

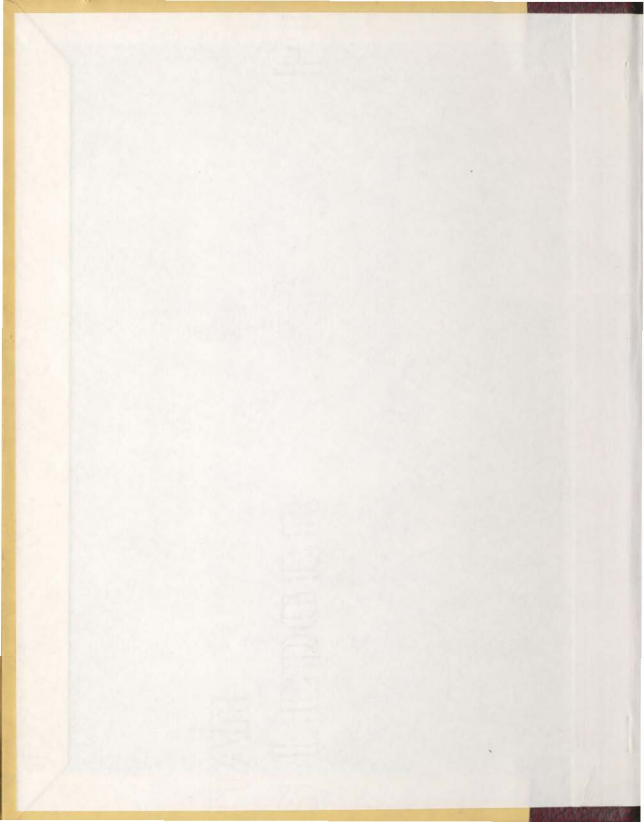
THE NEW EMISSION SPECTRUM OF SELENIUM MONOXIDE IN
THE REGION 3185 - 2690 Å

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THE NEW EMISSION SPECTRUM OF SELENIUM MONOXIDE IN
THE REGION 3185 - 2690 Å

by

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Submitted in partial fulfilment of the
requirements for the degree of Master of Science,
Memorial University of Newfoundland

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ABSTRACT

The emission spectrum of SeO excited in an electrodeless discharge tube containing selenium dioxide powder by a high power microwave generator revealed the existence of a new band system in the region 3185 - 2690 Å consisting of 48 bands degraded to longer wavelengths. The vibrational analysis suggests that the bands arise from the transition $C(^3\Pi) - X^3\Sigma^-$ (the states designated as C and D in earlier work by Reddy and Azam (1974) are hereafter to be referred to as D and E, respectively). Sub-systems, $C(^3\Pi_0) - X^3\Sigma^- (F_2, F_3)$, $C(^3\Pi_0) - X^3\Sigma^- (F_1)$, $C(^3\Pi_1) - X^3\Sigma^- (F_2)$, $C(^3\Pi_1) - X^3\Sigma^- (F_1)$ and $C(^3\Pi_2) - X^3\Sigma^- (F_1)$ of C-X have been identified. The separations between the band heads having the same vibrational assignments (v' , v'') with a common upper electronic substate are consistent with the expected value of $\sim 2\lambda$, $\lambda (= 86.4 \text{ cm}^{-1})$ being the spin-splitting constant of the $X^3\Sigma^-$ state known from earlier work (Barrow and Deutsch, 1963; Azam and Reddy, 1973). Derived constants (in cm^{-1}) of state C are as follows:

	T_e	ω_e	$\omega_e X_e$
$^3\Pi_2$	35312	582	3.7
$^3\Pi_1$	35237	585	4.0
$^3\Pi_0$	35150	581	3.5

In addition, 8 new emission bands of SeO degraded to longer wavelengths in the region 3040 - 2805 Å have been fitted into the vibrational scheme of the previously known $B^3\Sigma - X^3\Sigma^-$ system.

Finally, Morse potential curves have been drawn for several known electronic states of SeO.

CHAPTER I

INTRODUCTION

1.1 Electronic Spectra of the Analogous Molecules of O_2 , SO and SeO:

The electrons in the outermost shells of the constituent atoms of a molecule chiefly determine the type of molecular binding and the nature of the molecular states. In general, molecules having the same number of electrons in the outermost shells are expected, within the first approximation, to have similar electronic spectra. In particular, the analogous molecules O_2 , SO and SeO are expected to have similar electronic states because the outermost shells of each of the atoms O, S and Se contain four p-electrons. The electronic states of O_2 differ from those of SO and SeO at least in two respects: (i) because of the symmetry of the nuclei in O_2 , its electronic states are either even (g) or odd (u); (ii) since the oxygen nucleus has zero spin, the O_2 has only symmetric rotational levels. Even though the outermost electrons play a major role in determining the molecular properties mentioned above, the inner electrons and the masses of the nuclei are also of considerable importance. In fact, the relative positions of the electronic states and the nature of the coupling between electronic motion (orbital motion as well as spin) and the rotation of the nuclei are dependent to a considerable extent on the electrons of the inner shells. A detailed study of the electronic spectra of analogous molecules makes it possible for one to determine the nature of the coupling between the electronic motion and rotation of the nuclei in their various electronic states and to obtain a proper correlation between these states.

Extensive investigations have been carried out on the electronic band spectrum of O_2 . The number of electronic states for O_2 is at least 10 which have given rise to 14 band systems (see Rosen, 1970; p. 423). The ground electronic state is the common lower state for 9 of these band systems. Also, a number of Rydberg transitions (cf. Rosen 1970) and several double electronic transitions (see Findlay, 1970) have been observed for O_2 .

For SO , three electronic band systems all with a common lower (ground) state have been observed and its structure in all the four electronic states has been determined (Colin, 1968, 1969).

A general spectroscopic study of the electronic spectrum of SeO in emission has been recently initiated in our laboratory and some experimental results have already been published on this spectrum (see Azam and Reddy, 1973, and Reddy and Azam, 1974; also see section 1.2 in this thesis). The results presented in this thesis on the emission spectrum of SeO in the region $3185 - 2690 \text{ \AA}$ form a part of this systematic study.

1.2 Previous Work on the Electronic Band Spectrum of SeO :

(i) The Extensive $B^3\Sigma^- - X^3\Sigma^-$ System in the Region $5100 - 3100 \text{ \AA}$:

Asundi, Jan-Khan and Samuel (1936) observed 14 characteristic emission bands of SeO degraded to longer wavelengths in the region $3950 - 3230 \text{ \AA}$ by introducing SeO_2 powder in a bunsen flame and gave a tentative vibrational analysis of these bands. Later, Choong-Shin Piaw (1938) excited the spectrum of SeO in a high voltage transformer discharge tube by passing a slow stream of oxygen over heated selenium. He photographed 20 double-headed bands degraded to longer wavelengths in the region $3950 - 3100 \text{ \AA}$ and analyzed them into two systems. Subsequently, Barrow and Deutsch (1963) excited the emission spectrum of SeO in a radio-frequency discharge

through selenium vapour and oxygen and photographed it under high resolution. These authors have carried out the rotational analysis of 9 bands and designated the system as $A^3\Sigma^- - X^3\Sigma^-$, which was later referred to as $B^3\Sigma^- - X^3\Sigma^-$ by Azam and Reddy (1973) because this system is analogous to the system $B^3\Sigma^- - X^3\Sigma^-$ in O_2 as well as in SO . The spin-spin interaction constants λ'' and λ' of the $X^3\Sigma^-$ and $B^3\Sigma^-$ states, respectively, were found by Barrow and Deutsch (1963) to be very large. The double-headed nature of the bands was explained on the basis of the splitting of each band (v', v'') into three sub-bands, two of which arise from $F_2 - F_2$ and $F_3 - F_3$ transitions that lie close together, and one of which arises from $F_1 - F_1$ transitions which are separated by an amount $\sim 2(\lambda' - \lambda'')$ from the former. Haranath (1965) photographed 25 additional double-headed bands of the B-X system of SeO in the region 5100 - 3900 Å and assigned vibrational quantum numbers to them. These assignments were confirmed by the observed isotope heads of ^{80}SeO and ^{78}SeO .

(ii) Two Infrared Band Systems in the Region 10 780 - 9490 Å

Recently, in our laboratory, Azam and Reddy (1973) observed two emission band systems of SeO consisting of 46 bands degraded to longer wavelengths in the region 10 780 - 9490 Å. From a vibrational analysis of these bands, one of these systems has been assigned by these authors to the forbidden transition $b(1\Sigma^+) - X^3\Sigma^-$. The double-headed bands have been analyzed as belonging to the $1\Sigma^+ - X^3\Sigma^- (F_1)$ and $1\Sigma^+ - X^3\Sigma^- (F_2, F_3)$ sub-systems. The separations between the corresponding band heads of these two sub-systems are found to be consistent with the expected value $\sim 2\lambda$, λ being the spin-spin interaction constant of the $X^3\Sigma^-$ state, whose value was derived earlier by Barrow and Deutsch (1963). The vibrational assignments

of this system were confirmed by the observed isotope heads of ^{82}SeO , ^{80}SeO , ^{78}SeO and ^{76}SeO . The second band system, which consists of only one sequence of bands in the region $10\,780 - 10\,500 \text{ \AA}$, was tentatively assigned to the probable forbidden transition $a(1\Delta) - X^3\Sigma^-$ (Azam and Reddy, 1973).

