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A RAMAN SPECTROSCOPIC STUDY OF SOME LEWIS ACID - BASE SYSTEMS

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INTRODUCTION

The study of acid-base phenomena has led to some of the most vigorous controversies in the field of chemistry. Theories proposed by eminent workers have gained acceptance only to be discarded as subsequent experimental evidence pointed out omissions or contradictions. Accumulating experimental evidence has always seemed to indicate a much greater complexity in both reactions and products than had been suspected earlier. As a result the theoretical treatments have tended to become more and more general until they now are closely related to the electronic nature of chemical interaction.

The one-element theories of Lavoisier and Davy served adequately through most of the nineteenth century although the type of experimental evidence which would lead ultimately to the water-ion theory was initiated by Faraday as early as 1834. Work by van't Hoff, Ostwald, and others upon aqueous solutions of electrolytes led Arrhenius to a concept which is useful even today as an aid to understanding the behavior of aqueous solutions.

Subsequent theories tended to be closely related to the Arrhenius theory but of broader scope. In Franklin's theory of solvent systems emphasis is placed not just upon water and its ions. An acid, according to him, was defined as a solute giving rise to a cation characteristic of the solvent, and a base was defined as a solute giving rise to a characteristic anion. A typical neutralization reaction in liquid N_2O_4 might be:

$$NOCl + AgNO_3 = AgCl + N_2O_4$$

where NOCl is an acid because of its ionization into NO^+ and $AgNO_3$ a base due to its ionization to give NO_3^-.

Because of its ability to relate acid-base behavior in numerous solvents, the theory of solvent systems offered a real advantage over the water-ion concept. It suffered from disadvantages present in the earlier theory in that it was still limited to solvent systems and overemphasized the ionic character of neutralization processes.

These weaknesses were actually the strengths of the protonic concept which Brønsted and Lowry advanced in 1923. Since they defined acid and bases as proton donors and acceptors respectively, the neutralization process was no longer dependent upon the reaction medium or upon the mechanism of proton transfer. Many species, both molecular and ionic, which had long been known to affect acids after the fashion of alkalis could now be accepted as bases. However, an equal number of species were excluded from classification as acids because they did not contain hydrogen, despite their acid-like effect upon alkalis. This constituted a serious omission.

The electronic theory of G. N. Lewis was actually very closely akin to the Brønsted-Lowry concept. Instead of basing acid-base phenomena entirely upon proton transfer, Lewis saw this to be only a special case of the more general occurrence, electron sharing.

Actually there are three ways in which two atoms might apportion electrons. A complete transfer of one or more electrons would lead to the familiar electrovalent or ionic bond. A contribution of one electron by each to make a pair which is then shared by both gives the covalent bond so common in organic chemistry. Finally, one atom may have a pair of electrons which it can donate to form a dative bond. It was this ability to accept an unshared pair of electrons that Lewis found to be common to all acids.

Lewis developed his theory by first listing all the species which exhibited a characteristic set of "acid" properties. Luder and Zuffanti(1) describe these four "phenomenological criteria" as:

I. Neutralization. Acids and bases may combine more or less rapidly with each other.

II. Titration with Indicators. Acids and bases may be titrated against each other by the use of substances, usually colored, known as indicators.

III. Displacement. An acid or base will in general replace a weaker acid or base from its compounds.

IV. Catalysis. Acids and bases frequently act as catalysts.

Any substance displaying all four of these characteristics was then classified as an acid or base, depending upon its similarity to a known acid, hydrogen chloride, or the known bases, the alkalis. While the list of bases turned out to be identical with that under the Brønsted-Lowry theory, the compounds designated as acids included not only proton donors and the acids of the solvent systems theory, but also many more which had never before been recognized as such by any formal theory.

According to Lewis' electronic theory the neutralization process involved formation of a dative bond between the base and the acid, where the acid was any molecule, radical, or ion capable of accepting an electron pair or pairs, with the base playing the role of the electron pair donor. This brought many seemingly unrelated reactions into the realm of neutralization reactions, since any case of coordination now represented acid-base behavior. This more generalized extension of the theory proved a stimulus to the new areas included, catalysis and coördination chemistry, for example.

The catalytic function of acids and bases was noted by Lewis among his "phenomenological criteria." The nature of this function can often be shown to be the result of the formation of an unstable intermediate by the catalyst through donation or acceptance of an electron pair. The complex $CH_3Br:AlBr_3$ discussed in this research appears to be one such case.

The contribution of Lewis' electronic theory to the field of coordination chemistry has been of a much broader scope. The difficulties which were present in this area at the time the Lewis theory was being formulated, stemmed from failure to understand the wide variations in binding forces and their obvious interrelation. The situation can perhaps be best illustrated by example. The divergencies in binding forces can be seen in ammine complexes like $Ag(NH_3)_2Cl$ and $Co(NH_3)_6Cl_3$. The former is ionic, readily and reversibly dissociating on heating or in solution, while the latter loses only one mole of ammonia at 175°C and retains all six moles in sulfuric acid solution. The interrelation of the two types of bonds is seen in $Co(NH_3)_5Cl_3$ in which only two chloride ions can be precipitated by aqueous silver nitrate.

Werner, in his early work on the nature of coordination, postulated two different valence types. The first, designated "principal" or "primary" valences, described the customary affinity bonds which are now defined in terms of combining capacity with hydrogen. His "auxiliary" or "secondary" valences were originally conceived as being quite different since, unlike the primary valences, they did not allow ionization.

These fundamental postulates met widespread criticism and general acceptance of Werner's theories was postponed for many years. Werner himself recognized a connection between his primary and secondary valences and finally concluded that no clear-cut distinction between them was possible. In the light of current valence theory it can be seen that Werner's "primary" valences involved either electrostatic or covalent bonds, and hence showed a wide variation in properties; his secondary valences were the dative bonds encountered in Lewis acid-base interaction. The field of Lewis acid-base interactions now is considered to be but a specialized segment of the much broader field of coordination chemistry.

The older question of what is an acid no longer seems to be compelling in the light of Lewis' behavioristic approach. Current interest has turned to an examination of the nature of the acid-base interaction and its products. In general, this is achieved through investigations of acid-base systems to determine the number and nature of the complexes formed.

Nearly every available physico-chemical technique has been employed to gain information about the nature of acid-base interaction. Thermodynamic properties of the more stable complexes have been evaluated. Heat capacity data have revealed something of the internal energy of the complexes while entropies or free energy changes can be a measure of the spontaneity of their formation and permit calculation of equilibrium constants. Even very weakly bound aggregations have been detected using such classical methods as phase studies and conductivity measurements. Cryoscopic methods have the additional advantage of giving stoichiometry as well as melting points.

Other techniques, more recently developed, make available structural information about the complexes. Knowledge of geometrical configuration, an indirect contribution to an understanding of the bonding forces involved, can be obtained by the methods of x-ray and electron diffraction. Configurations can also be inferred from dipole moment measurements and reactivities can be better understood in the light of such data. Reference has been made to one convenient method of detecting the occurrence of complexation, that of ultraviolet spectroscopy. Since the electronic part of the complex is most directly involved in the process of ultraviolet absorption, combinations of too fleeting existence for observation by other means can be disclosed. Functional groups can be identified in many cases despite the limited view of the overall interaction which is provided by this technique.

The application of group theory to the field of vibrational spectroscopy has permitted a much broader use of the techniques of infrared and Raman spectroscopy to gain information regarding configuration and binding forces in the complexes resulting from acid-base interaction. Nuclear magnetic resonance, which gives a measure of the electron distribution about the nucleus, has not been applied to any extent in this field but appears a promising tool for investigation.

STATEMENT OF THE PROBLEM

Earlier work in this laboratory(2) on the nature of the Lewis acid-base interaction centered about the HCl - dimethyl ether system. The technique employed was that of vibrational spectroscopy which permits direct observation of frequencies associated with certain molecular motions. This feature makes it particularly useful for general exploratory work in detecting complex formation through changes in the characteristic spectra of the reacting components. In addition to establishing the existence of stable complexes, the spectral results also supply information about the nature of these complexes.

Of the two methods available for the examination of vibrational spectra, the technique of Raman spectroscopy was chosen over infrared in the previous work principally because it permits use of all-glass apparatus and cells. Other materials, such as the rock salt required for infrared cells, are difficult, if not impossible, to use in view of the reactivity and properties of the reagents. The Raman technique also allows observation of a broader spectral region and is more conveniently adaptable to a wide range of temperatures. Since this research was instituted as an extension of Vidale's work, these same advantages make the Raman technique preferable.

The HCl - dimethyl ether system was found to contain at least three discrete complexes. Besides a 1:1 molecular complex there were two others which appeared to be ionic in nature, resulting from proton transfer accompanied by further complexation on the chloride. However, complete characterization of these ionic species was not possible because of inherent spectroscopic limitations of the HCl molecule. Although HCl has one frequency and its shifts could be used to detect complex formation, the solvated Cl^- ion had frequencies which were either too low in magnitude or of too low intensity to give any information as to the nature of the anion(s) formed. This inability to obtain spectra of the anions prevented complete characterization of these higher order complexes, although much information could be gleaned from shifts in the DME skeletal frequencies.

In the present work a more complex Lewis acid was sought which, in mixtures with DME, might give rise to another series of complexes in which both anionic and cationic fragments could be characterized. Such a system might well provide information on the stoichiometry of the HCl - DME complexes in addition to being valuable as another example of acid-base interaction.

Conductivity measurements and other work by Kraus and coworkers (3,4) have indicated the possible existence of more than one complex in the aluminum bromide - DME system. Also, Brown's(5) recently proposed single bridge structure for compounds of the boron halides suggests the possibility of higher order complexes in their systems with some of the stronger Lewis bases such as DME. From the experimental standpoint, these strong Lewis acids are well suited to an investigation of the type contemplated. Their low boiling points permit the use of high vacuum techniques for both purification and sample preparation. The acids themselves have only three vibrational frequencies active in the Raman effect which would not unduly complicate the spectra and would minimize the chance of a superposition of bands of the pure acid and its complexes. In addition, these halides are sufficiently stable species that cationic fragments resulting from complexation should be characterizable.

An extension of the scope of the investigation could be achieved by substituting a weaker acid for the boron and aluminum trihalides and a weaker base for DME. Sulfur dioxide is suitable for comparison with the stronger acids because it has all of the experimental and spectroscopic advantages of the latter and evidence is available that it forms a 1:1 addition compound with DME in the solid phase.

Complexation of strong Lewis acids with the relatively weakly basic alkyl halides has been indicated by H. C. Brown(6) as a result of thermal analyses of several aluminum bromide-alkyl halide systems. Most of the latter are sufficiently volatile to permit the use of vacuum techniques. From the spectroscopic viewpoint, the alkyl halides seem satisfactory also, since their only band in the 0-1200 cm.$^{-1}$ region, in which all of the bands of the strong acids fall, is the R-X stretching frequency.

HISTORICAL BACKGROUND

Etherates of the boron halides were first observed in 1846 when Ebelman and Bouquet(7) noted the formation of white, crystalline solids on mixing boron trichloride and several alkyl ethers. They reported that the solid evolved HCl and left a solid residue which they called " methyl protoborate."

Much of this work was repeated in 1889 by Gatterman(8). He correctly postulated the formation of a 1:1 addition compound when boron trichloride is added to ether. He also noted the solubility of the complex in ether.

As a result of a vapor pressure-composition study of the system BCl_3 - dimethyl ether (referred to hereafter as DME), Wiberg(9) confirmed the stoichiometry of the complex and noticed its ready decomposition into methyl chloride and a series of esters. In succeeding papers(10), Wiberg identified these esters and listed their physical properties as well as those of DME:BCl_3. No thermodynamic or spectroscopic investigations have been reported.

Compound formation in the BF_3-DME system was first reported as a result of the vapor pressure lowering on mixing(11,12). However, the first attempt to identify the product was a thermal analysis study by Germann and Cleaveland(13) which showed a maximum melting point at -9°C for a concentration corresponding to an equimolar mixture.

Considerable effort has been expended upon the study of the BF_3-DME system, probably because of its marked catalytic properties, and numerous thermodynamic data are available such as the heat of formation of DME:BF_3 (13.3 kcal./mole)$^{(14)}$. Its ultraviolet spectrum has been examined by Dundermann and Bauer$^{(15)}$ and an electron diffraction study has been carried out by Bauer and coworkers$^{(16)}$. The ultraviolet spectrum indicated only a broadening of the characteristic ether absorption band and does not appear to offer any significant information. The diffraction study, however, and the concurrent dipole moment measurement led Korshak and Lebedev$^{(17)}$ to an explanation of its catalytic action. A Raman spectroscopic investigation of DME:BF_3 was also attempted by Dundermann and Bauer$^{(15)}$ in connection with the electron diffraction investigation, but no attempt was made to assign the observed bands. This study was hampered by the presence of fluorescent decomposition products in the samples and by inadequate filtering of the exciting radiation. As a result, continuous background radiation prevented attempts to detect the weaker bands and some confusion from the overlapping of spectra excited by the 4046 A and 4358 A mercury lines was reported. They did note, however, a complete disappearance of all spectral lines associated with BF_3, and of all skeletal motions of dimethyl ether. As a result they were able to conclude that a very strong interaction takes place leading to the formation of a stable 1:1 molecular addition complex.

It appears that some spectroscopic work on BF_3-etherates has been done by Bues$^{(18)}$ as part of a doctoral thesis in Germany. A footnote by Goubeau and Lücke$^{(19)}$ makes reference to a stretching frequency of an unspecified etherate of BF_3. Unfortunately a copy of the dissertation was not available.

The discovery of complex formation in the $AlBr_3$-MeBr system came as part of a series of investigations by H. C. Brown and coworkers into the nature of catalysis in the Friedel-Crafts reaction(20). Vapor pressure - composition curves, molecular weight data, and vapor pressure - temperature plots have given conclusive evidence for the existence of MeBr:$AlBr_3$ and MeBr:Al_2Br_6 in the solid state.

Compound formation in the SO_2 - DME system was first suggested in 1907 by Briner and Cardoso(21) as the result of a vapor pressure - composition study. A phase diagram reported by Baume(22,23) showed the existence of a stable 1:1 complex in the solid state. However, a Raman spectroscopic investigation by Wolkenstein(24) revealed only slight shifts in several of the DME bands and no changes whatever in the SO_2 frequencies. No thermodynamic data have been reported.

Martin and Hicks(25) detected a maximum freezing point in the BCl_3 - ethyl chloride system at a concentration corresponding to the formation of EtCl:2BCl_3. Because of the flatness of the maximum they predicted marked dissociation in the liquid phase. This same study reported only a simple eutectic point in the BCl_3 - methyl chloride system. No spectroscopic or thermodynamic data can be found.

For the remaining systems, BX_3 - methyl bromide, no information indicating or denying the existence of complexes has been reported.

A BRIEF REVIEW OF VIBRATIONAL THEORY

This topic is given more thorough treatments in several current texts(26,27,28). Only a small portion which is pertinent to the current investigation will be discussed below.

From the purely theoretical standpoint, one should be able to obtain all of the internal parameters of a molecular system from Schrödinger's amplitude equation for a conservative system of point particles. For a system consisting of a total of n electrons and nuclei this may be written in the following form:

$$\sum_{i=1}^{n} 1/m_i \nabla_i^2 \psi + 8\pi^2/h^2 (W - V) \psi = 0$$

where m_i is the mass of the ith particle, ∇_i^2 is the Laplace operator in the coordinates of the ith particle, ψ is the wave function of the molecule, W is the total energy of the molecular system, and V is its potential energy.

Solution of the wave equation has so far been possible for only the very simplest molecules. For such a complicated system as a polyatomic molecule, simplifying assumptions are required and only approximate solutions are possible even then. Born and Oppenheimer(29) have pointed out one such assumption which permits a separation of variables into nuclear and electronic components. They argued that because of the tremendous mass differences between the electrons and the nuclei, a solution could be obtained for the electrons alone, assuming a fixed configuration of the nuclei. By then substituting a characteristic electronic energy value, a function of the nuclear coordinates, into the complete wave equation one could obtain an equation for the vibration of the nuclei:

$$\sum_{i}^{N} 1/M_i \quad \nabla_i^2 \psi + 8\pi^2/h^2 \; [W - V] \; \psi = 0$$

where N is the number of nuclei, M_i is the mass of the ith nucleus, W is the total energy of the molecule and V its potential energy.

