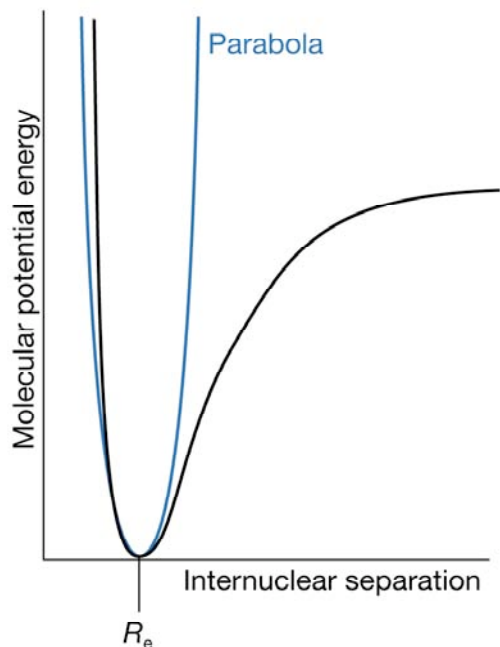


## Spectroscopy 1: rotational and vibrational spectra

### The vibrations of diatomic molecules



Consider a typical potential energy curve for a diatomic molecule. In regions close to  $R_e$  (at the minimum) the potential energy can be approximated by parabola:

$$V = \frac{1}{2} kx^2 \quad x = R - R_e$$

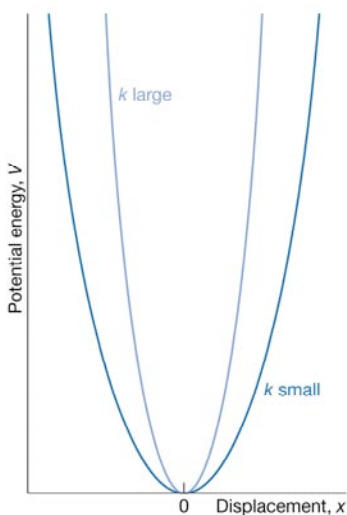
$k$  – the **force constant** of the bond. The steeper the walls of the potential, the greater the force constant. We can expand the potential energy around its minimum by using a Taylor series:

$$V(x) = V(0) + \left(\frac{dV}{dx}\right)_0 x + \frac{1}{2} \left(\frac{d^2V}{dx^2}\right)_0 x^2 + \dots$$

The term  $V(0)$  can be set arbitrarily to zero. The first derivative of  $V$  is 0 at the minimum. Therefore, if we can ignore all the higher terms for small displacements

$$V(x) = \frac{1}{2} \left(\frac{d^2V}{dx^2}\right)_0 x^2 \quad k = \left(\frac{d^2V}{dx^2}\right)_0$$

If the potential energy is sharply curved close to its minimum, then  $k$  will be large. Conversely, if the potential energy is wide and shallow, then  $k$  will be small.



The Schrödinger equation for the relative motion of two atoms of masses  $m_1$  and  $m_2$  with a parabolic potential energy is

$$-\frac{\hbar^2}{2m_{\text{eff}}}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi \qquad m_{\text{eff}} = \frac{m_1m_2}{m_1 + m_2}$$

We already now solutions of this harmonic oscillator equation:

$$E_v = (v+1/2)\hbar\omega \qquad \omega = (k/m_{\text{eff}})^{1/2} \qquad v = 0, 1, 2, \dots$$

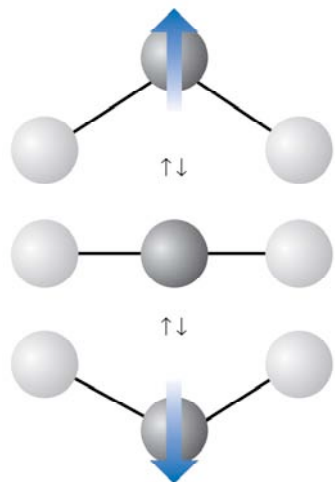
The **vibrational terms** of a molecule, the energies of its vibrational states in wavenumbers are denoted  $G(v)$ , with  $E_v = hcG(v)$ , so

$$G(v) = \left(v + \frac{1}{2}\right)\tilde{\nu} \qquad \tilde{\nu} = \frac{1}{2\pi c} \left(\frac{k}{m_{\text{eff}}}\right)^{1/2}$$

The vibrational terms depend on the effective mass of the molecule, not directly on its total mass. For a homonuclear diatomic molecule  $m_1 = m_2$  and the effective mass is half of the total mass:  $m_{\text{eff}} = 1/2 m$

An HCl molecule has a force constant of  $516 \text{ N m}^{-1}$ , a reasonably typical value. The effective mass of  $^1\text{H}^{35}\text{Cl}$  is  $1.63 \times 10^{-27} \text{ kg}$  (very close to the mass of the hydrogen atom). These values imply  $\omega = 5.63 \times 10^{14} \text{ s}^{-1}$ ,  $\nu = 89.5 \text{ Thz}$ ,  $\tilde{\nu} = 2990 \text{ cm}^{-1}$ ,  $\lambda = 3.35 \text{ mm}$ . These characteristics correspond to infrared.