(iii) The Far Ultraviolet Band Systems in the Region $2480 - 1800 \text{ \AA}$

The emission spectrum of SeO in the far ultraviolet region was first observed by Haranath (1964) who photographed 40 bands in the region $2400 - 1800 \text{ \AA}$ under low dispersion and analyzed the bands into four systems. Recently, in our laboratory, Reddy and Azam (1974) have photographed the far ultraviolet emission spectrum of SeO in the region $2480 - 1930 \text{ \AA}$ under better resolution and reanalyzed the vibrational structure of the bands. Beginning at the longer wavelength end, the spectrum was analyzed into five band systems which have been designated as $c(1\Sigma^+) - b(1\Sigma^+)$, $x_2 - x_1$, $y_2 - y_1$, $C(3\Pi) - X^3\Sigma^-$ and $D(3\Sigma^-) - X^3\Sigma^-$. The lower state of the c-b system was found to be the upper state of the infrared b-X system.

In the present work (see section 1:3), a new system of SeO has been observed and will be designated as system C-X; consequently, the earlier designations of C and D states by Reddy and Azam (1974) will be hereafter referred to as D and E, respectively.

(iv) Other Bands of SeO

Kushawaha and Pathak (1972) reported several weak emission bands of SeO in the region $6150 - 5250 \text{ \AA}$ and suggested the transition $b(1\Sigma^+) - X^3\Sigma^-$ for these bands. However, now it appears that this assignment is uncertain (see, for example, Azam and Reddy, 1973).

1.3 Present Work on the Emission Spectrum of SeO:

In the present investigation, the emission spectrum of SeO was excited by irradiating selenium dioxide powder contained in a quartz discharge tube by a high power microwave generator. A new band system of SeO consisting of 48 bands degraded to longer wavelengths in the region 3185 - 2690 Å has been observed for the first time. The vibrational analysis of the system suggests that it arises from the transition $C({}^3\Pi) - X({}^3\Sigma^-)$. The observed separations between band heads having the same vibrational quantum numbers v' and v'' with a common upper electronic substate are consistent with the expected value $\sim 2\lambda$, λ being the spin-spin interaction constant of the $X({}^3\Sigma^-)$ state, known from the earlier work of Barrow and Detusch (1963). Eight new emission bands degraded to longer wavelengths have been observed in the region 3040 - 2805 Å. These bands have been fitted into the vibrational scheme of the $B({}^3\Sigma^-) - X({}^3\Sigma^-)$ system of SeO. Also, the Morse potential curves for the states $X({}^3\Sigma^-)$, $b({}^1\Sigma^+)$, $B({}^3\Sigma^-)$ and $C({}^3\Pi)$ of SeO have been drawn.

CHAPTER 2

EXPERIMENTAL DETAILS

The experimental set-up used for the excitation of the SeO spectrum in the present work is the same as the one used recently in our laboratory by Azam (1973) who gave a detailed description of the apparatus and of the experimental procedure. A brief account of the experimental procedure is given in the following paragraphs..

2.1 Excitation of the Spectrum of SeO:

The emission spectrum of SeO was excited in an electrodeless discharge tube, 2.5 cm in diameter and 45 cm long, containing 30-40 gm of SeO₂ powder (Fig. 1). Samples of SeO₂ supplied by either the British Drug Houses Ltd., England, or Anachimia Chemicals Ltd., Montreal, or Alpha Inorganic Ventron, Beverly, Mass., U.S.A., were used. The discharge tube was first evacuated through a liquid nitrogen trap to pressures of the order of 10^{-5} torr by means of a high vacuum pumping system. The central portion of the discharge tube was then heated for a few minutes with a Bunsen burner and it was then irradiated by microwave radiation from a Raytheon Microwave Power Generator model PGM-100 (Fig. 2), having an output power in the range 250-800 W at a frequency of 2450 ± 50 MHz. The anode current of the Generator was kept at 260 mA which corresponds to 755 W (Hynes, 1968). It was necessary to excite the discharge initially with a tesla coil. The characteristic colour of the SeO discharge was bluish white.

The actual process involved in producing and sustaining an electrical discharge in a discharge tube consists of the following three

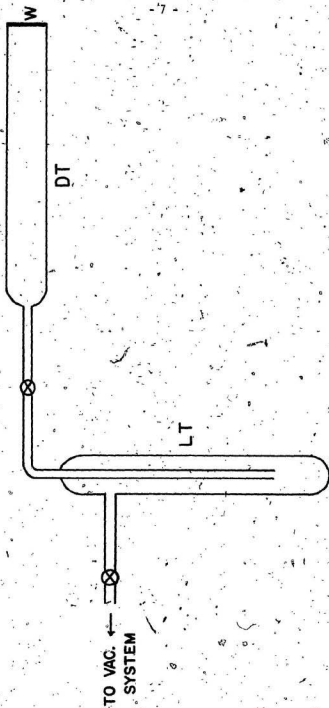


Fig. 1. Discharge tube and liquid nitrogen trap. W: Quartz window.

DT: Electrodeless discharge tube, LT: Liquid N₂ trap.

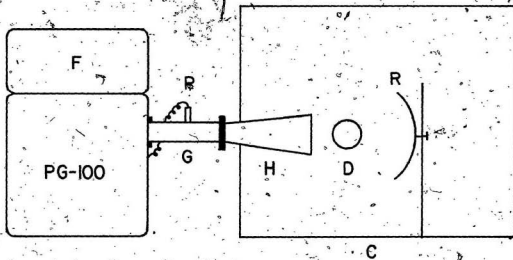


Fig. 2. Cross-sectional view of the experimental arrangement. PG-100: Microwave power generator, F: Filter unit, P: Probe, G: Rectangular waveguide, H: Horn, D: Discharge tube, R: Reflector, C: Copper net radiation cage.

steps: (i) Free electrons in the discharge tube are first accelerated by an electric field produced by a device such as a microwave power generator, a high-frequency valve oscillator, a high voltage a.c. or d.c. power supply unit or a tesla coil. (ii) The translational energy thus acquired by the electrons is then transformed into the internal energy of the atoms and molecules in the discharge tube as a result of a collision process, i.e., the atoms and molecules are excited to their higher energy states. In the case of molecules these higher energy states could be electronic, vibrational and rotational in nature; however, for atoms, these are only electronic in nature. (iii) The higher energy states of the atoms and molecules are inherently unstable and the excited atom or molecule gives up energy by dropping into a lower state with the emission of electromagnetic radiation of frequency ν' so that $h\nu'$ (h being the Planck's constant) is equal to the energy difference between the two states.

One of the important methods of obtaining the emission spectra of free radicals (i.e., species having a short life-time in gaseous phase under ordinary laboratory conditions), is by way of electrical discharges. In fact, the physical existence of diatomic radicals such as CH, NH, OH, C₂, He₂, etc., as well as of the molecular ions N₂⁺, CO⁺, CO₂⁺, etc., has been firmly established as a result of the identification of their spectra (see, for example, Herzberg, 1971). Molecules such as SO and SeO belong to this type of free radicals. The characteristic

emission spectrum of SeO obtained in the present work under continuous evacuation of the discharge tube containing SeO_2 shows that SeO_2 dissociates into SeO , oxygen and selenium. The presence of atomic lines of oxygen and selenium in the spectrum shows the existence of atomic oxygen and selenium in the discharge. No known emission bands of O_2 and Se_2 have been observed with the present method of excitation.

2.2 Photography:

The spectrum in the region $3200 - 2600 \text{ \AA}$ was photographed with a 2 m Littrow type Bausch and Lomb dual grating spectrograph (Fig. 3). The 1200 grooves/mm plane grating was used in its first order. The slit width was maintained at 0.20 mm. The reciprocal dispersion obtained with the grating varies from 4.19 \AA/mm at 2690 \AA to 4.07 \AA/mm at 3200 \AA . The experimental resolving power, $\lambda/d\lambda$, at 3000 \AA is 3625 for the slit width mentioned above, and this corresponds to a spectral resolution of $\sim 0.8 \text{ \AA}$.

Kodak 103 a-o plates were used to photograph the spectrum. These are sensitive in the region 2500 to 4500 \AA . Due to a large variation of intensity of the SeO bands in the region of interest, four different exposure times ranging from 2.5 minutes at longer wavelengths to 40 minutes at shorter wavelengths were used to photograph the spectrum.

