The diamagnetic properties of the $\cdot NF_2$ radical by magic doublet rotational Zeeman spectroscopy

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The magic doublets of 15 para- and 11 ortho-state rotational transitions of $\cdot NF_2$ were investigated up to fields of 2.6 T, and avoided crossings were observed. A truncated matrix deperturbation analysis yielded $\frac{1}{2}(2g_{aa}^c - g_{bb}^c - g_{cc}^c) = -0.003319(24)$ and $\frac{1}{2}(2g_{cc}^c - g_{aa}^c - g_{bb}^c) = 0.003700(18)$ for the two independent electronic g-tensor anisotropies (Bohr magnetons) as well as $g_{aa}^c = -0.4624(69)$, $g_{bb}^c = -0.0764(26)$, and $g_{cc}^c = -0.0482(24)$ for the rotational g-values (nuclear magnetons). The diamagnetic susceptibility contributions were found to be not negligible, and the two independent anisotropy parameters were determined with moderate accuracy. The zero-field rotational and hfs parameters were redetermined. The Colburn-Kennedy technique to prepare N₂F₄, the precursor of $\cdot NF_2$, was improved.

1. Introduction

The NF_2 radical exists in chemical equilibrium with its diamagnetic dimer, N_2F_4 , and can be kept in high concentration as a stable gas at temperatures above 70°C under low-pressure conditions [1]. This high temperature and a small dipole moment, $\mu_b = 0.14$ D [2], lead to weak signals in the rotational spectrum as transitions are normally split into six or even 18 components by the fine and hyperfine interactions. Brown et al. [2] were the first to record and assign a large number of transitions in the frequency range between 13.8 and 65.1 GHz. They determined the rotational and four centrifugal distortion constants as well as altogether 11 additional independent parameters covering the electron spin-rotation, the nitrogen and fluorine electron-nuclear, and the nitrogen quadrupolar interactions. Davies et al. [3], in the course of their diode laser investigation of the ν_1 band of $\cdot NF_2$, have fitted to the combined microwave [2] and infrared data and obtained a somewhat variant set of ground-state asymmetric rotor and fine structure parameters. The Zeeman effect of $\cdot NF_2$ was investigated in high fields by Uehara and Horiai [4] using LMR microwave double resonance avoided crossing techniques. The main result of this work [4] is the determination of the three diagonal ground-state electronic g-tensor elements. Attempts to include also the rotational g-factors in fitting the Zeeman splittings led to several distinct solutions depending on the chosen set of (zero-field) electron spin-rotation tensor elements.

The present work also aims at the determination of magnetic-field interaction parameters of the \cdot NF₂ radical. We concentrate, however, on Zeeman components which are highly insensitive to the applied fields yielding complementary information with respect to the previous investigation by Uehara and Horiai [4]. The splittings of these so-called magic doublets [5] are in first order independent on the bulk magnetic properties induced by the unpaired electron, thus leading to the possibility of accurately determining molecular diamagnetic quantities such as the two anisotropy parameters of the electronic g-tensor and the three rotational g-factors. Every rotational transition exhibits one magic doublet which is formed between substates of maximum angular momentum and maximum projection along and antiparallel to the field direction. It is then clear from the vector model or from first-order perturbation theory that the Zeeman energy contributions caused by the trace electronic spin term (as well as by all nuclear spin terms) are alike in the upper and lower states and therefore cancel. Fortu-

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nately, these transitions are the strongest in the hfs Zeeman pattern. The magic-doublet technique has previously been applied to $\cdot NO_2$ [5] and $\cdot ClO_2$ [6]. It was found in these cases that paramagnetic perturbations must be taken into account, meaning that deviations from the pure diamagnetic first- and second-order field dependences of the magic-doublet splittings were observed. In the present investigation on $\cdot NF_2$, several examples have been met where exceptionally strong perturbations with near-by rotational states even caused avoided crossings. The limited homogeneity of our high-field magnet does not allow one to follow the perturbed component through the complete crossing pattern, but this can eventually be "found" again at sufficiently strong fields where a nearly linear field dependence is re-established. In this way, it is possible to concentrate the measurements on high-field regions where the influence of perturbing matrix elements as for example the off-diagonal spin-rotation contribution is weak. Hence it is clear that the problems caused by the limited accuracy of zero-field parameters encountered by Uehara and Horiai [4] are greatly reduced in the magic-doublet technique.

In what follows, we will first give some experimental details including sample preparation, report then on the theoretical and computational means in evaluating the magic-doublet field splittings, and present the results.

2. Preparation of tetrafluorohydrazine

Tetrafluorohydrazine (N_2F_4) was first synthesized by Colburn and Kennedy [7] by reaction of nitrogen trifluoride (NF_3) with copper or other fluorine abstractors at elevated temperatures. We adopted this straightforward method and extended it by providing continuous check of the N_2F_4 yield via IR absorption and by modifying the purification procedure. N_2F_4 seems not to be available commercially at present so that it might be useful to report on details of our preparation:

2.1. Apparatus and reagents

Synthesis and purification of N_2F_4 were carried out in a helium-leak tested apparatus which also allowed the recovery of the unconverted NF₃ (Air Products) without contact to air. The NF₃ storage bomb equipped with a dual stage pressure adapter and a needle valve (Leybold) was connected in line to the flow reactor with IR cell, four traps and the vacuum pump (1 mPa). In the preparation runs the pump connection was replaced by an outlet to the atmosphere. Pressure adapter, needle valve, reactor and IR cell consisted of stainless steel. Lines to and from the reactor/IR unit were 6 mm copper pipes connected by Swagelok fittings. All other components were Duran glass sealed with silicon-free grease. The vertically mounted, cylindrical reactor (23 mm inner diameter, inside length $l_i = 224$ mm, walls 1 mm) was packed with 250 g of small (0.6×4 mm) copper sticks (Merck). Cu is reported [8] to be one of the most effective solid fluorine acceptors for the production of N_2F_4 . Heating wire was wound around the reactor, a NiCr/Ni thermocouple was welded on in the middle, and the feed-pipes were mantled for water cooling. The small volume IR cell (18 mm inner diameter, $l_i = 50$ mm, NaCl windows), operated with a Perkin-Elmer 457 grating IR spectrophotometer, was connected to the bottom of the reactor by a Whitey-stopcock (stainless steel, Teflon). The whole apparatus was swept with dry nitrogen and evacuated several times to remove oxygen and moisture which would lead to formation of nitrosyl fluoride (ONF), nitrogen dioxide (NO_2) [9] or highly dangerous difluoramine (HNF_2) [8,10]. The reactor was then heated to 310°C and pumped off for 16 hours. Oxygen impurities in NF₃ were removed by condensing the gas into a trap at -210° C (nitrogen slush) and pumping off the oxygen.

2.2. Preparation

The NF₃ gas was introduced from the storage bomb, held at -78 °C (ethanol/dry ice), through the graded needle valve by which the residence time in the reactor was adjusted to be 4 to 5 minutes. The temperature of the reactor was slowly increased from 350 °C to 490 °C to compensate the formation of copper fluorides on the

copper surface. When, after a couple of preparation cycles, this coating had gone too far it was removed by reacting with hydrogen at 400°C countercurrent to the normal gas flow. After such regeneration runs, the copper was extremely reactive and traces of N_2F_4 appeared already at 60°C. The N_2F_4 yield check was based on its very strong IR absorption at 959 cm⁻¹ just between two strong NF₃ bands, where the NF₃ background remained virtually unchanged owing to the low NF₃ conversion rate. Though the contact of crude N_2F_4 with the sodium chloride windows immediately caused stable background peaks [11], especially at 720 cm⁻¹, the yield check was not impaired. Having passed through the IR cell, the gas mixture was diluted by pure helium serving as a buffer gas. Flowing through the first two traps at -196°C (liquid nitrogen) the reaction products and NF₃ were withdrawn, and the remaining helium subsequently escaped from the apparatus through a bubbler at the end. When the reaction had stopped, the product mixture was condensed into the third trap at -196°C; the dissolved helium and nitrogen were pumped off. Then the unconverted NF₃ was separated by distillation from the third trap at -183°C (liquid oxygen) to the fourth trap at -196°C : 1.821(18) g/ml [12]).

