Molecular Structure and Spectra

How are molecules and solids held together?

**Bonds**
- **Ionic:** Coulomb attraction of a positive and a negative ion
- **Covalent:** sharing of electrons between two atoms
- **Dipole-Dipole:** electric forces between
  - two polar atoms/molecules
  - one polar and one non-polar atoms/molecules
  - two non-polar atoms/molecules
- **Metallic:** electrons shared by all the atoms in a solid (not discussed until chap. 10)

The type of bonding also plays a big role in determining the structure of solids.

To be stable, a molecule or solid must have lower energy than the constituents.
**Ionic Bonding**

An electron is transferred from one atom to the other to create two ions, one positive and one negative, which requires energy. The Coulomb force provides the attraction and lowers the energy of the system. The repulsion of the electron clouds increases the energy if the atoms get too close. So there is a minimum in the energy at a particular separation.

![Diagram showing ionic bonding](image)
Ionic Bond Energy

One important measure of the stability of the bond is $U(r)$, the total potential energy of the system compared to separate atoms, which is a function of the separation of the ions.

This energy comes from three contributions:

- $E_{ion}$ is the energy to transfer an electron from one atom to the other, which is positive. It is the difference between the ionization energy of one atom (the energy required to remove the highest energy electron from the atom) and the electron affinity of the other atom (the binding energy of the electron added to the other atom).
- $E_{Coulomb}$ is the energy due to the attractive electric force, which is negative.
- $E_{exclusion}$ is the energy due to the repulsion of the electron clouds, which is positive. This repulsion is not due to the Coulomb force between the electrons, but is instead due to the Pauli exclusion principle. We can’t have overlap between two electrons in the same state, that is, with the same quantum numbers. This results in an energy cost which increases steeply as the overlap of the electron orbitals increases.

\[
U(r) = E_{Coulomb}(r) + E_{ex}(r) + E_{ion} = -\frac{ke^2}{r} + \frac{A}{r^n} + E_{ion}
\]
Since alkali metals (Group I) have the lowest ionization energies and halogens (Group VII) have the highest electron affinities, the strongest ionic bonds are formed from one alkali and one halogen, NaCl for example.

<table>
<thead>
<tr>
<th>Alkali metal</th>
<th>Ionization energy (eV)</th>
<th>Halogen</th>
<th>Electron affinity (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>5.39</td>
<td>F</td>
<td>3.40</td>
</tr>
<tr>
<td>Na</td>
<td>5.14</td>
<td>Cl</td>
<td>3.62</td>
</tr>
<tr>
<td>K</td>
<td>4.34</td>
<td>Br</td>
<td>3.36</td>
</tr>
<tr>
<td>Rb</td>
<td>4.18</td>
<td>I</td>
<td>3.06</td>
</tr>
<tr>
<td>Cs</td>
<td>3.89</td>
<td>At</td>
<td>2.8</td>
</tr>
<tr>
<td>Fr</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Data from Handbook of Chemistry and Physics, 75th ed. (New York: Chemical Rubber Co., 1994).
$U(r)$, the total potential energy of the system
Covalent Bonding
Electrons are shared by two atoms.
The energy decrease is not from Coulomb interaction but a purely quantum-mechanical effect.

As an example, let’s look at two square wells.

If one electron is shared between the wells, it will be equally likely to be found in either one.

Either a symmetric or anti-symmetric wave function will give the same probabilities if the wells are separated.
However, if the wells are close together the symmetric and anti-symmetric wave function will give different probabilities and the energy of the states are now different.

Notice that the symmetric wave function is getting to look like the ground state for one well and the anti-symmetric state is getting to look like the first excited state.

The symmetric state is lower in energy than the anti-symmetric state if the wells are close together.

The symmetric state has a high probability of finding the electron between the wells while the anti-symmetric state has a low probability.

The idea of two degenerate states being split into two different energy states by an interaction will be a general theme.

