Diatomic vibrational spectra

Molecular vibrations

- Typical potential energy curve of a diatomic molecule:

- Parabolic approximation close to R_e:
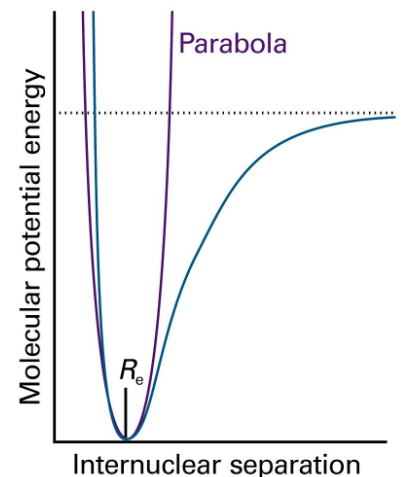
$$V = \frac{1}{2}kx^2 \qquad x = R - R_e$$

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k = force constant of the bond. The steeper the walls of the potential, the stiffer the bond, the greater the force constant.

- Connection between the shape of molecular potential energy curve and k: we expand $V(x)$ around $R = R_e$ by a Taylor series:

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

$\rightarrow$ $V(0)$ = constant set arbitrarily to zero.
$\rightarrow$ first derivative of V is 0 at the minimum.
$\rightarrow$ for small displacements we ignore all high terms.

Hence, the first approximation to a molecular potential energy curve is a parabolic potential with:

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

$\rightarrow$ if $V(x)$ is sharply curved, k is large.
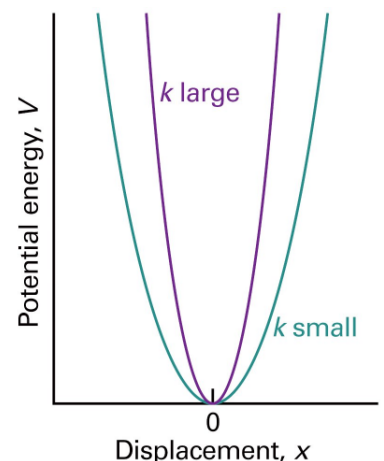$\rightarrow$ if $V(x)$ is wide and shallow, k is small.

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- Schrödinger equation for the relative motion of two atoms of masses m_1 and m_2 with a parabolic potential energy:

$$-\frac{\hbar^2}{2m_{eff}}\frac{d^2\Psi}{dx^2} + \frac{1}{2}kx^2\Psi = E\Psi$$

where m_{eff} = effective (or reduced) mass: $m_{eff} = \dfrac{m_1 m_2}{m_1 + m_2}$

- Use of $m_{eff} \rightarrow$ to consider the problem from the perspective of the motion of molecule as a whole.
  Example: homonuclear diatomic $m_1 = m_2 = m$: $m_{eff} = m/2$.
  XH, where $m_X \gg m_H$: $m_{eff} \approx m_H$.

- Same Schrödinger equation as for the particle of mass m undergoing harmonic motion. Therefore, the permitted vibrational energy levels are:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad \text{with:} \quad \omega = \sqrt{\frac{k}{m_{eff}}} \quad \text{and:} \; n = 0, 1, 2, \ldots$$

The vibrational wavefunctions are the same as those discussed for the harmonic oscillator. Important to notice that E_n depends on m_{eff} and not on the total mass.

Selection rules

- Gross selection rule for a change in vibrational state (absorption or emission): the electric dipole moment of the molecule (not necessarily permanent) must change when the atoms are displaced relative to one another.
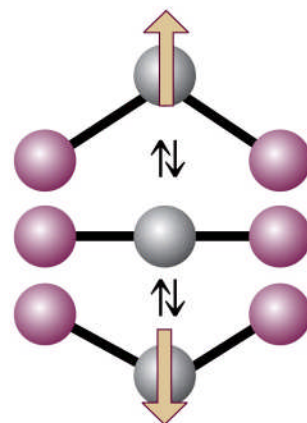

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- IR active molecules: heteronuclear diatomic.
  IR inactive molecules: homonuclear diatomic.

