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Thermal Emission Spectra of two New Diatomic Emitters - CrS and MnS

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Abstract: Band spectra of two hitherto unknown diatomic emitters - CrS and MnS have been observed in thermal emission using a vacuum graphite furnace. While the spectrum attributed to CrS lies in the spectral region $\lambda\lambda 3860 - 4650$, MnS bands fall in the region $\lambda\lambda 4200 - 5900$. Vibrational analyses of the bands observed in both the cases give spectroscopic constants which tally nicely with the mass-spectrometric data.

Diatom molecules involving transition group elements as one of the constituent atoms have always been of great theoretical interest as models to study the role of d-electrons in chemical bonding. While recent investigations in high temperature mass-spectrometry have put to evidence the existance of quite a good number of such diatoms, spectroscopic identification could, however, be made so far only for a few of them. Further, since the spectra of these molecules are most likely to involve higher multiplicities of electronic states, study of such molecules is quite useful to understand the complex role of high multiplicities in molecular spectra. Many of these molecules have been identified in stellar atmospheres as well and so this class of molecules as such is of great interest to astrophysicists too.

In extension to our investigations on the spectra of diatomic molecules involving atoms of the first transition series, we have recently identified two new diatomic emitters - CrS and MnS. Chromium and manganese lie as close neighbours in the first transition series of the periodic table and structurally chromium is quite interesting in the sense that it has only one unpaired s-electron in addition to the partially filled d-orbital, as distinct from the other members of the series.

An outline of our findings on these molecules is given below.

CrS (Chromium monosulphide)

Band spectrum attributed to the molecule CrS has been observed in thermal emission using a King's furnace. The bands are best observed by loading the furnace with appropriate proportional quantities of chromium and cadmium sulphide or zinc sulphide instead of CrS₃ or chromium plus sulphur. The above mixture was vaporised in the atmosphere of argon gas in the furnace at a temperature of about 2200⁰C. Red-degraded bands, characterised by well-marked sequences, have been obtained in the region 3860 - 4650 \AA . The main band-heads lie at wavelengths (\AA) given below.

3937.5 (4, 0) 4015.1 (3, 0) 4097.6 (2, 0) 4183.4 (1, 0)
4273.6 (0, 0) 4388.7 (0, 1) 4508.4 (0, 2) 4633.2 (0, 3).

The figures in the parenthesis show the vibrational transitions assigned. On detailed vibrational analysis, the following vibrational constants have been proposed.

$$\begin{array}{ll} \omega_e'' = 621.4 \text{ cm}^{-1} & \omega_e''x''_e = 4.1 \text{ cm}^{-1} \\ \omega_e' = 510.1 \text{ cm}^{-1} & \omega_e'x'_e = 2.1 \text{ cm}^{-1} \\ T_e = 234482 \text{ cm}^{-1} & \end{array}$$

The dissociation energy is found to be of the order of 23986 cm^{-1} which is about 11 percent less than the value proposed by J. Drowart, A. Pattoret and S. Smoes on the basis of mass-spectrometric studies.

MnS (Manganese monosulphide)

Band spectrum of this new molecule has also been observed in thermal emission using a King's Furnace. When a mixture containing appropriate proportions of manganese and cadmium sulphide or zinc sulphide is put in the graphite tube of the furnace and vaporized in the atmosphere of argon at a temperature of about 2200°C , red-degraded bands characterised by well-marked sequences have been recorded in the region $\lambda\lambda 4900-5890 \text{ \AA}$ and $\lambda\lambda 4200 - 4750 \text{ \AA}^\circ$. The main band-heads for both of the systems lie at wavelengths (\AA°) given below.

System I

4919.8 (4, 0) 5009.8 (3, 0) 5102.9 (2, 0) 5199.8 (1, 0)
 5300.8 (0, 0) 5440.9 (0, 1) 5586.5 (0, 2) 5739.9 (0, 3)

System II

4217.5 (3, 0) 4301.5 (2, 0) 4388.4 (1, 0) 4479 (0, 0)
 4576.6 (0, 1) 4679.9 (0, 2).

The figures in the parenthesis show the vibrational transitions assigned. After detailed vibrational analyses the following constants are proposed for the first system

$$\omega''_e = 490.4 \text{ cm}^{-1} \quad \omega''_{ex''_e} = 2.6 \text{ cm}^{-1} \quad T_e = 18920.3 \text{ cm}^{-1}$$

$$\omega'_e = 369.2 \text{ cm}^{-1} \quad \omega'_{ex'_e} = 1.16 \text{ cm}^{-1}$$

and for the second system $\omega'_e = 466.0 \text{ cm}^{-1}$ $\omega'_{ex'_e} = 2.0 \text{ cm}^{-1}$
 $T_e = 22332 \text{ cm}^{-1}$. Both the systems involve the ground state.

The dissociation energy of this molecule is found to be 23124 cm^{-1} which is very near to the value reported by J. Drowart, A. Pattoret and S. Smoes through their mass-spectrometric studies. Detailed account of these spectra are being published elsewhere.

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