## Selection rules



The gross selection rule – *the electric dipole moment of the molecule must change when the atoms are displaced relative to one another*. Such vibrations are said to be **infrared active**. The classical basis – the molecule can shake the electromagnetic field into oscillation and vice versa. Note that the molecule need not have a permanent dipole moment: the rule requires only a change in dipole moment, possibly from zero. Some vibrations do not affect the molecule's dipole moment (for example, the stretching motion of a homonuclear diatomic molecule), so they neither absorb nor generate radiation: such vibrations are **infrared inactive**. Homonuclear diatomic molecules are infrared inactive because their dipole moments remain zero however long the bond; heteronuclear diatomic molecules are infrared active.

Of the molecules  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{OCS}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_2=\text{CH}_2$ , and  $\text{C}_6\text{H}_6$ , all except  $\text{N}_2$  possess at least one vibrational mode changing dipole moment – all except  $\text{N}_2$  can show a vibrational absorption spectrum. Not all the modes of complex molecules are vibrationally active. The symmetric stretch of  $\text{CO}_2$ , in which the O-C-O bonds stretch and contract symmetrically is inactive because it leaves the dipole moment unchanged (at zero).

The specific vibrational selection rule, which is obtained from an analysis of the expression for the transition dipole moment and the properties of integrals over harmonic oscillator wavefunctions, is

$$\Delta v = \pm 1$$

Transitions with  $\Delta v = +1$  correspond to absorption and those with  $\Delta v = -1$  correspond to emission. It follows from the specific selection rules that the wavenumbers of allowed vibrational transitions (denoted  $\Delta G_{v+\frac{1}{2}}^1$  for the transition  $v+1 \leftarrow v$ ) are

$$\Delta G_{v+\frac{1}{2}}^1 = G(v+1) - G(v) = \tilde{\nu}$$

$\tilde{\nu}$  lies in the infrared region of the electromagnetic spectrum, so vibrational transitions absorb and generate infrared radiation.

At room temperature, almost all the molecules will be in their vibrational ground states initially and the dominant spectral transition will be the **fundamental transition**,  $1 \leftarrow 0$ . Then, the spectrum is expected to consist of a single absorption line. If the molecules are formed in a vibrationally excited state, such as when vibrationally excited HF molecules are formed in the reaction  $\text{H}_2 + \text{F}_2 \rightarrow 2\text{HF}^*$ , the transitions  $5 \rightarrow 4$ ,  $4 \rightarrow 3$ , ... may also appear in emission. In the harmonic approximation, all these lines lie at the same frequency, and the spectrum is also a single line. However, as we will see, the breakdown of the harmonic approximation causes the transitions to lie at slightly different frequencies, so several lines are actually observed.

### **Anharmonicity**

The vibrational terms obtained for a harmonic oscillator are only approximate because they are based on a parabolic approximation to the actual potential energy curve. A parabola cannot be correct because it does not allow a bond to dissociate. At high vibrational excitations the swing of the atoms (the spread of the vibrational wavefunction) allows the molecules to explore regions of the potential energy curve where the parabolic approximation is poor and additional terms in the Taylor expansion of  $V$  must be retained. The motion then becomes **anharmonic** – the restoring force is no longer proportional to the displacement.

## The convergence of energy levels

Instead of parabola one can use the **Morse potential energy**:

$$V = hcD_e \left\{ 1 - e^{-a(R-R_e)} \right\}^2 \quad a = \left( \frac{m_{eff} \omega^2}{2hcD_e} \right)^{1/2}$$

$D_e$  – the depth of the potential minimum. Near the well minimum the curve resembles a parabola, but unlike a parabola, it allows for dissociation at large displacements. The Schrödinger equation can be solved for the Morse potential and the permitted energy levels are:

$$G(v) = \left( v + \frac{1}{2} \right) \tilde{\nu} - \left( v + \frac{1}{2} \right)^2 x_e \tilde{\nu} \quad x_e = \frac{a^2 \hbar}{2m_{eff} \omega} = \frac{\tilde{\nu}}{4D_e}$$

