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A MEASUREMENT OF THE $J = 2 \leftarrow 1$ FINE-STRUCTURE INTERVAL FOR ^{28}Si AND ^{29}Si IN THE GROUND ^3P STATE[1]

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ABSTRACT

We report the first observation of the far-infrared laser magnetic resonance spectrum associated with the $J = 2 \leftarrow 1$ fine-structure interval of ^{28}Si and ^{29}Si in the ^3P ground state. In ^{28}Si this separation is 4378.3280(2) GHz, and for ^{29}Si it is 4378.3306(6) GHz. The magnetic hyperfine parameter A_2 has also been determined for ^{29}Si, apparently for the first time. The value obtained corresponds to a value for the electronic expectation value $\langle r^{-3} \rangle_l$ of 1.626×10^{31} m^{-3}. Zero-field transition frequencies for the hyperfine components of the $J = 2 \leftarrow 1$ transition in ^{29}Si are determined and will aid in their identification in interstellar sources.

Subject headings: atomic data — line: identification — ISM: atoms — radio lines: ISM

1. INTRODUCTION

There is growing interest in the measurement of the fine-structure intervals of light atoms in the far-infrared. These transitions provide a means of detecting such species in the more opaque parts of the interstellar medium and other astrophysical sources. The successful astrophysical observation of these transitions with modern heterodyne receivers such as those flown on the Kuiper Airborne Observatory requires a knowledge of the transition frequency to within a few MHz. Such accuracy is not available in the laboratory from optical spectroscopy but it can be achieved by far-infrared spectroscopy, either with the aid of a tunable coherent source (Evenson, Jennings, & Vanek 1988) or by laser magnetic resonance (LMR; Inguscio 1988). LMR is by far the more sensitive of these two techniques. Measurements have been made in this way of the fine-structure intervals in O atoms (Zink et al. 1991), C atoms (Cooksy et al. 1986a), Si atoms (Inguscio et al. 1984), N atoms in the ^2D metastable state (Bley et al. 1989), Mg atoms in the ^3P metastable state (Inguscio et al. 1985), N^+ atoms (Cooksy, Hovde, & Saykally 1986b), and C^+ atoms (Cooksy, Blake, & Saykally 1986c). In these experiments, the atoms were generated in the gas phase by chemical reactions or electric discharges. The limitation to further observations is the lack of available laser lines in this region of the spectrum (100–25 μm). We have recently made a simple improvement to the design of the far-infrared laser which makes it much more efficient 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 have not been identified previously. We have used these new lines to detect several other fine-structure transitions in atoms, one of them being the $^3P_2$–$^3P_1$ transition in Si reported in this *Letter*.

The $J = 1 \leftarrow 0$ transition in the ^3P ground state of ^{28}Si was detected by Inguscio et al. (1984) by LMR. They observed the same transition with four different laser lines and determined the g_J factor in the $J = 1$ level as well as the zero-field transition frequency. However, the $J = 2 \leftarrow 1$ transition was not detectable because, at the time, there were no known laser lines sufficiently close to the desired wavelength (68.47 μm). Our discovery of two new laser lines at 68.7 and 68.1 μm has enabled us to make this measurement. The sensitivity of the experiment was such that we were also able to detect the $J = 2 \leftarrow 1$ fine-structure transition in ^{29}Si in natural abundance (4.67%). Magnetic hyperfine structure from the $I = \frac{1}{2}$ nucleus has been observed for the first time.

Although the fine-structure transitions in Si have not yet been detected in an astrophysical source, they have been detected for the related species C and Si^+ (Phillips et al. 1980; Haas et al. 1991). These observations suggest that Si itself is likely to be detected in the near future. The measurements reported in this paper will help this search by defining the transition frequency much more precisely.

2. EXPERIMENTAL DETAILS

The LMR apparatus used in this work has been described in essence elsewhere (Sears et al. 1984). 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 thin (12.5 μm) polypropylene beam splitter set at the Brewster angle. The sample region is situated between the 38 cm, ring-shimmed, nickel-cobalt pole caps of an electromagnet that produces a homogeneous field region 7.5 cm in diameter. The field was stabilized with the signal from a rotating coil magnetometer that is calibrated from time to time against a proton fluxmeter. We estimate the field measurements to be accurate to 0.01 mT below 0.1 T and to $10^{-4}B_0$ above this flux density. When a transition in the atomic sample is tuned into resonance with the laser frequency by the magnetic field, the total far-infrared power inside the laser cavity changes and is modulated at 40 kHz by a pair of Helmholtz coils. The laser output is detected with a liquid-helium–cooled photoconductive bolometer, and the signal is passed to a lock-in amplifier. The modulation frequency is 4 times higher than we have used previously. This increases the sensitivity of the experiment by a factor of 3–4 by reducing the $1/f$ laser noise.

