



A study of the polarized infrared spectrum of maleic anhydride
by Wilbur Allen Layman

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemistry
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Abstract:

The vibrational spectrum of maleic anhydride has been studied using polarized infrared radiation. The observed polarization of spectral bands has been compared with the predicted polarization as determined from symmetry considerations of the crystal structure. Polarization properties, group frequencies and calculated force constants were utilized in making the vibrational assignments. Comparative assignments for succinic anhydride have also been determined.

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OF MALEIC ANHYDRIDE

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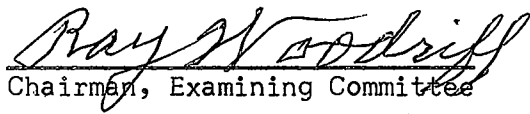
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ABSTRACT

The vibrational spectrum of maleic anhydride has been studied using polarized infrared radiation. The observed polarization of spectral bands has been compared with the predicted polarization as determined from symmetry considerations of the crystal structure. Polarization properties, group frequencies and calculated force constants were utilized in making the vibrational assignments. Comparative assignments for succinic anhydride have also been determined.

INTRODUCTION

There has been insufficient data available to classify completely the infrared absorption bands of the anhydrides. This is especially true for bands originating in carbon-oxygen motions. Most anhydrides exhibit two carbonyl stretching bands with variable intensity patterns. Contrary to the view of Bellamy(1), however, there are observable patterns in the separations and intensities of these bands. If the anhydrides are classified according to their cyclic and symmetric properties, the Sadtler spectra series contains seventeen cyclic, symmetric(2), twelve cyclic, non-symmetric(3) and nine non-cyclic, symmetric(4) anhydrides. In addition, Barnes and coworkers(5) report the spectra of two additional non-cyclic, symmetric and three cyclic, non-symmetric anhydrides. The spectra of all of these cyclic anhydrides exhibit two carbonyl absorption bands with the high frequency band possessing the lower intensity. If the cyclic anhydrides are also symmetric, the ratio of intensities for the two bands appears approximately constant from one anhydride to another. The cyclic, non-symmetric group contains slightly more variation in the intensity ratio. These observations concerning carbonyl band intensities have been partially substantiated by Dauben and Epstein(6). The non-cyclic anhydrides show considerably more variation in the band intensities and some have only one band in the carbonyl stretching region. This variation would be expected on the basis that the non-cyclic anhydrides do not have a rigid ring for restricting the carbonyl groups to a particular configuration and consequently independent vibration of each carbonyl unit is probable.

The majority of the work reported on anhydrides has dealt with the carbonyl bands(1,32). The fingerprint region of the spectrum has received only minor consideration. A thorough study of anhydrides should start with a simple cyclic type, thus providing the basis for further work. Such an investigation could eventually be expanded to include acyclic systems.

The primary objective of this investigation is to initiate such a study. Maleic anhydride has been selected for this purpose since it represents the simplest cyclic, symmetric anhydride available. Vibrational assignments are also reported for succinic anhydride, since the similarity of the two molecules enables a comparative treatment to be utilized. Polarized infrared radiation is used to determine the symmetry type of each observed absorption band. The use of polarized infrared radiation to establish the symmetry of the observed spectral bands is now firmly established(7-13).

EXPERIMENTAL CONSIDERATIONS

Instrument

A Beckman IR-4 optical null spectrometer with sodium chloride optics was used to record all infrared spectra. A beam condenser was used to reduce the beam size to 2 x 5mm for use with small sample areas. The polarizer was of the parallel silver chloride plate type and was mounted so that the radiation electric vector ($\vec{E}$) was parallel to the base of the instrument. A rotatable sample holder was obtained from Connecticut Instrument Company, calibrated over a 180 degree range in 1 degree intervals. The rotatable sample holder was used in preference to a rotatable polarizer because of inherent instrumental polarization effects. Thus the electric vector was held constant and any change in absorption was due to different sample orientations.

Frequency measurements were calibrated with the vacuum wavelength values for polystyrene reported by Plyler(14) and water vapor and carbon dioxide reported by Herzberg(15). The scanning speed was 0.08 μ /min, equivalent to a scanning time of about three and a half hours for a complete spectrum(640-4000 cm^{-1}). Identical instrument settings were used in obtaining all calibration spectra of the anhydrides. All spectra were taken using double beam operation except the calibration spectra of carbon dioxide and water vapor.

Polarized Spectra

Polarized spectra of maleic anhydride were obtained over a 180 degree range of sample rotation. The complete spectrum was run at each of ten different sample orientations to establish the functional relationship between band intensity and sample orientation.

The polarized spectra of maleic and succinic anhydrides for analysis were taken with the electric vector of the radiation perpendicular and parallel to the direction of crystal growth. These runs were made with identical instrument parameters.

Preparation of Oriented Films

Reagent grade anhydrides obtained from Eastman Chemical Co. were further purified by a repeated sublimation technique. An infrared spectra was run on the sample after each sublimation to serve as a check on the purification process. The sublimations were repeated until the infrared spectra indicated no change in the number of bands or the intensity of any band. Three sublimations satisfied this criterion. The spectra of succinic anhydride exhibited some broadening of the base of the CH stretching bands near 3000 cm^{-1} . This was probably due to the presence of some acid impurity formed from moisture in the air and appeared only with the thicker samples.

Four techniques were investigated to prepare an oriented film of the anhydrides. These were: flow of a solution over a cooled salt plate, slow withdrawal of a salt plate from a melt of the anhydride, slow

withdrawal of a salt plate from an acetone solution of the anhydride and crystalization in a temperature gradient between two salt plates. The latter two were the most promising, with the temperature gradient method yielding the most useful samples. The temperature gradient method was a modification of one suggested by Halverson and Francel(11). A thin film of the anhydride was deposited on one side of a salt plate and a second plate was then placed on top of the film. When the film melted, the plates were removed from the beaker and placed between two aluminum bars. One bar made contact with a small electric heater and the other with a container of flowing cold water. The heater was turned off and the system was allowed to cool slowly. This set up a temperature gradient across the salt plates, with a front that slowly moved from one side to the other. Microscopic observation of samples prepared in this manner showed striations in the sample which were parallel to the direction of the crystal growth. A similar observation was noted by Halverson and Francel. Although all samples prepared in this manner possessed some infrared polarization anisotropy, successive attempts were made to improve the orientation. The variation in polarization behavior of different samples indicated that the film was not a single crystal but rather a number of small crystals with some degree of orientation. It seemed reasonable to assume that the observed striations were indicative of the direction of the needle axis, or c-axis of the crystal.

The thickness of the film was difficult to control. Some films

were so thick that only the weak bands were useful in their corresponding spectra, while the thin films showed only the most intense bands. The film thickness probably varied between 0.01 to 0.1mm.

THEORY

Molecular Dynamics

The motion of the atoms in a polyatomic molecule may be described with the ordinary Cartesian coordinates x_k , y_k , and z_k of each atom k . If there are N atoms, $3N$ coordinates are required to describe their motion and the molecule has $3N$ degrees of freedom. If only the vibrational motion within the molecule is desired, the translational and rotational motions may be eliminated leaving $3N-6$ degrees of freedom for a non-linear molecule. Thus any motion that may occur in the molecule may be resolved into $3N-6$ genuine normal modes of vibration. In any normal mode of vibration all particles may move. However, they must all move with the same frequency and a constant phase relationship so that the particles pass thru their equilibrium positions at the same time. The displacements must be such that the center of mass remains fixed in position, with no resultant translation or rotation of the molecule as a whole.

The restoring force acting on each atom is proportional to the displacement, where the proportionality factor is the force constant. Thus the force constant is a measure of the restoring force acting upon an atom when displaced from its equilibrium configuration.

Any molecule may be classified according to one of the thirty-two molecular point groups on the basis of the symmetry of the molecule. Maleic and succinic anhydrides (assuming planar ring configurations) belong to the C_{2v} point group with a two-fold rotational axis and two mutually perpendicular symmetry planes parallel to the rotational axis.

The $3N-6$ normal modes of vibration may be grouped according to the effect of the symmetry operations upon the normal modes. Such a distribution for the maleic and succinic anhydrides is given in Appendix A.

An approximate description of the normal modes of vibration may be obtained by expressing the motions of the atoms in terms of symmetry coordinates. This effectively considers the motions as being essentially localized in certain portions of the molecule and does not require the center of mass to remain fixed. Symmetry coordinates are linear combinations of internal coordinates (bond lengths and angles). These combinations of equivalent internal coordinates must retain the same symmetry properties as the normal coordinate description. The symmetry coordinates are useful in providing an approximate coordinate description and in factoring the secular equation used in a calculation of force constants. The construction of the complete set of symmetry coordinates and their corresponding coordinate description is illustrated in Appendix B for maleic anhydride.

