Molecular Structure

Outline

1. Introduction

2. Chemical Bonds in Molecules
   - Ionic Bond
   - Covalent Bond
   - Other Mechanisms

3. Spectroscopy of Diatomic Molecules

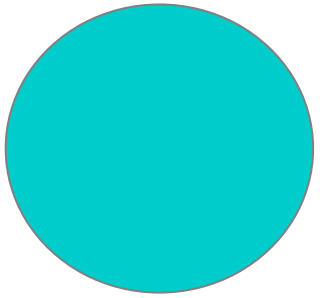
4. Summary

Introduction

Introduction

individual atoms

molecule



Molecule – the smallest constituent of a substance that retains its chemical properties

Examples:

hydrogen $1s^1$ — **H_2** — two protons sharing two bonding electrons

sodium chloride $1s^2 2s^2 2p^6 3s^1$ $1s^2 2s^2 2p^6 3s^2 3p^5$ — **NaCl** — Na^+ and Cl^- ions interacting via Coulomb interaction; Pauli exclusion

Types of Chemical Bonds

Main four types of chemical bonds

- ionic (e.g. NaCl)
- covalent (e.g. H_2)
- dipole-dipole (e.g. between HF molecules)
- metallic (e.g. copper)

Note. Usually chemical bonds are not entirely of one type, but are rather some combinations of various types.

Chemical Bonds (I)

The Ionic Bond

When do Atoms Form a Molecule?

Two atoms form a stable bound molecule if it results in lowering the total energy of the system

$$E_{\text{molecule}} < E_{\text{system of individual atoms}}$$

General mechanism

Trade-off between

attractive interaction between atoms/ions

and

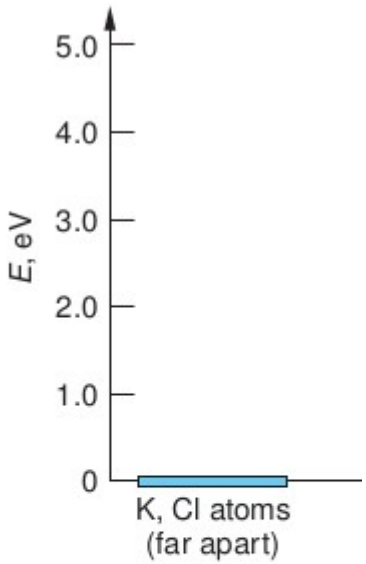
properties of electrons (Pauli Exclusion Principle)

resulting in formation of an equilibrium configuration (molecule).

Ionic Bond. Example: KCl

Stable potassium chloride molecule is formed if

$$E_{\text{KCl}} < E_{\text{K and Cl atoms (far apart and at rest)}}$$



Illustrations: Tipler's textbook

potassium (K) $\underbrace{1s^2 2s^2 2p^6 3s^2 3p^6}_{\text{Ar}}\, 4s^1$

chlorine (Cl) $1s^2 2s^2 2p^6 3s^2 3p^5 \longrightarrow$ short of one electron to "close" the orbital

---

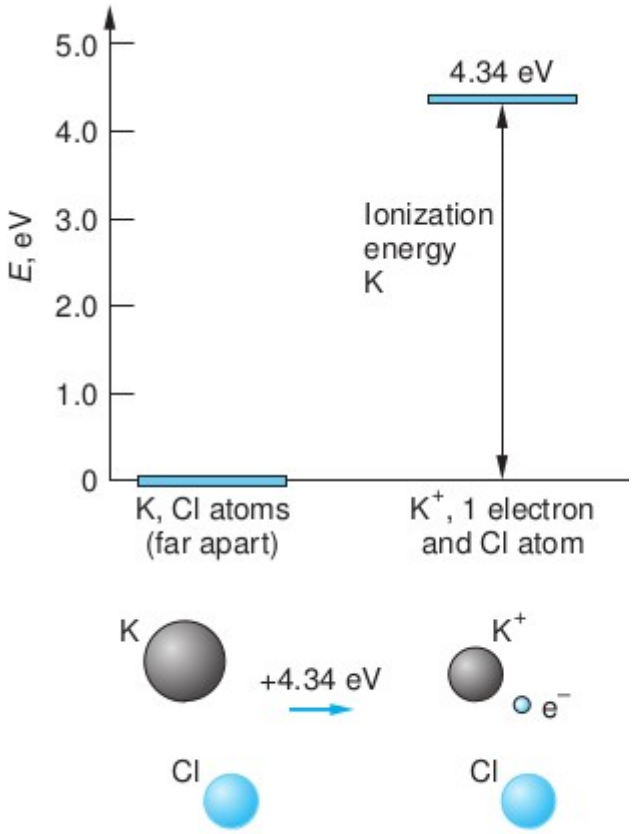
Note. In the following we always analyze the **ground state** of the molecule.

Ionic Bond. Example: KCl

Phase I *ionization of the potassium atom*
[needs energy 4.34 eV]

K⁺ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0$

Cl $1s^2 2s^2 2p^6 3s^2 3p^5$

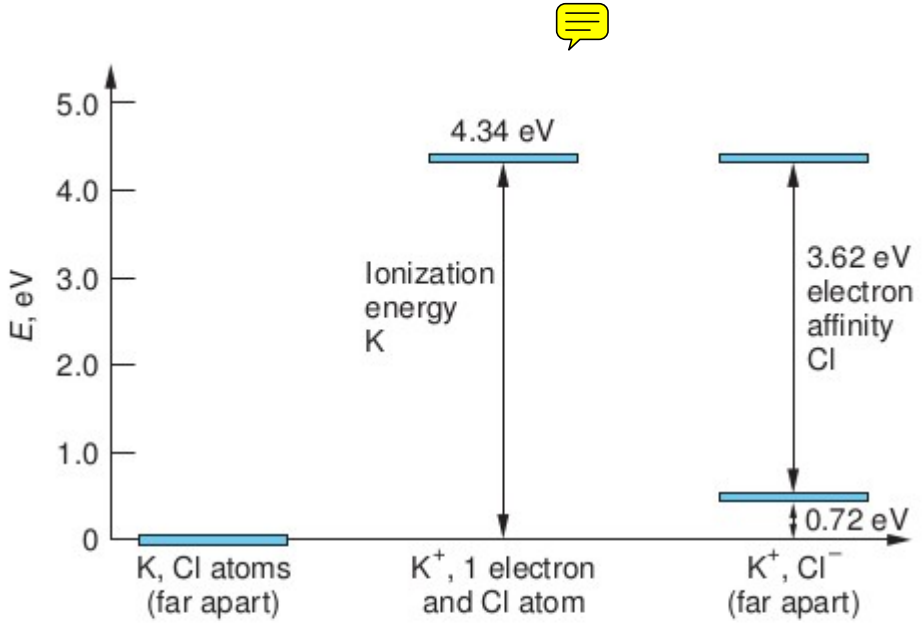


Ionic Bond. Example: KCl

Phase II *acquisition of the electron by the chlorine atom*
[releases energy 3.62 eV – **electron affinity** of Cl]

K^+ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0$

Cl^- $1s^2 2s^2 2p^6 3s^2 3p^6$



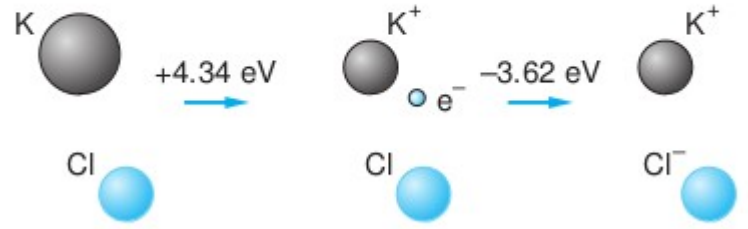


Table 9-1 Ionization energies of alkali metal atoms and electron affinities of halogen atoms

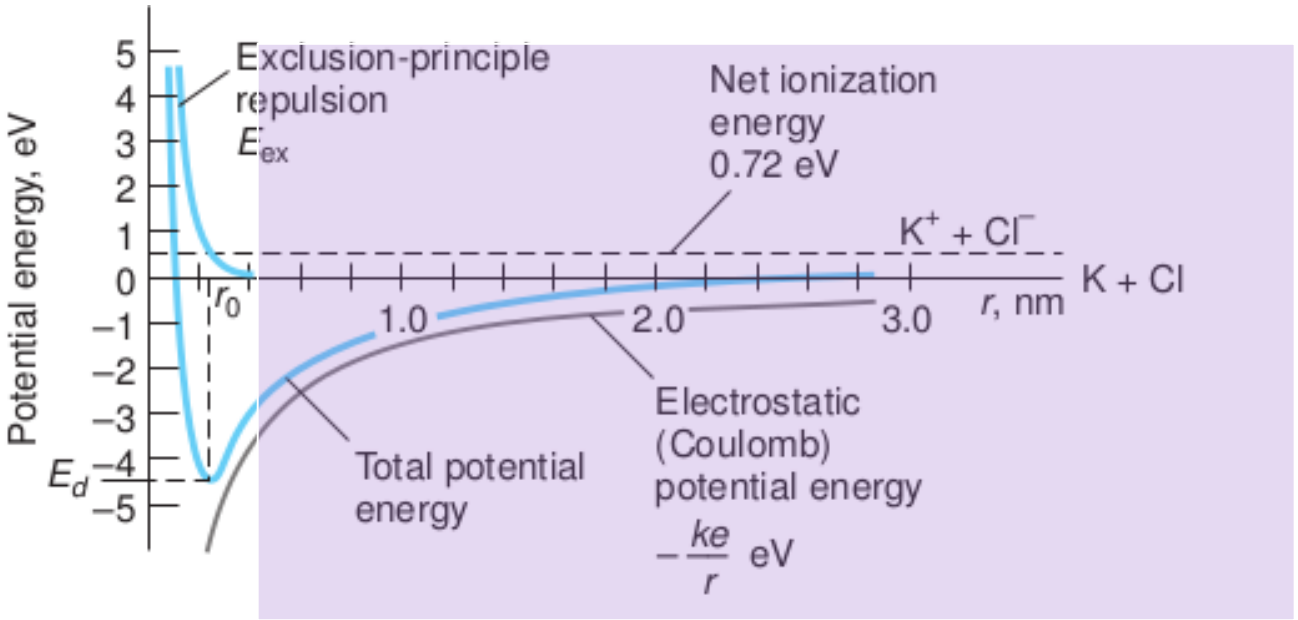
Alkali metal	Ionization energy (eV)	Halogen	Electron affinity (eV)
Li	5.39	F	3.40
Na	5.14	Cl	3.62
K	4.34	Br	3.36
Rb	4.18	I	3.06
Cs	3.89	At	2.8
Fr	4.07		

Source: Data from *Handbook of Chemistry and Physics*, 90th ed. (New York: Chemical Rubber Co., 2009).

+0.72 eV = net energy change in the process of formation of both ions

Ionic Bond. Example: KCl

Phase III *electrostatic attraction between the two ions*

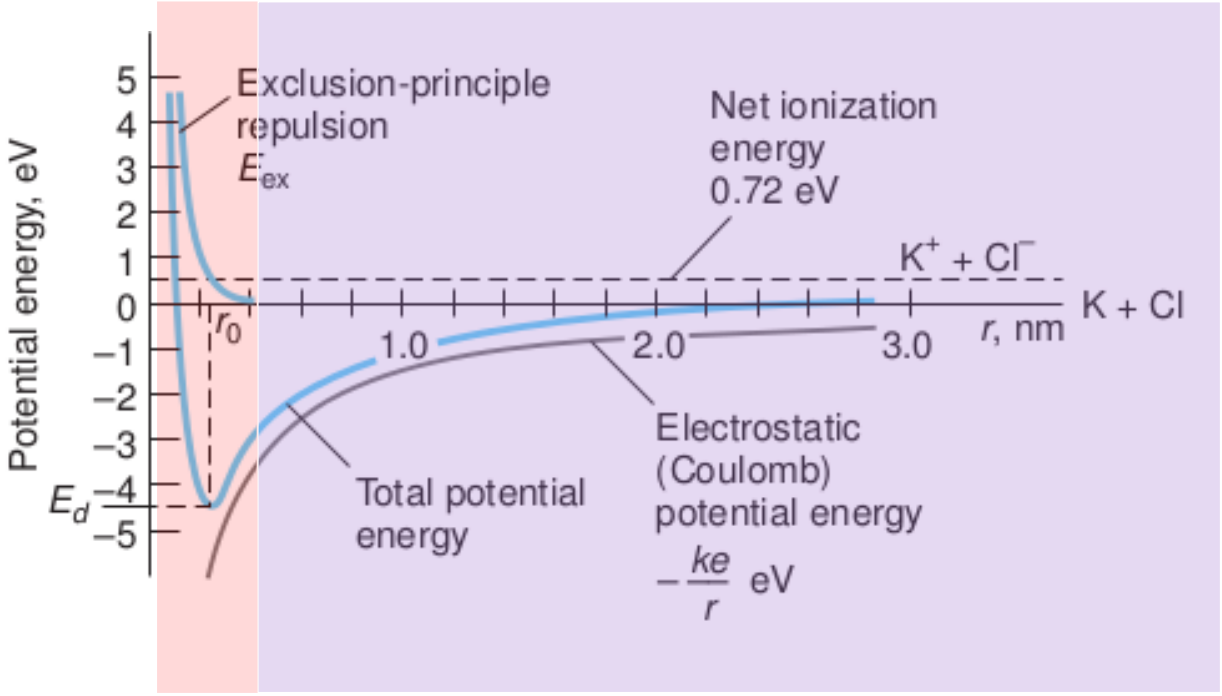


When the separation between the ions is less that 2.8 nm, the (negative) energy due to Coulomb attraction is greater in magnitude than the energy needed to create the ions (positive net ionization energy). The ions keep moving towards each other in order to further lower the total potential energy of the system.