We have modified the spectrometer in order to enhance its performance at short wavelengths (less than 100 μm). We have

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reduced the inside diameter of the polished copper pump tube from 50.8 to 19.1 mm (2 to 0.75 inch). This provides much better overlap between the pumped lasing gas and the far-infrared field within the laser cavity, and many more short-wavelength laser lines oscillate. In particular, we have used two such lines in CD_3OH to study the $J = 2 \leftarrow 1$ fine-structure transition in Si. One of them, lasing at 68.72 μm and pumped by the 10*R*(46) line of $^{12}CO^{16}O_2$, has been reported previously (Saykally et al. 1987), but the other, lasing at 68.09 μm and pumped by the 10*R*(36) $^{12}C^{16}O_2$ laser line, is new. We have determined the frequency of each line by measuring its beat frequency when mixed with a pair of CO_2 laser frequencies in a MIM diode. The results are as follows:

$$CD_3OH \text{ pump } 10R(46) \; \lambda = 68.72 \; \mu\text{m}$$
$$\nu = 4{,}362{,}722.7 \pm 0.5 \text{ MHz},$$
$$CD_3OH \text{ pump } 10R(36) \; \lambda = 68.09 \; \mu\text{m}$$
$$\nu = 4{,}401{,}127.0 \pm 0.5 \text{ MHz}.$$

These two frequencies lie very conveniently on either side of the $J = 2 \leftarrow 1$ transition frequency of Si.

The Si atoms were generated as in the previous work (Inguscio et al. 1984) by the reaction between F atoms and silane, SiH_4, in a discharge-flow system. The F atoms were produced by flowing a 10% mixture of fluorine in helium through a 2450 MHz discharge. The total pressure was about 35 Pa. The optimum Si signal was obtained with a partial pressure of SiH_4 of 1.5 Pa and corresponded to a maximum of the deep violet chemiluminescence produced by the reaction.

3. RESULTS, ANALYSIS, AND DISCUSSION

The LMR spectrum associated with the $J = 2 \leftarrow 1$ fine-structure transition of an atom in a ^3P state consists of three lines, $M_J = 2 \leftarrow 1$, $1 \leftarrow 0$, and $0 \leftarrow -1$ (or the negative of these values) with relative intensities 6:3:1. Since the g_J factors for Si in the $J = 1$ and 2 levels are identical to first order (1.50), all three resonances are expected to occur at the same field. In reality, second-order effects cause these transitions to occur at slightly different fields. For the spectrum recorded with the 68.7 μm laser line, the resonances occur at low enough fields that they are not fully resolved. The spectrum recorded is shown in Figure 1. The signal-to-noise ratio of this spectrum is so good that it is also possible to observe signals from ^{29}Si in natural abundance (4.67%). The hyperfine splitting for the $I = \frac{1}{2}$ nucleus produces resonances well outside the line width of the ^{28}Si signal (see Fig. 1). The signal-to-noise ratio of the spectrum recorded with the 68.1 μm line was even better because this laser line is significantly more powerful. The details of the observations for ^{28}Si and ^{29}Si are given in Tables 1 and 2; respectively.

The LMR spectra have been analyzed with a standard effective Hamiltonian for a Russell-Saunders atom as given, for example, by Cooksy et al. (1986a). Both the present and the previous data for ^{28}Si (Inguscio et al. 1984) are used to determine g_J factors for the $J = 1$ and 2 levels and the fine-structure intervals. The results are given in Tables 1 and 3. The value for the $J = 2 \leftarrow 1$ fine-structure interval of 4378.32796(16) GHz or 146.04530(1) cm^{-1} is consistent with the previous value from optical spectroscopy of 4378.23 GHz or 146.042 cm^{-1} (Bashkin & Stoner 1975) but is much more accurately determined.