While Born and Oppenheimer have shown that this substitution will permit a separation of the wave function into a product of an electronic and a nuclear wave function, no one has been able to obtain an exact solution for this characteristic electronic energy expression for a polyatomic molecule. Thus a complete solution of the vibrational problem from first principles is not feasible.

Since this same electronic energy function appears in the nuclear equation as V, the potential energy, it is necessary to develop such a function empirically in order to obtain a solution. If one assumes that in the course of a vibrational motion, the displacement of the atoms from their equilibrium positions is very small in comparison to the internuclear distances, V may be expanded as a Taylor series in powers of the displacement coordinates of the nuclei. Elimination of the first power terms can be justified through the choice of the zero value for energy, while the cubic and other higher order terms can be assumed not be contribute significantly because of the small displacements from the equilibrium positions. The resulting expression has only quadratic terms and is identical with the expression obtained if Hooke's Law (harmonic oscillator) forces are assumed between the nuclei.

With the potential energy of the molecular system so expressed, it is convenient to effect a linear transformation to a new set of displacement coordinates, called normal coordinates, which are linear combinations of stretching, bending, and twisting motions within the molecule. As a result of this change from external to internal coordinates, six coordinates (five, for linear molecules) which describe translational and rotational motions of the molecule may be factored out and the nuclear wave equation becomes separable into $3N - 6$ (or $3N-5$) one-dimensional wave equations, each expressed in terms of one of the normal coordinates.

While any actual motion of the molecule may be quite complicated, it may be considered as resolvable into components which are the normal coordinates. For each of the normal coordinates there are associated energy levels corresponding to the absorption of one or more quanta of energy into that particular vibrational mode. If one considers only "fundamental" frequencies; that is, the frequencies due to transitions between the lowest energy level of the molecule, or "ground" level, and the first excited level of only one normal coordinate, there will be $3N-6$ (or 5) such frequencies observable in the vibrational spectrum. It is general practice to associate each of these frequencies with some readily visualizable motion within the molecule in terms of bond extensions and angle deformations. Perhaps this is better described in terms of a specific example.

The vibrational motion of pyramidal XY_3 molecules such as NH_3 and PF_3 can be shown to be resolvable into six components, or normal

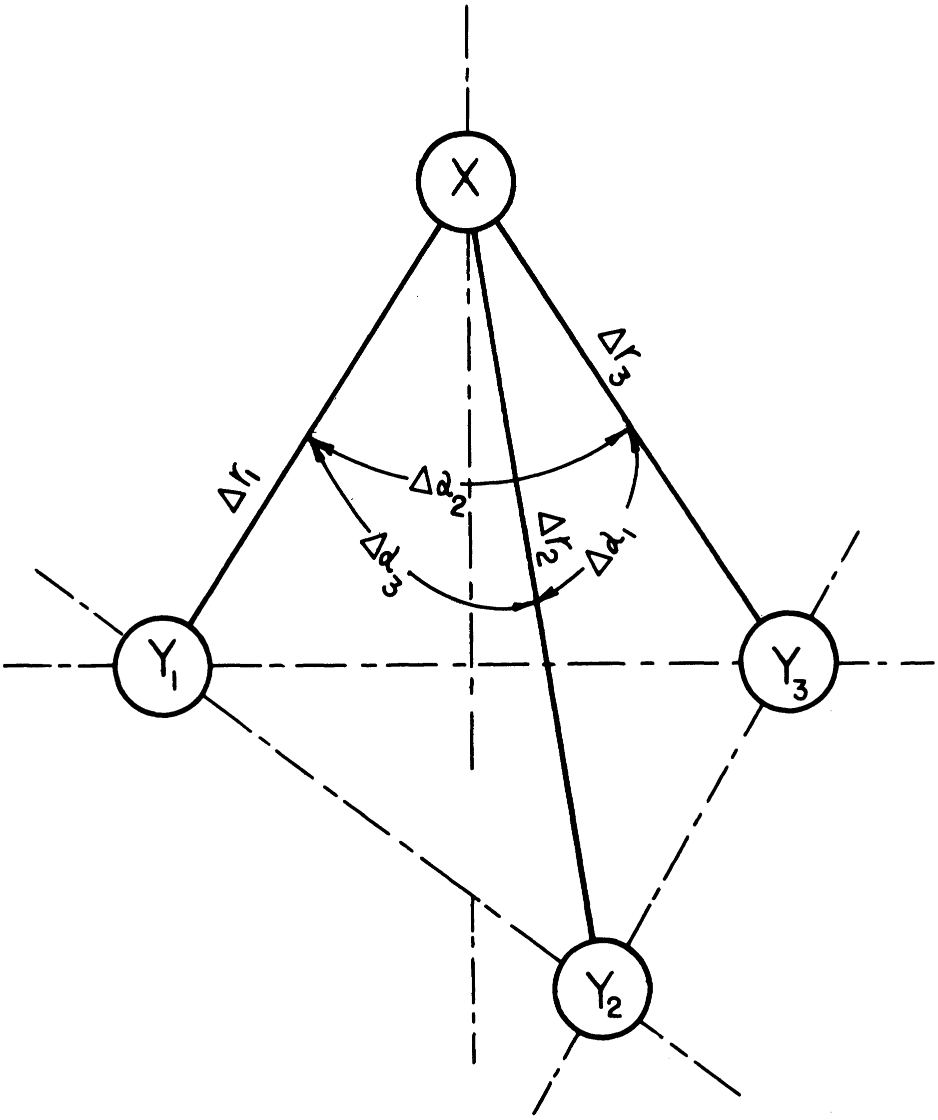

Figure 1. Internal Coordinates of Pyramidal X Y_3 Molecules.

coordinates. In terms of the bond extensions and angle deformations, one may write the following symmetry coordinates which have approximately the form of the normal coordinates:

$$S_1 = N_1(\Delta r_1 + \Delta r_2 + \Delta r_3)$$
$$S_2 = N_2(\Delta \alpha_1 + \Delta \alpha_2 + \Delta \alpha_3)$$
$$S_3 = N_3(\Delta r_2 - \Delta r_3)$$
$$S_4 = N_4(\Delta \alpha_2 - \Delta \alpha_3)$$
$$S_5 = N_5(2\Delta r_1 - \Delta r_2 - \Delta r_3)$$
$$S_6 = N_6(2\Delta \alpha_1 - \Delta \alpha_2 - \Delta \alpha_3)$$

The quantities Δr_i and $\Delta \alpha_i$ which describe the internal motions are illustrated in Figure 1 while N_i is a normalizing constant. In discussing the motions described by the normal coordinates which are approximated by S_1 and S_2, for example, are customarily referred to as symmetrical X-Y stretching and symmetrical Y-X-Y deformation motions while S_3, S_4, S_5 and S_6 are spoken of as their asymmetrical counterparts. However, because the symmetry coordinates usually only approximate the normal coordinates, there may be a slight amount of angle bending in the stretching motion, and vice versa, but frequently this amount is sufficiently small so that it can be ignored in qualitative discussions.

There are several factors which may serve to alter the observed number of vibrational frequencies from the 3N-6 (or 5) which are expected. One of these arises from molecular symmetry. As a consequence of the latter, the frequencies associated with two or more normal coordinates, and hence wave functions, have exactly the same energy value. In the example above, it is found that S_3 and S_5 give rise to identical frequencies, as do S_4 and S_6. As a result, one member of each "degenerate pair" of coordinates may be disregarded and the molecular system may be described using four rather than six normal coordinates for the purposes of numerical calculation of the frequencies. When two vibrational modes have exactly the same frequency, they, of course, cannot be distinguished experimentally and the number of bands observable thus becomes less than 3N-6.

An experimentally similar situation may arise when the energy differences between the ground level and two fundamental levels happen to be very nearly, although not exactly identical. Whether the associated spectral bands can be resolved under these circumstances depends upon the resolving power of the measuring instrument. If they cannot, the result is referred to as an "accidental" degeneracy.

A spectrum showing too many bands can result from the appearance of overtones, combination bands, and difference bands. Overtones result from transitions between the ground state and excited levels other than the first, or fundamental level. The result is the appearance of new bands at some multiple of the fundamental frequency. Combination bands on the other hand, arise from simultaneous transitions between the ground level and two or more fundamental levels, while difference bands involve transitions only between fundamental levels. The frequencies of these bands are approximately the sum and difference, respectively, of the fundamental frequencies concerned.

INFRARED AND RAMAN SPECTROSCOPY

In order to observe vibrational spectra one customarily irradiates a sample with electromagnetic radiation having at least the minimum energy per photon to cause a molecule to move from the ground state to a first excited level when one photon is observed. This establishes a lower limit to the frequency usable and is represented by infrared radiation with a wave length somewhere around one hundred microns. If radiation of higher frequency is used, a more complex interaction may take place. This may involve transitions to much higher vibrational levels or to higher electronic levels, or both. An upper limit to the frequency usually is determined by the dissociation energy of the weakest bond in the molecule. This generally is found in the ultraviolet region and is the basis of reaction initiation through ultraviolet irradiation.

In infrared spectroscopy the compound is irradiated with a continuous spectrum of infrared radiation covering a sufficient energy range to encompass transitions from the ground state to all of the fundamental vibrational levels. In passing through the sample, those photons whose energy corresponds to an energy of transition of the molecule interact strongly with a relatively high probability of being absorbed. The transmitted radiation is thus depleted and if analyzed for missing frequencies, the energy differences between various molecular levels can be established.

In Raman spectroscopy, monochromatic radiation of much greater energy than that required for vibrational transitions, usually visible light, is passed through the sample. This results in an interaction leading to a scattering of light by the molecule itself. In the vast majority of cases the molecule returns immediately to its initial state and the light scattered has exactly the same frequency as the exciting source (Rayleigh scattering). Occasionally however, the molecule may return to a vibrational level other than the one it was in initially. Light scattered in this case will differ in frequency from the Rayleigh scattering by the energy difference between the initial and the final level. Since most of the molecules participating in this scattering process are initially in the ground state, most of the scattered photons will have less energy than originally. However, some of the molecules at all times are in excited vibrational levels, the numbers being distributed in accord with the Boltzman distribution law. When these molecules are involved in the scattering process, they can impart this excitation energy to what would otherwise be Rayleigh scattered light, leading to the emission of a frequency higher than that of the exciting light.

On analyzing the total radiation scattered by the sample, one finds an intense band at the frequency of the exciting light and much weaker bands symmetrically placed on either side of it. Those on the low frequency side are known as "Stokes" lines and those of higher frequency as "anti-Stokes". The intensities of the anti-Stokes lines fall off very rapidly with increasing separation from the Rayleigh scattering since the population of the excited molecules responsible for these lines rapidly declines as the magnitude of the excitation energy increases.

It would seem that one could obtain identical information through the use of either infrared or Raman spectroscopy since both give information on molecular vibrational levels. For molecules having little or no symmetry this is roughly the case, but in many highly ordered molecular structures striking differences in transition probabilities, and hence intensities, arise because of the differing mechanisms of reaction with the incident radiation in the two techniques.

Infrared absorption occurs through changes in the molecular dipole moment as the nuclei are displaced from their equilibrium position. In any molecule the instantaneous value of the dipole moment can be expressed in terms of the normal coordinates:

$$M = M_o + \sum_{k} \left(\frac{\partial M}{\partial q_k}\right) q_k + 1/2 \sum_{k,\ell} \left(\frac{\partial^2 M}{\partial q_k \partial q_\ell}\right) q_k q_\ell + \dots$$

where M_o is the permanent moment corresponding to a non-vibrating molecule, and q_k and q_ℓ are any two of the $3N-6$ normal coordinates. If only one normal vibration takes place, the atoms oscillate in such a way that the normal coordinates may be represented by an expression describing simple harmonic motion about the equilibrium position:

$$q_k = A_k \cos\left(2\pi_k \nu\, t + \delta_1\right)$$

where A_k is the amplitude, ν_k the vibrational frequency, and δ_1 a phase constant. Upon substituting for q_k and q_ℓ one obtains for the dipole moment:

$$\begin{aligned} M = M_o &+ \sum_{k} \left(\frac{\partial M}{\partial q_k}\right) A_k \cos\left(2\pi\, \nu_k t + \delta_1\right) \\ &+ 1/4 \left(\frac{\partial^2 M}{\partial q_k \partial q_\ell}\right) A_k A_\ell \Big\{\cos\left[2\pi t(\nu_k + \nu_\ell) + \delta_1 + \delta_2\right] \\ &+ \cos\left[2\pi t(\nu_k - \nu_\ell) + \delta_1 - \delta_2\right]\Big\} + \dots\dots\dots\dots \end{aligned}$$

The term $(\partial M/\partial q_k)$ governs the appearance of fundamental frequencies. If the term is zero, that is, if the molecule undergoes no change in dipole moment as a result of the normal vibration described by q_k, the corresponding fundamental will not appear, or is said to be "infrared inactive". The value of the term $(\partial^2 M/\partial q_k \partial q_\ell)$ determines the activity of overtones, combinations, and difference bands. Non-zero values for $\ell = k$ permits overtones, while non-zero values for $\ell \neq k$ allow observation of $\nu_k + \nu_\ell$ and $\nu_k - \nu_\ell$.

Raman scattering depends upon a change in the amplitude of the dipole moment induced by the incident radiation. The magnitude of the induced moment, P, may be expressed as a product of the polarizability of the molecule, α, and the electric field vector, E, of the incident radiation of frequency ν_o, according to the equation $P = \alpha E$. As with the permanent dipole moment, the instantaneous value of α may be expressed in terms of the normal coordinates.

$$\alpha = \alpha_o + \sum_k \left(\frac{\partial \alpha}{\partial q_k}\right) q_k + 1/2 \sum_{k,\ell} \left(\frac{\partial^2 \alpha}{\partial q_k \partial q_\ell}\right) q_k q_\ell + \cdots\cdots$$

With the electric field expressed in the form: $E = E_o \cos 2\pi\nu_o t$, the expression for P becomes:

$$\begin{aligned} P = E_o\alpha_o \cos 2\pi\nu_o t + 1/2\, E_o A_k \sum_k \left(\frac{\partial \alpha}{\partial q_k}\right) \Big\{ &\cos[2\pi t(\nu_o + \nu_k) + \delta_k] \\ &+ \cos[2\pi t(\nu_o - \nu_k) - \delta_k] \Big\} + 1/8\, E_o A_k A_\ell \sum_{k\ell} \left(\frac{\partial^2 \alpha}{\partial q_k q_\ell}\right) \\ &\Big\{ \cos[2\pi t(\nu_o + \nu_k + \nu_\ell) + \delta_k + \delta_\ell] + \cos[2\pi t(\nu_o - k_k - \nu_\ell) - \delta_k - \delta_\ell] \\ &+ \cos[2\pi t(\nu_o + \nu_k - \nu_\ell) + \delta_k - \delta_\ell] + \cos[2\pi t(\nu_o - \nu_k + \nu_\ell) - \delta_k + \nu_\ell] \Big\} \end{aligned}$$

Looking at the equation term by term, one finds Rayleigh scattering predicted whenever a non-zero value for α_0, the polarizability of the non-vibrating molecule exists. Similarly a change in the induced moment as a result of the vibrational motion described by q_k makes the associated frequency "Raman active". Overtones, combinations, and difference bands are governed by a non-zero value for $(\partial^2\alpha/\partial q_k \partial q_\ell)$.

Raman scattered light which is observed at right angles to the incident beam is found to be partially polarized. According to classical theory isotropic molecules should scatter completely polarized light at right angles to the direction of the exciting radiation. Thus any depolarization results from the anisotropy of the molecule and vibrational motions which destroy some or all of the molecule's symmetry will give rise to vibrational bands which show a maximum depolarization. The depolarization ratio is determined by twice recording the vibrational spectrum of the compound, each time rejecting all components of the scattered light except that which is polarized first parallel, and second, perpendicular to the direction of the incident beam. Taking as the x-axis the direction of the propagation of the incident light, this depolarization ratio may then be defined as the ratio of the intensity of the scattered light whose electric vector is perpendicular to the yz plane, to that polarized parallel to this plane. Vibrational bands showing the maximum depolarization ratio, 6/7 may then be attributed to normal vibrations which destroy some or all of the molecule's symmetry while for vibrational motions which retain all symmetry elements, depolarization ratios ranging from zero to slightly less than 6/7 are found. Since the symmetry properties of the normal coordinates are known beforehand, knowledge of depolarization ratios can greatly facilitate the assignment of spectral bands to particular vibrational modes.