Ionic Bond. Example: KCl

Phase IV *trade-off between Coulomb attraction and Pauli exclusion principle repulsion; reaching the equilibrium*

When the ions get very close to each other, the wave functions of *3p* electrons in K^+ and *3p* electrons in Cl^- begin to overlap, giving rise to strong repulsion due to the Pauli Exclusion Principle. As a result of the trade-off between the 'Coulomb' and the 'Pauli' terms, the system of ions reaches a stable equilibrium forming a KCl molecule.



total potential energy

$$U(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} + \underbrace{E_{ion}}_{0.72\ \text{eV}} + E_{ex}$$

repulsion term

$$E_{ex} = \frac{A}{r^n}$$

$r_0 = 0.27$ nm, $E_d = 4.40$ eV

dissociation energy (energy needed to separate KCl into K and Cl atoms)

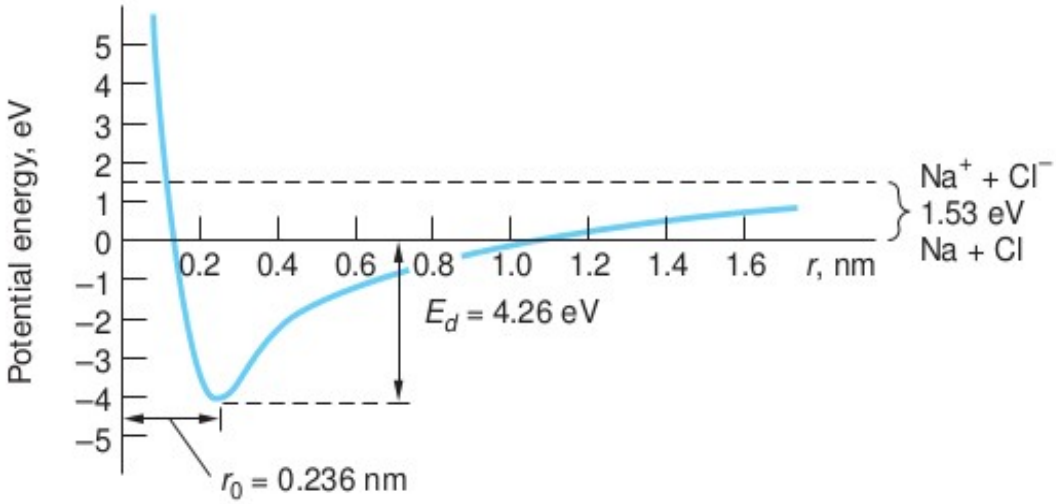
Ionic Bond. Parameters

Table 9-2 Dissociation energies E_d and equilibrium separations r_0 for several ionic molecules* in the gaseous state

Molecule	Dissociation energy (eV)	Equilibrium separation (nm)
NaCl	4.27	0.236
NaF	5.34	0.193
NaH	1.92	0.189
NaBr	3.81	0.250
LiCl	4.86	0.202
LiH	2.47	0.159
LiI	3.58	0.239
KCl	4.49	0.267
KBr	3.94	0.282
RbF	5.12	0.227
RbCl	4.43	0.279
CsI	3.50	0.332

*The two entries of molecules formed by an alkali atom and a hydrogen atom may seem odd, but hydrogen atoms, like those of a number of other elements, may form molecules as either positive or negative ions. The ionization energy of H is, of course, 13.6 eV; its electron affinity is 0.75 eV.

Source: Data from *Handbook of Chemistry and Physics*, 90th ed. (New York: Chemical Rubber Co., 2009).



Numerical Example: NaF

ionization energy of Na	5.14 eV
electron affinity of F	3.40 eV
equilibrium separation in NaF	0.193 nm
dissociation energy	4.99 eV

→ energy needed to form Na^+ and F^- ions from neutral atoms

$$E_{ion} = E_{\mathrm{Na}^+} - E_{\mathrm{F}^-} = (5.14 - 3.40)\ \mathrm{eV} = 1.74\ \mathrm{eV}$$

→ electrostatic (Coulomb) potential energy of the system of Na^+ and F^- ions at the equilibrium separation (with $E_{el} = E_{ion}$ at infinity)

$$E_{el} = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_0} + \boxed{E_{ion}} = -5.71\ \mathrm{eV}$$

→ energy due to Pauli repulsion at equilibrium separation

$$E_{ex} = |E_{el}| - |E_d| = (5.71 - 4.99)\ \mathrm{eV} = 0.72\ \mathrm{eV}$$

Numerical Example: NaF

ionization energy of Na	5.14 eV
electron affinity of F	3.40 eV
equilibrium separation in NaF	0.193 nm
dissociation energy	4.99 eV

→ values of *A* and *n* for

At the equilibrium separation $E_{ex}(r_0) = \dfrac{A}{r_0^n} = \dfrac{A}{(0.193\ \mathrm{nm})^n} = 0.72\ \mathrm{eV}$

At this separation, the Coulomb attraction and the Pauli repulsion balance each other (the corresponding forces are equal in magnitude).

$$\mathbf{F} = -\mathrm{grad}\, U$$

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_0^2} = 38.7\ \mathrm{eV/nm} = \frac{nA}{r_0^{n+1}} = \frac{n}{r_0}\underbrace{\frac{A}{r_0^n}}_{0.72\ \mathrm{eV}}$$

Hence $n \approx 10,\ A \approx 5.4 \times 10^{-8}\ \mathrm{eV \cdot nm}^{10}$

Ionic Bond. Summary

An ionic bond forms as a result of the trade-off between the Coulomb (long-range) interaction and the (short-range) interaction due to the Pauli Exclusion Principle.

The process can be discussed quantitatively in terms of the potential energy.

Factors neglected in the discussion:

→ zero-point oscillations energy (decreasing the magnitude of the dissociation energy);
the bond is treated as rigid

→ Van der Waals attraction (increasing the magnitude of the dissociation energy)

However, both effects are in this case relatively small.

Chemical Bonds (II)

The Covalent Bond

Introduction

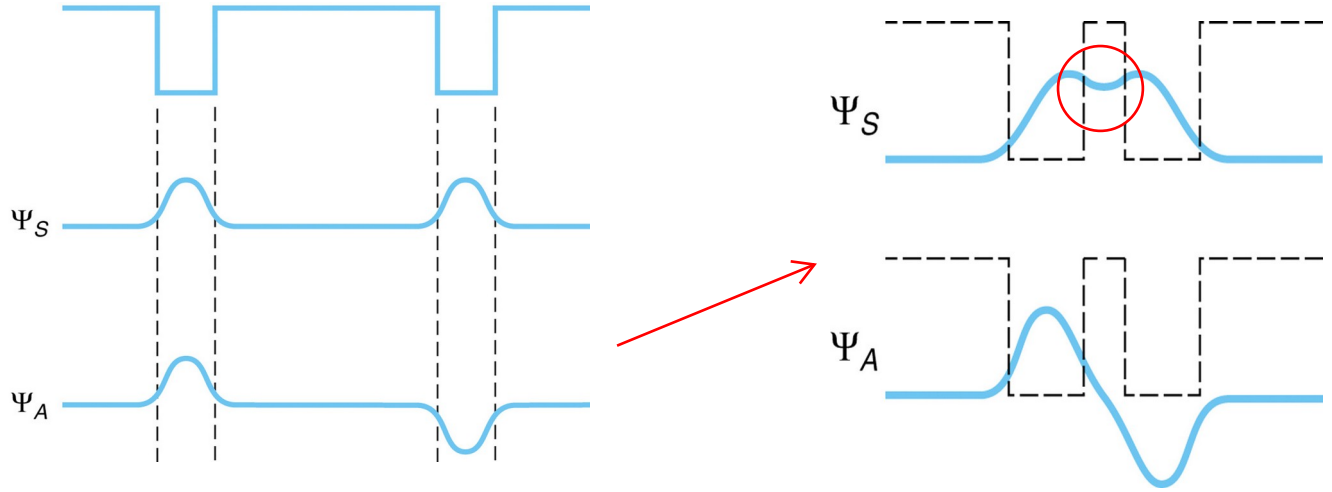
Protons in the H_2 molecule are bound by a different mechanism:

Detailed calculations show that the energy needed to create a H^+ and H^- pair is equal to 12 eV. When added to the (negative) electrostatic energy due to Coulomb interaction between the ions, cannot yield a negative value.

Bonding mechanism in the H_2 molecule is of purely quantum-mechanical origin.

Introduction. Single Electron in a Double Well

Two lowest eigenstates in a (square) double-well potential



Observations

- when the wells are far away from each other, energy levels are doubly-degenerate
- bringing the wells closer lifts the degeneracy; the energy level splitting increases with decreasing well separation
- when the separation is small, the even (space-symmetric) wave function is non-zero in the barrier region; probability of finding the electron there is much greater for the space-symmetric than for the space-antisymmetric wave function

http://phet.colorado.edu/en/simulation/covalent-bonds

Introduction. Two Electrons in a Double Well

Now, add one more electron. The complete wave function, combining both the spatial and spin parts, should be antisymmetric upon exchange of electrons (electrons are fermions).

spin-antisymmetric ←→ ***space-symmetric***

$$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

$S = 0$ (spin-singlet)

spin-symmetric ←→ ***space-antisymmetric***

$$|\uparrow\uparrow\rangle$$

$$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)$$

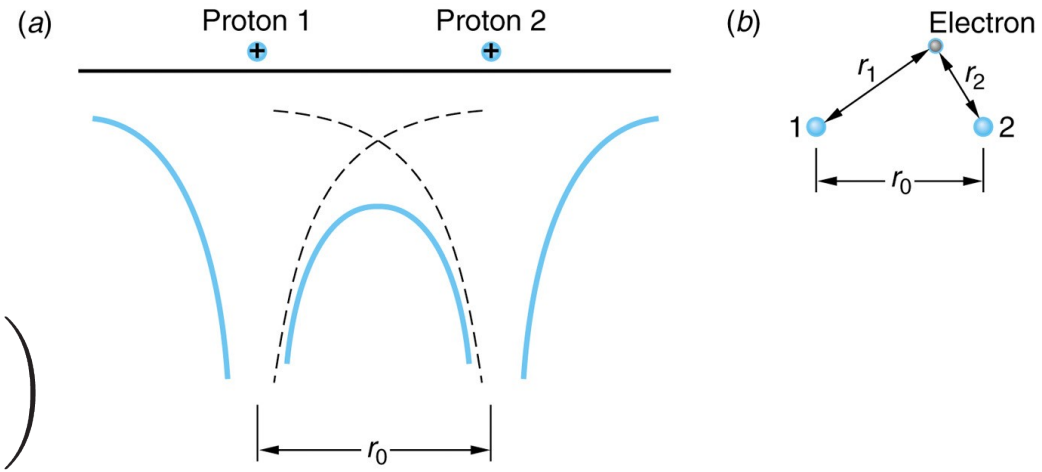
$$|\downarrow\downarrow\rangle$$

$S = 1$ (spin-triplet)

Note. Exchange symmetry is here equivalent to spatial symmetry.

