

New band system of MnSe molecule

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Abstract. Thermal emission spectrum of MnSe molecule, excited in high temperature graphite furnace, has been photographed in the spectral region $\lambda\lambda$ 4150–5800 Å at a reciprocal linear dispersion of 7.3 Å/mm. The study reveals the presence of two band systems viz. $A-X$ and $B-X$ in which $B-X$ is entirely new. While the system $A-X$ consists of 29 bands, the new system $B-X$ comprises of 24 single headed and red degraded bands. Vibrational analysis performed suggested that both the systems involve ground state ${}^6\Sigma$ with a vibrational frequency $\omega'_e = 361.0 \text{ cm}^{-1}$. Transition responsible for MnSe spectrum appears to be of the type ${}^6\Sigma - {}^6\Sigma$.

An estimation of the ground state vibrational frequency for MnTe molecule gives rise to its value as 280 cm^{-1} .

Keywords. Thermal emission; molecular spectra; vibrational analysis; spectra of inorganic diatomic molecule; transition elements.

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1. Introduction

Electronic spectrum of MnSe was observed by Monjajeb [1] for the first time twenty years ago from thermal emission in a King's furnace by heating a mixture of manganese and selenium or cadmium selenide or zinc selenide at 1800°C in argon atmosphere. Single headed bands shaded to red, occurring in the visible region $\lambda\lambda$ 4970–5600 Å, were attributed to a single system. However the analysis is based on the spectrograms taken under low dispersion (12–40 Å/mm) with Hilger E-492 spectrograph. Because MnSe has the same electronic structure as MnS, one can therefore assume that this system corresponds to the $A{}^6\Sigma - X{}^6\Sigma$ visible system of MnS molecule. Since the study of MnS molecule in thermal emission by Uttam *et al* [2] reveals the presence of two band systems viz. $A-X$ and $B-X$ in the visible region, we expect a new band system in the visible spectra of MnSe. Further the spectrum of MnSe is congested due to the presence of large number of isotopic abundance of selenium. Therefore we examined the thermal emission spectrum of MnSe molecule using high temperature graphite furnace at a comparatively higher dispersion (7.3 Å/mm) and higher resolution (0.1 Å) than that of Monjajeb [1].

Here we report the fresh results for MnSe molecule in the visible region $\lambda\lambda$ 4150–5800 Å.

2. Experimental details

A small quantity of intimate mixture of manganese metal powder (BDH) with selenium or some solid selenide like CdSe or ZnSe was put in the graphite tube of the Saha's

high temperature furnace [3]. After making necessary routine adjustments and evacuation of the furnace chamber, argon gas was filled at about pressure of 50 cm of mercury. The tube was heated electrically to around 1800°C. A host of well marked bands, all degraded to the red, appeared in the blue-green region. A two meter Plane Grating Spectrograph with a grating blazed at λ 5600 Å and total lines ruled 45600 was used to photograph these bands in first order at a reciprocal linear dispersion of 7.3 Å/mm. An exposure time of about 6–8 min was sufficient to record the spectrogram on ORWO 400 ASA black and white films. An iron dc arc spectrum was recorded for comparison. The measurements were made using CZ Abbe Comparator with a least count of 0.0001 cm.

3. Results and Analyses

The bands appear in two groups in the spectral region $\lambda\lambda$ 4800–5800 Å and $\lambda\lambda$ 4150–4600 Å. Each group consists of a single system. All the bands are red degraded. Because of the higher resolution and dispersion, a partial rotational structure has been resolved. The complete reproduction of the spectrum is given in figure 1. The following is the system wise description:

3.1 *A—X system* ($\lambda\lambda$ 4800–5800 Å)

This system appears in the region $\lambda\lambda$ 4800–5800 Å and is constituted of 29 red degraded bands. The (0,0) of the system lies at λ 5316 Å and is marked in figure 1. Observed band head data, their vibrational assignments and relative visual estimates of intensities are collected in table 1. The following equation [ref. 4] was found satisfactory to represent the wave numbers of the different band heads observed.

