Spectroscopy and Diatomic Molecules

- In a molecule nuclei are not fixed:
 - They can vibrate about an equilibrium position.
 - They can revolve around a molecule's centre of mass.
- Energy levels are associated with these motions.
- These may be accessed through quantum mechanics or through spectroscopy.
- Insights from quantum mechanics will be used to interpret molecular spectra.
- Consider a molecule of H₂ in the ground electronic state.
 - The E(R) may be obtained from quantum mechanics and represents the electronic energy of the molecule as a function of R, the separation of the two nuclei.
 - The Born-Oppenheimer approximation is used, which is based on the fact that nuclei are much heavier than electrons.

- This allows the Schrödinger equation to be separated into nuclear and electronic parts which are then solved separately, with the final wavefunction being the product of the nuclear and electronic wavefunctions.
- The Heisenberg uncertainty principle means that nuclei cannot be in fixed positions.
- The quantum mechanical description of the molecule gives the probability of the atoms in a molecule being is a particular position relative to each other.

Vibrations of Diatomic Molecules

- When the Born-Oppenheimer approximation is used, E(R) may be obtained from the electronic portion of the Schrödinger equation.
- E(R) becomes the effective potential energy for the nuclear portion of the equation.

• Thus the nuclear portion of the Schrödinger equation is:

$$\left(\frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B}\right)\Psi_{nucl}(R_n) = \left[E - E(R)\right]\Psi_{nucl}(R_n)$$

where R_n represents all the nuclear coordinates, E the total energy of the molecule.

- It is now assumed that the translational, rotational, and vibrational motions may be separated from one another.
 - Corrections for this inaccuracy will be applied later.
- This approximation gives:

$$\mathbf{H}_{nucl} = \frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} = \mathbf{H}_{trans} + \mathbf{H}_{vib} + \mathbf{H}_{rot}$$
$$E - E(R) = E_{trans} + E_{vib} + E_{rot}$$

• This means that the wavefunction is:

.

$$\Psi_{nucl}(R_n) = \Psi_{trans} \Psi_{vib} \Psi_{rot}$$

- Thus \mathbf{H}_{trans} and Ψ_{trans} depend only on the motion of the centre of mass.
- \mathbf{H}_{vib} and Ψ_{vib} depend only on the intermolecular separation.
- \mathbf{H}_{rot} and Ψ_{rot} depend only on the angular coordinates describing the orientation of the molecules in space.
- Each type of motion give an equation:

$$\mathbf{H}_{j}\Psi_{j}=E_{j}\Psi_{j}$$

- For translational motion, this is the equation for a particle in free space.
- Quantum and classical solutions give the same result.
- The operator for total energy may be rewritten in centre of mass coordinates:

$$[E - E(R)] = \left[\frac{p_X^2 + p_Y^2 + p_Z^2}{2M}\right] + \left[\frac{p_R^2}{2\mu} + V(R)\right] + \left[\frac{1}{2\mu R^2} \left(p_{\theta}^2 + \frac{p_{\phi}^2}{R^2 \sin^2 \theta}\right)\right]$$

where X, Y, Z are the coordinates of the centre of mass, M is the total mass, μ is the reduced mass, p_R is the radial momentum, and p_{θ} and p_{ϕ} are the components of the angular momentum.

- Consider now the vibrational motion of a diatomic.
- Since E(R) depends only on R, it may be identified as V(R).
- Thus the Schrödinger equation for vibrational motion is:

$$\mathbf{H}_{vib}\Psi_{vib} = \left[\frac{p_R^2}{2\mu} + E(R)\right]\Psi_{vib} = E_{vib}\Psi_{vib}$$

where $p_R = i\hbar(\partial/\partial R)$, the radial relative momentum operator.

- This equation can be solved to give the vibrational eigenfunctions Ψ_{vib} and the vibrational eigenvalues (energy levels) E_{vib} .
- The form of the solution depends on the functional form of ${\cal E}(R).$

- For most functional forms of E(R) only numerical solutions are feasible.
- As an approximation, E(R) will be replaced by a function of R for which exact solutions are possible.
- To determine what a suitable "replacement" function would be, the properties of the actual E(R) must be considered.
 - E(R) has a stable minimum where dE(R)/dR = 0at $R = R_e$.
 - Since dE(R)/dR gives the binding force, the force on either side of R_e will restore the separation to R_e .
 - There exist values of *E* such that the molecule is bound.
 - The resulting wave functions are oscillatory functions of R, decaying exponentially in the forbidden regions.

- The number of bound states that a diatomic may have depends on E(R) for the particular electronic state under consideration.
 - From spectroscopy, it is known that the H₂ molecule has 15 bound vibrational states (from v = 0 to v = 14) in the ground electronic state.
- For a model form for E(R), it will be assumed that the restoring force, dE(R)/dR, is proportional to the displacement from equilibrium:

$$F(R) \propto |R - R_e|$$

• This is consistent with the harmonic oscillator described by:

$$F(R) = -k(R - R_e)$$
 and $V(R) = \frac{1}{2}k(R - R_e)^2$

• If x is defined as $R - R_e$, then:

$$F(x) = -kx$$
 and $V(x) = \frac{1}{2}kx^2$

- This is the equation of a parabola.
- However, this does not behave like the potential for a real molecule since it predicts an infinite number of vibrational levels and does not asymptotically approach the dissociation limit.
- In spite of this, it does a reasonably good job of predicting the energy levels in the region near the equilibrium separation.
- The harmonic oscillator model predicts uniformly spaced energy levels.
- But how well does this model do?



Figure 7.1 Vibrational energy levels of the H₂ molecule. Solid lines (——) represent the experimental E(R) curve and energy levels; dashed lines (- - -) give the parabolic approximation described in the text and the first few of the corresponding harmonic oscillator levels; and the dotted line ($\cdot \cdot \cdot \cdot \cdot$) is a Morse potential fit. The inset shows an enlargement of the region near the minimum. The two "dissociation energies" are indicated: $D_e = 4.748 \text{ eV}, D_0 = 4.477 \text{ eV}.$

- Consider a "typical" diatomic:
 - The well depth is about 5 eV or 8×10^{-19} J.
 - The amplitude of the vibration is about 1 $Å(|R R_e| \le 0.5 Å).$
 - If it is assumed that at $|R R_e|$, V(R) is the well depth, then k may be determined.

$$k = \frac{2V(R)}{(R - R_e)^2} = \frac{2 \times 8 \times 10^{-19} \text{ J}}{(0.5 \times 10^{-1} \text{ m})^2} = 640 \text{ N m}^{-1}$$

- Once k has been determined, then it may be combined with the reduced mass of the diatomic under consideration to determine the oscillator frequency.
 - For the H₂ molecule, the reduced mass is about 8×10^{-28} kg.

