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Rotational analysis of the 0–9, 0–10 and 0–11 bands of the $A^2\Pi_u$–$X^2\Pi_g$ band system of $(^{16}O\ ^{18}O)^+$

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Abstract. High-resolution spectra of the 0–9, 0–10 and 0–11 bands of the $A^2\Pi_u$—$X^2\Pi_g$ system of $(^{16}O\ ^{18}O)^+$ ion have been studied for their rotational structure. This study enables a direct determination of the Λ-doubling parameters of the $A^2\Pi_u$ and $X^2\Pi_g$ states. The model of 'pure precession' explains, though not entirely, the Λ-doubling of the $X^2\Pi_g$ state as arising out of its interaction with the $B^2\ \Sigma_g^-$ state. The Λ-doubling in the $A^2\Pi_u$ state was found insignificant.

Keywords. $(^{16}O^{18}O)^+$; rotational analysis; Λ-doubling.

1. Introduction

Rotational analysis of the 0–9, 0–10 and 0–11 bands of the $A^2\Pi_u$–$X^2\Pi_g$ system of $(^{16}O\ ^{18}O)^+$ is presented here. There is no earlier available report on the high resolution studies of $(^{16}O\ ^{18}O)^+$ spectra. The corresponding band system of $^{16}O_2^+$, called the second negative system, is known for a long time and has been extensively studied by Stevens (1931) and Bozoky (1937). Using their data Albritton *et al* (1973) carried out a least squares analysis to determine various molecular constants of O_2^+. They stated that the data of Stevens and Bozoky used by them in their computational work were not very accurate. It was partly for this reason that we carried out a reinvestigation of the second negative band system of O_2^+ (Bhale and Narasimham 1976) after photographing several of its bands under higher resolution. Subsequently, Colbourn and Douglas (1977) also reported the rotational analysis of a few more bands of $^{16}O_2^+$, particularly those involving the lower vibrational quanta of the $X^2\Pi_g$ state. These studies, however, do not give a direct information of the Λ-doublings involved in the two $^2\Pi$ states of the transition because of the following reasons. O_2^+ is a homonuclear molecule with a nuclear spin of zero for ^{16}O. This means that only the symmetric component of the Λ-doublet appears for each J value of the two states. Thus, for any rotational line only one of the two Λ-components is observed and this prevents a direct determination of Λ-doublings. Although Stevens (1931) did calculate the Λ-doubling constants in his work on the second negative bands of O_2^+, his procedure was rather involved. He estimated these constants from the amount of staggerings in the $\triangle_1 F_1(J)$ and $\triangle_1 F_2(J)$ values. These differences, however, cannot be obtained directly in a $^2\Pi$—$^2\Pi$ transition because of the absence of Q branches. It was, therefore, thought worthwhile to study the aspect of Λ-doubling in a direct manner from the $(^{16}O\ ^{18}O)^+$ spectra where both the Λ-components occur with equal intensity.

2. Experimental

While recording the emission spectrum of $(^{16}O\ ^{18}O)^+$, one also gets the spectra due to $^{16}O_2^+$ and $^{18}O_2^+$. A given band of $(^{16}O\ ^{18}O)^+$ is sandwitched between the corresponding $^{16}O_2^+$ and $^{18}O_2^+$ bands. In order to carry out a satisfactory rotational analysis of a $(^{16}O\ ^{18}O)^+$ band, it has to be seen that the band of interest is not very much masked by either $^{16}O_2^+$ or $^{18}O_2^+$ band. To achieve this objective, it is necessary to choose bands having large isotope shifts. Because of the appreciable difference in the ω_e value of the $A^2\Pi_u$ and $X^2\Pi_g$ states, the bands of $v' = 0$ progression involving high v'' quantum numbers are observed to have considerable isotope shifts. Accordingly, the 0–9, 0–10 and 0–11 bands, lying at 4013·6 Å, 4278·7 Å and 4574·0 Å respectively, were chosen for the present studies. Isotope shift studies of these bands were reported earlier (Bhale and Rao 1968). The bands were photographed in the third order of a 3·4 m Ebert grating spectrograph at a dispersion of 0·5 Å/mm. The spectra were excited by microwaves of 2450 MHz at oxygen pressure of 0·1 torr. Spec-pure oxygen used for the experiment was enriched with 65% ^{18}O isotope. Exposures ranging from 1 to 3 hr were required on the 103 a-0 photographic emulsion. Atomic lines of thorium were used as the reference spectrum. Thorium spectrum was excited in an electrodeless discharge tube containing thorium iodide by microwaves of 2450 MHz. The plates were measured on a Zeiss Abbe comparator. Figure 1 shows a portion of the $A^2\Pi_u - X^2\Pi_{\frac{1}{2}g}$ transition of the 0–11 band.