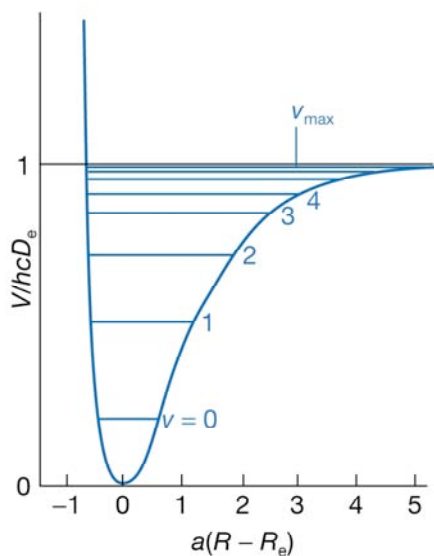
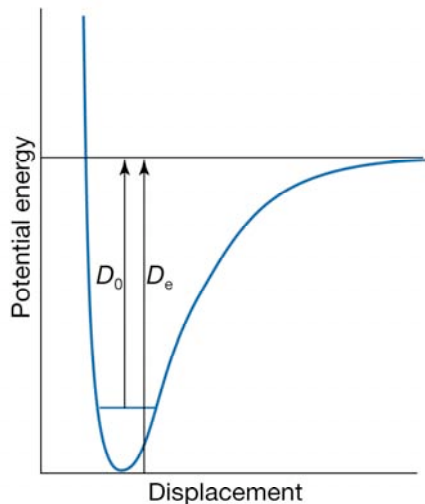
$x_e$  – the **anharmonicity constant**. The number of vibrational levels of a Morse oscillator is finite:  $v = 0, 1, 2, \dots, v_{max}$ . The second term in the expression for  $G$  subtracts from the first with increasing effect as  $v$  increases – the levels converge at high quantum numbers. In practice the more general expression is used to fit the experimental data and to find the dissociation energy of the

molecule:

$$G(v) = \left( v + \frac{1}{2} \right) \tilde{\nu} - \left( v + \frac{1}{2} \right)^2 x_e \tilde{\nu} + \left( v + \frac{1}{2} \right)^3 y_e \tilde{\nu} + \dots$$

$x_e, y_e$  – empirical constants characteristic of the molecule. When anharmonicities are present, the wavenumbers of transitions with  $\Delta v = +1$  are

$$\Delta G_{v+\frac{1}{2}} = \tilde{\nu} - 2(\tilde{\nu} + 1)x_e \tilde{\nu} + \dots$$



When  $x_e \neq 0$ , the transitions move to lower wavenumbers as  $\nu$  increases. Anharmonicity also accounts for the appearance of additional weak absorption lines corresponding to transitions  $2 \leftarrow 0, 3 \leftarrow 0, \dots$ , even though these first, second, ... **overtones** are forbidden by the selection rule  $\Delta\nu = \pm 1$ . The first overtone gives an absorption at

$$G(\nu + 2) - G(\nu) = 2\tilde{\nu} - 2(2\nu + 3)x_e\tilde{\nu} + \dots$$

The overtones appear because the selection rule is derived from the properties of harmonic oscillator wavefunctions, which are only approximately valid when anharmonicity is present. Therefore, the selection rule is also only an approximation. For an anharmonic oscillator, all values of  $\Delta\nu$  are allowed, but transitions with  $\Delta\nu > 1$  are allowed only weakly if the anharmonicity is slight.

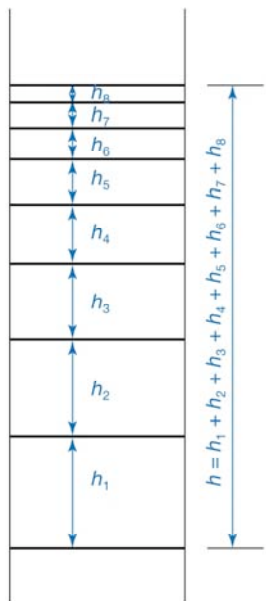
### The Birge-Sponer plot

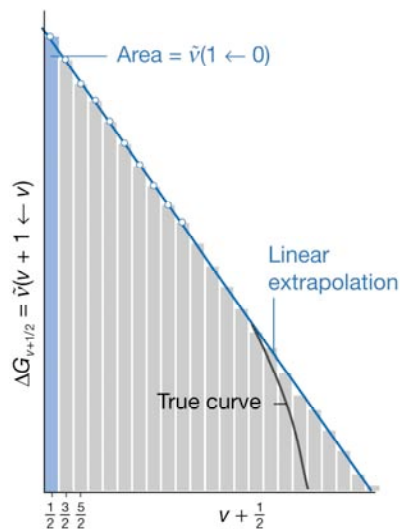
When several vibrational transitions are detectable, a **Birge-Sponer plot** may be used to determine the dissociation energy,  $D_0$ , of the bond. The sum of successive intervals  $\Delta G_{\nu+1/2}$  from the zero-point level to the dissociation limit is

the dissociation energy: 
$$D_0 = \Delta G_{1/2} + \Delta G_{3/2} + \dots = \sum_{\nu} \Delta G_{\nu+1/2}$$

The area under the plot of  $\Delta G_{\nu+1/2}$  against  $\nu + 1/2$  is

equal to this sum and therefore to  $D_0$ . The successive anharmonicity constant is taken into account and the inaccessible part of the spectrum can be estimated by linear extrapolation.



