DEDICATION

To my father and to my mother,
To Carmel and Aldona,
who have given me so much,
I dedicate this thesis.

"As we will all ultimately be judged, yet as the years pass we must surely judge ourselves."

Robert F. Kennedy
(1925-1968)
in "To Seek a Newer World"

"And to paraphrase that Irishman (Shaw) 'Old men dream dreams of things that were and say "Why?", but young men dream dreams of things that never were and say "Why not?"' Let us always have the spirit of young men."

John F. Kennedy
(1917-1963)
from a speech delivered to Dail Éireann June 1963
THE ELECTRONIC SPECTRA OF $S_2O$
THE ELECTRONIC SPECTRA

OF $S_2O$

by

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SCOPE AND CONTENTS:

Three electronic absorption systems of the S\textsubscript{2}O molecule, each having discrete vibrational structure, were observed in the spectral region 2000 - 7400 Å. Long pressure path lengths were used to observe very weak absorption bands. Two of these spectral systems have not been observed previously. Vibrational analyses of the spectral systems were made. The quasilinear character of the ground electronic state of S\textsubscript{2}O has been established.
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CHAPTER 1
Introduction

In this thesis the quantum mechanical structure and geometry of some of the energy states of the \( \text{S}_2\text{O} \) molecule will be discussed. The structural information was obtained by absorption spectroscopy of the \( \text{S}_2\text{O} \) molecule in the gas phase. In the first chapter of this thesis basic ideas, which are generally applicable to non-interacting isolated molecules in the gas phase and which are relevant to the discussion later in the thesis, will be summarised.

SECTION A: The Schrodinger Eqns. for Molecules


A molecule is a system of electrons and nuclei, in which the nuclei are separated by distances of the order of \( 10^{-7} - 10^{-8} \) cms. Quantum mechanics must be used in determining the properties of a molecule. Classical mechanics was used initially in explaining some of the properties of molecules. Much of the terminology used in classical mechanics is retained in the quantum mechanical description of molecules.
The quantum mechanical properties of an isolated molecule in its stationary states are obtained by solving the Schrödinger Equation,

\[
(\hat{H} - E^{(m)}) |\psi^{(m)}\rangle = 0,
\]

Eqn. 1.1

where \(E^{(m)}\) is the \(n^{th}\) energy eigenvalue associated with \(|\psi^{(m)}\rangle\), which is the eigenfunction of the \(m^{th}\) energy state is the Hamiltonian operator corresponding to the total energy of the electrons and nuclei.

The operator form of \(\hat{H}\) is normally described in coordinate representation rather than in momentum representation.

If spin and relativistic effects are ignored, the sum of the kinetic (\(T\)) and potential (\(V\)) energies, in a system in which energy is conserved, is given by (References (1) and (2)).

\[
\hat{H} = \hat{T} + \hat{V}
\]

\[
= -\frac{\hbar^2}{2} \left[ \sum_k \frac{1}{M_k} \nabla_k^2 + \sum_i \frac{\hbar^2}{m_e} \nabla_i^2 \right] + \sum_{k \geq 1} \sum_{k, l} \frac{z_k z_1 e^2}{r_{kl}} + \sum_{k \geq 1} \sum_{i} \frac{z_k e^2}{r_{ki}} + \sum_{i, j} \frac{e^2}{r_{ij}},
\]

Eqn. 1.2

where \(M_k\) denotes the mass of the \(k^{th}\) nucleus,

\(m_e\) denotes the mass of the electron,

\(\nabla_k^2\) is the Laplacian in which differentiation is with respect to nuclear coordinates,
\[ \nabla_i^2 \] is the Laplacian in which differentiation is
with respect to electron coordinates,
e is the electronic charge, and
\[ Z_k \] and \[ Z_j \] are the electronic charges on the \( k^{th} \) and
\( j^{th} \) nuclei respectively.

\( r_{kl}, r_{ki} \) and \( r_{ij} \) are the distances between
the \( k^{th} \) and \( l^{th} \) nuclei,
the \( k^{th} \) nucleus and the \( i^{th} \) electron, and between
the \( i^{th} \) and \( j^{th} \) electrons respectively.

\( (\hat{H} - E(m)) \mid \psi(m) \rangle = 0 \) is the equation for the
many body problem, which, in general, cannot be solved
exactly. The simplest type of molecule is the three body
molecule of the type \( H_2^+ (3)(4) \).

1.A.2. The \( H_2^+ \) molecule.

An algebraic solution of the Schrödinger
equation for the \( H_2^+ \) molecule is obtained in two steps.
The equation is first solved for fixed internuclear
distances \( R \). The solution yields energy eigenvalues \( U(m) \).
Each \( U(m) \) is the sum of both the potential energy of inter-
nuclear repulsion and of the potential and kinetic energy
of electronic motion about rigidly clamped nuclei.
Consequently each energy eigenvalue \( U(m) \) is a function of
\( R \) - the internuclear distance. This equation is solved
separately for all values of \( R \). The graph of \( U(R) \)
against \( R \) is called a potential curve. Potential curves
for stable and unstable electronic states are illustrated in Fig. 1.1 on page 5. The dissociation energies of the electronic states are also indicated.

The second step in the solution of the Schrödinger equation is the solution of the equation

\[ \left( \hat{T}_{\text{nuc}} + U(R) \right) - E_{\text{nuc}}^{(m)} \right| \Psi_{\text{nuc}}^{(m)} > = 0, \quad \text{Eqn. 1.3} \]

where \( \hat{T}_{\text{nuc}} \) is the kinetic energy of nuclear motion (unclamped nuclei),

\( U(R) \) is the potential function as defined in the previous paragraph,

\( E_{\text{nuc}}^{(m)} \) is the \( m \)th energy eigenvalue of the nuclear motion corresponding to

\( |\Psi_{\text{nuc}}^{(m)} > \) the eigenfunction describing the nuclear motion in the \( m \)th state.

This procedure is equivalent to factorising the wave function

\[ |\Psi_{\text{total}}^{(m)} >, \quad \text{which describes all the properties of the} \]

\( m \)th eigenstate of the molecule,

\[ |\Psi_{\text{total}}^{(m)} > = |\Psi_{\text{elect}}^{(m)} > |\Psi_{\text{nuc}}^{(m)} >, \quad \text{Eqn. 1.4(a)} \]

where \( |\Psi_{\text{elect}}^{(m)} > \) describes only the electronic motion in the \( m \)th eigenstate

and \( |\Psi_{\text{nuc}}^{(m)} > \) was previously defined.

The factorisation is equivalent to forming the sums

\[ \hat{\mathcal{H}}_{\text{total}} = \hat{\mathcal{H}}_{\text{elect}} + \hat{\mathcal{H}}_{\text{nuc}} \quad \text{Eqn. 1.4(b)} \]
(1) and (3) are potential curves for stable electronic states. The dissociation energies are $D_e(1)$ and $D_e(3)$.

(2) is the potential curve for an unstable electronic state. The dissociation energy, $D_e(2)$, is zero.
and

\[ \hat{\Psi}_{\text{total}} = \hat{\Psi}_{\text{elect.}} + \hat{\Psi}_{\text{nuc}} \]

\[ E_{\text{total}} = E_{\text{elect.}} + E_{\text{nuc}} \quad \text{Eqn. 1.5(c)} \]

In this procedure, it is assumed that there are no interactions between electronic and nuclear motions.


In molecular problems, where an exact analytical solution of the Schrodinger Equation is not possible, an approximate solution is obtained by assuming that

\[ |\Psi_{\text{total}}\rangle = |\Psi_{\text{elect.}}\rangle |\Psi_{\text{nuclear}}\rangle |\Psi_{\text{nuclear}}\rangle, \quad \text{Eqn. 1.5(a)} \]

\[ \hat{H}_{\text{total}} = \hat{H}_{\text{elect.}} + \hat{H}_{\text{nuclear}} \quad \text{Eqn. 1.5(b)} \]

and

\[ E_{\text{total}} = E_{\text{elect.}} + E_{\text{nuclear}} + E_{\text{nuclear}} \quad \text{Eqn. 1.5(c)} \]

Born and Oppenheimer (5) (and, recently, Liehr (6)) have outlined the conditions under which the separation process of Eqn. 1.5 is valid.

Let

\[ \chi = \left( \frac{m_e}{\bar{m}_k} \right)^{\frac{1}{2}} \]

where \( \bar{m}_k \) is the average mass of the nuclei and \( m_e \) is the electronic mass.

* For convenience, the superscript \( (m) \) will be omitted in the rest of the discussion.
In references (5) and (6) \( \psi_{\text{total}} \) is expanded in a power series in \( \chi \), and the domain of validity of the separation process in Eqn. 1.5 is established.*

SECTION B. Group Theory

1.B.1. Introduction.

Detailed treatments of group theoretical concepts and of the application of these concepts to molecular physics are given in the literature (1)(2)(3)(7)(8)(9)(10)(11)(12). Only those concepts relevant to the subject matter of this thesis will be summarised here. The Schönflies notation will be used. The group of symmetry elements describing the symmetry properties of a molecule all intersect at a common point and form the point group to which that molecule belongs.

The group character tables for all the representations for the point groups of interest in this thesis are given in Table 1.1. The character under the identity operator \( E \) is \( N \) for an \( N \)-fold degenerate representation. The representations \( \Gamma \) span a representation space and are mutually orthogonal.

* Most text books, however, refer to Eqn. 1.4, rather than to Eqn. 1.5, as the Born Oppenheimer Approximation.
Thus

\[ (\Gamma_i | \hat{O} | \Gamma_j) = 6_{ij}(\text{const}), \]

if \( \hat{O} \) is any operator which is totally symmetric with respect to all the symmetry elements of the group. If the point group is Abelian, i.e., all the operators commute, then all representations \( \Gamma \) are non-degenerate.

When the Born Oppenheimer Approximation is used three Schrödinger Equations must be solved

\[
(\hat{\mathcal{H}}_{\text{elect.}} - E_{\text{elect.}}) | \Psi_{\text{el.}} \rangle = 0 \quad \text{Eqn. 1.6(a)}
\]

\[
(\hat{\mathcal{H}}_{\text{vib.}} - E_{\text{vib.}}) | \Psi_{\text{vib.}} \rangle = 0 \quad \text{Eqn. 1.6(b)}
\]

\[
(\hat{\mathcal{H}}_{\text{rot.}} - E_{\text{rotation}}) | \Psi_{\text{rot.}} \rangle = 0 \quad \text{Eqn. 1.6(c)}
\]

Group theory requires that the wave functions \( | \Psi_{\text{elect.}} \rangle \) and \( | \Psi_{\text{vib.}} \rangle \) transform as an irreducible representation of the molecular point group, defined by the geometrical configuration of the nuclei in their equilibrium positions. \( | \Psi_{\text{rot.}} \rangle \) must transform as an irreducible representation of the point group describing the momental ellipsoid of the molecule.

The symmetry elements of linear triatomic molecules form the point groups \( D_{\infty h} \) and \( C_{\infty v} \). In the former point group an operator for inversion through the centre of symmetry is present. This inversion operator is absent
in the $C_{\infty v}$ point group. When a linear triatomic molecule is bent, the symmetry elements associated with the equilibrium geometrical configurations of the nuclei define the point groups $C_{2v}$ and $C_s$, corresponding to the point groups $D_{\infty h}$ and $C_{\infty v}$ in the linear conformations, respectively.

When the nuclei in a molecule can assume more than one equilibrium geometrical configuration and can easily move from one configuration to another, the molecule is said to be non rigid. The group theory of non-rigid molecules has been discussed by Longuet-Higgins(13), Watson(16), and Hougen(15) and Altman(16).

An asymmetric top is defined as a rotating object in which the three mutually-perpendicular moments of inertia of the object, $I_a$, $I_b$, and $I_c$, are all unequal. If $I_b = I_a > I_c$, the rotating object is called an oblate symmetric top. If $I_b = I_c < I_a$, the rotating object is called a prolate symmetric top. The rotational wave functions for an asymmetric top transform as the irreducible representations of the point group $D_2$. The rotational wave functions for a symmetric top transform as the irreducible representations of the point group $D_{\infty z}$. The group character tables of the point groups $C_{2v}$ and $D_2$ are isomorphous, as are the point groups $C_{\infty v}$ and $D_{\infty z}$. The group character tables of all the point groups mentioned here are given in Appendix 1.
1.B.2. Direct Products of Representations.

When a product of any function is taken the symmetry of the product function is determined, simply, from group theoretical arguments. Consideration will be given here only to the decomposition of direct products of representations into symmetric and antisymmetric products. The expression of point groups as semi-direct products of point groups will also be outlined.

Discussions of direct products of representations and their decomposition into symmetric and antisymmetric parts are given by Hammermesh (8), Landau and Lifschitz (9), and Wilson, Decius and Cross (12). Let \( \chi(G) \) represent the character for each element in the group \( G \). If there are two sets of \( \mathcal{N} \) fold degenerate wave functions, \( \psi_i \) and \( \phi_j \), which transform as the same representation \( \Gamma \) of the point group \( G \), then the direct product \( \Gamma \otimes \Gamma \) gives a representation of dimension \( \mathcal{N}^2 \). This reducible representation contains \( \mathcal{N}(\mathcal{N}+1) \) representations for symmetric wave function products of the type

\[
\psi_i \phi_j + \psi_j \phi_i
\]

and \( \mathcal{N}(\mathcal{N}-1) \) representations of the antisymmetric products of the type

\[
\psi_i \phi_j - \psi_j \phi_i
\]
For non-degenerate wave functions \( N = 1 \) and only the symmetric direct product can be formed.

The characters of the symmetric product are

\[
[\chi^2](G) = \frac{1}{2} \left\{ [\chi(G)]^2 + \chi(G^2) \right\}
\]

Eqn. 1.7(a)

The characters of the antisymmetric product are

\[
[\chi^2](G) = \frac{1}{2} \left\{ [\chi(G)]^2 - \chi(G^2) \right\}
\]

Eqn. 1.7(b)

Tables of double symmetric and antisymmetric direct products for various point groups are given in Table 57 of Herzberg (1) Vol. III.

Semi-direct products have been defined by Lomont (10) and by Altman* (16)(17)(18). The semidirect product is denoted by a \( \wedge \) sign. The concept of semidirect products has recently been used by Altman (18) to describe the point groups of non-rigid molecules.

* Definition of semidirect product as given in (16):
If two groups \( N \) and \( C \) are such that any element \( N_i \) of one group commutes with any element \( C_j \) of the other group

\( N_i C_j = C_j N_i \)

their group product (i.e., the set of all elements of the form \( N_i C_j \)) forms the group \( G \) which is the direct product of \( N \) and \( C \)

\( N \times C = G. \)

On the other hand if \( N \) and \( C \) do not commute in detail but rather

\( N C_j = C_j N \) for all \( C_j \in N \),

then the group product forms a group which is called the semidirect product of \( N \) and \( C \)

\( N \wedge C. \)

A triatomic molecule may have a linear or bent conformation. By the adiabatic principle the wave functions and energies of the eigenstates of molecule in the linear conformation must correlate with those of the same molecule in the bent conformation as the bond angle at the central atom is changed. The irreducible representations of the point groups of the linear and bent conformations of a molecule must also correlate, since the wave functions transform as these irreducible representations. The resolution of species of symmetric point groups into those of point groups of lower symmetry are given in Herzberg (2) Tables 55, 56, 57 and 58.


The spin wave function of a single electron \( |\text{spin} \, \frac{1}{2} \rangle \) exhibits a double degeneracy with respect to the time reversal operator. This double degeneracy is called a Kramers doublet. If \( \hat{R} \) is an operator which rotates the spin wave function through \( 2 \pi \), then

\[
\hat{R} |\text{spin} \, \pm \frac{1}{2} \rangle = - |\text{spin} \, \pm \frac{1}{2} \rangle
\]

Therefore \( \hat{R}^2 \), or rotation through \( 4 \pi \), is the equivalent of the identity operator. Thus, for a system with an unpaired electron, double groups as introduced by Bethe, must be used. The resolution of spin symmetry species
of the full rotation point group into the corresponding symmetry species of point groups of lower symmetry are given in Tables 55, 56, and 57 of Herzberg (2) Vol. III.

SECTION C: Electronic, Vibrational and Rotational Energy Terms.


From the work of Hund and Mulliken, the idea of individual electronic molecular orbitals, analogous to atomic orbitals, was developed. The electronic structure of a molecule was "built up" by feeding in electrons into such orbitals, in accordance with the Pauli Exclusion Principle. This procedure is called the Aufbau Prinzip. Exact analytical expressions for molecular orbital wave functions can be determined only for molecules like \( \text{H}_2^+ \). Approximate molecular orbital wave functions, for molecules where the Schrodinger equation cannot be solved exactly, are usually obtained by the L.C.A.O. method. The physical basis for this method is outlined below.

The Fourier theorem states that any arbitrary function \( \Psi \), which obeys the Dirichlet conditions**, can

* Linear combination of atomic orbitals.

** A function \( \Psi \) obeys the Dirichlet conditions if it is single valued, continuous, except for a finite number of discontinuities, and has a finite number of maxima and minima.
be expanded as a linear combination of any complete set of functions.

\[ \forall = \sum_{n=1}^{\infty} c_n \Phi_n \]

Every physically acceptable molecular orbital wave function obeys Dirichlet's conditions and so can be expanded

\[ |\forall > = \sum_{n=1}^{\infty} c_n |\Phi_n > \]  \hspace{1cm} \text{Eqn. 1.8}

where \( |\Phi_n > \) is any complete set of functions. Normally the set \( |\Phi_n > \) is the set of atomic orbital wave functions. It is found that a very good approximation to \( |\forall_{mol} > \) of the molecular orbital can be obtained by taking a linear combination of a small number of atomic orbital wave functions of appropriate symmetry; each atomic orbital wave function being localised on one of the nuclei in the molecule.

Each molecular orbital is designated by a number \( n \) and the symmetry of the wave function of the molecular orbital \( |ns > \). The number \( n \) is assigned empirically and indicates the relative energies of molecular orbitals of the same symmetry (e.g. the \( 3\pi \) orbital lies higher in energy than the \( 2\pi \) orbital, etc.).

The molecular wave functions of molecular orbitals which are completely filled with electrons, in accordance with the Pauli principle, transform as the totally symmetric
representations of the point group of the molecule. It is
assumed that the core atomic orbitals play very little part
in determining the properties of the molecule, and can
be considered as remaining as atomic orbitals centered
around each nucleus. Only the valence electrons of each
atom are considered as contributing to the formation of
molecular orbitals. Since the core electron atomic
orbitals, or the molecular orbitals formed from them, remain
filled with electrons in all the molecular states con­
sidered here, the symmetry of the total electronic wave
function is determined from those molecular orbitals
formed by a linear combination of the valence electrons
of the atoms of which the molecule is composed.


Energies of molecular orbitals and electronic
states are generally calculated by the Hartree Fock Self
Consistent Field method. This method is based on a process
of iteration of the approximations to the eigenfunctions
of the Schrodinger Equation, which lead to a minimisation
of the total energy, until self consistency is achieved
in the solution. This is called an L.C.A.O./S.C.F./M.O.
calculation if a linear combination of atomic orbital wave
functions was used as the initial approximation to the
molecular orbital wave function. The method of the
Hartree Fock calculation is dealt with extensively in the
If $|\psi_a\rangle$ and $|\psi_b\rangle$ are molecular orbital wave functions of the same molecule, but which transform as different irreducible representations of the molecular point group then all matrix elements

$$<\psi_a | \hat{H} | \psi_b> = 0 \quad \text{Eqn. 1.9}$$

This fact produces a great simplification in Hartree Fock Energy Calculations, since it eliminates many of the off-diagonal elements in the determinental equations that have to be solved.


Every molecule containing $N$ nuclei has $3N$ degrees of freedom of displacement. In a linear molecule five of these degrees of freedom, and in a non linear molecule six of these degrees of freedom are associated with translation and rotation of the molecule as a whole. Therefore there are $(3N-5)$ for a linear molecule and $(3N-6)$ for a non linear molecule degrees of freedom associated with the internal vibratory motions of the nuclei in the molecule.

Internal vibratory motions of polyatomic molecules are analysed into motions along separate normal coordinates and are identified by energy and symmetry. The theory of normal coordinate analysis is dealt with extensively in
the literature, especially (1)(2)(12).

Cartesian displacement coordinates, derived by linear transformation from normal coordinates, are frequently used to graphically depict normal vibrations. Fig. 1.2 shows the normal modes of vibration of molecules belonging to the point groups $C_\infty v$ and $C_s$, since these apply to the $S_2O$ molecule. The symmetry of a vibration is determined by applying the symmetry operations of the point group of the molecule to the schematic displacement vectors as shown in Fig. 1.2.

Simple normal coordinate analysis, in the harmonic approximation, requires that matrix elements

$$\langle \Psi(\nu_i) | \hat{H} | \Psi(\nu_j) \rangle = E_i \delta_{ij} \quad \text{Eqn. 1.10}$$

i.e., the normal vibrations do not interact. However this is no longer true in a higher approximation; for example the interaction of the bending vibration mode $\nu_2$ with the symmetric stretching mode $\nu_3$ in the ground electronic state of $S_2O$ is considered as in Chapter 4.

When several quanta of the same normal vibration are excited the symmetric direct product of the representations generated by the wave functions of the normal vibrations must be taken in order to determine the symmetry of the resultant vibrational state. This product differs from the ordinary direct product only when degenerate vibrational wave functions are involved. The
**Fig. 1.2 Normal Modes of Vibration**

<table>
<thead>
<tr>
<th>Point Group</th>
<th>Symmetry</th>
<th>Mode</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_\infty v$</td>
<td>$\sigma^+$</td>
<td>$\nu_1$</td>
<td>Non-degenerate symmetric stretching vibration</td>
</tr>
<tr>
<td>$\Pi$</td>
<td>$\nu_2$</td>
<td>Doubly degenerate symmetric bending vibration</td>
<td></td>
</tr>
<tr>
<td>$\sigma^+$</td>
<td>$\nu_3$</td>
<td>Non-degenerate symmetric stretching vibration</td>
<td></td>
</tr>
</tbody>
</table>

$h\nu_1 > h\nu_3$

<table>
<thead>
<tr>
<th>Point Group</th>
<th>Symmetry</th>
<th>Mode</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_s$</td>
<td>$a'$</td>
<td>$\nu_1$</td>
<td>Non-degenerate symmetric stretching vibration</td>
</tr>
<tr>
<td>$a'$</td>
<td>$\nu_2$</td>
<td>Non-degenerate symmetric bending vibration</td>
<td></td>
</tr>
<tr>
<td>$a'$</td>
<td>$\nu_3$</td>
<td>Non-degenerate symmetric stretching vibration</td>
<td></td>
</tr>
</tbody>
</table>

Schematic Vector Displacements (in Cartesian Coordinates) representing normal vibrations
symmetries of the product wave functions are listed in Herzberg (2) and in Wilson, Decius and Cross (12).


Potential curves as in Fig. 1.1 can be represented by analytic formula such as

\[
U(R) = \frac{1}{2}k(R-R_0)^2 + \text{terms of higher order in } (R-R_0)
\]

Eqn. 1.12

In normal coordinate analysis a harmonic force field for nuclear motion, is assumed and terms in \((R-R_0)\) of higher order than \((R-R_0)^2\) are ignored. The solution of the simple harmonic oscillator problem is well known and leads to

\[
E_{vib}(v_1, v_2, \ldots, v_3) = \sum_i h \omega_i (v_i + \frac{d_i}{2})
\]

Eqn. 1.13

where \(v_i\) is the number of quanta of the \(i^{th}\) vibration excited; \(h \omega_i\) is the energy of excitation of one quantum of normal vibrational motion of frequency \(\omega_i\), and \(d_i\) is the degeneracy of the \(i^{th}\) vibrational wave function. Thus in the simple harmonic oscillator approximation the energy difference between adjacent vibrational energy levels is constant.

In a linear triatomic molecule the degenerate vibrational wave function of the bending vibrational mode, \(v_2\), has a vibrational angular momentum associated with it. The
magnitude of this vibrational angular momentum is $\ell \hbar$ where

$$\ell = v_2, v_2^{-2}, v_2^{-4}, \ldots, 1 \text{ or } 0.$$ 


If terms in Eqn. 1.12 of higher order in $(R-R_0)$ than $(R-R_0)^2$ are treated as a perturbation to the simple harmonic oscillator the vibrational energies are given by an expression of the form

$$E_{\text{vib}}(v_1, v_2, v_3 \ldots) = \sum_i \hbar \omega_i(v_i + \frac{d_i}{2}) + \sum_{i,k} x_{ik}(v_i + \frac{d_i}{2})(v_k + \frac{d_k}{2})$$

$$+ \sum_{i,k} g_{ik} l_i l_k + \ldots \text{ other terms}$$

Eqn. 1.14

where $x_{ik}$ and $g_{ik}$ are anharmonicity constants.

For anharmonic vibrations the vibrational wave functions are not orthogonal, as in harmonic vibrations. Eqn. 1.10 does not hold and there is interaction between the "normal" modes of vibration* of the molecule.

When $\partial^3 U(R)/\partial R^3$ is $< 0$ the anharmonicity constant $x_{ik}$ is negative. The energy difference between

---

*The term normal mode of vibration can be applied only to harmonic vibrations. It is commonly used also in the description of anharmonic vibrations.
consecutive vibrational energy levels decreases with increasing quantum number of the vibrational energy levels being considered.

If \( \partial^3 U(R)/\partial^3 R \) is > 0, the anharmonicity constants are positive and the energy difference between consecutive vibrational energy levels increases with increasing quantum number of the vibrational energy levels being considered. The effects of anharmonicity on vibrational energy level patterns are shown in Fig. 1.3 for negative, zero and positive anharmonicity effects. Negative anharmonicity is normally observed in the vibrational energy level pattern of polyatomic molecule, while positive anharmonicity effects are rarely observed. The vibrational structures of the electronic spectra of the \( \text{S}_2\text{O} \) molecule contain striking examples of both negative and positive anharmonicity effects.


Consider a bent triatomic molecule of the type \( \text{BAA}^* \), where \( A \) and \( A^* \) are the same atomic species and the \( ^* \) just used for identification. If the bending vibration \( \nu_2 \) has, classically, a large amplitude of vibration then the transition

\[
\text{B} \quad \text{A} \to \text{A}^* \to \text{A} \quad \text{A}^* \to \text{B}
\]
Anharmonic oscillator energy levels when
\[ \frac{\partial^3 U(R)}{\partial^3 R} < 0 \]
i.e. negative anharmonicity

Harmonic oscillator energy levels, which are equally spaced. There are no anharmonic effects.
\[ \frac{\partial^3 U(R)}{\partial^3 R} = 0 \]

Anharmonic oscillator energy levels when
\[ \frac{\partial^3 U(R)}{\partial^3 R} > 0 \]
i.e. positive anharmonicity

Fig. 1.3
may occur. This transition is classified as an isodynamic operation (18). If this isodynamic operation is feasible, the vibrational wave functions will transform, not as the irreducible representations of the point group $C_s$, but as the irreducible representations of the point group $G_4^*$, which is isomorphous with the point groups $C_{2v}$, $C_{2h}$ etc. If this isodynamic operation is feasible, there will be a doubling of each vibrational energy level with respect to the vibrational energy level pattern obtained when the isodynamic operation is not feasible (23). The energy splitting between the doublets of vibrational energy levels can be treated by the same mathematical procedure as is used for the inversion doublets of the NH$_3$ molecule (18).

1.C.7. Rotational Energy Terms in Polyatomic Molecules.

A detailed rotational analysis of the vibrational bands of the electronic spectra of S$_2$O could not be achieved. Therefore this discussion of rotational energy terms contains only the material relevant to the subject matter of the thesis.

The simple theory of molecular rotation is based on the theory of the rigid rotator. In this theory the rotational energy levels of a polyatomic molecule are

\[ G_4 = C_s \wedge C_s \]
completely determined by the three principle moments of
inertia \( I_a \), \( I_b \), \( I_c \). These moments of inertia are
calculated from the bond lengths and bond angles of the
polyatomic molecule.

Four angular momentum quantum numbers are used
in characterising the energy states of the rotating
molecule.

