

Reinvestigation of the second negative ($A^2\Pi_u - X^2\Pi_g$) band system of O_2^+

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Abstract. The $A^2\Pi_u$ state of O_2^+ was earlier established as an inverted state contrary to previous assumptions. The rotational analysis of a few more bands of the $A-X$ system of O_2^+ has now been completed. These studies show that the spin-orbit coupling constant A in the $A^2\Pi_u$ state gradually varies with the vibrational quantum number v and is found to be positive for $v \geq 6$. It has also been observed that the spin-rotation interaction is not negligible in the $A^2\Pi_u$ state. The spin splitting constant γ is reported for various vibrational levels of this electronic state.

Keywords. O_2^+ ; rotational analysis; spin-orbit coupling constant.

1. Introduction

The second negative bands of O_2^+ involve the transition $A^2\Pi_u - X^2\Pi_g$. Stevens (1931) first analysed the rotational structure of these bands and showed that the $A^2\Pi_u$ state was regular with $A = +8.2 \text{ cm}^{-1}$. His conclusion was based on the identifications of first lines in the 0-8 and 1-7 bands. Later Bozoky (1937) analysed several other bands of this system but did not report any value for the spin-orbit or the spin-rotation coupling constant.

A close look at the intensities of rotational lines, especially those involving low J values, however, does not seem to favour a regular $A^2\Pi_u$ state. At low values of J , the rotational lines involving $F_1 \leftrightarrow F_2$ transitions (*i.e.*, $^5R_{21}$, $^6P_{21}$, $^6R_{12}$, $^6P_{12}$ branches) are more intense than the lines involving either $F_1 \leftrightarrow F_1$ or $F_2 \leftrightarrow F_2$ transitions (*i.e.*, R_1 , P_1 , R_2 and P_2 branches). Since the lower state $X^2\Pi_g$ is known to be a regular state ($A = 195 \text{ cm}^{-1}$), the observed intensity pattern can be explained only in terms of an inverted $A^2\Pi_u$ state. Similar considerations led Merer *et al* (1966) to establish the nature of the $A^2\Delta$ state of CCl .

2. Experimental techniques

For these studies the 1-7 and 0-8 bands (lying at 3492.9 \AA and 3829.5 \AA respectively) were chosen because they suffer from a minimum overlap from neighbouring bands. These were photographed in the third order of a 3.4 meter Ebert grating spectrograph at an inverse dispersion of 0.55 \AA/mm . Exposures of 30-40 minutes were required on Kodak SA-1 plates. O_2^+ spectrum was excited in oxygen at a pressure of 0.1 torr by microwaves of 2450 MHz. Thorium atomic lines were used as the reference spectrum. The plates were measured on a photoelectric comparator. Other bands of this system whose rotational analysis was done are

5-3, 6-3, 7-2 and 8-2. Out of these, the 5-3 and 6-3 bands were photographed in the fourth order while the 7-2 and 8-2 bands were recorded in the second order.

3. Analysis and discussion

3.1. Determination of A

The rotational constants B_v and D_v were obtained by the usual graphical methods. In the present section the determination of the spin-orbit coupling constant is discussed.

The rotational terms of the ${}^2\Pi$ state are given by the well-known formula of Hill and Van Vleck (1928)

$$F_1(J) = B_v [(J + \frac{1}{2})^2 - 1 - \frac{1}{2} \sqrt{Y(Y-4) + 4(J + \frac{1}{2})^2}] - D_v J^4 \quad (1)$$

$$F_2(J) = B_v [(J + \frac{1}{2})^2 - 1 + \frac{1}{2} \sqrt{Y(Y-4) + 4(J + \frac{1}{2})^2}] - D_v (J + 1)^4 \quad (2)$$

