Synthesis And Infrared-spectrum Of Propynl Boron Difluoride.

SYNTHESIS AND INFRARED SPECTRUM OF PROPYNYL BORON DIFLUORIDE

by

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To Jane

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ABSTRACT

The first known synthesis of propynyl boron difluoride, CH_3CCBF_2 has been carried out, and the infrared spectrum of the molecule has been determined. Propynyl boron difluoride was prepared by three methods: (1) by allowing a reaction mixture of BF_3 and BCl_3 to react with dipropynyl mercury; (2) by allowing a reaction mixture of BF_3 and BBr_3 to react with dipropynyl mercury; and (3) by fluorinating propynyl boron dichloride, a previously unknown molecule prepared by reacting BCl_3 with dipropynyl mercury. The melting point of propynyl boron difluoride was found to be -61.3°C. Vapor pressure data for liquid propynyl boron difluoride fit the equation: $\log_{10}P = -1622.8/T + 8.628$ from which the normal boiling point and heat of vaporization were estimated to be 9°C and 7.42 kcal/mole, respectively.

Infrared spectra of propynyl boron difluoride were recorded in the region from 4000 to 250 cm^{-1} by using a single beam grating instrument with a spectral slit width of approximately 0.3 cm^{-1}. The spectrum was compatible with a molecular model belonging to the G_{12} symmetry group with the two end groups rotating freely with respect to each other. The vibrational assignment was based on isotopic splitting, band shape considerations, and group frequencies. From the vibrational assignment and estimated rotational constants, standard thermodynamic quantities of propynyl boron difluoride were estimated over the temperature interval from

100°K to 1000°K.

The most outstanding feature of the gas phase infrared spectrum of propynyl boron difluoride was the appearance of Q-branch structure for the asymmetric methyl stretches. It was ascertained that this fine structure resulted from internal rotation of the methyl group, and an analysis of this band, using empirical relationships, resulted in a Coriolis coupling coefficient of +0.16.

CHAPTER I

INTRODUCTION

Infrared spectroscopy is a widely used spectrophotometric method for determining the structure of molecules in various physical states. This investigation is an example of the use of infrared techniques to determine the structure of a previously unknown gaseous organoborane. An analysis of the finer details of the infrared spectrum has also provided information related to the internal motions of the molecule.

Organoboranes were first synthesized in 1859 by Frankland, the father of organometallic chemistry, and since then, the number of alkyl and aryl boron compounds reported has increased rapidly [1]. However, of the organoboranes characterized, only a few contain an alkenyl substituent bonded to a boron atom, namely, the vinylboranes [2,3] and several unsaturated boronic acids [4]. The number of alkynyl boranes is even less. Until the recent synthesis of ethynyldihaloboranes [5], the only simple alkynyl boranes reported were amine complexes [6]. This work reports the synthesis of a second member of the alkynyldihaloboranes, namely propynyl boron difluoride, CH_3CCBF_2.

The first member of the alkynyldihaloborane series, ethynyl boron difluoride, $HCCBF_2$, was prepared in low yield by treating ethynyltrimethyl tin with boron trifluoride, a method similar to

the preparation of vinyl boron dihalides [3]. The structure and dipole moment of ethynyl boron difluoride have been determined from its microwave spectrum [7], and the parameters are presented in Table 1. These data indicate that the molecule has C_{2v} point

TABLE 1

Structural Parameters and Dipole Moment of Ethynyl Boron Difluoride

Structural Parameter	Value
$r_{C\equiv C}$	1.203Å (assumed)
r_{C-H}	1.060Å (assumed)
$<FBF$	118.2°
r_{B-C}	1.53Å
$\mu = 1.93 \pm 0.06D$	

group symmetry, the boron atom being co-linear with the ethynyl group and the off-axis fluorine atoms situated symmetrically about the figure axis. Preliminary infrared spectral results to characterize the molecule were reported [5] and are shown in Table 2, but an exhaustive study of the gas phase infrared spectrum of $HCCBF_2$ has not been reported. Apparently the half-life of approximately one minute precludes a detailed investigation of the gas phase infrared spectrum.

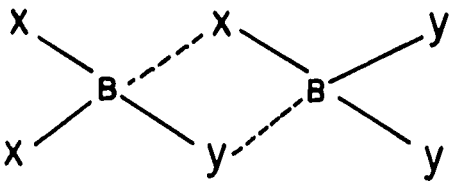
TABLE 2

Vibrational Frequencies for Ethynyl Boron Difluoride

Group Vibration	Wavenumber Value (cm^{-1})
C-H stretch	3310
C≡C stretch	2120
BF_2 stretches	1450 - 1300
≡C-H bending modes	725 - 650

Since propynyl boron difluoride is the second member of this series, it is reasonable that it should exhibit many properties characteristic of the alkynyldihaloboranes. For this reason alone, a study of the physical properties and the gas phase infrared spectrum of propynyl boron difluoride is in order.

Chemical interest in unsymmetrical boranes arises from the unusual bonding characteristics in boron compounds [1]. For example, the mixed fluoro, chloro, and bromo halides of boron have only a transient existence at ambient temperatures; i.e., BF_2Cl rapidly transforms into BF_3 and BCl_3. Similarly, $(CH_3)_2BCH_2CH_3$ disproportionates to $(CH_3)_3B$ and $(CH_3CH_2)_3B$. These transformations proceed by means of a four centered reaction species involving the p_z orbital of boron, e.g.



The experimental foundation for this mechanism is based on the relatively high chemical stability of the vinylalkylboranes. Apparently the p_z orbital of the boron atom in each of the vinylalkylboranes is involved in the π system of the vinyl substituent to prevent formation of the dimer [2]. Similar stabilities were found for the vinylhaloboranes [3].

By invoking the same reasoning, the alkynyldihaloboranes should be chemically stable at ambient temperatures; however, $HCCBF_2$ is not. This apparent contradiction is best explained by the strong electron-withdrawing character of the acetylenic group which results in an acidic boron atom, thereby permiting formation of the four centered intermediate. Since the electronegative character of the acetylenic group in propynyl boron difluoride will be decreased by the electropositive character of the methyl group, CH_3CCBF_2 was expected to have a greater chemical stability than $HCCBF_2$. In fact, propynyl boron difluoride proved to be more chemically stable than ethynyl boron difluoride.

From a spectroscopic point of view, a most interesting feature of this molecule is its six-fold potential barrier which inhibits rotation of the $CH_3C\equiv$ rotor with respect to the $\equiv CBF_2$ framework about their common axis. Consideration of internal rotation in CH_3CCBF_2 will constitute a major portion of this work.

For years, the magnitude and origin of the forces inhibiting internal rotation has been of interest. At present, these potential barriers are believed to arise primarily from the electrostatic inter-

actions of polar groups, from steric hinderance of the groups, and from partial double bond character between the groups. In spite of these ideas, it should be noted that at present there is no a priori way to predict accurate barrier heights.

The few data available concerning internal rotation have resulted in several empirical relationships [8] of importance in this investigation. First of all, when the symmetries of the two groups at the ends of axial bonds result in a six-fold potential barrier, the barrier height is very low. Three molecules in this category are methyl boron difluoride, nitromethane, and toluene, with barriers of 13.77 [9], 6.00 [10], and 13.94 cal/mole [11], respectively.

A second trend is the decrease in the potential barrier as the axial bond length increases. In considering the series CH_3CH_3, CH_3SiH_3, and CH_3GeH_3, the barrier decreases from 2.8, to 1.67, to 1.24 kcal/mole [12]. Even though the bonded atoms are different in each case, the trend is generally applicable. A related empirical relationship is the decrease in barrier on insertion of a -C≡C- functional group between axially bonded atoms. From examples cited in Table 3, it should be noted that such an insertion causes at least a ten-fold decrease in magnitude of the barrier. No exceptions to this trend have been reported.

Of less significance is the effect of substituting other atoms, such as halogen atom, for one or more of the hydrogen atoms in ethane, methyl silane, and acetaldehyde. The effect is not very

TABLE 3

Barriers to Internal Rotation* -- The Effect of the -C≡C- Group

Molecule	Barrier Height (cal/mole)	Molecule	Barrier Height (cal/mole)
CH_3CH_2Cl	3685	CH_3CCCH_2Cl	<100
CH_3CF_3	3500	CH_3CCCF_3	<300
CH_3SiF_3	1670	CH_3CCSiF_3	<3
CH_3CH_3	∿2800	CH_3CCCH_3	∿1.31
CH_3NO_2	6.03	CH_3BF_2	13.77

*See references 12, 13, 14.

large and at most produces changes of only 30 per cent when substitution is confined to one end of the molecule. Also, the effect does not always increase the barrier as does replacing the acetyl hydrogen with a halogen in acetaldehyde. The addition of one fluorine to ethane increases the barrier and the addition of a second fluorine produces little effect. Available data indicate that substitution of a chlorine always increases the barrier, but the values for CH_3CH_2F, CH_3CH_2Cl, and CH_3CH_2Br are suprisingly similar.

Application of these empirical relationships to propynyl boron difluoride indicates that the potential inhibiting internal rotation in this molecule must be exceptionally low, approaching free internal rotation. As a result, an anomalous vibration-rotation spectrum with rotational fine structure was expected for propynyl boron difluoride,

in spite of the unfavorably large principal moments of inertia for the molecule.

Rotational structure similar to that expected for CH_3CCBF_2 was observed in the infrared spectra of methyl boron difluoride and nitromethane. The line sequences observed in the absorptions of the asymmetric methyl vibrations of these two molecules were successfully analyzed by JONES and SHEPPARD [15] using a theoretical model in which free internal rotation was assumed. These infrared bands were found to be complex because of the interactions of internal rotation with overall rotation. SHEPPARD and WOODMAN [16] have presented a more detailed theoretical discussion of the problem, but an experimental attempt to resolve the problem further was unsuccessful, even with the most sophisticated instrumentation [17].

Since propynyl boron difluoride possesses a six-fold potential barrier similar to CH_3BF_2 and CH_3NO_2, and is a near prolate top with the axis of internal rotation coincident with the principal axis of the molecule, the complexities of the infrared spectrum were expected to be reduced. As a result, a detailed analysis of the vibration-rotation spectrum of CH_3CCBF_2 may better represent the gross effects of internal rotation in the infrared spectrum.

CHAPTER II

EXPERIMENTAL PROCEDURES

Preparation of Propynyl Boron Difluoride

Propynyl boron difluoride was prepared by allowing gaseous chlorodifluoroborane to react with solid dipropynyl mercury. The synthesis is outlined by the following reactions:

$$2KI + HgI_2 \rightarrow K_2HgI_4$$

$$2NaOH + K_2HgI_4 + 2CH_3CCH \rightarrow (CH_3CC)_2Hg + 2H_2O + 2KI + 2NaI$$

$$2BF_3 + BCl_3 \rightleftarrows 3BF_2Cl$$

$$2BF_2Cl + (CH_3CC)_2Hg \rightarrow 2CH_3CCBF_2 + HgCl_2$$

The gaseous nature and high chemical reactivity of the compounds involved in this synthesis necessitated the use of a glass vacuum system for their preparation and purification. The vacuum system consisted of a preparative section and a small manifold for filling infrared cells. The preparative section contained four U-tube traps, and a mercury manometer connected in series to a manifold. The filling manifold was merely a glass tube to which a mercury manometer and two ground glass outlets were attached. Since propynyl boron difluoride was found to attack ordinary hydrocarbon stopcock grease, all ground glass surfaces in the preparative section of the vacuum system were lubricated with Kel-F grease. A pressure of

approximately 10^{-6} torr was produced by a two stage, water cooled mercury diffusion pump coupled with a Welch model 1400 two stage mechanical pump.

Dipropynyl mercury

Dipropynyl mercury was prepared by allowing methyl acetylene to react with a basic solution of potassium mercuric iodide. In a typical preparation of K_2HgI_4 solution [18], 37.17 g (82.0 millimoles) anhydrous HgI_2 were added to 150 ml water, followed by the addition of 26.0 g (157 millimoles) anhydrous KI. The resulting solution was added slowly to a cooled solution of 58.2 g (1.45 moles) NaOH in 200 ml water contained in a 1 liter volumeteric flask. The K_2HgI_4 solution was diluted to 1 liter.

To prepare dipropynyl mercury [19], 500 ml (41.0 millimoles) basic K_2HgI_4 solution were added dropwise, under a methyl acetylene atmosphere, to a 1000 ml round bottom flask containing 200 ml of water which were continuously saturated with methyl acetylene. The reaction mixture was stirred continuously during the addition. The desired product formed as a flocculent white precipitate which was easily removed from solution by vacuum filtration. The precipitate was washed twice with cold water and sublimed in vacuo at 105°C. The dipropynyl mercury was characterized by a melting point of 204°C, (lit. 204±1°) and its reaction with HCl to yield CH_3CCH. The yield was 9.35 g $(CH_3CC)_2Hg$, or 82 per cent based on the HgI_2 consumed.

Propynyl boron difluoride

To prepare propynyl boron difluoride, gaseous chlorodifluoroborane was allowed to react with dipropynyl mercury. Even though the

mixed chlorofluoroboranes have not been isolated, BF_2Cl and BCl_2F do exist as independent species formed by halogen exchange in a mixture of boron trifluoride and boron trichloride [20]. The chlorodifluoroborane used for the synthesis of CH_3CCBF_2 was prepared by an exchange reaction of boron trichloride with an excess of boron trifluoride. A typical reaction mixture was 15.4 millimoles BCl_3 and 30.8 millimoles BF_3, contained by a 1100 ml round bottom flask. The formation of BCl_2F and BF_2Cl in the gaseous mixture was confirmed by a low resolution infrared spectrum recorded three hours after the mixture had warmed to room temperature.

In a typical preparation of propynyl boron difluoride, 0.15 g BF_2Cl reaction mixture were passed through a Pyrex reaction tube containing 0.40 g (1.45 millimoles) dipropynyl mercury. Because the ensuing reaction was rapid and highly exothermic, the gas flow through the reaction tube was controlled with a pin-hole regulator, which is shown in Fig. 1. The rate of the reaction could be followed conveniently by the darkening of the dipropynyl mercury in the Pyrex column: a typical reaction of this sort required approximately one hour. Because the amount of CH_3CCBF_2 produced was on the order of tenths of millimoles, six reactions were carried out in sequence. The resulting crude product was condensed in a -196°C U-tube trap. Low resolution infrared spectra of the gaseous products indicated the presence of propynyl boron difluoride, boron trifluoride, boron trichloride, propynyl boron dichloride, and methyl acetylene.

Propynyl boron difluoride was isolated from the undesired impurities by simple fractionation in the vacuum system. The reaction

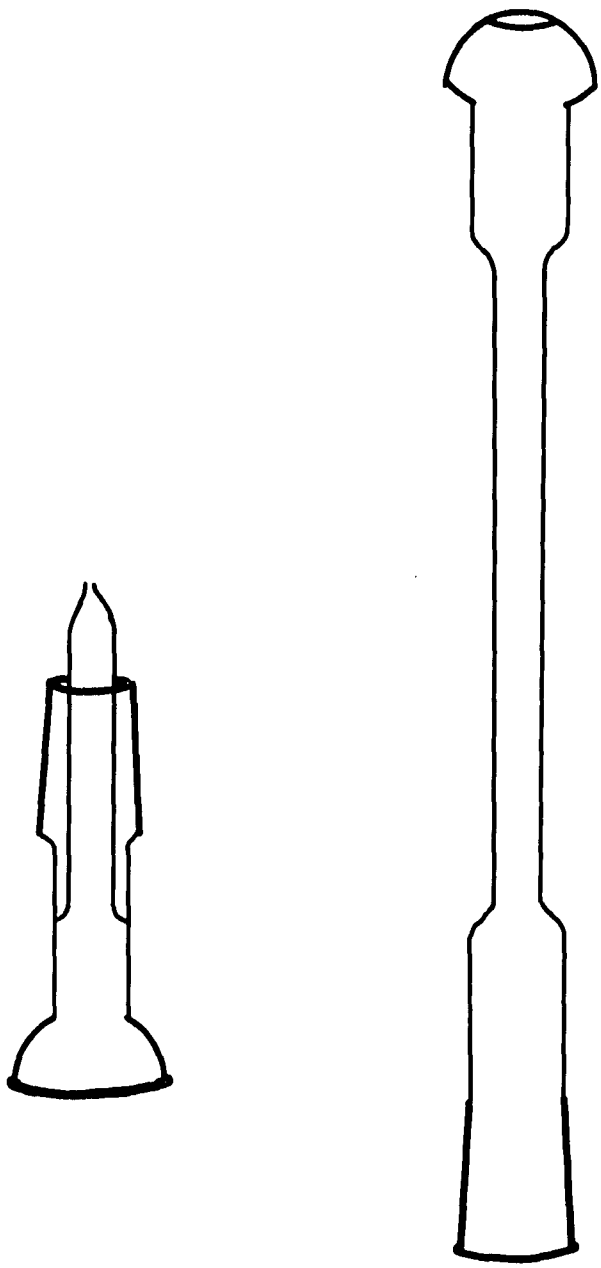


Fig. 1. Pin-hole regulator (left) and Pyrex reaction tube (right). The tapered ground glass joints are 12/30 ℨ, and the ball and socket joints are 18/9.

products were distilled from a -55°C U-tube trap; vapors emanating from this trap were passed through a -89°C U-tube trap and into an adjacent U-tube trap at -196°C. Nearly pure propynyl boron difluoride condensed in the -89°C U-tube trap, while boron trifluoride and methyl acetylene condensed in the -196°C trap. Other impurities remained in the -55°C U-tube trap. High purity samples of CH_3CCBF_2 were obtained by a similar redistillation of the -89°C fraction. The per cent yield for the sequence of six reactions was 4.5 per cent, based on the $Hg(CCCH_3)_2$ consumed. The purity of the sample was determined by infrared and mass spectra. A low resolution infrared spectrum of propynyl boron difluoride is shown in Fig. 2, and a mass spectrum of the compound in Fig. 3.

A second synthetic route to propynyl boron difluoride that was tried consisted of allowing a mixture of boron tribromide and boron trifluoride to react with dipropynyl mercury to form CH_3CCBF_2. However, the inconvenient low vapor pressure and high reactivity of BBr_3, plus a low final yield of only 3.6 per cent, did not warrant use of this method.

Propynyl boron difluoride was prepared by still a third method which is outlined by the following series of reactions:

$$(CH_3CC)_2Hg + BCl_3 \rightarrow CH_3CCBCl_2$$

$$CH_3CCBCl_2 \xrightarrow[-45°C]{SbF_3} CH_3CCBF_2$$

Propynyl boron dichloride, a previously unknown molecule, could be prepared in approximately 25 per cent yield by the reaction of BCl_3 with dipropynyl mercury. The freshly prepared CH_3CCBCl_2 was then

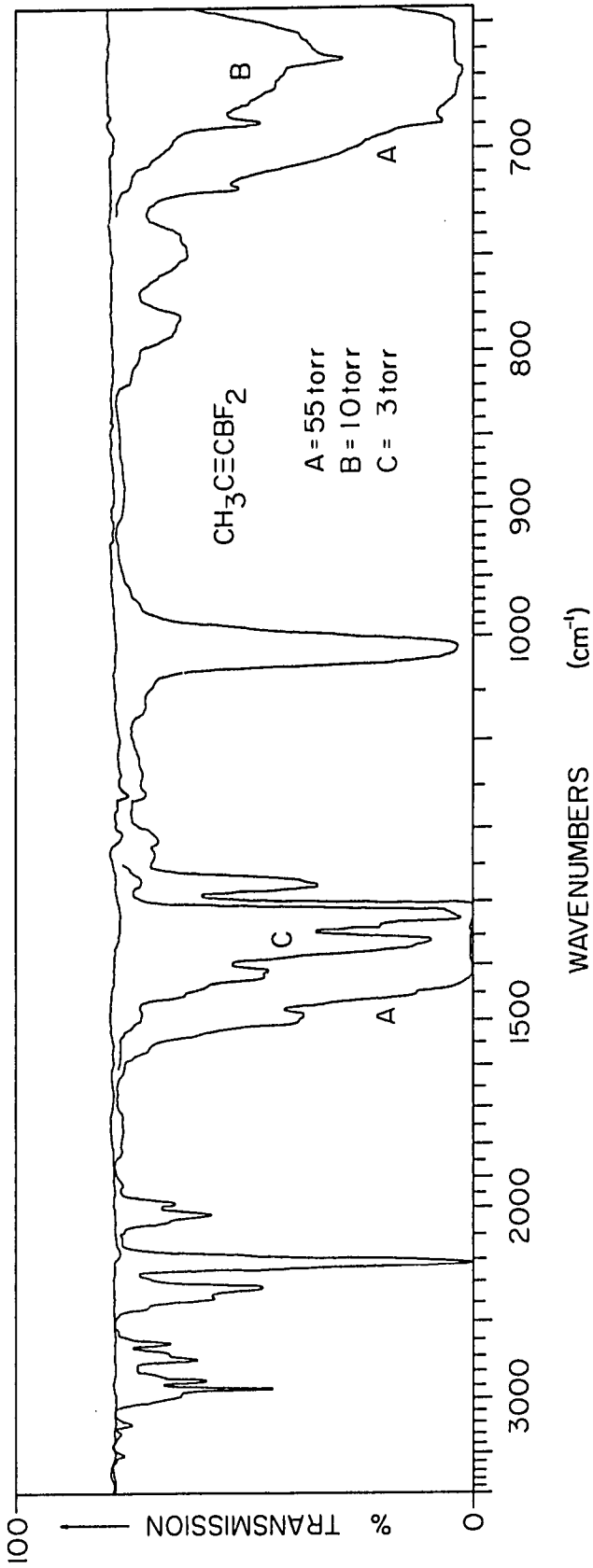


Fig. 2. Low resolution infrared spectrum of propynyl boron difluoride.

