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Technical Report

A VIBRATIONAL STUDY OF SOME LEWIS ACID-BASE COMPLEXES CONTAINING PHOSPHORUS AND BORON

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INTRODUCTION

In recent years a great deal of interest has been shown in the complexes which are formed from Lewis acids and bases. One reason for this interest is that the formation of the complex may stabilize either the Lewis acid or base, which may be unstable by itself. A good example of this is shown in the reactions of diborane with Lewis bases. Experimental evidence, primarily from kinetic studies, suggests that diborane dissociates into the borane group, BH_3, which is thought to be the principal intermediate in reactions involving diborane. The borane group has never been isolated and presumably has only a transitory existence. However, many complexes are known which contain the borane group joined to Lewis bases such as the amines, phosphines, ethers and the like. In all these complexes the BH_3 fragment is stabilized by the dative bond to the base. In many cases the complex is formed without the necessity of a bond rupture on the part of the parent Lewis acid or base prior to reaction. The only energies which are involved in the process of complex formation are those which pertain to the possible rearrangement of the parent species plus that of the dative bond formation in the complex. A spectroscopic study of such compounds could afford valuable insight into their chemical bonding and physical properties. From a spectroscopic point of view one would expect the principal differences which might appear to be largely a consequence of the dative bond formed in the complex.

A great deal of discussion has been given to the subject of bonding in Lewis acid-base complexes and to the interpretation of stabilities, heats of formation and other thermodynamic properties in terms of the electronic structures of the acid and base or the complex. Complexes containing phosphorus have received considerable attention particularly with respect to the role of the d-orbitals of the phosphorus. Traditional acid-base and coordination theories suggest that compounds of phosphorus(III) should serve as ligands in complex formation because of the lone pair of electrons on the phosphorus atom. It is evident that the nature of the groups attached to the phosphorus atom will greatly affect the availability of the lone-pair electrons. One would expect that electron withdrawing groups on the phosphorus, e.g. the halogens, would tend to make the lone-pair electrons less available for contribution. On the other hand, electron releasing groups such as CH_3-, CH_3NH-, $(CH_3)_2N$-, etc. would tend to release electrons to the phosphorus, thereby making the lone-pair electrons less tightly bound by the phosphorus and more available for coordinate bond formation.

Somewhat contrary to the above expectations based on simple theory, trifluorophosphine is known to form fairly stable complexes with transition metal ions of platinum (1,2) and nickel (3). In order to account for the unusual stability of the complexes, Chatt and Williams (1) proposed that a different type of bonding was present. They invoked the concept of π-bonding between the d-orbital electrons on the metal ion and the vacant orbitals on the ligand. As a corollary, it was postulated that PF_3 should not form a complex with Lewis acids such as BF_3, BH_3, or $AlCl_3$ (1,2) since these have no d-orbitals.

However, with the synthesis of F_3PBH_3 in this laboratory by Parry and Bissot (4), the ability of PF_3 to coordinate with the borane Lewis acid was demonstrated. Taylor and Bissot (5) have provided evidence from a Raman spectroscopic study that this complex probably has an ethane-like structure and contains a typical dative P-B bond. Although not in accord with Chatt's ideas, the formation of this complex was not entirely unexpected in view of the marked similarity of PF_3 and CO and the known existence of the compound H_3BCO (6).

Attempts have been made to rationalize the non-existence of F_3PBF_3 while still accounting for the existence of F_3PBH_3. Graham and Stone (7) proposed that the borane complex existed because in addition to the σ-dative bond formed from the lone-pair electrons on the phosphorus, there was additional π-bonding between the vacant 3d-orbitals of phosphorus and a "pseudo π orbital" provided by the delocalized electrons in the borane group. The non-existence of F_3PBF_3 was attributed to the fact that the fluorine atoms on the boron attract electrons to such an extent that delocalization cannot take place. Arhland, Chatt, and Davies (8) invoked a similar argument and attributed the existence of F_3PBH_3 to hyperconjugation effects.

It should be mentioned here that several workers have reported previously the synthesis of Cl_3PBBr_3 (9) and Cl_3PBF_3 (10) and it is surprising to note that very little has been mentioned in the literature (2) to explain the bonding in these complexes.

The synthesis of F_3PAlCl_3 in this laboratory by Alton (11) necessitated a re-examination of the bonding question since the formation of this complex could not be explained adequately by using either the π-bonding or delocalization concepts. Alton suggested that perhaps this bonding issue was not as complex as the previous authors tried to make it but could be explained in the more conventional terms of steric and electronic effects. For example, he tried to show by approximate calculations that more energy is required to deform planar BF_3 into the pyramidal configuration found in complexes than is needed for BH_3 (11), thereby making the F_3PBH_3 complex thermodynamically favored over F_3PBF_3. Also, from steric considerations, the smaller BH_3 is able to bring the bonding site on the boron closer to the phosphorus allowing for greater stability to be achieved upon complexation. The existence of F_3PAlCl_3 was attributed to the probable ease of deformation of $AlCl_3$ (11).

Subsequent to the discovery of F_3PBH_3 a new series of related compounds was synthesized by Kodama (12) in this laboratory. His work involved reactions in which ammonia and the methyl amines were used to substitute for fluorine in F_3PBH_3. Sr. Fleming (13) in continuing this work, studied the dimethylamine series in greater detail and by means of infrared and N.M.R. spectra was able to show fairly conclusively that the borane group was bonded to the phosphorus in the complexes.

Beyond this information, little or no structural data have been accumulated for these interesting complexes. Likewise no attempt has been made to gather information which might lead to a better understanding of the nature of the P-B dative bond.

STATEMENT OF PROBLEM

Although a large number of complexes containing phosphorus and boron are known, a number of questions concerning these complexes still remain unanswered. Structural data for them are relatively meager and in many cases only those physical properties are known which are used in their characterization. A spectroscopic investigation of these complexes would be of interest to supplement the data already accumulated and help provide a better understanding of these complexes.

Since the number of phosphorus-boron complexes is appreciable, a selection must be made for the present work. Several borane complexes, first investigated by Kokama (12), offer a very interesting series to study spectroscopically. These include the following: F_3PBH_3, $CH_3NHPF_2BH_3$, $(CH_3NH)_2PFBH_3$, $(CH_3)_2NPF_2BH_3$, $[(CH_3)_2N]_2PFBH_3$ and $(CH_3)_3PBH_3$. A Raman investigation of $(CH_3)_2NPF_2BF_3$ is also of interest for comparison with the preceding because of its unusual nitrogen-boron bonding.

Detailed information on the vibrational spectra of the preceding compounds would be of interest in connection with the general question of bonding since the vibrational frequencies can be directly related to bond strength. The actual calculation of force constants for molecules of the size being considered may not be a simple process and may not lead to an unequivocal answer. However, this is a problem in itself and is a step removed from the experimental one which is an essential prelude to any further theoretical work.

In addition to the information which may be garnered concerning bonding, the vibrational data may also provide a basis for the comparison of the properties of the Lewis acids, bases and complexes formed from them. Such data would contribute to the general fund of knowledge accumulated for other Lewis complexes in this laboratory and in addition would be pertinent to the general question of stability, strength of the dative bond, and related characteristics. A somewhat secondary but still useful benefit from this investigation would be the identification of characteristic frequencies which might be associated with certain groups of atoms found in these molecules.

The vibrational spectra of these complexes may be expected to be relatively complex due to the large number of atoms in the molecules. The large number of vibrational modes resulting may create difficulties in making assignments and increase the possibility of modes being accidentally degenerate. Due to the low symmetry of many of these molecules none of the vibrational modes are truly degenerate and this will increase the difficulty of interpretation of the spectra.

Since many of the bases of interest contain methyl groups, some simplification can be achieved by virtue of the fact that the methyl group frequencies are well known and easily identified. To a good approximation, the frequencies remaining after elimination of the methyl modes can be considered to arise from a molecule in which the methyl groups act as point masses. The problem can be simplified further by examining the vibrational spectrum of the ligand whenever possible and then comparing this spectrum to that of the complex. Polarization information and data obtained from isotopic substitution will also facilitate making assignments.

HISTORICAL BACKGROUND

Even though spectroscopic work on compounds containing phosphorus and boron is not voluminous, data for a large number of closely related compounds have been given in the literature.

Trifluorophosphine has been examined spectroscopically by several workers (14,15,16,17). Despite the relative simplicity of the molecule, a surprising amount of confusion has existed regarding the spectra and the assignment of fundamentals. For example, Yost and Anderson (14) assigned the frequencies 531 cm^{-1} and 486 cm^{-1} to the respective totally symmetric and degenerate P-F bending vibrations whereas Gutowsky and Liehr (15) reported the reverse of these assignments. Somewhat later, Wilson and Polo (16) assigned the frequency 487 cm^{-1} to the totally symmetric bending mode, a new band at 344 cm^{-1} to the doubly degenerate bending vibrations, and reported no evidence of a band at 531 cm^{-1}. A recent Raman investigation by Taylor (17) agreed with Wilson and Polo's findings, although polarization data were not obtained. The Wilson-Polo-Taylor assignment is probably correct and it is possible that the 531 cm^{-1} band reported earlier is due to a PF_2Cl impurity.

The complexation of PF_3 with a metal such as nickel (18,19) or Lewis acids like oxygen (15,20) and BH_3 (5) produces noticeable shifts in the P-F stretching and bending vibrations, the largest shifts occurring with P-F stretching motions. For example in comparing the frequencies of PF_3 (17) and F_3PBH_3 (5), the symmetric and degenerate P-F stretching frequencies at 874 and 832 cm^{-1} were found to shift to 944 and 958 cm^{-1} respectively, in the complex, while the symmetric and degenerate bending frequencies shift from 484 and 351 to 441 and 370 cm^{-1}, respectively. A similar shift is noted for the $Ni(PF_3)_4$ complex (19). In this case, the symmetric and doubly degenerate P-F stretching frequencies are 859 and 898 cm^{-1} while the symmetric and doubly degenerate bending frequencies have been assigned at 503 and 386 cm^{-1} respectively.

A Raman spectroscopic study of F_3PBH_3 and F_3PBD_3 carried out by Taylor and Bissot (5) allowed frequency assignments to be made for the eleven active fundamentals predicted for a C_{3v} structure. Frequencies were assigned on the basis of correlation made with Raman spectra of PF_3 and H_3BCO (21).

An infrared spectroscopic study of $(CH_3)_2NPF_2$, $(CH_3)_2NPF_2BH_3$, and $(CH_3)_2NPF_2BF_3$ has been reported by Sr. Fleming (13). Tentative assignments were made on the basis of correlations between the vibrational frequencies of these compounds and those of PF_3 (17), F_3PBH_3 (5), $(CH_3)_3N$ (22), $(CH_3)_2NH$ (22), $(CH_3)_2NPCl_2$ (23) and $(CH_3)_3NBF_3$ (24). Data obtained from N.M.R. studies and supplemented by the infrared data indicated that the BH_3

group bonded through the phosphorus atom while the BF_3 bonded through the nitrogen atom in these complexes. The infrared evidence was based on the intensities of two characteristic group frequencies, one described as a symmetric C_2-N-P stretch around 1007 cm^{-1} and the other as a N-P-F_2 stretch around 693 cm^{-1}. In the BH_3 complex, the relative intensity of a band assigned to a N-P-F_2 motion was lessened appreciably compared to the free ligand, while in the BF_3 complex the intensity of a band assigned to a C_2-N-P motion was diminished. The P-F symmetric and asymmetric stretching frequencies were in the range of 767 to 827 cm^{-1} and 814 to 880 cm^{-1} respectively. Some doubt remained concerning the correct assignment of the symmetric or asymmetric P-F stretching frequencies and also the assignments for the BH_3 deformation and rocking modes in the borane complex. Further spectroscopic study appears desirable to confirm the results and conclusions and to provide additional data.

An infrared spectroscopic analysis of $[(CH_3)_2N]_2PF$ and $[(CH_3)_2N]_2PFBH_3$ has been reported in the literature (13), and N.M.R. data have indicated the existence of a B-P bond in the latter. Tentative assignments have been made for a large number of vibrations, but a Raman investigation including a polarization study is desirable to observe some of the lower frequencies and to provide additional information about the symmetry of the vibrational bonds.

No detailed spectroscopic data concerning the

$CH_3NHPF_2BH_3$ and $(CH_3NH)_2PFBH_3$ complexes have been reported, except for some unpublished results by Kodama (25). No structural data have been accumulated or reported.

A great deal of information is available in the literature concerning trimethylphosphine. Its physical properties (26,27,28), spectral properties (29,30,31,32) and molecular parameters are known (33). Spectroscopic results include both infrared and Raman data although the earlier workers, Rosenbaum, Rubin and Sandberg (29), and Wagstaffe and Thompson (30) made no attempt to assign frequencies to the fundamental modes of vibration. Later Siebert (31) made some assignments using existing data and performed a few force constant calculations. Finally, Halmann (32) using infrared data made more complete assignments; however, these latter assignments were made without the use of polarization data and no attempt had been made to reproduce the earlier Raman data of Rosenbaum, Rubin and Sandberg (29).

Trimethylphosphine-borane is a very stable crystalline solid and its physical properties are known (34,35). However, its vibrational spectrum has not been published in the literature. Daasch and Smith (36) have studied an analogous complex, $(CH_3)_3PO$, and have reported both its infrared and Raman spectrum and have made assignments to its vibrational modes. These vibrational data should be of use in the present spectral study of $(CH_3)_3PBH_3$.

EXPERIMENTAL PROCEDURES

Preparation of Samples

Most of the samples used for the present spectroscopic study were prepared in this laboratory. The methods of preparation have been described in the literature, in previous dissertations or represent minor modifications of existing methods. Specific details of the preparation and purification of the samples are given in Appendix B.

Throughout the preparative work vacuum line techniques were used extensively since many of the materials involved are moisture or air sensitive and also possess toxic properties.

Trifluorophosphine-Borane, F_3PBH_3 and $F_3PB^{10}H_3$.

Trifluorophosphine-borane, F_3PBH_3, containing the natural isotope mixture of boron and hydrogen, was prepared by direct reaction of B_2H_6 and a five fold excess of PF_3. Due to the fact that a large quantity of this material was needed not only for the spectroscopic work but also for preparing other samples, the method of preparation as reported by Parry and Bissot (4) was modified slightly and scaled up. The pure F_3PBH_3 exhibited a vapor pressure of 23 mm at -111.8°C and melted at -116°C.

Trifluorophosphine-borane enriched in the boron-10 isotope was prepared similarly using somewhat smaller amounts of starting material and retaining a four to five fold excess of PF_3. The method of purification was identical to that of F_3PBH_3.

Methylaminodifluorophosphine-Borane, $CH_3NHPF_2BH_3$.

A procedure for the preparation of $CH_3NHPF_2BH_3$ has been described by Kodama (12) in which CH_3NH_2 was allowed to react with F_3PBH_3 under mild conditions. The conditions of the reaction which Kodama describes were followed with few modifications. However, the amounts of the reactants were doubled so that a larger quantity of product would be obtained. The pure liquid $CH_3NHPF_2BH_3$ obtained was stable at room temperature (melting point -65°C) and showed a vapor pressure of 9 mm at 25°C. This value compared favorably with 8.7 mm at 25°C reported by Kodama.

Bis(methylamino)fluorophosphine-Borane, $(CH_3NH)_2PFBH_3$.

Kodama (12) has reported that the disubstituted complex, $(CH_3NH)_2PFBH_3$, is formed by the reaction of CH_3NH_2 with F_3PBH_3 under relatively severe conditions. The procedure which he described was used for the present study. Pure $(CH_3NH)_2PFBH_3$, a colorless nonvolatile liquid, exhibited an infrared spectrum which was identical to that reported by Kodama (25).

Dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$.

Kodama (12) reported the preparation of $(CH_3)_2NPF_2$ by the reaction of $(CH_3)_2NPF_2BH_3$ with $(CH_3)_3N$ as shown by the equation:

$$(CH_3)_2NPF_2BH_3 + (CH_3)_3N \rightarrow (CH_3)_3NBH_3 + (CH_3)_2NPF_2$$

However, Sr. Fleming (13) has reported the formation of $(CH_3)_2NPF_2$ by the direct reaction of PF_3 and $(CH_3)_2NH$ and this method was used in the present study. The purified compound had a melting point of -87°C and showed a vapor pressure of 94 mm at 0°C which compared favorably with the value of 93.4 mm reported by Kodama and Sr. Fleming. The purity of the purified product was checked further by examining the infrared spectrum and comparing it to that reported by Sr. Fleming.

Dimethylaminodifluorophosphine-Borane, $(CH_3)_2NPF_2BH_3$ and $(CH_3)_2NPF_2B^{11}D_3$.

The synthesis of $(CH_3)_2NPF_2BH_3$ has been reported in the literature (12) by allowing F_3PBH_3 to react with $(CH_3)_2NH$ and also by the direct reaction of $(CH_3)_2NPF_2$ and B_2H_6. Sr. Fleming (13) found the latter method more satisfactory if sufficient amounts of $(CH_3)_2NPF_2$ were available. The latter method of preparation was employed for this work. The purified product (melting point -56.7°C) exhibited a vapor pressure of 17 mm at 25°C which compared favorably with 16.7 mm at 25.5°C reported by Kodama (12). An infrared spectrum of the product was identical to that recorded by Kodama (25) and Sr. Fleming (13).

A sample of $(CH_3)_2NPF_2B^{11}D_3$ enriched in boron-11 and deuterium was prepared by the direct reaction of excess

$(CH_3)_2NPF_2$ with $B_2^{11}D_6$ using the same procedure.

Dimethylaminodifluorophosphine-Boron Trifluoride, $(CH_3)_2NPF_2B^{11}F_3$ and $(CH_3)_2NPF_2B^{10}F_3$.

The method of preparation for $(CH_3)_2NPF_2BF_3$ has been reported by Sr. Fleming (13) and involved the direct reaction of $(CH_3)_2NPF_2$ with BF_3. This method was utilized for the present study with the exception that BF_3 enriched in boron-10 and 11 was used instead of the natural isotope of boron. The purified product exhibited a dissociation vapor pressure of 56 mm at 24°C and its infrared spectrum was identical to that reported by Sr. Fleming.

Bis(dimethylamino)fluorophosphine, $[(CH_3)_2N]_2PF$.

The method used to synthesize the $[(CH_3)_2N]_2PF$ ligand has been discussed by Sr. Fleming (13) and involved the reaction of $(CH_3)_2NPF_2$ with excess $(CH_3)_2NH$ in a sealed tube. The purified liquid $[(CH_3)_2N]_2PF$ exhibited a vapor pressure of 4 mm at 0°C and its infrared spectrum was the same as that reported by Sr. Fleming.

Bis(dimethylamino)fluorophosphine-Borane, $[(CH_3)_2N]_2PFB^{11}H_3$.

Kodama (12) has reported the formation of the $[(CH_3)_2N]_2PFBH_3$ complex by the reaction of $(CH_3)_2NH$ on $(CH_3)_2NPF_2BH_3$. A more straightforward reaction also was reported by him and later by Sr. Fleming (13) in which $[(CH_3)_2N]_2PF$ was allowed to react with B_2H_6 yielding the desired complex. The latter procedure was utilized for the present work, the only modification being that B_2H_6 enriched in the boron-11 isotope was used. The vapor pressure of the pure sample was not measurable at room temperature. Kodama (12) has reported the freezing point of the disubstituted complex as -15.2°C. The infrared spectrum of the sample was identical to that reported by Sr. Fleming (13).

Trimethylphosphine, $(CH_3)_3P$.

A sample of $(CH_3)_3P$ was obtained from the Evans Chemical Laboratory at Ohio State University through the generosity of Professor Sheldon Shore and Mr. Gerald Mc Achran. The $(CH_3)_3P$ had been prepared by the procedure of Mann and Wells (27) as described by the following reactions:

$$CH_3I + Mg \xrightarrow{\text{ether}} CH_3MgI$$

$$3\ CH_3MgI + PCl_3 \xrightarrow{\text{ether}} (CH_3)_3P + 3\ MgClI$$

$$(CH_3)_3P + AgI \xrightarrow[\text{KI sol'n}]{\text{sat.}} \underline{(CH_3)_3PAgI}$$

$$(CH_3)_3PAgI \xrightarrow{\Delta} (CH_3)_3P + AgI$$

The sample was purified in this laboratory by distilling it from a -25°C trap into a -196°C trap. The pure $(CH_3)_3P$ exhibited a vapor pressure of 15.9 cm at 0°C. Rosenbaum and Sandberg (28) also report a value of 15.9 cm for the vapor pressure of $(CH_3)_3P$ at 0°C.

Trimethylphosphine-Borane, $(CH_3)_3PBH_3$, $(CH_3)_3PB^{10}H_3$ and $(CH_3)_3PB^{11}D_3$.

The preparation of $(CH_3)_3PBH_3$ has been reported in the literature by Burg and Wagner (34) and also by Hewitt and Holliday (35). The method involves the direct reaction of $(CH_3)_3P$ and B_2H_6 with the formation of a volatile, white, crystalline solid. Burg and Wagner (34) have characterized the solid and have reported the following information: melting point is 103°—103.5°C, vapor pressure at 45.7°C is 2.2 mm, and $\log_{10} P_{mm} = 9.531\text{-}2933/T$.

A sample of $(CH_3)_3PBH_3$ containing the natural isotopes of boron and hydrogen was generously donated by Professor Sheldon Shore. Before use in this laboratory, the sample was freshly sublimed and stored in an evacuated tube.

A sample of $(CH_3)_3PB^{10}H_3$ containing the boron-10 enriched isotope was prepared by condensing about 1 ml of $(CH_3)_3P$ into a reaction tube with excess $B_2^{10}H_6$. Upon warming the tube to room temperature a white crystalline solid, $(CH_3)_3PB^{10}H_3$, formed. The reaction tube was placed in a 0°C bath and the volatile components were distilled away. The product was purified by sublimation.

A sample of $(CH_3)_3PB^{11}D_3$, enriched in boron-11 and deuterium, was prepared and purified in the same fashion.

Miscellaneous Procedures

Some discussion of general experimental procedures appears appropriate. As was mentioned earlier, vacuum line techniques were employed for the preparation and handling of the materials under investigation. It was found that some high vacuum greases were more compatible with these materials than were others. Kel-F Grease was found to be particularly suitable in the presence of BF_3 and the $(CH_3)_2$-NPF_2BF_3 complex. Dow Corning High Vacuum Silicone Grease and Apiezon N Grease were employed to a large extent in the handling of the borane complexes. $(CH_3)_2NPF_2$ and $[(CH_3)_2N]_2PF$ seemed to be reactive to the Dow Corning Silicone Grease so Apiezon N Grease was employed while handling these samples.

The vacuum line was cleaned periodically with alcoholic-KOH or $K_2Cr_2O_7$- H_2SO_4 depending on whether Silicone or Apiezon N Grease was used. In every case, after the line was clean the glass was treated with dilute HCl or HF. This was done because the samples under investigation are sensitive to the presence of bases, such as traces of the alcoholic-KOH cleaning solution.

It was also noted that mercury was readily absorbed by the samples, rendering them somewhat opaque. Care was taken to limit the exposure of the samples to mercury only for vapor pressure measurements.

In every case, the samples were stored in evacuated tubes which were pre-treated with acid or made of new pyrex. Also all samples were stored as solids at dry ice or liquid nitrogen temperatures to retard decomposition until they were ready for use.

Special precautions were taken to minimize hydrogen contamination of the deuterated samples during the preparation and handling of the samples. The vacuum system and all attachments were cleaned prior to use and then allowed to equilibrate with heavy water so as to reduce hydrogen exchange with water absorbed in the glass surface.

Spectroscopic Methods and Equipment

The infrared spectra of the compounds studied were obtained on a Perkin-Elmer Model 21 Spectrophotometer equipped with CaF_2, NaCl or KBr prisms. The spectra were calibrated in the appropriate regions from 4000-400 cm^{-1} using indene, H_2O vapor, NH_3, HCl, and HBr. Gaseous samples were examined in a ten cm cell having KBr windows and liquids were studied as a liquid film between KBr plates. The infrared spectra of solid samples were observed in transmission through a thin film by employing a modified version of the cold cell described by Wagner and Hornig (37). This cold cell was fitted with a bulb in which the sample could be kept at liquid nitrogen temperature until use. To prepare the film, the compound was allowed to evaporate at a low pressure and the vapor was sprayed directly on a KBr window kept in thermal contact with a liquid nitrogen reservoir. Nonvolatile liquid samples were examined in their solid states by placing a drop between two KBr plates and then inserting the assembly in the low temperature cell. The low temperature infrared cell is shown schematically in Figure 1.

In essence, the technique of Raman spectroscopy involves irradiating the sample with monochromatic light and observing the spectrum of scattered light. Since the Raman scattering phenomenon is intrinsically inefficient, an intense light source and high aperture spectrographic equipment are desirable. Special precautions must be taken to eliminate light scattered from sources other than the sample and to avoid fluorescence and Tyndall scattering from within the sample.

For the Raman spectroscopic study, samples were distilled into pyrex Raman tubes having an I.D. of 2 to 4 mm and an O.D. of 6 mm and then sealed off under vacuum. These tubes were fitted with optically clear flat ends so that with liquids and some solids, the Raman scattered light could be observed at right angles to the incident radiation produced by the Toronto Arc. These Raman tubes were used for a spectroscopic study of both liquid and solid samples.

The light source used for obtaining the spectra of liquids was a helical, mercury arc having large, water cooled mercury pools as electrodes as described by the workers at the University of Toronto (38,39). Solutions of ethyl violet in alcohol and KNO_2 in water were used to filter the mercury radiation so that mercury lines other than the 4358 Å were greatly reduced in intensity.

In obtaining a spectrum, the sample tube was placed in a specially constructed dewar flask in the center of the arc. The temperature of the sample was controlled by passing a stream of cold air in at the bottom of the dewar and up along the sample. The temperature of the air stream was monitored by a thermocouple and recording potentiometer and could be adjusted if desired, by a small heater arrangement to within ± 5°C of the desired temperature. The experimental setup for the Toronto arc, filters, and temperature control is given in detail elsewhere (40); however, the main features are shown in Figure 2. Polarization characteristics of liquid samples were studied by taking two equal exposures, during which times the incident radiation was polarized respectively parallel and perpendicular to the axis of observation by using appropriate polaroid filters.

The experimental arrangement used to obtain Raman spectra of solid samples is shown in Figure 3. Mercury light from two General Electric AH-4 lamps was passed through monochromator systems which contained condensing lenses, absorption filters and two interference filters which were adjusted to allow the maximum transmission of 4358 Å light. With this arrangement about 33% to 50% of the 4358 Å light was transmitted while reducing the intensity of the other mercury lines and the continuous background to

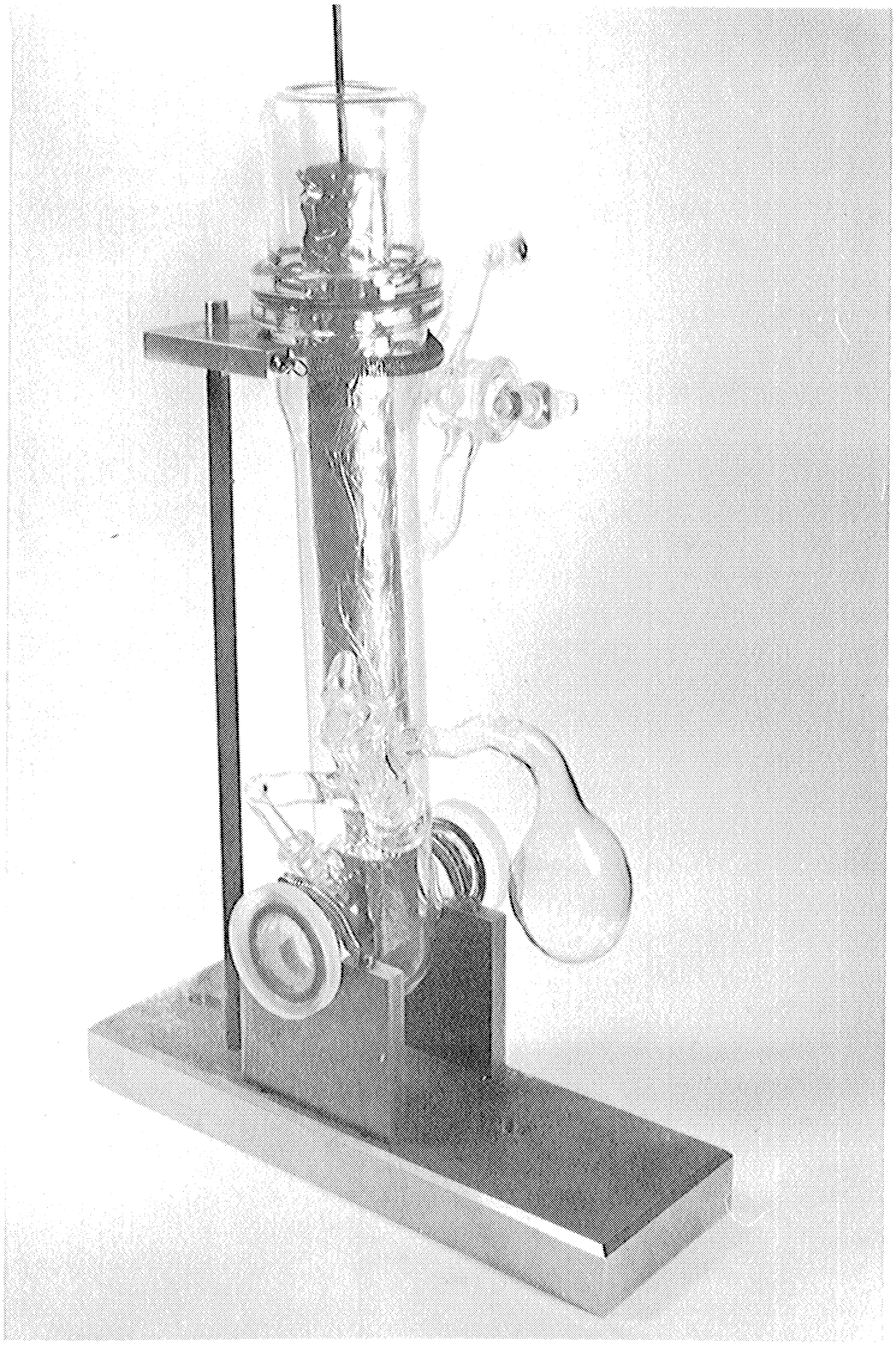


FIGURE 1 - THE LOW TEMPERATURE INFRARED CELL

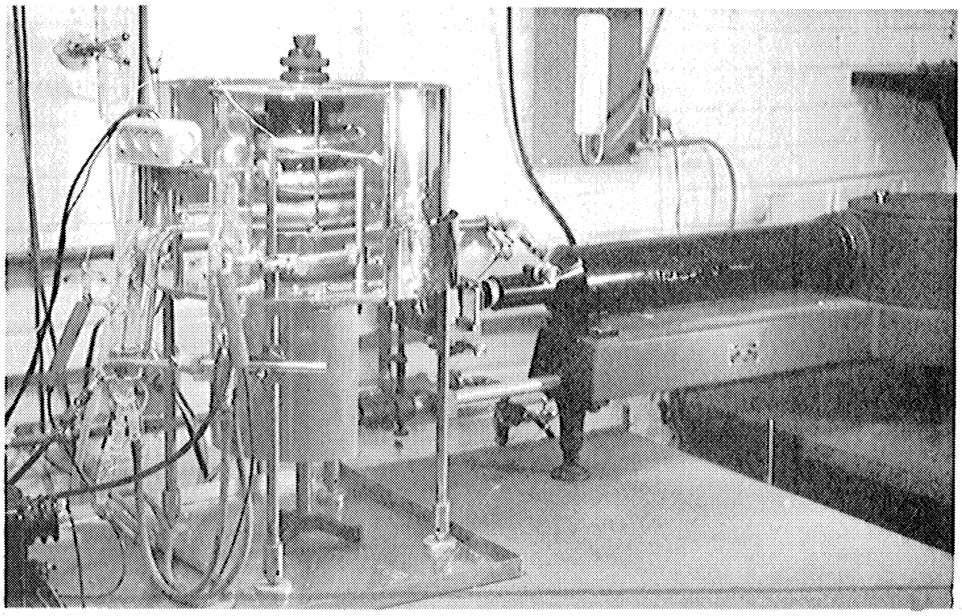


FIGURE 2 - THE EXPERIMENTAL ARRANGEMENT

FOR OBTAINING RAMAN SPECTRA

OF LIQUIDS

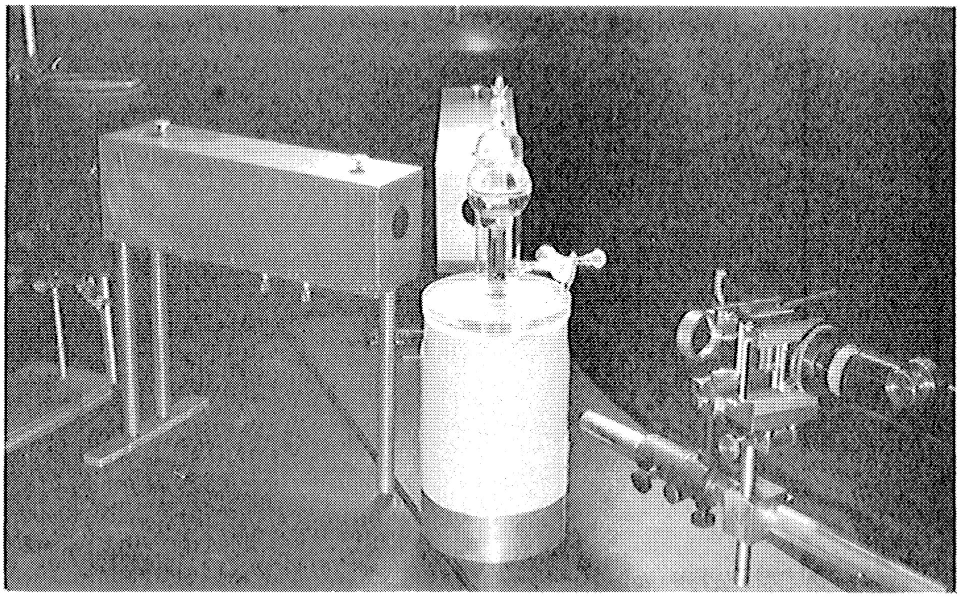


FIGURE 3 - THE EXPERIMENTAL ARRANGEMENT

FOR OBTAINING RAMAN SPECTRA OF SOLIDS

AT LOW TEMPERATURES

negligible values. In a few cases the Raman spectra of solid samples were taken with the Toronto arc serving as a light source and these spectra exhibited a higher general background, although below 400 cm^{-1} the background was lower. Since the solid samples were polycrystalline masses, it was not possible to determine the polarization characteristics of the observed frequencies.

When examining the spectra of solid samples a great deal of the incident mercury radiation is reflected from the crystal faces and therefore is scattered towards the spectrograph. This scattered light usually obscures the lower frequency Raman lines. This effect was reduced by allowing the scattered radiation to be reflected four times from two nearly parallel interference filters. The characteristics and the arrangement of these filters has been described by Dahl (41). By correctly adjusting the angles of the two filters with respect to each other and the incident beam, one is able to properly "tune" the interference filters to allow the passage of a maximum of scattered Raman radiation into the spectrograph and a minimum of scattered mercury light. With this arrangement it was estimated that about 65% of the Raman light above 200 cm^{-1} was transmitted while only about 0.4% of the mercury exciting 4358 Å light was transmitted (41). In some instances a Corning yellow filter, No. 3387, was placed in front of the slit to reduce further the mercury 4358 Å light.

The previously mentioned multireflection filter system also has been used with success in connection with liquids. The use of this arrangement allowed a Raman spectrum to be taken of slightly turbid liquid samples. In the present work, this proved quite helpful because a slight sediment appeared in many of the samples during exposure.

The low temperature cell used to obtain the Raman spectra of solid samples has also been described by Dahl (41). In this cell, the sample tube was placed in an evacuated chamber and brought into thermal contact with a low temperature reservoir by means of a copper rod. By utilizing this cell samples could be maintained at temperatures as low as -180°C during an exposure.

The spectrograph used for this investigation was a Gaertner two prism instrument having a dispersion of 180 cm^{-1} per millimeter in the blue region and a camera aperture of f:3.5.

The Raman spectra were recorded photographically on Eastman Kodak IIa-O plates with antihalation backing. These plates were sensitized by heating them in a vacuum desiccator at 55°C for 12 to 14 hours prior to use. The plates were developed for four minutes in Eastman Kodak D-19 developer at 20°C and were fixed with F-6 solution for ten minutes. Exposure times ranged from 1/4 to 10 hours for liquid samples and 1 to 72 hours for solid samples.

The position of the Raman lines were measured directly on the plates using a Mann comparator and also on tracings of the plates. The latter were made with a Leeds and Northrup, Knorr-Albers recording microphotometer and also by a Joyce-Loebl microphotometer. The respective tracings represented approximately 25 and 20 fold enlargements of the plates.

The Raman frequencies were calculated from the plate measurements by a computer program based on a quadratic interpolation of the dispersion curve for the spectrometer. Mercury lines at 4339.24 and 4916.04 Å were used as references for the Raman spectra of liquid samples. For spectra of solid samples argon reference lines were supplied by placing an argon spectrum above and below the Raman spectrum.

EXPERIMENTAL RESULTS AND INTERPRETATION

General Discussion of Spectra

Since the present study deals with an infrared and Raman investigation of samples in the gaseous, liquid and solid states, a brief discussion of the differences in spectra with physical state is appropriate at this point.

The change of state of a sample often results in a significant modification in the vibrational frequencies of the individual molecules or the intensities of the vibrational bands. The extent to which these modifications occur depends on intermolecular separation, the dielectric constant of the surrounding medium, the degree of molecular interaction and other less important factors. The vibrational spectra of gaseous samples frequently show resolved rotational structure. This rotational structure is normally "washed out" in the spectra of liquids but the vibrational bands tend to be somewhat broadened, perhaps due to increased molecular interactions. However, the vibrational spectra of solids, especially at low temperatures, tend to be much more complex. This increased complexity can be attributed to one or more of the following factors: splittings of degenerate bands as a result of decreased molecular symmetry, multiplets arising from the coupling of the vibrations of one molecule with others in the same unit cell, combinations of the molecular fundamentals with the lattice modes or resolution of otherwise accidentally degenerate fundamentals because of the greater sharpness of bands. The last named cause may be important in the present case due to the presence of different isotopic species which otherwise would contribute to the intensity of a single unresolved band. Other changes in intensity, both in fundamentals as well as the combinations or overtones, frequently occur between liquid or gas and the solid state and may contribute to the problem of interpretation.

Differences between the infrared and Raman spectrum of a compound are frequently observed. Molecular vibrations which absorb infrared radiation are often active in the Raman effect. However, the intensities of the vibrational bands may be markedly different in each case. This phenomenon is brought about by the fact that a particular vibration may not involve the dipole moment to the same extent as it does the polarizibility, thereby making the transition moment different in each case. Minor differences in the vibrational frequencies are also observed. Such variations may occur as a result of a difference in the physical state of the sample, experimental error in the measurements, crystal symmetry effects and intermolecular coupling, differences in resolving power of the spectrographic equipment, or the noncoincidence of the band maximum with the actual vibrational frequency.

Polarization Results

An important and useful feature in the analysis of Raman spectra is the study of the polarization characteristics of the scattered light. Theory predicts that if the incident light is polarized, with its electric vector parallel to the direction of observation, then the intensities of the Raman bands are less than if the incident light is perpendicularly polarized. The ratio of the parallel to perpendicular intensities can be shown theoretically to depend on the nature of the vibration. For vibrations which preserve the symmetry of the molecule the depolarization ratio may have any value between zero to 6/7 while for asymmetric vibrations the ratio is 6/7. This provides an important way of distinguishing between the totally symmetric and asymmetric vibrations. Unfortunately it is difficult experimentally to make accurate depolarization ratio measurements because of numerous instrumental and other factors which must be taken into account. If photographic plates are used, one has the additional handicap of a detector with a non linear response. In the present work, this factor made it difficult to identify unequivocally polarized lines whose depolarization ratio was close to 6/7, whose intensity was quite low or which were superimposed on a high intensity background caused by fluorescence or Tyndall scattering.

