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Chapter 6 Electronic Spectroscopy of Molecules

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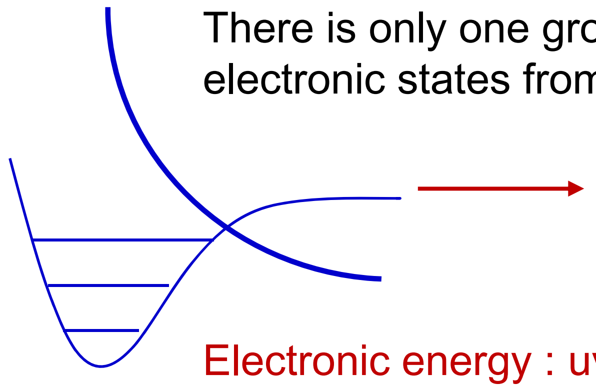
Structure of potential energy

Unbound state : No potential minimum
= No formation of molecule

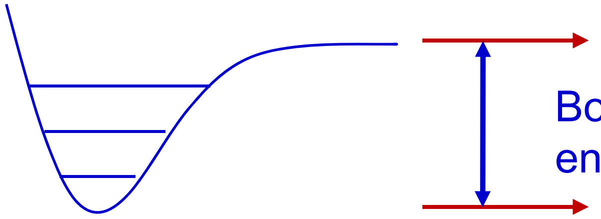
There is only one ground state, but many excited electronic states from atoms of excited states.



Ionization limit

Bound state :
potential minimum

Electronic energy : uv/visible energy



Ionization limit

Bond dissociation energy

Vibrational energy : IR

Rotational energy : MW energy

Changes in Molecular Structure upon Excitation

Rotational Excitation:

No change in Molecular Structure. Very small difference due to the centrifugal distortion

Vibrational Excitation:

Bond length increases with vibrational quantum number because of the shape of anharmonic potential

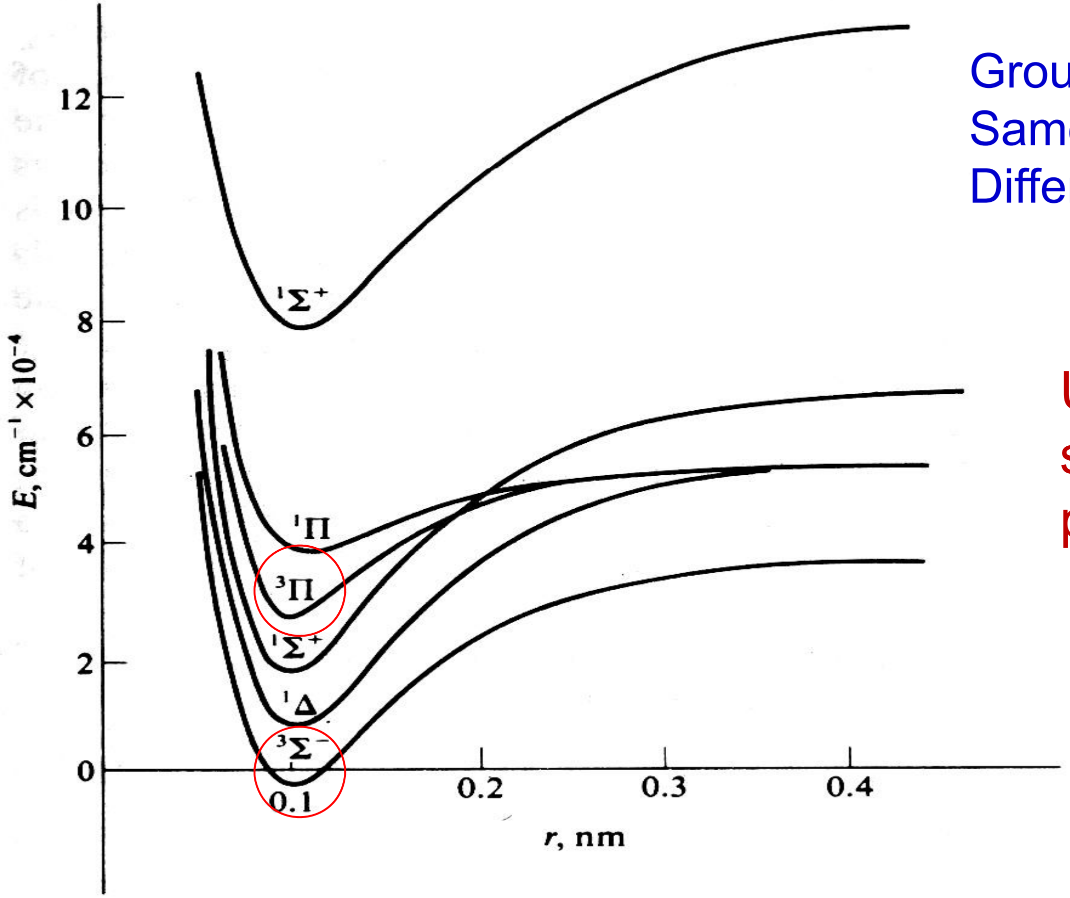
Electronic Excitation:

Large changes in molecular size as well as molecular shape because the bonds could break off upon electronic excitation.

Let's see the change of structure upon excitation.

Potential energy surface (PES) of bound states

There exist many excited bound states obtained from atoms of excited states.



Ground state: X state
Same spin states: A, B, C,
Different spin states: a, b, c,

Unbound states, not shown here, do not have potential minima.

FIGURE 6.2
Potential energy functions for the ground and five stable excited states of the NH molecule.

There is a large change in molecular structure with electronic excitation.

6.1 ELECTRONIC SPECTRA OF DIATOMIC MOLECULES

6.1.1 The Born-Oppenheimer Approximation

We have already studied this concept in rotational-vibrational interaction. Actually, there is an interaction between rotation and vibration. But we apply the same concept to electron and nuclear motions. Nuclear motion is related to rotation and vibration of molecules.

As a first approach to the electronic spectra of diatomic molecules we may use the Born–Oppenheimer approximation previously mentioned in Sec. 3.2; in the present context this may be written:

Now, extend to 3 different motions.

Total energy is sum of

$$\underline{E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}}} \tag{6.1}$$

which implies that the electronic, vibrational, and rotational energies of a molecule are completely independent of each other. We shall see later to what extent this approximation is invalid. A change in the total energy of a molecule may then be written:

Compare the energy size of each motion.

$$\Delta E_{\text{total}} = \Delta E_{\text{elec.}} + \Delta E_{\text{vib.}} + \Delta E_{\text{rot.}} \quad \text{J}$$

or

$$\Delta \varepsilon_{\text{total}} = \Delta \varepsilon_{\text{elec.}} + \Delta \varepsilon_{\text{vib.}} + \Delta \varepsilon_{\text{rot.}} \quad \text{cm}^{-1} \tag{6.2}$$

Rotational and vibrational motion belong to nuclear motion.

6.1.2 Vibrational Coarse Structure: Progressions

Without rotational

Since $\Delta E_{elec} > \Delta E_{vib} >> \Delta E_{rot}$

UV/visible IR far IR/MW

Initially, neglecting rotational changes in the transition

$$\underline{E_{\text{total}} = E_{\text{elec.}} + E_{\text{vib.}}} \quad \text{J}$$

Takes only two motions.

$$\varepsilon_{\text{total}} = \varepsilon_{\text{elec.}} + \varepsilon_{\text{vib.}} \quad \text{cm}^{-1}$$

$$\varepsilon_{\text{total}} = \underline{\varepsilon_{\text{elec.}}} + \underline{(v + \tfrac{1}{2})\bar{\omega}_e - x_e(v + \tfrac{1}{2})^2\bar{\omega}_e \quad \text{cm}^{-1}} \qquad (v = 0, 1, 2, \dots)$$

$$\bar{v}_{\text{spec.}} = \underline{(\varepsilon' - \varepsilon'')} + \{(v' + \tfrac{1}{2})\bar{\omega}'_e - x'_e(v' + \tfrac{1}{2})^2\bar{\omega}'_e\}$$
$$- \{(v'' + \tfrac{1}{2})\bar{\omega}''_e - x''_e(v'' + \tfrac{1}{2})^2\omega''_e\} \quad \text{cm}^{-1}$$

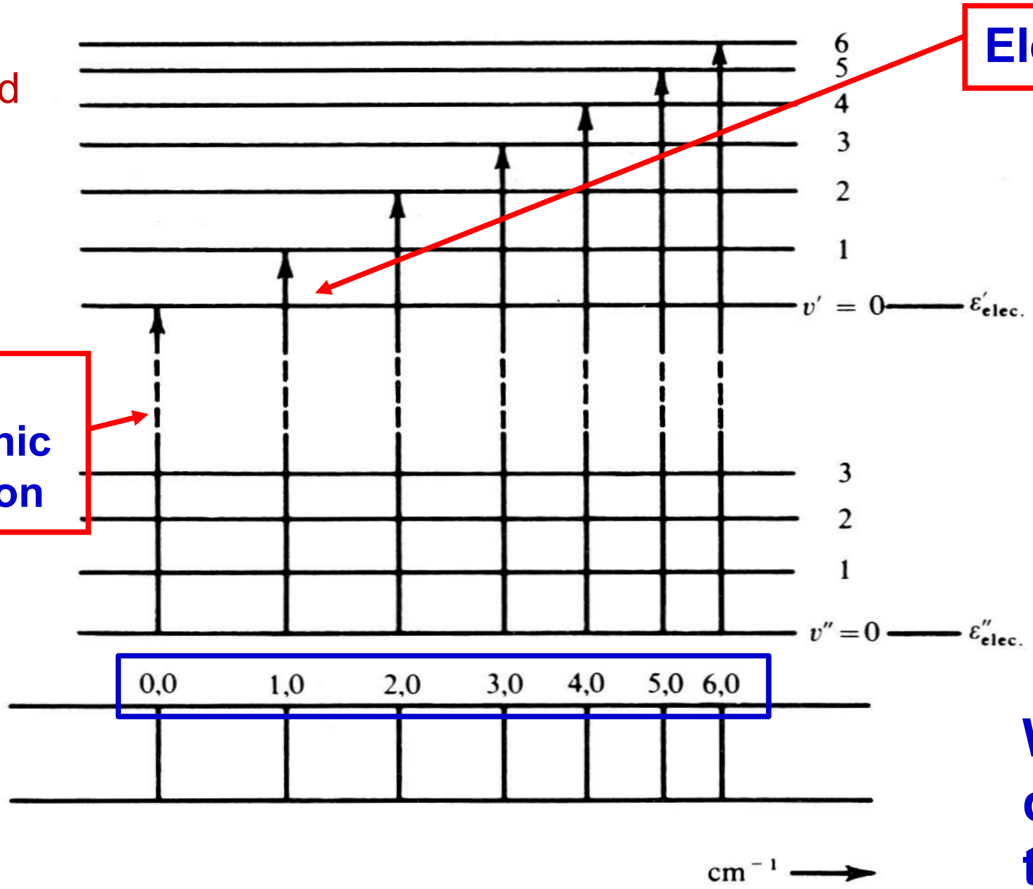
Vibrational frequencies depend on the electronic states.

Intensity of Vibronic Transitions

Excited states

Electronic + Vibrational

Pure electronic transition



The difference represents the vibrational energy at the upper state.

Ground state

What is the Intensity distribution of vibronic transitions ?

Figure 6.1 The vibrational 'coarse' structure of the band formed during electronic absorption from the ground ($v'' = 0$) state to a higher state.

The selection rule of vibronic (vibrational + electronic) transition is not limited.

6.1.3 Intensity of Vibrational-Electronic Spectra: the Franck-Condon Principle

vibronic

Franck-Condon principle: One of the most important rule explaining the transition intensity in vibronic transition.

Franck explained the intensity in terms of classical mechanics while Condon tried to describe the phenomena by quantum mechanics.

Franck-Condon principle: An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance and vibrating speed appreciably during the transition.

Another application of Born-Oppenheimer approximation

Quantum mechanical description (difficult)

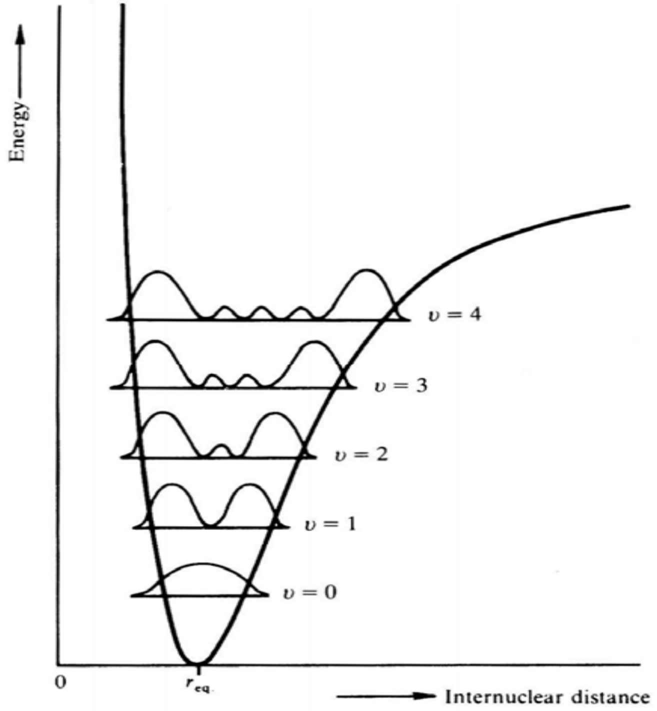


Figure 6.2 The probability distribution for a diatomic molecule according to the quantum theory. The nuclei are most likely to be found at distances apart given by the maxima of the curve for each vibrational state.

Overlap of wave functions connected by transition

The overlap is called as Franck-Condon factor

Transition probability is proportional to the overlap size of two wave function. If the integration of two wave function is zero, then two functions are orthogonal.

In harmonic oscillator, all wave functions are orthogonal.

The intensity of a vibronic transition is proportional to the square of the transition moment $\boldsymbol{R}_{ev}$ which is given by (*see* equation 2.21)

$$\boldsymbol{R}_{ev} = \int \underline{\psi_{ev}'}^{*}\underline{\boldsymbol{\mu}}\,\underline{\psi_{ev}''}\,\mathrm{d}\tau_{ev} \tag{6.123}$$

Transition expressed quantum mechanically.

where $\boldsymbol{\mu}$ is the electric dipole moment operator and ψ_{ev}' and ψ_{ev}'' are the vibronic wave functions of the upper and lower states, respectively. The integration is over electronic and vibrational coordinates. Assuming that the Born–Oppenheimer approximation (Section 1.3.3) holds, ψ_{ev} can be factorized into $\psi_e\psi_v$. In addition $\boldsymbol{\mu}$ can be broken down into $(\boldsymbol{\mu}_e + \boldsymbol{\mu}_n)$, which are the contributions from the electrons and nuclei, respectively. Then equation (6.123) becomes

$$\boldsymbol{R}_{ev} = \int \psi_e'^{*}\psi_v'(\boldsymbol{\mu}_e + \boldsymbol{\mu}_n)\psi_e''\psi_v''\,\mathrm{d}\tau_e\,\mathrm{d}r \tag{6.124}$$

Separate electronic and vibrational

Since the vibrational wave functions, given in equation (1.104) are always real, $\psi_v^{*} = \psi_v$. Since $\boldsymbol{\mu}_e$ is a constant with respect to ψ_v and $\boldsymbol{\mu}_n$ a constant with respect to ψ_e

$$\boldsymbol{R}_{ev} = \int \psi_e'^{*}\psi_e''\,\mathrm{d}\tau_e \int \psi_v'\boldsymbol{\mu}_n\psi_v''\,\mathrm{d}r + \int \psi_v'\psi_v''\,\mathrm{d}r \int \psi_e'^{*}\boldsymbol{\mu}_e\psi_e''\,\mathrm{d}\tau_e \tag{6.125}$$

Because electronic states are, of necessity, orthogonal

$$\int \psi_e'^{*}\psi_e''\,\mathrm{d}\tau_e = 0 \tag{6.126}$$

Franck-Condon factor (Integral)

so that

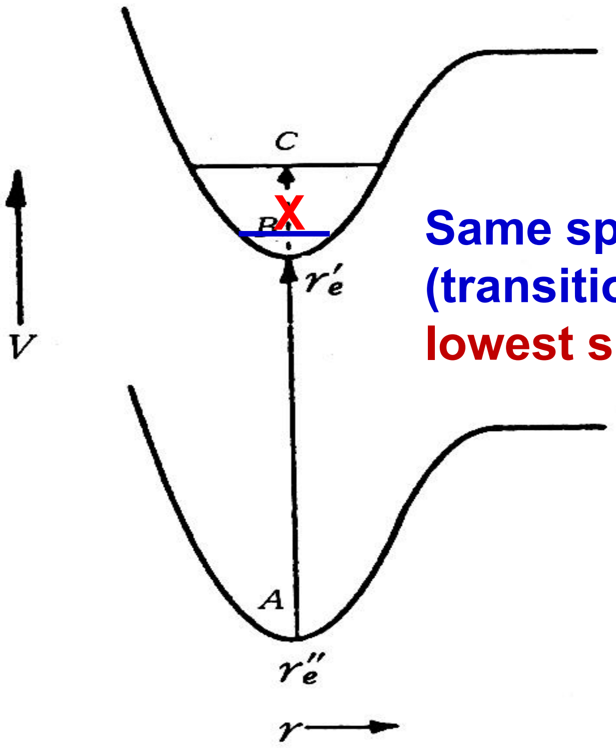
$$\boxed{\boldsymbol{R}_{ev} = \underline{\boldsymbol{R}_e} \int \psi_v'\psi_v''\,\mathrm{d}r} \tag{6.127}$$

Overlap of two wave functions

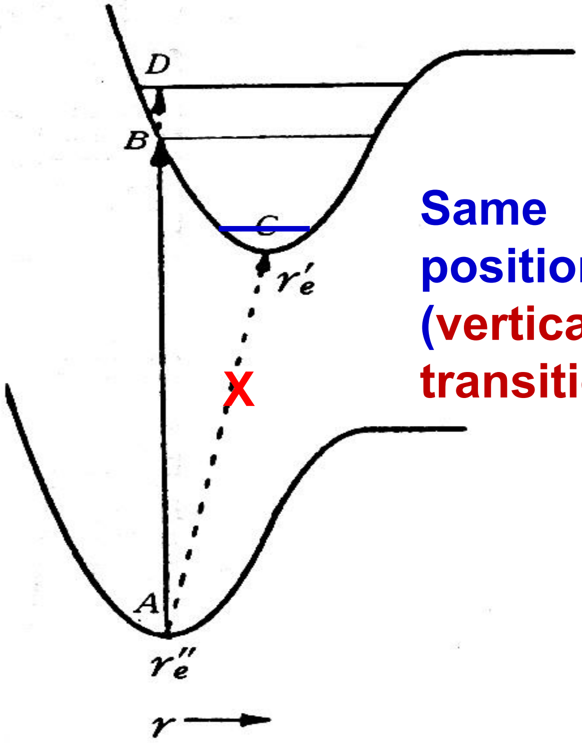
where $\boldsymbol{R}_e$ is the electronic transition moment.

Classical description

The motion of nuclei is much slower compared to that of electron, so that the position and speed of nuclei does not change during the electronic transition.

