# ACCURATE DETERMINATION OF THE FINE-STRUCTURE INTERVALS IN THE $^3P$ GROUND STATES OF $^{13}$C AND $^{12}$C BY FAR-INFRARED LASER MAGNETIC RESONANCE

A. L. COOKSY AND R. J. SAYKALLY[1]
Department of Chemistry, University of California at Berkeley

J. M. BROWN
Physical Chemistry Laboratory, Oxford University

AND

K. M. EVENSON
Time and Frequency Division, National Bureau of Standards

## ABSTRACT

In this work we present accurate values for the fine-structure intervals in the $^3P$ ground state of neutral atomic carbon-12 and carbon-13 as obtained from laser magnetic resonance spectroscopy. The rigorous analysis of $^{13}$C hyperfine structure, the measurement of resonant fields for $^{13}$C transitions at several additional far-infrared laser frequencies, and the increased precision of the $^{12}$C measurements permit significant improvement in the evaluation of these energies relative to earlier work. The $J = 2 \leftarrow 1$ interval is 809.3435(9) GHz in $^{12}$C and 809.3489(10) GHz in $^{13}$C, while we find values of 492.1611(12) GHz and 492.1628(20) GHz, respectively, for the $J = 1 \leftarrow 0$ splittings. These results will expedite the direct and precise measurement of these transitions in interstellar sources and should assist in the determination of the interstellar $^{12}$C/$^{13}$C abundance ratio.

Subject headings: atomic processes — interstellar: abundances — line identifications

## I. INTRODUCTION

Transitions within the $^3P$ ground-state fine-structure levels of neutral atomic carbon (C I) are expected to contribute substantially to the cooling of interstellar molecular clouds. In addition, the relative abundances of CO, C I, and C II are important probes of the chemistry and long-term dynamics of these clouds. The detection of $^{12}$C I in the interstellar medium (ISM) by Phillips et al. (1980) was facilitated by the prior observation and analysis of the same fine-structure transitions in the laboratory by laser magnetic resonance spectroscopy (LMR) (Saykally and Evenson 1980). Phillips et al. found strong C I lines deep within regions exhibiting strong CO emission, in contrast to the predictions of several chemical models existing at that time. This and subsequent work provide important evidence on which to base revised models of carbon chemistry in these sources (Frerking et al. 1986).

It would be useful to measure the $^{12}$C I/$^{13}$C I abundance ratio in the ISM, since this information is expected to clarify the reason for the high C I abundance in inner regions of molecular clouds and to characterize regions of star formation further. In the original laboratory study (Saykally and Evenson 1980), the $^{12}$C I spectrum was analyzed, and an estimate of the $^{13}$C I transition energy was also given, but no rigorous treatment of the $^{13}$C hyperfine structure was presented at the time. Additional measurements of both carbon isotopes have subsequently been obtained, and for each a more rigorous analysis has been performed, using these results in combination with the original data and correcting one of the original field measurements. In this paper we present accurate values for the fine-structure splittings of each of these isotopes in their ground states with the intent of facilitating the observation of $^{13}$C I and analysis of the carbon isotope ratio in the ISM.

## II. THEORY

The effective atomic Hamiltonian contains three terms:

$$\hat{H} = \hat{H}_0 + \hat{H}_Z + \hat{H}_M , \tag{1}$$

where $\hat{H}_0$ is the fine-structure term, $\hat{H}_Z$ the Zeeman interaction, and $\hat{H}_M$ the magnetic hyperfine structure contribution. To $\hat{H}_0$ we assign eigenvalues $E_J^0$ corresponding to the energy of the unperturbed fine-structure level. The atomic Zeeman Hamiltonian is written (Miller and Freund 1971)

$$\hat{H}_Z = [\mu_B(g_S \hat{S} + g_L \hat{L}) - \mu_N g_I(1 - \sigma)\hat{I}] \cdot B - \tfrac{1}{2}\chi_I B^2 - \chi_A T^{(2)}(B, B) \cdot T^{(2)}(L, L) , \tag{2}$$

where $B$ is the magnetic flux density, $\mu_B$ is the Bohr magneton, $\mu_N$ is the nuclear magneton, $\sigma$ is the nuclear diamagnetic shielding constant, and the isotropic and anisotropic diamagnetic susceptibilities are represented by $\chi_I$ and $\chi_A$, respectively. The first term in this expression, evaluated in an $LS$ coupled basis $|LSJM_J IM_I\rangle$ and neglecting diamagnetic effects, yields the diagonal terms $\mu_B g_J M_J B - \mu_N g_I(1 - \sigma)M_I B$ and off-diagonal terms, effectively $\langle LSJ \pm 1 \, M_J| \, \mu_B(g_S - g_L)\hat{S}_z B \, |LSJM_J\rangle$. The off-diagonal matrix

