SOME OXALYL HALIDES

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THE VIBRATIONAL SPECTRA

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OF

SOME OXALYL HALIDES

by

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SCOPE AND CONTENTS:

The infrared spectra of gaseous oxalyl fluoride, oxalyl chloride, and oxalyl chloride fluoride, and the Raman spectra of liquid oxalyl fluoride and liquid oxalyl chloride have been measured. A satisfactory analysis of these spectra has been obtained for all three molecules on the basis of the trans isomer. An I.B.M. 7040 digital computer has been programmed to calculate the fundamental frequencies, normal coordinates, Urey-Bradley force constants, and potential energy distributions in Urey-Bradley space.

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The two electronic band systems of oxalyl fluoride whose origins are located at 3082 Å and 3340 Å have been photographed in absorption under low resolution. These band systems have been assigned to ${}^{1}A_{u} \leftarrow {}^{1}A_{g}$ and ${}^{3}A_{u} \leftarrow {}^{1}A_{g}$ transitions respectively, and have been partially analyzed in terms of the vibrational energy levels associated with the combining electronic states.

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CHAPTER 1.

INTRODUCTION

I. THEORETICAL:

The total internal energy of a molecule is the sum of the kinetic and potential energies of the electrons and nuclei, (we ignore here the translational kinetic energy of the molecule and the energies due to electronic and nuclear spins). The quantum mechanical Hamiltonian operator, \mathcal{H} , corresponding to the internal energy has eigenfunctions, \mathcal{V}_{T} , and eigenvalues, \mathcal{E}_{T} , which satisfy the equation

$$\mathcal{F} \mathcal{V}_{\mathrm{T}} = \mathcal{E}_{\mathrm{T}} \mathcal{V}_{\mathrm{T}} \tag{1.1}$$

Equation (1.1) can be separated into equations for the electronic, vibrational, and rotational motions respectively. In order to achieve this, coordinate systems for the electrons and nuclei must be defined. The electronic coordinates, $r_i(x_i, y_i, z_i)$, are referred to a set of molecule-fixed Cartesian axes with origin at the centre of mass. The nuclear coordinates, R_i , consist of 3N-6 displacement coordinates, L_i , with origins at the equilibrium positions of the nuclei, and three Eulerian angles, (θ , φ , χ), which define the orientation of the molecule relative to space-fixed axes.

According to the Born-Oppenheimer approximation¹ the molecular Hamiltonian operator can be written as a sum of two components, i.e.,

$$\mathcal{H} = \mathcal{H}_{\mathrm{E}} + \mathcal{H}_{\mathrm{N}}$$

where \mathcal{H}_{E} is the Hamiltonian for the motion of the electrons in the Coulombic field of the nuclei and has eigenfunctions $\mathcal{V}_{E}(r_{i}, R_{i})$, and eigenvalues, E_{F} , which satisfy

$$\mathcal{H}_{E} \mathcal{V}_{E}(\mathbf{r}_{i}, \mathbf{R}_{i}) = \mathbf{E}_{E} \mathcal{V}_{E}(\mathbf{r}_{i}, \mathbf{R}_{i})$$
(1.2)

 \mathcal{H}_{N} is the sum of the operators for the kinetic and electrostatic repulsion energies of the nuclei which, together with the electronic energy, E_{E} , determine the potential field in which the nuclei move. \mathcal{H}_{N} has eigenfunctions, $\mathcal{M}_{N}(R_{i})$, and eigenvalues, E_{N} , which satisfy

$$(\mathcal{H}_{N} + E_{E}) \mathcal{V}_{N}(R_{i}) = \mathcal{E}_{T} \mathcal{V}_{N}(R_{i})$$
(1.3)

Thus, the molecular wave function, \mathcal{V}_{T} , of equation (1.1) becomes

$$\mathcal{V}_{\mathrm{T}} = \mathcal{V}_{\mathrm{E}}(\mathbf{r}_{\mathrm{i}}, \mathbf{R}_{\mathrm{i}}) \mathcal{V}_{\mathrm{N}}(\mathbf{R}_{\mathrm{i}})$$
(1.4)

In general, the nuclear energies are considered relative to the bottom of the potential well given by

$$V(R_{i}) = E_{E} + V_{N}$$

where V_N is the potential energy due to electrostatic repulsion of the nuclei. In spectroscopic discussions the electronic energy is taken as the minimum value of $V(R_i)$ and given the symbol E_e , i.e.,

$$\mathbf{E}_{e} = \mathbf{V}(\mathbf{R}_{i}^{O}) = \mathbf{E}_{E}(\mathbf{R}_{i}^{O}) + \mathbf{V}_{N}(\mathbf{R}_{i}^{O})$$

where R_{i}^{0} is the value of R_{i} for which $V(R_{i})$ is a minimum.

In the rigid rotor approximation for the rotational motion, the nuclear wave function, $\mathcal{V}_{N}(R_{i})$, becomes

$$\mathcal{V}_{N}(\mathbb{R}_{i}) = \mathcal{V}_{V}(\mathcal{J}_{i}) \mathcal{V}_{\mathbb{R}}(\theta, g, \chi)$$
(1.5)

Substitution of (1.5) into (1.3) gives the equations

$$\mathcal{H}_{\mathbf{V}}\mathcal{V}_{\mathbf{V}}(\mathcal{S}_{\mathbf{i}}) = \mathbb{E}_{\mathbf{V}}\mathcal{V}_{\mathbf{V}}(\mathcal{S}_{\mathbf{i}}) \tag{1.6}$$

for the vibrational motion, where E_{V} is measured relative to $E_{e} = V(R_{i}^{0})$, and

$$\mathcal{H}_{\mathrm{R}} \mathcal{V}_{\mathrm{R}}(\theta, \mathcal{G}, \chi) = \mathbb{E}_{\mathrm{R}} \mathcal{V}_{\mathrm{R}}(\theta, \mathcal{G}, \chi)$$
(1.7)

for the rotational motion.

As a result of the separation of the electronic, vibrational, and rotational motions, the total energy, \mathcal{E}_{T} , becomes

$$\mathcal{E}_{\mathrm{T}} = \mathrm{E}_{\mathrm{e}} + \mathrm{E}_{\mathrm{V}} + \mathrm{E}_{\mathrm{R}} \tag{1.8}$$

and the total wave function, \mathcal{V}_{T} , becomes

$$V_{\rm T} = V_{\rm e} V_{\rm V} V_{\rm R} \tag{1.9}$$

where the subscript of the electronic wave function, \mathcal{V}_{E} , in equation (1.2) has been changed for consistency with the conventional electronic energy $E_e = V_N + E_E$.

When a transition takes place between two states, V_T and V_T^* , energy is emitted or absorbed in the form of radiation with wave number (cm⁻¹)

$$O'' = \frac{E_T - E_T''}{hc}$$
(1.10)

where the single and double primes refer to the higher and lower energy states respectively, h, is Planck's constant, and, c, is the velocity of light.

The probability of transition between states ${\mathscr V}_{\mathtt{T}}^{*}$ and ${\mathscr V}_{\mathtt{T}}^{*}$ is

proportional to the square of the transition moment, $\stackrel{\rightarrow}{\mathbb{M}}$, which is given by

$$\vec{M} = \int \vec{V}_{T} \vec{v}_{T} \vec{V}_{T} dt \qquad (1.11)$$

where $\vec{\mu}$ is the dipole moment of the molecule. The transition is allowed if $\vec{M} \neq 0$.

INFRARED SPECTRA:

When a transition takes place between two vibrational states \mathscr{V}_V and

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 \mathcal{V}_V^n associated with the electronic ground state, radiation is emitted or absorbed in the infrared spectral region (~10-10,000cm⁻¹). The vibrational wave functions \mathcal{V}_V^n and \mathcal{V}_V^n are factors of the total wave functions \mathcal{V}_T^n and \mathcal{V}_T^n respectively, i.e.,

$$\begin{aligned}
\mathcal{V}_{T}^{n} &= \mathcal{V}_{e}^{n} \, \mathcal{V}_{V}^{n} \, \mathcal{V}_{R}^{n} \\
\mathcal{V}_{T}^{n} &= \mathcal{V}_{e}^{n} \, \mathcal{V}_{V}^{n} \, \mathcal{V}_{R}^{n}
\end{aligned}$$
(1.12)

where $\mathcal{V}_{e}^{!} = \mathcal{V}_{e}^{n}$ represents the electronic ground state, and $\mathcal{V}_{R}^{!} = \mathcal{V}_{R}^{n}$ for a simple vibrational transition.

For a simple vibrational transition, the dipole moment, $\vec{\mu}$, as a function of the internal coordinates, $\vec{\lambda}_i$, is given approximately by

$$\vec{\mu} = \vec{\mu}_{0} + \underbrace{\sum_{i} \left(\frac{\partial \vec{\mu}_{i}}{\partial \vec{J}_{i}} \right)_{o}}_{i} d\vec{J}_{i}$$
(1.13)

where $\overrightarrow{\mu}_{o}$ is the permanent dipole moment of the molecule.

Substitution of (1.13) and (1.12) for μ , Ψ_{T} , and Ψ_{T} , in (1.11)

gives the vibrational transition moment

$$\vec{M}_{V} = \int \psi_{V} \Delta \vec{u} \ \psi_{V}^{n} d\tau_{V} \qquad (1.14)$$

$$\int \psi_{e}^{n*} \psi_{e}^{n} d\tau_{e} = 1,$$

$$\int \psi_{R}^{n*} \psi_{R}^{n} d\tau_{R} = 1,$$

$$\int \psi_{T}^{n*} \psi_{T}^{n} d\tau = 0, \quad \text{and}$$

since

and

and

where

$\Delta \vec{\mu} = \underbrace{\mathcal{Z}}_{i} \left(\frac{\partial \vec{\mu}}{\partial \mathcal{L}_{i}} \right)_{o} d \mathcal{L}_{i}$	
$dT = dT dT dT dT_{R}$	

and

The vibrational transition moment, \widetilde{M}_{V} , is given relative to Cartesian axes fixed in the molecule. An infrared transition is allowed if \widetilde{M}_{V} is non-zero.

Each infrared band is composed of rotational fine structure which results from transitions between rotational levels associated with the combining vibrational states. If rotational-vibrational transition moments, $\overrightarrow{M_{VR}}$, are considered, a more complicated expression than (1.13) is required for the dipole moment.² In this thesis, only simple vibrational transitions will be discussed.

RAMAN SPECTRA:

Raman spectra result from transitions between vibrational levels of the ground state as do infrared spectra; however, the probability of a transition being observed in the Raman spectrum is proportional to the square of the polarizability rather than the square of the transition moment.

The induced dipole moment, P, is given by

(1.15)

$$\vec{P} = \alpha \vec{\mathcal{E}}$$
(1.16)

where $\tilde{\mathcal{E}}$ is the electric vector of the exciting radiation and ∞ is a dyadic, corresponding to the polarizability tensor which relates the Cartesian components of \tilde{P} and $\tilde{\mathcal{E}}$. For a simple vibrational transition the polarizability ∞ can be expressed as the linear expansion

$$\alpha = \alpha_{0} + \sum_{i} \left(\frac{\partial \alpha}{\partial l_{i}} \right)_{0} dd_{i}$$
 (1.17)

Substitution of (1.12) and (1.16) in equation (1.11) followed by substitution of (1.17) for α gives the polarizability tensor

$$\begin{aligned} & \alpha_{\rm V} = \int \gamma \sqrt[n]{\rm V} \, \Delta \alpha \, \gamma \sqrt[n]{\rm V} \, d \tau_{\rm V} \tag{1.18} \\ & \Delta \alpha = \sum_{\rm i} \left(\frac{\partial \alpha}{\partial {\rm I}_{\rm i}} \right) \, d {\rm A}_{\rm i} \end{aligned}$$

where

A transition is allowed in the Raman spectrum only if $\alpha_V \neq 0$. As is the case with infrared bands, each Raman vibrational band is composed of rotational fine structure.

VIBRONIC SPECTRA:

When a transition takes place between two electronic states V'_e and V'_e , radiation is usually emitted or absorbed in the visible or ultraviolet spectral regions, (~10,000-100,000cm⁻¹). The Franck-Condon principle states that the nuclei do not move significantly during the electronic transition; thus, the electric moment, \vec{m} , is not dependent upon the internal coordinates, \mathcal{A}_i .

Substitution of \vec{m} for $\vec{\mu}$ in equation (1.11) leads to the electronic transition moment

$$\vec{M}_{e} = \int \chi_{e}^{i*} \vec{M}_{e}^{n} d\tau_{e} \int \chi_{V}^{i*} \chi_{V}^{n} d\tau_{V}$$
(1.19)

An electronic transition is allowed if $\widetilde{M}_e \neq 0$. The spectrum consists of a series of bands due to transitions between vibrational levels of the combining electronic states. Each vibrational band consists of rotational fine structure due to transitions between rotational levels of the combining vibronic states $\mathcal{W}_e^* \mathcal{W}_V^*$ and $\mathcal{W}_e^* \mathcal{W}_V^*$.

A necessary condition that the transition moments be non-zero is that the integrands in (1.14), (1.18), and (1.19) transform like the totally symmetric representation of the molecular point group. The conditions under which the integrands are totally symmetric are easily obtained by the methods of group theory which will be discussed in later chapters.

II.HISTORICAL:

The three molecules studied here are oxalyl fluoride, oxalyl chloride,

and oxalyl chloride fluoride. Three possible isomeric forms for each of these molecules are shown in FIGURE 1.1.

FIGURE 1.1

ISOMERS OF THE OXALYL HALIDES



In general the isomers shown in FIGURE 1.1 belong to different point groups and the selection rules for allowed spectroscopic transitions are different. It is therefore feasible to determine the isomeric form of a molecule from an analysis of its molecular spectra.

Of the oxalyl halides studied here, only oxalyl chloride has been the subject of previous structural investigations. The earliest attempt at determining the structure of oxalyl chloride was made by Wierl using the electron diffraction technique; however, his results were inconclusive. More recently, Luvalle has determined that the structure is planar and trans by the same method. Luvalle's measurements of the interatomic distances have been reported by Allen and Sutton⁴ and are given in

TABLE 1.1.

TABLE 1.1

INTERATOMIC DISTANCES FOR OXALYL CHLORIDE4

C – C	1.50 ± 0.03 Å
C - Cl	1.72 ± 0.03 Å
C = 0	1.20 Å assumed
C - C = O	123 <u>+</u> 2°
C1 - C = 0	123 ± 2°

Groth and Hassel⁵have studied the crystal structure of solid oxalyl chloride by means of x-ray diffraction. The experimentally determined crystal space group is consistent with a centrosymmetric molecular configuration although there is evidence that the molecules are not strictly planar in the solid state.

The infrared and Raman spectra of oxalyl chloride have been studied by several investigators.⁶⁻¹³In addition, some of the frequencies of oxalyl chloride fluoride have been reported by Haszeldine and Nyman;¹⁴ however, no references to the infrared and Raman spectra of oxalyl fluoride are to be found in the literature.

The most complete vibrational analyses of the infrared and Raman

spectra of oxalyl chloride were reported by Saksena and Kagarise, and Ziomek, Meister, Cleveland, and Decker.¹² Saksena and Kagarise reported a marked temperature dependence of the intensity of certain bands, both in the infrared and Raman spectra. Bands whose intensity increased when the temperature was increased were assigned to the cis isomer. All other bands were assigned to the trans isomer. The energy difference, \triangle H, between the cis and trans isomers was calculated using the formula

$$\frac{\mathbf{I}_{t_{1}}}{\mathbf{I}_{t_{1}}} = \frac{\mathbf{I}_{t_{2}}}{\mathbf{I}_{t_{2}}} \exp \left[-\frac{\Delta H}{R} \left(\frac{1}{T_{1}} - \frac{1}{T_{2}}\right)\right]$$
(1.20)

due to Bernstein; I_{t_1} , I_{t_1} , I_{t_2} , and I_{t_2} are intensities of bands due to cis and trans isomers respectively at temperatures T_1 and T_2 . Using the intensities of Raman bands at 533cm⁻¹ (assigned to the cis C-Cl stretching mode) and 620cm⁻¹ (assigned to the trans C-Cl stretching mode), these authors obtained an energy difference, $\Delta H = 2.8$ K cal./mol between the cis and trans isomers. The product rule for cis and trans isomers given by Bernstein gave observed and calculated ratios of 2.44 and 2.5, respectively.

In a later experiment, Kagarise reported a marked difference between the infrared spectrum of liquid oxalyl chloride at room temperature and the infrared spectrum of the solid at -78°C. Two bands (at 520cm⁻¹ and 1050cm⁻¹) present at room temperature but absent at -78°C, were assigned to the cis isomer.

Ziomek et al. were able to make a complete assignment of all observed infrared and Raman frequencies on the basis of the trans structure alone; however, their analysis depended on the assignment of a depolarized Raman band, 355cm⁻¹, to an in-plane fundamental, and the assignment of a polarized Raman band, 465cm⁻¹, to an out-of-plane fundamental. The latter assignments contradict the symmetry selection rules for the trans isomer and leave this analysis open to question. Ziomek et al. carried out a normal coordinate analysis for both cis and trans models, in which they used a modified valence force field and initial force constants transferred from phosgene and ethane. The frequencies calculated for the trans isomer were in better agreement with the observed frequencies than were the frequencies calculated for the cis isomer.

The present analysis of the infrared and Raman spectra of oxalyl chloride has not explained the temperature dependence reported by Kagarise; however, the additional infrared data which has been obtained for the region 400-250 cm⁻¹, in particular, has made possible a more satisfactory assignment of bands which are definitely due to the trans isomer. In a later chapter detailed arguments will be advanced which indicate that the trans structure predominates at room temperature.

The ultraviolet band spectrum of oxalyl chloride which occurs in the region of 3700 Å has been reported several times. The most complete 18 previous analysis is that reported by Sidman. He observed that the absorption spectrum consisted of sharp vibrational structure superimposed on a background of continuous absorption. The intensity of the continuous absorption increased relative to the intensity of the sharp structure as the temperature of the absorption cell was raised. Sidman concluded that the sharp structure was due to a transition between electronic states of the trans isomer. He attributed the continuous absorption to a transition from the ground state of the cis isomer to a non-planar excited state. The overall transition was identified as of n $\rightarrow \pi^{\#}$ type, in which a non-bonding electron on the oxygen atom is excited into an unoccupied π^* orbital.

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Saksena and Jauhri preferred to assign the continuous spectrum to a

transition between electronic states of CL-C = 0 radicals which were considered to be formed by photochemical decomposition of the oxalyl chloride molecules. The sharp structure was then assigned to two overlapping band systems due to transitions between electronic states of both cis and trans isomers. There was no clear evidence which distinguished the bands due to one isomer from those due to the other; therefore, the assignments do not seem to be necessarily justified. It is also quite unlikely that a sufficient number of CL-C = 0 radicals to produce a spectrum would be formed during an exposure.

Kanda et al. observed a weak band system in absorption at 4100 Å. They also observed the phosphorescence emission spectrum of oxalyl chloride in cyclohexane at 90°K. The absorption and phosphorescence were both assigned to a singlet-triplet transition of the $n \rightarrow n^*$ type. Measurements of the oscillator strengths, f, for the singlet-triplet transitions of several oxalyl compounds were compared. These oscillator strengths are tabulated in TABLE 1.2.

TABLE 1.2

OSCILLATOR STRENGTHS OF THE SINGLET-TRIPLET

MOLECULE	APPARENT ELECTRONIC ORIGIN (cm ⁻¹)	OSCILLATOR STRENGTH
(COC1)2	24,374	1.34×10^{-7}
$(COBr)_2$	22,943	3.13×10^{-6}
(COCH3)2	19,500	1.12×10^{-7}

The investigation of the ultraviolet spectra of oxalyl fluoride was undertaken in order that a comparison could be made with the spectra of oxalyl chloride. As was the case with oxalyl chloride, the singletsinglet spectrum consists of sharp structure superimposed on a continuous background; however, there is a marked discontinuity in the continuum at about 2900 Å, where it becomes so intense that the sharp structure is almost completely absent. Sidman observed no such discontinuity in the continuum of the oxalyl chloride spectrum. The discontinuity is attributed to predissociation due to overlapping of the lower energy planar excited state with a higher energy excited state which is predicted to be non-planar.²⁴

In order to check the validity of the ground state assignments of the infrared and Raman frequencies, normal coordinate analyses were

15.

carried out for all three molecules. It was also hoped that the stretching force constants would give some indication of the bond strengths, and in particular, the C-C bond strength of oxalyl fluoride.

CHAPTER 2.

PREPARATION AND IDENTIFICATION OF OXALYL FLUORIDE AND OXALYL CHLORIDE FLUORIDE

I.INTRODUCTION:

A general method for the preparation of acyl fluorides has been reported by Tullock and Coffman.²¹ By their method a chlorine atom of an acyl chloride is exchanged for a fluorine atom of sodium fluoride. The reaction is carried out in a non-aqueous solvent of high dielectric constant. These authors prepared oxalyl fluoride (boiling point, 0-2°C.) from oxalyl chloride, using tetrahydrothiophene-l,l-dioxide as solvent. II.PROCEDURE:

The procedure used to prepare oxalyl fluoride was an adaptation of the method of Tullock and Coffman. It differed from their procedure in that the reaction was carried out at room temperature (22°C.), without reflux, for longer periods of time. Under these mild conditions, both oxalyl fluoride and oxalyl chloride fluoride (boiling point, -21°C./140mm.) were obtained. The apparatus which was used is shown in FIGURE 2.1. 100 g. of tetrahydrothiophene-1,1-dioxide (Matheson, Coleman, and Bell, m.p. 20-22°C.) and 52 g. of powdered sodium fluoride were placed in the two-necked 500 ml. flask A. Flask A was fitted with a dropping funnel, B, and connected to the rest of the apparatus. The system was evacuated and the mixture in flask A was stirred for 12 hr. with a magnetic stirrer.

After the stirring period, stopcock D was closed and air was let into the apparatus. TRAP IV was disconnected and replaced by a drying tube packed with $CaCl_2$. TRAP I was cooled in a dry ice-acetone bath (-78°C) and TRAPS II and III were immersed in liquid air (\sim -190°C). With stopcock C open, 21 ml. of oxalyl chloride were very slowly added from the dropping funnel to the contents of flask A. Some decomposition took place during the addition of the oxalyl chloride. Decomposition products condensed in TRAPS II and III (-190°C.) but not in TRAP I (-78°C.).

The reaction mixture was stirred for 4-12 hrs., longer time resulting in higher ratios of oxalyl fluoride to oxalyl chloride fluoride in the product. When the reaction period was over, TRAP IV was reconnected and immersed in liquid air. Stopcock D was opened and the reaction product was pumped off the reaction mixture and condensed in TRAP I (-78°C.). Warming of flask A made the release of products from the reaction mixture easier. Release of the products was noted by the effervescence of the mixture in flask A. When effervescence ceased, stopcock C was closed and the liquid air bath on TRAP II was replaced by a dry ice-acetone bath. All decomposition products then condensed in TRAP III. The contents of TRAP III were discarded and the contents of TRAPS I and II were distilled under vacuum into a sample tube. Unreacted oxalyl chloride was later removed from the reaction product by trap-to-trap distillation. The product sample which remained was a mixture of oxalyl fluoride, oxalyl chloride fluoride, and a trace of oxalyl chloride.

III.PURIFICATION:

A Perkin Elmer model 154 vapor fractometer was used to separate the components of the product sample. Since this instrument was designed for analytical purposes, its detector was intended for use with small quantities of material. For the large quantities of sample used in preparative work, a detector bypass device was provided with the instrument as an accessory. This bypass device allowed only a small fraction of a given sample to pass through the detector.

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FIGURE 2.1

PREPARATIVE APPARATUS





FRACTOMETER SAMPLING APPARATUS


Because oxalyl fluoride is a gas at room temperature, the syringe input to the fractometer could not be used; instead, a gas sampling device was employed. The analytical gas sampling valve on the fractometer was removed and replaced by the input apparatus shown in FIGURE 2.2.

The input apparatus was provided with pressure stopcocks A, A, B, and C. A and A were two-way stopcocks which could be turned so that the carrier gas, nitrogen, either bypassed the input system or flowed through it.

The typical sampling procedure was carried out as follows: Stopcocks A and A' were turned to bypass the input system; then, stopcock B was turned to open the input system to the vacuum pump. After evacuation of the input system, stopcock B was closed, and stopcock C was opened. 0.5 - 1 ml. of sample were distilled into TRAP D which was cooled in liquid air. Stopcock C was closed and the sample in TRAP D was warmed up to room temperature in order to vaporize the sample. Stopcocks A and A' were then turned so that the sample was swept out of the input system by the carrier gas. The carrier gas flow in the fractometer was sustained under a pressure of 15 p.s.i. The oxalyl

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fluoride fraction passed the detector at \sim 3-5 min. and oxalyl chloride fluoride passed the detector at \sim 9-11 min.

The packing which was used for the preparative column consisted of Chromasorb P (Johns-Manville 30/60 mesh) as support phase and fluorolube grease as stationary phase. The fluorolube grease made up 40% by weight of the packing.

The fluorolube was dissolved in ethyl ether and dry Chromasorb P was stirred in. After the mixture had been agitated for about 1 hr., the ether was stripped off by means of a rotary evaporator. The packing obtained was spread out on paper and placed in an oven at 110° C. for 4 hr. Two 1m. x 25mm. glass tubes, each tapered to 8mm. at both ends, were packed with the above material and connected in series with a short piece of Tygon tubing. The free ends of the column were connected to the detector block by short pieces of 7mm. glass tubing.

A sample gas chromatogram is given in FIGURE 2.3. Fractions were cut between X and X' for oxalyl fluoride and between Y and Y' for oxalyl chloride fluoride. U-tubes cooled in dry ice-acctone baths served as collecting vessels.



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IV.IDENTIFICATION OF COMPOUNDS:

Oxalyl fluoride and oxalyl chloride fluoride were identified from C^{13} satellite peaks observed in their fluorine nuclear magnetic resonance spectra. The analyses of these spectra have been reported by Gillespie and Bacon.²³ V. PURITY OF SAMPLES:

The gas chromatographically purified samples were checked for purity using an infrared spectrophotometer (Perkin-Elmer model 21, NaCl optics). The infrared spectrum of oxalyl chloride fluoride vapor showed no impurities up to 550mm. sample pressure. No spectra were recorded above this pressure because of the smallness of the sample (0.5ml.).

The spectrum of oxalyl fluoride vapor showed no impurities up to 300mm. sample pressure, where the strong 936cm⁻¹ band of oxalyl chloride fluoride appeared weakly. Since 5mm. pressure of oxalyl chloride fluoride produced 5-10% transmission at 936cm⁻¹, the percentage of oxalyl chloride fluoride present in oxalyl fluoride as an impurity was estimated to be less that 0.5%. The amount of oxalyl fluoride sample was approximately 2ml.

The pure samples described above were used for all the infrared work; however, these samples proved insufficient in amount for recording a Raman spectrum. In the case of oxalyl fluoride, a larger, relatively impure, sample (1-2% oxalyl chloride fluoride) was used for the Raman

spectrum.

CHAPTER 3.

INFRARED AND RAMAN SPECTRA

I. THEORETICAL:

A discussion of the selection rules for vibrational transitions observed in the infrared and Raman spectra requires a knowledge of the symmetry properties of the vibrational wave functions, \mathcal{M}_V , which are solutions of the equation

$$\mathcal{A}_{\mathrm{V}}\mathcal{V}_{\mathrm{V}} = \mathrm{E}_{\mathrm{V}}\mathcal{V}_{\mathrm{V}} \tag{1.6}$$

The wave functions, \mathcal{V}_V , are functions of 3N-6 displacement coordinates, \mathcal{J}_i , which were described in Chapter 1.

If the potential energy function is assumed to be harmonic, and the normal coordinates, Q_k , (to be discussed in Chapter 5) are chosen as

displacement coordinates, the potential energy is given by

$$V = \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2$$
(3.1)

where

$$\lambda_{k} = \left(\frac{\partial^{2} v}{\partial q_{k}^{2}}\right)_{0}$$

and the kinetic energy is given by

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$$T = \frac{1}{2} \sum_{k=1}^{3N-6} \hat{Q}_{k}^{2}$$
(3.2)

25 To a very good approximation, the quantum mechanical operator for

the kinetic energy can be written as

$$-\frac{1}{2^{n}} \sum_{k=1}^{3N-6} \frac{\partial^{2}}{\partial \varrho_{k}^{2}}$$
(3.3)

Thus, the operator \mathcal{A}_{v} is given by

$$\mathcal{A}_{V} = -\frac{1}{2} \bigwedge_{k=1}^{3N-6} \frac{\partial^{2}}{\partial Q_{k}^{2}} + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_{k} Q_{k}^{2}$$

which can be substituted into equation (1.6) to give

$$\begin{pmatrix} \frac{1}{2^{n}} \sum_{k=1}^{3^{n-6}} \frac{\partial}{\partial Q_{k}^{2}} + \frac{1}{2} \sum_{k=1}^{3^{n-6}} \lambda_{k} Q_{k}^{2} \end{pmatrix} \psi_{V} = E_{V} \psi_{V} \qquad (3.4)$$

Since the \mathbf{Q}_k are orthogonal, the wave function, $\mathcal{W}_V,$ can be written

as

$$\mathcal{V}_{V} = \frac{3N-6}{71} \mathcal{V}_{k}(Q_{k})$$

$$(3.5)$$

and consequently,

$$E_{V} = \sum_{k=1}^{3N-6} E_{k}$$
(3.6)

Substitution for E_V and V_V in equation (3.4) using equations (3.5) and (3.6) respectively gives 3N-6 equations of the simple harmonic ascillator

$$\begin{pmatrix} -\frac{1}{2}\hbar \frac{\partial^2}{\partial \varrho_k^2} + \frac{1}{2}\lambda_k \varphi_k^2 \end{pmatrix} \chi_k (\varrho_k) = E_k \chi_k (\varrho_k)$$

$$k = 1, 2, \dots 3N-6$$

$$(3.7)$$

Each of these equations can be solved to give

$$\begin{aligned}
\mathcal{V}_{k}(Q_{k}) &= \left[\left(\frac{\mathcal{Y}_{k}}{TT} \right)^{\frac{1}{2}} \frac{1}{\mathcal{V}_{k}} \frac{1}{\mathcal{V}_{k}^{2}} \right]^{\frac{1}{2}} \exp\left(-\frac{1}{2} \mathcal{V}_{k}^{2} Q_{k}^{2} \right) H_{V_{k}}(\mathcal{Y}_{k}^{\frac{1}{2}} Q_{k}) \quad (3.8) \\
& E_{k} &= \left(\mathcal{V}_{k}^{2} + \frac{1}{2} \right) \stackrel{\text{th}}{} \mathcal{Y}_{k}^{\frac{1}{2}} &= \left(\mathcal{V}_{k}^{2} + \frac{1}{2} \right) \stackrel{\text{th}}{} \mathcal{Y}_{k} \quad (3.9)
\end{aligned}$$

and

where V_k is the vibrational quantum number, $\mathcal{V}_k = \frac{\lambda_k^{\frac{1}{2}}}{2\pi}$ is the classical frequency, $V_k = \frac{2\pi \mathcal{V}_k}{\kappa}$, and $H_{V_k}(\chi_k^{\frac{1}{2}}Q_k)$ is the Hermite polynomial of degree V_k .

