The isotope Effect of the O_2 $a^1\Delta_g$ Rotational Constant

E. A. Cohen[1], M. Okunishi[2], and J. J. Oh[3]

Institute for Molecular Science
Okazaki, Myodaiji 444, Japan

and

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109, U. S. A.

[1] Visiting Scientist, IMS. Permanent address, JPL.
[2] Affiliation, IMS. Permanent address: Research Institute for Scientific Measurement, Tohoku University, Katahira, Aoba-ku, Sendai, 980, Japan
[3] Research Affiliate, JPL. Permanent Address: Sookmyung Women's University, Seoul 140-742, Korea

ABSTRACT

The pure rotational spectrum of $a^1\Delta_g$ oxygen in its first excited vibrational state as well as the ground vibrational state rotational spectra of $^{16}O^{18}O$ and $^{18}O_2$ in their a states have been observed. Precise parameters describing the spectra have been determined and an accurate value has been derived for the equilibrium interatomic distance in the Born-Oppenheimer limit.

INTRODUCTION

Watson [1,2] *has* shown that the isotope dependence of the Dunham coefficients for a diatomic molecule can be expressed in relatively simple form. For a homonuclear diatomic molecule the number of independent parameters required to fit the rotational spectra of several isotopic species is quite small and these may be well determined with a limited amount of data. A number of pure rotational transitions of $a^1\Delta_g$ O_2 in its $v = 1$ state as well as some $v = 0$ transitions for $^{16}O^{18}O$ and $^{18}O_2$ have been measured. When these measurements are combined with those previously reported for the ground vibrational level of the $a^1\Delta_g$ state of $^{16}O_2$ [3], they allow the determination of the deviation of the rotational constants from predictions based on the Born-Oppenheimer approximation. An isotopically independent value can then be derived for the equilibrium bond length, r_e^{BO}, in the Born-Oppenheimer limit. It is interesting to compare the Watson correction to the rotational constant of oxygen in its $a^1\Delta_g$ state with that obtained by Tiemann [4] for the $^3\Sigma_g^-$ O_2 electronic ground state.

EXPERIMENTAL DETAILS

The $a^1\Delta_g$ O_2 was made in a positive column discharge cell approximately 1 m long by 10 cm diameter. A similar sized hollow cathode cell produced several times less metastable O_2. Normal O_2 was slowly flowed through the discharge, but ^{18}O enriched samples were observed under static conditions.

Approximately 150 mTorr of pure 0_2 and a discharge current of ≈ 70ma were used. The signal from the isotopic species diminished markedly after several minutes in the discharge making detection of their $v = 1$ states impractical. All but the $J = 5 - 4$, $v = 1$ transition were measured using a millimeter spectrometer which has been described by Endo and Hirota [5]. That transition was measured using similar pressures and current with a spectrometer described by Birk, et al,, [6] with a rooftop reflector employed to double the effective absorption path to approximately 1,8 meters.

THEORY

The expression for the energy levels of a molecule in a ^{1}A state may be written

$$ * = \sum_{l,m} Y_{l,m}\left(v + \frac{1}{2}\right)^l [J(J-1\ 1)\ -4]^m + \gamma\left(\frac{q}{2}\right)[J(J+1)][J(J-1\ 1)\ 2] \tag{1} $$

The $Y_{l,m}$ are the usual Dunham coefficients, q is the A doubling constant, and $\gamma = (-.1\ )^J$ for the homonuclear species and $+1$ for $^{16}O^{18}O$.

It is assumed that the ordinary Dunham expressions for B_v and D_v are valid so that

$$ B_v = Y_{01} + Y_{11}\left(v + \frac{1}{2}\right) + Y_{21}\left(v + \frac{1}{2}\right)^2 + \cdots, \tag{2} $$

$$ - D_v = Y_{02} + Y_{12}\left(v + \frac{1}{2}\right) + \cdots, \tag{3} $$

and

$$ H_v = Y_{03} + \cdots. \tag{4} $$

4

Y_{03} is fixed by the relationship

$$Y_{03} = \frac{Y_{02}^2}{Y_{01}} \left(\frac{Y_{11}}{3(-Y_{02}Y_{01})^{1/2}} + 2 \right).$$ (5)

