A VIBRATIONAL STUDY OF SOME TRIHALOBOROXINES

By

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INTRODUCTION

The Problem

Vibrational analysis is a fundamental means of investigating the nature of the forces which govern the vibrational motions of molecules. The electronic energy of the system of nuclei and electrons of a molecule is dependent upon the nuclear coordinates, and is a minimum at the equilibrium position of the molecule. Displacement of a nucleus from equilibrium produces a corresponding increase in electronic energy (potential energy of the nuclei of the molecule) which is accompanied by a force tending to restore the nucleus to its equilibrium position. Such forces are best described in terms of chemical bonds and repulsive or attractive interactions between nonbonded atoms of molecules. The characterization of these forces yields valuable information concerning bonding and other interatomic interactions of molecules.

The primary purpose of this investigation was to perform a vibrational analysis of the planar vibrational modes of the fluorine-chlorine derivatives of the inorganic ring compound, boroxine.

The fluorine-chlorine derivatives of boroxine were chosen for this investigation because they form a series of structurally related compounds and because relatively little vibrational spectroscopic work has been done with compounds of this type. Boroxine, $(BOH)_3$, is a six-membered ring of alternating boron and oxygen atoms with a hydrogen atom bonded to each boron atom. The series of fluorine-chlorine boroxines consists of trifluoroboroxine, $(BOF)_3$; trichloroboroxine, $(BOCl)_3$, and the two mixed haloboroxines, $B_3O_3ClF_2$ and $B_3O_3Cl_2F$.

The experimental phase of this study involved preparing the trihaloboroxines and recording their infrared spectra. Common infrared sampling techniques were not adequate for studying these molecules because the trihaloboroxines are not stable when isolated at room temperature. However, they can be kinetically stabilized at low temperatures. Thus, a low temperature infrared cell was assembled for preparing and obtaining the spectra of the compounds.

The infrared data, together with some Raman data from the literature, was then applied to an overlay Urey-Bradley vibrational analysis of the trihaloboroxines.

During the course of this investigation the spectrum of boron trichloride was re-examined and, surprisingly, certain features of the reported spectrum of BCl_3 have been identified with trichloroboroxine. Several assignments of the BCl_3 spectrum were subsequently changed and these results have been incorporated into this study.

Normal Modes of Vibration

A molecule with N atoms has 3N degrees of freedom associated with its momentum coordinates. Three degrees of freedom are associated with the translation of the molecule as a whole, and, for non-linear molecules, three more are associated with rotation of the molecule. For linear molecules there are only two degrees of rotational freedom. The remaining 3N-6 or 3N-5 degrees of freedom correspond to vibrations of the molecule.

The vibrational motion of a polyatomic molecule is apparently disorderly; but the displacements of the nuclei from their equilibrium positions are the sum of the displacements due to special vibrations which are known as the normal modes of vibration of the molecule. In a normal mode the nuclei of a molecule move simultaneously subject to two conditions. Each nucleus will move with the same frequency about its equilibrium position and with the same phase factor. That is, the nuclei pass through the equilibrium configuration of the molecule simultaneously. There are as many normal modes of vibration as there are vibrational degrees of freedom, and the frequencies of the normal modes are the normal or fundamental frequencies of a molecule. In some molecules two or more normal modes will vibrate with exactly the same frequency; these are degenerate vibrational modes. Degenerate vibrations need not satisfy the second requirement of a normal mode.

The discussion of the normal modes of a molecule is aided by the introduction of a system of normal coordinates. Definition of normal coordinates is simplified by first defining a system of 3N mass-weighted cartesian displacement coordinates q_i^* by the set of equations

$$q_i^* = \sqrt{m_j}\,\Delta x_i \qquad \begin{matrix} j = 1,\ 2,\ \ldots,\ N \\ i = 1,\ 2,\ \ldots,\ 3N \end{matrix} \qquad [1]$$

where m_j is the mass of the jth atom and Δx_i is one of the three cartesian displacement coordinates of the jth atom. The normal coordinates Q_k may then be defined by the linear equations

$$Q_k = \sum_{i=1}^{3N} l_{ki} q_i^* \qquad k = 1,\ 2,\ \ldots,\ 3N \qquad [2]$$

where the coefficients l_{ki} are chosen so that in terms of the new coordinates the kinetic and potential energies, T and V respectively, have the forms

$$2T = \sum_{k=1}^{3N} \dot{Q}_k^2 \qquad 2V = \sum_{k=1}^{3N} \lambda_k Q_k^2 \qquad [3]$$

where $\dot{Q}_k$ is the time derivative of Q_k and the λ_k are directly related to the vibrational frequencies ν_k of the normal modes by

$$\lambda_k = 4\pi^2\nu_k^2 \ . \qquad [4]$$

Each of the normal coordinates is associated with a normal mode of a molecule. There are 3N normal coordinates since translational and rotational modes may be considered as normal modes with zero frequency. Vibrational or normal coordinate analysis allows one to deduce the normal coordinates of a molecule.

Potential Fields

Nakamoto (1) has pointed out that one of the fundamental problems in vibrational analysis is the selection of a suitable potential field which represents the interatomic forces in a molecule. The potential energy V of a molecule may be expressed as a power series in some set of 3N-6 independent internal coordinates R_t (i.e., coordinates which describe the internal configuration of the molecule without regard for its position as a whole in space)

$$2V = 2V_e + 2\Sigma \left(\frac{\partial V}{\partial R_t}\right)_{V_e} R_t + \Sigma\Sigma \left(\frac{\partial^2 V}{\partial R_t \partial R_{t'}}\right)_{V_e} R_t R_{t'} + \ldots \quad [5]$$

where V_e, the potential energy of the molecule in the equilibrium configuration, is arbitrarily set equal to zero. The R_t are assumed to be displacement coordinates, that is, the $R_t = 0$ in the equilibrium configuration. For a set of independent coordinates the potential energy is a minimum with respect to each coordinate at $V = V_e$, and all of the first order terms of the expansion vanish since $\left(\frac{\partial V}{\partial R_t}\right)_{V_e} = 0$. In practice cubic and higher terms are often dropped and in the resulting expression the potential energy is expressed as a sum of quadratic terms

$$2V = \Sigma\Sigma \left(\frac{\partial^2 V}{\partial R_t \partial R_{t'}}\right)_{V_e} R_t R_{t'} = \Sigma\Sigma f_{tt'} R_t R_{t'} \quad [6]$$

where the coefficients $f_{tt'}$ are the force constants for this particular potential function. The expression of the potential energy in the form of equation [6] implies harmonic motion, and although the motion of molecules is not harmonic, this approximation is sufficient for most purposes.

The determination of the force constants of a molecule is a key step toward understanding the nature of the bonding and the vibrational properties of the molecule. Attempts have been made to determine the force constants of simple molecules without a prior knowledge of the vibrational frequencies of the molecules. For example, Pohl, Rein and Appel (2) have calculated force constants for the hydrogen halides from the results of a simplified molecular orbital treatment of the molecules. In principle the vibrational frequencies of a molecule can be calculated if the force constants and geometry of the molecule are known. In practice the reverse is usually done; that is, the vibrational frequencies which can be measured by infrared and Raman spectroscopy are used to calculate the force constants and to determine the normal coordinates of a molecule. A detailed discussion of this procedure will not be given here, but the method of analysis used in this study of the haloboroxines is discussed in the Appendix.

Equation [6] expresses the potential energy in terms of the general valence force field where force constants are included for all cross terms ($t \neq t'$) between the internal coordinates. The general valence force field is satisfactory for simple molecules, but the large number of general valence force constants necessary for complex molecules prohibits the use of this force field. In order to determine the force constants of a molecule from spectroscopic data alone, there must be at least as many observed vibrational frequencies as there are force constants to evaluate. One technique for getting more data is to use the frequencies of isotopic molecules and to assume that isotopic substitution has no effect on the force constants. This technique is very effective in cases where the isotopes of hydrogen can be used, but it is less effective when isotopes of heavier atoms are involved.

The apparent necessity of simplifying the potential functions for complex molecules has led to the introduction of a number of approximate force fields which require fewer force constants than the general valence force field (3). One of the simplest approximations which has been used to reduce the number of independent force constants is the central force field. Under this approximation it is assumed that the forces holding the atoms in their equilibrium positions act only along the lines joining pairs of atoms and that every pair of atoms is connected by such a force. This force field has not been very successful and is now seldom used. The simple valence force field, which considers those forces which resist the extension or compression of valence bonds together with those which oppose changes in the angles between bonds, is better than the central force approximation, but it, too, often gives only a rough approximation.

Modifications of the valence force field by the inclusion of intuitively selected cross terms have met with considerably more success in defining potential functions for complex molecules than the central force and simple valence force fields. Several other more refined approximate force fields have been introduced in an effort to overcome the deficiencies of the simpler models. The orbital valency force field is unique in that the bending force constants are expressed in terms of parameters describing changes in the overlap of atomic orbitals, and the hybrid orbital force field relates stretch-bend interaction constants to the corresponding stretching constant through a model which allows for changes in hybridization of orbitals during bending (4,5). Another force field which has been widely used in recent years and the one which was chosen for this study is the Urey-Bradley force field (UBFF) (6). This particular approximation was first used extensively by Shimanouchi (7) and has been applied successfully to a wide variety of molecules. The UBFF combines features of the central and valence force fields by expressing the potential energy of a molecule as a sum of terms involving bond stretching (K) and bending (H) force constants as well as force constants between nonbonded atoms (F). Thus the UBFF consists of three types of force constants, all of which have clear-cut physical meaning.

The potential function for a molecule can be expressed in terms of the basic UBFF by an expression such as

$$2V_{UB} = 2\sum_i K_i' r_i \Delta r_i + \sum_i K_i (\Delta r_i)^2 + 2\sum_j H_j' (\Delta \alpha_j) + \Sigma H_j (\Delta \alpha_j)^2 + 2\sum_k F_k' q_k \Delta q_k + \sum_k F_k (\Delta q_k)^2 \qquad [7]$$

where r_i is an equilibrium bond distance, α_j a bond angle, and q_k an equilibrium distance between non-bonded atoms. The linear terms were retained in this power series expansion because the Δr's, $\Delta\alpha$'s, and Δq's are not mutually independent. The inclusion of non-bonded interactions is an attempt to take into account the effect of van der Waals forces; therefore, interaction terms are included for only those pairs of non-bonded atoms for which these forces would appear appreciable. In general the non-bonded distances q_k may be related to the bond distances r_i and bond angles α_j by a straightforward geometrical relation from which the Δq's can be expressed in terms of the Δr's and $\Delta\alpha$'s. The Δq_k can then be eliminated from equation [7] after which the linear terms in the Δr_i and $\Delta\alpha_j$ can be set equal to zero using the equilibrium condition $\left(\frac{\partial V}{\partial r_i} = \frac{\partial V}{\partial \alpha_j} = 0\right)$. The resulting potential function contains four types of force constants -- K, H, F and F'. At this point it is common practice to set F' equal to -0.1 F. This is based on the assumption that the repulsive energy between non-bonded atoms is proportional to $1/r^9$. It has been pointed out that this practice is unwarranted, but that in any case F' is probably small compared to F (8,9). Therefore, this questionable practice is still widely adherred to, thus reducing still further the number of force constants which must be evaluated. As a result the number of Urey-Bradley force constants (UBFC) for complex molecules is, in general, much smaller than the number of general valence force constants.

Another advantage of the UBFF is the transferability of force constants from molecule to molecule. That is, force constants which have been evaluated for one molecule can, in many cases, be used to calculate the frequencies of structurally related molecules. The transferability of UBFC has been studied extensively by Overend and Scherer (10,11) and by Shimanouchi and his co-workers (12) and has been found useful in the study of a variety of molecular types.

Overlay Technique

As a result of the transferability of UBFC, a technique known as the overlay method has evolved into a very useful tool in the determination of force constants. The overlay method is applicable when the force constants of a series of structurally related molecules are to be determined. Force constants corresponding to similar structural features are assumed to be completely transferable from molecule to molecule in such a series. Under this assumption the observed vibrational frequencies of all molecules of the series can be used to simultaneously evaluate all UBFC for the series, but each transferable constant must be evaluated only once for the whole series, not for each molecule separately. For example, the master set of UBFC for the series, BF_3, BF_2Cl, $BFCl_2$, and BCl_3, might include only one B-F stretching constant, one Cl-B-Cl bending constant, etc. Thus, the overlay technique allows the evaluation of a set of force constants for a series of molecules in cases where there is insufficient data to evaluate the constants for each molecule separately.

As in any method, the success or failure of the technique is reflected in the accuracy with which the vibrational frequencies are reproduced when calculated from the overlay force constants.

By using the overlay method the force constant problem can frequently be over determined; that is, the available data will be in excess of the minimum necessary to fix the force constants. In this case the force constants are adjusted to give the best reproduction of the observed frequencies. Overend and co-workers (10) have programmed an overlay normal coordinate analysis method for a digital computer by which force constants are adjusted by a least squares iterative procedure. This method is discussed in the Appendix.

The utility of the overlay technique has been demonstrated for organic molecules, and should be of equal value for inorganic molecular series provided series members have sufficiently similar structure (13,14). The halogen derivatives of boroxine should meet this requirement; and since the data obtained in this investigation was insufficient to evaluate the UBFC of the trihaloboroxines separately, the use of overlay calculations was a necessity. Thus, this investigation should give an indication of the applicability of the overlay technique to the normal coordinate analysis of inorganic molecules.

CHAPTER II

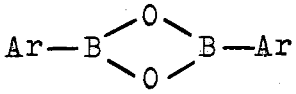
THE BOROXINES

The boroxines, which are characterized by a six membered ring of boron and oxygen atoms, make up an interesting series of compounds for which relatively little vibrational spectroscopic data is available. Because many of the organic derivatives of boroxine are considerably more stable at ambient temperatures than inorganic derivatives, they have received relatively more attention than the less stable inorganic compounds.

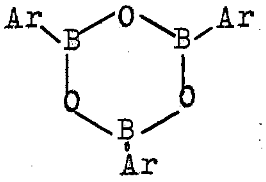
Michaelis and Becker (15) probably prepared the first organic boroxine when they made phenylboronic anhydride or triphenylboroxine, $(C_6H_5BO)_3$, by heating phenylboronic acid. A large number of boronic anhydrides have since been prepared by dehydration of the corresponding acids,

$$3RB(OH)_2 \longrightarrow (RBO)_3 + 3H_2O.$$

Molecular weight measurements of a number of arylboronic anhydrides by Kinney and Pontz (16) gave the first clues regarding the structures of the boroxines. These measurements showed them to have molecular weights corresponding to 2 or 3 times the equivalent weights. It was suggested that the anhydrides were mixtures of



and



Later the trimeric nature of the alkylboronic anhydrides was confirmed also by determination of their molecular weights.

In 1941 Bauer and Beach (17) performed an electron diffraction study of trimethylboroxine. Their results were concordant with a six-membered ring of alternating boron and oxygen atoms with the methyl groups bonded to the boron atoms. The study also indicated that all of the atoms except hydrogen were in a plane. Bond distances and bond angles were determined as follows:

B-C bond length = 1.57 ± 0.03A
B-O bond length = 1.39 ± 0.02A
BOB angle = 112 ± 4°

The cyclic structure of the inorganic boroxines was probably first proposed by Baumgarten and Bruns (18,19). They reported the formation of a supposed boron oxyfluoride $(BOF)_3$ as a product of reaction of BF_3 with a number of oxides including B_2O_3 and SiO_2. They proposed a heterocyclic ring structure for the compound which previously had been given as an addition compound.

Goubeau and Keller (20) prepared a white solid by dissolving B_2O_3 in BCl_3 at 300°C under pressure and then cooling the solution a few degrees. Since the ratio $B_2O_3:BCl_3=1:1$ was the limiting value of the reactivity of both components, they assumed that an unstable compound $(BOCl)_3$ was formed.

Later these same workers reported the preparation of several cyclic compounds of the type $(BOX)_3$ where X = F, Cl, Br, NMe_2, Me, or OMe (21).

