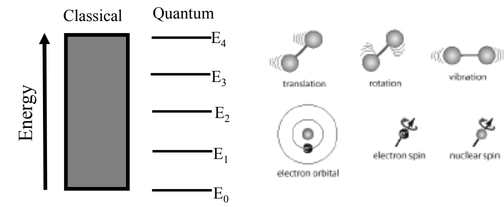
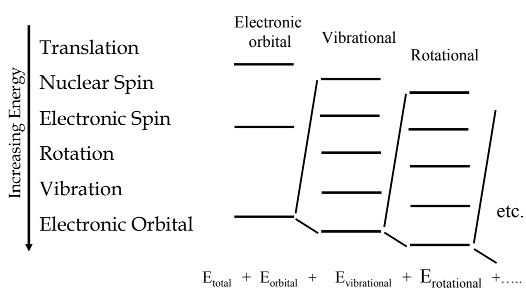
Molecular Spectroscopy

- Molecular Energy Levels
  - Vibrational Levels
  - Rotational levels
- Population of levels
- Intensities of transitions
- General features of spectroscopy
- An example: Raman Microscopy
  - Detection of art forgery
  - Local measurement of temperature

Molecular Energies

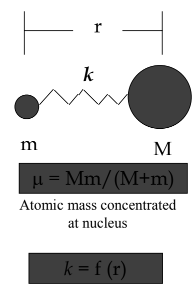


Molecular Energy Levels



Molecular Vibrations

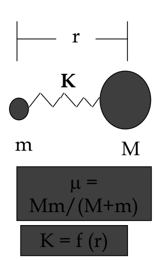
- Longitudinal Vibrations along molecular axis
- $E=(n+1/2)hf$ where f is the classical frequency of the oscillator
- $$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$ where k is the 'spring constant
- Energy Levels equally spaced
- How can we estimate the spring constant?



Molecular Vibrations

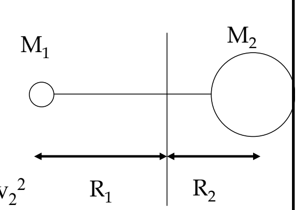
Hydrogen molecules, H_2, have ground state vibrational energy of 0.273eV. Calculate force constant for the H_2 molecule (mass of H is 1.008 amu)

- $E_{vib}=(n+1/2)hf \Rightarrow f=0.273\text{eV}/(1/2(h))$ $= 2.07\times10^{13}$ Hz
- To determine k we need μ
  $\mu=(Mm)/(M+m) = (1.008)^2/2(1.008)$ amu $=(0.504)1.66\times10^{-27}$kg $=0.837\times10^{-27}$kg
- $k= \mu(2\pi f)^2$ =576 N/m



Molecular Rotations

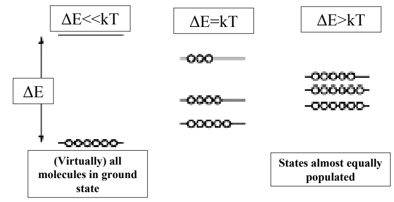
- Molecule can also rotate about its centre of mass
- $v_1 = \omega R_1$; $v_2 = \omega R_2$
- $L = M_1v_1R_1 + M_2v_2R_2$
  $= (M_1R_1^2 + M_2R_2^2)\omega$
  $= I\omega$
- $E_{KE} = 1/2M_1v_1^2 + 1/2M_2v_2^2$
  $= 1/2I\omega^2$



Molecular Rotations

- Hence, $E_{rot} = L^2/2I$
- Now in fact L^2 is quantized and $L^2 = l(l+1)h^2/4\pi^2$
- Hence $E_{rot} = l(l+1)(h^2/4\pi^2)/2I$
- Show that $\Delta E_{rot} = (l+1)\ h^2/4\pi^2/I$. This is not equally spaced
- Typically ΔE_{rot}=50meV (i.e for H_2)

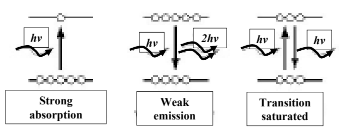
Populations of Energy Levels



- Depends on the relative size of kT and ΔE

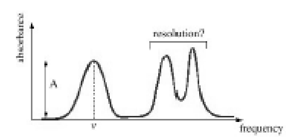
Intensities of Transitions

- Quantum Mechanics predicts the degree to which any particular transition is allowed.
- Intensity also depends on the relative population of levels



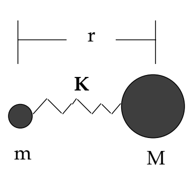
General Features of Spectroscopy

- Peak Height or intensity
- Frequency
- Lineshape or linewidth



Raman Spectroscopy

- Raman measures the vibrational modes of a solid
- The frequency of vibration depends on the atom masses and the forces between them.
- Shorter bond lengths mean stronger forces.

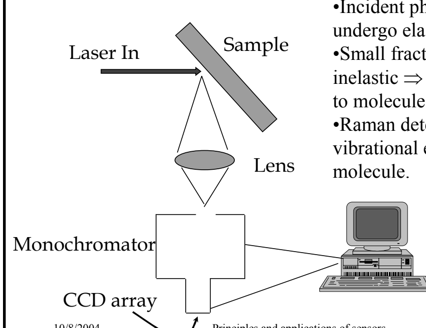


$f_{vib} = (K/\mu)^{1/2}$

$\mu = Mm/(M+m)$

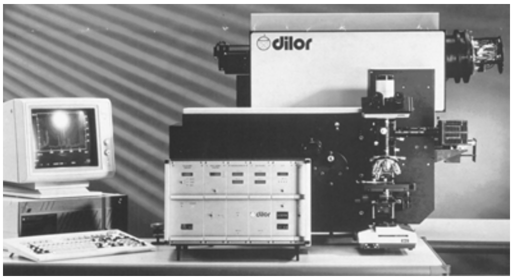
$K = f(r)$

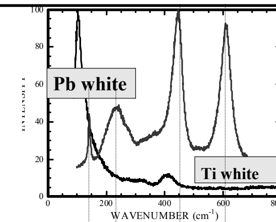
Raman Spectroscopy Cont...

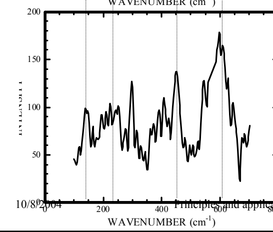


- Incident photons typically undergo elastic scattering.
- Small fraction undergo inelastic ⇒ energy transferred to molecule.
- Raman detects change in vibrational energy of a molecule.

Raman Microscope







Detecting Art Forgery

• Ti-white became available only circa 1920.

• The Roberts painting shows clear evidence of Ti white but is dated 1899

Tom Roberts, ‘Track To The Harbour’ dated 1899

Raman Spectroscopy and the Optical Measurement of Temperature

- Probability that a level is occupied is proportional to exp(ΔE/kT)