



Force constant vs. bond length relations [pt.1] : The use of frequency modulation to generate a reference beam for atomic absorption analysis [pt.2]  
by Andrew Mackie Held

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree. of  
DOCTOR OF PHILOSOPHY in Chemistry  
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Abstract:

In the first part quadratic, cubic, and quartic force constants have been calculated from the known spectroscopic constants of both ground and excited states of those diatomic molecules composed solely of elements of the first row of the periodic table. The calculated force constants have been compared with bond lengths, and correlations between the force constants and bond lengths have been noted. Force constants were also calculated using theoretical data, and the theoretical constants have been compared with the experimental constants. The force constant behavior is interpreted in terms of free-electron theory and a constant repulsion curve.

In the second part the feasibility of applying various physical effects in the frequency modulation of a light beam or source has been determined, as related to the generation of a reference beam for atomic absorption analysis. The Zeeman effect was found to be the best suited for such a purpose, and an apparatus for determining mercury, which utilizes this effect, was constructed and tested. Because of its background correction capability, the instrument can easily and reliably detect nanogram quantities of mercury without the use of chemical separation techniques.

I. FORCE CONSTANT vs. BOND LENGTH RELATIONS  
II. THE USE OF FREQUENCY MODULATION TO GENERATE A  
REFERENCE BEAM FOR ATOMIC ABSORPTION ANALYSIS

by

ANDREW MACKIE HELD

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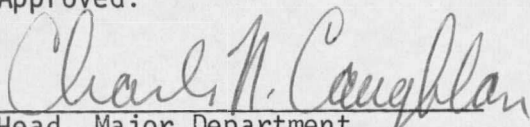
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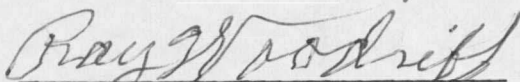
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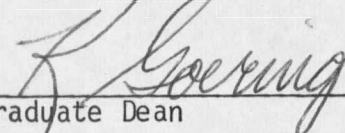
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## ABSTRACT

In the first part quadratic, cubic, and quartic force constants have been calculated from the known spectroscopic constants of both ground and excited states of those diatomic molecules composed solely of elements of the first row of the periodic table. The calculated force constants have been compared with bond lengths, and correlations between the force constants and bond lengths have been noted. Force constants were also calculated using theoretical data, and the theoretical constants have been compared with the experimental constants. The force constant behavior is interpreted in terms of free-electron theory and a constant repulsion curve.

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## PART I

### FORCE CONSTANT vs. BOND LENGTH RELATIONS

## INTRODUCTION

Many chemists and physicists have attempted to find a general empirical relation between the force constant, or stiffness, of a molecule and the internuclear distance, since, as Herzberg<sup>(1)</sup> states, ". . . no satisfactory theoretical relation between the force constant and the bond length has been found". Recently effort has been centered on the determination of relationships for particular atom pairs, and relations have been found which fit the experimental data quite closely. To date only the atom pairs carbon-oxygen, nitrogen oxygen, and nitrogen-nitrogen have been fitted to such a relation. This work, then, is an attempt to enlarge the number of known individual relations and to observe any general patterns arising from them, with the ultimate goal in mind of obtaining a general empirical force constant vs. bond length relation. These empirical relations and those for higher-order force constants will be of use in determining the general behavior of molecular potential energy curves and hopefully will guide the way toward the development of a satisfactory theoretical understanding of the relation between the force constant and the bond length.

One often hears of the importance of chemical intuition in studying the chemical bond. Yet, we seem to easily forget that the flowers of chemical intuition need the fertile soil of a large body of facts. The compilation and study of data on diatomic molecules has been

considered to be too far afield for the chemist, beneath the dignity of the physicist, and one of those things for which the spectroscopist never has enough time. The vast body of knowledge which we possess concerning the diatomic molecules has not been collected and used as it should in the study of the nature of the chemical bond, nor has it been used in the study of simple polyatomic molecules. It is in this never-never land between the diatomic and polyatomic molecules, where chemical intuition for lack of easily accessible data cannot be applied, that I have tried to reach.

The cataloguing of this vast body of data is the first step in the development of a "satisfactory theory." Just as the data collected by Tycho Brahe served for twenty-five years as the basis for Kepler's studies, the collected data can be analyzed until all the molecular properties are correlated with one another. We may then hope that the explanations for these correlations will provide the basis for some fundamental changes, just as Newton's predictive laws of motion superseded the explanations of Kepler.

## CHAPTER I

### Historical Review

The introduction of quantum mechanics in the 1920's made possible the interpretation of molecular spectra in terms of fundamental molecular constants. A. Kratzer<sup>(2)</sup>, in 1920, was the first person to observe a relation between vibrational frequency and bond length of a molecule. In 1925 R. Mecke<sup>(3)</sup> noticed that the vibrational frequency and the bond length followed approximately the relation

$$(\text{bond length})^2(\text{vibrational frequency}) = \text{Constant} \quad (1-1)$$

for different electronic states of the same molecule. In 1929 P. Morse<sup>(4)</sup> found that a single relation,

$$(\text{bond length})^3(\text{vibrational frequency}) = \text{Constant}, \quad (1-2)$$

could be used for the electronic states of different diatomic molecules, giving a probable error of less than four percent. Thus, from a single empirical relation, if the bond length were known for one state of a diatomic molecule, the vibrational frequency of that state could be determined within a few percent, or vice versa. Morse also noted that the best fit was obtained for molecules which were symmetric and therefore postulated the need for the introduction of an "unsymmetry factor" of the form  $(4m_1m_2/[m_1+m_2])^{1/4}$  where  $m_1$  and  $m_2$  are the masses of

the atoms, to correct for the deviation shown by very unsymmetric molecules such as the diatomic hydrides. He observed that the deviation of a state from the relation corresponded to a poor fit of the data for that state to a particular potential energy curve which is now commonly called the Morse potential function. The Morse relation was later improved by Clark<sup>(5)</sup> to

$$R_e^3 w_e n^{1/2} = C, \quad (1-3)$$

where  $n$  is the number of electrons outside the closed atomic shells,  $C$  is a constant that is the same for molecules with the same closed atomic shells, and  $R_e$  is the equilibrium bond length. The relation was then further modified<sup>(6,7,8,9)</sup> to make it hold for various isotopic molecules by introducing the force constant,  $K_e$ , in place of the vibrational frequency,  $w_e$ . The relation then becomes

$$R_e^6 K_e n = C. \quad (1-4)$$

Another relation having a slightly different form was proposed by Badger<sup>(10,11)</sup>:

$$K_e (R_e - d_{ij})^3 = C. \quad (1-5)$$

Here  $d_{ij}$  is a constant that is different for each type of molecule, and  $C$  is the same for all molecules. This relation, known as "Badger's rule,"

was found to be applicable to polyatomic molecules as well as to diatomic molecules and has found wide use. Glockler and Evans<sup>(12)</sup> later improved the accuracy of Badger's rule by giving C slightly different values for different types of molecules.

Starting in the 1930's, many attempts were made to find accurate but general and simple functions relating potential energy to interatomic distance and the force constant. Huggins<sup>(13,14)</sup>, by modifying the Morse potential function, obtained a force constant relation which was later further simplified to the form

$$\ln(K_e) = AR_e + B \quad (1-6)$$

by Wu and Chao<sup>(15)</sup>. At about the same time Linnett<sup>(16,17)</sup> suggested a new potential function which gave a force constant relation closely resembling the purely empirical relation which had been proposed by Morse. The validity of the various force constant and potential functions which were postulated, however, could not be tested simply because of a lack of detailed information on the force constants and potential functions of most molecules. Subsequent attempts to develop valid functions were also hampered by a lack of data to provide adequate testing.

Attempts have also been made to relate force constants to molecular constants other than the interatomic distance. Relations relating the force constant and bond length with the heat of dissociation were

proposed<sup>(18,19)</sup> but confirmation of the relations again could not be made because of large uncertainties in the values of the dissociation energies of many important molecules. Also, the dissociation energy depends upon the long range force fields to a much greater extent than do the force constant and bond length. The last major effort to devise a general force constant relation was made by Walter Gordy<sup>(20)</sup>, who took into account bond order,  $N$ , and electronegativity,  $x$ , as well as bond length,  $r$ , and obtained a formula,

$$K_e = aN(x_a x_b / r^2)^{3/4} + b, \quad (1-7)$$

with an average deviation of two percent for seventy-one cases.

In the last ten years spectroscopic constants have been determined for a large number of states of some of the simpler molecules. This has encouraged several authors to reformulate new force constant relations by concentrating on single molecules for which a large amount of data is present. In 1961 Ladd, et. al.<sup>(21)</sup> collected the available data on the carbon-oxygen bond and fit the force constants and bond distances to the relation

$$K_e = AR_e^n. \quad (1-8)$$

They later extended this work to a study of the nitrogen-oxygen bond<sup>(22)</sup> and obtained an accurate relation of the same form for it. In 1966

J. C. Decius<sup>(23)</sup> published a similar study of the nitrogen-nitrogen bond and found a relation of the same form which was valid over several orders of magnitude in the force constant.

No one, however, has published a comprehensive and up-to-date collection of the known spectroscopic constants, nor has anyone published a comprehensive study of the force constant relations for other types of chemical bonds, though some attempts have been made to observe correlations between the spectroscopic and molecular constants of ground-state molecules. Herschbach and Laurie<sup>(24)</sup> in 1961 studied the dependence of anharmonic potential constants on bond length for some ground-state molecules. Also, in 1964 Johnson<sup>(25)</sup> suggested the extension of force constant relations to the noble-gas or Lennard-Jones type atom pairs. In 1968, during the course of this work, Calder and Reudenberg<sup>(26)</sup> examined the spectroscopic constants and force constants of ground-state diatomic molecules and determined some relations between the constants.

## CHAPTER II

### Theoretical Review and General Theoretical Results

The force constant of a molecular bond is defined in terms of the potential energy function of that molecule. The problem of understanding molecular force constant relations, therefore, is essentially one of understanding the potential functions of molecules. The potential function is most readily defined within the context of the Born-Oppenheimer approximation,<sup>1</sup> which essentially states that the atomic nuclei are infinitely heavier or slower than the electrons. Under the Born-Oppenheimer approximation nuclei move sufficiently slowly so that they can be considered to be at rest for a given electronic state. Then for any internuclear distance,  $R$ , there will correspond an actual energy  $E(R)$ . The energy  $E(R_i)$  for a given internuclear separation,  $R_i$ , is called the "potential energy," though the term is inaccurate in that  $E(R_i)$  includes the kinetic energy of the electronic motion. Thus, the potential function or potential energy curve, which is defined as  $E(R)$ , includes both kinetic and potential energies.  $E(R)$ , however, acts as a potential energy for the nuclear motion, so that there is

---

<sup>1</sup>The Born-Oppenheimer approximation is sometimes called the adiabatic approximation; however, in modern usage<sup>(27)</sup> it is considered to be a special case of the adiabatic approximation.

some justification for the use of the term "potential energy."<sup>1</sup>

For a diatomic molecule the potential function,  $E(R)$ , closely approximates a parabola near the minimum. The nuclei of the molecule behave, therefore, very much like a harmonic oscillator near the equilibrium position. The force constant, being simply the curvature or second derivative of the curve at the minimum, allows the determination of the shape of the potential curve near the equilibrium position. A study of the relation of the harmonic oscillator force constant to other molecular constants then gives insight into the behavior of potential energy curves near the equilibrium position.

The harmonic oscillator approximation is, though, of limited value in any analysis of the shape of the potential curve; a much more flexible and accurate approximation may be used by making what is commonly called the "force constant" the first-order term in a power series expansion about the equilibrium internuclear distance,  $R_e$ . This ordinary force constant is then called the quadratic or harmonic force constant, and the higher order coefficients in the expansion are called the cubic, quartic, etc., force constants and represent the contribution of curves of the form

$$E = \frac{L_e}{6} (R - R_e)^3, \quad E = \frac{M_e}{24} (R - R_e)^4, \quad \dots \quad (2-1)$$

---

<sup>1</sup>The issue is further confused by the fact that through the use of the Hellman-Feynman theorem one may calculate the "potential energy" using only electrostatic repulsions and attractions.

to the shape of the potential curve near the minimum. An  $n$ th-order force constant, then, is also the  $n$ th-order derivative of the potential curve at the minimum. The shape of a potential curve near its minimum may then be easily analyzed, since the representation as a power series allows the decomposition of the curve form into contributions from various elementary curves.

To simplify the problem of comparing the relative shapes of the potential curves of different molecules, the power expansion may be carried out in terms of reduced coordinates. Such an expansion is called a Dunham<sup>(28)</sup> function and will be used here. The nomenclature and formulas needed to make the expansion are given in Appendix A.

We must remember, though, that the potential curve and force constant are only mental constructs, and information concerning molecules must ultimately be obtained from spectroscopic data. Formulas giving the values of the Dunham coefficients or force constants in terms of spectroscopic constants have been derived<sup>(28,29)</sup> and are reproduced in Appendix B. In this paper all forces are expressed in millidynes and bond lengths in Angstroms.

The various spectroscopic constants needed are in turn determined from the actual spectra. Analysis of the detailed structure of the spectra of diatomic molecules leads to the determination of the electronic energy levels, including the energy levels of the vibrationally and rotationally excited states. Using quantum mechanics, the

vibrational and rotational energy levels for each electronic state may be represented as a power series in terms of the vibrational and rotational quantum numbers,  $v$  and  $J$ :

$$E(v,J)/hc = w_e(v + 1/2) - w_e x_e(v + 1/2)^2 + \dots + B_v J(J + 1) - C_v J^2(J + 1)^2 + \dots \quad (2-2)$$

$w_e$  and  $w_e x_e$  are the equilibrium vibrational spectroscopic constants.  $B_v$  and  $C_v$  are rotational spectroscopic constants. The "term value"  $G$  will be used subsequently in the place of  $E/hc$ . Once the energy levels are known from the spectra the equilibrium constants can be determined. The rotational equilibrium constants,  $B_e$  and  $\alpha_e$ , are determined from the power series expression

$$B_v = B_e - \alpha_e(v + 1/2) + \dots \quad (2-3)$$

The equation

$$B_e(\text{cm}^{-1}) = 16.857/\mu R_e^2(\text{\AA}) \quad (2-4)$$

allows the determination of the equilibrium internuclear distance, once the reduced mass is known. Quite often (nearly always in the case of polyatomic molecules) only the fundamental vibrational frequency,  $\nu(1-0)$  or  $\Delta G(1/2)$ , is known. It is often used as an approximation for  $w_e$ . A

better approximation is

$$\Delta G(1/2) = w_e - 2w_e x_e \quad , \quad (2-5)$$

$w_e x_e$  may sometimes be estimated from the Morse relation

$$D_e = w_e^2 / 4w_e x_e \quad , \quad (2-6)$$

where  $D_e$  is the equilibrium dissociation energy, or from the well-known rule that  $w_e x_e / w_e$  is only slightly smaller than  $\alpha_e / B_e$ . Similarly, often only  $R_v = 0$ , or  $R_0$ , is known, so that  $R_e$  cannot be determined (again this is nearly always the case with polyatomic molecules). One is often forced to use  $\Delta G(1/2)$  and  $R_0$  in determining the force constant and bond length. No mention has been made in the literature of the magnitude of error incurred by the use of  $\Delta G(1/2)$  and  $R_0$ , and their substitution for  $w_e$  and  $r_e$  has implied that the error is rather small. Expressions for the magnitude of the deviation of  $\Delta G(1/2)$  from  $w_e$  and of  $R_0$  from  $R_e$  are derived in Appendix C. For a normal molecule  $w_e x_e / w_e$  and  $\alpha_e / B_e$  are usually less than 0.02. Using the expression derived in the appendix we then find that the use of  $\Delta G(1/2)$  gives a force constant which is low by eight percent or less, whereas  $R_0$  is only one-half percent or less larger than  $R_e$ . Whether the use of  $\Delta G(1/2)$  and  $R_0$  in combination with each other would result in a large error would depend upon the slope of the force constant vs. bond length curve.

It is possible to study the relative shapes of molecular potential curves then, providing that a sufficient number of spectroscopic constants are available for those molecules. In recent years large amounts of new spectroscopic data have become available, making it possible that an in-depth analysis might reveal some basic new relations governing the shapes and behavior of potential curves.

It will be advantageous to try at the very start to determine what additional factors can influence the relation between force constant and bond length. It is appropriate, then, to ask at this point what molecular properties might be expected to have an influence upon the relations. Any properties which would effect the shape of the potential curve would also be expected to have an influence upon the force constant and the bond length.

The dissociation energy of diatomic molecules has been related to the force constant and bond length by several authors<sup>(16,18)</sup>. It is well known that a high dissociation energy is associated with a large force constant and a small internuclear distance for a normal chemical bond. The dissociation energy also has long been recognized as a fundamental parameter in the determination of the shape of the potential energy function. Thus, the dissociation energy may be considered a probable contributing factor to force constant relations, and its influence should be examined carefully. However, reliable values for dissociation energies are not generally available. Also, it is almost certain that

the influence exerted by the dissociation energy will be extremely variable. Whenever accidental "level crossing" occurs the dissociation energy of the state will be anomalous, and the degree of influence of the dissociation energy will depend on whether or not it is possible to take the level crossing into account. The dissociation energy is also determined by long range forces, so that sometimes the dissociation energy will be anomalous even if level crossing does not occur. Thus a careful analysis of the influence of the dissociation energy would be somewhat premature.

The degree of ionic character of a bond is also an important factor in determining the shape of a potential curve. Ionic bonds are known to have potential curves of a different shape or form than covalent bonds<sup>(30,31,32)</sup>. About the only experimental measure of ionic character is the dipole moment; however, ionicity is a rather variable function of interatomic distance, so that the change in dipole moment with interatomic distance, i.e. the dipole derivative, would be important as well. It may be noted that for ground state molecules ionicity correlates rather well with the electronegativity difference between the constituent atoms. Excited states will vary considerably in ionic character even for homonuclear diatomic molecules, making the dipole moment and electronegativity concepts difficult to use. Since data concerning dipole moments and dipole derivatives are rather sparse, a systematic study of the influence of ionic character or ionicity cannot be made.

The number of electrons and protons in a molecular system is, of course, of extreme importance for any molecular property. Likewise, the empirical information on force constants and bond lengths collected here will show conclusively that the number of protons present influences the relation between force constant and bond length sufficiently to make classification of the relations in terms of atomic number absolutely essential. The influence of the atomic number upon the atomic core radii or radial electron densities is apparently the cause of the strong dependence upon the atomic numbers. The number of electrons present, though, will be shown to have no apparent effect upon the relations.

Since the force constant and bond length may be defined in terms of the vibrational and rotational spectroscopic constants, any relations between the spectroscopic constants will be reflected in the force constant vs. bond length relations, and vice versa. Thus the determination of force constant relations provides a means of studying the relations between spectroscopic constants as well.

The total electronic energy at the equilibrium distance might be expected to have some influence upon the force constant relations, since it plays an important role in theoretical problems. It will be shown that total energy correlates rather poorly with equilibrium distance and force constant; however, it will be of interest to check for a correlation of total energy with the deviation of force constants from "expected" values.

Finally, there are many theoretical properties such as "overlap population" and quantum number which one could attempt to relate to the force constant and bond length. Such an attempt, the author feels, would not be in keeping with the essentially phenomenological approach taken here, if the attempt were made on a large scale. The relations obtained will be certainly useful in evaluating various theoretical approaches and approximations, even though this thesis is to be considered an attempt to generate representation-independent concepts. Therefore, the compatibility of only some of the simpler molecular models with the force constant relations will be evaluated.

An effort will be made to provide a reasonable theoretical context for the interpretation of force constant relations. Since force constants are derivatives of the total energy, it is necessary only to relate the derivatives to the values of some fundamental theoretical constructs in order to provide such a theoretical context. The total potential and kinetic energies are two such fundamental constructs. Approximate electronic contributions may be obtained from one-electron energies determined from simple quantum-mechanical calculations.<sup>1</sup> The energies may then be related to the energy derivatives through the virial theorem. The virial theorem, though, does not by itself allow the unique determination of the kinetic and potential energies from the

---

<sup>1</sup>The nuclear-nuclear potential is simply  $Z_1 Z_2 / R$  where  $Z_1$  and  $Z_2$  are the atomic numbers. The nuclear kinetic energy is negligible under the Born-Oppenheimer approximation.

energy derivatives. By making some reasonable assumptions, however, the virial theorem may be used to determine the behavior of the force constants, or energy derivatives.

The virial theorem determines the relative magnitudes of the kinetic and potential energies of any molecular system. The general forms of the theorem given below<sup>(34)</sup> are valid for any diatomic molecule within the Born-Oppenheimer approximation.<sup>1</sup>

$$RE' + 2E = V, \quad RE' + E = -T, \quad (RT' + 2T) + (RV' + V) = 0 \quad (2-7)$$

T is the total kinetic energy, V is the total potential energy, and derivatives are indicated by primes. The theorem is valid for any value of the internuclear distance, R. Differentiation of the virial theorem allows expressions for the potential constant, to be derived: thus,

$$R_e K_e = -(T)'_{R_e} = (V)'_{R_e} \quad (2-8)$$

and

$$V' = V'_{\text{nuclear}} + V'_{\text{electronic}} \quad (2-9)$$

combine to give

$$R_e K_e = -Z_1 Z_2 / R_e^2 + (V_{\text{electronic}})'_{R_e} \quad (2-10)$$

---

<sup>1</sup>Again the nuclear kinetic energy is neglected.

Borkman and Parr<sup>(33)</sup> have recently used this theorem to interpret the behavior of potential constants and potential curves. Their work and that of Knoll<sup>(34)</sup> will serve largely as the basis for the present interpretation through the virial theorem. Borkman and Parr based their analysis upon the fact that the Born-Oppenheimer electronic energy satisfied the differential equation

$$R^2 E'' + 4RE' + 2E = (-1/R)(R^2 T)' , \quad (2-11)$$

which may be derived from the virial theorem. The author has shown in Appendix D, however, that the same method may be used to generate the more general differential equation

$$R^2 E'' + (n + 2)RE' + nE = -(R^n T)' / R^{n-1} , \quad (2-12)$$

where  $n$  is greater than one. If the right hand side of equation (2-12) is set identically equal to zero, then all of the solutions of the equation will be reciprocal functions of the form

$$V = A/R + V_n/R^n + V_0 \quad (2-13)$$

and

$$T = T_n/R^n + T_0 , \quad (2-14)$$

where

$$V_n/T_n = -(n - 2)/(n - 1) \quad (2-15)$$

If the right hand side of equation (2-12) is a constant, then the solutions will be of the form

$$V = A/R + V_n/R^n + V_0 \quad (2-16)$$

and

$$T = B/R^2 + T_n/R^n + T_0 \quad (2-17)$$

Thus the differential equation of Borkman and Parr forms a particularly simple case in which the homogenous solutions are of the form

$$V = -A/R + \text{Const.} \quad (2-18)$$

and

$$T = B/R^2 + \text{Const.} \quad (2-19)$$

The general solution to equation (2-12) is

$$E(R) = A/R + B/R^n - (1/R) \int T(R) dR \quad (2-20)$$

Since the general solution of the virial equation is

$$E(R) = A/R - (1/R) \int T(R) dR \quad (2-21)$$

it is seen that the method used by Borkman and Parr introduces extraneous solutions. The method employed by Knoll avoids this difficulty by using the virial theorem directly; therefore, it is to be preferred. The force constant relations derived by Borkman and Parr then arose essentially from their assumption that

$$T = T_0 + T_2/R^2 \quad (2-22)$$

rather than from their treatment of the virial theorem. I introduce as an assumption equation (2-13). This assumption, because of its more general nature, can be expected to fit the data much better than the assumption of Borkman and Parr.

It should be noted here that assuming a functional form for the kinetic energy, potential energy, or total energy automatically allows the determination, via the virial theorem, of the form for the other two types of energy. Thus it really makes no difference whether one works with  $T(R)$ ,  $V(R)$ , or  $E(R)$  in determining force constant relations or in determining energy relations from the force constant relations.

From the assumption of Borkman and Parr the relations

$$L_e = -6K_e/R_e \quad (2-23)$$

and

$$M_e = 36K_e/R_e^2 \quad (2-24)$$

and

$$K_e M_e / L_e^2 = 1 \quad (2-25)$$

are obtained by differentiation of the virial theorem and substitution.

From the author's assumption the relations

$$L_e = -(n + 4) K_e / R_e, \quad (2-26)$$

$$M_e = (n^2 + 7n + 18) K_e / R_e^2, \quad (2-27)$$

and

$$K_e M_e / L_e^2 = 1 + (2 - n) / (n + 4)^2 \quad (2-28)$$

are obtained, and again the relations of Borkman and Parr form a special case where  $n$  is equal to two.

There is another useful theorem which relates the energy to any parameter being used in the determination of the energy. It is called the Hellman-Feynman theorem and usually is written in the form

$$\frac{\partial E_n}{\partial \lambda} = \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n d\tau. \quad (2-29)$$

The formula is very useful because we can substitute the internuclear distance or the force constant in as a parameter. By using the internuclear distance as the parameter one obtains the "electrostatic theorem," which essentially states that the force on the nucleus can be

determined by simple electrostatics as the sum of the nuclear-nuclear repulsion and an electron-cloud attraction. The virial theorem may also be derived from this theorem<sup>(35)</sup>. Thus, by using the virial theorem we are actually also using the Hellman-Feynman theorem.

Before pursuing complicated or abstract models it is appropriate to ask if there are any simple classical models which one may use to account for the force constant relations. Indeed, there are several very simple classical models from which to choose to account for the basic exponential relation between force constant and bond length. The simplest model of all is that of two balls and a spring. If one varies only the length of the spring, then the relation

$$K_e = AY/R_e \quad (2-30)$$

holds, since Young's Modulus,  $Y$ , and the cross-sectional area,  $A$ , are constant and represents the force of restitution per unit length of spring. If we restrict the spring so that it has the same amount of material no matter what its equilibrium length is, then the relation becomes

$$K_e = VY/R_e^2, \quad (2-31)$$

where the volume,  $V$ , is constant. Still, the classical ball and spring model is unsatisfactory, as there is no way to further modify the model without making it seem somewhat contrived.

There does exist an extremely simple quantum - mechanical

model which, with the use of a few parameters, actually reproduces both qualitatively and quantitatively the basic relation between the force constant and bond length in molecules. It is called the free-electron model. Some attempts have been made to explain the basic force constant vs. bond length behavior using simple free-electron models<sup>(10,33,36,37)</sup>. The model, however, has not been carefully and extensively treated in any of the cases.

There are different types of free-electron models, the least sophisticated of which is the particle-in-a-box model. If we consider the valence or bonding electrons in the molecule as being constrained to move only along the axis in a region whose boundaries are at the nuclei, then we have a fairly satisfactory one dimensional particle-in-a-box model. It gives the relation

$$K_e = (h^2/4m_e)/R_e^4 \quad . \quad (2-32)$$

If we allow motion in all three dimensions and further assume that the boundaries in the lateral dimension remain constant, then we find that the force constant again varies as the inverse fourth power of the internuclear distance. In fact, the relation obtained is exactly equation (2-31). If the lateral boundaries are allowed to expand and contract along with the axial boundary one still obtains an inverse fourth power relation! It is important to remember that this model only assumes that the bonding or valence electrons behave as free electrons

confined to the region between the nuclei. No other assumptions are involved. The model may be modified by changing the number of electrons participating or by changing the rules for determining the boundaries. It is very easy to reproduce the empirical force constant to bond length relations by making such modifications. The inverse fourth order dependence of the force constant applies for any shape of box one chooses, as is shown in Appendix E.

One might hope also that there is some connection between the form of the potential energy curves of individual states and the form which the force constant vs. bond length relation takes for the multitude of states. There are many satisfactory mathematical forms for describing a potential energy curve<sup>(16,17,29,38-43)</sup>. Most of these forms can be made consistent with the empirical force constant relations because a separate set of parameters is used for each state. If one could reduce the number of empirical parameters in the potential energy curves to the point where a specific force constant bond length will be predicted, then one might gain some insight into the factors which could relate the force constant behavior to the form of the potential energy curve. Such models will be discussed later.

