



【Chapter 8 Molecules】

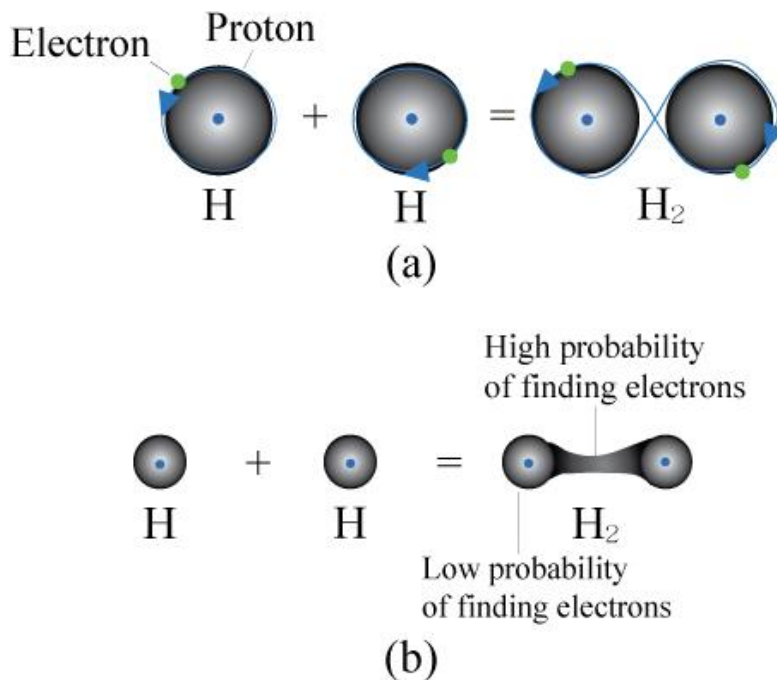


Figure 8.1 (see textbook) (a)Orbit model of the hydrogen molecule. (b)Quantum-mechanical model of the hydrogen molecule. In both models the shared electrons spend more time on the average between the nuclei, which leads to an attractive force. Such a bond is said to be covalent.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

- What holds atom together? Electric forces hold atoms together to form molecules.
- A molecule exists because its energy is less than that of the system of separate noninteracting atoms.

1. A covalent bond : pairs of e' are shared by two atoms.

example : H₂, the attractive force the e' exert on the protons is more than enough to counterbalancd the direct repulsion between them.

The balance occures at 7.42×10^{-11} m & $E = -4.5$ eV



By comparison



Easier to break up a molecule than to break up an atom

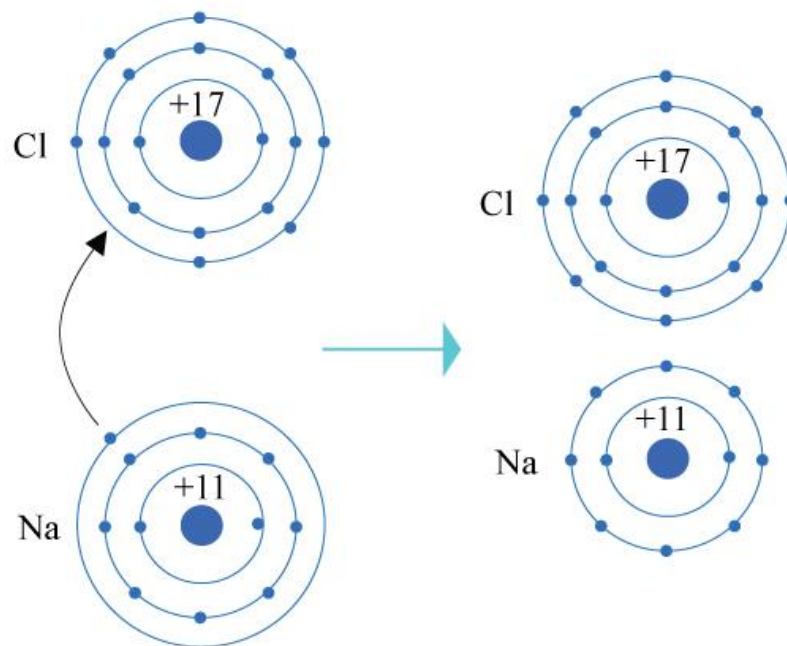


Figure 8.2 (see textbook) An example of ionic bonding. Sodium and chloride combine chemically by transfer of electrons from sodium atoms to chlorine atoms; the resulting ions attract each other electrically.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

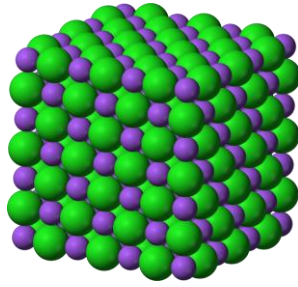


Figure 8.3 Scale model of an NaCl crystal. (source: wikipedia)

※References: Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris. Quantum Physics of atoms, molecules, Solids, nuclei and Particles. Eisberg & Resnick

2. An ionic bond : one or more e^- from one atom may transfer to the other and the resulting positive & negative ions attract each other. ex. : NaCl

In many molecules, an intermediate type of bond occurs in which the atoms share e^- to an unequal extent. ex : HCl

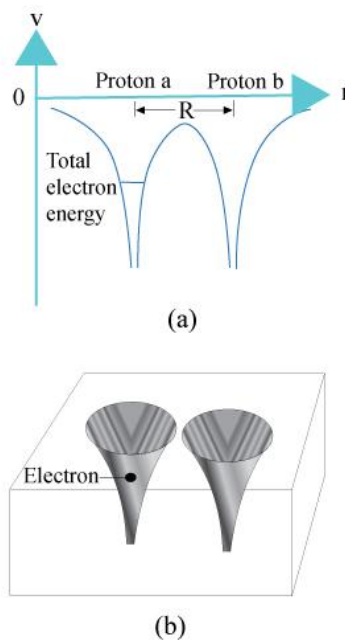


Figure 8.4 (see textbook) (a) Potential energy of an electron in the electric field of two nearby protons. The total energy of a ground-state electron in the hydrogen atom is indicated. (b) Two nearby protons correspond quantum-mechanically to a pair of boxes separated by a barrier.