2.3. Purification

The product was passed several times under dynamic vacuum through the traps at -120° C (ethanol slush) or -160° C (isopentane slush), -183° C and -196° C. N₂F₄ was found in good purity in the -160° C and -183° C traps and was identified by infrared spectroscopy [8,11,13] and mass spectrometry. At -196° C it still had a blue-purple taint from traces of nitrosodifluoramine (NF₂NO) [14]. The specimens which were used in the MW measurements were further purified by several freeze-pump cycles (-196° C, 1 mPa). Finally, the mass spectrometric purity ranged between 96% and 99%. The main impurities were nitrous oxide (N₂O) and silicon tetrafluoride (SiF₄). The over-all yield after nine preparation cycles including the test runs (which were not optimized, of course) was 32% in relation to converted plus exhausted NF₃. The loss of NF₃ by pumping off may be reduced using nitrogen slush instead of liquid nitrogen.

2.4. Caution

A gaseous mixture of N_2F_4 and carbonyl sulfide (OCS, widely used for calibration purposes in microwave spectroscopy) was stable at room temperature but violently exploded (harsh white flash) as soon as the trap was immersed in liquid nitrogen. Obviously, at normal pressure this reaction is kinetically hindered.

3. Spectrometer-magnet assembly

Several OKI klystrons in the frequency range between 46 and 85 GHz were used as radiation sources either directly or by frequency doubling and tripling. Phase stabilization to the primary standard XUC was carried out in two regulation loops as explained in detail previously [15].

Two copper X-band Stark effect cells for $\Delta M = 0$ and $\Delta M = \pm 1$ selection rules, supplied with an inner electrode septum of 1.20 m length to prevent modulation of molecules outside of the 0.5% homogeneous field region of our magnet [16], were passivated by N₂F₄ or ClF₅ (0.1–1 kPa, 100–150°C, several hours) before use and kept at temperatures near 90°C during measurements. Millimeter wave absorption as a function of frequency at various magnetic fields was detected with an InSb hot carrier bolometer as described previously [16].

The field distribution in the magnet was carefully measured with a Rawson-Lush rotating coil Gaussmeter calibrated in advance by NMR, at different current settings. The field near the center was also measured with a Bruker B-H11 D Hall Gaussmeter. These readings were used later to check the reproducibility of field strength at the different induction currents.

Under these conditions and at achievable linewidths between 200 and 400 kHz (fwhm) the errors of the data



Fig. 1. The $3_{21} \leftarrow 2_{12}$, $F = \frac{9}{2} \leftarrow \frac{7}{2}$ hfs component of $\cdot NF_2$ at increasing fields as indicated, $\Delta M_F = \pm 1$ selection rule. The gas temperature was 90°C, the pressure approximately 2 Pa. Marker distance 765.6 kHz, first marker (triangle) at 246891.406 MHz, sinusoidal 30 kHz, 4.9×10^5 V/m Stark effect modulation. At 3.8 mT, all Zeeman components $M_F \pm 1 \leftarrow M_F$, $|M_F| \langle \frac{7}{2}$ are shifted away leaving a clearly diminished signal intensity at the center. The $\pm \frac{9}{2} \leftarrow \pm \frac{7}{2}$ magic doublet starts to split at 73.2 mT. This (bottom) spectrum was obtained in 15 min time averaging adding 128 sweeps.

given below were mainly determined by the uncertainty in locating the center frequencies of the Zeeman components. Recordings of the magic doublet of the $3_{21} \leftarrow 2_{12}$ rotational transition at different fields are given in fig. 1.

4. Theoretical background

The zero-field Hamiltonian used in this work is given by

$$\hat{H}_{0} = \hat{H}_{rot} + \hat{H}_{SR} + \hat{H}_{Fermi}({}^{19}F) + \hat{H}_{DD}({}^{19}F) + \hat{H}_{Fermi}({}^{14}N) + \hat{H}_{DD}({}^{14}N) + \hat{H}_{Q}({}^{14}N) , \qquad (1)$$

where

$$\hat{H}_{\text{Fermi}}({}^{19}\text{F}) = \sum_{i=1}^{2} \hat{H}_{\text{Fermi}}({}^{19}\text{F}_{i}) , \qquad (1a)$$

and

$$\hat{H}_{\rm DD}(^{19}\rm F) = \sum_{i=1}^{2} \hat{H}_{\rm DD}(^{19}\rm F_{i}) .$$
(1b)

The fluorine interactions considered in this work can be described, for symmetry reasons, in terms of the total fluorine spin angular momentum operator, $\hat{I}^F = \hat{I}^{F_1} + \hat{I}^{F_2}$. In more detail, the energy operators read

$$\hat{H}_{\text{rot}} = \frac{1}{2} (B+C) \hat{N}^2 + [A - \frac{1}{2} (B+C)] \hat{N}_a^2 + \frac{1}{4} (B-C) (\hat{N}_+^2 + \hat{N}_-^2) - \Delta_N (\hat{N}^2)^2 - \Delta_{NK} \hat{N}^2 \hat{N}_a^2 - \Delta_K \hat{N}_a^4 - \delta_N \hat{N}^2 (\hat{N}_+^2 + \hat{N}_-^2) - \frac{1}{2} \delta_K [\hat{N}_a^2, \hat{N}_+^2 + \hat{N}_-^2]_+,$$
(2a)

$$H_{\rm SR} = \epsilon_{aa} N_a S_a + \epsilon_{bb} N_b S_b + \epsilon_{cc} N_c S_c , \qquad (2b)$$

$$\dot{H}_{\text{Fermi}}(L) = (0)_{IL} (\vec{I}^L \cdot \vec{S}) , \qquad (2c)$$

$$\hat{H}_{\rm DD}(L) = (aa)_{IL} \hat{I}_a^L \hat{S}_a + (bb)_{IL} \hat{I}_b^L \hat{S}_b + (cc)_{IL} \hat{I}_c^L \hat{S}_c , \qquad (2d)$$

and

.

$$\hat{H}_{Q}(^{14}N) = \frac{1}{2I_{N}(2I_{N}-1)} \left[\chi_{aa}(\hat{I}_{a}^{N})^{2} + \chi_{bb}(\hat{I}_{b}^{N})^{2} + \chi_{cc}(\hat{I}_{c}^{N})^{2} \right].$$
(2e)

L in eqs. (2c) and (2d) stands for ¹⁹F and ¹⁴N. Eq. (2a) represents Watson's A-reduced rotational Hamiltonian in standard notation [17]. Calculations will be carried out in the I^r representation, and $\hat{N}_{\pm} = \hat{N}_b \pm i \hat{N}_c$. Eqs. (2b)-(2e) give the electronic spin-rotation, Fermi contact, electron-nuclear dipole and ¹⁴N nuclear electric quadrupole coupling interactions, respectively, in the (a, b, c) principal inertia axis system specialized to a species of C_{2v} symmetry. Observe that $\sum_g (gg)_{IL} = 0$ and $\sum_g \chi_{gg} = 0$, g = (a, b, c). \hat{N} , \hat{S} , and \hat{I}^L mean the rotational, electronic and nuclear momentum operators. The validity of this effective Hamiltonian for the description of vibronic ground state hfs patterns of ² Σ radicals has been discussed previously in detail by Curl et al. [18] and by Brown [19]. In spite of the improved spectroscopic resolution now available, we will not consider the additional contributions of nuclear dipole-dipole and nuclear spin-rotation interactions, possible centrifugal-distortion variations of the interaction strengths given in eqs. (2b)-(2e), or nuclear shielding. A term in $(ab)_{IF}$ arising from the electron-nuclear dipole interaction of the two fluorine nuclei [19] was also disregarded. These simplifications are justified within the concept of the magic-doublet approach followed here and should not measurably effect the magnetic parameters to be determined.