Much of the available spectroscopic data for boroxine compounds concerns the more stable organic derivatives of the parent compound (22-24). The limited spectroscopic data which have been reported for inorganic boroxines include the Raman spectrum of trichloroboroxine and the infrared spectrum of trifluoroboroxine. Goubeau and Keller (24) obtained the Raman spectrum of $(BOCl)_3$ from a 75% solution of B_2O_3 in BCl_3. They assigned five Raman lines as fundamental frequencies of the haloboroxine. Fisher, Lehmann and Shapiro (25) have reported the infrared spectrum of a solid film of trifluoroboroxine in the NaCl spectral region (650 to 4000 cm^{-1}). They recorded the infrared absorption frequencies of both isotopically normal and B^{10}-enriched (ca. 95% B^{10}) trifluoroboroxine, and assigned four fundamental frequencies for the compound. They also pointed out that the small isotopic shift of about 2 cm^{-1} for the doubly degenerate out-of-phase stretching mode of the three B-F groups confirms the ring structure. Any other reasonable structure would exhibit a much larger isotope effect.

Ultee (26) has reported the infrared spectrum of the gaseous B_2O_3-BF_3 system at about 225° in which he observed bands assignable to trifluoroboroxine. The spectra which were obtained were difficult to interpret because of the strong absorption bands of BF_3, but the results seemed to agree reasonably well with those of Fisher, et al.

The infrared spectrum of the parent boroxine, $(BOH)_3$, has been reported by Gupta and Porter (27) who recorded the spectrum of the compound in the solid state at liquid nitrogen temperature. They observed two bands in the B-H stretching region which they assigned to the symmetric and asymmetric B-H stretching modes. They interpreted the presence of the symmetric B-H band as indicative of the fact that the molecule is not planar. Later Wason and Porter (28) reported the spectrum of gaseous boroxine which they found could be maintained for a period up to 2 hours at room temperature at pressures between 1.0 and 2.0 torr in the presence of excess argon. Gaseous boroxine exhibited only one B-H stretching frequency suggesting planar structure, and indicating that distortion of molecular symmetry due to interactions in the solid phase was responsible for the second B-H stretching band reported by Gupta and Porter.

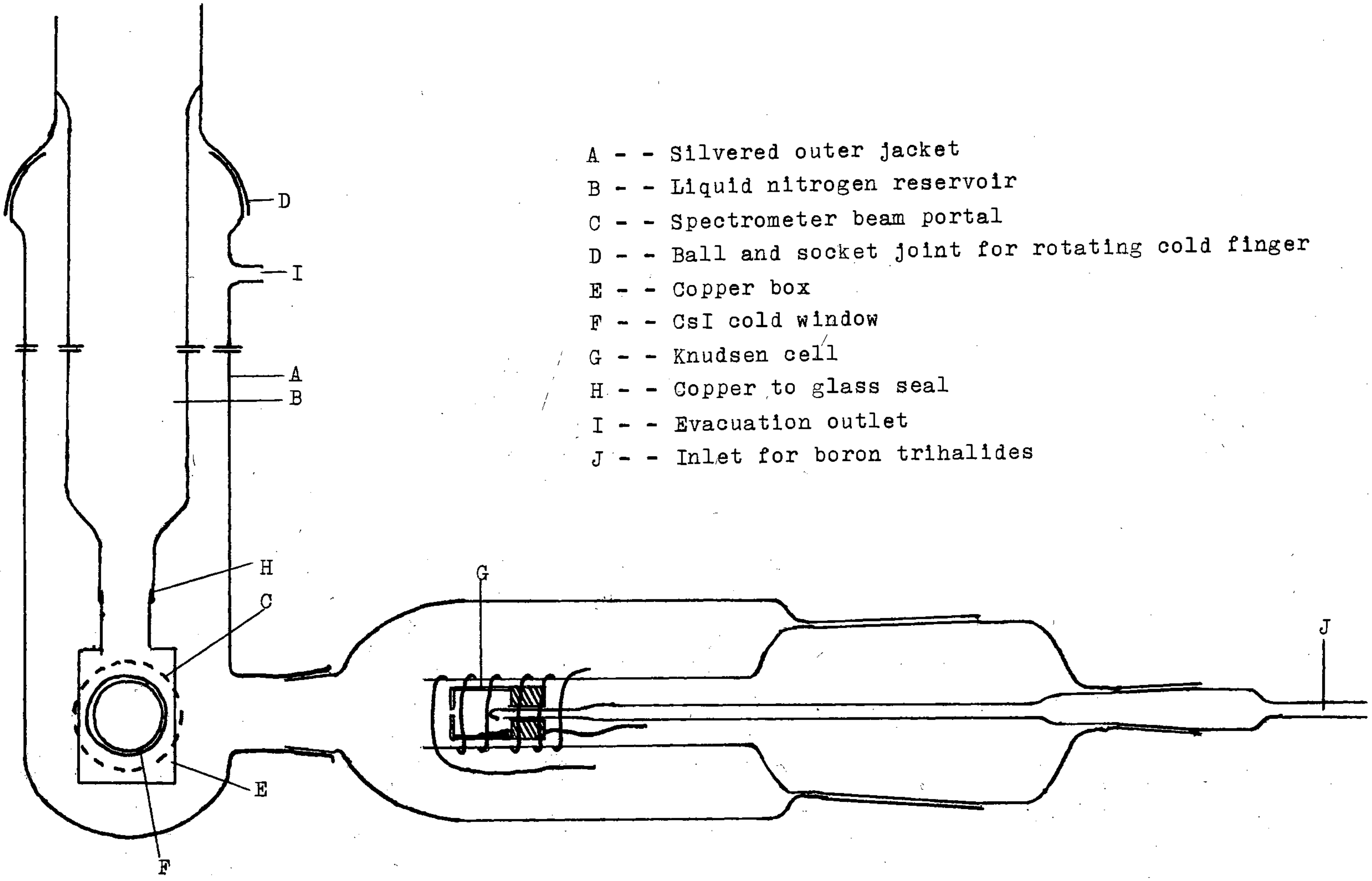
Thus, the planar cyclic structure of the boroxines seems to have been well established. The results of the present investigation should yield some conclusions regarding molecular geometry and should give some insight into the bonding of these compounds.

CHAPTER III

EXPERIMENTAL

As stated previously, the experimental phase of this study involved preparing the chlorofluoroboroxines and recording their infrared spectra. The experimental difficulties encountered in the work resulted primarily from the fact that the haloboroxines are not stable when isolated at room temperature. These species are the products of high temperature reactions, and Goubeau and Keller (21) reported that trifluoroboroxine is stable only above 250°. Trichloroboroxine seems to be somewhat more stable than the trifluoroderivative, but it, too, decomposes rapidly if isolated at room temperature. The preparation and infrared sampling methods used in this study resembled those of Fisher, Lehmann and Shapiro (25) who isolated trifluoroboroxine at liquid nitrogen temperature. They reported that trifluoroboroxine can be maintained at temperatures below -135°, at which temperature the rate of disproportionation becomes negligible.

The low temperature infrared cell used for obtaining the spectra of the haloboroxines was similar to one described by Schoen, Kuentzel and Broida (29). A diagram of the cell and the apparatus used for preparing the haloboroxines is shown in Figure 1. The low temperature cell was basically



A - - Silvered outer jacket
B - - Liquid nitrogen reservoir
C - - Spectrometer beam portal
D - - Ball and socket joint for rotating cold finger
E - - Copper box
F - - CsI cold window
G - - Knudsen cell
H - - Copper to glass seal
I - - Evacuation outlet
J - - Inlet for boron trihalides

Figure 1. Diagram of Low Temperature Infrared Cell and Trihaloboroxine Preparation Chamber

an evacuable glass Dewar which was designed for using liquid nitrogen as a coolant. The cell consisted of a silvered outer jacket A and an inner cold finger which included the liquid nitrogen reservoir B. The outer jacket contained three portals near the bottom of the cell. Polished cesium iodide windows were sealed to two of the portals C for transmission of the spectrometer beam through the evacuated cell. The third portal was simply a standard taper joint through which a sample could be introduced into the cell. The cell was designed so that the inner cold finger could be rotated around the vertical axis, even when the cell was evacuated, by means of a large ground glass joint D. Attached to the bottom of the cold finger was a copper box E which held a CsI window F on which samples were deposited for infrared investigation. This CsI window (cold window) was positioned in a one inch hole through the center of the copper box. The box was hollow so that liquid nitrogen could be circulated around the cold window and good thermal contact between the box and the window was achieved by packing indium between the window and the box. The temperature of the cold window was monitored by means of an iron-constantan thermocouple imbedded in the window.

The trihaloboroxines were prepared by the reaction

$$6BX_3 + 3SiO_2 \xrightarrow{\sim 500^{\circ}} 2(BOX)_3 + 3SiX_4.$$

Boron trifluoride and trichloride were obtained from the Matheson Company and purified by vacuum distillation. The purities of the boron trihalides were checked by recording their infrared spectra. After purification the appropriate boron trihalide was allowed to flow through a needle valve into the rear of a graphite Knudsen cell G (Figure 1) containing finely ground quartz. The rate of flow of the gas was estimated by means of a 1/16" variable area flowmeter with a sapphire float. The chamber in which the Knudsen cell was located was actually a part of the vacuum system of the low temperature cell. The Knudsen cell was positioned so that its 1 mm. exit orifice was directed toward the deposition port of the low temperature cell. The Knudsen cell was heated by a simple resistance heater consisting of about 18 turns of B and S No. 24 Chromel A wire wound around 25 mm Vycor tubing. During the flow of the boron trihalide into the reaction chamber, the Knudsen cell was maintained at about 500°, at which temperature the trihalide reacted with the ground quartz in the cell. The resulting reaction products, $(BOX)_3$, SiX_4 and unreacted BX_3, passed through the orifice of the Knudsen cell and impinged the cold CsI window of the low temperature cell. The temperature of the cold window was maintained such that the trihaloboroxine would condense but the boron trihalide and silicon tetrahalide could be removed by pumping. The temperature of the window was controlled by incremental additions of liquid nitrogen to the coolant reservoir of the cell. After deposition of a sample, the cold window was cooled to about -180° with liquid nitrogen and rotated 90° so that it was perpendicular to the radiation beam when positioned in the spectrometer. The spectrum was then recorded on the Beckman IR-7 spectrophotometer. The spectrum of each compound was recorded using both NaCl and CsI optics of the spectrometer so that the spectral region from 200 to 4000 cm^{-1} was investigated. Trifluoroboroxine and trichloroboroxine were prepared simply by reacting BF_3 and BCl_3, respectively, with the hot quartz. The mixed halogen boroxines could not be prepared separately. Mixtures of the trihaloboroxines, including the two mixed halogen compounds, were prepared by using mixtures of BF_3 and BCl_3 as the starting material. By varying the BF_3:BCl_3 ratio, bands of the spectra of the reaction products could be assigned to the proper mixed halogen boroxine. Typical conditions for preparing trifluoro-, trichloro- and the mixed halogen boroxines for spectral analysis are given in Table I.

TABLE I

TYPICAL DEPOSITION CONDITIONS FOR THE TRIHALOBOROXINES

	$(BOF)_3$		$(BOCl)_3$	Mixed Haloboroxines
	NaCl region	CsI region		
Estimated Rate of Flow of BX_3 moles/min.	$4x10^{-5}$	$4x10^{-5}$	$8x10^{-5}$	$2x10^{-5}$
Deposition Time, min.	8	50	60	50
Cold Window Temperature, °C	-145 to -150	-150 to -155	-90 to -95	-120 to -125
Knudsen Cell Temperature, °C	~500	~500	~500	~500

The spectra of both B^{10} enriched (ca. 96% B^{10}) and B^{11} enriched (ca. 90% B^{11}) trifluoroboroxine were recorded in addition to the spectrum of the compound containing boron in its natural isotopic abundance. The isotopically enriched trifluoroboroxine samples were prepared from enriched BF_3 which was obtained from Oak Ridge National Laboratory in the form of the complex $CaF_2 \cdot BF_3$. The BF_3 was released by heating the complex at 250-300°C. in a vacuum system and collecting the evolved BF_3 in a liquid nitrogen trap. The boron trifluoride was then purified by vacuum distillation and the purity was checked by recording the spectrum. In the spectra of both the B^{10} and B^{11} enriched samples of BF_3 there was one impurity band which could not be removed by distillation. This impurity band, at 1031 cm^{-1}, was probably due to SiF_4 which could have been formed by the reaction of the BF_3 with the hot pyrex container during the evolution of the gas.

The spectrum of B^{10} enriched trichloroboroxine was also recorded in addition to that of the natural compound. The B^{10} enriched boron trichloride used to make the $(B^{10}OCl)_3$ was prepared by heating B^{10} enriched boron trifluoride with $AlCl_3$ at 110° for about 20 hours (30). After several vacuum distillations the spectrum of the enriched BCl_3 still showed the presence of $B^{10}FCl_2$, but no further purification was attempted.

During the study of trichloroboroxine some interesting observations were made concerning boron trichloride as a result of the routine checks on the purity of the reactant gas. As stated previously the purity of each boron trihalide was checked by recording the spectrum of the gas and comparing it with reported spectra. The spectra of the gases were recorded in a 10 cm. gas cell at pressures varying from approximately 1 torr, for observation of the very strong bands, to about 175 torr.

Preliminary spectra of BCl_3 raised some questions concerning reported assignments of the compound so a more detailed study of the compound was made. In addition to the gas phase spectrum, the spectrum of a thin film of solid BCl_3 was recorded by depositing a sample on the cold window of the low temperature cell at liquid nitrogen temperature. An attempt was also made to check the BCl_3 for the presence of $(BOCl)_3$ by allowing the gas to impinge the cold window of the low temperature cell under conditions for the deposition of the boroxine compound. The resulting deposit was cooled to about -180° and the spectrum was recorded.

CHAPTER IV

INTERPRETATION OF SPECTRA

Planar trifluoro- and trichloroboroxine belong to symmetry point group D_{3h}. Each compound has 14 internal vibrations which are of the following symmetry species: $3A_1' + 2A_2' + 2A_2'' + 5E' + 2E''$. Of these the E' modes are both infrared and Raman active, the A_2'' modes are infrared active, the A_1' and E'' are Raman active, and the A_2' modes are inactive. Thus, there should be seven fundamental absorptions ($2A_2'' + 5E'$) in the infrared spectra of the isolated molecules. However, since sampling was in the solid state there was the possibility of splitting the degenerate modes and activation of certain inactive modes due to intermolecular interactions.

