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DIRECT MEASUREMENT OF FINE STRUCTURE IN THE GROUND STATE OF ATOMIC CARBON BY LASER MAGNETIC RESONANCE

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ABSTRACT

The fine-structure intervals in the ground $2\,^3P$ multiplet of ^{12}C I have been measured with high accuracy by laser magnetic resonance. The results are: $\Delta E(^3P_2\text{–}^3P_1) = 809.3446\ (29)$ GHz and $\Delta E(^3P_1\text{–}^3P_0) = 492.1623(7)$ GHz. These precise measurements have made possible the astronomical detection of far-infrared line emissions from ^{12}C atoms in several interstellar sources, as reported in the accompanying *Letter* by Phillips *et al.*
Subject headings: atomic processes — infrared: spectra

I. INTRODUCTION

The carbon atom has been studied for many years by optical spectroscopy. The cumulative results of these efforts are tabulated by Moore (1970) and Bashkin and Stoner (1975). Hyperfine splittings in ^{11}C and ^{13}C were measured with precisions of ~25 kHz (Wolber *et al.* 1970), and the *g*-factors to within a part in 10^5 (Wolber *et al.* 1970), but the separations between the fine-structure levels in the ^3P ground state have been known only with optical precision (~1 GHz). It is important for several reasons to know these fine-structure splittings more precisely. Carbon is one of the most abundant elements, exhibiting a cosmic abundance of 3×10^{-4} that of hydrogen; only hydrogen, helium, and oxygen are more abundant (Watson 1976). Much of this carbon is thought to be present in atomic form, some of it in cold clouds where it cannot be detected via its optical emission lines. It would be extremely valuable to be able to monitor C atoms in these regions (Phillips *et al.* 1980). Radio searches have been conducted at 372.5 MHz for the ^{13}C hyperfine transition in the $^3P_2$ state (Wolber *et al.* 1970), corresponding to the 21 cm H atom line, but these have not proved successful. Transitions between the fine-structure levels, occurring by emission in the far-infrared, would provide a convenient means to monitor C atom densities. Accurate laboratory measurements of the fine-structure intervals would greatly expedite astronomical searches for C atoms in the interstellar medium. Therefore, we sought to measure the fine-structure in ^{12}C and ^{13}C directly by far-infrared laser magnetic resonance (LMR). We have recently published results of a similar experiment performed on the $2\,^3P$ state of oxygen atoms (Saykally and Evenson 1979). In that case, O atoms were generated in a glow discharge through an oxygen-helium mixture, and the $J = 2 \rightarrow 1$ transition was tuned into coincidence with a continuous-wave laser line at 63.1 μm, producing a measurement of the $^3P_2\text{–}^3P_1$ interval accurate to 0.4 parts per million. The principal difficulty in performing the analogous experiment for C atoms was simply that of producing a sufficient number density.

II. EXPERIMENTAL TECHNIQUES

A methane-fluorine atom flame had been used previously to generate a number of transient species including CH, CH$_2$, CH$_2$F, CCH, and CF (Evenson *et al.* 1980), implying the presence of C atoms in the flame. Optical data (Bashkin and Stoner 1975) predict transitions near 370 and 610 μm. With this source we have indeed been able to observe both the $^3P_0 \rightarrow {}^3P_1$ and the $^3P_1 \rightarrow {}^3P_2$ transitions in ^{12}C and ^{13}C, using 10 different optically pumped far-infrared laser lines. The lines used are summarized in Table 1 and the transitions illustrated in Figure 1. The ^{12}C and ^{13}C spectra observed with the 380.6 μm line of DCOOD are shown in Figure 2. Since the ^{13}CH$_4$ sample was only 90% enriched, residual lines from ^{12}C are also visible on the lower trace.

By combining data from all 10 lines and using *g*-factors from the atomic beam experiments of Wolber *et al.* (1970), the ^{12}C fine-structure intervals have been obtained with precisions near 1×10^{-6}. The corresponding splittings in ^{13}C are estimated here, but an equally precise determination awaits further experimental efforts.