Nature of Polarized Infrared Absorption Spectra

The fundamental modes of vibration have been previously related to the atomic displacements within the molecule. If there is a net change in the dipole moment of the molecule during the fundamental vibration, the vibration is infrared active and appears in the spectra as a definite band. The nature of the infrared absorption process is interaction of the electric vector ($\vec{E}$) of the incident radiation with a vector ($\vec{M}$)

describing the change in dipole moment. The simplest way to describe this interaction is to use plane polarized radiation and one molecule. For a given fundamental vibration, the absorbance is proportional to $\cos^2 \Theta$, where the angle Θ is the angle between the vector defining the change in dipole moment and the radiation electric vector(13). If $\vec{E}$ and $\vec{M}$ are parallel, maximum absorbance will be obtained; if perpendicular there will be minimum absorbance. If definite statements are to be made concerning the infrared polarization of molecules, some knowledge of the change in dipole moment must be available. From considerations of normal coordinates or symmetry coordinates and their distribution among symmetry species, it is relatively easy to determine the direction of the change in dipole moment vector with respect to a particular symmetry vibration of the molecule. For example, this may be illustrated with some of the symmetry coordinates for maleic anhydride given in Appendix B. Using dots as atoms and lines for bonds, four symmetry coordinates for the maleic anhydride molecule are indicated in Figure 1. By vector addition, the resultant motion and consequently the change in dipole moment for Figure 1(a) is along the 2-fold rotational axis and in the plane of the molecule. For Figure 1(b) the dipole moment change is also in the plane of the molecule but will be perpendicular to the rotation axis. The latter condition is true because of the symmetry of the molecule. The fact that the molecule has a plane of symmetry perpendicular to the molecular plane implies that the magnitude of the two atomic displacements is the same with symmetrically opposed directions.

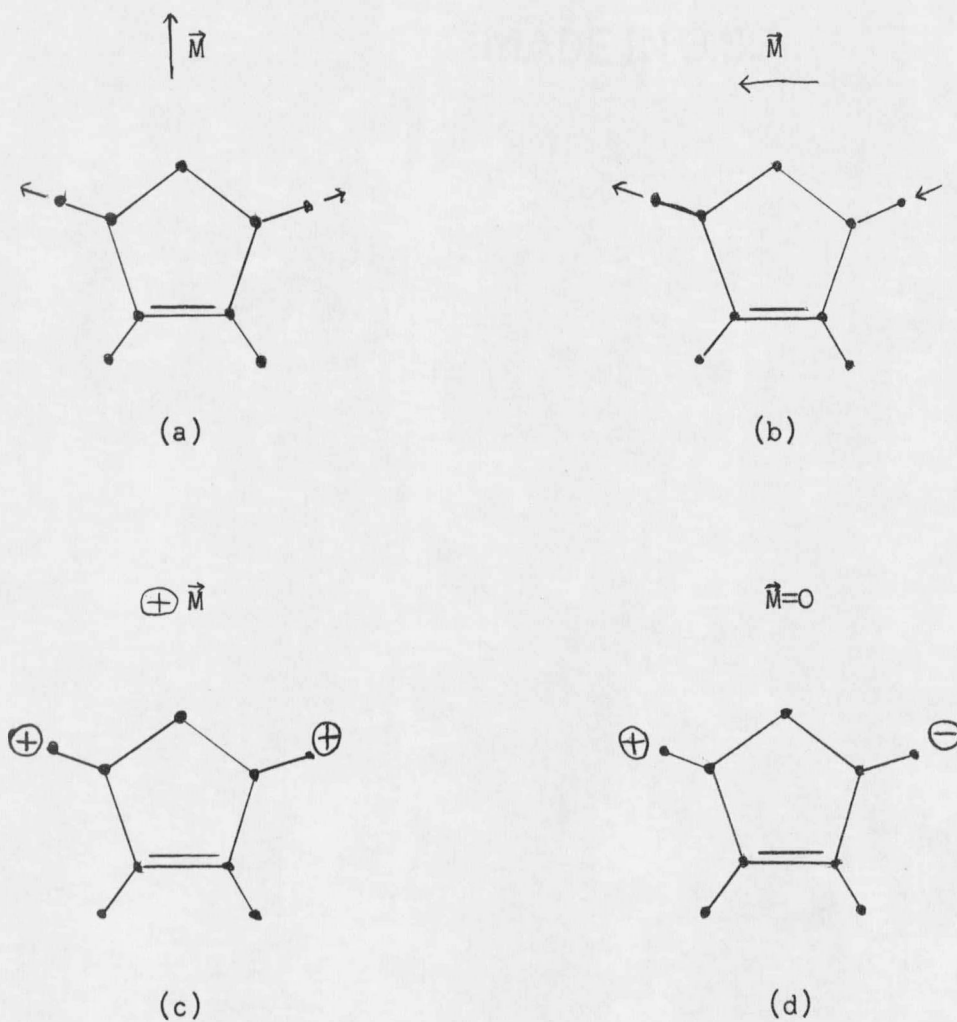


Figure 1 Motions Derived From Typical Symmetry Coordinates of Maleic Anhydride

(The arrows indicate the direction of atomic displacements in the plane of the molecule and the (+) and (-) refer to motion out-of and in-to the plane of the molecule.)

As a consequence, their combination will yield a resultant vector which is perpendicular to the rotational axis. Figure 1(c) displays a change in dipole moment perpendicular to the molecular plane and the motion in Figure 1(d) has no change in dipole moment since any displacement below the plane is offset by a corresponding displacement above the plane of the molecule. Thus the last motion is infrared inactive. Consequently the symmetry coordinates are useful in determining the direction of the electric vector for maximum absorption. The four fundamental vibrations described above are examples of the four symmetry species of the C_{2v} point group described in Appendix A. The motions in Figure 1(a), (b), (c) and (d) represent the symmetry species A_1 , B_1 , B_2 and A_2 respectively. Each example illustrates the direction of the change in dipole moment (and consequently the direction of maximum absorbance in a molecule) for all vibrations of that particular species. For any molecule belonging to the C_{2v} point group, these same general considerations are valid. The infrared polarization behavior is accordingly determined from the symmetry of the molecule.

The coordinate descriptions of the four fundamentals in Figure 1 represent carbonyl stretching (symmetric, asymmetric) and carbonyl bending (asymmetric, symmetric). The symmetry coordinates used in determining the infrared polarization properties consider the atomic displacements as essentially localized in a specific portion of the molecule. This gives rise to the term group frequency. Then, as a first approximation, many fundamental vibrations may be ascribed to a

particular functional group in the molecule. The force constant of a particular fundamental vibration is related to the frequency of the absorbed radiation by Hooke's Law for harmonic oscillators. Since the force constant is a function of the atoms involved in the vibration, one would expect that the group frequency would be approximately the same for a particular functional group in any molecule. This is a useful empirical concept although other environmental factors modify the picture.

VIBRATIONAL ASSIGNMENTS

The non-polarized and polarized spectra of maleic anhydride are given in Figures 2, 3 and 4. Similar spectra of succinic anhydride are given in Figures 5, 6 and 7 for comparison. From the concepts of polarization previously given, it has been demonstrated that the maximum absorption will occur for all A_1 species fundamentals if the radiation electric vector is parallel to the 2-fold rotational axis. Similarly maximum absorbance would occur for the B_1 species if $\vec{E}$ were in the molecular plane and perpendicular to the rotation axis. It follows that if the incident polarized radiation is normal to the molecular plane, the B_2 vibration would not appear.

The crystal structure of maleic anhydride has been determined by Marsh and coworkers(16) and is illustrated in Figure 8. They have indicated the structure to be a head to tail sequence along the c-axis. Since the c-axis is the needle axis, these head to tail sequences run parallel to the direction of the needle growth. The striations observed in the oriented films prepared for the polarized spectra were assumed to be indicative of needle direction. Further, it may be observed from the work of Marsh that the molecular planes are tilted with respect to the b-axis. They report this angle as 66 degrees which would enable absorption by the B_2 vibrations to occur since an incident beam normal to either the 001 or h00 is not normal to the molecular plane. Applying the cosine relationship (absorbance is proportional to $\cos^2 \Theta$) to each molecule and vectorially adding all components that belong to the same normal vibration in the unit cell, a resultant vector can be obtained