\( J \) is the quantum number for the total angular momentum
of the molecule \( \hbar \sqrt{J(J+1)} \).

\( M_h \) is the projection of the total angular momentum along
the \( Z \) axis of a laboratory fixed coordinate system.

\( K_h \) is the projection of the total angular momentum along
the \( z \) axis (determined by \( I_a \)) in the molecule fixed
coordinate system, and

\( S \) is the quantum number for the angular momentum associated
with electron spin \( \hbar \sqrt{S(S+1)} \).

The Hamiltonian of the rigid rotor is

\[
\hat{H} = J_x^2 / 2I_x + J_y^2 / 2I_y + J_z^2 / 2I_z
\]

Eqn. 1.15

where \( xyz \) is a molecule fixed coordinate system and
\( I_z \ll I_y \ll I_x \). As shown in the literature, especially (11)
(24) and (25), the only non-vanishing matrix elements in
the rotational Hamiltonian in matrix form are

\[
\langle J,K | \hat{H} | J,K \rangle = \hbar^2 / 4 \left\{ \frac{1}{I_x} + \frac{1}{I_y} \right\} \left\{ (J)(J+1) - K^2 \right\} + \frac{\hbar^2}{2I_z} K^2
\]

Eqn. 1.16(a)
and
\[ \langle J, K \pm 2 | \hat{H} | J, K \rangle = -\frac{\hbar^2}{4} \left( \frac{1}{I_x} - \frac{1}{I_y} \right) \left\{ (J)(J+1) - (K)(K+1) \right\}^{\frac{1}{2}} \]
\[ \times \left\{ (J)(J+1) - (K\pm1)(K\pm2) \right\}^{\frac{1}{2}} \]

Eqn. 1.16(b)

Let \( \hbar^2/2I_z = A; \hbar^2/2I_x = B \) and \( \hbar^2/2I_y = C \).

An asymmetry parameter \( \chi \) was introduced by Ray

\[ \chi = (2B - A - C)/(A - C) \]

Eqn. 1.17

For prolate and oblate symmetric tops, \( \chi \) has the limiting values of -1.0 and +1.0 respectively and has intermediate values for asymmetric tops of Fig. 1.4.

In the simple case of a prolate symmetric top \( B=C \) and the non-diagonal matrix elements of Eqn. 1.16(b) vanish. Only the diagonal elements are non-zero and give

\[ E_{\text{rot}}(J) = B(J)(J+1) + (A-B)K^2 \]

Eqn. 1.18

In a linear molecule, the rotational degree of freedom about the z axis, which occurs in a bent molecule, has been transformed into a vibrational degree of freedom. \( I_z \) is a physically meaningless quantity for a linear molecule if the nuclei are point masses, and if the electronic masses are ignored. So, for a linear molecule, in the rigid rotor approximation,
\[ E_{\text{rot}}(J) = B (J)(J+1) - K^2 \] \hspace{1cm} \text{Eqn. 1.19}

If rotation-vibration interactions are taken into account, centrifugal distortion energy terms of the form

\[ D_J(J)^2(J+1)^2 + D_{JK}(J)(J+1)K^2 + D_KK^4 \] \hspace{1cm} \text{Eqn. 1.20}

are added to Eqns. 1.18, 1.19. The D's are called centrifugal distortion constants. The energy terms in Eqn. 1.20 are of large magnitude in quasi linear electronic states where rotation-vibration interactions are very large. The structure of quasilinear states is discussed in detail in Chapter 3, Section D rather than in this general introductory chapter.

In symmetric top wave functions with \( K > 0 \), there is a double degeneracy with respect to the quantum number \( K \). By the adiabatic principle, the energy levels of prolate and oblate symmetric tops must correlate. This correlation is shown in Fig. 1.4. For asymmetric tops the degeneracy with respect to \( K \) is absent, and the rotational energy level pattern is more complex than the corresponding pattern for symmetric tops.

1.C.8. Summary of ideas in Section C.

Section C of this chapter dealt with the solution of the Schrödinger eqns. given in Eqn. 1.6.

\[ (\hat{\mathcal{H}}_{el} - E_{el})|\psi_{el}\rangle = 0 \] \hspace{1cm} \text{Eqn. 1.6(a)}
FIG. 1.4 Correlation of rotational energy levels between prolate and oblate symmetric top limits. The intermediate asymmetric top levels are also shown.
\[ (\hat{\mathbf{H}}_{\text{vib}} - E_{\text{vib}}) | \psi_{\text{vib}} \rangle = 0 \quad \text{Eqn. 1.6(b)} \]

\[ (\hat{\mathbf{H}}_{\text{rot}} - E_{\text{rot}}) | \psi_{\text{rot}} \rangle = 0 \quad \text{Eqn. 1.6(c)} \]

If coupling between electronic, vibrational and rotational motions is zero, then

\[ E_{\text{total}} = E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}} \quad \text{Eqn. 1.5(c)} \]

If these couplings are non-zero, then there are additional energy expression in Eqn. 1.5(c). These energy corrections are normally introduced by means of perturbation theory, in which Eqns. 1.5 and 1.6 are taken as the zeroth order approximation.

So far, only the stationary state energy levels have been considered. Section D of this chapter will deal with transitions between these energy levels and with the relative probabilities of these transitions.

 SECTION D: Transitions Between Energy Levels

1. D.1. Introduction.

Transitions can occur between energy levels of a molecule through various radiative mechanisms, e.g. electric dipolar, electric quadrupolar, magnetic dipolar, etc. interactions with electromagnetic radiation. In this section electric dipolar radiative transitions will
be considered. A very brief discussion of electric quadrupolar radiative transitions will also be given. Electric dipolar radiative transitions are responsible for most of the spectroscopic transitions observed in molecules. The other radiative mechanisms give spectra of very low intensity and are rarely encountered. A spectral system of the \( \text{S}_2^0 \) molecule, which has very low intensity, is observed in the spectral region 4,400 Å - 6700 Å and may be due to a quadrupolar radiative mechanism.


The electric dipole operator \( \hat{A} \) is

\[
\hat{A} = e \cdot \hat{r}
\]

Eqn. 1.21

By use of the Born Oppenheimer Approximation, electronic and vibrational transitions are considered separately from transitions between rotational energy levels.

So

\[
|\psi_{\text{total}}\rangle = |\psi_{\text{el}}\rangle |\psi_{\text{nuc}}\rangle
\]

Eqn. 1.22(a)

and

\[
\hat{A}_{\text{tot}} = \hat{A}_{\text{el}} + \hat{A}_{\text{nuc}}
\]

Eqn. 1.22(b)

The transition moment, \( R_{\text{if}} \), between initial and final energy states is

\[
R_{\text{if}} = \langle \psi_{\text{tot}}^f | \hat{A}_{\text{tot}} | \psi_{\text{tot}}^i \rangle
\]

Eqn. 1.23(a)
\[
\begin{align*}
&= \langle \Psi_{\text{nuc}}^f | \Psi_{\text{nuc}}^i \rangle \langle \Psi_{\text{el}}^f | \hat{\Lambda}_{\text{el}} | \Psi_{\text{el}}^i \rangle \\
&\quad + \langle \Psi_{\text{nuc}}^f | \hat{\Lambda}_{\text{nuc}} | \Psi_{\text{nuc}}^i \rangle \langle \Psi_{\text{el}}^f | \Psi_{\text{el}}^i \rangle \\
&\quad \quad \text{Eqn. 1.23(b)}
\end{align*}
\]

But \( \langle \Psi_{\text{el}}^f | \Psi_{\text{el}}^i \rangle = \delta_{if} \) * 

So for \( R_{if} \neq 0 \) both

\[
\langle \Psi_{\text{el}}^f | \hat{\Lambda}_{\text{el}} | \Psi_{\text{el}}^i \rangle \neq 0 \quad \text{Eqn. 1.24(a)}
\]

and \( \langle \Psi_{\text{nuc}}^f | \hat{\Lambda}_{\text{nuc}} | \Psi_{\text{nuc}}^i \rangle \neq 0 \quad \text{Eqn. 1.24(b)} \)

For Eqns. 1.24(a) and (b) to be valid, group theory requires that the direct products of the representations

\[
\Gamma(\Psi_{\text{el}}^f) \otimes \Gamma(\hat{\Lambda}_{\text{el}}) \otimes \Gamma(\Psi_{\text{el}}^i)
\]

and \( \Gamma(\Psi_{\text{vib}}^f) \otimes \Gamma(\Psi_{\text{vib}}^i) \)

both, must contain the totally symmetric irreducible

* This is correct only when the equilibrium geometry of the molecule in the two electronic states is the same. It is usually a good approximation. Even when

\[
\langle \Psi_{\text{el}}^f | \hat{\Lambda}_{\text{el}} | \Psi_{\text{el}}^i \rangle = 0
\]

for symmetry reasons, then the non-zero value of the second can give "vibronically" allowed spectra.

The nuclear motion modifies the electronic wave functions and so leads to a breach of the Born-Oppenheimer Approximation.
representation of the point group of the molecule.

Therefore, if an allowed electric dipole transition occurs between the states i and f, the direct product of the representations

\[ \Gamma(\psi_e^f) \otimes \Gamma(\psi_e^i) \]

contains the representation according to which at least one of the translation vectors \( T_x, T_y \), or \( T_z \) transforms.

As can be seen from Table 1.1, no electronic transition in any molecule which belongs to the \( C_s \) point group is forbidden for symmetry reasons only. In molecules which belong to the \( C_{\infty v} \) point group,

\( T_z \) transforms as the irreducible representation \( \Sigma^+ \).
\( T_x \) and \( T_y \) transform as the irreducible doubly degenerate representation \( \Pi \).

In molecules which belong to the point group \( C_{\infty v} \), the only transitions allowed by an electric dipole radiation mechanism are therefore

\[ \Sigma^+ \leftrightarrow \Sigma^+, \Pi \quad \Sigma^- \leftrightarrow \Sigma^-, \Pi \]
\[ \Pi \leftrightarrow \Sigma^+, \Sigma^-, \Pi, \Delta \]

etc.

i.e., \( \Delta \wedge = 0^{\pm 1} \) Eqn. 1.25

(where \( \wedge \hbar \) is the projection of the electronic angular momentum along the internuclear axis of the molecule).
The electric quadrupole moment tensor is

\[ d_{ik} = \sum e(3r_ir_k - \delta_{ik} r^2) \]

If a transition occurs between two energy states through an electric quadrupolar mechanism, the direct product of the representations

\[ \Gamma(\psi_f^e) \otimes \Gamma(\psi_i^e) \]

contains the representation according to which at least one of \( T_x^2, T_y^2, T_z^2, T_xT_y, T_yT_z \) or \( T_zT_x \) transform. Electronic transitions with \( \Delta \Lambda = 0, \pm 1, \pm 2 \) are allowed, e.g., the transition \( \sum^+ \leftrightarrow \Delta \) is allowed.

The intensity of an electronic transition between two energy levels in absorption is

\[ I_{i\rightarrow f} = \text{const} (\nu) h^2 \]  

Eqn. 1.26

where \( h\nu \) is the energy difference between the two energy levels.


In an allowed electric dipolar transition it is required that

\[ \langle \psi^f_{vib} | \psi^i_{vib} \rangle \neq 0 \]  

Eqn. 1.27

When Eqn. 1.27 is satisfied, \( n \) quanta of totally symmetric but only \( 2n \) quanta of antisymmetric (where \( n \) is an integer)
normal vibrations are observed in the vibrational structure of the electronic spectrum. The expression \( \langle \psi^f_{\text{vib}} | \psi^i_{\text{vib}} \rangle \) is called the vibrational overlap integral.

For an allowed electric dipolar electronic transition, the quantity \( \langle \psi^f_{\text{el}} | \hat{M}_{\text{el}} | \psi^i_{\text{el}} \rangle \) is a constant and so the intensities of the vibrational frequencies are proportional to

\[
I_{v_f} \leftrightarrow v_i = \text{const} \ n_{fi} \left| \langle \psi^f_{\text{vib}} | \psi^i_{\text{vib}} \rangle \right|^2, \text{ Eqn. 1.28}
\]

where \( h n_{fi} = E_f - E_i \)

Eqn. 1.28 is the quantum mechanical basis for the mathematical expression of the Franck Condon Effect. This Effect is discussed in detail in Chapter 3, Section D with special reference to the electronic spectra of \( S_2O \).

In a quadratic force field the selection rule which permits transitions between vibrational energy levels under an electric dipolar radiation mechanism is;

\[ \Delta v_j = \pm 1 \] for transitions between vibrational levels of the same electronic state

and \( \Delta v_j = 0, \pm 1 \) for transitions between vibrational energy levels of different electronic states.

When anharmonicity effects are large, these selection rules are abrogated, so that transitions for which

\[ \Delta v_j = 0, \pm 1, \pm 2, \pm 3, \pm \ldots \] etc.
are possible.


Selection rules, which indicate the conditions under which transition probabilities between rotational energy levels are non-zero, (from symmetry considerations alone) can readily be determined by the same group theoretical methods as outlined previously for electronic and vibrational selection rules.

For the transition moment of a rotational transition, allowed by electric dipolar radiation, to be non-zero, i.e.,

$$\langle \psi^f_{\text{rot}} | \hat{M}_{\text{rot}} | \psi^i_{\text{rot}} \rangle \neq 0,$$

it is required that the direct product

$$\Gamma(\psi^f_{\text{rot}}) \otimes \Gamma(\psi^i_{\text{rot}})$$

must contain an irreducible representation which transforms as $R_x, R_y$ or $R_z$ (the rotation operators). This leads to the selection rules

$$\Delta J = 0, \pm 1 \quad \Delta K = 0, \pm 1 \quad \text{Eqn. 1.29}$$

By use of the Wigner-Eckart theorem, the relative intensities of rotational transitions can be expressed in terms of the vector coupling or Clebsch Gordon Coefficients.
Use of this theorem provides an elegant way of deriving both selection rules and intensity expressions for transitions between rotational energy levels.

SECTION E: Electron Spin and the Zeeman Effect

1.E.1. Spin.

In the discussion given thus far, it has been assumed that the factorisation

$$|\Psi_{\text{tot}}\rangle = |\Psi_{\text{space}}\rangle |\beta\rangle \quad \text{Eqn. 1.30}$$

is possible, where $|\Psi_{\text{space}}\rangle$ is a wave function determined solely by ordinary three dimensional Cartesian coordinate space, and where $|\beta\rangle$ is the electron spin wave function determined solely by spin space coordinates. This factorisation leads to a rigorous selection rule $\Delta S = 0$ for all transitions. ($S$ was defined in 1.C.7.)

However, both the intrinsic electron spin angular momentum and the electronic orbital angular momentum have magnetic fields associated with them. These magnetic fields couple with each other. The resultant effects due to this coupling are called spin-orbit interaction. The factorisation of $|\Psi_{\text{tot}}\rangle$ into $|\Psi_{\text{space}}\rangle$ is no longer valid and transitions with $\Delta S = \pm 1$ can occur weakly.

In molecules such as $O_3$ and $SO_2$, the intensity ratio of transitions with $\Delta S = 0$ to those with $\Delta S = \pm 1$
is approximately

\[ 10^3 : 1 \]

1.E.2. The Zeeman Effect

The alteration of the spectrum of a molecule, due to shifts in its energy levels in the presence of a magnetic field, is called a Zeeman Effect. If a molecule is placed in a magnetic field, a laboratory fixed axis system is defined with respect to the applied magnetic field. The \((2S+1)\) fold spin degeneracy and the \(2J+1\) fold spatial degeneracy in \(\mathcal{N}\) are lifted. Small alterations in the energy levels of the molecule will occur.

If \(S > 0\), then \(M_s\) is the projection of \(\sqrt{S(S+1)} \mathbf{\hat{n}}\) along the direction of the applied magnetic field. The alteration in energy, when a magnetic field is applied, \(\Delta E\) is given by

\[ \Delta E = g \, M_s \, \mu_B \, H \quad , \quad \text{Eqn. 1.31} \]

where \(g\) is the spectroscopic splitting factor or Lande \(g\) factor and is 2 for free electrons, \(\mu_B\) is the Bohr magneton, and \(H\) is the strength of the applied magnetic field.

In general, the Magnetic fields which can be produced in the laboratory are much smaller than the high fields produced internally in polyatomic molecules.
and therefore the applied field produces only very small energy changes. Expressions for the change in energy due to the lifting of the \((2J+1)\) fold spatial degeneracy in \(M\) are given in Herzberg (2). They are not of major interest in the present thesis.

SECTION G: Molecular Spectroscopy


Molecular Spectroscopy is the study of the emission or absorption of electromagnetic radiation by molecules. This radiation forms the molecular spectrum.

The energy of the radiation is generally quoted in wave numbers according to \(E = h\sigma\), where \(c\) is the velocity of light

\[ \sigma \text{ units} \equiv \text{cm}^{-1} \equiv \text{kaysers} \]

where \(\sigma = 1/\lambda\) and \(\lambda\) is the wavelength of the radiation measured in cms. In experimental molecular spectroscopy, the transitions examined generally lie in the range

\[ 10^5 \text{ cm}^{-1} \text{ or } 10^7 \text{ to } 10^{-2} \text{ cm}^{-1} \text{ or } 10^{-5} \text{ eV}, \text{ approx.} \]

In general, transitions between

(i) different electronic states, lie in the energy range \(10^5 - 10^4 \text{ cm}^{-1}\) (approx.), i.e., in the ultraviolet, visible and near infrared regions of the spectrum.
(ii) vibrational energy levels, in the same electronic state, lie in the range $10^3 - 10^2 \text{ cm}^{-1}$ (approx.) i.e., in the infrared region of the spectrum.

(iii) rotational energy levels, without accompanying changes in the electronic or vibrational energies, lie in the energy range $10 - 10^{-2} \text{ cm}^{-1}$, i.e., in the far infrared and microwave regions of the electromagnetic spectrum.


In gas phase electronic molecular absorption spectroscopy, a cell is filled with the gas, the spectrum of which is to be examined. A continuum of radiation is passed through the cell. The continuum of radiation is usually obtained from a high pressure xenon arc or from an iodine-tungsten lamp. The beam of radiation emerging from the absorption cell is separated into its component wavelengths by a spectrometer. The spectrometer contains a diffraction grating or a dispersive prism.

The gas absorbs all radiation of frequency $\nu_j$, where $h\nu_j$ corresponds to the energy of an allowed transition between energy levels in the molecule. Each discrete absorption frequency produces a spectral line. In general, many stable electronic states exist for a given molecule and it will have several electronic spectral systems.

Spectral lines have finite width. The quantum theory of radiation predicts that a graph of intensity $I$
versus $\nu$ of each spectral line due to a non-interacting non-translating molecule, will have a Lorentzian Profile. In any gas absorption cell there are $10^{15}$ to $10^{25}$ molecules present. These molecules undergo translational motion and interact through collisions, producing Doppler and pressure broadening in the observed spectral lines.

For absorption of radiation by a molecule, an oscillator strength $f_{fi}$ is defined by Mulliken and Rieke (26) and see also (27).

$$f_{fi} = \frac{mc^2}{\pi e^2 N_i} f_{fi} k_{\nu} d_{\nu} = 4.3 \times 10^{-9} \int \varepsilon_{\nu} d\nu$$

where $m$ and $e$ are the electronic mass and charge respectively,

$N_i$ is the number of molecules, in the state $i$, per unit volume, and

$k_{\nu}$ and $\varepsilon_{\nu}$ are the absorption and extinction coefficients, respectively.


When an absorption spectrum is observed it is necessary to identify the molecule which causes the absorption. The oscillator strength of the spectral system is determined, if this is possible. If several electronic spectral systems of the same molecule are observed then it may be possible to assign the electronic states involved. Use of simple L.C.A.O./M.O. theory enables one to predict
the electronic states which can occur in the molecule and to predict, approximately, the energies of electronic transitions. The vibrational and rotational structures in each electronic spectral system must be consistent with the assignment of the electronic transitions. The depths of electronic potential wells are determined where possible. From a detailed analysis of rotational structures accurate bond lengths and bond angles of the molecule in the different electronic states may be readily determined. Thus molecular spectroscopy provides a very powerful tool for the determination of the quantum mechanical structure of molecules.
CHAPTER II

Experimental Work

Introduction:

This Chapter is divided into two sections, A and B. A review of previous work done on the \( S_2O \) molecule is given in Section A. The correct molecular formula of \( S_2O \) was not established until 1959 and the establishment of this formula is discussed in Section A. The experimental work of the author on \( S_2O \) is described in Section B.

SECTION A: Previous Experimental Work


In 1933 Schenk (28) obtained evidence of the existence of a new oxide of sulphur by streaming sulphur dioxide and sulphur vapour through a high voltage electrical discharge. The product was shown to possess a strong system of absorption bands in the region 2500 - 3400 Å. This product is now known to be \( S_2O \).

Schenk (28) (29) showed by quantitative analysis of the gaseous product collected in a liquid air trap that the ratio of sulphur to oxygen atoms was unity.
Schenk therefore assumed that the new oxide, which he had prepared, was identical with the diatomic molecule sulphur monoxide, which gives an electronic band spectrum in emission in the region 2400 - 4000 Å when sulphur dioxide is subjected to a high voltage condensed electrical discharge.

The emission spectrum of diatomic sulphur monoxide had previously been analysed in detail by Henri and Wolff (30) and by Martin (31). Since the spectrum of sulphur monoxide is not the same as the one Schenk found, his (Schenk's) assignment is in error. Apparently Schenk was not aware of the work of Henri and Wolff (30) and Martin (31). Cordes (32) in 1937 fitted the absorption bands of the discharge tube product to a vibrational energy level scheme, on the assumption that the bearer of the spectrum was an excited diatomic sulphur molecule, S₂.

Kondrat'eva and Kondrat'ev (33) repeated the quantitative analysis of Schenk (28) (29) and confirmed that the ratio of sulphur to oxygen atoms in the gaseous product from the discharge tube, which was condensed in a liquid air trap, was unity. They concluded that the chemical formula of the oxide prepared by Schenk (28) was S₂O₂.

The work of Kondrat'eva and Kondrat'ev (33) was mainly concerned with establishing the temperature
dependence of the equilibrium

\[ \text{S}_2\text{O}_2 \rightleftharpoons 2\text{SO} \]

over the range \(-60^\circ \text{C} \leftrightarrow +60^\circ \text{C}\). Since the intensity of the absorption bands of Schenk's oxide of sulphur did not vary appreciably in this temperature range Kondrat'eva and Kondrat'ev (33) concluded that the equilibrium mixture consisted principally of \(\text{S}_2\text{O}_2\).

In 1950 Vallance Jones (34) examined the infrared and ultraviolet spectra of Schenk's oxide of sulphur. In the infrared spectrum bands were observed at 679 cm\(^{-1}\) and 1165 cm\(^{-1}\). Vallance Jones (34) photographed the ultraviolet absorption spectrum in the second order of a 21 ft. concave grating between 2500 \(\Delta\) and 3500 \(\Delta\) and made a partial vibrational analysis of the bands in the 3193 \(\Delta\) to 3352 \(\Delta\) region. He divided the bands in this region into three progressions A, B and C. He showed that three members of the A progression were separated from the corresponding members of the B progression by 679 cm\(^{-1}\). This observation established that 679 cm\(^{-1}\) is a vibration frequency of the electronic ground state of the molecule.

As mentioned previously, Kondrat'eva and Kondrat'ev (33) had studied the temperature dependence of the absorption band intensities in the region of 3300 \(\Delta\). From this temperature dependence data, Vallance Jones (34)
tentatively assigned the origin band of the intense
electronic absorption band system of Schenk's oxide of
sulphur as the band at $3321 \text{ Å}$.


The conversion of sulphur dioxide and sulphur vapour into the new oxide of sulphur in the electrical discharge is less than 100%. Vallance Jones (34) carried out experiments to obtain the conditions of maximum yield of the new oxide of sulphur. The yield was estimated by comparison of the intensity of the ultraviolet absorption band system of the new oxide of sulphur with the intensity of the $1361 \text{ cm}^{-1}$ infrared absorption band of sulphur dioxide. The average yield of the reaction was $30 - 40\%$, i.e., the product of the discharge tube contained $60 - 70\%$ of sulphur dioxide plus sulphur vapour and $30 - 40\%$ of Schenk's new oxide of sulphur.


In 1959 Meschi and Myers (35) established that Schenk's oxide of sulphur was disulphur monoxide, $S_2O$. They examined the microwave spectrum of $S_2O$ in the spectral region $18,000 \text{ Mc/sec}$ to $43,000 \text{ Mc/sec}$. The microwave spectra of the isotopic species $S^{32}S^{32}O^{16}$ and $S^{34}S^{32}O^{16}$ were analysed.
The values obtained for the inertial constants A, B and C of S\textsubscript{2}O are given in Table 2.1. The values of these constants can readily be explained if disulphur monoxide has a bent S-S-0 structure. The observed microwave spectrum is consistent with that for a molecule with a dipole moment along two inertial axes. This observation excludes a bent S-0-S structure which would have a dipole moment along one inertial axis only. Both S\textsuperscript{32} and O\textsuperscript{16} have zero nuclear spin. Therefore a symmetrical S-0-S molecule with a twofold axis of symmetry would have missing rotational levels in a bent or linear conformation. This is not observed. The analysis of the microwave spectrum by Meschi and Myers (35) proved conclusively that Schenk's oxide of sulphur was an asymmetrical bent molecule S-S-0 with the S-S-0 angle of 118°.

Meschi and Myers (35) state that under the best possible experimental conditions, the method used by Schenk for the preparation of S\textsubscript{2}O gives a product containing approximately 50% of S\textsubscript{2}O and 50% of SO\textsubscript{2}. Since Schenk (28) (29) and Kondrat'eva and Kondrat'ev (33) examined a mixture of these two gases, their quantitative analytical results are not in conflict with the work of Meschi and Myers (35).

Meschi and Myers (35) predicted that one quantum of the bending vibrational motion, \(v_2\), of S\textsubscript{2}O, would
have an energy of approximately 360 cm\(^{-1}\). Blukis and Myers (36) observed an infrared absorption band at 388 cm\(^{-1}\) and assigned this to the bending vibrational mode \(\nu_2\) of the ground electronic state of \(\text{S}_2\text{O}\).

In 1966 Nagarayan (37) calculated the mean amplitudes of the vibrations of \(\text{S}_2\text{O}\) by the method of Cyvin (38). These amplitudes of vibration are given in Table 2.1. The mean amplitude of the bond angle bending vibration \(\nu_2\) is anomalously large in comparison with the same quantity for most other triatomic molecules.

Information on the structure of \(\text{S}_2\text{O}\) known prior to the commencement of the present work is summarised in Table 2.1.
Table 2.1.
Information on S₂O Known Prior to the Present Investigation

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>S₂O</th>
<th>Ref. (35)</th>
</tr>
</thead>
</table>

Geometrical Structure in the ground electronic state

- S
- S
  \[
  \text{the S0 bond length} = 1.46 \text{ Å} \\
  \text{the SS bond length} = 1.88 \text{ Å} \\
  \text{the SSO angle} = 118°
  \]
  
  Ref. (35)

Vibrational Frequencies of ground electronic state

- \( \nu_1 = 1165 \text{ cm}^{-1} \) Ref. (34)
- \( \nu_2 = 388 \text{ cm}^{-1} \) Ref. (36)
- \( \nu_3 = 679 \text{ cm}^{-1} \)

Inertial Constants of the ground electronic state

For \( S^{32}S^{32}O^{16} \)

- \( A_{000} = 1.39811 \text{ cm}^{-1} \) \( A_{010} = 1.41692 \text{ cm}^{-1} \)
- \( B_{000} = 0.16875 \text{ cm}^{-1} \) \( B_{010} = 0.16877 \text{ cm}^{-1} \)
- \( C_{000} = 0.15034 \text{ cm}^{-1} \) \( C_{010} = 0.15013 \text{ cm}^{-1} \)

For \( S^{34}S^{32}O^{16} \)

- \( A_{000} - C_{000} = 1.24606 \text{ cm}^{-1} \)
- \( B_{000} - C_{000} = 0.01741 \text{ cm}^{-1} \)

*Here 000 indicates the zeroth vibrational energy level and 010 indicates the energy level corresponding to the excitation of one quantum of bending vibrational motion \( \nu_2 \).
Table 2.1 continued

Ray's Asymmetry Parameter
For $S_{32}^{32}S_{0}^{16}$

\[
\begin{align*}
\kappa_{000} &= -0.97049 \\
\kappa_{010} &= -0.97057 \\
\end{align*}
\]

Mean Square Amplitudes of vibrations in ground electronic state

\[
\begin{align*}
\sigma_{SO}^{\text{stretch}} &= 0.0019272 \ \text{Å}^2 \\
\sigma_{SS}^{\text{stretch}} &= 0.0023619 \ \text{Å}^2 \\
\sigma_{SS}^{\text{bending}} &= 0.0098465 \ \text{Å}^2 \ \text{rads}^2. \\
\end{align*}
\]
Ref. (37)

Electronic spectral systems observed

An absorption band spectrum was observed in the region $2500 - 3400$ Å. A tentative assignment of the band at 3321 Å as the origin band of this spectral system was made by Vallance Jones (34).
SECTION B: Present Investigation on $S_2O$

2.3.1. Preparation of $S_2O$.

An apparatus similar to that described by Vallance Jones (34) was used to prepare $S_2O$ for the experimental investigations described in this section. A diagram of the apparatus is given in Fig. 2.1. Sulphur was placed in the round-bottomed flask and heated to boiling point. The heating jacket around the discharge region of the tube was maintained at 250° C.

