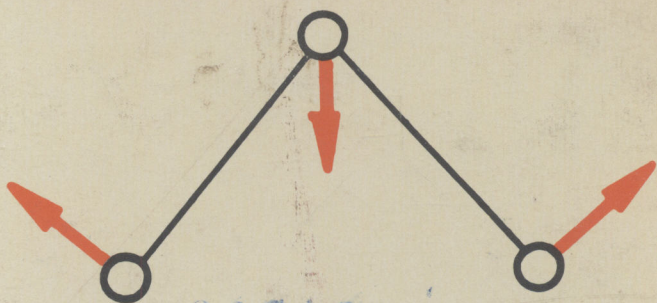
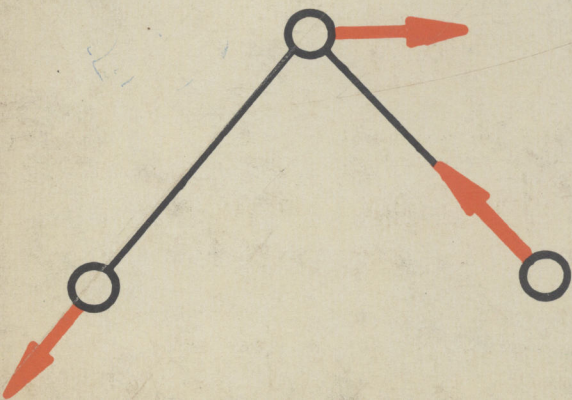


inorganic vibrational spectroscopy



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volume 1

Llewellyn H. Jones

Inorganic Vibrational Spectroscopy

Volume 1



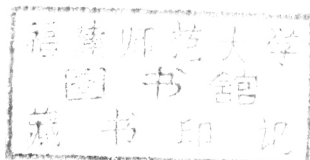
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Preface

An understanding of the forces which hold atoms together to form molecules has been a goal of chemists for many decades. These forces arise from mutual interactions of electrons and nuclei. The vibrational spectrum of a molecule, as observed in both infrared absorption and Raman studies, is a direct manifestation of these forces. The nuclei move with approximate harmonic motion under forces determined by the electronic configuration. The vibrational spectra tell us the frequencies of the oscillations. These frequencies are related to potential energy constants whose values are determined by the electronic structure.

If one can determine for a molecule meaningful potential constants, which describe the potential field under which the nuclei move, one has a valuable quantity for correlation with electronic structure. This book is intended to outline how one can go about determining the potential constants and evaluating their significance. It is written primarily for the inorganic chemist who has not specialized in this field but wishes to apply it either to his own work or toward evaluation of other workers' results and interpretations.

The potential constants mentioned above have generally been determined as force constants. While this book was in preparation, the author was made to realize, as pointed out by J. C. Decius several years ago, that in many ways *compliance constants* are more interesting than force constants. Therefore, I have used the term potential constants, covering both force constants and compliance constants, which are, of course, related. A section on compliance constants is included.

There are a large number of molecules for which normal coordinate treatments have been reported in the literature. Unfortunately, for most of these, rather gross approximations were necessary, which make the significance of the results highly questionable. It did not seem appropriate to discuss these dubious calculations at this time; therefore, the discussion of individual molecules in this book is limited to the few for which reliable potential constants are known.

Introduction

In recent years, vibrational spectroscopy has been used extensively for studying various properties of inorganic compounds. By *vibrational spectroscopy* is meant the determination of the energy levels of the various fundamental modes of vibration occurring in the molecules or complex ions* of interest. Many of these energy levels can be determined by observing the frequencies of transitions from one level to another using infrared absorption and Raman spectroscopy. A number of commercial instruments are available for observing infrared absorption spectra; in general, at least two will be required to study the range of interest to vibrational spectroscopists, namely $50\text{--}5000\text{ cm}^{-1}$. Raman spectra have come forth in much more limited volume but great strides are now being made in this direction with the availability of the laser source for Raman spectrometers.

This book will not go into experimental techniques† extensively but rather will start with the idea: “here we have the observed spectra; now what can we learn from it?” In other words, the purpose is to show what information can be obtained from the experimental data and how meaningful it is.

The most fundamental information to be obtained from vibrational spectra is a quantitative knowledge of the interatomic forces within a molecule. These forces can be treated approximately as Hooke’s Law springs placed appropriately about the molecule. The force constants of these springs then determine the frequencies of the fundamental vibrations. The binding forces are determined by the electronic configuration. Thus, from the observed vibrational frequencies, we can glean information about the force constants which hopefully can then be correlated with electronic structure and bonding theories. Often it is too complex a problem to calculate force constants, but the research worker will use the magnitude of a vibrational frequency as a semiquantitative measure of the

* Henceforth the word molecules shall include complex ions.

