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Observation of electric quadrupole transitions in the fundamental band of O_2 in the 1600-cm^{-1} region

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We have detected the electric quadrupole $S(5)$ and $S(7)$ transitions in the 1-0 band of $^{16}O_2$ using a tunable diode laser and a 40-m path of O_2 at pressures of 10 to 80 Torr. This is the first observation of quadrupole vibrational transitions in a molecule other than hydrogen. Each transition is observed to be a triplet due to the spin splitting of the O_2 rotational levels, and the measured separations of the lines, in the 0.02 to 0.04-cm^{-1} range, agree with values derived from microwave spectroscopy of O_2. The total integrated intensity of the O_2 1-0 quadrupole band was determined to be $(1.77 \pm 0.63) \times 10^{-5}$ $cm^{-1}/(m$ amagat). We were not able to detect magnetic-dipole transitions in the band, and thus determined a conservative upper limit of 0.86×10^{-5} $cm^{-1}/(m$ amagat) for the strength of a magnetic-dipole 1-0 band in O_2.

I. INTRODUCTION

The first observation of the electric quadrupole pure rotational spectrum of the H_2 molecule was reported in 1978 by Reid and McKellar,[1] who detected the $S_0(3)$ ($v=0$; $J=5 \leftarrow 3$) transition near 1035 cm^{-1} using a tunable diode laser and a long-path absorption cell. At that time, it was realized that the same apparatus could be used to search for vibration-rotation quadrupole transitions in such molecules as N_2 and O_2, provided that suitable diode lasers were available. Recently, diode lasers operating in the 1600-cm^{-1} region, close to the $v=1 \leftarrow 0$ band of O_2, were obtained[2] to study the detection of very low concentrations of NO_2. A further incentive to carry out a search for a weak O_2 vibration-rotation spectrum (due to electric quadrupole or magnetic-dipole transitions) was provided by the very recent observation of an unidentified line triplet in a long-path infrared atmospheric (solar) spectrum reported by Niple *et al.*[3,4] The center frequency of this triplet was found to be 1603.83 cm^{-1}, close to the expected position of the $S(7)$ ($v=1 \leftarrow 0$; $N=9 \leftarrow 7$) transition of O_2.

In the present paper, we report the laboratory observation of the $S(5)$ and $S(7)$ lines of the $1 \leftarrow 0$ electric quadrupole band of O_2. Each line is a closely spaced (0.03 cm^{-1}) triplet split by the spin structure of the O_2 $^3\Sigma_g^-$ ground electronic state. Our observations confirm the identification of the lines seen in the atmospheric spectrum as due to quadrupole transitions in O_2, and they represent the first detection of quadrupole vibration-rotation transitions in a molecule other than hydrogen. We have also searched for, but failed to detect, a magnetic-dipole transition, and are thus able to establish an upper limit for the strength of the O_2 1-0 magnetic-dipole band.

II. DETECTION AND FREQUENCY MEASUREMENTS

The apparatus employed here consists of a tunable diode laser and a multipass cell; and has been described in detail in previous publications.[1,2,5] The operating conditions (temperature and current) of the tunable diode laser are carefully adjusted to ensure single-mode operation in the required spectral region. The laser beam is then focused into a 1-m multipass cell,[2] and the output from the cell is focused in turn onto a HgCdTe infrared detector. A Ge etalon[5] or small infrared cell containing reference gases can be inserted into the laser beam to calibrate the spectra. Spectra are recorded on an X-Y plotter, and to achieve very high sensitivity we use second-harmonic detection techniques.[2]