Trifluoroboroxine

Although data was obtained for both B^{10} and B^{11} enriched compounds, the assignments of the spectra will be discussed in terms of the B^{11} isotopic compounds. The infrared spectrum from thin films of trifluoroboroxine is presented in Figure 2 and Table II. The results of this work are in qualitative agreement with the assignments reported by Fisher, et al (25), for the four fundamental absorptions in the NaCl spectral region. The band centers of some of the broad bands were

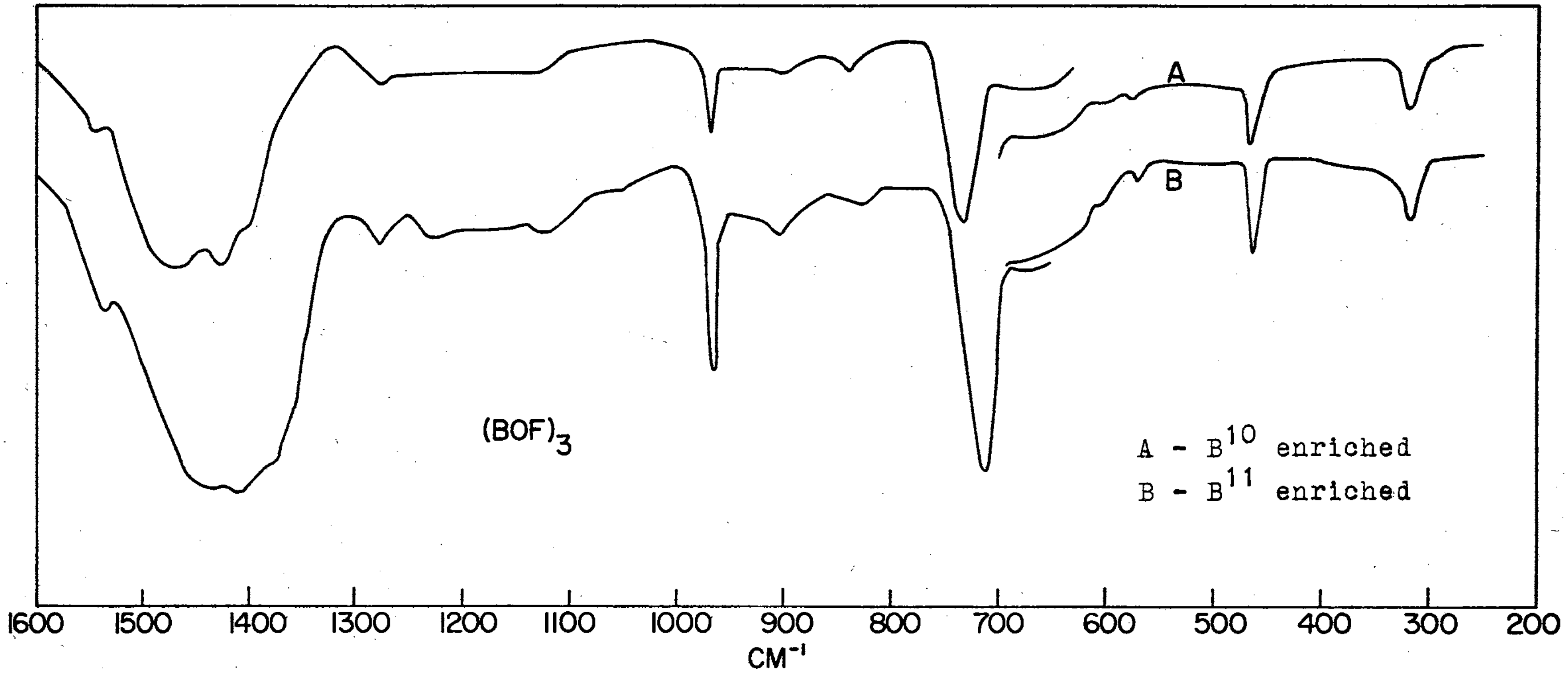


Figure 2. Infrared Spectrum of (BOF)$_3$

TABLE II

INFRARED SPECTRUM AND ASSIGNMENTS FOR $(BOF)_3$

$(B^{10}OF)_3$ cm^{-1}		$(B^{11}OF)_3$ cm^{-1}		Assignment
319	mw[1]	316	mw[1]	ν_{12}
465	mw, sp	462	mw, sp	ν_{11}
574	vw	570	vw	?
603	vw	601	vw	?
731	s, b	711	s, b	ν_6
838	w	826	vw, b	ν_2(?), $\nu_3+\nu_{12}$(?)
896	w, b	903	w, b	?
966	m, sp	964	m, sp	ν_{10}
1125	vw	1123	vw	$\nu_2 + \nu_{12}$ (?)
1275	w	1277	w	$\nu_{10} + \nu_{12}$
1403	m, sh	1373	ms, sh	ν_9
1422	ms, b	1400	ms, b	$\nu_{10} + \nu_{11}$
1468	s, vb	1436	s, vb	ν_8
1545	mw	1535	mw	$\nu_1 + \nu_{12}$(?)
1781	w	1776	w	$\nu_2 + \nu_{10}$(?)

---

[1] w = weak, m = medium, s = strong, v = very, sh = shoulder, b = broad, sp = sharp

very difficult to determine. In addition to the four fundamentals, several weak bands were observed in this region. Some of these bands were given combination assignments and one, occurring at 826 cm^{-1}, was assigned as the activated A_1' mode, ν_2.

The assignment of the bands in the region near 1400 cm^{-1} presented a special problem. The strong, broad absorption in this region could not be sufficiently resolved to determine accurately the centers of the separate bands. The contour of the absorption indicated that there were at least three strong overlapping bands in this region. From analogy with molecules of similar structure, such as mesitylene and trimethylboroxine, one would expect two fundamental absorptions in this part of the spectrum. These are the two doubly degenerate ring stretching modes, ν_8 and ν_9, which were assigned to absorptions at 1436 and 1373 cm^{-1}, respectively. A third component at about 1400 cm^{-1} was assigned as the combination, $\nu_{10} + \nu_{11}$, which is enhanced by Fermi resonance with the high frequency fundamental. Bands at 964 and 711 cm^{-1} were assigned as an E' out-of-phase B-F stretching mode, ν_{10}, and an A_2'' out-of-plane ring deformation mode, ν_6.

In addition to the four fundamentals previously reported, two bands occurring in the CsI spectral region were assigned as fundamental absorptions. A sharp band at 462 cm^{-1} was assigned as ν_{11}, which is an E' in-plane ring deformation. The other major feature of the CsI region, located at 316 cm^{-1}, was assigned as the B-F in-plane bending mode, ν_{12}. As is the case for some of the weak bands in the NaCl region, the very weak bands at 570 and 601 cm^{-1} could not be explained in the absence of Raman data. Only a single infrared active fundamental, the B-F out-of-plane wag, remains unassigned, and probably occurs below the lower limit of observation of this study.

As shown in Table IV, the assignments of the E' fundamentals for both $(B^{10}OF)_3$ and $(B^{11}OF)_3$ are complete. According to the Teller-Redlich product rule the ratio of the product of the frequencies of the E' modes for $(B^{10}OF)_3$ to the product of the E' frequencies for $(B^{11}OF)_3$ should be 1.076 (31). The observed frequency ratio is 1.064. This apparent discrepancy may be explained in part by the fact that even though B^{10} and B^{11} enriched compounds were used in the investigation, the presence of some B^{11} in the B^{10} enriched $(BOF)_3$ would tend to shift the apparent absorption frequencies to lower values and vice versa. Another possible contribution to the low frequency ratio is the effect of the Fermi resonance cited previously. If the $\nu_{10} + \nu_{11}$ band is in Fermi resonance with the high frequency fundamental, ν_8, as was suggested, then the effect should be stronger in $(B^{11}OF)_3$ and would, therefore, operate to diminish the frequency ratio.

Trichloroboroxine

The thin film infrared spectrum of $(BOCl)_3$ is presented in Figure 3 and Table III. Tentative assignment of the fundamental modes was made through analogy with $(BOF)_3$. However,

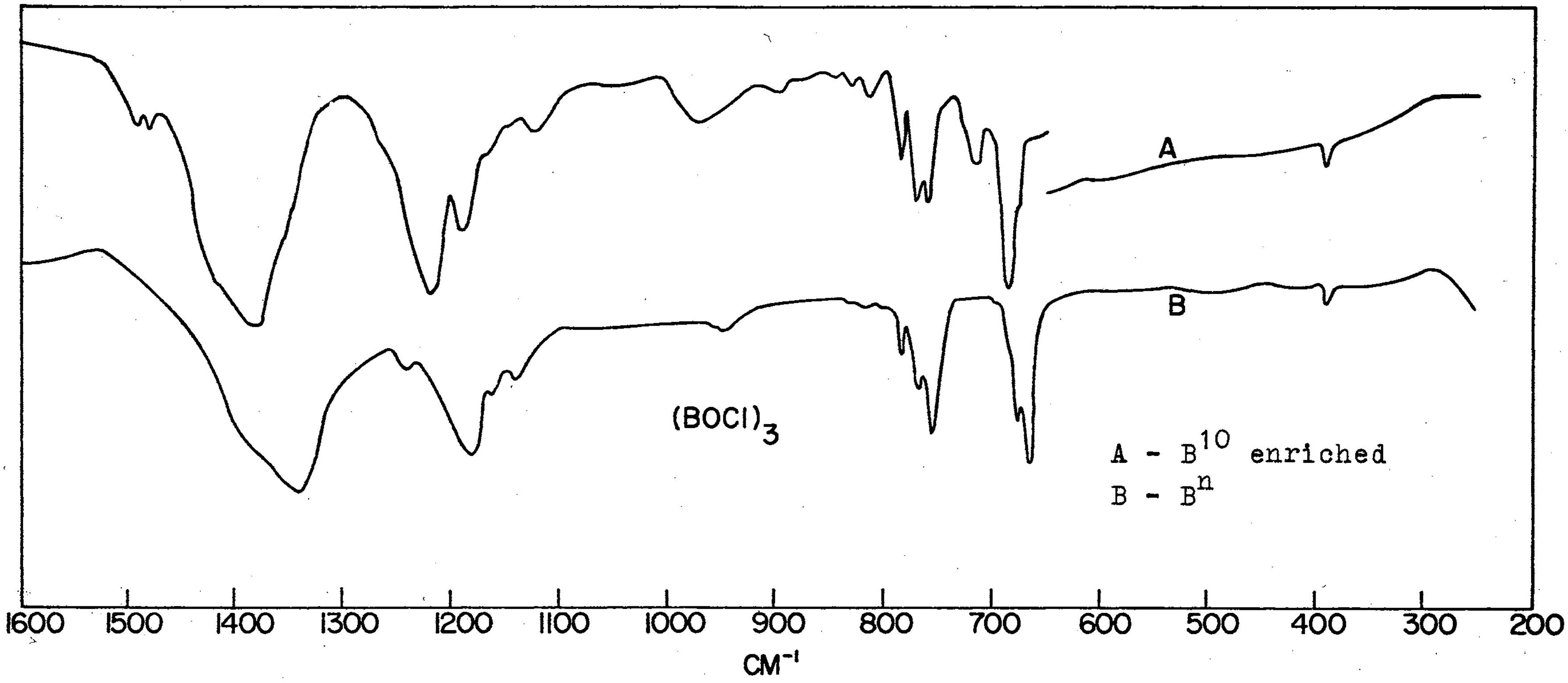


Figure 3. Infrared Spectrum of (BOCl)$_3$

TABLE III

INFRARED SPECTRUM AND ASSIGNMENTS FOR $(BOCl)_3$

cm^{-1}	$(B^{10}OCl)_3$	cm^{-1}	$(B^{11}OCl)_3$	Assignment
392	w[2]	390	w[2]	ν_{11}
		664	s	ν_6, B^{11}_3
		674	s	$\nu_6, B^{10}B^{11}_2$
675	w, sh	683	sh	$\nu_6, B^{10}_2B^{11}$
686	s			ν_6, B^{10}_3
716	m			?
		697	vw	$\nu_{11} + \nu_{13}$
760	m	755	s	ν_{10}
771	m	766	m	
786	m	782	mw	$2\nu_{11}$
815	mw			ν_2[3] (?)
830	w			$B^{10}_3O_3Cl_2F$
844	vw			?
897	w			?
975	mw, b	949	w	ν_3, BCl_3 $\nu_6 + \nu_{13}$
1125	w			?
1148	vw	1140	vw	$\nu_{10} + \nu_{11}$
1192	ms	1161	w	$\nu_1 + \nu_{12}$ $\nu_2 + \nu_{11}$
1220	s, b	1183	s, b	ν_9
		1241	w	?
1385	s, b	1345	s, b	ν_8
1414	m, sh	1390	m, sh	?
1481	w			$B^{10}_3O_3Cl_2F$
1493	w			?

---

[2] w, m, s = weak, medium, strong
v = very, sh = shoulder, b = broad.

[3] estimated as 820 from product rule

the $(BOCl)_3$ spectrum displayed features which had not been observed in the spectrum of the trifluoro- compound.

The assignment of bands at 1345, 1183, 760, and 390 cm^{-1} to the E$'$ fundamental modes, ν_8 through ν_{11}, was straightforward. Similarly the strong band at 664 cm^{-1} was readily assigned as the A_2'' ring puckering mode, ν_6. The other infrared active fundamentals, a chlorine in-plane rocking mode and a chlorine out-of-plane wagging mode were expected to have frequencies too low to be observed. However, the E$'$ rocking mode ν_{12} has been reported at 150 cm^{-1} in the Raman spectrum of $(BOCl)_3$ (24).

An interesting aspect of the trichloroboroxine spectrum was the observation of isotopic splitting for ν_6. Since the natural abundance ratio of boron isotopes, $B^{11}:B^{10} = 4:1$, the relative abundance of B_3^{11}, $B^{10}B_2^{11}$, $B_2^{10}B^{11}$, and B_3^{10} species of $(BOCl)_3$ prepared from natural BCl_3 should be approximately 64:48:12:1. The spectrum of $(BOCl)_3$ (Figure 3) containing boron in its natural isotopic abundance exhibits a strong band at 664 cm^{-1}, a slightly weaker band at 674 cm^{-1} and a weak shoulder at about 683 cm^{-1}. The positions and relative intensities of these bands is concordant with their assignment as ν_6 for $B_3^{11}O_3Cl_3$, $B^{10}B_2^{11}O_3Cl_3$, and $B_2^{10}B^{11}O_3Cl_3$, respectively. On the other hand, the spectrum of B^{10} enriched $(BOCl)_3$ exhibits a strong band at 686 cm^{-1} with a single shoulder at about 675 cm^{-1}. The $B^{11}:B^{10}$ ratio in the B^{10} enriched samples was approximately 1:24 so that the abundance ratio of the four isotopic species, from B_3^{11} to B_3^{10}, should be about 1:72:1728:13,824. Thus, the 686 cm^{-1} band was assigned as ν_6 for $B_3^{10}O_3Cl_3$ and the shoulder as ν_6 for $B_2^{10}B^{11}O_3Cl_3$. The apparent incongruity in the assignments of ν_6 for $B_2^{10}B^{11}O_3Cl_3$ from the spectra of natural and B^{10} enriched $(BOCl)_3$ can be explained by the fact that in both spectra the band occurs as a weak shoulder, but on opposite sides of strong bands. Thus it was not possible to observe the true position of this band, but its center probably occurs at about 680 cm^{-1}. Similar isotopic shifts undoubtedly produce splitting in ν_6 of $(BOF)_3$ which was not detected because of the greater bandwidth in the fluorine compound.

The region near ν_{10} also contains structure which has no counterpart in the spectrum of $(BOF)_3$. Here, however, the insensitivity of the intensities of the components to isotope ratios eliminated isotope shifts as the cause of the structure. The splitting of the pair of bands at 755 and 766 cm^{-1} was diminished, but not eliminated, in a matrix of BCl_3. Thus, these two components have been assigned to the E' mode, ν_{10}, split by a static field which must be less intense in a BCl_3 matrix than for the pure $(BOCl)_3$. The third band in this region, located at 782 cm^{-1}, was then assigned as the first overtone of ν_{11}. The intensity of the overtone band can be explained by Fermi resonance with ν_{10}.

Although the two fundamentals, ν_8 and ν_9, were too broad to allow the resolution of any crystal splitting, crystal effects undoubtedly contribute to the assymetry of these bands.

As noted previously, the Raman spectrum of $(BOCl)_3$ has been reported by Goubeau and Keller (24). These workers observed five Raman lines assignable as $(BOCl)_3$ fundamentals. They reported lines at 390 and 150 cm^{-1} which they assigned as ν_{11} and ν_{12}, the former of which was also observed in the infrared spectrum. The other three Raman lines, located at 1037, 807, and 333 cm^{-1} were assigned as the totally symmetric A_1' modes, ν_1, ν_2 and ν_3.

As shown in Table III some of the weaker bands have been given combinational assignments. Other weak bands which were observed in the spectrum of B^{10} enriched $(BOCl)_3$ have been assigned to $B_3O_3Cl_2F$. Since the BCl_3 used to prepare the enriched $(BOCl)_3$ was originally prepared from BF_3, small amounts of $B_3O_3Cl_2F$ could result from residual fluorine. In fact, as noted previously some $B^{10}FCl_2$ could be detected in the gas phase samples of the B^{10} enriched BCl_3.

Table IV lists the fundamental frequencies which have been observed for trifluoroboroxine and trichloroboroxine. There are a total of nine observed fundamentals for $(B^{11}OCl)_3$, eight of which are due to planar vibrations. For $(B^{11}OF)_3$ there are only six observed fundamental frequencies, not including ν_2 which is a questionable assignment. Thus, there are a total of 13 fundamental frequencies available for use in a normal coordinate analysis of the planar vibrational modes of the two symmetric trihaloboroxines. The difference in the masses of the B^{10} and B^{11} compounds is too small for the isotopic frequencies to be of any value in furnishing

TABLE IV

FUNDAMENTAL VIBRATIONS FOR THE HALOBOROXINES

D_{3h} Species	Number	Description[7]	$(B^{10}OF)_3$	$(B^{11}OF)_3$	$(B^{10}OCl)_3$	$(B^{11}OCl)_3$
A_1'	1	B-X stretch	-	-	-	1037[4]
	2	ring def.	838[6]	826[6]	815[6]	807[4]
	3	ring def.	-	-	-	333[4]
A_2''	6	ring pucker	731	711	686	664
	7	B-X o.p. bend	-	-	-	-
E'	8	ring stretch	1468	1436	1385	1345
	9	ring stretch	1403	1373	1220	1183
	10	B-X stretch	966	964	765	760
	11	ring def.	465	462	392	390
	12	B-X i.p. bend	319	316	151[5]	150[4]

---

[4] from Raman spectrum

[5] from product rule

[6] activated in solid state infrared

[7] i.p. = in-plane, o.p. = out-of-plane.

additional data for the normal coordinate calculations.

