THE $^{1}D_{2} \rightarrow ^{1}A_{1}$ ELECTRONIC TRANSITION
OF
SELENIUM DIOXIDE
THE $^1B_2 \rightarrow ^1A_1$ ELECTRONIC TRANSITION
OF
SELENIUM DIOXIDE

by

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A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University
October, 1972

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SCOPEx AND CONTENTS:
The B-X system of selenium dioxide was studied in absorption in the gas phase and has been assigned to the electronic transition $^1B_2 + ^1A_1$. A complete vibrational analysis of the electronic transition is presented. The geometry of the excited state has been determined completely from rotational analysis of the $^1_0$ vibronic band and further confirmed by Franck-Condon calculations. The previously unknown ground state fundamentals $v_1^*$ and $v_2^*$ have been determined along with the three fundamentals of the $^1B_2$ excited state. It is proposed that selenium dioxide has an asymmetric structure with unequal bond lengths in certain vibronic levels of the excited state involving $v_3$ as a result of a double-minimum potential along the $Q_3$ co-ordinate.
To

my Mother and Father

Dobby and Cathy
ACKNOWLEDGEMENTS

I would like to thank Dr. G.U. King for suggesting the SeO₂ problem and for many valuable discussions during the preparation of the thesis.

I am indebted to my colleagues, Mr. M. Danyluk, Mr. E. Farnworth, Mr. E. Finn, Mrs. D. Grange, Mr. F. Greening, Dr. K.G. Kidd, Mr. R. Lemanczyk, Mr. R. Netherlands, Mr. A. Van Putten and Mr. C.R. Subramanian for both their friendship and assistance. My thanks also to Dr. D.C. Moule for the use of his Ebert spectrograph and his willing assistance and hospitality while at Brock University.

I am grateful to the Ontario government for a Fellowship (1969) and to the National Research Council of Canada for Scholarships (1970-72).

Miss Susan Hawley (typing) and Mr. Dennis McEntee (printing), thank you, you both did a beautiful job.

To Mr. Greg McLean, I am especially grateful for the professional and arduous task of drawing most of the Figures in the thesis.

Anne, thank you for "The Summer of 72" - it was great!

Finally, 0.104 - You I shall never forget!
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1.1. Electronic, Vibrational and Rotational Motion of Molecules

Molecular spectroscopy is the study of the quantized electronic, vibrational and rotational motion of a molecule through its interaction with electromagnetic radiation. The complexity of most spectroscopic problems would be overwhelming were it not for the large inequality in mass between the electrons and nuclei in a molecule. Quantum mechanically this allows the nuclear and electronic motions to be considered largely independent of one another and the overall rovibronic (rotational-vibrational-electronic) wave function $\psi_{\text{ovr}}$ to be written as a product of an electronic part, vibrational part and rotational part.

$$\psi_{\text{ovr}} = \psi_{\text{o}} \psi_{\text{vib}} \psi_{\text{rot}} \psi_{\text{me}}$$

The factorization of the wave function into components due to electronic and nuclear motion is called the Born-Oppenheimer approximation.

In the zeroth-order Born Oppenheimer approximation, the time independent Schrödinger equation for the electronic and nuclear motion may be written,

$$H_0(r, Q_o) \psi_o(r, Q_o) = E_o(Q_o) \psi_o(r, Q_o)$$

$$[H_1(Q) + E_o(Q)] \psi_o(Q) = E_o \psi_o(Q)$$

where the Hamiltonian for the electronic and nuclear motion is given by

$$H_o(r, Q_o) = -\sum_i \frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial^2} - \sum_{i, \mu} \frac{2\mu^0}{r_{i\mu}} \sum_{i > j} \frac{2\mu^0}{r_{ij}}$$

$$H_1(Q) = -\sum_{\mu} \frac{\hbar^2}{2m} \frac{\partial^2}{\partial^2} + \sum_{\mu > \nu} \frac{2\mu^2 \nu}{r_{\mu \nu}}$$
The terms on the right-hand side of Equation (1.4) refer respectively to the kinetic energy of the individual electrons, attractive force of the ith electron for the jth nucleus and an electron-electron repulsion term; while the nuclear Hamiltonian $H_N$ in Equation (1.5) contains respectively a nuclear kinetic energy and repulsion term and

- $r$ is the electronic co-ordinates;
- $Q$ the nuclear displacement co-ordinates;
- $\hbar$ is Planck's constant divided by $2\pi$;
- $m_i$ and $m_a$ are the mass of the ith electron and the a-th nucleus;
- $v^2$ is the Laplacian operator;
- $Z_a$ is the atomic number of the a-th nucleus;
- $e$ is the charge of the electron; and
- $r_{ij}$ is the distance between particle i and j.

The solution of Equations (1.2) and (1.3) yield the electronic and nuclear energy levels and wave functions. It is transitions between the above energy levels which are of fundamental interest to the molecular spectroscopist.

1.2. Transition Probabilities

According to the Bohr theory, a transition from one stationary state in the molecule to another may occur with the quantized absorption or emission of radiation of wave number $\sigma$ given by

$$\sigma = \frac{E_n - E_m}{\hbar c} \quad E_n > E_m$$  \hspace{2cm} (1.6)

The transition probability that an oscillating electromagnetic field induces such a transition in a molecule, from state $m$ to state $n$ was first determined by Einstein and is given by

$$D_m = \frac{2\pi}{c^2} |\psi|^2$$  \hspace{2cm} (1.7)
where \( b_m \) is the Einstein probability coefficient, \( N = \langle \phi_m | \hat{T} | \phi_n \rangle \), the transition moment and \( |m|^2 \) is the transition probability between state \( m \) and \( n \), \( \hat{T} \) is the electric dipole operator.

1.3. Selection Rules

In order that an electric dipole transition occur between the states \( \phi_m \) and \( \phi_n \), the following integral must be non-zero,

\[
\langle \phi_m | \hat{T} | \phi_n \rangle \neq 0
\]  

(1.8)

In the language of group theory, the above integral will be non-zero only if the direct product of the representations of \( \phi_m \), \( \hat{T} \) and \( \phi_n \) contain the totally symmetric representation.

\[
\Gamma \phi_m \times \Gamma \hat{T} \times \Gamma \phi_n = \Gamma A_1
\]  

(1.9)

The application of the above selection rule to specific, electronic, vibrational and rotational transitions in SeO₂ is examined more fully in the subsequent chapters where the analysis of each is discussed in detail.

The remainder of the present chapter shall concern itself with the experimental aspects of the present work as well as a brief description of previous spectroscopic studies involving SeO₂.

1.4. Preparation of Isotopic Selenium Dioxide

Isotopically pure Se\textsuperscript{78} (93.3\%) and Se\textsuperscript{80} (95.6\%) and O\textsubscript{2}\textsuperscript{16} (99.9\%) were obtained from Union Carbide (Oak Ridge Laboratories). The three isotopic molecules Se\textsuperscript{78}O\textsubscript{2}, Se\textsuperscript{80}O\textsubscript{2} and Se\textsuperscript{50}O\textsubscript{2} were prepared by adding a stoichiometric amount of oxygen to 200 mg of selenium isotopes contained in a 50 cm all-quartz

\[ \text{An introductory knowledge of group theory is assumed throughout the thesis.} \]
\[ \text{Accounts of the application of group theory to molecular spectroscopic problems is given by King\textsuperscript{6}, Cotton\textsuperscript{7} and Hochstrasser\textsuperscript{6}.} \]
cell. The cell was wound with 0.5 ohm/ft. nichrome wire, wrapped with asbestos paper and heated electrically to 350°C. The oxidation was assumed to be complete after several hours.

In order to prevent condensation of selenium on the windows, a copper envelope was extended two inches beyond the windows at each end of the cell.

The entire spectrum of the B system could be obtained with SeO₂ pressures which varied from 0.5 mm to 10 mm. The temperature ranged from 120°C to 200°C. In order to photograph the much weaker C system to the red of the B system, it was necessary to heat the cell to around 350°C. At this temperature all of the SeO₂ is in the gas phase.

In order to minimize the decomposition of SeO₂ into Se + O₂, an additional 100 mm of oxygen gas was added to the cell. Spectra taken both in the presence as well as the absence of the additional oxygen, when compared, showed no visible affect of pressure broadening of the rotational fine structure.

The only other oxide of selenium is SeO₃. It presented no problem to the present investigation of SeO₂ since SeO₃ decomposes into SeO₂ on heating.

1.5. Previous Spectroscopic Studies of SeO₂

At least five electronic transitions have been observed in the gas phase spectrum of SeO₂ in the spectral region between 2000 Å - 6000 Å. Three of these transitions have been observed in absorption in the region 2070-2210 Å, 2300-3400 Å, and 3500-4000 Å and have been designated the A, B and C systems respectively.

Harmanath and Sivarayan² also observed two systems in emission with origins at 3110.9 Å and 3119.9 Å. The present investigation is concerned with the B system of SeO₂.
1.6. Gas Phase Emission Spectrum of $^{32}$O$_2$

Haranath and Sivararnurty$^{12}$ observed an emission spectrum extending from 2700-4700 Å. The bands below 3200 Å were assigned as belonging to the $B \rightarrow X$ system of $^{32}$O$_2$ previously reported by Duchesne and Rosen$^8$ under low resolution. The bands between 3200-4700 Å could not be associated with the $C \rightarrow X$ system observed by Rosen$^7$ and were assigned as belonging to two new systems, involving transitions from the upper state $v_2$ levels to the ground state $v_1$ levels. The observed frequencies are given in Table 1.1.

<table>
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<tr>
<th>System</th>
<th>Origin</th>
<th>$v'_1$ of Lower State</th>
<th>$v'_2$ of Excited State</th>
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<td>I</td>
<td>32145 cm$^{-1}$</td>
<td>910.5 cm$^{-1}$</td>
<td>182 cm$^{-1}$</td>
</tr>
<tr>
<td>II</td>
<td>32052 cm$^{-1}$</td>
<td>911.5 cm$^{-1}$</td>
<td>182 cm$^{-1}$</td>
</tr>
</tbody>
</table>

However, this emission work is of little use in the present study, because very few of the band frequencies reported by Haranath and Sivararnurty agree with the frequencies measured here, even in the origin region where isotopic shifts should be small. Haranath and Sivararnurty used selenium dioxide containing natural selenium and therefore would have observed bands due to both $^{70}$O$_2$ and $^{80}$O$_2$, but the absorption bands of these separate isotopic species show very little agreement with the reported emission bands in regions where the absorption and emission spectra overlap. An analysis of the emission spectra of the different isotopes under much higher resolution would be necessary for a satisfactory interpretation to be made.

All that can be said is that Haranath and Sivararnurty's two "electronic
origins" lie within ~ 100 cm\(^{-1}\) of the origin given here for the B system in absorption.

Their analysis postulates two separate electronic transitions with origins only 93 cm\(^{-1}\) apart. Although such a coincidence cannot be ruled out completely, it is highly unlikely that such systems are not related in some way. A possible alternate interpretation for the two emission systems observed by Haranath and Sivaramanmury is given below, on the assumption that they have indeed correctly identified emission due to SeO\(_2\).

From the hot band spectrum in the present investigation of the B System of SeO\(_2\), the ground state stretching frequency \(v_1\) is unambiguously determined to be 923 cm\(^{-1}\). This is in excellent agreement with the value of 922.0 determined by Cesaro et al.\(^{14-15}\) from recent low temperature infrared studies of SeO\(_2\) in an argon matrix.

The origin band for the B \(+\) X electronic transition in the present work is found with a high degree of certainty (from isotopic shifts as well as the analysis of the hot band spectrum) to lie at 31955.0 cm\(^{-1}\).

In view of the proximity of the origin of the B \(+\) X system to the origin of the two emission systems, one is tempted to think that the lower electronic state observed by Haranath and Sivaramanmury is in fact the ground electronic state. The anomaly, however, arises that the upper state of the B \(+\) X transition observed in absorption cannot be associated with either of the above two emission systems.

In order to rationalize this seemingly unexplainable contradiction the following alternate interpretation of Haranath and Sivaramanmury's emission work is offered. From the analysis of the hot band spectrum in the present investigation of the B \(+\) X system, the ground state totally symmetric stretching frequency \(v_1\) = 923 cm\(^{-1}\). The frequency of the second overtone, 3\(v_1\), is observed
to be 912 cm\(^{-1}\). The anharmonicity in \(v_1\) is, therefore, about 5.5 cm\(^{-1}\) per quantum excited. In the previous gas phase analysis of the B + X System Duchesne and Rosen\(^6\) misinterpreted the interval \((v'_1 + v'_2) = 910\) cm\(^{-1}\) as a sequence interval involving \(v''_1\). The interval between the last observed emission bands at 32145 and 32052 cm\(^{-1}\) reported by Haranath and Sivaramamurti was observed to be 911 cm\(^{-1}\).

It is possible that the bands observed by Haranath and Sivaramamurti at 32145 cm\(^{-1}\) and 32052 cm\(^{-1}\) do not terminate at the vibrationless level of the ground state but rather at the \(3v''_1\) level. This interpretation then extends the origin for the emission system \(\Delta \approx 3v''_1 = 2753\) cm\(^{-1}\) to the blue of the previously assigned origins. This explanation is, therefore, consistent with the ground state being the lower state to which the emission occurs, and removes the possibility that the upper state of the B System \(\left(^1\text{B}_2\right)\) is the emitting state, which is in agreement with Haranath and Sivaramamurti's observation.

The fact that the above two emission systems have not as yet been observed in absorption could, therefore, be attributed to the strongly overlapping \(B + X\) electronic transition which is approaching its intensity maximum in the region where the present interpretation suggests the origin for the emission systems should appear in absorption.

Reinvestigation of the emission work using isotopic \(\text{Sc}^{76}\text{O}_2\) and \(\text{Sc}^{78}\text{O}_2\) would unambiguously ascertain the validity of the present interpretation since the \(v_1\) levels are isotopically split by approximately 50 cm\(^{-1}\) per quantum excited, as is observed in the present analysis of the \(B + X\) System of \(\text{Sc} \text{O}_2\).

The remaining yet unexplained presence of two low lying excited electronic states separated by less than 160 cm\(^{-1}\) can possibly be accounted for in the following way.
The present work involving the \( \text{B}_2^+ + \text{A}_1 \) electronic transition of SeO\(_2\) suggests strong evidence for the presence of a double-minimum potential well in the antisymmetric stretching co-ordinate \( Q_3 \) of the \( \text{B}_2 \) excited electronic state. The \( 0^+ - 0^- \) splitting is observed to be 78 cm\(^{-1}\).

An alternate explanation for the two emission systems separated by only 100 cm\(^{-1}\) is the hypothesis of only one system containing two progressions originating on the levels \( (0^+ + n\nu_2) \) and \( (0^- + n\nu_2) \), \( n = 0, -1, \ldots, 4 \), the \( 0^+ - 0^- \) splitting being of the order of 100 cm\(^{-1}\). There is, of course, no basis for assuming the above explanation is correct, aside from the fact that apparently \( \nu_2' = 182 \) cm\(^{-1}\) for both systems. However, in view of the difference in \( \nu_2' = 260 \) cm\(^{-1}\) observed in the present analysis of the \( \text{B} + \text{X} \) system of SeO\(_2\) with \( \nu_2' = 182 \) cm\(^{-1}\) observed in emission by Haranath and Sivaramakumurti, it appears unlikely that the \( \text{B}_2 \) electronic state can be associated with either of the above two emission systems if their experimental frequencies are correct. A detailed discussion of the electronic states of SeO\(_2\) is deferred to Chapter Two.

1.7. Previous Gas Phase Investigations of the B System of SeO\(_2\) in Absorption

The \( \text{B} + \text{X} \) system of SeO\(_2\) has been studied under low resolution by several workers: Cheong Shin-Pieu\(^9\) (1938), Asumdi et al.\(^10\) (1937) and, more recently, by Duchesno and Rosen\(^8\) (1941).

Duchesno and Rosen were the first researchers to study the \( \text{B} \) system of SeO\(_2\) in the light of the Herzberg-Teller\(^17\) selection rules. Many of the gross experimental features and observations in their work are identical to the present investigation, although of course they worked with the natural selenium dioxide. The most notable feature is the presence of long progressions involving the upper state totally symmetric stretching frequency, \( \nu_1' = 660 \) cm\(^{-1}\).
This is the only upper state frequency reported by Duchesne and Rosen. This is in contrast to the present work where all three fundamentals are assigned. Duchesne and Rosen also incorrectly assigned the origin for the B + X electronic transition at 1300 cm\(^{-1}\) to the blue of the true origin, determined from isotopic shifts in the present analysis. This erroneous assignment resulted from their incorrectly assigning the frequency interval of 910 cm\(^{-1}\) to \(v_1\) when in fact the interval arises from the combination band \(v_1' + v_2' = 660\) cm\(^{-1}\) + 260 cm\(^{-1}\).

1.8. Infrared Studies of SeO\(_2\)

The infrared spectrum of SeO\(_2\) has been studied by Giguère and Falk in the gas phase and in rare gas matrices by Hastie et al. and just recently by Cesaro, Spoliti, Hinckcliffo and Ogden in argon matrices. A summary of ground state frequencies for SeO\(_2\) is given in Table 1.2.

<table>
<thead>
<tr>
<th>Table 1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground State Fundamentals for SeO(_2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Gas Phase</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1)</td>
<td>923 cm(^{-1})</td>
<td>923.4 cm(^{-1})</td>
</tr>
<tr>
<td>(v_2)</td>
<td>373 cm(^{-1})</td>
<td>372.5 cm(^{-1})</td>
</tr>
<tr>
<td>(v_3)</td>
<td>967 cm(^{-1})</td>
<td>967.6 cm(^{-1})</td>
</tr>
</tbody>
</table>

*Obtained from present gas phase analysis of B System of SeO\(_2\).*

1.9. Experimental Aspects of the Present Work

Low resolution spectra of Se\(_{70}\)O\(_{2}\), Se\(_{80}\)O\(_{2}\), and Se\(_{80}\)O\(_{2}\) were photographed in the second order of a 1.5 motor Bausch and Lomb model 11 spectrograph which has a resolving power of 70,000 and a reciprocal dispersion of 7.5 Å/mm. The slit width used was 82 microns. Kodak Spectrum Analysis No. 1
film was used in all instances. The spectrum was also photographed at a slightly higher dispersion on a 1.5 meter Hilger and Watts Littrow-Mounted quartz prism spectrophotograph.

The high resolution photographs were obtained in the first order of a 20-foot Ebert spectograph similar to the one described by King.\textsuperscript{19} The dispersion and theoretical resolving power of the instrument in the first order is 0.72 Å/μ and 150,000 respectively. A slit width of 30 microns was used. A few select bands were also photographed in the second order at a resolving power of 300,000 and dispersion of 0.36 Å/μ.

Several bands of the \textsuperscript{70}O\textsubscript{2} and \textsuperscript{80}O\textsubscript{2} were photographed at still higher dispersion in the 20th order on an Ebert spectograph located in Dr. D. C. Moule's laboratory at Brock University in St. Catharines, Ontario.\textsuperscript{*}

All of the absorption spectra were obtained using a 450 watt, high pressure Xenon arc, obtained from Corning Inc., as the continuous radiation source.

1.10 Measurement and Calibration of Spectra

The comparison spectrum, which was superimposed adjacent to the absorption spectrum, was an iron arc emission spectrum from a Pfund arc in the case of the Ebert and Dausch-and Lamb photographs and a neon filled hollow iron cathode discharge for the Hilger pictures and those obtained at Brock University.

The relative positions of the iron arc and selenium dioxide spectral lines were measured with a Neophoto travelling microscope having a precision of 0.0001 μ. The wavelength of the iron emission lines were taken from a

* I would like to express my appreciation to Dr. D. C. Moule for his willing assistance and hospitality while at Brock University.
tabulated list comprised by the spectroscopy division of the National Research Council of Canada.

The measured iron lines were then fitted to an equation of the form

$$Y = A_0 + A_1x + A_2x^2$$

by means of a least square computer program carried out on a CDC 6400 computer. Once the constants $A_0$, $A_1$ and $A_2$ were determined, the wavelength of the spectral lines were obtained by substituting their positions into the above equation.

The air wavelengths were converted to vacuum wavelengths by means of a formulae derived by Edlen\textsuperscript{20}. The vacuum wavelengths were then converted to vacuum wavenumbers.

1.11. Experimental Conditions

Selenium dioxide is a white crystalline solid which sublimes at 350°C. In order to photograph the gas phase spectrum, it was necessary to heat the cell electrically to temperatures ranging between 130°C and 200°C. Between these temperatures the vapor pressure of SeO\textsubscript{2} varies over the range 0.01 Torr to 10 Torr\textsuperscript{21}.

The exposure time for the high resolution Ebert photographs varied from 5 to 40 minutes with Kodak Spectrum Analysis No. 1 film.
CHAPTER TWO

ELECTRONIC STRUCTURE AND SPECTRA OF SELENIUM DIOXIDE

2.1. Introduction

In the electronic ground state, selenium dioxide is a bent symmetric
$AB_2$ type molecule containing eighteen valence electrons in its molecular
orbital framework, and as such is valence isoelectronic with $O_3$, $SO_2$ and $NO_2^-$. Since the present sophistication of quantitative molecular orbital calculations
has not yet been extended to include third row elements such as selenium the
theoretical discussion of the molecular orbitals and low lying electronic
states of $SeO_2\_2$ must proceed by comparison with the much studied isoelectronic
$SO_2$ and $NO_2^-$ molecules$^{22-25}$.

2.2. Molecular Orbital Calculations for $NO_2^-$

In the following section a brief summary of the one electron molecular
orbitals for $NO_2^-$ is discussed. Since the nature of the present work has been
spectroscopic and has not involved any numerical molecular orbital calculations,
the analytical methods used in calculations will not be discussed in the thesis.

The things that are of primary interest in so far as the present work is
cconcerned are:

(a) the ordering and nature of the highest filled molecular orbitals in
the ground state; and

(b) the electron configurations which are expected to give rise to the
first few low lying excited electronic states.

The ordering of the molecular orbitals for the nitrite ion$^{22}$ (isoelectronic
with $SeO_2$) are given in Figure 2.1. The relative ordering of the NO's remain
the same in the nitrite ion ($NO_2^-$), ozone ($O_3$) and sulfur dioxide ($SO_2$).$^{22}$
It therefore seems reasonable to assume the same ordering for SeO₂. However, it is difficult to say to what extent "d" orbital participation might affect this ordering.⁴

Maria et. al.⁵² have discussed the nature of the MO's involved in generating the low lying excited electronic states of some 18 electron molecules, isoelectronic with SeO₂. A brief summary of their results will be given below.

From Figure 2.1 it can be seen that the 1a₂(π), 4b₂(σ) and 6a₁(σ)
molecular orbitals are the last three occupied MO’s and the 2b₁(π) is the first unoccupied MO. The form of the above four MO’s is also shown in Figure 2.1 for SeO₂ and is assumed to be the same as NO₂⁻.