Another problem requiring some theoretical consideration is whether the force constants of polyatomic molecules and crystals are comparable in the same sense as those of diatomic molecules. For polyatomic molecules the potential energy is written out in terms of a "General Valence

Force Field" in which there is a force constant for each internal coordinate and an interaction force constant for each combination of two internal coordinates. The force constant then becomes a symmetric matrix of force constants, in which the diagonal constants are the force constants for the internal coordinates, and the off-diagonal elements correspond to corrections for the non-additivity in combinations of the internal coordinates. Since the internal coordinates are simply changes in the bond lengths and bond angles one would hope that the force constant corresponding to a particular bond would be analogous to the diatomic force constant for that bond. From an intuitive point of view one might wonder if this is actually true, since there is no physically realizable polyatomic vibration which can simulate completely the diatomic vibration. However, the force constants in the GVFF approximation correspond to vibrations that are not physically realizable either, so that the diagonal stretching force constants do correspond to diatomic vibrations. The off-diagonal elements represent coupling between the idealized individual oscillators. There is one catch, though. When a diatomic molecule vibrates, the non-binding electrons are free to relax into their optimum positions for each value of bond length. The molecule then follows its reaction coordinate during the vibration. By introducing the coupling constants in the GVFF method, one freezes the electrons in the other bonds, so that the idealized vibration of a single bond involves no relaxation of the electrons outside the bond in question. Instead this

relaxation of the electrons and nuclei is handled by the off-diagonal interaction constants. Thus, the idealized diatomic molecule of the GVFF method does not follow the actual reaction coordinate. Force constants computed by this method, then, would be expected to be higher than those of the corresponding actual diatomic molecules, especially if many other bonds are adjacent to the bond in question! This difference apparently has not been considered by any previous workers. It is possible to remove this constraint from the polyatomic force constants if the interaction force constants are known. One then has the problem of determining if a motion along the reaction coordinate is a better approximation than the constrained motion. If another bond is being appreciably strengthened while the bond in question is stretching, then the unconstrained force constant will be appreciably lower than that for the diatomic molecule!

Lattice vibrations in crystals do not admit a simple interpretation, principally because of the importance of long-range forces in crystals.

## CHAPTER III

### Procedure

No comprehensive listings are available of the spectroscopic constants of the known diatomic molecules; therefore, a literature search was conducted to obtain all of the spectroscopic data needed to determine the Dunham constants  $a_0$ ,  $a_1$ , and  $a_2$  for as many of the electronic states as possible of all of the known diatomic molecules and polyatomic molecules. Data on polyatomic molecules are, however, in almost every case insufficient for the calculation of these constants. The search encompasses all of the literature listed by Chemical Abstracts through December, 1970. The spectroscopic constants needed were  $w_e$ ,  $w_e x_e$ ,  $\alpha_e$ ,  $B_e$ , and  $r_e$  and are listed in Appendix F for most of the diatomic molecules for which the constants have been determined. The Dunham and Maclaurin expansion coefficients, or force constants, were calculated for these molecules using the SDX Sigma 7 computer on campus and are listed in Appendix G. For those molecules having a sufficiently large number of known electronic states a least-squares analysis of the quadratic force constant vs. bond length relation was carried out. Deviations of particular force constant values from the "expected" least-squares values were then calculated and compared with the higher-order force constants and with any molecular properties which might be expected to influence them. The results of the least-squares calculations are summarized in Appendix H.

## CHAPTER IV

### Data Analysis

#### Hydrogen-hydrogen Bond

The hydrogen molecule is the simplest molecular system known and will be treated in some detail, especially from the viewpoint of theory, since it is the only molecule for which accurate wave functions may be obtained without the use of a large amount of computer time. Also, current progress toward better quantum mechanical calculations is leading to increasingly complex wave functions, making it more and more difficult to relate them to qualitative ideas about chemical bonding. Only for hydrogen does the development of conceptual or intuitive interpretations seem likely to have a direct or apparent relation to the wave functions.

The only molecules in existence which have hydrogen-hydrogen bonds are the hydrogen molecule and the hydrogen molecule ions. The relation between force constant and bond length for the hydrogen-hydrogen bond, as obtained from a least squares analysis, is given in Appendix H and shown graphically in Figure 1 and Figure 2. These graphs exhibit some scattering, as do all force constant vs. bond length plots. One would, of course, wish to know the cause of this scattering. Also, were the cause known, appropriate corrections might be made to give a more nearly exact relation. I propose now to correlate the deviations of the individual states from the "expected" force constants to other

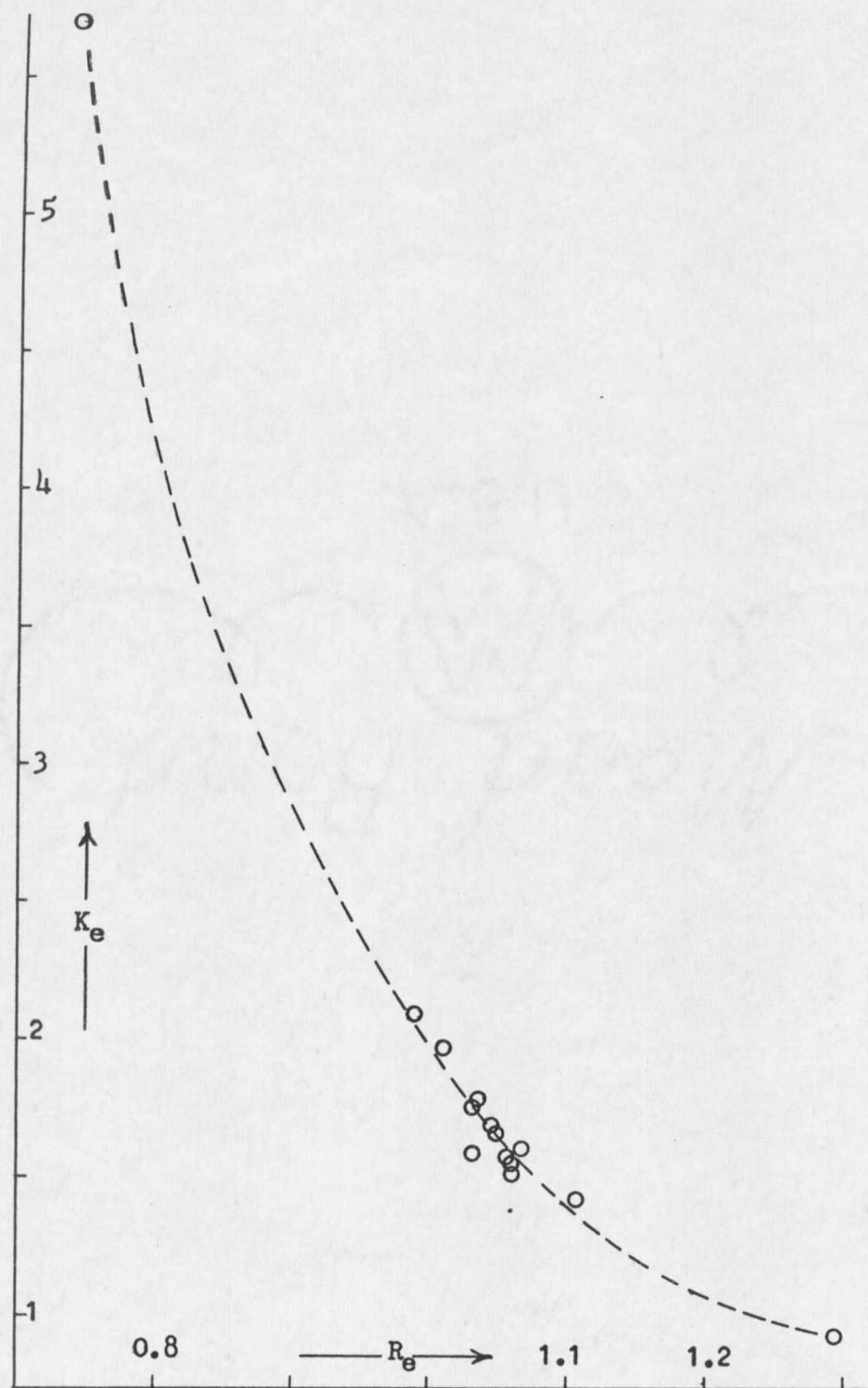


Figure 1. Hydrogen-hydrogen bond, long range graph

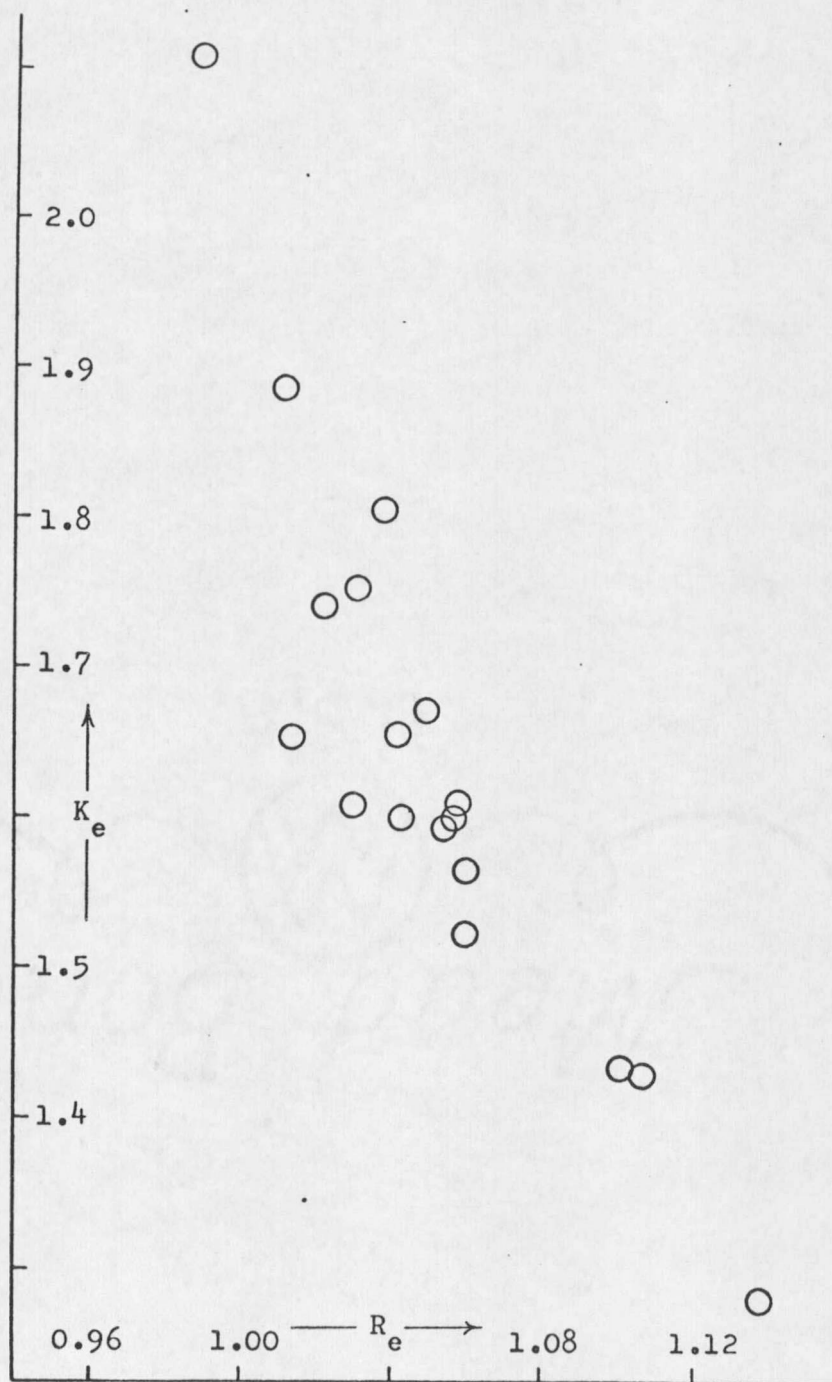


Figure 2. Hydrogen-hydrogen bond, short range graph

properties of the molecule. Because an ordinary least-squares analysis weights the end points heavily if they are somewhat isolated, the end points often will not be included in the analysis of the deviations. It is noted that the triplet states have a positive average deviation, whereas the deviation of the corresponding singlet states is negative, indicating that triplet states tend to have higher force constants than singlet states for a given equilibrium internuclear distance. No correlation of the deviations with any other properties is evident.

The simplest molecule within the hydrogen group and the simplest molecule of all is the hydrogen molecule ion,  $H_2^+$ . From Figure 2 we notice that the force constant and bond length of the hydrogen molecule ion are very close to those of many of the excited states of the hydrogen molecule. Thus, the relation between force constant and bond length would appear to be strictly a function of the number of protons present in the system rather than of the number of electrons present. With this in mind, let us re-examine some models:

The simplest model which will duplicate the force constant behavior is the free-electron model mentioned previously. Assuming that one electron in the molecule behaves as a particle-in-a-box with length  $R$  equal to the internuclear distance, the addition of an electron to the molecule immediately poses the problem of where to put the extra electron. If the extra electron is added to the box both the kinetic energy and its derivative must double, and the force constant must therefore also

double. Since this does not happen, we must conclude that there is not room for more than one electron in the box. The extra electron must then occupy a region whose boundaries do not change size with internuclear distance.

This model presents an interesting physical picture. If an electron is out of the binding or free-electron region the size of the region it occupies can be expected to be determined largely by the nuclear attraction potential of a single atom, and therefore is fairly constant. Electron-electron repulsion presumably keeps the electrons from occupying the same region simultaneously. This model, when assuming variation in the longitudinal direction only, predicts the force constant relation

$$K_e = 12.05 R_e^{-4} \quad (4-1)$$

for the hydrogen-hydrogen bond, which gives very high force constants compared to the experimentally determined relation,

$$K_e = 1.94 R_e^{-3.9} \quad (4-2)$$

Another possible explanation is that the force constant is determined by the nuclear-nuclear repulsion potential. Since the addition of an electron brings about no change in the nuclear-nuclear repulsion potential, the force constant relation would not be affected. This explanation requires, however, that the electron potential have a negligible curvature at the equilibrium distance, an unrealistic assumption. Also,

the force constant must vary as the inverse third power of distance. though the bare model is unacceptable, the explanation may be modified by assuming that electron-electron repulsion terms, in conjunction with the nuclear-nuclear repulsion, give rise to a common repulsive curve of the form  $AR^{-n}$ . There is some justification for believing that this total repulsion curve remains somewhat constant from state to state, since it is determined in large part by the non-bonding electrons<sup>(46)</sup>. In this case the force constant obeys the relation

$$K_e = n(n + 1)A/R^n + 2 \quad (4-3)$$

if the curvature of the total attraction potential is small relative to the curvature of the repulsive potential. The assumption of negligible curvature, though unrealistic as before, has some probability, since the electronic attraction potential in a molecule always has a point of inflection where the curvature is zero. It is also well known that a repulsive potentials of the form  $AR^{-n}$  nearly always give an excellent fit to the actual potential energy curves<sup>(16,17,38,39,43)</sup>. This explanation seems to serve rather well for most molecules. It requires that the addition of an electron not change the curvature of the electron-electron repulsion terms; that is, the electron-electron repulsion terms resulting from the addition of an electron must have a linear dependence upon the internuclear distance. One immediately notices that according to this model all the electron repulsion terms for the hydrogen-hydrogen

must be linear, since for  $H_2^+$  the total repulsion is the same as the nuclear-nuclear repulsion. Also, the contribution of the nuclear-nuclear repulsion to the force constant in  $H_2^+$  is 3.87 mdynes/A, whereas the actual force is only 1.56 mdynes/A, making it necessary to include the curvature of the attractive potential.

In the case of attractive potential having a significant influence upon the force constant, the form of the force constant relation is no longer a simple inverse power relation, and fitting of theoretical relations to empirical relations becomes slightly complicated. If the potential energy curve is expressed as a double-reciprocal function, one may cast the force constant relation into a simple reciprocal form. A double-reciprocal function will be tested on the ground state of carbon monoxide.

For the hydrogen-hydrogen bond one may rather easily calculate the exact potential energies if the electron-electron coulomb repulsion and spin-orbit interaction are not included. By comparing the actual relation and potential energy curves with those arising from the treatment neglecting electron-electron repulsion the influence of the electron-electron repulsion might be made clearer. Exact potential energies are available for the various states of the hydrogen molecule ion<sup>(46)</sup>. These exact energies may be used as molecular orbital energies, and the potential energy curves of the hydrogen molecule states may be calculated by assuming the wave function of the hydrogen molecule to be a

simple product of the exact one-electron wave functions of  $H_2^+$ . Once the energies are calculated they can be fitted to an analytical expression from which the force constant may be calculated. The results are compared graphically with the empirical data in Figure 3. We observe that the molecules not having electron-electron repulsion exhibit much larger scattering of the force constants than do the actual molecules. Consequently, the spin interactions and electron-electron coulomb terms decrease the scattering rather than add to it! The very nature of the exact quantum mechanical solutions, it seems does not allow an exact reciprocal relation between the force constant and the bond length. It is interesting in this connection to examine to what extent the scattering of the force constant values is related to the shapes of the potential energy curves. That there is some sort of connection is readily seen by observing the relation of the force constant deviation to the constant  $a_1$  and by plotting the contributing one-electron potential curves and their second derivatives. Figure 4 shows the correlation between the force constant deviation and the constant  $a_1$  for both the empirical and calculated data. There is no obvious correlation, though the empirical and calculated data seem to exhibit quite different trends. In Figure 5 the calculated potential curves for  $H_2^+$  are drawn. Their shapes are seen to be qualitatively different, especially for those derived from united atom states having different angular momenta. In Figure 6 the second derivatives of the potential curves of  $H_2^+$  are plotted. From it we see that the principle contribution to the force

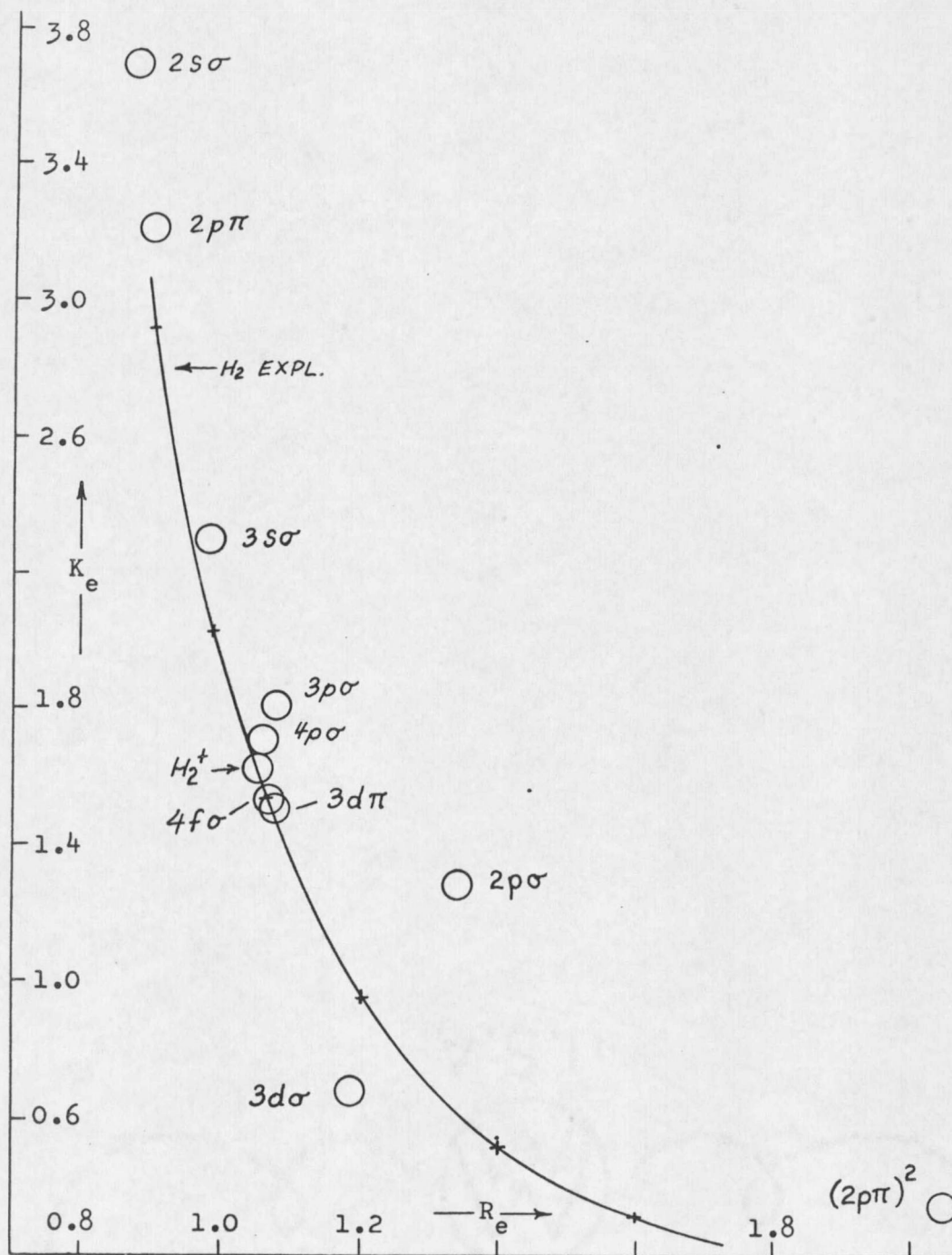


Figure 3. Hydrogen-hydrogen bond, theoretical

○ —  $H_2$  calc.