※References: Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris. Quantum Physics of atoms, molecules, Solids, nuclei and Particles. Eisberg & Resnick

【8.2 Electron sharing】

→ The mechanism of the covalent bond

- Consider H_2^+ molecule : a single e^- bonds two protons.

The electric field around a proton is in effect a box for e^- .

Two nearby protons correspond to a pair of boxes with a wall between them.

- In classical physics, e^- are not allowed to jump spontaneously to a neighboring proton.

In Q.M. there is a certain probability that an e^- trapped in one box will tunnel through the wall & get into the other box, and tunnel back. $\Rightarrow e^-$ is shared by protons.

- The probability of an e^- pass through the region of high potential energy between two protons depends on how far apart the protons are.

If proton-proton distance is 0.1 nm \Rightarrow energy 10^{-15} s e^- jump from a proton.

If distance is 1 nm \Rightarrow once per second.

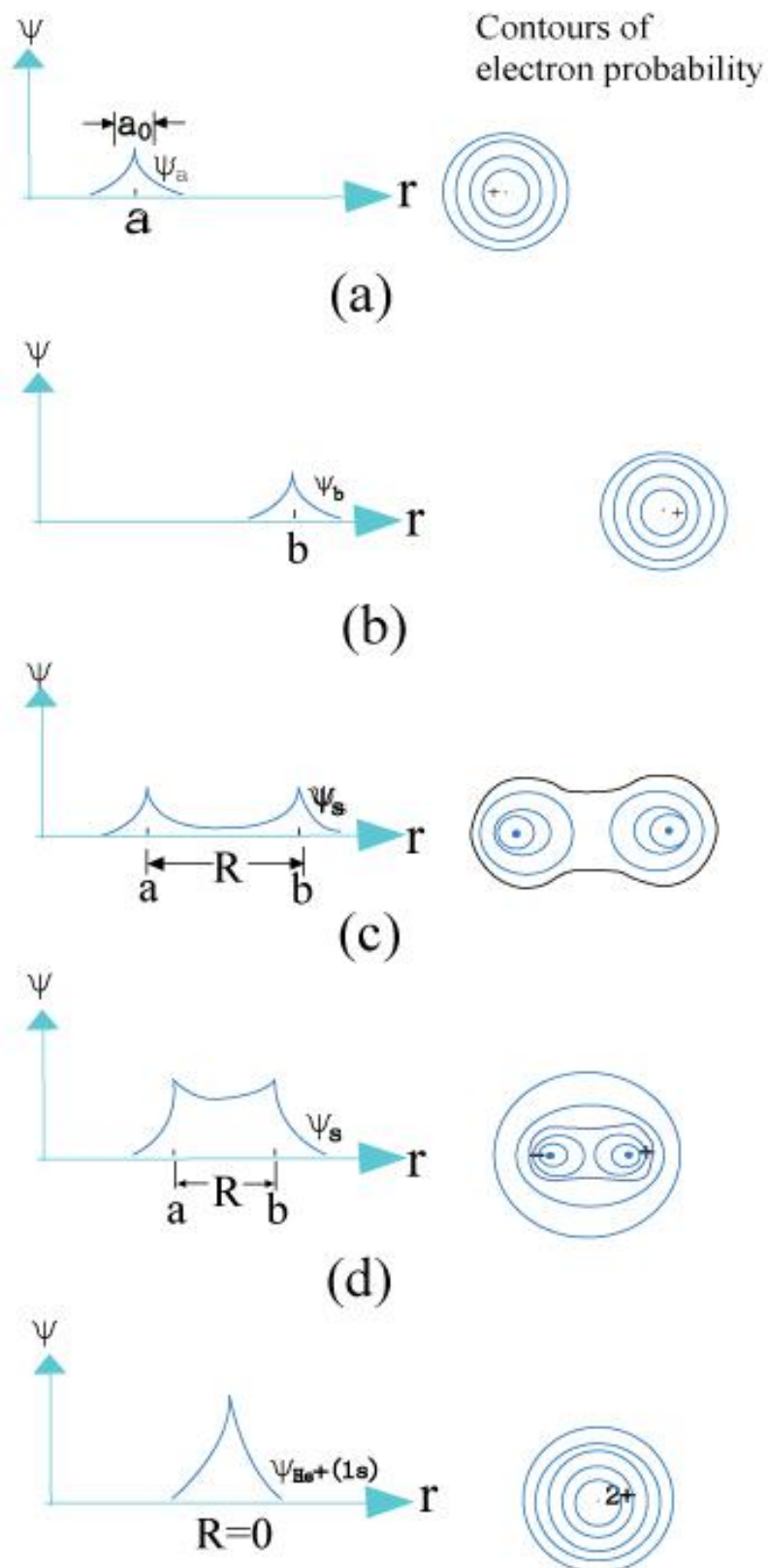


Figure 8.5 (see textbook) The combination of two hydrogen-atom 1s wave functions to form the symmetric H_2^+ wave function ψ_5 .

