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Band Spectrum of CdI Molecule in the Region 3586-3495 A. (*C*-System)

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The *C*-system of CdI has been obtained in emission using a high frequency oscillator and has been photographed in the first order of the two-metre plane grating spectrograph. Nearly 30 bands have been measured. The bands have been analysed under the assumption that the structure accompanying the three prominent bands is the vibrational structure of the system and not the rotational structure of a single band. The following vibrational quantum equation representing the bands has been derived:

$$\nu_{\text{head}}=28228\cdot25+[186\cdot36(v'+\tfrac{1}{2})-0\cdot68(v'+\tfrac{1}{2})^2]-[178\cdot25(v''+\tfrac{1}{2})-0\cdot60(v''+\tfrac{1}{2})^2]$$

WIELAND[1] has analysed the *D*-system of CdI with the (0,0) band at 3384 A. He has also reported three bands at 3586, 3563 and 3541 A., the last being the strongest of all. It has been suggested by Howell[2] that if these two groups of bands form the two components of a $^2\pi\rightarrow{}^2\Sigma$ transition with their (0,0) bands at 3384 and 3541 A. respectively, a doublet interval of about 1300 cm.$^{-1}$ is obtained which may not be considered so close to the anticipated value of 1140 cm.$^{-1}$; it is, however, of the right order. The work was repeated by Ramasastry and Rao[3] who listed a few additional bands of *D*-system on the shorter wavelength side and also observed the above three bands and assigned them to the missing component of the above transition (*C*-system). However, the vibrational constants of the *C*-system could not be derived as only three bands were observed by them and the dispersion used was not enough to resolve the structure

The aim of the present investigation is to check the above conclusion and to analyse the *C*-system if it could be extended further. The results obtained are reported here.

Experimental Procedure

The spectrum of CdI was excited in an electrodeless quartz discharge tube of length about 25 cm. and diameter 1·5 cm, with a flat quartz window on one end. A 125 W. oscillator working in the frequency range 10-15 Mc/s. served for excitation. It was found necessary to have controlled and careful heating with a burner to vaporize the substance and to have the discharge maintained golden yellow in colour. The spectra were photographed in the first order of a two-metre plane grating spectrograph having a dispersion of 7·35 A./mm. Ilford N.30 ordinary and N.40 process plates were used and an exposure of about an hour was found to be sufficient to record the spectrum. Iron arc spectrum was used as wavelength standards.

Results

The band spectrum of CdI in the region 3500-3600 A. has been reproduced in Fig 1 and some of the prominent bands have been marked on it. The vibrational structure of the (0,0), (0,1) and (0,2) bands could be clearly seen in the reproduction.

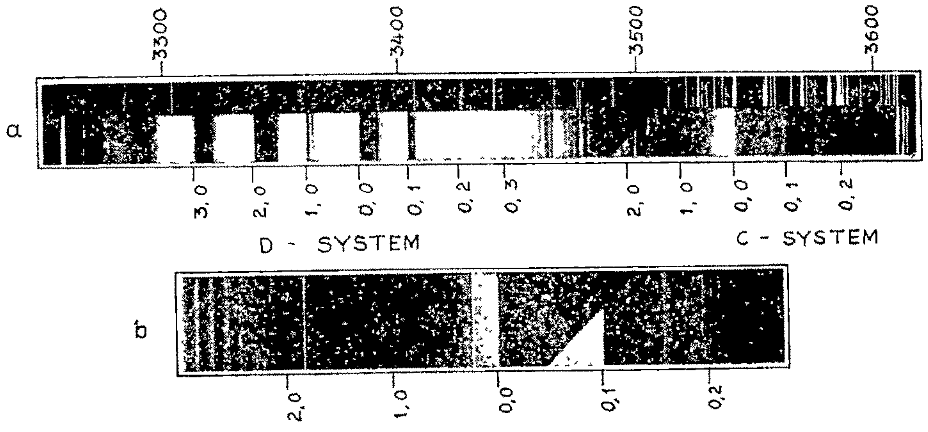

Fig. 1 — *C*-system of CdI bands taken with plane grating spectrograph in the first order [(a) taken with plane grating spectrograph in the first order, and (b) *C*-system with more magnification]

TABLE 1 — POSITION OF BAND HEADS, THEIR QUANTUM CLASSIFICATION NUMBER AND THE VISUALLY ESTIMATED INTENSITIES OF THE BAND SPECTRUM OF CdI MOLECULE IN REGION 3586-3495 A.

v', v''	Wavelength A.	Intensity	$\nu_{obs.}-\nu_{calc.}$ cm.$^{-1}$
0, 2	3585·85	2	0·0
1, 3	3584·52	2	0·1
2, 4	3583·27	2	−0·4
3, 5	3582·30	2	−2·9
4, 6	3580·94	2	−2·6
5, 7	3579·35	1	0·6
6, 8	3578·22	1	−0·2
7, 9	3576·99	1	0·6
8, 10	3575·92	1	−0·8
9, 11	3574·67	1	−0·1
0, 1	3563·36	4	0·2
1, 2	3562·20	4	0·2
2, 3	3561·12	4	−0·3
3, 4	3560·18	4	−1·7
4, 5	3558·99	4	−1·0
5, 6	3557·82	3	−0·3
6, 7	3556·53	3	1·6
7, 8	3555·69	3	0·0
8, 9	3554·77	2	−0·8
0, 0	3541·03	10	0·0
1, 1	3540·00	10	0·3
2, 2	3539·20	10	−1·1
3, 3	3538·11	9	−0·1
4, 4	3537·32	9	−1·2
5, 5	3536·25	8	0·0
6, 6	3535·32	8	0·3
7, 7	3534·49	7	−0·1
8, 8	3533·02	7	−1·2
1, 0	3517·98	3	0·0
2, 1	3517·15	2	0·1
2, 0	3495·29	2	0·9

The wavelengths of the bands, their visually estimated intensities and the assignment of the vibrational quantum numbers have been given in Table 1.

Discussion

In analysing the bands it was assumed that the structure accompanying the three prominent bands was the vibrational structure of the system and not the rotational structure of a single band. This conclusion was arrived at by the following reasons:

1. The molecule is sufficiently heavy and, with the dispersion used, it was not possible to resolve the rotational structure.
2. The vibrational constants of the two states involved are very near and, as such, the shading of the bands will not be prominent. The same has been observed in the case of *D*-system also.
3. Some of the higher members of *D*-system mix with the vibrational structure of the (0,0) band of the *C*-system and give a misleading appearance of long and extensive degradation to violet under low dispersion.

Taking the above aspects into consideration, the bands were analysed in the usual way[4] and following quantum equation was derived:

$$\nu_{\text{head}} = 28228{\cdot}25+[186{\cdot}36(v'+\tfrac{1}{2})-0{\cdot}68(v'+\tfrac{1}{2})^2]$$
$$-[178{\cdot}25(v''+\tfrac{1}{2})-0{\cdot}60(v''+\tfrac{1}{2})^2]$$

The values of $\nu_{obs.}-\nu_{calc.}$ given in column 4 of Table 1 indicate a close agreement. The exact doublet interval observed in the present analysis is 1300 cm.$^{-1}$.

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