

## Vibrational analysis of Fourier transform spectrum of the $B^3\Sigma_u^-(0_u^+)-X^3\Sigma_g^-(0_g^+)$ transition of $^{80}\text{Se}_2$ molecule

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**Abstract.** The emission spectra of  $B^3\Sigma_u^-(0_u^+)-X^3\Sigma_g^-(0_g^+)$  transition of the isotopic species  $^{80}\text{Se}_2$ , excited in an electrodeless discharge lamp by the microwave, was recorded on BOMEM DA8 Fourier transform spectrometer at an apodized resolution of  $0.035\text{ cm}^{-1}$ . Vibrational constants were improved by putting the wave number of band origins in Deslandre table. The vibrational analysis was supported by determining the Franck–Condon factor and  $r$ -centroid values.

**Keywords.** Fourier transform spectroscopy; electronic spectrum of selenium dimer; vibrational analysis; Franck–Condon factor;  $r$ -centroid values.

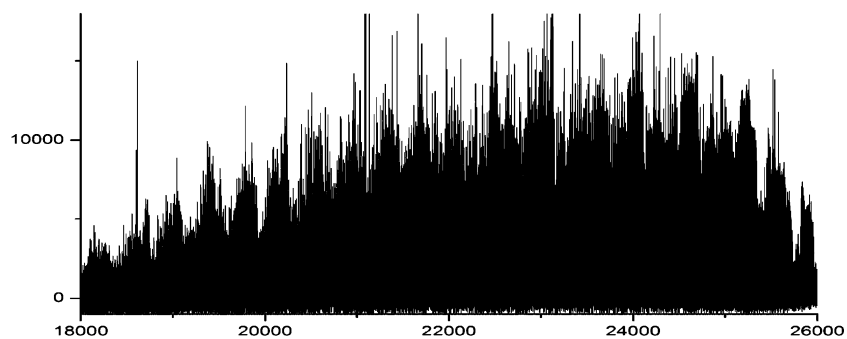
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### 1. Introduction

The electronic spectra of  $\text{O}_2$ ,  $\text{S}_2$ ,  $\text{Se}_2$  and  $\text{Te}_2$  dimers were investigated by several workers [1–25]. In all these molecules, the strongest band system  $B^3\Sigma_u^- - X^3\Sigma_g^-$  is allowed by electric dipole transition, viz. Schumann–Runge system of  $\text{O}_2$  molecule lying in the  $\lambda\lambda$  1750–5350 Å region, the  $\lambda\lambda$  2400–7000 Å region band system of  $\text{S}_2$ , the  $\lambda\lambda$  3250–6400 Å region band system of  $\text{Se}_2$  and the visible band system  $\lambda\lambda$  4250–6300 Å of  $\text{Te}_2$ . The ground state, the low-lying valence states and the Rydberg states were characterized for  $\text{O}_2$  and  $\text{S}_2$ . But for heavier molecules like  $\text{Se}_2$  and  $\text{Te}_2$ , information about the valence and Rydberg states is not very extensive. This is probably because in heavier molecules, the spin-orbit interaction becomes important and the spectra become very complex.

Barrow *et al* [5] recorded for the first time the bands of  $B^3\Sigma_u^- - X^3\Sigma_g^-$  system of both isotopes of selenium ( $^{80}\text{Se}_2$  and  $^{78}\text{Se}_2$ ) in absorption as well as in emission and performed vibrational analysis. In addition, they reported rotational analyses of many bands of both isotopes and concluded that the band system arose from  $0_u^+ - 0_g^+$  and  $1_u - 1_g$  components of a  $B^3\Sigma_u^- - X^3\Sigma_g^-$  transition in Hund's case 'c'. The observed bands were assigned to two subsystems, viz.  $B0_u^+ - X0_g^+$  and  $B1_u - X1_g$ . But, they reported only a few bands of  $B1_u - X1_g$  subsystem. Perturbations, diffuseness and pre-dissociation were observed in the band systems, but the nature of perturbing states was not characterized unambiguously. Later, from the observation of  $B0_u^+ - X0_g^+$  and  $B1_u - X1_g$  transitions in the resonance spectra of  $\text{Se}_2$  [8], lambda ( $\Lambda$ ) doubling was obtained for the  $X(2\lambda = 512.9 \pm 2 \text{ cm}^{-1})$  and  $B(2\lambda = 78.4 \pm 2 \text{ cm}^{-1})$  states. Jenouvrier [18] reported perturbation analyses and suggested that two electronic states, viz.  $A^3\Pi(1_u)$  and  $A^1\Pi(1_u)$ , were responsible for the perturbations and pre-dissociations in the upper state  $B$ . The study of laser-induced fluorescence and chemiluminescence spectra of selenium molecule [12,16,17] revealed the existence of  $A0_u^+$ ,  $b^1\Sigma_g^+$  and  $a^1\Delta$  states of  $\text{Se}_2$ . Balsubramanian [19] theoretically studied low-lying states of  $\text{Se}_2$  molecule. Recently, Saraswathy and Sunanda [25] have studied vibronic intensity distribution in the  $B0_u^+ - X0_g^+$  and  $B1_u - X1_g$  transitions and reported several new bands especially for the  $B1_u - X1_g$  system. Their vibrational assignments were supported by isotopic shift studies, Franck-Condon factors and  $r$ -centroid values. Later, Chakraborty and Pan [26] summarized different methods of calculation of Franck-Condon factors using spectroscopic constants.