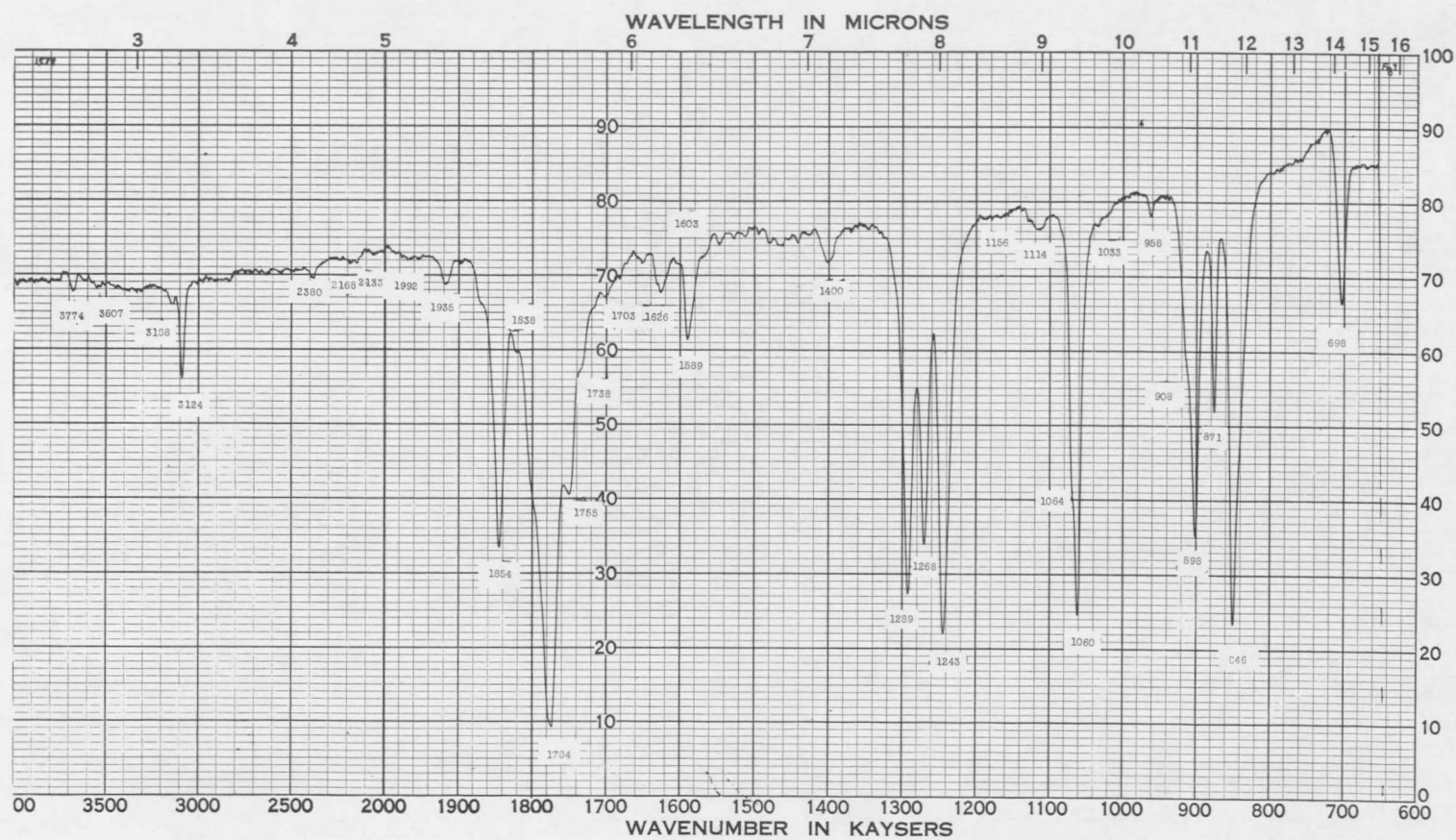


Figure 2. Infrared Spectra of Maleic Anhydride, Non-polarized

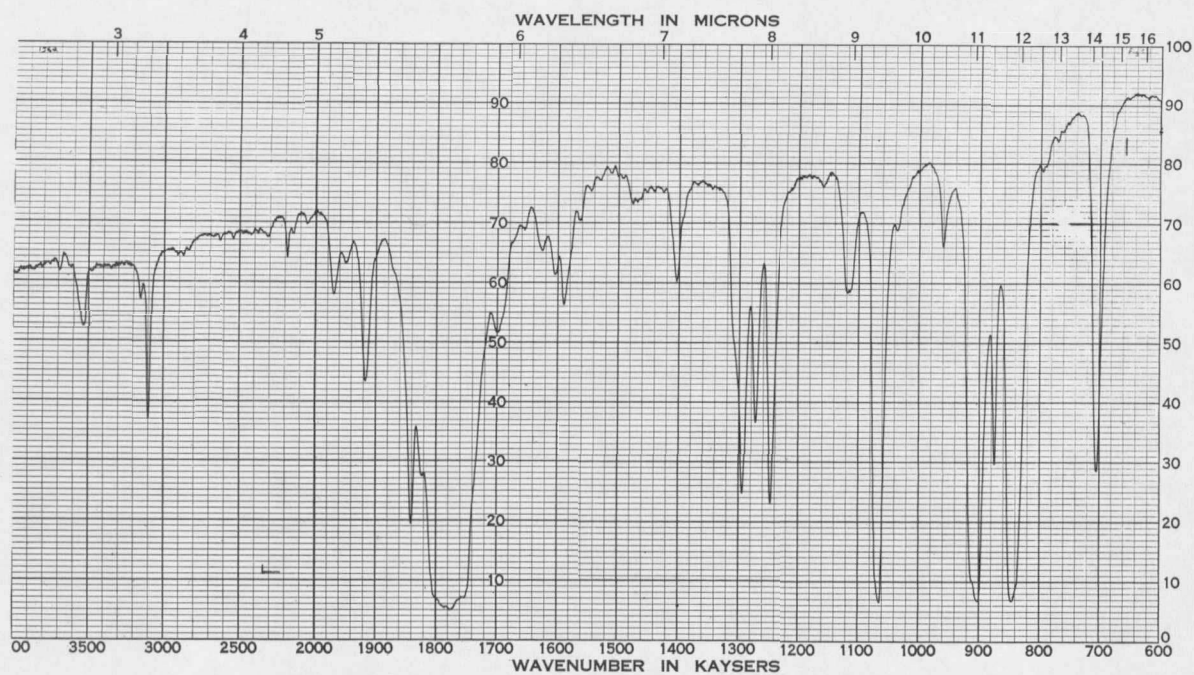


Figure 3. Infrared Spectra of Maleic Anhydride, Polarized Perpendicular

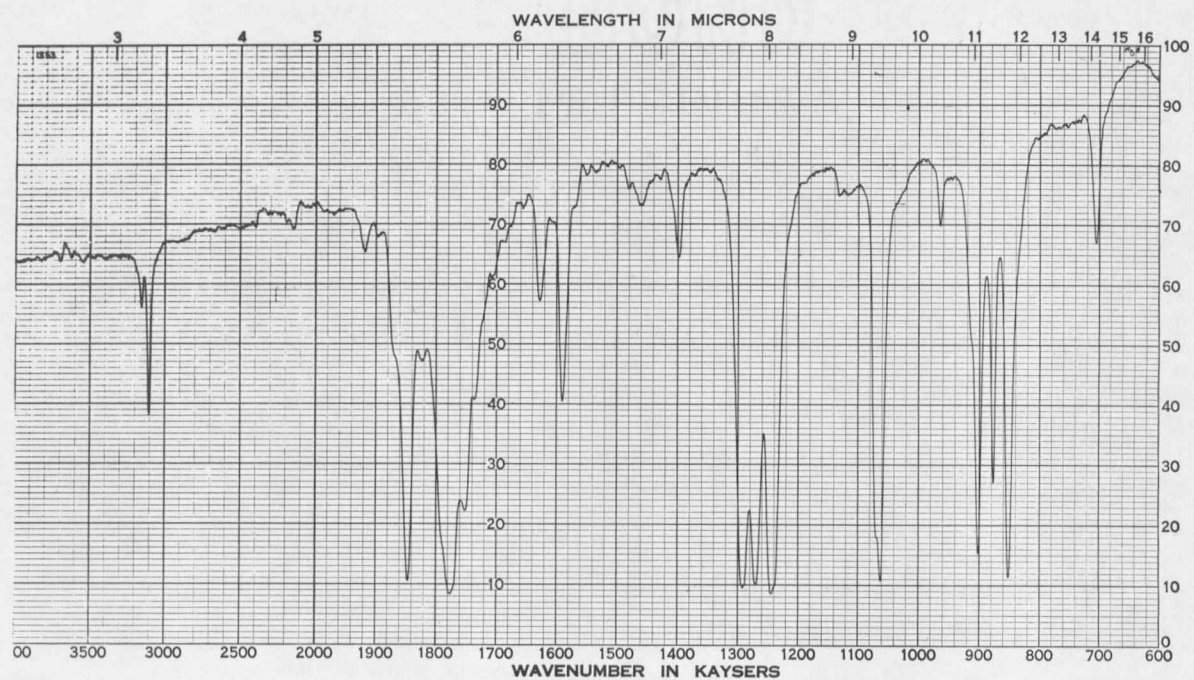


Figure 4. Infrared Spectra of Maleic Anhydride, Polarized Parallel

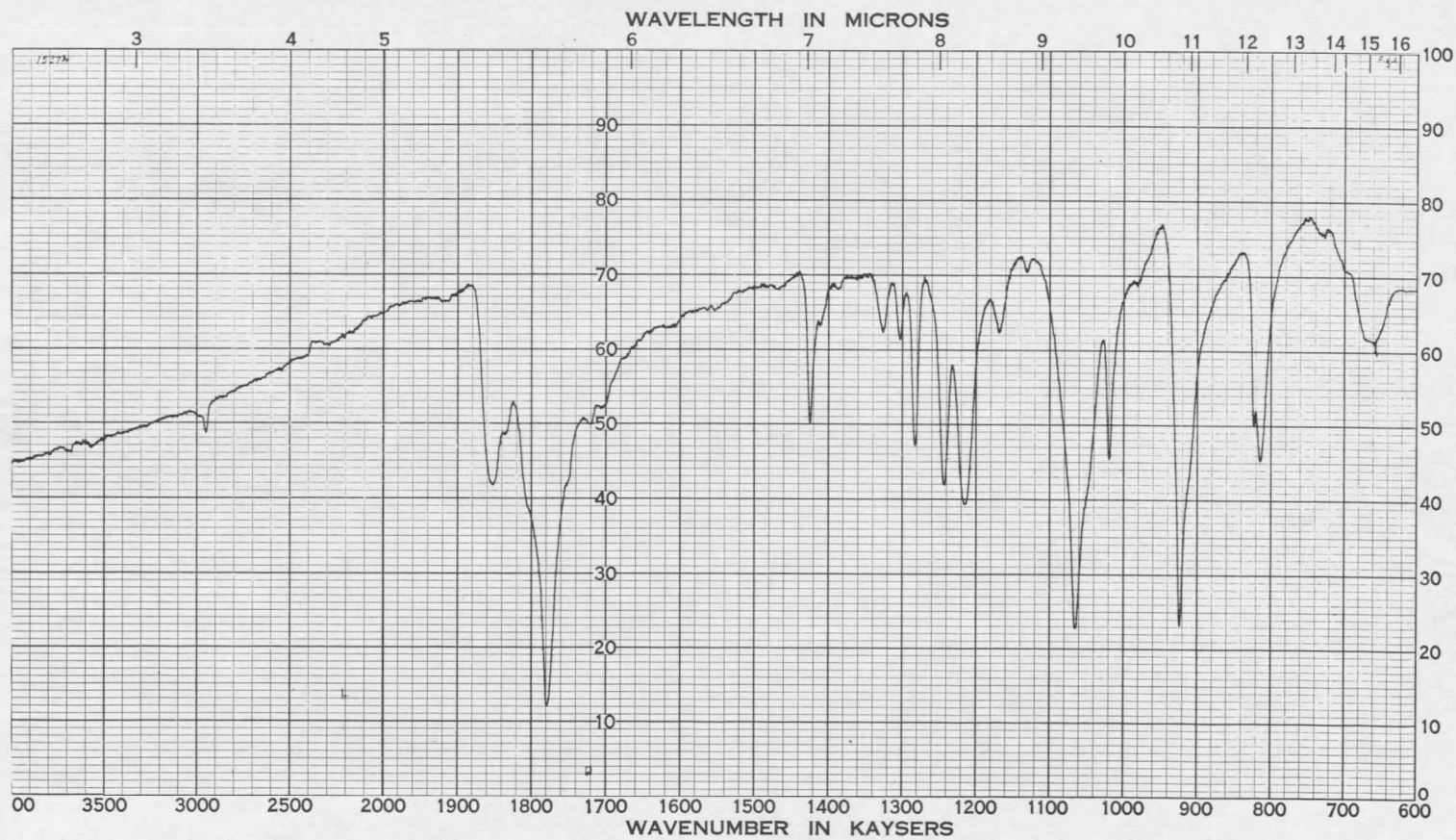


Figure 5. Infrared Spectra of Succinic Anhydride, Non-polarized

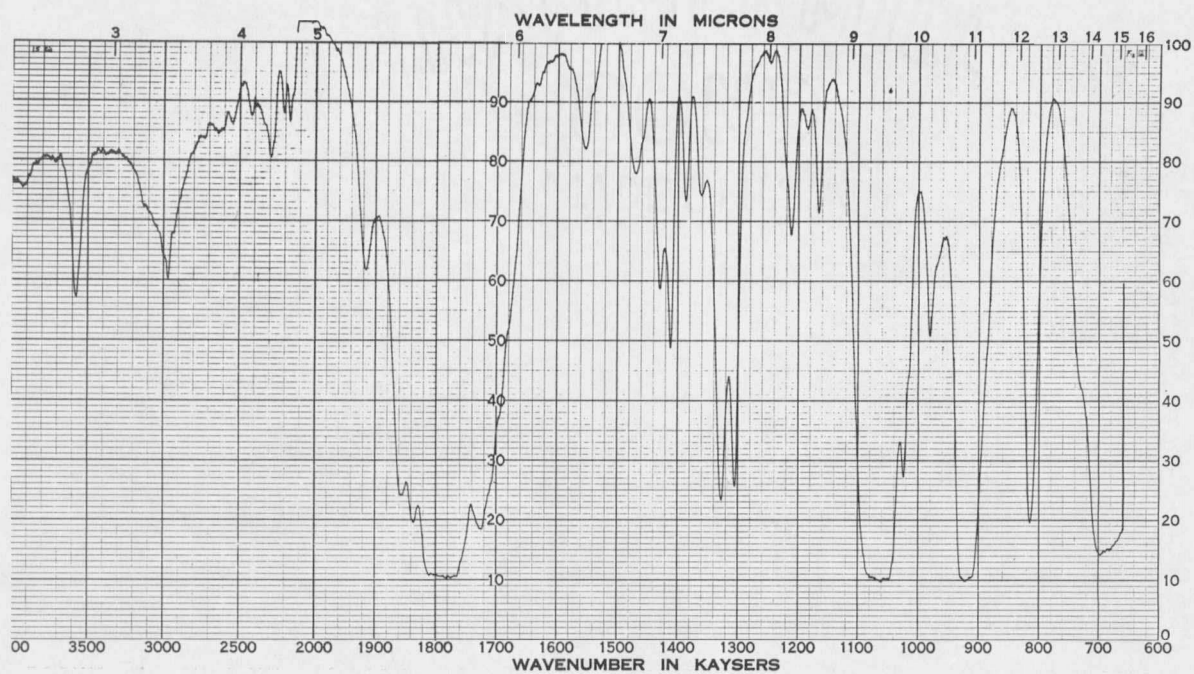


Figure 6. Infrared Spectra of Succinic Anhydride, Polarized Perpendicular

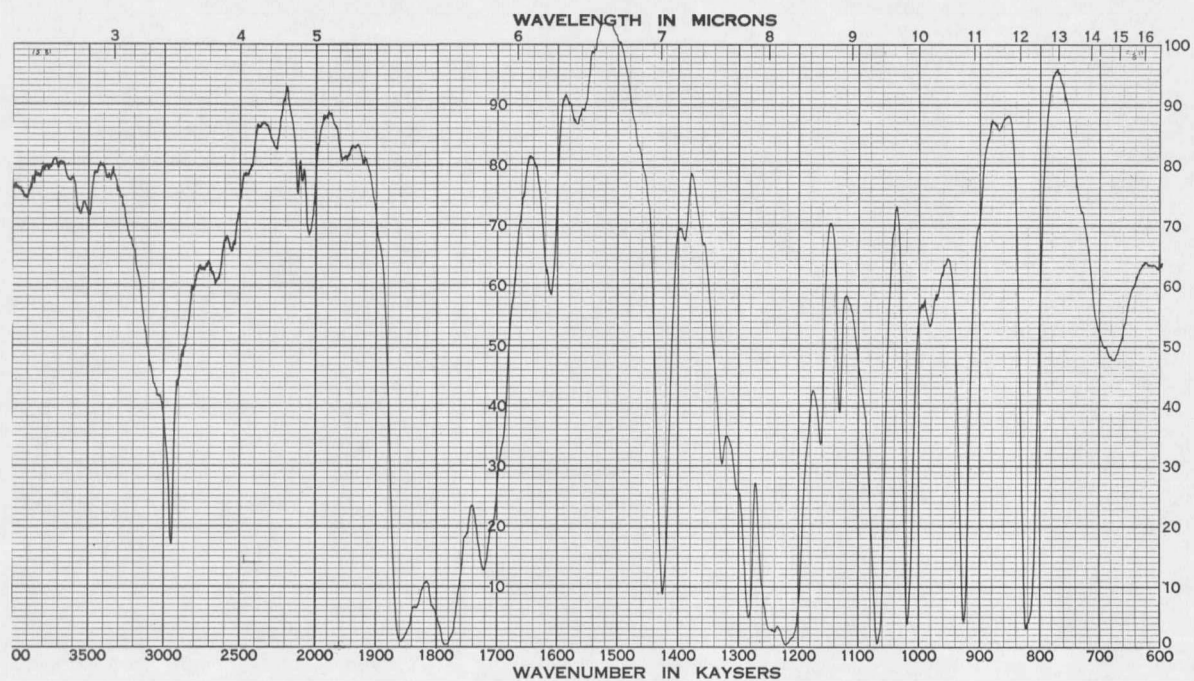
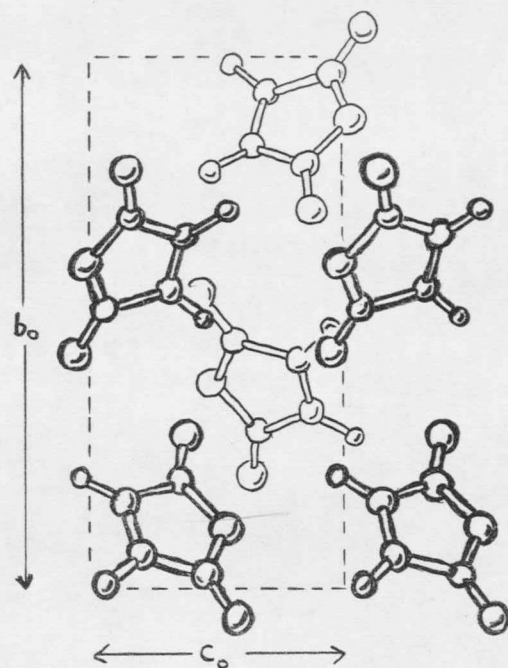
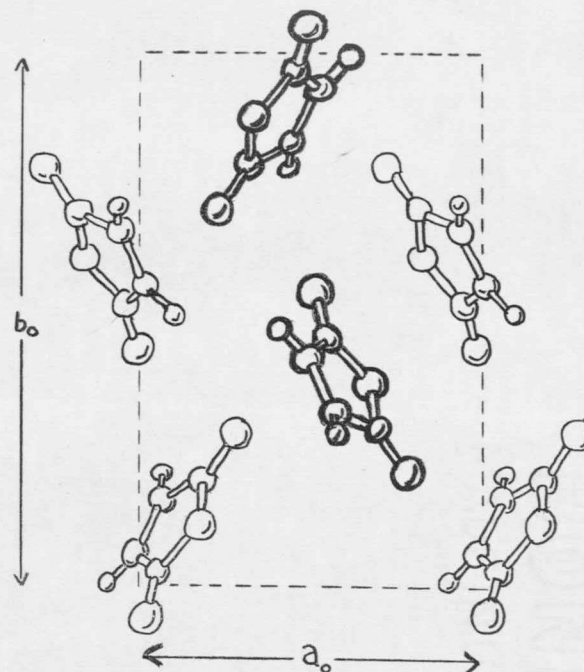


Figure 7. Infrared Spectra of Succinic Anhydride, Polarized Parallel



The structure viewed down the a-axis



the structure viewed down the c-axis

Figure 8 Crystal Structure of Maleic Anhydride

that represents each fundamental vibration. The plane upon which this vector is projected is determined by the way in which the cosine relation is used. A complete treatment may be made with the vectors projected upon all of the three planes involving the crystallographic axes. As a result of this treatment, it can be seen that each of the A_1 , B_1 , B_2 fundamental vibrations will have a changing dipole moment vector component perpendicular and parallel to the growth direction (c-axis). The magnitude of these two vectors will be different with the A_1 vibrations having the largest vector parallel to the growth axis and the B_1 and B_2 vibrations having the largest vector perpendicular to the growth axis. This indicates the direction of the radiation electric vector $\vec{E}$ to obtain maximum absorption.