A 60 cycle/sec 16 Kv. A.C. voltage was applied between the electrodes. The discharge current was approximately 30 ma. When $S_2O$ was being generated the colour of the discharge was blue, but had a green appearance when viewed through the layer of molten sulphur on the walls of the discharge tube. It was not possible to maintain the electrical discharge when the total pressure of gas in the discharge tube exceeded 8 mms Hg.

Solid sulphur was allowed to accumulate in the cool upper part of the generating tube. A constant downward flow of molten sulphur into the discharge region was maintained by heating this solid accretion of sulphur, in the upper part of the tube, at regular intervals. In this way a high pressure of sulphur vapour was maintained in the discharge region of the generating tube.
Fig. 2.1 Diagram of apparatus used for preparation of $\text{S}_2\text{O}$.

Voltage of 15 Kv. A.C. applied between the electrodes

Heating jacket at 250°C

Molten sulphur

Heating mantle
In the early part of the work sulphur dioxide was allowed to leak into the discharge tube through the needle valve. As the work progressed it was found to be more convenient to leak air rather than sulphur dioxide into the discharge tube. The use of air in place of sulphur dioxide produced no change in the relative intensities of the observed spectra of $S_2O$.

2.B.2. Properties of $S_2O$.

Disulphur monoxide is a gas at room temperature. It is metastable and has a mean life of several hours. $S_2O$ undergoes rapid photodecomposition in which free sulphur is produced. The particles of sulphur can be seen as specks in the path of the light beam. These particles settle on the walls and windows of the absorption cell. In order to minimise the deposition of these particles, the $S_2O$ was streamed in a continuous flow through the absorption cell. Even if all radiation of wavelength shorter than 5500 Å is absorbed by a filter before it enters the absorption cell, photodecomposition still occurs. Three spectral systems of the $S_2O$ molecule were observed in the region 2000 – 7400 Å. Each of the three systems had discrete band structure.

2.B.3. Absorption cells.

Four absorption cells were used in the present experimental work. Two single pass cells of length
10 cms and 1 m respectively were used to observe the strong bands of the 3077 Å absorption system. Two White type multiple reflection cells of length 1.7 m and 6.0 m respectively were used to observe the weaker bands of the 3077 Å system, the bands of the 4000 Å system and the bands of the 6000 Å system. Fig. 2.2 is a diagram of the optical arrangement of a White Type Multiple Reflection Cell. The maximum path length attained in the 1.7 m cell was approximately 50 m for 28 traversals; while the maximum path length attained in the 6 m cell was 500 m for 84 traversals. The construction and optical alignment procedure for a White type multiple reflection cell has been described by Herzberg and Bernstein (39). The "minus one image" method of alignment, given by these authors, was found to be extremely rapid and simple.

The total pressure of gas in the absorption cells was varied over the range

\[ 10^{-4} - 10^{-2} \text{ atmos. (approx.)} \]

It is plausible to assume that, as in the work of Vallance Jones (34) and Meschi and Myers (35), the maximum yield of S₂O in the electrical discharge is approximately 50%. Therefore the partial pressure of S₂O in the absorption cell was varied over the range
Fig. 2.2 Schematic drawing of optical adjustment of WHITE type multiple reflection cell. For clarity the optical path is illustrated in three sections.
\[ 5 \times 10^{-5} - 5 \times 10^{-3} \text{ atmos. (approx.)} \]

2.B.4. Observation of the spectra.

The absorption spectrum of \( S_2O \) in the region 1900 - 3000 Å was examined on a 1.5 m Littrow-mounted, quartz prism spectrograph made by Hilger and Watts. The absorption spectrum of \( S_2O \) in the region 2200 - 3700 Å was examined in the second order of a Bausch and Lomb, Model 11, 1.5 metre, concave grating spectrograph. The second order of the grating is used in the Model 11 spectrograph to observe spectra in the range 1850 - 3700 Å. The absorption bands of \( S_2O \) in the spectral range 3700 - 7400 Å were observed in the first order of a Bausch and Lomb Model 11 spectrograph.

The Bausch and Lomb Model 11 spectrograph has a dispersion of 15 Å/mm and a resolving power of 35,000 in the first order of the spectrum. The dispersion and resolving power in the second order of this spectrograph are 7.5 Å/mm and 70,000, respectively.

The spectrum in the region 2800 - 3200 Å was observed on a Cary 14 spectrophotometer. The absorption spectrum of \( S_2O \) was examined in the region 7500 Å - 25000 Å on the same Cary 14 spectrophotometer. This spectrophotometer is constructed such that only 10 cm absorption cells may readily be used on it.
2.B.5. High resolution spectrographs.

The absorption bands of $S_2O$ in the region 2600 - 3500 Å were photographed under high resolution in the first order of a 6 m Ebert spectrograph of the type described by King (40). The dispersion in this region and the resolving power were approximately 0.7 Å/mm and 150,000, respectively. The absorption bands between 3190 Å and 3380 Å were photographed in the second order of the same 6 m Ebert spectrograph. In the second order the dispersion and resolving power were 0.3 Å/mm and 300,000 (approx.), respectively.

All of the work described above was carried out at McMaster University.

In addition the absorption band at 3193 Å was photographed in the eighteenth order of a 10.5 m Ebert type spectrograph, in the Spectroscopic Laboratories of the Division of Pure Physics, National Research Council of Canada, Sussex Drive, Ottawa.*


In the National Research Council Laboratories, an experiment to determine whether the 3193 Å absorption

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* The author wishes to express his thanks to Dr. A. E. Douglas, of the Division of Pure Physics, for the use of this instrument Sept./Oct. 1966, and for helpful discussions on the 3077 Å spectral system of $S_2O$. He wishes to thank also Mr. F. Alberti for experimental assistance and advice.
band exhibited a Zeeman Effect*, was also carried out. A 1 m absorption cell, through which \( S_2O \) was continuously flowing, was placed inside the coil of a large solenoidal magnet. The solenoid was 1.2 metres in length. When a D.C. current of 80 amps. was passed through the coil of the solenoid, a magnetic field of strength 2,000 gauss was generated inside the solenoid. The flux lines of this magnetic field were parallel to the gas absorption cell.

The 3193 Å absorption band was photographed in the 18th order of the 10.5 m Ebert type spectrograph, when the magnetic field strength was zero, and when it was 2,000 gauss. No difference was detectable between the two spectra, i.e., a Zeeman effect was not observed.

2.7. Photographic Materials.

Except for the spectra recorded on the Cary 14 Spectrophotometer, all spectra were photographed. In the region 1900 - 4200 Å Kodak Spectrum Analysis #1, 35 mm film and 2 x 10 in. photographic plates were used with Kodak D19 as developer. The effective A.S.A. speed of the Spectrum Analysis #1 film is 40 (41). In the region 4100 - 6500 Å both Ilford FP3 35 mm film, with

* Dr. A. E. Douglas kindly permitted the author to use the large steady field solenoid at the N.R.C. laboratories for this experiment.
Kodak D19 as developer, and Kodak Tri-X 35 mm film with "Acufine" as developer, were used. The effective A.S.A. speeds of these films are 125 and 1,200, respectively (41). In the region 6000 Å - 7400 Å Kodak I N 35 mm film, with Kodak D19 as developer, was used. This is "fast" infrared film and has an effective A.S.A. speed of 10 (41). For the work at Ottawa Kodak 1-0 plates were used with Kodak D19 as developer.

2.B.8. Light sources.

The molecular spectra were photographed in absorption. A 450 watt, 23 amp, high pressure xenon arc lamp, supplied by Osram, was used as the source of the continuum of radiation in the region 1900 Å - 7400 Å. Xenon emission bands occur around 4200 Å and 7200 Å. The use of a tungsten lamp filled with iodine vapour was tried as a light source in these regions. However the intrinsic intensity of the beam of light obtained from this lamp is much lower than that obtained from the xenon arc. No useful spectra were obtained using this tungsten lamp.

Comparison spectra were recorded beside the molecular spectra. The atomic emission spectra of iron and neon were used for this purpose. These emission spectra were obtained from an iron hollow cathode tube which contained neon gas at low pressure. The hollow
cathode tube was made by the Jarrell Ash Co. The striking voltage was 185 volts D.C. The discharge current was maintained at 20 ma. The atomic spectral lines of iron and neon obtained by using an iron hollow cathode tube of this type are very sharp and do not display self reversal or Stark Effects frequently observed in the more common Pfund type iron arc. The emission lines of neon were very useful in the region 5500 - 7400 Å since there are very few iron arc emission lines here.

The National Research Council of Canada has tabulated the accurate wavelengths of the iron and neon emission lines observed in an iron hollow cathode discharge tube of the type described in the previous paragraph. These N.R.C. tables were used in the present work.

2.B.9. Description of observed spectra.

The observed spectra can be considered in four separate groups.

(a) 1900 - 2400 Å.

In this region there is an absorption continuum, the intensity of which increases towards shorter wavelengths. Since a maximum in this absorption continuum was not observed, it is difficult to assign this continuous spectrum to a specific electronic transition.
It is not discussed further in this thesis.

(b) 2300 - 3500 Å.

In this region of the spectrum there is a very intense absorption band system, with discrete band structure. A photograph of this spectrum is given in Fig. 4.1. It will be designated as the \( \tilde{E} \leftarrow \tilde{X} \) spectral system. Some of the bands show a discrete rotational structure while the other bands are diffuse. This is discussed in Chapter 4, Section B. All of the bands of this system show sharp degradation to the red. A list of band head wavenumbers of this system is given in Appendix IV. An estimated pressure path length of \( 10^{-5} \) to \( 10^{-3} \) m atmos. (approx.) of \( S_2O \) was used to observe the \( E \leftarrow X \) spectral system.

(c) 4000 - 4300 Å.

A spectral system is observed in this region. The system has discrete vibrational structure. The bands are red degraded but not as sharply as those of the \( \tilde{E} \leftarrow \tilde{X} \) system. It is probable that other absorption bands of this system lie in the region 3500 - 4000 Å. It was not possible to obtain photographs of the spectra in this wavelength region. (This is discussed later in this chapter under 2.B.12. "Experimental Difficulties".) The bands in the region 4000 - 4300 Å are assigned to the \( \tilde{D} \leftarrow \tilde{X} \) transition. A photograph of part of the
The intensity of the \( \tilde{D} \leftarrow \tilde{X} \) spectral system is approximately \( 10^2 \) weaker than the \( \tilde{E} \leftarrow \tilde{X} \) spectral system. An estimated pressure path length of \( S_2 \) of \( 10^{-3} \) to \( 10^{-2} \) m atmos. is used to observe the \( \tilde{D} \leftarrow \tilde{X} \) spectral system. A list of vibrational band wavenumbers is given in Appendix V.

(d) \( 4400 - 6700 \) Å

In this region there is a discrete absorption band spectrum. Each vibrational band has discrete rotational structure. The band system is designated the \( \tilde{C} \leftarrow \tilde{X} \) system. A photograph of the spectrum is given in Chapter 4 of this thesis. Absorption bands in the region \( 6400 - 6700 \) Å could not be photographed on the 6 m Ebert spectrograph. Kodak I N 35 mm film must be used in this region. Since this film has an A.S.A. speed of approximately 10 an exposure time of approximately 100 hours would be required to photograph bands on the 6 m Ebert spectrograph in the region \( 6400 - 6700 \) Å. The pressure path length used to observe this \( \tilde{C} \leftarrow \tilde{X} \) spectral system is in the range \( 10^{-3} \) - \( 10 \) m atmos. A list of band head wavenumbers for the vibrational bands of the \( \tilde{C} \leftarrow \tilde{X} \) system is given in Appendix VI.

The \( \tilde{D} \leftarrow \tilde{X} \) and \( \tilde{C} \leftarrow \tilde{X} \) spectral systems have not been observed previously. The analyses of the \( \tilde{E} \leftarrow \tilde{X} \),
the $\tilde{D} \leftarrow \tilde{X}$ and $\tilde{C} \leftarrow \tilde{X}$ spectral systems are given in Chapter 4 of this thesis.

2.B.10. Identification of bearer of the spectra.

The $\tilde{E} \leftarrow \tilde{X}$ spectral system in the region 2300 - 3500 Å is known from the work of Schenk (28) and Vallance Jones (34). The absorption spectrum of $\text{SO}_2$ occurring in the region 2400 - 3200 Å is also well known. The oscillator strength of the $\tilde{E} \leftarrow \tilde{X}$ spectral system is approximately ten times greater than the oscillator strength of the 2400 - 3200 Å absorption system of $\text{SO}_2$. Therefore, under favourable experimental conditions, when the yield of $\text{S}_2\text{O}$ is at a maximum, no trace of the absorption bands of $\text{SO}_2$ is seen on the photographic films of the $\tilde{E} \leftarrow \tilde{X}$ spectral system of $\text{S}_2\text{O}$.

The $\tilde{D} \leftarrow \tilde{X}$ and $\tilde{C} \leftarrow \tilde{X}$ spectral systems do not lie in the absorption regions of $\text{SO}_2$. The large 6 m multiple reflection cell was filled with $\text{SO}_2$ to a pressure of $\frac{1}{2}$ atm. No absorption bands of $\text{SO}_2$ were observed in the region 4500 Å - 7400 Å even when the pressure path length of $\text{SO}_2$ was 200 m atm.

The bands of the well known singlet triplet spectral system of $\text{SO}_2$ in the region 3600 - 4100 Å did not coincide with any of the bands of the $\tilde{D} \leftarrow \tilde{X}$ absorption system of $\text{S}_2\text{O}$. Therefore, none of the bands attributed to the $\tilde{E} \leftarrow \tilde{X}$, $\tilde{D} \leftarrow \tilde{X}$ and $\tilde{C} \leftarrow \tilde{X}$ spectral systems of $\text{S}_2\text{O}$ are absorption bands of $\text{SO}_2$. 
It is necessary to exclude the possibility that the $\tilde{C} \leftarrow \tilde{X}$ and $\tilde{D} \leftarrow \tilde{X}$ spectral systems are not due to a molecule $S$-$O$-$S$. $S$-$O$-$S$ and $S$-$S$-$O$ are isoelectronic and would be expected to have spectral absorption systems in the same region of the spectrum. Meschi and Myers (35) did not find any evidence for the existence of $S$-$O$-$S$. No additional spectral systems were seen in the region $2000 - 4000$ Å.

If the $\tilde{C} \leftarrow \tilde{X}$ and $\tilde{D} \leftarrow \tilde{X}$ spectral systems are due to a different absorbing molecule from that which produces the $\tilde{E} \leftarrow \tilde{X}$ system, then the intensities of the $\tilde{C} \leftarrow \tilde{X}$ and $\tilde{D} \leftarrow \tilde{X}$ systems, relative to the $\tilde{E} \leftarrow \tilde{X}$ system, should vary as experimental conditions in the discharge tube are varied. In fact, no change in relative intensities is observed when the experimental conditions are varied. By use of this argument, it is obvious that the $\tilde{C} \leftarrow \tilde{X}$ and $\tilde{D} \leftarrow \tilde{X}$ spectral systems are not due to sulphides, nitrogen, carbon, aluminum or silicon. If either the $\tilde{C} \leftarrow \tilde{X}$ or $\tilde{D} \leftarrow \tilde{X}$ system was due to a nitrogen compound of sulphur, a dramatic increase in absorption intensity should be observed when air, rather than sulphur dioxide, is leaked into the discharge tube. This is not observed.

Accordingly, all evidence indicates that the $\tilde{E} \leftarrow \tilde{X}$, $\tilde{D} \leftarrow \tilde{X}$ and $\tilde{C} \leftarrow \tilde{X}$ absorption systems are due to electronic transitions in the $S_2O$ molecule.

The positions of sharp band heads and rotational features, and of the lines of the iron-neon comparison spectra, were measured on each photograph of the spectrum with a McPherson travelling microscope, which has a precision of 0.001 mm. The wavelengths of the sharp band heads and rotational features were calculated. The Edlen vacuum wavelength correction, which compensates for the variation of the refractive index of air with wavelength, was added to band head wavelengths, as measured in air. This is equal to the wavelength which would be measured in vacuo. 

\[ \nu = \frac{1}{\lambda_{\text{vac}}} \]

where, \( \lambda_{\text{vac}} \) is measured in cms, was then calculated. This calculational process was performed on a computer.

Microdensitometer traces of all absorption bands were made on a Joyce-Loebl MK III C microdensitometer.

Measurements of the wavelengths of diffuse band heads were taken from microdensitometer tracings and converted to vacuum cm\(^{-1}\) by the process outlined above.

For sharp band heads, the estimated uncertainty in band head energies is ±1 cm\(^{-1}\). For very diffuse bands this uncertainty is ±10 cm\(^{-1}\).


The intensities of bands in the \( \tilde{E} \leftarrow \tilde{X} \) spectral system were measured as follows. Microdensitometer
traces of all the bands were made on a Joyce-Loebl Microdensitometer Model MK III C. This instrument measures the optical density of the photographic image. The optical density measured in this way is approximately proportional to the log of the transmission coefficient of the $S_2O$ gas for the various wavelengths examined. Thus the intensity figures quoted in this work are proportional to the log of the intensity of the absorption bands. For convenience the $O_0^0$ band of the $\tilde{E} \leftarrow \tilde{X}$ system was arbitrarily assigned an intensity figure of 100 and all other intensity figures were scaled proportionately.

For the $\tilde{D} \leftarrow \tilde{X}$ spectral system it was difficult to obtain accurate intensity measurements. Since the film of solid sulphur absorbs light and the absorption coefficient for this process increases rapidly with decreasing wavelength in the region of 4000 $\AA$, the light intensity over the spectral region examined - 4000 $\AA$ - 4300 $\AA$ was not uniform. The relative intensities of absorption bands for the $\tilde{D} - \tilde{X}$ spectral system were therefore estimated from photographic enlargements of the spectrum. Since the origin band of the system was not assigned, the most intense band was assigned an intensity value of 100. The intensity figures for the $\tilde{D} \leftarrow \tilde{X}$ spectral system are only useful as order of magnitude figures.

In the $\tilde{C} \leftarrow \tilde{X}$ spectral system a very wide range
of intensities was observed. In the region 4400 – 5500 Å, intensity measurements were obtained for intense absorption bands from microdensitometer traces as was done for the $\tilde{E} \leftarrow \tilde{X}$ spectral system. The intensities of bands in the region 6000 Å – 6700 Å could not be measured from microdensitometer traces since the wavelength response of the photographic materials used in this region of the spectrum is non-uniform. In this region of the spectrum, intensity figures of absorption bands were estimated from photographic enlargements of the spectrum. This procedure was also used to obtain intensity figures for the very weak bands in the region 4400 – 6000 Å. Since the origin band of the $\tilde{C} \leftarrow \tilde{X}$ spectral system has not been assigned, the absorption band with maximum intensity was arbitrarily assigned an intensity figure of 100 and all other intensity estimates were scaled proportionately.

A list of vibrational band head energies in cm$^{-1}$ and intensity measurements for these bands are given in Appendices IV, V and VI for the $\tilde{E} \leftarrow \tilde{X}$, $\tilde{D} \leftarrow \tilde{X}$ and $\tilde{C} \leftarrow \tilde{X}$ spectral systems, respectively.


The task of photographing the electronic spectra of $\text{S}_2\text{O}$ was a very laborious operation. Considerable care had to be exercised in the generation of the $\text{S}_2\text{O}$. The rate of inflow of sulphur dioxide, or air, into the
discharge tube was carefully controlled. If the rate of inflow was too high, the discharge between the electrodes ceased and instead a discharge took place between the electrodes and the heating jacket outside the discharge tube. When a discharge took place through the walls of the discharge tube, these walls were punctured and the discharge tube cracked at the point of puncture.

In the early stages of the experimental work, the average life time of a discharge tube, before cracking, was approximately five hours. With experience and care this average life time was extended to approximately 100 hours.

If the rate of flow of gas or air into the discharge tube is too low, sulphur dioxide, rather than disulphur monoxide, is produced. It is also necessary to reduce the rate of inflow of gas with time, because the cool parts of the system were rapidly clogged with solid sulphur. This clogging reduced the effectiveness of the pumping system. As a protective device, a liquid air trap was placed between the absorption cell and the pumping system. It was found necessary to clean out all half clogged tubes every two to three hours, even though wide bore tubing of 1.5 mm diameter was used throughout the apparatus.

The rapid photodecomposition of $S_2O$ inside the absorption cells also caused great experimental
difficulties. The windows of absorption cells and the multiple reflection mirrors of the 6 m cell were rapidly coated with a film of sulphur, which strongly absorbs light of all wavelengths less than 3900 Å. The absorption by a film of sulphur is particularly intense in the region 3500 - 3900 Å. Hence, it was not possible to photograph the absorption bands of S₂O in this spectral region.

To remove these films of sulphur, it was necessary to wash the windows of the absorption cells and the multiple reflection mirrors approximately every one hour. This was a tedious process since the whole apparatus was shut off during cleaning operations and required 20 - 30 minutes of heating up before S₂O could again be generated.

As can be seen from the above, the task of photographing the electronic spectra of S₂O was a very tedious operation. The absorption bands of the $\tilde{D} \leftarrow \tilde{X}$ and $C \ X$ systems could be observed through the spectrograph with the naked eye. Bands of these systems were photographed, not in order of wavelength, but when the absorption intensity was considered suitable by the experimenter.

The results of the experimental work are summarised in Fig. 2.3 and Table 2.2.
FIG. 2.3 ELECTRONIC SPECTRAL SYSTEMS OBSERVED

PRESSURE PATH LENGTHS USED IN OBSERVING THE ABSORPTION BANDS IN METER ATMOS.

ENERGY IN CMS.$^{-1}$

REGION OF CONTINUOUS ABSORPTION

$\tilde{E} \leftrightarrow \tilde{X}$ SYSTEM

$\tilde{D} \leftrightarrow \tilde{X}$ SYSTEM

EXPERIMENTALLY INACCESSIBLE REGION

$\tilde{C} \leftrightarrow \tilde{X}$ SYSTEM
Table 2.2  
Spectral Observations

<table>
<thead>
<tr>
<th>Wavelength Range</th>
<th>Instrumentation</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1900 - 2300 Å</td>
<td>Hilger Watts 1.5 m Littrow Mounted quartz spectrograph used.</td>
<td>Continuous absorption. Not assigned.</td>
</tr>
<tr>
<td>2300 - 3500 Å</td>
<td>1.5 m Bausch and Lomb Model 11 spectrograph; 6 m Ebert spectrograph; 10.5 m spectrograph used.</td>
<td>Intense absorption with discrete band structure. Some of the bands have rotational structure. Assigned ( \tilde{E} \leftarrow \tilde{X} ) system.</td>
</tr>
<tr>
<td>3500 - 4000 Å</td>
<td>No observations possible.</td>
<td></td>
</tr>
<tr>
<td>4000 - 4300 Å</td>
<td>1.5 m Bausch and Lomb Model 11 spectrograph and 6 m Ebert spectrograph used.</td>
<td>Weak absorption bands observed. Assigned as ( \tilde{D} \leftarrow \tilde{X} ) system.</td>
</tr>
<tr>
<td>4400 - 6700 Å</td>
<td>1.5 m Bausch and Lomb Model 11 spectrograph and 6 m Ebert spectrograph used.</td>
<td>Extremely weak absorption bands observed. Assigned as ( \tilde{C} \leftarrow \tilde{X} ) system.</td>
</tr>
<tr>
<td>6700 - 25000 Å</td>
<td>Cary 14 Spectrophotometer used.</td>
<td>Pressure path length available very low. No absorption systems observed.</td>
</tr>
</tbody>
</table>
Chapter III
Theoretical Considerations

Introduction.

In this chapter the energy states which the S\textsubscript{2}O molecule can occupy will be considered. This will be done by reference to molecules which have electronic and vibrational energy levels similar to those expected in the S\textsubscript{2}O molecule. The O\textsubscript{3} and SO\textsubscript{2} molecules have the same number of valence electrons - eighteen - as S\textsubscript{2}O. In the discussion in this chapter the series of molecules O\textsubscript{3}, SO\textsubscript{2} and S\textsubscript{2}O will be called an isoelectronic series.

The chapter is divided into four sections. In Section A the possible electronic states of S\textsubscript{2}O are considered using simple L.C.A.O./M.O. theory. The Renner Effect is discussed in Section B. In Section C the problem of quasilinear electronic states is considered. Those aspects of the Franck-Condon Effect, which are used in the explanation of the electronic spectra of S\textsubscript{2}O, are discussed in Section D.

In the fourth chapter of this thesis an analysis of the spectra of S\textsubscript{2}O is presented. The purpose of this third chapter is to provide a discussion of the spectra which could possibly be observed for the S\textsubscript{2}O molecule. The content of this chapter compliments that of Chapter Four.

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SECTION A: Possible Electronic States of $S_2O$


In the qualitative description of electronic states of triatomic molecules it is necessary to consider the molecule in both the linear and bent conformations. By the adiabatic principle the electronic states of the two conformations can be correlated. In the linear conformation both $O_3$ and $SO_2$ belong to the point group $D_{\infty h}$, while the $S_2O$ molecule in the linear conformation belongs to the point group $C_{\infty v}$. In the bent conformation $O_3$ and $SO_2$ belong to the point group $C_{2v}$ and $S_2O$ belongs to the point group $C_3v$.


The electronic states of the linear conformation of $S_2O$ will be considered first. The electron configurations for sulphur and oxygen atoms are

- Sulphur $KL\ 3s^2\ 3p^4$
- Oxygen $K\ 2s^2\ 2p^4$

As an approximation it will be assumed, that since the sulphur and oxygen atoms have the same number of valence electrons, and that in each molecule (of $O_3$, $SO_2$ and $S_2O$) each atom (sulphur and oxygen) contributes six valence
electrons to molecule formation, the molecular orbitals of $S_2O$ will be similar to those of $O_3$ and $SO_2$.

$O_3$ and $SO_2$ are classified as $AB_2$ type molecules. Molecular orbitals in $AB_2$ type molecules have been considered by Walsh (42). Since $S_2O$ in the linear conformation belongs to the point group $C_{\infty v}$, the indices $g$ and $u$, as used by Walsh (42) in describing $AB_2$ type linear molecules, are omitted in this discussion.

Hayes and Pfeiffer (43)* have recently carried out L.C.A.O./S.C.F./M.O. calculations for the $O_3$ and $SO_2$ molecules. Similar calculations for the $O_3$ molecule were carried out by Peyerimhoff and Buenker (44).

The approximate energy ordering of the molecular orbitals of the $O_3$ and $SO_2$ molecules in the linear conformation is given in Fig. 3.1.** The symmetry classification of each molecular orbital is shown in terms of the $C_{\infty v}$ point group. The calculations of Hayes and Pfeiffer (43) show that the energy ordering of the molecular orbitals is

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* The author wishes to thank Dr. Hayes for discussion and for communicating this paper to him prior to publication.

