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Hyperfine structure and isotope shift in the far-infrared ground-state transitions of atomic oxygen

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We have investigated the $^3P_2 \rightarrow {}^3P_1$ and $^3P_1 \rightarrow {}^3P_0$ atomic fine-structure transitions in isotopically enriched samples of oxygen by means of tunable far-infrared spectroscopy. Accurate frequency measurements (a few parts in 10^8) were made for all three stable isotopes and the ^{17}O hyperfine structure was resolved. The experimental values for the isotopic shift of ^{18}O relative to ^{16}O for the $J=2 \rightarrow J=1$ and $J=1 \rightarrow J=0$ fine-structure transitions are in agreement with theoretical calculations.

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Electronic transitions of important atomic species, such as carbon, oxygen, and ionic nitrogen, are not conveniently accessible to laser sources in the optical region. Indeed, far-infrared (FIR) spectroscopy is the only way by which ground-state transitions can be studied with high accuracy. On the other hand, detection of these weak lines is challenging because spectra are associated with fine-structure transitions which are magnetic dipole in nature. Until recently, only the high-sensitivity intracavity laser magnetic-resonance (LMR) technique had been successful, as discussed in [1]. Recently the group at NIST, Boulder [2] reported the first successful application of tunable far-infrared (TuFIR) spectroscopy to an atom, namely ^{16}O. This was possible because of skillful changes in the spectrometer, in particular the use of a double-pass absorption cell combined with a rotation of the FIR polarization. It is worth noting that the application of TuFIR yields transition frequencies which are more than one order of magnitude more accurate than those from LMR measurements. We decided to extend TuFIR measurements to ^{17}O and ^{18}O because isotope shift measurements, in this light and still theoretically tractable atom, are very interesting, as for instance discussed for transitions in the visible involving excited levels [3]. Also, probably because of an efficient production of atomic oxygen, we were able to use a single-pass cell and to keep the TuFIR apparatus in its simplest configuration, already applied to rotational spectroscopy of stable polar molecules [4–6]. In addition, the resolution of the hyperfine structure of ^{17}O fine-structure transitions provides a significant test of the accuracy by comparison with available precise data from EPR studies [7].

In our apparatus, radiation from a microwave synthesizer and from two frequency-stabilized CO_2 lasers is coupled onto a metal-insulator-metal (MIM) diode which generates FIR radiation. After passing through the absorption cell, the FIR radiation is detected by a silicon composite bolometer cooled to 1.4 K. For the present experiment, atomic oxygen was produced in a 3-m-long glow discharge cell. An oxygen-argon mixture (5–10 %) was used for a total pressure ranging from 1.1 to 1.7 Torr. The best signal-to-noise ratio for the $^3P_1 \rightarrow {}^3P_0$ transition was observed with currents of 80–90 mA, while lower currents (40–60 mA) were required for optimizing the detection of the $J=2 \rightarrow J=1$ transition. The efficiency of production of atomic oxygen increases with current; however, a good compromise with the discharge temperature has to be found to optimize population of the levels under investigation. To record the $J=2 \rightarrow J=1$ transition, the cell was cooled to the lowest temperature achievable with our apparatus (about −5 °C). Measurements were made by maintaining a slow flow of the gas mixture because a strong degradation of the signal was observed in sealed-off operation, probably due to an increase of the wall recombination rate.

Two different specimens of isotopically enriched oxygen were used for our measurements: a 50% ^{18}O–50% ^{16}O and a 48% ^{17}O–42% ^{18}O–10% ^{16}O mixture, for recordings involving ^{18}O and ^{17}O, respectively.

