ROTATIONAL ANALYSIS OF THE ÅNGSTRÖM BANDS AT λλ 6080 AND 6620 Å.U.

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Received March 20, 1936.

The Ångström bands of CO, though simple in structure, inasmuch as they are due to the transition $B^1\Sigma \rightarrow A^1\Pi$, have evoked considerable interest from more than one point of view. The rotational analysis of some of these bands was given by Hulthen.[1] The 0–0 and 1–0 bands were analysed by Jassé,[2] by Johnson and Asundi[3] and by Rosenthal and Jenkins.[4] The latter were able to show that pronounced perturbations of the rotational levels occurred in the bands they analysed, *viz.*, bands having $v'' = 0$, 1, 2 and 3, and especially in bands with $v'' = 0$ and 1, these perturbations occurred at relatively low J values in addition to perturbations at high J values observed in all bands. The displacements of the 0–1 and 1–1 bands previously observed by Johnson and Asundi was traced to this rotational perturbation very near to the origin in these cases. All these perturbations are definitely shown to be in the $A^1\Pi$ level. Further proof of this fact is given by similar perturbations observed by Read[5] in such of the fourth positive carbon bands as have initial levels of the same quantum number as the final levels of the Ångström bands. The initial state $B\ ^1\Sigma$ of these latter bands is also not without interest. Recently, Coster and Brons[6] have reported a sudden decrease in intensity of some of the rotational lines which they attribute to pre-dissociation of the molecule. The present paper deals with the rotational analysis of the 0–4 and 0–5 bands, preliminary results of which have been published before.[3] Measurements have been made on plates taken in the first order of a 21 ft. concave grating. The spectrum was produced in a usual discharge tube of CO and the data are confined to relatively low J values on account of the low temperature production of the bands.

Tables I and II contain the analysed wave-numbers (cm.$^{-1}$) *in vacuo* of the lines of the two bands. Table III contains the $\Delta_2F'(J)$ values observed in these bands and those calculated by Rosenthal and Jenkins. On account of the Λ-type doubling in the lower level, combination defects are to be expected, but these are negligible in such at least of the bands as are free from perturbations at low J values. Table IV gives the $R(J) - Q(J)$

and $Q(J+1) - P(J+1)$ values which should be equal if no combination defects were present, these being then $\Delta_1F'(J)$ values; also similarly the $R(J) - Q(J+1)$ and $Q(J) - P(J+1)$ values which would be $\Delta_1F''(J)$.

The agreement between the observed and calculated values of $\Delta_2F'(J)$ in Table III is quite satisfactory and affords proof of the correctness of the analysis. Reference to Table IV shows that combination defects are negligible for the 0–5 band at λ 6620. This indicates that there are probably no perturbations in this band upto the J values here observed. In order to ascertain this, the method used by Rosenthal and Jenkins of plotting deviation curves was adopted. Formulæ were developed to express the regular lines of each branch in the bands by the method of least squares and the observed *minus* calculated values were graphically plotted. The small residuals for the band at λ 6620 (the maximum *O–C* values being + 0·22 for P(1), + 0·20 for Q(13) and + 0·18 for R(3), indeed confirm that there are no perturbations in this band inside the observed limit. This is further corroborated by the recent work of Gerö[13] on the fourth positive carbon band ($v' = 5$, $v'' = 13$), which involves this same level. The first strong perturbation observed by Gerö at Q(30) is already outside the limit of the present observations. On the other hand, the band at λ 6080 shows considerable combination defects and correspondingly large residuals for the P and R branches, the Q branch, however, being more or less normal. The residuals increase towards small J values starting from + 0·06 at P(6) to + 0·94 at P(2) and from + 0·06 at R(6) to + 1·04 at R(2), and therefore point to $J = 0$ being perturbed as in the 0–1 or 1–1 bands, the perturbation being smaller than and opposite in sign to that observed in the latter bands. This perturbation, though small, appears to be genuine because firstly while $\Delta_2F'(J)$ values are proper, the combination defects are appreciable and secondly, the positive residuals increase towards $J = 0$ thus indicating a violet shift of the origin which has been already noticed.[3] Incidentally, a second perturbation at P(19) is indicated by the residuals, − 0·28, − 0·52 and − 0·43 for P(18), P(19) and P(20) respectively.