** The content and format of Fig. 3.1 has been taken from the work of Hayes and Pfeiffer (43).
FIG. 3.1

ENERGY ORDERING OF ORBITALS
IN THE LINEAR CONFORMATION

--- $3\pi$

--- $2\pi$

--- $4\sigma$

--- $1\pi$

--- $3\sigma$

--- $2\sigma$

--- $1\sigma$
the same for the $O_3$ and $SO_2$ molecules, when these molecules are in the linear conformation. It is plausible to assume that the qualitative energy ordering of the molecular orbitals will be the same also for the $S_2O$ molecule when it is in the linear conformation.

In order to obtain the ground state electron configurations of the molecules, the molecular orbitals are filled up with electrons in accordance with the Aufbau Prinzip. In the linear conformation of the $S_2O$ molecule all of the orbitals between $1\sigma$ and $2\pi$ are completely filled with electrons. There are two electrons in the $3\pi$ orbital.


In deriving the electronic states of $S_2O$, only these two $3\pi$ electrons need be considered. Since the two electrons are in the same orbital, by the Pauli Exclusion Principle, the product wave function of the two electrons must be antisymmetric with respect to exchange in both Cartesian and spin space. Therefore the symmetries of the electronic states formed by the $(3\pi)^2$ configuration are readily determined by taking the double antisymmetric product of the irreducible representations according to which both the space and spin wave functions transform,
i.e.,

\[ \chi^2(\pi, E_{\frac{1}{2}}) \]  

Eqn. 3.1

For the Cartesian space part \( \pi \otimes \pi \) yields

\[ \Sigma^+, \Delta \] symmetric product

\[ \Sigma^- \] antisymmetric product.

For the spin space part the product \( E_{\frac{1}{2}} \otimes E_{\frac{1}{2}} \) yields

\[ \Sigma^-, \Pi \] symmetric product

\[ \Sigma^+ \] antisymmetric product

Therefore the total antisymmetric wave functions have the symmetries

\[ (\Sigma^+ \text{ and } \Delta) \otimes (\Sigma^+) \]

\[ (\Sigma^-) \otimes (\Sigma^- \text{ and } \Pi) \]

In spin space, singlet wave functions transform as \( \Sigma^+ \) and triplet wave functions transform as \( (\Sigma^- \oplus \Pi) \). Therefore only the electronic states

\[ ^1\Sigma^+, ^1\Delta \] and \[ ^3\Sigma^- \]

can arise from the configuration \((3\pi)^2\). Of these three states the \[ ^3\Sigma^- \] state is expected to lie lowest in energy, according to Hund's rule. In general, in iso-electronic diatomic molecules the \( ^1\Delta \) state lies lower
in energy than the $^1\Sigma^+$ state arising from the same electron configuration. It is reasonable to assume that the same energy ordering of $^1\Sigma^+$ and $^1\Delta$ states also occurs in linear triatomic molecules.

3.A.4. Excited Electronic States in the Linear Conformation.

Calculations by Hayes and Pfeiffer (43) and by G. W. Robinson (45) on $O_3$ have shown that the next highest set of molecular electronic energy levels are obtained by the single electron promotion

$$\ldots (2\pi)^4 (3\pi)^2 \rightarrow \ldots (2\pi)^3 (3\pi)^3$$

In this configuration there are three equivalent electrons in both the $2\pi$ and $3\pi$ molecular orbitals. Therefore, the symmetries of the resultant electronic states are obtained by taking the simple direct product of the representations

$$(\text{Triple antisymmetric product of } \Pi, E_{1/2})$$

$$(\text{Triple antisymmetric product of } \Pi, E_{1/2})$$

For each triple antisymmetric product

$$\chi^3 (\Pi, E_{1/2})$$

the total antisymmetric product is $\Pi \otimes E_{1/2}$. Therefore, the symmetries of the electronic states which can arise...
from the configuration

\[ \ldots (2\pi)^3 (3\pi)^3 \]

are contained in

\[ \eta \otimes E_{\gamma/2} \otimes \eta \otimes E_{\gamma/2} \]

and are

\[ 3\Delta, \ 1\Delta, \ 3\Sigma^+, \ 1\Sigma^+, \ 3\Sigma^-, \ 1\Sigma^- \]

It is plausible to assume that the lower excited electronic states of the linear conformation of \( S_2O \) are similar to those of \( O_3 \) and \( SO_2 \) when these molecules are also in the linear conformation.

3.A.5. Molecular Orbitals for the Bent Conformation of \( S_2O \).

A qualitative correlation of single electron molecular orbital energies in a triatomic molecule of the type \( AB_2 \), between bent and linear conformations has been given by Walsh (42). A figure showing these correlations is usually called a Walsh Diagram. The recent L.C.A.O./S.C.F./M.O. calculations of Hayes and Pfeiffer (43) have given Walsh Diagrams for \( O_3 \) and \( SO_2 \) when the bond angle \( \beta AB \) is varied from 40° to 180° of Fig. 3.2.

In the bent conformation of a molecule there may be ambiguity in labelling the orbitals with a number \( n \),
Fig. 3.2.

WALSH DIAGRAM FOR MOLECULES
ISOELECTRONIC WITH $S_2O$

(ADAPTED FROM REF. 43)

BINDING ENERGY
OF A SINGLE
ELECTRON IN A
MOLECULAR
ORBITAL
INCREASING

$\theta$

BOND ANGLE

90° 180°
which indicates energy ordering. This ambiguity in labelling orbitals is due to the fact that on the Walsh Diagram the graphs of orbital energy versus bond angle, for different orbitals, may cross at angles different from 180°. To avoid the ambiguity, in Fig. 3.2, the angle 120° was chosen as a reference point and the orbitals were labelled in order of increasing energy at a bond angle of 120°.

3.4.6. Electronic States in the Bent Conformation of \( S_2O \).

As for the linear conformation, molecular orbitals are filled with electrons in accordance with the Aufbau Prinzip. In the bent conformation the molecule belongs to the \( C_2 \) point group and the molecular orbital electronic wave functions are all non-degenerate since the \( C_2 \) group is an Abelian Group. The spin wave functions are doubly degenerate - Kramers Doublets.

The ground electronic state arises from the configuration

\[ \ldots (6a')^2 (7a')^2 (3a'')^0 \]

when the BAB bond angle is approximately 120°.* The resultant electronic state is obtained by taking the

* The S-S=O angle is 118° in the ground electronic state - Meschi and Myers (35).
double antisymmetric product.

\[ \chi^2 (a', E_{\frac{1}{2}}) \]

\( a' \otimes a' \) yields \( A' \), which is symmetric and

\( E_{\frac{1}{2}} \otimes E_{\frac{1}{2}} \) yields \( A', A'', A'' \) as the symmetric product
and \( A' \) as the antisymmetric product.

In spin space, singlet wave functions transform as \( A' \) and
triplet wave functions transform as \( A' \oplus A'' \oplus A'' \) in the
C\(_s\) point group. Therefore the ground electronic state of
\( \text{S}_2 \text{O} \) is expected to be a \( ^1A' \) state.

This \( ^1A' \) state of the configuration

\[ \ldots (6a')^2 (\gamma a')^2 \]

of the bent conformation correlates with the \( ^1\Delta \) state
arising from the configuration

\[ \ldots (2\pi)^4 (3\pi)^2 \]

of the linear conformation, cf. Fig. 3.3.

In the bent conformation, the first electron
promotion is

\[ \ldots (\gamma a')^2 (3a'')^0 \rightarrow \ldots (\gamma a')^1 (3a'')^1 \]

Using the product of representations technique, as outlined above the configuration

\[ \ldots (6a')^2 (\gamma a')^1 (3a'')^1 \]
A schematic correlation between the linear and bent conformations of the electronic orbital configurations and the resultant electronic states in molecules which are isoelectronic with the $S_2O$ molecule.

![Diagram showing electronic states and configurations](image-url)
FIG. 3.4 POTENTIAL CURVES FOR MOLECULES WHICH ARE ISOELECTRONIC WITH $S_2O$. THESE CURVES ARE DERIVED FROM THE INFORMATION IN FIG. 3.3.
yields $^3A''$ and $^1A''$ states.
The $^3A''$ state of the configuration $\ldots (7a')^1 \ (3a'')^1$
correlates with the $^3\Sigma^-$ state of the $\ldots (2\pi)^4 \ (3\pi)^2$
configuration. The $^1A''$ state of the configuration
$\ldots (7a')^1 \ (3a'')^1$ correlates with the upper half of the
$^1\Delta$ state of the configuration $\ldots (2\pi)^4 \ (3\pi)^2$.

When the two electron promotion

\[ \ldots (6a')^2 \ (7a')^2 \ (3a'')^0 \rightarrow \ldots (6a')^2 \ (7a')^0 \ (3a'')^2 \]

occurs, giving the configuration

\[ \ldots (6a')^2 \ (7a')^0 \ (3a'')^2, \]

only an $^1A'$ state is possible. This $^1A'$ state correlates
with the $^1\Sigma^+$ electronic state of the configuration
$\ldots (2\pi)^4 \ (3\pi)^2$.

When the electron promotions

\[ \ldots (2a'')^2 \ (6a')^2 \ (7a')^2 \rightarrow \ldots (2a'')^2 \ (6a')^1 \ (7a')^2 \ (3a'')^1 \]

and

\[ (2a'')^2 \ (6a')^2 \ (7a')^2 \rightarrow \ldots (2a'')^1 \ (6a')^2 \ (7a')^2 \ (3a'')^1 \]

occur, the resultant electron configurations give
$^1,^3A''$ and $^1,^3A'$ states. These states correlate with the
$^3\Delta$ and $^1\Delta$ states of the $\ldots (2\pi)^3 \ (3\pi)^3$ configuration
of the linear conformation.
Only those states mentioned above are of interest to the subject matter of this thesis. The $^1\Sigma^+$ and $^1\Sigma^-$ states of $S_2O$ which arise from the configuration $... (2\pi)^3 (3\pi)^3$ in the linear conformation correlate with $^1\Sigma_A^+$ and $^1\Sigma_A^-$ states in the bent conformation of the molecule.


Absorption spectral systems for the $SO_2$ molecule are observed at 2900 Å and 3800 Å and are assigned as the transitions $\tilde{\Delta} \leftarrow \tilde{X}$ and $\tilde{\alpha} \leftarrow \tilde{X}$ respectively, cf. Herzberg (2). The $\tilde{\alpha} \leftarrow \tilde{X}$ system is assigned as a singlet singlet transition and the $\tilde{\alpha} \leftarrow \tilde{X}$ is assigned as the corresponding singlet triplet transition. The $\tilde{\alpha} \leftarrow \tilde{X}$ system shows a Zeeman Effect.

The bond angle O-S-O for the A state has not been determined. Merer (46) has carried out a rotational analysis of some of the bands of the $\tilde{\alpha} \leftarrow \tilde{X}$ spectral system and has concluded that the bond angle in the triplet a state is 126°.

The electronic configuration which gives the A and a states has not been completely determined, cf. Mulliken (47). Merer (46) assigned the electron configurations as

\[
(3b_2)^2 (4a_1)^1 (2b_1)^1 \text{ singlet } A^1B_1
\]

\[
\text{triplet } a^3B_1
\]
This assignment is in conflict with the L.C.A.O./S.C.F./M.O. calculations of Hayes and Pfeiffer (43). The assignment is also inconsistent in that, in the linear conformation such an assignment would require the ordering of states of the \( \ldots (1\pi_u)^4 (2\pi_u)^2 \) configuration to be \( ^1\Sigma^+_g, ^1\Delta_g \) and \( ^3\Sigma^+_g \), in order of increasing energy. This ordering is improbable. A more probable assignment is the assignment of the \( A \) and \( a \) states as being due to the configurations which correlate with the configuration \( \ldots (1\pi_g)^3 (2\pi_u)^3 \) of the linear conformation. Thus in the preceding discussion molecular orbital energies for \( \text{SO}_2 \) and \( \text{O}_2 \) were given but only the energies of the electronic states of \( \text{O}_2 \) were discussed.

SECTION B: The Renner Effect

3.B.1. Introduction.

In Section A of this chapter simple L.C.A.O./M.O. theory was used to derive the symmetries and approximate energy ordering of the electronic energy states. In this section a procedure is outlined which gives the same qualitative information about electronic energy states and which also gives information about the vibrational structure of these states.

Consider the triatomic molecules \( \text{O}_2, \text{SO}_2, \) and \( \text{S}_2\text{O} \) as being in the linear conformation. The Schrödinger

*Configuration interaction was applied for excited states.
Equations of the molecules may be solved by using the Born-Oppenheimer Approximation. The factorisation

$$\psi_{\text{tot}} = \psi_{\text{el}} \psi_{\text{vib}} \psi_{\text{rot}} \quad \text{Eqn. 3.2}$$

also Eqn. 1.5(a)

is valid provided there is no vibronic interaction between close lying electronic states and provided there are no degeneracies in any two of the wavefunctions

$$\psi_{\text{el}} ; \psi_{\text{vib}} \text{ or } \psi_{\text{rot}} .$$

In a linear triatomic molecule the wave functions of the $\Pi$, $\Delta$, $\Pi$ etc. electronic states are doubly degenerate; the wave functions of the bending vibrational mode $v_2$ are doubly degenerate; cf. Fig. 1.2, and the rotational wave functions are doubly degenerate with respect to the quantum number K, cf. 1.C.7. These degeneracies are removed if the interaction of electronic and nuclear motions is taken into account. These interactions are treated as perturbations to the Hamiltonian of the molecule in the linear conformation. The interaction of

(i) electronic and vibrational motions gives rise to Renner Coupling,

(ii) electronic and rotational motions gives rise to K-type Doubling,

(iii) vibrational and rotational motions gives rise to l-type Doubling.
3.B.2. Weak Renner Effect.

It was noted by Renner (48) that the absorption bands of the \( \text{CO}_2 \) molecule, in the region 1010 Å - 1070 Å, had a complex vibrational structure. This complexity was attributed, by Renner, to the coupling between the electronic angular momentum of a \( \Pi \) electronic state and the vibrational angular momentum of the doubly degenerate bending vibration. This type of coupling is now called the Renner Effect (48)(49)(2).

In a theoretical treatment of the Renner Effect, it is assumed that the coupling causes a separation of the potential energy curve of the doubly degenerate electronic state, along the normal coordinate of bending \( r_b \), into two separate potential energy curves \( U^+(r_b) \) and \( U^-(r_b) \). Renner (48) treated only the case where the minimum of \( U^+(r_b) \) and of \( U^-(r_b) \) coincided at \( r_b = 0 \).


The situation treated by Renner is called the dynamic Renner Effect since it can be observed only by excitation of the bending vibrational motion \( \nu_2 \). The coupling between the electronic and vibrational angular momentum is small in the dynamic Renner Effect. If this coupling is large, then \( U^-(r_b) \) curve may have a minimum at \( r_b \neq 0 \) and \( U^+(r_b) \) a minimum at \( r_b = 0 \), or both \( U^-(r_b) \) and \( U^+(r_b) \) may have minima at \( r_b \neq 0 \). These
three situations are illustrated in Fig. 3.5. For clarity in this discussion, they will be called Renner Effect Case (a), Renner Effect Case (b) and Renner Effect Case (c), respectively.

In the Renner Effect Case (b) and Case (c), an energy minimum is achieved by angular distortion of the molecule out of the linear conformation. The $U^+(r_b)$ and $U^-(r_b)$ may be considered as belonging to separate non-degenerate electronic states. However, when the vibrational energy levels of these "separate" electronic states are being considered it is necessary to take into account the fact that they correlate with a single doubly degenerate electronic state of the linear conformation of the molecule. The vibrational energy levels in the "separate" electronic states strongly perturb one another.

Renner Effect Case (b) and Renner Effect Case (c) are called the static Renner Effect. The distortion from the linear conformation is permanent and hence the separation of the $U^-(r_b)$ and $U^+(r_b)$ at $r_b \neq 0$ curves is permanent and does not depend on the excitation of bending vibrational motion as for Renner Effect Case (a).

A theoretical treatment of Renner Effect Case (a) was given by Renner (48); Case (b) was considered in a semi-empirical way by Pople and Longuet-Higgins (50) and Case (c) was considered by Dixon (51)(52)(53)(54), cf. Appendix II.
Fig. 3.5. Potential Curves for weak (a) and strong (b) and (c) Renner Effect.

Potential energy $U(r_b)$ is plotted on the ordinate. The bending coordinate is $r_b$. 

A theoretical analysis of the Renner Effect is given in Appendix II. The Renner Effect Case (a) is treated for a $^1\Delta$ state. Using the symmetry coordinates technique, as defined by Moffitt and Liehr (55), Herer and Travis (56) obtained energy expressions for the components of the vibrational energy levels of a $\Delta$ state, which exhibits a dynamic Renner Effect.

3.3.4. Magnitude of Renner Coupling.

The Renner Coupling constant is $\epsilon$ for a $\Pi$ state and $\eta/\omega_2$ for a $\Delta$ state. This constant gives the magnitude of the coupling between the electronic and vibrational angular momenta. The coupling constant can, in principle, be calculated, and it depends on the structure of the molecule. Normally, however, the coupling constant plays the role of a parameter*, the value of which is determined by the experimental data. As noted by Renner, the coupling is particularly strong if the doubly degenerate electronic state lies close to a $\Sigma$ state.* This latter

* "(...)" wird also in unserer Rechnung die Rolle eines Parameters spielen, der wegen seiner Abbildung
vom speziellen Bau der Elektronenhülle bei verschiedenen
Molekülen des $\Pi$-Typs und auch bei verschiedenen
Elektronenzuständen desselben Moleküls verschieden sein
wird. Die Störung (zwischen Elektronen und Knickeinrahm-
ungsbegegung) wird besonders groß werden, wenn der
$\Pi$-Term nahe an einen $\Sigma$-Term liegt." – quoted from
Renner (48).
fact can be illustrated quite simply. If, in a triatomic molecule which belongs to the point group \( C_{\infty v} \) having \( 1^\Sigma^+ \) and \( 1^\Delta \) states arising from the same \((\pi)^2\) electron configuration, a bending vibration \( \nu_2 \) is excited, then, when the \( 1^\Sigma^+ \) and \( 1^\Delta \) states are distorted by the vibration, the \( 1^\Sigma^+ \) state goes to a \( 1^A' \) state and the \( 1^\Delta \) state goes to a \( 1^A' \) and \( 1^A'' \) state momentarily. The \( 1^A' \) component of the \( 1^\Delta \) state and the \( 1^A' \) state of the \( 1^\Sigma^+ \) state repel each other. This may, equivalently, be described by saying that there is Renner Coupling in the \( 1^\Delta \) state. In this case, the coupling takes place via a close-lying electronic state of appropriate symmetry. If the \( 1^\Sigma^+ \) and \( 1^\Delta \) states lie close together in energy the magnitude of the Renner Coupling is particularly large.

The electronic spectral system of \( \text{NH}_2 \), which was examined by Dressler and Ramsay (57), was initially assigned as a bent to linear transition in absorption. For this spectral system of \( \text{NH}_2 \), the lower bent electronic state \( 2^B_1 \) and the upper linear (quasilinear) electronic state \( 2^A' \) both correlate with a single \( 2^\Pi_u \) electronic state of the linear conformation. In the linear conformation a \( 2^\Sigma_u^- \) state lies close to the \( 2^\Pi_u \) state previously mentioned. Theoretical treatments of the \( 2^B_1 \) and \( 2^A_1 \) states of \( \text{NH}_2 \) have been given by Pople and Longuet-Higgins (50) and by Dixon (52) (cf. also Appendix II, Sections B
and C). The approach in each of these papers is semi-empirical. No mention is made of the possible interaction of the $^2B_2\left(^2\sum_-^u\right)$ state with the $^2A_1$ and $^2B_1$ (or $^2\Pi_u$) state although, as pointed out by Renner, such interactions should lead to strong Renner coupling.

SECTION C: Quasilinearity


Quasilinearity was first treated theoretically by Thorson and Nakagawa (58) in an explanation of the infra-red spectrum of disiloxane ($\text{SiH}_2\text{O}_2$). Disiloxane can be considered as being an $AB_2$ type molecule and the theoretical treatment of Thorson and Nakagawa (58) dealt only with $AB_2$ type triatomic molecules. The mathematical arguments presented by these authors are outlined in Appendix III.

Dixon (51) and Johns (59) have discussed quasilinearity in triatomic molecules. The mathematical treatment of these authors (58), (51), (59) involves the solution of the two-dimensional isotropic simple harmonic oscillator which is perturbed by a potential hump*. The effect of the perturbation is that, for the lower vibra-

* cf. note in Appendix II on the use of the word "hump". 
tional energy levels, the molecule is stable in the bent conformation, while in the higher vibrational energy levels of the same electronic state it is stable in the linear conformation.

The analytic expression for the hump devised by Thorson and Nakagawa (58) is

$$\frac{k}{c^2 + r^2},$$

where $k/c^2$ is the hump height relative to the potential minimum for the bent molecule, and $r$ is the distance between the central atom and the line joining the two extremal atoms of the triatomic molecule. This is a Lorentzian hump. Dixon (51) used a Gaussian potential hump* 

$$\alpha \exp (-\beta r^2)$$

as a perturbation to the two-dimensional oscillator. The height of this Gaussian potential hump is $\alpha$ and $\beta$ indicates the width of the hump.

Johns (59) has used both Gaussian and Lorentzian potential humps in his calculations on the quasilinear $\tilde{A}^1A^*$ state of $\tilde{A}^1A^* \leftarrow \tilde{X}^1\Sigma^+$ spectral system of HCN

* A Gaussian barrier had previously been used by Chan and Steeleman (60) to express the barrier to inversion in ammonia.
analysed by Herzberg and Innes (61). Both Johns (59) and Dixon (51) have considered only the bending vibrational motion $v_2$ in a quasilinear electronic state and have shown that the properties outlined in 3.C.2. are characteristic of such a state.


Let

$$\Delta G_{v_1} = E_{v_1+1} - E_{v_1}$$

where $E_{v_1}$ is the energy of the $i^{th}$ quantum of the bending vibrational motion.

A graph of $\Delta G_{v_1}$ versus $E_{v_1}$ for a quasilinear electronic state is shown in Fig. 3.6. The value of $\Delta G_{v_1}$ decreases, passes through a minimum and then increases again. Thus the vibrational energy level pattern shows negative anharmonicity for small $v_1$ but as $v_1$ increases the anharmonicity becomes zero and then assumes a positive value. This behaviour is very characteristic of the bending vibrational motion in a quasilinear triatomic molecule.

Both Johns (59) and Dixon (51) indicate that the energy difference $E_{v_2 = 0} - E_{v_2 = k}$, where the anharmonicity changes from negative to positive at the $k^{th}$ vibrational energy level, is approximately equal to the hump height. Johns (59) has shown that, in a quasilinear state, there is a systematic increase in the inertial
Fig. 3.6. Effects of quasilinearity.
constant A and in the rotational distortion constant $D_k$ with increase in vibrational quantum number $v_2$. This is shown in Fig. 3.6 (b) and Fig. 3.6 (c). A correlation of the vibrational and rotational energy levels of a triatomic molecule in the linear and bent conformations is given in Fig. 3.7.

3.0.3. Interaction of Bending and Stretching Vibrational Motions in a Quasilinear State.

Freed and Lombardi (62) have given a very general treatment of the interactions of bending and stretching vibrational motions in a triatomic molecule which has a large classical amplitude of bending vibration in the bent conformation. The results obtained by these authors are not directly applicable to the discussion in Chapter 4. Thorson and Nakagawa (58) have given a semiqualitative treatment of the interaction of bending and stretching vibrational motions in an $AB_2$ quasilinear triatomic molecule. The mathematical details of the calculation of Thorson and Nakagawa are given in Appendix III.

If the stretching vibrational motion is described by a simple harmonic oscillator equation, the energy eigenvalues are

$$E_s = (N_s + \frac{1}{2})\hbar \omega_s \quad \text{Eqn. 3.2}$$

where $N_s$ is the number of quanta of stretching vibration excited
FIG. 3.7  CORRELATION OF THE ENERGY LEVELS OF A LINEAR MOLECULE WITH THOSE OF A BENT MOLECULE
and $\hbar \omega_s$ is the energy of one quantum of symmetric stretching vibration.

If the molecule has a large classical amplitude of bending vibration, the instantaneous moments of inertia of the molecule change appreciably during the bending motion. This change produces a strong coupling between bending and stretching vibrational motions and leads to energy shifts in Equation 3.2. These energy shifts are calculated in Appendix III.

$$E = \frac{1}{2} (2X_s + 2M/m)(N_s + \frac{1}{2})\hbar \omega_s \langle \alpha^2 \rangle_{n,l} \quad \text{Eqn. 3.3}$$

for an $AB_2$ type molecule

where

- $m$ is the mass of atom A,
- $M$ is the mass of atom B,
- $X_s$ is the constant which gives the strength of the coupling between the bending and symmetrical stretching vibrational motions,
  $$= \frac{1}{2} (\pi - BAB),$$
- $n$ is the mode of the bending vibration excited,
- $l$ is the order of the Associated Laguerre Polynomial, which is contained in the wave function for the bending vibrational motion of the molecule.

Thorson and Nakagawa (58) have discussed qualitatively the values of $\langle \alpha^2 \rangle_{n,l}$ which would be observed for a typical
quasilinear triatomic molecule. The quantities $<\alpha^2>_{n,l}$ and $<\alpha^2>_{n+1,l}$ (n=1, 2, 3 etc.) may differ greatly in numerical value. In general the numerical differences $<\alpha^2>_{n,l} - <\alpha^2>_{n+1,l}$ are very much smaller than $<\alpha^2>_{o,l} - <\alpha^2>_{1,l}$. The difference $<\alpha^2>_{o,l} - <\alpha^2>_{1,l}$ means that a vibrational level, corresponding to the excitation of stretching vibrational motion in the molecule is "apparently split" into two or more component levels having the same but different $n$ values.

This behaviour is characteristic of quasilinear electronic states. The apparent splitting of the $3^1_1$ and $3^0_2$ bands of the $\tilde{E} \leftarrow \tilde{X}$ system of $S_2O$ are attributed to this effect.

SECTION D: Vibrational Transitions and the Franck-Condon Principle


When a transition occurs between two electronic states in a molecule, the "electron jump" occurs, classically, in a time interval which is very much smaller than the period of time taken for the nuclei of the molecule to perform one complete cycle of vibration. This classical idea was first introduced by Franck (6) in an explanation of photochemical dissociation of simple
molecules. The postulate, made by Franck, implies that the geometrical configurations and momenta of the nuclei of the molecule are the same just before and just after electronic excitation, even though the equilibrium geometrical configuration of the nuclei may be different in the initial and excited electronic states.

Condon (64) expressed the postulate of Franck (63) in quantum mechanical terms and by use of the postulate he was able to give expressions for the relative intensities of the vibrational bands in the electronic spectra of several simple diatomic molecules. The Franck-Condon Principle may be illustrated in a graphical manner as in Fig. 3.8. In Fig. 3.8, U'(r) and U''(r) are cross-sections along the normal coordinate r of the potential surfaces of the electronic states E' and E". Using Fig. 3.8, the relative intensities of the vibrational bands involving the normal coordinate r in the transition E' \rightarrow E" may be predicted.

The most probable electronic transition is represented by a vertical straight line originating at the point A on the U''(R) curve and terminating at point B on the U'(R) curve.

\[ R_A = R_B \]

In the semiclassical treatment of the Franck-Condon Principle the point A is at the point of intersection of
Fig. 3.8. Franck-Condon Effect. "Vertical transitions"
for classical and quantum mechanical treatments.
the potential curve and the horizontal line denoting the vibrational energy level. In the quantum mechanical treatment, the point A is at the most probable value of \( r \) for a quantised oscillator.

The vibrational wave functions of a molecule are those of a quantised oscillator — the product of a Hermite Polynomial and an exponential function. The square of the wave function \( \psi_{\text{vib}}^2 \), gives the probability that the quantised normal vibration of the molecule, along the normal coordinate \( R \), has a value \( R = r \). The dotted lines in Fig. 3.8 indicate the squares of the appropriate vibrational wave functions. Condon (64) showed that the intensity of a transition between two vibrational energy levels is proportional to the square of the overlap integral of the vibrational wave functions

\[
\langle \psi_{v(f)} \mid \psi_{v(i)} \rangle^2
\]

This overlap integral was previously discussed on page 32 of Chapter 1.