Both the g_J factors, 1.500794(23) for $J = 1$ and 1.500642(12) for $J = 2$, are slightly smaller than the values expected from theoretical calculations (1.501097 and 1.500974; Veseth 1980). The theoretical values should be very reliable and indeed have been confirmed by an independent calculation reported by Inguscio et al. (1984). Values of g_J factors determined from

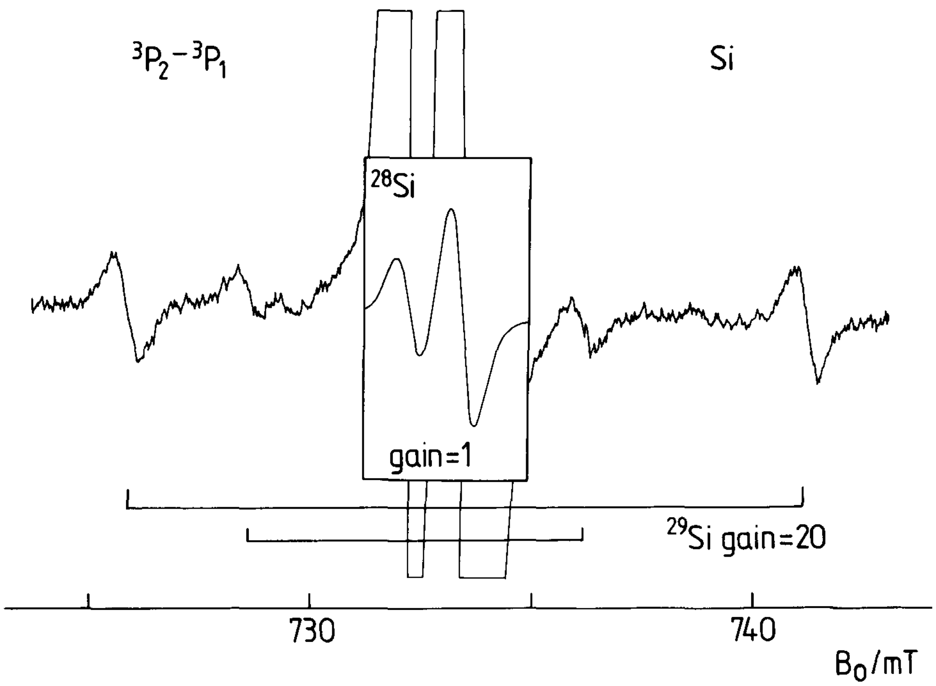

FIG. 1.—Far-infrared laser magnetic resonance spectrum associated with the $J = 2 \leftarrow 1$ transition of atomic silicon in its ground ^3P state, recorded with the 68.7 μm line of CD_3OH, pumped by the 10*R*(46) line of a CO_2 laser. The strong central doublet arises from ^{28}Si, and the weaker outlying lines are hyperfine components of ^{29}Si in natural abundance (4.68%). The spectrum is recorded with the oscillating magnetic field perpendicular to the applied magnetic field ($\Delta M_J = \pm 1$). The output time constant of the lock-in amplifier was 0.3 s.

TABLE 1

LASER MAGNETIC RESONANCE DATA FOR ^{28}Si ATOMS

J	M_J	ν_L/GHz	B_0/mT	(o–c)/MHz
$1 \leftarrow 0$	$1 \leftarrow 0$	2314.1113	112.12[a]	−0.1
	$1 \leftarrow 0$	2341.5089	1412.12[a]	0.4
	$1 \leftarrow 0$	2348.4384	1739.64[a]	3.2
	$-1 \leftarrow 0$	2278.7030	1579.00[a]	1.1
$2 \leftarrow 1$	$-1 \leftarrow 0$	4362.7227	742.18	−0.3
	$-2 \leftarrow -1$	4362.7227	743.37	0.1
	$1 \leftarrow 0$	4401.1270	1087.21	0.3
	$2 \leftarrow 1$	4401.1270	1084.99	−0.1
	$0 \leftarrow -1$	4401.1270	1083.91	0.4

[a] Measurements from the previous study (Inguscio et al. 1984).