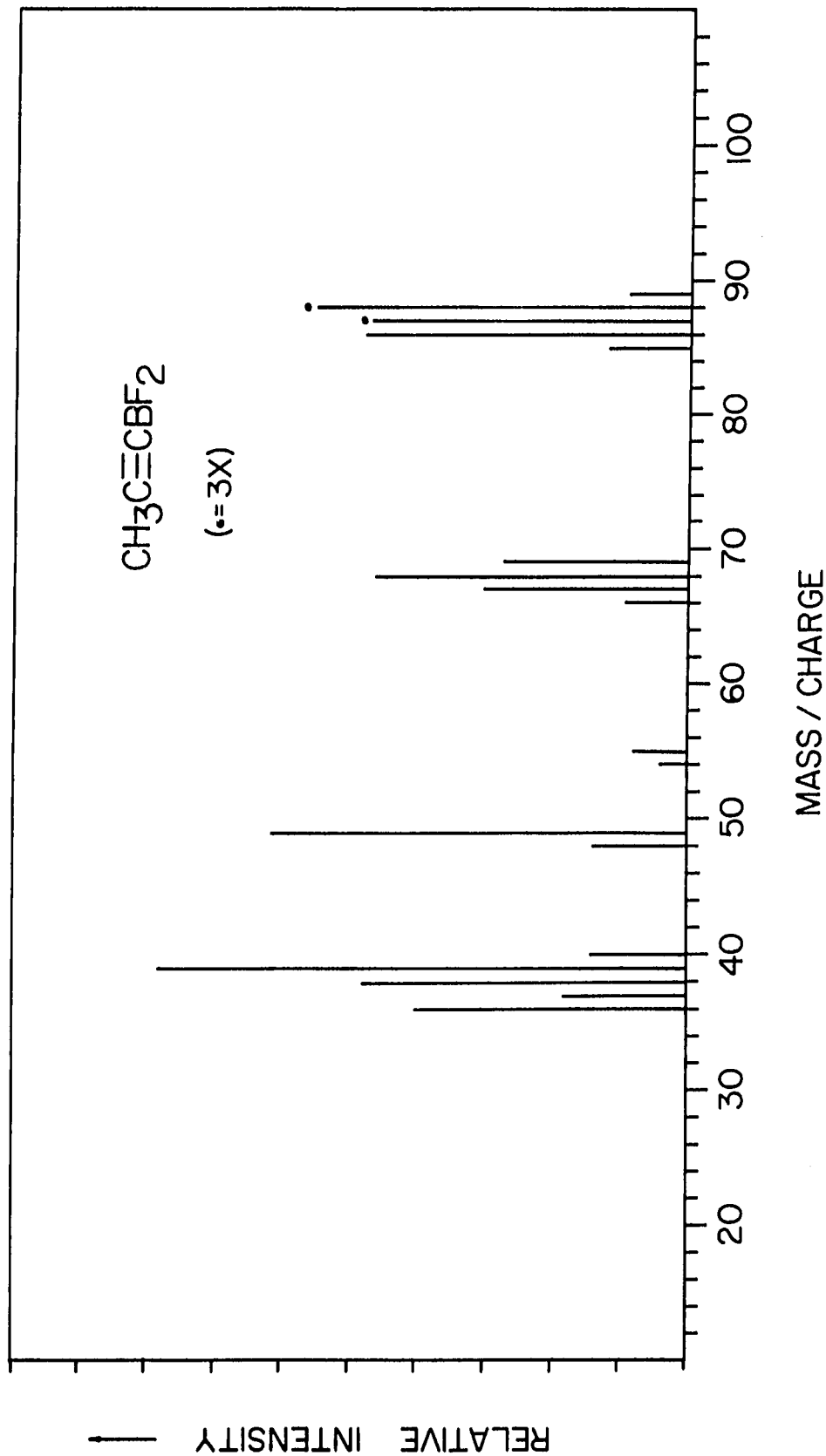


Fig. 3. Mass spectrum of propynyl boron difluoride.

fluorinated with SbF_3 to form propynyl boron difluoride. A typical reaction sequence is described as follows. Five and one-tenth millimoles BCl_3 were condensed into a one liter round bottom flask at -196°C which contained 0.7084 g (2.55 millimoles) $Hg(CCCH_3)_2$. The flask and its contents were warmed slowly to room temperature over a two and one-half hour period. Then the volatile reaction products were condensed in a U-tube trap of the vacuum system. The trap was surrounded by a -75°C bath and the volatile constituents were removed by cryogenic pumping. The propynyl boron dichloride which remained in the -75°C trap was transferred to a -196°C storage tube containing SbF_3 which had been dried previously in vacuo at 130°C for eight hours. The storage tube containing the reactants was gradually warmed to room temperature over a two day period. Propynyl boron difluoride began to form at -45°C. Since the per cent yield was extremely low and the reaction sequence was time consuming, this procedure was not pursued further.

Unfortunately, propynyl boron difluoride is highly reactive and chemically unstable at ambient temperatures. Apparent decomposition products are CH_3CCH, BF_3, and an intractable white crystalline-like substance which forms on the interior surfaces of the infrared cells. Because of this behavior, the gas phase infrared spectrum shown in Fig. 2 exhibits BF_3 absorptions, even though the sample was estimated to contain less than 2 per cent of this impurity. Methyl acetylene was not readily detected in the infrared spectrum; however, it did appear in the mass spectrum, shown in Fig. 3, and was probably present in concentrations of 5 per cent or less. Because

of the apparent chemical instability of the molecule, freshly distilled samples of propynyl boron difluoride were used for recording all infrared spectra and determining physical constants.

Physical Properties

Several physical constants of propynyl boron difluoride were determined during this investigation. The melting point was measured by the magnetic plunger method of STOCK [21], with the use of copper-constantan thermocouples and a Leeds & Northrup millivolt potentiometer to determine the temperatures, which were checked with a pentane thermometer. The average value of two measurements for the melting point was $-61.3\pm0.5°C$.

The vapor pressure of propynyl boron difluoride as a function of temperature was also determined over the temperature interval from 215.1°K to 260.4°K, by permitting a freshly distilled liquid sample to warm in a small tube which was connected to a mercury manometer. Temperatures of the sample tube were determined from the millivolt potential of copper-constantan thermocouples with a zero degree Centigrade reference junction, as measured with a Leeds & Northrup potentiometer. Vapor pressure data are presented in Table 4. Using the in-line computer program BMD05R [22], a least squares fit of these data to the Clausius-Clapeyron Equation resulted in the following equation:

$$\log_{10}P = -1622.8/T + 8.628$$

with a correlation coefficient of -0.99977. From this equation the normal boiling point of propynyl boron difluoride was estimated to

Table 4

Vapor Pressure Data for Propynyl Boron Difluoride

Temperature (°K)	Pressure (torr)	Pressure calc (torr)
215.1±0.3	12±1	12
218.0	15	15
220.5	19	19
223.4	24	23
227.7	32	32
231.1	41	40
234.7	51	52
238.5	65	67
242.0	80	84
244.7	97	99
247.2	115	116
249.7	135	134
251.9	155	153
254.7	182	181
257.4	216	211
260.4	250	249

be 282°K, the molar heat of vaporization was 7.42 kcal, and the Trouton constant was 26.3 cal/mole-deg.

Spectrometers

Two infrared spectrometers were used during this investigation. To monitor sample purity, low resolution spectra in the region from 4000 to 650 cm^{-1} were recorded with a Perkin-Elmer model 21 double beam prism instrument equipped with NaCl optics. Moderate resolution spectra (0.3 cm^{-1} resolution) from 4000 to 250 cm^{-1} were obtained with a Perkin-Elmer model 16 single beam, filter-grating spectrometer [23] which was calibrated using the vibration-rotation spectra of simple gases [24], or the pure rotational spectrum of water [25]. Conventional Pyrex gas cells of 10 cm path length, equipped with either NaCl, KBr, or CsBr windows, were used to obtain the vapor phase results. Polycrystalline thin film spectra of CH_3CCBF_2 were obtained at -196°C with a low temperature cell similar to that described by WAGNER and HORNIG [26].

A Spex model 1401 Raman spectrometer equipped with a Carson model 500 Ar^+/Kr^+ laser was used in several unsuccessful attempts to measure the Raman spectrum of CH_3CCBF_2. Initially, liquid samples sealed in Pyrex tubes 50 mm in length by 3 mm in diameter were used at ambient temperatures, but the samples decomposed rapidly when excited with each of the four available excitation lines: 4880 Å, 5145 Å, 5682 Å, 6471 Å. A subsequent attempt with a Harney-Miller low temperature cell revealed that propynyl boron difluoride does not lend itself to Raman techniques: the fluorescence of the samples was so intense that the attenuation required to bring the pen on scale washed out the Raman scattering.

Mass spectra were recorded with a Perkin-Elmer Hitachi model RMU-6E spectrometer.

CHAPTER III

THEORETICAL DISCUSSION

Introduction

To determine the structure of a molecule, one must first propose a model which is compatible with the observed spectrum of the molecule. Usually the proposed model is constructed from a judicious selection of known structural data for functional groups that are known to be present in the molecule. Then, if the moments of inertia of the molecule are sufficiently small, it is possible to determine accurately bond lengths and bond angles by suitable analysis of the observed spectral data. In this manner spectroscopists have determined exact structural parameters for many diatomic and simple polyatomic molecules. Unfortuately, for most polyatomic molecules, whose complex and unresolved spectra preclude a precise, unequivocal determination of their structural parameters, this method is impossible to use. For these molecules, the best spectroscopists can do is to confirm that the observed spectrum is consistent with that of a proposed molecular model. Such is the case for propynyl boron difluoride.

Another consideration of polyatomic molecules, such as CH_3CCBF_2, concerns the conformation of the molecule. Whenever two or more functional groups with off-axis atoms are chemically bonded, it is essential to consider the angular orientation of these groups

with respect to each other about their common bond. In most cases, the potential barrier inhibiting internal rotation of the groups is high with respect to the kinetic energy imparted at ambient temperatures. As a result, one functional group, called the rotor, executes torsional oscillations with respect to the other functional group, called the framework, and occasionally tunnels into a different potential well. On the other hand, if the potential inhibiting internal rotation is considerably less than kT, the rotor may rotate virtually freely with respect to the framework. In Chapter I, it was shown by empirical relationships that nearly free internal rotation was expected for CH_3CCBF_2.

Thus, the molecular model proposed for propynyl boron difluoride consisted of a methyl group and a BF_2 group bonded to opposite ends of an acetylenic functional group, with the two end groups rotating freely with respect to each other. The $CH_3C\equiv$ part of the molecule was defined as the rotor, and the $\equiv CBF_2$ part of the molecule as the framework. The assumed molecular configuration for propynyl boron difluoride, shown in Fig. 4, was based on known structural parameters of CH_3CCH [27] and $HCCBF_2$ [7]. From the structures of these two molecules, estimates of the moments of inertia for propynyl boron difluoride were calculated and appear in Table 5. Details of the calculation of the moments of inertia are presented in Appendix I.

To determine whether a proposed model is suitable, spectral properties of a molecule are predicted by applying group theory methods to the proposed model and comparing the results with the

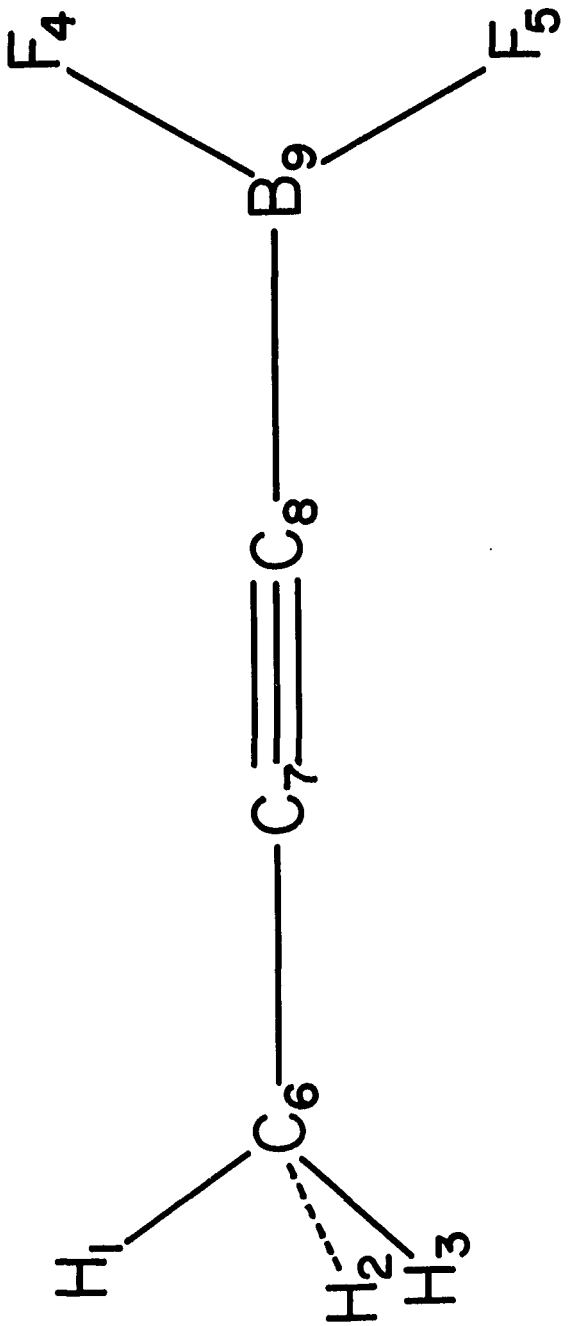


Fig. 4. Molecular configuration of propynyl boron difluoride.

TABLE 5

Bond Distances, Bond Angles and Principal Moments of Inertia of $CH_3C{\equiv}CBF_2$

Bond Distance Bond Angle	Approximate Value	Reference Molecule
-C-H	1.112 Å	$CH_3C{\equiv}CH$
-C-C-	1.458 Å	$CH_3C{\equiv}CH$
-C≡C-	1.207 Å	$CH_3C{\equiv}CH$
<H-C-H	108°	$CH_3C{\equiv}CH$
-C-B-	1.53 Å	$HC{\equiv}CBF_2$
-B-F	1.309 Å	$HC{\equiv}CBF_2$
<F-B-F	118°	$HC{\equiv}CBF_2$

$I_a = 84.86 \times 10^{-40}$ g-cm^2; $I_b = 543.6 \times 10^{-40}$ g-cm^2;
$I_c = 623.1 \times 10^{-40}$ g-cm^2

observed spectrum. The remainder of this chapter concerns itself with the prediction of spectral properties for propynyl boron difluoride, while the next chapter compares the predicted and observed results to establish that the proposed model was suitable.

In the present investigation, the spectral properties of importance were the number of fundamental vibrations of the molecule, the degeneracy and infrared activity of the vibrations, the approximate form of the normal modes of vibration, and the vibration-rotation selection rules. For rigid molecules, i.e. molecules with

high internal rotational barriers, the above properties can be determined easily by applying point group theory to their equilibrium molecular configurations, as described by WILSON, DECIUS, and CROSS [28]. However, propynyl boron difluoride is an example of a non-rigid molecule and it can be shown that the usual group theory arguments must be modified because certain symmetry elements of non-rigid molecules lead to configurations which cannot be attained by overall rotation or reflection of the molecule. Symmetry groups of non-rigid molecules have been discussed at length by LONGUET-HIGGINS [29] and others [30, 31a, 31b].

It may be shown that CH_3CCBF_2 belongs to the symmetry group G_{12} whose character table is shown in Table 6. The symmetry elements of this group are based on the following operations: (1) the identity operation, E; (2) permutation operations, e.g. (123); and (3) permutation-inversion operations, e.g. (23)*. To aid the reader, the effects of the G_{12} symmetry operations on CH_3CCBF_2 are shown in Fig. 5, where the methyl hydrogen atoms are designated by the numerals 1, 2, 3, and the fluorine atoms by the numerals 4 and 5. In the following sections of this chapter it will be shown how the selection rules for the vibration-rotation spectrum, as well as the approximate form of the normal modes of vibration, were determined using the G_{12} symmetry group.

Vibrational Selection Rules and Approximate Normal Vibrations

The vibrational selection rules were readily obtained by considering the symmetries of the wavefunctions for the various

vibrational states. In the harmonic oscillator limit, the wave-function for any vibrational state is represented by the following expression:

$$\psi_i(n) = N_i e^{-(\alpha_{i/2})q_i^2} H_n(\alpha_i^{1/2} q_i) \qquad (1)$$

where:

N_i = normalization constant

$\alpha_i = 2\pi \nu_{i/h}$ with ν_i = frequency of the i^{th} normal vibration

H_n = Hermitian polynomial

n = vibrational quantum number

q_i = displacement vector for a normal vibration

Table 6

G_{12} Symmetry Group

	E	(123) (132)	(23)* (31)* (12)*	(45)	(123)(45) (132)(45)	(23)(45)* (31)(45)* (12)(45)*
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

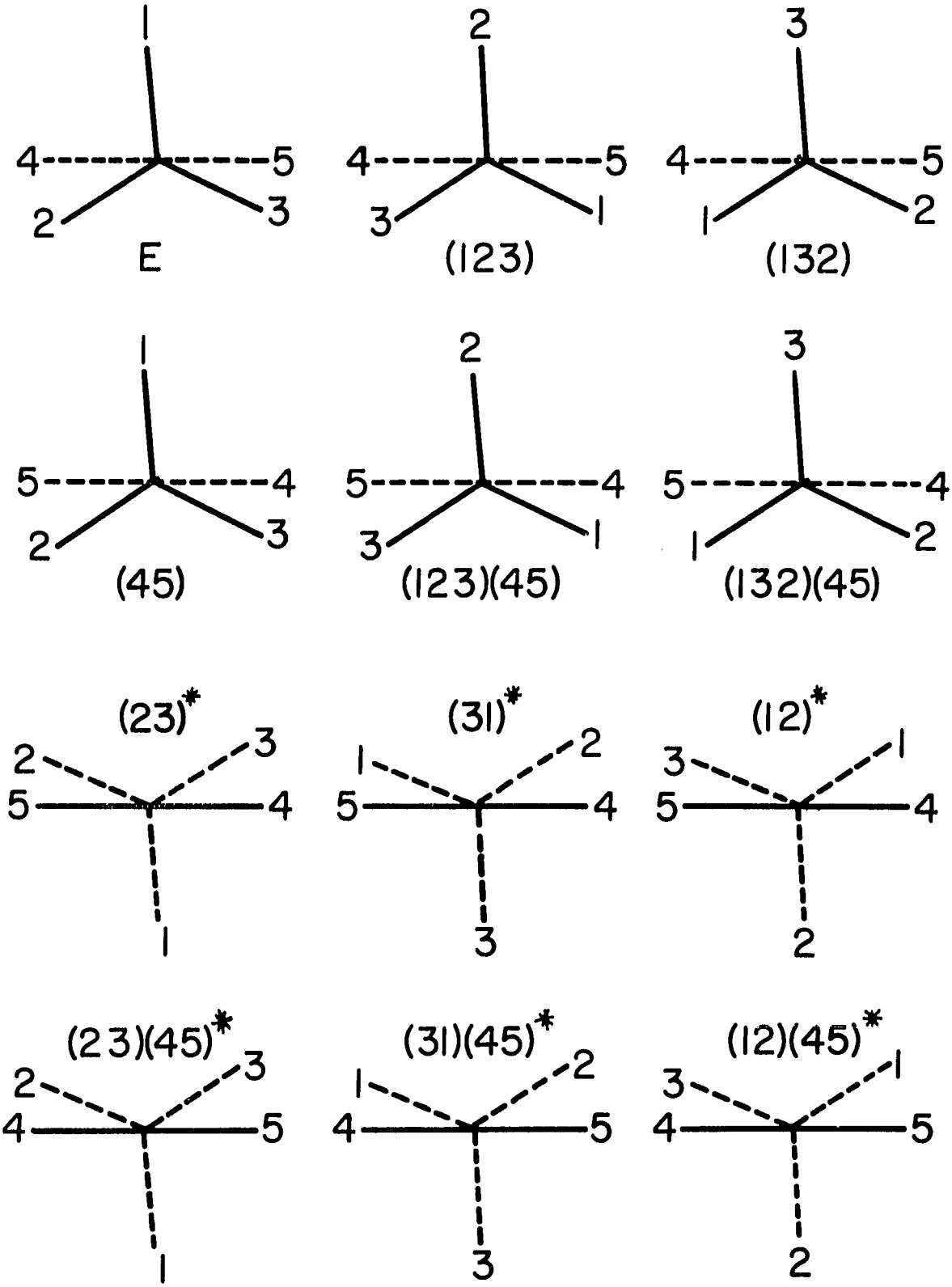


Fig. 5. Effects of the G_{12} symmetry operations on CH_3CCBF_2.