where $Y = A/B_v$. A plot of $\left\{ \frac{F_1(J) - F_2(J)}{B_v} \right\}^2$ against $(J + 1/2)^2$ gives a straight line whose intercept on the ordinate is equal to $Y(Y-4)$. The solution of the quadratic equation in Y gives two values for Y , symmetric about $Y = 2$, and from the experimental evidence it is decided which of these is correct. For this purpose, position of the level $J = 1/2$ offers the clue. This is the only J level which is single, other J levels occur in pairs, one of them going with the F_1 and the other with the F_2 series of rotational terms. It can be seen from Herzberg (1950) that if $Y > 2$, the $J' = 1/2$ level goes with the F_1 series, and if $Y < 2$, the $J' = 1/2$ level goes with the F_2 series. In the present case, depending upon the position of the $J = 1/2$ level, following first lines result in the P branches: for $Y > 2$, these are $P_1(1.5)$, ${}^oP_{12}(1.5)$, ${}^qP_{21}(2.5)$ and $P_2(2.5)$; and for $Y < 2$, these are $P_1(2.5)$, ${}^oP_{12}(2.5)$, ${}^qP_{21}(1.5)$ and $P_2(1.5)$.

3.2. Identification of the first lines

Stevens (1931) noted that the spin-orbit coupling constant for the $v = 0$ and 1 levels of the $A^2\Pi_u$ state could be either $+8.2$ or -4.0 cm^{-1} . To support his choice for $A' = +8.2 \text{ cm}^{-1}$, he cited the identification of $P_1(1.5)$ in the 0-8 and 1-8 bands, the identification of ${}^oP_{12}(1.5)$ in the 1-8 band and definite absence of $P_2(1.5)$ in the 1-7 band.

The first few members of the main branches P_1 and P_2 are weak even on overexposed plate the lines below $P_1(4.5)$ and $P_2(4.5)$ are not observed. Hence it is not possible to make any positive comment on Stevens' observation, as his conclusion is mostly based on the presence or absence of the low J members of P_1 and P_2 branches. However, we find that the satellite branches ${}^qP_{21}$ and ${}^oP_{12}$ are fairly intense even at very low J values. In figure 1, which shows the $\Pi_{1/2}$ sub-band of the 1-7 band, the lines of the ${}^qP_{21}$ branch are identified right up to the first member ${}^qP_{21}(1.5)$, marked with an arrow. The unambiguous identification of the ${}^qP_{21}(1.5)$ in the present case, as well as in case of the 0-8 band (Bhale 1972), clearly shows that the $J = 1/2$ level goes to the F_2 series in the upper state which, therefore, is an inverted state.