In practice it is found that equivalent results can be obtained if the sample is irradiated with light which is incident in the xy plane. With this arrangement two exposures must be taken; one with the incident radiation polarized in a plane parallel to the z-axis and another using light polarized perpendicular to it. Qualitative results can be obtained by comparing the spectrum resulting from normal incident light with that from light polarized parallel to the z axis.

EXPERIMENTAL PROCEDURES

Preparation of Materials

The compounds used in the preparation of samples were:

a. Aluminum bromide

b. Boron trichloride

c. Boron trifluoride

d. Dimethyl ether

e. Ethyl chloride

f. Methyl bromide

g. Methyl chloride

h. Sulfur dioxide

Aluminum bromide was synthesized from C. P. grades of aluminum turnings and bromine. The former was placed in a pyrex tube which was itself placed inside a tube furnace. Temperature control was maintained by inserting a thermocouple into the furnace and manually adjusting the voltage across its terminals by means of a Variac. After an initial incubation period during which the aluminum remained in contact with bromine vapors at 250°C, the reaction proceeded under its own heat. A temperature of about 35 °C was maintained through intermittent dropwise additions of bromine while the system was flushed with dry nitrogen to remove aluminum bromide from the reaction site as fast as it was formed. The product was triple distilled to remove the last traces of bromine before storage in weighed amounts in fragile glass bulbs.

All of the gaseous reagents not specifically stated as purchased elsewhere were obtained in cylinders from The Matheson Company, Inc. Most of these gases had been analyzed by the manufacturer and these results have been included in the discussions of their purification.

Although the boron trichloride had a minimum guaranteed assay of 98.5% BCl_3, it gave on condensation a yellow liquid phase containing copious quantities of a white solid which melted and dissolved at about 0°C. A careful fractionation separated BCl_3 from the solid and removed most of the yellow color. Complete decolorization was obtained by the action of freshly activated Norite upon the liquid at -78°C. According to the manufacturer, a typical analysis of the BCl_3 used showed the following impurities:

Si as $SiCl_4$	0.007%
S as S_2Cl_2	0.2%
C as $COCl_2$	0.8%
Free chloride as Cl_2................	0.2%

Only the most intense band of phosgene was detected in any spectra taken of systems containing BCl_3, and that as a weak line in a ten-fold overexposure of a sample of BCl_3 which had been fractionated but not treated with Norite.

The boron trifluoride used contained 98.5% BF_3, with SiF_4 and SO_2 presumably as the only principal contaminants, each present to the extent of 0.5%. Because of the proximity of their boiling points, a separation by fractionation was extremely difficult and since the impurities are both much weaker acids than BF_3, it was decided to use the material after only a single trap-to-trap distillation. None of their characteristic bands ever appeared in any of the many spectra recorded of systems containing BF_3 nor in the spectrum of BF_3 itself.

Analyses of DME indicated a purity of not less than 99.5% with the bulk of the impurity being moisture. Further purification was attempted, however, by passage of the gas through a column containing freshly activated alumina. The alumina was then regenerated and the process repeated.

Methyl bromide (MeBr hereafter) had a stated purity of 99.4%, the balance consisting of moisture and organic chlorides. It was condensed into a second cylinder containing 15 grams of aluminum bromide. After standing at room temperature for about a week, the gas was scrubbed by water in a 150 cm. scrubbing tower packed with short pieces of glass tubing. It was dried by passage first through a column containing calcium chloride and then through a second containing phosphorus pentoxide suspended upon glass beads. The MeBr was finally recondensed into a stainless steel cylinder for storage until used.

The methyl chloride had a stated purity of 99.5%, with moisture and residue as the only impurities. Therefore, it was used after only a single trap-to-trap distillation. Neither of the methyl halides showed bands attributable to impurities even in prolonged exposures.

Ethyl chloride was purchased from The Ohio Chemical and Surgical Equipment Company. No data on purity were available, so the liquid was carefully fractionated. The first and last cuts were rejected while the middle fraction was then used.

Since The Ansul Chemical Company's sulfur dioxide was sold as 99.9% pure, it was given only a single trap-to-trap distillation before use. Prolonged exposures of the liquid revealed only the bands of the pure compound.

Preparation of Samples

Because of the extreme reactivity of the acids with atmospheric moisture, it was necessary to handle the compounds in a closed system. A diagram of the vacuum line used both in the purification of materials and in sample preparation is shown in Figure 2.

The gaseous reagents were admitted through any of the stopcocks labeled "A". The presence of non-condensable gases often required a preliminary condensation and freezing in a pump-through trap, "B". The reagent was then permitted to warm up and expand back into the calibrated volume. By adjusting the pressure within this volume exact mole ratios having a desired total liquid volume could be obtained. Recondensation in trap B before distillation into the mixing bulb attached to the ground glass joint at C aided in the removal of entrained stopcock grease.

The two mixing devices used in sample preparation are shown in Figure 3. The upper one (A) was used solely for the preparation of solutions of the systems $AlBr_3$-MeBr and $AlBr_3$-MeBr-HBr. Prior to use the bottom of the apparatus was cut open, permitting introduction of a small weighed bulb of $AlBr_3$. The apparatus was then sealed, evacuated, and shaken vigorously to break the bulb. The other components of the system under investigation were introduced and solution effected. By inverting the apparatus the solution could be filtered through a sintered glass frit of "ultrafine" porosity into the Raman tube.

In most of the systems investigated, all of the reactants could be distilled. In such cases the bottom apparatus (B) was used. The gases were distilled from trap-to-trap until they were finally condensed atop one another in the final bulb; the preceding bulbs were then removed by sealing off. This series of trap-to-trap distillations was designed primarily to remove entrained stopcock grease. The final trap was then

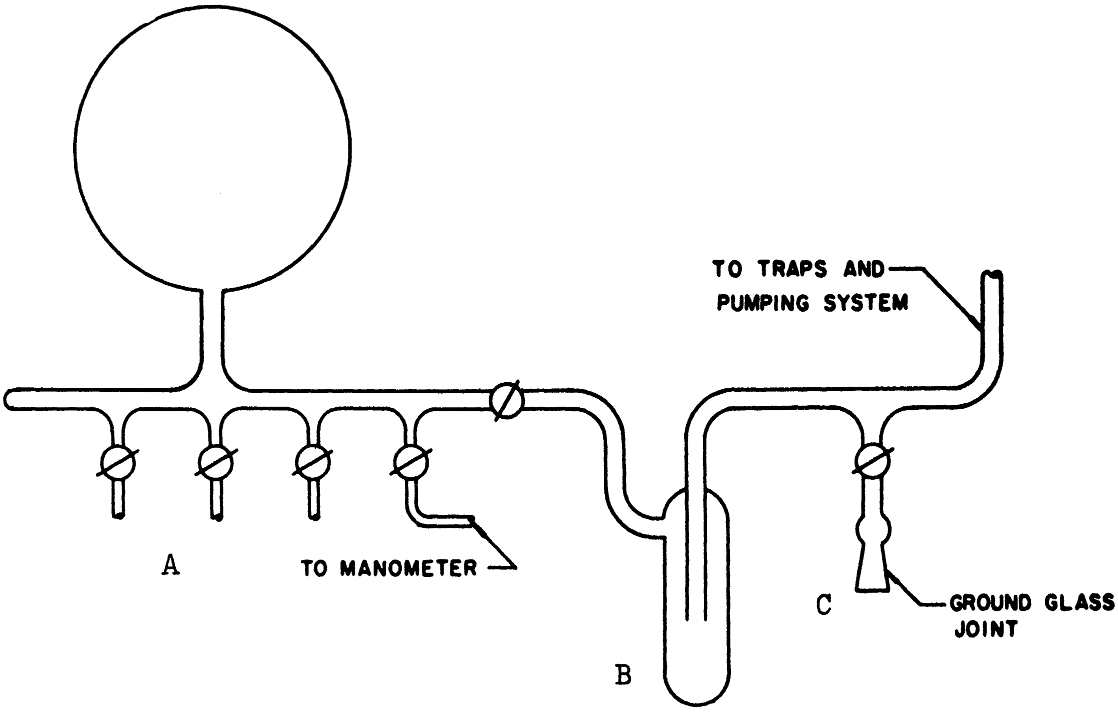

Figure 2. Vacuum Line Used in Sample Preparation.

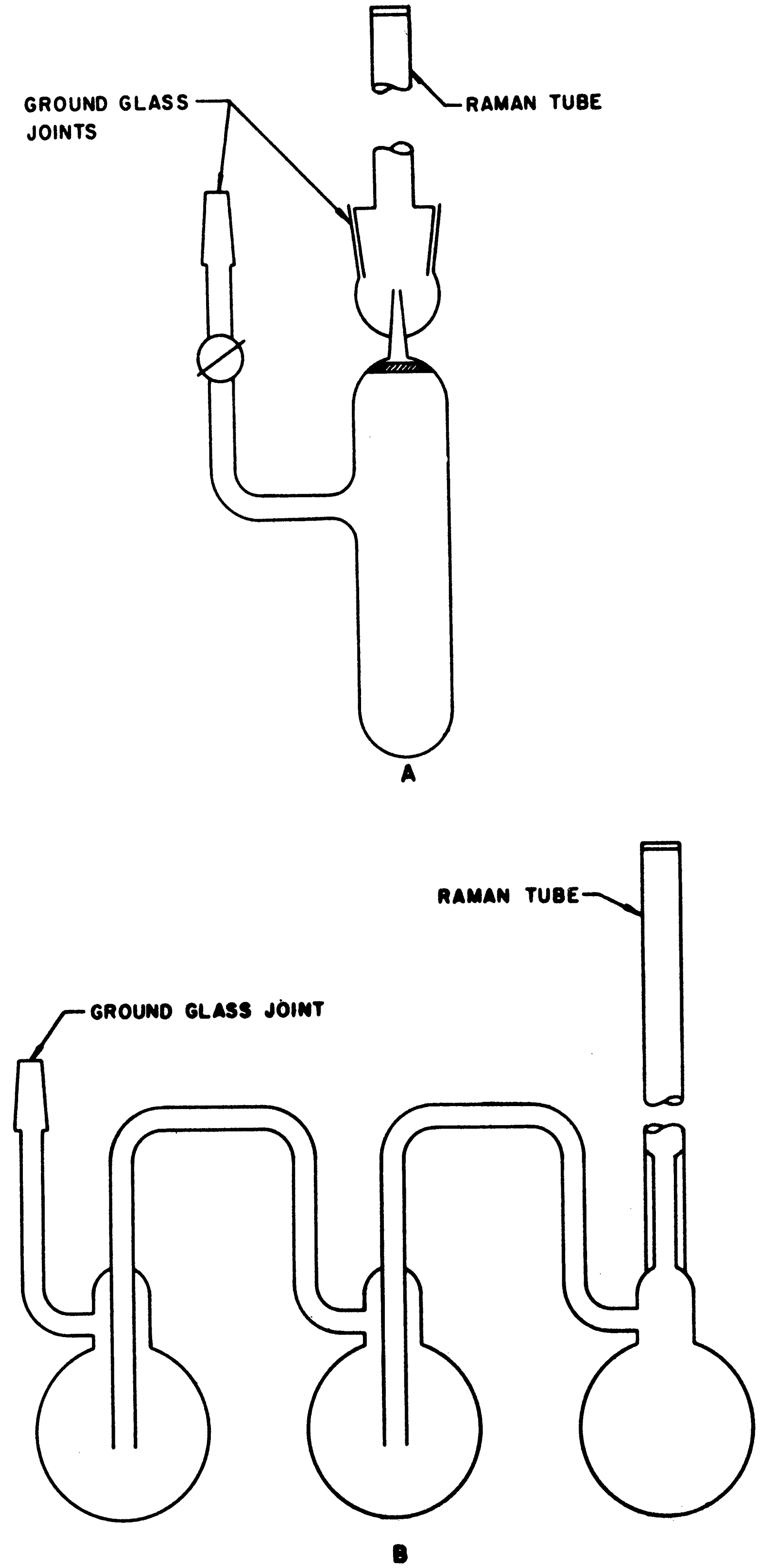

Figure 3. Apparatus Used in the Preparation of Raman Samples.

permitted to warm up to dry ice temperature and the interaction, often quite violent, took place. In many cases a prolonged swirling of the trap while in an appropriate cooling bath was necessary to effect solution, but in some a solution was obtained at once. The trap was then inverted so as to pour its contents into the Raman tube, which was then sealed off.

Spectrographic Equipment

Very little of the exciting radiation gives rise to Raman scattering and only a minute fraction of this scattered light can be collected and analyzed because of physical limitations. Thus the Raman spectroscopist must endeavor to obtain a monochromatic light scource of maximum intensity, collect as much of the Raman scattered light as possible, and yet prevent as much as possible of the exciting radiation which is not actually scattered by the sample from reaching the spectrograph. These requirements are approached by a variety of techniques.

The most satisfactory light source currently available is the helical Toronto-type low pressure, low temperature maecury arc. Most of the energy released from mercury's electronic transitions is concentrated in a few relatively intense bands. Those in the visible range are well separated, thus facilitating the task of obtaining monochromatic light. Continuous background radiation and pressure broadening of the exciting line are minimized through the use of large water cooled pools of mercury for electrodes which favor a low pressure in the arc. If the cold finger, by which the cooling is accomplished, extends well above the surface of the mercury pool into the arc proper, transferal of the mercury from one electrode to the other during operation is greatly reduced. The arc is in the form of a helix made of 32 mm. Pyrex tubing which is wound into three full turns. The arc is operated on 220 volts and normally draws about 24 amps.

Despite the fewness of the spectral lines from the mercury arc, it is desirable to utilize light filters to simplify interpretation and reduce the overlapping of spectra. Although there are very few intense bands in the visible range of mercury's spectrum, there are a number of very weak bands. These may obscure Raman bands unless removed from the incident light. Failure to reduce the intensity of the other intense lines can lead to overlapping Raman spectra. Spectra from the 4358 A. mercury line, which was used exclusively, were isolated through the simultaneous use of two filter solutions as shown in Figure 4. A nearly saturated solution of sodium nitrite in water was circulated through the outer filter jacket. This served two purposes: it reduced the intensities of the mercury lines at 4046 and 4078 A. to the point where Raman scattering resulting from them was no longer detectable, and because of its continuous circulation through a heat exchanger, it served to keep the heat of the arc away from the inner filter jacket and the sample.