TABLE 2

LASER MAGNETIC RESONANCE DATA FOR ^{29}Si ATOMS

J	M_J	M_I[a]	ν_L/GHz	B_0/mT	(o–c)/MHz
$2 \leftarrow 1$	$-2 \leftarrow -1$	$-\frac{1}{2}$	4362.7227	735.78	−0.1
	$-1 \leftarrow 0$	$-\frac{1}{2}$	4362.7227	738.59	0.3
	$-1 \leftarrow 0$	$\frac{1}{2}$	4362.7227	746.11	1.7
	$-2 \leftarrow -1$	$\frac{1}{2}$	4362.7227	751.09	−0.7
	$2 \leftarrow 1$	$-\frac{1}{2}$	4401.1270	1077.16	−0.5
	$1 \leftarrow 0$	$\frac{1}{2}$	4401.1270	1091.01	−0.7
	$2 \leftarrow 1$	$\frac{1}{2}$	4401.1270	1092.53	−0.0

[a] The transitions obey the selection rule $\Delta M_I = 0$.

these far-infrared LMR experiments have an accuracy of about 1 part in 10^4. There are two reasons for this. First, the laser is set manually to the top of the gain curve just before making the measurement so that the frequency used to record the spectrum can be uncertain by $\Delta\nu/\nu = \pm 3 \times 10^{-7}$ (several hundred kHz). Second, the magnetic field is calibrated on the laser axis, whereas the sample volume of Si atoms may lie off center (i.e., at a slightly lower flux density) because the sample is injected from the top of the laser cavity. The latter source of error is systematic and will tend to produce g_J factors slightly smaller than the correct values (as is observed).

TABLE 3

PARAMETERS DETERMINED FROM THE FAR-INFRARED LASER MAGNETIC RESONANCE SPECTRUM OF ATOMIC SILICON

Parameter	^{28}Si	^{29}Si
ΔE_{10}/GHz	2311.75574(12)[a]	2311.7571[b]
ΔE_{21}/GHz	4378.32796(16)	4378.33060(60)
$g_{J=1}$	1.500794(23)[c]	[d]
$g_{J=2}$	1.500642(12)[c]	[d]
A_1/MHz	...	1.84[e]
A_2/MHz	...	−160.74(73)
A_{10}/MHz	...	−88.51[e]
A_{21}/MHz	...	−101.65[e]

[a] The numbers in parentheses represent 1 standard deviation of the least-squares fit, in units of the last quoted decimal place.

[b] Estimated value.

[c] The uncertainty on the g-factors is 1 standard deviation of the least-squares fit. However these quantities are subject to systematic errors which are an order of magnitude large (see text).

[d] Assumed to be the same as for ^{28}Si.

[e] Value estimated from semiempirical values as described in the text.

The measurements on ^{29}Si atoms appear to be the first on this isotopic species. The isotopic shift in the $J = 2 \leftarrow 1$ fine-structure interval (^{29}Si − ^{28}Si) is $+2.6 \pm 0.6$ MHz, smaller than the corresponding quantity for ^{13}C − ^{12}C (+5.4 MHz) but in the same direction. The experimental shift for silicon is also in reasonably good agreement with the ab initio predictions of Veseth (1985) who calculated a shift of +12.2 MHz for ^{30}Si − ^{28}Si.

The observation and analysis of the ^{29}Si magnetic hyperfine structure provides valuable information on the electronic wavefunction for the atom in its ground state. As is well known, the observed splittings for an atom in a ^3P state depend on four hyperfine parameters, A_1, A_2, A_{10}, and A_{21} (see, e.g., Cooksy et al. 1986a). These in turn can be expressed in terms of three structural parameters, $\langle r^{-3}\rangle_l$, $\langle r^{-3}\rangle_s$, and $\psi(0)^2$:

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

$$\frac{A_2}{\text{Hz}} = \frac{g_N \mu_N \mu_B}{10^7 h}\left[\langle r^{-3}\rangle_l + \frac{g_s}{10}\langle r^{-3}\rangle_s + g_s \frac{4\pi}{3}\psi(0)^2\right], \quad (2)$$

$$\frac{A_{10}}{\text{Hz}} = \frac{g_N \mu_N \mu_B}{10^7 h}\sqrt{\frac{2}{3}}\left[2\langle r^{-3}\rangle_l - \frac{g_s}{2}\langle r^{-3}\rangle_s - g_s \frac{8\pi}{3}\psi(0)^2\right], \quad (3)$$

$$\frac{A_{21}}{\text{Hz}} = \frac{g_N \mu_N \mu_B}{10^7 h}\sqrt{\frac{1}{3}}\left[\langle r^{-3}\rangle_l + \frac{g_s}{5}\langle r^{-3}\rangle_s - g_s \frac{4\pi}{3}\psi(0)^2\right]. \quad (4)$$

