Laser Magnetic Resonance of the O_2 Molecule Using the 337-μm HCN Laser*

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We observed thirteen laser magnetic resonance lines (transitions between $[n=3, J=4]$ $\rightarrow$ $[n=5, J=5]$ for the oxygen molecule, using the 337-μm line of the HCN laser. The magnetic g factors ($g_\perp = 2.0044$, $g_z = 2.0020$, and $g_n = 0.000\,125$) give the best fit to the data. The zero-field frequency for the transition $(N=J=3) \rightarrow (N=J=5)$ obtained by using these sets of the magnetic g factors all agree with theoretical value of $775.700\,43$ $\pm 0.000\,01$ GHz if an experimental uncertainty of ± 1 G ($\pm 10^{-4}$ T) is allowed.

In a previous Letter, Evenson et $al.$[1] reported one laser magnetic resonance (LMR) line of the oxygen molecule at 16 418 G using the 337-μm line of the HCN laser. Here using the same laser line we report additional resonances of the oxygen molecule.

Since the oxygen molecule in its electronic ground state has an electronic spin of 1, each rotational state is a triplet. The transitions within each triplet have been observed[2-4] in microwave spectroscopy. The transitions between different rotational states are very weak, because they are magnetic dipole transitions allowed only through the coupling between the electronic spin and the end-over-end rotation (Kramers coupling[5]). Thus, if each triplet is designated by a "quantum number" n, which reduces to the quantum number of the end-over-end rotation N when the Kramers coupling is switched off, then the transitions in question are of the type $\Delta n = \pm 2$, and are forbidden in the limit of no Kramers coupling.

McKnight and Gordy[6] observed the transitions of $n = 1 \rightarrow 3$ in submillimeter wave spectroscopy, giving the only high-resolution zero-field observation of the rotational transitions. The present LMR resonances are due to the $n = 3 \rightarrow 5$ transitions.

Electron paramagnetic resonance (EPR) of this molecule has been observed in the X-band region by Tinkham and Strandberg,[7] Bauers, Kamper, and Lustig,[8] and Tischer.[9] The perturbation Hamiltonian due to an external magnetic field $\vec{B}$ is

$$H = \mu_B [g_\perp \vec{S} \cdot \vec{B} + (g_z - g_\perp) S_z B_z + g_n \vec{N} \cdot \vec{B}], \qquad (1)$$

where μ_B is the Bohr magneton (1.399 61 MHz/G); $\vec{S}$ and $\vec{N}$ are the electronic spin and end-over-end rotational angular momenta, respectively; S_z and B_z are the components of $\vec{S}$ and $\vec{B}$ along the molecular axis; and $g_\perp$, g_z, and g_n are the magnetic g factors. Tinkham and Strandberg[7] assumed that g_z is equal to the free-electron g factor, neglecting relativistic effects. Hendrie and Kusch[10] observed magnetic resonance of the oxygen molecular beam and analyzed their own data without the above assumption. Their theory was equivalent to that expressed in Eq. (1), and they obtained

$$g_\perp = 2.005\,169 \pm 0.000\,056,$$
$$g_z = 2.001\,939 \pm 0.000\,026, \qquad (2)$$
$$g_n = 0.000\,122 \pm 0.000\,015$$

(Their reported values are slightly different because they used an old value of the free-electron g factor.) Bauers, Kamper, and Lustig[8] obtained, from their EPR data, a rather different set of values:

$$g_\perp = 2.004\,838 \pm 0.000\,030,$$
$$g_z = 2.002\,025 \pm 0.000\,020, \qquad (3)$$
$$g_n = 0.000\,126 \pm 0.000\,012.$$

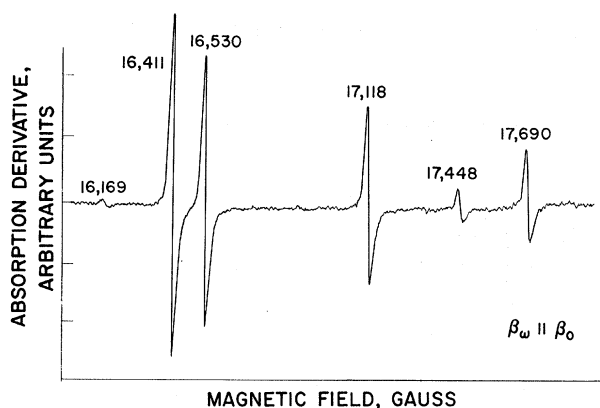Tischer's results[9] agreed with the latter set of values.

FIG. 1. Chart recorder trace showing LMR of the oxygen molecule for the parallel case.