The data of Marsh indicates that the maleic anhydride ring is slightly puckered at the ring oxygen. They have indicated it to be 0.03A out of the plane of the molecule. Since the ring has been assumed planar, the effect of slight deviation from planarity should be considered. The main effect is that the molecule does not actually have the C_{2v} symmetry that was assumed. This would tend to activate the infrared inactive A_2 species. Since the deviation from planarity is small, the intensity of any such activated band would be weak and possibly unobservable. This non-planarity could also cause some small decrease in the intensities of the A_1 and B_1 bands.

A sample rotation of 180 degrees was run for maleic anhydride to establish the cosine relation previously discussed. The spectra for

the 3607 cm^{-1} band is shown in Figure 9 for the ten different sample orientations. Other bands exhibited similar patterns. To illustrate the parallel and perpendicular polarization of the A_1 and B_1 carbonyl stretching fundamentals, the intensities of the bands subsequently assigned to A_1 carbonyl stretching were converted to absorbance values with a zero absorbance base line. A plot of these values as a function of sample orientation is shown in Figure 10 along with the theoretical $\cos^2 \Theta$ curve. Comparison of the A_1 and B_1 curves indicates that the right half of the A_1 curve has absorbance values that are too high to give a symmetrical curve. This accounts for the slight shift of the phase relation exhibited by the two curves, since there is undoubtedly band overlap. The strong B_1 band is probably making some contribution to the A_1 band intensity.

By the application of group theory, the 1st overtone of a B_1 band should be A_1 . This means that the 3607 cm^{-1} band should be A_1 if assigned as the 1st overtone of the B_1 C=O stretching vibration, however, it was observed to be B_1 in character. It is quite probable that this band is a combination of the A_1 and B_1 C=O str. with B_1 symmetry.

Table I summarizes the properties expected of the fundamentals for maleic anhydride. The infrared polarization refers to the relationship of the radiation electric vector $\vec{E}$ and the growth axis $\vec{G}$. The wave-numbers and infrared polarization of the observed bands have been tabulated in Table II.

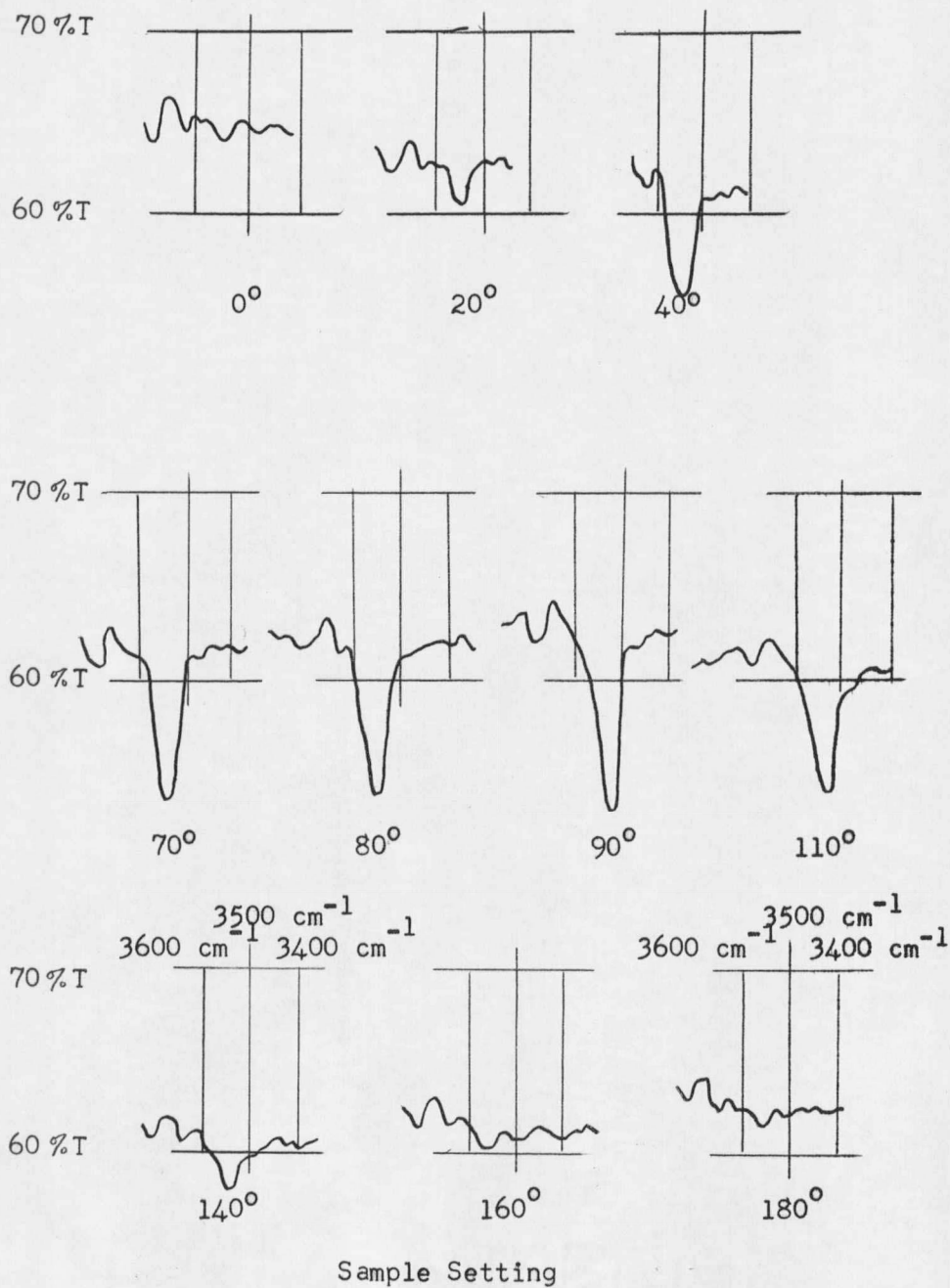


Figure 9

Combination band involving B₁ C=O str.
at different sample orientations

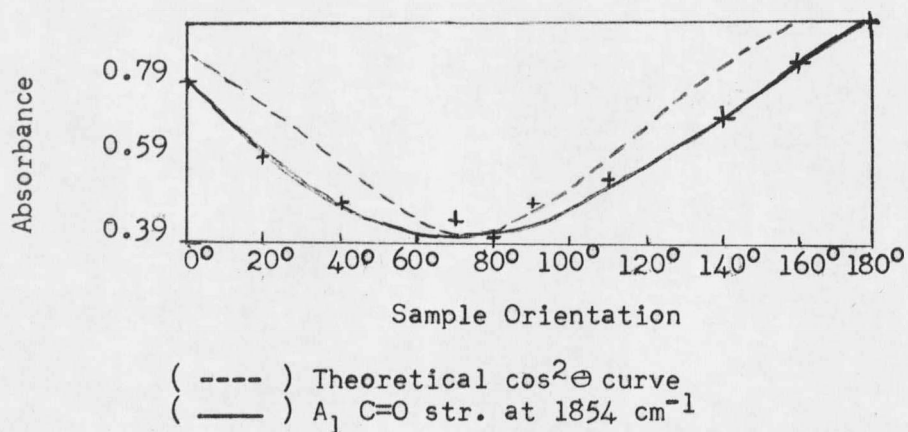
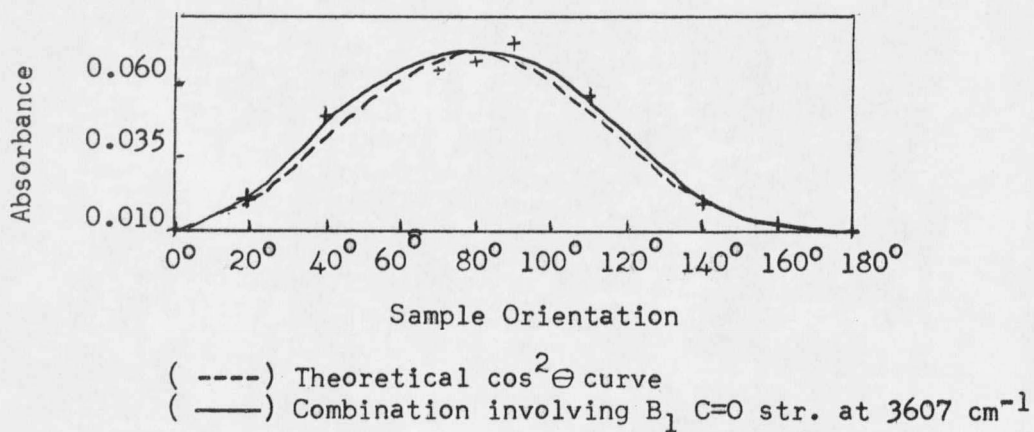