The 1a₂ MO is of σ nature and consists entirely of group orbitals (GO's) localized on the two end oxygen atoms. The 4b₂ MO (σ) is also localized primarily on the oxygen atoms and consists of the inplane overlap of the selenium 4p₂ AO with the oxygen GO's (2p_y₁ - 2p_y₂) and (2p_z₁ + 2p_z₂) and is antibonding in both combinations. The 6a₁ MO is also of σ type and results from overlap of the selenium 4p_y AO with the oxygen GO (2p_y₁ + 2p_y₂) and is bonding. The 2b₁ MO is π* in nature and results from the out of plane overlap of the selenium 4p_x atomic orbital with the oxygen GO (2p_x₁ + 2p_x₂). The overlap is bonding in nature.

2.3. Molecular Orbitals of SeO₂ (Linear Conformation)

It has long been recognized that the geometric shape of a molecule may be understood by considering the nature of the molecular orbitals comprising it. Mulliken⁴² in 1942 and Walsh⁴³ later in 1953 investigated the change in orbital

⁴Koothen and Sanny⁴² have recently shown the importance of 3d orbital participation in minimum basis set calculations on SO₂. In SeO₂ d orbitals will quite definitely be involved in the bonding.
Figure 2.1: Molecular orbitals of SeO₂ in the bent conformation. Orbital ordering is assumed to be the same as in NO₂ (Moldaen u.c.) for clarity. The dotted lines have been omitted. The 15 atomic orbitals have been omitted but have fallen into account in the numbering of the orbitals.
energy in going from bent (90°) to a linear conformation in AB₂ type molecules. These authors have shown that a redistribution of electronic charge resulting from an electronic transition can cause a change in geometry of the molecule in the excited electronic state. Therefore, for the sake of completeness, the molecular orbitals for ScO₂ in the linear conformation are shown in Figure 2.2. The ordering of the MO's in the linear conformation is not certain. The ordering given in Figure 2.2 is the same as for CO₂ determined by Rabalais et al.29

The variation in orbital energy with bond angle is given in Figure 2.3. Such a diagram is commonly referred to as a Walsh diagram.28

It can be seen from the Walsh diagram in Figure 2.3 that the 4σg, 3σu, 1πg, 5πg and 4πu orbitals favor the linear conformation while 1πu-1b₁ and 2πu favor the bent conformation. The addition of two electrons to the strongly bent-stabilized 6a₁ molecular orbital is primarily responsible for the bent ground state geometry of ScO₂, while CSO₂ with 16 valence electrons remains linear with a (1πg)₄ configuration.

2.4. Low Lying Excited States of ScO₂

According to the qualitative ordering of the one electron molecular orbitals of ScO₂ given in Figure 2.1, the ground state configuration is

\[ \ldots (1a_2)^2 (4b_2)^2 (6a_1)^2 \]

(2.4)

and, as is expected in accordance with Walsh's rules, the molecule is bent, having a \(^1\text{A}_{1}\) ground electronic state.9

The low lying excited electron configurations and the electronic states

---

*The basic group theoretical methods involved in determining the symmetry and multiplicity of electronic states resulting from electron configurations has been assumed throughout this thesis. A complete discussion of group theory and its application to molecular spectroscopy can be found in either of Horwberg36, King4, or Hochstrasser5.
Figure 2.2 Molecular orbitals of SeO₃ in the linear conformation. Orbital ordering is assumed to be the same as CO₂ (Bredlau et al.). For clarity, some of the dotted lines have been omitted. The 1s orbitals α and β have been omitted but have been taken into account in the numbering of the orbitals.
arising from each of these, in approximate order of increasing energy are given below:

\[
\begin{align*}
\ldots (1a_2)^2(4b_2)^2(6a_1)^1(2b_1)^1 & \quad 1,3_B^1 \\
\ldots (1a_2)^2(4b_2)^2(6a_1)^1(2b_1)^2 & \quad 1_A^1 \\
\ldots (1a_2)^2(4b_2)^1(6a_1)^2(2b_1)^1 & \quad 1,3_A^2 \\
\ldots (1a_2)^2(4b_2)^1(6a_1)^1(2b_1)^2 & \quad 1,3_B^2 \\
\ldots (1a_2)^1(4b_2)^2(6a_1)^1(2b_2)^1 & \quad 1,3_B^2 \\
\ldots (1a_2)^1(4b_2)^2(6a_1)^1(2b_2)^2 & \quad 1,3_A^2
\end{align*}
\]

Under \( C_{2v} \) symmetry, the three components of the dipole moment operator transform as \( A_1, B_1 \), and \( B_2 \). Therefore, transitions from the totally symmetric ground state to \( 1,3_A^2 \) states (2.7 and 2.10) are, within the Born-Oppenheimer approximation forbidden and could appear only weakly through a vibronic mechanism. Transitions to \( 1A_1 \) (2.6) and \( 1B_2 \) (2.8) are allowed but should be weak since double electron excitation is involved. The transitions \( 1B_1 \) (2.5) + \( \tilde{x}, 1A_1 \) and \( 1B_2 \) (2.9) – \( \tilde{x}, 1A_1 \) are electronically allowed and should appear in the visible or ultraviolet region of the spectrum in most 18-electron molecules. The \( 1B_1 + 1A_1 \) transition is expected to give rise to "perpendicular" Type C bands and should be accompanied by a moderate increase in bond angle and a small increase in bond length in the excited state. The \( 1B_2 + 1A_1 \) transition, on the other hand, should give rise to "parallel" Type A bands and should be accompanied by a decrease in bond angle and an increase in bond length in the excited state. The present work concerning the \( 1D_2 + \tilde{x}, 1A_1 \) transition in \( ScO_2 \) substantiates the above predictions for the excited \( 1B_2 \) state. The bond angle was found to decrease from 110.9° to 101.6° in the excited state while the bond length increased from 1.607 \( \text{Å} \) to 1.74 \( \text{Å} \).

Brand and Selim 

have recently shown the intense absorption
FIGURE 2.5 WELSH DIAGRAM FOR AB₂ TYPE MOLECULE. THE ORIENTATION OF THE ORBITALS AT RIGHT AND LEFT IS NOT UNIQUELY DETERMINED. THE 12 ORBITALS OF A AND B ARE OMITTED BUT HAVE BEEN TAKEN INTO ACCOUNT IN THE NUMBERING OF THE ORBITALS.
in SO₂ centered around 2350 Å to be due to the 1B₂ + X 1A₁ electronic transition. They also observed an increase in bond length while the bond angle decreased relative to the ground state in the 1B₂ excited state of SO₂. Merer⁴² and more recently Brand⁴¹ have shown the weak absorption in SO₂ around 3800 Å as due to the 3B₁ + X 1A₁ electronic transition. The spectral region around 2900 Å is thought to contain the 1B₁ + X 1A₁ transition, but this as yet has not been confirmed by rotation analysis.

The observed electronic transitions of SO₂ in the visible and ultraviolet region of the spectrum are in excellent agreement with the low lying excited states predicted from molecular orbital considerations.

The observed experimental data and assignments of the electronic transition for O₃, SO₂ and ND₂⁺ are given in Table 2.1 after Maria et al.²²

In ScO₂ unlike SO₂, the first observed low lying electronic transition is 3B₂ + X 1A₁, followed in energy by the 1B₂ + X 1A₁ transition. It is probable that the expected 1B₁ and 3B₁ electronic states in ScO₂ lie to the red of the 3B₂ excited state. Efforts are in progress to detect transitions to these electronic states. Weak rather than continuous absorption is observed in the spectral region >4800 Å, and it is possible that for some reason the 1,3B₁ excited states of ScO₂ are dissociative. This is in direct contrast to SO₂ where the 3B₁ + X 1A₁ electronic transition is sharp and discrete⁴².

Since it is possible for ScO₂ to become linear in an excited electronic state²⁸, it is important to know how the electronic states in each conformation correlate.

In the linear conformation, the ground state electron configuration is²⁸:

⁴¹ Present work.
⁴² R. McFarland, Private Communication.
<table>
<thead>
<tr>
<th>Transition</th>
<th>1B_2 + 1A_1</th>
<th>1A_2 + 1A_1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 eV (64)</td>
<td>ε_{max} 1.3</td>
<td>Indistinct</td>
</tr>
<tr>
<td>3.5 eV (45)</td>
<td>ε_{max} 5.3</td>
<td>Estimation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecule</th>
<th>3B_1 + 1A_1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur dioxide (SO_2)</td>
<td>3.2 eV (24, 42, 36, 47)</td>
</tr>
<tr>
<td>Nitrate ion (NO_2^-)</td>
<td>2.8 eV (59-52)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>ε_{max}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>2.5 x 10^{-5}</td>
</tr>
<tr>
<td>ε_{max}</td>
<td>0.2</td>
</tr>
<tr>
<td>ε_{max}</td>
<td>0.003</td>
</tr>
</tbody>
</table>
$$(1\pi_g)^4(2\pi_u)^2 \ 3\Sigma_g^+, 1\Delta_g, 1\Sigma_g^+$$

with the $3\Sigma_g^-$ state lying lowest in energy, followed by the $1\Delta_g$ and $1\Sigma_g^+$ in agreement with Hund's rules.

The first excited state configuration is assumed to be

$$...(1\pi_u)^3(2\pi_u)^3 \ 1,3\Delta_u, 1,3\Sigma_u^+, 1,3\Sigma_u^-$$

The manner in which the electronic states of bent ($C_{2v}$) and linear ($D_{oh}$) SeO$_2$ correlate with each other is shown in Figure 2.4.

Since in the present work, the molecule remains strongly bent in both electronic states, the Renner$^{33}$ effect and other phenomena relating to linear and quasi-linear$^{34}$ molecules will not be considered.

2.5. Double-Minima Potentials in $AB_2$ Type Molecules

Usually the geometric structure of a bent $AB_2$ molecule has $C_{2v}$ symmetry when the nuclei are in their equilibrium positions. However, there is evidence that occasionally a bent $AB_2$ molecule has an excited state with two equilibrium structures which deviate from $C_{2v}$ symmetry by $\Theta_0$, where $Q_0$ is a normal co-ordinate representing a small antisymmetric displacement$^{35}$. This means that the electronic state has a double-minima potential in the antisymmetric vibrational co-ordinate $Q_0^1$, and that the molecule will have a stable non-symmetric structure in these vibrational levels associated with $Q_0^1$ which lie well below the peak of the barrier. The molecular symmetry will be reduced from $C_{2v}$ to $C_5$ and these vibrational levels below the barrier may exhibit the consequence of $C_5$ symmetry (e.g., the $3\Sigma_0^+(0 \rightarrow 0)$ band should be an A-B hybrid type band). Above the barrier to inversion, the molecule freely moves from one structure to the other and the equilibrium symmetry becomes $C_{2v}$ again.

Conn$^{36-38}$ has postulated the existence of a double-minima potential in
Figure 2.4: Correlation of the electronic states of SO₂ in the linear and bent conformations. The ordering of the higher electronic states is only tentative pending further experimental work.
the 4758 Å electronic transition of C2O2 as well as the 2348 Å system of SO2 and the 2491 Å system of NO2. The present analysis of the 3120 Å system of SeO2 also strongly suggests the presence of a double-minimum potential well in the excited state Q3′ co-ordinate. A further discussion of double-minimum potentials is deferred to Chapter Three where the vibrational analysis is discussed in detail. The resolution of the symmetry species of C2v into those of Cs are given in Table 2.2.

Table 2.2

<table>
<thead>
<tr>
<th>C2v</th>
<th>Cs (σy2)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>A'</td>
<td>y (b-axis)</td>
</tr>
<tr>
<td>A2</td>
<td>A''</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>A''</td>
<td>x (c-axis)</td>
</tr>
<tr>
<td>B2</td>
<td>A'</td>
<td>z (a-axis)</td>
</tr>
</tbody>
</table>
CHAPTER THREE

VIBRATIONAL ANALYSIS OF SELENIUM DIOXIDE SPECTRUM

3.1. Description of SeO₂ Spectrum

At least five discrete electronic transitions have been observed in
the gas phase spectrum of the selenium dioxide molecule in the spectral region
between 2000 Å and 6000 Å. Three of these transitions have been observed
in absorption in the regions 2070-2210 Å, 2500-3400 Å, and 5500-5200 Å and
have been designated the A, B and C systems respectively. Haranath and
Sivaramanurty also claim to have observed two systems in emission with
origins at 3110 Å and 3119 Å. The present work is concerned primarily with
the B system of selenium dioxide.

3.2. The B System of SeO₂

The B system of SeO₂ has been photographed under both high and low
resolution using pure selenium and oxygen isotopes. Portions of the spectra
of the Se⁷⁰O₂¹⁶ and Se⁷⁰¹⁰O₂ molecules are shown under low dispersion in Figure
3.1.

The most prominent features in the spectrum are long progressions with
the frequency interval of approximately 650 cm⁻¹. This frequency can be
assigned to ν₁, the totally symmetric stretching frequency of the excited
state. Both the excited state bending frequency ν₂ = 260 cm⁻¹ and the asym-
metric stretching frequency of 1572 cm⁻¹ (2ν₃) appear in the spectrum as false
origins for totally symmetric progressions in ν₁. All three fundamental fre-
quencies have decreased in the excited state. The ground and excited state
frequencies, along with their percentage decreases, are summarized in Table 3.1.

Many of the bands in the system are double headed and several frequency
intervals are abnormally large. Each of these anomalies will be discussed separately, later in the chapter.

The strongest progression in the spectrum involves $\nu_1$ and originates on the unobserved $2^2_0$ level and contains twelve members. The intensity maximum occurs in the sixth member. The presence of such an extended progression in $\nu_1$ in combination with $\nu_2$ indicates a substantial change in both bond length and bond angle in the excited electronic state.

3.3. The Origin Band of the B System of SeO$_2$

The spectra of the two isotopic molecules Se$^{78}$O$_2$ and Se$^{78}$O$_2$ were photographed under high resolution and the positions of the band heads carefully determined using a travelling microscope accurate to 0.0001 centimeters. In Figure 3.2 is shown a plot of isotopic splitting against number of quanta of $\nu_1$ excited for the two isotopic molecules Se$^{78}$O$_2$ and Se$^{78}$O$_2$. The origin band for the electronic transition has an isotopic splitting of -8.9 cm$^{-1}$ for the Se$^{78}$O$_2$ and Se$^{78}$O$_2$ molecules, the heavier isotope band lying to the blue of the lighter one. The origin band for the Se$^{78}$O$_2$ isotope occurs at 31955.0 cm$^{-1}$. The origin band of the Se$^{76}$O$_2$ and Se$^{80}$O$_2$ molecules have an isotopic splitting of -2.4 cm$^{-1}$. For the Se$^{78}$O$_2$ and Se$^{78}$O$_2$ molecules, the isotopic splitting is found to be 30 cm$^{-1}$ per quanta of $\nu_1$ excited, with the lighter isotope to the blue of the heavier one. A similar plot using the isotopic splittings from the Se$^{78}$O$_2$ and Se$^{80}$O$_2$ molecules gives a value of 1.46 cm$^{-1}$ per quanta of $\nu_1$ excited. It is possible to observe three quanta of the ground state totally symmetric stretching frequency $\nu_1$, as hot bands to the red of the above assigned origin band. Figure 3.2 (lower curve) shows the

*Unless otherwise stated, all frequencies used in the text refer to the Se$^{78}$O$_2$ isotope.*
Figure 22. Isotopic splitting per quantum of $\gamma'$ excited in the 0-0 progression (upper curve) and isotopic splitting per quantum of $\gamma'_s$ excited in the hot band spectrum (lower curve). The isotopic molecules used were $36^{16}O_2$, $34^{16}O_2$, and $36^{18}O_2$. A similar plot using $56^{16}O_2$ and $56^{18}O_2$ shows an isotopic splitting of 1.46 cm$^{-1}$ per quantum of $\gamma'_s$ excited and extrapolates to the same origin.
corresponding plot for $v''_1$. As is expected there is a reversal in the direction of the isotopic splitting in the hot band spectrum to that in the cold band spectrum. The average splitting is $-47.0 \text{ cm}^{-1}$ per quanta of $v''_1$ excited with the heavier isotope now appearing to the blue of the lighter one.

The explanation for this reversal is simple, and can be understood with the aid of Figure 3.3.

3.4. Isotopic Splittings in Hot and Cold Bands of Electronic Transitions

A cold band in an electronic transition is due to a transition originating on the vibrationless level of the ground state and terminating on an excited state vibronic level, while a hot band transition originates from an excited vibronic level in the ground state and terminates on an excited state vibronic level. The transitions designated (a) in Figure 3.3 give cold bands while those designated (b) give hot bands. If, for the moment, we assume that the isotopic splitting of the vibrationless level in both the ground and excited state is too small to resolve, then for a decrease in frequency in going to the excited state as a result of a shallower potential well in this state, the levels will have a larger splitting in the ground than in the excited state. The level belonging to the lighter isotope will have a higher energy since it vibrates at a higher frequency. Since the splitting of the $v''_1 = 2$ isotopic levels in the ground state is larger than the $v'_1 = 2$ splitting in the upper state, then the bands of the lighter isotope will lie to the blue of the heavier in (a) but to the red of the heavier in (b). In the present case the origin band has an isotopic splitting of $-8.9 \text{ cm}^{-1}$, the heavier isotope origin band lying to the blue of the lighter one. This can be rationalized in the following way. Since the three fundamental frequencies decrease considerably in the excited state, therefore, the potential wells along these co-ordinates
will be shallower than the corresponding wells in the ground electronic state. Accordingly, the $v_i = 0$ vibrational levels will lie both closer together and closer to the bottom of the well in the excited state than in the ground state. The zero-point energy will, therefore, be less in the excited state than in the ground state. Since the isotopic splitting of the vibrationless level is larger in the ground than in the excited state, with the lighter isotope lying at higher energy, the origin band of the heavier isotope is expected to lie to the blue of the origin band for the lighter isotope and thus a reversal in the direction of the isotopic splitting is observed. The reversal in the direction of the isotopic splitting is shown in Figure 5.3 by the set of transitions labelled (c).

3.5. Ground State Fundamentals of ScO$_2$

The infrared spectrum of selenium dioxide has been studied in the gas phase by Giguère and Falk$^{10}$ and in the solid phase in rare gas matrices by Hastic et al.$^{15}$ and Cesaro et al.$^{14}$ The gas phase work of Giguère and Falk give $v_3'$ as 967 cm$^{-1}$ in good agreement with the value of 970.2 cm$^{-1}$ found in neon matrices by Hastic et al. and 965 cm$^{-1}$ reported by Cesaro et al. The weak $v_1''$ fundamental could not be definitely assigned in the gas phase because of overlap with the intense $v_3$ absorption. Duchesne and Rosen$^8$, however, assigned $v_1'' = 910$ cm$^{-1}$ from their analysis of the B system of selenium dioxide. The present analysis of the B system indicates 923 cm$^{-1}$ for the totally symmetric stretching frequency of the ground state. The interval of 910 cm$^{-1}$ attributed to $v_1''$ by Duchesne and Rosen was incorrectly interpreted. The isotopic analysis of ScO$_2$ unambiguously shows the 910 cm$^{-1}$ interval is in fact due to the excited state combination band $v_1' + v_2'$ where $v_1' = 660$ cm$^{-1}$ and $v_2' = 250$ cm$^{-1}$. Higher members of the excited state progression involving $v_1'$
Figure 3.5 The isotopic splitting of the $\gamma^0$ and $\gamma'$ levels in $\text{SO}_2^{16}$ and $\text{SO}_2^{32}$. The splitting is greatly exaggerated. The well is flatter in the excited state $\gamma'$ since the frequency was dropped and the $\text{SO}-\text{O}$ bond length increased.
show a frequency interval of approximately 650 cm\(^{-1}\). Hot band progressions in \(v_1\) originating on the \(1^0_1\) and \(1^0_2\) levels are quite weak with fewer members in the progression. Duchesne and Rensen incorrectly assigned the origin band for the transition 1375 cm\(^{-1}\) to the blue of the true origin. Prior to the present analysis the interval corresponding to \(v''_1\) and \(v''_2\) had not been observed in absorption in either the gas phase or in low temperature matrices. Takeo et. al.\(^{57}\), from the microwave spectrum of ScO\(_2\), have estimated \(v''_2 = 362 \pm 14\) cm\(^{-1}\), using Coriolis coupling constants and inertial defects. From the present work the frequency interval associated with \(v'_2\) has been observed to be 373 cm\(^{-1}\). This is in excellent agreement with the value of 372.5 recently determined by Cesaro et. al.\(^{14}\) from studies of ScO\(_2\) in an argon matrix.

3.6. Excited State Fundamentals of ScO\(_2\)

In the present vibrational analysis of the B system of ScO\(_2\), all three excited state fundamentals are assigned. By far the most active frequency in the spectrum is \(v'_1 = 660\) cm\(^{-1}\) which occurs in long progressions with as many as twelve members. The bending frequency \(v'_2 = 260\) cm\(^{-1}\) appears only in combination with \(v'_1\) and \(v'_3\) while the asymmetric stretching frequency \(2v'_3 = 1372\) cm\(^{-1}\) appear in the spectrum both as the fundamental and in combination with \(v'_1\) and \(v'_2\). The ground and excited state frequencies for the Sc\(^{76}\)O\(_2\)^{16} and Sc\(^{78}\)O\(_2\)^{18} molecules are summarized in Table 3.1.

3.7. Major Progressions in the B System of ScO\(_2\)

The majority of bands in the spectrum may be accounted for in terms of progressions in \(v'_1\). The following set as origins for a progression in this code: \(2^0_0, 2^1_0, 2^2_0, 3^0_0, 3^1_0, 3^2_0, 3^3_0, 3^4_0, 1^0_1, 1^1_1, 1^2_1, 1^3_1, 1^4_1\). The \(2^2_0\)^{10} progression contains the strongest bands in the spectrum. The wavelengths and assignments for the above progressions are given in Appendix I of the thesis. Since there are so many
Table 3.1
Ground and Excited State Fundamentals of $\text{Se}^{78,16} \text{O}_2$ and $\text{Se}^{76,18} \text{O}_2$

<table>
<thead>
<tr>
<th>Isotope $^\dagger$</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Ground State</th>
<th>Excited State</th>
<th>Percent Change on Excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Se}^{78,16} \text{O}_2$</td>
<td>$v_1$ ($a_1$)</td>
<td>923 cm$^{-1}$</td>
<td>660 cm$^{-1}$</td>
<td>-28.5%</td>
</tr>
<tr>
<td></td>
<td>$v_2$ ($a_1$)</td>
<td>373 cm$^{-1}$</td>
<td>255 cm$^{-1}$</td>
<td>-30.3%</td>
</tr>
<tr>
<td></td>
<td>$v_3$ ($b_2$)</td>
<td>967 cm$^{-1}$</td>
<td>$^\circ$</td>
<td>-29.1%</td>
</tr>
<tr>
<td>$\text{Se}^{78,18} \text{O}_2$</td>
<td>$v_1$ ($a_1$)</td>
<td>878 cm$^{-1}$</td>
<td>625 cm$^{-1}$</td>
<td>-28.9%</td>
</tr>
<tr>
<td></td>
<td>$v_2$ ($a_1$)</td>
<td>359 cm$^{-1}$</td>
<td>245 cm$^{-1}$</td>
<td>-31.8%</td>
</tr>
<tr>
<td></td>
<td>$v_3$ ($b_2$)</td>
<td>$^\circ$</td>
<td>$^\circ$</td>
<td>$^\circ$</td>
</tr>
</tbody>
</table>

*Evidence is presented which suggests the presence of a double-minimum potential in the asymmetric vibrational co-ordinate $Q_3$ in the excited state of $\text{SeO}_2$ and, therefore, it is not possible to assign a particular frequency to $v_3'$. However the interval $(0^0-1^0) = 2v_3'$ has been observed as 1372 cm$^{-1}$.