All vibrational ψ_i form the basis for the irreducible representation of the vibrational symmetry group of the molecule. For the vibrational ground state, the value of the Hermite polynomial, H_o, is 1, and insertion of this value into the above equation gives:

$$\psi_i(o) = N_i e^{-(\alpha_i/2)q_i^2} \qquad (2)$$

For both non-degenerate and degenerate vibrational modes, q_i^2 is unchanged by all symmetry operations. Therefore, $\psi_i(o)$ is a totally symmetric wavefunction and belongs to the totally symmetric representation, A_1' of the G_{12} symmetry group.

For excited vibrational states, $\psi_i(n)$ has the same symmetry as the n^{th} Hermite polynomial, since $\psi_i(n)$ is the product of the ground state exponential $e^{-(\alpha_i/2)q^2}$ and the n^{th} Hermite polynomial. Accordingly, for the first excited vibrational state, with $H_1 = 2(\alpha_i)^{1/2}q_i$, $\psi_i(1)$ has the same symmetry as q_i. For the second excited state, with $H_2 = 4\alpha_i q_i^2 - 2$, $\psi_i(2)$ has the same symmetry as q_i^2, which corresponds to the ground state symmetry. Investigation of the properties of the Hermite polynomial indicates that all even states are totally symmetric, while the odd states have the symmetry of q_i.

To determine the vibrational representation for the CH_3CCBF_2 molecule, we begin by recognizing that for any molecule with free internal rotation, there will be a total of 3N-7 normal modes of vibration. Since CH_3CCBF_2 is a nine atom molecule, 20 normal modes were predicted. Also, since the symmetry of

the i^{th} normal mode of vibration is well represented by the i^{th} symmetry coordinate, the symmetry species of the 3N-7 normal modes could be determined from a derivation of the symmetry coordinates. The symmetry coordinates, $S^{(\gamma)}$, were determined by the usual group theoretical methods [28], in which symmetry operations were performed on symmetrically equivalent sets of internal coordinates, listed in Table 7, using the following equation:

$$S^{(\gamma)} = N \sum_{R} \chi_{R}^{(\gamma)} RS_1 \qquad (3)$$

where:

N = normalization constant

RS_1 = coordinate to which displacement of internal coordinate S_1 is sent by operation R

$\chi_{R}^{(\gamma)}$ = the character of the γ^{th} symmetry species for operation R.

Because the rotor and framework were not identical, the symmetry of q_i was identical to that of $S^{(\gamma)}$. The symmetry coordinates, including their species, are presented in Table 8, where the redundant coordinates have been eliminated and the type of vibration represented by each symmetry coordinate is described. From this table, the vibrational representation for the CH_3CCBF_2 molecule was immediately seen to be $\Gamma_{vib} = 7A_1' + 5E' + 2A_1'' + A_2''$.

From the symmetries of the normal vibrations it was possible to determine the vibrational selection rules. At any moment, each of the 3N-7 normal vibrations of the molecule will be in a certain quantum state, where the wavefunction for the i^{th} vibrational mode

Table 7

Internal Coordinates for Propynyl Boron Difluoride

Internal Coordinate	Description
r_1, r_2, r_3	Change in C-H distances
s_1, s_2	Change in B-F distances
t	Change in C-C distance
u	Change in C≡C distance
v	Change in C-B distance
α_1, α_2, α_3	Change in C-C-H angles
β_{12}, β_{23}, β_{31}	Change in H-C-H angles
γ_1, γ_2	Change in C-B-F angles
δ	Change in F-B-F angle
ϕ_x	Change in C-C≡C angle
ψ_y	Change in C≡C-B angle
θ	Change in C-BF_2 dihedral angle

in the n^{th} state is $\psi_i(n)$. The total vibrational wavefunction ψ_v, then, is the product of all the $\psi_i(n)$, since all q_i are linearly independent. As a result, the total vibrational wavefunction can be expressed as the following:

$$\psi_v = \psi_1(n_1)\cdot\psi_2(n_2)\cdots\psi_{3N-7}(n_{3N-7}) = \prod_{i=1}^{3N-7} \psi_i(n_i) \qquad (4)$$

Table 8

Approximate Normal Modes of Vibration for Propynyl Boron Difluoride

Symmetry Coordinate	Designation	Description
$1/\sqrt{6}\ (2\Delta r_1 - \Delta r_2 - \Delta r_3)$	$\nu_8(e')$	CH_3 asymmetric stretch
$1/\sqrt{3}\ (\Delta r_1 + \Delta r_2 + \Delta r_3)$	$\nu_1(a_1')$	CH_3 symmetric stretch
Δu	$\nu_2(a_1')$	C≡C stretch
$1/\sqrt{6}\ (2\Delta\beta_{12}-\Delta\beta_{23}-\Delta\beta_{31})$	$\nu_9(e')$	CH_3 asymmetric deformation
$1/\sqrt{2}\ (\Delta S_1 - \Delta S_2)$	$\nu_{13}(a_1'')$	BF_2 asymmetric stretch
$1/\sqrt{3}\ (\Delta\beta_{12}+\Delta\beta_{23}+\Delta\beta_{31})$	$\nu_3(a_1')$	CH_3 symmetric deformation
$1/\sqrt{2}\ (\Delta S_1 + \Delta S_2)$	$\nu_4(a_1')$	BF_2 symmetric stretch
$1/\sqrt{6}\ (2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)$	$\nu_{10}(e')$	CH_3 rock
Δt	$\nu_5(a_1')$	C-C stretch
Δv	$\nu_6(a_1')$	C-B stretch
$1/\sqrt{2}\ (\Delta\gamma_1 - \Delta\gamma_2)$	$\nu_{14}(a_2'')$	BF_2 wag (out-of-plane)
$\Delta\delta$	$\nu_7(a_1')$	BF_2 scissors
$\Delta\phi_x$	$\nu_{11}(e')$	C≡C-B deformation
$\Delta\psi_y$	$\nu_{12}(e')$	C-C≡C deformation
$\Delta\theta$	$\nu_{15}(a_1'')$	BF_2 rock (in-plane)

When each $n_i = 0$, the molecule is in its vibrational ground state, but, if the molecule absorbs radiation so that only the j^{th} normal mode is excited to $n_j = 1$, the molecule has undergone a fundamental vibrational transition. Thus, for a fundamental transition of the j^{th} normal mode:

$$\prod_i \psi_i(o) \rightarrow \psi_j(n_j) \prod_{i \neq j} \psi_i(o) \tag{5}$$

or,

$$\psi_v^{\,o} \rightarrow \psi_v^{\,j} \tag{6}$$

For a transition to occur by absorption of infrared dipole radiation, it is necessary that one or more of the following integrals be non-zero:

$$\int \psi_v^{\,o}\, \phi_i\, \psi_v^{\,j} d\tau \tag{7}$$

where:

$$\phi_i = X', Y', Z', X'', Y'', \text{ or } Z''$$

X', Y', and Z' refer to the orientation of the oscillating dipole vector relative to the Cartesian coordinate system fixed in the rotor, while X'', Y'', and Z'' refer to analogous coordinates fixed in the framework. The integral, $\int \psi_v^{\,o}\, \phi_i\, \psi_v^{\,j}\, d\tau$, is non-zero only when the direct product, $\psi_v^{\,o} \times \phi_i \times \psi_v^{\,j}$, contains the totally symmetric representation. Since $\psi_v^{\,o}$ is totally symmetric, the direct product of ϕ_i and $\psi_v^{\,j}$ must contain a totally symmetric representation. As a result, the vibrational selection rules emerge. The j^{th}

fundamental will be infrared active if the vibrational mode belongs to the same representation as at least one of the Cartesian coordinates of either the rotor or the framework. The symmetries of the Cartesian coordinates for both parts of the molecule are presented in Table 9. By comparing the symmetries of these coordinates with the symmetries of the normal modes of vibration, Table 8, it was apparent that all fundamental vibrations of propynyl boron difluoride were infrared active.

Table 9

Symmetries of Molecular Fixed Cartesian Coordinate Vectors

CH_3-C≡ Rotor		≡C-B(F)F Framework	
Vectors	Symmetry	Vectors	Symmetry
X', Y'	E'	X''	A_2''
		Y''	A_1''
Z'	A_1'	Z''	A_1'

The Z vector is along the axis of internal rotation.

Vibration-Rotation Selection Rules and Rotational Energy Levels

In addition to their vibrational motions, gaseous molecules can also rotate in space. When the molecules are excited with infrared radiation, the rotational motion couples with the vibrations

giving rise to vibration-rotation transitions which occur as line sequences in infrared spectra. These line sequences arise from transitions to a different rotational level in the excited vibrational state, as prescribed by rotational selection rules. For rigid molecules, the theoretical aspects of the problem are well defined. However, for molecules with free internal rotation, the problem is much more complex because of the additional degree of rotational freedom. JONES and SHEPPARD [15] have considered the CH_3BF_2 type molecule in detail and an extension of their treatment to CH_3CCBF_2 has proven to be acceptable.

To a first approximation, the expression for the rotational energy levels of propynyl boron difluoride is [15, 32]:

$$F(J,K,k_1) = DJ(J+1) + A_1 k_1^2 + (A_2-D)(K^2-dKk_1) \qquad (8)$$

where:

$$D = \frac{1}{2}(B+C) \qquad B = \frac{\hbar}{4\pi I_b c} \qquad C = \frac{\hbar}{4\pi I_c c}$$

$$A_1 = \frac{\hbar I_a}{4\pi I_\alpha (I_a - I_\alpha) c} \qquad A_2 = \frac{\hbar}{4\pi (I_a - I_\alpha) c}$$

$$d = \frac{2A_2}{(A_2-D)}$$

I_a, I_b, and I_c are the principal moments of inertia of the molecule while I_α is the moment of inertia of the methyl group about the axis of internal rotation, and c is the velocity of light. J is the usual quantum number for total angular momentum, K corresponds to the quantum number for rotation about the figure axis, and k_1 is the quantum number corresponding to the angular momentum of the

methyl group about the axis of internal rotation. J has the subscripts K_{-1} and K_{+1}, which correspond to the levels in prolate and oblate symmetric tops, respectively.

An equation for the rotational transitions were derived by applying selection rules to equation (8). Initially the selection rules for CH_3CCBF_2 were based on those for a symmetric top, since propynyl boron difluoride proved to be a near prolate symmetric top with $\kappa = -0.96$ (κ, an asymmetry parameter, is -1.00 for a prolate symmetric top). Then, the selection rules were confirmed by symmetry considerations. In the limiting case of a true prolate symmetric top, consisting of a freely rotating rotor and framework (referred to as parts 1 and 2, respectively), the rotational selection rules are as follows [33]:

a. If the transition moment or dipole moment change is parallel to the top axis:

$$\begin{aligned} &\Delta J = 0, \pm 1 \qquad \Delta K = 0, \Delta k_1 = 0, \Delta k_2 = 0 \text{ for } K \neq 0 \\ &\Delta J = \pm 1 \qquad\quad \Delta K = 0, \Delta k_1 = 0, \Delta k_2 = 0 \text{ for } K = 0 \end{aligned} \tag{9}$$

where k_1 and k_2 are the rotational quantum numbers for each part and

$$K = k_1 + k_2. \tag{10}$$

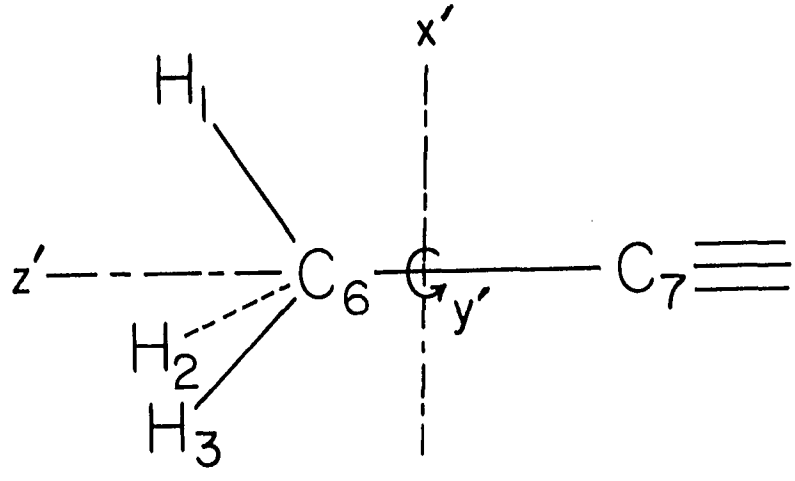
b. If the dipole moment change is perpendicular to the principal axis:

$$\Delta J = 0, \pm 1 \qquad \Delta K = \pm 1 \tag{11}$$

with $\Delta k_1 = \pm 1$, $\Delta k_2 = 0$ when the oscillating dipole is in part 1,

$\Delta k_1 = 0$, $\Delta k_2 = \pm 1$ when in part 2. By analogy, the same selection rules were assumed for propynyl boron difluoride. A discussion of symmetry substantiated the assumed selection rules.

To determine the symmetries of the rotational levels for the rotor, Cartesian axes were fixed to the rotor as shown below:



Associated with each symmetry element of the G_{12} molecular symmetry group was an equivalent rotation which took the rotor nuclei into the same spatial orientation. The relationship between the symmetry elements and the rotations is shown in Table 10, while the characters for the rotations [32, 27] are presented in Table 11. By combining Table 10 and Table 11 the representations for the rotational levels were deduced and used to determine the symmetries of the rotational levels for the rotor. These results are presented in Table 12.

Table 10

Equivalent Rotations for the Rotor

Symmetry Element	E	(123)	(23)*	(45)	(123)(45)	(23)(45)*
Equivalent Elements	E	C_3	C_{2x}	E	C_3	C_{2x}

Table 11

Characters of Rotational Functions: Rotor

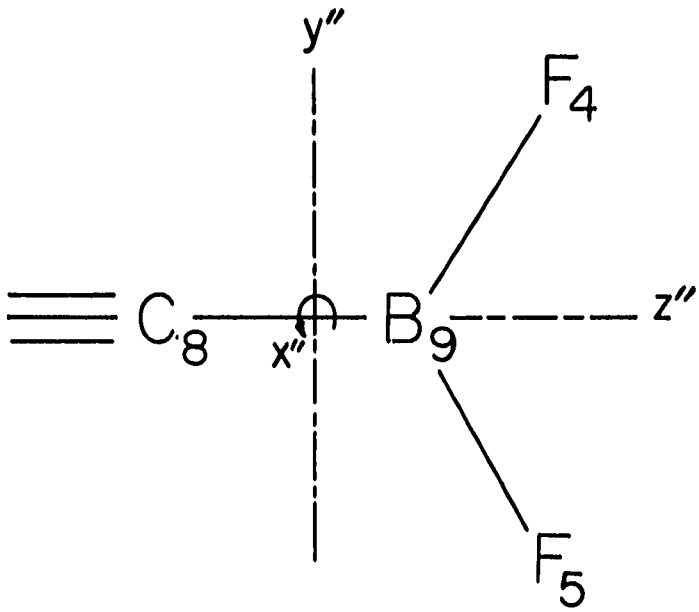
Symmetry Element	E	C_3	C_{2x}
K = 0	1	1	$(-1)^J$
K > 0	2	1	0

Table 12

Rotational Representations for Rotor

Symmetry Element	E	(123)	(23)*	(45)	(123)(45)	(23)(45)*	Species
K = 0, J even	1	1	1	1	1	1	A_1'
K = 0, J odd	1	1	-1	1	1	-1	A_2'
K > 0	2	1	0	2	1	0	E_1'

The framework was treated in an analogous manner to determine the species of the k_2 rotational levels. Cartesian axes were fixed to the framework as shown below:



As before, each symmetry element of the G_{12} group was identified with an equivalent rotation which is shown in Table 13. By using

Table 13

Equivalent Rotations for the Framework

Symmetry Element	E	(123)	(23)*	(45)	(123)(45)	(23)(45)*
Equivalent Rotation	E	E	C_{2x}	C_{2z}	C_{2z}	C_{2y}

the same relationships employed by LONGUET-HIGGINS [29], the characters for the equivalent rotations were determined as a function of the J and k_2 quantum numbers. The results are presented in Table 14. Then the symmetry species of the rotational levels

Table 14

Characters of Rotational Functions: The Framework

Symmetry Element	E	C_{2x}	C_{2y}	C_{2z}
K = 0	1	$(-1)^J$	$(-1)^J$	1
K > 0	2	0	0	$2(-1)^K$

were determined by combining the results of these two tables to form reducible representations for the rotational levels. The representations and symmetries of the framework levels are given in Table 15.

Table 15

Rotational Representations for Framework

Symmetry Element	E	(123)	(23)*	(45)	(123)(45)	(23)(45)*	Species
K = 0, J even	1	1	1	1	1	1	A_1'
K = 0, J odd	1	1	-1	1	1	-1	A_2'
K > 0, K even	2	2	0	2	2	0	$A_1'+A_2'$
K > 0, K odd	2	2	0	-2	-2	0	$A_1''+A_2''$

Determination of the rotational selection rules followed much of the same reasoning used by LONGUET-HIGGINS [29], who pointed out that there is a rigorous selection rule relating the over-all species of the levels which can combine. The dipole selection rule requires that $A_1'' \leftrightarrow A_2''$. This is so because the

absolute dipole moment of the molecule, a vector in laboratory coordinates, transforms as $3A_2'$ under G_{12} symmetry operations and the species of the over-all ground state wavefunction is either A_1'' or A_2''.

The selection rules were determined for internal transitions along either the X', Y', and Z' axes, or the X'', Y'', and Z'' axes. As indicated in the discussion of the vibrational selection rules, the direct product of the symmetry species of the upper and lower vibration-rotation states must result in a component with species identical to at least one of the Cartesian coordinate vectors, or there will be no dipole moment change. By using the symmetry species of the components of the internal dipole moments for parts 1 and 2, Table 9, the following selection rules emerged:

a. For the rotor:

$Z'(A_1')$ polarization: $A_1' \leftrightarrow A_1'$, $A_2' \leftrightarrow A_2'$, $E' \leftrightarrow E'$, etc.

$X', Y'\}(E')$ polarization: $A_1' \leftrightarrow E'$, $A_2' \leftrightarrow E'$, $E' \leftrightarrow E'$, $A_1'' \leftrightarrow E''$, $A_2' \leftrightarrow E''$, $E'' \leftrightarrow E''$.

b. For the framework:

$Z''(A_1')$ polarization: $A_1' \leftrightarrow A_1'$, $A_2' \leftrightarrow A_2'$, $E' \leftrightarrow E'$, etc.

$X''(A_2'')$ polarization: $A_1'' \leftrightarrow A_2'$, $A_2'' \leftrightarrow A_1'$, $E' \leftrightarrow E''$.

$Y''(A_1'')$ polarization: $A_1' \leftrightarrow A_1''$, $A_2' \leftrightarrow A_2''$, $E' \leftrightarrow E''$.

With a knowledge of the symmetry restrictions on the vibration-rotation transitions, it was possible to transpose these limitations to changes in J, k_1 and k_2. The changes in k_1

were determined first. As mentioned previously, the ground state is totally symmetric as the molecule is not rotating. For a Z' polarized transition, the product of the initial and final rotational states had to be A_1', according to the selection rule $A_1' \leftrightarrow A_1'$. Since the absolute dipole vector transforms as $3A_2'$, the product of the overall species of the two states was A_2'. This required the direct product of the rotational species to be A_2'. Consideration of the symmetries of the transitions of the sort $J = 0$ to $J = \pm 1$ indicated that $\Delta k_1 = 0$, which is consistent with symmetric top selection rules. For a perpendicular transition, where X' and Y' transform as a pair, the internal selection rule was $A_1' \leftrightarrow E'$, hence the product of the initial and final states was E'. As above, the product of the overall species of the two states had to be A_2', and the requirement on the overall species was such that the direct product of the rotational species was E'. But, of the final rotational states with $J = 1$, that with $k_1 = 1$ met the symmetry requirements. Also, that with $J = 0$ and $k_1 = 1$ met the symmetry requirements, while $J = 0$, $k_1 = 0$ were not satisfactory. These selection rules are consistent with selection rules for symmetric top molecules.