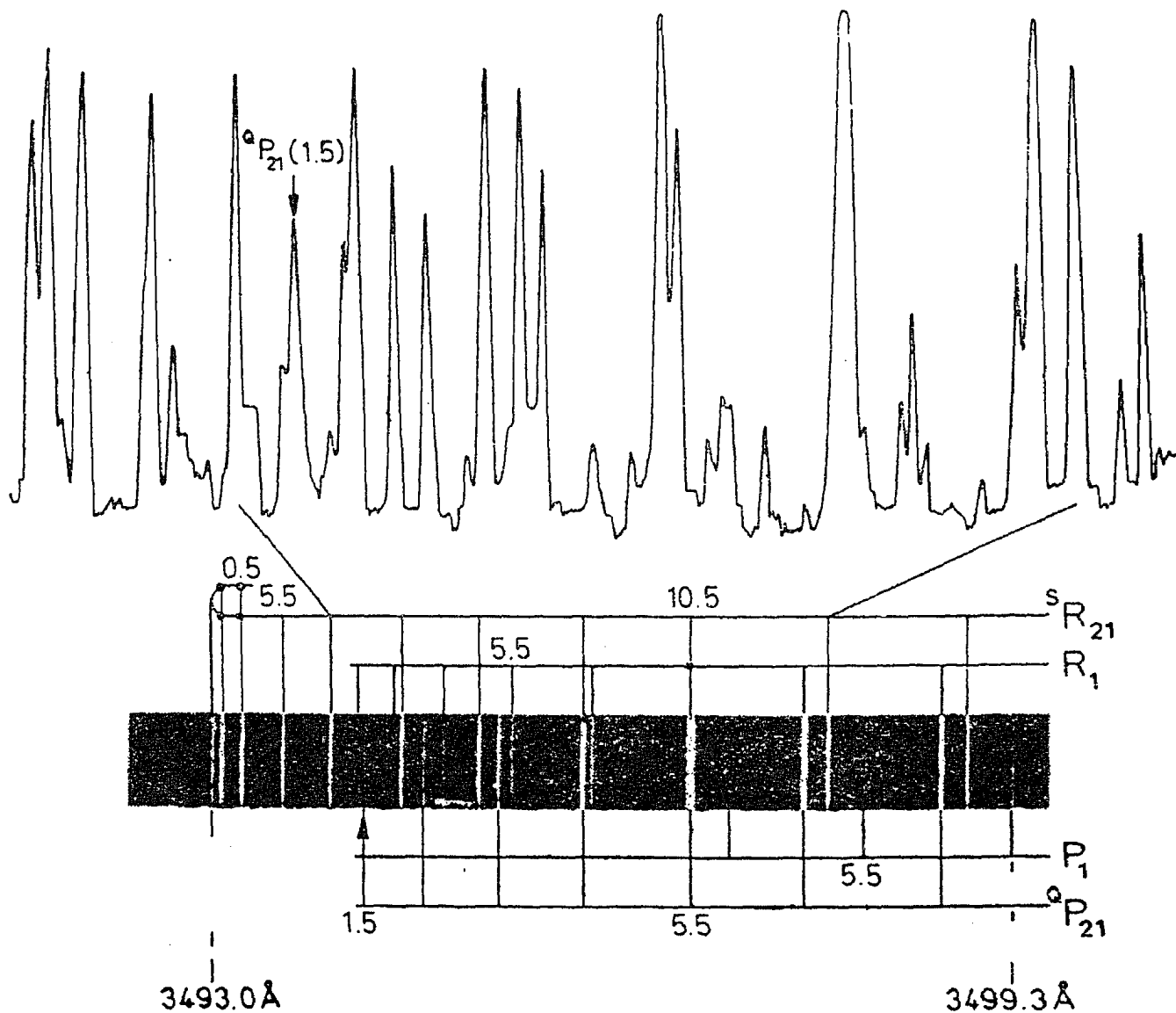


Figure 1. $A^2\Pi_u - X^2\Pi_{\frac{1}{2}g}$ sub-band of the 1-7 band of O_2^+ .

3.3. Intensity distribution in various branches

The second factor favouring the above interpretation is the intensity pattern of the rotational lines. Figure 1 shows that the rotational lines of the $^S R_{21}$ and $^Q P_{21}$ branches involving $J'' = 4.5, 5.5, 6.5$, etc., are more intense than the corresponding R_1 and P_1 lines. Similarly in the $\Pi_{3/2}$ sub-band, which is not shown in figure 1, the $^Q R_{12}$ and $^O P_{12}$ lines of low J values are more intense than the R_2 and P_2 lines. The former involve $F_1 \leftrightarrow F_2$ whereas the latter $F_1 \leftrightarrow F_1$, or $F_2 \leftrightarrow F_2$ transitions. These intensities can be qualitatively explained using the arguments of Merer *et al* (1966) according to which

if branches involving $F_1 \leftrightarrow F_2$ }
 transitions are more intense at } either $Y' < 2$ and $Y'' > 2$
 low values of J } or $Y' > 2$ and $Y'' < 2$

and

if branches involving $F_1 \leftrightarrow F_1$ }
 and $F_2 \leftrightarrow F_2$ transitions are } either $Y' > 2$ and $Y'' > 2$
 more intense at low values of J } or $Y' < 2$ and $Y'' < 2$

In case of the second negative bands of O_2^+ , the former situation holds and hence Y' will be less than Z , since it is well established that $Y'' > 2$ ($A'' \approx 195 \text{ cm}^{-1}$).

3.4. Quantitative studies of the intensity distribution

As a further confirmation of the inverted nature of the $A^2\Pi_u$ state a quantitative estimation of the intensities was carried out. For this purpose, after photographing the O_2^+ bands, an Fe arc spectrum was recorded through a 2 : 1 rotating step sector kept in front of the slit of the spectrograph. From this the plate emulsion was calibrated. The densities of various rotational lines were read on a microphotometer and following the procedure of respectra (Anderson 1956), intensity ratios between different pairs of lines were obtained.