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[1] Berkeley Miller Research Professor.

elements are given by the expression

$$\langle LSJM_J | \hat{H}_Z | LSJ - 1M_J \rangle = -\mu_B(g_S - g_L)\frac{B}{2J}\left[\frac{(J^2 - M_J^2)(J + L + S + 1)(J + L - S)(-J + L + S + 1)(J - L + S)}{(2J - 1)(2J + 1)}\right]^{1/2}. \quad (3)$$

The factors $g_J$ are approximated reasonably well by the values obtained from application of the Wigner-Eckart theorem:

$$g_J = \frac{1}{2}\left\{(g_L + g_S) + \frac{(g_L - g_S)[L(L + 1) - S(S + 1)]}{J(J + 1)}\right\}, \quad (4)$$

which gives $g_{J=1} \approx g_{J=2} \approx 3/2$ for a $^3P$ atom. Small deviations from equation (4) arise from $LS$-coupling breakdown, nuclear motion, and relativistic effects (Abragam and Van Vleck 1953). In the case of the carbon atom, the $g_J$ factors have been measured by atomic beam spectroscopy to a precision exceeding that required for our analysis (Wolber $et$ $al.$ 1970), and these values are employed here. The diamagnetic effects in equation (2) are below our resolution, but were included in the analysis for completeness. Further discussion of these diamagnetic contributions for the case of the isoelectronic species N II is available elsewhere (Cooksy, Hovde, and Saykally 1986).

$^{12}$C I has no nuclear hyperfine interaction, and in $^{13}$C I it is limited to that resulting from magnetic interactions of first order, since the nuclear spin $I = \frac{1}{2}$. The hyperfine Hamiltonian used here is identical to that employed by Harvey (1965) in his studies of $^{17}$O and $^{19}$F:

$$\hat{H}_M = 2g_I\mu_B^2\{\langle r_I^{-3}\rangle(\hat{L} \cdot \hat{I}) + \langle r_s^{-3}\rangle\xi[L(L + 1)(\hat{S} \cdot \hat{I}) - \tfrac{3}{2}(\hat{L} \cdot \hat{S})(\hat{L} \cdot \hat{I}) - \tfrac{3}{2}(\hat{L} \cdot \hat{I})(\hat{L} \cdot \hat{S})] + \tfrac{8}{3}\pi|\psi(0)|^2(\hat{S} \cdot \hat{I})\}, \quad (5a)$$

where

$$\xi = \frac{(2I + 1) - 4S}{S(2I - 1)(2I + 3)(2L - 1)}. \quad (5b)$$

The matrix elements of this Hamiltonian, given in alternate form in the Appendix, are

$$\langle LSJ'M_J'IM_I' | \hat{H}_M | LSJM_JIM_I \rangle = (-1)^{J'+J+I+L+S-M_J'-M_I'+1}2\sqrt{L(L + 1)(2L + 1)I(I + 1)(2I + 1)}\sqrt{(2J' + 1)(2J + 1)}$$

$$\times \begin{Bmatrix} L & J' & S \\ J & L & 1 \end{Bmatrix}\sum_{p=-1}^{1}(-1)^p\begin{pmatrix} J' & 1 & J \\ -M_J' & p & M_J \end{pmatrix}\begin{pmatrix} I & 1 & I \\ -M_I' & -p & M_I \end{pmatrix}c_{J',J}^{-1}A_{J',J}, \quad (6)$$

where $c_{J',J}$ is the coefficient appearing before $g_I\mu_B^2\langle r_I^{-3}\rangle$ in the expressions for the constants $A_{J',J}$ (e.g., for C I, $c_{1,1} = c_{2,2} = 1$, $c_{2,1} = 1/3^{1/2}$, and $c_{1,0} = 2(2/3)^{1/2}$; see eqs. [8] and [10] below). In the approximation that $J$ is a rigorously good quantum number, equation (5) may be substantially simplified to the form