*Not observed.

$^\dagger$The fundamental frequencies of $\text{Se}^{78,16} \text{O}_2$ are almost identical with those of $\text{Se}^{78,16} \text{O}_2$ and are therefore not shown.
long progressions of bands, all of type-A and further since the combination band \( v'_1 + v'_2 = 920 \text{ cm}^{-1} \) is almost identical with \( v''_1 = 923 \text{ cm}^{-1} \), there can occur quite strong Fermi resonances in the spectrum.

The three progressions in \( v'_1 \) originating on the levels \( 0^0_0, 2^1_0 \) and \( 2^2_0 \) are quite straightforward. Each contains twelve members with the sixth member being the strongest in each progression. The \( 2^1_0 \) and \( 2^2_0 \) bands, however, appear in absorption only in combination with \( v'_1 \); the \( v'_2 \) fundamental is not observed. It is possible that \( v'_2 \) also appears in combination with the \( 3^3_0 \) level. This hypothesis is discussed in greater detail later in the chapter.

The region of the \( 0-0 \) band is both very weak and badly overlapped.

The considerable overlap in this region is due to the presence of combination sequence bands of the type \( 1^1_0 + 1^2_0 \) and \( 1^1_1 + 1^2_1 \); the first occurs at almost an identical frequency to that of the origin band.

The hot band spectrum very clearly shows the three bands \( 1^0_1, 1^0_2 \) and \( 1^0_3 \). All three bands are themselves false origins for progressions in \( v'_1 \). Higher members in this progression further complicate the region of the origin band.

3.8. The Presence of Another Electronic Transition?

The hot band spectrum of the \( D \) system of \( SeO_2 \) was photographed under both high and low resolution and extends for 2750 \( \text{ cm}^{-1} \) to the red of the origin band. The origin band for the transition occurs at 31955 \( \text{ cm}^{-1} \). The ground state fundamentals \( v''_1 = 923 \text{ cm}^{-1} \) and \( v''_2 = 375 \text{ cm}^{-1} \) can be unambiguously assigned. The three hot bands in the spectrum appearing at 31032 \( \text{ cm}^{-1} \), 30115 \( \text{ cm}^{-1} \), and 29201 \( \text{ cm}^{-1} \), separated by the respective intervals 923.0 \( \text{ cm}^{-1} \), 910.4 \( \text{ cm}^{-1} \) and 912.0 \( \text{ cm}^{-1} \) have been assigned to the \( 1^0_1, 1^0_2 \) and \( 1^0_3 \) bands respectively.

*There is strong evidence showing the presence of a double-minima potential in the asymmetric stretching co-ordinate \( Q^5 \) of the excited state. The \( (0^0-0^0) \) splitting is observed to be 78 \( \text{ cm}^{-1} \) and can be associated with the frequency interval \( 3^5_0 \).
This assignment can be made with a high degree of certainty and is substantiated by the isotopic splitting for each band.

A puzzling thing about the above three hot bands is the fact that they appear to be doublets, each having an additional head at an average separation of 78 cm\(^{-1}\) to the blue. The calculated band contour of the 1\(^3\) band in the cold spectrum shows no indication of the presence of a second head in the band 78 cm\(^{-1}\) to the blue of the first head. From the rotational analysis of the 1\(^3\) band, the excited state was determined to be of B\(_2\) symmetry, the electric dipole for the electronic transition being polarized along the a-axis (i.e., the axis parallel to the line joining the oxygen nuclei) of the molecule. The possibility that both heads separated by 78 cm\(^{-1}\) could be associated with one vibronic band was, however, still considered.

If in fact the head 78 cm\(^{-1}\) to the blue is to be associated with the same vibrational band then one of the heads\(^*\) must be due to a q branch (\(\Delta K = 0\)) while the other is due to an s or o branch (\(\Delta K = \pm 2\)) in the K structure. The latter two branches are expected to be much weaker than the q branch since they acquire intensity only as a result of the asymmetry of the molecule or through a perturbation such as Coriolis coupling or centrifugal distortion.

The origin of the sub-bands (\(J = 0\)), in the q branch of a parallel transition of an asymmetric top, in the near prolate symmetric top approximation, is given by:

\[

\nu_{\text{sub}} = \nu_0 + [(\lambda' - \beta') - (\lambda'' - \beta'')] R^2

\]

(5.1)

where \(\beta = \frac{1}{2}(\beta + C)\) and the primes and double-primes refer to excited and ground state respectively.

\(^*\) In this context the word "head" is meant to indicate an accumulation of very closely spaced K sub-bands.
The sub-band origins for a parallel transition in the o and s branch of the K-structure is given by

\[ \nu_{\text{sub}} = \nu_o + 4(A' - B') \pm 4(A' - B')K \cdot [(A' - B') - (A'' - B'')] K^2 \]  

(3.2)

The value of \( K \) at the head is determined by differentiating Equation (3.2) and setting it equal to zero. The resulting equation is:

\[ K_{\text{HEAD}} = \frac{\pm 2(A' - B')}{[(A' - B') - (A'' - B'')]} \]  

(3.3)

Substitution of Equation (3.3) into (3.2) gives, for the separation of the heads in the q and o branch, and the q and s branch of the K-structure:

\[ \nu_o^s - \nu_q = 4(A' - B') \pm \frac{12(A' - B')^2}{[(A' - B') - (A'' - B'')]} \]  

(3.4)

From the microwave spectrum \(^{57}\), \((A'' - B'') = 0.712 \text{ cm}^{-1}\) while from the present rotational analysis \((A' - B') = 0.361 \text{ cm}^{-1}\). Substitution of these values into Equation (3.4) gives a head separation of \(\pm 5 \text{ cm}^{-1}\). The observed separation between the two heads in the spectrum is 78 \text{ cm}^{-1}. The hypothesis that the two heads belong to the oeo vibronic band is therefore rejected since the observed separation is much too large. The fact that both heads are of equal intensity is also strong evidence against both belonging to one and the same band, since the o and s branches would be expected to have considerably less intensity than the q branch.

It was therefore necessary to assign the four bands located at 32033.6 \text{ cm}^{-1}, 31110.8 \text{ cm}^{-1}, 30192.5 \text{ cm}^{-1} and 29209.5 \text{ cm}^{-1} to different vibronic transitions.

Khanna and Sivaraman\(^{12}\) studied the gas phase collision spectrum of ScO\(_2\) and observed a number of bands in the spectral region 4700 Å to 2750 Å.
The bands below $\lambda$ 3200 Å to $\lambda$ 2700 Å were assigned as belonging to the previously assigned B–X system of ScO$_2$ studied by Duchesne and Rosen in 1941. The remaining bands were assigned by Haranath and Sivaramakurty as belonging to two new systems of selenium dioxide with origins at 32145 cm$^{-1}$ and 32052 cm$^{-1}$. A summary of the vibrational constants determined by Haranath and Sivaramakurty is given in Table 3.2.

Table 3.2

Vibrational Frequencies of System-I and System-II

<table>
<thead>
<tr>
<th></th>
<th>$\nu_0$</th>
<th>$\nu_1$</th>
<th>$\nu_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>System-I</td>
<td>32145 cm$^{-1}$</td>
<td>910.5 cm$^{-1}$</td>
<td>182 cm$^{-1}$</td>
</tr>
<tr>
<td>System-II</td>
<td>32052 cm$^{-1}$</td>
<td>911.5 cm$^{-1}$</td>
<td>182 cm$^{-1}$</td>
</tr>
</tbody>
</table>

Both of the above emission systems could, if they terminate on the ground electronic state, appear in absorption in the same spectral region as the B System of ScO$_2$. An attempt was therefore made to try and observe their absorption spectrum in the hope of perhaps accounting for the four sequence bands discussed above.

The only conceivable assignment which could be made would be to assign the four vibronic bands located at 32033.8 cm$^{-1}$, 31110.8 cm$^{-1}$, 30192.5 cm$^{-1}$ and 29280.5 cm$^{-1}$ as the $\nu_0^0$, $\nu_1^0$, $\nu_2^0$, and $\nu_3^0$ of one of the two electronic states observed by Haranath and Sivaramakurty.

It was, however, not possible to observe the frequency interval of 182 cm$^{-1}$ anywhere in the spectrum, nor was it possible to assign any new frequency interval resulting from the presence of a close lying second electronic transition.
Since there are no excited state frequencies observed, along with the fact that the presence of a second electronic transition, only 78 cm⁻¹ away, is difficult to account for theoretically, the hypothesis of a second electronic transition was rejected. In the emission work of Haranath and Sivaramamurty both transitions were found to have the same intensity. It would be difficult to explain why only one of the two emission systems should appear in absorption if both were transitions terminating in emission on the ground state. The four vibronic bands mentioned above, though still unexplained, were assumed to be sequence bands associated in some way with the B System of SeO₂.

The possibility that the above vibronic bands were due to an impurity molecule such as Se₂ was excluded since the bands showed an 0¹⁸ isotopic shift when the Se⁷⁸O₁⁸ spectrum was photographed. Since isotopic selenium was used, the only other realistic impurity which was considered was Se₀. Along with the fact that the observed frequencies of the bands are different to those of Se₀ observed by Shin-Piao⁵⁸, the rotational structure appears much too complex to be associated with a diatomic molecule.

The isotopic splitting of all bands was found to be almost linear with displacement from the origin, regardless of the nature of the band. Since the four sets of bands were separated by only 78 cm⁻¹, both members of each set showed approximately the same isotopic shift; so the isotopic molecule gave no new information, other than the bands do in fact belong to SeO₂.

3.9. The Cold Spectrum of the B System of SeO₂

All of the bands in the cold spectrum can be accounted for by progressions in the excited state totally symmetric stretching frequency ν₁ = 660 cm⁻¹. Two interesting features are present in the spectrum.

1. There is an abnormally high intensity associated with the 3₀ transition
(see below).

2. Many, but not all, of the bands are double-headed.

3.10. Progressions in Anti-Symmetric Vibrations

According to the simple classical principle of Franck, the geometric conformation of the nuclei and their relative velocities does not change during an electronic transition. Therefore, the instantaneous symmetry of the equilibrium position of the nuclei is the same in both combining electronic states. The classical principles of Franck were later developed quantum mechanically by Condon; the combined treatment is now most often referred to as the Franck-Condon principle.

If a non-totally symmetric vibration is excited during an electronic transition (and once again it is assumed that the instantaneous symmetry of the excited state is the same as that of the ground electronic state) then this requires that the potential surfaces for all non-totally symmetric vibrations have their origins directly above one another. The potential well along $Q_3$, the asymmetric stretching normal coordinate, is shown in Figure 3.4 for two combining electronic states (the double minimum character is ignored in this section). The centers of the two wells must be directly above one another since any displacement along $Q_3$ in the excited state relative to that of the ground state will correspond to an equilibrium asymmetric structure in the excited state. This would then violate the initial assumption that the symmetry of the molecule remains unchanged during an electronic transition. Therefore, within the Franck-Condon approximation, the transition probability between two electronic states is proportional to the square of the matrix element

$$<\phi_0^*|\hat{T}|\phi_0>$$

(3.5)
where \( \psi \) and \( \phi \) are the electronic and vibrational wavefunctions respectively and \( \hat{r} \) is the electric dipole operator. The primes refer to the upper state while the double primes refer to the lower state.

Within the Born-Oppenheimer approximation, the nuclear and electronic motion may be considered independent and Equation (3.5) reduces to

\[
<\psi' | \hat{r} | \psi''> <\phi' | \phi''>
\]  

(3.6)

In order for an electronic transition to occur, Equation (3.6) must be non-zero. The transition probability will be different from zero only if the integrand of Equation (3.6) is totally symmetric.

The first integral of Equation (3.6), \( <\psi' | \hat{r} | \psi''> \), is the transition moment and is non-zero only if the direct product of the representations to which the electronic wavefunctions belong transform as one of the components of the electric dipole operator \( \hat{r} \), which transforms like the translations \( T_x \), \( T_y \), and \( T_z \). We, therefore, have the following selection rule:

\[
\Gamma \psi' \times \Gamma \psi'' = \Gamma T_i \quad i = x, y, z
\]  

(3.7)

The second integral of Equation (3.6), \( <\phi' | \phi''> \), is called the Franck-Condon overlap integral and is non-zero only if the following selection rule is satisfied:

\[
\Gamma \phi' \times \Gamma \phi'' = \Gamma A_1
\]  

(3.8)

If we assume transitions from the ground state occur from the vibrationless level, then \( \Gamma \phi'' = A_1 \) and, therefore, according to the Franck-Condon principle, within the Born-Oppenheimer approximation, the following vibrations may be excited:

1. Totally symmetric vibrations may change by any number of quanta.
2. Anti-symmetric vibrations must change by an even number, \( \Delta v = 0, 2, 4, \ldots \), where \( v \) is the vibrational quantum number.
If the symmetry is different in both states then only those vibrations will be excited which preserve the symmetry elements common to both states.

Therefore, according to the Franck-Condon principle, the 0→0, 1→1, ..., v→v transitions will be intense, with the higher members becoming progressively weaker due to their decreased Boltzmann factor.

Spencer and Toller have shown, for purely harmonic vibrations, that the ratio of the intensity of the 0→0 band, to that of all the other members in a progression involving an asymmetric vibration Q, is given by

\[
\frac{\frac{1}{2} (v^2 + v''^2)^{1/2}}{\text{intensity of all bands } 0→v \text{ in } Q} \quad v = 0, 2, 4, \ldots
\]  

where \(v'\) and \(v''\) are the frequencies in the two combining electronic states.

This means that even in the extreme case when the vibrational frequencies in the upper and lower state change by 50\%, the intensity of the 0→0 band amounts to 94.4 percent of the total intensity and only 5.6 percent is left for transitions from \(v'' = 0\) to \(v' \neq 0\) levels. Hence the \(3_0^2, 5_0^4\) and higher bands should be very weak and in all probability not be observed in the spectrum.

It is possible to rationalize the above results in the following manner. Since the potential wells for asymmetric vibrations belonging to different electronic states must be directly above one another, as shown in Figure 3.4, then transitions of the type 0→0, 1→1, etc., will have a larger Franck-Condon factor than transitions of the type 0→2 or 0→4. The actual intensity of any one band is proportional to

\[
\int \phi^* \phi'' \phi_{\text{vib}}^2 \phi_{\text{nuc}}^2 \, d\varepsilon \quad \text{(3.10)}
\]

where \(\phi'\) and \(\phi''\) are the vibrational wavefunctions of the combining states and the integration is over the nuclear co-ordinates. Each combining electronic state contains its own unique set of orthonormal vibrational wavefunctions.
Figure 3.4 Plot of potential energy versus the antisymmetric normal co-ordinate $Q_3$ for two combining electronic states. Since the symmetry must, according to the Franck-Condon principle be the same in both states, the potential wells along $Q_3$ must directly be one above one another.
In a symmetric triatomic molecule such as SeO\textsubscript{2}, the only asymmetric vibration is \(v_3\), the antisymmetrical stretching frequency. Therefore, for an electronic transition in SeO\textsubscript{2} involving \(v_3\), in the limit that \(v_3' = v_3''\), then the complete set of vibrational wavefunctions in both combining states are identical and transitions between levels whose vibrational quantum numbers differ, are forbidden by the orthogonality of the wavefunctions. Small differences in \(v_3\) and \(v_3'\) remove the orthogonality and transitions to higher vibronic levels may occur, but will be weak.

In the present analysis of the \(Q_0\) system of selenium dioxide the intensity ratio of the 0–0 band to the 3\^2 \(S_0\) band is approximately 0.2, or the 3\^2 \(S_0\) band is five times stronger than the 0–0 band. This is inconsistent with the above discussion concerning the expected intensity of the 3\^2 \(S_0\) band. There are two ways in which the 3\^2 \(S_0\) band can acquire intensity. Since the above arguments are based on the assumption of purely harmonic vibrations, therefore the inclusion of cubic and quartic terms in the potential energy render the vibrations anharmonic and the above arguments are no longer true.

Coen and his co-workers\textsuperscript{56,61} have suggested the possibility of the existence of a double-minimum potential in the anti-symmetrical vibrational co-ordinate of an excited state of SeO\textsubscript{2} as a possible explanation for the abnormally high intensity of the 3\^2 \(S_0\) band in the SeO\textsubscript{2} spectrum. There is also strong evidence for the existence of a double-minimum in the antisymmetric co-ordinate of the 2548 Å transition of SeO\textsubscript{2} \textsuperscript{57,62,63}, as well as the 2491 Å band system of the NO molecule\textsuperscript{30}. The present work indicates strong evidence\textsuperscript{*} for a double-minimum potential in the \(Q_0^*\) co-ordinate of the 3125 Å system of SeO\textsubscript{2}. It

\textsuperscript{*} The experimental observation of the 3\^2 \(S_0\) vibronic band (transition from the vibrational level of the ground state to the 0\^* level of \(Q_0^*\) in the excited state) appears to be at present the only existing experimental evidence for the presence of a double-minimum potential in the antisymmetric stretching co-ordinate of a symmetric bent \(AB_2\) type molecule.
appears as if there may be some common mechanism among seventeen, eighteen and nineteen electron bent symmetric triatomic molecules through which the $3^2_0$ transition gains intensity. Milliken has suggested that a double-minimum potential might occur if an electron occupies a $2b_1$-molecular orbital. The antibonding effect of this orbital is expected to be smaller for an unsymmetrical structure than for a symmetric one.

It will now be shown how, in the present analysis, the assumption of a double-minimum potential in the excited state asymmetric vibrational co-ordinate $Q_3^1$, accounts for the four as yet unexplainable sequence bands mentioned above, as well as the abnormally high intensity of the $2v_3^1$ transition.

### 3.11. A Double-Minimum In the Excited State Asymmetric Stretching Co-ordinate of $\text{SeO}_2$

As a result of the abnormally high intensity of the $3^2_0$ band, which could not be explained in terms of a harmonic potential in $Q_3$, it has been necessary to assume that there is a double-minimum potential with respect to the anti-symmetric stretching co-ordinates of the excited state. J. B. Coon has constructed a three parameter double-minimum potential function in a convenient form for general application, and tabulated the energy levels. The methods outlined by Coon have been applied in the present analysis to the $\text{SeO}_2$ molecule.

The double-minimum potential function used is of the form

$$V(Q) = \frac{1}{2} \lambda Q^2 + Q \exp(-\alpha Q^2) \quad (3.11)$$

where $Q$ is a mass-weighted co-ordinate defined by $2T = Q^2$. In order to apply the method outlined by Coon, it is necessary to experimentally determine at least three levels in the progression involving the asymmetric vibration. In the present calculation the frequency intervals between $0^2_0 (0^+)\text{, }3^2_0 (0^-)$ and
3^2_0 (1^+^-) bands were used.

The 3v'_3 vibronic band is also observed and is a false origin for a
totally symmetric progression involving v_1. The 4v'_3 vibronic band is not
observed; however, the higher members in the progression 3^2_0, 1^{01}_0
are observed. The lower members of both the 3^2_0 and 3^2_0 progressions are expected to be
weak due to a small Franck-Condon factor. In addition these bands lie in the
same region as many of the intense members of the strong 1^{01}_0, 1^{20}_0 and 1^{22}_0
progressions. The intense bands in these progressions are probably mainly
responsible for the lower members of the 3^2_0 and 3^2_0 progressions not being
observed in the spectrum. Extrapolation of the higher members in the 3^2_0
progression to the origin (3^2_0), further allowed the 4v'_3 band position to be
determined. The extrapolated value for the 4v'_3 (2^+^-) interval is 5084 cm^{-1}
with the 4v'_3 vibronic band lying approximately at 0^0_0 + 5084 = 35039 cm^{-1}.

The actual calculations and a fuller description of the double-minim parameters are given in Appendix II of the thesis. Only a brief summary of the
results will be given here.

The 0^0_0, 1^0_0, 2^0_0, 3^0_0 and 5^0_0 vibronic bands appear in the spectrum of the
Sc^{78}O_2 molecule at 31955.0 cm^{-1}, 32033 cm^{-1}, 33327 cm^{-1}, 34026.5 cm^{-1} and
35039 cm^{-1} (estimated) respectively. The interval ν'_3 = G(0^-) - G(0^0) is 78.9
cm^{-1} while the 2ν'_3 = G(1^-) - G(0^0) interval is observed to be 1372 cm^{-1}. The
3ν'_3 = G(1^-) - G(0^0) is observed as 2071.5 cm^{-1} and the extrapolated value of
4ν'_3 = 3034 cm^{-1}. The interval 4ν'_3 - 2ν'_3 = G(2^+^-) - G(1^+) is calculated to be
1712 cm^{-1}.

The energy levels for the first four levels of the double-minim will
have been calculated for ω = 0.6, 0.9, 1.2 and 1.5 for the isotopic molecules
Sc^{70}O_2, Sc^{70}O_2 and Sc^{80}O_2 and are calculated in Table 3.3. The corresponding
ω values and barrier heights are given in Table 3.4. The parameter ω determines
the shape of the potential function. For low \( \rho \) values the outer walls of the potential rise more steeply than the walls of the barrier. For \( \rho = 1.5 \) the minima are parabolic, while for larger values of \( \rho \) the walls of the barrier rise more steeply than the outer walls of the potential. In the present application to the excited state of \( \text{ScO}_2 \), \( \rho = 0.6 \) was found to give the best fit. The effect of the parameter \( \rho \) on the shape of the double-minimum potential is shown in Figure 3.5.

The barrier height separating the two minima is calculated to be 1986.5 cm\(^{-1} \) for \( \rho = 0.6 \) and the (0\(^0\)–0\(^-\)) separation is 79.2 cm\(^{-1} \). Coon\(^{61} \) has calculated the (0\(^0\)–0\(^-\)) interval to be 69 cm\(^{-1} \) in \( \text{C}_2\text{O}_2 \) and 103 cm\(^{-1} \) in the 2491 Å absorption system of the \( \text{NO}_2 \) molecule\(^{39} \). The double-minimum potential in the asymmetric vibrational mode of the 1\(^B_2 \) excited state of \( \text{ScO}_2 \) is shown in Figure 3.6 for \( \rho = 0.6 \).

