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ROTATIONAL ANALYSIS OF THE A-X SYSTEM OF CuI MOLECULE

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(Plate 6)

ABSTRACT. The emission bands of the A-X system of the CuI molecule lying in the region 5600-4750 Å have been photographed under higher dispersion and resolution. Rotational analysis of (1, 0), (0,0) and (0, 1) bands has been made. The transition involved is found to be $^1\Pi - {}^1\Sigma$. The rotational constant of the two states are as follows (cm^{-1}) units) :

$A\ ^1\Pi$ state : $B_0 = 0.0674$, $\alpha = 0.0001$, $q = 1.25 \times 10^{-4}$

$X\ ^1\Sigma$ state : $B_0 = 0.0732$, $\alpha = 0.0002$

INTRODUCTION

The visible bands of the CuI molecule were studied by Mulliken (1925) and by Ritschl (1927). Ritschl recorded the bands in absorption and classified them in four systems with a common ground state for all of them. Of these known systems, the rotational analysis of the E-X, C-X and D-X systems were made by Nair and Upadhya (1966). Later Rao and Rao (1966) also reported the rotational analysis of E, C and D systems. Since a discrepancy existed regarding the constants of the ground and excited states of these systems as reported by the two different workers, Nair and Rai (1967) from considerations of the expected periodic variation of the r_e-values in similar molecules indicated that the constants given by Rao and Rao (1966) were uncertain. In continuation of the work of Nair and Upadhya (1966) the present paper deals with the rotational analysis of the A-X system of the CuI molecule.

EXPERIMENTAL

The molecule has been excited in an electrodeless discharge tube by a 2450 mc/sec. Raytheon Microwave Oscillator. The rotational structures were photographed on a 10.6 metre grating spectrograph in the second order with a dispersion of 0.33 Å/mm. The overlapping structure of the less abundant species $Cu^{65}I^{127}$ has been eliminated by adjusting the time of exposure. Since emission bands of this system are weak, it required 10 hours of exposure on Kodak IIF

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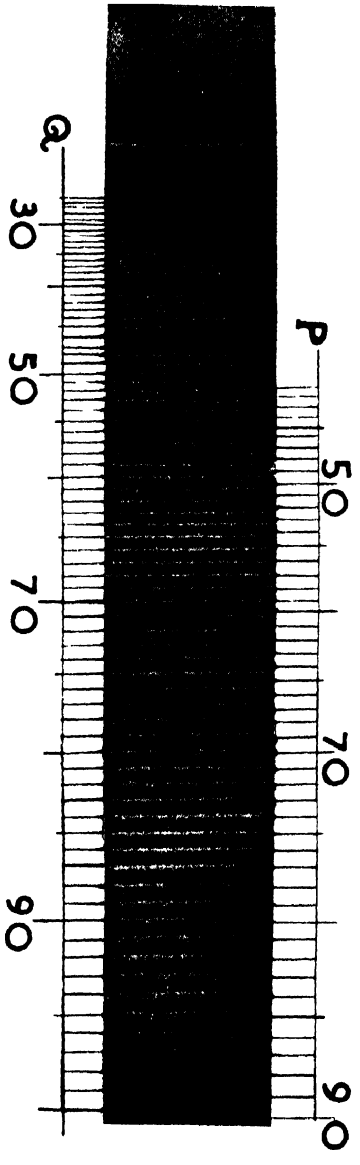

Fig. 1. Rotational structure of the 1,0 band of A-X system of CuI molecule.

Plates. Iron arc spectrum was used for comparison. The probable error in the measurement is estimated to be $\pm$ 0.04 cm^{-1}.

ANALYSIS AND DISCUSSION

The three bands (1, 0), (0,0) and (0, 1) were found suitable for measurement. The bands of the A system show two heads (fig. 1, plate 6), one being the R head and the other Q head. The R head is quite weak. Hence, in the resolved structure only two series of lines, Q and P could be picked. The fine structure analysis indicates that the transition is $^1\Pi - ^1\Sigma$. The Q branch is quite intense and runs to large J values. The P series is detected only at large J values and runs towards the lesser frequency side. Vaccum wave numbers and J assignments of the lines of the analysed bands are given in table 1.