The scrutiny of available literature about  $\text{Se}_2$  molecule reveals that different workers have reported different constants for different systems for the ground state as well as band-head data. In addition, the high resolution study of isovalent molecule  $\text{S}_2$  by Lindner *et al* [27] has yielded fruitful information. Because of the additional advantages of Fourier transform spectrometer such as fast scanning rate, low signal-to-noise ratio, free from stray light, high resolution and high sensitivity, it has been decided to investigate the spectra of  $^{80}\text{Se}_2$  molecule using Fourier transform spectrometer and microwave excitation technique in electrodeless discharge lamp.



**Figure 1.** Gross structure of FT high resolution spectrum of  $^{80}\text{Se}_2$  molecule.

$B^3\Sigma_u^-(0_u^+) - X^3\Sigma_g^-(0_g^+)$  transition of  $^{80}\text{Se}_2$  molecule

Natural selenium consists of five isotopes, namely,  $^{74}\text{Se}$ ,  $^{76}\text{Se}$ ,  $^{77}\text{Se}$ ,  $^{78}\text{Se}$  and  $^{80}\text{Se}$  with the abundance of 0.87%, 9.02%, 7.58%, 25.5% and 49.82% respectively. The isotope  $^{80}\text{Se}$  has the largest abundance, and so it will produce the most intense spectrum. In this paper, authors present the Fourier transform (FT) high-resolution spectrum of  $^{80}\text{Se}_2$  molecule excited by microwave in electrodeless discharge lamp. The vibrational constants of the  $B0_u^+ - X0_g^+$  system were improved using band-origin data obtained from the rotational analysis of  $^{80}\text{Se}_2$  molecule. This analysis was further supported by determining Franck Condon factor and  $r$ -centroid values.

## 2. Experimental details

The emission spectra of  $\text{Se}_2$  molecule was produced in a sealed electrodeless discharge lamp (EDL) made of quartz, about 5–6 cm long and with 6 mm internal diameter. The

**Table 1.** Band origin data of the  $B0_u^+ - X0_g^+$  subsystem of the  $\text{Se}_2$  molecule.

$(v', v'')$	$\nu_{\text{obs}} (\text{cm}^{-1})$	$\nu_{\text{cal}} (\text{cm}^{-1})$	$\Delta\nu (\text{cm}^{-1})$
(3, 3)	25,492.979	25,492.885	+0.094
(4, 3)	25,730.762	25,730.769	-0.007
(5, 3)	25,966.488	25,966.482	+0.006
(3, 4)	25,115.440	25,115.336	+0.104
(4, 4)	25,353.222	25,353.220	+0.002
(5, 4)	25,588.948	25,588.933	+0.015
(6, 4)	25,822.451	25,822.459	-0.008
(2, 5)	24,499.713	24,499.711	+0.002
(3, 5)	24,739.435	24,739.749	-0.014
(4, 5)	24,977.626	24,977.633	-0.007
(2, 6)	24,126.096	24,126.088	+0.008
(3, 6)	24,366.227	24,366.127	+0.100
(0, 7)	23,267.959	23,267.957	+0.002
(1, 7)	23,512.257	23,512.256	+0.001
(2, 7)	23,754.437	23,754.432	+0.005
(0, 8)	22,898.266	22,898.270	-0.004
(1, 8)	23,142.564	23,142.568	-0.004
(2, 8)	23,384.743	23,384.745	-0.002
(0, 9)	22,530.558	22,530.553	+0.005
(1, 9)	22,774.855	22,774.852	+0.003
(0, 10)	22,164.809	22,164.810	-0.001
(1, 10)	22,409.107	22,409.108	-0.001
(0, 11)	21,801.039	21,801.042	-0.003
(2, 11)	22,287.517	22,287.517	0.000
(0, 12)	21,439.248	21,439.251	-0.002
(2, 12)	21,925.726	21,925.727	-0.001
(0, 13)	21,079.441	21,079.441	+0.000
(2, 13)	21,565.919	21,565.916	+0.003