H_2^+ Ion

Coulomb double-well



Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_0}\right)$$

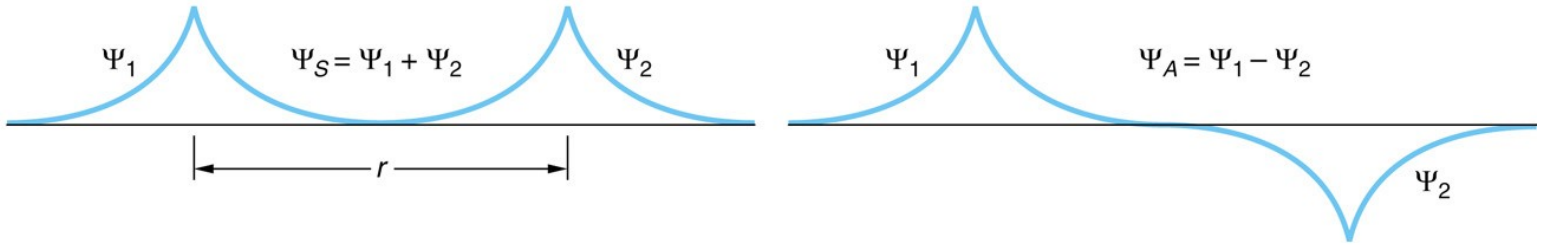
Space-symmetric and space-antisymmetric linear combinations

$$\psi_S = \frac{1}{\sqrt{2}}\left(\psi_{100}(r_1) + \psi_{100}(r_2)\right)$$

$$\psi_A = \frac{1}{\sqrt{2}}\left(\psi_{100}(r_1) - \psi_{100}(r_2)\right)$$

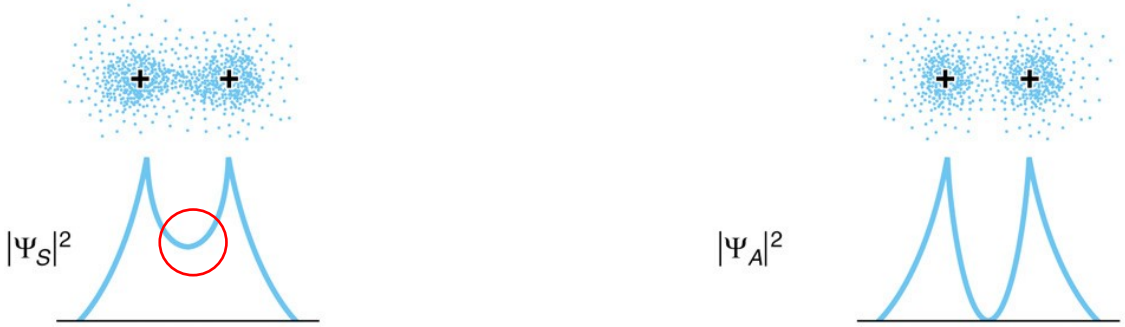
H_2^+ Ion. Illustration

protons
far apart



protons
close to
each other

probability
density



Conclusion

A stable molecular configuration is expected to form if the probability density is non-zero near the center (negative charge density between protons stabilizes the structure).

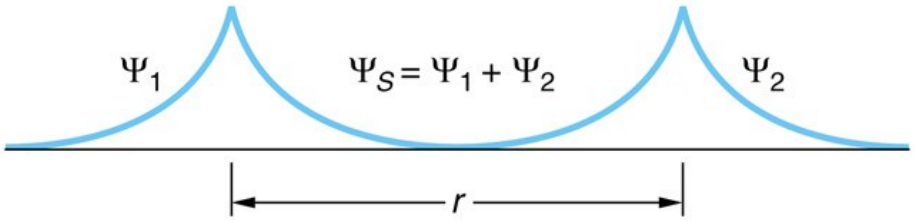
H_2^+ Ion. Quantitative Analysis

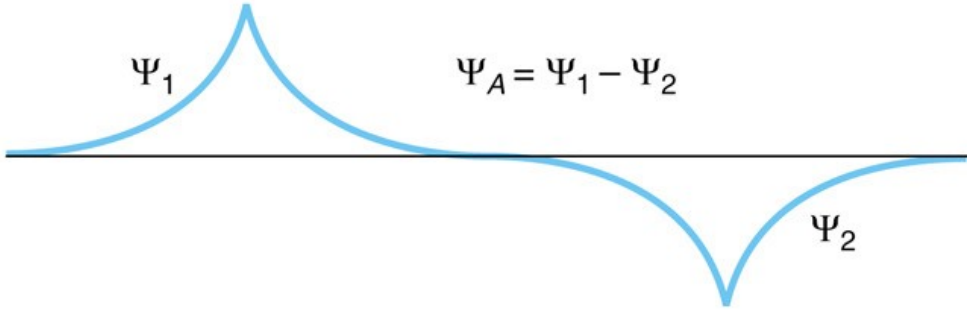
protons far apart ($r \to \infty$)

electron's energy E_s = -13.6 eV

proton-proton interaction energy U_p (Coulomb repulsion) negligible

no exclusion-principle repulsion (one electron in the system)





H_2^+ Ion. Quantitative Analysis

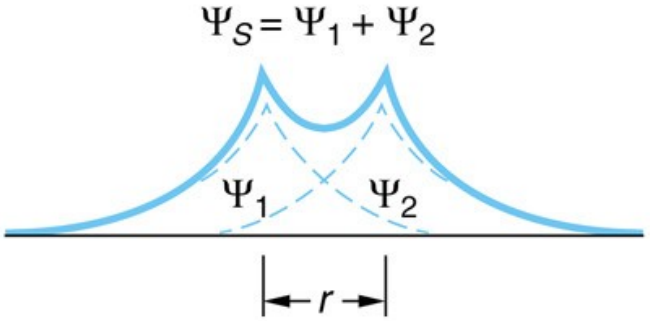
protons brought closer to each other

→ electron's energy decreases (bound more tightly)

→ U_p increases

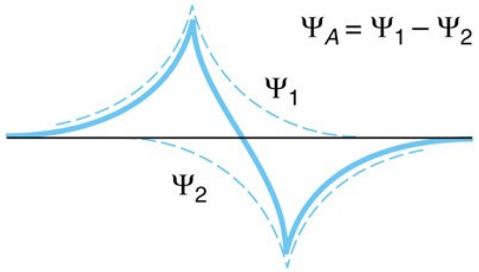
→ when $r \to 0$ electron's symmetric wave function corresponds to that of the ground state (n=1) of the Z = 2 atom (ion) with

$E_S = E_1 = -13.6 \times 2^2 / 1^2 = -54.4$ eV



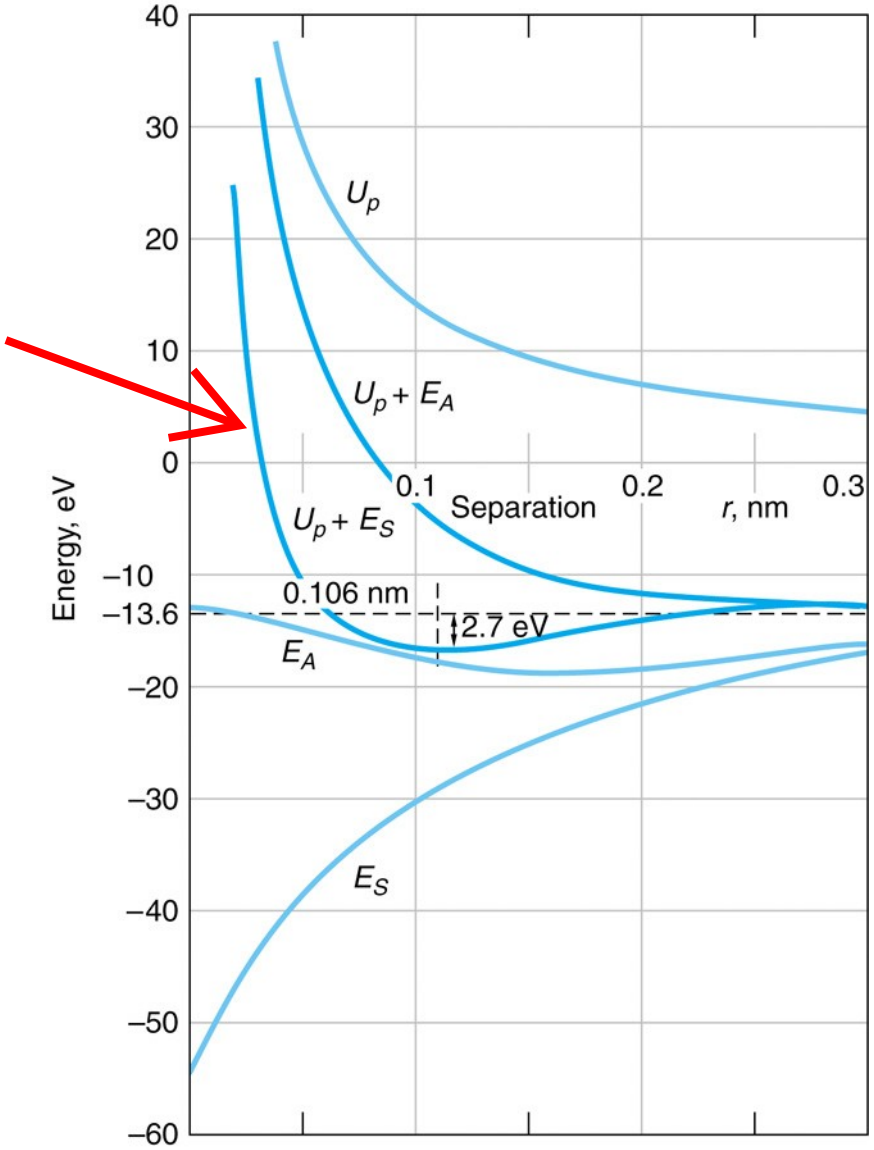
→ when $r \to 0$ electron's antisymmetric wave function corresponds to that of the first excited state (n=2) with

$E_A = E_2 = -13.6 \times 2^2 / 2^2 = -13.6$ eV



H_2^+ Ion. Quantitative Analysis

Energy as a function of ion separation



total energy of the H_2^+ ion:

$U_p + E_S$ *or* $U_p + E_A$

only in this case
a minimum is realized
(stable equilibrium)

$$E_{\text{total}} = U_p + E_S$$

→ equilibrium separation r_0 = 0.106 nm

→ binding energy

$$E_{\text{total}}(\infty) - E_{\text{total}}(r_0) = -13.6 - (-16.3) = 2.7 \text{ eV}$$

H_2 Molecule. Mechanism

Now, two electrons in the system – need to take into account the Pauli Exclusion Principle.

atoms far apart ($r \to \infty$)

→ energy of electrons: 2 x (-13.6 eV) = -27.2 eV;
wave functions: atomic orbitals with $n = 1$, $l = 0$, $m = 0$ (i.e. 1*s* state)