Spectroscopic Results and Assignments

Throughout the following section, vibrational frequencies and their assignments for a number of compounds will be discussed in detail. For clarity, it is desirable to define several terms which will be used in the following discussion. The terms symmetric and asymmetric most generally are employed in describing whether or not a particular fundamental vibration preserves or destroys some or all symmetry elements of the molecule. This strict definition will be used whenever possible; however, for molecules which have two or more chemically equivalent groups or which possess no molecular symmetry, further clarification is necessary. For compounds such as $(CH_3)_3P$ and $(CH_3)_2NPF_2$ which contain two or more chemically equivalent methyl groups, chemical knowledge tells us that the methyl group vibrations are influenced to a larger degree by local interactions than by the coupling of the motions of one methyl group with those of another. For this reason it appears more meaningful to define the methyl vibrations as being symmetric or asymmetric motions within the methyl group, i.e. with respect to local symmetry, and then compare the motions of one methyl group with another by using the terms "in phase" or "out-of-phase". This treatment is particularly useful in discussing the motions of molecules which have no symmetry, such as $CH_3NHPF_2BH_3$, for in this case the use of symmetrical or asymmetrical vibrations can refer only to the local symmetry of the group vibration. In addition, the numerous tabulated frequencies, band intensities and vibrational assignments necessitate an abbreviated notation in the tables. Therefore the following symbolism will be employed in the tables when referring to band intensities, structure and polarization characteristics: v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad, p = polarized and dp = depolarized. Also, the symmetry and the type of vibration will be represented as: s = symmetric, a = asymmetric, ν = stretch, δ = deformation, ρ = rock, ω = wag and τ = torsion.

Trifluorophosphine, PF_3.

In order to carry out a vibrational analysis of the compounds of principal interest in this work, it was desirable to record the vibrational spectrum of PF_3 and confirm previous assignments. Although PF_3 is a stable compound, the information concerning its vibrational spectrum is somewhat limited and the assignments of the fundamental modes of vibration have been subject to some uncertainty.

It is known that the PF_3 molecule has a regular triangular pyramidal configuration belonging to the C_{3v} point group (42,43,44). This model has four fundamental modes of vibration, all active in the infrared and Raman effect. Two of these fundamentals belong to the A_1 class and the other two belong to the doubly generate E class. The four vibrational modes may be described as: ν_1 and ν_2, the symmetric P-F stretching and deformation modes, and ν_3 and ν_4, the doubly degenerate asymmetric P-F stretching and bending vibrations respectively.

Yost and Anderson (14), the first to examine PF_3 spectroscopically, reported the vibrational frequencies given in Table 1. They assigned ν_1 and ν_3 to 890 cm^{-1} and 840 cm^{-1} and ν_2 and ν_4 to 531 cm^{-1} and 486 cm^{-1} respectively. Later, Gutowsky and Liehr (15) reported essentially the same results but reversed the assignments of ν_2 and ν_4 on the basis of band contour considerations. Wilson and Polo (16) observing the gaseous infrared spectrum found similar results for ν_1, ν_2, ν_3 but assigned the doubly degenerate bending vibration, ν_4, to a new band at 344 cm^{-1} and found no evidence of a band at 531 cm^{-1}. A more recent Raman investigation by Taylor (17) agreed with the findings of Wilson and Polo. Although polarization data were not obtained, the contours of bands in the spectrum of the gas supported their assignment. The previously reported band at 531 cm^{-1} possibly is due to an impurity.

Due to the conflicting earlier work, additional spectroscopic work was carried out to confirm the correct assignments of ν_2 and ν_4. In particular, the polarization properties of the bands were determined for liquid PF_3. The results clearly showed that the bands at 874 and 484 cm^{-1}

TABLE 1

THE OBSERVED RAMAN AND INFRARED FREQUENCIES OF PF_3

RAMAN					INFRARED			Assignment
(14) Gas	(14) Liquid	(17) Gas (20°C)	(17) Liquid (-90°C)[a]	Solid (-180°C)	(15) Gas	(16) Gas	Gas (4 mm)	
							920 w,sh	R branch
893 m	890 s	891 vs	874 s,p	858 vw,sh	891	892	891 s,sh	ν_1
		867 s,sh					862 vs	
851 m	840 s		832 vs,dp	809 w	844	860		ν_3
		846 s,sh					851 s,sh	
						833	833 m,sh	$\nu_2 + \nu_4$
						693		
	351 w				532			
							499 vw	R branch
487 ms	486 w	486 m	484 m,p	479 vw	486	487	485 w	ν_2
			351 w,dp			344		ν_4

[a] s = strong
m = medium
w = weak
v = very
sh = shoulder
br = broad
p = polarized
dp = depolarized

were polarized while the bands at 832 and 351 cm^{-1} were depolarized. The assignments of ν_1 to 874, ν_2 to 484, ν_3 to 832 and ν_4 to 351 cm^{-1} are in agreement with the assignments and frequencies reported by Wilson and Polo.

In addition, the Raman spectrum of solid PF_3 at -180°C and also the infrared spectrum of gaseous PF_3 at 20°C and 4 mm pressure were studied. As a consequence of this study, several features of the infrared and Raman spectra were observed that are worth mentioning. First of all, the band at 513 cm^{-1} as reported by Yost and Anderson and also by Gutowsky and Liehr was not observed which substantiates Wilson and Polo's findings. Secondly, in the infrared spectrum of gaseous PF_3, the bands at 902 and 499 cm^{-1} are proposed to be the R branches of ν_1 and ν_2 respectively. The very strong band at 862 cm^{-1} and the strong shoulder at 851 cm^{-1} remain to be assigned. The question arises: which of these two frequencies should be assigned to ν_3? It is evident that neither of these frequencies can be attributed to an overtone or combination band, nor is Fermi resonance likely in this case. Two possible explanations can be given. Either the higher band at 862 cm^{-1} can be attributed to the P branch of ν_1 and the band at 851 cm^{-1} assigned to ν_3, or these two bands are unresolved P and R branches of ν_3, the Q branch being absent. A study of band shapes and intensities for both the gaseous infrared and Raman spectra (17) indicates that perhaps the latter case is more likely correct. A simple doublet band outline for a degenerate Raman band has been observed in at least two other cases (39,45).

Trifluorophosphine-Borane, F_3PBH_3 and $F_3PB^{10}H_3$.

Electron diffraction studies of trifluorophosphine (43,44) and phosphoryl fluoride (46) have shown that these molecules are of C_{3v} symmetry having the fluorine atoms arranged at the corners of an equilateral triangle. In view of the known structure of $OCBH_3$ (47), the trifluorophosphine-borane complex would be expected to have an ethane-like configuration with C_{3v} symmetry, the threefold axis coinciding with the phosphorus-boron bond. For this configuration, there would be twelve vibrational frequencies with the symmetry distribution $5A_1 + A_2 + 6E$. Four of these are localized in the borane group, four in the trifluorophosphine group and four motions arise from the formation of the phosphorus-boron bond. A description of the fundamental vibrations and the symmetry species to which each belongs is given in Table 2. All of the vibrational modes are active both in the infrared and Raman effect except for the inactive (A_2) torsional mode.

The infrared and Raman spectra of solid F_3PBH_3 and $F_3PB^{10}H_3$ at -180°C are shown in Figures 4, 5 and 6. The observed vibrational frequencies and their assignments for the Raman and infrared spectra of solid F_3PBH_3 and $F_3PB^{10}H_3$ are given in Table 3. The Raman data reported by Taylor

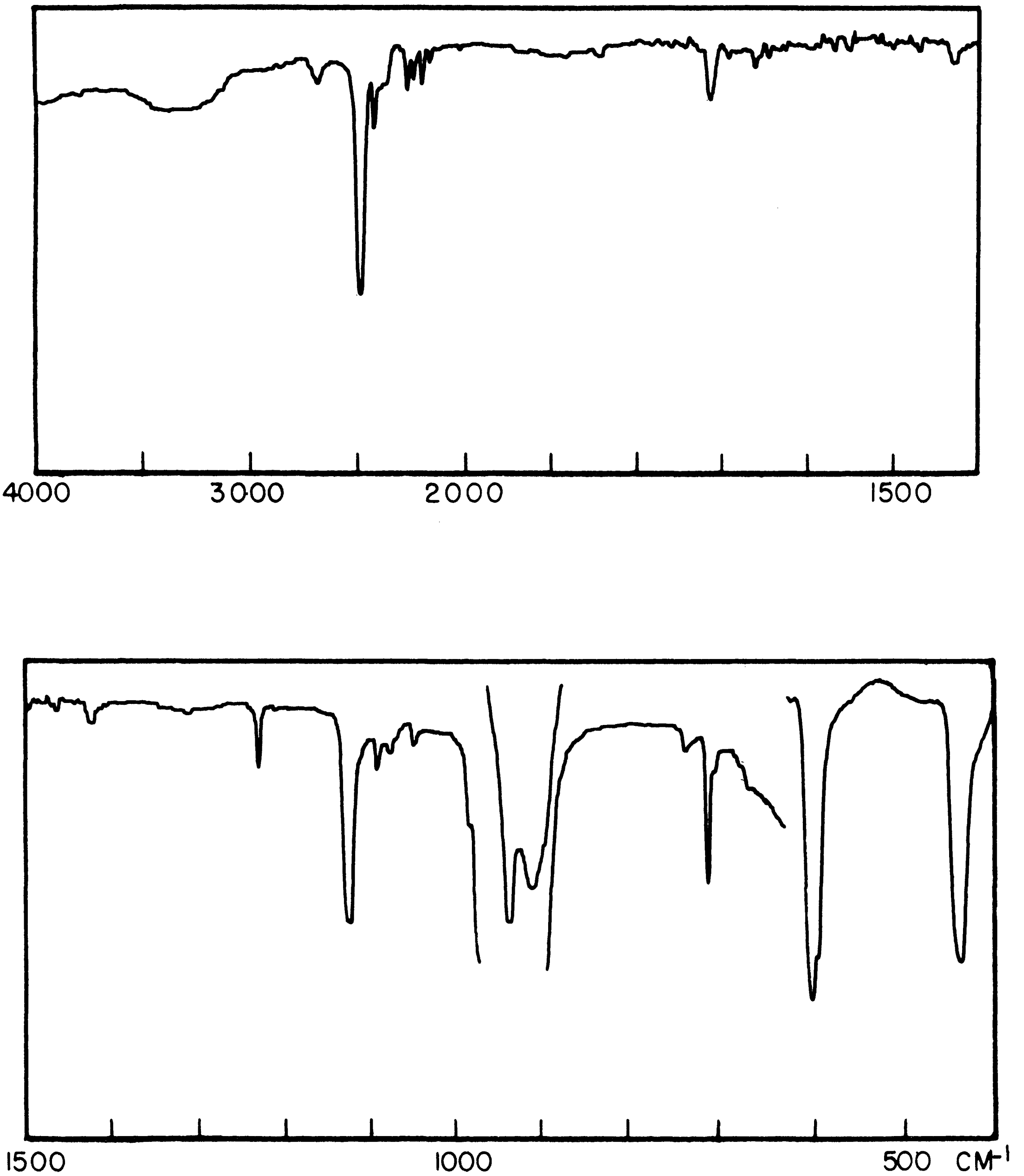


FIGURE 4 - THE INFRARED SPECTRUM OF SOLID $F_3PB^{10}H_3$ (-180°C)

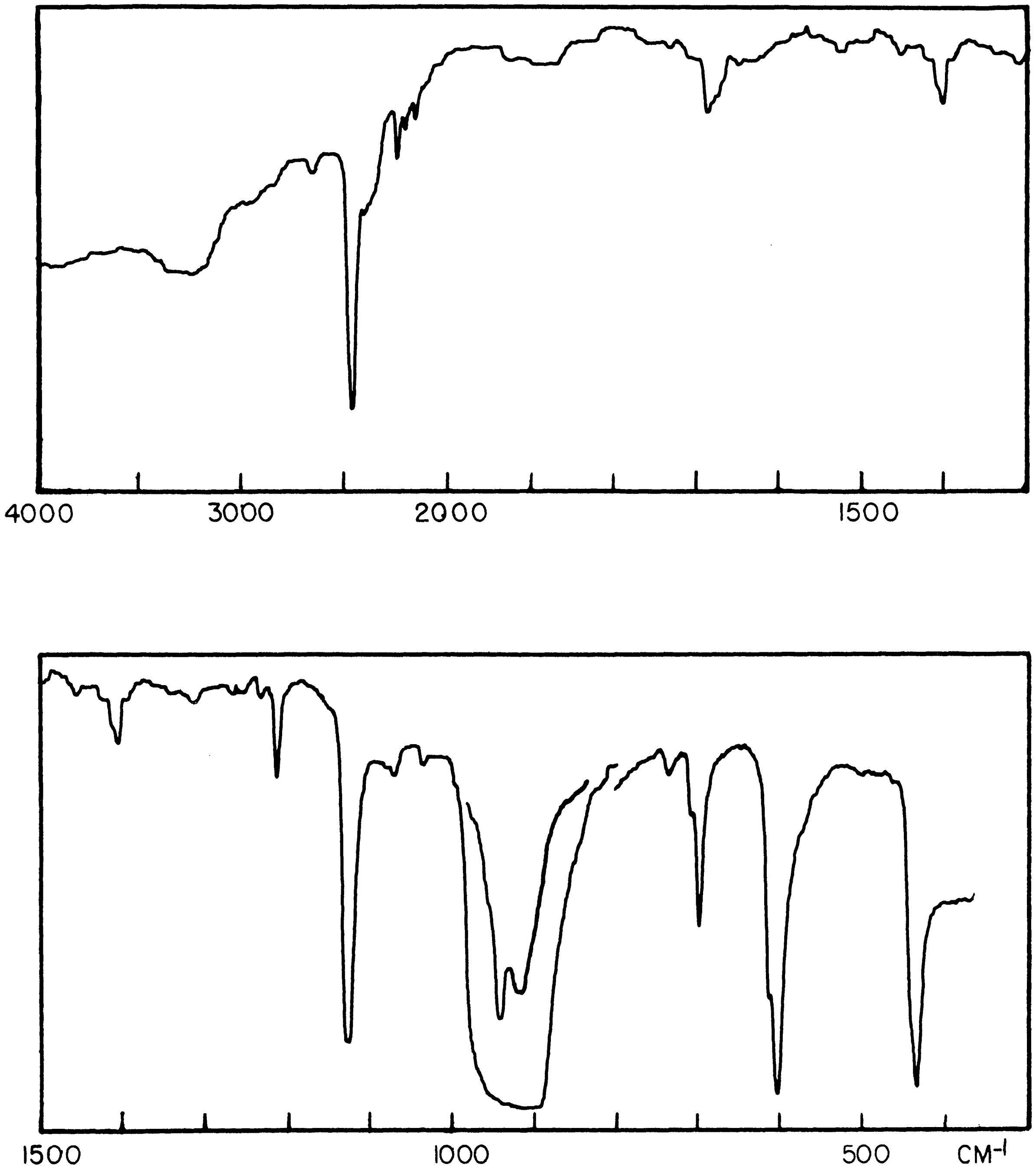


FIGURE 5 - THE INFRARED SPECTRUM OF SOLID F_3PBH_3 (-180°C)

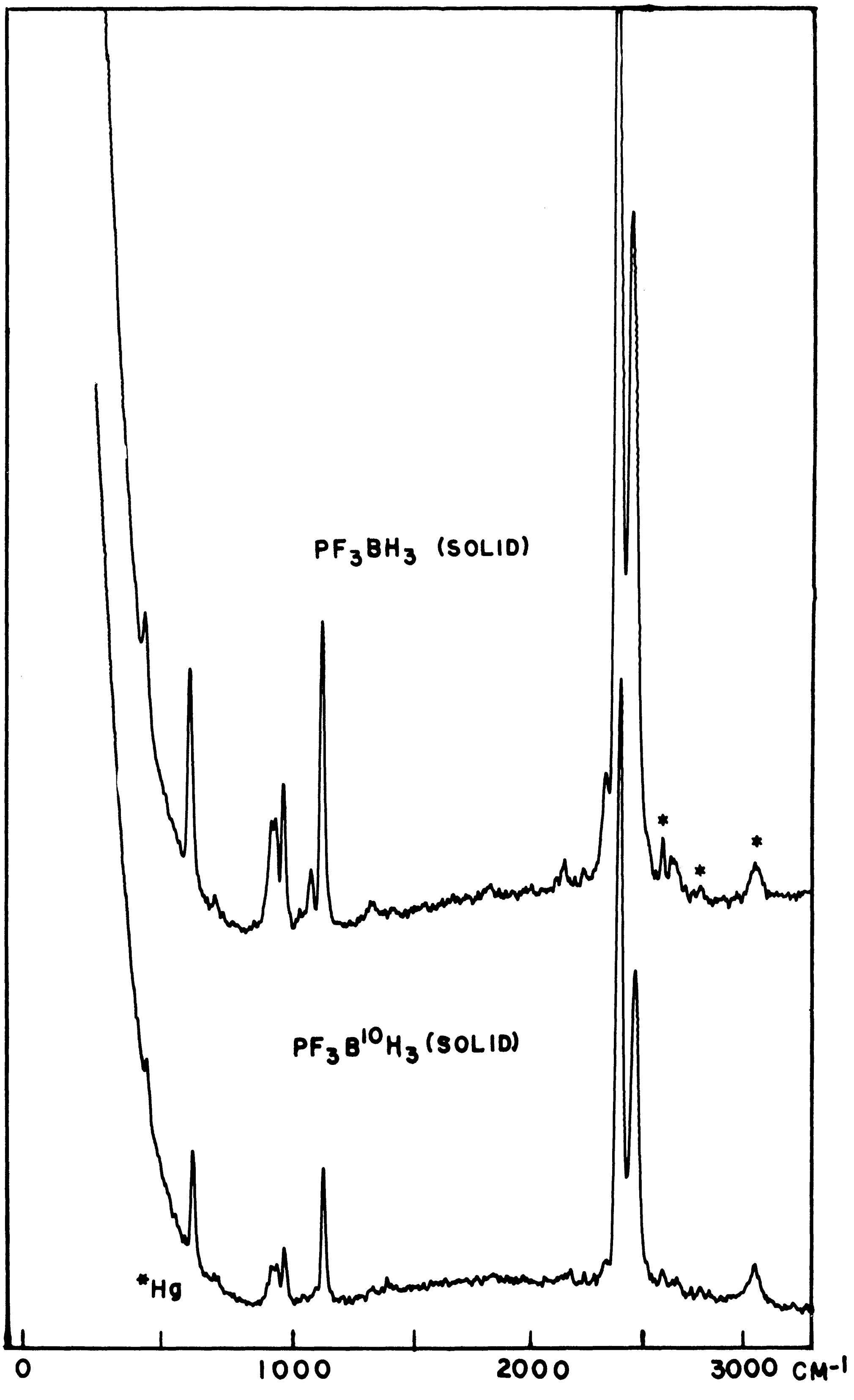


FIGURE 6 - THE RAMAN SPECTRA OF SOLID F_3PBH_3 AND $F_3PB^{10}H_3$ (-180°C)

TABLE 2

THE FUNDAMENTAL VIBRATIONS OF F_3PBH_3, C_{3v} SYMMETRY

Symmetry	Number	Description
A_1	1	B-H stretch
	2	BH_3 deformation
	3	P-F stretch
	4	P-B stretch
	5	PF_3 deformation
A_2	6	P-B torsion
E	7	B-H stretch
	8	BH_3 deformation
	9	P-F stretch
	10	BH_3 rock
	11	PF_3 deformation
	12	PF_3 rock

TABLE 3

THE OBSERVED INFRARED AND RAMAN FREQUENCIES OF F_3PBH_3 AND $F_3PB^{10}H_3$

		F_3PBH_3				$F_3PB^{10}H_3$				
Raman (5) liquid (-80°C)		Raman solid (-180°C)		Infrared solid (-180°C)		Raman solid (-180°C)		Infrared solid (-180°C)		Assignment
2655±5	vvw	2655	vw	2643±2	w			2654	vw	$\nu_7 + \nu_{12}$
2530	vvw									diborane?
				(2459	vs,sh)			(2469	m,sh)	
2455	vs,dp	2460	s			2471	ms			ν_7
				2450	vs			2456	vs	
2385	vs,p	2392	vs	2391	ms,sh	2397	s	2394	m	ν_1
2328±4	vvw	2336	w,sh	2340	w,sh,br	2337	vw,sh	2341	w,sh	$2\nu_3 + \nu_5$
2247±2	vw	2239	vvw	2231	w	2243	vvw	2239	w	$2\nu_8$
								2212	w	$\nu_1 - \nu_{12}$?
				2197	vw					$\nu_1 - \nu_{12}$?
								2173	w	$2\nu_4 + \nu_3$
2140±4	vw	2146	vvw	2146±5	vw			2137	vw	$2\nu_2$
2112	vvw	2113	vvw							diborane?
		1818	vvw					1831	vw,br?	$\nu_8 + \nu_{10}$
				1703	vw,br,sh			1704	m	$\nu_2 + \nu_4$ (B-10)
				1681	w			1676	vw	$\nu_2 + \nu_4$ (B-11)
				1668	w,sh?					$\nu_9 + \nu_{10}$

TABLE 3 - CONT'D.

Raman (5) liquid (-80°C)		F_3PBH_3 Raman solid (-180°C)		F_3PBH_3 Infrared solid (-180°C)		$F_3PB^{10}H_3$ Raman solid (-180°C)		$F_3PB^{10}H_3$ Infrared solid (-180°C)		Assignment
				1648	vvw			1650	vw	$\nu_3 + \nu_{10}$
								1636	vvw	$\nu_3 + \nu_{10}$?
								1560	vvw	$\nu_4 + \nu_9$?
								1542	vvw	$\nu_3 + \nu_4$?
				1523	vvw					$\nu_2 + \nu_5$
				1447	vvw			1460	vvw	$\nu_2 + \nu_{11}$
				1417	vvw,sh			1418	w	$\nu_5 + \nu_9$?
				1403	vw,sh?					$2\nu_{10}$ or $\nu_5 + \nu_9$
				1396	w	1391	vvw?			$2\nu_{10}$ or $\nu_5 + \nu_9$
		1328	vvw	1335	vvw?					$\nu_9 + \nu_{11}$
		1314	vw	1308	vw					$\nu_3 + \nu_{11}$, $\nu_8 + \nu_{12}$ or $\nu_4 + \nu_{10}$
				1227	vw			1227	m	$2\nu_4$ (B-10)
				1208	w			1208	vvw	$2\nu_4$ (B-11)
								1127	s,sh?	$\nu_3 + \nu_{12}$
1117	s,dp	1124	ms	1121	s	1127	m	1123	s	ν_8
						1092	vvw	1093	w	ν_2 (B-10)

TABLE 3- CONT'D.

Raman (5) liquid (-80°C)		F_3PBH_3 Raman solid (-180°C)		F_3PBH_3 Infrared solid (-180°C)		$F_3PB^{10}H_3$ Raman solid (-180°C)		$F_3PB^{10}H_3$ Infrared solid (-180°C)		Assignment
1077	w,p	1079	w	1079	w,sh			1078	vw	ν_2 (B-11)
				1068	w			1051	vw	$\nu_{10} + \nu_{11}$
1040±3	w,p	1030	vw,sh	1032	vvw					$\nu_4 + \nu_5$
957±3	m,dp	969	m	957±7	s,sh?	972	w	988±5	m,sh?	ν_9
944	m,p?	939	m	942	vs	944	w	943	vs	ν_3 or ν_9?
920	w,p	921	m	919	s	925	w	916	s	ν_3?
886±5	vw,p			892±5	w,sh?			902	s,sh?	$2\nu_5$ or $\nu_{10} + \nu_{12}$
				830±5	vw,vbr,sh					$\nu_5 + \nu_{11}$
799	vw									
				736	vw			736	w	$2\nu_{11}$
				709	w,sh			709	s	ν_{10} (B-10)
697±2	vw	701	vw	700	ms			702	w,sh	ν_{10} (B-11)
								662	vvw	Impurity
				616	s,sh	619	m	613	s	ν_4 (B-10)
607	s,p	608	m	606	s			606	s,sh	ν_4 (B-11)
441	m,p	438	w	436	s	449	vw	439	s	ν_5
370	vw									ν_{11}
197	m,dp									ν_{12}

and Bissot (5) for liquid F_3PBH_3 are also tabulated for purposes of comparison. The agreement between the frequencies reported here and those found previously by Taylor and Bissot (5) is quite satisfactory and most of the small differences which are observed can be attributed to experimental error or to a change of state of the sample.

The symmetric and asymmetric B-H stretching vibrations appear as a very characteristic and intense doublet in the region between 2350 and 2500 cm^{-1}. The asymmetric B-H stretching vibration, the higher band in the doublet, shows a single strong peak in the Raman spectrum, but in the solid infrared spectrum using CaF_2 optics a strong shoulder is observed on the high-frequency side of the fundamental. The shoulder and the fundamental are observed at 2459 cm^{-1} and 2450 cm^{-1} respectively for F_3PBH_3, and 2469 cm^{-1} and 2456 cm^{-1} respectively for $F_3PB^{10}H_3$. Since the shoulder cannot be identified with an isotope effect or a combination band, it probably arises from crystal splitting effects. The symmetric band occurring at 2392 cm^{-1} has a high intensity in the Raman effect but appears only as a medium intensity shoulder in the infrared.

The asymmetric and symmetric deformation modes of the borane group are found at 1124 cm^{-1} and 1079 cm^{-1} respectively for the compound containing the natural boron isotope. The asymmetric deformation mode appears as a strong band in both the infrared and Raman spectra, but the symmetric vibration is much weaker. A weak band at 1092 cm^{-1} is also observed in the spectrum of the B-10 compound and is assigned to the symmetric B-10 borane deformation mode.

The frequencies associated with the PF_3 group are similar to those of free PF_3 (16,17) and F_3PO (15,20), and a comparison of these P-F vibrations is shown in Table 4. In the region from 1000 cm^{-1} to 900 cm^{-1} three distinct bands are observed in the Raman spectrum: a medium intensity band at 969 cm^{-1} and two bands of lesser intensity at 939 cm^{-1} and 921 cm^{-1}. In the infrared spectra, however, two very strong bands are observed at 942 cm^{-1} and 919 cm^{-1}, each having a strong shoulder around 957 cm^{-1} and 892 cm^{-1} respectively. The shoulder at 892 cm^{-1}, appearing only in the infrared spectrum, is probably due to the overtone $2\nu_5$ or the combination $\nu_{10} + \nu_{12}$. The two higher frequencies, which are observed at 969 cm^{-1} and 939 cm^{-1} in the solid Raman spectrum and 957 cm^{-1} and 942 cm^{-1} in the solid infrared spectrum, also appear in the Raman spectrum of the liquid and are assigned to the asymmetric and symmetric P-F stretching motions respectively (5). The lower band at 921 cm^{-1} is also observed in the liquid spectrum and is attributed to a difference band, $\nu_8 - \nu_{12}$. However, in view of the fact that this band is very intense in the solid infrared spectra taken at -180°C, this assignment does not appear tenable. It must therefore be either a fundamental or a combination band. It is possible that the bands at

TABLE 4

A COMPARISON OF THE FUNDAMENTAL FREQUENCIES OF PF_3, $Ni(PF_3)_4$, OPF_3, $OCBH_3$ and F_3PBH_3 (CM^{-1})

PF_3(16)	$Ni(PF_3)_4$(19)	F_3PO(15)	$OCBH_3$(21)	F_3PBH_3(5)	Assignment
			2434	2455	asym. B-H stretch
			2380	2385	sym. B-H stretch
			2169		(sym. C-O stretch)
		1415			(sym. P-O stretch)
			1101	1117	asym. BH_3 deformation
			1073	1077	sym. BH_3 deformation
860	859	990		957	asym. P-F stretch
892	898	873		944	sym. P-F stretch
			816	697	asym. BH_3 rock
			692		(sym. B-C stretch)
				607	sym. P-B stretch
487	386	473		441	sym. PF_3 deformation
344	503	485		370	asym. PF_3 deformation
			317		(asym. BCO deformation)
		345		197	asym. PF_3 rock

921 cm^{-1} and 939 cm^{-1} are the P-F stretching fundamentals while the higher 969 cm^{-1} band is the combination. In this region only two possible combinations appear reasonable: $\nu_4 + \nu_{11}$ at about 977 cm^{-1} and $2\nu_{11} + \nu_{12}$ at about 937 cm^{-1}. The intensities of these proposed bands probably would be relatively weak unless resonance occurred with one of the P-F stretching fundamentals. If this were true, the band intensity might be appreciable and the band maximum might be shifted from the expected position. Although the intensities of the observed bands at 969 cm^{-1} and 939 cm^{-1} might be explained in terms of Fermi resonance, little or no apparent shifting is observed from the calculated frequencies of the combinations and no strong preference for either choice is indicated.

Another possibility is that the observed band at 921 cm^{-1} may be due to an overtone or combination of the inactive torsional mode with an E fundamental. Since the frequency of the torsional mode is not known, one cannot predict where such a band might be observed. None of the other bands observed in the spectra, however, require the assumption of a torsional frequency. At the present time, Taylor's assignments for the asymmetric and symmetric P-F stretching modes are considered to be correct, but the band at 921 cm^{-1} remains to be assigned. A normal coordinate treatment might help in resolving the uncertainties connected with these assignments.

Since the PF_3 deformation modes occur at much lower frequencies, only the symmetric PF_3 deformation vibration at 438 cm^{-1} was observed in infrared absorption, the asymmetric deformation frequency at 370 cm^{-1} (5) being too low to be recorded experimentally. The broadness of the exciting line also prevented it from being observed in the Raman effect.

The four fundamentals which remain are the BH_3 and PF_3 rocks, the P-B stretch, and the inactive P-B torsional mode. Of these, only the BH_3 rocking and P-B stretching vibrations are observed. The BH_3 rocking vibration is easily identified in the infrared spectrum and shows a typical boron-10 isotope effect. The observed frequencies for the boron-10 and 11 enriched samples are 709 cm^{-1} and 700 cm^{-1} respectively. Similarly, the P-B stretching vibration is shifted from 616 cm^{-1} to 606 cm^{-1} in the appropriately enriched samples.

The weaker bands shown in Figures 4, 5 and 6 are due to overtones and combinations, and the assignments for many of these are given in Table 3. Due to the fact that these assignments are somewhat arbitrary, they are not as certain as those for the fundamentals.

It should be mentioned here that many of the infrared tracings of solid F_3PBH_3 and $F_3PB^{10}H_3$ exhibit bands which do not appear in the Figures 4 or 5. These bands are attributed to volatile impurities, perhaps diborane, since their relative intensity depended on the treatment of the sample. If the sample of F_3PBH_3 is fractionated immediately before use and the less volatile fraction is used for examination, no evidence of these bands is observed in the infrared spectra. For purposes of record the following impurity bands are observed for solid F_3PBH_3: a strong band at 2340 cm^{-1} with a shoulder at 2358 cm^{-1}, a very weak band at 2261 cm^{-1} and a strong band at 663 cm^{-1} with a shoulder at 656 cm^{-1}. Similar bands are observed in the infrared spectrum of solid $F_3PB^{10}H_3$. The band at 2340 cm^{-1} also appears in the Raman spectra and Taylor (5) has attributed this band to the combination $2\nu_3 + \nu_5$, but in the light of the present study it probably should be ascribed to an impurity.

Methylaminodifluorophosphine-Borane, $CH_3NHPF_2BH_3$.

Virtually no experimental data are available which provide information about the structure of this compound. However, nuclear magnetic resonance studies indicate that the borane group bonds through the phosphorus atom in the similar compounds, $(CH_3)_2NPF_2BH_3$ and $[(CH_3)_2N]_2PFBH_3$ (13). Since these dimethylamine complexes are very similar chemically to the present methylamine complex, one might similarly expect P-B bonding in this compound. In addition, chemical arguments support the hypothesis that the pyramidal configurations of CH_3NH_2 and PF_3 are retained in the $CH_3NHPF_2BH_3$ complex. The application of these conditions leads to a structure which has no molecular symmetry or at best a "pseudo" C_s symmetry in which the carbon, nitrogen, phosphorus and boron atoms lie on a vertical reflection plane. Because the former configuration is more probable, the motions of the molecule will be discussed in terms of group or site symmetry rather than in terms of possible molecular symmetry.

Since this molecule contains thirteen atoms, there are thirty-three Raman and infrared active vibrational modes. Of these vibrations, nine are confined to the vibrations of the methyl group, nine involve predominantly the motions of the borane group, three are essentially N-H vibrations and the remaining twelve vibrations are primarily skeletal motions of the molecule, regarding the CH_3, BH_3 and NH groups as point masses. Although this vibrational classification is employed mostly for the sake of convenience, nevertheless such a classification is validated by the experimental observation that the hydrogen motions are well separated from the skeletal vibrations and probably are not coupled to the skeletal modes to any appreciable extent.

Both the infrared and Raman spectra of $CH_3NHPF_2BH_3$ for various sample states have been observed and are represented in Figures 7 through 10. The Raman polarization spectra of the liquid sample at -40°C have also been included in the List of Figures (see Figure 10) for assistance in making assignments. The large number of mercury lines which are observable in the Raman spectrum of the liquid sample (see

Figures 9 and 10) are a result of inadequate filtering of the incident mercury light. The observed infrared and Raman frequencies and their tentative assignments are listed in Table 5.

The very strong band appearing in the region from 3350 cm^{-1} to 3454 cm^{-1} in both the infrared and Raman spectra is obviously the N-H stretching vibration and correlates very well with the similar vibration at 3355 cm^{-1} for $(CH_3)_2NH$ (22). The frequency of this band shifts from 3454 cm^{-1}, to 3369 cm^{-1}, to 3362 cm^{-1} in the spectra of the respective gaseous, liquid and solid samples. Such shifting probably is indicative of appreciable hydrogen bonding in the condensed states.

In the C-H stretching region, two polarized bands at 2845 cm^{-1} and 2957 cm^{-1} and one depolarized band at 3004 cm^{-1} are clearly resolved in the Raman effect but are not completely resolved in the infrared spectrum. The assignment of the lower band at 2845 cm^{-1} to the symmetric C-H stretch and the two higher bands to asymmetric C-H stretching vibrations is consistent with the observations of CH_3NH_2 in which the corresponding bands are found near 2820 cm^{-1}, 2961 cm^{-1} and 2985 cm^{-1} (48,49). Other bands which are observed in this region of the spectrum are probably overtones or combinations of lower frequency fundamentals probably in resonance with themselves or with the C-H valency fundamentals.

