2

Basic Principles

1. ELECTROMAGNETIC RADIATION

All light (including infrared) is classified as electromagnetic radiation and consists of alternating electric and magnetic fields and is described classically by a continuous sinusoidal wave like motion of the electric and magnetic fields. Typically, for IR and Raman spectroscopy we will only consider the electric field and neglect the magnetic field component. Figure 2.1 depicts the electric field amplitude of light as a function of time.

The important parameters are the wavelength (λ, length of 1 wave), frequency (v, number cycles per unit time), and wavenumbers ($\bar{v}$, number of waves per unit length) and are related to one another by the following expression:

$$\bar{v} = \frac{v}{(c/n)} = \frac{1}{\lambda}$$

where c is the speed of light and n the refractive index of the medium it is passing through. In quantum theory, radiation is emitted from a source in discrete units called photons where the photon frequency, v, and photon energy, E_p, are related by

$$E_p = hv$$

where h is Planck's constant (6.6256×10^{-27} erg sec). Photons of specific energy may be absorbed (or emitted) by a molecule resulting in a transfer of energy. In absorption spectroscopy this will result in raising the energy of molecule from ground to a specific excited state
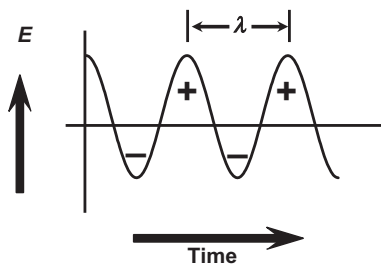

FIGURE 2.1 The amplitude of the electric vector of electromagnetic radiation as a function of time. The wavelength is the distance between two crests.
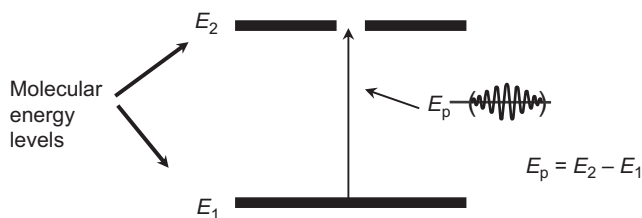
FIGURE 2.2   Absorption of electromagnetic radiation.

as shown in Fig. 2.2. Typically the rotational (E_{rot}), vibrational (E_{vib}), or electronic (E_{el}) energy of molecule is changed by $\triangle E$:

$$\Delta E = E_p = h\nu = hc\bar{\nu}$$

In the absorption of a photon the energy of the molecule increases and ΔE is positive. To a first approximation, the rotational, vibrational, and electronic energies are additive:

$$E_T = E_{el} + E_{vib} + E_{rot}$$

We are concerned with photons of such energy that we consider E_{vib} alone and only for condensed phase measurements. Higher energy light results in electronic transitions (E_{el}) and lower energy light results in rotational transitions (E_{rot}). However, in the gas-state both IR and Raman measurements will include $E_{vib} + E_{rot}$.

2. MOLECULAR MOTION/DEGREES OF FREEDOM

2.1. Internal Degrees of Freedom

The molecular motion that results from characteristic vibrations of molecules is described by the internal degrees of freedom resulting in the well-known $3n - 6$ and $3n - 5$ rule-of-thumb for vibrations for non-linear and linear molecules, respectively. Figure 2.3 shows the fundamental vibrations for the simple water (non-linear) and carbon dioxide (linear) molecules.

The internal degrees of freedom for a molecule define n as the number of atoms in a molecule and define each atom with 3 degrees of freedom of motion in the X, Y, and Z directions resulting in $3n$ degrees of motional freedom. Here, three of these degrees are translation, while three describe rotations. The remaining $3n - 6$ degrees (non-linear molecule) are motions, which change the distance between atoms, or the angle between bonds. A simple example of the $3n - 6$ non-linear molecule is water (H_2O) which has $3(3) - 6 = 3$ degrees of freedom. The three vibrations include an in-phase and out-of-phase stretch and a deformation (bending) vibration. Simple examples of $3n - 5$ linear molecules include H_2, N_2, and O_2 which all have $3(2) - 5 = 1$ degree of freedom. The only vibration for these simple molecules is a simple stretching vibration. The more complicated CO_2 molecule has $3(3) - 5 = 4$ degrees of freedom and therefore four vibrations. The four vibrations include an in-phase and out-of-phase stretch and two mutually perpendicular deformation (bending) vibrations.

The molecular vibrations for water and carbon dioxide as shown in Fig. 2.3 are the normal mode of vibrations. For these vibrations, the Cartesian displacements of each atom in molecule
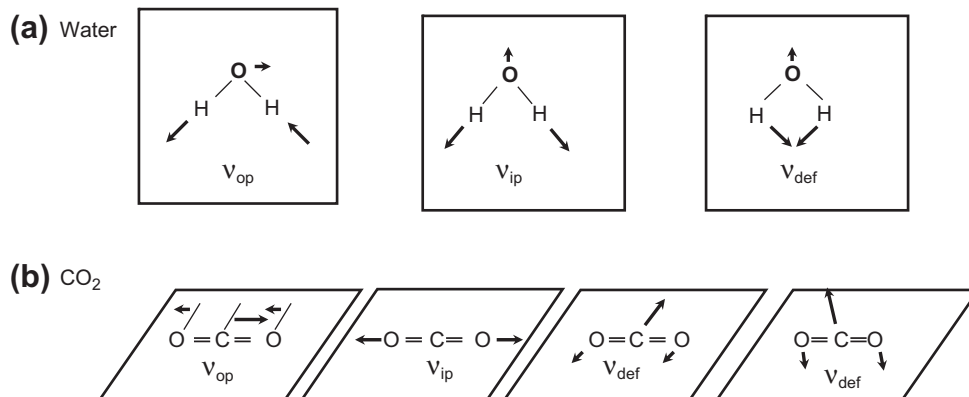
FIGURE 2.3 Molecular motions which change distance between atoms for water and CO_2.