Substitution of equations (3.8) and (3.9) into equations (3.5) and

(3.6) gives the total vibrational wave function

$$\begin{aligned}
\mathcal{V}_{\Psi} &= \prod_{k=1}^{5N-5} \mathcal{N}_{\Psi_{k}} \exp\left(-\frac{1}{2} \vartheta_{k}^{2} \varrho_{k}^{2}\right) H_{\Psi_{k}} \left(\begin{array}{c} \frac{1}{2} \varrho_{k} \\ k & \varrho_{k} \end{array}\right) \quad (3.10) \\
\mathcal{N}_{\Psi_{k}} &= \left[\left(\frac{\mathcal{V}_{k}}{2 \pi}\right)^{\frac{1}{2}} \frac{1}{\frac{\Psi_{k}}{2^{k} \Psi_{k}!}}\right]^{\frac{1}{2}}
\end{aligned}$$

where

and the total vibrational energy

$$E_{V} = \sum_{k=1}^{3N-6} (V_{k} + \frac{1}{2}) h z_{k}$$
(3.11)

Because of the assumption of a harmonic potential function, equation

(3.1), the eigenvalues and eigenfunctions given in equations (3.11) and (3.10), respectively, are not in exact agreement with experiment.

Experimentally, the vibrational energy levels decrease in separation as

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the vibrational quantum number increases, whereas the above theory predicts equally spaced levels. The observed vibrational transitions are found to obey the selection rule $\Delta V_k = \pm 1, \pm 2, \pm 3, \ldots$, whereas the simple harmonic oscillator selection rule is $\Delta V_k = \pm 1$.

II.SYMMETRY:

If a molecule possesses a set of symmetry elements, there is a corresponding set of symmetry operators which either exchange identical nuclei, or leave them unchanged. The symmetry operators, including the identity operator, constitute the elements of a point group.

Symmetry operators are given special symbols. The operator symbols which will be used in this chapter are listed and described in TABLE 3.1.







DESCRIPTION OF SYMMETRY SYMBOL OPERATOR Identity E Two-Fold Rotation C₂ Reflection in a plane \sim_h

Reflection in a plane perpendicular to the principal axis

Reflection in a plane in which the principal axis lies g,g = x,y,z

Inversion

i

 $\sigma_{v(gg')}$

In FIGURE 3.1 the symmetry elements of each molecule are shown. Cis oxalyl chloride fluoride has the same symmetry elements as trans oxalyl chloride fluoride. In TABLE 3.2 the point groups of the molecules are given together with the operators which make up each point group. The symmetry operators are referred to the Cartesian axes defined in FIGURE 3.1.

MOLECULE	POINT GROUP SYMMETRY OPERATORS	POINT GROUP
trans $(COF)_2$ trans $(COC1)_2$	E, $C_2(z)$, $\sigma_h(xy)$, i	C _{2h}
cis (COF) ₂ cis (COCl) ₂	E, $C_2(z)$, $\tilde{\sigma_V}(zx)$, $\tilde{\sigma_V}(yz)$	C _{2V}
COF.COC1	E, O(xy)	Cs

The character tables for the point groups C_{2h} , C_{2V} , and C_s are TABLE 3.3, TABLE 3.4, and TABLE 3.5, respectively. The irreducible representation or symmetry species appears in the first column of the character table. For example, the symmetry species of point group C_s are labelled A^{*} and A^{*}. The direct products obtained from multiplication of the corresponding characters belonging to two symmetry species are given in TABLES 3.6, 3.7, and 3.8.

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C _{2h}	E	C ₂ (z)	o _h (xy) i		
Ag	1	l	1	l	Rz	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}$
^A u	1	l	-1	-1	Tz	
Bg	l	-1	-1	l	R _x ,R	α_{yz}, α_{zx}
B _u	1	-1	l	-1	Tx, Ty	

THE CHARACTER TABLE FOR POINT GROUP C2h

TABLE 3.4

THE CHARACTER TABLE FOR POINT GROUP C2V

с _{2V}	E	C ₂ (z)	$\widetilde{O_V}(xz)$	O√(yz)		
Al	l	l	l	1	Tz	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
^A 2	1	l	-1	-1	Rz	α_{xy}
Bl	l	-1	1	-1	T _x ,R _y	$\propto_{\rm zx}$
B ₂	l	-1	-1	l		$lpha_{yz}$

C _s	Ε	$\sigma_{\rm h}({\rm xy})$		
A	1	l	T _x , T _y , R _z	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}$
A	1	-1	^T z, ^R x, ^R y	α_{yz}, α_{zx}

THE CHARACTER TABLE FOR POINT GROUP Cs

TABLE 3.6

THE DIRECT PRODUCTS TABLE FOR THE $\mathbf{C}_{2\mathbf{h}}$ POINT GROUP

	Ag	Au	Bg	Bu
Ag	Ag	Au	Bg	Bu
Au	Au	Ag	Bu	Bg
Bg	Bg	Bu	Ag	Au
Bu	Bu	Bg	A _u	Ag

	Al	^A 2	Bl	^B 2
Al	A _l	^A 2	Bl	^B 2
^A 2	A2	Al	^B 2	Bl
Bl	Bl	B ₂	Al	A2
^B 2	^B 2	Bl	A2	Al

THE DIRECT PRODUCTS TABLE FOR THE $\mathbf{C}_{\mathbf{2V}}$ point group

TABLE 3.8

THE DIRECT PRODUCTS TABLE FOR THE $\mathbf{C}_{\mathbf{S}}$ point group

 $\begin{array}{c|c} & A^{T} & A^{H} \\ \hline \\ A^{T} & A^{T} & A^{H} \\ A^{H} & A^{H} & A^{T} \\ \hline \end{array}$

III.VIBRATIONAL REPRESENTATIONS:

Let 3N-6 independent valence internal coordinates, S_k , be chosen as internal displacement coordinates; then, application of any symmetry operator, R, to these coordinates will produce a new set of coordinates, $S_k^{'}$, such that $\begin{bmatrix}
S_1^{'}\\S_2^{'}\\\vdots\\\vdots\\S_{3N-6}^{'}
\end{bmatrix} =
\begin{bmatrix}
R_{1,1} & R_{1,2} & \cdots & R_{1,3N-6}\\
R_{2,1} & R_{2,2} & \cdots & R_{2,3N-6}\\\vdots\\\vdots\\\vdots\\R_{3N-6,1} & R_{3N-6,2} & \cdots & R_{3N-6,3N-6}
\end{bmatrix}
\begin{bmatrix}
S_1\\S_2\\\vdots\\\vdots\\S_{3N-6}\\\vdots\\S_{3N-6}\end{bmatrix}$ (3.12)

where the matrix [R] is the symmetry transformation matrix which corresponds to the symmetry operator R. The set of transformation matrices generated by the application of the group symmetry operators, \mathcal{R} , to the coordinates, S_k , forms a representation of the molecular point group, because the matrices, [R], satisfy the same multiplication rules as the symmetry operators R. The coordinates, S_k , are said to form the basis of the representation.

The character of the matrix, $\chi_{\rm R}$, is defined by

$$\chi_{R}^{} = \sum_{i}^{l} R_{ii}^{} \qquad (3.13)$$

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The character X_R has the property of being invariant under change of coordinates, provided that the new coordinates are related to the S_k by a linear transformation. The representations generated by coordinates which are related by a linear transformation are called equivalent representations. The normal coordinates, Q_k , and the internal coordinates, S_k , generate equivalent representations.

The molecules considered here belong to point groups which do not have degenerate representations, and have no degenerate normal modes of vibration; hence, in the following, we shall only consider the nondegenerate case.

In the non-degenerate case, application of a group symmetry operation, \mathcal{R} , to a normal coordinate, Q_k , gives

$$\mathcal{K}Q_{k} = \pm Q_{k} \tag{3.14}$$

Thus, the character of the transformation for a single normal coordinate is given by

$$\chi_{R}^{(l)} = \pm 1 \tag{3.15}$$

where $\chi_{\mathbf{R}}^{(\mathcal{B})}$ is the character of the transformation $[\mathbf{\bar{R}}]$ in the irreducible

representation $\Gamma^{(1)}$. The character χ_{R} of the transformation of all the

normal coordinates can thus be given as

$$\chi_{R} = \sum_{\lambda=1}^{p} n^{(\lambda)} \chi_{R}^{(\lambda)}$$
(3.16)

(8) where n is the number of normal coordinates which generate the irreducible representation $\Gamma^{(3)}$ and p is the order of the group.

n () can be found from the formula

$$n^{(2)} = \frac{1}{g} \sum_{R}^{p} g_{R} \chi_{R}^{(b)} \chi_{R}$$
(3.17)

where g is the number of operators in the point group and g_R is the number of the operators in the Rth class. The total vibrational representation Γ_V can be expressed as the direct sum of the irreducible representations, $\Gamma_V^{(d)}$, of the 3N-6 normal coordinates, Q_k , i.e., p = (d) = (d)

$$\int_{V}^{T} = \sum_{k=1}^{P} n^{\binom{k}{k}} \int_{V}^{\binom{k}{k}} (3.18)$$

Since each non-degenerate wave function $\mathcal{V}_k(Q_k)$ is a function of only one Q_k , there are only as many fundamental levels as there are normal coordinates; thus, $n^{(k)}$ also represents the number of fundamental levels which can be classified under a given irreducible representation $\Gamma^{(k)}$

A knowledge of the normal coordinates is not required in order to

evaluate n from equation (3.17) since $\chi_{p}^{(i)}$ can be found from the representation for internal coordinates. The valence coordinates, S_{ν} , can be divided into classes which contain all the bonds or angles of a specific type in the molecule. For example, the carbon-halogen bonds r_x and r_x^{\dagger} of the (COX)₂ molecule form one class. Each class will transform under symmetry operation R, with character $\mathcal{X}_{_{\mathrm{R}}}(\mathbf{s})$. $\mathcal{X}_{_{\mathrm{R}}}(\mathbf{s})$ is substituted for $\chi_{_{\rm R}}$ in equation (3.17), to give

$$n^{\binom{k}{3}}(s) = \frac{1}{g} \sum_{R=1}^{p} g_R \chi_R^{\binom{k}{3}} \chi_R^{(s)}$$
 (3.19)

such that

 $n^{(2)} = \sum_{s} n^{(2)}(s)$ (3.20)The calculations of n for trans oxalyl halide, cis oxalyl halide, and

oxalyl chloride fluoride are given in TABLES 3.9, 3.10, and 3.11, respectively. The internal coordinates are defined in TABLE 3.12.

The characters $\chi_{_{\mathrm{R}}}$ (s) are arranged in a column below the character table. The values of n (s) are arranged in the columns to the right of the group table. For example, consider the calculation of $\mathcal{X}_{\mathsf{C}_{\mathsf{C}}}$ $(\mathbf{r}_{\mathbf{x}})$ for trans oxalyl halide given in TABLE 3.10. If the C2 operation is carried out on the $\mathbf{r}_{_{\mathbf{Y}}}$ the transformation is given by

$$\begin{bmatrix} \mathbf{r}_{\mathbf{x}} \\ \mathbf{r}_{\mathbf{x}} \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} \mathbf{r}_{\mathbf{x}} \\ \mathbf{r}_{\mathbf{x}} \end{bmatrix}$$
(3.21)

and thus, $\chi_{C_{2}}$ (r_x) = 0. In general, if a coordinate is changed by a symmetry operation it contributes nothing to $\mathcal{X}_{_{\mathrm{R}}}$ (s) while if the coordinate is left unchanged, it contributes 1 to $\mathcal{X}_{_{\mathrm{P}}}$ (s). If two coordinates are left invariant under a transformation, \mathcal{X}_{R} (s) = 2. n (s) is obtained by substitution of $\chi_{\rm R}$ (s) into equation (3.19). n^(X) is obtained from equation (3.20) and Γ_V from equation (3.18). IV.SYMMETRY OF THE TOTAL VIBRATIONAL WAVE FUNCTION:

The total wave function, \mathcal{V}_{v} , given by equation (3.6) can be rewritten as

$$\mathcal{V}_{V} = \frac{3N-6}{T} \mathcal{V}_{V}_{k}$$
(3.22)

where $\mathcal{V}_{V_k} = \mathcal{V}_k(Q_k)$ and V_k is the vibrational quantum number. Thus, the representation generated by \mathcal{W}_V is the direct product of the irreducible representations of the 3N-6 non-degenerate wave functions V. i.e., $\Gamma(\gamma_{V}) = \Gamma(\gamma_{V}) \otimes \Gamma(\gamma_{V}) \otimes \cdots \otimes \Gamma(\gamma_{V_{3N-6}}) \quad (3.23)$

where $\bigcap(\bigvee)$ denotes a representation.

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The simple harmonic ascillator wave functions \mathcal{W}_k given by equation

(3.9) can be written as

$$\mathcal{V}_{V_{k}} = \mathcal{N}_{k} U_{k} H_{V_{k}} (\mathcal{Y}_{k}^{\frac{1}{2}} Q_{k})$$
(3.24)

where $\mathcal{N}_{\mathbf{k}}$ is a normalization constant and

$$U_{k} = \exp(-\frac{1}{2} \partial_{k}^{2} Q_{k}^{2})$$
 (3.25)

Since U_k is an even function of Q_k ,

$$U_{k}(Q_{k}) = U_{k}(-Q_{k})$$
 (3.26)

Therefore, U_k is invariant under any symmetry operation \mathcal{R} since \mathcal{R} can only change the sign of Q_k or leave Q_k unchanged.

Since U_k is invariant under any symmetry operation \mathcal{R} , the wave function, \mathcal{W}_{V_k} , must generate the same representation as the Hermite polynomial $H_{V_k}(\mathcal{J}_k^{\frac{1}{2}}Q_k)$. i.e.,

$$\prod_{k} (\mathcal{V}_{V_{k}}) = \prod_{k} (\mathcal{Y}_{k}^{\frac{1}{2}} Q_{k})$$
 (3.27)

The Hermite polynomials, $H_{V_k}(\begin{cases} \frac{1}{2} \\ k \end{cases} Q_k)$, are given by

$$H_{V_{k}}(\gamma_{k}^{\frac{1}{2}}Q_{k}) = (2\gamma_{k}^{\frac{1}{2}}Q_{k})^{V_{k}} - \frac{V_{k}(V_{k}-1)}{1!} (2\gamma_{k}^{\frac{1}{2}}Q_{k})^{V_{k}-2} + (3.28)$$

$$\frac{\nabla_{k}(\nabla_{k}-1)(\nabla_{k}-2)(\nabla_{k}-3)}{2!} (2 \sqrt[3]{\frac{1}{2}} Q_{k})^{\nabla_{k}-4} + \cdots$$

If V_k is an even integer, $H_{V_k}(\overset{\sqrt{\frac{1}{2}}}{\otimes k} Q_k)$ is an even function of Q_k since

$$H_{V_{k}}(\gamma_{k}^{\frac{1}{2}} Q_{k}) = H_{V_{k}}(-\gamma_{k}^{\frac{1}{2}} Q_{k})$$

$$V_{k} = 0,2,4, \dots$$
(3.29)

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Hence, $H_{V_k}(V_k^{\frac{1}{2}}Q_k)$ is invariant under any symmetry operation \mathcal{R} , since \mathcal{R} can only change the sign of Q_k or leave Q_k unchanged. i.e.,

$$\int^{-1} (H_{V_{k}}(Y_{k}^{\frac{1}{2}} Q_{k})) = \int^{-1} (1)$$

$$V_{k} = 0, 2, 4, ...$$
(3.30)

where \sqcap (1) denotes the totally symmetric representation.

If
$$V_k$$
 is an odd integer, $H_{V_k}(v_k^{\frac{1}{2}}Q_k)$ is an odd function of Q_k

since

$$H_{V_{k}}(\vartheta_{k}^{\frac{1}{2}}Q_{k}) = -H_{V_{k}}(-\vartheta_{k}^{\frac{1}{2}}Q_{k})$$
(3.31)
$$V_{k} = 1,3,5, \dots$$

Thus,

$$(H_{V_{k}}(\gamma_{k}^{\frac{1}{2}} Q_{k})) = \Gamma(Q_{k})$$

$$V_{k} = 1,3,5, \dots$$

$$(3.32)$$

since if Q_k changes sign under any symmetry operation \mathcal{R} , $H_{V_k}(\mathcal{Y}_k^{\frac{1}{2}}Q_k)$ also changes sign.

Substitution in equation (3.27) for $\prod_{k} (V_{k}^{\frac{1}{2}} Q_{k})$ given by equations (3.30) and (3.32) gives the representation generated by $\mathcal{W}_{V_{k}}$. i.e.,

$$\Gamma(\psi_{v_{k}}) = \begin{cases} \Gamma(1) & v_{k} = 0, 2, 4, \dots \\ \Gamma(q_{k}) & v_{k} = 1, 3, 5, \dots \end{cases}$$
(3.33)

SYMMETRY OF THE VIBRATIONAL GROUND STATE

The ground state wave function ${\mathscr V}_{\mathbb V}^0$ is obtained by substitution of

$$V_{1} = V_{2} = \dots = V_{3N-6} = 0 \text{ in equation (3.22). i.e.,}$$

$$V_{V}^{0} = \frac{3N-6}{77} V_{0}$$

$$k = 1 \qquad (3.34)$$

From equation (3.33)

$$\int (\psi_{0_k}) = \int (1)$$
 (3.35)

Thus the representation generated by the ground state wave function \mathcal{V}_0^0 is given by

$$/ (\psi_{V}^{0}) = / (1) (3.36)$$

V.SYMMETRY OF VIBRATIONAL EXCITED STATES:

The wave function corresponding to the excited level in which n

quanta of the l^{th} vibration are excited is given by

where $V_{\ell} = n_{\ell}$ and all other $V_k = 0$. Thus from equations (3.23) and

(3.33) the representation generated by $\mathcal{W}_{V}^{n_{\ell}}$ is

$$\left(\gamma_{V}^{n_{\ell}} \right) = \begin{cases} \gamma^{(1)} & V = n = 0, 2, 4, \dots \\ & (3.38) \\ \gamma^{(1)} & V = n = 1, 3, 5, \dots \end{cases}$$

If $V_{\ell} = n_{\ell} = 1$, equation (3.37) gives the representation of the fundamental level of the ℓ^{th} vibration.

If $V_k \ge 2$, equation (3.37) gives the representation of an overtone level of the l^{th} non-degenerate vibration.

An excited level in which V_{ℓ} quanta of the ℓ^{th} vibration and $V_{\rm m}$ quanta of the mth vibration are excited is called a combination level. The corresponding wave function $V_{\rm V}^{V_{\ell},V_{\rm m}}$, from equation (3.23), is given

where V_{ℓ} , $V_{\rm m} > 0$ and all other $V_{\rm k} = 0$. Thus, the representation of the combination level is

$$\Gamma \left(\psi_{\mathbf{V}}^{\mathbf{V}_{\ell},\mathbf{V}_{\mathbf{m}}} \right) = \Gamma \left(\psi_{\mathbf{V}_{\ell}} \right) \otimes \Gamma \left(\psi_{\mathbf{V}_{\mathbf{m}}} \right)$$
 (3.40)

or



$$V_{m} = 0, 2, 4, ...$$

$$V_{m} = 0, 2, 4, ...$$

$$V = 1, 3, 5, ...$$

$$V = 0, 2, 4, ...$$

$$V_{m} = 1, 3, 5, ...$$

$$V_{m} = 1, 3, 5, ...$$

VIBRATIONAL REPRESENTATION OF TRANS OXALYL HALIDE

C _{2h}	E	с ₂	$\widetilde{\mathcal{O}_{h}}$	i	nrc)	nr _x	nr _o ()	n ⁽⁾	n(8)	n(?)	$n_{\omega}^{(2)}$	$n_{z}^{()}$	n(3)
Ag	1	1	l	1	1	l	1	1	1	12	0	0	5
. ^A u	1	l	-1	-1	0	0	0	0	0	0	1	1	2
Bg	1	-1	-1	1	0	0	· 0	0	0	0	l	0	1
Bu	1	-1	l	-1	0	l	1	1	l	1ª	0	0	4
$\chi_{\rm R}^{\rm (r_c)}$	1	1	l	l			×.						
$\mathcal{V}_{R}(r_{x})$	2	0	2	0									
$\chi_{\rm R}^{\rm (r_o)}$	2	0	2	0			(8)	15	y (8	γ			
$\chi_{\rm R}^{(\alpha)}$	2	0	2	0			n s	BR	, e _R Λ_R	Λ _R (s)			
$\chi_{R}(\beta)$	2	0	2	0			Γ _v :	$= 5A_g + 1$	2A _u + B _g	+ 4 ^B u			
$\chi_{\rm R}(\vec{\lambda})$	2	0	2	0	÷.		а.	. REDU	NDANT CO	ORDINATE			
$\chi_{\rm R}^{(\omega)}$	2	0	-2	0									
$\chi_{R}(z)$	1	l	-1	-1								.*	8

TABLE	3.	10
	~ ~	

								the set which the de	a 66 had do be fait				
C _{2V}	E	C2	0~V(2	x) 07(y	z) n ^(l) _r	n(?) n _{r_x}	nro ⁽³⁾	ner (V)	ns(V)	ng(8)	n (d)	$n_{\overline{z}}^{(i)}$	n(?)
۸ ₁	1	1	1	1	l	<u> </u>	l	1	1	1 ^a	0	0	5
A2	1	1	-1	-1	0	0	0	0	0	0	1	l	2
Bl	1	-1	l	-1	0	0	0	0	0	0	1	0	1
B ₂	1	-1	-1	1	0	l	1	1	1	la	0	0	4
$\chi_{\rm R}^{\rm (r_c)}$	1	1	1	ı									
$\mathcal{V}_{R}^{(r_{x})}$	2	0	0	2			,),						
$\chi_{\rm R}^{\rm (r_o)}$	2	0	0	2			$n_{s}^{(\ell)} =$	$\frac{1}{g} \sum_{R}'$	$\mathbf{g}_{\mathrm{R}} \chi_{\mathrm{R}}^{(\mathrm{Y})}$	$\chi_{\rm R}^{\rm (s)}$			
X _R (~)	2	0	0	2			Γ _v =	5A ₁ + 2A	2 + ^B 1 +	4B2			
X _R (3)	2	0	0	2			а.,	REDUND	ANT COOR	DINATE			
$\chi_{\rm R}^{(\delta)}$	2	0	0	2									
$\chi_{\rm R}^{(\omega)}$	2	0	0	-2									
$\chi_{R}^{(Z)}$	1	1	1	-1									46

VIBRATIONAL REPRESENTATION FOR CIS OXALYL HALIDE

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VIBRATIONAL REPRESENTATION FOR OXALYL CHLORIDE FLUORIDE

Cs	Е	0 ^h	nrc ^(d)	n _r ())	n() n _{r_{C1}}	n(1) n _{ro}	$n_{\alpha}^{(\delta)}$	n ⁽³⁾	n(8) 13'	ng(b)	n (7)	n _w (2)	$n_{\tau}^{(2)}$	n(1)
۹۱	1	1	1	1	2	2	1	1	1	1	1	0	0	9
Au	1	-1	0	0	0	0	0	0	0	0	0	2	1	3
$\chi_{\rm R}^{\rm (r_c)}$	1	1					¢							
$\chi_{\rm R}^{(\rm r_F)}$	1	1												
$\chi_{\rm R}^{\rm (r_{\rm Cl})}$	1	1	۰.	9										
$\chi_{\rm R}^{\rm (r_o)}$	2	2					$n^{(\gamma)} = 1$	5.	x ch	2 (9)				
$\chi_{\rm R}^{(\alpha)}$	2	2					"s (R	R	^R ⁽³⁾				
$\chi_{R}(\beta)$	1	l					v = 9A	' + 3A"						
$\chi_{\rm R}^{(3)}$	1	1	,			ŝ	a	REDUNDAN	T COORDI	NATE				
$\chi_{\rm R}^{(\prime)}$	1	1												
$\chi_{\mathbf{R}}^{(\delta)}$	1	1												
χ _R (ω)	2	-2									,			
$\chi_{R}^{(T)}$	1	-1												

,

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VI.SELECTION RULES:

INFRARED SPECTRUM

The transition moment, \overline{M}_V , for a simple vibrational transition was given by equation (1.14). This equation can be broken down into expression for the three Cartesian components of \overline{M}_V , i.e.,

A transition is allowed in the infrared spectrum if at least one of the integrands of (3.42) is totally symmetric; thus, the condition for an allowed transition is given by

$$\int (\psi_{V}^{*}) \otimes \int (\psi_{V}^{*}) = \int (\Delta \mu_{g})$$

$$g = x_{s} y_{s} z$$

$$(3.43)$$

 $\Delta \mu_g$ transforms as a translation, $T_g(g = x,y, \text{ or } z)$, along one of the Cartesian axes. The irreducible representations generated by T_x , T_y , and T_z are given in TABLES 3.3, 3.4, and 3.5. The condition expressed by equation (3.43) can thus be given as

$$\Gamma(\gamma_{\rm VI}) \otimes \Gamma(\gamma_{\rm VII}) = \Gamma({\rm T}_{\rm g}) \tag{3.44}$$

g = x, y, z

For example, a transition will be allowed in the infrared spectrum of trans oxalyl fluoride if

$$\Gamma(\psi_{V^{\dagger}}) \otimes \Gamma(\psi_{V^{\dagger}}) = B_{u} \text{ or } A_{u}$$
(3.45)

RAMAN SPECTRUM

Selection rules for simple vibrational transitions observed in the Raman spectrum are derived from the polarizability tensor given by equation (1.18). The elements of this tensor are given by

$$(\alpha_{V})_{gg'} = \int \gamma_{V'}^{*} (\Delta \alpha)_{gg'} \gamma_{V'} d \tau_{V}$$
(3.46)

A transition is allowed in the Raman spectrum if at least one of the integrands of equation (3.46) is totally symmetric, i.e.,

$$\Gamma'(\psi_{V_1}) \otimes \Gamma(\psi_{V_1}) = \Gamma(ad_{gg_1}) \tag{3.47}$$

The representations to which the $\varDelta d_{gg}$, belong are given in TABLES 3.3, 3.4, and 3.5.

When normal incident light is used as exciting line, the scattered light may be partially polarized. Conversely, if polarized incident light is used, the scattered light may be partially depolarized. The depolarization factor for a Raman line is given by

$$\rho = \frac{6\beta^2}{45\alpha^2 + 7\beta^2}$$

where

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

and

 $\beta = \frac{1}{2}(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2)$ and the α_{gg} , (g,g' = x,y,z) are given by (3.46).

If $\int (\alpha_{gg'})$ is a non-totally symmetric irreducible representation, the depolarization factor $\rho = 6/7$ since in this case $\alpha_{xx} = \alpha = \alpha = 0$. If $\int (\alpha_{gg'})$ is totally symmetric irreducible representation, $\rho \leq 6/7$ since in this case α_{xx}, α_{yy} , and α_{zz} can all be non-zero.

The selection rules for oxalyl fluoride, oxalyl chloride, and oxalyl chloride fluoride are summarized in TABLE 3.13. The selection rules for the staggered form (point group C_2 for $(COX)_2$) were established from the correlation tables given by Wilson, Decius and Cross. The C_{2V} and C_{2h} point groups each have the C_2 point group as a subgroup. The irreducible representations of the three point groups are correlated as

follows:



Thus, the vibrational representation of the staggered $(COX)_2$ isomer is

$$r_{V} = 7a + 5b$$

Note that small letters have been used to designate the irreducible representations of the normal modes. Throughout the remainder of this thesis this convention will be followed. In addition, the irreducible representations of combinations and overtones will be denoted with capital letters.

MOLECULE	\int_{V}	ACTIVE	RAMAN POLARIZATION	INFRARED ACTIVE
Trans Oxalyl Fluoride	$5a + 2a + b + 4b_u$	ag	p	au
Trans Oxalyl Chloride		bg	dp	b _u
Cis Oxalyl Fluoride	521+ 222+ b1+ 4b2	a1 a2	p dp	ື່
Cis Oxalyl Chloride		b1 b2	dp dp	bl b2
Oxalyl Chloride Fluoride	9a' + 3a"	a " a "	p dp	2#
Staggered Oxalyl Fluoride and Oxalyl Chloride	7a + 5b	a b	q qb	a b
Staggered	Completely as	symmetri	c with no	

Staggered Oxalyl Chloride Fluoride

symmetry selection rules.