→ proton-proton interaction energy U_p (Coulomb repulsion) negligible

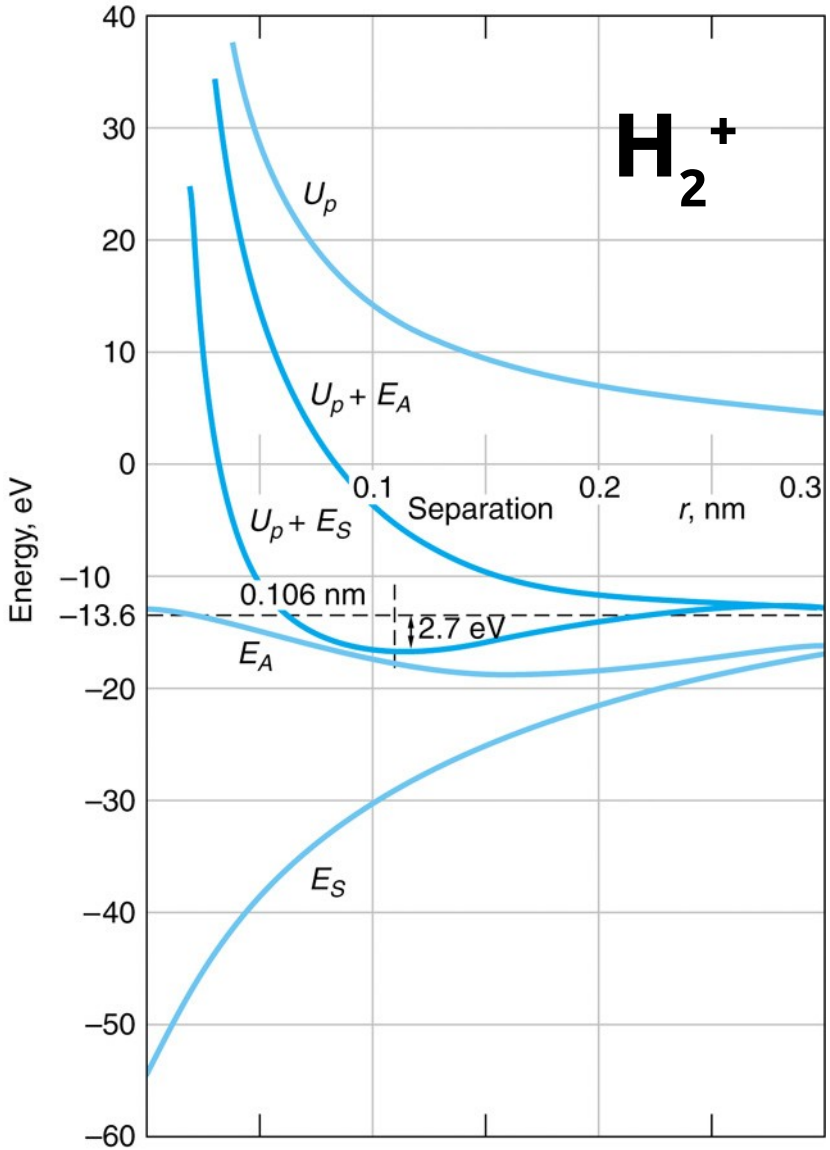
→ no exclusion-principle repulsion (no overlap between the wave functions)

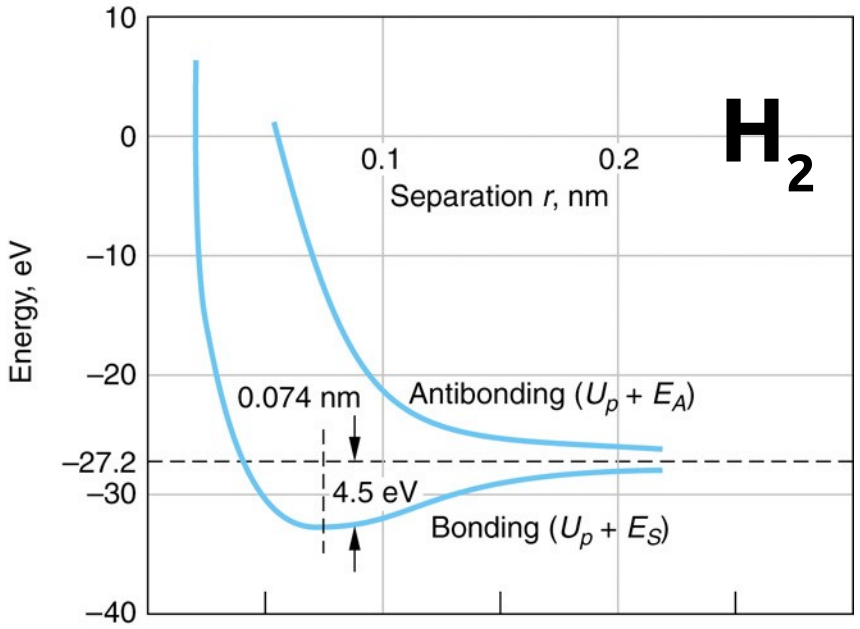
atoms brought close to each other ($r \to 0$)

→ wave functions of the electrons start to overlap; both atoms share the electrons

→ due to the Pauli Exclusion Principle, the symmetric spatial part of the (two-particle) wave function combines with antisymmetric (singlet) spin part, and the antisymmetric spatial part combines with the symmetric (triplet) spin part; singlet configuration gives a minimum in potential energy (stable bond)

H_2 Molecule vs H_2^+ Ion





Features (ion vs molecule)

→ binding energy: 2.7 vs. 4.5 eV

→ equilibrium separation: 0.106 vs. 0.074 nm

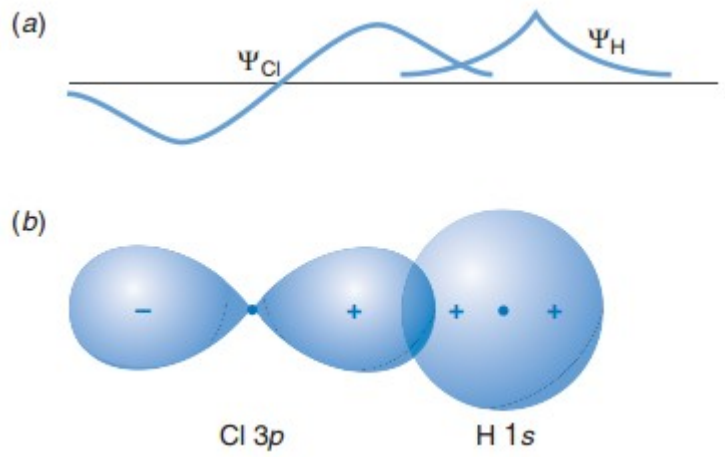
→ *increased charge concentration between protons results in a tighter bond*

Remarks

Requirement for covalent bonding

Overlap between the wave functions of the valence (outermost) electrons; two atoms share valence electrons – **covalent bond.**

H_2 is an example of *s-type* covalent-bond. If other atomic orbitals participate, other covalent bonds possible (p-p, s-p,...).



Why not He_2?

When two He atoms are brought close to each other, the bonding and anti-bonding orbitals form, but each may accommodate only two electrons. Hence two electrons occupy anti-bonding orbital.

Net effect: no stable bond. At low temperatures (or high pressures) He binds into He_2 but the mechanism is different.

Remarks. Parameters of Some s-bonded Covalent Molecules

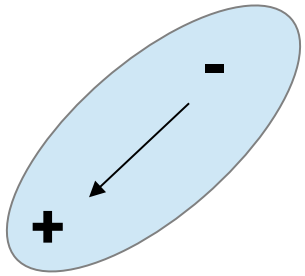
Table 9-3 Dissociation energies E_d and equilibrium separations r_0 for several covalent s-bonded molecules

Molecule	Dissociation energy (eV)	Equilibrium separation (nm)
H_2	4.52	0.074
Li_2	1.10	0.267
LiH	2.43	0.159
LiNa	0.91	0.281
Na_2	0.80	0.308
NaH	2.08	0.189
NaRb	0.61	0.359
K_2	0.59	0.392
KNa	0.66	0.347
Rb_2	0.47	0.422
Cs_2	0.43	0.450

Comment. Covalent or Ionic?

In *homonuclear* molecules, bonding is purely covalent.

In *heteronuclear* molecules, usually a mixture of covalent and ionic.



dipole moment - used to quantify to what extent is the bond ionic/covalent

$$|\mathbf{p}_{ionic}| = er_0$$

equilibrium separation

For a purely covalent bond, the dipole moment is expected to be zero.

The ratio $p_{measured} / p_{ionic}$ is a measure of the 'amount' of ionic bonding.

E.g. for NaCl $p_{measured} / p_{ionic} = 3.00 \times 10^{-29}$ C m/ 3.78×10^{-29} C m = 0.79
("bonding is 79% ionic, 21% covalent")

Chemical Bonds (III)

Dipole-Dipole Bonding Mechanism

and

the Lennard-Jones Potential

Introduction

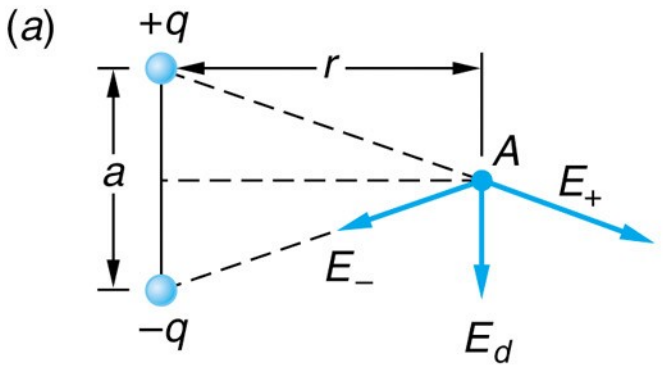
Dipole-dipole bonding (or *molecular bonding*) plays an important role in formation of molecule complexes from small molecules.

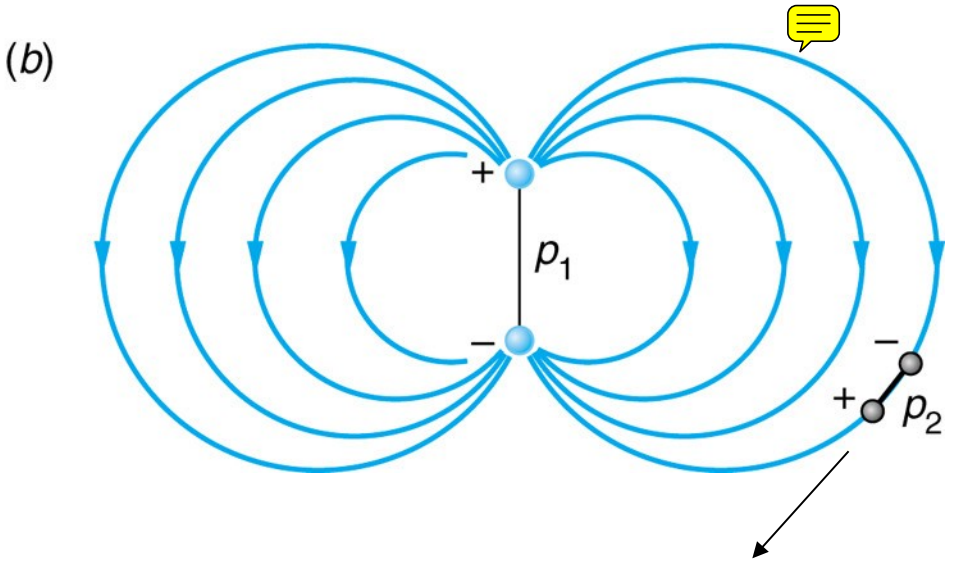
Any two molecules attract each other by (weak) electrostatic forces. When the temperature is low enough, these interactions are responsible for condensation of the matter into a liquid or solid (Helium-4 is an exception).

dipole-dipole interaction

Introduction. Electric Field of a Dipole

Dipole moment $\mathbf{p} = q\mathbf{a}$





Electric field of a dipole

$$\mathbf{E}_d = \frac{1}{4\pi\varepsilon_0}\left[\frac{\mathbf{p}}{r^3} - \frac{3(\mathbf{p}\cdot\mathbf{r})\mathbf{r}}{r^5}\right]$$

the electric field tries to re-orient the dipole so that it aligns along the field lines

Magnitude

$$|\mathbf{E}_d| \overset{r\gg a}{\sim} \frac{1}{r^3}$$

[weaker than that of a single charge]

Potential energy of dipole- dipole interaction

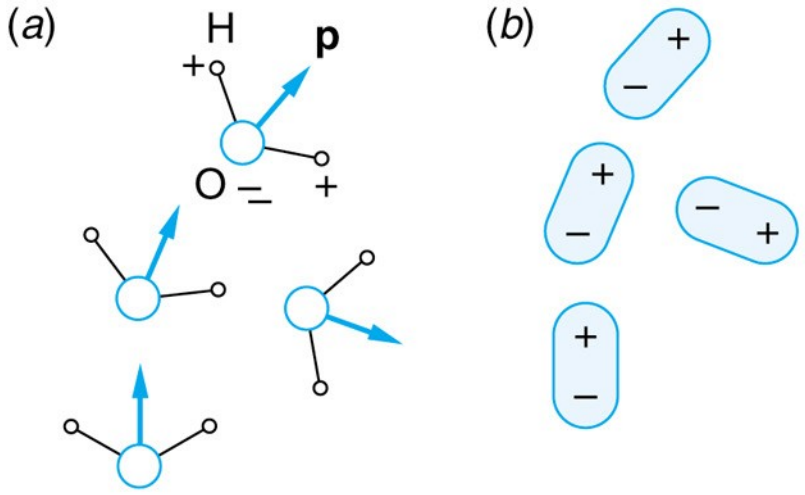
$$U = -\mathbf{p}_2 \cdot \mathbf{E}_d$$