In these four equations, g_N is the nuclear g-factor (−1.1106 for ^{29}Si), μ_N and μ_B are the nuclear and Bohr magnetons, respectively, and h is Planck's constant. The equations are written in SI units. Because $\langle r^{-3}\rangle_l \simeq \langle r^{-3}\rangle_s$ and $\psi(0)^2$ is approximately zero for electrons in the $3p$ orbital on the Si atom, the observed hyperfine splitting depends primarily on the parameter A_2. The value for A_1 is too small to place the ^{29}Si hyperfine doublet outside the ^{28}Si line width in the $J = 1 \leftarrow 0$ spectrum, and such features were consequently not observed in the previous work (Inguscio et al. 1984). However, the $J = 2 \leftarrow 1$ hyperfine splitting observed in the present study involves the splitting in the $J = 1$ level, which depends on A_1. Since we cannot determine both A_1 and A_2 from our measurements, we have estimated a value for A_1 and constrained it in the least-squares fit to the data. The required estimate is made using results given by Harvey, Evans, & Lew (1972). By scaling ab initio results, they estimate a value for $(4/3)\pi g_s \psi(0)^2$ for Si of 7.42×10^{29} m^{-3} or 0.11 au^{-3}. Their analysis of trends in expectation values for first and second row atoms also suggests (see Fig. 3*b* of their paper) that

$$\langle r^{-3}\rangle_s \simeq 1.06\langle r^{-3}\rangle_l \quad (5)$$

for Si. These two relationships can be used together with a preliminary value for A_2 to calculate values for A_1, A_{10}, and A_{21} using equations (1), (3), and (4) and so obtain a more accurate value for A_2 of −160.6 MHz. This value corresponds to a value for $\langle r^{-3}\rangle_l$ of 2.410 au^{-3} or 1.626×10^{31} m^{-3}, given the assumptions made above. A reliable calculation of this expectation value has apparently not yet been made. The present determination is clearly much more accurate than the estimate of 2.691 au^{-3} made using Herman and Skillman's wave function (Morton & Preston 1978) and can be used to make more reliable interpretations of ^{29}Si splittings in open shell molecules.

TABLE 4

FREQUENCIES AND INTENSITIES FOR THE FINE-STRUCTURE TRANSITIONS IN ATOMIC SILICON IN THE GROUND ^3P STATE

Transition	Frequency (GHz)	Relative Intensity[a]
^{28}Si $J = 1$–0	2311.75574(12)[b]	4.018
^{28}Si $J = 2$–1	4378.32796(16)	5.023
^{29}Si $J = 1$–0:		
$F = 1\frac{1}{2}$–$\frac{1}{2}$	2311.758(3)	2.679
$F = \frac{1}{2}$–$\frac{1}{2}$	2311.755(3)	1.340
^{29}Si $J = 2$–1:		
$F = 2\frac{1}{2}$–$1\frac{1}{2}$	4378.1691(10)	3.014
$F = 1\frac{1}{2}$–$\frac{1}{2}$	4378.5734(13)	1.674
$F = 1\frac{1}{2}$–$1\frac{1}{2}$	4378.5706(13)	0.335

[a] The relative intensity is given by the square of the magnetic dipole transition moment, $\langle LSJ'IF' \| (m/\mu_B) \| LSJIF \rangle^2$.

[b] Estimated uncertainty (1 σ) in units of the last quoted decimal place.

The zero field frequencies of ^{28}Si and ^{29}Si, calculated from the parameter values determined from the fit (Table 3) are given in Table 4, together with their relative intensities. The Einstein A coefficients are 8.283×10^{-6} and 4.221×10^{-5} s^{-1} for the $J = 1 \rightarrow 0$ and $J = 2 \rightarrow 1$ transitions, respectively. Although the transitions are magnetic dipole, the prospects are good for their detection, since Si has quite a high cosmic abundance. Measurements of the amounts of ^{29}Si relative to ^{28}Si may well be as informative on the processes of star formation as that which comes from the ^{13}C/^{12}C ratio

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