The experimentally observed intensity ratios were compared with the theoretically calculated ones, the latter having been obtained using the two alternate values of Y in question. The results of these studies are depicted in figure 2 where it is clearly seen that the observed intensities are explained only if the $A^2\Pi_u$ state is taken to be inverted. Theoretical intensity ratios shown in figure 2 are the ratios of the line strengths computed from Kovacs' intensity formulae (Kovacs 1969).

3.5. Determination of A and γ for different vibrational levels

Having established that the spin-orbit coupling constant is negative for the $v = 0$ and 1 levels of the $A^2\Pi_u$ state, its value was calculated for other vibrational levels too. The graphical method described in the previous section for the determination of A could not be used successfully for the vibrational levels 5, 6, 7 and 8 for the following reason. Because of the low values of A_v involved, the inter-

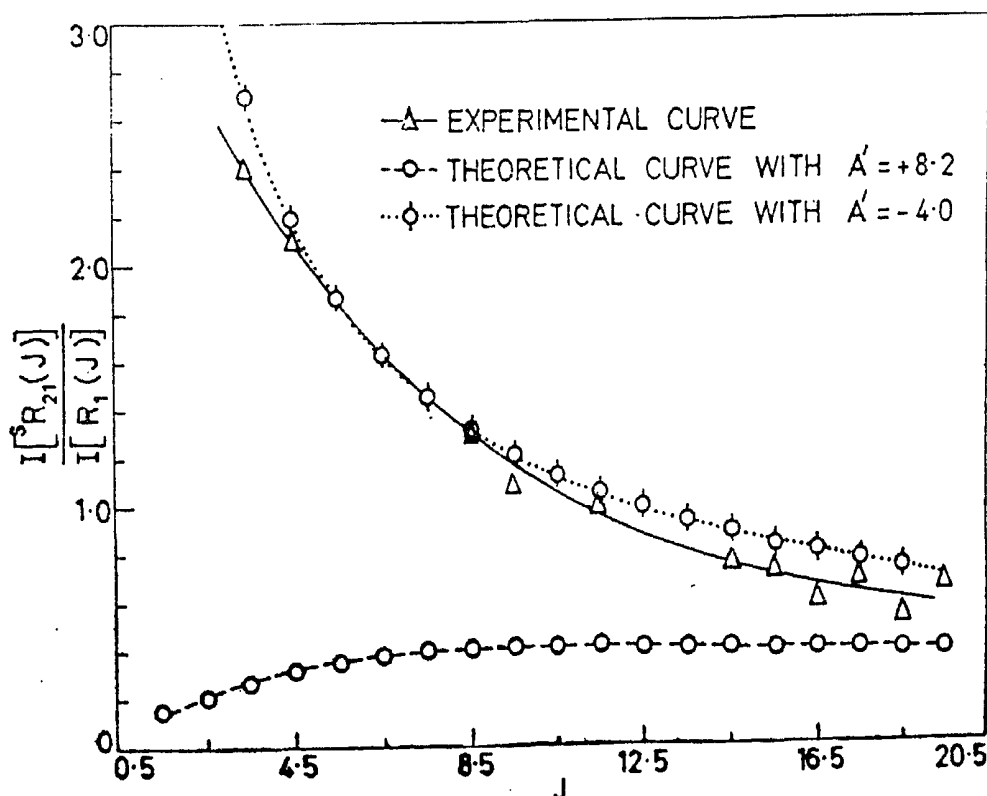


Figure 2. [Intensity of ${}^S R_{21}(J)$]/Intensity of $R_1(J)$ in the 0-8 band of the $A^2\Pi_u - X^2\Pi_g$ band system of O_2^+ .

