Luleå technical university
Physics
Hans Weber, 2009

Molecules

and

thermal motion – Statistical physics

Molecules

Electron structure and chemical binding

The binding that keeps atoms together in molecules is a quantal effect, as are most of the properties of atoms.

Ionic binding arises when the ionisation energies of the atoms are very different, and the atom with the largest ionisation energy is not a noble gas but has room for another electron in the valence shell. The quantum states for the electrons when the atoms come close are about the same as for the free atoms. One or several valence electrons will jump over to the lower lying state with higher ionisation energy.

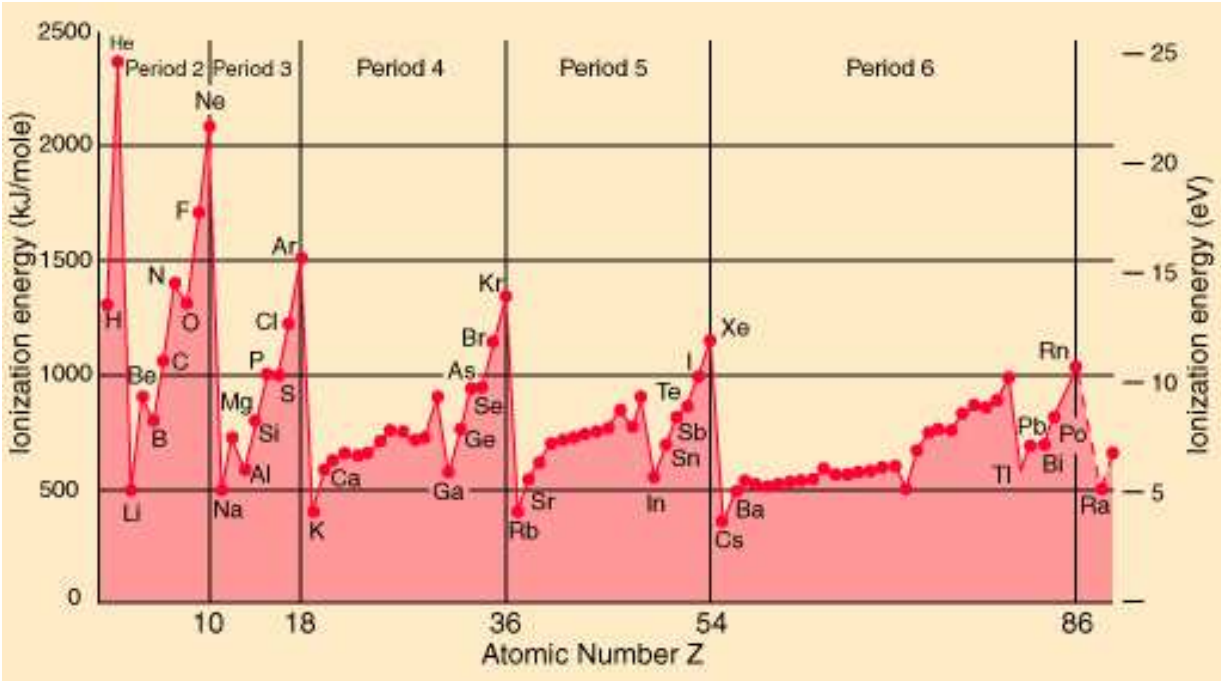

Figure 1: Ionisation energies, the points on the abscissa indicates closed shell. 1 kJ/mol = .010364 eV/atom. The picture is taken from hyperphysics.phy-astr.gsu.edu

Covalent binding appears when the ionisation energies are similar. The state that the electrons are in when the atoms are near each other are distributed over both atoms. Roughly, the wavefunctions are linear combinations of the two wavefunctions that are located around each atom when they are separated. If the phase factors of the states are chosen such that wavefunctions have the same phase in the region in between the atoms, then the two linear combinations are

$$\psi_1 = C(\phi_1 + \phi_2)/,\ \psi_2 = C(\phi_1 - \phi_2)/\sqrt{2}. \tag{1}$$

where ϕ_1 is the wavefunctions for one valence electron of atom 1 and ϕ_2 of for one valence electron of atom 2. The first one ψ_1 has an energy lower then for separated atoms, hence it is bonding. The second ψ_2 has an increased energy and is thus anti bonding. In most cases we have that one electron from each atom will occupy the bonding wavefunction. Qualitatively, these functions can be correct, but if the Schrödinger equation is solved, one will find that the states are somewhat modified. This can be illustrated by the one dimensional systems with two delta potentials or two wells close to each other. Linear combination of atomic orbitals (LCAO) is the commonly used term for states like ψ_1 and ψ_2.