$$\hat{H}_M = A_J\hat{I} \cdot \hat{J}, \quad (7)$$

where $A_J \equiv A_{J,J}$. The $A_J$ coefficients may then be written in terms of the radial integrals in equation (5), yielding

$$A_1 = g_I\mu_B^2[\langle r_I^{-3}\rangle - \langle r_s^{-3}\rangle + \tfrac{8}{3}\pi|\psi(0)|^2], \quad A_2 = g_I\mu_B^2[\langle r_I^{-3}\rangle + \tfrac{1}{5}\langle r_s^{-3}\rangle + \tfrac{8}{3}\pi|\psi(0)|^2]. \quad (8)$$

These $A_J$ coefficients have also been measured for $^{13}$C by atomic beam spectroscopy (Wolber $et$ $al.$ 1970; eq. [5] of Wolber $et$ $al.$ is corrected in eqs. [8], [10] of this paper).

There are also off-diagonal terms in $J$ from equation (5) proportional to the constants $A_{J,J-1}$ defined in Harvey's work (1965) by the equation

$$\langle JM_JIM_I | \hat{H}_M | J - 1M_JIM_I \rangle = M_I\sqrt{J^2 - M_J^2}A_{J,J-1}. \quad (9)$$

The matrix elements between states of different $M_I$ and $M_J$ are, in general, also nonzero. These hyperfine effects off-diagonal in $J$ are, at best, poorly resolved by LMR, but their inclusion improves the quality of the data fitted by a small margin. The magnitudes of these constants were estimated using theoretical values (Schaefer, Klemm, and Harris 1968) for $\langle r_s^{-3}\rangle$, $\langle r_I^{-3}\rangle$, and $|\psi(0)|^2$, and the expressions obtainable from equations (5) and (9):

$$A_{1,0} = \sqrt{\tfrac{2}{3}}g_I\mu_B^2[2\langle r_I^{-3}\rangle - \langle r_s^{-3}\rangle - \tfrac{16}{3}\pi|\psi(0)|^2], \quad A_{2,1} = \sqrt{\tfrac{1}{3}}g_I\mu_B^2[\langle r_I^{-3}\rangle + \tfrac{2}{5}\langle r_s^{-3}\rangle - \tfrac{8}{3}\pi|\psi(0)|^2]. \quad (10)$$

The values of these constants for $^{13}$C, as well as those of the other relevant constants used in the fit, are given in Table 1.

### III. RESULTS AND DISCUSSION

The experimental apparatus (Evenson 1981) and conditions (Saykally and Evenson 1980) used in this work were described previously. The data obtained from these measurements were fitted to the complete Hamiltonian using standard diagonalization and least-squares fitting routines, yielding accurate values for the zero-field fine-structure transition energies of $^{12}$C I and $^{13}$C I. Those are given in Table 2, and are illustrated for $^{13}$C in Figure 1. Comparison with the original data shows substantial improvement in the uncertainty of the $J = 2 \leftarrow 1$ $^{12}$C splitting, due to the inclusion of more precise field measurements and the correction of an earlier, incorrectly recorded measurement (the resonant field for the $J''$, $M_J'' = 1$, $-1$ transition at 783.4860 GHz is 12352.4 G). This value is therefore more accurate as well. The value for the $J = 1 \leftarrow 0$ splitting in $^{12}$C obtained from LMR is now in better agreement with the more precise value found by heterodyne spectroscopy of the ISM (Frerking $et$ $al.$ 1986). It is likely that the

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TABLE 1

CONSTANTS IN ANALYSIS OF LMR SPECTRUM OF
$^3P$ $^{13}$C I AND $^{12}$C I

| Parameter | Value |
|---|---|
| $g_{J=1}$ | 1.501122[a] |
| $g_{J=2}$ | 1.501109[a] |
| $g_I(^{13}C)$ | 1.404398[b] |
| $A_1(^{13}C)$ | 2.838 MHz[a] |
| $A_2(^{13}C)$ | 149.055 MHz[a] |
| $A_{1,0}(^{13}C)$ | 73.5 MHz[c] |
| $A_{2,1}(^{13}C)$ | 88.0 MHz[c] |
| $\chi_I$ | $2.72 \times 10^{-9}$ MHz/G$^2$ [d] |
| $\chi_A$ | $1.632 \times 10^{-9}$ MHz/G$^2$ [d] |
| $\sigma$ | $2.6073 \times 10^{-4}$ [d] |

[a] Wolber *et al.* 1970. The $g_J$ values have been corrected for an improved value of $\mu_B$.
[b] Royden 1954.
[c] From the calculated results of Schaefer, Klemm, and Harris 1968.
[d] Schaefer and Klemm 1970.

