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# Fine-structure spectrum of the FO radical, observed by far-infrared laser magnetic resonance

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The fine-structure transition  ${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{3/2}$  of the free radical FO has been detected by far-infrared laser magnetic resonance. All the observed transitions are magnetic dipole in character. The spin-orbit constant  $A_0$  has been determined experimentally; its value of  $-196.108\,686(50)\text{ cm}^{-1}$  is consistent with previous estimates. The analysis of a set of 290 transitions leads to the determination of a number of molecular parameters including rotational, centrifugal distortion, spin-orbit, lambda-doubling, magnetic hyperfine, and Zeeman terms. All four magnetic hyperfine structure constants  $a$ ,  $b_F$ ,  $c$ ,  $d$  for the  ${}^{19}\text{F}$  nucleus have been determined and are discussed in terms of the expectation values of the appropriate operators over the electronic wave function. © 1999 American Institute of Physics. [S0021-9606(99)01315-X]

## INTRODUCTION

The first experimental detection of the FO radical was made by McKellar<sup>1</sup> in 1979 through the observation of its infrared spectrum. He recorded the fundamental vibration-rotation band associated with the lower spin component  ${}^2\Pi_{3/2}$  by CO<sub>2</sub>-laser magnetic resonance (LMR) spectroscopy and determined the band origin  $\nu_0$ , the rotational constant  $B_0$ , the centrifugal distortion correction  $D_0$ , the hyperfine parameter  $h_{3/2} = a + \frac{1}{2}(b+c)$ , the vibrational differences  $B_1 - B_0$ ,  $h_1 - h_0$ , and the spin-orbit constant  $A_0$ . Since the observations were confined to the  $\Omega = 3/2$  spin component,  $A_0$  could not be determined directly, and in fact the reported value of  $-177.3(57)\text{ cm}^{-1}$  was not very accurate. Subsequently, the same vibrational band was reinvestigated by diode laser spectroscopy,<sup>2</sup> leading to a better determination of  $B_0$ ,  $B_1$ ,  $D_0$ ,  $D_1$  because it was now possible to study FO in both spin components.

Burkholder *et al.*<sup>3</sup> recorded the 1-0 and 2-0 bands in both  ${}^2\Pi_{3/2}$  and  ${}^2\Pi_{1/2}$  spin components by Fourier transform IR spectroscopy. In 1988 the same infrared bands and a number of  $\Delta v = 1, 2, 3$  bands were recorded in a Fourier transform emission experiment by Hammer *et al.*<sup>4</sup> The set of reported data was fitted to an effective Hamiltonian which included rotational, centrifugal distortion, spin-orbit, and lambda-doubling terms. Nuclear hyperfine structure was not resolved.  $A_0$  was estimated to be  $-198.3(67)\text{ cm}^{-1}$  in Ref. 3 and  $-193.28(97)\text{ cm}^{-1}$  in Ref. 4, still indirectly and subject to quite a large uncertainty. As pointed out by the authors of Ref. 4, the comparison of all the available experimental determinations and theoretical calculations suggested that  $A_0$  could lie between  $-180$  and  $-200\text{ cm}^{-1}$ ; that is to say, a major parameter of FO was still very poorly determined.

The best way to measure the spin-orbit splitting is the

direct detection of the fine-structure transition  ${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{3/2}$  in the far-infrared region. This is the aim of the present work. The LMR technique was chosen because of its high sensitivity and its ability to discriminate between open-shell and closed-shell molecules, which are usually present in much higher amounts; also, the only intense sources in the far-infrared (FIR) region are fixed-frequency lasers. In a Hund's case (a) limit, the fine-structure transition is electric dipole forbidden but magnetic dipole allowed and hence it is expected to be three or four orders of magnitude weaker than a normal, electric dipole allowed transition. On the other hand, Brown, Cole, and Honey,<sup>5</sup> in their work on the fine-structure spectrum of NO, pointed out that magnetic dipole allowed transitions were about 18 times stronger than electric dipole forbidden transitions. The same ratio is 20 for SeH<sup>6</sup> and 140 for BrO;<sup>7</sup> it depends on the magnitude of the electric dipole moment and the spin-orbit splitting.

Burkholder *et al.*<sup>3</sup> have also considered the production of FO by the reaction between F atoms and ozone and emphasized that, in the presence of excess ozone, there is no net loss of FO radicals. FO is produced by the reaction



and destroyed by the reaction



Thus two F atoms are produced in the latter process and can react with further ozone molecules, thereby regenerating the FO radical. This was confirmed in our experiments where we observed a surprisingly long lifetime of the signal (see the experimental section). These considerations and the high intrinsic sensitivity of LMR gave us confidence in our approach to the experiment, despite the expected low intensity of the magnetic dipole transitions.

No pure rotational or electron paramagnetic resonance spectra of FO have been reported in the literature. McKellar<sup>8</sup>

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combined LMR spectroscopy and Stark spectroscopy to demonstrate that the electric dipole moment of FO is 0.0043(4) D for the  $v=0$  level and 0.0267(9) D for  $v=1$ . The exceptionally small value of  $\mu$  has therefore precluded any detection of rotational spectra so far but the strong variation of  $\mu$  with the vibrational excitation makes the infrared spectra relatively easy to observe. This is supported by theoretical calculations by Langhoff, Bauschlicher, and Partridge.<sup>9</sup> Their predictions for  $\mu_{v=0}$  (−0.0089 D with the negative end on the F atom) and  $\mu_{v=1}$  (−0.0318 D) show quite good agreement with McKellar's experimental values. The computed curve of the dipole moment as a function of the internuclear distance shows a steep slope for bond lengths less than 0.16 nm, confirming the large change of  $\mu$  passing from  $v=0$  to  $v=1$ .

In the present paper, we report the successful detection of magnetic dipole, fine-structure transitions of the FO radical in the  $v=0$  level of the  $X^2\Pi$  state. The measurements are more accurate than any which precede it and allow, among other things, the first direct determination of the spin–orbit coupling constant and of all four magnetic nuclear hyperfine parameters.

## EXPERIMENTAL DETAILS

The far-infrared spectrometer used for the experiment has been described elsewhere.<sup>10</sup> Very recently<sup>11</sup> some changes have been made: the Zeeman modulation frequency has been raised to 40 kHz to improve the sensitivity and the diameter of the pump tube has been reduced in order to produce better performance of the laser at wavelengths shorter than 100  $\mu\text{m}$ . This has been proved to be particularly important for our experiment since the fine structure transitions of FO are around 50  $\mu\text{m}$ . The detector used was a liquid-helium-cooled gallium–germanium photoconductor.

FO was produced by reacting F atoms with  $\text{O}_3$ . The F atoms were generated by flowing a 10%  $\text{F}_2$  in He mixture through a microwave discharge. Ozone was introduced into the cell by flowing He over silica gel, on which ozone was adsorbed. The  $\text{O}_3$ /silica gel trap was placed in an ethanol–dry ice bath to regulate the amount of  $\text{O}_3$  evaporated. The best signals were observed with 24 Pa (180 mTorr) of  $\text{F}_2$ /He and 9.3 Pa (70 mTorr) of  $\text{O}_3$ /He. As described in the Introduction, the production of FO was sustained by an excess of

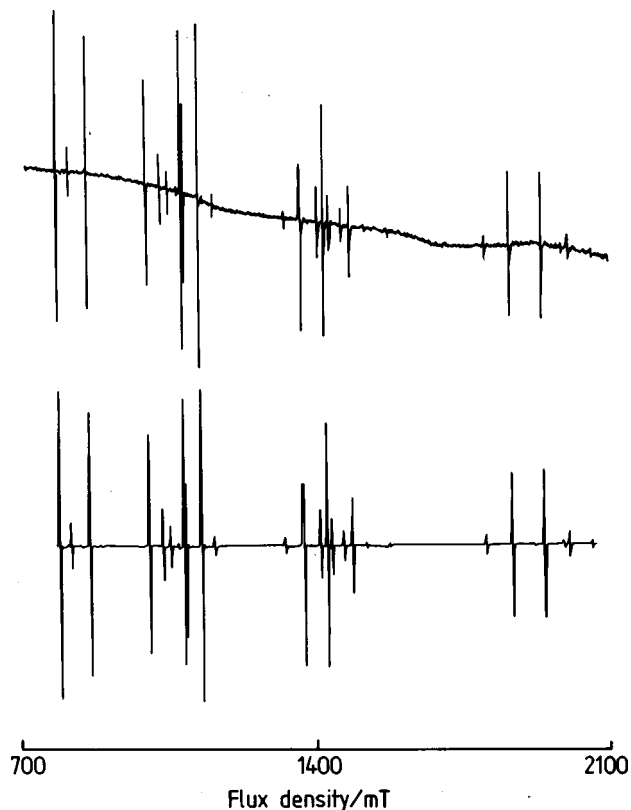


FIG. 1. Experimental (the upper trace) and simulated (the lower trace) far-infrared laser magnetic resonance spectrum of the  $R(4\frac{1}{2})$  fine-structure transition of FO observed at 209.819 231  $\text{cm}^{-1}$  in perpendicular polarization ( $\Delta M_J = \pm 1$ ).

$\text{O}_3$ , even in the absence of further F atoms. The interesting result is that, if the microwave discharge is switched off and the flow of ozone is maintained, the signal is maintained for a few minutes. This is not due to a very long lifetime of FO but to the regeneration of fluorine atoms by the reaction of two FO molecules. Signals of lower intensity were also observed reacting F atoms (42.7 Pa 10%  $\text{F}_2$ /He) with  $\text{O}_2$  (100 Pa).

The spectra were recorded on an  $xy$  plotter as a function of the magnetic flux density. Since  $1-f$  detection with magnetic modulation was employed, the first derivative of the absorption profile was observed. Figure 1 shows a long sur-

TABLE I. FIR laser lines used to record LMR spectra for FO.

$\text{CO}_2$ laser line <sup>a</sup>	Laser gas	Wavelength/ $\mu\text{m}$	Frequency/MHz	Assigned FO transitions
10R(46)	$\text{CH}_3\text{OH}$	52.004	5 764 826.7	$P(2\frac{1}{2})$
10R(56)	$\text{CD}_3\text{OH}$	51.478	5 823 660.9*	$P(1\frac{1}{2})$
10R(20)	$\text{CD}_3\text{OH}$	50.629	5 921 370.4*	$Q(1\frac{1}{2}), Q(2\frac{1}{2})$
10R(24)	$\text{CD}_3\text{OH}$	49.973	5 999 028.8*	$Q(11\frac{1}{2}), Q(12\frac{1}{2}), Q(13\frac{1}{2}), Q(14\frac{1}{2})$
10R(52)	$\text{CH}_3\text{OH}$	49.694	6 032 811.3*	$Q(15\frac{1}{2}), Q(16\frac{1}{2}), Q(17\frac{1}{2})$
9P(12)	$^{13}\text{CH}_3\text{OH}$	49.455	6 061 914.8*	$Q(17\frac{1}{2}), Q(18\frac{1}{2}), Q(19\frac{1}{2}), Q(20\frac{1}{2})$
9R(6)	$\text{CD}_3\text{OH}$	48.721	6 153 279.0*	$R(2\frac{1}{2})$
9R(8)	$\text{CH}_3\text{OD}$	47.660	6 290 222.3*	$R(4\frac{1}{2})$
9P(10)	$\text{CH}_3\text{OH}$	46.165	6 493 911.5	$R(7\frac{1}{2})$

<sup>a</sup>Reference 28. The lines marked with an asterisk have been frequency measured for this work.