Coster and Brons[12] find a perturbation in this band at about $J = 31$ for this level but Gerö[13] has shown, from a study of the Herzberg and the fourth positive carbon bands involving this level that perturbations occur at $J = 0$, 23 and 37. The present results confirm the perturbation at $J = 0$ but the data are not sufficient to confirm the other perturbations. The very small perturbation at about $J = 19$ has not been recorded previously and may not be real.

Rosenthal and Jenkins[4] have come to the conclusion that the perturbations are caused by the rotational terms of the electronic state $a\,^3\Pi$. Watson[7]

from Zeeman effect results also favours this interpretation. Coster and Brons[12] classify them as due to the already known states $a'^3\Sigma^+$ and $d^3\Pi$ and to certain $e^3\Sigma^-$ and $^1\Pi$ states which are still unknown. In view of the multiple perturbations in each band, such an explanation appears quite plausible. Except for the hypothetical $^1\Pi$ state, all perturbing levels would then, however, be triple. This creates a theoretical difficulty pointed out by them, which concerns the condition that for the two terms to perturb they must have the same symmetry with respect to interchange of the point co-ordinates of the electrons, that is, they must be terms of equal multiplicity.[8] There is, however, a possibility of explaining some of these perturbations as due to the ground $X^1\Sigma$ state of the molecule. It is of course not possible to extrapolate with much accuracy but if we do so from the equation given by Read[5] for the fourth positive carbon bands, we obtain for the vibrational terms of the ground level, values which are comparable with those of the $A^1\Pi$ state which is perturbed, as in the following table :—

$X^1\Sigma$ Level		$A^1\Pi$ Level	
v	Energy cm.$^{-1}$	v	Energy cm.$^{-1}$
		0	65809
40	66865	1	67297
41	68006	2	68739
42	69124	3	70151
43	70217	4	71527
44	71288	5	72869

If the extrapolation gave correct values, from this table one would expect that of all levels, only $v = 3$ of $A^1\Pi$ state would exhibit near $J = 0$, a perturbation due to $v = 43$ of $X^1\Sigma$ state. This, however, has no support from experimental evidence and therefore the coincidence is simply fortuitous and the extrapolation is certainly only approximate. We know, however, that $v = 1$ of $A^1\Pi$ state is perturbed near $J = 0$ and if we assume that this perturbation is caused by $v = 40$ of $X^1\Sigma$ state, it is possible that a similar perturbation near the origin at $v = 4$ of the $A^1\Pi$ state is caused by $v = 44$ of the $X^1\Sigma$ state within the errors of extrapolation. It appears as if some of the perturbations, therefore, are definitely due to the ground level of the

TABLE I.

Analysis of 0–4 *Band at* λ 6080 *Å.U.*

(*Figures in brackets denote estimated Intensities.*)

J	P-Branch	Q-Branch	R-Branch
1	....	16450·48 (6)	....
2	16444·81 (0)	452·37 (2)	16464·10 (0)
3	443·52 (6)	454·97 (3)	470·71 (1)
4	443·13 (3)	458·53 (4)	478·13 (1)
5	443·52	462·95 (4)	486·45 (2)
6	445·01 (5)	468·25 (8)	495·61 (2)
7	447·33 (4)	474·49 (8)	505·67 (2)
8	450·48	481·48 (8)	516·64 (2)
9	454·50 (4)	489·41 (7)	528·43 (2)
10	459·36 (3)	498·19 (7)	541·09 (2)
11	465·06 (4)	507·84 (7)	554·59 (2)
12	471·73 (3)	518·39 (7)	
13	479·21 (3)	529·82 (7)	
14	487·63 (2)	542·01 (5)	
15	496·84 (2)	555·21 (5)	
16	506·95 (2)		
17	518·14 (1)		
18	529·82		
19	542·55 (0)		
20	556·32 (0)		

TABLE II.