The inner filter jacket was sealed and easily removable. Several of these filter jackets were available, each filled with a solution adapted to some special purpose. Generally a solution of ethyl violet in isopropyl alcohol was used. This removed the multitude of weak mercury lines in the 4700 to 5000 A. region and reduced the intensity of the 4916 A. line to the point where Raman scattered light arising from it could not be detected

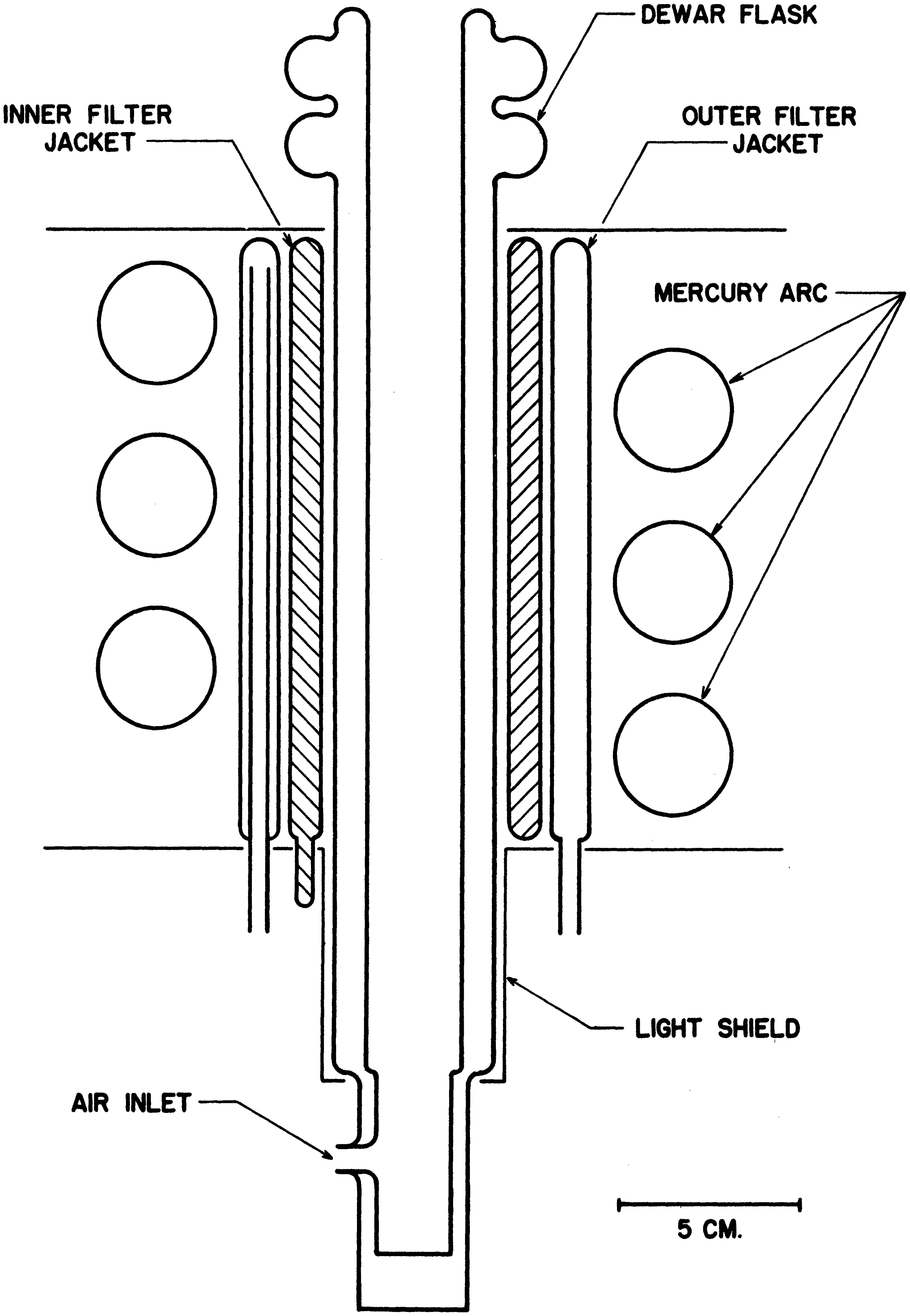

Figure 4. Raman Light Source Assembly.

When spectral bands of very low frequency were being studied, it was helpful to substitute a solution of praeseodymium chloride. This served to reduce the background radiation in the region close to the 4358 A. exciting line. During polarization studies, the inner filter jacket was replaced by collimating baffles. These helped approximate the theoretical requirement that polarized spectra be observed at right angles to the plane of the incident radiation.

Spectra of samples at very low temperatures were obtained through the insertion of a specially constructed Dewar flask into the space inside the inner filter jacket. The temperature of the interior could be maintained anywhere in the range of 0 to -55°C by passing precooled air into the air inlet at the bottom. This stream of air was first dried by anhydrous calcium chloride and then cooled as it passed through a copper coil which was immersed in a dry ice - isopropanol slush. For lower temperatures it was necessary to pass nitrogen gas through the copper tubing. In this way temperatures down to -130°C could be maintained for relatively long periods of time.

A rough control of temperature was possible by regulation of the rate of flow of the gas, but a more satisfactory continuous monitoring and control system was available. This consisted of a thermocouple in the air stream alongside the sample tube connected to a Leeds and Northrup strip chart recorder. The temperature of the air stream could be adjusted on demand by a small electrical heater in the stream immediately following the cooling coil. In normal operation, a fluctuation of about five degrees was observed in the air stream in the area of the sample tube. There was in addition a thermal gradient of approximately ten degrees along the length of the Raman tube.

Alignment of the optical system was greatly facilitated through the use of the sample holder shown in Figure 5. This fitted snugly inside the Dewar flask, which was itself firmly mounted in the light source assembly. The sample holder was fitted with a series of adapters in order to permit use with a variety of sizes of Raman tubes. It could also be used to support a wrapping of Polaroid film for polarization studies.

In order to minimize the amount of stray light reaching the spectrograph, only the Raman scattering perpendicular to the plane of the exciting light was analyzed. This was accomplished by using as a sample tube a cylinder of Pyrex tubing whose lower surface consisted of a plane window. By illuminating only the central segement of the tube and blackening the curved outer surfaces above and below this section, most of the incident illumination could be excluded from the Raman and Rayleigh scattered light. In addition, extreme care was exercised to exclude from the sample tube any dust or other foreign matter which might cause Tyndall scattering. This was done by steaming out the interior of the tube before use, careful purification of all sample materials, and especially by filtering samples whenever possible.

The Raman scattered light was analyzed with a Gaertner two-prism spectrograph having a dispersion of about 180 cm.$^{-1}$ per millimeter in the blue region.

The spectra were recorded photographically using Eastman-Kodak 103a-J plates with an antihalation backing. This particular combination of emulsion

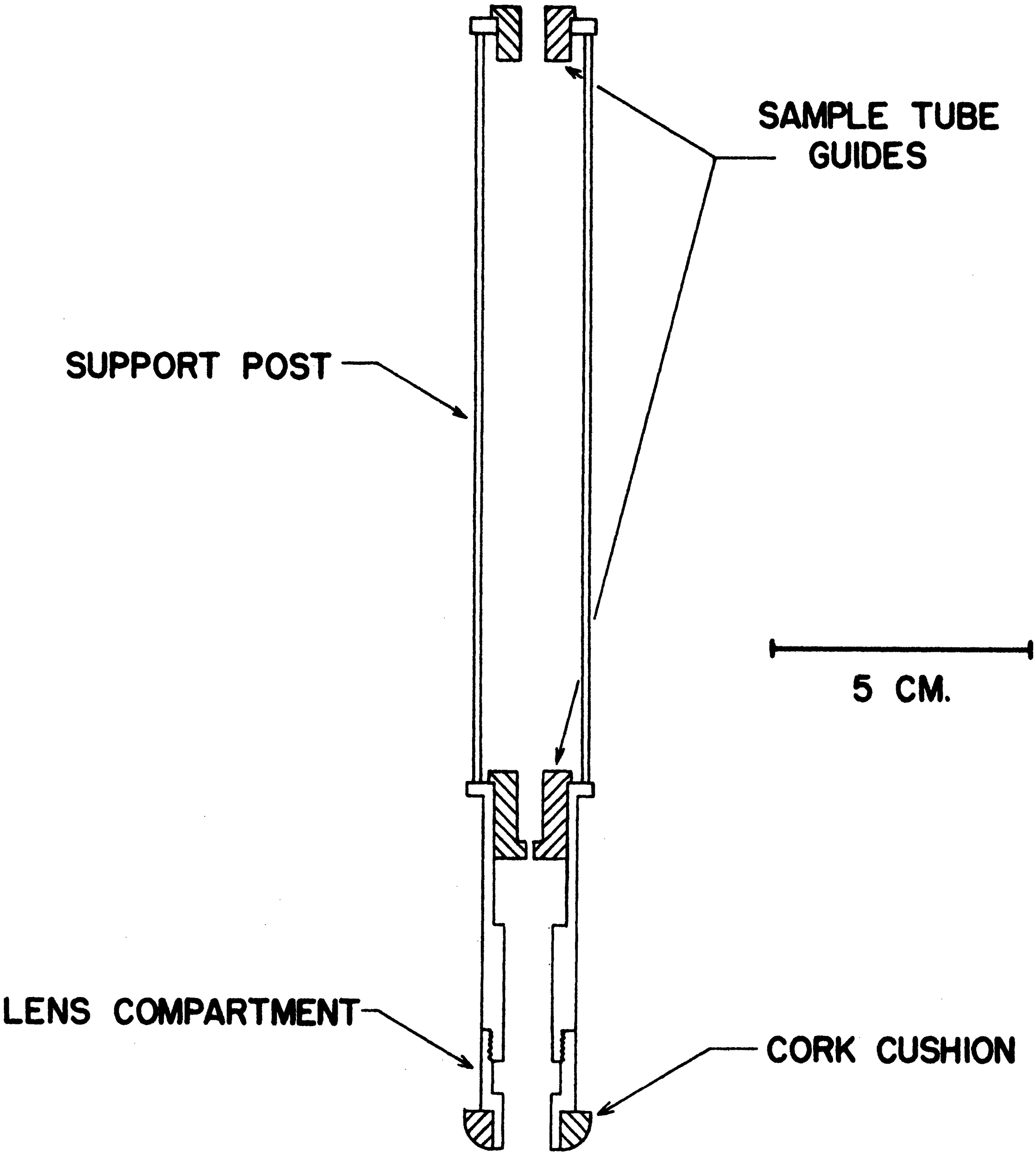

Figure 5. Sample Tube Holder.

and sensitivity was chosen because of high response to light of low intensity in the blue region. The plates were developed for four minutes at 20°C in D-19 solution and fixed in F-6.

Most of the plates so obtained were measured using two techniques. The first of these was the use of a comparator which measured directly the distances of the Raman lines along the plate and could be read to the nearest 0.001 mm. The frequencies of the Raman bands could then be calculated from a dispersion curve based on the spectrum of argon. In the other method, microphotometer tracings, representing about a twenty-six fold enlargement of the plates, were obtained with a Leeds and Northrup microphotometer. The distance between peaks could then be measured by means of a modified cathetometer and the displacements from the exciting line calculated from a second dispersion curve, again based upon the argon spectrum.

EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

Raman Spectra of Pure Components

Since complex formation was to be detected through changes in the vibrational spectra of the pure components, it was necessary that these spectra be available. Although all had been reported in the literature, they were recorded once again primarily for the purpose of detecting impurities. The spectrum of aluminum bromide only will be reported here briefly since for the other molecules both the number of bands and their frequencies has been well established by earlier workers.

Subsequent to the time that Rosenbaum(30) and Gerding and Smit(31,32) reported the Raman spectrum of liquid aluminum bromide, the bridge structure has been proven conclusively. From group theoretical considerations it can be shown that of the 18 fundamental frequencies expected for this model only 9 are active in the Raman effect, while 8 others are infrared active and one is inactive in both. Thus a complete assignment of the vibrational frequencies of aluminum bromide would require knowledge of its infrared and Raman spectra, including its polarized Raman spectrum. In addition, it would be desirable to have similar data for the other aluminum halides in order that the assignments be unequivocal. The only such data which were available for the aluminum halides prior to this research were their Raman spectra obtained using natural incident light. Because of the magnitude of the undertaking and the experimental difficulties certain to be encountered, especially in the recording of infrared spectra, it was decided to make no attempt at assigning the vibrational frequencies of aluminum bromide. The Raman spectrum of aluminum bromide is shown in Figure 6 and the frequencies obtained are compared in Table I with the results of the earlier workers.

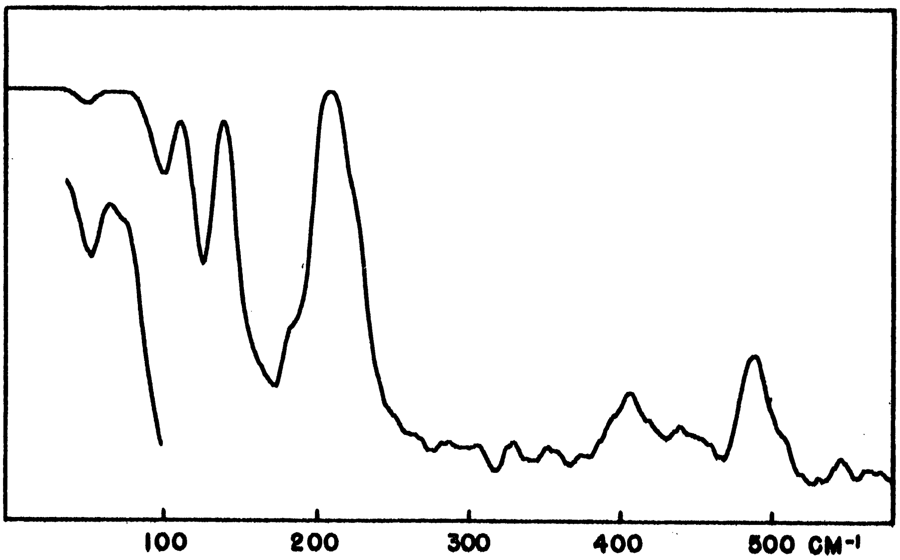

Figure 6. The Raman Spectrum of Al_2Br_6.

TABLE I

VIBRATIONAL FREQUENCIES (IN $cm.^{-1}$) OF Al_2Br_6

Rosenbaum	Gerding and Smit	This Research
67	73	67
79.3		78
112.8	112	111
140.3	140	140
185	176	183
208.2	204	209
223	221	223
	291	
407	407	402
		440
488	491	489

Systems Showing No Interaction in the Liquid Phase

Spectra of equimolar solutions of BCl_3 and methyl chloride, BCl_3 and methyl bromide, and BF_3 and methyl bromide were recorded at -55°C in the first two cases and at -90°C in the last. All showed only the superimposed spectra of the pure components with no frequencies shifted.

Systems Showing Interaction But Not Complexation in the Liquid Phase

BCl_3-Ethyl Chloride

At -55°C the spectrum of a mixture containing two moles of BCl_3 per mole of ethyl chloride was that of the reagents. However, at -100°C the C-Cl stretching frequency, which occurs at 655 cm^{-1} in ethyl chloride, appeared at 642 cm^{-1}. This indicates a slight weakening of the C-Cl bond due to the action of BCl_3. None of the frequencies of BCl_3 were shifted, none of the other frequencies of ethyl chloride were affected, and no new bands were found. Thus the interaction appears to be a solvent effect rather than a case of complexation.

SO_2-DME

A brief temperature-pressure study of an equimolar mixture of SO_2 and DME was conducted to see if any pronounced interaction could be detected. The results are shown in Table II, in which the observed pressures are compared with those of an ideal solution.

TABLE II

VAPOR PRESSURE (IN mm.) OF AN EQUIMOLAR MIXTURE OF SO_2 AND DME

t(°C.)	$P_{ideal\ sol.}$	$P_{obs.}$
-78	25	5
-23	580	265
0	1500	749

This pronounced vapor pressure lowering is certainly indicative of interaction, but not necessarily of complexation.

The Raman spectroscopic investigation by Wolkenstein(24) was conducted at room temperature with a sample containing sulfur dioxide and DME in the ratio 3:2. This work has been extended in the present case by examining 1:1 mixtures at -25 and -55°C. The study of HCl-DME complexes by Vidale and Taylor(2) showed the sketetal frequencies of DME to be a very sensitive indicator of complexation; that is, these frequencies were markedly shifted, usually to lower values, by interaction with the acid. The effect upon these frequencies by SO_2 is given in Table III.

TABLE III

THE EFFECT OF SO_2 AND HCl UPON THE SKELETAL FREQUENCIES (IN cm.$^{-1}$) OF DME

	C-O asym. stretch	C-O sym. stretch	COC deformation
Pure DME	1095	920	420
DME-SO_2 mixture (3:2) at room temperature *	1088	908	411
DME-SO_2 mixture (1:1) at -25°C.	1086	910	417
DME-SO_2 mixture (1:1) at -55°C.	1087	904	420
DME-HCl mixture (1:1) at -90°C.	1077	886	420

However, the frequencies of SO_2 itself in these solutions are exactly the same as those of the pure liquid. The smaller shifts in the skeletal

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* From Wolkenstein(24)

frequencies of DME together with the lack of an effect on the SO_2 frequencies is interpreted only as an indication of a slightly temperature dependent solvent effect occurring in the liquid phase. The situation further differs from the DME-HCl case in that two sets of frequencies corresponding to complexed and uncomplexed DME were never observed. Thus both DME:SO_2 and EtCl:2BCl_3 reported from phase studies appear to be crystal lattice compounds which exist only in the solid state.

Systems Showing Complexation

Aluminum Bromide - Dimethyl Ether.

