$^{19}F^+$ atom in its ground ^3P state: The $J=0\leftarrow1$ fine-structure interval

John M. Brown*
The Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, England

Lyndon R. Zink and Kenneth M. Evenson
Time and Frequency Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80303

(Received 1 December 1997)

The $J=0\leftarrow1$ fine-structure transition in the atomic ion F^+ in its ground ^3P state has been detected in the laboratory by far-infrared laser magnetic resonance. The fine-structure interval has been measured accurately as 4 453 253.2±1.6 MHz (148.544 537±0.000 053 cm^{-1}) which corresponds to a wavelength of 67.319 877 ±0.000 015 μm. The hyperfine splitting for the ^{19}F nucleus was also observed and its measured value is in fair agreement with predictions based on *ab initio* wave functions. [S1050-2947(98)07204-7]

PACS number(s): 32.30.−r, 32.60.+i, 32.10.Fn

I. INTRODUCTION

Laser magnetic resonance (LMR) has proved itself to be a very powerful technique for the direct and accurate measurement of fine-structure intervals in atoms and molecules, in both far-infrared and mid-infrared regions [1,2]. In the far-infrared region, the intervals have been measured for O atoms [3,4], C atoms [5,6], Si atoms [7], N atoms in the metastable ^2D state [8], Mg atoms in the metastable ^3P state [9], and for two atomic ions, N^+ [10] and C^+ [11]. In these experiments, the atoms were generated in the gas phase by chemical reactions or electric discharges. The obstacle to extension of these observations to shorter wavelengths in the far infrared (100–25 μm) was the lack of available laser lines in this region of the spectrum. We have recently made a simple improvement to the design of the far-infrared laser which increases its efficiency at short wavelengths. In consequence, the laser in our LMR spectrometer can be made to oscillate on many more lines in this spectral region, several of which had not been discovered previously. We have used these new lines to detect several other fine-structure transitions in atoms, including the $^3P_2$-$^3P_1$ transition in Si [12], the $^3P_0$-$^3P_1$ transition in S [13], the $^5D_0$-$^5D_1$ and $^5D_1$-$^5D_2$ transitions in atomic Fe [14], the $^3P_1$-$^3P_0$ transition in P^+ [15], the $^2P_{3/2}$-$^2P_{1/2}$ transition in Al [16], and the $^6D_{1/2}$-$^6D_{3/2}$ and $^6D_{3/2}$-$^6D_{5/2}$ transitions in Fe^+ [17].

We have also developed a new design of microwave discharge source for the production of ions and molecules in excited states in the sample region of the LMR spectrometer. With this source, we have been able to record the spectrum of N^+ in its ground ^3P state with a much better signal-to-noise ratio than previously. In particular, we have detected the $J=1\leftarrow0$ transition and measured its frequency accurately [18]. We have also used the discharge source to make the measurements of the F^+ ion at 67.3 μm reported in this paper.

F^+ is isoelectronic with atomic O and has an inverted ^3P ground state, arising from the $2p^4$ configuration. The relative positions of its spin-orbit components are shown in Fig. 1. These values are taken from Moore's compilation [19] and are based on even earlier optical measurements by Edlén [20]. Rather surprisingly, no improvement on these numbers appears to have been made in the intervening 60 years. F^+ is a small enough species that its structure can be calculated by *ab initio* methods. For example, configuration interaction

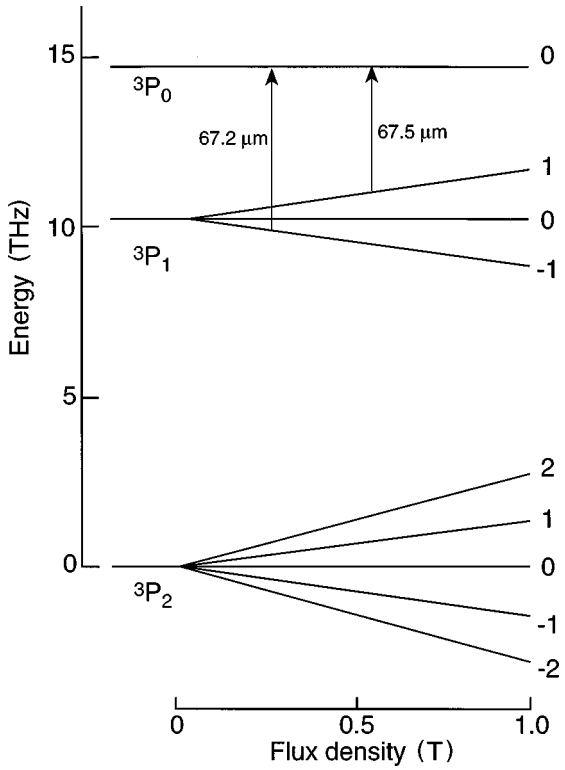

FIG. 1. The energy level diagram for the F^+ atom in its ground ^3P state, at zero field and in the presence of an applied magnetic field. The Zeeman splittings are exaggerated for the sake of clarity. The detected transitions are indicated at the observed magnetic fields. The separation between the $J=1$ and 2 levels corresponds to a wavelength of 29.3 μm.

