



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  
Montana State University  
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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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Head, Major Department



Chairman, Examining Committee



Dean, Graduate Division

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TABLE OF CONTENTS

	Page
LIST OF TABLES. . . . .	v
LIST OF FIGURES . . . . .	vi
ABSTRACT. . . . .	vii
I. INTRODUCTION. . . . .	1
II. EXPERIMENTAL CONSIDERATIONS . . . . .	3
A. Instrument. . . . .	3
B. Polarized Spectra . . . . .	4
C. Preparation of Oriented Films . . . . .	4
III. THEORY. . . . .	7
A. Molecular Dynamics. . . . .	7
B. Nature of Polarized Infrared Absorption Spectra . . . . .	8
IV. VIBRATIONAL ASSIGNMENTS . . . . .	13
V. PROPOSED FUTURE RESEARCH. . . . .	35
VI. APPENDIX. . . . .	37
A. Decomposition of Genuine Vibrations . . . . .	37
B. Symmetry Coordinates of Maleic Anhydride. . . . .	38
C. Method of Calculating Force Constants . . . . .	41
VII. LITERATURE CITED. . . . .	47

LIST OF TABLES

Table	Page
I. Expected Properties of Maleic Anhydride Fundamentals . . . .	23
II. Observed Properties of Maleic Anhydride Fundamentals . . . .	24
III. Assignment Discrepancies Compared with Mirone and Chiorboli. . . . .	30
IV. Vibrational Assignments of Maleic and Succinic Anhydride . .	31
V. Force Constants. . . . .	32
VI. Distribution of Fundamental Vibrations Among Symmetry Species. . . . .	37
VII. Distribution of Internal Coordinates for Maleic and Succinic Anhydrides. . . . .	38
VIII. Symmetry Coordinates of Maleic Anhydride . . . . .	40
IX. <u>G</u> Matrix for Maleic Anhydride. . . . .	44

LIST OF FIGURES

Figure	Page
1. Motions Derived from Typical Symmetry Coordinates of Maleic Anhydride . . . . .	10
2. Infrared Spectra of Maleic Anhydride, Non-polarized. . . . .	14
3. Infrared Spectra of Maleic Anhydride, Polarized Perpendicular. . .	15
4. Infrared Spectra of Maleic Anhydride, Polarized Parallel . . . . .	15
5. Infrared Spectra of Succinic Anhydride, Non-polarized. . . . .	16
6. Infrared Spectra of Succinic Anhydride, Polarized Perpendicular. .	17
7. Infrared Spectra of Succinic Anhydride, Polarized Parallel . . . .	17
8. X-ray Structure of Maleic Anhydride. . . . .	18
9. Combination Band Involving $B_1$ C=O Stretching Vibration at Different Sample Orientations. . . . .	21
10. Band Intensity as a Function of Sample Orientation . . . . .	22
11. Carbon-carbon Double Bond Stretching Motions . . . . .	25
12. Internal Coordinates for Maleic Anhydride. . . . .	39

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  $\mu$ /min, equivalent to a scanning time of about three and a half hours for a complete spectrum(640-4000  $\text{cm}^{-1}$ ). 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  $3000\text{ cm}^{-1}$ . 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 crystallization 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  $\Theta$  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.

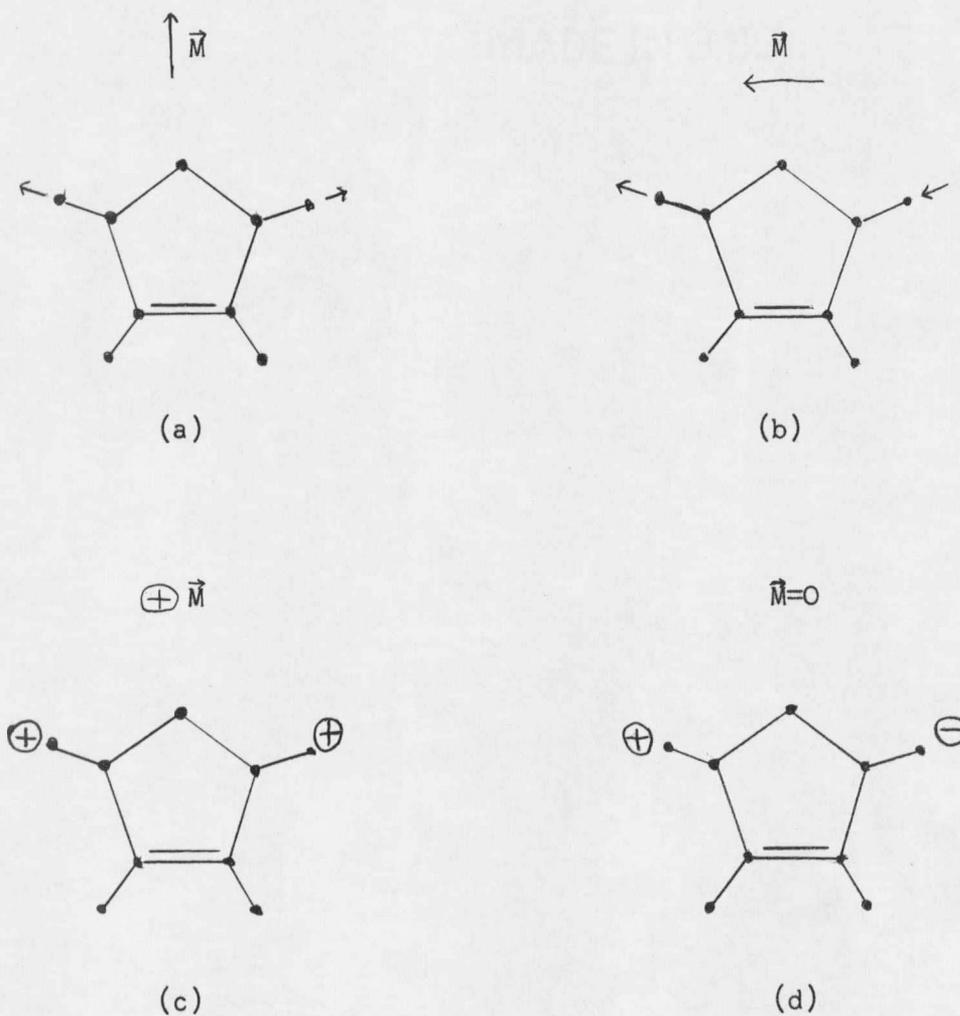


Figure 1 Motions Derived From Typical Symmetry Coordinates of Maleic Anhydride

(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







































































