PRESENTATION

By

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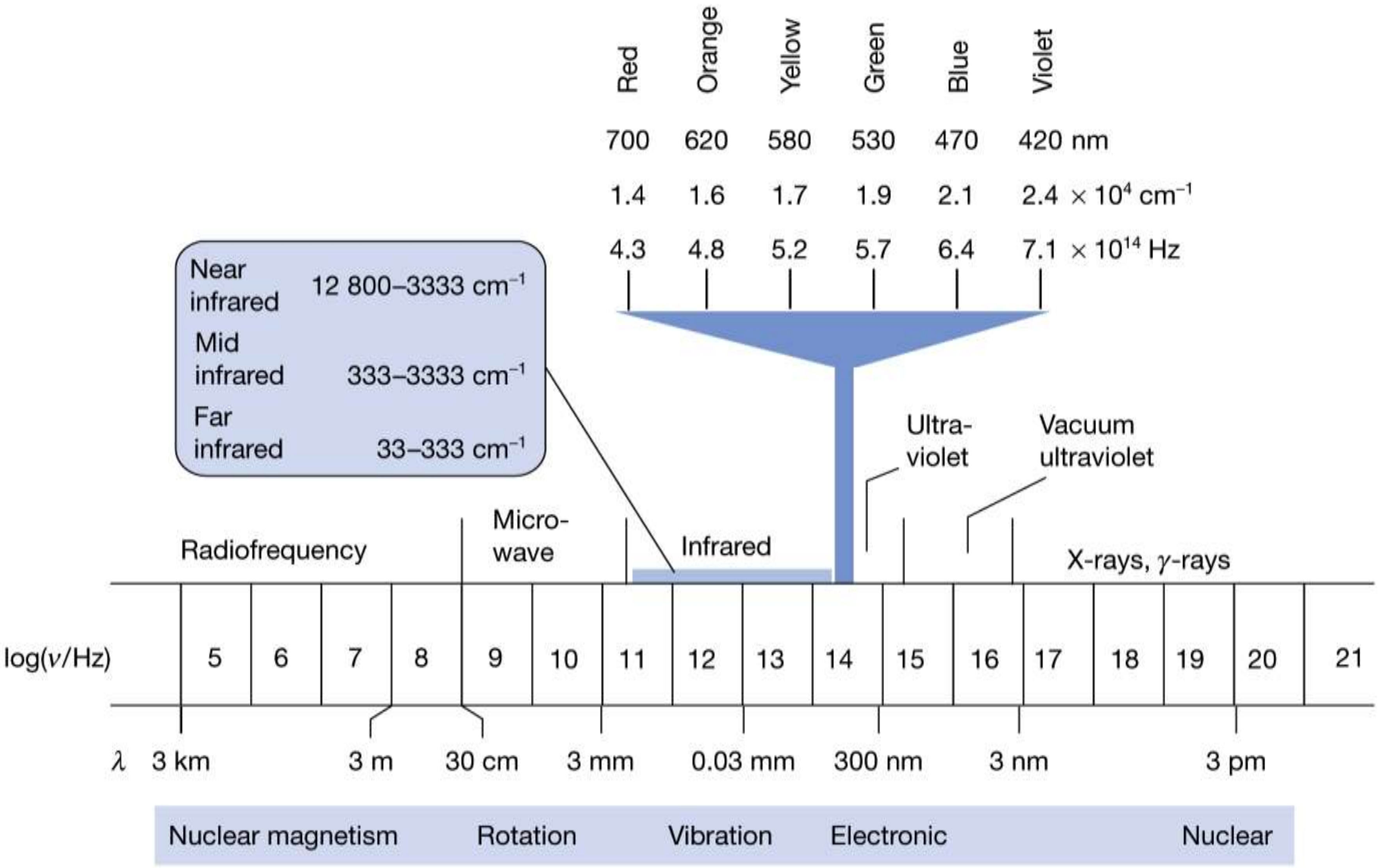
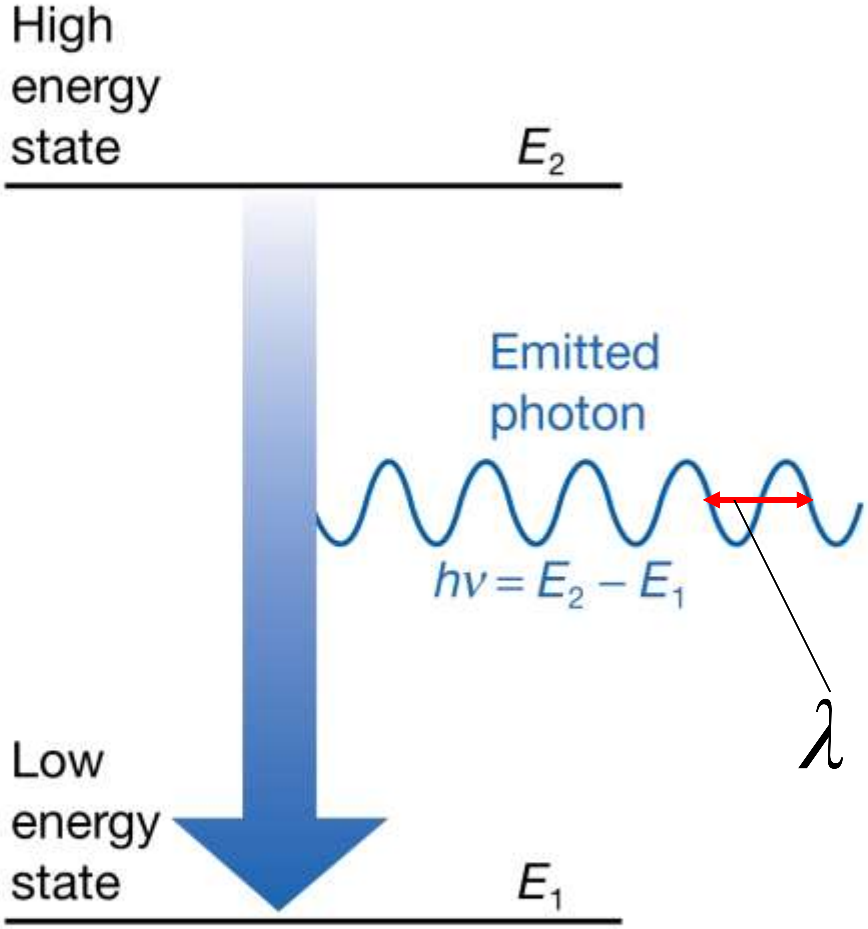
Regions of the Electromagnetic spectrum