  Not all the modes of polyatomic molecules are vibrationally active (e.g.: the symmetric stretch of CO_2, in which the C –O–C bonds stretch and contract symmetrically is inactive.

- Specific selection rules: analysis of the expression of the transition dipole moment and the properties of integrals over harmonic oscillator wavefunctions, gives (tedious calculation):

$$\Delta n = \pm 1 \qquad \text{with} \begin{cases} \Delta n = +1 \ \rightarrow \text{absorption} \\ \Delta n = -1 \ \rightarrow \text{emission} \end{cases}$$

- It follows that the allowed $n+1 \leftarrow n$ vibrational transitions are:

$$\overline{\nu} = \frac{E_{n+1} - E_n}{hc} = \frac{\hbar\omega}{hc} = \frac{\sqrt{k/m_{eff}}}{2\pi c}$$

  $\overline{\nu}$ lies in the infrared, so vibrational transitions absorb and generate infrared radiation. The vibrational spectrum provides the force constant of the bond.

- At room temperature $k_B T/hc \approx 200 \ cm^{-1}$ << most vibrational wavenumbers.
  $\rightarrow$ Boltzmann: most molecules in their ground states.
  $\rightarrow$ dominant spectral transition: fundamental transition $1 \leftarrow 0$.
  $\rightarrow$ spectrum consists of a single absorption line.

  If the molecules are formed in their vibrationally excited state (e.g. , $H_2 + F_2 \rightarrow 2HF^*$) , transitions $5 \rightarrow 4$, $4 \rightarrow 3$, … may also appear (in emission).
  $\rightarrow$ all these lines lie at the same frequency
  $\rightarrow$ spectrum expected to consist of a single line.
  $\rightarrow$ NO! Breakdown of the harmonic approximation.

Anharmonicity

- Harmonic oscillator is only a parabolic approximation to the actual molecular potential energy curve:
  $\rightarrow$ does not allow a bond to dissociate.
  $\rightarrow$ at high vibrational excitations, not enough spread of the vibrational wavefunction.

  Hence the additional terms in the Taylor expansion of V must be retained.

- The motion is anharmonic (restoring force no longer proportional to the displacement)

- Because the actual curve is less confining than a parabola, we can anticipate that the energy levels become less widely spaced at high excitations.

The convergence of energy levels

- One approach to anharmonicity is the Morse potential energy:

$$V = hcD_e \left(1 - e^{-a(R-R_e)}\right)^2$$

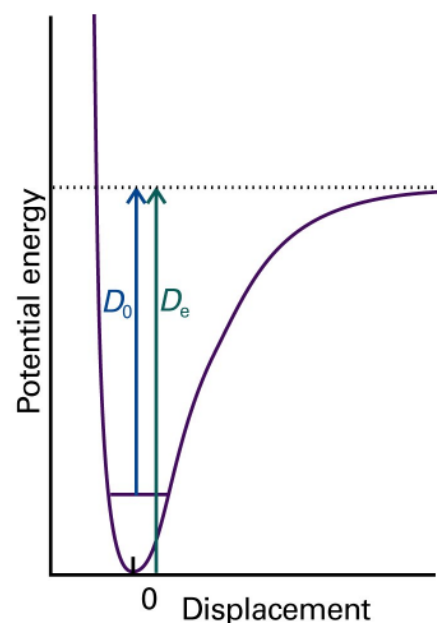$$\text{with } a = \left(\frac{m_{eff}\,\omega^2}{2hcD_e}\right)^{1/2}$$

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D_e = depth of the potential minimum, D_0 = dissociation energy.

$\rightarrow$ at R close to R_e, parabolic behaviour (cf. Taylor expansion).
$\rightarrow$ allows for dissociation at large displacements.