The relevant magnetic-field perturbations can be written [5]

$$\hat{H}_z = -\mu_{\rm B} g_{\rm e} B_z \hat{S}_z \tag{3a}$$

$$-\mu_{\rm B}B_z \sum_{g,\gamma} \tilde{g}^{\rm e}_{gg} \hat{\Phi}_{gz} \hat{\Phi}_{g\gamma} \hat{S}_{\gamma} \tag{3b}$$

$$-\mu_{\rm N}B_z[g_{IF}\hat{f}_z^{\rm F}+g_{IN}\hat{f}_z^{\rm N}] \tag{3c}$$

$$-\mu_{\rm N}B_z \sum_g g_{gg}^{\rm r} \hat{\varPhi}_{gz} \hat{N}_g \tag{3d}$$

$$-\frac{1}{2}B_{z}^{2}\sum_{g}\xi_{gg}\Phi_{gz}^{2},$$
 (3e)

where $B = (0, 0, B_z)$ is the external magnetic field, g sums over the molecular axes (a, b, c), γ over the spacefixed axes (x, y, z), and $\Phi_{g\gamma}$ is the direction-cosine operator connecting the g and γ axes. g_e means the (negative) bulk molecular electronic g-factor, g_{IF} that of the fluorine nucleus, and g_{IN} that of the nitrogen nucleus, while g_{aa}^r, g_{bb}^r and g_{cc}^r are the rotational g-factors. Finally, $\bar{g}_{aa}^e = \frac{1}{3}(2g_{aa}^e - g_{bb}^e - g_{cc}^e)$ and $\xi_{aa}^e = \frac{1}{3}(2\xi_{aa} - \xi_{bb} - \xi_{cc}) - and$ similarly for the b and c components – are the anisotropy parameters of the electronic g-tensor and of the magnetic susceptibility tensor, respectively. Normally, eq. (3a) is called the paramagnetic contribution, eq. (3c) is

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Fig. 2. Contributions to the matrix elements in the truncated scheme used to determine the perturbations of the magic-doublet level D_0 . J=N+S, J'=J or J+1, $F_1=J+I_F$, $F'_1=F_1$ or F_1+1 , $F=F_{max}=F_1+I_N$, F'=F or F+1. M: $\hat{H}_{SR}+\hat{H}_{DD}(^{19}F)+\hat{H}_{DD}(^{14}N)+\hat{H}_Q+\hat{H}_{Zd}$, A: $\hat{H}_{DD}(^{19}F)+\hat{H}_{DD}(^{14}N)+\hat{H}_Q+\hat{H}_{Zd}$, B: $\hat{H}_{DD}(^{14}N)+\hat{H}_Q+\hat{H}_{Zd}$, C: \hat{H}_{Zd} , D_i: $\hat{H}_{rot}+\hat{H}_{SR}+\hat{H}_{Fermi}(^{19}F)+\hat{H}_{Fermi}(^{14}N)+\hat{H}_{DD}(^{19}F)+\hat{H}_{DD}(^{14}N)+\hat{H}_Q+\hat{H}_{Zd}$, U: $\hat{H}_{Fermi}(^{19}F)+\hat{H}_{Fermi}(^{14}N)+\hat{H}_{DD}(^{19}F)+\hat{H}_{DD}(^{14}N)+\hat{H}_Q+\hat{H}_{Zp}+\hat{H}_{Zd}$, V: $\hat{H}_{Fermi}(^{14}N)+\hat{H}_{DD}(^{14}N)+\hat{H}_Q+\hat{H}_{Zp}+\hat{H}_{Zd}$, V: $\hat{H}_{Fermi}(^{14}N)+\hat{H}_{DD}(^{14}N)+\hat{H}_Q+\hat{H}_{Zp}+\hat{H}_{Zd}$, X: $H_{Zp}+\hat{H}_{Zd}$, V: $\hat{H}_{Fermi}(f_{N})+\hat{H}_{DD}(f_{N})+\hat{H}_{Q}+\hat{H}_{Zp}+\hat{H}_{Zd}$, Abbreviations were used in the Zeeman operators: $\hat{H}_{Zp}=\hat{H}_{Zp}(g_e)$ for the paramagnetic (see eq. (3a)), $\hat{H}_{Zn}=\hat{H}_{Zn}(g_{I^N})+\hat{H}_{Zn}(g_{I^N})$ for the nuclear (see eq. (3c)), and $\hat{H}_{Zd}=\hat{H}_{Zd}(g^e)+\hat{H}_{Zd}(g^e)+\hat{H}_{Zd}(\xi)$ for the diamagnetic contributions (see eqs. (3b), (3d), (3e)). The matrix is diagonal in $M_F=\pm (N+\frac{1}{2}+I_F+1)$ so that perturbation by levels with N' < N does not occur.

called the nuclear magnetic term, and eqs. (3b), (3d) and (3e) form the diamagnetic part which is of most interest in this work.

Calculations in the field-on case will be carried out in the asymmetric-rotor basis $|N\tau\rangle$ which diagonalizes \hat{H}_{rot} , eq. (2a). For any given rotational level $N\tau$, two magic-doublet states $|FM_F\rangle = |F_{max} \pm F_{max}\rangle$ exist which are characterized by maximum angular momentum $F=N+S+I^F+I^N$ and its two maximum components F_z along and antiparallel to the field axis. Nuclear spin statistics lead to the restrictions that [2] the fluorine spins form triplets ($I^F=1$) in symmetric rotational states ($N_{K_aK_c}=N_{ee}$ or N_{oo}) and singlets ($I^F=0$) in antisymmetric ones (N_{eo} or N_{oo}).

In the coupling scheme $\hat{J} = \hat{N} + \hat{S}$, $\hat{F}_1 = \hat{J} + \hat{I}^F$, $\hat{F} = \hat{F}_1 + I^N$ the magic-doublet states can be written as [5]

$$|N\tau \pm N\rangle |S \pm S\rangle |I_{\rm F} \pm I_{\rm F}\rangle |I_{\rm N} \pm I_{\rm N}\rangle = |N\tau S J_{\rm max} I_{\rm F} (F_1)_{\rm max} I_{\rm N} F_{\rm max} \pm (M_{\rm F_{\rm max}})_{\rm max}\rangle.$$
(4)

This indicates that the magic-doublet state wave functions are identical in the coupled and uncoupled schemes. To simplify the notation we will further take advantage of the identity $(M_F)_{max} = (M_{Fmax})_{max}$. The total energy operator, $\hat{H} = \hat{H}_0 + \hat{H}_Z$, is diagonal in M_F . The two functions in eq. (4) can, therefore, only be perturbed by levels of equal or higher N. Adjacent K_a levels of the same N-block do not yield significant perturbations because they are either not connected or their energy separation is too large compared with the Zeeman shifts of the doublets. The perturbation scheme we used in practice is shown in fig. 2. The detailed matrix element expressions are given in the appendix. We use prolate symmetric-rotor functions for the matrix elements off-diagonal in N [18]. This is a justified approximation (the asymmetry parameter of $\cdot NF_2$ is $\kappa = -0.943$).

5. Deperturbation approach

The diagonal matrix element D_0 , fig. 2, represents the unperturbed magic-doublet level for a given rotational state $N\tau$. Its field contribution reads [5]

$$\langle N\tau S J' I_F F'_1 I_N F' M'_F | \hat{H}_Z | N\tau S J_{\max} I_F (F_1)_{\max} I_N F_{\max} \pm (M_F)_{\max} \rangle$$

$$= \delta_{J'J_{\max}} \delta_{F'_{1}(F_{1})_{\max}} \delta_{F'_{F\max}} \delta_{M'_{F^{\pm}}(M_{F})_{\max}}$$

$$\times [\mp \mu_{B}g_{e}B_{z}S$$
(5a)

$$\mp 2\mu_{\rm B}B_z S \frac{1}{(2N+3)(N+1)} \sum_g \bar{g}_{gg}^{\rm e} \langle \hat{N}_g^2 \rangle \tag{5b}$$

$$\mp \mu_{\rm N} g_{I\rm F} B_z I_{\rm F} \mp \mu_{\rm N} g_{\rm IN} B_z I_{\rm N} \tag{5c}$$

$$\mp \mu_{\rm N} B_z \frac{1}{(N+1)} \sum_g g_{gg}^{\rm r} \langle \hat{N}_g^2 \rangle \tag{5d}$$

$$-B_{z}^{2}\frac{1}{(2N+3)(N+1)}\sum_{g}\xi_{gg}\langle\hat{N}_{g}^{2}\rangle],$$
(5e)

where it is easily seen that the parts (5a) and (5c) do not show rotational dependence. Cancellation of these dominating electronic and nuclear field energy contributions in appropriate (magic) rotational Zeeman transitions leads to the favourable effect of small doublet splittings as they are usually observed in diamagnetic molecules. Thus, from good estimates of the D_0 differences of various rotational transitions it is possible to obtain the seven independent diamagnetic parameters entering eq. (5) $-\bar{g}_{aa}^e, \bar{g}_{cc}^e, g_{aa}^r, g_{bb}^r, g_{cc}^r, \xi_{aa}$ and ξ_{cc} – by linear regression.

Such estimates have been obtained in a quickly converging iterative perturbation procedure as follows. Using the field parameters from the *n*th iteration step as well as g_e , g_{I^F} , g_{I^N} given in table 1 and the zero-field constants given in table 2, the matrix from fig. 2 was set up numerically for the rotational levels investigated, diagonalised, and a set of predicted frequency displacements obtained by level subtraction at different magnetic fields. Comparison of these numbers with the corresponding ones obtained via eqs. (5) yielded the frequency perturbation corrections which were applied to the experimental Zeeman displacements to arrive at the next better estimate of D_0 differences and in turn the field parameters of the (n+1)th step. The procedure converged to the parameter set given in table 1. The treatment of the electronic bulk g_e -factor is discussed below.