THE ENERGIES OF ELECTROMAGNETIC WAVES



$$c = \lambda \upsilon \qquad \bar{\upsilon} = \frac{1}{\lambda}$$

$$E = h\nu = h\frac{c}{\lambda} = hc\bar{\upsilon}$$

$$E = N_A h\nu = N_A h\frac{c}{\lambda} = N_A hc\bar{\upsilon}$$

$\bar{\upsilon}$ **(nu-bar) represents wavenumber, the number of wavelengths in 1 cm**

The rotational energy levels E_J of a diatomic molecule, in the rigid rotor approximation, are given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

Where the moment of inertia $I = \mu r^2$ in which r is the internuclear distance and $\mu = m_1 m_2 / (m_1 + m_2)$

is the reduced mass for nuclei of masses m_1 and m_2.

The vibrational energy levels E_v of a diatomic molecule, treated by the harmonic oscillator approximation, are given by

$$\boldsymbol{E_v = h v_0 \left(v + \tfrac{1}{2}\right)}$$

It is convenient to divide the values of energy by *hc*. The resultant quantity is known as ‘term value’ and has dimensions of wavenumber.

Thus, the rotational term values are given by

$$\boldsymbol{F(J) = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) = \overline{B} J(J+1)}$$

where $I = \mu r_0^{\;2}$

For a non rigid rotor the expression is modified to

$$F(J) = \overline{B} J(J+1) - \overline{D} J^2 (J+1)^2$$

Where $\overline{D}$ is the centrifugal distortion constant.

$$\overline{D} = \frac{4\overline{B}^3}{\overline{\nu}_0^2} \qquad \text{and} \qquad \overline{\nu}_0 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Where:
c is the speed of light
k is the Hooke's law force constant
r_0 is the vibrationally-averaged bond length

μ is the reduced mass
h is Planck's constant

The vibrational term values are given by

$$G(v) = \frac{E_v}{hc} = \bar{v}_0 (v + \tfrac{1}{2})$$

where, $\bar{v}_0 (= \frac{v_0}{c})$ is the vibration wavenumber.

The vibrational term values $G(v)$ are modified in case of anharmonic oscillator and are given by

$$G(v) = \bar{v}_e (v + \tfrac{1}{2}) - \bar{v}_e x_e (v + \tfrac{1}{2})^2 + \bar{v}_e y_e (v + \tfrac{1}{2})^3 + \ldots\ldots..$$

Where $\bar{v}_e$ is the vibration wavenumber, which a classical oscillator would have for an infinitesimal displacement from equilibrium. The terms x_e, y_e, … are anharmonic constants.

When the molecule has both vibrational and rotational energy the total term values *S* are given by the sum of the rotational term values *F*(*J*) and the vibrational term values *G*(*v*).

$$S(v, J) = G(v) + F(J)$$

$$= \bar{v}_e(v + \tfrac{1}{2}) - \bar{v}_e x_e (v + \tfrac{1}{2})^2 + \ldots\ldots\ldots + \bar{B}J(J+1) - \bar{D}J^2(J+1)^2$$

Neglecting the small centrifugal distortion constant

$$S(v, J) = \bar{v}_e(v + \frac{1}{2}) - \bar{v}_\mathrm{e}(v + \frac{1}{2})^2 + \ldots\ldots\ldots + \bar{B}J(J+1)$$

The selection rules are:

$\Delta v = \pm 1, \pm 2, \pm 3, \ldots..$

$\Delta J = \pm 1$

Considering only $v = 0 \rightarrow v = 1$ transition,

$$\bar{v} = S(1, J') - S(0, J'') = \bar{v}_0 + \bar{B}J'(J'+1) + \bar{B}J''(J''+1)$$

For $\Delta J = -1$ ($J' = J'' - 1$), we get the *P*-branch

$$\bar{v}_P(J'') = \bar{\omega}_0 - 2BJ''$$

For $\Delta J = +1$ ($J' = J'' + 1$), we get the *R*-branch

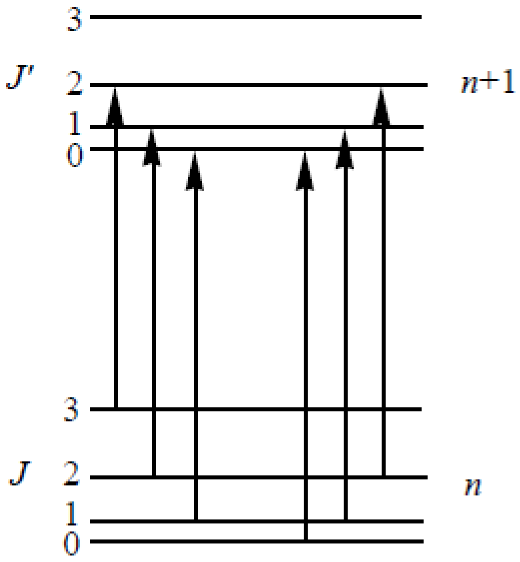
$$\bar{v}_R(J'') = \bar{\omega}_0 + 2B(J''+1)$$