CHAPTER 4.

ANALYSIS OF THE INFRARED AND RAMAN SPECTRA

I.EXPERIMENTAL:

a) INFRARED SPECTRA:

The infrared spectra of the vapours of oxalyl fluoride, oxalyl chloride, and oxalyl chloride fluoride were recorded from 4000cm⁻¹ to 250cm⁻¹ on a Perkin-Elmer model 521 grating infrared spectrophotometer. The infrared spectrum of oxalyl fluoride was also recorded in the range 400 - 200cm⁻¹ on a Beckman IR9 infrared spectophotometer equipped with a cesium iodide prism. For spectra recorded on the Perkin-Elmer instrument, slit widths ranged from 195 microns at 4000cm⁻¹ to 1578 microns at 250cm⁻¹. The wave numbers of the bands were calibrated against the values for bands due to polyethylene film, atmospheric water vapour and atmospheric carbon dioxide.

Sets of lOcm. gas cells were equipped with NaCl, KBr and polyethylene windows. The NaCl and KBr windows were attached to the cells by means of zinc gaskets. Polyethylene windows were butted against the ends of the cells and held firmly in position by means of a specially constructed

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metal frame.

The vapour pressures used in the cells varied between 1mm. and 800mm. for oxalyl fluoride, 1mm. and 550mm. for oxalyl chloride fluoride, and 1mm. and 125mm. for oxalyl chloride.

Uncertainties in the measurements of the apparent band origins were estimated to be ± 5 cm⁻¹ for oxalyl fluoride, and $\pm 5 - 10$ cm⁻¹ for oxalyl chloride and oxalyl chloride fluoride.

b) RAMAN SPECTRA:

The Raman spectra of liquid oxalyl fluoride and liquid oxalyl chloride were recorded photographically using a Hilger E612 glass-prism spectrograph. This spectrograph has a linear dispersion of 23 Å/mm. in the vicinity of 4358 Å. The exciting line, Hg4358 Å, was produced by a vertically mounted Toronto - type mercury arc which had a striking potential of 250 V.D.C. and an operating current of 12 amperes.

The Raman cell was assembled as shown in FIGURE 4.1. A sample was distilled under vacuum into TUBE A which was then sealed off. A filter of saturated ammonium nitrite solution which was circulated through the jacket C, enabled the exciting line, Hg4358 Å, to be isolated from $^{\circ}$ Hg4046 Å and Hg4076 Å. The circulating filter solution was cooled externally by inserting in it a coiled metal tube through which cold water flowed. Additional cooling of the cell was obtained by blowing cold air through the annular space D; thus, the sample temperature was kept at room temperature (22°C.).

Spectra were recorded on Kodak IIa-O spectroscopic plates. Exposure times for ~ 5 ml. samples were $\sim 1 - 60$ min. for oxalyl fluoride and $\sim 1 - 10$ min. for oxalyl chloride.

Densitometer records of the photographic plates were obtained with a Leeds and Northrup microphotometer. A dispersion curve constructed to the same scale as the microphotometer records was obtained from spectra of mercury and iron arc lines. The wave numbers of the Raman bands were determined from their microphotometer records by interpolation, using the dispersion curve.

Depolarization ratios of the bands were obtained by the method of 27 Edsall and Wilson. Polaroid cylinders were slipped around TUBE B so that incident light was polarized either perpendicular or parallel to the axis of TUBE A. Exposures of equal duration for each direction of polarization were recorded adjacent to each other on the same photographic plate.

In order to make quantitative measurements of the depolarization ratios of the spectral bands, the photographic plates were calibrated for relative intensity, I, as a function of optical density. The slit of the spectrograph was illuminated directly with an ordinary 30 watt frosted light bulb. Exposures of the continuum for equal exposure times were recorded on a photographic plate for slit widths which were chosen in the ratio 1:2:4:8 . . . It was assumed that the intensity of the continuum emitted by the bulb was constant over the spectral region of interest (4358 - 4900 Å) and that the intensity was proportional to the slit width.

The continua on the photographic plates were microphotometered to give curves of optical density, $D(\mathcal{V})$ Vs. $\mathcal{V}(cm^{-1})$, (the wave number being obtained from the dispersion curve) for each slit width. The optical density, $D(\mathcal{V})$, of the emulsion, is given by

$$D(\mathcal{D}) = \log \frac{I_{m}}{I_{m}(\mathcal{D})}$$

where I_m^o and $I_m(p)$ are respectively the intensities of the light incident on the photographic plate and of the light transmitted by the photographic plate.

Curves of optical density, $\mathbb{D}(\mathcal{V}_R)$ Vs. log (I) (I \propto slit width) were constructed for each observed wave number (\mathcal{V}_R) of the Raman spectrum. The optical density of a Raman band with wave number \mathcal{V}_R was converted to intensity by interpolating log(I) from the curve and converting log (I) to relative intensity (I).

The depolarization ratio $\ensuremath{\rho_{\rm R}}$ of a band with wave number $\ensuremath{\mathcal{D}_{\rm R}}$ was calculated from

$$\mathcal{P}_{\mathrm{R}} = \frac{\mathrm{I}_{\mathrm{II}}}{\mathrm{II}_{\mathrm{II}}}$$

where I_{1} is the intensity of the band for incident light polarized perpendicular to the axis of TUBE A (FIGURE 4.2) and I,, is the intensity of the band for light polarized parallel to the axis of TUBE A.

As a check on the validity of the above method, it was used to measure depolarization ratios for the 459cm⁻¹ and 317cm⁻¹ bands of carbon tetrachloride. These results are compared with those of Koningstein and Bernstein (hereafter called KB) in TABLE 4.1.

TABLE 4.1

DEPOLARIZATION RATIOS OF SOME CC1, BANDS

\mathcal{D}_{R}	KB	PRESENT VALUE	THEORETICAL	
459	0.17	0.21	0	
317	1.14	1.096	0.86 (6/7)	

The values of $\rho_{\rm R}$ determined by the procedure described above are in reasonable agreement with KB's values but neither set of experimental values agrees with the theoretical values predicted in Chapter III. The reasons for this disagreement are described elsewhere. A band was considered to be depolarized if its experimentally determined depolarization ratio was greater than 0.86.

II.ROTATIONAL ISOMERISM:

In the following sections, the classical description of normal modes and frequencies of vibrations will often be used instead of the quantummechanical one for the sake of simplicity.

On the basis of the selections rules given in TABLE 3.13, the predicted spectra of the three possible isomers (trans, cis, and staggered)

of oxalyl chloride and oxalyl fluoride are different in the following respects:

(i) The trans isomer (point group C_2h) is centro-symmetric; therefore, vibrational modes which are active in the Raman spectrum (5a and b) are inactive in the infrared spectrum while modes active in the infrared (4b and 2a) are inactive in the Raman.

On the other hand, ten vibrational modes of the cis isomer $(5a_1, 4b_2, and b_1)$ are active in both spectra. The two a_2 modes, are active in the Raman, but not in the infrared.

All twelve modes of the staggered isomer (point group C_2) are active in both spectra.

(ii) Only one strong depolarized band is predicted in the Raman spectrum of the trans isomer (due to the b mode) while seven depolarized bands (2a₂, b₁, and 4b₂) are predicted for the cis isomer, and five depolarized bands (5b) are predicted for the staggered isomer. In the light of these differences, it should be possible to determine which isomer is most stable at room temperature from a qualitative consideration of the spectra. If the Raman spectrum has less than five depolarized bands, and there are fewer than ten Raman frequencies coincident with infrared frequencies, it can be assumed that the most stable isomer is the trans isomer. This assumption may be justified by subsequent complete assignment of all the spectral frequencies. On the other hand, if there are more than seven depolarized Raman bands and at least ten Raman frequencies which are coincident with infrared frequencies, the cis isomer can be assumed to be most stable.

On the basis of the above, it would be difficult in practice to distinguish between cis and staggered isomers because of the activity of combination bands. Likewise, a mixture of trans and staggered isomers would be very difficult to distinguish from a mixture of cis and trans isomers.

The LCAO (LINEAR COMBINATION OF ATOMIC ORBITALS) molecular orbitals (see FIGURE 6.1) show that π -bonding is possible across the carboncarbon bond in the planar isomers but not in the staggered isomer. As a result, the staggered isomer is expected to be much less stable than the planar isomers are predicted to be, and consideration of the staggered isomer can be safely dropped at this point.

Cis and trans oxalyl chloride fluoride belong to the same point group (C_s) and hence have the same symmetry selection rules. Spectra for these two isomers are therefore predicted to be qualitatively identical. III.ASSIGNMENT OF SPECTRAL FREQUENCIES TO MOLECULAR VIBRATIONAL MODES:

To a limited extent, spectral frequencies can be correlated with certain atomic groups or bonds in a molecule. For example, any molecule with a C = 0 bond gives rise to a band in the region $1600-1900 \text{ cm}^{-1}$, thus, even though the molecule as a whole is in motion, such a frequency is assigned to the carbonyl stretching mode. If a molecule has two carbonyl groups, two frequencies can appear in the carbonyl region. In addition, if the two carbonyl groups are related by symmetry, one frequency can be assigned to a symmetric carbonyl stretching mode and the other to an antisymmetric stretching mode. Symmetric modes are those for which the molecular symmetry is maintained during a vibrational cycle and antisymmetric modes are those for which vibration distorts or lowers the

In TABLE 4.2 the expected frequency regions for valence bond stretching motions of the oxalyl halides are given.

TABLE 4.2

SPECTRAL REGIONS FOR VALENCE STRETCHING MODES

BOND	SPECTRAL REGION (cm ⁻¹)
C==0	1700-1900 ^a
C-C	800-1200 ^b
C-F	1000-1400
C-Cl	600-800

- a. Spectral region shifted to higher frequency (cm⁻¹) due to OL-halogen substitution.
- b. Upper limit taken as C-C stretching frequency of glyoxal. Lower limit taken as C-C single bond frequency.

In general, frequencies are difficult to correlate with bending modes of individual angles particularly in planar molecules; thus, frequencies are assigned as in-plane, out-of-plane, and torsional bending modes of the whole molecule.

In the present case, frequencies of strong bands were first identified

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as fundamentals. Frequencies were assigned to valence stretching modes on the basis of their spectral regions. Bending frequencies were assigned by comparison with the bending frequencies of similar molecules (carbonyl fluoride, carbonyl chloride fluoride, etc.) whose normal coordinates were known.

Assignments of infrared frequencies can be simplified if the contours of the bands in the vapour spectrum are resolved. For a given asymmetric top molecule, three types of band contour are possible. These are called A, B, and C types according to whether the transition moment is parallel to the a, b, or c inertial axes respectively where

$$I_a < I_b < I_c$$
 (4.1)

The principal moments of inertia, I_a , I_b , and I_c are the roots of the 30 secular determanant

where the x, y, and z axes (fixed in the molecule) are chosen arbitrarily and I_{xx} , I_{yy} , I_{zz} , I_{xy} , I_{xz} , and I_{yz} are given by equations of the form

63.

$$I_{xx} = \sum_{i}^{l} m_{i} (y_{i}^{2} + z_{i}^{2})$$

$$(4.3)$$

$$I_{xy} = \sum_{i} m_{i} x_{i} y_{i}$$
(4.4)

Band contours due to unresolved rotational structure are estimated from the band contours calculated by Badger and Zumwalt using the calculated values of I_a , I_b , and I_c .

In the planar molecules studied here, the C-axis is directed normal to the plane. An out-of-plane vibration for which the dipole moment change (transition moment) is parallel to the C-axis gives rise to a C-type band. In-plane transition moments can have components along both A and B axes and hence hybrid AB-type bands are possible.

In the Raman spectrum of the liquid, band contours are not resolved; however, the band depolarization ratios $\rho_{\rm R}$ indicate whether the corresponding molecular vibration is symmetric or antisymmetric. Symmetric modes give rise to polarized bands ($\rho_{\rm R} \leq 0.86$) while antisymmetric modes give rise to depolarized bands ($\rho_{\rm R} > 0.86$). In the special case of the trans isomer of (COX)₂ there is only one depolarized band which is due to a symmetric out-of-plane bending mode.

In the spectral analyses which follow, the frequencies assigned to

the normal modes are numbered according to the following convention:

- (i) The assigned frequencies are grouped together according to the irreducible representations of the normal modes.
- (ii) The frequencies within each group are arranged in descending order of magnitude.
- (iii) The frequency groups are arranged in the order in which the corresponding irreducible representations are listed in the point group character table (TABLES 3.3, 3.4, 3.5).
- (iv) Beginning with the frequencies assigned to the totally symmetric modes, the frequencies are numbered

$$\mathcal{V}_1, \mathcal{V}_2, \mathcal{V}_3, \dots$$
 etc.

For example, the vibrational representation of trans oxalyl fluoride is

$$\Gamma_{\rm V} = 5a_{\rm g} + 2a_{\rm u} + b_{\rm g} + 4b_{\rm u}$$

The frequency numbering is as follows:

The irreducible representation is placed in brackets after the

frequency assignment, eg. $\mathcal{V}_{10}(b_u)$, $\mathcal{V}_{1}(a_g)$, etc. In addition, it is convenient to use the frequency assignments $\mathcal{V}_{1}(a_g)$, etc. to identify also the normal modes of vibration themselves.

IV.VIBRATIONAL ANALYSIS OF OXALYL FLUORIDE:

The infrared spectrum of oxalyl fluoride vapour is given in FIGURE 4.2. The Raman spectrum of the liquid is given in FIGURE 4.3. The frequencies (cm^{-1}) , depolarization ratios and assignments are given in TABLE 4.3.

The Raman spectrum has only one depolarized band (420cm⁻¹), and it was assumed that a satisfactory vibrational analysis could be obtained on the basis of the trans isomer alone. Furthermore, no satisfactory analytical scheme could be found which assumed that either pure cis isomer or a mixture of cis and trans isomers was present.

In the infrared spectrum, the contours of several bands are resolved. On the basis of an assumed geometry (CHAPTER 5, TABLE 5.3) the band contours were calculated for trans oxalyl fluoride at 300°K. The calculated band contours are given in FIGURE 4.4. The central branch of a band is called the Q branch. The other two branches are called the P (low frequency side) and R (high frequency side) branches. The different







66a.



RAMAN SPECTRUM OF OXALYL FLUORIDE



66b.

FIGURE 4.4

BAND CONTOURS FOR OXALYL FLUORIDE





separation $\Delta \mathcal{V}_{PR}^{(cm^{-1})}$ of the P and R branch maximum was considered to be the main distinguishing feature between the A and C-type bands. For an A-type band, $\Delta \mathcal{V}_{PR} = \sim 15 \text{ cm}^{-1}$, while for a C-type band $\Delta \mathcal{V}_{PR} = \sim 10 \text{ cm}^{-1}$. Identification of the band types was complicated by the possibility of hybrid bands with both A and B character; however, the $\Delta \mathcal{V}_{PR}$ value did provide a guide to identification.

Bands with the contour of the 1870cm^{-1} band (which has no Q branch) were identified as B-type bands. The 1098cm^{-1} and 1269cm^{-1} were both taken to be AB-type hybrid bands. Identification of the band type of the 672cm^{-1} band was difficult because of its intense Q branch; nevertheless, since $\Delta \mathcal{V}_{PR}$ was approximately 15cm^{-1} , this band was taken as an A-type band. It should be noted that in TABLE 4.3, 672cm^{-1} is assigned to an in-plane fundamental coincident with an out-of-plane combination frequency. This accounts for the complexity of the band. No C-type bands were resolved well enough for any positive identifications of them to be made from their contours.

Vibrational analysis began with a consideration of the Raman spectrum. The 420cm⁻¹ band is the only strong depolarized spectral band, and was

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assigned to the symmetric out-of-plane bending mode $\mathcal{V}_{8}(b_{g})$. The five strongest polarized bands are at frequencies 1872cm⁻¹, 1286cm⁻¹, 809cm⁻¹, 565cm⁻¹, and 292cm⁻¹. Frequencies were assigned to stretching modes on the basis of the spectral ranges given for bond frequencies in TABLE 4.2; thus, 1872cm⁻¹ was assigned to the symmetric carbonyl stretching mode $\mathcal{D}_{1}(a_{g})$, 1286cm⁻¹ was assigned to the C-F symmetric stretching mode $\mathcal{D}_{2}(a_{g})$, and 809cm⁻¹ was assigned to the C-C stretching mode $\mathcal{V}_{3}(a_{g})$. The frequencies 565cm⁻¹ and 292cm⁻¹ were tentatively assigned to the symmetric in-plane bending modes $\mathcal{V}_{\underline{\lambda}}(\underline{a}_{\underline{R}})$ and $\mathcal{V}_{\underline{5}}(\underline{a}_{\underline{R}})$ on the basis of their intensities. The strongest bands in the infrared spectrum are located at 1870cm⁻¹, 1269cm⁻¹, 1098cm⁻¹, 798cm⁻¹, 672cm⁻¹, 408-438cm⁻¹, and 255cm⁻¹. Stretching frequencies were assigned according to the bond frequency ranges given in TABLE 4.2; thus, 1870cm⁻¹ was assigned to the antisymmetric carbonyl stretching mode $\mathcal{V}_{0}(b_{u})$ and 1098 cm^{-1} was assigned to the antisymmetric C-F stretching mode $\mathcal{V}_{10}(b_u)$. The alternative assignment of 1269cm⁻¹ as $\mathcal{V}_{10}(b_u)$, would leave the very intense spectral band (1098cm⁻¹) to

be explained as a combination band. Since combination bands are, in general, expected to be weak, this alternative assignment was not considered

to be justified.

The antisymmetric modes should give rise to bands in the same general spectral regions as the corresponding symmetric bending modes. On this basis 1269cm⁻¹ and 798cm⁻¹ were dropped from consideration as fundamental.

The modes $\mathcal{V}_{11}(\mathbf{b}_{u})$, $\mathcal{V}_{12}(\mathbf{b}_{u})$, $\mathcal{V}_{6}(\mathbf{a}_{u})$, and $\mathcal{V}_{7}(\mathbf{a}_{u})$ remained to be assigned at this point. Brand and Williamson have assigned a frequency 134cm⁻¹ to the torsional mode $\mathcal{V}_{7}(\mathbf{a}_{u})$ of glyoxal; thus, it was expected that the torsional mode $\mathcal{V}_{7}(\mathbf{a}_{u})$ of oxalyl fluoride would have a frequency in the same general region, which was not accessible to either of the infrared spectrophotometers used in the investigation. It was, therefore, assumed that $\mathcal{V}_{11}(\mathbf{b}_{u})$, $\mathcal{V}_{12}(\mathbf{b}_{u})$, and $\mathcal{V}_{6}(\mathbf{a}_{u})$ could be chosen from the strong bands at $672 \mathrm{cm}^{-1}$, $406-438 \mathrm{cm}^{-1}$, and $255 \mathrm{cm}^{-1}$.

The lowest in-plane skeletal mode of biacetyl has been assigned a frequency of 257cm⁻¹ by Noack and Jones. It seemed, therefore, reasonable to assign 255cm⁻¹ to the in-plane bending mode $\mathcal{V}_{12}^{\prime}(b_{u})$.

The 406-438cm⁻¹ band(s) appear(s) as two sharp spikes of about equal intensities at 406cm⁻¹ and 438cm⁻¹.

Since the 406cm⁻¹ and 438cm⁻¹ bands appeared with equal intensities, they were considered as a possible Fermi resonance doublet. As shown in Chapter 3, Fermi resonance occurs when a combination (or overtone) level and a fundamental level with wave functions of the same symmetry occur at the same energy in zeroth order approximation (Simple Harmonic Oscillator Approximation). The only possible combination which can occur in the 406-438cm⁻¹ region is $292cm^{-1}$ (Raman $\mathcal{V}_{5}(a_{g})$) + 114-146cm⁻¹ (infrared). Since the mode $\mathcal{V}_{7}(a_{u})$ (the torsional mode) was expected in the region 114-146cm⁻¹, the symmetry of this combination was taken as $\mathbf{A}_{_{\mathcal{G}}} \otimes \mathbf{A}_{_{\mathbf{U}}} \to \mathbf{A}_{_{\mathbf{U}}}; \text{ thus, only a fundamental of } \mathbf{A}_{_{\mathbf{U}}} \text{ symmetry could be involved}$ in the Fermi resonance. On the basis of the foregoing argument, 422cm⁻¹ $(\frac{438-406}{2} + 406)$ cm⁻¹ was assigned to the out-of-plane antisymmetric bending mode $\mathcal{V}_{6}(a_{u})$. It is noted that the corresponding symmetric bending mode $\mathcal{V}_{g}(b_{g})$ was assigned a frequency 420cm⁻¹.

The unassigned frequencies of both infrared and Raman spectra were assigned as combination or overtone frequencies in a straightforward manner. It is noted that only antisymmetric (A_u or B_u) combinations are active only in the infrared spectrum while either A_g or B_g combinations are active only in the Raman spectrum. Overtones are active only in the Raman spectrum.

The combination and overtone frequencies were assigned by comparison with the frequencies calculated from combination of assigned fundamental frequencies. In general, the agreement between observed and calculated values was very good; however, the 1269cm⁻¹ infrared frequency proved difficult to assign.

The 1269cm⁻¹ band appears with appreciable intensity in the infrared spectrum and yet 1269cm⁻¹ must be assigned as a combination frequency. (As pointed out previously, 1269cm⁻¹ can be assigned neither to $\mathcal{V}_{10}(b_u)$ nor to an antisymmetric bending mode.) The nearest calculated combination frequency is $565(\mathcal{V}_4(a_g)) + 672(\mathcal{V}_{11}(b_u)) = 1247$ cm⁻¹ which is not in good agreement with the observed frequency. Furthermore, if 1269cm⁻¹ is a combination, the high intensity of the band must be explained. The only apparent conclusion which can be drawn is that the combination

 $\mathcal{V}_{4}(a_{g}) + \mathcal{V}_{11}(b_{u})$ (1247cm⁻¹) is involved in a resonance-type interaction with the fundamental $\mathcal{V}_{10}(b_{u})$. This would mean that 1098cm⁻¹ was not the zeroth order frequency (simple harmonic oscillator value) of $\mathcal{V}_{10}(b_{u})$, and that the true zeroth order value is somewhat higher. Since no other assignment seemed to be possible, 1269cm^{-1} was assigned to the combination $\mathcal{V}_4(a_g) + \mathcal{V}_{11}(b_u)$.

The 1745cm⁻¹ band was assigned to the difference combination $\mathcal{V}_1(a_g) - \mathcal{V}_7(a_u)$ for which the transition originates in the thermally populated torsional fundamental energy level. The calculated value of $\mathcal{V}_7(a_u)$ was 1872-1745 = 127cm⁻¹. This frequency was confirmed by the assignment of the Raman frequency 262cm⁻¹ to the overtone $2\mathcal{V}_7(a_u) =$ 254cm⁻¹ and the infrared active combination $\mathcal{V}_5(a_g) + \mathcal{V}_7(a_u) = 292 +$ 127 = 419cm⁻¹ which was involved in the Fermi resonance.

In general, the assignments of the infrared and Raman active fundamentals were well confirmed by the overtone and combination analysis. The assumption of the trans isomer alone as a model appears to be justified.

The assignments of the fundamentals were checked by carrying out a normal coordinate analysis which further supported the above assignment (see Chapter 5). In addition, from the calculated normal coordinates and potential energy distribution (Chapter 5) a more detailed picture of the vibrational modes was obtained.

TABLE 4.3

OBSERVED FREQUENCIES AND ASSIGNMENTS FOR OXALYL FLUORIDE

INFR	ARED (vapour	•)	RAM	AN (liquid)		CALCULATED	ASSIGNMENT	SYMMETRY
(cm ⁻¹)	Intensity	Band Typo	(cm ⁻¹)	Relative Intensity	Polari- zation	Freq. (cm ⁻¹)		
129						129	\mathcal{V}_{η}	8.
255	mw					255 ^C	212	b,
	*		292	6	р	292 ^C	$\overline{\mathcal{V}_5}$	e,
408 438	\mathbf{W}^{l_A}	C?				422 ^d	F.R. 726 + 77	au; Au
			420	16	dp	-	28	bg
502	mw	В				547	$v_5 + v_{12}$	B
540	mw	A?				549	$v_7 + v_8$	Bu
672	S	A? 0 ?	565 br.	3	p	565 ⁰ 672 ⁰	v_{11} v_{11} ; v_{8} + v_{12}	ag bu; Au
			627	W	р			Ag ·
500		5	121	Ψ.	p	1.00	COF.COC1 impurity	, O
798	ms	В	809	38	р	820 810 ^C	$\overline{\nu}_4 + \overline{\nu}_{12}$ $\overline{\nu}_3$	Bu ag
820 sh.	m					841	$v_{6} + v_{8}$	Au
			831 sh.	W	р	840	228	Ag
			1095	W	р	1101	23+25	Ag
1098	WS	AB				1098	7 ² 10	bu
1210	m					1231	$v_3 + v_6$	Au
1269	S	AB	1226	VW	?	1229 1237	$v_3 + v_8$ $v_1 + v_2$	B B
							4	u

73.

TABLE 4.3 - CONTINUED

			1286	5	p	1283	V2	a
1470	VVW					1481	V3 + 211	B
1510	VW					1518	$v_8 + v_{10}$	A
1599	VW	В			a.	1608	$v_{10} + 2v_{12}$	B
			1604	VVW	p?	1618	22/3	A
1685	VW					1708	V2+V6	A
1745	VW					127	Vi -Vy	A
			1787		р		COF.COCL impurity	4
1870	VVS	В				1857	Vg	b
		κ, s.	1872	100	р	1884	Vi	ຂັ
1896	ms					1907	$v_{3} + v_{10}$	B
2078	VW					2127	V1 + V12	B
2148	W					2162	25+29	B
2370	W					2384	$v_{2} + v_{10}$	B
2470	VVW					2472	$v_{3}^{2} + v_{1}^{2} + v_{10}^{2}$	B
2523	VW					2544	$\mathcal{V}_1 + \mathcal{V}_{11}$	B
2671	VVW					2679	23+29	B
2971	VW					2970	$v_{1} + v_{10}$	B
3070	VW					3099	$\mathcal{V}_3 + \mathcal{V}_8 + \mathcal{V}_9$	A
3130	VW					3156	$\mathcal{D}_2 + \mathcal{D}_9$	B
3634	VVW					3670	22/2 +2/10	Bu
3718	mw	В				3742	2,+20	B
3766	VW					3779	2+23+210	B,
4140+	VW					4162	$\overline{\mathcal{V}}_1 + \overline{\mathcal{V}}_8 + \overline{\mathcal{V}}_9$	A

4

74.

4224 WW

4256 $V_1 + V_2 + V_{10}$ Bu

+ - Obtained with Perkin-Elmer model 21 Infrared Spectrophotometer equipped with CaF2 optics.

SYMBOLS:

- sh. shoulder band
- vvs very, very strong
- vs very strong
- s strong
- m medium
- w weak
- vw very weak
- vvw very, very weak
- br. broad
 - p polarized
- dp depolarized
- F.R. Fermi resonance
 - C calculated in normal coordinate analysis
 - d mean of the Fermi resonance doublet 406 438cm⁻¹.

V.VIBRATIONAL ANALYSIS OF OXALYL CHLORIDE:

The infrared spectrum of oxalyl chloride vapour and the Raman spectrum of the liquid are given in FIGURES 4.5 and 4.6. In TABLE 4.4 the infrared frequencies obtained here for the vapour are listed together with the frequencies reported by Saksena and Kagarise for the vapour and with 12those obtained by Ziomek et al. for the liquid.

The present infrared results for the vapour are in general agreement with those of Saksena and Kagarise with the exception of the following:

- (i) The doublet frequencies 980-988cm⁻¹ and 1060-1077cm⁻¹
 observed by Saksena and Kagarise (hereafter referred to as SK) were observed here as the single frequencies 975cm⁻¹
 and 1058cm⁻¹.
- (ii) The frequencies 1262cm⁻¹, 1970cm⁻¹, 2060cm⁻¹, 2100cm⁻¹, and 2160cm⁻¹ had been previously observed by SK only when the sample was at 150°C. These frequencies were observed here with the sample at room temperature.
- (iii) Several new vapour frequencies were observed here which had not been reported by SK but which agreed well with the



INFRARED SPECTRUM OF OXALYL CHLORIDE



76a.







liquid frequencies obtained by Ziomek et al.(hereafter called ZMCD).

(iv) The band observed by SK at 2855cm⁻¹ was identified here as an impurity band due to HCl on the basis of its rotational structure. When the sample was carefully degassed before use, this band was not observed except at high vapour pressure. (Degassing was effected by repeated vaporization and condensation of the sample. Non-condensible material

was pumped off before each successive vaporization.)

¹² The infrared spectrum of the liquid observed by ZMCD shows evidence of molecular association. The vapour bands at 778cm⁻¹ and 725cm⁻¹ appear in the liquid spectrum as a very broad band whose intensity maximum is located at 752cm⁻¹, and the vapour bands at 3560cm⁻¹ and 3635cm⁻¹ are observed as a single band at 3740cm⁻¹ in the liquid spectrum (according to ZMCD's results for the liquid). The 1058cm⁻¹ band in the liquid spectrum appears with somewhat greater intensity relative to the 1752cm⁻¹ band than does the 1058cm⁻¹ band relative to the 1790cm⁻¹ band in the vapour spectrum. The vapour bands at 1790cm⁻¹ and 1862cm⁻¹ are shifted to

77.