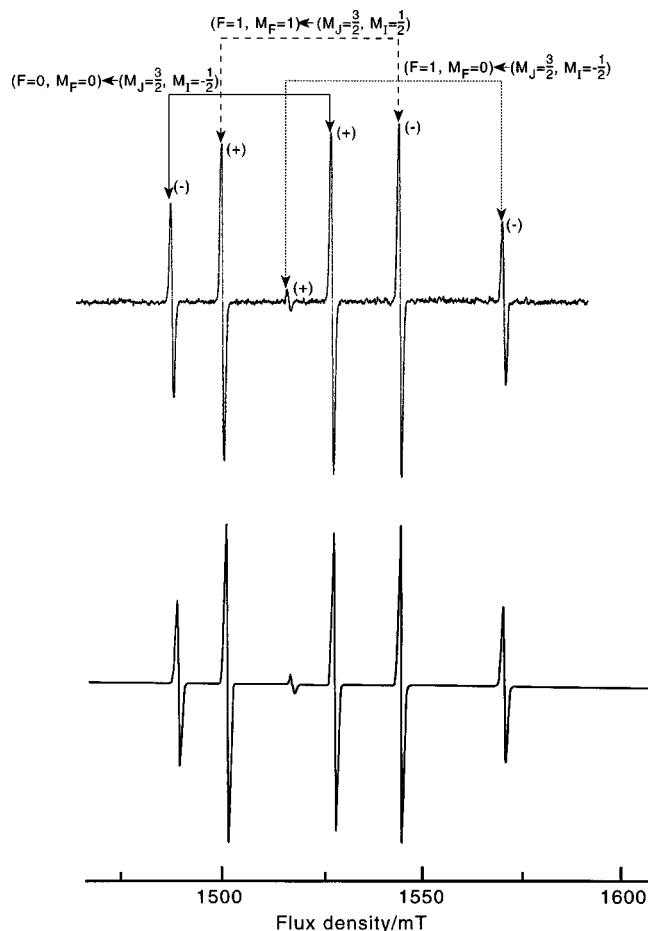


FIG. 2. Experimental (the upper trace) and simulated (the lower trace) far-infrared laser magnetic resonance spectrum of the  $P(1\frac{1}{2})$  fine-structure transition of FO observed at  $194.256\,417\text{ cm}^{-1}$  in perpendicular polarization ( $\Delta M_J = \pm 1$ ). Note the complicated hyperfine structure because of the difference in coupling schemes in the lower and upper states.

vey scan of the  $R(4\frac{1}{2})$  transition. The spectra have been recorded in both parallel ( $B_\omega \parallel B_0$ ) and perpendicular ( $B_\omega \perp B_0$ ) polarizations. Typical measurement scans covered 40 mT and were performed back and forth to correct shifts due to the time constant. The magnet was periodically calibrated with a NMR gaussmeter: the overall fractional uncertainty is  $\pm 1 \times 10^{-4}$  above 0.1 T and  $\pm 1 \times 10^{-5}$  below 0.1 T. We estimate an experimental uncertainty of  $\pm 2 \times 10^{-4}$  T for an individual resonance.

We used nine FIR laser lines to make our observations (see Table I) and seven of their frequencies have been measured for the first time in this experiment. Their frequency was determined by measuring the beat frequency when the FIR radiation was mixed with the radiation from two frequency-stabilized  $\text{CO}_2$  lasers in a metal-insulator-metal (MIM) diode.<sup>12</sup>

## RESULTS AND ANALYSIS

Nine laser lines, listed in Table I, have been used to record all of the spectra reported in this paper. The total range explored is about  $24\text{ cm}^{-1}$  and covers part of the  $P$ ,  $Q$ , and  $R$  branches of the fine-structure transition. Examples of

typical spectra are shown in Figs. 1–3. We have recorded and assigned 290 lines corresponding to 17 rotational transitions with  $J$  ranging from  $\frac{1}{2}$  to  $20\frac{1}{2}$ . All the observed resonances are magnetic dipole in origin. The spectrum of the  $(J=18\frac{1}{2}, F=19, M_F=-19, -) \leftarrow (J=18\frac{1}{2}, M_I=-\frac{1}{2}, M_J=-\frac{39}{2}, -)$  transition showed a Lamb dip, at low pressure and modulation amplitude, which indicates that the signals are strong enough to reach saturation and also that there is no underlying structure in the Doppler profile (see Fig. 4). No evidence for FO in vibrationally excited states has been found and all of the recorded lines have been assigned to fine-structure transitions in  $v=0$ .

By comparison of our spectra with the LMR spectra reported by Mizushima, Evenson, and Wells<sup>13</sup> in their work on the corresponding fine-structure transition of NO, we identified the different  $Q$  branches of our spectrum and obtained a rough idea of the value of  $J$ . Using the parameters of FO already known from literature<sup>3,4</sup> and hyperfine constants scaled from the corresponding parameters of CF,<sup>14</sup> the high- $J$   $Q$  branch was tentatively assigned.  $A_0$  was changed step by step in order to match the calculated pattern with the experimental pattern. Once the first transition was identified, the spectroscopic constants were refined and new predictions made. The analysis of the spectra was lengthy and elaborate because of our ignorance of some basic parameters and the unusual Zeeman patterns,<sup>7</sup> which arise from the different nuclear spin coupling schemes in the upper and lower levels.

For a molecule in a  $^2\Pi$  state there are two possible values,  $3/2$  and  $1/2$ , for magnitude of the projection  $\Omega$  of the angular momentum  $\mathbf{J}$  on the internuclear axis. The two spin components,  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$ , show very different behavior in the presence of an external magnetic field. For a molecule which conforms closely to Hund's case (a) coupling, such as FO ( $A_0 \approx -196\text{ cm}^{-1}$ ,  $B_0 \approx 1\text{ cm}^{-1}$ ) the first-order Zeeman contribution to the total energy is given by

$$E_{Zee} = g_J \mu_B B M_J, \quad (3)$$

where  $g_J$  is the  $g$  factor for the rotational level  $J$ ,  $\mu_B$  is the Bohr magneton,  $B$  is the magnetic flux density, and  $M_J$  is the projection of  $\mathbf{J}$  on the laboratory-fixed  $Z$  axis. The  $g$  factor is given by

$$g_J = \frac{(\Lambda + \Sigma)(\Lambda + g_S \Sigma)}{J(J+1)}, \quad (4)$$

where  $\Lambda$  and  $\Sigma$  are, respectively, the projections of  $\mathbf{L}$  and  $\mathbf{S}$  on the internuclear axis. According to Eq. (4)  $g_J$  is nearly zero for the  $^2\Pi_{1/2}$  state, while it is nonvanishing for the  $^2\Pi_{3/2}$  state; in other words, the  $^2\Pi_{1/2}$  state is essentially diamagnetic. As a result, the energy level patterns for the two types of state in a magnetic field are considerably different. In Fig. 5 the energy level diagram for the  $P(1\frac{1}{2})$  transition at a flux density of 1.5 T is given.

For the lower state ( $J=3/2$ ) the interaction with a magnetic field produces four  $M_J$  components,  $3/2, 1/2, -1/2, -3/2$ , spread over  $1.7\text{ cm}^{-1}$ . Each  $M_J$  level is in turn split into two levels by magnetic hyperfine interaction ( $I_F=1/2$ ) and a further two by lambda-doubling effects. The finer splittings between these four sublevels cannot be appreciated on

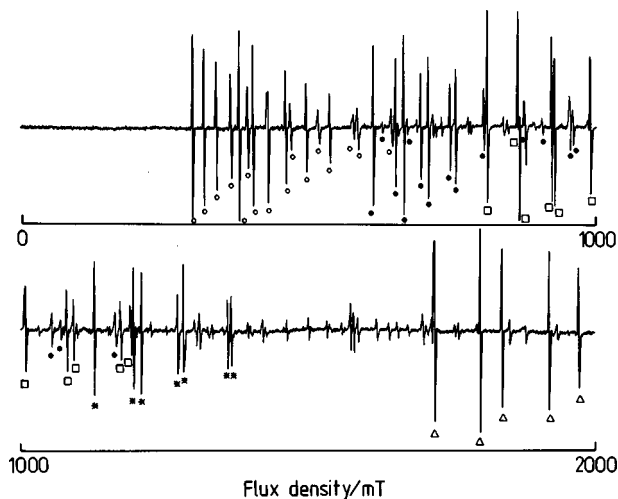


FIG. 3. Experimental far-infrared laser magnetic resonance spectrum of the  $Q(15\frac{1}{2})$ ,  $Q(16\frac{1}{2})$ ,  $Q(17\frac{1}{2})$  transitions of FO observed at  $201.232\,924\text{ cm}^{-1}$  in parallel polarization ( $\Delta M_J=0$ ). The measured lines are identified as follows:  $\square$ — $Q(15\frac{1}{2})_+$ ,  $\triangle$ — $Q(15\frac{1}{2})_-$ ,  $\circ$ — $Q(16\frac{1}{2})_+$ ,  $\bullet$ — $Q(16\frac{1}{2})_-$ ,  $*$ — $Q(17\frac{1}{2})_-$ .

