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DIRECT MEASUREMENT OF THE FINE-STRUCTURE INTERVAL AND g_J FACTORS OF SINGLY IONIZED ATOMIC CARBON BY LASER MAGNETIC RESONANCE

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ABSTRACT

We present the results of laser magnetic resonance measurements performed on the ground ^2P state of singly ionized atomic carbon (C II). The $^2P_{3/2} \leftarrow {}^2P_{1/2}$ fine-structure intervals of both $^{12}C^+$ and $^{13}C^+$ have been determined with a precision of approximately 1 ppm, and the g_J factors to approximately one part in 10^4. Specifically, we find that $g_{J=1/2} = 0.66576(11)$ and $g_{J=3/2} = 1.33412(11)$, while for $^{12}C^+$ $\Delta E_0(^2P_{3/2} \leftarrow {}^2P_{1/2}) = 1900536.9(1.3)$ MHz, with $\Delta E_0(^2P_{3/2} \leftarrow {}^2P_{1/2}) = 1900545.8(2.1)$ and $\Delta E(^2P_{3/2} \leftarrow {}^2P_{1/2}, F = 2 \leftarrow 1) = 1900466.1(2.3)$ MHz in $^{13}C^+$. The highly precise values of the ^{12}C II and ^{13}C II fine-structure intervals verify the already secure far-infrared astronomical identification of C^+ and should allow the interstellar $^{12}C/^{13}C$ ratio to be unambiguously determined in a number of environments.

Subject headings: laboratory spectra — line identification — molecular processes

I. INTRODUCTION

Observations made possible by the dramatic improvements in astronomical instrumentation during the past decade have now confirmed the theoretical expectation that the far-infrared (FIR) fine-structure lines of atomic carbon and oxygen in various ionization states would provide an important cooling mechanism for the interstellar gas (Dalgarno and McCray 1972). These species have energy levels and excitation densities that are well matched to the physical state of both the neutral and ionized regions in which they are prevalent and are therefore quite efficient sources of energy loss. Particularly important are the transitions of O (O I) and C^+ (C II) which, because of their high abundance in the warm photodissociation regions commonly associated with giant molecular cloud complexes, may contain up to 1% of the total bolometric luminosity of "typical" gas-rich galaxies (Watson 1984; Crawford *et al.* 1985). Measurement of the intensities and velocity profiles of FIR fine-structure emission lines can also yield considerable insight into the chemistry and dynamics of molecular clouds, star formation processes, and galactic morphology. Indeed, the detection of intense 610 μm neutral carbon (C I) emission by Phillips *et al.* (1980) has led to a number of revisions in the chemical modelling of dense interstellar clouds, while the 158 μm [C II] line has been used, among other things, to examine the validity of CO as a tracer of H_2 (Crawford *et al.* 1985). The detailed structure of the $C^+/C/CO$ transition in molecular clouds can profoundly influence the chemical composition of dense clouds and therefore the star formation process, but it must usually be probed indirectly via velocity shifts and line profiles because the transition regions are often spatially unresolved. For detailed studies of the dynamics and chemistry of such objects it is therefore imperative to know the rest frequencies of the transitions under study to considerably better accuracy than the currently available spectral resolution.

Because of the reactive nature of most atoms and the relative lack of intense radiation sources in the FIR, atomic fine-structure lines have proven difficult to study in the laboratory. Far-infrared laser magnetic resonance (FIR LMR) spectroscopy is an extremely powerful tool for the study of molecular rotational spectra but is less applicable to the investigation of atomic species due to the small number of fine-structure transitions in any given species and the incomplete coverage of even the most versatile FIR LMR spectrometers. Nevertheless, to date the fine-structure lines of C (Saykally and Evenson 1980; Cooksy *et al.* 1986), O (Davies *et al.* 1978; Saykally and Evenson 1979), and Si (Inguscio *et al.* 1984) have been measured in the FIR, while several isotopes of Cl (Dagenis, Johns, and McKellar 1976), Hg (Johns, McKellar, and Riggin 1977), and metastable Kr and Xe (Sears and McKellar 1982) have been detected with infrared systems. The inherently high sensitivity of the LMR technique was essential for the detection of these electric dipole-forbidden transitions, but the extension of LMR spectroscopy to ionic species such as C^+ has proven difficult due to their extreme reactivity under normal laboratory conditions. Utilizing advances in ion production technology, we have recently detected the first ionic fine-structure transition in the laboratory, the $^3P_2 \leftarrow {}^3P_1$ 121 μm line of N^+ (N II) (Cooksy, Hovde, and Saykally 1986). In this *Letter* we report the detection of the 158 μm $^2P_{3/2} \leftarrow {}^2P_{1/2}$ transitions of $^{12}C^+$ and $^{13}C^+$ with similar techniques, thereby confirming the astronomical detection of this feature (Russell *et al.* 1980). It is hoped that the measurement of these lines will permit an accurate determination of the interstellar $^{12}C/^{13}C$ and $^{14}N/^{15}N$ isotopic rations free from the deleterious effects of