The fine-structure separation, ν_0, was calculated from the LMR spectra with the use of the second-order Zeeman equation:

$$\nu_L = \nu_0 + \mu_0 H[(g_J' - g_J'')M_J'' \pm g_J'] + cH^2 \ , \quad (1)$$

where ν_L is the laser frequency, ν_0 is the zero-field fine-structure transition frequency, μ_0 is the Bohr magneton, c is the coefficient of the second-order Zeeman shift, H is the magnetic flux density, and g_J represents the *g*-factor of the state J. Primes and double primes refer to the upper and lower states of the transition, respectively, and the upper and lower signs refer respectively to $\Delta M_J = \pm 1$ selection rules. Equation (1) applies to perpendicular polarization of the laser magnetic field relative to the static magnetic

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field. For a ^3P state only $\Delta M = \pm 1$ magnetic dipole transitions can be observed in a LMR experiment. The first-order Zeeman energy in a state coupled according to $J = L + S$ is simply $g_J M_J \mu_0 H$; second-order contributions calculated according to standard tensor methods are listed in Table 2 and shown in Figure 3. The third-order corrections to the Zeeman energy vanish in LS coupling, and fourth-order terms are totally negligible at the level of LMR precision (Radford and Hughes 1959), as is the diamagnetic contribution.

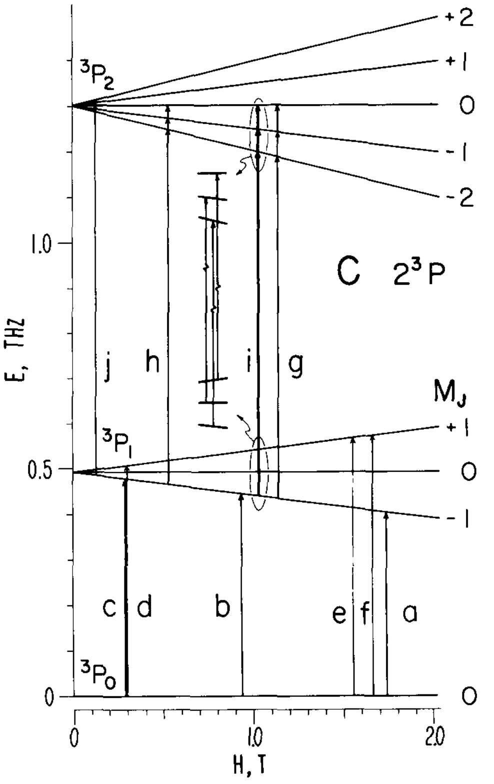

FIG. 1.—Zeeman energy-level diagram with observed transitions identified (see Table 1). The three M_J components (separated by second-order effects) are illustrated in the inset for the *i* spectrum.

The LMR spectrometer used in these experiments has been described previously (Evenson *et al.* 1977). Briefly, it consists of a far-infrared gain cell pumped transversely by a grating-tuned CO_2 laser, and separated from the intracavity sample region by a polypropylene beam splitter. The sample region is located between the pole faces of a 37.5 cm electromagnet providing about a 1 cm^3 region of homogeneous field. A double-wall concentric flow tube extends to the perimeter of the laser tube. Fluorine atoms, produced in a 2450 MHz discharge through a dilute mixture of F_2 in He, flow down the inner tube and mix with CH_4, which flows down between the walls producing a bright flame

TABLE 2

CALCULATED SECOND-ORDER CORRECTIONS AND INTENSITIES FOR ZEEMAN COMPONENTS OF THE ^3P FINE-STRUCTURE TRANSITIONS

$M_J'' \rightarrow M_J'$	$c(\times 10^{-2}$ MHz/tesla$)^2$	I[a]
$1 \rightarrow 0$	$7/12\ \epsilon_2 = 1.4119$	1
$1 \rightarrow 2$	$1/4\ \epsilon_2 = 0.60509$	6
$0 \rightarrow 1$	$1/12\ \epsilon_2 - 2/3\ \epsilon_1 = -1.2416$	3

$\epsilon_1 = \mu_0^2/(E_1 - E_0) = 3.98024 \times 10^{-2}$ MHz/tesla^2
$\epsilon_2 = \mu_0^2/(E_2 - E_1) = 3.42035 \times 10^{-2}$ MHz/tesla^2

[a] For $\Delta J = +1$, from Table 10–1 of Townes and Schawlow 1955.