We can add a second electron to the ground state of the two well system as long as they have opposite spins (so $S=0$) so the total wave function is anti-symmetric. Two electrons in the anti-symmetric state would need the same spin ($S=1$).
If we replace the square wells with protons, our Hamiltonian will be

\[
H_{op} = \frac{p_{op}^2}{2m} + ke^2 \left( -\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_0} \right).
\]
Symmetric and anti-symmetric combinations of the ground state solutions to Schrödinger’s equation for two separations of the protons:
At large separation of the protons, the energy of both the symmetric and anti-symmetric solutions is the same as the energy of the ground state of one hydrogen atom, \(-13.6\, \text{eV}\).

As the protons separation is decreased, the symmetric and anti-symmetric solutions split in energy. At small separations, the anti-symmetric solution looks like the first excited state of helium \((Z=2, n=2, E=-13.6\, \text{eV})\) while the symmetric solution looks like the ground state \((Z=2, n=1, E=-54\, \text{eV})\).

To both of these we need to add the energy due to the repulsion of the protons, \(U_p\).

The result gives a minimum in energy for the symmetric state, but no minimum for the anti-symmetric state.

Symmetric solution - bonding state
Anti-symmetric solution - non-bonding state
We can add a second electron to the symmetric state as long as it has the opposite spin so that the total wave function is anti-symmetric, so \( S=0 \) in the ground state, a singlet state.

To add a second electron to the anti-symmetric state, the spins must be aligned, so \( S=1 \), a triplet state.
Hydrogen is s-bonded since both electrons are in s states.

Flourine is p-bonded since both electrons are in p states.
<table>
<thead>
<tr>
<th></th>
<th>$N_2$</th>
<th>$O_2$</th>
<th>$F_2$</th>
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<tbody>
<tr>
<td>2$p$ electrons (total)</td>
<td>6</td>
<td>8</td>
<td>10</td>
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<tr>
<td>Binding energy (eV)</td>
<td>9.8</td>
<td>5.1</td>
<td>1.6</td>
</tr>
<tr>
<td>Equilibrium separation (nm)</td>
<td>0.11</td>
<td>0.12</td>
<td>0.14</td>
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</table>
Hydrogen fluoride, HF
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Dissociation energy (eV)</th>
<th>Equilibrium separation (nm)</th>
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<tr>
<td>HF</td>
<td>5.90</td>
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<td>HCl</td>
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</tr>
<tr>
<td>HI</td>
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<tr>
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<td>0.156</td>
</tr>
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<td>KCl</td>
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<td>0.267</td>
</tr>
<tr>
<td>Molecule</td>
<td>Bond angle (°)</td>
<td>Molecule</td>
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<tr>
<td>----------</td>
<td>---------------</td>
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</tr>
<tr>
<td>H₂O</td>
<td>104.5</td>
<td>NH₃</td>
</tr>
<tr>
<td>H₂S</td>
<td>93.3</td>
<td>PH₃</td>
</tr>
<tr>
<td>H₂Se</td>
<td>91.0</td>
<td>AsH₃</td>
</tr>
<tr>
<td>H₂Te</td>
<td>89.5</td>
<td>SbH₃</td>
</tr>
</tbody>
</table>
Hybridization - mixing of atomic orbitals

\[ \psi_1 = \frac{1}{2} (s + p_x + p_y + p_z) \]

\[ \psi_2 = \frac{1}{2} (s + p_x - p_y - p_z) \]

\[ \psi_3 = \frac{1}{2} (s - p_x - p_y + p_z) \]