• Therefore the oscillator frequency is:

$$\nu(H_2) = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{1/2} = \frac{1}{2\pi} \left(\frac{640 \text{ N m}^{-1}}{8 \times 10^{-28} \text{ kg}}\right)^{1/2}$$
$$= \frac{(80 \times 10^{28} \text{ s}^{-2})^{1/2}}{2\pi} = 1.5 \times 10^{14} \text{ s}^{-1}$$

• When this frequency is converted into wavenumbers:

$$\frac{\nu}{c} \equiv \overline{\nu} = 5000 \text{ cm}^{-1}$$

• Since the spacing of vibrational levels is $h\nu$, this can now be calculated:

$$\Delta E(H_2) = h\nu(H_2) = (6.6 \times 10^{-34} \text{ Js})(1.5 \times 10^{14} \text{ s}^{-1}) \approx 10^{-19} \text{ Js}$$

- For the harmonic oscillator, the lowest energy level is $\frac{1}{2}h\nu$ above the minimum.
- When the harmonic oscillator energy levels are compared with the actual levels as determined by spectroscopy, it is observed that while the first two levels agree well, the higher levels do not.
 - Because at room temperature, only the lowest two or three vibrational levels have non-negligible populations, the harmonic oscillator approximation has proved to be quite useful.
- This approximation does break down for molecules with very shallow or non-parabolic wells.
- The vibrational energy levels of a real molecule may be fitted to a power series in $(v + \frac{1}{2})$.

• The first order term may be identified with a harmonic oscillator, $(v + \frac{1}{2})h\nu_e$.

• For H₂,
$$\nu_e = 1.3192 \times 10^{14} \text{ s}^{-1}$$
.

- This indicates that the harmonic oscillator model can predict within 10% the ground state energy of the molecule.
- The suitability of the harmonic oscillator model may also be assessed by isotope effects.
- E(R) is the same for all isotopic combinations of the same atoms, since the electronic structure of a diatomic is determined by the nuclear charge.
- For a given E(R), the harmonic oscillator model predicts that $\nu_e \propto \mu^{-1/2}$ or that $\mu^{-1/2}\nu_e$ is a constant.
- For isotopic analogues of H₂, this works well.

Table 7.1 Test of Harmonic Oscillator Model with VibrationalConstants of H2 Isotopes

(Atomic masses: ¹ H, 1.00782 amu; D, 2.01410 amu)								
	Reduced Mass,	Vibrational Frequency,	$\frac{\mu^{1/2} V_e}{10^{14} \text{amu}^{1/2} \text{s}^{-1}}$					
Molecule	μ (amu)	$v_e \times 10^{-14}(s^{-1})$						
¹ H ₂	0.50391	1.3192	0.9365					
¹ HD	0.67171	1.1429	0.9367					
D ₂	1.00705	0.9345	0.9378					

- The deviations may be accounted for by the fact that E(R) is not perfectly parabolic.
- The harmonic oscillator vibrational energy levels are:

$$E_{vib}(v) = (v + \frac{1}{2})h\nu_0$$

where ν_0 is the oscillator frequency and v is the vibrational quantum number of the diatomic molecule.

• The vibrational wavefunctions are $\Psi_v(z)$ (see Table 4.1), where z is a dimensionless displacement variable:

$$z \equiv \left(\frac{4\pi^2 \mu \nu_0}{h}\right)^{1/2} \left(R - R_e\right)$$

• v gives the number of nodes in the wavefunction and v+1 gives the number of maxima in the wavefunction.

n	$H_n(z)$	$\psi_n(z)$
0	1	$(m\omega/\hbar\pi)^{1/4}e^{-z^{2/2}}$
1	2z ·	$(m\omega/\hbar\pi)^{1/4}(2\cdot 1)^{-1/2}e^{-z^2/2}2z$
2	$4z^2 - 2$	$(m\omega/\hbar\pi)^{1/4}(4\cdot 2)^{-1/2}e^{-z^2/2}(4z^2-2)$
3	$8z^3 - 12z$	$(m\omega/\hbar\pi)^{1/4}(8\cdot 6)^{-1/2}e^{-z^2/2}(8z^3-12z)$
4	$16z^4 - 48z^2 + 12$	$(m\omega/\hbar\pi)^{1/4}(16\cdot 24)^{-1/2}e^{-z^2/2}(16z^4 - 48z^2 + 12)$

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Table 4.1 Harmonic Oscillator Wave Functions



(a)



Figure 4.4 The quantum mechanical harmonic oscillator. (a) Potential energy curve, energy levels E_n and superimposed wave functions $\psi_n(z)$, where $z \equiv (m\omega/\hbar)^{1/2}x$. (b) Probability densities for n = 0, 1, 4, 10, with the dashed lines (- -) giving the probabilities for classical oscillators of the same energies.

- As v increases the harmonic oscillator model becomes less accurate and the oscillator behaves more like a classical oscillator.
- In connection with E(R) there are two representations of dissociation energy that are widely used.
 - D_e is the depth of the well. This is of interest to theoreticians.
 - D₀ is the difference between the zero point energy and the dissociation limit. This is of interest to experimentalists and represents bond energy.
 - For the harmonic oscillator:

$$D_e = D_0 + (v + \frac{1}{2})h\nu_0$$

- For a more accurate representation of the energy levels of the diatomic molecule, anharmonic corrections may be applied to the harmonic oscillator model.
- The harmonic oscillator models assumes that E(R) is parabolic, while it actually rises more steeply at small R and becomes less steep at large R.
- Therefore, the correction should be positive for $R < R_e$ and negative for $R > R_e$.
- The term $(R R_e)^n$ where n is odd will change sign in the appropriate direction at R_e .
- Since a parabola involves $(R R_e)^2$, n = 3 will give the next lowest power term.
- The higher power corrections to the harmonic oscillator model are referred to as the anharmonicity.