The selection rules for k_2 were determined in an analogous manner. For an X" polarized transition in the framework, the product of the initial and final states had to be A_2'', and the direct product of the rotational species had to be A_1''. Of the final rotational states with $J = 1$, only that with $k_2 = 1$ was

allowed. For a Y" polarized transition, the direct product of initial and final states had to be $A_1"$, and the product of rotational species had to be $A_2"$. The resulting selection rules were $\Delta J = 0, \pm 1 \quad \Delta k_2 = \pm 1$. The symmetry of Z" polarized rotation-vibration required the product of internal species to be A_2'. Since the overall species had to be A_2', the direct product of rotational species was A_2'. Thus, $\Delta k_2 = 0$ for $\Delta J = 0, \pm 1$. The vibration-rotation selection rules are summarized in Table 16.

Table 16

Vibration-Rotation Selection Rules

Rotor	Polarization	Framework	Polarization
		$\Delta J=0,\pm1;\ \Delta k_2=\pm1$	$X(A_2")$
$\Delta J=0,\pm1,\Delta k_1=\pm1$	$X,Y(E')$		
		$\Delta J=0,\pm1;\ \Delta k_2=\pm1$	$Y(A_1")$
$\Delta J=\pm1,\Delta k_1=0,k=0$	$Z(A_1')$		
$\Delta J=0,\pm1,\Delta k_1=0,k\neq0$		$\Delta J=\pm1;\ \Delta k_2=0$	$Z(A_1')$

Further Spectral Considerations

Because rotational fine structure was observed in only the CH_3 asymmetric stretch, $\nu_8(e')$, the most important selection rules were those pertaining to the perpendicular vibrations in the rotor. Furthermore, only the transitions arising from $\Delta J = 0$ were considered

since transitions of the type $\Delta J=\pm 1$ contribute only to the unresolved background in spectra of symmetric tops [33]. Applying the pertinent selection rules, i.e. $\Delta J = 0$, $\Delta k_1 = \pm 1$, for the asymmetric methyl vibrations to equation (8) resulted in the following expressions:

For $\Delta K=1$, $\Delta k_1=+1$:

$$\nu = \nu_0 + A_1 + (A_2-D)(1-d) + [2A_1-d(A_2-D)]k_1 + (A_2-D)(2-d)K \quad (12)$$

For $\Delta K=-1$, $\Delta k_1=-1$:

$$\nu = \nu_0 + A_1 + (A_2-D)(1-d) - [2A_1-d(A_2-D)]k_1-(A_2-D)(2-d)K \quad (13)$$

Transition due to $\Delta k_1=+1$ were called ${}^{R}Q_{k_1}$ lines, while transitions due to $\Delta k_1=-1$ were called ${}^{P}Q_{k_1}$ lines. The above equations were readily combined to give:

$$\nu = \nu_0 + A_1 + (A_2-D)(1-d) \pm [2A_1-d(A_2-D)]k_1 \pm (A_2-D)(2-d)K \quad (14)$$

where ν is the frequency of the Q-branches and ν_0 is the origin of the band. The plus sign is for the ${}^{R}Q_{k_1}$ branches, while the minus sign is for the ${}^{P}Q_{k_1}$ branches.

From eqn. (14) it was not immediately apparent that the prescribed selection rules would give rise to a regularly spaced series of lines, since, for any k_1 transition, there appeared to be no predetermined value for K. JONES and SHEPPARD [15] have shown that the greatest contribution to the Q-branch lines comes from levels where $K = \frac{1}{2}dk_1$. Consequently, eqn. (14) was simplified further to:

$$\nu = \nu_0 + [A_1+(A_2-D)(1-d)] \pm [2A_1-\tfrac{1}{2}d^2(A_2-D)]k_1 \quad (15)$$

At this point, it was clear that a regularly spaced series of lines was expected for the perpendicular methyl vibrations.

A working expression to estimate the frequencies of the Q-branches was easily obtained by substituting the appropriate parameters into eqn. (15). Unfortunately, all the parameters were functions of the moments of inertia of the molecule which have not been experimentally determined, however the estimated values for the moments of inertia of propynyl boron difluoride given in Table 5 proved to be sufficient for this analysis. Thus, the following empirical relationship emerged:

$$\nu^{sub} = \nu_0 + 5.104 \pm 10.193k_1 \qquad (16)$$

In the initial expression for the Q-branch frequencies, the effect of the differences in rotational constants between the upper and lower states was not considered. In the equation for the Q-branches of a symmetric top, the effect appears as a coefficient of K^2, where K has the same significance as k_1 in propynyl boron difluoride. By analogy, the difference, attributed to the change in A_1, was included as a coefficient of k_1^2 in the expression for the subbands of CH_3CCBF_2. As a result, eqn. (16) became:

$$\nu^{sub} = \nu_0 + 5.104 \pm 10.193\ k_1 + (A'-A'')k_1^2 \qquad (17)$$

Because the vibrational transitions in question were from a non-degenerate ground state to a degenerate excited state, Coriolis interactions in the degenerate states were approximated. By analogy

with Equation 14 of JONES and SHEPPARD [15], consideration of the Coriolis effects resulted in the following expression:

$$\nu^{sub} = \nu_0 + 5.104\ (1-\zeta_i^2) \pm 10.193(1-\zeta_i)k_1 + (A'-A'')k_1^2 \quad (18)$$

where ζ_i is the Coriolis coupling coefficient. By comparing the above expression for the Q-branches with an experimentally determined expression, it is possible to determine the band center and the Coriolis coefficient.

For all other vibrations, where Δk_1 = 0, A, B, and C type band contours typical of asymmetric molecules were expected [15,35]. Because of the large moments of inertia for overall rotation, resolved rotational structure was not expected. Accordingly, the normal vibrations with dipole moment changes along the I_a inertial axis were expected to exhibit gas phase infrared bands with PQR branch structure (type A bands) similar to that of unresolved perpendicular bands of true prolate symmetric tops. Those vibrations having dipole moment changes parallel to the I_b inertial axis were expected to give rise to type B bands which are characterized by prominent P and R branches and the absence of a central Q branch. A type C band, with a prominent Q branch, was expected for absorptions caused by vibrations with dipole moment change along the I_c axis.

The separations between maxima of the various bands were approximated by the method of SETH PAUL and DIJKSTRA [36]. The P-R separation for the type A band is given by the following expression:

$$\Delta\nu_{PR}(\text{A band}) = 10\ S\ (\tilde{\beta})(\beta T/9)^{1/2}\ cm^{-1} \quad (19)$$

T is temperature in degrees Kelvin, and $S(\tilde{\beta})$ is the separation function which is given by the following:

$$S(\tilde{\beta}) = 10^{0.721/(\tilde{\beta}+4)^{1.13}} \quad (20)$$

where:

$$\tilde{\beta}+1 = A/2\beta \qquad \text{and} \qquad \beta = BC/(B+C)$$

The P-R separations of B and C bands were determined from $\Delta\nu_{PR}$(A band) by the following relationshps:

$$\Delta\nu_{PR}(\text{B band}) = 5/6 \quad \Delta\nu_{PR}(\text{A band}) \quad cm^{-1} \quad (21)$$

$$\Delta\nu_{PR}(\text{C band}) = 3/2 \quad \Delta\nu_{PR}(\text{A band}) \quad cm^{-1} \quad (22)$$

The calculated separations for CH_3CCBF_2 are presented in Table 17.

Table 17

PR Separations at T = 300°K

Band Type	A	B	C
Separation (cm^{-1})	10.1	8.4	15.1

A precise, detailed analysis of this internal rotational phenomenon would be extremely difficult. As JONES and SHEPPARD indicated, it would require accurate consideration of the asymmetry of the molecule, differences in rotational constants for various vibrational states, Coriolis effects for the degenerate states, and Coriolis effects between the methyl vibrations and the BF_2 vibrations.

CHAPTER IV

SPECTRAL RESULTS

In the previous chapter, a specific molecular model was proposed for propynyl boron difluoride, and spectral properties of the model were predicted. The purpose of this chapter is to confirm the proposed molecular model by comparing predicted spectral properties with the observed infrared spectrum.

Prism Resolution Spectra

A low resolution infrared spectrum of gaseous propynyl boron difluoride was shown in Fig. 2, and from this scan eight normal vibrational frequencies were readily assigned using nothing more than characteristic group frequencies. Thus, the carbon-hydrogen stretches occurred as a pair of absorptions in the region from 2900 to 3100 cm^{-1}. The CH_3 asymmetric stretches were assigned to the absorption at 2980 cm^{-1}, a shoulder on the 2930 cm^{-1} absorption of the CH_3 symmetric stretching vibration. The acetylenic carbon-carbon stretch, expected to occur near 2150 cm^{-1}, was located at 2210 cm^{-1}. The absorptions in the region from 1300 to 1450 cm^{-1} were attributed to the BF_2 stretching vibrations with the BF_2 asymmetric stretch being observed as an isotopically split absorption; the $B^{10}F_2$ asymmetric stretch absorbing at 1420 cm^{-1}, and the $B^{11}F_2$ asymmetric stretch at 1361 cm^{-1}. The BF_2 symmetric stretch occurred at 1323 cm^{-1}, however isotopic splitting was not

resolved. The carbon-carbon single bond stretch caused the absorption at 1020 cm^{-1}, while the absorption at 775 cm^{-1} was assigned to the carbon-boron stretch. The one remaining major absorption at 663 cm^{-1} was assigned to the out-of-plane BF_2 wagging vibration. As mentioned in Chapter II, propynyl boron difluoride decomposes slowly forming BF_3 and CH_3CCH. While CH_3CCH absorptions were not readily apparent in the low resolution infrared spectrum, the absorptions at 690, 719, 1497, and 1446 cm^{-1} were readily assigned to BF_3 fundamentals. All other absorptions in Fig. 2 were due to overtone or combination bands of CH_3CCBF_2.

Grating Resolution Spectra

The normal modes of vibration of propynyl boron difluoride are characterized by atomic displacements that were fairly localized with the functional groups. This permitted the fundamental vibrations to be categorized as CH_3 group vibrations, BF_2 group vibrations, or skeletal vibrations. The assignment of the various vibrational frequencies was based on the spectral properties proposed in Chapter III, or by analogy with spectral results for structurally similar molecules.

CH_3 Group Vibrations

There can be little doubt about the assignment of the asymmetric carbon-hydrogen stretching vibrations. They appeared in the 3000cm^{-1} region as an absorption with well-defined rotational structure, as shown in Fig. 6. By employing sum and difference relationships for the analysis of this band, the equations determined for the Q-branches listed in Table 18 were:

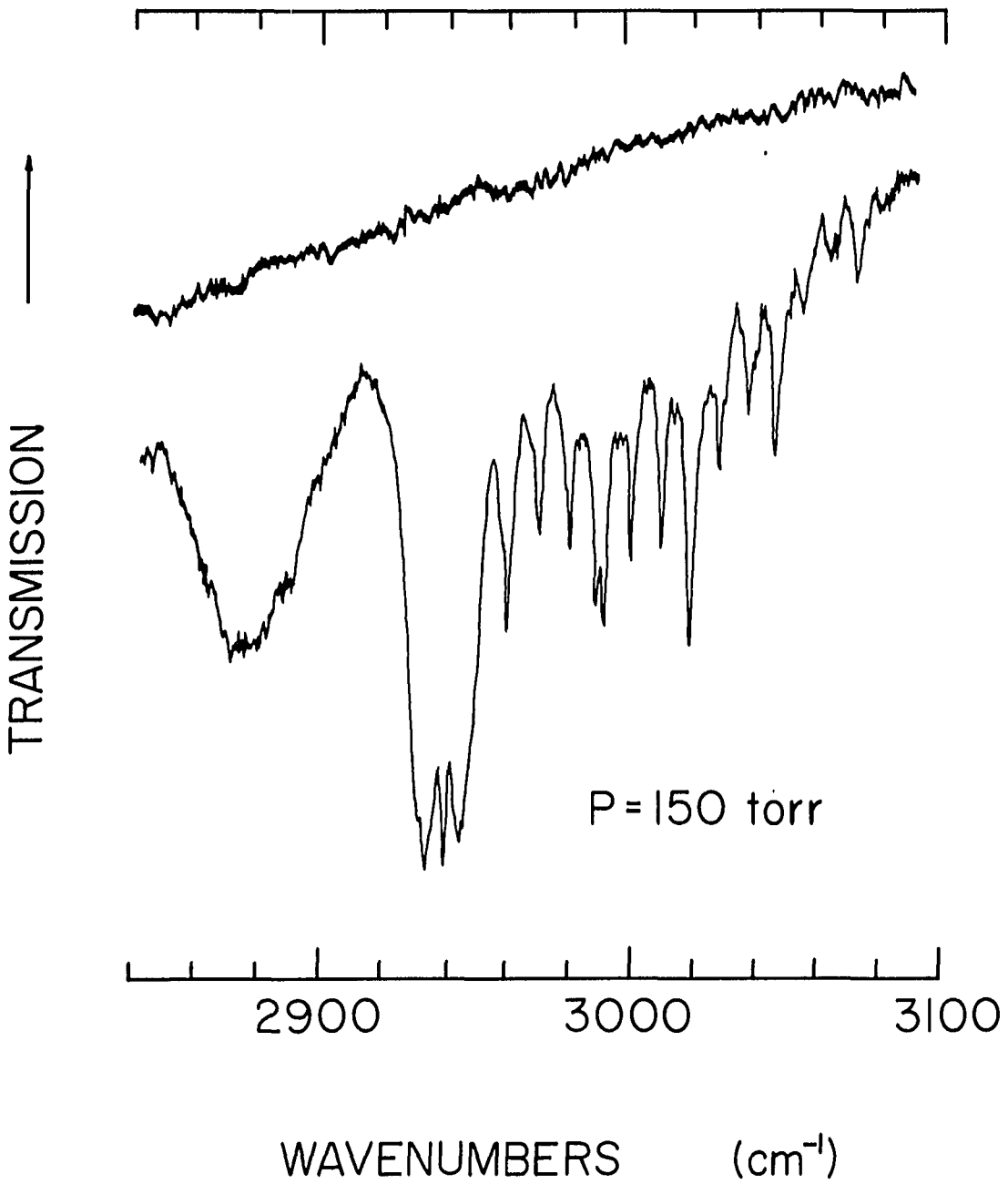


Fig. 6. Grating resolution spectrum of the asymmetric and symmetric methyl stretching modes of propynyl boron difluoride/ Scanning speed was 8 cm^{-1}/min and the theoretical spectral slit width was 0.2 cm^{-1}.

Table 18

Q-Branch Wavenumbers for $\nu_8(e')$ of Propynyl Boron Difluoride

k_1	$^RQ_{k_1}$		$^PQ_{k_1}$	
	Observed	Calculated	Observed	Calculated
0	3019.7	3019.5	--	--
1	3029.1	3029.0	3009.8	3009.7
2	3038.5	3038.4	3000.1	3000.0
3	3047.8	3047.7	2989.4	2989.8
4	3056.3	3056.8	2979.2	2979.7
5	3065.6	3065.7	2968.9	2969.3
6	3074.7	3074.5	2959.0	2958.8

$$^{R}Q_{k_1} + {}^{P}Q_{k_1} = 6037.59 - 0.1420k_1^2 \quad (23)$$

$$^{R}Q_{k_1} - {}^{P}Q_{k_1} = 19.15k_1 \quad (24)$$

and the equation for the Q-branches was determined to be:

$$\nu = 3018.80 \pm 9.58k_1 - 0.0710k_1^2 \quad (25)$$

By comparing the above expression with eqn. (18), the Coriolis coefficient for $\nu_8(e')$ of propynyl boron difluoride was estimated to be $\zeta_8 = +0.16$, which compared well with values of +0.150 and +0.125 for the analogous absorptions for nitromethane and methyl boron difluoride, respectively, as determined by JONES and SHEPPARD [15]. The ν_8 band center for propynyl boron difluoride was calculated to be 3014.3 cm^{-1}, and A' - A'' = -0.0710 cm^{-1}. It is possible that the additional line at 2991.3 cm^{-1} was a hot band [37,38,39].

The other degenerate methyl vibrations of CH_3CCBF_2, namely, the asymmetric methyl deformation, $\nu_9(e')$, and the methyl rocking vibration, $\nu_{10}(e')$, were not observed in the gas phase infrared spectrum. The methyl deformation was obscured by the very intense BF_2 stretching absorptions, but a reasonable estimate of its frequency was obtained from its first overtone which occurred at 2874 cm^{-1} [33,38,40,41,42], in Fermi resonance with $\nu_1(a_1')$ [43]. As a result, $\nu_9(e')$ was estimated to occur at a wavenumber value a little greater than 1437 cm^{-1}, one-half 2874 cm^{-1}. That $\nu_{10}(e')$ was not observed in the gas phase infrared spectrum was not

unexpected, as the methyl rocking vibration is generally a weak absorption which must be observed under conditions of high sample pressure or long path-length. Since the nature of CH_3CCBF_2 precluded using either method, a polycrystalline thin film spectrum of the 1000 cm^{-1} region was recorded, and an infrared absorption at 1022 cm^{-1} was assigned as $\nu_{10}(e')$.

The symmetric methyl stretching and deformation vibrations, $\nu_1(a_1')$ and $\nu_3(a_1')$, respectively, were assigned as follows. As expected, $\nu_1(a_1')$ appeared as a well defined type A band at 2938.6 cm^{-1}, but $\nu_3(a_1')$, obscured by the BF_2 vibrations, was not so readily assigned. From a polycrystalline thin film spectrum of the 1350 cm^{-1} region, $\nu_3(a_1')$ appeared as an absorption at 1378 cm^{-1}.

BF_2 Group Vibrations

In addition to band shape and group frequency considerations, the assignment of the fundamental vibrations associated with the BF_2 group was based on the effects of isotopic splitting, as the natural abundance of B^{10} is 18.83 per cent, while B^{11} is 81.17 per cent. The BF_2 stretching vibrations gave rise to the four major bands in the region from 1440 to 1320 cm^{-1}, and are shown in Fig. 7. The weakest absorption in this region, at 1422 cm^{-1}, was assigned to the $B^{10}F_2$ asymmetric stretching vibration, $\nu_{13}(a_1'')$, while the stronger band at 1373 cm^{-1} was assigned to the $B^{11}F_2$ asymmetric stretch. The band shapes observed for these fundamentals were consistent with the contours expected for a type B band.

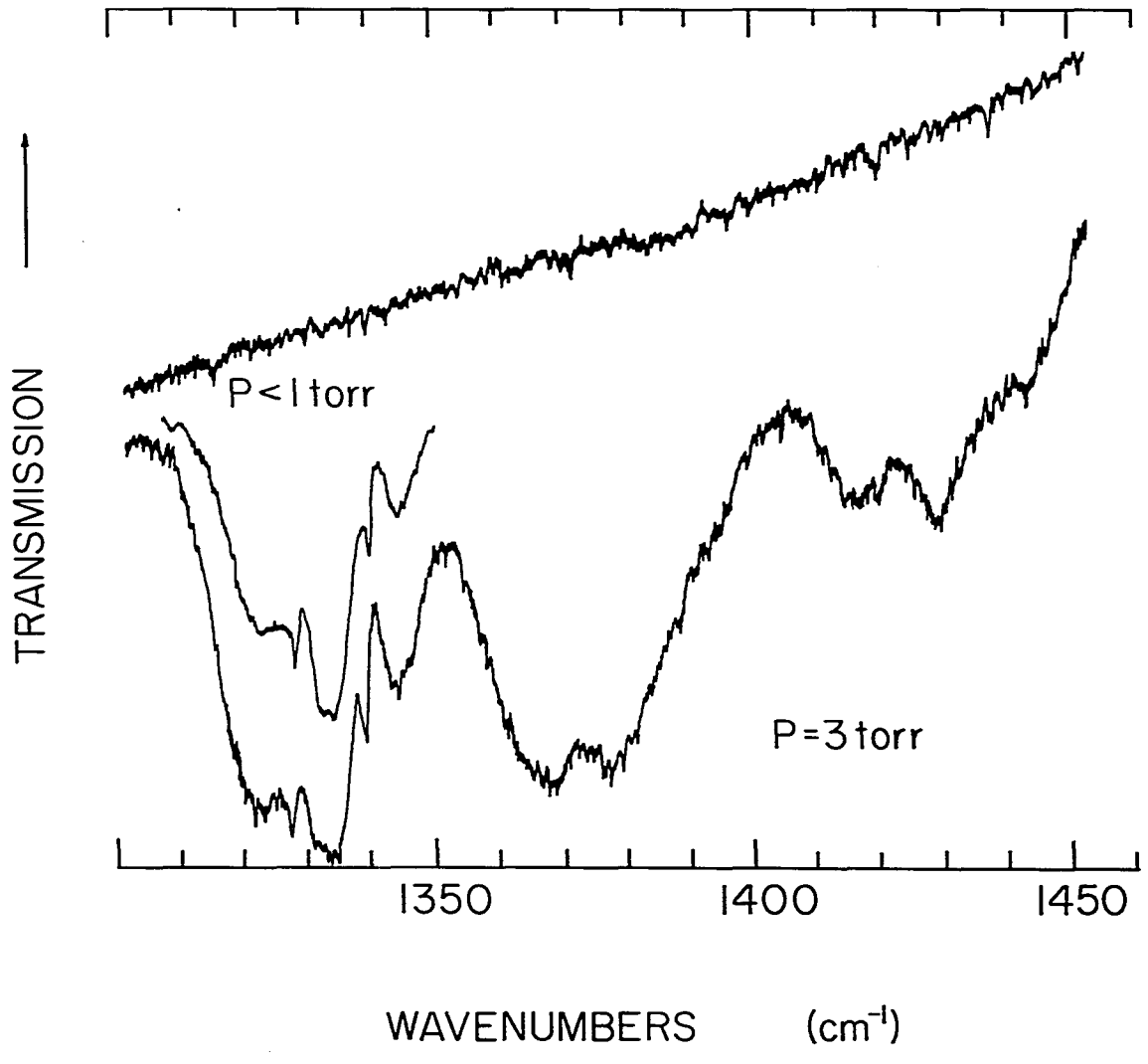


Fig. 7. Grating resolution spectrum of the asymmetric and symmetric BF_2 stretching vibrations recorded at 4 cm^{-1}/min with a spectral slit width of 0.2 cm^{-1}.