TABLE 4.4

COMPARISON	OF	OBSERVED	INFRARED	FREQUENCIES	
		(cm	-1)		

VAPO	DUR		LIQUID
ll SK	PRESENT		2MCD ¹²
	360		
	486		488
	520		532
	593		594
	668		-
724	725		-
777	778		_ 752
795	798		-
-	938		942ª
980 988	975		986
1060 1077	1058		1058
1262 ^b	1265		-
	1407		1388
	1580		_
1790	1790		1754
1852	1862		1826
1970 ^b	1984		1964 ^a
2060 ^b	2065		
2100 ^b	2115		
2160 ^b	2160		
	2270	20	
2530	2565		2510
2855°	-		2830
	3560		371.0
	3635		-
			5140

a - bands observed by SK
b - bands observed with sample at 150°C. by SK
c - band due to HCL

1754cm⁻¹ and 1826cm⁻¹ respectively in the liquid spectrum.

In TABLE 4.5 the Raman frequencies and relative intensities obtained by SK, ZMCD, and those obtained here are presented for comparison. The present results do not agree with those of SK in that (i) the 175-201. doublet observed by SK was observed here as a single broad band with maximum at 174cm⁻¹ and (ii) the 465cm⁻¹ band observed by SK appeared as the doublet 452-462cm⁻¹ here. (On this point, the present results also disagree with those of ZMCD who observed a triplet, 443-465-483cm⁻¹.) The relative intensities obtained here disagree significantly with those of both SK and ZMCD. (In particular, refer to the relative intensities of the 619cm⁻¹ and 1778cm⁻¹ bands given in TABLE 4.6.) A shoulder band was observed here on the low frequency side of the 1078cm⁻¹ band. This shoulder band was not reported by either ZMCD or SK.

The disagreement about the relative intensities of the Raman bands cited above is difficult to explain. The photographic plates used here were calibrated for spectral sensitivity by the procedure outlined in section I of this chapter. The plate sensitivity was found to vary little over the region (\sim 4358-4900 Å) where Raman bands were observed. Further-

79.

TABLE 4.5

			(cm ⁻¹)		
S	11 K	Z	MCD ¹²	PRE	SENT
	I		I		I
175	12	193	5	174	lOvb
201	8	-	-	-	-
276	396	261 279	33	274	41
350	6	354	3	349	7
400	0	-	-	_	-
465	50vb	443 465 483	28 30	452 462	14
519	8	522	7	-	-
533	20	533	12	529	25
619	92	620	100	618	95
672 ^a	-	-	-		-
707	2	709	l	703	4
809	lvb	802	VW	792	2vb
****		4005	-	sh.	-
1078	14	1081	5	1077	22
1230	0			-	
1417	1.	1416	VW	1412	2
1530	0	-		-	-
1778	67		57	1779	100

OBSERVED RAMAN FREQUENCIES AND RELATIVE INTENSITIES

SYMBOLS:

b - broad

vb - very broad

vw - very weak sh - shoulder band

a - observed by Kohlrausch and Wittek

I - relative intensity (In general, the most intense spectral band is assigned a relative intensity of 100. Other band intensities are taken relative to this. SK have simply used a variation of the above method.)

more, spectra recorded on different plates, with a variety of exposures, gave the same relative intensities. In all exposures the sample temperature was kept at approximately 22°C. Neither SK nor ZMCD reported the sample temperatures at which their Raman intensities were measured. The photographically obtained results of ZMCD are, however, in good agreement with the photoelectric results of SK. In view of the temperature dependence of the band intensities in the Raman spectrum (see Chapter 1) the disagreement between the relative intensities obtained here and those reported by the other workers was not considered to be serious.

The Raman instruments used by SK appear to have better dispersion and resolution than any of the instruments used by other workers (including the present ones). SK resolved the band at 174cm⁻¹, observed in the present work, into a doublet 175cm⁻¹-201cm⁻¹, whereas they did not report the 452-462cm⁻¹ doublet observed here. In view of SK's apparently better measurements, their Raman frequencies were used in the present vibrational analysis.

V.a.ROTATIONAL ISOMERISM:

In order to discuss the rotational isomerism of oxalyl chloride a

diagram (schematic) of the potential energy as a function of the torsional angle, θ , is given in FIGURE 4.7 in which it is assumed that the trans form is most stable.





(V_o,V_o-zero point energy levels of cis and trans isomers respectively) ll SK concluded from the temperature dependence of the band intensities in

the Raman spectrum that cis and trans isomers were both responsible for the Raman spectral bands. They assigned the 533 cm^{-1} band to the symmetric C-Cl stretching mode of this cis isomer and the 619 cm^{-1} band to the symmetric C-Cl stretching mode of the trans isomer. They measured the ratio of the relative intensity of the 533 cm^{-1} band (I_{533}) to that of the 619 cm^{-1} band (I_{619}) at -10° C. and 85° C. This ratio, R(T), may be compactly written as

$$R(T) = \frac{I_{533}(T)}{I_{619}(T)}$$

where T is the temperature ($^{\circ}$ K). Using the Bernstein formula (equation 1.20), SK obtained the enthalpy difference between cis and trans isomers as \triangle H = 2.8 Kcal/mol.

The conclusions drawn by SK from the temperature dependence of the Raman band intensities are open to the following criticism:

- (i) Bernstein has recommended that liquid spectra should not be used in the determination of AH since the temperature dependence of spectral band intensities of liquid spectra could be affected by association in the liquid.
- (ii) The calculation of \triangle H by SK was based on measurement of $R(T) = I_{533}/I_{619}$ at only two temperatures (-10°C and +85°C). In a proper application of equation 1.20 the intensity ratio, R(T), should have been measured at several temperatures and a plot of log R(T) Vs. 1/RT should have been made. Linearity of this curve would then indicate genuine rotational isomerism.

(iii) The fraction of cis isomer present in a given sample at

room temperature can be calculated from

$$\frac{N_{cis}}{N_{cis} + N_{trans}} = \exp - \frac{\Delta H}{RT} = \exp - \frac{\Delta H(cm^{-1})}{kT(cm^{-1})}$$

Assuming that $\triangle H = 2.8$ Kcal (980cm⁻¹), as measured by SK, and kT = 208cm⁻¹ (k = Boltzman's constant, R = ideal gas constant), the calculated fraction of cis isomer in a given sample at room temperature is ~ 0.007 (or 0.7%).

The relative intensities of the 533 cm⁻¹ and 619 cm⁻¹ Raman bands given by SK are 20 and 92 respectively; thus, if of it is assumed that these measurements were made at room temperature, the ratio $R(T_{i})$ (T = room temperature) is

emperature, the ratio
$$H(T)$$
 (T = room temperature) 1

$$R(T_r) = \frac{I_{533}(T_r)}{I_{619}(T_r)} = \frac{20}{92} \quad 0.2 \text{ or } 20\%$$

Since at room temperature less than 1% (0.7%) of the sample is cis isomer, it follows from $R(T_r) = \sim 20\%$ that the intrinsic intensity of the 533cm⁻¹ band (assigned to cis isomer by SK) would be at least twenty times the intrinsic intensity of the 619cm⁻¹ band (assigned to trans isomer
by SK) for equal quantities of cis and trans isomers. Such a difference in intrinsic intensities is highly unlikely since the C-Cl bond polarizabilities (which substantially determine the band intensities) for cis and trans isomers could hardly be expected to differ by a factor of twenty; thus, assumption of SK's value of ΔH leads to an unreasonable conclusion about the intrinsic Raman band intensities.
(iv) There are only three depolarized bands in the Raman spectrum (201cm⁻¹, 350cm⁻¹, and 809cm⁻¹). If both cis and trans isomers were present, at least eight depolarized bands are expected to be observed. (b_g(trans); 2a₂ +4b₂ +b₁(cis))

(v) Although SK observed a marked temperature dependence of the Raman band intensities, they apparently did not observe any significant temperature dependence of infrared bands in the vapour spectrum over the temperature range 22°C-150°C.
(vi) SK assigned the infrared vapour frequencies 520cm⁻¹, 798cm⁻¹, and 1058cm⁻¹ to the cis isomer. All these frequencies were observed by them in the spectrum of the liquid at

room temperature but bands at 520cm⁻¹ and 1058cm⁻¹ were 13 not observed by Kagarise in the spectrum of the solid at -78°C. Kagarise assumed that the solid consisted entirely of trans isomer. Since the 520cm⁻¹ and 1058cm⁻¹ bands were absent in the solid spectrum, they were assigned to the cis isomer; however, the 798cm⁻¹ band is present in the solid spectrum (\sim 815cm⁻¹) and cannot be assigned to the cis isomer. Other bands present in the solid spectrum in the spectral region (600-800 cm⁻¹) are at \sim 700 cm⁻¹, ~750cm⁻¹, and 790cm⁻¹. These bands should correspond to the vapour bands at 668cm⁻¹, 725cm⁻¹, and 778cm⁻¹ respectively: so none of these frequencies provides a reasonable alternative assignment of the cis fundamental expected in this region (C-Cl antisymmetric stretching mode, (b_2)).

At the very least, comparison of the liquid and solid spectra neither supports nor disproves the existence of cis isomer at room temperature. (vii) In the infrared spectrum of the cis isomer, the intensity

of the band due to the C-C stretching mode would be expected to be weak relative to the bands due to the C-Cl and C=O stretching modes. The pure C-C stretching motion i.e.



(the vectors indicate displacements of the carbon atoms) involves no change in dipole moment. In the observed infrared spectrum the 1058cm^{-1} band (assigned to the C-C stretching mode of the cis isomer by SK) appears with much greater intensity than the 520cm^{-1} band (assigned to the symmetric (a₁) C-Cl stretching mode of the cis isomer by Kagarise); thus, assignment of 1058cm^{-1} to the C-C stretching mode by SK is apparently not justified.

The above arguments strongly suggest that the temperature dependence of the spectral band intensities cannot be explained on the basis of rotational isomerism. As is the case with oxalyl fluoride, biacetyl and glyoxal, it should therefore be expected that a satisfactory vibrational analysis can be obtained on the basis of the trans isomer alone.

V.b.FREQUENCY ASSIGNMENTS FOR OXALYL CHLORIDE:

The assignments of the infrared and Raman frequencies of oxalyl chloride are given in TABLE 4.6.

Vibrational analysis began with a consideration of the Raman spectrum. The five strongest polarized bands have frequencies 1778cm⁻¹, 1078cm⁻¹, 619cm⁻¹, 465cm⁻¹, and 276cm⁻¹. Frequencies were assigned to the stretching modes on the basis of the spectral regions given in TABLE 4.2; thus, 1778cm⁻¹ was assigned to the symmetric carbonyl stretching mode $\mathcal{V}_{1}(a_{\rho})$, 1078cm⁻¹ was assigned to the C-C stretching mode $\mathcal{V}_2(a_g)$ and 619cm⁻¹ was assigned to the symmetric C-Cl stretching mode $\mathcal{V}_3(a_g)$. 465cm⁻¹ and 276cm⁻¹ were tentatively assigned to in-place bending modes $\mathcal{V}_{\mu}(a_g)$ and $\mathcal{V}_{5}(a_{g})$ respectively on the basis of their relatively high intensities. Of the three depolarized bands at 809cm⁻¹, 350cm⁻¹, and 201cm⁻¹, the latter is the most intense and was assigned to the symmetric out-of-plane bending mode $\mathcal{V}_{g}(b_{p})$.

The strongest infrared bands are located at 1790cm⁻¹, 1058cm⁻¹, 778cm⁻¹, 520cm⁻¹, and 360cm⁻¹. 1790cm⁻¹ was assigned to the antisymmetric carbonyl stretching mode $\mathcal{V}_{9}(b_{u})$, and 778cm^{-1} was assigned to the antisymmetric C-Cl stretching mode $\mathcal{V}_{10}(bu)$.

The frequencies of the remaining four fundamental vibrational modes are expected to be in the same frequency range as the corresponding frequencies of symmetric bending modes i.e. below 600cm⁻¹. The band at 1058cm⁻¹ was not considered to be a fundamental frequency.

Two of the fundamental frequencies ($\mathcal{V}_{\gamma}(a_u)$ and $\mathcal{V}_{12}(b_u)$) are not expected to lie within the spectral region covered by the Perkin-Elmer 521 grating infrared spectrophotometer (4000-250cm⁻¹). As in the case of oxalyl fluoride, the torsional mode $\mathcal{V}_{\gamma}(a_u)$ of oxalyl chloride is expected to have a frequency of less than 150cm⁻¹. The corresponding torsional frequency is at 134cm⁻¹ in glyoxal. In addition, the $\mathcal{V}_{12}(b_u)$ of oxalyl chloride is expected to have a frequency lower than 255cm⁻¹ (the frequency assigned to $\mathcal{V}_{12}(b_u)$ of oxalyl fluoride) since heavier atoms in a molecule tend to lower the frequencies of the bending modes. $\mathcal{V}_6(a_u)$ and $\mathcal{V}_{11}(b_u)$ could be chosen from the frequencies 520cm⁻¹, 486cm⁻¹, and 360cm⁻¹.

In the case of oxalyl fluoride the frequency assigned to $\mathcal{V}_{11}(b_u)$

 (672 cm^{-1}) was higher than the frequency assigned to $\mathcal{V}_6(a_u)$ (422 cm⁻¹). This would indicate 520 cm⁻¹ as the antisymmetric in-plane bending mode $\mathcal{V}_{11}(b_u)$ of oxalyl chloride. 486 cm⁻¹ was not considered for this fundamental because the band at this wave number was somewhat weaker than the 520 cm⁻¹ band.

The antisymmetric out-of-plane bending mode $\mathcal{V}_{6}(a_{u})$ of oxalyl fluoride has been assigned a frequency of $422 \mathrm{cm}^{-1}$. Since the corresponding frequency for oxalyl chloride was expected to be lower (due to the heavier mass of the molecule) than $422 \mathrm{cm}^{-1}$, $360 \mathrm{cm}^{-1}$ was tentatively assigned to the antisymmetric out-of-plane bending mode, $\mathcal{V}_{6}(a_{u})$, of oxalyl chloride. The unobserved fundamental frequencies $\mathcal{V}_{11}(b_{u})$ and $\mathcal{V}_{7}(a_{u})$ were obtained by analysis of unassigned frequencies below $600 \mathrm{cm}^{-1}$. The infrared frequency $486 \mathrm{cm}^{-1}$ was taken to be a combination frequency which could be assigned as the sum of either of the Raman frequencies $20 \mathrm{cm}^{-1}$ or $276 \mathrm{cm}^{-1}$ and an unobserved infrared frequency. The calculated unobserved infrared frequencies in each case were

$$486 \text{ cm}^{-1} - 201 \text{ cm}^{-1} = 285 \text{ cm}^{-1}$$

 $486 \text{ cm}^{-1} - 276 \text{ cm}^{-1} = 210 \text{ cm}^{-1}$

and

The former calculated frequency 285cm^{-1} was not observed even though it lies within the spectral range covered by the spectrophotometer. It was not considered to give a correct assignment of 486cm^{-1} . On the other hand, 210cm^{-1} calculated in the latter case fell within the region where the antisymmetric in-plane bending fundamental was expected; and so, 210cm^{-1} was assigned to the antisymmetric in-plane bending mode $\mathcal{V}_{12}(b_u)$.

Before the assignment of a torsional frequency was made, a complete assignment of the remaining unassigned bands as overtones and combinations was attempted. It was found that the Raman frequencies 519cm^{-1} and 350cm^{-1} (depolarized band) could not be assigned. It was therefore assumed that these frequencies could be explained as combinations involving the torsional frequency.

519cm⁻¹ could be explained as the combination

 $360 \text{ cm}^{-1} (\mathcal{V}_6(a_u)) + 159 \text{ cm}^{-1} = 519 \text{ cm}^{-1}$

In addition, 350cm⁻¹ could then be assigned as the combination

$$210 \text{cm}^{-1} (\mathcal{V}_{12}(b_u)) + 159 \text{cm}^{-1} = 369 \text{cm}^{-1}$$

Hence, 159cm⁻¹ was provisionally assigned to the torsional mode $\mathcal{V}_{7}(a_{u})$.

With the exception of two extremely weak bands which are probably

TABLE 4.6

OBSERVED FREQUENCIES AND ASSIGNMENTS FOR OXALYL CHLORIDE

INFRARED (vapour)		RA	RAMAN ⁺ (liquid)			ASSIGNMENT	SYMMETRY
(cm ⁻¹)	Intensity	(cm ⁻¹)	Relative Intensity	Polari- zation	Freq. (cm ⁻¹)		
159 ^C						7 n	a
210 ^C			,			7/12	b,
		175	12	р	189	$\mathcal{V}_{1} = \mathcal{V}_{5}$	u
		201	8	dp	201	ν_8	b
	· · · ·	276	39b	р		\mathcal{V}_5	ີຂູ
		350	6	dp	369	$\mathcal{V}_{7} + \mathcal{V}_{12}$	B
360	ms					26	au
		400	0	р	402	27/8	Ag
		465	50vb	р		\mathcal{P}_{μ}	ag
486	m		•				
		51.9	8	р	519	26+27	Ag
520	ms					ν_{11}	bu
		533	20	р	552	225	Ag
593	W				636	$v_5 + v_6$	· A _u
		619	92	р		\overline{v}_3	ag
668	m				675	$v_4 + v_{12}$	Bu
		672	VW	?	679	$v_7 + v_{11}$	Bg
		707	2	р	720	226	Ag
725	W				721	28 + 211	A

92.

TABLE 4.6 - CONTINUED

778	VVS				778	210	b
		809	lvb	dp	820	23+28	B
938	VW				919	2 - 27	A
975	VW				979	マ3+26	A
1058					1056	2 5+2/10	B
		1050sh.	?	?b	1084	V3+24	A g
		1078	14	р		\mathcal{V}_2	ಷ್ಟಿ
		1230	0	?	1238	22/3	Ą
1265	VW				1288	V2 + V12	B
1407	VVW				1399	23+210	B
		1417	1	р		?	B
		1530	0	?	1543	ショ+シ,	A
1580	VW				1598	$\vec{v_2} + \vec{v_{11}}$	B
		1778	67	р		2 T	a,
1790	VVS		*			z,	ູ
1862	ms				1869	22+2/10	B
1984	W				1990	V1 + V12	B
2065	VW				2070	V5 + 20	B
2115	VW				2138	21+26	A
2160	VW					?	u
2270	Vы				2300	$\mathcal{V}_1 + \mathcal{V}_{11}$	B,
2565	VW				2560	2 + 210	B
0							

93.

TABLE 4.6 - CONTINUED

2560	W	$3570 \nu_1 + \nu_9$	B
3635	WW	$3634 \nu_1 + \nu_2 + \nu_{10}$	B
5140 ^a	-	5370 329	Bu

a - values taken from the liquid spectrum (see TABLE 4.3)

b - low frequency shoulder on 1078cm⁻¹ band observed in our Raman spectrum

+ - Raman frequencies, relative intensities, and polarizations observed by SK

C - calculated in normal coordinate analysis

SYMBOLS:

- vvs very, very strong
 - ms medium strong
 - w weak
 - vw very weak
 - vvw very, very weak
 - m medium
 - vb very broad

due to ternary combinations, all spectral bands are explained by this analysis. As in the case of oxalyl fluoride the assignments of the inplane fundamentals were checked by carrying out a normal coordinate analysis (Chapter 5).

VI.VIBRATIONAL ANALYSIS OF OXALYL CHLORIDE FLUORIDE:

The infrared spectrum of oxalyl chloride fluoride vapour is given in FIGURE 4.8. The frequencies and assignments are given in TABLE 4.7.

Several of the band contours were resolved in the infrared spectrum. By analogy with the band contours of oxalyl fluoride, bands with contours like that of the 1858cm⁻¹ band were identified as B-type bands. No other contour types were resolved well enough to enable a positive identification. In general, however, any bands with sharp central "spikes" were taken as possible C-type bands.

Oxalyl chloride fluoride can be regarded as a simple combination of the Cl-CO group from oxalyl chloride and the F-CO group from oxalyl fluoride. Frequencies for oxalyl chloride fluoride were calculated as the arithmetic means of the corresponding assigned a_g , a_u , b_g , and b_u frequencies of the "parent" molecules. This calculation is given in

FIGURE 4.8 INFRARED SPECTRUM OF OXALYL CHLORIDE FLUORIDE



95a.

TABLE 4.8

EXPECTED FREQUENCIES FOR OXALYL CHLORIDE FLUORIDE

	(COCL) ₂ Observed	ARIT	COF.COCL HMETIC MEAN	(COF) ₂ OBSERVED
a.,	1778	21	1825	1872
0	1078		1182	1286
	619		714	809
	465		515	565
	276		284	292
a,	360	an	391	422
u	159 ^C		143	127 ^C
'n	203	6 ¹¹	217	1.20
ິຮ	201	d		420
b _u	1790	a!	1830	1870
	778		438	1098
	520		596	672
	210 ^C		233	255

C - calculated from overtone and combination frequencies.

96.

TABLE 4.8. The arithmetic mean frequencies calculated for COC1.COF were used as a guide in carrying out the spectral analysis. Frequencies of the strongest bands in the vicinities of these calculated frequencies were taken as fundamentals.

Frequencies were assigned to the stretching modes on the basis of the bond frequency ranges given in TABLE 4.2; thus, 1858cm^{-1} and 1790cm^{-1} were assigned to the carbonyl stretching modes $\mathcal{V}_1(a^{\dagger})$ and $\mathcal{V}_2(a^{\dagger})$ respectively, 1197cm^{-1} was assigned to the C-F stretching mode $\mathcal{V}_3(a^{\dagger})$, 932cm^{-1} was assigned to the C-C stretching mode $\mathcal{V}_4(a^{\dagger})$, and 713cm^{-1} was assigned to the C-Cl stretching mode $\mathcal{V}_5(a^{\dagger})$.

The strongest observed bands with frequencies so far unassigned which occur in the vicinities of arithmetic mean frequencies of TABLE 4.9 are 570cm⁻¹, 491cm⁻¹, 409cm⁻¹, and 360cm⁻¹. 570cm⁻¹ and 491cm⁻¹ were tentatively assigned to the in-plane bending modes $\mathcal{V}_6(a^{\circ})$ and $\mathcal{V}_7(a^{\circ})$ respectively. 409cm⁻¹ was taken to correspond to the calculated aⁿ frequency 391cm⁻¹ and was thus assigned to the out-of-plane bending mode $\mathcal{V}_{10}(a^n)$. 360cm⁻¹ does not agree well with any of the calculated arithmetic means except 311cm⁻¹, and was tentatively assigned to the outof-plane bending mode $\mathcal{V}_{11}(a^n)$. A very weak band was observed in the spectrum at 287cm⁻¹. The frequency 287cm⁻¹ agreed well with the calculated arithmetic mean 284cm⁻¹ and was therefore assigned to the in-plane bending mode $\mathcal{V}_8(a^n)$.

The frequencies of the modes $\mathcal{V}_{9}(a^{*})$ and $\mathcal{V}_{12}(a^{*})$ could not be assigned and were presumably not observed. The remaining unassigned but observed frequencies were analyzed as overtones and combinations.

After an identification of fundamentals, overtones, and combinations had been made, the bands at 1990cm⁻¹, and 1059cm⁻¹ remained unassigned. If 1059cm⁻¹ is assumed to be a combination involving 932cm⁻¹ ($\mathcal{V}_{\mu}(a^{i})$), the frequency 127cm⁻¹ is obtained for an unobserved fundamental. If 1990cm⁻¹ is assumed to be a combination involving 1858cm⁻¹ ($\mathcal{V}_{1}(a^{i})$), the frequency 132cm⁻¹ is calculated for the unobserved fundamental. The average frequency (132 + 127)/2 = 129cm⁻¹ was assigned to the torsional mode $\mathcal{V}_{12}(a^{n})$. Since no unassigned bands remained, it proved to be impossible to calculate the frequency of $\mathcal{V}_{9}(a^{i})$ in this manner.

A normal coordinate analysis was carried out for the in-plane vibrations as a check on the above assignment.

TABLE 4.7

OBSERVED FREQUENCIES AND ASSIGNMENTS FOR OXALYL CHLORIDE FLUORIDE

INFRARED (vapour)			CALCULATED	ASSIGNMENT	SYMMETRY
(cm ⁻¹)	Intensity	Band Type	FREQUENCY		
			132	212	a n
287	VVW			Va	a
360	nw			νı	a"
409	mw			\mathcal{V}_{10}	a."
491	m	А		V7	at
570	mw			V6	a'
658	mw		647	$\mathcal{V}_{8} + \mathcal{V}_{11}$	пА
713	VS	A		v_5	2 ¹¹
770	m		778	$v_{7} + v_{8}$	Ап
932	Vs	А		\mathcal{V}_{1}	a'
1059	W		1064	$z_{1}^{+} + z_{12}^{-}$	A"
1110	W		1122	25+210	A 1
1197	VS	B?		23	a."
1300	W		1292	2, +22	ми
1418	W	B?	1426	$2v_5$	¹ A
1520	VW		1502	2, +26	1 A
1563	VW		1557	$\mathcal{D}_3 + \mathcal{D}_{11}$	An
1648	VW		1645	$\mathcal{V}_{L} + \mathcal{V}_{5}$	۲.
1690	VW		1688	$\mathcal{V}_3 + \mathcal{V}_7$	

99.

1790	VB	В		ν_2	at
1858	VS	В		ν_1	at
1990	VW		1990	$v_{1} + v_{12}$	¹¹ A
2129	mw		2129	V3 + 24	1 A
2340	W				
2354	W		2349	21+29	A
2402	W		2394	22/3	1 A
2560	VVW		2571	$v_{1} + v_{5}$	A *
2710	W		2722	V2 + 24	1 A
3060	W		3055	$\mathcal{V}_1 + \mathcal{V}_3$	A
3558	mw	A	3580	27/2	A.ª
3622	W		3648	$z_1 + z_2$	A *
3700	mw	В	3716	22/1	A,

- SYMBOLS:
 - w weak
 - vw very weak
 - vvw very, very weak
 - m medium
 - mw medium weak
 - vs very strong

VII.SUMMARY OF CHAPTER 4.

From the qualitative features of the infrared and Raman spectra of oxalyl fluoride and oxalyl chloride it was concluded that both molecules were planar and trans. This conclusion was justified by subsequent complete analyses of their spectra. By analogy it is also concluded that oxalyl chloride fluoride is planar and trans.

CHAPTER 5.

NORMAL COORDINATE ANALYSIS

I.CLASSICAL TREATMENT OF MOLECULAR VIBRATIONS:

In the classical treatment of molecular vibrations, the molecular model consists of N mass points (representing the N nuclei) held together by massless springs (representing the bonds). The motion of the molecule can be described in terms of 3N displacement coordinates. If Cartesian displacement coordinates are used, the displacement of the ith nucleus from its equilibrium position is represented by a vector $\overrightarrow{\mathcal{O}_1}$ whose massweighted Cartesian components are $m_1^{\frac{1}{2}} \bigtriangleup x_1$, $m_1^{\frac{1}{2}} \bigtriangleup y_1$, and $m_1^{\frac{1}{2}} \bigtriangleup z_1$. The origin of these mass-weighted displacement coordinates is fixed at the equilibrium position of the ith nucleus. The 3N mass-weighted Cartesian displacement coordinates can be written in general form as

$$\mathcal{Y}_{1}, \mathcal{Y}_{2}, \cdots \mathcal{Y}_{3N} \tag{5.1}$$

If the molecular motion is constrained so as to eliminate translational and rotational motion, six of the 3N mass-weighted Cartesian coordinates are redundant. This leaves a non-linear molecule with 3N-6 degrees of freedom for vibration; so, in a treatment of molecular vibrations using 3N mass-weighted Cartesian displacement coordinates, six null frequencies are calculated in addition to the genuine frequencies of vibration.

The potential energy of the molecule can be represented by a Taylor series in the γ_i 's, i.e.

$$\mathbf{V} = \mathbf{V}_{0} + \sum_{\mathbf{i}=1}^{N} \left(\frac{\partial \mathbf{V}}{\partial \eta_{\mathbf{i}}} \right) \eta_{\mathbf{i}} + \frac{1}{2!} \sum_{\mathbf{i},\mathbf{j}=1}^{N} \left(\frac{\partial^{2} \mathbf{V}}{\partial \eta_{\mathbf{i}} \partial \eta_{\mathbf{j}}} \right) \eta_{\mathbf{i}} \eta_{\mathbf{j}} + \cdots$$
(5.2)

 V_o is the energy of the molecule with the nuclei at their equilibrium positions and can be set equal to zero. The second term of the expansion is also zero, $\operatorname{since}\left(\frac{\partial V}{\partial \gamma_i}\right)_o = 0$ is the condition that V be a minimum when the nuclei are each at their equilibrium positions. In the simple harmonic oscillator approximation, terms of higher order than quadratic in equation (5.2) are neglected and the potential energy becomes

$$V = \frac{1}{2} \sum_{i,j=1}^{3N} f_{ij} \gamma_i \gamma_j \qquad (5.3)$$

where

$$f_{ij} = \left(\frac{\partial^2 v}{\partial \eta_i \partial \eta_j}\right)_{o}$$

The kinetic energy, T, is given by

$$T = \frac{1}{2} \sum_{i=1}^{3N} \gamma_i^2$$
(5.4)

The treatment of the problem is greatly simplified if matrix notation is

introduced at this point. In matrix notation, the kinetic and potential

energies, T and V, are given by

$$2T = [\dot{\eta}]^{t}[\dot{\eta}]$$
(5.5)

and

$$2V = [\gamma]^{t} [f] [\gamma]$$
(5.6)

where $[\dot{\eta}]$ and $[\eta]$ are column vectors of the $\dot{\eta}_i$ and the η_i respectively and the row vectors $[\dot{\eta}]^t$ and $[\eta]^t$ are the matrix transposes of $[\dot{\eta}]$ and $[\eta]$ respectively. The elements of the matrix [f] are the f_{ij} given in equation (5.3).

