

THE DIRECT MEASUREMENT OF THE $3^3P_0-3^3P_1$ FINE-STRUCTURE INTERVAL AND THE g_J -FACTOR OF ATOMIC SILICON BY LASER MAGNETIC RESONANCE¹

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ABSTRACT

Laser magnetic resonance measurements have been performed on the ground $3p^2\ ^3P$ multiplet of atomic silicon. The $J = 1 \leftarrow 0$ fine-structure interval and the g -factor of the 3P_1 state have been determined with high precision. The results are: $\Delta E(^3P_1-^3P_0) = 2,311,755.6(7)$ MHz and $g_J(^3P_1) = 1.500830(70)$. Single-configuration calculations of $g_J(^3P_1)$ and $g_J(^3P_2)$, with accurate Hartree-Fock wave functions, were performed. The calculated value $g_J(^3P_1) = 1.501095$ shows an unexpectedly large difference from the experimental value.

Subject headings: atomic processes — interstellar: molecules — laboratory spectra — Zeeman effect

I. INTRODUCTION

Far-infrared laser magnetic resonance (LMR) is a new and powerful spectroscopic technique for studying molecules. This has already been proven by applying it successfully to detect and study the rotational spectra of transient molecular species, many of which have long been of great interest in astrophysics (Evenson *et al.* 1980).

The applicability of LMR to atoms, however, meets with some difficulties. Mainly, a near coincidence between a laser line and an atomic transition may not be available; in contrast, a number of rotational transitions are available from even a simple molecule. Besides this, since atomic transitions in the far-infrared are magnetic dipole in nature, the sensitivity of LMR spectroscopy to atomic transitions is greatly reduced. This is particularly severe when the production of a high atomic density is limited as it is for the nonvolatile elements. To date, only atomic oxygen⁴ and atomic carbon have been measured (Davies *et al.* 1978; Saykally and Evenson 1979, 1980). In this *Letter*, we report LMR measurements on silicon atoms.

There are several reasons for studying the silicon atom. Its cosmic abundance relative to hydrogen is 2.5×10^{-5} . This makes it the sixth most abundant element after hydrogen, helium, oxygen, nitrogen, and carbon. Its 3P ground-state fine-structure splitting lies at far-infrared frequencies and is

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⁴An incorrect value of the laser frequency was used in the calculation of the $^3P_1-^3P_2$ oxygen frequency difference (Saykally and Evenson 1979). The correct value of the $^3P_1-^3P_2$ interval of oxygen is $4,744,774.0 \pm 2$ MHz [$158.26862(7)$ cm⁻¹].

known from laboratory optical spectroscopy measurements, although only to within 200 MHz (Moore 1970; Bashkin and Stoner 1975). Far-infrared spectroscopy at the wavelengths of the fine structure of silicon is then a very convenient way to measure its density, particularly in cold interstellar clouds for in those no optical lines are emitted. However, the astronomical search for silicon by infrared spectroscopy has so far been unsuccessful (Watson and Storey 1980). An accurate value of the fine-structure separation of silicon would expedite this astronomical search as in the case of atomic carbon (Saykally and Evenson 1980; Phillips *et al.* 1980).

The near coincidence of the ground-state fine-structure line of silicon with at least four laser lines makes this atom particularly amenable to study by LMR spectroscopy. We have determined its fine-structure splitting from an LMR experiment. In addition to this, we have also obtained the g_J -factors of silicon to sufficient accuracy for a meaningful comparison with theoretical values.

II. EXPERIMENTAL

The LMR apparatus used in this experiment has been previously described (Evenson 1981). Briefly, it consists of a far-infrared gain cell pumped transversely by a grating-tuned CO₂ laser and separated from the intracavity sample region by a polypropylene beam splitter at Brewster angle to the far-infrared laser cavity. The sample region is placed between the ring-shimmed Hyperco 38 cm pole caps of an electromagnet producing a homogeneous field region 7.5 cm in diameter.

Two coaxial flow tubes extend to the perimeter of the laser tube where fluorine atoms, produced in a 2450 MHz discharge in a dilute mixture of F₂ in He in the inner tube, mix with silane (SiH₄) flowing down between the walls of the two tubes. The reaction of the flowing F atoms with the silane

produces a deep violet flame in the laser cavity and produces free Si atoms. Optimum conditions for production of silicon atoms are obtained at a total pressure of 34 Pa and the following composition: He, 87%, F₂, 9%; and SiH₄, 4%. This is almost exactly the same composition which maximizes LMR spectral intensities for SiH recently observed in the same apparatus (Brown and Evenson 1984).