Y_{21} is not determinable from these measurements but is available from CARS data [7]. It is the largest source of uncertainty in the reported parameters. It is further assumed that except for Y_{01}, the usual isotope relationship

$$Y'_{lm} = Y_{lm}\left(\frac{\mu}{\mu'}\right)^{(l+2m)/2}$$ (i)

is valid within experimental uncertainties where μ is the reduced mass using atomic masses. For a homonuclear diatomic molecule the expression given by Watson [1,2] becomes

$$Y_{01} = B_e^{BO} \left(1 - 2m_e \frac{d_0}{\mu} \right)$$ (7)

where

$$B_e^{BO} = \frac{h}{8\pi^2 \mu (r_e^{BO})^2}$$ (8)

is the Born-Oppenheimer rotational constant and is exactly proportional to μ^{-1}. The d_0 constant includes contribut ions from the 1)unham correction to Y_{01} found in the standard texts [7] as well as adiabatic and non-adiabatic corrections. The non-adiabatic part of d_0 is related to the rotational g factor expressed in nuclear magnetons by

$$d_O^n = -\frac{\mu g_1}{2m_p}$$ (9)

This last contribution is expected to be the dominant one.

RESULTS AND DISCUSSION

The newly measured transitions are listed in Table 1 along with those reported in Ref. 3. These have been fitted using a general fitting routine [9] to the parameters listed in Table 2 with their isotope dependences fixed as indicated. The observed minus calculated frequencies using these parameters are shown with the measured frequencies in Table 1. The parameters listed in Table 2 are *effective* parameters since they have been determined with the assumption that $Y_{21} = 0$. The parameters which are affected by Y_{21} have their dependence on this parameter shown in the last column.

Y_{21} is reported by Nich and Valentini [7] based upon analysis of CARS spectra of highly excited products of photodissociated ozone. Their value for Y_{21} of - 1.35(17) MHz is quite reasonable, but their value for B_1 - B_0 of - 518.3(8) MHz is in serious disagreement with the effective Y_{11} value of - 51 3.087(6) MHz in Table 2. Brault [10] has provided measurements of the $a \leftarrow X$ 1 ← 0 and 0 – 0 bands for $^{16}O_2$ as well as the 0 --0 bane] of $^{16}O^{18}O$. These measurements, whit.]1 were made at high resolution with the McMath-Pierce Fourier transform spectrometer at the National Solar Observatory, Kitt Peak, Arizona, are perfectly consistent with the data and parameters reported here. If the CARS spectra are fitted simultaneously with the $^{16}O_2$ $v = 0$ and $v = 1$ rotational spectra, there is a significant deterioration in the overall quality of the fit from that reported in Ref. 7. Moreover, the value of Y_{21} becomes approximately -4.3 MHz. 'J 'his is not on] y quite different from

6

that in Ref. 6, but it seems too large in magnitude. The Ref. 7 value of Y_{21} is not much different from what one might estimate from a Morse potential with the reported $\omega_e x_e$. The discrepancy between this work and the CARS data disappears if one assumes that the calibration of the CARS spectra was in error. This would leave the reported value of Y_{21} essentially unchanged within its uncertainty. Irrespective of the source of discrepancy between the CARS and the present value of $B_1 - B_0$, there seems to be no doubt from the CARS data that Y_{21} is negative.

'Table 3 contains the **derived** constants r_e^{BO} and d. These are reported both for $Y_{21} = 0$ and for Y_{21} as given in Ref. 7. The derivatives with respect to Y_{21} are also shown. The uncertainties of the $Y_{21} = 0$ parameters reflect only the uncertainties of the effective parameters in 'Table 2. The uncertainties of the parameters derived with the literature value of Y_{21} include the reported uncertainty of the CARS determination. Derived rotational constants for the ground and first excited states of all three species are also listed as are the Y_{01}'s. Effective r_e's have been calculated from the Y_{01}'s using the relationship

$$Y_{01} = \frac{h}{8\pi^2 \mu r_e^2} \tag{lo}$$

These are also shown in Table 3.

