between the chemical shift and the reciprocal temperature provided the complex is in a low-spin electron configuration and the system is in a liquid phase. Only those results will be considered in the following discussion which are characterized by a single ^{15}N absorption with a Lorentzian line shape. These data are marked by solid lines in Fig. 2.

For low-spin ferriporphyrins with one unpaired electron ($S = 1/2$) the ^{15}N-NMR chemical shift is composed of three different contributions: the pseudocontact term (superscript ps), the contact term (superscript c), and the diamagnetic term (superscript dia), viz.,

$$(\Delta H/H) = (\Delta H/H)^{\mathrm{ps}} + (\Delta H/H)^{\mathrm{c}} + (\Delta H/H)^{\mathrm{dia}}. \quad (1)$$

The diamagnetic term in Eqn (1) can be neglected to a very good approximation in the following discussion, since all chemical shift data in the present study are referred to the diamagnetic ZnTPP complex in chloroform solution.

For complexes with an electron spin quantum number S, where thermal population of excited electron states is negligibly small, the Fermi contact term can be expressed as [16 – 18]

$$(\Delta H/H)^{\mathrm{c}} = -[A \cdot \beta \cdot S(S+1) \cdot 2\pi \cdot \bar{g}]/(3\,\gamma_{\mathrm{N}} \cdot kT) \quad (2)$$

with $\bar{g} = 1/3 \cdot (g_{\mathrm{xx}} + g_{\mathrm{yy}} + g_{\mathrm{zz}})$ and A, the hyperfine coupling constant which measures the electron spin density at the position of the interacting nuclear spin.

The pseudocontact shift reflects both, the magnetic dipolar interaction between the unpaired electron and the nuclear spin, and the interaction between the nuclear magnetic moment and the magnetic field generated by the orbital motion of the unpaired electron. The corresponding Hamiltonian is given as,

$$\boldsymbol{H} = 2\hbar \cdot \gamma_{\mathrm{N}} \cdot \beta \{[3\,(\boldsymbol{r}_{\mathrm{M}} \cdot \boldsymbol{S})(\boldsymbol{r}_{\mathrm{M}} \cdot \boldsymbol{I})/r_{\mathrm{M}}^5 - (\boldsymbol{S} \cdot \boldsymbol{I})/r_{\mathrm{M}}^3] + (\boldsymbol{l} \cdot \boldsymbol{I})/r_{\mathrm{M}}^3\} \quad (3)$$

where $\boldsymbol{r}_{\mathrm{M}}$ is the radius vector, $\boldsymbol{r}_{\mathrm{M}} = \boldsymbol{r} + \boldsymbol{R}$. Here, $\boldsymbol{r}$ is the radius vector of the electron at the electron bearing nucleus, for example, the central metal ion, and $\boldsymbol{R}$ is vector pointing from the NMR nucleus to the paramagnetic center. For protons where the unpaired spin resides more or less in an *s*-orbital, the last term in the curl bracket can be neglected. Under these conditions a simple relation holds provided the paramagnetic center and the proton are well separated, *i.e.*, $|\boldsymbol{R}| \gg |\boldsymbol{r}|$. With the same restrictions as for Eqn (2) it follows [16 – 18]

$$(\Delta H/H)^{\mathrm{ps}}_{^1\mathrm{H}} = (\Delta H/H)^{\mathrm{d}} = -\beta^2 \frac{S(S+1)}{3kT}\left(\frac{3\cos^2\theta - 1}{R^3}\right) \cdot F(g) \quad (4)$$

with θ the angle between the vector $\boldsymbol{R}$ and the symmetry axis and $F(g)$ a function of the principal g-values.

Since the contribution of the orbital term to the pseudocontact shift depends on the inverse cube of the distance (cf. Eqn (3) – second term in the curl bracket) of the electron from the nucleus under study, the effect of unpaired spin in a *p*-orbital centered on the ligand nucleus can be quite large, even though the unpaired spin density itself might be small. Consequently the full Hamiltonian (Eqn. (3)) has to be considered for an interpretation of the ^{15}N-NMR shifts of the pyrrole nitrogen atoms in low-spin ferriporphyrins.