• Defining $x = R - R_e$, an anharmonic oscillator may be described by:

$$V(R) = \frac{1}{2}kx^2 - \frac{1}{3}k'x^3$$

$$F(R) = -kx + k'x^2$$

- For most molecules, the anharmonic correction shifts the position of the energy levels that would be populated at room temperature by about 1%.
- It still does not do a good job at describing the higher vibrational energies, because even with anharmonic corrections, the model V(R) does not level off to the dissociation limit.
- This can be addressed to some extent by adding higher order terms.

The vibrational energy may also be expressed as a power series in v + ¹/₂:

$$E_{vib}(v) = h\nu_e \left[(v + \frac{1}{2}) - x_e (v + \frac{1}{2})^2 + y_e (v + \frac{1}{2})^3 + \cdots \right]$$

where v = 0, 1, 2, ... and $\nu_e, x_e, y_e, ...$ are determined from spectroscopic data.

- ν_e, x_e, y_e, \ldots may be related to E(R).
- This is not trivial.
- A functional form that is closed for E(R) needs to be assumed.
- One particularly convenient one is the Morse potential:

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

- D_e is the well depth.
- a may be shown to be $a = \pi \nu_e (\mu/D_e)^{1/2}$.
- The Morse potential has the property of rising more steeply at small R and levels off to the dissociation limit at large R such that $V(0) = \infty$ and $V(\infty) = D_e$.
- When the Schrödinger equation is solved using the Morse potential, the eigenvalues match the sum of the first two terms in the power series expansion of E(vib) in terms of $(v + \frac{1}{2})$.
- The Morse potential is shown in Figure 7.1 and matches the true potential poorly at large R.
- Information about energy levels may be obtained experimentally by observing transitions between them with spectroscopy.

- Transitions can be induced by radiation and observed as discrete spectral lines in an absorption spectra.
- For most heteronuclear molecules, the vibrational absorption spectra lie in the near infrared in the region corresponding to (0.6-12) $\times 10^{13}$ s⁻¹ or 200 4000 cm⁻¹ or 2.5 50 μ m.
- Isolated homonuclear molecules do not exhibit vibrational spectra.
- Consider the interaction of radiation with a diatomic.
- A photon may be considered as a oscillating electric field that interacts with the electrons of the molecule (see Figure 7.2).
- A heteronuclear diatomic molecule has a dipole moment which oscillates as the molecule oscillates.



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Figure 7.2 Interaction between an electric field and an oscillating (molecular) dipole. (a) The forces exerted on the dipole by the field, which alternately tend to compress or stretch the dipole as the field direction changes. (b) Field varies much faster than the molecular vibration ($\nu >> \nu_e$); here and in the subsequent diagrams, the instantaneous forces on the dipole are indicated by arrows. (c) Field varies much slower than the molecular vibration ($\nu << \nu_e$). (d) Field and dipole oscillate at the same frequency ($\nu = \nu_e$), but 90° out of phase. As shown here, the dipole absorbs energy from the field; for a field phase 180° different, the forces are reversed and the dipole gives up energy to the field.

- Consider a photon with a wavelength greater than any dimension of the molecule.
- The electric field is uniform in space but oscillates with time.
- The component of this field that is parallel to the axis of a bond exerts an instantaneous force on the dipole that will either compress or stretch the bond.
- Whether or not this will affect the vibration will depend on whether the frequency of the photon matches the frequency of the molecular vibration.
- If the frequency of the photon is higher than that of the molecular vibration, then the field of the photon reverses in less than one period of the molecular vibration.

- If the frequency of the photon is lower than that of the molecular vibration, then the field varies slowly over many vibrational periods and would eventually effect the average value of *R* over the period of the photon, but will not change the state of the molecule.
- If the frequency of the photon closely matches the frequency of the vibration and is in the right phase with respect to the vibration then there will be energy exchange between the molecule and the field.
 - If the field is stretching the molecule while it is expanding and compresses it while the molecule is contracting, then the molecule will be excited.
 - If the field is stretching the molecule while it is contracting and compresses it while the molecule is expanding, then the molecule will be deexcited.
 - This is typical of electric dipole transitions.

- If a molecule is homonuclear, then there is no dipole and an oscillating electric field can exert no net force on the vibrating molecule.
- This why homonuclear diatomics do not have vibrational spectra.
- Classical mechanics cannot account for the quantization of molecules or spectra.
- A quantum mechanical approach is needed.
- The quantum mechanical treatment gives as the transition probability:

$$\mu_{v,v'} = \int_0^\infty \Psi_{v'}^*(R)\mu(R)\Psi_v(R)dR$$

describing the transition between v and v'.

- $\mu(R)$ is the instantaneous dipole moment of the molecule.
- Ψ_v and $\Psi_{v'}$ are the vibrational wavefunctions for states v and v'.
- In the case of a molecule with no dipole, $\mu(R)$ is always zero, and thus the transition probability is rigourously zero.
- In order to probe experimentally the vibrational levels of a homonuclear diatomic, the vibrational transitions accompanying electronic transitions need to be probed.
- Quantum mechanics also give rise to selection rules.
- Consider a heteronuclear diatomic.
- For the integral to be nonzero, in addition to $\mu(R) \neq 0$, the properties of the wavefunctions must be considered.

- The integral will be nonzero only when v and v' differ by 1.
- This gives the selection rule $\Delta v = \pm 1$.
- A heteronuclear diatomic that is described as a harmonic oscillator changes energy one vibrational quantum at a time.
- But real molecules are not harmonic.
- The vibrational wavefunctions of a real molecule may be described as a linear combination of the harmonic oscillator wavefunctions.
- This means that the transition probabilities for transitions that are not $\Delta v = \pm 1$ can be nonzero.
- However the probabilities of these other transitions are much smaller.



Figure 7.3 Schematic representation of molecular vibrational absorption spectra (neglecting rotational effects). (a) Harmonic oscillator model: $\Delta v = \pm 1$ only, all transitions at the same frequency v_0 . (b) Real diatomic molecule: The energy levels are not evenly spaced, so one can observe a band of lines beginning near v_e ; since the selection rule is not rigorous, there is a weaker band $(\Delta v = \pm 2)$ near $2v_e$, and still weaker bands at $3v_e$, $4v_e$, . . . Within each band, the intensity of a given line is proportional to the population of the initial state; the intensities as drawn here correspond to a gas with $hv_e/k_BT \approx 1.8$ (cf. Chapter 21).