the scale of the diagram, being much smaller than the separation between the  $M_J$  components. In this situation the nuclear spin  $\mathbf{I}$  is decoupled from  $\mathbf{J}$  so that  $J, M_J, I, M_I$  and the parity are all good quantum numbers. For the upper  $J=1/2$  state in the same field, the Zeeman levels are spread over a much narrower range of energy ( $0.036\text{ cm}^{-1}$ ) and there is no clear magnetic structure. In this case the nuclear spin remains coupled and only  $F$  ( $\mathbf{F}=\mathbf{J}+\mathbf{I}$ ), its projection on the field axis  $M_F$  and the parity are good quantum numbers. The  $J=1/2$  eigenfunctions in the coupled representation can be expressed as a linear combination of the decoupled basis set  $|JM_JIM_I\rangle$  and, in the specific case of the  $P(1\frac{1}{2})$  transition in FO they are, neglecting  $J$  and  $I$ :

$$\begin{aligned}
 |F=1, M_F=-1, -\rangle &= |M_J=-\frac{1}{2}, M_I=-\frac{1}{2}, -\rangle, \\
 |F=1, M_F=0, -\rangle &= 0.735|M_J=-\frac{1}{2}, M_I=\frac{1}{2}, -\rangle \\
 &\quad + 0.677|M_J=\frac{1}{2}, M_I=-\frac{1}{2}, -\rangle, \\
 |F=1, M_F=1, -\rangle &= |M_J=\frac{1}{2}, M_I=\frac{1}{2}, -\rangle, \\
 |F=1, M_F=0, +\rangle &= 0.609|M_J=-\frac{1}{2}, M_I=\frac{1}{2}, +\rangle \\
 &\quad + 0.792|M_J=\frac{1}{2}, M_I=-\frac{1}{2}, +\rangle, \\
 |F=1, M_F=1, +\rangle &= |M_J=\frac{1}{2}, M_I=\frac{1}{2}, +\rangle, \\
 |F=1, M_F=-1, +\rangle &= |M_J=-\frac{1}{2}, M_I=-\frac{1}{2}, +\rangle, \\
 |F=0, M_F=0, -\rangle &= -0.677|M_J=-\frac{1}{2}, M_I=\frac{1}{2}, -\rangle \\
 &\quad + 0.735|M_J=\frac{1}{2}, M_I=-\frac{1}{2}, -\rangle, \\
 |F=0, M_F=0, +\rangle &= -0.792|M_J=-\frac{1}{2}, M_I=\frac{1}{2}, +\rangle \\
 &\quad + 0.609|M_J=\frac{1}{2}, M_I=-\frac{1}{2}, +\rangle,
 \end{aligned}$$

where the calculations have been made for a flux density of 1.5 T and use the molecular parameters in Table III. The

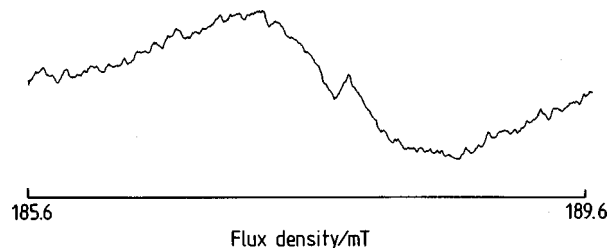


FIG. 4. A spectrum of the  $(J=18\frac{1}{2}, F=19, M_F=-19, -) \leftarrow (J=18\frac{1}{2}, M_I=-\frac{1}{2}, M_J=-\frac{39}{2}, -)$  transition of FO observed at  $202.203\,713\text{ cm}^{-1}$  in parallel polarization ( $\Delta M_J=0$ ) showing a single Lamb dip. Total pressure 22 Pa (165 mTorr), scan time 5 min, time constant 1 s, sensitivity  $100\text{ }\mu\text{V}$ , modulation 0.1 mT.

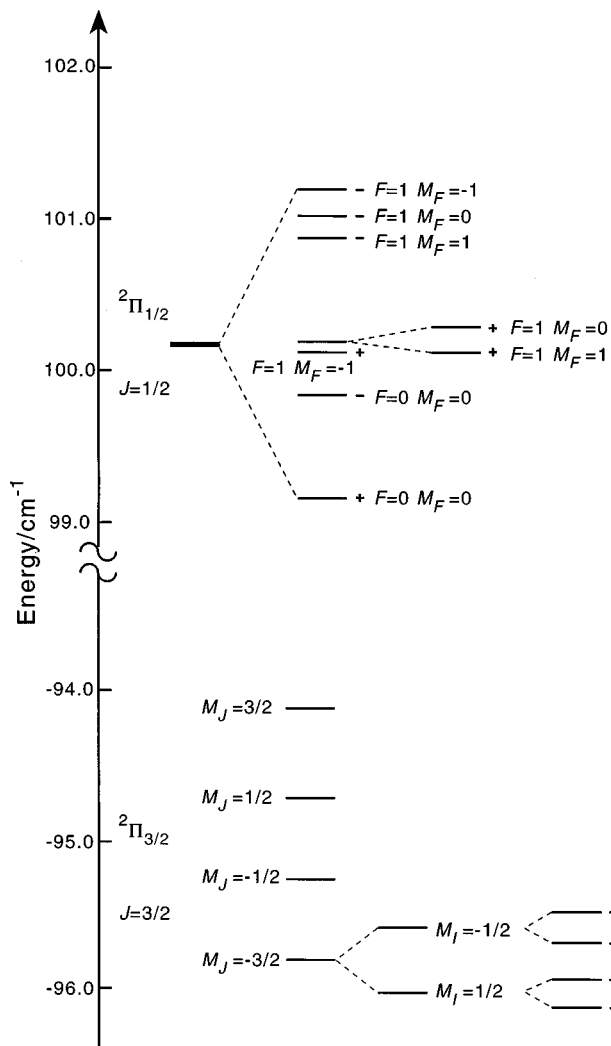


FIG. 5. Energy level diagram for the  $P(1\frac{1}{2})$  fine-structure transition of FO calculated in a flux density of 1.5 T. For the  $2\Pi_{3/2}$  component, the fluorine nuclear spin is decoupled and every  $M_J$  level is split into two levels by the nuclear hyperfine interaction, each of which is further split by the effect of lambda doubling. The four energy levels associated with each single  $M_J$  component are not visible on the present scale; an enlargement is shown for  $M_J=-3/2$ . For the  $2\Pi_{1/2}$  component, the nuclear spin remains coupled to the overall rotational angular momentum  $\mathbf{J}$ ; the quantum numbers  $F$  and  $M_F$  are therefore appropriate. The energy levels in the  $2\Pi_{1/2}$  component have been expanded, since their separation is not visible on the present scale. Note that the levels  $(F=1, M_F=0, +)$  and  $(F=1, M_F=1, +)$  are overlapped.

$P(1\frac{1}{2})$  transition is shown in Fig. 2, where the simulated spectrum is also given. The six peaks correspond to the transitions:

$$(i) \quad |F=0, M_F=0, -\rangle \leftarrow |M_J=\frac{3}{2}, M_I=-\frac{1}{2}, -\rangle,$$

$$B_0 = 1489.17 \text{ mT},$$

$$(ii) \quad |F=1, M_F=1, +\rangle \leftarrow |M_J=\frac{3}{2}, M_I=\frac{1}{2}, +\rangle,$$

$$B_0 = 1501.60 \text{ mT},$$

$$(iii) \quad |F=1, M_F=0, +\rangle \leftarrow |M_J=\frac{3}{2}, M_I=-\frac{1}{2}, +\rangle,$$

not measured,

$$(iv) \quad |F=0, M_F=0, +\rangle \leftarrow |M_J=\frac{3}{2}, M_I=-\frac{1}{2}, +\rangle,$$

$$B_0 = 1528.97 \text{ mT},$$

$$(v) \quad |F=1, M_F=1, -\rangle \leftarrow |M_J=\frac{3}{2}, M_I=\frac{1}{2}, -\rangle,$$

$$B_0 = 1545.84 \text{ mT},$$

$$(vi) \quad |F=1, M_F=0, -\rangle \leftarrow |M_J=\frac{3}{2}, M_I=-\frac{1}{2}, -\rangle,$$

$$B_0 = 1571.73 \text{ mT}.$$

Transitions (i), (iii), (iv) and (vi) involve heavily mixed basis functions and are in part forbidden because of the decoupled selection rule  $\Delta M_I=0$ .

As mentioned before, we cannot analyze the data in terms of a single coupling scheme. We chose to calculate the eigenvalues for the two spin components in the most appropriate basis sets, that is **I**-decoupled  $|\eta\Lambda\rangle|S\Sigma\rangle|JM_J\Omega\rangle|IM_I\rangle$  for  $^2\Pi_{3/2}$  and **I**-coupled  $|\eta\Lambda\rangle|S\Sigma\rangle|JIFM_F\rangle$  for  $^2\Pi_{1/2}$ . The set of data has been fitted with an effective Hamiltonian<sup>15,16</sup> of the form

$$H_{\text{eff}} = H_{\text{so}} + H_{\text{rot}} + H_{\text{cd}} + H_{\text{LD}} + H_{\text{cdLD}} + H_{\text{hfs}} + H_Z, \quad (5)$$

where

$$H_{\text{so}} = A_0 L_z S_z + \frac{1}{2} A_D [N^2, L_z S_z]_+, \quad (6)$$

$$H_{\text{rot}} = B_0 N^2, \quad (7)$$

$$H_{\text{cd}} = -D_0 N^4 + H_0 N^6, \quad (8)$$

$$H_{\text{LD}} = \frac{1}{2}(p+2q)(e^{2i\phi} S_- J_- + e^{-2i\phi} S_+ J_+) - \frac{1}{2}q(e^{2i\phi} J_-^2 + e^{-2i\phi} J_+^2), \quad (9)$$

$$H_{\text{cdLD}} = \frac{1}{4}(p_D+2q_D)[N^2, e^{2i\phi} S_- J_- + e^{-2i\phi} S_+ J_+]_+, \quad (10)$$

$$H_{\text{hfs}} = aI_z L_z + b(I_x S_x + I_y S_y) + (b+c)I_z S_z + \frac{1}{2}d(e^{-2i\phi} I_+ S_+ + e^{2i\phi} I_- S_-), \quad (11)$$

$$H_Z = g_L \mu_B B_0 L_z + g_S \mu_B B_0 S_z - g_r \mu_B B_0 N_z + g_l \mu_B (S_x B_x + S_y B_y) - g_N \mu_N B_0 I_z - g'_r \mu_B (e^{-2i\phi} N_+ B_+ + e^{2i\phi} N_- B_-) + g'_l \mu_B (e^{-2i\phi} S_+ B_+ + e^{2i\phi} S_- B_-). \quad (12)$$

$H_{\text{so}}$  is the spin-orbit operator including the centrifugal distortion correction.  $H_{\text{rot}}$  is the rotational operator and  $H_{\text{cd}}$  is the rotational centrifugal distortion contribution.  $H_{\text{LD}}$  is the

lambda-doubling term and  $H_{\text{cdLD}}$  its centrifugal distortion correction.  $H_{\text{hfs}}$  represents the magnetic hyperfine interaction Hamiltonian and  $H_Z$  is the Zeeman Hamiltonian.

The selection rules for LMR transitions are  $\Delta J=0, \pm 1$ ,  $\Delta M_I=0, \Delta M_J=0, \pm 1$ . If the laser magnetic field (or electric field in case of electric dipole transitions) is parallel to the external magnetic field the selection rule  $\Delta M_J=0$  applies. If they are perpendicular  $\Delta M_J=\pm 1$  holds. As pointed out by Brown, Carrington, and Sears,<sup>5</sup> the optimum polarization is parallel for  $Q$  transitions and perpendicular for  $R$  and  $P$  transitions. This rule has been experimentally confirmed by our spectra. Only for the  $R(4\frac{1}{2})$ ,  $Q(1\frac{1}{2})$ , and  $Q(2\frac{1}{2})$  transitions have equally intense lines been detected in both parallel and perpendicular polarizations.