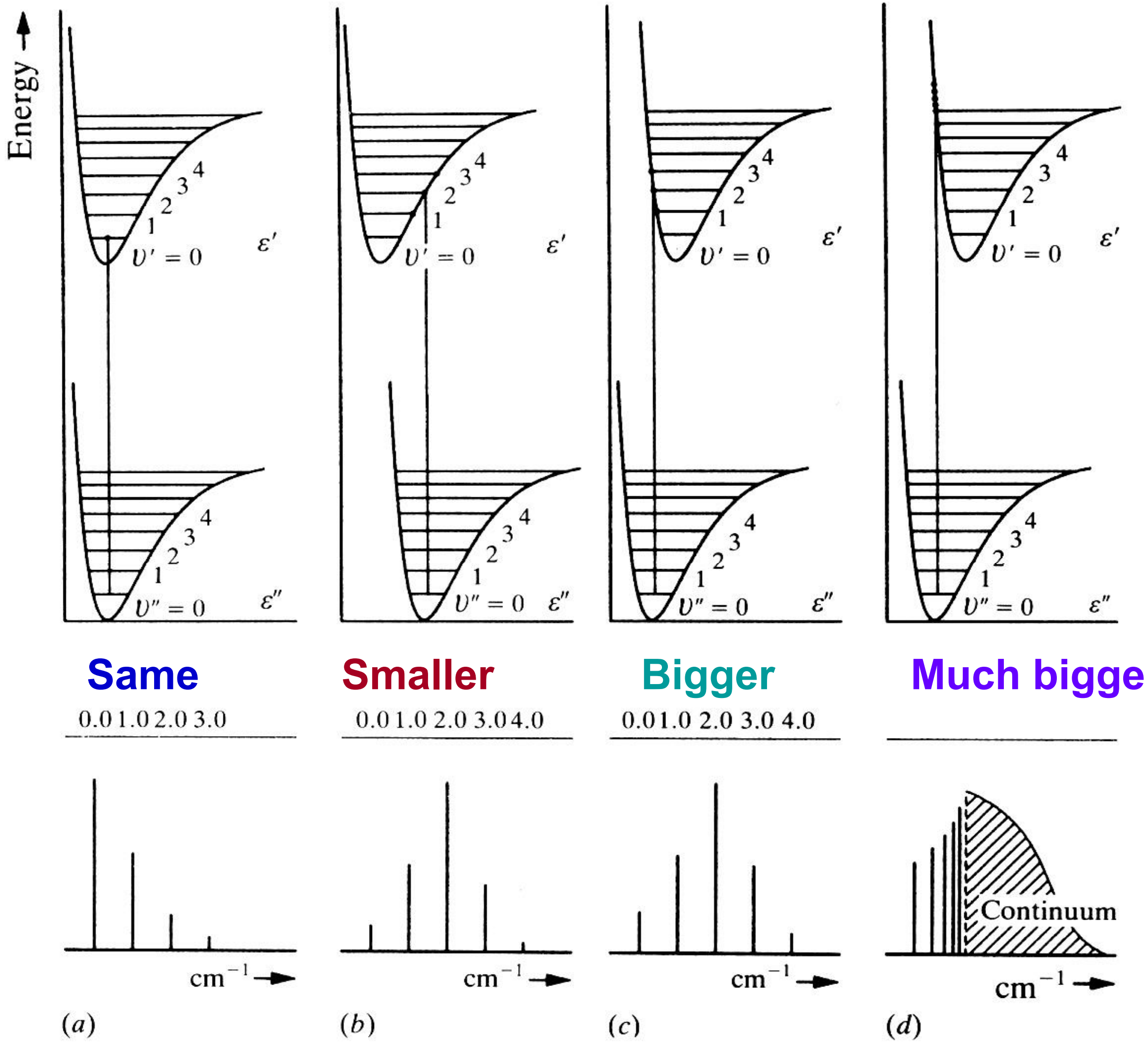


Same speed (transition to lowest speed)



Same position (vertical transition)

4 different cases described by classical method



Same

Smaller

Bigger

Much bigger

Intensity at different nuclei positions

We can explain the intensity of vibronic transitions.

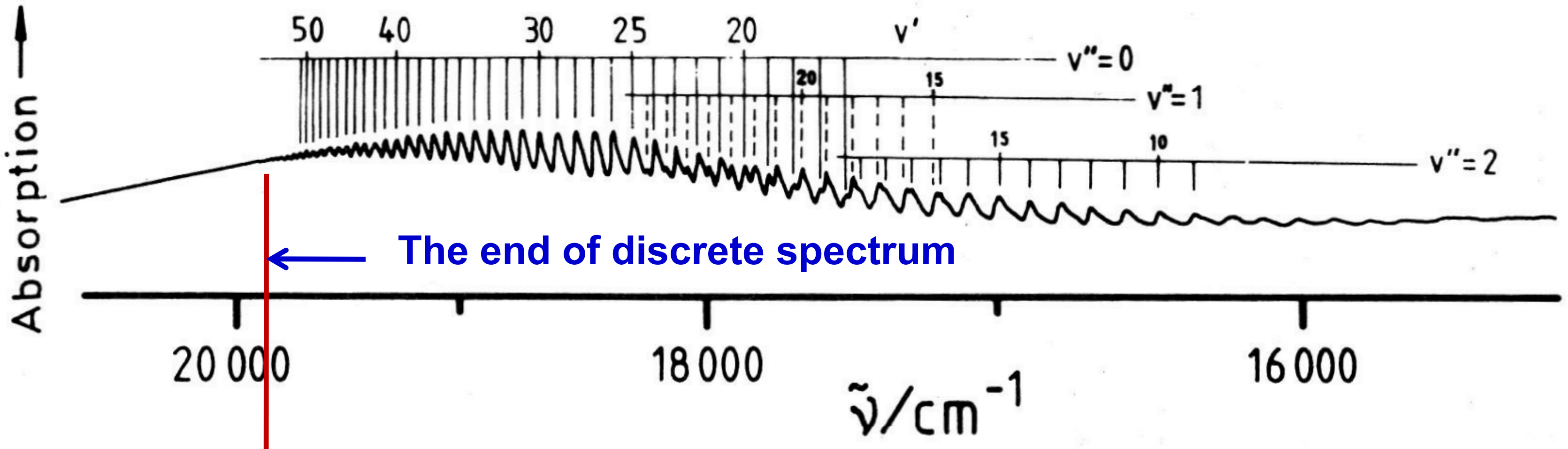
Iodine spectrum

Figure 6.3 The operation of the Franck–Condon principle for (*a*) internuclear distances equal in the upper and lower states, (*b*) upper state internuclear distance a little less than that in the lower state, (*c*) upper state distance a little greater than in the lower, and (*d*) upper state distance considerably greater.

Iodine spectrum

Iodine spectrum is the reference spectrum for calibration of wavelength in the uv and visible region due to the existence of so many lines in the visible region.

Several tens of thousand transitions are possible because of dissociation of I_2.



The end of discrete spectrum

Progressions with $v''=0$, 1 and 2 in the $B^3\Pi_{0+u}$—$X^1\Sigma_g^+$ system of the I_2 molecule

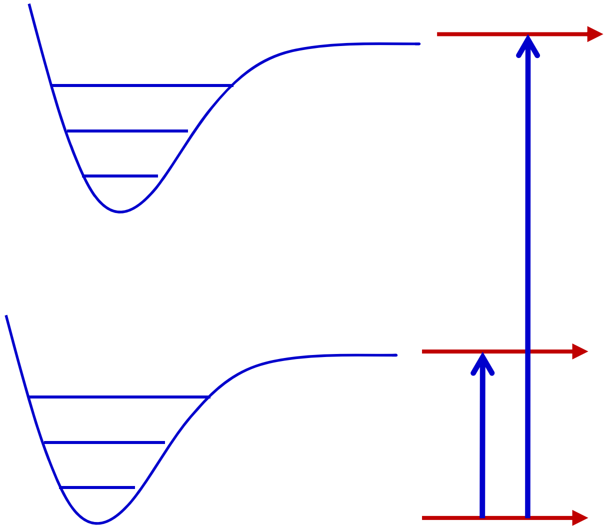
Start of continuum : End of the bound state

What is dissociation? How to predict the dissociation energy?

6.1.4 Dissociation Energy and Dissociation Products

How to obtain the dissociation energy, D_0 experimentally?
There are two different dissociations of molecules:
Dissociation in the ground and excited electronic states

What spectrum do you expect from this diagram?



The end of bound state

The separation between two neighboring two vibrational levels decreases with increasing v.

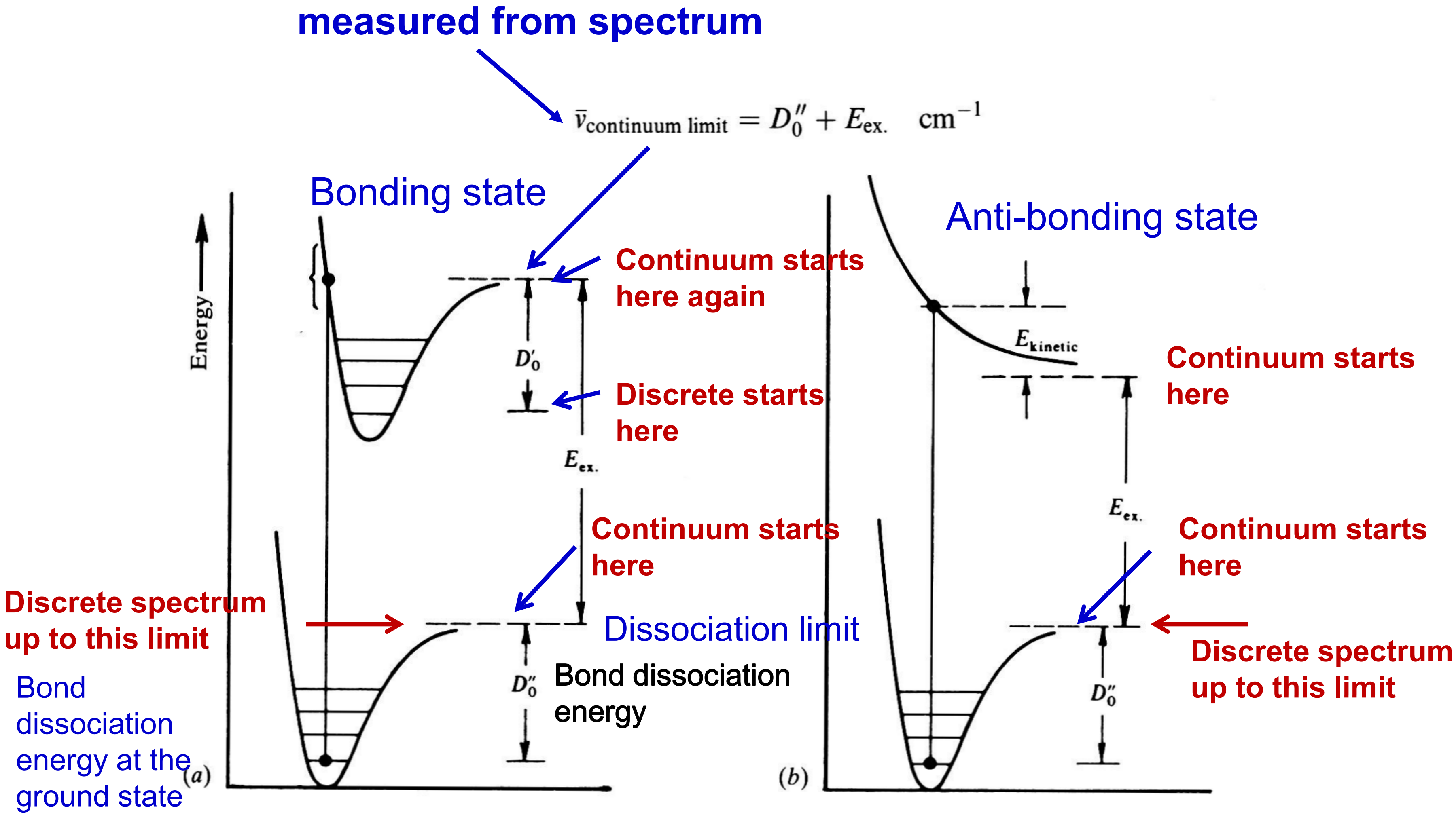
Transition to unbound states shows a continuum spectrum.

The end of bound state

Transition to bound states shows a discrete spectrum.

If dissociation occurs, a continuum spectrum will be observed.

We can determine the dissociation energy from the measured continuum frequency.



measured from spectrum

$$\bar{\nu}_{\text{continuum limit}} = D_0'' + E_{\text{ex.}} \quad \text{cm}^{-1}$$

Bonding state

Continuum starts here again

Discrete starts here

Continuum starts here

Discrete spectrum up to this limit

Dissociation limit

Bond dissociation energy

Bond dissociation energy at the ground state

Anti-bonding state

Continuum starts here

Continuum starts here

Discrete spectrum up to this limit

Figure 6.4 Illustrating dissociation by excitation into (*a*) a stable upper state and (*b*) a continuous upper state.

What is the difference between two spectra? They show different patterns.

We can calculate the bond dissociation energy from vibrational energy.

We have already seen in Chapter 3 (cf. Eq. (3.12)) that the vibrational energy levels may be written:

How many vibrational levels are in a bounded state?

$$\varepsilon_v = (v + \tfrac{1}{2})\bar{\omega}_e - x_e(v + \tfrac{1}{2})^2\bar{\omega}_e \quad \mathrm{cm}^{-1} \tag{6.8}$$

And so the separation between neighbouring levels, $\Delta\varepsilon$, is plainly:

The separation between two neighboring two vibrational levels decreases with increasing v and will be zero at dissociation limit.

$$\begin{aligned}\Delta\varepsilon &= \varepsilon_{v+1} - \varepsilon_v \\ &= \bar{\omega}_e\{1 - 2x_e(v + 1)\} \quad \mathrm{cm}^{-1}\end{aligned} \tag{6.9}$$

$\Delta\varepsilon$ is getting smaller with v.

This separation obviously decreases linearly with increasing v and the dissociation limit is reached when $\Delta\varepsilon \to 0$. Thus the maximum value of v is given by $v_{\max.}$, where:

$$\bar{\omega}_e\{1 - 2x_e(v_{\max.} + 1)\} = 0$$

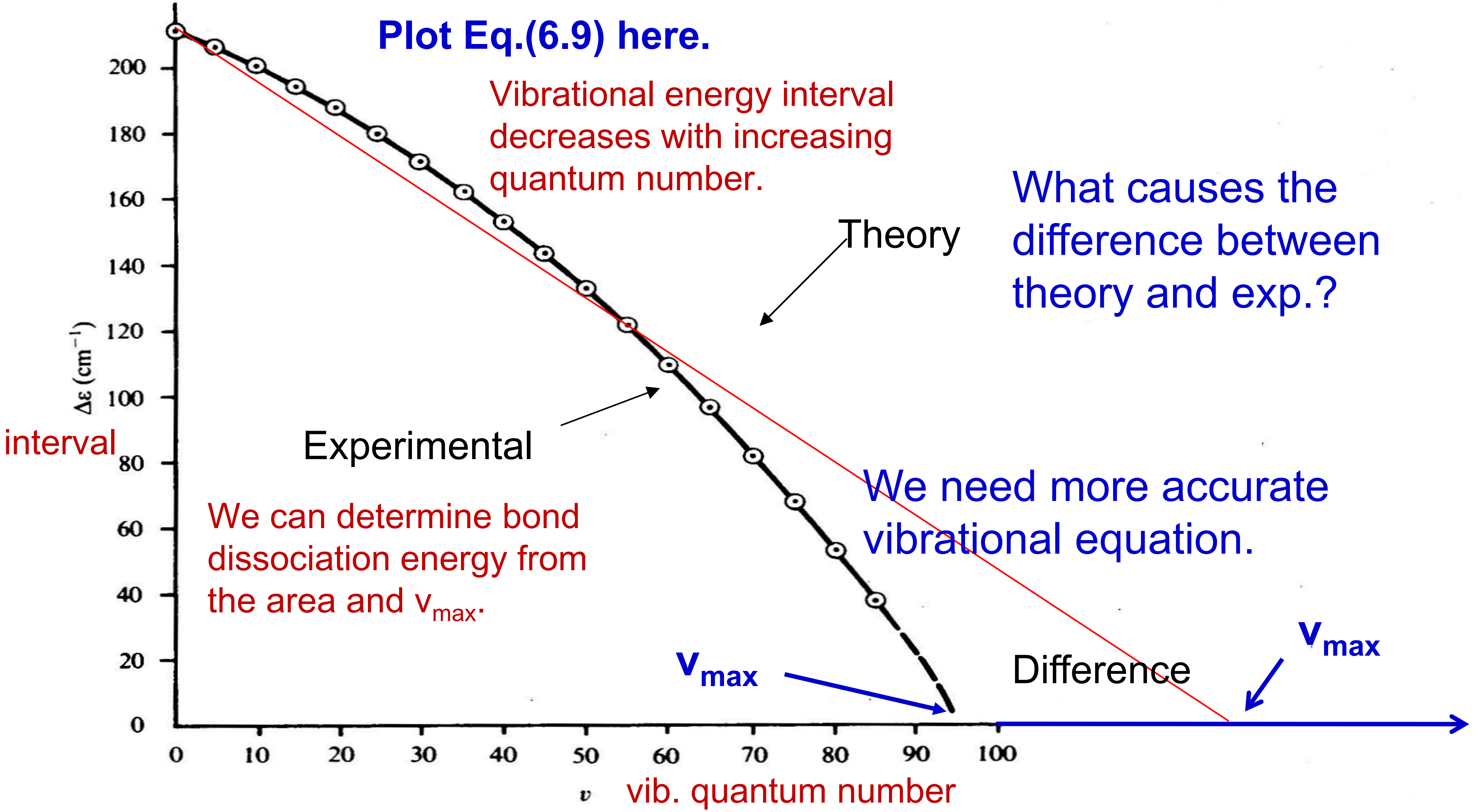
i.e.

There are 50 vib. levels in a given electronic state.

$$v_{\max.} = \frac{1}{2x_e} - 1 \tag{6.10}$$

We recall that the anharmonicity constant, x_e, is of the order of 10^{-2}; hence $v_{\max.}$ is about 50.

Birge-Sponer extrapolation
for bond dissociation energy and v_{max}



Plot Eq.(6.9) here.

Vibrational energy interval decreases with increasing quantum number.

Theory

What causes the difference between theory and exp.?

interval

Experimental

We can determine bond dissociation energy from the area and v_{max}.

We need more accurate vibrational equation.

v_{max}

Difference

v_{max}

vib. quantum number

Figure 6.5 Birge–Sponer extrapolation to determine the dissociation energy of the iodine molecule, I_2. (*Taken from the data of R. D. Varma,* J. Chem. Phys., **32**, *p. 738, 1960, by kind permission of the author.*)

6.1.5 Rotational Fine Structure of Electronic-Vibration Transitions

include rotational energy for higher resolution

To a very good approximation we can ignore centrifugal distortion and we have the energy levels of a rotating diatomic molecule (cf. Eqs (2.11) and (2.12)) as:

$$\varepsilon_{\text{rot.}} = \frac{h}{8\pi^2 Ic} J(J+1) \underline{= BJ(J+1) \quad \text{cm}^{-1}} \quad (J = 0, 1, 2, \dots) \qquad (6.12)$$

where I is the moment of inertia, B the rotational constant, and J the rotational quantum number. Thus, by the Born–Oppenheimer approximation, the total energy (excluding kinetic of translation) of a diatomic molecule is: together

$$\varepsilon_{\text{total}} = \boxed{\varepsilon_{\text{elec.}} + \varepsilon_{\text{vib.}}} + \underline{BJ(J+1)} \quad \text{cm}^{-1} \qquad (6.13)$$

Changes in the total energy may be written:

Rotational energy difference

$$\Delta\varepsilon_{\text{total}} = \Delta\{\varepsilon_{\text{elect.}} + \varepsilon_{\text{vib.}}\} + \Delta\{BJ(J+1)\} \quad \text{cm}^{-1} \qquad (6.14)$$

and the wavenumber of a spectroscopic line corresponding to such a change becomes simply:

$$\underline{\bar{\nu}_{\text{spect.}} = \bar{\nu}_{(v',v'')} + \Delta\{BJ(J+1)\} \quad \text{cm}^{-1}} \qquad (6.15)$$

We will learn the notation of electronic state later.

Rotational selection rule in rovibronic spectrum

$\Delta J = \pm 1$ only for $^1\Sigma \rightarrow {}^1\Sigma$ transition

$\Delta J = 0$, or ± 1 for other transition

We will learn term symbol of molecules later.

We have studied that B’ is different from B”.

$$\bar{\nu}_{\text{spect.}} = \bar{\nu}_{(v',v'')} + \underline{B'J'(J'+1) - B''(J''+1)} \quad \text{cm}^{-1}$$

Taking the P, R, and Q branches in turn: **We have already studied this.**

1. P branch: $\Delta J = -1,\ J'' = J' + 1$

$$\Delta\varepsilon = \bar{\nu}_P = \bar{\nu}_{(v',v'')} - (B' + B'')(J'+1) + (B' - B'')(J'+1)^2 \quad \text{cm}^{-1} \qquad \text{where } J' = 0, 1, 2, \ldots \tag{6.20a}$$

2. R branch: $\Delta J = +1,\ J' = J'' + 1$

$$\Delta\varepsilon = \bar{\nu}_R = \bar{\nu}_{(v',v'')} + (B' + B'')(J''+1) + (B' - B'')(J''+1)^2 \quad \text{cm}^{-1} \qquad \text{where } J'' = 0, 1, 2, \ldots \tag{6.20b}$$

These two equations can be combined into:

$$\boxed{\bar{\nu}_{P,R} = \bar{\nu}_{(v',v'')} + \underset{+}{(B' + B'')m} + \underset{+/-}{(B' - B'')m^2} \quad \text{cm}^{-1} \qquad \text{where } m = \pm 1, \pm 2, \ldots} \tag{6.20c}$$

3. Q branch: $\Delta J = 0,\ J' = J''$ if possible

$$\Delta\varepsilon = \bar{\nu}_Q = \bar{\nu}_{(v',v'')} + (B' - B'')J'' + (B' - B'')J''^2 \quad \text{cm}^{-1} \qquad \text{where } J'' = 1, 2, 3, \ldots \tag{6.21}$$

We already studied this one in the chapter 3.