change periodically with the same frequency and go through equilibrium positions simulta-
neously. The center of the mass does not move and the molecule does not rotate. Thus in
the case of harmonic oscillator, the Cartesian coordinate displacements of each atom plotted
as a function of time is a sinusoidal wave. The relative vibrational amplitudes may differ in
either magnitude or direction. Figure 2.4 shows the normal mode of vibration for a simple
diatomic such as HCl and a more complex totally symmetric CH stretch of benzene.
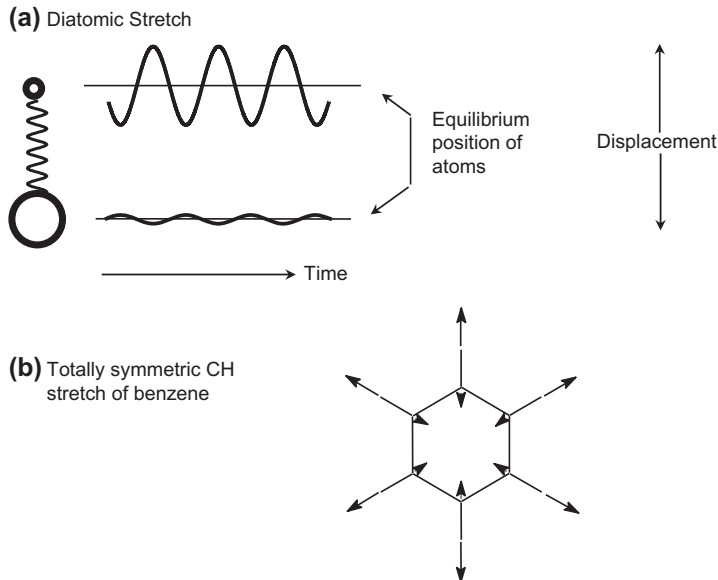

FIGURE 2.4 Normal mode of vibration for a simple diatomic such as HCl (a) and a more complex species such
as benzene (b). The displacement versus time is sinusoidal, with equal frequency for all the atoms. The typical
Cartesian displacement vectors are shown for the more complicated totally symmetric CH stretch of benzene.

3. CLASSICAL HARMONIC OSCILLATOR

To better understand the molecular vibrations responsible for the characteristic bands observed in infrared and Raman spectra it is useful to consider a simple model derived from classical mechanics.[1] Figure 2.5 depicts a diatomic molecule with two masses m_1 and m_2 connected by a massless spring. The displacement of each mass from equilibrium along the spring axis is X_1 and X_2. The displacement of the two masses as a function of time for a harmonic oscillator varies periodically as a sine (or cosine) function.

In the above diatomic system, although each mass oscillates along the axis with different amplitudes, both atoms share the same frequency and both masses go through their equilibrium positions simultaneously. The observed amplitudes are inversely proportional to the mass of the atoms which keeps the center of mass stationary

$$-\frac{X_1}{X_2} = \frac{m_2}{m_1}$$

The classical vibrational frequency for a diatomic molecule is:

$$\nu = \frac{1}{2\pi}\sqrt{K(\frac{1}{m_1} + \frac{1}{m_2})}$$

where K is the force constant in dynes/cm and m_1 and m_2 are the masses in grams and ν is in cycles per second. This expression is also encountered using the reduced mass where

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad \text{or} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

In vibrational spectroscopy wavenumber units, $\bar{\nu}$ (waves per unit length) are more typically used
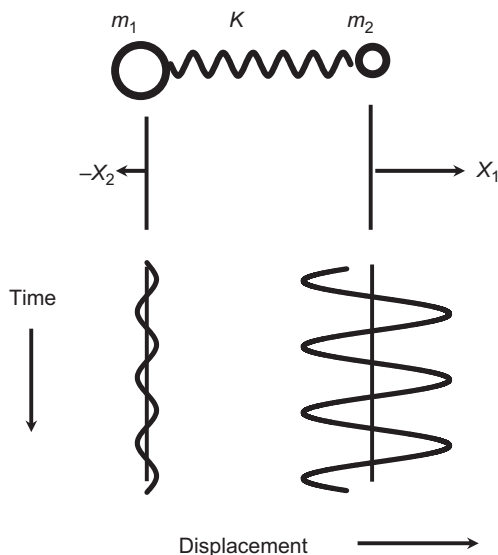

FIGURE 2.5 Motion of a simple diatomic molecule. The spring constant is K, the masses are m_1 and m_2, and X_1 and X_2 are the displacement vectors of each mass from equilibrium where the oscillator is assumed to be harmonic.

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{K\left(\frac{1}{m_1} + \frac{1}{m_2}\right)}$$

where $\bar{\nu}$ is in waves per centimeter and is sometimes called the frequency in cm^{-1} and c is the speed of light in cm/s.

If the masses are expressed in unified atomic mass units (u) and the force constant is expressed in millidynes/Ångström then:

$$\bar{\nu} = 1303\sqrt{K\left(\frac{1}{m_1} + \frac{1}{m_2}\right)}$$

where $1303 = [N_a \times 10^5]^{1/2}/2\pi c$ and N_a is Avogadro's number (6.023×10^{23} mole^{-1})

This simple expression shows that the observed frequency of a diatomic oscillator is a function of

1. the force constant K, which is a function of the bond energy of a two atom bond (see Table 2.1)
2. the atomic masses of the two atoms involved in the vibration.

TABLE 2.1   Approximate Range of Force Constants for Single, Double, and Triple Bonds

Bond type	K (millidynes/Ångström)
Single	3–6
Double	10–12
Triple	15–18

Table 2.1 shows the approximate range of the force constants for single, double, and triple bonds.

Conversely, knowledge of the masses and frequency allows calculation of a diatomic force constant. For larger molecules the nature of the vibration can be quite complex and for more accurate calculations the harmonic oscillator assumption for a diatomic will not be appropriate.

The general wavenumber regions for various diatomic oscillator groups are shown in Table 2.2, where Z is an atom such as carbon, oxygen, nitrogen, sulfur, and phosphorus.

TABLE 2.2   General Wavenumber Regions for Various Simple Diatonic Oscillator Groups

Diatomic oscillator	Region (cm^{-1})
Z–H	4000–2000
C≡C, C≡N	2300–2000
C=O, C=N, C =C	1950–1550
C–O, C–N, C–C	1300–800
C–Cl	830–560

4. QUANTUM MECHANICAL HARMONIC OSCILLATOR

Vibrational spectroscopy relies heavily on the theoretical insight provided by quantum theory. However, given the numerous excellent texts discussing this topic only a very cursory review is presented here. For a more detailed review of the quantum mechanical principles relevant to vibrational spectroscopy the reader is referred elsewhere.[2-5]

For the classical harmonic oscillation of a diatomic the potential energy (PE) is given by

$$PE = \frac{1}{2} KX^2$$

A plot of the potential energy of this diatomic system as a function of the distance, X between the masses, is thus a parabola that is symmetric about the equilibrium internuclear distance, X_e. Here X_e is at the energy minimum and the force constant, K is a measure of the curvature of the potential well near X_e.