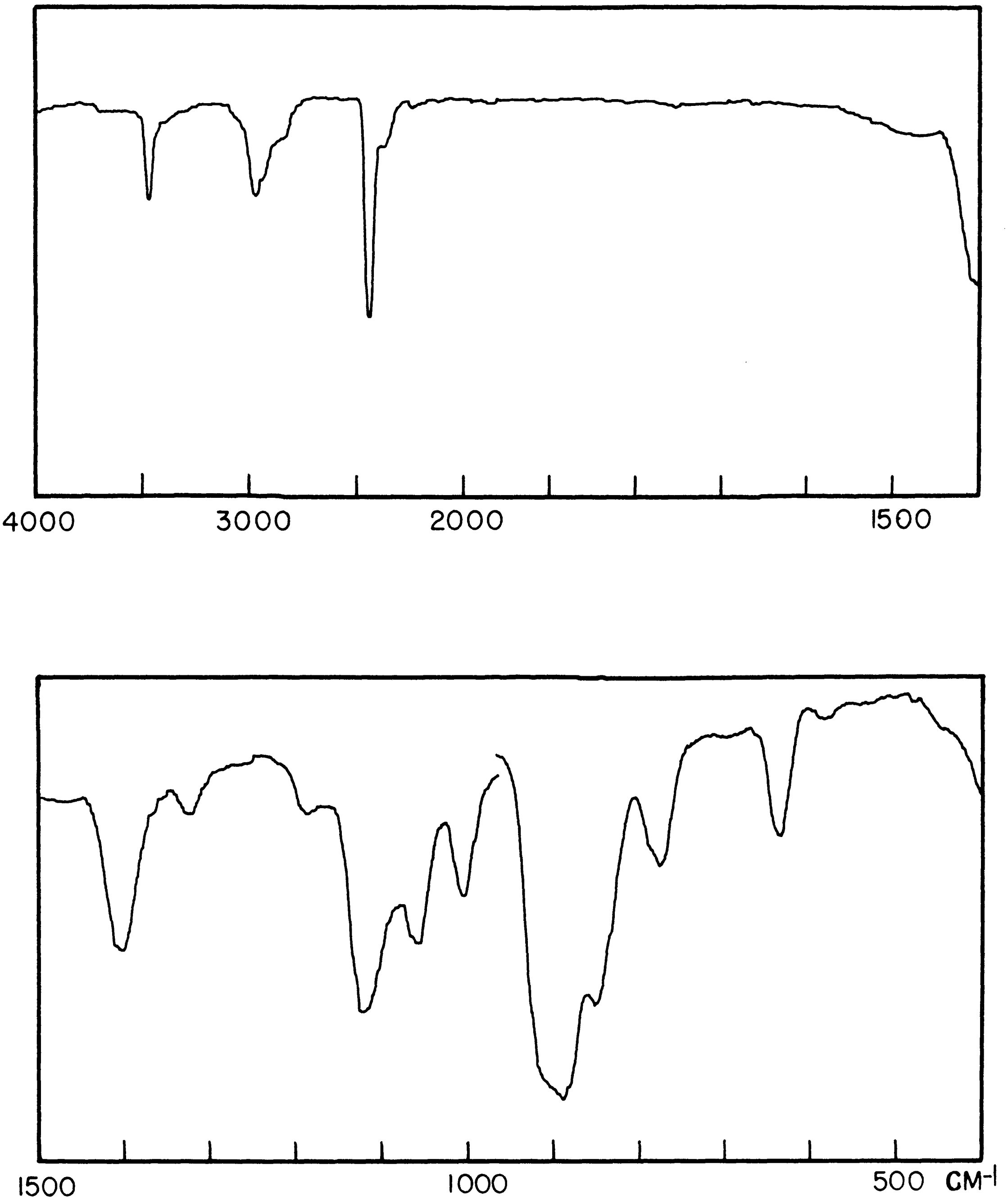


FIGURE 7 - THE INFRARED SPECTRUM OF GASEOUS $CH_3NHPF_2BH_3$ (6 mm)

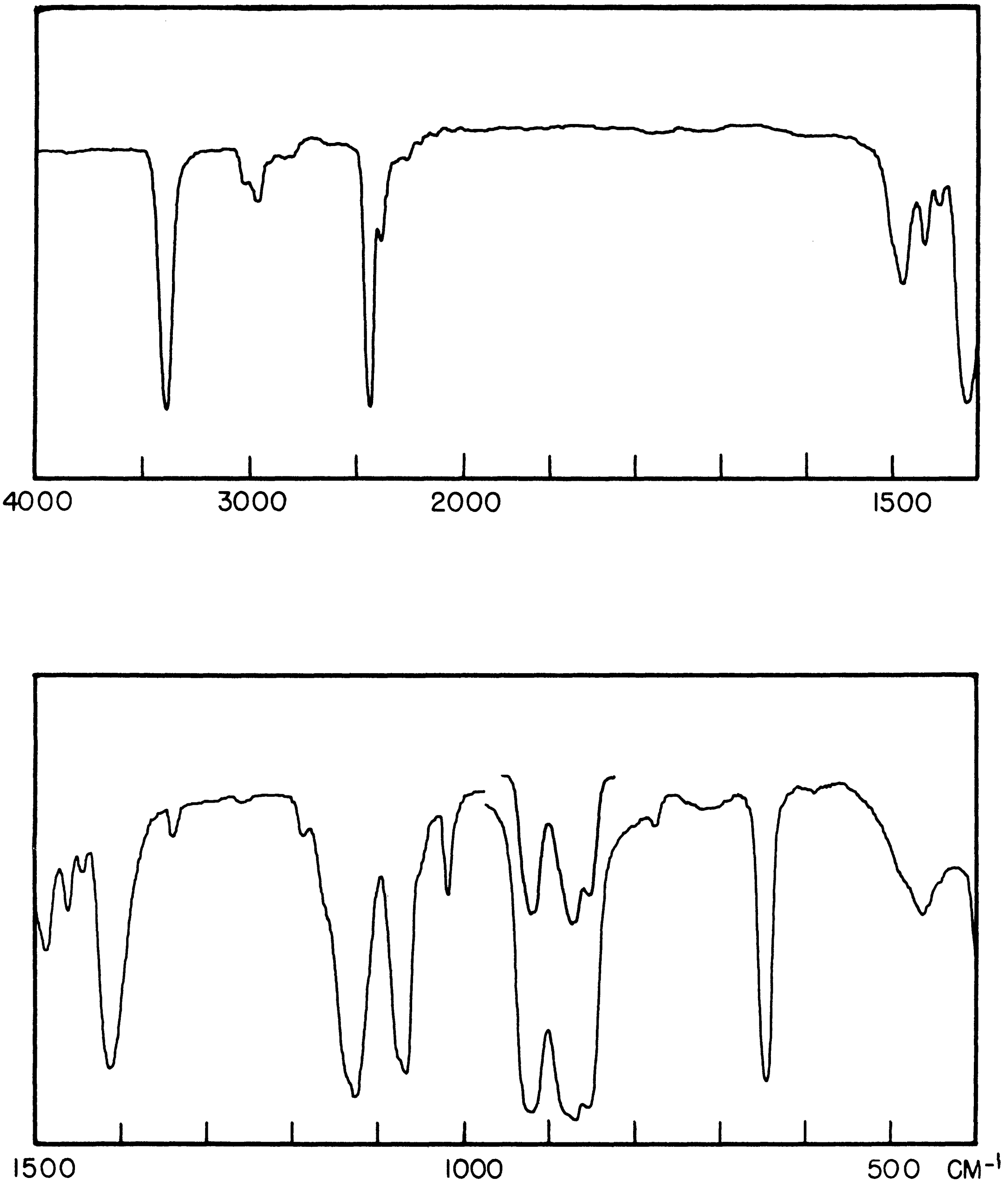


FIGURE 8 - THE INFRARED SPECTRUM OF SOLID

$CH_3NHPF_2BH_3$ (-180°C)

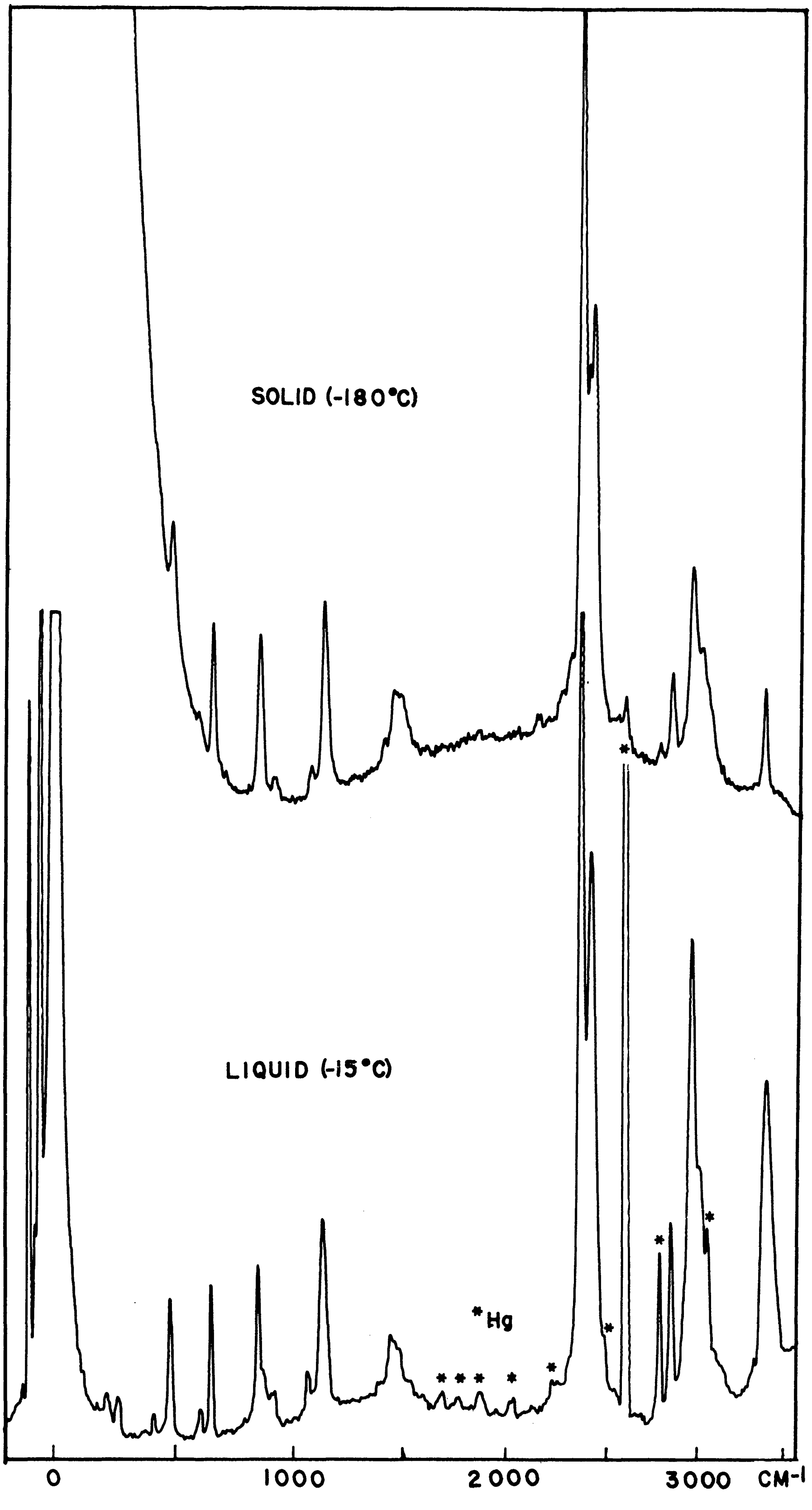


FIGURE 9 - THE RAMAN SPECTRA OF SOLID (-180°C) AND LIQUID (-15°C) $CH_3NHPF_2BH_3$

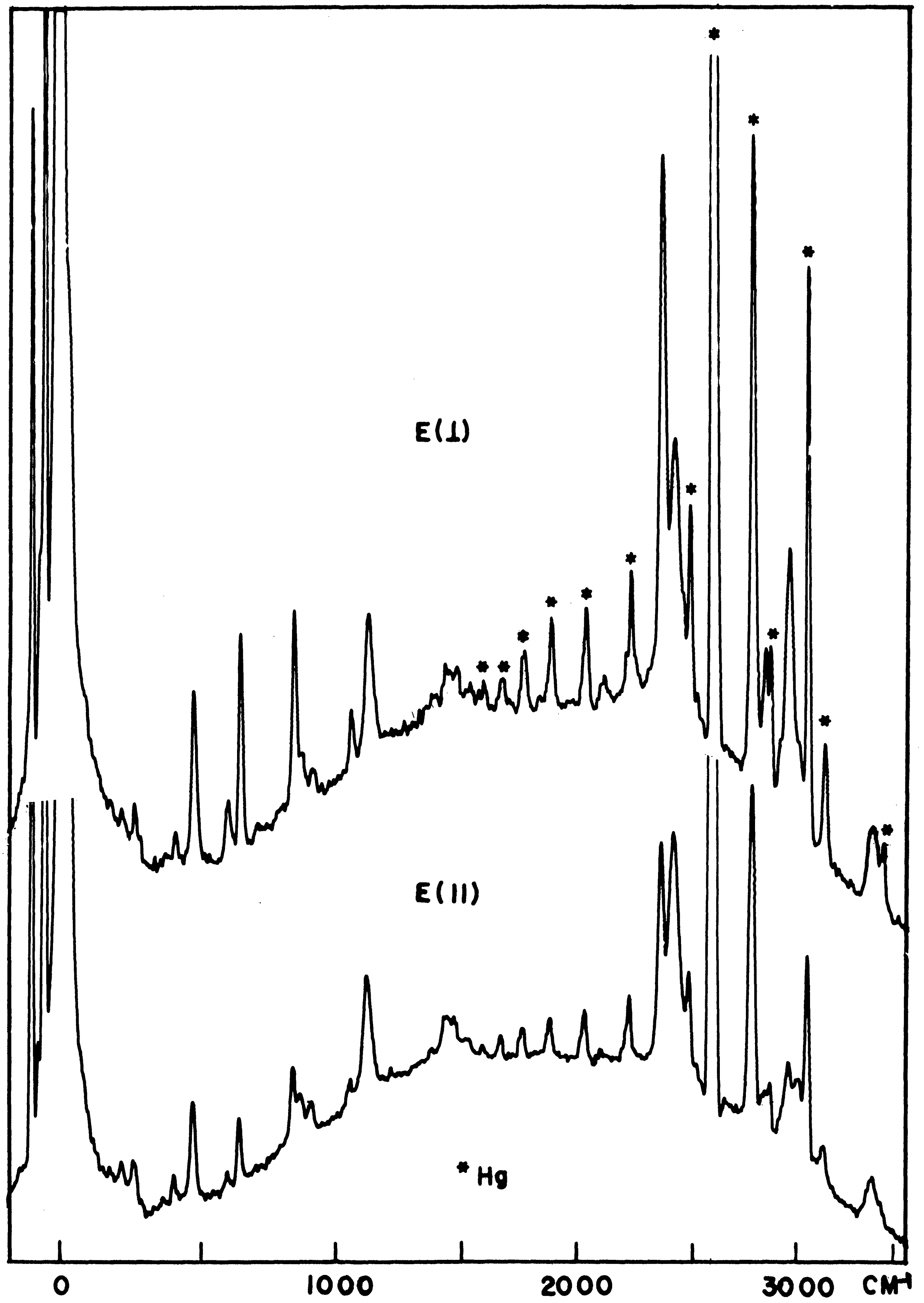


FIGURE 10 - THE POLARIZED RAMAN SPECTRA OF LIQUID

$CH_3NHPF_2BH_3$ (-40°C)

TABLE 5

THE OBSERVED INFRARED AND RAMAN FREQUENCIES OF $CH_3NHPF_2BH_3$

Infrared		Raman		
gas (6mm)	solid (-180°C)	liquid (-15°C)	solid (-180°C)	Assignment
3454±10 w	3353 vs	3369 vs,p	3362 s	N-H stretch
3028±10 vw,sh?	2997 w,sh	3004 s,sh,dp	3015 s,sh,br	asym. C-H stretch
2961±10 w		2957 vs,p	2956 vs	asym. C-H stretch?
2929±10 w,sh	2938 w			1454 + 1479 = 2933
		2911 w,sh?		2 x 1458 = 2916
2827±10 vw,sh	2839 vw,sh	2845 s,p	2848 ms	sym. C-H stretch
	2794 vw,sh?			2 x 1405 = 2810
2438±10 ms	2413 s	2425 vs,p	2432 vs	asym. B-H stretch
			2407 vs,sh	917 + 1489 = 2406?
2365±10 w,sh	2370 m,sh	2369 vw,p	2369 vs	sym. B-H stretch
			2312 m,sh	1135 + 1181 = 2316
		2253 w,sh?	2264 w,sh	2 x 1125 = 2250?
2233±10 vw	2242 w,sh			2 x 1125 = 2250?
	2186 vvw,sh?		2162 vw	705 + 1455 = 2160
			2143 vw	2 x 1077 = 2154
	2115±5 vvw,sh?	2114 vvw?		646 + 1479 = 2125
		1536 w,sh	1545 vw,sh?	2 x 773 = 1546
	1494 w,sh?			369 + 1125 = 1494

TABLE 5 - CONT'D.

Infrared		Raman		
gas (6mm)	solid (-180°C)	liquid (-15°C)	solid (-180°C)	Assignment
	1479 ms	1483 m,sh,dp	1489 ms,sh	asym. CH_3 deformation
	1454 m,sh	1458 m,sh,dp	1455 ms	asym. CH_3 deformation
	1439 m,sh	1438 m		asym. CH_3 deformation?
1400 m	1405 vs	1393 w,sh	1410 w,sh	sym. CH_3 deformation
1323 w,sh	1335 w			465 + 867 = 1332
1186 w,sh	1185 w,sh	1182 vvw,sh??	1181 vw,sh??	CH_3 rock
1120 ms	1125 s	1131 s,p?	1135 vw	asym. BH_3 deformation and/or CH_3 rock?
1059 m,sh	1076 s,sh? 1066 s	1064 m,p	1077 w	sym. BH_3 deformation and/or C—N-P stretch
1008 m,sh	1018 m	1020 vvw??		C—N-P stretch
908 s,sh?	915 vs	914 w,dp	917 w	BH_3 rock?
883 vs,br	867 vs	877 m,sh,dp?		asym. P-F stretch
845 s,sh	849 vs,sh	843 s,p	851 vs	sym. P-F stretch
770 m,sh	773 w,sh	796 vvw,sh?		NH rock and/or N—P-F_2 stretch
		708 vvw?	705 vvw?	NH rock and/or N—P-F_2 stretch
	668 vw,sh			211 + 465 = 676

TABLE 5 - CONT'D.

Infrared		Raman		
gas (6mm)	solid (-180°C)	liquid (-15°C)	solid (-180°C)	Assignment
	652 m,sh			P-B stretch (B-10)?
636 m	646 s	640 s,p	647 s	P-B stretch (B-11)
584 vvw,br		596 w,p	591 vvw?	skeletal
	465 m	467 s,p	475 vw	PF_2 deformation
	401 m	400 w		skeletal
		369 vvw?		C-N-P deformation?
		255 w,sh,p?		CH_3 torsion
		211 w,sh,p?		PF_2 rock?
		169 vw,sh		skeletal

The very strong doublet which is observed in both the Raman and infrared spectra around 2369 cm^{-1} and 2425 cm^{-1} is most assuredly the symmetric and asymmetric B-H stretching vibrations in view of a similar doublet at 2385 cm^{-1} and 2455 cm^{-1} in the Raman spectrum of F_3PBH_3 (5). Since the lower band is strongly polarized while the upper is only weakly polarized, the lower band is assigned to the symmetric B-H stretch and the upper to the asymmetric vibration. The influence of the rest of the molecule apparently is not sufficient to cause an observable splitting of the two asymmetric modes which form a degenerate pair in the case of full C_{3v} symmetry. The strong shoulder appearing between the two lines of the doublet in the solid Raman spectrum is probably an overtone or combination, perhaps 917 + 1489 = 2406.

In the methyl deformation region from 1400 cm^{-1} to 1500 cm^{-1} several clearly resolved bands are observed in the solid infrared spectrum but are not well resolved in the Raman effect. The very strong infrared band at 1405 cm^{-1} and the weak Raman shoulder at 1393 cm^{-1} are probably the totally symmetric methyl deformation vibration while the asymmetric methyl deformations are most likely found as one or more of the bands in the triplet at 1438 cm^{-1}, 1458 cm^{-1} and 1483 cm^{-1}. The tentative assignments of the asymmetric CH_3 deformations to the two higher bands at 1458 cm^{-1} and 1483 cm^{-1} are preferred because these correlate better with the respective assignments in methylamine at 1459 cm^{-1} and 1476 cm^{-1} (49). The great intensity change of the symmetrical deformation vibration between the infrared and Raman spectra may be somewhat surprising but Barcelo and Bellanato (22) report similar observations for the symmetric methyl deformation of CH_3NH_2 at 1410 cm^{-1}.

Because the methyl rocking vibrations are found in the same region of the spectrum as the asymmetric borane deformations, their assignments are not certain and deuteration of the borane group will be necessary to make unambiguous assignments. Since methyl rocks are found at 1130 cm^{-1} and 1195 cm^{-1} in the infrared spectrum of CH_3NH_2 (48), one or both of the bands at 1131 cm^{-1} and 1182 cm^{-1} in the spectrum of $CH_3NHPF_2BH_3$ may be methyl rocking vibrations. On the other hand, the 1131 cm^{-1} band is quite likely the asymmetric BH_3 deformation mode on the basis of its intensity in the infrared and Raman spectra and its agreement with the asymmetric BH_3 deformation observed around 1120 cm^{-1} in F_3PBH_3, $CH_3NH_2BH_3$ and for other amine boranes.

Many of the observable bands below 1100 cm^{-1} are very difficult to identify and therefore their assignments are not at all certain. Two such bands are observed around 1020 cm^{-1} and 1064 cm^{-1}. The C-N stretch for methylamine is generally agreed to be the band at 1044 cm^{-1} (22,48,49). Bellamy has cited evidence for a coupled $\begin{matrix}C\\C\end{matrix}\!\!>\!N\text{-}P$ motion in many dimethylaminophosphines (51). The extrapolation of this hypothesis to the present case, results in the assumption that the normal vibration for the C-N stretch probably contains some N-P stretching as well, thereby yielding a C-N-P coupled motion. With the present information at hand, one is not able to make an unequivocal assignment of either of these frequencies to the proposed C-N-P stretch, although the higher frequency at 1064 cm^{-1} is favored because experimental evidence tends to show that the C-N stretching frequency oftentimes increases with added substitution on the carbon or nitrogen atoms (13,52). However, the higher 1064 cm^{-1} frequency may be the symmetric BH_3 deformation vibration because similar vibrations have been observed at 1073 cm^{-1} for $OCBH_3$ (21), at 1077 cm^{-1} for F_3PBH_3 (5) and at 1070 cm^{-1} for $(CH_3)_3PBH_3$. Isotopic substitution of deuterium in the borane group will be necessary for further clarification of these assignments.

Three very strong infrared bands at 849 cm^{-1}, 869 cm^{-1} and 915 cm^{-1} are also observed in the Raman effect, but the intensities of the upper two Raman bands are considerably diminished. Polarization measurements indicate that the two higher bands are depolarized while the lower more intense band is strongly polarized. Although all three of these bands are observed in the P-F stretching region from 720 cm^{-1} to 950 cm^{-1} (53,54), the bands at 849 cm^{-1} and 867 cm^{-1} are probably the respective symmetric and asymmetric

P-F stretching vibrations. These frequencies may be correlated with those observed for $Ni(PF_3)_4$ at 859 cm^{-1} and 898 cm^{-1} (19), for $Ni(PF_2CH_3)_4$ at 723 cm^{-1} and 781 cm^{-1} (19) and for $(CH_3)_2NPF_2$ at 743 cm^{-1} and 792 cm^{-1}. The higher band at 915 cm^{-1} may be the asymmetric P-F stretch but is more likely a BH_3 rock. Even though borane rocking modes are sometimes found at lower frequencies, this assignment is consistent with that observed for $OCBH_3$ at 816 cm^{-1} (21) and for various amine-boranes around 900 cm^{-1} (50).

Two bands are observed in the 700-800 cm^{-1} region which may be the N-H rocking and $N\text{-}P\text{-}F_2$ stretching vibrations. One of the bands, at 773 cm^{-1}, appears as a very weak to medium intensity shoulder in the infrared and Raman spectra. The other is observed only as a very weak Raman line at 708 cm^{-1}. Evidence for the fact that the N-P stretch in aminophosphines is probably coupled to neighboring vibrations has been reported by Bellamy (51), Sr. Fleming (13) and others (23). Because such a group vibration, e.g. $N\text{-}P\text{-}F_2$ stretch, probably has its greatest amplitude along the N-P bond, its frequency should not be too different from that of P-N stretching motion which is oftentimes found in the region from 680 cm^{-1} to 750 cm^{-1} (53,54). Since the similar group vibration is observed at 705 cm^{-1} in the spectrum of $(CH_3)_2NPF_2$, the assignment of the $N\text{-}P\text{-}F_2$ stretch to the lower frequency at 708 cm^{-1} is preferred, but the higher assignment to the 773 cm^{-1} band cannot be ruled out.

The NH_2 rocking motion of CH_3NH_2 has generally been assigned to a band around 724-780 cm^{-1} (22,48). A similar band for the N-H rock has been reported at 724 cm^{-1} for $(CH_3)_2NH$ (22) and around 730 cm^{-1} for various dialkylamines (52). Therefore the assignment of the 773 cm^{-1} frequency to a NH rocking vibration is consistent with the present data on the alkylamines.

The strong polarized band at 646 cm^{-1} is assigned to the P-B stretching vibration. The medium intensity shoulder seen at 652 cm^{-1} in the solid infrared spectrum may be the boron-10 component of the P-B vibration. Although this assignment is somewhat higher than that observed for F_3PBH_3 at 607 cm^{-1}, for $(CH_3)_2NPF_2BH_3$ at 591 cm^{-1} and for $(CH_3)_3PBH_3$ at 571 cm^{-1}, the intensity of the band in question is comparable to that observed for similar phosphine-boranes. A lower band at 596 cm^{-1} has a frequency which is expected more for a P-B stretch, but its intensity is so weak in the infrared and Raman spectra that it is not considered to be the P-B stretch, but rather an unassigned skeletal vibration.

Several observed vibrations remain to be assigned. The strong, polarized band at 467 cm^{-1} is probably the PF_2 deformation mode which may be regarded as a remnant of the symmetric PF_3 deformation of F_3PBH_3 at 441 cm^{-1}. The very weak band at 369 cm^{-1} has been tentatively assigned to the C-N-P deformation because of its close proximity to the C-N-C deformation vibration at 383 cm^{-1} for dimethylamine. The weak shoulder at 255 cm^{-1} is considered to be the methyl torsion because of its low intensity and its nearness to the 269 cm^{-1} torsional motion of CH_3NH_2 (55). Although the assignment of the 211 cm^{-1} frequency to a PF_2 rock is uncertain, it is justified on the basis that a similar PF_3 rock is observed in the spectrum of F_3PBH_3 at 197 cm^{-1} (5). The remaining bands at 169 cm^{-1} and 400 cm^{-1} are probably skeletal vibrations but they have not been given specific assignments because of the lack of knowledge concerning many of the lower fundamental frequencies.

Bis(methylamino)fluorophosphine-Borane, $(CH_3NH)_2PFBH_3$.

The structure of $(CH_3NH)_2PFBH_3$ is unknown; however, a phosphorus-boron bond is postulated by analogy to the bis-(dimethylamino)fluorophosphine-borane complex. In addition, the assumption that the nitrogen and phosphorus atoms remain at the apexes of the generic NH_3 and PF_3 pyramids is based largely upon chemical knowledge of similar compounds. It is reasonable to assume that this molecule has no molecular symmetry, but a symmetrical orientation of the CH_3NH-groups about the phosphorus atom could lead to a configuration having C_s symmetry. Since the methylamine groups probably experience some rotation around the N-P bonds, it is likely that more than one rotational isomer exists at room temperature. Therefore no attempt will be made to define the orientation of one methylamine group with respect to the other.

The vibrational spectrum of this compound is expected to be very complex due to the existence of these rotational isomers and because a total of forty-eight fundamentals may be observed in both the infrared and the Raman effect. Although some resolution may be achieved between the eighteen methyl group vibrations, the nine borane group vibrations, the six NH group vibrations and the fifteen skeletal vibrations, extensive band overlapping and vibrational coupling present severe difficulties in establishing assignments for the fundamentals.

Infrared spectra of liquid and solid films were studied at 25°C and -180°C respectively and are represented in Figures 11 and 12. Also the Raman spectrum of the liquid sample at 0°C was observed along with the polarized spectra, but only the former is presented in Figure 13. The observed infrared and Raman frequencies are listed in Table 6 along with their tentative assignments. For the most part, the infrared spectrum of $(CH_3NH)_2PFBH_3$ closely resembles that of the difluoro-complex. However, striking differences are observed between the infrared and Raman spectra of the present compound. The unusually weak scattering ability of this complex along with the presence of fluorescent impurities presented severe difficulties to observing the Raman spectrum. On the other hand, the infrared spectrum exhibited many strong absorption bands, several of which were

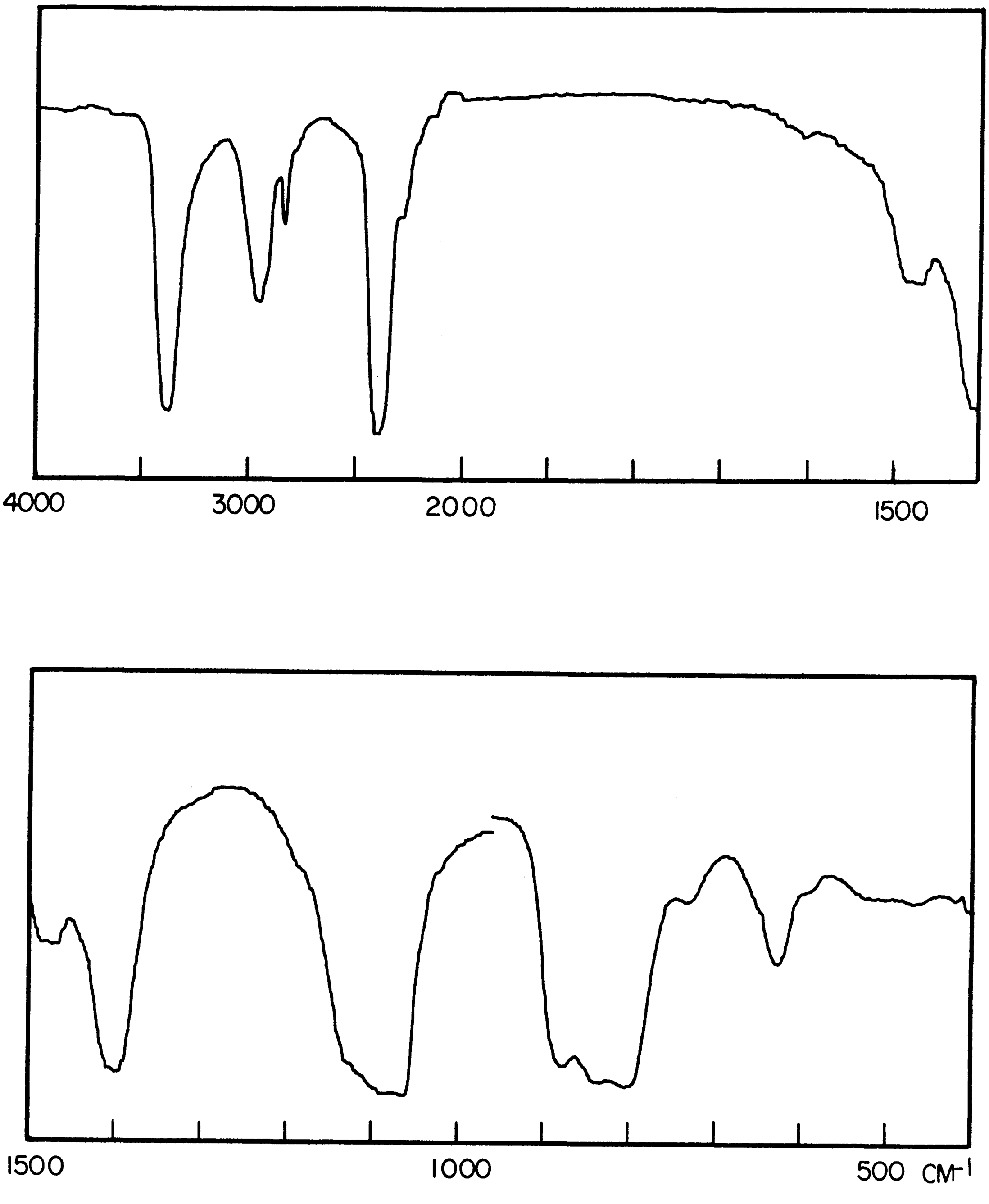


FIGURE 11 - THE INFRARED SPECTRUM OF LIQUID $(CH_3NH)_2PFBH_3$ (25°C)

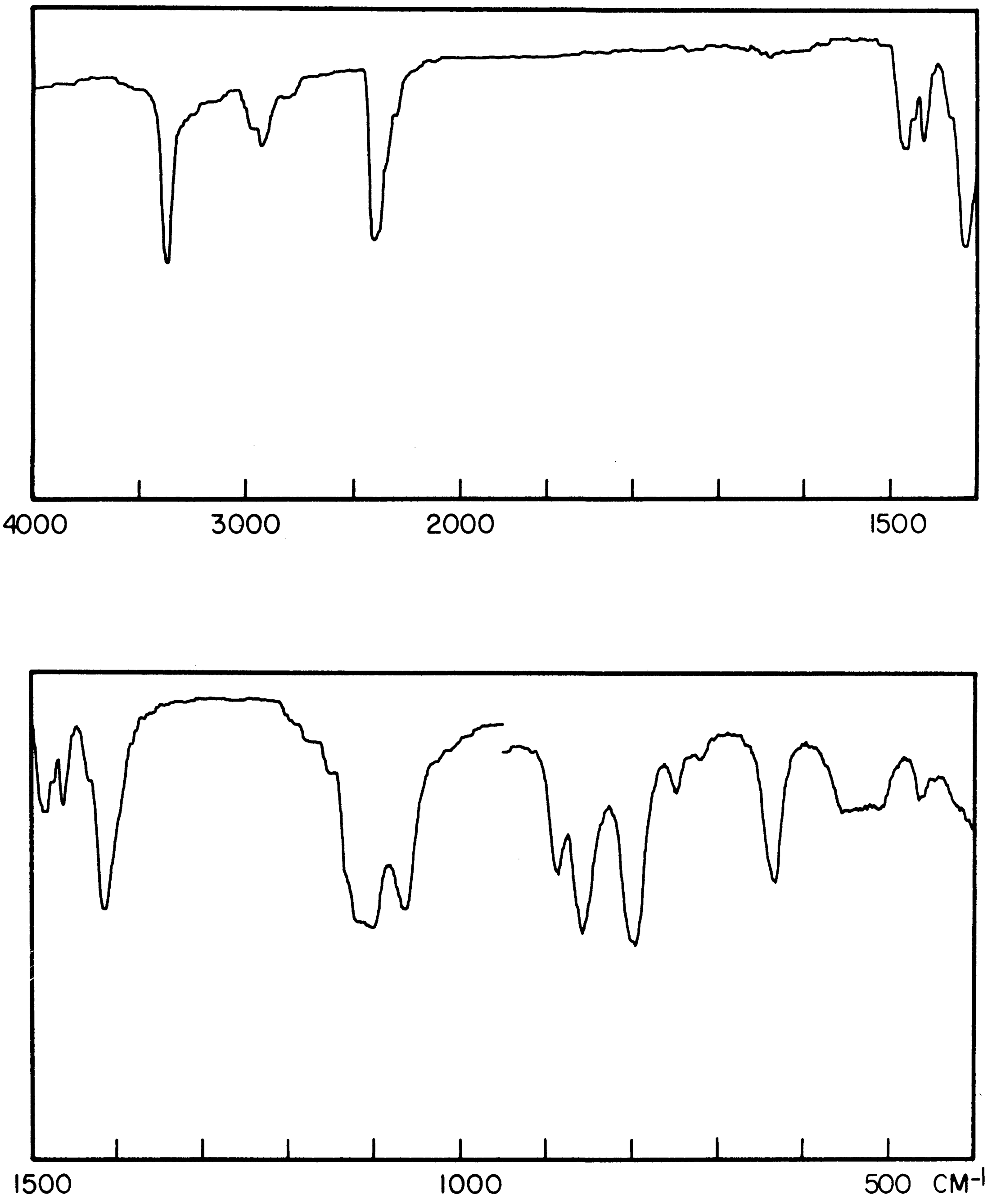


FIGURE 12 - THE INFRARED SPECTRUM OF SOLID

$(CH_3NH)_2PFBH_3$ (-180°C)

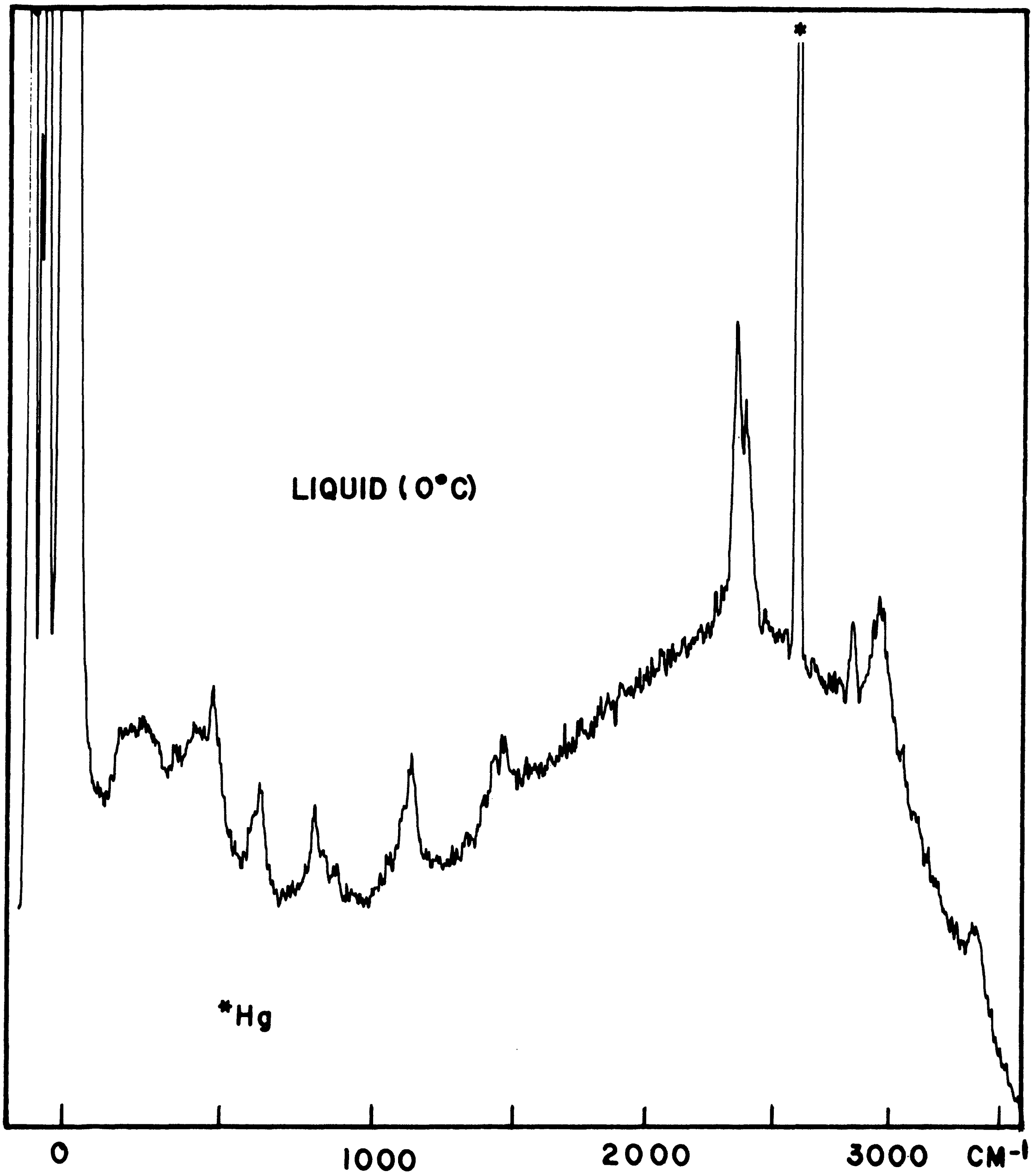


FIGURE 13 - THE RAMAN SPECTRUM OF LIQUID $(CH_3NH)_2PFBH_3$ (0°C)

TABLE 6

THE OBSERVED INFRARED AND RAMAN FREQUENCIES OF $(CH_3NH)_2PFBH_3$

Infrared		Raman	Assignment
liquid(20°C)	solid(-180°C)	liquid(0°C)	
3365 vs	3343±10 s	3366 vw	N-H stretch
2940 m	2954±10 w,sh	2947 w,p?	asym. C-H stretch
2905 m,sh	2910±10 w	2912 w,sh,p?	asym. or sym. C-H stretch
2828 w	2802±10 vw,sh?	2830 w,p	sym. C-H stretch
2388 vs	2380±10 s	2391 m,sh,dp	asym. B-H stretch
2359 s,sh		2350 ms,p	sym. B-H stretch
2265 m,sh	2288±10 w,sh		2 x 1136 = 2272 2 x 1147 = 2294
2121 vw,sh?			2 x 1063 = 2126
1595 vvw,sh?			2 x 800 = 1600
1476 m,sh,br?	1473 m		asym. CH_3 deformation
1461 m,sh,br?	1465 w,sh 1453 m	1460 vw	asym. CH_3 deformation
	1422 w,sh	1432 vw	asym. CH_3 deformation ?
1390 vs,br	1404 s		sym. CH_3 deformation
	1169 vw,sh		CH_3 rock
	1147 w,sh	1136 w,dp	asym. BH_3 deformation and/or CH_3 rock?
1088 vs,br	1117 s,sh? 1100 s	1098 vw,sh?	sym. BH_3 deformation and/or out of phase $(C—N)_2$-P stretch?

TABLE 6 - CONT'D.

Infrared		Raman	Assignment
liquid(20°C)	solid(-180°C)	liquid(0°C)	
1063 vs,br	1062 s	1056 vvw,sh?	in phase (C—N)$_2$-P stretch
875 vs,br	877 m,sh	874 vvw	BH_3 rock?
837 vs,br?	842 s	836 vw,sh	P-F stretch?
800 vs,br	793 s	801 vw,p?	P-F stretch
	749 w,sh		NH rock and/or N_2—P-F stretch
729 w,sh	720 vw,sh		NH rock and/or N_2—P-F stretch
651 w,sh?			skeletal?
629 m	631 s	623 w,p?	P-B stretch
590 w,sh,br?		589 vw,sh,p?	skeletal
	532 w,vbr??		
	462 vw	467 w,p?	PF rock
424 vvw?			skeletal?
		407 vvw?,p?	skeletal
		347 vvw?	skeletal

very broad in the liquid spectrum. By cooling the sample to -180°C, the infrared bands were considerably sharpened, causing components of the band envelopes to be resolved. The increased resolution in the solid spectrum may result partly from the curtailment of internal rotation within the molecule as a consequence of increased barriers in the solid state as well as reduction of the thermal motion.

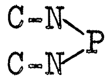
The very strong infrared band and the very weak Raman band around 3365 cm^{-1} is most certainly the N-H stretching vibration in view of the similar vibration found near 3369 cm^{-1} in the spectra of $CH_3NHPF_2BH_3$.

The methyl stretching and deformation vibrations in the 2900 cm^{-1} and 1450 cm^{-1} regions show no peculiarities and are in fact nearly identical to those of the monosubstituted complex. Reference may be made to the previous section for specific information concerning these vibrations.

As in the spectra of $CH_3NHPF_2BH_3$ and similar fluorophosphine-borane complexes, the B-H stretching vibrations are observed as a very characteristic doublet around 2359 cm^{-1} and 2388 cm^{-1}. The lower band is definitely polarized and is assigned to the symmetric stretch while the higher 2388 cm^{-1}, depolarized band is the asymmetric B-H stretching vibration. The medium intensity shoulder found in the infrared at 2265 cm^{-1} is probably an overtone, perhaps 2 x 1147 = 2294, rather than a B-H stretching fundamental.

The frequencies below 1200 cm^{-1} are very difficult to assign because of extensive overlapping of the fundamentals. Many of these assignments are uncertain and several alternate possibilities may exist. The first of such difficulties arises in identifying the methyl rocking vibrations. The very weak shoulder at 1169 cm^{-1} in the solid infrared spectrum is in all probability a methyl rock, but a lower depolarized band at 1136-1147 cm^{-1} may either be a methyl rock or the asymmetric BH_3 deformation. The assignment of this band to the BH_3 fundamental is preferred because similar absorption is observed for $(CH_3)_2NPF_2BH_3$ at 1128 cm^{-1}, for $[(CH_3)_2N]_2PFBH_3$ at 1131 cm^{-1} and for $(CH_3)_3PBH_3$ at 1137 cm^{-1}.

Similar difficulties are encountered in establishing the identity of bands between 1000-1100 cm^{-1}. Two partially resolved, very strong infrared bands are observed in this region: one at 1063 cm^{-1} and the other at 1088 cm^{-1}. These bands are resolved further in the solid infrared spectrum and both are present in the Raman effect. Since the C-N stretch for CH_3NH_2 is observed at 1044 cm^{-1}, either or both of these bands may be attributed to the proposed C-N-P group vibration. The modification of the C-N-P group to the



$\begin{matrix} C\text{-}N \\ C\text{-}N \end{matrix}\!>\!P$

entity may cause the frequency to be split, perhaps to 1063 cm^{-1} and 1088 cm^{-1}, but no definite evidence for such splitting has been observed. Justification for such a postulate may be found in the 942, 991 cm^{-1} C_2-N-P stretching doublet of $[(CH_3)_2N]_2PF$ and the 969, 999 cm^{-1} doublet of $[(CH_3)_2N]_2PFBH_3$. In addition to the previous possibilities the higher, 1088 cm^{-1} band may be the symmetric BH_3 deformation vibration. No definite choice is made concerning these assignments and isotopic substitution of the borane group will be required to resolve the difficulty.