6.1.6 The Fortrait Diagram

p=- for P-branch
p=+ for R-branch

$$\bar{\nu}_{P,R} = \bar{\nu}_{(v',v'')} + (B' + B'')p + (B' - B'')p^2 \qquad (6.22a)$$

$$\bar{\nu}_{Q} = \bar{\nu}_{(v',v'')} + (B' - B'')q + (B' - B'')q^2 \qquad (6.22b)$$

If possible.

$$\frac{\mathrm{d}\bar{\nu}_{P,R}}{\mathrm{d}p} = B' + B'' + 2(B' - B'')p = \boxed{0}$$

Minimum or maximum

In vibrational transition, bond length always increases with vibrational quantum number.

Position of band head

$$p = -\frac{B' + B''}{2\boxed{(B' - B'')}} \text{ for band head}$$

In electronic transition, bond length may vary with excitation, increase or decrease .

- for B’ < B” (r’>r”) : Bandhead at R-branch

+ for B’ > B” (r’<r”) : Bandhead at P-branch

Interval difference in P- and R-Branches

$$\bar{\nu}_{P,R} = \bar{\omega}_o + \underset{+}{\boxed{(B_1 + B_0)}}\,m + \overset{-}{\boxed{(B_1 - B_0)}}\,m^2 \quad \mathrm{cm}^{-1} \qquad (m = \pm 1, \pm 2, \ldots)$$

m= +: R-branch

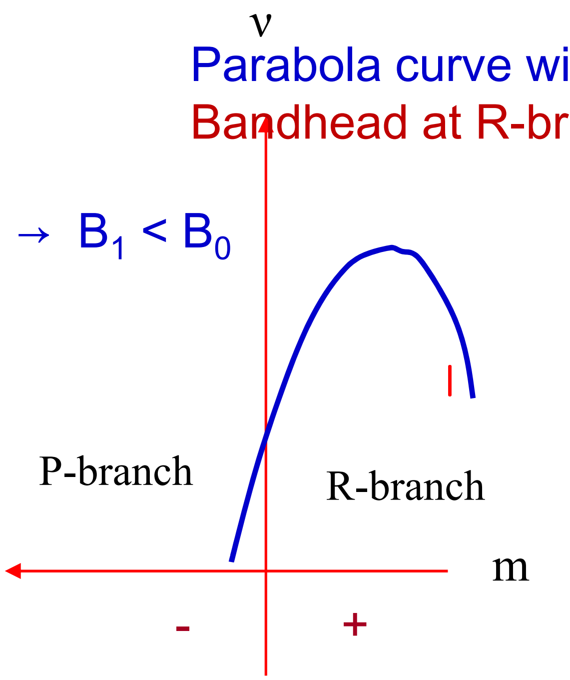
m= -: P-branch

because $B_e > B_0 > B_1 > B_2$

Parabola curve with maximum.

Bandhead at R-branch

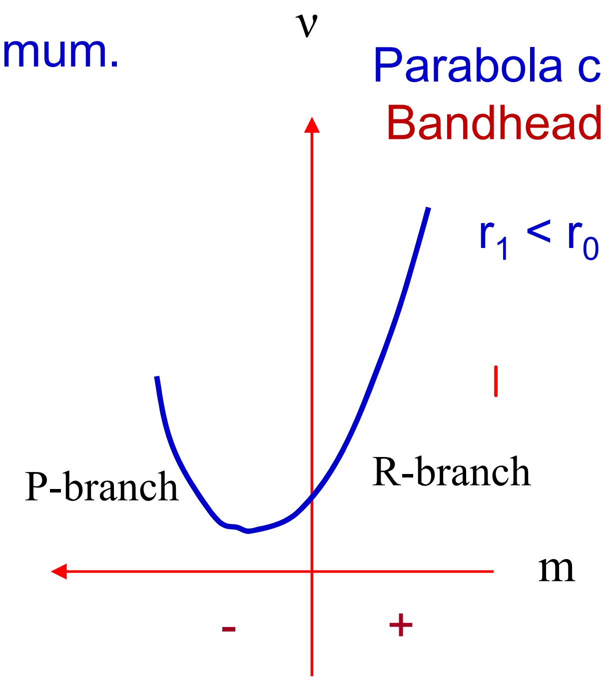
$r_1 > r_0 \rightarrow B_1 < B_0$



Parabola curve minimum.

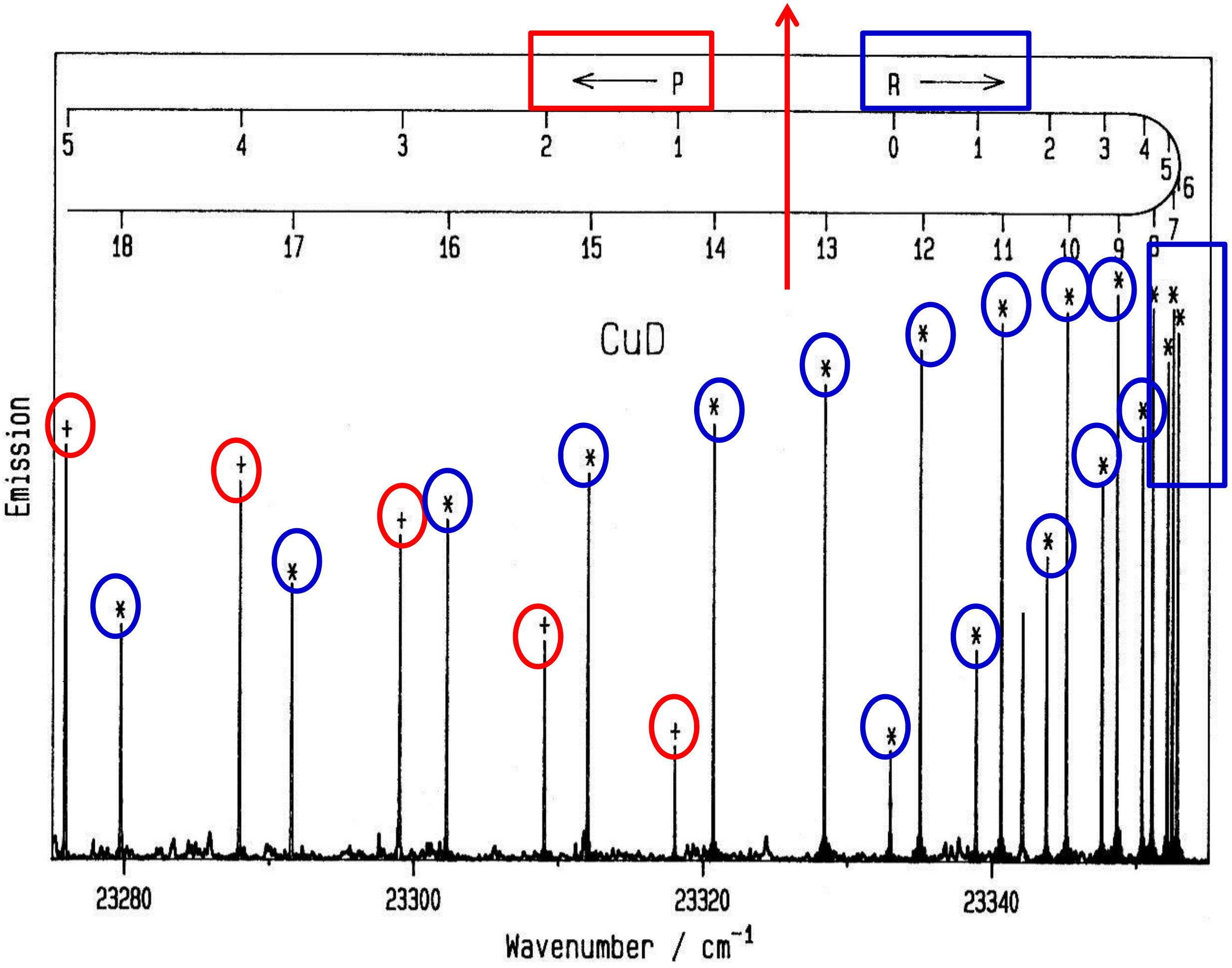
Bandhead at P-branch

$r_1 < r_0 \rightarrow B_1 > B_0$



Now, we can explain why the spacing is getting smaller with J number in R-branch.

Pure vibration: Band origin



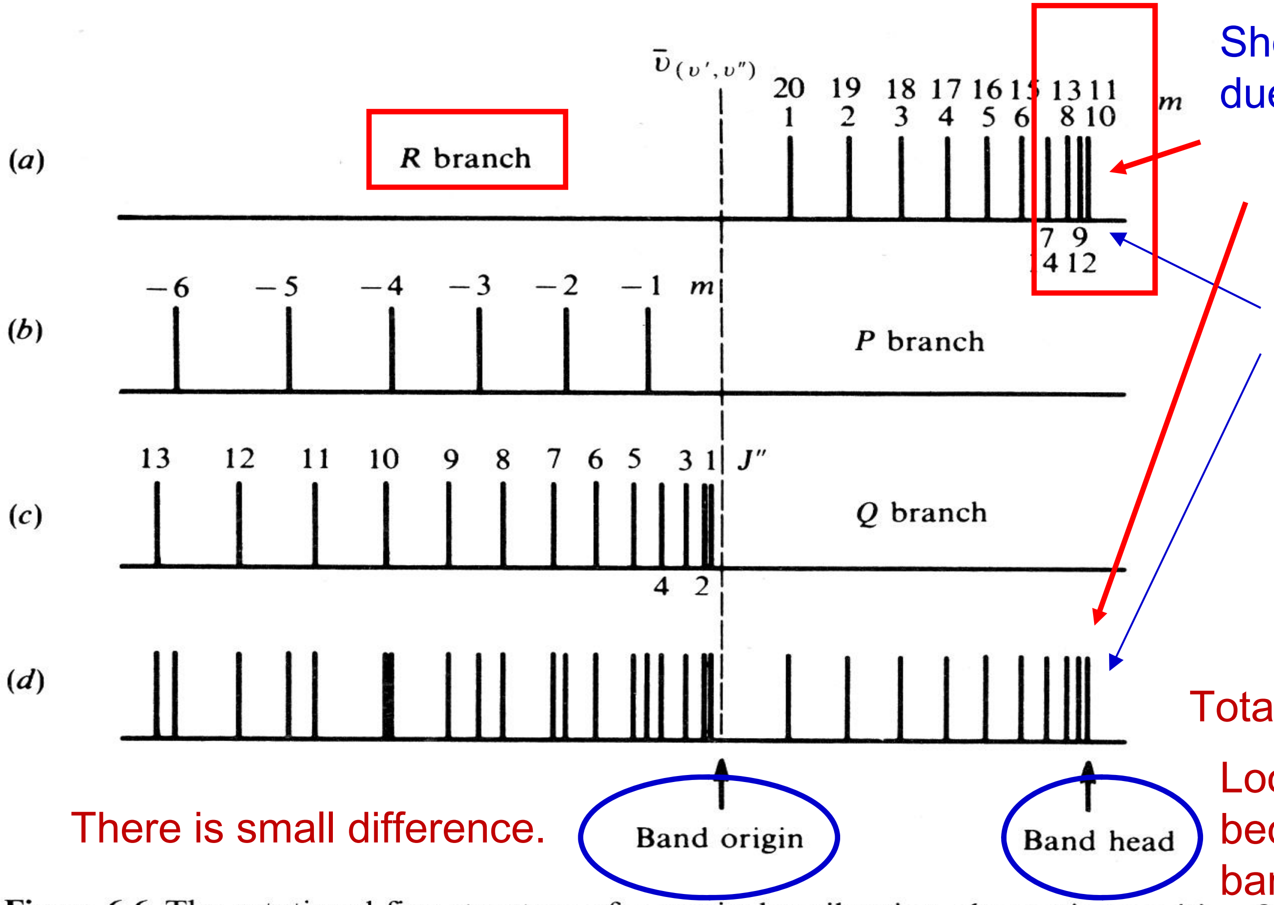
Turn back here.

Band head

Figure 9.12. The 0–0 band of the CuD $A^1\Sigma^+–X^1\Sigma^+$ system.[3] The peaks marked with + are *P* branch transitions, while those marked with * belong to the *R* branch.

Transition and band head

Band head at R- branch



Shows strongest intensity due to overlap of bands

Band head at R-branch

Total spectrum

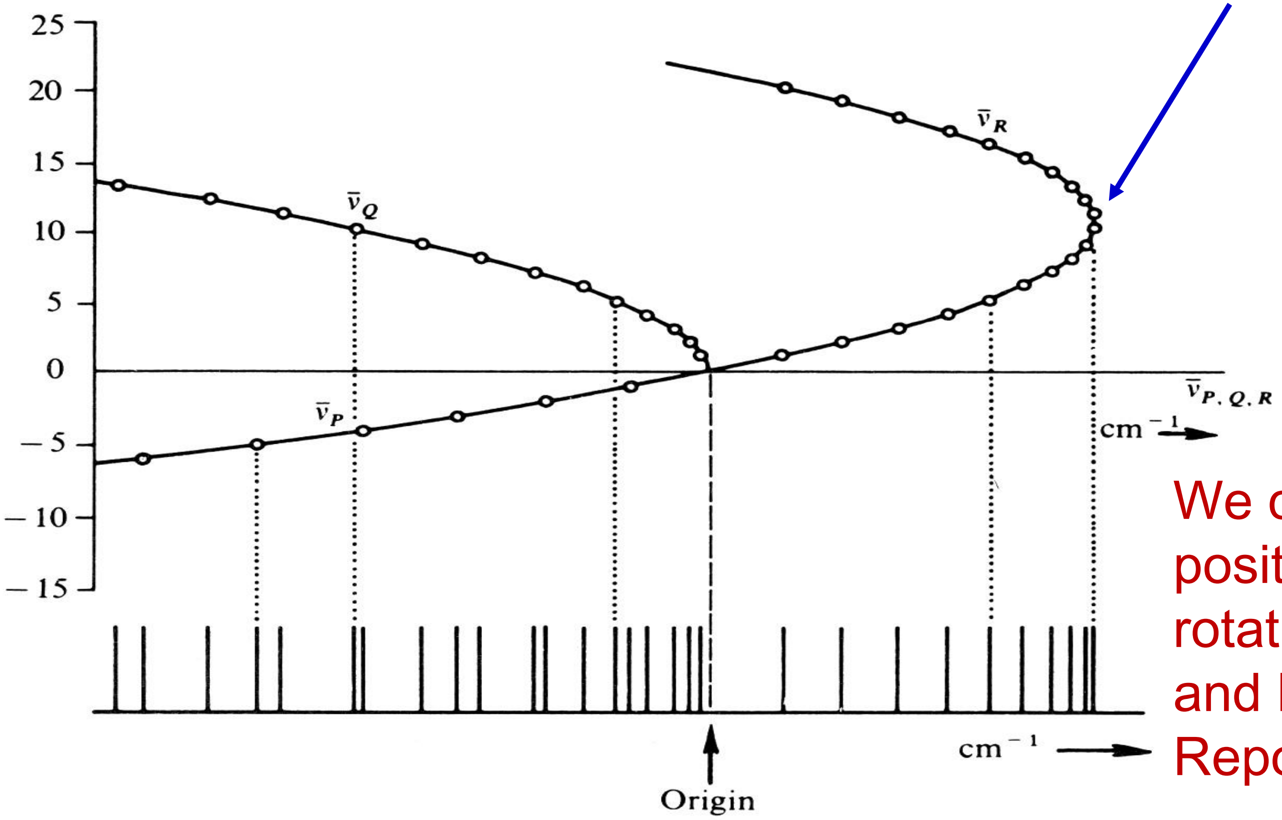
Looks like very strong because of overlap of many bands.

There is small difference.

Figure 6.6 The rotational fine structure of a particular vibration–electronic transition for a diatomic molecule. The *R*, *P*, and *Q* branches are shown separately at (*a*), (*b*), and (*c*), respectively, with the complete spectrum at (*d*).

Position of band head

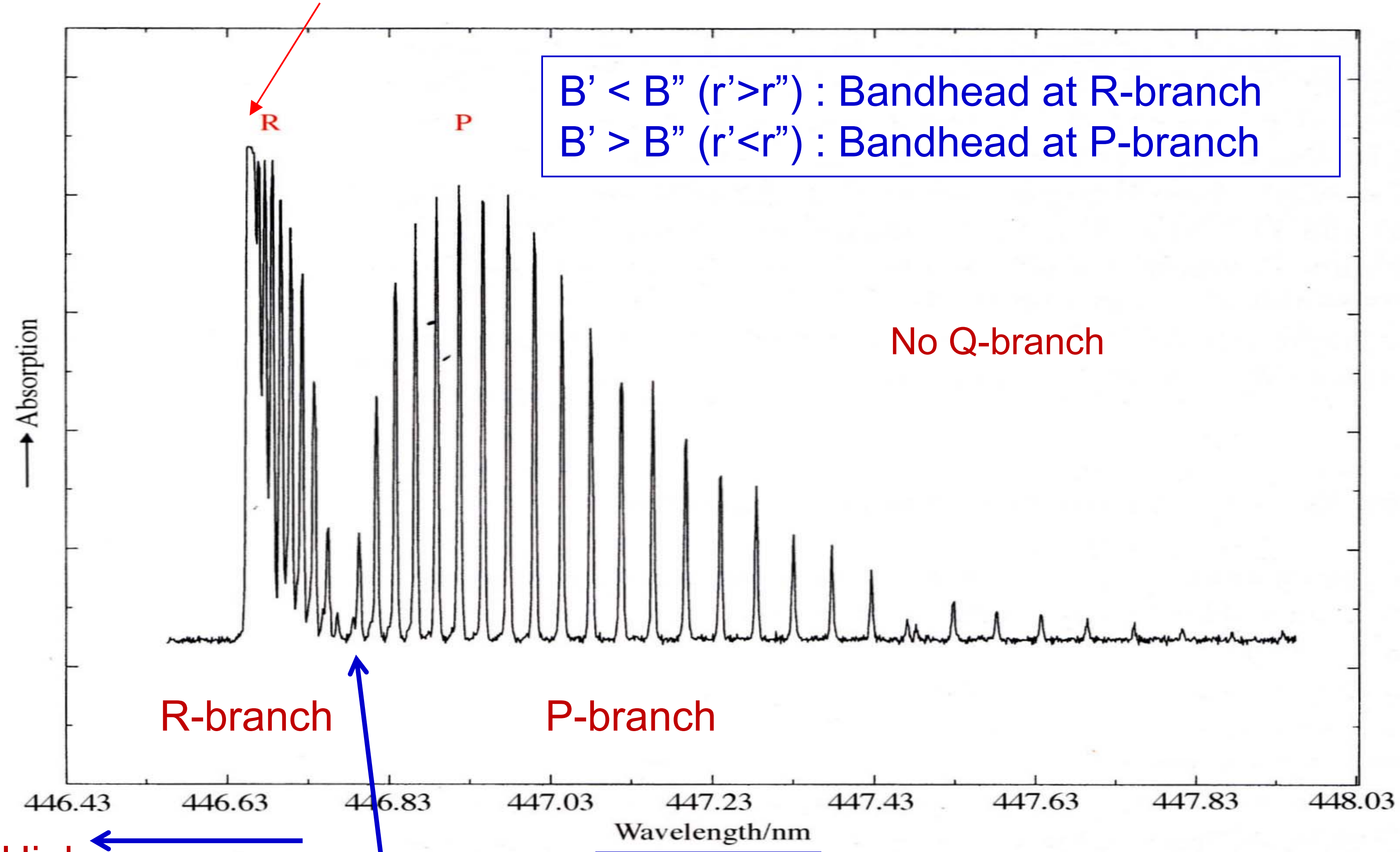
- for B' < B" (r'>r") : Bandhead at R-branch
+ for B' > B" (r'<r") : Bandhead at P-branch



We can predict the position of band head from rotational constants, B' and B". (see problem #6 in Report #5)

Figure 6.7 The Fortrat diagram sketched for a 10 per cent difference between B' and B'' (with $B' < B''$). The spectrum illustrated at the foot is identical with that of Fig. 6.6(d).

