Vibrational spectroscopy

Infrared Spectrometry

Region	Energy (kJ/mol)	Wavenumber (cm^{-1})	Wavelength (μm)
Near IR	150-50	12,800-4000	0.78-2.5
Mid IR	50-2.5	4000-200	2.5-50
Far IR	2.5-0.1	200-10	50-1000

Energy of IR photon is insufficient to cause electronic excitation but can cause vibrational or rotational excitation

The frequency dependence of force constant, a classical-mechanical approximation.

0.Classical approximation
Model: a spring and ball *system* is attached to a wall.

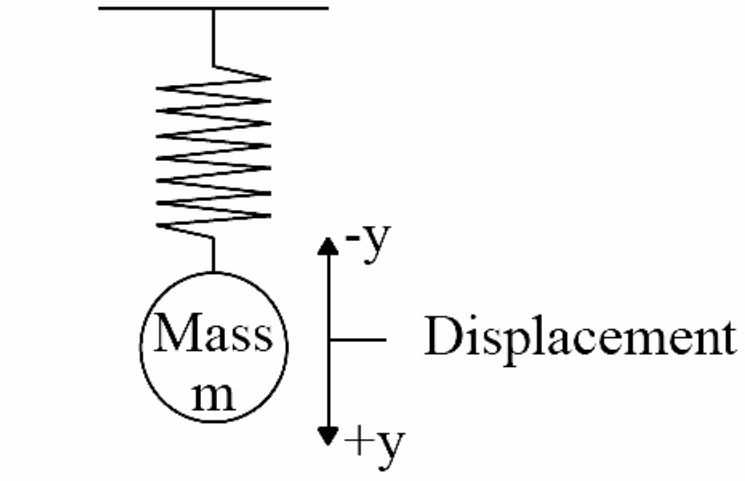


Figure 1. Classical vibration motion.

The force acting on the system is proportional to the force constant, *k,* and displacement, *x*, measured from the equilibrium position of system

$$F = -kx \qquad 1.$$

The oscillating mass, *m,* acquires an acceleration, *a*, and from Newton II. law

$$F = ma = m\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} \qquad 2.$$

The solution of this derivative should met the conditions

1. the function is periodic,
2. the second derivative of x is equal to the original function multiplied by $-k/m$.

The second condition: $m\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -kx$, and

$$\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -x\frac{k}{m}. \qquad 3.$$

The function fulfils the conditions if:

$$x = A\cos(2\pi\nu \cdot t + b) \qquad 4.$$

where v is the frequency of vibration, and b is the phase of vibration.
If $b = 0$, the first and second derivative of equation 4.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -A2\pi\nu \cdot \sin(2\pi\nu \cdot t)$$

$$\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -A4\pi^2\nu^2 \cdot \cos(2\pi\nu \cdot t) \qquad 5.$$

When Equations 3. and 4. are compared

$$\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -4\pi^2\nu^2 \cdot x \qquad 6.$$

From Equations 3. and 6. we have,

$$-x\frac{k}{m} = -4\pi^2\nu^2 \cdot x$$

and finally we get the frequency dependence:

$$\nu = \frac{1}{2\pi} \cdot \sqrt{\frac{k}{m}} \qquad 7.$$

For a chemical bond force constant is called bond strength.

1. *Diatomic molecules*

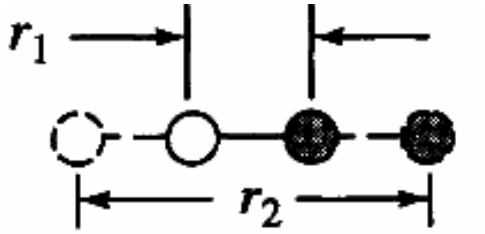


Figure 2. Equilibrium distance: r_1, displacement: $r_2 - r_1$.

For a diatomics with atomic masses m_1 and m_2 Eq. 7 is given

$$\nu = \frac{1}{2\pi} \cdot \sqrt{\frac{k}{\mu}} \qquad 7a.$$

where

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

μ is the reduced mass representing a single mass having the same vibrating properties as m_1 and m_2 produce.