The total energy of the molecule as function of the distance r between the two atoms will depend on which of the states ψ_1 and ψ_2, that the valence electrons occupy. In figure 2 the total energy are shown for the two cases that there is an electron in the lower level or that there is an electron in the upper level. Both energies are large and positive at small distances, due to the repulsion between the nuclei and the squeezing of the other electrons, rising their kinetic energies. Normally there are two electrons in the bonding

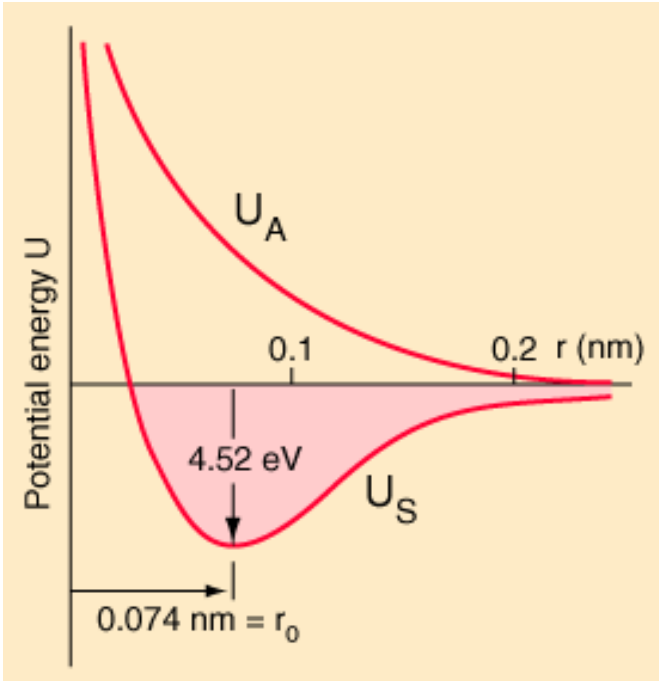

Figure 2: The total energy of the neutral Hydrogen molecule (H_2) as function of the distance between the atoms. The lower curve corresponds to one electron put into the bonding state and the upper having one electron the anti-bonding state. The minimum in the energy of the lower curve will approximately give the bond length of the chemical bond between the two atoms

state, which approximately doubles the binding energy. If all valence states were doubly occupied but the states ϕ_1 and ϕ_2 which were singly occupied before the atoms came close, then all the valence states may now be maximally occupied, except for the anti bonding state, which on the other hand is lifted high up in energy.

If the valence states have $l > 0$, then we have a chose which states to put into the LCAO wavefunctions. There are states with different m quantum numbers to chose from and even linear combinations of them. It is the linear combination with a positive interference of the atomic states in between the atoms that gives the bonding wavefunction. The binding becomes stronger the larger amplitude the atomic wavefunctions have in this region. This indicates how the wavefunctions are chosen. For example, one does not expect that

$$\Phi_{2,1,m} = R_{2,1}(r)Y_{1,m}, \quad m = \pm 1, \tag{2}$$

will enter into the LCAO directly as they do not stretch out in any specific direction, where the other atom may be placed. The following functions are more promising in this respect, as they stretch out along the x, y and z directions,

$$\Phi_{2,1,x} \quad = \quad (\Phi_{2,1,-1} - \Phi_{2,1,1})/\sqrt{2} = R_{2,1}(r)\sqrt{\frac{3}{4\pi}}\frac{x}{r}, \tag{3}$$

$$\Phi_{2,1,y} = i(\Phi_{2,1,-1} + \Phi_{2,1,1})/\sqrt{2} = R_{2,1}(r)\sqrt{\frac{3}{4\pi}}\frac{y}{r}, \tag{4}$$

$$\Phi_{2,1,z} = \Phi_{2,1,0} = R_{2,1}(r)\sqrt{\frac{3}{4\pi}}\frac{z}{r}. \tag{5}$$

Note, that these functions are eigenstates to the atomic Hamiltonian just as much as the states in (2) are. When states are degenerate, any linear combination of them will also be an eigenstate. The angular dependence of these wavefunctions are presented in figure 3. It is clear from the figure that the wavefunctions $\Phi_{2,1,x}$, $\Phi_{2,1,y}$ and $\Phi_{2,1,z}$ is equally