Band head at R-branch



B' < B" (r'>r") : Bandhead at R-branch
B' > B" (r'<r") : Bandhead at P-branch

No Q-branch

R-branch

P-branch

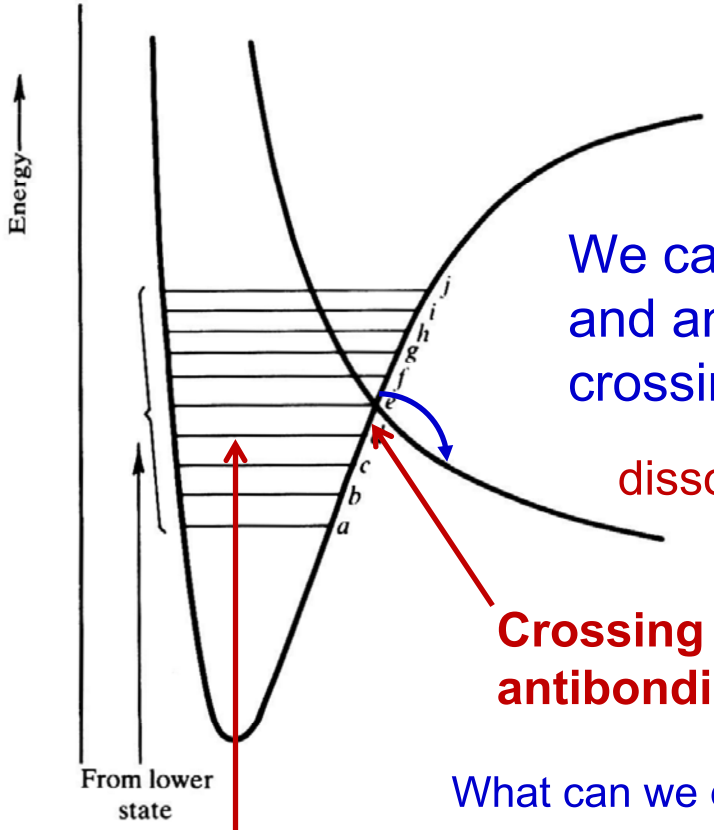
Higher energy

Band origin

Figure 11.5 Rotational fine structure of a $^1\Sigma^+ - {}^1\Sigma^+$ electronic transition of RhN

6.1.7 Predissociation

Dissociation prior to (before) dissociation limit



We can see predissociation if bonding and antibonding potentials curves are crossing.

dissociate

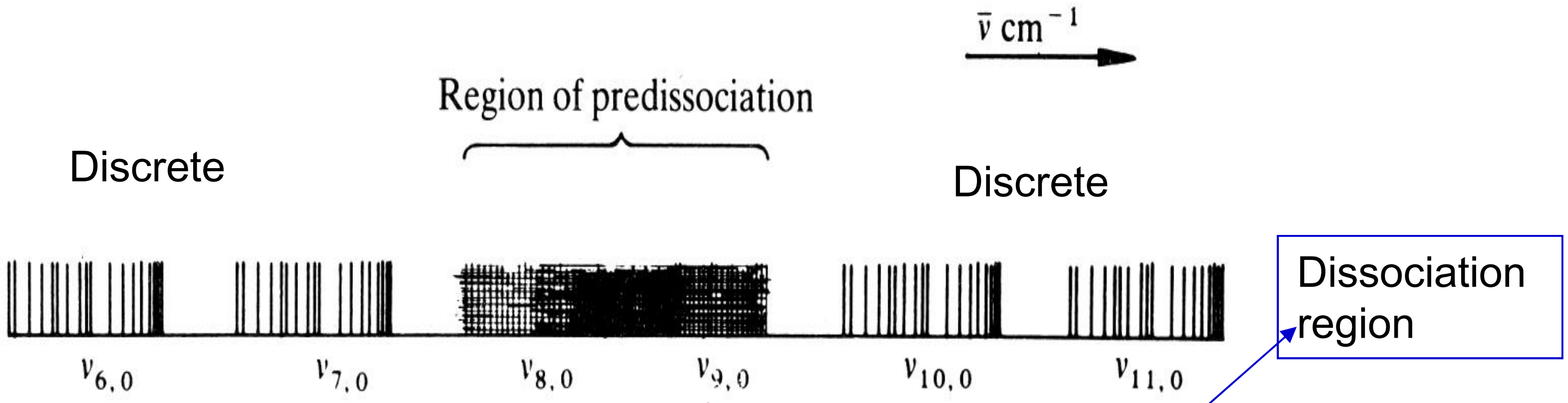
Crossing of bonding and antibonding potentials

What can we expect from the crossing?

Figure 6.9 Showing the occurrence of predissociation during transitions into a stable upper state intersected by a continuous state.

Transition from ground state

Discrete → Continuum (predissociation) → Discrete → Continuum (dissociation)



Discrete

Discrete

Dissociation region

Figure 6.8 Diagrammatic illustration of the appearance of predissociation. The rotational fine structure is clearly defined for vibrational transitions both above and below the predissociation region, but in this region the fine structure becomes blurred and lost.

Continuum

6.1.8 Diatomic Molecules: A Summary

What information can we get from spectrum?

- Rotational spectrum : Molecular structure
- Vibrational spectrum : Bond strength
- Electronic spectrum : Electronic structure
- Rovibronic spectrum : Molecular structure at excited vibrational and electronic states
- Problem : How to obtain the rovibronic spectrum with a good S/N and resolving power? Many experimental techniques have been developed to increase the S/N and resolution.

Changes in Molecular Structure upon Excitation

Molecules may change their structures with uv/visible radiation.

Rotational Excitation:

No change in Molecular Structure. Very small difference due to the centrifugal distortion

Vibrational Excitation:

Bond length increases with vibrational quantum number because of the potential shape of anharmonic oscillator

Electronic Excitation:

Large changes in molecular size as well as molecular shape because the bonds could break off upon electronic excitation.

6.2 ELECTRONIC STRUCTURE OF DIATOMIC MOLECULES

6.2.1 Molecular Orbital Theory

Studied in general chemistry

Many theories have been well developed to explain experimental observations. There are mainly two theories adapted for explanation in undergraduate levels.

Outmost electrons

Valence bond theory: Using valence electrons

Easy but not correct

Promotion

Carbon uses sp^3 orbital in CH_4

Hybridization

Molecular orbital theory: Using all electrons

More reasonable

including inner core electrons

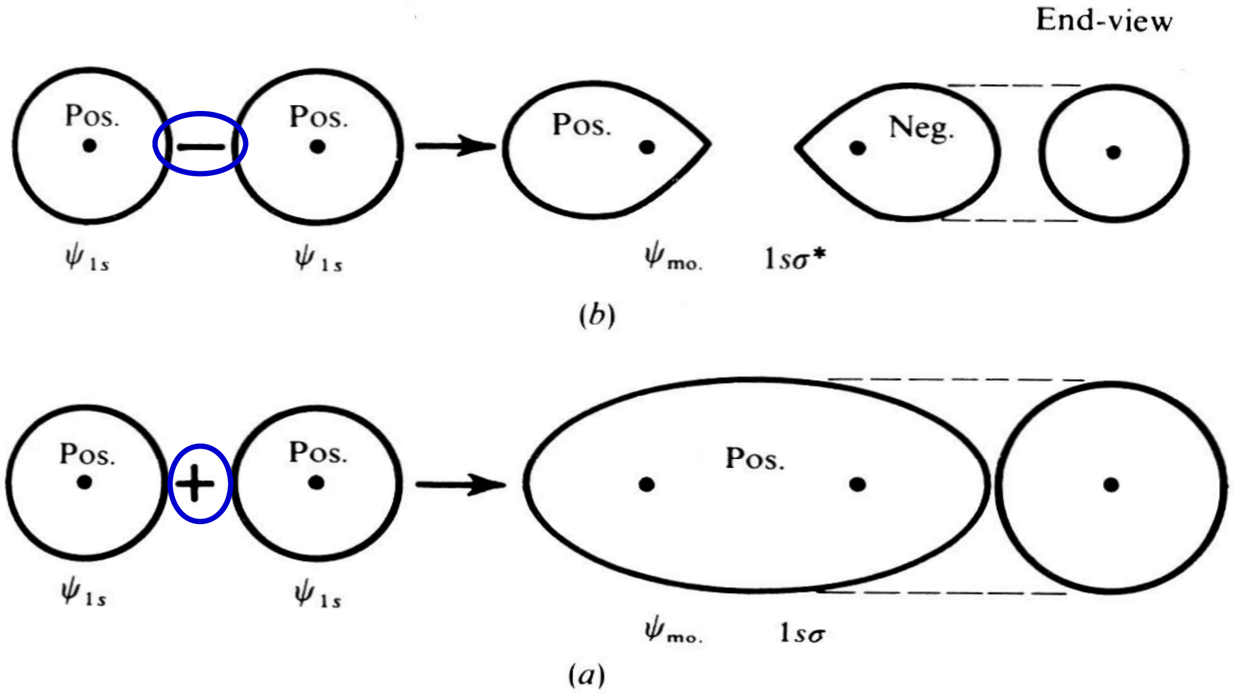
Explain magnetic property

Valence bond theory

- We have already learned this theory at general chemistry because this is very simple concept.
- However, we cannot explain many properties of atoms with this theory. These are bond strength and electron spin characters.
- It can be understood by promotion and hybridization of valence electrons to form bonding. However, antibonding character cannot be explained.
- The simplest cases are sp^3, $sp^2 + p$, and $sp + p^2$. Also d orbitals can participate to bonding for dsp^2, d^2sp^3,

6.2.2 The shape of Some Molecular Orbitals

The basic concept of Molecular Orbital Theory is Linear Combination of Atomic Orbitals (LCAO) : Sum and difference combinations



Difference combination : antibonding orbital

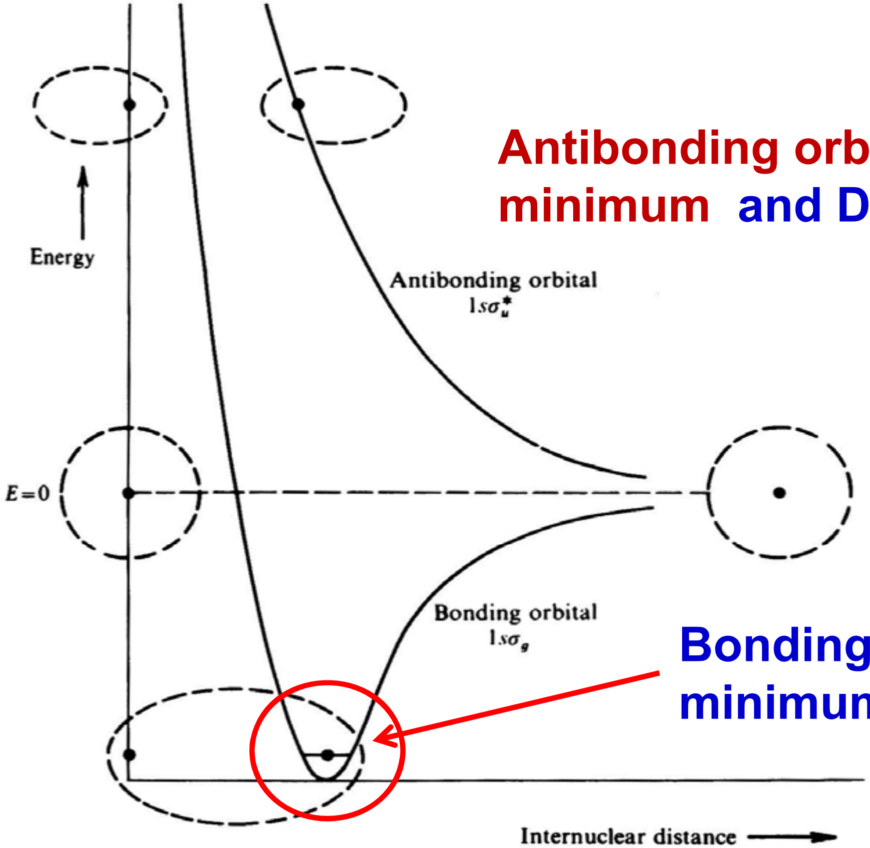
Sum combination : Bonding orbital

Figure 6.10 The formation of (*a*) a bonding $1s\sigma$ orbital and (*b*) an antibonding $1s\sigma^*$ orbital from two atomic $1s$ orbitals.

Combination of s orbitals

Bonding and antibonding orbitals

Making Molecular Orbitals from Atomic Orbitals, there are two types of bonding; bonding and antibonding orbitals

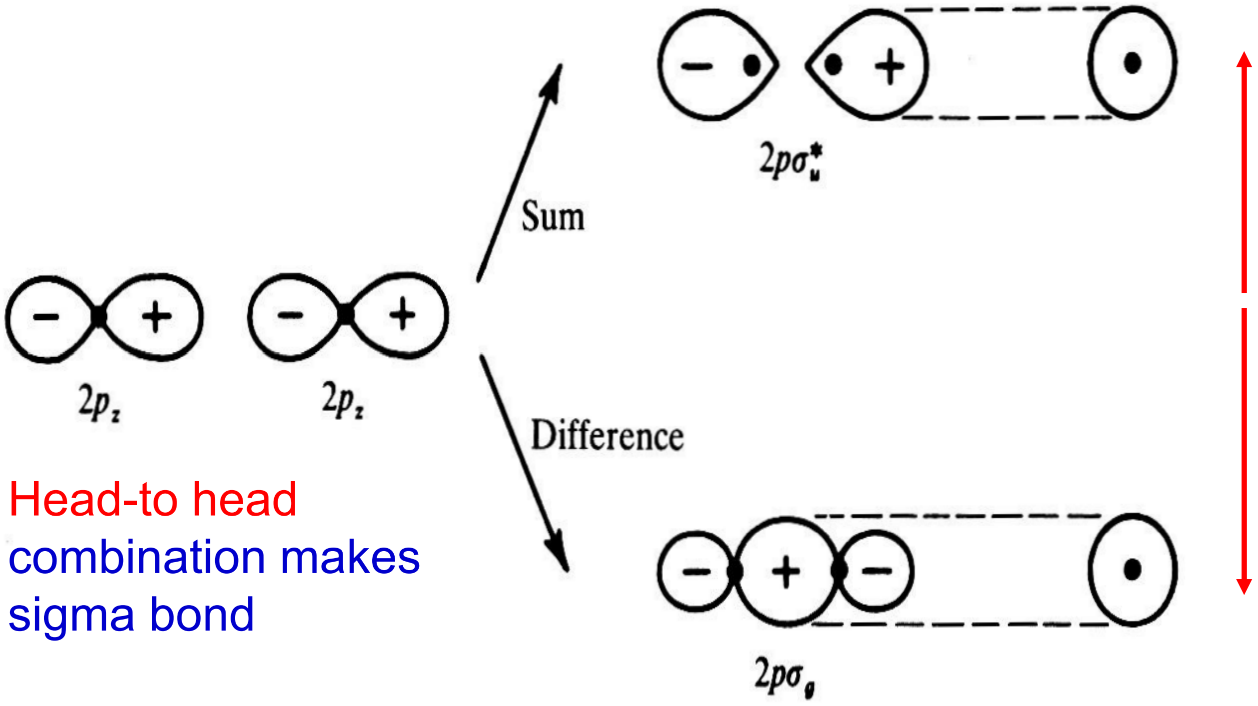


Antibonding orbitals: No potential minimum and Dissociation into atoms

Bonding orbitals: Potential minimum and stable at minimum.

Figure 6.11 The variation of energy with internuclear distance in the bonding and antibonding orbitals, $1s\sigma_g$ and $1s\sigma_u^*$.

Shape of MO (σ-bonding)



Lose stabilization energy

Gain stabilization energy

Head-to head combination makes sigma bond

Figure 6.12 The formation of bonding ($2p\sigma_g$) and antibonding ($2p\sigma_u^*$) orbitals from two atomic $2p_z$ orbitals, where the z axis is taken as the internuclear axis.

Combination of p orbitals

Shape of MO (π-bonding)

Combination of p orbitals

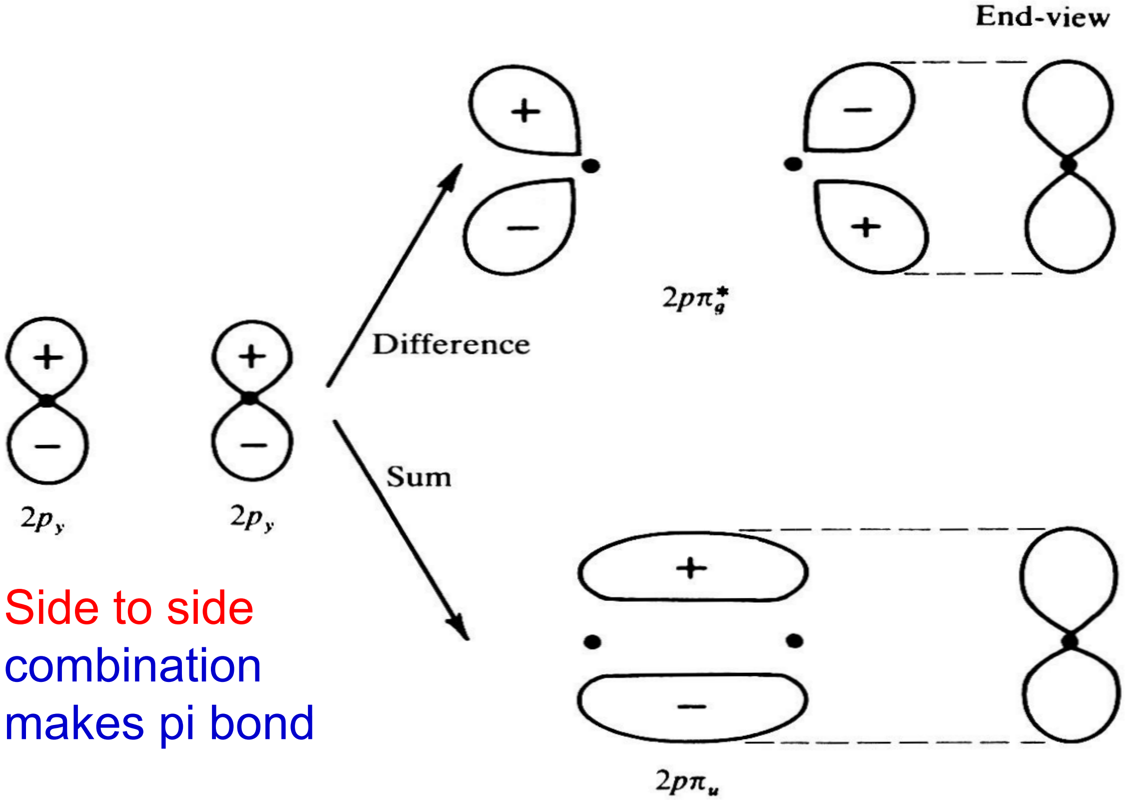


Figure 6.13 The formation of bonding ($2p\pi_u$) and antibonding ($2p\pi_g^*$) orbitals from two atomic $2p_y$ orbitals, the z axis being the internuclear axis. Atomic $2p_x$ orbitals would form identical molecular orbitals except that all lobes would be rotated through a right angle about the z axis.

Head to head combination

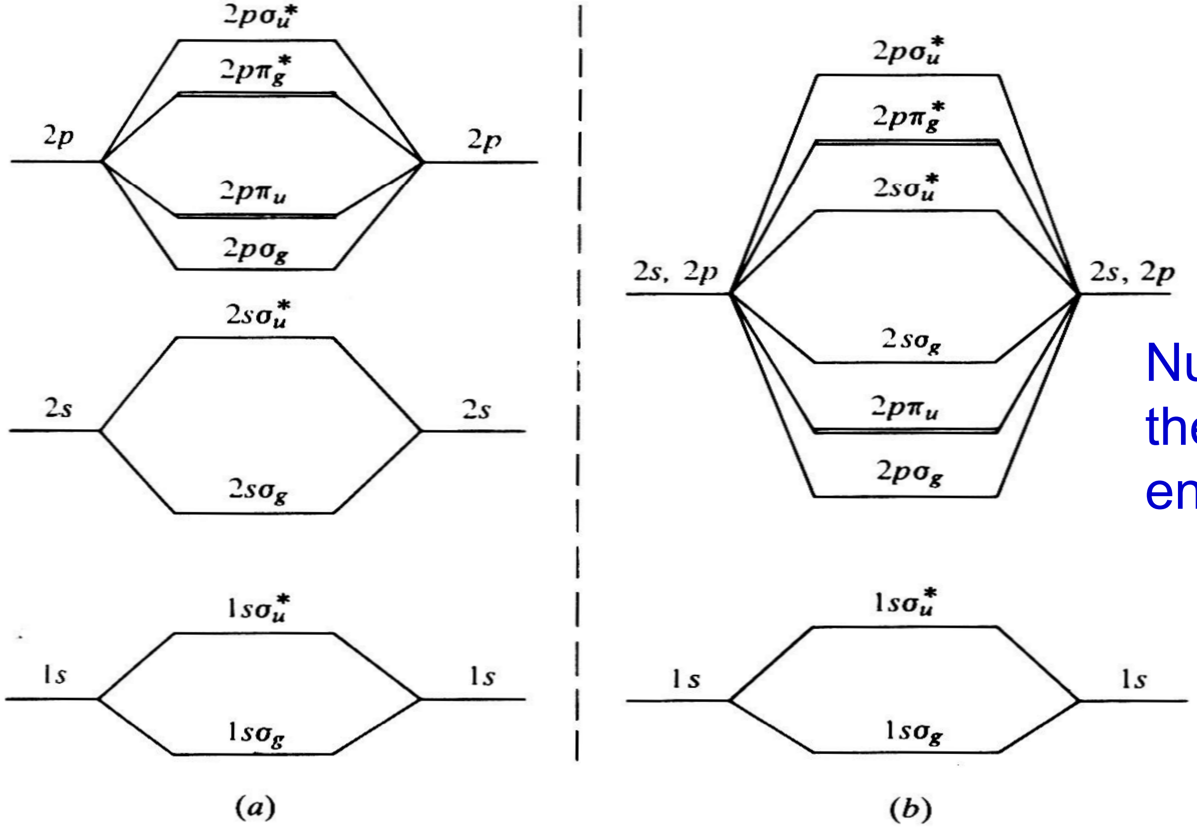
Side to side combination makes pi bond

Summary of MO diagram

Other diatomic molecules

H_2

We can construct all MOs.