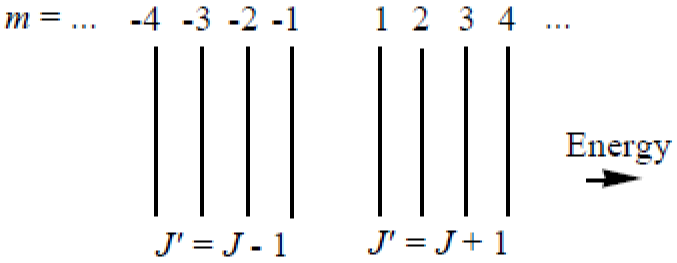
Thus, the zero gap $\bar{v}_R(0)$ - $\bar{v}_P(1)$ is $4\overline{B}$

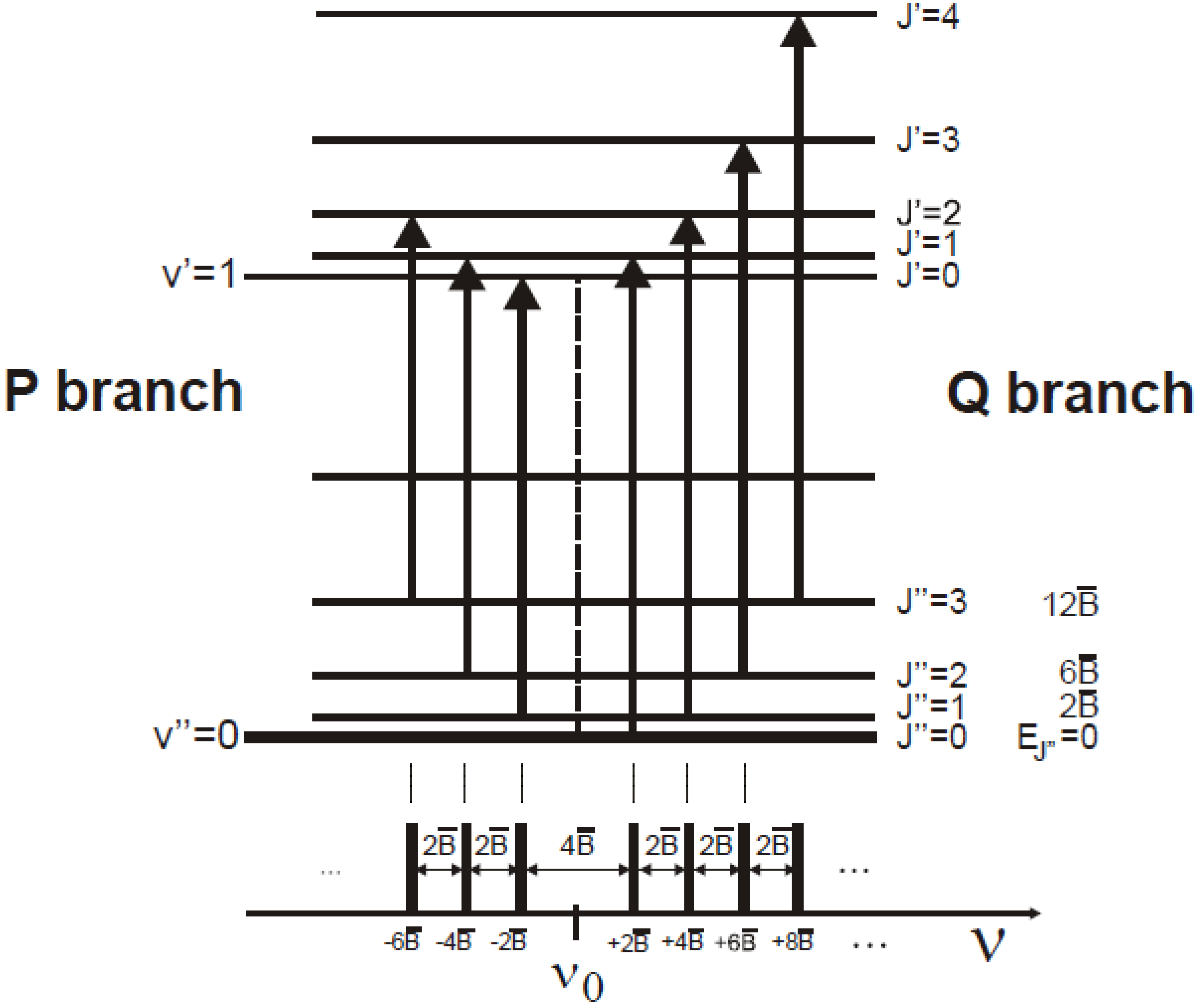
and the spacing between the adjacent *R*-branch lines and also between the adjacent *P*-branch lines is 2*B.*