The separations and band shapes observed for the BF_2 symmetric stretching vibrations agreed quite well with the predicted separations for type A bands. The $B^{10}F_2$ symmetric stretch, $\nu_4(a_1')$ was assigned to the band at 1328.3 cm^{-1}. As previously mentioned, the weak shoulder at 1446 cm^{-1} was due to $\nu_3(e')$ of $B^{11}F_3$.

The BF_2 out-of-plane wagging vibration, $\nu_{15}(a_2'')$, was expected to occur as a type C band with a strong central Q-branch. As shown in Fig. 8, such an absorption was observed at 665.5 cm^{-1} and accordingly was assigned to the ν_{15} mode. The Q-branches at 719.0 and 691.5 cm^{-1} were $\nu_2(a_2'')$ of $B^{10}F_3$ and $B^{11}F_3$, respectively.

The absorptions of the remaining two BF_2 vibrations, the BF_2 scissors vibration, and the BF_2 in-plane rocking vibration, were observed at longer wavelengths. The symmetric deformation, $\nu_7(a_1')$, occurred at 499 cm^{-1}, on the higher wavenumber side of the $\nu_4(e')$ absorption of BF_3 at 480 cm^{-1}, and is shown in Fig. 9. The peculiar shape of this band precluded an assignment based on band shape considerations, but the frequencies for the analogous vibrations in CH_3BF_2 and CD_3BF_2 substantiated this assignment. Also, the infrared spectrum of a polycrystalline thin film of CH_3CCBF_2 indicated that the 498 cm^{-1} absorption was a single CH_3CCBF_2 absorption. The absorption of the BF_2 in-plane rock, $\nu_{14}(a_1'')$ was observed as a type B band at 307 cm^{-1} and is shown in Fig. 9. That this doublet was not the result of two fundamental vibrations of CH_3CCBF_2 was substantiated by a thin film spectrum in which a single absorption at 320 cm^{-1} was observed. The

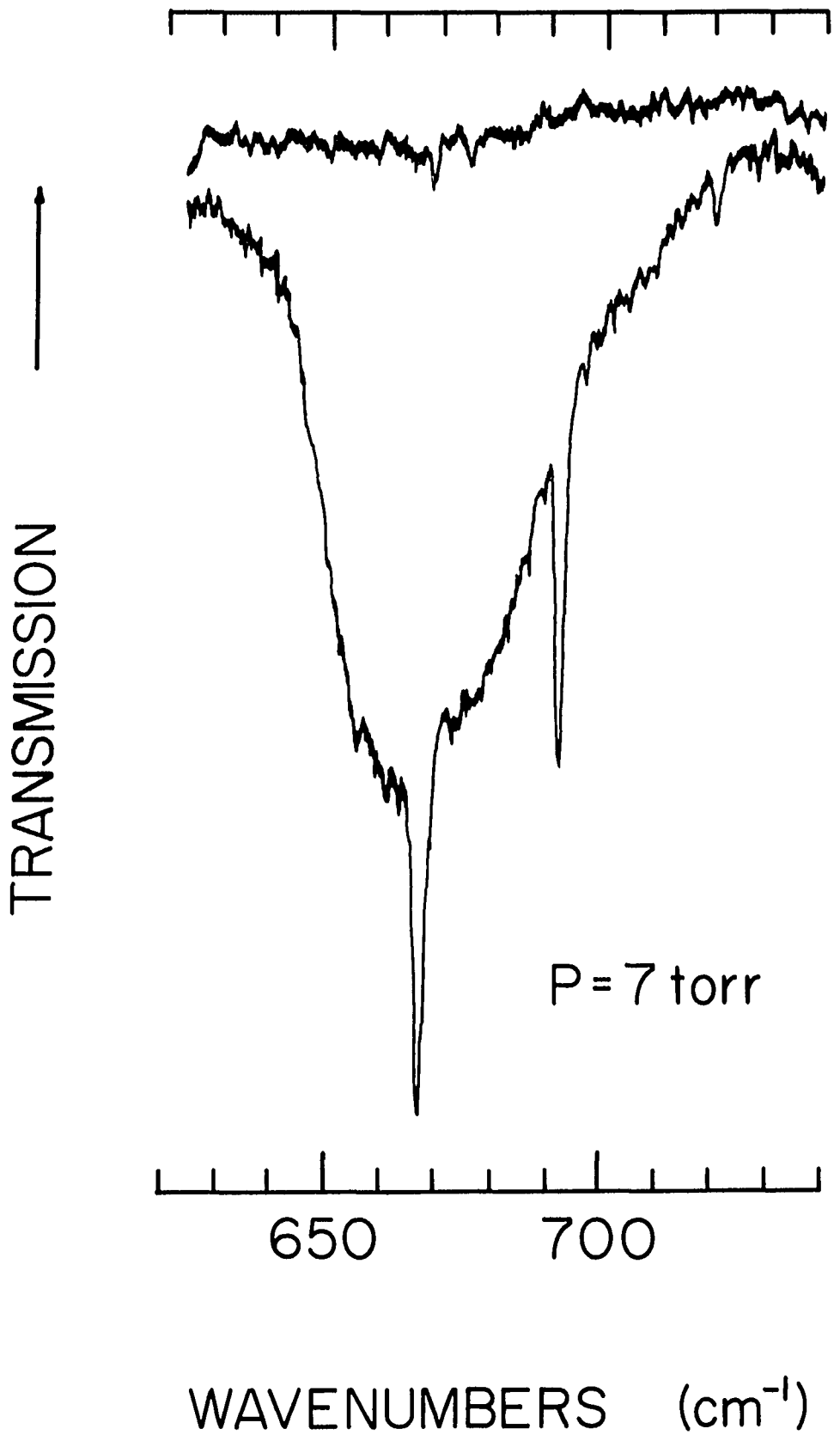


Fig. 8. Grating resolution spectrum of the out-of-plane BF_2 wagging vibration recorded at 5 cm^{-1}/min with a spectral slit width of 0.1 cm^{-1}.

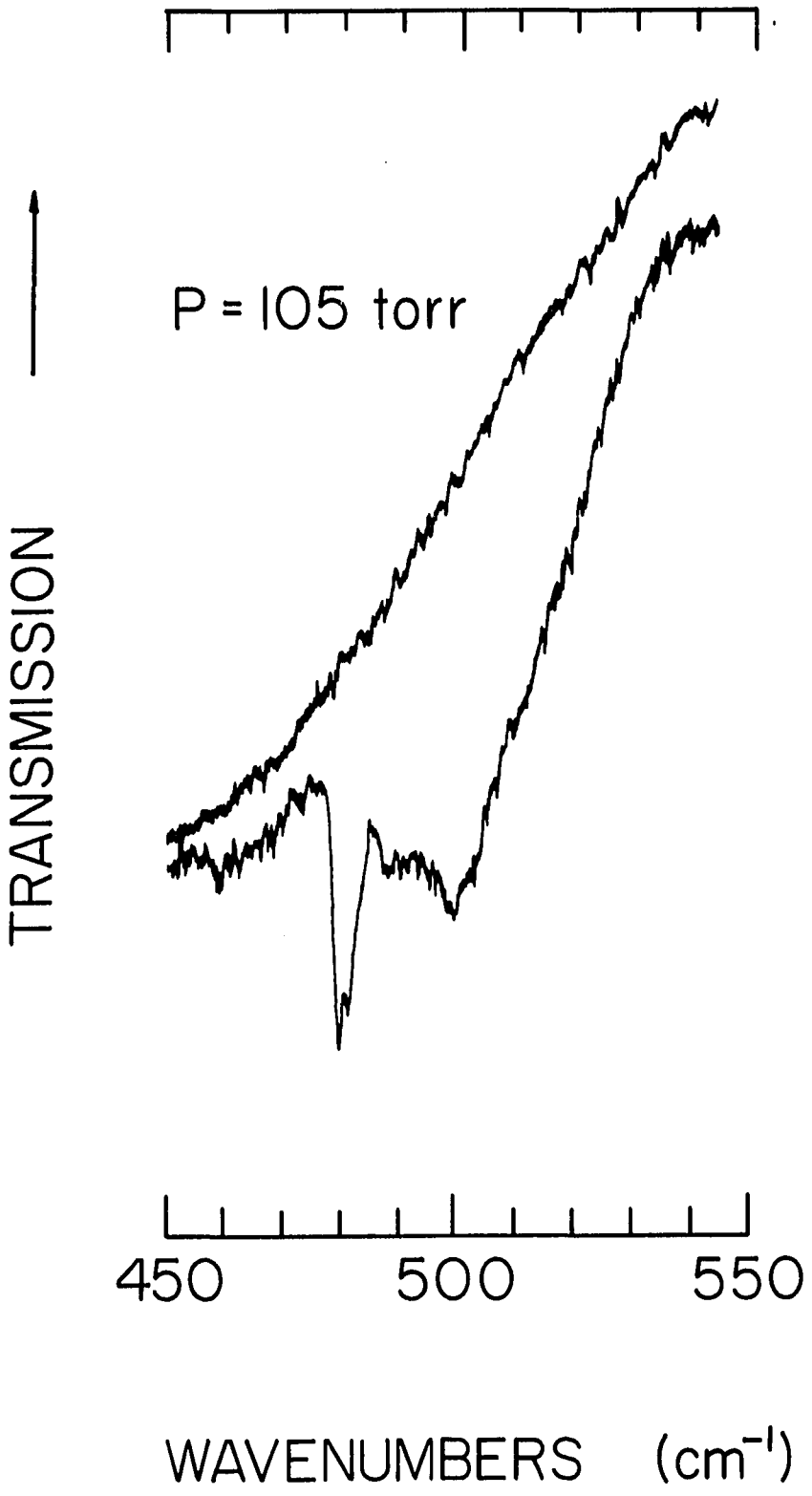


Fig. 9. Grating resolution spectrum of the BF_2 scissoring mode recorded at 5 cm^{-1}/min with a spectral slit width of 0.3 cm^{-1}.

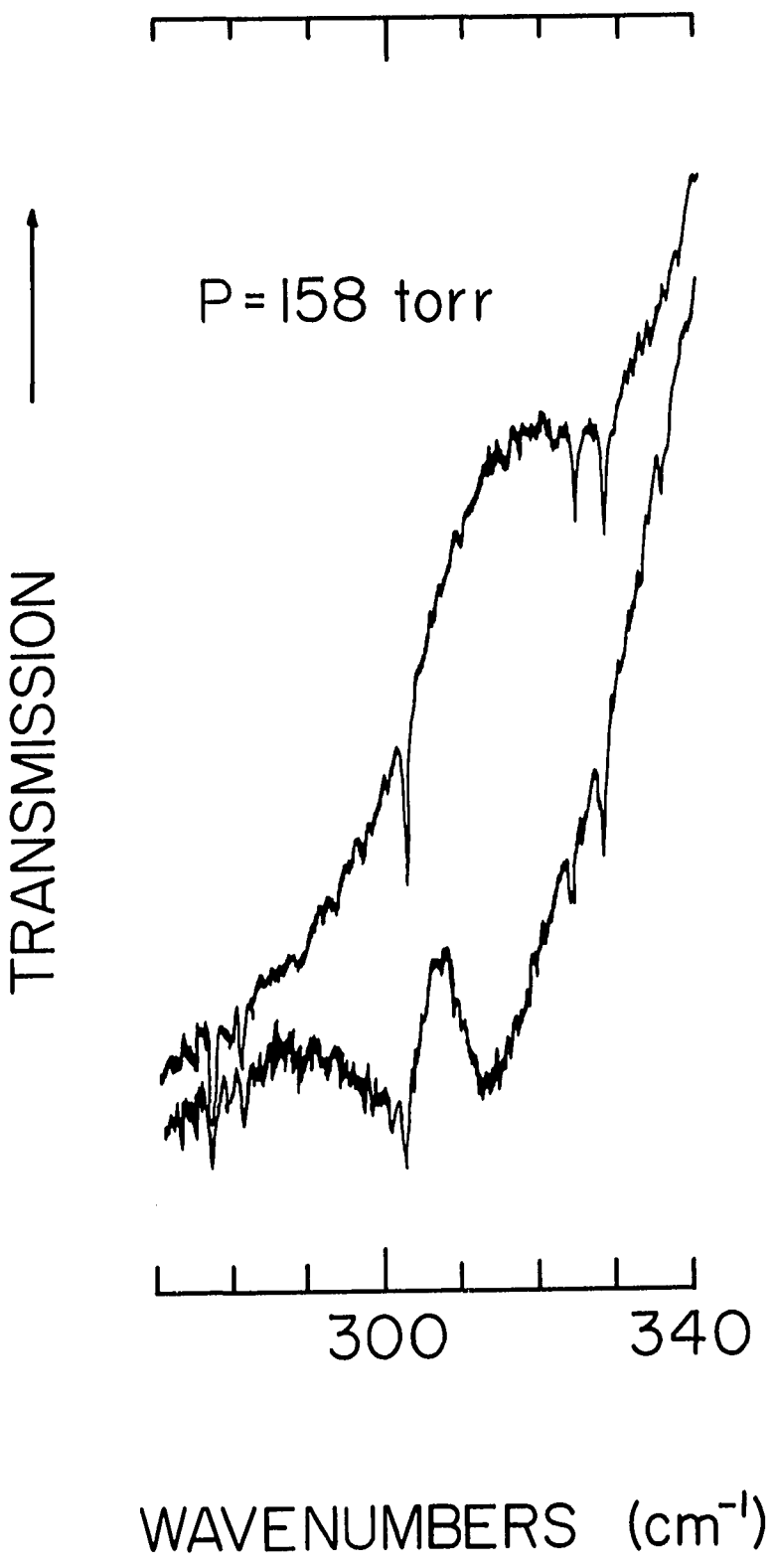


Fig. 10. Grating resolution spectrum of the in-plane BF_2 rocking mode recorded at 4 cm^{-1}/min with a spectral slit width of 0.4 cm^{-1}.

vibrational assignment for the BF_2 vibrations is summarized in Table 19. This table also demonstrates that the assignment of the BF_2 group vibrations compares favorably with analogous vibrations of other molecules.

Skeletal Vibrations

The seven remaining fundamental vibrations are all associated with the linear skeletal chain. The carbon-carbon stretches were more readily assigned than the carbon-boron stretching and skeletal bending vibrations. The intense band at 2228 cm^{-1} was attributed to the acetylenic carbon-carbon stretching vibration, $\nu_2(a')$. As shown in Fig. 11, there was a reproduceable series of lines on the high wavenumber side of this band which were interpreted as "hot" bands, as this is not an unusual feature of the acetylenic carbon-carbon stretch [44]. The wavenumber values of these lines were 2231.3, 2238.8, and 2235.0 cm^{-1}. The C-C stretching vibration, $\nu_5(a_1')$, was assigned to a less intense absorption at 1018.5 cm^{-1}, shown in Fig. 12. The PQR structure of this absorption was consistent with the type A contour expected for this vibration. The absorption of the carbon-boron stretch, $\nu_6(a_1')$, was not assigned as readily, even though it was expected as a isotopically split type A band at approximately 750 cm^{-1}. Instead, two weak, structureless absorptions were observed in this region, one at 747 cm^{-1}, and the other at 782 cm^{-1}, as shown in Fig. 13. In the low resolution polycrystalline thin film spectrum of this region, an absorption with suggested isotopic splitting was observed at

Table 19

BF_2 Group Vibrational Frequencies

Group Vibration	$ClB^{11}F_2$ [20]	$BrB^{11}F_2$ [20]	$CH_3B^{11}F_2$ [17]	$CD_3B^{11}F_2$ [17]	$CH_3C{\equiv}CB^{11}F_2$*
ν_2 BF_2	1421	1417	1366	1348	1373
ν_S BF_2	1242	1208	1249	1193	1328
ν B-C	--	--	774	718	782
γ BF_2	604	568	908	812	666
δ_S BF_2	427	330†	485	470	499
δ_a BF_2	366	346†	346	305	307

† Calculated values

* This work

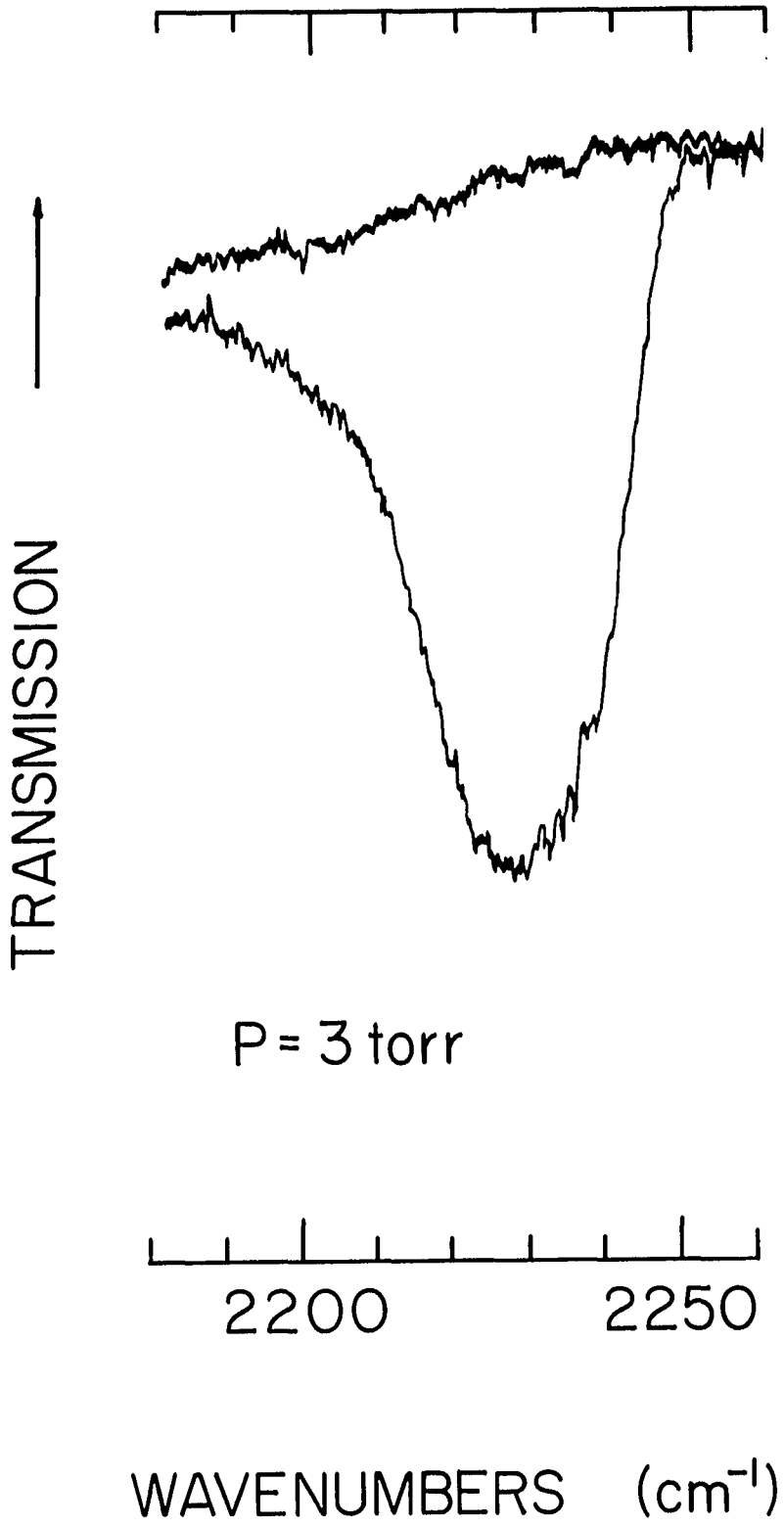


Fig. 11. Grating resolution spectrum of the acetylenic carbon-carbon stretching mode recorded ar 4 cm^{-1}/min with a spectral slit width of 0.3 cm^{-1}.

