Short Communication

Vibrational numbering in the $A^2\Pi_i$ state of ClO

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(Received January 15, 1976)

The ClO radical was first identified by Pannetier and Gaydon [1] in experiments on the emission spectra of hydrogen/oxygen flames containing small amounts of chlorine. Head measurements were reported for nineteen red-degraded bands in the near ultra-violet region. Although the nature of the two electronic states was unknown, vibrational assignments were given, and indicated that the spectrum is characterized by simple progressions from a few low-lying levels of the excited electronic state.

The same band system was observed later by Porter [2] during the flash photolysis of Cl_2/O_2 mixtures. The absorption spectrum of ClO was found to show a strong progression from $v'' = 0$ to a wide range of levels in the excited state, including levels close to the dissociation limit. On the basis that the absorption and emission data should extrapolate to a common system origin, Porter reported the first absolute vibrational numbering for the ground state. Table 1a shows a Deslandres array of the emission heads [1] with the numbering obtained by Porter [2].

The first experimental insight on the nature of the transition was obtained by the observation [2] of a second weaker progression in the absorption spectrum, which was identified as the second component of a

n's data.

ı [1], ground state numbering by Porter [2]

7	8	9	10	11	12	13	14
25,265 (750)	24,515						
(541)							
25,806 (757)	25,049 (749)	24,300 (727)	23,573 (712)	22,861			
			(493)				
			24,066 (725)	23,341 (708)	22,633		
					(429)		
					23,062 (642)	22,420	
							22,206

7	8	9	10	11	12	13	14
26,027 (762)	25,265 (750)	24,515					
25,806 (757)	25,049 (749)	24,300^b					
		25,049 (749)	24,300^b (727)	23,573 (712)	22,861		
		—	24,066 (725)	23,341^b (708)	22,633		
						23,341^b (708) 22,633	
						23,062 (642) 22,420^b	22,420^b
							22,206

entries are for $^2\Pi_{1/2}-^2\Pi_{1/2}$ and $^2\Pi_{3/2}-^2\Pi_{3/2}$ respectively.
appear twice in the Table.

An extremely satisfactory reconciliation of this conflict is shown in Table 1b, in which the same heads of Table 1a have been reassigned taking account of both spin components of the $^2\Pi_i-^2\Pi_i$ system. Thus, for example, the $v' = 0$ progression of Table 1a is reassigned as the $v' = 0$ progression for the $^2\Pi_{1/2}-^2\Pi_{1/2}$ component. Since the separation between the heads of the two sub-systems is near 200 cm^{-1}, the determination by Basco and Morse [5] of the ground state spin-orbit coupling constant, $A = -318 \pm 5$ cm^{-1}, leads to an estimate of $A \sim -520$ cm^{-1} for the same constant of the excited state. For a temperature of 2000 K, the ratio of the populations of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ components of the A-state would be ~ 0.7, so that the $^2\Pi_{1/2}-^2\Pi_{1/2}$ sub-bands would be expected to be observed for excitation in a flame.

The reassignments in Table 1b indicate that the progression assigned by Pannetier and Gaydon [1] as $v' = 1$ is in fact the $v' = 0$ progression of the $^2\Pi_{3/2}-^2\Pi_{3/2}$ sub-system. In other words, it is concluded that the vibrational numbering in the A state of ClO should be reduced by unity. Extrapolation to the origin of the $^2\Pi_{3/2}-^2\Pi_{3/2}$ sub-system is just as satisfactory as that obtained by Porter [2] with incorrect assignments. Furthermore, the revised assignments of Table 1b are strongly supported by a consideration of intensity distributions. The absence of $v' = 1$ bands in the region where the $v' = 0$ bands are most intense is in accord with qualitative Franck-Condon (FC) behaviour, and with preliminary calculations [6] of the FC-factors from RKR potential energy curves. An unambiguous confirmation of the renumbering has also been obtained from recent work [7] in this laboratory on the emission spectrum of ClO at high resolution.

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