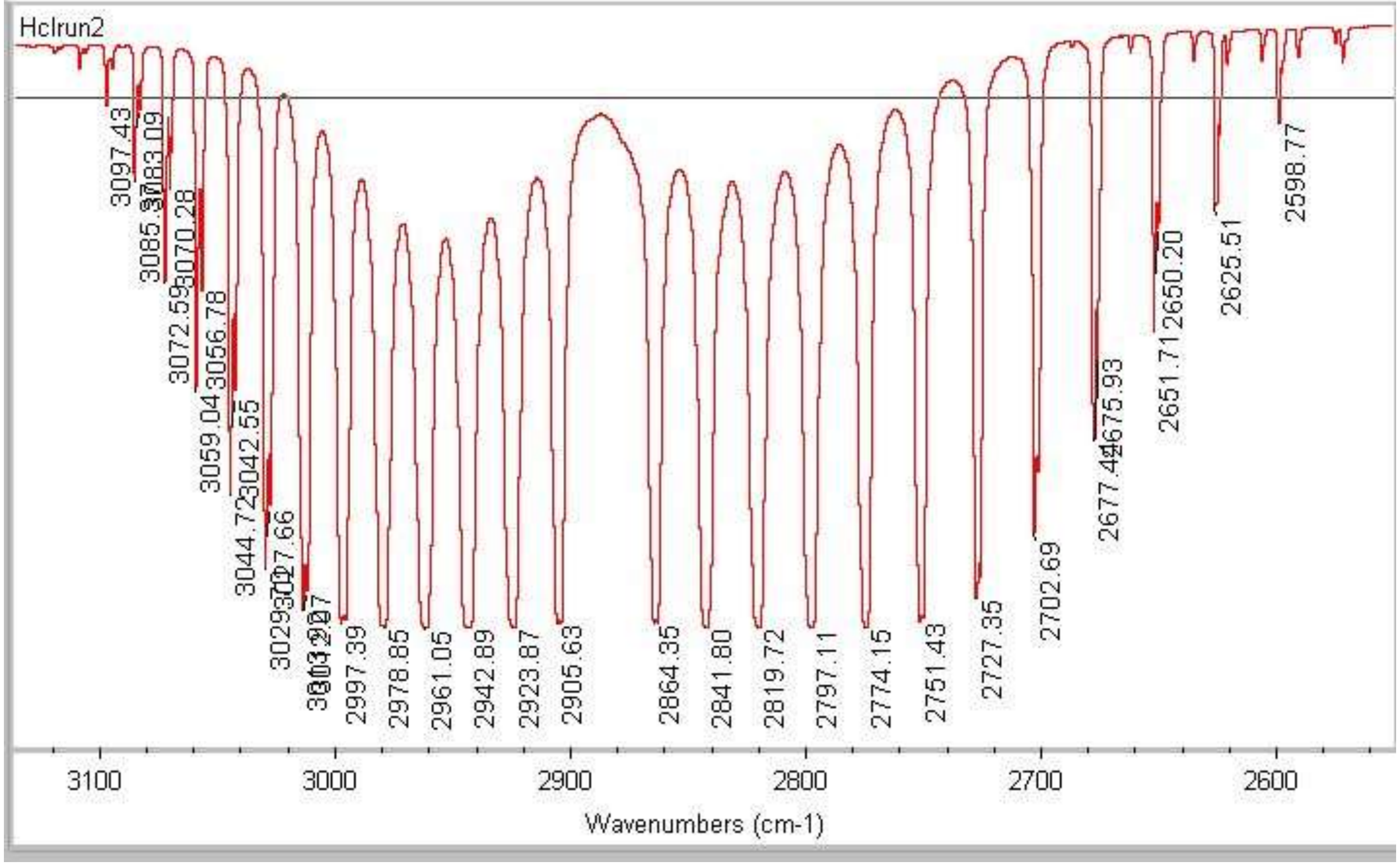
After assignment and measurement of the wavenumbers of the rotational lines of the *P*-branch, a graph of $\bar{v}_P(J'')$ versus *J”* is a straight line with slope – 2*B*.

Similarly, a graph of $\bar{v}_R(J'')$ versus *J”* + 1 for the *R*-branch is a straight line with slope 2*B*.


3
J′
2
1
0
n+1
3
J
2
1
0
n


m = …
-4
-3
-2
-1
1
2
3
4
…
Energy
J′ = J - 1
J′ = J + 1


J'=4
J'=3
J'=2
J'=1
v'=1
J'=0
P branch
Q branch
J"=3 12$\bar{B}$
J"=2 6$\bar{B}$
J"=1 2$\bar{B}$
v"=0
J"=0 $E_{J"}$=0
2$\bar{B}$ 2$\bar{B}$ 4$\bar{B}$ 2$\bar{B}$ 2$\bar{B}$ 2$\bar{B}$
...
...
-6$\bar{B}$ -4$\bar{B}$ -2$\bar{B}$ +2$\bar{B}$ +4$\bar{B}$ +6$\bar{B}$ +8$\bar{B}$ ...
ν_0
ν

HcIrun2
3097.43
3085.97
3083.09
3072.59
3070.28
3059.04
3056.78
3044.72
3042.55
3027.66
2997.39
2978.85
2961.05
2942.89
2923.87
2905.63
2864.35
2841.80
2819.72
2797.11
2774.15
2751.43
2727.35
2702.69
2677.44
2675.93
2651.71
2650.20
2625.51
2598.77
3100
3000
2900
2800
2700
2600
Wavenumbers (cm-1)

A close look at the vibration-rotation spectrum of a diatomic molecule reveals that the band is not quite symmetrical but shows a convergence in the *R* branch and a divergence in the *P* branch.

This behaviour is due mainly to the inequality of B_0 and B_1 and there is enough information in the band to be able to determine these two quantities separately. The method used is called the **method of combination differences**.

The principle is that, if we wish to derive information about a series of lower states and a series of upper states, between which transitions are occurring, then differences in wavenumber between transitions with a common upper state are dependent on properties of the lower states only. Similarly differences in wavenumber between transitions with a common lower state are dependent on properties of the upper states only.

In case of a vibration-rotation band, since all pairs of transitions

R (J) and P (J + 2) have a common upper state with J' = J + 1,

$\bar{\nu}[R(J) - \bar{\nu}[P(J+2)]$ must be a function of B_0 only

$$\bar{\nu}[R(J)] - \bar{\nu}[P(J+2)] = \omega_0 + B_1 (J+1)(J+2) - B_0 J (J+1)$$
$$- [\omega_0 + B_1 (J+1)(J+2) - B_0 (J+2)(J+3)]$$

$$= 2 B_0 (2J + 3)$$

Thus a graph of $\bar{\nu}[R(J)] - \bar{\nu}[P(J+2)]$ versus $2J + 3$ is a straight line of slope $2B_0$.

