17

NEW BANDS OF THE ASUNDI BAND-SYSTEM OF CO

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ABSTRACT. A large number of bands has been recorded in an uncondensed discharge through a tube containing $SnBr_4$ at very low pressure and carbon as the usual impurity. Most of them are found to belong to the Asundi system ($a'^3\Sigma \rightarrow a^3\pi$) of CO. The following is the equation found to represent satisfactorily these bands as well as the already known ones of this system:

$$\nu = 6953.6 + (1208.6\ v' - 9.5\ v'^2) - (1726.5\ v'' - 14.4\ v''^2)$$

$$\text{or, } \nu_r = 7213.8 + (1218.1\ u' - 9.5\ u'^2) - (1740.9\ u'' - 14.4\ u''^2)$$

where, $u = v + \frac{1}{2}$ and the v' numbering is that proposed by Gerö and Lorinczi. A few bands which cannot find suitable places in the system appear to be fragments of an unknown system.

INTRODUCTION

The spectrum of CO has been the subject of much investigation due, among other causes, to its occurrence in almost all discharge tubes where CO or CO_2 occurs as impurity. Presence of other substances has often introduced many peculiarities in the spectrum of CO. An interesting example of the effect of foreign gases is provided by Merton and Johnson's method of production and isolation of the triplet bands of CO. Thus, if in a tube, having carbon electrodes and helium under high pressure, and, showing the comet-tail bands of CO, a trace of hydrogen is introduced, the comet-tail system disappears and the triplet system takes its place. Again if in a tube, having argon under high pressure and carbon electrodes, and showing the Swan bands, a trace of hydrogen is introduced, the Swan bands disappear and the triplet bands take their place. Before the discovery and classification of the triplet bands by Merton and Johnson, some bands were known to be associated with Angstrom bands in the red and yellow regions. These bands and those discovered by Merton and Johnson were collectively called as triplet system, though no satisfactory classification was forthcoming. Later on, Asundi (1929) photographed the bands associated with Angstrom bands in the red and yellow regions, which were tentatively included previously in the triplet system. He had no helium or hydrogen in his tube, yet he obtained a few bands of Merton and Johnson, although very weak. He measured those bands in the visible and the photographic infra-red and came to the conclusion that a large majority of them could not go with the Triplet system. For such bands he gave an analysis and showed that their

upper state is the then newly discovered level at 58927 cm^{-1} (Hopfield and Birge, 1927) of CO, and the lower state coincides with the lower state of the third positive bands of CO. He represented these bands by the following equation :—

$$\nu = 10491 + (1154.4\ v' - 9.5\ v'^2) - (1721.5\ v'' - 13.7\ v''^2) \quad \ldots \quad (1)$$

These bands which were also previously observed by McLennan, Smith and Peters (1925) are known as Asundi bands.

Later work done so far on the Asundi bands is summarised below :—

(1) Estey (1930), on the basis of a private communication from Birge that the upper level ($a'^3\Sigma$) is at 57763 cm^{-1}, proposed an increment of one unit in the v' numbering given by Asundi.

(2) Schmid and Gerö (1937) estimated the ν-values for bands from $v'=8$ onwards (with a few exceptions) from perturbations of $a'^3\Sigma$ level by $b^3\Sigma$ level and by an extrapolation obtained the energy of dissociation of CO as 11.06 volts. They also reported some new bands which they interpreted as members of the Asundi system with high v' values.

(3) Gerö (1938) performed the rotational analysis of two of these bands—(30,1) and (34,0)—and found the structure to be analogous to that of the bands recorded by Asundi.

(4) Gerö and Lorinczi (1939) proposed an increase of three units in the v' numbering given by Asundi.

Observation of bands with high quantum numbers by Gerö and others suggested an attempt at extending the known bands with low quantum numbers. A tube with a bulb containing $MgCO_3$ (to serve as a source of CO_2) gave only further evidence of some bands between successive Angstrom bands. The faint traces obtained on the plates were unsuitable for measurements. Next, while preparing a tube for studying the emission from $SnBr_4$ vapour, however, it was observed that in the initial stages, when pressure of CO was sufficient and that of $SnBr_4$ vapour low, bands similar to the known Asundi bands were well developed. The present paper deals with these additional bands. Measurements and analysis indicate that a large number of these bands can be included in the Asundi system.