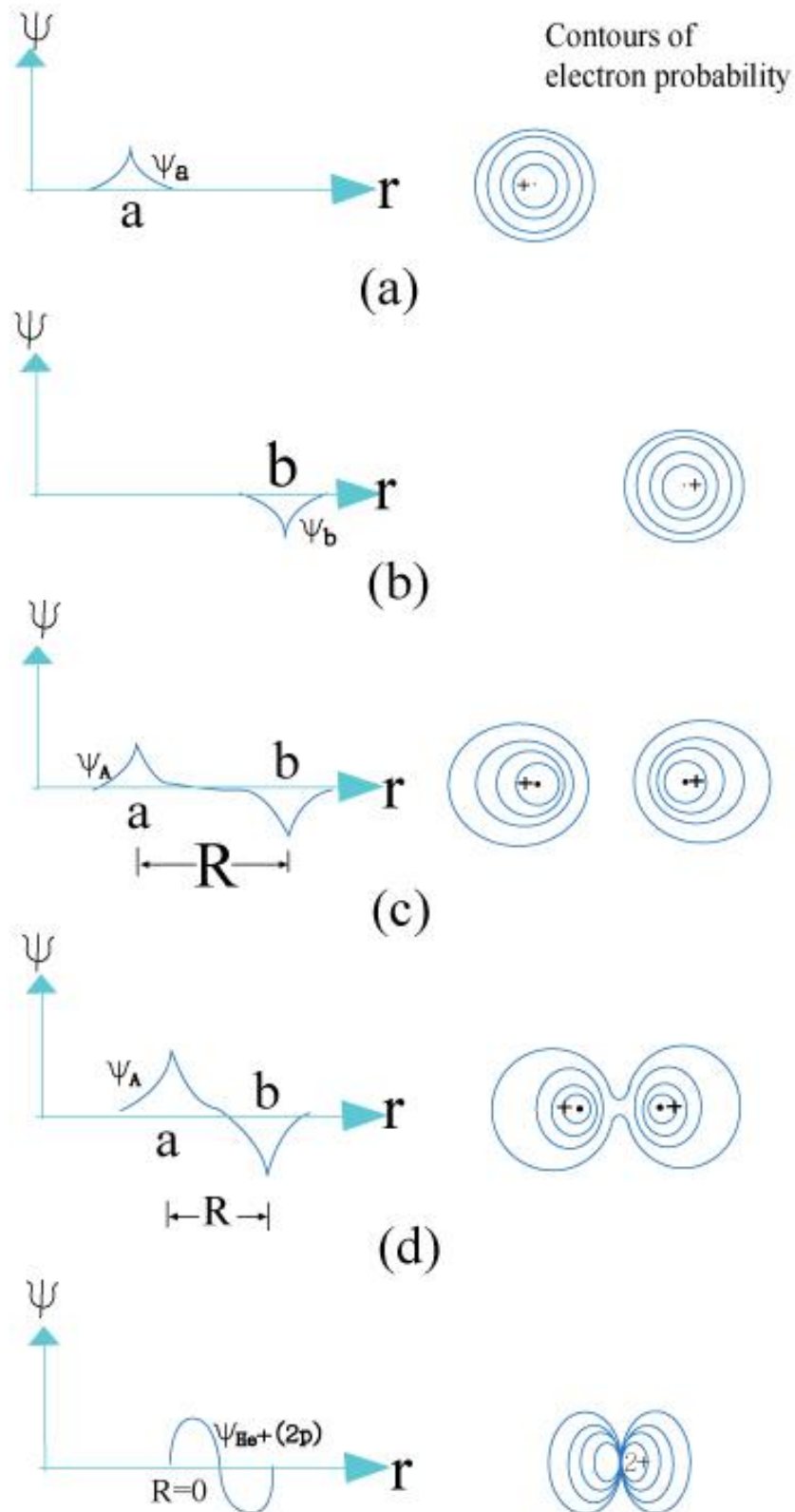


Figure 8.6 (see textbook) The combination of two hydrogen-atom 1s wave functions to form the antisymmetric H_2^+ wave function ψ_A

※References: Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris. Quantum Physics of atoms, molecules, Solids, nuclei and Particles. Eisberg & Resnick

2p state of He^+ is an excited state

1s state is the ground state

\Rightarrow H_2^+ in the antisymmetric state have more energy than when it is in the symmetric state.

Figure 8.7 (see textbook) Electron, proton repulsion, and total energies in H_2^+ as a function of nuclear separation R for the symmetric and antisymmetric states. The antisymmetric state has no minimum in its total energy.

※References: Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris. Quantum Physics of atoms, molecules, Solids, nuclei and Particles. Eisberg & Resnick

System Energy

- For symmetric case

When R is large \Rightarrow electron energy $E_s = -13.6 \text{ eV}$

The potential energy U_p of protons

$$U_p = \frac{e^2}{4\pi\epsilon_0 R}$$

When $R = 0 \Rightarrow$ electron energy E_s equal that of the He^+ ion

$\Rightarrow E^2(4x)$ that of H atom $\Rightarrow E_s = -54.4 \text{ eV}$

$E_s^{\text{total}} = E_s + U_p \rightarrow$ has a min.

- For antisymmetric case.

When $R = 0 \rightarrow 2p$ state of He^+

$$2p \text{ state of } \text{He}^+ \rightarrow E_n \frac{Z^2}{n^2} = -13.6 \text{ eV}$$

\therefore when $R \rightarrow \infty \Rightarrow E_A \rightarrow -13.6 \text{ eV}$ electron energy \sim
const (but small dip) The dip is not enough to form bond.

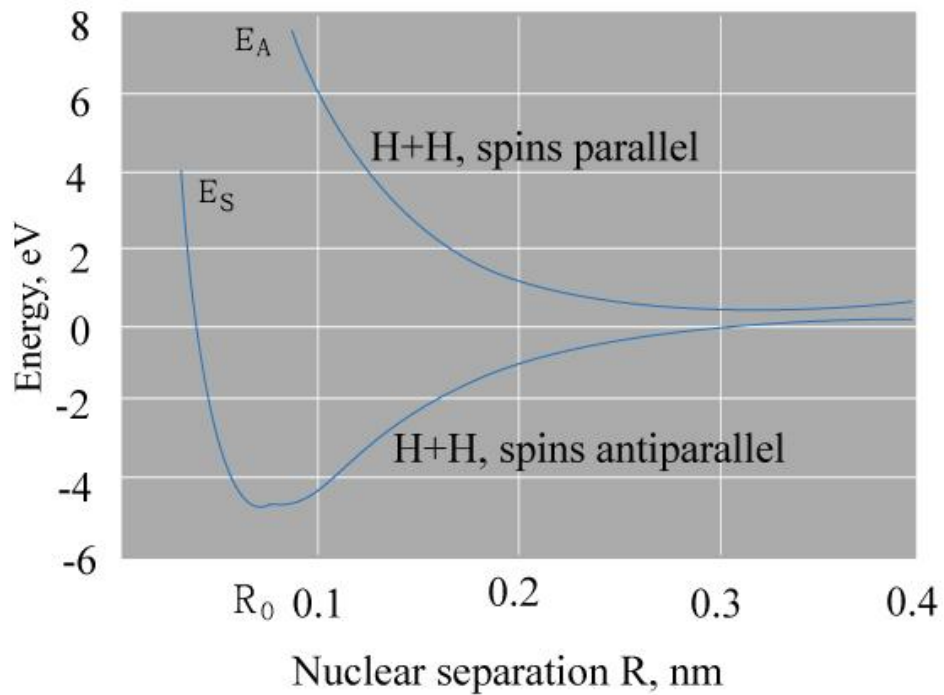


Figure 8.8 (see textbook) The variation of the energy of the system H+H with their distances apart when the electron spins are parallel and antiparallel.

