

NEW EMISSION BANDS OF CO AND CO⁺

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ABSTRACT

Some new electronic band systems in CO and CO⁺ have been observed in emission, using high voltage (30 KV) D.C. discharge through relatively low pressure CO₂. The emission spectrum was photographed on Hilger large quartz, Steinheil two prism quartz and Bausch and Lomb 1.5 metre grating spectrographs. The spectrum covers the range 2100–5600 Å. In addition to the band systems usually observed in this region for CO and CO⁺, about 55 new bands have also been photographed. The majority of the new bands could be arranged in three band systems, two of which are proposed to be due to CO and one band system to CO⁺. Vibrational constants of the three band systems have been determined.

A CONSIDERABLE amount of work has been done on CO and CO⁺ molecules by a large number of workers¹⁻⁴⁴. In the case of the CO molecule, about 35 electronic states [Asundi¹⁰ (d), Tanaka¹¹] and for the CO⁺ molecule four electronic states are known⁴¹⁻⁴⁴. The observed electronic band systems for these molecules cover a wide range from near-infrared to vacuum-ultraviolet region.

In the present work a large number of new bands have been photographed in a high voltage (30 KV) D.C. discharge through CO₂ gas at relatively low pressure. The spectra were photographed on Hilger large quartz, Steinheil two prism quartz and Bausch and Lomb 1.5 metre grating spectrographs, in the region 2100–5600 Å. The accuracy of measurements is estimated to be ± 4 cm⁻¹. The intensities of the observed bands were measured on a recording densitometer.

In the present method of excitation, about 55 new bands, which do not belong to any known band system of CO and CO⁺ molecules, also appear (Fig. 1). A majority of these new bands are degraded to red and some are degraded to violet. The wide wavelength range of the new bands indicated that all the bands may not belong to a single band system. It was found possible to arrange most of the new bands in three Deslandres Tables. It appears that two of the new band systems are due to CO and one band system is due to CO⁺.

The bands observed in the 3414–3997 Å region (system I) are probably due to the transition T → P of CO (Table I). Tanaka¹¹ has reported the positions of the ν_{00} bands of T ← X and P ← X transitions at 154362 and 126410 cm⁻¹ respectively. In the present case the 0-0 band of system I is observed at 27953 cm⁻¹, which is in good agreement with Tanaka's data. The slight differences between the vibrational constants observed in the present case and those reported by Tanaka may be explained by the fact that Tanaka's observations were made in the vacuum-ultraviolet region with possibly greater uncertainty.

The red degraded bands observed in the 3536–4687 Å region (system II) could be arranged in another