The apparatus used to record the spectra shown in Figs. 1 and 2 is described by Wells and Evenson.[11] The O_2 pressure was 7.5 Torr, and a modulation field of 8 G was used. No saturation of the molecule was observed. A different version[12] of the LMR (previously called LEPR) spectrometer was used to check the magnetic gradient of the 15-in. magnet which was equipped with 6-in. Rose shimmed pole caps.

The field strength at each resonance was measured by a gaussmeter located just outside the resonance cell. A correction was made to convert the field strength outside to that inside the cell, and was found to be as large as 5.7 G at these field strengths. This correction made the uncertainty in the field-strength measurement about 1.5 G with a possible systematic error of the order of 1 G for all observed resonance lines.

All observed resonance lines and their assignments are given in Tables I and II. Figure 3 shows relevant energy levels and one typical LMR transition.
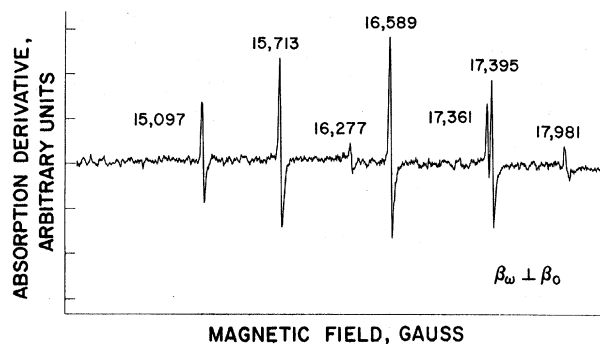

FIG. 2. Chart recorder trace showing LMR of the oxygen molecule for the perpendicular case.

TABLE I. Observed resonance fields (in kG) and calculated perturbation energies (in GHz). Parallel case. (a) Using (4); average, 115.045 GHz. (b) Using (3); average, 115.055 GHz. (c) Using (2); average, 115.064 GHz.

B	M	(a)	(b)	(c)
16.169	1	115.043	115.054	115.060
16.411	−4	115.058	115.064	115.076
16.530	−3	115.045	115.059	115.069
17.118	−2	115.043	115.056	115.063
17.448	0	115.042	115.051	115.056
17.690	−1	115.041	115.051	115.057

Theoretical calculation was done in the NSJM representation, taking $N = 1$, 3, 5, 7, and 9. The values of the zero-field molecular parameters B_0, B_1, B_2, λ_0, λ_1, μ_0, and μ_1 are taken to be 43.100 518, -1.4496×10^{-4}, -1.6×10^{-10}, 59.501 342, 5.847×10^{-5}, $-0.252 586 5$, and -2.464×10^{-7} GHz, respectively. These are the values found by Welch and Mizushima[13] by fitting all existing mi-
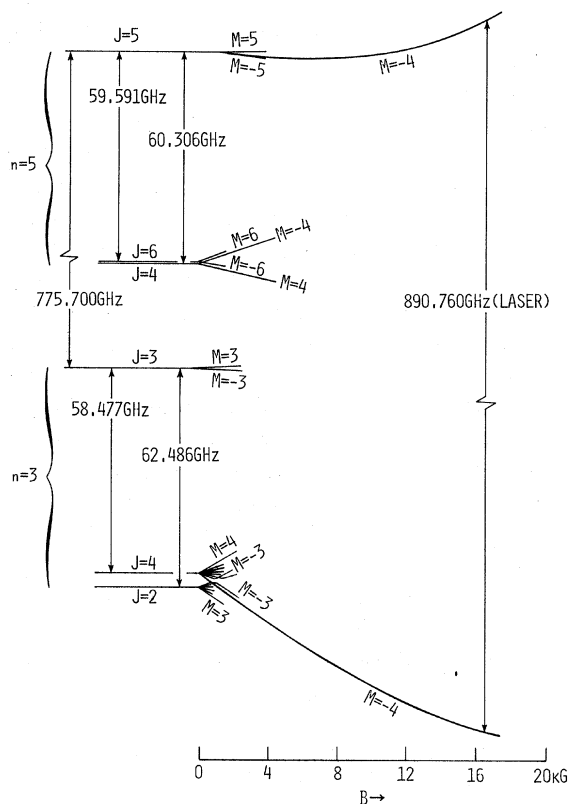

FIG. 3. Schematic energy-level diagram. The zero-field energy separations within each triplet are observed in microwave spectroscopy. Only the strongest LMR transition, $M = -4 \to -4$, is shown explicitly.