Fig. 3.9 shows how the Franck-Condon Principle applies to the vibrational band intensities associated with an electronic transition between a bent ground electronic state and a linear excited electronic state in a triatomic molecule. This figure is used to explain the vibrational band intensities observed in the electronic spectra of \( \text{S}_2\text{O} \).
Fig. 3.9. Franck–Condon Effect in a triatomic molecule. A bent-linear transition is shown. $|\psi_v|^2$ is also shown.
The potential curves in Fig. 3.9 are cross-sections through cylindrically symmetric potential surfaces*. In a triatomic XYZ molecule the potential surface along the normal coordinate which describes the bending vibrational motion is cylindrically symmetric about the energy = U axis. The cylindrical symmetry is due to the fact that, in the linear conformation the bending vibration can take place in any of the infinity of planes which intersect along the internuclear axis - the z axis - of the molecule; and in the bent conformation the plane of the molecule can rotate about the axis on which the X and Z atoms lie. For these cylindrically symmetric potential surfaces the bending vibrational motion and the rotational motion are coupled and the wave functions of the energy levels, in the potential wells, are described by Associated Laguerre Polynomials. (cf. Appendix III, Equation A.III.5.)


The band due to the transition between the zeroth vibrational energy level of the ground state and the zeroth vibrational energy level of the excited state is called the origin band of the electronic spectral system. The origin band is designated \( \Delta_0^0 \). A vibrational band is designated \( \Delta_1^0 \) if it is due to the transition

\* cf. Fig. A.III.2.
$Cv'_A \leftarrow Bv''_A$.

$v_A$ indicates the vibrational energy level due to the excitation of $v_A$ quanta of the normal vibration $v_A$.

Intercombination bands are indicated $A_B^C D_E^F$ etc. The set of bands

$$\ldots, A_B^{C+2}, A_B^{C+1}, A_B^C, \ldots$$

form a progression.

The set of bands

$$\ldots, A_B^C, A_B^{C+1}, A_B^{C+2}, \ldots$$

form a progression which is technically called a "hot band" progression. A hot band progression arises from excited vibrational levels in the ground electronic state and the relative intensities of members of this progression may be altered by change in temperature of the molecular sample.

The set of bands

$$\ldots, A_B^{C+2}, A_B^{C+1}, A_B^C, \ldots$$

form a sequence of bands.


Experimental observations on the vibrational structure of many vibronic transitions in molecules, indicate that, if there is a large change in the normal coordinate $r$, as between the ground and excited electronic states, then the vibrational band spectrum observed, due to
a transition between these levels, will consist of long intense progressions in the normal vibration associated with the normal coordinate $r$.

Dressler and Ramsay (57) have used a simple formula to estimate the difference in bond angle, $\Delta \theta$, between the ground $^2B_1$ electronic state and the low lying $^2A_1(\nu_2\Pi_u)$ electronic state of the NH$_2$ molecule,

$$E = \frac{1}{2}k_\theta (\Delta \theta)^2$$

where $E$ is the energy difference between the $0^0_0$ band and the most intense absorption band in the $2^J_0$ progression of the $^2A_1 \leftarrow ^2B_1$ spectral system and where $k_\theta$ is the force constant for the bending vibrational motion $\nu_2$ of the $^2B_1$ state.


A Deslandres Table is a rectangular tabular array of the wavenumbers of the vibrational bands of an electronic spectral system. In each horizontal row of the table, the wavenumbers of a $\nu'$ progression, of the normal vibration $\nu_i$ are arranged in order; while in each vertical column the wavenumbers of a $\nu''$ progression in the same normal vibration are arranged in order. This arrangement is discussed in Herzberg Vol. I, Ref. (65)*. Each

* The horizontal and vertical arrangements are the reverse of those given in Herzberg Vol. I. The arrangement above is more convenient for absorption spectroscopy.
diagonal column of the tabular array contains the set of bands forming a sequence. For polyatomic molecules a super Deslandres Table may be formed, (cf. Herzberg Vol. III Ref. (2)) and each element of this Table may itself be a simple Deslandres table.


A parabola can be drawn on a Deslandres table through those elements of the tabular array which correspond to the most intense vibrational bands of the spectral system for which the table was constructed. This parabola is called a Condon parabola (64). Two cases will be considered

(i) When the sequence of bands of which the origin band is the first member is the most intense feature of the vibrational band structure of the spectral system, the two branches of the Condon Parabola lie close to the diagonal of the Deslandres Table. An analysis of this type of spectrum shows that the change in the normal coordinate, corresponding to the normal vibration for which the Deslandres Table was constructed, is very small.

(ii) When long progressions of bands form the most intense feature of the vibrational band structure of the spectral system, the two branches of the
Deslandres Table showing tabular array of progressions and sequences.

Fig. 3.10. Deslandres Table & Condon Parabolae
Condon parabola are separated, in the asymptotic limit by a large angle. An analysis of this type of spectrum shows that the change in normal coordinate, corresponding to the normal vibration, for which the Deslandres Table was constructed, is very large.

This type of spectrum is observed in a bent linear transition in a triatomic molecule as in Fig. 3.9. This figure is a section through two potential surfaces for a triatomic molecule along one normal coordinate - the normal coordinate of bending vibrational motion and illustrates the section for a bent and for a linear state. The $\tilde{E} \leftarrow \tilde{X}$ and $\tilde{C} \leftarrow \tilde{X}$ spectral systems of $S_2O$ are of the type described in (ii), (with respect to bending motion).


The vibrational structure of an absorption spectral system due to an allowed transition from a bent ground electronic state to a linear excited state of a triatomic molecule should display the following features.

(i) There are long progressions in the bands due to the bending vibrational motion $v_2$. 
(ii) The branches of the Condon parabola are, in the asymptotic limit, separated by a large angle.

(iii) The vibrational bands of the system are red degraded.

Feature (iii) may be understood in the following way.

The degradation of a vibrational band is dependent on the rotational structure of the band. As shown in Chapter I, Equations 1.18 and 1.19 the rotational energy levels of a linear triatomic molecule are given by

\[ E'(J) = B'[J(J+1) - K^2] \]

and the rotational energy levels of the same molecule in an electronic state which is stable in a bent conformation, are

\[ E''_{\text{rot}}(J,K) = B''(J)(J+1) + (A'' - B'')K^2 \]

when the asymmetry parameter \( \kappa \) is \( \approx -1.0 \). When \( \kappa \) is approximately \(-1.0\) the molecular system is nearly a prolate symmetric top and \( A'' > B'' \) while \( B'' \) and \( B' \) are almost equal. Therefore the rotational structure involving rotational energy levels determined by \( J \) and \( K \) in the ground state but by \( B(J)(J+1) \) only in the excited state must be red degraded. In the ground state of \( S_2O \), \( \kappa \) is approximately \(-1.0\) and so in this state the molecule is considered to be a prolate symmetric top.
In the \( \tilde{E} \) and \( \tilde{C} \) electronic states the molecule is in the linear conformation and in the \( \tilde{E} \leftarrow \tilde{X} \) and \( \tilde{C} \leftarrow \tilde{X} \) transitions the features described here are observed.

As shown in Section C of this chapter when a triatomic molecule goes from a bent to a linear conformation the inertial constant \( A \) increases, not to infinity, but to \( \frac{1}{2} \omega_2 \) of the linear conformation.* Therefore each vibrational band in the linear conformation is a \( K \) sub-band. Transitions between the rotational levels of the bent electronic state determined by \( A'B' \) \( J \) and \( K \) and those of the linear electronic state determined by \( (A' \leftarrow \frac{1}{2} \omega_2 e) \), \( B' \), \( J \) and \( K \), are violet degraded i.e. the total intensity envelope of the whole spectral system is violet degraded.

The ideas discussed in this chapter will be used to explain the observed spectra of \( S_2O \) in Chapter 4.

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* cf. Fig. 37, page 96.
CHAPTER IV

Analysis of Experimental Data

Introduction.

As mentioned in Chapter II, which dealt with the experimental work on the \( S_2O \) molecule, three absorption systems, each with discrete vibrational band structure, were observed in the spectral region \( 2300 - 7400 \) Å. They are:

(i) \( \tilde{E} \leftarrow \tilde{X} \) System: Absorption bands of this system were observed in the spectral region \( 2300 - 3500 \) Å.

(ii) \( \tilde{D} \leftarrow \tilde{X} \) System: Due to the experimental difficulties outlined in Chapter II 2.3.12, only a fragment of this spectral system was observed in the region \( 4000 - 4300 \) Å.

(iii) \( \tilde{C} \leftarrow \tilde{X} \) System: Absorption bands of this system were observed in the region \( 4400 - 6700 \) Å.

The \( \tilde{D} \leftarrow \tilde{X} \) and \( \tilde{C} \leftarrow \tilde{X} \) systems have not been reported previously. Absorption bands of the \( \tilde{E} \leftarrow \tilde{X} \) system in the region \( 3350 - 3500 \) Å have not been reported previously. Extremely long absorption pressure path lengths were used in the present work and thus very weak absorption bands could be observed.
Since the three band systems were observed in absorption it is reasonable to assume that they originate in a common ground state* and involve transitions to three different excited electronic states. From the analysis of the three different absorption band systems information on the quantum mechanical structure of the $\tilde{X}$, $\tilde{C}$, $\tilde{D}$ and $\tilde{E}$ electronic states of $S_2O$ is obtained.

This chapter is divided into four subsections. Section A deals with the relative intensities of the three absorption band systems. In Section B an analysis of the $\tilde{E} \leftarrow \tilde{X}$ absorption band system is presented. Section C deals briefly with the $\tilde{D} \leftarrow \tilde{X}$ absorption band system. In Section C, a partial analysis of the $\tilde{C} \leftarrow \tilde{X}$ absorption band system is presented. In Chapter V some conclusions on the structure of the electronic states of $S_2O$ are given.

SECTION A: Intensities


Comparisons of intensities of electronic transitions are frequently expressed in terms of oscillator strengths of the transitions. A short discussion of oscillator strengths was given in Chapter I, page 39.

* cf. Section D for further discussion.
If a beam of electromagnetic radiation of frequency \( \nu \) and intensity \( I_0 \) passes through a column of gas of length \( \ell \) cms, with a concentration of gas of c moles/litre, and emerges with an intensity \( I \), due to the absorption of \( (I_0 - I) \) of the radiation by the molecules of gas

then the absorbance

\[
A = \log_{10} \left( \frac{I_0}{I} \right) = \epsilon \nu \ell c,
\]

where \( \epsilon \nu \) is the molar extinction coefficient.

Mulliken and Rieke (26) have shown that the oscillator strength of the transition causing the absorption is

\[
f = 4.3 \times 10^{-9} \int \epsilon \nu \ dv.
\]

They have also shown that if the intensity envelope of the complete spectral system is triangular in shape a good approximation to \( \int \epsilon \nu \ dv \) is \( \Delta \nu /2 \Delta \nu \). \( \Delta \nu /2 \Delta \nu \) is the width in cm\(^{-1}\) of the intensity envelope of the whole spectral system at an intensity value equal to half the intensity maximum.


The absorption band spectrum of the \( \tilde{E} \leftarrow \tilde{X} \) spectral system of \( S_2O \) was observed on a Cary 14 Spectrophotometer. The discrete band structure of the spectral system was
observed. The effective path length of absorbing gas was approximately 5 cm (± 2 cm). The total pressure of gas in the absorption cell was approximately 1 mm Hg.

Valance Jones (34) and Meschi and Myers (35) have shown that when S\(_2\)O is generated in the manner described in Chapter II, the resultant gas mixture contains approximately 50% S\(_2\)O and 50% SO\(_2\). Therefore the estimated partial pressure of S\(_2\)O in the absorption cell is ½ mm Hg.

Under these conditions, the absorbance, A, of the \(\tilde{E} \leftarrow \tilde{X}\) spectral system was approximately 4 x 10\(^{-2}\). Therefore the extinction coefficient \(\varepsilon_\nu\) is approximately 10\(^3\). The intensity envelope for the \(\tilde{E} \leftarrow \tilde{X}\) absorption band spectrum is triangular in shape. The width observed at half maximum intensity \(\Delta \nu_{1/2}\) was approximately 5 x 10\(^3\) cm\(^{-1}\). Therefore the oscillator strength of the transition

\[
f = \varepsilon_\nu \Delta \nu_{1/2} \times 4.3 \times 10^{-9}
\]

\[
= 2 \times 10^{-2}, \text{ approximately.}
\]

This calculation is an order of magnitude calculation. Therefore it is significant to quote only

\[f(\tilde{E} \leftarrow \tilde{X}) \text{ lies in the range } 10^{-2} - 10^{-1}\]

Direct absorbance measurements were not made on the Cary 14 spectrophotometer for the \(\tilde{C} \leftarrow \tilde{X}\) and \(\tilde{D} \leftarrow \tilde{X}\)
absorption band systems. The absorption intensities of these spectral systems are very much lower than the absorption intensity of the $\tilde{E} \leftarrow \tilde{X}$ spectral system and the long absorption path lengths required to observe the bands of these systems cannot easily be used on a Cary 14 spectrophotometer. The pressure path lengths required to observe the $\tilde{D} \leftarrow \tilde{X}$ and $\tilde{C} \leftarrow \tilde{X}$ absorption band systems were approximately $10^2$ and $10^5$ (respectively) greater than the pressure path length used to observe the $\tilde{E} \leftarrow \tilde{X}$ absorption band systems. Therefore, the oscillator strengths of the $\tilde{E} \leftarrow \tilde{X}$, $\tilde{D} \leftarrow \tilde{X}$ and $\tilde{C} \leftarrow \tilde{X}$ absorption systems are approximately in the ratio $1 : 10^{-2} : 10^{-5}$, respectively. The approximate oscillator strengths are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Spectral System</th>
<th>Approximate Oscillator Strength $f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{E} \leftarrow \tilde{X}$</td>
<td>$10^{-2}$ ... $10^{-1}$</td>
</tr>
<tr>
<td>$\tilde{D} \leftarrow \tilde{X}$</td>
<td>$10^{-4}$ ... $10^{-3}$</td>
</tr>
<tr>
<td>$\tilde{C} \leftarrow \tilde{X}$</td>
<td>$10^{-7}$ ... $10^{-6}$</td>
</tr>
</tbody>
</table>
SECTION B: The $\tilde{E} \leftarrow \tilde{X}$ System

4.B.1. Description of Spectrum.

Absorption bands of this spectral system were observed in the region 2300 Å - 3500 Å. The intensity maximum of the system occurs at approximately 2800 Å. The spectrum is illustrated in Fig. 4.1. The photograph of the spectrum in Fig. 4.1 was taken in the second order of the 1.5 m Bausch and Lomb Model 11 spectrograph.

Fig. 4.2 is a photograph of the rotational structure of the absorption bands at 3307 Å and 3321 Å. This photograph was taken in the 1st Order of the 6 m Ebert spectrograph - the high resolution spectrograph.

The vibrational bands of the spectral system are, on the basis of appearance, divided into three groups:

(i) bands in the spectral region 3193 - 3500 Å. (the bands at 3208 Å, 3222 Å, 3248 Å and 3291 Å are excepted from this grouping.) These bands are all sharply degraded to the red and they all show fine rotational structure, even when observed on the Bausch and Lomb Model 11 spectrograph - the low resolution spectrograph.

(ii) bands in the spectral region 2819 - 3193 Å. (with the exception of bands at 2830 Å, 2860 Å and 2890 Å.) The bands at 3208 Å, 3222 Å, 3248 Å and 3291 Å are included in this group. All of the bands in this group are sharply
The intensity maximum in the A progression is at approximately 35,500 cm\(^{-1}\) and in the C progression at approximately 34,500 cm\(^{-1}\). Rotational structure may be seen in bands at the low energy side of the spectrogram. The diffuse character of the bands at the high energy side of the spectrogram may also be seen. Quantum number assignments of the bands are also shown. These assignments will be discussed later in this chapter.
The 3.077 Å (\( ^3\Delta \rightarrow ^3\Pi \) transition) absorption spectrum of the \( S_2O \) molecule (near U.V. system)

Fig. 4.1
Fig. 4.2

HIGH RESOLUTION EBERT SPECTROGRAM SHOWING
THE FINE ROTATIONAL STRUCTURE OF THE
ABSORPTION BANDS AT 30,099 cm\(^{-1}\) AND AT
30,229 cm\(^{-1}\).

The sharp heads and strong red degradation
of the bands in this region of the spectrum
is clearly illustrated in this photograph,
which was taken in the 1\(^{st}\) order of the
6 m Ebert Spectrograph.
Fig. 4.2 High resolution spectrogram showing the rotational structure which is typical of bands of the \( \tilde{E} \leftrightarrow \tilde{X} \) system.
degraded to the red and are similar in appearance to the bands in group (i). None of the bands in group (ii) show any resolved rotational structure even when observed on the 6 m Ebert spectrograph, which has a theoretical resolving power of 300,000 in the second order of diffraction.

(iii) bands in the region 2300 Å - 2819 Å region. The bands at 2830 Å, 2860 Å and 2890 Å are included in this group. All bands in group (iii) are diffuse in appearance - the diffuseness being more marked for bands at shorter wave lengths. No resolved rotational structure was observed for any of these bands. Bands close to 2900 Å show a distinct red degradation, while bands close to 2300 Å are very diffuse and do not show any distinct degradation.

Bands with maximum absorption intensity occur at 2800 Å approximately. The intensity of bands in the region 2800 - 2300 Å falls off slowly towards shorter wave lengths. The intensities of bands in the region of 2300 Å are approximately 10% of the maximum intensity (which occurs at 2800 Å approximately.) The intensity of bands in the region 2800 - 3500 Å falls off rapidly towards longer wave lengths. The intensities of the absorption bands at 3500 Å are approximately 0.01% of
the intensities of the bands at 2800 Å. A list of band head wave numbers and intensities of the bands of the $E \leftrightarrow \tilde{X}$ system is given in Appendix IV.

4.B.2. Ordering of Bands into Progressions.

Vallance Jones (34) arranged the eleven bands lying between 3193 Å and 3151 Å into three progressions which he called the A, B and C progressions. He showed that three members of the B progression were separated from three members of the A progression by 679 cm$^{-1}$. An infrared absorption band at this same frequency was observed by Vallance Jones (34). Meschi and Myers (35) have assigned this absorption band at 679 cm$^{-1}$ as being due to the excitation of one quantum of the stretching vibration $\nu_3$ of the ground $\tilde{X}$ state of $S_2C$.

Table 4.2 is a Table similar to that given by Vallance Jones (34). The band head energies used in the table were taken from the measurements made in the present work. Bands to longer wave length than 3351 Å are included in the table. Bands to shorter wave length than 3193 Å are not included in Table 4.2. (This omission is explained in the discussion of hump heights since the hump height changes when stretching vibrational motions are excited.)

Table 4.2 shows that four members of the C progressions are separated from the corresponding members.
### Table 4.2

<table>
<thead>
<tr>
<th>A cm⁻¹</th>
<th>B cm⁻¹</th>
<th>ΔE cm⁻¹</th>
<th>A cm⁻¹</th>
<th>C cm⁻¹</th>
<th>ΔE cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>31308*</td>
<td>30629*</td>
<td>679</td>
<td>31308</td>
<td>29955</td>
<td>1353</td>
</tr>
<tr>
<td>30909*</td>
<td>30229*</td>
<td>680</td>
<td>30909</td>
<td>29557</td>
<td>1352</td>
</tr>
<tr>
<td>30506*</td>
<td>29826*</td>
<td>680</td>
<td>30506</td>
<td>29154</td>
<td>1352</td>
</tr>
<tr>
<td>30099</td>
<td>29419</td>
<td>680</td>
<td>30099</td>
<td>28747</td>
<td>1352</td>
</tr>
<tr>
<td>29689</td>
<td>29008</td>
<td>681</td>
<td>29689</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Bands assigned in Table II, page 1267, of Vallance Jones (34).
of the A progression by 1352 cm\(^{-1}\), approximately.

\[1352 \text{ cm}^{-1} \text{ is approximately } 2 \times 679 \text{ cm}^{-1}.\]

Therefore, the energy interval 1352 cm\(^{-1}\) is identified as \(2 \nu^m\) of the \(\tilde{X}\) ground electronic state.

The energy differences between successive members of the A, B and C progressions are approximately 390 cm\(^{-1}\). Blukis and Myers (36) have observed an infrared absorption band at 388 cm\(^{-1}\), which is identified as the energy of one quantum of bending vibrational motion \(\nu^m_2\) in the \(\tilde{X}\) ground state. Therefore the A, B and C bands are identified as progressions in the bending vibrational motion \(\nu_2\).

The A, B and C series of bands extend a considerable distance towards higher energies with slightly altered wave number intervals and with much greater intensity. In the next section it will be shown that these extensions of the A, B and C series result from progressions in the upper state vibrational bending motion \(\nu^o_2\). The frequency \(\nu^o_2\) is only slightly different from the frequency \(\nu^m_2\).

The assignment of these bands depends upon the identification of the origin band of the system. All bands

(i) of the A progression between 2300 and 2941 \(\AA\),
(ii) of the B progression between 2870 and 3183 \(\AA\) and
(iii) of the C progression between 2300 and 3338 \(\AA\) show a double or triple headed structure.
4.3. Assignment of the \( \psi_0 \) band.

The graphs of \( \Delta G_{v_2} \) (the energy difference between successive members of a progression of bands) versus energy was plotted for the A, B and C progressions. This is shown in Fig. 4.3. The graph shows a sudden discontinuity of approximately 14 cm\(^{-1}\) in the A progression at 32487 cm\(^{-1}\) (3077 Å), in the B progression at (31796; 31807) cm\(^{-1}\) and in the C progression at (31158; 31173) cm\(^{-1}\). The band at 32487 cm\(^{-1}\) is assigned as the origin, \( \psi_0 \), band and the A progression of bands is assigned as the set of bands

\[ (\ldots \, 2^n_0 \, \text{and} \, 2^0_n \, \ldots \ldots) . \]

The double headed band at (31796; 31807) cm\(^{-1}\) is assigned as the \( 3_1^0 \) band and the B progression of bands is assigned as

\[ (\ldots \, 2^n_0 \, 3_1^0 \, \text{and} \, 2^0_n \, 3_1^0 \, \ldots \ldots) . \]

---

Schenk (28) assumed that the molecule now known to be \( \text{S}_2\text{O} \) was \( \text{S}_2\text{O}_2 \). Kondrat'eva and Kondrat'ev (33) wished to examine the equilibrium

\[ \text{S}_2\text{O}_2 \rightleftharpoons 2\text{S}_2 \]

and the temperature dependence of this interconversion process. They concluded that the degree of dissociation of what they believed to be \( \text{S}_2\text{O}_2 \) into \( \text{S}_0 \) was very small. It is now known that the molecule is in fact the triatomic molecule \( \text{S}_2\text{O} \) and not the tetra-atomic molecule \( \text{S}_2\text{O}_2 \).

Kondrat'eva and Kondrat'ev measured the absorption intensity of the vibrational bands at 30099 cm\(^{-1}\) and 30506 cm\(^{-1}\) (members of the A progression) and 30229 cm\(^{-1}\) and 30629 cm\(^{-1}\) (members of the B progression). A single pass 10 cm
absorption gas cell was used by Kondrat'eva and Kondrat'ev. The effective temperature of the central 6 cm of this cell was varied from -60° C to +60° C. It was observed that the absorption intensity of the vibrational bands at 30229 cm⁻¹ and 30629 cm⁻¹ changed relative to the absorption intensity of the vibrational bands at 30099 cm⁻¹ and 30506 cm⁻¹. The absolute absorption intensities of these latter bands was not observed to change under the experimental conditions used. Vallance Jones (34) also believed the S₂O molecule to be S₂O₂. On the basis of the intensity observations of Kondrat'eva and Kondrat'ev, he tentatively assigned the band at 30099 cm⁻¹ as the O₀ band of the absorption band spectrum. This assignment is quoted in Herzberg Vol. III.

The present assignment of the band at 32487 cm⁻¹ does not conflict with the intensity observations of Kondrat'eva and Kondrat'ev. Vallance Jones did not observe the vibrational bands at 29689 cm⁻¹, 29274 cm⁻¹, 28860 cm⁻¹. All of these bands are members of the A progression. There is no discontinuity in \( G_{\nu_2} = E_{\nu_2+1} - E_{\nu_2} \) at 30099 cm⁻¹ such as occurs at 32487 cm⁻¹. If 30099 cm⁻¹ is assumed to be the O₀ band then energy level diagrams (as in Figs. 4.4 and 4.5) are complex and exceedingly difficult to explain. The intensity measurements of Kondrat'ev and Kondrat'eva were carried out with a short absorption path length of gas, over small temperature range and over such a small region of the total absorption spectrum that it cannot be regarded as conclusive that the absolute intensity of the band at 30099 cm⁻¹ does not change in temperature, while all other bands do show a temperature effect. The values for the absorption coefficients only varied by approximately 1% in the work of Kondrat'eva and Kondrat'ev (33).

The assignment of the O₀ band as the band at 32487 cm⁻¹ provides a much greater degree of internal consistency in the analysis of the spectrum.
A PLOT OF $\Delta G(v_2)$ AGAINST $E(v_2)$ FOR THE A, B & C PROGRESSIONS
The double headed band at (31158; 31173) cm$^{-1}$ is assigned as the $3_2^0$ band and the C progression of bands is identified as

\[ (\ldots \; 2_n^0 3_2^0 \; \text{and} \; 2_n^0 3_2^0 \; \ldots ) \]

where $n = 1, 2, 3, \ldots$ etc.

The intensity of the origin band is 100 (cf. Chapter II 2.B.12), the intensity of the $3_1^0$ band is 7.5 and the intensity of the $3_2^0$ band is 1.8.

A super-Deslandres table of the bands of the $\tilde{E} \leftarrow \tilde{X}$ system is given in Table 4.3. An energy level diagram for the vibrational structure of the ground X state is given in Fig. 4.4 and for the vibrational structure of the E state in Figure 4.5. The ground and excited state progressions formed by the A, B and C series of bands are also shown on these energy level diagrams. The assignment of the band at 32487 cm$^{-1}$ (3077 Å) as the origin band gives a consistent vibrational energy level scheme for both the $\tilde{X}$ and $\tilde{E}$ electronic states.

No progressions in the vibrational mode $v_1''$ could be identified in the $\tilde{E} \leftarrow \tilde{X}$ spectral system. This may be due to the fact that $v_1''$ contains no angle-bending component of motion, whereas $v_2''$ does (cf. Fig. 1.2, page 18) and hence $v_1''$ is not active, but $v_2''$ is active in the spectrum in accordance with the Franck-Condon Principle.
### SUPER DESLANDRES TABLE OF THE 3077Å ABSORPTION SPECTRUM OF $S_0O$

$\left( \tilde{E}'A \rightarrow \tilde{X}'A'' \ \text{TRANSITION} \right)$

<table>
<thead>
<tr>
<th>$v'_r$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v''_r$</td>
<td>1296</td>
<td>33250</td>
<td>33629</td>
<td>34008</td>
<td>34377</td>
<td>34746</td>
<td>35123</td>
<td>35479</td>
<td>35862</td>
<td>36227</td>
<td>36550</td>
<td>36952</td>
<td>37**</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34000</td>
<td>34351</td>
<td>34712</td>
<td>35060</td>
<td>35427</td>
<td>35800</td>
<td>36123</td>
<td>36450</td>
<td>36830</td>
<td>37**</td>
<td>37**</td>
<td>37**</td>
<td>37**</td>
<td></td>
</tr>
</tbody>
</table>

### Band Progressions

- **A Progression**
  - $2^+_a$ Bands
  - $3^+_2^+$ Bands
  - $3^+_2^+$ Bands

- **B Progression**
  - $3^+_2^+$ Bands
  - $3^+_2^+$ Bands

- **C Progression**
  - $3^+_2^+$ Bands
  - $3^+_2^+$ Bands

**Note:** All bands are mentioned but specific details are not provided in the table.
Vibrational energy levels of the $\tilde{X}'A'$ state and the transitions observed between these levels and the zeroth vibrational energy level of the $\tilde{E}'A'$ state. Energies are in cm$^{-1}$.