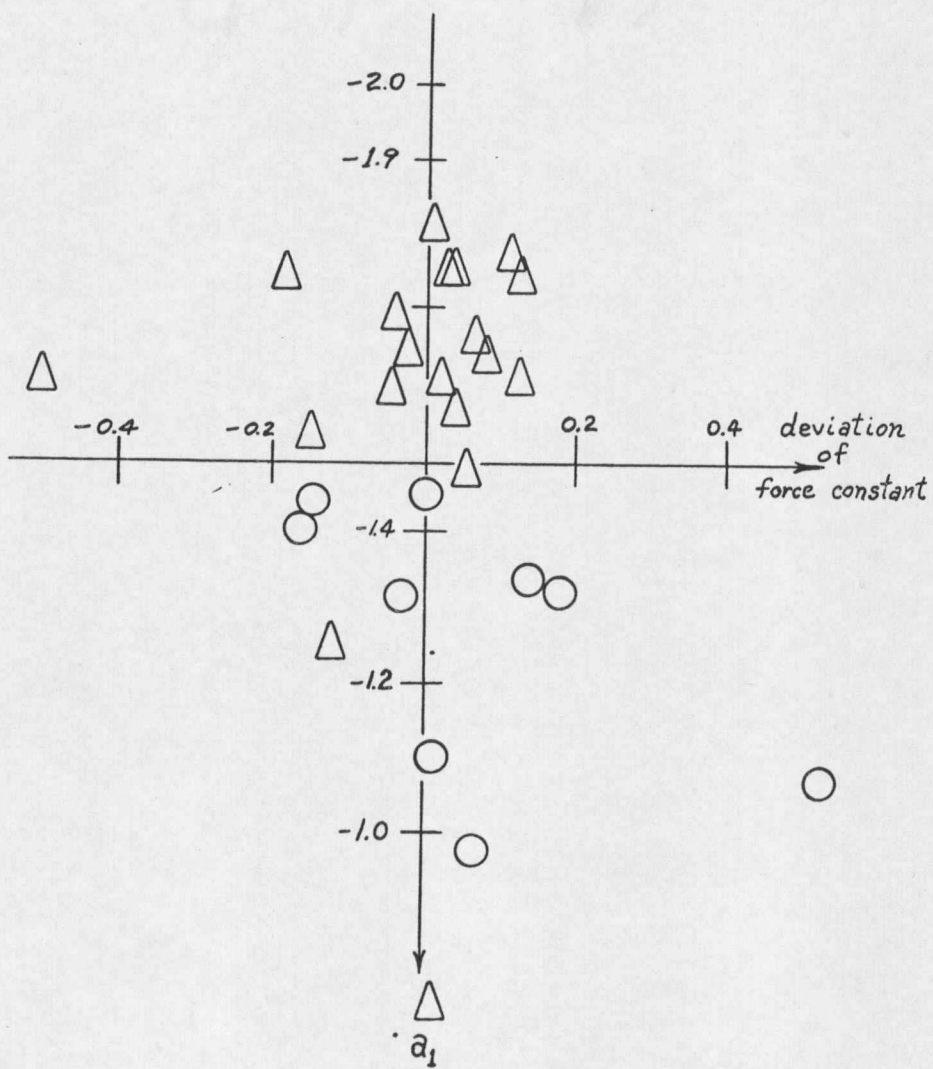
$$\Delta - H_2 \text{ expl.}$$


Figure 4. Force constant deviation for hydrogen

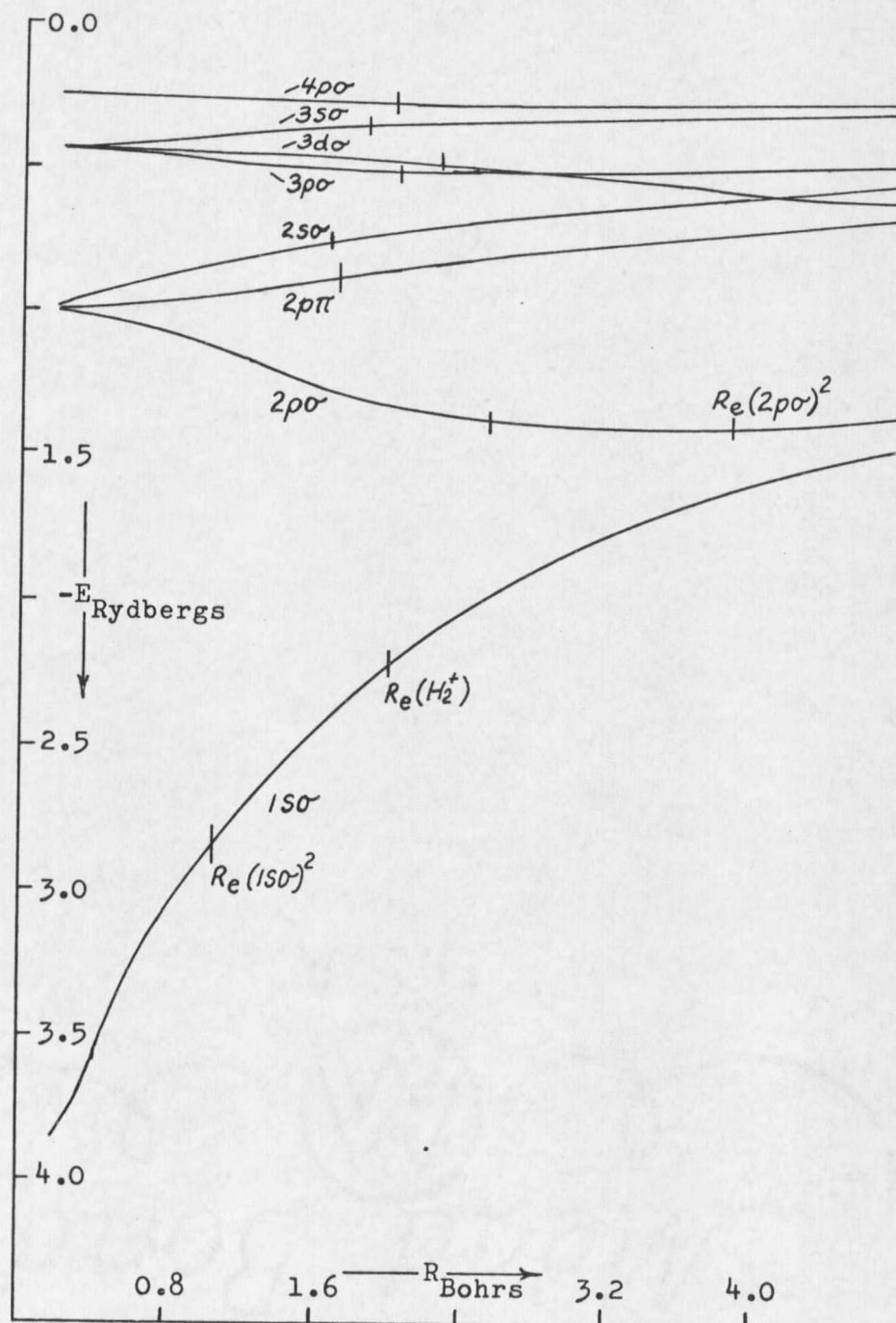


Figure 5. Potential energy curves for hydrogen

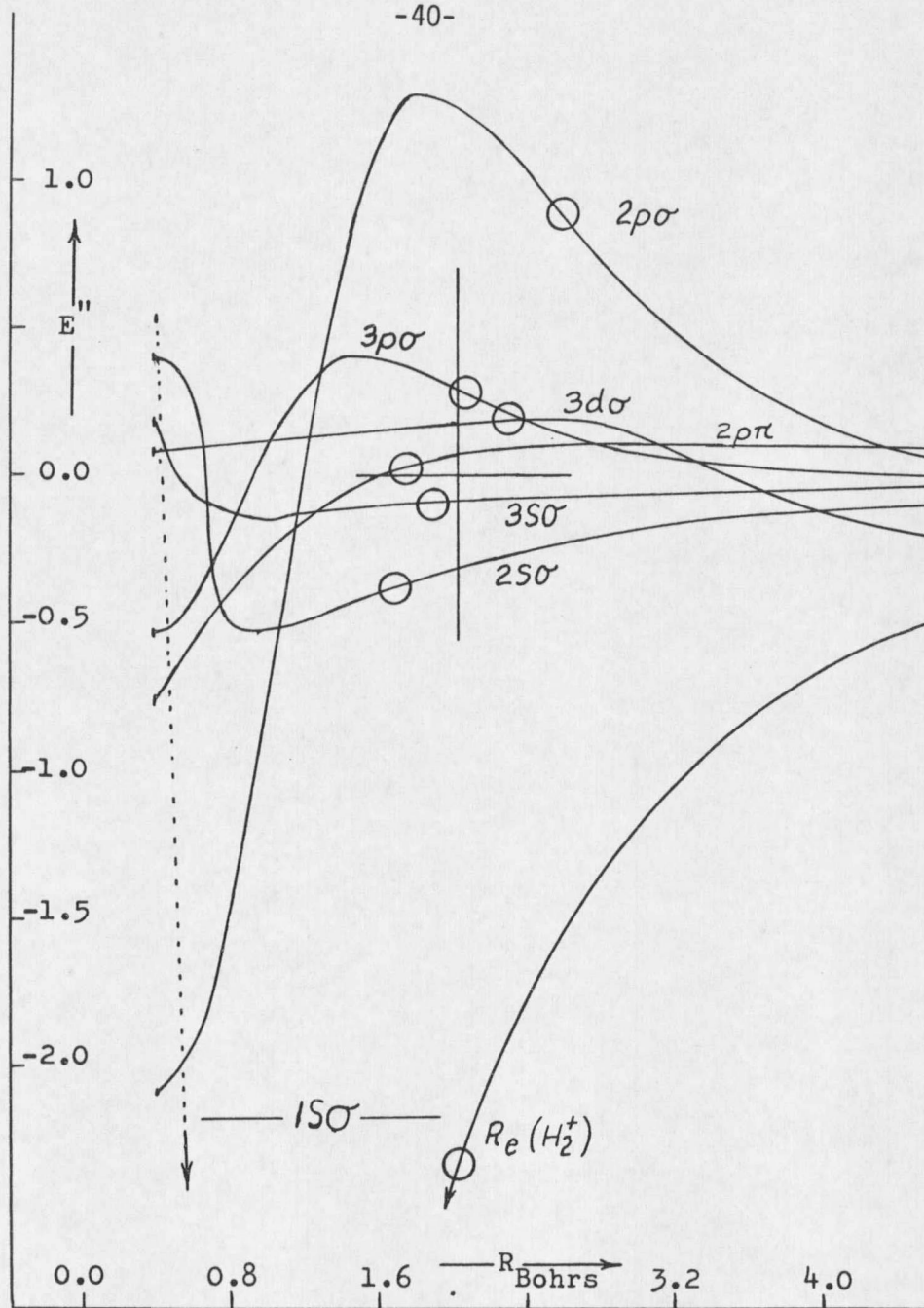


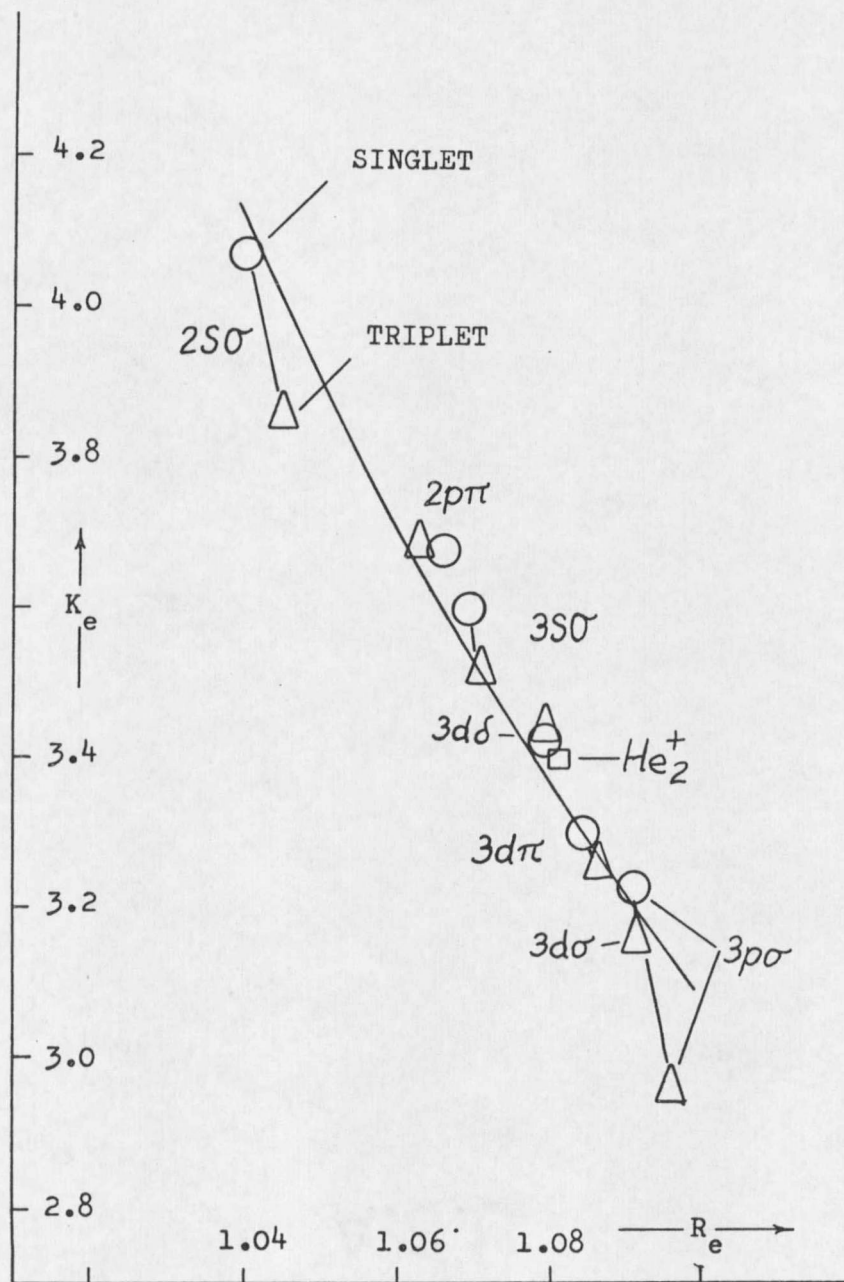
Figure 6. Second derivatives of the potential curves

constant, after the nuclear-nuclear repulsion, is from the ground-state orbital. The contribution from other  $H_2^+$ -type orbitals is seen to be small in comparison and, strangely enough, of about the same magnitude as the change in the ground-state contribution.

No mention has been made of the negative ion states of hydrogen. Though experimental observations on these states are inconclusive, calculations indicate that the force constants and bond lengths are often nearly the same as those of the corresponding states of hydrogen<sup>(47)</sup>. Also, the best calculated values<sup>(48)</sup> for the excited states of the hydrogen molecule show about the same amount of scatter as do the experimental data, with no apparent systematic differences between the calculated and experimental values.

#### Helium-helium Bond

The relation between force constant and bond length for the helium-helium system is shown graphically in Figure 7. The relation is seen to be quite different from that of the hydrogen-hydrogen system. The obvious explanation for this change is that the hydrogen molecules, being one and two electron systems, have no core, or non-valence electrons. The presence of core electrons may be expected to have a large influence upon the force constant relations because the internuclear distance at which repulsive forces become strong now is determined by the repulsion of the core electrons as well as the nuclear-nuclear repulsion. The force constants for the helium-helium bond fit the free-electron model much better than do those for the hydrogen-hydrogen bond.



The helium-helium curve also shows some new regularities. First, the triplet states for each configuration have a lower force constant to bond length ratio than the corresponding singlet states in all cases except the 3d  $\delta$  states, in which the singlet and triplet have almost identical ratios. Second, the deviation of single force constant values from the least-squares values correlates fairly well with the Dunham constant  $a_1$ , which measures the cubic contribution to the potential energy curve. Figure 8 shows this correlation. A high value for  $a_1$  is associated with a relatively low value of the force constant, indicating that high values of the cubic force constant tend to depress the quadratic force constant. It is shown in Appendix I that, if one assumes the validity of equation (2-13), the kinetic energy can be expressed in the form

$$T = T_0 + T_1/(R^{-3}a_1^{-4}) \quad , \quad (4-4)$$

which shows a direct relation between the cubic force constant and the form of the kinetic-energy curve.

The  $\text{He}_2^{++}$  ion in the ground state has not been observed, though it can be expected to be stable even though its dissociation energy is negative<sup>(49)</sup>. I have calculated the quadratic and cubic force constants from the theoretical data and find that the quadratic constant is anomalously low and the cubic constant anomalously high. Since the shape of the potential energy curve is also somewhat anomalous, this comes as

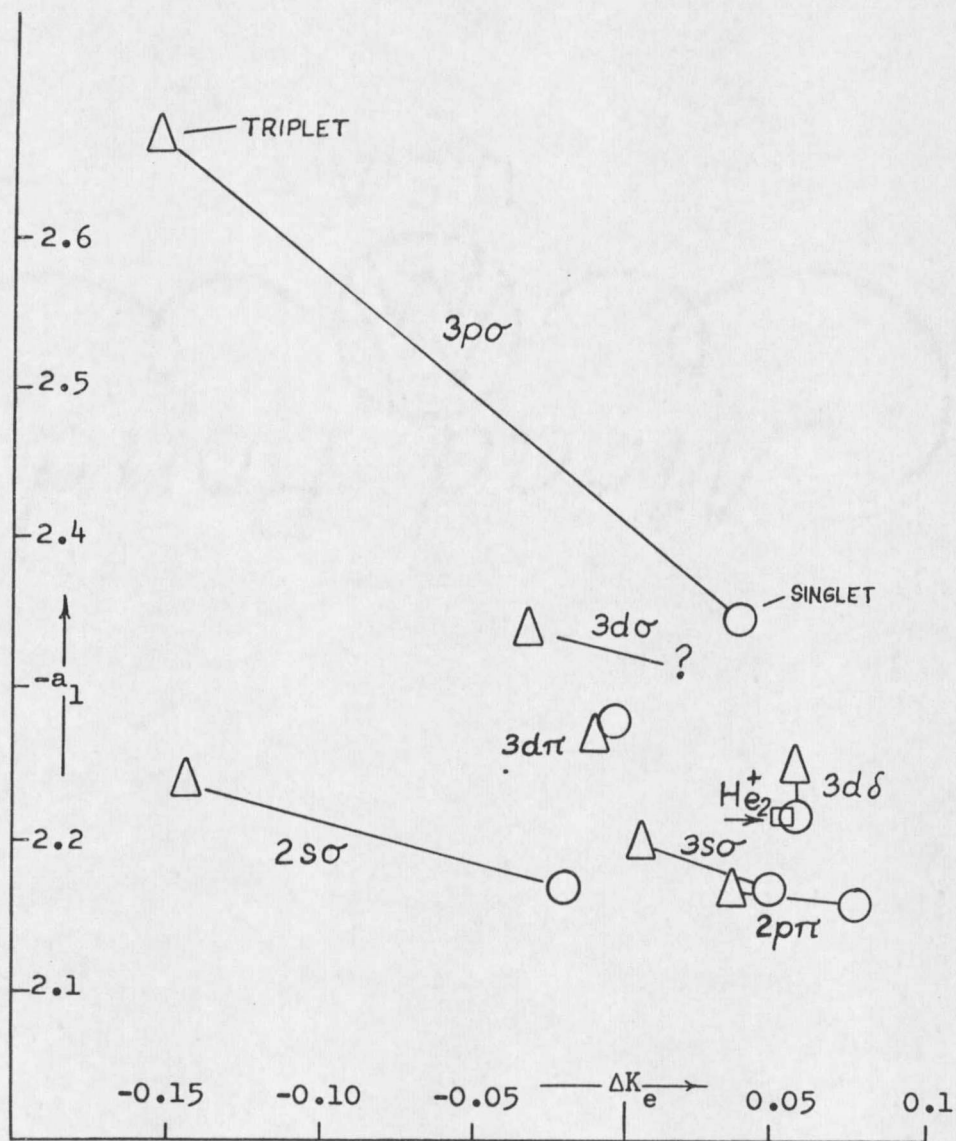


Figure 8. Force constant deviation for helium molecules

no surprise.

#### Helium-hydrogen Bond

The ground state of the HeH molecule, like the He<sub>2</sub> ground state, is unstable. Accurate experimental data are not available for this system. Exact calculations<sup>(50)</sup> show that the HeH<sup>+2</sup> molecule has only one bound state, the 2pσ state. The HeH<sup>+</sup> molecule is known experimentally only from mass spectroscopic studies. Therefore, the theoretical values of Michels<sup>(51)</sup> are used. For the excited states of the HeH molecule the calculations of Michels and Harris<sup>(52)</sup> have been used. Because there are only a few normal states for the helium-hydrogen bond, none of which have been empirically determined, a reliable force constant vs. bond length relation cannot be established. However, it is interesting to see if the relation obtained from the calculations is close to being a mean of the hydrogen-hydrogen and helium-helium relations. Inspection of Figure 9 reveals that the three states having short bond lengths are very close to the hydrogen-hydrogen curve, while the state with the long bond length has an anomalously high force constant, as seems to often be the case with very long bonds.

#### Lithium-lithium Bond

Lithium is the element of lowest atomic weight which contains a closed-shell core of non-valence electrons. As would be expected, the Pauli repulsion between the core electrons prevents the formation of strong short bonds. The result is that the force constant vs. bond

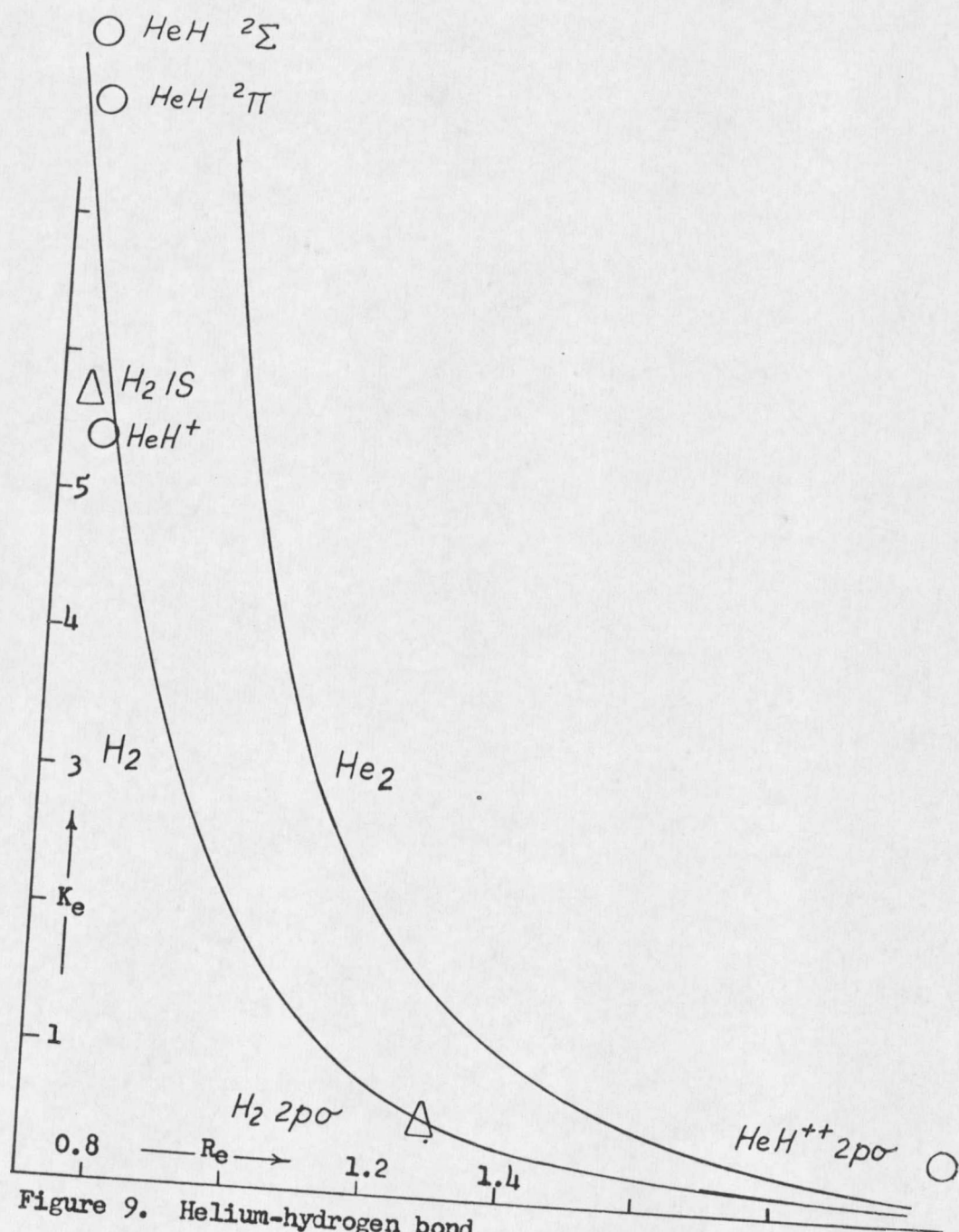


Figure 9. Helium-hydrogen bond

length relation is not easily compared to the relations for other bonds.

#### Lithium-helium Bond

The lithium-helium molecule has only very slightly bound states having dissociation energies of less than 0.07 eV.<sup>(53)</sup> and therefore will not be considered.

#### Lithium-hydrogen Bond

The relation between force constant and bond length for this bond is shown along with that for diatomic lithium in Figure 10. Again only three states are known and these states fall in a region apart from most bonds.

#### Beryllium-hydrogen Bond

To date the only observed states of diatomic molecules containing beryllium bonded to itself or to a lighter atom are four states of BeH and BeH<sup>+</sup>. They are shown in Figure 11.

#### Boron-boron Bond

Surprisingly, only two states are known for the diatomic boron molecule. We must therefore use the results of theoretical calculations if we are to find out anything about the boron-boron force constant relation. Fortunately, Bender and Davidson<sup>(54)</sup> have conducted a very thorough theoretical investigation of the electronic states of B<sub>2</sub>. Using a curve-fitting routine we can estimate the equilibrium force constants and bond lengths from their results. The values obtained are plotted in Figure 12. The two observed states are denoted by large circles. Extremely large

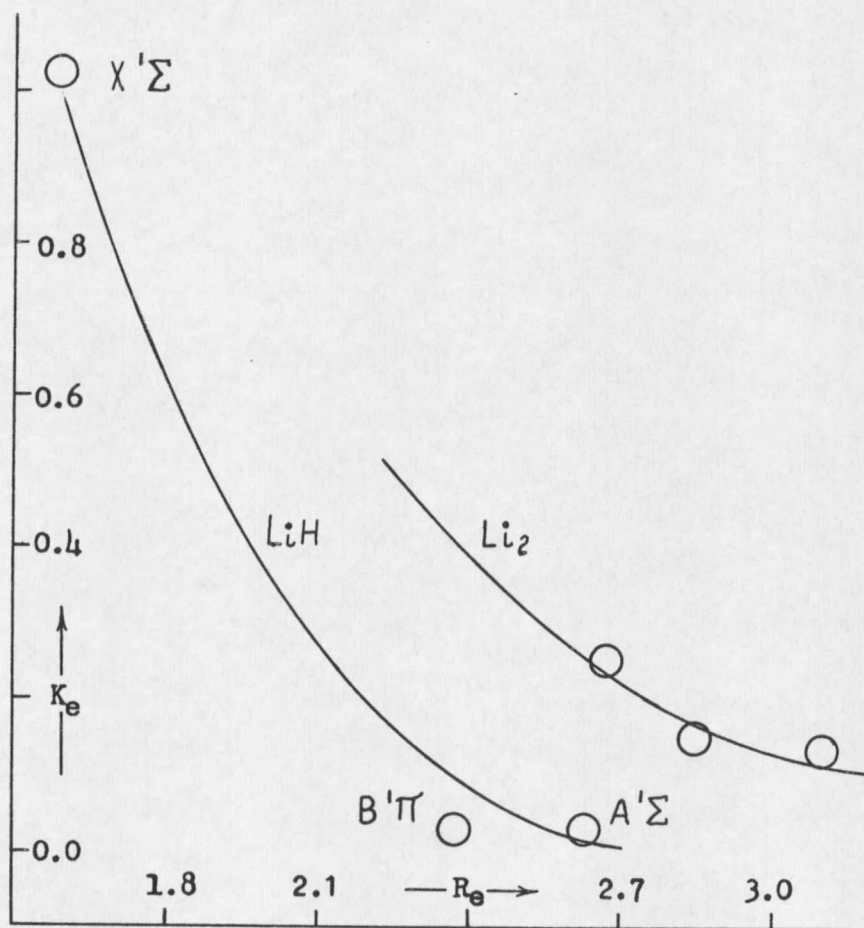


Figure 10. Lithium-hydrogen and lithium-lithium bonds

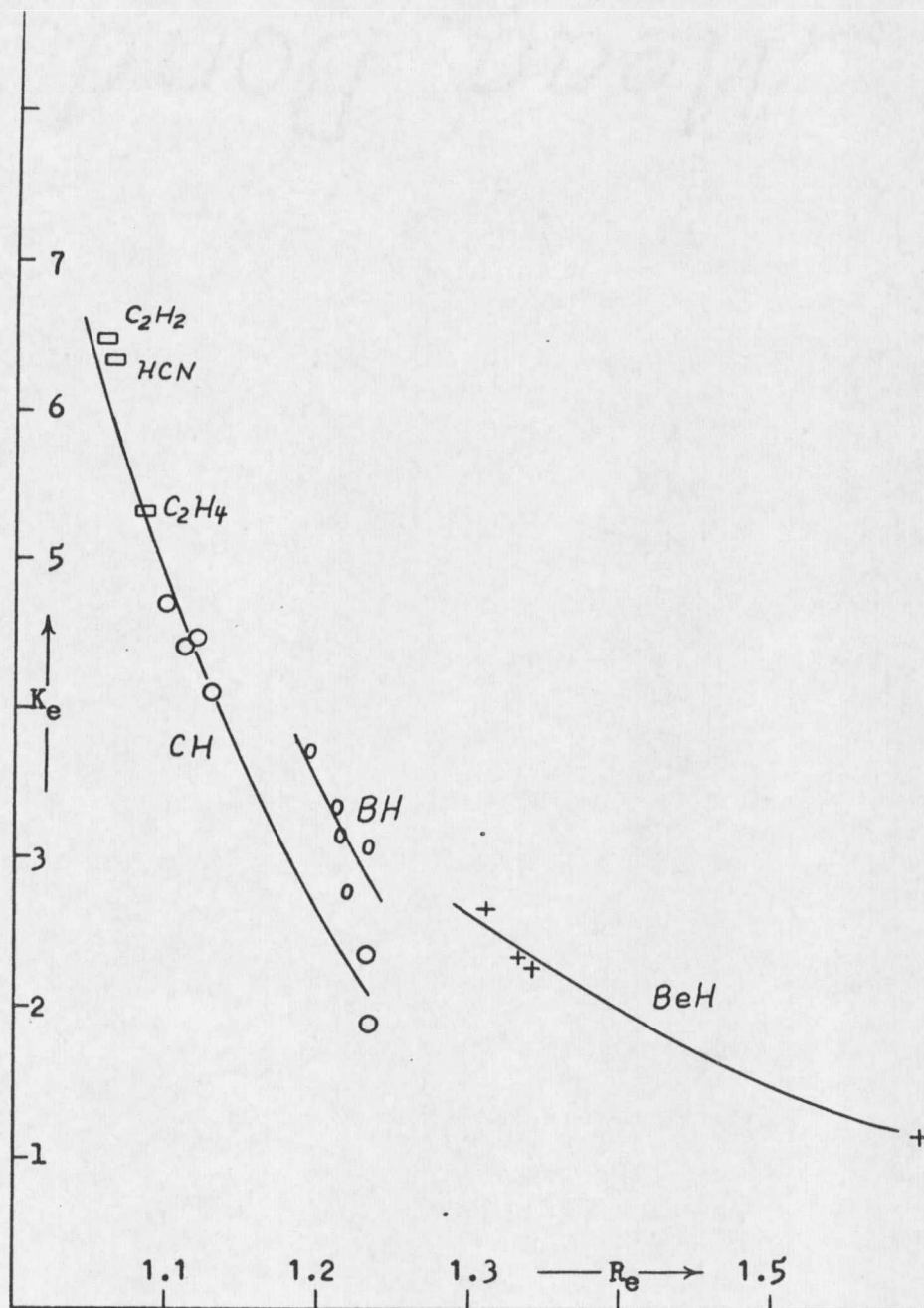


Figure 11. Hydrides of beryllium, boron, and carbon

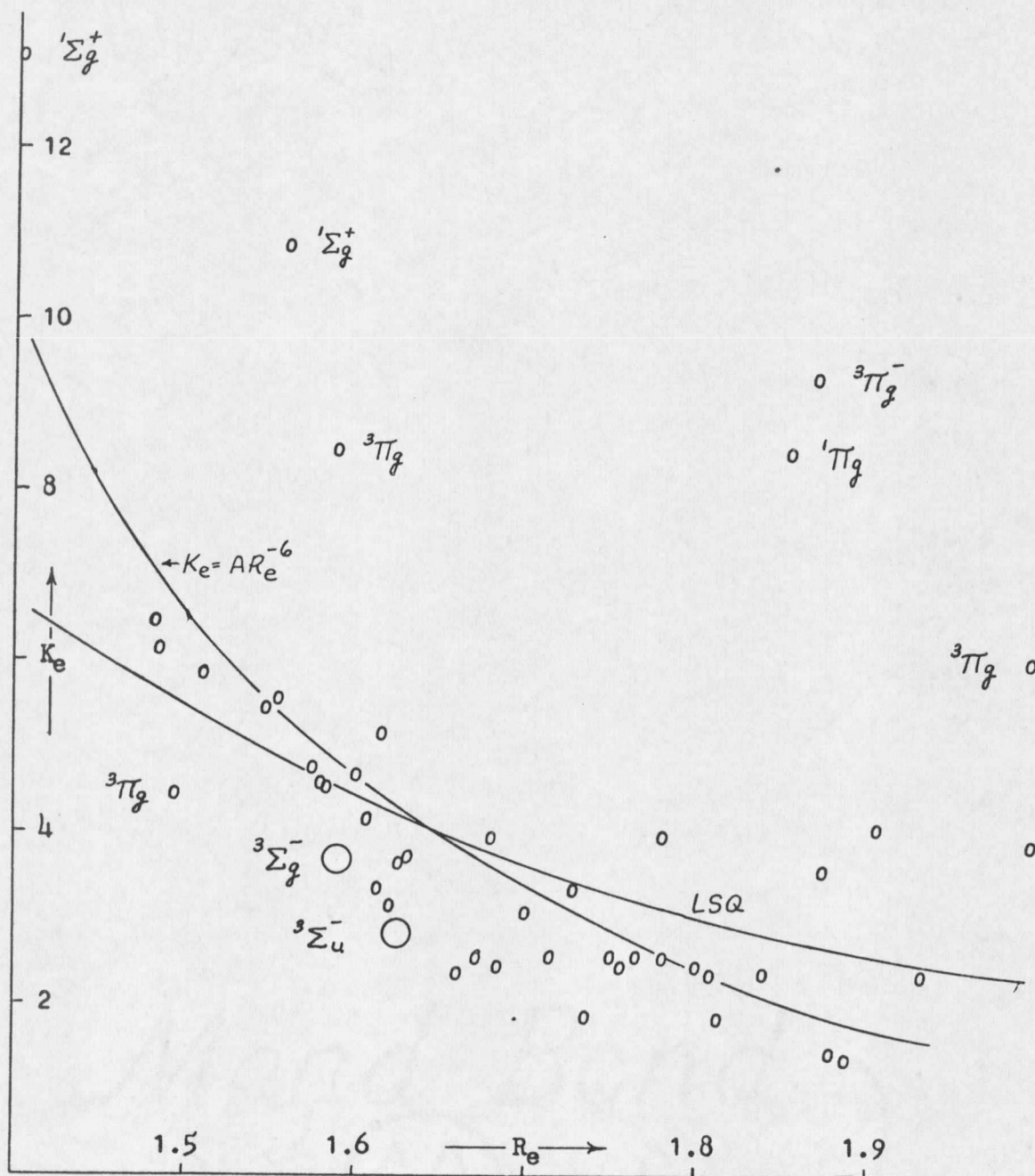


Figure 12. Boron-boron bond

deviations from the least-squares values exist, making the least-square relation dubious even though over forty electronic states were used. Again the cause of the large deviations is of particular interest. In this case the large deviations are shown chiefly by highly anharmonic g states.