From quantum mechanics we know that molecules can only exist in quantized energy states. Thus, vibrational energy is not continuously variable but rather can only have certain discrete values. Under certain conditions a molecule can transit from one energy state to another ($\Delta v = \pm 1$) which is what is probed by spectroscopy.

Figure 2.6 shows the vibrational levels in a potential energy diagram for the quantum mechanical harmonic oscillator. In the case of the harmonic potential these states are equidistant and have energy levels E given by

$$E_i = \left(v_i + \frac{1}{2} \right) hv \quad v_i = 0, 1, 2...$$

Here, v is the classical vibrational frequency of the oscillator and v is a quantum number which can have only integer values. This can only change by $\Delta v = \pm 1$ in a harmonic oscillator model. The so-called zero point energy occurs when $v = 0$ where $E = \frac{1}{2} hv$ and this vibrational energy cannot be removed from the molecule.
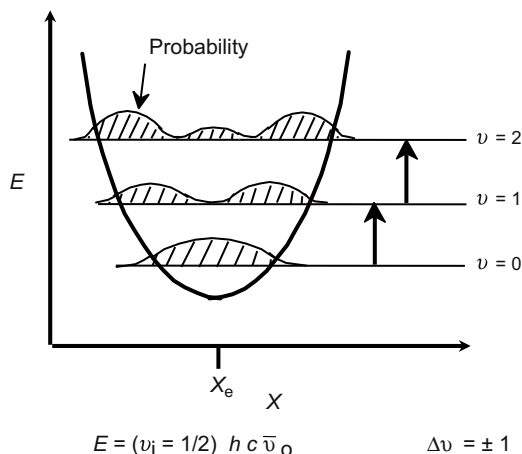

$$E = (v_i = 1/2) \; h \, c \, \bar{v}_0 \qquad\qquad \Delta v = \pm 1$$

FIGURE 2.6   Potential energy, E, versus internuclear distance, X, for a diatomic harmonic oscillator.
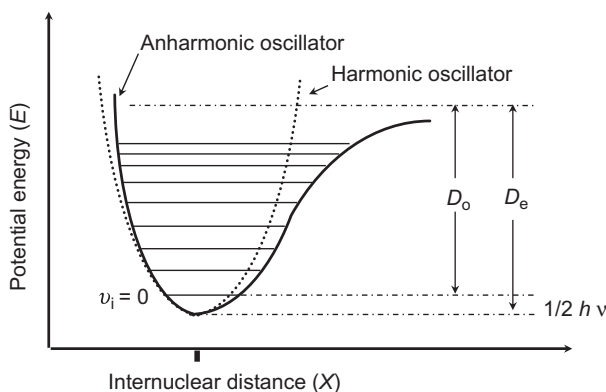
FIGURE 2.7 The potential energy diagram comparison of the anharmonic and the harmonic oscillator. Transitions originate from the $\upsilon = 0$ level, and D_o is the energy necessary to break the bond.

Figure 2.6 shows the curved potential wells for a harmonic oscillator with the probability functions for the internuclear distance X, within each energy level. These must be expressed as a probability of finding a particle at a given position since by quantum mechanics we cannot be certain of the position of the mass during the vibration (a consequence of Heisenberg's uncertainty principle).

Although we have only considered a harmonic oscillator, a more realistic approach is to introduce anharmonicity. Anharmonicity results if the change in the dipole moment is not linearly proportional to the nuclear displacement coordinate. Figure 2.7 shows the potential energy level diagram for a diatomic harmonic and anharmonic oscillator. Some of the features introduced by an anharmonic oscillator include the following.

The anharmonic oscillator provides a more realistic model where the deviation from harmonic oscillation becomes greater as the vibrational quantum number increases. The separation between adjacent levels becomes smaller at higher vibrational levels until finally the dissociation limit is reached. In the case of the harmonic oscillator only transitions to adjacent levels or so-called fundamental transitions are allowed (i.e., $\triangle \upsilon = \pm 1$) while for the anharmonic oscillator, overtones ($\triangle \upsilon = \pm 2$) and combination bands can also result. Transitions to higher vibrational states are far less probable than the fundamentals and are of much weaker intensity. The energy term corrected for anharmonicity is

$$E_\upsilon = h\nu_e\left(\upsilon + \frac{1}{2}\right) - h\chi_e\nu_e\left(\upsilon + \frac{1}{2}\right)^2$$

where $\chi_e\nu_e$ defines the magnitude of the anharmonicity.

5. IR ABSORPTION PROCESS

The typical IR spectrometer broad band source emits all IR frequencies of interest simultaneously where the near-IR region is 14,000–4000 cm^{-1}, the mid-IR region is

$4000-400$ cm^{-1}, and the far-IR region is $400-10$ cm^{-1}. Typical of an absorption spectroscopy, the relationship between the intensities of the incident and transmitted IR radiation and the analyte concentration is governed by the Lambert−Beer law. The IR spectrum is obtained by plotting the intensity (absorbance or transmittance) versus the wavenumber, which is proportional to the energy difference between the ground and the excited vibrational states.

Two important components to the IR absorption process are the radiation frequency and the molecular dipole moment. The interaction of the radiation with molecules can be described in terms of a resonance condition where the specific oscillating radiation frequency matches the natural frequency of a particular normal mode of vibration. In order for energy to be transferred from the IR photon to the molecule via absorption, the molecular vibration must cause a change in the dipole moment of the molecule. This is the familiar selection rule for IR spectroscopy, which requires a change in the dipole moment during the vibration to be IR active.

The dipole moment, μ, for a molecule is a function of the magnitude of the atomic charges (e_i) and their positions (r_i)

$$\mu = \sum e_i r_i$$

The dipole moments of uncharged molecules derive from partial charges on the atoms, which can be determined from molecular orbital calculations. As a simple approximation, the partial charges can be estimated by comparison of the electronegativities of the atoms. Homonuclear diatomic molecules such as H_2, N_2, and O_2 have *no* dipole moment and are IR inactive (but Raman active) while heteronuclear diatomic molecules such as HCl, NO, and CO do have dipole moments and have IR active vibrations.