ception the ordinate, which gives $A_v(A_v - 4B_v)$ is usually too small to be read accurately. A small error in its reading causes a large swing in the value of A_v . In fact for $v = 6$, it is difficult to decide whether the intercept is positive or negative, and so the sign of A_v itself remains uncertain. Hence the expressions of Hill and Van Vleck's (1928) written in the case (b) approximation were used. These are:

$$F_1(N) = B_v \left[N(N+1) - 1 + \frac{Y(Y-4)}{8(N+1)} + \dots \right] + \frac{1}{2} \gamma N, \quad (3)$$

$$F_2(N) = B_v \left[N(N+1) - 1 - \frac{Y(Y-4)}{8N} + \dots \right] - \frac{1}{2} \gamma (N+1) \quad (4)$$

In the above expressions the terms in D_v have been neglected. Additional terms $\frac{1}{2} \gamma N$ and $\frac{1}{2} \gamma (N+1)$ take into account the magnetic interaction of \vec{N} and \vec{S} (Mulliken 1930).

Subtracting (3) from (4) we get

$$F_2(N) - F_1(N) = \frac{B_v Y(Y-4)}{4} \frac{(N + \frac{1}{2})}{N(N+1)} - \gamma (N + \frac{1}{2}) \quad (5)$$

γ is usually quite small, and hence the splitting of N doublets is predominantly due to the term in Y , except for large values of N . However, for values of Y near 0 or 4, it is the term in γ which predominates. A graph between $[F_2(N) - F_1(N)] / [(N + \frac{1}{2})]$ against $1/[N(N+1)]$ would be a straight line with slope $[B_v Y(Y-4)]/4$ and its intercept on the ordinate the spin-splitting constant γ . The quantity $F_2(N) - F_1(N)$ was obtained for the vibrational levels $v = 0, 1, 5, 6, 7$ and 8 and from this A_v and γ were obtained using the relation (5).

3.6. Calculation of $F_2(N) - F_1(N)$

Since the second negative bands involve the transition $A^2\Pi_u - X^2\Pi_g$, the Q branches which are expected to be very weak are not observed and as such, a direct determination of $F_2(N) - F_1(N)$ cannot be made. For getting these differences, a procedure first adopted by Stevens (1931) has been followed which, with slight modifications, is given below:

It is clear from eq. (5) that if the contribution due to the term in γ is small,

$$F_2(N) - F_1(N) \text{ is positive if } 0 > Y > 4$$

and

$$F_2(N) - F_1(N) \text{ is negative if } 0 < Y < 4$$

so that $F_2(N)$ lies above $F_1(N)$ if Y is less than zero or greater than 4, whereas $F_2(N)$ lies below $F_1(N)$ if Y is between 0 and 4 (Herzberg 1950). The two possibilities are shown in figure 3.

In order to calculate $|F_2(N) - F_1(N)|$, which we will designate by ϵ_N , the following procedure is adopted:

- (i) The $F_2(J) - F_1(J)$ differences for the upper state are calculated. These are obtained from the combination relations,