**Table 2.** Comparison of vibrational constants ( $\text{cm}^{-1}$ ) of  $^{80}\text{Se}_2$  molecule.

Workers	$\omega'_e$	$\omega_e x'_e$	$\omega_e y'_e \times 10^{-3}$	$\omega''_e$	$\omega_e x''_e$	$\omega_e y''_e \times 10^{-3}$
Barrow <i>et al</i> [5]	246.291	1.016	-5.490	385.303	0.9663	-0.818
Sunanda <i>et al</i> [26]	246.291	1.016	-7.800	385.303	0.9776	-0.680
Present findings	246.405	1.049	-2.718	385.374	0.9759	-0.374

quartz tube was evacuated and baked (degassed) well and finally filled with isotopically-rich  $^{80}\text{Se}$  (99.8%) and argon gas at a pressure of about 2–5 mm of mercury. The EDL was excited by microwave (2450 MHz) at a power of 150 W such that the bands were sufficiently intense to be observed. The glow was focussed onto the emission port of the Fourier transform spectrometer using a spherical lens. The spectra were recorded in the region 18,000–26,000  $\text{cm}^{-1}$  on BOMEM DA8 Fourier transform spectrometer at an apodized resolution of 0.035  $\text{cm}^{-1}$  using a quartz UV beam splitter, photomultiplier

**Table 3.** Calculated values of the Franck–Condon factor (FCF) for the  $\text{Se}_2$  molecule:  $B^3\Sigma_u^-(0_u^+) - X^3\Sigma_g^-(0_g^+)$  subsystem.

$v'/v''$	0	1	2	3	4	5	6	7	8
0	0.0000	0.0000	0.0002	0.0010	0.0036	0.0102	0.0235	0.0450	0.0733
1	0.0000	0.0002	0.0015	0.0063	0.0184	0.0407	0.0695	0.0926	0.0952
2	0.0001	0.0011	0.0059	0.0200	0.0456	0.0743	0.0853	0.0646	0.0250
3	0.0004	0.0035	0.0157	0.0417	0.0708	0.0773	0.0474	0.0085	0.0037
4	0.0010	0.0087	0.0311	0.0631	0.0741	0.0441	0.0052	0.0081	0.0417
5	0.0025	0.0174	0.0492	0.0724	0.0508	0.0081	0.0067	0.0403	0.0403
6	0.0053	0.0296	0.0639	0.0628	0.0185	0.0019	0.0342	0.0396	0.0062
7	0.0098	0.0436	0.0692	0.0389	0.0006	0.0223	0.0419	0.0106	0.0055
8	0.0162	0.0568	0.0622	0.0139	0.0066	0.0399	0.0211	0.0009	0.0298
9	0.0247	0.0660	0.0450	0.0007	0.0254	0.0349	0.0015	0.0192	0.0305
10	0.0347	0.0686	0.0241	0.0040	0.0383	0.0148	0.0053	0.0326	0.0087
11	0.0457	0.0637	0.0074	0.0183	0.0348	0.0008	0.0229	0.0220	0.0006
12	0.0565	0.0523	0.0001	0.0327	0.0192	0.0044	0.0310	0.0040	0.0149
13	0.0663	0.0370	0.0035	0.0381	0.0043	0.0189	0.0212	0.0015	0.0268
14	0.0740	0.0213	0.0144	0.0320	0.0003	0.0292	0.0056	0.0145	0.0193
15	0.0789	0.0086	0.0271	0.0189	0.0081	0.0263	0.0001	0.0251	0.0042
16	0.0807	0.0013	0.0364	0.0061	0.0205	0.0139	0.0083	0.0213	0.0007
17	0.0794	0.0004	0.0388	0.0001	0.0284	0.0025	0.0202	0.0083	0.0110
18	0.0756	0.0054	0.0341	0.0030	0.0270	0.0006	0.0245	0.0002	0.0212
19	0.0701	0.0152	0.0244	0.0129	0.0178	0.0085	0.0178	0.0042	0.0196
20	0.0635	0.0282	0.0129	0.0251	0.0065	0.0202	0.0063	0.0158	0.0083

$B^3\Sigma_u^-(0_u^+) - X^3\Sigma_g^-(0_g^+)$  transition of  $^{80}\text{Se}_2$  molecule

detector and appropriate filter. A total of 191 scans were co-added to get good  $S/N$  ratio.