The IR absorption process involves absorption of energy by the molecule if the vibration causes a change in the dipole moment, resulting in a change in the vibrational energy level. Figure 2.8 shows the oscillating electric field of the IR radiation generates forces on the
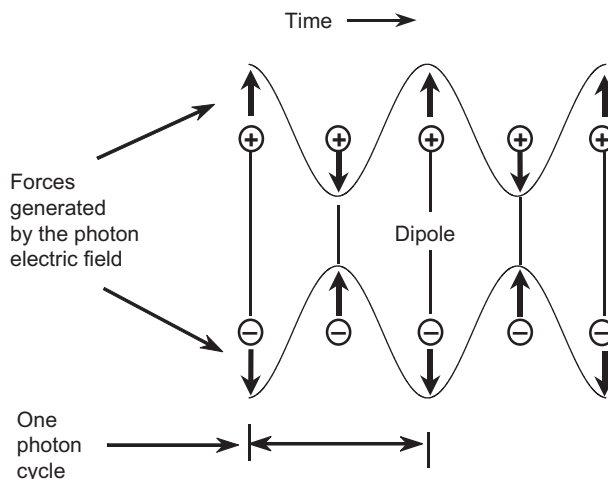

FIGURE 2.8   The oscillating electric field of the photon generates oscillating, oppositely directed forces on the positive and negative charges of the molecular dipole. The dipole spacing oscillates with the same frequency as the incident photon.

molecular dipole where the oscillating electric field drives the oscillation of the molecular dipole moment and alternately increases and decreases the dipole spacing.

Here, the electric field is considered to be uniform over the whole molecule since λ is much greater than the size of most molecules. In terms of quantum mechanics, the IR absorption is an electric dipole operator mediated transition where the change in the dipole moment, μ, with respect to a change in the vibrational amplitude, Q, is greater than zero.

$$\left(\frac{\partial \mu}{\partial Q}\right)_0 \neq 0$$

The measured IR band intensity is proportional to the square of the change in the dipole moment.

6. THE RAMAN SCATTERING PROCESS

Light scattering phenomena may be classically described in terms of electromagnetic (EM) radiation produced by oscillating dipoles induced in the molecule by the EM fields of the incident radiation. The light scattered photons include mostly the dominant Rayleigh and the very small amount of Raman scattered light.[6] The induced dipole moment occurs as a result of the molecular polarizability α, where the polarizability is the deformability of the electron cloud about the molecule by an external electric field.

Figure 2.9 shows the response of a non-polar diatomic placed in an oscillating electric field. Here we represent the static electric field by the plates of a charged capacitor. The negatively charged plate attracts the nuclei, while the positively charged plate attracts the least tightly
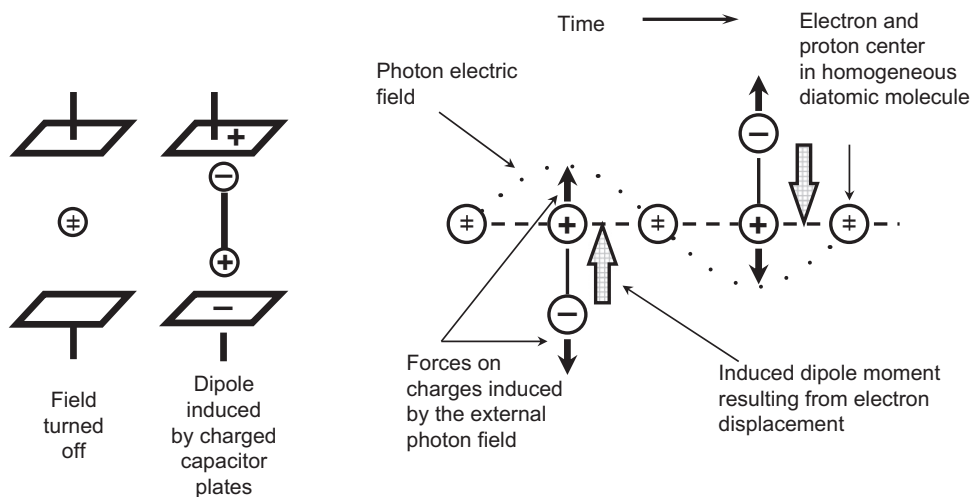

FIGURE 2.9 Induced dipole moment of a homonuclear diatomic originating from the oscillating electric field of the incident radiation. The field relative to the proton center displaces the electron center. The charged plates of a capacitor, which induces a dipole moment in the polarizable electron cloud, can represent the electric field.
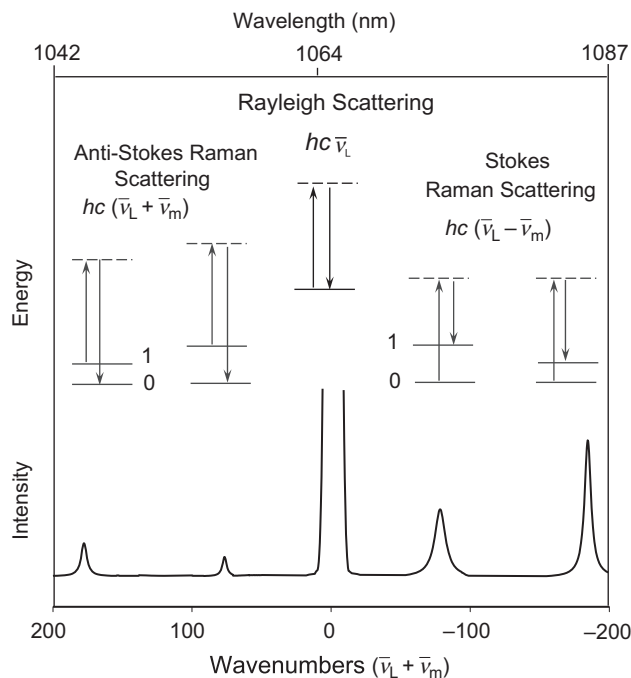
FIGURE 2.10 Schematic illustration of Rayleigh scattering as well as Stokes and anti-Stokes Raman scattering. The laser excitation frequency (v_L) is represented by the upward arrows and is much higher in energy than the molecular vibrations. The frequency of the scattered photon (downward arrows) is unchanged in Rayleigh scattering but is of either lower or higher frequency in Raman scattering. The dashed lines indicate the "virtual state."

bound outer electrons resulting in an induced dipole moment. This induced dipole moment is an off-resonance interaction mediated by an oscillating electric field.