Dipole-dipole force magnitude $\sim \frac{1}{r^4}$
[attractive, relatively weak/short range]

Polar Molecules

Intermolecular bonding mechanism:

dipole-dipole attraction + *nuclear repulsion (protons)* + *Pauli repulsion*



bonding energy ~0.5 eV/molecule
[10% of the strength of the H—OH bond]

weak bonding

Digression: hydrogen bond and DNA

Non-polar Molecules. Induced Dipole Moment

Electric charge in a non-polar molecule may be rearranged if it is placed in an external electric field (e.g. that of a dipole).

non-polar molecule (zero dipole moment) —*external electric field*→ *induced dipole moment*

$$\mathbf{p}_2 = \alpha \mathbf{E}_d$$

polarizability (characteristics of a non-polar molecule; tells about how easy can the molecule be polarized)

Potential energy of polar-nonpolar molecule interaction

$$U = -\mathbf{p}_2 \cdot \mathbf{E}_d = -\alpha E_d^2 \sim -\frac{1}{r^6}$$

(Attractive) force magnitude $\sim \frac{1}{r^7}$

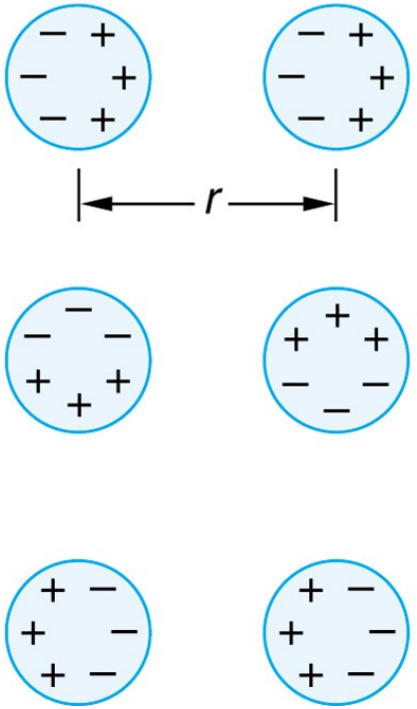
London Dispersion Force (also called Van der Waals Attraction)

Distribution of charge is, on average, symmetric in non-polar molecules.

However, instantaneous fluctuations in the electron distribution are not symmetric and tend to be correlated with those of nearby molecules. Hence, the instantaneous dipole moment is, in general, not zero.

The fluctuations of the instantaneous dipole moments produce net attraction force of the magnitude

$$\sim \frac{1}{r^7}$$



(Total) Van der Waals Force

Components

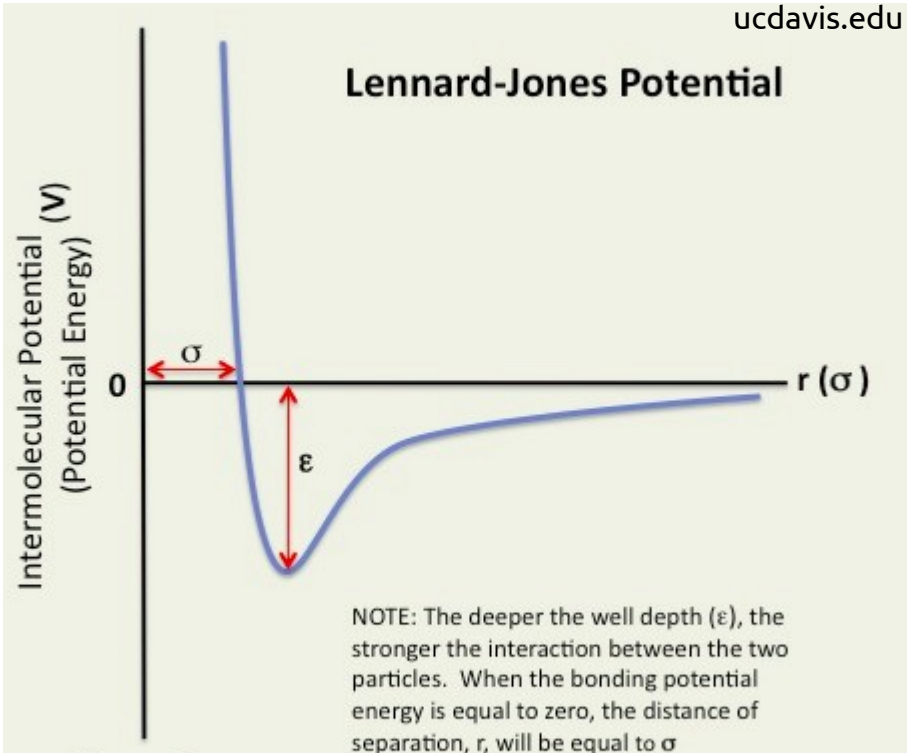
→ *Repulsive* component resulting from the Pauli exclusion principle that prevents the collapse of molecules.

→ *Attractive* or *repulsive* electrostatic interactions between permanent charges or dipoles.

→ Polarization term, i.e. *attractive* interaction between a dipole and an induced dipole.

→ *Attractive* London dispersion force.

$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$



Spectroscopy of Diatomic Molecules

Introduction

Molecules, like atoms, may emit and absorb electromagnetic radiation to transfer form one state (energy level) to another.

The structure of energy levels of molecules is more rich than that of atoms: systems of particles (molecules) have more degrees of freedom than individual particles (atoms).

The energy levels of a molecule may be classified into the following groups :

→ vibrational levels (due to vibrations of atoms around equilibrium positions

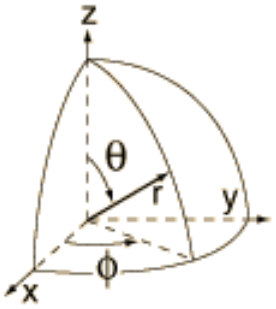
→ rotational levels (due to rotations of the molecule about an axis through its center of mass)

→ electronic levels (excitation of electrons)

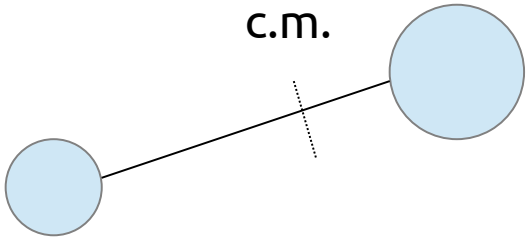
Rotational Energy Levels

Rotational Energy Levels. Introduction

Recall: *energy spectrum of a quantum mechanical rigid rotor*

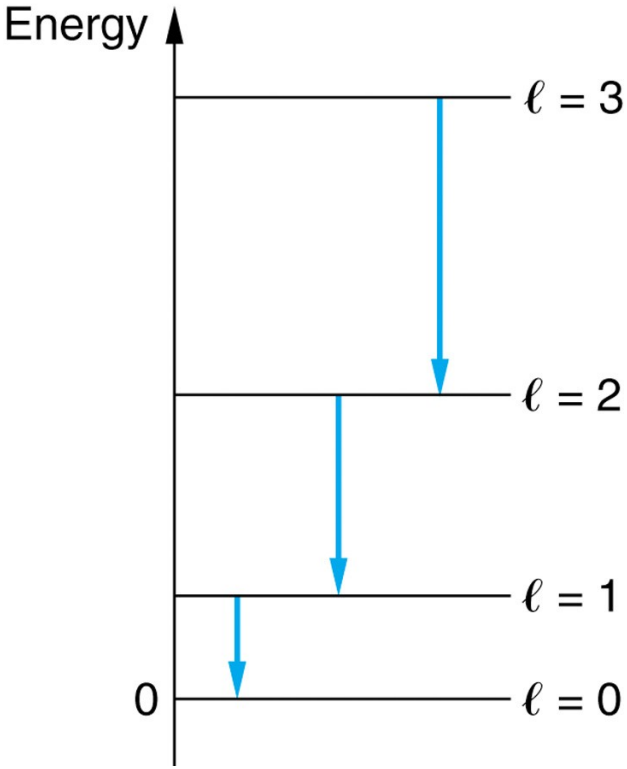


$$\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}\right]+E\Psi=0$$



$$E_l = \frac{\hbar^2 l(l+1)}{2I} = l(l+1)E_{rot}$$

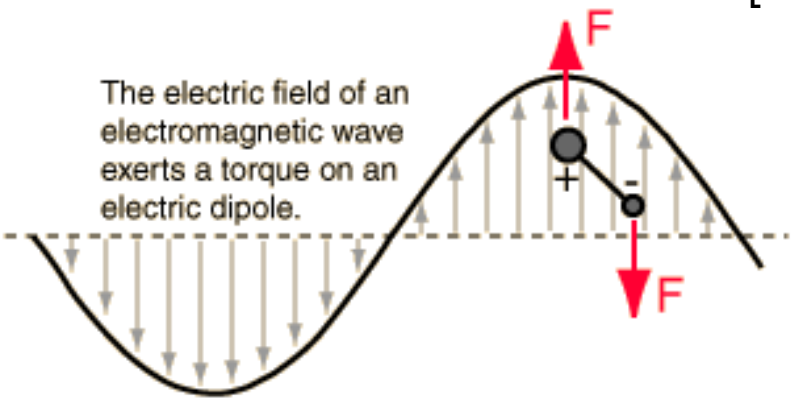
$$E_{rot} = \frac{\hbar^2}{2I}$$



Rotational Energy Levels. Introduction

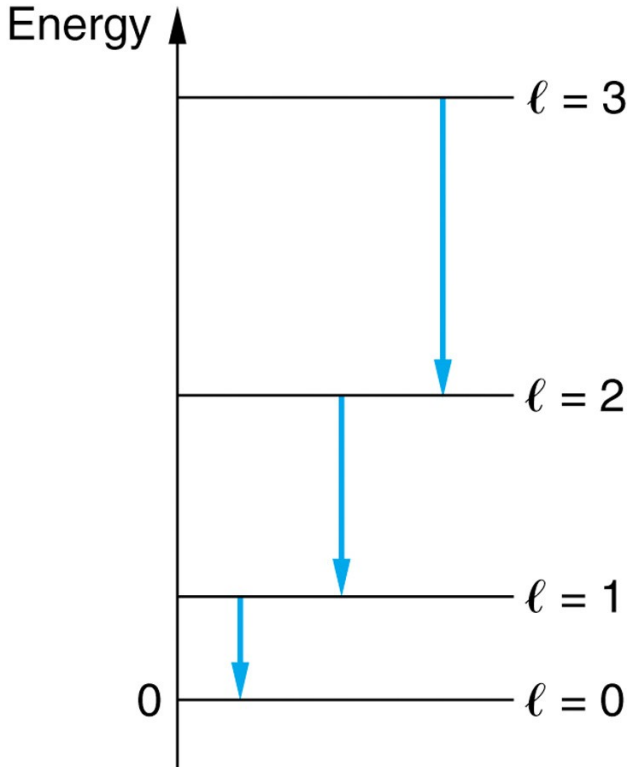
Comments (1) All diatomic molecules have rotational energy levels. However those without a permanent dipole moment cannot emit or absorb electromagnetic radiation as a result of transitions between rotational levels only. Therefore they do not reveal a pure rotational spectrum.