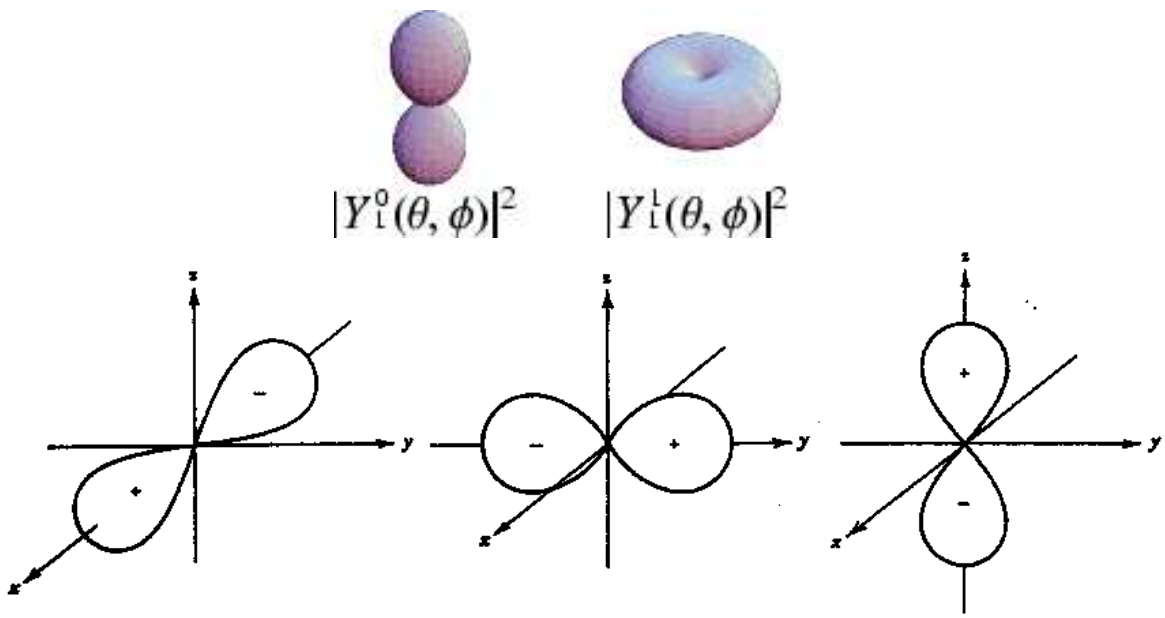

Figure 3: The top figures show the angular dependence of $Y_{l,m}$, for $l = 1$, $m = 0, \pm 1$, below are shown the angular dependence for $\Phi(2,1,x)$, $\Phi(2,1,y)$ and $\Phi(2,1,z)$.

much on one side of the atom as the opposite side. For many atoms the valence states belong to several different l-values. For example, for bor, carbon, nitrogen and oxygen both the 2s and the 2p are valence states. In such cases, it is often a linear combination of the s- and p-states that make up the atomic states ϕ_i in the linear combinations used to approximate the states in the molecule. These so called hybrid states give an explanation for many features of B, C, N and O atoms in molecules. The sp^3 orbitals

$$\chi^{(1)} = (\Phi_{2,0,0} + \Phi_{2,1,x} + \Phi_{2,1,y} + \Phi_{2,1,z})/\sqrt{4} \tag{6}$$

$$\chi^{(2)} = (\Phi_{2,0,0} + \Phi_{2,1,x} - \Phi_{2,1,y} - \Phi_{2,1,z})/\sqrt{4} \tag{7}$$

$$\chi^{(3)} = (\Phi_{2,0,0} - \Phi_{2,1,x} + \Phi_{2,1,y} - \Phi_{2,1,z})/\sqrt{4} \tag{8}$$

$$\chi^{(4)} = (\Phi_{2,0,0} - \Phi_{2,1,x} - \Phi_{2,1,y} + \Phi_{2,1,z})/\sqrt{4} \tag{9}$$

explain the bindings of the carbon atom in e.g. CH_4. The sp^3-states are tetrahedrally oriented which gives the position of the hydrogen atoms in CH_4.