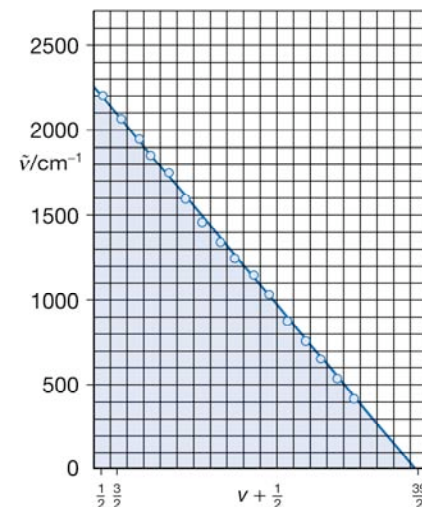


terms decrease linearly when only the  $x_e$  Most actual plots differ from the linear plot, so the value of  $D_0$  obtained in this way is usually an overestimate of the true value.

*Example. Using a Birge-Sponer plot.*

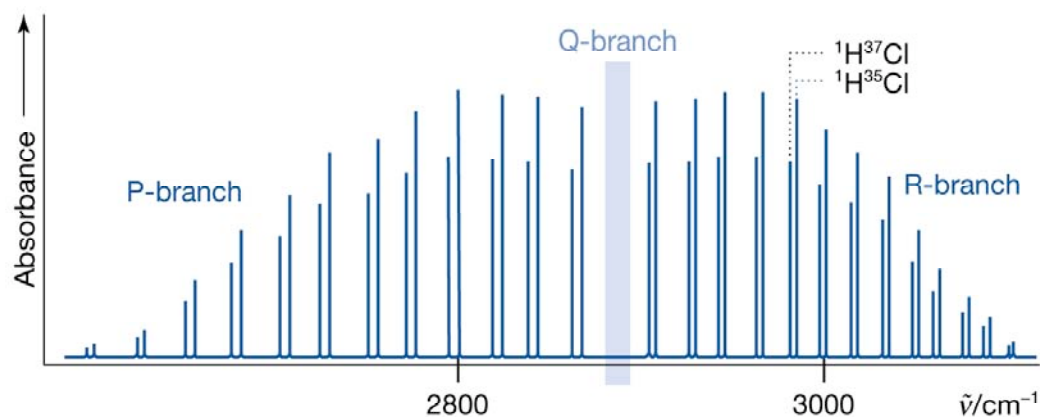
The observed vibrational intervals of  $\text{H}_2^+$  lie at the following values for  $1 \leftarrow 0, 2 \leftarrow 1, \dots$  respectively (in  $\text{cm}^{-1}$ ): 2191, 2064, 1941, 1821, 1705, 1591, 1479,

1368, 1257, 1145, 1033, 918, 800, 677, 548, 411. Determine the dissociation energy of the molecule. We plot the points and make a linear extrapolation. The area under the curve is calculated as 214. Each square corresponds to  $100 \text{ cm}^{-1}$ ; so the dissociation energy is  $21400 \text{ cm}^{-1} = 256 \text{ kJ mol}^{-1}$ .

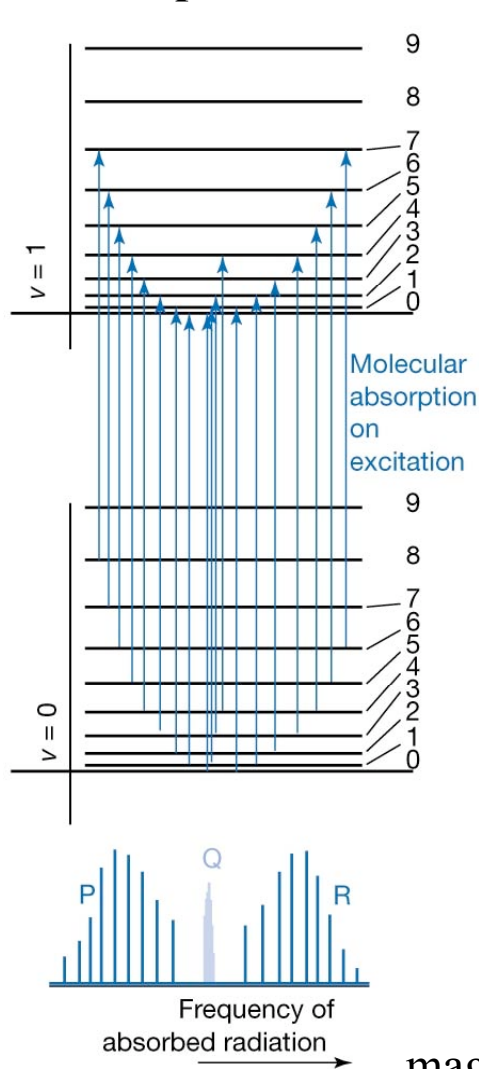


### Vibration-rotation (rovibrational) spectra

Each line of the high-resolution vibrational spectrum of a gas-phase heteronuclear diatomic molecule is found to consist of a large number of closely spaced components (**band spectra**). The separation between the components is of the order of  $10 \text{ cm}^{-1}$  – the structure is due rotational transitions accompanying the vibrational transition.