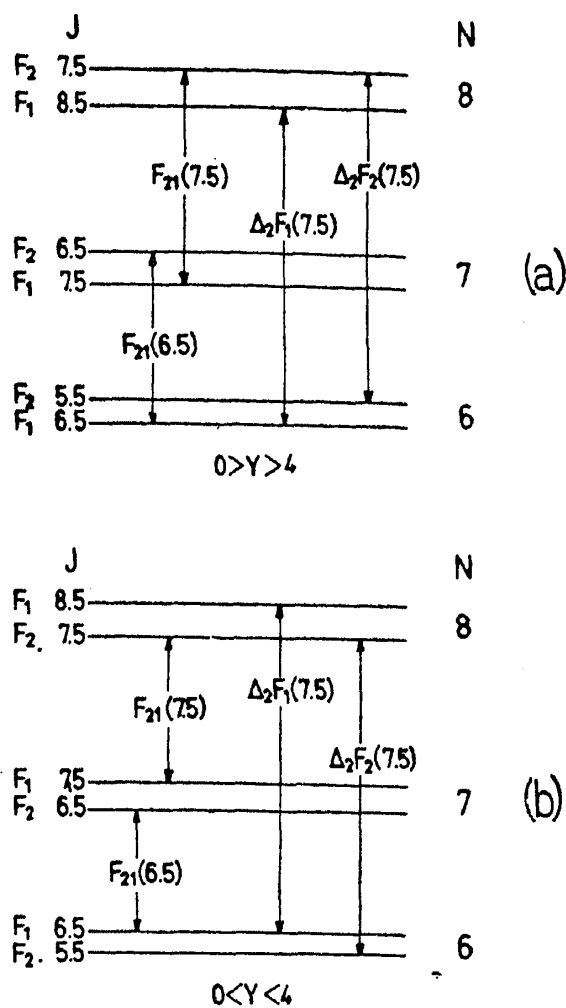


Figure 3. Calculation of $F_2(N) - F_1(N)$ in the $A^2\Pi_u$ state of O_2^+ .

$$\begin{aligned}
 F_{21}(J) &= F_2(J) - F_1(J) = {}^S R_{21}(J-1) - R_1(J-1) \\
 &= R_2(J-1) - {}^Q R_{12}(J-1) = {}^Q P_{21}(J+1) - P_1(J+1) \\
 &= P_2(J+1) - {}^O P_{12}(J+1).
 \end{aligned}$$

(ii) $\Delta_2 F_1(J)$ and $\Delta_2 F_2(J)$ for the upper state are calculated from the usual combination relations, e.g.,

$$\Delta_2 F_1(J) = R_1(J) - P_1(J) = {}^Q R_{12}(J) - {}^O P_{12}(J)$$

and

$$\Delta_2 F_2(J) = {}^S R_{21}(J) - {}^Q P_{21}(J) = R_2(J) - P_2(J).$$

It can be verified from figure 3 (a) that

$$F_{21}(J) + F_{21}(J+1) = \Delta_2 F_1(J+1) + \epsilon_{N=J+1/2} + \epsilon_{N=J+3/2} \quad (6)$$

$$F_{21}(J) + F_{21}(J+1) = \Delta_2 F_2(J) + \epsilon_{N=J-1/2} + \epsilon_{N=J+1/2}. \quad (7)$$

Adding (6) and (7) we get

$$2\{F_{21}(J) + F_{21}(J+1)\} = \Delta_2 F_1(J+1) + \Delta_2 F_2(J) + 4\epsilon_{N=J+1/2}. \quad (8)$$

In writing the above expression, it has been assumed that ϵ_N is a slowly varying function of N , so that to a first approximation

$$\epsilon_{N-1} + \epsilon_{N+1} = 2\epsilon_N.$$

ϵ_N values are calculated using the relation (8). Figure 3 (b) depicts the case when Y lies between 0 and 4. Calculation of ϵ_N still remains the same, but for the difference that in eqs (6) and (7) the terms of ϵ_N now carry a negative sign. Following this procedure the N -doublet separation ϵ_N has been calculated for the vibrational levels $v = 0, 1, 5, 6, 7$ and 8 . A plot of $\epsilon_N/(N + 1/2)$ vs $1/N(N + 1)$ was used to get the values of A_v and γ for various vibrational levels [see eq. (5)]. The slopes obtained for the vibrational levels $v = 5$ and 6 were 1.6 cm^{-1} and 0.3 cm^{-1} respectively; these values excluded the possibility of A_v being positive for $v = 5$ and negative for $v = 6$.

4. Conclusions

Thus we found A_v to be negative for $v = 0, 1$ and 5 and positive for $v = 6, 7$ and 8 . The same conclusion was also drawn by Albritton *et al* (1973) but their values of A_v for $v = 5, 6, 7$ and 8 are slightly different from the present values, as can be seen from table 2. This could possibly be due to the omission of the constant γ , which is observed to assume significant values for higher v values. The agreement between the observed and the calculated N -doublet splittings using the present A_v and γ values is quite good as can be seen from table 1. The N -doublet splittings for various vibrational levels are shown graphically in figure 4.