$$\begin{aligned} \nu &= 18850.7 + 270.5(v' + 1/2) - 1.75(v' + 1/2)^2 \\ &\quad - 361.0(v'' + 1/2) + 2.25(v'' + 1/2)^2. \end{aligned}$$

3.2 *B—X system* ($\lambda\lambda$ 4150–4600 Å)

This system lies in the region $\lambda\lambda$ 4150–4600 Å and consists of 24 single headed, red degraded relatively faint bands. The (0,0) of the system was located at λ 4293.9 Å. Table 2 provides the observed wave numbers in vacuum, visual estimates of their intensities and the vibrational assignments to the attributed bands. The following equation [ref. 4] accounts fairly well for the wave numbers of the different band heads forming this system.

$$\begin{aligned} \nu &= 23323.1 + 278.0(v' + 1/2) - 1.00(v' + 1/2)^2 \\ &\quad - 361.0(v' + 1/2) + 2.25(v'' + 1/2)^2. \end{aligned}$$

4. Discussion

The thermal emission spectrum of MnSe molecule consists of two systems designated as *A* and *B* in the visible region. As already mentioned, Monjajeb [1] had proposed only a tentative analysis of system *A* and suggested the probable value of the ground state vibrational frequency to be 360.0 cm⁻¹. The ω_e'' value obtained here is 361.0 cm⁻¹, which agrees with that of Monjajeb [1]. The remaining system *B* is faint. However,

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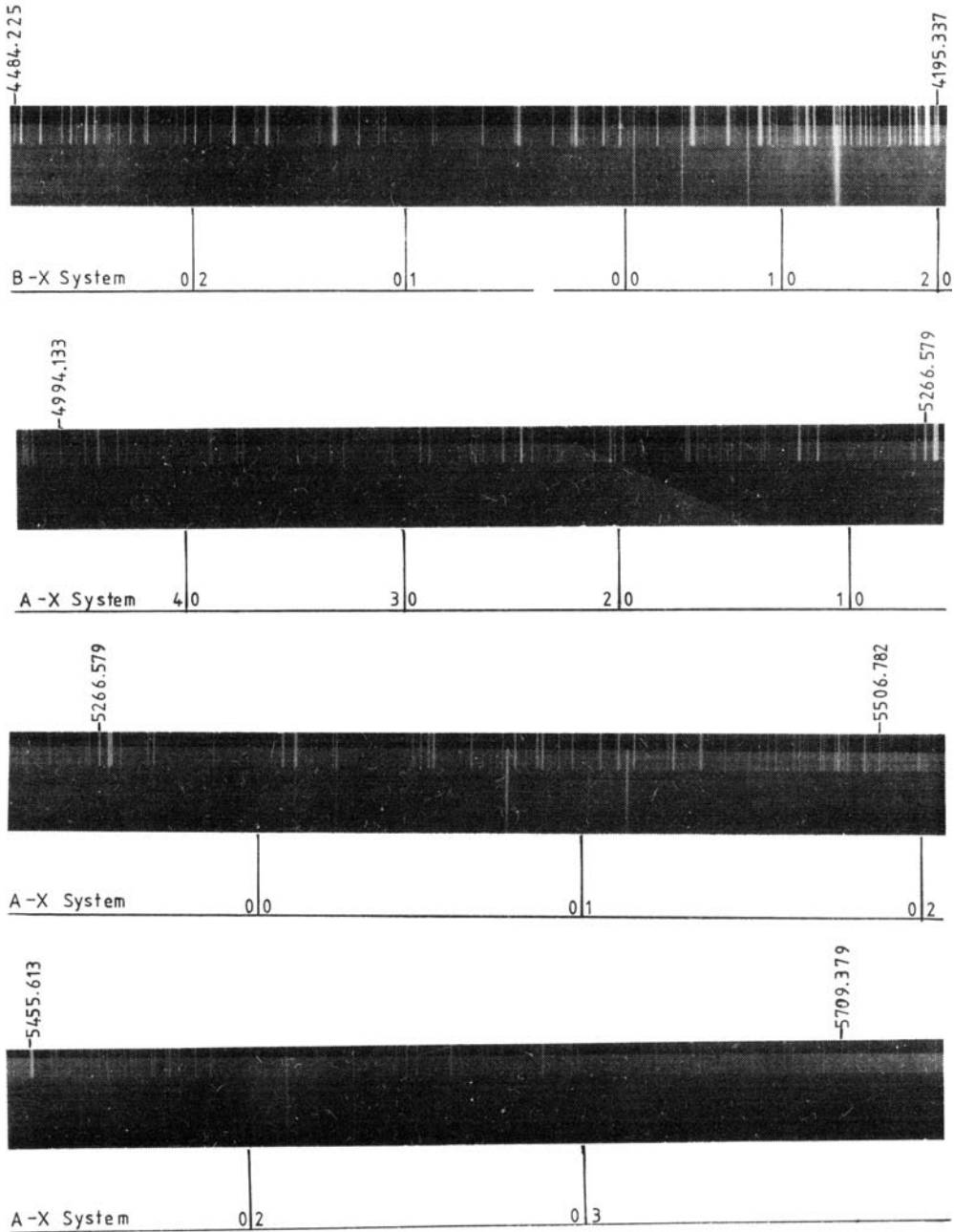