3. Analysis and discussion

3.1. *Determination of B_v, D_v, and A_v*

The rotational constants B_v and D_v were determined graphically from the second combination difference using the relation

$$\triangle_2 F(J) = (4\,B_v - 6\,D_v)\,(J + \tfrac{1}{2}) - 8\,D_v\,(J + \tfrac{1}{2})^3$$

and the spin-orbit coupling constant was calculated from the graph of $[\{F_1(J) - F_2(J)\}/B_v]^2$ vs $(J+\frac{1}{2})^2$ in which the intercept on the ordinate gives $Y(Y-4)$ where $Y=A/B$. The lower state $X^2\Pi_g$ is known to be regular, as is also evident from the higher Λ-doubling seen in the higher frequency sub-band, and accordingly the positive value for A'' was chosen. For the $A^2\Pi_u$ state, which was established to be inverted (Bhale 1972), the negative value for the constant A' was taken.

3.2. *Isotopic calculations*

The theoretical relations between rotational constants for isotopically substituted molecules are related to the ratio of their reduced masses (Herzberg 1950). Let the reduced masses of $^{16}O_2$ and $(^{16}O\ ^{18}O)$ be designed by μ and μ^i respectively. Then from the ratio $\mu/\mu^i=\rho^2$, ρ can be found out, which in the present case is 0·971765. With the superscript i denoting the constants of $(^{16}O\ ^{18}O)^+$, the isotopic relations are

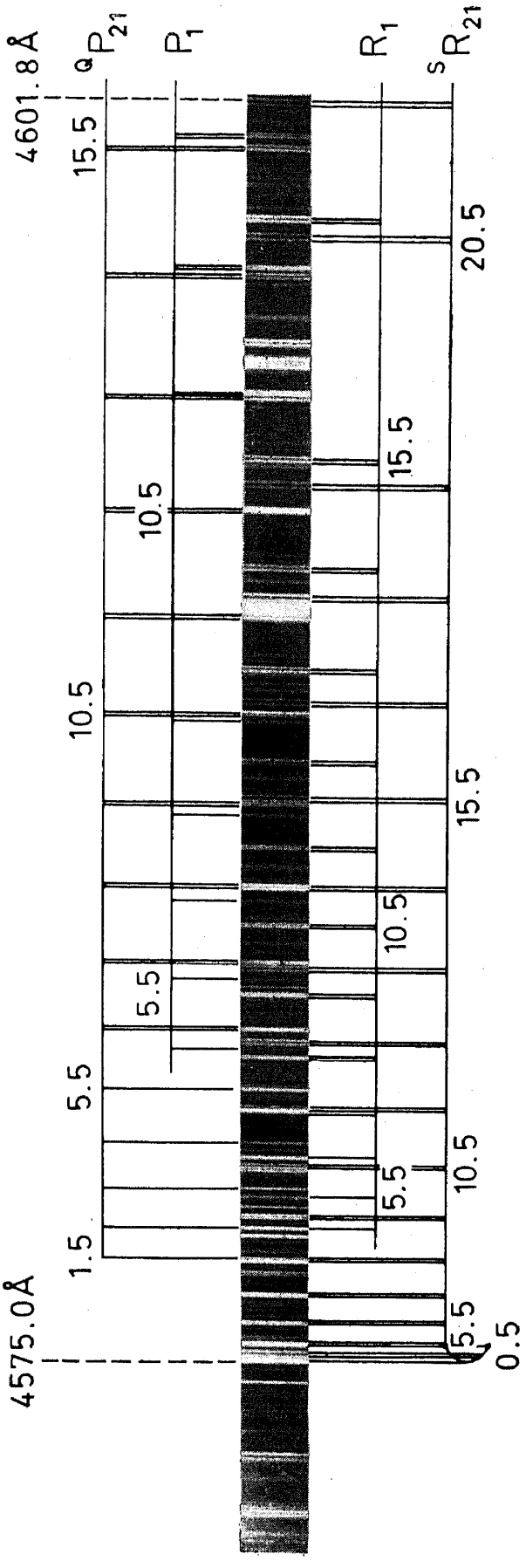

Figure 1. Part of the 0-11 band of the $A^2\Pi_u \rightarrow X^2\Pi_{(1/2)g}$ transition of $(^{16}O\ ^{18}O)^+$ ion

