Investigation of the $b\,^1\Sigma_g^+(v=0)\leftarrow X\,^3\Sigma_g^-(v=0)$ magnetic-dipole transitions in $^{18}O_2$

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We report an investigation of the $b\,^1\Sigma_g^+(v=0)\leftarrow X\,^3\Sigma_g^-(v=0)$ band of $^{18}O_2$. The weak magnetic-dipole transitions around 761 nm were observed using a high-sensitivity absorption spectroscopy apparatus based on a DFB diode laser source and a multipass absorption cell. We accurately measured the wavelength of several lines and deduced the rotational constants for the $b\,^1\Sigma_g^+(v=0)$ electronic state. We also studied the line broadening in the presence of different isotopic species and determined the pressure broadening coefficients. We discuss the interest of these data in view of a possible test of the symmetrization postulate for ^{18}O nuclei. [S1050-2947(97)03405-7]

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I. INTRODUCTION

In this paper we report the observation of the $b\,^1\Sigma_g^+(v=0)\leftarrow X\,^3\Sigma_g^-(v=0)$ spectrum of the isotopic $^{18}O_2$ molecule around 761 nm. These extremely weak lines (peak absorption coefficient $\sim 10^{-6}$ cm^{-1}) correspond to magnetic-dipole and electric-quadrupole transitions; their transition strength, however, has essentially magnetic-dipole character. They were early observed for other isotopic species, namely, $^{16}O^{16}O$, $^{18}O^{16}O$, and $^{17}O^{16}O$ [1], but observations were not reported until recently for the isotopic dimer $^{18}O_2$. The only data existing in the literature for visible transitions of $^{18}O_2$ were obtained by Hill and Schawlow for the $b\,^1\Sigma_g^+(v=2)\leftarrow X\,^3\Sigma_g^-(v=0)$ band near 635 nm by using laser intracavity absorption spectroscopy [2]. The rotational spectrum of $^{18}O_2$ was instead investigated extensively using Raman [3,4] and microwave [5,6] techniques.

As is well known, the spectra of $^{18}O_2$ (as well as the spectra of $^{16}O_2$) have a rather peculiar feature. Because the nuclei are identical spin-0 particles, and according to the spin-statistic theorem the overall wave function of the molecule must be symmetric under the exchange of the nuclei, only alternate rotational levels are allowed [7]. This suggested the possibility of performing an accurate test of the symmetrization postulate of quantum mechanics (and/or of the spin statistic theorem) by searching for molecules in the forbidden states [8]. Experiments were recently performed by our group [9] and by Hilborn and Yuca [10] setting a limit of 5×10^{-7} for the maximum fraction of $^{16}O_2$ molecules in the forbidden symmetry states. The lack of accurate observations of the $^{18}O_2$ spectra makes it particularly interesting to perform a similar test for this molecule.

The motivation of this work was therefore twofold. First, the detection of these transitions allowed us to obtain several molecular constants that were not known for $^{18}O_2$. In particular, by measuring the wavelength of the transitions, we deduced the rotational constants of the $b\,^1\Sigma_g^+(v=0)$ electronic state and by studying the line profile we obtained the pressure broadening coefficients. Second, this experiment can be considered preliminary to a test of the symmetrization postulate for ^{18}O nuclei. The knowledge of the molecular constants obtained in this work is important in order to calculate the positions of the forbidden lines to be searched. The knowledge of the pressure broadening coefficient is also important in this respect in order to calibrate the sensitivity of the apparatus.

II. EXPERIMENTAL APPARATUS

The experimental apparatus used in this work was similar to the one described in Ref. [9]. It consisted of a spectrometer based on a diode laser radiation source and a multipass absorption cell. The laser source was a distributed feedback diode laser emitting 5-mW cw in a single mode at 761 nm. It was temperature stabilized and driven by a low-noise current supply. The emission linewidth was about 20 MHz. The frequency drift was measured to be less than 0.2 MHz/s. An optical isolator at the output of the laser was used in order to avoid perturbations due to stray reflections from optical components.