\[ \psi_4 = \frac{1}{2} (s - p_x + p_y - p_z) \]
<table>
<thead>
<tr>
<th></th>
<th>Linear</th>
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<th>Tetrahedral</th>
<th>Trigonal Bipyramidal</th>
<th>Octahedral</th>
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<tr>
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<td>one $s$</td>
<td>one $s$</td>
<td>one $s$</td>
<td>one $s$</td>
</tr>
<tr>
<td>mixed</td>
<td>one $p$</td>
<td>two $p$</td>
<td>three $p$</td>
<td>three $p$</td>
<td>three $p$</td>
</tr>
<tr>
<td>Hybrid orbitals</td>
<td>two $sp$</td>
<td>three $sp^2$</td>
<td>four $sp^3$</td>
<td>five $sp^3d$</td>
<td>six $sp^3d^2$</td>
</tr>
<tr>
<td>formed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unhybridized</td>
<td>two $p$</td>
<td>one $p$</td>
<td>none</td>
<td>four $d$</td>
<td>three $d$</td>
</tr>
<tr>
<td>orbitals</td>
<td></td>
<td></td>
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<tr>
<td>remaining</td>
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<td>Orientation</td>
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<td><img src="example.com" alt="Trigonal Bipyramidal" /></td>
<td><img src="example.com" alt="Octahedral" /></td>
</tr>
</tbody>
</table>
Dipole-Dipole Bonding (two polar molecules)

The electric field from a dipole is

$$ \vec{E}_d = k \left( \frac{\vec{p}}{r^3} - \frac{3(\vec{p} \cdot \vec{r})\vec{r}}{r^5} \right) $$

If the magnitude of the dipole moment is expressed as $p = qa$ and for $r \gg a$, then

$$ E_d = \frac{kqa}{r^3} = \frac{kp}{r^3} $$

The potential energy of a second dipole in the electric field of the first is

$$ U = -\vec{p} \cdot \vec{E}_d $$

The potential energy is proportional to $1/r^3$ and the force is proportional to $1/r^4$. The force between polar molecules is generally a few tenths of an electron volt. If hydrogen is involved its called hydrogen bonding. This force is responsible for polar molecules condensing to liquids and solids at relatively high temperatures, e.g. water. Directionality of bonding results in ordered crystals.
**Induced Dipole (one polar, one non-polar molecule)**

The degree to which a non-polar molecule will become polarized in an electric field depends on its polarizability, $\alpha$, such that $\vec{p} = \alpha \vec{E}$.

So if a non-polar molecule is near a polar molecule, it will have an induced dipole moment and there will be a potential energy,

$$U = -\vec{p}_2 \cdot \vec{E}_d = -\alpha \vec{E}_d \cdot \vec{E}_d = -\alpha \vec{E}_d^2 = -\alpha \kappa^2 p_1^2 / r^6$$

and a force which is proportional to $1/r^7$, so it is weak and very short-range.

**Fluctuating Dipole (two non-polar molecules)**

Molecules which have no permanent dipole moment still have an instantaneous dipole moment that fluctuates quickly. If the fluctuations of two neighboring non-polar molecules (e.g. He) becomes correlated, there is a net attractive force and a negative energy. Just as above, the potential energy is proportional to $1/r^6$ and the force is proportional to $1/r^7$. This force is called the van der Waals force or the London dispersion force.
Rotational Energy Levels

We will consider only diatomic molecules for simplicity, but the ideas extend to polyatomic molecules.

\[ E = \frac{L^2}{2I} = \frac{l(l + 1)\hbar^2}{2I} = l(l + 1)E_{or} \]

\[ E = 12E_{or} \]

\[ E = 6E_{or} \]

\[ E = 2E_{or} \]

\[ E = 0 \]

\[ I = m_1r_1^2 + m_2r_2^2 = \mu r_0^2 \]