- In Figure 7.3 are shown the spectrum predicted by a harmonic oscillator and the spectrum predicted by an anharmonic oscillator.
- Since the spectrum is determined by the spacing of the energy levels, the harmonic oscillator spectrum has only one line.
- The spectrum that arises from the anharmonic oscillator has a series of lines with different values of Δv .
 - The transition between v = 0 and v = 1 requires more energy than the transition between v = 1 and v = 2, therefore the line arising from the latter will be at a lower frequency than the line arising from the former.
 - Transitions for which $\Delta v = 2$ will be at a higher frequency than those for $\Delta v = 1$.

- The relative intensity of the lines contains information about the relative populations of the initial states.
- For real molecules, vibrational transitions are accompanied by changes in rotational states.
 - This means that vibrational spectra contain bands of closely spaced rotational-vibrational lines.
- As shown in Table 7.2, vibrational constants vary among molecules.
- Part of this variation is due the electronic structure of the molecule.
- Part of this variation is due to the reduced mass.
- The values shown may be corrected for differences in the reduced mass for the isotopic analogues.

			$\tilde{V}_e(\text{cm}^{-1})$	$\overline{\tilde{V}_e} x_e$	$\tilde{V_e} Y_e$	D ₀	Be	α
Molecule	μ (amu)	R_e (Å)	$(\tilde{V}_e \equiv V_e/c)$	(cm ⁻¹)	(cm ⁻¹)	(eV)	(cm ⁻¹)	(cm ⁻¹)
¹ H ₂	0.50391	1.7412	4400.39	120.815	0.7242	4.4773	60.864	3.0764
HD $(^{1}H^{2}H)$	0.67171	0.7412	3812.29	90.908	0.504	4.5128	45.663	2.0034
$D_2(^2H_2)$	1.00705	0.7412	311.70	61.82	0.562	4.5553	30.457	1.0786
First-row home	onuclear molecule	<i>es</i>						
⁷ Li ₂	3.50800	2.6725	351.44	2.592	-0.0058	1.12	0.6727	0.00704
$^{11}B_2$	5.50465	1.590	1051.3	9.4		2.9	1.212	0.014
¹² C ₂	6.00000	1.2425	1854.71	13.340	-1.172	6.24	1.8198	0.01765
¹⁴ N ₂	7.00154	1.094	2358.07	14.188	0.0124	9.7598	1.9987	0.01781
¹⁶ O ₂	7.99745	1.2075	580.19	11.98	0.0475	5.1156	1.4456	0.01593
¹⁹ F ₂	9.49910	1.409	919.0	13.6		1.604	0.8901	0.0146
Other homonu	clear molecules							
²³ Na ₂	11.4949	3.0786	159.23	0.726	-0.0027	0.75	0.1547	· 0.00079
³⁹ K ₂	19.48185	3.923	92.64	0.354		0.51	0.0562	0.00022
⁸⁵ Rb ₂	42.4558	4.20	57.28	0.96	-0.0008	0.47	0.0127	0.0000264
¹³³ Cs ₂	66.9525	4.58	41.99	0.080	0.0002	0.45		
³⁵ Cl ₂	17.48222	1.9878	559.71	2.70		2.484	0.2441	0.00153
⁷⁹ Br ⁸¹ Br	39.9524	2.2809	323.33	1.081		1.9708	0.0811	0.00032
$^{127}I_2$	63.4502	2.6666	214.52	0.607	-0.0013	1.5437	0.0374	0.00012
Hydrides								
⁷ Li ¹ H	0.88123	1.5954	1405.65	23.200	0.1633	2.429	7.5131	0.2132
¹² C ¹ H	0.92974	1.124	2859.1	63.3		3.47	14.448	0.530
¹⁶ O ¹ H	0.94808	0.9706	3735.21	82.81		4.392	18.871	0.714
¹ H ¹⁹ F	0.95705	0.9168	4139.04	90.05	0.932	5.86	20.9560	0.7958
¹ H ³⁵ CI	0.97959	1.2746	2991.09	52.82	0.2244	4.4361	10.5936	0.3072
¹ H ⁸¹ Br	0.99511	1.4145	2649.21	45.22	0.0029	3.755	8.4651	0.2333
${}^{1}H^{127}I$	0.99988	1.6090	2308.09	38.981	-0.1980	3.053	6.5108	0.1686
Other heteroni	uclear molecules							
⁷ Li ¹⁹ F	5.12381	1.5638	910.34	7.929		5.94	1.3454	0.02030
⁹ Be ¹⁶ O	5.76432	1.3310	1487.32	11.830	0.0224	4.60	1.6510	0.0190
¹¹ B ¹⁴ N	6.16351	1.281	1514.6	12.3		3.99	1.666	0.025
¹² C ¹⁴ N	6.46219	1.1720	2068.70	13.144		7.567	1.8991	0.01735
¹² C ¹⁶ O	6.85621	1.1283	2169.82	13.294	0.0115	11.09	1.9313	0.01751
¹⁴ N ¹⁶ O	7.46676	1.1508	1904.03	13.97	-0.0012	6.50	1.7046	0.0178
²³ Na ³⁵ Cl	13.8707	2.3606	366	2.05		4.25	0.2181	0.00161
³⁹ K ⁷⁹ Br	26.0850	2.8207	213	0.80	0.0011	3.925	0.0812	0.00040

Table 7.2 Vibrational and Rotational Constants of Some Diatomic Molecules

Rotations of Diatomic Molecules

- Consider the rotational behaviour of diatomic molecules.
- It will be assumed that the rotational motion can be separated from the translational and vibrational motions.
- The rigid rotator model will be used.
- The diatomic molecule will be treated a a rigid symmetric top which has two equal moments of inertia:

$$I_0 \equiv I_x = I_y \neq I_z$$

where the z axis is the bond axis.

• The Hamiltonian of the rigid symmetric top is:

$$\left| \mathbf{H}_{rot} = \frac{1}{2I_0} \mathbf{L}^2 + \frac{1}{2} \left(\frac{1}{I_z} - \frac{1}{I_0} \right) L_z^2 \right|$$

- \mathbf{L}^2 and L_z^2 are the angular momentum operators.
- The eigenvalues of \mathbf{H}_{rot} are:

$$E_{rot} = \frac{\hbar^2}{2} \left[\frac{J(J+1)}{I_0} + l_z^2 \left(\frac{1}{I_z} - \frac{1}{I_0} \right) \right]$$

• For a diatomic molecule:

$$I_z \equiv \sum_i m_e(x_i^2 + y_i^2)$$

and is very small since it is due to the electrons and the fact that the atoms have nonzero radii.