EXPERIMENTAL

The discharge tube employed was a Π type one, 30 cm. long and 1.2 cm. in diameter. It had aluminium electrodes, 20 cm. apart, and drying tubes containing KOH, NaOH and anhydrous $CaCl_2$ on both sides : one side leading to the pump and the other to a bulb containing $SnBr_4$. The solid $SnBr_4$ (since room temperature was below 31°C) was allowed to evaporate of its own accord under reduced pressure. The usual carbon impurity in the tube itself was sufficient to produce intense Angstrom bands. As the pressure of $SnBr_4$

vapour in the tube increased gradually (though still very low), the Angstrom bands slightly weakened and the new bands belonging to the Asundi system developed distinctly.

The tube was excited by an uncondensed discharge from a transformer giving about 7000 volts, fed by A.C. obtained from a 1/4 kilowatt rotary convertor working off the D.C. 220 volts mains.

For the resolving instrument a two-prism glass spectrograph, constructed in this laboratory by the author, having dispersion of 80Å/mm. at 6500Å, 31Å/mm. at 5070Å, 17Å/mm. at 4500Å, and 8Å/mm. at 3800Å was used. Exposures of about one to two hours were necessary for photographing the bands on Ilford HP3 plates.

Wavenumbers in vacuo of band-heads were obtained from Kayser's Schoringungs zahlen from the mean wavelengths in air from measurements of three independent plates. The ν values are expected to be correct to about ± 4 cm^{-1}.

ANALYSIS

The analysis of these bands presents the usual difficulties which are encountered in all such extended systems. A small change in vibrational functions used may not apparently make any appreciable difference in the representation of bands with low quantum numbers but it may produce large deviations for high quantum numbers. Hence the vibrational function of initial or final (or both) state given from an analysis of a few bands is liable to modifications if it is to represent a greater amount of data to a good degree of approximation.

From his analysis of the Asundi Bands observed by him, Asundi derived the following equation :—

$$\nu_h = 10491 + (1154.4\ v' - 9.5v'^2) - (1721.5\ v'' - 13.7\ v''^2) \qquad (1)$$

He observed : "Assuming a transition to exist between the new level at 58927 ν as the initial level and the final level at 48438 ν of the third positive carbon bands as the final level, it will give rise to bands whose heads can be represented by

$$\nu_h = 10489 + (1155\ v' - 9\ v'^2) - (1726.5\ v'' - 14.4\ v''^2) \quad \ldots \quad (2)$$

The equation representing the new bands is very close to this. There is a possibility of considerable error in the measurements of the bands of higher wave-lengths because the dispersion of the instrument falls rapidly in that region. Therefore the discrepancy between the two equations may be taken to be within the limits of experimental error."

The function $(1726.5\ v'' - 14.4\ v''^2)$ is well-established and reliable, being common also to third positive carbon bands, 5B bands, 3A bands, and the Cameron bands. Thus there are two ways open for us : (*a*) to use equation (2) as such ; (*b*) to use equation (2) with the first function $(1155\ v' - 9v'^2)$ modified to a desirable extent.

(a) Using equation (2) as such the observed-calculated values of wave numbers of bands observed by Asundi are given in Table I and of bands observed by the present author are given in Table II.

TABLE I

ν_{vac}	v'	v''	O-C cm^{-1}	ν_{vac}	v'	v''	O-C cm^{-1}
11636.0	1	0	+ 1.0	14693.2	7	2	−44.4
12158.5	3	1	− 2.4	14953.2	4	0	−11.3
22761.8	2	0	− 1.2	15348.5	6	1	−34.4
13237.0	4	1	−15.9	15702.0	8	2	−55.6
13668.4	6	2	−31.2	16011.0	5	0	−28.0
13861.5	3	0	− 8.5	16375.0	7	1	−45.9
14048.0	8	3	−55.1	17057.2	6	0	−37.8
14301.8	5	1	−25.1	17389.2	8	1	−51.7