Figure 10 Band Intensity as a Function of Sample Orientation

TABLE I

Expected Properties of Maleic Anhydride

Specie	Localized description	Approx. infrared region (cm ⁻¹)*	Infrared polarization**
A ₁	CH str.	ca 3100	parallel
	C=O str.	1800-1850	"
	C=C str.	ca 1600	"
	CH bend	800-1400	"
	C-O str.	900-1300	"
	C-C str.	800-1200	"
	Ring bend	600-800	"
	C=O bend	400-700	"
B ₁	CH str.	ca 3100	perpendicular
	C=O str.	1750-1800	"
	CH bend	600-1000	"
	C-O str.	900-1300	"
	Ring bend	600-1000	"
	C=O bend	400-700	"
A ₂	CH bend	800-1400	infrared inactive
	Ring bend	?	"
	C=O bend	400-700	"
B ₂	CH bend	600-800	perpendicular
	Ring bend	?	"
	C=O bend	400-700	"

* Reference 32

** Angle between growth axis and radiation vector

TABLE II

Observed Properties of Maleic Anhydride Fundamentals

σ (wavenumber) cm ⁻¹ in vac.	Infrared polarization*	Absorbance maximum	variation of absorbance
698	90	0.499	78.2
846	90	1.065	23.0
871	0	0.559	31.4
898	90	1.054	31.8
908	90	0.980	80.4
958	90	0.072	22.2
1060	90	1.059	22.6
1064	0 ?	0.966	33.6
1243	0	1.218	61.3
1268	0	1.039	70.3
1289	0	1.079	58.9
1400	90 ?	0.123	41.5
1589	0	0.375	67.0
1626	0	0.162	74.0
1755	90	1.005	48.2
1784	90	1.262	26.8
1854	0	0.998	61.0
1935	90	0.195	81.0
3124	0 ?	0.309	26.7
3188	90 ?	0.104	51.9
3607	90	0.076	85.5

* The polarization is expressed in degrees between growth axis and the radiation vector.

There are eight A_1 and seven B_1 fundamentals for maleic anhydride. Of these, the following may be readily identified.

	A_1 (cm^{-1})	B_1 (cm^{-1})
CH stretching	3124	3188
C=O Stretching	1854	1784
C=C stretching	1589	----

Discussion of the C=O stretching mode will be made later.

If the motion of the carbon atoms in the C=C stretching vibration is along the direction of the bond, the dipole moment change would be negligibly small and would not appear in the spectra even though theoretically it should be infrared active. Since the C-C-C angle is near 108 degrees as indicated by x-ray data(16), the C=C stretching motion in the normal coordinate description is more accurately described as shown in Figure 11.

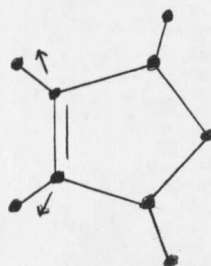


Figure 11 Carbon-carbon Double Bond Stretching Motions

This provides some change in dipole moment and would be expected to appear with weak to medium intensity in the infrared spectra.

The remaining five pairs of A_1 and B_1 fundamentals were somewhat more difficult to assign. One would expect the A_1 and B_1 C-O stretching bands to occur in the region of 1000 to 1300 cm^{-1} . The only band in

this region conforming to B_1 polarization was observed at 1060 cm^{-1} and thus assigned to the B_1 C-O stretching mode. Three A_1 bands were observed between 1200 and 1300 cm^{-1} . The band at 1243 cm^{-1} was selected for the A_1 C-O stretching because of its similarity to a band in the spectra of succinic anhydride. These ring atoms are in similar molecular environments in both maleic and succinic anhydrides and hence should show comparable absorption bands in both spectra.

The average C-C stretching vibration occurs near 900 cm^{-1} . Due to the possibility of resonance occurring in the ring, the C-C stretching motion was predicted to have some double bond character. This has been confirmed by the x-ray data of Marsh and coworkers(16) who report 15% double bond character. On this basis, the average C-C stretching mode in maleic anhydride probably would be closer to 1000 cm^{-1} . Consequently the A_1 and B_1 C-C stretching vibrations are assigned to the bands at 1064 and 898 cm^{-1} respectively. These bands are slightly more intense than would be expected for the C-C bands. They are probably not simple carbon to carbon stretching motions, but include some carbon-oxygen motion. This also would be reason to expect them at a higher frequency.

The A_1 and B_1 CH in-plane bending vibrations are assigned to the bands at 1268 and 908 cm^{-1} respectively. It is a possibility that the 898 cm^{-1} band previously assigned to the B_1 C-C stretching could have been interchanged with the 908 cm^{-1} band of the CH bending vibration since both are B_1 bands. The CH bending would be expected to occur

at a higher frequency than the C-C stretching vibration and thus the 908 cm^{-1} band is better located for the CH bending vibrations. Another possibility that was considered, assigned the 1060 cm^{-1} band (previously assigned to B_1 C-O stretching) as the B_1 CH bend and the 898 cm^{-1} band as the B_1 C-O stretching vibration. This would make a better fit for the CH bending vibration but gives a separation of about 350 cm^{-1} for the two C-O stretching bands, which is unusually large.

The A_1 and B_1 ring bending vibrations are assigned to the bands at 871 and 698 cm^{-1} respectively. This is in agreement with similar assignments of the A_1 and B_1 bands of pyrrole(20) at 711 and 647 cm^{-1} and of furan(21) at 725 and 624 cm^{-1} . They are both five-membered heterocyclic rings and should have ring bending modes comparable with maleic anhydride. The A_1 , B_1 and B_2 C=O bending vibrations are expected to occur below the range of the sodium chloride prisms and are not assigned. This assumption is based on similar assignments for acetone(22) and methyl acetate(23) in the region of 500 to 600 cm^{-1} .

The remaining band to be assigned is the B_2 CH bending vibration, which probably occurs around 600 to 800 cm^{-1} . The band at 698 cm^{-1} (previously assigned to ring bend) is considered as a possibility. The only other B polarized band in this region is at 846 cm^{-1} . However this is at too high a frequency for the ring bend and thus is considered to be the B_2 CH bending vibration.

The only remaining band in the spectra of moderately strong intensity was observed at 1289 cm^{-1} . This band is one of three that appeared

between 1200 and 1300 cm^{-1} . Two possible interpretations are considered for this band. The carbon-carbon stretching fundamental would be a reasonable assignment if the bond has a large degree of double bond character. The other possibility is interaction of an overtone or combination of a lower band, enhanced by Fermi resonance* with the band at 1268 cm^{-1} of the same symmetry. The first possibility can be eliminated by comparing the spectra of maleic and succinic anhydride. The same set of three bands appears in the spectra of succinic anhydride. Since the succinic anhydride molecule does not have the same opportunity for double bond character in the C-C bonds, the Fermi resonance interpretation is considered as most likely.

Because of the similarity in structure of maleic and succinic anhydrides a comparative assignment can be made for succinic anhydride. Any difference in their spectra is expected to be due to the change in the carbon-hydrogen portion of the molecule and the C=C double bond region. Succinic anhydride would have two CH bending vibrations in each symmetry species as determined by the symmetry coordinates of the molecule. There would be an A_1 and B_1 CH_2 scissoring vibration near 1450 cm^{-1} . The pair observed at 1420 and 1408 cm^{-1} is found to agree with the infrared polarization of the A_1 and B_1 scissoring vibration. The pair of bands at 1211 and 1164 cm^{-1} are considered to be the CH_2 in-plane wagging vibrations. These would be analogous to the CH motions

* Fermi resonance - mixing of closely spaced energy levels of the same symmetry, with subsequent splitting to give two bands of nearly the same intensity.

found in maleic anhydride at 1268 and 908 cm^{-1} . Since the C-C bonds in succinic anhydride do not have the resonance possibility existing in maleic anhydride, they are expected to occur at a lower frequency. The A_1 C-C stretching vibration is found to have shifted from 1064 cm^{-1} down to 1014 cm^{-1} in making the comparison. The B_1 C-C stretching vibration is assigned at 919 cm^{-1} . The A_2 and B_2 CH_2 twisting vibrations would be expected to occur near 1300 cm^{-1} with weak to medium intensity and are assigned to the bands at 1300 and 1324 cm^{-1} respectively. The A_2 and B_2 CH_2 out-of-plane rocking vibrations are assigned to the pair at 818 and 810 cm^{-1} . The A_2 mode would not normally be expected to occur unless coupled with some lattice vibrations as indicated by Hornig(17). The remaining fundamentals are assigned by direct analogy.

Since this investigation was initiated, Mirone and Chiorboli(18)* have reported a complete vibrational assignment of maleic anhydride. Their work is based upon non-polarized infrared (solid and vapor state) and Raman spectra. Their work confirms the 846 cm^{-1} band as the CH bending vibration as assigned. A number of disagreements occur, however, between this work and that of MC. These discrepancies are tabulated in Table III. Their assignment of the B_1 C=O stretching vibration to a band in the 1250 cm^{-1} region is not compatible with the polarized infrared spectra. No band is observed in the region of 1070 to 1300 cm^{-1} with B_1 polarization. Based upon the polarized spectra, there is no alternative choice for the A_1 C=O stretching fundamental. Their assign-

* Hereafter referred to as MC.

ment of the C-C stretching vibration is considered to be too low in view of the partial double bond character. Their assignment of the A_1 ring bend at 640 cm^{-1} is not observed in the polarized spectra, undoubtedly due to low intensity. It is obvious that these discrepancies point out the need for further work in this area.