The data have been analyzed using a linearized least-squares procedure. Since the Zeeman effect mixes energy levels with different  $J$  according to the selection rule  $\Delta J=\pm 1$ , a suitably truncated basis set for the matrix of the Hamiltonian must be chosen ( $\Delta J=\pm 2$  in our case) in order to ensure that the calculations are accurate enough.  $H_0$  was fixed to a calculated value (see Ref. 17) and  $p_D+2q_D$  was constrained to the previous value determined in Ref. 3. The observed lines are given in Table II. For each rotational transition, identified by the usual notation  $P(J)$ ,  $Q(J)$  or  $R(J)$ , the lower level is labeled by the quantum numbers  $M_J$  and  $M_I$ , and the upper level by  $F$  and  $M_F$ . The parity is defined for both levels, according to the selection rule for magnetic dipole transitions  $\pm \leftarrow \pm$ . For each transition the laser frequency, the differences observed-calculated from the fit, the tuning rates, and the weights are also given. The tuning rate, defined as the variation of the transition frequency with respect to the magnetic flux density  $B_0$ , is in MHz/mT. We chose to give a weight of 0.1 to the transitions with o-c between 6 and 10 MHz and a weight of 0 to the transitions with o-c greater than 10 MHz; virtually all these data points corresponded to resonances at high magnetic fields where the measurements are less accurate. The quality of the fit (Table III) is satisfactory and only a few lines, mostly partially overlapped or at high fields, have been given a lower weight. The standard deviation of the fit is 1.9 MHz, consistent with the expected experimental uncertainty.

We fitted  $A_D$  and constrained  $\gamma$  to zero, but in principle an equivalent fit can be made with the opposite choice. When we tried such a calculation, we obtained a significant worsening of the quality of the fit with a standard deviation of 3.0 MHz. Since we are confident that our set of data is not affected by severe systematic errors, this suggests that there are may be other contributions from parameters not accounted for in the effective Hamiltonian (see Discussion and Conclusions).

## DISCUSSION AND CONCLUSIONS

The main goal of the present work was the determination of the spin-orbit coupling constant  $A_0$  for FO in its ground  $^2\Pi$  state. This parameter has been determined with great accuracy and the fit as a whole shows a marked improvement in the precision of most of the other parameters. The two exceptions are the rotational and centrifugal distortion con-

TABLE II. The  ${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{3/2}$  transitions of FO observed by far-infrared LMR.

	$F$	$M_F$	$\leftarrow$	$M_I$	$M_J$	$p$	$\nu_L$ (MHz)	$B_0$ (mT)	o-c (MHz)	$\partial\nu/\partial B_0$ (MHz/mT)	wt
$P(2\frac{1}{2})$	2	2		1/2	5/2	—	5 764 826.7	1778.74	−0.9	−10.9	1.0
	2	1		−1/2	5/2	—		1807.11	−0.0	−10.9	1.0
	1	1		−1/2	5/2	—		1831.51	−0.0	−10.9	1.0
	1	1		−1/2	5/2	+		1839.71	−8.7	−10.9	0.1
	2	2		1/2	5/2	+		1880.46	−0.6	−10.9	1.0
$P(1\frac{1}{2})$	0	0		−1/2	3/2	—	5 823 660.9	1489.17	−2.0	−15.1	1.0
	1	1		1/2	3/2	+		1501.60	−2.3	−15.0	1.0
	0	0		−1/2	3/2	+		1528.97	1.5	−15.0	1.0
	1	1		1/2	3/2	—		1545.84	−0.2	−15.0	1.1
	1	0		−1/2	3/2	—		1571.73	−0.3	−14.9	1.0
$Q(1\frac{1}{2})$	2	2		1/2	1/2	—	5 921 366.7	1295.46	3.7	−15.4	1.0
	2	1		−1/2	3/2	—		1321.56	−2.1	−15.4	1.0
	1	1		−1/2	3/2	—		1339.43	3.2	−15.4	1.0
	1	1		−1/2	3/2	+		1346.74	−0.1	−15.4	1.0
	2	2		1/2	3/2	+		1369.56	−0.9	−15.4	1.0
	2	1		−1/2	3/2	+		1400.17	2.2	−15.3	1.0
	2	1		1/2	3/2	—		1301.42	3.6	−15.4	1.0
	1	1		1/2	3/2	—		1318.74	−0.6	−15.4	1.0
	1	1		1/2	3/2	+		1326.25	−2.4	−15.4	1.0
	2	0		−1/2	3/2	—		1328.14	−2.1	−15.3	1.0
	1	0		−1/2	3/2	—		1348.31	3.6	−15.3	1.0
	1	0		−1/2	3/2	+		1360.90	−0.5	−15.3	1.0
	2	1		1/2	3/2	+		1379.70	−1.1	−15.3	1.0
	2	0		−1/2	3/2	+		1408.18	−41.9	−15.2	0.0
$Q(2\frac{1}{2})$	3	3		1/2	5/2	+	5 921 366.7	1908.66	−1.6	−10.9	1.0
	3	2		−1/2	5/2	+		1940.85	−0.2	−10.9	1.0
	2	2		−1/2	5/2	+		1968.26	7.6	−10.9	0.1
	2	2		−1/2	5/2	—		2017.10	9.8	−10.9	0.1
	3	3		1/2	5/2	—		2051.37	18.9	−10.9	0.0
	3	2		−1/2	5/2	—		2091.93	30.5	−10.8	0.0
	3	2		1/2	5/2	+		1924.56	1.7	−10.9	1.0
	2	2		1/2	5/2	+		1951.24	−0.0	−10.9	1.0
	3	1		−1/2	5/2	+		1958.09	−0.2	−10.8	1.0
	2	1		−1/2	5/2	+		1990.43	8.0	−10.7	0.1
	2	1		−1/2	5/2	—		2046.38	17.3	−10.8	0.0
	3	2		1/2	5/2	—		2075.70	25.6	−10.8	0.0
$Q(11\frac{1}{2})$	12	−12		−1/2	−23/2	+	5 999 028.8	1202.87	1.8	7.0	1.0
	11	−11		1/2	−23/2	+		1259.35	−0.4	7.0	1.0
	12	−11		−1/2	−21/2	+		1315.06	−0.3	6.4	1.0
	11	−10		1/2	−21/2	+		1379.02	10.2	6.4	1.0
	12	−10		−1/2	−19/2	+		1449.60	1.3	5.8	1.0
	12	−9		1/2	−19/2	+		1460.84	−4.8	5.7	1.0
	11	−9		1/2	−19/2	+		1527.57	−0.4	5.8	1.0
	12	−9		−1/2	−17/2	+		1615.16	1.1	5.2	1.0
$Q(12\frac{1}{2})$	12	−8		−1/2	−15/2	+	5 999 028.8	1819.88	16.4	4.6	0.0
	12	−12		1/2	−25/2	—		76.05	0.3	6.8	1.0
	12	−11		1/2	−23/2	—		82.72	1.4	6.2	1.0
	12	−10		1/2	−21/2	—		91.19	−0.2	5.7	1.0
	12	−9		1/2	−19/2	—		101.14	0.0	5.1	1.0
	12	−8		1/2	−17/2	—		113.47	0.5	4.6	1.0
	12	−7		1/2	−15/2	—		129.21	1.8	4.0	1.0
	12	−6		1/2	−13/2	—		151.01	−1.8	3.5	1.0
	12	−5		1/2	−11/2	—		179.55	−0.2	2.9	1.0
	12	−4		1/2	−9/2	—		221.75	0.6	2.4	1.0
	12	−12		1/2	−25/2	+		801.68	3.9	6.9	1.0
	12	−11		1/2	−23/2	+		872.30	2.4	6.3	1.0
	13	−13		−1/2	−25/2	+		886.49	2.5	6.9	1.0
	12	−10		1/2	−21/2	+		956.49	0.3	5.8	1.0
	13	−12		−1/2	−23/2	+		962.55	−0.2	6.3	1.0
	13	−11		−1/2	−21/2	+		1052.16	1.1	5.8	1.0
	12	−9		1/2	−19/2	+		1057.70	1.8	5.2	1.0
	13	−10		−1/2	−19/2	+		1160.24	2.5	5.3	1.0

TABLE II. (Continued.)

