

Laser magnetic-resonance measurement of the 3P_1 - 3P_2 fine-structure splittings in ${}^{17}\text{O}$ and ${}^{18}\text{O}$

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(Received 8 April 1993)

The 3P_1 - 3P_2 fine-structure splittings of ${}^{17}\text{O}$ and ${}^{18}\text{O}$ have been measured by far-infrared laser magnetic-resonance spectroscopy. The signals for ${}^{17}\text{O}$ were detected with a sample in its natural abundance (0.038%). The isotopic shifts from the corresponding interval in ${}^{16}\text{O}$ are +13.0 MHz for ${}^{17}\text{O}$ and +23.5 MHz for ${}^{18}\text{O}$, in accord with theoretical expectations.

PACS number(s): 32.30.Bv

I. INTRODUCTION

The fine-structure intervals of the oxygen atom in its ground 3P state fall in the far-infrared (FIR) region of the spectrum. The transitions between these levels provide a simple, direct, and sensitive method of monitoring O atoms, both in the atmosphere [1] and in astrophysical sources [2,3]. Although these intervals have been known for a long time from optical measurements [4], they have been measured much more accurately in recent years by direct, FIR techniques. The frequencies of ${}^{16}\text{O}$ were first refined by laser magnetic resonance (LMR), by Davies *et al.* [5] for the $J=0\leftarrow 1$ transition, and by Saykally and Evenson [6] for the $J=1\leftarrow 2$ transition. These values have been improved still further by Zink *et al.* [7], who used a tunable FIR source and so were able to dispense with the magnetic field.

In this paper, we report the observation of the LMR spectrum associated with the $J=1\leftarrow 2$ transition for the ${}^{17}\text{O}$ and ${}^{18}\text{O}$ isotopes. The ${}^{17}\text{O}$ spectrum was recorded using a sample in natural abundance (0.038%). By using the g_J factors measured in the EPR spectrum of ${}^{16}\text{O}$ by Radford and Hughes [8], and the ${}^{17}\text{O}$ hyperfine parameters measured by Harvey [9], we have determined much-improved values for the $J=1\leftarrow 2$ fine-structure intervals for these isotopes. In the course of these experiments, we have been able to make observations of saturation dips on the LMR signals for ${}^{16}\text{O}$.

II. EXPERIMENTAL DETAILS

The FIR LMR spectrometer has been described in detail elsewhere [10]. Briefly, it consists of a transversely pumped gain cell which is 56 cm long and is separated from the sample region by a 12.5- μm -thick polypropylene beam splitter set at Brewster's angle. The magnetic field is provided by an electromagnet with an 8-cm gap. The FIR power is coupled out with a movable 45° mirror and detected by a liquid-helium-cooled photoconductive detector. The signal is Zeeman-modulated at 40 kHz and detected with a lock-in amplifier tuned to the same frequency. The magnetic field is controlled by a rotating coil magnetometer, located on the axis of the field and

close to the absorption region. The small correction for the difference between the field at the sample and that at the probe position is measured with a proton NMR fluxmeter.

The present measurements were made with the 63.1- μm line of ${}^{13}\text{CH}_3\text{OH}$ pumped by the 9P(12) line of a ${}^{12}\text{C}{}^{16}\text{O}_2$ laser. Because our measurement of the fine-structure interval depends directly on the knowledge of the laser frequency as used in the experiment, we have carefully remeasured the frequency as $4751\,341.8\pm 0.5$ MHz. The oxygen atoms were generated by flowing molecular oxygen at 160 Pa (1.2 Torr) through a microwave discharge.

III. RESULTS AND DISCUSSION

The LMR spectrum of ${}^{16}\text{O}$ recorded with the 63.1- μm laser consists of a single line at about 0.313 T [6]. This line is composed of three unresolved Zeeman components whose separation is less than the Doppler linewidth [14.7-MHz full width at half maximum (FWHM) at 300 K]. By reducing the total pressure to 13 Pa (100 mTorr), lowering the modulation amplitude, and maximizing the intracavity laser power, we have been able to resolve the two stronger Zeeman components as Lamb dips (Fig. 1).

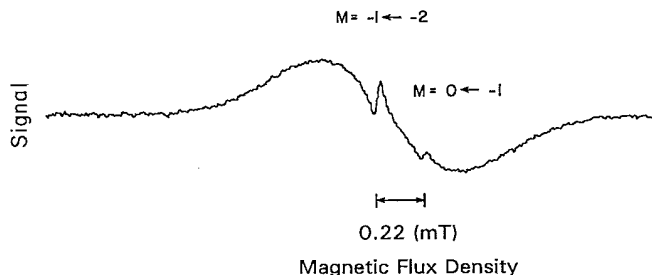


FIG. 1. Lamb dips recorded in the laser magnetic-resonance spectrum of atomic oxygen at 63.1 μm . The total sample pressure was 13 Pa (100 mTorr). The transition involved is the magnetic dipole transition between the 3P_1 and 3P_2 spin components. Three Zeeman components are expected: $M_J = -1\leftarrow -2$, $0\leftarrow -1$, and $1\leftarrow 0$ with relative intensities 6:3:1. The weakest of the three falls at almost the same field as the strongest, and so it is not seen in this spectrum.