From molecular orbital (MO) calculations on ferriporphyrin complexes [19, 20] it is known that the metal character of the 3d orbitals in the low-spin electron configuration is reduced by about 20 to 40% depending on the interaction between the Fe^{3+}-ion and the axially bound ligands. For a calculation of the pseudocontact shift of the pyrrole nitrogen a molecular orbital approximation seems to

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* Note added in proof: Spectra of the low temperature range $200\text{ K} \gtrsim T \gtrsim 187$ K for [Fe(III)TPP(Py)$_2$]Cl are shown and discussed in addition with results for [Fe(III)TPP(CH$_3$-Im)$_2$]Cl at $T > 300$ K in the report of the 'XIVth European Congress on Molecular Spectroscopy', which will be published in a special volume of Journal of Molecular Structure, 1979/80.

be physically more reasonable than any pure electrostatic model, which necessarily leads to a higher number of adjustable parameters. Therefore, a separation of the different contributions to the chemical shifts in Eqn (1) is extremely difficult and cannot be accomplished at the present moment from these data alone.

More information on the magnetic behavior of the pyrrole nitrogen can be extracted, however, from an analysis of the corresponding NMR relaxation times T_1 and T_2. There are two contributions, namely magnetic dipole-dipole interaction between the nucleus and the unpaired electron (superscript d) and the isotropic electron-nucleus spin exchange (superscript c) causing spin relaxation by their temporal variations. The measured relaxation rate $(1/T_{1,2})$ is the sum of both fractions,

$$(1/T_\mathrm{i}) = (1/T_\mathrm{i})^\mathrm{d} + (1/T_\mathrm{i})^\mathrm{c} \quad \text{with} \quad i=1,2 \qquad (5)$$

where the dipolar relaxation rates are given as [21, 22]

$$(1/T_\mathrm{i})^\mathrm{d} = F \cdot \left[A_\mathrm{i} \cdot \tau_{\mathrm{d}1} + \frac{B_\mathrm{i} \cdot \tau_{\mathrm{d}2}}{1 + (\omega_\mathrm{S} \cdot \tau_{\mathrm{d}2})^2} \right]; \quad i=1,2 \qquad (6\,\mathrm{a})$$

with

$$F = (\mu_0/4\,\pi)^2\,[\gamma_\mathrm{N}^2 \cdot \beta^2 \cdot S\,(S+1)]/(15 \cdot R^6). \qquad (6\,\mathrm{b})$$

For paramagnetic compounds with axially symmetric *g*-tensors the coefficients A_i and B_i in Eqn (6a) are somewhat lengthy functions of $g_\parallel$ and $g_\perp$ and will not be represented here (cf. refs. 23, 24).

For the so-called scalar relaxation rates$(1/T_{1,2})^\mathrm{c}$ the following relation holds [21, 22],

$$(1/T_\mathrm{i})^\mathrm{c} = 4/3 \cdot \pi^2 \cdot S\,(S+1) \cdot A^2 \left[C_\mathrm{i} \cdot \tau_{\mathrm{A}1} + \frac{D_\mathrm{i} \cdot \tau_{\mathrm{A}2}}{1 + (\omega_\mathrm{S} \cdot \tau_{\mathrm{A}2})^2} \right] \quad \text{with} \quad i=1,2. \qquad (7)$$

The coefficients C_i, D_i are: $C_1=0$; $C_2=1$; $D_1=2$; $D_2=1$.

Both parameters *R* and *A* in Eqns (6) and (7) are defined as in Eqns (2), (4). The correlation times in Eqns (6) and (7) have the following meanings:

$$\begin{aligned} 1/\tau_{\mathrm{d}i} &= 1/\tau_\mathrm{c} + 1/\tau_{\mathrm{s}i} && (8\,\mathrm{a}) \\ 1/\tau_{\mathrm{A}i} &= 1/\tau_\mathrm{b} + 1/\tau_{\mathrm{s}i}. && (8\,\mathrm{b}) \end{aligned} \quad \text{with} \quad i=1,2$$

$\tau_{\mathrm{s}i}$ stands for the electron spin-lattice and spin-spin relaxation time, respectively. τ_c describes the tumbling motion around the vector $\boldsymbol{R}$ and τ_b symbolizes the mean lifetime of the considered nucleus fixed at the paramagnetic center.