TABLE II. Observed resonance fields (in kG) and calculated perturbation energies (in GHz). Perpendicular case. (a) Using (4); average, 115.043 GHz. (b) Using (3); average, 115.057 GHz. (c) Using (2); average, 115.064 GHz.

| | M | | | | |
B	$n=3$	$n=5$	(a)	(b)	(c)
15.097	−4	−3	115.036	115.060	115.071
15.713	−3	−2	115.045	115.058	115.067
16.277	1	2	115.049	115.054	115.060
16.589	−2	−1	115.042	115.053	115.060
17.361	0	1	115.038	115.048	115.052
17.395	−1	0	115.039	115.049	115.054
17.981	−3	−4	115.058	115.074	115.080

crowave and infrared transition frequencies. For the present magnetic perturbation calculation, however, other sets of values [9,14] would give essentially the same result. For the magnetic g factors, two sets of values given in (2) and (3) already exist. LMR of O_2 using the 78- and 118-μm H_2O laser[13] on the $N=13 \rightarrow 15$ and $21 \rightarrow 23$

transitions provided another set:

$$g_\perp = 2.0044 \pm 0.0008,$$

$$g_z = 2.0020 \pm 0.0001, \tag{4}$$

$$g_n = 0.000\,125 \pm 0.000\,08,$$

which gives a slightly better fit to that data. Calculation of the magnetic perturbation energies at observed magnetic resonance fields was done using these three sets of values of the g factors, and the results are shown in Tables I and II. The perturbation energies (frequencies) given there correspond to the calculated transition frequencies minus the zero-field energy separation between the $N=J=3$ levels.

The standard deviation for the thirteen data points of the calculated perturbation frequencies is 6.8, 7.1, and 9.7 MHz for the sets (4), (3), and (2), respectively, showing that the set (4) is slightly better than the others.

From the observed frequency of the laser line,[15] 890.761 ± 0.001 GHz, the zero-field energy separation between the $N=J=5$ and $N=J=3$ levels is obtained as

$$E(N=J=5) - E(N=J=3) = \begin{cases} 775.716 \pm 0.007 \text{ GHz} & (5a) \\ 775.704 \pm 0.007 \text{ GHz} & (5b) \\ 775.696 \pm 0.010 \text{ GHz}. & (5c) \end{cases}$$

Theoretically, this energy difference should be

$$E(N=J=5) - E(N=J=3) = 18(B_0 + \tfrac{2}{3}\lambda_1 - \mu_1) + 756B_1 + 25\,272B_2. \tag{6}$$

When the above cited set of values of the molecular parameters[13] is used, we obtain 775.700 43 GHz ± 0.000 01 from this theoretical formula. Comparing this result with (5a), (5b), and (5c), we see that the sets (2) and (3) are better than (4). If, however, we assume a systematic error of 1 G in our field measurement, the set (4) is also acceptable.

[1]K. M. Evenson, H. P. Broida, J. S. Wells, R. J. Mahler, and M. Mizushima, Phys. Rev. Lett. 21, 1038 (1968).
[2]Old references can be found in P. F. Wacker, M. Mizushima, J. D. Peterson, and J. R. Ballard, Microwave Spectral Tables Diatomic Molecules, National Bureau of Standards Monograph No. 70 (U. S. GPO, Washington, D. C., 1964), Vol. 1.
[3]R. W. Zimmerer and M. Mizushima, Phys. Rev. 121, 152 (1961).
[4]B. G. West and M. Mizushima, Phys. Rev. 143, 31 (1966).
[5]H. A. Kramers, Z. Phys. 53, 422 (1929).
[6]J. S. McKnight and W. Gordy, Phys. Rev. Lett. 21, 1787 (1968).
[7]M. Tinkham and M. W. P. Strandberg, Phys. Rev. 97, 951 (1955).
[8]K. D. Bauers, R. A. Kamper, and C. D. Lustig, Proc. Roy. Soc., Ser. A 251, 565 (1959).
[9]R. Tischer, Z. Naturforsch. 22A, 1711 (1967).
[10]J. M. Hendrie and P. Kusch, Phys. Rev. 107, 716 (1957).
[11]J. S. Wells and K. M. Evenson, Rev. Sci. Instrum. 41, 226 (1970).
[12]K. M. Evenson and M. Mizushima, to be published.
[13]W. M. Welch and M. Mizushima, Phys. Rev. A 5, 2692 (1972).
[14]T. T. Wilheit and A. H. Barrett, Phys. Rev. A 1, 213 (1970).
[15]K. M. Evenson, J. S. Wells, L. M. Matarrese, and L. B. Elwell, Appl. Phys. Lett. 16, 159 (1970).