Analysis of 0–5 *Band at* λ 6620 *Å.U.*

(*Figures in brackets denote estimated Intensities.*)

J	P-Branch	Q-Branch	R-Branch
1	15104·24 (0)	15108·07 (1)	15115·62 (1)
2	102·12 (1)	109·93 (2)	121·67 (0)
3	100·89 (5)	112·72 (5)	128·24 (2)
4	100·89	116·38 (5)	135·86 (2)
5	101·50 (3)	121·00 (7)	144·41 (4)
6	103·17 (7)	126·55 (8)	153·87 (3)
7	105·73 (5)	132·96 (8)	164·15 (4)
8	109·20 (8)	140·38 (10)	175·43 (3)
9	113·59 (6)	148·62 (8)	187·61 (4)
10	118·90 (6)	157·83 (9)	200·68 (4)
11	125·14 (5)	167·97 (8)	214·70 (4)
12	132·36 (5)	179·03 (6)	(masked by Hα)
13	140·38	191·02 (6)	245·53 (2)
14	149·45 (5)	203·90 (5)	
15	159·29 (3)	217·86 (6)	
16	170·24 (3)	(masked by Hα)	
17	182·06 (2)	248·20 (6)	
18	194·79 (1)	264·69 (5)	
19	208·47 (0)	282·26 (7)	

TABLE III.

$\Delta_2F'(J)$ *Values.*

Calculated Values are from Rosenthal and Jenkins (l.c.).

J	Observed R(J)−P(J)		Calculated
	λ 6080 Å.U.	λ 6620 Å.U.	
1	..	11·38	11·62
2	19·29	19·55	19·47
3	27·19	27·35	27·26
4	35·00	34·97	35·05
5	42·91	42·93	42·83
6	50·60	50·70	50·62
7	58·34	58·42	58·40
8	66·16	66·23	66·18
9	73·93	74·02	73·96
10	81·73	81·78	81·74
11	89·53	89·56	89·51
12	..	..	97·27
13	..	105·15	105·04

molecule. It is further likely that the state K at 38820 cm.$^{-1}$, discovered by Kaplan[9] is responsible for some of the perturbations. The band which involves this state is reported to possess a structure similar to the fourth positive carbon bands. Therefore it is probable that K is a singlet level.

In addition to perturbations, the Ångström and certain other bands of the CO molecule are reported to exhibit the phenomenon of predissociation.[10] Brons has recently given[11] an interpretation of this and attributes the predissociation in the Ångström bands as due to a molecular term arising out of $C(^1S) + O(^3P)$. This term can only be a triplet term which according to

TABLE IV.

Term Differences.

J	λ 6080 Å.U.				λ 6620 Å.U.			
	$\Delta_1F'(J)$		$\Delta_1F''(J)$		$\Delta_1F'(J)$		$\Delta_1F''(J)$	
	R(J) − Q(J)	Q(J+1)−P(J+1)	R(J)−Q(J+1)	Q(J)−P(J+1)	R(J) − Q(J)	Q(J+1) − P(J+1)	R(J)−Q(J+1)	Q(J)−P(J+1)
0	..	..	..	..	..	3·83	..	..
1	..	..	..	..	7·55	7·81	5·69	5·95
2	11·37	11·47	9·13	8·85	11·74	11·83	8·95	9·04
3	15·74	15·40	12·18	11·84	15·52	15·49	11·86	11·83
4	19·60	19·43	15·18	15·01	19·48	19·50	14·86	14·88
5	23·50	23·24	18·20	17·94	23·41	23·38	17·86	17·83
6	27·36	27·16	21·12	20·92	27·32	27·23	20·91	20·82
7	31·18	31·00	24·19	24·01	31·19	31·18	23·78	23·76
8	35·16	34·91	27·23	26·98	35·05	35·03	26·81	26·79
9	39·02	38·83	30·24	30·05	38·99	38·93	29·78	29·72
10	42·90	42·78	33·25	33·13	42·85	42·85	32·71	32·69
11	46·75	46·66	36·20	36·13	46·73	46·67	35·67	35·66
12		50·61		39·18	..	50·64	..	38·65
13		54·38		42·19	54·51	54·45	41·63	41·57
14		58·37		45·17		58·57		44·61
15				48·26		..		47·62
16						66·14		..
17						69·90		53·41
18						73·79		56·22

Kronig's theory[8] should not perturb or predissociate the singlet level $B^1\Sigma$ of the Ångström bands. Similarly, most of the other correlations that he gives indicate a direct violation of the selection rule. We believe that these predissociations, if real, have to be explained in a different way, especially in view of the very low value for the energy of dissociation which comes out by this correlation. We intend to discuss this in detail in a separate communication.†

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† This number p. 562.