When a transition in the atom is tuned into coincidence with the laser frequency by the magnetic field, the total far-infrared power inside the laser cavity changes and is modulated at 10 kHz by a pair of Helmholtz coils. The laser output is detected with a helium-cooled germanium bolometer, and the signal is fed to a lock-in amplifier. The demodulated output signal is approximately equal to the first derivative of the absorption signal.

The Zeeman spectrum of silicon in its ground state can be calculated with the second-order equation:

$$\nu_L = \nu_0 + \mu_B [(g'_j - g''_j) M'_j \pm g'_j] B + CB^2, \quad (1)$$

where ν_L is the laser frequency, ν_0 is the zero-field fine-structure transition frequency, μ_B is the Bohr magneton, C is the coefficient of the second-order Zeeman shift, B is the magnetic field, and g_j is the g -factor of the J state. Primes refer to the upper, and double primes to the lower, states of the transition. The plus and minus signs correspond to the $\Delta M = \pm 1$ transitions. The first-order Zeeman energy is simply given by $g_j \mu_B B M_j$, and second-order contributions, calculated according to standard methods, are given by Townes and Schawlow (1955, Table 10-1). Those contributions are shown in Figure 1, where $\epsilon_1 = 84.74 \text{ MHz T}^{-2}$ and $\epsilon_2 = 44.74 \text{ MHz T}^{-2}$. The third-order corrections vanish in LS coupling, the fourth-order terms are totally negligible for a 3P state at the level of LMR precision (Radford and Hughes 1959), and also the diamagnetic contribution is negligible.

The $1 \rightarrow 2$ transition occurs at $68.47 \mu\text{m}$ (4378 GHz), and it is not at present accessible to LMR because there are no laser lines sufficiently near in frequency. In contrast to this, the $0 \rightarrow 1$ transition occurs at $129.68 \mu\text{m}$ (2312 GHz) and can be observed with at least four laser lines. In Figure 2 the Zeeman energy level diagram is shown together with the observed transitions.

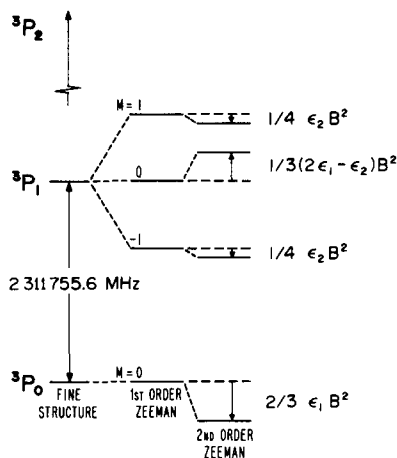


FIG. 1.—Energy-level diagram of the 3P_0 and 3P_1 states, including second-order Zeeman shifts, for Si ($1s^2 2s^2 2p^6 3s^2 3p^2$).

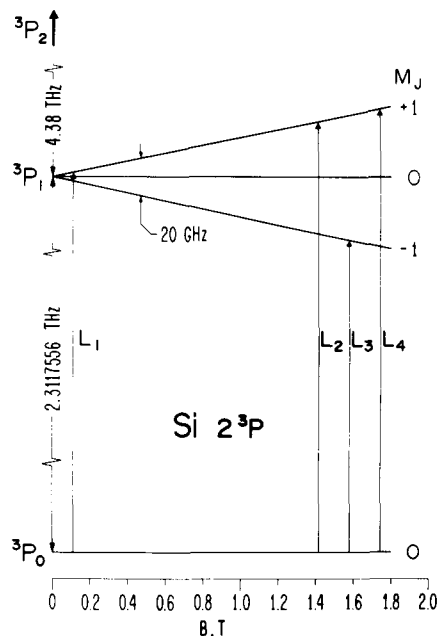


FIG. 2.—Zeeman energy-level diagram with the observed coincidences with four laser lines (Table 1).