※References: Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris. Quantum Physics of atoms, molecules, Solids, nuclei and Particles. Eisberg & Resnick

【8.4 H₂ molecule】

- H₂ molecule has two e', both e' can share the same orbital (same wave function $\varphi_{n\ell m_\ell}$) if their spins are antiparallel.
- Comparing H₂ & H₂⁺ => bounding energy of H₂ is not of H₂⁺ ∴ repulsion between two e'. In H₂, (same as H₂⁺) symmetric wave function φ_s leads to bound state.
- However, based on exclusion principle, the systems of e' are described by antisymmetric wave functions.

But the bound state in H₂ corresponds to both e' being described by a symmetrical wave function φ_s => contradict.

- The complete wave function $\Psi(1,2) = \varphi(1,2)s(1,2)$
 $\varphi(1,2)$ spatial wave function → e' coordinates
 $s(1,2)$ spin function → spin orientation
- The exclusion principle requires the complete wave function be antisymmetric to an exchange of both coordinates and spins, not $\varphi(1,2)$ only
 $\Psi = \varphi_s S_A$ or $\Psi = \varphi_A S_s$

- If spins of two e' are parallel => spin function is symmetric.

=> Φ needs to be antisymmetric.

- (2) If spins of two e' are antiparallel => spin function is

antisymmetric => Φ needs to be symmetric.

From detailed calculation of SH eq. => case (2) is the case

for H_2 (see fig 8.8)

Figure 8.10 (see textbook) The formation of $ss\sigma$, $pp\sigma$, and $pp\pi$ bonding molecular orbitals. Two p_y atomic orbitals can combine to form a $pp\sigma$ molecular orbital in the same way as shown for two p_x atomic orbitals but with a different orientation.

※References: Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris. Quantum Physics of atoms, molecules, Solids, nuclei and Particles. Eisberg & Resnick

- Molecular bonds are classified by Greek letters according to their angular momenta L about the bond axis (i.e. z axis).

σ corresponds to $L = 0$, π corresponds to $L = \hbar$

- H_2O molecule : one 2p orbital in O is fully occupied by two e', the other two 2p orbital are only singly occupied and so can join with the 1s orbital of two H atoms to form $sp\sigma$ bonding orbital. The mutual repulsion between H nuclei widens the angles between the bond axes from 90° to 104.5°

Figure 8.13 (see textbook) The bonds in the CH_4 (methane) molecule involve sp^3 hybrid orbitals.

※References: Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris. Quantum Physics of atoms, molecules, Solids, nuclei and Particles. Eisberg & Resnick

- * Hybrid orbital → The way in H₂O can not be used for CH₄
- A C has two e' in 2s and once' in each of two 2p orbital => expect CH₂ with two spσ bonding => not the case. (i.e. 2s does not participate bonding)
- Linear combinations of both the 2s & 2p atomic orbital of C contribute to each molecular orbital in CH₄
- 2s & 2p wave functions are both solutions of the same SH eq. if the corresponding energies are the same, which is not the case in isolated C atom.

In an CH₄ molecule, the E field experienced by outer C e' is affected by the nearby H nuclei => energy difference between 2s & 2p can disappear.

- Hybrid orbital that consist of mixtures of s & p orbital occur when bonding energies are greater than pure orbital. In CH₄, hybrid orbital are mixture of one 2s & 3 2p orbital => sp³ hybrids.

Figure 8.15 (see textbook) The benzene molecule. (a)The overlap between the sp² hybrid orbitals in the C atoms with each other and with the s orbitals of the H atoms lead to σ bonds. (b)Each C atom has a pure p_x orbital occupied by one electron. (c)The bonding π molecule orbitals formed by the six p_x atomic orbitals constitute a continuous electron probability distribution around the molecule that contains six delocalized electrons

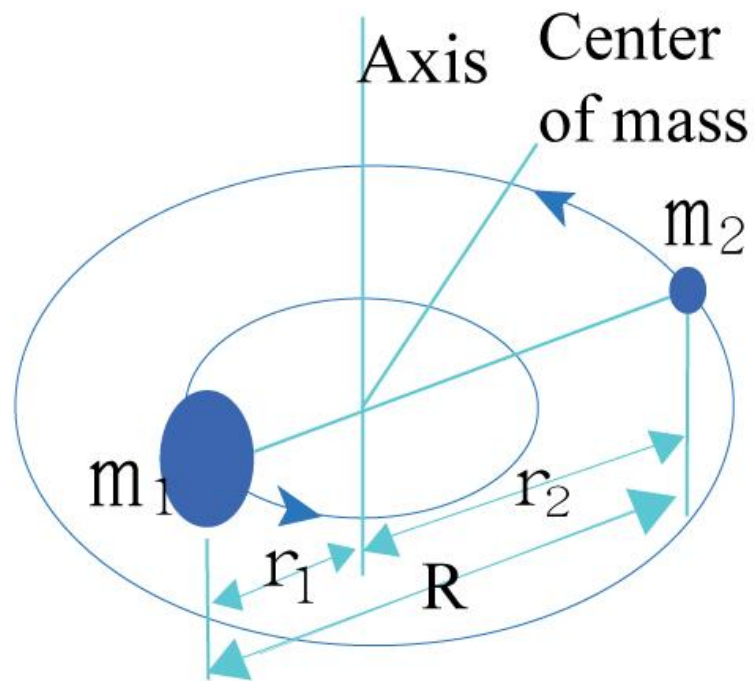


Figure 8.16 (see textbook) A diatomic molecule can rotate about its center of mass.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum
Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