### 3. Results and discussion

The high-resolution Fourier transform spectrum of  $^{80}\text{Se}_2$  molecule was recorded in the spectral region 18,000–26,000  $\text{cm}^{-1}$ . The gross structure of FT spectrum of  $^{80}\text{Se}_2$  is shown in figure 1. The observed bands were classified into a single system  $B^3\Sigma_u^- - X^3\Sigma_g^-$ . As selenium diatomic is a heavier molecule, spin-orbit interaction becomes important and Hund's coupling case 'c' holds. The  $B^3\Sigma_u^- - X^3\Sigma_g^-$  system was divided into two subsystems:  $B0_u^+ - X0_g^+$  and  $B1_u - X1_g$ . A total of 155 bands were recorded in which 103 bands belonged to  $B0_u^+ - X0_g^+$  subsystem, whereas 52 bands were attributed to  $B1_u - X1_g$  subsystem. The vibrational assignments proposed by Saraswathy and Sunanda [25] were found to be correct. It could be seen that the  $B0_u^+ - X0_g^+$  subsystem was stronger than the  $B1_u - X1_g$  subsystem. We could analyse rotational structure of 28 bands of the

**Table 4.** Calculated values of the Franck–Condon factor (FCF) for the  $\text{Se}_2$  molecule:  $B^3\Sigma_u^-(0_u^+) - X^3\Sigma_g^-(0_g^+)$  subsystem.

$v'/v''$	9	10	11	12	13	14	15	16	17
0	0.1031	0.1265	0.1370	0.1317	0.1133	0.0876	0.0612	0.0388	0.0223
1	0.0717	0.0340	0.0050	0.0029	0.0284	0.0656	0.0948	0.1041	0.0937
2	0.0006	0.0131	0.0474	0.0667	0.0516	0.0185	0.0001	0.0135	0.0485
3	0.0348	0.0564	0.0379	0.0059	0.0048	0.0357	0.0584	0.0457	0.0142
4	0.0470	0.0150	0.0009	0.0277	0.0488	0.0293	0.0019	0.0105	0.0428
5	0.0069	0.0065	0.0376	0.0365	0.0060	0.0063	0.0368	0.0410	0.0121
6	0.0084	0.0379	0.0260	0.0003	0.0185	0.0396	0.0179	0.0002	0.0239
7	0.0352	0.0227	0.0000	0.0233	0.0336	0.0058	0.0075	0.0350	0.0251
8	0.0251	0.0000	0.0222	0.0298	0.0024	0.0132	0.0336	0.0110	0.0030
9	0.0016	0.0168	0.0294	0.0025	0.0137	0.0305	0.0055	0.0083	0.0318
10	0.0081	0.0300	0.0055	0.0100	0.0289	0.0048	0.0098	0.0294	0.0068
11	0.0266	0.0128	0.0040	0.0276	0.0074	0.0075	0.0275	0.0053	0.0089
12	0.0230	0.0000	0.0229	0.0135	0.0030	0.0258	0.0070	0.0075	0.0261
13	0.0051	0.0122	0.0215	0.0000	0.0216	0.0119	0.0036	0.0247	0.0050
14	0.0012	0.0243	0.0040	0.0125	0.0189	0.0002	0.0218	0.0087	0.0057
15	0.0143	0.0160	0.0022	0.0227	0.0020	0.0147	0.0151	0.0014	0.0222
16	0.0231	0.0019	0.0161	0.0115	0.0046	0.0206	0.0003	0.0176	0.0101
17	0.0158	0.0028	0.0208	0.0001	0.0185	0.0063	0.0088	0.0169	0.0004
18	0.0031	0.0151	0.0095	0.0069	0.0168	0.0007	0.0196	0.0018	0.0140
19	0.0009	0.0206	0.0001	0.0187	0.0033	0.0128	0.0105	0.0047	0.0177
20	0.0112	0.0119	0.0062	0.0160	0.0017	0.0189	0.0000	0.0180	0.0034