$$\left.\begin{aligned} B_e^{\,i} &= \rho^2\ B_e \\ \alpha_e^{\,i} &= \rho^3\ \alpha_e \end{aligned}\right\} \tag{1}$$

$$D_e^{\,i} = \rho^4\ D_e. \tag{2}$$

The constant B_e for O_2^+ was taken from Bhale and Rao (1968) while α_e and D_e were taken from Herzberg (1950) and inserting these in the above relations the constants $B_e^{\,i}$, $\alpha_e^{\,i}$ and $D_e^{\,i}$ were calculated. Now finally making use of the relation

$$B_v^{\,i} = B_e^{\,i} - \alpha_e^{\,i}\,(v + \tfrac{1}{2}) \tag{3}$$

the different values of $B_v^{\,i}$ were computed. These are compared in table 1 with the values of $B_v^{\,i}$ obtained by the present analysis where it can be seen that the agreement between the two sets is quite good. It is further noticed that the centrifugal distortion constant D does not vary appreciably for $v'' = 9$, 10 and 11. Its value has been compared with $D_e^{\,i}$ obtained from relation (2).

3.3 *Λ-doubling in the* $A^2\,\Pi_u$ *and* $X^2\,\Pi_g$ *states*

Thet heoretical expressions for the separation of the Λ-doublets for a regular $^2\Pi$ state approaching Hund's case (a) are given by Mulliken and Christy (1931) as

$$^2\Pi_{1/2} : \triangle\nu_{dc}\,(J) = -\,p\,(J + \tfrac{1}{2}) \tag{4}$$

and

$$^2\Pi_{3/2} : \triangle\nu_{dc}\,(J) = \left(-\frac{p}{Y^2} + \frac{2q}{Y}\right)\left(J - \frac{1}{2}\right)\left(J + \frac{1}{2}\right)\left(J + \frac{3}{2}\right) \tag{5}$$

where p and q are Λ-doubling constants. The separations of the Λ-components for various branches of the 0–9, 0–10, and 0–11 bands are shown in tables 2 and 3. Now confining only to the $\Pi_{1/2}$ sub-band it can be seen from table 2 that, within the experimental error, the separation between the two Λ-components of the $^SR_{21}$, $^QP_{21}$, R_1 and P_1 branch lines involving a common J'' is almost the same. This means that the upper state Λ-doubling is negligible and the observed Λ-splitting

Table 1. Molecular constants (in cm^{-1}) of the $A^2\Pi_u$ and $X^2\Pi_g$ State of $(^{16}O\ ^{18}O)^+$ obtained from the analysis of 0-9, 0-10 and 0-11 bands.

		B_v		$D_v \times 10^{-6}$		A_v
		Obsd	Calc	Obsd	Calc	
$A^2\,\Pi_u$ state:	0	0·9940	0·99383	5·6	5·79	−3·5
$X^2\,\Pi_g$ state:	9	1·4257	1·42489	5·8		193·9
	10	1·4067	1·40669	5·5	6·1	193·0
	11	1·3880	1·38849	5·4		191·9
		p=0·031		q=0·0024		

Table 2. Λ-doublet separation (in cm^{-1}) in the rotational lines of $A^2\Pi_u - X^2\Pi_{\frac{1}{2}g}$ components of the second negative bands of $(^{16}O\ ^{18}O)^+$ ion.

