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ATOMIC SULFUR: FREQUENCY MEASUREMENT OF THE $J = 0 \leftarrow 1$ FINE-STRUCTURE TRANSITION AT 56.3 MICRONS BY LASER MAGNETIC RESONANCE[1,2]

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ABSTRACT

The $J = 0 \leftarrow 1$ fine-structure transition in atomic sulfur (S I) in its ground ^3P state has been detected in the laboratory by far-infrared laser magnetic resonance. The fine-structure interval has been measured accurately as 5,322,492.9 ± 2.8 MHz which corresponds to a wavelength of 56.325572 ± 0.000030 μm.

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

1. INTRODUCTION

Atomic sulfur had an inverted fine structure in its ground ^3P state, which arises from the $3s^23p^4$ electronic configuration. In this paper, we report the direct observation of the $J = 0 \leftarrow 1$ fine-structure transition in the laboratory. This transition is magnetic dipole in character. The observation was made by laser magnetic resonance (LMR) and yields an accurate determination of its transition frequency of 5,322,492.9 ± 2.8 MHz.

With improvements in observational techniques, it is becoming apparent that sulfur is an important element in astrophysics, commensurate with its cosmic abundance (1.6×10^{-5}). Several sulfur-containing molecules have now been detected in interstellar clouds by radio astronomy (see, for example, Thaddeus, Guélin, & Linke 1981; Saito et al. 1987; Yamamoto et al. 1987; Turner 1992). These observations suggest that the abundance of S relative to O in these clouds is very similar to its terrestrial ratio (about 1:43). Atomic S has also been detected, in the neighborhood of the protostar IRc2 by observation of its 25.2 μm fine-structure transition ($J = 1 \leftarrow 2$) from the Kuiper Airborne Observatory by Haas, Hollenbach, & McKee (1991). This observation provides strong support for a wind shock near this star. Indeed, the fine structure transition in S has emerged as an important new diagnostic for interstellar shocks because it is uncontaminated by emission from any associated photodissociation region where sulphur exists predominantly as S^+ (Tielens & Hollenbach 1985). In addition, abundance effects are unimportant because the gas phase depletion of S is relatively small.

The increasing use by astronomers of heterodyne receivers on airborne platforms to detect atomic and molecular lines in the far-infrared has identified a need for much more accurate measurements of fine-structure intervals in atoms. The frequencies must be known to within a few megahertz to be useful for these purposes. Neither fine-structure interval of atomic S in its ground ^3P state is known particularly well. The best available determinations come from optical spectroscopy (Eriksson 1978) with an uncertainty of 0.0071 cm^{-1} or 212 MHz for the $J = 1 \leftarrow 2$ transition and 0.03 cm^{-1} or 900 MHz for the $J = 0 \leftarrow 1$ transition.

Several atomic fine-structure intervals below 100 cm^{-1} have been measured to the desired accuracy in the laboratory by far-infrared LMR (Inguscio 1988). Although many more such intervals exist which are greater than 100 cm^{-1}, only one (the $J = 1 \leftarrow 2$ transition of O in its ^3P state at 63 μm; see Saykally & Evenson 1979) had been detected in this region until recently. The reason for this dearth of observations was the lack of suitable far-infrared laser lines with wavelengths less than 100 μm. A modification of the laser cavity of our LMR system has enabled us to operate it on many new lines between 50 and 100 μm. We have consequently been able to make the first direct observation of fine-structure transitions of several other atoms. We have recently reported our measurement of the $J = 2 \leftarrow 1$ fine structure intervals of ^{28}Si and ^{29}Si at 68.5 μm (Brown, Zink, & Evenson 1994). Here, we report the detection of the $J = 0 \leftarrow 1$ transition of atomic S in its ground ^3P state at 56.3 μm and an accurate determination of its transition frequency. A single, blended line from all three naturally occurring isotopes was observed.