The bands were also photographed in higher orders of the 1200 grooves/mm grating but, in this case, the rotational structure of the bands

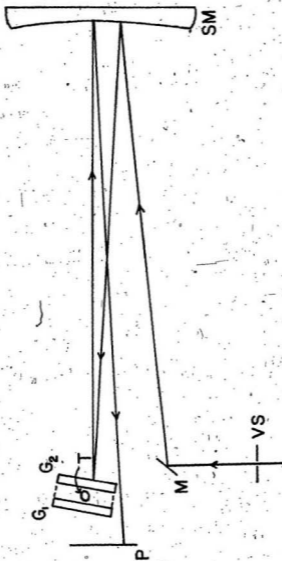


Fig. 3. Optical arrangement of the Bausch and Lomb dual grating spectrograph. SM: Spherical mirror, S: Variable slit, M: Plane mirror, P: Photographic plate, G₁ and G₂: Two gratings with 1200 grooves/mm and 600 grooves/mm, T: Turret axis.

is resolved in such a way that it was not possible to locate the heads accurately.

2.3 Measurement of the Spectrum:

A linear comparator model M1205C having a least count of 0.001 mm (supplied by Gaertner Optical Co., Chicago) was used to measure the spectrum. The readings, however, were estimated correct to 0.0001 mm. The wavelengths, λ_{air} , of iron arc lines were used to determine the constants a_0 , a_1 , and a_2 of the expression

$$\lambda_{\text{air}} = a_0 + a_1 d + a_2 d^2$$

by the method of least squares fit. The accuracy of these constants was tested by calculating the wavelengths of the other standard lines in the same spectral region whose d values had been measured. The accuracy of measurement for sharp lines in the first order spectra is better than 0.03 Å. However, the accuracy of measurement for diffuse band heads is considerably less (~ 0.08 Å). Edlen's (1953) formula for the refractive index,

$$n = 1 + 6432.8 \times 10^{-8} + \frac{2949810}{146 \times 10^8 - \nu^2} + \frac{25540}{41 \times 10^8 - \nu^2}$$

$$\text{where } \nu = \frac{10^8}{n \lambda_{\text{air}} (\text{Å})}$$

was used to convert wavelengths in air to vacuum wavenumbers, ν . An iterative method was employed to do the computations on an IBM-370 computer and the iteration was continued until the absolute difference between the successive values of ν was satisfactory. Several other calculations were done on a Hewlett-Packard Calculator model 9100A.

CHAPTER 3

RESULTS AND DISCUSSION

In the previous chapter, a brief description of the experimental method used in the excitation and photography of the emission spectrum of SeO and details concerning measurement of the spectrum are given. In the present chapter, the experimental data of a new band system of SeO, which is designated as $C(^3\Pi) - X(^3\Sigma^-)$, and its vibrational analysis will be presented. Also included in this chapter is the new data on the band heads of the previously known $B(^3\Sigma^-) - X(^3\Sigma^-)$ system of SeO. Expressions used in the vibrational analysis of the electronic band spectra are given in section 3.1; section 3.2 presents the vibrational structure of a $^3\Pi - ^3\Sigma^-$ system in which the $^3\Sigma^-$ state has a large spin splitting constant; the rest of this chapter is devoted to the results and discussion.

3.1 Expressions used in the Vibrational Analysis of the Electronic Band Systems:

The total energy E of a diatomic molecule (neglecting its spin and translational energies) can be expressed, to a good approximation, as the sum of its electronic energy E_e , vibrational energy E_v and rotational energy E_r . Thus

$$E = E_e + E_v + E_r, \quad E_e > E_v > E_r \quad (1)$$

or, in wavenumber units,

$$T = T_e + G(v) + F(J), \quad (2)$$

where v and J are the vibrational and rotational quantum numbers, respectively. Each electronic state may have a number of vibrational levels and

each vibrational level, in turn, may have a number of rotational states. The vibrational and rotational term values are given, respectively, by

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \dots$$

$$\omega_e \gg \omega_e x_e \gg \omega_e y_e \quad (3)$$

and

$$F(J) = B_v J(J+1) - D_v J^2(J+1)^2 + \dots$$

$$B_v \gg D_v \quad (4)$$

Using equation (2) for the term values of a molecule, the wavenumbers of the spectral lines corresponding to the transitions between two electronic states (in emission or absorption) are given by

$$\nu = (T'_e - T''_e) + (G' - G'') + (F' - F'') \quad (5)$$

where the single primed letters refer to the upper state and the double primed letters refer to the lower state. Thus, the emitted or absorbed wavenumbers may be regarded as the sum of three terms (not all of which need be positive),

$$\nu = \nu_e + \nu_v + \nu_r \quad (6)$$

For a given transition, $\nu_e = T'_e - T''_e$ is a constant. Since, in general, F is small compared to G , $\nu_r (= F' - F'')$ may be neglected when only the vibrational structure of a band system is of interest. Thus, the wavenumber of a band head in an electronic band system is represented as (neglecting the cubic and higher order terms in equation (3)),

$$\nu = \nu_e + \omega'_e(v' + \frac{1}{2}) - \omega'_e x'_e(v' + \frac{1}{2})^2$$

$$- [\omega''_e(v'' + \frac{1}{2}) - \omega''_e x''_e(v'' + \frac{1}{2})^2] \quad (7)$$

The separation between the vibrational states v and $v + 1$ of a given electronic state can then be defined as,

$$\begin{aligned} \Delta G_{v+\frac{1}{2}} &= G(v+1) - G(v) \\ &= (\omega_e - \omega_e x_e) - 2\omega_e x_e (v + \frac{1}{2}) \end{aligned} \quad (8)$$

The second difference is given by

$$\begin{aligned} \Delta^2 G_{v+1} &= \Delta G_{v+\frac{3}{2}} - \Delta G_{v+\frac{1}{2}} \\ &= -2\omega_e x_e \end{aligned} \quad (9)$$

3.2: The Vibrational Structure of a $^3\Pi - ^3\Sigma$ Transition:

For a $^3\Sigma$ electronic state of a diatomic molecule, the quantized component of the orbital electronic angular momentum along the internuclear axis, $\Lambda = 0$ and the total spin, $S = 1$ so that the multiplicity, $2S + 1 = 3$. The reasons of the multiplet structure have been discussed by Kramers (1929) and Schlapp (1937). The magnetic interaction between the spin, S and Λ does not arise in a $^3\Sigma$ state because $\Lambda = 0$. It was shown, however, by Kramers (1929) that the spin-spin interaction of the uncompensated electrons is equivalent to an interaction between S and the figure-axis. Kramers calculated the energy levels and found that each rotational level N was split by the interaction into three, corresponding to three different ways of constructing a total angular momentum J ($= N - 1, N, N + 1$) out of N and $S = 1$. Another effect is due to the interaction between the uncompensated spins and the magnetic field set up by the rotation of the molecule as a whole. There is a further cause of fine structure - although on the average the electronic orbital angular momentum of the molecule in a Σ state is

null this angular momentum has a precessing component perpendicular to the figure-axis, which interacts with the total spin S . These effects together give, for the three energy levels associated with a given value of N in a $^3\Sigma$ state, the following expressions (Schlapp, 1937):

$$\begin{aligned}
 F_1(N) &= B_V N(N+1) + (2N+3)B_V - \lambda_V - \sqrt{(2N+3)^2 B_V^2 + \lambda_V^2 - 2\lambda_V B_V} \\
 &\quad + \gamma_V (N+1) \\
 F_2(N) &= B_V N(N+1) \\
 F_3(N) &= B_V N(N+1) - (2N-1)B_V - \lambda_V \\
 &\quad + \sqrt{(2N-1)^2 B_V^2 + \lambda_V^2 - 2\lambda_V B_V} - \gamma_V N
 \end{aligned}
 \tag{10}$$

Here F_1 , F_2 and F_3 refer to the levels with $J = N+1$, N , $N-1$, respectively, and N is the quantum number representing the angular momentum apart from the spin of the electrons. (Note: $J = N+S$, $N+S-1$, ..., $|N-S|$.) B_V is the rotational constant, and λ_V and γ_V are, respectively, the spin-spin and spin-rotation interaction constants.

For a $^3\Pi$ state, $\Lambda = 1$ and $S = 1$ so that the resultant electronic angular momentum about the internuclear axis, Ω ($= \Lambda + S$, $\Lambda + S - 1$, ..., $|\Lambda - S|$) takes the values 2, 1 and 0. In the customary notation in molecular spectroscopy, the three substates, $^{2S+1}\Lambda_\Omega$, of a triplet Π state are represented by $^3\Pi_2$, $^3\Pi_1$ and $^3\Pi_0$. Apart from this, each substate is doubly degenerate because Λ can take two values, $+\Lambda$ and $-\Lambda$. This doubling is called Λ -type doubling which is usually very small.