## Spectral branches



A detailed analysis of the quantum mechanics of simultaneous vibrational and rotational changes shows that the rotational quantum number  $J$  changes by  $\pm 1$  during the vibrational transition of a diatomic molecule. If the molecule also possesses angular momentum about its axis, as in the case of the electronic angular momentum of the paramagnetic molecule NO, then the selection rules also allow  $\Delta J = 0$ .

The appearance of the rovibrational spectrum of a diatomic molecule can be discussed in terms of the combined vibration-rotation terms,  $S$ :

$$S(\nu, J) = G(\nu) + F(J)$$

If we ignore anharmonicity and centrifugal distortion,

$$S(\nu, J) = \left( \nu + \frac{1}{2} \right) \tilde{\nu} + BJ(J+1)$$

When the vibrational transition  $\nu + 1 \leftarrow \nu$  occurs,  $J$  changes by  $\pm 1$  and in some cases by 0 (when  $\Delta J = 0$  is allowed). The absorptions then fall into three groups called **branches** of the spectrum. The **P branch** consists of all transitions with  $\Delta J = -1$ :

$$\tilde{\nu}_P(J) = S(\nu + 1, J - 1) - S(\nu, J) = \tilde{\nu} - 2BJ$$

This branch consists of lines at  $\tilde{\nu} - 2B$ ,  $\tilde{\nu} - 4B, \dots$  with an intensity distribution reflecting both the populations of the rotational levels and the

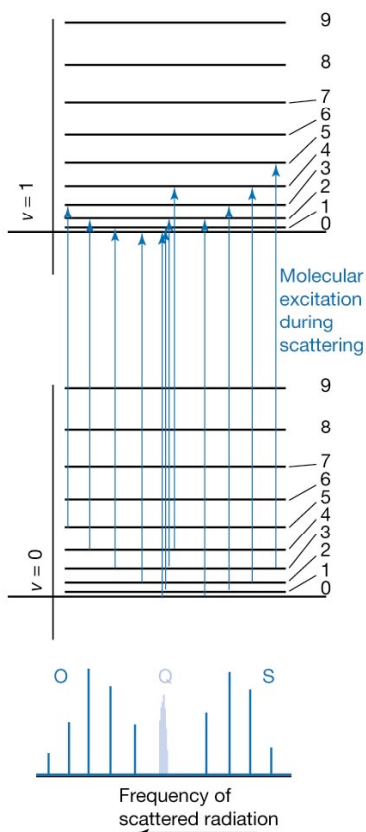
magnitude of the  $J - 1 \leftarrow J$  transition moment. The **Q branch** consists of all lines with  $\Delta J = 0$ , and its wavenumbers are  $\tilde{\nu}_Q(J) = S(\nu + 1, J) - S(\nu, J) = \tilde{\nu}$  for all  $J$

This branch, when it is allowed (NO), appears at the vibrational transition number. When it is forbidden we see a gap in the spectrum (HCl).



The **R branch** consists of lines with  $\Delta J = +1$ :  $\tilde{\nu}_R(J) = S(\nu+1, J+1) - S(\nu, J) = \tilde{\nu} + 2B(J+1)$

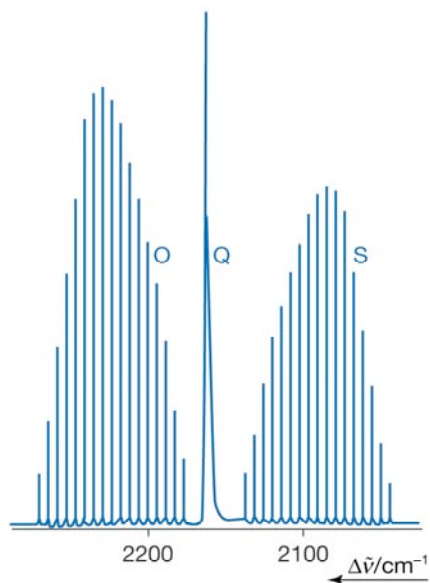
This branch consists of lines displaced from  $\tilde{\nu}$  to high wavenumbers by  $2B, 4B, \dots$ . The separation between the lines in the P and R branches of a vibrational transition gives the value of  $B$  – the bond length can be deduced without needing to take a pure rotational spectrum. However, the latter is more precise.



### Vibrational Raman spectra of diatomic molecules

The gross selection rule for vibrational Raman transitions – *the polarizability should change as the molecule vibrates*. As homo-nuclear and heteronuclear diatomic molecules swell and contract during a vibration, the control of the nuclei over the electrons varies, and hence the molecular polarizability changes. Both types of diatomic molecule are therefore vibrationally Raman active. The specific selection rule -  $\Delta \nu = \pm 1$ . The lines to high frequency of the incident radiation, the anti-Stokes lines correspond to  $\Delta \nu = -1$  and the lines to low frequency, the Stokes lines, correspond to  $\Delta \nu = +1$ . The intensities of the lines are governed largely by the Boltzmann populations of the vibrational states involved in the transition – the anti-Stokes lines are usually weak because very few molecules are in an excited vibrational state initially.