Mixed Halogen Boroxines

The mixed halogen boroxines, $B_3O_3ClF_2$ and $B_3O_3Cl_2F$, belong to symmetry point group C_{2v}. Since there will be no degenerate vibrational modes in these molecules, each molecule has 21 internal vibrations of the following symmetry species: $8A_1 + 2A_2 + 4B_1 + 7B_2$. All except the A_2 modes should be infrared active and all species should exhibit Raman activity. Thus, there should be 19 infrared active fundamentals in each of the mixed halogen molecules, 15 of which are due to planar (A_1 and B_2) vibrational modes.

Study of the mixed halogen boroxines was complicated by the fact that they could not be prepared and studied separately. The reactions of mixtures of BF_3 and BCl_3 with SiO_2 yields not only $B_3O_3ClF_2$ and $B_3O_3Cl_2F$, but $(BOF)_3$ and $(BOCl)_3$ are also possible products. Because of the instability of these boroxine derivatives, they could not be conveniently separated after preparation; therefore, the infrared spectra of the mixed halogen boroxines were enriched by the presence of several compounds. Bands were assigned to the proper mixed halogen molecule by varying the BF_3:BCl_3 ratio of the reactant gas, but detailed assignment was possible only in the light of the force constant calculations. Figures 4 and 5 show the results of two attempts to obtain the spectra of the mixed halogen compounds. Figure 4 is the spectrum of the product of a reaction for which the initial BF_3:BCl_3 ratio was

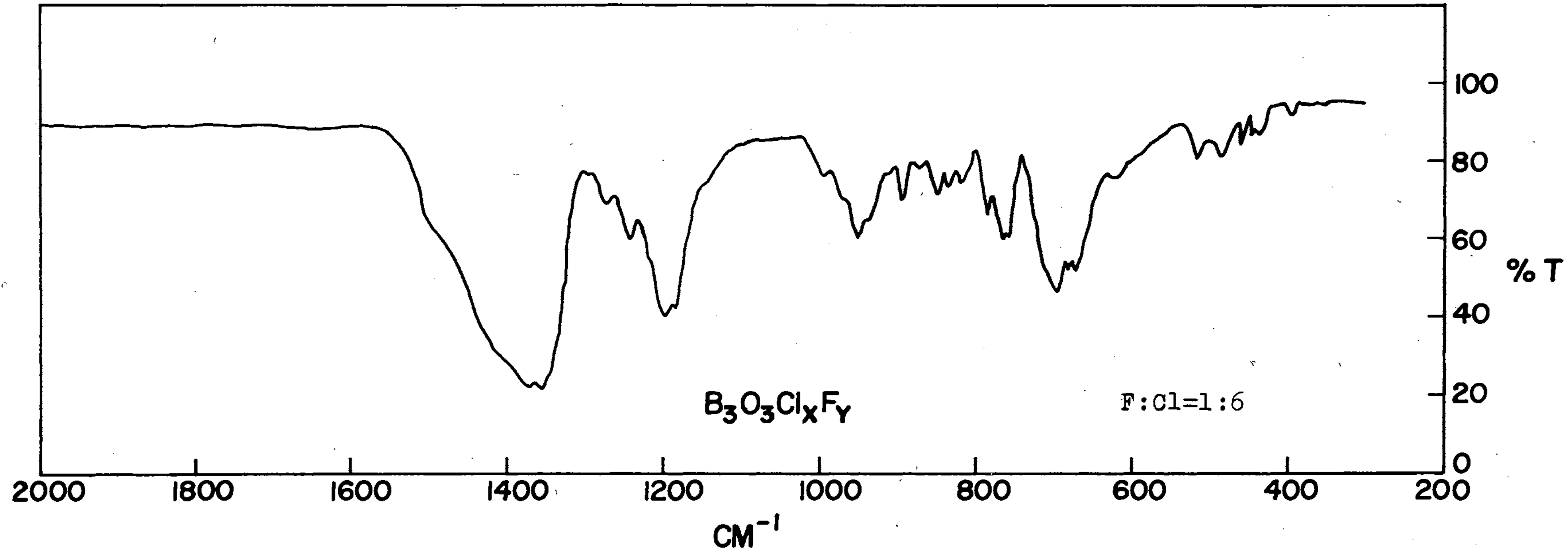


Figure 4. Infrared Spectrum of Mixed Halogen Boroxine for which the initial F:Cl ratio was about 1:6.

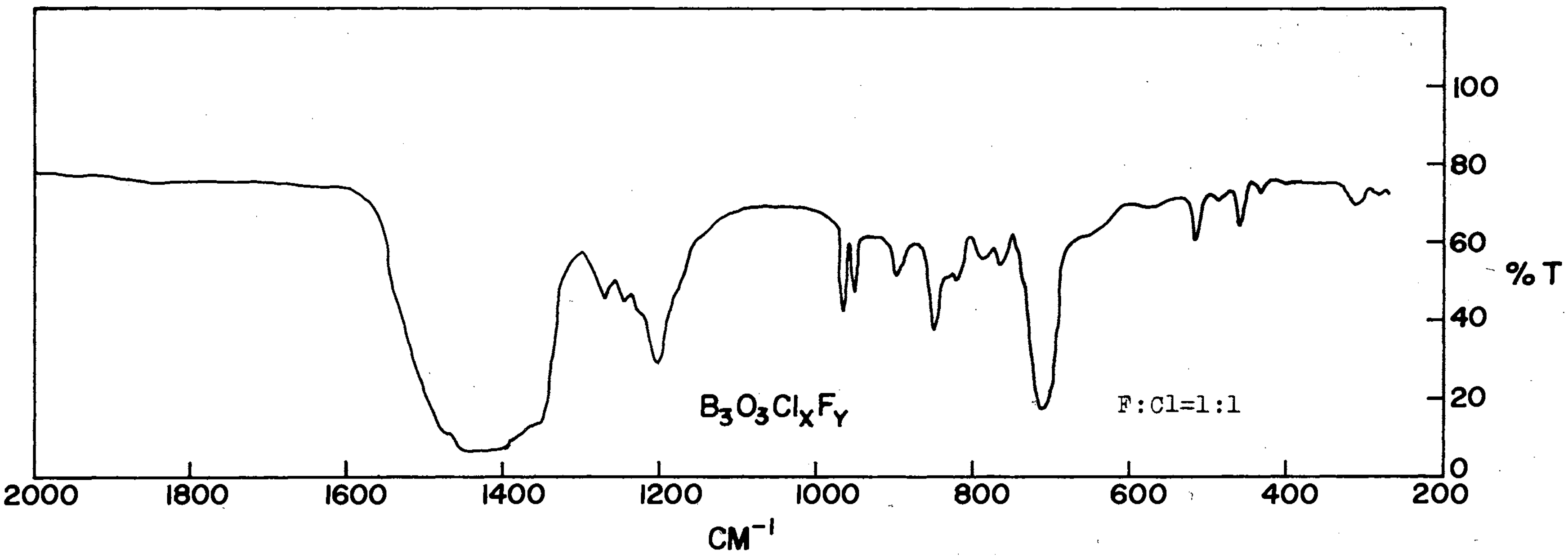


Figure 5. Infrared Spectrum of Mixed Halogen Boroxine for which the initial F:Cl ratio was about 1:1.

about 1:6; for Figure 5 the initial BF_3:BCl_3 ratio was about 1:1. Except for the qualitative discussion that follows, the specific assignments of the mixed halogen boroxines will not be considered until the results of the force constant calculations are discussed.

Since only planar modes were to be considered in the normal coordinate calculations of this study, it was necessary to attempt to determine which bands were due to planar vibrations and which were a result of out-of-plane vibrations. The symmetry species of the vibrations of the mixed haloboroxines may be considered to be derived from the trifluoro- and trichloro- derivatives in the following way:

$$\begin{tikzcd}
(BOX)_3 \arrow[r] & B_3O_3X_2Y \\
D_{3h} \arrow[r] & C_{2v} \\
3A_1' \arrow[r] & 3A_1 \\
2A_2' \arrow[r] & 2B_2 \\
5E' \arrow[r] \arrow[dr] & 5A_1 \\
 & 5B_2 \\
2A_2'' \arrow[r] & 2B_1 \\
2E'' \arrow[r] \arrow[dr] & 2A_2 \\
 & 2B_1
\end{tikzcd}$$

Each of the mixed boroxines has a total of 6 out-of-plane vibrational modes, $4B_1 + 2A_2$, but only the B_1 modes are allowed under infrared selection rules. As indicated above two of the B_1 vibrations may be considered to be derived from the two A_2'' modes of the symmetric boroxines. The A_2''

vibrations are infrared active, but only one of these modes has been assigned in each of the symmetric boroxines studied. The out-of-plane ring puckering mode has been assigned to a band occurring at 711 cm^{-1} in $(BOF)_3$ and at 664 cm^{-1} in $(BOCl)_3$. Thus, one of the B_1 bands in each of the mixed boroxines would be expected to occur in the region between these two extremes. Bands were observed in this region, but because of the overlapping of the bands, it was difficult to make exact assignments. The frequency of the ring puckering mode appeared to be about 700 cm^{-1} for $B_3O_3ClF_2$ and 675 cm^{-1} for $B_3O_3Cl_2F$. The frequency of the other B_1 mode "derived" from an A_2'' mode was probably below the lower limit of observation of this study since neither the B-F nor the B-Cl out-of-plane bending vibration was observed in the symmetric compounds.

The other pair of B_1 modes of each mixed boroxine is "derived" from the E" modes of the symmetric compounds. From analogy with mesitylene and trimethylboroxine one can conclude that one of the E" modes of the symmetric boroxines is probably well below 300 cm^{-1}, thereby indicating that one of the resulting B_1 modes of each of the mixed boroxines is below 300 cm^{-1}. A second E" mode is probably somewhat higher in frequency for the symmetrical trihaloboroxanes (597 cm^{-1} for $(BOCH_3)_3$); therefore, one of the B_1 modes of each of the mixed boroxines which is "derived" from an E" mode might lie in the range of infrared observation with CsI optics. It appears quite probable that not more than a total of four (two from each compound) of the infrared bands above 300 cm^{-1}

which are assignable to the two mixed haloboroxines are due to out-of-plane vibrations. Two of these modes have been assigned since their counterparts in the symmetric boroxines are also infrared active, but the other two which probably absorb in the CsI spectral region have not been definitely assigned.

Boron Trichloride

Boron trichloride has four fundamental vibrations, three of which are infrared active. Two of the fundamentals, ν_2 and ν_3, have been observed in the infrared spectrum, and assignments have been made for several overtone and combination bands (32-34). Anderson, Lassettre, and Yost (35) assigned a Raman line occurring at 253 cm^{-1} as ν_4 for liquid BCl_3. A gas phase value of 243 cm^{-1} has been estimated for ν_4 from combination tones in the infrared spectrum.

The gas phase data obtained during this study is presented in Table V, together with the assignments reported by Scruby, Lacher, and Park (33). A band observed at 256 cm^{-1} was assigned as ν_4. This band showed PQR structure with a 20 cm^{-1} separation of the P and R branches.

The present assignment for the quartet of bands from 714 to 736 cm^{-1} differs from that of Scruby, et al. The bands at 714, 721, and 727 cm^{-1} are assigned as three components of the combination tone, $\nu_1 + \nu_4$, which is split as a result of a chlorine isotope effect. The natural abundance ratio of BCl_3^{35}:$BCl_2^{35}Cl^{37}$:$BCl^{35}Cl_2^{37}$:BCl_3^{37} should be about

TABLE V

THE INFRARED SPECTRUM FOR BCl_3 IN THE GAS PHASE

A COMPOSITE OF NATURAL AND B^{10} ENRICHED SPECTRA

Scruby et al.		This work		
cm^{-1}	Assignment	cm^{-1}		Assignment
		256	m[8]	ν_4^{11}
		457	s	ν_2^{11}
		477	ms	ν_2^{10}
		524	w	
		624	w	
715	$\nu_3-\nu_4^{11}$	714	mw	$(\nu_1+\nu_4)BCl^{35}Cl_2^{37}$
722	$\nu_1+\nu_4$	721	m	$(\nu_1+\nu_4)BCl_2^{35}Cl^{37}$
728	$3\ \nu_4^{11}$	727	m	$(\nu_1+\nu_4)BCl_3^{35}$
735	$3\ \nu_4^{10}$	736	w	R branch of $(\nu_1+\nu_4)$
955	ν_3^{11}	954	vs	ν_3^{11}
995	ν_3^{10}	993	vs	ν_3^{10}
1203	$\nu_3+\nu_4^{11}$	1205	m	$\nu_3+\nu_4^{11}$
1241	$\nu_3+\nu_4^{10}$	1245	w	$\nu_3+\nu_4^{10}$
		1304	w	ν_1 of $B^{11}FCl_2$
		1317	w	
1376	$3\ \nu_2^{11}$	1378	ms	
1395	$2\ \nu_1+\nu_2^{11}$	1408	m	
1420	$\nu_1+\nu_3^{11}$, $3\ \nu_2^{10}$	1423	s	$\nu_1+\nu_3^{11}$
1464	$\nu_1+\nu_3^{10}$	1461	ms	$\nu_1+\nu_3^{10}$

TABLE V

(Continued)

Scruby et al.		This work		
cm^{-1}	Assignment	cm^{-1}		Assignment
1672	$\nu_1 + \nu_3 + \nu_4{}^{11}$			
1916	$2\ \nu_3{}^{11}$	1909	ms	$2\ \nu_3{}^{11}$
1948	$2\ \nu_3{}^{10}$	1988	m	$2\ \nu_3{}^{10}$

---

[a] w, m, s = weak, medium, strong and v = very.

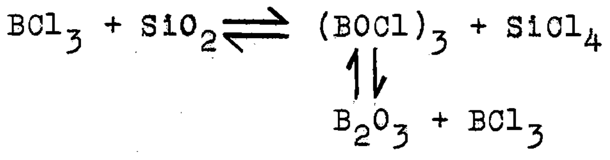
27:27:9:1. Since the bands at 727 and 721 cm^{-1} have approximately equal intensities while the 714 cm^{-1} component is considerable less intense, their assignment as $\nu_1 + \nu_4$ for the three most abundant isotopic species seems reasonable. These assignments are supported by the fact that Delhaye and Delhaye-Buisett (36) have observed isotopic structure for ν_1 of BCl_3 in the Raman spectrum of the compound. They reported two lines of about equal intensity at about 470 cm^{-1} and a less intense line at a lower frequency. Although the exact frequencies of the lines were not reported, the separation of adjacent features appeared to be about 4 cm^{-1}. The fourth component of the quartet of bands under consideration occurs at 736 cm^{-1} in the gas phase spectrum, but it was absent in the spectrum of the solid. It has, therefore, been identified with part of the band envelope (R branch) of the $\nu_1 + \nu_4$ components.

Perhaps the most interesting observation concerning BCl_3

was that previously reported BCl_3 spectra apparently contained a strong band which originated, not in BCl_3, but in $(BOCl)_3$. Scruby, et al., observed the band at 1376 cm^{-1} and gave it the very improbable assignment of $3\nu_2$ for $B^{11}Cl_3$. In this work a band was observed at 1378 cm^{-1} in natural BCl_3 and at 1408 cm^{-1} in B^{10} enriched BCl_3. The intensity of this band could be reduced considerably, compared to the intensity in the spectrum reported by Scruby, et al., but it could not be completely eliminated by vacuum distillation of the gas. If a sample of the "purified" gas was allowed to remain in an infrared gas cell for several hours, the intensity of this unusual band increased as shown in Figure 6.

The 1378 cm^{-1} band was believed to be due to the presence of a small amount of $(BOCl)_3$ vapor in the BCl_3. The presence of the trichloroboroxine was confirmed by passing the gas over a cold window of the low temperature cell under conditions for the deposition of $(BOCl)_3$ except that the gas was not heated. The spectrum of the condensed phase was weak, but showed the two strongest bands of solid trichloroboroxine at 1345 and 1180 cm^{-1}.