#### Boron-hydrogen Bond

Boron has not been known to bond to atoms lighter than itself other than hydrogen. Spectroscopic constants have been determined for three states of boron hydride, though the results are not known to be accurate. The data indicate the force constant relation shown in Figure 11.

The boron-hydrogen system is the first that we have encountered for which polyatomic molecules are known. We must now ask if we can expect the same correlations between force constant and bond length for polyatomics. Part of the problem is that of defining the force constant for polyatomic molecules. The constant which corresponds to the quadratic force constant of diatomic molecules is the diagonal bond-stretch force constant which appears in a normal-coordinate analysis. Since normal-coordinate analyses have not been performed on many polyatomic molecules, we are rather limited in the selection of polyatomics we may use. Thus, though the species  $\text{BH}_2$  and  $\text{B}_2\text{H}_6$  are well-known, there is not sufficient information on them for the calculation of meaningful force constants.

The analysis of force constants for polyatomic molecules is generally

too complex (actually the amount of data is too small) to allow the consideration of anharmonic terms. We have already seen that the anharmonic terms play an important part in the relations. We know that the the consideration of anharmonicity leads to force constants which show considerably less scattering than force constants determined without anharmonic corrections.

#### Carbon-carbon Bond

The graph of force constant vs. bond length for the diatomic carbon species is shown in Figure 13. Only one state, the  $E^1\Sigma$  state, seems to deviate significantly from the pattern, though the status of the  $b^3\Pi$  state is not known because of its isolation. As expected, the E state is highly anharmonic, with a very high  $a_1$  value. The b state also has an unusually high anharmonicity, making it suspect as well, though its anharmonicity is of a different character than that of the E state. The E state also has the highest zero-point energy and lowest dissociation energy of any of the states. The E state has not been assigned an electron configuration, as there are several possibilities.

The simplest polyatomic molecule with a carbon-carbon bond is acetylene. A carbon-carbon stretching force constant which includes anharmonic corrections has been determined by Suzuki and Overend<sup>(55)</sup>. It is slightly larger than the force constant expected from the graph of diatomic force constants. The high value may be the result of the neglect of relaxation effects that is inherent in the treatment of polyatomic

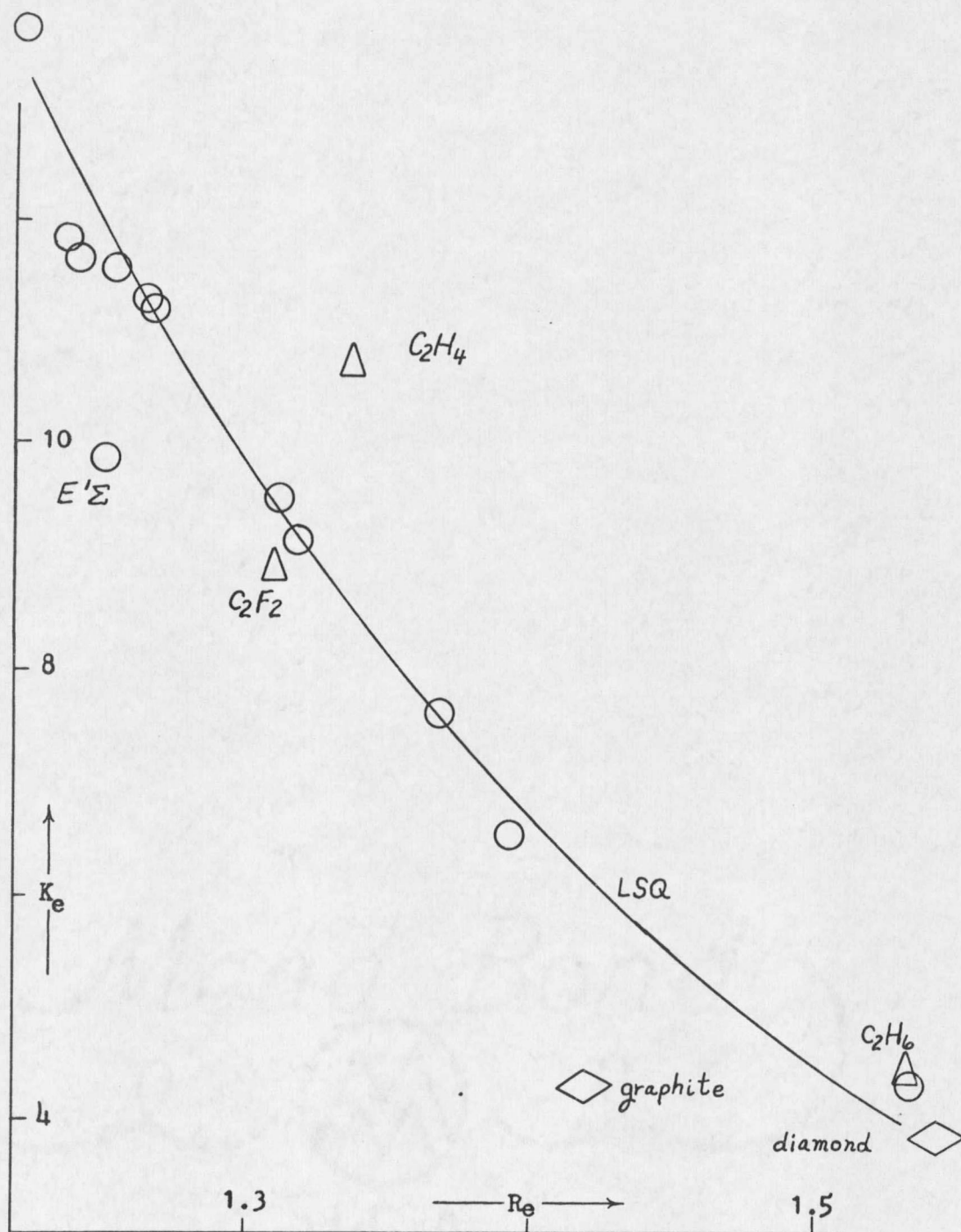


Figure 13. Carbon-carbon bond

molecules. Also, the exponent value for the diatomic relation appears to be low and might, therefore, give low force constant values for very small internuclear distances.

Ethylene has also been studied carefully by taking anharmonicity into account<sup>(56)</sup>. The carbon-carbon stretching force constant is considerably higher than the least-squares value. This time the only apparent explanation is that the difference is due to the relaxation effects discussed at the end of the theory section. For molecules of which anharmonicity has not been considered, the agreement with the diatomic values should generally be better because the error will compensate for the difference due to the relaxation effect. Thus, the force constant determined for  $C_2F_2$ <sup>(57)</sup> is in fairly good agreement with the diatomic results. The force constant for ethane<sup>(58)</sup>, which includes a correction for anharmonicity, also appears to be high.

Quite recently a new determination has been made of the force constant of the carbon-carbon bond in graphite<sup>(59)</sup>, which affords us our first chance to compare our results with those for a solid. When compared with the empirical curve, the force constant determined for graphite is seen to be ridiculously low! Close perusal of the article reveals, however, that the force constant was calculated directly from the observed Raman vibrational frequency; thus, the force constant corresponds directly to the normal mode and is therefore not the force constant for a simple bond stretch, but rather a bond stretch in combination

with adjacent bond compressions. That is, the force constant represents an extreme form of relaxation of electrons from one bond to another, resulting in a force constant considerably lower than that for a diatomic molecule. The force constant for diamond<sup>(60)</sup>, which was determined with a valence force field rather than directly, is in good agreement with the diatomic curve.

#### Carbon-boron Bond

Diatomic boron carbide was not known to exist until 1964, and there still are no spectroscopic data available for this species. Kouba and Ohm<sup>(61)</sup> have recently attacked this problem from a theoretical basis and calculated theoretical spectroscopic constants for all the possible states of diatomic boron carbide. Their data are used to obtain the totally theoretical graph of force constant vs. bond length displayed in Figure 14. Several of the states have rather abnormal force constants. The force constants of the states having large internuclear distances correlate rather poorly with distance.

#### Carbon-hydrogen Bond

Simple compounds of carbon with beryllium, lithium, and helium are not known. In the case of the carbon-hydrogen bond the bond distances for the diatomic states are all larger than those for the polyatomic molecules, as is shown in Figure 11. Rather than make a comparison between the diatomic and polyatomic force constants for this bond, we are perhaps better off using them together to get a force constant relation which is

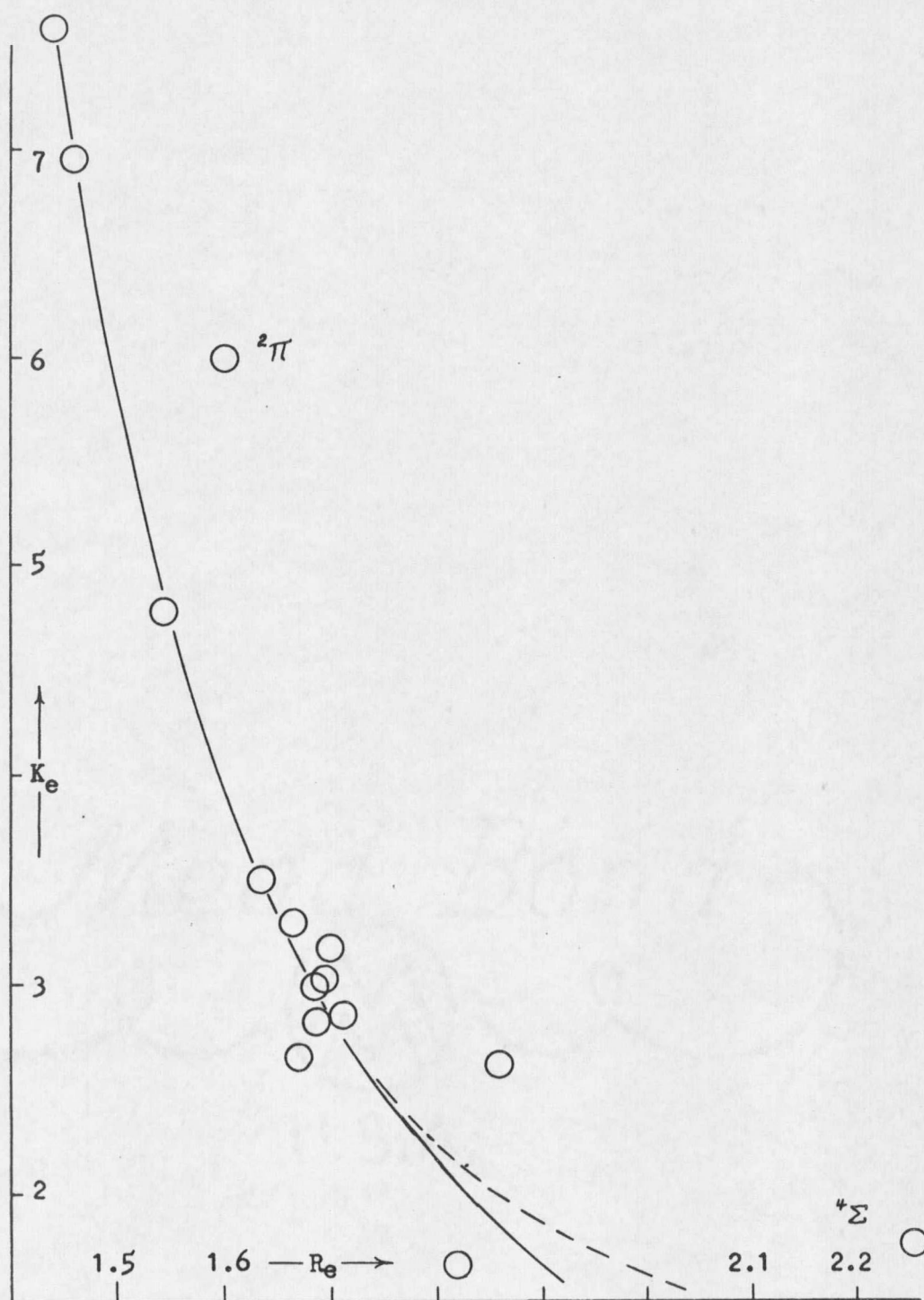


Figure 14. Carbon-boron bond

valid over a wide range of distance. Again the force constant values for the polyatomics<sup>(55,56,62)</sup> appear to be slightly high and are corrected for anharmonicity.

#### Nitrogen-nitrogen Bond

Here we encounter our first bond for which an empirical force constant vs. bond length relation has been reported<sup>(23)</sup>. The reported relation was determined by using force constants calculated from the frequency of the fundamental 0 - 1 transition rather than from the equilibrium force constants used here. Figure 15 shows the relation and force constants as determined by the author. The polyatomic force constants fall below the least-squares line, except for  $N_2H_6^{++}$ . However, the force constants of all of the polyatomics having this bond are difficult to analyze and have been determined by neglecting the anharmonicity; therefore, the force constants can be expected to be low. Remembering that the extra atoms on polyatomic molecules would be expected to increase the force constant of a bond, it comes as no surprise that  $N_2H_6^{++}$ , which has six extra atoms, has a relatively high force constant.

#### Carbon-nitrogen Bond

The force constant vs. bond length graph in Figure 16 shows two rather abnormal states. One state has such a high force constant that one must seriously doubt the validity of the spectroscopic data from which it was determined. A reanalysis of the data would certainly be

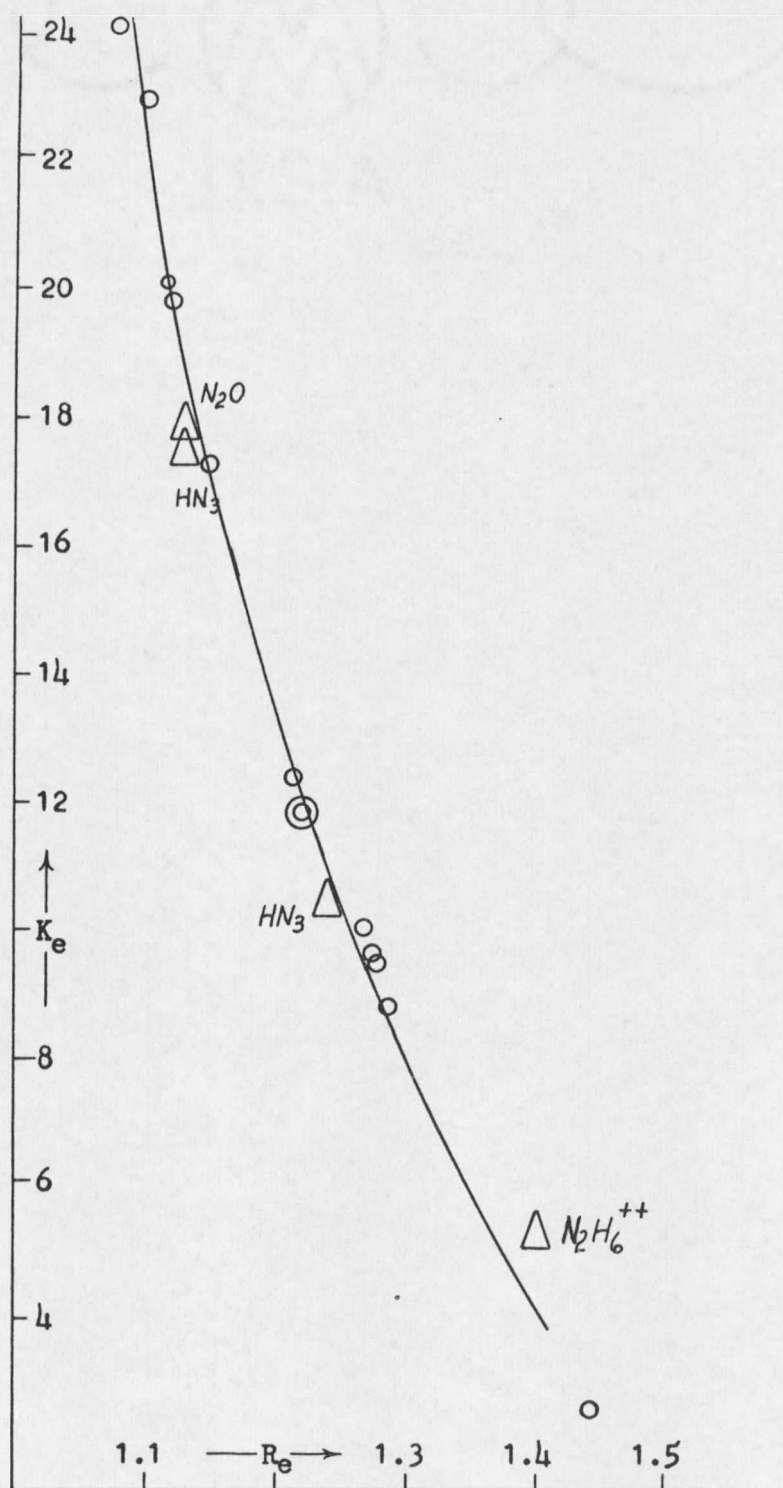


Figure 15. Nitrogen-nitrogen bond

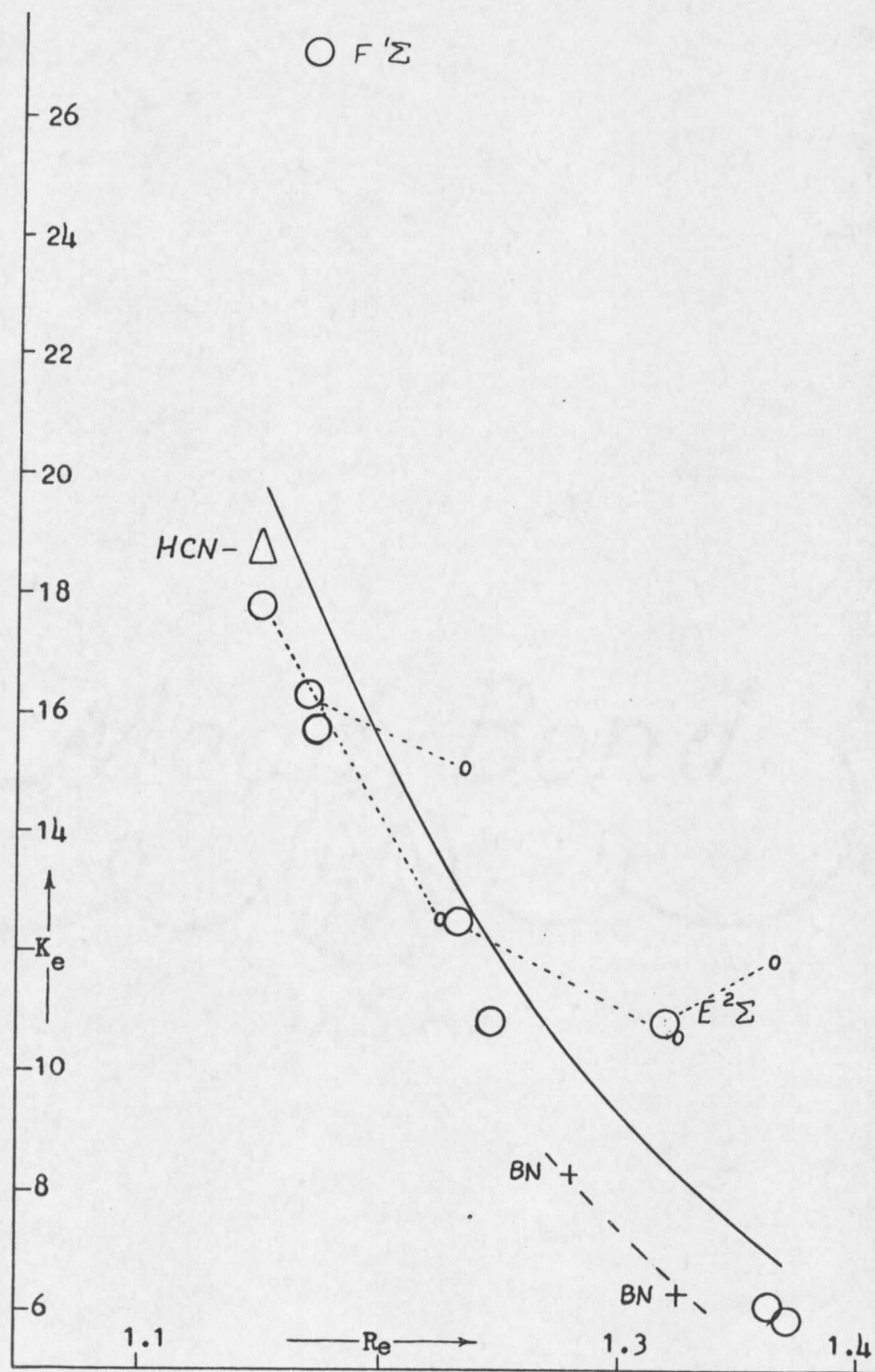


Figure 16. Carbon-nitrogen and boron-nitrogen bonds

in order, as often the spectrum of one molecule is mistaken for that of another. The other abnormal state is, as might be expected, abnormally harmonic. Schaeffer and Heil<sup>(63)</sup> have calculated theoretical spectroscopic constants for many of the states of CN. The theoretical force constant relation shows an extremely large scattering.

#### Boron-nitrogen Bond

The two known states of diatomic boron-nitride have been included in Figure 16. They exhibit force constants which are lower than the expected carbon-nitrogen values; thus, the usual periodic trends for the force constant relations is in this case reversed.

#### Nitrogen-hydrogen Bond

The nitrogen-hydrogen relation in Figure 17 covers only a very narrow range. None of the diatomic states for this bond seem to exhibit any abnormal behavior.

#### Oxygen-oxygen Bond

Figure 18 shows the various states of diatomic oxygen. Again no marked irregularities are present.

#### Nitrogen-oxygen Bond

This bond may vary considerably in stiffness and bond length, as is shown in Figure 19. Many simple polyatomic molecules contain the nitrogen-oxygen bond, so that there has been considerable interest in the bond's characteristics. Ladd, et. al.<sup>(22)</sup> in 1966 surveyed the known diatomic and polyatomic states and calculated a force constant vs. bond