TABLE 1

EXPERIMENTAL DATA FOR ^{12}C I

TRANSITION				H_0 (Tesla)	LASER LINE (see Fig. 1)	λ_L (μm)	LASING GAS	ν_L[a] (GHz)
J''	J'	M_J''	M_J'					
0	1	0	−1	1.7442	a	657.2	(CH_2F_2)	456.1411
0	1	0	−1	0.94442	b	634.5	(CH_2CHCl)	472.5035
0	1	0	−1	0.27448	c	616.3	(CH_2DOH)	486.4111
0	1	0	+1	0.28101	d	601.9	(CH_2CHCl)	498.0824
0	1	0	+1	1.55965	e	570.6	(CH_3OH)	525.4279
0	1	0	+1	1.6716	f	568.0	(CH_2CHCl)	527.8540
		0	−1	1.2220				
1	2	−1	−2	1.2358	g	382.6	(CH_2F_2)	783.4860
		+1	0	1.2413				
		0	−1	0.52467				
1	2	−1	−2	0.52722	h	375.5	($C_2H_2F_2$)	798.2870
		+1	0	0.52830				
		0	−1	1.02133				
1	2	−1	−2	1.03058	i	380.6	(DCOOD)	787.7555
		+1	0	1.03472				
		−1	0	0.13573				
1	2	+1	+2	0.13581	j	369.4	(CH_3OH)	812.1954
		0	+1	0.13599				

[a] Far-infrared laser frequencies are tabulated by Knight 1979.

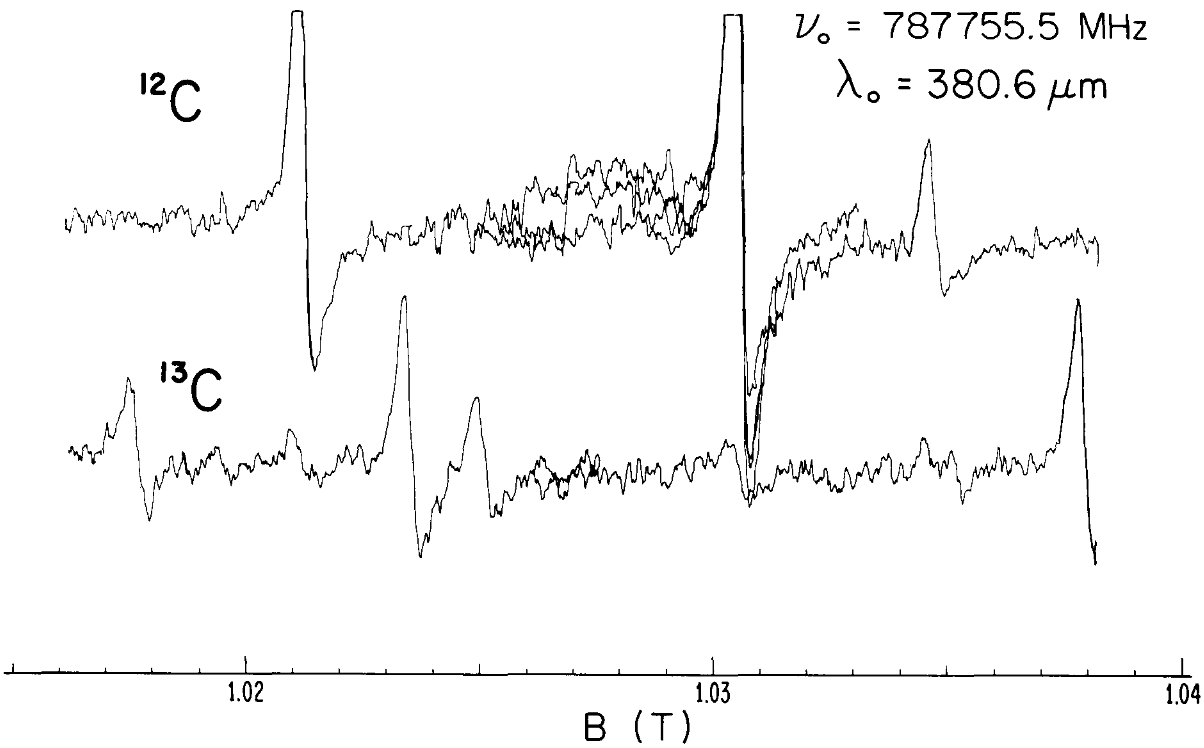

FIG. 2.—The $J = 1 \rightarrow 2$ transitions of ^{12}C and ^{13}C observed with the 380.6 μm laser line of DCOOD. A 0.3 s time constant was used to record these spectra.