Table 1

The Zeeman parameters of $\cdot NF_2$ determined in this work and comparison with literature data. For definitions see eqs. (3). The errors given in parentheses, in units of the least significant figure, are standard deviations. Electronic magnetic moments in units of μ_B , rotational in units of μ_N

Parameter	This work *)	Ref. [4]	Curl's	
		fit a	fit c	relationship [23]
<u></u> <u> </u> <u> </u>	-0.003319(24)	-0.003313(20)	-0.003320(20)	-0.00326768(22)
8 cc	0.003700(18)	0.003677(27)	0.003675(27)	0.00370053(32)
graa	-0.4624(69)	0.069(13)	-0.594(13)	
g ^r _{bb}	-0.0764(26)	0.0312(37)	-0.1377(37)	
gr	-0.0482(24)	0.0	0.0	
Eng	-0.113(81)MHz/T ^{2 c)}			
Ē.	-0.073(55)MHz/T ²			
8e	-2.00485(25)	-2.005312(11)	-2.005340(11)	-2.00580242(20)

^{a)} The nuclear g-values used in the fit are $g_{IF} = 2.628867(1)$ and $g_{IN} = 0.4037607(1)$ [24]. The values of fundamental constants were taken from Cohen and Taylor [25].

^{b)} $g_{i}^{\epsilon} = g_{s} + (\epsilon_{i}/2A_{i}), i = a, b, c, A_{i} = \text{rotational constant}, g_{s} = (\text{negative})$ free-electron g-factor. Errors given in parentheses are induced by those of ϵ_{i} and A_{i} in table 2.

c) $1 \text{ MHz/T}^2 \cong 3.9903133 \times 10^{-4} \text{ J/(T}^2 \text{ mol}).$

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Table 2

Zero-field parameters of $\cdot NF_2$ used in this work and comparison with literature data, see text. Errors given in parentheses in units of the least significant figure are standard deviations with the exception of those in the last column which are three standard deviations. All entries in MHz

Parameter	This work	Ref. [2] ^{a)}	Ref. [3]	
A	70496.3314(74)	70496(2)	70495.3(21)	
В	11872.4517(24)	11872.24(20)	11872.14(39)	
С	10136.2259(30)	10136.46(20)	10136.04(36)	
$10^{3}\Delta_{N}$	14.601(15)		14.12(30)	
$10^3 \Delta_{NK}$	-54.55(21)		-51.4(24)	
Δ_{K}	1.8978(12)		1.8740(87)	
$10^3 \delta_N$	2.7630(50)		3.02(23)	
$10^3 \delta_{\kappa}$	67.26(75)		43(23)	
€aa	-951.799(22)	-951.79	-940.4(252)	
ϵ_{bb}	-92.9866(94)	-92.86	-90.2(84)	
€cc	4.4075(87)	4.49	6.0(86)	
(0) _{/F}	164.445(42)	164.39		
(aa) ₁ ,	-241.724(40)	-241.75		
(<i>bb</i>) _{/F}	-226.440(41)	- 226.48		
(<i>CC</i>) ₁ F	468.164(45)	468.22		
(0) _{/N}	46.609(35)	46.57		
(aa) _{IN}	-47.689(39)	-47.72		
(<i>bb</i>) _{/N}	-50.472(33)	- 50.47		
(CC) _{IN}	98.161(34)	98.19		
Xaa ^{b)}	5.495(87)	5.59		
Хьь	-0.667(47)	-0.73		
Xcc	-4.828(40)	- 4.86		

^{a)} Centrifugal distortion constants given in ref. [2] are not compatible with those defined in the first column.

^{b)} The parameter $(ii)_Q = \chi_u/2I_N(2I_N-1), i=a, b, c [18]$ is sometimes used instead of χ_u .

Vastly distinctive perturbation behaviours as a function of field strength were found, and are illustrated in figs. 3-5a. Fig. 3 shows the rare case where the field dependence of both measured doublet members (entries connected by solid lines) is virtually linear. The two slopes are, however, markedly different. As expected, the deperturbation results in a symmetric first order dependence (entries connected by broken lines), as required by eqs. (5a)-(5d). Note that here and in the following two figures the influence of the susceptibility term (eq. (5e)) is too small to become visible. It can be shown [5] that the lower and upper branches are perturbed by the near-by state 615 in second order mainly via the spin-rotation term (see M in fig. 2). In fig. 4 it is seen that the high-frequency branch is strongly perturbed by at least two fine-structure levels of close rotational states which would require a deperturbation approach of higher than second order. The magnetic-field dependence near 2.5 T is already very strong and would eventually turn into an avoided-crossing pattern if higher fields were available. An example of avoided crossing is shown in fig. 5a. As the crossing takes place near 1.5 T, it was possible to follow the pattern to higher field strengths. The perturbations of the 1_{10} state are caused by the 2_{12} rotational state where the $|2_{12} \frac{1}{2} \frac{3}{2} 0 \frac{3}{2} 1 \frac{5}{2}$ hfs level contributes most. However, as is demonstrated in fig. 5b, there is a significant admixture of still other hfs components. Again the deperturbation procedure ends up in the expected symmetric first-order pattern. It should be emphasized that the solid and broken curves in figs. 3, 4 and 5a are not obtained by fitting to the entries separately in each figure but are predicted using the parameters in tables 1 and 2 where the former resulted from a combined least squares fit to all deperturbed field functions as described above.



Fig. 3. Experimental (solid lines) and deperturbed (broken lines) field dependences of the $5_{15} \leftarrow 4_{04}$ magic-doublet components of $\cdot NF_2$ near 157 GHz. The M_F quantum numbers are $-\frac{15}{2} \leftarrow -\frac{13}{2}$ (upper branch) and $+\frac{15}{2} \leftarrow +\frac{13}{2}$ (lower branch). The experimental errors are not resolvable on this scale. $\Delta \nu_+$ and $\Delta \nu_-$ designate the deperturbed branches according to the absolute signs of magic M_{Fmax} quantum numbers, see text. Hence here and in the following two figures the frequency differences between the squares and triangles represent the second- and higher-order perturbation contributions at a given field strength.

6. Zero-field parameters



Our results are in good agreement with those of Brown et al. [2] which are reproduced, with the exception of the centrifugal parameters, in the third column of table 2 for comparison. A discussion of the centrifugal part is not suitable as the data from ref. [2] cannot be uniquely transferred into the representation chosen here. The accuracy of the rotational constants was increased considerably. This is mainly due to the inclusion of the 23 new rotational transitions in table 3. The results of Davies et al. [3], given in the last column of table 2 for comparison, deviate more but are in most cases compatible on the basis of three standard deviations. The disagreement in the spin-rotation parameter ϵ_{aa} is, however, unexpectedly large.



Fig. 4. Measured and deperturbed $3_{21} \leftarrow 3_{12}$ magic doublets near 173 GHz, cf. fig. 3. The M_F quantum numbers are $+\frac{9}{2}$ (upper branch) and $-\frac{9}{2}$ (lower branch).



Fig. 5. (a) Measured and deperturbed field dependences of the $1_{10} \leftarrow 1_{01}$ magic-doublet components near 60 GHz, cf. fig. 3. The upper $(M_F = +\frac{5}{2} \leftarrow +\frac{5}{2})$ frequency component shows an avoided crossing. (b) Field dependence of the 1_{10} magic doublet energy level $M_F = +\frac{5}{2}$ and the perturbing 2_{12} levels causing the avoided crossing frequency pattern shown in fig. 5a. The levels (solid lines) are designated by E_i , i=0, ..., 4 according to the ordering of states chosen in fig. 2. The matrix elements D_i (broken lines) are also given. The 1_{01} level is not perturbed in our scheme.