In a typical Raman experiment, a laser is used to irradiate the sample with monochromatic radiation. Laser sources are available for excitation in the UV, visible, and near-IR spectral region (785 and 1064 nm). Thus, if visible excitation is used, the Raman scattered light will also be in the visible region. The Rayleigh and Raman processes are depicted in Fig. 2.10. No energy is lost for the elastically scattered Rayleigh light while the Raman scattered photons lose some energy relative to the exciting energy to the specific vibrational coordinates of the sample. In order for Raman bands to be observed, the molecular vibration must cause a change in the polarizability.

Both Rayleigh and Raman are two photon processes involving scattering of incident light ($hc\bar{v}_L$), from a "virtual state." The incident photon is momentarily absorbed by a transition from the ground state into a virtual state and a new photon is created and scattered by a transition from this virtual state. Rayleigh scattering is the most probable event and the scattered intensity is ca. 10^{-3} less than that of the original incident radiation. This scattered photon results from a transition from the virtual state back to the ground state and is an elastic scattering of a photon resulting in no change in energy (i.e., occurs at the laser frequency).

   Raman scattering is far less probable than Rayleigh scattering with an observed intensity that is ca. 10^{-6} that of the incident light for strong Raman scattering. This scattered photon results from a transition from the virtual state to the first excited state of the molecular vibration. This is described as an inelastic collision between photon and molecule, since the molecule acquires different vibrational energy $(\bar{\nu}_m)$ and the scattered photon now has different energy and frequency.

   As shown in Fig. 2.10 two types of Raman scattering exist: Stokes and anti-Stokes. Molecules initially in the ground vibrational state give rise to Stokes Raman scattering $hc(\bar{\nu}_L - \bar{\nu}_m)$ while molecules initially in vibrational excited state give rise to anti-Stokes Raman scattering, $hc(\bar{\nu}_L + \bar{\nu}_m)$. The intensity ratio of the Stokes relative to the anti-Stokes Raman bands is governed by the absolute temperature of the sample, and the energy difference between the ground and excited vibrational states. At thermal equilibrium Boltzmann's law describes the ratio of Stokes relative to anti-Stokes Raman lines. The Stokes Raman lines are much more intense than anti-Stokes since at ambient temperature most molecules are found in the ground state.

   The intensity of the Raman scattered radiation I_R is given by:

$$I_R \propto \nu^4 I_o N \left(\frac{\partial \alpha}{\partial Q}\right)^2$$

where I_o is the incident laser intensity, N is the number of scattering molecules in a given state, ν is the frequency of the exciting laser, α is the polarizability of the molecules, and Q is the vibrational amplitude.

   The above expression indicates that the Raman signal has several important parameters for Raman spectroscopy. First, since the signal is concentration dependent, quantitation is possible. Secondly, using shorter wavelength excitation or increasing the laser flux power density can increase the Raman intensity. Lastly, only molecular vibrations which cause a change in polarizability are Raman active. Here the change in the polarizability with respect to a change in the vibrational amplitude, Q, is greater than zero.

$$\left(\frac{\partial \alpha}{\partial Q}\right) \neq 0$$

   The Raman intensity is proportional to the square of the above quantity.

7. CLASSICAL DESCRIPTION OF THE RAMAN EFFECT

   The most basic description of Raman spectroscopy describes the nature of the interaction of an oscillating electric field using classical arguments.[6] Figure 2.11 schematically represents this basic mathematical description of the Raman effect.

   As discussed above, the electromagnetic field will perturb the charged particles of the molecule resulting in an induced dipole moment:

$$\mu = \alpha E$$

where α is the polarizability, E is the incident electric field, and μ is the induced dipole moment. Both E and α can vary with time. The electric field of the radiation is oscillating
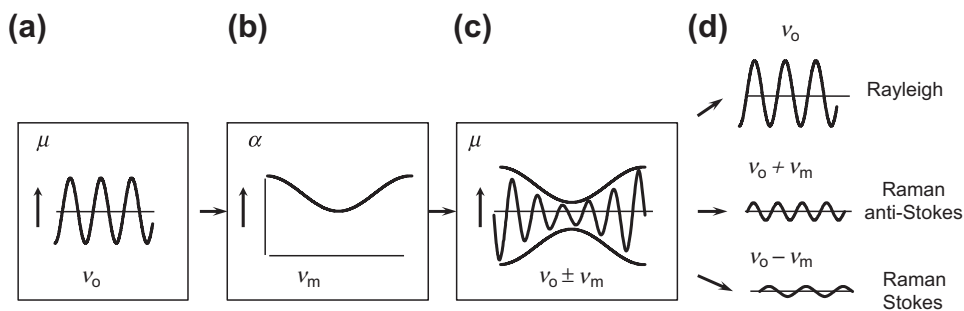
FIGURE 2.11   Schematic representing Rayleigh and Raman scattering. In (a) the incident radiation makes the induced dipole moment of the molecule oscillate at the photon frequency. In (b) the molecular vibration can change the polarizability, α, which changes the amplitude of the dipole moment oscillation. The result as shown in (c) is an amplitude modulated dipole moment oscillation. The image (d) shows the components with steady amplitudes which can emit electromagnetic radiation.

as a function of time at a frequency ν_0, which can induce an oscillation of the dipole moment μ of the molecule at this same frequency, as shown in Fig. 2.11a. The polarizability α of the molecule has a certain magnitude whose value can vary slightly with time at the much slower molecular vibrational frequency ν_m, as shown in Fig. 2.11b. The result is seen in Fig. 2.11c, which depicts an amplitude modulation of the dipole moment oscillation of the molecule. This type of modulated wave can be resolved mathematically into three steady amplitude components with frequencies ν_0, $\nu_0 + \nu_m$, and $\nu_0 - \nu_m$ as shown in Fig. 2.11d. These dipole moment oscillations of the molecule can emit scattered radiation with these same frequencies called Rayleigh, Raman anti-Stokes, and Raman Stokes frequencies. If a molecular vibration did not cause a variation in the polarizability, then there would be no amplitude modulation of the dipole moment oscillation and there would be no Raman Stokes or anti-Stokes emission.

8. SYMMETRY: IR AND RAMAN ACTIVE VIBRATIONS

The symmetry of a molecule, or the lack of it, will define what vibrations are Raman and IR active.[5] In general, symmetric or in-phase vibrations and non-polar groups are most easily studied by Raman while asymmetric or out-of-phase vibrations and polar groups are most easily studied by IR. The classification of a molecule by its symmetry enables understanding of the relationship between the molecular structure and the vibrational spectrum. Symmetry elements include planes of symmetry, axes of symmetry, and a center of symmetry.