(2) For molecules with a permanent dipole moment, only transitions between adjacent rotational levels are possible.



selection rule
[molecules with a dipole moment]

$$\Delta l = \pm 1$$



mechanism of transitions between rotational levels
[interaction with e-m (i.e. time-dependent) field]

Rotational Energy Levels. Selection Rule

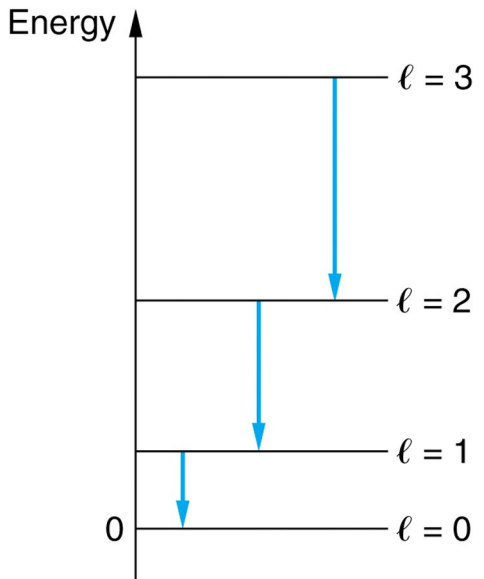
absorption (of a quantum of electromagnetic radiation)

$$l \longrightarrow l+1 \Rightarrow E_{l+1} - E_l = \frac{[(l+1)(l+2) - l(l+1)]\hbar^2}{2I} = \frac{(l+1)\hbar^2}{I}$$

emission (of a quantum of electromagnetic radiation)

$$l \longrightarrow l-1 \Longrightarrow E_l - E_{l-1} = \frac{[l(l+1) - (l-1)l]\,\hbar^2}{2I} = \frac{l\hbar^2}{I}$$

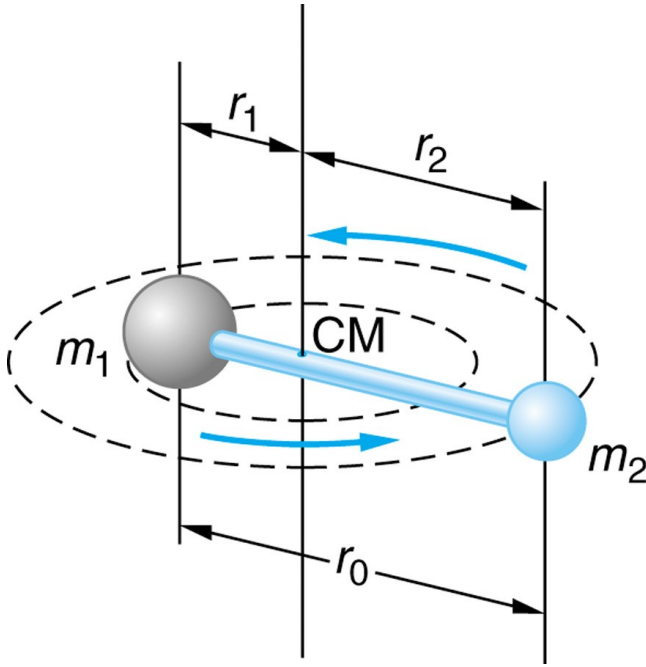
Comment. Energies of these types of transitions usually correspond to the *microwave* part of the electromagnetic spectrum.



Rotational Energy Levels. Application

Determining the moment of inertia of a diatomic molecule
[rotating about the center of mass]

$$I = m_1 r_1^2 + m_2 r_2^2$$



Center of mass

$$\frac{m_1 r_1 - m_2 r_2}{m_1 + m_2} = 0 \Longrightarrow r_2 = \frac{m_1}{m_2} r_1$$

Distance between atoms $\quad r_0 = r_1 + r_2 \Longrightarrow r_0 = r_1 + \frac{m_1}{m_2} r_1$

Hence $\quad r_1 = \frac{m_2}{m_1 + m_2} r_0, \qquad r_2 = \frac{m_1}{m_1 + m_2} r_0$

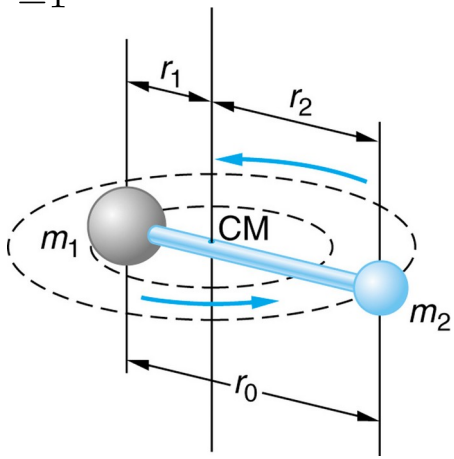
Rotational Energy Levels. Application

Moment of inertia about the center of mass

$$I = m_1 r_0^2 \left(\frac{m_2}{m_1+m_2}\right)^2 + m_2 r_0^2 \left(\frac{m_1}{m_1+m_2}\right)^2 = \frac{m_1 m_2}{m_1+m_2} r_0^2 \underbrace{\left(\frac{m_2}{m_1+m_2} + \frac{m_1}{m_1+m_2}\right)}_{=1}$$

Eventually, the moment of inertia

$$I = \mu r_0^2$$



$$\mu = \frac{m_1 m_2}{m_1+m_2}$$

reduced mass

Note. For homo-atomic molecules

$$m_1 = m_2 = m \Longrightarrow \mu = \frac{m}{2}, \qquad I = \frac{1}{2} m r_0^2$$

Rotational Energy Levels. Example

The energy of a photon absorbed in transition between the rotational levels with l=0 and l=1 in a CO molecule has been measured at 4.77 x 10^{-4} eV.

What is the length of the bond in the CO molecule?

$$I = \mu r_0^2 \Longrightarrow r_0 = \sqrt{\frac{I}{\mu}}$$

$$\Delta E = E_{l=1} - E_{l=0} = \frac{\hbar^2}{I} \Longrightarrow I = \frac{\hbar^2}{\Delta E}$$

Hence $$r_0 = \sqrt{\frac{\hbar^2}{\mu \Delta E}} = \sqrt{\frac{\hbar^2}{\Delta E}\frac{m_C + m_O}{m_C m_O}}$$

$m_C = 12 \text{ u} = 12 \times 1.66 \times 10^{-27} \text{ kg}$

$m_O = 16 \text{ u} = 16 \times 1.66 \times 10^{-27} \text{ kg}$

$$r_0 = 0.133 \text{ nm}$$

Rotational Energy Levels. Comments

→ energy of rotational levels (as well as spacing between them) is of the order of ~0.1 meV ~ 1 meV;
much less than that of electronic levels (~ eV)

→ recall that the characteristic thermal energy at room temperature $k_B T$ ~ 26 meV; transitions between rotational levels may be thermally induced (collisions between molecules)

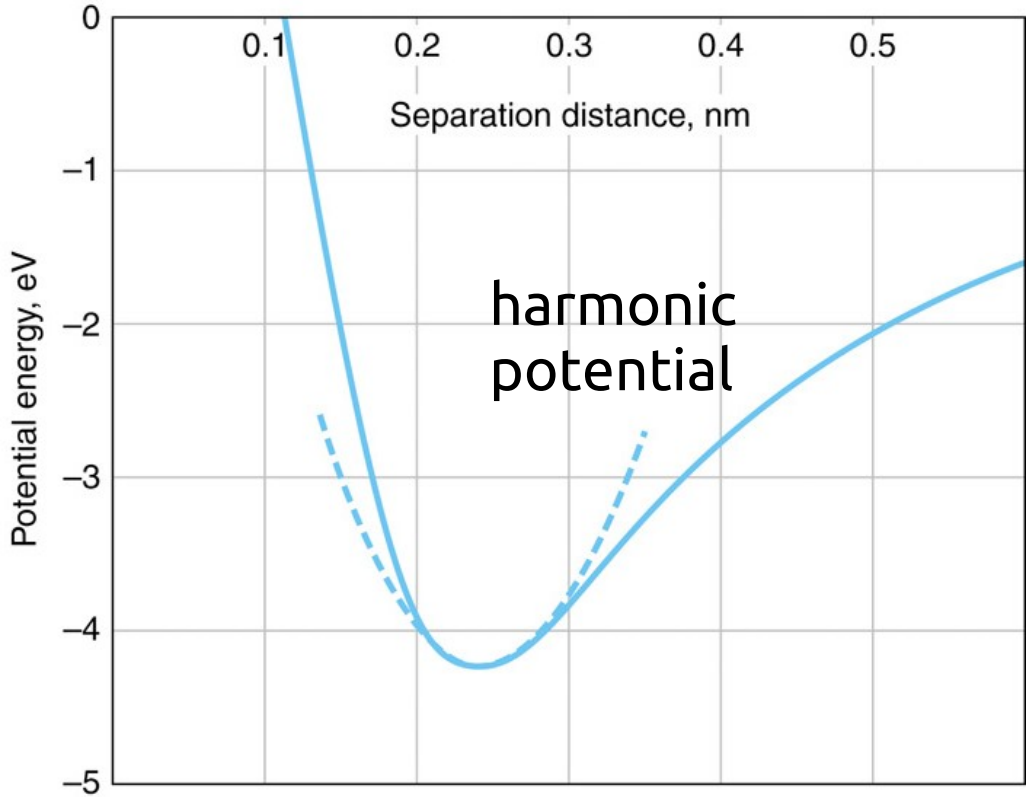
→ thermally-induced transitions between electronic levels not possible at room temperature

Vibrational Energy Levels

Vibrational Energy Levels. Introduction

Observation (*harmonic approximation*)

Potential well of any shape can be approximated by the potential energy of a harmonic oscillator, provided the system is close to a stable equilibrium (energy of the system is close to a local minimum of the potential energy).



6-12 potential

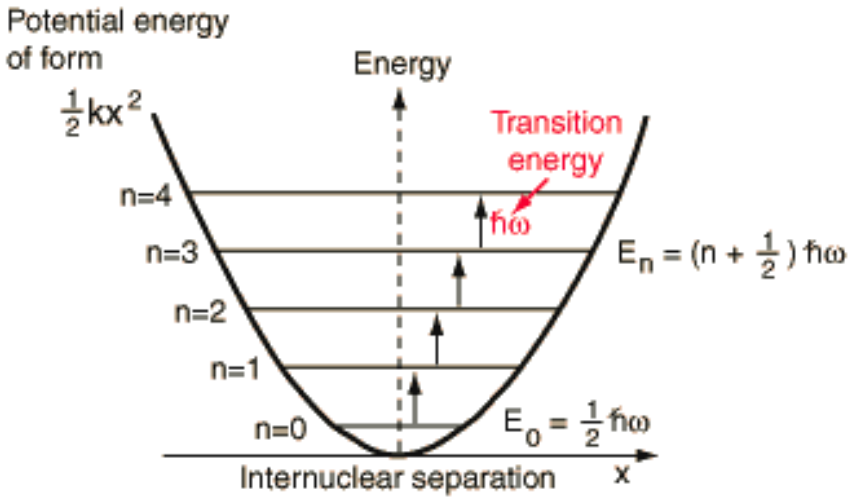
“small oscillations”

Vibrational Energy Levels. Introduction

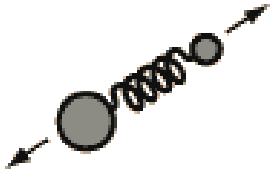
Energy spectrum of a quantum harmonic oscillator

$$E_\nu = \hbar\omega\left(\nu + \frac{1}{2}\right) = E_{vib}\left(\nu + \frac{1}{2}\right)$$

where $\nu = 0, 1, 2, \ldots$



equally-spaced energy levels



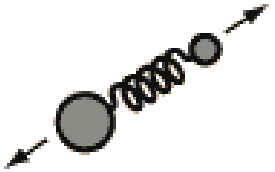
x=0 represents the equilibrium separation between the nuclei.

Vibrational Energy Levels. Introduction

Natural angular frequency of oscillations of a diatomic molecule

$$\omega = \sqrt{\frac{k}{\mu}}$$

effective force constant



x=0 represents the equilibrium separation between the nuclei.

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

reduced mass

Comments

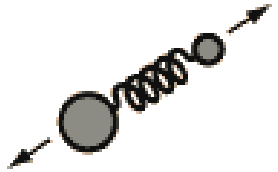
(1) *Selection rule* – only transitions between adjacent vibrational levels possible.

(2) Typical energy of transitions between vibrational levels is ~0.1 eV, i.e. much higher than the typical rotational energy as well as than the typical thermal energy scale at room temperature (26 meV). Transitions between vibrational levels cannot be easily induced by collisions between molecules at usual temperatures.