The J numbering was fixed by comparing $\Delta_1 F(J)$ values for common vibrational levels and employing the usual procedure (Herzberg, 1957). The rotational constant were obtained by the graphical method from the relation :

$$\frac{\Delta_1 F(J)}{J+1} = 2B_v - 4D_v(J+1)^2$$

where $\Delta_1 F''(J) = Q(J) - P(J+1)$ and $\Delta_1 F'(J) = Q(J+1) - P(J+1)$. The band origins were determined from the intercepts of the graphs by plotting $Q(J)$ against $J(J+1)$. The α value for the upper $^1\Pi$ state was determined graphically using the relation,

$$Q_{v'v''}(J) - Q_{v'v''}(J) = \Delta' G - (B_{v'_1} - B_{v'_2})J(J+1)$$

In table 1 the $\Delta_1 F''(J)$ values of the previous analysis for the $E(3, 0)$ band and

$$\begin{aligned}\Delta_1 F''(J) + \Delta_1 F''(J-1) &= Q(J) - P(J+1) + Q(J-1) - P(J) \\ &= \Delta_2 F''(J) + \Delta\nu_{cd}(J-1) + \Delta\nu_{cd}(J)\end{aligned}$$

values for $A(0, 0)$ and A (1, 0) bands are given. Since the two sets of values are very close,it is confirmed that the transition is to the ground state. The regularly increasing difference in the two values is due to combination defect on account of Λ-type doubling in the upper $^1\Pi$ state. The mean value of the Λ-splitting coefficient, q was found to be 1.25×10^{-4} cm^{-1}, from this table from the relation :

$$\Delta\nu_{cd}(J-1) + \Delta\nu_{cd}(J) = 2qJ^2$$

The band origins and the rotational constants are summarised in table 3.

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Table 1

Vacuum wave numbers and J assignments of the A bands of CuI

J	0,0		1,0		0,1	
	$Q(J)$	$P(J)$	$Q(J)$	$P(J)$	$Q(J)$	$P(J)$
25	19703.33		19914.15		19438.66	
26	03.11		13.88		38.38	
27	02.93		13.61		38.10	
28	02.67		13.39		37.65	
29	02.32		13.04		37.23	
30	01.94		12.71		36.72	
31	01.58		12.42		36.27	
32	01.25		12.05		35.85	
33	19700.89		11.81		35.42	
34	00.49		11.43		34.95	
35	00.10		11.00		34.51	
36	19699.70		10.63		34.08	
37	99.29		10.28		33.62	
38	98.92		09.86		33.15	
39	98.51		09.45		32.65	
40	98.00		08.95		32.13	
41	97.55	19692.17	08.57	19902.95	31.62	
42	97.06	91.62	08.15	02.35	31.10	
43	96.58	91.04	07.62	01.98	30.54	
44	96.06	90.32	07.10	01.37	30.02	
45	95.53	89.62	06.63	19900.78	29.45	
46	95.09	89.03	06.13	00.14	28.96	19422.82
47	94.63	88.34	05.57	19899.52	28.34	22.15
48	93.88	87.64	05.06	98.86	27.81	21.57
49	93.34	86.94	04.50	98.18	27.10	20.78
50	92.75	86.31	04.13	97.46	26.35	19.81
51	92.17	85.62	03.47	96.75	25.79	19.00
52	91.62	84.96	02.95	96.01	25.14	18.35
53	91.04	84.24	02.35	95.32	24.49	17.63
54	90.32	83.53	01.73	94.60	23.63	16.81
55	89.91	82.74	01.13	93.89	22.96	16.06
56	89.33	81.88	19900.50	93.11	22.28	15.23
57	88.62	81.12	19899.90	92.56	21.57	14.43
58	87.98	80.31	99.21	91.98	20.90	13.56
59	87.28	79.77	98.57	90.99	20.19	12.78
60	86.61	78.87	97.88	90.09	19.43	11.97

Table 1 (*Contd.*)