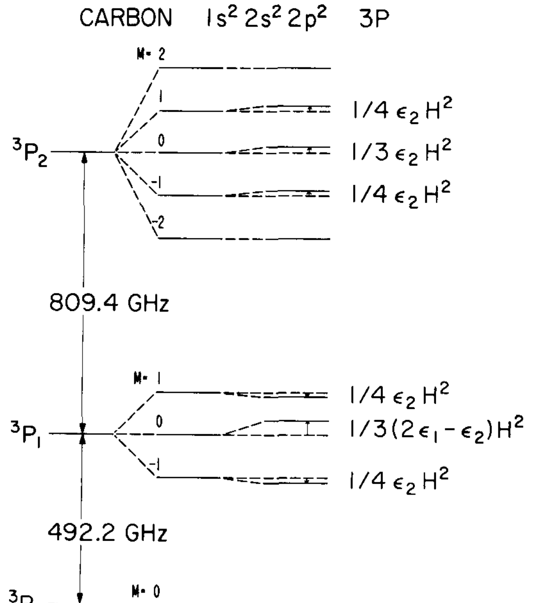

FIG. 3.—Energy-level diagram for the 2 ^3P state of ^{12}C I. Second-order Zeeman shifts are given in terms of ϵ_J defined in Table 2.

in the homogeneous field region of the laser cavity. As a transition in the atom is tuned into coincidence with the laser frequency by the magnetic field, the total power inside the laser cavity changes and is modulated at 5 kHz by a set of Helmholtz coils. The output of the laser is monitored by a helium-cooled germanium bolometer whose voltage output is then fed into a lock-in amplifier. The demodulated output signal is approximately the first derivative of the absorption spectrum as a function of magnetic field.

The optimum fluorine-atom/methane flame was obtained at total pressures near 133 Pa (133 Pa = 1 torr), with the following composition: 0.1% CH_4/1.4% F_2/98.5% He. This is considerably richer in F_2 than the flames that maximize CH or CH_2 LMR spectral intensities, and of about the same composition as that used to obtain the maximum CF intensities. The C-atom density was a very sensitive function of the flame composition.

Other sources were tried, viz., N atoms + C_2N_2 and O atoms + C_2H_2, but no C atom signals were observable with them. This implies C atom densities at least 20 times smaller in these sources, which are known to produce this species (Gaydon 1974), than those in the F-atom/methane flame. These estimates come from our signal-to-noise ratio of 20. To help verify that hydrogen was not directly involved in the spectrum, CD_4 was substituted for CH_4, and the spectrum was reproduced.

The $J = 0 \rightarrow 1$ transition, predicted to occur at

491.6 GHz, was observed with the six laser lines listed in Table 1. Three of these lines are lower in frequency than the zero field splitting (ν_0), and correspond to $\Delta M_J = -1$ transitions, while the three lines that are higher in frequency than ν_0 correspond to $\Delta M_J = +1$ transitions. Only $\Delta M_J = \pm 1$ transitions can be observed here because $M_J'' = 0$ (see eq. [1]). With the 616.3 μm line of CH_2DOH, the shift in resonant field due to the normal mass effect was observed for ^{13}C by replacing $^{12}CH_4$ with a sample of 90% $^{13}CH_4$. This shift was measured to be $+0.0001$ T ($+1.0$ gauss). The hyperfine splitting for this transition is calculated to be $\sim$1.4 gauss, and was not resolvable.

The $J = 1 \rightarrow 2$ transition was detected with four different laser lines near 809.4 GHz; three of these are below ν_0 and correspond to the $\Delta M_J = -1$ selection rule, while one is above ν_0 and corresponds to $\Delta M_J = +1$. Unlike the $J = 0 \rightarrow 1$ transition, which has only one Zeeman component, the $J = 1 \rightarrow 2$ transition has three Zeeman components distinctly separated by second-order mixing of the fine-structure levels. For a rigorously linear Zeeman effect these would occur at the same magnetic field. In the spectra shown in Figure 2, the frequency of the laser is less than that of the transition; therefore, the Zeeman component with the largest second-order effect that *decreases* the separation will occur at the lowest field. Thus the $M_J = 0 \rightarrow -1$ component appears first (see insert in Fig. 1), followed by $M_J = -1 \rightarrow -2$ and $M_J = -1 \rightarrow 0$ in the respective 3:6:1 intensity ratio.