• Also:

$$I_0 = \mu R^2$$
- Therefore $I_z << I_0$.
- The energy associated with the L_z term may be either vary large or very small depending on the electronic state and is constant for that electronic state.
 - Therefore it can be included with the electronic part of the Hamiltonian.
- Thus the rotational energy of the molecule may be written as:

$$E_{rot} = \frac{J(J+1)\hbar^2}{2I_0} = \frac{J(J+1)\hbar^2}{2\mu R_e^2}$$

where J = 0, 1, 2, ... and J is the rotational quantum number.

• This equation has the form of the rigid rotator equation.

- Each energy level has a degeneracy of 2J + 1.
- The angular momentum about an axis through the center of mass is $M_J\hbar$.
- M_J has 2J + 1 allowed values, $J, J 1, \ldots, -J + 1, -J$.
- The rotational wavefunctions are the spherical harmonics $Y_{J,M_J}(\theta,\phi)$.
- The limitations on the validity of this model are due to the fact that real molecules vibrate.
- A further understanding of this may be gained by examining the rotational and vibrational periods.
- The angular momentum of diatomic molecule with fixed R is $\mu R_e^2 \omega$ and the rotational energy is $E_{rot} = \frac{1}{2} \mu R_e^2 \omega^2$.
- The eigenvalue for angular momentum is $L^2 = J(J+1)\hbar^2$.

• Combining these gives:

$$\omega = \frac{\left[J(J+1)\right]^{1/2} \hbar}{\mu R_e^2} = \left(\frac{E_{rot}}{\mu R_e^2}\right)^{1/2}$$

- Equipartion predicts an average value of kT as the rotational energy of a diatomic molecule.
 - For a hydrogen molecule at room temperature the average period is:

$$\tau_{rot} = \frac{2\pi}{\omega} = 2\pi \left(\frac{\mu R_e^2}{2k_B T}\right)^{1/2}$$

$$= 2\pi \left[\frac{(8.3676 \times 10^{-28} \text{ kg})(0.7412 \times 10^{-10} \text{ m})}{2(1.381 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})} \right]^{1/2}$$

$$= 2\pi (5.55 \times 10^{-28} \text{ s}^2)^{1/2} = 1.48 \times 10^{-13} \text{ s}$$

- The vibrational period is the reciprocal of the frequency.
 - For a harmonic oscillator model of the hydrogen molecule, this is:

$$\tau_{vib} = \nu_e^{-1} = (1.3192 \times 10^{14} \text{ s}^{-1})^{-1} = 7.58 \times 10^{-15} \text{ s}$$

- This means that a hydrogen molecule will vibrate about 20 times in the course of one rotational period.
- Thus it may be assumed that the effects of vibration will average out over the course of one rotation and an average (rigid) bond length may be assumed.
- However the rigid rotator model is inadequate for spectroscopy.

- The average R value should increase with the vibrational quantum number v.
- Rigorously, R_e^{-2} should be replaced by the value of R^{-2} averaged over a vibrational period and

$$\langle R^{-2} \rangle_v < R_e^{-2}$$

• The rotational energy levels can be approximated by:

$$E_{rot} = J(J+1)hcB_v = J(J+1)hc\left[B_e - \alpha_e\left(v + \frac{1}{2}\right) + \dots\right]$$

where

$$B_e = \frac{h}{4c\mu R_e^2},$$

 α_e is a constant, B_v is the rotational state v, and B_e is the rigid rotator value.

• For H₂:

 $\frac{1.0546 \times 10^{-34} \text{ J s}}{8\pi (2.9979 \times 10^{-8} \text{ m/s})(8.368 \times 10^{-28} \text{ kg})(0.7412 \times 10^{-10} \text{ m})^2}$

$$= B_e = 60.9 \text{ cm}^{-1}$$

which agrees well with experiment.

- α_e is determined experimentally to be \approx 3.0 cm⁻¹.
- Measurements of B_e are used to determine R_e .
- Molecules with large R_e have small B_e .
- The rigid rotator model assumes that the nuclei are point masses.
- This assumption breaks down if the electronic state of the molecule does not have zero angular momentum relative to the nuclei.

• Consider the eigenvalue equation for the symmetric top:

$$E_{rot} = J(J+1)hcB_v + M_J^2hc(A-B_v)$$

where $A \equiv \hbar/4\pi c I_z$.

• The quantum numbers J and M_J are defined by:

$$\left|\mathbf{J}\right|^2 = J(J+1)\hbar^2 \text{ and } J_z = M_J\hbar$$

which are the square and z component of the total angular momentum of the molecule.

- Electronic and nuclear motions contribute to J.
- J_z is almost entirely due to the angular momentum of electrons about the bond axis.

- L, the orbital electronic angular momentum, and S can couple with each other and the nuclear angular momentum in many ways.
- Consider the simplest case.
 - For most electronic states, the orbital electronic angular momentum is strongly coupled to the bond axis.
 - Only the *z* component is quantized.
 - Therefore:

$$\left|L_z\right| = \Lambda\hbar$$

• If the electronic state is a singlet state with **S** = 0 (i.e. all the electrons are paired), L_z is the only contribution to J_z .

• Therefore:

$$\left|J_{z}\right| = \Lambda \hbar \text{ and } \left|M_{J}\right| = \Lambda$$

• The eigenvalue equation becomes:

$$E_{rot} = J(J+1)hcB_v + \Lambda^2 hc(A - B_v)$$

where

$$\Lambda = 0, 1, 2, \dots$$
 and $J = \Lambda, \Lambda + 1, \Lambda + 2, \dots$

- Although the second term is part of the electronic hamiltonian, it is important to consider the restrictions that it places on allowed quantum numbers.
- Rotational transitions occur if the molecule has a dipole.
- A homonuclear diatomic does not have a pure rotational spectrum.