The $(BOCl)_3$ apparently enters the system through the reaction of BCl_3 with the SiO_2 of the pyrex containers, after which some decomposes so that the equilibrium conditions for the following reactions are satisfied.



$$\begin{tikzcd}BCl_3 + SiO_2 \arrow[r, shift left] & (BOCl)_3 + SiCl_4 \arrow[l, shift left] \arrow[d, shift left] \\ & B_2O_3 + BCl_3 \arrow[u, shift left]\end{tikzcd}$$

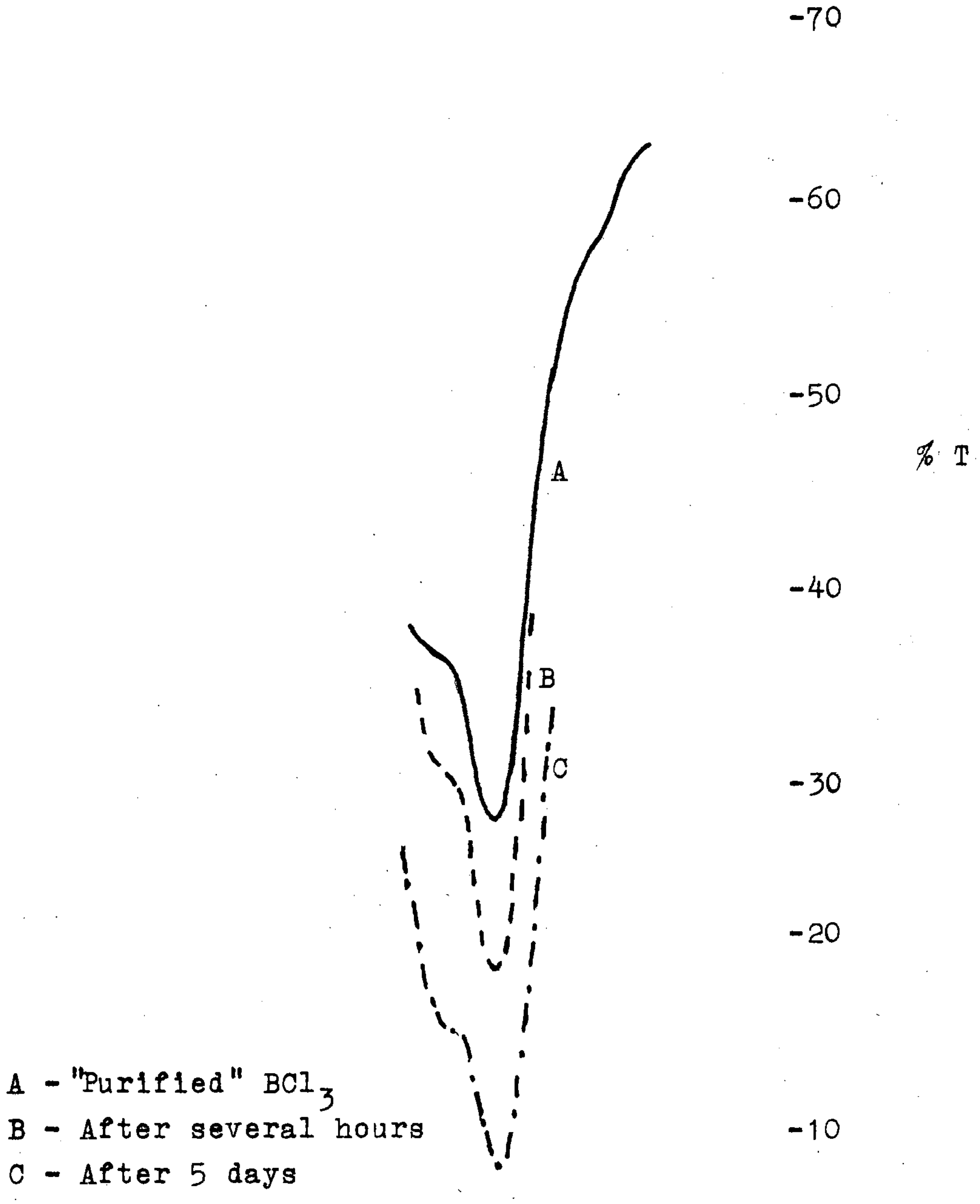


Figure 6. Intensity Changes of 1378 cm^{-1} Band in the Spectrum of a Sample of BCl_3 Gas at Intervals after Purification; 175 mm pressure in 10 cm gas cell.

CHAPTER V

FORCE CONSTANT ANALYSIS

The basic Urey-Bradley Force Field for the planar modes of a trihaloboroxine is defined by the equation

$$\begin{aligned}2V_{UB} = {} & 2\overset{3}{\Sigma}K'(BX)r_{BX}\Delta r_{BX} + \overset{3}{\Sigma}K(BX)\ (\Delta r_{BX})^2 + 2\overset{6}{\Sigma}K'(BO)r_{BO}\Delta r_{BO} + \\ & \overset{6}{\Sigma}K(BO)\ (\Delta r_{BO})^2 + 2\overset{3}{\Sigma}H'(BB)\Delta\alpha + \overset{3}{\Sigma}H(BB)\ (\Delta\alpha)^2 + \\ & 2\overset{3}{\Sigma}H'(OO)\Delta\beta + \overset{3}{\Sigma}H(OO)\ (\Delta\beta)^2 + 2\overset{6}{\Sigma}H'(OX)\Delta\phi + \\ & \overset{6}{\Sigma}H(OX)\ (\Delta\phi)^2 + 2\overset{6}{\Sigma}F'(OX)q_{OX}\Delta q_{OX} + \overset{6}{\Sigma}F(OX)\ (\Delta q_{OX})^2 + \\ & 2\overset{6}{\Sigma}\frac{C'(BO)}{2}q_{BO}\Delta q_{BO} + \overset{6}{\Sigma}\frac{C(BO)}{2}(\Delta q_{BO})^2 + 2\overset{3}{\Sigma}F'(OO)q_{OO}\Delta q_{OO} \\ & + \overset{3}{\Sigma}F(OO)\ (\Delta q_{OO})^2 + 2\overset{3}{\Sigma}F'(BB)q_{BB}\Delta q_{BB} + \overset{3}{\Sigma}F(BB)\ (\Delta q_{BB})^2 \quad [8]\end{aligned}$$

where the internal coordinates are defined in Figure 7.

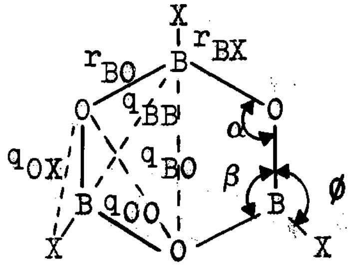


Figure 7. Internal Coordinates for Trihaloboroxines

A total of twelve Urey-Bradley force constants (UBFC) were used in the overlay calculations for the four trihaloboroxines. These force constants are listed in Table VI. Details of the overlay calculation are discussed in the Appendix. As usual it was assumed that F′=-F/10, although, as noted in the introduction, this practice is of questionable merit.

TABLE VI

FORCE CONSTANTS FOR THE TRIHALOBOROXINES

Force Constant	Description
K(BF)	B-F Stretching
H(OF)	O-B-F Bending
F(OF)	O-F Non-bonded
K(BO)	B-O Stretching
H(BB)	B-O-B Bending
H(OO)	O-B-O Bending
F(BB)	B-B Non-bonded
F(OO)	O-O Non-bonded
C(BO)	B-O Non-bonded
K(BCl)	B-Cl Stretching
H(OCl)	O-B-Cl Bending
F(OCl)	O-Cl Non-bonded

The exact geometry of the trihaloboroxines has not been determined, but trimethylboroxine has been examined by electron diffraction (37). The results of the electron diffraction study gave a value of 1.39 ± 0.02A for the B-O bond distance and $112 \pm 4^{\circ}$ for the B-O-B bond angle of trimethylboroxine. This B-O bond distance was assumed to be transferable to the haloboroxines, but the assumption of a value of 112° for the B-O-B angle in the haloboroxines resulted in a negative B-O-B bending constant. More feasible results were obtained by assuming a value of 120° for all of the ring angles, and these are the results which are reported. Values for B-F and B-Cl bond distances were transferred from BF_3 and BCl_3, respectively. Thus, the following values were assumed for the equilibrium bond distances and bond angles:

B-F bond	1.30 A
B-Cl bond	1.75 A
B-O bond	1.39 A
B-O-B angle	120°

The first step in the force constant calculations involved a zero order calculation of the frequencies of trichloro- and trifluoroboroxine. That is, initial guesses for the force constants were used to calculate the frequencies of the two molecules. The initial force constants were transferred from molecules having similar bonds such as BF_3, BCl_3 and B_2O_3. The zero order frequencies $\nu(0)$ are compared with the observed frequencies ν_{obs} in Table VII. The initial force constants $\Phi(0)$ are also presented in the table. Although the agreement between observed and zero order frequencies was not good, the frequency assignments seemed to be satisfactory.

The next step was to adjust the initial force constants by a two molecule overlay calculation to give the best agreement between observed and calculated frequencies. The initial force constants were adjusted by an iterative procedure to give a minimum value for the weighted sum of square errors, S, of the frequency parameters. The quantity S can be expressed as

$$S = \sum_k p_k \, (\lambda_k + \Delta \lambda_k - \lambda_k^o)^2 \qquad [9]$$

where the p_k are weighting factors, the λ_k and λ_k^o are the calculated and observed frequency parameters, respectively, and $\Delta \lambda_k$ is a correction to be added to the calculated frequency.

TABLE VII

RESULTS OF TWO MOLECULE OVERLAY CALCULATIONS

	Frequencies					
	$(B^{11}OF)_3$ cm^{-1}			$(B^{11}OCl)_3$ cm^{-1}		
Symmetry	ν_{obs}	$\nu(0)$	$\nu(1)$	ν_{obs}	$\nu(0)$	$\nu(1)$
A_1'		1522	1384	1037	1270	1067
		845	854	807	804	807
		569	511	333	360	342
A_2'		1696	1438		1673	1409
		581	632		389	423
E'	1436	1649	1463	1345	1598	1359
	1373	1498	2339	1183	1343	1146
	964	1032	961	760	761	738
	462	435	452	390	366	376
	316	325	338	150	160	171

Force Constants

(The units are in mdyne/A except for bending constants which are in 10^{-11} erg/rad^2)

	$\Phi(0)$	$\Phi(1)$
K(BF)	6.0	5.470
H(OF)	0.35	0.641
F(OF)	0.9	0.708
K(BO)	7.0	4.873
H(BB)	0.4	0.352
H(OO)	0.4	0.250
F(BB)	0.5	0.092
F(OO)	0.4	0.807
C(BO)	0.1	0.288
K(BCl)	3.0	2.260
H(OCl)	0.24	0.215
F(OCl)	0.25	0.679

Initial attempts to adjust all twelve of the force constants simultaneously in the two molecule problems were unsuccessful because the problem would not converge to a minimum value for S. The problem could be made to converge by constraining the bending force constants to reasonable values and allowing all other force constants to be adjusted. The non-bonded constants were then constrained to the values which were obtained in the initial calculation and the bending constants were adjusted. By alternately constraining the bending and non-bonded constants the fit was improved until there was little change in S on successive trials. Table VII presents the results of the calculations for the two molecule overlay. The table gives the final calculated frequencies $\nu(1)$ for trifluoro- and trichloroboroxine together with the final force constants $\Phi(1)$ from the two molecule overlay.

The force constants obtained from the two molecule overlay were used to make a zero order calculation of frequencies of the two mixed halogen boroxines. That is, the frequencies of $B_3O_3ClF_2$ and $B_3O_3Cl_2F$ were calculated directly from the force constants $\Phi(1)$ obtained from $(BOF)_3$ and $(BOCl)_3$. These zero order frequencies were used to make specific assignments of the observed frequencies of the two mixed halogen molecules. Table VIII presents the calculated zero order frequencies $\nu(0')$ together with the observed frequencies.

After making assignments of the observed frequencies of the mixed trihaloboroxines, a four molecule overlay calculation was performed, again by alternately constraining bending

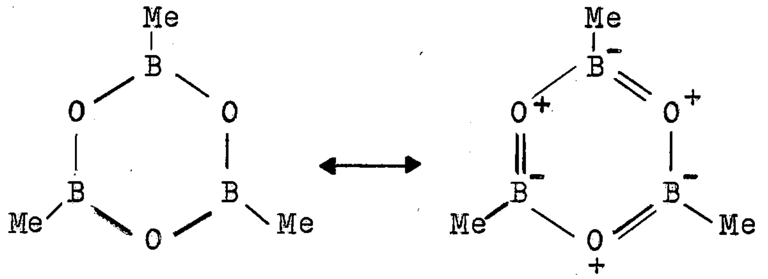
TABLE VIII

RESULTS OF ZERO ORDER CALCULATIONS FOR $B_3^{11}O_3ClF_2$ AND $B_3^{11}O_3Cl_2F$

	$B_3^{11}O_3ClF_2$ cm^{-1}		$B^{11}O_3Cl_2F$ cm^{-1}	
Symmetry	ν_{obs}	$\nu(0')$	ν_{obs}	$\nu(0')$
A_1		1435		1439
	1374	1358	1242	1296
		1157		1107
	847	862	832	885
		788	783	803
		481	434	463
		385		357
	312	317		175
B_2		1457		1427
	1413	1429	1352	1380
	1267	1299	1197	1173
	950	949	762	745
		579	483	518
	457	451	394	377
		215		250

and nonbonded force constants in successive trials. A total of 29 observed frequencies were used to determine 12 UBFC. The results of these calculations are shown in Tables IX and X where $\nu(2)$ are the frequencies calculated from the resulting force constants $\Phi(2)$.

Thus far, the potential function which was used for the trihaloboroxines contained only Urey-Bradley type terms. There have been suggestions by some workers that the boroxine ring might possess some aromatic character in which case a modified UBFF might give better results. Lehmann, Wilson, and Shapiro (38) have reported mass spectral data which indicates that trimethylboroxine exhibits some aromaticity. They observed a striking similarity between the fragmentation pattern of trimethylboroxine and mesitylene, and concluded that $(BOCH_3)_3$ has considerable aromatic character with resonance involving structures of the type



Fisher, Lehmann, and Shapiro (25) pointed out that the increased electronegativity of fluorine over the methyl group should make trifluoroboroxine even more aromatic than trimethylboroxine. This conclusion is supported by the increase in ring-stretching frequencies of trifluoroboroxine (1436 and 1373 cm^{-1}) over trimethylboroxine (1384 and 1227 cm^{-1}).

TABLE IX

RESULTS OF FOUR MOLECULE OVERLAY

$(B^{11}OF)_3$
cm^{-1}

Symmetry	ν_{obs}	$\nu(2)$	$\nu(3)$	$\nu(4)$	$\nu(5)$
A_1'		1376	1372	1372	1373
		853	854	860	864
		494	493	495	497
A_2'		1426	1417	1416	1415
		643	643	646	637
E'	1436	1469	1471	1470	1461
	1373	1336	1337	1342	1344
	964	939	940	939	942
	462	448	448	447	449
	316	338	338	339	336
Average % error		3.44	3.44	3.45	3.04

$(B^{11}OCl)_3$
cm^{-1}

Symmetry	ν_{obs}	$\nu(2)$	$\nu(3)$	$\nu(4)$	$\nu(5)$
A_1'	1037	1071	1070	1070	1086
	807	798	797	795	795
	333	339	339	346	349
A_2'		1389	1380	1379	1381
		390	388	375	382
E'	1345	1340	1344	1342	1343
	1183	1141	1142	1139	1148
	760	741	741	741	745
	390	371	371	372	376
	150	159	159	155	158
Average % error		2.95	2.86	2.89	2.96

TABLE IX
(Continued)

$(B_3^{11}O_3ClF_2)$
cm^{-1}

Symmetry	ν_{obs}	$\nu(2)$	$\nu(3)$	$\nu(4)$	$\nu(5)$
A_1		1433	1435	1435	1430
	1374	1350	1350	1353	1355
		1165	1165	1166	1172
	847	857	858	862	869
		790	789	788	788
		471	470	472	474
		379	379	380	382
	312	318	318	320	320
B_2		1464	1465	1464	1455
	1413	1418	1409	1409	1408
	1267	1276	1277	1276	1283
	950	923	923	922	925
		577	577	576	571
	457	448	447	447	449
		200	200	195	198
Average % error		1.54	1.57	1.76	1.78

$(B_3^{11}O_3Cl_2F)$
cm^{-1}

Symmetry	ν_{obs}	$\nu(2)$	$\nu(3)$	$\nu(4)$	$\nu(5)$
A_1		1444	1444	1443	1436
	1242	1267	1268	1266	1273
		1105	1105	1103	1115
	832	868	868	869	877
	783	797	796	794	793
	434	457	457	457	459

TABLE IX
(Continued)

Symmetry	ν_{obs}	$\nu(2)$	$\nu(3)$	$\nu(4)$	$\nu(5)$
		($B_3^{11}O_3Cl_2F$) (Continued) cm^{-1}			
A_1		353	353	358	361
		163	162	158	161
B_2		1415	1409	1410	1409
	1352	1363	1363	1362	1363
	1197	1182	1183	1185	1189
	762	754	754	756	758
	483	505	505	500	500
	394	371	371	371	375
		238	237	233	286
Average % error		2.97	2.94	2.75	2.75

TABLE X

FORCE CONSTANTS OBTAINED FROM FOUR MOLECULE OVERLAY CALCULATIONS

(The units are in mdyne/A except for bending constants which are in 10^{-11} erg/rad^2.)