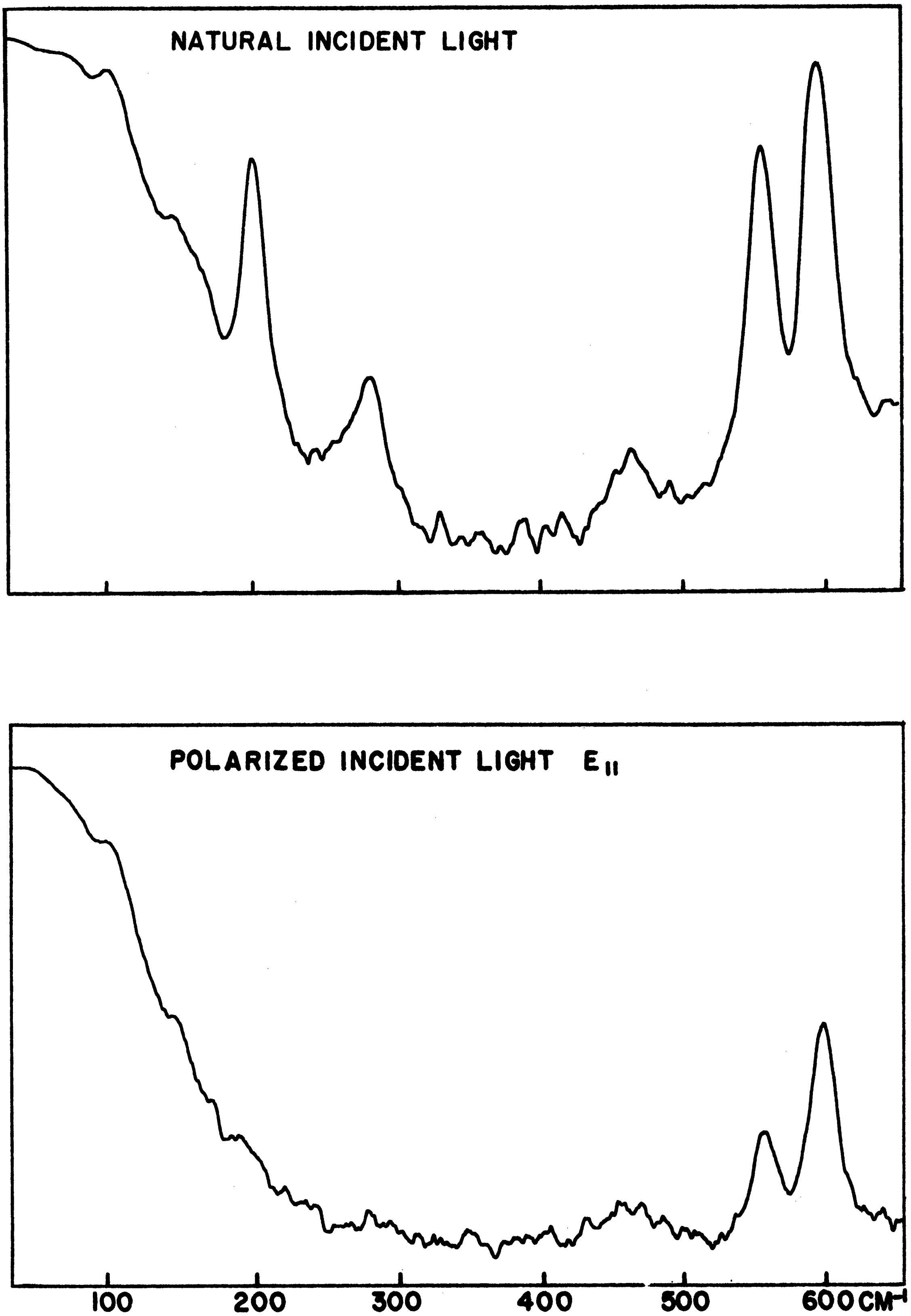
Products resulting from the interaction of $AlBr_3$ and DME were found to be ill-suited to Raman spectroscopic study because of their slow decomposition into products which fluoresce in the visible region. The rate of this decomposition increased so rapidly with temperature that the Raman spectrum of the molten complex could not be recorded despite its low melting point (47°C.). Since examination of the solid appeared out of the question using the Raman technique, the possibility of studying the complex in solution was considered.

Of the many proposed solvents which were examined only CS_2, SO_2 and MeBr appeared to offer sufficient promise to warrant closer study. Sulfur dioxide instantly dissolved ether-rich mixtures but greatly accelerated their decomposition while neither the 1:1 complex nor $AlBr_3$ was significantly soluble in SO_2. Despite the very low solubility reported by Foster and Kraus(33) for DME:$AlBr_3$ in MeBr (0.3 moles per liter at -78°C), it was hoped that increased solubility at higher temperatures might compensate for the accompanying increased rate of decomposition. Unfortunately, such was not the case. Lastly, carbon disulfide itself was found to decompose under the intense light of the Toronto arc and was eliminated. Since the possibility of further work appeared discouraging, the investigation of the system was discontinued.

Aluminum Bromide - Methyl Bromide

The same general solubility problems encountered in the $AlBr_3$-DME system were present here since the 1:1 ratio marks the upper limit of solubility of $AlBr_3$ in MeBr. No suitable solvent could be found for acid-rich mixtures, but MeBr served as an excellent solvent for the 1:1 complex. As in the case of DME:$AlBr_3$, these solutions slowly decomposed to give products which fluoresced in the visible region. However, the rate of decomposition was much slower and satisfactory spectra were recorded. Polarized spectra required much longer exposures and were therefore more seriously affected by this decomposition. As a result, the assignment of the vibrational bands is hampered by the necessarily underexposed polarized spectrum. The spectra obtained are shown in Figure 7.

Vapor pressure measurements by Brown and Wallace(20) have indicated that in all mixtures of MeBr and $AlBr_3$ in which the MeBr/$AlBr_3$ ratio is unity or greater, the only complex species present is MeBr:$AlBr_3$. This conclusion is confirmed by the small number of vibrational bands in the 0-500 $cm.^{-1}$ region, since a complex containing Al_2Br_6 would be expected to show at least ten bands in this region (see Figure 6) whereas the pyramidal $AlBr_3$ structure would show a maximum of seven. Since only five vibrational bands in the 0-500 $cm.^{-1}$ region could be assigned to fundamental frequencies, the structure by Brown and Wallace seems quite reasonable.



RAMAN SPECTRA OF AlBr$_3$:CH$_3$Br

Figure 7

The intense band at 595 cm.$^{-1}$ is the C-Br stretching frequency of the solvent, MeBr. The corresponding band in the 1:1 complex appears about 40 cm.$^{-1}$ below it, which is an energy difference of 0.12 kcal per mole. The intense band at 200 cm.$^{-1}$ is analogous to the intense, strongly polarized bands found by Gerding(34,35) in several $AlCl_3$ complexes at frequencies near the most intense band of pure Al_2Cl_6. In each case these bands were assigned to the Al-Cl stretching frequency. The most intense line in the Al_2Br_6 spectrum occurs at 209 cm.$^{-1}$. This band and the strong, completely polarized band at 200 cm.$^{-1}$ in MeBr:$AlBr_3$ are clearly Al-Br stretching frequencies. Asymmetric stretching bands are customarily found at slightly higher frequencies, are much broader, and appear with very little reduction in intensity in spectra observed using polarized incident radiation. Despite the reduction in intensity of the broad band at 277 cm.$^{-1}$ in going from natural to polarized incident radiation, this has been assigned to the asymmetric Al-Br stretching mode because of its contours and position. Because the polarized spectrum was grossly underexposed, the fact that this band appears at all in the latter may be evidence for its unsymmetrical nature. The lower-lying bands have been assigned to deformations largely through the process of elimination. A tabulation of the frequencies, their polarization, and relative intensities is given in Table IV together with a set of tentative assignments, assuming C_{3v} symmetry.

The Systems: Boron Trihalide - Dimethyl Ether

Raman Spectrum of DME:BF_3.

The slow decomposition into fluorescent products which interfered so seriously with Raman spectroscopic analyses of DME:$AlBr_3$ and MeBr:$AlBr_3$ appeared

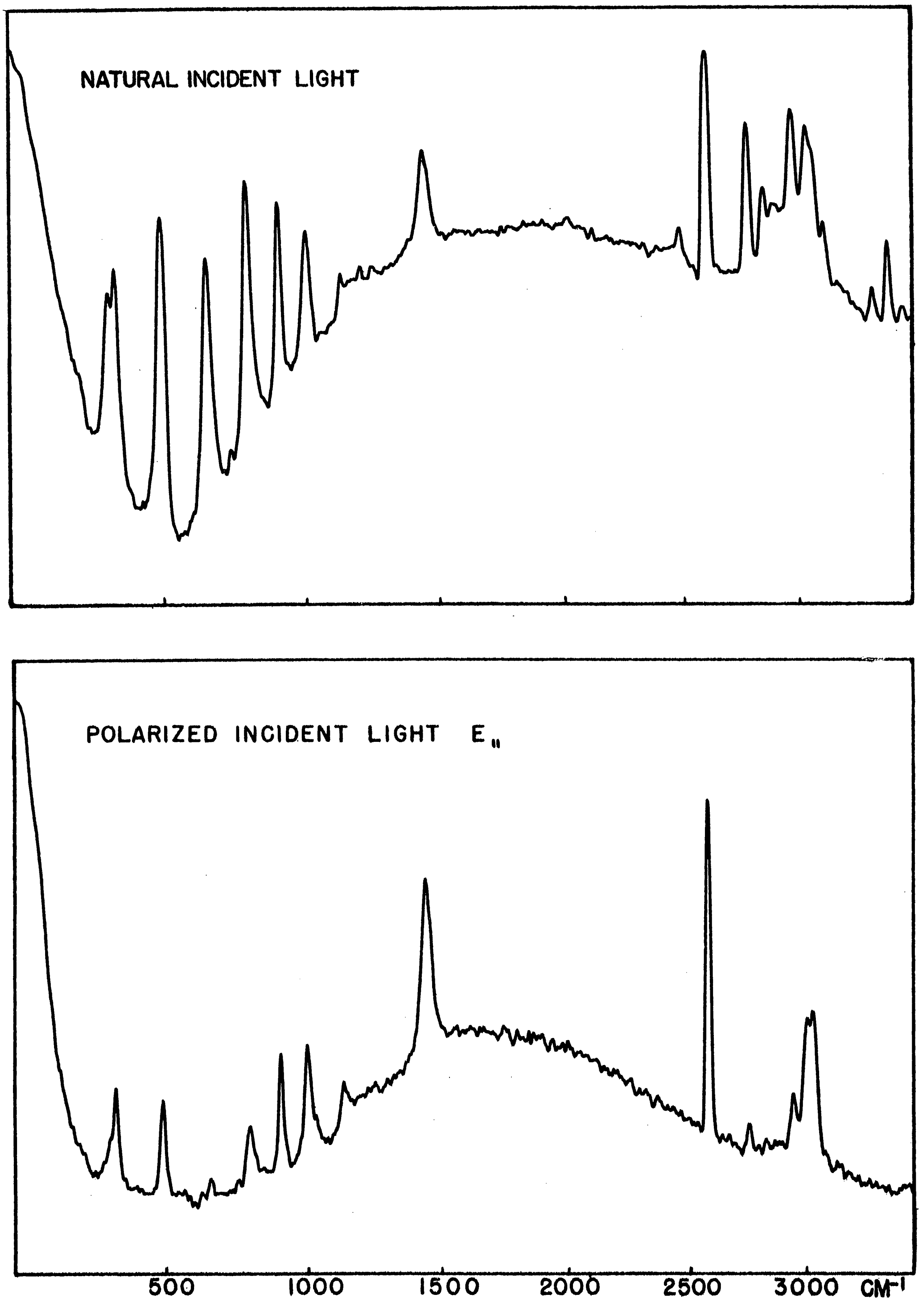
TABLE IV

THE RAMAN SPECTRUM OF $MeBr:AlBr_3$

Frequency ($cm.^{-1}$)	State of Polarization	Intensity	Tentative Assignment
71	Depol.	w	$AlBr_3$ wag or rock (e)
102	Depol.	m	$AlBr_3$ def. (e)
149	-	w	$AlBr_3$ def. (a_1)
199	Pol.	s	Al-Br str. (a_1)
277	Depol.	m	Al-Br str. (e)
454	Depol.	w	554.3 - 101.7 = 452.6
467	-	w	276.8 + 199.4 = 476.2
554	Pol.	s	C-Br str. (a_1)

here also, but at a rate sufficiently low that spectra could be recorded using both natural and polarized incident radiation. These are shown in Figure 8. In the discussion of the frequencies of the BF_3:DME complex, a natural grouping is to consider three sets of bands, (1) those derived from free DME bands, (2) those derived from free BF_3 bands, and (3) those arising as a consequence of the formation of the B-O link.

The spectral bands of DME:BF_3 which arise from motions of the methyl groups should have nearly the same frequencies as the corresponding bands of DME. As result, bands in the 3000, 1450, and 1000-1200 $cm.^{-1}$ regions are to be expected from C-H stretching, CH_3 deformation, and CH_3 rocking modes. The effect of complexation should be more pronounced in the case of the so-called skeletal motions, viz. the symmetric and



RAMAN SPECTRA OF $(CH_3)_2\ O:BF_3$

Figure 8

asymmetric C-O stretching and the deformation of the C-O-C angle. Vidale and Taylor(2) found these frequencies reduced by as much as 10% as a result of complexation with the halogen acids. By analogy, the corresponding bands in DME:BF_3 should be a strong, polarized band between 800 and 850 cm.$^{-1}$ and an only slightly less intense, depolarized band in the 900-1000 cm.$^{-1}$ region. The C-O-C deformation frequency, occurring at 420 cm.$^{-1}$ in DME would be expected to be shifted downward to perhaps 350-375 cm.$^{-1}$. This band should also be polarized.

Accordingly the intense, polarized line at 806 cm.$^{-1}$ and its depolarized neighbor at 921 have been assigned to the symmetric and asymmetric C-O stretching motions. The only polarized line below 420 cm.$^{-1}$ is found at 326 cm.$^{-1}$ and has been assigned to the C-O-C deformation.

The assigning of frequencies contributed to the complex by the BF_3 group is rendered more difficult by the scarcity of spectral data of molecules containing this grouping. However, a wealth of data on molecules containing the CF_3 group and the same symmetry (a single reflection plane) is available. The C-F stretching and CF_3 deformation frequencies of eight such compounds have been assembled in Table V. The polarized bands have been designated (a') and the depolarized by (a") which respectively preserve and destroy the plane of symmetry of the molecule during the course of the vibration. Generalizing from these data, one may attribute to the CF_3 group three stretching and three bending frequencies, the former occurring between 1100 and 1300 cm.$^{-1}$ and the latter between 500 and 700 cm.$^{-1}$. In addition, two of each group of three will be polarized, that is, suffer a reduction in intensity when

TABLE V

TYPICAL VALUES OF THE C-F STRETCHING AND THE CF_3 DEFORMATION FREQUENCIES ($cm.^{-1}$)

Compound	C-F Stretch			CF_3 Deformation			Ref.
	a'	a'	a"	a'	a'	a"	
CF_3CF_2Cl	1224	1349	1240	560	647	593	36
CF_3CFCl_2	1247	1292	1218	505	588	559	36
CF_3CH_2Cl	1152	1262	1285	(455)	639	537	37
CF_3CHCl_2	1140	1270	1226	526	671	554	37
CF_3CH_2Br	1075	1240	1135	526	632	539	38
CF_3CH_2I	1098	1210	1252	513	626		39
CF_3CO_2H	1128	1199	1240	566	580	507	40
CF_3COCl	1190	1279	1237	584	710		39

radiated with incident radiation which is polarized parallel to the axis the sample tube. Although it is not indicated in Table V, the intensities all of these bands are very low. Except for the higher-frequency CF_3 deformation, every band listed was classified by the author as "weak" or "very weak".

The method of transferring these values to anticipated frequencies of the BF_3 group is based upon a comparison of the frequencies of CF_4 and BF_4^-. That this can be done has been demonstrated by Woodward and Nord(41) who compared the vibrational frequencies of $GaBr_4^-$ and $InBr_4^-$ with those of the isoelectronic species $GeBr_4$ and $SnBr_4$. A constant difference of about 10%

was noted, with the ions having the lower values. A similar comparison of BF_4^- and CF_4 is given in Table VI.