The vibrational problem is most easily formulated in terms of the Lagrangian, \prec , which is defined in non-matrix notation by

$$\mathcal{Z} = \mathbf{T} - \mathbf{V} \tag{5.7}$$

The equations of motion expressed in terms of \mathscr{L} are

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{g}_{i}}\right) - \left(\frac{\partial \mathcal{L}}{\partial g_{i}}\right) = 0$$

$$i = 1, 2, 3, \dots 3N$$
(5.8)

where the g form a set of generalized coordinates. II.NORMAL COORDINATES:

When mass-weighted Cartesian coordinates, \mathcal{I}_i , are used, the equations of motion (5.8) are complicated by the presence of terms $f_{ij}(i \neq j)$ in the potential energy expression (5.3). In the simple harmonic oscillator

(5.10)

approximation there exists a set of coordinates called normal coordinates, Q_i , in terms of which the kinetic and potential energy expressions are given by

$$2T = \begin{bmatrix} \dot{q} \end{bmatrix}^{t} \begin{bmatrix} \dot{q} \end{bmatrix}$$
(5.9)
$$2V = \begin{bmatrix} q \end{bmatrix}^{t} \begin{bmatrix} \Lambda \rceil \begin{bmatrix} q \end{bmatrix}$$
(5.10)

and

where the elements λ_i of [A] are given by

$$\lambda_{\mathbf{i}} = \left(\frac{\partial^2 \mathbf{v}}{\partial \mathbf{Q}_{\mathbf{i}}^2}\right)_{\mathbf{0}}$$

In terms of the normal coordinates, the Lagrangian becomes (in matrix notation)

$$\mathcal{L} = \left[\dot{q} \right]^{t} \left[\dot{q} \right] - \left[q \right]^{t} \left[\Lambda \right] \left[q \right]$$
(5.11)

and the equations of motion (5.8) become (in matrix notation)

$$\begin{bmatrix} \ddot{q} \end{bmatrix} - \begin{bmatrix} \Lambda \end{bmatrix} \begin{bmatrix} q \end{bmatrix} = 0 \tag{5.12}$$

Solution of (5.12) leads to 3N roots which are the elements of [A], i.e. the λ_i . The roots λ_i are related to the frequency $\mathcal{V}(\sec^{-1})$ by ³⁴

$$\lambda_{i} = 4\pi^{2} \nu_{i}^{2} \qquad (5.13)$$

$$A_{i} = 4\pi^{2} c^{2} \mathcal{V}_{i}^{2}$$
(5.14)

or

for \mathcal{V}_i expressed in wave numbers (cm⁻¹).

In practise, the normal coordinates are not known in advance and so

direct solution of equation (5.12) in terms of normal coordinates is not possible. Instead, the normal coordinates are usually determined in terms of some other set of coordinates which are more easily defined. In the present case, the normal coordinates were calculated in terms of massweighted Cartesian coordinates by the following procedure.

A transformation matrix [Y] is sought such that

$$[\gamma] = [\gamma] [Q]$$
(5.15)

Substitution of $[\eta]$ from (5.15) in equations (5.5) and (5.6) gives

$$2T = \left[\dot{q}\right]^{t} \left[Y\right]^{t} \left[Y\right] \left[\dot{q}\right]$$
(5.16)

and

$$2V = [Q]^{t} [Y]^{t} [f] [Y] [Q]$$
(5.17)

From a comparison of equations (5.16) and (5.17) with (5.9) and (5.10) respectively, it is seen that

$$[Y]^{t}[Y] = [E]$$
(5.18)

where [E] is the unit matrix, and

$$[Y]^{t}[f] [Y] = [\Lambda]$$
 (5.19)

From (5.18) it is seen that the transformation given by equation (5.15) is orthogonal. i.e. $[Q] = [Y]^t[\eta]$

From (5.19) it is seen that the columns of [Y] and the elements of $[\Lambda]$

are the characteristic vectors $[Y_i]$ and roots λ_i of the matrix [f].

Application of equation (5.19) is not generally of any practical use since it is the roots λ_i which are observed experimentally and not the force constants. In principle, the elements f_{ij} of [f] could be adjusted systematically until the calculated roots λ_i agreed with the experimental values λ_i^{obs} . The [f] matrix has $(3N)^2$ elements while there are at most only 3N values of λ_i available experimentally; hence, an unambiguous determination of the force constants by such a procedure would be impossible.

The problem becomes somewhat more tractable if the potential energy is expressed in internal valence coordinates, S_i. In terms of these coordinates, the potential energy is given by

$$2V = [s]^{t} [\#] [s]$$
 (5.20)

where the elements of $[\mathcal{F}]$ are given by

$$\mathcal{F}_{ij} = \left(\frac{\partial^2 v}{\partial s_i \partial s_j}\right)_{o}$$

Let the transformation from normal coordinates to internal coordinates be

$$[S] = [L][Q]$$
(5.21)

In addition, let the transformation from mass-weighted Cartesian

coordinates to internal coordinates be

$$[s] = [D][\eta]$$
(5.22)

Comparison of equations (5.21), (5.22), and (5.15) for L gives

$$\begin{bmatrix} L \end{bmatrix} = \begin{bmatrix} D \end{bmatrix} \begin{bmatrix} Y \end{bmatrix}$$
(5.23)

Substitution of [S] from (5.21) in equation (5.20) followed by substitution of [L] from (5.23) gives

 $2\mathbf{V} = \left[\mathbf{Q}\right]^{\mathsf{t}} \left[\mathbf{Y}\right]^{\mathsf{t}} \left[\mathbf{D}\right]^{\mathsf{t}} \left[\mathbf{Y}\right] \left[\mathbf{D}\right] \left[\mathbf{Y}\right] \left[\mathbf{Q}\right] \tag{5.24}$

Comparison of (5.24) with (5.17) gives

$$[f] = [D]^{t} [\#] [D]$$
 (5.25)

Substitution for [f] from (5.25) in (5.19) gives

$$[\mathbf{Y}]^{\mathsf{r}} [\mathbf{D}]^{\mathsf{r}} [\mathcal{F}] [\mathbf{D}] [\mathbf{Y}] = [\mathcal{A}]$$
(5.26)

which after premultiplication by [Y] gives

$$\begin{bmatrix} D \end{bmatrix}^{t} \begin{bmatrix} \forall \end{bmatrix} \begin{bmatrix} D \end{bmatrix} \begin{bmatrix} Y \end{bmatrix} = \begin{bmatrix} Y \end{bmatrix} \begin{bmatrix} A \end{bmatrix}$$
 (5.27)

where equation (5.18) has been used.

Equation (5.27) is the form of the vibrational equation which was used in the present normal coordinate analysis. In order to make use of this equation it was necessary to obtain the [D] matrix and a good approximation for the [F] matrix. For a planar molecule, the potential energy (equation 5.3) must be invariant under reflection in the plane. Such a symmetry operation carried out on the out-of-plane Cartesian displacement coordinates however, changes their signs. If an out-of-plane Cartesian displacement coordinate, say $m_1^{\frac{1}{2}} \Delta z_i$, occurs in a cross term, eg. $m_1^{\frac{1}{2}} \Delta x_i \cdot m_1^{\frac{1}{2}} \Delta z_i$, with an in-plane coordinate, $m_1^{\frac{1}{2}} \Delta x_i$, the potential energy changes sign under the symmetry operation. It is, therefore, concluded that no cross terms $\gamma_i \gamma_j$ can occur between in-plane and out-of-plane displacement coordinates in the potential energy expressions (5.3), (5.10), and (5.20).

In the present case, all the molecules studied were found to be planar (Chapter 4). The in-plane normal coordinates could be calculated in terms of just 2N in-plane mass-weighted Cartesian coordinates. III.CALCULATION OF THE D MATRIX:

As was shown in section II, the [D] matrix was defined by

$$[S] = [D][\gamma]$$
(5.22)

where the elements [S] are the internal valence coordinates and the elements of $[\gamma]$ are the mass-weighted Cartesian coordinates. Let the transformation from mass-weighted Cartesian coordinates γ_i to nonmass-weighted Cartesian coordinates, q_i , be

$$[\gamma] = [m^{\frac{1}{2}}][q] \qquad (5.28)$$

where $\left[m^{\frac{1}{2}}\right]$ is a diagonal matrix with elements $m_{i}^{\frac{1}{2}}$. The inverse trans-

$$\left[q\right] = \left[m^{\frac{1}{2}}\right]^{-1} \left[\gamma\right] \tag{5.29}$$

Let the transformation from internal coordinates, S_i, to non-mass-

weighted Cartesian displacement coordinates be given by

$$[s] = [B][q]$$
(5.30)

Substitution for [q] from (5.29), and comparison with (5.22) gives

$$\left[D \right] = \left[B \right] \left[m^{\frac{1}{2}} \right]^{-1}$$
(5.31)

In non-matrix notation (5.30) may be represented by

$$S_{t} = \sum_{i=1}^{3N} B_{ti} q_{i}$$
(5.32)

where the q_i are the displacement coordinates $(\Delta x_1, \Delta y_1, \Delta z_1 \dots \Delta x_{3N}, \Delta y_{3N}, \text{ and} \Delta z_{3N})$.

In terms of the nuclear displacement vectors $\overrightarrow{\rho_{\infty}}$ which were defined in section I, (5.32) may be rewritten in the form

$$S_{t} = \sum_{\alpha=1}^{N} \overline{A}_{t\alpha} \cdot \overline{A}_{\alpha} \qquad (5.33)$$

where

$$\vec{p}_{\alpha} = \Delta x_{\alpha} \vec{i} + \Delta y_{\alpha} \vec{j} + \Delta z_{\alpha} \vec{k}$$
(5.34)

The $\mathcal{A}_{t\alpha}$ vectors are defined as follows:

Let all nuclei except \propto be at rest in their equilibrium positions. The direction of $\overrightarrow{\mathcal{A}}_{t\alpha}$ is the direction for which displacement of nucleus \propto produces the greatest increase in S_t . $|\overrightarrow{\mathcal{A}}_{t\alpha}|$ is equal to the increase in S_t produced by unit displacement of nucleus \propto .

The vectors $\vec{\lambda}_{t\alpha}$ are obtained by vector analysis in terms of the bond lengths and valence angles and a set of unit vectors $\vec{e}_{q,p}$ which define unit displacements along the bonds. The vector $\vec{e}_{q,p}$ points from nucleus α to nucleus β in the bond $\mathbf{r}_{q,\beta}$. It is also noted that $\vec{e}_{q,p} = -\vec{e}_{\beta\alpha}$. The $\vec{\lambda}_{t\alpha}$ vectors have been given by Wilson, Decius, and Cross for several different types of valence internal coordinates. In The present case, only valence bond stretching and valence angle bending coordinates were used. The $\vec{\lambda}_{t\alpha}$ vectors for each of these cases are given in TABLE 5.1 with reference to the parameters $\vec{\lambda}_{t\alpha}$, $\vec{e}_{q,\beta}$, $\mathbf{r}_{q,\beta}$, and $\vec{\phi}_{\alpha,\beta}\gamma$ which are defined in FIGURE 5.1.

FIGURE 5.1

DEFINITION OF THE S_t VECTORS

Ztac oc B



VALENCE ANGLE BENDING

VALENCE BOND STRETCHING

TABLE 5.1

INTERNAL COORDINATE S _t	Ī ta
∆ r _{α/3}	$\vec{\lambda}_{ta} = \vec{e}_{a,\beta} = -\vec{e}_{\beta\alpha}$ $\vec{\lambda}_{t\beta} = \vec{e}_{\beta\alpha} = -\vec{e}_{\beta\alpha}$
Adaps?	$\overline{\mathcal{A}}_{t\alpha} = \frac{\cos(\phi_{\alpha,\beta}) \cdot \overline{\mathcal{E}}_{\beta\alpha}) - \overline{\mathcal{E}}_{\beta\gamma}}{r_{\beta\alpha} \cdot \sin \phi_{\alpha\beta\gamma}}$
	$\vec{A}_{t\beta} = \left[(r_{\beta\alpha} - r_{\beta\gamma} \cos \phi_{\alpha\beta\gamma}) \vec{e}_{\beta\alpha} + (r_{\beta\gamma} - r_{\beta\alpha} \cos \phi_{\alpha\beta\gamma}) \vec{e}_{\beta\gamma} \right] / (r_{\beta\alpha} \cdot r_{\beta\gamma}).$
	$\vec{\mathcal{A}}_{ty} = \frac{\cos(\phi_{\alpha\beta}\gamma \cdot \vec{e}_{\beta\gamma}) - \vec{e}_{\beta\alpha}}{r_{\beta\gamma} \sin \phi_{\alpha\beta}\gamma}$

EXPRESSIONS FOR THE Dital

Before the $\vec{A}_{t\alpha}$ can be used in equation (5.33) the $\vec{e}_{\alpha\beta}$ must be obtained in terms of \vec{i} , \vec{j} , and \vec{k} . Let the position of each nucleus α in the molecule be given by three Cartesian coordinates X_{α} , y_{α} , z_{α} with respect to the Cartesian axes defined in FIGURE 3.1; then, if each bond $r_{\alpha\beta}$ can be represented by the vector $\vec{r}_{\alpha\beta}$ which is given by $\vec{r}_{\alpha\beta} = (x_{\beta} - x_{\alpha})\vec{i} + (y_{\beta} - y_{\alpha})\vec{j} + (z_{\beta} - z_{\alpha})\vec{k}$ The $\overrightarrow{\mathcal{C}}_{\alpha_{\beta}}$ vectors are then given by

or

$$\vec{e}_{\alpha\beta} = \vec{r}_{\alpha\beta} / (\vec{r}_{\alpha\beta} \cdot \vec{r}_{\alpha\beta})^{\frac{1}{2}}$$
or
$$\vec{e}_{\alpha\beta} = \cos\theta_{x} i + \cos\theta_{y} j + \cos\theta_{z} k \qquad (5.35)$$
where $\cos\theta_{x}$, $\cos\theta_{y}$, and $\cos\theta_{z}$ are the direction cosines of $\vec{e}_{\alpha\beta}$

relative to the molecule fixed Cartesian axes defined in FIGURE 3.1. The angles, θ_{i} , (i = x, y, z) can easily be obtained in terms of the valence angles from Euclidean geometry.

The expressions for the internal coordinates S₊ can now be obtained from equations (5.35) and (5.33) and TABLE 5.1. In the expressions obtained for the S_t , the coefficients B_{ti} of each Cartesian coordinate, \boldsymbol{q}_i , are selected as the elements of the [B] matrix. The [D] matrix is obtained from equation (5.31).

In the present case it was convenient to use internal coordinates which were all expressed in the same units. Valence angle bending coordinates $\Delta \phi_{\alpha\beta}$ were multiplied by $(r_{\alpha\beta} \cdot r_{\beta\beta})^{\frac{1}{2}}$ to give them the same units as the valence stretching coordinates $\bigtriangleup r_{\alpha\beta}$. Consequently, the coefficients B_{ti} (or D_{ti}) involving a bending coordinate $(\Delta \phi_{\sigma,s})$ were also multiplied by $(r_{\alpha\beta} \cdot r_{\beta\beta})^{\frac{1}{2}}$.

The matrix elements ${\rm D}_{\rm ti}$ were derived here using the foregoing

procedure for any molecule of the type $\begin{array}{c} X \\ Z \\ Y \end{array} \begin{array}{c} Y^{1} \\ Z \\ Y \end{array}$. The numbering

of the nuclei is given in FIGURE 5.2.

FIGURE 5.2

NUMBERING OF NUCLEI FOR X Y Z - Z' X' Y'



The [S] and [7] vectors were defined as follows:

$$\begin{bmatrix} \triangle r_{12} \\ \Delta r_{23} \\ \triangle r_{16} \\ \Delta r_{24} \\ \Delta r_{15} \\ (r_{23} \cdot r_{24})^{\frac{1}{2}} \triangle \phi_{324} \\ (r_{13} \cdot r_{16})^{\frac{1}{2}} \triangle \phi_{516} \\ (r_{12} \cdot r_{24})^{\frac{1}{2}} \triangle \phi_{124} \\ (r_{12} \cdot r_{23})^{\frac{1}{2}} \triangle \phi_{215} \\ (r_{12} \cdot r_{23})^{\frac{1}{2}} \triangle \phi_{123} \\ (r_{12} \cdot r_{16})^{\frac{1}{2}} \triangle \phi_{216} \end{bmatrix}$$

$$\begin{bmatrix} \gamma \end{bmatrix} = \begin{bmatrix} m_{1}^{\frac{1}{2}} \triangle y_{1} \\ m_{2}^{\frac{1}{2}} \triangle x_{2} \\ m_{2}^{\frac{1}{2}} \triangle x_{3} \\ m_{4}^{\frac{1}{2}} \triangle x_{4} \\ m_{5}^{\frac{1}{2}} \triangle x_{5} \\ m_{5}^{\frac{1}{2}} \triangle x_{5} \\ m_{5}^{\frac{1}{2}} \triangle x_{6} \\ m_{6}^{\frac{1}{2}} \triangle x_{6} \end{bmatrix}$$

$$\mu_i = 1/m_i$$
.

TABLE 5.2

[D] - MATRIX ELEMENTS FOR X Y Z - Z' X' Y'

 $D_{1,2} = \mu_1^{\frac{1}{2}}; \quad D_{1,4} = -\mu_2^{\frac{1}{2}}$ $D_{2,3} = -\sin\phi_{123}\mu_2^{\frac{1}{2}}; D_{2,4} = -\cos\phi_{123}\mu_2^{\frac{1}{2}}; D_{2,5} = \sin\phi_{123}\mu_3^{\frac{1}{2}}; D_{2,6} = \cos\phi_{123}\mu_3^{\frac{1}{2}}$ $D_{3,1} = \sin \phi_{216} \mu_1^{\frac{1}{2}}; D_{3,2} = \cos \phi_{216} \mu_1^{\frac{1}{2}}; D_{3,11} = -\sin \phi_{216} \mu_6^{\frac{1}{2}}; D_{3,12} = -\cos \phi_{216} \mu_6^{\frac{1}{2}}$ $D_{4,3} = \sin\phi_{124}\mu_2^{\frac{1}{2}}; D_{4,4} = -\cos\phi_{124}\mu_2^{\frac{1}{2}}; D_{4,7} = -\sin\phi_{124}\mu_4^{\frac{1}{2}}; D_{4,8} = \cos\phi_{124}\mu_4^{\frac{1}{2}}$ $D_{5,1} = -\sin \phi_{215} \mu_1^{\frac{1}{2}}; D_{5,2} = \cos \phi_{215} \mu_1^{\frac{1}{2}}; D_{5,9} = \sin \phi_{215} \mu_5^{\frac{1}{2}}; D_{5,10} = -\cos \phi_{215} \mu_5^{\frac{1}{2}}$ $D_{6,3} = \mu_2^{\ddagger} (r_{23} - r_{24} \cos \phi_{324}) \sin \phi_{123} - (r_{24} - r_{23} \cos \phi_{324}) \sin \phi_{124} / ((r_{23} r_{24})^{\ddagger})$ $\sin\phi_{324}$) $D_{6,4} = \mu_2^{\frac{1}{2}} (r_{23} - r_{24} \cos \phi_{324}) \cos \phi_{123} + (r_{24} - r_{23} \cos \phi_{324}) \cos \phi_{124} / ((r_{23} r_{24})^{\frac{1}{2}})$ $\sin \phi_{324})$ $D_{6,5} = \mu_3^{\frac{1}{2}} \left(\cos\phi_{324}\sin\phi_{123} + \sin\phi_{124}\right) / \sin\phi_{324} \left(r_{24}/r_{23}\right)^{\frac{1}{2}}$ $D_{6,6} = \mu_3^{\ddagger} \left(\cos\phi_{324}\sin\phi_{123} - \cos\phi_{124}\right) / \sin\phi_{324} \left(r_{24}/r_{23}\right)^{\ddagger}$ $D_{6,7} = -\mu_{4}^{2} (\sin\phi_{124}\cos\phi_{324} + \sin\phi_{124}) / \sin\phi_{324} (r_{23}/r_{24})^{\frac{1}{2}}$ $D_{6,8} = \mu_{4}^{\frac{1}{2}} \left(\cos\phi_{324}\cos\phi_{124} - \cos\phi_{123}\right) / \sin\phi_{324} \left(r_{23}/r_{24}\right)^{\frac{1}{2}}$ $D_{7,1} = \mu_1^{\frac{1}{2}} (r_{16} - r_{15} \cos \phi_{516}) \sin \phi_{216} - (r_{15} - r_{16} \cos \phi_{516}) \sin \phi_{215} / ((r_{16} r_{15})^{\frac{1}{2}})$ $\sin\phi_{516}$) $D_{7,2} = \mu_1^{\frac{1}{2}} (r_{16} - r_{15} \cos \phi_{516}) \sin \phi_{216} + (r_{15} - r_{16} \cos \phi_{516}) \cos \phi_{215} / ((r_{16} r_{15})^{\frac{1}{2}})$ $\sin\phi_{516}$) $D_{7,9} = \mu_5^{\frac{1}{2}} \left(\sin \phi_{215} \cos \phi_{516}^{+} \sin \phi_{216} \right) / \sin \phi_{516} \left(r_{16} / r_{15} \right)^{\frac{1}{2}}$ $D_{7,10} = -\mu_5^{\frac{1}{2}} (\cos\phi_{516}\cos\phi_{215} - \cos\phi_{216}) / \sin\phi_{516} (r_{16}/r_{15})^{\frac{1}{2}}$ $D_{7,11} = -\mu_{6}^{\frac{1}{2}} \left(\cos\phi_{516}\sin\phi_{216} + \sin\phi_{215}\right) / \sin\phi_{516} \left(r_{15}/r_{16}\right)^{\frac{1}{2}}$ $D_{7,12} = \mu_{\delta}^{\frac{1}{2}} \left(\cos\phi_{516}\cos\phi_{216} - \cos\phi_{215}\right) / \sin\phi_{516} \left(r_{15}/r_{16}\right)^{\frac{1}{2}}$

TABLE 5.2 - CONTINUED

 $D_{8,1} = \mathcal{M}_{1}^{\frac{1}{2}} (r_{2\mu}/r_{12})^{\frac{1}{2}}; \quad D_{8,3} = -\mathcal{M}_{2}^{\frac{1}{2}} (r_{2\mu}-r_{12}\cos\phi_{12\mu})/(r_{12}\cdot r_{2\mu})^{\frac{1}{2}}$ $D_{8,L} = \mu_2^{\frac{1}{2}} (r_{12}/r_{2L})^{\frac{1}{2}} \sin \phi_{12L}; \quad D_{8,7} = -\mu_L^{\frac{1}{2}} (r_{12}/r_{2L})^{\frac{1}{2}} \cos \phi_{12L}$ $D_{8,8} = -\mu_{h}^{\frac{1}{2}} (r_{12}/r_{2h})^{\frac{1}{2}} \sin\phi_{12h}$ $D_{9,1} = \mu_1^{\frac{1}{2}} (r_{15} - r_{12} \cos \phi_{125}) / (r_{12} \cdot r_{15})^{\frac{1}{2}}; \quad D_{9,2} = -\mu_1^{\frac{1}{2}} (r_{12} / r_{15})^{\frac{1}{2}} \sin \phi_{215}$ $D_{9,3} = -\mu_2^{\frac{1}{2}} (r_{15}/r_{12})^{\frac{1}{2}}; \quad D_{9,9} = \mu_5^{\frac{1}{2}} (r_{12}/r_{15})^{\frac{1}{2}} \cos \phi_{215}; \quad D_{9,10} = \mu_5^{\frac{1}{2}} (r_{12}/r_{15})^{\frac{1}{2}}$ sin Ø215 $D_{10,1} = -\mu_1^{\frac{1}{2}} (r_{23}/r_{12})^{\frac{1}{2}}; \quad D_{10,3} = \mu_2^{\frac{1}{2}} (r_{23}-r_{12}\cos\phi_{123})/(r_{12}\cdot r_{23})^{\frac{1}{2}}$ $D_{10,L} = \mu_2^{\frac{1}{2}} (r_{12}/r_{23})^{\frac{1}{2}} \sin \phi_{123}; \quad D_{10,5} = \mu_3^{\frac{1}{2}} (r_{12}/r_{23})^{\frac{1}{2}} \cos \phi_{123}$ $D_{10,6} = -\mu_3^{\frac{1}{2}}(r_{12}/r_{23})^{\frac{1}{2}} \sin \phi_{123}$ $D_{11,1} = -\mu_1^{\frac{1}{2}} (r_{16} - r_{12} \cos \phi_{216}) / (r_{12} r_{16})^{\frac{1}{2}}; \quad D_{11,2} = -\mu_1^{\frac{1}{2}} (r_{12} / r_{16})^{\frac{1}{2}} \sin \phi_{216}$ $D_{11,3} = \mu_2^{\frac{1}{2}} (r_{16}/r_{12})^{\frac{1}{2}}; \quad D_{11,11} = \mu_6^{\frac{1}{2}} (r_{12}/r_{16})^{\frac{1}{2}} \cos \phi_{216}; \quad D_{11,12} = \mu_6^{\frac{1}{2}} (r_{12}/r_{16})^{\frac{1}{2}}$ $\sin\phi_{216}$

The [D] matrices for oxalyl chloride, oxalyl fluoride, and oxalyl chloride fluoride were calculated by substituting the appropriate masses, band lengths, and angles into the expressions given in TABLE 5.2.

The geometrical parameters used for oxalyl chloride have previously been given in TABLE 1.1; however, for oxalyl fluoride and oxalyl chloride fluoride, the values given in TABLE 5.3 had to be assumed for these parameters. In the case of oxalyl fluoride, values for the C-F and C=O

36 bond lengths were transferred from acetyl fluoride. A comparison of the $CCO = 127^{\circ}5'$ of acetyl chloride with that of acetyl fluoride (CCO =128°21') shows that in changing from the chloride to the fluoride the CCO opens up by about 1° ; therefore, since $CCO = 123^{\circ}$ for oxalyl chloride, $CCO = 124^{\circ}$ was assumed for oxalyl fluoride. $CCCI = 112^{\circ}39^{\circ}$ in acetyl chloride while in acetyl fluoride $CCF = 110^{\circ}18^{\circ}$ or about 3° less; therefore, since $CCCl = 114^{\circ}$ in oxalyl chloride, $CCF = 111^{\circ}$ was assumed for oxalyl fluoride. The C-C bond length for oxalyl fluoride was transferred from oxalyl chloride. The geometrical parameters of oxalyl chloride fluoride were estimated from the parameters of oxalyl chloride and oxalyl fluoride.

To the right of each set of parameters in TABLE 5.3, the molecular formulae are given. The numbers in brackets correspond to the numbers used for the general X Y Z - Z' Y' X' molecule in FIGURE 5.2.

TABLE 5.3

BOND LENGTHS AND ANGLES FOR THE OXALYL HALIDES

$$(COC1)_{2} d(C-C) = 1.50 \text{ Å} d(C-C1) = 1.72 \text{ Å} d(C=O) = 1.20 \text{ Å} C - C = 0 = 123^{\circ} O - C - C1 = 123^{\circ} C - C - C1 = 114^{\circ} (COF)_{2} d(C-C) = 1.50 \text{ Å} d(C=O) = 1.181 \text{ Å} C - C = 0 = 124^{\circ} O - C - F = 125^{\circ} C - C - F = 111^{\circ} COC1.COF d(C-C) = 1.50 \text{ Å} d(C=O) = 1.19 \text{ Å} d(C=O) = 1.19 \text{ Å} C - C = 0 = 123^{\circ} O - C - C1 = 123^{\circ} O - C - F = 125^{\circ} C - C - F = 125^{\circ} C - C - F = 125^{\circ} O - C - C1 = 123^{\circ} O - C - C1 = 123^{\circ} O - C - C = 123^{\circ} O - C - C1 = 124^{\circ} C - C - C1 = 114^{\circ} C - C - C = 112^{\circ}$$

C1(3) O(5)C(2) C(1)O(4) C1(6)





MASSES

SES $m_c = 12.011; m_0 = 16.000; m_F = 19.000; m_{c1} = 35.457$
The calculation of the [D] matrix was programmed in FORTRAN IV for the IBM 7040 computer. Since this program was not completely general, (it only calculated [D] matrices for molecules of the form XYZ - Z'X'Y') it will not be discussed in detail here. The input consisted of the bond lengths $\binom{0}{A}$, angles (degrees), and atomic masses. Using these parameters, the computer evaluated the expressions given in TABLE 5.2. The calculated [D] matrix was printed out and also punched on cards which were used as input for a later program. The calculated [D] matrix for oxalyl fluoride is given as an example in TABLE 5.4.

The potential energy in terms of valence internal coordinates was given by equation (5.20), i.e.,

$$2V = [s]^{t} [\mathcal{F}] [s]$$

The $[\neq]$ matrix defined in this way is symmetric about its leading diagonal. The diagonal elements are the so-called valence force constants (i.e., valence bond stretching and valence angle bending force constants) while the off-diagonal elements, i.e.,

$$\mathcal{F}_{tu} = \left(\frac{\partial^{2} v}{\partial^{S_{t}} \partial^{S_{ju}}}\right)_{o} \qquad t \neq u$$

TABLE 5.4

[D] MATRIX OF OXALYL FLUORIDE

	∠y」	Ax1	♪ y ₂	∆x ₂	<i>م</i> y ₃	∆x ₃		Δx_4	$ r_5 $	$\triangle x_5$	۵y ₆	≏x ₆
s ₁		0.28854		-0.28854					ж., К			×
⁵ 2			-0.26938	0.10340	0.21418	-0.08222	,					
^s 3	0.26938	-0.10340	8								-0.21418	0.08222
s ₄	×	*	0.23921	0.16135			-0.20726	-0.13980				
⁸ 5	-0.23921	-0.16135			×				0.20726	0.13980		
s ₆			0.07571	-0.50771	0.07692	0.20039	-0.14942	0.22152				0.00000
^s 7	-0.07571	0.50771	a.						-0.15762	0,23368	-0.07692	-0.20039
sg	0.25592		-0.43784	0.26971			0.15762	-0.23368				
s ₉	0.43784	-0.26971	-0.25592									
s ₁₀	-0.27353		0.38261	0.28416	-0.08673	-0.22593					0.08673	0.22593
s _ມ	-0.38261	0.28416	0.27353								0.00019	н

120.

are the intersection constants.