Force Constant	$\Phi(2)$	$\Phi(3)$	$\Phi(4)$	$\Phi(5)$
K(BF)	5.517	5.483	5.416	5.318
H(OF)	0.763	0.765	0.779	0.741
F(OF)	0.585	0.583	0.577	0.586
K(BO)	4.758	4.776	4.796	4.825
H(BB)	0.138	0.136	0.095	0.067
H(OO)	0.460	0.461	0.474	0.381
F(BB)	0.008	-0.007	0.043	0.146
F(OO)	0.807	0.806	0.849	0.923
C(BO)	0.296	0.302	0.276	0.294
K(BCl)	2.604	2.598	2.530	2.485
H(OCl)	0.149	0.140	0.039	0.039
F(OCl)	0.618	0.623	0.704	0.731
ρ		0.018	0.023	0.026

However, mass spectral data for trifluoroboroxine does not verify this (39). There appear to be several major broken ring fragments in the mass spectrum of trifluoroboroxine while broken ring fragments are much less prominent in the spectrum of trimethylboroxine.

The basic Urey-Bradley force field has been found inadequate for aromatic molecules. However a modification of the UBFF including terms which take care of the stretch-stretch interactions characteristic of aromatic systems has been applied successfully to a number of aromatic molecules

(40-43). Since there is some evidence for aromaticity in the boroxines, force constant calculations were made using a modification of the UBFF, known as the Kekulé model. The Kekulé model was introduced by Scherer and Overend (40) in the study of the planar vibrations of benzene. The potential energy for the trihaloboroxines can be expressed in terms of the Kekulé model by

$$2V = 2V_{UB} + 2\rho\Big[\sum^{6}(\Delta r_{BO})_i(\Delta r_{BO})_{i+1} + \sum^{3}(\Delta r_{BO})_i(\Delta r_{BO})_{i+3} - \sum^{6}(\Delta r_{BO})_i(\Delta r_{BO})_{i+2}\Big] \qquad [10]$$

where ρ is known as the Kekulé constant. If there is actually resonance stabilization of the boroxine ring, it should be reflected in the value obtained for the Kekulé constant. In Tables IX and X the results of calculations obtained using the Kekulé potential function are compared with the results obtained using the basic UBFF. The force constants presented under $\Phi(2)$ (UBFF) and $\Phi(3)$ (Kekulé model) were obtained by alternately constraining bending and non-bonded constants as previously described. The corresponding calculated frequencies are listed under $\nu(2)$ and $\nu(3)$. The force constant set $\Phi(4)$ was obtained by using $\Phi(2)$ as initial force constants and allowing all 13 force constants, including ρ, to be adjusted simultaneously. By using the refined force constants as input, the problem could be made to converge while allowing all force constants to be adjusted.

As shown in the Appendix the observed frequencies are part of the input for the computer method used in the force constant calculations. When a molecule possesses doubly degenerate modes of vibration, each observed frequency of the degenerate vibrations can be entered twice in the frequency input. This, in effect, gives the degenerate frequencies twice the weight of nondegenerate frequencies in determining the force constants of the molecule. The force constant sets $\Phi(1)$ through $\Phi(4)$ were obtained from calculations in which the degenerate frequencies were weighted on the same basis as the nondegenerate frequencies. The force constant set $\Phi(5)$ and the calculated frequencies $\nu(5)$ were obtained from a four molecule overlay in which the E' frequencies of $(BOF)_3$ and $(BOCl)_3$ were given double weight (entered twice in input), and in which all 13 force constants were adjusted simultaneously.

All force constant calculations were made using data from boron-11 isotopic compounds. The frequency shifts due to the boron isotope effect are not large enough for the frequencies of the boron-10 compounds to be of any value as additional data for the evaluation of force constants, but they can be used to confirm the frequency assignments. The force constant set $\Phi(4)$ was used to calculate the frequencies of the boron-10 trihaloboroxines. Table XI presents the observed and calculated frequencies for the B-10 compounds together with the calculated and observed isotopic shifts $(\nu_k^{10}-\nu_k^{11})$. The largest discrepancies between observed and calculated isotopic shifts occur for ν_8 and ν_9 of $(BOF)_3$. This is probably a result of the effect of the Fermi resonance which has been discussed previously and of the difficulty in locating the band centers of the two broad fundamental bands.

The potential energy distribution (PED) in Urey-Bradley space gives the fractional contributions of each UBFC to the different normal modes. The determination of the PED is discussed in the Appendix. Examination of the PED allows one to roughly deduce the contributions of the various internal coordinates to each normal coordinate. The PED for the trihaloboroxines calculated from the force constant set $\Phi(4)$ together with a qualitative description of the normal modes is tabulated in Table XII.

TABLE XI

FREQUENCIES OF BORON-10 TRIHALOBOROXINES AND ISOTOPIC SHIFTS

	$(B^{10}OF)_3$		Isotopic Shifts $\nu_i^{10}-\nu_i^{11}$	
Symmetry	ν_{obs}	$\nu(4)$(Calcd.)	Observed	Calculated
A_1'		1426		54
		860		0
		499		4
A_2'		1462		46
		652		6
E'	1468	1519	32	49
	1403	1395	30	53
	966	941	2	2
	465	451	3	4
	319	339	3	0

TABLE XI
(Continued)

	$(B^{10}OCl)_3$		Isotopic Shifts $\nu_i^{10}-\nu_i^{11}$	
Symmetry	ν_{obs}	$\nu(4)$(Calcd.)	Observed	Calculated
A_1'		1114		44
		798		3
		347		1
A_2'		1418		39
		382		7
E'	1385	1380	40	38
	1220	1181	37	42
	765	751	5	10
	392	374	2	2
		155		0
	$(B_3^{10}O_3ClF_2)$			
A_1		1484		49
	1427	1406	53	53
	1261	1204		38
	855	864	8	2
		798		10
		476		4
		382		2
	314	321	2	1
B_2		1513		49
	1465	1454	52	45
		1323		47
	954	924	4	2
		582		6
	462	451	5	4
		196		1

TABLE XI
(Continued)

	$(B_3^{10}O_3Cl_2F)$		Isotopic Shifts $\nu_i^{10}-\nu_i^{11}$	
Symmetry	ν_{obs}	$\nu(4)$(Calcd.)	Observed	Calculated
A_1	1478	1492		49
		1311		45
	1122	1145		42
	833 (?)	873	1	4
	787	800	4	6
	440	461	6	4
		359		1
		158		0
B_2		1457		47
	1394	1401	42	39
	1239	1223	42	38
	770	767	8	11
	484(?)	506	1	6
		374		3
		234		1

TABLE XII

DISTRIBUTION OF POTENTIAL ENERGY AMONG PLANAR INTERNAL COORDINATES OF THE TRIHALOBOROXINES

$(B^{11}OF)_3$		A_1'			A_2'			E'		
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}
ν_{obs}, cm^{-1}						1436	1373	964	462	316
$\nu(4)$, cm^{-1}	1372	860	495	1416	646	1470	1342	939	447	339
K(BF)	66.9	1.6	20.1	0.0	0.0	31.6	20.2	29.3	6.6	1.0
H(OF)	3.5	9.1	10.4	7.2	63.7	6.7	15.6	6.6	14.7	46.2
F(OF)	0.9	1.8	24.4	3.2	32.8	1.1	2.6	18.7	9.1	31.1
K(BO)	18.2	31.9	18.7	92.7	3.6	50.6	59.4	34.6	3.1	20.0
H(BB)	0.8	2.2	2.5	0.0	0.0	0.5	0.2	0.5	3.8	0.2
H(OO)	4.2	11.0	12.6	0.0	0.0	4.9	0.6	0.0	17.6	0.0
F(BB)	0.9	0.2	1.6	0.0	0.0	0.0	0.5	0.0	1.2	0.1
F(OO)	2.0	37.1	5.9	-0.8	0.0	2.5	0.2	8.9	24.8	1.0
C(BO)	2.6	4.9	3.6	0.0	0.0	1.8	0.3	1.2	19.0	0.2
ρ	0.1	0.2	0.1	-2.2	-0.1	0.2	0.3	0.2	0.0	0.1
Description of normal mode	Sym. B-F Str.	Sym. Ring Def.	Sym. Ring Def.	Ring Str.	B-F Wag	Ring Str.	Ring Str.	B-F Str.	Ring Def.	B-F wag

TABLE XII (Continued)

$(B^{11}OCl)_3$	A_1'			A_2'		E'				
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}
ν_{obs}	1037	807	333			1345	1183	760	390	150
$\nu(4)$	1070	795	346	1379	375	1342	1139	741	372	155
K(BCl)	36.4	9.7	28.6	0.0	0.0	4.1	14.4	42.2	13.0	0.8
H(OCl)	0.2	0.9	0.4	0.2	6.9	0.4	0.7	0.5	0.7	5.9
F(OCl)	-0.4	4.8	42.6	4.6	92.6	4.5	3.2	21.4	24.9	88.6
K(BO)	46.5	12.6	10.6	98.5	0.5	83.2	72.5	9.8	2.5	3.6
H(BB)	0.8	4.3	1.7	0.0	0.0	0.6	0.2	1.7	3.3	0.1
H(OO)	4.0	21.4	8.6	0.0	0.0	3.7	3.1	4.3	16.3	0.0
F(BB)	1.4	0.7	1.0	0.0	0.0	0.1	0.6	0.3	1.1	0.0
F(OO)	5.1	41.7	4.2	-0.8	0.0	2.1	3.9	13.0	21.3	0.8
C(BO)	5.8	3.9	2.2	0.0	0.0	1.0	1.1	6.8	17.0	0.2
ρ	0.2	0.1	0.1	-2.3	0.0	0.4	0.3	0.0	0.0	0.0
Description of normal mode	Sym. B-Cl Str.	Sym. Ring Def.	Sym. Ring Def.	Ring Str.	B-Cl wag	Ring Str.	Ring Str.	B-Cl Str.	Ring Def.	B-Cl Wag

TABLE XII (Continued)

$B_3^{11}O_3ClF_2$

	A$_1$								B$_2$						
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_{15}	ν_{16}	ν_{17}	ν_{18}	ν_{19}	ν_{20}	ν_{21}
ν_{obs}		1374		847				312		1413	1267	950		457	
$\nu(4)$	1435	1353	1166	862	788	472	380	321	1464	1409	1276	922	576	447	195
K(BF)	26.3	33.3	5.3	6.0	3.4	14.0	0.3	0.0	35.6	2.6	16.0	26.8	0.2	7.2	0.2
H(OF)	7.4	11.5	5.3	5.4	5.8	11.1	11.9	34.0	5.3	6.5	4.2	4.6	50.3	14.6	4.5
F(OF)	1.2	2.1	2.5	4.4	5.4	17.6	6.7	22.9	0.7	2.2	1.6	17.2	27.5	10.0	3.5
K(BCl)	0.6	0.1	18.2	3.9	30.8	2.7	10.1	8.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H(OCl)	0.0	0.0	0.2	0.0	0.3	0.0	0.5	0.1	0.0	0.0	0.4	0.2	1.0	0.0	5.4
F(OCl)	0.7	0.1	0.2	2.5	8.9	2.4	18.7	12.4	0.3	1.1	2.7	1.9	11.5	0.2	79.5
K(BO)	55.0	48.2	54.3	36.5	6.7	13.0	6.8	17.3	47.5	90.0	74.4	37.5	8.2	3.6	5.4
H(BB)	0.7	0.5	0.4	1.3	2.6	2.7	3.2	0.1	0.4	0.0	0.3	0.6	0.2	3.5	0.1
H(OO)	4.1	1.7	4.7	5.9	11.6	13.8	11.8	2.4	5.2	0.2	0.2	0.0	0.0	17.6	0.0
F(BB)	0.2	0.6	0.7	0.2	0.6	1.4	0.8	0.3	0.1	0.0	0.5	0.1	0.0	1.2	0.0
F(OO)	1.9	0.6	5.6	28.6	19.7	12.1	17.3	1.0	2.8	-0.6	-0.5	9.5	0.8	23.6	1.0
C(BO)	1.6	1.1	2.4	4.9	4.1	9.1	11.8	1.2	1.9	0.1	0.1	1.4	0.3	18.5	0.3
ρ	0.3	0.2	0.3	0.2	0.0	0.1	0.0	0.1	0.2	-2.0	0.2	0.2	0.0	0.0	0.0
Description of normal mode	Ring Str.	B-F Str.	Ring Str.	Ring Def.	B-Cl Str.	Ring Def.	Ring Def.	B-F Wag	Ring Str.	Ring Str.	Ring Str.	B-F Str.	B-F Wag	Ring Def.	B-Cl Wag

TABLE XII (Continued)

$B_3^{11}O_3Cl_2F$

	A$_1$								B$_2$						
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_{15}	ν_{16}	ν_{17}	ν_{18}	ν_{19}	ν_{20}	ν_{21}
ν_{obs}		1242		832	783	434				1352	1197	762	483	394	
$\nu(4)$	1443	1266	1103	869	794	457	358	158	1410	1362	1185	756	500	371	233
K(BF)	39.9	20.1	2.1	13.6	2.7	9.9	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H(OF)	4.0	0.2	0.0	0.9	2.6	12.5	0.1	0.0	8.9	1.4	7.1	5.2	36.8	0.1	11.4
F(OF)	0.2	1.4	0.8	8.2	2.9	12.8	0.4	0.2	2.3	0.2	1.6	3.1	20.6	0.2	7.7
K(BCl)	0.3	1.1	25.0	4.8	18.0	1.8	23.2	0.4	0.4	1.8	14.3	43.6	0.3	12.5	1.6
H(OCl)	0.0	0.5	0.4	0.3	0.7	0.0	0.5	5.9	0.0	0.3	0.3	0.2	2.1	0.9	4.4
F(OCl)	1.0	3.0	1.0	5.3	6.3	2.1	36.6	88.3	1.2	4.3	1.3	17.2	26.1	26.2	66.4
K(BO)	43.6	70.9	56.5	40.6	9.2	7.5	8.1	3.7	87.7	89.2	64.0	8.0	8.7	2.6	7.8
H(BB)	0.4	0.5	0.6	0.9	3.8	3.2	2.3	0.1	0.3	0.4	0.0	1.3	0.6	3.2	0.1
H(OO)	5.3	0.9	3.9	1.9	17.7	15.8	11.2	0.0	0.6	1.9	4.1	4.1	0.7	15.9	0.0
F(BB)	0.2	0.5	1.0	0.2	0.7	1.3	1.1	0.0	0.0	0.0	0.5	0.3	0.1	1.0	0.0
F(OO)	3.0	-0.1	4.8	19.2	31.6	18.5	9.7	0.9	-0.4	0.5	5.2	11.0	2.7	20.8	0.4
C(BO)	2.0	0.6	3.5	4.1	3.7	14.5	6.7	0.2	0.2	0.6	1.3	6.0	1.4	16.5	0.1
ρ	0.2	0.3	0.3	0.2	0.0	0.0	0.0	0.0	-1.3	-0.6	0.2	0.0	0.0	0.0	0.0
Description of normal mode	B-F Str.	Ring Str.	B-Cl Str.	Ring Str.	Ring Def.	Ring Def.	Ring Def.	B-Cl Wag	Ring Str.	Ring Str.	Ring Str.	B-Cl Str.	B-F Wag	Ring Def.	B-Cl Wag

CHAPTER VI

DISCUSSION OF RESULTS

The agreement between the observed and calculated frequencies of the trihaloboroxines is not exceptionally good; the average per cent error of the frequencies is about 2.7 for $\nu(4)$. This is not an unexpected result considering the source and nature of the experimental data. The observed vibrational data were condensed phase frequencies where intermolecular interactions must certainly have an effect on the vibrations of the molecules. In addition, the exact frequencies of some of the observed bands were difficult to determine because of broadening.