† For experimental techniques see, for example, *An Introduction to Infrared Spectroscopy* by W. Brügel (Wiley, New York, 1962) and *Chemical Infrared Spectroscopy* by W. J. Potts, Jr. (Wiley, New York, 1963).

bond strength. For gross effects, this is often informative if used judiciously. However, the relations between frequencies and force constants are usually not simple for polyatomic molecules and the force constants are much more directly related to electronic structure.

This volume of *Inorganic Vibrational Spectroscopy* is devoted primarily to the determination of force constants from vibrational frequencies, a discussion of the meaning of force constants, and an indication of how they can best be correlated with electronic structure and bonding theories. In order to determine force constants from vibrational frequencies, it is important to use the theory of molecular vibrations as described in the literature. Though the theory will not be covered in detail in this book, the main results and their use in determining force constants will be included. Examples are given in the appendices to illustrate the procedures. Though the detail presented in these examples may seem unnecessary to some, it is felt that it will be helpful to the chemist wishing to start in the field of vibrational spectroscopy.

Though force constants have been calculated for a large number of molecules in the past few decades, most of the results are based on some very arbitrary assumptions because of lack of information. With the availability of vibrational spectra of isotopic species and other types of pertinent data, more meaningful force constants are now being reported in the literature. Many of these will be discussed in detail in this volume after the necessary procedures of calculation are outlined.

For many purposes, compliance constants are more useful than force constants. Compliance constants are elements of the inverse of the force constant matrix. Though they have received little attention in the literature, they are reported along with the force constants for a number of systems in this book. A discussion of their importance is presented in Sect. 1.13.

For many systems there is just not enough information available to calculate force constants (or compliance constants) and it may be a long time before the situation improves significantly. However, a good deal of information about stereochemistry and electronic structure can be obtained from vibrational frequencies and band intensities without force constant calculations. This arises because the characteristics of the observed spectrum, such as intensity and infrared or Raman activity, are determined by the arrangement of electrons and atoms within a molecule. Also it is often possible to obtain important evidence concerning crystal structure from infrared and Raman studies of crystalline solids, especially of single crystals. Often vibrational spectra are used for analysis for studying concentrations in equilibrium mixtures, etc. It is planned to publish later, a second volume of *Inorganic Vibrational Spectroscopy* which will be devoted to these other, less quantitative applications of vibrational spectra.

Inorganic Vibrational Spectroscopy

Volume 1

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Chapter 1

Force Constants: Their Interpretation and Determination

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1.1. DIATOMIC MOLECULES

Chemical bonds are found to behave like Hooke's Law springs for small displacements. Hooke's Law is given by the expression

$$F = -kX \quad (1.1-1)$$

If X is a displacement of a Hooke's Law spring from its equilibrium length, F is the force tending to restore it to equilibrium. The proportionality constant k is called the force constant. Thus, when we speak of a bond force constant, we mean the restoring force resulting from a small unit displacement from the equilibrium length. It is, therefore, also a measure

of the force necessary to stretch the bond a small amount. This is an important quantity as it is determined by the electronic configuration in the molecule and thus gives information about the electronic structure and bonding. The *force constant* is a direct measure of the *bond strength* determined by the electronic distribution when the nuclei are at their equilibrium positions. Note that this is a different "bond strength" than the energy required to break a bond. More will be said about this in the next section.

A diatomic molecule acting under Hooke's Law forces is a harmonic oscillator. The potential energy (V) is

$$V = \frac{1}{2}kX^2 \quad (1.1-2)$$

and the molecule is found to vibrate with a frequency

$$\nu = (k/4\pi^2\mu)^{1/2} \quad (1.1-3)$$

The quantity X is a displacement of the bond length from its equilibrium value and μ is the reduced mass [$M_1M_2/(M_1 + M_2)$] of the diatomic molecule. The quantum mechanical solution to the harmonic oscillator problem shows (2) that the vibrational energy levels can be expressed by the relation

$$G_v = \nu(v + \frac{1}{2}) \quad (1.1-4)$$

where $v = 0, 1, 2, \dots$. In vibrational spectroscopy, the frequency ν and thus the energy G is generally expressed in units of waves per centimeter (cm^{-1}) which is, of course, the reciprocal of wavelength. This unit cm^{-1} is sometimes referred to as a wave number.