TABLE II

No.	ν_{vac}	v'	v''	O-C cm^{-1}	No.	ν_{vac}	v'	v''	O-C cm^{-1}
1	15439.0 15467.2	11	4	37.8	9	17627.4 17666.7 17700.5 17726.5	10	2	−17.1
2	15510.9 15608.5	20	9	− 8.4	10	17780.1	19	7	−25.0
3	15975.6 16009.2	5	0	−29.8	11	18222.2	14	4	2.8
4	16230.6 16295.4 16315.4 16338.0	12	4	−39.4	12	18352.3 18400.6 18428.7 18440.8	9	1	3.9
5	16977.0 17013.1 17032.8 17072.4	6	0	−22.6	13	18460.1 18531.2	18	5	8.8
6	17128.8 16198.7	22	9	27.8	14	18553.6 18573.2 18594.6 18617.2	20	7	8.1
7	17297.4 17315.7 17327.1	13	4	19.7	15	19019.9 19086.7	15	4	−26.7
8	17398.6 17504.9	15	5	−11.6	16	19170.9	8	0	17.9
					17	19618.9 19663.7	12	2	6.1

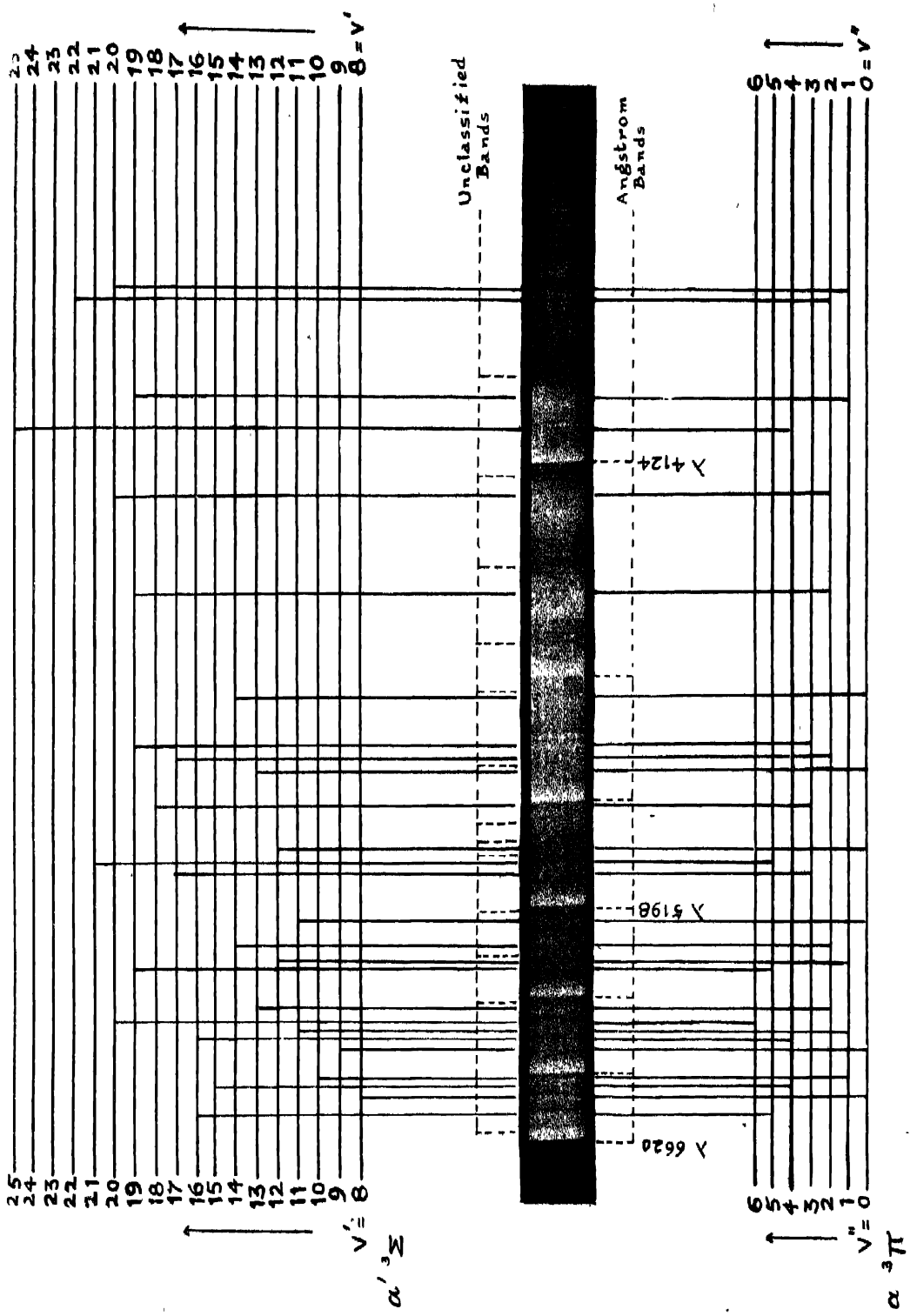
Unclassified Bands
Angstrom Bands
λ 4124
λ 5198
λ 6620
v' = 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
v" = 0 1 2 3 4 5 6
$a'^3\Sigma$
$a^3\Pi$