$J = 2 \leftarrow 1$ transition in both isotopes will soon be observed with comparable precision, since Jaffe *et al.* (1985) have now observed this line in the ISM, and further studies are planned. The $^{13}$C splittings are now known to nearly the precision of the $^{12}$C splittings, and with greater accuracy than the values cited in the original work as a result of the complete analysis of hyperfine effects. The $^{13}$C I $J = 1 \leftarrow 0$ is not a convenient candidate for interstellar searches because the small hyperfine splitting and smaller isotope shift place these lines within 5 MHz of the $^{12}$C I transition frequency.

Veseth's (1985) recent detailed theoretical calculations of the isotope shifts in the neutral atomic carbon fine structure encouraged us to determine the experimental uncertainty in the shift directly by least-squares analysis. The observed shifts $[E(^{13}C)-E(^{12}C)]$ are 5.4(1.3) MHz and 1.7(2.5) MHz for the $2 \leftarrow 1$ and $1 \leftarrow 0$ transitions, respectively, where the uncertainties cited are two standard deviations. Veseth's ab initio calculations place these values at $-4.5$ MHz and $-3.1$ MHz, respectively. His results give excellent agreement with the observed shifts in neutral oxygen, chlorine, and bromine, but even this thorough treatment is insufficient for the cases of singly ionized neon and argon. Hence, this small discrepancy between the theoretical and experimental carbon data is not surprising.

An accurate knowledge of the abundance of $^{13}$C I relative to $^{12}$C I will be quite valuable in the analysis of cold interstellar sources, particularly in regions of star formation, where this ratio can be profoundly influenced by the expelled products of intrastellar nuclear synthesis. The improved values for the rest frequencies of the transitions in the ground-state carbon atom should facilitate studies of the chemistry and dynamics of these and other interesting sources. Moreover, the recent measurement of the fine-structure interval in the $^2P$ ground state of C II by LMR (Cooksy, Blake, and Saykally 1986) will permit the same type of measurement to be made for the singly ionized form of carbon as well.

TABLE 2

FINE-STRUCTURE INTERVALS AND TRANSITION FREQUENCIES DETERMINED BY LMR

A.

| Interval | This Work | Original Work[a] | Astronomical Data[b] |
|---|---|---|---|
| $^{12}$C: | | | |
| $\Delta E_{10}$ (GHz) | 492.1611(12)[c] | 492.1623(9)[c] | 492.1607(1)[d] |
| $\Delta E_{21}$ (GHz) | 809.3435(9)[c] | 809.3446(36)[c] | ... |
| $^{13}$C: | | | |
| $\Delta E_{10}$ (GHz) | 492.1628(20)[d] | 492.164(2)[d] | ... |
| $\Delta E_{21}$ (GHz) | 809.3489(10)[c] | 809.346(4)[d] | ... |

B.

| $^{13}$C Transition Frequencies | $\nu$ (GHz) | Relative Intensity[e] |
|---|---|---|
| $J', F' \leftarrow J'', F''$: | | |
| $1, \frac{3}{2} \leftarrow 0, \frac{1}{2}$ | 492.1600(20)[d] | 33.3 |
| $1, \frac{1}{2} \leftarrow 0, \frac{1}{2}$ | 492.1642(20)[d] | 66.7 |
| $2, \frac{5}{2} \leftarrow 1, \frac{3}{2}$ | 809.1282(10)[c] | 33.3 |
| $2, \frac{3}{2} \leftarrow 1, \frac{1}{2}$ | 809.1240(10)[c] | 6.7 |
| $2, \frac{3}{2} \leftarrow 1, \frac{3}{2}$ | 809.4966(10)[c] | 60.0 |