The calculated and observed energy levels of the double-minimum well along \( Q_3' \) appear to be best for \( \rho = 0.6 \). The calculated value for the 3\( v_3' \) (1\(^-\)) level of 2085.6 cm\(^{-1} \) is in excellent agreement with the observed value of 2071.5 cm\(^{-1} \). The calculated value for 4\( v_3' \) (2\(^6\)) is poorer. The poorer agreement for the 4\( v_3' \) level may possibly be due to an anharmonicity in the double-minimum well. The potential used by Coon\(^{35} \) reduces to a harmonic potential for large values of \( v_3' \); therefore, the calculated level will be in error if any anharmonicity is present. It is difficult to know at what value of \( v_3' \) in the double-minimum well does anharmonicity become important.

The barrier height \( (B_{v_0}) \) and the shape of the potential surface (\( \rho \)) are assumed to be invariant to isotopic substitution. Comparison of the barrier height in all three isotopes for \( \rho = 0.6 \) shows that the agreement is excellent for \( \text{Sc}^{70}\text{O}_2 \) and \( \text{Sc}^{60}\text{O}_2 \), and within 5% for the \( \text{Sc}^{70}\text{O}_2 \) isotopes. While the interchange of some of the structure to another primarily occurs
Table 3.3

Calculated Energy Levels of the Double-Minimum Potential Well

for the Asymmetric Stretching Coordinate $Q_3$ of the $^1B_2$ Excited State

of Se$^{78}O_2$, Se$^{79}O_2$ and So$^{80}O_2$ in cm$^{-1}$ for the Shape Parameter $\rho = 0.6, 0.9, 1.2$ and 1.5

<table>
<thead>
<tr>
<th>Selenium Isotope</th>
<th>$\nu_1$</th>
<th>0.6</th>
<th>0.9</th>
<th>1.2</th>
<th>1.5</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se$^{78}O_2$</td>
<td>0 ($0^+$)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>1 ($0^-$)</td>
<td>79.2</td>
<td>78.05</td>
<td>77.4</td>
<td>79.13</td>
<td>78.9</td>
</tr>
<tr>
<td></td>
<td>2 ($1^+$)</td>
<td>1372.5</td>
<td>1372.2</td>
<td>1372.6</td>
<td>1372.6</td>
<td>1372.6</td>
</tr>
<tr>
<td></td>
<td>3 ($1^-$)</td>
<td>2055.6</td>
<td>2015.4</td>
<td>1952.2</td>
<td>1905.6</td>
<td>2071.5</td>
</tr>
<tr>
<td></td>
<td>4 ($2^+$)</td>
<td>3177.2</td>
<td>3084.0</td>
<td>2993.8</td>
<td>2893.84</td>
<td>3034.0</td>
</tr>
<tr>
<td>So$^{80}O_2$</td>
<td>0 ($0^+$)</td>
<td>0.0</td>
<td>0.0</td>
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<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
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<td>1 ($0^-$)</td>
<td>73.4</td>
<td>61.99</td>
<td>02.8</td>
<td>78.23</td>
<td>77.9</td>
</tr>
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<td>3 ($1^-$)</td>
<td>2052.9</td>
<td>2046.9</td>
<td>1954.1</td>
<td>1897.9</td>
<td>2067.2</td>
</tr>
<tr>
<td></td>
<td>4 ($2^+$)</td>
<td>3163.5</td>
<td>3137.0</td>
<td>2931.1</td>
<td>2837.7</td>
<td>3030.0</td>
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<tr>
<td>Se$^{79}O_2$</td>
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<td>0.0</td>
<td>0.0</td>
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<td>76.5</td>
<td>79.05</td>
<td>02.77</td>
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<td>1599.55</td>
<td>1599.55</td>
<td>1518.74</td>
<td>1509.52</td>
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<td>3 ($1^-$)</td>
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<td>1935.29</td>
<td>1891.66</td>
<td>1827.96</td>
<td>1953.27</td>
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<td>2029.58</td>
<td>2289.93</td>
<td>2777.93</td>
<td>2905.0</td>
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$\nu_3 (2^+)$ is estimated from extrapolation of So$^{80}O_2$ progression.
Table 3.4

Calculated B Values and Barrier Heights $D_{\nu_0}$ (cm$^{-1}$) for the Asymmetric Stretching Co-ordinate $Q_3$ of the $^1B_2$ Excited State of Se$^{78}O_2^+$, Se$^{78}O_2^+$ and Se$^{80}O_2^+$ for the Shape Parameter $\rho = 0.6, 0.9, 1.2$ and 1.5

<table>
<thead>
<tr>
<th>Selenium Isotope</th>
<th>$\rho$</th>
<th>0.6</th>
<th>0.9</th>
<th>1.2</th>
<th>1.5</th>
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<td>Se$^{78}O_2^+$</td>
<td>$B$</td>
<td>1.0337</td>
<td>1.3557</td>
<td>1.6305</td>
<td>1.9094</td>
</tr>
<tr>
<td></td>
<td>$\nu_0$</td>
<td>1067.6</td>
<td>1492.3</td>
<td>1252.94</td>
<td>1099.68</td>
</tr>
<tr>
<td></td>
<td>$D_{\nu_0}$</td>
<td>1936.57</td>
<td>2039.55</td>
<td>2042.91</td>
<td>2099.72</td>
</tr>
<tr>
<td>Se$^{80}O_2^+$</td>
<td>$D$</td>
<td>1.35906</td>
<td>1.6346</td>
<td>1.9142</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\nu_0$</td>
<td>1551.67</td>
<td>1694.39</td>
<td>1240.86</td>
<td>1095.98</td>
</tr>
<tr>
<td></td>
<td>$D_{\nu_0}$</td>
<td>2035.1</td>
<td>2080.95</td>
<td>2041.38</td>
<td>2097.93</td>
</tr>
<tr>
<td>Se$^{78}O_2^{10}$</td>
<td>$D$</td>
<td>1.34075</td>
<td>1.6155</td>
<td>1.8375</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\nu_0$</td>
<td>1784.37</td>
<td>1416.95</td>
<td>1197.75</td>
<td>1051.3</td>
</tr>
<tr>
<td></td>
<td>$D_{\nu_0}$</td>
<td>1979.1</td>
<td>1899.77</td>
<td>1932.53</td>
<td>1934.3</td>
</tr>
</tbody>
</table>
Figure 9.9 The effect of the parameter $p$ on the shape of the double-minimum potential. After $p = 0.9$ and $p = 1.9$, the minima are parabolic.
Figure 36 The double minimum potential in the antisymmetric stretching coordinate of the $^3B_2$ excited state of $\text{SO}_2$. The value of $C(\phi^*) = 0.97$ cm$^{-1}$ and the barrier height is 1906.6 cm$^{-1}$. 
along \( Q_3 \) there are small changes along \( Q_1 \) and \( Q_2 \) as well. Small differences in the barrier height are therefore expected since the normal co-ordinates are slightly different for all three isotopes and may be involved to different extents in each isotope in the motion which converts one isodynamic structure of selenium dioxide into the other.

The selenium dioxide molecule is the first molecule in which it has been possible to experimentally observe transitions to the \( 5^1_0 \) (0\(^-\)) and \( 3^3_0 \) (1\(^-\)) levels. It is felt that this observation is strong evidence for the existence of a double-minima potential in the \( Q_3 \) co-ordinate of \( \text{SeO}_2 \). The 78 cm\(^{-1}\) interval between the \( 1^0_2 - 1^2_3 \) and \( 1^0_2 - 1^0_3 \) bands of the \( \text{Se}^{78}\text{O}_2 \) molecule is shown in Figure 3.7.

Both the \( 5^1_0 \) and \( 3^3_0 \) vibronic bands have a noticeably different band profile from all other bands in the spectrum. The transition to the level \( v_3 = 1 \) originating on the four levels \( 0^0_0, 1^0_2, 1^0_3 \) and \( 1^0_3 \) in all cases show a very sharp line-like head which is the most prominent feature of the band. The sub-band structure (K-structure) is very irregular and it is difficult to unambiguously assign the various sub-bands. This is in direct contrast to all of the other bands in the spectrum where the quadratic nature of the sub-bands is quite distinct, and as many as fifteen sub-bands can be easily assigned. The rotational structure of the \( 5^1_0 \) vibronic band is discussed in detail in Chapter Four.

The \( 3^3_0 \) vibronic band is also quite different in band profile to the other vibronic bands in the spectrum. The band contains fewer sub-bands and unlike all of the other bands in the spectrum which are strongly red degraded, the \( 3^3_0 \) vibronic band lacks a head.

The \( 3^3_0 \) and \( 3^3_1 \) bands are expected to be almost co-incident. Due to the extended Franck-Condon maximum in the excited state \( v_1 \) progression (sixth
member), the $3^2_0$ band is not likely to be observed and the observed headless band is probably the pure $3^3_0$ band.

Since the $3^3_0$ band is expected to be a B-type band whereas the $3^2_0$ band is A-type, then no Fermi resonance can occur between the upper levels of those transitions, and the headless feature of the $3^3_0$ band cannot be attributed to a Fermi resonance since both levels must be of the same symmetry for such a perturbation to occur.

The band profile could however be altered due to a Coriolis-type perturbation involving the $3^3_0$ and the $3^2_0$ levels. The selection rule for Coriolis-type perturbations between vibronic levels has been given by Jahn\textsuperscript{70}. An interaction can occur only if the direct product for the irreducible representations to which the two vibrational wavefunctions belong transform or has a component that transforms like a rotation. Since the direct product

$$
\Gamma^3_0 \times \Gamma^2_0 = \Gamma^2_2 \times \Gamma^1_2 = \Gamma^2_2
$$

then a Coriolis perturbation can occur between these levels as a result of rotation about the c-axis of the molecule, perpendicular to the molecular plane. It is difficult to know to what extent Coriolis perturbations have altered the rotational structure of the $3^3_0$ vibronic band. It is doubtful that the Coriolis perturbation alone is responsible for the headless feature of the band.

The asymmetric stretching vibration of ScO$_2$ is an in-plane vibration of $B_2$ symmetry and therefore odd quanta of this vibration are forbidden in the zeroth order Born-Oppenheimer approximation and should not appear in the spectrum. The $3^1_0$ ($v_3^1$) and $3^3_0$ ($5v_3^1$) bands however appear in the spectrum and are reasonably strong bands.

The antisymmetric stretching co-ordinate of the excited $1B_2$ electronic
Figure 3.7

2nd order Bausch & Lomb photograph of the $1_2^0$ and $1_3^0$ bands of $\text{Se}^7\text{O}_2^{16}$ showing the $1_23_1^0$ and $1_33_1^0$ bands 78 cm$^{-1}$ to the blue. The $1_22_1^0$ and $1_22_2^0$ vibronic bands are also shown.
state is believed to have a double-minimum potential well, the barrier to
inversion being \( \approx 2000 \text{ cm}^{-1} \) \((\alpha \approx 0.6)\). The \( v_3^1 = 1 (0^-) \) level is very close
to the bottom of the well \((78 \text{ cm}^{-1}) \) and therefore when the \( \text{SeO}_2 \) molecule is
in this vibronic level it will tunnel from one asymmetric structure to the
other with only low probability. In fact, when the molecule is in the \( \tilde{3}_0^1 \)
\((0^-) \) vibronic level, it effectively has an equilibrium asymmetric structure
with one bond length longer than the other. The symmetry of the molecule is
therefore reduced from \( C_{2v} \) to \( C_5 \). Under \( C_5 \) symmetry both the \( A_1 \) and \( B_2 \)
vibrations become \( A' \) and transitions from the vibrationless level in the
ground state to the \( 0^+ \) and \( 0^- \) levels of \( Q^3_3 \) in the excited state are allowed
and expected to have comparable intensity. Transitions to both the \( 0^+ \) and \( 0^- \)
levels of the excited state are experimentally observed with almost identical
intensity.

The \( 3_0^1 \) vibronic band is also allowed under \( C_{2v} \) symmetry when in a higher
approximation it is considered how nuclear displacements affect the interactions
between electronic states. Herzberg and Teller \(^{17} \) have shown that when vibronic
coupling is important the electronic and vibrational motions cannot be considered
independent and the vibronic transition moment which now must be non-zero takes
the form

\[
\langle \psi' | \phi' | (r, Q) | \overline{\phi} | \psi'' | (r, Q) \rangle \neq 0 \tag{3.13}
\]

where the product \( \phi(r, Q) \overline{\phi}(Q) \) is the vibronic wave function and \( r \) and \( Q \) are the
electronic and nuclear co-ordinates respectively. \( \overline{\phi} \) is the electric dipole
operator.

In order for the integral of Equation (3.13) to be non-zero, the
following direct product must be totally symmetric

\[
\Gamma_0^0 \phi' \times \Gamma_0 \phi'' = \Gamma A_1 \tag{3.14}
\]
Since the ground state is totally symmetric and the excited state has been shown to be electronically of $B_2$ symmetry, then (3.14) becomes

$$B_2 \times B_2 \times \Gamma \times A_1 \times A_1 = A_1 \quad (3.15)$$

and Equation (3.15) will be non-zero if there is a component of the dipole operator $\tilde{r}$ which transforms as $A_1$. Since the component of $\tilde{r}$ along the b-axis passing through the selenium atom is of $A_1$ symmetry, then Equation (3.15) is non-zero and the $3_0^1$ transition is therefore vibronically allowed; the intensity is said to be "stolen" or "borrowed" from an allowed $1A_1 \rightarrow 1A_1 \tilde{r}$ electronic transition with the $3_0^1$ band then having the polarization of the transition from which the intensity derives. Therefore the $3_0^1$ band is expected to be a perpendicular type-B band in $C_{2v}$ symmetry approximation.

If the intensity derives from a change in selection rules resulting from a reduction in symmetry ($C_{2v} \rightarrow C_5$) rather than through a vibronic mechanism, then the $3_0^1$ band is expected to be an A-B hybrid type band consisting of a superposition of a parallel type-A and perpendicular type-B band. The intensity of each band type will be determined by the direction of the electric dipole with respect to the a and b axes of the molecule. The rotational structure of the $3_0^1$ band will be discussed later in Chapter Four.

The $3_0^3 (1^7)$ level lies above the barrier to inversion and therefore when the molecule is in the $3_0^3$ vibronic level it can classically move freely from one asymmetric structure to the other. The equilibrium structure is symmetric and the electronic and vibrational wave functions must be classified under $C_{2v}$ symmetry. The only mechanism by which the $3_0^3$ band can then acquire intensity is the vibronic one, and the band is expected to be B-type. All

---

A rotational analysis of the $1_0^5$ vibronic band has shown this band to be A-type and therefore the excited electronic state to be of $B_2$ symmetry.
that can be said with regards to the experimentally observed $3_0$ band is that it is headless and in no way resembles the band profile of A-type bands which have a head and are strongly red degraded. If the intensity of the $3_0^2$ transition is borrowed from another allowed electronic transition, then one might expect to see an intensity alternation between the even and odd numbers of the $3_0^n$ progression. This is not apparent and is perhaps due to overlap with adjacent bands.

The interval of 78 cm$^{-1}$ which has been assigned to the ($0^+ - 0^-$) splitting was also tried as an assignment for the ($0^- - 1^+$) splitting, it being concurrently assumed that the ($0^+ - 0^-$) splitting was too small to be resolved experimentally. The above assumption results in an extremely high barrier (a consequence of the small ($0^+ - 0^-$) splitting). An extremely high barrier height would be inconsistent with the observed spectrum since the perturbation is obvious, as manifested in the abnormally high intensity of the $3_0^2$ and $3_0^3$ vibronic bands. For this reason the assignment of the 78 cm$^{-1}$ interval to the ($0^- - 1^+$) splitting was rejected.

The presence of a double minimum potential, with the relatively low barrier height of 2000 cm$^{-1}$ in the asymmetric stretching vibrational coordinate of the excited state of SeO$_2$ suggests that the molecule is non-rigid in the excited state and as such should be classified according to a non-rigid point group. A brief discussion of isodynamic operations, and the Schrödinger super group with respect to SeO$_2$ is given below. For an excellent account of non-rigid point groups, the reader is referred to articles by Altman and Longuet-Higgins where the basic principles are presented and applied to several non-rigid molecules.


Non-rigid molecules are those for which there are several equilibrium
configurations that cannot be transformed one into another by a Schrödinger group operation (reflection or rotation) but have, nevertheless, identical energies. Such configurations are called isodynamic configurations, and the operations that transform one isodynamic structure into another are called isodynamic operations. They are not symmetry operations, but rather motions (translations or rotations) of an atom or group of atoms with respect to the rest of the molecule. Isodynamic operations involve the displacement of material points, and are denoted by a superscript I added to the conventional symmetry operations.

The symmetry groups of non-rigid molecules possess, therefore, two subgroups: one is that of all the symmetry operations of the Schrödinger group (rotations and reflections) and the other is the Isodynamic group, containing all of the isodynamic operations belonging to the molecule.

Therefore for non-rigid molecules the familiar interpretation of symmetry operations breaks down and an entirely new system of operations is necessary. They are constructed as follows: \( E, E^0 \) and \( P \) are respectively the identity operation, the inversion of all particle positions and a permutation of the position and spins of identical nuclei. \( P^0 \) is the product \( E^0 P = P E^0 \). Any of these operations is feasible when it can be achieved without passing over an insurmountable energy barrier. The molecular symmetry group is then the set of all feasible \( P \) (including \( E \)), and all feasible \( P^0 \).

The two isodynamic structures of \( \text{SeO}_2 \) of importance in the present analysis result from the asymmetric vibrational motion of the molecule in the \( ^1\text{B}_2 \) excited state, and are shown in Figure 3.9.

The two isodynamic structures in Figure 3.8 occur in the \( \text{SeO}_2 \) molecule as a result of the asymmetric vibrational motion shown below in Figure 3.9.

In going from structure (a) to (b) in Figure 3.9, the Se atom moves
Figure 3.8: The isodynamic operation \((\alpha')^{T}\), which is a displacement of the \(3\theta\) atom perpendicularly to the \(xy\) plane, into its reflected position with respect to it. The \(y\) axis is directed perpendicular to the plane of the paper. (Apted Altman)

Figure 3.9: Asymmetrical vibrational motion of \(3\theta\).
across a potential well with a minimum where it crosses the x axis. The splitting of the levels in the double-minimum potential well depends on the magnitude of the perturbation matrix element $\int \phi_d H' \phi_d \, dr$ where the perturbation term $H'$ is small if the depth of the well is large. An alternate way of viewing the perturbation is in terms of the barrier height separating the two isodynamic structures. The lower the barrier height the stronger the perturbation and consequently the greater will be the splitting of the levels in the well. The isodynamic operation $(a^\dagger)$ may be thought therefore as a tunnelling through the potential barrier separating the two configurations of Figure 5.8.

3.13. Quasilinear Molecules

Quasilinearity has been treated theoretically by Thorson and Nakagawa in an explanation of the infrared spectrum of disiloxane and in triatomic molecules by Dixon and Johns. The mathematical treatment of these authors involves the solution of the two-dimensional harmonic oscillator which is perturbed by a potential hump. The effect of the perturbation is that, for the lower vibrational levels, the molecule is stable in the bent conformation while in the higher vibrational levels the molecule is stable in the linear conformation. Both Johns and Dixon considered only the vibrational motion involving $v_2$ in a quasilinear electronic state. Quasilinearity as described above is then only important in linear to bent or bent to linear transitions involving long progressions of the upper state bending frequency $v_2$.

In the present analysis of the $\text{SeO}_2$ molecule, the prominent frequency in the spectrum is the upper state symmetric stretching frequency while $v_2$ appears only in combination with $v_1$ and $v_3$. However, the molecule becomes more bent in the excited state at equilibrium, with a bond angle of $2\theta = 101^\circ$.

*Present rotational analysis of the $1\tilde{a}$ vibrionic band.*
compared to be value of $2\alpha = 113.8^\circ$ observed in the ground state. For this reason quasilinearity was not considered important in the present work.


The missing piece to the puzzle in the present analysis was the assignment of the 32033.0 cm$^{-1}$ band to the $3^1_0$ transition. The observed intensities of both the $0^0_0$ and $3^1_0$ band are about the same, as is expected since in $C_s$ symmetry (equilibrium symmetry of the excited state in this vibronic level), both the $0^0_0$ and $3^1_0$ ($0^0_0$) levels are of $A'$ symmetry and thus transitions from the vibrationless level of the ground state are electronically allowed to each of these vibronic levels of the excited state. Transitions from ground state $v_1^i$ levels to $v_3^i$ levels of the excited state are shown in Figure 3.10. The vibrational and vibronic symmetry of the levels is also shown.

Progressions in both the excited state symmetric and antisymmetric stretching frequencies appear in the spectrum. The longest progressions involve $v_1^i$ and contain as many as thirteen members. A progression of four members involving $v_2^i$ is observed. The enormous intensity of the higher members in the $v_2^i$ progression results from the presence of a double-minimum potential well along $Q_3$. The excited state bending frequency $v_2^i$ appears in the spectrum only in combination with $v_1^i$ and $v_3^i$. There was considered, however, an alternate assignment to the $v_2^i$ progression in the present analysis which involves the assignment of a $v_2^i$ progression containing six members.

Both assignments will be discussed briefly.

In the present analysis $v_1^i = 669$ cm$^{-1}$ and $v_2^i = 239$ cm$^{-1}$ while $v_3^i = 923$ cm$^{-1}$. Therefore, on the basis of an observed 239 cm$^{-1}$ interval between successive bands, it is very difficult to distinguish between a $v_2^i$
Figure 3.10: Transitions from the ground state totally symmetric vibrational levels $v_0$ to the excited state asymmetric vibrational levels $v_3$. The transitions shown are observed experimentally.
progression and a group of sequence bands of the type \( \nu_n^D = n(923-660) = n\text{260} \).

In the spectrum of the \( \text{So}^{78}\text{O}_2^{16} \) isotope, eight vibronic bands are
observed with the energies shown below. The two possible assignments con-
sidered are also shown.