TABLE VI

THE VIBRATIONAL SPECTRA OF BF_4^- AND CF_4 (cm.$^{-1}$)

	$\nu_1(A_1)$	$\nu_3(F_2)$	$\nu_4(F_2)$	$\nu_2(E)$	Ref.
BF_4^-	769	984	524	352	42
CF_4	904	1265	630	437	27
BF_4^-/CF_4	0.85	0.78	0.83	0.81	

Assuming that frequencies associated with the BF_3-group will also be approximately 80% of the corresponding CF_3-group frequencies, one would expect three stretching frequencies between 900 and 1100 cm.$^{-1}$ and three deformations in the region from 400 to 560 cm.$^{-1}$. It can be seen that there is an overlapping of the B-F stretching and CH_3 rocking bands and neither can be assigned with any certainty. On the other hand, the only band in the 400-560 cm.$^{-1}$ region is found at 503 cm.$^{-1}$ and must be the intense, symmetric BF_3-deformation frequency.

In addition to the bands derived from the original molecules forming the complex, there will be six new bands arising because of the loss of translational and rotational degrees of freedom in the separate components. In the case of the $R_2O:BX_3$ complexes, these new vibrational motions, which are characteristic of the complex itself, may be approximately described as a B-O stretching vibration, rocking motions of the BF_3 group both in the plane of the DME and out of the plane, similar rocking motions of the DME portion of the molecule in plane and out of plane, and a twisting of the BF_3 end around its axis with respect to the other end of the complex. Goubeau and Lücke(43) have reported the B-O stretching frequencies of a series of methyl esters of BF_3 as falling in the range from 630 to 770 cm.$^{-1}$. Therefore, the 664 cm.$^{-1}$ band, which is relatively intense and polarized, has been assigned to this motion.

The strong, depolarized band at 348 cm.$^{-1}$ has been assigned to a rocking motion of the BF_3 group. Although values for this frequency were not included in Table V, all of the compounds listed there have a strong band in the region between 250 and 350 cm.$^{-1}$ which is due to such a motion. There is the possibility that this is one of the BF_3 deformation frequencies instead, but because of its intensity, the assignment to a rocking motion is more likely. Vibrational frequencies associated with three other motions characteristic of the complex itself, namely the BF_3 torsional motion and the in-plane and out-of-plane DME rocking motions, could not be assigned because all of the observed bands could be accounted for otherwise. A BF_3 twisting frequency probably would be of rather low intensity and moreover would be expected at a rather low frequency, probably less than 100 cm.$^{-1}$. Failure to observe it must then be attributed to a combination of these factors and is not unexpected. The DME rocking motions would also be expected in this region and may not have been observed becuase of their low intensity. Broadening of the 4358 A. mercury line which occurred in all solutions prepared using BF_3 may well have prevented observation of these bands.

A summary of the frequency values, polarizations, intensities, and assignments is given in Table VII.

TABLE VII

THE RAMAN SPECTRUM OF $(CH_3)_2O:BF_3$

Frequency (cm.$^{-1}$)	Intensity	State of Polarization	Assignment
326	m	Pol.	C-O-C deformation
348	s	Depol.	BF_3 rock or BF_3 deformation
503	s	Pol.	BF_3 deformation
664	s	Pol.	B-O stretch
806	s	Pol.	C-O stretch
921	m		C-O stretch
1021	m		B-F stretch or CH_3 rock
1149	w		B-F stretch or CH_3 rock
1222	vw		CH_3 rock or CH_3 deformation
1262	vw		CH_3 rock or CH_3 deformation
1271	vw		CH_3 rock or CH_3 deformation
1455	s	Depol.	CH_3 deformation
2861	m	Pol.	*
2894	s	Pol.	*
2981	m	Depol.	C-H stretch
3049	m	Depol.	C-H stretch

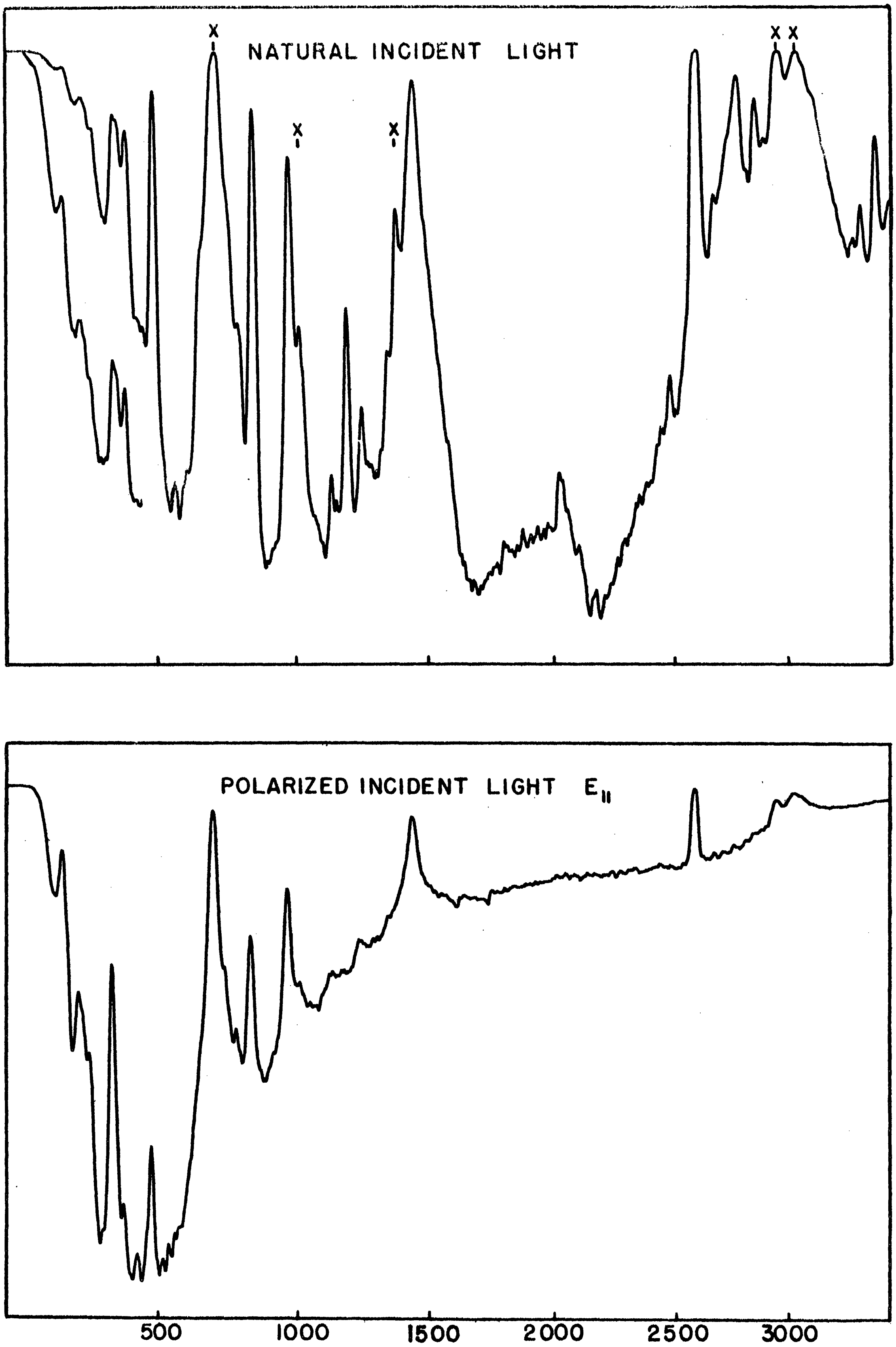
* These bands may be the fundamentals of symmetric C-H stretching frequencies or the first overtone of the CH_3 deformation in strong Fermi resonance with the stretching frequencies.

Raman Spectrum of DME:BCl_3

Spectra obtained through the use of both natural and polarized incident radiation are shown in Figure 9. Since methyl chloride was employed as a solvent, its spectrum is superimposed upon that of the solute. The symbol "x" indicates bands due to the solvent.

As in the preceding section, the spectrum will be considered as being made up of three groups of bands; those arising from BCl_3, those arising from DME, and new bands attributable to motions of the complex which in its components represented rotational and translational motions. Looking first at DME's contributions to the spectrum of the complex, one may argue through the same reasoning as in the BF_3 case that the bands occurring in the 1100 - 3000 $cm.^{-1}$ region can be assigned at once to C-H stretching, CH_3 deformation, and CH_3 rocking motions of the methyl group. The intense, strongly polarized band at 845 and its only slightly less intense neighbor at 976 $cm.^{-1}$ are immediately recognizable as the symmetric and asymmetric C-O stretching frequencies while the C-O-C deformation frequency must be one of the two polarized members of the triplet which covers the region between 350 and 400 $cm.^{-1}$. In fact, it can only be the band at 371 since the alternative assignment would represent a shift of only 20 $cm.^{-1}$ from its position in DME. In view of the corresponding value in DME:BF_3 (326 cm^{-1}) a greater shift is indicated.

Frequencies of the complex which may be considered as derived from BCl_3 may be deduced by examining a series of compounds containing the CCl_3-grouping. The stretching and deformation frequencies of such a series are given in Table VIII.



RAMAN SPECTRA OF $(CH_3)_2\ O{:}BCl_3$

Figure 9

TABLE VIII

TYPICAL VALUES OF THE C-Cl STRETCHING AND THE CCl_3 DEFORMATION FREQUENCIES ($cm.^{-1}$)

Compound	C-Cl Stretch			CCl_3 Deformation			Ref.
	a'	a'	a"	a'	a'	a"	
CCl_3CH_2Cl	549	747	717	242	334	307	44
CCl_3CHCl_2	584	725	773	224	327	327	44
CH_2CHCCl_3	538	792		281	315	436	45

These indicate that C-Cl stretching frequencies occur in the region between 550 and 800 $cm.^{-1}$, while CCl_3 deformations are found at lower values, 250 - 400 $cm.^{-1}$. Preliminary studies by Greenwood(49) indicate that the vibrational frequencies of BCl_4^- are about 85% of the corresponding frequencies of CCl_4. Assuming that frequencies associated with the BCl_3-group will also be approximately 80% of the corresponding CCl_3-group frequencies, one would expect three B-Cl stretching frequencies between 450 and 800 $cm.^{-1}$ and three BCl_3 deformations in the region from 200 to 400 $cm.^{-1}$.

The intensities of the C-Cl stretching frequencies show a definite pattern. The lowest frequency, found between 500 and 600 $cm.^{-1}$, is of the three, usually the most intense band in the entire spectrum and it is also strongly polarized. Such a band in the spectrum of DME:BCl_3 is found at 494 $cm.^{-1}$ and must therefore be assigned to one of the symmetric B-Cl stretching modes.

The only other strongly polarized band in this region appears at 664 $cm.^{-1}$ and must be attributed to the B-O stretching motion. The bands

TABLE IX

THE RAMAN SPECTRUM OF $(CH_3)_2O:BCl_3$

Frequency (cm.$^{-1}$)	Intensity	State of Polarization	Assignment
178	w		DME rock
189	m	Depol.	BCl_3 rock
242	m		BCl_3 rock or BCl_3 deformation
282	w	Depol.	BCl_3 rock or BCl_3 deformation
358	s	Depol.	BCl_3 deformation
371	s	Pol.	C-O-C deformation
399	s	Pol.	BCl_3 deformation
494	s	Pol.	B-Cl stretch
664	m	Pol.	B-O stretch
755	m		B-Cl stretch
795	w		B-Cl stretch
845	s	Pol.	C-O stretch
976	s	Depol.	C-O stretch
1136	w		CH_3 rock
1157	vw		CH_3 rock
1180	m	Pol.	CH_3 rock
1245	w		CH_3 deformation
1349	m		CH_3 deformation
1447	s	Depol.	CH_3 deformation

C-H stretching frequencies have been omitted because of interference by solvent bands.

Conclusions Drawn From a Comparison of the Two Spectra

Errors made in assigning spectral bands can often be detected by comparing corresponding bands in a series of related compounds. One such comparison is given in Table X in which the frequencies of the skeletal motions of DME are compared with those of DME:BCl_3 and DME:BF_3.

TABLE X

A COMPARISON OF THE SKELETAL FREQUENCIES OF DME, DME:BCl_3, AND DME:BF_3 (cm.$^{-1}$)

	C-O sym. stretch	C-O asym. stretch	COC deformation
DME	920	1095	420
DME:BCl_3	845	976	371
DME:BF_3	806	921	326

The formation of a strong dative bond between oxygen and boron would be expected to cause these frequencies to appear in the complexes at lower values than in free DME, the amount of lowering depending upon both the mass of the coordinating group and its acid strength. Since the two C-O stretching and the C-O-C deformation frequencies were found at lower values in DME:BF_3 than in DME:BCl_3 despite the greater mass of BCl_3, one could then argue that BF_3 is a stronger acid than BCl_3.

The observation of B-O stretching frequencies at exactly the same positions in DME:BF_3 and DME:BCl_3, however, is surprising. One would expect this frequency to be lower in the latter case because of the greater mass of BCl_3 and also because BF_3 is generally considered to be a stronger

Lewis acid than BCl_3. Two explanations of this anomaly can be suggested: first, the geometry of the system may be such that the B-O stretching frequency is practically independent of the mass of the halogen atoms, and second, the B-O stretching force constant may be different in DME:BCl_3 than in DME:BF_3 such that fortuitously it exactly compensates for the mass effect.

To study the effect of mass and geometry upon the B-O stretching frequency, a simplified model system, XYZ_3, having a 3-fold symmetry axis, was considered and the effect of various ZYZ angles upon its calculated vibrational frequencies was followed. In order that the model system be as closely related as possible to the dimethyl etherates of the boron halides, the mass of X was chosen to be that of oxygen,* Y that of boron, while the mass of Z varied from 19 to 80 atomic weight units. This artificial system is roughly equivalent to a simple mechnaical model of a X_3B-O molecule whose force constants are unaffected by molecular geometry. In carrying out the calculations, a consistent set of force constants was selected and the totally symmetric vibrational frequencies of X_3B-O were calculated as a function of the angle variable. The details of these calculations are given in the Appendix, but the effect of the ZYZ angle upon the X-Y stretching frequency is shown in Figure 10 in which the calculated value of the X-Y stretching frequency is plotted against the mass of X for four different values of α, the Z-Y-Z angle. From this figure it can be seen that the B-O stretching frequency in the dimethyl etherates of the boron halides can be expected to be appreciably mass dependent for all of a series of X-B-X angles ranging from 106° to 119°.

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* Perhaps a larger value should have been chosen but 16 was selected as a first approximation.