For the initial experiments, we adjusted the diode laser to tune from 1603.5 to 1064.1 cm^{-1} in a single mode. This range covers the unidentified triplet of Niple *et al.*[3] and the expected position of the $S(7)$ quadrupole line of O_2, which should be the strongest feature in the band at room temperature. The multipass cell was set for 40-m path length and was initially filled with air at 36-Torr pressure. A small cell containing NO_2 at low pressure was also placed in the laser beam. Figure 1 shows the results obtained as the laser was tuned and conventional amplitude detection was employed. The AFGL tapes[6,7] were used to identify both the NO_2 lines appearing in the reference cell and some weak atmospheric HDO lines appearing in the 40-m path length of air. The reference cell was then removed, and a high sensi-

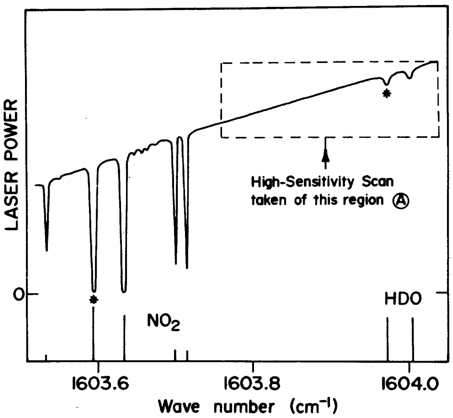

FIG. 1. Diode laser scan of the 1603.8-cm^{-1} region using conventional amplitude detection. The laser beam passes through a 40-m path length of air at 36 Torr, and a 10 cm reference cell containing <1 Torr of NO_2. The weak HDO lines arise from residual water vapor in the long-path cell. Calculated line positions, shown at the bottom of the figure, are taken from the AFGL tapes, (Refs. 6 and 7) and lines marked with an asterisk were used as reference lines (see Table I).

tivity scan was taken near 1603.8 cm^{-1} using second-harmonic detection. However, in this initial experiment using air in the multipass cell, no absorption lines could be seen near 1603.8 cm^{-1}. We estimate typical noise levels during these measurements to be equivalent to an absorption coefficient of ~5×10^{-7} m^{-1}.

The air in the multipass cell was then replaced with pure O_2 at 36 Torr, the scan was repeated, and a clearly identifiable triplet appeared above the noise level. Figure 2 shows typical results.

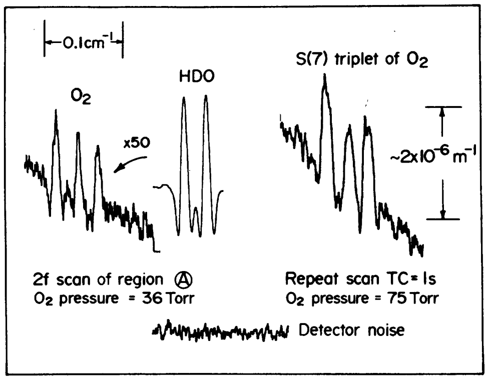

FIG. 2. High-sensitivity diode laser scans of the $S(7)$ triplet of O_2 in region A of Fig. 1. For these scans, the NO_2 cell was removed, and second-harmonic detection was used. The first scan was taken with an O_2 pressure of 36 Torr and the second with 75 Torr; the diode laser current (wavelength) modulation amplitude was optimized in each case. The sensitivity is close to detector noise limited due to the relatively low power available in this laser mode.

Simple tests confirmed that the three lines were not associated with any contaminants in the cell or the ambient air, and the gas from two cylinders of O_2 from different manufacturers gave identical results. We were thus confident that the observed lines were due to oxygen. Their absolute and relative positions identified them unambiguously as the $J=10\leftarrow8$, $9\leftarrow7$, and $8\leftarrow6$ spin components of the $S(7)$ $(N=9\leftarrow7)$ quadrupole transition of $^{16}O_2$.