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fractionation that plague molecular tracers of the dense interstellar gas.

II. EXPERIMENTAL

The LMR spectrometer used in our study of the C^+ and N^+ ions has been described in detail elsewhere (Ray, Lubic, and Saykally 1982). Briefly, the spectrometer consists of an optically pumped far-infrared molecular laser containing an intracavity sample cell placed between the pole pieces of a 0–20 kilogauss Varian 15" electromagnet, a liquid-helium cooled Ga:Ge bolometer, and associated detection electronics. A rotatable polyproplylene beam splitter set at the Brewster angle separates the gain and sample regions of the FIR laser cavity. The FIR gain cell is transversely pumped by a 80 watt CO_2 laser, with power coupled out to the bolometer by an adjustable copper mirror inserted into the laser mode. If necessary, an iris may be used to suppress higher order transverse modes in the FIR laser. By superposing a 2–6 kHz sinusoidal magnetic field of about 30 G onto the slowly swept DC field any absorption from paramagnetic species is converted into a phase coherent signal which is detected by the bolometer and processed in a lock-in amplifier. For the weakest transitions studied here it was necessary to signal average several scans in order to accurately measure the line position. The resonant fields were measured and calibrated to an accuracy of ± 2 G with an NMR gaussmeter probe.

Like N^+, the C^+ ions were generated in a 12–17 kHz AC discharge between two brass shimstock electrodes housed in the sample cell. The simple reaction

$$He^+ + CO \rightarrow C^+ + O + He$$

proceeds quite rapidly to produce C^+ and has the added advantage that the less reactive neutral oxygen species may be used to estimate optimum reaction conditions. As judged initially by the [O I] line at 145 μm and subsequently by the 158 μm [C II] transition, optimized conditions for C^+ production were approximately 50–70 millitorr of CO in 900 millitorr of He, with a discharge current of about 50 mA. The search problem for the 158 μm line was greatly reduced by the astronomical rest frequency estimate of Crawford *et al.* (1985), determined from observations of the Orion molecular cloud. Figure 1 shows a recording of the $M_J = -3/2 \rightarrow -1/2$ component of the [C II] line under typical operating conditions.

III. THEORY

The effective Hamiltonian employed in our analysis of C^+ has been thoroughly described in our study of N^+ (Cooksy, Hovde, and Saykally 1986). We give here a brief summary of the perturbations treated and the results for the case of C^+ that differ from our earlier work. The effective Hamiltonian is written as

$$H = H_O + H_Z + H_M, \tag{1}$$

where H_O is the phenomenological fine structure Hamiltonian, H_Z is the Zeeman term, and H_M is the magnetic hyperfine term.

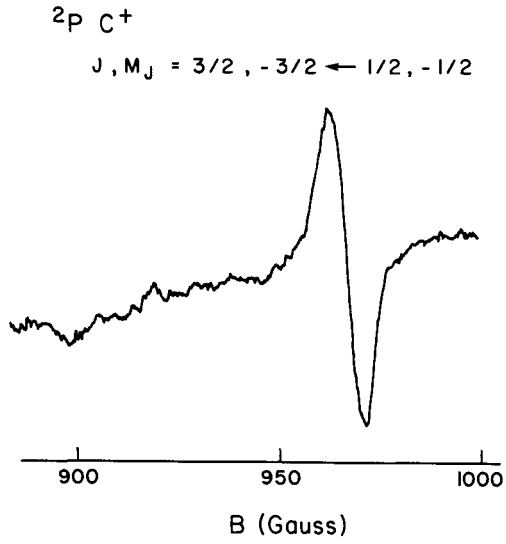

FIG. 1.—Signal-averaged LMR spectrum of the $M_J = -3/2 \leftarrow -1/2$ fine-structure transition in $^2P\ ^{12}C^+$ at 1898.2799 GHz and 967.0 G.