A typical recording of the $^3P_2 \rightarrow {}^3P_1$ transition at 63 μm is shown in Fig. 1 for the ^{18}O-enriched sample. Two scans were averaged together, with a lock-in time constant of 300 ms and a modulation depth of 5.6 MHz. Similar recordings were obtained for the other fine-structure transition at 145.5 μm. In ^{17}O, the presence of a nuclear dipole moment $I=\frac{5}{2}$ gives rise to a hyperfine structure, as schematically shown in Fig. 2, where all the observed components have also been indicated. In Fig. 3 the experimental recording of three hyperfine com-

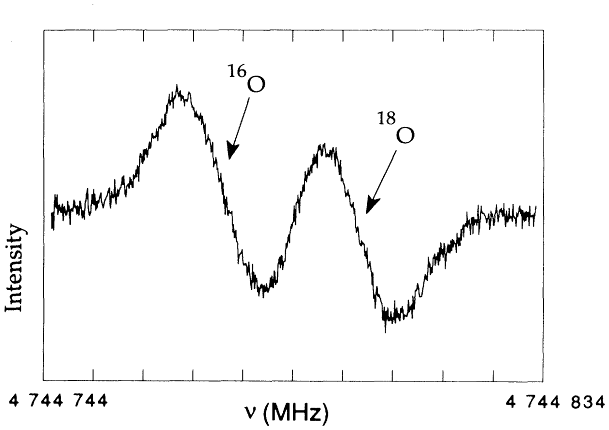

FIG. 1. First derivative recording of $^3P_2 \rightarrow {}^3P_1$ transition for both ^{16}O and ^{18}O.

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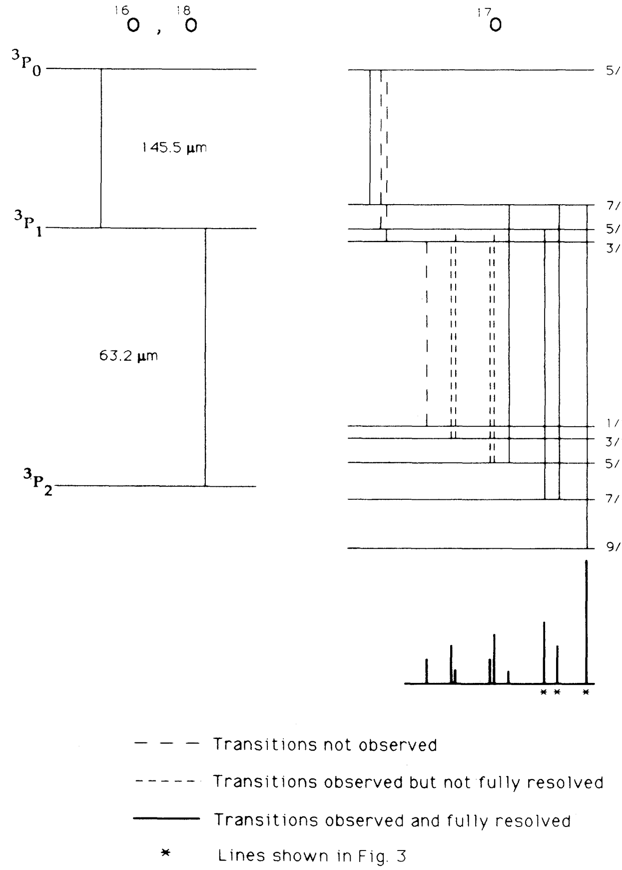

FIG. 2. Level scheme of the fine and hyperfine structures for the ^3P ground state of ^{16}O, ^{17}O, and ^{18}O. The bars below the ^{17}O level scheme are the relative intensities of all the hyperfine components of the $^3P_2 \rightarrow {}^3P_1$ transition for ^{17}O.