Figure 1. Thermal emission spectrum of MnSe molecule at a reciprocal linear dispersion of 7.3 \AA/mm .

well marked and intense $\Delta v = 0$ and ± 1 sequences are present. This situation is helpful in determining the ground state vibrational constants with reasonable certainty. Figure 2 displays a smooth curve demonstrating the variation of ω_e'' values for diatomic MnO, MnS and MnSe with the number of electrons in these molecules.

Table 1. Band head data of MnSe molecule: *A—X* system.

$\nu_{\text{obs}}(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$ (Obs-Cal)	Int.	Analysis (v', v'')	$\nu_{\text{obs}}(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$ (Obs-Cal)	Int.	Analysis (v', v'')
17749.8	0.2	1	(0, 3)	19072.3	-0.3	3	(1, 0)
17675.0	1.4	1	(1, 4)	18978.8	-0.8	1	(2, 1)
18098.3	1.2	2	(0, 2)	18886.8	-0.8	1	(3, 2)
18917.2	0.6	2	(1, 3)	19335.8	-0.3	3	(2, 0)
18936.2	-0.9	3	(2, 4)	19239.9	0.3	2	(3, 1)
18450.2	1.1	4	(0, 1)	19143.2	-0.9	1	(4, 2)
18365.2	1.1	1	(1, 2)	19597.1	1.0	2	(3, 0)
18280.4	0.3	1	(2, 3)	19496.8	0.7	1	(4, 1)
18198.2	1.1	1	(3, 4)	19398.5	1.4	1	(5, 2)
18805.6	0	4	(0, 0)	19853.0	0.4	2	(4, 0)
18715.8	-0.3	1	(1, 1)	19751.0	1.0	1	(5, 1)
18627.5	-0.1	1	(2, 2)	19647.5	0.9	1	(6, 2)
18539.8	-0.3	1	(3, 3)	20106.8	1.2	1	(5, 0)
18454.2	0.6	1	(4, 4)	20099.6	1.0	1	(6, 1)
				19891.4	-1.2	1	(7, 2)

Table 2. Band head data of MnSe molecule: *B—X* system.