	$F$	$M_F$	$\leftarrow$	$M_I$	$M_J$	$p$	$\nu_L$ (MHz)	$B_0$ (mT)	o-c (MHz)	$\partial\nu/\partial B_0$ (MHz/mT)	wt
$Q(13\frac{1}{2})$	12	-8		1/2	-17/2	+		1182.77	2.6	4.7	1.0
	13	-9		-1/2	-17/2	+		1294.27	-1.2	4.7	1.0
	12	-7		1/2	-15/2	+		1341.81	0.0	4.1	1.0
	13	-8		-1/2	-15/2	+		1460.84	4.5	4.2	1.0
	14	14		1/2	27/2	-	5 999 028.8	344.58	-0.8	-6.7	1.0
	14	13		-1/2	27/2	-		363.21	-0.2	-6.6	1.0
	14	13		1/2	25/2	-		373.29	-1.5	-6.3	1.0
	14	12		-1/2	25/2	-		391.33	-1.7	-6.1	1.0
	14	12		1/2	23/2	-		406.33	-2.8	-5.8	1.0
	14	11		-1/2	23/2	-		425.02	-1.1	-5.6	1.0
	13	13		-1/2	27/2	-		430.28	-2.5	-6.7	1.0
	13	13		1/2	25/2	-		445.45	5.8	-6.4	1.0
	14	11		1/2	21/2	-		445.45	-3.7	-5.3	1.0
	13	12		-1/2	25/2	-		464.82	1.1	-6.2	1.0
	14	10		-1/2	21/2	-		464.82	-3.2	-5.1	1.0
	13	12		1/2	23/2	-		483.47	-2.8	-5.9	1.0
	14	10		1/2	19/2	-		493.09	-2.4	-4.8	1.0
	13	11		-1/2	23/2	-		504.70	-0.5	-5.7	1.0
	14	9		-1/2	19/2	-		514.34	-0.2	-4.6	1.0
	13	11		1/2	21/2	-		530.20	-2.5	-5.4	1.0
	14	9		1/2	17/2	-		552.67	2.8	-4.3	1.0
	13	10		-1/2	21/2	-		552.67	-0.9	-5.2	1.0
	14	8		-1/2	17/2	-		575.27	0.6	-4.1	1.0
	13	10		1/2	19/2	-		586.77	-1.5	-4.8	1.0
	13	9		-1/2	19/2	-		610.99	-1.6	-4.7	1.0
	13	13		-1/2	27/2	+		1217.35	1.1	-6.7	1.0
	14	14		1/2	27/2	+		1275.29	-1.6	-6.7	1.0
	13	12		-1/2	25/2	+		1315.06	-2.1	-6.2	1.0
	14	13		1/2	25/2	+		1378.55	-0.2	-6.2	1.0
	13	11		-1/2	23/2	+		1431.23	0.7	-5.6	1.0
	14	12		1/2	23/2	+		1499.58	-0.6	-5.7	1.0
	13	10		-1/2	21/2	+		1569.16	-1.4	-5.1	1.0
	14	11		1/2	21/2	+		1643.86	-1.4	-5.2	1.0
	13	9		-1/2	19/2	+		1737.59	-0.8	-4.6	1.0
$Q(14\frac{1}{2})$	15	15		1/2	29/2	+	5 999 028.8	1674.97	-0.1	-6.7	1.0
	15	14		-1/2	29/2	+		1709.27	-23.2	-6.5	0.0
	14	14		-1/2	29/2	+		1763.83	0.3	-6.6	1.0
	15	14		1/2	27/2	+		1799.81	-0.1	-6.2	1.0
$Q(15\frac{1}{2})$	16	-16		-1/2	-31/2	+	6 032 811.3	810.90	2.9	7.2	1.0
	15	-15		1/2	-31/2	+		863.66	3.1	7.2	1.0
	16	-14		1/2	-29/2	+		865.51	-1.8	6.6	1.0
	15	-14		1/2	-29/2	+		924.37	-0.7	6.8	1.0
	16	-14		-1/2	-27/2	+		928.42	1.1	6.3	1.0
	15	-13		1/2	-27/2	+		993.28	0.6	6.3	1.0
	16	-13		-1/2	-25/2	+		1000.87	0.5	5.9	1.0
	15	-12		1/2	-25/2	+		1073.72	-1.0	5.8	1.0
	16	-12		-1/2	-23/2	+		1085.70	-1.0	5.4	1.0
	15	-11		1/2	-23/2	+		1167.48	1.1	5.4	1.0
	16	-11		-1/2	-21/2	+		1185.35	1.4	5.0	1.0
	15	-15		1/2	-31/2	-		1718.98	-3.2	7.3	1.0
	16	-16		-1/2	-31/2	-		1798.69	-1.4	7.3	1.0
	15	-14		1/2	-29/2	-		1836.54	-0.1	6.8	1.0
	16	-15		-1/2	-29/2	-		1920.37	-4.3	6.9	1.0
	15	-13		1/2	-27/2	-		1972.59	-5.7	6.4	1.0
	16	-14		-1/2	-27/2	-		2060.53	-13.8	6.4	0.0
$Q(16\frac{1}{2})$	16	16		-1/2	33/2	-	6 032 811.3	609.55	-0.8	-7.1	1.0
	16	16		1/2	31/2	-		626.29	0.3	-6.9	1.0
	16	15		-1/2	31/2	-		648.58	-1.5	-6.7	1.0
	17	17		1/2	33/2	-		662.77	-2.5	-7.1	1.0
	16	15		1/2	29/2	-		669.42	-3.4	-6.4	1.0
	16	14		-1/2	29/2	-		693.86	2.0	-6.3	1.0
	17	16		1/2	31/2	-		706.80	1.5	-6.7	1.0
	16	13		-1/2	27/2	-		745.23	0.9	-5.8	1.0



TABLE II. (Continued.)

	$F$	$M_F$	$\leftarrow$	$M_I$	$M_J$	$p$	$\nu_L$ (MHz)	$B_0$ (mT)	o-c (MHz)	$\partial\nu/\partial B_0$ (MHz/mT)	wt
	17	15		1/2	29/2	—		756.03	0.5	−6.3	1.0
	16	12		−1/2	25/2	—		805.15	0.4	−5.4	1.0
	16	11		−1/2	23/2	—		876.15	1.8	−4.9	1.0
	17	13		1/2	25/2	—		878.95	3.7	−5.4	1.0
	17	12		1/2	23/2	—		955.30	−0.5	−5.0	1.0
	16	10		−1/2	21/2	—		960.10	−1.1	−4.5	1.0
	17	11		1/2	21/2	—		1047.05	−1.2	−4.5	1.0
	16	9		−1/2	19/2	—		1062.83	−1.8	−4.0	1.0
	17	10		1/2	19/2	—		1158.74	−0.2	−4.1	1.0
	16	−16		1/2	−33/2	+		293.31	−0.5	7.2	1.0
	16	−15		1/2	−31/2	+		312.55	−0.5	6.8	1.0
	16	−14		1/2	−29/2	+		334.15	1.5	6.3	1.0
	16	−13		1/2	−27/2	+		359.29	1.7	5.9	1.0
	17	−17		−1/2	−33/2	+		374.34	1.4	7.2	1.0
	16	−12		1/2	−25/2	+		388.48	2.0	5.4	1.0
	17	−16		−1/2	−31/2	+		397.93	2.0	6.8	1.0
	17	−15		−1/2	−29/2	+		424.52	3.8	6.4	1.0
	17	−14		−1/2	−27/2	+		455.51	2.5	5.9	1.0
	16	−10		1/2	−11/2	+		463.75	2.3	4.6	1.0
	17	−13		−1/2	−25/2	+		491.54	0.2	5.5	1.0
	16	−9		1/2	−19/2	+		513.53	1.7	4.1	1.0
	17	−12		−1/2	−23/2	+		533.08	1.0	5.1	1.0
	16	−8		1/2	−17/2	+		575.01	1.4	3.7	1.0
	17	−11		−1/2	−21/2	+		582.56	0.9	4.6	1.0
	17	−10		−1/2	−19/2	+		641.78	2.6	4.2	1.0
$Q(17\frac{1}{2})$	18	18		1/2	35/2	—	6 032 811.3	1122.30	1.9	−7.1	1.0
	18	17		1/2	33/2	—		1190.75	1.4	−6.7	1.0
	17	17		−1/2	35/2	—		1204.42	0.0	−7.1	1.0
	18	16		1/2	31/2	—		1267.72	−1.3	−6.3	1.0
	17	16		−1/2	33/2	—		1278.89	2.7	−6.7	1.0
	18	15		1/2	29/2	—		1356.06	0.3	−5.9	1.0
	17	15		−1/2	31/2	—		1362.49	0.5	−6.3	1.0
	18	−18		−1/2	−35/2	+	6 061 914.8	1752.14	−0.5	7.7	1.0
	17	−17		1/2	−35/2	+		1801.61	−0.6	7.7	1.0
	18	−17		−1/2	−33/2	+		1855.28	−1.7	7.2	1.0
$Q(18\frac{1}{2})$	17	−16		1/2	−33/2	+		1911.05	−1.6	7.2	1.0
	18	−16		−1/2	−33/2	+		1971.43	−4.4	6.8	1.0
	19	−19		−1/2	−39/2	—	6 061 914.8	187.80	−0.9	7.6	1.0
	19	−18		−1/2	−35/2	—		198.06	0.7	7.2	1.0
	19	−17		−1/2	−33/2	—		209.73	1.1	6.8	1.0
	19	−16		−1/2	−31/2	—		222.81	1.9	6.4	1.0
	18	−18		1/2	−39/2	—		236.68	−0.9	7.6	1.0
	19	−15		−1/2	−29/2	—		236.68	8.5	6.0	0.1
	18	−17		1/2	−35/2	—		250.22	0.8	7.2	1.0
	19	−14		−1/2	−27/2	—		255.23	0.2	5.6	1.0
	18	−16		1/2	−33/2	—		265.56	1.5	6.7	1.0
	19	−13		−1/2	−25/2	—		275.34	−1.2	5.2	1.0
	18	−15		1/2	−31/2	—		283.25	0.1	6.3	1.0
	19	−12		−1/2	−23/2	—		298.39	−0.4	4.8	1.0
	18	−14		1/2	−29/2	—		303.08	0.6	5.9	1.0
	18	−13		1/2	−27/2	—		325.72	2.1	5.5	1.0
	18	−12		1/2	−25/2	—		352.30	2.2	5.1	1.0
	18	−18		1/2	−37/2	+		1193.59	0.1	7.7	1.0
	18	−17		1/2	−35/2	+		1261.52	1.7	7.2	1.0
	19	−19		−1/2	−39/2	+		1270.12	2.1	7.7	1.0
	18	−16		1/2	−33/2	+		1338.14	−0.3	6.8	1.0
	19	−18		−1/2	−37/2	+		1341.41	0.8	7.3	1.0
	19	−17		−1/2	−33/2	+		1421.10	−0.1	6.9	1.0
	18	−15		1/2	−31/2	+		1424.26	−0.6	6.4	1.0
	19	−16		−1/2	−33/2	+		1511.31	−4.4	6.5	1.0
	18	−14		1/2	−29/2	+		1521.91	0.1	6.0	1.0
	19	−15		−1/2	−29/2	+		1612.11	0.4	6.1	1.0
	18	−13		1/2	−27/2	+		1634.15	−1.4	5.6	1.0
	19	−14		−1/2	−27/2	+		1728.14	0.9	5.7	1.0

TABLE II. (Continued.)

