THE EMISSION SPECTRUM OF CARBON MONOSELENIDE

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by

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ABSTRACT

The emission spectrum of CSe was excited in an electrodeless discharge tube containing a mixture of carbon and selenium in the presence of argon by means of a high power microwave generator. Spectra were photographed on a 2 m Bausch and Lomb dual grating spectrograph in the first order of a grating with 1200 grooves/mm. Thirty-seven characteristic bands of CSe were obtained in the spectral region 3060 - 2680 Å. In addition to the previously known $A^1\Pi - X^1\Sigma^+$ system, a new band system has been identified for the first time. The wavenumbers of the band heads of the new system are represented by the relation,

$$\nu = 34702.2 + 954.9(v' + \tfrac{1}{2}) - 6.9(v' + \tfrac{1}{2})^2 - \left[1039.9(v'' + \tfrac{1}{2}) - 8.4(v'' + \tfrac{1}{2})^2\right] .$$

By correlating the ω_e values of different electronic states of the analogous molecules CO, CS and CSe it is suggested that the transition giving rise to the new band system of CSe is probably $a^3\Pi - X^1\Sigma^+$.

A complete rotational analysis of the 0,1 band and a partial rotational analysis of the 1,2 , 1,1 , 0,0 , 2,1 and 1,0 bands of the $A^1\Pi - X^1\Sigma^+$ system, photographed at high resolution in the fifth order of the grating, are also reported. The rotational constants obtained for the lower and upper states are as follows:

$B''_v = 0.577 - 0.0045\ (v'' + \tfrac{1}{2})\ \mathrm{cm}^{-1}$

$D'' = 3 \times 10^{-6}\ \mathrm{cm}^{-1}$

$r''_e = 1.673\ \text{Å}$

$B'_0 = 0.484\ \mathrm{cm}^{-1}$

$B'_1 = 0.489\ \mathrm{cm}^{-1}$

$B'_2 = 0.478\ \mathrm{cm}^{-1}$

$D' = 1 \times 10^{-6}\ \mathrm{cm}^{-1}$

$r'_0 = 1.827\ \mathrm{cm}^{-1}$

$$\nu_{00} = 35135.51\ \mathrm{cm}^{-1}\ .$$

The values of B'_e and α'_e could not be determined from the obtained rotational constants because of perturbations in the upper state.

CHAPTER 1

INTRODUCTION

1.1 Electronic Spectra of Diatomic Molecules Formed of Carbon With the Sixth Group Elements O, S and Se:

With the advent of quantum mechanics in the 1920's extensive study of the electronic band spectra of diatomic molecules was begun. Very considerable advances have been made since then in our understanding of the structure of a large number of molecules. From a detailed analysis of the electronic spectrum of a molecule, it is possible to make an accurate determination of its electronic, vibrational and rotational levels. As a result one can obtain precise information about the structure of the electrons in the molecule and about the vibrational and rotational frequencies of its nuclei. Important properties such as the nature of the chemical valence of the molecule can be understood from its electronic configuration. Forces between the atoms of the molecule and its dissociation energies can be readily obtained from its vibrational frequencies. Moments of inertia of the molecule and the nature of the coupling between its electronic and rotational motions can be determined accurately from a study of the rotational fine structure of its electronic bands. Furthermore, from an analysis of the electronic band spectrum of a molecule one can obtain other important information such as potential energy curves of different electronic states of the molecule, perturbations between energy levels of the various electronic states, transition probabilities and life times in the states and dipole moments of the molecule in various electronic states.

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. Considering the diatomic molecules CO, CS and CSe (formed of C and the elements O, S and Se of the sixth group of the periodic table), one expects within a first approximation similar electronic spectra because the outermost shells of electrons, $2p^4$, $3p^4$ and $4p^4$ for O, S and Se, respectively, are the same except for the principal quantum number. However, the relative positions of the energy levels and the nature of the coupling between the electronic and rotational motions in these analogous molecules depend also on the innermost shells of electrons of their constituent atoms. To obtain a proper correlation of the electronic states of these molecules and to determine the nature of their coupling from their spectra it is necessary to discover as many band systems as possible for each of these molecules and, if possible, to analyze the rotational fine structure of the band systems found.

The study of the electronic band spectrum of CO, both in emission and absorption, the modern investigation of which began with the work of Birge (1926), has led to great advances in our understanding of its structure in the electronic ground state as well as in a large number of excited states. The number of electronic states so far observed for CO is at least 24 and its band systems extend from 600 Å in the vacuum ultraviolet region to 8600 Å in the near infrared region. For a comprehensive review of the literature on the spectrum of CO and for a compilation of data on band positions, energy levels, molecular constants, potential energy curves and other molecular properties derived from its spectrum, the reader is referred to the recent review paper by Krupenie (1966) (see also Herzberg et al, 1970, and the references therein).

The electronic band spectrum of CS has not been studied as extensively as that of CO. For CS, five electronic band systems involving five excited electronic states and a common ground electronic state have been observed experimentally in the spectral region 3860 - 2400 Å (see Barrow et al, 1960, and the references therein, and Tewarson and Palmer, 1968).

The work on the electronic band spectrum of CSe is, however, very meagre. Only one band system has been observed in emission in the spectral region 3055 - 2750 Å (see Section 1.2). A further careful study of the electronic band spectra of CS and CSe is therefore considered worthwhile. The present thesis embodies the results obtained from an investigation of the emission spectrum of CSe.

1.2 Previous Work on the Electronic Band Spectrum of CSe:

Rosen and Désirant (1935) were the first to observe the emission spectrum of CSe which was excited in an electrodeless discharge in a silica tube containing selenium and carbon. The spectrum was photographed in the spectral region 3055 - 2775 Å on a spectrograph having a reciprocal dispersion of 14 Å/mm at 3000 Å. The band system obtained was analyzed as consisting of 10 bands. The band heads of the system could be represented by the approximate formula:

$$\nu = 35250 + 830(v' + \tfrac{1}{2}) - \left[1037(v'' + \tfrac{1}{2}) - 8(v'' + \tfrac{1}{2})^2\right] .$$

Rosen and Désirant tentatively assigned the transition $A^1\Pi - X^1\Sigma^+$ to this system, in analogy with the $A^1\Pi - X^1\Sigma^+$ systems of CO and CS.

Barrow (1939) reinvestigated the emission spectrum of CSe in the ultraviolet region using a positive column heavy current discharge through a silica tube containing aluminum, selenium and a small amount of hydrocarbon grease. The spectrum of CSe was photographed in the region 3054 - 2760 Å on a 2.4 m concave grating spectrograph with a reciprocal dispersion of 7.42 Å/mm and on a large quartz littrow instrument having reciprocal dispersions of 2.40 Å/mm and 3.90 Å/mm at 2600 Å and 3000 Å, respectively. In all, twelve band heads were assigned vibrational quantum numbers. The band heads associated with the v' = 1 level were found to be affected by perturbations of the order of 10 cm^{-1}. With the exception of the bands affected by these perturbations, the data of the band heads could be represented by the formula:

$$\nu = 35238.0 + 835.7(v' + \tfrac{1}{2}) - 2.2(v' + \tfrac{1}{2})^2 - \left[1036.0(v'' + \tfrac{1}{2}) - 4.8(v'' + \tfrac{1}{2})^2\right] - 1.3(v' + \tfrac{1}{2})(v'' + \tfrac{1}{2}) .$$

Laird and Barrow (1953) made a further study of the ultraviolet band spectrum of CSe which was excited in an electrodeless discharge through methylene chloride (CH_2Cl_2) and selenium vapor. This was photographed on a quartz littrow spectrograph (see Barrow, 1939). Vibrational assignments were made for sixteen band heads and seven band heads were left unassigned. These authors also performed a partial rotational analysis of seven assigned bands and found no evidence against the view that the main system of CSe is a $^1\Pi$ - $^1\Sigma^+$ transition, in which the $^1\Pi$ state is greatly perturbed. This analysis by Laird and Barrow partly answered the criticism of Howell (1947) who claimed that the main system of CSe (as well as the corresponding system of CS) is really a $^3\Pi$ - $^1\Sigma$ transition, analogous to the Cameron bands of CO.

1.3 The Present Study of the Emission Spectrum of CSe:

The emission spectrum of CSe was excited in an electrodeless discharge tube containing a mixture of carbon and selenium, in the presence of argon, by means of a high power microwave generator. Thirty-seven characteristic bands of CSe were obtained in the spectral region 3060 - 2680 Å. In addition to the previously known $A^1\Pi$ - $X^1\Sigma^+$ system, a new band system has been identified for the first time. The vibrational constants obtained from the analysis reveal that the new band system and the A - X system have a common lower electronic state. By correlating the ω_e values of different electronic states of the analogous molecules CO, CS and CSe it is suggested that the transition giving rise to the new band system of CSe is probably $a^3\Pi$ - $X^1\Sigma^+$. Finally a complete rotational analysis of the 0,1 band, and a partial rotational analysis of several other bands, of the $A^1\Pi$ - $X^1\Sigma^+$ system, photographed at high resolution, have been done yielding rotational constants of the states A and X.

CHAPTER 2

EXPERIMENTAL METHOD

The emission spectrum of carbon monoselenide was excited in a quartz discharge tube containing equal amounts of carbon and selenium powders in the presence of argon gas by means of microwave radiation. In this chapter the apparatus used and the experimental procedure adopted will be described.

2.1 Spectrographs:

(a) Hilger and Watts Medium Quartz Prism Spectrograph:

For the preliminary investigation of the emission spectrum of CSe, a medium quartz prism spectrograph, supplied by Hilger and Watts, Ltd., London, England, was employed. The maximum aperture of this instrument is f/12. The best focus of the spectrograph can be obtained by adjusting the position of the slit and the tilt of the plate holder. The spectral region 10000 - 2000 Å can be photographed on a single plate. The reciprocal dispersions for this instrument are 11.3 Å/mm and 15.7 Å/mm at 2720 Å and 3060 Å, respectively.