1.1 *Harmonic oscillator*.
When $F = -kx$ law is valid harmonic oscillator approximation can be applied for the description of energetics of molecular vibrations.

The displacement, can be defined as (see Figure 2.),

$$x = r_2 - r_1,$$

and x can be positive, when bond is stretched or that can be negative, when restoring force makes the bond distance less than the equilibrium bond distance.

The equilibrium condition: $F = 0$, $x = 0$.

Potential energy, V_v.

$$-\frac{dV_v}{dx} = F \qquad 8.$$

$$\int dV_v = -\int F dx = k \int x dx$$

$$V_v = \frac{1}{2} k \cdot x^2 \qquad \text{or} \qquad V_v = \frac{1}{2} k \cdot (r_2 - r_1)^2 \qquad 9.$$

The graph of this function is a perfect parabola (see Figure 3.)

Quantum mechanical energy term
According to the law of classical mechanics a diatomics can have any amplitude, consequently can take any potential energy on parabola.
By the law of quantum mechanics, the allowed energies of a diatomics are restricted to the vibrational levels.

$$E_v = (v + 1/2) \cdot h\nu \qquad 10.$$

In equation 10 v represents the quantum number, v = 1, 2, 3 ... . The change in quantum number for a harmonic oscillator is called vibration selection rule:

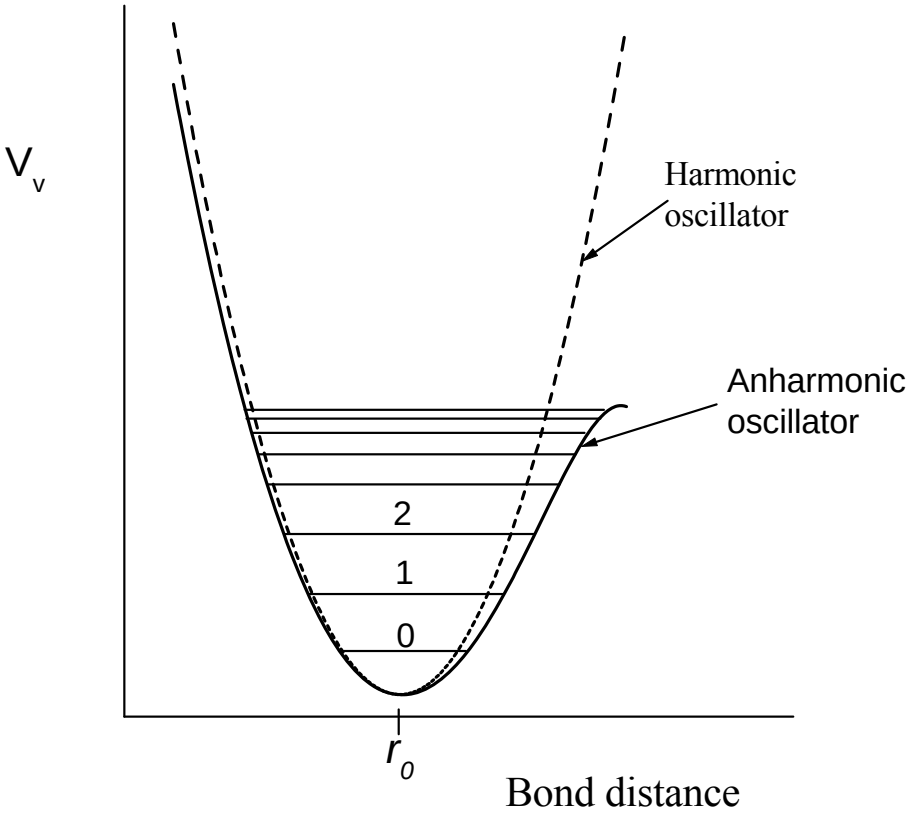
$$\Delta v = \pm 1$$

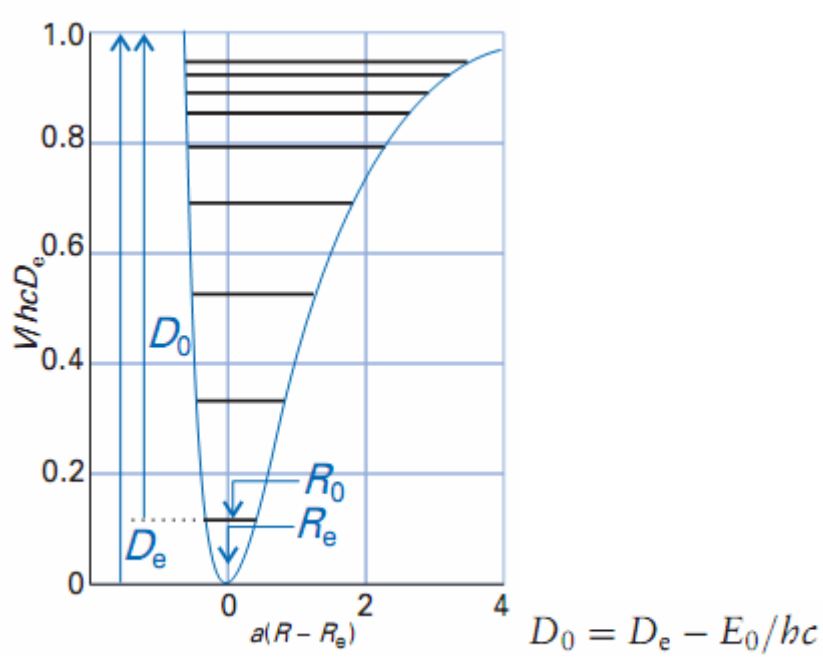
It means that the vibrating system can exclusively absorb the energy difference between two subsequent vibrational level.

In equations (see Figure 3.) we show

$$E_0 = (0 + 1/2) \cdot h\nu$$
$$E_1 = (1 + 1/2) \cdot h\nu$$
$$\Delta E_v = E_1 - E_0 = h\nu \qquad 11.$$

The energy difference, ΔE_v is quantized, and equal to the energy of exciting photon, $h\nu$. Equation 11. denotes that the energy difference is independent of the level number, so the levels are *equidistant*.





$D_0 = D_e - E_0/hc$

Figure 3. Potential energy distance functions. Harmonic oscillator: dotted line, anharmonic oscillator: solid line.

The shape of parabola depends on the force constant (see Eq. 9.). The stronger the bond the narrower the parabola. The lengths of a level is equal to *twice of the amplitude* of the motion.
Eq. 9 can be given also in terms of force constant and reduced mass,

$$V_{\mathrm{v}} = \frac{1}{2} k \cdot (r_2 - r_1)^2 = \frac{1}{2} \cdot \nu^2 \cdot 4\pi^2 \mu \cdot (r_2 - r_1)^2$$

1.2 *Anharmonic oscillator*.
The harmonic oscillator approximation refers to the lowest energy vibration levels, where amplitude is small. The anharmonic oscillator approximation models the true function well (solid line on Fig. 3.). A power series gives the energy in wavenumber term

$$\tilde{\nu} = \frac{E_{\mathrm{v}}}{hc} = \omega_0 \left((\mathrm{v} + 1/2) - x_e (\mathrm{v} + 1/2)^2 + y_e (\mathrm{v} + 1/2)^3 \right) \qquad 12.$$

Where ω_0, x_e, y_e are constants.

Selection rule: $\Delta \mathrm{v} = \pm 1, \pm 2, \pm 3 \ldots$ etc. (overtones). Levels are not equidistant, which concludes the form of Eq. 12.
At room temperature the 0^{th} level is densely populated, therefore the $0 \rightarrow 1$ transition is observed in common, for which *harmonic oscillator* model fits perfectly well. The intensity of first overtone band is 1/10 of ground vibrational band.

Types of Molecular Vibrations

Stretch: change in bond length	Bend: change in bond angle
Stretch symmetric	scissoring
Stretch asymmetric	wagging
	rocking
	twisting/torsion

General selection rule:
Molecule must have a change in dipole moment due to vibration or rotation to absorb IR radiation.