7. Results and discussion

The diamagnetic Zeeman parameters aimed at in this work, obtained with the iteration procedure explained above, are given in the second column of table 1. Their statistical correlations can be found in table 4. The corresponding perturbational first-order, deperturbed frequency information from the last iteration step is presented in table 3. These data contain, according to eqs. (5b), (5d), and (5e), the first- and second-order rotational Zeeman effects and can, therefore, be decomposed in a linear $(\Delta \nu_{g})$ and a quadratic $(\Delta \nu_{q})$ field contribution given by

$$\Delta \nu_{\varrho}/B_z = \mu_{\rm B}(m_a \bar{g}_{aa}^e + m_c \bar{g}_{cc}^e) + \mu_{\rm N}(n_a g_{aa}^r + n_b g_{bb}^r + n_c g_{cc}^r)$$
(6a)

and

$$\Delta \nu_{\rm q}/B_z^2 = m_a \bar{\xi}_{aa} + m_c \bar{\xi}_{cc} , \qquad (6b)$$

where

$$m_{i} = \frac{\langle \hat{N}_{i}^{\prime 2} \rangle - \langle \hat{N}_{b}^{\prime 2} \rangle}{(2N'+3)(N'+1)} - \frac{\langle \hat{N}_{i}^{\prime \prime 2} \rangle - \langle \hat{N}_{b}^{\prime \prime 2} \rangle}{(2N''+3)(N''+1)}, \quad i=a,c$$

and

$$n_j = \frac{\langle \hat{N}_j^{\prime 2} \rangle}{N+1} - \frac{\langle \hat{N}_j^{\prime \prime 2} \rangle}{N^{\prime \prime}+1}, \quad j = a, b, c.$$

Table 3

Zero-field and deperturbed magic-doublet Zeeman data of the ground state rotational transitions of $\cdot NF_2$ investigated in this work. The F quantum numbers are (2N+3)/2 for para (eo, oe) and (2N+5)/2 for ortho states (ee, oo). $\Delta \nu_e$ and $\Delta \nu_q$ measure the linear and quadratic molecular Zeeman effect, respectively, obtained by deperturbation (see eqs. (6) and text). Their theoretical values (columns 4 and 6) were calculated with the parameters in tables 1 and 2. The standard deviations of the fits are 0.034 MHz/T for the first-order and 0.073 MHz/T² for the second-order Zeeman effects, respectively

Rotational transition	ν ₀ ^{a)} (MHz)	$\frac{\Delta \nu_{\rm g}/B_{\rm z}}{(\rm MHz/T)}$		$\frac{\Delta \nu_q / B_z^2}{(MHz/T^2)}$		
$N'_{K'_{a}K'_{c}} \leftarrow N''_{K''_{a}K''_{c}}$		obs. ^{b)}	obscalc.	obs. ^{b)}	obscalc.	
1 ₁₁ ←0 ₀₀	80415.470(15)	-1.515(17)	-0.102	-0.117(14)	-0.098	
1 ₁₀ ←1 ₀₁	60101.669(10) °)	-11.419(49)	-0.017	0.062(192)	+0.066	
$2_{12} \leftarrow 1_{01}$	100760.379(10)	1.416(18)	+0.048	-0.031(17)	-0.009	
$2_{20} \leftarrow 1_{11}$	222886.270(17)	-10.259(33)	+ 0.099	0.071(22)	+0.068	
$2_{11} \leftarrow 2_{02}$	61871.504(10) °)	-8.661(65)	-0.021	0.018(92)	+0.007	
$3_{13} \leftarrow 2_{02}$	120283.041(11)	2.833(33)	+0.055	0.005(29)	+0.028	
$2_{20} \leftarrow 2_{11}$	175443.417(10)	-8.933(19)	+0.004	-0.087(21)	-0.045	
$2_{21} \leftarrow 2_{12}$	180550.207(10)	-17.202(18)	-0.012	0.007(15)	+0.013	
$3_{21} \leftarrow 2_{12}$	246897.961(28)	-10.349(25)	+0.013	-0.055(166)	-0.067	
$3_{12} \leftarrow 3_{03}$	64695.241(10) ^{c)}	-7.951(25)	-0.028	0.032(28)	+0.014	
4 ₁₄ ←3 ₀₃	138879.951(10)	3.534(58)	+0.007	-0.041(160)	-0.017	
$3_{21} \leftarrow 3_{12}$	173149.813(10)	-3.525(34)	+0.043	-0.010(40)	+0.024	
$3_{22} \leftarrow 3_{13}$	183192.074(10)	-13.023(26)	+0.034	0.019(14)	+0.011	
4 ₁₃ ←4 ₀₄	68399.344(10)	-7.861(13)	-0.013	0.015(9)	-0.008	
5 ₁₅ ← 4 ₀₄	156849.525(15)	3.917(12)	+0.015	-0.007(17)	+0.017	
4 ₂₃ ←4 ₁₄	186854.594(11)	-11.140(28)	-0.021	0.000(29)	-0.015	
$5_{14} \leftarrow 5_{05}$	73394.778(10)	-8.053(13)	+0.003	0.010(15)	-0.017	
6 ₁₆ ←5 ₀₅	174073.752(19)	4.016(10)	-0.013	-0.044(129)	-0.021	
5 ₂₃ ←5 ₁₄	166742.665(13)	0.285(9)	+0.004	-0.006(9)	+0.020	
6 ₀₆ ← 5 ₁₅	83150.998(10)	-3.019(20)	-0.001	-0.027(53)	-0.048	
6 ₂₄ ←6 ₁₅	163068.288(15)	0.842(42)	-0.012	-0.033(61)	-0.011	
7 ₀₇ ← 6 ₁₆	108606.760(12)	-3.162(19)	+0.010	0.008(21)	-0.011	
5 ₃₂ ←6 ₂₅	165409.026(25)	-8.468(34)	+0.023	0.010(61)	+0.022	
7 ₂₅ ←7 ₁₆	159290.186(11)	0.948(34)	-0.032	-0.106(201)	-0.087	
8 ₀₈ ← 7 ₁₇	134050.977(13)	-3.071(29)	+0.030	0.040(108)	+0.023	
9 ₀₉ ←8 ₁₈	159473.562(22)	-2.849(50)	+0.039	-0.101(363)	-0.116	

a) Errors estimated.

^{b)} Errors are standard deviations.

^{c)} These transitions have also been observed in ref. [2], all others are new.

 <u></u> <u></u> <u></u> <u></u> <u></u>	1.00					
<u></u>	-0.67	1.00				
8 aa	-0.95	0.67	1.00			
8 bb	0.17	0.45	-0.03	1.00		
g^{r}_{cc}	0.31	-0.79	-0.27	-0.29	1.00	
Ē.,	1.00					
ξ _{cc}	-0.63	1.00				

 Table 4

 Correlation matrices of the first- and second-order molecular Zeeman parameters in table 1

Let us define ν_+ as the magic-doublet branch formed by the energy difference between the deperturbed states $|F'_{\max}(M'_F)_{\max}\rangle$ and $|F''_{\max}(M''_F)_{\max}\rangle$, and correspondingly ν_- as the branch formed by the deperturbed states $|F'_{\max} - (M'_F)_{\max}\rangle$ and $|F''_{\max} - (M''_F)_{\max}\rangle$ where primes designate higher, and double primes lower rotational levels. $\Delta \nu_+ = \nu_+ - \nu_0$ and $\Delta \nu_- = \nu_- - \nu_0$ are then, consequently, the field-dependent perturbation first-order displacements from zero-field frequency shown as triangles in figs. 3-5a. The assignment of the branches to either $(M_F)_{\max}$ or $-(M_F)_{\max}$ is unique because the absolute signs of the five g-parameters appearing in eq. (6a) are determined relative to g_e and the known nuclear g-values contained in the energy matrix, fig. 2. Unperturbed magic doublets would not contain this sign information because of the isotropic behaviour of the expressions (5a) and (5c).

Using the definitions just introduced we obtain the relations

$$\Delta \nu_{g} = -\frac{1}{2}(\nu_{+} - \nu_{-}) = -\frac{1}{2}(\Delta \nu_{+} - \Delta \nu_{-}) \text{ and } \Delta \nu_{q} = -\frac{1}{2}(\nu_{+} + \nu_{-}) - \nu_{0} = -\frac{1}{2}(\Delta \nu_{+} + \Delta \nu_{-})$$

which serve to set up the experimental numerical values for the left-hand side of the equation systems (6a) and (6b), respectively. The values are given, for all magic-doublet transitions investigated in this work, in the third and fifth columns of table 3. Eight different field settings have been measured on the average for each rotational transition (compare figs. 3-5a). The errors in parentheses are standard deviations of the mean values of $\Delta \nu_{g}/B_{z}$ and $\Delta \nu_{g}/B_{z}^{2}$, respectively, calculated for the different field strengths.

The two electronic g-anisotropies and three rotational g-values in table 1 are the results of a linear leastsquares fit to the 26 entries in the third column of table 3, according to eq. (6a). The residuals in the fourth column are small enough to confirm the present approach as a correct one for understanding the Zeeman effect of a freely rotating $\cdot NF_2$ radical. Note that 11 of the investigated transitions involve ortho states (parallel fluorine spins) which are observed and analysed for the first time in magnetic fields. A close inspection of the original Zeeman data shows that in some cases $(1_{11} \leftarrow 0_{00}$ is one), the predicted frequencies start to deviate by more than the experimental accuracy at higher fields. We think that this could be avoided by adding matrix elements of the type $\langle N|N+2 \rangle$ to the truncated scheme of fig. 2. Exceptionally low weights were introduced for data of this kind.