As expected, the major contribution to d_0 is from the term related to the rotational g factor shown in Eq. 9. Using Miller's [13] value of $-0.2266(22)$ for g_r in Eq. 9, one obtains $d_O^n = -0.900(9)$. Miller reports g_r in Bohr magnetons with two standard errors. Here g_r is stated in nuclear magnetons

7

with one standard error. Both d_O and d_O^n are almost the same as Tiemann [4] determined for the $X^3\Sigma_g^-$ state. Tiemann's conclusion that the adiabatic correction is small compared to the non-adiabatic one is equally applicable to the $a^1\Delta_g$ state. Arrington, et al., [14] have also determined g_r for a' Δ_g oxygen and report a values of - 0.313 nuclear magnetons. Although they were unable to identify the source of the discrepancy with Miller's work, it is clear that the magnitude of their g_r is too great to be consistent with the d_O determined here or with any d_O's derived with Y_{21}'s that are within the limits imposed by the CARS data. The results obtained here are, however in agreement with Miller's finding that g_r was very close to that of the $X^3\Sigma_g^-$ State.

Finally, the precision to which r_e^{BO} can be determined is comparable to that of the fundamental constants relating it to the rotational constant. For $Y_{21} = 0$, $r_e^{BO} = 1.21\ 557202(25)$ Å where the uncertainty reflects only the experimental uncertainty in B_e^{BO}. The uncertainties in $B \times I$ and the atomic masses have been ignored as have possible higher order contributions to the molecular parameters. The actual uncertainty in r_e^{BO} is primarily due to the uncertainty in Y_{21} with $\partial r_e^{BO}/\partial Y_{21} = -6.9 \times 10^{-6}$ Å/MHz. If the CARS determination of Y_{21} is accurate to its quoted uncertainty, then $r_e^{BO} = 1.2155f3]\ 3(12)$ Å. Table 3 shows that r_e for $^{16}O_2$ determined in the usual way from Y_{01} is about 8×10^5 Å longer than r_e^{BO} and that there is a shortening of r_e of $\approx 4.6 \times 10^{-6}$ Å for each ^{18}O substitution. Most of this

8

apparent shortening with isotopic substitution is due to the contribution of g_r to d_0. Less than 10% of the effect is due to the combination of the Dunham and adiabatic corrections.

CONCLUSIONS

Measurements of the rotational spectra of $a^1 \Delta_g$ oxygen in its first excited vibrational state along with ground vibrational state measurements of the two ^{18}O substituted species have provided precise values for the rotational and centrifugal distortion constants. Using the formalism developed by Watson, an accurate value has been determined for the interatomic distance in the Born-Oppenheimer limit. The derived molecular parameters have been compared with those obtained from CARS studies and with those expected from previous determinations of the rotational g factor. It is pleasing to show that the Watson description of the isotopic dependence of Y_{01} works well for the excited delta state of O_2.

ACKNOWLEDGMENTS

REFERENCES

[1.] J. K. G. Watson, J. Mol. Spectrosc., 45 *(1977)* 99.

[2.] J. K. G. Watson, J. Mol. Spectrosc., 80 (1980) 411.

[3.] K. W. Hillig II, C. C. W. Chiu, W. G. Read, and E. A. Cohen, J. Mol. Spectrosc., 109 (1 985) 205.

[4.] E. Tiemann, J. Mol. Spectrosc., 90 (1982) 60.

[5.] Y. Endo and E. Hirota, J. Chem. Phys., 86 (1987) 4319.

[6.] M. Birk, R. R. Friedl, E. A, Cohen, S. P. Sander, and H. M. Pickett, J. Chem. Phys., 91 (1989) 6588.

[7.] J.-C. Nieh and J. J. Valentini, J. Phys. Chem., 91 (1987) 1370.

[8.] C. H. Townes and A. 1,. Schawlow, Microwave Spectroscopy, McGraw Hill Book Company, Inc., New York, 1955, pp 9-14.

[9.] H. M. Pickett, J. Mol. Spectrosc., 148 (1991) 371.

[10.] J. W. Brault, personal communication.