As noted in Chapter IV, frequencies have been assigned for all planar infrared active modes of trifluoro- and trichloroboroxine, although it was necessary to rely on Raman data for ν_{12} of $(BOCl)_3$. Assignments of the mixed halogen boroxines were made by comparing the observed frequencies with the frequencies calculated from force constants transferred from $(BOF)_3$ and $(BOCl)_3$ (Table VIII). Each mixed halogen boroxine should have 15 in-plane infrared active modes--eight (ν_1-ν_8) of A_1 symmetry and seven (ν_{15}-ν_{21}) of B_2 symmetry. Only three observed frequencies were assigned as A_1 modes and four as B_2 modes for $B_3O_3ClF_2$. For $B_3O_3Cl_2F$, four A_1 and five B_2 modes were assigned frequencies. This leaves eight planar modes for $B_3O_3ClF_2$ and six modes for $B_3O_3Cl_2F$ which have not been given frequency assignments. Absorptions of some modes were probably too weak to be observed under the existing experimental conditions; others, especially those in the region from 1300 to 1500 cm^{-1}, were undoubtedly masked out by other absorptions.

There was one band occurring at 892 cm^{-1} in the spectra of the mixed halogen boroxines which defied assignment. This band was not originally assigned to either of the mixed halogen boroxines because of the apparent insensitivity of its intensity to the F:Cl ratio. Re-examination of the spectra indicated that the intensity of this band was more closely related to the intensities of the $B_3O_3Cl_2F$ bands than it appeared to be on first glance. The overlapping of bands of different compounds complicated the estimation of intensities, but it is possible that the 892 cm^{-1} band is assignable to $B_3O_3Cl_2F$. If this is the case the most logical assignment is ν_4 which was originally given a frequency assignment of 832 cm^{-1}. All calculations were made using the 832 cm^{-1} assignment for ν_4 of $B_3O_3Cl_2F$; but, except for its uncertain intensity behavior, the assignment of 892 cm^{-1} for ν_4 is more desirable.

The calculated frequencies $\nu(4)$ (see Table IX) give the best least squares fit of calculated to observed frequencies for the case in which the degenerate and nondegenerate modes were weighted on the same basis. The average per cent error in frequencies is slightly less for $\nu(5)$, the calculated frequencies for the case in which degenerate frequencies were doubly weighted. However, there is no real justification for doubly weighting the degenerate frequencies. The differences in the values of the force constants obtained for the two cases are within the uncertainties of the results. Thus, one set of force constants is not necessarily better than the other.

The force constants which have been determined for the trihaloboroxines are certainly not to be interpreted as the true harmonic force constants of the isolated molecules. They must be regarded as apparent force constants since intermolecular effects present in the condensed trihaloboroxines have not been taken into consideration, nor have the frequencies been corrected for anharmonicity. In addition, the geometrical parameters used to evaluate the G matrix were approximate since the exact geometry of the trihaloboroxines was not known.

Despite the uncertainties in the values of the force constants, present results permit some interesting conclusions. For one thing the question of the aromaticity of the boroxine ring may be considered in the light of information which has been obtained.

The force constant of the B-O stretching motion should be directly related to the bond order of the B-O bond and, hence, to the aromaticity of the ring. According to Goubeau (45) the value for the B-O single bond stretching force constant is about 4.6 mdynes per Angstrom. This is comparable to the value of 4.64 for K(BO) of BO_3^{3-} which is probably a fair representation of the B-O single bond. The K(BO) value for the trihaloboroxines was found to be about 4.8 mdynes per Angstrom which is not far removed from the quoted single bond value. In general the force constants of a bond are quite sensitive to the bond order. For example, the C-C single bond force constant is about 4.5 mdynes/A while the force constant for the C-C bond in benzene is approximately 5.6 mdynes/A and that for the double bond is nearly 9.5 mdynes/A (31,40).

Another factor to be considered is the very small value which was obtained for the Kekulé constant. The value of ρ for the trihaloboroxines is in the neighborhood of 0.02 mdynes/A. This is very small compared to values of ρ for organic aromatic compounds; i.e., the values of ρ for benzene, pyridine, and pyrazine are respectively, 0.35, 0.41, and 0.23 mdynes/A. Thus, these results suggest that the boroxine ring in the trihaloboroxines has very little, if any, aromatic character. This argument for nonaromaticity is by no means conclusive, but should definitely be taken into consideration.

Taking a rather naïve approach, Beyer, et al, (46) have suggested that the frequencies of the ring stretching vibrations of structurally similar compounds might give an indication of the relative aromaticity of the compounds. Table XIII presents their comparison of some symmetrically fluorinated ring systems together with the ring frequencies of trifluoroboroxine.

TABLE XIII

DEGENERATE RING STRETCHING VIBRATIONS OF SYMMETRICALLY FLUORINATED RING SYSTEMS

Compound	Phase	ν cm^{-1}	
1,3,5-Trifluorobenzene	Gas	1618	1473
Cyanuric Fluoride, $(FCN)_3$	"	1585	1427
B-Trifluoroborazine	"	1510	1401
Trifluoroboroxine	Solid	1436	1373

Although the solid phase ring frequencies are quoted for $(BOF)_3$, it is probable that the gas frequencies are also lower than those of the other compounds cited. If the ring vibration frequencies can be directly related to the aromaticity, then the boroxine ring has less aromatic character than the borazine, triazine, or benzene rings.

It is interesting to compare the final force constants of the four molecule overlay $\Phi(4)$ with similar force constants of other molecules. Table XIV presents such a comparison. Inspection of the table indicates that the force constants for the boron-halogen stretching motion K(BX) are about 10% less in the trihaloboroxines than in the boron trihalides. There is evidence that the bonds in BF_3 and BCl_3 have some double bond character (47,48). Thus, the decrease in K(BX) on going from BX_3 to $(BOX)_3$ indicates that the B-X bond in the latter has less double bond character;

TABLE XIV

COMPARISON OF TRIHALOBOROXINE FORCE CONSTANTS WITH SIMILAR FORCE CONSTANTS FROM OTHER MOLECULES

Trihaloboroxine Modified UBFC		Comparative Force Constants				
F.C.	Φ(4)[1]	F.C.	Value[1]	Force Field[3]	Molecule	Reference
K(BF)	5.416	K(BF)	6.04	UB	$B^{11}F_3$	(49)
H(OF)	0.779	H(FBF)	0.358[2]	UB	$B^{11}F_3$	(49)
F(OF)	0.577	F(FF)	0.927	UB	$B^{11}F_3$	(49)
K(BO)	4.796	K(BO)	4.64	UB	BO_3^{3-}	(49)
H(BB)	0.095					
H(OO)	0.474	H(OBO)	1.376[2]	UB	BO_3^{3-}	(49)
F(BB)	0.043					
F(OO)	0.849	F(OO)	1.05	UB	BO_3^{3-}	(49)
C(BO)	0.276					
K(BCl)	2.530	K(BCl)	2.963	UB	$B^{11}Cl_3$	Unpublished[4]
H(OCl)	0.039	H(ClBCl)	0.245	UB	$B^{11}Cl_3$	"
F(OCl)	0.704	F(ClCl)	0.536	UB	$B^{11}Cl_3$	"
ρ	0.023	ρ	0.35	Kek	Benzene	(40)
		ρ	0.41	Kek	Pyridine	(42)
		ρ	0.23	Kek	Pyrazine	(43)

[1] The units are in mdynes/A^{0} except for bending constants which are in 10^{-11} erg/rad^2.

[2] Bending constants have been multiplied by the appropriate factor to make the units consistent with Φ(4).

[3] UB = Urey Bradley; Kek = Kekulé Model

[4] The force constants for $B^{11}Cl_3$ were calculated from the frequencies obtained in this study.

i.e., resonance structures involving B-X double bond are less important in $(BOX)_3$ than in BX_3.

The values obtained for H(BB), H(OO), F(BB), and H(OCl) are of questionable significance because their dispersions are of the same order of magnitude as the force constants themselves. One interesting observation was made concerning the non-bonded O-O force constant. Janz and Mikawa (49) have published a paper concerning Urey-Bradley calculations of planar XY_3 type molecules in which they plotted the distance between non-bonded oxygen atoms versus the value for F(OO). Out of six points representing six molecules and ions, five lay on a smooth curve. The F(OO) value for the boroxine ring lies very near this curve. This may be fortuitous since the geometry of the trihaloboroxines was assumed initially.

SUMMARY

The primary purpose of this investigation was to perform a vibrational analysis of the fluorine-chlorine derivatives of boroxine. This was achieved by first recording the infrared spectra of $(BOF)_3$, $B_3O_3ClF_2$, $B_3O_3Cl_2F$ and $(BOCl)_3$, and then applying the data to an overlay calculation of the Urey-Bradley force constants of the four molecules.

Because of the unstable nature of the trihaloboroxines, the infrared spectra were recorded from kinetically stabilized solid films maintained at about -180°. Complete frequency assignments were made for the planar infrared active modes of $(BOF)_3$ and $(BOCl)_3$, and partial assignments were made for the two mixed halogen boroxines.

The infrared data, together with some Raman data obtained from the literature, was then used to determine the Urey-Bradley force constants of the four fluorine-chlorine boroxines. The overlay technique was employed by necessity since there was insufficient data to solve the vibrational problem for each molecule separately. The Urey-Bradley force constants were calculated by means of a least squares iterative procedure programed for a digital computer. The results of the calculations also included the potential energy distribution and the transformation matrix from normal to internal coordinates for each molecule, as well as the dispersions of the

force constants and calculated frequencies.

Although the fit of the calculated vibrational frequencies to the observed frequencies was by no means excellent, the results were good considering the fact that solid phase anharmonic frequencies were used and that broadening made frequency assignment difficult. These results show that the overlay technique can be applied to this molecular type. While the UBFF appears to provide a fair vibrational model for the trihaloboroxines, it is known to have certain deficiencies and could probably be improved by inclusion of additional terms.

More experimental data would be needed to better determine the values of the force constants, i.e., to decrease the dispersions on the calculated force constants. Additional Raman frequencies for these compounds would probably be an accessible type of data. It would be interesting to compare observed Raman frequencies with the frequencies which are predicted by the present calculations.

It would also be advantageous if the gas phase frequencies of the trihaloboroxines could be applied to the vibrational problem instead of condensed phase frequencies. The results from gas phase data should give a more realistic description of the trihaloboroxine molecules. The instability of the gaseous trihaloboroxines would present experimental difficulties which must be surmounted before meaningful results could be obtained. As noted in Chapter II, Wason and Porter (28) were successful in maintaining gaseous $(BOH)_3$ for a limited period of time by diluting with inert gases. A similar approach might be applicable to the trihaloboroxine systems.

After a thorough study of the trihaloboroxines, a logical step would be the application of the information and techniques to other boroxine derivatives and related molecules.

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APPENDIX

Wilson's FG Matrix Method

The molecular vibrational problem involves setting up the molecular equations of motion from expressions for the kinetic and potential energy of the system of nuclei of a molecule, and then solving the equations of motion for the vibrational properties of the system. The solution of the equations of motion yields expressions for the vibrational frequencies of the system in terms of the nuclear masses, geometry and force constants of the molecule, and allows one to deduce the normal coordinates of the molecule.

The treatment of molecular vibrations can be systematized by the use of the FG matrix method introduced by E. B. Wilson (3). Under this method both the kinetic and potential energies are expressed in terms of the internal coordinates R_t of a molecule. The potential energy (harmonic approximation) can immediately be written in terms of the internal coordinates by

$$2V = \Sigma\Sigma f_{tt'} R_t R_{t'} \qquad [A-1]$$

where the coefficients $f_{tt'}$ are the force constants for the general valence force field. In matrix notation equation [A-1] can be expressed as

$$2V = R'FR \qquad [A-2]$$

where F is the force constant matrix and R' is the transpose of R which is the vector of internal coordinates.

The expression for the kinetic energy of a molecule in terms of the internal coordinates is not as obvious as that for the potential energy. However, in terms of the cartesian displacement coordinates Δx_i of the nuclei the kinetic energy has the simple form

$$2T = \sum_{i=1}^{3N} m_j \Delta \dot{x}_i^2 \qquad [A-3]$$

or if mass weighted cartesian displacement coordinates q_i^* are used the expression becomes

$$2T = \sum_{i=1}^{3N} \dot{q}_i^{*2} \qquad [A-4]$$

Since $\Delta \dot{x}_i = \dot{x}_i$, the delta can be dropped in the discussion of the time derivatives of the cartesian displacement coordinates. By inspection of the geometry of a molecule, one can relate the time derivatives of the internal coordinates to the $\dot{x}_i$ by an expression of the form

$$\dot{R}_t = \sum_{i=1}^{3N} B_{ti} \dot{x}_i \qquad [A-5]$$

or in matrix notation

$$\dot{R} = B\dot{x}. \qquad [A-6]$$

$\dot{R}$ is a column matrix or vector with 3N-6 rows, $\dot{x}$ is a vector with 3N rows, and B is a 3N-6 x 3N transformation matrix.

The $\dot{R}_t$ can be expressed in terms of the $\dot{q}_i^*$ by

$$\dot{R}_t = \sum_{i=1}^{3N} D_{ti} \dot{q}_i^* \qquad [A-7]$$

where

$$D_{ti} = B_{ti}(m_i)^{-\frac{1}{2}}$$

or

$$\dot{R} = D\dot{q}^{*}. \qquad [A\text{-}8]$$

The inverse transformation of equation [A-8] is the desired relation for inserting into the kinetic energy expression; but, since D is not a square matrix, the inverse transformation cannot be readily obtained. The coordinate system on which the q_i^* are based is defined such that there is no net translational or angular momentum of the molecule with respect to the coordinate system. Thus, the transformation matrix from mass weighted coordinates to internal coordinates can be made square by introducing the conditions of zero translational and angular momentum into the expression to give

$$\dot{\mathcal{R}} = \begin{bmatrix} \dot{R} \\ \dot{r} \end{bmatrix} = \begin{bmatrix} D \\ D_o \end{bmatrix} \dot{q}^{*} = \mathcal{D}\dot{q}^{*}. \qquad [A\text{-}9]$$

D_o is an additional six rows which correspond to the six conditions of zero momentum and $\dot{r}$ is a column of six zeros. $\mathcal{D}$ is 3N x 3N and the inverse can, in principle, be calculated

$$\mathcal{D}^{-1} = [Y Y_o]. \qquad [A\text{-}10]$$

$\mathcal{D}^{-1}$ has been arbitrarily partitioned into Y which is 3N x 3N-6 and Y_o which is 3N x 6.

The desired relation can now be written as

$$\dot{q}^{*} = \mathcal{D}^{-1}\dot{\mathcal{R}} \qquad [A\text{-}11]$$

and the kinetic energy can be expressed as

$$2T = \dot{q}^{*\prime}\dot{q}^{*} = \dot{\mathcal{R}}'(\mathcal{D}^{-1})'\mathcal{D}^{-1}\dot{\mathcal{R}}. \qquad [A\text{-}12]$$

This expression for the kinetic energy can be expanded as

$$2T = [\dot{R}'\dot{r}'] \begin{bmatrix} Y' \\ Y_o' \end{bmatrix} [YY_o] \begin{bmatrix} \dot{R} \\ \dot{r} \end{bmatrix} \qquad [A\text{-}13]$$

$$= [\dot{R}'Y' + \dot{r}'Y_o'] \; [Y\dot{R} + Y_o\dot{r}] \qquad [A\text{-}14]$$

$$= \dot{R}'Y'Y\dot{R} + \dot{R}'Y'Y_o\dot{r} + \dot{r}'Y_o'Y\dot{R} + \dot{r}'Y_o'Y_o\dot{r} \qquad [A\text{-}15]$$

Since $\dot{r}$ is a zero matrix, the last three terms are zero and

$$2T = \dot{R}'Y'Y\dot{R} \qquad [A\text{-}16]$$

Thus, the problem has been reduced from 3N to 3N-6 dimensions. The evaluation of Y is the next step.