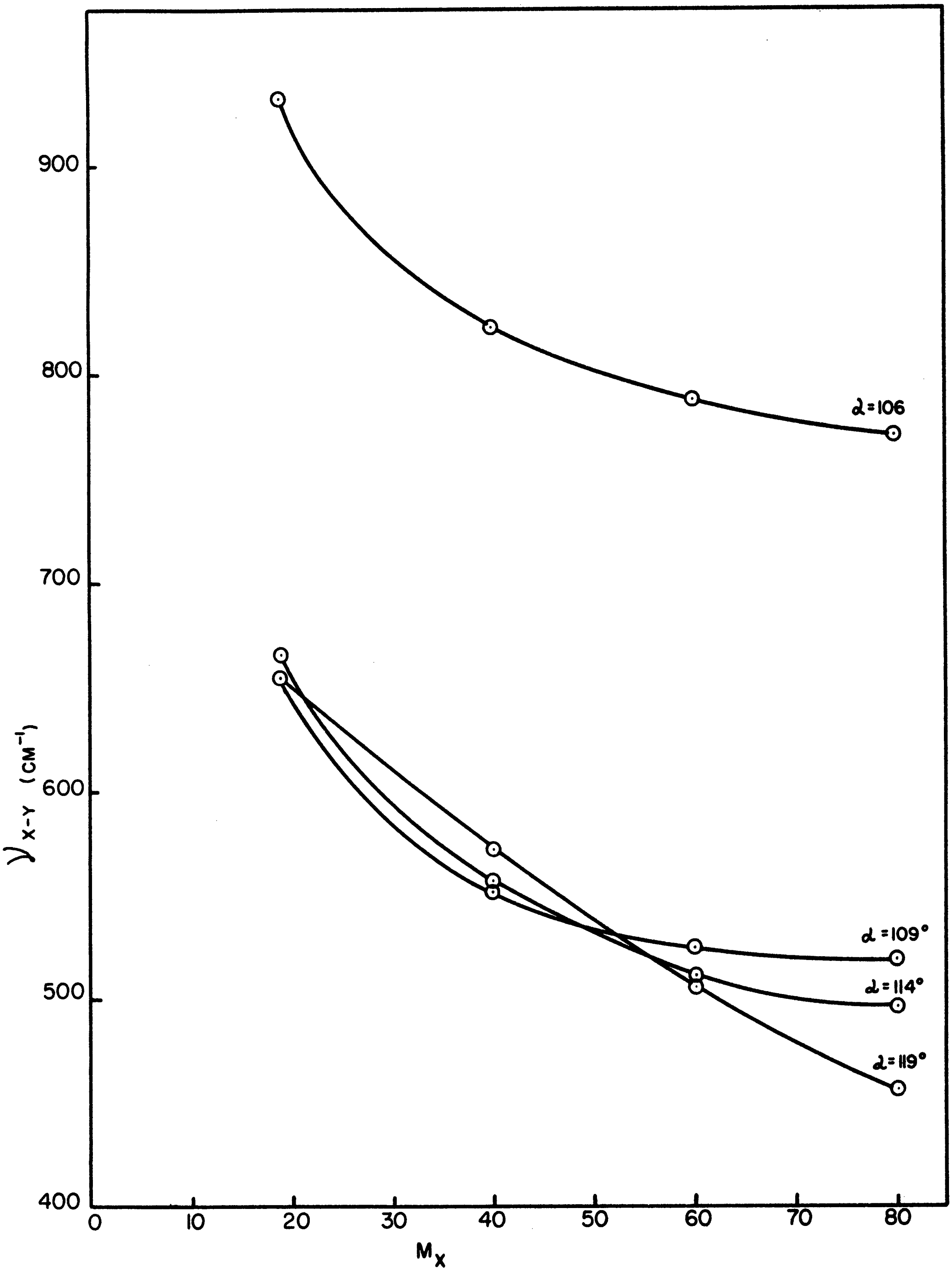


Figure 10. The Mass Dependence of ν_{X-Y} for Various ZYZ Angles.

These results appear to eliminate the first explanation of the coincidence of the B-O stretching frequencies of DME:BF_3 and DME:BCl_3 as being due to geometrical factors. To obtain positive evidence for the second explanation, one would have to investigate other systems involving other ethers and perhaps use BBr_3 and BI_3 as acids as well as BCl_3 and BF_3. The second explanation lends credence to Brown's contention that BCl_3 is the stronger acid(50) Further investigation of this point appears desirable.

A rough check of the assignments of the B-X stretching and BX_3 deformation frequencies of DME:BF_3 and DME:BCl_3 can be made by comparing these frequencies with those of BX_3 and BX_4^-. In Table XI the B-F stretching and deformation frequencies of DME:BF_3 are compared with those of BF_3 and BF_4^-.

TABLE XI

A COMPARISON OF THE B-F STRETCHING AND THE BF_3 DEFORMATION FREQUENCIES OF BF_3, DME:BF_3, AND BF_4^- (cm.$^{-1}$)

	B-F stretch		BF_3 deformation	
	(sym.)	(asym.)	(sym.)	(asym.)
BF_3	888	1446	480	691
DME:BF_3	(1021)	(1222)	348	503
BF_4^-	767	984	353	524

One would expect these frequencies to approach those of BF_4^- in complexes with strong Lewis base and with the exception of the stretching frequency at 1021 cm.$^{-1}$ this is observed. As was mentioned earlier, the B-F stretching frequencies are of very low intensity and are overlapped by methyl-group rocking frequencies. Therefore the band at 1021 cm.$^{-1}$ may be incorrectly assigned and may instead be either a methyl group rocking frequency or the second, asymmetric, B-F stretch.

A similar comparison of DME:BCl_3 is not possible because of the lack of spectral data for BCl_4^-, but a comparison with BCl_3 shows the symmetric B-Cl stretching frequency of DME:BCl_3 also above the corresponding

TABLE XII

A COMPARISON OF THE B-Cl STRETCHING AND THE BCl_3 DEFORMATION FREQUENCIES OF BCl_3 AND DME:BCl_3 (cm.$^{-1}$)

	B-Cl stretch		BCl_3 deformation	
	(sym.)	(asym.)	(sym.)	(asym.)
BCl_3	471	958	243 (242)	462
DME:BCl_3	494 755	795	(282)358	399

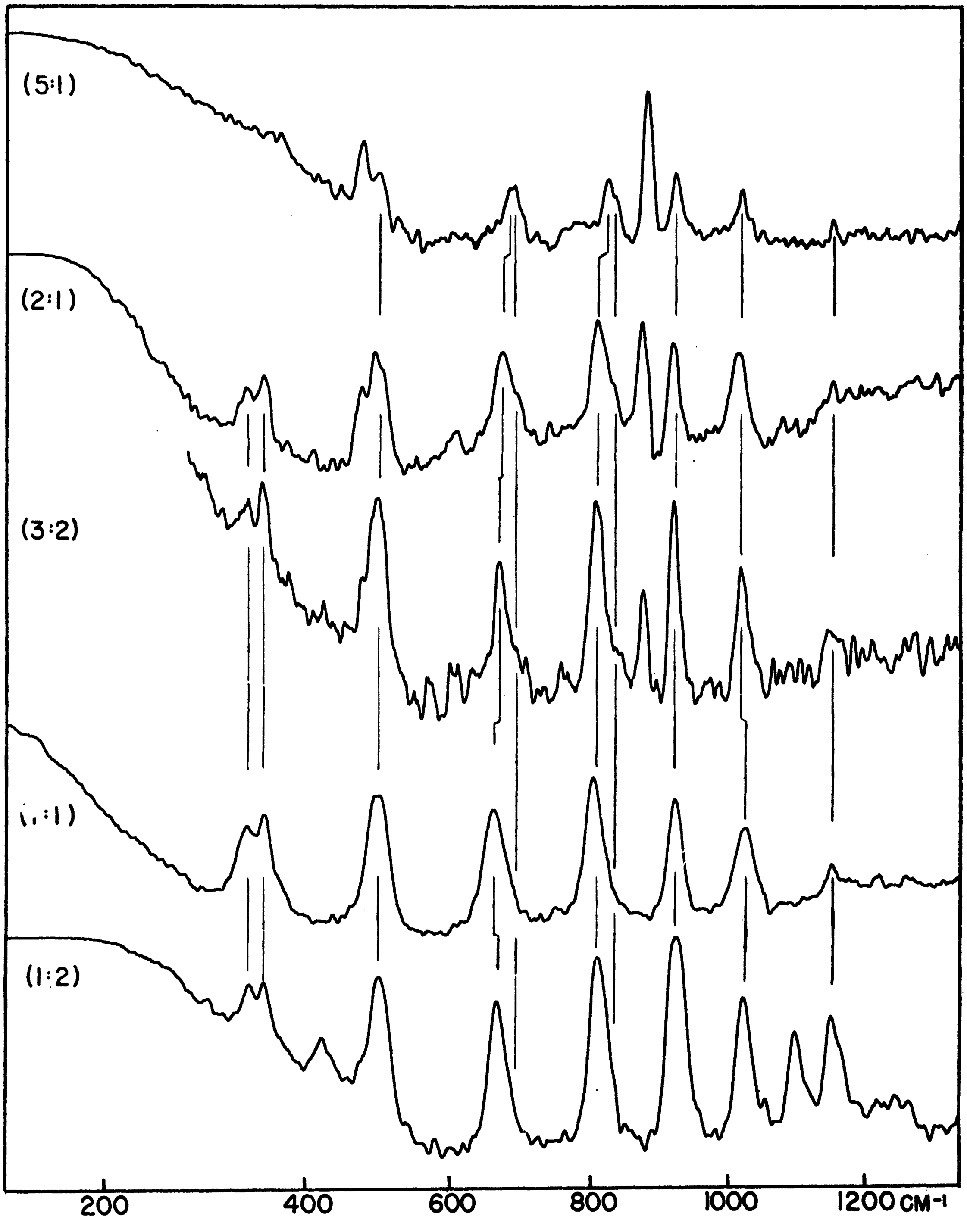
band of BCl_3. In this case, however, the assignment of the band of the etherate is more certain and thereby, in a sense, justifies the assignment in the BF_3 case. Further work with other complexes of BF_3 and BCl_3 with Lewis bases will be necessary before unequivocal assignments can be made for DME:BF_3.

The Spectra of BX_3:DME in Ether-Rich Solutions

One of the goals of this research was the study of acid-rich mixtures of a strong Lewis acid and DME in hope of observing higher order complexes as in the DME-HCl system. However, the possibility of higher order complexes in which more than one mole of ether was present per mole of acid was not ignored since several workers have reported such complexes in systems involving DME or diethyl ether and strong Lewis acids such as AlX_3 and GaX_3(46), $TiCl_4$(47) and $SnCl_4$(48). As a result, a series of Raman spectra of solutions having various BX_3-DME ratios were recorded and are shown in Figures 11 and 12. Since no changes were noted in the C-H stretching or CH_3 deformation regions, these parts have not been included.

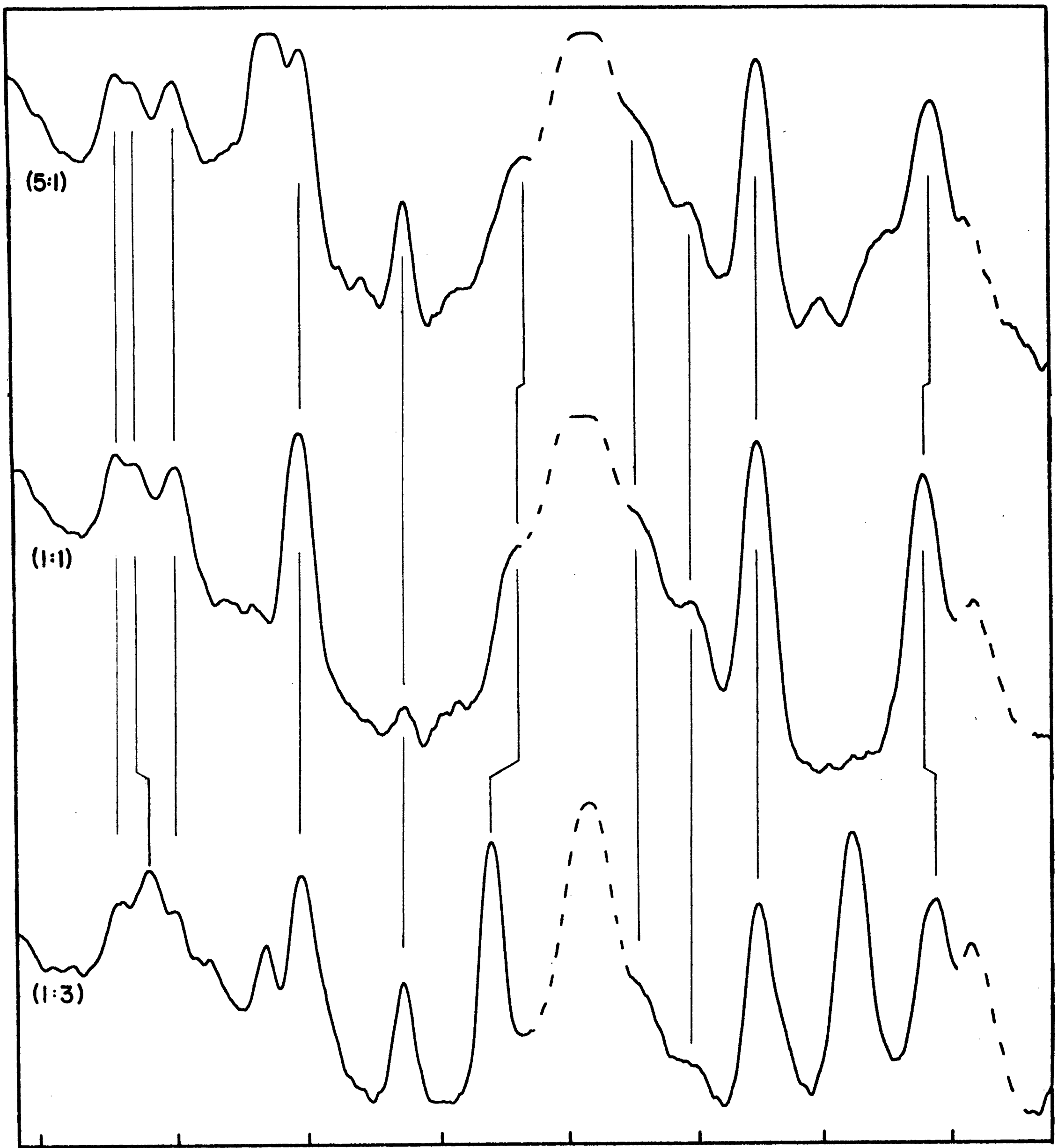
The presence of excess DME actually has very little effect upon the spectrum of DME:BF_3. The only band of the complex which appears to be affected is the B-O stretching band which is shifted from 664 $cm.^{-1}$ in the 1:1 mixture to 673 $cm.^{-1}$ in the excess ether solution. Such a small change can be attributed to solvent effects. The skeletal bands of DME appear at 420, 920, and 1095 $cm.^{-1}$ in the mixture, the increased relative intensity of the band at 920 $cm.^{-1}$ being due to a superposition of bands of the ether and the complex.

At a first glance, the effect of DME appears more pronounced in the case of DME:BCl_3 since several new bands appear. Several of these new bands indicate the presence of a significant amount of methyl chloride, however, and since none was used for solvent purposes, this can only have come from the decomposition of DME:BCl_3. Wiberg and Sütterlin(20) have studied this decomposition and have found the products to be methyl chloride and several methyl chloroborates. The additional new bands at 469 and 573 $cm.^{-1}$ are undoubtedly due to one of these esters, probably BCl_2OCH_3, while the other new bands (at 420, 920, and 1095 $cm.^{-1}$) are due to the DME present in the mixture. Some interaction of DME with DME:BCl_3 is indicated, however, by shifts in the skeletal frequencies of the latter. The C-O-C deformation



0-1200 REGION FOR VARIOUS BF_3-$(CH_3)_2O$ RATIOS

Figure 11



300-1000 REGION FOR VARIOUS BCl_3-$(CH_3)_2O$ RATIOS

Figure 12

band at 371 cm.$^{-1}$ appears at 378 cm.$^{-1}$ with a noticeable gain in intensity. The B-O stretching frequency is shifted downward in this case, occurring at 641 cm.$^{-1}$. The asymmetric C-O stretching frequency, on the other hand, has been shifted from 976 to 987 cm.$^{-1}$. The fact that all of the bonds about the oxygen atom have been affected is, in one sense, a verification of the correctness of the assignments of the bands associated with the DME part of the complex.

The Spectra of BX_3:DME in Acid-Rich Solutions

The addition of excess BF_3 to DME:BF_3 introduces several additional bands into the vibrational spectrum besides those of the free acid. A band at 690 cm.$^{-1}$ appears in the 3:2 mixture as a shoulder on the B-O stretching band and finally becomes equally intense in the 5:1 mixture. Similar behavior is shown by the band at 833 cm.$^{-1}$ which appears in the 3:2 mixture as a weak shoulder on the symmetrical C-O stretching band. This shoulder gains intensity in solutions containing more acid until it appears equally intense in the 5:1 mixture. The B-O and symmetrical C-O stretching frequencies are at the same time shifted to higher and higher frequencies, the B-O stretching frequency going from 664 cm.$^{-1}$ to 667 in the 3:2 mixture, to 673 in the 2:1 solution, and appearing finally at 685 cm.$^{-1}$ in the 5:1 ratio. Clearly a new species is present, but whether it has come from interaction of DME:BF_3 with BF_3 or from decomposition of the complex cannot be stated with absolute certainty. However, because of the regular gradations in intensity obtained from freshly prepared samples, the former seems more likely.