The positions of the three O_2 lines were measured relative to both the NO_2 and HDO lines using a calibrated Ge etalon.[5] From these diode laser scans, we can determine line separations to ±0.003 cm^{-1} or better, but the absolute frequencies of the NO_2 and HDO reference lines are not known with confidence to this precision. Consequently, we report two separate sets of values for the O_2 frequencies depending on the reference line used. Any future improvement in the absolute frequency of the NO_2 or HDO lines will lead to a better value for the O_2 line frequencies. The results of these frequency measurements are given in Table I, where they are compared to some previous experimental values from Raman,[8,9] electronic,[10,11] and microwave[12] spectroscopy. In the Raman spectrum, the triplet structure of $S(7)$ has not yet been resolved, but the measured line positions of Fletcher and Rayside[8] and Loete and Berger[9] agree with the center of gravity of the present values to within ~0.06 and ~0.02 cm^{-1}, respectively. Furthermore, in both cases [8,9] the fitted $S(7)$ frequencies agree better with our value. Line positions for the 1-0 band of O_2 may also be obtained directly from the "experimental" term values derived by Veseth and Lofthus[10] from measurements of the red atmospheric bands $(^1\Sigma_g^+\leftarrow{}^3\Sigma_g^-)$ in the electronic spectrum of O_2 by Babcock and Herzberg.[11] Again, the agreement is quite good (see Table I). Finally, the separations of the O_2 lines measured here may be compared directly with combination differences obtained from the microwave spectrum of O_2 in the $v=0$ and 1 states (see Amano and Hirota).[12] The agreement of the very accurate microwave values with our line separation measurements is within 0.0004 and 0.0005 cm^{-1} (12 and 15 MHz), providing a convincing proof that our observed spectrum is indeed due to O_2 quadrupole transitions.

These laboratory measurements enabled us to identify confidently the triplet observed by Niple *et al.*[3,4] as due to the $S(7)$ quadrupole transition of atmospheric oxygen.[13] Their measured line positions agree well with ours (see Table I), and the relative and absolute line intensities are also consistent with this identification. A search for other O_2 quadrupole lines in the infrared solar spectrum also led to the tentative identification[14] of the $S(5)$

TABLE I. Experimental line frequencies for the $S(7)$ triplet of the 1-0 band of O_2.

Source	Line positions (cm^{-1})			Splittings (cm^{-1})	
	$J=10\leftarrow 8$	$9\leftarrow 7$	$8\leftarrow 6$		
Present results:					
HDO reference[a]	1603.8053	1603.8350	1603.8589	0.0297	0.0239[c]
NO_2 reference [b]	1603.799	1603.829	1603.853		
Solar spectrum[d]	1603.799	1603.828	1603.852	0.029	0.024
Electronic spectrum[e]	1603.775	1603.821	1603.801	0.046	−0.020
Raman spectrum		1603.780[f] 1603.821[g]			
Microwave spectrum[h]				0.02933	0.02438

[a] HDO reference line (Ref. 7) at 1603.974 cm^{-1}. The measured separation of the HDO and O_2 lines is accurate to 0.001 cm^{-1}, but the HDO position is less accurately known.

[b] NO_2 reference line (Ref. 6) at 1603.593 cm^{-1}. The measured separation of the NO_2 and O_2 lines is accurate to 0.003 cm^{-1}, and the absolute NO_2 position probably has about the same accuracy.

[c] The uncertainty in the splitting measurement is ±0.0007 cm^{-1}.

[d] Niple *et al*. (Ref. 3) and Goldman *et al* (Ref. 13).

[e] Term values derived by Veseth and Lofthus (Ref. 10) from the results of Babcock and Herzberg (Ref. 11).

[f] Fletcher and Rayside (Ref. 8).

[g] Loete and Berger (Ref. 9).

[h] Amano and Hirota (Ref. 12) accurate to ±0.00001 cm^{-1}.

triplet near 1592.9 cm^{-1}, but no other lines in the band appear to lie in a satisfactory atmospheric window.[14] We therefore tuned our diode laser to the 1593 cm^{-1} region in order to search for $S(5)$; at high sensitivity with pure O_2 in the cell, a second triplet was detected. Measurements of the line frequencies and separations are given in Table II, where they are compared to other values as in Table I. The $S(5)$ triplet was somewhat weaker than $S(7)$ (as expected) and the laser performance was not as good around 1593 cm^{-1}, so the measurements in Table II are slightly less accurate than those in Table I.