<table>
<thead>
<tr>
<th>Position</th>
<th>( \text{cm}^{-1} )</th>
<th>( \Delta \text{ cm}^{-1} )</th>
<th>Assignment 1</th>
<th>Assignment 2</th>
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</thead>
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<td>262_1</td>
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<tr>
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<tr>
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<td></td>
<td>324_7</td>
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</tr>
</tbody>
</table>

Assignments Two above has the following serious difficulty. The higher

members in the \( \nu_2 \) progression show a reasonably constant interval of approx-

imately \( 262 \text{ cm}^{-1} \). However the interval between the \( 2^1_0 \) and the \( 0^0_0 \) band is not

\( 262 \text{ cm}^{-1} \) but rather \( 322 \text{ cm}^{-1} \). To account for this abnormally high interval it

could be postulated that perhaps the above progression in \( \nu_2 \) was in fact a pro-

gression in combination with one quantum of \( \nu_3 \), i.e., \( 2^1_0 \text{3}^0_0 \), \( n = 0, 1, \ldots, 6 \). How-

ever, the interval between the origin band and the \( 2^1_0 \text{3}^0_0 \) band is not

\( 262 \times 78 = 340 \text{ cm}^{-1} \) but only \( 322 \text{ cm}^{-1} \). The barrier height to inversion along

\( \nu_3 \) between the two asymmetric structures is expected to be a function of the

bond angle \( 2\alpha \), and consequently the \( (0^0_0 - 0^0_0) \) splitting is a function of the

bond angle. The hypothesis was then made that in fact the interval of \( 322 \text{ cm}^{-1} \)
could be associated with the combination band \( 2^1_0 \text{3}^0_0 = 262 \times 60 = 322 \text{ cm}^{-1} \). The

interaction between \( Q_2^0 \) and \( Q_3^0 \) was considered responsible for reducing the
(0^+ - 0^-) splitting in Q' from 78 cm^{-1} to 60 cm^{-1}. If in fact this hypothesis is correct, then a very serious problem results. Why does the (0^+ - 0^-) interval remain constant when additional quanta of v_2 are excited? Since excitation of successive quanta of v_2 increases the angular displacement of the oxygen atoms, it seems unreasonable to assume that Q_3 should be sensitive to the first quantum of v_2 excited yet almost completely insensitive to excitation of additional quanta of v_2. For this reason Assignment Two was discarded.

Assignment One removes the above problem. The band located at 33327.6 cm^{-1} is assigned to the 3^0 transition. This assignment is also strongly suggested by the fact that there is a strong v_1 progression which extrapolates to this band as a false origin, i.e., 3^01^0 progression. It is otherwise impossible to satisfactorily assign a false origin for this progression. The vibronic band located at 33594.5 is then easily assigned as 5^22^0.

The four bands to the red of the 3^0 band located at 33066.2 cm^{-1}, 32801.3 cm^{-1}, 32539.2 cm^{-1} and 32277.1 cm^{-1} are assigned to the four sequence bands 3^01^1, 3^01^2, 3^01^3 and 3^01^5 respectively. This seems a reasonable assignment since v_1 is by far the most active frequency in both the hot and the cold spectrum. In addition the three sequence bands 1^1, 1^2 and 1^3 appear strongly in the spectrum. The 1^0 band may appear weakly but lies in a region that is both weak and strongly overlapped by the 302 spectrum.

The 3^0 transition is not observed but is thought to occur around 35039 cm^{-1} from extrapolation of the 1^02^0 progression to its origin. It was not possible to observe the 5^0, 3^0 or higher members in the v_3 progression. This is probably a result of the intense members of the 1^0, 1^22^0 and 1^02^0 progression which fall in the same region as where the 3^0 and 3^0 bands are expected to appear.

The 1^D_2 + 1^A_1 electronic transition extends from approximately 28000
to 45000 cm\(^{-1}\), the origin for the transition occurring at 31955 cm\(^{-1}\). The bands in the region of the origin band are weak and badly overlapped. Vibronic bands appearing in the region 35500 cm\(^{-1}\) to 33900 cm\(^{-1}\) are sharp and red degraded. The sub-bands (K-structure) are sharp and distinct.

Bands to the blue of 35500 cm\(^{-1}\) become progressively more diffuse with the distinct rotational fine structure now becoming smeared and the individual sub-bands no longer distinguishable. It appears as if the \(^1\mathbf{B}_2\) excited state of \(\text{SeO}_2\) is being prodissociated in the region to the blue of 36000 cm\(^{-1}\) by another electronic state. It is also possible that the \(^1\mathbf{B}_2\) electronic state is itself becoming dissociative to the blue of 36000 cm\(^{-1}\) thus accounting for the diffuse bands in this region.

The most striking features of the hot spectrum (to the red of the origin band) are the sets of paired sequence bands \(1^0, 1^0_{00}; 1^2, 1^2_{00}; \) and \(1^0, 1^0_{30};\) The intensity of members in the same set are about equal. The quanta of the ground state bending vibration \(v_2 = 372 \text{ cm}^{-1}\) are also observed in the hot spectrum and originate on the \(0^0_0, 1^0_1, 1^0_2\) and \(1^0_3\) vibronic levels. Regions of the hot band spectrum are weak and badly overlapped due to the co-incidental overlap of these bands with members of excited state \(v_1\) progression originating on the \(1^1_0, 1^1_2\) and \(1^1_3\) vibronic levels.

### 3.15. Fluctuations in Excited State \(v_1\) Progressions

The most prominent frequency in the spectrum is the excited state totally symmetric stretching frequency \(v_1 = 660 \text{ cm}^{-1}\) and appears most strongly in the three progressions \(1^1_{00}, 1^1_{02}^1, \text{ and } 1^1_{02}^2\). The \(v_1\) interval of 660 cm\(^{-1}\) appears to randomly fluctuate \(\pm 10 \text{ cm}^{-1}\) in all three progressions.

Since \(v_1 = 660 \text{ cm}^{-1}\), \(v_2 = 280 \text{ cm}^{-1}\) and \(v_1 = 923 \text{ cm}^{-1}\), therefore \(v_1 = v_2 = v_1\) and the odd member of the \(1^0\) progression can be in Fermi resonance.
with the \((m+1)\)th member of the \(1_{1}^{n+1}\) progression. Similarly, the \(m\)th member of the \(1_{2}^{n+1}\) progression can interact strongly with the \((m+1)\)th member of the \(1_{2}^{n+2}\) progression. Also the \(m\)th member of the \(1_{0}^{n}\) progression is expected to fall very close to the \((m+2)\)th member of the \(1_{2}^{n+2}\) progression.

Many of the bands in the \(1_{0}^{n}\), \(1_{2}^{n+1}\) and \(1_{2}^{n+2}\) progressions appear to be double-headed. The two heads however belong to separate vibronic bands resulting from the coincidental overlap of members in other progressions as a result of the fact that \(v_1 + v_2 \sim v_1''\).

The rotational fine structure (K-structure) of all the resolvable bands in the \(1_{0}^{n}\), \(1_{2}^{n+1}\) and \(1_{2}^{n+2}\) progressions was also measured and the head to origin distance compared. This separation was found to randomly fluctuate. Since it is the frequencies of the heads of the bands which were used in the vibrational analysis, then the small changes (2-3 cm\(^{-1}\)) in the head to origin separation might well also be partly responsible for the small fluctuation in the \(v_1\) interval observed in those progressions.

III. An Anomalously Large Frequency Difference

The two vibronic bands located at 35010.3 cm\(^{-1}\) and 34506.5 cm\(^{-1}\) have a separation of 703.9 cm\(^{-1}\) and have been assigned to the \(1_{1}^{5}\) and \(1_{1}^{6}\) transitions. The observed interval is considerably larger than the expected interval of 660 cm\(^{-1}\). The assignment is based on the fact that the earlier members in the \(1_{1}^{n}\) progression are also observed but with the correct interval of ~660 cm\(^{-1}\). Since the strongest members in the \(1_{0}^{n}\) progression are the 5th and 6th, the two corresponding sequence bands \(1_{1}^{5}\) and \(1_{1}^{6}\) are expected to appear and not probably be the strongest members in the \(1_{1}^{n}\) progression. The separation between these two bands is anomalously large in all three isotopic molecules studied and therefore cannot be attributed to a perturbation of the Fermi
resonance type.

Since the intensity of both bands is comparable to that of the intense members in the $l_0^\text{n}$ progression, it is unlikely that they could originate from higher ground state levels than in the present assignment.

An alternate assignment for the $l_1^5$ band is $3^2_02^1_0$; however, this band would then be expected to be a B-type band. The observed band is unfortunately identical in structure to the $l_0^3$ band which rotational band contour analysis has conclusively shown to be A-type. An alternate assignment for these bands consistent with their observed intensity is not obvious.
CHAPTER FOUR

ROTATIONAL ANALYSIS OF SELENIUM DIOXIDE

4.1. Moments of Inertia

The moments of inertia of a rigid molecule about each of the three axes passing through the center of mass are defined by

\[I_x = \sum_i P_i (y_i^2 + z_i^2)\]
\[I_y = \sum_i P_i (x_i^2 + z_i^2)\]  \hspace{1cm} (4.1)
\[I_z = \sum_i P_i (x_i^2 + y_i^2)\]

where \((x_i, y_i, z_i)\) are the co-ordinates of the \(i\)th atom with mass \(P_i\).

If we define the products of inertia by the equations

\[I_{xy} = \sum_i P_i x_i y_i\]
\[I_{yz} = \sum_i P_i y_i z_i\]  \hspace{1cm} (4.2)
\[I_{xz} = \sum_i P_i x_i z_i\]

with \(I_{xy} = I_{yx}\), etc., then the equation

\[I_x x^2 + I_y y^2 + I_z z^2 - 2I_{xy} xy - 2I_{yz} yz - 2I_{xz} xz = 1\]  \hspace{1cm} (4.3)

represents a quadratic surface, called the \(\text{mm}\)mental ellipsoid. The ellipsoid itself has three axes, \(a\), \(b\) and \(c\), called the principal axes of the \(\text{mm}\)mental ellipsoid. In terms of these axes the ellipsoid is given by

\[I_a a^2 + I_b b^2 + I_c c^2 = 1\]  \hspace{1cm} (4.4)

in which the products of inertia have vanished. The three principal axes are chosen such that the moments of inertia about them have the order of magnitude \(I_c > I_b > I_a\).
The moments of inertia in the principal axes system in which the products of inertia are zero are obtained by solving the determinantal equation:

\[
\begin{vmatrix}
I_{xx} - \lambda & -I_{xy} & -I_{xz} \\
-I_{xy} & I_{yy} - \lambda & -I_{yz} \\
-I_{xz} & -I_{yz} & I_{zz} - \lambda
\end{vmatrix} = 0
\]  

(4.5)

We, therefore, wish to find the transformation matrix \( S \) relating the arbitrary axes \((x, yz)\) and the principal axes \((a, b, c)\). The transformation matrix \( S \) can then be used to diagonalize the matrix \( \Lambda \), formed from the coefficients in Equation (4.5), by means of the similarity transformation \( S^{-1}\Lambda S = \Lambda \). The diagonal matrix \( \Lambda \) will have the form

\[
\begin{pmatrix}
I_a \\
I_b \\
I_c
\end{pmatrix}
\]  

(4.6)

and contains as its elements the required coefficients in Equation (4.4).

Molecules are classified according to the relative magnitude of their principal moments of inertia in the following way:

i) \( I_a = I_b = I_c \) - spherical top

ii) \( I_a = 0 \) \( I_b = I_c \) - linear (symmetric top)

iii) \( I_a < I_b = I_c \) - prolate symmetric top

iv) \( I_a = I_b > I_c \) - oblate symmetric top

v) \( I_a < I_b < I_c \) - asymmetric top

\( \text{ScO}_2 \), shown in Figure 4.1, is a bent triatomic molecule with all three moments of inertia different, and so such is classified as an asymmetric top molecule.

There is, however, a particular value of the angle \( 2\alpha = 2\beta \), given by
Figure 4.1  SO$_2$ molecule, showing the directions of the principal moments of inertia.
Equation 4.7 for which $I_a = I_b = \frac{1}{2} I_c$, in which case the molecule is an accidental oblate symmetric top and as such will display all of the physical features of a true symmetric top molecule.

$$\tan \alpha_S = \sqrt{\frac{N_{Se}}{N_{Se} + Z_0}}$$  \hspace{1cm} (4.7)

A value of $2\alpha_S = 84.8^\circ$ is the angle for which the ScO$_2$ molecule is an accidental oblate symmetric top. From recent microwave studies of ScO$_2$ by Takeo et al., the ground state bond angle was determined to be $2\alpha = 115^\circ 50'$. The degree of asymmetry of an asymmetric top molecule is commonly determined by a dimensionless parameter $\kappa$ (kappa) given by

$$\kappa = \frac{2B - A - C}{A - C} \hspace{1cm} -1 \leq \kappa \leq +1$$  \hspace{1cm} (4.8)

which in the prolate limit ($B = C$) has the limiting value $-1$, while in the oblate symmetric top limit ($A = B$), $\kappa = +1$. In the ground state of ScO$_2$ $\kappa = -0.81$, which is sufficiently close to $-1$, that ScO$_2$ might be expected to behave as a near prolate symmetric top. From the present rotational analysis of the $B$ system of ScO$_2$ the excited state bond angle has been found to have the value $2\alpha = 101^\circ$. The molecule is, therefore, a stronger asymmetric top ($\alpha = 0.53\alpha$) in the excited state, than in the ground electronic state.

4.2. Rotational Structure of Parallel and Perpendicular Electronic Transitions

The rotational energy levels of a prolate symmetric top are given by

$$F_y (J, K) = B_y J (J + 1) + (A_y - B_y) K^2$$  \hspace{1cm} (4.9)

where $J$ is the total angular momentum and $K$ the component of the total angular
momentum about the top axis. $A_v = \hbar^2/2I_o$ and $B_v = \hbar^2/2I_b$ are the rotational constants of the $v$th vibrational level in $\text{cm}^{-1}$.

The selection rules governing the allowed rotational transitions accompanying a vibronic transition are determined by the polarization of the electronic transition. If the change of the dipole moment of the electronic transition is parallel to the top axis (parallel band), we have the following selection rules\(^8\) for the quantum numbers $J$ and $K$,

$$\Delta K = 0, \quad \Delta J = 0, \pm 1 \quad \text{if } K \neq 0$$

$$\Delta K = 0, \quad \Delta J = \pm 1 \quad \text{if } K = 0 \quad (4.10)$$

and if the transition is perpendicular to the top axis (perpendicular band) we have

$$\Delta K = \pm 1, \quad \Delta J = 0, \pm 1 \quad (4.11)$$

The top axis in ScO$_2$ is the $a$-axis in Figure 4.1. The symmetry in the $C_{2v}$ point group and classification of the possible electronic transitions as to parallel or perpendicular is given in Table 4.1. The co-ordinate system used for the polarizations given is that shown in Figure 4.1.

Table 4.1

<table>
<thead>
<tr>
<th>Symmetry of Excited State</th>
<th>Polarization of Transition</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$y$</td>
<td>perpendicular</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$z$</td>
<td>perpendicular</td>
</tr>
<tr>
<td>$B_3$</td>
<td>$x$</td>
<td>parallel</td>
</tr>
<tr>
<td>$D_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
For an asymmetric top the quantum number $K$ is not strictly defined but for a molecule such as ScO$_2$ which is nearly a prolate symmetric top, we may expect the selection rules $\Delta K_p = 0$ and $\Delta K_p = \pm 1$ to apply to parallel and perpendicular transitions respectively. $K_p$ then gives the component of the total angular momentum along the "pseudo" unique axis of the near prolate symmetric top. For parallel bands it follows from Equation (4.9) that

$$v = v_o + B_1 J'(J'^{+}1) - B_2 J''(J''^{+}1) + [(A' - B') - (A'' - B'')] K_p^2$$  \hspace{1cm} (4.12)

while for perpendicular transitions

$$v = v_o + B_1 J'(J'^{+}1) - B_2 J''(J''^{+}1) + (A' - B') K_p + [(A' - B') - (A'' - B'')] K_p^2$$  \hspace{1cm} (4.13)

where the primes and double primes refer to the excited and ground state respectively, $K_p$ is the ground state value, and $B = \frac{1}{2}(B - C)$.

The formulae for a perpendicular transition given by Equation (4.13) is to be used with the (+) sign in the linear term for an $r$ branch ($\Delta K_p = +1$) and with a (-) sign for a $p$ branch ($\Delta K_p = -1$). However, both the $r$ and $p$ branch together may be represented by a single equation of the form

$$v = v_o + B_1 J'(J'^{+}1) - B_2 J''(J''^{+}1) - \frac{1}{2}(A' - B') - (A'' - B'') K_p$$

$$+ [(A' - B') + (A'' - B'')] K_p + [(A' - B') - (A'' - B'')] K_p^2$$  \hspace{1cm} (4.14)

where $K$ is a convenient index number with the value $K = K_p + \frac{1}{2}$ for the $r$ branch ($\Delta K_p = +1$) and $K = -K_p + \frac{1}{2}$ for the $p$ branch ($\Delta K_p = -1$).

We may speak of $K$-structure and $J$-structure when discussing the rotational fine structure of vibrational bands. It is convenient to think of $K$ and $J$ structure in terms of sub-bands. A sub-band in the $K$ structure corresponds to the set of rotational transitions for a fixed $K''$ and $\Delta K_p$ but differing values of $J''$ and $\Delta J$ in Equations (4.12), (4.13) and (4.14). Each sub-band (constant $K_p$) is then expected to contain a $P$, $Q$ and $R$ branch.
corresponding to \( J = -1, 0, 1 \), respectively. The total rotational fine structure of a vibronic band is then the sum of all the sub-bands of differing \( K_p \). Usually the distance between lines is much smaller in the \( J \)-structure than in the \( K \)-structure and we may therefore regard the set of transitions with \( J = 0, K_p = 0, 1, 2, \ldots, n \) in Equations (4.12), (4.13) and (4.14) as giving the positions of sub-band origins in the vibronic band.

From Equations (4.12), (4.13) and (4.14), levels which differ only in the sign of \( K_p \) have the same energy and are therefore degenerate. In passing from a symmetric to an asymmetric top, the molecule no longer possesses a unique axis (i.e., an axis about which a component of angular momentum is conserved). The \( K \) degeneracy is removed (\( K \)-type doubling) and for each value of \( J \) there are \( 2J+1 \) different energy levels. The quantum number \( K \) is no longer defined for an asymmetric top. The \( 2J+1 \) components for each value of \( J \) are for convenience designated by a subscript \( \tau \) added to \( J \) such that \( \tau \) takes the values

\[
\tau = -J, -J+1, -J+2, \ldots, J
\]  

(4.15)

Unlike symmetric top molecules, the energy levels of an asymmetric top molecule cannot be represented by a single quantitative formula. For a discussion of the energy levels of asymmetric tops, the reader is referred to Herzberg.

4.3. Rotational Selection Rules for Asymmetric Top Molecules

Then the molecule is a strongly asymmetric top, the selection rule \( \Delta K = 0, \pm 1 \) is no longer valid since \( K \) is no longer a good quantum number. Rather we must now apply the general selection rules for \( K_a \) and \( K_c \) developed by Gross, Källner and King. \( K_a \) and \( K_c \) are the quantum numbers for rotation about the \( a \) and \( c \) axes in the limiting cases of prolate and oblate symmetric tops respectively. The correlation of the asymmetric top rotational levels
with those of the prolate and oblate symmetric top limits is shown in Figure 4.2. For $K_a$ and $K_c$ we have the following selection rules.\(^{90}\)

If the transition moment is in the $a$-axis

$$\Delta K_a = 0, \pm 2, \ldots$$

if the transition moment is in the $b$-axis

$$\Delta K_b = \pm 1, \pm 3, \ldots$$

and if the transition moment is in the $c$-axis

$$\Delta K_c = \pm 1, \pm 3, \ldots$$

(4.16) (4.17) (4.18)

An alternate way of stating these selection rules is in terms of the parity of the rotational levels. Only the following transitions may occur.\(^{82}\)

If the transition moment is in the $a$-axis

$$++ \leftrightarrow --$$

and

$$-- \leftrightarrow +-$$

(4.19)

if the transition moment is in the $b$-axis

$$++ \leftrightarrow --$$

and

$$-- \leftrightarrow +-$$

(4.20)

and if the transition moment is in the $c$-axis

$$++ \leftrightarrow --$$

and

$$-- \leftrightarrow +-$$

(4.21)

In order to designate the various branches for the rotational structure of an asymmetric top, we require two superscripts to be added to the usual $P$, $Q$, $R$ symbols (which give the $\Delta J$ value for the transition). The first of these superscripts indicates $\Delta K_a$, the second the $\Delta K_c$ value. The $B \leftrightarrow X$ transition of $\text{SO}_2$ is shown in the present work to be a parallel transition with the transition moment polarized along the $a$-axis of the molecule. The excited electronic state is therefore of $C_2$ symmetry. In accordance with the selection rules given by Equations (4.16) and (4.19) the following branches may occur in an $A$-type band of an asymmetric top such as $\text{SO}_2$. 

...
with similar Q and P branches.

The principal sub-branches of the asymmetric rotor are those for which both \( \Delta K_a \) and \( \Delta K_c \) change by 0 or \( \pm 1 \), since they become the p, q and r branches in both the prolate and oblate symmetric limiting cases\(^{90}\). Branches which correspond to forbidden transitions in the limiting prolate and oblate symmetric tops will not be considered in this discussion. The reader is referred to Cross, Hainer and King\(^{90}\) for further discussion of these forbidden branches.

In the general case of the asymmetric rotor for a transition parallel to the a-axis, \( \Delta K_a = 0, \pm 2, \pm 4, \text{ etc.} \) and \( \Delta K_c = \pm 1, \pm 3, \text{ etc.} \). However, not all combinations of \( \Delta K_a \) and \( \Delta K_c \) are possible because the sum \( K_a \pm K_c \) for each combining level is either equal to \( J \) or \( J\pm 1 \). The permitted values of \( \Delta(K_a \pm K_c) \) are given in Table 4.2.

<table>
<thead>
<tr>
<th>Parity of Initial Level</th>
<th>P</th>
<th>Q</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>even</td>
<td>-1,0</td>
<td>0,1</td>
<td>1,2</td>
</tr>
<tr>
<td>odd</td>
<td>-1,-2</td>
<td>0,-1</td>
<td>1,0</td>
</tr>
</tbody>
</table>

The symmetry of the rotational levels shown in Figure 4.2 have been determined with respect to both the rotational sub-group \( (C_2) \) after Dennison\(^{88}\) and the full molecular symmetry group \( (C_{2v}) \) after Haugon\(^{91}\).
Since rotation of $\text{ScO}_2$ by 180° about any of the three principal axes of the molecular ellipsoid leads to an orientation which has the same probability as the original orientation then the rotational wavefunction can only be multiplied by +1 or by -1 when any of the operations $C_2^a$, $C_2^b$, $C_2^c$ are carried out.

Since $C_2^b$ is always the product of $C_2^c$ and $C_2^a$, it is sufficient to designate the four symmetry species as $\leftrightarrow$, $+-$, $-\leftrightarrow$, and $-+$, where the first sign refers to the behaviour with respect to $C_2^c$ and the second with respect to $C_2^a$.

Dennison has shown that the highest level $J_{\pm J}$ for each set of a given $J$ is $+$ with respect to $C_2^c$, the next two $-$, the two next are $+$ and so on. The lowest level $J_{-J}$ of each set is $+$ with respect to $C_2^a$, the next two $-$, the next two $+$ and so on. Figure 4.2 show the result for $J = 0$ to $J = 3$ for $\text{ScO}_2$.

The symmetry of rotational wave functions with respect to the full molecular point group were determined using the methods outlined by Hougen, where reflection at a plane of symmetry is equivalent to a two-fold rotation about an axis perpendicular to that plane. The results are summarized in Table 4.3.