With respect to the apparatus of Ref. [9], in this experiment we used a smaller-volume Herriott-type multipass cell. The absorption path length was 36 m. A 50% ^{18}O enriched sample was used; the amount of the most abundant species in the sample was $^{16}O_2\sim28\%$, $^{18}O_2\sim31\%$, and $^{16}O^{18}O\sim37\%$. The total pressure in the cell was measured by means of a capacitive gauge.

For the wavelength measurements, a dual-beam detection system was used. The laser beam was split into two parts by a beam splitter. One beam passed through the absorption cell, while the other beam provided a reference signal. In this way, we eliminated the background signal due to the change of the laser intensity during the frequency scan, which would have biased the determination of the line center. The beams had the same path length in air. Each beam was focused by a 10-cm-focal-length lens into a Si photodiode preamplifier. The intensity of the two beams was adjusted to be the same at the photodetectors. The absorption signal was recorded using a wavelength modulation technique. The laser frequency was modulated at $f=40$ kHz by adding a small sinu-

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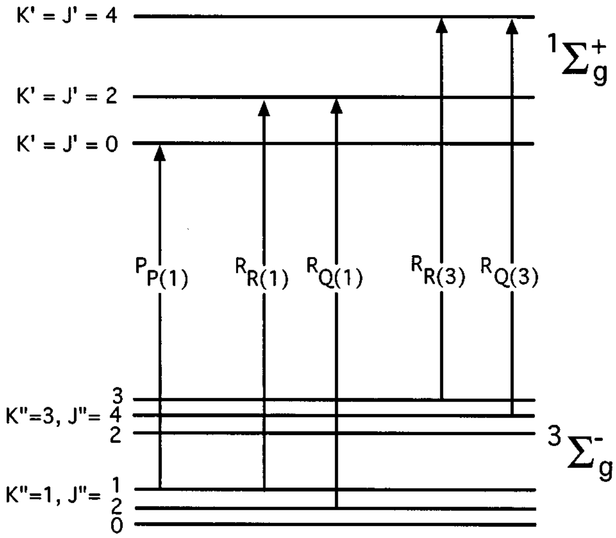

FIG. 1. Partial scheme showing the $^{18}O_2$ energy levels (not to scale) and the type of transitions investigated in this work.

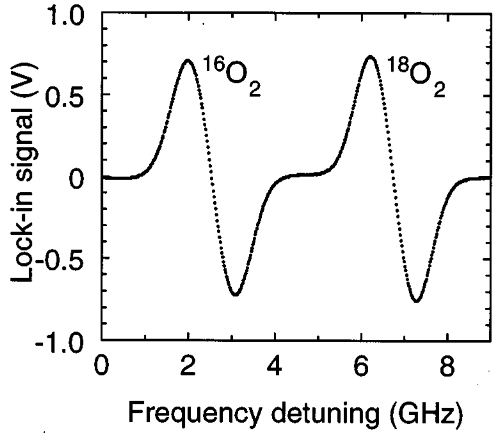

FIG. 2. Example of the detection of the magnetic-dipole lines for two isotopic species of oxygen. The signals shown correspond to the $^RR(7)$ line of $^{16}O_2$ and to the $^RQ(5)$ line of $^{18}O_2$ as observed using the wavelength-modulation technique with a total pressure of 20 Torr of isotopically enriched gas in the cell.

soidal modulation to the injection current of the diode. Using a lock-in amplifier with the same modulation as the reference signal, the derivative of the difference of the outputs of the photodetectors was obtained. For the wavelength measurement we measured the position of the zero of the signal corresponding to the center of the line. We set a modulation index equal to 1.6 for the optimum first-harmonic signal. The laser wavelength was measured with a traveling Michelson interferometer and a wavelength-stabilized He-Ne laser as a reference. The accuracy of this system was 1 part in 10^7. The measured values for the wavelength were corrected with a factor 0.999 998 9 in order to take into account the change in the index of refraction between 760 nm and the reference He-Ne wavelength. The accuracy of our measurements was tested by measuring the wavelength of the $^RR(3)$,$^RR(5)$, and $^RR(7)$ lines of $^{16}O_2$. The measured wavelengths are 761.5291(1) nm, 761.2551(1) nm, and 761.0030(1) nm, which agree, within the experimental accuracy, with those reported in the literature [1,11].