In reality, a diatomic molecule is not a true harmonic oscillator. Analytic functions which approximate the observed potential curves are discussed by Herzberg (3). These will not be discussed here, but the qualitative aspects will be brought out. As the molecule is displaced from its equilibrium atomic separation, the electrons will rearrange themselves to accommodate to the new configuration. This, in effect, changes the forces holding the atoms together. Thus, k in Eq. (1.1-2) is essentially a function of X . The potential curve near the minimum (for infinitesimal displacements) is well approximated by a parabola. Thus we may write

$$k = k_e + g(X) \quad (1.1-5)$$

$$V = \frac{1}{2}k_eX^2 + \frac{1}{2}X^2f(X) \quad (1.1-6)$$

where $f(X)$ is some function which goes to zero as X goes to zero. The equilibrium force constant, k_e , is then a measure of the strength of the

bond at the minimum in the potential curve. The corresponding energies in terms of cm^{-1} of the various vibrational levels are then given by

$$G(v) = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3 - \omega_e z_e(v + \tfrac{1}{2})^4 \quad (1.1-7)$$

By observing the fundamental and various overtone transitions, one can determine the values of ω_e (the fundamental harmonic frequency) and the various anharmonicity constants, $\omega_e x_e$, $\omega_e y_e$, etc. For example, for H^{35}Cl the energy levels of the first five vibrationally excited states have been determined (4). From them, the data of Table 1.1-1 is calculated.* The coefficients of higher terms are essentially zero.

TABLE 1.1-1
VIBRATIONAL CONSTANTS OF H^{35}Cl

$\omega_e = 2991.03 \text{ cm}^{-1}$
$\omega_e x_e = 52.89 \text{ cm}^{-1}$
$\omega_e y_e = 0.247 \text{ cm}^{-1}$
$\omega_e z_e = 0.0146 \text{ cm}^{-1}$

If we knew the frequencies of only the fundamental and first overtone, we would neglect $\omega_e y_e$ and $\omega_e z_e$ and calculate $\omega_e = 2990.0$, $\omega_e x_e = 52.0$. The observed fundamental transition is 2885.9. Thus, neglect of $\omega_e y_e$ and $\omega_e z_e$ has only a small effect (0.07% in force constant) while neglect of $\omega_e x_e$ introduces a large error of about 3.5% in the harmonic frequency or 7% in the harmonic force constant. Of course, a rather large anharmonicity exists for HCl ; it is generally much smaller for nonhydrogen containing molecules ($\omega_e x_e = 13.3 \text{ cm}^{-1}$ and $\omega_e y_e = +0.011 \text{ cm}^{-1}$ for CO). Thus one can obtain quite a good estimate of ω_e if only two transitions are observed and $\omega_e y_e$ is neglected. However, one must keep in mind that the only really meaningful force constant is the k_e of Eq. (1.1-5), and

$$k_e = 4\pi^2 \mu \omega_e^2 \quad (1.1-8)$$

If the anharmonic corrections are unknown, one must live with this uncertainty in the results.

In summary, then, ω_e is a hypothetical frequency for infinitesimal vibrations. It is obtained by extrapolation of the observed vibrational levels to the bottom of the potential well. It is important as data for

* These values, calculated by the author, differ slightly from those listed in (4).

calculation of the harmonic force constant k_e which is a measure of the forces holding the atoms together at their equilibrium length, r_e . Actually the molecule is constantly in vibration, the atoms moving apart and together about r_e . As the distance between atoms changes, the electronic configuration and thus the binding force changes also. For a measure of the binding force at the minimum of energy, which is related to the equilibrium electronic configuration, we should calculate k_e as in Eq. (1.1-8).

1.2. BOND STRENGTH

There are various definitions of "bond strength" in the literature, as well as much use of the term without definition. In this book, bond strength

TABLE 1.2-1
FORCE CONSTANTS AND DISSOCIATION ENERGY
FOR HI AND Cl₂

	k_e (m dyn Å ⁻¹)	D_0 (eV)
HI	3.14	3.056
Cl ₂	3.33	2.475

is used synonymously with force constant. As discussed in Sect. 1.1, this means the force necessary to stretch a bond by a small unit amount from its equilibrium length. This seems to be the best criterion for comparing the "strength" of the binding forces among different bonds.

The force constant is, of course, a different measure of strength than the dissociation energy. When a bond stretches enough to dissociate, its electronic structure (and apparent force constant) changes considerably. Usually bonds with larger force constants also have greater dissociation energies; however, there are exceptions as seen in Table 1.2-1. Thus it takes more energy to stretch a Cl—Cl bond by a small amount (compared to equilibrium bond length) than to stretch an H—I bond by the same amount; however, it takes less energy for complete separation of the two Cl atoms than for separation of the H and I atoms. By the force constant criterion, Cl₂ has a stronger bond than HI.

Cleveland has proposed (5) another definition of bond strength for a diatomic molecule. He feels that the most important measure of strength is the maximum force required in pulling the atoms apart. However, this

maximum occurs when the molecule is stretched considerably from its equilibrium length and the electronic configuration has certainly changed. Thus, this measure of strength is not closely related to the binding forces at the equilibrium configuration. It is dependent on the anharmonicities involved. It is essentially a compromise between force constant and dissociation energy, more related to the latter.