The two susceptibility anisotropies in table 1, determined by a linear least-squares fit to the data in the fifth column of table 3, show the expected order of magnitude for a molecule like $\cdot NF_2$. Their errors are, however, more than a factor of three larger than those achievable in microwave Zeeman spectroscopy of diamagnetic molecules. This will partly be due to the increased linewidth in the mm range, but probably also reflects small model failures caused by the matrix truncation. Thus, we will not discuss the susceptibility anisotropies in further detail.

The molecular Zeeman parameters must depend on the exact bulk g_e value used in the matrix elements in fig. 2. From the microwave laser double resonance work of Uehara and Horiai one can deduce the gas phase (fit c) value [4] $g_e = -2.005340(11)$, while ESR inert gas matrix results [20,21] range between -2.0044 and -2.0053. We have varied g_e systematically in our analysis as shown in fig. 6, and found an absolute minimum of the sum of squares of frequency residuals, S, at $g_e = -2.00485(25)$. The error is a conservative estimate based on the width of the minimum, fig. 6. The seven least-squares parameters in table 1 are obtained with this value which has to be compared with the most recent theoretical result [22], $g_e = -2.0041$. The g_e -values of several sources, including Curl's relationship [23], have been collected in the last row of table 1. The sensitivity of the diamagnetic least-squares parameters to the choice of g_e is rather low, a fact which is one of the advantages of the magic-doublet method: varying g_e over the range including all values in table 1 leads to changes of \bar{g}_{u}^e , g_{u}^r , and $\bar{\xi}_{u}$, i=a, b, c less than the corresponding standard deviations in table 1.

Uchara and Horiai [4] have analysed their double resonance Zeeman data in terms of the complete electronic g-tensor and of g_{aa}^r and g_{bb}^r , constraining g_{cc}^r to zero. We have included their fit a and fit c results in table 1, in a somewhat modified form suitable for comparison with our data. In fit a, most of the zero-field data were fixed to the diode laser results [3], while for those in fit c the obviously more correct microwave values [2] were used (see table 2). As one can see there is a dramatic difference in the rotational g-values of both fits which was



Fig. 6. The (weighted) sum of squares of frequency residuals, S, of the fitting procedure described in the text as a function of the bulk electronic g-factor, g_e . The minimum occurs at $g_e = -2.00485$, the value chosen for getting the final results, second column of table 1.

attributed [4] to the distinct sets of spin-rotation parameters used. The fact that the fit c parameters resemble ours much more than the fit a ones supports this explanation. Comparison of the sets of rotational g-values in table 1, including their accuracies, again reveals that the magic-doublet method is best suited for the determination of diamagnetic properties. In view of the fact that the method of Uehara and Horiai [4] depends much more on the correct choice of zero-field parameters, the high degree of consistency of all g_e anisotropies given in table 1 seems rather surprising.

This statement even includes the estimates obtained with the well-known relation of Curl [23] which involves the rotation and spin-rotation constants. As was the case earlier for $\cdot ClO_2$ [6], it is found that the predicting power of the relation is good to two significant figures for anisotropies.

As one may suspect the rotational g-factors of \cdot NF₂ are similar to those of \cdot NO₂ which were previously determined to $g_{aa}^r = -2.23(2)$, $g_{bb}^r = -0.080(5)$, and $g_{cc}^r = -0.055(5)$ [26]. The large negative value in the *a*-direction is caused mainly by the unusually large rotational constant A of approximately 240 GHz as compared with 70 GHz in the case of \cdot NF₂.

8. Conclusion

The Zeeman splittings of the magic doublets of a large body of 26 ground state rotational transitions of $\cdot NF_2$ have been investigated in the mm range in fields up to $B_z = 2.6$ T, and analysed by diagonalizing a truncated energy matrix. 11 of the transitions took place between ortho states (parallel fluorine spins). Their inclusion necessarily complicated the field Hamiltonian but helped to break parameter correlations. The zero-field parameters necessary for determining the doublet perturbations by nearby rotational states were redetermined on the basis of the early microwave data of Brown et al. [2] and 23 newly observed rotational transitions. The results (table 2) were found in close agreement with those of [2] but are considerably more accurate.

The final result (table 1) consists of the two independent electronic g-tensor anisotropies which are in agreement with the MW IR double resonance work of Uehara and Horiai [4], and a complete set of accurate rotational g-factors. The two independent susceptibility anisotropy parameters also included in the fit show the expected (small) order of magnitude but are relatively inaccurate. There are indications that extension of the energy matrix (to take into account more distant perturbers) might remove residual descrepancies and increase the quality of the parameters further.

Complete avoided crossing patterns were observed in this work meaning that the low spectral field sensitivity of the magic doublets was recovered at larger fields behind the crossings. Thus, inhomogeneity broadening could be avoided at the highest fields, a fact which is an important advantage of the method.

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Appendix

All matrix elements necessary to set up the matrix in fig. 2 are collected here, with the exception of the rotational part. They have been derived by standard decoupling methods [27] taking advantage of literature results as indicated.

Nonzero matrix elements diagonal in N

Quantum numbers: $S = \frac{1}{2}$, J = N + S, J' = J or J + 1, $F_1 = J + I_F$, $F'_1 = F_1$ or $F_1 + 1$, $F = F_1 + I_N$, F' = F or F + 1 and $I_F = I_{F_1} + I_{F_2} = 0$ or 1; j = a, b, c.

1. Electron spin-rotation interaction [28]

$$\langle N\tau SJ I_{\rm F} F_1 I_{\rm N} F | \hat{H}_{\rm SR} | N\tau SJ I_{\rm F} F_1 I_{\rm N} F \rangle = \frac{J(J+1) - N(N+1) - S(S+1)}{2N(N+1)} \sum_{j} \epsilon_{jj} \langle \hat{N}_j^2 \rangle . \tag{A.1}$$

2. Fermi interactions

$$\langle N\tau S J' I_{\rm F} F_{1} I_{\rm N} F | \hat{H}_{\rm Fermi}(^{19}{\rm F}) | N\tau S J I_{\rm F} F_{1} I_{\rm N} F \rangle = (0)_{I^{\rm F}}(-1)^{N+S+J+J'+I_{\rm F}+3F_{1}+2I_{\rm N}+2F+1} \\ \times \begin{cases} F_{1} & I_{\rm F} & J' \\ 1 & J & I_{\rm F} \end{cases} \begin{cases} N & S & J' \\ 1 & J & S \end{cases} [(2J+1)(2J'+1)(2S+1)(S+1)S(2I_{\rm F}+1)(I_{\rm F}+1)I_{\rm F}]^{1/2}, \qquad (A.2) \end{cases}$$

 $\langle N\tau S J' I_{\rm F} F'_1 I_{\rm N} F | \hat{H}_{\rm Fermi}(^{14}N) | N\tau S J I_{\rm F} F_1 I_{\rm N} F \rangle$

$$= (0)_{I^{N}} (-1)^{N+S+2J'+I_{F}+2F_{1}+I_{N}+F} \begin{cases} F & I_{N} & F'_{1} \\ 1 & F_{1} & I_{N} \end{cases} \begin{cases} J' & F'_{1} & I_{F} \\ F_{1} & J & 1 \end{cases} \begin{cases} N & S & J' \\ 1 & J & S \end{cases}$$

$$\times [(2F_{1}+1)(2F'_{1}+1)(2J+1)(2J'+1)(2S+1)(S+1)S(2I_{N}+1)(I_{N}+1)I_{N}]^{1/2}.$$
(A.3)