Three broad, very strong infrared bands are observed at 800 cm^{-1}, 837 cm^{-1} and 875 cm^{-1}. They also appear in the Raman effect and the 800 cm^{-1} band seems to be polarized. Although all of these bands are found in the P-F stretching region, the assignment of the 800 cm^{-1} band to the P-F stretching fundamental is preferred because of its greater band intensity. The 875 cm^{-1} band may be a BH_3 rocking vibration, but the 837 cm^{-1} band remains to be assigned.

The assignments for the very weak shoulders at 720 cm^{-1} and 749 cm^{-1} are uncertain but are probably the NH rocking vibration and/or the N_2-P-F group frequency with no preference being given to either assignment. A definite possibility exists that both of these bands are components of the N_2-P-F group frequency in view of the fact that this frequency appears to be split at 644 cm^{-1}, 689 cm^{-1} and at 685 cm^{-1}, 706 cm^{-1} in the spectra of $[(CH_3)_2N]_2PF$ and of $[(CH_3)_2N]_2PFBH_3$ respectively.

A medium to strong intensity band at 629 cm^{-1} is observed in the liquid and solid infrared spectra and is seen as a weakly polarized, weak band in the Raman effect.

This vibration is assigned to the P-B stretch, because of its strong band intensity in the infrared. Although the assignment of this vibration to a lower, very weak, band at 590 cm^{-1} correlates better with the observed P-B vibrations of similar fluorophosphine-borane complexes, the very low intensity of the latter band removes it from serious consideration and instead it may be an unassigned skeletal vibration. The very weak band at 462 cm^{-1} is assigned to a PF rocking motion to agree with the related PF_2 deformation vibration of $CH_3NHPF_2BH_3$ assigned at 467 cm^{-1}.

The remaining bands at 651 cm^{-1}, 590 cm^{-1}, 424 cm^{-1}, 407 cm^{-1} and 347 cm^{-1} are all very weak to weak in intensity and are probably skeletal vibrations. Further classification of these is impossible at this time. The weak, very broad 532 cm^{-1} band has not been termed a skeletal mode because of its doubtful origin. The frequencies which are assigned to combinations or overtones are considered to be tentative and may be seen in Table 6.

Dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$.

Although no structural data have been reported in the literature for $(CH_3)_2NPF_2$, it is logical to assume that the pyramidal configurations of $(CH_3)_2NH$ and PF_3 are retained with the formation of $(CH_3)_2NPF_2$. Sr. Fleming (13) has invoked theoretical arguments along with experimental evidence to show that $(CH_3)_2NPF_2$ probably has a structure in which the methyl groups and the fluorine atoms are in a trans configuration, although a gauche configuration cannot be completely ruled out. Assuming the trans configuration, one would expect that this molecule possesses only one element of symmetry, a vertical reflection plane, σ_v, and would belong to the C_s point group.

The C_s symmetry of the molecule requires that it have thirty active vibrational modes, of which sixteen are of the A' symmetry species and fourteen are of the A" symmetry species. Eighteen of the total number of vibrations are localized primarily in the C_2NPF_2 framework of the molecule. A complete numerical listing of the fundamental vibrational modes along with a description of each mode is given in Table 7.

Since the atomic masses in the $(CH_3)_2NPF_2$ skeleton are very similar, one may expect the skeletal modes to involve extensive coupling of the individual bond stretching and deformation motions. This is particularly true in the case of ν_9 and ν_{11}, which appear to be modes involving the symmetric stretching of all the bonds in the C_2-N-P and N-P-F_2 groups. This is indicated by the fact that they do not occur at quite the positions at which "pure" C-N and N-P frequencies occur.

The observed Raman spectra of liquid and solid $(CH_3)_2NPF_2$ at -32°C and -180°C respectively are shown in Figure 14 and the polarization spectra for the liquid sample are shown in Figure 15. As an aid in making assignments to the vibrational modes in the molecule the observed Raman frequencies of the sample are compared to published infrared frequencies of $Ni(PF_2CH_3)_4$ (19), $(CH_3)_2NH$ (22) and $(CH_3)_2NPCl_2$ (23) in Table 8. Also, the observed infrared frequencies of $(CH_3)_2NPF_2$, reported by Sr. Fleming (13) and Schmutzler (56), are tabulated along with the present Raman results in Table 9. An inspection of this table reveals that the observed Raman frequencies agree with the infrared values, within the range of experimental error. This table also includes the vibrational assignments which were deduced from the present investigation. Although most of the assignments for the skeletal modes appear fairly certain, the assignments for the overtones, combinations and methyl group vibrations are less certain and should be considered only tentative.

The infrared spectrum of the sample for the most part resembles that of the Raman effect, however, some striking differences also appear. Such differences are present in the C-H stretching region from 2800 cm^{-1} to 3000 cm^{-1} where only three bands were observed in the infrared spectrum (13) while at least five bands are clearly resolved in the Raman spectrum. These bands are probably components of the six symmetric and asymmetric C-H stretching vibrations. However, there is a distinct possibility that one or more of these bands may be due to overtones of the deformation modes.

The methyl deformation frequencies in the region from 1300 cm^{-1} to 1500 cm^{-1} are well characterized and tentative

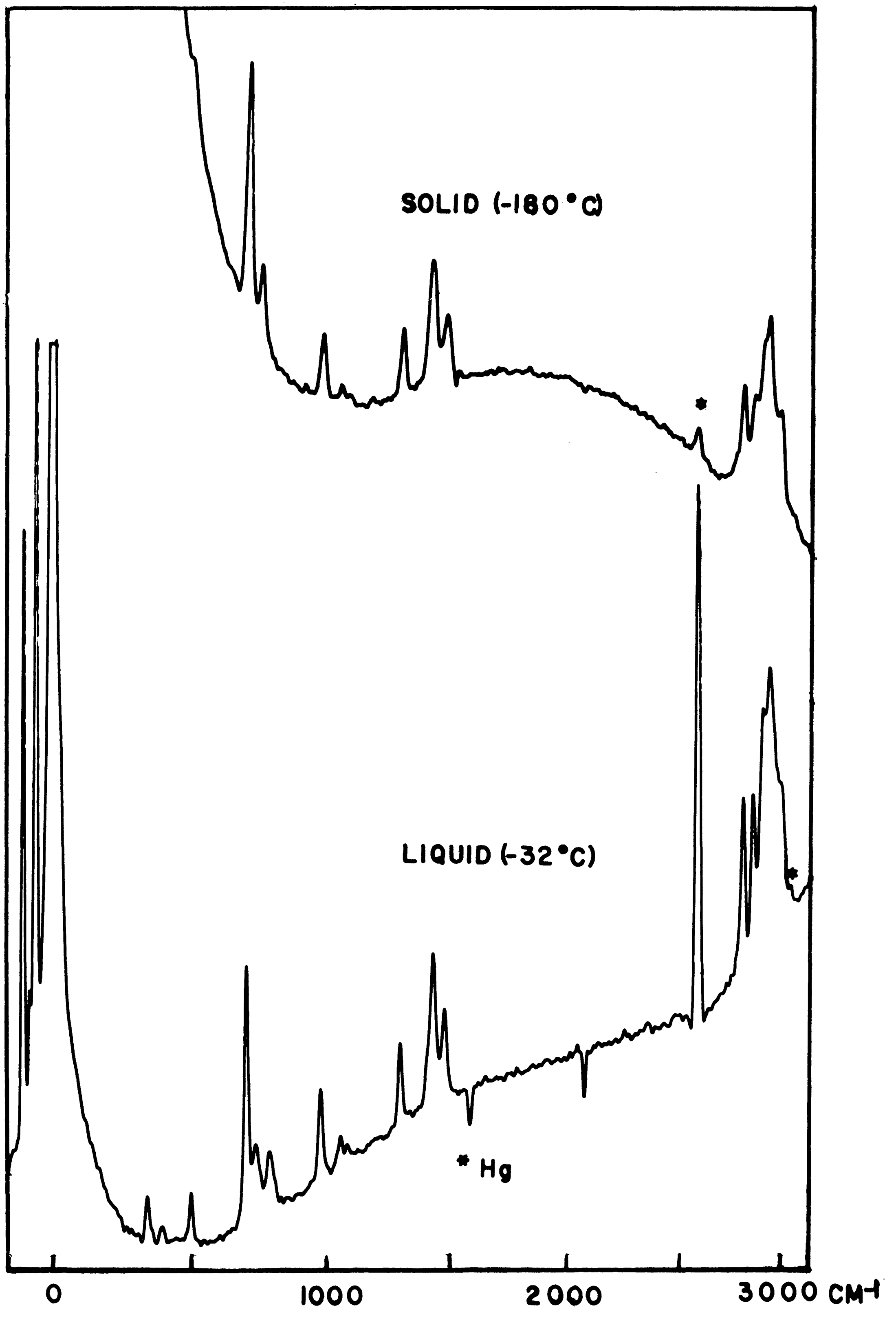


FIGURE 14 - THE RAMAN SPECTRA OF SOLID (-180°C) AND LIQUID (-32°C) $(CH_3)_2NPF_2$

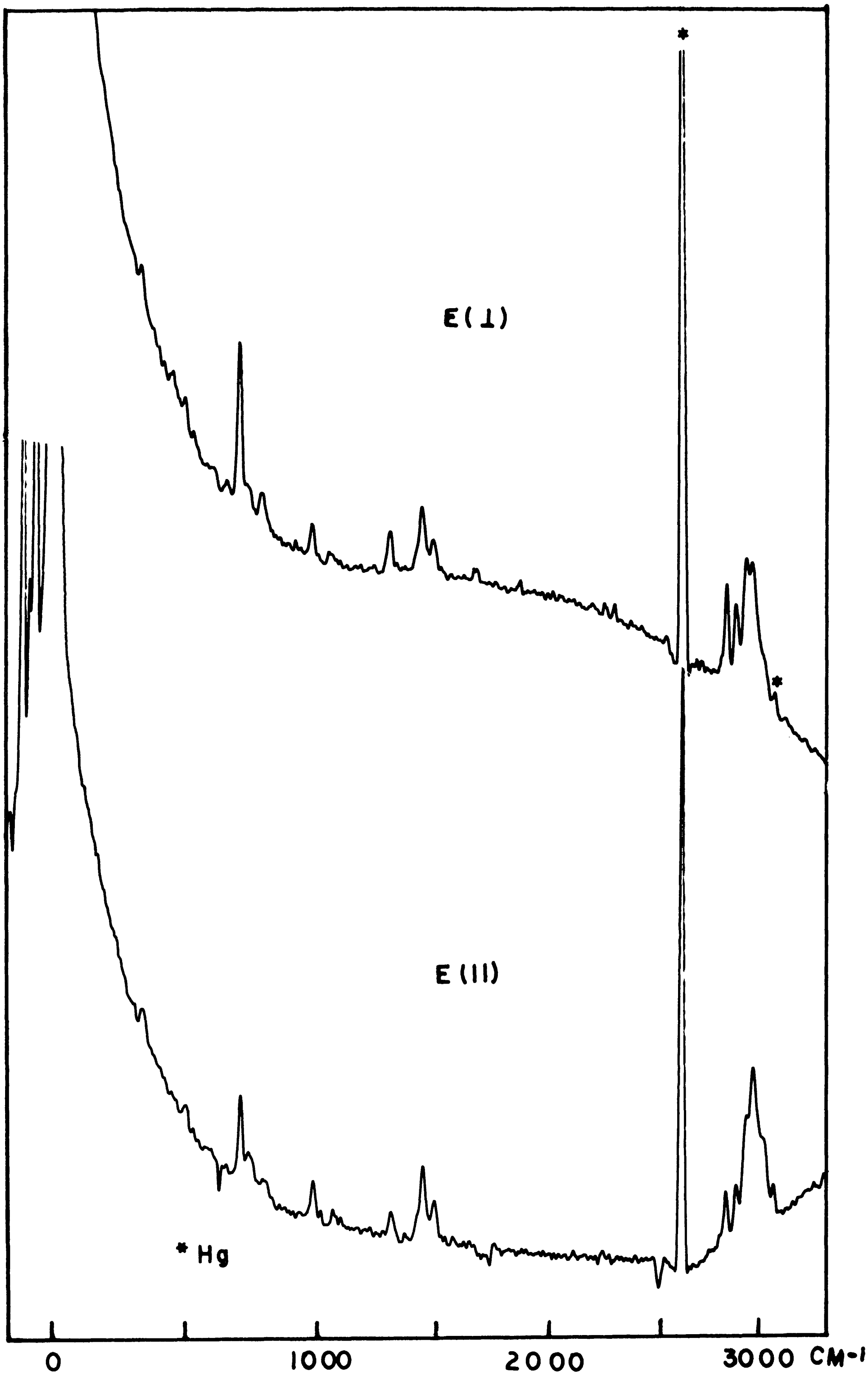


FIGURE 15 - THE POLARIZED RAMAN SPECTRA OF LIQUID $(CH_3)_2NPF_2$ (-32°C)

TABLE 7

THE FUNDAMENTAL VIBRATIONS OF $(CH_3)_2NPF_2$, C_s SYMMETRY

Symmetry	Number	Description
A'	1	in phase asymmetric C-H stretch
	2	in phase asymmetric C-H stretch
	3	in phase symmetric C-H stretch
	4	in phase asymmetric CH_3 deformation
	5	in phase asymmetric CH_3 deformation
	6	in phase symmetric CH_3 deformation
	7	CH_3 rock (out of C-N-C plane)
	8	CH_3 rock (in C-N-C plane) or CH_3 wag
	9	C_2—N-P stretch
	10	P-F stretch
	11	N—P-F_2 stretch
	12	F-P-F deformation
	13	C-N-C deformation
	14	NC_2 rock
	15	PF_2 rock
	16	CH_3 torsion
A''	17	out of phase asymmetric C-H stretch
	18	out of phase asymmetric C-H stretch
	19	out of phase symmetric C-H stretch
	20	out of phase asymmetric CH_3 deformation
	21	out of phase asymmetric CH_3 deformation
	22	out of phase symmetric CH_3 deformation

TABLE 7 - CONT'D.

Symmetry	Number	Description
A''	23	CH_3 rock (out of C-N-C plane)
	24	CH_4 rock (in C-N-C plane) or CH_3 wag
	25	C-N stretch
	26	P-F stretch
	27	NC_2 wag
	28	PF_2 wag
	29	CH_3 torsion
	30	P-N torsion

TABLE 8

A COMPARISON OF THE OBSERVED VIBRATIONAL FREQUENCIES OF $Ni(PF_2CH_3)_4$, $(CH_3)_2NH$, $(CH_3)_2NPCl_2$ AND $(CH_3)_2NPF_2$

$Ni(PF_2CH_3)_4(\ell)$ Infrared(19)	$(CH_3)_2NH(g)$ Infrared(22)	$(CH_3)_2NPCl_2(\ell)$ Infrared(23)	$(CH_3)_2NPF_2(\ell, -30°C)$ Raman	Assignment and Symmetry
	3355			[N-H stretch (a')]
	2967	2840 ms	2998 s,sh,dp	asym. C-H stretch (a")
			2945 vs,dp?	sym. or asym. C-H stretch (a" or a')
	2912		2912 vs,p?	asym. C-H stretch (a')?
	2855		2861 s,p	asym. C-H stretch (a')?
	2802	2790 mw	2814 s,p	sym. C-H stretch (a' and a"?)
	1496	1478 ms	1487 m,dp	asym. CH_3 deformation (a")
	1466	1450 ms	1439 s,dp	asym. CH_3 deformation (a')
	1404		1414 w,sh,dp?	sym. CH_3 deformation (a")?
		1287 ms	1306 m,p	sym. CH_3 deformation (a' and a"?)
	1245			[CH_3 rock (a")]
	1155	1175 ms	1103 vw	CH_3 rock (a' and/or a")

TABLE 8 - CONT'D.

$Ni(PF_2CH_3)_4(\ell)$ Infrared(19)	$(CH_3)_2NH(g)$ Infrared(22)	$(CH_3)_2NPCl_2(\ell)$ Infrared(23)	$(CH_3)_2NPF_2(\ell$, -30°C$)$ Raman	Assignment and Symmetry
	1024	1063 m	1071 w,dp?	C-N stretch (a")
		978 vs	989 m,dp?	C_2-N-P stretch (a')
	930			[C-N stretch (a')]
781			792 m,p?	P-F stretch (a")
723			743 m,dp?	P-F stretch (a')
	724			[NH bend (a")]
			705 vs,p	N-P-F_2 stretch (a')
		690 s		[N-PCl_2 or C_2N-P stretch (a')]
485 442			495 w	PF_2 deformation (a')
	(397)		393 vw	C-N-C deformation (a')
			336 w	skeletal
(290)				[CH_3 twist (a')]
(250)				[CH_3 twist (a")]
			168 vvw	PF_2 rock (a') and/or PF_2 wag (a")

TABLE 9

THE OBSERVED INFRARED AND RAMAN FREQUENCIES OF $(CH_3)_2NPF_2$

Infrared Gas(13)	 Liquid(56)	 Solid(13) (-180°C)	Raman Liquid (-30°C)	 Solid (-180°C)	Assignment
		3002 vw	2998 s,sh,dp	2996 s	ν_{17},ν_{18}
2925 m		2932 mw	2945 vs,dp?	2935 vs	ν_{19}? or ν_1?
	2908 s		2912 vs,p?	2906 vs,sh	ν_1?
2865 sh			2861 s,p	2867 s	ν_2?
2820 w	2808 s	2817 vw	2814 s,p	2815 s	ν_3,ν_{19}?
	1691 w				705 + 990 = 1695
		1498 w			728 + 764 = 1492
1507-	1484 s	1490 m	1487 m,dp	1495 m	ν_{20},ν_{21}?
	1468 w	1473 w			707 + 764 = 1471
		1463 w			393 + 1073 = 1466
	1450 s	1455 m			ν_{21}?
1432 w		1433 w	1439 s,dp	1432 s	ν_4?
		1430 vw			707 + 728 = 1435
			1414 w,sh,dp?		ν_5 or ν_{22}
1307 m	1308 vs	1313 s	1306 m,p	1315 m	ν_6,ν_{22}?
		1233 vw			499 + 728 = 1227
		1206 m			ν_{23}?
1195 m	1182 vs	1191 s			ν_7,ν_{23} or ν_{25}?
		1145 vw			ν_8 or ν_{24}

TABLE 9 - CONT'D.

Infrared Gas(13)	 Liquid(56	 Solid(13) (-180°C)	Raman Liquid (-30°C)	 Solid (-180°C)	Assignment
			1103 vw	1107 m	ν_8 or ν_{24}
1073 w	1068 s	1073 m	1071 w,dp?	1075 m	ν_{25}
		1002 sh			2 x 499 = 998
989 s	990 vs	994 s	989 m,dp?	999 m	ν_9
814 s	800 vs	764 s	792 m,p?	759 m	ν_{26}
770 s	743 vs	728 m	743 m,dp?		ν_{10}
704 m	705 s	707 vs	705 vs,p	704 s	ν_{11}
501 w,br		499 w	495 w	494 w	ν_{12}
		486 vvw			skeletal?
			393 vw		ν_{13}?
			336 w		skeletal?
			168 vvw		ν_{15} or ν_{28}?

frequency assignments have been made for these vibrations with the assistance of polarization data.

Although considerable vibrational data have appeared in the literature concerning dimethylamine and dimethylamino-derivatives, there seems to be some disagreement about the assignments for the methyl rocking and asymmetric C-N stretching vibrations. The methyl rocking and the asymmetric C-N stretching frequencies most generally have been assigned to bands in the regions 1125-1260 cm^{-1} and 1015-1090 cm^{-1} respectively for $(CH_3)_2NH$ (22,57,58), for $[(CH_3)_2NH_2]Cl$ (58), and for $[(CH_3)_2NH_2]I$ (59). On the other hand, evidence for a higher frequency asymmetric C-N stretch around 1020-1220 cm^{-1} (for secondary aliphatic amines) has been cited by Bellamy (51) and Stewart (52). In addition, Goubeau, Rahtz and Becher (60) and also Banister and co-workers (61) have assigned the asymmetric C-N stretch in $(CH_3)_2NBCl_2$ to a band around 1143 cm^{-1} and the methyl rocks to bands near 1199 cm^{-1} and 978-1068 cm^{-1}. The higher C-N frequency assignment is substantiated further by the observation of an asymmetric C-C stretching frequency near 1170 cm^{-1} in the 2-methylalkanes (51). With the present information at hand, one is not able to make definite assignments to the methyl rocks and asymmetric C-N stretch without further spectroscopic data of $(CD_3)_2NH$ and some of its derivatives.

A very strong band around 1190 cm^{-1} is observed in the infrared spectrum of $(CH_3)_2NPF_2$ (13,56) but not in the Raman.

The assignment of this frequency to a methyl rock (13), perhaps the methyl rocking motions perpendicular to the C-N-C plane, is consistent with similar assignments for $(CH_3)_2NH$. A very weak band at 1103 cm^{-1} is observed in the Raman spectrum but not in the infrared and is thought to be one or both of the in C-N-C plane methyl rocking motions. The remaining torsional frequencies were not observed in the Raman spectrum but are probably found near 260 cm^{-1} as evidenced by far infrared studies of $(CH_3)_2NH$ (62).

The tentative assignments for the asymmetric C-N stretching and the symmetric C_2-N-P group vibrations have been made identical to those of Sr. Fleming (13). The respective motions are observed in the Raman as a weak band at 1071 cm^{-1} and as a medium band at 989 cm^{-1}. Polarization data for these bands are of little value because the band intensities are too small to determine depolarization ratios accurately. The asymmetric C-N stretch frequency at 1071 cm^{-1} correlates well with that reported for $(CH_3)_2NH$ (22) and for $(CH_3)_2NPCl_2$ (23), while both the position and existence of the C_2-N-P group vibration at 989 cm^{-1} is cited by Bellamy (51) and also by Holmstedt and Larsson (63).

The intense infrared bands at 743 cm^{-1} and 792 cm^{-1} without doubt are the symmetric and asymmetric P-F stretching vibrations, because similar bands are found at 874 cm^{-1} and 832 cm^{-1} for PF_3 (17), at 944 cm^{-1} and 957 cm^{-1} in F_3PBH_3 (5), and at 723 cm^{-1} and 781 cm^{-1} in $Ni(PF_2CH_3)_4$ (19). However, there is some question as to which mode is higher in frequency, the asymmetric or symmetric vibration. In PF_3 the symmetric mode is higher while in F_3PBH_3 the asymmetric mode is higher. Raman polarization results favor the lower frequency as the asymmetric mode but the bands are sufficiently weak in the Raman effect to make accurate determination of the depolarization ratio impossible. Therefore the higher frequency was assigned to the asymmetric mode in accordance with the present P-F stretching assignments for F_3PBH_3 and fluorophosphine derivatives.

Several workers have attempted to establish a frequency region for the P-N stretching vibration (51,53,54,63). Although the intensity and position of the N-P stretching band seem to be influenced by neighboring groups, it is quite frequently found in the region from 680 cm^{-1} to 750 cm^{-1}. Therefore the strong band at 705 cm^{-1} very likely is the symmetric $N\text{-}P\text{-}F_2$ stretching group frequency in agreement with the assignment proposed by Sr. Fleming (13). It is also interesting to note that a similar group vibration is known to occur in the infrared spectrum of $(CH_3)_2NPCl_2$ at 690 cm^{-1} (23).

A weak band at 495 cm^{-1} is found in both the infrared and Raman spectra and is probably the symmetric PF_2 deformation frequency because the comparable band in PF_3 is found around 484 cm^{-1} and at 482 cm^{-1} in $Ni(PF_2C_6H_5)_4$ (19). The very weak absorption band at 393 cm^{-1} is considered to be the NC_2 deformation frequency in agreement with the assignment of a weak Raman band at 390 cm^{-1} (57) and a far infrared band at 383 cm^{-1} (62) for $(CH_3)_2NH$. Stewart also reports that this deformation mode appears in the infrared around 427 ± 14 cm^{-1} for a large number of dialkylamines (25).

Three bands remain to be assigned: a very weak infrared band at 486 cm^{-1} (13) and two weak Raman bands at 336 cm^{-1} and 168 cm^{-1}. The low band at 168 cm^{-1} may be one of the PF_3 rocking modes because the corresponding degenerate vibration in F_3PBH_3 is found near 197 cm^{-1} (5). No attempt has been made to characterize the other two bands because little or no data is avilable concerning the possible frequencies of the NC_2 rocks and the P-N torsional vibration.

Dimethylaminodifluorophosphine-Borane, $(CH_3)_2NPF_2BH_3$ and $(CH_3)_2NPF_2B^{11}D_3$.

This molecule at most may have C_s molecular symmetry assuming a similar symmetry for the free ligand, $(CH_3)_2NPF_2$, and knowing that a phosphorus-boron dative bond is present as shown by nuclear magnetic resonance studies (13). The hypothesis that this molecule belongs to the C_s point group requires that it have forty-two fundamental vibrations with the symmetry distribution 23A' + 19A". Of these modes, thirty may be considered as belonging to the $(CH_3)_2NPF_2$ ligand, six involve the vibrations of the borane group and six motions arise as a consequence of the dative bond formed between the

Lewis base and the borane Lewis acid. A complete listing of the fundamental vibrations and descriptions of their motions are tabulated in Table 10.

The observed Raman spectra of liquid (-24°C) and of solid (-180°C) $(CH_3)_2NPF_2BH_3$ are shown in Figure 16 and the polarized Raman spectra may be seen in Figure 17. In addition, infrared absorption spectra of gaseous and liquid $(CH_3)_2NPF_2$-$B^{11}D_3$ were observed and are represented in Figures 18 and 19 respectively. Raman spectra of the liquid and solid deuterated samples were also recorded and are shown in Figures 20 and 21. The observed Raman vibrational frequencies of $(CH_3)_2NPF_2BH_3$ agree, within the limits of experimental error, with the infrared values reported in the literature (13). The observed infrared and Raman frequencies and their tentative assignments, for both the natural hydrogen and the deuterated borane complexes, are given in Tables 11 and 12 respectively. For purposes of comparison, several vibrational frequencies are exhibited in Table 13 which are particularly sensitive to isotopic substitution in the borane group. A more detailed discussion of these figures and tables follows.

The vibrational spectra of $(CH_3)_2NPF_2BH_3$ and of the borane 11-d_3 complex are remarkably similar to that of the free ligand. The most evident similarities are found in the methyl group stretching and deformation regions around 2900 cm^{-1} and 1450 cm^{-1} respectively. Because the intensities,

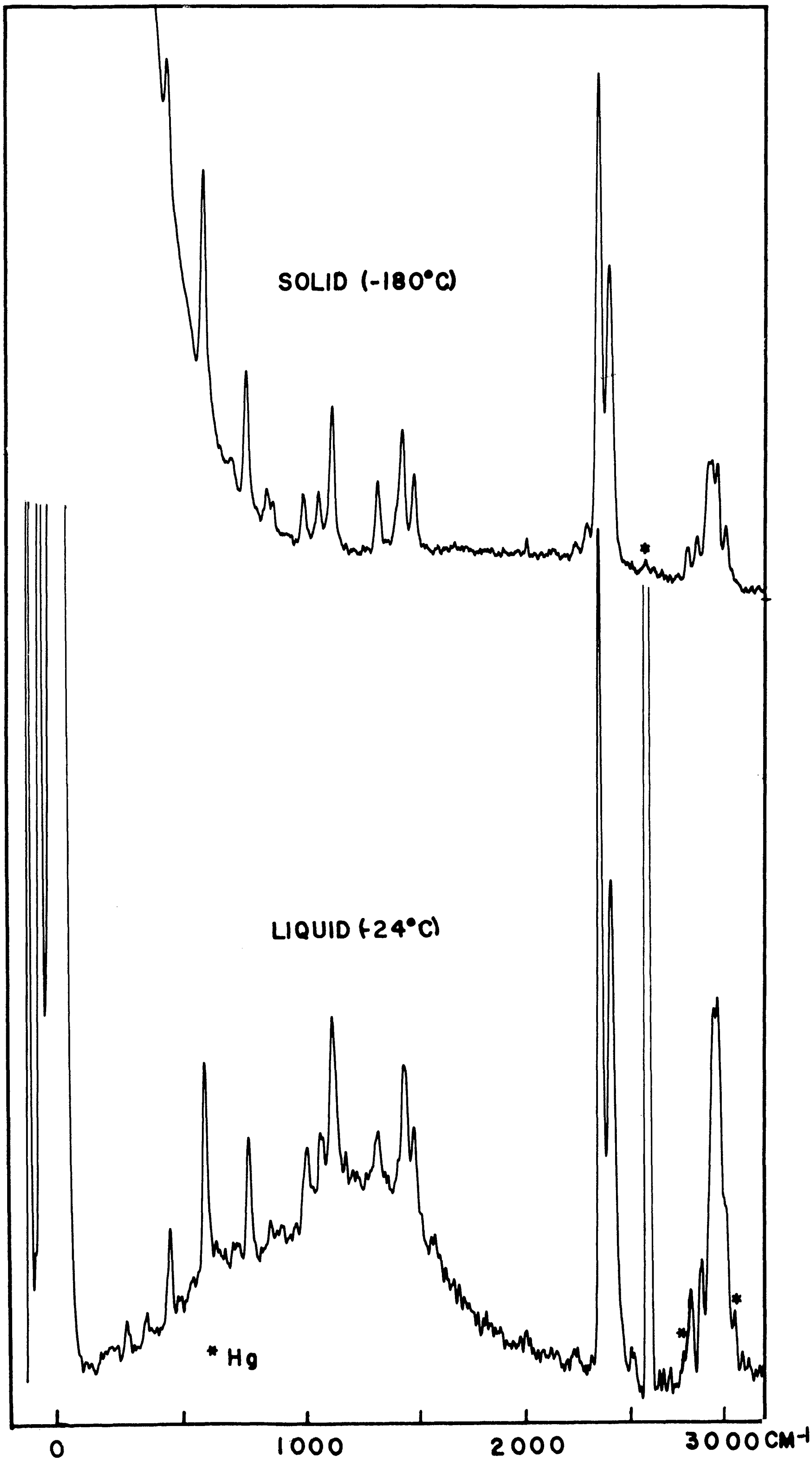


FIGURE 16 - THE RAMAN SPECTRA OF SOLID (-180°C) AND LIQUID (-24°C) $(CH_3)_2NPF_2BH_3$

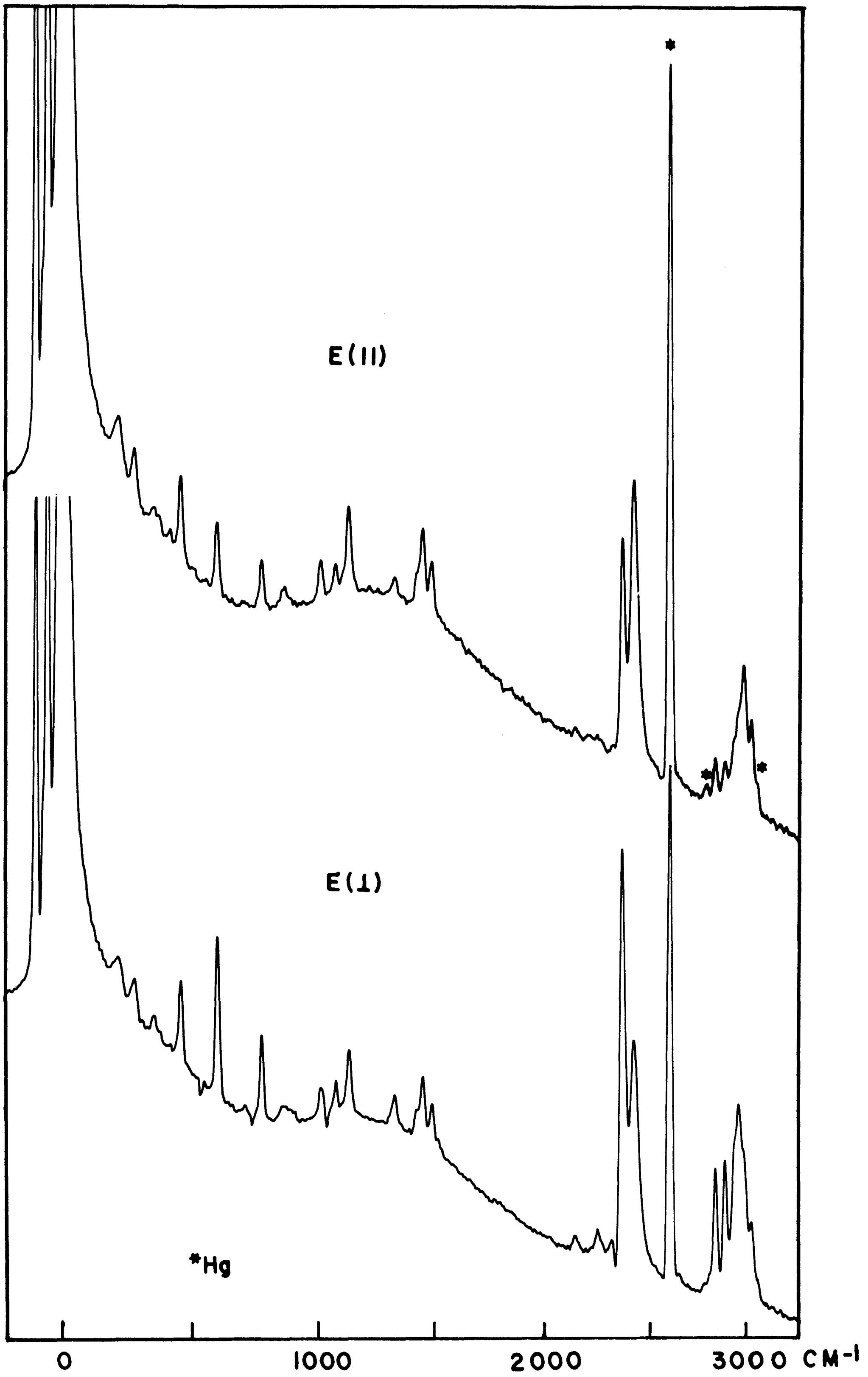


FIGURE 17 - THE POLARIZED RAMAN SPECTRA OF LIQUID $(CH_3)_2NPF_2BH_3$ (-15°C)

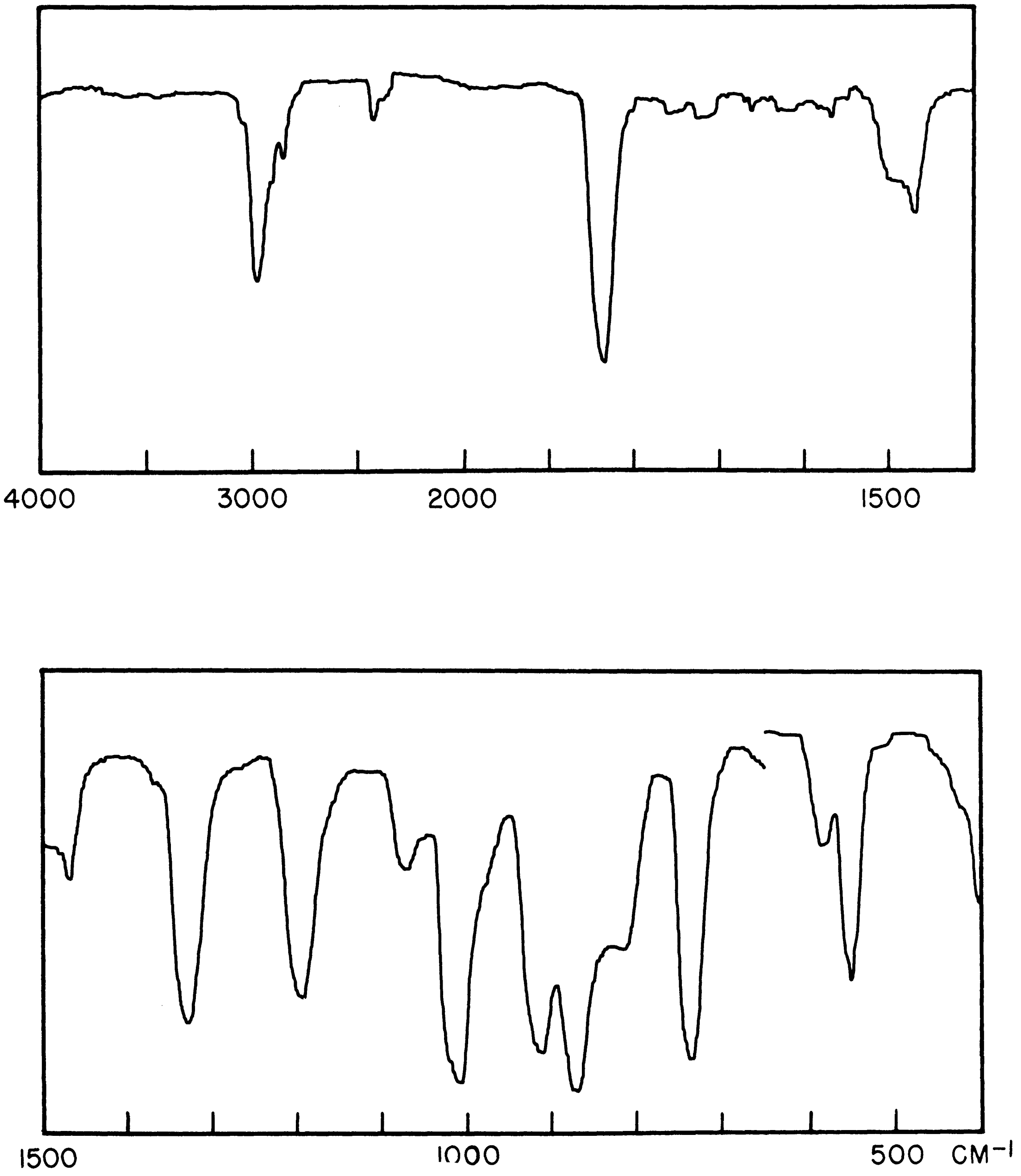


FIGURE 18 - THE INFRARED SPECTRUM OF GASEOUS $(CH_3)_2NPF_2B^{11}D_3$ (11 mm)

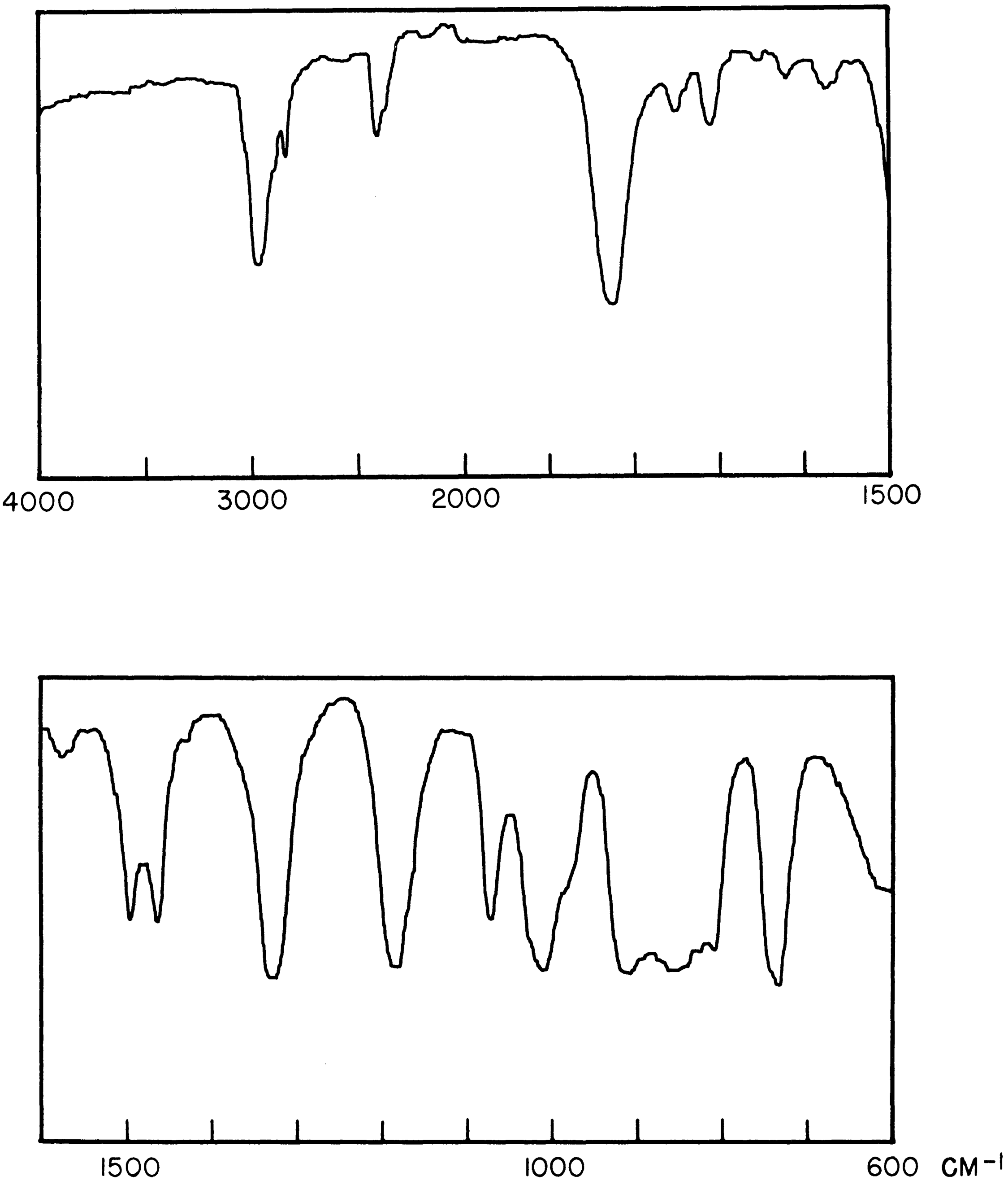


FIGURE 19 - THE INFRARED SPECTRUM OF LIQUID $(CH_3)_2NPF_2B^{11}D_3$ (25°C)