(b) Bausch and Lomb Dual Grating Spectrograph:

The emission spectrum of CSe was photographed on a dual grating spectrograph supplied by Bausch and Lomb Optical Company, Rochester, New York, U.S.A. A schematic diagram of the instrument is given in Fig. 1. Light from a discharge tube (not shown in the figure) enters the spectrograph through the variable slit S and is incident on the spherical mirror

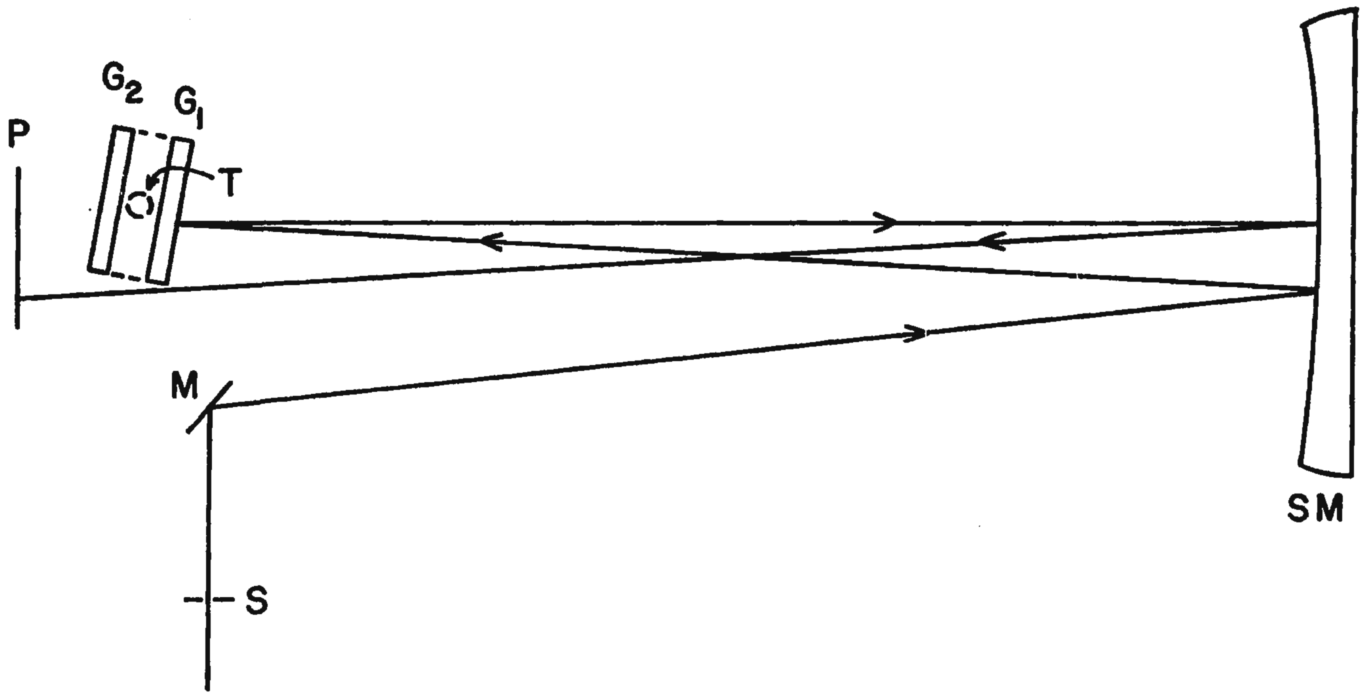

Fig. 1. Optical Arrangment of the Bausch and Lomb Dual Grating Spectrograph.

SM after having been reflected at the plane mirror M. It is then dispersed by grating G_1 or G_2, which can be set into position by means of a rotatable turret T, and later focussed by the mirror SM on to the photographic plate P. The spectrograph is of the littrow-type and the spherical mirror SM having a radius of curvature of 200 cm acts as the collimator. The plate holder can be raised manually or automatically. A Hartmann diaphragm attached to the spectrograph in front of the slit enables spectra to be photographed in juxtaposition. The numerical aperture of the spectrograph is f/15.5. G_1 and G_2 are echelle-type plane gratings, also supplied by Bausch and Lomb, each having a ruled width of 128 mm and a groove length of 102 mm. They have 1200 grooves/mm and 600 grooves/mm, respectively. The slit width was maintained at 0.2 mm. The spectra were photographed in the first and fifth orders of the grating having 1200 grooves/mm. The reciprocal dispersions obtained with this grating are as follows: 4.11 Å/mm at 2715 Å and 4.08 Å/mm at 2995 Å, in the first order; and 0.47 Å/mm at 2779 Å and 0.33 Å/mm at 3047 Å in the fifth order. The specifications of the grating are as follows:

Blazed Wavelength:	1.0 micron (first order)
Blaze Angle:	36^{o} 52'
Resolving Power ($\lambda/\Delta\lambda$):	70% of the theoretical value (153600 in the first order)
Efficiency:	62% at 9000 Å 66% at 1.0 micron 70% at 1.1 microns
Ghost Intensity:	1% of the parent line in the 2nd order at 5461 Å

2.2 Microwave Generator:

The emission spectrum of the CSe vapor was excited by radiation from the microwave power generator model PGM-100 supplied by the Raytheon Company, Waltham, Mass., U.S.A. The microwave generator consists of a fixed frequency, air-cooled, CW-type magnetron oscillator. A full wave rectified power supply unit is provided with the magnetron, the average anode current being held constant by a magnetic regulator. Thus, variations in the magnetron impedance with load and life are overcome and a constant power output is achieved. A cross-sectional view of the experimental arrangement is presented in Fig. 2. Shown are the microwave power generator PGM-100, its filter unit F, the slotted waveguide G and the horn H. Also shown are the probe P, the discharge tube D, the metallic reflector R and the microwave radiation cage C. The filter unit F supplied with the generator provides a microwave power output having a modulation of about 10% in the detected R.F. envelope when switched into the magnetron plate supply. The microwave power generator with filter connected provides a variable output power in the range 250 to 800 watts at a fixed frequency of 2450 ± 25 MHz.

The slotted waveguide G and the horn H are connected to the microwave power generator as shown in Fig. 2. The waveguide has inner dimensions of 4.3" x 2.2" and a slot is provided in the waveguide to enable probe P to be inserted. The wavelength of the radiation within the waveguide is 14.8 cm. Further details on the construction of the waveguide and horn have been described by Ali (1969). The horn H, the discharge tube D and the metallic reflector R are enclosed in a cage C

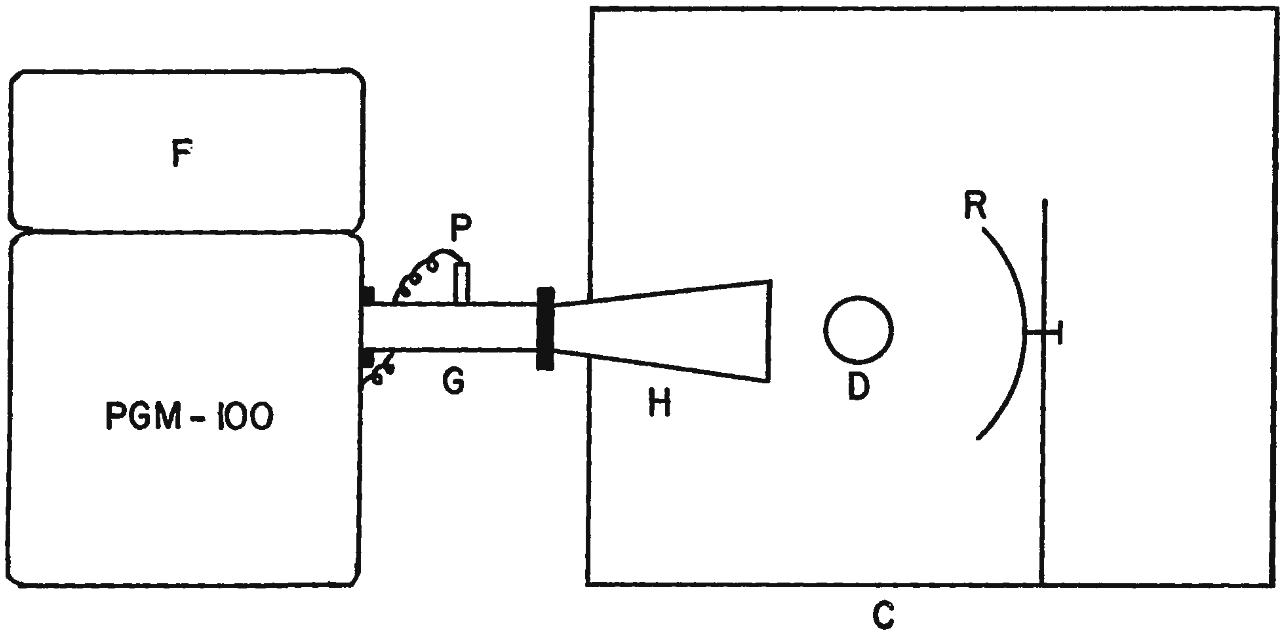

Fig. 2. Cross-Sectional View of the Experimental Arrangment.

made with copper screening of mesh size 0.1 cm x 0.15 cm. Rubber mats were placed on the bottom of the cage to absorb scattered radiation. For the same reason, clay bricks were placed along the wall of the cage behind the reflector R. A photograph of the experimental arrangement with the spectrograph removed is given in Fig. 3.

2.3 Mechanism of Electrical Discharges:

The basic process involved in producing and maintaining an electrical discharge in any discharge tube consists of the following three steps: (i) Free electrons are first accelerated by a potential difference or an electrical energy from a device such as a microwave power generator. (ii) The kinetic energy thus acquired by the free electrons is then transformed into the internal energy of the atoms or molecules in the discharge tube as a result of a collision process, i.e., the atoms or molecules are excited to their higher internal energy states. This internal energy could be electronic, vibrational and rotational in nature in the case of molecules. (iii) The internal energy of the atoms or molecules is finally dissipated as radiation (light quanta) as they relax back to their lower energy states. The free electrons are then accelerated again by the external power source, and the whole process is repeated.

In the excitation of certain molecular discharges, it is sometimes necessary to introduce inert gas at low pressure into the discharge tube to sustain the discharge. In the present investigation, the characteristic CSe spectrum was excited by a microwave power generator. Argon at low pressure was used as the carrier gas of the discharge. It

Fig. 3. Photograph of the Experimental Arrangement.

was sometimes found necessary to initiate the discharge with the help of a tesla coil. The details of the discharge tube and the gas handling system are described in the next section.

2.4 Discharge Tube and Gas Handling System:

The quartz discharge tube used for the excitation of the CSe spectrum was 18" long and 25 mm in diameter and its schematic diagram is shown in Fig. 4. The quartz window, 2mm thick, was fused at one end of the discharge tube. The other end of the discharge tube was connected by means of a graded seal to a pyrex stopcock which enables the discharge tube to be isolated from the rest of the system. Before the graded seal was fused to the discharge tube, a mixture of equal quantities of carbon (supplied by Leybold Company) and selenium (supplied by The British Drug Houses, Ltd.) was placed in the discharge tube. The discharge tube was then connected to a gas handling system and to a high vacuum pumping system through the liquid nitrogen trap.

As mentioned earlier in this chapter, it was necessary to excite the CSe spectrum in the presence of argon at low pressure. The gas handling system used in order to purify and later to admit the argon gas into the discharge tube is shown in Fig. 5. Ultra pure argon (99.999% purity), supplied by Matheson of Canada, Ltd., was introduced from a cylinder into the storage bulbs C_1 and C_2 through cold trap A and the quartz tubing B which was 20" long and 19 mm in diameter and contained copper turnings. The storage bulbs are in turn connected to the discharge tube and the vacuum system as shown. A manometer M was used to measure the gas pressure in the storage bulbs. The entire gas handling system