3. Electron-nuclear dipole-dipole interactions

$$\langle N\tau S J' I_{\rm F} F_{1} I_{\rm N} F | \hat{H}_{\rm DD}(^{19}{\rm F}) | N\tau S J I_{\rm F} F_{1} I_{\rm N} F \rangle$$

$$= \left[\sum_{J} (jj)_{I^{\rm F}} \langle \hat{N}_{J}^{2} \rangle \right] (-1)^{N+S+2J+I_{\rm F}+3F_{1}+2I_{\rm N}+2F} \frac{\left[(2J+1) (2J'+1) (2I_{\rm F}+1) (I_{\rm F}+1)I_{\rm F} \right]^{1/2}}{(2N-1) (2N+3)N(N+1)}$$

$$\times \left\{ F_{1} I_{\rm F} J' \right\} \left[3\left[(2N+1) (N+1)N \right]^{1/2} \left[S(S+1) + N(N+1) - \frac{1}{2}J' (J'+1) - \frac{1}{2}J(J+1) \right] \left\{ S N J' \\ 1 J N \right\}$$

$$+ (-1)^{J'-J} \times 2\left[(2S+1) (S+1)S \right]^{1/2} N(N+1) \left\{ N S J' \\ 1 J S \right\} \right],$$

$$(A.4)$$

$$\langle N\tau SJ' I_{\rm F} F'_{1} I_{\rm N} F | \hat{H}_{\rm DD}(^{14}{\rm N}) | N\tau SJ I_{\rm F} F_{1} I_{\rm N} F \rangle = \left[\sum_{j} (jj)_{I^{\rm N}} \langle \hat{N}_{j}^{2} \rangle \right] (-1)^{N+S+2J'+I_{\rm F}+2F_{1}+I_{\rm N}+F+1} \\ \times \frac{\left[(2F_{1}+1)(2F'_{1}+1)(2J+1)(2J'+1)(2I_{\rm N}+1)(I_{\rm N}+1)I_{\rm N} \right]^{1/2}}{(2N-1)(2N+3)N(N+1)} \begin{cases} F & I_{\rm N} & F'_{1} \\ 1 & F_{1} & I_{\rm N} \end{cases} \begin{cases} J' & F'_{1} & I_{\rm F} \\ F_{1} & J & 1 \end{cases} \\ \times \left[(-1)^{J-J'} \times 3[(2N+1)(N+1)N]^{1/2}[S(S+1)+N(N+1)-\frac{1}{2}J'(J'+1)-\frac{1}{2}J(J+1)] \begin{cases} S & N & J' \\ 1 & J & N \end{cases} \right] \\ + 2[(2S+1)(S+1)S]^{1/2}N(N+1) \begin{cases} N & S & J' \\ 1 & J & S \end{cases} \end{cases} \right].$$
(A.5)

4. Quadrupole interaction

$$\langle N\tau SJ' I_{\rm F} F'_{1} I_{\rm N} F | \hat{H}_{\rm Q}(^{14}{\rm N}) | N\tau SJ I_{\rm F} F_{1} I_{\rm N} F \rangle = \left[\sum_{j} \chi_{jj} \langle \hat{N}_{j}^{2} \rangle \right] (-1)^{N+S+J+J'+I_{\rm F}+2F_{\rm I}+I_{\rm N}+F} \\ \times \frac{\left[(2F_{1}+1)(2F_{1}'+1)(2J+1)(2J'+1) \right]^{1/2}}{2(2N+3)(N+1)} \left[\frac{(2I_{\rm N}+3)(2I_{\rm N}+1)(I_{\rm N}+1)(2N+3)(2N+1)(N+1)}{I_{\rm N}(2I_{\rm N}-1)N(2N-1)} \right]^{1/2} \\ \times \begin{cases} F & I_{\rm N} & F_{1}' \\ 2 & F_{1} & I_{\rm N} \end{cases} \begin{cases} J' & F_{1}' & I_{\rm F} \\ F_{1} & J & 2 \end{cases} \begin{cases} N & J' & S \\ J & N & 2 \end{cases}.$$
 (A.6)

5. Paramagnetic field interaction

$$\langle N\tau S J'_{\bullet} I_{F} F'_{1} I_{N} F' M_{F} | \hat{H}_{ZP}(g_{e}) | N\tau S J I_{F} F_{1} I_{N} F M_{F} \rangle = \mu_{B} g_{e} B_{z} (-1)^{N+S+2J'+I_{F}+F_{1}+F_{1}+I_{N}+F+F'-M_{F}} \\ \times [(2F+1)(2F'+1)(2F_{1}+1)(2F_{1}+1)(2J+1)(2J+1)(2J'+1)(2S+1)(S+1)S]^{1/2} \\ \times \begin{pmatrix} F' & 1 & F \\ -M_{F} & 0 & M_{F} \end{pmatrix} \begin{cases} F'_{1} & F' & I_{N} \\ F & F_{1} & 1 \end{cases} \begin{cases} J' & F'_{1} & I_{F} \\ F_{1} & J & 1 \end{cases} \begin{cases} S & J' & N \\ J & S & 1 \end{cases} .$$
(A.7)

6. Nuclear magnetic field interactions

$$\langle N\tau SJ I_{\rm F} F'_{1} I_{\rm N} F' M_{\rm F} | \hat{H}_{\rm Zn}(g_{I^{\rm F}}) | N\tau SJ I_{\rm F} F_{1} I_{\rm N} F M_{\rm F} \rangle = \mu_{\rm N} g_{I^{\rm F}} B_{z}(-1)^{J+I_{\rm F}+2F'_{1}+I_{\rm N}+F+F'_{-}-M_{\rm F}+1} \\ \times [(2F+1)(2F'+1)(2F_{1}+1)(2F'_{1}+1)(2I_{\rm F}+1)(I_{\rm F}+1)I_{\rm F}]^{1/2} \\ \times \begin{pmatrix} F' & 1 & F \\ -M_{\rm F} & 0 & M_{\rm F} \end{pmatrix} \begin{cases} F'_{1} & F' & I_{\rm N} \\ F & F_{1} & 1 \end{cases} \begin{cases} I_{\rm F} & F'_{1} & J \\ F_{1} & I_{\rm F} & 1 \end{cases},$$

$$\langle N\tau SJ I_{\rm F} F_{1} I_{\rm N} F' M_{\rm F} | \hat{H}_{\rm Zn}(g_{I^{\rm N}}) | N\tau SJ I_{\rm F} F_{1} I_{\rm N} F M_{\rm F} \rangle = \mu_{\rm N} g_{I^{\rm N}} B_{z}(-1)^{F_{1}+I_{\rm N}+2F'-M_{\rm F}} \\ \times [(2F+1)(2F'+1)(2I_{\rm N}+1)(I_{\rm N}+1)I_{\rm N}]^{1/2} \begin{pmatrix} F' & 1 & F \\ -M_{\rm F} & 0 & M_{\rm F} \end{pmatrix} \begin{cases} I_{\rm N} & F' & F_{1} \\ F & I_{\rm N} & 1 \end{cases}.$$

$$(A.9)$$

7. Diamagnetic field interactions

$$\langle N\tau S J' I_{\rm F} F'_{1} I_{3} F' M_{\rm F} | \hat{H}_{Zd}(g^{*}) | N\tau S J I_{\rm F} F_{1} I_{N} F M_{\rm F} \rangle$$

$$= \mu_{\rm B} B_{\rm f} \left[\sum_{j} g_{jj}^{*} \langle \hat{N}_{j}^{2} \rangle \right] (-1)^{N+S+2j'+I_{\rm F}+F_{\rm F}+F_{\rm F}+F_{\rm F}'-M_{\rm F}+1} \\ \times \frac{\left[(2F+1)(2F'+1)(2F_{1}+1)(2F_{1}+1)(2F_{1}+1)(2J+1)(2J'+1) \right]^{1/2}}{(2N-1)(2N+3)N(N+1)} \\ \times \left(\int_{-M_{\rm F}}^{F'} 0 M_{\rm F} \right) \left\{ F'_{\rm F} F_{\rm I} I_{\rm N} \right\} \int_{-F_{\rm I}}^{F'} F_{\rm I} I_{\rm I} \left\{ F'_{\rm I} I_{\rm I} \right\} \\ \times \left[3(-1)^{J-F} [(2N+1)(N+1)N]^{1/2} [S(S+1)+N(N+1)-\frac{1}{2}J'(J+1)-\frac{1}{2}J(J+1)] \left\{ \int_{J}^{N} \int_{-N}^{J'} S_{\rm I} \right\} \right] \\ + 2[(2S+1)(S+1)S]^{1/2}N(N+1) \left\{ \int_{J}^{S} \int_{-S}^{J'} I_{\rm I} \right\} \\ + 2[(2S+1)(S+1)S]^{1/2}N(N+1) \left\{ \int_{J}^{S} S_{\rm I} I_{\rm I} \right\} \\ = \mu_{\rm N} B_{\rm f} \left[\sum_{j} g_{jj}^{*} \langle \hat{N}_{j}^{2} \rangle \right] (-1)^{N+S+J+f'+F_{\rm F}+F_{\rm I}} + I_{\rm N}+F_{\rm F}+F'-M_{\rm F}} \\ \times \left[(2F+1)(2F'+1)(2F_{\rm I}+1)(2F'_{\rm I}+1)(2F'_{\rm I}+1)(2J'+1)(2J'+1)(2J'+1)(N+1)N]^{1/2} [N(N+1)]^{-1} \\ \times \left(\int_{-M_{\rm F}}^{F'} 0 M_{\rm F} \right) \left\{ F'_{\rm I} F'_{\rm I} I_{\rm N} \right\} \\ = -B_{\rm f} \left[\sum_{j} \xi_{jj}^{*} \langle \hat{N}_{j}^{2} \rangle \right] \left[(-1)^{2(N+S+I_{\rm F}+K-H_{\rm F})+J+F_{\rm I}+F_{\rm I}+F_{$$

Nonzero matrix elements off-diagonal in N

Symmetric-rotor functions $|NK\gamma\rangle$, $K=K_a$ are used [29]. The terms involving δ_{1K} are valid for on levels; for on levels they have opposite signs [18].