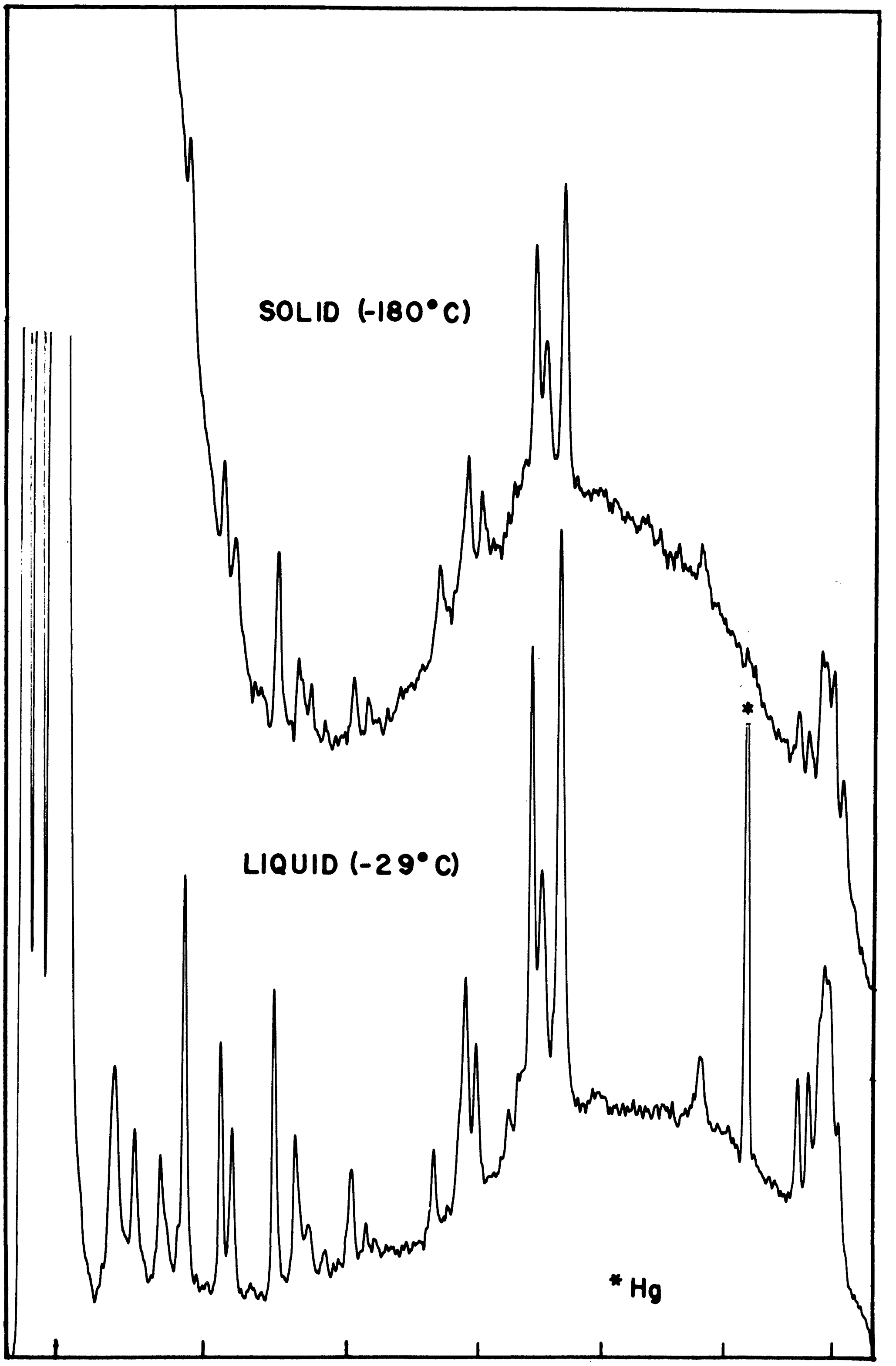


FIGURE 20 - THE RAMAN SPECTRA OF SOLID (-180°C) AND LIQUID (-29°C) $(CH_3)_2NPF_2B^{11}D_3$

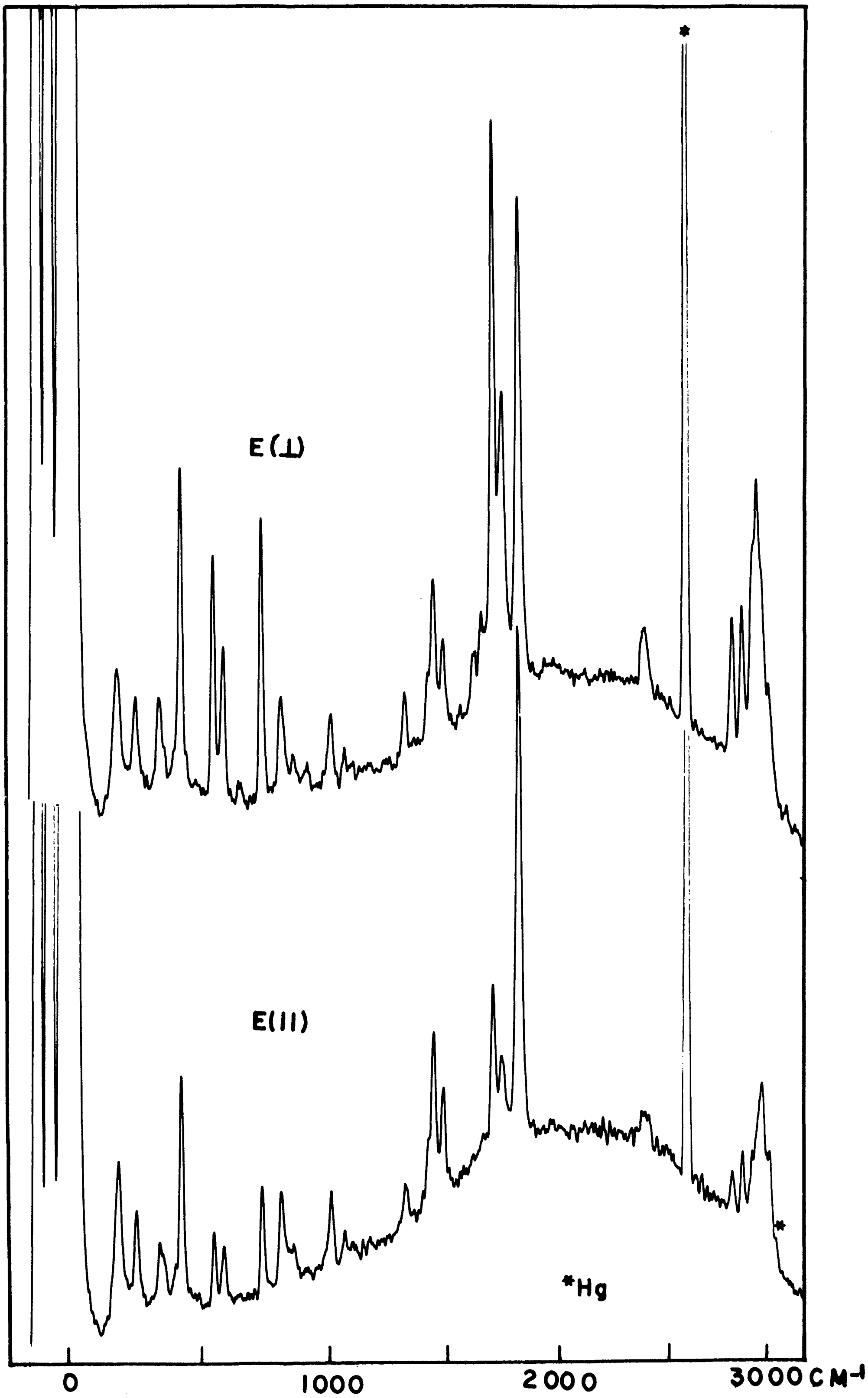


FIGURE 21 - THE POLARIZED RAMAN SPECTRA OF LIQUID $(CH_3)_2NPF_2B^{11}D_3$ (-29°C)

TABLE 10

THE FUNDAMENTAL VIBRATIONS OF $(CH_3)_2NPF_2BH_3$, C_s SYMMETRY

Symmetry	Number	Description
A'	1	in phase asymmetric C-H stretch
	2	in phase asymmetric C-H stretch
	3	in phase symmetric C-H stretch
	4	asymmetric B-H stretch
	5	symmetric B-H stretch
	6	in phase asymmetric CH_3 deformation
	7	in phase asymmetric CH_3 deformation
	8	in phase symmetric CH_3 deformation
	9	asymmetric BH_3 deformation
	10	symmetric BH_3 deformation
	11	CH_3 rock (out of C-N-C plane)
	12	CH_3 rock (in C-N-C plane) or CH_3 wag
	13	BH_3 rock
	14	C_2—N-P stretch
	15	P-F stretch
	16	N—P-F_2 stretch
	17	P-B stretch
	18	N-P-B deformation
	19	F-P-F deformation
	20	C-N-C deformation
	21	C_2N rock
	22	PF_2 rock
	23	CH_3 torsion

TABLE 10 - CONT'D.

Symmetry	Number	Description
A''	24	out of phase asymmetric C-H stretch
	25	out of phase asymmetric C-H stretch
	26	out of phase symmetric C-H stretch
	27	asymmetric B-H stretch
	28	out of phase asymmetric CH_3 deformation
	29	out of phase asymmetric CH_3 deformation
	30	out of phase symmetric CH_3 deformation
	31	asymmetric BH_3 deformation
	32	CH_3 rock (out of C-N-C plane)
	33	CH_3 rock (in C-N-C plane) or CH_3 wag
	34	BH_3 wag
	35	C-N stretch
	36	P-F stretch
	37	F-P-B deformation
	38	C_2N wag
	39	PF_2 wag
	40	CH_3 torsion
	41	BH_3 torsion
	42	C_2N torsion or P-N torsion

TABLE 11

THE OBSERVED INFRARED AND RAMAN VIBRATIONAL FREQUENCIES OF $(CH_3)_2NPF_2BH_3$

Infrared		Raman		Assignment
gas(25°C)	liquid(25°C)	liquid(-24°C)	solid(-180°C)	
3014 vw		3011 s,sh,dp	3015 m,sh	ν_{24},ν_{25}
		2971 vs,p	2972 ms	2 x 1486 = 2972
2945 m	2937 w	2941 vs,sh,p	2942 ms	ν_{26}?
	2917 w	2917 s,sh,p	2917 ms,sh	ν_1?
2885 w,sh		2875 m,sh,p	2864 m,sh	ν_2?
2820 w	2810 vw	2827 m,sh,p	2813 m,sh	ν_3,ν_{26}?
2620 vw,br				2 x 1325 = 2650
2440 s	2413 ms	2421 vs,dp	2419 vs	ν_4,ν_{27}
2375 w	2348 w,sh	2366 vs,p	2364 vs	ν_5
			2311 vw	1128 + 1180 = 2308
2245 vw	2228 vw	2249 vw,p	2251 vw	2 x 1128 = 2256
		2144 vw,p		2 x 1074 = 2148
1470- 1490 sh	1486 w	1486 w,sh,dp	1492 m	ν_{28}
1465 m	1455 w	1445 m,dp	1439 ms	ν_{29},ν_6?
		1418 w,sh,dp	1413 w,sh	ν_7?
1320 ms	1323 m	1325 w,p	1331 m	ν_8,ν_{30}
1187 m	1180 ms			ν_{11},ν_{32} or ν_{35}?
1121 w	1125 w	1128 m,dp	1130 ms	ν_9,ν_{31}
		1108 w,sh		ν_{12},ν_{33}

TABLE 11 - CONT'D.

Infrared		Raman		Assignment
gas(25°C)	liquid(25°C)	liquid(-24°C)	solid(-180°C)	
1071 m	1070 mw	1074 w,p?	1072 m	ν_{35} and ν_{10}?
1010 vs	1006 s	1013 w,dp?	1008 m	ν_{14}
891-873 vs,br	880 s	862 vw,dp?	877 w	ν_{36}
	851 s		853 w	ν_{15}
753 s	765 ms	768 m,p	767 ms	ν_{13}
701 w	694 vw	705 vw	705 vw	ν_{16}
		660 vvw	659 vvw	skeletal
586 mw	586 mw	591 m,p	590 ms	ν_{17}
441 vvw,br	443 vvw,br	447 m,p?	445 w	ν_{19}
		408 vvw		ν_{20}
		376 vvw		skeletal
		344 w,p?	346 vw	skeletal
		270 w,dp?		ν_{23} and/or ν_{40}
		211 w,dp?		skeletal

TABLE 12

THE OBSERVED INFRARED AND RAMAN VIBRATIONAL FREQUENCIES OF $(CH_3)_2NPF_2B^{11}D_3$

Infrared		Raman		Assignment
gas(11mm)	liquid(25°C)	liquid(-30°C)	solid(-180°C)	
3020±10 vw,sh	3008±10 w,sh	3009 w,sh,dp	3024 vw	ν_{24},ν_{25}
		2974 m,sh,p	2980 w	2 x 1488 = 2976
2948±10 s	2942±10 ms	2945 m,p	2948 w	ν_{26}?
		2923 m,sh,p	2918 w	ν_1?
2880±10 m,sh	2867±10 m,sh	2872 w,p	2867 vw	ν_2?
2829±10 w,sh	2816±10 m,sh	2826 w,p	2819 vw	ν_3,ν_{26}?
2405±10 w	2385± 5 w	2395 vw,p	2388 vvw	1070 + 1322 = 2392
2355±10 w,sh	2357± 5 w,sh			ν_5 (BH_3)
1827 s	1819 s	1818 vs,dp	1822 s	ν_4,ν_{27}
1792 vvw,sh				
1752- 1732 vw,br	1746 w,sh	1743 ms,p	1750 m	2 x 873 = 1746 or ν_5?
1717- 1697 vvw,br	1704 w,sh	1705 vw,p	1708 ms	ν_5
	1649 vvw	1652 vw,sh,p?	1656 vvw	737 + 912 = 1649
	1616 vw	1618 vw,sh,p?		2 x 814 = 1628
	1569 vw			252 + 1322 = 1574
	1507 w,sh?			183 + 1322 = 1505
1492 m,sh	1488 ms	1485 w,dp	1496 w	ν_{28}
1460 m	1454 ms	1446 m,dp	1445 w	ν_{29},ν_6?

TABLE 12 - CONT'D.

Infrared		Raman		Assignment
gas(11mm)	liquid(25°C)	liquid(-30°C)	solid(-180°C)	
	1419 vw,sh	1420 w,sh,dp		ν_7?
1321 s	1322 s	1323 w,p	1434 w	ν_8,ν_{30}
1189 s	1178 s			ν_{11},ν_{32} or ν_{35}?
		1101 vvw	1104 vvw	ν_{12},ν_{33}
1071 w	1070 ms	1069 vvw	1070 vw	ν_{35}
1007 vs	1007 s	1017 w	1019 vw	ν_{14}
		980±5 ms,sh?		252 + 737 = 989
913 s	912 s,br	916 vvw,p?	911 vvw	ν_{10}
	894 s,sh?			
873 vs	870- 850 s,br	860 vw,sh,dp?	862 vw	ν_{36}
	826 s,sh			
817 ms,sh	810 s	814 w,dp?	818 w	ν_9,ν_{31}
745 s,sh	747 s,sh			
738 s	737 s	736 ms,p	743 m	ν_{15}
		651 vvw?		skeletal
584 w		588 w,p	596 vw	ν_{13}
552 ms		549 m,p	552 w	ν_{17}
		423 s,p	435 vw	ν_{19}
		398 vvw,sh		ν_{20}
		340 v,p		skeletal
		252 w		ν_{23} and/or ν_{40}
		183 m,dp		skeletal

TABLE 13

A COMPARISON OF SOME ISOTOPE DEPENDENT VIBRATIONS OF $(CH_3)_2NPF_2BH_3$ AND $(CH_3)_2NPF_2B^{11}D_3$ (CM^{-1})

Assignment*		$(CH_3)_2NPF_2BH_3$	$(CH_3)_2NPF_2B^{11}D_3$	Frequency Ratio
ν_4, ν_{27}	ν^aB-H	2418	1821	1.33
ν_5	ν^sB-H	2362	1706	1.38
ν_9, ν_{31}	$\delta^a BH_3$	1128	815	1.38
ν_{10}	$\delta^s BH_3$	(1072)	913	(1.17)
ν_{13}	ρ BH_3	767	589	1.30
ν_{34}	ω BH_3	----	----	----
ν_{41}	τ BH_3	----	----	----
ν_{17}	ν P-B	589	551	1.07

*ν = stretch, δ = deformation, ρ = rock, ω = wag and τ = torsion

shapes and frequencies of these bands are nearly identical to those of the ligand and to a lesser degree those of dimethylamine, their assignments are based upon those observed for the latter two compounds. Although these are somewhat arbitrary, they are probably as reliable as those reported for dimethylamine and its derivatives. Reference may be made to Tables 11 and 12 for specific assignments to these vibrations.

The very strong doublet which appears near 2362 cm^{-1} and 2418 cm^{-1} in the Raman spectrum of $(CH_3)_2NPF_2BH_3$ is most certainly due to components of the symmetric and asymmetric borane stretching fundamentals, since they are not present in the spectrum of the ligand and because they shift to 1706 cm^{-1} and 1821 cm^{-1} upon deuteration. The weak to medium intensity band at 1746 cm^{-1}, found in the infrared and Raman spectra of the deuterated sample, is considered to be an overtone of ν_{36} rather than the symmetric B-H stretching fundamental because its intensity is considerably weaker than the other two bands. The relatively low ratio of the 2362 cm^{-1} and 1746 cm^{-1} frequencies, 1.35, also gives credence to this assignment. Since only one asymmetric B-H stretching vibration is observed, the influence of the ligand is probably not sufficient to cause an observable splitting of ν_4 and ν_{27}.

A strong band is observed near 1185 cm^{-1} in the infrared spectra of both isotopic samples, but is absent in the Raman effect. Sr. Fleming has assigned this band to a methyl rock (13).

However, in view of the fact that some workers have assigned the asymmetric C-N stretch of various secondary aliphatic amines to bands in this region, this assignment remains uncertain. Of the two possibilities, the former is given more weight because it agrees with the majority of the assignments reported in the literature. A lower band at 1105 cm^{-1}, appearing only in the Raman effect, probably is a methyl rock since a similar band is observed in the Raman spectrum of the free ligand.

A moderately intense, depolarized band is observed near 1128 cm^{-1} in both the infrared and Raman spectra of the non-deuterated sample. Since this band is absent in the spectrum of the deuterated sample, it is assigned to the asymmetric borane deformation modes, ν_9 and ν_{31}. This assignment correlates quite well with the known asymmetric borane deformation of $(CH_3)_3NBH_3$ at 1169 cm^{-1} (69), of $(CH_3)_3PBH_3$ at 1136 cm^{-1} and of F_3PBH_3 at 1117 cm^{-1} (5). Upon deuteration this vibration shifts to 815 cm^{-1} yielding an isotopic frequency ratio of 1.38.

The assignments of the C_2-N-P group vibration and of the asymmetric C-N stretch to bands at 1008 cm^{-1} and 1072 cm^{-1} respectively are made in agreement with those proposed by Sr. Fleming (13). The assignment of the higher frequency bears further explanation because other possibilities exist. Although the asymmetric C-N stretch in many dialkylamines has been reported to be near 1160 cm^{-1} (52), the majority of workers place it in the 1025-1100 cm^{-1} region. Therefore, in keeping with the majority, the assignment of the C-N fundamental to the 1072 cm^{-1} band is preferred. Because of the closeness of this band to the observed symmetric borane deformation vibrations in $OCBH_3$ (21), F_3PBH_3 and $(CH_3)_3PBH_3$ at 1073 cm^{-1}, 1077 cm^{-1} and 1070 cm^{-1} respectively, it is likely that the band envelope also contains the borane deformation fundamental. If this were the case, deuteration of the sample would cause this frequency to shift to around 850 cm^{-1} as is observed for many borane complexes.

Several vibrational bands are observed in the region 725-925 cm^{-1} for both isotopic varieties of the complex. In the infrared spectrum of the non-deuterated sample three bands are observed: a medium strong band at 767 cm^{-1} and a strong doublet at 851 cm^{-1} and 880 cm^{-1}. The identical bands appear in the Raman effect but their intensities are reversed. Although Sr. Fleming assigned the two lower bands to P-F stretching fundamentals and the higher to a borane rock (13), it is believed that these bands are better assigned by reversing the order of the previous assignments. These are reversed on the basis that the P-F stretching fundamentals of $(CH_3)_2NPF_2BF_3$, tentatively assigned to bands at 850 cm^{-1} and 880 cm^{-1}, coincide exactly with those of the borane complex. Even though polarization data are inconclusive, the higher vibration at 880 cm^{-1} is assigned to the asymmetric P-F stretch and the lower to the symmetric fundamental by analogy to similar compounds. The remaining polarized band at 767 cm^{-1}, assigned to the borane rock, shifts to 589 cm^{-1} upon deuteration. This frequency shift is larger than expected (ratio of the frequencies = 1.30), however it may be justified in view of the strong vibrational coupling observed in the spectrum of the deuterated sample. In the region in question, the vibrational spectrum of the deuterated sample is not well understood because of its complexity. Four bands around 738 cm^{-1}, 815 cm^{-1}, 865 cm^{-1} and 913 cm^{-1} are clearly observed along with several shoulders. Of these bands, the two near 815 cm^{-1} and 865 cm^{-1} appear to be depolarized, while the 738 cm^{-1} band is definitely polarized and the polarization of the 913 cm^{-1} band is questionable. The 815 cm^{-1} band has been previously assigned to the asymmetric borane-d_3 deformation. The band at 865 cm^{-1} is not affected by isotopic borane substitution and probably is the asymmetric P-F stretch. The two bands at 738 cm^{-1} and 913 cm^{-1} cannot be explained on the basis of Fermi resonance or overtones, and their strong band intensities suggest that they are fundamentals. Because both the expected symmetric borane-d_3 deformation and the symmetric P-F stretch are found near 850 cm^{-1}, these modes may be expected to couple very strongly with each other, thereby causing their frequencies to split. If this is true, then the 738 cm^{-1} band may be the symmetric P-F stretch and the 913 cm^{-1} band may very well be the symmetric borane-d_3 deformation vibration. The exceptionally low frequency ratio of the borane deformation fundamentals, (1072)/913 = 1.17, is probably the result of such coupling. The observed shoulders remain unassigned.

Assignments to the remaining observed frequencies require little discussion and will only be enumerated. A weak band at 700 cm^{-1} is observed in both the infrared and Raman spectra of the non-deuterated sample, but is absent in the spectra of the deuterated compound. The assignment of the N-P-F_2 stretch to this vibration by Sr. Fleming (13) remains unchanged in the present work. The polarized band near 589 cm^{-1} in the hydrogen compound shifts to 551 cm^{-1} upon deuteration, and is most assuredly the P-B stretching vibration. This assignment correlates very well with the observed P-B stretch in F_3PBH_3 at 607 cm^{-1}. The polarized band near 444 cm^{-1} and 430 cm^{-1} in the respective natural hydrogen and deuterated samples is assigned to the PF_2 deformation in view of a similar vibration of the ligand near 393 cm^{-1}. The weak Raman bands at 408-398 cm^{-1} and at 270-252 cm^{-1} are assigned to the C_2N deformation and methyl torsional modes respectively by analogy to similar vibrations in dimethylamine at 383 cm^{-1} and 257 cm^{-1} (62). Several skeletal vibrations are observed below 600 cm^{-1} and no attempt has been made to characterize them. The assignments for combinations and overtones which are listed in Tables 11 and 12 are quite arbitrary because of uncertainties involved with the selection of the fundamentals.

Dimethylaminodifluorophosphine-Boron Trifluoride, $(CH_3)_2NPF_2$-$B^{10}F_3$ and $(CH_3)_2NPF_2B^{11}F_3$.

Nuclear magnetic resonance studies have indicated that the boron trifluoride Lewis acid does not bond through the phosphorus atom of $(CH_3)_2NPF_2$ as does the borane group, but rather through the nitrogen atom (13). Although the bonding site in the boron trifluoride complex is different than in the borane complex, the molecule is expected to have essentially the same C_s molecular symmetry.

Analogous to the previously mentioned borane complex, this molecule possesses forty-two Raman and infrared active fundamental vibrations: six of which may be regarded as involving primarily motions of the boron trifluoride group, six result from the formation of the B-N dative bond and the remaining fundamentals may be considered as belonging to the Lewis base.

Raman spectra of $(CH_3)_2NPF_2BF_3$ at -78°C, enriched in the boron-10 and 11 isotopes, were studied and are represented in Figure 22. Although this compound is reported to have a very intense infrared absorption spectrum (13), its Raman spectrum is very weak. The weak scattering ability of this compound is probably the primary factor contributing to the low intensity of the Raman spectrum. The observed infrared and Raman frequencies of $(CH_3)_2NPF_2B^{11}F_3$ are compared with those of $(CH_3)_2NPF_2$ and of $(CH_3)_3NB^{11}F_3$ in Table 14. In addition, the reported infrared frequencies, their observed

Raman counterparts and their tentative assignments are listed in Table 15 for both the boron-10 and 11 trifluoride complexes. For the most part, the present assignments are identical to those reported for the infrared results (13). Therefore, only those frequencies and their assignments which are different will be mentioned in the following discussion.

The bands associated with the methyl stretching motions in the 2800-3050 cm^{-1} region are decidedly different in the infrared and the Raman spectra and also between the spectra of the ligand, of the borane complex and of the boron trifluoride complex. The C-H stretching frequencies are extremely broad and low in intensity in the solid infrared spectrum. However, in the Raman effect a medium strong doublet is observed at 2980 cm^{-1} and 3044 cm^{-1}. The lower band correlates very well with the asymmetric C-H stretching vibrations of the ligand at 2998 cm^{-1} and of the borane complex at 3011 cm^{-1}, but the assignment for the 3044 cm^{-1} band is more doubtful. The frequency of the latter band coincides exactly with a frequently observed weak mercury emission line of the source, however, its surprising intensity in the present spectra leads to the conclusion that this band is due to an asymmetric C-H stretching fundamental rather than the mercury line. The very weak infrared band at 2907 cm^{-1} (13) is absent in the Raman effect and is also probably a methyl stretching fundamental. The characteristic symmetric C-H stretching vibration, found near 2815 cm^{-1} in similar dimethylamino-compounds, is clearly missing in both the

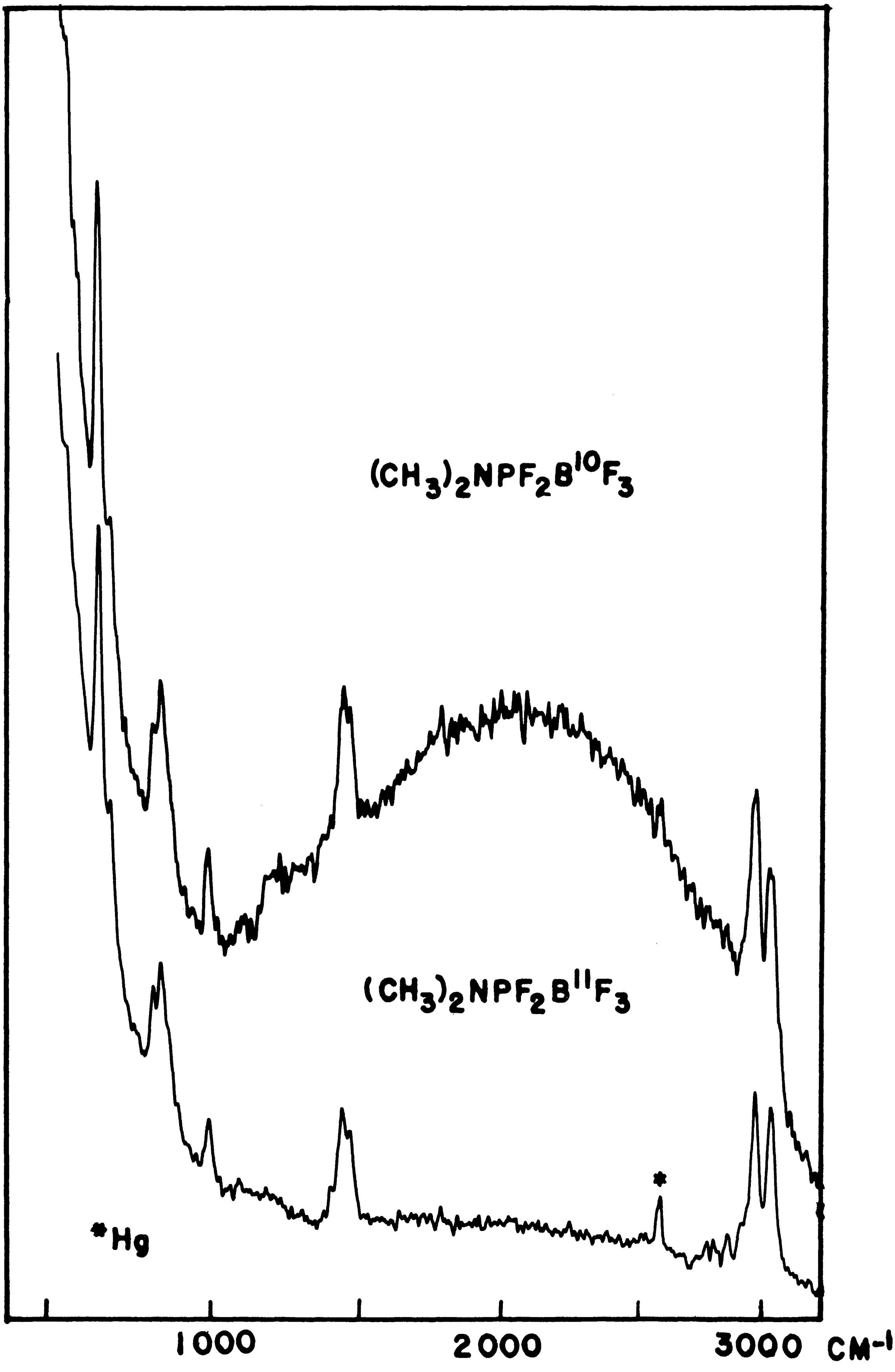


FIGURE 22 - THE RAMAN SPECTRA OF $(CH_3)_2NPF_2B^{10}F_3$ AND $(CH_3)_2NPF_2B^{11}F_3$ (-78°C)

TABLE 14

A COMPARISON OF OBSERVED INFRARED AND RAMAN FREQUENCIES OF $(CH_3)_3NB^{11}F_3$, $(CH_3)_2NPF_2$ AND $(CH_3)_2NPF_2B^{11}F_3$

$(CH_3)_3NB^{11}F_3$(24)		$(CH_3)_2NPF_2$(liquid)		$(CH_3)_2NPF_2B^{11}F_3$		Assignment and Symmetry
Infrared	Raman	Infrared(56)	Raman	Infrared(13)	Raman	
3033 w	3030 s				3043 ms	asym. C-H stretch (a")
3013 m						
			2998 s,sh,dp		2978 ms	asym. C-H stretch (a")
2971 sh 2954 s	2967 s	2945 vs,dp				
2924 vw		2908 s	2912 vs,p?	2908 vw,br		asym. C-H stretch (a')?
2890 w	2889 m					
2868 vw			2861 s,p		2871 vw?	asym. C-H stretch (a')?
2845 vw						
2807 vw	2802 sh	2808 s	2814 s,p			
		1691 w				
				1506 vw		417+1101=1518
				1496 vw		650+850=1500
1487 m		1484 s	1487 m,dp	1486 w		asym. CH_3 deformation (a")
1480 w				1474 w	1474 w,sh	asym. CH_3 deformation (a")

TABLE 14 - CONT'D.

$(CH_3)_3NB^{11}F_3$ (24)		$(CH_3)_2NPF_2$ (liquid)		$(CH_3)_2NPF_2B^{11}F_3$		Assignment and Symmetry
Infrared	Raman	Infrared(56)	Raman	Infrared(13)	Raman	
1469 w	1473 vs	1468 w		1465 vw		asym. CH_3 deformation (a')
1454 w				1456 vw		561+907=1468
		1450 s	1439 s,dp	1445 vw	1445 m	asym. CH_3 deformation (a')
				1431 vw		561+880=1441
				1424 vw		417+1008=1425
1412 vw	1413 vw		1414 w,sh,dp?	1414 mw,br	1403 vw,sh?	sym. CH_3 deformation (a' or a")?
		1308 vs	1306 m,p			
1271 vw						
1255 w	1253 w			1235 w		CH_3 rock (a")?
1208 w				1200 mw		CH_3 rock or wag (a' and/or a")?
1175 sh	1178 vvw	1182 vs		1171 ms,br		CH_3 rock (a' and/or a") or C-N stretch (a")?
1142 s,br				1151 vs		asym. B-F stretch (a' and/or a")
				1121 mw		2 x 561 = 1122
1104 m	1105 w		1103 vw	1101 mw		CH_3 wag (a' and/or a")?
		1068 s	1071 w,dp?			
1017 vw						

TABLE 14 - CONT'D.

$(CH_3)_3NB^{11}F_3$(24)		$(CH_3)_2NPF_2$(liquid)		$(CH_3)_2NPF_2B^{11}F_3$		Assignment and Symmetry
Infrared	Raman	Infrared(56)	Raman	Infrared(13)	Raman	
991 w	988 s					
841 s	842 s	990 vs	989 m,dp?	1008 w	1003 w	C_2—N-P stretch (a')
				921 vw,sh		B(10)-F stretch (a')
932 s	935 w,sh			907 m		B(11)-F stretch (a')
		800 vs	792 m,p?	880 s	879 w,sh?	P-F stretch (a")
		743 vs	743 m,dp?	850 s	852 m	P-F stretch (a')
				827 s	827 w,sh	2 x 417 = 834?
		705 s	705 vs,p	692 s	690 vw	N—P-F_2 stretch (a')
692 m	694 s			650 ms	653 ms	B-N stretch (a')
640 vw						
547 w	545 vw			561 m	551 vw	BF_3 deformation (a')
519 vw,sh	513 vw				509 vvw?	skeletal?
			495 w	473 mw		PF_2 deformation (a')
464 vvw?						
				440 vw		skeletal
430 w	428 vvw					
	372 vw		393 vw	417 vw		C_2N deformation (a')?
340 w						
320 w			336 w			
			168 vvw			

TABLE 15

THE OBSERVED INFRARED AND RAMAN VIBRATIONAL FREQUENCIES OF $(CH_3)_2NPF_2B^{10}F_3$ AND $(CH_3)_2NPF_2B^{11}F_3$

$(CH_3)_2NPF_2B^{10}F_3$		$(CH_3)_2NPF_2B^{11}F_3$		Assignment and Symmetry
Infrared(13)	Raman	Infrared(13)	Raman	
	3044 w		3043 ms	asym. C-H stretch (a")
	2981 ms		2978 ms	asym. C-H stretch (a")
	2965 m,sh?			
	2948 w,sh?			
2907 vw		2908 vw,br		asym. C-H stretch (a')?
	2873 vw?		2871 vw?	asym. C-H stretch (a')?
1507 vw		1506 vw		417 + 1101 = 1518
1497 vw		1496 vw		650 + 850 = 1500
1485 w		1486 w		asym. CH_3 deformation (a")
1473 w	1474 m,sh	1474 w	1474 w,sh	asym. CH_3 deformation (a")
1466 vw		1465 vw		asym. CH_3 deformation (a')
1457 vw		1456 vw		561 + 907 = 1468
	1445 m	1445 vw	1445 m	asym. CH_3 deformation (a')
		1431 vw		561 + 880 = 1441
		1424 vw		417 + 1008 = 1425
	1410 vw,sh?	1414 mw,br	1403 vw,sh?	sym. CH_3 deformation (a' or a")?
1242 m		1235 w		CH_3 rock (a")?
1216 m				562 + 654 = 1216?
1201 s		1200 vw		CH_3 rock or wag (a' and/or a")?

TABLE 15 - CONT'D.

$(CH_3)_2NPF_2B^{10}F_3$		$(CH_3)_2NPF_2B^{11}F_3$		Assignment and
Infrared(13)	Raman	Infrared(13)	Raman	Symmetry
1189 s		1171 ms,br		CH_3 rock (a' and/or a") or C-N stretch (a")
1162 m				asym. B(10)-F stretch (a' and/or a")
1152 mw,sh		1151 vs		asym. B(11)-F stretch (a' and/or a")
		1121 mw		2 x 562 = 1122
		1101 mw		CH_3 wag (a' and/or a")?
1010 w	1006 w	1008 w	1003 w	C_2—N-P stretch (a')
921 s		921 vw,sh		B(10)-F stretch (a')
908 w		907 m		B(11)-F stretch (a')
884 s	878 w,sh	880 s	879 w,sh?	P-F stretch (a")
853 s	852 m	850 s	852 m	P-F stretch (a')
830 s	827 w,sh	827 s	827 w,sh	2 x 417 = 834?
699 s	698 vw	692 s	690 vw	N—P-F_2 stretch (a')
654 m	656 ms	650 ms	653 ms	B-N stretch (a')
	605 vvw?			
562 ms	558 vw	561 m	551 vw	BF_3 deformation (a')
511 vw	509 vvw?		509 vvw?	skeletal?
480 m		473 mw		PF_2 deformation (a')
445 vw		440 vw		skeletal
416 vw		417 vw		C_2N deformation (a')?

infrared and Raman spectra of the present boron trifluoride complex.

The vibrations associated with the methyl deformation modes show no peculiarities except for the fact that the totally symmetric methyl deformation vibration near 1315 cm^{-1} in the spectra of $(CH_3)_2NPF_2$ and $(CH_3)_2NPF_2BH_3$ is absent in the present spectra. The assignment of the 1235-1242 cm^{-1} medium infrared band to the symmetric methyl deformation mode by Sr. Fleming (13) is probably incorrect, and is better assigned to a methyl rocking fundamental in view of a similar vibration found near 1255 cm^{-1} in the spectrum of $(CH_3)_3NBF_3$ (24).

Several infrared bands are observed in the 1150-1200 cm^{-1} region for the different isotopic samples, but are absent in the Raman effect (see Table 15). The previous assignment of the asymmetric B(11)-F stretch to the 1152 cm^{-1} band appears to be correct (13). However, the assignment of the boron-10 fundamental to the 1189 cm^{-1} band in the spectrum of $(CH_3)_2NPF_2B^{10}F_3$ may be more correctly assigned to the 1162 cm^{-1} band in view of a similar vibration of $(CH_3)_3NB^{10}F_3$ at 1165 cm^{-1} (24). The remaining band at 1171 cm^{-1} or 1189 cm^{-1} is probably a methyl rocking vibration or the asymmetric C-N stretch by analogy to the observations for $(CH_3)_2NPF_2$ and $(CH_3)_2NPF_2BH_3$, with no preference being given to either assignment.