TABLE II (*contd.*)

No	ν_{vac}	v'	v''	O-C cm^{-1}	No.	ν_{vac}	v'	v''	O-C cm^{-1}
18	19767.5 19815.3 19839.7 19860.2	14	3	15.1	28	22478.2 ? 22511.1 ? 22559.4	19	4	50.0
19	19908.0 19924.3 20006.4	16	4	17.0	29	23024.4 23083.9	12	0	30.9
20	20021.8 20032.9 20049.0 20078.8	18	5	−11.7	30	23186.2	14	1	3.3
21	20161.4 ?	9	0	6.4	31	23270.4	16	2	0.8
22	20382.1 ?	11	1	−19.8	32	23317.1	18	3	7.0
23	20516.4 20578.9 20597.5	13	2	9.9	33	23962.6	13	0	−20.4
24	21057.4 21141.1	10	0	2.1	34	24010.4 24031.7 24053.1 24082.1	15	1	5.2
25	21267.0 21300.1 21344.7	12	1	3.8	35	24115.8	17	2	−11.8
26	21402.7 21420.6	14	2	Masked by a Herzberg band.	36	24566.1	26	6	−29.3
27	22014.5 22036.8	11	0	Masked by an Angström band.	37	24722.2 24752.2 24776.8	24	5	24.3
					38	24839.0 24861.8	14	0	−33.2
					39	24924.4 24943.1 24956.8	16	1	3.9
					40	25466.0 25486.1	25	5	19.6
					41	25529.7 25614.7	23	1	− 2.7

A survey of the Tables I and II shows that whereas the O-C values in Table II are both positive as well as negative the O-C values in Table I are all, except one, negative and increase rapidly with the quantum numbers. It is incomprehensible that the equation should behave in a divergent manner up to some quantum numbers and in an irregular manner afterwards. When an attempt was made to introduce a third degree term in the vibration function of the initial state, keeping equation (2) as a first approximation, it was found that again the equation remained divergent up to certain quantum numbers and then deviated irregularly. Also it was noted that the situation became rather worse ; the absolute magnitude of error became one and a half times that of the original. Hence it was decided to use equation (2) with a modification in the initial vibration function.

(b) Accepting for the vibration function of the final state that known from other systems mentioned above, it was found that the most suitable equation representing the bands recorded by Asundi would be:

$$\nu_h = 10493.9 + (1151.6v' - 9.5v'^2) - (1726.5v'' - 14.4v''^2) \quad \ldots (3)$$

Table III shows the comparison between the values calculated from equation (3) and those observed by Asundi.

TABLE III

No.	ν_{vac}	v'	v''	O-C cm^{-1}	No.	ν_{vac}	v'	v''	O-C cm^{-1}
1	11636.0	1	0	0	9	14693.2	7	2	−1.0
2	12158.5	3	1	7.4	10	14953.2	4	0	4.9
3	12761.8	2	0	2.7	11	15348.5	6	1	0.9
4	13237.0	4	1	0.8	12	15702.0	8	2	−1.3
5	13668.4	6	2	2.3	13	16011.0	5	0	3.4
6	13864.5	3	0	1.3	14	16375.0	7	1	−2.5
7	14048.0	8	3	−0.8	15	17057.2	6	0	−4.3
8	14301.8	5	1	−0.5	16	17389.2	8	1	2.6

Though both equations (1) and (3) represent Asundi's data to the same extent of accuracy, equation (3) is preferred since it contains the better known term $(1726.5\ v'' - 14.4\ v''^2)$ for the lower state. Equation (3) may now be extrapolated to correspond to the increase of three units in v' numbering proposed by Gero and Lorenzei. It becomes:

$$\nu_h = 6953.6 + (1208.6\ v' - 9.5\ v'^2) - (1726.5\ v'' - 14.4\ v''^2) \quad \ldots (4)$$

This equation for the band-heads may be written in the less convenient, but theoretically more significant, form as:

$$\nu_e = 7213.8 + (1218.1\ u' - 9.5u'^2) - (1740.9\ u'' - 14.4\ u''^2) \quad \ldots (4a)$$

where $u = v + 1/2$.