The number of force constants which have to be determined from the observed frequencies can be greatly reduced if a special model is used to give the potential energy expression. One such model is the Urey-Bradley-Schimanouchi model.³⁸ This assumes that there are three types of force constants, valence bond stretching, valence angle bending, and those between non-bonded atoms. The latter non-bonded type constants are designed to account for Van der Waals repulsions between the nonbonded atoms. The potential for this model is given by

$$2V = \sum_{i} 2K'_{i} r_{i}(\Delta r_{i}) + K_{i}(\Delta r_{i})^{2} + \sum_{i \leq k} 2H'_{ij}r_{o}^{2}(\Delta \phi_{ij}) + H_{ij}(r_{o}\Delta \phi_{ij})^{2} + \sum_{i \leq k} 2F'_{ij} q_{ij}(\Delta q_{ij}) + F_{ij}(\Delta q_{ij})^{2} + \sum_{i \leq k} 2C'_{ik} p_{ik}(\Delta p_{ik}) + C_{ik}(\Delta p_{ik})^{2} + \sum_{i \leq k} 2C'_{ik} p_{ik}(\Delta p_{ik}) + C_{ik}(\Delta p_{ik})^{2}$$
where $r_{o} = (r_{i}r_{j})^{\frac{1}{2}}$ and r_{i}, ϕ_{ij}, q_{ij} , and p_{ik} are defined in FIGURE 5.3.

FIGURE 5.3

DEFINITION OF r_i , ϕ_{ij} , q_{ij} , and p_{ik} *



* Note that the indexing of the bonds and angles used here is different

here from that used in the calculation of the [D] matrix. In the latter case, the bonds and angles were indexed according to the numbers attached to the atoms, a, b, c, and d in FIGURE 5.2, while in the present case the bonds are numbered and the angles are indexed according to the bonds that contain them.

The force constants
$$F'_{ij} = \left(\frac{\partial v}{\partial q_{ij}}\right)_{o}$$
 and $F_{ij} = \left(\frac{\partial^2 v}{\partial q_{ij}}\right)_{o}^{2}$
are called "gem-type" while $C'_{ik} = \left(\frac{\partial v}{\partial p_{ik}}\right)_{o}^{2}$ and $C_{ik} = \left(\frac{\partial^2 v}{\partial p_{ik}}\right)_{o}^{2}$ are called "cis-type".

The coordinates $\triangle r_i$, $\triangle \phi_{ij}$, $\triangle q_{ij}$, and $\triangle p_{ik}$ are not independent and hence the equilibrium condition

dV = 0

does not imply that

$$\left(\frac{\partial \mathbf{v}}{\partial \mathbf{r}_{\mathbf{i}}}\right)_{\mathbf{o}} = \left(\frac{\partial \mathbf{v}}{\partial \phi_{\mathbf{i}\mathbf{j}}}\right)_{\mathbf{o}} = \left(\frac{\partial \mathbf{v}}{\partial q_{\mathbf{i}\mathbf{j}}}\right)_{\mathbf{o}} = \left(\frac{\partial \mathbf{v}}{\partial p_{\mathbf{i}\mathbf{k}}}\right)_{\mathbf{o}} = 0$$

If the redundant coordinates, $\bigtriangleup q_{ij}$, and $\bigtriangleup p_{ik}$, are removed by substitution 39 of expressions of the form

$$\Delta p_{ik} = \Delta p_{ik} (\Delta r_i, \Delta r_j, \Delta r_k, \Delta \phi_{ij}, \Delta \phi_{jk})$$
(5.38)

and

into (5.36), it is found that

$$\left(\frac{\partial V}{\partial r_{i}}\right)_{o} = \left(\frac{\partial V}{\partial \phi_{ij}}\right)_{o} = 0$$

but that $\left(\frac{\partial V}{\partial q_{ij}}\right)_{o} \neq 0$ and $\left(\frac{\partial V}{\partial p_{ik}}\right)_{o} \neq 0$
Substitution of equations (5.37) and (5.38) into (5.36) also introduces
terms linear with respect to the F'_{ij} , F_{ij} , C'_{ij} , and C_{ij} into the
potential energy and hence into the elements \mathcal{F}_{tu} of the $[\mathcal{F}]$ matrix.
The coefficients of these force constants in the linear terms form
elements of the $[Z]$ matrix. (To be described later.)

Since the [#Jmatrix is symmetric about its diagonal, matrix operations can be conveniently carried out using only its upper right triangular half (including the diagonal elements). The numbering of the elements in this triangular form with reference to the internal coordinate vector [S] is given by

[s]t	302	$[s_1]$	s ₂	s ₃	 •	s _{ns}]	
[¥]	11	F	F2 F3	F4 F5 F6	 •		(5.39)
						$\mathcal{F}\left(\frac{n_{s}(n_{s}+1)}{2}\right)$	

123.

In this form, the $[\mathcal{H}]$ matrix may be treated as a vector with $n_s(n_s+1)/2$ elements where n_s is the total number of internal coordinates. The elements \mathcal{H}_n of the triangular matrix are related to those of the square matrix elements \mathcal{H}_n by

$$n = \begin{cases} u(u-1)/2 + t & t < u \\ t(t+1)/2 & t = u \\ t(t-1)/2 + u & u < t \end{cases}$$
 (5.40)

Note that t and u are also the indices of internal coordinates \mathbf{S}_{t} and $\mathbf{S}_{u}.$

Let the force constants K_i, H_{ij}, K_{ij}, etc., be generalized as the force constant vector

$$[\mathcal{G}] = (\mathcal{G}_1, \mathcal{G}_2, \dots, \mathcal{G}_{n_{\mathcal{G}}})$$
(5.41)

where the column vector $[\mathcal{G}]$, has been written horizontally for convenience and $n_{\mathcal{G}}$ = number of force constants. Let the [Z] matrix be defined such that

$$[\mathcal{F}] = [\mathbf{z}][\boldsymbol{\varphi}] \tag{5.42}$$

or, in non-matrix notation

$$\mathcal{F}_{n} = Z_{nk} \mathcal{G}_{k}$$
(5.43)

The [Z] matrix consists of the coefficients of the \mathcal{P}_{k} 's in the

 $[\mathcal{H}]$ matrix. The diagonal force constants (K_i and H_{ij}) have coefficients that are unity but the coefficients of the repulsive force constants which result from the substitutions of (5.37) and (5.38) into (5.36) are more complex. The latter coefficients have been tabulated by Overend and Scherer and are given for F'_{ij} and F_{ij} in TABLE 5.5 and in TABLE 5.6 for C'_{ik} and C_{ik} . The nomenclature of Overend and Scherer has been adjusted for the fact that the angles ϕ_{ij} are multiplied here by $(r_i r_j)^{\frac{1}{2}}$. This is consistent with the nomenclature in FIGURE 5.3.

The first column of each of TABLES 5.7 and 5.8 is headed $S_t S_u$ where t and u are also the indices of \mathcal{F}_{tu} or \mathcal{F}_n . The position of a given coefficient in the (\mathcal{F}) matrix is given by index n which is calculated from t and u using equation (5.40). The position of an element of the [Z] matrix, i.e., Z_{nk} is given by n and k which is the index of $\mathcal{P}_k = F_{ij}$, C_{ik} , etc.

In all the molecules studied here, the F_{ij}^{i} and C_{ik}^{i} were eliminated by the approximations $F_{ij}^{i} = -0.1F_{ij}$ and $C_{ik}^{i} = -0.1C_{ik}^{i}$. This approximation has been justified independently both by Linnet and Heath, and Shimanouchi. When this approximation is used the [2] matrix columns in TABLE 5.5 for

TABLE 5.5



COEFFICIENTS IN [Z] MATRIX DUE TO THE F_{ij}^{i} and F_{ij}

 $s_{ij} = (r_i - r_j \cos \phi_{ij})/q_{ij}$ $t_{ij} = (r_i \sin \phi_{ij})/q_{ij}$

TABLE 5.6

Z DUE TO THE C. AND C. COEFFICIEN'TS OF

StSu $(\Delta r_i)^2$ $(\Delta r_{\rm L})^2$ $(\Delta r_i)^2$ $(\triangle r_i)(\triangle r_k)$ $(\Delta r_i)(\Delta r_i)$ $(\Delta r_k)(\Delta r_j)$ $r_i r_i (\triangle \phi_{ij})^2$ $r_k r_i (\Delta \phi_{ik})^2$ $((\mathbf{r}_{i}\mathbf{r}_{j})^{\frac{1}{2}} \Delta \phi_{ij})((\mathbf{r}_{i}\mathbf{r}_{k})^{\frac{1}{2}} \Delta \phi_{ik})$ $(\Delta r_i)(r_i r_i)^{\frac{1}{2}}(\Delta \phi_{ii})$ $(\Delta \mathbf{r}_k)(\mathbf{r}_i\mathbf{r}_j)^{\frac{1}{2}}(\Delta \phi_{ij})$ $(\Delta r_{i})(r_{i}r_{j})^{\frac{1}{2}}(\Delta \phi_{ij})$ $(\triangle r_i)(r_i r_k)^{\frac{1}{2}}(\triangle \phi_{ik})$ $(\Delta r_k)(r_j r_k)^{\frac{1}{2}}(\Delta \phi_{jk})$ $(\Delta \mathbf{r}_{i})(\mathbf{r}_{i}\mathbf{r}_{k})^{\frac{1}{2}}(\Delta \phi_{ik})$

ik
c'_{ik}
$(1 - v_{ik}^2)$
$(1 - v_{ki}^2)$
$(b_{ik})^2$
$\cos(\phi_{ij} + \phi_{jk}) - v_{ik}v_{ki}$
$(a_{ik}v_{ik} - \cos\phi_{ij})$
$(a_{ik}v_{ki} - \cos\phi_{jk})$
$(r_{i}/r_{j}) (v_{ik}p_{ik}/r_{i}) + (1 - u_{ik}^{2})$
$(r_{k}/r_{j})(v_{ki}p_{ik}/r_{k}) + (1 - u_{ki}^{2})$
$-((\mathbf{r}_{\mathbf{i}}\mathbf{r}_{\mathbf{k}})^{\frac{1}{2}}/\mathbf{r}_{\mathbf{j}})\cos(\phi_{\mathbf{j}\mathbf{k}}+\phi_{\mathbf{i}\mathbf{j}})+u_{\mathbf{i}\mathbf{k}}u_{\mathbf{k}\mathbf{i}}$
$(r_i r_j)^{\hat{z}} u_{ik} (p_{ik} + r_i v_{ik})$
$(r_i/r_j)^{\ddagger} v_{ki}u_{ik} - \sin(\phi_{jk} + \phi_{ij})$
$(r_i/r_j)^{\frac{1}{2}}(\sin\phi_{ij} - a_{ik}u_{ik})$
$(r_k/r_j)^{\ddagger} v_{ik}u_{ki} - \sin(\phi_{jk} + \phi_{ij})$
$(r_k/r_j)^{\frac{1}{2}} u_{ki} (p_{ik} + r_k v_{ki})/r_k$
$(r_k/r_j)^{\frac{1}{2}} (\sin\phi_{jk} - a_{ik}u_{ki})$

127.

$$\begin{aligned} \mathbf{a}_{ik} &= (\mathbf{r}_{j} - \mathbf{r}_{i} \cos \phi_{ij} - \mathbf{r}_{k} \cos \phi_{jk}) \\ \mathbf{u}_{ik} &= (\mathbf{a}_{ik} \sin \phi_{ij} + \mathbf{b}_{ik} \cos \phi_{ij}) \\ \mathbf{v}_{ik} &= (\mathbf{a}_{ik} \cos \phi_{ij} - \mathbf{b}_{ik} \sin \phi_{ij}) \end{aligned}$$

$$b_{ik} = (r_i \sin \phi_{ij} - r_k \sin \phi_{jk})$$
$$u_{ki} = (a_{ik} \sin \phi_{jk} - b_{ik} \cos \phi_{jk})$$
$$v_{ki} = (a_{ik} \cos \phi_{jk} + b_{ik} \sin \phi_{jk})$$

 F_{ij}^{i} and F_{ij} are brought together so that (new coefficient of F_{ij})=(coefficient of F_{ij})-O.l(coefficient F_{ij}^{i}) in each row of TABLE 5.5. The same relation applies to the coefficients of C_{ij} given in TABLE 5.6.

The construction of the [2] matrix will be illustrated for the case of trans oxalyl fluoride. The numbering of the bonds is given in FIGURE 5.4 for this molecule.

FIGURE 5.4

FORCE CONSTANTS AND BOND NUMBERINGS FOR (COF)



In this figure, the atoms are also numbered for convenient reference to FIGURE 5.1, and the various types of force constant are indicated. With reference to FIGURES 5.1 and 5.4, the [S] vector is given for oxalyl

fluoride by

$$\begin{bmatrix} \triangle^{r}_{12} \\ \triangle^{r}_{23} \\ \triangle^{r}_{16} \\ \triangle^{r}_{24} \\ \triangle^{r}_{15} \\ (r_{23}r_{24})^{\frac{1}{2}} \triangle \phi_{324} \\ (r_{15}r_{16})^{\frac{1}{2}} \triangle \phi_{516} \\ (r_{12}r_{23})^{\frac{1}{2}} \triangle \phi_{215} \\ (r_{12}r_{23})^{\frac{1}{2}} \triangle \phi_{215} \\ (r_{12}r_{16})^{\frac{1}{2}} \triangle \phi_{216} \end{bmatrix} = \begin{bmatrix} \triangle^{r}_{1} \\ \triangle^{r}_{2} \\ \triangle^{r}_{2} \\ (r_{2}r_{3})^{\frac{1}{2}} \triangle \phi_{23} \\ (r_{2}r_{3})^{\frac{1}{2}} \triangle \phi_{23} \\ (r_{1}r_{3})^{\frac{1}{2}} \triangle \phi_{45} \\ (r_{1}r_{3})^{\frac{1}{2}} \triangle \phi_{45} \\ (r_{1}r_{2})^{\frac{1}{2}} \triangle \phi_{124} \\ (r_{1}r_{2})^{\frac{1}{2}} \triangle \phi_{124} \\ (r_{1}r_{2})^{\frac{1}{2}} \triangle \phi_{124} \\ (r_{1}r_{2})^{\frac{1}{2}} \triangle \phi_{14} \\ (r_{1}r_{2})^{\frac{1}{2}} \triangle \phi_{12} \\ (r_{1}r_{5})^{\frac{1}{2}} \triangle \phi_{15} \end{bmatrix} = \begin{bmatrix} S_{1} \\ S_{2} \\ S_{3} \\ S_{4} \\ S_{5} \\ S_{5} \\ S_{6} \\ (r_{5}, 44) \\ S_{7} \\ S_{8} \\ S_{9} \\ S_{10} \\ S_{11} \end{bmatrix}$$

The force constant vector $[\varphi]$ for oxalyl fluoride is given by

$$\begin{bmatrix} \varphi_{1} \\ \varphi_{2} \\ \varphi_{3} \\ \varphi_{4} \\ \varphi_{5} \\ \varphi_{6} \\ \varphi_{7} \\ \varphi_{8} \\ \varphi_{9} \\ \varphi_{10} \end{bmatrix} = \begin{bmatrix} K_{1} \\ K_{2} = K_{5} \\ K_{3} = K_{4} \\ H_{13}^{=} H_{14} \\ H_{23}^{=} H_{45} \\ H_{12}^{=} H_{15} \\ H_{13}^{=} F_{14} \\ F_{23}^{=} F_{45} \\ F_{12}^{=} F_{15} \\ C_{24}^{=} C_{35} \end{bmatrix} = \begin{bmatrix} K_{C} \\ K_{F} \\ K_{O} \\ H_{OC} \\ H_{CX} \\ H_{CX} \\ F_{OC} \\ F_{OX} \\ F_{OX} \\ F_{OX} \\ F_{OX} \\ H_{CX} \\ F_{OC} \\ F_{OX} \\ F_{OX} \\ F_{OX} \\ F_{OX} \\ H_{CX} \\ H_{$$

(5.45)

130.

For oxalyl fluoride the number of internal coordinates S_t (in-plane only) is eleven (i.e., $n_s = 11$). The number of force constants is ten (i.e., $n_{g} = 10$). The triangular form of the [\neq 7 matrix has $n_s(n_s + 1)/$ 2 = 66 elements and the dimensions of the [2] matrix are 66 x 10.

In the following, the columns of the [Z] matrix are given as $[Z_k]$ (k = l, n_{φ}) corresponding to the $\varphi_k(k = l, n_{\varphi})$. Where two or more force constants are equal (eg. $\varphi_7 = F_{13} = F_{14}$) the coefficients of φ_k each appear in the same column.

As an example, consider column $[Z_3]$ where $\varphi_3 = K_3 = K_4$. In the potential energy expression (5.36), the force constants K_3 and K_4 appear only in the terms $K_3(\bigtriangleup r_3)^2$ and $K_4(\bigtriangleup r_4)^2$; hence, these force constants appear only in the diagonal elements of the $[\mathcal{H}]$ matrix and their coefficients in the [Z] matrix are unity. From (5.44), $\bigtriangleup r_3 = S_4$, $S_t = S_u = S_4$ (or t = u = 4), and the position of the unit coefficient of K_3 is at n = 10 (from equation 5.40) in column $[Z_3]$. Similarly, $\bigtriangleup r_4 = S_5$ and the unit coefficient of $K_4(=K_3)$ appears at n = 15 in the same column.

As a further illustration, consider $[Z_7]$ where $\varphi_7 = F_{13} = F_{14}$. The

force constant F_{13} occurs in potential energy terms involving $\triangle r_1$, $\triangle r_3$, and $(r_1r_3)^{\frac{1}{2}} \triangle \phi_{13}$; therefore, in TABLE 5.7, $\triangle r_i = \triangle r_1 = S_1$, $\triangle r_j = \triangle r_3$ $= S_4$, and $(r_ir_j)^{\frac{1}{2}} \triangle \phi_{ij} = (r_1r_3)^{\frac{1}{2}} \triangle \phi_{13} = S_8$. For example, consider the calculation of n for $S_tS_u = S_sS_s = \triangle r_j(r_ir_j)^{\frac{1}{2}} \triangle \phi_{ij}$ where n gives the position of element Z_{n7} in $[Z_7]$. Substitution of t = 4 and u = 8in equation (5.40) gives n = 32. In a similar way, the values of n for all Z_{n7} can be calculated. Since $F_{13} = F_{14}$, the coefficients of F_{14} fall in column $[Z_7]$ of the [Z] matrix as do those of F_{13} . IVa. [Z] MATRIX CALCULATION WITH A DIGITAL COMPUTER:

The [Z] matrix has a large number of zero elements. For example, consider column $[Z_3]$ of the [Z] matrix for oxalyl fluoride whose elements were derived above. There are 66 elements in this column while only two elements are non-zero (i.e., $Z_{10,3}$ and $Z_{15,3}$). The inclusion of all these zero elements in the [Z] matrix makes an unnecessary demand on computer storage space; therefore, in the present calculations another matrix called the [Z'] matrix was defined.

The $\begin{bmatrix} 2 \end{bmatrix}$ matrix is obtained by leaving out all the zero elements of each column of the $\begin{bmatrix} 2 \end{bmatrix}$ matrix and collapsing all the non-zero elements

together. Inspection of TABLE 5.5 shows that any column, $[Z_{A}^{\prime}]$ where $\varphi_{k} = F_{ij}$ will have six elements or some multiple of six elements. For example, take the case $\varphi_{7} = F_{13} = F_{14}$ considered above for oxalyl fluoride. F_{13} and F_{14} will each contribute six non-zero elements to column $[Z_{7}^{\prime}]$ for a total of twelve non-zero elements. In a similar way, inspection of TABLE 5.8 shows that any column $[Z_{k}^{\prime}]$ where $\varphi_{k} = c_{ik}$ can have fifteen elements or a multiple of fifteen elements. The $[Z_{7}^{\prime}]$ matrix for oxalyl fluoride is given in TABLE 5.7.

Each element of the [Z'] matrix is given by $Z'_{n'k}$ where n' is not directly related to index n of Z_{nk} . An indicial matrix [K'] is defined whose elements $K'_{n'k}$ are the indices, n, of the elements Z_{nk} . There is a one-to-one correspondence between the elements of the [Z'] matrix and the elements of the [K'] matrix. For example, $Z'_{n'k}$ corresponds to $K'_{n'k}$. If $K'_{n'k} = n$ it can be seen that

or $Z'_{n'k} = Z_{K'_{n'k}k}$

The [K'] matrix of oxalyl fluoride is given in TABLE 5.8.

 $Z_{n^{i}k}^{i} = Z_{nk}$

The calculation of the [Z] and [K] matrices was programmed for the

TABLE 5.7

Чı	Y2	Ф3	94	P 5	φ6	cp 7	98	99	P 10	
1.000	1.000	1.000	1.000	1.000	1.000	0.813	0.795	0.684	0.085	
	1.000	1.000	1.000	1.000	1.000	0.697	0.734	0.609	1.010	
			×			0.294	0.291	0.387	0.801	1.010+
						0.797	0.807	0.710	0.510	0.801
*			• • • • • • • • • • • • • • • • • • •		_	0.393	0.380	0.436	0.368	0.510
They	are calcu	lated to e	ight decim	al places l	pà.	0.342	0.353	0.401	0.934	0.368
the	computer.					0.813	0.795	0.684	0.632	0.434
this the	column she	ould contin	nue from t	he bottom (of	0.697	0.734	0.609	0.667	0.632
		10				0.294	0.291	0.387	0.542	0.667
						0.797	0.807	0.710	0.176	0.542
						0.393	0.380	0.436	0.762	0.176
				0.342	0.353	0.401	0.495	0.762		
									0.660	0.495
									0.245	0.660
									0.621	0.245

134.

0.085 0.621

TABLE 5.8

[K'] MATRIX FOR OXALYL FLUORIDE

	φ_1	\mathscr{P}_2	φ_3	<i>\$</i> 4	Ф5	Р6	Ф7	\$P8	φ_9	φ_{10}	
	1	3	10	36	21	55	1	3	1	3	6+
		6	15	45	28	66	10	10	3	15	10
							36	21	55	l	1
							7	8	2	12	9
*	· . '						29	17	46	2	4
							32	19	47	11	7
this co	lumn shou	ald con	ntinue f	rom the	bottom		1	6	l	55	66
or one	COLOURI HE	saueu ç	P10*				15	15	6	45	36
							45	28	66	54	63
							11	13	4	47	58
							37	24	56	50	59
							41	26	58	46	56
										38	31
							*			41	32
										37	29

+

IBM 7040 computer in FORTRAN IV language. With this program it is possible to calculate the [Z'] and [K'] matrices for any molecule. Input to the program consists of bond lengths and angles, and indices of the internal coordinates, S_t , which correspond to them. The bond lengths and angles are used to evaluate the expressions given in TABLES 5.5 and 5.6. The indices are used to calculate the elements of [K'] using equation (5.40). V.CALCULATIONS OF FORCE CONSTANTS FROM OBSERVED FREQUENCIES:

The secular equation (5.27) is solved to give the eigenvector $[Y_{l}]$ and calculated eigenvalues λ_{l}^{c} , i.e.,

$$[D]^{t}[7][D][Y_{l}] = [Y_{l}]\lambda_{l}^{c}$$

$$[J] = [z][\varphi]$$
(5.46)

where

Since $[\mathscr{P}]$ is not generally known in advance, it is usually approximated and hence the calculated roots, λ_{ℓ}^{c} , do not agree with the observed parameters ($\lambda_{\ell}^{o} = 4\pi^{2}c^{2}\lambda_{\ell}^{o^{2}}$). The assumed force constants are therefore adjusted systematically until the agreement between λ_{ℓ}^{o} and λ_{ℓ}^{c} is acceptable.

A correction to $[\mathcal{P}]$ is sought such that $\lambda_{\mathcal{L}}^{c} - \lambda_{\mathcal{L}}^{o} = 0$. Let the $(i-1)^{th}$ set of force constants be $[\varphi^{i-1}]$ and let the corresponding calculated roots be $[\Lambda^{i-1}]$. The difference between the observed and calculated roots be given by

$$\left[\mathcal{E}^{i-1}\right] = \left[\mathcal{N}^{\circ}\right] - \left[\mathcal{N}^{i-1}\right] \tag{5.47}$$

A set of corrections to the force constants, $[\Delta \phi^{i-1}]$, is sought such that

$$\begin{bmatrix} J^{\varphi} \end{bmatrix} \begin{bmatrix} \Delta \varphi^{i-1} \end{bmatrix} = \begin{bmatrix} \varepsilon^{i-1} \end{bmatrix}$$
(5.45)

where $[J^{\mathcal{G}}]$ is the Jacobian matrix whose elements are

$$J_{\ell k}^{q} = \frac{\partial \lambda_{\ell}}{\partial \mathcal{G}_{k}}$$

Calculation of this matrix will be discussed later.

It has been assumed in (5.48) that for small changes $\Delta \lambda_{\perp}, \Delta \varphi_{\perp}$ a linear relationship exists between λ_{\perp} and φ_{\perp} . Since the relationship is not linear for large $[\Delta \varphi^{i-1}]$, usually several cycles of refinement are required in which $[\varphi]$ is adjusted by a small amount for each cycle. In particular, for the (i-1)th cycle, a set of residuals is defined by

$$[\mathbf{r}] = [J^{\varphi}] [\Delta \varphi] - [\mathcal{E}]$$
(5.49)

where the superscript (i-1) has been temporarily dropped for convenience. The sum of the squares of the residuals is given by

$$\mathbf{X} = [\mathbf{r}]^{\mathsf{T}} [\mathbf{W}] [\mathbf{r}] \tag{5.50}$$

where [W] is a diagonal matrix whose elements W_i are the weighting factors which will be described later.

Substitution of [r] from (5.49) into (5.50) followed by expansion and rearrangement gives

$$X = [\Delta \phi]^{t} [J \varphi]^{t} [W] [J \varphi] [\Delta \varphi] - 2[\mathcal{E}]^{t} [W] [J] [\Delta \varphi] \quad (5.51)$$

Minimizations of X with respect to [$\Delta \varphi$] gives

$$\begin{bmatrix} \frac{\partial \mathbf{x}}{\partial \Delta \phi} \end{bmatrix} = 0 = 2 \left[\Delta \varphi \right]^{t} \left[\mathbf{y}^{2} \right]^{t} \left[\mathbf{w} \right] \left[\mathbf{y}^{2} \right] - 2 \left[\mathcal{E} \right]^{t} \left[\mathbf{w} \right] \left[\mathbf{y}^{2} \right] \quad (5.52)$$

Rearrangement of (5.52) gives

$$\left[\Delta \mathcal{G}^{i-1}\right] = \left[\left[J\mathcal{G}\right]^{t}\left[W\right]\left[J\mathcal{G}\right]^{-1}\left[J\mathcal{G}\right]^{t}\left[W\right]\left[\mathcal{E}^{i-1}\right]\right]$$
(5.53)

where the superscript (i-1) has been reinstated. The ith set of force constants thus becomes

$$[g^{i}] = [g^{i-1}] + [\Delta g^{i-1}]$$

$$(5.54)$$

These $[cp^{i}]$ are now inserted into (5.26) and a new set of calculated roots λ_{ℓ}^{i} is obtained for which $[\mathcal{E}^{i}] \leq [\mathcal{E}^{i-1}]$. The cycling is continued until the sum of the squares of the residuals, X is a minimum. Note that equation (5.4) consists of n pequations in n unknowns

where n_{γ} is the number of observed frequencies. If $n_{\gamma} > n_{\varphi}$ equation (5.43) is soluble; however, if $n_{\gamma} < n_{\varphi}$ the above treatment does not apply and certain further approximations (such as transferring force constants from related molecules) must be made.

WEIGHT MATRIX, [W]:

The elements W_i of the weight matrix used here are given by

$$W_{i} = \left(\frac{1}{\lambda_{i}^{\circ}}\right)$$

140.

(5.55)

As pointed out by Overend and Scherer this choice of weight matrix fits the calculated roots to the observed roots on a percentage basis. When a frequency (and hence, root) was not observed experimentally, it was given a weight, $W_i = 0$, in the calculation. Va. THE JACOBIAN MATRIX, [J9]:

If the [7] matrix in equation (5.46) is perturbed by an amount $[\Delta F]$, the corresponding change in the l^{th} root is Δh_l and equation (5.46) becomes

 $\int DJ^{t} [\mathcal{F} + \Delta \mathcal{F}] [D] [Y, J \approx [Y,] (\lambda_{\ell}^{\circ} + \Delta \lambda_{\ell})$

$$[D]^{t}[J][D][Y_{l}] + [D]^{t}[\Delta J][D][Y_{l}] \approx [Y_{l}] \lambda_{\ell}^{2} + (Y_{l}] \Delta \lambda_{\ell} \quad (5.56)$$

where it is assumed that for a small change $in[\mathcal{F}]$, $[Y_{\mathcal{L}}]$ is changed by a negligible amount.

Combination of (5.46) and (5.56) gives

$$[D]^{t}[\Delta \neq J[D][Y_{\ell}] \gtrsim [Y_{\ell}] \Delta \lambda \ell \qquad (5.57)$$

Premultiplication of (5.57) by $\begin{bmatrix} \mathbf{x} \end{bmatrix}^{t}$ gives

$$[\mathbf{L}_{\mathcal{J}}^{\mathsf{T}}[\Delta \mathcal{F}][\mathbf{L}_{\mathcal{J}}] \approx \Delta \lambda \boldsymbol{\ell} \tag{5.58}$$

$$[L] = [D] [Y] \sim (5.23)$$

$$[\mathbf{Y}]^{\mathsf{t}}[\mathbf{Y}] = [\mathbf{E}] \tag{5.18}$$

since

and

or

Since the g, are linearly related to [7],

$$[\Delta f] = [z] [\Delta \varphi]$$
(5.59)

and (5.58) becomes

$$[I_{j}]^{t}[Z][I_{j}][\Delta \varphi] = \Delta \lambda e \qquad (5.60)$$

Comparison of (5.60) with (5.48) shows that

$$[L_{j}^{t}[Z_{j}]] = [J_{j}^{\varphi}]$$
(5.61)

since $[J_{j}^{\varphi}]$ is the l^{th} row of $[J^{\varphi}]$.