Vibrational assignments to bands appearing in the 800-900 cm^{-1} region also bear explanation. In this region, three infrared and Raman bands are observed at 827 cm^{-1}, 852 cm^{-1} and 880 cm^{-1}; and their frequencies are not affected by isotopic substitution of the boron atom. Previously, the 880 cm^{-1} band was assigned to the asymmetric P-F stretching vibration and 827 cm^{-1}, 850 cm^{-1} bands were considered to be a Fermi doublet, with the lower band being assigned to the symmetric P-F stretch (13). The present work suggests that the assignment to the 880 cm^{-1} band is correct, but the symmetric P-F fundamental may be better assigned to the 850 cm^{-1} band because of its stronger intensity in the Raman effect and because the fundamental is also observed in the spectrum of the borane complex at 852 cm^{-1}. The 827 cm^{-1} vibration may be an overtone of the 417 cm^{-1} band.

Although the previous assignment of the B-N stretch and the N-P-F_2 group frequency to the respective infrared bands at 654 cm^{-1} and 690-699 cm^{-1} seem to be correct (13), further explanation is desirable. The N-P-F_2 group motion is assigned to the higher frequency because a similar vibration is observed in the spectrum of the ligand at 705 cm^{-1}. It is interesting to note that the infrared intensity of this fundamental is about the same as that found in the spectrum of the ligand, but is considerably diminished in the infrared spectrum of the borane complex. The identical vibration in the Raman effect appears much weaker in the boron trifluoride and borane complexes than in the ligand. Even though the B-N stretching vibration of $(CH_3)_3NBF_3$ is also observed near 690-700 cm^{-1} (24), it is believed to shift to 653 cm^{-1} in the present complex.

The 561 cm^{-1} band, observed in both the infrared and Raman effect, is reassigned to the symmetric BF_3 deformation rather than the asymmetric vibration on the grounds that the symmetric mode is found at 545 cm^{-1} in the spectrum of $(CH_3)_3NBF_3$ (24). The infrared band at 416 cm^{-1} is assigned to the C_2-N deformation mode by analogy to the 393 cm^{-1} vibration of the ligand.

The remainder of the absorptions appearing in the spectra of the boron-10 and 11 trifluoride complexes do not require discussion since their relationships to the vibrations of the free ligand are quite evident. The uncertainties of these assignments are considered to be the same as those of the free ligand.

Bis(dimethylamino)fluorophosphine, $[(CH_3)_2N]_2PF$.

No experimental data are available bearing on the structure of this compound although chemical arguments favor a bond configuration around the phosphorus similar to that in $(CH_3)_2NPF_2$. The structure of $[(CH_3)_2N]_2PF$ may be one of no symmetry or, at most, the molecule may have a plane of symmetry and belong to the C_s point group. However, even if this molecule were assumed to have C_s symmetry, the orientation of the dimethylamine groups around the central phosphorus atom would remain unknown.

There are several difficulties in interpreting the vibrational spectrum of this compound. This molecule has a total of fifty-four Raman and infrared active vibrations which may be subdivided into thirty-six methyl group vibrations and eighteen skeletal modes. Also, many of the vibrations, especially those of the methyl groups, may be expected to be accidentally degenerate. In addition, many fundamentals of the same symmetry are found in the same region of the spectrum, thereby increasing the probability of interaction or coupling between various groups of the molecule. In any case, detailed assignments to numbered vibrations, such as those made for dimethylaminodifluorophosphine, have much less meaning here and therefore no attempt will be made to present a systematic numbering and description of the vibrational modes. However, it is possible to give assignments to the more characteristic group frequencies and to define the symmetry of the vibrations in terms of the local symmetry of the group.

The observed Raman spectra of $[(CH_3)_2N]_2PF$ in the liquid (-45°C) and solid (-180°C) states are shown in Figure 23 and the supplementary polarization spectra of the liquid are represented in Figure 24. An inspection of these tracings reveals several interesting features. As is true for most of the aminophosphines in this work, it is very difficult to prepare a sample of $[(CH_3)_2N]_2PF$ which is completely devoid of fluorescent impurities and minute suspended particles. These impurities have the general effect of increasing the background of the Raman spectra. Fluorescence and increased light scattering from the crystal faces is particularly evident in the spectrum of the solid sample while the Tyndall scattering, seen in the liquid spectra, was kept to a minimum in Figure 23 by the use of an interference filter rejection unit. In general, the spectrum of the disubstituted ligand (Figure 23) closely resembles that of $(CH_3)_2NPF_2$ (Figure 14) and the noticeable differences and similarities will be discussed later. The observed Raman frequencies and the reported infrared values (13) along with their present assignments are tabulated in Table 16.

The observed vibrational bands of the methyl stretching and deformation modes closely resemble those of other dimethylaminophosphines and no peculiarities are observed in these regions of the spectrum. However, it is interesting to note that at least five Raman bands are clearly resolved in the methyl stretching region while the infrared spectrum shows only the absorption envelope. On the other hand, the infrared spectrum of the methyl deformation region shows much more structure than does the Raman effect, perhaps due to the appearance of more overtones. Because the bands overlap extensively in these regions, their assignments are somewhat arbitrary and they may be modified when deemed necessary. Reference may be made to Table 16 for specific vibrational assignments in these regions.

Several bands are observed in the methyl rocking region from 1100 cm^{-1} to 1250 cm^{-1}. The very weak band at 1257 cm^{-1}

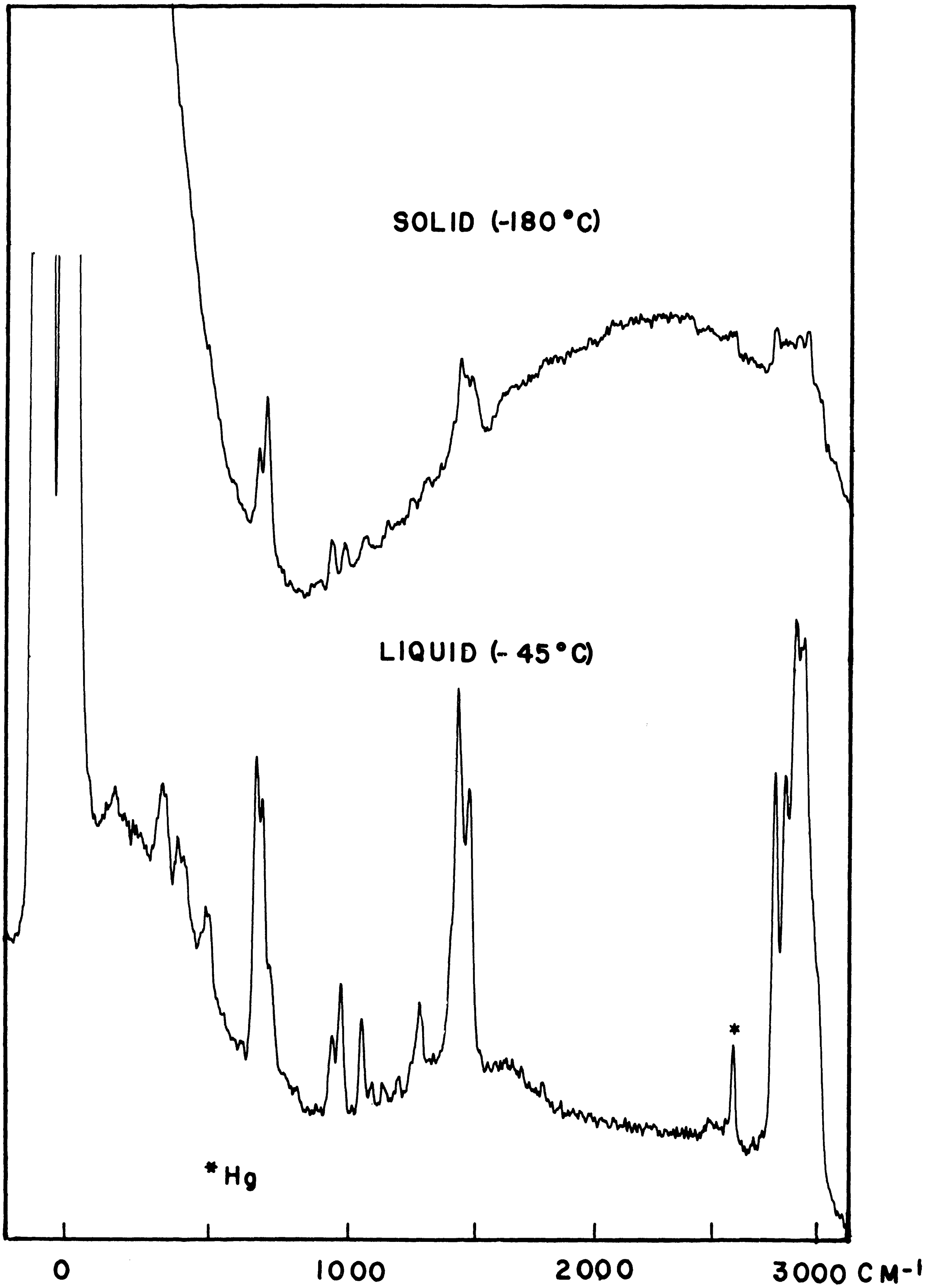


FIGURE 23 - THE RAMAN SPECTRA OF SOLID (-180°C) AND LIQUID (-45°C) $[(CH_3)_2N]_2PF$

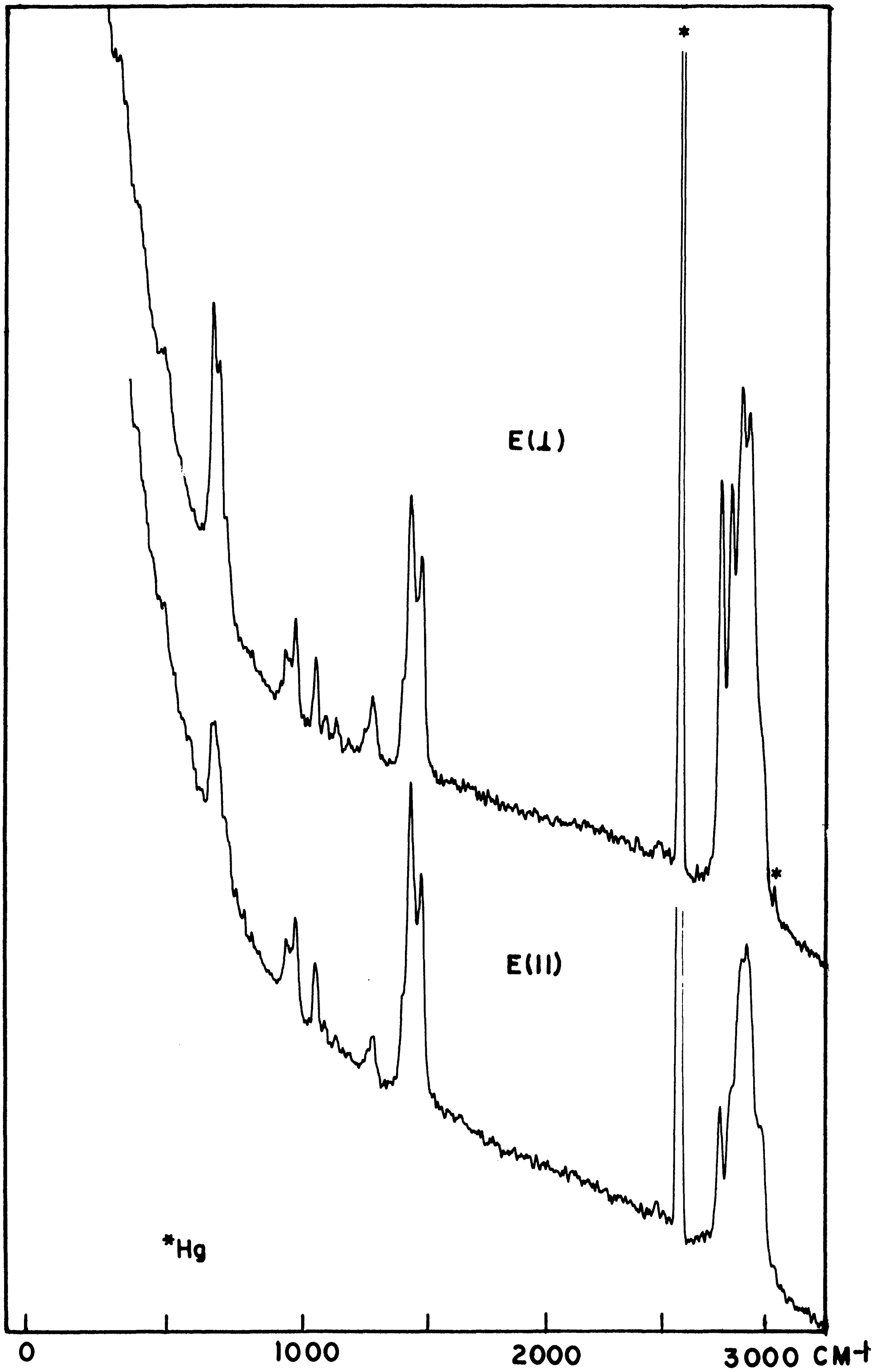


FIGURE 24 - THE POLARIZED RAMAN SPECTRA OF LIQUID

$[(CH_3)_2N]_2PF$ (-45°C)

TABLE 16

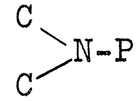
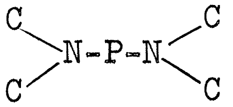
THE OBSERVED INFRARED AND RAMAN FREQUENCIES OF $[(CH_3)_2N]PF$

Infrared(13) gas	Raman liquid(-45°C)	Raman solid(-180°C)	Assignment
	2992 s,sh,dp	2994 vvw	out of phase asym. C-H stretch
	2925 vs,p	2936 w	out of phase sym. C-H stretch
2882 s	2885 vs,p	2902 w	in phase asym. C-H stretch ?
2842 sh	2837 s,sh,p	2837 w	in phase asym. C-H stretch ?
2795 m	2790 s,sh,p	2789 w	in phase sym. C-H stretch
	2542 vvw?		
	2503 vw?		
1504 w			
1494 w			
1485 w			
1479 w	1479 s,sh,dp	1491 vw,sh	out of phase asym. CH_3 deformation
1469 mw,br			
1463 m			out of phase asym. CH_3 deformation
1453 mw			
1448 w			
1434 vvw	1432 s,dp	1438 w	in phase asym. CH_3 deformation
	1402 m,sh,dp	1401 vw,sh	in phase asym. CH_3 deformation

TABLE 16 - CONT'D.

Infrared(13)	Raman		Assignment
gas	liquid(-45°C)	solid(-180°C)	
1280 m	1284 m,p	1304±10 vvw	in phase sym. CH_3 deformation
	1257 w,sh,dp?	1242 vvw	asym. CH_3 rock (out of C-N-C plane)
1199 m	1195 vw	1209 vvw	CH_3 rock (out of C-N-C plane) or asym. C-N stretch ?
1164 mw,sh	1141 vw	1147 vvw	CH_3 rock (in or out of C-N-C plane)
	1098 vw		CH_3 rock or asym. C-N stretch?
1057 mw	1059 m	1064 vw	asym. C-N stretch
985- 975 s,sh	980 ms	991 vw	out of phase $(C_2\text{-}N)_2\text{-}P$ stretch
949 vs	944 m,sh	942 vw	in phase $(C_2\text{-}N)_2\text{-}P$ stretch
	817 vvw?		
745 s	716 m,sh,p?		P-F stretch
677 s	689 s,sh,p	702 ms	asym. $N_2\text{-}P\text{-}F$ stretch
	644 s,p	672 m	sym. $N_2\text{-}P\text{-}F$ stretch
	612 vvw?		
496 w,br	497 w,sh? 486 w	490 vvw	P-F rock or wag
403 w,br	408 vw		$C_2\text{-}N$ deformation
	386 vw		$C_2\text{-}N$ deformation?
	329 w,br		skeletal
	165 vvw?		skeletal

is probably a methyl rocking vibration. However, the methyl rocking assignment to the 1195 cm^{-1} band is questionable in view of the present uncertainty connected with the location of the asymmetric C-N stretching frequency in dimethylamine derivatives. In addition, the medium weak shoulder at 1164 cm^{-1} in the infrared and the very weak Raman line at 1141 cm^{-1} are probably methyl rocking vibrations on the basis of similar bands found for $(CH_3)_2NH$ (22) and $(CH_3)_2NPCl_2$ (23). The assignment for the very weak Raman line at 1098 cm^{-1} is uncertain but it may be a methyl rock or less likely a component of the asymmetric C-N stretch.

The tentatively assigned asymmetric C-N stretching motion in $(CH_3)_2NPF_2$ shifts from 1071 cm^{-1} to 1059 cm^{-1} in the disubstituted compound. The Raman band at 989 cm^{-1}, which was attributed to the  $C_2{>}N\text{-}P$ group stretch in $(CH_3)_2NPF_2$, clearly splits in the Raman spectrum of $[(CH_3)_2N]_2PF$ yielding a doublet at 944 cm^{-1} and at 980 cm^{-1}. This doublet is also observed as a strong band at 949 cm^{-1} and shoulder at 973-985 cm^{-1} in the infrared spectrum. It is interesting to note that Evleth, Freeman and Wagner (64) also report a very strong infrared doublet at 958 cm^{-1} and 978 cm^{-1} which is characteristic of the C_2-N-P group in $[(CH_3)_2N]_2PCl$. It is very probable that this doublet arises from the in and out of phase C_2-N-P group motions in the  $C_2{>}N\text{-}P\text{-}N{<}C_2$ skeleton of the molecule.

Sr. Fleming observed a strong infrared band around 745 cm^{-1} which she attributed to the P-F stretch (13). No such band at this frequency is observed in the Raman effect, but a medium intensity shoulder did appear at 716 cm^{-1} on the high side of a strong doublet at 664 cm^{-1} and 689 cm^{-1} in the liquid spectrum. Although this frequency is somewhat lower than the expected P-F stretching range, 750 cm^{-1}-900 cm^{-1}, reported by Bellamy (51), this band shows the same downward shift in frequency as was observed for PF_3 and $(CH_3)_2NPF_2$ when the sample was condensed to a liquid or a solid.

A strong band at 677 cm^{-1} is observed in the infrared spectrum and is assigned to the N_2-P-F group vibration. However, in the Raman spectrum this band appears clearly as a polarized, strong doublet at 664 cm^{-1} and 689 cm^{-1}. This splitting is most likely the result of symmetric and asymmetric motions of the N_2-P-F group. Similar observations are reported for $(CH_3)_2NPOCl_2$ and $[(CH_3)_2N]_2POCl$ where the N-P-Cl_2 frequency at 723 cm^{-1} in $(CH_3)_2NPOCl_2$ splits to 672 cm^{-1} and 755 cm^{-1} in the monochloro- compound (23). Since this frequency does not shift appreciably from compound to compound, the motion is probably localized to a large extent in the N-P bonds.

A broad, weak absorption band is reported at 496 cm^{-1} in the infrared spectrum (13). Similar bands, appearing in the liquid and solid Raman spectra, are found at 486 cm^{-1}, 497 cm^{-1} and 490 cm^{-1} respectively. Since the absorption occurs at virtually the same frequency as the P-F_2 deformation in $(CH_3)_2NPF_2$, it seems logical to assume that this absorption is the result of the P-F rocking or wagging motion, a remnant of the PF_2 deformation in the difluoro-compound.

A broad, weak infrared band at 403 cm^{-1} is also seen in the Raman effect as a very weak band at 408 cm^{-1} and has been assigned by Sr. Fleming to a $(CH_3)_2N$- deformation mode (13). The assignment of this band is consistent with the findings of Stewart in which he observed that the corresponding vibration occurred at 427 ± 14 cm^{-1} for a large number of dialkylamines (52). A lower band at 386 cm^{-1} is also observed in the Raman spectrum and no doubt is a skeletal motion. Due to its closeness to the 408 band it might also be assigned to a $(CH_3)_2N$- deformation, but this postulate is only a conjecture. The weak Raman band at 329 cm^{-1} and the very weak band at 165 cm^{-1} are probably skeletal vibrations, however, no attempt has been made to characterize them.

Bis(dimethylamino)fluorophosphine-Borane, $[(CH_3)_2N]_2PFB^{11}H_3$.

The structure of $[(CH_3)_2N]_2PFBH_3$ is unknown; however, nuclear magnetic resonance data have indicated that the borane group is bonded to the phosphorus atom in this complex (13). Since no attempt was made to discuss the vibrations of the ligand in relation to possible symmetry elements of the molecule, the same procedure will be used in the present discussion. If this molecule has no symmetry, all sixty-six of its fundamental vibrations may be observed in the infrared and Raman effect. Of these vibrations thirty-six involve the motions of the methyl groups, nine are localized primarily in the borane group and the remaining twenty-one vibrations are predominantly skeletal vibrations of the molecule.

As was seen for $(CH_3)_2NPF_2$ and its borane adduct, the Raman and infrared spectra of $[(CH_3)_2N]_2PFBH_3$ closely resemble that of the ligand, $[(CH_3)_2N]_2PF$. The observed Raman spectra of liquid and solid samples are represented in Figure 25, while the polarized spectra are shown in Figure 26. Similar to the observations of $[(CH_3)_2N]_2PF$, the Raman spectrum of liquid $[(CH_3)_2N]_2PFBH_3$ contains an abnormally high background due to Tyndall scattering within the sample. The observed Raman frequencies, band intensities, polarization data and assignments are listed in Table 17 along with the reported infrared data (13).

In view of the similarities in the spectra of the ligand and the complex, a detailed discussion of the methyl frequencies is omitted here and reference may be made to preceeding sections for further details. A broad infrared band of medium intensity is observed at 1194-1167 cm^{-1} but does not appear in the Raman spectrum. The assignment of this band to a methyl rocking motion by Sr. Fleming (13) is supported by the observation that rocking motions oftentimes exhibit bands which are much weaker in the Raman effect than in the infrared. Although this vibration may be correlated with the observed methyl rocking vibrations of the ligand at 1164 cm^{-1} and 1199 cm^{-1}, the correctness of the present

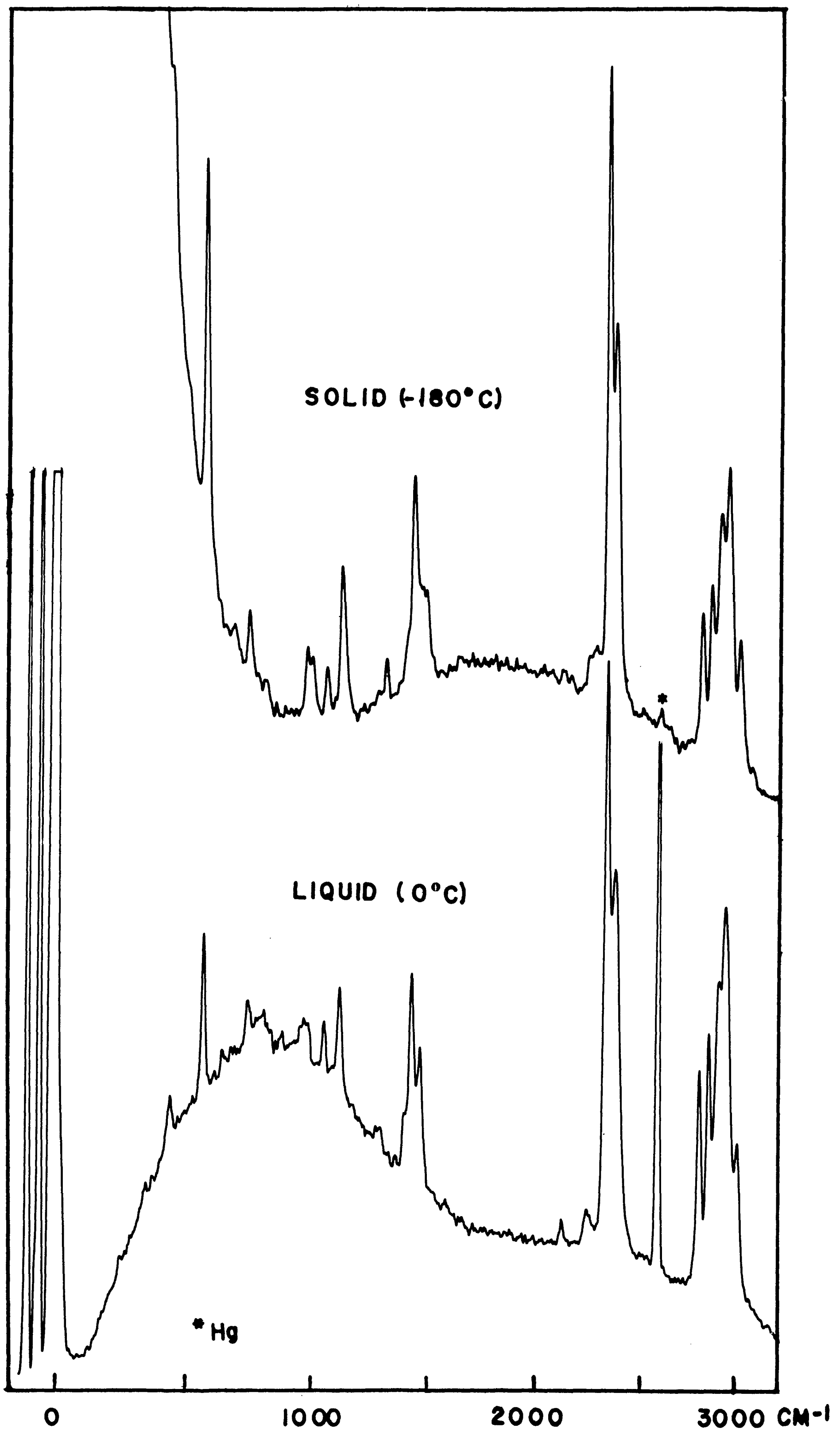


FIGURE 25 - THE RAMAN SPECTRA OF SOLID (-180°C) AND LIQUID (0°C) $[(CH_3)_2N]_2PFB^{11}H_3$

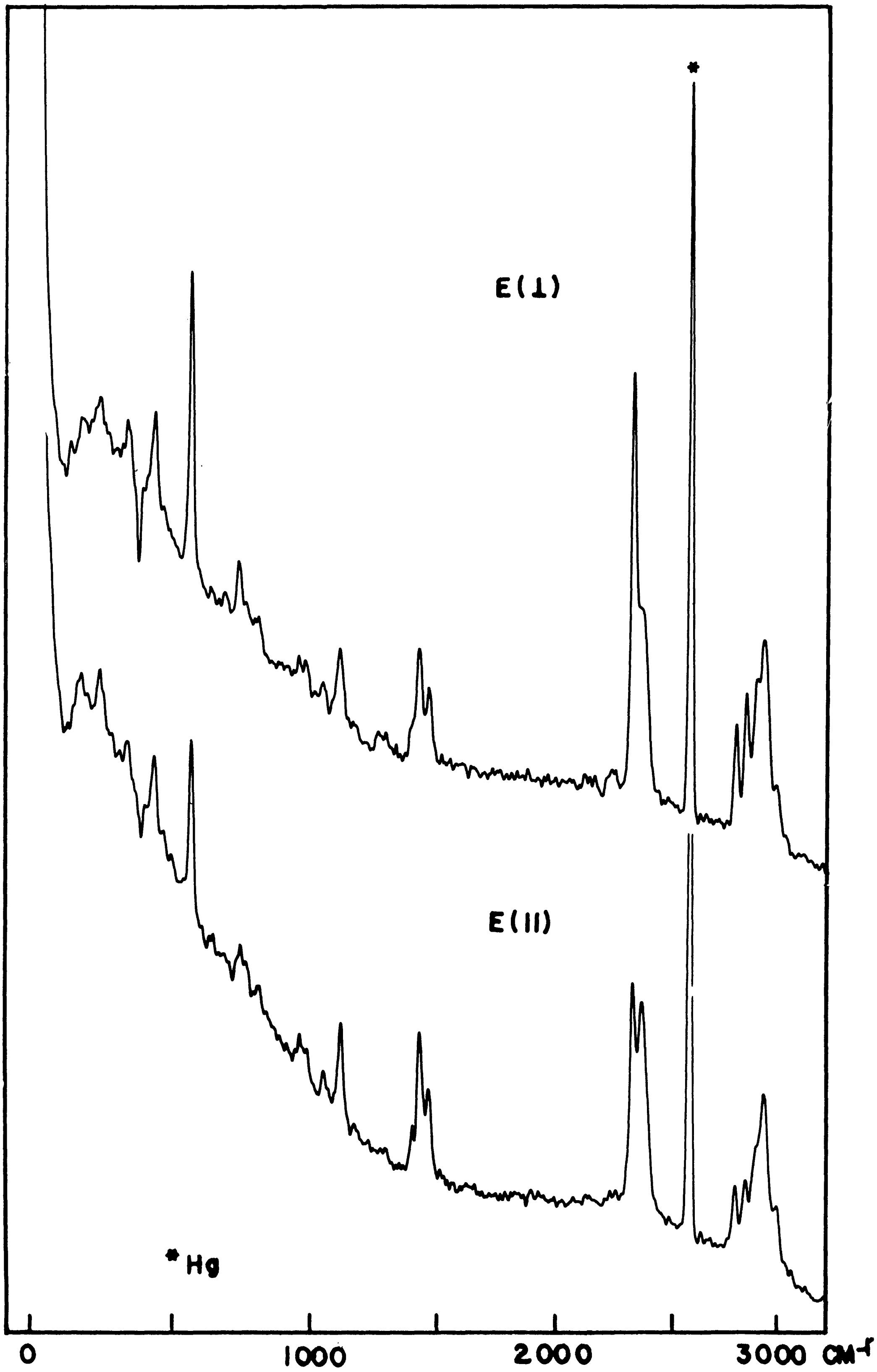


FIGURE 26 - THE POLARIZED RAMAN SPECTRA OF LIQUID $[(CH_3)_2N]_2PFB^{11}H_3$ (0°C)

TABLE 17

THE OBSERVED INFRARED AND RAMAN FREQUENCIES OF $[(CH_3)_2N]_2PFB^{11}H_3$

Infrared (13) liquid (25°C)	Raman liquid(0°C)	Raman Solid(-180°C)	Assignment
2991 sh	3006 m,sh,dp	3001 w,sh	out of phase asym. C-H stretch
2924 m	2945 s,p	2946 m	out of phase sym. C-H stretch
	2905 s,sh,p	2904 m,sh	in phase asym. C-H stretch
2855 sh	2854 m,sh,p	2856 w,sh	in phase asym. C-H stretch
2810 w	2810 m,sh,p	2807 w,sh	in phase sym. C-H stretch
2389 s	2387 s,sh,dp	2379 s,sh	asym. B-H stretch
	2343 vs,p	2343 vs	sym. B-H stretch
		2286 vw	977 + 1311 = 2288
2249 vw	2249 vw	2246 vw	2 x 1131 = 2262
2199 vvw			1060 + 1131 = 2191
2134 vvw	2137 vvw		2 x 1068 = 2136
1489- 1475 br,sh	1481 m,sh,dp	1493 w,sh	out of phase asym. CH_3 deformation
1460 m		1467 w,sh?	out of phase asym. CH_3 deformation
	1441 m,dp	1437 m	in phase asym. CH_3 deformation
1416 vvw	1411 w,sh,dp	1408 vw,sh	in phase asym. CH_3 deformation
1310 ms	1305 vvw	1311 vw	in phase sym. CH_3 deformation

TABLE 17 - CONT'D.

Infrared (13)	Raman		Assignment
liquid (25°C)	liquid(0°C)	Solid(-180°C)	
	1283 vvw	1280 vvw	CH_3 rock (in C-N-C plane)
1194-1167 m,br			CH_3 rock (in and/ or out of C-N-C plane)
1134 w	1131 w,dp	1126 w	asym. BH_3 deformation
1068 m	1060 w,dp?	1064 vw	asym. C-N stretch
998-	999 vw?	1000 vw	out of phase $(C_2-N)_2-P$ stretch
973 s	969 vw?	977 vw	in phase $(C_2-N)_2-P$ stretch
821 s	811 vvw?	809 vvw	BH_3 rock
775 ms	773 vvw	771 vvw	BH_3 rock or skeletal
750 s	747 w,p	743 vw	P-F stretch
706 mw			asym. N_2-P-F stretch
685 w	683 vvw?	680 vvw	sym. N_2-P-F stretch
574 w	569 m,p	570 s	P-B stretch
	438 w,p?	438 vvw	PF rock or C_2-N deformation
	340 vw		skeletal
	243 vw		skeletal
	180 vvw		skeletal
	140 vvw?		skeletal

assignment is no better than the assignments of the free base. Therefore, the assignment of this band to a methyl rock is questionable in view of the present uncertainty involved with the location of the asymmetric C-N stretching vibration in the ligand and in related dimethylamine derivatives.

The borane stretching motions are easily identified in the Raman spectrum as a very strong, well resolved doublet at 2343 cm^{-1} and 2387 cm^{-1} respectively. The lower band is most assuredly the symmetric stretching motion because it is strongly polarized while the upper band is depolarized. Sr. Fleming (13) observed the asymmetric B-H stretching motion at 2389 cm^{-1} in the infrared. However, her assignment of the symmetric stretch to a weak band at 2249 cm^{-1} does not appear correct in view of the Raman results.

A weak depolarized band at 1131 cm^{-1}, observed in both the infrared and Raman effect, is believed to be the asymmetric borane deformation vibration. Even though this band is found very near to a methyl rocking band at 1141 cm^{-1} in the spectrum of the ligand, it is not assigned to the rocking mode because of its relatively strong intensity in the Raman effect.

Three strong infrared bands appear at 750 cm^{-1}, 775 cm^{-1}, and 821 cm^{-1} while the respective bands are observed in the Raman effect as a weak, polarized line at 747 cm^{-1}, a very weak line at 773 cm^{-1} and an extremely weak line at 811 cm^{-1}. Since the borane rocking and P-F stretching motions are expected in this region (50,53), a choice must be made concerning these assignments. Although Sr. Fleming has assigned the P-F stretch to the 821 cm^{-1} band (13), it is believed that this vibration is better assigned to the 747 cm^{-1} band, because the latter is definitely polarized and has a somewhat stronger intensity than the others in the Raman effect. In addition, this frequency correlates reasonably well with the corresponding Raman frequency of the ligand at 716 cm^{-1}. The highest band at 821 cm^{-1} or 811 cm^{-1} is most likely a borane rocking vibration and this assignment is substantiated by the fact that no similar band is observed in the spectrum of the ligand. The band at 773 cm^{-1} is identified with less certainty but is probably a skeletal vibration or borane rock, perhaps a motion out of the hypothetical symmetry plane of the molecule.

Many of the skeletal motions of the borane complex may be identified by their analogous vibrations in the free ligand. The vibrational assignment to the depolarized, weak to medium intensity band around 1060 cm^{-1} is such an example. Since a similar vibration is found at 1059 cm^{-1} in the spectrum of the ligand which was tentatively assigned to the asymmetric C-N stretching motion, the present band is also thought to be the C-N stretching fundamental. It should be noted that any uncertainty in the original assignment would certainly be carried over to the present situation. In another case, the in and out of phase $(C_2\text{-}N)_2\text{-}P$ group stretching motion, observed as a medium intensity doublet at 944 cm^{-1} and 980 cm^{-1} in the Raman spectrum of the ligand, also is clearly observed in the solid Raman spectrum of the complex at 977 cm^{-1} and 1000 cm^{-1} respectively. However, these motions remain unresolved in the infrared spectra, both of the ligand and its borane complex. The symmetric and asymmetric N_2-P-F coupled motions of the complex are more difficult to observe in the Raman effect, because their band intensities are so weak. The asymmetric motion is probably the medium weak infrared band at 706 cm^{-1} (13), but no such band is observed in the Raman effect. The corresponding symmetric motion is probably the weak, infrared band at 685 cm^{-1} and the very weak Raman band at 683 cm^{-1}. The intensities of these Raman bands decrease markedly upon borane complexation, as was observed in the infrared, and their frequencies shift from 664 cm^{-1} and 689 cm^{-1} in the ligand to 683 cm^{-1} and 706 cm^{-1} in the complex.

The weak infrared band at 574 cm^{-1} and the polarized, medium intensity Raman band at 569 cm^{-1} are probably the P-B stretching vibration. This assignment correlates well with the similar vibration in F_3PBH_3 at 607 cm^{-1} and in $(CH_3)_2NPF_2BH_3$ at 591 cm^{-1}.

The weak, slightly polarized Raman line at 438 cm^{-1} is believed to be a P-F rocking vibration or a $(CH_3)_2$-N deformation. Since the respective vibrations in the ligand are probably those found near 490 cm^{-1} and 408 cm^{-1}, one is not able to make a more definite assignment to this frequency.

Four very weak Raman lines which appear at 340 cm^{-1}, 243 cm^{-1}, 180 cm^{-1} and 140 cm^{-1} are probably skeletal vibrations, but more specific assignments are impossible because of a general lack of knowledge concerning many of the deformations and torsional modes of the molecule.

Trimethylphosphine, $(CH_3)_3P$.

Trimethylphosphine has been shown by electron diffraction and microwave studies to have a pyramidal structure (33,65,66). It is assumed in this study that it has real or effective C_{3v} symmetry in that the methyl groups are in their most symmetrical orientation or are rotating sufficiently fast to have an effective cylindrical symmetry. This assumption is consistent with the spectroscopic data reported in the literature (29,30,31,32), although the question of whether the symmetry is C_{3v} or only C_3 has never been investigated critically.

The C_{3v} symmetry requires that trimethylphosphine have twenty-two fundamental vibrations with the symmetry distribution $7A_1 + 4A_2 + 11E$. Of the eighteen active vibrations, only four are skeletal vibrations (two in the A_1 class and two in the E class) while the remaining fourteen are methyl group vibrations. The numbering used for the fundamentals and the descriptive notation are listed in Table 18.

The Raman spectra of liquid (-40°C) and solid (-141°C) trimethylphosphine are shown in Figures 27 and 28. The observed vibrational frequencies and their assignments are given in Table 19. The observed frequencies agree, within experimental error, with those reported in the literature (29,30,31,32), and their assignments for the most part are identical to those of the earlier workers. Variations in the assignments from the previous to the present work will be cited later. The spectroscopic results of this investigation are compared to those of other workers in Table 20.