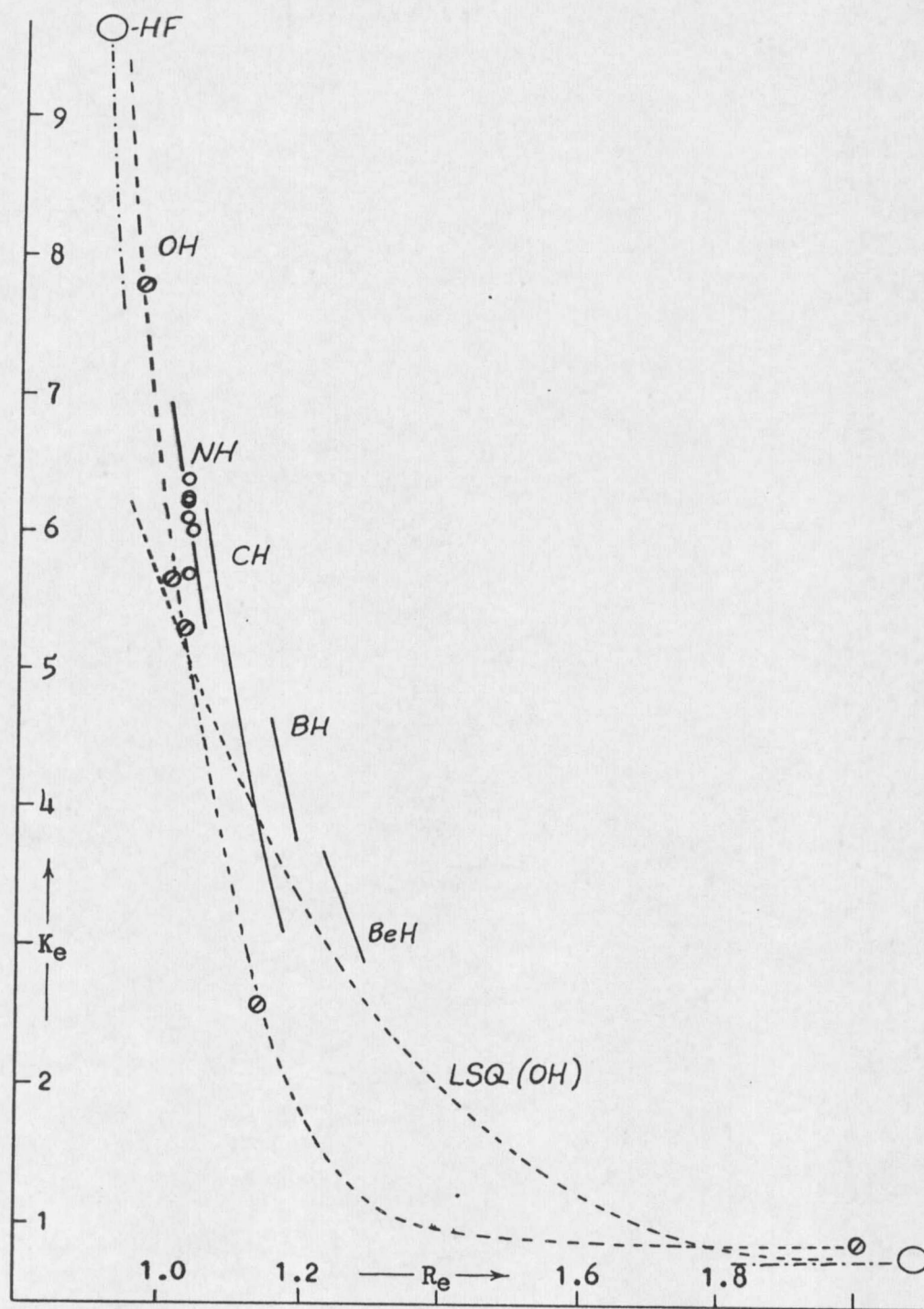


Figure 17. Nitrogen-hydrogen and oxygen-hydrogen bonds

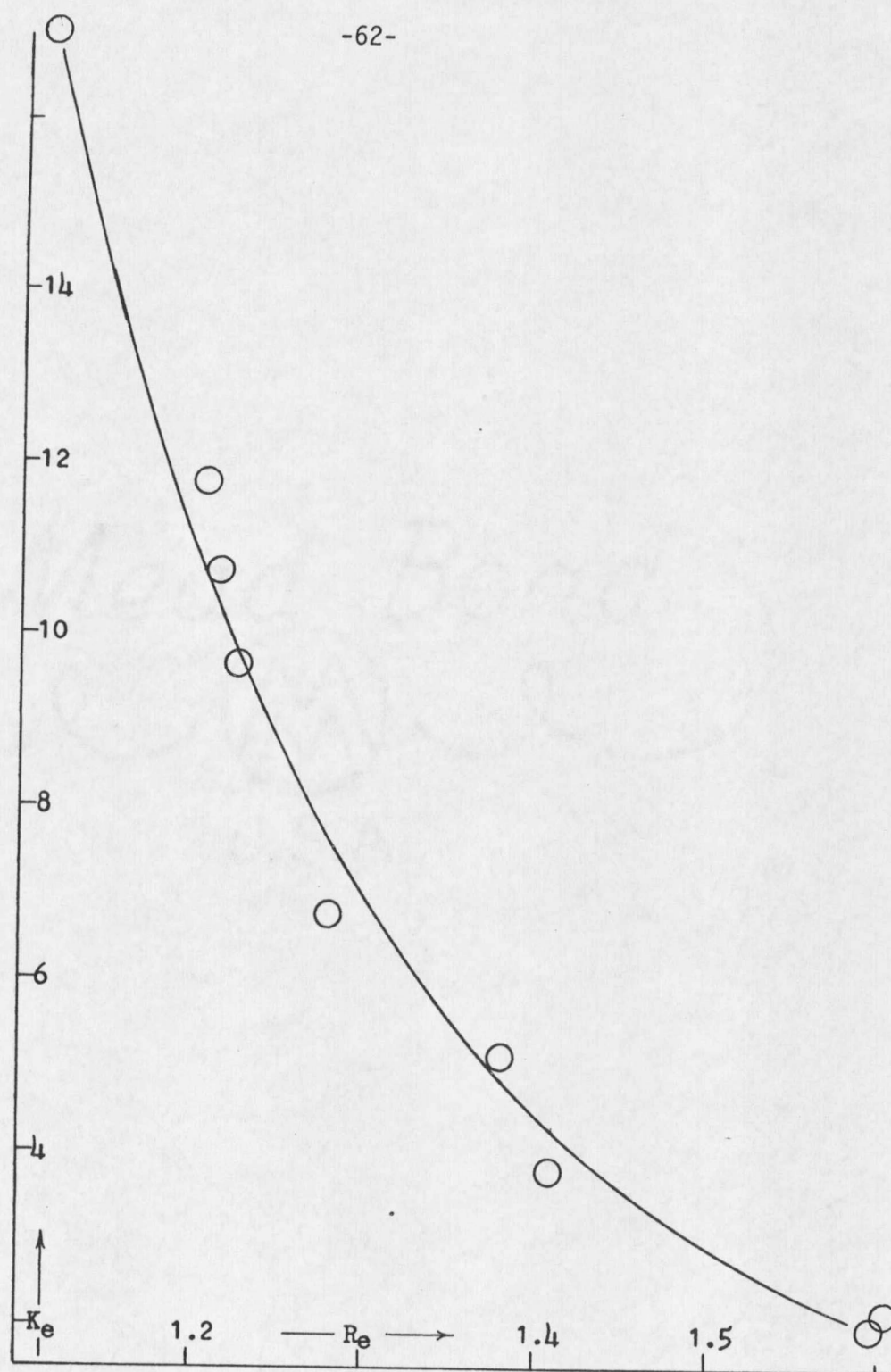


Figure 18. Oxygen-oxygen bond

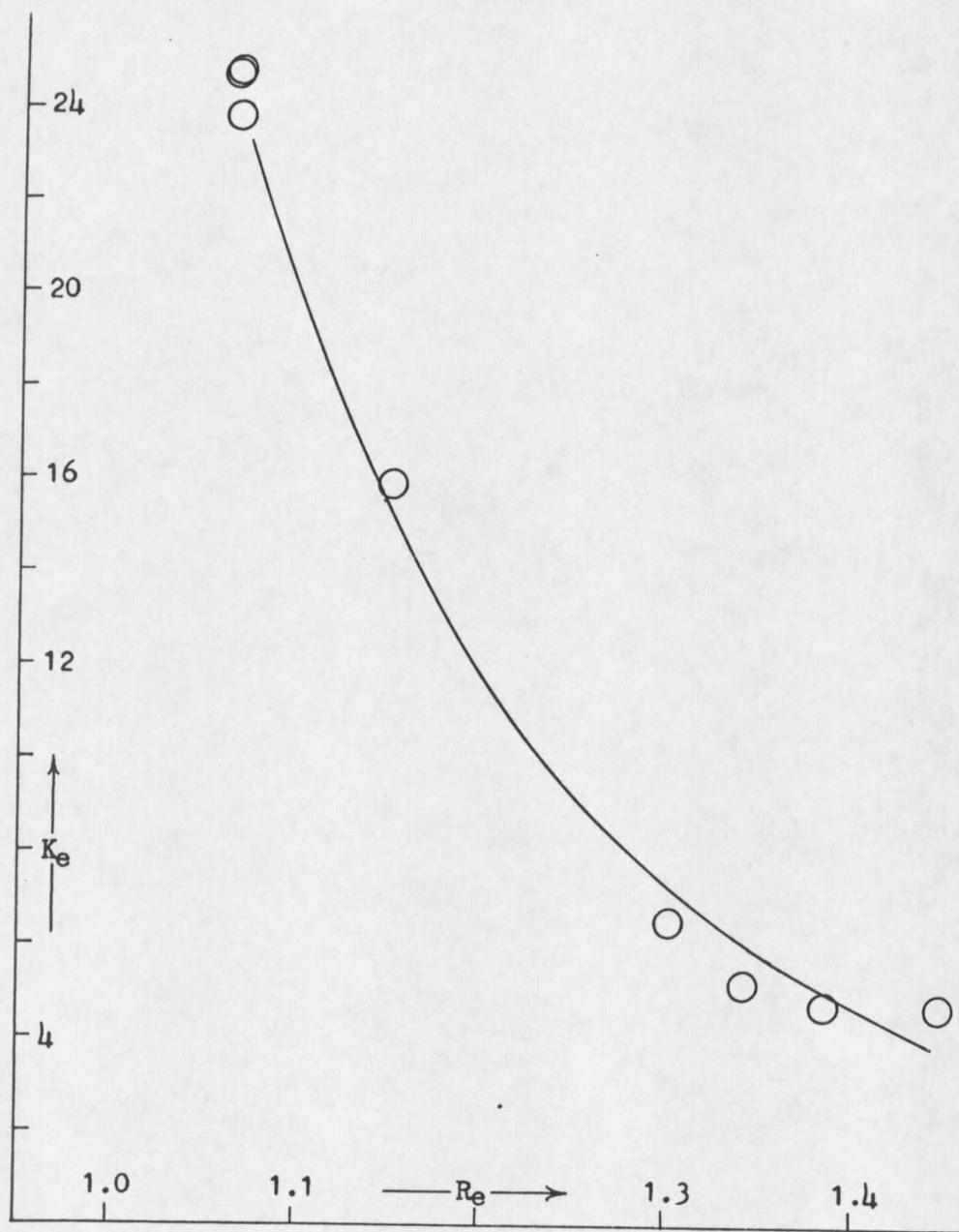


Figure 19. Nitrogen-oxygen bond

length relation. The data available has not changed much since then.

#### Carbon-oxygen Bond

Ladd, et. al.<sup>(21)</sup> studied the force constants for the carbon-oxygen bond in 1964. They were the first to recognize that the force constant of a bond is fairly insensitive to the hybridization. The scattering of the force constants of the various states plotted in Figure 20 follows the usual trends.

The ground state of carbon monoxide has been extensively studied and therefore was chosen as a test case for the determination of a double-reciprocal function to represent the potential curve and force constant relation. The potential curve is best represented by a function having exponents equal to 2.95 and 1.85 for the repulsive and attractive parts respectively. If the attractive portion doesn't contribute to the curvature at the minimum, then the force constant relation must vary as  $R^{-4.95}$ . This follows also if the attractive portion remains constant. Since the force constant varies as  $R^{-6}$ , the use of the common repulsive potential is not completely satisfactory.

#### Boron-oxygen Bond

Three states are known for diatomic boron oxide, and they are represented in Figure 21.

#### Beryllium-oxygen Bond

Four states are known for diatomic beryllium oxide, and they are compared with the boron-oxygen bond in Figure 21. The usual trend toward

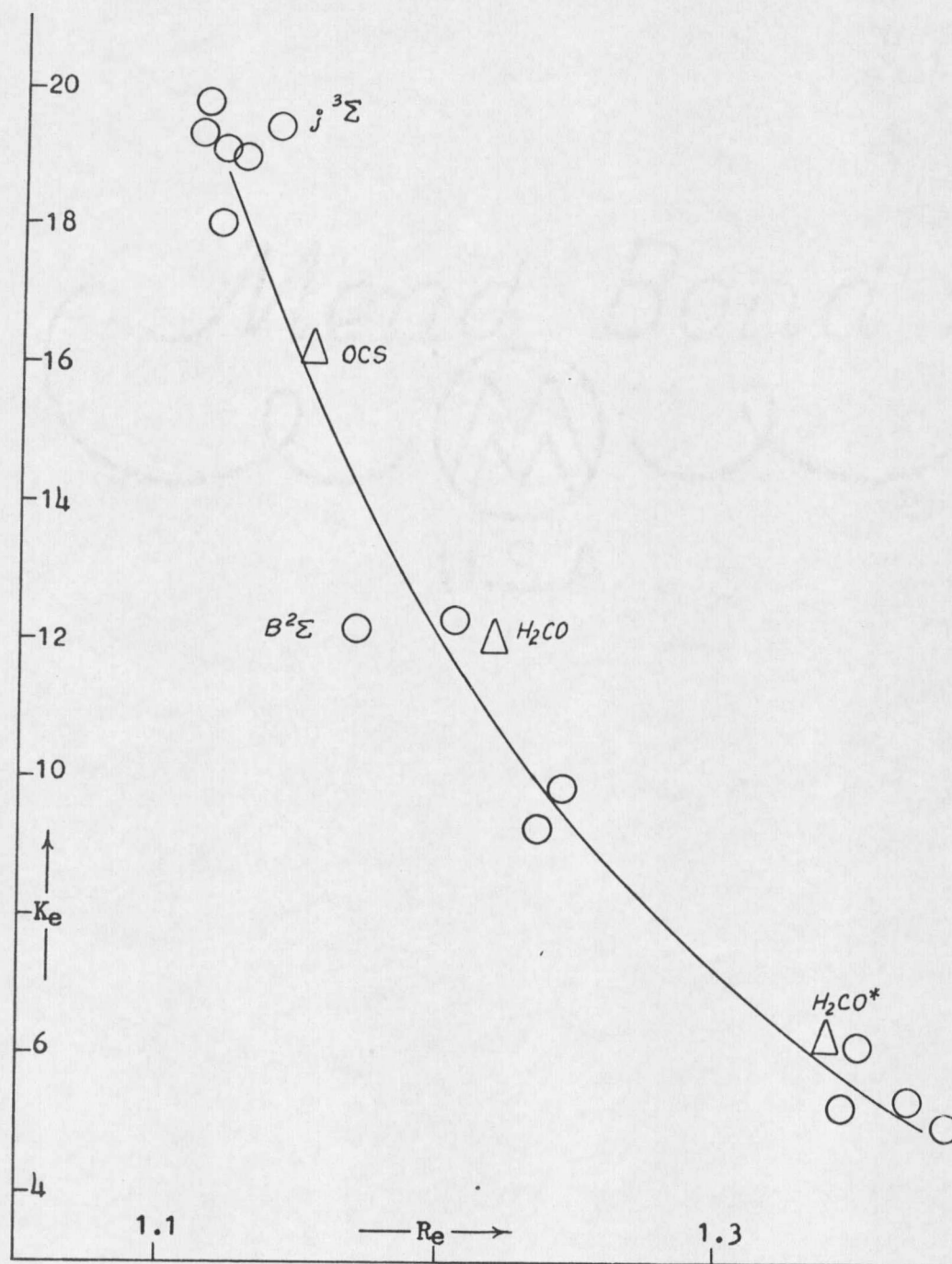


Figure 20. Carbon-oxygen bond

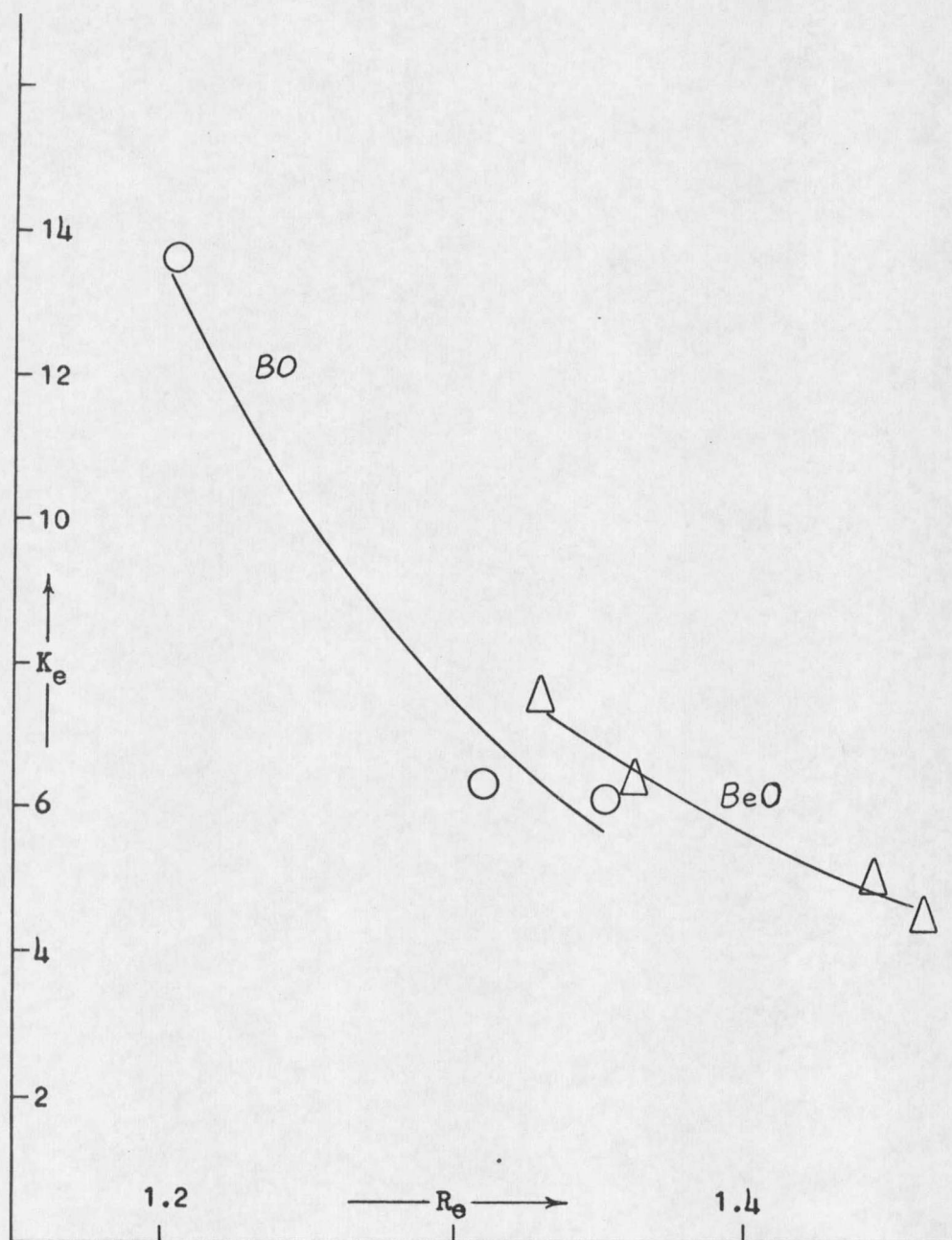


Figure 21. Boron-oxygen and beryllium-oxygen bonds

reduction of the force constant as the atomic number increases is evident.

#### Hydrogen-oxygen Bond

Electronic states of the OH molecule are represented in Figure 17. The least-squares fit for the force constants is extremely interesting in that it predicts a curve which is inconsistent with the curves for the other hydrides. We must be careful, then, not to always believe the least-squares results, as they are constrained to follow an exponential function having a constant exponent. The data for OH indicate clearly that a different form of function could give a much better fit to the data. We have seen before that long bonds tend to have a high force constants relative to the least-squares curve; again, the use of a different form of function would seem appropriate if a relation valid over a large range is to be found. Thus, a relation of the form

$$K_e = AR_e^{-1} + BR_e^{-n} \quad (4-5)$$

would be suitable from an experimental point of view as well as from a theoretical point of view.

#### Fluorine Bonds

The force constants and bond lengths for the fluorine-containing diatomic molecules are plotted in Figure 22. Again a reciprocal relation between atomic number and force constant appears. Here, though, the relation breaks down for the fluorine-fluorine, nitrogen-fluorine,

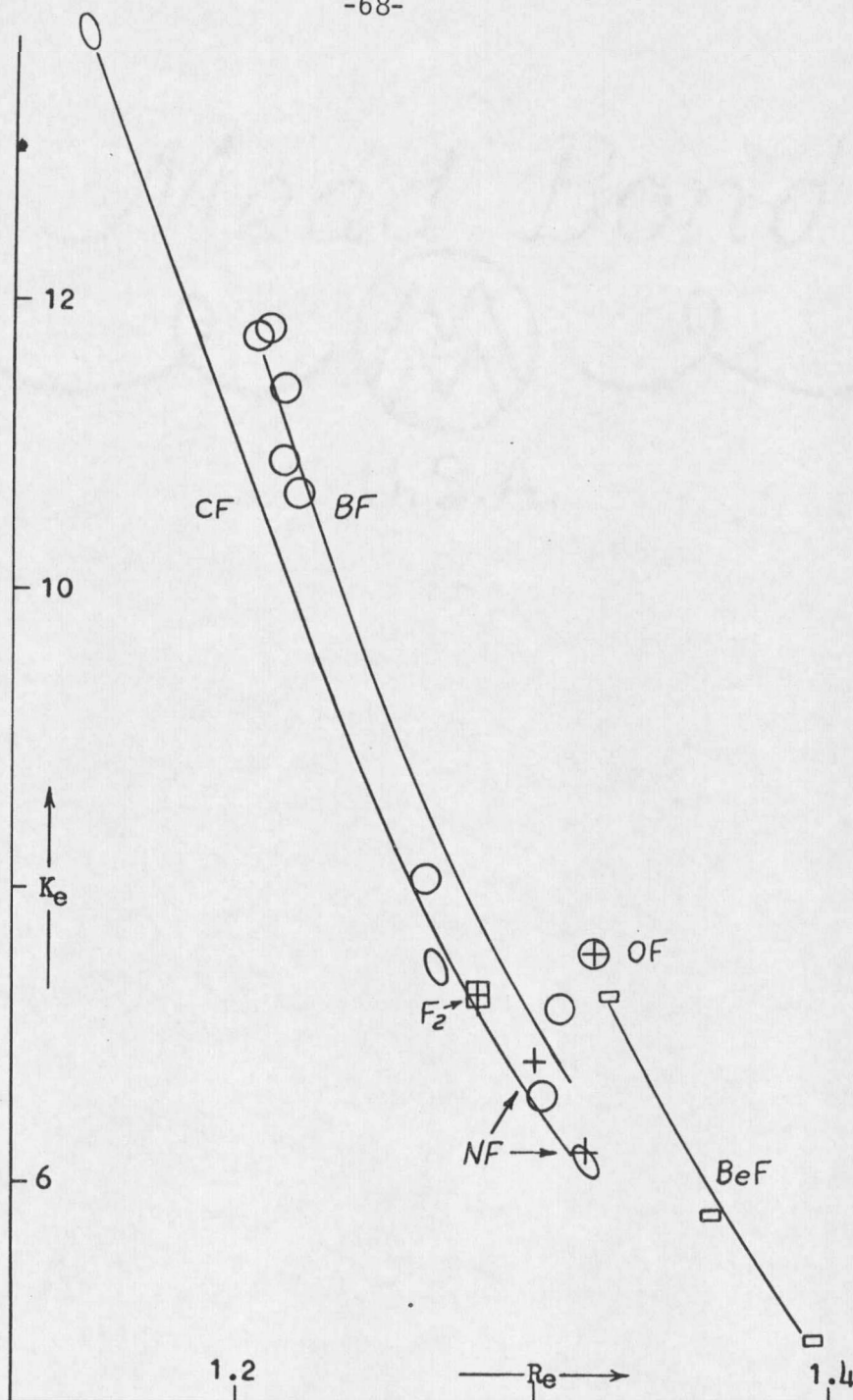


Figure 22. Bonds containing fluorine

and especially oxygen-fluorine bonds, for which very few data are available. Thus one remains uncertain as to whether any meaning should be attached to the apparent violation of this "reciprocity" rule.

## CHAPTER V

### Conclusion

This study, though for the author a long and sometimes arduous task, merely scratches the surface of a field of study which has in recent years been sadly neglected. The force constant relations for bond combinations including elements not in the first row of the periodic chart have not yet been determined. Many bond properties have not been related with the force constant behavior, though the existence of such relationships is very probable. Alternate functional forms for the relations need to be tried. The free-electron theory, for example, lends itself particularly well to the equation

$$K_e = A(R_e - d)^{-m} ,$$

where  $m$  is set at four. The parameter  $d$  could be used as a measure of the sum of the ionic radii of the atoms.  $d$  may be obtained from the usual exponential function by use of the equation

$$d = (-mR_e/n + R_e) ,$$

where  $n$  is the exponent of the normal exponential relation. The comparison of diatomic force constants with those of polyatomic molecules could be carried further in cases where the force fields of the polyatomic molecules are well known. Also, the manner in which force constants change as calculations are changed is of increasing interest to theoreticians.

A universal formula for the force constant vs. bond length relation has not been found which works appreciably better than those presently in use. The scatter of force constants of individual states from one another was shown to be largely systematic rather than random. The changes brought about by changing the number or distribution of protons in a system were found to exhibit definite but not absolute trends.

## APPENDIX A

### POWER SERIES EXPANSION OF THE POTENTIAL CURVE

#### Maclaurin expansion

$$E(R) = \frac{E_e^{(2)}}{2} (R - R_e)^2 + \frac{E_e^{(3)}}{6} (R - R_e)^3 + \frac{E_e^{(4)}}{24} (R - R_e)^4 + \dots \quad (A-1)$$

$E_e^{(2)}$  = quadratic force constant,  $K_e$

$E_e^{(3)}$  = cubic force constant,  $L_e$

$E_e^{(4)}$  = quartic force constant,  $M_e$

#### Dunham or reduced-coordinate expansion

$$r = \frac{R - R_e}{R_e}$$

$$E(r) = a_0 r^2 (1 + a_1 r + a_2 r^2 + \dots) \quad (A-2)$$

$$a_0 = \frac{K_e}{2} \cdot R_e^2 \quad a_1 = \frac{L_e}{3K_e} \cdot R_e \quad a_2 = \frac{M_e}{12K_e} \cdot R_e^2$$

## APPENDIX B

### EXPANSION COEFFICIENTS IN TERMS OF SPECTROSCOPIC CONSTANTS

Dunham coefficients:

$$a_0 = \frac{\omega_e^2}{4B_e} \quad (B-1)$$

$$a_1 = -1 - \frac{\omega_e \alpha_e}{6B_e} \quad (B-2)$$

$$a_2 = \frac{5a_1^2}{4} - \frac{2\omega_e x_e}{3B_e} \quad (B-3)$$

Maclaurin coefficients:

$$K_e = \frac{\omega_e^2}{2B_e R_e} \quad (B-4)$$

$$L_e = 3K_e \frac{-B_e^2 - \omega_e \alpha_e}{R_e B_e} \quad (B-5)$$

$$M_e = \frac{6\omega_e^2}{R_e^4 B_e} \left( \frac{5a_1^2}{4} - \frac{2\omega_e x_e}{3B_e} \right) \quad (B-6)$$

## APPENDIX C

### ERRORS INCURRED IN THE USE OF $\Delta G(1/2)$ AND $R_o$

$$\frac{\Delta G(1/2)}{w_e} \approx \frac{w_e - 2w_e x_e}{w_e} = 1 - \frac{2w_e x_e}{w_e} \quad (C-1)$$

is well known<sup>(1)</sup>, and

$$R_o/R_e = (B_e/B_o)^{1/2} \quad (C-2)$$

follows from equation (2-4). If  $\alpha_e/B_e \ll 1$  substitution of

$$B_o \approx B_e - (1/2)\alpha_e \quad (C-3)$$

into (C-2) yields

$$R_o/R_e \approx 1 + \alpha_e/4B_e \quad (C-4)$$

Likewise, assuming  $w_e x_e/w_e$  to be small, substitution of

$$K = \text{Const. } w^2 \quad (C-5)$$

into (C-1) gives

$$K(\Delta G)/K_e \approx 1 - 4w_e x_e/w_e \quad (C-6)$$

If the ratios  $w_e x_e/w_e$  and  $\alpha_e/B_e$  are fixed, then the use of the approximate constants will give a force constant relation having the same exponential dependence as the equilibrium relation.

## APPENDIX D

### DERIVATION OF EQUATION (2-16)

According to the virial theorem

$$RE' + E = -T \quad . \quad (D-1)$$

Differentiation of (D-1) gives

$$RE'' + 2E' = -T' \quad . \quad (D-2)$$

Multiplication of (D-1) times  $nR^{n-1}$  and of (D-2) times  $R^n$  and adding gives

$$-(R^n T)' / R^{n-1} = R^2 E'' + (n+2)RE' + nE \quad (D-3)$$

after collecting like terms.

## APPENDIX E

### FORCE CONSTANT RELATIONS FOR THE FREE-ELECTRON THEORY

Suppose that

$$T = AR^{-2} = AR_e^{-2} \quad (E-1)$$

for  $R$  near to  $R_e$ . Then

$$(dT/dR)_{R_e} = -2AR_e^{-3}. \quad (E-2)$$

Substitution of (E-2) into the virial relation

$$R_e K_e = -(T')_{R_e} \quad (E-3)$$

gives

$$K_e = 2AR_e^{-4}. \quad (E-4)$$

For a one-dimensional particle in a box

$$T = (h^2/8m)R^{-2}, \quad (E-5)$$

where  $h^2/8m$  is constant and  $R$  is the length of the box. If the length  $R$  is taken as equal to  $R_e$ , then an inverse fourth order dependence of the force constant on  $R_e$  is implied. Likewise, assuming a three-dimensional box having constant lateral dimensions give the relation

$$T = (h^2/8m)R_e^{-2} + \text{Constant},$$

which gives the exact same force constant relation as the one-dimensional box, since the relation is obtained by differentiation of the expression for kinetic energy. If the lateral dimensions are in proportion to the length one obtains

$$T = (h^2/8m)(1 + [R_e/R_a]^2 + [R_e/R_b]^2)R_e^{-2} \quad (\text{E-7})$$

where  $R_a$  and  $R_b$  are the lateral dimensions of the box. Again one obtains an inverse fourth-order dependence for the force constant.

I now introduce as a theorem the statement that any box which maintains a constant shape will give an inverse fourth order dependence for the force constant, no matter what its initial shape is. If we can prove that the energy is proportional to  $1/h^2$ , where  $h$  is a one-dimensional scale factor which measures the change in size of the box along each dimension, then the theorem will follow from the argument used at the beginning of this section. An increase in size of any box can be compensated for by changing the coordinate system by a scale factor,

$$x' = x/h, \quad (\text{E-8})$$

so that in the new coordinate system the box appears not to have changed size. By transforming coordinates the potential energy and boundary conditions are effectively unchanged. The only change is in the form of the

Laplacian operator, which becomes multiplied by the constant  $1/h^2$ . Rewriting the wave equation, we obtain

$$\nabla^2 \psi(x') = h^2 K E' \psi(x') \quad , \quad (E-9)$$

which is identical to the original wave equation,

$$\nabla^2 \psi(x) = K E \psi(x) \quad , \quad (E-10)$$

except that the energy  $E$  is replaced by  $h^2 E'$ . Thus

$$E' = \frac{1}{h^2} E \quad (E-11)$$

which was to be proven.