The selection rules in Hund's case (a) are:

$$\begin{aligned} \Delta S &= 0, \\ \Delta \Omega &= 0, \pm 1 \end{aligned} \tag{11}$$

The former is satisfied already in a ${}^3\Pi - {}^3\Sigma$ transition. On the basis of the latter, the following six sub-systems are possible,

$$\begin{aligned} &{}^3\Pi_0 - {}^3\Sigma^-(F_1), \quad {}^3\Pi_0 - {}^3\Sigma^-(F_2), \\ &{}^3\Pi_0 - {}^3\Sigma^-(F_3), \quad {}^3\Pi_1 - {}^3\Sigma^-(F_1), \\ &{}^3\Pi_1 - {}^3\Sigma^-(F_2), \quad {}^3\Pi_2 - {}^3\Sigma^-(F_1). \end{aligned}$$

A schematic energy level diagram showing these six sub-systems is shown in Fig. 4. In this figure it is assumed that the ${}^3\Pi$ state is regular and is approaching Hund's case (a). The Λ -type doubling is not shown. For a molecule such as SeO, the ground electronic state $\chi^3\Sigma^-$ has a large spin-spin interaction constant λ and a negligibly small spin-rotation interaction constant γ . In general, if λ is very large (or more precisely B/λ is very small), for each value of N , the F_2 and F_3 levels will be very close together with the F_1 level separated from them by an amount equal to $\sim 2\lambda$. In Fig. 4, the separation between the F_2 and F_3 levels is rather exaggerated for the sake of clarity. The quantum numbers Ω of the resultant electronic angular momentum about the internuclear axis are formally assigned to the ${}^3\Sigma$ state in order to indicate the relation to the ${}^3\Pi - {}^3\Sigma$ transition. In Fig. 4 the transitions have been shown exactly the way they are developed in the spectrum.

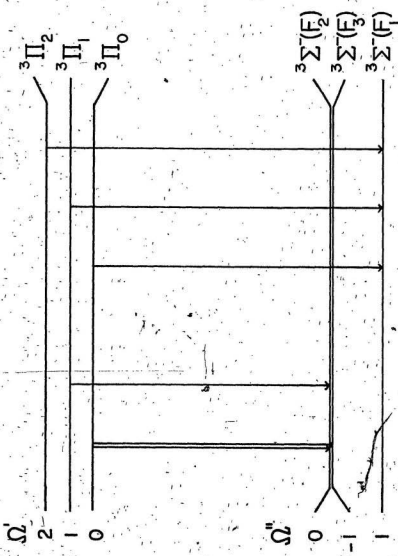


Fig. 4. Schematic diagram showing the sub-systems of a $3\Pi - 3\Sigma$ band system.
(See text for details.)

3.3 The C-X System:

Vibrational Analysis:

The general appearance of the bands of the C-X system of SeO in the region 3185 - 2690 Å is shown in plates I and II. The bands are degraded to longer wavelengths and are intense in the longer wavelength region and weak in the shorter wavelength region. The vibrational analysis of this system was somewhat complicated due to the overlap of several bands of the B-X system of SeO (Barrow and Deutsch, 1963). In addition to the bands reported earlier, eight new bands of the B-X system have been photographed in the present work (see section 3.4).

From the rotational analysis of the $B^3\Sigma^- - X^3\Sigma^-$ system of SeO, Barrow et al. (1963) have shown that in the $X^3\Sigma^-$ state the term value of the F_1 level with respect to the F_2 level is -172 cm^{-1} and that F_2 and F_3 levels lie very close together.

An attempt to fit all the observed bands of SeO in the region 3185 - 2690 Å in the B-X system was not successful. It was then realized that the separations of the intense band heads at 2830.9 Å (35314 cm^{-1}), 2905.6 Å (34406 cm^{-1}), 2983.5 Å (33508 cm^{-1}) and 3064.8 Å (32619 cm^{-1}) are 908, 898 and 889 cm^{-1} , respectively. These separations are found to be in good agreement with the $\Delta G_{v+\frac{1}{2}}$ values (905, 897 and 888 cm^{-1}) of the ground state obtained from the analysis of the B-X system (Choong, 1938; Barrow et al., 1963) (also see Azam and Reddy, 1973). The close proximity of these separations suggests that the lower state of the new system is the ground state $X^3\Sigma^-$. Another clue which helped to guess the nature of the ground and upper electronic states of the new system is the separations between various band heads in a group. For example, the following separations are noted for the five bands near 3000 Å.

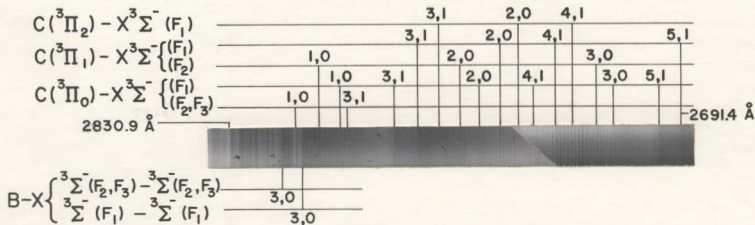
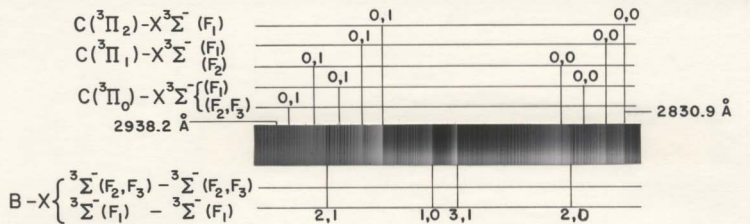
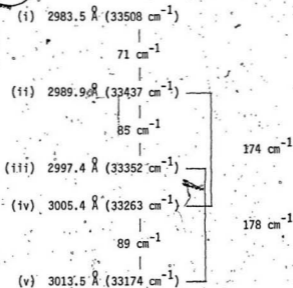


Plate II The $C(^3\Pi) - X^3\Sigma^-$ and $B^3\Sigma^- - X^3\Sigma^-$ Systems of SeO in the Region 2940 - 2690 Å



In this group of bands, the separations between the band heads (ii) and (iv) on one hand and (iii) and (v) on the other are 174 and 178 cm⁻¹, respectively. These separations are close to the value of $|-172|$ cm⁻¹, the separation between the sublevels F₁ and F_{2,3} of the X³Σ⁻ state. This observation also favours the assignment of the lower state of the new system as the ground state X³Σ⁻. The average separation between the band heads (ii) and (iii), and (iv) and (v) is 87 cm⁻¹ and the separation between (i) and (ii) is 71 cm⁻¹. This indicates that the upper state has three sub-states and may possibly be a ³Π state.

Due to unusually large separation between X³Σ⁻ (F₁) and X³Σ⁻ (F₂) sublevels and closely-lying X³Σ⁻ (F₂) and X³Σ⁻ (F₃) sublevels of the ground state of the SeO molecule, the following sub-systems should be observed in the C(³Π) - X³Σ⁻ system which are allowed by the selection rules Δn = 0, ±1 (see Fig. 4):

$$(i) C(^3\Pi_0) - X^3\Sigma^-(F_1)$$

$$(ii) C(^3\Pi_0) - X^3\Sigma^-(F_2, F_3)$$

$$(iii) C(^3\Pi_1) - X^3\Sigma^-(F_1)$$

$$(iv) C(^3\Pi_1) - X^3\Sigma^-(F_2)$$

$$(v) C(^3\Pi_2) - X^3\Sigma^-(F_1)$$

In the observed spectrum, the sub-systems $C(^3\Pi_1) - X^3\Sigma^-(F_1)$ and $C(^3\Pi_1) - X^3\Sigma^-(F_2)$ are developed well with an average separation of 173 cm^{-1} between the corresponding band heads. The sub-system $C(^3\Pi_0) - X^3\Sigma^-(F_1)$ itself is strong but the bands, belonging to the sub-system $C(^3\Pi_0) - X^3\Sigma^-(F_2, F_3)$ are diffuse. The sub-system $C(^3\Pi_2) - X^3\Sigma^-(F_1)$ is moderately intense.

Assuming the C state to be a regular $^3\Pi$ state, the sub-system with the highest T_e value has been assigned as the $(^3\Pi_2) - ^3\Sigma^-(F_1)$ transition. The other subsystems in the decreasing order of T_e values are $(^3\Pi_1) - ^3\Sigma^-(F_1)$, $(^3\Pi_1) - ^3\Sigma^-(F_2)$, $(^3\Pi_0) - ^3\Sigma^-(F_1)$, $(^3\Pi_0) - ^3\Sigma^-(F_2, F_3)$.