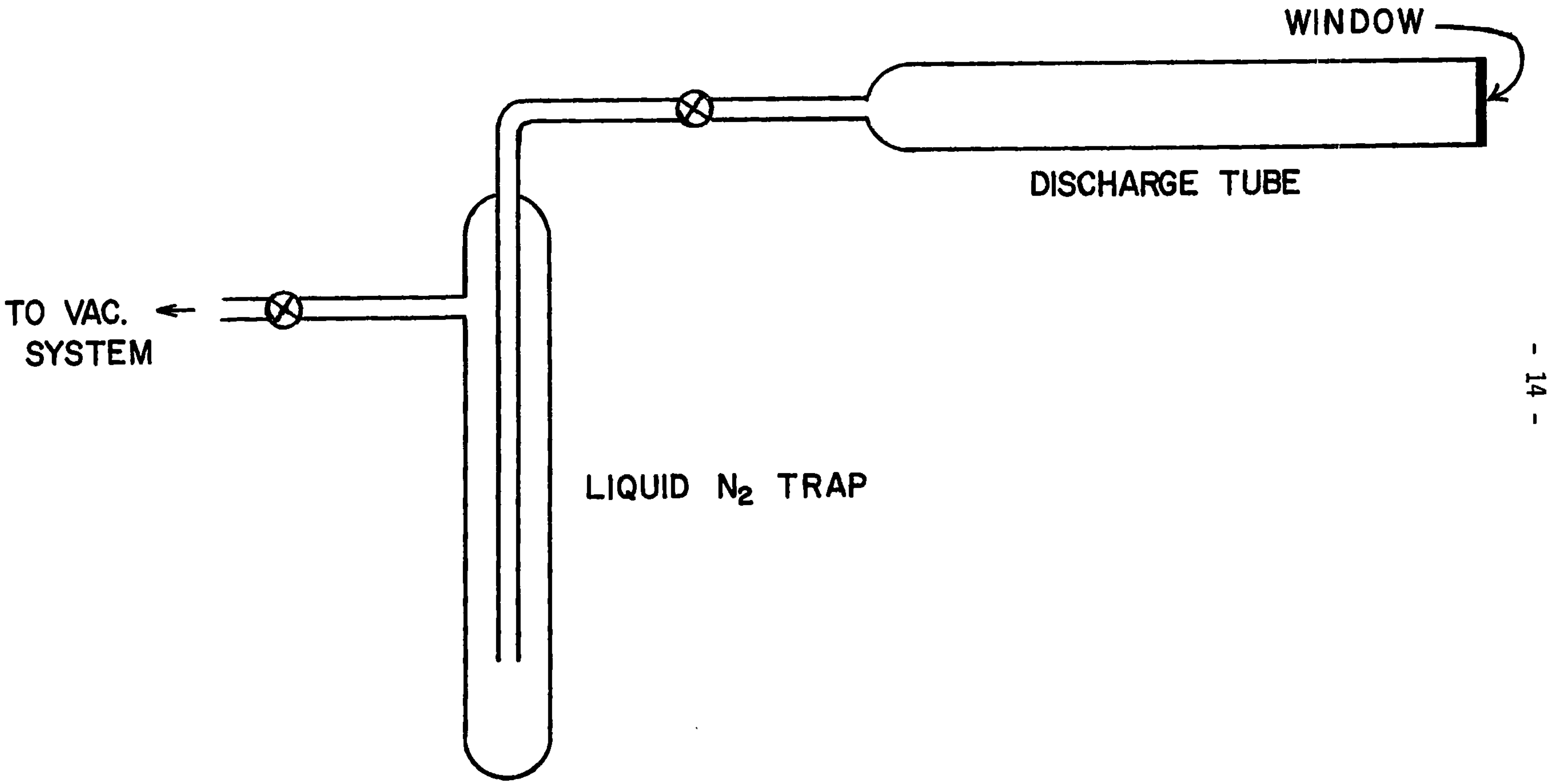

Fig. 4. Discharge Tube and Liquid Nitrogen Trap.

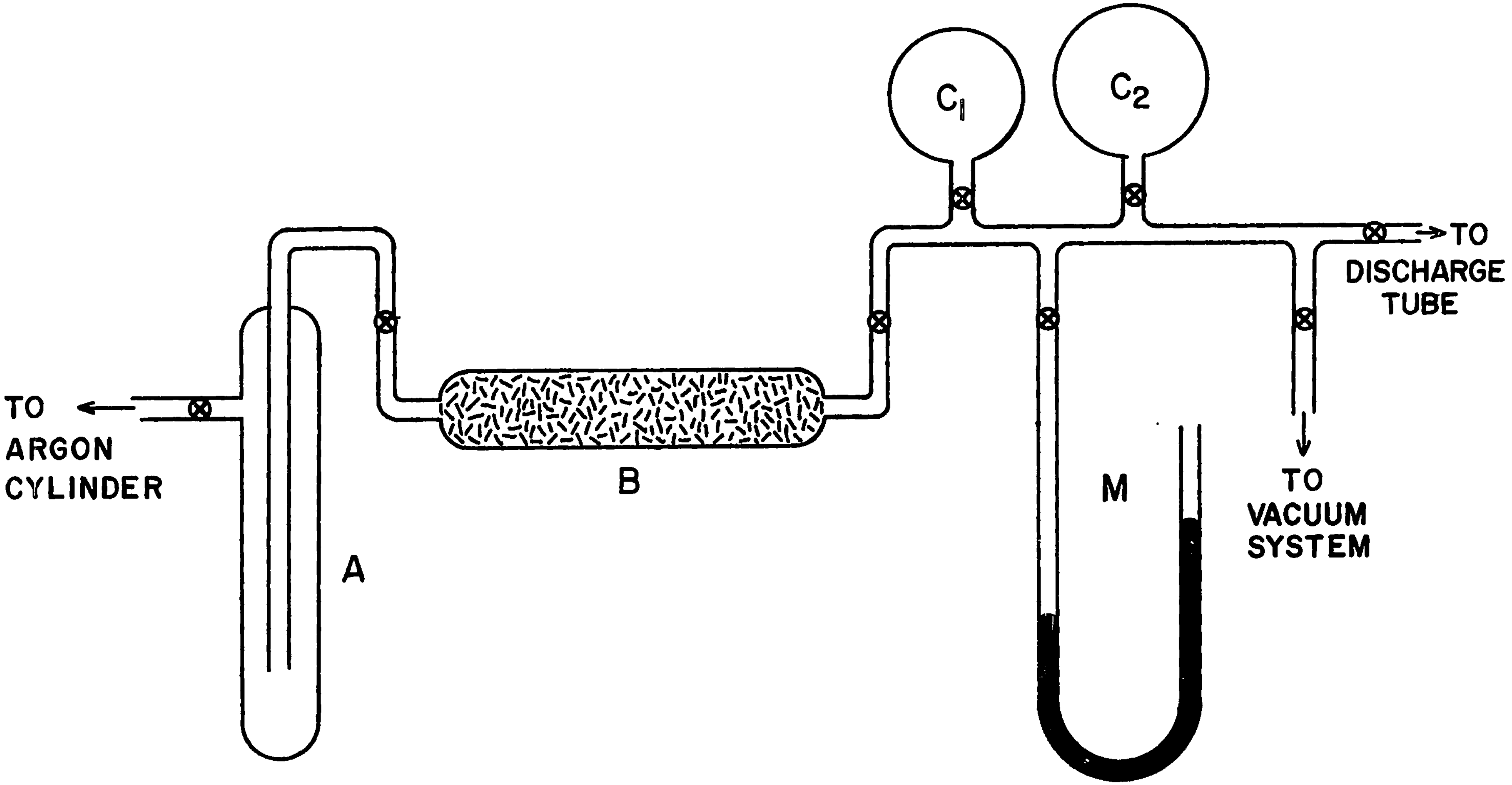

Fig. 5. Schematic Diagram of Gas Handling System.

was first evacuated to a pressure of the order of 10^{-6} torr. All the stopcocks in the system were then closed isolating the various components. Next argon was introduced into the liquid nitrogen trap A at about a pressure of 10 p.s.i. It was then allowed to evaporate and to pass through the heated copper turnings in the quartz tubing B to remove all traces of impurity including water vapor. The purified argon was then stored in the glass reservoirs C_1 and C_2 until used in the experiment.

2.5 Experimental Procedure:

The discharge tube (see Fig. 4) containing a mixture of carbon and selenium powders, of approximately 10 grams each, was optically aligned with respect to the slit of the spectrograph so that the collimator of the spectrograph was filled uniformly with light from the discharge tube. The discharge tube was then connected to a high vacuum pumping system, consisting of a rotary pump in conjunction with an oil diffusion pump, and was evacuated to a pressure of about 5×10^{-7} torr. Traces of water vapor were removed from the discharge tube by initially heating it with a bunsen burner. Condensation of vapors on the window of the discharge tube, while the discharge was on, was prevented by heating the window under a low bunsen flame. Care was taken that the flame did not enter the optical path of the radiation from the discharge tube. Argon gas from reservoirs C_1 or C_2 (see Fig. 5) was slowly admitted at low pressure into the discharge tube. The gas pressure required to sustain the discharge was in the range 1 to 4 mm of Hg. When the desired gas pressure was attained in the discharge tube, the stopcock connecting the discharge tube to the rest of the system was closed. The discharge tube was then irradiated by the high power microwave generator using the desired output power. A tesla coil was sometimes needed to initiate the discharge. The metallic reflector R (see Fig. 2) was adjusted until the most intense discharge as well as the lowest standing wave ratio (VSWR), hereafter referred to as r, were obtained. The procedure followed in determining r was described previously by Ali (1969). The details are as follows: A probe P capable of being moved along a slotted section of waveguide G (see Fig. 2) was connected to a Wheatstone Bridge circuit. A graph of distance along the slotted section versus the resistance required to balance the circuit was plotted. The resultant graph had a number of maxima and minima positions. The square roots of the ratios between the resistances corresponding to maxima and minima of voltage were found and equated to r. Since the manufacturers of the microwave generator set the limit of the value of r at 2 for maximum power output in phase, the reflector was adjusted until a calculated value of $r < 2$ was achieved. The final value of r was found to be in the range 1.26 to 1.31. The power received P_r was then computed by means of the equation

$$P_r = P_a \left[4r/(1 + r)^2\right] , \tag{1}$$

where P_a is the power available. Hynes (1968) obtained a calibration curve of anode current versus power output using a water load in conjunction with this microwave generator. At the normal operating anode current of 260 ma it was determined from this curve that P_a was 755 watts. The corresponding value of P_r was found to be 740 watts.

Preliminary spectra were recorded using a Hilger and Watts medium quartz prism spectrograph. Spectra were photographed using Kodak

SWR, 103a-O, Panchromatic Type B, 1N and 1Z plates so that a complete study from the ultraviolet to the photographic infrared region could be made. These were taken at a slit width of 0.01 mm for various exposure times in the range 1 second to 30 minutes, depending on the type of plate used. Using the same slit width, d.c. iron arc spectra were recorded in juxtaposition to the CSe spectra as the wavelength calibration. This was accomplished using a Hartmann diaphragm. The iron arc used was operated at a voltage of 125 volts and a current of 4 amps. Final spectra in the ultraviolet region were taken on the Bausch and Lomb dual grating spectrograph in the first and fifth orders of a grating with 1200 grooves/mm. Exposure times were in the range ½ to 1 hour for the first order plates and 2 to 6 hours for the fifth order plates. Iron arc spectra were recorded in the same manner as on the medium quartz plates. The overlapping of different orders was eliminated by means of the interference filter SWP-3340 specially obtained from Baird Atomic, Inc. The transmission curve of this filter is given in Fig. 6.