2.Vibrations of polyatomic molecules, normal modes
For a molecule with *N* atoms, each atom has three *motional degrees of freedom*- one each for the translation about the x, y, and z Cartesian axes of the molecule-based coordinate system. Thus, the molecule possesses a total of 3*N* degrees of freedom.

Chemical bonds, which for the moment can be thought of a spring connectors between atoms, serve to *constrain* the motion of the atoms to well defined vibrational modes.

Linear molecules have three unique translations, but only two unique rotations. (The rotation about the bond axis does not count, since it changes neither positions of the atoms, nor does it change the angular momentum). Thus, from the total of 3*N* degrees of freedom, we subtract three translations (on the x, y, and z directions) and two rotations, leaving 3*N*-5 vibrational degrees of freedom.

For a diatomic molecule, 3*N*-5 vibrational degrees of freedom is consistent with the single vibration along the bond axis.
Consider now carbon dioxide, O=C=O. The 3*N*-5 rule for vibrational degrees of freedom predicts 4 vibrations. If the molecule lies along the *z*-axis, these vibrations are the symmetric stretch, the anti-symmetric stretch, and a symmetric bend in each of the *xz* and *yz* planes.

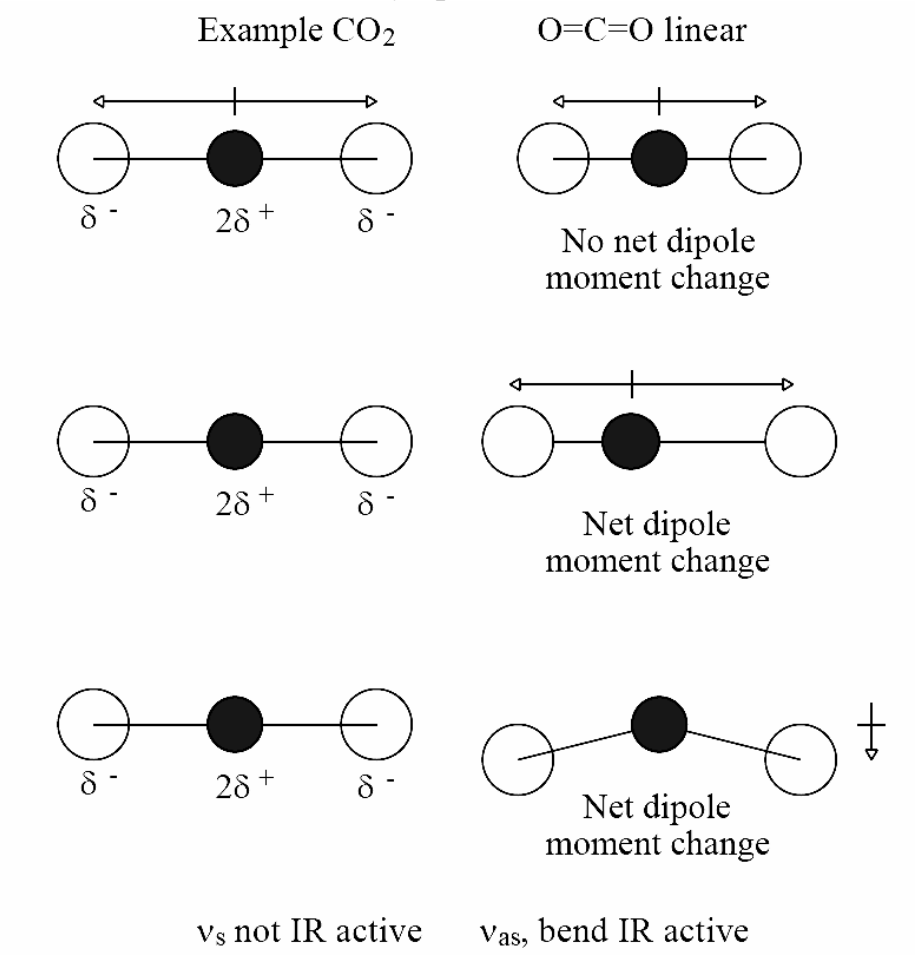


Figure 4.