It was not possible to observe any additional O_2 quadrupole lines in the laboratory due to difficulties in obtaining good single-mode behavior of the diode laser in the regions of the $S(3)$, $S(9)$, or $S(11)$ lines. To detect these transitions, or any of the stronger lines of the Q and O branches, requires a sensitivity of $\leqslant 5\times 10^{-7}$ m^{-1}, which is close to the

TABLE II. Experimental line frequencies for the $S(5)$ triplet of the 1-0 band of O_2.

Source	Line Positions (cm^{-1})			Splittings (cm^{-1})	
	$J=8\leftarrow 6$	$7\leftarrow 5$	$6\leftarrow 4$		
Present results[a]	1592.849	1592.884	1592.919	0.0351	0.0353[b]
Solar spectrum[c]	1592.843	1592.878	1592.921	0.035	0.043
Electronic spectrum[d]	1592.815	1592.864	1592.913	0.049	0.049
Raman spectrum		1592.837[e] 1592.864[f]			
Microwave spectrum[g]				0.03415	0.03472

[a] NO_2 reference line (Ref. 6)1592.954 cm^{-1}. The measured separation of the NO_2 and O_2 lines is accurate to 0.003 cm^{-1}, and the NO_2 position probably has about the same accuracy.

[b] The uncertainty in the splitting measurement is ±0.001 cm^{-1}.

[c] Niple *et al*. (Ref. 3) and Goldman *et al*. (Ref. 13).

[d] Term values derived by Veseth and Lofthus (Ref. 10) from the results of Babcock and Herzberg (Ref. 11).

[e] Fletcher and Rayside (Ref. 8).

[f] Loete and Berger (Ref. 9).

[g] Amano and Hirota (Ref. 12) accurate to ± 0.00001 cm^{-1}.

optimum performance of our laser absorption spectrometer. However, it was possible to operate the laser with reasonable sensitivity in the region of 1601.9 cm^{-1} in order to search for the $J=8 \leftarrow 7$ component of $S(7)$, which would be one of the strongest transitions (see below) in the magnetic-dipole 1-0 band of O_2. No absorption was observed, and it was possible to place an upper limit of 10^{-6} m^{-1} on the line-center absorption coefficient.

III. INTENSITY MEASUREMENTS

The optimum signal to noise ratio that we could attain for $S(7)$ using a 1-s time constant was ~6:1 (see Fig. 2). While this was adequate for accurate frequency measurements, it made it difficult to estimate accurate relative and absolute line intensities. We took many scans of the $S(7)$ region at pressures ranging from 10 to 80 Torr of O_2, and from these we estimated approximate peak absorption coefficients at line center. (The second-harmonic detection technique is not very suitable for the determination of integrated absorption coefficients.) It was found that the O_2 lines were dominated by pressure broadening above ~40 Torr, and hence that the line-center absorption coefficient was approximately independent of pressure in the 40–80-Torr range. The absorption coefficient could be reduced by a factor of 2 by pumping the cell down to a pressure of 13 Torr. These observations are consistent with the pressure broadening coefficients of ~0.1 cm^{-1}/atm(FWHM) determined by Raman spectroscopy.[8, 9, 15]