2.6 Measurement of Spectra:

All spectral measurements were made on a linear comparator Model M1205C supplied by the Gaertner Optical Instrument Company, Chicago, Illinois, U.S.A. The comparator is capable of reading to 0.001 mm. In the spectral region of interest the band heads or the rotational lines of the CSe spectrum and a number of sharp standard iron arc lines, photographed in juxtaposition to the former, were measured. The wavelengths of several iron arc lines were then used to obtain the constants a_o, a_1 and a_2 of the following equation by means of a least squares fit:

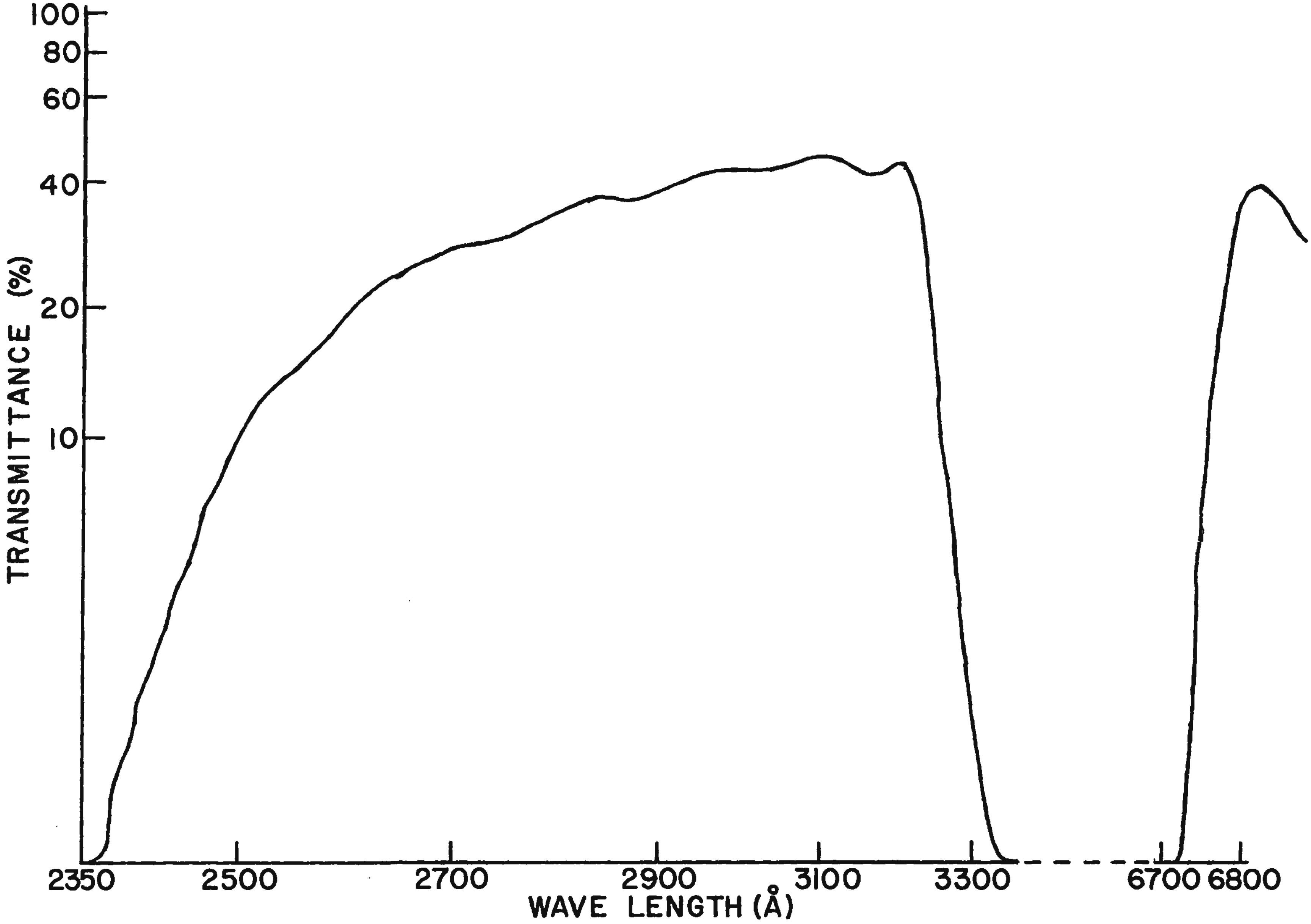

Fig. 6. Transmittance Curve of Filter SWP-3340.

$$\lambda_{air} = a_0 + a_1 d + a_2 d^2 \quad , \tag{2}$$

where λ_{air} is the wavelength of an iron arc line in air and d is the corresponding comparator reading. The accuracy of the constants was tested by calculating, in the same spectral region, the λ values of other reference lines whose d's had been measured. For sharp lines the accuracy of measurement was better than 0.02 Å in the first order and 0.005 Å for the fifth order plates. The wavelengths of the CSe spectrum were then obtained from Eq. (2). The vacuum wavenumbers (σ in cm^{-1}) could have been directly obtained from Coleman <u>et al</u> (1960). However, since a large number of rotational lines were measured for the CSe spectrum, an IBM 370 computer was used to convert the values of λ_{air} to σ using Edlén's (1953) formula for the refractive index, n, of air,

$$n = 1 + 6432.8 \times 10^{-8} + \frac{2949810}{146 \times 10^{8} - \sigma^2} + \frac{25540}{41 \times 10^{8} - \sigma^2} \quad , \tag{3}$$

where

$$\sigma\ (cm^{-1}) = \frac{10^8}{n\ \lambda_{air}(Å)} \quad . \tag{4}$$

Calculations were made using an iterative method, the iterations being continued until the absolute difference between successive values of σ was $\leq 10^{-10}\ cm^{-1}$.

CHAPTER 3

VIBRATIONAL STRUCTURE OF THE EMISSION SPECTRUM OF CSe

3.1 Introduction:

The details of the apparatus and of the experimental procedure followed in obtaining the emission spectrum of CSe in the ultraviolet region were described in detail in Chapter 2. A brief resumé of the experimental conditions is as follows: Preliminary spectra were taken on a Hilger and Watts medium quartz prism spectrograph. Final spectra were photographed on a Bausch and Lomb dual grating spectrograph. Iron arc lines were used as the wavelength standards. The spectra were measured on a Gaertner linear comparator. The band head data reported in this chapter are taken from the measurements of the first order grating plates. The accuracy of the data for the sharp band heads is estimated to be ~ 0.02 Å while it is less for the diffuse band heads.

3.2 Expressions Used in the Vibrational Analysis of the Electronic Band Spectra:

Neglecting the energy of translation and the nuclear spin of a molecule, its total energy E can be expressed, to a good first approximation, as the sum of its electronic energy E_e, vibrational energy E_v and rotational energy E_r (see Herzberg, 1950, Chapter III). Thus,

$$E = E_e + E_v + E_r \tag{1}$$

or, in wavenumber units

$$T = T_e + G(v) + F(J) \ . \tag{2}$$

When only the vibrational structure of an electronic band system is considered, the term E_r (or F(J)) in Eq. (1) (or Eq. (2)) can be omitted. The wavenumber (in cm^{-1}) of a band head is then represented as:

$$\nu = (T'_e - T''_e) + G'(v') - G''(v'')$$

$$\text{or} \quad \nu = \nu_e + G'(v') - G''(v''). \tag{3}$$

Here single- and double-primed letters refer to the upper and lower electronic states, respectively. Each electronic state may have a number of vibrational levels whose term values G(v) are given by

$$G(v) = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3 + \dots \ . \tag{4}$$

Neglecting the cubic and higher order terms in Eq. (4) and substituting into Eq. (3) gives

$$\begin{aligned} \nu = \nu_e &+ \omega'_e(v' + \tfrac{1}{2}) - \omega'_e x'_e(v' + \tfrac{1}{2})^2 \\ &- \left[\omega''_e(v'' + \tfrac{1}{2}) - \omega''_e x''_e(v'' + \tfrac{1}{2})^2\right] \ . \end{aligned} \tag{5}$$

The interval between vibrational states v and v + 1 of a given electronic state can be defined (again neglecting the cubic terms in Eq. (4)) as:

$$\begin{aligned} \Delta G_{v+\frac{1}{2}} &= G(v + 1) - G(v) \\ &= \omega_e - 2\omega_e x_e \ (v + 1) \\ &= (\omega_e - \omega_e x_e) - 2\omega_e x_e \ (v + \tfrac{1}{2}) \ . \end{aligned} \tag{6}$$

The second differences are

$$\Delta^2 G_{v+1} = \Delta G_{v+3/2} - \Delta G_{v+\frac{1}{2}} = -\ 2\omega_e x_e \ . \qquad (7)$$

3.3 Vibrational Structure of the Ultraviolet Band Spectrum of CSe:

In all, thirty-seven characteristic band heads of CSe have been measured in this experiment in the spectral region 3060 - 2680 Å. The general appearance of the bands photographed on the medium quartz prism spectrograph and on the grating spectrograph in the first order is shown in spectrograms (a) and (b), respectively, of Plate I. A few iron arc line wavelengths are marked on the spectrograms to indicate the spectral region. All the bands are degraded to longer wavelengths. The OH band at 3064 Å prevented observations on the long wavelength side.

The $A^1\Pi - X^1\Sigma^+$ system which was previously studied by Rosen and Désirant (1935), Barrow (1939) and Laird and Barrow (1953) has been reinvestigated in the present work. Furthermore, a new band system has been identified in the spectral region 2980 - 2735 Å and analyzed for the first time. A probable transition has been proposed for the new band system on the basis of a correlation of the vibrational frequencies of the electronic states of CSe with those of the known electronic states of the analogous molecules CO and CS.

(i) The A - X System:

The A - X system as photographed in this experiment consists of fourteen bands and is shown in Plate II. The wavelengths and the vacuum wavenumbers of the band heads, the visual estimates of their relative intensities and their vibrational quantum numbers are listed in

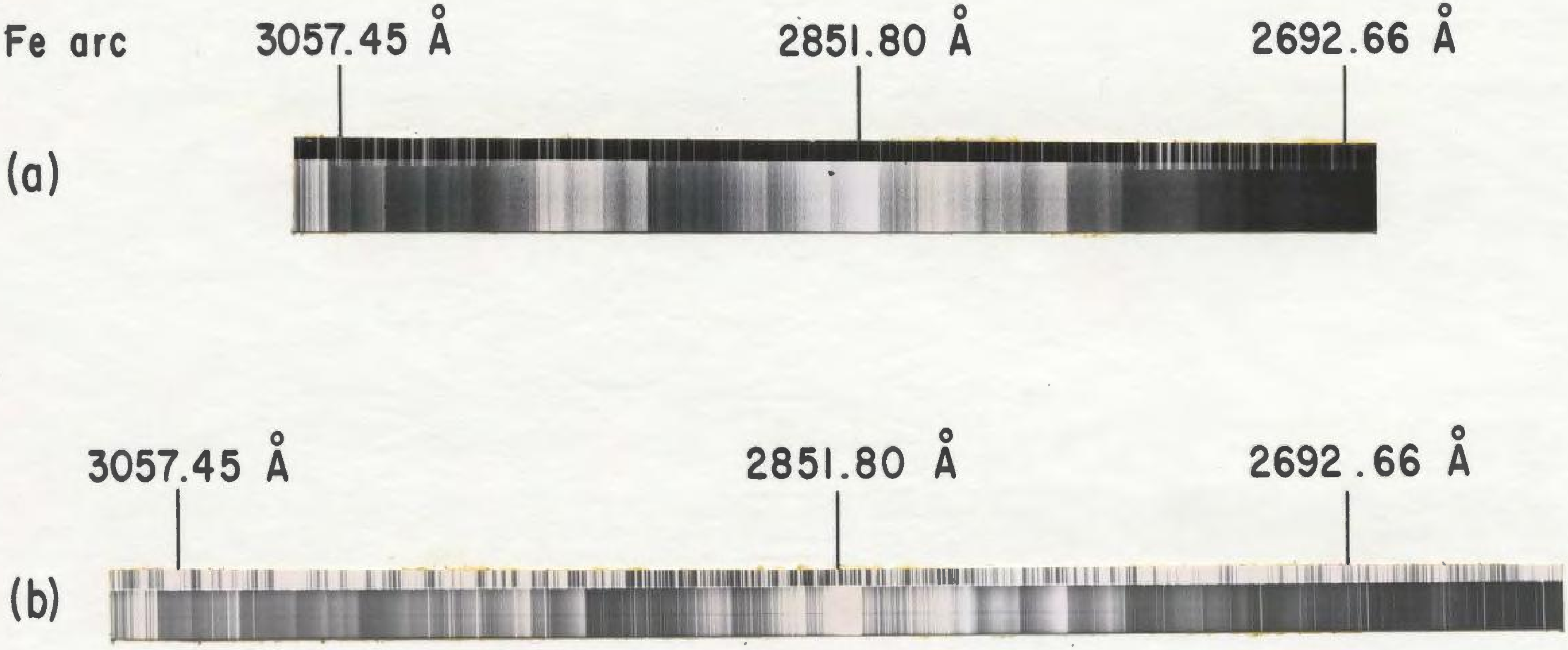

PLATE I : THE EMISSION SPECTRUM OF CSe IN THE REGION 3060 - 2680 Å.
(a) Spectrum Photographed On Medium Quartz Spectrograph
(b) First Order Spectrum Photographed On Grating Spectrograph