$B0_u^+ - X0_g^+$  subsystem which were 5-3, 6-4, 4-3, 5-4, 3-3, 4-4, 3-4, 4-5, 3-5, 2-5, 3-6, 2-6, 2-7, 1-7, 2-8, 0-7, 1-8, 0-8, 1-9, 0-9, 2-11, 0-10, 0-11, 2-12, 2-13, 0-12, 1-10 and 0-13. The vibrational constants were improved using band-origin measurements and Deslandre's table. The band origins were determined by generating  $R_0$  and  $P_1$  values in each band by interpolation and then taking the average [28]. The wave number of band origins of all the observed bands were fitted simultaneously by means of least square fit computer programme. We could report  $\omega_e x'_e$  and  $\omega_e y''_e$  values for the two states accurately due to high resolution data. The vibrational constants thus obtained are given below:

$$\begin{aligned} \nu_{00} &= 25980.270 \pm 0.038 \text{ cm}^{-1} \\ \omega'_e &= 246.405 \pm 0.008, \quad \omega_e x'_e = 1.0487 \pm 0.0034, \\ \omega_e y'_e &= -0.002718 \pm 0.00034 \text{ cm}^{-1} \\ \omega''_e &= 385.374 \pm 0.014, \quad \omega_e x''_e = 0.9759 \pm 0.0016, \\ \omega_e y''_e &= -0.00374 \pm 0.00062 \text{ cm}^{-1}. \end{aligned}$$

**Table 5.** Calculated values of the Franck–Condon factor (FCF) for the  $\text{Se}_2$  molecule:  $B^3\Sigma_u^-(0_u^+) - X^3\Sigma_g^-(0_g^+)$  subsystem.

$v'/v''$	18	19	20	21	22	23	24	25
0	0.0117	0.0056	0.0025	0.0010	0.0004	0.0001	0.0000	0.0000
1	0.0719	0.0481	0.0284	0.0150	0.0071	0.0031	0.0012	0.0004
2	0.0813	0.0948	0.0868	0.0660	0.0430	0.0245	0.0123	0.0055
3	0.0001	0.0188	0.0552	0.0834	0.0894	0.0756	0.0532	0.0320
4	0.0538	0.0303	0.0034	0.0057	0.0366	0.0710	0.0868	0.0797
5	0.0013	0.0277	0.0515	0.0394	0.0097	0.0012	0.0257	0.0618
6	0.0423	0.0206	0.0000	0.0183	0.0470	0.0432	0.0141	0.0002
7	0.0006	0.0160	0.0402	0.0251	0.0008	0.0137	0.0436	0.0440
8	0.0303	0.0279	0.0019	0.0122	0.0381	0.0264	0.0013	0.0122
9	0.0135	0.0016	0.0276	0.0281	0.0023	0.0114	0.0371	0.0255
10	0.0067	0.0303	0.0135	0.0016	0.0271	0.0267	0.0017	0.0126
11	0.0281	0.0062	0.0072	0.0295	0.0115	0.0024	0.0280	0.0239
12	0.0041	0.0101	0.0268	0.0043	0.0093	0.0289	0.0083	0.0046
13	0.0092	0.0244	0.0022	0.0128	0.0247	0.0019	0.0130	0.0273
14	0.0235	0.0024	0.0125	0.0217	0.0004	0.0168	0.0211	0.0002
15	0.0049	0.0094	0.0211	0.0004	0.0168	0.0173	0.0002	0.0210
16	0.0044	0.0213	0.0014	0.0141	0.0166	0.0003	0.0207	0.0114
17	0.0199	0.0047	0.0093	0.0181	0.0000	0.0188	0.0104	0.0033
18	0.0110	0.0035	0.0196	0.0007	0.0152	0.0121	0.0022	0.0211
19	0.0000	0.0183	0.0044	0.0097	0.0155	0.0005	0.0196	0.0050
20	0.0120	0.0114	0.0035	0.0186	0.0002	0.0170	0.0078	0.0060

$B^3\Sigma_u^-(0_u^+) - X^3\Sigma_g^-(0_g^+)$  transition of  $^{80}\text{Se}_2$  molecule