2. EXPERIMENTAL DETAILS

The LMR apparatus used in this work has been described elsewhere (Sears et al. 1982), and the details are not repeated here. As described in our earlier paper (Brown et al. 1994), we have recently increased the sensitivity by raising the Zeeman modulation frequency from 13 to 40 kHz. We have also modified the spectrometer to enhance its performance at wavelengths shorter than 100 μm by reducing the inside diameter of the polished copper pump tube from 50.8 mm to 19.1 mm (from 2 inches to $\frac{3}{4}$ inch). This provides much better overlap between the pumped lasing gas and the far-infrared radiation field within the laser cavity, and many more short wavelength laser lines oscillate. In particular, we have used two such lines of CD_3OH to study the $J = 0 \leftarrow 1$ fine structure transition in S. Both of them have been reported previously by Sigg, Bluyssen, & Wyder (1984) but could not be made to lase in the previous configuration of the LMR spectrometer with the larger bore pump tube. Both lased readily in the new arrangement. Since their wavelengths had been measured to an accuracy of only

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[2] Contribution of US Government, nor subject to copyright.

about 0.5 μm, we determined the frequency of each line by measuring its beat frequency when mixed with a pair of CO_2 laser frequencies in a metal-insulator-metal (MIM) diode. The results, which are about 4000 times more accurate than the wavelength values, are as follows:

$$\lambda = 56.54\ \mu\mathrm{m}\ \mathrm{CD_3OH}\quad \text{pump 9R(6)}$$

$$\nu = 5{,}302{,}545.3 \pm 0.7\ \mathrm{MHz}\ ,$$

$$\lambda = 56.62\ \mu\mathrm{m}\ \mathrm{CD_3OH}\quad \text{pump 10R(30)}$$

$$\nu = 5{,}294{,}509.2 \pm 0.7\ \mathrm{MHz}\ .$$

These two frequencies both lie below that of the $J = 0 \leftarrow 1$ transition in S.

The S atoms were generated by the reaction between F atoms and hydrogen sulfide, H_2S, 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 (260 mtorr), and the optimum S signal was obtained with a partial pressure of H_2S of about 1.5 Pa (10 mtorr).

3. RESULTS, ANALYSIS, AND DISCUSSION

The energy levels of atomic S in its inverted ^3P ground state are shown in Figure 1. It can be seen that the LMR spectrum associated with the $J = 0 \leftarrow 1$ fine-structure transition of an atom in a ^3P state consists of a single transition, $M_J = 0 \leftarrow 1$ (or $0 \leftarrow -1$ if the laser frequency is less than the atomic interval). The observed spectrum for S is shown in Figure 2. All three naturally occurring isotopes of S contribute to this signal, although it arises predominantly from ^{32}S (The abundances are ^{32}S 95.0%, ^{33}S 0.75% and ^{34}S 4.2%). Neither the isotope shifts (Veseth 1985) nor the nuclear hyperfine splittings for ^{33}S in the $J = 1$ level are large enough to place the signals from the less abundant isotopes outside the main line shape. The orbital and spin contributions to the nuclear hyperfine splitting in the $J = 1$ level to a large extent cancel; furthermore, the magnetic moment of the ^{33}S nucleus is rather small (0.6438 nuclear magnetons). The detailed measurements of the resonance field strengths, B_0, for the two observed LMR spectra for S are given in Table 1.

The LMR spectra have been analyzed with a standard effective Hamiltonian for a Russell-Saunders atom. The experimental measurements depend primarily on the $J = 0$–1 fine-structure interval and the g_J-factor for the $J = 1$ level. The $J = 1$–2 interval and the g-factor for $J = 2$ have only a weak, indirect effect on the resonance positions. The g-factors for atomic S in the $^3P_2$ and $^3P_1$ levels have been measured very accurately in an electron paramagnetic resonance (EPR) experiment (Brown 1966). Because we cannot hope to match this accuracy in a far-infrared LMR experiment, we have fitted the model to the two data points, constraining the g-factors to their EPR values. A much improved value for the $J = 0 \leftarrow 1$ transition frequency of 5322.4929 ± 0.0028 GHz is determined in the fit, the results of which are given in Tables 1 and 2. The best previously available value for this fine structure interval