The double bond of C_2H_4 involve the sp^2-hybrid states,

$$\chi^{(1)} = \Phi_{2,1,z} \tag{10}$$

$$\chi^{(2)} = \frac{1}{\sqrt{3}}\Phi_{2,0,0} + \sqrt{\frac{2}{3}}\Phi_{2,1,x} \tag{11}$$

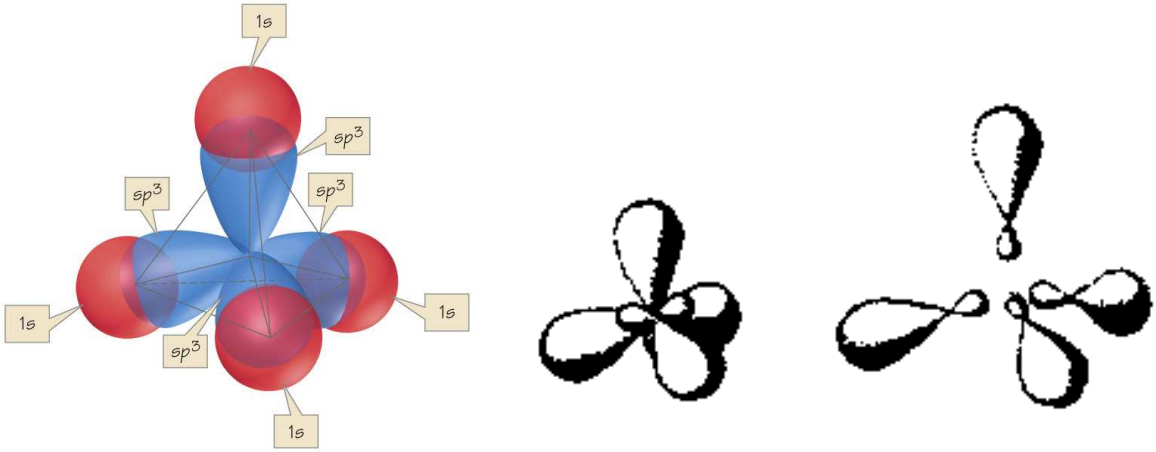

Figure 4: To the left a hybrid orbital of s- and p-states, to the right the sp^3 orbitals for CH_4 are shown. The four sp3 hybrid orbitals of the C atom (purple) have been modified to eliminate the small lobes directed toward the centre of the structure; they are not involved in orbital overlaps. The hydrogen orbitals are 1s (red). The molecular geometry is tetrahedral; the s bond angles are 109.5^o.

$$\chi^{(3)} = \frac{1}{\sqrt{3}}\Phi_{2,0,0} - \frac{1}{\sqrt{6}}\Phi_{2,1,x} + \frac{1}{\sqrt{2}}\Phi_{2,1,y} \tag{12}$$

$$\chi^{(4)} = \frac{1}{\sqrt{3}}\Phi_{2,0,0} - \frac{1}{\sqrt{6}}\Phi_{2,1,x} - \frac{1}{\sqrt{2}}\Phi_{2,1,y}, \tag{13}$$

which are illustrated in figure 5. It is the $\chi^{(1)}$ that together with the one of the hybrid states make up the double bond.

The dynamics of the atoms – diatomic molecules

The energy of the valence electrons decreases as the distance between the atoms decrease until the atoms come close enough the energy start increase. For a diatomic molecule this give rise to the potential energy $V(r)$ which is a function of the distance r between the atoms. This potential energy can be used to calculate the relative motion of the two atoms if that motion is slow enough, so that the motion of the electrons is 'fast'[1] enough to adjust to the varying positions of the atoms. The Schrödinger equation for this relative motion of the atoms is

$$\left(-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right) u_E = E u_E. \tag{14}$$

The reduced mass $\mu = M_1 M_2/(M_1 + M_2)$ and M_1, M_2 are the masses of the atoms. As the potential only depends on $r = |\mathbf{r}|$ the hamilton operator is rotationally invariant. The wavefunction u_E that represents the state of atoms can be written as

$$u_E(\mathbf{r}) = \frac{w_{n,l}(r)}{r} Y_{lm}(\theta, \phi) \tag{15}$$

where the function w_{nl} is a solution to

$$-\frac{\hbar^2}{2\mu}\frac{d^2 w_{nl}}{dr^2} + \left(\frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r)\right) w_{nl}(r) = E w_{nl}(r). \tag{16}$$

[1] 'fast' means here that the energy differences between different electron states is much larger than the energy differences between the states of the relative motion of the atoms