The spectrum of DME:BCl_3 in solution with excess BCl_3 does not indicate interaction of the complex and the excess acid. The new bands are those of BCl_3, their overtones, and one of the bands (575 cm.$^{-1}$) which in ether-rich solutions were attributed to the decomposition of the 1:1 complex. The other may be obscured by the BCl_3. The B-O stretching frequency appears at 666 vm.$^{-1}$ in the 5:1 mixture and the asymmetric C-O stretch at 984 cm.$^{-1}$

It is of interest to note that the effect of an excess of either DME or acid upon the dimethyl etherates of the boron halides is upon bonds about the oxygen atom. Although the formation of higher order complexes is suggested only in the case of BF_3:DME with excess BF_3, the shifting of the frequencies associated with these bonds suggested that the point of attack of excess component is at the oxygen atom and is not at the first boron atom through formation of a single-bridged structure.

The Effect of HCl Upon DME:BCl_3

The Raman spectrum of a 1:1 mixture of DME:BCl_3 and HCl was recorded to check the possibility that HCl might complex with DME:BCl_3, giving perhaps $(DME:H)^+$ and BCl_4^-. The spectrum showed that in the liquid phase no interaction occurs. There remains the possibility that if BCl_3 were added to DME:HCl, a new species might be formed. However, Laubengayer and Smith(51) prepared $(Me_3N)_2SnCl_4$ and admitted BF_3 to the system. The resulting interaction resulted in displacement of the weaker acid, $SnCl_4$, by BF_3 and led to the formation of $Me_3N:BF_3$. Drawing an analogy from this instance, displacement of HCl from DME:HCl by addition of BCl_3 seems likely, but a final answer can only come from further experimental work.

SUMMARY

Earlier work in this laboratory by Vidale and Taylor(1) involved a study of the interaction of HCl and dimethyl ether (DME). This system was of particular interest not only as a case of very strong hydrogen bonding but also because of the number of discrete species which are formed as a result of acid-base interaction. The technique employed was that of vibrational spectroscopy and of the two methods available for the analysis of vibrational spectra, the Raman technique was chosen over infrared because it permitted use of all-glass apparatus, allowed observation of a broader spectral region and was more conveniently adaptable to a wide range of temperatures.

One portion of this previous investigation which could not be resolved involved the characterization of all the species present in the DME - HCl system. The existence of a 1:1 molecular complex was confirmed but the remaining complexes, at least two in number, which appeared to be ionic in nature and resulting from proton transfer, could not be characterized, partly because of inherent spectroscopic limitations of the HCl molecule.

In the present work a more complex Lewis acid was sought which in mixtures with DME, might give rise to another series of complexes in which both cationic and anionic fragments could be characterized. Such a system might well provide information on the stoichiometry of the DME - HCl complexes in addition to being valuable as another example of acid-base interaction.

The interaction of many strong Lewis acids with DME to give stable 1:1 addition complexes is quite general and complexes containing two moles of ether per mole of acid are not uncommon. Brown's recently proposed single-bridge structure for compounds of the boron halides(5) suggested additional complexes containing more than one mole of acid per mole of base. Thus, systems of the boron halides offered reasonable promise of giving rise, in mixtures with DME, to another series of complexes whose study would be of considerable interest.

Raman spectra have been obtained of mixtures of the boron halides with DME in which the concentrations of acid/base varied from 5/1 to 1/3 at temperatures just above their freezing points. All of these spectra showed the spectrum of a 1:1 addition complex plus new bands which, in the DME-BCl system are attributed to decomposition of the 1:1 complex rather than to formation of a higher order complex. In the DME - BF_3 system, however, the results indicate a second complex which is found only in acid-rich solutions. In both systems addition of excess acid or base to solutions of the 1:1 complex caused a shifting of several frequencies which is attributed to a solvent effect.

A detailed study of the vibrational spectra of the 1:1 complexes is presented in which the spectra are considered as being made up of three sets of bands:

A. those derived from dimethyl ether

B. those derived from BX_3

C. new bands arising as a consequence of the formation of the B-O bond.

Frequencies associated with the methyl group of DME are not noticeably affected by complexation but the skeletal frequencies appear at lower values in the complexes. In this respect BF_3 has a greater effect than BCl_3. Bands derived from the parent acids are shifted in a manner similar to that observed in the formation of BF_4^- from BF_3(42). Of interest among the frequencies arising from complex formation is the B-O stretching frequency. Its appearance at 664 $cm.^{-1}$ in both DME:BF_3 and DME:BCl_3 is interpreted as indicating greater acid strength for BCl_3.

Spectra of mixtures of strong Lewis acids and weaker bases and of a weaker acid, SO_2, and DME are also discussed. In only one system, methyl bromide - aluminum bromide, was a complex species, MeBr:$AlBr_3$, observed in the liquid phase. The vibrational frequencies of this species, considered by some to be an unstable intermediate in Friedel-Crafts catalysis, are assigned to various motions of the complex.

The question of trends in the acid strengths of the boron halides is perhaps typical of the many unanswered questions which one encounters in the field of molecular addition compounds. Many of these questions can be traced to a lack of fundamental knowledge of the properties of the compounds involved and to the limited number of experimental techniques which have been applied. The two are related to the nature of the compounds themselves but as a result most of the information currently available is in the form of thermodynamic data obtained from thermal dissociation studies or calorimetry. The development of spectroscopic techniques has permitted study of a whole new range of systems which had not been tractable previously.

It would be of interest to extend the current investigation of acid-base interaction by studying several related systems whose spectra could be analyzed more easily. These proposed systems should have two properties which would facilitate this analysis. Their components should contain a minimum number of atoms and their 1:1 addition compounds should possess a high degree of molecular symmetry, preferably at least a three-fold rotation axis in order to reduce the number of observed bands through degeneracy. The advantages of such systems would actually be two-fold. The reduction of the number of observed spectral bands would facilitate the assigning of these bands to particular vibrational motions while the highly symmetrical structure would permit a normal coordinate treatment of the complex and thereby give a measure of the binding forces of the molecule in terms of force constants. An example of such a series can be found in the 1:1 addition complexes of ammonia and the Group III halides. A spectroscopic investigation of these species would not only give information about the binding forces in a series of related compounds but would also serve as a check on the assignments which were made for the dimethyl etherates of BF_3 and BCl_3.

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APPENDIX

The method which was employed to study the effect of geometry upon the vibrational frequencies of the XYZ_3 model system is that outlined in Wilson, Cross, and Decius(24). Only a small portion which contains a slight modification of Wilson's method will be discussed below.

It can be shown that the potential and kinetic energies of vibration may be written in matrix form:

$$2V = \tilde{x}\, f\, x \qquad \text{(A-1)}$$

$$2K = \tilde{\dot{x}}\, g^{-1}\, \dot{x} \qquad \text{(A-2)}$$

where x is a column vector of internal displacement coordinates, $\tilde{x}$ is the transposed (row) vector, f is a matrix of force constants, and g^{-1} is a kinetic energy matrix whose elements are expressed in terms of masses, bond lengths and angles. The form of the secular determinant obtained from the energy expressions given in (A-1) and (A-2) is:

$$|f - g^{-1}\lambda| = 0 \qquad \text{(A-3)}$$

where $\lambda = 4\pi^2\nu^2$. By multiplying (A-3) through by the determinant g, the inverse kinetic energy matrix, and rearranging, one can obtain the secular determinant in the form:

$$|fg - I\lambda| = 0 \qquad \text{(A-4)}$$

The f-matrix is symmetrical about its diagonal and has for its elements two types of valence force constants; the "principal" valence force constants lie along the diagonal while the "interaction" terms fill out the rest of the matrix. Often the magnitudes of these interaction terms are sufficiently small that they may be equated to zero;

in the XYZ_3 case only two such terms were retained. The f-matrix which was employed in the XYZ_3 system is shown below with half the interaction terms omitted because of symmetry.

$$f = \left|\begin{array}{cccccccccc}
k_r & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 & k_r & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 & & k_r & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 & & & k_D & k_{D\alpha} & k_{D\alpha} & k_{D\alpha} & k_{D\beta} & k_{D\beta} & k_{D\beta} \\
 & & & & k_\alpha & 0 & 0 & 0 & 0 & 0 \\
 & & & & & k_\alpha & 0 & 0 & 0 & 0 \\
 & & & & & & k_\alpha & 0 & 0 & 0 \\
 & & & & & & & k_\beta & 0 & 0 \\
 & & & & & & & & k_\beta & 0 \\
 & & & & & & & & & k_\beta
\end{array}\right| \qquad (A-5)$$

The method by which the g-matrix elements are determined is given by Wilson. Since the elements in terms of atom masses and internal coordinates are fairly complex expressions, the matrix is represented symbollically below, the rows and columns being labeled with the appropriate internal displacements coordinates so that the notation may be understood. Terms having identical subscripts are the same because of the symmetry of the model. In addition, symmetry of the matrix has led to omission of half of the interaction terms, as in the case of the f-matrix.

$$\begin{array}{c|cccccccccc}
 & r_1 & r_2 & r_3 & D & \alpha_1 & \alpha_2 & \alpha_3 & \beta_1 & \beta_2 & \beta_3 \\
\hline
r_1 & g_{11} & g_{12} & g_{12} & g_{14} & g_{16} & g_{15} & g_{15} & g_{18} & g_{19} & g_{19} \\
r_2 & & g_{11} & g_{12} & g_{14} & g_{15} & g_{16} & g_{15} & g_{19} & g_{18} & g_{19} \\
r_3 & & & g_{11} & g_{14} & g_{15} & g_{15} & g_{16} & g_{19} & g_{19} & g_{18} \\
D & & & & g_{44} & g_{19} & g_{19} & g_{19} & g_{48} & g_{48} & g_{48} \\
\alpha_1 & & & & & g_{55} & g_{56} & g_{56} & g_{59} & g_{58} & g_{58} \\
\alpha_2 & & '' & & & & g_{55} & g_{56} & g_{58} & g_{59} & g_{58} \\
\alpha_3 & & & & & & & g_{55} & g_{58} & g_{58} & g_{59} \\
\beta_1 & & & & & & & & g_{88} & g_{89} & g_{89} \\
\beta_2 & & & & & & & & & g_{88} & g_{89} \\
\beta_3 & & & & & & & & & & g_{88}
\end{array} \qquad \text{(A-6)}$$

Since the expressions for the g-matrix elements have been tabulated in Appendix VI of Wilson, Cross, and Decius, they will not be repeated here. However, a translation of the notation employed above into that used by Wilson is given:

$g_{11} = g_{rr}^{2}$

$g_{12} = g_{rr}^{1}$

$g_{14} = g_{rr}^{1}$

$g_{15} = g_{r\varphi}^{2}$

$g_{16} = g_{r\varphi}^{1}(\tfrac{1}{1})$

$g_{18} = g_{r\varphi}^{2}$

$g_{19} = g_{r\varphi}^{1}(\tfrac{1}{1})$

$g_{44} = g_{rr}^{2}$

$g_{48} = g_{r\varphi}^{2}$

$g_{55} = g_{\varphi\varphi}^{3}$

$g_{56} = g_{\varphi\varphi}^{2}(\tfrac{1}{1})$

$g_{58} = g_{\varphi\varphi}^{2}(\tfrac{1}{1})$

$g_{59} = g_{\varphi\varphi}^{1}(\tfrac{1}{1})$

$g_{88} = g_{\varphi\varphi}^{3}$

$g_{89} = g_{\varphi\varphi}^{2}(\tfrac{1}{1})$

Wilson has shown that equation (A-4) can be further simplified by the use of symmetry coordinates rather than internal coordinates. For pyramidal molecules such as XYZ_3 the change from the internal coordinates r_i, D, α_i, and β_i to symmetry coordinates, S_i, may be expressed as

$$S_i = U x_i \qquad \text{(A-7)}$$

where U, the transformation matrix has the form

$$U = \begin{vmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/\sqrt{c} & 1/\sqrt{c} & 1/\sqrt{c} & b/\sqrt{c} & b/\sqrt{c} & b/\sqrt{c} \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/\sqrt{2} & -1/\sqrt{2} \end{vmatrix} \qquad \text{(A-8)}$$

with $b = 3 \cos \beta/\cos \alpha/2$ and $c = 3(1 + b^2)$.

In terms of the symmetry coordinates the secular equation may be written:

$$|FG - \lambda I| = 0 \qquad \text{(A-9)}$$

where $F = U f \tilde{U}$ and $G = U g \tilde{U}$ (A-10)

The F and G matrices obtained according to (A-10) are not only symmetrical but are also factored into two 3 x 3 matrices as shown below for the F matrix.

$$\left|\begin{array}{ccc|ccc} F_{11} & F_{12} & F_{13} & & & \\ F_{12} & F_{22} & F_{23} & & 0 & \\ F_{13} & F_{23} & F_{33} & & & \\ \hline & & & F_{44} & F_{45} & F_{46} \\ & 0 & & F_{45} & F_{55} & F_{56} \\ & & & F_{46} & F_{56} & F_{66} \end{array}\right|$$

in which the upper block corresponds to totally symmetric (A_1) vibrations and the lower section to antisymmetric (E) vibrations. The product, the FG matrix, is similarly factored, but is not symmetrical. For the purposes of these calculations only the totally symmetric frequencies were considered. The frequency values together with the values of the F and G-matrix elements are given below:

$$\nu_1 = 1020 \text{ cm.}^{-1}$$
$$\nu_2 = 664 \text{ cm.}^{-1}$$
$$\nu_3 = 554 \text{ cm.}^{-1}$$

$$F_{11} = 7.34 \qquad F_{22} = 2.29$$
$$F_{12} = F_{21} = 0.5 \qquad F_{23} = F_{32} = -1.0$$
$$F_{13} = F_{31} = 0 \qquad F_{33} = 1.75$$

$$G_{11} = g_{11} + 2g_{12}$$
$$G_{12} = G_{21} = \sqrt{3}\, g_{14}$$
$$G_{13} = G_{31} = (1/\sqrt{1 + b^2})(2g_{15} + g_{16} + bg_{18} + 2bg_{19})$$
$$G_{22} = g_{44}$$
$$G_{23} = G_{32} = (3/\sqrt{c})(g_{19} + bg_{48})$$
$$G_{33} = (1/1 + b^2)(g_{55} + 2g_{56} + 4bg_{58} + 2bg_{59} + b^2g_{88} + 2b^2g_{89})$$

Since it was assumed that the binding forces were to remain fixed in order that the effect of various masses and angles could be determined, the same F-elements were used throughout. The numerical values of the G-elements are:

α = 106°

M_Z	G_{11}	G_{12}	G_{13}	G_{22}	G_{23}	G_{33}
19	0.09032	-0.06083	-0.07302	0.15330	0.12762	0.41295
40	0.06270	"	"	"	"	0.38231
60	0.05437	"	"	"	"	0.37307
80	0.05020	"	"	"	"	0.36845

α = 109° 28'

19	0.08290	-0.05241	-0.08584	0.15330	0.14600	0.29646
40	0.05528	"	"	"	"	0.26868
60	0.04695	"	"	"	"	0.26031
80	0.04278	"	"	"	"	0.25610

α = 114°

19	0.06956	-0.03921	-0.05797	0.15330	0.13802	0.23929
40	0.04194	"	"	"	"	0.21784
60	0.03361	"	"	"	"	0.21136
80	0.02944	"	"	"	"	0.20813

α = 119°

19	0.05538	-0.01583	-0.01264	0.15330	0.10069	0.06842
40	0.02776	"	"	"	"	0.06257
60	0.01943	"	"	"	"	0.06081
80	0.01526	"	"	"	"	0.05992

The frequencies calculated from the roots of the secular equation for the X-Y stretching motion (ν_2) have already been given in Figure 12 but are included with the Y-Z stretching frequency (ν_1) and the ZYZ deformation frequency (ν_3) in the tables below.

$\alpha = 106^\circ$

M_Z	ν_1	ν_2	ν_3
19	1048	933	565
40	963	822	500
60	944	787	460
80	936	770	434

$\alpha = 109^\circ\ 28'$

M_X	ν_1	ν_2	ν_3
19	1021	655	556
40	916	554	479
60	890	523	399
80	878	517	349

$\alpha = 114^\circ$

M_Z	ν_1	ν_2	ν_3
19	910	665	522
40	796	550	453
60	775	510	396
80	767	496	351

$\alpha = 119^\circ$

M_Z	ν_1	ν_2	ν_3
19	816	656	65
40	652	570	imag.
60	624	505	imag.
80	620	456	imag.