TABLE III

Assignment Discrepancies Compared With Mirone and Chiorboli(18)

	<u>This work</u>	<u>MC</u>
G-O stretching A_1	1243 cm^{-1}	1068 cm^{-1}
B_1	1060 cm^{-1}	1268 cm^{-1}
C-C stretching A_1	1064 cm^{-1}	871 cm^{-1}
Ring bending A_1	871 cm^{-1}	640 cm^{-1}

A summary of the vibrational assignments for maleic and succinic anhydrides is given in Table IV.

An approximate force constant calculation has been made for the A_1 and B_1 in-plane motions and is given in Appendix C. The calculations are based on the assigned fundamentals. The results are indicated in Table V. Although the calculations are crude and contain a number of approximations, the results are essentially in agreement with expected values. The largest discrepancy is in the C-C stretching force constant which was found to be somewhat low considering that it has some double bond character. This is probably due, in part, to the assumption that the reduced mass for all ring vibrations would be the same.

TABLE IV

Vibrational Assignments of Maleic and Succinic Anhydrides

		maleic anhydride	succinic anhydride
A ₁	CH str.	3124	2968
	C=O str.	1854	1860
	C=C str.	1589	----
	CH bend	1268	1420 scissor
		----	1211 wag
	C-O str.	1243	1239
	C-C str.	1064	1014
	Ring bend	871	700
	C=O bend	unassigned	unassigned
B ₁	CH str.	3188	3008
	C=O str.	1784	1786
	CH bend	908	1408 scissor
		----	1164 wag
	C-O str.	1060	1060
	C=C str.	898	919
	Ring bend	698	661 ?
	C=O bend	unassigned	unassigned
A ₂	CH str.	----	? (unresolved)
	CH bend	766	818 rock
		----	1300 twist
	Ring bend	unassigned	unassigned
	C=O bend	unassigned	unassigned
B ₂	CH str.	----	? (unresolved)
	CH bend	846	810 rock
		----	1324 twist
	Ring bend	unassigned	unassigned
	C=O bend	unassigned	unassigned

All units are cm⁻¹

TABLE V

A_1 and B_1	Calculated	Force Constants	
		Expected range*	Interaction constant
C=O str.	12.4	11.8 - 13.4	1.11
C=C str.	9.5	9.5 - 9.9	----
C-O str.	5.00	5.0 - 5.8	1.83
C-C str.	3.63	4.5 - 5.6	1.45
Ring bend**	2.33	?	1.18
C=O bend**	0.91	?	-0.65

All units of 10^5 dynes/cm.

* Reference 19, pg. 175, 176

**Vibrational assignments taken from Mirone and Chiorboli(18) for additional required parameters.

The interaction force constants between identical functional groups turned out to be quite large. This is expected on the basis of two factors, the close proximity of certain identical groups and a rigid, slightly strained ring. It is expected that the interaction constant for two C=O groups would be the largest due to their close proximity in the ring. The calculations confirmed this with a value of 1.83×10^5 dynes/cm.

The origin of the two bands in the carbonyl stretching region has been discussed by Bellamy(1) and also by Jones and Sandorfy in Weissberger's text on Chemical Application of Spectroscopy(32). The general opinion has been that these two bands represent the in-phase (A_1 at 1800 to 1850 cm^{-1}) and the out-of-phase (B_1 at 1750 to 1800 cm^{-1}) motions due to simple mechanical coupling. Another possibility is that both carbonyl bands are together in the 1750 to 1800 cm^{-1} region and the 1800 to 1850 cm^{-1} band is an overtone enhanced by Fermi resonance with the strong carbonyl band at 1750 to 1800 cm^{-1} . If this were the case, both bands would be of the same symmetry species. The polarized spectra indicates that these bands belong to different symmetry species, however, thus eliminating the Fermi resonance interpretation. The polarized spectra may also be used to eliminate the possibility of the two bands arising from two carbonyl groups, each in a different molecular environment. The x-ray data indicates that the angle between the carbonyl groups is about 145 degrees. Since the phase relation determined from the polarized spectra is approximately 90 degrees, this con-

jecture is doubtful. Thus it appears that the two carbonyl bands are basically due to the mechanically coupled carbonyl vibrators.

PROPOSED FUTURE RESEARCH

This study constitutes only a small portion of the work that can be done in this area. A study of the mono- and di-deuterated maleic anhydrides would prove invaluable in providing further confirmation for the assignments made in this study. Since deuteration does not appreciably change the force constants for the maleic anhydride molecule, the frequency shifts of the CH vibrations would be due to the mass change. The shift could be calculated and checked with the spectra for agreement. Since the force constants do not change, this would give three sets of data (hydrogen, mono- and di-deuterated), enabling a more complete force constant calculation to be made on maleic anhydride. Also mono-deuteration would break the C_{2v} symmetry, thus ensuring the appearance of the A_2 vibrations.

The mono- and di-halogen derivatives of maleic anhydride could profitably be studied. Due to the size and electronegativity of the halogens, they would probably affect the ring force constants as opposed to deuteration. This should cause some shift of the vibrational frequencies involving ring motions.

Similar studies could be expanded into other cyclic anhydrides and eventually into the acyclic group.

The corresponding imides should provide interesting analogies because of their similarity in structure. The anhydrides have a ring oxygen where as the imides have an isoelectronic NH group, roughly of the same size.

Solvent effect studies could also be made on all of the above

proposed anhydrides and imides not only in the carbonyl stretching region, as used by Bellamy(24) but in the fingerprint region as well. Observation of frequency and intensity variation with solvent polarity would provide information as to bands with similar solvent effects, thus indicating A_1 and B_1 pairs which arise from motions of the same atoms.

APPENDIX A

Decomposition of Genuine Vibrations

The (3N-6) fundamentals of non-linear molecules may be grouped together according to the effect that various symmetry operations have upon the molecular motions. This classification is based upon the application of group theory. Maleic and succinic anhydrides are essentially planar molecules which belong to the C_{2v} point group. The distribution of the fundamental modes among the various symmetry species of the C_{2v} point group may be calculated according to the procedure of Herzberg(25). This calculation is based upon the number of sets of equivalent atoms that are situated on various symmetry elements. The results of these calculations are summarized in Table VI.

TABLE VI

Distribution of Fundamental Vibrations Among Symmetry Species

	A_1	A_2	B_1	B_2	3N-6
Maleic anhydride	8	3	7	3	21
Succinic anhydride	9	5	8	5	27

The first four column headings are shorthand descriptions of symmetry behavior. The A and B refer to symmetric or asymmetric behavior with respect to rotation about the principal axis of symmetry (in this case the two-fold rotational axis thru the ring oxygen and bisecting the opposite carbon-carbon double bond). The subscripts 1 and 2 refer to symmetric or asymmetric behavior with respect to reflection in the molecular plane.

APPENDIX B

Symmetry Coordinates of Maleic Anhydride

Symmetry coordinates are linear combinations of internal coordinates (changes in bond lengths and angles). Decius(26) has given a set of equations which may be used to determine the distribution of internal coordinates among the stretching(d), in-plane bending(ϕ), out-of-plane bending(γ) and bond torsion(τ) internal coordinates. This set of internal coordinates completely describes the motions within the molecule. The results of applying these equations to maleic and succinic anhydride are given in TABLE VII.

TABLE VII

Distribution of Internal Coordinates for Maleic and Succinic Anhydrides

	n_d	n_ϕ	n_γ	n_τ	$3N-6$
Maleic anhydride	9	6	4	2	21
Succinic anhydride	11	8	6	2	27

n = number of indicated coordinates needed

The choice of linear combinations of internal coordinates is not arbitrary but must conform to certain requirements. The combinations must be constructed from sets of equivalent orthonormal internal coordinates, and transform according to the symmetry species of the point group to which the molecule belongs. The internal coordinates for maleic anhydride are illustrated in Figure 12, from which it can be seen that the sets of equivalent internal coordinates for maleic anhydride are:

$$\begin{array}{llll}
 d_1, & d_2; & d_3, & d_4; & d_5, & d_6; & d_7, & d_8; & d_9 \\
 \phi_1, & \phi_2; & \phi_3, & \phi_4; & \phi_5, & \phi_6 \\
 \gamma_1, & \gamma_2; & \gamma_3, & \gamma_4; & \tau_1, & \tau_2
 \end{array}$$

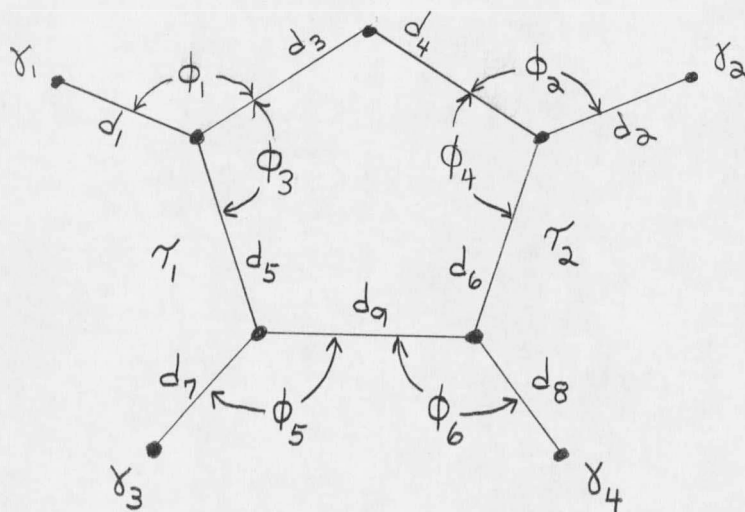


Figure 12 Internal Coordinates for Maleic Anhydride

The prescription for the symmetry coordinates is given by Meister and Cleveland(27) as:

$$R_j = \sum_k U_{jk} r_k, \quad B-1$$

where the R_j is the j th symmetry coordinate required for normalization and orthogonality and r_k is the appropriate internal coordinate. The resulting symmetry coordinates for maleic anhydride are collected in Table VIII.