FIG. 4.4
Fig 4.5 Transitions originating in the \((0,0,0)\) and \((0,0,2)\) levels of the \(X^2E_a\) state. Energies are in cm\(^{-1}\). The \((0,0,0)\) levels are shown as the zero points of the energy scale.
for a bent to linear transition. No bands which could be assigned to \( \text{ln}_o \) or \( \text{3n}_o \) were identified in the spectrum.

4.B.4. The \( \tilde{X} \) ground electronic state of \( \text{S}_2\text{O} \).

During the present investigation of \( \text{S}_2\text{O} \), absorption path lengths of gas of from 10 cm to 0.5 Km were used to observe the spectra. In the \( \tilde{X} \) ground state, ten members of the progression \( 2^0_n \) - the A progression - eight members of the progression \( 2^0_1 2^0_n \) - the B progression - and seven members of the progression \( 2^0_2 2^0_n \) - the C progression - were observed.

The vibrational energy level structure of the \( \tilde{X} \) ground state of \( \text{S}_2\text{O} \) shows the following features, which are characteristic of quasilinear electronic states.

(i) The energy intervals in the \( 2^0_n \) progression

\[
G_{v_2}'' = E_{v_2}'' + 1 - E_{v_2}'
\]

decrease at first and then systematically increase as \( v_2'' \) increases. This behaviour is characteristic of a quasi-linear molecule cf. Thorson and Nakagawa (58), Dixon (51) and Johns (59). The same qualitative behaviour is observed in the \( 2^0_1 2^0_n \) progression of bands. In the \( 2^0_2 2^0_n \) progression \( \Delta G_{v_2}'' \) systematically increases with \( n \) for all values of \( v_2'' \).
(ii) The ground state vibrational levels in which single and double quanta of the symmetric stretching vibration \( v''_3 \) and \( 2v''_3 \) are excited appear to have two components. No apparent splitting is observed in the bands which involve the excitation of symmetric bending vibrations \( v''_2 \) only. This is discussed by Thorson and Nakagawa (58).

The force constant calculations of Nagarajan (37) have shown that the root mean square value of the classical amplitude of the bending vibration \( v''_2 \) is approximately 9° in the zeroth vibrational level of the ground \( X \) electronic state of \( S_2O \). This is a large value for the classical amplitude of bending vibration for a triatomic molecule and this large value is characteristic of a quasilinear electronic state.

Meschi and Myers (35) have observed that the inertial constant \( A \) of the 0,1,0 vibrational level of the ground \( X \) state of \( S_2O \) was greater than the \( A \) constant for the zeroth vibrational energy level of the same \( \tilde{X} \) state of \( S_2O \).

\[
A_{010} = 1.4169 \text{ cm}^{-1} \quad A_{000} = 1.3981 \text{ cm}^{-1}
\]

This is characteristic of a quasilinear electronic state, cf. Johns (59).

These four observations establish that the \( \tilde{X} \) ground state of \( S_2O \) must be considered as a quasilinear state as described in Section C of Chapter III and in Appendix III.

If the $\tilde{X}$ state of $S_2O$ is a quasilinear state then the height $E$ of the potential hump, which distorts the molecule from the linear into the bent conformation, must be estimated. No absolute method for the determination of hump heights is yet available in the literature. A discussion of the presently available methods of determining hump heights are given here.

The Lorentzian and Gaussian approximations to the shape of the potential hump in a quasilinear electronic state were discussed in Chapter III Section C. Both Johns (59) and Dixon (51) imply, but do not state explicitly, that irrespective of which form - Gaussian or Lorentzian - is used to describe the potential hump, the energy difference

$$E_{v_2=0} - E_{v_2=k} = E \text{ (approx.)}$$

where $v_2=k$ is the vibrational energy level at which the anharmonicity changes from negative to positive, and where $E$ is the hump height. This reasoning would suggest a hump height of approximately $1200 \text{ cm}^{-1}$ in the ground $\tilde{X}$ state of $S_2O$ when no quanta of symmetric vibration are excited (i.e., in the A progression of bands). The hump height would be approximately $800 \text{ cm}^{-1}$ when one quantum of stretching vibrational motion $\nu''_2$ is excited and is $400 \text{ cm}^{-1}$, or less, when two quanta of the stretching vibrational motion $\nu''_2$ are excited. There is a reduction
in the apparent hump height when the stretching vibrational motion $\nu_2$ is excited. The vector displacements for the vibrational mode $\nu_2$ as shown in Fig. 1.2, page 18, indicate that this mode contains a bond angle bending component. Therefore, during the vibration $\nu_2$ the molecule tends to "straighten out", i.e., move towards a linear conformation.

However, the assignment of 1200 cm$^{-1}$ as the potential hump height in the $\tilde{X}$ state of $\text{S}_2\text{O}$ when neither of the stretching vibrational motions are excited is not consistent with other calculations. Dixon (51) has shown that the potential hump height $\mathcal{E}$, when stretching vibrational motions are not excited is given by

$$\mathcal{E} = \frac{q_0^2 \omega}{4s_0^2} \left[ \frac{1}{\ln(\eta)} - \frac{1}{\ln(\eta)} - 1 \right] = \frac{q_0 \omega}{4s_0^2} \chi,$$

$q_0$ is the displacement of the central atom of the triatomic molecule in the bent conformation, from the position which it would occupy on the internuclear axis if the molecule were in the linear conformation. $q_0$ is measured in Å;

$s_0$ is the amplitude of the bending vibration in the zeroth vibrational energy level. $s_0$ is measured in Å;

where $\omega$ is the energy of the symmetric bending vibration $\nu_2$.
\( \chi \) is a slowly varying function of \( \eta \); and \( \eta = 2 \alpha \beta \) as discussed in Chapter III 3.C.2.

For the ground state of \( \tilde{X} \) of \( \text{S}_2\text{O} \)

\[
q_0 = 0.81 \, \text{Å} \quad s_0 = 0.09 \, \text{Å} \quad \omega = 395 \, \text{cm}^{-1}
\]

and for a typical quasilinear molecule \( \chi \) is approximately 0.8***.

From this calculation the hump height

\[ \varepsilon = 6,500 \, \text{cm}^{-1} \text{ approx.} \]

This is much larger than the previously estimated value of 1200 \( \text{cm}^{-1} \). However, there is no reason to believe that either method of calculation would give particularly accurate values. As Fig. 4.3 shows, the slope of \( \Delta G_{\nu_2} \) curve only changes sign slowly, and there is no reason to assume an exact correspondence between the hump height and the point where the anharmonicity constant changes sign.

* Calculated from the geometry of \( \text{S}_2\text{O} \) in the ground \( X \) state.

** Calculated from the value of \( \sigma_0^2 \) as given by Nagarajan (37).

*** \( \chi \) is a very slowly varying function of the product \( 2 \alpha \beta \). Even when \( \eta = 2 \alpha \beta \) is changed by 100%, \( \chi \) changes by less than 15%. The value of \( \chi = 0.8 \) is used for this order of magnitude calculation of \( \varepsilon \) - the hump height.
The occurrence of positive anharmonicity in the energy level pattern of the bending vibrational motion $v_2$ below the potential hump height can be accounted for in the following manner. The Lorentzian and Gaussian analytical forms of the potential energy hump are chosen simply for ease of computation, and may be quite unrealistic for the ground $\tilde{X}$ state of the $S_2O$ molecule. A potential hump with small width but large height in energy units is shown in Fig. 4.6. The wave functions for the vibrational rotational energy levels will overlap in the region underneath the potential hump. When appreciable overlap occurs the probability of the molecule being in the linear conformation is increased. If the form of potential hump in Fig. 4.6 is realistic for the ground $\tilde{X}$ state of $S_2O$, then positive anharmonicity in the energy level pattern of the bending vibrational motion $v_2$ can occur at energy levels below the top of the potential hump.

4.3.6. Excitation of quanta of stretching vibration in the $X$ state.

The vibrational bands at $(31796)$ cm$^{-1}$ and $(31158)$ cm$^{-1}$ have been assigned as the $3_1^0$ and $3_2^0$ bands. Both bands are double headed. The separation of the two heads in the $3_1^0$ band is 11 cm$^{-1}$ and in the $3_2^0$ band is 15 cm$^{-1}$. As can be seen from the energy level diagrams, Figs. 4.4 and 4.5 on pages 129 and 130, these splittings are not due to
FIG. 4.6. POTENTIAL CURVES SHOWING TUNNELING INTO THE REGION BENEATH THE HUMP.
rotational branch leads but occur in the energy levels associated with excitation of the stretching vibrational motion $\nu''_2$ in the $X$ ground state of $S_2O$.

In the infrared absorption bands observed by Vallance Jones (34), the band corresponding to the excitation of one quantum of symmetric stretching vibrational motion $\nu''_2$ contained three peaks — one at 670 cm$^{-1}$, one at 679 cm$^{-1}$ and one at 691 cm$^{-1}$; while the infrared absorption band corresponding to the excitation of one quantum of symmetric stretching vibrational motion $\nu''_1$ has two peaks — one at 1159 cm$^{-1}$ and the other at 1173 cm$^{-1}$.

There are two possible explanations for the observation of a splitting in the energy levels associated with stretching vibrational motions in the $\tilde{X}$ electronic state.

(i) Since the mean amplitude of bending vibration $\nu''_2$ in the $X$ state of S-S-O has a large classical amplitude the $S_2O$ molecule may be classified as a non-rigid molecule. The operation

\[
\begin{align*}
\text{I} & \quad \text{(1) (2)} \\
0 \quad \begin{array}{c} \\
S-S \\
\end{array} & \quad \rightarrow \\
\end{align*}
\]

\[
\begin{align*}
\text{II} & \quad \text{(1) (2)} \\
\begin{array}{c} \\
S-S \\
\end{array} \quad 0
\end{align*}
\]

which switches the oxygen atom is an isodynamic operation. Configurations I and II are not superimposable by simple rotation. If the oxygen switching is a feasible operation
then the wave functions of the $S_2O$ molecule transform as the irreducible representations of the Abelian point group $G_4$ which is isomorphous with $C_{2v}$. The effect of this is to produce a small splitting* of each vibrational energy level into two components. These components are classified $+$ and $-$ according as the wave function of each component remains unchanged or changes sign on reflection in the plane of the molecule. Transitions from both of these components to the single upper vibrational level $(0,0,0)$ of the E state can occur.

However, the use of this effect as an explanation for the observed splitting of the $3_1^0$ and $3_2^0$ bands is not accepted in this work. An effect of this kind should be larger in vibrational bands involving the excitation of quanta of bending vibration $\nu_{3n}^0$. No splitting of similar magnitude is observed in the $2_n^0$ progression of bands.

A second mechanism to explain the splittings is that proposed by Thorson and Nakagawa (58). This explanation is considered in detail in Chapter III Section C and in Appendix III. It is a characteristic of quasilinear electronic states that vibrational bands associated with stretching vibrational motions in such a state show side band effects, i.e., show an apparent splitting which is absent from vibrational bands associated with the bending vibrational motion of the molecule. This explanation is assumed to be the correct one.

* Private Communication, Altman (23).
The symmetries of the components of the "split" vibrational energy levels were not assigned by Thorson and Nakagawa (58). From the energy level diagrams Figs. 4.4 and 4.5 it is seen that the two components of the $3_1^0$ and $3^0_2$ are not of the same symmetry. For further discussion cf. 4.B.13.


All vibrational bands involving transitions from the vibrational energy levels of the $\tilde{X}$ ground state to the $(0 0 0)$ energy level of the $E$ electronic state of $S_2O$ (cf. Fig. 4.4) have sharp heads and are sharply degraded to the red. In this set of bands the

$$0^0_0, \ 2^0_1, \ 2^0_2, \ 3^0_1, \ 2^0_1 3^0_1, \ 3^0_2, \ 2^0_1 3^0_2$$

do not show a resolved rotational structure, whereas all the other bands of the set do.

The most likely explanation is that the group of bands, for which rotational structure was not observed do in fact have rotational structure, in which, however, the separation of the rotational spectral lines is less than width due to the Doppler and pressure broadening of these rotational lines. The observation of discrete rotational structure for the $2^0_3, 2^0_4$ etc. bands excludes the possibility that the diffuseness in the $0^0_0, 2^0_1$ etc. bands is due to a diffuseness in the $(0 0 0)$ level of the $\tilde{E}$ state. The
observation of transitions in the microwave region of the spectrum between the lower rotational energy levels of the (0,0,0) and (0,1,0) vibrational energy levels of the X ground electronic state of $S_2O$ excludes dissociation in these vibrational energy levels.

In a quasilinear electronic state of a molecule, the inertial constant $A$, and Ray's asymmetry parameter are functions of the number of quanta of bending vibrational motion excited. Both $A$ and $\kappa$ increase rapidly with $v_2$ (59). This type of behaviour is shown in Fig. 3.6. It is probable that $A_{(030)}''$ is sufficiently large and that the rotational energy levels of the $v_2'' = 3$ vibrational energy level are separated by a sufficiently large energy gap from one another that the rotational lines of the $2^0\tilde{3}$ band do not overlap each other and so are resolved as rotational lines by the spectrograph. If the symmetric stretching vibration $v_3''$ is excited, the potential hump to linearity is reduced and the constants

$$A_{(021)}'' \text{ and } A_{(022)}''$$

of the $\tilde{X}$ electronic state are also sufficiently large to allow the observation of resolved rotational structure. Photographs of bands showing resolved rotational structure are given in Fig. 4.2.

A photograph of the vibrational band at 31,508 cm$^{-1}$,
which shows resolved rotational structure, was taken on the 10.5 m Ebert spectrograph, of resolving power 600,000, at the National Research Council Laboratories in Ottawa. This vibrational band, which is similar to the bands in Fig. 4.2 in structure, shows an extremely complicated structure formed by the appearance of many rotational branches. The energy spacing between successive members of some of these branches can be fitted to an empirical formula

\[ E = T(2N + 1) \]

In some rotational branches, \( T = 1.0 \text{ cm}^{-1} \) and \( N = 0, 1, 2 \) etc., while in other branches \( T \) also = 1.0 cm\(^{-1}\) and \( N = 1, 2, 3 \) etc., but \( N \neq 0 \). The value of \( T \) could not be identified with any of the known inertial constants of the molecule. The number \( N \) could not be identified as the quantum number \( K \) or \( J \).

A comparison between the photograph of the 31308 cm\(^{-1}\) band of \( S_2O \) and a photograph of the rotational structures of the spectrum of \( \text{CSe}_2 \) taken on the same 10.5 m spectrograph showed that most of the "rotational lines" in the 31308 cm\(^{-1}\) band of \( S_2O \) are probably due to many single spectral lines which occur close together in energy and are blended into one apparent rotational line. A rotational analysis of the 31,308 cm\(^{-1}\) band of \( S_2O \) could not be made in spite of considerable time devoted
to the task of rotational analysis. It appears that such an analysis will only be achieved on the experimental side when the band can be photographed under very much higher resolution than is currently available and when ways are found to introduce isotopes of oxygen or sulphur into the molecule to obtain different molecular isotopic species, and on the theoretical side when analytical expressions for the rotational levels of quasilinear states of molecules have been worked out.

4.3.8. The Electronic spin of the \( \tilde{X} \) state.

As previously discussed in Chapter II, the \( 31308 \, \text{cm}^{-1} \) (3193 Å) band of the \( \tilde{E} \leftarrow \tilde{X} \) spectral system does not show a Zeeman Effect. If either the \( \tilde{E} \) or the \( \tilde{X} \) state of the \( S_2O \) molecule has an electronic spin of unity, then in a magnetic field the spin angular momentum vector could have three quantised components along the direction of the magnetic field, i.e., \( M_S = 0, \pm 1 \). It is shown in Herzberg Vol. III (2) that an energy term \( \Delta E \) must be considered in the presence of a magnetic field. The energy \( \Delta E \) is added to the rotational energies.

\[
E = -g M_S \mu_B H,
\]

where \( g \) = the Landé g factor which = 2 for free electrons,
\( \mu_B \) = the Bohr magneton = \( 4.67 \times 10^{-5} \, \text{cm}^{-1}/\text{Gauss} \).
and \( H \) = strength of applied magnetic field in gauss.

In the Zeeman Effect experiment carried out in the National Research Council Laboratories, Ottawa, \( H = 2,000 \) gauss so \( \Delta E = 0.2 \) cm\(^{-1} \), approximately. Energy shifts of 0.2 cm\(^{-1} \) in the rotational structure of a vibrational band should readily be observable on the 10.5 m Ebert spectrograph at N.R.C., Ottawa. At the very least, the effect of the magnetic field would be to "blur" the rotational lines in the spectrum (Douglas (66)) and this was not observed.

Since no Zeeman Effect is observable for the 31,308 cm\(^{-1} \) band of the \( \tilde{E} \leftarrow \tilde{X} \) spectral system it is necessary to conclude that the electronic spin angular momentum of both the \( X \) and \( E \) electronic states is zero.

4.3.9. The Symmetry of the \( \tilde{X} \) electronic state.

The \( \tilde{X} \) electronic state of \( S_2O \) is stable in the bent conformation. The electronic spin angular momentum associated with the \( \tilde{X} \) state is zero, i.e., it is a singlet state. The \( S_2O \) molecule contains an even number of electrons and in the ground state the molecular orbitals are doubly occupied. Therefore, the ground state of \( S_2O \) is the \( X'A' \) state, i.e., the ground state is totally symmetric with respect to the operations of the point group to which the molecule belongs. In the \( O_2 \) and \( SO_2 \) molecules the ground states are \( ^1A_1 \) states.
The calculations of Robinson (27) on $O_3$ show that the ground $X^{1\Lambda_1}$ state correlates with the $^1\Delta_g$ state of the configuration \((\pi^e_u)^4(2\pi^e_u)^2\) of the linear conformation. It is reasonable to assume that the corresponding $X^{1\Lambda'}$ state of $S_2O$ correlates with the $^1\Delta$ state of the configuration \((2\pi)^4(3\pi)^2\) of the linear conformation, see Fig. 3.2. The results of the spectroscopic analyses are consistent with this assignment.

If the $X^{1\Lambda'}$ state of $S_2O$ is derived from the \(1\) \(((2\pi)^4(3\pi)^2)\) state of the linear conformation then the potential curve for the $\bar{X}$ state can be derived by considering strong Renner Coupling, either case (b) or case (c) in the linear $^1\Delta$ state, see Fig. 3.5 page 88. An exact analytical treatment of Renner Coupling and the influence of nearby electronic states on the magnitude of the coupling would be helpful in determining the quasi-linear character of the $\bar{X}^{1\Lambda'}$ state of $S_2O$.

4.B.10. Geometry of the $\bar{E}$ electronic state.

The vibrational bands of the $\bar{E} \leftarrow \bar{X}$ spectral system are all sharply degraded to the red. Very long progressions

\[ (\ldots 2^n_0 \ldots 2^o_n \ldots ) \]

\[ (\ldots 2^{n_2}_0 2^o_{n_1} \ldots 2^{o_2}_n \ldots ) \]

\[ (\ldots 2^{n_2}_0 2^o_{n_2} \ldots 2^{o_2}_n \ldots ) \]
are observed. The Franck Condon Principle implies that there is a large change in the normal coordinate associated with the bending vibrational motion $\nu_2$ when the molecule is excited from the $\tilde{X}$ ground state to the $\tilde{E}$ excited electronic state, i.e., there is a large difference in the S-S-O bond angle between the $\tilde{E}$ and $\tilde{X}$ states.

Dressler and Ramsay (57) used a simple calculation to determine the difference in bond angle between the $^2B_1$ ($^2 \Pi_u$) and $^2A_1$ ($^2 \Pi_u$) states in NH$_2$.

Let $\Delta \theta$ be the difference in bond angle.

Let $k_6$ be the force constant for the bending vibrational motion $\nu_2$.

Let $\Delta E$ be the energy difference between the origin band and the bands which show maximum absorption intensity.

Then $\frac{k_6}{2}(\Delta \theta)^2 = \Delta E$.

For the $\tilde{X}$ state (and also approximately for the $\tilde{E}$ state) of S$_2$O the value of $k_6$ is approximately $6 \times 10^3$ cm$^{-1}$/rad. The origin band occurs at 3248 cm$^{-1}$ and the bands with maximum absorption intensity at approximately 35,500 cm$^{-1}$. Therefore $\Delta E$ is approximately 3000 cm$^{-1}$. Therefore $\Delta \theta \approx 1$ rad.

(This calculation is an order of magnitude calculation.)

See intensity measurements Appendix IV.
Therefore, if the bond angle $\Theta$ in the $\tilde{X}$ state is 118° the bond angle in the $E$ state is

$$118^\circ \pm 57^\circ \text{ i.e. approx. } 60^\circ \text{ or } 180^\circ$$

If the latter bond angle is chosen, then $S_2O$ would have an acute angled triangular form, which is improbable.

If the bond angle 180° for the $E$ electronic state is the correct choice, the $E \leftarrow X$ spectral system should show the characteristics of an electronic transition between a bent and a linear electronic state. These characteristics were listed in Section D of Chapter III. The sharp red degradation of the vibrational bands of the $E \leftarrow X$ system is characteristic of a linear $\leftarrow$ bent transition. Therefore the geometry of the $E$ electronic state of $S_2O$ is assigned a linear electronic state.

It was not possible to carry out Franck-Condon Effect calculations to determine the difference in geometry between the ground $\tilde{X}$ state and the $\tilde{E}$ excited state. These calculations use overlap integrals (cf. page 33). The exact analytical form of the wave functions in the $\tilde{X}$ and $\tilde{E}$ states are unknown and the harmonic oscillator approximation - the normal approximation used in such calculations would hardly seem appropriate for quasilinear $\tilde{X}$ state.
4.3.11. The Electronic spin of the $\tilde{E}$ state.

The 3193 Å band of the $\tilde{E} \leftarrow \tilde{X}$ spectral system does not show a Zeeman Effect in a magnetic field of 2000 gauss. From the absence of the Zeeman Effect it is necessary to assume that the $\tilde{E}$ state of $\text{S}_2\text{O}$ molecule has zero electronic spin angular momentum.

4.3.12. Vibrational Structure of the $\tilde{E}$ state.

The bands of the $\tilde{E} \leftarrow \tilde{X}$ spectral system which involve transitions to the excited vibrational levels of the E state are nearly all double or triple headed. This is shown in Fig. 4.1. In Fig. 4.5 the vibrational energy levels $v_2' = 0$ to $v_2' = 5$ of the $E$ state are shown and transitions from the (000) (001) and (002) vibrational energy levels of the $\tilde{X}$ ground state to the levels of the $E$ state are also shown. The energy level diagram was constructed from band head wave numbers. Since the band head wave numbers are not determined to an accuracy of better than $\pm 1 \text{ cm}^{-1}$, the accuracy in determining the energies of the vibrational energy levels is $\pm 2 \text{ cm}^{-1}$.

From the experimental data, the vibrational energy levels $v_2' = 0$ and $v_2'' = 1$ of the $\tilde{E}$ state are observed to consist of a single level; the $v_2' = 2$ level is observed to consist of two components separated by 26 cm$^{-1}$; and the $v_2' = 3$, 4 and 5 vibrational levels are each observed to consist of three components. The identification of the component levels is difficult since the uncertainty
in band head measurements of the bands $2^6_0$, $2^7_0$ etc.,
$2^6_1$, $2^7_1$ etc., is ± 2 cm$^{-1}$ and greater and accurate
combination differences cannot be obtained. The levels
$v'_2 = 6, 7$ etc. of the $\tilde{E}$ state are therefore not shown
in Fig. 4.5.

4.B.13. Symmetry of the $\tilde{E}$ state.

The $\tilde{E}$ state of $S_2O$ is a linear state. If the $\tilde{E}$
state is a $\Sigma$ state then the energy levels (0, $v_2$ 0) are
given by

$$E(v_2) = (v_2+1) \hbar \omega_2 + x_{22}(v_2+1)^2 + \varepsilon \ell^2 + \text{smaller terms}$$

where $\ell = v_2, v_2-2, \ldots 1$ or 0

On the basis of this formula the energy level $E(v_2)$ consists
of as many components as there are values of $\ell$. $\hbar \ell$ is
the vibrational angular momentum along the internuclear
axis of the linear molecule.

If $E$ is a $\Sigma$ state, the level

$v_2 = 0$ has 1 component $\Sigma$
$v_2 = 1$ has 1 component $\Pi$
$v_2 = 2$ has 2 components $\Sigma, \Delta$ separated by $4\varepsilon$
$v_2 = 3$ has 2 components $\Pi, \tilde{\Pi}$ separated by $8\varepsilon$
$v_2 = 4$ has 3 components $\Gamma, \Delta, \Sigma$ separated by $12\varepsilon, 4\varepsilon$
$v_2 = 5$ has 3 components $\Pi, \tilde{\Pi}, \Pi$ separated by $16\varepsilon, 8\varepsilon$, etc.

In Fig. 4.5

2 components of the (0 2 0) level are observed and they
are separated by 26 cm\(^{-1}\).

3 components (rather than 2) of the (030) level are observed with separations 8 cm\(^{-1}\) and 32 cm\(^{-1}\).

3 components of the (040) level are observed with separations 8 cm\(^{-1}\) and 39 cm\(^{-1}\).

3 components of the (050) level are observed with separations 26 cm\(^{-1}\) and 52 cm\(^{-1}\).

From this data it is not possible to form a consistent value of \(g\) and thus it is concluded that the \(\tilde{E}\) state is not a \(\Sigma\) state.

The \(\tilde{E}\) state of \(\text{S}_2\text{O}\) is not the \(^1\Lambda''\) state which correlates with the upper half of the \(^1\Delta\) state of the configuration \(\ldots(2\pi)^4(3\pi)^2\). A \(^3\Lambda''\) or \(^3\Sigma^+\) state lies below this \(^1\Lambda''\) state but no other states lie below the \(^3\Lambda''\) or \(^3\Sigma^+\) state. However two spectral systems lying to the red - to lower energies - of the \(\tilde{E} \leftrightarrow \tilde{X}\) system are observed experimentally.

In \(\text{O}_2\) and \(\text{SO}_2\) the next singlet electronic state higher in energy than the \(^1\Lambda''(\frac{1}{2}\Delta)\) state and which is not a \(\Sigma\) state arises from the configuration \(\ldots(1\pi \Sigma)^3(2\pi \Sigma)^3\). It is a \(^1\Delta_u\) state. A reasonable assignment of the \(\tilde{E}\) state, within the L.C.A.O./M.O. approximation used is as the \(^1\Delta\) state of the \(\ldots(2\pi)^3(3\pi)^3\) configuration.

A $1\Delta$ state is expected to show a Renner Effect. Weak Renner Coupling was discussed in Appendix II Section A. For the $l = 0$ one component level - of $\Delta$ symmetry occur

\[ l = 1 \text{ two component levels of } \Pi \text{ and } \Phi \text{ symmetry occur} \]
\[ l = 2 \text{ four component levels of } \Sigma^+, \Pi, \Delta, \Sigma^- \text{ symmetry occur etc. cf. Merer and Travis (56)} \]

\[ K = |\chi + l| \]

Levels for which $(v_2^2 - 2) \neq K$ and $v_2 \neq K$ occur in pairs and the mutual "repulsion" of energy levels of the same symmetry gives a complex vibrational energy level pattern. Transitions to all the components are not observed. From the experimental data available it is not possible to assign symmetries to the components of the vibrational energy levels observed in the $1\Delta$ state. The symmetries to be assigned to the (000) level, to the two components of the (001)" and (002)" levels of a quasilinear electronic state have not yet been determined theoretically. It would appear, however, that the symmetries of the two components of the levels (001)" and (002)" are possibly the same, but are different from the symmetry which must be assigned to the (000)" level to account for the energy level diagram Fig. 4.5. This problem requires theoretical clarification before definite symmetry assignments can be made.
4.B.15. Resume of data on \( \tilde{E} \leftarrow \tilde{X} \) system.

From the long "hot band" progressions observed the quasilinear character of the \( \tilde{X} \) state was established. The \( \tilde{E} \) state on the basis of the simple L.C.A.O./M.O. approximation used is assigned as a \( ^1\Delta \) state.