Similarly, since all pairs of transitions *R* (*J*) and *P* (*J*) have common lower states,

$\bar{\nu}[R(J)-\bar{\nu}[P(J)]$ must be a function of B_1 only

$$\bar{\nu}[R(J)-\bar{\nu}[P(J)]= \omega_0 + B_1 (J+1)(J+2) - B_0 J (J+1)$$

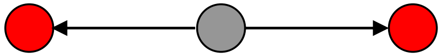
$$- [\omega_0 + B_1 (J-1)(J) - B_0 J(J+1)]$$

$$= 2 B_1 (2J+1)$$

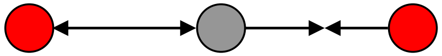
Thus a graph of $\bar{\nu}[R(J)]-\bar{\nu}[P(J)]$ versus $2J + 1$ is a straight line of slope $2B_{1.}$

Vibrational Modes and IR Absorption

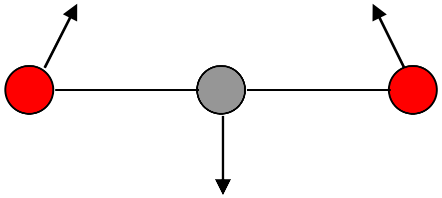
- Number of modes:
  - Linear: $3n - 5$ modes
  - Non-linear: $3n - 6$ modes
- Types of vibrations:
  - Stretching
  - Bending
- Examples:
  - CO_2 has $3 \times 3 - 5 = 4$ normal modes



Symmetric
No change in dipole
IR-inactive



Asymmetric
Change in dipole
IR-active



Scissoring
Change in dipole
IR-active

- IR-active modes require dipole changes during rotations and vibrations!

INFRARED ABSORPTION BANDS

POSITION	REDUCED MASS	LIGHT ATOMS HIGH FREQUENCY
	BOND STRENGTH (STIFFNESS)	STRONG BONDS HIGH FREQUENCY
STRENGTH	CHANGE IN ‘POLARITY’	STRONGLY POLAR BONDS GIVE INTENSE BANDS
WIDTH	HYDROGEN BONDING	STRONG HYDROGEN BONDING GIVES BROAD BANDS

INFRARED (VIBRATIONAL) SPECTROSCOPY

Bond →	C-H	C-D	C-O	C-Cl
ν/cm^{-1} →	3000	2200	1100	700
Bond →	C≡O	C=O	C-O	
ν/cm^{-1} →	2143	1715	1100	

REGIONS OF THE INFRARED SPECTRUM

4000-3000 cm^{-1}	**3000-2000 cm^{-1}**	**2000-1500 cm^{-1}**	**1500-1000 cm^{-1}**
O-H **N-H** **C-H**	**C≡C** **C≡N**	**C=C** **C=O**	**C-O** **C-F** **C-Cl** deformations

Increasing energy

←

increasing frequency

←

INTERPRETATION OF INFRARED SPECTRA

- An element of judgement is required in interpreting IR spectra but you should find that it becomes relatively straightforward with practice.
- It is often possible to assign the peaks in the 1600-3600 cm^{-1} region by consulting tables or databases of IR spectra. When making an assignment, give both the type of bond and the type of vibration, *e.g.* O-H stretch or C-H bending vibration.
- The most useful regions are as follows:

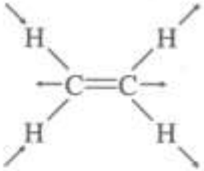
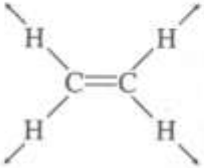
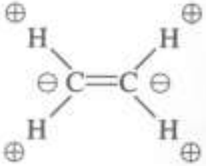
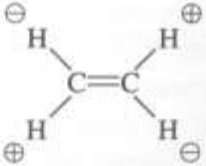
  1680-1750 cm^{-1}: C=O stretches feature very strongly in IR spectra and the type of carbonyl group can be determined from the exact position of the peak.

  2700-3100 cm^{-1}: different types of C-H stretching vibrations.

  3200-3700 cm^{-1}: various types of O-H and N-H stretching vibrations.