【8.6 Rotation Energy Levels】

Molecular energy states arise from (1) the rotation of a molecule as a whole (2) vibrations of its atoms relative to one another (3) changes in its electronic configuration

(1) Rotational states are separated by quite small energy intervals ($\sim 10^{-3}$ eV)

→ microwave region (0.1mm~1cm)

(2) Vibrational states separated by ~ 0.1 eV → infrared region (1 μ m~0.1mm)

(3) Molecular electronic states separated by \sim eV → visible & UV region

- For diatomic molecules

The moment of inertia of this molecule about an axis passing through its center of mass $\Rightarrow I = m_1 r_1^2 + m_2 r_2^2$

From the definition of center of mass $\Rightarrow m_1 r_1 = m_2 r_2 \Rightarrow$

$$I = \frac{m_1 m_2}{m_1 + m_2} (r_1 + r_2)^2 = m' R^2$$

$$\Rightarrow \text{reduced mass } m' = \frac{m_1 m_2}{m_1 + m_2}$$

Angular momentum L

$L = I\omega$ (ω : angular velocity)

L is quantized

If we denote rotational quantum number J

$$\Rightarrow L = \sqrt{J(J+1)}\hbar \quad J = 0, 1, 2, 3, \dots$$

$$\text{rotational energy levels } E_J = \frac{1}{2} I\omega^2 = \frac{L^2}{2I} = \frac{J(J+1)\hbar^2}{2I} \quad (\text{see ex 8.1})$$

- Rotational spectra : arise from transitions between rotational energy states.

Only molecules that have electric dipole moments can absorb or emit photons.

For a rigid diatomic, the selection rule for rotational transitions is $\Delta J = \pm 1$

In practice, rotational spectra are always obtained in absorption.

$$\nu_{J \rightarrow J+1} = \frac{\Delta E}{h} = \frac{E_{J+1} - E_J}{h} = \frac{\hbar}{2\pi I} (J+1) \Rightarrow \text{equally spaced.}$$

From the data, I can be calculated. Bond length in molecular can be got. (see ex 8.2)

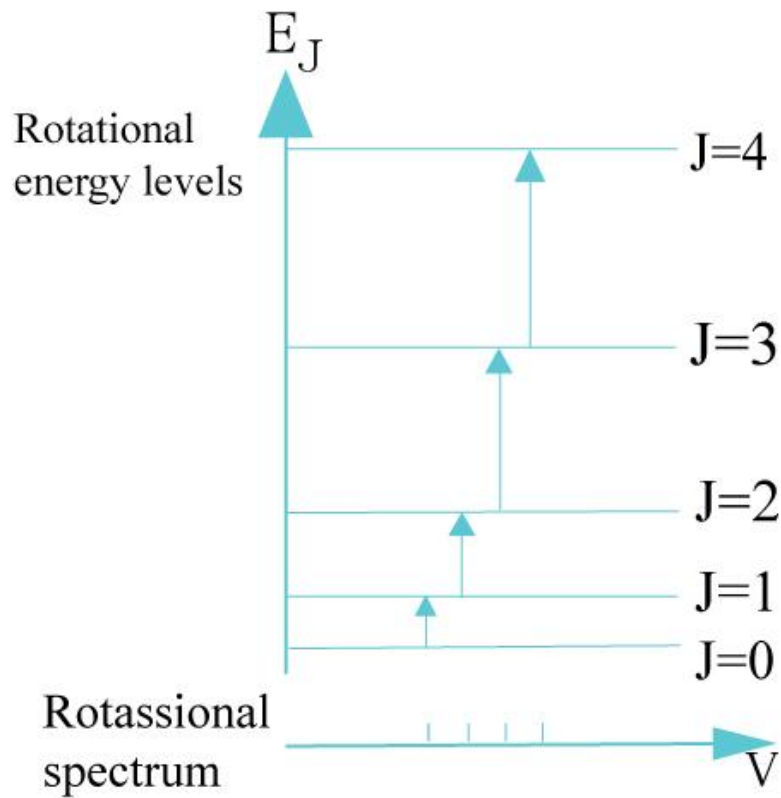


Figure 8.17 (see textbook) Energy levels and spectrum of molecular rotation.

Figure 8.18 (see textbook) The potential energy of a diatomic molecule as a function of internuclear distance.

Two-body oscillator

$$v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m'}} \quad (8.15)$$

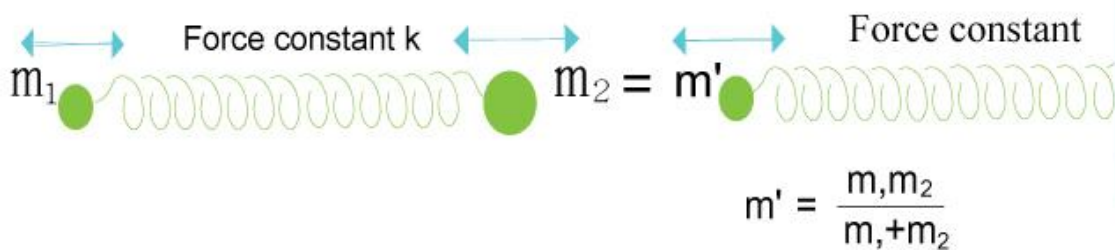


Figure 8.18 (see textbook) A two-body oscillator behaves like an ordinary harmonic oscillator with the same spring constant but with the reduced mass m'

※References: Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris. Quantum Physics of atoms, molecules, Solids, nuclei and Particles. Eisberg & Resnick

【8.7 Vibrational Energy Levels (for diatomic molecule)】

- Near the minimum of U-R curve (fig 8.18) → parabolic

$$\Rightarrow U = U_0 + \frac{1}{2}k(R - R_0)^2 \quad R_0 : \text{equilibrium separation}$$

$$F = -\frac{dU}{dR} = -k(R - R_0) \Rightarrow \text{interatomic force (restoring force)}$$