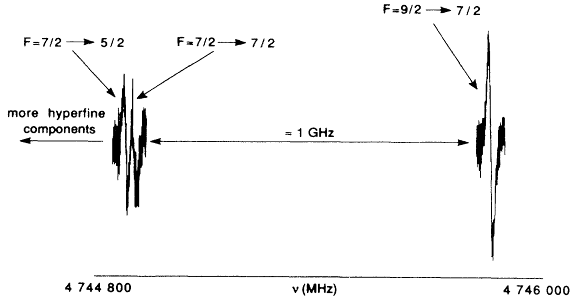

FIG. 3. Experimental recording of three components of the $^3P_2 \rightarrow {}^3P_1$ transition for ^{17}O. Two separate recordings, one for the $F=\frac{9}{2} \rightarrow \frac{7}{2}$ component, and another for both $F=\frac{7}{2} \rightarrow \frac{5}{2}$ and $F=\frac{7}{2} \rightarrow \frac{7}{2}$, are shown together.

ponents of the $J=2 \rightarrow J=1$ transition is shown. For all the measurements, center frequencies were determined by fitting experimental data using a computer program kindly provided by K. Chance of the Harvard Smithsonian Center for Astrophysics. The program takes into account spectrometer parameters such as modulation amplitude and baseline curvature. Each fit gave an error in the range of a few tens of kHz; however, repeated measurements gave a reproducibility of about 100 kHz, probably due to a standing wave producing a baseline oscillation. The uncertainty in the frequency lock of the CO_2 lasers produces a contribution of 8.5 kHz from each laser, thus 12 kHz from the two combined [8]. Several measurements have been performed on each far-infrared transition, and results reported in Table I reflect the weighted average.

We have remeasured both ^{16}O fine-structure transitions, obtaining values which are in good agreement with those previously found in [2]. Only a datum for ^{18}O was previously published [1]. Our result is in agreement and about one order of magnitude more accurate. While the present investigation was being performed, the group in Boulder has increased the sensitivity of LMR to the level of observing signals from ^{17}O in natural abundance [9]. They also measured ^{18}O in an enriched sample, and their values for the two isotopes, relative to the $^3P_2 \rightarrow {}^3P_1$ transition, extrapolated at zero magnetic field, are in excellent agreement with our measurements (see Table I).

To measure the isotope shift between ^{16}O and ^{18}O transitions, simultaneous recordings of the same transition for the two isotopes were performed.

For ^{17}O, we were able to record hyperfine components for both the fine-structure transitions. Only one component was resolved for the $J=1 \rightarrow J=0$ transition, because the other two components originating from the $J=1$ multiplet completely overlapped with the ^{18}O line. The large uncertainty assigned to the resolved component is a consequence of the strong overlapping with the ^{16}O line, also present in the recording.

The two hyperfine components of ^{17}O, starting from the $F=\frac{7}{2}$ hyperfine level, were fitted by fixing their frequency difference to the value of the splitting between the $J=1$, $F=\frac{5}{2}$, and $F=\frac{7}{2}$ levels, calculated using the data from [7]. This splitting $\Delta\nu=22.042$ MHz was also used, with the same procedure, for the fit of the transitions starting from the $J=2$, $F=\frac{5}{2}$ level. In this case, because of the presence of two unresolved transitions ($J=2$, $F=\frac{5}{2} \rightarrow J=1$, $F=\frac{5}{2}$, $F=\frac{3}{2}$) their center of gravity was considered and so the frequency difference between this unresolved line and the $J=2$, $F=\frac{5}{2} \rightarrow J=1$, $F=\frac{7}{2}$ transition was fixed in the fit at $\Delta\nu=23.68$ MHz.

To check the accuracy of our measurements, we subtracted the $J=2$, $F=\frac{7}{2} \rightarrow J=1$, $F=\frac{7}{2}$ frequency from that of the $J=2$, $F=\frac{9}{2} \rightarrow J=1$, $F=\frac{7}{2}$ transition, to obtain the frequency separation between the $^3P_2$ $F=\frac{9}{2}$ and $^3P_2$ $F=\frac{7}{2}$ hyperfine levels. This value was compared with the more accurate value (some tens of kHz estimated uncertainty) of the hyperfine separation from electron-paramagnetic-resonance (EPR) data [7]. The two estimations agree within 2 kHz.

A worse agreement with EPR measurements of hyperfine frequencies is observed when weaker or partially overlapping transitions are considered, which give a

TABLE I. Frequency measurements of $^3P_2$-$^3P_1$ and $^3P_1$-$^3P_0$ transitions.