III. RESULTS AND DISCUSSION

Using equation (1), the relevant data in Table 3, and the tabulated second-order Zeeman corrections in Table 2, we used each of the six measurements of the $J = 0 \rightarrow 1$ transition and the four measurements of the $J = 1 \rightarrow 2$ transitions to determine the $^3P_1$–$^3P_0$ and $^3P_2$–$^3P_1$ fine-structure intervals of ^{12}C. The results are presented in Table 3. The error limits in these results correspond to the 90% confidence intervals determined from the Student t-distribution.

While our refinement of the second-order corrections to the Zeeman effect, arising from terms off-diagonal in J, could in principle affect the determination of the g-factors, Wolber *et al.* (1970) chose sets of Zeeman levels such that these quadratic dependences canceled each other. Their resulting g-factors are then independent of the fine-structure intervals.

TABLE 3

FINE-STRUCTURE INTERVALS DETERMINED BY LASER MAGNETIC RESONANCE

	^{12}C (GHz)[a,b]	^{13}C (GHz)	^{12}C (GHz)[c]
$\Delta E(^3P_2$–$^3P_1)$	809.3446 (29)	809.346 (4)	809.4
$\Delta E(^3P_1$–$^3P_0)$	492.1623 (7)	492.164 (2)	491.7

[a] Uncertainties for ^{12}C are 90% confidence limits, those for ^{13}C are estimated.

[b] Calculated with $\mu_0 = 1.399612 \times 10^{+4}$ MHz/tesla (Cohen and Taylor 1973); $g_J(J = 1) = 1.501122(13)$ (Wolber *et al.* 1970); $g_J(J = 2) = 1.501109(15)$ (Wolber *et al.* 1970). These g-factors are corrected for the improved value of μ_0 given here. Second-order corrections are given in Table 2.

[c] Optical data (Bashkin and Stoner 1975).

The most important feature of this work is the establishing of precise rest frequencies for ^{12}C I fine-structure transitions. These frequencies provided the basis for the successful astronomical detection of neutral carbon atoms in interstellar sources (Phillips *et al.* 1980). Similar transitions between fine-structure levels of the ^3P ground states of O I and O III have recently been observed in emission from several H II regions by far-infrared astronomy (Melnick, Gull, and Harwit 1979; Moorwood *et al.* 1978; Story, Watson, and Townes 1979), using grating, Fabry-Perot, and Michelson spectrometers.

C I has an ionization potential of 11.26 eV, compared to 13.598 eV for H I. Therefore, carbon will be present largely in ionized form in diffuse ($n \sim 10$–10^3 cm^{-3}) regions of the interstellar medium, but will be present in neutral form when the density of H_2 molecules and dust grains is sufficient to shield inner regions of clouds from the ionizing UV photons. Therefore, the "dark" or "molecular" types of clouds should be sources of C I far-infrared emission, excited by collisions with other species. In such regions this emission is likely to be an important cooling mechanism.

The ratios of $^{13}C/^{12}C$ and N/O abundances are regarded at present as the most sensitive indicators for the amount of matter returned to the interstellar medium (ISM) after nuclear processing in stellar interiors (Watson 1976). Consequently, present understanding of mass exchange between stars and the ISM depends on measurement of these isotope ratios. Except for atomic deuterium, only molecular observations have effected detection of the less-abundant isotopes, and because of the relatively high abundance of ^{13}C, the $^{13}C/^{12}C$ ratio has been the most studied among the heavier elements. Uncertainties involved in separating chemical fractionation effects lead to uncertainties in the actual isotopic abundances. Therefore, direct measurement of the $^{12}C/^{13}C$ ratio would be quite valuable. Although our preliminary measurements of the ^{13}C spectra have yielded an estimate of the ^{13}C fine structure (Table 3), a precise analysis will require additional data which we will obtain in the future.

In summary, by combining measurements from the laser magnetic resonance spectra of ground-state carbon atoms with accurate g-factors measured earlier, we have deduced precise values for transitions between the fine-structure levels, which occur in the far-infrared, for ^{12}C I. With far-infrared receivers of sufficient resolving power, these transitions can now be observed in emissions from interstellar sources. Further detection of these transitions should lead to a great deal of information regarding atomic abundances, isotope ratios, chemical fractionation effects, processes involving interstellar dust grains, and the general physical conditions that prevail in the interstellar medium.

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