The matrix Y can be deduced by first considering the relations

$$\mathcal{D}^{-1}\mathcal{D} = [YY_o] \begin{bmatrix} D \\ D_o \end{bmatrix} = [YD + Y_oD_o]$$
$$= I_{3N \times 3N} \qquad [A\text{-}17]$$

and

$$\mathcal{D}\mathcal{D}^{-1} = \begin{bmatrix} D \\ D_o \end{bmatrix} [YY_o] = \begin{bmatrix} DY & DY_o \\ D_oY & D_oY_o \end{bmatrix}$$
$$= I_{3N \times 3N} \qquad [A\text{-}18]$$

where I is the identity matrix. From equation [A-18] one can deduce that

$$DY = I_{3N-6 \times 3N-6}. \qquad [A\text{-}19]$$

If equation [A-17] is transposed to give

$$D'Y' + D_o'Y_o' = I_{3N \times 3N} \qquad [A\text{-}20]$$

and then multiplied on the left by D and on the right by Y to give

$$DD'Y'Y + DD_o'Y_o'Y = DY = I_{3N-6 \times 3N-6} \quad [A-21]$$

another useful relation can be obtained. The matrices D and D_o must be orthogonal so DD_o' is a zero matrix. Therefore, the second term on the left side of equation [A-21] is eliminated and

$$DD'Y'Y = I. \quad [A-22]$$

It follows that

$$Y'Y = (DD')^{-1} = G^{-1} \quad [A-23]$$

where the matrix G is defined as DD'.

The kinetic energy can now be written as

$$2T = \dot{R}'G^{-1}\dot{R}. \quad [A-24]$$

In view of the relation between the components of D and B, the elements of G are

$$G_{tt'} = \sum_{i=1}^{3N} \frac{B_{ti}B_{t'i}}{m_i} . \quad [A-25]$$

The elements of G can now be calculated since the elements of B can be determined from consideration of molecular geometry.

Now both the potential and kinetic energies have been expressed in terms of the internal coordinates as

$$2V = R'FR \quad [A-26]$$

and

$$2T = \dot{R}'G^{-1}\dot{R} . \quad [A-27]$$

The equations of motion of the molecule could be obtained directly from these expressions for T and V by the application of Lagrange's equation

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{R}_t} + \frac{\partial V}{\partial R_t} = 0 \quad t=1,2,\ldots 3N-6. \quad [A-28]$$

However, it is probably more informative to consider the vibrational problem in terms of the normal coordinates.

The Vibrational Secular Equation

The normal coordinates of a molecule are defined such that the expressions for the potential and kinetic energies have the form

$$2V = Q'\Lambda Q = \sum_k \lambda_k Q_k^2 \qquad [A-29]$$

and

$$2T = \dot{Q}'\dot{Q} = \sum_k \dot{Q}_k^2 \qquad [A-30]$$

where Q is a column matrix of the normal coordinates Q_k and Λ is a diagonal matrix of the λ_k.

It has been stated previously that the λ_k are related to the vibrational frequencies ν_k by

$$\lambda_k = 4\pi^2\nu_k^2. \qquad [A-31]$$

This relation is easily verified by considering the equations of motion in terms of the normal coordinates

$$\ddot{Q}_k + \lambda_k Q_k = 0 \quad k=1,2,\ldots,3N-6. \qquad [A-32]$$

These equations are obtained from Lagrange's equation and the expressions for V and T in equations [A-29] and [A-30]. Possible solutions of these equations are the vibrational type solutions

$$Q_k = A_k \cos(2\pi\nu_k t + \epsilon) \qquad [A-33]$$

where A_k is the amplitude, t the time, and ϵ the phase. Substitution of this solution into the equations of motion gives

$$-4\pi^2\nu_k^2A_k \cos(2\pi\nu_k t + \epsilon) + \lambda_k A_k \cos(2\pi\nu_k t + \epsilon) = 0 \qquad [A\text{-}34]$$

and obviously

$$\lambda_k = 4\pi^2\nu_k^2. \qquad [A\text{-}35]$$

The normal coordinates are related to the internal coordinates by the transformation matrix L

$$R = LQ \qquad [A\text{-}36]$$

or

$$Q = L^{-1}R. \qquad [A\text{-}37]$$

Substitution of equation [A-36] into equations [A-26] and [A-27] gives expressions for T and V in the form

$$2T = \dot{Q}'L'G^{-1}L\dot{Q} \qquad [A\text{-}38]$$

$$2V = Q'L'FLQ \qquad [A\text{-}39]$$

Comparison of equations [A-38] and [A-39] with equations [A-29] and [A-30] yields the equations

$$L'G^{-1}L = I \qquad [A\text{-}40]$$

$$L'FL = \Lambda. \qquad [A\text{-}41]$$

Solving equation [A-40] for L' and substituting in equation [A-41] gives

$$L^{-1}GFL = \Lambda \qquad [A\text{-}42]$$

or

$$GFL = L\Lambda. \qquad [A\text{-}43]$$

Thus, L is the matrix which diagonalizes the matrix GF by a similarity transformation. The columns of L are the eigenvectors of the matrix GF and the elements of Λ are the eigenvalues. Equation [A-43] is one form of the secular equation for the vibrational problem and the solution of this equation yields the vibrational properties of the molecule in question. For a nontrivial solution the secular determinant must vanish, i.e.,

$$|GF - \Lambda| = 0. \qquad [A-44]$$

Schachtschneider and Snyder (13) have reported a method for the solution of secular equation [A-44] by means of a digital computer. Although the matrix GF is not symmetric, it can be diagonalized by diagonalizing two symmetric matrices. First, G is diagonalized by solving the secular equation

$$GA = A\Gamma \qquad [A-45]$$

where A is the eigenvector matrix of G, and Γ is the diagonal matrix of eigenvalues of G. A new matrix W can now be defined by

$$W = A\Gamma^{\frac{1}{2}} \qquad [A-46]$$

and applied to F to give

$$H = W'FW. \qquad [A-47]$$

H is a symmetric matrix, since A must be orthogonal and Γ is diagonal, and it can be diagonalized by solving

$$HC = C\Lambda. \qquad [A-48]$$

Substituting the expression of H given in equation [A-47] into equation [A-48] gives

$$W'FWC = C\Lambda. \qquad [A-49]$$

Multiplying on the left by W gives

$$WW'FWC = WC\Lambda \qquad [A-50]$$

and since

$$WW' = G \qquad [A\text{-}51]$$

equation [A-50] takes the form

$$GFWC = WC\Lambda . \qquad [A\text{-}52]$$

By comparison of equations [A-43] and [A-52] one can deduce that

$$L = WC. \qquad [A\text{-}53]$$

Thus, the transformation matrix from normal to internal coordinates can be evaluated by diagonalizing the matrices G and H.

Schachtschneider and Snyder point out several advantages of this method of solving the secular equation [A-43]:

(1) Very fast machine methods, such as Jacobi's method, can be used for diagonalizing the symmetric matrices G and H.

(2) L^{-1} is easily obtained as

$$L^{-1} = C'\Gamma^{-1}W' \qquad [A\text{-}54]$$

since

$$\Gamma^{-1}W' = \Gamma^{-\frac{1}{2}}A' = W^{-1} \qquad [A\text{-}55]$$

(3) Redundant coordinates need not be removed before diagonalizing G. Frequently, it is convenient to use a set of internal coordinates which includes more than the necessary 3N-6 coordinates. In this case the matrix G will have a number of zero eigenvalues equal to the number of redundant coordinates. This will in turn yield a W matrix with zero columns corresponding to the number of redundancies. The resulting matrix H which is constructed using the transformation W will be a 3N-6 x 3N-6 matrix. Thus, the redundancies have been eliminated from the

secular equation when it is expressed in terms of equation [A-48].

Symmetry Considerations

Through the application of group theory the symmetry of a molecule can be utilized to factor the determinant of equation [A-44] into a number of determinants of lower order. This can be accomplished through the introduction of symmetry coordinates, each of which belongs to one of the symmetry species of the molecular point group.

Techniques have been published for systematically setting up symmetry coordinates S_s as linear combinations of internal coordinates R_t according to

$$S_s = \sum_t U_{st} R_t \qquad [A\text{-}56]$$

or in matrix form

$$S = UR \qquad [A\text{-}57]$$

where U is an orthogonal matrix, i.e., $U^{-1} = U'$(3). Thus,

$$R = U'S \qquad [A\text{-}58]$$

and

$$R' = S'U \qquad [A\text{-}59]$$

can be substituted into the expressions for T and V to give

$$2T = \dot{R}'G^{-1}\dot{R} = \dot{S}'UG^{-1}U'\dot{S} \qquad [A\text{-}60]$$

$$= \dot{S}'\mathcal{G}^{-1}\dot{S} \qquad [A\text{-}61]$$

and

$$2V = R'FR = S'UFU'S \qquad [A\text{-}62]$$

$$= S'\mathcal{F}S \qquad [A\text{-}63]$$

where

$$\mathcal{G}^{-1} = UG^{-1}U' \qquad [A-64]$$

$$\mathcal{F} = UFU'. \qquad [A-65]$$

The resulting $\mathcal{G}^{-1}$ and $\mathcal{F}$ matrices will be factored into square blocks along the diagonals, each factored block corresponding to the symmetry coordinates belonging to one symmetry species of the molecular point group. It can easily be shown that there can be no cross terms between symmetry coordinates of different species in the expressions for T and V. As a result of this each factored block can be considered separately and a secular determinant can be formed for each symmetry species where the order of the determinant is equal to the number of normal vibrations of that particular species. Thus, by the use of symmetry coordinates, the vibrational problem can be reduced to several smaller problems, each of which may be solved separately. For example, the treatment of the previous section could be applied to the symmetrized secular equation

$$\mathcal{G}\mathcal{F}\mathcal{L} = \mathcal{L}\Lambda \qquad [A-66]$$

where $\mathcal{L} = UL$ and each symmetry block could be considered separately.

Evaluation of Force Constants

The iterative method which was used to evaluate the force constants is based on a procedure described by King (50). The potential energy is expressed in the usual Urey-

Bradley form

$$\begin{aligned} 2V = &\sum_i [2K_i' r_i \Delta r_i + K_i(\Delta r_i)^2] \\ &+ \sum_j [2H_j' \Delta \alpha_j + H_j(\Delta \alpha_j)^2] \\ &+ \sum_k [2F_k' q_k \Delta q_k + F_k(\Delta q_k)^2] \end{aligned} \qquad [A-67]$$

and the redundant coordinates Δq_k (displacements between nonbonded atoms) are removed. Substitution of the minimum condition $\left(\frac{\partial V}{\partial r_i} = \frac{\partial V}{\partial \alpha_j} = 0\right)$ leaves V as a function of variables which may be independent or may still include redundancies. The potential energy now appears as

$$2V = R'FR \qquad [A-68]$$

in which the elements of the F matrix are linear functions of the Urey Bradley force constants Φ_j

$$f_{tt'} = \sum_j Z^j_{tt'} \Phi_j \qquad [A-69]$$

the coefficients $Z^j_{tt'}$ being determined by the molecular geometry. The $Z^j_{tt'}$ can be defined so that the $f_{tt'}$ are the elements of the F matrix or the elements of the $\mathcal{F}$ matrix. The elements of the F matrix can be arranged into an F vector and the $Z^j_{tt'}$ become the elements of a transformation matrix defined by

$$F^V = Z\Phi \qquad [A-70]$$

where F^V is the F vector and Φ is a vector of UBFC.

If the exact UBFC are known, then the F matrix can be reconstructed from the F vector and the secular equation

$$GFL = L\Lambda \qquad [A-71]$$

can be solved for eigenvectors L_k and eigenvalues λ_k. Since the force constants are usually not known but are approximated, the calculated λ_k will be significantly different from the observed frequency parameters ($\lambda_k^{obs} = 4\pi^2\nu_k^2$). The initial force constants are then refined so that the fit between observed and calculated λ's is improved. Assuming the zeroth order normal coordinates (normal coordinates calculated from the initial force constants) to be fairly close to the true ones, then the secular equation can be written as

$$[G(F_o+\Delta F)]L_o \approx L_o\Lambda^{obs} \qquad [A\text{-}72]$$

where ΔF are the corrections to the force constant matrix and L_o is the normal coordinate transformation for the zeroth order secular equation

$$GF_oL_o = L_o\Lambda_o\ . \qquad [A\text{-}73]$$

Combining equations [A-72] and [A-73] gives

$$G(\Delta F)L_o \approx L_o(\Lambda^{obs} - \Lambda_o) = L_o(\Delta\Lambda). \qquad [A\text{-}74]$$

Since the eigenvectors of the secular equation are normalized so that

$$L'FL = \Lambda \qquad [A\text{-}75]$$

and

$$L'G^{-1}L = I \qquad [A\text{-}76]$$

equation [A-74] can be reduced to

$$L_o'\Delta FL_o = \Delta\Lambda. \qquad [A\text{-}77]$$

Equation [A-77] can be rewritten as a series of equations, one for each root, of the form

$$\Delta\lambda_k = \sum_{t}\sum_{t'}(L_o)_{tk}(L_o)_{t'k}\Delta f_{tt'} \qquad [A\text{-}78]$$

or a new matrix, the Jacobian J, can be defined by

$$\Delta \Lambda^{V} = J(\Delta F^{V}) \qquad [A\text{-}79]$$

where the ΔF^{V} and $\Delta \Lambda^{V}$ are column matrices or vectors. Since the $f_{tt'}$ are linear functions of the Φ_j equation [A-69] also holds for the difference form

$$\Delta F^{V} = Z\Delta\Phi. \qquad [A\text{-}80]$$

Substitution for ΔF^{V} in [A-79] gives

$$\Delta\Lambda^{V} = JZ\Delta\Phi \qquad [A\text{-}81]$$

The dimension of the matrix JZ is n x m where n is the number of vibrational frequencies and m is the number of UBFC.

If n = m then expression [A-81] gives n equations which can, in principle, be solved to give n corrections to the force constants. If $n > m$, then the method of least squares provides a convenient method of solving for the $\Delta\Phi_j$. The least squares method consists of minimizing the weighted sum of the squared errors S defined by

$$S = \sum_k p_k((\lambda_o)_k + \Delta\lambda_k - \lambda_k^{obs})^2 \qquad [A\text{-}82]$$

The p_k are weighting factors and are usually taken as $1/\lambda_k$ and the $\Delta\lambda_k$ are the elements of the $\Delta\Lambda^{V}$ of equation [A-81]. The minimization condition, leads to the normal equation

$$(JZ)'P\,\Delta\Lambda^{V} = (JZ)'P(JZ)\,\Delta\Phi \qquad [A\text{-}83]$$

where P is the diagonal matrix of weighting factors p_k. The solutions $\Delta\Phi$ of this equation are the least square corrections to the UBFC. However, since the $(L_o)_{tk}$ of equation

[A-78] were only approximate, the corrected force constants will still deviate from the best values and the perturbation must be repeated using the revised normal coordinates to set up a new J matrix. The cycle is repeated until further refinement produces no change in the resulting force constants.

The program "Overend" was used for the calculation of the UBFC. The program will not be discussed in detail for similar programs have been described in the literature by Overend and Scherer (10) and by Schachtschneider and Snyder (13).

As described previously, this program employs the W matrix to introduce the kinetic energy in the vibrational problem. The W matrix and the Z matrix are determined by separate programs and are part of the input for the program "Overend". This program is capable of evaluating a set of force constants for a series of molecules. The required input is as follows:

(1) A vector of approximate UB force constants Φ_o.

(2) A Z matrix.

(3) A W matrix.

(4) The values of the observed frequencies.

(5) A weight matrix P, usually taken as Λ^{-1}.

Items (2) through (5) are repeated for each molecule of the series. The output from the program "Overend" includes the following:

(1) The final UB force constants.

(2) The calculated frequencies for each molecule.

(3) The L matrix for each molecule.

(4) The potential energy distribution for each molecule. The distribution of potential energy among the internal coordinates is determined by forming the matrix product

$$\Lambda^{-1} J Z \Phi^{*}$$

where Φ^{*} is a diagonal matrix of UB force constants (51).

(5) Dispersions and co-error matrices for the calculated frequencies and force constants.

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