The relative intensities of the three components of $S(7)$ are predicted (see below) to be 1.00, 0.87, and 0.78 in order of increasing wave number (left to right in Fig. 2). Our signal-to-noise ratio, and the closeness of the three lines, preclude a very accurate measurement of relative intensity, but the first line at lowest wave number does appear to be somewhat more intense in our scans.[16] The average value of the limiting peak absorption for the three lines was estimated to be $(2.1 \pm 0.4) \times 10^{-6}$ m^{-1}. Assuming a pressure broadening coefficient of 0.10 ± 0.03 cm^{-1}/atm, the resulting combined intensity for the $S(7)$ triplet is $(0.99 \pm 0.35) \times 10^{-6}$ cm^{-1}/(m atm) at 293 K, which leads to a value of $(1.77 \pm 0.63) \times 10^{-5}$ cm^{-1}/(m amagat) for the total 1-0 band quadrupole intensity. In terms of the quadrupole transition matrix element, the experimental value is $\langle 1|Q|0\rangle = 0.145 \pm 0.026$ DÅ. This is equivalent to 0.108 ± 0.019 ea_0^2 in atomic units, or to $(0.486 \pm 0.086) \times 10^{-40}$C m^2 in SI units. Note that the largest error source in this intensity determination comes from the pressure broadening coefficient.

The value of the quadrupole transition moment, $\langle 1|Q|0\rangle$, also enters into the theoretical expression for the intensity of the collision-induced 1-0 band of oxygen. From their study of this spectrum, Shapiro and Gush[17] determined a value of $Q' = 1.6$ ea_0 for the rate of change of the quadrupole moment with internuclear distance, which is equivalent to a value of $\langle 1|Q|0\rangle = 0.110$ ea_0^2. This is remarkably close to our value of $\langle 1|Q|0\rangle = 0.108$ ea_0^2, but the agreement may be regarded as fortuitous considering the large uncertainty in our value and the many approximations involved in the theory of collision-induced absorption.

The upper limit of 10^{-6} m^{-1} for the line-center absorption coefficient of the $J=8 \leftarrow 7$ component of $S(7)$ near 1601.9 cm^{-1} that was mentioned above may be used to determine a limit for the strength of the magnetic-dipole 1-0 band of O_2. This value implies that the total integrated intensity of the magnetic-dipole 1-0 band must be less than 0.86 $\times 10^{-5}$ cm^{-1}/(m amagat), that is, less than half the observed intensity of the quadrupole band.

IV. DISCUSSION AND CONCLUSIONS

In the preceding section, we alluded to the expected relative intensities of the various electric quadrupole and magnetic-dipole transitions in O_2. These may be determined by standard techniques, and we present in Table III a partial listing of relative line strengths which have been calculated using the computer program of Johns and Lepard.[18, 19] The list should prove helpful in clarifying the expected structure of the band. In the $^3\Sigma_g^-$ ground electronic state of O_2, each rotational level N is split by fine-structure interactions into three levels with resultant angular momentum $J = N + S = N-1$, N, and $N+1$. For $^{16}O_2$, only those levels with odd values of N are allowed by nuclear-spin statistics. The selection rules are $\Delta N = 0$, ± 2, $\Delta J = 0$, ± 1, and ± 2 for electric quadrupole transitions, and $\Delta N = 0$, ± 2, $\Delta J = 0$, and ± 1 for magnetic-dipole transitions. Thus, for example, an S-branch transition with $\Delta N = +2$ has six possible quadrupole components and three possible magnetic-dipole components, as shown in Table III. However, the three quadrupole transitions with $\Delta J = \Delta N = +2$ are much stronger than the remaining $\Delta J = 0$ and $+1$ transitions, and likewise the two magnetic-dipole transitions with $\Delta J = +1$ are much stronger than the remaining $\Delta J = 0$ transition. Specifically, the $J = 8 \leftarrow 8$ component of $S(7)$ is located just 0.042 cm^{-1} above the last member of the observed $S(7)$ triplet in Fig. 2, but was not observed. This is not surprising since it is predicted to be relatively weak for both quadrupole and dipole absorption. The $J = 8 \leftarrow 7$ component of $S(7)$ at 1601.89 cm^{-1}is one of the three or four strong-

TABLE III. Predicted relative intensities for electric quadrupole and magnetic-dipole transitions in the 1-0 band of O_2 at 293 K.[a].