- Schrödinger equation can be solved and the permitted energy levels are:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega - \left(n + \frac{1}{2}\right)^2 x_e \hbar\omega$$

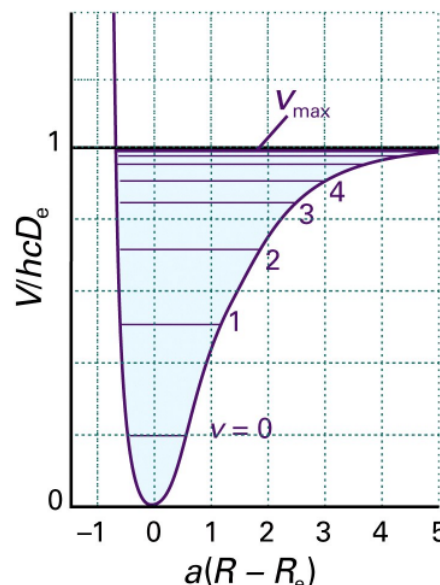$$\text{with } x_e = \frac{a^2\hbar}{2m_{eff}\,\omega} = \frac{\bar{\nu}}{4D_e}$$

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x_e = anharmonicity constant.

$\rightarrow$ # of vibrational levels is infinite, and $n = 0, 1, 2,\ldots, n_{max}$.
$\rightarrow$ 2nd term in E_n substracts from 1st with increasing effect as n increases. Hence, convergence of the levels at high quantum numbers.

- Although the Morse oscillator is quite useful theoretically, in practice we fit the experimental data with the more general expression:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega - \left(n + \frac{1}{2}\right)^2 x_e \hbar\omega + \left(n + \frac{1}{2}\right)^3 y_e \hbar\omega + \ldots$$

x_e, y_e, … = empirical dimensionless constants characteristic of the molecule $\rightarrow$ allowing to find its dissociation energy.

- Transitions with $\Delta n = +1$: $\quad \Delta E_{n+1/2} = \hbar\omega - 2(n+1)x_e\hbar\omega + \ldots$

Wavenumbers: $\qquad\qquad\qquad \bar{\nu} = \frac{\hbar\omega}{hc} - 2(n+1)x_e\frac{\hbar\omega}{hc} + \ldots$

$\rightarrow$ when $x_e > 0$, transitions move to lower $\bar{\nu}$ as n increases.

- Anharmonicity accounts for the appearance of additional weak absorption lines (transitions $2 \leftarrow 0$ or $3 \leftarrow 0,\dots$) even though these overtones are forbidden by the selection rule $\Delta n = \pm 1$.

First overtone absorption: $\mathrm{E}_{n+2} - \mathrm{E}_n = 2\hbar\omega - 2(2n+3)x_e\hbar\omega + \dots$

$\rightarrow$ selection rule is derived from the harmonic oscillator wavefunctions $\rightarrow$ approximation! All Δn values allowed, but $\Delta n > 1$ transitions allowed only weakly if anharmonicity is slight.

The Birge-Sponer plot

- Graphical technique: the Birge-Sponer plot is used to determine the dissociation energy, D_0, of the bond $\rightarrow$ if we write $\Delta \mathrm{E}_{n+1/2} = \mathrm{E}_{n+1} - \mathrm{E}_n$ ($n+1 \leftarrow n$) then:

$$D_0 = \Delta \mathrm{E}_{1/2} + \Delta \mathrm{E}_{3/2} + \dots$$
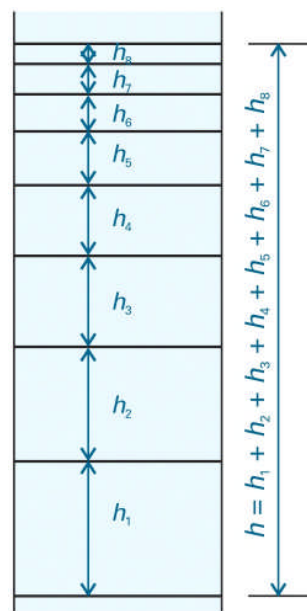$$= \sum_n \Delta \mathrm{E}_{n+1/2}$$