In non-matrix notation each element $(J^{\varphi})_{\ell k}$ is given by

$$(J^{q})_{lk} = \sum_{t=1}^{n_{s}} \sum_{u=1}^{n_{s}} L_{lt} L_{u} Z_{nk}$$
 (5.62)

where subscript n of Z_{nk} is given in terms of t and u by equation (5.40).

VD. POTENTIAL ENERGY DISTRIBUTION:

The potential energy is given by

$$2\mathbf{V} = [\mathbf{Q}]^{t} [\mathbf{Y}]^{t} [\mathbf{D}]^{t} [\mathbf{F}] [\mathbf{D}] [\mathbf{Y}] [\mathbf{Q}]$$
(5.24)

The contribution to the potential energy by any normal vibration $\lambda_{\mathscr{L}}$

is given by

$$2V_{\lambda_{\ell}} = [Y_{\ell}]^{t} [D]^{t} [\mathcal{F}] [D] [Y_{\ell}] = \lambda_{\ell}$$
(5.63)

since $Q_{\mathcal{L}}^2 = 1$, by definition, and where equation (5.26) has been used.

Since $[L_{2} = [D][Y_{2}]$ (equation (5.23)) it is seen that (5.63) becomes

$$\lambda_{I} = [L_{I}J^{t}(F)[L_{I}]$$
(5.64)

Furthermore, it is noted that if $[\mathcal{F}]$ is written in the form

$$[77 = [z](\varphi] \tag{5.42}$$

equation (5.64) becomes

$$\lambda_{I} = [L_{I}]^{\dagger} [Z] [L_{I}] [\varphi]$$
(5.65)

or

$$\lambda_{\ell} = \left[J_{\ell}^{\mathcal{G}} \right] \left[\mathcal{G} \right] \tag{5.66}$$

where $[J_{\ell}^{\varphi}]$ is given by (5.61).

In (5.66) the contribution of each φ_k to potential energy $2V_{\lambda \ell}$ is given by

$$\lambda_{\ell k} = (J^{\varphi}_{\ell k}) \varphi_{k}$$
 (5.67)

since from (5.63)

2V Ne = Ne

Thus, it is seen from (5.66) that

$$\lambda_{l} = \sum_{k=1}^{n_{\varphi}} J_{lk}^{\varphi} \cdot \varphi_{k}$$
(5.68)

If the potential energy $2V_{\lambda,\ell}$ given by (5.68) is normalized to unity, then

$$\frac{1}{\lambda \iota} \sum_{k=1}^{n_{\varphi}} J_{\ell k}^{\varphi} \cdot \varphi_{k} = 1$$
 (5.69)

and each element of the sum (5.69),

$$\frac{1}{\lambda_{\ell}} \cdot J_{\ell k}^{\varphi} \cdot \mathcal{G}_{k}$$
(5.70)

is an element of the potential energy distribution matrix which shall be designated $[V_{3}]$. It can be seen from (5.70) that such a matrix is given by

$$\begin{bmatrix} \mathbf{v}^{\varphi}_{\lambda} \end{bmatrix} = \begin{bmatrix} \mathbf{J}^{\varphi} \end{bmatrix} \begin{bmatrix} \mathbf{N} \end{bmatrix}^{-1} \begin{bmatrix} \varphi^* \end{bmatrix}$$
(5.71)

where $[g^*]$ is a diagonal matrix formed from the \mathcal{G}_k 's. It can be seen that is [4] were written as a column vector (5.71) would become a column vector with elements given by (5.68).

VC.CALCULATION OF FORCE CONSTANTS ON A DIGITAL COMPUTER:

The IEM 7040 digital computor has been programmed in FORTRAN IV to calculate force constants. A block diagram of the computer program is given in FIGURE 5.5. This diagram shows the essential features of the program although some incidental steps in the calculations and input are not included.

The most important features of the program are as follows:

(i) The integer n_I (see diagram) is the number of cycles of refinement which are desired. The integer I is increased by l after each cycle until I = n_I. At this point [7], [√], [√], [√], [V^P_λ], [L], [J^P], and [9] are printed

out. In order to follow the course of the refinement, $[JJ, [v], [g], and [\Delta g]$ are printed out in every cycle.

(ii) The [Z] matrix does not appear explicitly in the calculations of [J], and [JY].

Equation (5.42) for [77] can be rewritten as

$$\begin{bmatrix} \neq J \end{bmatrix} = \sum_{k=1}^{n_{\varphi}} \varphi_{k} \cdot \begin{bmatrix} z_{k} \end{bmatrix}$$
(5.72)

The columns $\begin{bmatrix} Z_k \end{bmatrix}$ are constructed one by one from $\begin{bmatrix} Z_k' \end{bmatrix}$ and $\begin{bmatrix} K_k' \end{bmatrix}$ and the products $\mathcal{G}_k[Z_k]$ are accumulated in the $[\mathcal{F}]$ matrix.

The expression for the l^{th} row of $(J \mathcal{P}_{J})$, i.e.,

 $[J_{\ell}^{\varphi}]$ (equation (5.62)) can be rewritten as

$$\begin{bmatrix} J_{\ell}^{\mathcal{G}} \end{bmatrix} = \begin{bmatrix} L_{\ell} \end{bmatrix}^{t} \sum_{k=1}^{d} \begin{bmatrix} Z_{k} \end{bmatrix} \begin{bmatrix} L_{\ell} \end{bmatrix}$$
(5.73)

Thus, each column $[J_k^{\mathcal{Y}}]$ is given by

$$[J_{k}^{\mathscr{P}}] = [L]^{t} [Z_{k}] [L]$$
(5.74)

The $[J\mathcal{Y}]$ matrix is constructed column by column where the $[Z_k]$ are obtained one by one from $[Z_k']$ and $[K_k']$. (iii) The matrix $(D)^t [\mathcal{F} \mathcal{J} [D \mathcal{J}$ is diagonalized to give [Y] and FAJ by the Eigen-Jacobi method.

The author is indebted to Dr. K. Ramaswamy for the diagonalization subroutine.

(iv) The roots λ_{ℓ}^{c} obtained by the Eigen-Jacobi method are not arranged in descending order of magnitude. A subroutine has been written which arranges the roots λ_{ℓ}^{c} and their corresponding eigenvectors $[Y_{\ell}]$ in descending order.

The author is indebted to Dr. D.J. Kenworthy for a very helpful discussion on this point.

(v) The matrix [J^J^t [W][J^g] was diagonalized by a sub routine given to the author by Dr. D.J. Kenworthy. The
 matrix is reduced to an equivalent triangular form which
 is then inverted. This method of matrix inversion is less

sensitive than others to the degree of singularity of the matrix. In the course of a calculation $[J\overline{J}^{t}(W)][J^{\varphi}]$ may become nearly singular.

FIGURE 5.5

COMPUTER PROGRAMME FOR FORCE CONSTANT CALCULATIONS



VI.CALCULATIONS:

The previously outlined calculation was carried out for the trans isomer of oxalyl fluoride, oxalyl chloride, and oxalyl chloride fluoride.

In order that the least squares procedure outlined in section V can be carried out, the condition $n_{\mathcal{V}} > n_{\mathcal{G}}$ must be met. This condition is met neither for the in-plane nor the out-of-plane vibrations of the above molecules. Nevertheless, in the case of the in-plane vibrations, it was feasible to transfer the values of certain force constants from similar molecules and to constrain them. Constraints were applied by omitting the appropriate columns of the Jacobian matrix when it was used in the calculation of $[\mathcal{A}\mathcal{G}]$. When this was done, the calculated corrections, $\mathcal{A}\mathcal{G}_k^{}$, to the constrained force constants were zero.

For each molecule, the frequencies of only two of the three out-ofplane fundamental modes were observed in the spectra, while at least three force constants, torsional, out-of-plane bending, and torsional-bending interaction, would have to be calculated from these observed frequencies. Furthermore, the out-of-plane force constants of similar molecules have not been determined and hence, a force constant transfer is impossible. VIa.OXALYL FLUORIDE:

The force constant vector of oxalyl fluoride was defined in equation (5.45). The [Z'], [K'], and [D] matrices were given previously as examples.

The initial force constants were transferred from other molecules. These force constants form the vector $\left[\varphi^{(1)}\right]$ which is given in TABLE 5.9.

TABLE 5.9

TRIAL FORCE CONSTANTS FOR OXALYL FLUORIDE

[9 (ma	(1)] d./A)**	MOLECULE	[4(1)] (md./A)
K _C	4.896	sym-trichlorobenzene ⁵¹	2.000
KF	4.528	carbonyl fluoride45	4.500
KO	12.85	21 12	12.000
HOC	0.408	acetyl chloride46	0.500
HOF	0.286* + .	carbonyl fluoride45	0.286
H	0.100* +	perfluoroethylene ^{4,2}	0.000+
FOC	0.497	acetyl chloride46	1.200
FOF	1.578	carbonyl fluoride	1.200
FCF	1.37	perfluoroethylene ⁴²	1.200
COF	0.000		0.000

These force constants have been adjusted to take account of the scaling factors $(r_i r_j)^{\hat{z}}$, of the $\bigtriangleup \phi_{ij}$.

+ These are constrained force constants.

** md./A = millidynes/A where the bond lengths are in Angstroms, the angles are in radians, and the masses are in atomic units.

The trial force constant vector $\left[\varphi^{(1)} \right]$ given in TABLE 5.9 was used in several trial calculations in which various sets of force constants in $\left[\mathcal{O}^{(1)} \right]$ were constrained while the remainder were varied. It was found that the most suitable force constants to constrain were ${\rm H}_{\rm OF}$ and H_{CF} . If $H_{CF} = 0.100 \text{ md./A}$, the value of F_{CF} converges to a negative value, while if $H_{CF} = 0.000$, F_{CF} converges to a small but positive value. It was also found that ${\rm K}_{\rm C}$ has a much smaller value for oxalyl fluoride than for sym-trichlorobenzene. The trial force constants $\left[\varphi^{(1)}\right]$ were adopted in the final calculations, since these force constants were closer in magnitude to the converged values than were the force constants $[q^{(1)}]$ and hence, fewer cycles of convergence were required.

The observed and calculated frequencies of the in-plane modes of oxalyl fluoride are given in TABLE 5.10. The potential energy distributions and calculated force constants are given in TABLE 5.11.

The normal coordinate diagrams were obtained from the eigenvectors $[Y_k]$. It is noted from equation (5.15) that

$$Q_{k} = \left[Y_{k}^{\dagger}\right] \left[\eta\right]$$
(5.75)

The eigenvectors $\begin{bmatrix} Y_k \end{bmatrix}$ are normalized and their elements Y_{ik} are the normalized amplitudes of vibration of the atoms in Cartesian space.

- (i) A scale diagram of the molecule was constructed.
- (ii) The Y_{ik} were plotted as the Cartesian components of the atomic displacements. (Note that each Y_{ik} is the normalized coefficient of an γ_i which is a Cartesian displacement coordinate of a given atom.)

The normal coordinate diagrams for the vibrational modes of trans oxalyl fluoride are given in FIGURE 5.7. The diagrams provide a quantitative description of the normal modes for which only qualitative descriptions were given in Chapter 4.

The potential energy distributions show the relationships between the Urey-Bradley force constants and the normal frequencies. For example, 809cm^{-1} (assigned in Chapter 4 to the C-C stretching mode $\mathcal{P}_{3}^{\prime}(a_{\mathrm{g}})$) is determined by the values of K_{C} , K_{F} , F_{OC} , and F_{OF} ; thus, it is seen that the low frequency is not due entirely to the low value of K_{C} . The frequency 1286cm⁻¹ (assigned in Chapter 4 to the symmetric C-F stretching mode $\mathcal{P}_{2}^{\prime}(a_{\mathrm{g}})$) is primarily determined by the potential energy term in K_{F} ; however, there are significant contributions from terms in K_{C} and H_{OC} . The involvement of H_{OC} in the 1286cm⁻¹ normal mode can be seen from the

TABLE 5.10

OBSERVED AND CALCULATED FREQUENCIES OF OXALYL FLUORIDE

SYMMETRY	FREQUENCIES	ERROR
	OBS. CALC.	(%)
ag	ν_{1} 1872 1884	0.64
		0.15
	z 809 810	0.12
	Z 4 565 565	0
	2 5 292 292	0
bu	- 1870 1858	0.64
	1098 1099	0.09
	2 ₁₁ 672 672	0
	→ ₁₂ 255 255	0

151.

TARIE	5	77
TUDTIC	20	diale

			IA Y TLATI TIRATIC	~~ <i>1</i> /21/216/21/	ONTON OF	OMMIN IN	00112010 214	01.123.1 131.1A	DITUT DI VOI	5	
2	(cm ⁻¹)	K	c ^K F	ĸ _o	H _{OC}	H _{OF}	H _{CF}	F _{OC}	F _{OF}	F _{CF}	C _{OF}
ag	1872		2 8	82	4	0	0	l	1	0	2
0	1286	2	1 41	5	16	6	0	5	5	0	1
	809	2	2 19	3	0	7	0	20	27	1	l
	565		4 10	2	28	L.	0	38	10	0	4
	292		7 8	0	11	19	0	2	17	1.6	20
bu	1870	(0 6	87	0	0	0	5	l	0	l
	1098	(0 74	2	5	5	0	5	8	2	0
	672	(D 5	l	17	23	0	10	43	0	2
	255	(2 1	1	19	10	0	11	9	9	41
[\varphi]	(md./A)	2.04	0 4.817	12.228	0.482	0.286+	0.000*	1.066	1.282	0.119	0.185

POTENTIAL ENERGY DISTRIBUTION OF OXALYL FLUORIDE IN UREY-BRADLEY SPACE

+ constrained values.

152.

NORMAL COORDINATE DIAGRAMS OF OXALYL FLUORIDE


normal coordinate diagram (FIGURE 5.7). Extension of the C-F bonds in this mode produces bending of the C-CO angles.

In general it is seen from the potential energy distributions and normal coordinate diagrams, that the concept of bond frequencies, which was discussed briefly in Chapter 4, is not supported except for the carbonyl stretching and antisymmetric C-F stretching frequencies.

Discussion of the calculated force constants is deferred until after the results for oxalyl chloride, and oxalyl chloride fluoride are given.

In addition to the potential energy distributions and force constants, calculated [FJ and [L] matrices were obtained. These matrices are given in the APPENDIX.

VID.OXALYL CHLORIDE:

The [ZJ, [K], and [D] matrices of oxalyl chloride are given in the APPENDIX.

The initial set of force constants $[\varphi^{(1)}]$ used for the oxalyl chloride calculations was transferred from other molecules and is given in TABLE 5.12.

TABLE 5.12

	an a weat - and		A R R R A R R R R R R R R R R R R R R R
[cp (m	(1)] d./Å)	MOLECULE	[g (1)'] (md./Å)
к _с Ксі	2.040 ⁺ 1.990 ⁺	oxalyl fluoride phosgene ⁴⁵	2.040 ⁺ 1.990
KO	12.231	oxalyl fluoride	11.772
HOC	0.482 +	82 82	0.482
HOCI	0.214*+	phosgene ⁴⁵	0.214+
HCCI	0.000+	28	0.000+
FOC	1.065	oxalyl fluoride	0.592+
FOCI	0.860	phosgene ⁴⁵	1.093*
FCCI	0.920	perchloroethylene 42	0.722
COCI	0.000+	610,00 mg 40,00	0.000

* Adjusted to account for the scaling factor $(r_i r_j)^{\frac{1}{2}}$ of $\triangle \phi_{ij}$.

TRIAL FORCE CONSTANTS FOR OXALYL CHLORIDE

+ Constrained force constants

Only eight of the nine in-plane frequencies of this molecule were observed experimentally, while ten force constants were to be determined from them. The unobserved fundamental frequency, $\nabla_{12}^{\prime}(b_u)$ was given zero weight in the calculations by putting $W_{12} = 0$ in the weight matrix. Several trial calculations in which various sets of constraints were employed, showed the calculated corrections to K_c and H_{CC} were not independent. In other words, in a given cycle of convergence, a small positive correction to K_{C} resulted in a negative correction to H_{OC} and vice versa. If convergence was allowed to proceed, K_{C} converged to a reasonable value, (3.494 md./A), but H_{OC} converged to a negative value, (-0.799 md./A). The finally adopted constraints in $[\wp^{(1)}]$ are given in TABLE 5.12.

It was found that the value of C_{OC1} was principally dependent on the unobserved frequency $\mathcal{V}_{12}(b_u)$. Since $\mathcal{V}_{12}(b_u)$ had been given zero weight in the calculations of $[\mathcal{G}]$, it was, therefore, not possible to get a good value of C_{OC1} by using a simple procedure. The following procedure was adopted.

- (i) The calculations were carried out with $[\varphi^{(1)}]$ as the trial force constant vector.
- (ii) The values of F_{OC} , F_{OC1} , F_{CC1} which were calculated with the trial set $[\mathcal{G}^{(1)}]$ were transferred to $[\mathcal{G}^{(1)}]$ and constrained. The constraints on C_{OC1} and K_{C1} were released in $[\mathcal{G}^{(1)}]$.
- (iii) The calculations were carried out again with the trial force constant vector (g⁽¹⁾) which is given in TABLE 5.12.

The frequencies calculated with $[g^{(1)}]$ and $[g^{(1)}]$ are given in TABLE 5.13 under the columns headed I and II, respectively. The calculated frequencies in column II were taken as the best values because they agreed best with the observed frequencies. The agreement between observed and calculated frequencies was considered to be sufficiently good to confirm the assignments given in Chapter 4.

The potential energy distributions and calculated force constants are given in TABLE 5.14. The normal coordinate diagrams are presented in FIGURE 5.8. Calculated (\neq] and [L] matrices are given in the APPENDIX.

The most striking feature of the potential energy distribution is the low contribution (13%) made by the potential energy term in K_{Cl} to the 619cm⁻¹ mode. In Chapter 4, 619cm⁻¹ was assigned to the symmetric C-Cl stretching mode $\gamma_3^2(a_g)$. With reference to the normal coordinate diagram for this mode (FIGURE 5.8) it is also seen that the normalized amplitudes of the chlorine atoms are small relative to those of the other atoms. In the classical approximation, it is noted that each potential energy term is proportional to the normalized amplitude TABLE 5.13

OBSERVED AND CALCULATED FREQUENCIES OF OXALYL CHLORIDE

SYMMETRY			FREQU	ENCIES (cm	-l)		ER	ROR
			OBS.	CALC.		*	(%)
				I	II		I	II
ag	·	\mathcal{V}_1	1778	1806	1806		1.2	1.2
		ν_2	1078	1103	1093		2.3	1.4
		ν_3	619	632	629		2.1	1.6
		\mathcal{P}_4	465	435	431		6.4	7.2
		25	276	269	279		2.5	1.1
b _u		v_9	1790	1761	1759		1.6	1.6
		210	778	823	797		5.8	2.4
		211	520 .	529	521		1.7	0.2
		\mathcal{V}_{12}	210 ^a	182	207			

a calculated from overtone or combination frequencies

MA TOT 10	1	-	£.
TABLE	2.	J.	L

		A CANNELLING	269 and 6 miles and an an	6 2×60,2 V 6 4 V	11 OL 0224133		LJ 22.11 (J 21)2J.	a 20° a 64 base dad <u>a</u> d da	011000		
	$\mathcal{V}(\mathrm{cm}^{-1})$	к _с	KCI	K _O	H _{OC}	HOCL	H _{CCL}	F_{OC}	F _{OC1.}	F _{CC1}	COCI
8.	1778	3	2	88	. 3	0	0	0	1	2	l
5	1078	33	14	0	28	9	0	5	4	6	1
	619	16	13	5	12	1	0	25	18	8	2
	465	7	22	1	12	6	0	15	35	0	2
	276	0	12	0	l	13	0	0	8	56	2
b.	1790	0	l	93	0	0	0	3	1	0	1
u	778	0	33	0	18	16	0	7	8	18	1
	520	0	24	0	8	9	0	3	51	3	1
	210 ⁸	0	1	0	21	4	0	8	7	37	22
[\$]	(md./A)	2.040+	1.649	11.666	0.482+	0.214	0.000+	0.592	1.093	0.722	0.100

POTENTIAL ENERGY DISTRIBUTION OF OXALYL CHLORIDE IN UREY-BRADLEY SPACE

a calculated from overtone or combination frequencies

+ transferred

158.



NORMAL COORDINATE DIAGRAMS OF OXALYL CHLORIDE



squared times the force constant. The normalized amplitudes of the carbon atoms, for example, are greater than those of the chlorine atoms In addition, $K_{C} > K_{Cl}$, thus, the potential energy term in K_{C} should indeed contribute more to the potential energy than the term in K_{Cl} . VIc.OXALYL CHLORIDE FLUORIDE:

The [2'], [K'], and [D] matrices of this molecule are presented in the APPENDIX.

The initial set of force constants $[\varphi^{(1)}]$ were transferred from oxalyl chloride and oxalyl fluoride. The values of the force constants K_0 , H_{0C} , and F_{0C} were taken as the arithmetic means of the values obtained for the "parent" molecules. The vector $[\varphi^{(1)}]$ in this case was given by

$$\left[\mathscr{P}(1) \right] = \begin{pmatrix} K_{C} \\ K_{F} \\ K_{C1} \\ K_{O} \\ H_{OC} \\ H_{OC} \\ H_{OF} \\ H_{CC1} \\ H_{CF} \\ H_{CC1} \\ H_{CF} \\ H_{CC1} \\ F_{CC} \\ F_{CC} \\ F_{CC} \\ F_{OF} \\ F_{CC1} \\ F_{CC1} \\ F_{CC} \\ F_{CC1} \\ F_$$

The internal coordinates S_{t} are given by equation (5.44).

The frequencies of only eight of all nine in-plane modes were observed. There are sixteen force constants in $[\varphi^{(1)}]$; therefore, the values of at least nine force constants had to be constrained in order that the least squares procedure could be applied. Trial calculations in which various constraints were employed led either to poor calculated frequencies or to unacceptable force constants. The least squares procedure, therefore, was not applied. The frequencies calculated directly from $\left[\varphi^{(1)}\right]$ are presented in TABLE 5.15. The agreement between the observed and calculated frequencies is not excellent but is, however, sufficiently good to confirm the fundamental frequencies obtained from the spectral analysis in Chapter 4. The agreement between these observed and calculated frequencies also shows that the force constants calculated for oxalyl fluoride and oxalyl chloride are reasonable.

The potential energy distributions are given in TABLE 5.16. The normal coordinate diagrams are given in FIGURE 5.9.

VId.FORCE CONSTANTS:

The accuracy of the force constants calculated here may be quite

TABLE 5.15

OBSERVED AND CALCULATED FREQUENCIES OF OXALYL CHLORIDE FLUORIDE

SYMMETRY

a

	FREQU	JENCIES (cm	·1)	ERROR
	OBS.	CALC.		(%)
v_1	1859	1839		l
\mathcal{P}_2	1790	1795		0.3
23	1197	1326		11
24	932	908		2.6
25	713	708		.7
26	570	582		2.1
27	491	466		5.1
28	278	294		5.8
29		222		

TABLE	5.16	
to a black dealder	10000	

POTENTIAL ENERGY DISTRIBUTION OF OXALYL CHLORIDE FLUORIDE IN UREY-BRADLEY SPACE

	2/(cm ⁻¹)	K _C	K _F	KCI	ĸ _o	H _{OC}	H _{OF}	HOCI	H _{CF}	Нссі	\mathbf{F}_{OC}	F _{OF}	FOCL	F _{CF}	Fccl	COCI	C _{OF}
a'	1858	l	7	0	85	3	0	0	0	0	2	1	0	0	0	0	1
	1790	l	0	1	92	1	0	0	0	0	4	1	1	0	2	l	0
	1197	16	36	0	5	12	5	l	0	0	3	15	0	0	5	0	0
	932	18	17	16	0	17	0	11	0	0	9	4	5	2	0	1	0
	713	11	8	10	3	11	7	l	0	0	22	15	3	0	6	2	0
	570	2	10	5	1	19	9	4	0	0	16	13	17	0	2	0	2
	491	4	2	23	1	11	l	4	0	0	16	2	32	0	2	3	0
	278	2	1	5	1	8	12	5	0	0	2	15	3	8	23	15	2
	222 ^C	0	0	0	l	19	l	6	0	0	9	1	7	3	24	15	15
[\$]	$(md./A)^+$	2.040	4.817	1.649	11.986	0.412	0.286	0.214	0.000	0.000	0,829	1.282	1.093	0.118	0.722	0.185	0.100
	+ all val	ues tr	ansfer	red				c cal	Lculate	ed in r	ormal	coord	inate a	analys:	is		

162.



NORMAL COORDINATE DIAGRAMS FOR OXALYL CHLORIDE FLUORIDE



dependent on the nature of the constraints which were applied in the above calculations. As a result, small deviations of the above force constants from those calculated for other molecules may not be considered to be significant; however, an attempt should be made to explain the very low values obtained here for K_C and F_{CF} .

The value obtained here for $K_{\rm C}$ is 2.040 md./Å. The value of $K_{\rm C}$ for the single bond in the halogenated ethanes varies from 2.00 - 3.00 md./Å. The low value of $K_{\rm C}$ for the oxalyl halides may indicate that the C-C bond in these molecules is very weak. In molecules of similar structure, particularly oxalic acid, it has been established that the C-C bond length is at least as long as the typical single-bond value; in the well-known case of the planar moleculer N_2O_4 , the central bond is extraordinarily long. There is, hence, no particular reason to expect a large value for $K_{\rm C}$ here on account of double-bond character.

The value of F_{CF} is known to vary from molecule to molecule. In TABLE 5.17 some sample values of F_{CF} are given. To the extent that the repulsive force constants are due to Van der Waals repulsions between non-bonded atoms, the variations of F_{CF} can be explained. The Van der Waals forces between non-bonded atoms are qualitatively dependent on the distances between the non-bonded atoms and on the electron densities on the atoms. The relatively small variations in F_{CF} shown by the first four molecules in TABLE 5.17 have been attributed by Scherer et al.⁴³ to variations in the F . . . C distances. The difference between the F_{CF} value of oxalyl fluoride and those of the other molecules appears to be too large to be accounted for in this way. It is possible that the low F_{CF} value for oxalyl fluoride results from a changed electron density distribution on the interacting atoms, as a result of the high electronegativities of the fluorine and oxygen atoms with respect to the carbon atoms to which they are attached.

TABLE 5.17

VARIATION OF FCF

F _{CF} o(md./A)		MOLECULE
1.3 1.073 1.37		38 C ₂ F ₆ 44 CH ₂ CF ₂ 42 C ₂ F ₄
0.946		sym-trifluorobenzene47
0.119		(COF)2

CHAPTER 6

ULTRAVIOLET SPECTRA OF OXALYL FLUORIDE

A detailed analysis of the ultraviolet spectra of oxalyl fluoride is presently being pursued by Mr. W. Balfour of this research group. In the following, only the results of a preliminary investigation of the spectra as observed under low resolution are described, and a very tentative vibrational analysis is presented.

I.MOLECULAR ORBITALS OF OXALYL FLUORIDE:

The ground state vibrational analysis of oxalyl fluoride has shown that the molecule is.planar and trans. The related molecule glyoxal is known to be planar and trans in both the ground state and the lowest excited state.⁵⁰ The following discussion is based on the assumption of this geometry.

The single electron LCAO/MO's of exalyl fluoride are given schematically in FIGURE 6.1. The relative energies which are schematically represented in FIGURE 6.1 are those adopted by Sidman and McClure for biacetyl.⁴⁸ The σ (bonding) orbitals and the non-bonded p orbitals on the fluorine atoms are not given in this figure. The σ^{\times} (antibonding) orbitals should be higher in energy than the orbitals shown in FIGURE 6.1.

The molecular orbitals can be classified under the irreducible

165.

FIGURE 6.1











a'u



<u>++</u> 77

<u>**</u> 11

representations (symmetry species) of the molecular point group (TABLE 3.3)

 C_{2h} , of trans oxalyl fluoride. The symmetry species of the molecular orbitals in FIGURE 6.1 are given by the symbols listed beneath the column headed SYMMETRY. Note that lower case letters are used for these symbols when they refer to molecular orbitals. Single and double primes are used to distinguish between the symmetry species' of lower and higher energy /T-orbitals, respectively.

II.ELECTRONIC STATES:

The electron configuration of the electronic ground state of trans exalyl fluoride is given by

 $(a_{u}^{'})^{2} (b_{g}^{'})^{2} (a_{g}^{'})^{2} (b_{u}^{'})^{2}; {}^{1}A_{g}$

(We ignome here the σ electrons and the non-bonded electron pairs on the fluorine atoms.) The numerical superscripts of the lower case symbols give the number of electrons in the orbital.

The symmetry species of an electronic state is given by the direct product of the symmetry species of the single-electron orbitals that are occupied by electrons. For example, the symmetry species of the electronic ground state (6.1) is given by $a_u \otimes a_u \otimes b_g \otimes b_g \otimes a_g \otimes a_g \otimes b_u \otimes b_u = A_g$ (6.2) The prefixed superscript on ${}^{1}A_g$ in (6.1) is the multiplicity of the electronic state. Since all the electrons are spin paired in the ground state, it is a singlet state and its multiplicity is 1.