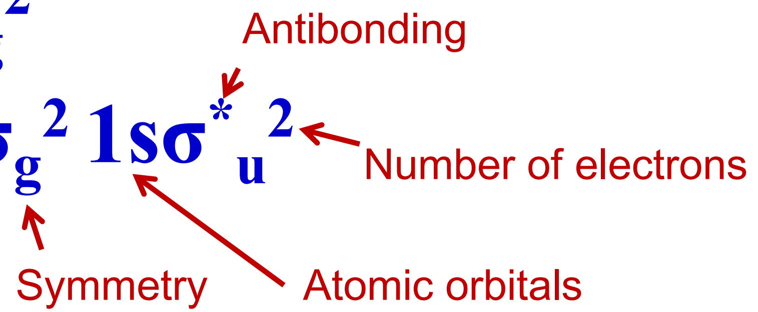
Nuclear charge changes the sequence of the energy levels

Figure 6.14 Schematic molecular orbital energy level diagrams for (*a*) simple diatomic molecules other than hydrogen and (*b*) the hydrogen molecule.

Electronic configuration of diatomic molecules

All MOs are marked by Greek alphabets.

- $H_2 : 1s\sigma_g{}^2$
- $He_2 : 1s\sigma_g{}^2\ 1s\sigma^*{}_u{}^2$



Antibonding

Number of electrons

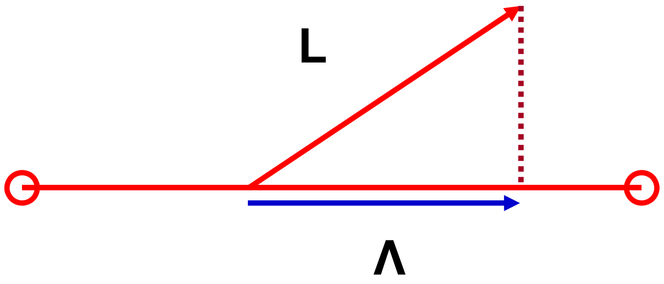
Symmetry

Atomic orbitals

- Li_2
- Be_2
- B_2
- $N_2 : 1s\sigma_g{}^2\ 1s\sigma_u{}^{*2}\ 2s\sigma_g{}^2\ 2s\sigma_u{}^{*2}\ 2p\sigma_g{}^2\ 2p\pi_u{}^4$
- O_2
- F_2

Difference between atoms and molecules

- Atoms: Spherically symmetric, the electronic energy depends on the distance from nucleus only.
- Molecules: For linear molecules, it is cylinderically symmetric. So the electronic energy depends on the position along symmetric axis.



For nonlinear molecules, it is too complicate to describe the energy, so we use the point group to identify

Notation of states

- Electrons: All little English alphabet ,$1s^2\ 2p^4$
- Atoms: All capital English alphabet given by term symbol.

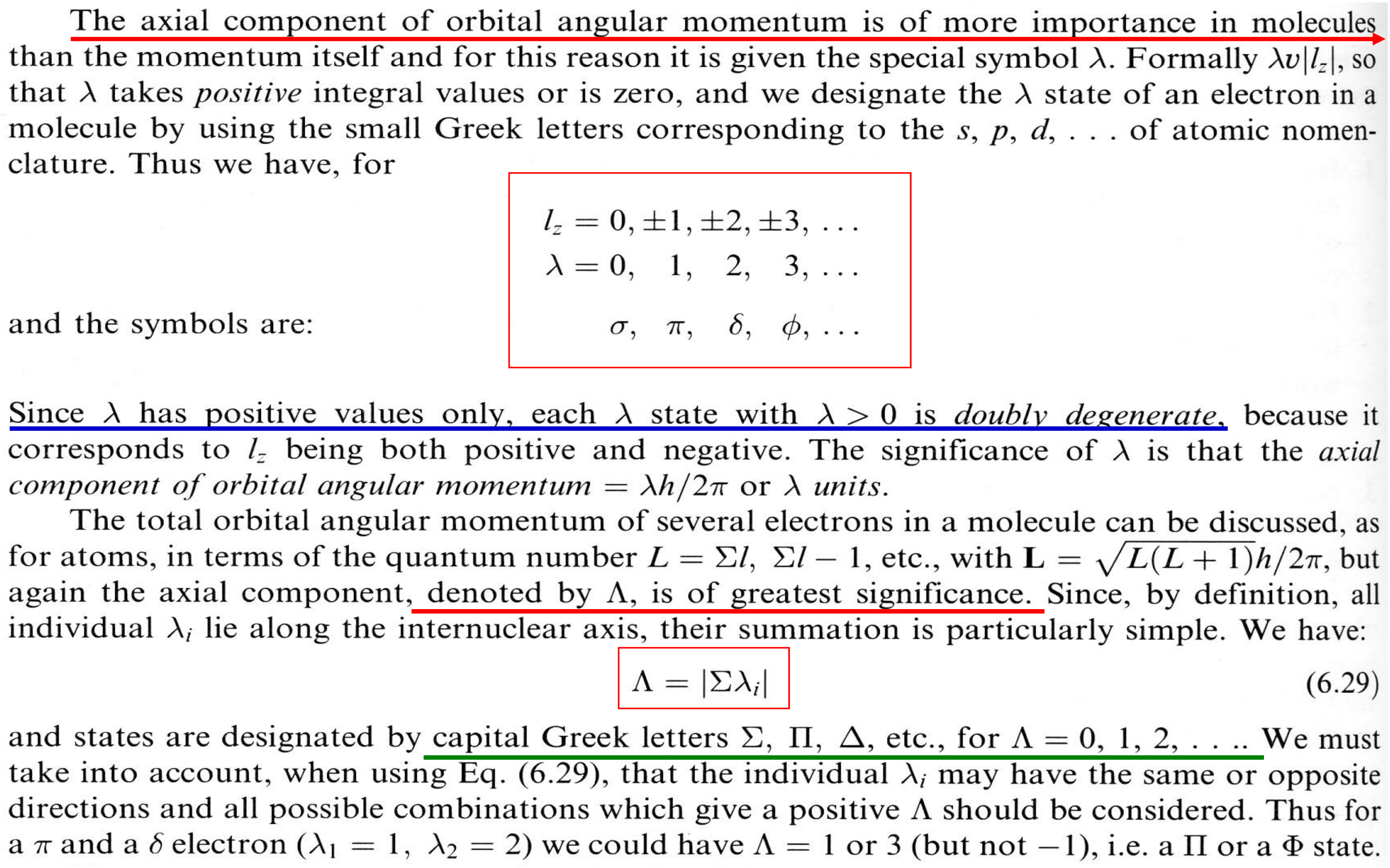
$${}^{2s+1}L_J$$

- Molecules:

For diatomic and linear molecules : All Greek alphabet

For other types of molecules : Use of Character table

6.2.3 Electronic Angular Momentum in Diatomic Molecules: Classification of States



The axial component of orbital angular momentum is of more importance in molecules than the momentum itself and for this reason it is given the special symbol λ. Formally $\lambda v|l_z|$, so that λ takes *positive* integral values or is zero, and we designate the λ state of an electron in a molecule by using the small Greek letters corresponding to the s, p, d, . . . of atomic nomenclature. Thus we have, for

$$\boxed{\begin{array}{l} l_z = 0, \pm 1, \pm 2, \pm 3, \ldots \\ \lambda = 0, \quad 1, \quad 2, \quad 3, \ldots \\ \qquad \sigma, \quad \pi, \quad \delta, \quad \phi, \ldots \end{array}}$$

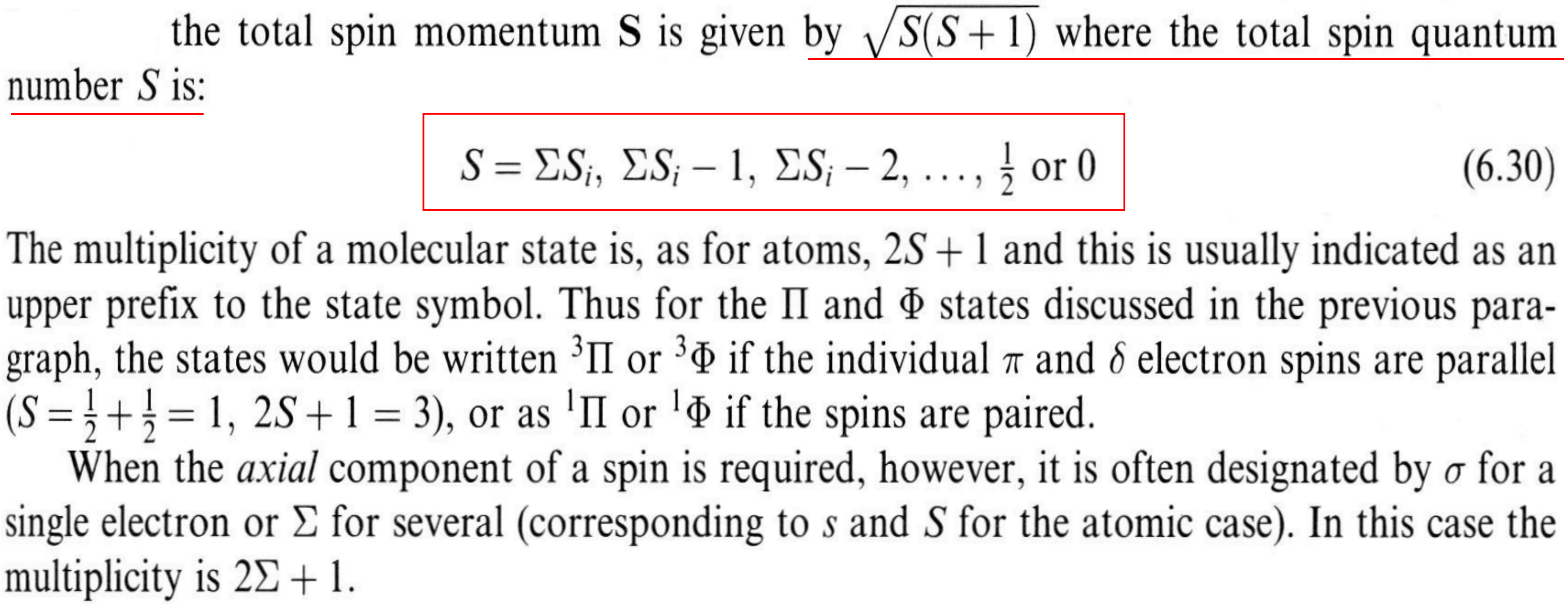
and the symbols are: σ, π, δ, ϕ, . . .

Since λ has positive values only, each λ state with $\lambda > 0$ is *doubly degenerate*, because it corresponds to l_z being both positive and negative. The significance of λ is that the *axial component of orbital angular momentum* $= \lambda h/2\pi$ or λ *units*.

The total orbital angular momentum of several electrons in a molecule can be discussed, as for atoms, in terms of the quantum number $L = \Sigma l$, $\Sigma l - 1$, etc., with $\mathbf{L} = \sqrt{L(L+1)}h/2\pi$, but again the axial component, denoted by Λ, is of greatest significance. Since, by definition, all individual λ_i lie along the internuclear axis, their summation is particularly simple. We have:

$$\boxed{\Lambda = |\Sigma\lambda_i|} \tag{6.29}$$

and states are designated by capital Greek letters Σ, Π, Δ, etc., for $\Lambda = 0, 1, 2, \ldots.$. We must take into account, when using Eq. (6.29), that the individual λ_i may have the same or opposite directions and all possible combinations which give a positive Λ should be considered. Thus for a π and a δ electron ($\lambda_1 = 1$, $\lambda_2 = 2$) we could have $\Lambda = 1$ or 3 (but not -1), i.e. a Π or a Φ state.



the total spin momentum **S** is given by $\sqrt{S(S+1)}$ where the total spin quantum number S is:

$$\boxed{S = \Sigma S_i,\ \Sigma S_i - 1,\ \Sigma S_i - 2,\ \ldots,\ \tfrac{1}{2} \text{ or } 0} \qquad (6.30)$$

The multiplicity of a molecular state is, as for atoms, $2S+1$ and this is usually indicated as an upper prefix to the state symbol. Thus for the Π and Φ states discussed in the previous paragraph, the states would be written $^3\Pi$ or $^3\Phi$ if the individual π and δ electron spins are parallel ($S = \frac{1}{2} + \frac{1}{2} = 1,\ 2S+1 = 3$), or as $^1\Pi$ or $^1\Phi$ if the spins are paired.

When the *axial* component of a spin is required, however, it is often designated by σ for a single electron or Σ for several (corresponding to s and S for the atomic case). In this case the multiplicity is $2\Sigma + 1$.

Term symbol of molecules: $^{2s+1}\Lambda_{\Omega}$

Similar to atomic term symbols

Σ, Π, Δ for Λ=0, 1, 2,

Finally, we consider the axial component of the *total* electronic angular momentum, i.e. the sum of the axial components of spin and orbital motion. In general the total momentum is strongly coupled to the axis and its axial component is more significant than the momentum itself. If we write the axial component as Ω we have simply:

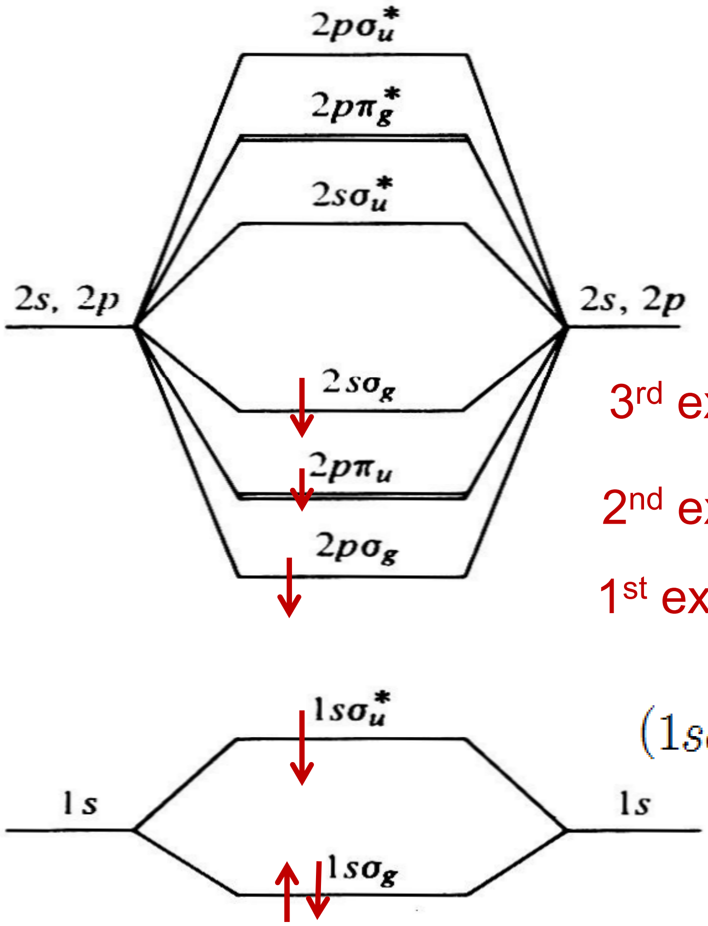
Total angular momentum

$$\boxed{\Omega = |\Lambda + \Sigma|} \qquad (6.31)$$

but we must remember that Λ and Σ may have the same or opposite directions along the internuclear axis. Thus in the $^3\Pi$ state described above we have $\Lambda = 1$, $\Sigma = 1$; hence $\Omega = 2$ or 0. The $^1\Pi$ state has $\Lambda = 1$, $\Sigma = 0$; hence we have $\Omega = 1$ only. These states would be indicated by writing their Ω values as subscripts: $^3\Pi_2$, $^3\Pi_0$, $^3\Pi_1$.

We can construct term symbol of linear molecules which is similar to atomic term symbol. Orbital, spin, and total angular momenta are express in term symbol.

MO diagram of H_2 molecule



3rd excited state $(1s\sigma_g)^1(2s\sigma_g)^1$ $^1\Sigma_g^+$

2nd excited state $(1s\sigma_g)^1(2p\pi_u)^1$ $^1\Pi_u$

1st excited state $(1s\sigma_g)^1(2p\sigma_g)^1$ $^1\Sigma_u^+$

$(1s\sigma_g)^1(1s\sigma_u^*)^1$ No bond formed

Ground state $(1s\sigma_g)^2\,{}^1\Sigma_g^+$

Two electrons in atomic ground state

6.2.4 An Example: The Spectrum of Molecular Hydrogen

Thus the ground state of molecular hydrogen can be written:

Two electrons are in a single MO orbital with $\lambda_1=0$. $\lambda_2=0$; Thus $\Lambda=0$
$s_1=s_2=1/2$; Thus s=0 for paired electrons

Hydrogen atom: $^2S_{1/2}$

$$\boxed{\text{Ground state:} \quad (1s\sigma_g)^2\ {}^1\Sigma_g^+}$$

A large number of excited singlet states also exist; let us consider some of the lower ones for which one electron only has been raised from the ground state into some higher molecular orbital, i.e. singly excited states. We can ignore promotion into any of the starred states of Fig. 6.14(*b*), since this would lead to the formation of an unstable molecule and immediate dissociation (cf. Fig. 6.11, where the placing of an electron in each of the σ_g and σ_u^* orbitals produces dissociation into two H atoms). Thus we may consider the three possible excited states $(1s\sigma_g 2s\sigma_g)$, $(1s\sigma_g 2p\sigma_g)$, and $(1s\sigma_g 2p\pi_u)$.

Construct term symbols from atomic orbitals.

Taking $(1s\sigma_g 2s\sigma_g)$ first: here both electrons are σ electrons; hence $\Lambda = \lambda_1 + \lambda_2 = 0$ and, since we are considering only singlet states, $S = 0$ also. Further, since both constituent orbitals are *even* and *symmetrical*, the overall state will be the same, and we have $(1s\sigma_g 2s\sigma_g)\ {}^1\Sigma_g^+$.

Now $(1s\sigma_g 2p\sigma_g)$: here we again have a $^1\Sigma$ state since both electrons are σ, but the overall state is now *odd* (*u*); this may be rationalized if we think of one electron as rising from a hydrogen atom in the *even* 1*s* state and the other from an *odd* 2*p* state, the combination of an odd and an even state leading to an overall odd state. Thus $(1s\sigma_g 2p\sigma_g)\ {}^1\Sigma_u^+$.

Finally the $(1s\sigma_g 2p\pi_u)$: now $\Lambda = \lambda_1 + \lambda_2 = 1$, since one electron is in a π state and, again since one electron originates from a $2p$ orbital, the combined state is u: ${}^1\Pi_u$.