A comparative study can be made with the constants obtained from the present analysis and those reported by Bozoky (1937) and Albritton *et al* (1973). It can be seen from table 2 that the constant obtained from the analysis of the 0-8 and 1-7 bands shows good agreement. However, present B_v' values for the vibrational levels 5, 6, 7 and 8 show a systematic variation when compared with the values of Albritton *et al*. Their values seem to be consistently low as compared

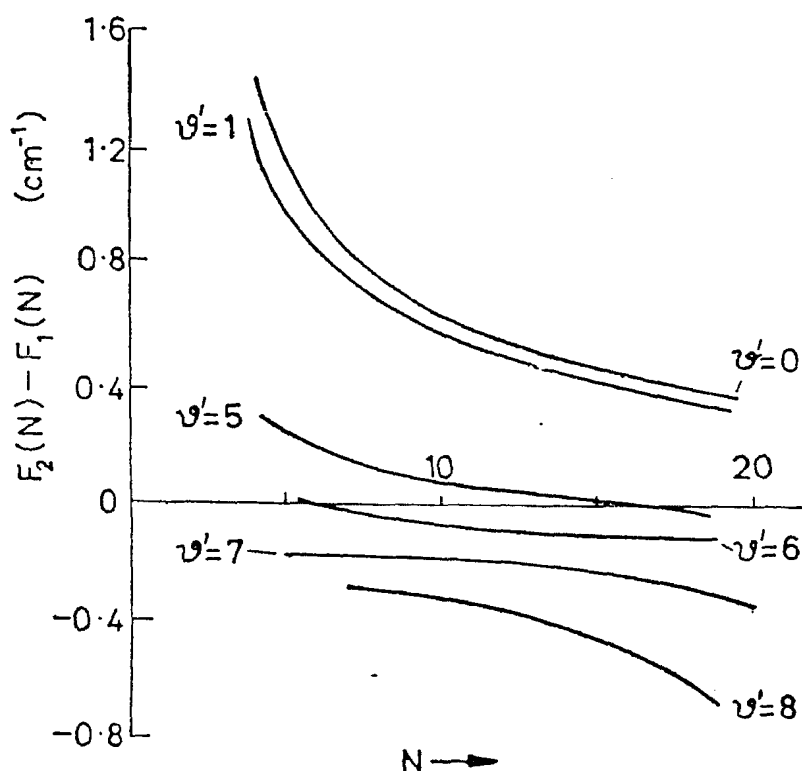


Figure 4. $F_2(N) - F_1(N)$ vs. N for various vibrational levels of the $A^2 \Pi_u$ state.

Table 1. N -doublet splittings $F_2(N) - F_1(N)$, expressed in cm^{-1} , in the vibrational levels of the $A^2\Pi_u$ state

N	$v' = 0$		$v' = 1$		$v' = 5$		$v' = 6$		$v' = 7$		$v' = 8$	
	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.
4	1.417	1.401	1.210	1.203	0.302	0.332						
5	1.142	1.148	0.995	0.988	0.196	0.359			-0.192	-0.186		
6	0.956	0.977	0.850	0.844	0.164	0.207	-0.031	-0.081	-0.185	-0.183		
7	0.847	0.851	0.716	0.737	0.133	0.168	-0.008	-0.087	-0.182	-0.185	-0.307	-0.300
8	0.749	0.756	0.662	0.658	0.077	0.136	-0.012	-0.091	-0.145	-0.188	-0.235	-0.314
9	0.701	0.686	0.591	0.600	0.086	0.110	-0.097	-0.083	-0.230	-0.196	-0.347	-0.329
10	0.635	0.623	0.554	0.548	0.092	0.089	-0.078	-0.085	-0.187	-0.203	-0.350	-0.348
11	0.592	0.576	0.595	0.509	0.061	0.068	-0.070	-0.088	-0.175	-0.212	-0.353	-0.367
12	0.542	0.542	0.481	0.482	0.056	0.106	-0.084	-0.092	-0.210	-0.222	-0.357	-0.389
13	0.500	0.502	0.481	0.449	0.040	0.034	-0.122	-0.095	-0.347	-0.231	-0.317	-0.408
14	0.472	0.477	0.411	0.429	0.008	0.021	-0.098	-0.099	-0.222	-0.243	-0.430	-0.429
15	0.452	0.452	0.399	0.410	-0.004	0.007	-0.098	-0.104	-0.225	-0.254	-0.410	-0.453
16	0.419	0.431	0.438	0.393	-0.012	-0.005	-0.132	-0.107	-0.210	-0.266	-0.630	-0.475
17	0.402	0.414	0.382	0.381	0.000	-0.017	-0.111	-0.112	-0.260	-0.278	-0.745	-0.498
18	0.404	0.403	0.349	0.373	-0.015	-0.026	-0.115	-0.116	-0.285	-0.290	-0.830	-0.522
19	0.367	0.389	0.320	0.363	-0.050	-0.037	-0.128	-0.121	-0.352	-0.303	-0.745	-0.546
20	0.356	0.372							-0.342	-0.315	-0.665	-0.569
21									-0.365	-0.328	-0.900	-0.596
22									-0.365	-0.339	-0.800	-0.619