**Table 4.3**

| Classification of Asymmetric Rotational Levels According to $C_{2v}$ Point Group |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $C_2^c(x)$   | $C_2^a(x)$       | $C_2^b(y)$       | $\sigma_{yz}(C_2^c)$ | $\sigma_{xy}(C_2^a)$ | Symmetry  |
| $+$          | $+$              | $+$              | $+$               | $+$               | $A_1$    |
| $+$          | $+$              | $+$              | $+$               | $+$               | $D_2$    |
| $-$          | $-$              | $-$              | $+$               | $-$               | $D_1$    |
| $-$          | $-$              | $-$              | $-$               | $-$               | $A_2$    |
Figure 4.2  Correlation of asymmetric top with prolate and olate symmetric top rotational levels. The symmetry of the asymmetric rotor functions have been determined with respect to the C₆ₐ point group after Hougen.
The rovibronic symmetry of a particular level is then easily determined from the symmetry of the direct product

\[ \Gamma_{\text{VIB}} \times \Gamma_{\text{ROT}} \times \Gamma_{\text{EL}} = \Gamma_{\text{ROVIBRANIC}} \]  

(4.23)

The general selection rule for an electric dipole transition between two rovibronic states of species \( \Gamma' \) and \( \Gamma'' \) is given by \( ^90 \)

\[ \Gamma' \times \Gamma'' = \Gamma_{T_i} \times \Gamma_{R_i} \]  

(4.24)

Therefore, in order for a rovibronic transition to be dipole allowed the symmetry of the direct product of the combining states must be the same as the symmetry of a component of the direct product of a translation \( T_i \) and the corresponding rotation \( R_i \) about the \( \text{axis} \), where \( i = x, y, z \) determines the polarization of the transition. For molecules of \( C_{2v} \) symmetry (SeO₂) the three direct products \( \Gamma_{T_i} \times \Gamma_{R_i} = A_2 \). Therefore, the general rovibronic selection rule of Equation (4.24) becomes

\[ \Gamma' \times \Gamma'' = A_2 \]  

(4.25)

where \( \Gamma' \) and \( \Gamma'' \) are the rovibronic symmetry of the upper and lower state respectively.

4.4. Nuclear Statistical Weights for SeO₂

The nuclear statistical weights for each rotational level of SeO₂ are easily determined by considering the total wave function \( \psi_{\text{TOT}} \) given by

\[ \psi_{\text{TOT}} = \psi_{\text{el}} \psi_{\text{vib}} \psi_{\text{rot}} \psi_{\text{n.s.}} \]  

(4.26)

where \( \psi_{\text{el}}, \psi_{\text{vib}}, \psi_{\text{rot}}, \) and \( \psi_{\text{n.s.}} \) are the electronic, vibrational, rotational, and nuclear spin wave functions respectively. Consider the behavior of each wave function with respect to \( C_2^b \) (interchange of identical nuclei). Since the nuclear spin of \( O^{16} \) is zero, \( \psi_{n.s.} \) must be symmetric and therefore trans-
form as $A_1$. Since the nuclei have integral spin (zero in this case), they obey Bose-Einstein statistics and $\psi_{\text{TOT}}$ must be symmetric with respect to the interchange. Therefore, it follows that the rovibronic wave function $\psi_{\text{rot}} \psi_{\text{vib}} \psi_e$ must be of a symmetry.

The ground electronic state of SeO$_2$ is known to be of $A_1$ symmetry while the upper state in the B $\rightarrow$ X electronic transition has been shown to be of $B_2$ symmetry from the present work. Therefore, only the A levels of SeO$_2$ are populated in the ground state and transitions may occur to only the B levels of the $^1B_2$ excited state.

4.5. Intensity of Rotational Transitions

The intensity of a rotational transition in absorption is proportional to the product

$$ I(J,K) = C A_{KJ} \varepsilon_{KJ}^2 F(K,J) hc/kT $$

(4.27)

where $C$ is a constant independent of $K$ and $J$ but depending on the vibrational transition and which may be determined if the absolute intensity of the absorption lines has been measured. $\varepsilon_{KJ}$ and $F(K,J)$ are respectively the statistical weight and term value of the lower state and $A_{KJ}$ is proportional to the square of the transition moment $R_x^2 + R_y^2 + R_z^2$ summed over all orientations of $J$. For a parallel transition of a symmetric top ($\Delta K = 0$), Dennison has shown that $A_{KJ}$ is

for $\Delta J = +1$: $A_{KJ} = \frac{(J+1)^2 - K^2}{(J+1)(2J+1)}$ (4.28)

for $\Delta J = 0$: $A_{KJ} = \frac{K^2}{2J(2J+1)}$ (4.29)

for $\Delta J = -1$: $A_{KJ} = \frac{J^2 - K^2}{2J(2J+1)}$ (4.30)
The statistical weights $g_{KJ}$ are $2J+1$ for $K = 0$ and $2(2J+1)$ for $K \neq 0$.

The relative intensity of the P, Q and R branch in a symmetric top molecule has been determined by Tellor as a function of $I_a/I_b$ and is shown in Figure 4.3. The relative intensity distribution within the P and R branches of a sub-band is essentially determined by the population of the lower levels irrespective of $K$; the total relative intensity of the P and R branch being determined by the number of molecules in a level with a given $J$ value (summed over all $K$ values).

The intensity of lines in the Q branch is zero for $K = 0$ and increases rapidly with $K > 0$, but decreases rapidly with increasing $J$.

The ratio $I_a/I_b = 3.3$ for ScO$_2$. Therefore the intensity of the Q branch is expected to be larger than the intensity of the P and R branches. Since the band is strongly red degraded, the R branch should form a head and probably be the most prominent feature in the spectrum. The Q branch lines should also be prominent in the spectrum with the P branch possibly being too weak to observe above the background.

4.6. Rotational Analysis of $1^3$ Vibronic Band

The ground state rotational constants for ScO$_2$ have been determined by Takeo, Hirota and Morino from microwave studies. An appropriate set of rotational constants was obtained for the excited state in the following way. The origin of the $K_p$ sub-band ($J = 0$ in Equations (4.12), (4.13) and (4.14)) minus the origin of the $K_p + 1$ sub-band is given by

$$[(A' - \tilde{B}^r) - (A'' - \tilde{B}''^r)][K_p - (K_p + 1)^2] = -[(A' - \tilde{B}^r) - (A'' - \tilde{B}''^r)]2K_p + 1$$

(4.31)

Therefore a plot of the first difference in the $K_p$ structure verses $K_p$ should give a straight line with slope $-2[(A' - \tilde{B}^r) - (A'' - \tilde{B}''^r)]$. The ground
Figure 4.5 Relative intensity of p, q, and r branch as a function of $I_0$ in a parallel case of a symmetric top.
state constants are known, therefore it is possible to determine the excited state difference $A'-\tilde{B}'$. Figure 4.4 shows a plot of $\Delta v$ verses $K_p$ for the $1^3_0$ vibronic band of Se$^{78}O_2^{16}$. The slope is found to equal $-0.71875$ which gives $A'-\tilde{B}' = 0.36339 \text{ cm}^{-1}$ for the excited state.

The sub-band heads were also fitted by least squares to Equations (4.12) and (4.14) which are both quadratic equations. The value of $A'-\tilde{B}'$ obtained from the quadratic coefficient is $0.36046 \text{ cm}^{-1}$ which is in good agreement with the value of $A'-\tilde{B}' = 0.36339 \text{ cm}^{-1}$ obtained from the $\Delta v$ verses $K_p$ plot.

The linear coefficient in Equation (4.13) changes with the $K_p$ numbering of the sub-bands while the quadratic coefficient is independent of the $K_p$ numbering. The correct $K_p$ numbering for a perpendicular band gives $A_1 = \pm(A'-\tilde{B}')$ while for a parallel band $A_1 = 0$ (i.e., Equation (4.13) reduces to Equation (4.12)). The calculated $K_p$ numbering for a parallel and perpendicular transition for the $1^3_0$ band of Se$^{70}O_2^{16}$ are given in Table 4.4. The first few sub-bands corresponding to low $K_p$ values were omitted in the above least square fit since for low $(J,K)$ the molecule is only poorly approximated as a near prolate symmetric top. The corresponding plot of $\Delta v$ against $K_p$, along with the $K_p$ numbering for assumed parallel and perpendicular bands for the Se$^{70}O_2^{16}$ and Se$^{80}O_2^{16}$ molecules are given in Appendix III.

From the least square procedure outlined above, it was possible to determine the $K_p''$ numbering for the sub-bands. It was, however, not possible to distinguish between a parallel and perpendicular transition since the $K_p$ numberings determined in each case were very similar. However, the number of sub-bands which appear in the spectrum between the head and the sub-band located at 33876.903 cm$^{-1}$ was closer to six rather than eight. For this reason
Figure 4.4 Plot of Q branch head separation (Δν) against U_p for the 1₁₅ vibronic band of \textit{so}_{2014}. From a least square fit of the above points the intercept is found to be \(-0.042\).
Table 4.4

Numbering for Sub-Band Origins of $1^3 \text{Vibronic Band of Se}^{78,16}_2$

Assuming a Parallel Band $^*$

<table>
<thead>
<tr>
<th>$K_p$</th>
<th>$\nu$ (Experimental) cm$^{-1}$</th>
<th>$\nu$ (Calculated) cm$^{-1}$</th>
<th>Deviation (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>33876.903</td>
<td>33876.701</td>
<td>-0.201</td>
</tr>
<tr>
<td>8</td>
<td>33870.817</td>
<td>33871.022</td>
<td>0.205</td>
</tr>
<tr>
<td>9</td>
<td>33864.355</td>
<td>33864.638</td>
<td>0.283</td>
</tr>
<tr>
<td>10</td>
<td>33857.765</td>
<td>33857.550</td>
<td>-0.21</td>
</tr>
<tr>
<td>11</td>
<td>33849.902</td>
<td>33849.757</td>
<td>-0.14</td>
</tr>
<tr>
<td>12</td>
<td>33841.250</td>
<td>33841.259</td>
<td>-0.05</td>
</tr>
<tr>
<td>13</td>
<td>33831.884</td>
<td>33832.057</td>
<td>0.17</td>
</tr>
<tr>
<td>14</td>
<td>33822.285</td>
<td>33822.150</td>
<td>-0.13</td>
</tr>
<tr>
<td>15</td>
<td>33811.477</td>
<td>33811.539</td>
<td>0.06</td>
</tr>
</tbody>
</table>

$^*$From a similar least square analysis assuming a perpendicular band, the sub-band at 33876.903 cm$^{-1}$ is assigned to the value $K_p^" = 9$. 
a parallel transition is favored over a perpendicular one.

In order to determine the polarization of the transition and consequently the symmetry of the excited electronic state, a rotational analysis was carried out by the band contour method. The analysis was performed using a computer program written by Pierrre [unpublished; see (7)]. The program calculates the frequency and intensity of individual rotational lines in asymmetric top approximation. The line intensities are then distributed according to a Gaussian function. The nuclear statistical weights for individual rotational lines are entered as input data in the program. The contours calculated for a particular vibronic band are then compared with a microdensitometer tracing of the same band. If the contour and trace do not match then the rotational constants are systematically varied until both are the same. Contours for both parallel and perpendicular transitions were calculated. The perpendicular contours in no way resembled the experimental profile of the band, while parallel contours resembled the experimental trace both in head position and intensity distribution. The calculated and observed contours for a transition polarized parallel to the top axis are shown in Figure 4.5 for the $^1\Sigma_0^+$ vibronic band. The excited state rotational constants for Ce$^{79}O_2$ which give the contour in Figure 4.5 are: $A = 0.60657$ cm$^{-1}$, $B = 0.29221$ cm$^{-1}$ and $C = 0.19721$ cm$^{-1}$. The moments of inertia for CeO$_2$ are related to the bond length and bond angle (see Figure 4.1) according to the following simple relations

$$I_x = mr^2\cos^2\alpha$$  \hspace{1cm} (4.32)

$$I_y = 2mr^2\sin^2\alpha$$  \hspace{1cm} (4.33)

---

*I would like to thank Dr. Glenn Eddle for writing the plot sub-routine used in the present band contour work.*
\[ I_z = I_x + I_y = 2m(\mu_3/\mu)r^2\sin^2\alpha \]  
\[ \mu = 2m/M(2n + 1) \]  
\[ \mu_3 = \mu[1 + (\mu/2m)\cot^2\alpha] \]

and M and \( n \) are the selenium and oxygen masses respectively. An excited state bond length of 1.74 Å and bond angle \( 2\alpha = 101.0^\circ \) was calculated from the moments of inertia determined by the band contour method. The value of \( \Delta v' = 0.36186 \text{ cm}^{-1} \) determined from the band contour, is in good agreement with the value 0.36046 cm\(^{-1}\) obtained from the average of the second difference in the \( K \)-structure using the least square method discussed earlier.

The excited state geometry determined above for \( \text{Se}^{78}O_{26} \) was then used with the aid of Equations (4.32) to (4.36) to calculate the rotational constants corresponding to this geometry for the isotopic molecules \( \text{Se}^{78}O_{26} \) and \( \text{Se}^{80}O_{26} \). The observed and calculated contour for \( \text{Se}^{80}O_{26} \) is shown in Figure 4.6. The agreement between the observed and calculated contours for the \( \text{Se}^{78}O_{26} \) isotope was much poorer. The tabulated rotational constants for all three isotopic molecules are given in Table 4.5.

**Table 4.5**

Rotational Constants of \( \text{Se}^{78}O_{26} \), \( \text{Se}^{78}O_{28} \) and \( \text{Se}^{80}O_{26} \) Molecules

Corresponding to the \( \text{Ib}_2 \) Excited State Geometry with Symmetric Bond Lengths of 1.74 Å and Bond Angle \( 2\alpha = 101.0^\circ \)

<table>
<thead>
<tr>
<th></th>
<th>( \text{Se}^{78}O_{26} )</th>
<th>( \text{Se}^{78}O_{28} )</th>
<th>( \text{Se}^{80}O_{26} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.68535 cm(^{-1})</td>
<td>0.68535 cm(^{-1})</td>
<td>0.68215 cm(^{-1})</td>
</tr>
<tr>
<td>B</td>
<td>0.29221 cm(^{-1})</td>
<td>0.29127 cm(^{-1})</td>
<td>0.29221 cm(^{-1})</td>
</tr>
<tr>
<td>C</td>
<td>0.19721 cm(^{-1})</td>
<td>0.19571 cm(^{-1})</td>
<td>0.19574 cm(^{-1})</td>
</tr>
</tbody>
</table>
Figure 4.5 observed (lower) and calculated (upper) contour for the $1^0$ vibrionic band of $3e^{-}$.
4.7. Prominent Features of $^1_0$ Vibronic Band

The $^3_0$ vibronic band is A-type and thus corresponds to a $^1\text{B}_2 + ^1\text{A}_1$ vibronic transition with the electric dipole polarized parallel to the top axis. Since only totally symmetric vibrations are excited in this transition, the electronic transition itself is therefore $^1\text{B}_2 + ^1\text{A}_1$. The $^3_0$ band is red degraded forming two principal heads separated by approximately 7 cm$^{-1}$. The more intense of these lies to the red forming the high frequency limit of the $^q\text{R}$-sub-branches ($^q\text{R}$ sub-branch in the prolate symmetric top limit).

The weaker head to the blue corresponds to the forbidden ($\Delta K_a = \pm 2$) symmetric rotor sub-branch $^s\text{R}$. This is the same type of head formation recently observed by Brand and Shrikameswaran$^{92}$ in the $^0_0$ band of the $^1\text{B}_2 + ^1\text{A}_1$ electronic transition of the sulfur dioxide. The most prominent feature in sub-bands of high $K$ is the $^q_0$ branch head and to a less extent initial lines of the $^q_0$ branch. A first order Ebert photograph of the $^3_0$ vibronic band of Se$^{76}$O$_2^{16}$ is shown in Figure 4.7.

4.8. Rotational Structure of $^0_2^1_0$ Vibronic Band

The vibrational analysis has led to strong evidence for the presence of a double-minimum potential well along $Q_2$ in the excited $^1\text{B}_2$ electronic state of selenium dioxide. The transition from the vibrationless level of the ground state to the $Q_2$-level of $Q_3$ in the excited state has been assigned. This transition is labelled the $^3_0$ vibronic band, at $32043.0$ cm$^{-1}$.

As discussed earlier in Chapter Three this band is expected to be of $B_2$ symmetry ($C_{2v}$ classification) or an AB-Type hybrid band ($C_3$ classification).

An extensive attempt was made to analyse the $^0_2^1_0$ band by the band contour method. Unfortunately it was not possible to fit the observed contour to calculated A, D or AD hybrid bands. The difficulty in obtaining a good fit
Figure 4.7

First order Ebert photograph of $1^3_{0}$ vibronic band of Se$^{78}$O$_2^{16}$. 
results from the fact that if the band is an AB-hybrid then the observed heads within the band will be most often due to coincidental overlap of the superimposed parallel A-type band and perpendicular B-type. The profile of the $3^1_0$ band (the $1^0_{2^1}0$ band was actually used in the analysis since it is free of overlapping sequence bands) is very distinctly different from the observed "pure" A-type bands. A first order Ebert photograph of the $1^0_{2^1}0$ band obtained at McMaster University and a 20th order Ebert photograph taken in Dr. D. C. Moule's laboratory at Brock University in St. Catharines, Ontario, are shown in Figure 4.8. It is unfortunate that it was not possible to analyse this band in detail since the determination of its band type would provide confirmation of the vibrational analysis given in the present work. Certainly, Figure 4.8 shows that the band type must be quite different from the observed type A bands (see Figure 4.7).
Figure 4.8
First order (a) and 20th order (b) Ebert photograph of 1241 \text{ cm}^{-1}
vibronic band of \text{ SeO}_2.
CHAPTER FIVE
FRANCK-CONDON CALCULATIONS

5.1. Introduction

In the present work the Franck-Condon principle was used to determine completely the structure of the \( ^1\text{B}_2 \) electronic state of selenium dioxide. The methods outlined by Coon et al. \(^71\) were applied and the results are discussed. In order to perform the above calculation it was necessary to have made a normal co-ordinate analysis, or have at least an approximate set of normal coordinates for the excited state. The results of the normal co-ordinate analyses are discussed along with a brief description of the methods used in the normal co-ordinate analysis. The Franck-Condon calculations require only \( Q_1 \) and \( Q_2 \). \( Q_3 \) was also calculated, although in practice the molecule has a double-minimum potential along \( Q_3 \). It was necessary to assume a symmetric harmonic model for \( Q_3 \). Also the value \( v_3 \) = 686 cm\(^{-1}\) was obtained by taking one half of the observed \( 2v_3 \) = 1372 cm\(^{-1}\).

5.2. Normal Co-ordinate Analysis (Ground Electronic State)

The normal co-ordinates for selenium dioxide were obtained using a Urey-Bradley \(^72,73\) force field and a general quadratic force field as an approximation to the potential function for the molecule. The computer program for the former was set up in a method similar to that described by Overend and Scherer \(^74\), and the final normal co-ordinates obtained by the Wilson F-G method \(^75\). A brief description of the procedure is outlined below.

In the Urey-Bradley \(^76\) force field we take account of bond-stretching force constants \( K \), angle bending force constants \( H \) and repulsive force constants \( F \). However, the non-bonding interaction between the oxygen nuclei
is not independent of \( \Delta r_1 \) and \( \Delta \phi \) and consequently is a redundant co-ordinate and must therefore be removed. The redundant co-ordinate arises due to the fact that we have four co-ordinates \( \Delta r_1, \Delta r_2, \Delta \phi \) and \( \Delta \phi \) (see Fig. 5.1) but only three vibrational degrees of freedom. In general the number of adopted co-ordinates should equal the number of vibrational degrees of freedom.

The non-bonding distance \( q \) (Fig. 5.1) is given by the cosine law as

\[
q^2 = r_1^2 + r_2^2 - 2r_1r_2\cos \phi
\]  

(5.1)

and the redundant condition is

\[
\Delta q = s\Delta r_1 + s\Delta r_2 + t(r_0\Delta \phi) + \left[ r_1^2(\Delta r_1)^2 + r_2^2(\Delta r_2)^2 - s^2(r_0\Delta \phi)^2 \right] - 2t^2(\Delta r_1)(\Delta r_2) + 2ts(\Delta r_1)(r_0\Delta \phi) + 2ts(\Delta r_2)(r_0\Delta \phi) \right]/2q_o
\]  

(5.2)

where \( s \) and \( t \) are given by

\[
s = r_0(1 - \cos \phi_o)/q_o
\]  

(5.3)

\[
t = r_0(\sin \phi_o)/q_o
\]  

(5.4)

Substitution of Equation (5.2) for \( \Delta q \) gives the Urey-Bradley potential energy for \( \text{SeO}_2 \) as

\[
V = \frac{1}{2}(H + s^2F - t^2F')(\Delta r_1)^2 + \frac{1}{2}(H + s^2F - t^2F')(\Delta r_2)^2
\]

(5.5)

\[
+ \frac{1}{8}(H + t^2F - s^2F')(r_0\Delta \phi)^2 + (s^2F - t^2F')(\Delta r_1)(\Delta r_2)
\]

\[
+ ts(F + F')(\Delta r_1)(r_0\Delta \phi) + ts(F + F')(\Delta r_2)(r_0\Delta \phi)
\]

The value of \( F \) and \( F' \) are dependent and usually assumed to be related in the following way:

\[
F' = -0.1 F
\]  

(5.6)

The potential energy, expressed in internal co-ordinates, is given by
Figure 6.1 Geometry of $\text{SeO}_2$ molecule
\[ V = \frac{1}{2} f_{11}(\Delta r_1)^2 + \frac{1}{2} f_{22}(\Delta r_2)^2 + \frac{1}{2} f_{33}(r_0 \Delta \phi)^2 \]
\[ + f_{12}(\Delta r_1)(\Delta r_2) + f_{13}(\Delta r_1)(r_0 \Delta \phi) + f_{23}(\Delta r_2)(r_0 \Delta \phi) \]
which when expressed in matrix notation is
\[ V = \frac{1}{2} \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \\ r_0 \Delta \phi \end{bmatrix} \begin{bmatrix} f_{11} & f_{12} & f_{13} \\ f_{21} & f_{22} & f_{23} \\ f_{31} & f_{32} & f_{33} \end{bmatrix} \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \\ r_0 \Delta \phi \end{bmatrix} \]  
\[ (5.8) \]

The individual elements \( f_{ij} \) of the \( F \) matrix are linear functions of the Urey-Bradley force constants \( \phi_k \) of Equation (5.5);
\[ F_{ij} = \sum_k a_{jk} \phi_k \]
\[ (5.9) \]

the coefficients \( a_{jk} \) being determined by the molecular geometry. The transformation of the potential energy from Urey-Bradley space to internal co-ordinate space is effected by a transformation matrix \( Z \).