The diagonal elements of H_Z may be explicitly expressed as

$$\langle LSJM_J IM_I | H_Z | LSJM_J IM_I \rangle = \mu_B g_J M_J B - \mu_N g_I (1 - \sigma) M_I B - \tfrac{1}{2}\chi_I B^2 - \chi_A \langle LSJM_J | T^{(2)}(\boldsymbol{B}, \boldsymbol{B}) \cdot T^{(2)}(\boldsymbol{L}, \boldsymbol{L}) | LSJM_J \rangle, \tag{2}$$

where σ is the nuclear shielding constant and χ_I is the isotropic diamagnetic Zeeman interaction. If we neglect the anisotropic diamagnetic Zeeman effect (the term in χ_A), the $\Delta M_I = 0$ selection rule implies that, for allowed transitions, only the first term of expression (2) has a first-order effect on the transition energy in a magnetic field. For a ^2P atom, the gyromagnetic factors are approximately $g_{J=1/2} \approx 2/3$ and $g_{J=3/2} \approx 4/3$. Because the g_J are significantly different for the two J levels, the energies of the M_J components of the $^2P_{3/2} \leftarrow {}^2P_{1/2}$ transition will change at different rates in a magnetic field. Lines of lower tunability [which is simply $\mu_B(g_{J=3/2} M_{J=3/2} - g_{J=1/2} M_{J=1/2})$] will be broader and will appear at higher magnetic fields than their faster tuning counterparts.

The magnetic hyperfine Hamiltonian is (Abragam and Pryce 1951)

$$H_M = 2 g_I \mu_B^2 \{ \langle r_l^{-3} \rangle (\boldsymbol{L} \cdot \boldsymbol{I}) + \langle r_s^{-3} \rangle \xi [L(L+1)(\boldsymbol{S} \cdot \boldsymbol{I}) - \tfrac{3}{2}(\boldsymbol{L} \cdot \boldsymbol{S})(\boldsymbol{L} \cdot \boldsymbol{I}) - \tfrac{3}{2}(\boldsymbol{L} \cdot \boldsymbol{I})(\boldsymbol{L} \cdot \boldsymbol{S})] + \tfrac{8}{3}\pi |\Psi(0)|^2 (\boldsymbol{S} \cdot \boldsymbol{I}) \}, \tag{3}$$

where

$$\xi = \frac{(2I+1) - 4S}{S(2I-1)(2I+3)(2L-1)}.$$

The matrix elements are functions of the constants (evaluated here for ^2P atoms)

$$A_{1/2} = g_I \mu_B^2 \left[\frac{8}{3}\langle r_l^{-3}\rangle + \frac{8}{3}\langle r_s^{-3}\rangle - \frac{16\pi}{9}|\Psi(0)|^2 \right],$$

$$A_{3/2} = g_I \mu_B^2 \left[\frac{4}{3}\langle r_l^{-3}\rangle - \frac{4}{15}\langle r_s^{-3}\rangle + \frac{16\pi}{9}|\Psi(0)|^2 \right],$$

and

$$A_{3/2\,1/2} = g_I \mu_B^2 \left[\frac{2}{3}\langle r_l^{-3}\rangle - \frac{1}{3}\langle r_s^{-3}\rangle - \frac{16\pi}{9}|\Psi(0)|^2 \right]. \quad (4)$$

We currently lack the precision to determine the constant off-diagonal in J, $A_{1/2\,3/2}$, but have included it in our analysis by utilizing the ab initio values of Schaefer and Klemm (1970) for $\langle r_l^{-3}\rangle$, $\langle r_s^{-3}\rangle$, and $|\Psi(0)|^2$. It is worth noting that due to the magnitude of the diagonal constants $A_{1/2}$ and $A_{3/2}$, terms off-diagonal in M_I and M_J are by no means negligible, contributing energies of as much as 50 MHz to the LMR transitions observed at low magnetic fields.

IV. RESULTS AND DISCUSSION

Four laser lines were available with which to investigate the LMR spectrum of C^+. The transitions resonant with each of these frequencies were the two $\Delta M_J = -1$ and the $\Delta M_J = 0$, $M_J = -1/2$ components as pictured for $^{13}C^+$ in Figure 2. Of these, the $M_J = -3/2 \leftarrow -1/2$ line has the greatest intensity and tunability. The $M_J = -1/2 \leftarrow -1/2$ component has only one-third of this intensity and is broader by nearly a factor of four, and it could not be resolved in this study.