Group Theory is the mathematical discipline, which applies symmetry concepts to vibrational spectroscopy and predicts which vibrations will be IR and Raman active.[1,5] The symmetry elements possessed by the molecule allow it to be classified by a point group and vibrational analysis can be applied to individual molecules. A thorough discussion of Group Theory is beyond the scope of this work and interested readers should examine texts dedicated to this topic.[7]
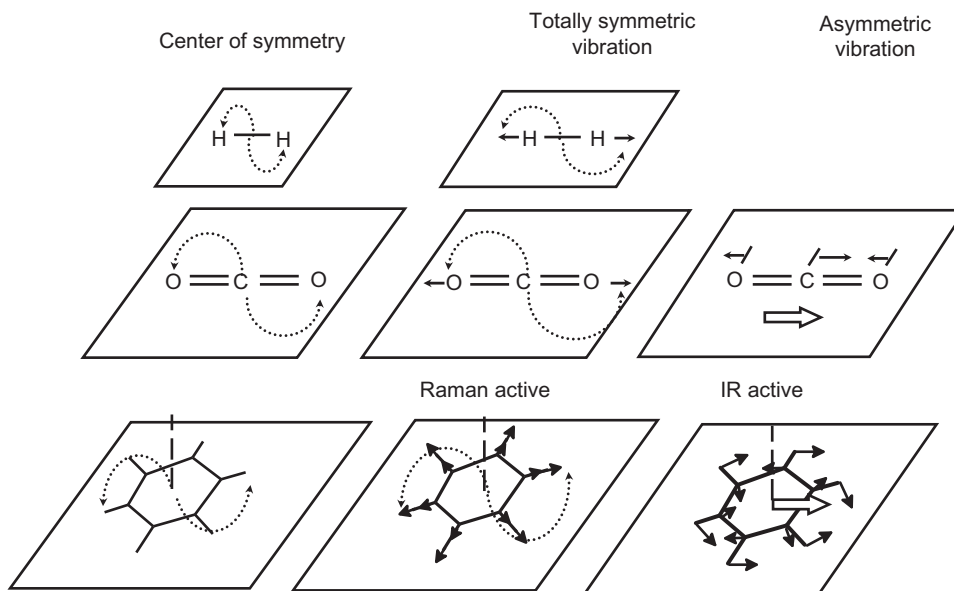
FIGURE 2.12   The center of symmetry for H_2, CO_2, and benzene. The Raman active symmetric stretching vibrations above are symmetric with respect to the center of symmetry. Some IR active asymmetric stretching vibrations are also shown.

For small molecules, the IR and Raman activities may often be determined by a simple inspection of the form of the vibrations. For molecules that have a center of symmetry, the rule of mutual exclusion states that no vibration can be active in both the IR and Raman spectra. For such highly symmetrical molecules vibrations which are Raman active are IR inactive and vice versa and some vibrations may be both IR and Raman inactive.

Figure 2.12 shows some examples of molecules with this important symmetry element, the center of symmetry. To define a center of symmetry simply start at any atom, go in a straight line through the center and an equal distance beyond to find another, identical atom. In such cases the molecule has no permanent dipole moment. Examples shown below include H_2, CO_2, and benzene and the rule of mutual exclusion holds.

In a molecule with a center of symmetry, vibrations that retain the center of symmetry are IR inactive and may be Raman active. Such vibrations, as shown in Fig. 2.12, generate a change in the polarizability during the vibration but no change in a dipole moment. Conversely, vibrations that do not retain the center of symmetry are Raman inactive, but may be IR active since a change in the dipole moment may occur.

For molecules without a center of symmetry, some vibrations can be active in both the IR and Raman spectra.

Molecules that do not have a center of symmetry may have other suitable symmetry elements so that some vibrations will be active only in Raman or only in the IR. Good examples of this are the in-phase stretches of inorganic nitrate and sulfate shown in Fig. 2.13. These are Raman active and IR inactive. Here, neither molecule has a center of symmetry but the negative oxygen atoms move radially simultaneously resulting in no dipole moment change.

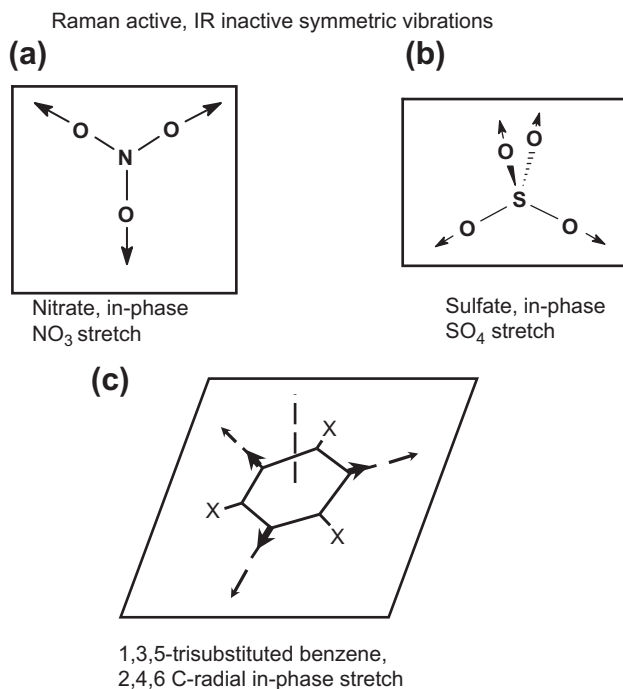Raman active, IR inactive symmetric vibrations

FIGURE 2.13   Three different molecules, nitrate, sulfate, and 1,3,5-trisubstituted benzene molecules that do not have a center of symmetry. The in-phase stretching vibrations of all three result in Raman active, but IR inactive vibrations.

Another example is the 1,3,5-trisubstituted benzene where the C-Radial in-phase stretch is Raman active and IR inactive.

In Figure 2.14 some additional symmetry operations are shown, other than that for a center of symmetry for an XY_2 molecule such as water. These include those for a plane of symmetry, a two-fold rotational axis of symmetry, and an identity operation (needed for group theory) which makes no change. If a molecule is symmetrical with respect to a given symmetry element, the symmetry operation will not make any discernible change from the original configuration. As shown in Fig. 2.14, such symmetry operations are equivalent to renumbering the symmetrically related hydrogen (Y) atoms.