5.3. Construction of the \( Z \) Matrix

We are seeking a transformation matrix \( Z \) of the form
\[ F = Z \Phi \]
\[ (5.10) \]

The elements of the \( F \) matrix are ordered in the following way:
\[ F = \begin{bmatrix} f_1 & f_2 & f_3 & 0 \\ f_3 & f_5 & f_6 \end{bmatrix} \]
\[ (5.11) \]

the matrix being symmetric about the main diagonal.

The individual elements of the \( Z \) matrix are, therefore, easily obtained by equating coefficients of Equation (5.5) with those of Equation (5.7). The \( Z \) matrix elements are given in Table 5.1.
Table 5.1

<table>
<thead>
<tr>
<th></th>
<th>( \kappa )</th>
<th>( \eta )</th>
<th>( \eta^T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\Delta r_1)^2)</td>
<td>1.0</td>
<td>0</td>
<td>0.86325</td>
</tr>
<tr>
<td>((\Delta r_1)(\Delta r_2))</td>
<td>0</td>
<td>0</td>
<td>0.98912</td>
</tr>
<tr>
<td>((\Delta r_2)^2)</td>
<td>1.0</td>
<td>0</td>
<td>0.86325</td>
</tr>
<tr>
<td>((\Delta r_1)(\rho \Delta \phi))</td>
<td>0</td>
<td>0</td>
<td>0.68714</td>
</tr>
<tr>
<td>((\Delta r_2)(\rho \Delta \phi))</td>
<td>0</td>
<td>0</td>
<td>0.68714</td>
</tr>
<tr>
<td>((\rho \Delta \phi))</td>
<td>0</td>
<td>1.0</td>
<td>0.72199</td>
</tr>
</tbody>
</table>

5.4. G Matrix for \( \text{SeO}_2 \)

In terms of mass-weighted cartesian co-ordinates, \( \eta_1 \), the kinetic energy \( T \), in matrix notation is given by,

\[
ZT = \eta^T \eta
\]

(5.12)

where \( \eta^T \) and \( \eta \) are a row and column vector respectively. The kinetic energy then takes the simple form of a sum of square terms when expressed in mass-weighted cartesian co-ordinates.

The potential energy is, however, expressed in internal co-ordinates. Therefore, the mass-weighted cartesian co-ordinates are transformed to internal co-ordinates \( \eta_1 \) by a transformation matrix \( D \).

\[
R = D\eta.
\]

(5.13)

However, since there are only 61-6 internal co-ordinates but 56 mass-weighted cartesian co-ordinates, \( D \) is a non-square matrix with 56 rows and 61 columns. Since \( D \) is a non-square matrix, it cannot be inverted to give the matrix \( R \) which we seek.
Wilson\textsuperscript{75} has shown, however, that the kinetic energy is given by

\[ 2T = \hat{R}^t G^{-1} \hat{R} \]  \hspace{1cm} (5.14)

where \( DD^t = G \) is a square matrix of dimension \( 3N-6 \) and thus possesses an inverse.

The \( G \) matrix elements are determined from the molecular geometry and are tabulated in Table 5.2. The \( G \) matrix is symmetric about the main diagonal.

\begin{table}[h]
\centering
\caption{G Matrix Elements for \( \text{SO}_2 \) in Internal Co-ordinates}
\begin{tabular}{c c c c}
\hline
& \( \Delta r_1 \) & \( \Delta r_2 \) & \( r_0 \Delta \phi \) \\
\hline
\( \Delta r_1 \) & \( \mu_{\text{Se}} + \mu_0 \) & \[ \] & \[ \] \\
\hline
\( \Delta r_2 \) & \( (t^2 - 5^2) \mu_{\text{Se}} + \mu_0 \) & \[ \] & \[ \] \\
\hline
\( r_0 \Delta \phi \) & \( -2t^2 \mu_{\text{Se}} \) & \( -2t^2 \mu_{\text{Se}} \) & \( 4s^2 \mu_{\text{Se}} + 2\mu_0 \) \\
\hline
\end{tabular}
\end{table}

The normal co-ordinates \( Q \) are related to the internal co-ordinates \( R \) by the transformation matrix \( L \)

\[ R = LQ \]  \hspace{1cm} (5.15)

where \( L \) is chosen such that the kinetic and potential energy have a diagonal form when expressed in terms of the normal co-ordinates.

\[ 2V = L^t \hat{Q} L Q = Q^t \hat{A} Q \]  \hspace{1cm} (5.16)

\[ 2T = L^t \hat{Q} L G^{-1} L Q = Q^t \hat{E} Q \]  \hspace{1cm} (5.17)

where \( \hat{A} \) is a diagonal matrix whose diagonal elements will be the quantity

\[ A_L = 4r^2 c^2 v_L^2 \] and \( E \) is the unit matrix. Therefore,

\[ L^t \hat{Q} L = \Lambda \] and \[ L^t G^{-1} L = E \]  \hspace{1cm} (5.18)
In the Wilson formalism the secular equation takes the form

$$|GF - EA| = 0$$  \( (5.19) \)

The GF matrix is diagonalized by \( L^{-1}GL = A \) or \( GF = LA \) where \( A \) is the diagonal matrix consisting of the eigenvalues and \( L \) consists of the corresponding eigenvectors.

5.5. Calculation of Urey-Bradley Force Constants from Observed Frequencies

In the present analyses a trial set of Urey-Bradley force constants \( \phi \) were assumed, and the elements of the \( F \) matrix calculated according to Equation (5.10). The GF matrix was then formed and subsequently diagonalized yielding a set of calculated eigenvalues \( \lambda_i^c \) which could then be compared with the observed eigenvalues \( \lambda_i^o \) obtained from the experimentally observed frequencies. A Jacobian subroutine was used to obtain a corrected set of Urey-Bradley force constants such that the difference \( (\lambda_i^o - \lambda_i^c) = 0 \).

The elements of the Jacobian matrix \( J_{ik}^\phi \) are given by

$$J_{ik}^\phi = \frac{3\lambda_i^c}{\partial \phi_k}$$  \( (5.20) \)

The construction of the Jacobian is identical with that outlined by Subramanian and will not be duplicated here.

5.6. Normal Co-ordinate Analysis (General Quadratic Force Field)

The set of frequencies obtained using a Urey-Bradley force field were reasonably close to the experimentally observed frequencies. The assumption of only one type of stretching force constant (Urey-Bradley force field) is probably most responsible for the slight disagreement between the calculated and observed \( v_i^1 \) and \( v_3^3 \) frequencies. The calculated frequencies for \( v_i^1 \) and \( v_3^3 \) were 662 cm\(^{-1}\) and 685 cm\(^{-1}\) while the observed frequencies are
660 cm\(^{-1}\) and 686 cm\(^{-1}\) respectively. In order to obtain slightly better agreement for these frequencies, a general quadratic force field was assumed rather than a Urey-Bradley force field.

The excited state normal co-ordinates were, therefore, obtained using a general quadratic force field according to the methods outlined by Shimamouchi\(^{77}\). A brief description of the method is given below.

According to Shimamouchi, the reason it is often difficult to obtain a convergent set of force constants is the fact that we are trying to adjust force constants for which no information is given by the data on the frequencies. The divergence also occurs when the number of force constants to be adjusted is larger than the number of physical observables.

To avoid the divergence problem Shimamouchi suggests that the force constants to be determined be separated into two sets, \(k_A\) and \(k_B\); the \(k_A\) set being those force constants for which the frequencies give information and which can be freely adjusted. The \(k_B\) set contains those force constants which cannot be estimated for which the frequencies contain little information. In the present work the diagonal force constants were classified in the \(k_A\) set while the off-diagonal force constants constituted the \(k_B\) set.

A trial set of \(k_A\) force constants was then adjusted from the normal equation\(^{77}\):

\[
J_A \Delta k_A = J_A \Delta u^0
\]

(5.21)

the values of the elements of \(k_B\) being assumed to be zero. \(J_A\) is the Jacobian matrix for the \(k_A\) set and is of the form:

\[
J = \frac{\partial^2 (v_1, v_2, v_3)}{\partial (\xi_{11})^2}
\]

(5.22)

\(u\) is a diagonal weighting matrix, the elements of which are given by

\[
\sqrt{u_{11}} = \frac{1}{\lambda_1^2}
\]

(5.23)
where $\lambda_1 = 4\pi^2 c^2 v_1^2$ and $\Delta v^o$ is the frequency-deviation vector

$$\Delta v^o = v^\text{obs} - v^o$$

and $v^o$ is the value calculated from the trial set of force constants $k^o$.

When the final converged set of $k_A$ force constants is determined, we calculate the $p_{AB}$ matrix defined by

$$\Delta k^B_A = p_{AB} \Delta k_B$$ \hspace{1cm} (5.24)$$

where $\Delta k^B_A$ is the correction which must be made to the converged $k_A$ set when the $k_B$ is varied by $\Delta k_B$.

In the present work it was possible to obtain the three excited state frequencies with the inclusion of only diagonal force constants, the off-diagonal force constants being zero or very small. This, therefore, suggests that in the excited state the motion along one normal co-ordinate is largely independent of the motion along the other two normal co-ordinates. Since no correction to the convergent set of diagonal force constants was required, a discussion of the procedures involved will not be given. The methods are, however, clearly outlined by Shimomouchi.[77]

For the Franck-Condon calculations (Coon's Method[35]), it is necessary to have the normal co-ordinates for only the totally symmetric vibrations $v_1$ and $v_2$. Therefore it is convenient to use symmetry co-ordinates $s_i$ given by (see Figure 5.1)

$$s_1 = (\Delta r_1 + \Delta r_2)/\sqrt{2}$$ \hspace{1cm} (A1) \hspace{1cm} (5.25)

$$s_2 = r_0^o \Delta \phi$$ \hspace{1cm} (A1) \hspace{1cm} (5.26)

$$s_3 = (\Delta r_1 - \Delta r_2)/\sqrt{2}$$ \hspace{1cm} (B2) \hspace{1cm} (5.27)

The potential energy in symmetry co-ordinates then becomes

$$V = \frac{1}{2}(f_{11} + f_{12}) s_1^2 + \frac{1}{2} f_{22} s_2^2 + \frac{1}{2}(f_{11} - f_{12}) s_3^2 + \sqrt{2} f_{13} s_1 s_2$$ \hspace{1cm} (5.28)
and we now have the four independent force constants $f_{11} + f_{12}$, $f_{33}$, $f_{11} - f_{12}$, and $f_{13}$ in place of the four force constants $f_{11}$, $f_{33}$, $f_{12}$ and $f_{13}$ associated with internal displacement co-ordinates.

The G matrix in symmetry co-ordinates is shown in Table 5.3 after Shinanouchi.

Table 5.3

G Matrix for SeO$_2$ in Symmetry Co-ordinates

(after Shinanouchi)

| $\Delta r_1 + \Delta r_2$ | $r_0 \Delta \phi$ | $(\Delta r_1 - \Delta r_2)/2$ |
| $A_1$: | $2t^2 \mu_{Se} + \nu_0$ | $-2\sqrt{2} \tau \mu_{Se}$ | $4s^2 \mu_{Se} + 2\nu_0$ |
| $\tau \Delta \phi$ | $-2\sqrt{2} \tau \mu_{Se}$ | |
| $B_2$: | $(\Delta r_1 - \Delta r_2)/2$ | $2s^2 \mu_{Se} + \nu_0$ |

The ground and excited state G and F matrix are given in Tables 5.4 and 5.5 for internal co-ordinates and Tables 5.6 and 5.7 for symmetry co-ordinates respectively.

The Urey-Bradley force constants for the ground and excited electronic state are shown in Table 5.8 and the L matrix (symmetry co-ordinates) is shown in Table 5.9.

Cartesian and mass-weighted cartesian displacement co-ordinates were also calculated using a computer program obtained from the "Quantum Chemistry Program Exchange" at Indiana University. Since an arbitrary co-ordinate system was used in the program, the original cartesian co-ordinates of the atoms are tabulated in Table 5.10. The normal co-ordinates in terms of mass-

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*I would like to thank Dr. D. C. Kale for providing us with a copy of this program.*
Table 5.4

G Matrix for the $^1A_1$ Ground and $^1B_2$ Excited Electronic State
of Se$^{78}O_2^{16}$ for Internal Co-ordinates (units are a.u.)

<table>
<thead>
<tr>
<th></th>
<th>$\Delta r_1$</th>
<th>$\Delta r_2$</th>
<th>$r_o\Delta \phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>State</td>
<td>$\Delta r_1$</td>
<td>0.07535</td>
<td>-0.00517</td>
</tr>
<tr>
<td></td>
<td>$\Delta r_2$</td>
<td>-0.00517</td>
<td>0.07535</td>
</tr>
<tr>
<td></td>
<td>$r_o\Delta \phi$</td>
<td>-0.01174</td>
<td>-0.01174</td>
</tr>
<tr>
<td>Excited</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>State</td>
<td>$\Delta r_1$</td>
<td>0.07535</td>
<td>-0.00244</td>
</tr>
<tr>
<td></td>
<td>$\Delta r_2$</td>
<td>-0.00244</td>
<td>0.07535</td>
</tr>
<tr>
<td></td>
<td>$r_o\Delta \phi$</td>
<td>-0.01259</td>
<td>-0.01259</td>
</tr>
</tbody>
</table>

Table 5.5

F Matrix for the $^1A_1$ Ground and $^1B_2$ Excited Electronic State
of Se$^{78}O_2^{16}$ for Internal Co-ordinates (units are n dyne/Å)

<table>
<thead>
<tr>
<th></th>
<th>$\Delta r_1$</th>
<th>$\Delta r_2$</th>
<th>$r_o\Delta \phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>State</td>
<td>$\Delta r_1$</td>
<td>7.1738</td>
<td>-0.20811</td>
</tr>
<tr>
<td></td>
<td>$\Delta r_2$</td>
<td>0.20811</td>
<td>6.83191</td>
</tr>
<tr>
<td></td>
<td>$r_o\Delta \phi$</td>
<td>0.05593</td>
<td>0.05616</td>
</tr>
<tr>
<td>Excited</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>State</td>
<td>$\Delta r_1$</td>
<td>3.499</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>$\Delta r_2$</td>
<td>0.0</td>
<td>0.2648</td>
</tr>
<tr>
<td></td>
<td>$r_o\Delta \phi$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
### Table 5.6

$G$ Matrix for the $^1A_1$ Ground State and $^1B_2$ Excited Electronic State of Se$^{78,16}$O$_2$ for Symmetry Co-ordinates (units are a.u.$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>$(\Delta r_1 + \Delta r_2)/2$</th>
<th>$r_0 \Delta \phi$</th>
<th>$(\Delta r_1 - \Delta r_2)/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ground State</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\Delta r_1 + \Delta r_2)/2$</td>
<td>0.070175</td>
<td>-0.01660</td>
<td>0.0</td>
</tr>
<tr>
<td>$r_0 \Delta \phi$</td>
<td>-0.01660</td>
<td>0.161065</td>
<td>0.0</td>
</tr>
<tr>
<td>$(\Delta r_1 - \Delta r_2)/2$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.080532</td>
</tr>
<tr>
<td><strong>Excited State</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\Delta r_1 + \Delta r_2)/2$</td>
<td>0.072906</td>
<td>-0.017817</td>
<td>0.0</td>
</tr>
<tr>
<td>$r_0 \Delta \phi$</td>
<td>-0.017817</td>
<td>0.155604</td>
<td>0.0</td>
</tr>
<tr>
<td>$(\Delta r_1 - \Delta r_2)/2$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.077802</td>
</tr>
</tbody>
</table>

### Table 5.7

$F$ Matrix for the $^1A_1$ Ground State and $^1B_2$ Excited Electronic State of Se$^{78,16}$O$_2$ for Symmetry Co-ordinates (units are n dynes/Å)

<table>
<thead>
<tr>
<th></th>
<th>$(\Delta r_1 + \Delta r_2)/2$</th>
<th>$r_0 \Delta \phi$</th>
<th>$(\Delta r_1 - \Delta r_2)/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ground State</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\Delta r_1 + \Delta r_2)/2$</td>
<td>7.109766</td>
<td>-0.011575</td>
<td>0.0</td>
</tr>
<tr>
<td>$r_0 \Delta \phi$</td>
<td>-0.011575</td>
<td>0.524665</td>
<td>0.0</td>
</tr>
<tr>
<td>$(\Delta r_1 - \Delta r_2)/2$</td>
<td>0.0</td>
<td>0.0</td>
<td>6.84006</td>
</tr>
<tr>
<td><strong>Excited State</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\Delta r_1 + \Delta r_2)/2$</td>
<td>3.49973</td>
<td>-0.00208</td>
<td>0.0</td>
</tr>
<tr>
<td>$r_0 \Delta \phi$</td>
<td>-0.00208</td>
<td>0.26479</td>
<td>0.0</td>
</tr>
<tr>
<td>$(\Delta r_1 - \Delta r_2)/2$</td>
<td>0.0</td>
<td>0.0</td>
<td>3.56316</td>
</tr>
</tbody>
</table>
Table 5.8.

Urey-Bradley Force Constants for Se$_{78}O_{16}$ in the Ground and Excited Electronic State

<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>H</th>
<th>F+F'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground</td>
<td>6.852</td>
<td>0.439</td>
<td>0.17</td>
</tr>
<tr>
<td>Excited</td>
<td>3.590</td>
<td>0.328</td>
<td>-0.080</td>
</tr>
</tbody>
</table>

Table 5.9

$L$ and $L^{-1}$ Matrix for the Ground and Excited State of Se$_{78}O_{16}$ using Symmetry Co-ordinates (units are a.m.u.$^{-1/2}$)

<table>
<thead>
<tr>
<th></th>
<th>L$^0$ Matrix</th>
<th>L$^{-1}$ Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.26472</td>
<td>3.75248</td>
</tr>
<tr>
<td></td>
<td>0.008998</td>
<td>-0.085687</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>-0.076114</td>
<td>0.724837</td>
</tr>
<tr>
<td></td>
<td>0.394045</td>
<td>2.521233</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Excited</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.269869</td>
<td>3.681271</td>
</tr>
<tr>
<td></td>
<td>0.008741</td>
<td>-0.083240</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>-0.078539</td>
<td>0.747926</td>
</tr>
<tr>
<td></td>
<td>0.386568</td>
<td>2.56995</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>3.585130</td>
</tr>
</tbody>
</table>

The $L$ Matrix has been normalized in the sense $L^0 = G$ and gives the symmetry co-ordinates in terms of the normal co-ordinates ($S = LQ$), while $L^{-1}$ is related to the reverse transformation ($Q = L^{-1}S$).
Table 5.10
Original Cartesian Co-ordinates for Se\textsuperscript{78}O\textsubscript{2}\textsuperscript{16} in the Ground
and Excited Electronic State

<table>
<thead>
<tr>
<th>Atom</th>
<th>Ground State</th>
<th>Excited State</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>O\textsubscript{1}</td>
<td>-1.4676</td>
<td>0.0</td>
</tr>
<tr>
<td>Se</td>
<td>0.1393</td>
<td>0.0</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>0.7887</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 5.11
Calculated and Observed Frequencies for the \textsuperscript{1}A\textsubscript{1} Ground
and \textsuperscript{1}B\textsubscript{2} Excited Electronic State of Se\textsuperscript{78}O\textsubscript{2}\textsuperscript{16}

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Urey-Bradley Force Field</th>
<th>General Quadratic Force Field</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground State</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v\textsubscript{1}</td>
<td>966.8 cm\textsuperscript{-1}</td>
<td>923 cm\textsuperscript{-1}</td>
<td>923 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>v\textsubscript{2}</td>
<td>922.5 cm\textsuperscript{-1}</td>
<td>373 cm\textsuperscript{-1}</td>
<td>373 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>v\textsubscript{3}</td>
<td>374.0 cm\textsuperscript{-1}</td>
<td>967 cm\textsuperscript{-1}</td>
<td>967 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>Excited State</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v\textsubscript{1}</td>
<td>669 cm\textsuperscript{-1}</td>
<td>660 cm\textsuperscript{-1}</td>
<td>660 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>v\textsubscript{2}</td>
<td>260 cm\textsuperscript{-1}</td>
<td>260 cm\textsuperscript{-1}</td>
<td>260 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>v\textsubscript{3}</td>
<td>683.5 cm\textsuperscript{-1}</td>
<td>606 cm\textsuperscript{-1}</td>
<td>686 cm\textsuperscript{-1}</td>
</tr>
</tbody>
</table>
weighted cartesian and cartesian displacement co-ordinates are given in Table 5.12.

The agreement between the observed and calculated frequencies for the Urey-Bradley and general quadratic force field are given in Table 5.11 for both the ground and excited state.

The normal co-ordinates for SeO₂ are shown in Figure 5.2 in terms of the mass-weighted cartesian displacement co-ordinates given above in Table 5.12.

5.7. Franck-Condon Calculations (Coon's Method)²

The present interest in carrying out Franck-Condon calculations was to elucidate the geometric structure of selenium dioxide in the ¹B₂ excited electronic state. The transition probability for an electronic transition from the ground electronic state φ₀ to an excited electronic state φ₁ is given by the square of the transition moment ú₂₁ as:

\[ ú₂₁ = \langle φ₁ | T | φ₀ \rangle \langle φ₀ | φ₁ \rangle \]

(5.29)

where φ₀ is the vibrationless level of the ground electronic state and φ₁ the wth vibrational level of the excited electronic state. The intensity of a particular vibronic band in the electronic transition is, therefore, given by the Franck-Condon overlap integral \( \langle φ₁ | φ₀ \rangle \) between the ground and excited state vibrational wavefunctions. The magnitude of this integral is accordingly related to the change in structure of the molecule going from the ground to excited electronic state. It should, therefore, be possible to relate the intensity distribution within a vibrational progression to the change in the molecular geometry accompanying the electronic transition. This is the basis of the Coon method.

In order to carry out the above Franck-Condon calculation it was, therefore, necessary to have completed a vibrational analyses and measured
Figure 5.2 Normal co-ordinates of $\text{ScO}_{16}$ in terms of mass-weighted Cartesian displacement co-ordinates.
Table 5.12

Normal Co-ordinates for Se$^{76}$O$_2^{16}$ in the $^1A_1$ Ground and $^1B_2$ Excited Electronic State in Terms of Cartesian and Mass-Weighted Cartesian Co-ordinates. The upper numbers refer to the mass-weighted co-ordinates. The displacements are given along the three principle axes of the molecule.