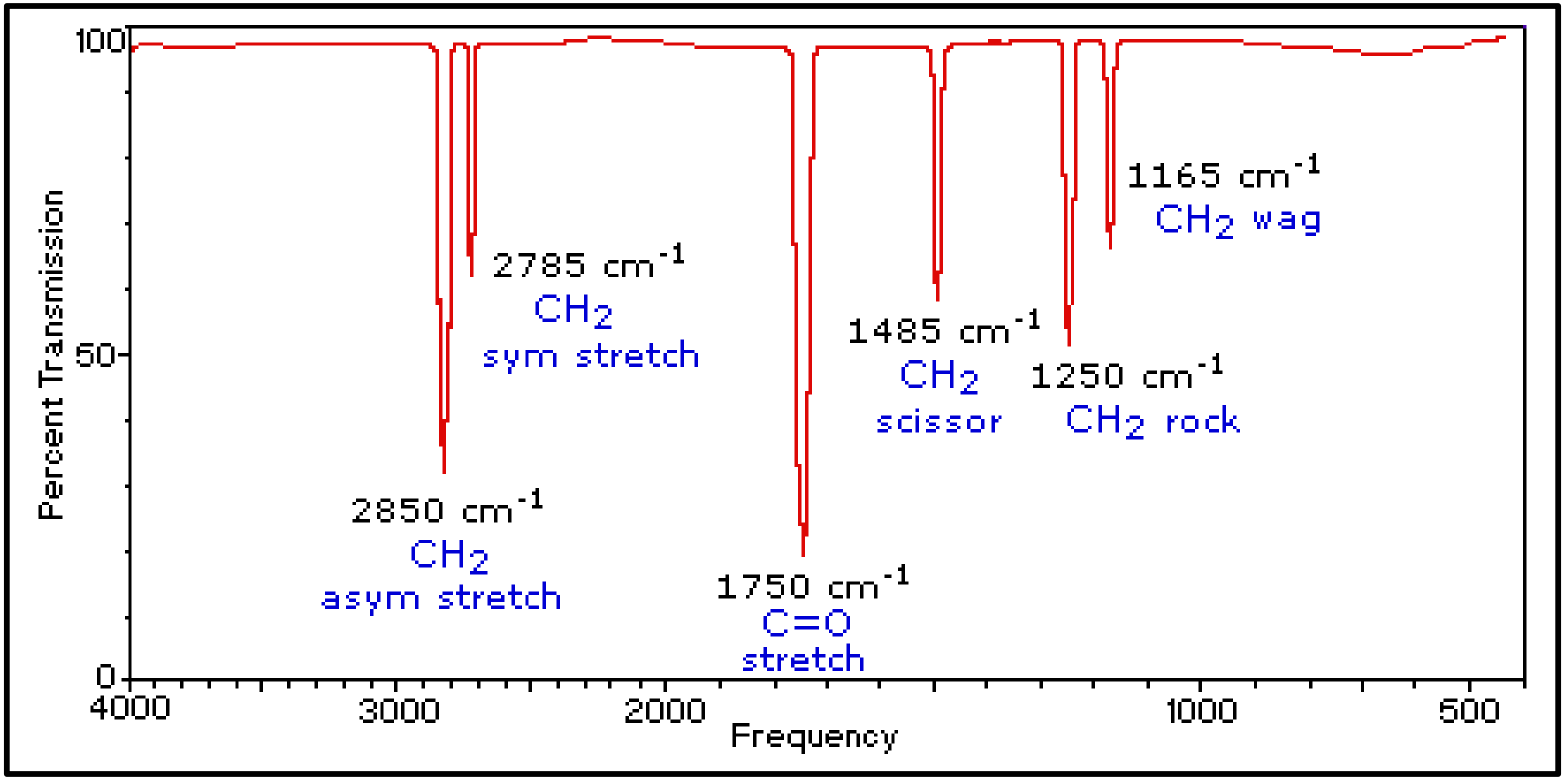
- Too many bonds absorb in the region of 600-1600 cm^{-1} to allow confident assignment of individual bands. However, this region is useful as a fingerprint of a molecule, *i.e.* if the spectrum is almost identical to an authentic reference spectrum then the structure can be assigned with some confidence

Vibrational Modes: Examples

Molecule	Motion	
(a) $CH_3—CH_3$	C—C stretching	Inactive
(b) $CH_3—CCl_3$	C—C stretching	Active
(c) SO_2	Symmetric stretching	Active
(d) $CH_2═CH_2$	C—H stretching: 	Active
(e) $CH_2═CH_2$	C—H stretching: 	Inactive
(f) $CH_2═CH_2$	CH_2 wag: 	Active
(g) $CH_2═CH_2$	CH_2 twist: 	Inactive

IR Spectra: Formaldehyde

- Certain types of vibrations have distinct IR frequencies – hence the chemical usefulness of the spectra
- The gas-phase IR spectrum of formaldehyde:



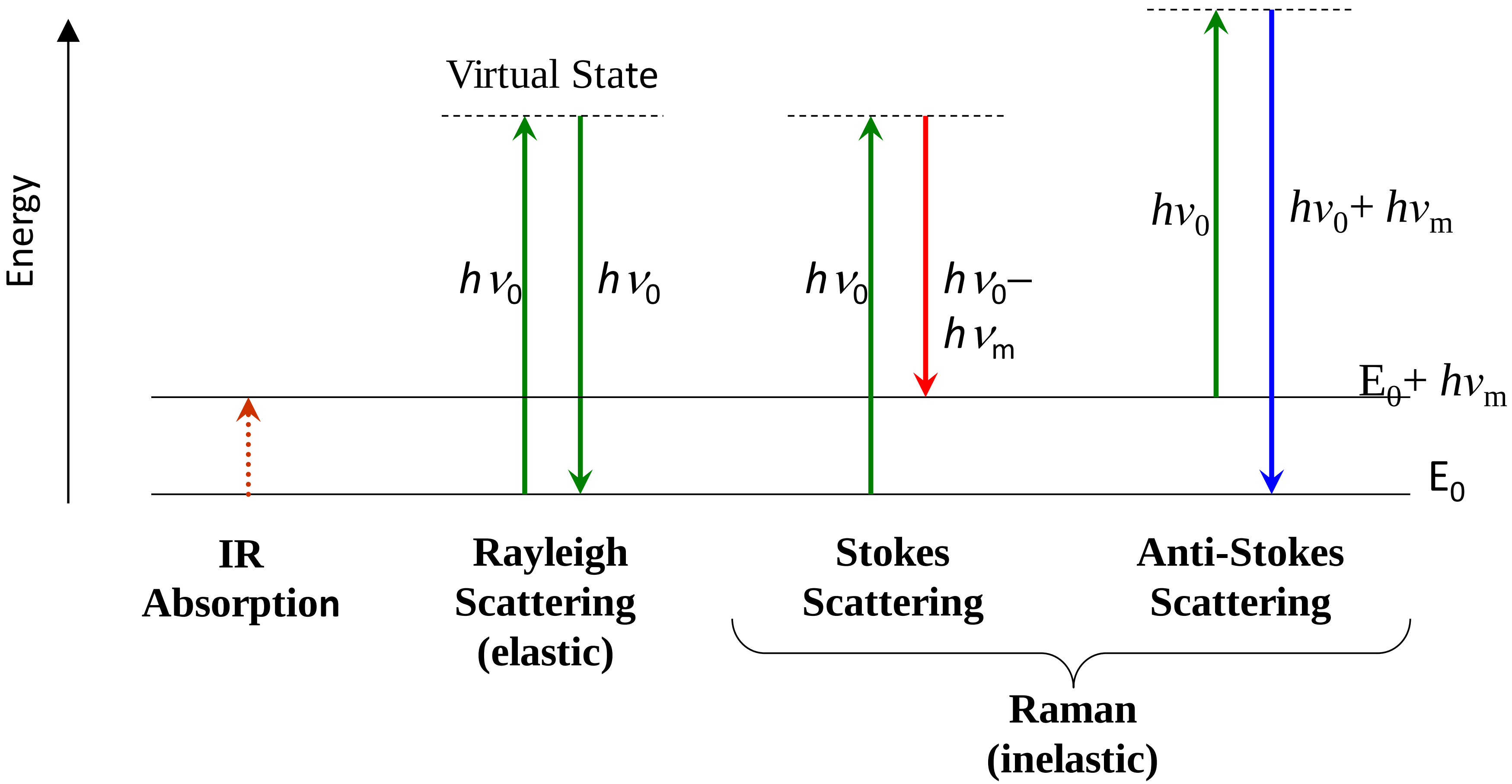
Rayleigh and Raman Scattering

- Rayleigh scattering:
  - occurs when incident EM radiation induces an oscillating dipole in a molecule, which is re-radiated at the same frequency
- Raman scattering:
  - occurs when monochromatic light is scattered by a molecule, and the scattered light has been weakly modulated by the characteristic frequencies of the molecule

- Raman spectroscopy measures the difference between the wavelengths of the incident radiation and the scattered radiation.

RAMAN SPECTROSCOPY

Energy Scheme for Photon Scattering



The Raman effect comprises a very small fraction, about 1 in 10^7 of the incident photons.

Raman-Active Vibrational Modes

- Modes that are more polarizable are more Raman-active

- Examples:
  - N_2 (dinitrogen) symmetric stretch
    - cause no change in dipole (IR-inactive)
    - cause a change in the polarizability of the bond – as the bond gets longer it is more easily deformed (Raman-active)
  - CO_2 asymmetric stretch
    - cause a change in dipole (IR-active)
    - Polarizability change of one C=O bond lengthening is cancelled by the shortening of the other – no net polarizability (Raman-inactive)

- Some modes may be both IR and Raman-active, others may be one or the other!

The Raman Depolarization Ratio

- Raman spectra are excited by linearly polarized radiation (laser).
- The scattered radiation is polarized differently depending on the active vibration.
- Using a polarizer to capture the two components leads to the depolarization ratio *p*:

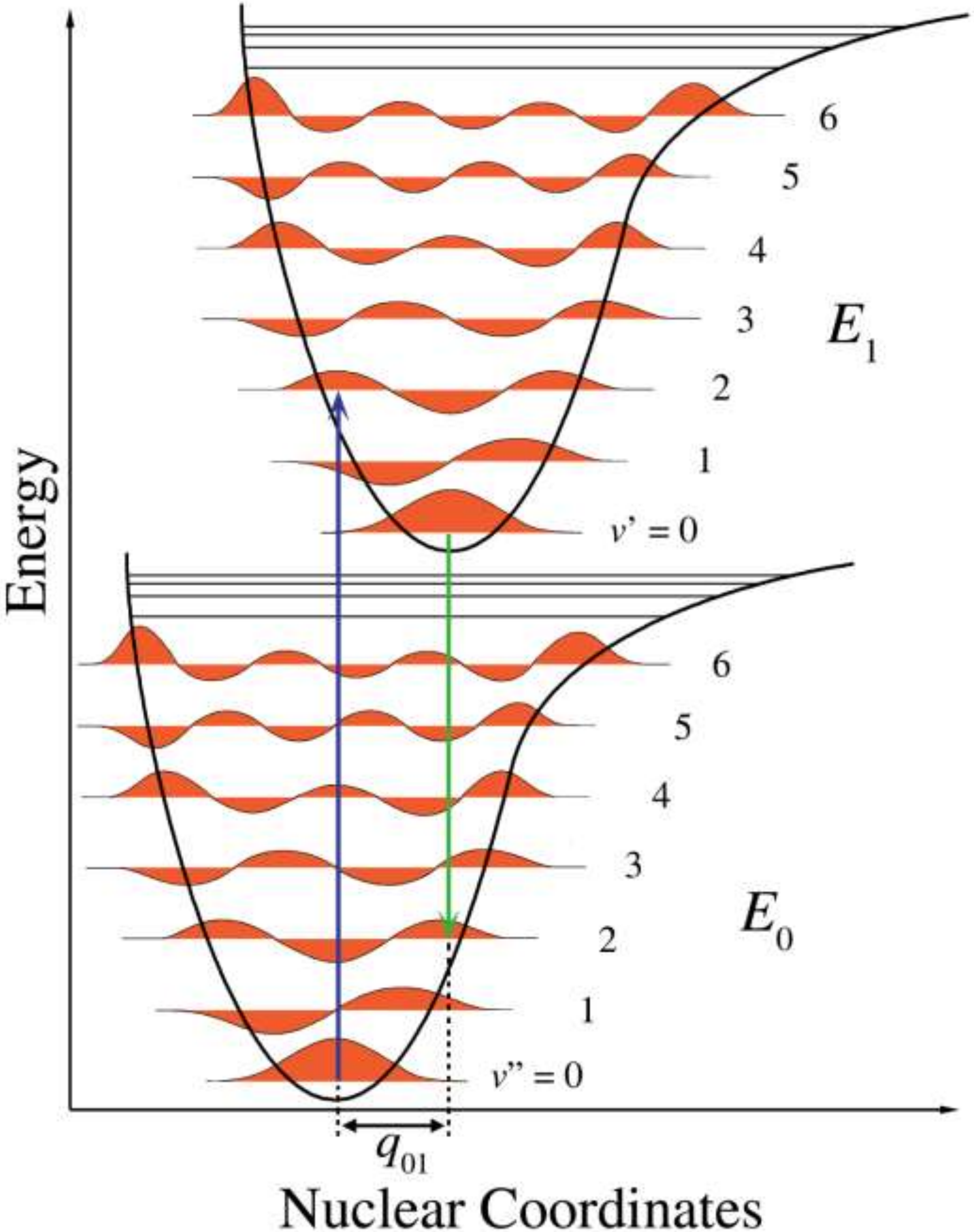
$$p = \frac{I_{\perp}}{I_{=}}$$

- The depolarization ratio *p* can be useful in interpreting the actual vibration responsible for a Raman signal.

ELECTRONIC SPECTROSCOPY

$$E_{vr}(n,v) = T_n + \bar{\nu}_e\left(v + \frac{1}{2}\right) - \bar{\nu}_e x_e\left(v + \frac{1}{2}\right)^2$$

$$\boxed{\Delta E_{vr}(v') = T' + \bar{\nu}_e'\left(v' + \frac{1}{2}\right) - \bar{\nu}_e' x_e'\left(v' + \frac{1}{2}\right)^2 - \bar{\nu}_e''\left(\frac{1}{2}\right) + \bar{\nu}_e'' x_e''\left(\frac{1}{4}\right)}$$


Energy
6
5
4
3
E_1
2
1
$v' = 0$
6
5
4
3
E_0
2
1
$v'' = 0$
q_{01}
Nuclear Coordinates

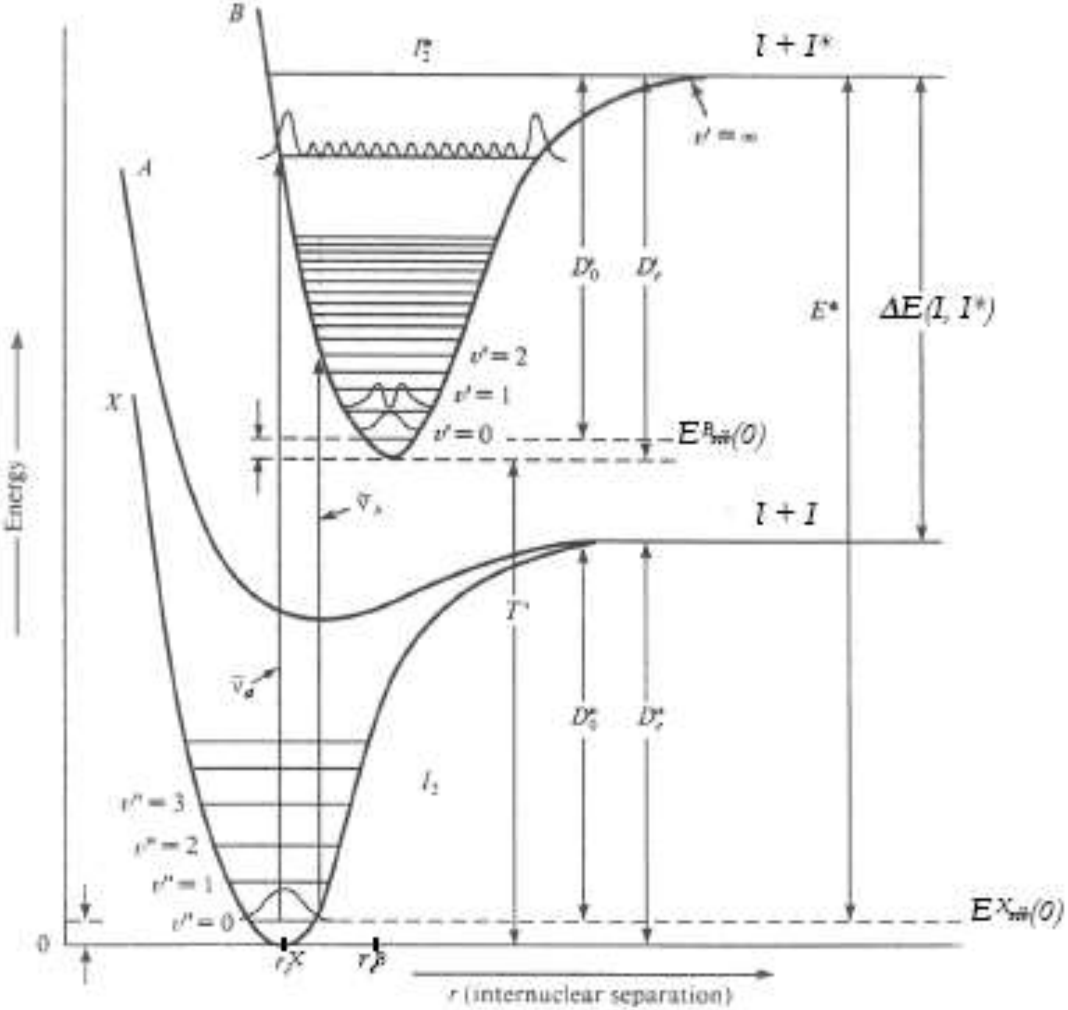


Figure 1: A potential energy diagram for I_2[1]. The curve X describes the ground electronic state, and the curves A and B describe excited electronic states. The horizontal lines within the curves indicate the vibrational energy levels within the particular electronic state.