1.3. DETERMINATION OF VIBRATIONAL FREQUENCIES OF POLYATOMIC MOLECULES

The theory of molecular vibrations has been presented in the literature (6-8), and it will not be developed in this book. However, many of the results will be given for later application to specific molecules. In order to determine force constants for a molecule one must know most of its vibrational frequencies.

1.3.1. Vibrational Energy Levels

The vibrational potential of a polyatomic molecule is exceedingly more complicated than that of a diatomic molecule. The internal configuration for a molecule of N atoms can be defined by $3N - 6$ coordinates. Thus, the configuration of a triatomic molecule, XYZ , is completely defined by the XY distance, the YZ distance, and the XYZ angle. These distances and angles are referred to as *internal coordinates* as they define the arrangement of atoms within the molecule but say nothing about its orientation in space, which is of no concern in discussing the pure vibrations of an isolated molecule. The three coordinates mentioned above for XYZ are not unique; the XZ distance would serve in place of one of the others.

The potential energy is a function of the displacements of these internal coordinates from their equilibrium positions. Analogous to Eq. (1.1-6) for diatomic molecules, it can be written as

$$2V = \sum_{ij} F_{ij} S_i S_j + \sum_{ijk} F_{ijk} S_i S_j S_k + \cdots$$

The S_i are displacements of the various internal coordinates from their equilibrium positions. The F_{ij} are the quadratic force constants. The F_{ijk} are "cubic" constants; the cubic terms are negligible for small displacements. The potential function will be discussed further in Sect. 1.9, 1.10, and 1.12.

The forces holding the atoms together are approximately harmonic, resulting in normal vibrations of $n = 3N - 6$ nearly harmonic oscillators ($n = 3N - 5$ for linear molecules). The vibrational energy to second order

in vibrational quantum number is given by Eq. (1.3-1).

$$G_{v_1, v_2, \dots} = \sum_i \omega_i (v_i + \frac{1}{2}d_i) + \sum_i \sum_{j>i} X_{ij} (v_i + \frac{1}{2}d_i)(v_j + \frac{1}{2}d_j) + W(l_i, l_j, \dots) \quad (1.3-1)$$

In Eq. (1.3-1) the ω_i are the fundamental vibrational frequencies at infinitesimal amplitude (they are actually extrapolations from observed frequencies to the values at infinitesimal amplitude). Thus they are the harmonic oscillator frequencies which would arise from the forces imposed by the equilibrium electronic configuration. They are referred to in this book as the harmonic frequencies. The d_i are the degeneracies of the frequencies ω_i . For nonlinear molecules, $\sum_i d_i = 3N - 6$; for linear molecules, $\sum_i d_i = 3N - 5$. The X_{ij} are anharmonic constants arising primarily from cubic and higher terms in the potential function. They correspond to the $\omega_e x_e$ of diatomic molecules. The v_i are the quantum numbers of the various vibrational modes in energy level $G_{v_1, v_2, \dots}$. The term W is a function of the internal angular momentum quantum numbers l_i, l_j , etc. It is zero for nondegenerate vibrations. The quantities l_i may have the values $v_i, v_i - 2, \dots, 1$, or 0 for degenerate vibrations.

The first sum on the right in Eq. (1.3-1) is that derived from a quadratic potential function, for which the normal vibrations are true harmonic oscillations. If cubic and higher terms in the potential function are significant, we must include the second sum of anharmonic terms (including W) to reproduce the observed energy level pattern. Higher terms, such as those involving $(v_i + \frac{1}{2}d_i)(v_j + \frac{1}{2}d_j)(v_k + \frac{1}{2}d_k)$, are expected to be very small as found for diatomic molecules [see Eq. (1.1-7) and Table 1.1-1]. This is born out in practice for the few cases where evidence is available. If a sufficient number of combination and overtone transitions are observed, for which $\sum_i \Delta v_i > 1$, it is possible to calculate the anharmonic corrections, X_{ij} and W of Eq. (1.3-1). Illustration of this procedure is given in Appendix I. In most cases, most of the anharmonic constants are unknown and therefore neglected. The calculated force constants are then only an approximation to the true harmonic force constants and must be treated as such. In a few cases, a sufficient number of vibrational levels has been determined to calculate many or all of the anharmonic corrections, X_{ij} and W , of Eq. (1.3-1). In later chapters, specific cases will be discussed.

Another factor which must be considered in evaluating the energy levels of polyatomic molecules is Fermi resonance. It may happen that two vibrational levels belonging to different vibrations (or combinations of vibrations) will have nearly the same energy. If these two levels have the