TABLE VIII

Symmetry Coordinates of Maleic Anhydride

Coordinate Description	A_1	B_1
C=O str.	$R_1 = \frac{1}{\sqrt{2}}(d_1 + d_2)$	$R_9 = \frac{1}{\sqrt{2}}(d_1 - d_2)$
C=O str.	$R_2 = \frac{1}{\sqrt{2}}(d_3 + d_4)$	$R_{10} = \frac{1}{\sqrt{2}}(d_3 - d_4)$
C-C str.	$R_3 = \frac{1}{\sqrt{2}}(d_5 + d_6)$	$R_{11} = \frac{1}{\sqrt{2}}(d_5 - d_6)$
C=O bend	$R_4 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$	$R_{12} = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$
Ring bend	$R_5 = \frac{1}{\sqrt{2}}(\phi_3 + \phi_4)$	$R_{13} = \frac{1}{\sqrt{2}}(\phi_3 - \phi_4)$
CH bend	$R_6 = \frac{1}{\sqrt{2}}(\phi_5 + \phi_6)$	$R_{14} = \frac{1}{\sqrt{2}}(\phi_5 - \phi_6)$
C-H str.	$R_7 = \frac{1}{\sqrt{2}}(d_7 + d_8)$	$R_{15} = \frac{1}{\sqrt{2}}(d_7 - d_8)$
C=C str.	$R_8 = d_9$	- - - - -
	A_2	B_2
C=O bend	$R_{16} = \frac{1}{\sqrt{2}}(\gamma_1 + \gamma_2)$	$R_{19} = \frac{1}{\sqrt{2}}(\gamma_1 - \gamma_2)$
Ring bend	$R_{17} = \frac{1}{\sqrt{2}}(\tau_1 + \tau_2)$	$R_{20} = \frac{1}{\sqrt{2}}(\tau_1 - \tau_2)$
CH bend	$R_{18} = \frac{1}{\sqrt{2}}(\gamma_3 + \gamma_4)$	$R_{21} = \frac{1}{\sqrt{2}}(\gamma_3 - \gamma_4)$

APPENDIX C

Method of Calculating Force Constants

The force constant analysis follows that of Meister and Cleveland (27). The method consists of analyzing the vibrational motions of atoms in a molecule as a set of coupled harmonic oscillators. A single harmonic oscillator may be described as the kinetic energy of the moving mass balanced against a restoring force (potential energy) proportional to the displacement of the mass from an equilibrium position. Using matrix notation, and remembering that the appropriate positions and velocities are expressed in terms of symmetry coordinates, the problem reverts to a solution of the following secular equation:

$$\begin{vmatrix} \underline{F} \underline{G} - \lambda \underline{E} \end{vmatrix} = 0, \quad \text{C-1}$$

where $\underline{F}$ is a matrix representing the possible restoring forces in the molecule, $\underline{G}$ is a matrix identified with kinetic energy components ordered in the same fashion as the potential energy, λ is a characteristic solution (equal to $4\pi^2 c^2 \nu^2$), and $\underline{E}$ is a unit matrix. Since symmetry coordinates are employed, the secular equation is automatically block diagonalized into factors corresponding to the various symmetry species of the appropriate point group. Consequently, since $\underline{G}$ is a matrix with elements specified by structural parameters (atomic masses, bond lengths, bond angles), substitution of assigned frequencies (ν) of a particular symmetry species yields a set of equations which define the $\underline{F}$ matrix, an ordered array of the force constants for the particular vibrational modes of the chosen symmetry species. This treatment is therefore composed of the following parts; defining a model, preparing the $\underline{F}$ and $\underline{G}$ matrices

and solving the resulting force constant equations.

Model

The model chosen is a restricted maleic anhydride molecule in which the hydrogen atoms are considered an integral part of the carbon to which they were bonded (that is, the CH moves as a unit). This provided a simpler system to work with but as a consequence gives no information about the force constants of the CH motions. The internal coordinates and symmetry coordinates are the same as given in Appendix B for maleic anhydride with the elimination of those involving hydrogen.

F Matrix

The force constant matrix as given by Meister and Cleveland is

$$\underline{F} = \underline{U} \underline{f} \underline{U}'$$

The U matrix represents an ordered array of the internal coordinate coefficients required to orthonormalize the symmetry coordinates and the prime defines the transpose matrix of U. The f matrix is an ordered array of the individual force constants obtained by assigning a force constant to all possible paired combinations of the internal coordinates. Multiplication of these matrices and subsequent simplification as a result of some identical elements gives four force constant matrices, one for each of the symmetry species of the C_{2v} point group with the fundamental force constants along the diagonal and interaction constants off the diagonal.

G Matrix

The non-zero g elements were evaluated with the aid of the tabulated equations of Decius(28). The numerical values of the G matrix elements are indicated in Table IX.

Force Constant Equations

The expanded form of the secular equation is given by Wilson, Decius and Cross(29) as:

$$\sum_{s=0}^n \left[(-1)^s \lambda^{n-s} \sum \left(\underline{G}(s) \quad \underline{F}(s) \right) \right] = 0 \quad C-2$$

The $\underline{G}$ and $\underline{F}$ terms are corresponding s -rowed minors of the determinants of the G and F matrices and n is the order of the determinants. In principle this equation may be solved for the force constants if the frequencies are known or vice-versa. All too often, the problem of too many force constants for the number of frequencies prevents an exact solution, as is the case for maleic anhydride. As a simplifying assumption, the off-diagonal force constants were assumed to be small enough to neglect. These force constants are interaction constants between non-identical functional groups and thus necessarily smaller than the fundamental constants.

Since λ_n represents the collection of roots of the secular equation,

$$(\lambda - \lambda_n)^n = 0 \quad C-3$$

may be written as an analogous power series equation in λ . Equating coefficients of the second terms gives:

$$\sum_{n=1}^n \lambda_n = \sum \underline{G}(1) \underline{F}(1) \quad C-4$$

If this equation is applied separately to the A_1 and B_1 factors and

TABLE IX
G Matrices

A_1	8.782	-2.696	-2.696	0	-3.016d	-1.804d
		8.064	-2.200	0	-0.765d	-0.392d
			10.036	-1.036	0.383d	-3.492d
				10.036	0	3.734d
					1.543d ²	-1.560d ²
						9.044d ²
B_1	8.762	-2.696	-2.696	-3.016d	-1.804d	
		9.500	-2.200	-6.159d	-5.786d	
			10.036	0.383d	-3.492d	
				2.507d ²	-2.438d ²	
					10.276d ²	
A_2	25.716d ²	17.183d ²				
		20.342d ²				
B_2	22.184d ²	17.183d ²				
		15.304d ²				

the results subtracted, the following relation is obtained.

$$\sum_{A_i} \lambda_{r_i} - \sum_{B_i} \lambda_{r_i} = \sum_{A_i} F^{(1)}_{G^{(1)}} - \sum_{B_i} F^{(1)}_{G^{(1)}} \quad C-5$$

However this equation contains n fundamental force constants and n interaction constants (between identical functional groups). Assuming that the fundamentals follow a harmonic oscillator description with the reduced mass of each fundamental the same in all cases, simple proportions may be set up to give additional equations. Taking the C=O and C-O stretching modes as examples, the average of their corresponding λ 's should be proportional to the fundamental force constant and their deviation from the average should be proportional to the interaction constant of two identical functional groups. By setting up proportions comparing all force constants to the C-O force constants, the above equation may be reduced to two unknowns, the fundamental and interaction force constants of the C-O functional group. Examples of these proportions are given below.

$$\frac{\lambda_{A_1} \text{ C=O} + \lambda_{B_1} \text{ C=O}}{\lambda_{A_1} \text{ C-O} + \lambda_{B_1} \text{ C-O}} = \frac{f_{\text{C=O}}}{f_{\text{C-O}}}$$

$$\frac{\lambda_{A_1} \text{ C=O} - \lambda_{B_1} \text{ C=O}}{\lambda_{A_1} \text{ C-O} - \lambda_{B_1} \text{ C-O}} = \frac{f_{\text{C=O interaction}}}{f_{\text{C-O interaction}}}$$

It is possible to transfer force constants from one molecule to another provided they exist in a similar molecular environment(30). Nakamoto and coworkers(31) have determined the force constant for a number of oxalato metal complexes. From the comparative molecular structures, their value of 5.00×10^5 dynes/cm. for the C-O fundamental

stretching force constant was considered applicable to maleic anhydride. The use of this value reduces the force constant equation to one unknown, the interaction constant between two C=O functional groups. From this result, other force constants may be obtained from similar force constant proportions. The results of these calculations are tabulated in Table V and have been previously discussed.

The magnitude of error introduced by the assumptions of this treatment is uncertain, however the intended purpose is not to make a rigorous treatment but to obtain additional information to substantiate the vibrational assignments.

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