		ν (MHz)[a]	
Isotope	^3P transition	(This work)	(Previous)[b]
^{16}O	$J=2 \rightarrow J=1$	4 744 777.49(15)	4 744 777.49(16)[c]
^{16}O	$J=1 \rightarrow J=0$	2 060 068.63(20)	2 060 069.09(10)[c]
^{18}O	$J=2 \rightarrow J=1$	4 744 801.37(19)	4 744 801.0(4)[d]
^{18}O	$J=1 \rightarrow J=0$	2 060 079.24(15)	2 060 079.0(12)[e]
^{17}O	$J=1,\ F=\frac{7}{2} \rightarrow J=0,\ F=\frac{5}{2}$	2 060 061.3(12)	/
^{17}O	$J=2,\ F=\frac{9}{2} \rightarrow J=1,\ F=\frac{7}{2}$	4 745 899.35(30)	/
^{17}O	$J=2,\ F=\frac{7}{2} \rightarrow J=1,\ F=\frac{7}{2}$	4 744 908.75(40)[f]	/
^{17}O	$J=2,\ F=\frac{7}{2} \rightarrow J=1,\ F=\frac{5}{2}$	4 744 886.71(35)[f]	/
^{17}O	$J=2,\ F=\frac{5}{2} \rightarrow J=1,\ F=\frac{7}{2}$	4 744 145.9(15)[g]	/
^{17}O	$J=2,\ F=\frac{5}{2} \rightarrow J=1,\ F=\frac{5}{2},\frac{3}{2}$	4 744 122.17(40)[g]	/
^{17}O	$J=2,\ F=\frac{3}{2} \rightarrow J=1,\ F=\frac{5}{2},\frac{3}{2}$	4 743 579.18(65)	/
^{17}O	$J=2 \rightarrow J=1$ Center of gravity	4 744 790.76(25)	4 744 790.5(3)[d]
^{18}O-^{16}O	$J=2 \rightarrow J=1$	$\Delta\nu=23.88(20)$	23.5(6)[d] Calc. 27.5[h]
^{18}O-^{16}O	$J=1 \rightarrow J=0$	$\Delta\nu=10.61(20)$	Calc. 10.8[h]
^{17}O-^{16}O	$J=2 \rightarrow J=1$	$\Delta\nu=13.27(40)$	13.0(4)[d]

[a] Numbers in parentheses are 1σ uncertainties of the last digits.
[b] References are shown in square brackets.
[c] Reference [2].
[d] Reference [9].
[e] Reference [1].
[f] Frequency difference for these two lines is kept fixed in the fit at values from [7].
[g] Frequency difference for these two lines is kept fixed in the fit at values from [7].
[h] Reference [10].

larger uncertainty in the frequency determination.

Our measurements on ^{17}O transitions have permitted an ordering of the hyperfine levels composing the ^{17}O ground-state multiplet. In [7] only a tentative assignment of the $J=1$ hyperfine constant signs was made. This assignment has been confirmed with no further doubt, comparing different transitions between the $J=1$ and 2 hyperfine structure multiplets. Moreover, our accurate measurement of fine-structure separations in the ground state provide an experimental test of the calculated isotopic shifts for ^{16}O-^{18}O by Veseth [10]. His calculated values are 27.5 and 10.8 MHz for the isotopic shifts of $^3P_2 \rightarrow {}^3P_1$ and $^3P_1 \rightarrow {}^3P_0$ transitions, respectively.

These values, calculated by many-body perturbation theory, are in good agreement with our experimental data.

In conclusion, we have demonstrated that tunable far-infrared spectroscopy in its simplest configuration can be successfully extended to the precise measurement of isotopic and hyperfine structure on magnetic dipole transitions of oxygen.

The sensitivity and accuracy demonstrated should enable extension to other important elements and more refined theoretical analysis of atomic structure.

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