# APPENDIX F

| STATE | RE | WE | WEXE | AE | BE | REF |
|-------|----|----|------|----|----|-----|
|-------|----|----|------|----|----|-----|

## H2

|      |        |         |        |        |         |      |
|------|--------|---------|--------|--------|---------|------|
| X1S  | .7416  | 4401.20 | 21.340 | 3.0620 | 60.8530 | 68   |
| X2S  | 1.0600 | 2297.00 | 62.000 | 1.4000 | 29.8000 | 64   |
| A3S  | .9887  | 2664.80 | 71.650 | 1.6710 | 34.2160 | 64   |
| B1S  | 1.2925 | 1375.40 | 20.420 | .9200  | 20.0350 | 64.6 |
| B1S  | 1.1380 | 2074.90 | 13.400 | 1.4900 | 25.8000 | 64.6 |
| B1S  | 1.1110 | 2197.50 | 68.100 | 2.3500 | 27.1000 | 64.6 |
| C3P  | 1.0376 | 2465.00 | 61.400 | 1.4250 | 31.0700 | 64.6 |
| C1P+ | 1.0220 | 2420.40 | 55.600 | 1.7600 | 32.0000 | 64.6 |
| C1P- | 1.0310 | 2431.20 | 60.900 | 1.8300 | 31.5000 | 64.6 |
| D1P- | 1.0420 | 2361.50 | 69.100 | 1.9600 | 30.8000 | 64.6 |
| D1P+ | 1.0140 | 2358.20 | 68.500 | 2.0000 | 32.5000 | 64.6 |
| D3P  | 1.0496 | 2371.60 | 66.270 | 1.5450 | 30.3640 | 64   |
| D4P+ | 1.0300 | 2329.70 | 63.000 | .6400  | 31.6000 | 64.6 |
| D4P- | 1.0580 | 2330.20 | 63.300 | 1.1100 | 29.9000 | 64.6 |
| D5P- | 1.0430 | 2323.60 | 62.100 | 1.4500 | 30.8000 | 64.6 |
| D5P+ | 1.0540 | 2316.30 | 63.900 | .5400  | 30.1000 | 64.6 |
| E1S  | 1.0120 | 1784.40 | 48.110 | .6760  | 16.3690 | 67   |
| E3S  | 1.1070 | 2195.80 | 65.800 | 1.5150 | 27.3000 | 1    |
| I3P- | 1.0700 | 2253.55 | 67.050 | 1.5060 | 29.2200 | 65   |
| I1P- | 1.0690 | 2259.15 | 78.410 | 1.5800 | 29.2600 | 65   |
| J3D- | 1.0540 | 2345.26 | 66.560 | 1.6900 | 30.0850 | 65   |
| J1D- | 1.0540 | 2341.15 | 63.200 | 1.7200 | 30.0800 | 65   |
| N3P  | 1.0570 | 2322.00 | 62.900 | 1.3000 | 29.9300 | 1    |

## HE2

|     |        |         |        |       |        |      |
|-----|--------|---------|--------|-------|--------|------|
| A1S | 1.0400 | 1861.30 | 35.100 | .2280 | 7.7870 | 69.7 |
| B1P | 1.0660 | 1765.80 | 34.390 | .2160 | 7.4030 | 69.7 |
| C1S | 1.0910 | 1653.40 | 41.000 | .2450 | 7.0680 | 69.7 |
| D1S | 1.0690 | 1746.40 | 35.540 | .2180 | 7.3650 | 69.7 |
| F1P | 1.0840 | 1670.60 | 40.030 | .2350 | 7.1560 | 69.7 |
| F1D | 1.0790 | 1706.60 | 35.060 | .2250 | 7.2300 | 69.7 |
| A3S | 1.0450 | 1809.90 | 38.900 | .2440 | 7.7100 | 69.7 |
| B3P | 1.0630 | 1769.10 | 35.020 | .2200 | 7.4470 | 69.7 |
| C3S | 1.0960 | 1583.80 | 52.700 | .3100 | 7.0050 | 69.7 |
| D3S | 1.0710 | 1728.00 | 36.130 | .2240 | 7.3410 | 69.7 |

| STATE | RE     | WE      | WEXE   | AE    | BE     | REF  |
|-------|--------|---------|--------|-------|--------|------|
| F3S   | 1.0910 | 1635.80 | 44.410 | .2460 | 7.0710 | 69.7 |
| F3P   | 1.0860 | 1661.50 | 44.790 | .2330 | 7.1360 | 69.7 |
| F3D   | 1.0790 | 1706.80 | 35.100 | .2290 | 7.2300 | 69.7 |
| X2S   | 1.0810 | 1698.50 | 35.250 | .2240 | 7.2110 | 69.7 |

L12

|     |        |        |       |       |       |   |
|-----|--------|--------|-------|-------|-------|---|
| X1S | 2.6720 | 351.43 | 2.592 | .0070 | .6727 | 1 |
| A1S | 3.1080 | 255.46 | 1.574 | .0054 | .4974 | 1 |
| B1P | 2.9360 | 269.69 | 2.744 | .0080 | .5572 | 1 |

L1H

|     |        |         |        |       |        |    |
|-----|--------|---------|--------|-------|--------|----|
| X1S | 1.5950 | 1405.65 | 23.200 | .2130 | 7.5130 | 1  |
| A1S | 2.5960 | 234.41  | 28.950 | .0783 | 2.8190 | 1  |
| B1P | 2.3780 | 215.50  | 42.400 | .9860 | 3.3830 | 74 |

BEH

|     |        |         |        |       |         |   |
|-----|--------|---------|--------|-------|---------|---|
| X2S | 1.3430 | 2058.60 | 35.500 | .3000 | 10.3080 | 1 |
| A2P | 1.3330 | 2087.70 | 39.800 | .3290 | 10.4700 | 1 |
| X1S | 1.3120 | 2221.70 | 39.800 | .2930 | 10.8000 | 1 |
| A1S | 1.6090 | 1476.10 | 14.800 | .1250 | 7.1830  | 1 |

B2

|     |        |         |       |       |        |   |
|-----|--------|---------|-------|-------|--------|---|
| X3S | 1.5890 | 1051.30 | 9.400 | .0140 | 1.2120 | 1 |
| A3S | 1.6250 | 937.40  | 2.600 | .0110 | 1.1600 | 1 |

BH

|      |        |         |        |       |         |    |
|------|--------|---------|--------|-------|---------|----|
| X1S+ | 1.2324 | 2366.90 | 49.390 | .4120 | 12.0210 | 75 |
| A1P  | 1.2190 | 2251.00 | 56.670 | .8350 | 12.2950 | 75 |
| B1S+ | 1.2160 | 2399.90 | 69.520 | .4850 | 12.3390 | 75 |
| C1S+ | 1.2130 | 2474.70 | 54.420 | .4320 | 12.4100 | 75 |
| C1D  | 1.1960 | 2610.00 | 46.620 | .3900 | 12.7570 | 75 |

| STATE | RE | WE | WEXE | AE | BE | REF |
|-------|----|----|------|----|----|-----|
|-------|----|----|------|----|----|-----|

C2

|     |        |         |        |       |        |    |
|-----|--------|---------|--------|-------|--------|----|
| X1S | 1.2425 | 1854.70 | 13.340 | .0170 | 1.8980 | 76 |
| B1P | 1.3184 | 1608.30 | 12.080 | .0170 | 1.6160 | 76 |
| C1P | 1.2552 | 1809.10 | 15.810 | .0180 | 1.7830 | 76 |
| D1S | 1.2378 | 1829.60 | 13.970 | .0200 | 1.8330 | 76 |
| E1S | 1.2517 | 1671.50 | 40.020 | .0420 | 1.7930 | 76 |
| X3P | 1.3119 | 1641.30 | 11.670 | .0170 | 1.6320 | 76 |
| A3S | 1.3693 | 1470.40 | 11.190 | .0160 | 1.4980 | 76 |
| A3P | 1.2660 | 1788.20 | 16.440 | .0160 | 1.7530 | 76 |
| B3P | 1.5350 | 1106.60 | 39.260 | .0240 | 1.1920 | 76 |
| F3S | 1.3930 | 1360.50 | 14.800 | .0400 | 1.4480 | 77 |
| C2  | 1.2233 | 1968.70 | 14.430 | .0180 | 1.8770 | 78 |
| C2- | 1.2682 | 1781.00 | 11.580 | .0170 | 1.7460 | 78 |

BC

|      |        |         |        |       |        |    |
|------|--------|---------|--------|-------|--------|----|
| 2S+  | 1.6930 | 949.00  | 8.490  | .0192 | 1.0340 | 61 |
| 2S1  | 1.6870 | 917.00  | 13.240 | .0154 | 1.0410 | 61 |
| 2S2  | 1.4380 | 1504.00 | 23.640 | .0192 | 1.4320 | 61 |
| 2S3  | 2.4380 | 680.00  | 5.370  | .0003 | .4990  | 61 |
| 2P1  | 1.5440 | 1194.00 | 17.240 | .0172 | 1.2430 | 61 |
| 2P2  | 1.8590 | 883.00  | 4.980  | .0028 | .8580  | 61 |
| 2P3  | 1.5990 | 1339.00 | 64.920 | .0316 | 1.1590 | 61 |
| 2D1  | 1.6870 | 944.00  | 11.380 | .0134 | 1.0410 | 61 |
| 2D2  | 2.3370 | 390.00  | 15.870 | .0270 | .5420  | 61 |
| 4S1  | 1.6650 | 991.00  | 10.390 | .0128 | 1.0690 | 61 |
| 4S2  | 1.6360 | 1022.00 | 11.610 | .0120 | 1.1070 | 61 |
| 4S2+ | 1.6720 | 888.00  | 62.140 | .0414 | 1.0590 | 61 |
| 4S3  | 2.2570 | 723.00  | 3.160  | .0006 | .5810  | 61 |
| 4S5  | 2.3920 | 1103.00 | 6.340  | .0016 | .5180  | 61 |
| 4P1  | 1.4600 | 1441.00 | 30.780 | .0246 | 1.3890 | 61 |
| 4P3  | 1.8180 | 702.00  | 17.860 | .0188 | .8960  | 61 |
| 4P6  | 2.3230 | 668.00  | 4.330  | .0023 | .5490  | 61 |
| 4F1  | 1.7130 | 920.00  | 13.970 | .0151 | 1.0100 | 61 |
| 6P1  | 1.7030 | 973.00  | 9.790  | .0121 | 1.0210 | 61 |

CH

|      |        |         |        |       |         |    |
|------|--------|---------|--------|-------|---------|----|
| X2P  | 1.1200 | 2858.50 | 63.000 | .5300 | 14.4570 | 79 |
| A2D  | 1.1020 | 2930.70 | 96.650 | .6970 | 14.9360 | 79 |
| C2S+ | 1.1140 | 2840.20 | 25.960 | .7180 | 14.6030 | 79 |

| STATE | RE     | WE      | WEXE   | AE    | BE      | REF |
|-------|--------|---------|--------|-------|---------|-----|
| *S    | 1.1309 | 2739.70 | .000   | .4917 | 14.1770 | 80  |
| *P    | 1.2345 | 1865.35 | 15.850 | .9414 | 11.8990 | 80  |
| *D    | 1.2320 | 2075.50 | 76.300 | .6200 | 11.9370 | 81  |

N2

|      |        |         |        |        |        |    |
|------|--------|---------|--------|--------|--------|----|
| X1S  | 1.0970 | 2359.61 | 14.456 | 1.7600 | 1.9990 | 82 |
| A1S  | 1.2750 | 1530.25 | 12.070 | .0170  | 1.4800 | 83 |
| A1P  | 1.2200 | 1666.05 | 13.550 | .0170  | 1.5640 | 83 |
| A1P* | 1.2200 | 1694.21 | 13.950 | .0180  | 1.6170 | 83 |
| W1D  | 1.2680 | 1559.24 | 11.890 | .0170  | 1.4980 | 83 |
| B11S | 1.4450 | 762.90  | 3.950  | .0080  | 1.1530 | 84 |
| C11S | 1.1200 | 2193.10 | 22.070 | .0200  | 1.9200 | 84 |
| A3S  | 1.2860 | 1460.60 | 13.851 | 1.7980 | 1.4550 | 82 |
| B3S  | 1.2780 | 1516.88 | 12.180 | .0170  | 1.4740 | 83 |
| B3P  | 1.2130 | 1733.40 | 14.120 | .0180  | 1.6370 | 83 |
| C3P  | 1.1490 | 2047.20 | 28.450 | .0190  | 1.8250 | 83 |
| X2S  | 1.1160 | 2207.19 | 16.136 | .0200  | 1.9320 | 1  |
| B2S  | 1.0750 | 2419.84 | 23.190 | .0195  | 2.0830 | 1  |
| SG+  | 1.6100 | 1135.00 | 6.300  | .0060  | .9000  | 1  |
| 3DG  | 1.7500 | 684.00  | 20.900 | .0190  | .7800  | 1  |

CN

|      |        |         |        |       |        |    |
|------|--------|---------|--------|-------|--------|----|
| X2S  | 1.1718 | 2068.70 | 13.144 | .0173 | 1.8996 | 1  |
| A2P  | 1.2327 | 1814.43 | 12.883 | .0175 | 1.7165 | 1  |
| B2S  | 1.1506 | 2164.13 | 20.250 | .0221 | 1.9700 | 1  |
| E2S  | 1.3210 | 1681.43 | 3.600  | .0064 | 1.4870 | 85 |
| F2D  | 1.3710 | 1239.50 | 12.750 | .0187 | 1.3834 | 86 |
| *B1P | 1.2470 | 1688.35 | 15.120 | .0191 | 1.6770 | 87 |
| *A1S | 1.1727 | 2033.05 | 16.140 | .0188 | 1.8964 | 88 |
| *F1S | 1.1710 | 2670.50 | 46.900 | .0320 | 1.9030 | 88 |
| *C1S | 1.3630 | 1265.00 | 11.000 | .0020 | 1.4030 | 88 |

NH

|      |        |         |        |       |         |    |
|------|--------|---------|--------|-------|---------|----|
| A1D  | 1.0330 | 3314.00 | 63.000 | .6700 | 16.7800 | 89 |
| A1D* | 1.0370 | 3362.00 | 16.000 | .7320 | 16.6800 | 89 |
| B1S* | 1.0350 | 3347.00 | 70.700 | .6050 | 16.7300 | 90 |

| STATE | RE     | WE      | WEXE   | AE    | BE      | REF |
|-------|--------|---------|--------|-------|---------|-----|
| B1S*  | 1:0350 | 3396:00 | 13:000 | :7120 | 16:7300 | 89  |
| X3S-  | 1:0370 | 3203:20 | 78:300 | :6480 | 16:6700 | 91  |
| X3S*  | 1:0410 | 3300:00 | 20:000 | :7600 | 16:5600 | 89  |

02

|     |        |         |        |       |        |      |
|-----|--------|---------|--------|-------|--------|------|
| X3S | 1:2074 | 1580:36 | 12:070 | :0160 | 1:4457 | 1    |
| B3S | 1:6040 | 676:80  | 9:293  | :0110 | :8190  | 92   |
| A1D | 1:2155 | 1509:30 | 12:900 | :0170 | 1:4264 | 1    |
| B1S | 1:2267 | 1432:69 | 13:950 | :0180 | 1:4004 | 1    |
| 1SU | 1:5970 | 650:50  | 17:040 | :0205 | :8260  | 93   |
| X2P | 1:1160 | 1903:85 | 16:180 | :0200 | 1:6920 | 1,94 |
| A2P | 1:4090 | 895:60  | 13:400 | :0190 | 1:0617 | 1    |
| A4P | 1:3810 | 1035:69 | 10:390 | :0160 | 1:1047 | 1    |
| B4S | 1:2800 | 1196:77 | 17:090 | :0220 | 1:2873 | 1    |

N0

|      |        |         |        |       |        |    |
|------|--------|---------|--------|-------|--------|----|
| G2S  | 1:3426 | 1085:54 | 11:080 | :0204 | 1:2520 | 95 |
| X2P  | 1:1508 | 1903:85 | 13:970 | :0178 | 1:7050 | 1  |
| A2S  | 1:0637 | 2371:30 | 14:480 | :0164 | 1:9952 | 1  |
| B2P  | 1:4480 | 1036:96 | 7:603  | :0116 | 1:0760 | 1  |
| B12P | 1:3850 | 1038:41 | 7:603  | :0189 | 1:1770 | 1  |
| B12D | 1:3020 | 1217:40 | 15:610 | :0210 | 1:3320 | 96 |
| D2S  | 1:0650 | 2327:00 | 23:000 | :0160 | 1:9920 | 1  |
| E2S  | 1:0661 | 2373:60 | 15:800 | :0182 | 1:9863 | 1  |

C0

|     |        |         |        |       |        |    |
|-----|--------|---------|--------|-------|--------|----|
| A1P | 1:2356 | 1515:40 | 17:200 | :0205 | 1:6104 | 97 |
| B1S | 1:1197 | 2112:70 | 15:220 | :0261 | 1:9612 | 97 |
| C1S | 1:1219 | 2175:92 | 14:760 | :0196 | 1:9533 | 97 |
| 1S  | 1:1283 | 2169:82 | 13:294 | :0175 | 1:9313 | 97 |
| A3S | 1:3519 | 1230:65 | 11:013 | :0187 | 1:3453 | 97 |
| A3P | 1:2058 | 1743:55 | 14:470 | :0195 | 1:6911 | 97 |
| B3S | 1:1130 | 2188:00 | 30:000 | :0420 | 1:9860 | 97 |
| D3D | 1:3700 | 1152:58 | 7:281  | :0168 | 1:3099 | 97 |
| E3S | 1:3834 | 1113:67 | 9:596  | :0181 | 1:2848 | 97 |
| J3S | 1:1410 | 2196:00 | 15:000 | :0200 | 1:8890 | 97 |

| STATE | RE     | WE      | WEXE   | AE    | BE     | REF |
|-------|--------|---------|--------|-------|--------|-----|
| X2S   | 1.1152 | 2214.24 | 15.164 | .0190 | 1.9772 | 97  |
| A2P   | 1.2438 | 1562.06 | 13.532 | .0194 | 1.5894 | 97  |
| B2S   | 1.1688 | 1734.18 | 27.927 | .0303 | 1.7999 | 97  |
| 2D    | 1.3460 | 1144.00 | 33.300 | .0240 | 1.3570 | 97  |

Bθ

|      |        |         |        |       |        |   |
|------|--------|---------|--------|-------|--------|---|
| X2S+ | 1.2050 | 1885.44 | 11.770 | .0165 | 1.7800 | 1 |
| A2P  | 1.3520 | 1260.70 | 11.160 | .0196 | 1.4132 | 1 |
| B2S+ | 1.3110 | 1280.30 | 10.070 | .0180 | 1.5030 | 1 |

BEθ

|      |        |         |        |       |        |    |
|------|--------|---------|--------|-------|--------|----|
| X1S  | 1.3310 | 1487.32 | 11.830 | .0190 | 1.6510 | 1  |
| A1P  | 1.4630 | 1144.24 | 8.415  | .0163 | 1.3661 | 1  |
| B1S  | 1.3620 | 1370.82 | 7.745  | .0154 | 1.5760 | 1  |
| A3P* | 1.4480 | 1213.00 | 8.600  | .0160 | 1.3970 | 98 |

θH

|      |        |         |        |       |         |     |
|------|--------|---------|--------|-------|---------|-----|
| X2P  | .9706  | 3735.20 | 82.810 | .7140 | 18.8710 | 1   |
| A2S  | 1.0120 | 3180.60 | 94.930 | .8070 | 17.3550 | 1   |
| C3S+ | 2.0450 | 1232.90 | 19.100 | .0780 | 4.2470  | 99  |
| +3P  | 1.1400 | 2145.20 | 84.500 | .8340 | 13.6620 | 100 |
| +3S- | 1.0290 | 3077.30 | 58.600 | .7640 | 16.7920 | 100 |

F2

|     |        |         |       |       |        |   |
|-----|--------|---------|-------|-------|--------|---|
| B1P | 1.2820 | 1139.80 | 9.700 | .0140 | 1.0800 | 1 |
|-----|--------|---------|-------|-------|--------|---|

θF

|     |        |         |       |       |        |     |
|-----|--------|---------|-------|-------|--------|-----|
| 2P* | 1.3210 | 1211.00 | 5.150 | .0097 | 1.1040 | 101 |
|-----|--------|---------|-------|-------|--------|-----|

| STATE    | RE     | WE      | WEXE   | AE     | BE      | REF  |
|----------|--------|---------|--------|--------|---------|------|
| NF       |        |         |        |        |         |      |
| X3S      | 1.3170 | 1141.37 | 8.990  | .0150  | 1.2060  | 102  |
| B1S      | 1.3000 | 1197.49 | 8.640  | .0145  | 1.2377  | 102  |
| CF       |        |         |        |        |         |      |
| X2P      | 1.2670 | 1308.10 | 11.100 | .0184  | 1.4170  | 103  |
| A2P      | 1.1480 | 1779.00 | 29.800 | .0245  | 1.7250  | 103, |
| B2S+     | 1.3180 | 1191.00 | 19.400 | .0250  | 1.3200  | 105  |
| BF       |        |         |        |        |         |      |
| X1S      | 1.2630 | 1402.10 | 11.800 | .0160  | 1.5170  | 106  |
| A1P      | 1.3040 | 1264.96 | 12.500 | .0180  | 1.4226  | 106  |
| 3S1S     | 1.2076 | 1692.90 | 12.400 | .0178  | 1.6590  | 106  |
| 3P1S     | 1.2207 | 1613.20 | 14.500 | .0194  | 1.6238  | 106  |
| 4P1S     | 1.2153 | 1666.60 | 12.700 | .0174  | 1.6381  | 106  |
| 3P1P     | 1.2190 | 1673.00 | 14.000 | .0169  | 1.6290  | 106  |
| A3P      | 1.3080 | 1323.90 | 9.200  | .01580 | 1.4130  | 106  |
| B3S+     | 1.2150 | 1629.30 | 22.260 | .0200  | 1.6385  | 106  |
| D3P      | 1.2103 | 1696.81 | 11.000 | .0176  | 1.6518  | 106  |
| BEF      |        |         |        |        |         |      |
| X2S      | 1.3600 | 1266.90 | 9.350  | .0176  | 1.4890  | 107  |
| A2P      | 1.3940 | 1171.20 | 8.530  | .0175  | 1.4200  | 107  |
| C2S      | 1.3250 | 1419.70 | 9.900  | .0140  | 1.5700  | 108  |
| HF       |        |         |        |        |         |      |
| X1S      | .9168  | 4138.32 | 89.880 | .7980  | 20.9560 | 109  |
| V1S      | 2.0916 | 1158.50 | 17.750 | .0173  | 4.0263  | 110  |
| *STOP* Q |        |         |        |        |         |      |

# APPENDIX G

| STATE | A0    | A1    | A2   | KE    | LE     | ME     |
|-------|-------|-------|------|-------|--------|--------|
| H2    |       |       |      |       |        |        |
| X1S   | 1.581 | =1.61 | 1.90 | 5.748 | =37.36 | 237.90 |
| X2S   | .879  | =1.60 | 1.83 | 1.565 | =7.10  | 30.54  |
| A3S   | 1.031 | =1.63 | 1.94 | 2.109 | =10.45 | 50.24  |
| B1S   | .469  | =1.53 | 2.23 | .561  | =1.99  | 8.99   |
| B1S'  | .829  | =1.77 | 1.00 | 1.280 | =5.98  | 11.90  |
| B1S   | .885  | =2.17 | 4.22 | 1.434 | =8.41  | 58.84  |
| C3P   | .971  | =1.61 | 1.91 | 1.804 | =8.38  | 38.37  |
| C1P+  | .909  | =1.69 | 2.43 | 1.741 | =8.65  | 48.52  |
| C1P=  | .932  | =1.75 | 2.53 | 1.753 | =8.91  | 50.02  |
| D1P=  | .899  | =1.81 | 2.61 | 1.656 | =8.65  | 47.84  |
| D1P+  | .850  | =1.74 | 2.40 | 1.653 | =8.53  | 46.25  |
| D3P   | .920  | =1.66 | 2.00 | 1.670 | =7.93  | 36.37  |
| D4P+  | .853  | =1.25 | .62  | 1.608 | =5.85  | 11.28  |
| D4P=  | .902  | =1.48 | 1.33 | 1.611 | =6.77  | 23.05  |
| D5P=  | .870  | =1.59 | 1.82 | 1.600 | =7.33  | 32.19  |
| D5P+  | .885  | =.77  | =.67 | 1.594 | =3.49  | =11.61 |
| E1S   | .966  | =1.75 | 1.87 | 1.886 | =9.79  | 41.33  |
| E3S   | .877  | =1.74 | 2.19 | 1.431 | =6.76  | 30.76  |
| I3P=  | .863  | =1.66 | 1.92 | 1.508 | =7.03  | 30.42  |
| I1P=  | .866  | =1.69 | 1.80 | 1.516 | =7.21  | 28.72  |
| J3D=  | .908  | =1.73 | 2.27 | 1.634 | =8.05  | 40.00  |
| J1D=  | .905  | =1.74 | 2.39 | 1.629 | =8.08  | 42.08  |
| N3P   | .895  | =1.56 | 1.65 | 1.601 | =7.10  | 28.33  |

## HE2

|     |       |       |      |       |        |        |
|-----|-------|-------|------|-------|--------|--------|
| A1S | 2.209 | =2.17 | 2.86 | 4.085 | =25.53 | 129.70 |
| B1P | 2.091 | =2.16 | 2.73 | 3.681 | =22.38 | 106.30 |
| C1S | 1.921 | =2.35 | 3.04 | 3.227 | =20.87 | 99.05  |
| D1S | 2.056 | =2.17 | 2.67 | 3.599 | =21.91 | 100.82 |
| F1P | 1.937 | =2.28 | 2.76 | 3.296 | =20.78 | 92.77  |
| F1D | 2.000 | =2.22 | 2.95 | 3.436 | =21.25 | 104.53 |
| A3S | 2.110 | =2.24 | 2.90 | 3.864 | =24.83 | 123.05 |
| B3P | 2.087 | =2.17 | 2.75 | 3.694 | =22.62 | 107.84 |
| C3S | 1.778 | =2.67 | 3.88 | 2.961 | =21.62 | 114.74 |
| D3S | 2.020 | =2.20 | 2.75 | 3.522 | =21.67 | 101.42 |

| STATE | A0    | A1   | A2   | KE    | LE    | ME     |
|-------|-------|------|------|-------|-------|--------|
| F3S   | 1.879 | 2.34 | 2.67 | 3.157 | 20.33 | 84.84  |
| F3P   | 1.921 | 2.27 | 2.24 | 3.258 | 20.40 | 74.24  |
| F3D   | 2.001 | 2.25 | 3.07 | 3.437 | 21.47 | 108.77 |
| X2S   | 1.987 | 2.22 | 2.90 | 3.400 | 20.94 | 101.20 |

L12

|     |      |      |      |      |     |     |
|-----|------|------|------|------|-----|-----|
| X1S | .912 | 1.91 | 1.97 | .255 | .55 | .85 |
| A1S | .652 | 1.93 | 2.54 | .135 | .25 | .43 |
| B1P | .648 | 2.16 | 2.54 | .150 | .33 | .53 |

L1H

|     |       |      |       |       |      |       |
|-----|-------|------|-------|-------|------|-------|
| X1S | 1.306 | 1.88 | 2.38  | 1.027 | 3.64 | 11.52 |
| A1S | .097  | .62  | 7.32  | .029  | .02  | .37   |
| B1P | .068  | 4.09 | 12.60 | .024  | .12  | .64   |

BEH

|     |       |      |      |       |       |       |
|-----|-------|------|------|-------|-------|-------|
| X2S | 2.042 | 1.97 | 2.55 | 2.264 | 9.96  | 38.39 |
| A2P | 2.067 | 2.04 | 2.69 | 2.327 | 10.70 | 42.26 |
| X1S | 2.269 | 1.93 | 2.20 | 2.637 | 11.64 | 40.44 |
| A1S | 1.506 | 1.60 | 1.81 | 1.164 | 3.46  | 9.77  |

B2

|     |       |      |      |       |       |       |
|-----|-------|------|------|-------|-------|-------|
| X3S | 4.528 | 2.67 | 3.74 | 3.587 | 18.08 | 63.75 |
| A3S | 3.762 | 2.28 | 4.99 | 2.849 | 11.98 | 64.57 |