The unoccupied π orbitals a_u and b_g are called π orbitals. It can be seen from FIGURE 6.1 that the lowest energy excited state may be reached by promotion of an electron from one of the n orbitals into the a_u (π) orbital. Such a transition is called an $n \rightarrow \pi$ transition. III.VIERONIC TRANSITIONS:

The electronic transition moment, $\overline{M_e}$, which is given by equation (1.19) has Cartesian components which are given by

$$(M_e)_g = \int \psi_e^{i*} m_g \psi_e^{i*} dz_e \int \psi_V^{i*} \psi_V^{i*} dz_V$$

$$(6.3)$$

$$g = x, y, z$$

The simultaneous conditions that (M_e) be non-zero are given by

(i)
$$\Gamma'(\psi'_e) \otimes \Gamma'(\psi''_e) = \Gamma'(\mathbf{m}_g) = \Gamma'(\mathbf{T}_g)$$
 (6.4)

and

(ii)
$$\Gamma(\gamma_{V}) \otimes \Gamma(\gamma_{V}^{"}) = \Gamma(1)$$
 (6.5)

where $/^{(1)}$ is the totally symmetric symmetry species.

The lowest energy $n \rightarrow \pi^*$ transitions are given by

$$(a_{u}^{'})^{2} (b_{g}^{'})^{2} (a_{g}^{'})^{2} (b_{u}^{'})^{2}; {}^{1}A_{g} \longrightarrow$$
 (6.6)

$$(a_{u}^{'})^{2} (b_{g}^{'})^{2} (a_{g}^{'})^{1} (b_{u}^{'})^{2} (a_{u}^{''})^{1}; {}^{1}A_{u}(I); {}^{3}A_{u}(I)$$

and
$$(a_{u}^{i})^{2} (b_{g}^{i})^{2} (a_{g})^{2} (b_{u}^{i})^{2}; {}^{1}A_{g} \longrightarrow$$
 (6.7)
 $(a_{u}^{i})^{2} (b_{g}^{i})^{2} (a_{g}^{i})^{2} (b_{u}^{i})^{1} (a_{u}^{i})^{1}; {}^{1}B_{g}(I); {}^{3}B_{g}(I)$

From the selection rule (6.4) and TABLE 3.3, it is seen that the ${}^{3}A_{u} \leftarrow {}^{1}A_{g}$ and ${}^{1}A_{u} \leftarrow {}^{1}A_{g}$ transitions are allowed while the ${}^{1}B_{g} \leftarrow {}^{1}A_{g}$ and ${}^{3}B_{g} \leftarrow {}^{1}A_{g}$ transitions are unallowed by symmetry. In (6.6) and (6.7) the Roman Numeral I has been placed in brackets after the excited state symmetry species in order to distinguish this lower energy excited state from higher energy excited states with the same symmetry.

Although the ${}^{3}A_{u} \leftarrow {}^{1}A_{g}$ transition is allowed by symmetry it is spin forbidden. Inclusion of the spin-orbit interaction terms in the electronic Hamiltonian, mixes the wave functions of singlet and triplet energy states. As a result, this transition may become allowed, although the corresponding spectrum will not be very intense.

As a rule, it has been found that the triplet states lie lower in energy than the singlet states; thus, the ${}^{3}A_{u}(I) \leftarrow {}^{1}A_{g}$ transition should be observed at longer wave length (lower energy) than the ${}^{l}A_{u}(I) < {}^{l}A_{g}$ transition.

IV.EXPERIMENTAL:

The spectral region 2000 - 7000 \mathring{A} was surveyed photographically with a Bausch and Lomb 1.5 meter grating spectrograph, model 11. Since the singlet-triplet absorption spectrum was expected to be very weak, a 1.85 meter multiple reflection cell was employed giving absorbing paths of up to 100 m. This multiple reflection cell was similar to the one described by Moule⁴⁹ except that the controls for adjusting the positions of the mirrors were outside the cell. A weak band spectrum was observed in the region of 3340 \mathring{A} with a pressure-path length of 3.21 meter.atmospheres. Another more intense band spectrum was observed in the region of 3082 \mathring{A} with a pressure-path length of 0.019 meter.atmospheres.

V.SPECTRAL ANALYSIS:

No absorption was obtained to the long wavelength side of the above spectra and so these were assigned to the lowest energy $n \Rightarrow \frac{\pi}{77}$ transitions. The weaker 3340 Å band system was assigned to the ${}^{3}A_{u}(I) = {}^{1}A_{g}$ transition. The 3082 Å band system was assigned to the

$l_{A_{u}}(I) \ll l_{g}$ transition.

Va. THE 3082 Å SYSTEM:

The frequencies (cm^{-1}) of the strongest bands of the spectrum and a partial vibrational analysis are presented in TABLE 6.1.

The strong band at 32,445.4cm⁻¹ was identified as the origin band. To the red of this origin in the region 32,445.4 - 31,642.2 cm⁻¹, bands at intervals of 803.2cm⁻¹ and 317.7cm⁻¹ were assigned to ground state quanta of $\mathcal{V}_{3}^{"}$ and $\mathcal{V}_{5}^{"}$. To the violet of the origin, the intervals 282.6cm⁻¹, 542cm⁻¹, 1146cm⁻¹, 1278cm⁻¹, and 1371cm⁻¹ were assigned to the excited state vibrations \mathcal{D}_5' , \mathcal{D}_1' , \mathcal{D}_3' , \mathcal{D}_2' , and \mathcal{D}_1' . That \mathcal{D}_3' (1146cm⁻¹) is greater than $\mathcal{V}_{3}^{"}(803.2 \mathrm{cm}^{-1})$ which was assigned in Chapter 4 to the C-C stretching mode, is consistent with the fact that in the excited state, the $a_{u}^{"}(\mathcal{T}^{*})$ orbital is bonding across the C-C bond should make this bond stronger. The frequency assigned to the excited state carbonyl stretching mode, $\mathcal{V}_1(a_g)$, i.e. 1371cm⁻¹ is of the same magnitude as the frequencies assigned to this mode in glyoxal (1391cm⁻¹) and in oxalyl chloride (1422 cm^{-1}) .

Groups of bonds separated by the interval 97.2cm⁻¹ are prominant

in the spectrum. Brand observed similar groups of bands separated by 100cm^{-1} in the near ultraviolet spectrum of glyoxal. Following Brand's assignment of the 100cm^{-1} of the glyoxal spectrum, the present 95cm^{-1} interval was assigned to positively running sequences in the torsional vibration, \mathcal{V}_{γ} .

The bands become increasingly diffuse toward the violet as the discontinuity in the underlying continuum is reached. This diffusness was attributed to predissociation. The predissociating state is probably the ${}^{1}A_{u}(II)$ excited state whose electron configuration is given by

$$(a_{u}')^{2} (b_{g}')^{2} (a_{g})^{2} (b_{u})^{1} (b_{g}')^{1}; {}^{1}A_{u}(II)$$
 (6.8)

52 Theory predicts that this state is probably unstable with respect to dissociation and, in any case, should have a rotated non-planar configuration.

Vb.THE 3340 Å BAND SYSTEM:

The frequencies of the strong bands and a partial analysis of this spectrum are given in TABLE 6.2.

The strong band at 29,943.3 was taken as the origin band. Analysis of this system follows closely that of the 3082 Å system. To the red

of the origin, the interval 230cm⁻¹ was assigned to the overtone of the ground state torsional mode. Apparently, no other hot bands were observed. To the violet side of the origin, the observed intervals 287cm⁻¹, 1148cm⁻¹, 1241cm⁻¹, 1444cm⁻¹ were assigned to the excited state frequencies $\mathcal{V}_{5}^{'}, \mathcal{V}_{3}^{'}, \mathcal{V}_{2}^{'}, \mathcal{V}_{1}^{'}$. The excited state quantum of $\mathcal{V}_{4}^{'}$ was apparently not observed.

The prominant 100cm⁻¹ interval observed here was assigned to sequences in the torsional vibration.

The values of the assigned fundamental frequencies of ground state, singlet excited state (${}^{1}A_{u}(II)$, and triplet excited state (${}^{3}A_{u}(I)$ are given in TABLE 6.3.

TABLE 6.1

VIBRATIONAL ANALYSIS OF THE STRONG BANDS OF THE 3082 A SYSTEM

(cm ⁻¹)	INTENSITY	NOTATION	ASSIGNMENT
31,642.2	VW	3 ⁰ 1	$\overline{\nu}_0 - \overline{\nu}_3^{"}$
31,740.5	VW	$3_{1}^{0} + 7_{1}^{1}$	20-23-27+27
31,837.6	VVW	$3_1^0 + 7_2^2$	Vo-V3-27+27
32,018.2	VW		
32,127.7	VW	5 ⁰	V- V5
32,214	VW	70	Vo - 2V7
32,312	m	~	
32,404	m .	$5\frac{1}{7}$	アローア·+ア
32,445.4	ms	origin	Vo
32,542.6	ms	77	アレージョナンク
32,617	ms		0
32,652	ms	72	$v_0 - 2v_7 + 2v_7$
32,728	. ms	5	Vot V5
32,737	m	73	$v_0 - 3v_7 + 3v_7$
32,824.0	ŝ		0 1 1
32,891	m		
32,912.8	S		
32,987.4	VS	40	アーキア
33,003.0	m	5 ² 0	V0 + 2V5
33,067.1	m		U
33,082.3	ms	40 + 71	マレヤレーショナショ
33,098.4	m		
33,111.3	ms		
33,177.5	W	$4_0^1 + 7_2^2$	$V_0 + V_1 - 2V_7 + 2V_7$
33,200.4	mw		
33,265.7	nw	$4_0^{\perp} + 5_0^{\perp}$	V0 + V1 + V5
33,275.1	W	$40^{1} + 73^{3}$	ン0+2-327+327
33,289.9	mw		1 1
33,354.2	mw		

TABLE 6.1 - CONTINUED

33,461.9	mw		
33,542.2	W	402	70+274
33,548.3	mw		
33,591.4	mw	30	V0+V3
33,672.2	mw		
33,724.0	m	2_0^1	$\mathcal{V}_0 + \mathcal{V}_2^{\prime}$
33,816	m	11	マ + マー
33,893	RED EDGE OF	CONTINUUM	<u> </u>

TABLE 6.2

VIBRATIONAL ANALYSIS OF STRONG BANDS OF THE 3340 A SYSTEM

(cm^{-1})	INTENSITY	NOTATION	ASSIGNMENT
29,712.8	VVW	702	$v_0 - 2v_7''$
29,864.7	m		
29,912.1	mw	51	V0+V5-V5
29,943.3	S	origin	Zo
30,043.3	S	77	20+27-27
30,143.7	m	7^{2}_{2}	$\gamma + 2(\gamma - \eta - \eta)$
30,230.3	m	50	20+25
30,330.3	m	$5^{1}_{0} + 7^{1}_{1}$	アレキンデキアラーアラ
30,429.4	m	50 2	$v_{0}+v_{5}+2(v_{7}-v_{7})$
30,529.5	m	$5^{1}_{0} + 7^{3}_{3}$	シー+シェ+3(シーシー)
30,715.4	mw	0)	
30,810.0	mw		
30,910.9	mw		
31,091.6	mw	30	20+23
31,184.9	m	20	$\nu_0 + \nu_2$
31.437.4	m	l	$v_0 + v_1$
		•	- ans

MADIT	6 0
LADLL	0.3

ASSIGNED GROUND STATE AND EXCITED STATE FUNDAMENTAL FREQUENCIES (cm⁻¹)

GROUND STATE			EXCITED STATES		
	1	A.g	l _{Au} (I)	³ A _u (I)	
as	\mathbb{V}_1	1872	1371	1444	
	ν_2	1286	1278	1241	
	\mathcal{V}_3	809	1146	1148	
	VL	565	542		
	ν_5	292	282.6	287	
au	V6	419			
	V7	127 ^a	212 ^b	215 ^b	
bgd	ν_{8}	420			
b _u	7/9	1870			
	710	1098			
	\mathcal{V}_{11}	672			
	2/12	255			

a

a calculated from overtone and combination frequencies b calculated from $(\mathcal{V}_{7}^{!} - \mathcal{V}_{7}^{'!}) + \frac{(2\mathcal{V}_{7}^{'!})}{2}$

CHAPTER 7

CONCLUSIONS

The limiting factor in the present vibrational analyses of the oxalyl halides is the lack of observed infrared frequencies below 200cm⁻¹ in the case of oxalyl fluoride, and below 250cm⁻¹ in the cases of oxalyl chloride fluoride.

A satisfactory analysis of the available infrared and Raman spectral frequencies of oxalyl fluoride and oxalyl chloride has been obtained on the assumption of the trans isomer alone. It seems likely that oxalyl chloride fluoride has the same configuration. In the absence of low observed frequencies it has been necessary to assign the normal frequencies of the torsional vibrations as values calculated from overtone and combination frequencies. In the cases of oxalyl chloride and oxalyl chloride fluoride, only eight of the nine in-plane fundamental frequencies were observed experimentally.

The assigned fundamental frequencies were checked by normal coordinate analysis. Here, several difficulties were encountered:

(i) In all the molecules studied here, there were fewer observed

frequencies than force constants, i.e., $n_{T} < n_{\varphi}$; thus, certain force constants had to be transferred from other molecules and constrained in the calculation while the remainder were varied.

- (ii) Only the Raman frequencies of liquid oxalyl fluoride and liquid oxalyl chloride were available. It is a known fact that liquid frequencies may be shifted from the corresponding gas phase values by undetermined amounts.
- (iii) In the case of oxalyl chloride, the converged values of K_{C} and H_{OC} were found to be correlated, with the result that a large number of constrained force constants were required.

Notwithstanding the above difficulties, the calculated and observed fundamental frequencies agree sufficiently well to confirm the frequency assignments for the in-plane normal modes. Although the force constants obtained with our rigidly constrained force field can not be considered to be precise, qualitative conclusions can be drawn from them. The relatively low value of $K_{\rm C}$ (2.040 md./ ${}^{\rm O}_{\rm A}$) indicates that the C-C bonds in all three molecules studied here are fairly weak. To the extent that the magnitudes of the repulsive force constants F_{ij} are determined by interatomic repulsions, the low value of F_{CF} (0.119 md./Å) obtained here for oxalyl fluoride, when compared with its value in other molecules, indicates that the electron distribution on carbon is different here than in other molecules.

The list of molecules containing the oxalyl group 0=C-C=0 whose structures have been determined to be planar and trans in spectroscopic studies is growing. Including the present molecules, the list is:

> glyoxal³² biacetyl³³ oxalyl bromide¹⁹ oxalyl chloride oxalyl fluoride oxalyl chloride fluoride

This is not to suggest that the cis form is unstable or non-existent; however, there is no concrete evidence to support its existence.

In the analysis of the ultraviolet spectrum of oxalyl fluoride, obtained under low resolution, a weak band spectrum at 3340 Å was assigned to the ${}^{3}A_{u}(I) \leftarrow {}^{1}A_{g}$ transition and a stronger system at 3082 Å was

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APPENDIX
[D] MATRIX OF OXALYL CHLORIDE

	∠y1	C1X1	Ay ₂	$\triangle x_2$	Ay3	Δx_3	ay4	Δx_{4}	Ay5	ax5	ay ₆	∠x ₆
s ₁	 Indextable thread of a construction of a set of a construction of a set of a construction of a construction of a set of a construction of a construction of a set of a construction of a construction	0.28855	general en al fan de la Radio de la Carlo de la Radio de la Carlo de la Carlo de la Carlo de la Carlo de la Car	-0.28855	den genetisment für 2000 och som etter so			NAMENIA DALLA CONTRACTORIA CON DURANTE	ing de la ser a ser se san de la de la ser de la de	na men kongelen kalanda kaland		REPAILED A CLASSE DAVID DAVID DAVID DAVID CLASSE
^S 2			-0.26361	0.11737	0.15342	0.06831						
s ₃	0.26361	-0.11737									-0.15342	0.06831
S4			0.24200	0.15716			-0.20967	-0.13616				
s ₅	-0.24200	-0.15716							0.20967	0.13616		
s ₆			0.09012	-0.50991	0.05706	0.12815	-0.16301	0.251.02				
s ₇	-0.09012	0.50991							0.16301	-0.25102	-0.05706	-0.12815
S ₈	0.25809		-0.43380	0.27057			0.1.5223	-0.23442				
s ₉	0.43380	-0.27057	-0.25809						-0.15223	0.23442		
S10	-0.30899		0.41860	0.24617	-0.06379	-0.14327						
s ₁₁	-0.41.860	-0.21;617	0.30899								0.06379	0.14327
	1											

β

[z'] MATRIX OF OXALYL CHLORIDE

9 1	\$2	\mathcal{P}_3	94	φ_5	\$96	\mathcal{P}_7	\$28	\$9	P 10	
1.000	1.000	1.000	1.000	1.000	1.000	0.803	0.832	0.628	0.191	0.191
	1.000	1.000	1.000	1.000	1.000	0.692	0.656	0.717	0.868	0.868
						0.301	0.295	0.365	0.763	0.763
						0.791	0.785	0.730	0.585	0.585
						0.397	0.403	0.388	0.455	0.455
						0.348	0.326	0.429	0.849	0.849
						0.803	0.832	0.628	0.660	0.660
						0.692	0.656	0.717	0.728	0.728
						0.301	0.295	0.365	0.542	0.542
						0.791	0.785	0.730	0.294	0.294
						0.397	0.403	0.388	0.823	0.823
						0.348	0.326	0.429	0.654	0.654
									0.433	0.433
									0.448	0.448
									0.639	0.639

\mathcal{S}_1	\mathscr{G}_2	\$3	\mathcal{P}_{4}	<i>Р</i> 5	<i>\$</i> 6	97	\$P_8	\$9	P 10	
1	3	10	36	21	55	1	3	1	3	6
	6	15	45	28	66	10	10	3	15	10
				•		36	21	55	1	1
						7	8	2	12	9
						29	17	46	2	l_{\diamond}
						32	19	47	11	7
						1	6	1	54	66
						15	15	6	45	36
						45	28	66	54	63
						11	13	4	47	58
						37	24	56	50	59
						41	26	58	46	56
									38	31
									41	32
									37	29

[K'] MATRIX OF OXALYL CHLORIDE

[D] MATRIX OF OXALYL CHLORIDE FLUORIDE

	∆y ₁	Δx_1	$ riangle \mathbb{Y}_2$	$\triangle x_2$	Δy_3	Δx_3	$ r_4$	$\bigtriangleup x_4$	Δy_5	∠∆ x ₅	$\triangle y_6$	$\Delta_{\mathbb{X}_6}$
S1		0.28854		-0.28854								
S2			-0.26938	0.10340	0.21418	0.08222						
^S 3	0.26361	-0.11737									-0.20967	-0.13616
s4			0.23921	0.16135			-0.20726	-0.13980				
s ₅	-0.23921	-0.16135						,	0.20726	0.13980		
⁸ 6			0.07571	-0.50771	0.07692	0.20039	-0.14942	0.22152				
s ₇	-0.09021	0.50991							0.16301	-0.25102	-0.05706	-0.12815
s ₈	0.25592		-0.43784	0.26971			0.15762	-0.23368				
s ₉	0.43380	-0.27057	-0.25809						-0.15223	0.23442		
s ₁₀	-0.27353		0.38261	0.28416	-0.08673	-0.22593						
s ₁₁	-0.41860	-0.24617	0.30899								0.0637	9 0.143
	1											

[Z'] MATRIX OF OXALYL CHLORIDE FLUORIDE

91	φ_2	Ŷ3	\mathcal{G}_{k}	P5	\$96	\$7	SP 8	<i>G</i> 9	\$P10	\mathcal{P}_{11}	P12	\$13	914	\$15	916
1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.809	0.792	0.832	0.684	0.832	0.081	0.184
			1.000	1.000					0.702	0.738	0.656	0.609	0.656	1.021	0.899
						•			0.295	0.291	0.295	0.387	0.295	0.806	0.761
									0.798	0.807	0.785	0.710	0.785	0.507	0.587
									0.392	0.379	0.403	0.436	0.403	0.364	0.450
									0.345	0.355	0.326	0.401	0.326	0.941	0.861
									0.809					0.638	0.668
									0.702					0.674	0.727
									0.295					0.549	0.587
									0.798					0.173	0.291
									0.392					0.771	0.734
									0.345					0.667	0.658
														0.243	0.338
														0.494	0.457
														0.628	0.637
															മ

j.

[K'] MATRIX OF OXALYL CHLORIDE FLUORIDE

91	Ŷ2	P3.	\mathcal{P}_4	P5	\$6	\$7	P8	SP 9	\$P_10	φ_{11}	φ_{12}	I 13	924	9° 15	\$P 16
1	3	6	10	86	21	28	55	66	1	3	6	1	1	3	6
			15	45					10	10	15	3	6	15	10
								•	36	21	28	55	66	1	1
									7	8	13	2	4	12	9
									29	11	24	46	56	2	4
									32	19	26	47	58	21	7
									1					55	66
									15					45	36
									45					54	63
									11					47	58
									37					50	59
									41					46	56
														38	31
														41	32
														37	29

Sl	^s 2	s ₃	s ₄	s ₅	⁵ 6	s ₇	sg	s ₉	s ₁₀	s ₁₁
4.230	0.152	0.152	1.022	1.022	0.000	0.000	0.533	0.533	0.174	0.174
	5.925	0.000	1.034	0.094	0.488	0.000	0.000	0.045	0.030	0.000
		5.925	0.094	1.034	• 0.000	0.488	0.045	0.000	0.000	0.080
			14.099	0.000	0.453	0.000	0.456	0.000	0.000	0.141
				14.099	0.000	0.453	0.000	0.456	0.141	0.000
					0.659	0.000	0.000	0.000	0.000	0.000
						0.659	0.000	0.000	0.000	0.000
							0.918	0.000	0.000	0.100
								0.918	0.100	0.000
									0.163	0.000
										0.163

[F] MATRIX OF OXALYL FLUORIDE

Sl	s ₂	^S 3	SI4	s ₅	^S 6	⁸ 7	S ₈	s ₉	s ₁₀	s ₁₁
4.050	0.573	0.573	0.553	0.553	0.000	0.000	0.298	0.298	0.345	0.345
	3.096	0.000	0.858	0.058	0.440	0.000	0.000	0.034	0.339	0.000
		3.096	0.058	0.857 .	0.000	0.440	0.034	0.000	0.000	0.339
			12.879	0.000	0.355	0.000	0.250	0.000	0.000	0.071
				12.879	0.000	0.356	0.000	0.250	0.071	0.000
					0.536	0.000	0.000	0.000	0.000	0.000
						0.536	0.000	0.000	0.000	0.000
							0.733	0.000	0.000	0.058
								0.733	0.583	0.000
									0.329	0.000
										0.329

[77 MATRIX OF OXALYL CHLORIDE

s ₁	S2	s3	$S_{l_{\downarrow}}$	s ₅	⁵ 6	s ₇	S ₈	s ₉	S ₁₀	S ₁₁
4.288	0.151	0.612	0.747	1.322	0.000	0.000	0.388	0.441	0.175	0.357
	5.919	0.000	1.035	0.094	0.000	0.000	0.000	0.045	0.079	0.000
		3.051	0.059	0.858	0:000	0.441	0.034	0.000	0.000	0.264
			13.603	0.000	0.456	0.000	0.331	0.000	0.000	0.073
				13.603	0.000	0.356	0,000	0.377	0.143	0.000
		1			0.659	0.000	0.000	0.000	0.000	0.000
						0.536	0.000	0.000	0.000	0.000
							0.799	0.000	0.000	0.059
								0.851	0.102	0.000
									0.164	0.000
										0.279

[J MATRIX OF OMALYL CHLORIDE FLUORIDE

	Q	Q2 Q9	Q3 Q10	Q _{1,} Q _{1,1}	Q ₅ Q ₁₂
S1	0.14463169	-0.31490055	-0.20200682	0.06344168	0.04019185
		0.00000005	-0.0000003	0.00000000	0.0000001
s2	0.12786752	0.20386630	-0.03811525	-0.04322515	0.02008465
		-0.11030357	0.23306143	-0.03778683	0.00594354
s3	0.12786752	0.20386630	-0.03811525	-0.04322515	0.02008465
		+0.11030357	-0.23306143	+0.03778683	0.00594354
S4	-0.26541468	0.04236962	-0.02236873	0.01167755	-0.00225022
~		0.26875287	0.02294594	-0.01034027	0.00450628
S5	-0.26541468	0.04236962	-0.02236873	0.01167755	-0.00225022
		-0.26875287	-0.02294594	+0.01034027	-0.00450628
s ₆	0.08111158	-0.33197189	-0.21073060	-0.11277386	-0.12878685
		-0.10784886	-0.25811581	-0.32522135	-0.08044736
s7	0.08111158	-0.33197189	-0.21073060	-0.11277386	-0.12878685
		+0.10784886	40.25811581	+0.32522135	40.08044736
s ₈	0.30378198	0.40527444	0.02879412	0.23177954	-0.07541594
		-0.00726174	0.19841989	0.21384754	-0.08655932

[L] MATRIX OF OXALYL FLUORIDE

[L] MATRIX OF OXALYL FLUORIDE

	Ql	Q2 Q9	Q3 Q10	Q ₄ Q ₁₁	Q ₅ Q ₁₂
s ₉	0.30378198	0.40527444	0.02879412	0.23177954	-0.07541594
		+0.00726174	-0.19841989	- 0.21384754	+0.08655932
s ₁₀	-0.41613861	-0.05887670	0.20681654	-0.12058121	0.22580914
		0.12935777	0.07894281	0.13811282	0.18321811
S ₁₁	-0.41613861	-0.05887670	0.20681654	-0.12058121	0.22580914
		-0.12935777	-0.07894281	-0.13811282	-0.18321811

[L] MATRIX OF OXALYL CHLORIDE

	Ql	Q ₂	83	QL	Q ₅
		Q.9	Qlo	QII	Q12
s ₁	0.17297002	0.33928287	-0.13331709	0.06021191	-0.00986437
		0.0000000	-0.C0000001	0.00000000	0.00000000
s ₂	0.09365889	-0.17082068	-0.09444903	-0.08478745	-0.04089847
		-0.08393831	0.19283254	-0.10703278	-0.00691788
S3	0.09365889	-0.17082068	0.09444:903	0.08478745	-0.04089847
		-0.08393831	-0.19283254	0.10703278	0.00691788
S4	-0.26883868	-0.00666405	-0.02234958	0.00760288	0.00244208
		+0.26992266	-0.00223711	-0.00397586	0.00169017
S5	-0.26883868	-0.00666405	-0.02234958	0.00760288	0.00244208
		-0.26992266	+0.00223711	+0.00397586	-0.00169017
s ₆	0.10301221	0.37697429	-0.07624638	-0.12560328	0.11994186
		-0.11.360707	-0.37207865	-0.18773959	-0.04584338
S7	0.10301221	0.37697429	-0.07624638	-0.12560328	0.11994186
·		+0.11360707	+0.37207865	+0.18773959	+0.04584338
S8	0.26127515	-0.45088260	-0.17208188	0.11583165	0.02081075
		0.00442764	0.26731912	0.11827042	-0.07506904

[L] MATRIX OF OXALYL CHLORIDE - CONTINUED

	Q	Q2 Q9	Q ₃ Q ₁₀	Q ₄ Q ₁₁	Q ₅ Q ₁₂
s ₉	0.26127515	-0.45088260	-0.17208188	0.11583165	0.02081075
		• 0.00442764	-0.26731912	-0.11827042	-0.07506904
S10	-0.42797476	0.11833510	0.29126574	0.00175289	-0.15901412
		0.12171575	0.09595710	0.06830366	0.14112855
s ₁₁	-0.42797476	0.11833510	0.29126574	0.00175289	-0.15901412
		-0.12171575	-0.09595710	-0.06830366	-0.14112855

[L] MATRIX OF OXALYL CHLORIDE FLUORIDE

	Q1	Q2 Q6	Q3 Q7	Q14 Q8	Q5 Q9
S ₁	-0.11795316	0.07438099	-0.28807663	0.20760429	-0.12515155
eb.		0.04787266	0.04916828	-0.02460288	-0.00412596
S2	-0.17274600	-0.01986625	0.28001673	0.13116995	-0.07074419
~		-0.06534111	-0.02570509	-0.01006345	0.00289337
S2	-0.04169543	0.12759140	0.05589974	-0.21889418	-0.13332510
5		0.07430014	-0.13284257	-0.03756538	-0.00747555
S,	0.36572637	0.09171653	0.05393551	0.00854026	-0.02260729
4		0.00577266	0.00788018	-0.00066847	-0.00267637
Sr	0.08720683	-0.36972127	0.03212003	-0.00782653	-0.01128422
-5		0.01408210	0.00320786	0.00519604	0.00301059
⁵ 6	-0.10504271	-0.06235217	-0.44588372	-0.02436228	-0.27662090
		-0.24852988	-0.07456566	0.14422001	0.03548884
^S 7	-0.01383312	0.13312671	-0.16541635	0.49028425	0.11010276
		0,19249392	-0.15341499	0.10459420	-0.08992113
Sa	-0.27894484	0.15443542	0.45152975	-0.03264802	0.00214228
8		0.27848490	0.09681498	0.08899693	0.08420295
	1				

[L] MATRIX OF OXALYL CHLORIDE FLUORIDE - CONTINUED

	Ql	Q2 Q6	Q3 Q7	Q4 Q8	Q5 Q9		
⁵ 9	-0.25159516	0.14654693	0.24573552	-0.41313964	-0.25798319		
		-0.00459284	0.14510915	0.02709732	-0.06583482		
^S 10	0.41308781	-0.09397026	0.01994852	0.06184069	0.30700102		
		-0.01729409	-0.01924475	-0.25556845	-0.12892438		
S ₁₁	0.31668041	-0.3242890]	-0.10925810	-0.05353588	0.18576373		
×		-0.20971661	-0.00220427	-0.14938131	0.17935358		