*Author to whom correspondence should be addressed. Address correspondence to The Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, England. FAX: (44)-1865-275410. Electronic address: jmb@physchem.ox.ac.uk

wave functions for F^+ in its ^3P state have been computed by Schaefer and Klemm and have been used to predict first-order expectation values for the operators involved in the nuclear hyperfine interactions of this atom [21]. The results reported in this paper provide an experimental test of these calculations.

II. EXPERIMENTAL DETAILS

The LMR spectrometer used in this work has been described elsewhere [22] and the details are not repeated here. As described in our recent paper [12], we have improved the sensitivity of the apparatus by raising the Zeeman modulation frequency to 40 kHz. We have also modified the spectrometer to enhance its performance at wavelengths shorter than 100 μm by reducing the inside diameter of the polished copper pump tube from 50.8 to 19.1 mm (from 2 to $\frac{3}{4}$ in.). This provides much better overlap between the pumped lasing gas and the far-infrared radiation field within the laser cavity and many more short wavelength laser lines oscillate. In particular, we have used two such lines to study the $J=0\leftarrow 1$ fine-structure transition in F^+. One was the 67.5 μm line of CH_3OH, pumped by the $9R(18)$ line of CO_2, which has been reported previously by Petersen *et al.* [23]. This line did not lase in the previous configuration of the LMR spectrometer with the larger bore pump tube but did so fairly readily in the new arrangement. The other laser line was the 67.2 μm line of NH_3, pumped by the $9R(30)$ line of CO_2 which lased spectacularly well with the narrow-bore pump tube; we had not attempted to use this line before. Some of its characteristics became apparent with use and marked it out as an unusual lasing transition. The far-infrared line has been assigned to the Sa $R(5,0)$ transition of NH_3 in the $\nu_2=1$ vibrational level and has been shown to arise from stimulated Raman emission by Willenberg, Hübner, and Heppner [24]. The offset of the $9R(30)$ line of CO_2 required to pump the infrared transition in NH_3 is 185 MHz. The laser line is strong and its frequency shows a remarkably strong pressure dependence (on the order of 0.1 MHz/m Torr for a lasing gas pressure of 0.5 Torr). Because its frequency is determined directly by the CO_2 frequency, it must be simultaneously measured during the LMR measurement of F^+. The wavelength of this line had been estimated quite accurately at 67.234 μm by Landsberg [25] and we have determined its frequency by measuring the beat frequency when it was mixed with a pair of CO_2 laser frequencies in a metal-insulator-metal (MIM) diode. The value obtained at the maximum of the gain curve (which was about 70 MHz wide in our laser), pulled by the frequency of the CO_2 laser, was 4 459 003 MHz with an uncertainty of 3 MHz; this corresponds to a wavelength of 67.233 07 μm.

The normal procedure for measuring a resonance in a far-infrared LMR experiment is to set the laser line manually to the top of the gain curve, record the resonance without delay, and measure the magnetic flux density at the line center. It is assumed that the laser frequency does not drift during the course of the measurement. Such a procedure would be very unreliable in the case of the 67.2 μm line of NH_3 because of its strong dependence on the frequency of the CO_2 laser. In this case therefore, we monitored the beat frequency from the MIM diode as the spectrum was being recorded and made simultaneous measurement of the laser frequency and the resonance field at the line center.

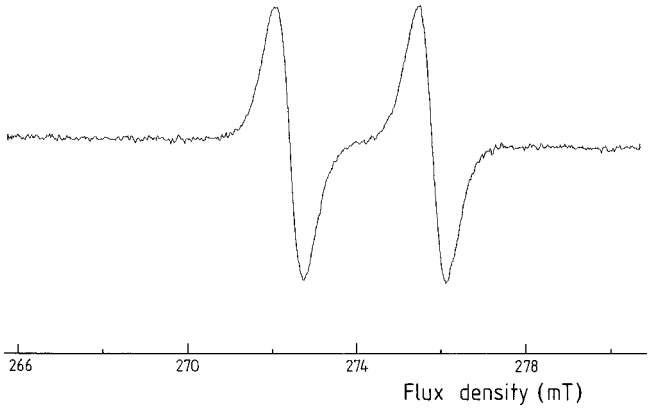

FIG. 2. The far-infrared LMR spectrum of the F^+ atom recorded with the 67.2 μm Raman laser line of NH_3. The output time constant of the lock-in amplifier was 0.1 s. The splitting arises from the nuclear hyperfine structure for $^{19}F^+$ nucleus ($I=\frac{1}{2}$).