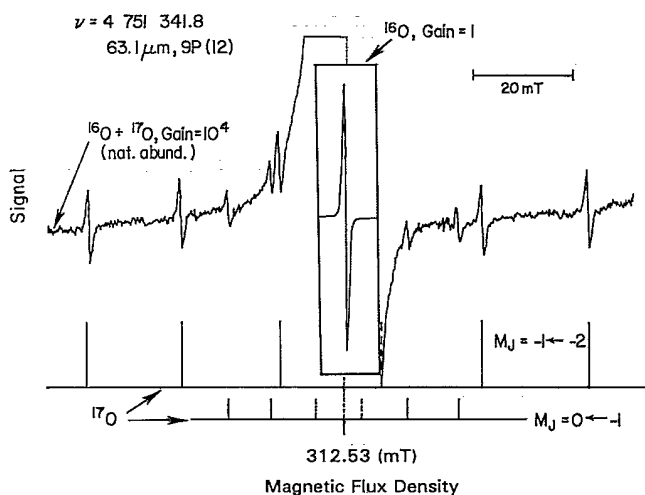


FIG. 2. The FIR LMR spectrum of ^{17}O recorded in natural abundance (0.038%) with the $63.1\text{-}\mu\text{m}$ line of $^{13}\text{CH}_3\text{OH}$ pumped by the $9P(12)$ line of the CO_2 laser. The individual ^{17}O lines are over four orders of magnitude weaker than the corresponding ^{16}O transition, which is shown in the inset recorded under the same conditions.

The recording of the saturation dips for an atomic magnetic dipole transition in the FIR has not previously been reported.

The ^{17}O and ^{18}O spectra were both recorded with Doppler limited linewidths at a total O_2 pressure of 160 Pa (1.2 Torr). The ^{17}O spectrum, recorded in natural abundance, is shown in Fig. 2. The nuclear hyperfine splitting for ^{17}O ($I = \frac{5}{2}$) is the greatest in the $J=2$ level and is large enough to shift the individual hyperfine lines well outside the main ^{16}O line shape. Since the line intensity for ^{17}O is diluted among $(2I+1)=6$ hyperfine components, the ^{16}O resonance is 1.61×10^4 times stronger than ^{17}O and corresponds to a signal-to-noise ratio of 4.8×10^5 with a time constant of 300 ms. Although ^{18}O is more abundant (0.204%) than ^{17}O , its LMR spectrum shows no hyperfine structure; the isotope shift from ^{16}O is

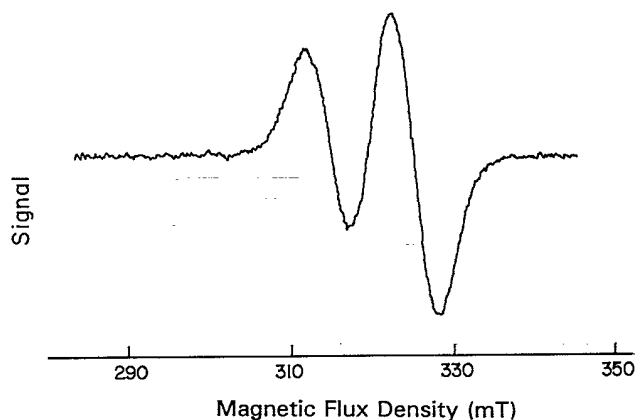


FIG. 3. The LMR spectrum associated with the $^3P_1\text{-}^3P_2$ fine-structure transition of atomic oxygen, using a sample enriched in ^{18}O (approximately 50%). The separation between the two line centers is measured as 1.12 mT after correcting for the overlap of the two line shapes.

TABLE I. Observed resonances associated with the $^3P_1\text{-}^3P_2$ fine-structure transition of ^{17}O recorded with the $63.1\text{-}\mu\text{m}$ line of $^{13}\text{CH}_3\text{OH}$. Laser frequency is $4\,751\,341.8 \pm 0.5$ MHz.