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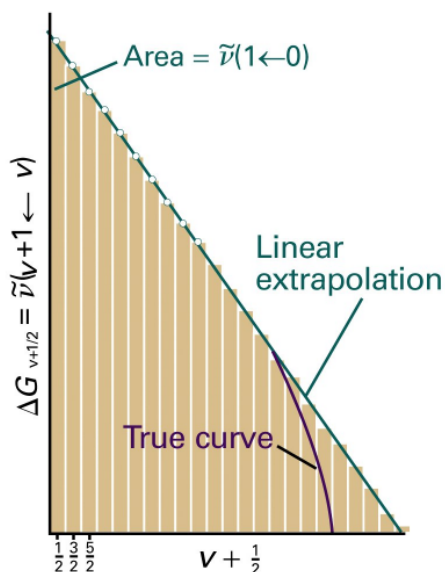

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Hence, D_0 = area under the plot of $\Delta \mathrm{E}_{n+1/2}$ against $n+1/2$

$\rightarrow$ terms decrease linearly when x_e is taken into account.
$\rightarrow$ inaccessible part of the spectrum estimated by linear extrapolation.
$\rightarrow$ most actual plots are not linear (as shown here) so the D_0 value obtained is an overestimate.

Vibration-Rotation spectra

High resolution vibrational
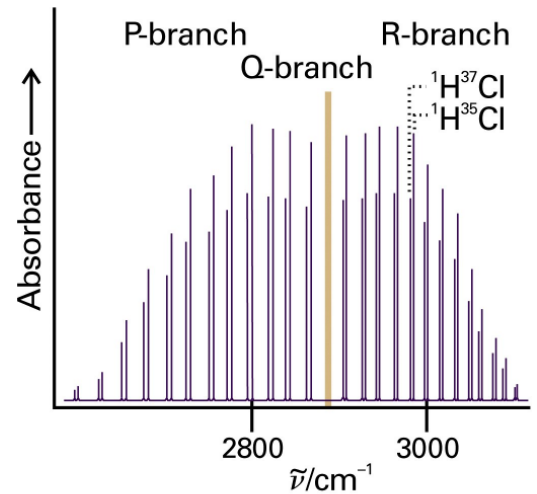spectrum of gas-phase HCl

P-branch   R-branch
Q-branch $^1H^{37}Cl$
              $^1H^{35}Cl$

Absorbance

2800   3000
$\tilde{\nu}$/cm^{-1}

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- For a heteronuclear diatomic molecule:
  $\rightarrow$ each line = large number of closely spaced components.
  $\rightarrow$ separation < 10 cm^{-1} $\rightarrow$ suggestive of rotational transitions.

- Hence, molecular spectra are often called band spectra.

- Rotational change is expected since (classically) the transition leads to a sudden increase/decrease in instantaneous bond length. Therefore, rotation is retarded/accelerated by a vibrational transition (think "ice-skaters").

Spectral branches of diatomic molecules

- Detailed quantum mechanical analysis of simultaneous vibration and rotation changes shows that the rotational quantum number J changes by ±1 during the vibrational transition. If the molecule also possesses angular momentum about its axis, then the selection rules also allow $\Delta J = 0$.

- Appearance of the diatomic V-R spectrum discussed in terms of the combination (ignoring anharmonicity and centrifugal distortion):

$$E_{n,J} = E_n + E_J = \left(n + \frac{1}{2}\right)\hbar\omega + BJ(J+1)$$

- B should depend on the vibrational state because, as n increases, the molecule swells slightly and the moment of inertia changes. We will ignore this for the time being.