SECTION C: The \( \tilde{D} \leftarrow \tilde{X} \) spectral system

4.C.1. Description of system.

Absorption bands due to this system were observed in the region 4000 - 4300 Å. Due to the experimental difficulties outlined in Chapter II, it was not possible to make observations in the region 3500 - 4000 Å. It is probable that bands of the \( \tilde{D} \leftarrow \tilde{X} \) system are present in the region 3500 - 4000 Å.

The profiles of the vibrational bands are different from those for the \( \tilde{E} \leftarrow \tilde{X} \) and \( \tilde{C} \leftarrow \tilde{X} \) systems. On the low resolution spectrograph - 1st order of the Bausch and Lomb Model II 1.5 m concave grating spectrograph - the bands appear diffuse and show marginal degradation to the red. Under high resolution - 1st order of the 6 m Ebert spectrograph - some rotational structure is partly resolved.

A list of the energies of fifteen vibrational band heads and intensities observed in the region 4000 - 4300 Å is given in Appendix V. A photograph of some
of these bands as observed on the low resolution spectrograph is given in Fig. 4.7.

4.6.2. Analysis.

Since only a fragment of this absorption system was observed a comprehensive analysis was not possible. In Table 4.3 (a) seven bands have been arranged into two progressions. The energy differences between successive members of each progression and the energy differences between corresponding members of the two progressions are also given. These differences are approximately 395 cm\(^{-1}\) and 685 cm\(^{-1}\) which correspond to the energies of the bending vibrational motion \(V_2\) and the stretching vibration \(V_{\tilde{3}}\), respectively, of the \(\tilde{X}^1A'\) ground state of S\(_2\)O. The \(0^0\) band was not identified. It would appear however that it lies at approximately 25,000 cm\(^{-1}\), and the limited region of the observed system is confined to "hot band" transitions.

A rather distinctive feature of this spectral system is the presence of groups of three bands separated by approximately 100 cm\(^{-1}\). These groups are shown in Table 4.3 (b)
Table 4.3 (a)

<table>
<thead>
<tr>
<th>1st Progression</th>
<th>2nd Progression</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>24982 (70)</td>
<td>24298 (50)</td>
<td>684 cm⁻¹</td>
</tr>
<tr>
<td>392 cm⁻¹</td>
<td>392 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>24590 (60)</td>
<td>24906 (70)</td>
<td>684 cm⁻¹</td>
</tr>
<tr>
<td>393 cm⁻¹</td>
<td>394 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>24197 (30)</td>
<td>23512 (50)</td>
<td>685 cm⁻¹</td>
</tr>
<tr>
<td>401 cm⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23796 (30)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3 (b)

Groups of three bands separated by approx. 100 cm⁻¹

<table>
<thead>
<tr>
<th>23,325</th>
<th>23,796</th>
<th>24,096</th>
<th>24,881</th>
</tr>
</thead>
<tbody>
<tr>
<td>23,415</td>
<td>23,906</td>
<td>24,197</td>
<td>24,982</td>
</tr>
<tr>
<td>23,512</td>
<td>23,998</td>
<td>24,298</td>
<td>....</td>
</tr>
</tbody>
</table>
4.0.3. Spin Symmetry and Geometry of the $\tilde{D}$ state.

Due to the limited amount of experimental data obtained on the $\tilde{D} \leftarrow \tilde{X}$ spectral system it is not possible to make a definite assignment of the electronic spin, symmetry and geometry of the $\tilde{D}$ electronic state of $S_2O$. By comparison of the $\tilde{D} \leftarrow \tilde{X}$ spectral system with the $\tilde{E} \leftarrow \tilde{X}$ spectral system it is possible, however, to make some statements about these properties.

As mentioned previously in Chapter III triplet and singlet states are observed in $SO_2$ at $T_e = 25766$ cm$^{-1}$ and $T_e = 29622$ cm$^{-1}$ respectively (2). The energy difference between this singlet state and triplet state is 4000 cm$^{-1}$ or $\approx$ eV approximately $3^3\Delta_u$ and a $1^1\Delta_u$ states arise from the electronic configuration

$$\cdots \quad (1\sigma_e^3 \quad (2\pi_u)^3$$

of the $O_2$ molecule in the linear conformation. In the bent conformation of $O_2$, $3^3B_2, 1^1B_2, 3^3A_2$ and $1^1A_2$ states are obtained which correlate with the $3^3\Delta_u$ and $1^1\Delta_u$ states of the linear conformation. From the calculations of Robinson (45) the energy difference between the singlet and corresponding triplet state arising from the same electronic configuration is approximately 1 eV in either the linear or bent conformation.

The origin band of the $\tilde{E}^1A \leftarrow \tilde{X}^1A'$ system of $S_2O$ state is at 32487 cm$^{-1}$. The origin band of $\tilde{D} \leftarrow \tilde{X}^1A'$
system is at $\sim 25000 \text{ cm}^{-1}$. The energy separation of the $\tilde{E}^1\Delta$ and $\tilde{D}$ states of $S_2O$ is therefore $\sim 7500 \text{ cm}^{-1}$ or 1 eV. It is therefore possible that the $\tilde{D}$ electronic state is a triplet electronic state arising from the same electronic configuration as the $\tilde{E}^1\Delta$ state. The oscillator strength of the $\tilde{D} \leftarrow \tilde{X}^1A'$ spectral system is a factor of approximately $10^2$ weaker than the oscillator strength for the $\tilde{E}^1\Delta \leftarrow \tilde{X}^1A'$ spectral system. This oscillator strength ratio is consistent with the assignment of the $\tilde{D}$ electronic state of $S_2O$ as a triplet electronic state arising from the same electronic configuration as the $\tilde{E}^1\Delta$ state.

It is not possible to determine the geometrical conformation of the $\tilde{D}$ state of $S_2O$ from the limited amount of experimental data, although the activity of $\nu_2^\prime$ in the spectrum would suggest a change of bond angle on excitation. The vibrational bands of the $\tilde{D} \leftarrow \tilde{X}$ spectral system do not have extremely sharp heads at the violet end of each band and are not very sharply degraded to the red as are the bands of the $\tilde{E} \leftarrow \tilde{X}$ and $\tilde{C} \leftarrow \tilde{X}$ spectral systems. Therefore it is not possible to assign definitely the $\tilde{D} \leftarrow \tilde{X}$ spectral system as due to a bent to linear transition or to assume that the $\tilde{D}$ electronic state of $S_2O$ is stable in the linear conformation. In the $^3\tilde{a}$ state of $SO_2$ the O-S-O bond angle is considerably less than the bond angle for the $^1\tilde{a}$ state which arises from the same
configuration cf. Merer (46). A similar situation may probably exist for the \( \tilde{D} \) state of \( S_2O \).

Theoretical treatments of the \( \tilde{D} \) state of \( S_2O \) would be extremely complex since both Renner Coupling as described in Appendix III and spin orbit coupling for a triplet state would have to be taken into account. A Zeeman Effect experiment would have to be carried out before a definite assignment of the \( \tilde{D} \) state as a triplet state could be made and a rotational analysis would have to be carried out before a definite assignment of the geometry of the \( \tilde{D} \) state could be made.

SECTION D: The \( \tilde{C} \leftarrow \tilde{X} \) Absorption System

4.D.1. Description of the \( \tilde{C} \leftarrow \tilde{X} \) spectral system.

Absorption bands of this spectral system were observed in the spectral region \( 4300 - 6700 \) Å. A photograph of the spectrum as obtained on the low resolution 1.5 m Bausch and Lomb Model 11 spectrograph is given in Fig. 4.7. In Fig. 4.8 the rotational structure of the absorption band at \( 50283 \) Å \( \bigcirc \) (19881) is shown. This structure is typical of the rotational structure of the bands of the \( \tilde{C} \leftarrow \tilde{X} \) system. A list of band head wave numbers and band intensities is given in Appendix VI.

All bands of the \( \tilde{C} \leftarrow \tilde{X} \) spectral system of \( S_2O \) show a discrete resolved rotational structure even when
Fig. 4.7

LOW RESOLUTION SPECTROGRAMS OF THE \( \tilde{\text{C}} \leftarrow \tilde{\text{X}} \)
AND PART OF THE \( \tilde{\text{D}} \leftarrow \tilde{\text{X}} \) SPECTRAL SYSTEMS IN
THE ENERGY RANGE 17000 cm\(^{-1}\) TO 24000 cm\(^{-1}\).

Only a small fragment of the \( \tilde{\text{D}} \leftarrow \tilde{\text{X}} \) system
is shown here since it is difficult to
obtain a good spectrogram of the system.
The absorption bands of the \( \tilde{\text{C}} \leftarrow \tilde{\text{X}} \) system
in the region 17000 - 15000 cm\(^{-1}\) are not
shown for the same reason. This photo-
graph was obtained in the 1\(^{\text{st}}\) Order of a
1.5 m concave grating Bausch and Lomb
Model 11 spectrograph.
Fragment of the \( \tilde{C} - \tilde{X} \) System. Members of the A and B progressions are shown.

\( \tilde{D} - \tilde{X} \) System

\[
\begin{array}{cccccccc}
  k+8 & k+7 & k+6 & k+5 & k+4 & k+3 & k+2 \\
  k+16 & k+15 & k+14 & k+13 & k+12 & k+11 & k+10 \\
  k+9 & k+8 & k+7 & k+6 & k+5 & k+4 & k+3 \\
\end{array}
\]

ENERGY IN CM\(^{-1}\)

Fig. 4.7 The \( \tilde{D} + \tilde{X} \) and the \( \tilde{C} + \tilde{X} \) spectral systems of \( S_2O \) in the spectral region \( 4080 \, \text{Å} - 5790 \, \text{Å} \).
A HIGH RESOLUTION SPECTROGRAM OF THE 19881 cm$^{-1}$ BAND OF THE $\tilde{C} \leftarrow \tilde{X}$ SYSTEM.

This photograph was taken in the 1$^{\text{st}}$ Order of the 6 m Ebert spectrograph and clearly shows the red degradation of the bands.
FIG. 4.8 HIGH RESOLUTION SPECTROGRAM SHOWING THE ROTATIONAL STRUCTURE WHICH IS TYPICAL OF BANDS OF THE $\tilde{C} \leftrightarrow \tilde{X}$ SYSTEM.
observed on the low resolution spectrograph. Each band has an extremely sharp head at the violet end of the band and is very sharply degraded to the red. The most intense absorption bands occur in the region 4500 - 5500 Å. The oscillator strength of the \( \tilde{\tilde{\Sigma}} \leftarrow \tilde{\tilde{\Pi}} \) transition is of the order of magnitude \( 10^{-6} - 10^{-7} \).


The dominant feature of the \( \tilde{\tilde{\Sigma}} \leftarrow \tilde{\tilde{\Pi}} \) spectral system of \( S_2^0 \) is a long intense progression of absorption bands. At the long wavelength end of this progression the energy separation between consecutive members of the progression is approximately 450 cm\(^{-1}\) while at the short wavelength end of the progression this energy separation between consecutive members has dropped to 340 cm\(^{-1}\) (approximately). Seventeen members of this progression are observed. For discussion purposes it will be called the B progression.

Four other progressions are observed. They are labelled the A, C, D and E progressions. Six members of the A progression, four members of the C progression, five members of the D progression and five members of the E progression are observed. The wave numbers of bands in the A, B, C, D and E progressions are given in Table 4.4. The 16024 cm\(^{-1}\) band of the B progression is arbitrarily assigned the number k.
Table 4.4

Progressions of Bands in the $\tilde{C} \leftarrow \tilde{X}$ system and differences between successive members of progressions.

<table>
<thead>
<tr>
<th>Number</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>k+16</td>
<td>22394</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k+15</td>
<td>22056</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>k+14</td>
<td>21715</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k+13</td>
<td>21372</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>k+12</td>
<td>21014</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>k+11</td>
<td>20645</td>
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</tr>
<tr>
<td>k+10</td>
<td>20277</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k+9</td>
<td>19881</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k+8</td>
<td>20976</td>
<td>19483</td>
<td></td>
<td>411</td>
<td>407</td>
</tr>
<tr>
<td>k+7</td>
<td>20565</td>
<td>19076</td>
<td></td>
<td>410</td>
<td>417</td>
</tr>
<tr>
<td>k+6</td>
<td>20155</td>
<td>18659</td>
<td></td>
<td></td>
<td>17599</td>
</tr>
</tbody>
</table>
Table 4.4 cont'd

<table>
<thead>
<tr>
<th>Number</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>k+6</td>
<td>20155</td>
<td>18659</td>
<td>17599</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>417</td>
<td>417</td>
<td></td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>k+5</td>
<td>19738</td>
<td>18242</td>
<td>17179</td>
<td>16697</td>
<td></td>
</tr>
<tr>
<td></td>
<td>427</td>
<td>427</td>
<td></td>
<td>420</td>
<td>420</td>
</tr>
<tr>
<td>k+4</td>
<td>19311</td>
<td>17815</td>
<td>16759</td>
<td>16277</td>
<td></td>
</tr>
<tr>
<td></td>
<td>441</td>
<td>439</td>
<td></td>
<td>439</td>
<td>441</td>
</tr>
<tr>
<td>k+3</td>
<td>18870</td>
<td>17376</td>
<td>16566</td>
<td>16320</td>
<td>15836</td>
</tr>
<tr>
<td></td>
<td>449</td>
<td>447</td>
<td>437</td>
<td>446</td>
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<tr>
<td>k+2</td>
<td>18421</td>
<td>16929</td>
<td>16129</td>
<td>15874</td>
<td>15389</td>
</tr>
<tr>
<td></td>
<td>452</td>
<td>447</td>
<td></td>
<td></td>
<td>461</td>
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<tr>
<td>k+1</td>
<td>16477</td>
<td>15682</td>
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<td>14928</td>
<td></td>
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<tr>
<td></td>
<td>453</td>
<td>460</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>16024</td>
<td>15222</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.5

Table of Energy differences in cm\(^{-1}\) between corresponding members of the progressions.

<table>
<thead>
<tr>
<th></th>
<th>(A_{k+n})</th>
<th>(-B_{k+n})</th>
<th>(-C_{k+n})</th>
<th>(D_{k+n})</th>
<th>(-E_{k+n})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k+8)</td>
<td>1494</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k+7)</td>
<td>1489</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k+6)</td>
<td>1496</td>
<td>1060</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k+5)</td>
<td>1496</td>
<td>1065</td>
<td>1545</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k+4)</td>
<td>1496</td>
<td>1056</td>
<td>1538</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k+3)</td>
<td>1494</td>
<td>810</td>
<td>1057</td>
<td>1540</td>
<td></td>
</tr>
<tr>
<td>(k+2)</td>
<td>1492</td>
<td>800</td>
<td>1055</td>
<td>1540</td>
<td>1549</td>
</tr>
<tr>
<td>(k+1)</td>
<td>795</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k)</td>
<td>802</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Energy differences between corresponding members of the A, B, C, D and E progressions are given in Table 4.4. The most intense bands of the spectral system from the B progression. The bands in the A progression are of much weaker intensity than bands in the B progression and the bands of the C, D and E progressions are extremely weak and are observed only at a pressure path length of approximately 10 m atm.

The energy of bending vibrational motion \( \nu_2 \) in the \( ^1X \) state of \( \text{S}_2\text{O} \) is approximately 395 cm\(^{-1}\). The energy difference between successive members of the B progression as shown in Table 4.4 varies from 453 to 338 cm\(^{-1}\). It is reasonable therefore to assign the energy differences in the range 453 to 338 cm\(^{-1}\) as the energies of successive quanta of bending vibrational motion \( \nu_2 \) in the C state of \( \text{S}_2\text{O} \). Since the B progression is the most intense progression it is assigned as the \(( \ldots \nu_0^1 \ldots )\) progression.

Members of the A progression are 1495 cm\(^{-1}\) to higher energy than the members of the B progression. It is not possible to assign this energy difference with certainty. 1495 cm\(^{-1}\) may be the energy of one quantum of stretching vibrational motion \( \nu_1 \) in the C state of \( \text{S}_2\text{O} \) or it may be the energy of two quanta of stretching vibrational motion \( \nu_3 \) in the C state. If the later
alternative were correct than a progression of bands, the members of which are separated by approximately 750 cm$^{-1}$ from the corresponding members of the B progression should be observed. No such progression is observed. Therefore it is tentatively assumed that the first alternative is correct and that the A progression is in fact the set of bands.

\[ (\ldots 1^1_0 2^n_0 \ldots ) \]

Members of the C progression are approximately 802 cm$^{-1}$ to lower energy than the members of the B progression. The intensity ratio of corresponding members of the B and C progressions is approximately 10 : 1. The energy value 802 cm$^{-1}$ cannot be identified with any single quantum of vibrational motion in the ground electronic state. However

\[ 802 \text{ cm}^{-1} \text{ is approx. } 2 \nu^2 \]

and so a tentative assignment of the C progression is

\[ (\ldots 2^n_0 2^0_2 \ldots ) \quad - \text{C progression} \]

Bands which could be identified as

\[ (\ldots 2^n_0 2^0_1 \ldots ) \]

were not observed. The failure to observe these bands is discussed later in this section of the chapter.
The energy levels \((0,1,1)\) and \((1,1,0)\) of the \(\tilde{X}^{1}A'\) state of \(S_2O\) are

\[
\begin{align*}
1063 & \text{ cm}^{-1} \quad \text{and} \quad 1548 \quad \text{cm}^{-1} \\
1072 & \quad \text{cm}^{-1} & 1563 \quad \text{cm}^{-1}
\end{align*}
\]

above the \((0,0,0)\) level of the same state. Members of the D and E progressions, which are of extremely low intensity are 1059 cm\(^{-1}\) and 1544 cm\(^{-1}\) to lower energy than the corresponding members of the intense B progression. Therefore the D and E progressions are tentatively assigned as originating on the \((0 1 1)\) and \((1 1 0)\) vibrational energy levels of the \(\tilde{X}^{1}A'\) state of \(S_2O\). The bands of the D and E progressions are assigned as the set of bands

\[
(\ldots \, 2^n \, 2^0 \, 3^0 \ldots \ldots) \quad \text{D progression, and}
\]

\[
(\ldots \, 2^n \, 1^0 \, 2^0 \ldots \ldots) \quad \text{E progression.}
\]

The tentative assignment of the C, D and E progressions given above requires that the bands in these progressions are due to transitions from energy levels \((0 2 0)\), \((0 1 1)\) and \((1 1 0)\) of the \(\tilde{X}\) state to the vibrational

* Obtained from an analysis of the \(\tilde{E} \leftrightarrow \tilde{X}\) system.

** Obtained by a combination of the infra red data obtained by Vallance Jones (34) and data obtained in the analysis of the \(\tilde{E} \leftrightarrow \tilde{X}\) system.
energy levels \((0, k+n, 0)\) of the \(C\) state. The \((0\ 2\ 0)\), \((0\ 1\ 1)\) and \((1\ 1\ 0)\) levels lie \(802\ \text{cm}^{-1}\), \(1060\ \text{cm}^{-1}\) and \(1549\ \text{cm}^{-1}\) above the \((0\ 0\ 0)\) level of the \(\tilde{X}\) state. These energy levels will be relatively unpopulated compared to the levels \((0\ 1\ 0)\), \((0\ 0\ 1)\) etc. which lie at \(392\ \text{cm}^{-1}\), \(679\ \text{cm}^{-1}\) etc. above the \((0\ 0\ 0)\) of the \(\tilde{X}\) state. However the \(\tilde{X}\) state is a quasilinear state and overlapping of the wave functions into the region beneath the potential hump, as shown in Fig. 4.6, is greater in the \((0\ 2\ 0)\), \((0\ 1\ 1)\) etc. levels than in the \((0\ 1\ 0)\), \((0\ 0\ 1)\) etc. levels i.e., the molecule is in a more linear conformation in these vibrational energy states. The Franck-Condon Principle implies that the intensities of transitions from the "more linear" energy levels are greater than those for the "more bent" energy levels. This application of the Franck-Condon Principle explains the observation of the \(C, D\) and \(E\) progressions if the tentative assignment of these progressions is correct. The intensities of the \(C, D\) and \(E\) progressions are very weak.

4.D.3. The assignment of the \(0^0_o\) band of the \(\tilde{C} \leftarrow \tilde{X}\) system.

The origin band of \(\tilde{C} \leftarrow \tilde{X}\) system was not assigned.
In order to make a definite assignment of the \(0^0_o\) band it would be necessary to observe the progression of bands

\[ \ldots 2^n_n \ldots 0^0_o \ldots 2^0_o \ldots \]
In this set of bands a discontinuity in the $\Delta G_{v_2}$ versus $E(v_2)$ graph (cf. Fig. 4.3) of 453 cm$^{-1}$ to 395 cm$^{-1}$ would occur at the $0^0$ band. However no progressions of hot bands involving $v_2''$ could be observed, probably because of their low intensity. The $\tilde{C} \leftarrow \tilde{X}$ system is so weak that the bands observed could only be obtained under limitingly high pressure path length. If the $\tilde{C} \leftarrow \tilde{X}$ transition is a linear $\leftrightarrow$ bent transition progressions in $v_2''$ will be very much weaker than progressions in $v_1'$, as was observed for the $\tilde{E} \leftarrow \tilde{X}$ spectral system. It is probable that the band at 16024 cm$^{-1}$ in the B progression is either $0^0$ or $2^k$ where $k$ is an integer close to zero. Thus the zeroth vibrational energy level of the $\tilde{C}$ state of $S_2O$ lies $\sim 16000$ cm$^{-1}$ above the zeroth vibrational level of the $\tilde{X}^1A'$ state of the molecule.


The B progression of the $\tilde{C} \leftarrow \tilde{X}$ spectral system of $S_2O$ shows a long progression of bands due to excitation of the bending vibrational motion $v_2'$. Therefore, as discussed in the Section D of Chapter III on the Franck-Condon Principle, there is a large change in the S-S-O bond angle on going from the $\tilde{X}$ ground state to the $\tilde{C}$ excited state. All bands of the $\tilde{C} \leftarrow \tilde{X}$ system are sharply degraded to the red. If the bond S-S-O angle in the $\tilde{C}$ state was larger than in the $\tilde{X}$ state, but yet less than
180° the bands of the \( \tilde{C} \leftarrow \tilde{X} \) spectral system would be violet degraded. Therefore as discussed in Chapter III Section D, the S-S-O angle in the \( \tilde{C} \) electronic state is 180° if the molecule is stable in the linear conformation in the \( \tilde{C} \) state of \( S_2O \).


The B progression of the \( \tilde{C} \leftarrow \tilde{X} \) spectral system has been assigned as the

\[
(\ldots 2^N_0 \ldots)
\]

set of bands. From the data on this long progression of bands the anharmonicity and dissociation energy of the \( \tilde{C} \) electronic state along the normal coordinate of bending vibrational motion may be determined.

For a linear electronic state of a molecule

\[
E(v_2) = (v_2 + 1)\hbar \omega_2 + \chi_{22}(v_2 + 1)^2 + g \hat{J}^2 + \text{other terms}
\]

If

\[
\Delta G(v_2) = E(v_2 + 1) - E(v_2)
\]

is plotted against \( v_2 \) a straight line graph of slope \( 2\chi_{22} \).

(In plotting the graph it is assumed that \( E(v_2) \) is chosen

* The bands of the \( (\ldots 2^N_0 \ldots) \)-B progression of the \( \tilde{C} \leftarrow \tilde{X} \) transition do not have multiple heads. Therefore the term in \( g \hat{J}^2 \) for the \( \tilde{C} \) state is very small and is neglected in this calculation.
FIG. 4.9

ANHARMONICITY IN "C STATE

\[ \Delta G_{V_2} \]

vs.

\[ V_2 \]
for \( \alpha = 0 \) or 1.) Fig. 4.9 shows this graph for the \( \tilde{C} \) state of \( S_2O \). The slope of the graph is 8.6 cm\(^{-1}\) so the anharmonicity constant is approximately 4.3 cm\(^{-1}\)

\[
x_{22} \text{ for the } \tilde{C} \text{ state } = 4.3 \text{ cm}^{-1}
\]

A graph of \( \Delta G(v_2) \) versus \( E(v_2) \) is plotted for the \( \tilde{C} \) electronic state of \( S_2O \) in Fig. 4.10. The zero point on the \( E(v_2) \) scale was chosen as 16000 cm\(^{-1}\) since the zeroth vibrational level of the \( \tilde{C} \) state lies at approximately 16000 cm\(^{-1}\). The intercept of the graph on the \( E(v_2) \) axis is equal to the dissociation energy of the \( \tilde{C} \) electronic state along the normal coordinate describing the bending motion of the molecule - \( q_2 \). The intercept is at approximately 12000 cm\(^{-1}\) or 1.5 eV approximately. Therefore

\[
D_e(q_2) \text{ for the } \tilde{C} \text{ state of } S_2O = 12000 \text{ cm}^{-1}
\]

4.D.6. Spin and symmetry of the \( \tilde{C} \) electronic state of \( S_2O \).

It is not possible to make a definite assignment of the spin and symmetry of the \( \tilde{C} \) electronic state from the experimental data available. The \( \tilde{C} \leftrightarrow \tilde{X} \) transition* can

*The transition does not originate on the \( 3\Sigma^- \) electronic state of the \( \ldots(2\pi)^4(3\pi)^2 \) configuration. If it did then intensity considerations would require that the \( A3\sigma^+ \) or \( A3\Sigma^- \) should lie at \( T_e \approx 4500 \text{ cm}^{-1}\). This state should strongly perturb the upper vibrational levels of the \( \tilde{X} \) state. "Hot band" progressions up to 3740 cm\(^{-1}\) to the red of the \( 0\tilde{B} \) band are observed in the \( E \leftrightarrow \tilde{X} \) system. No perturbations are observed so the \( A \) state is at a much higher energy than 4500 cm\(^{-1}\) above the \( \tilde{X} \) state.
FIG. 4.10

Dissociation Energy in $\tilde{C}$ State

$\Delta G_{V_2}$ vs. $E_{V_2}$ (cm$^{-1}$)

$\Delta G_{V_2}$

$E_{V_2}$ (cm$^{-1}$)

0 2500 5000 7500

450 400 300 250
be transition (1) \(3A''\) or \(3 \Sigma^- \leftarrow \tilde{X} 1A'\); (2) \(1A''(\frac{3}{2} \Delta) \leftarrow \tilde{X} 1A'\) or (3) \(1A'\) or \(1 \Sigma^+ \leftarrow \tilde{X} 1A'\). If the transition is the first alternative then the transition \(1A''(\frac{3}{2} \Delta) \leftarrow \tilde{X} 1A'\) should be observed to higher energies and with greater intensity. Only one strong spectral absorption system is observed in the region \(2300 - 6700 \text{ Å}\). Therefore the \(\tilde{C} \leftarrow \tilde{X}\) transition is not the \(3A''\) or \(3 \Sigma^- \leftarrow \tilde{X} 1A'\) transition. The transition \(1A''(\frac{3}{2} \Delta) \leftarrow \tilde{X} 1A'\) should be an intense allowed electric dipole transition. Within the framework of the simple L.C.A.O./M.O. approximation used in Section A of Chapter III the transition \(1 \Sigma^+ \leftarrow \tilde{X} 1A'\) should involve a "two electron jump"

\[
\text{... (6a')}^2 (7a')^0 (3a'')^2 \rightarrow \text{... (6a')}^2 (7a')^2 (3a'')^0
\]

in the bent conformation of both electronic states and an electric quadrupolar transition**

\[
1 \Sigma^+ \leftarrow 1 \Delta
\]

---

** The \(3A''\) or \(3 \Sigma^-\), the \(1A''(\frac{3}{2} \Delta)\) and the \(1A'\) or \(1 \Sigma^+\) states all arise from the configuration \(\ldots (2 \pi)^4 (3 \pi)^2\) of the linear conformation.

** "Vibronically Allowed" transitions do not occur in molecules which belong to the point groups \(C_\pi\) and \(C_v\), since there are no antisymmetric vibrations in such molecules.
in the linear-quasilinear conformations. No spectrum of a polyatomic molecule has ever been definitely assigned to a "two electron jump" or to an electric quadrupolar transition. The possibility of the $\tilde{C} \leftarrow \tilde{X}$ transition being due to such a radiative mechanism cannot be completely excluded. If such a transition causes the $\tilde{C} \leftarrow \tilde{X}$ system then the $\tilde{C}$ state is a $^1 \Sigma^+$ state.