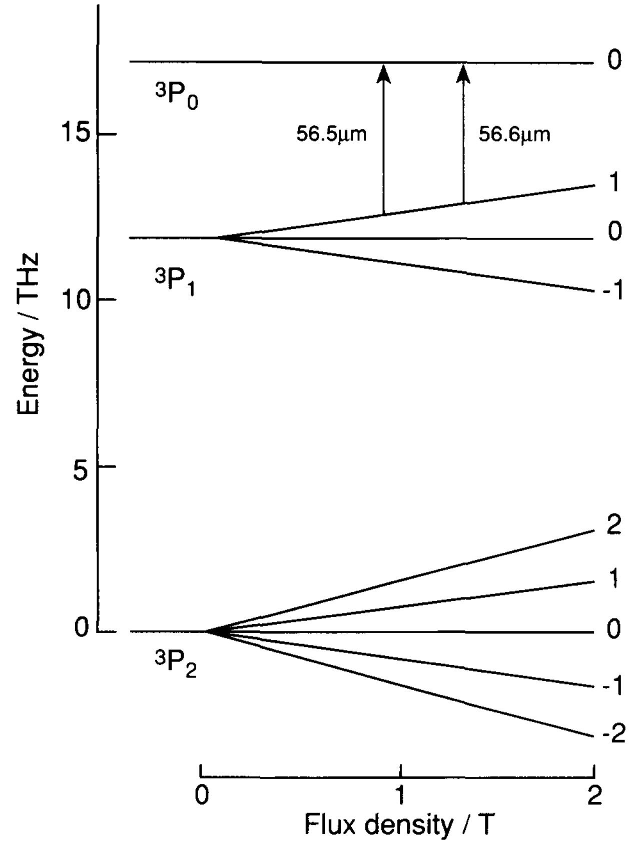

FIG. 1.—The energy level diagram for the ground ^3P state of atomic sulfur, in the presence of a variable magnetic field. The Zeeman components are labeled by their M_J values. The Zeeman splittings are exaggerated for the sake of clarity. The two transitions between the $J = 0$ and 1 components which were observed in the present work are indicated.

TABLE 1

LASER MAGNETIC RESONANCE DATA FOR S ATOMS

J	M_J	ν_L (GHz)	B_0 (mT)	(Observed − Calculated) (MHz)
$0 \leftarrow 1$..........	$0 \leftarrow 1$	5302.5453[a]	930.37	−0.2
$0 \leftarrow 1$..........	$0 \leftarrow 1$	5294.5092[b]	1333.76	+0.2

[a] The 56.54 μm line of CD_3OH, pumped by the 9R(6) line of a CO_2 laser.

[b] The 56.62 μm line of CD_3OH, pumped by the 10R(30) line of a CO_2 laser.

TABLE 2

PARAMETER VALUES USED IN THE INTERPRETATION OF THE FAR-INFRARED LASER MAGNETIC RESONANCE SPECTRUM OF ATOMIC SULPHUR

Parameter	Value	Reference
ΔE_{01}(GHz)..........	5322.4929(28)[a,b]	1
	5324.16(90)[c]	2
ΔE_{12}(GHz)..........	11873.43(21)[c]	2
$g_{J=1}$	1.501029(42)[c]	3
$g_{J=2}$	1.500541(24)[c]	3

[a] The figures in parentheses give the accuracy of the fine-structure interval, in units of the last quoted decimal place and estimated as described in the text.

[b] This frequency corresponds to a vacuum wavelength of 56.325572 ± 0.000030 μm.

[c] The figures in parentheses give the author's estimate of uncertainty, in units of the last quoted decimal place.

REFERENCES.—(1) Present work; (2) Eriksson 1978; (3) Brown 1966.