• For heteronuclear diatomics, the rotational spectrum has a selection rule for electric dipole transitions of

$$\Delta J = \pm 1$$

• Therefore, the only allowed pure rotational transitions have:

$$\Delta E = 2J'hcB_v$$
 or $\overline{\nu} = 2J'B_v$

where J' is the quantum number of the upper state.

- The rigid rotator model predicts a pure rotational spectrum consisting of a series of evenly spaced lines, beginning with $\overline{\nu} = 2B_v$ and continuing in intervals of $2B_v$ (see Figure 7.4).
- The series is usually found in the far infrared or in the microwave region.



Figure 7.4 Pure rotational absorption spectrum of a diatomic molecule. Given the selection rule $\Delta J = \pm 1$, there is a series of lines with the constant wavenumber spacing $2B_{\nu}$. The intensities of the lines are proportional to the populations of the initial states, and as drawn here correspond to a gas with $B_{\nu}hc/k_BT \approx 0.1$ (cf. Chapter 21).

- The spacing of rotational lines is one of the best methods of determining bond lengths.
- Generally the spectrum is best resolved if the gas is at low pressure.
- Usually the frequency of radiation is varied and absorbance determined from the power loss from the source to the detector.
- The first spectra were obtained by using a prism between the source and the sample to vary the wavelength and a photographic plate to detect the photons transmitted.
- With current technology, it is possible to obtain spectra very accurately and in great detail.
- To a first approximation, lines in a rotational spectra are equally spaced. and B_v may be estimated as half the spacing in wavenumbers.

Spectra of Diatomic Molecules

- When $h\nu$ equals the energy difference between two energy levels a transition may be induced.
- In the microwave and far infrared regions, pure rotational spectra may be observed.
- In the near and middle infrared regions, vibrational spectra may be observed.
 - Vibrational transitions are accompanied by rotational transitions.
- Radiation in the visible and ultraviolet region may cause electronic transitions.
 - These are usually accompanied by vibrational and rotational transitions.
- Higher energies such as those in the X-ray region may cause excitation of inner core electrons.



re 7.5 Energy levels of the N₂ molecule. (a) Electronic states, with vibrational levels (v = 0, 1, 2, ...) shown in the lowest three. [Not n is the $W^3\Delta_u$ state; this state has about the same minimum energy as the $B^3 \prod_g$ (see Table 7.6), but its R_e is not known.] The energy zero ground electronic-vibrational state ($X^1\Sigma_g^+$, v = 0). After W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. 1227 (1965). (b) Rotational structure of the two lowest vibrational levels of the ground state; the energy zero is the same as in (a).

- There are two main classes of spectroscopy:
 - In emission spectroscopy, the sample is excited (thermally, electrically, or in some other way), then the emitted radiation is observed as it relaxes to an equilibrium state.
 - If the sample is excited by radiation, then it is fluorescence spectroscopy.
 - In absorption spectroscopy, the sample is placed between the light source and the detector.
 - As the sample absorbs radiation, the molecules are excited to higher levels.
 - The absorbance is determined from the measurement at the detector of the attenuation of the original light source.
- Consider now the basic components of a spectrometer.

- The sample:
 - May be liquid or gas.
 - Must be in a holder that is transparent to the radiation being used.
 - For UV below 2000 Å, air is opaque and the spectrum must be taken in a vacuum.
- Radiation source:
 - There are number of light sources, depending on the wavelength of interest.
 - For UV and visible ranges, light sources include tungsten filament lamps and electrical discharges.
 - For IR, heat rods of a refractory material are used.
 - In the microwave region, Klystron tubes are used.
 - Radiowave generators are used at longer wavelengths.

- Optical system:
 - The purpose of the optical system is to select the wavelength of the radiation.
 - This may be done by using either a prism or a diffraction grating as a dispersing element.
 - It is also possible to use a tunable laser as the light source.
 - Radio and microwaves are also tunable.
 - If the light source is tunable, a dispersing element is not needed.
- Detector:
 - The first spectrophotometers used photographic emulsions on plates with the intensity of a line determined by the extent of darkening.

- (Continued:)
 - More recent spectrophotometers use electronic means of detection with photosensitive semiconductors, photoelectric cells, thermocouples and bolometers, and crystal diodes.
 - Computerized postprocessing is used to give the relationship between intensity and wavelength or wavenumber.
- A transition between bound states of a molecule has a definite energy and frequency ($\Delta E = h\nu$).
- There are a number of factors that lead to the observation of non-zero line widths.
 - The natural line width is the consequence of the uncertainty priniciple.

- Doppler broadening is due to the fact that molecules are moving randomly with some moving toward or away from the detector.
- Pressure broadening is due to the perturbation of energy levels do to interactions with other molecules.
 - Pressure broadening can be controlled by controlling the density and pressure of the sample.

Simultaneous vibration-rotation spectra

- For most diatomic molecules in the ground electronic state, pure vibrational transitions are forbidden.
- The selection rules are:

$$\Delta v = \pm 1$$
 and $\Delta J = \pm 1$

 $(\Delta v = \pm 1$ is only approximately true for real oscillators.)



Figure 7.6 The infrared spectrum of HCl vapor associated with transitions (a) $v=0 \rightarrow v=1$ and (b) $v=0 \rightarrow v=2$. The individual rotation vibration lines are all doublets because of the presence of the isotopic species H³⁵Cl and H³⁷Cl; the former is the more intense. Number above spectral lines specify ΔJ . From C. F. Meyer and A. A. Levin, *Phys* Rev. 34, 44 (1929).



Figure 7.7 Schematic representation of a vibration-rotation band in the infrared spectrum of a diatomic molecule in a Σ electronic state. Each line in the band corresponds to a transition between a lower level v'', J'' and an upper level v', J', with J' = J'' - 1 in the P branch and J' = J'' + 1 in the R branch. The lines are labeled with the running number m, defined in Eq. 7.29. The band origin \tilde{v}_0 corresponds to the forbidden transition v'; $J' = 0 \leftrightarrow v''$; J'' = 0. The spectrum is drawn for $B_{v'} < B_{v''}$ so that the band converges to a head (not shown) in the R branch.