The study of the line broadening as a function of gas pressure was performed instead by recording directly the absorption profile without lock-in detection. An accurate calibration of the recorded spectra was provided by a Fabry-Pérot interferometer with a free-spectral range of 1.5 GHz. Data were recorded on a digital oscilloscope and stored in a personal computer.

III. RESULTS

In this work, we observed the $^PP(1)$, $^RR(K'')$, and $^RQ(K'')$ transitions of $^{18}O_2$, with K'' ranging between 1 and 13. The notation used is $^{\Delta K}\Delta J(K'')$, K'' being the rotational quantum number in the electronic ground state. Figure 1 shows a partial scheme of the $^{18}O_2$ energy levels and the transitions observed in this work. A typical spectrum is shown in Fig. 2, recorded using first derivative detection. The signals shown correspond to the $^RR(7)$ and $^RQ(5)$ lines of $^{16}O_2$ and $^{18}O_2$, respectively. The gas pressure in the cell was 20 Torr. The good signal-to-noise ratio and the symmetry of the recorded signals allowed an accurate determination of the center of the line for the wavelength measurement. The wavelengths and the corresponding frequencies of the $^{18}O_2$ transitions measured in this work are listed in Table I. We found that the measured frequencies deviate by about 3 GHz from those calculated from a simple isotope scaling rule using the molecular constants of $^{16}O_2$ given in Ref. [1].

The data in Table I can be used to deduce a variety of molecular constants. As a preliminary test of the procedure, we deduced the fine-structure separations for the rotational levels $K''=1-13$ of the ground electronic state by subtracting the $^RR(K'')$ frequency from the $^RQ(K'')$ frequency. The values we obtained are in good agreement with the more accurate direct measurements of Ref. [5].

We then calculated the molecular constants for the $b\,^1\Sigma_g^+(v=0)$ state. The spacing $\Delta E'(K')=E'(K')-E'(K'-2)$ between the rotational levels K' and

TABLE I. Measured wavelength (*in vacuo*) and frequency of the $^{18}O_2$ lines detected in this work.

Line	Wavelength[a] (nm)	Frequency[a] (cm^{-1})
$^PP(1)$	762.0478	13122.5364
$^RQ(1)$	761.5062	13131.8694
$^RQ(3)$	761.2402	13136.4581
$^RQ(5)$	760.9949	13140.6925
$^RQ(7)$	760.7694	13144.5876
$^RQ(9)$	760.5639	13148.1392
$^RQ(11)$	760.3775	13151.3623
$^RQ(13)$	760.2109	13154.2444
$^RR(1)$	761.6171	13129.9573
$^RR(3)$	761.3542	13134.4911
$^RR(5)$	761.1105	13138.6967
$^RR(7)$	760.8865	13142.5646
$^RR(9)$	760.6819	13146.0996
$^RR(11)$	760.4966	13149.3027
$^RR(13)$	760.3308	13152.1701

[a]The relative uncertainty of these values is one part in 10^7.

TABLE II. Spacing (in cm^{-1}) between the rotational levels of the $b\,^1\Sigma_g^+$(v=0) state of $^{18}O_2$.

K'	From ^RR lines[a]	From ^RQ lines[a]	Average value[a]
2			7.421 [b]
4	17.314	17.314	17.314
6	27.208	27.207	27.208
8	37.089	37.093	37.091
10	46.970	46.966	46.968
12	56.846	56.848	56.847
14	66.710	66.708	66.709

[a]The uncertainty in these values is ~ 0.003 cm^{-1}.

[b]This value was obtained as the difference between the frequencies of the $^RR(1)$ and $^PP(1)$ lines.