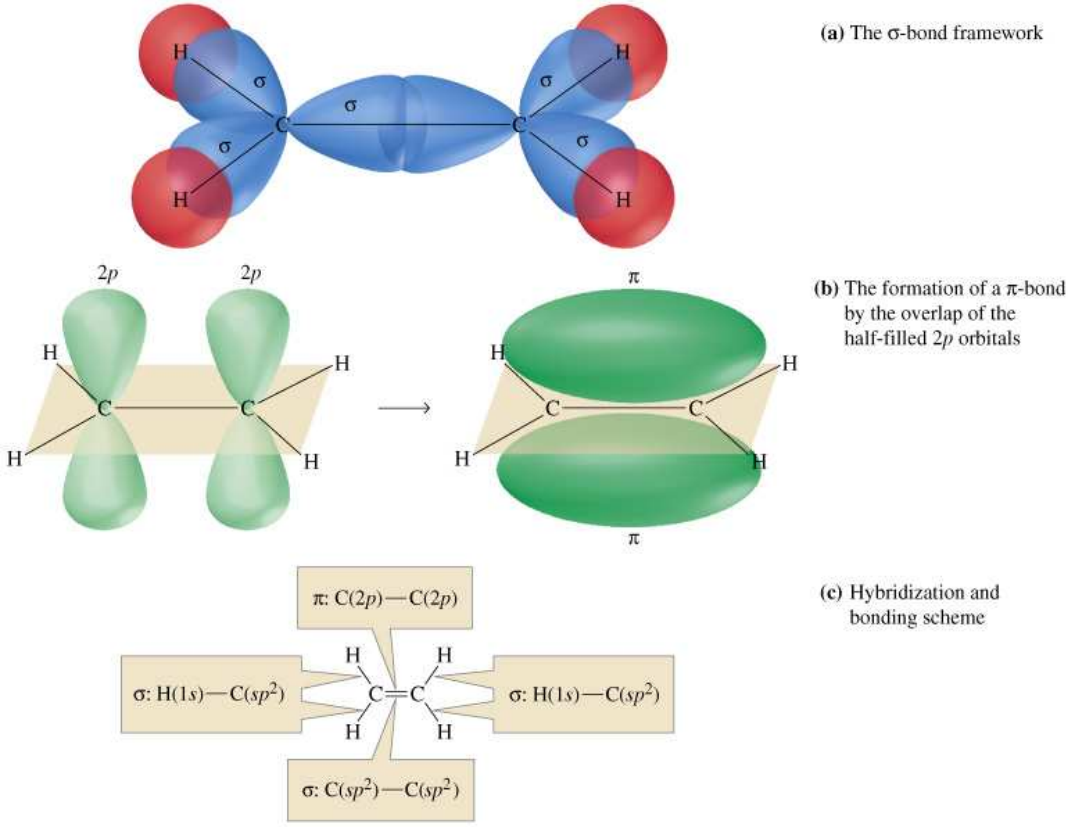

Figure 5: Carbon double bond in C_2H_4. The stronger bond in the double bond consist of the bonding linear combination between the two different $\chi^{(2)}$ from the two carbon atoms. The other bond is given by the bonding linear combination of the two $\chi^{(1)}$ orbitals that are perpendicular to the plane of the molecule.

Let us approximate the potential energy

$$V(r) \approx -V_0 + \frac{1}{2}k\left(r - r_0\right)^2. \tag{17}$$

For $l = 0$ we get a spectrum

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right),\ n = 0, 1, 2, \ldots \tag{18}$$

This is shown by changing to the variable $r' = r - r_0$. As previously we have that $\omega = \sqrt{k/\mu}$. For HCl and CO is the energy difference between the states $\hbar\omega = 0,36$ eV and $0,27$ eV, respectively. When you increase l, the centrifugal term changes the radial part w_{nl} only marginally and the energy increases with

$$E_l = \frac{\hbar^2 l(l+1)}{2I}, \tag{19}$$

where $I = \mu r_0^2$ is the moment of inertia of the molecule. The total energy is then given by

$$E_{nl} = E_n + E_l = \hbar\omega\left(n + \frac{1}{2}\right) + \frac{\hbar^2 l(l+1)}{2I}. \tag{20}$$

The radial factor w_{nl} appearing in the expression in the wavefunction is for $l = 0$

$$w_{n,0}(r) = H_n\left(\frac{r - r_0}{b}\right) exp\left(-\frac{(r - r_0)^2}{b^2}\right) \tag{21}$$

where $b = \sqrt{\hbar/m\omega}$. For $l \neq 0$ the function w_{nl} is approximately the same as w_{n0}. The energy difference between states with different l values are much less than $\hbar\omega$. For a molecule with two different kinds of atoms all integer values of $l = 0, 1, 2, \ldots$ [2] why the spectra has the appearance shown in figure 6.