The data obtained are given in Table 1. Measurements taken for both isotopes were combined in a least-squares analysis, the results of which comprise Table 2. We have failed thus far to resolve the hyperfine components of the $M_J = -1/2 \leftarrow 1/2$ transition in $^{13}C^+$ and therefore cannot adequately evaluate the independent parameters $A_{1/2}$ and $A_{3/2}$. We have been able to determine the value of the coupled term $1/4A_{1/2} - 3/4A_{3/2}$ to within small uncertainty, however, and can use this to precisely predict the frequency of the J, $F = 3/2,2 \leftarrow 1/2,1$ transition, the strongest of the zero-field $^2P_{3/2} \leftarrow {}^2P_{1/2}$ components. The ab initio hyperfine constants of Schaefer and Klemm (1970) have proved capable of reproducing experimental measurements in ^2P atoms to 2% or better, and we have therefore used these calculations to estimate the frequencies of the weaker zero-field transitions, which are listed together with the $3/2,2 \leftarrow 1/2,1$ frequency in Table 3. Schaefer and Klemm's constants predict the measured combination of the hyperfine constants to within 2.5%, from which we estimate a 2 σ uncertainty of $\pm$10–15 MHz for the weaker zero-field hyperfine lines. The

TABLE 1

A. RESONANT FIELDS FOR ^{12}C II MEASURED IN THIS WORK

Transition $M_J' \leftarrow M_J''$	Lasing Gas	Laser Frequency (GHz)	Field (G)
$-3/2 \leftarrow -1.2$	$^{13}CH_3OH$	1898.2799	967.0
$-1/2 \leftarrow 1/2$	$^{13}CH_3OH$	1898.2799	1613.2
$-3/2 \leftarrow -1/2$	CH_2F_2	1891.2743	3968.4
$-3/2 \leftarrow -1/2$	CH_2DOH	1882.9063	7556.0
$-1/2 \leftarrow 1/2$	CH_2DOH	1882.9063	12650.5
$-3/2 \leftarrow -1/2$	CH_3OH	1877.5085	9872.1
$-1/2 \leftarrow 1/2$	CH_3OH	1877.5085	16544.1

B. RESONANT FIELDS FOR ^{13}C II MEASURED IN THIS WORK

Transition M_J', M_J'', M_I	Lasing Gas	Laser Frequency (GHz)	Field (G)
$-3/2, -1/2, -1/2$	CH_2DOH	1882.9063	7525.3
$-3/2, -1/2, 1/2$	CH_2DOH	1882.9063	7604.0
$-3/2, -1/2, -1/2$	CH_3OH	1877.5085	9841.9
$-3/2, -1/2, 1/2$	CH_3OH	1877.5085	9917.3

TABLE 2

CONSTANTS FOR C II DETERMINED BY LMR

Constant	Value
$E(^{12}C^+ {}^2P_{3/2} \leftarrow {}^2P_{1/2})$	1900.5369(13) GHz
$E(^{13}C^+ {}^2P_{3/2} \leftarrow {}^2P_{1/2})$	1900.5458(21) GHz
$g_{J=1/2}$	0.66576(11)
$g_{J=3/2}$	1.33412(11)
$\frac{1}{4}(A_{1/2} - 3A_{3/2})$	80.3(7) MHz

NOTE.—Numbers in parentheses represent 2 σ, 95% confidence limits.