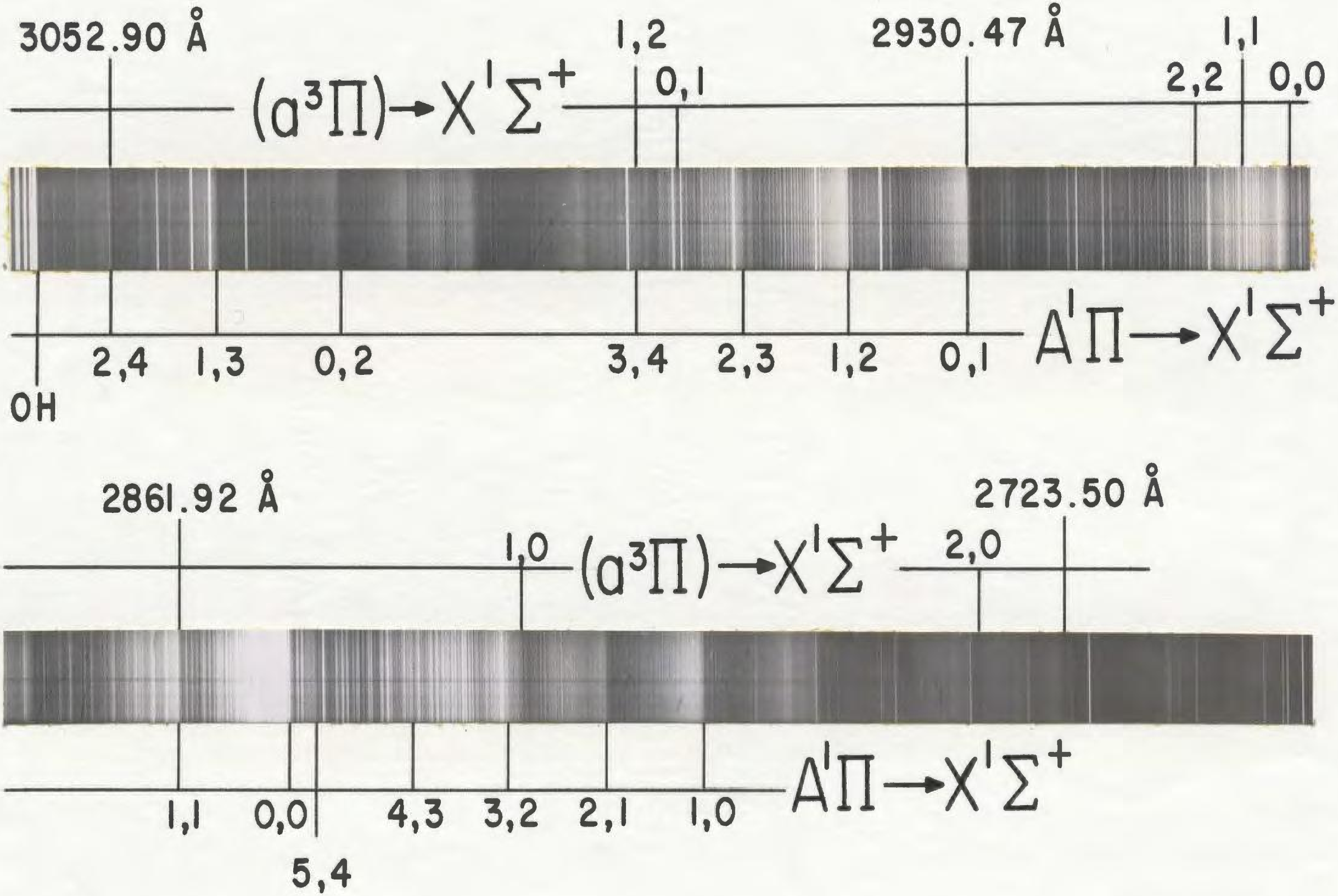

PLATE II : THE ULTRAVIOLET BAND SYSTEMS OF CSe IN THE REGION 3060 - 2680 Å.
(First Order Grating Spectrograms)

Table I. For the purpose of comparison, the wavenumbers of the band heads as presented by Laird and Barrow (1953) are also included in the same table. The vibrational quantum numbers assigned to the bands were determined by fitting the wavenumbers of the band heads in a Deslandres vibrational scheme which is shown in Table II. The bands fall into a narrow Franck-Condon parabola. As can be seen from Table II, the vibrational intervals of the lower state X and the upper state A are as follows:

State X:	State A:
$\Delta G''_{\frac{1}{2}} = 1028.4 \text{ cm}^{-1}$	$\Delta G'_{\frac{1}{2}} = 816.5 \text{ cm}^{-1}$
$\Delta G''_{3/2} = 1014.1 \text{ cm}^{-1}$	$\Delta G'_{3/2} = 836.6 \text{ cm}^{-1}$
$\Delta G''_{5/2} = 1004.5 \text{ cm}^{-1}$	$\Delta G'_{5/2} = 825.9 \text{ cm}^{-1}$
$\Delta G''_{7/2} = 990.0 \text{ cm}^{-1}$	

A straight line fit of the $\Delta G''_{v+\frac{1}{2}}$ values against $v'' + \frac{1}{2}$ was made by a least squares method and the values of $(\omega''_e - \omega''_e x''_e)$ and $-2\omega''_e x''_e$ have been obtained from the intercept and the slope, respectively. The vibrational constants thus obtained are as follows:

$$\omega''_e = 1036.0 \text{ cm}^{-1} \; ; \quad \omega''_e x''_e = 4.9 \text{ cm}^{-1} \, .$$

The large value of $\Delta G'_{3/2}$ as compared to $\Delta G'_{\frac{1}{2}}$ indicates that one of the levels $v' = 0$, 1, or both, are greatly perturbed. If higher vibrational quanta $\Delta G'_{v+\frac{1}{2}}$ had been observed it would have been possible to obtain more accurate information on the level (or levels) perturbed. However, with the limited data available, it is not possible to comment further on this aspect. From the rotational analysis of some bands of

TABLE I

Band Heads of System A - X[a]

λ_{air} (Å)	ν_{vac} (cm^{-1})	Intensity[b]	v', v"	ν_{vac} (cm^{-1}) (Laird and Barrow, 1953)
3052.90	32746.2	w	2 , 4	32752.6
3037.67	32910.4	m	1 , 3	32911.0
3020.05	33102.4	w	0 , 2	33101.9
2977.79	33572.1	w	3 , 4	33570.3
2962.52	33745.2	m	2 , 3	33745.8
2947.69	33914.9	s	1 , 2	33916.6
2930.47	34114.2	m	0 , 1	34114.4
2861.92	34931.3	s	1 , 1	34934.3
2844.83	35141.2	vs	0 , 0	35141.1
2840.49	35194.9	w	5 , 4	35191.8
2825.25	35384.7	w	4 , 3	35392.6
2810.39	35571.8	m	3 , 2	35571.7
2794.84	35769.7	m	2 , 1	35769.4
2779.96	35961.1	s	1 , 0	35960.9

[a]: All bands 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 A - X System

v' \ v''	0		1		2		3		4	Mean $\Delta G'_{v+\frac{1}{2}}$
0	35141.2	1027.0	34114.2	1011.8	33102.4					
	819.9		817.1		812.5					816.5
1	35961.1	1029.8	34931.3	1016.4	33914.9	1004.5	32910.4			
			838.4				834.8			836.6
2			35769.7				33745.2	999.0	32746.2	
									825.9	825.9
3					35571.8				33572.1	
4							35384.7			
5									35194.9	
Mean $\Delta G''_{v+\frac{1}{2}}$		1028.4		1014.1		1004.5		999.0		

the A - X system, given in Chapter 4, it is possible to state that the A - X band system involves a $^1\Pi$ - $^1\Sigma^+$ transition.

(ii) The New Band System:

The new band system, consisting of seven bands degraded to longer wavelengths, is shown in Plate II. The wavelengths, vacuum wavenumbers and visual estimates of the relative intensities of the bands along with their vibrational quantum numbers are listed in Table III. A Deslandres vibrational scheme of the system is presented in Table IV. The values of the vibrational quanta of this system, obtained from the Deslandres scheme, are as follows:

<u>Lower State</u>:

$$\Delta G''_{\frac{1}{2}} = 1023.1 \text{ cm}^{-1}$$

$$\Delta G''_{3/2} = 1006.3 \text{ cm}^{-1}$$

<u>Upper State</u>:

$$\Delta G'_{\frac{1}{2}} = 941.1 \text{ cm}^{-1}$$

$$\Delta G'_{3/2} = 927.3 \text{ cm}^{-1} \quad .$$

The values of ω_e and $\omega_e x_e$ for the lower and upper states of the new system were obtained using Eqs. (6) and (7). The band origin ν_e of the system was determined from Eq. (3) by substituting the calculated values of $G'(v')$ and $G''(v'')$ and the corresponding observed values of ν for all the seven bands. The mean value of ν_e obtained is 34702.2 (±0.5) cm^{-1}. Thus, the wavenumbers of the band heads of the new system can be represented by the formula (see Eq. (5)):

TABLE III

Band Heads of the New System[a]

λ_{air} (Å)	ν_{vac} (cm^{-1})	Intensity[b]	v', v"	$\nu_{obs} - \nu_{calc}$
2977.79	33572.1	w	1 , 2	+0.3
2972.08	33636.6	w	0 , 1	-0.4
2897.72	34499.8	vw	2 , 2	+0.7
2891.13	34578.4	w	1 , 1	+0.3
2884.29	34660.4	m	0 , 0	+0.3
2808.10	35600.8	m	1 , 0	-0.4
2736.84	36527.7	w	2 , 0	-0.8

[a]: All bands degraded to longer wavelengths.

[b]: See footnote of Table I for abbreviations used.