In gas-phase spectra, the Stokes and anti-Stokes lines have a branch structure due to simultaneous rotational transitions that accompany the vibrational excitation.



The selection rules are  $\Delta J = 0, \pm 2$ , and give rise to the **O branch** ( $\Delta J = -2$ ), the **Q branch** ( $\Delta J = 0$ ), and the **S branch** ( $\Delta J = +2$ ):

$$\tilde{\nu}_Q(J) = \tilde{\nu}_i - \tilde{\nu} \quad \tilde{\nu}_O(J) = \tilde{\nu}_i - \tilde{\nu} - 2B + 4BJ \quad \tilde{\nu}_S(J) = \tilde{\nu}_i - \tilde{\nu} - 6B - 4BJ$$

Unlike in infrared spectroscopy, a Q branch is obtained for all linear molecules. The information available from vibrational Raman spectra adds to that from infrared spectroscopy because homonuclear diatomics can also be studied. The spectra can be interpreted in terms of the force constants, dissociation energies, and bond lengths.

## The vibrations of polyatomic molecules

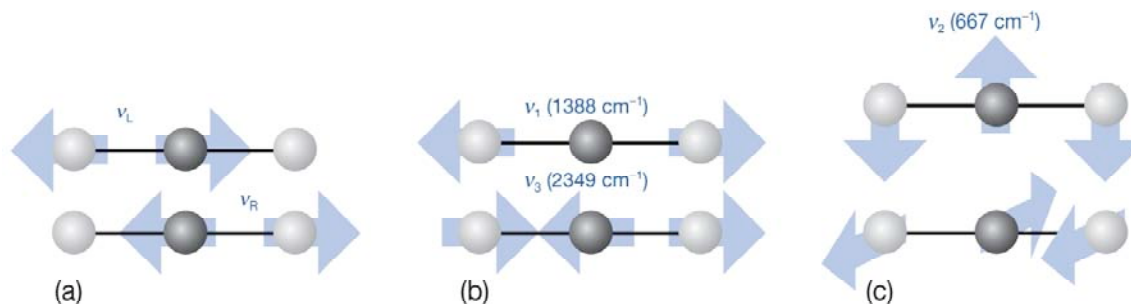
There is only one mode of vibration for a diatomic molecule, the bond stretch. In polyatomic molecules there are several modes of vibration because all the bond lengths and angles may change and the vibrational spectra are very complex. However, they can be used to obtain information about the molecular structure.

### Normal modes

For a nonlinear molecule with  $N$  atoms, there are  $3N - 6$  independent modes of vibration. If the molecule is linear, there are  $3N - 5$  independent vibrational modes. For example,  $\text{H}_2\text{O}$  is a nonlinear triatomic molecule and has three modes of vibrations;  $\text{CO}_2$  is a linear triatomic molecule and has four modes of vibration (and only two modes of rotation). Even a middle-sized molecule such as naphthalene ( $\text{C}_{10}\text{H}_8$ ) has 48 distinct modes of vibration.

## Combinations of displacements

Consider  $\text{CO}_2$  as an example. The choice for the four modes of vibration can be the stretching of one  $\text{C}=\text{O}$  bond ( $\nu_L$ ), the stretching of the other ( $\nu_R$ ), and two perpendicular bending modes ( $\nu_2$ ).



The disadvantage of such description: when one  $\text{CO}$  bond vibration is excited, the motion of the  $\text{C}$  atom sets the other  $\text{CO}$  bond in motion, so the energy flows back and forth between  $\nu_L$  and  $\nu_R$ . Moreover, the position of the center of mass of the molecule varies in the course of either vibration.

It is better to take linear combinations of  $\nu_L$  and  $\nu_R$ . One combination is  $\nu_1 = \nu_L + \nu_R$  – the **symmetric stretch**. Another mode is  $\nu_3 = \nu_R - \nu_L$  – the **antisymmetric stretch**. Both modes are independent in the sense that, if one is excited, then it does not excite the other. They are two of the ‘normal modes’ of the molecule, its independent, collective vibrational displacements. The two other normal modes are the bending modes  $\nu_2$ . In general, a **normal mode** is an independent, synchronous motion of atoms or groups of atoms that may be excited without leading to the excitation of any other normal modes.