BH

|      |       |      |      |       |       |        |
|------|-------|------|------|-------|-------|--------|
| X1S+ | 2.314 | 2.12 | 2.90 | 3.047 | 15.76 | 69.92  |
| A1P  | 2.046 | 3.07 | 8.73 | 2.754 | 20.83 | 194.09 |
| B1S+ | 2.318 | 2.27 | 2.71 | 3.135 | 17.59 | 68.91  |
| C1S+ | 2.451 | 2.16 | 2.89 | 3.331 | 17.77 | 78.56  |
| C1D  | 2.652 | 2.04 | 2.78 | 3.708 | 18.99 | 86.41  |

| STATE | A0     | A1   | A2    | KE     | LE     | ME      |
|-------|--------|------|-------|--------|--------|---------|
| C2    |        |      |       |        |        |         |
| X1S   | 9.000  | 2.46 | 2.87  | 11.659 | 69.22  | 260.18  |
| B1P   | 7.948  | 2.74 | 4.43  | 9.146  | 57.12  | 280.00  |
| C1P   | 9.115  | 2.71 | 3.25  | 11.571 | 74.87  | 286.36  |
| D1S   | 9.068  | 2.82 | 4.83  | 11.838 | 80.77  | 447.35  |
| E1S   | 7.738  | 4.64 | 12.03 | 9.877  | 109.83 | 909.77  |
| X3P   | 8.197  | 2.75 | 4.66  | 9.525  | 59.81  | 309.37  |
| A3S   | 7.167  | 2.75 | 4.45  | 7.645  | 46.02  | 217.96  |
| A3P   | 9.058  | 2.55 | 1.89  | 11.303 | 68.35  | 159.68  |
| B3P   | 5.101  | 4.12 | .79   | 4.330  | 34.83  | 17.40   |
| F3S   | 6.348  | 5.33 | 28.64 | 6.542  | 75.04  | 1158.81 |
| C2    | 10.254 | 2.68 | 3.83  | 13.704 | 89.94  | 420.69  |
| C2*   | 9.021  | 2.66 | 4.39  | 11.218 | 70.46  | 367.56  |

|      |        |      |       |       |       |        |
|------|--------|------|-------|-------|-------|--------|
| BC   |        |      |       |       |       |        |
| 2S+  | 4.325  | 3.84 | 12.96 | 3.018 | 20.54 | 163.77 |
| 2S1  | 4.011  | 3.17 | 4.10  | 2.819 | 15.90 | 48.69  |
| 2S2  | 7.844  | 3.35 | 3.00  | 7.587 | 52.97 | 131.94 |
| 2S3  | 4.602  | 1.14 | 5.56  | 1.548 | 2.17  | 17.38  |
| 2P1  | 5.695  | 3.22 | 3.68  | 4.778 | 29.85 | 88.41  |
| 2P2  | 4.512  | 1.56 | .83   | 2.611 | 6.57  | 7.51   |
| 2P3  | 7.682  | 6.25 | 11.48 | 6.009 | 70.46 | 323.81 |
| 2D1  | 4.251  | 2.95 | 3.56  | 2.987 | 15.65 | 44.80  |
| 2D2  | 1.394  | .97  | 11.41 | .510  | 3.26  | 12.79  |
| 4S1  | 4.562  | 2.85 | 3.67  | 3.291 | 16.90 | 52.33  |
| 4S2  | 4.685  | 2.67 | 1.91  | 3.501 | 17.13 | 29.91  |
| 4S2+ | 3.698  | 6.46 | 13.10 | 2.645 | 30.68 | 148.75 |
| 4S3  | 4.468  | 1.21 | 1.78  | 1.754 | 2.83  | 7.37   |
| 4S5  | 11.663 | .10  | 8.15  | 4.077 | .49   | 69.67  |
| 4P1  | 7.423  | 4.06 | 5.85  | 6.965 | 58.14 | 229.53 |
| 4P3  | 2.731  | 3.74 | 4.19  | 1.653 | 10.20 | 25.16  |
| 4P6  | 4.036  | .15  | 5.23  | 1.496 | .29   | 17.40  |
| 4F1  | 4.161  | 3.27 | 4.14  | 2.836 | 16.24 | 48.05  |
| 6P1  | 4.604  | 2.88 | 3.99  | 3.175 | 16.12 | 52.45  |

|      |       |      |      |       |       |        |
|------|-------|------|------|-------|-------|--------|
| CH   |       |      |      |       |       |        |
| X2P  | 2.807 | 2.21 | 3.19 | 4.475 | 26.47 | 136.53 |
| A2D  | 2.856 | 2.53 | 3.66 | 4.703 | 32.34 | 170.19 |
| C2S+ | 2.743 | 2.59 | 2.66 | 4.421 | 30.88 | 113.67 |

| STATE | AO    | A1   | A2   | KE    | LE    | ME     |
|-------|-------|------|------|-------|-------|--------|
| +S    | 2.629 | 2.12 | 5.60 | 4.111 | 23.09 | 216.12 |
| +P    | 1.452 | 3.07 | 5.27 | 1.906 | 14.20 | 79.04  |
| +D    | 1.792 | 2.51 | 3.58 | 2.361 | 14.40 | 66.89  |

N2

|      |        |        |          |        |          |            |
|------|--------|--------|----------|--------|----------|------------|
| X1S  | 13.831 | 174.21 | 37932.19 | 22.986 | 10951.10 | 8694462.00 |
| A1S  | 7.857  | 2.98   | 5.66     | 9.666  | 67.76    | 403.79     |
| A1P  | 8.813  | 2.93   | 4.95     | 11.842 | 85.32    | 472.95     |
| A1P* | 8.815  | 2.94   | 5.08     | 11.845 | 85.74    | 485.24     |
| W1D  | 8.059  | 2.97   | 5.72     | 10.025 | 70.41    | 428.35     |
| B11S | 2.507  | 1.77   | 1.61     | 2.401  | 8.80     | 22.22      |
| C11S | 12.439 | 2.98   | 3.46     | 19.833 | 158.47   | 656.41     |
| A3S  | 7.281  | 207.75 | 53943.34 | 8.805  | 4267.26  | 3446411.00 |
| B3S  | 7.752  | 2.98   | 5.58     | 9.492  | 66.36    | 388.97     |
| B3P  | 9.114  | 2.94   | 5.06     | 12.389 | 90.10    | 511.05     |
| C3P  | 11.404 | 2.95   | .46      | 17.275 | 132.90   | 72.00      |
| X2S  | 12.521 | 2.97   | 5.47     | 20.107 | 160.59   | 1058.94    |
| B2S  | 13.959 | 2.81   | 2.47     | 24.159 | 189.62   | 618.57     |
| SG*  | 7.108  | 2.40   | 2.54     | 5.484  | 24.54    | 64.50      |
| 3DG  | 2.979  | 4.56   | 8.13     | 1.945  | 15.21    | 61.96      |

CN

|      |        |      |       |        |        |         |
|------|--------|------|-------|--------|--------|---------|
| X2S  | 11.187 | 2.66 | 4.22  | 16.294 | 110.87 | 600.43  |
| A2P  | 9.524  | 2.80 | 4.77  | 12.535 | 85.30  | 472.11  |
| B2S  | 11.805 | 3.05 | 4.81  | 17.835 | 142.01 | 776.80  |
| E2S  | 9.441  | 1.81 | 2.49  | 10.821 | 44.51  | 184.99  |
| F2D  | 5.515  | 3.02 | 5.25  | 5.868  | 38.76  | 196.49  |
| +B1P | 8.441  | 2.91 | 4.58  | 10.856 | 76.03  | 383.86  |
| +A1S | 10.823 | 2.77 | 3.93  | 15.740 | 111.59 | 539.22  |
| +F1S | 18.609 | 4.93 | 13.99 | 27.142 | 343.01 | 3322.05 |
| +C1S | 5.664  | 1.21 | 3.38  | 6.097  | 16.30  | 133.29  |

NH

|      |       |      |      |       |       |        |
|------|-------|------|------|-------|-------|--------|
| A1D  | 3.250 | 2.31 | 4.19 | 6.092 | 40.94 | 287.15 |
| A1D* | 3.365 | 2.47 | 3.02 | 6.258 | 44.80 | 210.61 |
| B1S* | 3.325 | 2.21 | 3.26 | 6.208 | 39.69 | 227.01 |

| STATE | AO    | A1   | A2   | KE    | LE    | ME     |
|-------|-------|------|------|-------|-------|--------|
| B1S*  | 3.423 | 2.44 | 2.94 | 6.391 | 45.20 | 210.32 |
| X3S*  | 3.056 | 2.24 | 3.17 | 5.684 | 36.92 | 200.95 |
| X3S*  | 3.266 | 2.52 | 3.13 | 6.027 | 43.84 | 209.12 |

B2

|     |        |      |      |        |        |         |
|-----|--------|------|------|--------|--------|---------|
| X3S | 8.579  | 3.02 | 5.81 | 11.769 | 88.21  | 562.55  |
| B3S | 2.777  | 2.85 | 2.59 | 2.159  | 11.51  | 26.05   |
| A1D | 7.930  | 3.10 | 6.00 | 10.735 | 82.18  | 522.89  |
| B1S | 7.278  | 3.19 | 6.09 | 9.674  | 75.51  | 469.94  |
| 1SU | 2.544  | 4.26 | 8.90 | 1.995  | 15.95  | 83.58   |
| X2P | 10.638 | 3.22 | 6.56 | 17.082 | 147.71 | 1079.49 |
| A2P | 3.752  | 3.52 | 7.04 | 3.779  | 28.29  | 160.78  |
| A4P | 4.822  | 3.26 | 7.04 | 5.056  | 35.84  | 223.96  |
| B4S | 5.525  | 3.65 | 7.78 | 6.744  | 57.66  | 384.51  |

NB

|      |        |      |      |        |        |         |
|------|--------|------|------|--------|--------|---------|
| G2S  | 4.674  | 3.35 | 8.17 | 5.186  | 38.87  | 281.92  |
| X2P  | 10.557 | 2.94 | 5.36 | 15.942 | 122.31 | 774.76  |
| A2S  | 13.995 | 2.63 | 3.80 | 24.738 | 183.37 | 995.86  |
| B2P  | 4.962  | 2.73 | 4.62 | 4.734  | 26.79  | 125.06  |
| B12P | 4.549  | 3.36 | 9.82 | 4.743  | 34.53  | 291.24  |
| B12D | 5.525  | 3.40 | 6.65 | 6.519  | 51.09  | 306.86  |
| D2S  | 13.499 | 2.56 | .52  | 23.802 | 171.90 | 130.60  |
| E2S  | 14.085 | 2.82 | 4.67 | 24.785 | 197.02 | 1222.51 |

C8

|     |        |      |       |        |        |         |
|-----|--------|------|-------|--------|--------|---------|
| A1P | 7.081  | 3.00 | 4.10  | 9.276  | 67.49  | 299.14  |
| B1S | 11.302 | 3.39 | 9.19  | 18.029 | 163.72 | 1585.11 |
| C1S | 12.036 | 2.86 | 5.21  | 19.126 | 146.42 | 949.65  |
| 1S  | 12.106 | 2.70 | 4.51  | 19.018 | 136.41 | 808.10  |
| A3S | 5.590  | 3.12 | 6.72  | 6.117  | 42.38  | 270.01  |
| A3P | 8.927  | 2.98 | 5.41  | 12.279 | 91.08  | 547.91  |
| B3S | 11.970 | 4.88 | 19.74 | 19.326 | 254.37 | 3694.73 |
| D3D | 5.036  | 2.88 | 6.64  | 5.366  | 33.81  | 227.95  |
| E3S | 4.794  | 3.04 | 6.54  | 5.009  | 32.97  | 205.31  |
| J3S | 12.677 | 3.05 | 6.34  | 19.475 | 156.25 | 1138.91 |

| STATE | A0     | A1   | A2   | KE     | LE     | ME     |
|-------|--------|------|------|--------|--------|--------|
| X2S   | 12.313 | 2.79 | 4.62 | 19.803 | 148.63 | 882.02 |
| A2P   | 7.623  | 3.00 | 5.58 | 9.856  | 71.35  | 426.91 |
| B2S   | 8.297  | 3.70 | 6.76 | 12.147 | 115.33 | 720.98 |
| 2D    | 4.789  | 3.48 | 1.18 | 5.287  | 41.07  | 41.28  |

B0

|      |       |      |      |        |       |        |
|------|-------|------|------|--------|-------|--------|
| X2S+ | 9.917 | 2.64 | 4.28 | 13.660 | 89.66 | 483.19 |
| A2P  | 5.585 | 3.06 | 6.46 | 6.111  | 41.52 | 258.97 |
| B2S+ | 5.416 | 2.70 | 4.65 | 6.302  | 38.94 | 204.48 |

BE0

|      |       |      |      |       |       |        |
|------|-------|------|------|-------|-------|--------|
| X1S  | 6.653 | 2.73 | 4.52 | 7.511 | 46.18 | 230.20 |
| A1P  | 4.759 | 2.67 | 4.78 | 4.447 | 24.31 | 119.06 |
| B1S  | 5.921 | 2.42 | 4.02 | 6.384 | 33.98 | 166.14 |
| A3P* | 5.230 | 2.66 | 4.72 | 4.989 | 27.47 | 134.86 |

0H

|      |       |      |      |       |       |        |
|------|-------|------|------|-------|-------|--------|
| X2P  | 3.671 | 2.25 | 3.39 | 7.794 | 54.16 | 336.78 |
| A2S  | 2.895 | 2.42 | 3.68 | 5.653 | 40.56 | 243.44 |
| C3S+ | 1.777 | 1.89 | 1.46 | .850  | 2.35  | 3.56   |
| +3P  | 1.673 | 2.60 | 4.31 | 2.574 | 17.60 | 102.45 |
| +3S  | 2.800 | 2.39 | 4.81 | 5.290 | 36.85 | 288.43 |

F2

|     |       |      |      |       |       |        |
|-----|-------|------|------|-------|-------|--------|
| B1P | 5.973 | 3.28 | 7.46 | 7.269 | 55.79 | 395.98 |
|-----|-------|------|------|-------|-------|--------|

0F

|     |       |      |      |       |       |        |
|-----|-------|------|------|-------|-------|--------|
| 2P* | 6.596 | 2.61 | 5.38 | 7.560 | 44.75 | 279.74 |
|-----|-------|------|------|-------|-------|--------|

| STATE    | AO    | A1    | A2     | KE     | LE     | ME       |
|----------|-------|-------|--------|--------|--------|----------|
| NF       |       |       |        |        |        |          |
| X3S      | 5.364 | 2.96  | 6.00   | 6.185  | 41.73  | 256.58   |
| B1S      | 5.753 | 2.89  | 5.78   | 6.809  | 45.39  | 279.42   |
| CF       |       |       |        |        |        |          |
| X2P      | 5.996 | 3.00  | 6.01   | 7.471  | 53.03  | 335.72   |
| A2P      | 9.111 | 3.44  | 3.29   | 13.826 | 124.33 | 413.58   |
| B2S+     | 5.336 | 3.85  | 8.71   | 6.144  | 53.81  | 369.71   |
| BF       |       |       |        |        |        |          |
| X1S      | 6.435 | 2.62  | 3.43   | 8.068  | 50.30  | 207.91   |
| A1P      | 5.585 | 2.88  | 4.47   | 6.569  | 43.45  | 207.46   |
| 3S1S     | 8.578 | 2.82  | 4.99   | 11.765 | 82.56  | 483.17   |
| 3P1S     | 7.958 | 2.98  | 5.13   | 10.682 | 78.18  | 441.61   |
| 4P1S     | 8.420 | 2.80  | 4.64   | 11.402 | 78.84  | 429.76   |
| 3P1P     | 8.532 | 2.78  | 3.90   | 11.484 | 78.45  | 361.80   |
| A3P      | 6.160 | 18.46 | 421.68 | 7.201  | 304.89 | 21296.98 |
| B3S+     | 8.045 | 3.02  | 2.37   | 10.900 | 81.36  | 209.57   |
| D3P      | 8.655 | 2.82  | 5.53   | 11.818 | 82.73  | 535.42   |
| BEF      |       |       |        |        |        |          |
| X2S      | 5.353 | 2.68  | 4.77   | 5.788  | 34.17  | 178.96   |
| A2P      | 4.797 | 2.69  | 5.07   | 4.937  | 28.62  | 154.50   |
| C2S      | 6.375 | 2.34  | 2.66   | 7.262  | 38.54  | 132.21   |
| HF       |       |       |        |        |        |          |
| X1S      | 4.058 | 2.25  | 3.49   | 9.656  | 71.20  | 480.76   |
| V1S      | 1.655 | 1.21  | 1.12   | .757   | 1.31   | 2.33     |
| *STOP* 0 |       |       |        |        |        |          |

# APPENDIX H

## FORCE CONSTANT RELATIONS OBTAINED BY LEAST-SQUARES ANALYSIS

| <u>MOLECULE</u> | <u>EXPONENT</u> | <u>CONSTANT</u> |
|-----------------|-----------------|-----------------|
| H <sub>2</sub>  | 3.91            | 1.94            |
| He <sub>2</sub> | 5.27            | 5.05            |
| HeH             | 3.53            | 2.50            |
| Li <sub>2</sub> | 4.36            | 18.0            |
| LiH             | 7.97            | 38.9            |
| BeH             | 3.83            | 7.16            |
| B <sub>2</sub>  | 2.91            | 17.5            |
| BH              | 7.72            | 14.3            |
| C <sub>2</sub>  | 5.07            | 36.6            |
| BC              | 5.75            | 60.0            |
| CH              | 7.31            | 9.8             |
| N <sub>2</sub>  | 7.10            | 46.8            |
| CN              | 6.27            | 48.6            |
| NH              | 17.9            | 11.1            |
| O <sub>2</sub>  | 5.95            | 32.8            |
| NO              | 5.99            | 35.1            |
| CO              | 640             | 39.1            |
| BO              | 7.45            | 53.2            |
| BeO             | 5.09            | 31.6            |
| OH              | 2.75            | 55.0            |
| CF              | 5.94            | 31.2            |
| BF              | 6.93            | 43.0            |

## APPENDIX I

### Relation of Cubic Force Constant to Kinetic Energy

If one assumes that the kinetic energy of a molecule obeys the equation

$$T = T_0 + T_1 R^{-n} \quad (I-1)$$

near the equilibrium distance, then by differentiating we find that

$$T''/T' = \frac{n+1}{-R} \quad (I-2)$$

From differentiation of the virial theorem, relations between the force constants and the kinetic energy derivatives can be obtained<sup>(33)</sup>, which when combined give the relation

$$\frac{(T)_{R_e}''}{(T)_{R_e}'} = \frac{3 + 3a_1}{R_e} \quad (I-3)$$

By combining (I-3) with (I-2) one obtains

$$n = -3a_1 - 4, \quad (I-4)$$

thus relating the form of the kinetic energy curve to the cubic force constant.

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PART II

THE USE OF FREQUENCY MODULATION TO GENERATE A REFERENCE

BEAM FOR ATOMIC ABSORPTION ANALYSIS

## INTRODUCTION

The broad application of atomic absorption spectroscopy to chemical analysis was first realized by A. Walsh<sup>(1)</sup> in 1955. Since then atomic absorption analysis has become the principal method used in trace-element analysis. Research in atomic absorption analysis is presently centered upon devising ways to increase the sensitivity and accuracy of the method. In recent years the sensitivity of the method has been increased to the point where quantities as small as  $10^{-12}$  grams may be detected, and sensitivities are approaching the theoretical limits. To increase the accuracy of the method it is necessary to develop a way of correcting for the unwanted absorption and scattering by the sample. Chemical treatment of the sample to separate the matrix constituents from the element to be analyzed is a generally unsatisfactory approach, though a certain amount of chemical treatment can be very helpful. The second possibility is to make a correction for the unwanted absorption by the use of a reference beam. Double-beam or reference-beam methods, however, have been difficult to apply effectively to atomic absorption spectrochemical analysis. At present there are no truly satisfactory methods of compensating for the absorption and scattering of light by species other than the analyte atoms. Two basic approaches may be taken to provide such a background correction.

A classical double-beam spectrometer may be constructed using a beam splitter and beam condensor. The successful use of a double-beam

system requires that one be able to duplicate precisely the chemical composition of the sample while the element being analyzed is completely removed. This cannot usually be done. One must also duplicate the conditions under which the sample is introduced into the absorption cell or region. Since atomic absorption is observed only in atomized samples, duplication of such conditions can also be extremely difficult.

The magnitude of the background absorption may also be estimated by monitoring absorption at a wavelength near the wavelength being used. This method has the drawback that absorption of light by the unwanted species is frequently frequency dependent, giving an error in the background reading. Nevertheless, this approach is far more practical than the use of a dual-beam spectrometer. The currently available instrumentation utilizes this method to obtain background corrections. In order to monitor absorption at a second wavelength one must (a) add a second light source, (b) merge the beam from the second source with that from the principle source, and (c) provide a means for separately detecting the light from the second source. These requirements may all be met by simply frequency modulating the principle light source and using an A. C. or phase sensitive detector. However, presently other methods are being used for correcting atomic absorption measurements.

The principal method<sup>(2,3)</sup> being used is to mount a deuterium lamp near the source for the atomic line, merge the beam from the deuterium lamp with that of the primary lamp, and detect the reference light by

the use of a chopper arrangement similar to that used in most separated-double-beam systems. The frequency spread of the light detected from the deuterium lamp is determined by the spectral slit width of the monochromator and includes the sample or resonance frequency. Since light from the deuterium lamp is partially attenuated by the analyte atoms, it is not a true reference beam.

Abbott and Skogerboe<sup>(4)</sup> have used the continuum emission of electrodeless discharge lamps as a reference, thereby eliminating the need for a second lamp when the electrodeless discharge lamp emits the line desired for atomic absorption analysis.

Other methods<sup>(5)</sup> have been suggested for making this correction, but they are not commonly used.

## CHAPTER I

### Theory

There are many possible methods for frequency modulating a beam of light or a light source. For each method one must devise a means of assessing its effectiveness relative to other methods. For this reason I have chosen two elements, sodium and mercury, to use as examples (or test cases) for each method. These two elements represent extreme ends of the spectrum for many critical elemental properties. For example, wave length of emission and atomic weight. They are also generally the easiest elements to use in the actual testing of possible methods because of their high vapor pressures. For both sodium and mercury a minimum wavelength shift of about 0.05 Angstroms is needed for clear resolution of the reference and sample beams. The methods which may be used will be categorized by the physical effects they take advantage of.

#### Doppler Effect

The Doppler effect is familiar to everyone as the increase or decrease in the apparent frequency of sound emitted by a source traveling toward or away from the observer, respectively. The effect may be observed for both transverse and longitudinal waves. If  $f$  is the observed frequency of the waves and  $f_0$  is the frequency of the waves as measured by an observer at rest with respect to the source, then

$$f = f_0(1 + v/c) \quad , \quad (1-1)$$

where  $c$  is the velocity of propagation of the waves and  $v$  is the relative velocity of the source toward the observer. For light waves one may also write

$$\lambda = \lambda_0(1 - v/c) , \quad (1-2)$$

where  $v/c$  is much smaller than one and  $\lambda$  is the wavelength<sup>(6)</sup>.

The Doppler effect is one of the principal causes of line broadening. Since the average velocity of the atoms depends on the temperature, the magnitude of the Doppler broadening for an atomic line also depends on the temperature. By increasing the temperature of a source one may widen the line considerably. If one could rapidly change the temperature of an atomic light source, one could alternately emit a narrow and then a broad line, thereby generating a sample-and-reference beam for atomic absorption analysis. Simply broadening a line, however, as previously indicated, does not generate a true reference beam. I will therefore not consider methods which produce an effect in a random fashion, creating a simple broadening of the line. Nearly all effects may also be produced in a selective fashion, creating a change in the frequency of the light without appreciably changing the width of the line. Pursuing this line of thought, we try to devise a light source in which all the emitting atoms are travelling at high velocity toward or away from the detector. A hollow-cathode lamp may be constructed which will allow the ions to accelerate through a voltage drop before acquiring an

electron and emitting light. Such a lamp is easily constructed and used for demonstrating the Doppler effect in hydrogen<sup>(6)</sup>. However, to modulate the light from the lamp one must either change the voltage drop or pressure in the cell rather quickly. Large changes in the intensity of the light would be expected to accompany such changes, and emission from unaccelerated atoms would always be present, so the frequency modulation could not be achieved without the addition of cumbersome side effects. A frequency shift of 0.05 Angstrom would require that the ions experience a voltage drop of about 400 volts for mercury and about 10 volts for sodium.

A rapid change in path length could also be brought about by the use of rotating or vibrating mirrors. For such a method to be practical a change of the order of  $10^5$  cm/sec. would be needed. The use of a front-surface mirror on a piezoelectric crystal warrants investigation in this regard, as there would be no side effects expected for such a device.

#### Dynamic Refractive Index Change

Generalizing upon the discussion of the Doppler effect in the previous section, we consider the effective optical path length rather than the physical distance of the optical path. Calling  $L$  the physical distance and  $n$  the index of refraction of the medium through which the radiation passes, we define the optical path length,  $x$ , by the equation

$$x = nL. \quad (1-3)$$

In the previous section the case where  $n$  is held constant and  $L$  is varied was discussed as a method for producing a change in path length. In this section the case where  $L$  is held constant and  $n$  is varied is discussed. Since the optical path length is changed, a frequency shift must occur. The same equations apply for the usual Doppler effect, except that  $x$  is used instead of  $L$ .

The problem of devising a method for frequency modulating a light beam is now reduced to simply finding a way of rapidly changing the index of refraction of part of the medium through which light passes. This method has the advantage that it involves the light beam itself rather than the source of light and thereby minimizes chemical side effects.

The well-known dependence of the refractive index of a medium upon the transverse electric field, called the Kerr effect, allows one to bring about a frequency modulation of light by applying an electric field which is amplitude modulated. When an electric field is imposed on an isotropic dielectric, the dielectric reacts as a uniaxial crystal with its optic axis parallel to the electric field. Light polarized parallel to the field will therefore see an index of refraction,  $n_p$ , which is different from the index of refraction,  $n_s$ , seen by light polarized perpendicular to the field. The indices, according to the Langevin-Born theory<sup>(7)</sup>, are determined by the equations

$$n_p = n_0 = 2\lambda BE^2/3 \quad (1-4)$$

and

$$n_s = n_0 - \lambda B E^2 / 3 , \quad (1-5)$$

where B is the Kerr constant for the dielectric and E is the electric field. Kupper and Funfer<sup>(8)</sup>, using a travelling-wave Kerr cell, created a frequency shift on the order of 0.4 Angstrom. Likewise, Stauffer<sup>(9)</sup>, using a similar Kerr cell arrangement, has observed a broadening of two mercury lines having a separation of 0.045 Angstrom to the point where they could hardly be resolved. Burdette and Hughes<sup>(10)</sup> recently measured the difference in frequency of the perpendicular and parallel polarized components of the light beam in a Kerr cell. Using the Doppler-shift formula

$$\lambda = \lambda_0 (1 - n' L / c) \quad (1-6)$$

along with the Langevin-Born theory, the expression for the change in frequency of light polarized parallel to the field becomes

$$\Delta \nu = 4 B L E E' / 3 . \quad (1-7)$$

Thus, the frequency shift can be increased by superposing a larger constant potential as well as by increasing the amplitude and frequency of the alternating potential. Equation (1-7) must be considered only an approximate equation, however, since the Langevin-Born theory breaks down for very high frequencies of the alternating potential. To achieve a frequency shift of more than 0.01 Angstrom a voltage drop of at least 10,000 volts per centimeter and a powerful high-frequency voltage source

of about 2,000 megacycles per second would be needed. A pulsed electric field could be generated, though, without the use of expensive equipment.

A transverse magnetic field may be used in an analogous manner to induce birefringence in materials. This effect, called the Cotton-Mouton effect, allows one to produce a frequency shift in much the same manner as with the Kerr effect. The Cotton-Mouton effect is much weaker than the Kerr effect. High-frequency alternating magnetic fields are also difficult to obtain. Thus, Cotton-Mouton effect appears to be less advantageous to use than the Kerr effect.

A longitudinal magnetic field also produces a change in the refractive indices of a material. The effect, called the Faraday effect, results in equal but opposite changes in the indices of refraction,  $n_+$  and  $n_-$ , for right-circularly and left-circularly polarized light in the medium. A changing longitudinal magnetic field splits a monochromatic beam of light into two components having different frequencies, an ideal situation for the generation of a reference beam. The Faraday effect is normally considered in terms of the rotation of plane polarized light which it produces. The magnitude of the rotation is proportional to the Verdet constant,  $V$ , of the material. The angle of rotation,  $\phi$ , is given by

$$\phi = V \int_0^L H(L) dL, \quad (1-8)$$

where  $H$  is the magnetic field intensity and  $L$  is the path length<sup>(11)</sup>. The

rotation may also be determined from the Fresnel equation<sup>(12)</sup>,

$$\phi = (n_- - n_+)L/2\lambda . \quad (1-9)$$

For any of the methods discussed the ratio  $(\lambda - \lambda_0)/\lambda_0$  must be greater than  $10^{-5}$  for the method to be useful. This means, using equation (1-6), that  $dn/dt$  must be at least  $3 \cdot 10^5$ . Accordingly, if an alternating magnetic field of about one megacycle per second or a pulsed field having a duration of about one microsecond is used, then the magnetic field at its maximum must produce a change in the index of refraction of about 0.03 times the normal value with a 10 centimeter cell. Such changes cannot be achieved with normal dielectrics. Therefore, a useful frequency shift is not easily created using the Faraday effect, though in special restricted cases the Faraday effect could be used.

Mechanically induced changes in the refractive index are very small and occur rather slowly, so that the frequency shifts so generated are negligible.

#### Interruption Broadening

It is well known in radio science that any amplitude modulation of a wave can also be considered as a frequency modulation in which "side bands" are generated. If a carrier wave of frequency  $\nu_0$  is sinusoidally amplitude modulated at a frequency  $\nu_m$ , then the carrier wave is actually decomposed into two waves having frequencies of  $\nu_0 + \nu_m$  and  $\nu_0 - \nu_m$ . The observed amplitude modulation is then the result of the beating of

the two side bands. Therefore, if one can produce a high-frequency amplitude modulation of a light beam, then one has automatically also produced the desired frequency modulation. For our purposes  $\nu_m$  must be at least  $10^9$  cycles/sec. E. Rupp<sup>(13)</sup> in 1928 performed an experiment to verify this phenomenon. He passed light from a thallium resonance lamp through a Kerr shutter operated at  $10^9$  cycles/sec. and found that the light was not appreciably absorbed by thallium vapor. One cannot be sure, however, whether the frequency change he observed was produced by the shutter action or by the change in index of refraction in the Kerr cell. At any rate, there is no doubt that, if one could devise a shutter having a frequency of  $10^{10}$  cycles/sec., then a nearly ideal reference beam for atomic absorption would be realized.