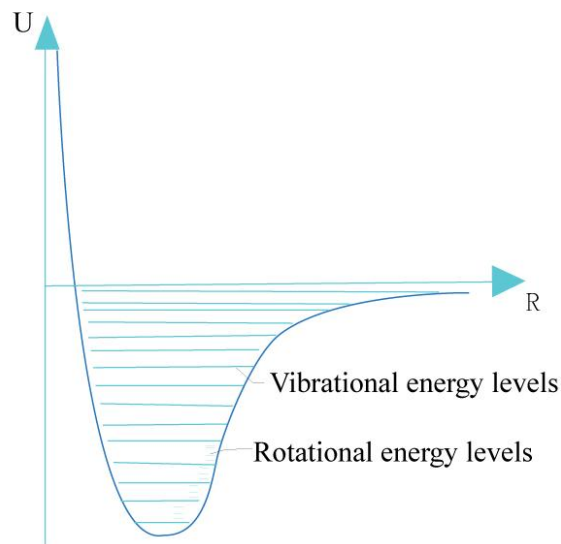


Figure 8.20 (see textbook) The potential energy of a diatomic molecule as a function of interatomic distance, showing vibrational and rotation energy levels.

※References: Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris. Quantum

Physics of atoms, molecules, Solids, nuclei and Particles. Eisberg & Resnick

- Classically, the frequency of vibrating body of m connected

to a spring of force constant k is
$$v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

For two-body oscillator $\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m'}}$ $m' = \frac{m_1 m_2}{m_1 + m_2}$

For harmonic oscillator $E = \left(\nu + \frac{1}{2} \right) h \nu_0$

ν : vibrational quantum number $\nu : 0, 1, 2, 3, \dots$

The lowest vibration state $\nu = 0 \Rightarrow E_0 = \frac{1}{2} h \nu_0 = 0 \Rightarrow$

uncertainty principle.

If oscillating particle were stationary $\Rightarrow \Delta x = 0 \Rightarrow \Delta p \rightarrow \infty$

- vibrational energy levels

$$E_\nu = \left(\nu + \frac{1}{2} \right) \hbar \sqrt{\frac{k}{m}}$$

The higher vibrational states do not obey above eq.

∴ potential energy curve is not parabolic.

\Rightarrow spacing between adjacent levels of ν for higher vibration states.

- selection rule for vibrational states

$$\Delta \nu = \pm 1$$

see Ex 8.3

* Vibration-Rotation Spectra

Pure vibrational spectra are observed only in liquid where interactions between adjacent molecules inhibit rotation.

$\therefore E_{\text{vibration}} \gg E_{\text{rotational}} \Rightarrow$ freely moving molecules in a gas are rotating

The spectra of molecules do not show isolated lines corresponding to each vibrational transition, but a large number of closely spaced lines due to transitions between the various rotational states. \Rightarrow vibration-rotation band

- To a first approximation, the vibrations & rotations of a molecule take place independently of each other

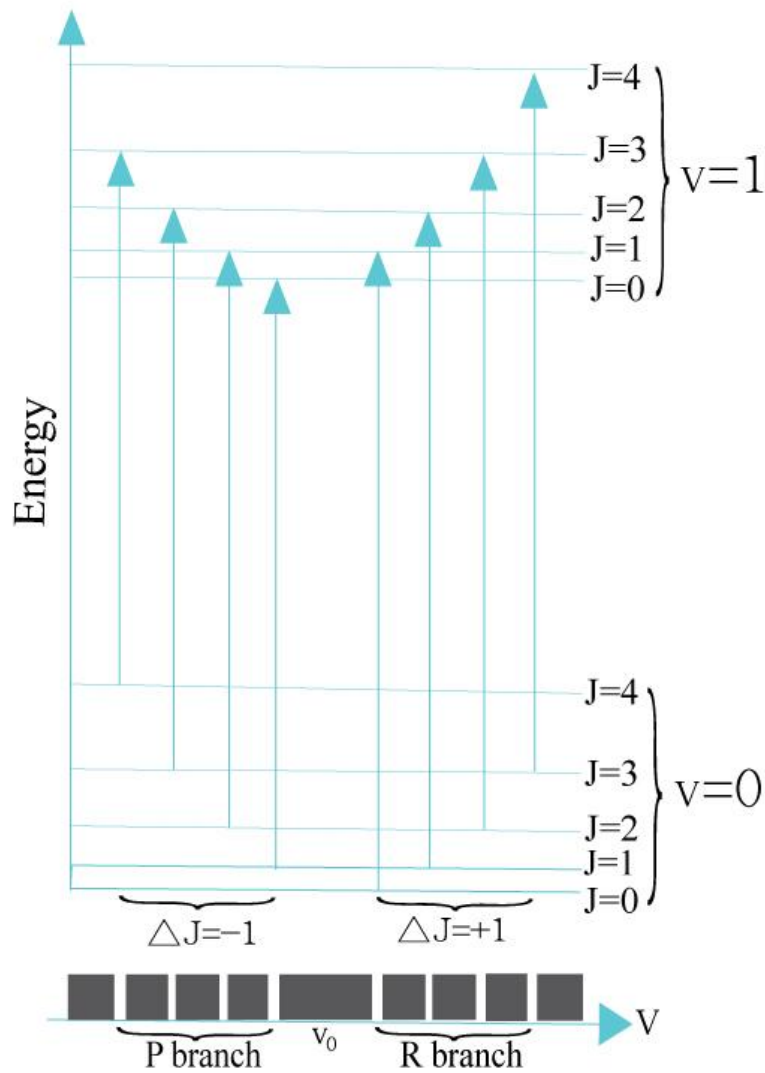


Figure 8.21 (see textbook) The rotation structure of the $v=0 \rightarrow v=1$ vibrational transitions in a diatomic molecule. there is no line at $v=v_0$ (the Q branch) because of the selection rule $\Delta J=1$

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris.Quantum

Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

For diatomic molecule
$$E_{v,J} = \left(v + \frac{1}{2} \right) \hbar \sqrt{\frac{k}{m'}} + J(J+1) \frac{\hbar^2}{2I}$$

- For $v = 0 \rightarrow v = 1$ transitions

- The spacing between p & R branch is $\Delta v = \frac{\hbar}{2\pi I}$

⇒ moment of inertia of a molecule can be found from its IR vibration-rotation spectrum (or from microwave pure-rotation spectrum)

vibrational spectra a valuable tool indeterming molecular structures.