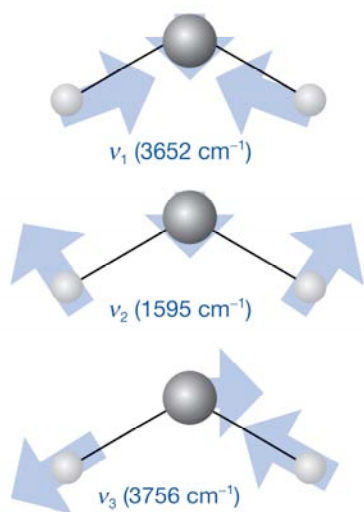
Each normal mode,  $q$ , behaves like an independent harmonic oscillator (if anharmonicities are neglected), so each has a series of terms

$$G_q(\nu) = \left( \nu + \frac{1}{2} \right) \tilde{\nu}_q \quad \tilde{\nu}_q = \frac{1}{2\pi c} \left( \frac{k_q}{m_q} \right)^{1/2}$$

$\tilde{\nu}_q$  - the wavenumber of mode  $q$  depending on the force constant  $k_q$  for the mode and on the effective mass  $m_q$  of the mode. The effective mass of the mode – a measure of the mass that is swung around about by the vibration and in general is a complicated function of the masses of the atoms. For example, in the symmetric stretch of  $\text{CO}_2$ , the C atom is stationary, and the effective mass depends on the masses of only the O atoms. In the antisymmetric stretch and  $\tilde{\nu}_q$  in the bends, all three atoms move, so all contribute to the effective mass.

The three normal modes of  $\text{H}_2\text{O}$  also include the symmetric O-H stretch, the antisymmetric stretch, and an H-O-H bend. The bending mode has a lower frequency than the others.

In general, the frequencies of bending motions are lower than those of stretching modes. However, only in special cases the normal modes are purely stretches or purely bends. Generally, a normal mode is a composite motion of simultaneous stretching and bending of bonds. Also, heavy atoms usually move less than light atoms in normal modes.



## Infrared absorption spectra of polyatomic molecules

The gross selection rule – *the motion corresponding to a normal mode should be accompanied by a change of dipole moment.*

For example, the symmetric stretch of CO<sub>2</sub> leaves the dipole moment unchanged (at zero), so this mode is infrared inactive. However, the antisymmetric stretch changes the dipole moment because the molecule becomes unsymmetrical as it vibrates, so this mode is infrared active. Because the dipole moment change is parallel to the principal axis, the transitions arising from this mode are classified as **parallel bends** in the spectrum. Both bending bonds are infrared active, they are accompanied by a changing dipole perpendicular to the principal axis – a **perpendicular band** in the spectrum. The perpendicular bands eliminate the linearity of the molecule, and as a result a Q branch is observed; a parallel band does not have a Q branch.

The active modes are subject to the specific selection rule  $\Delta v_q = \pm 1$  in the harmonic approximation, so the wavenumber of the fundamental transition (the ‘first harmonic’) of each active mode is  $\tilde{\nu}_q$ . From the analysis of the spectrum, a picture may be constructed of the stiffness of various parts of the molecules – we can establish the molecule’s **force field**, the set of force constants corresponding to all displacements of the atoms. One very important application of infrared spectroscopy – chemical analysis.

The vibrational spectra of different groups in a molecule give rise to absorptions at characteristic frequencies. Their intensities are also transferable between molecules.

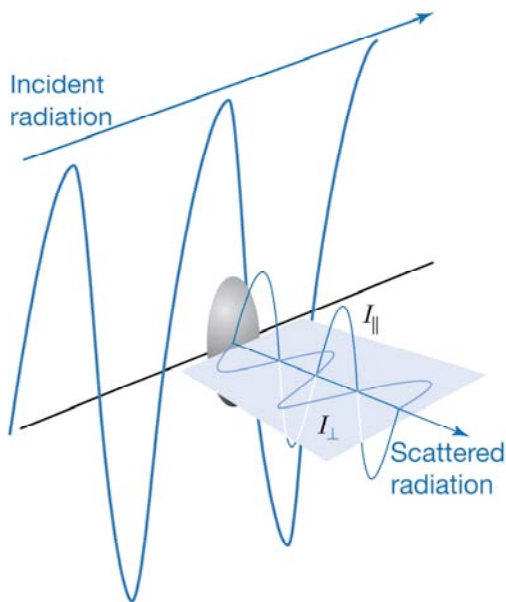
Consequently, the molecules in a sample can often be identified by examining its infrared spectra and referring to a table of characteristic frequencies and intensities.

## Vibrational Raman spectra of polyatomic molecules

The normal modes of vibration of molecules are Raman active if they are accompanied by a changing polarizability. For example, the symmetric stretch of CO<sub>2</sub> alternately swell and contracts the molecule, so the mode is Raman active. The other modes of CO<sub>2</sub> leave the polarizability unchanged, so they are Raman inactive.

**The exclusion rule: If the molecule has a center of symmetry, then no modes can be both infrared and Raman active.**

(A mode may be inactive in both.) In general, it is necessary to use group theory to predict whether a mode is infrared or Raman active.