All bands of the $\tilde{C} \leftarrow \tilde{X}$ spectral system show an extensive fine rotational structure, cf. Fig. 4.8. These rotational structures are very complex. Quadratic progressions of spectral lines and progression of spectral lines with constant energy spacing are observed. It was not possible, as for the $\tilde{E} \leftarrow \tilde{X}$ system, to fit these progressions to any of the known molecular parameters and so an analysis of these rotational structures was not carried out. A rotational analysis of the $\tilde{C} \leftarrow \tilde{X}$ system will have to be carried out before it is possible to assign the spin and symmetry of the $\tilde{C}$ state with certainty.


An examination of the absorption spectrum of $\text{SO}_2$ was carried out in the spectral region 6700 to 25000 Å. No absorption systems were observed in this region. However the pressure path length used was very small due to the construction of the Cary 14 Spectrophotometer.
If the $\tilde{C}$ state is the $^1\Sigma^+$ state then the transitions $^1\Lambda''(\frac{3}{2} \Delta) \leftrightarrow X^1\Lambda'$ and $^3\Lambda''$ or $^3\Sigma^-$ $\leftrightarrow X^1\Lambda'$ should be observed in the infra red region of the spectrum. Therefore it would be desirable to examine the absorption spectrum of $S_2O$ in the infra red region of the spectrum at much greater pressure path lengths than were available during the present work.
CHAPTER V

Conclusions

Three spectral systems of the $S_2O$ molecule have been observed. Two of these systems have not been reported previously. These two systems were observed by using White type multiple reflection cells and an absorbing path length of up to $\frac{1}{2}$ Km was used.

A simple L.C.A.O./M.O. theory was developed to account for the observed spectra. Within the framework of this theory a $^1\Delta$ state arising from the electronic configuration ...$(2\pi)^3 (3\pi)^3$ is expected to show a weak Renner Effect while the $^1\Delta$ state arising from the configuration $(2\pi)^4 (3\pi)^2$ is expected to show a strong Renner Effect either Case (b) or Case (c). This strong effect may be due to the interaction of this $^1\Delta$ state with the $^1\Sigma^+$ state of the same configuration. The observed spectra are consistent with the L.C.A.O./M.O. theory.

The quasilinear character of the ground electronic state of the molecule was established. Very few electronic states which display a quasilinear character have been observed and much theoretical investigation of the phenomenon of quasilinearity must be carried out in future work. It is probable that rotational analyses of the $\tilde{E} \leftarrow \tilde{X}$, $\tilde{D} \leftarrow \tilde{X}$ and $\tilde{C} \leftarrow \tilde{X}$ systems will not be
achieved until analytical expressions for the rotational energy levels of a quasilinear state are available in tractable form.

It is doubtful if more information can be obtained on the quantum mechanical structure of $S_2O$ by the technique of absorption spectroscopy in the 1900 - 7400 Å spectral range with the experimental apparatus presently available and with the present theoretical understanding of the phenomenon of quasilinearity.
Bibliography


45. Reference 27, pgs. 186 - 190.


64. E. Condon, Phys. Rev. 28 1182 (1926).


APPENDIX I

Point Groups and Character Tables

The Schoenflies Notation.

\( \hat{E} \) is the identity operator

\( \hat{C}_n(l) \) is an operator denoting rotation through an angle \( 2\pi/n \) about the \( l \) axis

\( \hat{\sigma}_{ij} \) is an operator denoting reflection in the plane containing the orthogonal intersecting vectors \( i \) and \( j \)

\( \hat{R} \) is rotation by \( 2\pi \) (cf. Chapter 1, Section E)

By convention the principal axis - the axis of highest symmetry coincides with the \( z \) axis.

Character Table for \( C_s \) Point Group

<table>
<thead>
<tr>
<th>( C_s )</th>
<th>( \hat{E} )</th>
<th>( \hat{\sigma}_{xz} )</th>
<th>( \hat{R} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A' )</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( A'' )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>( E_{\frac{3}{2}} )</td>
<td>2</td>
<td>0</td>
<td>-2</td>
</tr>
</tbody>
</table>
Character Table for the $C_{2v}$ and $D_2$ Point Groups

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$D_2$</th>
<th>( \hat{E} )</th>
<th>( \hat{C}_2(z) )</th>
<th>( \hat{\sigma}_{xz} )</th>
<th>( \hat{\sigma}_{yz} )</th>
<th>( \hat{R} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>( A )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>( B_1 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>( B_2 )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>( B_3 )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$E_{1/2}$</td>
<td>( E_{1/2} )</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-2</td>
</tr>
</tbody>
</table>

$T_z$ for $C_{2v}$

$T_z$ for $D_2$; $R_z$ for both $D_2$ and $C_{2v}$

$T_y, R_y$ for $D_2$; $T_x, R_y$ for $C_{2v}$

$T_x, R_x$ for $D_2$; $T_y, R_x$ for $C_{2v}$

Character Table for the $C_{\infty v}$ and $D_{\infty z}$ Point Groups

<table>
<thead>
<tr>
<th>$D_{\infty z}$</th>
<th>( \hat{E} )</th>
<th>( \hat{C}_2 )</th>
<th>( \hat{\sigma}_v )</th>
<th>( \hat{R} )</th>
<th>( \hat{2}^{n} \hat{R} )</th>
<th>( \hat{2}^{n} \hat{R} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\infty v}$</td>
<td>( \hat{E} )</td>
<td>( \hat{C}_2 )</td>
<td>( \hat{\sigma}_v )</td>
<td>( \hat{R} )</td>
<td>( \hat{2}^{n} \hat{R} )</td>
<td>( \hat{2}^{n} \hat{R} )</td>
</tr>
<tr>
<td>$\Sigma^+$</td>
<td>1</td>
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<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Sigma^-$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
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<td>2</td>
<td>2cosn$\Phi$</td>
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</tr>
<tr>
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<td>2</td>
<td>2cos2n$\Phi$</td>
<td>2cos2n$\Phi$</td>
</tr>
<tr>
<td>$E_{1/2}$</td>
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<td>2cos$n\Phi$</td>
<td>0</td>
<td>-2</td>
<td>2cos$n\Phi$</td>
<td>2cos$n\Phi$</td>
</tr>
<tr>
<td>$E_{3/2}$</td>
<td>2</td>
<td>2cos$3/2n\Phi$</td>
<td>0</td>
<td>-2</td>
<td>-2cos$3/2n\Phi$</td>
<td>-2cos$3/2n\Phi$</td>
</tr>
</tbody>
</table>

$T_z$ for $C_{\infty v}$

$R_z$ for $C_{\infty v}$

$T_{x,y}, R_{x,y}$ for $D_{\infty z}$

$T_x, R_x$ for $D_{\infty z}$
APPENDIX II
Renner Effect

SECTION A: The Dynamic Renner Effect in a $^1\Delta$
Electronic State

Definitions.

When a linear triatomic molecule undergoes a bending vibration, the central atom of the molecule moves a distance $r$ from the molecular axis. Let $\varphi$ be the angle between the plane, in which the bending takes place and a fixed plane through the internuclear axis. Let $\beta$ be the angle between the plane in which the electrons giving rise to the electronic angular momentum $\Lambda\hbar$ is situated and the same fixed reference plane as used to define $\varphi$. cf. Fig. A.II.1. $\beta$ is the angular displacement coordinate conjugate to the axial angular momentum of all the electrons. $\varphi$ is the angular displacement coordinate conjugate to the vibrational angular momentum, $l\hbar$, of the degenerate vibrational state. Let $\alpha = (\beta - \varphi)$.

The electronic wave function of a linear molecule has the form

$$|\psi_e\rangle = f \exp(\pm i \Lambda \beta) \quad \text{Eqn. A.II.A.1.}$$

where $\exp(\pm i \Lambda \beta)$ expresses the cylindrical symmetry of the electron distribution about the internuclear axis of
the linear molecule, and where \( f \) contains all other terms of the electronic wave function. If \( \Lambda > 0 \) then \( |\Psi_e > \) is doubly degenerate.

The wave function for the bending vibrational motion of a linear triatomic molecule has the form

\[
|\Psi_{\text{vib}} > = \rho(r_b) \exp(\pm i l \varphi) \quad \text{Eqn. A.II.A.2.}
\]

where \( \rho(r_b) \) expresses all terms other than \( \exp(\pm i l \varphi) \) in the vibrational wave function.

The Coupling Hamiltonian.

If the Born Oppenheimer Approximation is assumed, even though \( |\Psi_e > \) and \( |\Psi_{\text{vib}} > \) are both doubly degenerate, the vibronic wave function is written as the product

\[
|\Lambda, v, l > = |\Psi_e > |\Psi_{\text{vib}} >
\]

\[
= \left[ f \exp(\pm i \Lambda \beta) \right] \left[ \rho(r_b) \exp(\pm i l \varphi) \right] \quad \text{Eqn. A.II.A.3.}
\]

The energy of coupling between electronic and vibrational angular momenta is expressed in a series containing terms of the type

\[
V_r^\Lambda \left[ \exp(i \Lambda \alpha) + \exp(-i \Lambda \alpha) \right]
\]

where \( \alpha = (\beta - \varphi) \).
The most general form of the Hamiltonian giving the energy of coupling is

\[ H' = V_o(r) + V_1 r_b^\wedge \left[ \exp(i\wedge \alpha) + \exp(-i\wedge \alpha) \right] \]

\[ + V_2 r_b^{2\wedge} \left[ \exp(i2\wedge \alpha) + \exp(-i2\wedge \alpha) \right] \]

\[ + V_3 r_b^{3\wedge} \left[ \exp(i3\wedge \alpha) + \exp(-i3\wedge \alpha) \right] \]

\[ + \ldots \text{ etc.} \quad \text{Eqn. A.II.A.4.} \]

Since \( H' \) must be symmetric in \( r_b \) for all values of \( \wedge \)
the coefficients \( V_1, V_3, V_5 \) etc. must be zero. Terms containing \( r_b^{4\wedge} \) and higher powers of \( r_b \) are generally omitted to simplify the mathematical treatment. The term \( V_o \) merely adds a constant energy and so is neglected.

Therefore for a \( \Delta \) electronic state, the
Hamiltonian for the coupling of vibrational and electronic angular momenta is

\[ H' = \eta r^4 \cos 4(\beta - \alpha) \quad \text{Eqn. A.II.A.5.} \]

where \( \eta \) is a constant and is treated as a coupling parameter.

Perturbation Treatment of the Dynamic Renner Effect.

Let \( H_o \) be the Hamiltonian for the two dimensional isotropic oscillator. When Renner coupling is zero, \( H_o \) describes the bending vibrational motion of a linear
triatomic molecule. The eigenvalues of

\[ \mathcal{H}_0 |\Lambda, v, \ell > = E |\Lambda, v, \ell > \]

are \( E = (v_2 + 1)\omega_2 + \varepsilon_{22} \ell^2 \) \( \text{Eqn. A.II.A.6.} \)

where \( \omega_2 \) is the bending frequency

and \( \varepsilon_{22} \) is the anharmonicity constant associated with the

vibrational angular momentum \( \hbar \ell \)

In the matrix form of \( \mathcal{H}_0 \) the non-diagonal elements are zero. The terms of Eqn. A.II.A.6 are the diagonal elements.

To obtain expressions for the vibrational energy levels in the dynamic Renner Effect, the matrix form of \( \mathcal{H}_0 + \mathcal{H}' \) must be diagonalized. The coordinates \( q_1 \) and \( q_2 \) were introduced by Moffitt and Liehr (55), and

\[ q_1 + iq_2 = r_b \exp \i \varphi \]

\[ q_1 - iq_2 = r_b \exp -\i \varphi \] \( \text{Eqn. A.II.A.7.} \)

So \( \mathcal{H}' \) of Eqn. A.II.A.5 becomes

\[ \mathcal{H}' = \frac{\hbar}{8} \eta [ (q_1 - iq_2)^4 \exp(4i\beta) + (q_1 + q_2)^4 \exp(-4i\beta) ] \]

\( \text{Eqn. A.II.A.8.} \)

The operator \( \exp 4i\beta \) can connect only the wave functions

\[ |\Lambda = -2 > \text{ with } |\Lambda = +2 > \]

and the operator \( \exp -4i\beta \) can connect only the wave
functions

\[ |\Lambda = +2 \rangle \quad \text{with} \quad |\Lambda = -2 \rangle \]

Therefore the only non-vanishing matrix elements in the matrix form of \( \mathcal{H}' \) are

\[ \frac{1}{2} \eta \langle 2, v_2, K-2 | (q_1-iq_2)^4 \exp 4i\beta | -2, v_2, K+2 \rangle \quad \text{and} \]

\[ \frac{1}{2} \eta \langle -2, v_2, K+2 | (q_1+iq_2)^4 \exp -4i\beta | 2, v_2, K-2 \rangle \]

where the wave function basis set is \( |\Lambda, v_2, l \rangle \) and \( K = |\Lambda + l \rangle \). Merer and Travis (56) have diagonalised the matrix \( (\mathcal{H}^0 + \mathcal{H}') \) for a \( \Delta \) electronic state (actually for a \( 2\Delta \) electronic state) and have given resultant expressions for the vibrational energy levels.

Energy Expressions.

For the general case of the four states of given \( K \), belonging to a level of given \( v_2 \) (that is, where \( K \neq v_2 \) and \( K \neq v_2 + 2 \)) the energies are

\[ E^+ = (v_2+1)\omega_2 + \frac{1}{2}P - Q + \frac{S}{P} \quad \text{(a)} \]


and

\[ E^- = (v_2+1)\omega_2 - \frac{1}{2}P - Q - \frac{S}{P} \quad \text{(b)} \]

where

\[ P = \frac{1}{2} \left\{ 64K^2g_{22}^2 + 36 \eta^2 \left[ v_2^2 - K^2 \right] \left[ (v_2+2)^2 - k^2 \right] \right\}^{1/2}, \]

\[ Q = \left( \eta^2 / \omega_2 \right)(v_2+1) \left\{ 17v_2(v_2+2) + 3k^2 \right\} + g_{22}(k^2+4), \]
\[ S = 4 \left( \eta^2 / \omega_2 \right) (v_2 + 1) K^2 g_{22}^2 \left( 17v_2(v_2+2) - 15K^2 + 72 \right) \]

The states for which \( K = v_2 \) and \( K = v_2 + 2 \), lie at the centre of the splitting pattern and the energies are

\[ E(K=v_2) = (v_2+1) \omega_2 - \left( \eta^2 / \omega_2 \right) (K)(K+1)(K+2)(K+3) \]
\[ + g_{22} (K-2)^2 \quad \text{Eqn. A.II.A.10 (a)} \]

\[ E(K=v_2+2) = (v_2+1) \omega_2 - \left( \eta^2 / \omega_2 \right) (K-1)(K+1)(K+2) \]
\[ + g_{22} (K-2)^2 \quad \text{Eqn. A.II.A.10 (b)} \]

and

\[ E(K=v_2+2) - E(K=v_2) \]
\[ = 4 \left( \eta^2 / \omega_2 \right) (v_2+1)(v_2+2)(7v_2-3) + 4g_{22}(v_2-1) \quad \text{Eqn. A.II.A.11.} \]

The theory outlined above adequately describes the vibrational energy levels of the dynamic Renner Effect in a \(^1\Delta\) state of a linear triatomic molecule.
APPENDIX II

SECTION B: Renner Effect Case (b)

In this case the potential curve $U^+(r_b)$ has a minimum at $r_b = 0$ and the potential curve $U^-(r_b)$ has a minimum at $r_b \neq 0$. If, for convenience, $h \nu_2 = 1$ and $k = 1$ where $\nu_2$ if the frequency of the bending vibration in the electronic state described by the $U^+(r_b)$ potential function and

$k$ is the elastic force constant for the vibrational bending motion $\nu_2$.

Analytic expressions for $U^+(r_b)$ and $U^-(r_b)$ are set up on a semi-empirical basis by Pople and Longuet-Higgins (50).

$$U^+(r_b) = \frac{1}{2}r^2 + hr^4 \quad \text{Eqn. A.II.B.1 (a)}$$

$$U^-(r_b) = (\frac{1}{2} - f)r^2 + gr^4 \quad \text{Eqn. A.II.B.1 (b)}$$

where $h$ and $g$ are anharmonicity constants for the upper and lower potential curves, respectively and $g > 0$ and $f$ which gives a measure of the potential hump height is $> \frac{1}{2}$.

The constants $V_0$ and $V_2$ (cf. Eqn. 4 of Section A of this Appendix) are

A.10
By simultaneously diagonalising \((\mathcal{H}_0 + \mathcal{H}')\), the vibrational energy levels associated with the upper potential curve \(U^+(r_b)\) are given by

\[
E^+(v_2, K) = (v_2+1) + \frac{3}{2}h(v_2+1)^2
- \frac{1}{8}k^2 \left\{ 5h-g + \frac{2f}{v_2+1} \right\}
\]

Eqn. A.II.B.3.

Ramsay and Dressler (44) fitted the vibrational energy levels of the \(^2A(\frac{1}{2}\Pi_u)\) state of \(\text{NH}_2\) to the expression given in Eqn. A.II.B.3. above.
APPENDIX II

SECTION C: Renner Effect Case (c)

The situation in which both the $U^-(r_b)$ and the $U^+(r_b)$ portions of the potential curve have minima at $r_b \neq 0$ has been treated by Dixon (52). It is assumed that the potential hump in both states can be expressed analytically in Gaussian form (cf. Chapter 3, Section C on quasilineararity and Appendix III).

The $U^-(r_b)$ and $U^+(r_b)$ portions of the potential curve are considered as potential curves of separate electronic states. In these two electronic states the molecule is stable in the bent conformation. Rotation about the molecule fixed z axis is coupled to the bending vibration and the resultant wave functions are of the form of the associated Laguerre polynomials. The vibrational energies are calculated using a computer and the calculation is repeated until a good fit with the experimental data is obtained.
APPENDIX III

Quasilinearity

Introduction.

Consider a triatomic molecule of the $AB_2$ type. Let $R_{12}$ and $R_{23}$ be the A-B bond lengths. Let $\Delta_{12}$ and $\Delta_{23}$ be the small extensions of $R_{12}$ and $R_{23}$ during stretching vibrational motions ($\nu_1$ and $\nu_3$). Let $s$ and $a$ be symmetry coordinates defined by

$$s = (1/\sqrt{2}) (\Delta_{12} + \Delta_{23})$$

$$a = (1/\sqrt{2}) (\Delta_{12} - \Delta_{23})$$

Let $m$ be the mass of atom A and $M$ be the mass of atom B. Let $R$ be the displacement of atom A from the line joining the B atoms. Let $\mu = 2Mm/(m+2M)$. cf. Fig. A.III.1.

If centrifugal distortion during rotation is neglected, and if vibration rotation coupling and vibration-vibration interaction terms are considered to be zero, then the total kinetic energy is

A.13
The potential energy associated with symmetric and antisymmetric stretching motions is

\[ \frac{1}{2} k_s s^2 + \frac{1}{2} k_a a^2 \]

where \( k_s \) and \( k_a \) are the elastic constants for symmetric and antisymmetric bond stretching motions respectively.

Thorson and Nakagawa (58) introduced the potential energy term

\[ P.E. = \frac{1}{2} k_p r^2 + \frac{K}{c^2 + r^2} \]  
Eqn. A.III.2.

This potential energy term is independent of \( \Phi \) and so is cylindrically symmetric. The term \( K/(c^2 + r^2) \) is a Lorentzian term which introduces a potential hump into the quadratic potential surface of the simple harmonic oscillator. The potential surface of the simple harmonic oscillator is defined by

\[ P.E. = \frac{1}{2} k_p r^2 \]
A potential energy surface of the form given in Eqn. A.III.2 results in a non-linear electronic state of the molecule. cf. Fig. A.III.2. The hump* height is $K/c^2$ relative to the potential minimum for the bent molecule. Therefore the total Hamiltonian is

\[
\mathcal{H} = \frac{1}{2M}p_s^2 + \frac{1}{2}k_s s^2 + \frac{1}{2\mu}p_a^2 + \frac{1}{2}k_a a^2
\]

\[
+ \frac{1}{2\mu}\left[p_r^2 + p_r^2/r^2\right] + \frac{1}{2}k_r r^2 + K(c^2 + r^2)
\]

Eqn. A.III.3.

The Solution of the Schrodinger Equation.

Let the Schrodinger equation for the molecule be

\[
\hat{\mathcal{H}} \psi = E \psi
\]

* The term "hump" rather than "barrier" is used. The term "barrier" is reserved to describe the maximum in the potential surface of a molecule such as between inversion configurations of ammonia. The potential hump, with respect to the bending vibration of a tri-atomic molecule is illustrated in Fig. A.III.2. The potential hump is cylindrically symmetric about the $E$ axis, and so a transition from one side of the potential well to the other side can be achieved by simple rotation, cf. Johns (56).
\[ U = \text{Potential Energy} \]

\[ \rightarrow \quad \text{Bending Coordinate} \]

Fig. A.3.2.
Thorson and Nakagawa (58) assumed that

$$\Psi = X(s) X(a) \Psi(r, \varphi)$$

where $X(s)$ and $X(a)$ are wave functions of one dimensional simple harmonic oscillators with natural frequencies of

$$(k_s/\mu)^2 = \omega_s$$

and

$$(2k_a/\mu)^2 = \omega_a$$

The wave function $\Psi(r, \varphi)$ satisfies the Schrödinger Equation

$$\left\{ \frac{1/2 \mu}{(r^2 \varphi^2} + \frac{1/2 k_r r^2}{2} + \frac{K}{(c^2 + r^2)} \right\} \Psi = \mathcal{E} \Psi$$


The solution of Eqn. A.III.4 is obtained by separation of the variables

$$\Psi(r, \varphi) = F_n(l)(r) \exp(i l \varphi)$$

Eqn. A.III.5.

where $\varphi$ is as defined in Fig. A.III.2.

and $l$ is an integer $= 0, \pm 1, \pm 2, \text{ etc.}$

The term $\exp(i l \varphi)$ expresses the cylindrical symmetry of $\Psi(r, \varphi)$ about the line joining the B atoms.

If the substitutions

$$u = r \left\{ \mu k_r \right\}^{1/2}/\gamma$$

and

$$B = c^2 \left\{ \mu k_r \right\}^{1/2}/\gamma$$

are made in Eqn. A.III.4.
Then
\[ F_n \ell (u) = \exp(-u^2/2) u \ell (B+u^2) \sum_{k=0}^{\ell} A(n,k,\ell) L_{\ell+k} (u^2) \]


where the \( A(n,\ell,k) \) are numerical coefficients, and the \( L_{\ell+k}(u^2) \) are the normalised associated Laguerre polynomials of degree \( k \) and order \( \ell \), and \( n \) indicates that the \( n \)th mode of vibration-rotation is being considered.

Dixon (51) has solved an equation similar to Eqn. A.III.4 except in that the term \( K/c^2 + r^2 \) was replaced by a term \( \alpha \exp(-\beta r^2) \) - a Gaussian hump of total height \( \alpha \). This type of term - a Gaussian term - was also used by Chan and Stelman (60) to give an analytical expression to the barrier to inversion in ammonia.

The potential energy expression used by Dixon (51) is
\[ V = \gamma k r^2 + \alpha \exp(-\beta r^2) \]

Eqn. A.III.7.

The Interaction of Bending and Stretching Vibrations in a Quasilinear Electronic State.

The following semiqualitative treatment of the interaction of bending and stretching vibrations in a quasilinear electronic state was given by Thorson and Nakagawa (58). A more general form of the potential energy
term than that given in Eqn. A. III.3. is

\[ V = V_0(r) + \frac{1}{2}k_s s^2 + k_s X_s s \dot{\alpha}^2 \]

\[ + \frac{1}{2}k_a a^2 + k_a X_a a \dot{\alpha}^2 \]

Eqn. A. III.8.

where \( V_0(r) = \frac{1}{2}k_r r^2 + k/(c^2 + r^2) \),

\( X_s \) is the constant denoting the strength of the coupling between the bending vibrational motion \( V_2 \) and the symmetric stretching motion \( V_3 \) (in \( AB_2 \) type molecules),

\( X_a \) is a similar quantity but is defined for asymmetric stretching motion \( V_1 \) (in \( AB_2 \) type molecules),

is as defined in Fig. A. III.1.

The moments of inertia of a quasilinear molecule, with a large classical amplitude of bending vibration, will vary during the course of the bending motion. The Hamiltonian for the symmetric stretching vibration is therefore

\[ \hat{H} = \hat{H}_s + \hat{H}_{s,b} \]

\[ = \left\{ \frac{p_s^2}{2M} + \frac{1}{2}k_s s^2 \right\} + \left\{ (2M/m) \alpha^2 \left( \frac{p_s^2}{2M} \right) + k_s X_s s^2 \alpha^2 \right\} \]

A.21

The solution to the equation

\[ \hat{H}_s X(s) = E_s X(s) \]

is already given

\[ E_s = \hbar \omega_s = \hbar (k_s/M)^{\frac{1}{2}} \] Eqn. A.III.10

Thorson and Nakagawa (58) treated \( \hat{H}_s^* \) as a perturbation to the simple harmonic oscillator defined by Eqn. A.III.10.

Let \( |N_s\rangle \) be the wave function of the \( N_s \) th symmetric stretching vibration of the molecule being considered. Then in a first order perturbation treatment the diagonal matrix elements of the Hamiltonian \( \hat{H}_s \) are

\[
\left\{ (2M/m) \langle N_s | (p_s^2/2M) | N_s \rangle + 2X_s \langle N_s | k_s s^2 | N_s \rangle \right\} \langle n \ell | \alpha^2 | n \ell \rangle
\]

where \( n \) and \( \ell \) are quantum numbers as defined for Eqn. A.III.6.

But

\[
\langle N_s | (p_s^2/2M) | N_s \rangle = \langle N_s | k_s s^2 | N_s \rangle
\]

\[ = \frac{\hbar}{2}(N_s + \frac{1}{2}) \hbar \omega_s \]

for a simple harmonic oscillator of frequency \( \omega_s \).

Therefore the perturbation shifts in energy, due to the interaction of the bending and symmetric stretching vibrational motions, for a given value of \( N_s \), \( n \) and \( \ell \) are
\[ E_{sb} = (X_s + M/m)(N_s + \frac{1}{2}) \hbar \omega_s \langle \alpha^2 \rangle_{nl} \]

Eqn. A.III.11.

Normally in electronic states of triatomic molecules which have large classical amplitudes of bending vibrations the averaged values

\[ \langle \alpha^2 \rangle_{ol} \text{ and } \langle \alpha^2 \rangle_{nl} \text{ (where n=1,2,3,... etc.)} \]

are numerically different. The difference may be very large, especially near the top of the potential hump (cf. Fig. A.III.2.) and this leads to an apparent "splitting" of the bands involving the vibrational motions \( \nu_1 \) and \( \nu_3 \). This "splitting" of bands involving the excitation of stretching vibrational motions is characteristic of a quasilinear electronic state of a molecule.
APPENDIX IV

Band heads in wavenumbers, assignments, and intensities (cf. pg. 63, 2.B.12) of bands in the $\tilde{E} \leftarrow \tilde{X}$ spectral system. Assignments are in the notation suggested by Brand and Watson in J. Mol. Spectry. 10, 166 (1963).

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From approx. 37500 cm\(^{-1}\) to higher wavenumbers the absorption bands are very diffuse and it is difficult to obtain accurate band head wavenumbers and intensities. The diffuse band structure is readily observed up to 43000 cm\(^{-1}\).
Table of wave numbers of bands and intensities observed in the region 4000 - 4300 Å.

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*Probably due to the overlap of two or more vibrational bands.
Appendix VI

A list of band head wave numbers, intensities and assignments of the absorption bands of the \( \tilde{\Sigma} \leftarrow \tilde{\Xi} \). Since the \( \tilde{\Gamma}_0 \) band was not assigned the bands are labelled according to the progression and number assigned in Table 4. Unassigned bands are marked U.A.

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