Except of the hyperfine coupling constant *A*, all parameters in Eqns (6) and (7) are known from corresponding EPR and proton NMR studies on [Fe(III)TPP(Py)$_2$]Cl and [Fe(III)TPP(CH$_3$-Im)$_2$]Cl in chloroform in the considered temperature range [11, 24]. Table I lists some of these parameters at two different temperatures. The three components of the *g*-tensor, which where obtained by EPR measurements at 4 K, reveal that rhombic distortions exist at low temperatures. The existence of only one single ^{15}N-NMR signal for the four pyrrole nitrogen atoms clearly indicates that this magnetic inequivalence in the porphyrin ring plane is averaged out for both complexes in the liquid phase at temperatures where the NMR is observed ($T \gtrsim 200$ K), *i.e.*, the complexes are in an axial magnetic symmetry. A result which corroborates corresponding findings from ^{1}H-NMR [11, 24]. The components $g_\parallel$ and $g_\perp$ are defined as in Ref. 24, *viz.*,

$$g_1 = g_\parallel \quad \text{and} \quad g_\perp = [1/2\,(g_2^2 + g_3^2)]^{1/2}.$$

In Ref. 11 it was already shown that for the present low-spin complexes the correlation times in Eqn (8) are determined exclusively by $\tau_{\mathrm{s}i}$, the electron spin relaxation time, with $\tau_{\mathrm{s}1} = \tau_{\mathrm{s}2}$. Using the parameters listed in Table I, it is possible to calculate separately from the measured spin-lattice or spin-spin relaxation times the magnitude of the hyperfine coupling constant *A*. Good agreement exists – within experimental error – between the values extracted independently from T_1 and T_2.

Although the experimentally observed shifts are linear functions of the reciprocal temperature, extrapolation to infinitely high temperatures ($T^{-1} = 0$) does not give a zero intercept as required by Eqn (1) if the shifts are referred to $(\Delta H/H)^\mathrm{dia}$ as for the present case. The deviations for [Fe(III)TPP(Py)$_2$]Cl and [Fe(III)TPP(CH$_3$-Im)$_2$]Cl are $(\Delta H/H)_{1/T=0} = +1475$ ppm and $(\Delta H/H)_{1/T=0} = -390$ ppm, respectively. At least for the pyridine complex this value is far beyond experimental uncertainty. A similar behavior observed for the corresponding proton NMR

	[Fe(III)TPP(Py)$_2$]Cl	[Fe(III)TPP(CH$_3$ – Im)$_2$]Cl
$T \cdot \mathrm{K}^{-1}$	253	293
$T_1 \cdot \mathrm{s}^{-1}$	$(2.95 \pm 0.15) \cdot 10^{-3}$	$(2.6 \pm 0.3) \cdot 10^{-4}$
$T_2 \cdot \mathrm{s}^{-1}$	$(1.57 \pm 0.10) \cdot 10^{-3}$	$(2.31 \pm 0.23) \cdot 10^{-4}$
$\tau_S \cdot \mathrm{ps}^{-1}$	3.5 ± 0.18 *	13 ± 0.7 *
$g_1; g_2; g_3$	2.45; 2.15; 1.89 *	2.9; 2.3; 1.5 *
$g_\parallel; g_\perp$	2.45; 2.02 **	2.9; 1.94 **
$R \cdot \mathrm{nm}^{-1}$	0.2 *	0.2 *
$\lvert A \rvert \cdot \mathrm{MHz}^{-1}$	3.4 ± 0.2	5.5 ± 0.3

* Data from corresponding proton NMR and EPR measurements [11, 24].
** see text.