Non-linear polyatomic molecules have three unique rotational degrees of freedom, so they all have 3*N*-6 vibrational degrees of freedom. Consider now the non-linear molecule water: its three vibrations are the symmetric and anti-

symmetric O-H stretches, and the bending motion in the molecular plane. All vibrational motions change the molecular dipole moment, so all are infrared active, or electric-dipole allowed transitions.

	Mechanical degree of freedom			
molecule	total	translation	rotation	vibration
linear	3N	3	2	3N-5
non-linear	3N	3	3	3N-6

A chemical group can have both stretching and deformational vibration infrared active. In this case the stretching band always appears at greater energies than the deformational one. E.g. see table below

Table

Group frequency / cm^{-1}	Functional group / assignment
2970 - 2950	C-H in CH_3- / asym. stretch
1470 - 1430	C-H in CH_3- / asym. bending
1370 - 1365	C-H in CH_3- / sym. bending

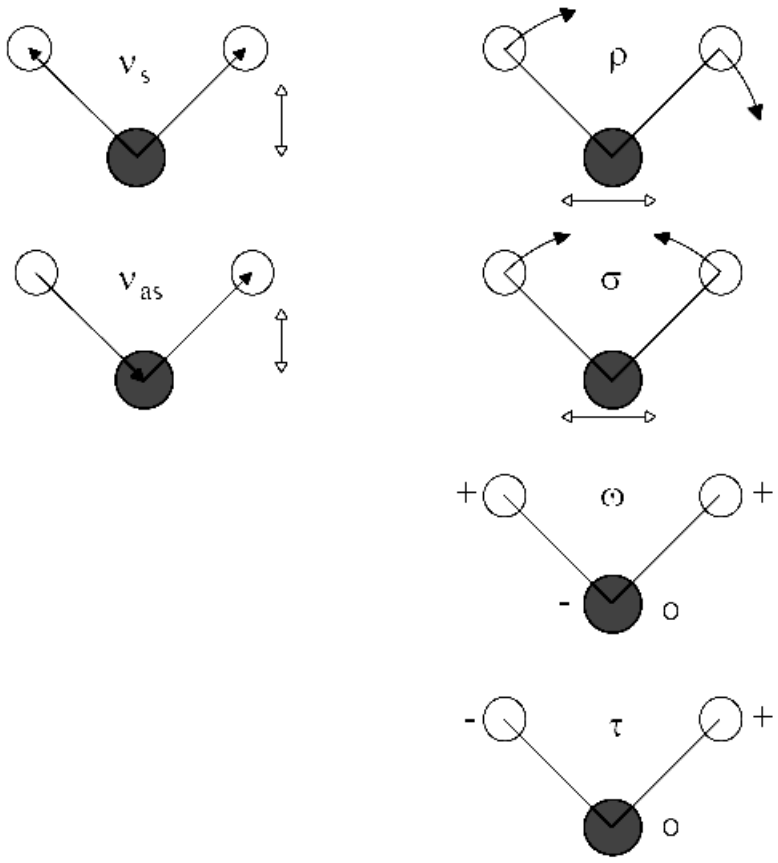


Figure 5. Types of molecular vibrations for a triatomic non-linear molecule.

3.Isotope effect
From Equations 7a and 10 we get

$$E = \left(\mathrm{v} + 1/2\right)h \cdot \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Turning to wavenumber term

$$\tilde{\nu} = \left(\mathrm{v} + 1/2\right)\frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad 13.$$

From assignment of spectral data the wavenumber of an absorption band and the reduced mass, μ of oscillating atoms in the IR range is known. The force constant, k for a particular vibration can be calculated by using Eq. 13.