The wavelengths $\lambda(\text{\AA})$, vacuum wavenumbers $\nu(\text{cm}^{-1})$, the visual estimates of their relative intensities and their vibrational quantum numbers of the bands of all the above sub-systems have been listed in Table I. The Deslandre's vibrational schemes for these sub-systems are given in Tables II, III and IV, respectively.

The values of $\Delta G_{v+1/2}$ are plotted against the corresponding $v + 1/2$ values for the lower and upper states of each of the sub-systems as shown in Fig. 5. These plots give straight lines which can be represented by the equation (8). The intercepts and slopes of the straight lines which

TABLE I

Band Heads of the $C(3\Pi) - X^3\Sigma^-$ System^a
in the Region 3185 - 2690 Å

λ (air) (Å)	$\nu_{\text{obs.}}$ (vacuum) (cm^{-1})	Relative Intensity ^b	ν', ν''	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
<u>Sub-system $C(3\Pi_0) - X^3\Sigma^-(F_1)$</u>				
3165.6	31581	m	0,4	+1
3079.5	32464	m	0,3	+2
2997.4	33352	s	0,2	0
2918.9	34250	s	0,1	0
2843.6	35156	m	0,0	0
2797.8	35732	vw	1,0	+2
2780.8	35951	w	3,1	0
2754.2	36297	w	2,0	0
2738.7	36504	w	4,1	0
2712.4	36857	w	3,0	0
2698.2	37051	w	5,1	+1
<u>Subsystem $C(3\Pi_0) - X^3\Sigma^-(F_2, F_3)$</u>				
3013.5	33174	vw	0,2	
2934.5	34067	w	0,1	
2858.6	34972	vw	0,0	
2812.4	35546	vw	1,0	
2794.7	35771	vw	3,1	

TABLE I (continued)

λ (air) (\AA)	$\nu_{\text{obs.}}$ (vacuum) (cm^{-1})	Relative Intensity ^b	ν', ν''	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
<u>Sub-system C($^3\Pi_1$) - X$^3\Sigma^-(F_1)$</u>				
3156.5	31671	m	0,4	-1
3100.1	32248	w	1,4	-1
3071.5	32548	m	0,3	-1
3018.0	33125	m	1,3	-1
2989.9	33437	m	0,2	+1
2911.8	34334	s	0,1	0
2836.7	35242	m	0,0	0
2791.0	35820	vw	1,0	+1
2773.5	36045	w	3,1	+4
2747.3	36388	w	2,0	0
2731.5	36600	w	4,1	+6
2691.4	37144	w	5,1	+5
<u>Sub-system C($^3\Pi_1$) - X$^3\Sigma^-(F_2)$</u>				
3174.0	31497	w	0,4	0
3116.7	32076	w	1,4	+2
3087.9	32375	m	0,3	0
3033.7	32954	w	1,3	+1
3005.4	33263	m	0,2	-1
2926.3	34163	m	0,1	+1

TABLE I (continued)

λ (air) (Å)	$\nu_{\text{obs.}}$ (vacuum) (cm^{-1})	Relative Intensity ^b	ν', ν''	$\nu_{\text{obs.}}$ - $\nu_{\text{calc.}}$
Sub-system $C(^3\Pi_1) - X^3\Sigma^-(F_2)$ (continued)				
2850.6	35070	m	0,0	-1
2804.3	35649	vw	1,0	+1
2787.4	35865	w	3,1	-1
2760.5	36214	vw	2,0	-2
2718.5	36774	w	3,0	0
Sub-system $C(^3\Pi_2) - X^3\Sigma^-(F_1)$				
3149.2	31745	w	0,4	+2
3093.0	32321	w	1,4	+3
3064.8	32619	m	0,3	-1
3011.5	33197	w	1,3	+2
2983.5	33508	s	0,2	0
2905.6	34406	m	0,1	0
2830.9	35314	m	0,0	-1
2768.5	36110	vw	3,1	+2
2742.2	36456	vw	2,0	-1
2726.7	36663	vw	4,1	+3

a: All bands are degraded to longer wavelengths.

b: Abbreviations used: vs, s, m, w and vw denote very strong, strong, medium, weak and very weak, respectively.

TABLE II

Vibrational Scheme of the Sub-system $C(\pi_0) - X^3-$

v' \ v''	0	1	2	3	4	Mean $\Delta v_{v'+1, v''}$
0	35156 (F_1) 184	34250 (F_1) 183	898 33352 (F_1) 178	888 32464 (F_1)	883 31581 (F_1)	
1	34972 (F_2) 576 574	905 34067 (F_2) 576 574	893 33174 (F_2) 576 574			576 (F_1) 574 (F_2)
2	35732 (F_1) 186 35546 (F_2) 565					565 (F_1)
	36297 (F_1) 560					560 (F_1)

- 26 -

TABLE II (continued)

v^R	0	1	2	3	4	Mean $\Delta G^{\circ}_{v^R+v^S}$
3	36857 (F_1)	906 35951 (F_1) 180 35771 (F_2) 553				553 (F_1)
4		36504 (F_1)				547 (F_1)
5		37051 (F_1)				
Mean $\Delta G^{\circ}_{v^R+v^S}$	906 (F_1) 905 (F_2)		898 (F_1) 893 (F_2)	888 (F_1)	883 (F_1)	

TABLE III

Vibrational Scheme of the Sub-system $C(3\pi_1) - \chi^3\Sigma^-$

$v'' \backslash v'$	0	1	2	3	4	Mean $\Delta G, \text{cm}^{-1}$
0	35242 (F_1) 172	34334 (F_1) 171	33437 (F_1) 174	32548 (F_1) 173	31671 (F_1) 174	877
	35070 (F_2) 578	34163 (F_2) 900	33263 (F_2) 888	32375 (F_2) 577	31497 (F_2) 577	877
1	35820 (F_1) 171			33125 (F_1) 171	32248 (F_1) 172	877
	35649 (F_2) 568			32954 (F_2) 565	32076 (F_2) 565	878
2	36388 (F_1) 174					878
	36214 (F_2) 560					878

560 (F_2)

TABLE III (continued)

V^m	0	1	2	3	4	Mean $\Delta G^m_{V^m+1}$
3		36045 (F_1)				
	36774 (F_2)	909	35865 (F_2)			
		555				555 (F_1)
4		36600 (F_1)				
		544				544 (F_1)
5		37144 (F_1)				
Mean $\Delta G^m_{V^m+1}$	908 (F_1) 908 (F_2)		897 (F_1) 900 (F_2)	889 (F_1) 888 (F_2)	877 (F_1) 878 (F_2)	

TABLE VI

Vibrational Scheme of the Sub-system $C(\Pi_2) - X^3 - (F_1)$

v''	0	1	2	3	4	Mean $\Delta G^0_{v''+1/2}$			
0	35314	908	34406	898	33508	889	32619	874	31745
1							578	576	575
2	36456						33197	876	32321
3		36110							
4		553							553
Mean $\Delta G^0_{v''+1/2}$		908					898	889	875

Y

TABLE V

Values of Mean $\Delta G_{V+\frac{1}{2}}$ and $\Delta^2 G_V$
of the C-X System of SeO

$v + \frac{1}{2}$	$\Delta G'_{V+\frac{1}{2}}$ (cm^{-1})	$\Delta^2 G'_V$ (cm^{-1})	$\Delta G''_{V+\frac{1}{2}}$ (cm^{-1})	$\Delta^2 G''_V$ (cm^{-1})
<u>Sub-system $C(^3\Pi_0) - X^3\Sigma^- (F_1)$</u>				
0.5	576		906	
		-11		-8
1.5	565		898	
		-5		-10
2.5	560		888	
		-7		-5
3.5	553		883	
		-6		
4.5	547			
<u>Sub-system $C(^3\Pi_1) - X^3\Sigma^- (F_1)$</u>				
0.5	577		908	
		-9		-11
1.5	568		897	
				-8
2.5			889	
				-12
3.5	555		877	
		-11		
4.5	544			

TABLE V (continued)

$v + \frac{1}{2}$	$\Delta G'_{V+\frac{1}{2}}$ (cm^{-1})	$\Delta^2 G'_V$ (cm^{-1})	$\Delta G''_{V+\frac{1}{2}}$ (cm^{-1})	$\Delta^2 G''_V$ (cm^{-1})
Sub-system $C(^3\Pi_1) - X^3\Sigma^-(F_2)$				
0.5	579		908	
		-14		-8
1.5	565		900	
				-12
2.5			888	
				-10
3.5			878	
Sub-system $C(^3\Pi_2) - X^3\Sigma^-(F_1)$				
0.5	575		908	
				-10
1.5			898	
				-9
2.5			889	
				-14
3.5	553		875	