	$F$	$M_F$	$\leftarrow$	$M_I$	$M_J$	$p$	$\nu_L$ (MHz)	$B_0$ (mT)	o-c (MHz)	$\partial\nu/\partial B_0$ (MHz/mT)	wt
	18	-12		1/2	-25/2	+		1763.25	0.7	5.2	1.0
	19	-13		-1/2	-25/2	+		1862.28	0.2	5.3	1.0
	18	-11		1/2	-23/2	+		1914.85	-0.2	4.8	1.0
$Q(19\frac{1}{2})$	20	20		1/2	39/2	-	6 061 914.8	309.61	-3.0	-7.6	1.0
	20	19		-1/2	39/2	-		325.72	-18.0	-7.3	0.0
	20	19		1/2	37/2	-		328.28	30.7	-7.4	0.0
	20	18		-1/2	37/2	-		341.22	0.1	-7.0	1.0
	20	18		1/2	35/2	-		347.45	-0.2	-6.9	1.0
	20	17		-1/2	35/2	-		360.55	0.8	-6.6	1.0
	20	17		1/2	33/2	-		368.91	-0.1	-6.5	1.0
	20	16		-1/2	33/2	-		382.74	4.0	-6.3	1.0
	19	19		-1/2	39/2	-		386.61	-2.5	-7.6	1.0
	20	16		1/2	31/2	-		392.31	-4.4	-6.1	1.0
	19	19		1/2	37/2	-		392.31	-0.8	-7.4	1.0
	20	15		-1/2	31/2	-		407.15	2.8	-5.9	1.0
	19	18		-1/2	37/2	-		407.15	-2.3	-7.2	1.0
	19	18		1/2	35/2	-		414.90	-3.5	-7.0	1.0
	20	15		1/2	29/2	-		420.80	2.3	-5.7	1.0
	19	17		-1/2	35/2	-		430.09	-3.0	-6.8	1.0
	20	14		-1/2	29/2	-		434.72	-0.1	-5.5	1.0
	19	19		-1/2	39/2	+		1384.91	0.2	-7.5	1.0
	20	20		1/2	39/2	+		1434.02	-1.2	-7.5	1.0
	19	18		-1/2	37/2	+		1460.83	0.9	-7.1	1.0
	20	19		1/2	37/2	+		1512.73	-0.0	-7.1	1.0
	19	17		-1/2	35/2	+		1545.44	0.1	-6.7	1.0
	19	16		-1/2	33/2	+		1640.69	-0.3	-6.3	1.0
	20	17		1/2	33/2	+		1698.87	-0.1	-6.3	1.0
	19	15		-1/2	31/2	+		1748.60	-0.9	-5.9	1.0
	20	16		1/2	31/2	+		1810.30	-0.2	-5.9	1.0
	19	14		-1/2	29/2	+		1872.13	-0.4	-5.5	1.0
	20	15		1/2	29/2	+		1937.50	-0.4	-5.5	1.0
$Q(20\frac{1}{2})$	21	21		1/2	41/2	+	6 061 914.8	1941.29	-0.8	-7.5	1.0
$R(2\frac{1}{2})$	4	4		1/2	5/2	-	6 153 279.0	992.23	-0.1	-11.9	1.0
	4	3		-1/2	5/2	-		1021.04	-1.3	-11.8	1.0
	3	3		-1/2	5/2	-		1049.00	-3.7	-11.9	1.0
	3	3		-1/2	5/2	+		1137.92	-7.5	-11.9	0.1
	4	4		1/2	5/2	+		1164.58	-5.3	-11.9	1.0
	4	3		1/2	3/2	-		1619.03	3.5	-7.6	1.0
	4	2		-1/2	3/2	-		1656.23	0.6	-7.5	1.0
	3	3		1/2	3/2	-		1659.37	0.2	-7.6	1.0
	3	2		-1/2	3/2	-		1702.18	-1.1	-7.5	1.0
	3	2		-1/2	3/2	+		1838.23	-7.7	-7.6	0.1
	4	3		1/2	3/2	+		1886.63	-8.0	-7.6	0.1
$R(4\frac{1}{2})$	6	5		1/2	9/2	-	6 290 222.3	779.39	-1.1	-8.6	1.0
	6	4		-1/2	9/2	-		808.68	-3.2	-8.4	1.0
	5	4		-1/2	9/2	-		854.26	-1.5	-8.5	1.0
	6	4		1/2	7/2	-		1000.02	-0.6	-6.7	1.0
	6	3		-1/2	7/2	-		1033.72	-2.7	-6.6	1.0
	5	4		1/2	7/2	-		1055.61	-1.2	-6.8	1.0
	5	4		-1/2	9/2	+		1085.58	-1.2	-8.5	1.0
	5	3		-1/2	7/2	-		1092.89	-1.8	-6.6	1.0
	6	5		1/2	9/2	+		1126.59	1.6	-8.5	1.0
	5	3		-1/2	7/2	+		1387.42	-1.0	-6.6	1.0
	6	3		1/2	5/2	-		1387.42	0.0	-4.9	1.0
	6	4		1/2	7/2	+		1441.53	0.2	-6.7	1.0
	6	2		-1/2	5/2	-		1432.74	-0.6	-4.8	1.0
	5	3		1/2	5/2	-		1465.07	-1.3	-4.9	1.0
	6	3		-1/2	7/2	+		1485.11	-0.2	-6.5	1.0
	5	2		-1/2	5/2	-		1517.31	-0.0	-4.8	1.0
	5	2		-1/2	5/2	+		1918.91	-0.5	-4.9	1.0
	6	3		1/2	5/2	+		1991.95	2.8	-4.9	1.0
	6	6		1/2	9/2	-		768.28	-1.2	-8.7	1.0

TABLE II. (Continued.)

	<i>F</i>	<i>M<sub>F</sub></i>	←	<i>M<sub>I</sub></i>	<i>M<sub>J</sub></i>	<i>p</i>	<i>ν<sub>L</sub></i> (MHz)	<i>B<sub>0</sub></i> (mT)	o-c (MHz)	<i>∂ν/∂B<sub>0</sub></i> (MHz/mT)	wt
	6	5		−1/2	9/2	−		797.13	−1.9	−8.5	1.0
	5	5		−1/2	9/2	−		840.46	0.2	−8.6	1.0
	6	5		1/2	7/2	−		981.96	−0.8	−6.8	1.0
	6	4		−1/2	7/2	−		1015.14	0.3	−6.7	1.0
	5	5		1/2	7/2	−		1034.24	0.1	−6.9	1.0
	5	5		−1/2	9/2	+		1066.23	0.5	−8.6	1.0
	5	4		−1/2	7/2	−		1070.53	0.9	−6.8	1.0
	6	6		1/2	9/2	+		1108.19	−0.7	−8.6	1.0
	6	5		−1/2	9/2	+		1142.79	1.2	−8.5	1.0
	5	5		1/2	7/2	+		1313.29	0.4	−7.0	1.0
	5	4		−1/2	7/2	+		1356.19	1.7	−6.8	1.0
	6	4		1/2	5/2	−		1354.08	3.1	−5.0	1.0
	6	3		−1/2	5/2	−		1396.86	0.3	−4.9	1.0
	6	5		1/2	7/2	+		1411.98	−0.0	−6.8	1.0
	5	4		1/2	5/2	−		1424.55	−0.9	−5.1	1.0
	6	4		−1/2	7/2	+		1454.28	1.7	−6.7	1.0
	5	3		−1/2	5/2	−		1473.89	−1.2	−4.9	1.0
	5	4		1/2	5/2	+		1798.48	−1.2	−5.2	1.0
	5	3		−1/2	5/2	+		1859.66	−0.9	−5.0	1.0
	6	4		1/2	5/2	+		1936.67	2.1	−5.1	1.0
	6	3		−1/2	5/2	+		1997.68	6.9	−4.9	0.1
<i>R</i> (7 <sup>1</sup> / <sub>2</sub> )	9	9		1/2	15/2	+	6 493 911.5	695.29	−0.3	−7.0	1.0
	8	8		−1/2	15/2	+		780.13	0.4	−7.0	1.0
	9	8		1/2	13/2	+		800.33	−1.7	−6.1	1.0
	8	7		−1/2	13/2	+		896.64	0.5	−6.1	1.0
	9	7		1/2	11/2	+		942.44	0.3	−5.2	1.0
	9	6		−1/2	11/2	+		976.75	−0.7	−5.1	1.0
	8	6		−1/2	11/2	+		1054.80	0.3	−5.2	1.0
	9	6		1/2	9/2	+		1143.76	−0.2	−4.3	1.0
	9	5		−1/2	9/2	+		1186.25	1.4	−4.2	1.0
	8	6		1/2	9/2	+		1234.53	1.3	−4.4	1.0
	8	8		−1/2	15/2	−		1242.78	1.4	−7.0	1.0
	8	5		−1/2	9/2	+		1282.22	2.1	−4.2	1.0
	9	9		1/2	15/2	−		1298.19	1.7	−7.0	1.0
	8	7		−1/2	13/2	−		1428.20	0.7	−6.1	1.0
	9	8		1/2	13/2	−		1492.57	1.3	−6.1	1.0
	9	4		−1/2	7/2	+		1509.75	0.6	−3.3	1.0
	8	6		−1/2	11/2	−		1679.09	−0.1	−5.2	1.0
	9	7		1/2	11/2	−		1754.51	0.5	−5.2	1.0

stants *B*<sub>0</sub> and *D*<sub>0</sub>, which are better determined in the Fourier transform investigation,<sup>4</sup> possibly because more high-*J* lines were included. The determination of the full set of magnetic hyperfine parameters arises from the detection of resolved hyperfine structures involving both spin states and both lambda doublets. All these parameters have been fitted in the present analysis and are shown in Table III. The zero-field transitions predicted using the final parameters of Table III are given in Table IV.

The magnitude  $|A|$  of the spin-orbit interaction term can be estimated from the atomic spin-orbit constants  $\xi_F$  and  $\xi_O$  according to the equation

$$|A| = c_F^2 |\xi_F| + c_O^2 |\xi_O|, \tag{13}$$

once the expansion coefficients of the atomic orbitals are known. Where possible, the coefficient *c<sub>F</sub>* is evaluated from the hyperfine structure parameters. Although several methods have been used in previous work,<sup>18,19</sup> we think that the most reliable procedure is based on the relationship  $c_F^2 = \frac{2}{3} h_{3/2} / A_{3/2}$ , where *A*<sub>3/2</sub> is the magnetic hyperfine parameter

determinable for atomic F in the <sup>2</sup>*P*<sub>3/2</sub> state and *h*<sub>3/2</sub> is equal to  $a + (1/2)(b + c)$ . If the overlap integral is included,<sup>18</sup> *c*<sub>F</sub><sup>2</sup> and *c*<sub>O</sub><sup>2</sup> turn out to be 0.226 and 0.844, respectively, and  $|A|$  is 188 cm<sup>−1</sup>, which is close to the experimental value. If the calculation is repeated with different methods (such as estimating *c<sub>F</sub>* from atomic and molecular values for the  $J = \frac{1}{2}$  and  $\Omega = \frac{1}{2}$  components),  $|A|$  varies between 176 and 206 cm<sup>−1</sup>.

The lambda-doubling parameters have been reliably determined; however, the set of data is not extended enough to allow the determination of the centrifugal distortion correction, which has been constrained to the literature value.<sup>3</sup>

The magnetic hyperfine constants are related to the electronic wave functions<sup>20</sup> and provide useful information on the distribution of the unpaired electron(s) in the molecule. The hyperfine parameter *a* is related to the orbital distribution  $\langle r^{-3} \rangle_I$ , where *r* is the distance between the unpaired electron and the F nucleus; the Fermi contact parameter *b<sub>F</sub>* is a measure of the spin density at the nucleus  $|\Psi(0)|^2$ ; *c* and *d* are associated to the angular spin distribution,  $\langle (3 \cos^2 \theta$

TABLE III. Molecular parameters obtained for FO in the  $^2\Pi$  state.