J	0,0		1,0		0,1	
	$Q(J)$	$P(J)$	$Q(J)$	$P(J)$	$Q(J)$	$P(J)$
61	85.95	78.12	97.17	89.27	18.70	11.11
62	85.30	77.13	96.49	88.46	17.98	10.25
63	84.49	76.34	95.78	87.69	17.20	09.47
64	83.81	75.49	95.07	86.78	16.45	08.34
65	83.08	74.82	94.32	85.92	15.67	07.60
66	82.30	74.00	93.60	85.05	14.92	06.67
67	81.59	73.09	82.83	84.30	14.09	05.90
68	80.80	72.15	92.12	83.49	13.28	05.08
69	80.05	71.39	91.41	82.55	12.50	04.11
70	79.23	70.44	90.64	81.65	11.65	03.16
71	78.47	69.48	89.68	80.73	10.84	02.21
72	77.58	68.65	88.92	79.76	09.96	01.28
73	76.80	67.78	88.06	78.99	09 10	00.24
74	76.09	66.80	87.21	78.03	08.14	19399.32
75	75.27	65.99	86.36	77.05	07.34	98.29
76	74.34	65.05	85.50	75.80	06.57	97.26
77	73.44	64.08	84.58	74.84	05.59	96.13
78	72.63	63.10	83.70	73.89	04.95	95.28
79	71.81	62.09	82.79	72.98		
80	70.90	60.84	81.84	71.78		
81	70.09	59.84	80.92	70.77		
82	69.26	58.81	79.96	69.65		
83	68.30	57.88	78.99	68.58		
84	67.35	56.83	78.03	67.52		
85	66.36	55.62	77.05	66.30		
86	65.32	54.50	75.88	65.16		
87	64.24	53.40	74.92	64.01		
88	63.36	52.33	73.98	62.87		
89	62.46	51.24	73.08	61.72		
90	61.10	50.05	72.07	60.53		
91			70.96			
92			69.92			
93			68.84			
94			67.73			
95			66.65			
96			65.49			
97			64.38			
98			63.26			
99			62.09			
100			60.98			

Table 2

Λ-type splitting in the $v = 0$ level of the $A\ ^1\Pi$ state of CuI

J	$\Delta_2F''(J)$ $E(3, 0)$ band	$\Delta_1F''(J)+\Delta_1F''(J-1)$ $=\Delta_2F''(J)+\Delta\nu_{cd}(J-1)$ $+\Delta\nu_{cd}(J)$ mean of A (0,0) and $A(1, 0)$ bands	$\Delta\nu_{cd}(J-1)+$ $\Delta\nu_{cd}(J)=2qJ^2$
41	12.12	11.76	0.36
42	12.38	11.95	0.43
43	12.72	12.28	0.44
44	12.97	12.64	0.33
45	13.28	12.88	0.40
46	13.59	13.18	0.41
47	13.84	13.53	0.31
48	14.13	13.77	0.36
49	14.49	13.96	0.53
50	14.74	14.31	0.43
51	15.04	14.61	0.43
52	15.35	14.85	0.50
53	15.62	15.18	0.44
54	15.88	15.39	0.49
55	16.17	15.70	0.47
56	16.50	16.06	0.46
57	16.80	16.19	0.61
58	17.07	16.33	0.74
59	17.42	16.67	0.75
60	17.65	17.00	0.65
61	18.01	17.21	0.80
62	18 26	17.46	0.80
63	18.49	17.80	0.69
64	18.85	18.06	0.79
65	19.16	18.23	0.83
66	19.36	18.43	0.98
67	19.70	18.65	1.05
68	19.99	18 88	1.11
69	20.30	19.17	1.13
70	—	19.51	—
71	20.89	19.70	1.19
72	21.20	19.74	1.46
73	21.47	19 89	1.58
74	21.73	20.24	1.49
75	22.01	20.52	1.49
76	22.29	20.85	1.44
77	22.65	20.98	1.67
78	22.88	21.15	1.73
79	23.20	21.52	1.68
80	23.61	22.02	1.59
81	23.88	22.19	1.69
82	24.08	22.35	1.73
83	24.39	22.65	1.74
84	24.64	22.85	1.79
85	24.95	23.20	1.75
86	25.21	23.60	1.61
87	25.50	23.76	1.74
88	25.87	23.87	2.00
89	26.26	24.36	1.90

Table 3
Rotational constants and Band origins for the $A-X$ system of CuI (cm^{-1})

Band	Bv′	Bv″	
0,0	0.0674	0.0730	19707.40
0,1	0.0674	0.0732	19442.93
1,0	0.0673	0.0730	19917.40

$B_e' = 0.06745$, $B_e'' = 0.0733$
$\alpha' = 0.0001$, $\alpha'' = 0.0002$
$r_e'' = 2.38$ Å, $q = 1.25 \times 10^{-4}$
$r_e' = 2.48$ Å

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