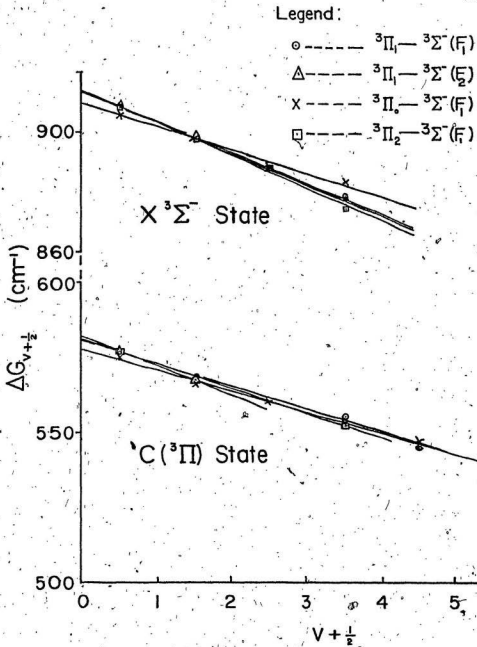


Fig. 5. Plots of $\Delta G_{v+\frac{1}{2}}$ vs. $v+\frac{1}{2}$ for the $X \ ^3\Sigma^-$ and $C(\ ^3\Pi)$ states of SeO .

are determined by a least-squares method give $(\omega_e - \omega_e x_e)$ and $2\omega_e x_e$, respectively. The values of ω_e and $\omega_e x_e$ determined in this way for each sub-system were used to calculate the sub-system origins from equation (7). In calculating the average values of ν_e for different sub-systems, the ν_e values corresponding to the following weak or diffuse band heads were excluded:

<u>Sub-system</u>	<u>Bands excluded</u>
$C(^3\Pi_0) - X^3\Sigma^-(F_1)$	(1,0), (0,3)
$C(^3\Pi_1) - X^3\Sigma^-(F_1)$	(3,1), (4,1), (5,1)
$C(^3\Pi_1) - X^3\Sigma^-(F_2)$	None
$C(^3\Pi_2) - X^3\Sigma^-(F_1)$	(4,1), (1,4)

For the sub-system $C(^3\Pi_0) - X^3\Sigma^-(F_2, F_3)$ data is insufficient to calculate the vibrational constants. The molecular constants obtained for the different sub-systems of SeO are given below in cm^{-1} .

For $C(^3\Pi_0) - X^3\Sigma^-(F_1)$:

$$\begin{aligned} \nu_e &= 35322 \\ \omega_e' &= 581 & \omega_e' x_e' &= 3.5 \\ \omega_e'' &= 914 & \omega_e'' x_e'' &= 4.0 \end{aligned}$$

For $C(^3\Pi_1) - X^3\Sigma^-(F_1)$:

$$\begin{aligned} \nu_e &= 35408 \\ \omega_e' &= 585 & \omega_e' x_e' &= 4.0 \\ \omega_e'' &= 918 & \omega_e'' x_e'' &= 5.1 \end{aligned}$$

For $C(3\Pi_1) - X^3\Sigma^- (F_2)$:

$$v_e = 35237$$

$$\omega_e' = 587 \quad \omega_e' x_e' = 4.8$$

$$\omega_e'' = 919 \quad \omega_e'' x_e'' = 5.1$$

For $C(3\Pi_2) - X^3\Sigma^- (F_1)$:

$$v_e = 35484$$

$$\omega_e' = 582 \quad \omega_e' x_e' = 3.7$$

$$\omega_e'' = 920 \quad \omega_e'' x_e'' = 5.4$$

The T_e value of the present system is 35150 cm^{-1} which lies between the B state and the old C state. Therefore, the upper state in the present system has been labelled as the $C(3\Pi)$ state and the previous designations of the states C and D (Reddy and Azam, 1974) are hereafter to be referred to as $D(3\Pi)$ and $E(3\Sigma^-)$, respectively.

Finally, the wavenumbers of the band heads of the sub-systems are represented by the following equations:

$$(i) \quad C(3\Pi_0) - X^3\Sigma^- (F_1):$$

$$v = 35322 + 581 (v' + \frac{1}{2}) - 3.5 (v' + \frac{1}{2})^2 \\ - [914 (v'' + \frac{1}{2}) - 4.0 (v'' + \frac{1}{2})^2]$$

$$(ii) \quad C(3\Pi_1) - X^3\Sigma^- (F_1):$$

$$v = 35408 + 585 (v' + \frac{1}{2}) - 4.0 (v' + \frac{1}{2})^2 \\ - [918 (v'' + \frac{1}{2}) - 5.1 (v'' + \frac{1}{2})^2]$$

$$(iii) C({}^3\Pi_1) - \chi^3\Sigma^-(F_2):$$

$$\begin{aligned} v &= 35237 + 587 (v' + \frac{1}{2}) - 4.8 (v' + \frac{1}{2})^2 \\ &- [919 (v'' + \frac{1}{2}) + 5.1 (v'' + \frac{1}{2})^2] \end{aligned}$$

$$(iv) C({}^3\Pi_2) - \chi^3\Sigma^-(F_1):$$

$$\begin{aligned} v &= 35484 + 582 (v' + \frac{1}{2}) - 3.7 (v' + \frac{1}{2})^2 \\ &- [920 (v'' + \frac{1}{2}) + 5.4 (v'' + \frac{1}{2})^2] \end{aligned}$$

The wavenumbers of the band heads of the sub-systems were calculated by means of the above equations. The values of ($v_{obs.} - v_{calc.}$) were determined and are listed in Table I. The differences range from 0 to 6 cm^{-1} .

The vibrational constants for the ground state obtained in the present investigation are in good agreement with those obtained from the rotational analysis of the $B^3\Sigma^- - \chi^3\Sigma^-$ system by Barrow and Deutsch (for F_1 state: $\omega_e = 914.69 \text{ cm}^{-1}$, and $\omega_e x_e = 4.52 \text{ cm}^{-1}$; for F_2 state: $\omega_e = 915.43 \text{ cm}^{-1}$, and $\omega_e x_e = 4.52 \text{ cm}^{-1}$). The average difference between the F_1 and F_2 sublevels of the ground state turns out to be 174 cm^{-1} which compares favourably with the value $|-172| \text{ cm}^{-1}$ given by Barrow and Deutsch. These small discrepancies are expected because of the fact that the above authors have used band origins in their calculations, whereas band heads have been used in the present work.

3.4 Extension of the $B^3\Sigma^- - \chi^3\Sigma^-$ System:

In the region $3040 - 2800 \text{ \AA}$, eight new bands were observed which are degraded to longer wavelengths. These bands did not fit in the

$C(^3\Pi) - X^3\Sigma^-$ system. On further investigation it was found that they belong to the B-X system and fit in its Deslandre's vibrational scheme.

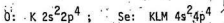
Table VI lists the wavelengths (\AA), wavenumbers (cm^{-1}), visual estimates of the intensities and the vibrational quantum numbers of these bands.

In Table VII, a part of the vibrational scheme of the B-X system has been given which shows the newly found bands along with a few bands observed by previous workers (Asundi, et al., Choong-Shin Piau, Barrow et al). Out of eight new bands observed, seven fit into the $B^3\Sigma^- - X^3\Sigma^- (F_1)$ sub-system and one fits into the $B^3\Sigma^- - X^3\Sigma^- (F_2, F_3)$ sub-system. The inconsistency in $\Delta G_{v+\frac{1}{2}}$ values has been attributed to the highly perturbed/upper state, as shown by Barrow and Deutsch (1963).

3.5 Molecular Constants and the Electronic Configurations of SeO:

The spectroscopic constants of all the known electronic states of the SeO molecule are summarized in Table VIII and its energy level diagram is given in Fig. 6. Potential curves are given in the Appendix.

The electronic configurations of the O and Se atoms are:



The ground state electron configuration of SeO is then written as (see Mulliken, 1932, and Herzberg, 1950, Chapter VI):

$$KKLM(\sigma\sigma)^2(\gamma\sigma)^2(\omega\pi)^4(x\sigma)^2(v\pi)^2 \dots 3\Sigma^-, 1\Delta, 1\Sigma^+ \quad (11)$$

The electron configuration of the low lying excited states of SeO are:

$$KKLM(\sigma\sigma)^2(\gamma\sigma)^2(\omega\pi)^4(x\sigma)^2(v\pi)(u\sigma) \dots 1\Pi, 3\Pi_r, \quad (12)$$

TABLE VI

New Band Heads of the $B^3\Sigma^- - X^3\Sigma^-$ System^a of SeO

λ (air) (Å)	$\nu_{\text{obs.}}$ (vacuum) (cm^{-1})	Relative Intensity ^b	ν', ν''
3039.0	32895	m	3,3
2967.3	33691	s	1,1
2959.2	33784	m	3,2
2890.3	34588	s	1,0
2882.6	34681	s	3,1
2847.4	35109	s	2,0
2815.1	35513	w	3,0
2809.1	35588	w	3,0

a: All bands are degraded to longer wavelengths

b: Abbreviations used: s, m and w denote strong, medium and weak, respectively.