The observed wave numbers of the band origin along with their vibrational assignments are listed in table 1. The determined constants are in close agreement with the earlier reported values [5,25]. Difference in the values of the vibrational constants is perhaps, due to the band origins generated by FT-data and not due to the band-head values. The comparison between the reported and obtained vibrational constants in the present study is given in table 2. The analysis is also supported by calculating the Franck–Condon factor (FCF) and  $r$ -centroid values of  $^{80}\text{Se}_2$  molecule. The ‘TRAPRB’ programme developed by Jarman and McCallum [29] has been used to compute FCF and  $r$ -centroid values using the presently determined spectroscopic constants and rotational constants reported by Tandon [28]. The calculated values of Franck–Condon factor (FCF) and  $r$ -centroid values are shown in tables 3–8. The plot of the ground state vibrational frequency ( $\omega_e$ ) and  $1/r_e\sqrt{\mu}$  for the  $\text{O}_2$ ,  $\text{S}_2$ ,  $\text{Se}_2$  and  $\text{Te}_2$  molecules [11] is a straight line (figure 2) which shows the accuracy of the determined constants. This is also in agreement with the criteria suggested by Zavitas [30]. The plot of wave number for  $\Delta v = 0$  sequence against the corresponding  $r$ -centroid values is found to be a straight line (figure 3) except for a few

**Table 6.** Calculated values of the  $r$ -centroid for the  $\text{Se}_2$  molecule:  $B^3\Sigma_u^-(0_u^+) - X^3\Sigma_g^-(0_g^+)$  subsystem.

$v'/v''$	0	1	2	3	4	5	6	7	8
0	2.2997	2.3123	2.3048	2.3075	2.3003	2.3633	2.3164	2.3297	2.3431
1	2.2917	2.3041	2.3165	2.3290	2.3417	2.3545	2.3674	2.3804	2.3936
2	2.2837	2.2961	2.3083	2.3207	2.3332	2.3458	2.3585	2.3712	2.3837
3	2.2760	2.2882	2.3003	2.3126	2.3249	2.3373	2.3496	2.3610	2.3793
4	2.2683	2.2805	2.2925	2.3046	2.3167	2.3287	2.3394	2.3566	2.3679
5	2.2608	2.2729	2.2848	2.2968	2.3086	2.3195	2.3359	2.3468	2.3587
6	2.2534	2.2654	2.2772	2.2890	2.3003	2.3173	2.3263	2.3380	2.3484
7	2.2461	2.2581	2.2698	2.2814	2.2880	2.3066	2.3180	2.3287	2.3456
8	2.2390	2.2509	2.2725	2.2736	2.2879	2.2985	2.3096	2.3292	2.3356
9	2.2319	2.2438	2.2553	2.2632	2.2796	2.2907	2.2986	2.3161	2.3270
10	2.2249	2.2368	2.2482	2.2616	2.2721	2.2829	2.2978	2.3078	2.3180
11	2.2180	2.2299	2.2411	2.2538	2.2648	2.2719	2.2891	2.2998	2.3208
12	2.2112	2.2232	2.2321	2.2467	2.2576	2.2716	2.2815	2.2909	2.3064
13	2.2044	2.2166	2.2283	2.2398	2.2500	2.2635	2.2741	2.2904	2.2983
14	2.1977	2.2102	2.2215	2.2332	2.2497	2.2564	2.2662	2.2804	2.2906
15	2.1911	2.2043	2.2149	2.2268	2.2389	2.2496	2.2722	2.2729	2.2821
16	2.1845	2.2007	2.2085	2.2209	2.2321	2.2429	2.2560	2.2658	2.2836
17	2.1779	2.1806	2.2022	2.2227	2.2257	2.2360	2.2489	2.2585	2.2723
18	2.1713	2.1806	2.1960	2.2048	2.2196	2.2318	2.2423	2.2427	2.2651
19	2.1646	2.1750	2.1899	2.1995	2.2139	2.2245	2.2361	2.2493	2.2582
20	2.1578	2.1688	2.1841	2.1933	2.2093	2.2181	2.2303	2.2419	2.2509

bands. This deviation may be due to the fluctuation in intensity of the observed bands as explained by Saraswathy and Sunanda [25].