- When the vibrational transition $n+1 \leftarrow n$ occurs, J changes by ±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:

- **P branch**: lines with $\Delta J = -1$:

$$\Delta E_J(P) = E_{n+1,J-1} - E_{n,J} = \hbar\omega - 2BJ$$

$\rightarrow$ lines at $\overline{\nu} - 2\overline{B}, \overline{\nu} - 4\overline{B},...$

- **Q branch**: lines with $\Delta J = 0$:

$$\Delta E_J(Q) = E_{n+1,J} - E_{n,J} = \hbar\omega = hc\overline{\nu}$$

$\rightarrow$ for all J values. Appears at the vibrational transition $\overline{\nu}$. (Forbidden in HCl, hence the gap.)

- **R branch**: lines with $\Delta J = +1$:

$$\Delta E_J(R) = E_{n+1,J+1} - E_{n,J} = \hbar\omega + 2B(J+1)$$

$\rightarrow$ lines at $\overline{\nu} + 2\overline{B}, \overline{\nu} + 4\overline{B},...$
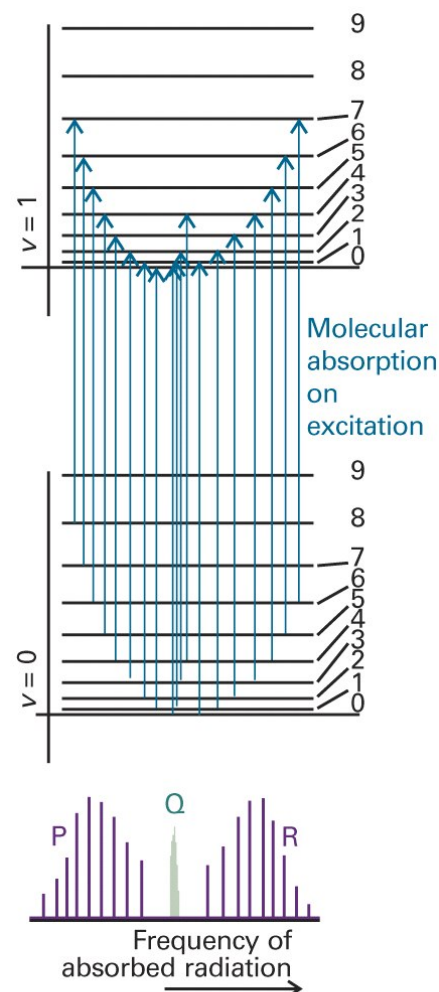

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- Line intensities = reflecting both the population of rotational levels and the magnitude of the $J-1 \leftarrow J$ transition moment.

- The separation between lines in the P and R branches of a vibrational transition gives the value of $\overline{B}$ (or B), hence the bond length (as with a pure rotational microwave spectrum).

Combination differences

- Rotational constants of vibrationally excited state n: B_n:
  - $\rightarrow$ Anharmonicity : $B_1 < B_0$ in general (because extended bond)
  - $\rightarrow$ Q branch (if it exists): series of closely spaced lines.
  - $\rightarrow$ R branch: lines converge slightly as J increases.
  - $\rightarrow$ P branch: lines diverge.

$$\bar{\nu}_P(J) = \bar{\nu} - \left(\bar{B}_1 + \bar{B}_0\right)J + \left(\bar{B}_1 - \bar{B}_0\right)J^2$$

Hence: $\quad \bar{\nu}_Q(J) = \bar{\nu} + \left(\bar{B}_1 - \bar{B}_0\right)J(J+1)$

$$\bar{\nu}_R(J) = \bar{\nu} + \left(\bar{B}_1 + \bar{B}_0\right)(J+1) + \left(\bar{B}_1 - \bar{B}_0\right)(J+1)^2$$

- Combination differences: method to determine $\bar{B}_0$ and $\bar{B}_1$ individually (widely used in spectroscopy):

- Transitions $\bar{\nu}_R(J-1)$ and $\bar{\nu}_P(J+1)$ have a common upper state, dependence on B_0 only:

$$\bar{\nu}_R(J-1) - \bar{\nu}_P(J+1) = 4\bar{B}_0\left(J + \frac{1}{2}\right)$$

- Similarly, $\bar{\nu}_R(J)$ and $\bar{\nu}_P(J)$ have a common lower state, dependence on B_1 only:

$$\bar{\nu}_R(J) - \bar{\nu}_P(J) = 4\bar{B}_1\left(J + \frac{1}{2}\right)$$

- Therefore, plot of the combination difference against $J + \frac{1}{2}$ $\rightarrow$ straight line of slope $4B_0$ (any deviation from straight line = consequence of centrifugal distortion).