TABLE IV

Vibrational Scheme of the New System

v'' v'	0		1		2	Mean $\Delta G'_{v+\frac{1}{2}}$
0	34660.4	1023.8	33636.6			
	940.4		941.8			941.1
1	35600.8	1022.4	34578.4	1006.3	33572.1	
	926.9				927.7	927.3
2	36527.7				34499.8	
Mean $\Delta G''_{v+\frac{1}{2}}$		1023.1		1006.3		

$$\nu = 34702.2 + 954.9\,(v' + \tfrac{1}{2}) - 6.9\,(v' + \tfrac{1}{2})^2 - \left[1039.9\,(v'' + \tfrac{1}{2}) - 8.4\,(v'' + \tfrac{1}{2})^2\right] \tag{8}$$

As a check on the assignment of v' and v", the wavenumbers of all the band heads were calculated by means of Eq. (8). The last column of Table III gives the differences between the observed and calculated wavenumbers. These residuals were found to have an absolute value of ≤ 0.8 cm^{-1}. From the vibrational analysis it seems reasonable to state that none of the seven bands assigned to the new system is perturbed. The lower state vibrational frequency ω_e of this system, 1039.9 cm^{-1} is in close proximity to that of the lower state frequency, 1036.0 cm^{-1} of the $A^1\Pi$ - $X^1\Sigma$ system (see Section 3.3(i)). It can be concluded that the A - X system and the new system have a common lower electronic state, namely, $X^1\Sigma^+$.

(iii) Unassigned Bands of CSe:

Sixteen band heads in the region 3015 - 2685 Å could not be fitted into either the A - X or the new system. The wavelengths and vacuum wavenumbers of these band heads are listed in Table V. As noted by Laird and Barrow (1953), a few of these heads may perhaps be due to large perturbations in the rotational levels of the A - X system. Some bands of CSe may also lie in the OH band at 3064 Å. It is possible that another new band system might be identified if OH is suppressed completely in the discharge. The characteristic band at 2761 Å may belong to a different system of CSe.

TABLE V

Unassigned Bands of CSe[a]

λ_{air} (Å)	ν_{vac} (cm^{-1})	Intensity[b]
3010.55	33206.9	w
3005.16	33266.4	w
3001.06	33311.9	w
2985.03	33490.7	w
2980.80	33538.2	w
2942.49	33974.9	w
2930.04	34119.2	w
2923.63	34194.0	vw
2887.90	34617.1	m
2849.25	35086.7	s
2766.25	36139.4	w
2761.02	36207.8	w
2729.91	36620.4	vw
2723.50	36706.6	vw
2705.88	36945.6	vw
2689.04	37176.9	vw

[a]: All bands degraded to longer wavelengths.

[b]: See footnote of Table I for abbreviations used.

3.4 Electron Configurations of the Low-Lying States of CO, CS and CSe:

The electron configuration of the C atom is represented by

$C : K2s^2 2p^2$

and the electron configurations of O, S and Se atoms by

$O : K2s^2 2p^4$

$S : KL3s^2 3p^4$

$Se : KLM4s^2 4p^4$.

In deriving the possible molecular electronic states of the analogous molecules CO, CS and CSe one need not take into account the closed K, L and M shells since they contribute $\Lambda = 0$ and $S = 0$. Here, Λ is the quantum number of the electronic angular momentum along the internuclear axis of a molecule and S is the resultant spin of the electrons. Using the standard notation of Mulliken (1932) (see also Herzberg, 1950, Chapter VI), the ground state electron configurations of CO, CS and CSe are represented by

$$(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2 : X^1\Sigma^+ \quad . \tag{9}$$

The expected low-lying upper electron configurations are

$$(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)(v\pi) : {}^3\Pi_r,\ {}^1\Pi \tag{10}$$

and

$$(z\sigma)^2(y\sigma)^2(w\pi)^3(x\sigma)^2(v\pi) : {}^3\Sigma^+,\ {}^3\Sigma^-,\ {}^3\Delta,\ {}^1\Sigma^+,\ {}^1\Sigma^-,\ {}^1\Delta \quad . \tag{11}$$

Higher excited states can be obtained by bringing an electron either from the $(x\sigma)^2$ orbital to $u\sigma$ instead of $v\pi$ as in the configuration given by expression (10) or from the $(w\pi)^4$ orbital to $u\sigma$ instead of $v\pi$ as in the configuration given by expression (11). The number of electronic states resulting from a few of these configurations is very large.

For CO the low-lying electronic states $a^3\Pi_r$ and $A^1\Pi$ arising from expression (10) and $a'^3\Sigma^+$, $e^3\Sigma^-$, $d^3\Delta_i$ and $I^1\Sigma^-$ arising from expression (11) have been identified. However, the $^1\Delta$ and $^1\Sigma^+$ states remain unobserved (see Table VI). For CS the states $a^3\Pi$, $A^1\Pi$, $a'^3\Sigma^+$ and $e^3\Sigma^-$ arising from the configurations have been identified (see Table VI). However, one of its low-lying states, $a^*\Pi$, does not arise from either of the configurations described by expressions (10) or (11). It may possibly arise from a different electron configuration. Prior to the present investigation, only one band system $A^1\Pi$ - $X^1\Sigma^+$ was known for CSe.

3.5 Probable Transition of the New Band System of CSe:

In the absence of a detailed rotational analysis of a band system, it is not possible to establish the exact nature of its electronic transition. However, one may be able to predict the probable transition by correlating the vibrational frequencies of the system with those of the analogous molecules for which the corresponding electronic transitions have been established. These predictions, however, must be confirmed by a detailed rotational analysis.

If the analogous molecules CO, CS and CSe have (i) the same electron configuration and (ii) the same type of coupling, then a close correspondence between their ω_e values can be expected. The reason for this is that the excitation of electrons to the same type of level will

TABLE VI

Comparison of CO, CS and CSe

State^a	T_o (cm^{-1})	ω_e (cm^{-1})	ω'_e/ω''_e	Observed Transitions	References
CO					
$A^1\Pi$	64746.5	1515.61	0.698	A ↔ X	Krupenie (1966)
$I^1\Sigma^-$	64546.65	1092.03	0.503	I ← X	Herzberg *et al* (1966)
$e^3\Sigma^-$	63708.92	1113.67	0.513	e ← X; e → a	Krupenie (1966)
$d^3\Delta_i$	60624.0	1168.18	0.538	d ← X; d → a	Herzberg *et al* (1970)
$a'^3\Sigma^+$	55353.91	1230.651	0.567	a' ↔ X; a' ↔ a	Krupenie (1966)
$a^3\Pi$	48473.97	1743.55	0.804	a ↔ X (Cameron Bands)	"
$X^1\Sigma^+$	0	2169.8233	1.000	———	"
CS					
$e^3\Sigma^-$	$\leq$39160.8	$\geq$ 742	$\geq$0.577	e ← X	Barrow *et al* (1960)
$a'^3\Sigma^+$	$\leq$38851.8	$\geq$ 739	$\geq$0.575	a' ← X	"
$A^1\Pi$	38797.6	1073.4	0.835	A ↔ X	"
$a^*\Pi$	$\leq$38613.9	$\geq$ 780	$\geq$0.607	a* ← X	"
($a^3\Pi$)	27681±10	1138±10	0.89	a → X	Tewarson and Palmer (1968)
$X^1\Sigma^+$	0	1285.08	1.000	———	Barrow *et al* (1960)

TABLE VI (Continued)

Comparison of CO, CS and CSe

State[a]	T_o (cm^{-1})	ω_e (cm^{-1})	ω_e'/ω_e''	Observed Transitions	References
			CSe		
$A^1\Pi$	35134.6	840	0.811	A → X	Laird and Barrow (1953)
$(a^3\Pi)$	34660.1	954.9	0.922	a → X	Present Work
$X^1\Sigma^+$	0	1036.0	1.000	———	"

[a]: States enclosed in parentheses are obtained from vibrational analyses only.

be accompanied by corresponding changes in the force constants which will be reflected in the ω_e values. A comparison of the low-lying electronic states of CO and all the observed electronic states of CS and CSe with respect to their ω_e values is very instructive. In Table VI are listed the electronic states, their term values T_0, the corresponding ω_e values and the observed transitions for CO, CS and CSe. The computed values of ω_e'/ω_e'' are also shown in the same table. Here, ω_e'' refers to the ground state vibrational frequency while ω_e' refers to the vibrational frequencies of the various excited states. From Table VI, it can be seen that the ratios for the A states of CO, CS and CSe are 0.698, 0.835 and 0.811, respectively. The ratio obtained for the upper state of the new system of CSe is 0.922. This value agrees with the ratios found for the $a^3\Pi$ states of CO and CS, namely, 0.804 and 0.89, respectively.

On the basis of this favourable comparison of the vibrational frequencies it is now suggested that the upper state of the new band system is probably the $a^3\Pi$ state and that the transition involved is $a^3\Pi - X^1\Sigma^+$, analogous to the Cameron bands of CO and to the bands of CS observed by Tewarson and Palmer (1968). However, it must be pointed out that we have not been able to assign for each v'- and v"-numbering the triple heads corresponding to the three sub-bands due to the $^3\Pi_0 - {}^1\Sigma^+$, $^3\Pi_1 - {}^1\Sigma^+$ and $^3\Pi_2 - {}^1\Sigma^+$ transitions. It seems probable that the new system of CSe identified by us is one of the three possible subsystems of $a^3\Pi - X^1\Sigma^+$. A detailed rotational analysis of this band system may provide an answer to this problem.

CHAPTER 4

ROTATIONAL ANALYSIS OF THE $A^1\Pi$ - $X^1\Sigma^+$ SYSTEM OF CSe

4.1 Introduction:

In the present chapter we report the rotational analysis of the $A^1\Pi$ - $X^1\Sigma^+$ system of carbon monoselenide. Of the several bands photographed on the Bausch and Lomb dual grating spectrograph in the fifth order of the grating with 1200 grooves/mm, the 0,1 band at 2930 Å was relatively well developed even though partially overlapped by some weaker bands. In the present work a complete rotational analysis of the 0,1 band has been made. A partial rotational analysis has also been done for the 1,2 , 0,0 , 1,1 , 1,0 and 2,1 bands. A complete analysis was not possible for these bands due to the following reasons: (i) inadequate resolution of the instrument, (ii) overlapping of these bands by other bands and (iii) possible perturbations in the energy levels. An attempt to do the rotational analysis of some of the stronger bands of the $(a^3\Pi)$ - $X^1\Sigma^+$ system was unsuccessful because of the same reasons.