$(K'-2)$ can be determined from the distance between the two nearest $^RR(K'')$ or $^RQ(K'')$ lines. Indeed, if we define $\Delta\nu_R(K'')=\nu[^RR(K'')]-\nu[^RR(K''-2)]$ and $\Delta\nu_Q(K'')=\nu[^RQ(K'')]-\nu[^RQ(K''-2)]$, it is straightforward to show that

$$\Delta\nu_R(K)=\Delta E'(K+1)-\Delta E_2(K),$$

$$\Delta\nu_Q(K)=\Delta E'(K+1)-\Delta E_1(K), \qquad (3.1)$$

where $\Delta E_i(K'')=F_i(K'')-F_i(K''-2)$ is the spacing between the F_i fine-structure components of the K'' and $(K''-2)$ rotational levels in the ground state. Using the values in Table I for the line frequencies and taking $\Delta E_1(K)$ and $\Delta E_2(K)$ from Ref. [5], we determined the separations $\Delta E'(K')$ for $K'=4-14$. Two independent determinations of each spacing, except for $\Delta E'(2)$, can be obtained from $\Delta\nu_R(K)$ and $\Delta\nu_Q(K)$. The $\Delta E'(2)$ spacing was obtained from the difference between the $^RR(1)$ and the $^PP(1)$ line frequencies. The results are reported in Table II.

In terms of the B_0 and D_0 rotational constants, $E'(K')$ is given by

$$E'(K')=B_0[K'(K'+1)]-D_0[K'(K'+1)]^2. \qquad (3.2)$$

Table III gives the values of the rotational constants B_0 and D_0 of the $b\,^1\Sigma_g^+(v=0)$ state obtained by fitting the measured spacings between rotational levels to the expression for $\Delta E'(K')$ derived from Eq. (2).

Combining our value of B_0 with the value of B_2 measured in Ref. [2], we determined the vibration-rotation constant α and the equilibrium rotational constant B_e, which enter in the first-order expression of B_v [7]:

$$B_v=B_e-\alpha(v+1/2). \qquad (3.3)$$

TABLE III. Molecular constants (in cm^{-1}) for the $b\,^1\Sigma_g^+$(v=0) state of $^{18}O_2$.

Constant	Experimental value	Isotopic substitutional value
B_0	1.23680(14)	1.23686
D_0	$4.0(5)\times10^{-6}$	4.3×10^{-6}
α	0.0150(3)	0.0152
B_e	1.2443(2)	1.2445

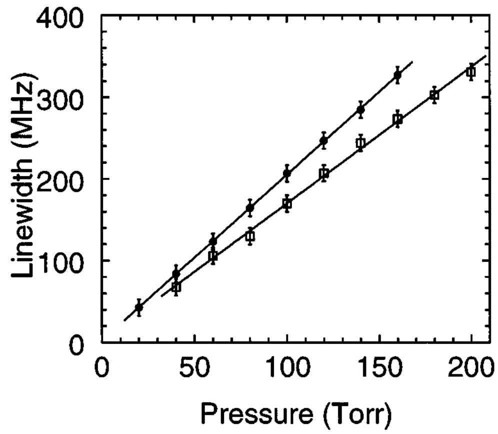

FIG. 3. Homogeneous linewidth of the $^RR(11)$ line of $^{18}O_2$ as a function of pressure. The square points correspond to the linewidths (half-width at half maximum) obtained with a partial pressure of 5 Torr of the isotopically enriched mixture and different values of $^{16}O_2$ pressure. Round points give instead the values obtained by varying the pressure of the enriched gas.

The values of B_e and α obtained in this work are given in Table III. In the table the values calculated from the isotope substitution rule using the $^{16}O_2$ constants from Ref. [1] are also reported for comparison. The two sets of constants are in agreement within the accuracy of our measurements.

Using the values of B_0 and B_e, it is possible to calculate, for the $b\,^1\Sigma_g^+(v=0)$ state, the effective internuclear distance r_o and the equilibrium internuclear distance r_e, which are given by [7]

$$r_{o,e}=\sqrt{\frac{h}{8\pi^2c\mu B_{o,e}}}, \qquad (3.4)$$

where h is the Planck constant, c is the speed of light, and μ is the reduced mass of the molecule. Using the value for the ^{18}O mass of $2.987\,635(36)\times10^{-23}$ g, we obtain $r_o=1.230\,70(6)$ Å and $r_e=1.226\,98(9)$ Å.

The value of r_e we deduced for the $b\,^1\Sigma_g^+(v=0)$ excited state is consistent, within the experimental uncertainties, with the corresponding value of 1.226 90 (1) Å calculated for $^{16}O_2$ taking the data in Ref. [1]. At the level of accuracy of our experiment, possible corrections to the r_e value due to deviations from an adiabatic Born-Oppenheimer potential are too small to be detected. Indeed, previous measurements on the electronic ground state also gave the same r_e value for the $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ isotopic molecules [12].