$\nu_{\text{obs}}(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$ (Obs-Cal)	Int.	Analysis (v', v'')	$\nu_{\text{obs}}(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$ (Obs-Cal)	Int.	Analysis (v', v'')
22226.2	0.3	1	(0, 3)	22635.3	-1.1	1	(4, 5)
22157.3	-1.6	1	(1, 4)	23281.9	0	3	(0, 0)
22093.5	-0.9	1	(2, 5)	23200.9	-0.5	2	(1, 1)
22032.0	-0.4	1	(3, 6)	23123.3	-0.1	2	(2, 2)
22574.2	0.8	2	(0, 2)	23048.7	0.8	2	(3, 3)
22502.6	0.7	1	(1, 3)	22973.6	-1.3	2	(4, 4)
22432.8	-0.1	2	(2, 4)	23557.4	-0.5	1	(1, 0)
22365.5	-0.9	1	(3, 5)	23474.7	-0.7	2	(2, 1)
22924.3	-1.1	2	(0, 1)	23396.3	0.9	2	(3, 2)
22848.7	-0.7	2	(1, 2)	23832.3	0.4	2	(2, 0)
22774.4	-1.5	2	(2, 3)	23746.3	-1.1	2	(3, 1)
22703.5	-1.4	2	(3, 4)	23666.1	0.7	1	(4, 2)

The present ω_e'' value for MnSe fits in the curve very well. Thus the ground state vibrational frequency for MnSe can be accepted as 361 cm^{-1} .

It is clear from the analysis that the vibrational constants of the lower state of the proposed system (*B* system) are identical with those of the ground state of the MnSe molecule. Further the general appearance of the bands and the simultaneous recording of the well-known visible system of MnSe are also strongly in favour of attributing these bands to the diatomic MnSe molecule. This evidently confirms that the carrier of the bands has been rightly identified as MnSe.

The $\Delta v = 0$ sequence is easily identified among the observed bands and those involving higher vibrational levels are found to be diffuse in appearance. The diffuseness increases as one moves away from the system origin and can be explained to

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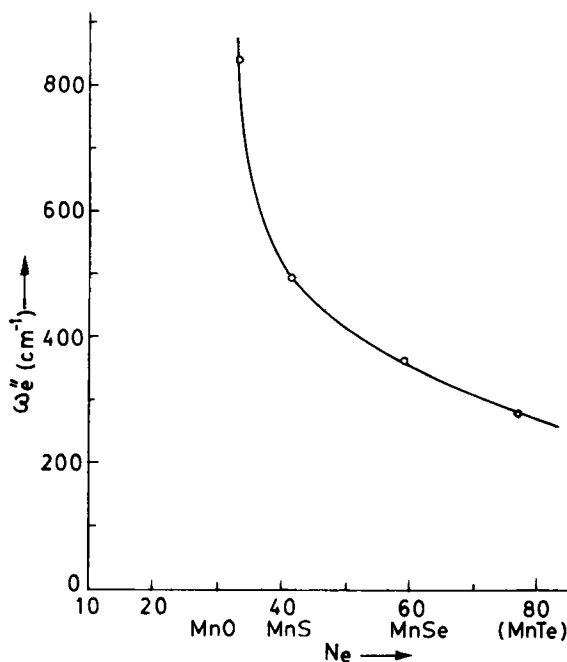
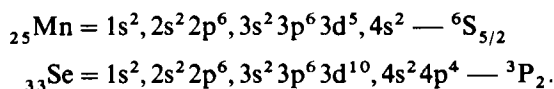


Figure 2. Variation of ground state frequency (ω_e'') vs number of electrons (Ne).

be due to the presence of large number of isotopes of selenium. The separate identification of the isotopic heads is not possible due to the faint spectrum.

The normal state electronic configurations of Mn and Se are given by:



Our study of MnS molecule [2] reveals that the ground state is ${}^6\Sigma$. Since MnSe has the same electronic structure (isovalent) as MnS and the chances of observing the transition which involves the ground state are higher in thermal emission, it is reasonable to assume that the ground state of MnSe is also ${}^6\Sigma$. Thus the optically allowed transitions are ${}^6\Sigma\text{—}{}^6\Sigma$ and ${}^6\Pi\text{—}{}^6\Sigma$. Since in the present study systems $A\text{—}X$ and $B\text{—}X$ consist of single headed bands analogous to MnS [2] molecule, therefore these systems involve ${}^6\Sigma\text{—}{}^6\Sigma$ transition.