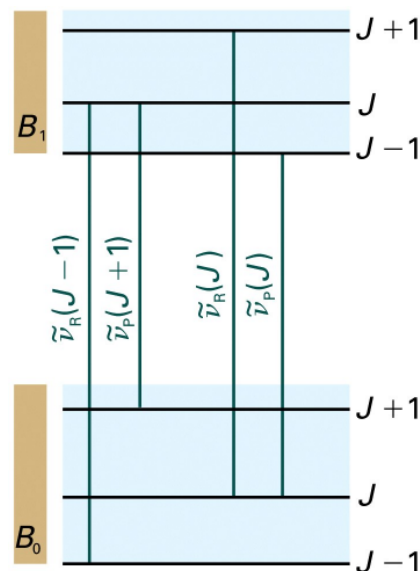Figure 13-36
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- The two rotational constants of $^1H^{35}Cl$ found in this way are $\bar{B}_0$ = 10.440 cm^{-1} and $\bar{B}_1$ = 10.136 cm^{-1}.

Vibrational Raman spectra of diatomic molecules

- Gross selection rule for vibrational Raman: polarizability should change as molecule vibrates. Hence, both homo- and hetero-nuclear diatomic molecules are vibrationally Raman active.

- Specific selection rule (harmonic approx.): $\Delta n = \pm 1$:
  → lines to high ν of incident radiation (anti-Stokes): $\Delta n = -1$.
  → lines to low ν of incident radiation (Stokes): $\Delta n = +1$.

- Line intensities → Boltzmann populations of vibrational states involved in transition, hence anti-Stokes lines (excited states) are weaker.

- Stokes and anti-Stokes lines have also a branch structure arising from rotational transitions accompanying the vibrational excitation.

- Selection rules (as in pure rotational Raman): $\Delta J = 0, \pm 2$: O branch: $\Delta J = -2$; Q branch: $\Delta J = 0$; S branch: $\Delta J = +2$.

$$\overline{\nu}_O(J) = \overline{\nu}_i - \overline{\nu} - 2B + 4BJ$$

Hence: $\overline{\nu}_Q(J) = \overline{\nu}_i - \overline{\nu}$

$$\overline{\nu}_S(J) = \overline{\nu}_i - \overline{\nu} - 6B - 4BJ$$

→ a Q branch exists for all linear molecules!

Molecular excitation during scattering

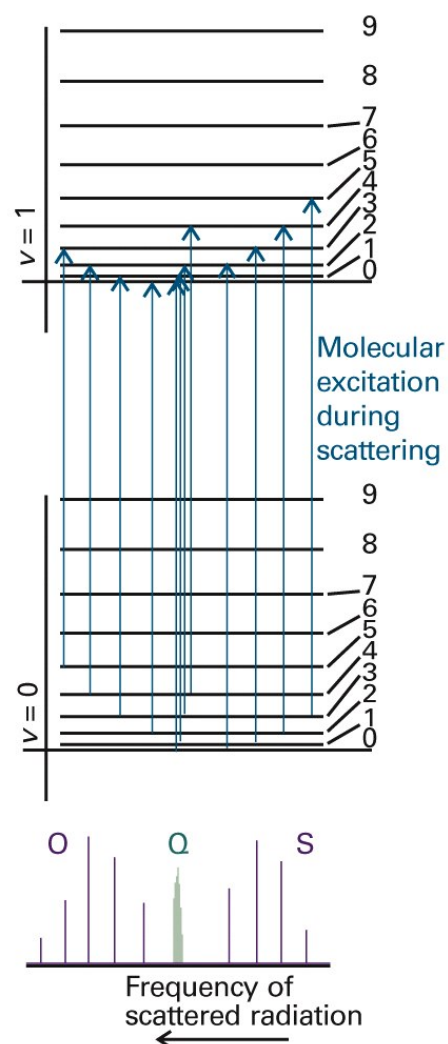Frequency of scattered radiation

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The vibrations of polyatomic molecules