Figure 2.15 shows the Cartesian displacement vectors (arrows) of the vibrational modes Q_1, Q_2, and Q_3 of the bent triatomic XY_2 molecule (such as water), and shows how they are modified by the symmetry operations C_2, σ_v, and σ'_v. For non-degenerate modes of vibration such as these, the displacement vectors in the first column (the identity column, I) are multiplied by either $(+1)$ or (-1) as shown to give the forms in the other three columns. Multiplication by $(+1)$ does not change the original form so the resulting form is said to be symmetrical with respect to that symmetry operation. Multiplication by (-1) reverses all the vectors of the original form and the resulting form is said to be anti-symmetrical with respect to that symmetry element. As seen in Fig. 2.15, Q_1 and Q_2 are both totally
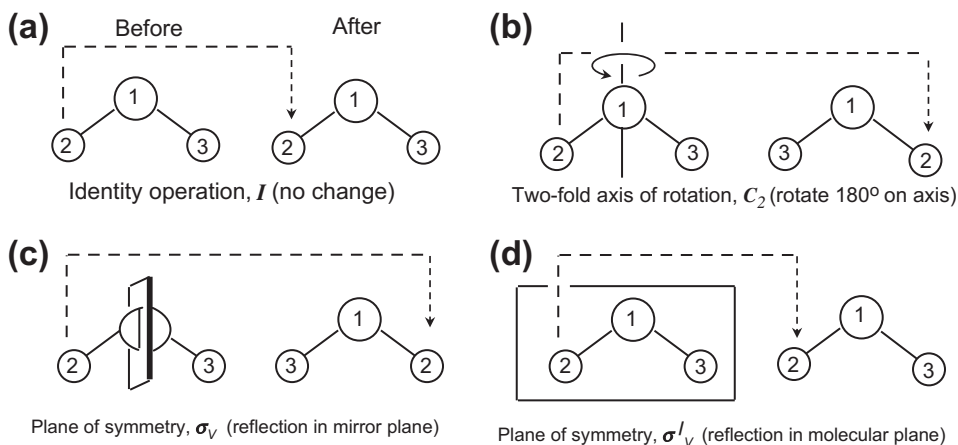
FIGURE 2.14 Symmetry operations for an XY_2 bent molecule such as water in the equilibrium configuration.
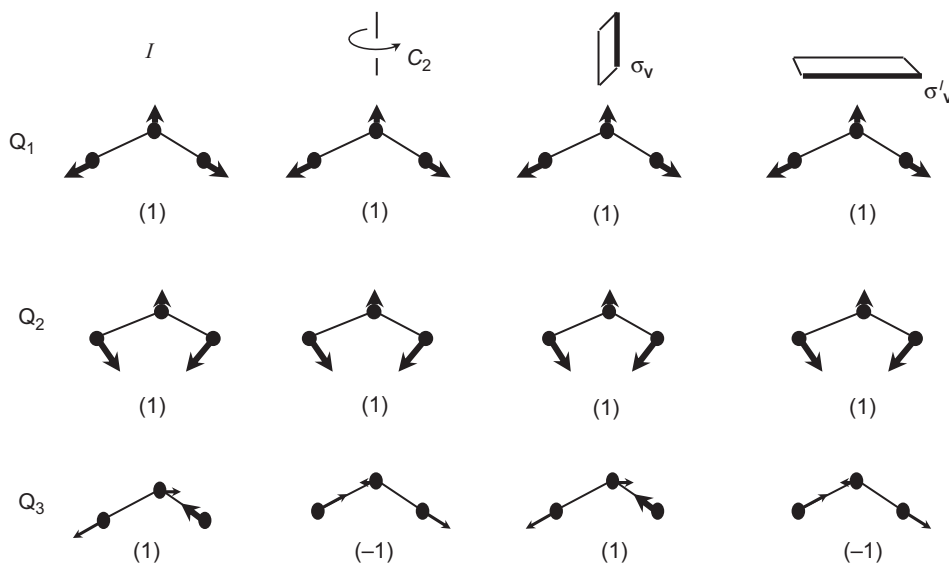

FIGURE 2.15 The bent symmetrical XY_2 molecule such as H_2O performing the three fundamental modes Q_1, Q_2, and Q_3. The vectors in column one (identity I) are transformed by the C_2, σ_v, and σ'_v, operations into the forms in the remaining columns, where the vectors are like those in column one multiplied by (+1) symmetrical or (−1) anti-symmetrical.

symmetric modes (i.e., symmetric to all symmetry operations), whereas Q_3 is symmetric with respect to the σ'_v operation but anti-symmetric with respect to the C_2 and σ_v operations. The transformation numbers (+1 and −1) are used in group theory to characterize the symmetries of non-degenerate vibrational modes. From these symmetries one can deduce that Q_1, Q_2, and Q_3 are all active in both the IR and Raman spectra. In addition,

the dipole moment change in Q_1 and Q_2 is parallel to the C_2 axis and in Q_3 it is perpendicular to the C_2 axis and the σ_v, plane.

Doubly degenerate modes occur when two different vibrational modes have the same vibrational frequency as a consequence of symmetry. A simple example is the C—H bending vibration in Cl_3C—H molecule where the C—H bond can bend with equal frequency in two mutually perpendicular directions. The treatment of degenerate vibrations is more complex and will not be discussed here.

9. CALCULATING THE VIBRATIONAL SPECTRA OF MOLECULES

The basis of much of the current understanding of molecular vibrations and the localized group vibrations that give rise to useful group frequencies observed in the IR and Raman spectra of molecules is based upon extensive historical work calculating vibrational spectra. Historically, normal coordinate analysis first developed by Wilson with a GF matrix method and using empirical molecular force fields has played a vital role in making precise assignments of observed bands. The normal coordinate computation involves calculation of the vibrational frequencies (i.e., eigenvalues) as well as the atomic displacements for each normal mode of vibration. The calculation itself uses structural parameters such as the atomic masses and empirically derived force fields. However, significant limitations exist when using empirical force fields. The tremendous improvements in computational power along with multiple software platforms with graphical user interfaces enables a much greater potential use of *ab initio* quantum mechanical calculational methods for vibrational analysis.