The dissociation energy, using Birge-Sponer extrapolation formula, is given by

$$D_0 = \omega_e''^2 / 4\omega_e'' x_e''.$$

Substituting the constants we find $D_0 = 14480 \cdot 1 \text{ cm}^{-1} = 1.80 \text{ eV}$ which is quite reasonable.

The VI sub-group of the periodic table consists of five elements viz. O, S, Se, Te and Po. The diatomics with manganese of each one of them have been investigated spectroscopically except MnTe and MnPo. The transition $A\text{—}X$ has been observed in each case of MnO, MnS and MnSe. This transition is characterized by well marked sequences. Table 3 displays the relevant data for these molecules with reference to system $A\text{—}X$. The ω_e'/ω_e'' and D_0 values for MnO, MnS and MnSe have been

Table 3. Spectroscopic constants for the $A-X$ system.

	MnO	MnS	MnSe
$\omega_e''(\text{cm}^{-1})$	839.6	490.6	361.0
$\omega_e'(\text{cm}^{-1})$	762.8	371.8	270.5
ω_e'/ω_e''	0.9085	0.7579	0.7493
$D_0(\text{cm}^{-1})$	29842.2	33428.9	14480.1
$\nu_{00}(\text{cm}^{-1})$	17909.0	18858.1	18805.6

Table 4. Comparative data for the different diatomic molecules.

Molecule	Ne	ω_e''	$\omega_e''^{-2} \times 10^{-7}$	Molecule	Ne	ω_e''	$\omega_e''^{-2} \times 10^{-7}$
PbO	90	721.0	19.2	BiO	91	692.4	20.9
PbS	98	429.4	54.2	BiS	99	408.7	59.9
PbSe	116	277.6	129.8	BiSe	117	265.6	141.8
PbTe	134	211.9	222.7	BiTe	135	208.5	230.0
SbO	59	816.0	15.0	SnO	58	822.1	14.8
SbS	67	482.4	43.0	SnS	66	487.3	42.1
SbSe	85	326.1	94.1	SnSe	84	331.2	91.2
SbTe	103	284.4	123.6	SnTe	102	259.5	148.5
AlO	21	979.2	10.4	MnO	33	839.6	14.2
AlS	29	617.1	26.6	MnS	41	490.6*	41.6
AlSe	47	467.6	45.7	MnSe	59	361.0&	76.7
AlTe	65	415.0	58.1	MnTe	77	280.0#	124.9

(All ω_e'' values are in cm^{-1} units),

(Ne: Number of electrons; #: expected value; &: present value, *: ref. [2]. All other values taken from ref. [5])

calculated on the basis of molecular constants taken from [5], [2] and present study respectively.

The behaviour of ground state vibrational frequencies is quite satisfactory and the plot of the number of electrons (Ne) against (ω_e'') values is a smooth curve (figure 2). According to Howell [6], the similarity of the ratio ω_e'/ω_e'' in such cases indicates that the same type of relative loosening takes place in the molecular binding on examination. That a similar situation exists in the present case of MnS and MnSe also can be readily inferred from table 4 where the ratio ω_e'/ω_e'' is strikingly similar for MnS and MnSe. The dissociation energy D_0 has been calculated for these molecules with the help of vibrational constants. Since sufficient vibrational quanta have been observed in the ground state, the extrapolated values described in the table appear to be reasonably accurate.

Our attempts fail to record the electronic band spectra due to MnTe molecule and hence, we do not have much information about this molecule. However, from the information available for MnO, MnS and MnSe some predictions can be made for MnTe.