- Some representative spectra are shown in Figures 7.6 and 7.7.
- For each vibrational transition, there is an entire family of vibration-rotation lines.
- The lines are nearly equally spaced with a gap in the middle.
 - This gap corresponds to the position of a hypothetical line with $\Delta J = 0$.
 - Such a transition is forbidden for a Σ state.
 - The position of this missing line is referred to a the null line or band origin with wavelength $\overline{\nu}_0$.
 - The group of lines with $\overline{\nu} < \overline{\nu}_0$ is the *P* branch.
 - The group of lines with $\overline{\nu} > \overline{\nu}_0$ is the R branch.
- By convention, a single prime denotes the upper state, while a double prime denotes the denotes the lower state.

- The P branch corresponds to J' = J'' 1
- The R branch corresponds to J' = J'' + 1
- The wavenumbers associated with the transitions are:

$$\overline{\nu} = \frac{E' - E''}{hc} = \overline{\nu}_0 + B'_v J' (J' + 1) - B''_v J'' (J'' + 1)$$

where

$$\overline{\nu}_0 = \frac{E'_{vib} - E''_{vib}}{hc}$$

• $\overline{\nu}$ may be rewritten as:

$$\overline{\nu} = \overline{\nu}_0 + (B'_v + B''_v)m + (B'_v - B''_v)m^2$$

where m = -J'' for the *P* branch and m = J'' + 1 in the *R* branch.

- For a rigid rotator, $B'_v = B''_v$, and the lines are evenly spaced.
- For a real rotator, B_v increases with v, therefore $B'_v < B''_v$ for any real infrared emission.
- This means that the quadratic term is negative and the spaces between successive lines decreases with increasing *m*.
- There can exist some value $\overline{\nu}$ such that the spacing would decrease to zero.
- At values of m above this mean that $\overline{\nu}$ would start to increase with m
- This gives rise to the band head in the R branch, usually at very high values of m which means that it is usually difficult to observe.

- If the ground state is not a Σ state, then ΔJ = 0 transitions (Q branch) are allowed in addition to ΔJ = ±1.
- For the *Q* branch:

$$\overline{\nu}_Q = \overline{\nu}_0 + (B'_v + B''_v)J + (B'_v - B''_v)J^2$$

- Since the spacing between the energy levels increase smoothly, the is no band head.
- The lines in the Q branch are very close together and, when not resolved, appear as a single intense line.
- Molecules may also scatter radiation.
- Radiation leaves the molecule in a different direction than before it interacted with the molecule.

- This is a two step process.
 - First the photon is absorbed, leaving the molecule in an unstable state that is not a quantum state, i.e. a forced oscillation.
 - Secondly, a photon is emitted in any direction that returns the molecule to a stable state.
 - Unlike fluorescence or phosphorescence there is no stable state in between.
 - Fluorescence involves excitation to a stable, but excited, electronic state of the same multiplicity.
 - This excited state may last a few picoseconds, then emit a photon to a lower state (usually the ground state) of the same multiplicity.
 - Phosphorescence involves excitation to a stable, but excited, electronic state of different multiplicity.

- This excited state can last for hours, then emit a photon to a lower state (usually the ground state) of the original multiplicity.
- In the case of scattering, if the incident and scattered photon have the same energy, it is elastic and is classified as Rayleigh scattering.
- If the incident and scattered photons have different energy, then the process is Raman scattering and it gives rise to a spectrum.
- A schematic spectrum is shown in Figure 7.8
- The incident light is a monochromatic beam with photons of a single wavelength.
- The resulting scattering is observed by a detector placed at right angles to the incident beam.
- Rayleigh scattering will be the dominant process.



Figure 7.8 Schematic Raman spectrum of a diatomic gas. Three vibrational bands are shown, each with its rotational fine structure. The intense line at the exciting frequency v_{exc} is due mainly to Rayleigh scattering; in the other bands the center line is the unresolved Q branch.

- All other lines are the result of Raman scattering.
- If ν_{exc} is the incident frequency, then the frequency ν observed for the line is due to a transition with

$$\Delta E = h(\nu_{exc} - \nu)$$

- This frequency shift $\nu_{exc} \nu$ is independent of ν_{exc} and depends only the energy of the transition.
- If the frequency shift is to a lower energy $(\nu_{exc} > \nu)$, then the lines are Stokes lines.
- If the frequency shift is to a higher energy $(\nu_{exc} < \nu)$, then the lines are anti-Stokes lines.
- Associated with each vibrational transition are bands of closely spaced lines due to the accompanying rotational transitions.

- At room temperature most molecules are in the lowest vibrational state.
- Therefore the most likely transition is with $\Delta v = +1$ and the Stokes bands will be stronger than the anti-Stokes lines.
- The Raman scattering is due to the interaction of the dipole of the molecules with the electric field associated with the photon.
- The incident light beam of frequency ν_{exc} has an electric field that oscillates with the same frequency.
- This causes an induced dipole in the molecule because the electrons in the molecule tend to follow this field.
- The total molecular dipole is $\mu_0 + \mu_{ind}$ where

$$\mu_{ind} = \alpha \mathbf{E} = \alpha \mathbf{E}_0 \cos 2\pi \nu_{exc} t$$

- In this case E is the oscillating field and α is the molecular polarizability.
- The previous equation may be rewritten as:

$$\mu_{n'n} = \int \dots \int \psi_{n'}^* \nu_0 \psi_n d\tau + \mathbf{E} \int \dots \int \psi_{n'}^* \alpha \psi_n d\tau$$

where $\mu_{n'n}$ is the probability of a transition between states n and n'.

- Consider a transition with $\nu_{n'n} \equiv |E_{n'n} E_n|/h$
- This rovibrational transition may occur in two ways:
 - The first case is when there is a permanent dipole and absorption and emission in the infrared or microwave occurs in the usual way.
 - The second case is the Raman scattering process and is due to the second term of the equation.

- Raman scattering can occur if the scattered light has the frequency $\nu_{exc} \pm \nu_{n'n}$.
- This means that if $\nu_{exc} >> \nu_{n'n}$, then the scattered light is in the same region of the electromagnetic spectrum as the incident light.
- The second integral term will vanish if α does not change, which occur only if the molecule has zero polarizability.
- All diatomic molecules, both homonuclear and heteronuclear, have non-zero polarizability, therefore all diatomic molecules can have Raman spectra.
- Because the mechanisms are different, the selection rules differfor Raman spectroscopy.
- The vibrational selection rules are the same.