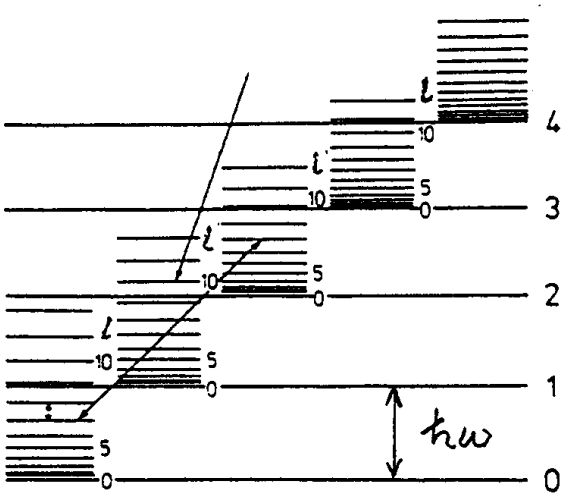

Figure 6: Energy levels for a diatomic molecule. The long horisontal lines mark the $l = 0$ levels, with the vibrational quantum number n to the right. The states with higher l-values (the rotational bands) give a dense sequence of states for each n-value. The arrows shows possible transitions.

It is also possible for the electrons to be in different levels, giving additional excited states. The energy difference between the different electronic levels are normally many times bigger than $\hbar\omega$.

When the molecule emits or absorbs a photon it changes from one state to another. The energy difference between the states is equal to the energy of the photon. This process is the quantum physics counterpart to the emission or reception of electromagnetic waves of a dipole antenna. The intensity of the transition between the states A and B is proportional to

$$| < A|x|B > |^2 + | < A|y|B > |^2 + | < A|z|B > |^2. \tag{22}$$

We see that the states must have different parities, else there will be no dipole radiation. Other types of radiation may be possible but its intensities are several orders of magnitude lower.

The parity of the states of the type $R_{nl}Y_{lm}$ is given by $(-1)^l$. For dipole radiation it is also so that l can only be changed by one unit (the total angular momentum is conserved).This results in the rule $\Delta l = \pm 1$. In the approximation that the radial motion is that of an harmonic oscillator, there is also the rule that $\Delta n = 0, \pm 1$.

The energies of the emitted photons in transitions with $\Delta n = 0$, are $\hbar^2 l_1/I$, where l_1 is the angular momentum quantum number for the initial state. The final state l_2-value is $l_1 - 1$ as the energy of the molecule is lowered when a photon is emitted. Accordingly the photon energies are

$$\frac{\hbar^2}{I}, \quad 2\frac{\hbar^2}{I}, \quad 3\frac{\hbar^2}{I}, \quad 4\frac{\hbar^2}{I}, \quad \ldots \tag{23}$$

[2] If the atoms belong to the same nucleide the nuclear spin will influence which angular momentum values appear.

The photon energies in transitions with $\Delta n = -1$ are $h\nu \pm \hbar^2 l_1/I$ depending on if l is lowered or raised by one unit. There therefore two series of spectral lines,

$$E_{\text{foton}} = h\nu + \frac{\hbar^2}{I}, \quad h\nu + 2\frac{\hbar^2}{I}, \quad \ldots \tag{24}$$

and

$$E_{\text{foton}} = h\nu - \frac{\hbar^2}{I}, \quad h\nu - 2\frac{\hbar^2}{I}, \quad \ldots . \tag{25}$$