The energies of these three states increase in the order of the constituent molecular orbitals, as shown in Fig. 6.14(*b*), i.e.:

The energy of molecular orbitals depends on the energy of atomic orbitals, as shown in Fig. 6.14

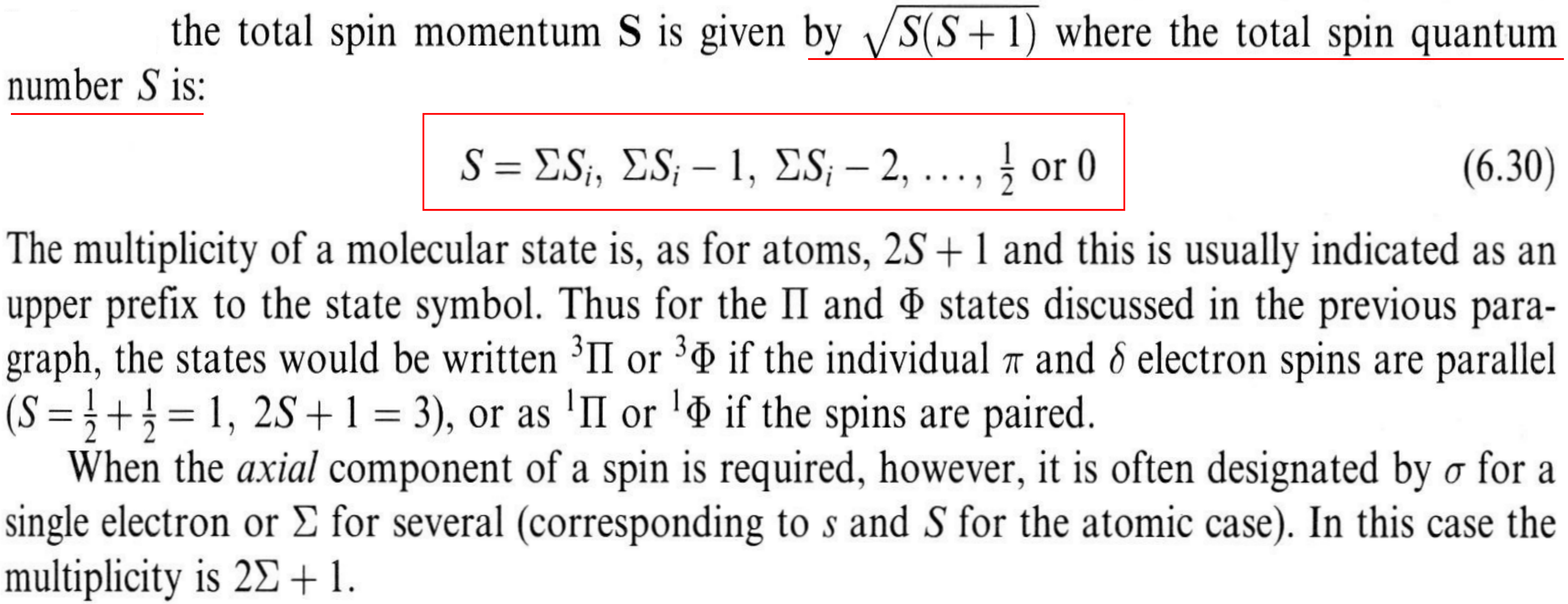
$$\boxed{{}^1\Sigma_u^+ < {}^1\Pi_u < {}^1\Sigma_g^+}$$

We have already studied how to construct term symbols of molecules.

Similar states are obtained by excitation to the $3s$ and $3p$ states, to the $4s$ and $4p$ states, etc. Also for $n = 3, 4, \ldots$ there exists the possibility of excitation to the nd orbital. It may be shown by methods similar to those above that interaction between $1s$ and nd electrons can lead to the three configurations and state symbols in increasing energy:

$$(1s\sigma\, nd\sigma)\ {}^1\Sigma_g^+ < (1s\sigma\, nd\pi)\ {}^1\Pi_g < (1s\sigma\, nd\delta)\ {}^1\Delta_g$$

The sequence in the singlet states



the total spin momentum **S** is given by $\sqrt{S(S+1)}$ where the total spin quantum number S is:

$$\boxed{S = \Sigma S_i,\ \Sigma S_i - 1,\ \Sigma S_i - 2,\ \ldots,\ \tfrac{1}{2} \text{ or } 0} \tag{6.30}$$

The multiplicity of a molecular state is, as for atoms, $2S+1$ and this is usually indicated as an upper prefix to the state symbol. Thus for the Π and Φ states discussed in the previous paragraph, the states would be written $^3\Pi$ or $^3\Phi$ if the individual π and δ electron spins are parallel ($S = \frac{1}{2} + \frac{1}{2} = 1,\ 2S+1 = 3$), or as $^1\Pi$ or $^1\Phi$ if the spins are paired.

When the *axial* component of a spin is required, however, it is often designated by σ for a single electron or Σ for several (corresponding to s and S for the atomic case). In this case the multiplicity is $2\Sigma + 1$.

Term symbol of molecules: $^{2s+1}\Lambda_{\Omega}$

Similar to atomic
term symbols

Σ, Π, Δ for Λ=0, 1, 2,

Selection rule

Some of these energy levels are shown at the left of Fig. 6.15. Transitions between them can occur according to the *selection rules*:

1. $$\Delta\Lambda = 0, \pm 1 \qquad (6.32)$$

Vertical transitions are also possible.

Thus transitions $\Sigma \leftrightarrow \Sigma$, $\Sigma \leftrightarrow \Pi$, $\Pi \leftrightarrow \Pi$, etc., are allowed, but $\Sigma \leftrightarrow \Delta$, for example, is not.

2. $$\boxed{\Delta S = 0} \qquad (6.33)$$

No crossing between singlet and triplet

Same as atoms

For the present we are concerned only with singlet states so this rule does not arise.

3. $$\boxed{\Delta\Omega = 0, \pm 1} \qquad (6.34)$$

Same as atoms

This follows directly from 1 and 2 above.

4. There are also restrictions on symmetry changes. Σ^+ states can undergo transitions only into other Σ^+ states (or, of course, into Π states) while Σ^- go only into Σ^- (or Π). Symbolically:

$$\Sigma^+ \leftrightarrow \Sigma^+ \quad \Sigma^- \leftrightarrow \Sigma^- \quad \Sigma^+ \not\leftrightarrow \Sigma^- \qquad (6.35)$$

And finally:

$$g \leftrightarrow u \quad g \not\leftrightarrow g \quad u \not\leftrightarrow u \qquad (6.36)$$

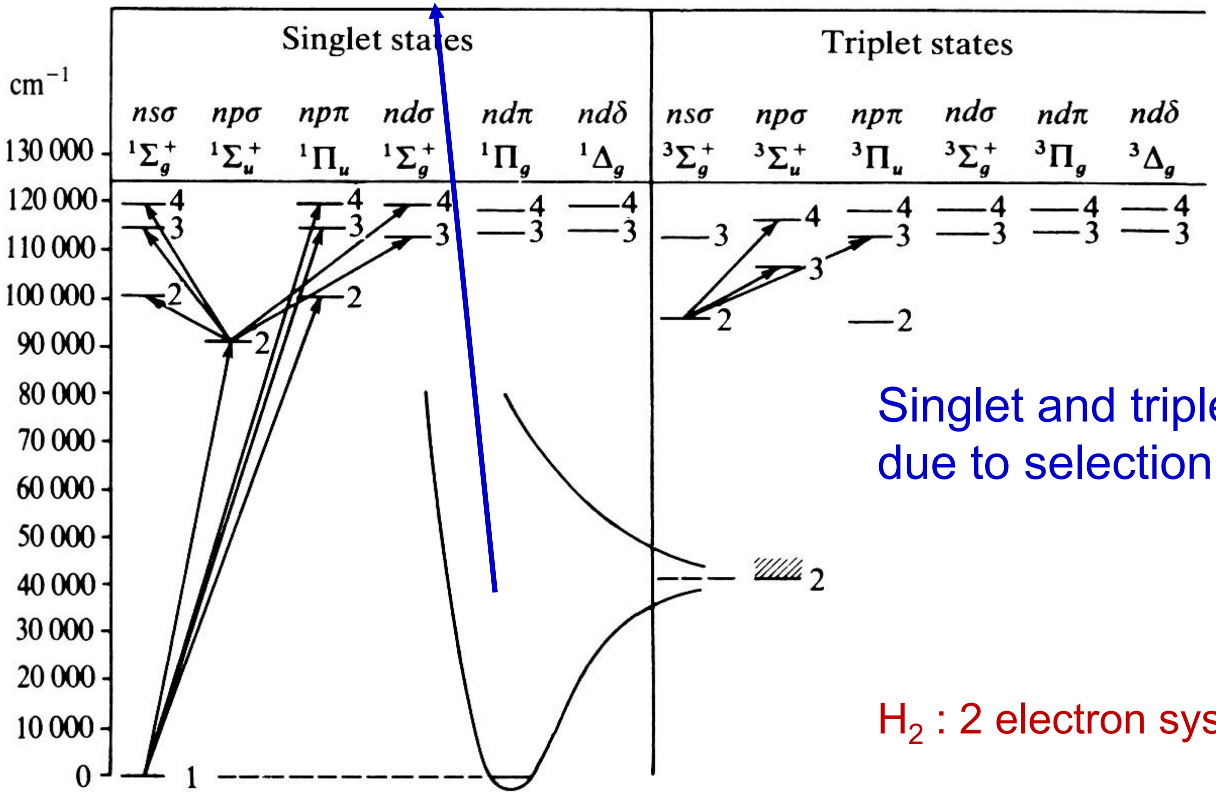
Forbidden transition

We have additional selection rule from symmetry.

Singlet and Triplet

Selection rule: $\Delta S = 0$, $\Delta\Lambda = 0, \pm 1$, $\Delta\Omega = 0, \pm 1$

No change in spin state during transition



Singlet and triplet are separated due to selection rule of $\Delta S=0$

H_2 : 2 electron system

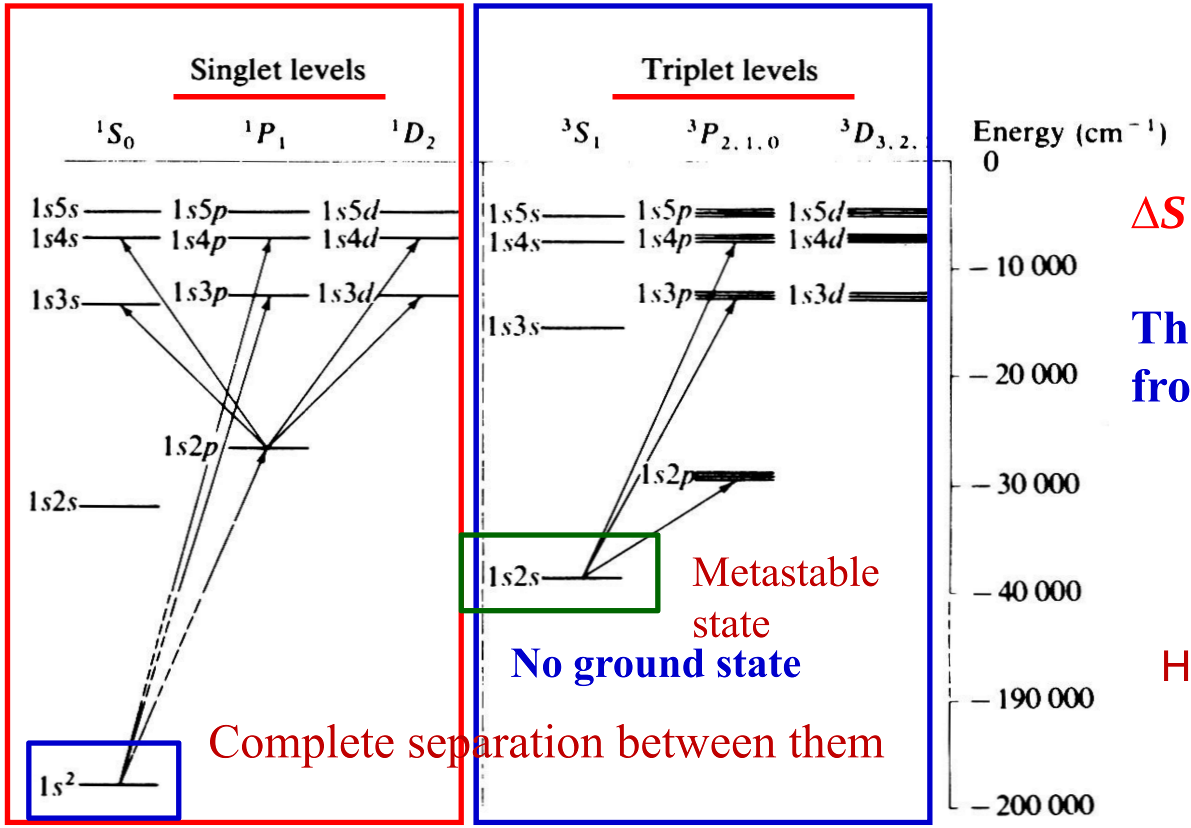
Figure 6.15 The singlet and triplet energy levels of the hydrogen molecule. One electron only is assumed to undergo transitions, the other remaining in the $1s\sigma$ state.

5.4.5 The Spectrum of Helium and the Alkaline Earths

Two electrons give two types of spin states, singlet and triplet

Selection rule: $\Delta S = 0$, $\Delta L = \pm 1$, $\Delta J = 0, \pm 1$

No change in spin state during transition



Metastable state

No ground state

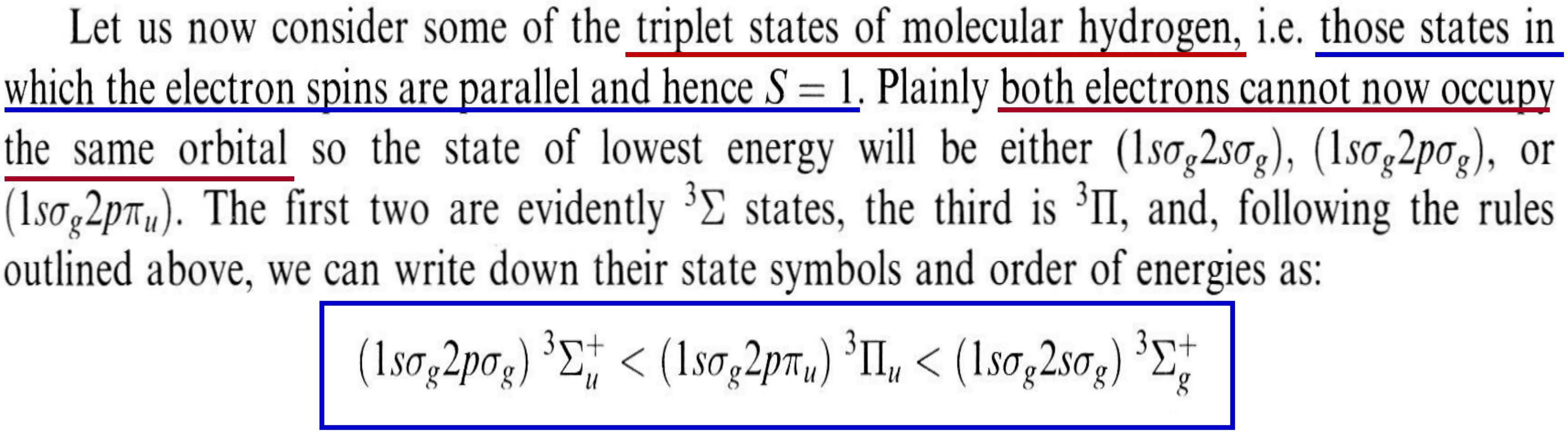
Complete separation between them

Figure 5.11 Some of the energy levels of the electrons in the helium atom, together with a few allowed transitions.

$\Delta S = 0$: very important

The singlet is separated from the triplet.

He : 2 electron system



Let us now consider some of the triplet states of molecular hydrogen, i.e. those states in which the electron spins are parallel and hence $S = 1$. Plainly both electrons cannot now occupy the same orbital so the state of lowest energy will be either $(1s\sigma_g 2s\sigma_g)$, $(1s\sigma_g 2p\sigma_g)$, or $(1s\sigma_g 2p\pi_u)$. The first two are evidently $^3\Sigma$ states, the third is $^3\Pi$, and, following the rules outlined above, we can write down their state symbols and order of energies as:

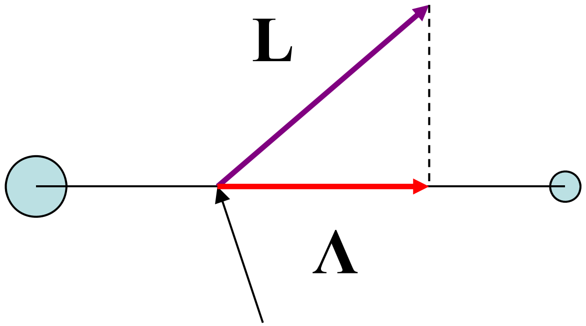
$$\boxed{(1s\sigma_g 2p\sigma_g)\ ^3\Sigma_u^+ < (1s\sigma_g 2p\pi_u)\ ^3\Pi_u < (1s\sigma_g 2s\sigma_g)\ ^3\Sigma_g^+}$$

The sequence in the triplet states

Notation of Molecular Electronic States

Atoms : LS-coupling or jj-coupling and Term symbol : $^{2S+1}L_J$

Linear molecules : Very similar to atoms except for orbital angular momentum L. In molecules, we use the component of orbital angular momentum along the molecular axis.



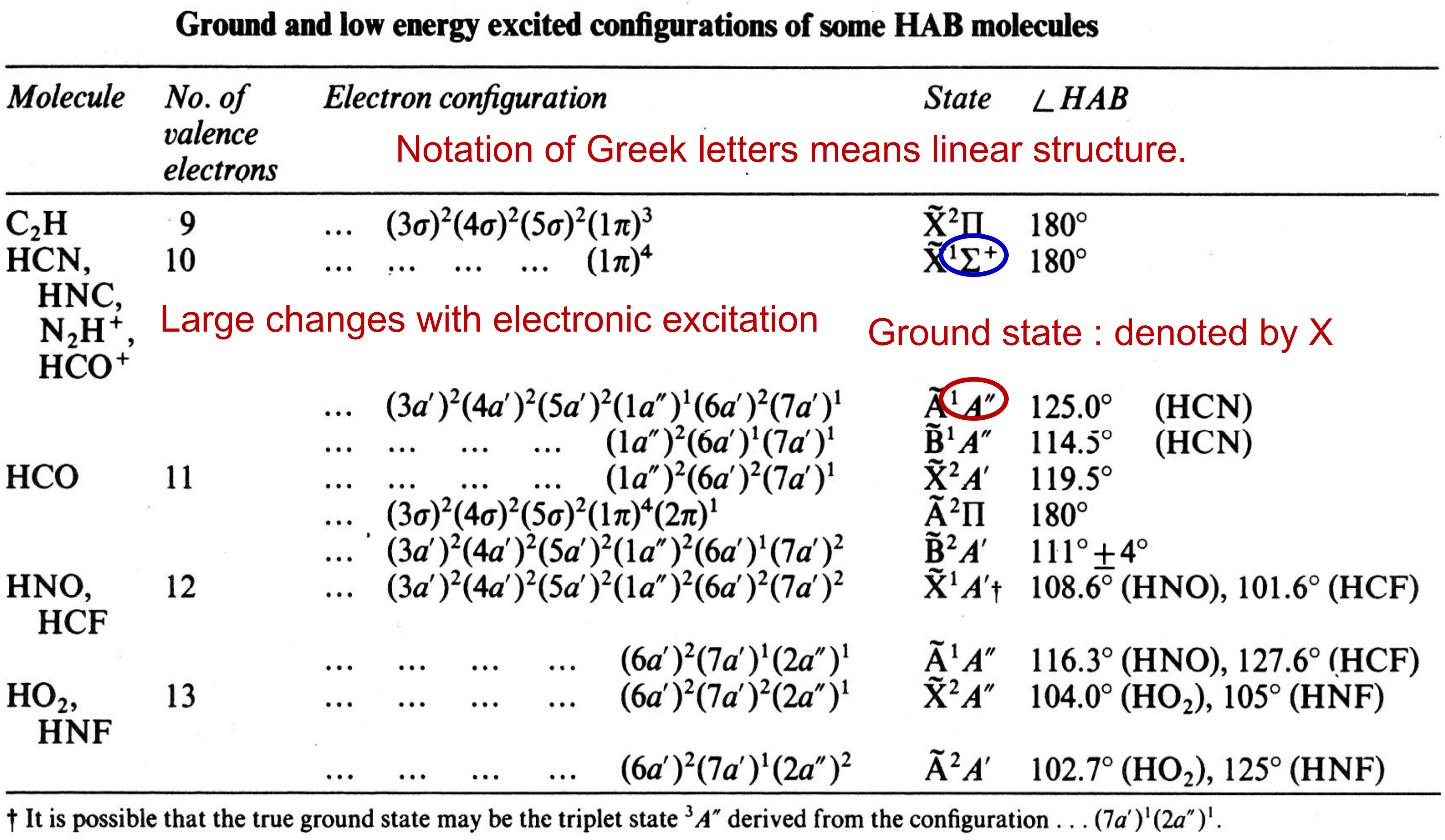
$^{2S+1}\Lambda_\Omega$

Term symbol of linear molecules

Center of mass (COM)