The standard method for calculating the fundamental vibrational frequencies and the normal vibrational coordinates is the Wilson GF matrix method.[8] The basic principles of normal coordinate analysis have been covered in detail in classic books on vibrational spectroscopy.[1,4,5,8] In the GF matrix approach a matrix, **G**, which is related to the molecular vibrational kinetic energy is calculated from information about the molecular geometry and atomic masses. Based upon a complete set of force constants a matrix, **F**, is constructed which is related to the molecular vibrational potential energy. A basis set is selected that is capable of describing all possible internal atomic displacements for the calculation of the **G** and **F** matrices. Typically, the molecules will be constructed in Cartesian coordinate space and then transformed to an internal coordinate basis set which consists of changes in bond distances and bond angles. The product matrix **GF** can then be calculated.

The fundamental frequencies and normal coordinates are obtained through the diagonalization of the **GF** matrix. Here, a transformation matrix **L** is sought:

$$L^{-1} \, GFL \, = \, \Lambda$$

Here, Λ is a diagonal matrix whose diagonal elements are λ_i's defined as:

$$\lambda_i \, = \, 4\pi^2 c^2 \, v_i^{-2}$$

Where the frequency in cm^{-1} of the *i*th normal mode is $\bar{v}_i^2$. For the previous equation, it is the matrix $\mathbf{L}^{-1}$ which transforms the internal coordinates, **R**, into the normal coordinates, **Q**, as:

$$Q \, = \, L^{-1}R$$

In this equation, the column matrix of internal coordinates is **R** and **Q** is a column matrix that contains normal coordinates as a linear combination of internal coordinates.

In the case of vibrational spectroscopy, the polyatomic molecule is considered to oscillate with a small amplitude about the equilibrium position and the potential energy expression is expanded in a Taylor series and takes the form:

$$V = V_0 + \sum_{i=1}^{3N} \left(\frac{\partial V}{\partial q_i}\right)_e dq_i + \frac{1}{2}\sum_{i=1}^{3N}\sum_{j=1}^{3N} \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_e dq_i dq_j + \cdots$$

expressed in internal coordinates, $q_{i,}$, which are directly connected to the internal bond lengths and angles. The above expression is simplified:

1. The first term $V_o = 0$ since the vibrational energy is chosen as vibrating atoms about the equilibrium position.
2. At the minimum energy configuration the first derivative is zero by definition.
3. Since the harmonic approximation is used all terms in the Taylor expansion greater than two can be neglected.

This leaves only the second order term in the potential energy expression for V. Using Newton's second law, the above is expressed as:

$$\frac{d^2 q_i}{dt^2} = -\left(\frac{\partial V}{\partial q_i}\right) = -\sum_{j=1}^{3N}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_e q_j$$

The above equation of motion is solved to yield a determinant whose eigenvalues $(m\omega^2)$ provides the vibrational frequencies (ω). The eigenvectors describe the atomic displacements for each of the vibrational modes characterized by the eigenvalues. These are the normal modes of vibration and the corresponding fundamental frequencies.

The force constant f_{ij} is defined as the second derivative of the potential energy with respect to the coordinates q_i and q_j in the equilibrium configuration as:

$$f_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)$$

In order to obtain the molecular force field with the force constants given by the above equation, a variety of computational methods are available. In general, the calculations of the vibrational frequencies can be accomplished with either empirical force field method or quantum mechanical methods.[9,10] The quantum mechanical method is the most rigorous approach and is typically used for smaller to moderately sized molecules since it is computationally intensive. Since we are examining chemical systems with more than one electron, approximate methods known as *ab initio* methods utilizing a harmonic oscillator approximation are employed. Because actual molecular vibrations include both harmonic and anharmonic components, a difference is expected between the experimental and calculated vibrational frequencies. Other factors that contribute to the differences between the calculated and experimental frequencies include neglecting electron correlation and the limited size of the basis set. In order to obtain a better match with the experimental frequencies, scaling factors are typically introduced.

Quantum mechanical *ab initio* methods and hybrid methods are based upon force constants calculated by Hartree-Fock (HF) and density functional based methods. In general, these methods involve molecular orbital calculations of isolated molecules in a vacuum, such that environmental interactions typically encountered in the liquid and solid state are not taken into account. A full vibrational analysis of small to moderately sized molecules typically takes into account both the vibrational frequencies and intensities to insure reliable assignments of experimentally observed vibrational bands.

The *ab initio* Hartree-Fock (HF) method is an older quantum mechanical based approach.[9,10] The HF methodology neglects the mutual interaction (correlation) between electrons which affects the accuracy of the frequency calculations. In general, when using HF calculations with a moderate basis set there will be a difference of ca. 10−15% between the experimental and calculated frequencies and thus a scaling factor of 0.85−0.90. This issue can be resolved somewhat by use of post-HF methods such as configuration interaction (CI), multi-configuration self-consistent field (MCSF), and Møller Plessant perturbation (MP2) methods. Utilizing configuration interaction with a large basis set leads to a scaling factor between 0.92 and 0.96. However, use of these post-HF methods comes with a considerable computational cost that limits the size of the molecule since they scale with the number of electrons to the power of 5−7.

The *ab initio* density functional theory (DFT) based methods have arisen as highly effective computational techniques because they are computationally as efficient as the original HF calculations while taking into account a significant amount of the electron correlation.[9,10] The DFT has available a variety of gradient-corrected exchange functions to calculate the density functional force constants. Popular functions include the BLYP and B3LYP. The scaling factors encountered using a large basis set and BLYP or B3LYP often approach 1 (0.96−1.05).

Basis set selection is important in minimizing the energy state of the molecule and providing an accurate frequency calculation. Basis sets are Gaussian mathematical functions representative of the atomic orbitals which are linearly combined to describe the molecular orbitals. The simplest basis set is the STO-3G in which the Slater-type orbital (STO) is expanded with three Gaussian-type orbitals (GTO). The more complex split-valence basis sets, 3-21G and 6-31G are more typically used. Here, the 6-31G consists of a core of six GTO's that are not split and the valence orbitals are split into one basis function constructed from three GTO's and another that is a single GTO. Because the electron density of a nucleus can be polarized (by other nucleus), a polarization function can also be included. Such functions include the 6-31G* and the 6-31G**.

Accurate vibrational analysis requires optimizing the molecular structure and wavefunctions in order to obtain the minimum energy state of the molecule. In practice, this requires selection of a suitable basis set method for the electron correlation. The selection of the basis set and the HF or DFT parameters is important in acquiring acceptable calculated vibrational data necessary to assign experimental IR and Raman spectra.

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