Since the bands associated with the methyl group vibrations are well separated from the skeletal frequencies, the two groups are relatively easy to identify. The very strong bands at 2958 cm^{-1} and 2891 cm^{-1} are assigned to asymmetric and symmetric C-H stretching vibrations on the basis of intensity and polarization measurements. Although six fundamentals must be present in these two bands, it is not possible to resolve them. However, it is observed that the asymmetric and symmetric methyl deformation bands at 1417 cm^{-1} and 1288 cm^{-1} respectively are split in the solid Raman spectrum due to the increased line sharpness at low temperatures. The methyl rocking and wagging vibrations are tentatively assigned to the bands appearing at 940 cm^{-1} and 823 cm^{-1} respectively. These assignments are made on the basis that the higher band is weakly polarized while the lower band is depolarized. In addition neither of the bands can be satisfactorily described as an overtone or combination. Although Siebert (31) and Halmann (32) assign somewhat higher frequencies to these vibrations, it is felt that these assign-

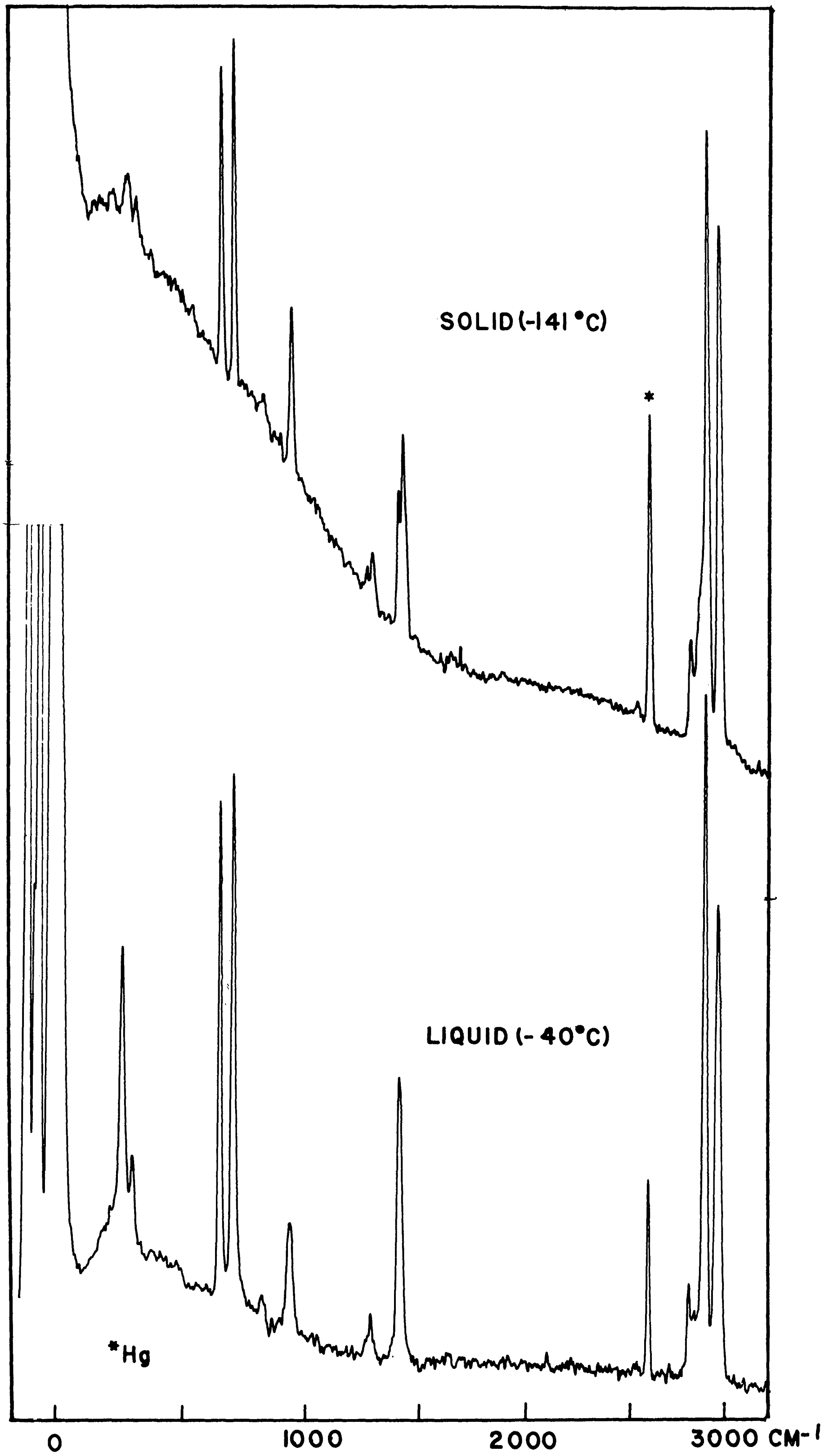


FIGURE 27 - THE RAMAN SPECTRA OF SOLID (-141°C) AND LIQUID (-40°C) $(CH_3)_3P$

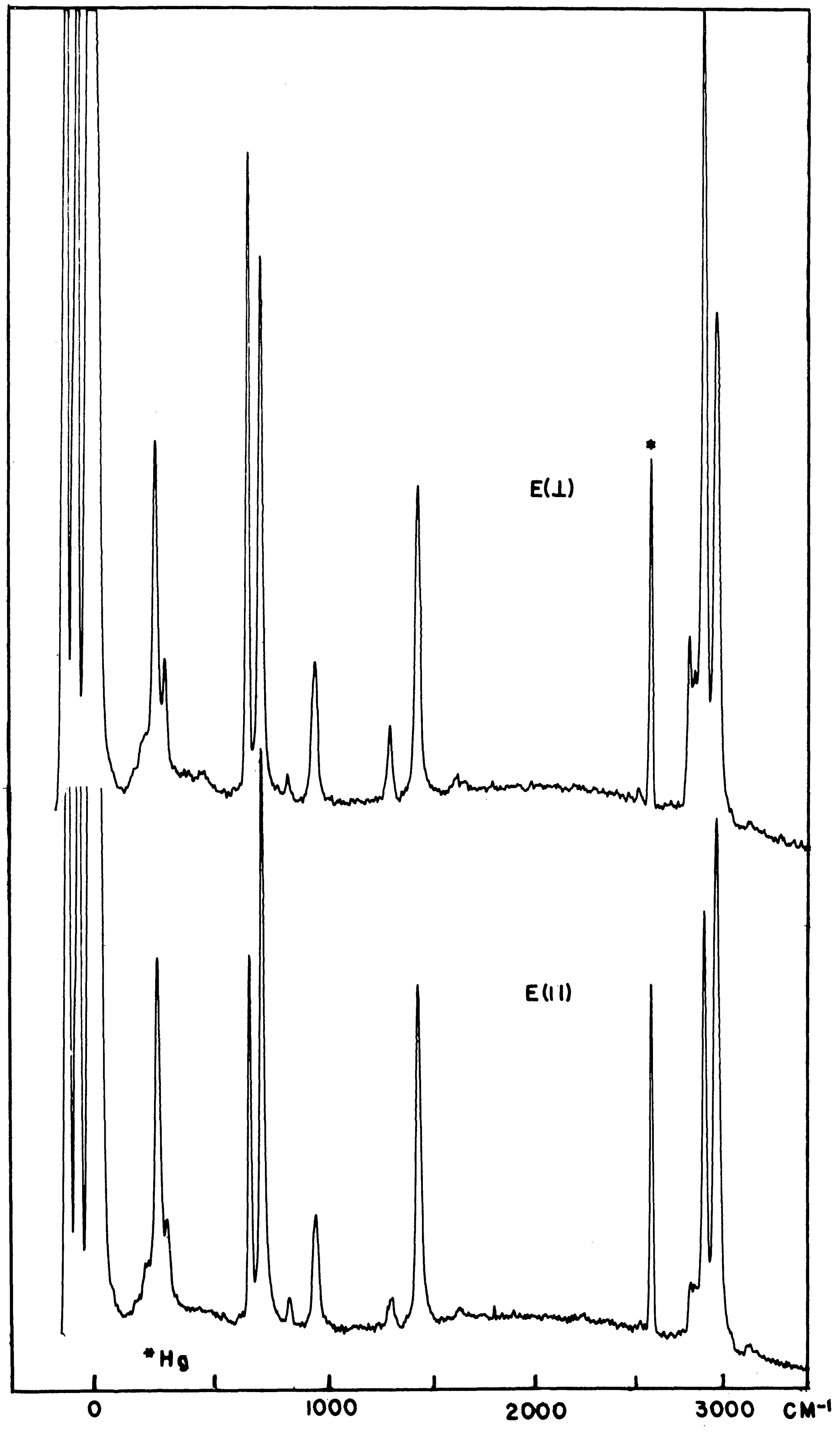


FIGURE 28 - THE POLARIZED RAMAN SPECTRA OF LIQUID

$(CH_3)_3P$ (-40°C)

TABLE 18

THE FUNDAMENTAL VIBRATIONS OF $(CH_3)_3P$, C_{3v} SYMMETRY

Symmetry	Number	Description
A_1	1	in phase asymmetric C-H stretch
	2	in phase symmetric C-H stretch
	3	in phase asymmetric CH_3 deformation
	4	in phase symmetric CH_3 deformation
	5	CH_3 rock
	6	C-P stretch
	7	C_3P deformation
A_2	8	out of phase asymmetric C-H stretch
	9	out of phase asymmetric CH_3 deformation
	10	CH_3 rock
	11	CH_3 torsion
E	12	out of phase asymmetric C-H stretch
	13	out of phase asymmetric C-H stretch
	14	out of phase symmetric C-H stretch
	15	out of phase asymmetric CH_3 deformation
	16	out of phase asymmetric CH_3 deformation
	17	out of phase symmetric CH_3 deformation
	18	CH_3 rock
	19	CH_3 wag
	20	C-P stretch
	21	C_3P deformation
	22	CH_3 torsion

TABLE 19

THE OBSERVED RAMAN VIBRATIONAL FREQUENCIES OF LIQUID AND SOLID $(CH_3)_3P$

Liquid (-40°C)		Solid (-141°C)		Assignment
3155	vvw			$\nu_2 + \nu_{21}$? or $\nu_{22} + \nu_{12}$?
2958	vs,dp	2959	vs	ν_1, ν_{12}, ν_{13}
2891	vs,p	2897	vs	ν_2, ν_{14}
2841	w,sh,p	2856	w,sh	$2\ \nu_{15}$ or $2\ \nu_{16}$
2808	w,sh,p	2806	w,sh	$2\ \nu_3$
2749	vvw			$\nu_{22} + 2\ \nu_{17}$
2537	vvw	2538	vvw	$2\ \nu_{17}$
1600	vvw			$\nu_3 + \nu_{22}$?
		1444	w,sh	
1417	s,dp	1427	m	ν_{15}, ν_{16}
		1407	w,sh	ν_3
1288	vw,p	1292	vw	ν_4
		1272	vvw,sh	ν_{17}
940	w,p	943	w	ν_5, ν_{18}?
900	vvw,sh?	900	vvw?	ν_5?, $\nu_6 + \nu_{21}$?
823	vw,dp	827	vvw	ν_{19}
705	vs,dp	703	m	ν_{20}
650	vs,p	652	m	ν_6
591	vvw?			$2\ \nu_7$
549	vvw?			$2\ \nu_{21}$
		368	vvw?	
297	w,sh,p	307	vw	ν_7
258	m,dp	272	vw	ν_{21}
210	vw,sh,dp	212	vvw	ν_{22}
		159	vvw?	
		136	vvw?	

TABLE 20

A COMPARISON OF THE OBSERVED VIBRATIONAL FREQUENCIES OF TRIMETHYLPHOSPHINE AND RELATED COMPOUNDS (CM^{-1})

		$(CH_3)_3P$				$(CH_3)_3PO$(36)		$(CH_3)_3N$(22)
		IR(g) (32)	Raman (29,31)	Raman(ℓ)$^+$	Raman(s)$^+$	IR	Raman	IR(g)
	A_1 Species							
ν_1	C-H asym. stretch	2970	2969	2958	2959		2999	2967
ν_2	C-H sym. stretch	2850	2894	2891	2897		2923	2777
ν_3	CH_3 asym. deformation	1417	1421		1406	1340?	1415	1466
ν_4	CH_3 sym. deformation	1310	1312	1288	1292	1340		1402
ν_5	CH_3 rock	960	973	940	943	872		1183
ν_6	C-P (C-N) stretch	652	653	650	652		671	826
ν_7	C_3P (C_3N) deformation		263	297	307		256	365*
	A_2 Species							
ν_8-ν_{11}	Forbidden in Infrared and Raman Spectra							
	E Species							
ν_{12},ν_{13}	C-H asym. stretch	2970	2969	2958	2959		2999	2967
ν_{14}	C-H sym. stretch	2920	2954	2891	2897		2923	2822
ν_{15},ν_{16}	CH_3 asym. deformation	1430	1421	1417	1427	1437		1466
					1406?	1420		
ν_{17}	CH_3 sym. deformation	1298	1293	1288	1292?	1305		1402
					1272	1292		
ν_{18}	CH_3 rock	1067	1072?	940	943	950	937	1272

TABLE 20 - CONT'D.

		$(CH_3)_3P$				$(CH_3)_3PO$(36)		$(CH_3)_3N$(22)
		IR(g) (32)	Raman (29,31)	Raman(ℓ)$^+$	Raman(s)$^+$	IR	Raman	IR(g)
ν_{19}	CH_3 wag	947	948	823	827	866	866	1104
ν_{20}	C-P (C-N) stretch	715				750	756	1043
		707	708	705	703			
ν_{21}	C_3P (C_3N) deformation		305	258	272		311	425*
ν_{22}	CH_3 torsion			210	212		(~275)	264*

$^+$ This work

* Values obtained from Raman data

ments are more consistent with the methyl rocking and wagging frequencies reported in the literature for $(CH_3)_3PO$ (36), $(CH_3)_2PH$ (67), and $(CH_3)_3SiCl$ (68). The remaining methyl group vibration, the degenerate methyl torsion, is assigned to a weak shoulder at 210 cm^{-1} in the Raman spectrum. This frequency is in good agreement with the value previously reported for $(CH_3)_3P$ at 223 cm^{-1} (66) and is consistent with the values reported for $(CH_3)_3N$ at 264 cm^{-1} (22) and for $(CH_3)_2PH$ at 236 cm^{-1} (67).

The four remaining bands in the Raman spectrum of $(CH_3)_3P$ are due to the skeletal motions of the molecule: the asymmetric and symmetric C-P stretching vibrations and the asymmetric and symmetric C_3P deformation vibrations. The components of the very strong doublet appearing at 705 cm^{-1} and 650 cm^{-1} are assigned to the asymmetric and symmetric C-P stretching vibrations respectively. The two deformation modes are found at 297 cm^{-1} and 258 cm^{-1}. Since the stronger, low frequency band at 258 cm^{-1} is clearly depolarized while the weaker band appears to be weakly polarized, the higher frequency is assigned to the symmetric deformation and the lower to the asymmetric deformation mode. The presently observed skeletal frequencies agree very well, within experimental error, with those appearing in the literature (29,30,31,32) and the assignments for the C-P stretching motions are identical to those reported earlier (31,32). However, the assignments for the skeletal deformation modes are the reverse of those reported by Siebert (31) based on the Raman data published by Rosenbaum, Rubin and Sandberg (29). Although this previous work included some polarization studies, no polarization data were obtained for the bands in question. The literature assignments were apparently based on analogy with $(CH_3)_3N$, where the symmetric deformation mode is lower. The present assignments for the C_3P deformation modes are further substantiated by microwave studies (66) in which the deformation frequencies are determined from relative intensity measurements on the vibrational satellite lines in the microwave spectrum.

It should be noted here that there is a suggestion of two very low lines at 159 cm^{-1} and 136 cm^{-1} in the solid Raman spectrum. However, since these are very weak in intensity and possibly are caused by lattice vibrations, they are neglected in the present discussion.

Trimethylphosphine-Borane, $(CH_3)_3PB^{10}H_3$, $(CH_3)_3PBH_3$, and $(CH_3)_3PB^{11}D_3$.

Such compounds as PF_3 and PCl_3 are known to retain their C_{3v} symmetry upon formation of their respective oxides, F_3PO and Cl_3PO (42,43,44,46). Therefore, it is not illogical to assume that the trimethylphosphine skeleton retains its C_{3v} symmetry with the formation of trimethylphosphine-oxide or the isoelectronic trimethylphosphine-borane.

The species and qualitative description of the fundamental modes of vibration for trimethylphosphine-borane are given in Table 21. It is noted that for a C_{3v} configuration, this molecule must have thirty vibrational frequencies classified as $10A_1 + 5A_2 + 15E$. Of these frequencies, the A_1 and E are active in both the infrared and Raman effect, while those belonging to the A_2 class are inactive in both.

For convenience, as was done in the case of trimethylphosphine, the fundamentals are divided into three groups: the methyl group vibrations, the vibrations involving the borane group and the skeletal vibrations. Since in reality interaction between the skeletal, methyl and borane vibrations certainly exists, this model is only an approximate one.

Three isotopic varieties of trimethylphosphine-borane, $(CH_3)_3PB^{10}H_3$, $(CH_3)_3PBH_3$ and $(CH_3)_3PB^{11}D_3$, were examined spectroscopically. Each of these species was studied in the infrared as a solid film at -180°C and the observed spectra are shown in Figures 29, 30 and 31. Since infrared studies involving the use of KBr pellets at room temperature yielded essentially the same spectra, they are not shown here. In addition, the Raman spectrum of each of these samples was studied at -10°C and -145°C. Only the spectra at -10°C are shown in Figure 32, since the differences from the spectra at -145°C are slight. The observed Raman and infrared frequencies along with their tentative assignments are given in Tables 22, 23 and 24. A comparison of the observed fundamentals for the different isotopic varieties is given in Table 25.

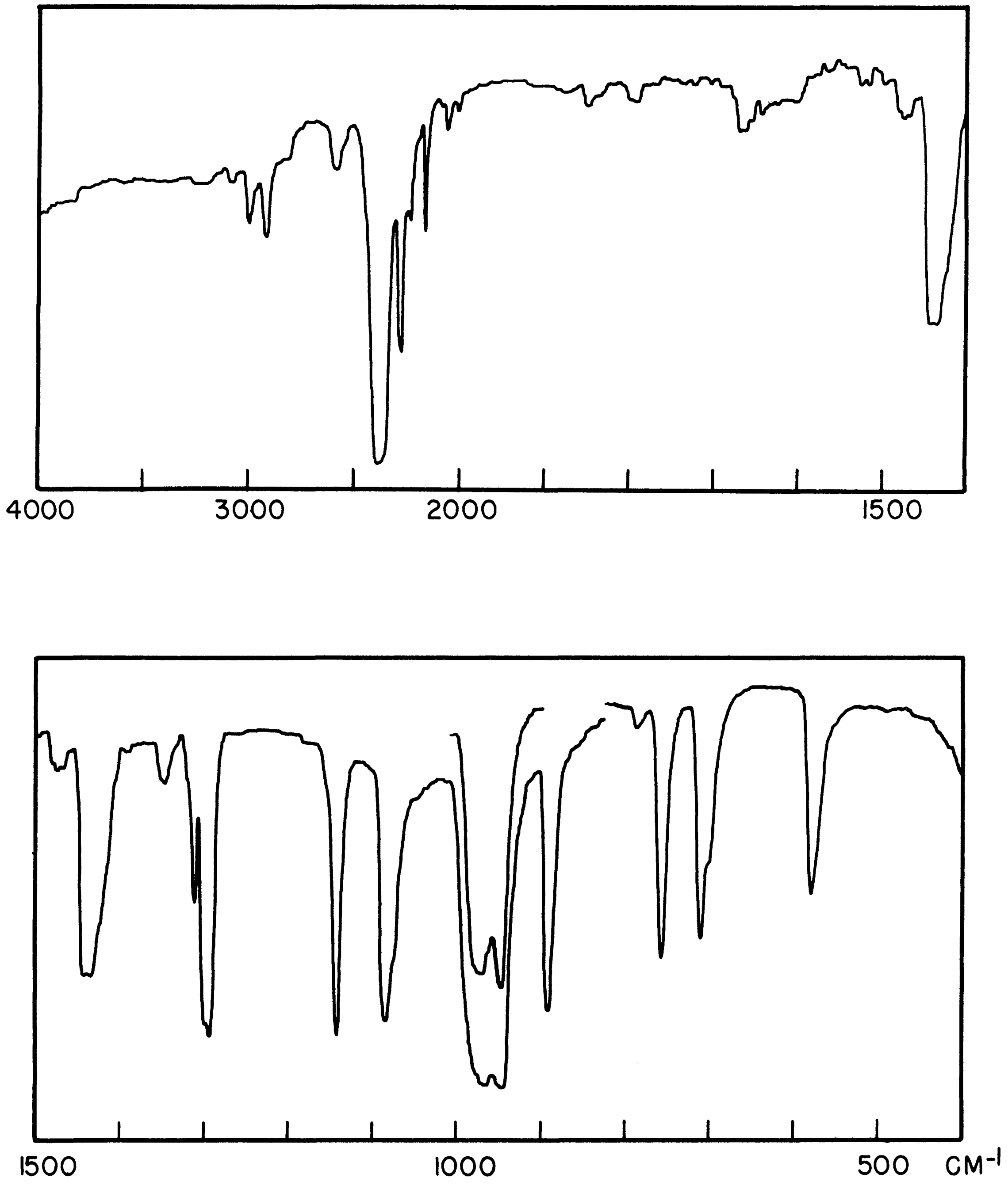


FIGURE 29 - THE INFRARED SPECTRUM OF $(CH_3)_3PB^{10}H_3$ (-180°C)

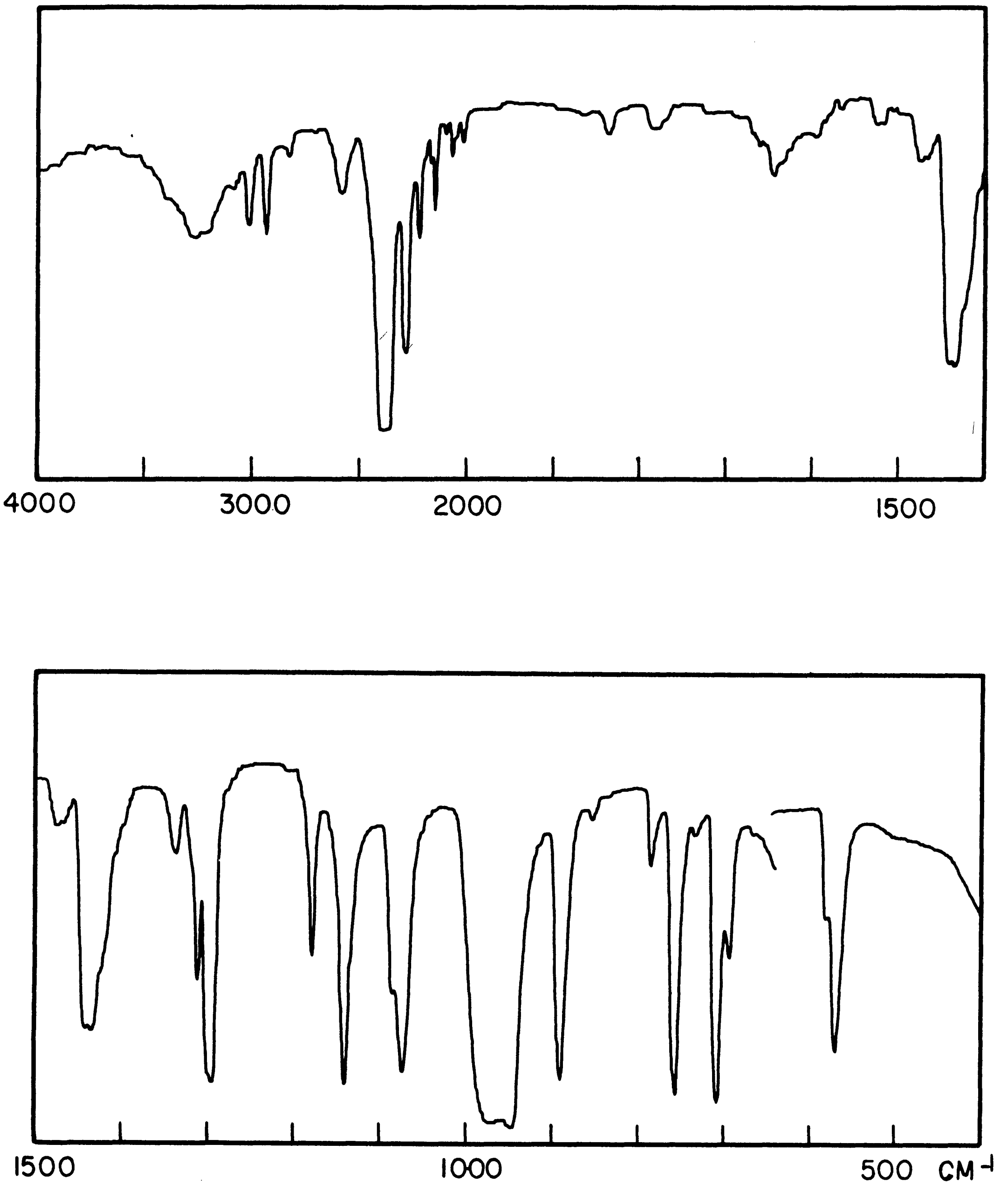


FIGURE 30 - THE INFRARED SPECTRUM OF $(CH_3)_3PBH_3$ (-180°C)

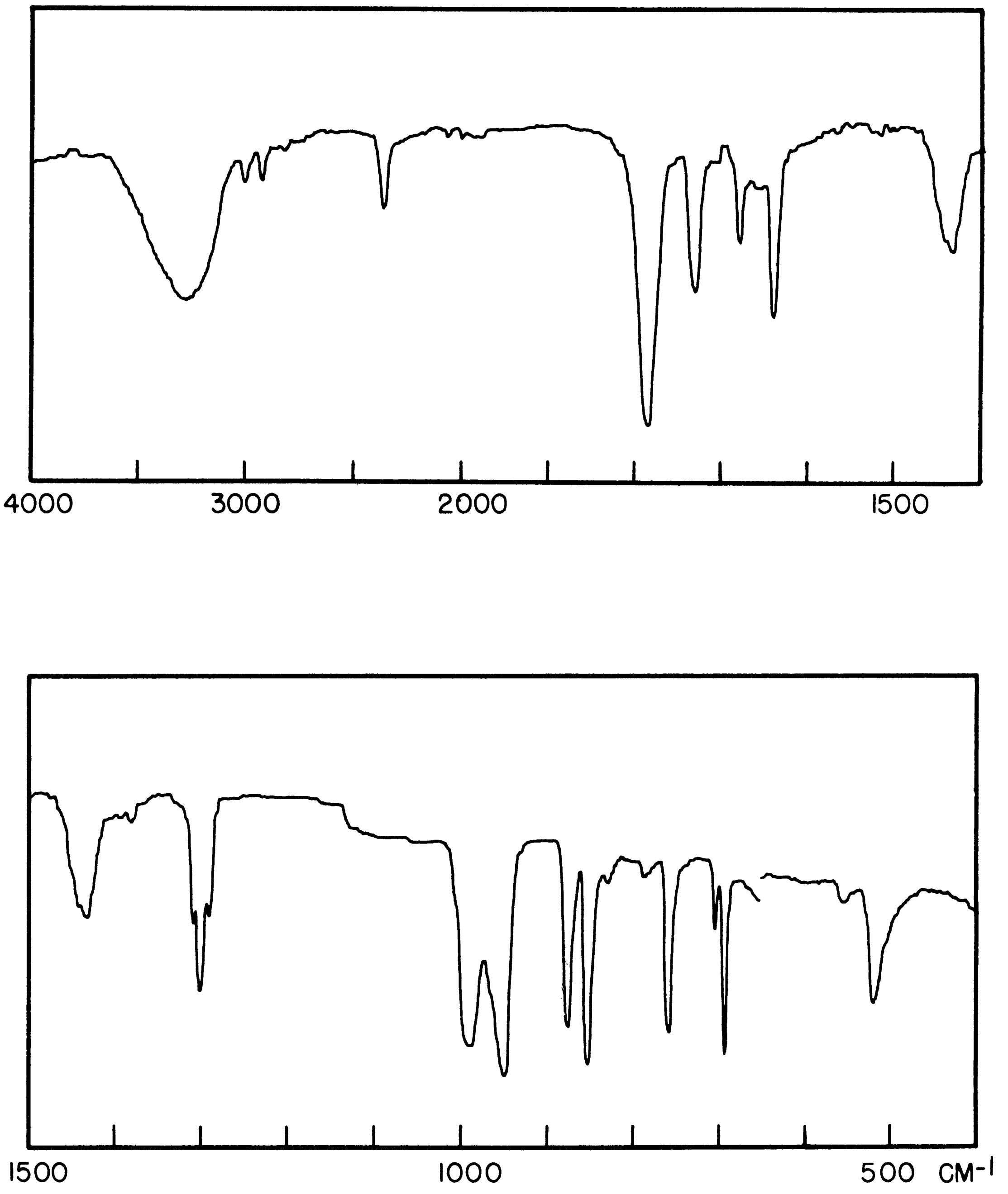


FIGURE 31 - THE INFRARED SPECTRUM OF $(CH_3)_3PB^{11}D_3$ (-180°C)

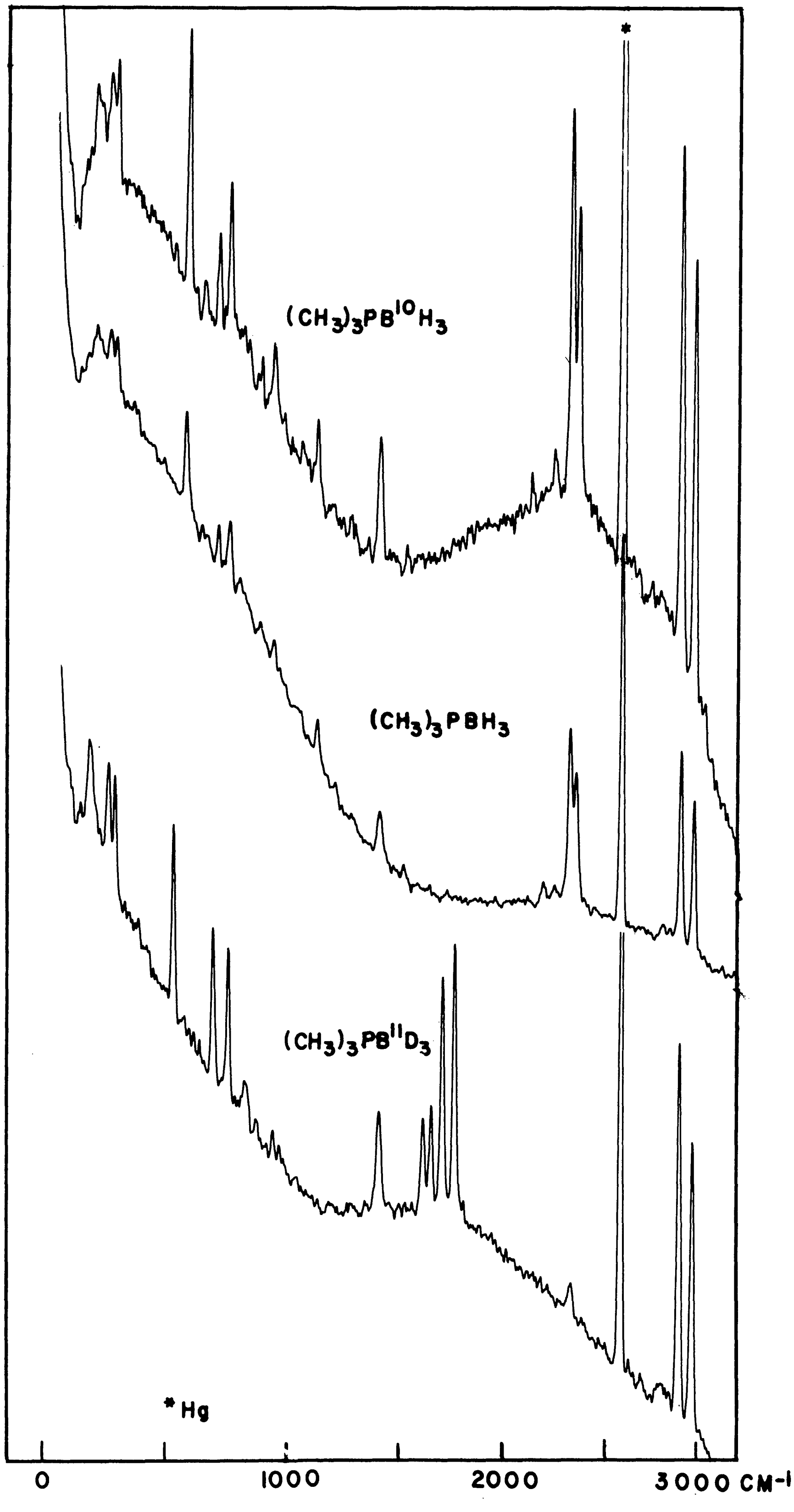


FIGURE 32 - THE RAMAN SPECTRA OF $(CH_3)_3PB^{10}H_3$, $(CH_3)_3PBH_3$, $(CH_3)_3PB^{11}D_3$ (-10°C)

TABLE 21

THE FUNDAMENTAL VIBRATIONS OF $(CH_3)_3PBH_3$, C_{3v} SYMMETRY

Symmetry	Number	Description
A_1	1	in phase asymmetric C-H stretch
	2	in phase symmetric C-H stretch
	3	B-H stretch
	4	in phase asymmetric CH_3 deformation
	5	in phase symmetric CH_3 deformation
	6	B-P stretch
	7	BH_3 deformation
	8	CH_3 rock
	9	C-P stretch
	10	C_3P deformation
A_2	11	out of phase asymmetric C-H stretch
	12	out of phase asymmetric CH_3 deformation
	13	CH_3 rock
	14	CH_3 torsion
	15	BH_3 torsion (around molecular axis)
E	16	out of phase asymmetric C-H stretch
	17	out of phase asymmetric C-H stretch
	18	out of phase symmetric C-H stretch
	19	B-H stretch
	20	out of phase asymmetric CH_3 deformation
	21	out of phase asymmetric CH_3 deformation

TABLE 21 - CONT'D.

Symmetry	Number	Description
E	22	out of phase asymmetric CH_3 deformation
	23	BH_3 deformation
	24	CH_3 rock
	25	CH_3 wag
	26	C-P stretch
	27	BH_3 rock
	28	C_3P deformation
	29	CH_3 torsion
	30	C_3P rock or C-P-B deformation

TABLE 22

THE OBSERVED RAMAN AND INFRARED FREQUENCIES OF $(CH_3)_3PB^{10}H_3$

Raman				Infrared		Assignment
-15°C		-145°C		-180°C		
3045	vvw	3042	vvw	3052±10	vw	$\nu_3 + \nu_9$?
		3028	vvw			
2988	s	2988	s	2977±10	w	ν_1, ν_{16}, ν_{17}
2915	s	2917	s	2898±10	w	ν_2, ν_{18}
2860	vvw	2863	vvw			$2\nu_{20,21}$
2814	vvw	2818	vvw			$\nu_{10} + 2\nu_{26}$
				2788±10	w,sh?	
				2564±10	w	$2\nu_5$
2373	m	2374	m	2360±5	vs	ν_{19}
2338	ms	2339	s	2340±5	vs,sh	ν_3
2258	vvw	2253	vvw	2258±5	s,sh	$2\nu_{23}$
				2215±5	w,sh	$\nu_7 + \nu_{23}$
2141	vvw			2142±5	w,sh	$2\nu_7$ or $\nu_9 + \nu_{20,21}$
				2070	vvw	$\nu_8 + \nu_{23}$
				2040	vw	$\nu_5 + \nu_{26}$
				1990	vw	$\nu_5 + \nu_9$ or $\nu_9 + \nu_{22}$
				1838	vw	$\nu_7 + \nu_{26}$
				1785	vw	$\nu_7 + \nu_9$ or $2\nu_{27}$
				1655	w	$\nu_8 + \nu_9$ or $\nu_{20,21} + \nu_{30}$
				1645	w,sh	$\nu_{26} + \nu_{27}$
				1633	vw,sh	$\nu_8 + \nu_9$?
				1592	vw,sh	$\nu_9 + \nu_{27}$
				1517	vw	$\nu_5 + \nu_{29}$
				1508	vw	$2\nu_{26}$
				1466	w	$\nu_9 + \nu_{26}$
				1457	w,sh	$\nu_6 + \nu_{27}$
				1435	s	ν_{20}, ν_{21}
1418	w	1421	m	1426	s	ν_4
				1383	vvw	

TABLE 22 - CONT'D.

Raman -15°C		Raman -145°C		Infrared -180°C		Assignment
				1338	w	$\nu_7 + \nu_{28}$
				1305	m,sh	ν_{22}
				1294	s,sh	
				1288	s	ν_5
				1175	vw,sh	$\nu_{10} + \nu_{27}$?
1134	vw	1137	w	1138	s	ν_{23}
				1082	s	ν_7 (B-10)
		1076	vvw?	1072	ms,sh	ν_7 (B-11)
				970	vs	ν_{24}
945	vvw	945	vw	948	vs	ν_8
886	vvw	885	vvw	891	s	ν_{27}
829	vvw?					ν_{25}?
808	vvw?					$\nu_6 + \nu_{30}$?
				786	vw	$\nu_6 + \nu_{29}$?
				762	s,sh?	
755	w	757	m	757	s	ν_{26}
707	vw	709	w	714	s	ν_9
				701	m,sh	
647	vvw	644	vvw			
580	m	581	s	583	m	ν_6 (B-10)
288	vw	288	w			ν_{10}
261	vw	260	w			ν_{28}
		232	vw			ν_{30}?
209	vw	208	w			ν_{29}
169	vvw,sh					
147	vvw,sh					

TABLE 23

THE OBSERVES RAMAN AND INFRARED FREQUENCIES OF $(CH_3)_3PBH_3$

Raman				Infrared		Assignment
-10°C		-150°C		-180°C		
				3057	vvw	$\nu_3 + \nu_9$?
2984	s	2987	s	2983	w	$\nu_1, \nu_{16}, \nu_{17}$
				2960	w,sh	ν_1?
2914	s	2915	s	2915	w	ν_2, ν_{18}
2854	vvw	2855	vvw	2851	vvw	$2\nu_{20,21}$
2808?	vvw	2809?	vvw	2803	vw	$\nu_{10} + 2\nu_{26}$
				2561	w	$2\nu_5$
2366	ms	2365	ms	2371	vs	ν_{19}
2335	s	2336	s	2328	vs	ν_3
2258	vw	2258	vw	2257	s	$2\nu_{23}$
				2200	w	$\nu_7 + \nu_{23}$
				2148	vvw,sh	$2\nu_7$ or $\nu_9 + \nu_{20,21}$
				2126	w	$\nu_4 + \nu_9$
				2075	vvw	$\nu_8 + \nu_{23}$
				2046	vw	$\nu_5 + \nu_{26}$
				2000	vvw	$\nu_5 + \nu_9$ Or $\nu_9 + \nu_{22}$
				1827	vw	$\nu_7 + \nu_{26}$
				1774	vw	$\nu_7 + \nu_9$ or $2\nu_{27}$
				1651	vw,sh	$\nu_8 + \nu_9$ or $\nu_{20,21}+\nu_{30}$
				1633	w	$\nu_8 + \nu_9$?
				1586	vw,sh	$\nu_9 + \nu_{27}$
				1516	vw	$\nu_5 + \nu_{29}$
				1507	vw	$2\nu_{26}$
				1465	w	$\nu_9 + \nu_{26}$
				1456	w	$\nu_6 + \nu_{27}$
				1432	s	ν_{20}, ν_{21}
1419	w	1420	w	1425	s	ν_4
				1327	w,sh	$\nu_7 + \nu_{28}$
				1303	m,sh	ν_{22}

TABLE 23 - CONT'D.

Raman -10°C		Raman -150°C		Infrared -180°C		Assignment
				1294	vs,sh	ν_5
				1288	vs	
				1172	m	$\nu_{10} + \nu_{27}$?
1134	vw	1136	vw	1137	s	ν_{23}
				1082	m,sh	ν_7 (B-10)
				1070	ms	ν_7 (B-11)
				973	vs	ν_{24}
944	vvw	948	vw	948	vs	ν_8
892	vvw	889	vvw	889	s	ν_{27}
				854	vvw,sh	$\nu_6 + \nu_{10}$
808	vvw?	808	vvw,br?			$\nu_6 + \nu_{30}$?
				787	w	$\nu_6 + \nu_{29}$?
				761	s,sh?	
757	w	757	w	757	s	ν_{26}
				735	vvw	
705	vw	707	vw	711	s	ν_9
				695	m,sh	
650	vw	647	vw			
				584	m,sh	ν_6 (B-10)
570	w	571	w	571	ms	ν_6 (B-11)
286	vw	287	vw			ν_{10}
261	vw	259	vw			ν_{28}
288	vw,sh	230	vw			ν_{30}?
211	vw	204	vw			ν_{29}
176	vvw,sh	169	vvw			
145	vvw,sh	146	vvw			

TABLE 24

THE OBSERVED RAMAN AND INFRARED FREQUENCIES OF $(CH_3)_3PB^{11}D_3$

Raman				Infrared		Assignment
-10°C		-145°C		-180°C		
		3053	vvw?			
3034	vvw?					
2986	s	2986	ms	2982±10	vw	$\nu_1, \nu_{16}, \nu_{17}$
2916	s	2915	ms	2903±10	vw	ν_2, ν_{18}
		2860	vvw			$2\nu_{20,21}$
				2801±10	vvw	$\nu_{10} + 2\nu_{26}$
2344	vw	2347	vvw	2338±5	w	ν_3 (B-H)
				2040	vvw	$\nu_5 + \nu_{26}$
				1980	vvw	$\nu_5 + \nu_9$ or $\nu_9 + \nu_{22}$
1769	ms	1769	m	1774	vs	ν_{19}
1713	ms	1717	w	1720	m	ν_3
1660	w	1662	w	1669	w	$\nu_7 + \nu_{25}$ or $2\nu_{25}$?
1622	w	1625	w	1630	m	$\nu_8 + \nu_9$? or $\nu_{23} + \nu_{26}$
1503	w					$2\nu_{26}$
				1432	m,sh	ν_{20}, ν_{21}
1419	vw	1422	w	1422	m	ν_4
1361	vvw?	1370	vvw?	1371	vvw?	$2\nu_9$
				1301	m,sh	ν_{22}
				1293	ms	
				1283	m,sh	ν_5
				986	ms	ν_{24}
934	vvw	942	vvw	949	s	ν_8
				873	m	ν_{23}
				851	ms	ν_7
820	vw	819	vvw?	830	vvw,sh	ν_{25}?
				785	vvw	$\nu_6 + \nu_{29}$?
749	w	753	w	757	m	ν_{26}
				706	w,sh	ν_{27}

TABLE 24 - CONT'D.