[a] Saykally and Evenson 1980.
[b] Frerking *et al.* 1986.
[c] Uncertainties cited are 95% confidence limits.
[d] Uncertainties cited are estimated.
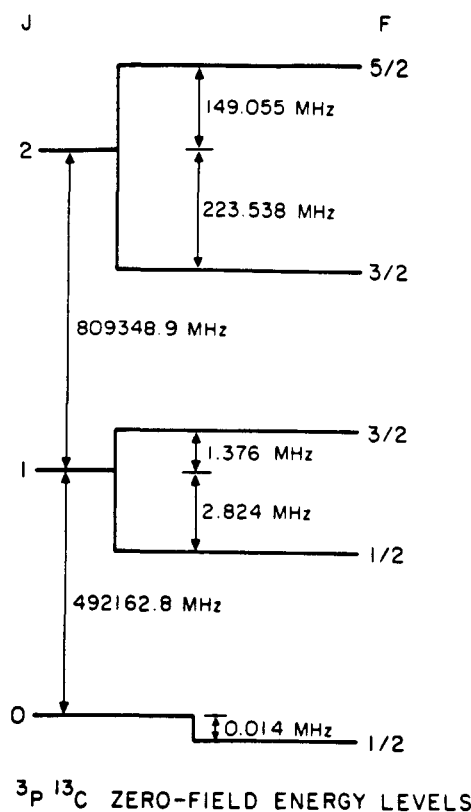[e] Townes and Schawlow 1955.

FIG. 1.—Zero-field energy level diagram for $^{13}$C I, illustrating the fine-structure separations evaluated in this work along with the hyperfine interactions determined by Wolber et al. (1970).

## APPENDIX

An alternative form of equation (6) which gives the matrix elements of $\hat{H}_M$ in more explicit form is

$$\langle LSJ'M'_J IM'_I | \hat{H}_M | LSJM_J IM_I \rangle = g_I \mu_B \sum_p (-1)^p (-1)^{J'-M_{J'}+I-M_I} \begin{pmatrix} J' & 1 & J \\ -M'_J & p & M_J \end{pmatrix} \begin{pmatrix} I & 1 & I \\ -M'_I & -p & M_I \end{pmatrix}$$

$$\times [I(I+1)(2I+1)]^{1/2} \langle LSJ' \| T^{(1)}(B_J) \| LSJ \rangle , \tag{A1a}$$

where $B_J$ is the magnetic field strength at the nucleus due to the electrons. The reduced matrix element is given by

$$\langle LSJ' \| T^{(1)}(B_J) \| LSJ \rangle = 2\mu_B [(2J'+1)(2J+1)]^{1/2} [\langle r_l^{-3} \rangle (-1)^{L+S+J'+1} \begin{Bmatrix} S & L & J' \\ 1 & J & L \end{Bmatrix} [L(L+1)(2L+1)]^{1/2}$$

$$+ \langle r_s^{-3} \rangle \xi \left[ L(L+1)(-1)^{L+S+J'+1} \begin{Bmatrix} L & S & J' \\ 1 & J & S \end{Bmatrix} [S(S+1)(2S+1)]^{1/2} \right.$$

$$\left. - \tfrac{3}{4}(-1)^{L+S+J+1} \begin{Bmatrix} S & L & J' \\ 1 & J & L \end{Bmatrix} [L(L+1)(2L+1)]^{1/2} [J'(J'+1) + J(J+1) - 2L(L+1) - 2S(S+1)] \right]$$

$$+ \frac{8\pi}{3} |\psi(0)|^2 (-1)^{L+S+J'+1} \begin{Bmatrix} L & S & J' \\ 1 & J & S \end{Bmatrix} [S(S+1)(2S+1)]^{1/2} \right] . \tag{A1b}$$

By straightforward application of equations (7) and (9), one may then use the results of the above expressions to relate the coefficients $A_{J',J}$ to the parameters $\langle r_l^{-3} \rangle$, $\langle r_s^{-3} \rangle$, and $|\psi(0)|^2$. This has been done for the case of $^3P$ atoms in equations (8) and (10).

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J. M. BROWN: Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford, OX1 3QZ, England, UK

A. L. COOKSY and R. J. SAYKALLY: Department of Chemistry, University of California, Berkeley, CA    94720

K. M. EVENSON: Time and Frequency Division, National Bureau of Standards, Boulder, CO    80302