The F^+ ions were formed in the sample region with a new microwave source which has been developed specifically for the production of ions and other transient species. The details of its design and construction have been given elsewhere [26]. The source was designed to operate in high magnetic fields (indeed its performance is enhanced by the presence of a magnetic field) and to produce a plasma which extends out into the far-infrared radiation field. The discharge produces considerable noise on the far-infrared laser output and the microwave power was often reduced to improve the signal-to-noise ratio. The typical microwave power fed to the cavity was 30 W. The F^+ ions were formed by flowing ultrahigh-purity helium through the discharge with a small amount of molecular fluorine added. Typical pressures employed were 0.09 Pa (0.7 mTorr) of F_2 and 133 Pa (1 Torr) of He. Both these pressures were fairly critical, particularly that of F_2.

III. RESULTS AND ANALYSIS

The energy levels of F^+ in its inverted ^3P ground state are shown in Fig. 1. The LMR spectrum associated with the $J=0\leftarrow 1$ fine-structure transition consists of a single Zeeman component, $M_J=0\leftarrow 1$ (or $0\leftarrow -1$ if the laser frequency is less than the atomic interval). An example of the observed spectrum of F^+, recorded with the 67.2 μm line of NH_3, is shown in Fig. 2. There is a clear doublet structure, arising from the nuclear hyperfine interaction of the ^{19}F nucleus which has $I=\frac{1}{2}$. The excellent signal-to-noise ratio is a tribute to the sensitivity of the technique. The measurements for the two spectra recorded are given in Table I.

The LMR spectra have been analyzed with a standard effective Hamiltonian for a Russell-Saunders atom, as described, for example, by Cooksy *et al.* [6]. The experimental measurements for F^+ depend primarily on the $J=0\leftarrow 1$ fine-structure interval ΔE_{01} and on the g_J factor and the nuclear hyperfine parameter for the $J=1$ level, $g_{J=1}$ and A_{11}, respectively. The $J=1\leftarrow 2$ interval, the g factor, and hyperfine parameter for $J=2$ and the other hyperfine parameters have only a slight, indirect effect on the resonance positions. The g factors for F^+ in the $^3P_2$ and $^3P_1$ levels have not yet been

TABLE I. Observed resonances associated with the $^3P_0-^3P_1$ fine-structure transition of $^{19}F^+$.

Transition					
J	M_J	M_I	ν_L (GHz)	B_0 (mT)	Observed-calculated resonances (MHz)
$0\leftarrow1$	$0\leftarrow1$	$\frac{1}{2}\leftarrow\frac{1}{2}$	4441.6752[a]	550.07	4.6
		$-\frac{1}{2}\leftarrow-\frac{1}{2}$	4441.6752[a]	553.25	3.2
	$0\leftarrow-1$	$\frac{1}{2}\leftarrow\frac{1}{2}$	4458.9942[b]	271.61	−1.3
		$-\frac{1}{2}\leftarrow-\frac{1}{2}$	4458.9942[b]	274.95	−2.8
		$\frac{1}{2}\leftarrow\frac{1}{2}$	4459.0001[b]	271.91	−1.7
		$-\frac{1}{2}\leftarrow-\frac{1}{2}$	4459.0001[b]	275.18	−1.8

[a]The 67.5 μm line of CH_3OH, pumped by the $9R$ (18) line of the CO_2 laser.
[b]The 67.2 μm Raman laser line of NH_3, pumped by the $9R$ (30) line of the CO_2 laser.

measured but $g_{J=1}$ can be approximated reliably by the value for the isoelectronic species, O, which has been measured as 1.500 986 [27]. The value for $g_{J=2}$ for F^+ is almost certainly lower than that for O because of larger spin-orbit mixing of the $^3P_2$ state with the $^1D_2$ state at 20 873 cm^{-1}. However, the small expected change in this g factor has an insignificant effect on the $J=0\leftarrow1$ spectrum.