[11.] E. R. Cohen and B. N. Taylor, Rev. Mod. Phys., 57 (1987) 1121.

[12.] G. Audi and A. H. Wapstra, Nut]. Phys. A, 565 (1993) 1.

[13.] T. A. Miller, *J. Chem. Phys 54, 330336* (1971).

[14.] C. A. Arrington, Jr., A. M. Falick, and R. J. Myers, J. Chem. Phys., 55 (1971) 909.

Table 1. Fitted Transitions for $a\,^1\Delta_g\,O_2$.

$J' - J''$	Frequency(unc.)/MHz	O.-C.
	$^{16}O_2\ v = 0$	
3 ---2	255017.937(30)	-0.006
4 --3	*340006.779(20)*	*-0.013*
5 - - 4	424980.983(20)	0.020
6 — 5	509936.752(20)	--0.015
7 --6	594870.607(40)	0.035
8 -- 7	679778.668(40)	0.038
9 - 8	764657.384(40)	-0.018
10- 9	849502.992(40)	-0.008
	$^{16}O_2\ v = 1$	
3 - 2	251939.375(30)	-0.006
4 --3	335901 .979(30)	0.009
5 -- 4	419849.813(30)	-0.004
	$^{16}O^{18}O\ v = 0$	
3 - 2	240862.786(30)	-0.008
4 --3	321135.098(30)	-0.019
	$^{18}O_2\ v = 0$	
3 --2	226703.708(20)	0.005
4 --3	302258.092(20)	0.015
5—4	377800.850(20)	-0.010

Table 2. Molecular Parameters for Fitting the Spectra.[a]

Effective Parameter	'Value/h411z	Reduced Mass Dependence	$\partial/\partial Y_{21}$
B_e^{BO}	42766.5220(172)	- 1	0.4854
$Y_{11} \approx \alpha_e$	--513 .0870(64)	- 1.5	--2.0000
$Y_{02} \approx - D_e$	- 0.152616(92)	- 2	
$Y_{12} \approx \beta_e$	–0.000660(175)	- 2.5	
$2m_e d_O B_e^{BO}/\mu$	5.4586(184)	- 2	-0.2646
$Y_{03} \approx H_e$ (fixed)	--0.637 x 10-"[7]	- 3	
9	--0.4 9(51) x_1 0 -[5] - 4		

a. Numbers in parentheses arc approximately one standard error.

<div align="center">Table 3. Derived Molecular Parameters.[a,b]</div>

Parameter	$^{16}O_2$	$^{16}O^{18}O$	1802	$\partial/\partial Y_{21}$ [c]
		$Y_{21} = 0$		
$r_c^{BO}/\text{Å}$		$1.21\,557202(25)^d$		$-6.9 \times 10\text{-G}$
d_O		$0.9372\,(33)^d$		-0.0454
Y_{01}/MHz	42761.0634(42)'	40380 .582.4	38000,0676	0.75
$r_e/\text{Å}$	1.21564960(6)	1.21564527	1.21564093	$-.1_c] \times 10^{-5}$
B_0/MHz	42504.5199(23)	40145.1629	37785.1581	
B_1/MHz	**41991.4329(64)**	**39674.3238**	**37355.3392**	
D_0/MHz	**0.152946(21)**	0,136381	0.120766	
D_1/MHz	**0.153606(174)**	0.136953	0.121258	
		$Y_{21} = -1.35(17)$ MHz^f		
$r_e^{BO}/\text{Å}$		$1.21558133(120)^d$		
d_O		$0.9985(84)^d$		
Y_{01}/MHz	42760.0508(1300)	40379.6450	37999.2031	
$r_e/\text{Å}$	1.21 566400(200)	1,21565938	1,21565476	

a. $B \times I = 505379.07$ MHz·amu·Å^2, Ref. 11.
b. $M(^{16}O) = 15.9949146223$ amu, $M(^{18}O) = 17.9991604$ amu, Ref. 12.
c. For $^{16}O_2$ only with Y_{21} in MHz.
d. Isotope independent.
e. The uncertainties are approximately the same for all isotopes and entirely correlated.
f. From Ref. 7.