Vibrational Energy Levels. Application

Determining the force constant of a chemical bond

Molecule (polar)	Frequency x10^{13} Hz	Force constant N/m
HF	12.4	970
HCl	8.66	480
HBr	7.68	410
HI	6.69	320
CO	6.42	1860
NO	5.63	1530



x=0 represents the equilibrium separation between the nuclei.

$$\omega = \sqrt{\frac{k}{\mu}}$$

$$f = \frac{\omega}{2\pi}$$

Comment

The natural frequency cannot be found directly from the spectroscopic data, because there is no $l = 0$, $\nu = 0$ to $l = 0$, $\nu = 1$ transition; the rotational quantum number must change by one. It can be approximated by the midpoint between the $l = 1$, $\nu = 0 \rightarrow l = 0$, $\nu = 1$ transition and the $l = 0$, $\nu = 0 \rightarrow l = 1$, $\nu = 1$ transition. This assumes that the difference between the $l = 0$ and $l = 1$ levels is the same for the ground and first excited state, which amounts to assuming that the first excited vibrational state does not stretch the bond. This "rigid-rotor" model cannot be exactly correct, so it introduces some error.
For more detailed explanation, see *Absorption Spectra*.

http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/

Vibrational Energy Levels. Numerical Example

Estimate the force constant of the chemical bond in a CO molecule, if the vibrational frequency is found to be 6.42 x 10^{42} Hz.

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{k\frac{m_C + m_O}{m_C m_O}}$$

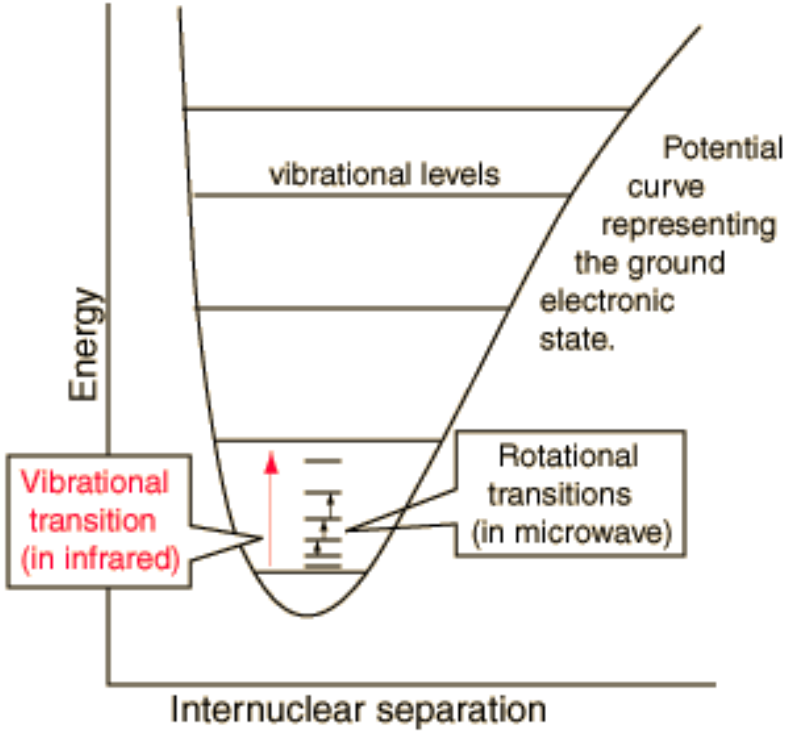
$$k = (2\pi f)^2 \frac{m_C m_O}{m_C + m_O}$$

$$k = 1860 \text{ N/m}$$

Spectroscopy of Diatomic Molecules

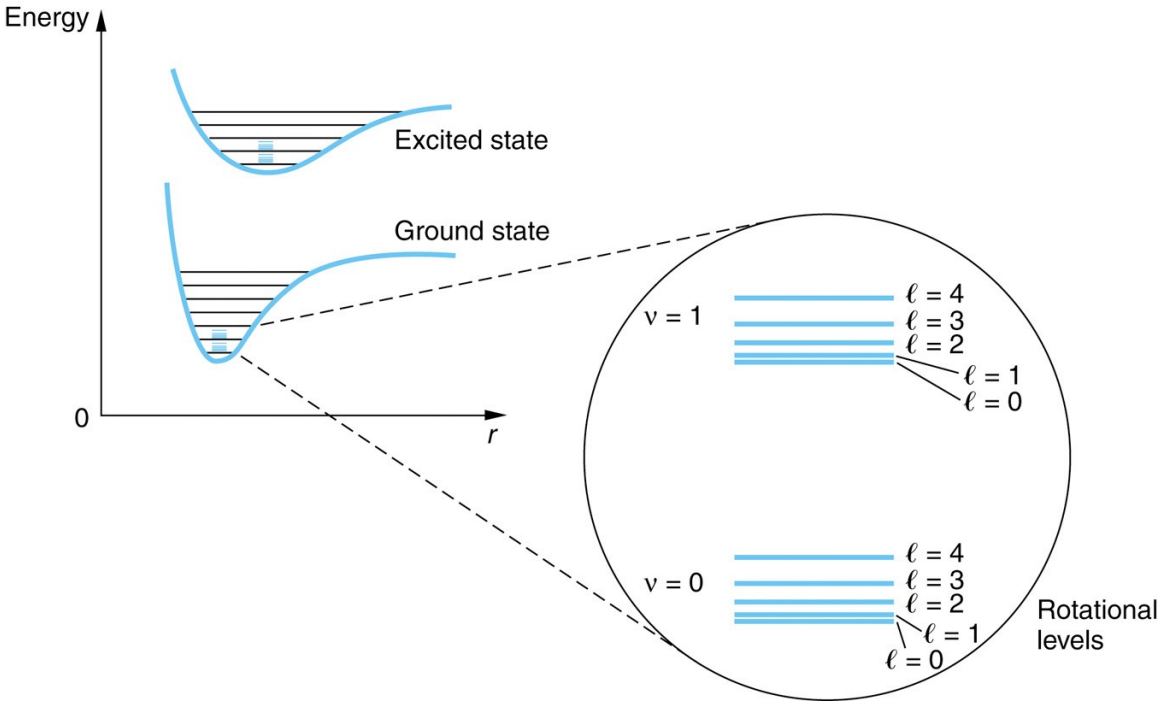
Spectra. Introduction

Schematic representation of vibrational and rotational levels of a diatomic molecule in the (electronic) ground state



Spectra. Introduction

Schematic representation of electronic, vibrational, and rotational energy levels of a diatomic molecule

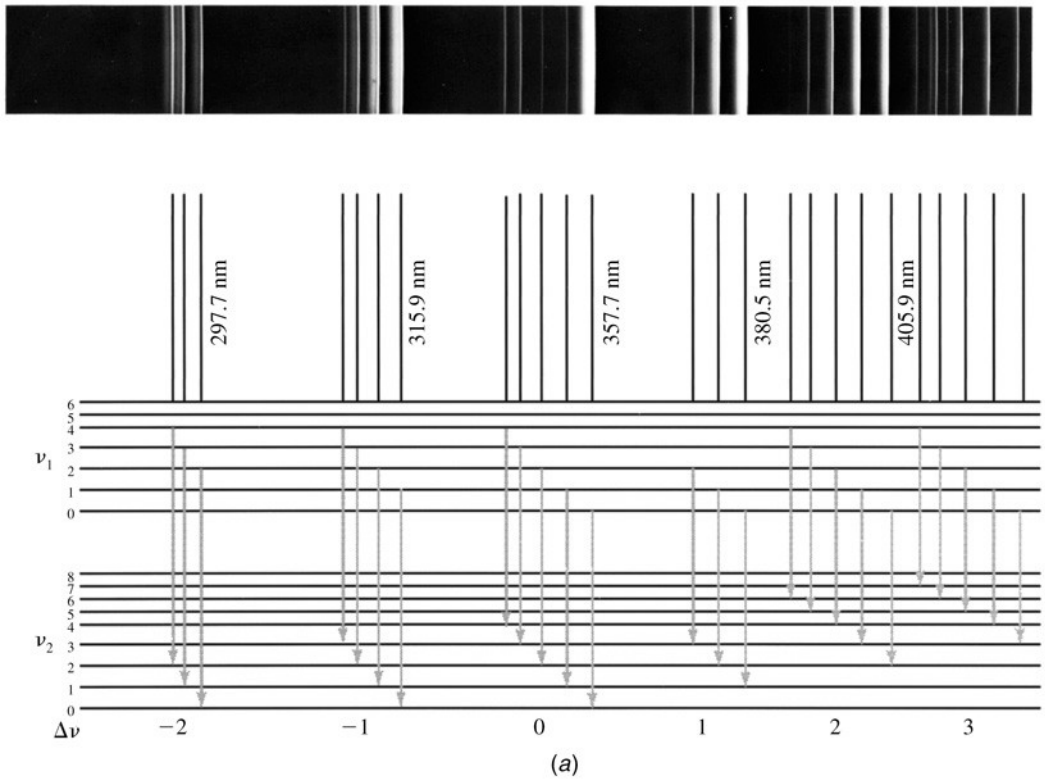


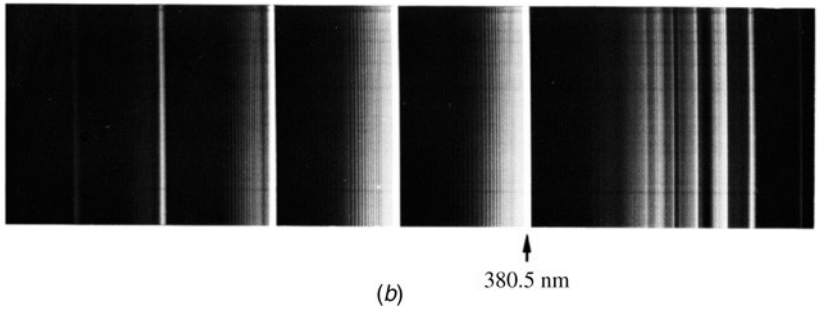
Comments

(1) Due to limited validity of the harmonic approximation, higher vibrational levels are not equally-spaced.

(2) The shape of the potential energy (consequently, the force between the two atoms) is different for the ground state and the excited (electronic) states. Hence the natural angular frequency of vibrations is different. Consequently, for transitions between vibrational levels of different electronic states, the selection rule $\Delta\nu = \pm 1$ does not hold.

Example. Emission Spectrum of N_2





"fine structure" due to transitions between rotational levels

Infrared Absorption Spectra

Introduction

Usually, in molecular spectroscopy the infrared part of the electromagnetic spectrum is used. Hence there are no excitations to higher electronic states, and vibrational/rotational levels belonging to the ground (electronic) state are studied.

Main features

(1) Room temperatures (~300 K) are too low to excite molecules to higher vibrational levels, hence the predominant absorption is due to transitions from the vibrational ground state ($\nu = 0$) to the first excited state ($\nu = 1$).

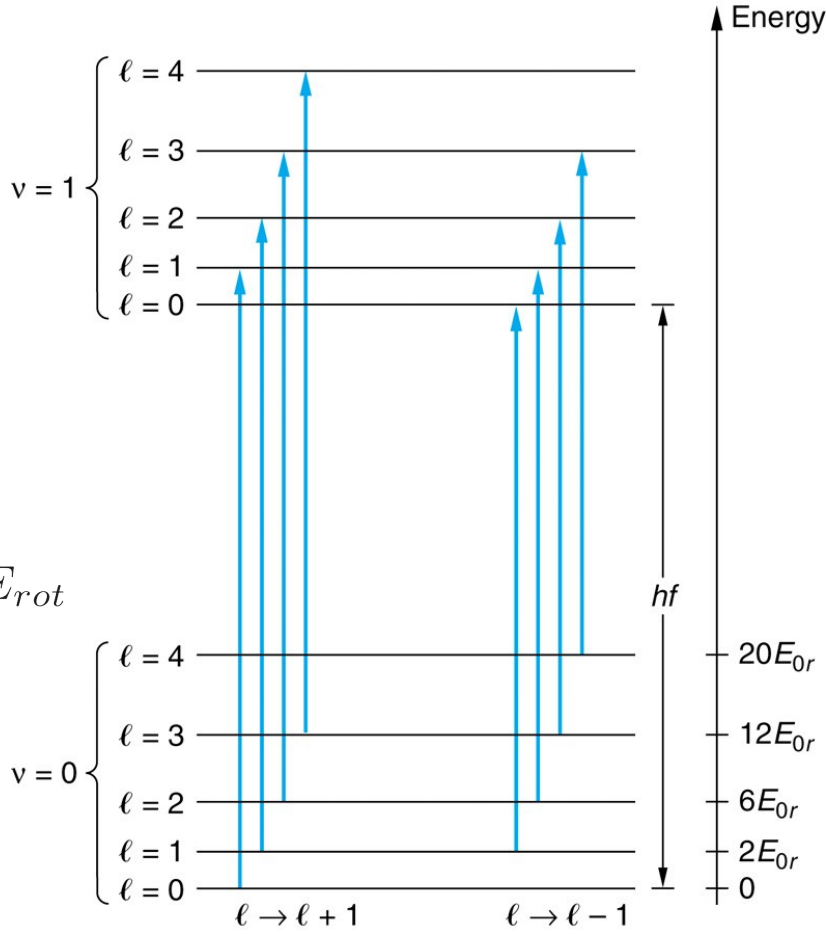
(2) Room temperature is high enough to induce transitions between rotational levels.