An isotope substitution causes change in reduced mass and consequently in wavenumber of the band position. The force constant remains the same by isotope exchange of ^{35}Cl to ^{37}Cl in HCl. The wavenumber shift of H-Cl stretching can be given from Eq. 13.

$$\tilde{\nu} = const.\mu^{-1/2}$$

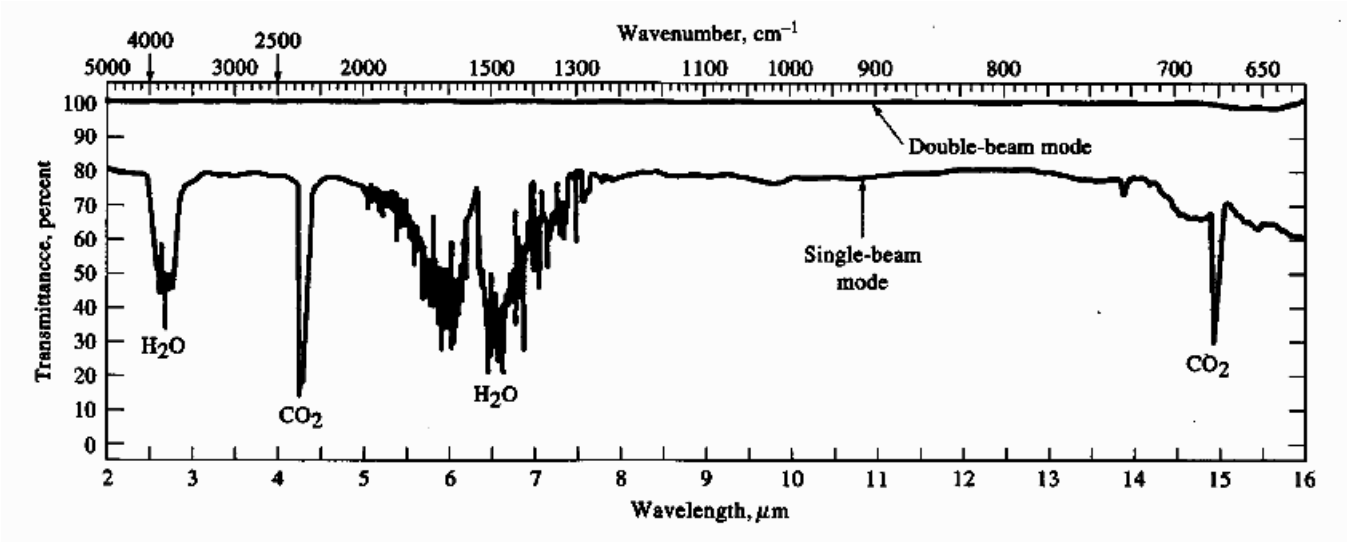
Recalling:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu\left({}^{1}\mathrm{H}\ {}^{35}\mathrm{Cl}\right) = \frac{1 \cdot 35}{1 + 35} = 0.9722 \qquad \frac{1}{\mu\left({}^{1}\mathrm{H}{}^{35}\mathrm{Cl}\right)} = 1.0286$$

$$\mu\left({}^{1}\mathrm{H}\ {}^{37}\mathrm{Cl}\right) = \frac{1 \cdot 37}{1 + 37} = 0.9737 \qquad \frac{1}{\mu\left({}^{1}\mathrm{H}{}^{37}\mathrm{Cl}\right)} = 1.0270$$

The lighter isotope (^{35}Cl) has a band at higher wavenumber.



The IR spectrum of laboratory air.

Table 1 Saturated aliphatic (alkane/alkyl) group frequencies

Group frequency (cm^{-1})	Functional group/assignment
	Methyl ($-CH_3$)
2970–2950/2880–2860	Methyl C–H asym./sym. stretch
1470–1430/1380–1370	Methyl C–H asym./sym. bend
1385–1380/1370–1365	*gem*-Dimethyl or "iso"- (doublet)
1395–1385/1365	Trimethyl or "*tert*-butyl" (multiplet)
	Methylene ($>CH_2$)
2935–2915/2865–2845	Methylene C–H asym./sym. stretch
1485–1445	Methylene C–H bend
750–720	Methylene $-(CH_2)_n-$ rocking ($n \geq 3$)
1055–1000/1005–925	Cyclohexane ring vibrations
	Methyne ($>CH-$)
2900–2880	Methyne C–H stretch
1350–1330	Methyne C–H bend
1300–700	Skeletal C–C vibrations
	Special methyl ($-CH_3$) frequencies
2850–2815	Methoxy, methyl ether O–CH_3, C–H stretch
2820–2780	Methylamino, N–CH_3, C–H stretch