The nuclear hyperfine splitting for an atom in the $^3P_1$ component is expected to be small because the electron orbital and spin contributions to a large extent cancel; the splitting for the $^3P_0$ component is rigorously zero. However, the splitting for the $^3P_2$ component and the off-diagonal hyperfine terms are expected to be large because of the large magnetic moment of the ^{19}F nucleus (5.2577 nuclear magnetons). Fortunately, high-quality *ab initio* wave functions are available for F^+ from Schaefer and Klemm [21] and we have used these to calculate values for the indirect hyperfine parameters. The parameters are constrained to these values in our fit.

The results of a least-squares fit to the experimental data are given in Tables I (residuals) and II (parameter values).

TABLE II. Parameters determined from the far-infrared laser magnetic resonance spectrum of $^{19}F^+$.

Parameter	Present work	Previous values
ΔE_{01} (GHz)	4453.2532(16)[a]	4461[b]
ΔE_{12} (GHz)	10 247[c]	
$g_{J=1}$	1.500 986[d]	
$g_{J=2}$	1.500 921[d]	
A_1 (MHz)	68.3(32)	19.0
A_2 (MHz)	2765[e]	
A_{01} (MHz)	1255[e]	
A_{12} (MHz)	1632[e]	

[a]Determined from the present fit. The number in parentheses is one standard deviation of the least-squares fit.
[b]Determined from optical data [19].
[c]Parameter constrained to this value, determined from optical data [19].
[d]g factors taken from the electron paramagnetic resonance measurements of ^{16}O by Radford and Hughes [27].
[e]Parameters constrained to this value, estimated from *ab initio* wave functions [21].

The fairly small residuals in Table I show that the measurements are consistent with the assumed value for $g_{J=1}$. Although it would be possible to reduce the size of the residuals by adjustment of $g_{J=1}$ to a smaller value, the systematic nature of the residuals much more likely reflects the fact that the F^+ atoms are formed (and detected) on the fringes of the far-infrared radiation field, in a region where the magnetic flux density is slightly smaller than the value in the center of the field gap. Through these measurements, a much improved value for the $J=0\leftarrow1$ transition frequency has been determined. The best previously available value was 148.8 ±0.1 cm^{-1} (4461$\pm$3 GHz) from optical spectroscopy [19]. Table II also shows that a value for the nuclear hyperfine parameter A_1 has been measured for the first time. The sign of this parameter (in other words, the M_I assignment in the spectrum) has been chosen so that it is as close as possible to the value calculated with Schaefer and Klemm's wave function [21].

IV. DISCUSSION

The observation of the $J=0\leftarrow1$ transition of F^+ in its ground ^3P state has enabled us to measure the fine-structure interval almost four orders of magnitude more accurately than previously. This result is primarily of theoretical interest and will provide a searching test of the best available wave functions [21]. It will also enable spin-orbit parameters to be estimated more reliably in fluorine-containing molecules where the bonding is ionic in character.

We have also measured a single hyperfine parameter for F^+ in the $J=1$ level, A_1, which is related to the expectation values of atomic operators as follows [12]:

$$A_1\ (\mathrm{Hz}) = \frac{g_N\mu_N\mu_B}{10^7 h}\left\{\langle r^{-3}\rangle_{\ell} - \frac{1}{2}\,g_s\langle r^{-3}\rangle_s + g_s\,\frac{4\pi}{3}\,\psi(0)^2\right\}. \quad (1)$$

The orbital and spin dipolar contributions to this parameter cancel each other to a large extent (these are the first two terms in braces on the right-hand side). In consequence, the splitting depends significantly on the third contribution, which arises from the Fermi contact interaction. The three expectation values in Eq. (1) have been calculated by

Schaefer and Klemm [21]. Using the polarization wave functions (which are preferable because they correspond to a ''Pauling point'' in the theoretical treatment), the values in atomic units are

$$\langle r^{-3}\rangle_{\ell} = 8.4088, \quad \tfrac{1}{2} g_s \langle r^{-3}\rangle_s = 9.1178,$$

$$|\Psi(0)|^2 = 0.093\,56.$$

Substitution of these values into Eq. (1) gives a value for A_1 of 19.0 MHz whereas the experimentally determined value in Table II is 68.3 ± 3.2 MHz. Of the three contributions in Eq. (1), the Fermi contact term is much the most difficult to estimate. If the other two values are completely reliable, the experimental value for A_1 implies that $|\Psi(0)|^2$ has a value of 0.1170(55) a.u. In other words, only a small adjustment of the theoretical quantity is needed to bring the calculated parameter value into line with the experimental one. The *ab initio* value for $|\Psi(0)|^2$ is expected to be a slight underestimate [28] which is also in agreement with our observations. The zero-field frequencies of the hyperfine components of the $J = 0 \leftarrow 1$ can be calculated from the values given in Table II as

$$J = 0 \leftarrow 1, \quad F = \tfrac{1}{2} \leftarrow 1\tfrac{1}{2}, \quad \nu = 4453.2866(20) \text{ GHz},$$

$$F = \tfrac{1}{2} \leftarrow \tfrac{1}{2}, \quad \nu = 4453.1854(31) \text{ GHz}.$$