N	J	Frequency[b](cm^{-1})	Intensity[c]	
			Electric quadrupole	Magnetic dipole
	4←2	1581.87	4.36	0
	5←3	1581.80	5.53	0
S(3)	6←4	1581.75	7.37	0
	4←4	1581.73	0.02	0.35
	4←3	1579.79	0.72	5.98
	5←4	1583.75	0.54	7.11
	6←4	1592.919	6.61	0
	7←5	1592.884	7.65	0
S(5)	8←6	1592.849	9.21	0
	6←6	1592.89	0.008	0.21
	6←5	1590.91	0.44	8.15
	7←6	1594.87	0.35	9.14
	8←6	1603.859	7.82	0
	9←7	1603.835	8.70	0
S(7)	10←8	1603.805	10.00	0
	8←8	1603.90	0.002	0.14
	8←7	1601.89	0.27	9.16
	9←8	1605.85	0.27	10.00
	10←8	1614.67	8.02	0
	11←9	1614.65	8.73	0
S(9)	12←10	1614.63	9.76	0
	10←10	1614.77	0.001	0.09
	10←9	1612.73	0.17	9.08
	11←10	1616.69	0.15	9.76

[a] Calculated using the computer program of Johns and Lepard (Refs. 18 and 19). Only four S-branch transitions are listed here.

[b] Frequencies given to 0.01 cm^{-1} are calculated; those given to 0.001 cm^{-1} are measured (see Tables I and II).

[c] Intensities are normalized to 10.00 for the strongest line in the band. Note that the electric quadrupole and magnetic-dipole intensity scales are not connected.

est magnetic-dipole transitions at room temperature, but as mentioned above, we were not able to detect any absorption in this region, thus establishing an upper limit for the strength of the magnetic-dipole band. From Table III it can be seen that there is also a quadrupole contribution to this component, but it is predicted to be only about 3% of the strength of the observed S(7) lines, which is well below our limit of detection.

The present observation of quadrupole transitions and apparent absence of magnetic-dipole transitions contrasts with the presence of the well-known fine-structure and rotational magnetic-dipole spectra of O_2 in the microwave and millimeter regions,[12] and the absence of corresponding quadrupole spectra. In simple terms, this contrast may be explained by the fact that the magnetic-dipole moment of O_2 is fixed to the molecule and rotates with it, thus giving the rotational spectrum. However, the value of the magnetic moment is not expected to depend significantly on vibrational motion (i.e., internuclear distance) and thus there is no vibrational spectrum. On the other other hand, the molecular quadrupole moment is expected to depend quite strongly on vibrational motion. Note that a pure rotational quadrupole spectrum (as in H_2)[1] should be present for O_2, but it will be very weak, in part because of the strong (ν^3) frequency dependence of quadrupole absorption intensity.

Brault[20] has recently observed electric quadrupole transitions of O_2 in long-path atmospheric spectra around 7600 Å. These electronic transitions belong to the $b \leftarrow X$ "red atmospheric bands" of O_2, the intensity of which arises predominantly from magnetic-dipole absorption. The intensity of these weak electronic transitions appears to be about six times smaller than the intensity of the vibrational transitions reported here. Brault was able to detect these lines because his solar spectra were ground based, in contrast to the balloon-based spectra.[3,4,13]

Electric quadrupole vibrational spectra were first observed by Herzberg[21] in H_2, and since then have been further studied in H_2,[22] HD,[23] and D_2.[24] However, the present results constitute the first detection of vibrational or rotational quadrupole transitions in any molecule other than hydrogen. Our laboratory results have led to the identification[13] of the $S(5)$ and $S(7)$ transitions in the 1-0 band of O_2 in long-path atmospheric (solar) spectra, and also to the realization[13] that some previously unidentified lines in the 2400 cm^{-1} region of the solar spectrum are due to electric quadrupole transitions in the 1-0 band of N_2.

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