Absorptive Transitions

Transitions from $\nu = 0$ *and* $l = l$ allowed by the selection rules

$$E_l = \frac{\hbar\omega}{2} + l(l+1)E_{rot}$$

$$E_{l+1} = \frac{3\hbar\omega}{2} + (l+1)(l+2)E_{rot} \qquad E_{l-1} = \frac{3\hbar\omega}{2} + (l-1)lE_{rot}$$



Corresponding energies

$$\Delta E_{l\to l+1} = E_{l+1} - E_l = \hbar\omega + 2(l+1)E_{\text{rot}}$$

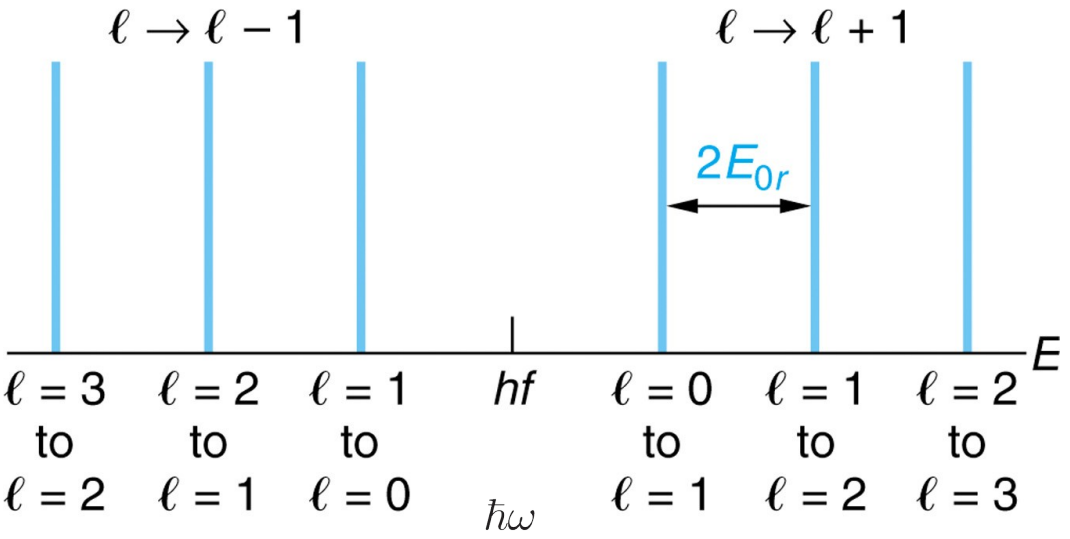
$$\Delta E_{l\to l-1} = E_{l-1} - E_l = \hbar\omega - 2lE_{\text{rot}}$$

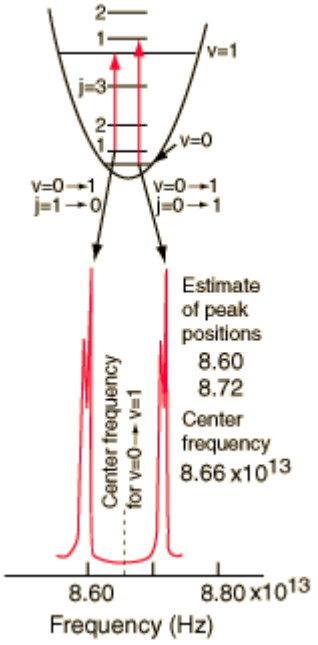
Absorption Spectrum

Energies of transitions from $\nu = 0$ *and* $l = l$ allowed by the selection rules

$$\Delta E_{l\to l+1} = E_{l+1} - E_l = \hbar\omega + 2(l+1)E_{\text{rot}}$$

$$\Delta E_{l\to l-1} = E_{l-1} - E_l = \hbar\omega - 2lE_{\text{rot}}$$



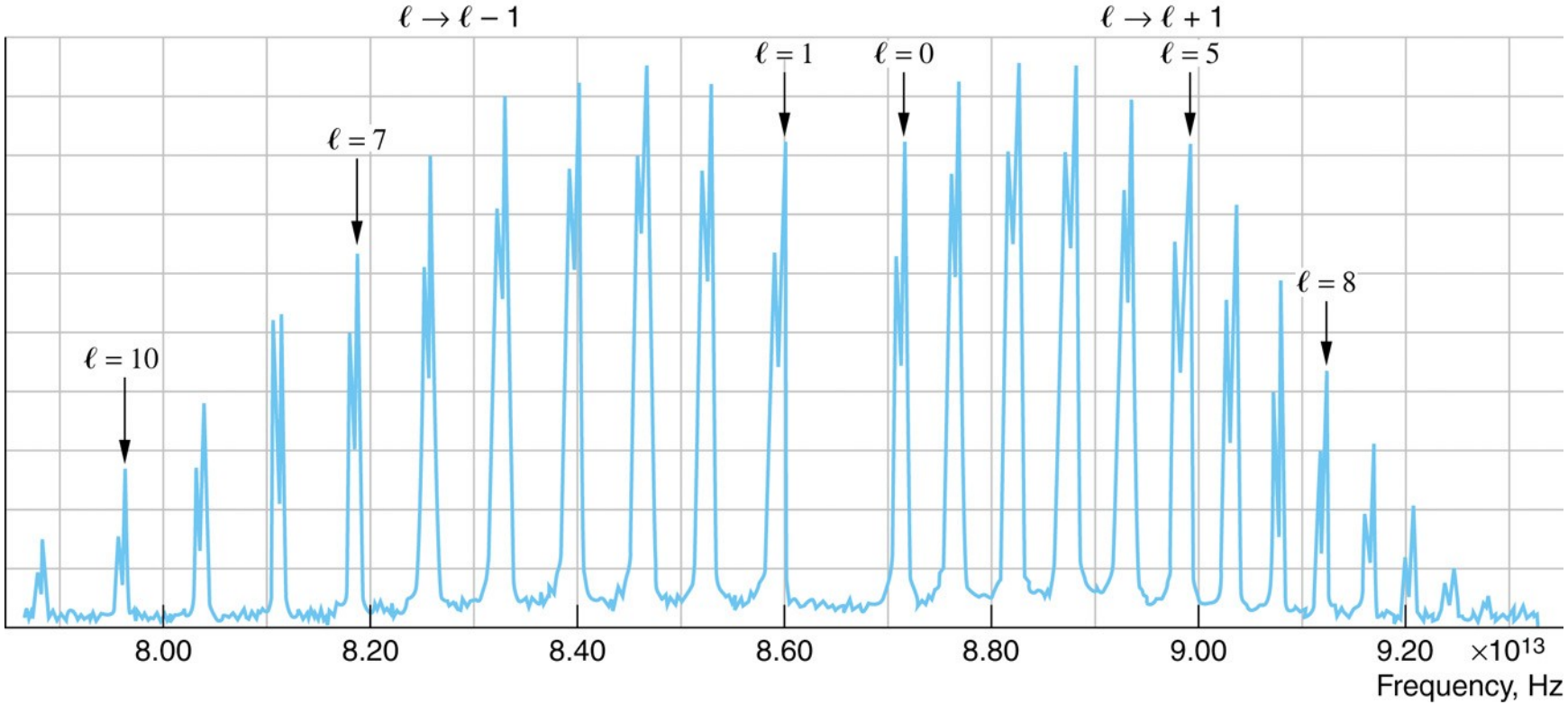


Observations

(1) Equally-spaced peaks are expected to be seen in the absorption spectrum of a diatomic molecule for transitions from the (vibrational) ground state.

(2) The energy corresponding to the center of the gap yields the natural angular frequency of oscillations.

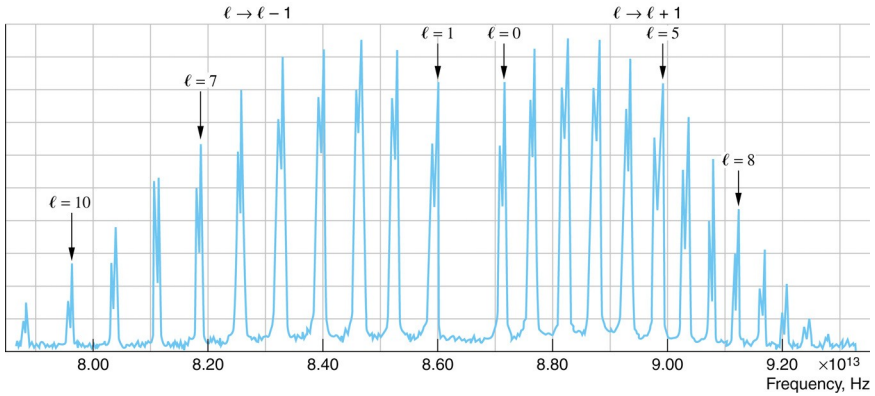
Absorption Spectrum. Example: HCl



Comment. The double-peak structure is due to presence of two isotopes of Cl (35 and 37, with the abundance ratio 3:1).

Absorption Spectrum. Example: HCl

Why are the intensities of the absorption processes (heights of absorption lines) not equal?



If, initially, all rotational levels were equally populated, then the absorption intensities would be equal. However, the levels are populated according to

$$n(E_l) = g(E_l)e^{-\frac{E_l}{k_B T}} = (2l+1)\exp\left\{-\left[\frac{\hbar\omega}{2} + l(l+1)E_{rot}\right]/k_B T\right\}$$

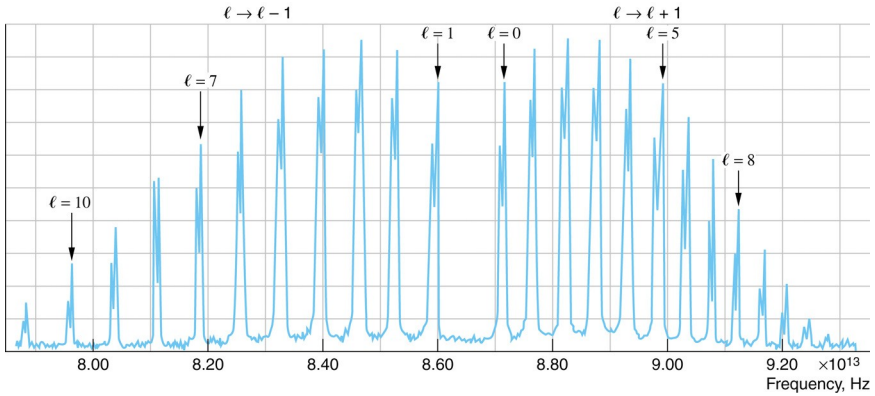
Comment: Usually the state with $l = 0$ is not the most populated one at room temperature. Notice that both factors in n depend on l. The former increases the population (with increasing l), whereas the latter makes it decrease. The value maximizing the population is

$$\frac{dn(E_l)}{dl} = 0 \Longrightarrow l_{max} = \frac{1}{2}\left(\sqrt{\frac{4k_B T}{\frac{h^2}{\mu r^2}}} - 1\right)$$

At room temperature ($k_B T \sim 26$ meV), $l_{max} \approx 3$ (cf. the figure above).

Absorption Spectrum. Example: HCl

Why is the spacing between adjacent peaks not exactly constant?



We have assumed that the moment of inertia is constant.
In fact diatomic molecules are not rigid rotors. Rotational motion of a molecule tends to increase the distance between the atoms (hence increase the moment of inertia), and decrease the rotational energy E_{rot}.

Summary

Summary

→ quantum mechanics provides tools for a detailed analysis of bonding mechanisms and microscopic structure of molecules (i.e. systems of atoms)

→ microscopic parameters of molecules (such as the binding energy, equilibrium separation, bonding force constant) can be found quantitatively

→ quantum mechanics allows to estimate the relevant energy scales for various excitations of the molecule interacting with electromagnetic radiation

→ study of transitions between different energy levels (spectroscopy) of molecules allows to characterize them quantitatively in a precise and consistent manner