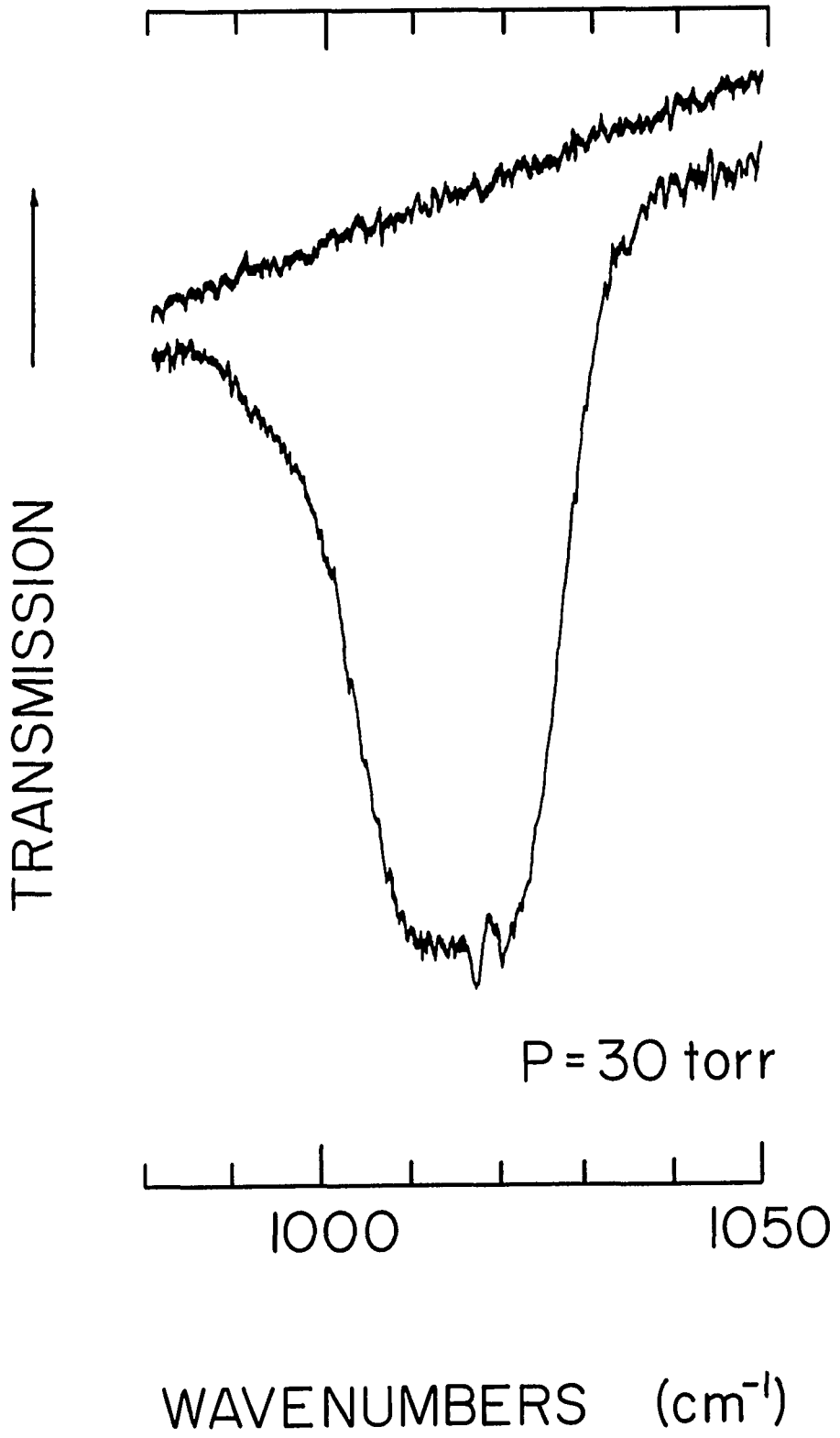


Fig. 12. Grating resolution spectrum of the carbon-carbon single bond stretching mode recorded at 4 cm^{-1}/min with a spectral slit width of 0.2 cm^{-1}.

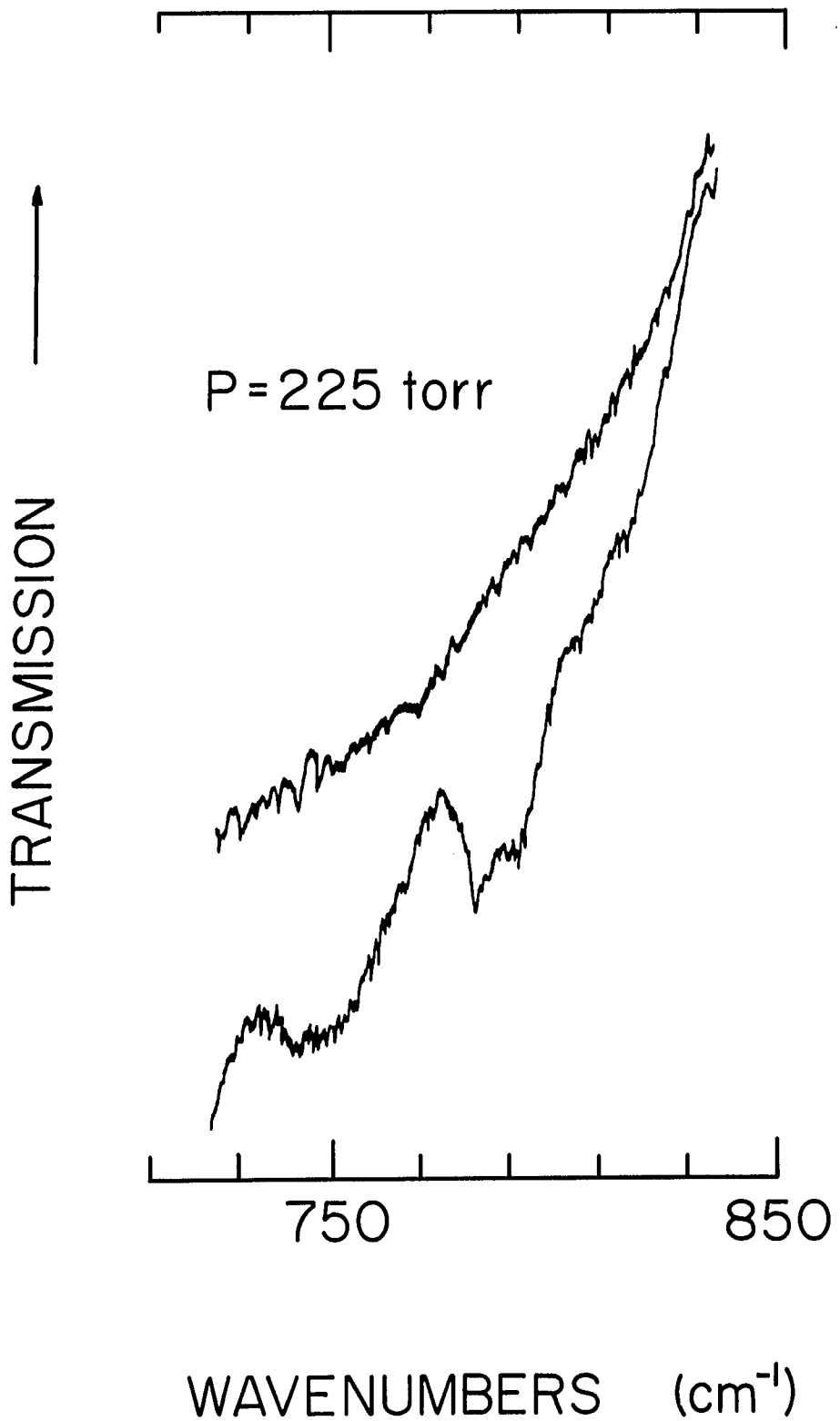


Fig. 13. Grating resolution spectrum of the boron-carbon stretching mode recorded at 8 cm^{-1}/min with a spectral slit width of 0.2 cm^{-1}.

770 cm^{-1}. As a result, the 782 cm^{-1} absorption was assigned to the carbon-boron stretch. The ambiguous nature of this absorption appears to be an intrinsic characteristic of the carbon-boron stretch as similar difficulties were encountered in determining the spectra of CH_3BF_2 and CD_3BF_2 [17].

The two doubly degenerate skeletal bending vibrations were assigned to the remaining absorptions in the region from 500 to 250 cm^{-1}. Their assignments were based strictly on characteristic group frequencies. The absorption of the C-C≡C bend, $\nu_{12}(e')$, was assigned to the infrared band at 371 cm^{-1}, shown in Fig. 14, while the 406 cm^{-1} absorption, shown in Fig. 15, was attributed to the C≡C-B bend, $\nu_{11}(e')$. The line at 375 cm^{-1} on the shoulder of the 371 cm^{-1} absorption was attributed to a "hot" band as the 371 cm^{-1} absorption was not isotopically split in the thin film spectrum. As shown in Table 20, the assignment $\nu_{12}(e')$ agrees with other results; $\nu_{11}(e')$ was assigned to the remaining absorption in this region. Table 20 summarizes and compares the assignment of the CH_3-C≡C vibrations with spectral results for other molecules possessing this group. Table 21 summarizes the vibrational assignment which confirmed the model proposed for propynyl boron difluoride. The assignment of the weaker absorptions attributed to overtone and combination modes are listed in Table 22.

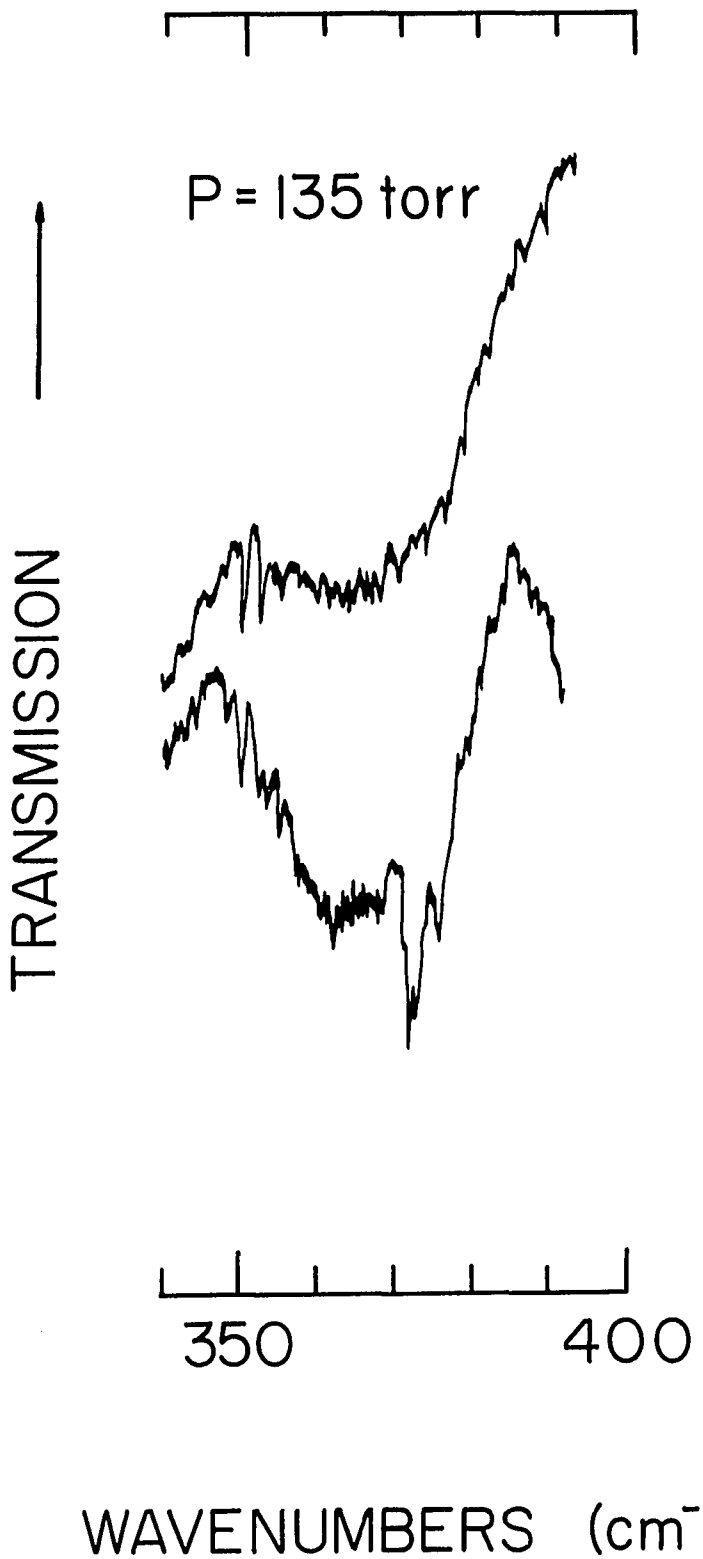


Fig. 14. Grating resolution spectrum of the C-C≡C bending mode of propynyl boron difluoride recorded at 4 cm^{-1}/min with a spectral slit width of 0.3 cm^{-1}.

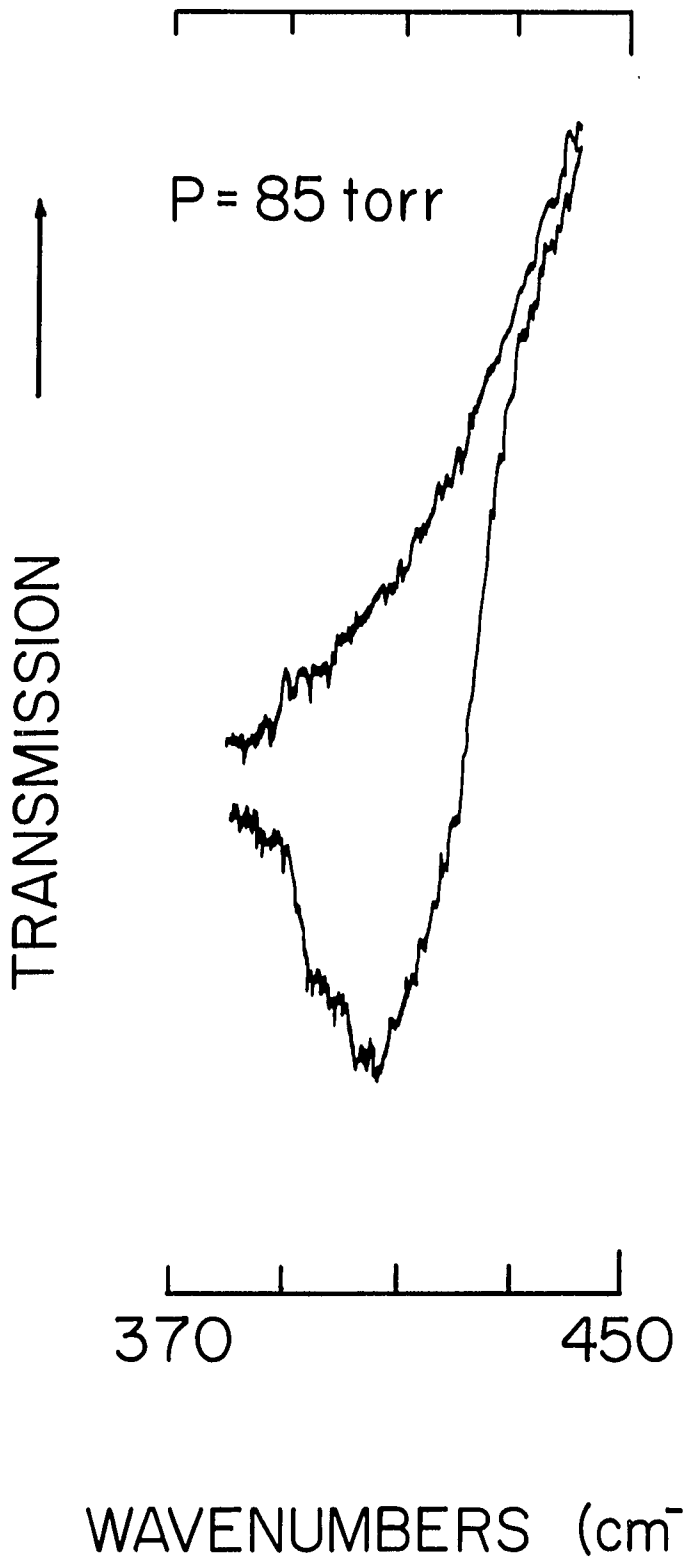


Fig. 15. Grating resolution spectrum of the B-C≡C bending mode of propynyl boron difluoride recorded at 6 cm^{-1}/min with a spectral slit width of 0.3 cm^{-1}.

Table 20

$CH_3C{\equiv}C$ Group Vibrational Frequencies

Group Vibration	$CH_3C{\equiv}CH$ (cm^{-1})	$CH_3C{\equiv}CCl$ [10] (cm^{-1})	$CH_3C{\equiv}CBr$ [9] (cm^{-1})	$CH_3C{\equiv}CI$ [9] (cm^{-1})	$CH_3C{\equiv}CCH_2Cl$ [11] (cm^{-1})	$CH_3C{\equiv}CCH_2Cl$ [5] (cm^{-1})	$CH_3C{\equiv}C\text{-}BF_2$ [6] (cm^{-1})
ν_a CH_3	3008	2980	2979	2997	2990	2990	3014
ν_s CH_3	2941	2939	2952	2936	2920	2920	2939
$\nu C{\equiv}C$	2142	2267	2248	2220	2242	2242	2228
δ_a CH_3	1452	1454	1452	1450	1440	1440	1437*
δ_s CH_3	1382(1,R)	1395	1375	1373	1380	1378	1378(p)
$\nu C\text{-}C$	931	1084	1045	1020	1159	1159	1019
ρCH_3	1053	1033	1034	1033	1030	1031	1022(p)
$C\text{-}C{\equiv}C$	328	358	343(1,R)	343(1,R)	--	--	371

1 - liquid phase, R = Raman spectrum, P = infrared spectrum of polycrystalline thin film,
* Calcaulted from first overtone, P = from the infrared spectrum of a polycrystalline thin film at -196°C.

Table 21

Fundamental Vibrational Wavenumbers for Propynyl Boron Difluoride

Wavenumber	Assignment	Approximate Normal Mode
2944.1 R 2938.6 Q 2932.8 P	$\nu_1(a_1')$	CH_3 symmetric stretch
2228	$\nu_2(a_1')$	C≡C stretch
1378*	$\nu_3(a_1')$	CH_3 symmetric deformation
1344.5 R 1339.6 Q 1333.0 P	$\nu_4(a_1')$	$B^{10}F_2$ symmetric stretch
1333.0 R 1328.3 Q 1323.1 P	$\nu_4(a_1')$	$B^{11}F_2$ symmetric stretch
1020.6 R 1018.5 Q 1012.5 P	$\nu_5(a_1')$	C-C stretch
782	$\nu_6(a_1')$	C-B stretch
499	$\nu_7(a_1')$	BF_2 scissors
$3014.3^{R}Q_0$	$\nu_8(e')$	CH_2 asymmetric stretch
1437†	$\nu_9(e')$	CH_3 asymmetric deformation
1022*	$\nu_{10}(e')$	CH_3 rock
406	$\nu_{11}(e')$	B-C≡C bend
371	$\nu_{12}(e')$	C≡C-C bend
1428 R 1422 1417 P	$\nu_{13}(a_1'')$	$B^{10}F_2$ asymmetric stretch
1377 R 1373 1369 P	$\nu_{13}(a_1'')$	$B^{11}F_2$ asymmetric stretch
307	$\nu_{14}(a_1'')$	BF_2 rock (in-plane)
665.5	$\nu_{15}(a_2'')$	BF_2 wag (out-of-plane)

†Calculated from first overtone, * from the infrared spectrum of a polycrystalline thin film at -196°C.

Table 22

Overtone and Combination Wavenumbers of Propynyl Boron Difluoride

Wavenumber	Assignment
2874	$2\nu_9(A_1' + E')$
2738	$2\nu_{13}(A_1')$
2699	$\nu_{13} + \nu_4(A_1'')$
2633	$2\nu_4(A_1')$
2421	$\nu_{13} + \nu_5(A_1'')$
2383	$\nu_{13} + \nu_5(A_1'')$
2337	$\nu_4 + \nu_5(A_1')$
1276	$2\nu_{15}(A_1')$
747	$2\nu_{12}(A_1' + E)$
600	$2\nu_{14}(A_1')$

CHAPTER V

THERMODYNAMIC PROPERTIES

In the previous chapter, a detailed account of the spectrum of propynyl boron difluoride was presented, and it was demonstrated that the observed spectrum was consistent with a specified molecular model. The purpose of this chapter was to use the estimated molecular configuration and the infrared spectrum to calculate standard thermodynamic quantities of propynyl boron difluoride. In this case, the calculated thermodynamic quantities are probably more reliable than those which would be calculated from direct thermal data because of the chemical instability of propynyl boron difluoride.