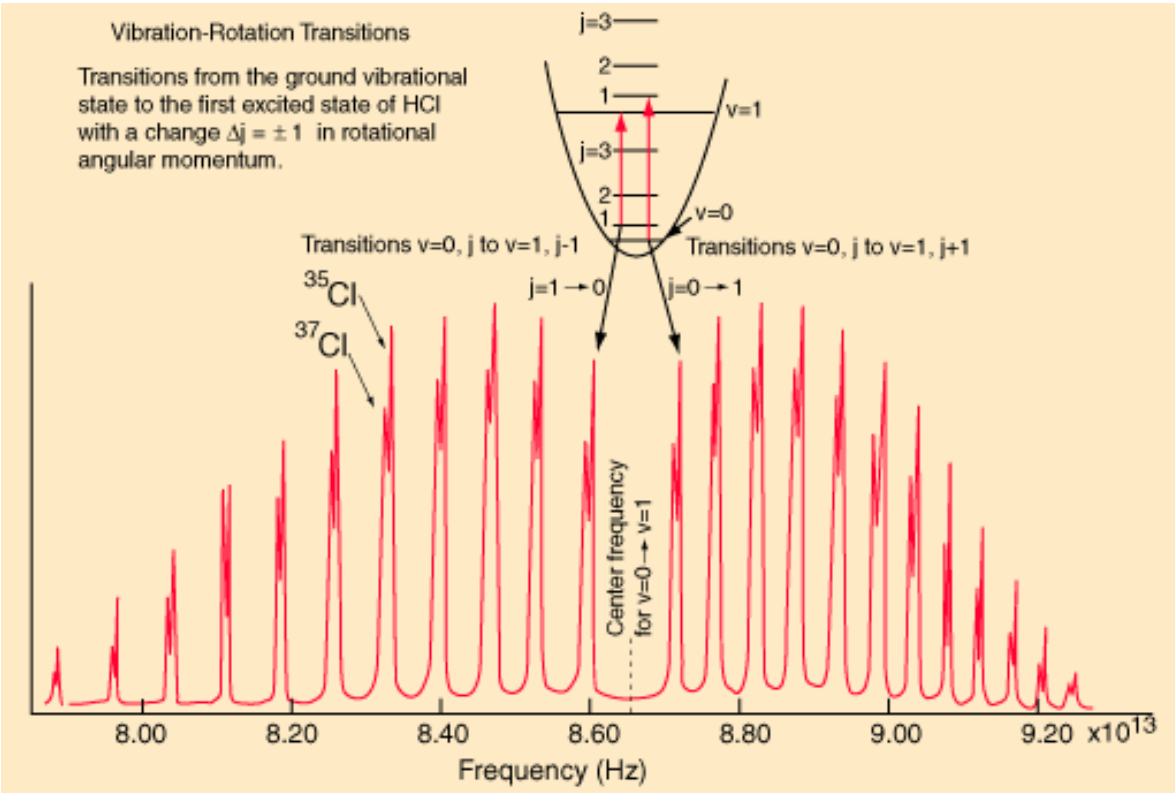

Figure 7: The absorption lines shown involve transitions from the ground to first excited vibrational state of HCl, but also involve changes in the rotational state. The rotational angular momentum changes by 1 during such transitions. If you had a transition from j=0 in the ground vibrational state to j=0 in the first excited state, it would produce a line at the vibrational transition energy. As observed, you get a closely spaced series of lines going upward and downward from that vibrational level difference. The splitting of the lines shows the difference in rotational inertia of the two chlorine isotopes Cl-35(75.5The picture is taken from hyperphysics.phy-astr.gsu.edu

Excersises from McMurry, Quantum Mechanics

4.10 The observed rotational spectrum of the hydrogen chloride molecule consists of a set of equally spaced lines produced by the emission (or absorption) of electric dipole radiation. If the spacing is 20.68 cm^{-1}, calculate the moment of inertia of the HCl molecule. What are the energies of its four lowest rotational energy levels? Assuming that the moment of inertia of a diatomic molecule is of the form $I = mr^2$, estimate the mean separation r of the atom in the molecules. (Here $m = m_H m_{Cl}/(m_H + m_{Cl})$ is the reduced mass of the molecule. Use the mass of the isotope ^{35}Cl: $m_{Cl} = 35m_H$.

4.11 Light can be scattered from molecules that have no permanent electric dipole moment through first inducing such a moment. If there is no change in the rotational state of the molecule, the light is scattered with no change in its frequency (**Rayleigh scattering**). However, the rotational state of the molecule may be changed from one characterised by the quantum number l to one corresponding to $l' = l \pm 2$ (**Raman scattering**). Show that in this case the frequency of the scattered light differs from that of the incident light by $\Delta\nu = B(4l + 6)$, where B is a constant characteristic of the molecule, and $l = 0, 1, 2, ...$

5.5 Treat a simple pendulum of mass 0.001 kg and period 1 s quantum mechanically, and calculate its zero-point energy. If it is oscillating with amplitude 0.01 m, use classical mechanics to find its energy. If this energy is an eigenvalue E_n, estimate the value of n.

5.6 From the position of the broad vibrational spectral line in hydrogen chloride, centred on 2886 cm^{-1}, calculate the zero-point energy of the $H^{35}Cl$. (See Problem 4.10 for the mass of the molecule containing this isotope of chlorine.) Calculate the amplitude of the classical oscillator with this energy. (for comparison, the mean separation of the atoms in the molecule was calculated in Problem 4.10.)

5.8 Draw a sketch to illustrate the vibrational energy levels of a diatomic molecule, for $n = 0$ and $n = 1$, showing the fine structure due to rotational levels from $l = 0$ to 4. Indicate on your diagram the electric dipole transitions that produce

(a) the purely rotational millimetre and sub millimetre spectrum.