For nonlinear molecules :

Use of symmetry properties (Character table in group theory)



Ground and low energy excited configurations of some HAB molecules

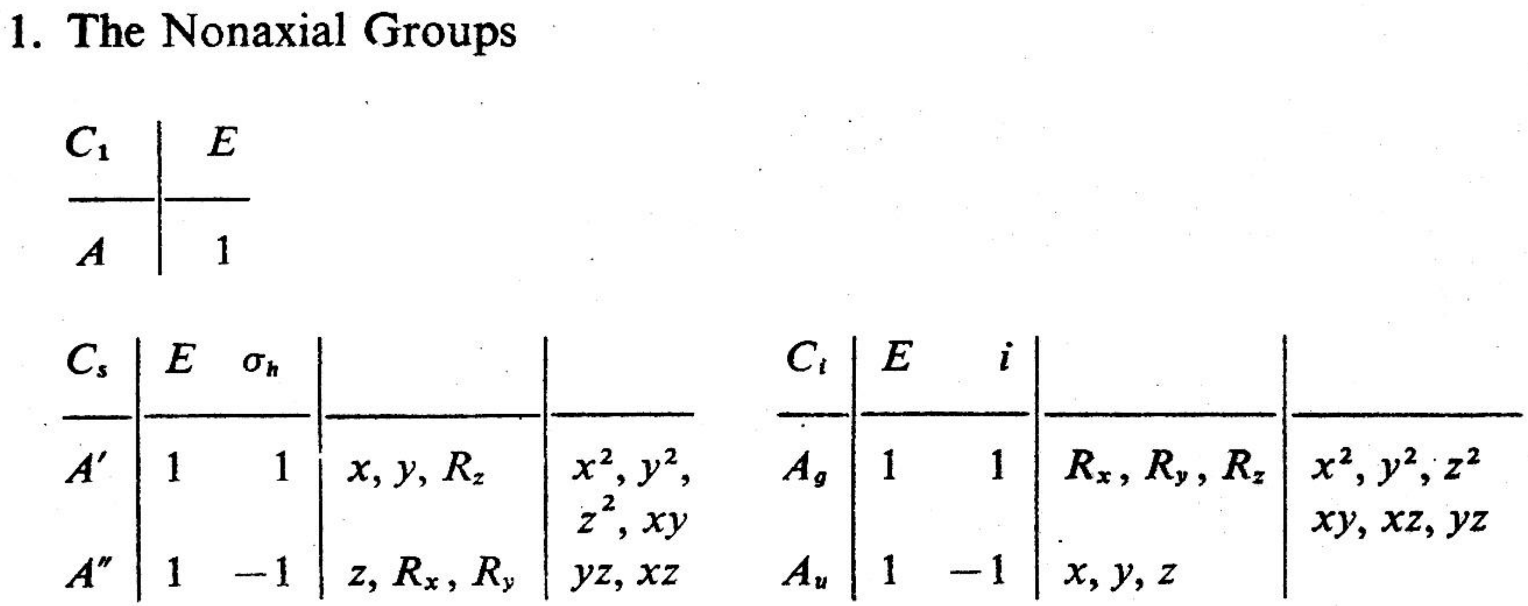
Notation of Greek letters means linear structure.

Large changes with electronic excitation

Ground state : denoted by X

Molecule	*No. of valence electrons*	*Electron configuration*	*State*	*∠HAB*
C_2H	9	… $(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^3$	$\tilde{X}\,^2\Pi$	180°
HCN, HNC, N_2H^+, HCO^+	10	… … … … $(1\pi)^4$	$\tilde{X}\,^1\Sigma^+$	180°
		… $(3a')^2(4a')^2(5a')^2(1a'')^1(6a')^2(7a')^1$	$\tilde{A}\,^1A''$	125.0° (HCN)
		… … … … $(1a'')^2(6a')^1(7a')^1$	$\tilde{B}\,^1A''$	114.5° (HCN)
HCO	11	… … … … $(1a'')^2(6a')^2(7a')^1$	$\tilde{X}\,^2A'$	119.5°
		… $(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4(2\pi)^1$	$\tilde{A}\,^2\Pi$	180°
		… $(3a')^2(4a')^2(5a')^2(1a'')^2(6a')^1(7a')^2$	$\tilde{B}\,^2A'$	111° ± 4°
HNO, HCF	12	… $(3a')^2(4a')^2(5a')^2(1a'')^2(6a')^2(7a')^2$	$\tilde{X}\,^1A'$†	108.6° (HNO), 101.6° (HCF)
		… … … … $(6a')^2(7a')^1(2a'')^1$	$\tilde{A}\,^1A''$	116.3° (HNO), 127.6° (HCF)
HO_2, HNF	13	… … … … $(6a')^2(7a')^2(2a'')^1$	$\tilde{X}\,^2A''$	104.0° (HO_2), 105° (HNF)
		… … … … $(6a')^2(7a')^1(2a'')^2$	$\tilde{A}\,^2A'$	102.7° (HO_2), 125° (HNF)

† It is possible that the true ground state may be the triplet state $^3A''$ derived from the configuration . . . $(7a')^1(2a'')^1$.



1. The Nonaxial Groups

C_1	E
A	1

C_s	E	σ_h		
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A''	1	-1	z, R_x, R_y	yz, xz

C_i	E	i		
A_g	1	1	R_x, R_y, R_z	x^2, y^2, z^2 xy, xz, yz
A_u	1	-1	x, y, z	

Character table

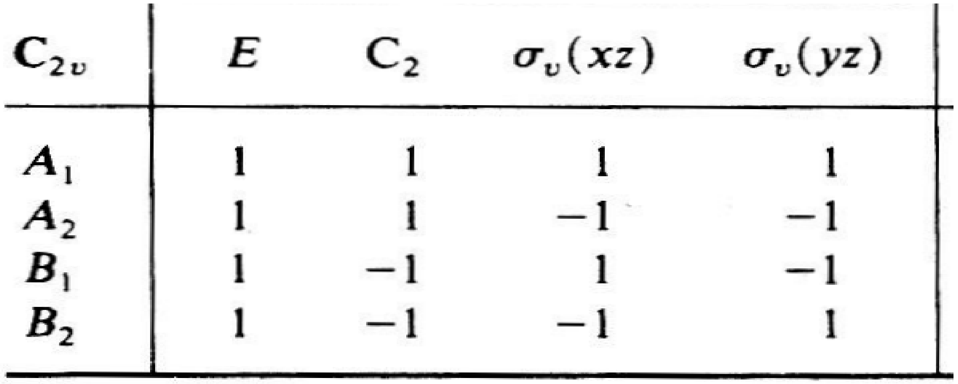
Four symmetry species

symmetry operation

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

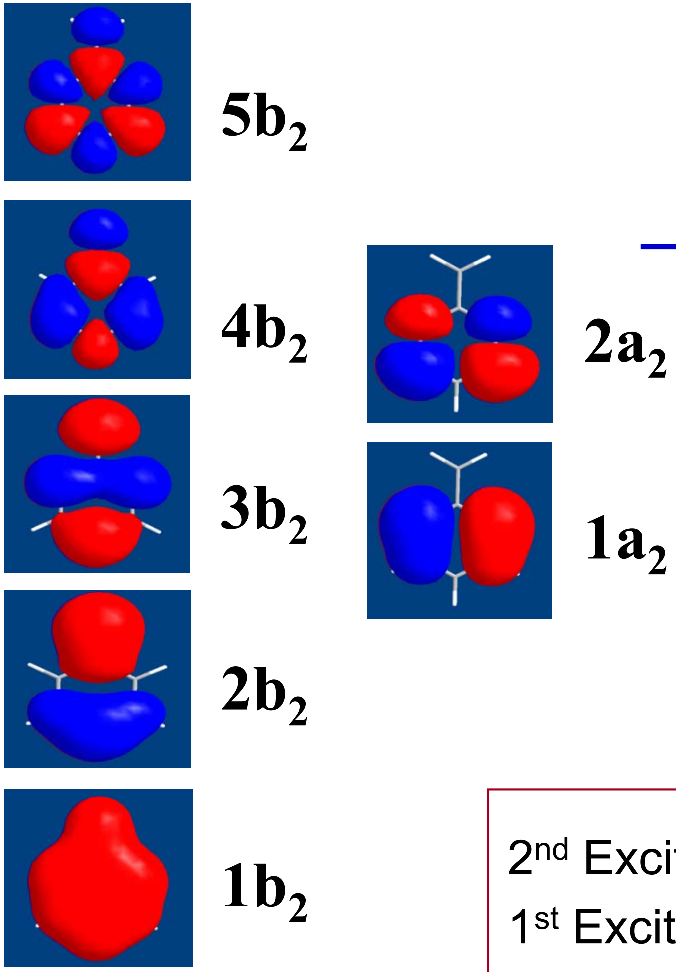
C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2-y^2, xy), (xz, yz)$

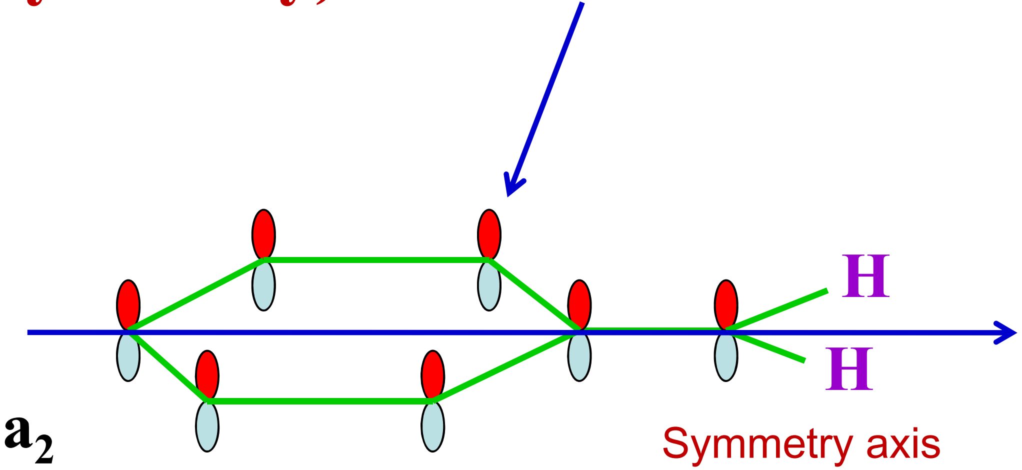
Character table



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

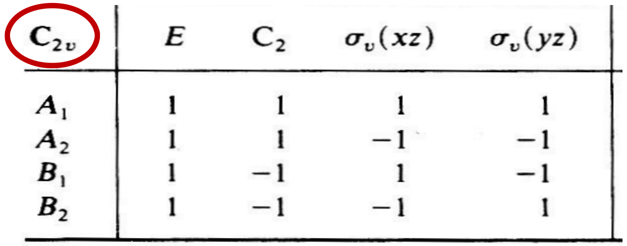
Benzyl radical (C_{2v} symmetry) of seven π electrons





Symmetry axis

The symmetry operation produce only a_2 and b_2 symmetry species in C_{2V} character table..



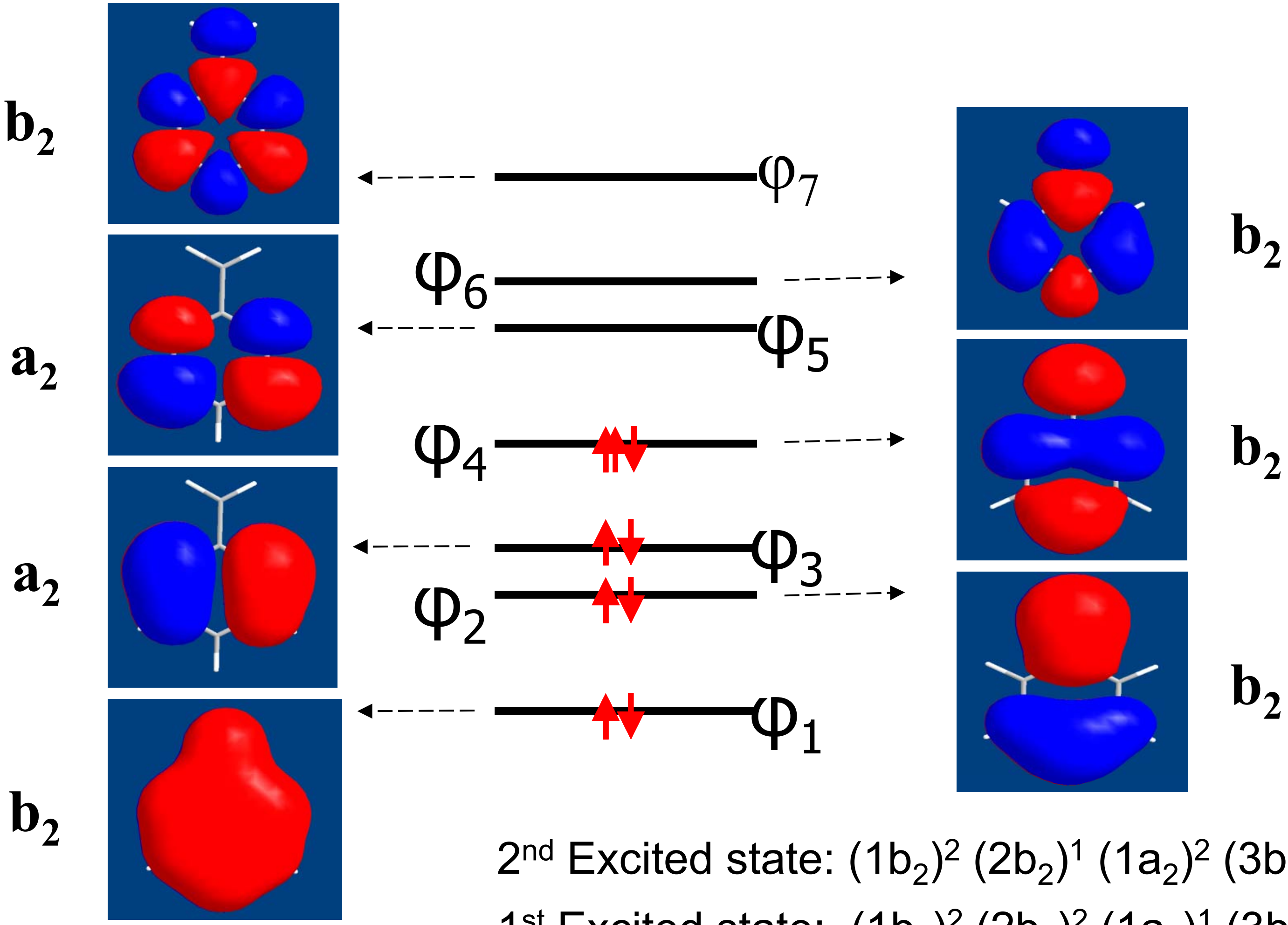
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

2nd Excited state: $(1b_2)^2\ (2b_2)^1\ (1a_2)^2\ (3b_2)^2$ **2^2B_2**

1st Excited state: $(1b_2)^2\ (2b_2)^2\ (1a_2)^1\ (3b_2)^2$ **1^2A_2**

Ground state: $(1b_2)^2\ (2b_2)^2\ (1a_2)^2\ (3b_2)^1$ **1^2B_2**

Molecular orbitals of benzyl radical

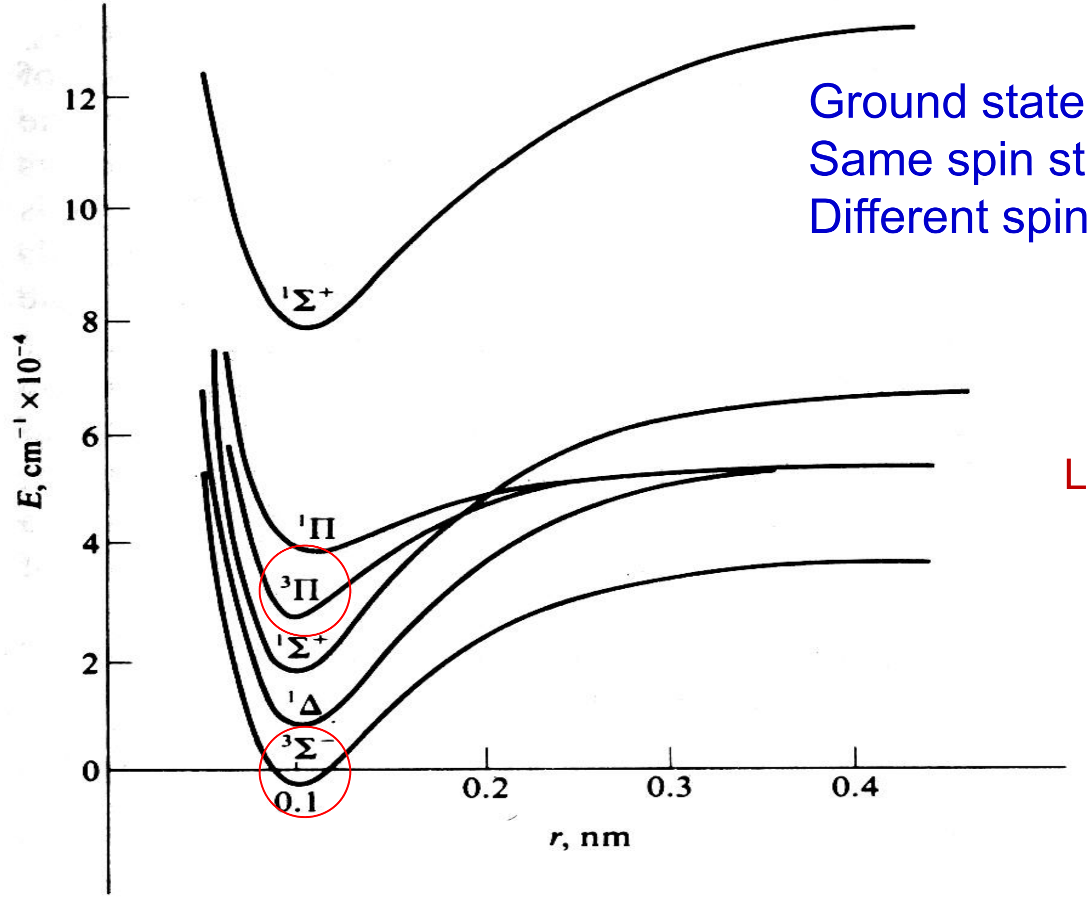


2nd Excited state: $(1b_2)^2\ (2b_2)^1\ (1a_2)^2\ (3b_2)^2$ **2^2B_2**

1st Excited state: $(1b_2)^2\ (2b_2)^2\ (1a_2)^1\ (3b_2)^2$ **1^2A_2**

Ground state: $(1b_2)^2\ (2b_2)^2\ (1a_2)^2\ (3b_2)^1$ **1^2B_2**

Ground state: X state
Same spin states: A, B, C, (capital)
Different spin states: a, b, c, (little)

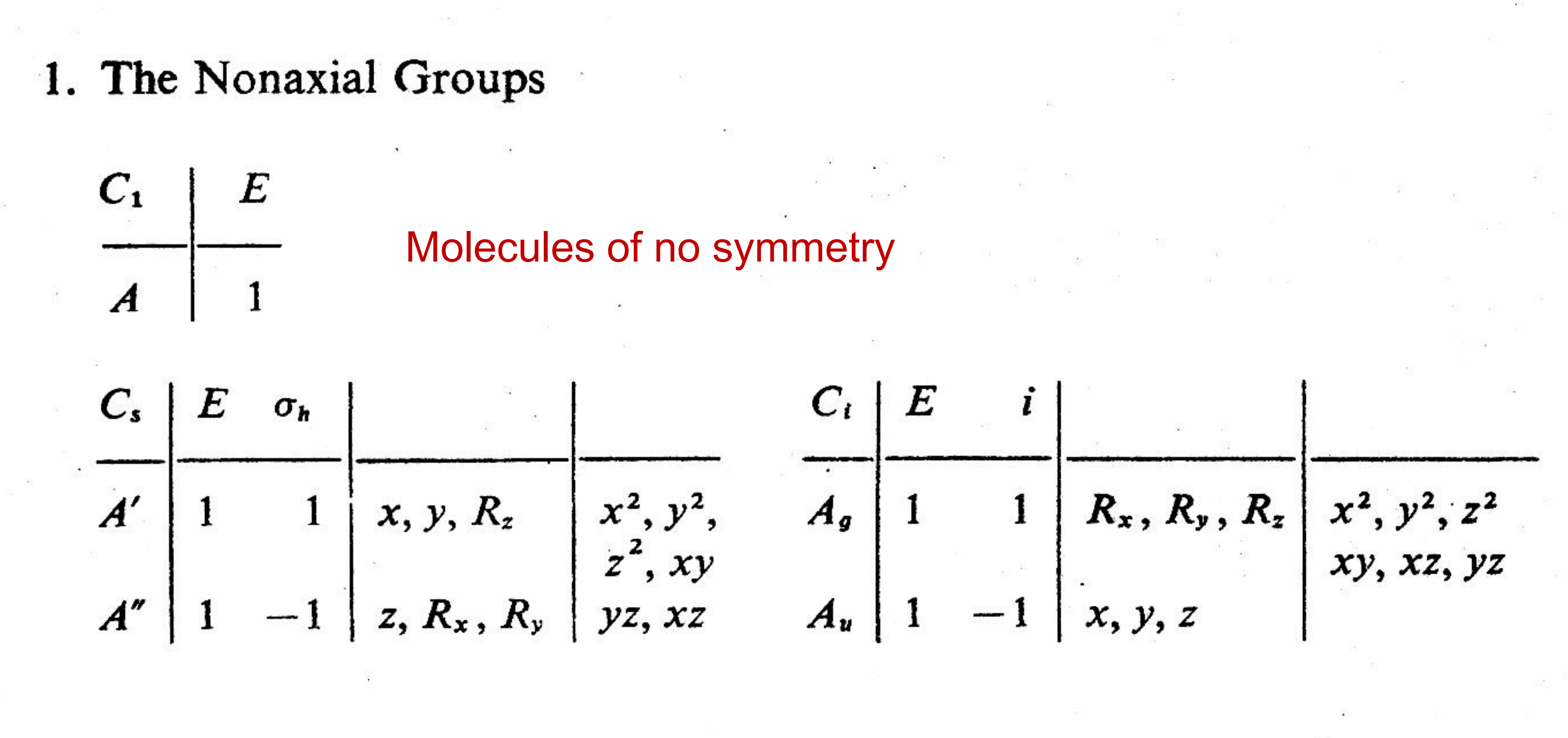


Linear molecules

FIGURE 6.2
Potential energy functions for the ground and five stable excited states of the NH molecule.