<table>
<thead>
<tr>
<th>Ground State</th>
<th>$\Delta_a$</th>
<th>$\Delta_b$</th>
<th>$\Delta_c$</th>
<th>$\Delta_a$</th>
<th>$\Delta_b$</th>
<th>$\Delta_c$</th>
<th>$\Delta_a$</th>
<th>$\Delta_b$</th>
<th>$\Delta_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>-0.5457</td>
<td>0.3786</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.3430</td>
<td>0.0</td>
<td>0.5457</td>
<td>0.3786</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>-0.1364</td>
<td>0.0946</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.0388</td>
<td>0.0</td>
<td>0.1364</td>
<td>0.0946</td>
<td>0.0</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>0.4496</td>
<td>0.4594</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.4163</td>
<td>0.0</td>
<td>-0.4496</td>
<td>0.4594</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>0.1124</td>
<td>0.1148</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.0471</td>
<td>0.0</td>
<td>-0.1124</td>
<td>0.1148</td>
<td>0.0</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>0.5219</td>
<td>-0.3400</td>
<td>0.0</td>
<td>-0.4730</td>
<td>0.0</td>
<td>0.5219</td>
<td>0.3400</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1305</td>
<td>-0.0805</td>
<td>0.0</td>
<td>-0.0535</td>
<td>0.0</td>
<td>0.1305</td>
<td>0.0850</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Excited State</th>
<th>$\Delta_a$</th>
<th>$\Delta_b$</th>
<th>$\Delta_c$</th>
<th>$\Delta_a$</th>
<th>$\Delta_b$</th>
<th>$\Delta_c$</th>
<th>$\Delta_a$</th>
<th>$\Delta_b$</th>
<th>$\Delta_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>-0.02896</td>
<td>0.04306</td>
<td>0.0</td>
<td>-0.30015</td>
<td>-0.28644</td>
<td>0.0</td>
<td>0.69143</td>
<td>0.58915</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>-0.00724</td>
<td>0.01077</td>
<td>0.0</td>
<td>-0.03400</td>
<td>-0.03245</td>
<td>0.0</td>
<td>0.17288</td>
<td>0.14731</td>
<td>0.0</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>0.50162</td>
<td>0.41945</td>
<td>0.0</td>
<td>0.00405</td>
<td>-0.37675</td>
<td>0.0</td>
<td>-0.51056</td>
<td>0.41208</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>0.12543</td>
<td>0.10488</td>
<td>0.0</td>
<td>0.00046</td>
<td>-0.04268</td>
<td>0.0</td>
<td>-0.12766</td>
<td>0.10304</td>
<td>0.0</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>0.69769</td>
<td>-0.58244</td>
<td>0.0</td>
<td>-0.32608</td>
<td>0.0</td>
<td>0.00550$^6$</td>
<td>0.01083</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.17445</td>
<td>-0.14563</td>
<td>0.0</td>
<td>-0.03694</td>
<td>0.0</td>
<td>0.00271</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the relative intensity of several vibronic bands. In order to evaluate the overlap integrals of Equation (5.29) the ground state L matrix is required and thus the necessity for doing the normal coordinate analysis.

The vibrational wavefunctions \( \phi_v \) in Equation (5.29) are assumed to be of the form

\[
\phi_v = \prod_{i=1}^{3} \phi_i(Q_i) \tag{5.30}
\]

where the product is taken over the \( 3N-6 = 3 \) normal co-ordinates \( Q_i \). The transition moment of Equation (5.29) upon substitution of (5.30) is

\[
M_{\mu\nu}^{10} = R_c \int \prod_{i=1}^{3} \phi_i(Q_i) \prod_{\mu=1}^{3} \phi_\mu(Q_\mu) dQ_1 dQ_2 dQ_3 \tag{5.31}
\]

In order to evaluate this integral it is necessary to specify the transformation between the ground and excited state normal co-ordinates. Duschinsky has shown what the required transformation is of the form

\[
Q''_k = \sum_j (a_{kj}Q'_j + d_i) \tag{5.32}
\]

That is, the ground state co-ordinates \( Q'' \) are related to the excited state co-ordinates \( Q' \) by means of a rotation plus a translation.

Coon, however, assumes the above transformation can be effected in the following way:

\[
Q'' = Q' \cdot D \tag{5.33}
\]

Since the internal displacement co-ordinates of the molecule are related to the normal co-ordinates by:

\[
R'' = L'' Q'' \tag{5.34}
\]

Substitution of Equation (5.33) into (5.34) with \( Q' = 0 \) for the equilibrium
excited state configuration gives, as a first approximation to the excited state structure,

\[ R'' = L'D \]

The elements of the \( R \) matrix are related to the experimentally measured intensities, and are obtained in the following way

\[
\frac{R(1,0)}{R(0,0)} = \frac{\sqrt{2} \beta_1^2 \gamma}{(1 + \beta^2)} = 8\pi^2 c v_i^1 \left( \frac{(v_i^{''})^2 d_i^2}{(v_i^1 + v_i^{''})^2} \right)
\]

\[ (5.36) \]

\[
\frac{R(2,0)}{R(0,0)} = \frac{1}{\sqrt{2}(1 + \beta^2)} \left[ \frac{2B^2 \gamma^2}{(1 + \beta^2)} + (1 - \beta^2) \right]
\]

\[ (5.37) \]

where

\[
\beta_i = \frac{a_i''/a_i^1}, \quad \gamma_i = -a_i'd_i, \quad \text{and} \quad a_i^2 = 4\pi^2 c v_i^1/h
\]

\[ (5.38) \]

Since in the present work, the excited state \( L \) matrix was available, the change in the internal co-ordinates could be obtained directly from the relationship

\[ R' = L'D \]

\[ (5.39) \]

which is equivalent to Coad's second approximation to the excited state structure.

Since the spectrum contained progressions in both the upper state totally symmetric stretching frequency \( \nu_1^1 \), and angle bending frequency \( \nu_2^1 \), it was possible to obtain changes in both the bond length and bond angle. The calculated values for \( \alpha \), \( \beta \) for specific vibronic bands are given in Table 5.13.

Since the sign of the individual \( d_i \) is undetermined in Equation (5.39), there are \( 2^n \) possible upper state geometries consistent with the observed intensities where \( n \) is the number of totally symmetric upper state normal co-
ordinates. Since a rotational analysis was performed on the $1^3_0$ band, the upper state geometry was known and thus the proper choice of sign for $d_1$ and $d_2$ determined.

The calculated values of $d_1$ and $d_2$, along with the vibronic band used, are given in Table 5.14.

In the Franck-Condon calculations the units of $d$ are $g^{1/2}$ cm. The L matrix must have the units $g^{-1/2}$. It is therefore necessary to convert the L matrix given in Table 5.9 from a.m.u. to g. Since $LL^T = G$, and $G$ has the units (a.m.u.)$^{-1}$, the required units for $L(g^{-1/2})$ are obtained by multiplying each element of the L matrix by $1.0/(1.66024)^{1/2} = 0.77609$. The L matrix with units $g^{-1/2}$ used in the Franck-Condon calculation is shown in Table 5.15.

5.8. Conclusions and Discussion

The fundamental frequencies for selenium dioxide may be accounted for easily using a general quadratic force field and slightly less accurately with the assumption of a Urey-Bradley force field (see Table 5.11).

The geometry determined by means of the Franck-Condon principle, gives $r(Se-O)$ as 1.71 Å and $\theta(O-Se-O)$ as 93.48°. This is in reasonable agreement with $r = 1.74$ Å and $\theta = 101.0^\circ$ determined by rotational analysis of the $1^3_0$ vibronic band. The geometry determined from rotational analysis is probably most reliable since the former requires an estimate of the intensity of several bands involving $v_1$ and $v_2$. The intensities were measured from an expanded trace obtained photo-electrically from a Cary 14 spectrophotometer. The discrepancy between the geometry calculated by means of the Franck-Condon Principle and that determined from rotational analysis probably lies in the estimate of intensities used in the former calculation.
### Table 5.13

**Vibrational Frequencies and Parameters used in Franck-Condon Calculations for SeO₂**

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<tr>
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<th>Ground State</th>
<th>Excited State</th>
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</thead>
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<tr>
<td>( \nu_1 )</td>
<td>923 cm(^{-1} )</td>
<td>660 cm(^{-1} )</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>373 cm(^{-1} )</td>
<td>260 cm(^{-1} )</td>
</tr>
<tr>
<td>( \alpha_1 )</td>
<td>(40.618 \times 10^{19})</td>
<td>(34.349 \times 10^{19})</td>
</tr>
<tr>
<td>( \alpha_2 )</td>
<td>(25.718 \times 10^{19})</td>
<td>(21.559 \times 10^{19})</td>
</tr>
</tbody>
</table>

\( \beta_1 = 1.1825 \) \( \beta_2 = 1.197 \)

*Units of \( \alpha \) are cm/\( \text{sec}^3 \).m.org.

### Table 5.14

**Calculate Values of \( d_1 \) and \( d_2 \) for the \( {1\text{B}_2} \) Electronic State of SeO₂**

<table>
<thead>
<tr>
<th>Band (a) ((\nu_1^0, \nu_2^0))</th>
<th>Band (b) ((\nu_1^0, \nu_2^0))</th>
<th>( dx \times 10^{20} ) ( g^{1/2} \text{cm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,0)</td>
<td>(2,0)</td>
<td>( d_1 = 0.5032 )</td>
</tr>
<tr>
<td>(2,1)</td>
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<td>( d_1 = 0.645 )</td>
</tr>
<tr>
<td>(3,1)</td>
<td>(3,0)</td>
<td>( d_1 = 0.645 )</td>
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</tbody>
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### Table 5.15

**L Matrix Used in Franck-Condon Calculation**

(units are \( g^{-1/2} \))

<table>
<thead>
<tr>
<th>( (\Delta \nu_1^0 \cdot \Delta \nu_2^0)/2 )</th>
<th>( r_0 \Delta \phi )</th>
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</tr>
<tr>
<td>( r_0 \Delta \phi )</td>
<td>-0.06093</td>
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CHAPTER SIX

CONCLUSIONS

The B-System of selenium dioxide has been analysed in detail. The extensive absorption system extending from 3400 Å - 2400 Å has been shown to result from a $^1B_2 + \tilde{x},^1A_1$ electronic transition. A vibrational analysis of the electronic transition has successfully account for all the vibronic bands (>100) and yielded the three excited state fundamental frequencies. In addition gas phase values for the ground state totally symmetric stretching and bending frequencies were determined for the first time. The spectrum has been extended ~2000 cm$^{-1}$ to the red of previous investigations.

A rotational analysis of the $^1\tilde{S}_0$ vibronic band has been carried out using the band contour method, and the excited state geometry completely determined. A normal co-ordinate analysis of the ground and excited state was performed and Franck-Condon calculations were carried out to further confirm the excited state geometry determined by rotational analysis.

Perhaps the most interesting aspect of the present work is the suggestion of a double-minima potential well along $Q_2$ in the excited $^1D_2$ electronic state of SeO$_2$. The $S_1$ and $S_0$ bands have been assigned. To the author's knowledge selenium dioxide is the only symmetric triatomic molecule in which transitions to excited state double-minima levels have been observed. It is felt this observation is the only existing confirmation for the possible presence of a double-minima along the asymmetric stretching coordinate in certain excited electronic states of symmetric-bent AB$_2$ type molecules.
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APPENDIX I

Frequencies of the Observed Band Heads in the $^1B_2 \rightarrow ^1A_1$ Electronic Transition of Se$^{78}O_2$, Se$^{76}O_2$, and Se$^{80}O_2$ Grouped into Progressions

Legend

The frequencies of the observed band heads of Se$^{78}O_2$, Se$^{76}O_2$ and Se$^{80}O_2$ are given in cm$^{-1}$. All bands listed are observed at pressures which varied between 0.01 Torr and 10 Torr in a 50 cm quartz cell.

The relative intensities given are only rough visual estimates relative to neighbouring bands. The abbreviations used in the Table are:

- $v = very$
- $w = weak$
- $s = strong$
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<th>$\text{Se}^{78} \text{O}_2^{16}$ (cm$^{-1}$ vac.)</th>
<th>$\text{Se}^{80} \text{O}_2^{16}$ (cm$^{-1}$ vac.)</th>
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<th>Se$^{80}<em>{2}$O$</em>{2}$ (cm$^{-1}$ vac.)</th>
<th>Assignment</th>
<th>Intensity</th>
</tr>
</thead>
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<tr>
<td>30192.4</td>
<td>30291.6</td>
<td>30195.3</td>
<td>$1^0_{230}$</td>
<td>vww</td>
</tr>
<tr>
<td>29280.4</td>
<td>29427.9</td>
<td>-</td>
<td>$1^0_{330}$</td>
<td>vvvw</td>
</tr>
<tr>
<td>31687.3</td>
<td>31710.3</td>
<td>31689.8</td>
<td>$1^1_1$</td>
<td>w</td>
</tr>
<tr>
<td>32330.0</td>
<td>32325.6</td>
<td>32324.5</td>
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<td>w</td>
</tr>
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<td>32980.1</td>
<td>32948.1</td>
<td>32974.9</td>
<td>$1^3_1$</td>
<td>s</td>
</tr>
<tr>
<td>33640.7</td>
<td>33560.6</td>
<td>33634.5</td>
<td>$1^4_1$</td>
<td>s</td>
</tr>
<tr>
<td>34306.5</td>
<td>34202.6</td>
<td>34305.6</td>
<td>$1^5_1$</td>
<td>vs</td>
</tr>
<tr>
<td>35010.3</td>
<td>34872.6</td>
<td>35004.7</td>
<td>$1^6_1$</td>
<td>vs</td>
</tr>
<tr>
<td>31582.0</td>
<td>31605.</td>
<td>31585.</td>
<td>$2^0_{1}$</td>
<td>vuu</td>
</tr>
<tr>
<td>31208.2</td>
<td>31252.</td>
<td>-</td>
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<td>30732.</td>
<td>30675.</td>
<td>$1^0_{221}$</td>
<td>vvv</td>
</tr>
<tr>
<td>30285.</td>
<td>30379.</td>
<td>30295.</td>
<td>$1^0_{222}$</td>
<td>vvv</td>
</tr>
<tr>
<td>29753.4</td>
<td>-</td>
<td>29758.1</td>
<td>$1^0_{212}$</td>
<td>vvv</td>
</tr>
<tr>
<td>29380.1</td>
<td>-</td>
<td>-</td>
<td>$1^0_{220}$</td>
<td>vvv</td>
</tr>
<tr>
<td>31378.5</td>
<td>-</td>
<td>31379.9</td>
<td>$1^0_{22151}$</td>
<td>w</td>
</tr>
<tr>
<td>31616.2</td>
<td>-</td>
<td>31611.9</td>
<td>$1^0_{322}$</td>
<td>vvv</td>
</tr>
<tr>
<td>31877.8</td>
<td>-</td>
<td>31878.3</td>
<td>$1^0_{232}$</td>
<td>vvv</td>
</tr>
<tr>
<td>32142.5</td>
<td>32146.</td>
<td>32142.8</td>
<td>$1^0_{332}$</td>
<td>vvv</td>
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<tr>
<td>32404.6</td>
<td>32594.6</td>
<td>32405.</td>
<td>$1^0_{330}$</td>
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<tr>
<td>32502.4</td>
<td>32296.9</td>
<td>32502.1</td>
<td>$2^0_{310}$</td>
<td>w</td>
</tr>
<tr>
<td>30748.3</td>
<td></td>
<td></td>
<td>$1^2 + 1^2_{2131}$</td>
<td>vvv</td>
</tr>
</tbody>
</table>
APPENDIX II

Double-Minimum Potential Calculations for the $^1B_2$ Excited State
of ScO$_2$

In order to explain the abnormally high intensity of the $2\nu_3$ band in
the electronic spectrum resulting from the $^1B_2$ -- $^1A_1$ transition of ScO$_2$, it
was necessary to suggest the presence of a double minimum in the potential
well along the excited state asymmetrical stretching co-ordinate $Q_3$.

The methods used are those outlined by Coon and his co-workers$^{35}$. The
double-minimum potential function is of the "Gaussian barrier type" and can be
written

$$V(Q) = \frac{1}{2} aQ^2 + A \exp (-a^2Q^2) \quad (a.1.)$$

where $Q$ is a mass weighted co-ordinate defined by $2T = Q^2$.

The minima of the potential function are determined by differentiating
$a.1$ with respect to $Q$ and equating the result to zero. The two minima $Q_m$ are
given by

$$Q_m = (1/a^2)\ln(2a^2A/a) \quad (a.2)$$

A shape function $\rho$, which determines the anharmonicity of the outer
walls of the well relative to the walls of the barrier is defined by

$$a^2 = a^0 1/2a \quad (a.3)$$

Coon$^{35}$ then defines a frequency $\nu_0$ given by the relation

$$\lambda = (2\pi c \nu_0) \quad (a.4)$$

A dimensionless parameter $B$ is then defined so that the barrier height is $B\hbar \nu_0$
which with the aid of Equations (a.1), (a.2) and (a.3) give the barrier height \( b \) in cm\(^{-1} \) as

\[
b = b_0 \tag{a.5}
\]

The actual determination of the energy levels in the double-minimum potential well was done in the following way for \( \rho = 0.6 \). From the spectrum, using the experimentally observed levels \( 0^0 \), \( 3^1 \) and \( 3^2 \) the following ratio was determined

\[
\frac{G(1^+) - G(0^0)}{G(0^-) - G(0^0)} = \frac{1372.6}{78.9} = 17.3967 \tag{a.6}
\]

From the tables of energy levels \( G/v_0 \) as a function of \( B \) provided by Coon, the above ratio is plotted against \( B \) as shown in Figure A.1. The value of \( B = 1.0637 \) was found to correspond to the above ratio of 17.3967.

A plot of \( G(1^+)/v_0 - G(0^+)/v_0 \) against \( B \), then yields the correct value for \( G(1^+)/v_0 - G(0^+)/v_0 \) corresponding to the value of \( B_{\text{calc.}} \) determined above. This plot is shown in Figure A.2. From Figures A.1 and A.2, \( B_{\text{calc.}} = 1.0637 \) and \( G(1^+)/v_0 - G(0^+)/v_0 \approx 0.735076 \).

The value of \( v_0 \) is then calculated from the identity

\[
v_0 = \frac{G(1^+) - G(0^0)}{G(1^+)/v_0 - G(0^+)/v_0} = \frac{1372.6}{0.735076} = 1867.6 \tag{a.7}
\]

With the aid of \( v_0 \) previously determined, the barrier height \( b \) is given by

\[
b = b_0 v_0 = 1.0637 \times 1867.6 = 1988.57 \text{ cm}^{-1} \tag{a.8}
\]

The energy levels may then be calculated using the tables provided by Coon. The resulting double-minimum potential well with the first four calculated levels is given in Figure A.3.
The two minima of the potential well are located at \( Q_0 \) where

\[
Q_0^2 = \frac{2 \hbar B}{e^2 - p - 1} \frac{h}{4 \nu_0^2 c \nu_0}
\] (a.9)

Substituting \( p = 0.6, B = 1.0657 \) and \( \nu_0 = 1867.6 \text{ cm}^{-1} \) into (a.9) gives

\[ Q_0^2 = 0.1722 \times 10^{-40} \text{ g cm}^2. \]

For small displacements the kinetic energy is given by \( 2T = \mu r^2 \) where

\[
\mu = \frac{2mM}{2m \sin^2 \alpha + M}
\] (a.10)

and \( m \) and \( M \) are the mass of the oxygen and selenium atom, respectively. \( \alpha \) is the 0-Se-0 bond angle in the excited state (101.0°). Substitution of \( m = 15.99491 \text{ g}, M = 77.9173 \) and \( \sin 101^\circ = 0.7716 \) into Equation gives \( \mu = 25.706 \text{ g}. \)

Therefore, using \( 2T = Q^2 \) and setting \( Q = Q_0 \) we have

\[
Q_0^2 = \mu r_0^2
\] (a.11)

Insertion of \( Q_0 = 0.1722 \times 10^{-40} \text{ g cm}^2 \) and \( \mu = 25.706 \text{ g} \) into (a.11) gives \( r_0 = 0.0818 \text{ Å}. \)

Therefore in certain vibronic levels involving \( v_0 \), the equilibrium geometry of SeO\(_2\) is asymmetric with bond lengths \( r_{\text{sym}} \pm 0.0818 \text{ Å} \) where \( r_{\text{sym}} \) is the equilibrium bond lengths of the symmetric structure.

From a rotational band contour analysis of the \( 1^3 \) vibronic band, assuming a symmetric structure, the equilibrium bond length of SeO\(_2\) in this vibronic level was found to be 1.74 Å. Therefore at the potential minima along \( Q_3 \) of the excited \( 1^3 \text{B}_2 \) electronic state of SeO\(_2\) the bond lengths are approximately 1.74 ± 0.032 Å.
\[
\frac{C(1^\circ)_{/0}}{C(0^\circ)_{/0}} / \frac{C(0^\circ)_{/0}}{C(0^\circ)_{/0}} - C(0^\circ)_{/0} = 17.397 \text{ using the double-minimum potential levels provided by Coon}^{35}
\]
Figure A.2.2. Determination of the value of $\frac{c(1)}{\nu_0} - \frac{c(\sigma)}{\nu_0}$ corresponding to $\beta_{cal} = 1.04$ with the aid of the energy levels by coon.
Figure A.2.5 The double-minimum potential in the antisymmetric stretching coordinate of the \( ^3\Sigma^+ \) excited state of \( \text{Se}^{78}\text{O}_{16} \). The value of \( C(0^\circ) = 897.0 \text{ cm}^{-1} \).
APPENDIX III

Energy of Sub-Band Origins and ν Versus Kp Plots for $^{78}O_2$ and $^{80}O_2$ Molecules

Table A.3.1

K numbering for sub-band origins of the $^3_0$ vibronic band of $^{78}O_2$, assuming the transition is polarized parallel to the top axis.

<table>
<thead>
<tr>
<th>K''</th>
<th>ν (Experimental) cm⁻¹</th>
<th>ν (Calculated) cm⁻¹</th>
<th>Deviation (cm⁻¹)</th>
</tr>
</thead>
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<tr>
<td>8</td>
<td>33798.813</td>
<td>33798.768</td>
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<tr>
<td>9</td>
<td>33793.710</td>
<td>33793.703</td>
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<tr>
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<td>33788.042</td>
<td>33788.055</td>
<td>0.013</td>
</tr>
<tr>
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<td>33781.729</td>
<td>33781.807</td>
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<tr>
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<td>33774.866</td>
<td>33774.965</td>
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<tr>
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<td>33741.664</td>
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</table>

AIII.1
Table A.5.2

K numbering for sub-band origins of the $1^3_0$ vibronic band of Se$_{80.0_{16}}$,
assuming the transition is polarized parallel to the top axis.

<table>
<thead>
<tr>
<th>$k''$</th>
<th>$\nu$ (Experimental) cm$^{-1}$</th>
<th>$\nu$ (Calculated) cm$^{-1}$</th>
<th>Deviation (cm$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>8</td>
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<td>0.259</td>
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</table>
Figure A.34. Plot of peak branch head separation (Δν) against $K_p$ for the 10$^{th}$ vibronic band of $SO_2·CO_2$. From a least square fit of the above points the intercept is found to be 0.046.
Figure A.5.2: Plot of & Baudin head separation (Δv) against kuper for the 16 vibronic band of \( \text{SO}_2 \). From a least square fit of the above points the intercept is found to be 0.284.