\[ \mu = \frac{m_1m_2}{m_1 + m_2} \]
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Equilibrium separation $r_0$ (nm)</th>
<th>Frequency $f$ (Hz)</th>
<th>$E_{or}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>0.074</td>
<td>$1.32 \times 10^{14}$</td>
<td>$7.56 \times 10^{-3}$</td>
</tr>
<tr>
<td>$Li_2$</td>
<td>0.267</td>
<td>$1.05 \times 10^{13}$</td>
<td>$8.39 \times 10^{-5}$</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.121</td>
<td>$4.74 \times 10^{13}$</td>
<td>$1.78 \times 10^{-4}$</td>
</tr>
<tr>
<td>$LiH$</td>
<td>0.160</td>
<td>$4.22 \times 10^{13}$</td>
<td>$9.27 \times 10^{-4}$</td>
</tr>
<tr>
<td>$HCl^{35}$</td>
<td>0.127</td>
<td>$8.97 \times 10^{13}$</td>
<td>$1.32 \times 10^{-3}$</td>
</tr>
<tr>
<td>$NaCl^{35}$</td>
<td>0.251</td>
<td>$1.14 \times 10^{13}$</td>
<td>$2.36 \times 10^{-5}$</td>
</tr>
<tr>
<td>$KCl^{35}$</td>
<td>0.279</td>
<td>$8.40 \times 10^{12}$</td>
<td>$1.43 \times 10^{-5}$</td>
</tr>
<tr>
<td>$KBr^{79}$</td>
<td>0.294</td>
<td>$6.93 \times 10^{12}$</td>
<td>$9.1 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Symmetric molecules such as $H_2$ or $O_2$ have no electric dipole moment. The vibration or rotation of these molecules does not involve a changing dipole moment and there is no vibrational-rotational electric dipole absorption or radiation for these molecules.
**Vibrational Energy Levels**

Since the curve of potential energy is close to a parabola near the minimum, a diatomic molecule has quantized energy levels similar to a harmonic oscillator.

\[ E_v = (v + \frac{1}{2})\hbar f = (v + \frac{1}{2})\hbar \omega = (v + \frac{1}{2})\hbar \sqrt{\frac{K}{\mu}} \]

More accurately, we have an anharmonic oscillator and the spacings of the levels are not quite equal.
Since the separation of the atoms is larger in the excited state than the ground state, the moment of inertia is different and the rotational energies are different. Since the shape of the potential energy curve is different, the force constant is different and the vibrational energies are different.
Emission Spectra

When a molecule makes a transition from one vibrational state to another, the change in the vibrational quantum number must be $+1$ or $-1$, so the energy of the photon is $hf$. When the molecule makes a transition from an excited electronic state to a lower energy state, it may also change its vibrational state, but in this case there is no selection rule for changes in $\nu$. 
If a molecule does not have a permanent dipole moment (e.g. any homonuclear diatomic), it can’t change rotational states by emitting a photon. If it does have a permanent dipole moment, it can make a purely rotational transition and emit a photon as long as the change in the rotational quantum number is +1 or -1.

All molecules can change rotational states while making transitions between electronic energy levels as long as the change in the rotational quantum number is +1 or -1.
Absorption Spectra

At room temperature, most molecules are in the electronic and vibrational ground states but in a rotationally excited state. These molecules can absorb an infrared photon and transition to the first vibrationally excited state. However, they must also change rotational states such that $\Delta l = +1$ or $\Delta l = -1$.

\[
E_{v=0,l} = \frac{1}{2} hf + l(l + 1)E_{0r}
\]
\[
E_{v=1,l+1} = \frac{3}{2} hf + (l + 1)(l + 2)E_{0r}
\]
\[
E_{v=1,l-1} = \frac{1}{2} hf + (l - 1)lE_{0r}
\]

\[
\Delta E_{l\rightarrow l+1} = hf + 2(l + 1)E_{0r}
\]
\[
\Delta E_{l\rightarrow l-1} = hf - 2lE_{0r}
\]

\[
n(E_l) = g(E_l)e^{-E_l/kT}
\]
\[
n(E_l) = (2l + 1)e^{-[hf/2 + l(l+1)E_{0r}]/kT}
\]
\[
n(E_l) \propto (2l + 1)e^{-l(l+1)h^2/2kt}
\]
\[
l_{\text{max}} = \frac{1}{2} \left[ \sqrt{\frac{4kT}{\hbar^2}} - 1 \right]
\]
Interaction of radiation with molecules

(a) Fluorescence
(b) Resonance absorption
(c) Stimulated emission
(d) Rayleigh scattering
(e) Compton effect
(f) Raman scattering
(g) Photoelectric effect
**Fluorescence**
Absorption of a photon (or some other process) puts molecule into electronically excited state. Photon(s) are given off as molecule transitions to lower electronic state.