J	0-9 band				0-10 band				0-11 band			
	$^sR_{21}$	$^QP_{21}$	R_1	P_1	$^sR_{21}$	$^QP_{21}$	R_1	P_1	$^sR_{21}$	$^QP_{21}$	R_1	P_1
3·5	—	—	—	—	0·14	—	—	—	—	—	—	—
4·5	—	—	—	—	0·14	—	—	—	—	—	—	—
5·5	—	—	—	—	0·19	—	—	—	0·17	—	—	—
6·5	0·24	0·17	—	—	0·23	0·17	—	—	0·24	0·17	—	—
7·5	0·24	0·27	—	—	0·26	0·23	—	—	0·26	0·21	—	—
8·5	0·26	0·24	0·22	0·19	0·28	0·28	0·29	0·20	0·34	0·19	0·16	—
9·5	0·32	0·31	0·22	0·25	0·29	0·31	0·29	0·28	0·31	0·24	0·28	—
10·5	0·29	0·35	0·36	0·24	0·37	0·30	0·28	0·23	0·33	0·36	0·28	0·34
11·5	0·37	0·37	0·40	0·31	0·40	0·30	0·30	0·27	0·43	0·34	0·29	0·34
12·5	0·36	0·36	0·38	0·36	0·37	0·37	0·33	0·27	0·37	0·34	0·36	0·25
13·5	0·38	0·40	0·40	0·33	0·38	0·42	0·36	0·31	0·40	0·42	0·38	0·34
14·5	0·51	0·41	0·38	0·39	0·49	0·49	0·37	0·41	—	0·40	0·39	0·36
15·5	0·54	0·45	0·42	0·37	0·44	—	0·41	0·39	0·46	0·44	0·43	0·39
16·5	0·40	0·43	0·46	0·44	0·51	0·52	0·39	0·44	0·46	0·45	0·45	0·47
17·5	0·51	0·47	0·46	0·45	0·52	0·47	0·47	0·41	0·50	0·48	0·47	0·45
18·5	0·52	0·44	0·47	0·43	0·55	0·49	0·46	0·40	0·53	0·47	0·49	0·51
19·5	0·56	0·45	0·51	0·64	0·60	0·54	0·51	0·48	—	0·53	0·54	0·48
20·5	0·55	0·37	0·53	0·55	0·58	0·62	0·54	0·50	0·58	0·56	0·58	0·60
21·5	0·62	0·88	0·54	0·57	0·61	0·62	0·59	0·54	0·58	—	0·54	0·53
22·5	0·64	0·67	0·62	0·78	0·58	0·65	0·56	0·56	0·59	—	0·61	0·60
23·5	—	0·54	0·49	0·59	0·56	0·63	0·64	0·47	0·66	—	0·65	0·57
24·5	—	—	0·63	—	0·66	0·57	0·63	0·58	—	—	0·64	0·61
25·5	—	—	0·59	—	—	0·65	0·63	0·66	—	—	0·65	0·62
26·5	—	—	0·77	—	—	0·69	0·72	—	—	—	0·76	0·63
27·5	—	—	—	—	—	—	0·73	0·71	—	—	0·71	—
28·5	—	—	—	—	—	0·78	0·71	—	—	—	—	—
29·5	—	—	—	—	—	0·77	0·78	—	—	—	—	—

Table 3. Λ-doublet separation (in cm^{-1}) in the rotational lines of the $A^2\Pi_u - X^2\Pi_{\frac{3}{2}g}$ components of the second negative bands of $(^{16}O\ ^{18}O)^+$ ion

J	0-9 band				0-10 band				0-11 band			
	R_2	P_2	$^QR_{12}$	$^OP_{12}$	R_2	P_2	$^QR_{12}$	$^OP_{12}$	R_2	P_2	$^QR_{12}$	$^OP_{12}$
10·5	—	—	—	—	—	—	—	—	—	—	—	—
11·5	—	—	—	—	—	0·11	—	—	—	—	—	—
12·5	—	—	—	—	—	0·15	—	—	0·12	—	—	—
13·5	—	—	—	—	0·16	0·19	0·16	—	—	—	—	—
14·5	0·21	0·20	—	—	0·14	0·16	0·14	0·19	0·19	—	—	—
15·5	0·19	0·16	—	—	0·23	0·19	0·19	0·08	0·21	—	—	—
16·5	0·32	0·21	—	—	0·27	0·22	0·21	—	0·32	—	—	—
17·5	0·16	0·26	0·20	0·17	0·24	0·23	—	0·22	0·23	0·22	—	—
18·5	0·22	0·39	0·21	0·18	0·24	—	0·26	—	0·23	—	—	—
19·5	0·25	0·22	0·18	—	0·29	0·22	0·42	—	—	0·34	—	—
20·5	0·29	0·30	0·30	—	0·21	0·29	0·25	—	0·35	0·27	—	—
21·5	0·42	—	0·28	—	0·31	—	0·23	—	0·28	0·28	—	—
22·5	0·29	—	0·27	—	0·31	—	—	—	0·32	0·31	—	—
23·5	0·29	—	—	—	0·31	—	—	—	—	0·33	—	—
24·5	0·32	—	—	—	0·33	—	—	—	0·32	—	—	—
25·5	—	—	—	—	0·29	—	—	—	0·36	—	—	—

is essentially due to the $X^2\Pi_g$ state. By directly measuring the Λ-splitting for the various J'' values in the $\Pi_{1/2}$ and $\Pi_{3/2}$ sub-bands the Λ-doubling constants were determined using eqs (4) and (5).