Table 2. Molecular constants (in cm^{-1}) of the $A^2\Pi_u$ and $X^2\Pi_g$ states of O_2^+

Vibrational level	B_v		$D_v \times 10^{-6}$			A_v		$\gamma \times 10^{-3}$		
	Present	Albritton <i>et al</i> (1973)	Bozoky (1937)	Present	Albritton <i>et al</i> *	Bozoky	Present		Albritton <i>et al</i>	Stevens (1931)
$A^2\Pi_u$ state:										
0	1.0525	1.0520	1.0522	6.5	5.97		-3.5	-3.7		-4.0
1	1.0330	1.0323	1.0328	6.8	6.06		-3.1	-3.1		-5.0
5	0.9517	0.9496	0.9513	7.5	6.16	$D' = 6.5-6.6$	-1.21	-0.95	$A' = 8.2$	6.0
6	0.9300	0.9289	0.9300	7.8	6.29		0.33	0.45		5.5
7	0.9095	0.9073	0.9082	8.4	6.44		0.77	1.12		14.0
8	0.8865	0.8823	0.8862	8.4	6.6		1.22	2.0		26.0
$X^2\Pi_g$ state:										
2	1.6413	1.6407	1.6425	5.0	5.40		199.2	198.12		
3	1.6222	1.6217	1.6227	5.9	5.43	$D'' = 6.8-6.9$	198.6	197.77	$A'' = 195$	
7	1.5440	1.5438	1.5432	6.5	5.59		195.4	194.84		
8	1.5237	1.5241	1.5234	6.4	5.63		194.4	193.88		

* These D_v values are theoretically computed.

to ours and the disagreement increases with the increase in the vibrational quanta. A possible explanation for this could be the fact that Albritton *et al* have kept values of D' , and D'' , fixed in the final calculations. Values for these were computed earlier from the RKR potential energy curves of the $A^2\Pi_u$ and $X^2\Pi_u$ states, which were plotted using the preliminary values of B_v and band origins. Values of D' , and D'' , so obtained were then kept fixed and the remaining constants were evaluated by the least-squares procedure. Now let us assume that the values of D' , and D'' , which were kept fixed in the final calculations, were slightly different from their actual values. It would naturally bring about a change in other constants and more so in the values of B'_v and B''_v , because of their strong correlation with D' , and D'' . It can be further noted that Bozoky's values of B'_v and B''_v are in good agreement with the present values, whereas those obtained by Albritton *et al*, while making use of Bozoky's data, show the disagreement. It appears, therefore, that the slight disagreement in the two sets of constants is due to the different methods of their evaluation. As mentioned earlier, the constants in the present analysis as well as in the case of Bozoky were obtained by the usual graphical techniques whereas Albritton *et al* obtained them from a least-squares fit.

As stated earlier, the disagreement in the A_v values reported in table 2 could be attributed to the fact that Albritton *et al* have neglected the spin-rotation interaction which according to them was found statistically insignificant. However, we find that almost for all the vibrational levels the graphs of $[F_2(N) - F_1(N + \frac{1}{2})]$ against $1/[N(N + 1)]$ have fairly high intercepts on the ordinate, showing thereby that the spin-rotation interaction is not negligible. It is found that the spin-rotation interaction increases with the increase in vibrational quanta.

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