Raman				Infrared		Assignment
-10°C		-145°C		-180°C		
685	w	688	vw	696	m	ν_9
645	vvw?	641	vvw?			
				562	vw	$2\nu_{10}$
521	m	523	w	527	w	ν_6
282	w	283	vw			ν_{10}
256	w	255	vw			ν_{28}
		223	vw			ν_{30}?
209	vvw,sh??					ν_{29}
188	vw	186	vw			
144	vw					
101	vvw,sh?					

TABLE 25

FREQUENCY ASSIGNMENTS OF THE FUNDAMENTAL VIBRATIONS OF TRIMETHYLPHOSPHINE-BORANE

Symmetry Class	No.	Notation[a]	Assignment[b]		
			$(CH_3)_3PB^{10}H_3$	$(CH_3)_3PBH_3$	$(CH_3)_3PB^{11}D_3$
A_1	1	ν-CH	2988	2985	2986
	2	ν-CH	2913	2915	2915
	3	ν-BH	2339	2333	1717
	4	δ-CH_3	1422	1421	1421
	5	δ-CH_3	1288	1288	1283
	6	ν-BP	582	571	524
	7	δ-BH_3	1082	1070	851
	8	ρ-CH_3	946	947	942
	9	ν-CP	710	708	690
	10	δ-C_3P	288	287	283
A_2	11-15	Inactive			
E	16	ν-CH	2988	2985	2986
	17	ν-CH	2988	2985	2986
	18	ν-CH	2913	2915	2915
	19	ν-BH	2371	2367	1771
	20	δ-CH_3	1435	1432	1432
	21	δ-CH_3	1435	1432	1432
	22	δ-CH_3	1294	1294	1293
	23	δ-BH_3	1136	1136	873
	24	ρ-CH_3	970	973	986
	25	ω-CH_3	829		823
	26	ν-CP	756	757	753
	27	ρ-BH_3	887	890	706
	28	δ-C_3P	260	260	256
	29	τ-CH_3	209	205	209
	30	ρ-Me_3P	232	229	223

[a] Symbols used: ν = stretching, δ = deformation, ρ = rocking, ω = wagging, τ = torsion

[b] All frequencies in cm^{-1}.

The vibrational modes of $(CH_3)_3PBH_3$ are assigned to the observed frequencies using the isotopic data and also by comparison with the assignments for $(CH_3)_3P$ (discussed in the previous section) and those for $(CH_3)_3PO$ (36), $(CH_3)_3N$ (22), $(CH_3)_3NBH_3$ (69) and for other amine-boranes (50).

The absorption bands associated with the methyl vibrations are easily identifiable by their band positions and their strong band intensities. Since the polycrystalline nature of the samples prevented polarization measurements in the present case, some uncertainty in the assignments must result. Nevertheless, tentative methyl stretching, deformation, rocking and torsional modes are assigned to the observed frequencies and these are shown in Tables 22 to 25. A detailed discussion of the methyl stretching and deformation frequencies is omitted since they are virtually the same as those reported earlier for $(CH_3)_3P$.

The methyl rocking and wagging modes are not easily identified because their frequencies occur in the same region as the borane rocking vibration and the isotopic borane-d_3 deformation vibrations. However, the methyl rocking and wagging vibrations are assigned to bands observed at 947 cm^{-1}, 973 cm^{-1} and 829 cm^{-1} respectively while the borane rocking mode is seen at 890 cm^{-1} and the borane-11-d_3 deformation modes are placed at 851 cm^{-1} and 873 cm^{-1}. The methyl vibrations are distinguished from those of the borane group, because their frequencies are relatively insensitive to isotopic substitution in the borane group. The remaining degenerate methyl torsional mode is found at 223 ± 20 cm^{-1} for $(CH_3)_3P$ (66) and is assigned to a very weak band at 205 cm^{-1} in the borane complex.

The basis for many of the assignments of the borane group is not immediately apparent and some discussion is necessary. The B-H symmetric and asymmetric vibrations, ν_3 and ν_{19} respectively, appear as a very strong doublet in both the infrared and Raman spectra at about 2333 cm^{-1} and 2367 cm^{-1}. The strong band in the infrared at 2258 cm^{-1} appears to be a combination or an overtone, possibly $2\nu_{23}$. For the deuterated sample, four bands appear between 1600 cm^{-1} and 1800 cm^{-1} in both the infrared and Raman spectra (see Figures 31 and 32). Because only two bands are expected in this region, the more complex spectrum must be due to the presence of overtones or perhaps combinations. Since fundamentals normally are more intense than the combinations, the bands at 1717 cm^{-1} and 1771 cm^{-1} are assigned to the symmetric and asymmetric B-D stretching vibrations, ν_3 and ν_{19}, respectively. The isotope frequency ratios calculated on the basis of these assignments are 1.36 and 1.34 lending additional support to the correctness of these assignments. The remaining two bands at 1662 cm^{-1} and 1625 cm^{-1} for the deuterated sample involve combinations or overtones, perhaps $\nu_7 + \nu_{25}$ or $2\nu_{25}$ and $\nu_8 + \nu_9$ or $\nu_{23} + \nu_{26}$ respectively; the fundamentals remain somewhat uncertain. The borane deformation modes, ν_7 and ν_{23}, are observed at 1070 cm^{-1} and 1136 cm^{-1} in the hydrogen species and shift to 851 cm^{-1} and 873 cm^{-1} in the deuterated sample. Lastly, the degenerate borane rocking vibration, ν_{27}, is observed at 890 cm^{-1} as a strong band in the infrared and a very weak band in the Raman and shifts to 706 cm^{-1} upon deuteration.

The skeletal vibrations are perhaps the most interesting to study spectroscopically, since they are pertinent to the discussion of bonding and stability of the borane complex. The skeletal motions of the molecule involve only the motions of the C_3P-B framework under the assumption that the methyl and borane groups behave as point masses. Such a molecular model has six vibrational modes, four of them originating in the trimethylphosphine ligand and two of them arising from the formation of the phosphorus-boron bond. Since the configuration of trimethylphosphine is not expected to change significantly upon complexation with the borane Lewis acid, the C-P stretching and C_3P deformation frequencies of the complex are not expected to be very different from those of the free base. In reality the symmetric and asymmetric C-P stretching frequencies shift from 650 cm^{-1} and 705 cm^{-1} in the free base to 708 cm^{-1} and 757 cm^{-1} respectively in the complex. However the C_3P deformation frequencies show almost no effect upon complexation, the symmetric and asymmetric frequencies moving respectively from 297 cm^{-1} and 258 cm^{-1} to 287 cm^{-1} and 260 cm^{-1}. The two remaining vibrations are the symmetric P-B stretching motion and the degenerate C_3P rocking or the C-P-B angle deformation motion. The P-B stretching frequency, ν_6, at 571 cm^{-1} in the natural borane compound is easy to recognize because of its relatively strong band intensity in the infrared and its large isotopic dependence. The assignment for the degenerate $(CH_3)_3P$- rocking vibration is not altogether certain, but its frequency is expected to be quite low. In fact Rice, Galiano and Lehmann (69) have assigned the 226 cm^{-1} frequency to the corresponding vibration for $(CH_3)_3NBH_3$. Several low lying bands are found in the Raman spectrum of $(CH_3)_3PBH_3$ and the very weak band at 229 cm^{-1} is tentatively assigned to the rocking mode by analogy to that of $(CH_3)_3NBH_3$.

Although all of the active vibrations are assigned frequencies, several bands are observed to which no assignments can be given. Of these, two or three very weak bands are observed below 200 cm^{-1} in the Raman spectrum. Because these lines are uncertain and are of dubious origin, they are not used in the assignments. The very broad infrared band which appears from 3200 cm^{-1} to 3260 cm^{-1} in some of the figures is attributed to an O-H band from the KBr windows. The assignments to the fundamental vibrations, for the most part, appear reasonably certain. However, the assignments of the overtones and combinations are much less certain and oftentimes several possibilities exist.

SUMMARY

Raman and infrared spectra of a number of phosphine Lewis bases and their borane complexes have been studied in this work. An attempt has been made to describe the vibrational modes of these molecules by means of symmetry analyses and the group vibration approximation. On this basis, the observed vibrational frequencies have been assigned to the fundamental modes of vibration and in some cases to overtones or to combinations of the fundamentals.

Since the group vibration approximation has been employed extensively throughout this investigation, it is worth while at this point to review its validity. This approximation has been used largely in connection with organic compounds, and it has been particularly successful in describing the motions of small isolated groups which are not incorporated into the molecular framework. For example, the methyl group stretching and deformation vibrations for a large number of compounds have been found in the 2800-3000 cm^{-1} and the 1400-1500 cm^{-1} regions respectively, and they do not appear to shift appreciably from one compound to another. In the present case this has also been observed, the $-BH_3$, $-CH_3$ and -N-H group frequencies being easy to identify and remaining relatively constant in all the complexes studied.

In general, the group vibration approximation has been studied less extensively in connection with inorganic than

with organic compounds, largely because it has proved less successful when applied to low frequency vibrations arising from various individual oscillators comprising a heavy molecular framework. However, these more complex skeletal modes often retain a certain degree of similarity in related molecules having the same general structure, thus frequency comparisons may still be informative even though a particular mode cannot be localized within a certain bond. A correlation diagram of the skeletal vibrations for the substituted fluorophosphine compounds, studied in this work, is represented in Figure 33. It is clearly evident from the diagram that certain vibrations do not shift appreciably from one compound to another. However, others, such as the P-F stretching and deformation vibrations, appear to be influenced by neighboring groups and these motions may involve a sensitive coupling with other skeletal vibrations.

In the case of $(CH_3)_3P$, a comparison of the skeletal modes of the ligand with those of $(CH_3)_3PBH_3$ in Table 26 reveals that the C_3P deformation frequencies do not change a great deal when $(CH_3)_3P$ complexes with the borane group. However, both the symmetric and asymmetric C-P stretching vibrations shift appreciably upon complexation. This frequency shift probably is, to a great extent, the result of coupling between the C-P and P-B vibrations, but it is not possible to separate this from the effect of a possible change in the C-P force constant without a normal coordinate calculation.

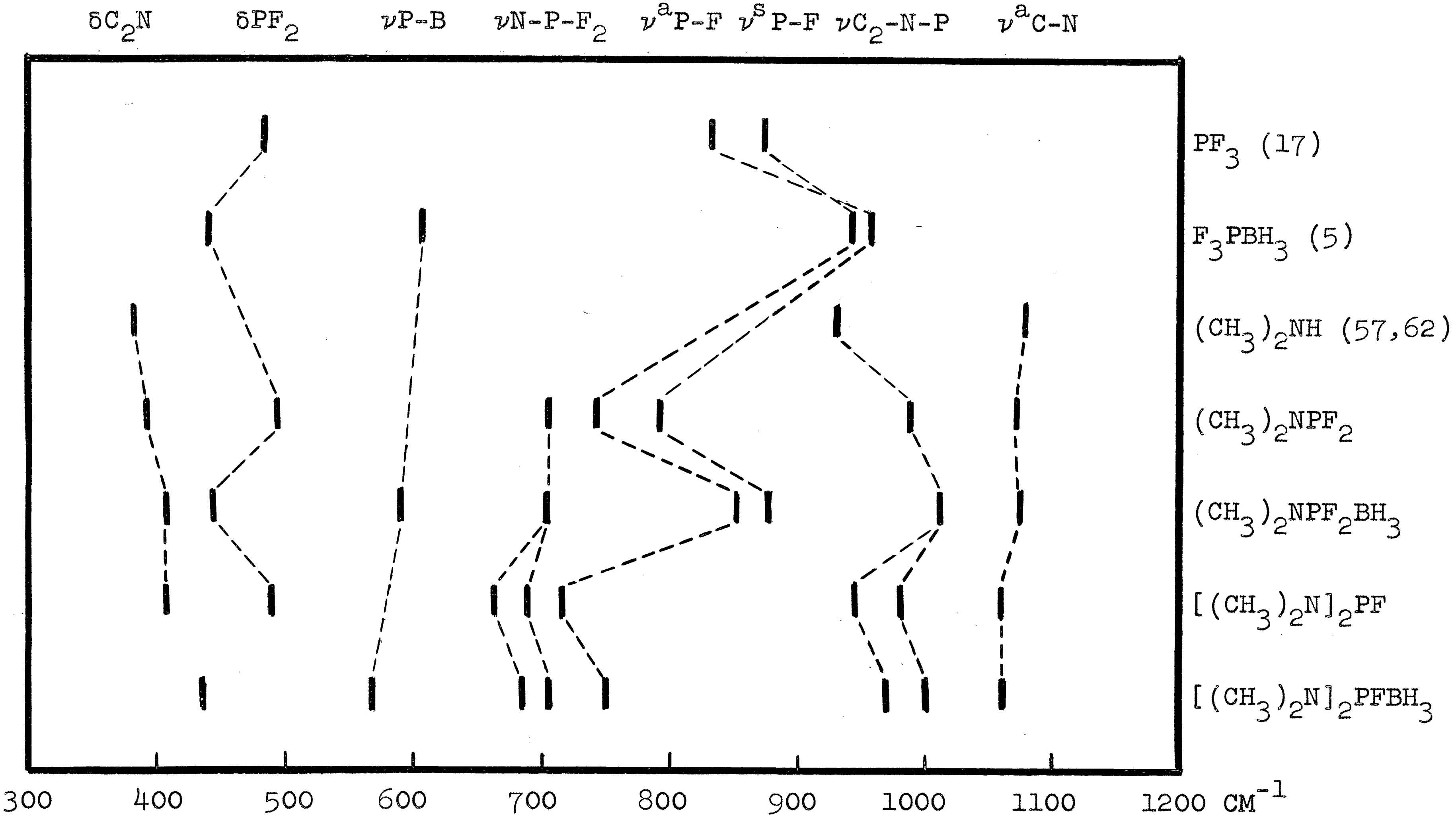


FIGURE 33 - A CORRELATION DIAGRAM FOR SOME FUNDAMENTAL VIBRATIONS OF PF_3, F_3PBH_3, $(CH_3)_2NH$, $(CH_3)_2NPF_2$, $(CH_3)_2NPF_2BH_3$, $[(CH_3)_2N]_2PF$ AND $[(CH_3)_2N]_2PFBH_3$

TABLE 26

A COMPARISON OF THE SKELETAL VIBRATIONS OF $(CH_3)_3P$ AND $(CH_3)_3PBH_3$

$(CH_3)_3P$	$(CH_3)_3PBH_3$	Description of Vibration
650	708	C-P symmetric stretch (a_1)
297	287	C_3P symmetric deformation (a_1)
	571	P-B stretch (a_1)
705	757	C-P asymmetric stretch (e)
258	260	C_3P asymmetric deformation (e)
	229	C_3P rock (e)

The borane stretching vibrations of the various phosphine-boranes studied appear to be good group vibrations by virtue of their separation from other molecular frequencies. As a consequence, one may expect that the effect of the dative bond on the borane group will be reflected directly in the magnitude of the B-H frequencies with relatively little complication by coupling effects. Previous work, in this laboratory and elsewhere, has shown that these vibrations can be correlated qualitatively with the strength of the Lewis base which is complexed with the borane group. If these B-H stretching vibrations are arranged in systematically decreasing order of magnitude, one obtains the effect shown in Figure 34. A more uniform trend is shown by the weighted average of the borane stretching fundamentals, since the use of the average eliminates coupling effects within the borane group itself. It can be seen that the trend established by the B-H frequencies, shown in Figure 34, agrees with the generally accepted order of base strengths as established from other experimental results. In like manner, the borane stretching fundamentals of the phosphine-borane complexes reported in this work, or preferably their weighted averages, may be arranged in systematic order. Such a listing is depicted in Figure 35. Chemical knowledge generally agrees that dimethylamine is a stronger base than methylamine and that the methoxy group is more basic than the methyl group. In addition, the strength of the fluorophosphines, as Lewis bases, is expected to increase with increased substitution of amine groups for fluorine atoms on the phosphorous. Analogous to the previously mentioned trend in Figure 34 and in accordance with chemical intuition concerning the basicity of phosphine Lewis bases, the borane stretching vibrations of phosphine-borane complexes are seen to shift systematically to lower frequencies with increased base strength of the ligand. Such a trend may be useful in predicting the stabilities of these complexes and predicting displacement reactions. An attempt to correlate the B-H stretching fundamentals of the ether and the amine complexes in Figure 34 with those of the phosphine series in Figure 35 was not successful. This may be because oxygen and nitrogen are first row elements while phosphorus is a second row element. A correlation involving borane complexes of

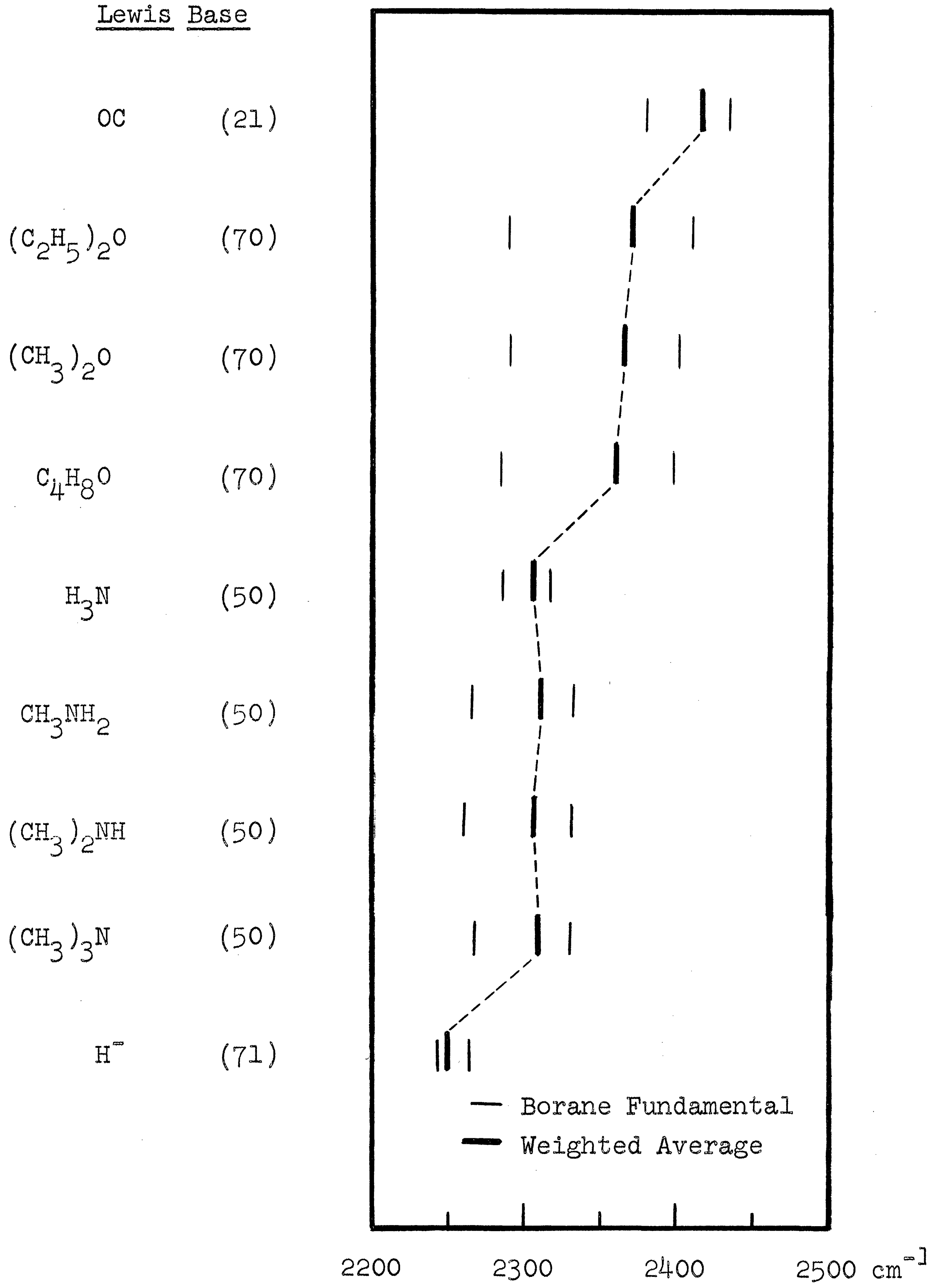


FIGURE 34 - A CORRELATION DIAGRAM FOR THE BORANE STRETCHING FUNDAMENTALS OF VARIOUS BORANE LEWIS ACID-BASE COMPLEXES

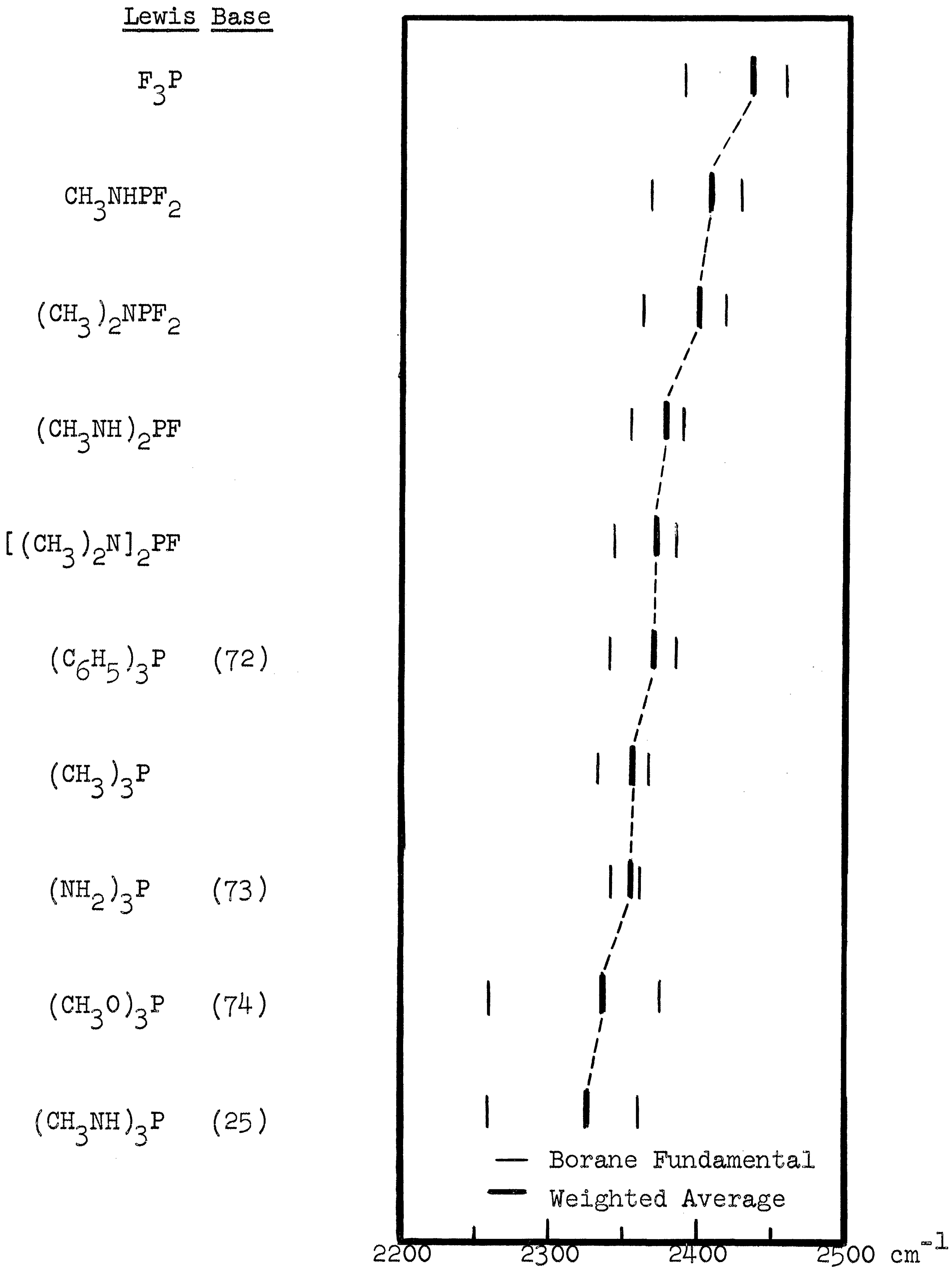


FIGURE 35 - A CORRELATION DIAGRAM FOR THE BORANE STRETCHING FUNDAMENTALS OF SOME PHOSPHINE-BORANE COMPLEXES

phosphorus and sulfur might be informative in this respect.

The extension of the previously mentioned trends to the phosphorus-boron bond vibrations is of interest, since these vibrations are relevant to the discussion of bonding and to the stability of the complexes. In the analogous amine-borane series, Cluff has found that the B-N dative bond frequency decreases in a continuous and regular fashion with the number of methyl groups attached to the nitrogen (50). Taylor has carried out a normal coordinate analysis of the vibrational frequencies of H_3NBH_3 and $(CH_3)_3NBH_3$, and he has found that this frequency decrease is due to a decrease in the B-N force constant accompanied by a simultaneous increase in the coupling between the B-N stretching and the C-N stretching and deformation modes (75). The observed phosphorus-boron stretching vibrations of several phosphine-borane complexes are listed in Table 27. Although vibrational data concerning the trisubstituted aminophosphine-boranes are not available, a similar trend appears to be present here as is found for the amine-boranes. For example, the dative bond vibrations of the disubstituted aminophosphine-boranes are observed at lower frequencies than those of the monosubstituted complexes. Attempts to correlate the stretching vibrations of the phosphorus-boron bonds with the base strength of the ligands are only partly successful. In general the dative bond vibrations in phosphine-boranes appear to shift to lower frequencies with increased base strength of the ligand, with the noted exception of the methylaminophosphine-boranes.

TABLE 27

THE P-B STRETCHING VIBRATIONS OF SEVERAL PHOSPHINE-BORANE COMPLEXES

Compound		P-B Stretching Frequency (cm^{-1})
F_3PBH_3		607
$CH_3NHPF_2BH_3$		642
$(CH_3)_2NPF_2BH_3$		589
$(CH_3NH)_2PFBH_3$		628
$[(CH_3)_2N]_2PFBH_3$		571
$(C_6H_5)_3PBH_3$	(72)	608
$(CH_3)_3PBH_3$		571

With the presently available information, very little more can be said about the strength or the stability of the dative bond in the phosphine-borane complexes. A complete vibrational analysis involving a normal coordinate treatment will be a necessary preliminary to further conclusions, since the phosphorus-boron stretching mode appears to be mixed with those of the ligand skeleton, and the extent and the nature of the mixing is uncertain. In order to explain fully the chemical properties of the phosphine-borane complexes, thermodynamic data will be necessary in addition to vibrational data.

APPENDIX A

Preparation and Purification of Materials

Methylamine.

Anhydrous methylamine was purchased from the Matheson Company and purified by fractionating it through a -78°C trap into a -196°C trap to remove any trace of water. The vapor pressure of the amine was within 2 or 3 mm of the value of 100 mm at -43.7°C reported by Stull (76).

Dimethylamine.

A commercial cylinder of anhydrous dimethylamine was purchased from the Matheson Company. Before use, traces of water were removed by fractionating the dimethylamine through a -78°C trap into a -196°C trap. Previous work in this laboratory has shown that the dimethylamine is relatively free of other impurities. The vapor pressure of the purified dimethylamine gave a pressure of 40 mm at -39.8°C (76).

Trifluorophosphine.

Trifluorophosphine was prepared by fluorinating PCl_3 with ZnF_2 using the method described by Williams (77) as modified by Sr. Fleming (13). The impure PF_3 was purified by passing it through Dowex-3 to remove traces of HCl followed fractionation from a -150°C trap to one held at -196°C.

Potassium Fluoborate.

Potassium fluoborate 92.0% enriched in boron-10 was obtained from A.E.C. stock held by the Michigan Chemical Company. A sample 99.4% enriched in boron-11 was obtained from the Union Carbide Nuclear Company.

Boron Trifluoride.

The isotopically enriched boron trifluoride was prepared by thermally decomposing a 50% mixture of LiF and the appropriate isotopically enriched KBF_4. The decomposition was accomplished by heating the mixture in a stainless steel tube to around 650°C under vacuum and condensing the products in a liquid nitrogen trap. The crude BF_3 was purified by condensing it on NaF at -126°C to remove traces of SiF_4 followed by fractionation from a -150°C trap into one held at -196°C. All ground glass connections were lubricated with Kel-F grease.

Diethyl Ether.

Analytical, reagent grade, anhydrous diethyl ether was obtained from the Mallinckrodt Chemical Works. This was dried and stored over calcium hydride.

Boron Trifluoride Etherate.

Boron-10 and -11 trifluoride etherates were prepared by direct reaction of the isotopically enriched BF_3 and anhydrous ether. This reaction was brought about by allowing BF_3 to transfer slowly from a -126°C trap on the vacuum line into a -78°C trap containing a large excess of ether. The latter trap was stirred continuously with a magnetic stirrer until the reaction was complete. The excess ether was stripped from the etherate by evaporation and the crude boron trifluoride etherate was purified by fractional distillation at 53°C and 30 mm pressure.

Diborane.

Diborane containing the natural boron isotope ration (boron-10:boron-11::1:4) was obtained from Callery Chemical Company and was purified by fractionation from a -126°C trap, through a -150°C trap, to a -196°C trap. The purified material was recovered from the -196°C trap and stored in liquid nitrogen until use.

A cylinder of diborane containing boron-10 in 93% enrichment was obtained from Arthur D. Little, Inc. through the courtesy of Amos J. Leffler. Another sample of diborane, enriched to 92% in boron-10, was given to the author by A. J. Dahl of this laboratory. Both of these samples were purified by fractional distillation.

Isotopically pure B_2H_6 (99.4% enriched in boron-11) was prepared by using the method described by Shapiro, Wiess, et al. (78) and more recently by A. R. Emery (40) and C. L. Cluff (50) in which an ether solution of $B^{11}F_3{:}O(C_2H_5)_2$ was reduced by $LiAlH_4$ according to the equation:

$$3\ LiAlH_4 + 4\ (C_2H_5)_2O{:}B^{11}F_3 \rightarrow 2\ B_2H_6 + 3\ LiF + 3\ AlF_3 + 4\ (C_2H_5)_2O.$$

In a typical reaction, 10 ml of $B^{11}F_3{:}O(C_2H_5)_2$ were reacted with a slurry of 2.3 g of $LiAlH_4$ in 30 ml of ether to give about one ml of $B_2{}^{11}H_6$. The diborane was purified by passing it through a -150°C trap into a trap held at -196°C. The purity of the diborane was checked by comparing its vapor pressure at -111.8°C with the value reported in the literature.

The preparation of $B_2{}^{11}D_6$ required a slightly different procedure because the deuterium could most easily be obtained as LiD. The method of preparation was essentially the same as that described by Finholt (79), and later by Emery (40) and Cluff (50) in which $LiAlD_4$ was prepared <u>in situ</u> by the addition of an ether solution of aluminum chloride etherate to a slurry of LiD. The $B_2{}^{11}D_6$ obtained in this reaction was purified by passing it through a -150°C trap into a -196°C trap and its vapor pressure was checked with that reported in the literature.

Metal Hydrides.

The $LiAlH_4$, $LiAlD_4$, and LiD were obtained from Metal Hydrides, Incorporated, Beverly, Massachusetts. The isotopic purity of the latter two compounds was stated to be 98% and 96.6% respectively.

APPENDIX B

Preparation and Purification of Samples

F_3PBH_3.

A typical preparation involved the reaction of 86.1 mM of PF_3 (5.7 fold excess) with 15.7 mM of B_2H_6 in a high pressure stainless steel reaction vessel which could withstand pressure up to 1500 lb./sq. in. The reaction tube was allowed to stand for 4 days at room temperature and then was connected to the vacuum line to strip the product F_3PBH_3 from the unreacted PF_3 and B_2H_6. The fractionation was accomplished by distilling the F_3PBH_3 through a -128°C trap, into a -155°C trap and collecting the more volatile components in a -196°C trap. The less volatile impurities remained in the -128°C trap while the pure F_3PBH_3 remained in the -155°C trap.

$CH_3NHPF_2BH_3$.

In a typical preparation, a 3.4 mM of F_3PBH_3 was dissolved in about 20 ml of diethyl ether at -111°C by first condensing the sample of F_3PBH_3 and then the ether into a reaction tube using liquid nitrogen. The tube was allowed to warm very slowly, with the pressure in the tube being monitored until the F_3PBH_3 and ether had melted and had gone into solution completely. At no time were the contents of the tube allowed to warm above -111°C. These precautions were necessary because F_3PBH_3 decomposes rapidly in the gaseous phase but is somewhat more stable in solution.

After the solution of F_3PBH_3 was complete, CH_3NH_2 vapor was introduced over the surface of the solution while stirring, until 9.0 mM had been completely absorbed. After stirring for 30 minutes at -111°C, the solution was gradually warmed to -78°C at which temperature a white precipitate slowly formed. The mixture was allowed to stand for 16 hours at -78°C after which the volatile components were distilled from the tube through a trap at -78°C into a trap at -196°C. The reaction tube was then warmed slowly to 0° and the distillation was stopped. Diethyl ether and CH_3NH_2 were trapped in the -196°C trap and a mixture of diethyl ether and $CH_3NHPF_2BH_3$ was retained in the -78°C trap.

The final mixture of diethyl ether and $CH_3NHPF_2BH_3$ was separated by fractionating it from a trap at -35°C through a trap at -65°C into a trap at -196°C. The $CH_3NHPF_2BH_3$ was retained in the -65°C trap. About 2.23 mM of $CH_3NHPF_2BH_3$ was collected giving a yield of 65.7% based on the F_3PBH_3 used.

$(CH_3NH)_2PFBH_3$.

A sample of F_3PBH_3 (3.8 mM) was dissolved in 15 ml of diethyl ether at -111°C. The same procedure for bringing about the solution of F_3PBH_3 in diethyl ether was used as was mentioned previously for the preparation of $CH_3NHPF_2BH_3$.

An excess of CH_3NH_2 (47.4 mM) was frozen into the reaction tube with liquid nitrogen, the reaction tube sealed off and the system allowed to warm to -111°C. The solution was stirred for 20 minutes with a magnetic stirrer and then warmed to -78°C. The mixture was maintained at this temperature and stirred for 10 to 12 hours. Finally the reaction tube was allowed to warm to room temperature and maintained for 2 to 3 days.

After opening the tube to the vacuum system and removing the volatile components, 10 ml of fresh diethyl ether were condensed into the tube and the ether insoluble $CH_3NH_2 \cdot HF$ salt was removed by vacuum line filtration through a glass frit. The diethyl ether was then distilled from the filtrate leaving the nonvolatile liquid, $(CH_3NH)_2PFBH_3$. The yield of crude product was almost quantitative based upon the amount of PF_3BH_3 used.

The sample of $(CH_3NH)_2PFBH_3$ prepared this way had a slight yellowish color. The sample was passed through charcoal followed by an ether wash. The diethyl ether was removed by evaporation and the $(CH_3NH)_2PFBH_3$ remained as a colorless liquid.

<u>$(CH_3)_2NPF_2$.</u>

A 13.5 mM sample of PF_3 was condensed with liquid nitrogen in a thin layer inside a reaction tube and then 20.3 mM of $(CH_3)_2NH$ was condensed on top of the PF_3. The reaction vessel was repeatedly warmed to room temperature and then cooled down with liquid nitrogen until no further drop in pressure was noted in the system.

The product was purified by distillation from a -46°C trap through traps held at -95°C and -196°C, the $(CH_3)_2NPF_2$ remaining in the -95°C trap. Traces of $(CH_3)_2NH$ and $[(CH_3)_2N]_2PF$ were removed from the sample by condensing the mixture on a small amount of anhydrous $CoBr_2$. The system was warmed to room temperature and the resulting green solution allowed to stand for one hour before fractionating through a -95°C trap to a -196°C trap. The purified ligand was recovered from the -95°C trap while $(CH_3)_2NH_2$ and $[(CH_3)_2N]_2PF$ remain behind as complexes of $CoBr_2$. Using this method of preparation a yield of about 85% was usually obtained for the $(CH_3)_2NPF_2$.

$(CH_3)_2NPF_2BH_3$.

In the usual preparation, an excess of the ligand was condensed in a tube with a few millimoles of B_2H_6 at -196°C. The mixture was alternately warmed to room temperature and then cooled with liquid nitrogen several times to insure complete reaction of the reagents after which it was fractionated through a -78°C trap to a -196°C trap. Unreacted B_2H_6 was collected in the -196°C trap while crude $(CH_3)_2NPF_2BH_3$ was retained in the -78°C trap. The complex was purified further by distilling it from a trap held at -45°C into a trap held at -78°C.

$(CH_3)_2NPF_2B^{11}F_3$.

About 2.0 mM of $(CH_3)_2NPF_2$ were condensed in the bottom of a reaction tube along with 2.5 mM of $B^{11}F_3$. The reaction tube was warmed slowly to room temperature. As the gaseous $B^{11}F_3$ reacted with the liquid $(CH_3)_2NPF_2$, $(CH_3)_2NPF_2B^{11}F_3$ a white crystalline solid formed. When the system had reached equilibrium the reaction vessel was placed in a -64°C slush bath and the volatile components were distilled from the tube through traps held at -95°C and -196°C. Unreacted $(CH_3)_2NPF_2$ and $B^{11}F_3$ were collected in the -95°C and -196°C trap respectively. The impure $(CH_3)_2NPF_2B^{11}F_3$ was purified by sublimation from a trap held at -23°C.

$[(CH_3)_2N]_2PF$.

A sample of $(CH_3)_2NPF_2$ (4.2 mM) was condensed into a thick walled reaction vessel along with 12.6 mM of $(CH_3)_2NH$. The tube was sealed off and allowed to warm to room temperature and was maintained at this temperature for three days.

The tube was then cooled down in liquid nitrogen, the tube opened to the vacuum line, and the contents fractionated through traps held at -78°C, -95°C and -196°C. Dimethylamine was recovered from the -196°C trap, $(CH_3)_2NPF_2$ from the -95°C trap, and $[(CH_3)_2N]_2PF$ was recovered from the -78°C trap, leaving a white, nonvolatile, solid residue in the reaction tube.

The sample of $[(CH_3)_2N]_2PF$ initially gave a vapor pressure of 14 mm at 0°C as compared to 3.6 mm reported by Kodama (25) and Sr. Fleming (13). An infrared analysis indicated that the sample of $[(CH_3)_2N]_2PF$ contained $(CH_3)_2NPF_2$ as an impurity. The more volatile $(CH_3)_2NPF_2$ impurity was removed by vaporization while the sample tube was maintained at -63.5°C, until the vapor pressure and the infrared spectrum of the sample was identical to that reported by Sr. Fleming (13).

$\underline{(CH_3)_2N_2PFB^{11}H_3}$.

A sample of $[(CH_3)_2N]_2PF$ (5.0 mM) was condensed into a reaction tube along with 6.0 mM of $B_2{}^{11}H_6$ (boron-11 enriched). The reaction tube was allowed to warm to room temperature and after the reaction mixture had equilibrated the contents of the tube were fractionated through a -35°C trap to one held at -196°C. The unreacted diborane was recovered from the -196°C trap and impure $[(CH_3)_2N]_2PFB^{11}H_3$ remained in the -35°C trap. The impure product was purified by distilling it from a 0°C trap into a -196°C trap. The product was recovered from the -196°C trap and any less volatile impurities remained behind in the 0°C trap.

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