#### Scattering Processes

Scattering processes provide a simple and extremely effective means of changing the frequency of light. Unfortunately, the intensity of scattering is always low compared to the intensity of the incident radiation, making the use of scattering extremely difficult in practice. There are many types of inelastic scattering in which large frequency shifts are produced, chief among them being the Raman effect. Many elastic scattering processes also produce large frequency changes; Thompson scattering from high speed electrons can even result in the production of X rays.

### Stark Effect

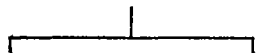
An electric field will split the energy levels of atoms and consequently result in a change in the frequency of emission or absorption of the atoms. The effect need not be considered in detail because (a) the splitting even for large electric fields is very small and (b) it results in the dissociation of electrons and diffuse spectra before the splitting becomes large. In mercury, for example, an electric field of 100,000 V/cm. produces a frequency shift in the 2537 Angstrom line of only  $5 \times 10^{-4}$  Angstrom<sup>(14)</sup>.

### Zeeman Effect

The origin of the Zeeman effect is the change due to a magnetic field in the energy levels of the atoms. It was first observed as a splitting into three components of the emission line of mercury in a magnetic field. Later observations on other spectral lines revealed splitting into more than three components; such splittings were called the anomalous Zeeman effect, whereas the triplet splitting was designated the normal Zeeman effect, since it is explainable in terms of classical theory. Basically, the normal Zeeman effect is due to the orbital magnetic moment of the electrons and the anomalous effect is due to the spin magnetic moment of the electrons.

When a spectral line splits in a magnetic field the components into which it splits are polarized either parallel or perpendicular to the magnetic field if viewed perpendicular to the field.

The former are called the  $\pi$  components and the latter the  $\sigma$  components. Drawings are commonly used to describe the nature of the Zeeman splitting for a particular line;  $\pi$  components are drawn above the horizontal and  $\sigma$  components below, the length of the vertical lines being proportional to intensity and frequency being plotted along the abscissa. Thus the drawing for a normal Zeeman splitting is



If the spectral line is viewed along the magnetic field, only the  $\sigma$  components are visible, and they become left and right circularly polarized. According to the classical theory<sup>(6)</sup> the displacement of  $\Delta\nu$ , of each  $\sigma$  component is given by

$$\Delta\nu = eB/4\pi m_e \quad , \quad (1-10)$$

where  $e$  and  $m_e$  are the charge and mass of the electron and  $B$  is the magnetic flux density.

The magnitude and character of the splitting of a spectral line depends upon how the energy levels are split for both of the electronic states involved in the transition. For the mercury 2537 Angstrom line a simple triplet is observed in which the splitting is  $3/2$  larger than the classically predicted value. We therefore say that the  $g$  value for the transition is  $3/2$ . In the case of the sodium  $D_1$  line, two  $\sigma$  components and two  $\pi$  components are found, the  $\sigma$  components being displaced  $4/3$  of the expected classical value, while

the  $\pi$  components are displaced a smaller amount. Again splittings large enough to be useful are not easy to obtain. The fields required to displace the  $\sigma$  components 0.05 Angstrom are about eleven kilogauss for mercury and about two kilogauss for sodium.

There are many ways in which one might take advantage of the Zeeman effect to produce a reference system. One might, for example, apply a longitudinal magnetic field (though in some cases a transverse field could be used) to the sample, thereby changing its resonance frequency rather than that of the light and using the Zeeman effect in absorption. Some of the possible experimental configurations using the Zeeman effect will be described in the next chapter. A practical system for the analysis of sodium which utilizes a magnetic field has already been built by D. Woodriff<sup>(15)</sup>.

## CHAPTER II

### Experiments Using the Zeeman Effect

Mercury has a sufficiently high vapor pressure ( $10^{-3}$  Torr) at room temperature that a one centimeter cell with a drop of mercury in it will absorb a large portion of the resonance light from a mercury lamp. For the sake of convenience, mercury was used as a test element in all of the experiments. For mercury a vapor lamp may be used in place of the usual hollow-cathode lamp. It has the advantage of being small and relatively inexpensive.

The first experiments were conducted using a modified Beckman DB spectrophotometer. The modified instrument has been described by Woodruff, Culver, and Olson<sup>(16)</sup>. It is helpful to know some of the details of how the modified DB works in order to understand how and to what extent it can be used in taking advantage of the Zeeman effect. The instrument in the double-beam mode measures the relative intensities of two beams which are generated by a vibrating mirror system after the light has passed through a low-resolution grating monochromator. The ratio  $(I_r - I_s)/I_r$  is measured, where  $I_r$  is the intensity of the reference beam and  $I_s$  is the intensity of the sample beam. By placing two Glan-type polarizers in the sample compartment, the instrument theoretically becomes capable of measuring either the degree of polarization of a single beam or the relative intensities of two colinear perpendicularly polarized beams. Generally the magnetic field

is horizontal, so that a horizontal polarizer is used for the sample beam and a vertical polarizer for the reference beam.

Many more practical problems arise when polarized light is used than when polarization is neglected. Optical components, for example, can rotate or partially depolarize the polarized light. The DB, however, was tested and found to cause rotation of less than one degree and only about two percent depolarization.

Another common practical problem in atomic absorption analysis is the presence of interfering emission due to other elements or other lines of same element. For the DB no change in the sensitivity for the simple atomic absorption of mercury was observed as the slit width was changed, indicating that there are no appreciable interfering lines within about 50 Angstroms of the 2537 A resonance line.

A third problem, which naturally becomes very important when a magnetic field is present, is the susceptibility of the intensity and linewidth of the resonance line to change as conditions change. The apparent width of the resonance line was found to depend largely upon the temperature of the light source. Since the absorbing atoms are at room temperature in the atomic absorption apparatus used by author, a considerable increase in sensitivity can be achieved by maintaining the lamp at a low temperature. An air stream was therefore used with the mercury vapor lamp. Likewise, a water cooled hollow-cathode lamp would be expected to give a narrow resonance line and high sensitivity. The

intensity of resonance emission generally increases as the temperature of the lamp increases; however, for mercury an increase in the temperature appears to decrease the intensity if the temperature is above a certain level. This effect may be the result of distillation of mercury away from the emitting portion of the lamp. The mercury Pen-ray lamp, when operated on D.C. current, shows a marked decrease in intensity after operating for several minutes; again, distillation of mercury is the suspected cause. Intensity of emission also generally increases as the current or voltage is increased. The actual intensity of a lamp, therefore, is determined by the combined influences of current and temperature. A magnetic field also causes a large change in emission intensity. For example, placing the mercury Pen-ray lamp in an 8kG. magnetic field more than doubles the steady-state intensity of the lamp. If this magnetic field is then turned off quickly, the intensity will momentarily double again before turning to its original intensity. Similarly, if the field is above about 4 kilogauss and is increasing rapidly, the intensity momentarily drops before going to the steady-state value. Since the behavior of emission sources in magnetic fields is extremely important for this project, I shall undertake to explain these phenomena.

One possible cause for the change in steady-state intensity with magnetic field is the orbiting of all the ions about the magnetic field lines. If the radii of the orbits are about as large or larger than the

mean free path length for collisions with the atoms whose radiation is being monitored, then the intensity of the resonance radiation will increase as the magnetic field is increased.<sup>1</sup> However, if the magnetic field is increased to the point where the orbits become much smaller than the mean free path length, then the collision rate will go down and the intensity will start to decrease as the magnetic field is increased. For the mercury discharge lamp the intensity stops increasing with the magnetic field at about eight to ten kilogauss. If the pressure in the lamp is assumed to be about one millimeter of mercury, then, by the orbiting electron approach, the intensity reversal should occur at approximately ten kilogauss, in agreement with the experimental results. Also, the current in the lamp decreases slightly as the magnetic field is increased, so that an increase in the conductivity of the plasma is not responsible for the increased intensity.

For the hollow-cathode lamp there are additional factors which should be taken into account in any explanation of the intensity changes in a magnetic field. Much time and effort would be required to determine experimentally the relative magnitude of contributions from various factors; therefore, I will simply enumerate the possibilities. First,

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<sup>1</sup>In any discharge lamp the intensity of the resonance radiation is governed largely by the frequency with which free electrons collide with gaseous neutral atoms. A particle which is travelling in a helical path sweeps out a larger area per unit time than a particle moving in a straight line and is less likely to collide with a wall.

in any commercial hollow-cathode lamp ferromagnetic materials are used to support the cathode and anode and are used in the socket pins. This means (a) that it is difficult to put the lamp in a high magnetic field without introducing considerable strain on the lamp, and (b) that the magnetic field in the hollow-cathode will not be homogeneous. Second, the materials used to make the cathode are not usually disclosed and, in fact, are often considered a trade secret. Whether the cathode material is diamagnetic, paramagnetic, or ferromagnetic is very important in predicting the behavior of the lamp in a magnetic field, since the magnitude and homogeneity of the field is determined largely by the magnetic properties of the cathode. Finally, the magnetic properties of the atoms of the emitting element and of the carrier gas are important, especially when the field is not homogeneous.

A detailed account of the behavior of the atoms in a glow discharge in a magnetic field is beyond the scope of this paper and somewhat superfluous in view of the lack of extensive experimental evidence on the behavior of hollow-cathode lamps in a magnetic field. Only one paper<sup>(17)</sup> has been published in this area, and it does not treat the problem thoroughly. For the commercial mercury hollow-cathode lamp an increase in the steady-state intensity of about 15 percent is observed when a 400 gauss field is applied. This behavior is consistent with several mechanisms.

The anomalous time-dependent behavior of the mercury vapor lamp

has been determined (a) not to be caused by the effect of the changing magnetic field on the electronics, (b) not to be caused by changes in the current, (c) to occur with both A.C. and D.C. current, (d) to occur with both resonance and non-resonance lines of both argon and mercury, and (e) to occur only when the magnetic field is over about 5 kilogauss and to increase as the field is further increased. The orbiting behavior of electrons in a slowly varying magnetic field is easily determined from the fact that the magnetic moment of the electron remains constant as the field is changed. Thus, when the magnetic field is increased the electrons gain energy, whereas when the field is decreased the electrons lose energy to the magnetic field. We observe, however, that as the field is increased, less energy is emitted from the atoms, so the changes are truly anomalous! An increase or decrease in the oscillator strengths of the atomic transitions is extremely unlikely; so the effect must be related to the frequency with which the atoms collide with electrons. Since the discharge seems to develop some instabilities near 5 kilogauss, which probably are related to the magnitude of the Lorentz force,

$$\vec{F} = q\vec{E} \times \vec{B} \quad ,$$

one would suspect that this force might also be important for the time-dependent phenomena observed. We know that according to Maxwell's equations, a changing magnetic field must induce a curl in any perpendicular

electric field. Using these equations one finds that the Lorentz force pushes the ions and electrons toward a region of low electric field when the magnetic field is increasing and toward a region of high electric field when the magnetic field is decreasing. Thus the discharge is probably more difficult to sustain while the magnetic field is increasing and easier to sustain when the field is decreasing, accounting for the observed anomalous changes in intensity.

Finally, a special problem which arises whenever mercury is determined by atomic absorption is the interference of ozone. Although it is known that ozone has a broad and strong continuum absorption band centered at about 2550 Angstroms, the interference of ozone in the atomic absorption analysis of mercury has been mentioned only once to the author's knowledge<sup>(18)</sup>. Apparently no one has considered that the mercury lamp might have an effect upon the air in the optical path. Most mercury lamps have quartz windows which transmit the 1850 Angstrom line of mercury as well as the commonly known 2537 Angstrom line, thus produce ozone photochemically for the surrounding air<sup>(19)</sup>. The ozone concentration would be expected to build up to a fairly high level if the air in the optical path is confined or stagnant. In the apparatus used by the author a 2 percent increase in apparent intensity was found by sweeping fresh air through a one-half meter confined section of the optical path. Also, fluctuations of about one percent were observed when air was swept from the lamp toward the optical path. Therefore, in any

accurate analysis care should be taken to avoid this interference by excluding oxygen or the 1850 Angstrom radiation from the optical path.

Because of the radical changes in intensity which take place when a mercury lamp is placed in a magnetic field, all the experimental configurations which require that the lamp be placed in a rapidly changing magnetic field were discontinued. Configurations which require an A. C. magnet were also eliminated because of the high cost of constructing such a magnet with a peak-to-peak field in the kilogauss range. The only configurations, then, which were seriously considered after preliminary study were those requiring a fixed magnetic field around the lamp or the sample chamber or both. With a single D. C. magnet two basic configurations are possible. First, the magnet may be placed around the lamp, causing the lamp to emit normal resonance light polarized parallel to the field as well as perpendicularly-polarized frequency-shifted light of equal intensity. Second, the magnet may be placed about the absorption cell, causing light polarized parallel to the field to be absorbed in a normal manner while light polarized perpendicular to the field is absorbed only at shifted frequencies.

The first experiments were conducted using a hand magnet rated at 4300 gauss<sup>1</sup> with a one-centimeter spectrophotometer cuvette serving as the sample chamber. These first experiments were encouraging in that a

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<sup>1</sup>The field intensity of the magnet was determined with a commercial Hall-effect gaussmeter borrowed from the physics department.

definite increase in the percent transmission of the sample was observed when the magnetic field was added. However, the change was too small (about twenty percent of maximum) to make the method really useful for analysis without sensitive electronic equipment. Fortunately, a Varian series variable D.C. electromagnet was graciously made available to us by Dr. John Hanton, so that the effects of a varying magnetic field upon the equipment used in these experiments could be measured. It was then possible, in turn, to predict with some confidence the type of configuration which would be the most useful to construct. The configuration finally chosen for testing is shown in Figure 23. The detector assembly consists of an IP-28 photomultiplier tube (as well as a power supply and oscilloscope) with a 2520 Angstrom interference filter serving as the monochromator. The use of an interference filter normally is not recommended because of the danger of other atomic lines interfering with the desired line. However, by using the Zeeman effect apparatus such lines do not interfere. The key idea of the system is the use of a rotating polarizer to create an A.C. signal at the detector which corresponds to  $I_s - I_r$ . It is also useful to keep track of the absolute value of  $I_r$ , so that the ratio  $(I_r - I_s)/I_r$  may be measured. The sample chamber is simply a glass tube with silica plates on each end. It is about fourteen inches long and has connecting tubes for the entrance and exit of gas. Compressed air is bubbled through a solution containing the sample and one milliliter of twelve percent

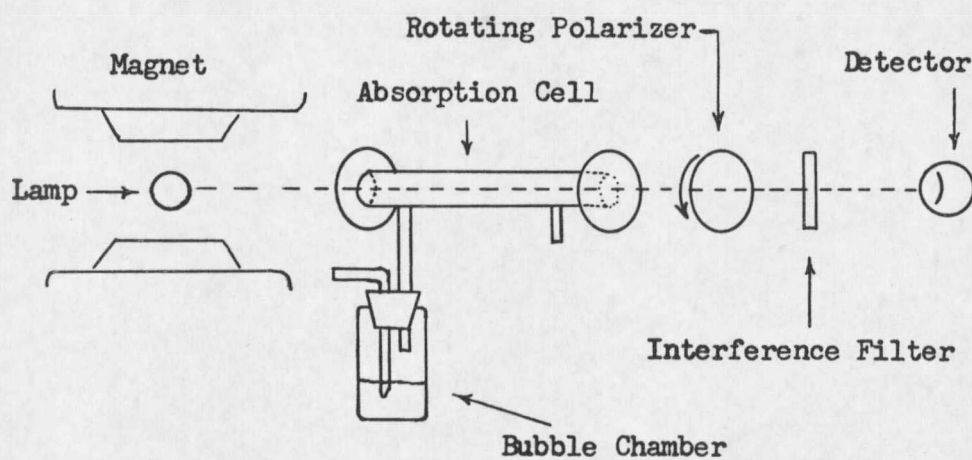


Figure 23. Diagram of experimental apparatus

stannous chloride solution made up to a total volume of about thirty milliliters with distilled water. The air then carries the mercury vapor picked up from the solution over to the sample chamber. A mixing time of about two minutes is used to allow all of the mercury to be reduced to the elemental state before letting the air bubble through it. A flow rate of about 0.4 cubic feet per hour and a magnetic field of 14,000 Gauss were used in most of the experiments. The signal from the photomultiplier appears on an oscilloscope, and any absorption due to mercury shows up as a thirty cycle-per-second sine wave, whereas the background absorption shows up only as a change in the D. C. signal level. The signal observed using a 14,000 Gauss magnetic field and a one-centimeter cell containing saturated mercury vapor is shown in Figure 24.

The sensitivity of the apparatus was measured as a function of the magnetic field strength; a plot of  $I_r/I_s$ , which is a measure of sensitivity, vs. the magnetic field strength is shown in Figure 25. Most of the irregularities in the curve are due to the hyperfine splitting of the mercury line<sup>(20)</sup>. The absolute sensitivity of the apparatus at 14,000 Gauss is illustrated by the calibration curve in Figure 26. One of the factors preventing the method from being more accurate is the relatively high noise level of the output signal. This noise originates largely from the fluctuations of lamp intensity, power-supply voltage, and photomultiplier amplification, and could probably be reduced by a factor

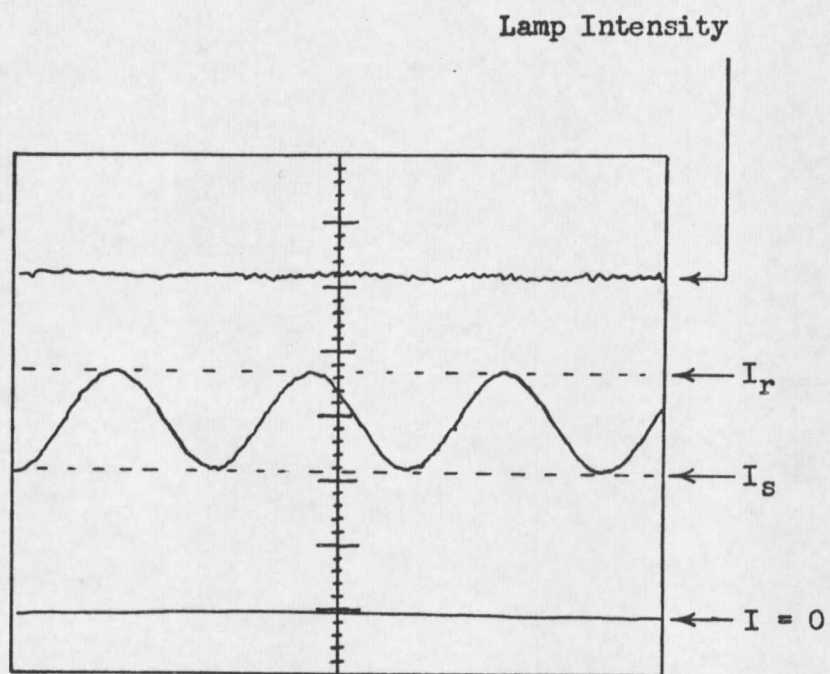


Figure 24. Diagram of observed signal

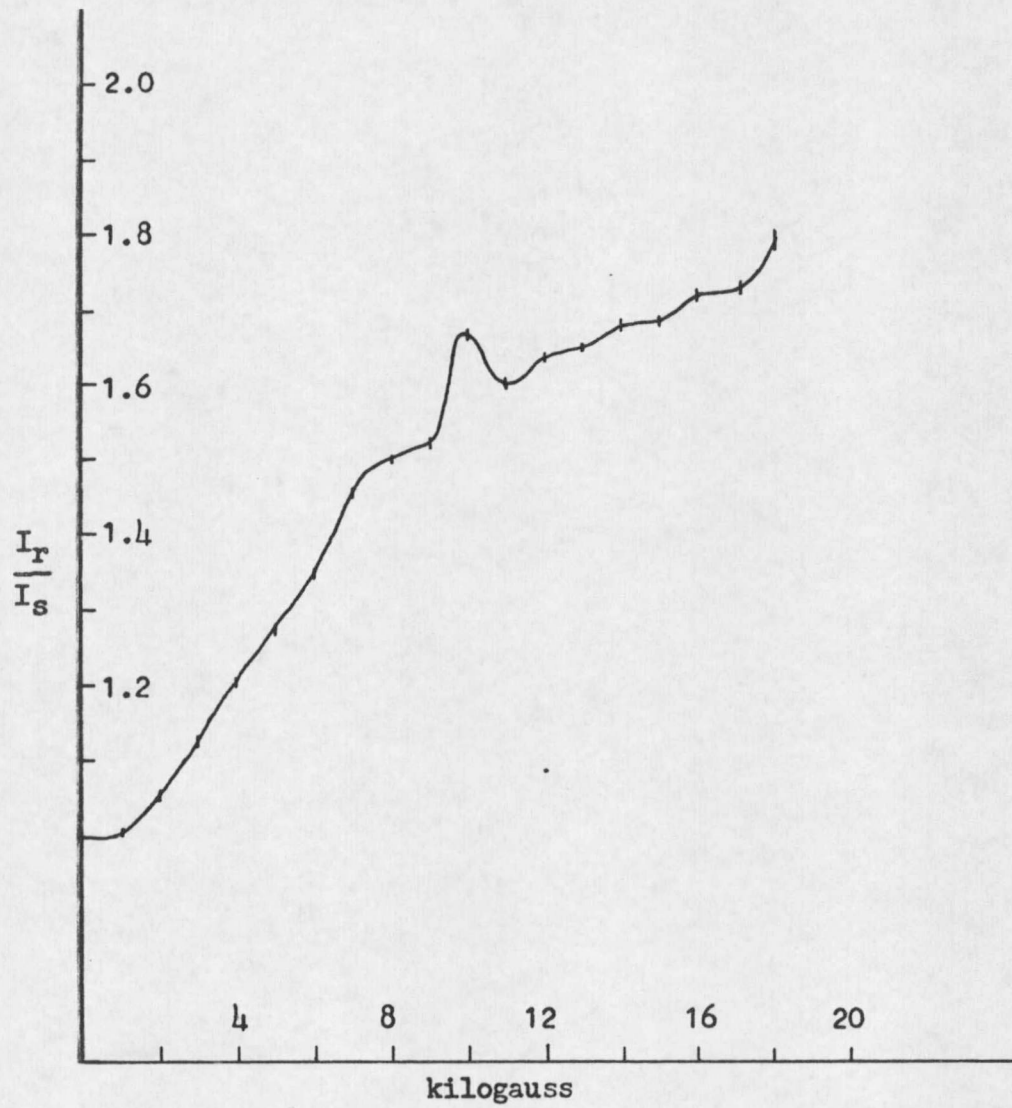


Figure 25. Sensitivity vs. magnetic field strength

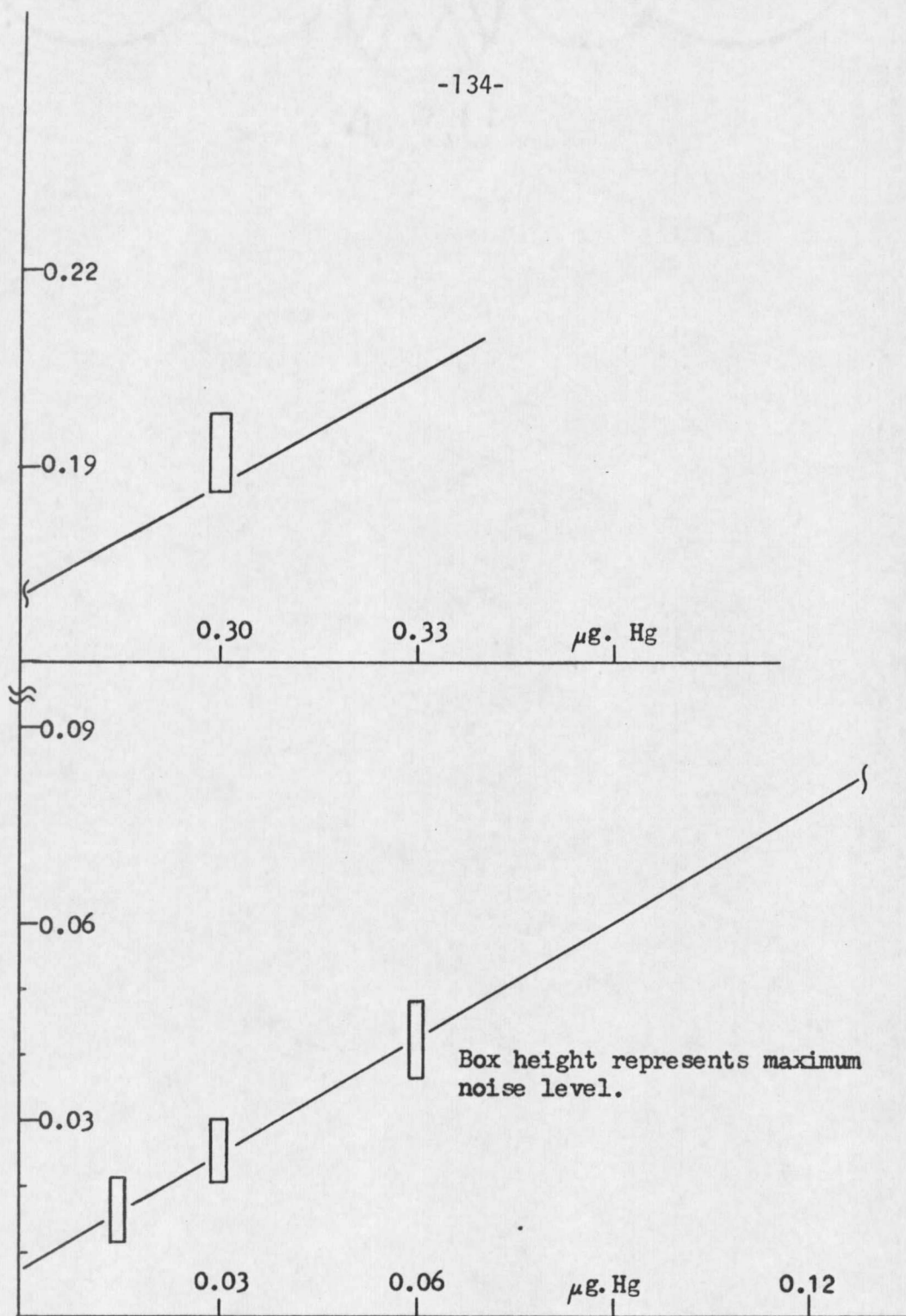


Figure 26. Optical density vs. quantity of mercury

of ten or more by the installation of better electronic equipment.

Background signals are observed in almost every determination, even though reagent-grade mercuric chloride was used, indicating that such an instrument would be very unreliable in the single-beam mode.

Absorbances as great as 0.2 were observed for water vapor alone. Other workers have also noticed large background absorptions in the determination of mercury by atomic absorption<sup>(21)</sup>. I have added impurities such as benzene and toluene to the samples and have observed only increases in the background absorption, thus substantiating the hypothesis that only mercury will absorb so as to give an A. C. signal.

## CHAPTER III

### Conclusion

The experiments, both hypothetical and real, described herein introduce a new method for changing atomic absorption analysis from a single-beam to a double-beam method. The success of the experiments using the Zeeman effect, along with comparison to results not correcting for background absorption, demonstrates the advantage of using a double-beam system, at least in the analysis of mercury. I have shown that many problems must be overcome in order to build a reliable frequency-modulated apparatus, but that, if the problems can be overcome, as in the case of mercury analysis of the Zeeman effect, that an analytical instrument of high accuracy and reliability can be built. The elimination of background absorption allows one to confidently measure (without performing chemical separations) quantities of mercury which are orders of magnitude smaller than the quantities which can be determined by the single-beam method. The apparatus is extremely simple in that it performs a dual-beam experiment with only a single source and a single detector. With only mercury 199 isotope in the lamp, the magnetic field needed to effect a complete separation of the split lines from the absorption profile can be reduced to about<sup>(22)</sup> ten kilogauss, so that the apparatus can be made portable. A smaller magnetic field could also be used with an evacuated absorption cell similar

to that constructed by Goleb<sup>(23)</sup>, since the absorption profile is much narrower in a low-pressure cell. Similarly, resonance lamps<sup>(24,25)</sup> emit very narrow lines, thereby allowing the complete separation of Zeeman-split lines with a lower magnetic field.

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