A complete discussion of the hyperfine interactions in F^+ in its ground state must await measurements on the $J = 2$ level; the hyperfine splittings in this level will be very much larger. In principle, it should be possible to detect the $J = 1 \leftarrow 2$ fine-structure transition by LMR also. A laser line with a wavelength of 29.26 ± 0.07 μm would be required for this experiment. Although such a line has not yet been identified [29], there is every chance that one will be at some time in the future.

ACKNOWLEDGMENTS

We thank Andy Cooksy for helpful advice on the use of his Russell-Saunders computer program. The research was supported by NASA Contract No. W-19, 167.

[1] M. Inguscio, Phys. Scr. **37**, 699 (1988).
[2] P. B. Davies, J. Phys. Chem. **85**, 2599 (1981).
[3] R. J. Saykally and K. M. Evenson, J. Chem. Phys. **71**, 1564 (1979).
[4] J. M. Brown, K. M. Evenson, and L. R. Zink, Phys. Rev. A **48**, 3761 (1993).
[5] R. J. Saykally and K. M. Evenson, Astrophys. J. **238**, L107 (1980).
[6] A. L. Cooksy, R. J. Saykally, J. M. Brown, and K. M. Evenson, Astrophys. J. **309**, 828 (1986).
[7] M. Inguscio, K. M. Evenson, V. Beltrán-López, and E. Ley-Koo, Astrophys. J. **278**, L127 (1984).
[8] U. Bley, F. Koch, F. Temps, P. B. Davies, and I. H. Davis, J. Chem. Phys. **90**, 628 (1989).
[9] M. Inguscio, K. R. Leopold, J. S. Murray, and K. M. Evenson, J. Opt. Soc. Am. B **2**, 1566 (1985).
[10] A. L. Cooksy, D. C. Hovde, and R. J. Saykally, J. Chem. Phys. **84**, 6101 (1986).
[11] A. L. Cooksy, G. A. Blake, and R. J. Saykally, Astrophys. J. **305**, L89 (1986).
[12] J. M. Brown, L. R. Zink, and K. M. Evenson, Astrophys. J. **423**, L151 (1994).
[13] J. M. Brown, K. M. Evenson, and L. R. Zink, Astrophys. J. **431**, L147 (1994).
[14] J. M. Brown and K. M. Evenson, Astrophys. J. **441**, L97 (1995).
[15] J. M. Brown, K. M. Evenson, L. R. Zink, and E. C. C. Vasconcellos, Astrophys. J. **464**, L203 (1996).
[16] J. M. Brown and K. M. Evenson (unpublished).
[17] J. M. Brown, H. Körsgen, and K. M. Evenson (unpublished).
[18] J. M. Brown, T. D. Varberg, K. M. Evenson, and A. L. Cooksy, Astrophys. J. **428**, L37 (1994).
[19] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circular No. 467 (U.S. GPO, Washington, DC, 1949), Vol. I, p. 62.
[20] B. Edlén, Z. Phys. **93**, 433 (1935).
[21] H. F. Schaefer III and R. A. Klemm, Phys. Rev. A **1**, 1063 (1970).
[22] T. J. Sears, P. R. Bunker, A. R. W. McKellar, K. M. Evenson, D. A. Jennings, and J. M. Brown, J. Chem. Phys. **77**, 5348 (1982).
[23] F. R. Petersen, K. M. Evenson, D. A. Jennings, and A. Scalabrin, IEEE J. Quantum Electron. **16**, 319 (1980).
[24] G. D. Willenberg, U. Hübner, and J. Heppner, Opt. Commun. **33**, 193 (1980).
[25] B. M. Landsberg, Appl. Phys. **23**, 127 (1980).
[26] T. D. Varberg, K. M. Evenson, and J. M. Brown, J. Chem. Phys. **100**, 2487 (1994).
[27] H. E. Radford and V. W. Hughes, Phys. Rev. **114**, 1274 (1959).
[28] H. F. Schaefer III (private communication).
[29] N. G. Douglas, in *Millimetre and Submillimetre Wavelength Lasers*, edited by H. K. V. Lobsch, Springer Series in Optical Sciences Vol. 61 (Springer-Verlag, Berlin, 1989).