4.2 Expressions Used in the Rotational Analysis of a $^1\Pi$ - $^1\Sigma^+$ System:

The wavenumbers of the rotational levels of a specific vibrational band in an electronic band system are given by

$$(1) \qquad \nu = \nu_0 + F'_v(J') - F''_v(J'')$$

where ν_0 $(= \nu_e + \nu_v)$ is a constant, called the band origin, and $F'_v(J')$ and $F''_v(J'')$ are the rotational terms of the upper and lower states, respectively. Neglecting the dependence of these terms on the electronic angular momentum quantum number Λ, $F_v(J)$ for a non-rigid rotator may be written as:

$$F_v(J) = B_vJ(J + 1) - D_vJ^2(J + 1)^2 + \dots , \tag{2}$$

where

$$B_v = B_e - \alpha_e(v + \tfrac{1}{2}) + \dots \ . \tag{3}$$

The rotational constant B_e is related to the equilibrium internuclear distance r_e by

$$B_e = h/8\pi^2cI_e , \quad \text{where } I_e = \mu r_e^2 . \tag{4}$$

Here I_e is the moment of inertia of the molecule, h is Planck's constant, c is the speed of light and μ is the reduced mass of the molecule. If at least one of the two electronic states of a band has $\Lambda \neq 0$, the selection rule for the rotational quantum number J is

$$\Delta J \ (= J' - J'') = +1, 0, -1, \tag{5}$$

giving the R, Q and P branches, respectively. The wavenumbers of these branches are given by the formulae:

$$R(J) = \nu = \nu_0 + F_v'(J + 1) - F_v''(J) , \tag{6}$$

$$Q(J) = \nu = \nu_0 + F_v'(J) - F_v''(J) , \tag{7}$$

$$P(J) = \nu = \nu_0 + F_v'(J - 1) - F_v''(J) , \tag{8}$$

where $J = J''$. If we substitute Eq. (2) in Eqs. (6), (7) and (8), neglecting the small stretching term D_v, the following equations are obtained:

(9) $$R(J) = \nu_0 + 2B'_v + (3B'_v - B''_v)J + (B'_v - B''_v)J^2 ,$$

(10) $$Q(J) = \nu_0 + (B'_v - B''_v)J + (B'_v - B''_v)J^2 ,$$

(11) $$P(J) = \nu_0 - (B'_v + B''_v)J + (B'_v - B''_v)J^2 .$$

The relative J numbering for the individual rotational lines of a band is obtained with the help of the following combination differences:

(12) $$R(J) - Q(J) = F'_v(J + 1) - F'_v(J) = \Delta_1 F'_v(J) ,$$

(13) $$Q(J + 1) - P(J + 1) = F'_v(J + 1) - F'_v(J) = \Delta_1 F'_v(J) ,$$

(14) $$R(J) - Q(J + 1) = F''_v(J + 1) - F''_v(J) = \Delta_1 F''_v(J) ,$$

(15) $$Q(J) - P(J + 1) = F''_v(J + 1) - F''_v(J) = \Delta_1 F''_v(J) .$$

Using Eq. (2) it can be shown that

(16) $$\Delta_1 F'_v(J) = 2B'_v(J + 1) - 4D'_v(J + 1)^3$$

and

(17) $$\Delta_1 F''_v(J) = 2B''_v(J + 1) - 4D''_v(J + 1)^3 \quad .$$

4.3 Rotational Analysis and Results:

(i) Analysis:

Of the six bands for which a rotational analysis was carried out, the structure of the 0,1 band appeared relatively less complex. The rotational structure of this band, photographed in the fifth order of the grating instrument is shown in Plate III. The experimental resolution

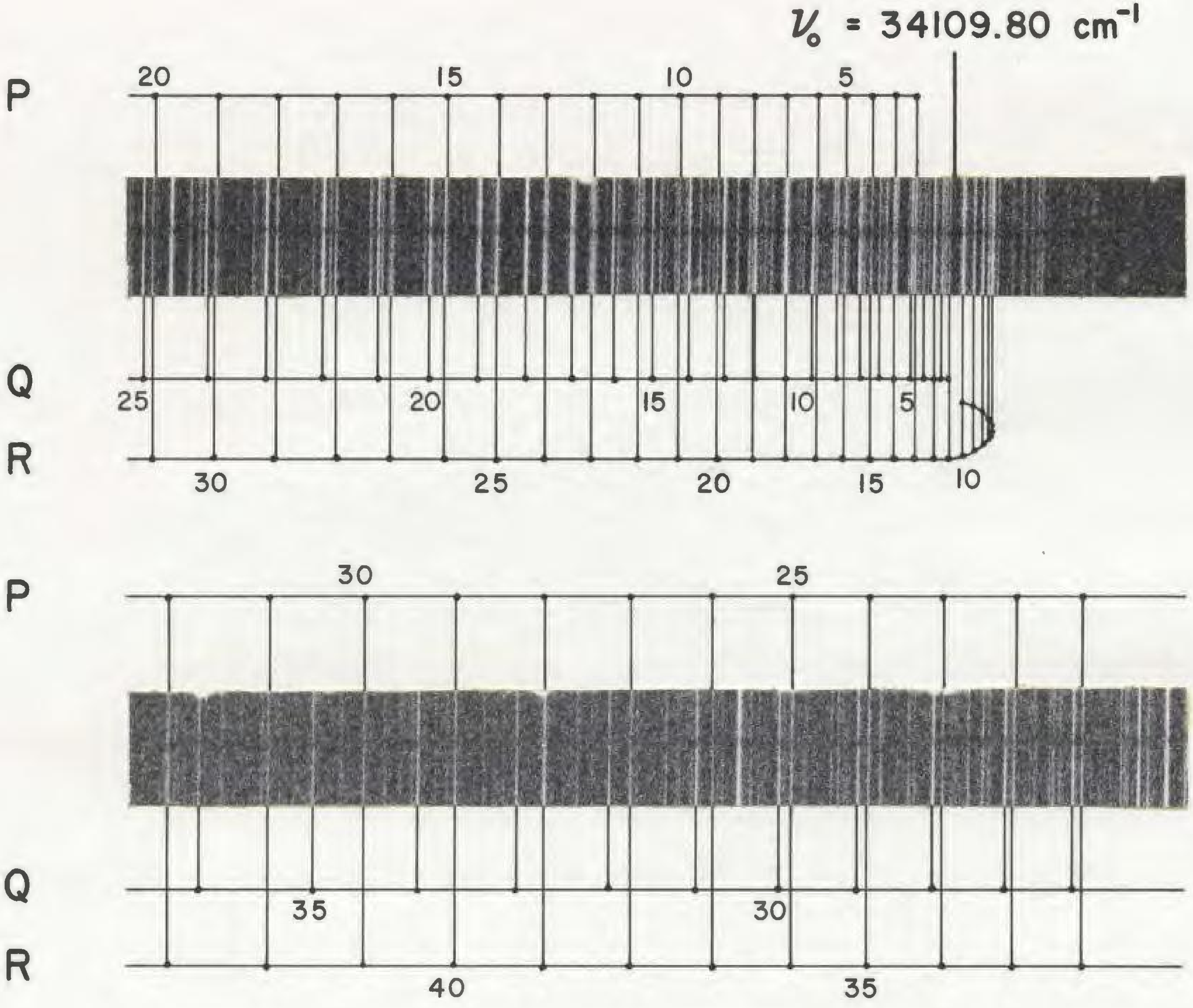

PLATE III : THE 0,1 BAND OF THE $A^1\Pi - X^1\Sigma^+$ SYSTEM OF CSe.

in the region of interest was found to be better than 0.4 cm^{-1}. For the 0,1 band there is some overlapping from a weaker unassigned band at 2930.04 Å. For all the bands analyzed it was relatively easy to pick out an intense branch, which was presumed to be the Q branch. The resolved structure of the 0,1 band was analyzed as the R, Q and P branches of a $^1\Pi$ - $^1\Sigma^+$ transition. The relative J numbering for all the three branches of the 0,1 band was fixed by forming combination differences (see below).

Five other bands for which a partial rotational analysis was made are 1,2 , 1,1 , 0,0 , 2,1 and 1,0. A complete analysis of these bands was not possible due to the difficulties mentioned in Section 4.1. The picking out of the relatively intense Q branch lines did not cause much difficulty while an attempt to analyze the R and P lines was unsuccessful. The rotational structures of the 0,0 and 1,2 bands, also photographed in the fifth order of the grating spectrograph, are shown in Plate IV. The wavenumbers of the lines of the R, Q and P branches of the 0,1 band and those of the Q lines of the other five bands are given in Tables VII and VIII, respectively. The relative numbering for the 1,2 , 1,1 and 1,0 bands became somewhat simplified because of the perturbation observed at J = 15 in the vibrational level v' = 1 of the $A^1\Pi$ state (see 1,2 band in Plate IV and also Table VIII).

(ii) Molecular Constants:

Equation (10) (see Section 4.2) can be simplified to give the following:

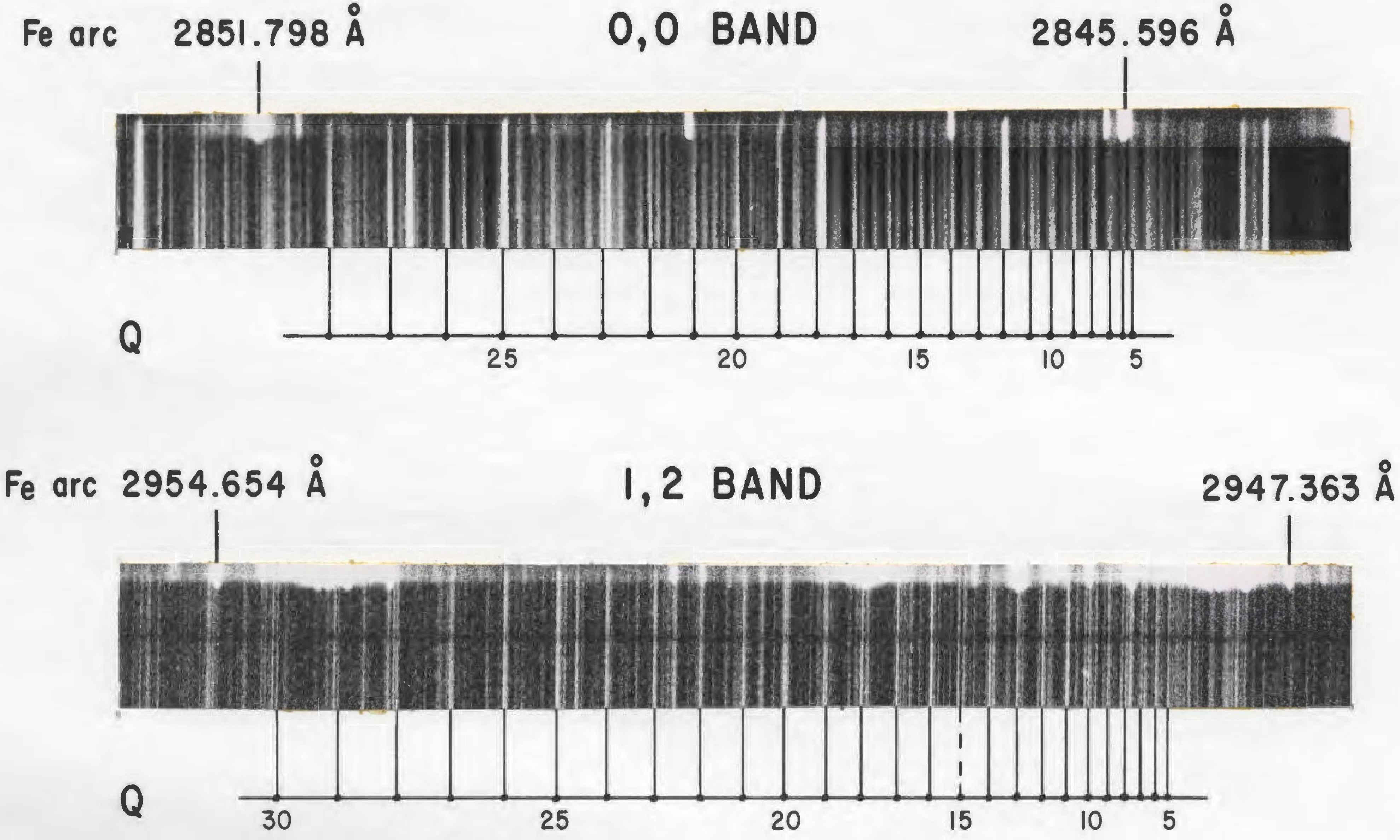

PLATE IV : THE 0,0 AND 1,2 BANDS OF THE $A^1\Pi - X^1\Sigma^+$ SYSTEM OF CSe.