Propynyl boron difluoride was considered to be an ideal gas at one atmosphere pressure with the total energy of the molecule equal to the sum of the translational, rotational, internal rotational, vibrational, and electronic energies. Thus it was possible to calculate each contribution to the thermodynamic quantities by using the following relationships:

For molar heat capacity:

$$C_p^{\circ} = R[T^2(\partial^2 \ln Q/\partial T^2) + 2T(\partial \ln Q/\partial T)] \qquad (26)$$

For molar entropy:

$$S^{\circ} = R(\ln Q + T(\partial \ln Q/\partial T) \qquad (27)$$

For molar free energy:

$$(H^\circ - H_o^\circ) = RT + RT^2(\partial \ln Q/\partial T) \quad (28)$$

For molar enthalpy:

$$-(G^\circ - H_o^\circ) = R\ln Q \quad (29)$$

where Q is the partition function for the molecule. Since most molecules have electronic ground states in which the electrons are paired to yield zero spin and zero orbital angular momentum, electronic contributions were neglected.

The translational contributions to thermodynamic properties are independent of spectroscopic data, as they can be calculated from kinetic theory. The equations used were [45]:

$$S^\circ_{TR} = R(3/2 \ln M + 5/2 \ln T) - 2.315 \text{ cal/deg.} \quad (30)$$

$$-[(G^\circ - H_o^\circ)/T]_{TR} = R(3/2 \ln M + 5/2 \ln T) - 7.283 \text{ cal/deg.} \quad (31)$$

$$(H^\circ - H_o^\circ)_{TR} = 5/2\ RT \quad (32)$$

$$(C_p{}^\circ)_{TR} = 5/2\ R \quad (33)$$

where T is temperature in degrees Kelvin, M is the mass of the molecule in atomic mass units, and R is the universal gas constant in calories/mole-degree.

The rotational contributions to the thermodynamic quantities are a function of the principal moments of inertia of the molecule, its symmetry, and the temperature. The equations used for propynyl boron difluoride were:

$$S^\circ_{ROT} = R[1/2\ \ln(D \times 10^{117}) + 3/2\ \ln T - \ln\sigma] - 0.033 \text{ cal/deg.} \quad (34)$$

$$-[(G^\circ - H^\circ_o)/T]_{ROT} = R[1/2\ \ln(D \times 10^{117}) + 3/2\ \ln T - \ln\sigma] - 3.014 \text{ cal/deg.} \quad (35)$$

$$(H^\circ - H^\circ_o)_{ROT} = 3/2\ RT \quad (36)$$

$$(Cp^\circ)_{ROT} = 3/2\ RT \quad (37)$$

where σ is the symmetry number, and D is the product of the moments of inertia, $I_a \cdot I_b \cdot I_c$, each in cgs units. Since the moments of inertia of CH_3CCBF_2 were not spectroscopically determined, the estimates cited in Table 5 were used.

The vibrational contributions were determined from the frequencies of the fundamental absorptions. At a specific temperature, the total vibrational contribution equals the sum of the contributions from each of the twenty vibrational frequencies weighted for their appropriate degeneracies. The equations used to calculate the contribution from each frequency were:

$$S^\circ_{VIB} = R[u/(e^u-1) - \ln(1-e^{-u})] \quad (38)$$

$$-[(G^\circ - H^\circ_o)/T]_{VIB} = -R\ \ln(1-e^{-u}) \quad (39)$$

$$(H^\circ - H^\circ_o)_{VIB} = RT\ u/(e^u-1) \quad (40)$$

$$(Cp^\circ)_{VIB} = -R\ u^2 e^u/(e^u-1)^2 \quad (41)$$

where

$$u = h\nu c/kT = 1.4387\ \nu/T$$

and ν represents the fundamental frequency in cm^{-1}.

The internal rotational contributions to the thermodynamic quantities are a function of the reduced moment of inertia of the molecule and the symmetry number for internal rotation. By applying the fundamental equations listed at the beginning of this chapter, the following expressions for the internal rotational contributions emerged:

$$S^{\circ}_{IROT} = R[\ln Q_F + 1/2] \tag{42}$$

$$-[(G^{\circ} - H^{\circ}_o)/T]_{IROT} = R \ln Q_F \tag{43}$$

$$(H^{\circ} - H^{\circ}_o)_{IROT} = 1/2\ RT \tag{44}$$

$$(Cp^{\circ})_{IROT} = 1/2\ R \tag{45}$$

Q_F is the partition function for free internal rotation and is defined as follows [45]:

$$Q_F = \frac{2.7935}{n} (10^{38} I_R T)^{1/2} \tag{46}$$

where T is temperature in degrees Kelvin, I_R is the reduced moment of inertia, and n is the number of times per revolution that the molecule attains an equilibrium configuration. The reduced moment of inertia for a symmetric top rotor attached to an asymmetric framework is defined by the following equation:

$$I_R = A[1 - \sum_{i=1}^{3} (\alpha_i^2 A/I_i)] \tag{47}$$

A is the moment of inertia of the symmetric top rotor about the axis of internal rotation, α_i is the direction cosine between the

axis of internal rotation and the i^{th} principal axis for overall rotation of the molecule, and I_i is the i^{th} principal moment of inertia for overall rotation.

A computer program (Appendix II) was written to calculate thermodynamic properties for non-linear molecules, including molecules with free internal rotation. In this investigation, the gas phase absorptions of the asymmetric methyl rocking vibrations were not observed, as previously explained. However, with the intention of determining reasonable estimates for the thermodynamic properties of propynyl boron difluoride, the wavenumber values estimated from overtones and polycrystalline spectra were used. The contributions from translation, rotation, vibration, and internal rotation from 100 to 1000°K are presented in Tables 23, 24, 25, and 26, respectively, while the total contributions are in Table 27. The input data for the computer program are displayed in the computer printout, Appendix II.

Table 23

Translational Contributions to the Thermodynamic Properties of Propynyl Boron Difluoride

T(°K)	$Cp°/_R$	$(H°-H°_o)/_{RT}$	$-(G°-H°_o)/_{RT}$	$S°/_R$
100	2.50	2.50	14.6	17.1
200	2.50	2.50	16.3	18.8
298.16	2.50	2.50	17.3	19.8
300	2.50	2.50	17.3	19.8
400	2.50	2.50	18.0	20.5
500	2.50	2.50	18.6	21.1
600	2.50	2.50	19.0	21.5
700	2.50	2.50	19.4	21.9
800	2.50	2.50	19.8	22.3
900	2.50	2.50	20.1	22.6
1000	2.50	2.50	20.3	22.8

Table 24

Rotational Contributions to the Thermodynamic Properties of Propynyl Boron Difluoride

T(°K)	$Cp°/_R$	$(H°-H°_o)/_{RT}$	$-(G°-H°_o)/_{RT}$	$S°/_R$
100	1.50	1.50	10.5	12.0
200	1.50	1.50	11.6	13.1
298.16	1.50	1.50	12.2	13.7
300	1.50	1.50	12.2	13.7
400	1.50	1.50	12.6	14.1
500	1.50	1.50	12.9	14.4
600	1.50	1.50	13.2	14.7
700	1.50	1.50	13.4	14.9
800	1.50	1.50	13.6	15.1
900	1.50	1.50	13.8	15.3
1000	1.50	1.50	14.0	15.5

Table 25

Vibrational Contributions to Thermodynamic Properties of Propynyl Boron Difluoride

T(°K)	Cp°/R	$(H^\circ-H_o^\circ)/RT$	$-(G^\circ-H_o^\circ)/RT$	S°/R
100	0.688	0.128	0.0242	0.152
200	3.49	1.11	0.378	1.48
298.16	5.87	2.30	1.04	3.34
300	5.92	2.32	1.06	3.37
400	7.98	3.48	1.88	5.37
500	9.71	4.56	2.78	7.34
600	11.1	5.54	3.70	9.24
700	12.3	6.43	4.62	11.0
800	13.3	7.23	5.53	12.8
900	14.1	7.95	6.43	14.4
1000	14.8	8.60	7.30	15.9

Table 26

Internal Rotational Contributions to the Thermodynamic Properties of Propynyl Boron Difluoride

T(°K)	$Cp^\circ/_R$	$(H^\circ-H^\circ_o)/RT$	$-(G^\circ-H^\circ_o)/RT$	$S^\circ/_R$
100	0.500	0.500	0.0491	0.549
200	0.500	0.500	0.396	0.896
298.16	0.500	0.500	0.595	1.10
300	0.500	0.500	0.598	1.10
400	0.500	0.500	0.742	1.24
500	0.500	0.500	0.854	1.35
600	0.500	0.500	0.945	1.45
700	0.500	0.500	1.02	1.52
800	0.500	0.500	1.09	1.59
900	0.500	0.500	1.15	1.65
1000	0.500	0.500	1.20	1.70

Table 27

Thermodynamic Quantities for Propynyl Boron Difluoride

T(°K)	$Cp°/R$	$(H°-H°_o)/RT$	$-(G°-H°_o)/RT$	$S°/R$
100	5.19	4.63	25.2	29.8
200	7.99	5.61	28.6	34.3
298.16	10.4	6.80	31.1	37.9
300	10.4	6.82	31.1	38.0
400	12.5	7.98	33.3	41.2
500	14.2	9.06	35.2	44.2
600	15.6	10.0	36.9	46.9
700	16.8	10.9	38.5	49.4
800	17.8	11.7	40.0	51.8
900	18.6	12.4	41.4	53.9
1000	19.3	13.1	42.8	55.9

APPENDIX I

PRINCIPAL MOMENTS OF INERTIA AND RELATED CONSTANTS

APPENDIX I

PRINCIPAL MOMENTS OF INERTIA AND RELATED CONSTANTS

By using the assumed molecular parameters presented in Table 2, the principal moments of inertia for propynyl boron difluoride were estimated. Consideration of the molecular configuration indicated that the smallest moment of inertia, I_a, would be about the axis co-linear with the C-C≡C-B skeletal chain. The largest moment of inertia, I_c, was expected to have an axis perpendicular to the unique plane described by the BF_2 atoms and intersecting the I_a inertial axis at the center of mass of the molecule. The intermediate inertial axis, I_b, then would be mutually perpendicular to and intersecting the other inertial axes at the center of mass.

Center of Mass

The center of mass of CH_3CCBF_2 was determined from torque moments about an axis perpendicular to the principal symmetry axis of the molecule; i.e., the center of mass is the point at which $\sum_i m_i r_i = 0$, where m_i is the mass of the i^{th} atom, r_i is the perpendicular distance of the i^{th} atom from the axis about which the moments are being considered, and the index i includes all atoms of the molecule. To simplify the calculation, the center of mass of the CH_3 group was determined first, then the molecule could be considered as X-C≡C-BF_2 from an inertial view point, where X represents a point with a mass equivalent to that of the CH_3 group

and located at the center of mass of the CH_3 group. The center of mass of the CH_3 group was located by using the law of cosines and the torque moment method. This point was estimated to be 0.1751 Å beyond the terminal carbon of the skeletal chain and on the I_a inertial axis. By using similar relationships and considering the CH_3 group as a point mass of 15.03 amu, the center of mass of the molecule was determined to be 1.039 Å from the boron atom on the I_a inertial axis.

Principal Moments of Inertia

The I_a moment of inertia was determined with the following expression:

$$I_a = 3m_H r_H^2 + 2m_F r_F^2 \qquad (1a)$$

where

m = the mass of an atom

r_F = 1.309 Å sin 59° = 1.114 Å

$r_H = [2(1.112)^2 - 2(1.112)^2 \cos 108.4°]^{1/2}/2\cos 30°$

= 1.041 Å

From this, $I_a = 84.86 \times 10^{-40}$ g-cm^2. The A rotational constant, which is related to I_a by the following relationship:

$$A(cm^{-1}) = h/8\pi^2 c I_a, \qquad (2a)$$

was determined to be 0.330 cm^{-1}.

The I_b moment of inertia was determined from the following expression:

$$I_b = m_{CH_3} r_{CH_3}^2 + m_C r_{C_7}^2 + m_C r_{C_8}^2 + m_B r_B^2 + 2m_F r_F^2 \qquad (3a)$$

where:

m = the mass of the atom under consideration

r_{CH_3} = 2.840 Å + 0.491 Å = 3.331 Å

r_{C_7} = 1.207 Å + 0.491 Å = 1.698 Å

r_{C_8} = 0.491 Å

r_B = 1.039 Å

r_F = 1.309 Å cos 59° + 0.674 Å = 1.713 Å,

with the subscripted carbon atoms referring to the atoms as they are labelled in Fig. 4. I_b was calculated to be 543.6 x 10^{-40} g-cm^2, and from a relationship analogous to eqn. (2a), B was determined to be 0.051 cm^{-1}.

I_c, the largest moment of inertia, was calculated by using the following expression:

$$I_c = m_{CH_3} r_{CH_3}^2 + m_C r_{C_7}^2 + m_C r_{C_8}^2 + m_B r_B^2 + 2m_F r_F^2 \quad (4a)$$

with the same parameters for eqn. (3a), except

$$r_F^2 = (1.713)^2 + (1.122)^2 = 4.193 \text{ Å}^2$$

As a result, I_c = 623.1 x 10^{-40} g-cm^2, and the C rotational constant was 0.045 cm^{-1}.

κ, The Asymmetry Parameter

The asymmetry parameter, a numerical representation of the symmetry of a molecule, is determined from the A, B, and C rotational

constants with the following relationship:

$$\kappa = (2B-A-C)/(A-C) \qquad (5a)$$

For oblate and prolate symmetric top molecules, κ has exact values of +1 and -1, respectively. The value of the asymmetry parameter for propynyl boron difluoride is -0.96, a near prolate value.

Related Constants

To solve the rotational problem, eqn. (8), several constants were required. These constants are functions of the principal moments of inertia of propynyl boron difluoride, and their numerical values are presented below.

$$A_1 = \frac{hI_a}{8\pi^2 I_\alpha (I_a - I_\alpha)_c} = 5.504 \text{ cm}^{-1} \qquad D = \frac{1}{2}(B+C) = 0.048 \text{ cm}^{-1}$$

$$A_2 = \frac{h}{8\pi^2 (I_a - I_\alpha)_c} = 0.3525 \text{ cm}^{-1} \qquad d = \frac{2A_2}{A_2 - D} = 2.311$$

As mentioned previously, I_α is the moment of inertia for rotation of the methyl group about the axis of internal rotation. This is the first term of eqn. (1a) and equals 5.435×10^{-40} g-cm^2.