TABLE VII

Vibrational Scheme[†] of the $B^3\Sigma^- - X^3\Sigma^-$ System of SeO

	0	1	2	3	4	5			
0			32284 (F ₁)	888.1	31395.9 (F ₁)	876.8	30519.2 (F ₁)		
			74		75.2		76.5		
			32210 (F ₂)	889.3	31320.7 (F ₂)	878.0	30442.7 (F ₂)		
			517.0		511.7		508.1		
			516.7		519.7		517.9		
1	34588 (F ₁)*	897	33691 (F ₁)*	890.0	32801.0 (F ₁)	893.4	31907.6 (F ₁)	880.3	31027.3 (F ₁)
					74.3		67.2		66.7
					32726.7 (F ₂)	886.4	31840.4 (F ₂)	879.8	30960.6 (F ₂)
		508			499.0		506.7		507.3
					526.9		524.7		521.8
2	35109 (F ₁)*	910	34199 (F ₁)	899.0	33300.0 (F ₁)	885.6	32414.4 (F ₁)	879.8	31534.6 (F ₁)
			42		46.4		49.3		52.2
			34157 (F ₂)		33253.6 (F ₂)	885.5	32365.1 (F ₂)	882.7	31482.4 (F ₂)
	479		482		484		480.6		
3	35588 (F ₁)*	907	34681 (F ₁)*	897	33784 (F ₁)*	889	32895 (F ₁)*		
	75								
	35513 (F ₂)*								

[†] Only a part of the vibrational scheme of B-X system is shown.

*New bands observed in the present work.

TABLE VIII
Molecular Constants (in cm^{-1}) of the SeO Molecule

State	T_e	ω_e	$\omega_e x_e$	B	a	$r_0(\text{\AA})$	λ	Observed Transition	Reference
ν_2	$\nu_1 + 47830$	974	6.0	—	—	—	—	$\nu_2 - \nu_1$	Reddy & Azam (1974)
ν_1	ν_1	906	21.0	—	—	—	—	—	"
ν_2	$\nu_1 + 46009$	993	2.0	—	—	—	—	$\nu_2 - \nu_1$	"
ν_1	ν_1	877	8.0	—	—	—	—	—	"
$c(1^2)$	53080	954	13.0	—	—	—	—	$\nu_2 - \nu_1$	"
$F(3^2)F_2$	51422	955	9.3	—	—	—	0.36	E-X	"
F_1	51350	955	8.5	—	—	—	—	E-X	"
$D(2b)$	40873	1034	9.3	—	—	—	—	O-X	"
$C(3^2b)$	35312	582 (F_1)	3.7 (F_1)	—	—	—	—	C-X	Present Work
$C(2^2b)$	35237	587	4.8	—	—	—	—	C-X	"
$C(2^2a)$	35150	581 (F_1)	3.5 (F_1)	—	—	—	—	C-X	"
$B(3^2)F_2$	34012.2*	$\Delta G_3 = 515.7$	—	$B_0 = 0.3391$	—	$\nu_0 = 1.931$	$\lambda_0 = 51$	B-X	Barrow & Deutsch (1963)
F_1	33910	522.3	3.9	$B_0 = 0.3332$	—	—	—	B-X	"
$b(1^2)$	9570.7	834.9	5.5	—	—	—	—	b-X	Azam & Reddy (1973)
$a(1^2)$	9519.4*	—	—	—	—	—	—	a-X	"
$X(3^2)F_2$	0.0	915.43	4.52	$B_e = 0.4705$	0.0033	$\nu_e = 1.640$	$\lambda_0 = 86.4$	—	Barrow & Deutsch (1963)
F_1	-172	914.69	4.52	$B_e = 0.4655$	0.0032	—	—	—	"

* T_{00} value.

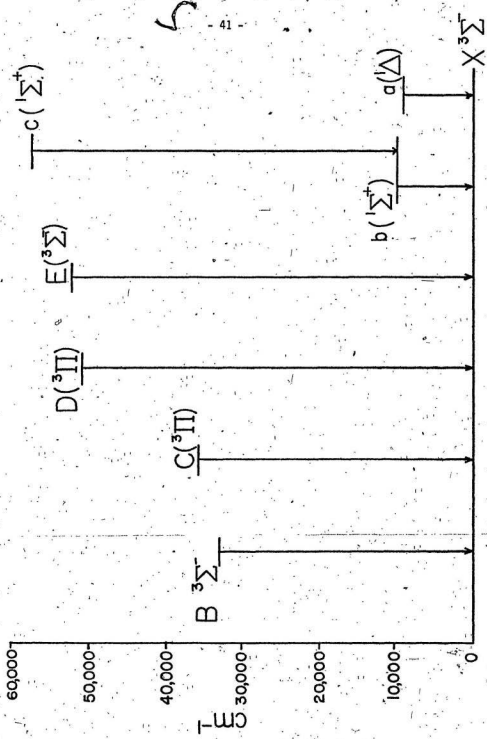


Fig. 6. Energy level diagram of SeO.

$$\begin{aligned}
 & \text{KKLM}(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)(v\pi)^2(y\sigma) \dots 1_{\Sigma^+}, 1_{\Sigma^-}, \\
 & 1_{\Delta}, 3_{\Sigma^+}, 3_{\Sigma^-}(2), 3_{\Delta}, 5_{\Sigma^-}, \quad (13)
 \end{aligned}$$

$$\text{KKLM}(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)(v\pi)^3 \dots 1_{\Pi}, 3_{\Pi_i} \quad (14)$$

Higher electronic states of SeO require excitation of electron(s) from the $(w\pi)^4$ orbital. The three states arising from the ground electronic configuration π^2 (expression (11)) are attributed to $X^3_{\Sigma^-}$, $a(1_{\Delta})$ and $b(1_{\Sigma^+})$ (Azam and Reddy, 1973). States $c(1_{\Sigma^+})$, $B^3_{\Sigma^-}$ and $E(3_{\Sigma^-})$ probably belong to the configuration given by expression (13). States $C(3_{\Pi})$ and $D(3_{\Pi})$ may arise from configurations (12) and (14). Definite conclusions concerning several of these electronic states and the question whether a given 3_{Π} state is regular or inverted must await detailed rotational analysis of the band systems of SeO arising from these states.

APPENDIX

Morse Potential Curves for the $X^3\Sigma^-$, $b(1\Sigma^+)$, $B^3\Sigma^-$ and $C(3\Pi)$ States of the SeO Molecule:

In principle, true potential energy curves for electronic states of a molecule can be constructed point for point without assuming any analytic expression for the potential function if a sufficiently large number of vibrational and rotational states are observed for these electronic states (e.g. the Klein-Rydberg method, see Herzberg, 1950, p. 102). The true curves obtained in this way are generally in fairly close agreement with the curves obtained by the Morse potential function. Moreover, the Morse curve is much simpler to calculate and, hence, it is frequently used for the representation of the potential curves (see, for example, Colin, 1969).

The Morse potential function for a diatomic molecule is written as

$$U(r - r_e) = D_e \left[1 - e^{-\beta(r - r_e)} \right]^2 \quad (A-1)$$

where D_e is the dissociation energy (in cm^{-1}), referred to the minimum of the curve; β is a constant depending on certain molecular parameters of the molecule, r is the internuclear separation and r_e is its value at the equilibrium position. If the vibrational levels of an electronic state are observed up to the dissociation limit, the dissociation is obtained directly with great accuracy. However, in the absence of such information, D_e is obtained from a linear extrapolation of the vibrational levels which gives rise to the relation

$$D_e = \frac{\omega_e^2}{4\omega_e x_e} \quad (\text{A-2})$$

For O_2 , SO and S_2 , this relation leads to dissociation energies which are too large by a factor about 1.25 (see, for example, Barrow and Deutsch, 1963). In the present work, the same correction factor has been applied in calculating the dissociation energies from equation (A-2) for the states X, b, B and C of SeO . The quantity β is given by

$$\begin{aligned} \beta &= \sqrt{\frac{2\pi^2 c \mu_A}{D_e h}} \omega_e \\ &= 1.2177 \times 10^7 \omega_e \sqrt{\frac{\mu_A}{D_e}} \end{aligned} \quad (\text{A-3})$$

where μ_A is the reduced mass of the molecule in atomic units. Birge (1925) and Mecke (1925) gave the following empirical relation which is valid for different electronic states of a given molecule:

$$r_e^2 \omega_e = \text{constant} \quad (\text{A-4})$$

For SeO , the r_e value in the X state was derived by Barrow and Deutsch from the rotational analysis of the B-X system. The approximate values of r_e for the states B, b and C were calculated from the r_e value of state X by means of Eq. (A-4). Table IX lists the important spectroscopic constants of these states which are needed to sketch the Morse potential curves. Finally, the calculated Morse potential curves for the X, b, B and C states of SeO are shown in Fig. 7.