Parameter <sup>a</sup>	This work	Previous works
$B_0$	31 539.819(94)	31 539.450(33) <sup>b</sup>
$D_0$	0.129 79(44)	0.128 935(33) <sup>b</sup>
$10^7 H_0$	-0.39 <sup>c</sup>	
$A_0/\text{cm}^{-1}$	-196.108 686(50)	-193.28(97) <sup>b</sup>
$A_D$	12.052(10)	16.8(16) <sup>b</sup>
$p+2q$	428.104(61)	438.7(18) <sup>b</sup>
$10^2(p_D+2q_D)$	-0.45	-0.45(120) <sup>c</sup>
$q$	-1.5255(94)	-2.1 <sup>b</sup>
$a$	779.4(16)	696(18) <sup>d</sup>
$b$	406.3(20)	
$b+c$	-196.1(22)	
$d$	977.79(46)	
$g_L$	0.999 34(14)	
$g_S$	2.001 11(22)	
$10^4 g_I$	0.112 7(28)	
$10^4 g_r$	-0.93(17)	
$10^4 g'_r$	0.477(68)	
$10^2(g'_I - g'_r)$	0.688 6(37)	
$g_N$	5.257 73	
$\sigma^f$	1.9	
No. of trans.	290	

<sup>a</sup>Values in MHz where appropriate. The numbers in parentheses represent one standard deviation of the least-squares fit, in units of the last quoted decimal place. Parameters with no standard deviation are held fixed in the present analysis.

<sup>b</sup>Reference 4.

<sup>c</sup>Reference 3.

<sup>d</sup>Reference 1. This is a value for  $h_{3/2}=a+1/2(b+c)$ . Our value for this parameter is 681.4(19) MHz.

<sup>e</sup>Calculated value.

<sup>f</sup> $\sigma$  is the overall standard deviation of the fit.

$-1/r^3\rangle_s$  and  $\langle(\sin^2\theta)/r^3\rangle_s$ , respectively, where  $\theta$  is the angle between the vector  $\mathbf{r}$  and the internuclear axis. The above-mentioned expectation values for FO, CF,<sup>21</sup> and the F atom<sup>22</sup> are given in Table V.

The spin average  $\langle r^{-3}\rangle_s$  can be calculated from  $d+c/3$  by giving  $\langle\pi|\sin^2\theta|\pi\rangle$  a value of 4/5 and  $\langle\pi|3\cos^2\theta-1|\pi\rangle$  a value of -2/5, which are correct for atomic  $p_\pi$  orbitals and good approximations for molecular  $\pi$  orbitals. The ratios  $\langle r^{-3}\rangle_s:\langle(3\cos^2\theta-1)/r^3\rangle_s:\langle(\sin^2\theta)/r^3\rangle_s$ , expected to be 1: -0.4: 0.8 for a  $p_\pi$  atomic orbital are 1: -0.52: 0.84 for FO and 1: -0.35: 0.78 for CF.<sup>14</sup> These values, greater than the corresponding atomic ratios, suggest that the unpaired electron in FO is in an orbital which is slightly polarized from a pure  $p$  orbital.

A full set of  $g$  factors, shown in Table III, has been determined in the present work (see Refs. 16 and 23 for a detailed description of the Zeeman parameters). Estimates of some of the  $g$  factors can be obtained from the relationships

$$g_I = -\gamma/2B, \quad (14)$$

$$g'_I \approx p/2B, \quad (15)$$

$$g'_r \approx -q/B, \quad (16)$$

$$g'_I - g'_r \approx (p+2q)/2B. \quad (17)$$

TABLE IV. Predicted fine-structure transitions of FO in zero magnetic field.

Transition	$\nu$ (MHz)	$p$	$\nu$ (MHz)	$p$
$P(10\frac{1}{2})$	5 317 782.5	+	5 313 496.8	-
$P(9\frac{1}{2})$	5 370 246.3	+	5 374 103.4	-
$P(8\frac{1}{2})$	5 431 083.1	+	5 427 654.6	-
$P(7\frac{1}{2})$	5 485 721.6	+	5 488 721.5	-
$P(6\frac{1}{2})$	5 547 018.2	+	5 544 447.0	-
$P(5\frac{1}{2})$	5 603 829.9	+	5 605 972.3	-
$P(4\frac{1}{2})$	5 665 583.0	+	5 663 869.2	-
$P(3\frac{1}{2})$	5 724 563.5	+	5 725 848.7	-
$P(2\frac{1}{2})$	5 786 767.6	+	5 785 911.0	-
$P(1\frac{1}{2})$	5 847 909.6	+	5 848 337.9	-
$Q(1\frac{1}{2})$	5 943 652.0	+	5 942 796.2	-
$Q(2\frac{1}{2})$	5 944 193.1	+	5 945 475.9	-
$Q(3\frac{1}{2})$	5 947 942.2	+	5 946 233.5	-
$Q(4\frac{1}{2})$	5 948 916.4	+	5 951 049.5	-
$Q(5\frac{1}{2})$	5 954 796.2	+	5 952 240.4	-
$Q(6\frac{1}{2})$	5 956 203.9	+	5 959 180.1	-
$Q(7\frac{1}{2})$	5 964 198.9	+	5 960 804.8	-
$Q(8\frac{1}{2})$	5 966 040.8	+	5 969 850.0	-
$Q(9\frac{1}{2})$	5 976 130.2	+	5 971 909.3	-
$Q(10\frac{1}{2})$	5 978 407.1	+	5 983 036.3	-
$R(1\frac{1}{2})$	6 101 077.5	+	6 102 361.2	-
$R(2\frac{1}{2})$	6 167 571.8	+	6 165 860.7	-
$R(3\frac{1}{2})$	6 231 275.6	+	6 233 413.8	-
$R(4\frac{1}{2})$	6 299 882.6	+	6 297 317.5	-
$R(5\frac{1}{2})$	6 363 981.8	+	6 366 973.5	-
$R(6\frac{1}{2})$	6 434 681.1	+	6 431 263.4	-
$R(7\frac{1}{2})$	6 499 156.6	+	6 503 000.2	-
$R(8\frac{1}{2})$	6 571 924.8	+	6 567 655.8	-
$R(9\frac{1}{2})$	6 636 754.9	+	6 641 448.8	-
$R(10\frac{1}{2})$	6 711 565.7	+	6 706 447.3	-

The calculated values for  $g'_r$  ( $0.484\times 10^{-4}$ ) and  $g'_I - g'_r$  ( $0.6787\times 10^{-2}$ ) are in excellent agreement with the observed values  $0.477\times 10^{-4}$  and  $0.6886\times 10^{-2}$ .

The orbital  $g$  factor  $g_L$  can be expressed as a sum of a main term (1.0) plus relativistic ( $\langle\delta g_{\text{rel}}\rangle_{\text{av}}$ ), orbit-orbit ( $\langle\delta g_{\text{orb}}\rangle_{\text{av}}$ ), and nonadiabatic ( $\Delta g_L$ ) contributions.<sup>10,24</sup> The electron spin  $g$  factor corrected for quantum electrodynamic and relativistic effects is  $g_S=2.002\,32(1+\langle\delta g_{\text{rel}}\rangle_{\text{av}})$ . The relativistic correction can therefore be estimated from the experimental value for  $g_S$  and is  $-6.0\times 10^{-4}$  for FO. Assuming that the orbit-orbit and nonadiabatic contributions are negligible compared with the relativistic term,<sup>10</sup>  $g_L$  can be calculated using the relationship  $g_L=1.0+\langle\delta g_{\text{rel}}\rangle_{\text{av}}=1.0-6.0\times 10^{-4}=0.9994$ , which is in excellent agreement with the experimental value 0.999 34(14). The nonadiabatic contribution can also be estimated from the relationship  $\Delta g_L=q/2B$ . The calculated value of  $2.4\times 10^{-5}$  confirms that the contribution  $\langle\delta g_{\text{rel}}\rangle_{\text{av}}$  is dominant. This relativistic contribution can be calculated from the corresponding

TABLE V. Hyperfine structure parameters (in MHz) and expectation values of distribution functions over the electronic wave function (in  $m^{-3}$ ) of  $^{19}\text{F}$  for FO, CF, and atomic fluorine.

Parameter	FO <sup>a</sup>	CF <sup>b</sup>	F <sup>c</sup>
$a$	779.4(16)	705.94(14)	
$b_F$	205.5(15) <sup>d</sup>	151.19(49)	
$c$	-602.4(30) <sup>d</sup>	-351.6(14)	
$d$	977.79(46)	792.195(98)	
$10^{-30}\langle r^{-3} \rangle_l$	10.485	9.502	4.96
$10^{-29}\Psi(0)^2$	3.2997	2.429	4.84
$10^{-30}\langle (3\cos^2\theta-1)/r^3 \rangle_s$	-5.4027	-3.151	
$10^{-30}\langle (\sin^2\theta)/r^3 \rangle_s$	8.7691	7.100	
$10^{-30}\langle r^{-3} \rangle_s$	10.452	9.075	5.49

<sup>a</sup>This work.<sup>b</sup>Reference 21.<sup>c</sup>Reference 22.<sup>d</sup>Derived parameter.

atomic values for F<sup>10</sup> and O,<sup>24</sup> which are, respectively,  $-1.8$  and  $-1.3 \times 10^{-4}$ . It is given by

$$\langle \delta g_{\text{rel}} \rangle_{\text{av,FO}} = c_F^2 \langle \delta g_{\text{rel}} \rangle_{\text{av,F}} + c_O^2 \langle \delta g_{\text{rel}} \rangle_{\text{av,O}}, \quad (18)$$

using values for the coefficients  $c_F^2$  and  $c_O^2$  determined from the magnetic hyperfine parameters. The result is  $-1.5 \times 10^{-4}$ , which is remarkably different from the experimental value of  $-6.0 \times 10^{-4}$  but consistent with the values calculated by Veseth<sup>25</sup> for other molecules, such as OH, SH, NO, NS, and ClO.

If values for  $B$  and  $\gamma$  are known, the parameter  $g_I$  should be predictable from Curl's relationship, Eq. (14). Although we know the value for  $B$  very precisely, we have not determined a value for the spin-rotation parameter  $\gamma$  in our fit because it is completely correlated with the parameter  $A_D$ . Brown and Watson<sup>26</sup> have shown that, in a fit of the parameters of a  $^2\Pi$  Hamiltonian to a set of data, one can either chose to constrain  $\gamma$  to zero and determine a value for the effective centrifugal distortion correction to the spin-orbit coupling  $\tilde{A}_D$ , where

$$\tilde{A}_D = A_D - \gamma \frac{2B}{(A-2B)} \quad (19)$$

or one can constrain  $A_D$  to zero and determine a value for an effective spin-rotation parameter  $\tilde{\gamma}$ , where

$$\tilde{\gamma} = \gamma - A_D \frac{(A-2B)}{2B}. \quad (20)$$

We can estimate the value for  $\gamma$  by using Eq. (20) and substituting the values of  $A_D$  (strictly  $\tilde{A}_D$ ),  $A$  and  $B$  from Table III. This is actually a value for  $\tilde{\gamma}$  but, if  $A_D$  happened to be very small, it would be close to the true value for  $\gamma$ . Substitution of this value in Eq. (14) gives a value for  $g_I$  of  $-0.018$ , which is very different from the experimental value of  $0.01127$ . Similar behavior is shown for the energy levels of CF;<sup>21</sup> the authors in that case suggested that the discrepancy was attributable to an inexact interpretation of the effective parameters in the Hamiltonian (in other words, the assumption which we have made that  $A_D$  is very small is not valid).