**Resonance Absorption**
Excited state is first excited state, so emitted photon is same energy as absorbed photon.
**Rayleigh Scattering**
Scattering of a photon from a molecule in which there is no change in frequency. The intensity of the scattered radiation is proportional to $f^4$ (its why the sky is blue).

**Compton Scattering**
Energy of photon is large enough to ionize the molecule, so electron ends up as free particle. Conservation of energy and momentum gives the Compton shift in frequency.
**Raman Scattering**

The scattered photon leaves the molecule in a higher (lower) vibrational or rotational state and therefore the scattered photon has a lower (higher) frequency. The energy of the incident photon does not need to match a characteristic energy of the molecule.

**Photoelectric effect**

Absorption of a photon and ionization of the molecule. For a molecule this can’t conserve energy and momentum without another particle being involved.
**Stimulated Emission** - The presence of a photon with an energy matching the transition energy, increases the probability of emission. The emitted photon goes in the same direction as the existing photon and with the same phase.

Calling the lower state $I$ and the upper state $2$, the energy difference between the two states is $E_2 - E_1 = hf_{12}$. The probability per unit time of absorption if the system is in state $I$ is $B_{12}u(f)$, where $B_{12}$ is called the Einstein coefficient of absorption and $u(f)$ is the energy density at a frequency $f$.

The probability per unit time of spontaneous emission if the system is in state $2$ is $A_{21}$. The lifetime of the state is $t_s = 1 / A_{21}$.

The probability per unit time of stimulated emission at a frequency $f$ is $B_{21}u(f)$, where $B_{21}$ is called the Einstein coefficient of stimulated emission.

If the two states have the same degeneracy and are in equilibrium, then

$$\frac{N_2}{N_1} = e^{-\frac{(E_2 - E_1)}{kT}} = e^{-\frac{hf}{kT}}.$$
In equilibrium the number of absorptions per unit time must be equal to the number of emissions, both spontaneous and stimulated.

\[ N_1 B_{12} u(f) = N_2 (A_{21} + B_{21} u(f)) \]

Rearranging to solve for \( u(f) \) gives

\[
u(f) = \frac{A_{21}}{B_{21}} \left( \frac{N_1 B_{12}}{N_2 B_{21}} - 1 \right) = \frac{A_{21}}{B_{21}} \left( \frac{B_{12}}{B_{21}} e^{hf/kT} - 1 \right).
\]

Recall Planck's law that says \( u(f) = \frac{8\pi hf^3}{c^3} e^{hf/kT} - 1 \).

This implies that \( B_{21} = B_{12} \) and \( \frac{A_{21}}{B_{21}} = \frac{8\pi hf^3}{c^3} \).

Notice that the ratio of spontaneous emission to stimulated emission is proportional to \( f^3 \).
When \( hf \gg kT \), spontaneous emission dominates over stimulated emission.
When \( hf \ll kT \), stimulated emission is the dominant de-excitation mechanism.
Lasers

Light Amplification by Stimulated Emission of Radiation

To get functioning laser in a medium (gas or crystal), you need more photons emitted than absorbed. So you need more stimulated emission than absorption. But the relative probability coefficients of the two are equal, so you need to get a much higher population in the excited state, $N_2 > N_1$, so that $N_2 B_{21} u(f) > N_1 B_{12} u(f)$.

Since in thermal equilibrium the lower state is more populated than the upper state, this is called a population inversion.