- The harmonic oscillator model predicts a vibrational selection rule of $\Delta v = \pm 1$, but due to the anharmonicity of real oscillators, overtones are observed for $\Delta v = \pm 2, \pm 3 \dots$
- In Raman spectroscopy, it is possible to have a pure rotational spectrum with $\Delta v = 0$.
- The rotational selection rules depend on the nature of the electronic state.
 - For diatomic molecules in a Σ state, the selection rules for Raman spectroscopy are:

$$\Delta J = 0, \pm 2$$

Therefore, each band will have an S branch (ΔJ = 2), an O branch with ΔJ = −2, and a Q branch with ΔJ = 0.

- For diatomic molecules in an electronic state with $\Lambda \neq 0$, the rotational selection rule is $\Delta J = 0, \pm 1, \pm 2$ and Pand R branches are observed in additon to O, Q, and S.
- Raman spectroscopy provides access to transitions that are forbidden in infrared spectroscopy.
- Its main drawback is that the transitions are weak with low intensity.
 - This is because they are second order in the dipole moment and depend on the fourth order term of the matrix elements.
- However the frequency range of Raman spectra is determined by the frequency of the incident radiation, so any convenient exciting line can be observed.
 - Usually ν_{exc} is in the visible or ultraviolet range.

- It is possible to increase the intensity of lines in Raman spectra by using an exciting frequency that is resonant with the absorption frequency.
- Surface-enhanced Raman spectroscopy, involves having deposited the molecule of interest on the surface of a metal.
 - The conduction electrons of the metal further polarize the electrons of the scattering molecule.
- Another important type of spectroscopy involves electronic transitions.
 - Transitions are generally observed in the visible and ultraviolet regions of the electromagnetic spectrum.
 - A given electronic transition is associated with a series of bands, one for each of the accessible vibrational transitions (Figure 7.9).



Figure 7.9 A typical electronic absorption spectrum of a gas undergoing a rapid reaction. The spectrum shows the presence of three diatomic molecules, CH, NH, and CN, none of which is stable under ordinary conditions. The numbers are wavelengths, in angstroms, of the band heads. This spectrum was taken with what is called a "medium dispersion" prism spectrograph, exhibiting the spectral range from about 200 to 700 nm (2000 to 7000 Å) on a 10-in. photographic plate. The photograph is printed in negative so absorption lines appear white. From D. W. Cornell, R. S. Berry, and W. Lwowski, J. Am. Chem. Soc. **88**, 544 (1966).
- Within each band are contributions for each possible rotational transition associated with that vibrational transition.
- Electronic spectra have *band heads*.
 - A band head is a sharply defined edge on one side of the band.
 - As in the case of vibrational-rotational spectra, the band head is formed when successive lines become so close to each other as to "pile" up on each other.
 - The rotational selection rule is $\Delta J = 0, \pm 1$ except in the case where both the initial and final electronic states are Σ states when $\Delta J = 0$ is forbidden.
 - However, in constrast to the case with vibrational-rotational spectra, B'_v and B''_v can be very different in value with the result that m does not have to be large at the band head (see Figure 7.10).



Figure 7.10 Structure of an electronic band spectrum. The upper part of the figure is what is known as a *Fortrat diagram*, showing the parabolic curves describing the three branches according to Eqs. 7.29 and 7.30. Below are shown the corresponding spectral lines of the three branches (which would be superimposed in the actual spectrum). The spectrum illustrated has a head in the *P* branch, at about m = -9.

- The reason B'_v and B''_v are different has to do with the position of the minimum and the shape of the potentials corresponding to the different electronic states.
 - The position of the minimum will affect the moment of inertia.
- There are no vibrational selection rules in electronic transitions.
 - Selection rules arise from the coupling of rotational and electronic angular momentum, both of which are not affected by vibration.
- Instead vibrational transitions are dominated by the Franck-Condon Principle.
 - The Franck-Condon Principle is a consequence of the fact that nuclei are heavier than electrons and move more slowly.



Figure 7.11 Illustration of the Franck–Condon principle. (a) Stable excited state: Any v' - v'' transition is possible, but the most likely are between states having maximum values of $|\psi_{vib}|^2$ (cf. Fig. 4.4) at nearly the same *R*. Here, for example, an excitation from v'' = 0 is most likely to yield v' = 3, and the state v' = 0 is most likely to decay to v'' = 2, as indicated by the vertical arrows. (b) Two ways to obtain a continuous spectrum: excitation to an unstable state (A), or to a stable state (B) at a level above its dissociation limit.

- According to the Franck-Condon Principle an electronic transition occurs so quickly that the electrons do not have time to move.
- This can be illustrated by a vertical line (constant *R*) between vibrational levels of the two electronic curves (See Figure 7.11).
- Rigorously this violates the uncertainty principle.
- Instead the quantum mechanical wavefunctions for the relevant vibrational states need to be considered.
 - The wavefunction gives rise to the density distribution and the most probable value of R
 - For low v values, R is near the position of the minimum of the potential.
 - As v increases, the most probable values of R are near the vibrational turning points.

- How well the most probable values of *R* match affects the intensity of the transition.
- When the Franck-Condon principle predicts an upper state above the dissociation limit for the electronically excited curve, a continuous absorption spectrum is observed.
- Selection rules do affect which electronic transitions are allowed.
 - Total angular momentum must be conserved.
 - In the case of a diatomic molecule, this consists of contributions from nuclear rotation, orbital angular momentum, and electronic spin.
 - All these couple with one another.
 - Spin-orbit coupling can be ignored in some cases.

- For symmetric molecules, properties of the wavefunction must also be considered.
- An electronic transition changes the parity of the wavefunction.
 - A wavefunction with even parity (gerade or g) will be transformed to a wavefunction with uneven parity (ungerade or u).
 - Similarly, a wavefunction with uneven parity (*ungerade* or *u*) will be transformed to a wavefunction with even parity (*gerade* or *g*).
- At the same time, the symmetry of the wavefunction must be preserved.
 - A wavefunction must be either symmetric or antisymmetric.

- Isotope effects are important in spectroscopy.
 - Affect spacing of both vibrational and rotational lines.
 - For vibrational lines, the spacing is proportional to $(1/\mu)^{1/2}$.
 - For rotational lines, the spacing is proportional to $(1/\mu)$.
 - Note that μ is always less than the mass of the lighter atom in the diatomic.
- When multiple isotopic analogs are present in a sample, each will have its own spectrum, often overlapping with the spectra of the other isotopic analogues present.