(b) the vibrational-rotational lines in the fundamental band.

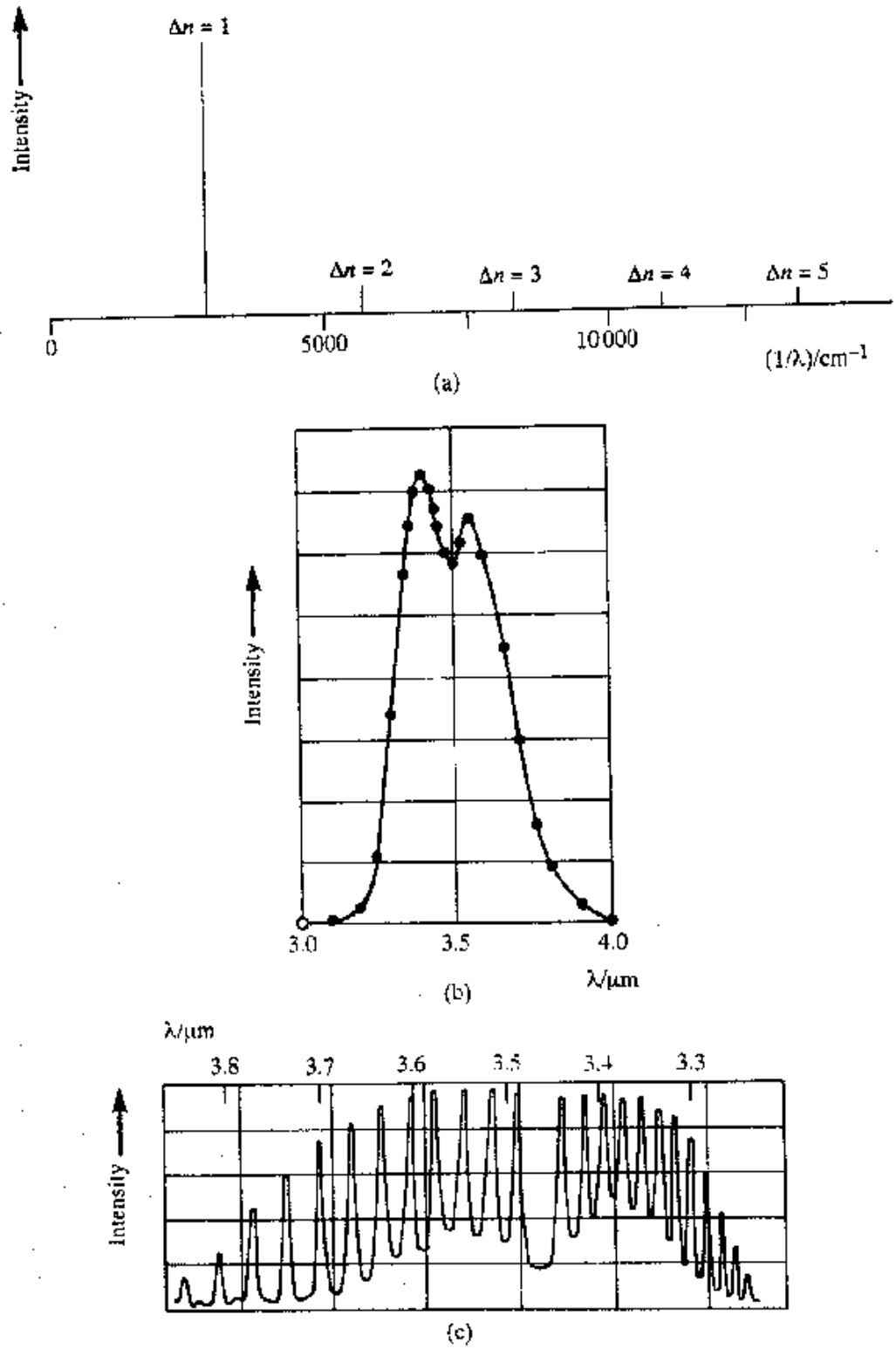

Figure 5.4 The infrared absorption spectrum of HCl (adapted from Figures 30–32, pp. 53–55, of [4]). (a) At very low resolution the intense line is the fundamental band, and the higher bands (which arise from anharmonicity) actually fall off in intensity about five times more rapidly than indicated. (b) At slightly higher resolution the fundamental band appears to be split into two. (c) At still higher resolution the rotational fine structure of the fundamental band is visible.

Figure 8: Figure from McMurry, Quantum Mechanics