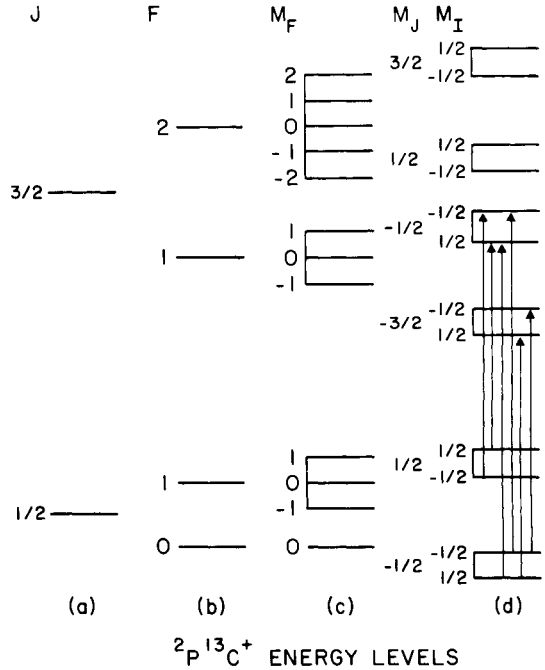

FIG. 2.—Energy level diagram of ^2P $^{13}C^+$. (*a*) The unperturbed fine-structure levels. (*b*) The zero-field doublet hyperfine splitting. (*c*) The Zeeman effect in a weak magnetic field. (*d*) The Zeeman effect in a strong field, with the transitions observable at the available laser frequencies illustrated.

TABLE 3

ESTIMATED ZERO-FIELD TRANSITION FREQUENCIES FOR ^{13}C II

Transition $F' \leftarrow F''$	Frequency (GHz)	Relative Intensity	$\Delta(^{13}$C II ^{12}C II) (km s^{-1})
$2 \leftarrow 1$	1900.4661(23)[a]	44.4%	−11.2
$1 \leftarrow 1$	1900.136(10)[b]	20.0	−63.2
$1 \leftarrow 0$	1900.950(15)[b]	35.6	65.2

[a] Determined in this work.

[b] Estimated using values of $A_{1/2}$ and $A_{3/2}$ obtained from the ab initio constants of Schaefer and Klemm 1970.

$F = 2 \leftarrow 1$ [^{13}C II] component lies only 14 km s^{-1} from the [^{12}C II] fine-structure line and will therefore be difficult to observe even in the most narrow-line sources. However, as Table 3 shows, the weaker hyperfine satellites still retain nearly 50% of the transition intensity and lie some 60–70 km s^{-1} from the stronger [^{12}C II] line.

In view of Veseth's recent theoretical work on isotopic shifts in atomic fine-structure states (Veseth 1985), we have also analyzed the $[\Delta E_0(^{13}\mathrm{C}) - \Delta E_0(^{12}\mathrm{C})]$ shift in ^2P C$^+$ and obtain a value of 8.9(1.5) MHz for this parameter. Because further investigation into the theory of fine-structure shifts is at present hampered by the paucity of precise experimental data, we hope such data will encourage continuing efforts in the field.

The variation of the ^{13}C/^{12}C and N/O isotopic ratios with galactic radius strongly constrains models of star formation and mass exchange between stellar interiors and the interstellar medium. Molecular tracers of dense interstellar gas can be strongly affected by chemical fractionation processes that render the accurate determination of isotopic ratios extremely difficult. For example, the molecular ^{13}C and D content in the cores of cool, dense interstellar clouds may be strongly enhanced or depleted by the exothermic reactions

$$^{13}\mathrm{C}^+ + {}^{12}\mathrm{CO} \rightarrow {}^{12}\mathrm{C}^+ + {}^{13}\mathrm{CO} + 35\ \mathrm{K}$$

and

$$\mathrm{H}_3^+ + \mathrm{HD} \rightarrow \mathrm{H}_2\mathrm{D}^+ + \mathrm{H}_2 + 298\ \mathrm{K}.$$

Atomic species are largely unaffected by these processes because of the higher temperatures and low molecular abundances in the H II regions and photodissociation zones where such species are prevalent. Thus, the far-infrared fine structure lines of C, N, and O should be excellent tracers of atomic abundances and isotope ratios throughout the galaxy. Indeed, Lester *et al.* (1983) have used the [N III] and [O III] lines to examine the large scale galactic N/O abundance gradient. The present work and our recent investigation of the laboratory spectra of C I and N II provide the necessary rest frequencies for a more thorough investigation of the ^{13}C/^{12}C and N/O galactic abundance ratios which is now possible with the advent of high-resolution far-infrared astronomical receivers and airborne observing platforms.

To summarize, far-infrared laser magnetic resonance spectroscopy has been used to precisely determine the g_J factors and fine-structure intervals of the ^{12}C and ^{13}C isotopes of singly ionized atomic carbon. The resulting transition frequencies will be of considerable use in detailed investigations of atomic abundances, isotope ratios, molecular cloud morphology, interstellar mass exhange, and star-formation processes.

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