Table IV gives the bands observed by Asundi as well as those observed by the present author. ν-values calculated from equation (4) are also indicated.

TABLE IV

No.	ν_{vac} Asundi	ν_{vac} Garg	I	ν_{cal}	v'	v''	O-C cm^{-1}
1	—						
	—						
	—						
	11636.0			11636.0	4	0	0 A
2	12072.5						
	—						
	—						
	12158.5			12151.1	6	1	7.4 A
3	12674.0						
	—						
	—						
	12761.8			12759.1	5	0	2.7 A
4	13157.7						
	—						
	—						
	13237.0			13236.2	7	1	0.8 A
5	13585.1						
	—						
	—						
	13668.4			13666.1	9	2	2.3 A
6	13776.0						
	—						
	—						
	13864.5			13863.2	6	0	1.3 A
7	—						
	—						
	—						
	—						
	14048.0			14048.8	11	3	−0.8 A
8	—						
	—						
	—						
	—						
	14301 8			14302.3	8	1	−0.5 A
9	14612.7						
	—						
	—						
	14693.2			14694.2	10	2	−1.0 A

Some of the bands listed in Table II cannot be accommodated in the analysis given in Table IV. Such bands are given in Table V. A similar case is obtained in the wellknown triplet carbon bands where a few weak bands still remain unaccounted for. It may be that the bands put in Table V here and those unaccounted for in the triplet carbon system form together a new system that remains to be investigated further.

TABLE V

ν_{vac}	I	Remarks	ν_{vac}	I	Remarks
15439.0 15467.2	5	Probably Triplet carbon (0, 0)	22036.8	4	Probably Triplet carbon (8,1)
17700.5 17726.5 17780.1	5	Probably Triplet carbon (2, 0)	22478.2 22511.1 22559.4	6	Probably a Triplet carb6n (unassigned)
18400.6 18428.7 18446.8 18460.1	6	Probably a Triplet carbon (unassigned)	23186.2 23270.4 23317.1	7	
19170.9	8	Probably Triplet carbon (5, 1)	24010.4 24031.7 24053.1 24082.1 24115.8	6	
19908.0 19924.3	6		24839.0 24861.8 24924.4 24943.1 24956.8	6	
20161.4	9	Probably Triplet carbon (6,1)			
20382.1	6				
21141.1	7	Probably Triplet carbon (7, 1)			

An inspection of Table IV shows that bands with v' equal to 15 or lower have O-C values well within errors of observation. From $v'=16$ onwards the O-C values have a tendency to increase. It is difficult to say whether such irregular deviations are due to any perturbations. For example there are four bands with $v'=19$ with residuals $+7.2, -17.0, -8.2, +1.4$, and three bands with $v'=20$ with residuals $+19.0, +32.4, +1.2$. In some cases such irregular deviations might be due to a possibility of wrong identification of the particular subhead used to calculate the O-C values.

Schmid and Gerö's (1937) estimated term values of the vibrational levels of the $a'\,^3\Sigma$ level cannot be represented by a usual function with any reasonable error however large. It may, therefore, be said that the perturbations observed by them are due to some level other than $a'^3\Sigma$. The two bands at 33548 and 37447 cm^{-1} reported by Schmid and Gerö as having quantum numbers (32, 1) and (36, 0) in the Asundi system do not fit in the proposed equation (4) except as bands (32, 1) and (38, 1) respectively. Even then the residuals will be -30 and -3 cm^{-1} respectively. The changes in the v' values may be likely because the extrapolation of rotational constants used by Schmid and Gerö is rather long. But the same cannot be said of v'' values. Hence with due reservation it seems that these two bands may belong to a new system along with the other bands given in Table V and the unassigned bands of the triplet system.

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