Table I. Experimental relaxation times (T_1, T_2) and the hyperfine coupling constant, A, of the ^{15}N-pyrrole nitrogen in low-spin ferritetraphenylporphyrin complexes with pyridine and 1-methylimidazole, together with some parameters which determine the NMR relaxation behavior.

absorption was explained by a temperature dependence of the hyperfine coupling constant A [11, 24]. Within the experimental error interval (*cf.* Table I) no such temperature dependence of A was found for the ^{15}N resonance of the two low-spin complexes in the temperature range investigated in the present study (*cf.* Fig. 2 – solid lines). Whether this deviations are caused by the pseudocontact shift, for example, by second order effects has to be postponed until a future investigation.

In order to demonstrate the expected limitation of Eqn (4), Table II collects some experimental and calculated shift values. For the determination of $(\Delta H/H)^{\mathrm{c}}$ negative values of the hyperfine coupling constants in Table I have been assumed. This is certainly a somewhat arbitrary assumption which cannot be proved at the present moment. However, the discrepancy between $(\Delta H/H)^{\mathrm{d}}$ and $(\Delta H/H)^{\mathrm{ps}}$ would be unreasonable high for $A > 0$, so that the present choice appears to be more likely. Very recently Golding *et al.* [25] calculated chemical shifts in paramagnetic systems by a nonmultipole expansion method. There, it was shown that for small values of R ($\lesssim 0.15$ nm) considerable deviations from the simple relation (4) may occur. Consideration of the orbital term in Eqn (3) and bonding effects of the coordinated ligands result in relatively complicated isoshielding diagrams [26]. Only a similar numerical analysis for the present systems possibly would allow a final decision on the sign of A.

It should be noted that the magnitude of A, as extracted from the present NMR measurements, are in good agreement with corresponding values reported from an electron nuclear double resonance experiment on some low-spin complexes of hemoglobin and myoglobin [27], though the experimental conditions are different (temperature, ligands, etc.). At low temperatures ($T \lesssim 4$ K) the hyperfine coupling constant, or more precisely its z-component, was found to differ for the four pyrrole nitrogen atoms in low-spin ferriporphyrins. A result which is not unexpected if the distortions from axial magnetic symmetry at low temperatures are considered as it was discussed above.

Conclusions

As a result of the extreme short electron spin relaxation times τ_S in comparison with the correlation time τ_c for the rotational diffusion of the [Fe(III)TPP(L)$_2$]Cl low-spin complexes, it is possible to detect the ^{15}N-NMR absorption of the pyrrole nitrogen atoms directly bound to the paramagnetic Fe^{3+}-ion. Although a complete analysis of the chemical shift data is strongly hampered by the great number of unknown parameters, the knowledge of the magnitude of A, the hyperfine coupling constant, which was extracted from NMR relaxation time measurements on these nuclei, reduces some of these difficulties; and it appears that these data

	[Fe(III)TPP(Py)$_2$]Cl	[Fe(III)TPP(CH$_3$ – Im)$_2$]Cl
$T \cdot \mathrm{K}^{-1}$	253	293
$(\Delta H/H)^{\mathrm{exp}}$	2.32 ± 0.02	2.33 ± 0.02
$(\Delta H/H)^{\mathrm{c}}$	1.15 ± 0.06	1.66 ± 0.08
$(\Delta H/H)^{\mathrm{ps}}$	1.17 ± 0.08	0.67 ± 0.10
$(\Delta H/H)^{\mathrm{d}}$	-0.142	-0.206

Table II. ^{15}N chemical shifts (in units of ppt) of the pyrrole nitrogen in low-spin complexes of ferritetraphenylporphyrin.

might be of some interest for future molecular orbital calculations on low-spin ferriporphyrin complexes, where, for example, the resonance integral β(Fe-N), which reflects chemical bonding between the nitrogen and metal orbitals, has been used as an adjustable parameter [20].

Finally one should mention that a relaxation analysis as it was performed in the present study does not generally yield a separation of the hyperfine coupling constant, since the orbital term as discussed in connection with Eqn (3) also may contribute to the overall measured relaxation times. From the identity of A within the experimental error interval, however, extracted independently from T_1 and T_2 these contributions can be expected to be small in relation to the experimental uncertainties. This assumption also is supported by the relatively good agreement between the values of A from the present investigation and corresponding Endor experiments [27].

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