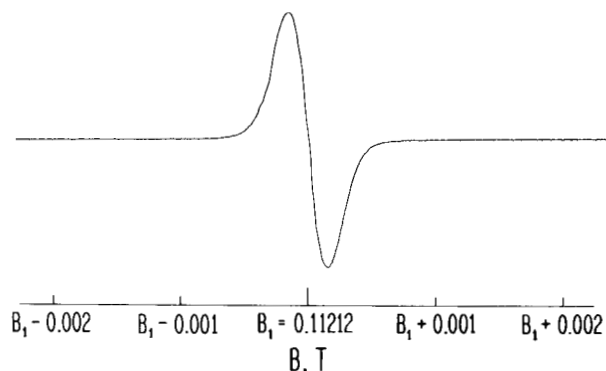
III. EXPERIMENTAL RESULTS

The experimental data are given in Table 1. Four different lines were used from three different isotopic species of methyl alcohol. The far-infrared frequencies have a fractional accuracy of 2×10^{-7} imposed by the limit in reproducing the setting of the cavity length to the peak output power of the laser lines. There is one report (Lawandy and Koepf 1980) of uncertainties 5 times greater than the number reported here. They report that this is due to a pressure shift; however, we have tried unsuccessfully to repeat their measurements (Inguscio, Petersen, and Evenson 1983). We have found shifts of similar magnitude due to line competition and believe that is the effect which they observed. Our LMR spectrometer is operated single-mode, single-frequency; hence, it does not suffer from these uncertainties. The first three laser lines appear in the compilation of Knight (1981). The fourth line was recently discovered in this laboratory by pumping $^{13}\text{CD}_3\text{OH}$ with the 10 R(22) CO₂ laser line (Petersen *et al.* 1984). LMR signals are recorded with a good signal-to-noise ratio as is shown in Figure 3 for the lowest magnetic field transition. The signal-to-noise ratio is significantly larger than that reported for carbon (Saykally and Evenson 1980). This is largely due to the higher transition probability brought about by the higher frequency of the Si transition. The line width (FWHM) in the recording of Figure 3 is 0.00032 T corresponding to about 6 MHz.

Accurate values for ν_0 and g_j are obtained by substituting the experimental data of Table 1 into equation (1) and solving the resulting simultaneous equations. Determinations of these values were made with data from all pairs of lines, except the pair 2 and 4 which yields inherently poor values for ν_0 and g_j on account of the proximity of the respective laser frequencies. The final results are shown in Table 2 together with the previously known, less accurate value.

TABLE I
 EXPERIMENTAL LMR DATA FOR Si: $^3P_1-^3P_0$ TRANSITION

LASER LINE	B (teslas)	TRANSITION		λ_L (μm)	LASING GAS	ν (MHz)
		M_J''	M_J'			
L_1	0.11212(1)	0	1	129.5	CH ₃ OH	2,314,111.3
L_2	1.41212(10)	0	1	128.3	CD ₃ OH	2,341,508.9
L_3	1.57900(10)	0	-1	131.6	CD ₃ OH	2,278,703.0
L_4	1.73964(17)	0	1	127.7	¹³ CD ₃ OH	2,348,438.4


 FIG. 3.—LMR signal of Si from the 129.5 μm , 2,314,111.3 MHz line of CH₃OH at 0.11212 T. This signal was recorded with a 0.1 s time constant.

IV. THEORETICAL

Atomic g_J -factors have been the subject of detailed calculations with the general objective of testing the theory of atomic magnetism (Abragam and Van Vleck 1953; Kambe and Van Vleck 1953). Different types of wave functions—Hartree-Fock (HF), unrestricted HF (UHF), and spin extended HF (SEHF)—have been used in these calculations (Beltrán-López *et al.* 1968; Beltrán-López *et al.* 1969; Beltrán-López and González 1970; Veseth 1980). In general, for the lighter atoms ($Z < 12$), calculated values agree with measurements to within a few parts per million. Sometimes, simple HF wave functions give excellent agreement, whereas in others a more elaborate wave function, such as SEHF, yields slight improvements. However, no systematic advantage of one type of wave function over the others has yet been established, as is well illustrated by the HF and SEHF calculated g_J factors in the 3P_1 and 3P_2 states of carbon. These, while in mutual agreement, deviate from the experimental value⁵ by the relatively large amount of about 100×10^{-6} . On the other hand, for heavier atoms, only HF calculations have been made. For the alkaline atoms, K and Rb, the experimental and calculated g_J factors differ by a few millionths and tens of millionths respectively. For the halogens Cl, Br, and I, this difference amounts to several times 10×10^{-6} . The g_J factors for the other $3p$ -row elements have also been calculated, but only that of Al is known also from experiment; it differs from theory by as much as 672×10^{-6} .