J	Transition M_J	M_I^a	Flux density (mT)	Expt.—Calc. (MHz)
1←2	-1←-2	$-\frac{5}{2}$	259.12	-1.1
		$-\frac{3}{2}$	278.37	0.5
		$-\frac{1}{2}$	298.48	0.4
		$\frac{1}{2}$	340.69	-0.3
		$\frac{3}{2}$	362.56	0.3
		$\frac{5}{2}$	288.04	0.3
0←-1	-1	$-\frac{5}{2}$	296.76	0.4
		$-\frac{3}{2}$	325.27	0.7
		$-\frac{1}{2}$	335.72	-1.2
		$\frac{1}{2}$		
		$\frac{3}{2}$		
		$\frac{5}{2}$		

^aThe observed transitions all obey the selection rule $\Delta M_I = 0$.

not large enough to place the signal outside the dominant ^{16}O line shape. We therefore recorded its spectrum with an enriched sample of ^{18}O (50%) as shown in Fig. 3. The shift from the ^{16}O resonance is measured to be 1.12 ± 0.02 mT to lower field, after correcting for the partial overlap of the two line shapes.

The measurements of the resonances for ^{17}O are given in Table I. The positions of these lines depend on (i) the zero-field separation of the $J=2$ and 1 fine-structure levels, (ii) the magnetic and electric nuclear hyperfine interactions, and (iii) the g factors for the O atom in the 3P_2 and 3P_1 levels.

The second and third of these quantities have been measured much more accurately by gas-phase EPR. The hyperfine parameters were measured by Harvey [9] and

TABLE II. Parameters for ^{17}O (in MHz).

ΔE_{01}	2 060 069.09 ^a
ΔE_{12}	4 744 790.52(26) ^b
$g_{J=1}$	1.500 986 ^c
$g_{J=2}$	1.500 921 ^c
A_{11}	4.738 ^d
A_{22}	-218.569 ^d
A_{10}	-91.7 ^d
A_{21}	-126.6 ^d
B	-0.5219 ^{d,e}

^aValue taken from ^{16}O (Zink *et al.*) [7].

^bValue determined from fit of the present data set. The number in parentheses is one standard deviation of the least-squares fit.

^c g factors taken from the EPR measurements of Radford and Hughes [8].

^dHyperfine parameters determined in the EPR experiments of Harvey [9].

^eThe electric-quadrupole parameter B in the model of Cooksy, Høyde, and Saykally [11] is related to the parameter b_J used by Harvey [9] by

$$b_J = B[3X(X+1) - 4J(J+1)L(L+1)] \\ \times I(2I+1)/[(J+1)(2J+3)],$$

where $X = S(S+1) - L(L+1) - J(J+1)$. Thus for ^{17}O , $b_1 = -10B$ and $b_2 = 20B$.

the g factors by Radford and Hughes [8]. We have therefore fitted our data using these parameter values to determine the fine-structure splitting for ^{17}O . The details of the standard Russell-Saunders model used are given in a paper by Cooksy, Hovde, and Saykally [11]. The results of our fit are given in Tables I (residuals) and II (parameters for ^{17}O); each data point was given unit weight. The 3P_1 - 3P_2 fine-structure interval is determined to be $4\,744\,790.52 \pm 0.26$ MHz, where the estimated error is one standard deviation of the fit. The corresponding quantity for ^{18}O is determined from the value for ^{16}O , $4\,744\,777.49 \pm 0.16$ MHz, measured by Zink *et al.* [7]. The oxygen atom transition concerned tunes at a rate of 21.008 MHz/mT, so the fine-structure interval for ^{18}O is determined to be $4\,744\,801.0 \pm 0.5$ MHz. The isotopic shifts in the fine-structure interval are therefore +13.0 MHz for ^{17}O and +23.5 MHz for ^{18}O .

The identical frequencies were measured by De Natale *et al.*, using tunable FIR methods on isotopically enriched samples [12]. The results of their measurements, which are more accurate than ours since they are made in the absence of a magnetic field, are

$$\nu_{J=1 \leftarrow 2} = \begin{cases} 4\,744\,790.76 \pm 0.25 \text{ MHz} & \text{for } ^{17}\text{O} \\ 4\,744\,801.37 \pm 0.19 \text{ MHz} & \text{for } ^{18}\text{O} \end{cases}$$

The agreement with our measurements is very good.

These are some of the most accurate measurements of the isotopic dependence of atomic-fine-structure intervals that have been made. The shift of ^{18}O is almost exactly, but not quite, twice that of ^{17}O , as might be expected. Veseth [13] has calculated the isotopic shifts in the fine-structure interval for several light atoms by use of many-body perturbation theory. The value calculated for the ^{18}O - ^{16}O shift in the 3P_1 - 3P_2 intervals is +27.5 MHz, in good agreement with the experimental value. The agreement is even more impressive when it is realized that the calculated value is the sum of three larger, counteracting contributions.

ACKNOWLEDGMENT

We are particularly grateful to Andy Cooksy for a copy of his computer program, which we used to fit the experimental results.

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