APPENDIX II

COMPUTER PROGRAM

```
      PROGRAM PRR(INPUT,OUTPUT)
000003 COMMON STR(11), GTR(11),HTR(11),CTR(11),SRO(11),GRO(11),HRO(11),
     1CRO(11),SVIBT(11),GVIBT(11),HVIBT(11),CVIBT(11),TEMP(11),
     2SRI(11),GRI(11),HRI(11),CRI(11),
     3STOT(11),GTOT(11),HTOT(11),CTOT(11)
C
C          THIS PROGRAM IS DESIGNED TO CALCULATE THERMODYNAMIC
C     QUANTITIES FOR NON-LINEAR POLYATOMIC MOLECULES FROM 100 TO
C     1000 DEGREES KELVIN.  DETAILED DISCUSSION OF THE CALCULATION CAN
C     BE FOUND IN CHAPTER 27 OF THERMODYNAMICS, BY G.N. LEWIS AND
C     MERLE RANDALL, MCGRAW-HILL, 1961.
C
C          THE REQUIRED INPUT DATA ARE AS FOLLOWS.
C
C     FOR TRANSLATIONAL CONTRIBUTIONS
C          WM=MOLECULAR WEIGHT
C
C     FOR ROTATIONAL CONTRIBUTIONS
C          SIGMA= SYMMETRY NUMBER WHICH IS DISCUSSED IN HERZBERG(II,
C               P.508)
C          AI,BI,CI= PRINCIPAL MOMENTS OF INERTIA IN CGS UNITS
C
C     FOR VIBRATIONAL CONTRIBUTIONS
C          NDATA= THE NUMBER OF VIBRATIONAL FREQUENCIES (EITHER 3N-6 OR
C               3N-7)
C          W= THE VIBRATIONAL FREQUENCIES IN WAVENUMBERS
C               (INCLUDE A DATA CARD FOR EACH)
C
C     FOR FREE INTERNAL ROTATIONAL CONTRIBUTIONS
C          AN=THE SYMMETRY NUMBER FOR INTERNAL ROTATION  AS DISCUSSED IN
C               LEWIS AND RANDALL, OP. CIT., P.438.
C          RI= THE REDUCED MOMENT OF INERTIA AS DISCUSSED IN LEWIS AND
C               RANDALL, IBID., P.440.   (CGS UNITS)
C
C
C          AT MODERATE TEMPERATURE MOST MOLECULES HAVE ELECTRONIC
C     STATES IN WHICH THE ELECTRONS ARE PAIRED TO YIELD ZERO ELECTRON
C     SPIN AND ZERO ORBITAL ANGULAR MOMENTUM.  AS A RESULT THE MOST POP
C     ULATED ELECTRONIC STATE IS A SINGLE  QUANTUM STATE WITH NO
C     ELECTRONIC CONTRIBTION TO THERMODYNAMIC QUANTITIES--THUS NO
C     PROVISIONS FOR ELECTRONIC CONTRIBUTIONS HAVE BEEN INCLUDED.
C
C          THIS PROGRAM CAN BE MODIFIED TO CALCULATE ANY COMBINATION OF
C     CONTRIBUTIONS BY ANSWERING A SERIES OF YES OR NO QUESTIONS WHICH
C     ARE FORTRAN STATEMENTS LOCATED AT THE BEGINNING OF THE PROGRAM.
C          Q1= CALCULATE TRANSLATIONAL CONTRITUTIONS
C          Q2= CALCULATE ROTATIONAL CONTRIBUTIONS
C          Q3= CALCULATE VIBRATIONAL CONTRIBUTIONS
C          Q4= CALCULATE INTERNAL ROTATIONAL CONTRIBUTIONS
C
C          DATA CARDS MUST APPEAR BEHIND THE 789 CARD IN THE ORDER IN
C     WHICH THEY WILL BE READ.  SUPERFLUOUS DATA SHOULD NOT BE INCLUDED,
C     E.G. IF Q1=XNO, THEN THE WM DATA CARD SHOULD NOT BE INCLUDED IN
C     THE DECK.  (XNO IS USED TO INDICATE NO.)
C
C     MARCH 23, 1970                              P. ROBERT REED, JR.
C
```

```
000003          YES=1.234567
000004          XNO=0.00000
000005          Q1=YES
000007          Q2=YES
000007          Q3=YES
000010          Q4=YES
000011          IF(Q1.NE.YES)GO TO 202
000013          CALL TRANS
000014      202 IF(Q2.NE.YES)GO TO 203
000016          CALL ROT
000017      203 IF(Q3.NE.YES)GO TO 204
000021          CALL VIB
000022      204 IF(Q4.NE.YES)GO TO  205
000024          CALL FRROT
000025      205 PRINT 206
000031      206 FORMAT(1H1, 7X,47HTOTAL CONTRIBUTIONS TO THERMODYNAMIC QUANTITIES/
                1/3X,4HTEMP,7X,7HENTROPY,4X,8HFREE EN.,5X,8HENTHALPY,4X,9HHEAT CAP.
                2//)
000031          I=1
000032      207 STOT(I)=STR(I)+SRO(I)+SVIBT(I)+SRI(I)
000037          GTOT(I)=GTR(I)+GRO(I)+GVIBT(I)+GRI(I)
000043          HTOT(I)=HTR(I)+HRO(I)+HVIBT(I)+HRI(I)
000050          CTOT(I)=CTR(I)+CRO(I)+CVIBT(I)+CRI(I)
000055          PRINT 208, TEMP(I),STOT(I),GTOT(I),HTOT(I),CTOT(I)
000072      208 FORMAT(5E12.5)
000072          I=I+1
000074          IF(I.LT.12)GO TO 207
000076          CALL EXIT
000077          END
```

```
                SUBROUTINE TRANS
000002          COMMON STR(11), GTR(11),HTR(11),CTR(11),SRO(11),GRO(11),HRO(11),
               1CRO(11),SVIBT(11),GVIBT(11),HVIBT(11),CVIBT(11),TEMP(11),
               2SRI(11),GRI(11),HRI(11),CRI(11),
               3STOT(11),GTOT(11),HTOT(11),CTOT(11)
C
C                    CALCULATIONS ARE BASED ON IDEAL GAS APPROXIMATION
C
C                   0                   0  0                   0  0                   0
C         STR = S /R,  GTR = -(G -H )/RT,  HTR = (H -H )/RT,  CTR = C /R
C                                    0                   0
C
000002          READ 1,WM
000010        1 FORMAT(E12.5)
C                    PRINT OUT LABELLED DATUM, CHECK
000010          PRINT 6
000014        6 FORMAT(1H1,2X,55HTRANSLATIONAL CONTRIBUTIONS TO THERMODYNAMIC QUAN
               1TITIES,//)
000014          PRINT 7, WM
000022        7 FORMAT(10X,5HINPUT,10X,18HMOLECULAR WEIGHT =,E12.5,4H AMU,//)
000022          PRINT 8
000026        8 FORMAT(3X,4HTEMP,7X,7HENTROPY,4X,8HFREE EN.,5X,8HENTHALPY,4X,9HHEA
               1T CAP.,/)
C                    BEGIN CALCULATIONS
000026          XLNMW=1.50000*ALOG(WM)
000031          I=1
000032          TEMP(I)=100.0
000035        5 XLNT=2.50000*ALOG(TEMP(I))
000042        2 SUMTR=XLNMW+XLNT
000044          STR(I)=SUMTR-1.1551
000047          GTR(I)=SUMTR-3.6656
000052          HTR(I)=2.50000
000054          CTR(I)=2.50000
C                    PRINT RESULTS
000056          PRINT 3,TEMP(I),STR(I),GTR(I),HTR(I),CTR(I)
000100        3 FORMAT(5E12.5)
000100          IF(TEMP(I).EQ.298.16)RETURN
C                    CHANGE TEMPERATURE AND BEGIN CALCULATIONS AGAIN
000104          I=I+1
000106          TEMP(I)=TEMP(I-1)+100.0
000111          IF(TEMP(I).EQ.1100.)GO TO 4
C                    A CHECK POINT TO MAKE CERTAIN THINGS DO NOT GET OUT OF
C                    HAND -- IF TEMP GOES ABOVE 1100., THESE CALCULATIONS
C                    WILL BE TERMINATED
000114          IF(TEMP(I).GT.1100.)RETURN
000117          GO TO 5
000120        4 TEMP(I)=298.16
000123          GO TO 5
000123          END
```

```
                SUBROUTINE ROT
000002          COMMON STR(11), GTR(11),HTR(11),CTR(11),SRO(11),GRO(11),HRO(11),
               1CRO(11),SVIBT(11),GVIBT(11),HVIBT(11),CVIBT(11),TEMP(11),
               2SRI(11),GRI(11),HRI(11),CRI(11),
               3STOT(11),GTOT(11),HTOT(11),CTOT(11)
      C
      C                 CALCULATIONS ARE BASED ON RIGID ROTOR APPROXIMATION
      C
      C                  0                 0  0                  0  0                  0
      C        SRO = S /R,  GRO = -(G -H )/RT,  HRO = (H -H )/RT,  CRO = C /R
      C                                    0                    0
      C
      C                 READ DATA
000002                READ 11,SIGMA,AI,BI,CI
000016           11   FORMAT(4E12.5)
000016                PRINT 19
000022           19   FORMAT(1H1,2X,53HROTATIONAL CONTRIBUTIONS TO THERMODYNAMIC QUANTIT
               1IES ,//)
      C                 PRINT OUT LABELLED INPUT DATA, CHECK
000022                PRINT 12,SIGMA,AI,BI,CI
000036           12   FORMAT(3X,15HINPUT   SIGMA =,E12.5,3X,9HAI,BI,CI=,3E12.5,//)
000036                PRINT 18
000042           18   FORMAT(3X,4HTEMP,8X,7HENTROPY,6X,8HFREE EN.,3X,8HENTHALPY,3X,10HHT
               1AT CAPAC,/)
      C                 BEGIN CALCULATIONS
000042                SIG=ALOG(SIGMA)
000044                XLNMNT=0.50000*ALOG((AI*BI*CI)*(10.**117))
000055                I=1
000056                TEMP(I)=100.0
000061           15   SUMRO=XLNMNT+1.50000*ALOG(TEMP(I))-SIG
000070                SRO(I)=SUMRO-0.0166
000074                GRO(I)=SUMRO-1.5169
000076                HRO(I)=1.50000
000101                CRO(I)=1.50000
      C                 PRINT RESULTS
000102                PRINT 13,TEMP(I),SRO(I),GRO(I),HRO(I),CRO(I)
000125           13   FORMAT(5E12.5)
000125                IF(TEMP(I).EQ.298.16)RETURN
      C                 CHANGE TEMP AND BEGIN CALCULATIONS AGAIN
000131                I=I+1
000133                TEMP(I)=TEMP(I-1)+100.0
000136                IF(TEMP(I).EQ.1100.)GO TO 14
      C                 A CHECK POINT TO MAKE CERTAIN THINGS DO NOT GET OUT OF
      C                 HAND -- IF TEMP GOES ABOVE 1100., THESE CALCULATIONS
      C                 WILL BE TERMINATED
000141                IF(TEMP(I).GT.1100.)RETURN
000144                GO TO 15
000145           14   TEMP(I)=298.16
000150                GO TO 15
000150                END
```

```
            SUBROUTINE VIB
000002      COMMON STR(11), GTR(11),HTR(11),CTR(11),SRO(11),GRO(11),HRO(11),
           1CRO(11),SVIBT(11),GVIBT(11),HVIBT(11),CVIBT(11),TEMP(11),
           2SRI(11),GRI(11),HRI(11),CRI(11),
           3STOT(11),GTOT(11),HTOT(11),CTOT(11)
000002      DIMENSION W(99)
      C
      C                CALCULATIONS ARE BASED ON HARMONIC OSCIL. APPROX.
      C
      C                 0              0  0               0  0               0
      C       SVIB= S /R,  GVIB= -(G -H )/RT,  HVIB= (H -H )/RT,  CVIB= C /R
      C                              0                  0
      C                READ NUMBER OF FREQUENCIES
000002      READ30,NDATA
000010   30 FORMAT(I2)
000010      PRINT 33,NDATA
000016   33 FORMAT(1H1,2X,53HVIBRATIONAL CONTRIBUTIONS TO THERMODYNAMIC QUANTI
           1TIES//15X,22HNUMBER OF FREQUENCIES=,I2/)
      C                READ FREQUENCY
000016      READ 38,(W(J),J=1,NDATA)
000031   38 FORMAT(F8.2)
000031      DO 200 J=1,NDATA
000033      PRINT 133, W(J)
000041   133 FORMAT(10X,F8.2)
000041   200 CONTINUE
000044      PRINT 131
000047   131 FORMAT(1X/3X,4HTEMP,9X,7HENTROPY,5X,8HFREE EN.,5X,9HENTHALPY,3X,
           111HHEAT CAPAC./)
000047      I=1
000050      TEMP(I)=100.0
      C                INITIALIZE TOTAL CONTRIBUTIONS
000053   35 SVIBT(I)=0.0
000055      GVIBT(I)=0.0
000057      HVIBT(I)=0.0
000060      CVIBT(I)=0.0
      C                CALCULATE CONTRIBUTIONS FROM EACH FREQUENCY
000062      DO 100 J=1,NDATA
000063      U=1.4837*(W(J)/TEMP(I))
000067      XP=EXP(-U)
000072      RXP = 1.0/XP
000074      XLN = ALOG(1.0-XP)
000100      GVIB = -(XLN)
000101      HVIB = (U*XP)/(1.0-XP)
000105      SVIB = (U/((1.0/XP)-1.0))-XLN
000110      CVIB = (U*U*(RXP))/(((RXP)-1.0)*((RXP)-1.0))
000115      SVIBT(I)=SVIBT(I)+SVIB
000120      GVIBT(I)=GVIBT(I)+GVIB
000123      HVIBT(I)=HVIBT(I)+HVIB
000126      CVIBT(I)=CVIBT(I)+CVIB
000131  100 CONTINUE
      C                PRINT TOTAL VIBRATIONAL CONTRIBUTIONS AT GIVEN TEMP
000134      PRINT 132,TEMP(I),SVIBT(I),GVIBT(I),HVIBT(I),CVIBT(I)
000157   132 FORMAT(5E12.5)
000157      IF(TEMP(I).EQ.298.16)GO TO 36
      C                INCREASE TEMP AND BEGIN CALCULATIONS AGAIN
000162      I=I+1
000163      TEMP(I)=TEMP(I-1)+100.0
```

```
000167          IF(TEMP(I).EQ.1100.)GO TO 34
      C                   A CHECK POINT TO MAKE CERTAIN TEMP DOES NOT EXCEED 1100.
000172          IF(TEMP(I).GT.1100.)GO TO 36
000175          GO TO 35
000175       34 TEMP(I)=298.16
000200          GO TO 35
000200       36 RETURN
000201          END
```

```
                SUBROUTINE  FRROT
000002          COMMON STR(11), GTR(11),HTR(11),CTR(11),SRO(11),GRO(11),HRO(11),
               1CRO(11),SVIBT(11),GVIBT(11),HVIBT(11),CVIBT(11),TEMP(11),
               2SRI(11),GRI(11),HRI(11),CRI(11),
               3STOT(11),GTOT(11),HTOT(11),CTOT(11)
      C
      C                  CALCULATIONS ARE BASED ON RIGID ROTOR APPROXIMATION
      C
      C                 0                 0  0                 0  0                  0
      C       SRI = S /R,  GRI = -(G -H )/RT,  HRI = (H -H )/RT,  CRI = C /R
      C                                  0                   0
      C
000002          I=1
000003          TEMP(I)=100.0
      C                 READ DATA
000006          READ41,AN,RI
000015       41 FORMAT(2E12.5)
      C                 PRINT OUT LABELLED INPUT DATA, CHECK
000015          PRINT 46, AN, RI
000025       46 FORMAT(1H1,2X,61HINTERNAL ROTATIONAL CONTRIBUTIONS TO THERMODYNAMI
               1C QUANTITIES//3X,5HINPUT,3X,3HAN=,E12.5,3X,3HRI=,E12.5//3X,4HTEMP,
               28X,7HENTROPY,6X,8HFREE EN.,3X,8HENTHALPY,3X,10HHEAT CAPAC,3X,9HPAR
               3TITION/)
      C                 BEGIN CALCULATIONS
000025       45 PART=(2.79350/AN)*SQRT(TEMP(I)*RI)*(10.**19)
000040          GRI(I)=ALOG(PART)
000045          SRI(I)=GRI(I)+0.50000
000050          HRI(I)=0.50000
000052          CRI(I)=0.50000
      C                 PRINT RESULTS
000053          PRINT 42, TEMP(I),SRI(I),GRI(I),HRI(I),CRI(I),PART
000100       42 FORMAT(6E12.5)
000100          IF(TEMP(I).EQ.298.16)RETURN
      C                 CHANGE TEMP AND BEGIN CALCULATIONS AGAIN
000104          I=I+1
000106          TEMP(I)=TEMP(I-1)+100.0
000111          IF(TEMP(I).EQ.1100.)GO TO 44
      C                 A CHECK TO MAKE CERTAIN TEMP DOES NOT EXCEED 1100.
000114          IF(TEMP(I).GT.1100.)RETURN
000117          GO TO 45
000120       44 TEMP(I)=298.16
000123          GO TO 45
000123          END
```

TRANSLATIONAL CONTRIBUTIONS TO THERMODYNAMIC QUANTITIES

INPUT MOLECULAR WEIGHT = 8.78700E+01 AMU

TEMP	ENTROPY	FREE EN.	ENTHALPY	HEAT CAP.
1.00000E+02	1.70616E+01	1.45512E+01	2.50000E+00	2.50000E+00
2.00000E+02	1.87945E+01	1.52941E+01	2.50000E+00	2.50000E+00
3.00000E+02	1.98081E+01	1.73077E+01	2.50000E+00	2.50000E+00
4.00000E+02	2.05273E+01	1.80269E+01	2.50000E+00	2.50000E+00
5.00000E+02	2.10852E+01	1.85848E+01	2.50000E+00	2.50000E+00
6.00000E+02	2.15410E+01	1.90406E+01	2.50000E+00	2.50000E+00
7.00000E+02	2.19264E+01	1.94260E+01	2.50000E+00	2.50000E+00
8.00000E+02	2.22602E+01	1.97598E+01	2.50000E+00	2.50000E+00
9.00000E+02	2.25547E+01	2.00543E+01	2.50000E+00	2.50000E+00
1.00000E+03	2.28181E+01	2.03177E+01	2.50000E+00	2.50000E+00
2.98160E+02	1.97928E+01	1.72924E+01	2.50000E+00	2.50000E+00

ROTATIONAL CONTRIBUTIONS TO THERMODYNAMIC QUANTITIES

INPUT SIGMA = 1.00000E+00 AI,BI,CI= 8.49000E-39 5.44000E-38 6.23000E-38

TEMP	ENTROPY	FREE EN.	ENTHALPY	HEAT CAPAC
1.00000E+02	1.20248E+01	1.05245E+01	1.50000E+00	1.50000E+00
2.00000E+02	1.30645E+01	1.15642E+01	1.50000E+00	1.50000E+00
3.00000E+02	1.36727E+01	1.21724E+01	1.50000E+00	1.50000E+00
4.00000E+02	1.41042E+01	1.26039E+01	1.50000E+00	1.50000E+00
5.00000E+02	1.44389E+01	1.29386E+01	1.50000E+00	1.50000E+00
6.00000E+02	1.47124E+01	1.32121E+01	1.50000E+00	1.50000E+00
7.00000E+02	1.49436E+01	1.34433E+01	1.50000E+00	1.50000E+00
8.00000E+02	1.51439E+01	1.36436E+01	1.50000E+00	1.50000E+00
9.00000E+02	1.53206E+01	1.38203E+01	1.50000E+00	1.50000E+00
1.00000E+03	1.54786E+01	1.39783E+01	1.50000E+00	1.50000E+00
2.98160E+02	1.36635E+01	1.21632E+01	1.50000E+00	1.50000E+00

VIBRATIONAL CONTRIBUTIONS TO THERMODYNAMIC QUANTITIES

NUMBER OF FREQUENCIES=20

3014.30
3014.30
2938.60
2228.00
1437.00
1437.00
1378.00
1382.40
1330.40
1022.00
1022.00
1019.50
782.00
665.50
499.00
405.70
405.70
371.00
371.00
307.40

TEMP	ENTROPY	FREE EN.	ENTHALPY	HEAT CAPAC.
1.00000E+02	1.51827E-01	2.41999E-02	1.27527E-01	6.97517E-01
2.00000E+02	1.48501E+00	3.77727E-01	1.10729E+00	7.43223E+00
3.00000E+02	3.37350E+00	1.05554E+00	2.31736E+00	9.91623E+00
4.00000E+02	5.36526E+00	1.88367E+00	3.48250E+00	1.09103E+01
5.00000E+02	7.37926E+00	2.77838E+00	4.59089E+00	1.17237E+01
6.00000E+02	9.24036E+00	3.69915E+00	5.54221E+00	1.11331E+01
7.00000E+02	1.10498E+01	4.62022E+00	6.42856E+00	1.23173E+01
8.00000E+02	1.27596E+01	5.53173E+00	7.22785E+00	1.32993E+01
9.00000E+02	1.43752E+01	6.42544E+00	7.94972E+00	1.41263E+01
1.00000E+03	1.59007E+01	7.29741E+00	8.60337E+00	1.48264E+01
2.98160E+02	3.33723E+00	1.04135E+00	2.29588E+00	5.97514E+00

INTERNAL ROTATIONAL CONTRIBUTIONS TO THERMODYNAMIC QUANTITIES

INPUT AN= 5.00000E+00 RI= 5.09000E-40

TEMP	ENTROPY	FREE EN.	ENTHALPY	HEAT CAPAC	PARTITION
1.00000E+02	5.49175E-01	4.91747E-02	5.00000E-01	5.00000E-01	1.05040E+00
2.00000E+02	8.95748E-01	3.95748E-01	5.00000E-01	5.00000E-01	1.48550E+00
3.00000E+02	1.09848E+00	5.98481E-01	5.00000E-01	5.00000E-01	1.81935E+00
4.00000E+02	1.24232E+00	7.42322E-01	5.00000E-01	5.00000E-01	2.10081E+00
5.00000E+02	1.35389E+00	8.53894E-01	5.00000E-01	5.00000E-01	2.34877E+00
6.00000E+02	1.44505E+00	9.45054E-01	5.00000E-01	5.00000E-01	2.57295E+00
7.00000E+02	1.52213E+00	1.02213E+00	5.00000E-01	5.00000E-01	2.77911E+00
8.00000E+02	1.58890E+00	1.08890E+00	5.00000E-01	5.00000E-01	2.97099E+00
9.00000E+02	1.64779E+00	1.14779E+00	5.00000E-01	5.00000E-01	3.15121E+00
1.00000E+03	1.70047E+00	1.20047E+00	5.00000E-01	5.00000E-01	3.32167E+00
2.98160E+02	1.09540E+00	5.95405E-01	5.00000E-01	5.00000E-01	1.81376E+00

TOTAL CONTRIBUTIONS TO THERMODYNAMIC QUANTITIES

TEMP	ENTROPY	FREE EN.	ENTHALPY	HEAT CAP.
1.00000E+02	2.97874E+01	2.51591E+01	4.62763E+00	5.18751E+00
2.00000E+02	3.42397E+01	2.96317E+01	5.60723E+00	[illegible]
3.00000E+02	3.79528E+01	3.11341E+01	6.81795E+00	1.04153E+01
4.00000E+02	4.12401E+01	3.32568E+01	7.98259E+00	1.24811E+01
5.00000E+02	4.42173E+01	3.51557E+01	9.06098E+00	1.42124E+01
6.00000E+02	4.69388E+01	3.68959E+01	1.00422E+01	1.56391E+01
7.00000E+02	4.94409E+01	3.85117E+01	1.09285E+01	1.68173E+01
8.00000E+02	5.17526E+01	4.00241E+01	1.17278E+01	1.77998E+01
9.00000E+02	5.38982E+01	4.14478E+01	1.24497E+01	1.86263E+01
1.00000E+03	5.58970E+01	4.27939E+01	1.31033E+01	1.93264E+01
2.98160E+02	3.78889E+01	3.10923E+01	6.79588E+00	1.03751E+01

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  08/28/70 SCOPE 3.2 - VER 4.01 LEHIGH U. 08/27/70
09.33.44.UREED3B
09.33.44.UREED01,A2163,CM45000,P1,T10,*REED*,URUN
09.33.44..
09.33.45.RUN(S)
09.33.49.SETCORE.
09.33.49.LGO.
09.33.52.EXIT
09.33.52.EXECUTION COST OF THIS JOB $      0.56
09.33.52.AUTHORIZED BALANCE IS  $    23.18
09.33.52.JULIAN DATE OF AUTHORIZATION EXPIRATION IS  70365.
09.33.52.PRIORITY SYSTEM RESOURCE UNITS      4.11
09.33.52.CP   002.310 SEC.
09.33.52.PP   005.208 SEC.
       09.35.56.    UREED3B 000737 LINES PRINTED  /// END OF LIST ///   LP  22
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VITA

Paul Robert Reed, Jr. was born on April 21, 1944, in Bellefonte, Pennsylvania, the son of Mr. and Mrs. Paul Robert Reed. He was graduated from Upper Darby High School, Upper Darby, Pennsylvania, in June, 1962.

In September, 1962, Mr. Reed entered Ursinus College, Collegeville, Pennsylvania, as a Wilkinson Scholar. He received a Bachelor of Science in Chemistry from this institution in June, 1966. During the Summer of 1966, Mr. Reed was employed as a chemist in the research laboratory of Sun Oil Company, Marcus Hook, Pennsylvania.

In September, 1966, Mr. Reed entered Lehigh University, as a graduate teaching assistant. Two years later he received a National Defense Educational Act Title IV Fellowship which he held until August, 1970.

Mr. Reed is co-author of the following:

(1) A paper entitled "The Vibrational Spectrum of Sulfuryl Bromide Fluoride," presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March, 1968;

(2) An article entitled "Vibrational Spectrum of Sulfuryl Bromide Fluoride," published in Spectrochimica Acta, Volume 24A, pages 1795 to 1801, 1968;

(3) An article entitled "The Vibrational Spectra of Methyl Boron Difluoride and Methyl-d_3 Boron Difluoride," published in Spectrochimica Acta, Volume 26A, pages 1087 to 1095, 1970;

(4) A paper entitled "Propynyl Boron Difluoride: It's Synthesis and Infrared Spectrum," presented at the 25th Symposium on Molecular Spectroscopy and Structure, The Ohio State University, Columbus, Ohio, September, 1970;

(5) A communication entitled "The Raman Spectrum of Gaseous Methyl Boron Difluoride," which appeared in the Raman Newsletter, January, 1970.

Mr. Reed is a member of the American Chemical Society and an associate member of the Society of the Sigma Xi. He is married to the former Jane Thomas Helinek of Spring Mount, Pennsylvania.