Quantum numbers: N' = N+1, $S = \frac{1}{2}$, J = N+S, J' = J or J+1, $F_1 = J+I_F$, $F'_1 = F_1$ or F_1+1 , $F = F_1+I_N$, $F' = F_1$ or F+1 and $I_F = I_{F_1} + I_{F_2} = 0$ or 1.

We define

$$f[(aa)_{P}, (cc)_{P}, N, K, J'] = \frac{1}{2(N+1)} K[(N+1)^{2} - K^{2}]^{1/2} \times \left[\begin{cases} J' & S & N+1 \\ 1 & N & S \end{cases} \begin{cases} N & J' & S \\ J & N & 1 \end{cases} \left(\frac{2N+1}{N} \right)^{1/2} + \begin{cases} J' & S & N+1 \\ 1 & N+1 & S \end{cases} \left\{ N+1 & J' & S \\ J & N & 1 \end{cases} \left(\frac{2N+3}{N+2} \right)^{1/2} \right] \times \left[3(aa)_{P} + \delta_{1K}(-1)^{N+1} \left[\frac{1}{2}(N+1) \right] \left[2(cc)_{P} + (aa)_{P} \right] \right],$$
(A.13)

 $P = I^{\mathsf{r}}$ or I^{N} . In eq. (A.19), $(jj)_{P}$ is replaced by $\bar{g}_{jj}^{\mathsf{e}}, j = a, c$.

1. Electron spin-rotation interaction [18]

$$(jj)_{S} = \epsilon_{jj} - \frac{1}{3} \sum_{i} \epsilon_{i}, \quad i, j = a, b, c, \qquad (A.14)$$

$$\langle N+1 K\gamma' SJ I_{\rm F} F_1 I_{\rm N} F | \hat{H}_{\rm SR} | N K\gamma SJ I_{\rm F} F_1 I_{\rm N} F \rangle = \frac{-1}{4(N+1)} K[(N+1)^2 - K^2]^{1/2} \\ \times [3(aa)_S + \delta_{1K}(-1)^{N+1} [\frac{1}{2}(N+1)] [2(cc)_S + (aa)_S]].$$
(A.15)

2. Electron-nuclear dipole-dipole interactions [18]

$$\langle N+1 K \gamma' S J' I_{\rm F} F_{1} I_{\rm N} F | \hat{H}_{\rm DD}(^{19}{\rm F}) | N K \gamma S J I_{\rm F} F_{1} I_{\rm N} F \rangle = (-1)^{2S+J'+I_{\rm F}+F_{1}} \\ \times [(2J+1)(2J'+1)(2I_{\rm F}+1)(I_{\rm F}+1)I_{\rm F}(2S+1)(S+1)S]^{1/2} \begin{cases} F_{1} & I_{\rm F} & J' \\ 1 & J & I_{\rm F} \end{cases} f[(aa)_{I^{\rm F}}, (cc)_{I^{\rm F}}, N, K, J'] \\ (A.16) \end{cases}$$

$$\langle N+1 K \gamma' S J' I_{\rm F} F_{1}' I_{\rm N} F | \hat{H}_{\rm DD}(^{14}{\rm N}) | N K \gamma S J I_{\rm F} F_{1} I_{\rm N} F \rangle = (-1)^{2S+J'+I_{\rm F}+I_{\rm N}+F} \\ \times [(2J+1)(2J'+1)(2F_{1}+1)(2F_{1}'+1)(2I_{\rm N}+1)(I_{\rm N}+1)I_{\rm N}(2S+1)(S+1)S]^{1/2}$$

$$\times \begin{cases} F & I_{\rm N} & F_1' \\ 1 & F_1 & I_{\rm N} \end{cases} \begin{cases} J' & F_1' & I_{\rm F} \\ F_1 & J & 1 \end{cases} f[(aa)_{I^{\rm N}}, (cc)_{I^{\rm N}}, N, K, J'].$$
(A.17)

3. Quadrupole interaction [18,30]

$$\langle N+1 \ K \ \gamma' \ S \ J' \ I_{\rm F} \ F'_1 \ I_{\rm N} \ F | \ \hat{H}_{\rm Q}(^{14}{\rm N}) | \ N \ K \ \gamma \ S \ J \ I_{\rm F} \ F_1 \ I_{\rm N} \ F \rangle = (-1)^{N+1+S+J+J'+I_{\rm F}+2F_1+I_{\rm N}+F+1} \\ \times [(2F_1+1)(2F_1'+1)(2J+1)(2J'+1)]^{1/2} \begin{cases} F \ I_{\rm N} \ F_1' \\ 2 \ F_1 \ I_{\rm N} \end{cases} \begin{cases} J' \ F_1' \ I_{\rm F} \\ F_1 \ J \ 2 \end{cases} \begin{cases} N+1 \ J' \ S \\ J \ N \ 2 \end{cases} \\ \times \left[4 \binom{N \ 2 \ N+1}{N \ 0 \ -N} \binom{I_{\rm N} \ 2 \ I_{\rm N}}{-I_{\rm N} \ 0 \ I_{\rm N}} \right]^{-1} \frac{1}{2(N+1)} K[(N+1)^2 - K^2]^{1/2} \\ \times \left[\binom{N+1 \ 1 \ N}{-N \ 0 \ N} \binom{N \ 1 \ N}{-N \ 0 \ N} \binom{2N+1}{N} \binom{N+1 \ 1 \ N+1}{-(N+1) \ 0 \ N+1} \binom{N+1 \ 1 \ N}{-N \ 0 \ N} \binom{2N+3}{N+2}^{1/2} \right] \\ \times [3\chi_{aa} + \delta_{1K}(-1)^{N+1} [\frac{1}{2}(N+1)] [2\chi_{cc} + \chi_{aa}]].$$

$$\begin{aligned} 4. Diamagnetic field interactions [18] \\ < N+1 K \gamma' S J' I_F F'_1 I_N F' M_F | \hat{H}_{Zd}(g^e) | N K \gamma S J I_F F_1 I_N F M_F \rangle \\ = \mu_B B_i (-1)^{2S+J'+I_F+I_N+F_F+F-M_F} \\ \times [(2F+1)(2F'+1)(2F_1+1)(2F_1'+1)(2J+1)(2J'+1)(2S+1)(S+1)S]^{1/2} \\ \times \begin{pmatrix} F & 1 & F \\ -M_F & 0 & M_F \end{pmatrix} \begin{pmatrix} F'_1 & F'_1 I_N \end{pmatrix} \begin{pmatrix} J'_1 & F'_1 & I_F \\ F_1 & J & J \end{pmatrix} f [g_{aa}^e g_{bc}^e, N, K, J'] , \quad (A.19) \\ < N+1 K \gamma' S J' I_F F'_1 I_N F' M_F | \hat{H}_{Zd}(g') | N K \gamma S J I_F F_1 I_N F M_F \rangle \\ = \mu_N B_i (-1)^{N+1+S+J+J'+I_F+F_1+F_1+F_1+F_1+F_2+F_2-M_F} \\ \times [(2F+1)(2F'+1)(2F_1+1)(2F_1+1)(2J+1)(2J'+1)]^{1/2} \\ \times \begin{pmatrix} F & 1 & F \\ -M_F & 0 & M_F \end{pmatrix} \begin{pmatrix} F'_1 & F' & I_N \\ F & F_1 & J \end{pmatrix} \begin{cases} J' & F'_1 & I_F \\ F_1 & J & J \\ F_1 & F' & J \\ F_1 & F' & J \\ F_1 & J & J \\ F_1 & J & J \\ F_1 & J & J \\ F_1 & F' & J \\ F_1 & J & J \\ F_1 & J' & J \\ F_1 & J$$

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