The present experimental value of $g_J(^3P_1)$ for Si, 1.500830, differs from the HF value calculated by Veseth (1980),

1.501097, by 267×10^{-6} . In view of this large discrepancy, we decided to do our own HF calculation. This was done with the Kambe-Van Vleck (1953) theory and accurate HF wave functions for Si (Clementi and Roetti 1974). In Table 2 we list the calculated values for the various corrections to the g_J factor as well as those of Veseth for comparison. From this it can be seen that both HF calculations of g_1 and g_2 are in agreement to within 2×10^{-6} . It should be noted, however, that $\delta g_{LS} = \{\zeta(3p)/[E(^1D) - E(^3P)]\}^2/2$, which is due to departures from LS coupling, cannot be reliably predicted when one uses the values of the spin-orbit coupling constant $\zeta(3p)$ and the energy difference of the excited levels $E(^3P)$ and $E(^1D)$ from a HF calculation minimizing the energy of the 3P_0 ground state. In fact, the HF values of the energy interval, $\Delta E(^1D-^3P) = 8614 \text{ cm}^{-1}$, from Clementi and Roetti and the spin-orbit parameter, $\zeta(3p) = 130.252 \text{ cm}^{-1}$ (Froese Fischer 1977), depart considerably from the empirical values $\Delta E(^1D-^3P) = 6145.7 \text{ cm}^{-1}$ and $\zeta(3p) = 148.5 \text{ cm}^{-1}$ (Garstang 1951). Using the latter values, the estimate for the δg_{LS} amounts to -292×10^{-6} .

As compared to the results in other atoms, the differences between experimental and calculated g_J -factors in C, Al, and Si are unexpectedly large. In C and Si, this may be related to the fact that the observed g_J -factors correspond to excited levels. This is in contrast to other atoms where the measured and calculated g_J -factors belong to the ground state and agree to within a few millionths. The large values of δg_{LS} suggest that other configurations may yield important contributions to the g_J -factors in C and Si.

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⁵The experimental values used for this comparison are those of Wolber *et al.* as corrected by Saykally and Evenson (1980) by using a more accurate value for the Bohr magneton than Wolber *et al.* used.

TABLE 2
EXPERIMENTAL RESULTS AND CALCULATED VALUES OF FINE-STRUCTURE INTERVAL
AND g_J -FACTORS IN SILICON

A. FINE-STRUCTURE INTERVAL $E(^3P_1) - E(^3P_0)$				
	Source	Value		
	This work	2.3117556 ^a (7) THz		
	Previous work	2.3118 ^b THz		
	Calculated	1.9528 ^c THz		
B. g_J -FACTORS				
	Method	$g(^3P_1)$	$g(^3P_2)$	
	Experimental result ...	1.500830(70)	...	
	Calculated values	1.501097	1.500972 ^c	
		1.501097 ^d	1.500794 ^f	
			1.500974 ^d	
C. RELATIVISTIC AND DIAMAGNETIC CORRECTIONS TO g_J				
PARAMETER	$g(^3P_1)$		$g(^3P_2)$	
	This Work	Veseth 1980	This Work	Veseth 1980
δg_1	-75.1×10^{-6}	-75.1×10^{-6}	-75.1×10^{-6}	-75.1×10^{-6}
δg_2	+89.2	+89.1	+53.5	+53.5
δg_3	-73.1	-72.5	-48.6	-48.2
δg_4	-2.5	-3.5	-2.5	-3.5
Isotropic effect (δg_{iso})	-1.2	-0.6	-1.2	-0.6
Departure from LS coupling (δg_{LS})	0	0	-114 ^g -292 ^h	-112 ...

^aDetermined with $\mu_B = 1.399612 \times 10^4$ MHz T⁻¹ (Cohen and Taylor 1973).

^bPrevious experimental value (Moore 1970).

^cFrom data by Froese Fischer 1977.

^dVeseth 1980.

^eCalculated with $\delta g_{LS} = -114 \times 10^{-6}$.

^fCalculated with $\delta g_{LS} = -292 \times 10^{-6}$.

^gFrom data by Clementi and Roetti 1974.

^hEstimated from experimental data by Garstang 1951.

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