### Depolarization

The assignment of Raman lines to particular vibrational modes is aided by noting the state of polarization of the scattered light. The **depolarization ratio**,  $\rho$ , of a line – the ratio of the intensities of the scattered light with polarizations perpendicular and parallel to the plane of polarization of the incident radiation:

$$\rho = \frac{I_{\perp}}{I_{\parallel}}$$

To measure  $\rho$ , the intensity of a Raman line is measured with a polarizing filter first parallel and then perpendicular to the polarization incident beam. If the emergent light is not polarized, then both intensities are the same and  $\rho$  is close to 1; if the light retains its initial

polarization, then  $I_{\perp} = 0$ , so  $\rho = 0$ . A line is classified as **depolarized** if it has  $\rho$  close to or greater than 0.75 and as **polarized** if  $\rho < 0.75$ . Only totally symmetrical vibrations give rise polarized lines. Vibrations that are not totally symmetrical give rise to depolarized lines.

## Resonance Raman spectra

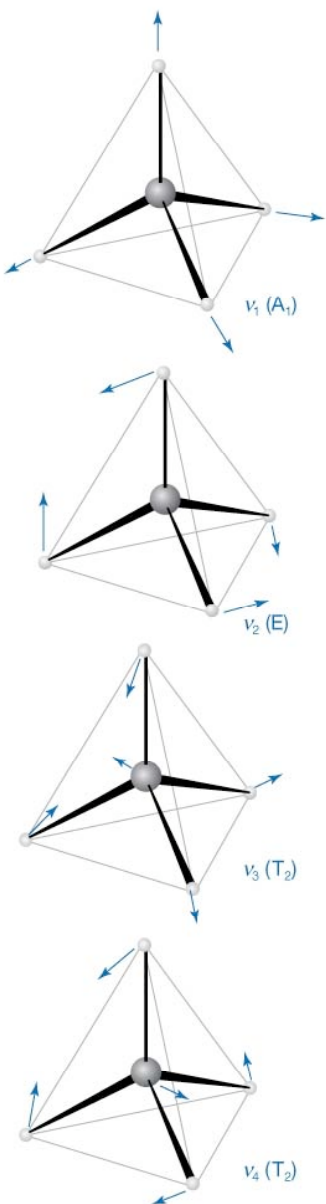
A modification of the basis Raman effect – involves using incident radiation that nearly coincides with the frequency of an electronic transition of the sample – **resonance Raman spectroscopy**. Characterized by a much greater intensity in the scattered radiation. Furthermore, usually only a few vibrational modes contribute to the more intense scattering, the spectrum is greatly simplified. Resonance Raman spectroscopy is used to study biological molecules that absorb strongly in the ultraviolet and visible regions of the spectra.

## Symmetry aspects of molecular vibrations

Each normal mode must belong to one the symmetry species of the molecular point group. To determine the symmetry species of a normal mode, one needs to apply symmetry operations of the molecular point group, see how the vectors showing the displacements of atoms change, to determine the characters corresponding to each symmetry operation, and to compare with the rows of the group's character table. For example, in H<sub>2</sub>O the characters of the symmetric stretch and bending modes are:  $\chi(E) = 1$ ,  $\chi(C_2) = 1$ ,  $\chi(\sigma_v) = 1$ , and  $\chi(\sigma_v') = 1$ , so they span A<sub>1</sub>. On the other hand, the antisymmetric stretch exhibits the following characters:  $\chi(E) = 1$ ,  $\chi(C_2) = -1$ ,  $\chi(\sigma_v) = -1$ , and  $\chi(\sigma_v') = 1$ , and this mode belongs to B<sub>2</sub> symmetry.

To judge the activities of vibrational modes – check the character table of the molecular point group for the symmetry species spanned by *x*, *y*, and *z* and apply the following rule:

**If the symmetry species of a normal mode is the same as any of the symmetry species of *x*, *y*, or *z*, then the mode is infrared active.**



*Example. Which modes of CH<sub>4</sub> are infrared active?*

The symmetry species of the normal modes are  $A_1 + E + T_2$ . According to the  $T_d$  character table, the functions  $x$ ,  $y$ , and  $z$  span  $T_2$ . Therefore, only the  $T_2$  modes are infrared active. The distortion accompanying these modes lead to a changing dipole moment. The  $A_1$  mode, which is inactive, is the symmetrical ‘breathing’ mode of the molecule.

### Raman activity of normal modes

Group theory provides a recipe for judging the Raman activity of a normal mode. In this case, the symmetry species of the quadratic forms ( $x^2$ ,  $xy$ , etc.) listed in the character table are noted and then we use the rule:

**If the symmetry species of a normal mode is the same as the symmetry species of a quadratic form, then the mode may be Raman active.**

To decide which of the vibrations of CH<sub>4</sub> are Raman active, refer to the  $T_d$  character table. The quadratic forms span  $A_1 + E + T_2$ , therefore all the normal modes are Raman active. The  $T_2$  modes can be easily assigned because these are the only modes both infrared and Raman active. In Raman spectra, the  $A_1$  mode is polarized, while the  $E$  mode is depolarized.