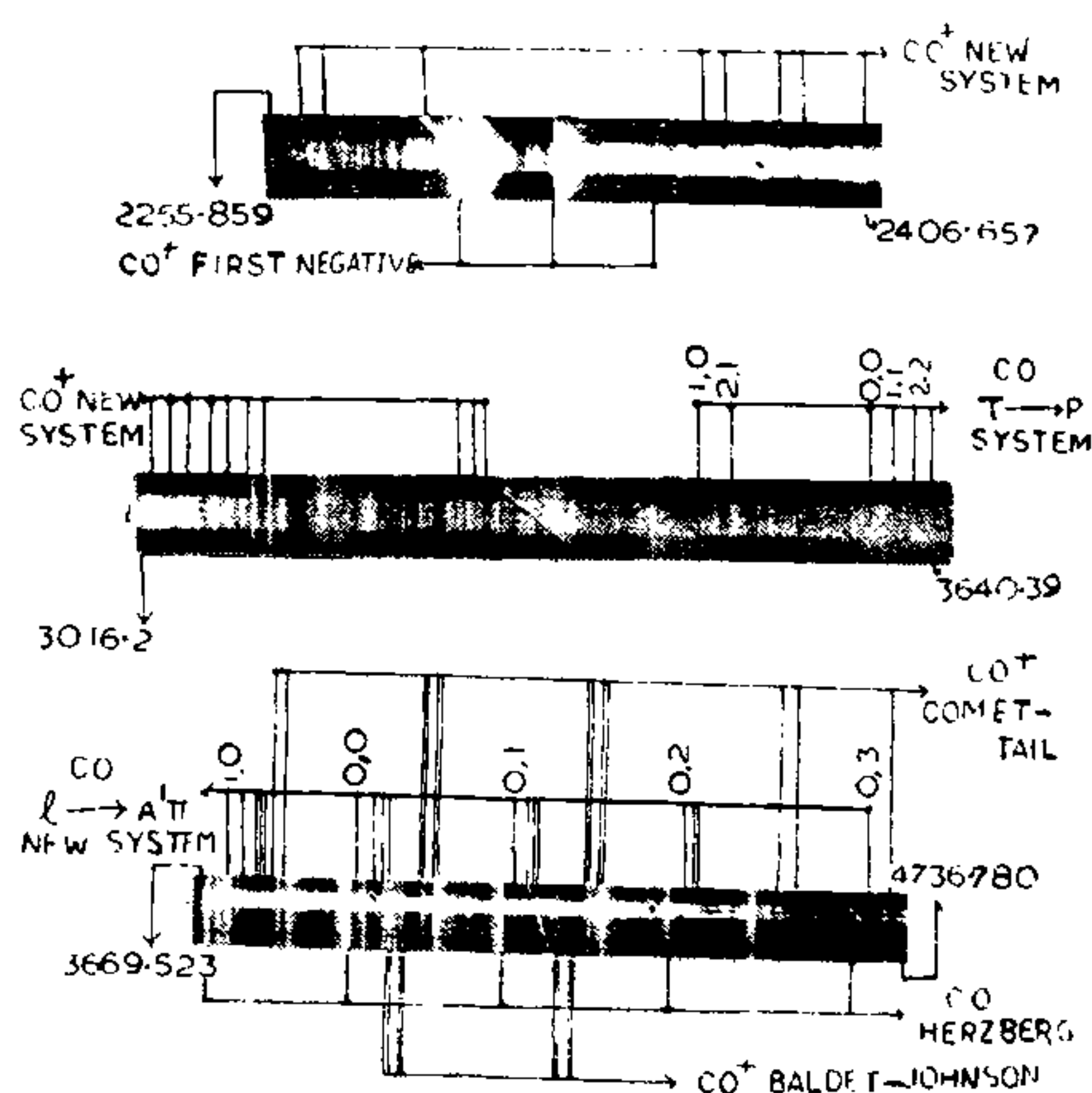


FIG. 1. Emission spectrum in 2255–4736 Å region.

Deslandres Table. The 0-0 band of this system is observed at 25593 cm⁻¹ and may be considered due to the $j \rightarrow D$ transition (90988–65391 – 25597 cm⁻¹) of CO. But the vibrational frequencies observed for the upper and lower electronic states of the band system II do not correspond to the j and D states of CO (2196 and 1080 cm⁻¹) [Tilford *et al.*³⁸ (b^o)]. Furthermore, the bands corresponding to the $j \rightarrow D$ transition should be degraded to violet, whereas the bands of this system are degraded to red. The observed vibrational constants for the lower electronic state of this band system agree with those of A¹Π state of CO¹⁻⁸ (b). Assuming the lower electronic state to be the A¹Π state of CO, and taking the 0-0 band at 25593 cm⁻¹, the upper electronic state should lie at 90339 cm⁻¹. However, no electronic state lying at 90339 cm⁻¹ is reported in literature for CO [Asundi¹⁰ (d)]. It appears that a singlet electronic state does not lie at 90339 cm⁻¹, otherwise the corresponding absorption from the ground state should have been observed by earlier workers. The appearance of this band system in emission may be explained by assuming a triplet

TABLE I

Vibrational assignment of $T \rightarrow P$ CO—System I

ν (cm ⁻¹)	I	Assignments (ν' , ν'')
25011	95	0, 2
26329	100	1, 2
26452	97	0, 1
27486	88	3, 3
27622	92	2, 2
27756	97	1, 1
27953	99	0, 0
29052	46	2, 1
29285	53	1, 0

$$\nu = 27953 + (1329 \cdot 75 \nu' - 11 \cdot 75 \nu'^2) - (1556 \cdot 17 \nu'' - 41 \cdot 17 \nu''^2).$$

TABLE II

Vibrational assignment of $I \rightarrow A^1\Pi$ CO Bands—Systems II

ν (cm ⁻¹)	I	Assignments (ν' , ν'')
21329	14	0, 3
22646	19	2, 4
22654	22	1, 3
22700	28	0, 2
23965	25	3, 4
23975	26	2, 3
24034	27	1, 2
24117	29	0, 1
25266	96	4, 4
25291	100	3, 3
25350	65	2, 2
25466	68	1, 1
25593	77	0, 0
26577	11	5, 4
26612	13	4, 3
26665	22	3, 2
26807	29	2, 1
26942	90	1, 0
28273	56	2, 0

$$\nu = 25593 + (1343 \cdot 95 \nu' - 4 \cdot 71 \nu'^2) - (14 \cdot 9582 \nu'' - 23 \cdot 17 \nu''^2).$$

state to lie at 90339 cm⁻¹. The corresponding absorption from the ground electronic state will be too weak to be observed under ordinary conditions. Since the pressure of the gas inside the discharge tube was relatively low, the mean free path may be large enough to permit the build up of high population density of molecules in the upper triplet state without collisional deactivation. Electron scattering experiments for singlet-triplet transitions (Dunham⁴⁷ Skerble⁴⁸) show that there are several triplet states in the vicinity of 11.280 eV [Tilford³⁸ (a)]. The proposed triplet electronic state (I) would lie at 11.1986 eV. The observed

TABLE III

Vibrational assignment of CO⁺—System III

ν (cm ⁻¹)	I	Assignments (ν' , ν'')
30842	44	
..	..	1, 6
31016	53	
30917	47	0, 5
32456	83	
32353	91	3, 7
32690	78	
32584	83	2, 6
32945	79	
32837	78	1, 5
..	..	
33059	65	0, 4
34792	19	
34687	100	2, 5
35088	13	
34982	19	1, 4
35359	79	
35254	29	0, 3
36934	13	
36829	19	2, 4
37599	16	
37503	17	0, 2
39880	16	
39794	18	0, 1
41420	47	
..	..	2, 2
41833	30	
41728	31	1, 1
42234	80	
42125	94	0, 0
43710	52	
43592	58	2, 1
44165	32	
44056	53	1, 0

$$\nu = 42125/42234 + (1968 \cdot 56 \nu' - 38 \cdot 07 \nu'^2) - (2359 \cdot 61 \nu'' - 23 \cdot 36 \nu''^2).$$

band system II (Table II) may be due to $I \rightarrow A^1\Pi$ transition.

A number of red degraded bands observed in the region 2269–3241 Å are doublet bands and are proposed to be due to CO⁺. However, it should be mentioned that the observed vibrational constants for the upper and lower electronic states of the band

system III (Table III) are not in agreement with those of any known electronic state of CO⁺ molecule.

Attempts are being made to photograph some of the strong bands of these three band systems on a 35' grating spectrograph so that their rotational structure could be resolved and definite assignments of the electronic states involved could be made.

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