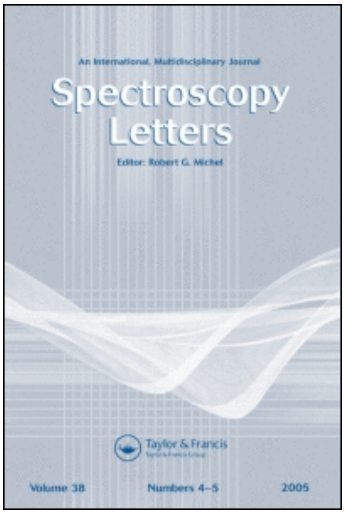

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On Thermal Excitation of the Diatom - CaF

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ON THERMAL EXCITATION OF THE DIATOM - CaF

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Abstract: Electronic spectrum of the diatomic molecule CaF was investigated in thermal emission using a high temperature vacuum graphite furnace. The ultraviolet system $C\ ^2\Pi - X\ ^2\Sigma$ for which only fragmentary data were available so far, was recorded in much extended form with bands showing clear multiplet sub-heads. In other systems too, numerous new sequences and additional bands have been reported.

Mitscherlich (1864), Fabry (1905) and Datta (1921) were probably the earliest workers to observe bands due to the molecule calcium monofluoride. These authors reported CaF bands using different sources but their observations were mostly qualitative. More systematic investigations were, later on, taken up by Walter and Barratt (1928), Johnson (1929) and Harvey (1931), who besides fairly extending the earlier data, also made satisfactory vibrational analysis of the bands observed. Fowler (1941) further explored these spectra in absorption and reported as many as six different band systems right upto 2550 Å in the ultraviolet region.

However, while spectra observed in emission were generally overlapped by numerous unwanted atomic lines and spurious bands, which invariably presented difficulties in

precisely identifying and measuring the different multiplet band-heads, absorption spectrograms were deficient otherwise. Many of the bands which were distinctly visible in emission, were altogether absent in absorption records.

Thermal excitation as employed in the present investigation was found to provide excellant spectra of this molecule. The spectra obtained were almost free from the crowding of undesired atomic lines and spurious bands. We got much extended vibrational structure and with better contrast to reveal multiplet structure of the bands clearly.

A small quantity (about 1 gm) of pure solid CaF_2 (Rieden de Haen, Germany) was vaporized to a temperature around 2400 ^{o}C in an atmosphere of pure argon using a King's furnace. Well-defined red-degraded bands, extending right from visible to the near-ultraviolet, were photographed on Ilford R-40 and HP-3 panchromatic plates. Hilger (E-492) large quartz spectrograph were employed to record all the spectra in a time range of about five to ten minutes.

Numerous additional bands and band sequences were identified practically in all the systems observed. A consolidated account of these findings is presented in Table I.

System-B was recorded with as many as twenty new members in different sequences along with an entirely new sequence $\Delta v = + 2$. The multiplet sub-heads of bands in system-C observed in the region ($\lambda\lambda$4085 - 3208) were found almost clearly distinguishable in most of the cases. Eleven

Table 1

Band System	Absorption	Emission	Thermal Emission (present authors)	Vibrational constants (cm^{-1}) Upper State $\omega_{e'}$	Upper State $\omega_{e'}x_{e'}$	Ground State $\omega_{e''}$	Ground State $\omega_{e''}x_{e''}$
A $^2\Pi - X\ ^2\Sigma$	Harvey (1931) λλ6297 - 5830	Johnson (1929) Harvey (1931) λλ6297 - 5830	λλ6300 - 5800	593.4 592.0	3.11 3.43	587.1	2.74
B $^2\Sigma - X\ ^2\Sigma$	Harvey (1931) λλ5422 - 5145	Johnson (1929) Harvey (1931) λλ5422 - 4145	λλ 5422 - 5000	566.7	2.82		
C $^2\Pi - X\ ^2\Sigma$	Fowler (1941) λλ3525 - 3220	Datta (1921) λλ3371 - 3524	λλ3820 - 3207	481.7	2.02		
	Q_1 18 heads R_1 11 heads R_2 12 heads R_{21} 4 heads		Q_1 56 heads R_1 34 heads R_2 38 heads R_{21} 25 heads				
D $^2\Sigma - X\ ^2\Sigma$	Fowler (1941) λλ3245 - 3081 (23 bands)	-	λλ3372 - 3050 (35 bands)	650.7	2.89		
E $^2\Pi - X\ ^2\Sigma$	Fowler (1941) λλ3035 - 2754 (20 bands)	-	λλ 3035 - 2800 (28 bands)	646.3	3.24		
F $^2\Sigma - X\ ^2\Sigma$	Fowler (1941) λλ2700 - 2554 (14 bands)	-	Only feeble impression (Not measured)	681.7	3.55		

heads due to R_1, twelve heads due to R_2 and four R_{21} heads have been reported in this system. This system was first identified by Fowler who pointed out that it could not be photographed by earlier workers as it was intrinsically weak. Fowler in his report did not mention the presence of any strong sequence beyond $\Delta v = -2$ while we could observe sequences upto $\Delta v = -7$ in addition to $\Delta v = +2$ sequence.

In system D, only $\Delta v = 0, 1$, two sequences could be identified by Fowler. With the observation of $\Delta v = -$ ve sequences, a better vibrational analysis has been possible for this system. The other systems too, have been recorded in much extended ranges.

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