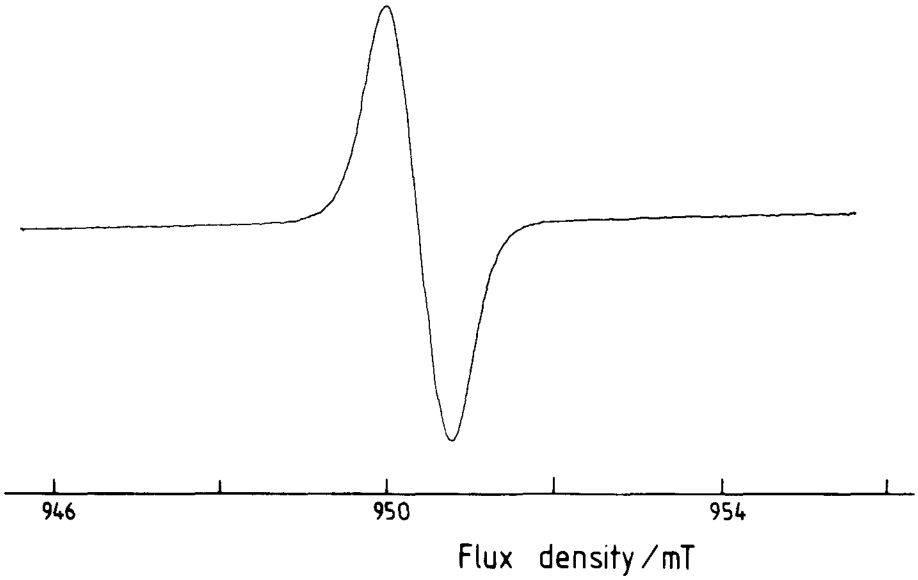

FIG. 2.—The far-infrared laser magnetic resonance spectrum associated with the $J = 0 \leftarrow 1$ transition of atomic S in its ground ^3P state, recorded with the 56.5 μm line of CD_2OH, pumped by the 9R(6) line of a CO_2 laser. The spectrum was recorded with the oscillating magnetic field perpendicular to the applied magnetic field, permitting $\Delta M_J = \pm 1$ transitions. The output time constant of the lock-in amplifier was 0.3 s. The signal arises from all naturally occurring isotopes of S.

was $177.59_5 \pm 0.03$ cm^{-1}, or 5324.16 ± 0.90 GHz (Eriksson 1978), which differs from our value by 1.7 GHz, about 2 σ. The small residuals in Table 1 show that our measurements are consistent with the EPR value for $g_{J=1}$ of 1.501029, to within experimental error. The uncertainty in the value determined for ΔE_{01} depends on several factors: the uncertainty in the laser frequencies as used in the experiment, the errors in the flux density measurements, and the uncertainty in the $g_{J=1}$ value as determined by Brown (1966). We estimate the combined effect of these various sources of error to be ± 2.8 MHz (1 σ).

The 25.2 μm fine-structure transition in S has already proved itself useful for astronomical purposes (Hollenbach & McKee 1989; Haas et al. 1991). It may well be that the 56.3 μm transition will also be useful as a probe of the local environment. Its Einstein A-coefficient is 3.033×10^{-4} s^{-1}, not much smaller than that of the 25.2 μm transition (1.403×10^{-3} s^{-1}). We have not been able to observe the ^{33}S hyperfine splitting in the $J = 0$–1 transition. The abundance of ^{33}S is low, and the splitting is too small in the $J = 1$ level to place the ^{33}S hyperfine quartet outside the ^{32}S Doppler line width at these wavelengths. The hyperfine splitting in the $J = 2$ level is much larger, and its effects should be easily resolved for the 25.2 μm transition. Although we have not yet performed a LMR experiment at such short wavelengths, there is a very convenient far-infrared laser line in CH_3OH, pumped by the 9P(26) line of a CO_2 laser, at 25.27 μm (Henningsen 1986). A frequency measurement of this line is required to see if it is close enough for the 25.2 μm transition in S to be detected.

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