TABLE IX

Constants for the Plot of the Morse Potential Function

$$\nu_A (^{80}\text{SeO}) = 13.3317^a \text{ a.m.u.}$$

State	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	r_e (\AA)	D_e^* (cm^{-1})	β (\AA^{-1})
$C(^3\Pi_0)$	35150 ^e	581 ^e	3.5 ^e	2.06	19289	1.86
$B^3\Sigma^-(F_1)$	33910 ^a	522.3 ^a	3.9 ^a	2.17	13990	1.96
$b(^1\Sigma^+)$	9570.7 ^d	834.9 ^d	5.5 ^d	1.72	27509	2.24
$X^3\Sigma^-(F_2)$	0.0 (T_{00}) ^a	915.43 ^a	4.52 ^a	1.64 ^a	37080	2.11

*Corrected values (see text).

^aBarrow and Deutsch (1963): for B state T_{00} is given.^dAzam and Reddy (1973).^ePresent work.

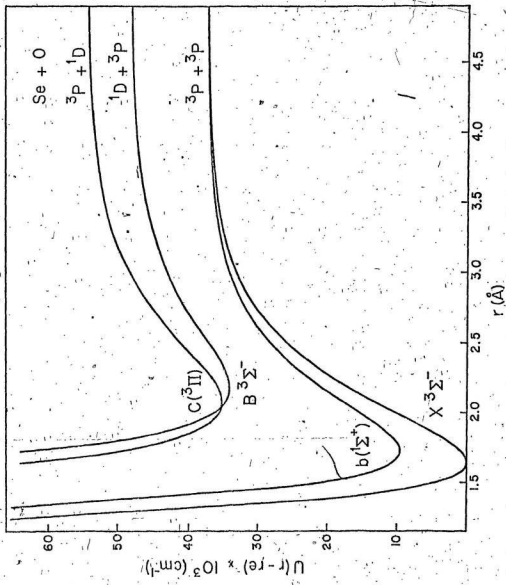


Fig. 7. Morse potential energy curves for X, b, B and C states of SeO.

Several comments are necessary concerning each electronic state:

The $X^3\Sigma^-$ state:

The vibrational levels of the $X^3\Sigma^-$ state are known up to $v = 19$ (Haranath, 1964). The vibrational and rotational constants given in Table VIII are those derived by Barrow and Deutsch (1963) from the rotational analysis of the $B^3\Sigma^- - X^3\Sigma^-$ system. The curve in Fig. 7 corresponds to $X^3\Sigma^- (F_2)$ as F_2 indicates the zero level. The dissociation energy of the ground state, D_0 , has been estimated by Barrow et al. to be about 100 kcal/mole⁻¹. The dissociation products are the ground state atoms Se(³P) and O(³P).

The $b^1\Sigma^+$ state:

The low lying states $a(^1\Delta)$ and $b(^1\Sigma^+)$ which arise from the ground state atoms have both been observed (Azam and Reddy, 1973). Constants for the $b(^1\Sigma^+)$ have been derived from the analysis of the $b-X$ system. However, the $a(^1\Delta)$ state was not well developed and only one sequence consisting of four bands has been observed; hence, its constants are undetermined. The $b^1\Sigma^+$ state dissociates into the ground state atoms Se(³P) + O(³P), its dissociation energy being 27509 cm⁻¹.

The $B^3\Sigma^-$ state

The $B^3\Sigma^-$ state is highly perturbed (Barrow et al., 1963) and appears to be predissociated at $v \geq 3$, but in the absence of detailed study this does not give a precise value of the dissociation energy. However, this has been calculated by the extrapolation method for $B^3\Sigma^- (F_1)$ sub-state. This state dissociates at an energy level (taking that of $X^3\Sigma^-$ to be zero) 10820 cm⁻¹. This indicates that the dissociation products are

$\text{Se}(^1\text{D}) + \text{O}(^3\text{P})$ which correspond to the atomic energy level 3576.08 cm^{-1} (see Atomic Energy Levels by C. E. Moore, National Bureau of Standards, Circular 467). The discrepancy is attributed to the fact that only two points are available to the $\Delta G_{v+1/2}$ vs. $(v+1/2)$ plot and hence the extrapolation is very crude.

The $\text{C}(^3\Pi)$ state:

This state also seems to predissociate around $v \geq 5$. The dissociation energy of the $\text{C}(^3\Pi_0)$ substate turns out to be $\sim 19390 \text{ cm}^{-1}$. This value indicates that the state C dissociates very likely into the ground state $\text{Se}(^3\text{P})$ atom and the excited $\text{O}(^1\text{D})$ atom, although there exists some discrepancy between the estimated dissociation energy from Eq. (16) and the one obtained from the atoms $\text{Se}(^3\text{P})$ and $\text{O}(^1\text{D})$, mainly because of the crude extrapolation made.

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REFERENCES

- Azam, M. 1973. M.Sc. Thesis, Memorial University of Newfoundland.
- Azam, M. and Reddy, S. P. 1973. Can. J. Phys. 51, 2166.
- Azundi, R. K., Jan-Khan, M., and Samuel, R. 1936. Proc. Roy. Soc. A, 157, 28.
- Barrow, R. F. and Deutsch, E. W. 1963. Proc. Roy. Soc. 82, 548.
- Choong, S.-P. 1938. Ann. Phys., Paris 10, 173.
- Colin, R. 1968. Can. J. Phys. 46, 1539.
- Colin, R. 1969. Can. J. Phys. 47, 979.
- Edlen, B. 1953. J. Opt. Soc. Amer. 43, 339.
- Findlay, F. D. 1970. Can. J. Phys. 48, 2107.
- Haranath, P. B. V. 1964. J. Mol. Spectrosc. 13, 168.
- Haranath, P. B. V. 1965. Indian J. Pure & Applied Phys. 3, 75.
- Herzberg, G. 1950. Spectra of Diatomic Molecules, 2nd ed. (D. Van Nostrand Co., Inc., Princeton, New Jersey).
- Herzberg, G. 1971. The Spectra and Structures of Simple Free Radicals (Cornell University Press).
- Hynes, D. L. 1968. B.Sc. Honours (Dissertation, Memorial University of Newfoundland).
- Kushawaha, V. S. and Pathak, C. M. 1972. Spectrosc. Lett. 5, 393.
- Kramers, H. A. 1929. Zeits. f. Physik 53, 422.
- Moore, C. E., Atomic Energy Levels (Circular A67 of National Bureau of Standards, 1969).
- Morse, P. M. 1929. Phys. Rev. 34, 57.
- Reddy, S. P. and Azam, M. 1974. J. Mol. Spectrosc. 49, 461.
- Schlapp, R. 1937. Phys. Rev. 51, 342.

GENERAL REFERENCES

- All, M. K. 1969. M.Sc. Thesis, Memorial University of Newfoundland.
- Duchesne, J. and Rosen, B. 1941. *Physica* VIII, 540.
- Duchesne, J. and Rosen, B. 1947. *J. Chem. Phys.* 15, 631.
- Gatterer, A. and Junkes, J. 1956. *Arc Spectrum of Iron*, 2nd ed. (Specola Vaticana, Citta del Vaticano).
- Gaydon, A. G. 1968. *Dissociation Energies and Spectra of Diatomic Molecules*, 3rd ed. (Chapman and Hall Ltd., London).
- Harrison, G. R. 19 . *M.I.T. Wavelength Tables* (John Wiley and Sons, New York).
- Herzberg, G. 1950. *Spectra of Diatomic Molecules*, 2nd ed. (D. Van Nostrand Co., Inc., Princeton, New Jersey).
- Hynes, D. L. 1968. B.Sc. Honours Dissertation, Memorial University of Newfoundland.
- Mulliken, R. S. "Interpretation of Band Spectra",
Parts I, II(a) and II(b), *Rev. Mod. Phys.* Vol. 2 (1930)
Part II(c), *Rev. Mod. Phys.* Vol. 3 (1931)
Part III, *Rev. Mod. Phys.* Vol. 4 (1932).
- Sawyer, R. A. 1951. *Experimental Spectroscopy*, 2nd ed. (Chapman and Hall Ltd., London).
- Pearse, R. W. B. and Gaydon, A. G. 1963. *The Identification of Molecular Spectra*, 3rd ed. (Chapman and Hall Ltd., London).
- "Spectroscopic Data Relative to Diatomic Molecules", 1970. Established under the direction of B. Rosen (Pergamon Press, New York).

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