The constraint of the parameter  $A_D$  or  $\gamma$  to zero in the fit has the effect of modifying several parameters in the Hamiltonian. If we apply Brown and Watson's unitary transformation to the Zeeman Hamiltonian, we can show that the parameter  $g_I$  is one which is affected and so becomes an effective parameter  $\tilde{g}_I$  where

$$\tilde{g}_I = g_I - \frac{\gamma}{(A-2B)}(g_L + g_S), \quad (21)$$

if  $\gamma$  is constrained to zero or

$$\tilde{g}_I = g_I - \frac{A_D}{2B}(g_L + g_S), \quad (22)$$

if  $A_D$  is constrained to zero. Thus the value determined in the fit,  $\tilde{g}_I$ , will differ from the value  $g_I$  according to whichever of these two equations applies. If we accept the correctness of Curl's relationship, Eq. (14), and substitute for  $g_I$  in Eq. (21), we can rearrange the result to give an expression for  $\gamma$  in terms of experimentally determinable parameters:

$$\gamma = - \frac{2B(A-2B)\tilde{g}_I}{\{A-2B[1-(g_L+g_S)]\}}. \quad (23)$$

Substitution of values from Table III in Eq. (23) gives a value for  $\gamma$  (the true spin-rotation constant) of  $-734.3$  MHz, from which we determine that the true value for  $g_I = -\gamma/2B$  is  $0.01164$ . This latter value is now much closer to the effective value for  $\tilde{g}_I$  of  $0.01127$  than our earlier estimate because the correction term on the right-hand side of Eq. (21) is comparatively small. If this determination of the value for  $\gamma$  is valid, we can use it to derive a value for  $A_D$  from that of the experimentally determined parameter  $\tilde{A}_D$  by use of Eq. (19). In this case, the value for  $A_D$  is  $19.847$  MHz, compared with  $\tilde{A}_D = 12.052$  MHz. A detailed description of the contact transformation of the Zeeman Hamiltonian is given in the Appendix.

In this paper we have described the detection of the fine-structure transition  $^2\Pi_{1/2} \leftarrow ^2\Pi_{3/2}$  in the FO radical by far-infrared laser magnetic resonance. The spin-orbit constant  $A_0$ , all four magnetic hyperfine parameters  $a$ ,  $b_F$ ,  $c$ ,  $d$ , and a full set of  $g$  factors have been determined for the first time. The recorded data form the most accurate measurements on FO to date. Given sufficient sensitivity, it should be possible to detect magnetic dipole, pure rotational transitions in the microwave region. The predicted frequencies are given in Table VI. We intend to make these observations in the near future.

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TABLE VI. Predicted magnetic dipole rotational transitions of FO in the  $^2\Pi_{3/2}$  spin state.

$J'$	$F'$	$\leftarrow$	$J$	$F$	$p$	$\nu$ (MHz)
5/2	3		3/2	2	+	156 827.1
5/2	3		3/2	2	-	156 828.1
5/2	2		3/2	1	+	157 019.5
5/2	2		3/2	1	-	157 020.1
7/2	4		5/2	3	+	219 598.4
7/2	4		5/2	3	-	219 595.8
7/2	3		5/2	2	+	219 686.7
7/2	3		5/2	2	-	219 684.7
9/2	5		7/2	4	+	282 339.4
9/2	5		7/2	4	-	282 345.0
9/2	4		7/2	3	+	282 390.9
9/2	4		7/2	3	-	282 395.3
11/2	6		9/2	5	+	345 073.6
11/2	6		9/2	5	-	345 063.6
11/2	5		9/2	4	+	345 105.6
11/2	5		9/2	4	-	345 097.2
13/2	7		11/2	6	+	407 768.1
13/2	7		11/2	6	-	407 784.5
13/2	6		11/2	5	+	407 791.8
13/2	6		11/2	5	-	407 806.0
15/2	8		13/2	7	+	470 476.0
15/2	8		13/2	7	-	470 450.9
15/2	7		13/2	6	+	470 490.8
15/2	7		13/2	6	-	470 468.8

## APPENDIX: TRANSFORMATION OF THE ZEEMAN AND MAGNETIC HYPERFINE STRUCTURE HAMILTONIANS

In a previous paper,<sup>26</sup> Brown and Watson transformed the spin-orbit Hamiltonian and demonstrated that  $\gamma$  and  $A_D$  are totally correlated for a molecule in a  $^2\Pi$  state. In this section, we will apply the same contact transformation to the Zeeman and magnetic hyperfine structure Hamiltonians.

Generally speaking, the procedure consists of calculating an effective Hamiltonian  $\tilde{H}$  from an original operator  $H$  through a unitary transformation of the form

$$\tilde{H} = e^{iU} H e^{-iU} = H + i[U, H] + \dots, \quad (\text{A1})$$

where  $U$  is a suitable operator. The appropriate choice for  $U$  is  $\theta\{L_z(J_x S_y - J_y S_x)\}$  where  $\theta$  is a parameter which will be defined later.

For the moment let us consider just the Zeeman Hamiltonian, which has the form

$$H_Z = g_L \mu_B B_0 L_z + g_S \mu_B B_0 S_z - g_r \mu_B B_0 N_z + g_I \mu_B (S_x B_x + S_y B_y), \quad (\text{A2})$$

where the smaller terms, depending on  $g_N$ ,  $g_r'$  and  $g_l'$  have not been included [see Eq. (10)]. The calculation of the commutator  $[U, H_Z]$  gives five terms:

$$(i) \quad i \mu_B B_0 \theta g_L (\Phi_{Zx} S_x + \Phi_{Zy} S_y) L_z^2, \quad (\text{A3})$$

$$(ii) \quad -i \mu_B B_0 \theta \{g_S [\Phi_{Zx} (J_x - S_x) + \Phi_{Zy} (J_y - S_y)] + (g_l + g_r) (\Phi_{Zx} J_x + \Phi_{Zy} J_y)\} L_z S_z, \quad (\text{A4})$$

$$(iii) \quad i \mu_B B_0 \theta (g_S + g_r) \Phi_{Zz} L_z (\mathbf{J} \cdot \mathbf{S} - J_z S_z), \quad (\text{A5})$$

$$(iv) \quad -i \mu_B B_0 \theta (g_S + g_l + g_r) \Phi_{Zz} L_z (S^2 - S_z^2), \quad (\text{A6})$$

$$(v) \quad i \mu_B B_0 \theta g_r (\Phi_{Zx} S_x + \Phi_{Zy} S_y) L_z J_z, \quad (\text{A7})$$

where  $\Phi_{Ff}$  is a direction cosine. Terms (i) and (iii) are contributions to  $g_l$  and give rise only to matrix elements off-diagonal in  $\Omega$  and  $\Sigma$ . The expectation value of term (ii) is zero when calculated over the Hermitian average. Term (iv) is a contribution to  $g_L$  and term (v) is not considered because it is negligible. For a  $^2\Lambda$  state, the matrix elements of term (i) diagonal in  $J$  and  $M_J$  and off-diagonal in  $\Omega$  are of the form

$$i \mu_B B_0 \theta g_L \Lambda^2 M_J \frac{[(J - \Omega)(J + \Omega + 1)]^{1/2}}{2J(J + 1)}, \quad (\text{A8})$$

where the corresponding matrix elements of term (iii) are

$$i \mu_B B_0 \theta g_S \Lambda^2 M_J \frac{[(J - \Omega)(J + \Omega + 1)]^{1/2}}{2J(J + 1)}. \quad (\text{A9})$$

Brown and Watson showed<sup>26</sup> that, if  $A_D$  is fitted and  $\gamma$  is constrained to zero, the transformation parameter  $\theta$  should be set equal to  $\gamma/[(A - 2B)\Lambda^2]$ . Substituting these matrix elements in Eq. (A1), we obtain the effective values for  $\tilde{g}_l$  and  $\tilde{g}_L$ ,

$$\tilde{g}_l = g_l - \frac{\gamma}{(A - 2B)} (g_L + g_S), \quad (\text{A10})$$

$$\tilde{g}_L = g_L + \frac{\gamma}{2(A - 2B)\Lambda^2} (g_S + g_l + g_r). \quad (\text{A11})$$

The same transformation also modifies the nuclear hyperfine Hamiltonian. The untransformed hyperfine Hamiltonian is given by

$$H_{\text{hfs}} = a I_z L_z + b (I_x S_x + I_y S_y) + (b + c) I_z S_z + \frac{1}{2} d (e^{-2i\phi} I_+ S_+ + e^{2i\phi} I_- S_-). \quad (\text{A12})$$

The first term does not contribute to the transformed Hamiltonian because it commutes with  $U$ . The second and fourth terms have zero matrix elements when the Hermitian average is taken. The third term is the only one which needs to be calculated. The evaluation of the commutator gives

$$[U, (b + c) I_z S_z] = i \theta (b + c) (\mathbf{J} \cdot \mathbf{S} - J_z S_z) L_z I_z \quad (\text{A13})$$

and the matrix elements diagonal in  $J$ ,  $M_J$ , and  $M_I$ , and off-diagonal in  $\Omega$  are

$$i \theta (b + c) \Lambda^2 \frac{[(J - \Omega)(J + \Omega + 1)]^{1/2}}{2J(J + 1)} M_J M_I. \quad (\text{A14})$$

Substituting  $\theta = \gamma/[(A - 2B)\Lambda^2]$  we obtain

$$- \frac{\gamma}{(A - 2B)} (b + c) \frac{[(J - \Omega)(J + \Omega + 1)]^{1/2}}{2J(J + 1)} M_J M_I. \quad (\text{A15})$$

The magnetic hyperfine matrix elements off-diagonal in  $\Omega$  and diagonal in  $J$ ,  $M_J$ , and  $M_I$  are

$$\left(b_F - \frac{c}{3}\right) \frac{[(J-\Omega)(J+\Omega+1)]^{1/2}}{2J(J+1)} M_J M_I. \quad (\text{A16})$$

Since  $b_F - c/3 = b$  we can finally write the effective hyperfine parameter

$$\tilde{b} = b - \frac{\gamma}{(A-2B)}(b+c), \quad (\text{A17})$$

where  $\gamma$  is constrained to zero in the fit. The parameter determined in a fit of data which show nuclear hyperfine structure is  $\tilde{b}$ , not  $b$ . Care must therefore be taken in the interpretation of such parameters in terms of the electronic structure of the molecule.

Similar modifications of nuclear hyperfine parameters have been described by Adam *et al.*<sup>27</sup> However, their effects arise from mixing with different (but nearby) electronic states whereas that given in Eq. (A17) arises entirely within the  $^{2S+1}\Lambda$  state, from the procedure adopted to fit the experimental measurements.

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