TABLE VII

Observed Wavenumbers of the Rotational Lines of the 0,1 Band in the $A^1\Pi$ - $X^1\Sigma^+$ System

J	R(J)*	Q(J)	P(J)*
0	34110.73		
1	111.49	34109.73	
2	112.09	109.25	34107.37
3	112.56	108.68	105.94
4	112.80	108.01	104.27
5	112.80	107.10	102.48
6	112.80	105.94	100.45
7	112.56	104.84	098.26
8	112.09	103.46	095.74
9	111.49	101.86	093.45
10	110.73	100.14	090.73
11	109.73	098.26	087.89
12	108.68	096.11	084.71
13	107.37	093.90	081.36
14	105.94	091.48	077.98
15	104.27	088.88	074.35
16	102.48	086.10	070.56
17	100.45	083.26	066.71
18	098.26	080.02	062.62

TABLE VII (Continued)

Observed Wavenumbers of the Rotational Lines of the 0,1 Band in the $A^1\Pi$ - $X^1\Sigma^+$ System

J	R(J)	Q(J)	P(J)
19	34095.74	34076.71	34058.34
20	093.45	073.31	053.90
21	090.73	069.65	049.30
22	087.89	065.81	044.52
23	084.71	061.86	039.55
24	081.36	057.64	034.39
25	077.98	053.26	029.00
26	074.35	048.67	023.51
27	070.56	043.89	017.78
28	066.71	038.88	011.80
29	062.62	033.64	005.63
30	058.34	028.16	33999.28
31	053.90	022.40	992.61
32	049.30	016.31	985.67
33	044.52	009.88	
34	039.55	003.07	
35	034.39	33995.75	
36	029.00	987.86	
37	023.51		

TABLE VII (Continued)

Observed Wavenumbers of the Rotational Lines of the 0,1 Band in the $A^1\Pi - X^1\Sigma^+$ System

J	R(J)	Q(J)	P(J)
38	34017.78		
39	011.80		
40	005.63		
41	33999.28		
42	992.61		
43	985.67		

*: In the region of the P branch, R and P lines not resolved.

TABLE VIII

Observed Wavenumbers of the Rotational Lines of the Q Branches of Several Bands of the $A^1\Pi - X^1\Sigma^+$ System

Band J	1,2	1,1	0,0	2,1	1,0
1					35953.06
2					952.44
3					951.96
4					951.24
5	33909.47		35132.58		950.64
6	908.57		131.76		949.58
7	907.32		130.59		948.39
8	906.16	34922.28	129.05	35756.65	947.03
9	904.77	920.83	127.32	754.90	945.44
10	903.24	919.29	125.38	753.05	943.74
11	901.58	917.43	123.59	751.24	941.90

TABLE VIII (Continued)

Observed Wavenumbers of the Rotational Lines of the Q Branches of Several Bands of the $A^1\Pi - X^1\Sigma^+$ System

J \ Band	1,2	1,1	0,0	2,1	1,0
12	33899.64	34915.46	35121.33	35749.18	35939.80
13	897.64	913.39	118.90	746.56	937.61
14	895.40	911.21	116.56	744.33	935.22
15	*	*	113.79	741.45	*
16	890.89	906.32	110.92	738.49	930.15
17	888.22	903.38	107.85	735.41	927.17
18	885.41	900.58	104.64	731.99	924.23
19	882.56	897.46	101.25	728.51	920.97
20	879.34	894.21	097.57	724.87	917.56
21	876.19	890.80	093.78	721.24	914.04
22	872.83	887.23	089.79	717.22	910.33

TABLE VIII (Continued)

Observed Wavenumbers of the Rotational Lines of the Q Branches of Several Bands of the $A^1\Pi - X^1\Sigma^+$ System

J \ Band	1,2	1,1	0,0	2,1	1,0
23	33869.26	34883.58	35085.61	35713.01	35906.39
24	865.52	†	081.29	708.74	902.32
25	861.69	875.44	†	704.02	898.01
26	857.57	871.39	071.91	699.41	893.59
27	853.39	866.90	066.88	694.38	888.85
28	849.13			689.24	884.17
29	844.59			683.81	
30	839.82			678.23	

*: Perturbed line.

†: Line not measured (overlapped by a foreign line).

$$Q(J) = \nu_0 + (B'_v - B''_v)J(J + 1) \; . \tag{18}$$

According to Eq. (18), if Q(J) is plotted against J(J + 1), a straight line is obtained whose intercept on the ordinate axis gives the band origin ν_0 and whose slope gives $(B'_v - B''_v)$. The values of ν_0 and $(B'_v - B''_v)$ were determined for all the six bands by the method of least squares using Eq. (18). The values obtained are listed in Table IX.

Since the R, Q and P branches are identified for the 0,1 band, it was possible to determine the values of the rotational constants B'_0 and B''_1 and the stretching constants D'_0 and D''_1. The details of this determination are as follows: The mean values of the combination differences $\Delta_1 F'_v(J)$ for the upper state v' = 0 were obtained using Eqs. (12) and (13). Similarly, $\Delta_1 F''_v(J)$ for the lower state v" = 1 were obtained from Eqs. (14) and (15). According to Eq. (16) or (17), when $\Delta_1 F_v(J)/(J + 1)$ is plotted against $(J + 1)^2$ a straight line graph is obtained and its intercept (on the ordinate axis) and slope give $2B_v$ and $- 4D_v$, respectively. Such plots for the v" = 1 and v' = 0 levels are shown in Fig. 7. Values of J = 12 to 27 were used in these plots. Measurements of the lines with J < 12 were considered to be less accurate and were neglected in determining the rotational constants. Lines with J > 27 appeared perturbed and were also neglected. The values of the constants of the 0,1 band obtained by a least squares fit of the data plotted in Fig. 7 are as follows:

$$B'_0 = (0.484 \pm 0.001)\ \text{cm}^{-1} \qquad B''_1 = (0.569 \pm 0.001)\ \text{cm}^{-1}$$

$$D'_0 = (3 \pm 1) \times 10^{-6}\ \text{cm}^{-1} \qquad D''_1 = (1 \pm 1) \times 10^{-6}\ \text{cm}^{-1} \; .$$

TABLE IX

ν_0 and ($B_v' - B_v''$) Values Obtained from the Analysis of the Q Branches

Band	ν_0 (cm^{-1})	$B_v' - B_v''$ (cm^{-1})
1,2	33911.76	-0.077
0,1	34109.80	-0.087
1,1	34928.16	-0.081
0,0	35135.51	-0.091
2,1	35763.26	-0.091
1,0	35953.08	-0.085

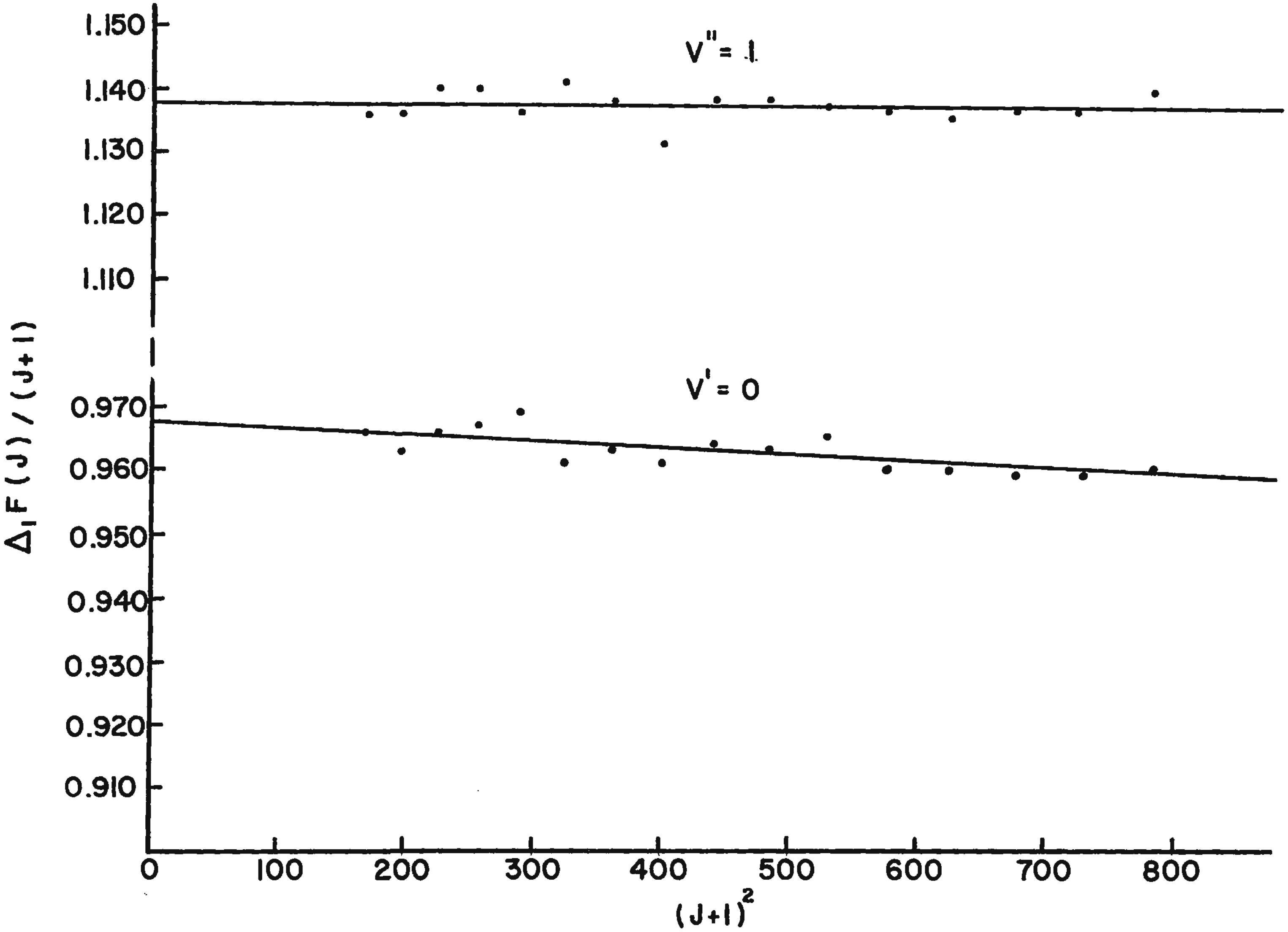

Fig. 7. Plots of $\Delta_1 F(J)/(J + 1)$ versus $(J + 1)^2$ for the v' = 0 and v" = 1 States of the $A^1\Pi$ - $X^1\Sigma^+$ Transition.

The values of B' and B" for the other bands are derived using the values of B'_o and B''_1 listed above and the values of $(B'_v - B''_v)$ given in Table IX. Finally, the rotational constants derived for the A - X system of CSe are summarized in Table X. B_e and α_e have been determined using Eq. (3), and r'_o and r''_e have been calculated from Eq. (4).

TABLE X

Molecular Constants of the $A^1\Pi$ - $X^1\Sigma^+$ System of CSe

$X^1\Sigma^+$ (cm^{-1})	$A^1\Pi$ (cm^{-1})
$B_o = 0.575$	$B_o = 0.484$
$B_1 = 0.569$	$B_1 = 0.489$
$B_2 = 0.566$	$B_2 = 0.478$
$B_e = 0.577$	
$\alpha_e = 0.0045$	
$D = 3 \times 10^{-6}$	$D = 1 \times 10^{-6}$
$r_e = 1.673$ (Å)	$r_o = 1.827$ (Å)
$\nu_{oo} = 35135.51$	

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