- Diatomic molecule = one vibrational mode: the bond stretch. Polyatomic molecule = several modes of vibrations: all bonds and angles.

Normal modes

- We consider a molecule of N atoms:
  - $\rightarrow$ nonlinear: $3N - 6$ independent vibrational modes.
  - $\rightarrow$ linear: $3N - 5$ independent vibrational modes.

Indeed, a full molecular description requires $3N$ coordinates (x,y,z for each atom). With physically sensible grouping:

$\rightarrow$ 3 coords needed for translational motion of centre of mass.

$\rightarrow$ 2 angles needed for special orientation of molecular axis.

$\rightarrow$ 1 angle (if nonlinear!) needed for orientation around the molecular axis.
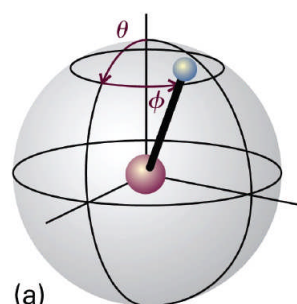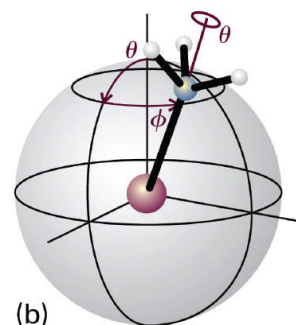
$\rightarrow$ the remaining are vibrational modes.

(a)

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(b)

- Examples:

H_2O = nonlinear triatomic, 3 vibration modes, 3 rotation modes.
CO_2 = linear triatomic, 4 vibration modes, 2 rotation modes.
Naphthalene $C_{10}H_8$ = 48 distinct modes of vibration.

- A possible choice for the 4 modes of CO_2:

   $\rightarrow$ stretching of one bond (mode ν_L),
   $\rightarrow$ stretching of the other bond (ν_R),
   $\rightarrow$ and 2 perpendicular bend modes (ν_2).
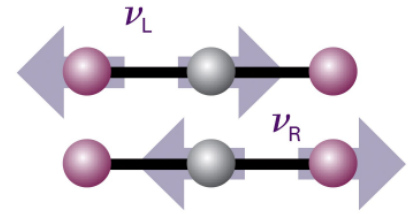
   Disadvantages: non-independent (energy flows backwards and forwards between ν_L and ν_R); position of centre of mass varies.

- Better, simpler description: linear combinations of ν_L and ν_R:

   $\rightarrow$ ν_1 = symmetric stretch
   $\rightarrow$ ν_3 = antisymmetric stretch
   $\rightarrow$ ν_2 (2x) = bending modes

   Advantages: ν_1 and ν_2 independent, that is, one does not excite the other.
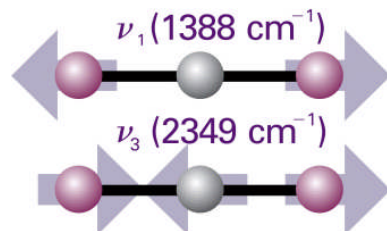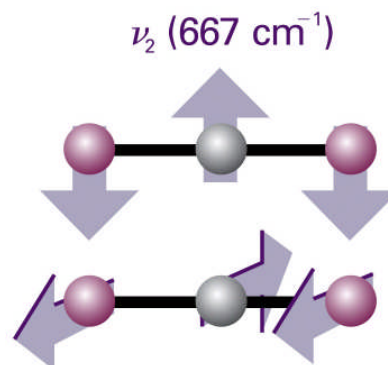

- Normal mode = independent, synchronous motion of atoms or group of atoms that may be excited without leading to the excitation of any other normal mode and without involving translation or rotation of the molecule as a whole.