The study of the calculated FC factors for each progression reveals that there is a gradual rise and fall in the FCF values. But, exact nature of the values depends on the relative positions of the potential energy curves of the ground and upper states. In fact there should be two values of FCFs in a row and the loci of such points which represent the Condon parabola. But in many cases, for e.g.,  $^{80}\text{Se}_2$ , it so happens that the minima of the potential energy curves of the upper and lower states are largely shifted ( $r'_e = 2.45 \text{ \AA}$ ;  $r''_e = 2.17 \text{ \AA}$ ). In such a case, in emission the FCF overlap is appreciable only from one end of the potential curve. Also, for these systems  $\Delta v = 0$  is usually not the strongest. Also it can be seen that the sequences  $\Delta v = 1, 2, 4, 5, \dots$  are not the strongest even if two maxima are observed in higher sequences.

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**Table 7.** Calculated values of the  $r$ -centroid for the  $\text{Se}_2$  molecule:  $B^3\Sigma_u^-(0_u^+)-X^3\Sigma_g^-(0_g^+)$  subsystem.

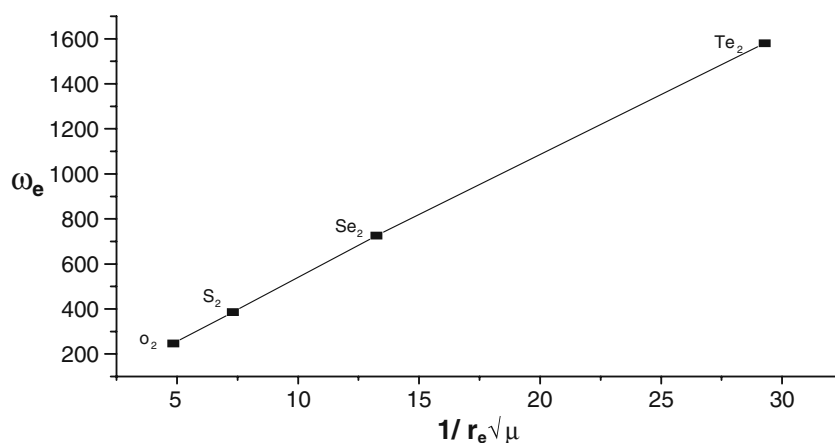
$v'/v''$	9	10	11	12	13	14	15	16	17
0	2.3168	2.3306	2.3447	2.3589	2.4734	2.4881	2.5030	2.5181	2.5335
1	2.4069	2.4202	2.4321	2.4531	2.4646	2.4786	2.4931	2.5079	2.5230
2	2.3894	2.4134	2.4261	2.4395	2.4531	2.4665	2.4605	2.4995	2.5133
3	2.3900	2.4027	2.4156	2.4270	2.4476	2.4591	2.4727	2.4866	2.5000
4	2.3803	2.3922	2.4153	2.4218	2.4346	2.4476	2.4566	2.4797	2.4924
5	2.3695	2.3879	2.3988	2.4112	2.4222	2.4425	2.4538	2.4670	2.4795
6	2.3659	2.3769	2.3888	2.3882	2.4179	2.4300	2.4422	2.4777	2.4734
7	2.3558	2.3673	2.4502	2.3954	2.4072	2.4177	2.4378	2.4489	2.4615
8	2.3468	2.3175	2.3740	2.3854	2.3936	2.4143	2.4258	2.4371	2.4587
9	2.3342	2.3535	2.3645	2.3726	2.3924	2.4036	2.4135	2.4335	2.4444
10	2.3343	2.3444	2.3539	2.3718	2.3823	2.3917	2.4110	2.4218	2.4321
11	2.3250	2.3353	2.3530	2.3619	2.3717	2.3900	2.4002	2.4097	2.4295
12	2.3168	2.3885	2.3423	2.3525	2.3713	2.3794	2.3892	2.4081	2.4182
13	2.3076	2.3236	2.3337	2.4294	2.3596	2.3696	2.3886	2.3971	2.4063
14	2.3084	2.3152	2.3238	2.3407	2.3506	2.3813	2.3770	2.3867	2.4055
15	2.2971	2.3071	2.3245	2.3320	2.3387	2.3578	2.3676	2.3889	2.3944
16	2.2894	2.2970	2.3139	2.3235	2.3403	2.3488	2.3447	2.3748	2.3844
17	2.2820	2.2976	2.3060	2.3004	2.3306	2.3394	2.3564	2.3657	2.3941
18	2.2733	2.2885	2.2981	2.3133	2.3225	2.3446	2.3473	2.3529	2.3730
19	2.2757	2.2811	2.2767	2.3049	2.3131	2.3295	2.3384	2.3558	2.3638
20	2.2648	2.2734	2.2880	2.2970	2.3139	2.3212	2.2849	2.3457	2.3524