The values of p and q as obtained from the present analysis are 0·031 cm^{-1} and 0·0024 cm^{-1} respectively. Earlier values for these constants as reported by Stevens (1931) in the case of $^{16}O_2^+$ ion are 0·036 cm^{-1} and 0·0027 cm^{-1}. He analysed the 0–8, 1–8, 0–7 and 1–7 bands of the second negative system and made use of the staggerings in the $\triangle 1\, F_1''(J)$ and $\triangle 1\, F_2''(J)$ values to get these constants for the $X^2\Pi_g$ state. As he did not notice any staggering in the $\triangle 1\, F_1'(J)$ and $\triangle 1\, F_2'(J)$ values, he rightly concluded that the initial $A^2\Pi_u$ state had Λ-splitting too small to be experimentally measured.

3.4. *Origin of* Λ*-doubling in the* $X^2\Pi_g$ *state*

As stated earlier in eq. (4), for a regular state, close to Hund's coupling case (a), Λ-doubling is given by

$$\triangle\nu_{dc}(J) = -p\,(J+\tfrac{1}{2})$$

The negative sign of $\triangle\nu_{dc}$ in $X^2\Pi_{(1/2)g}$ sub-state shows that one or more $^2\Sigma_g^-$ states is the main contributor to the Λ-doubling in the ground state of O_2^+. The only $^2\Sigma_g^-$ state known for O_2^+ is the $B^2\,\Sigma_g^-$ state at 20·3 eV with respect to the $X^3\,\Sigma_g^-$ state of O_2, its corresponding state in the isoelectronic molecule NO being the $G^2\,\Sigma^-$. Taking the analogy of NO (Lofthus and Miescher 1964), it can be assumed that $B^2\,\Sigma_g^-$ is the main contributor to the Λ-doubling of the $X^2\pi_g$ state. Using the approximation of ' pure precession ', the theory gives

$$p = \frac{2\,A\,B\,l\,(l+1)}{\nu\,(\Pi,\,\Sigma)} \text{ and } q = \frac{2\,B^2\,l\,(l+1)}{\nu\,(\Pi,\,\Sigma)} \qquad (6)$$

where l is the effective electron angular momentum, $\nu\,(\Pi,\,\Sigma)$ is the effective separation of the $^2\Pi$ state from the interacting $^2\Sigma^-$. Taking $l = 1$, $B = 1{\cdot}4896$ (average of B_e for the $X^2\,\Pi_g$ and $B^2\,\Sigma_g^-$ states), since B_e for the $B^2\,\Sigma_g^-$ state is not known it is assumed that its value will be close to the B_e value of the $b^4\,\Sigma_g^-$ state — because the two electronic states have almost identical ω_e values, $A = 195$ cm^{-1} and $\nu\,(\Pi,\,\Sigma) = 66340$ cm^{-1} (Rosen 1970), we get $p = 0{\cdot}016$ cm^{-1}, the observed value for the same being 0·031 cm^{-1}. Similarly, the value of q obtained from eq. (6) is 0·00012 cm^{-1} whereas its experimental value is 0·0024 cm^{-1}. It must be noted here that in the case of the ground state of NO the model of ' pure precession ' gives

Table 4. Λ-doublet constants for the $X^2\Pi$ state of NO (Lofthus and Miescher 1964)

Observed values based on microwave data cm^{-1}		Calculated values based on ' pure precession ' cm^{-1}	
p	q	p	q
0·0117	0·000077	0·0115	0·00014

remarkably good agreement between the experimental and theoretical (based on 'pure precession') values of the Λ-doubling constants (see table 4). But the same is not the case for the $X^2\,\Pi_g$ state of $(^{16}O\ ^{18}O)^+$. As for p, the disagreement is not very serious. The 'pure precession' does lead to the proper sign and the correct order of magnitude. But in the case of the constant q even the order of magnitude agreement is not there. One must conclude that the $B^2\,\Sigma_g^-$ state is not the sole contributor to p and q. In the absence of evidence for any other nearby $^2\Sigma$ state no further comments could be made.

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