   $\rightarrow$ key to describe polyatomic molecular vibrations.

- Each normal mode, q, behaves like an independent harmonic oscillator (if anharmonicities are neglected), with:

$$E_n(q) = \left(n + \frac{1}{2}\right)\hbar\omega_q = \left(n + \frac{1}{2}\right)hc\bar{\nu}_q \quad \text{with} \quad \bar{\nu} = \frac{\sqrt{k_q/m_q}}{2\pi c}$$

$\bar{\nu}_q$ = wavenumber of the mode q ; k_q = force constant for the mode q; m_q = effective mass for the mode q.

- The effective mass of the mode = measure of the mass that is swung about by the vibration = complicated function of the masses of the atoms. Example for CO_2:

  → symmetric stretch: C atom stationary, m_q depends on the masses of only the O atoms.

  → antisymmetric stretch and the bends: all 3 atoms move, so all contribute to m_q.

- In general for normal modes (example H_2O):

  → frequencies of bending motions are lower than those of stretching modes.

  → normal mode = composition of stretching and bending of bonds (not the case for CO_2).

  → heavy atoms move less than light atoms.

ν_1 (3652 cm^{-1})

ν_2 (1595 cm^{-1})
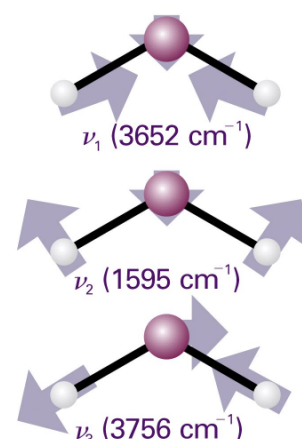
ν_3 (3756 cm^{-1})

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Infrared absorption spectra of polyatomic molecules

- Gross selection rule for infrared activity of a normal mode: it should be accompanied by a change of dipole moment. Decided by inspection. Example, for CO_2:

  $\rightarrow$ symmetric stretch is infrared inactive: dipole moment unchanged (at zero)

  $\rightarrow$ antisymmetric stretch is infrared active: dipole moment changes parallel to molecular axis because molecule becomes unsymmetrical as it vibrates; parallel band.

  $\rightarrow$ both bending modes are infrared active: dipole moment changes perpendicular to the principal axis; perpendicular band. Molecular linearity eliminated, hence a Q branch is observed.

- Specific selection rule for a normal mode: $\Delta n_q = \pm 1$ (harmonic approximation).

- Spectrum analysis provides a picture of the stiffness of the various parts of the molecule, that is, its force field = set of force constants corresponding to all displacements of the atoms.

- Complications: anharmonicities, molecular rotation (e.g. hindered in liquids or solids).

- In liquids, lifetimes of rotational states are very short, hence rotational energies are ill-defined:

  $\rightarrow$ lifetime broadening > 1 cm^{-1} can easily result.

  $\rightarrow$ rotational structure of vibrational spectrum is blurred.

  $\rightarrow$ infrared spectra in condensed phases usually consists of broad lines spanning the entire range of the resolved gas-phase spectrum, and showing no branch structure.

Vibrational Raman spectra of polyatomic molecules

- Gross selection rule for vibrational Raman activity of a normal mode: it should be accompanied by a changing polarizability. Decided by inspection (usually difficult). Example, for CO_2:

  $\rightarrow$ symmetric stretch is Raman active: alternate swelling and contraction changes polarizability.
  $\rightarrow$ other modes are Raman inactive.

- Detailed treatment leads to the exclusion rule: If the molecule has a centre of symmetry, then no modes can be both infrared and Raman active. A mode may be inactive in both. This rule applies to CO_2, but not H_2O or CH_4.