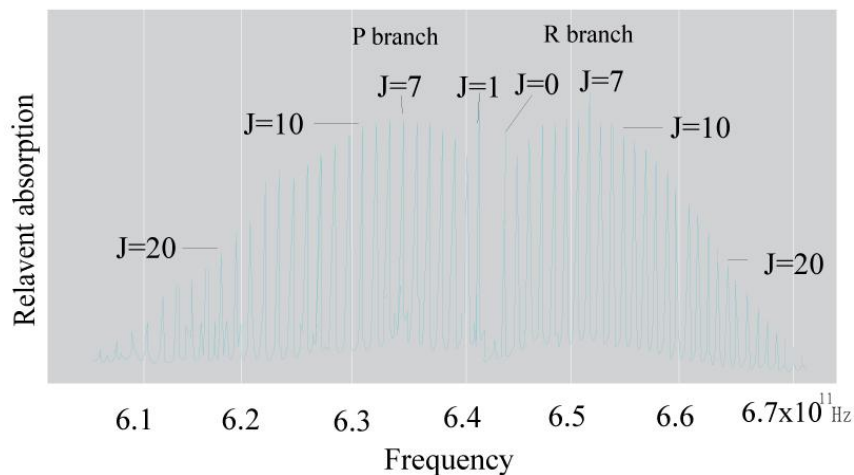


Figure 8.22 (see textbook) The $\nu=0 \rightarrow \nu=1$ vibrational-rotation absorption band in CO under high resolution. The lines are identified by the value of J in the initial rotational state.

※References: Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris. Quantum Physics of atoms, molecules, Solids, nuclei and Particles. Eisberg & Resnick

For example, thioacetic acid

Either $\text{CH}_3\text{CO-SH}$ or $\text{CH}_3\text{CS-OH}$

IR absorption spectrum contains a line at frequency equal to vibrational frequencies of $\text{C}=\text{O}$ and $-\text{SH}$ group.

⇒ confirm $\text{CH}_3\text{CO-SH}$.

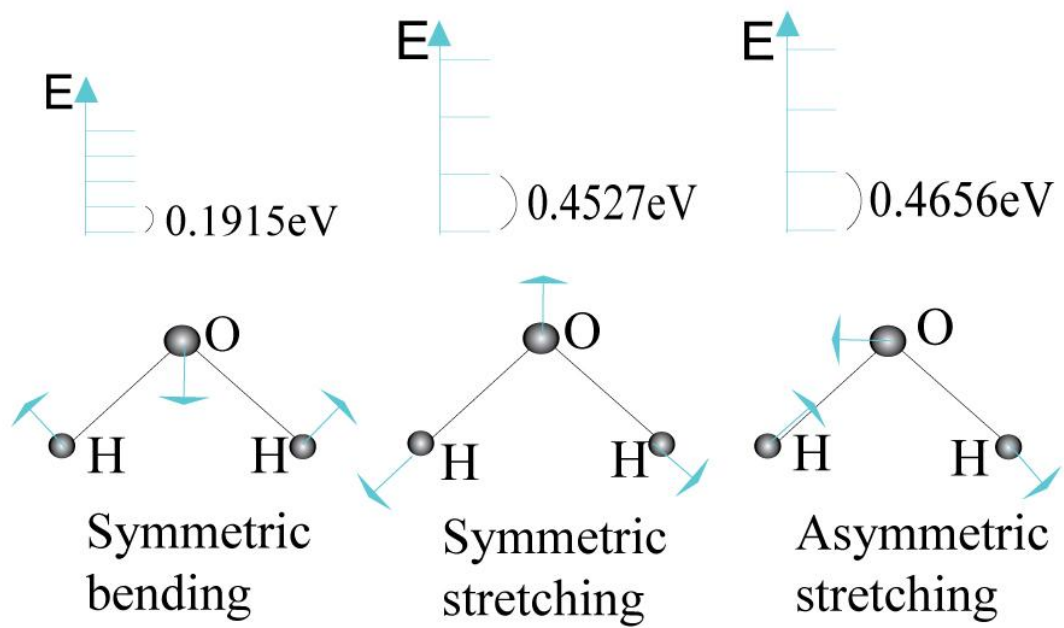


Figure 8.23 (see textbook) The normal modes of vibration of the H_2O molecule and the energy levels of each mode.