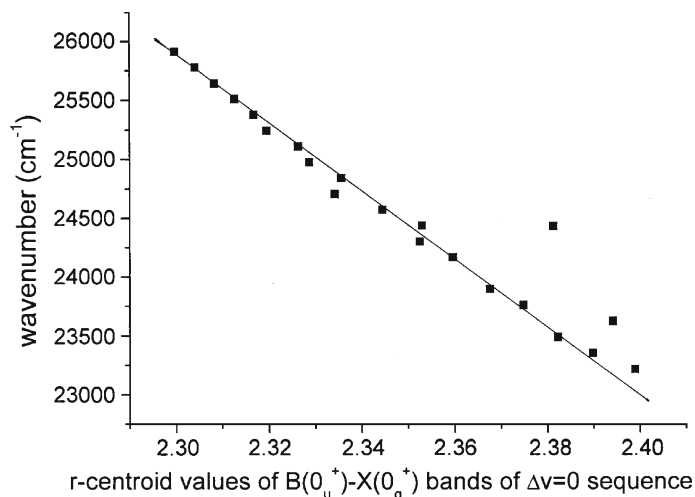
$B^3\Sigma_u^-(0_u^+) - X^3\Sigma_g^-(0_g^+)$  transition of  $^{80}\text{Se}_2$  molecule

**Table 8.** Calculated values of the  $r$ -centroid for the  $\text{Se}_2$  molecule:  $B^3\Sigma_u^-(0_u^+) - X^3\Sigma_g^-(0_g^+)$  subsystem.

$v'/v''$	18	19	20	21	22	23	24	25
0	2.5492	2.5651	2.5812	2.5977	2.6144	2.6314	2.6488	2.6664
1	2.5383	2.5539	2.5698	2.5860	2.6024	2.6191	2.6362	2.6535
2	2.5281	2.5433	2.5588	2.5747	2.5908	2.6072	2.6239	2.6409
3	2.5456	2.5342	2.5486	2.5639	2.5796	2.5957	2.6121	2.6288
4	2.5065	2.5206	2.5321	2.5564	2.5695	2.5848	2.6008	2.6171
5	2.5049	2.5126	2.5265	2.5409	2.5543	2.5821	2.5908	2.6061
6	2.4864	2.4996	2.4651	2.5330	2.5468	2.5614	2.5754	2.6206
7	2.4637	2.4932	2.5061	2.5195	2.5242	2.5537	2.5673	2.5821
8	2.4680	2.4807	2.4885	2.5133	2.5259	2.5395	2.5465	2.5745
9	2.4560	2.4801	2.4873	2.5000	2.5085	2.5333	2.5459	2.5596
10	2.4525	2.4632	2.4749	2.4998	2.5067	2.5195	2.5267	2.5532
11	2.4402	2.4503	2.4713	2.4821	2.4937	2.5177	2.5262	2.5391
12	2.4272	2.4478	2.4587	2.4680	2.4899	2.5012	2.5124	2.5356
13	2.4259	2.4363	2.4434	2.4661	2.4773	2.4840	2.5086	2.5204
14	2.4149	2.4222	2.4437	2.4545	2.4520	2.4845	2.4960	2.4844
15	2.4031	2.4226	2.4327	2.4301	2.4618	2.4727	2.5162	2.5032
16	2.4034	2.4119	2.4169	2.4402	2.4506	2.4861	2.4801	2.4908
17	2.3920	2.4004	2.4198	2.4295	2.5866	2.4581	2.4683	2.4906
18	2.3823	2.4016	2.4093	2.4105	2.4370	2.4469	2.4693	2.4762
19	2.4325	2.3898	2.3979	2.4172	2.4264	2.4558	2.4545	2.4634
20	2.3710	2.3799	2.3989	2.4066	2.3924	2.4338	2.4427	2.4630



**Figure 2.** Plot between ground state vibrational frequency ( $\omega_e''$ ) and  $1/r_e \sqrt{\mu}$  for  $\text{O}_2$ ,  $\text{S}_2$ ,  $\text{Se}_2$  and  $\text{Te}_2$  molecules.



**Figure 3.** Plot between wave number of the band-heads and  $r$ -centroid values.

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