We also determined the zero line frequency ν_{00} by subtracting from the $^PP(1)$ frequency the spacing between the $K=0$ level and the F_2 component of the $K=1$ rotational level of the ground electronic state. We find $\nu_{00}=13\,125.092(3)$ cm^{-1}. The value of ν_{00} given by the isotopic substitution expression using the $^{16}O_2$ molecular constants of Ref. [1] is 13 125.193 cm^{-1}. As mentioned above, using this value led to a wrong determination of the positions of $^{18}O_2$ lines that are correctly accounted for by the value we obtained experimentally.

In this work we also measured the pressure broadening of $^{18}O_2$ lines in presence of $^{16}O_2$ and in the presence of the isotopically enriched mixture. The recorded line shapes were fitted with a Voigt profile and the homogeneous width was deduced. The results obtained for the ${}^{R}R(11)$ line are reported in Fig. 3. The square points correspond to the linewidths (half-width at half maximum) obtained with a partial pressure of 5 Torr of the isotopically enriched mixture and different values of ${}^{16}O_2$ pressure. Round points give instead the values obtained varying the pressure of the enriched gas. The pressure broadening coefficients we deduced are 1.67(6) MHz/Torr in the first case and 2.03(7) MHz/Torr in the second case. For comparison, the self-broadening coefficient for the same transition in ${}^{16}O_2$ is 1.86(2) MHz/Torr [13]. The difference between the broadening coefficients can be interpreted as an indication of the importance of resonant exchange processes in the collisional broadening of oxygen lines [14]. A more quantitative analysis of this effect would require, however, isotopically pure samples and a systematic analysis of the broadening of lines involving different rotational levels, which was beyond the scope of the present work.

IV. CONCLUSION

We performed a spectroscopic investigation of the $b\,{}^1\Sigma_g^+(v=0) \leftarrow X\,{}^3\Sigma_g^-(v=0)$ band of ${}^{18}O_2$. We measured the wavelength of several lines and deduced the rotational constants B_0 and D_0 of the excited electronic state. Combining our data with existing data for other levels, we determined several molecular constants of ${}^{18}O_2$. We measured also the pressure broadening coefficient in the presence of different isotopic species. The data we obtained have an intrinsic interest because of the lack of spectroscopic data for this molecule. They are also important in view of a future test of the validity of the symmetrization postulate for ${}^{18}O$ nuclei.

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[1] H.D. Babcock and L. Herzberg, Astrophys. J. **108**, 167 (1948).
[2] W.T. Hill and A.L. Schawlow, J. Opt. Soc. Am. B **5**, 745 (1988).
[3] W.G.M. Edwards, F.A.M. Good, and D.A. Long, J. Chem. Soc. Faraday Trans. II **72**, 865 (1976).
[4] R.C. Herney and F.P. Molanovic, Can. J. Spectrosc. **21**, 162 (1976).
[5] W. Steinbach and W. Gordy, Phys. Rev. A **8**, 1753 (1973).
[6] Y. Endo and M. Mizushima, Jpn. J. Appl. Phys. **22**, L534 (1983).
[7] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, 1950).
[8] G.M. Tino, Nuovo Cimento D **16**, 523 (1994).
[9] M. de Angelis, G. Gagliardi, L. Gianfrani, and G. M. Tino, Phys. Rev. Lett. **76**, 2840 (1996).
[10] R.C. Hilborn and C.L. Yuca, Phys. Rev. Lett. **76**, 2844 (1996).
[11] D.E. Burch and D.A. Gryvnak, Appl. Opt. **8**, 1493 (1969).
[12] W. Steinbach and W. Gordy, Phys. Rev. A **11**, 729 (1975).
[13] K.J. Ritter and T.D. Wilkerson, J. Mol. Spectrosc. **121**, 1 (1987).
[14] M. de Angelis, L. Gianfrani, F. Pavone, A. Sasso, and G.M. Tino, Nuovo Cimento D **18**, 557 (1996).