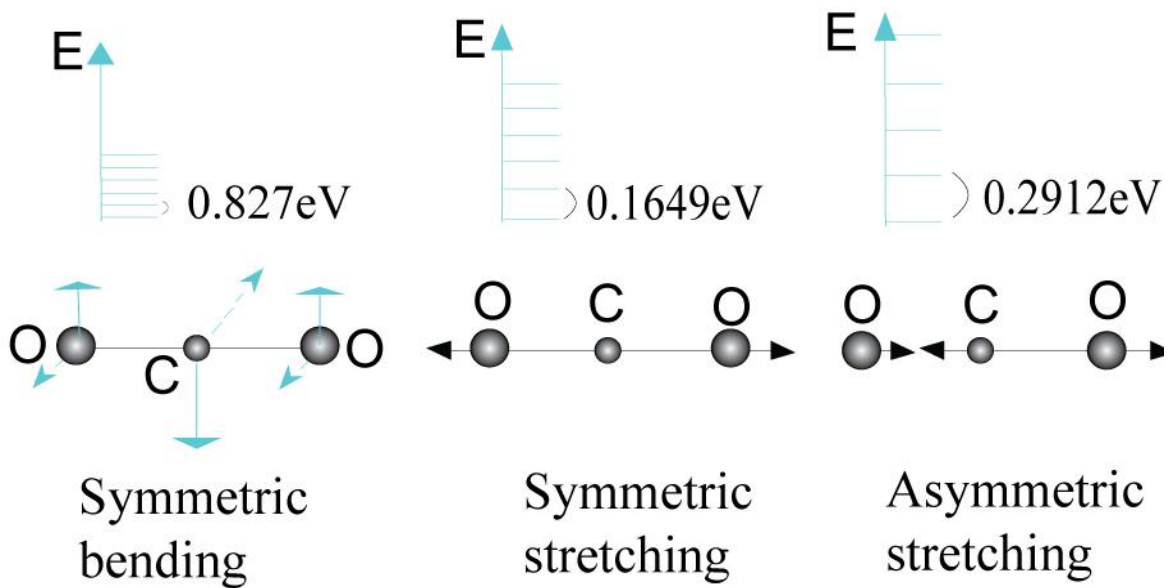


Figure 8.24 (see textbook) The normal modes of vibration of the CO_2 molecule and the energy levels of each mode. The symmetric bending mode can occur in two perpendicular planes.

Figure 8.25 (see textbook) A portion of the band spectrum of PN.

※References: Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris. Quantum

Physics of atoms, molecules, Solids, nuclei and Particles. Eisberg & Resnick

【8.8 Electronic Spectra of Molecules】

The molecule's e⁻ can be excited to higher energy levels. Electronic transitions involve radiation in visible or UV parts of spectrum. Each transition appears as a series of closely spaced lines, due to the presence of different rotational & vibrational states in each electronic state.

A molecule in an excited electronic state can lose energy and return to its ground state in various ways.

(1) emit a photon of the same frequency as that of the photon it absorbed.

→ returned to ground state in a single step.

(2) fluorescence : molecule gives up some of its vibrational energy in collisions with other molecule.

=> downward radiative transition originated from a lower vibrational level in the upper electronic state.

=> Fluorescent radiation is therefore of lower frequency than that of the absorbed radiation

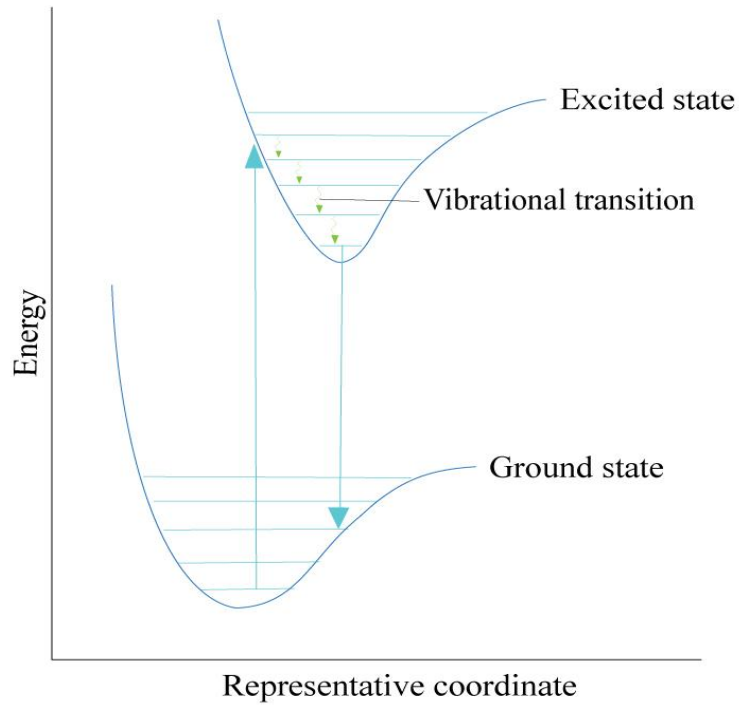


Figure 8.26 (see textbook) The origin of fluorescence. The emitted radiation is lower in frequency than the absorbed radiation.

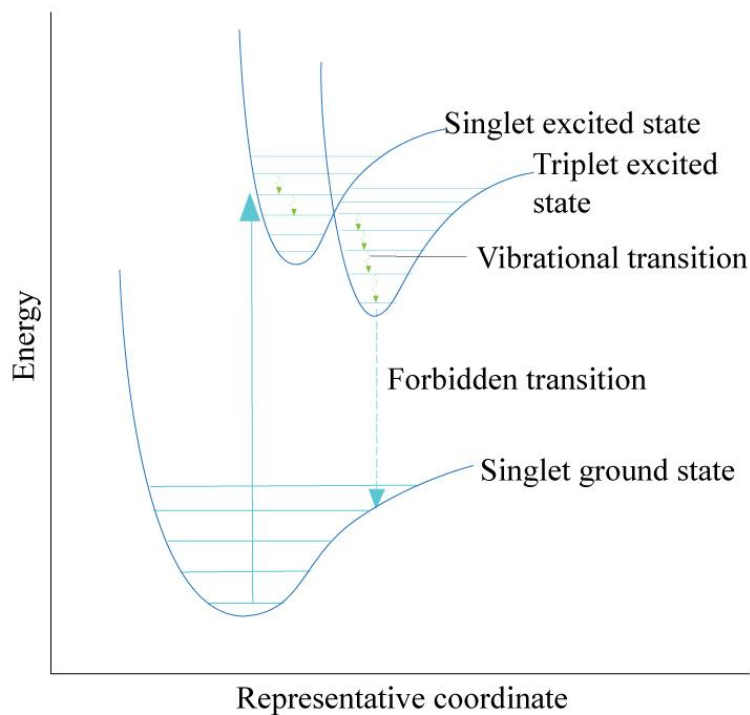


Figure 8.27 (see textbook) The origin of phosphorescence. The final transition is delayed because it violates the selection rules for electronic transitions.

※References: Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, Randy Harris. Quantum Physics of atoms, molecules, Solids, nuclei and Particles. Eisberg & Resnick

- In molecular spectra

Radiative transition between electronic states of different total spin are prohibited.

- From triplet to singlet transitions have long half-lives result in phosphorescent radiation.