The plot of $\omega_e''^{-2}$ values versus electron number for different diatomics of this

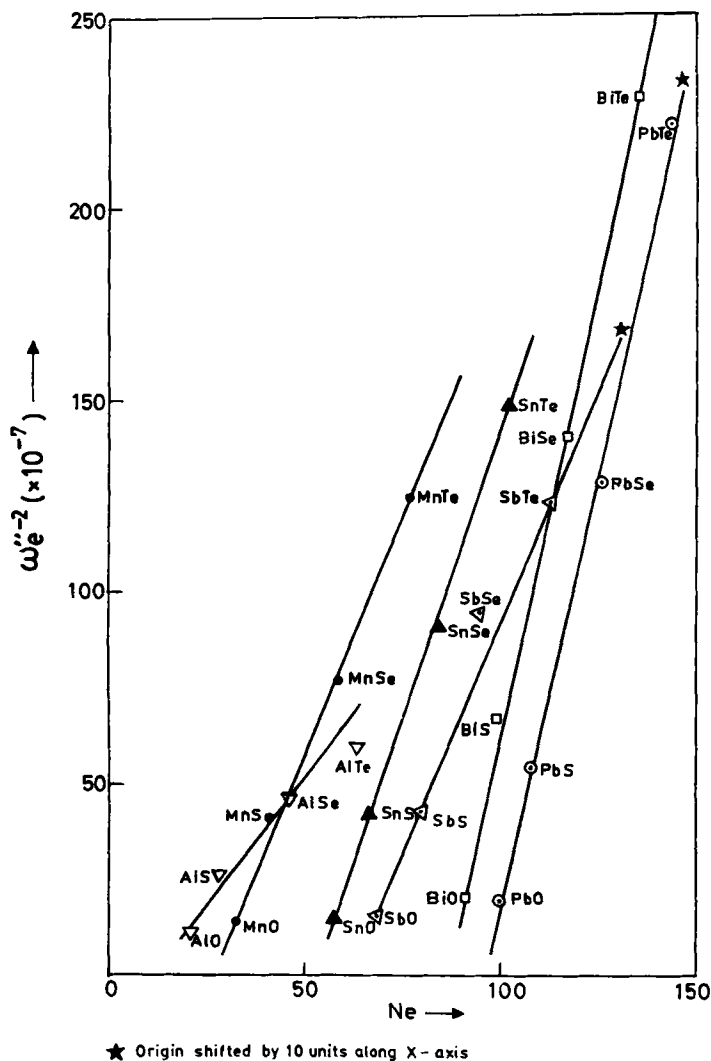


Figure 3. Variation of $\omega_e''^{-2}$ vs number of electrons (Ne).

molecular group involving manganese gives rise to a straight line. Spectroscopic constants for the diatomic combinations of many other atoms with O, S, Se and Te were also reviewed in this connection and table 4 presents the comparative data. If one plots $\omega_e''^{-2}$ values versus electron numbers straight lines are obtained for such of these molecular group vide figure 3. According to this trend in the group wise behaviour of molecular constants one can safely expect the ω_e'' value for MnTe to be around 280 (cm^{-1}).

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References

- [1] A Monjajeb, '*Electronic spectra of certain transient gaseous diatomics at high temperature*'
D. Phil Thesis, University of Allahabad, Allahabad, India, (1973)
- [2] K N Uttam, R Gopal and M M Joshi, *Indian J. Phys.* **B67**, 183 (1993)
- [3] M N Saha, N K Sur and K Majumdar, *Z. Phys.* **40**, 648 (1927)
- [4] G Herzberg, *Molecular spectra and molecular structure* (Spectra of Diatomic Molecules,
D Van Nostrand Company, New York, 1950) Vol. I pp 151
- [5] K P Huber and G Herzberg, *Molecular spectra and molecular structure* (Constants of
Diatomic Molecules, D Van Nostrand Company, New York, 1979) Vol. IV
- [6] H G Howell, *Proc. R. Soc. (London)*, **A153**, 683 (1936)