Singlet and triplet states are possible.

For nonlinear molecules, we use the symmetry species given in character table.



1. The Nonaxial Groups

C_1	E
A	1

Molecules of no symmetry

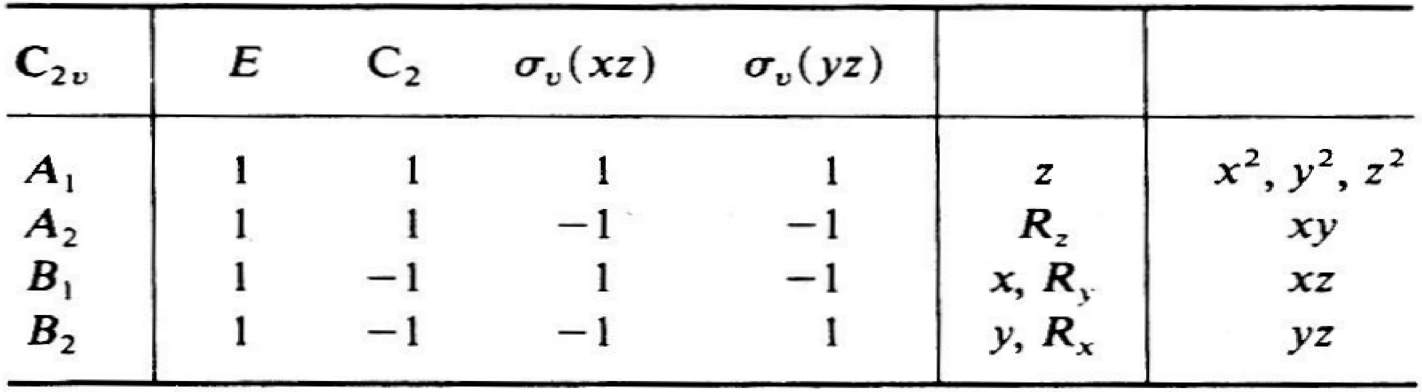
C_s	E	σ_h		
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A''	1	-1	z, R_x, R_y	yz, xz

C_i	E	i		
A_g	1	1	R_x, R_y, R_z	x^2, y^2, z^2 xy, xz, yz
A_u	1	-1	x, y, z	

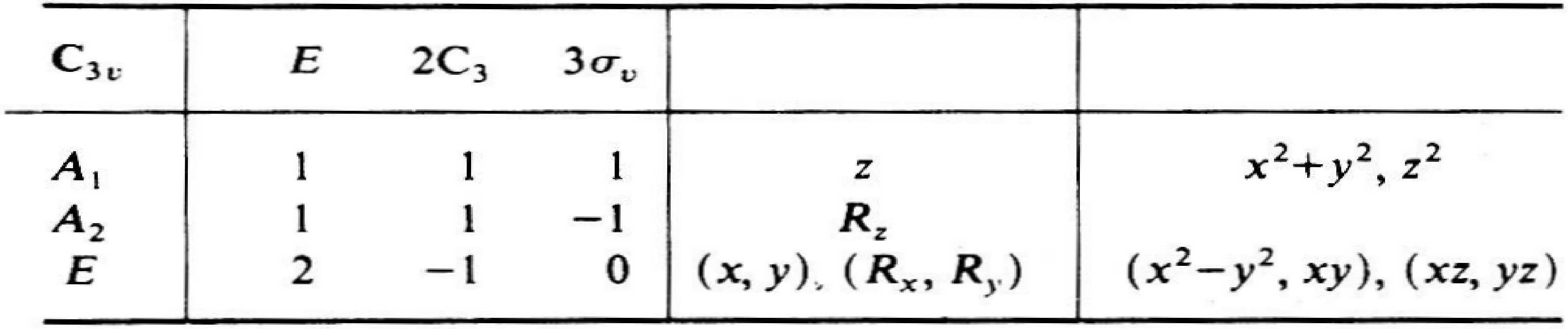
http://webbook.nist.gov/chemistry/name-ser.html

Character table

H_2O belongs to C_{2V} symmetry



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz



C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2-y^2, xy), (xz, yz)$

Vibronic Spectrum of Benzene

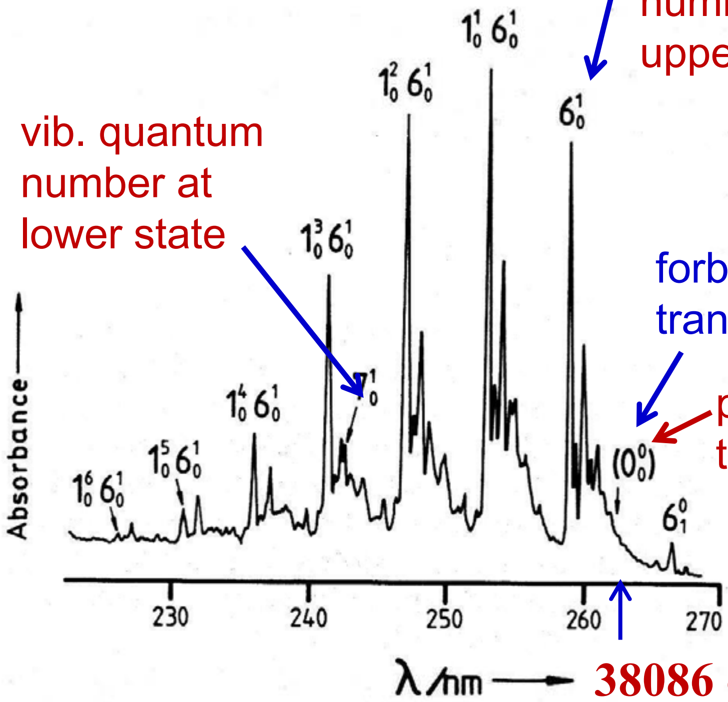
Notation of transition state of polyatomic molecules which has many vibrational modes.

vib. quantum number at upper state

vib. quantum number at lower state

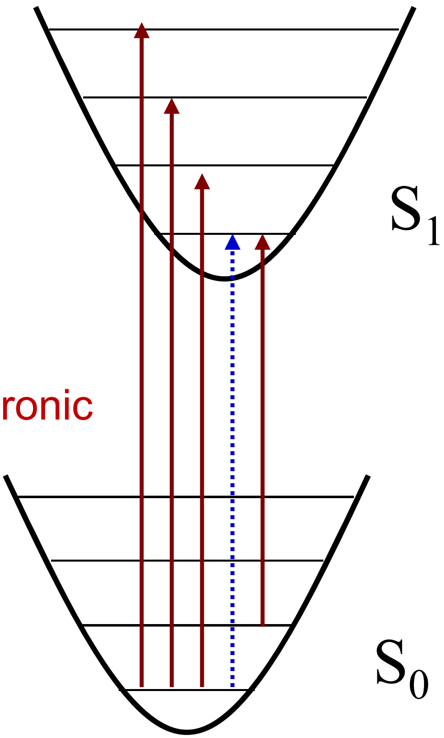
forbidden transition

pure electronic transition



38086 cm^{-1}

Figure 6.92 Low resolution $\tilde{A}^1B_{2u}$—$\tilde{X}^1A_{1g}$ absorption spectrum of a 1 cm path of benzene vapour above the liquid at room temperature and atmospheric pressure



Why we cannot observe the pure electronic transition of benzene?

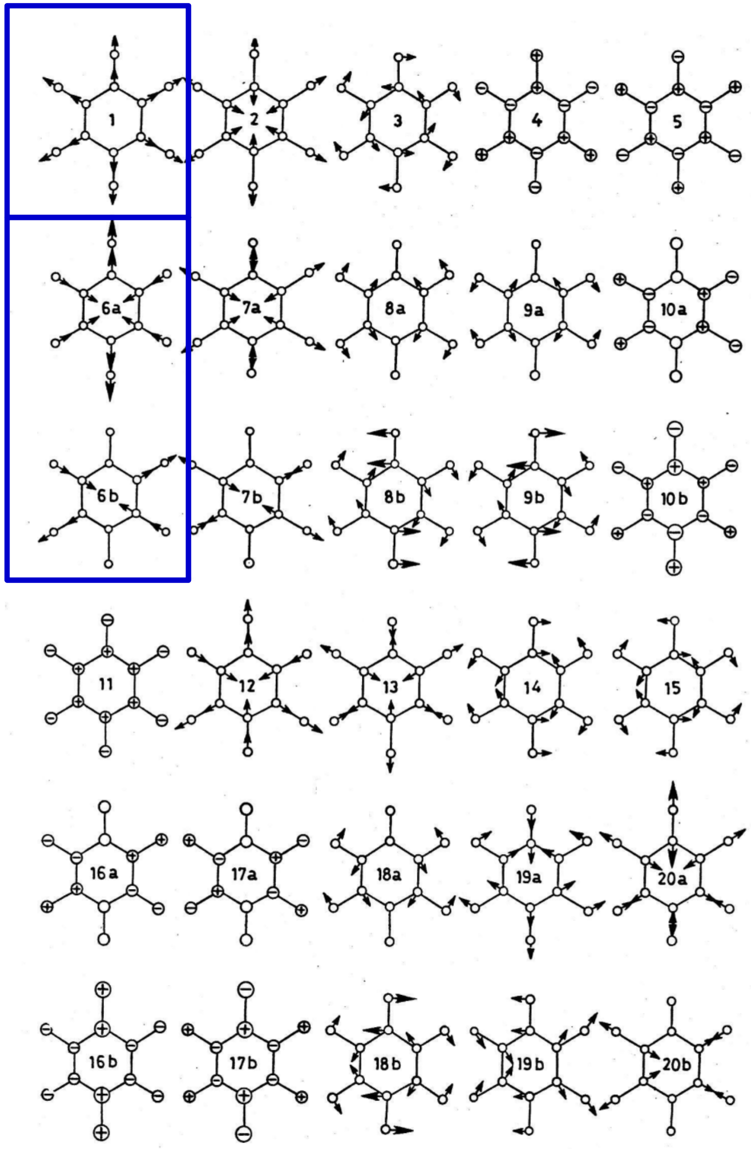
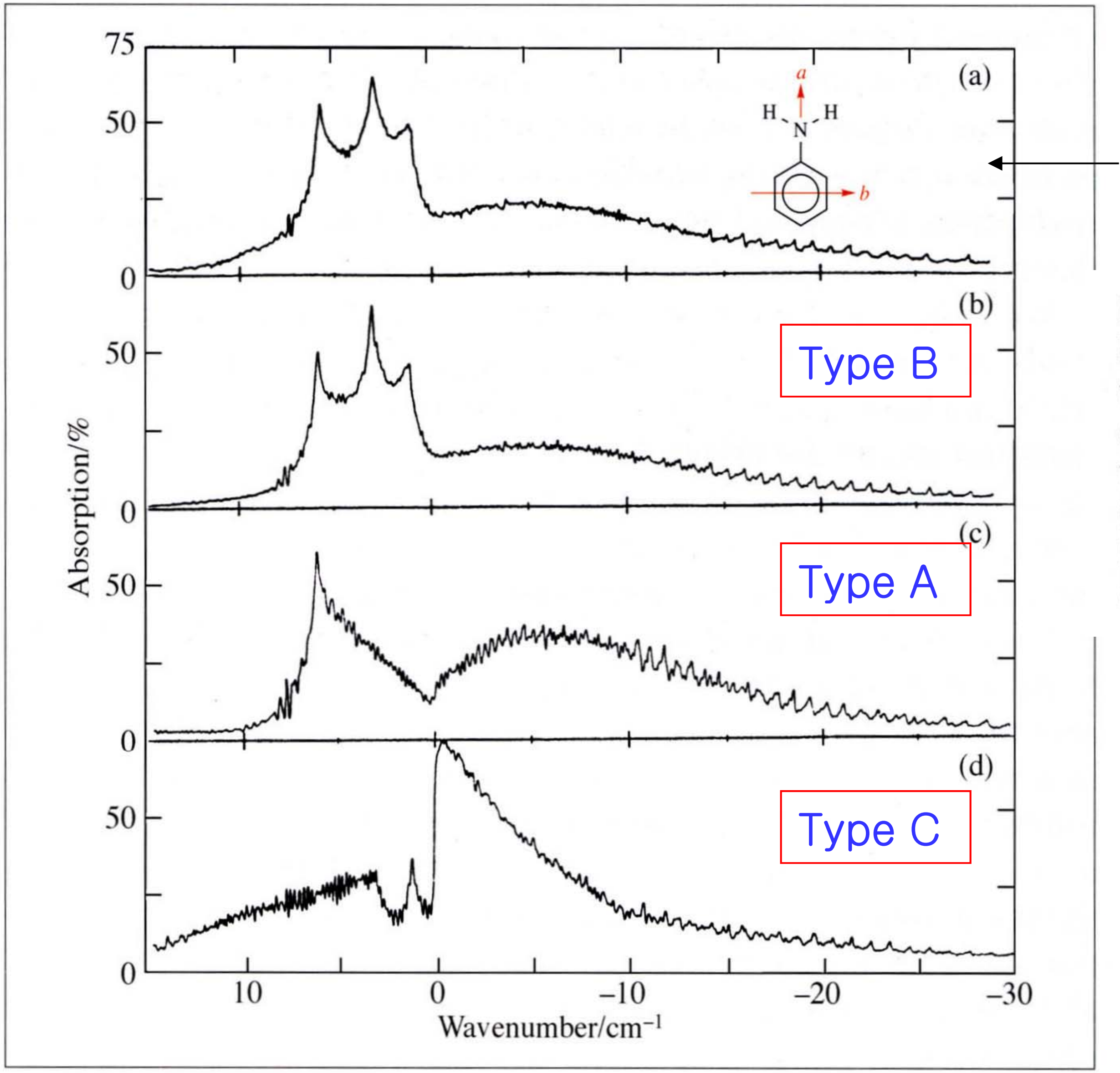


Fig. 1. Normal vibrations of benzene

Vibrational modes of benzene : There are a total of 30 vibrational degrees of freedom and 20 modes because some of them are degenerate.

Mode 1 is forbidden. Mode 6 (6a and 6b) is allowed. Thus the combination band of mode 1 and 6 is allowed transition.



Observation

Figure 11.8 (a) Observed type B and computed (b) type B, (c) type A and (d) type C rotational contours for aniline, using rotational constants for the 0–0 band (after J. Christoffersen, J. M. Hollas and G. H. Kirby, *Mol. Phys.*, 1969, **16**, 448)

How to generate the calculated spectrum?

We have already studied a, b, and c type transitions, the orientation of transition dipole moment along a, b, and c axes.

Making a calculated spectrum

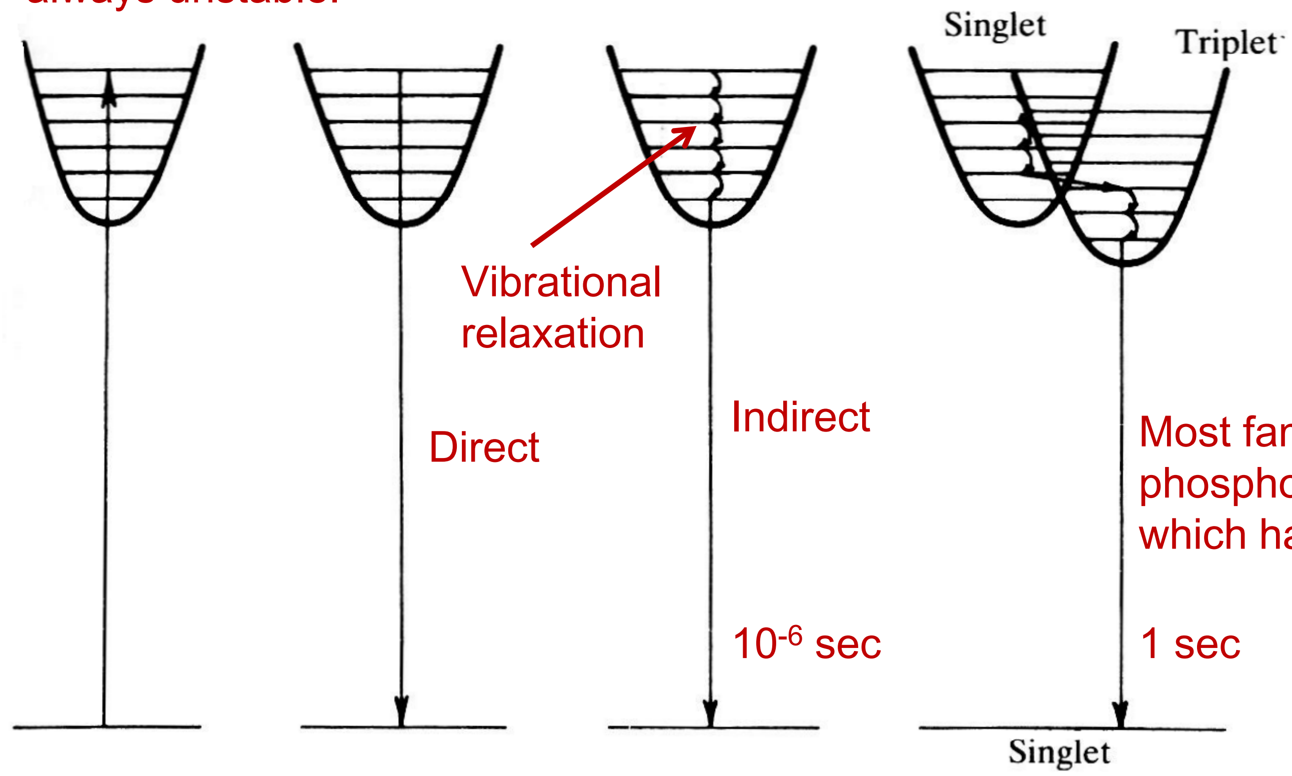
- We can obtain the spectroscopic data from the experimental observation by comparing the calculated spectrum.
- How can we make the calculated spectrum? To make this, we need the information on 1) rotational constant, 2) vibrational frequency, 3) electronic transition energy, 4) selection rule applied to each transition, and 5) temperature.

Relaxation process

Excited state is always unstable.

Lose energy

Crossing from singlet to takes a long time.



Vibrational relaxation

Direct

Indirect

10^{-6} sec

Most famous one is the phosphorescence from P which has about 10 min.

1 sec

(*a*) Absorption (*b*) Re-emission (*c*) Fluorescence (*d*) Phosphorescence

Figure 6.20 Showing the various ways in which an electronically excited molecule can lose energy.

How to predict the molecular geometry?

6.3 ELECTRONIC SPECTRA OF POLYATOMIC MOLECULES

6.3.1 Change of Shape on Excitation

AH_2 [H_2O]

polyvalent central atom

Think about two limiting cases.

p-orbital : 90°

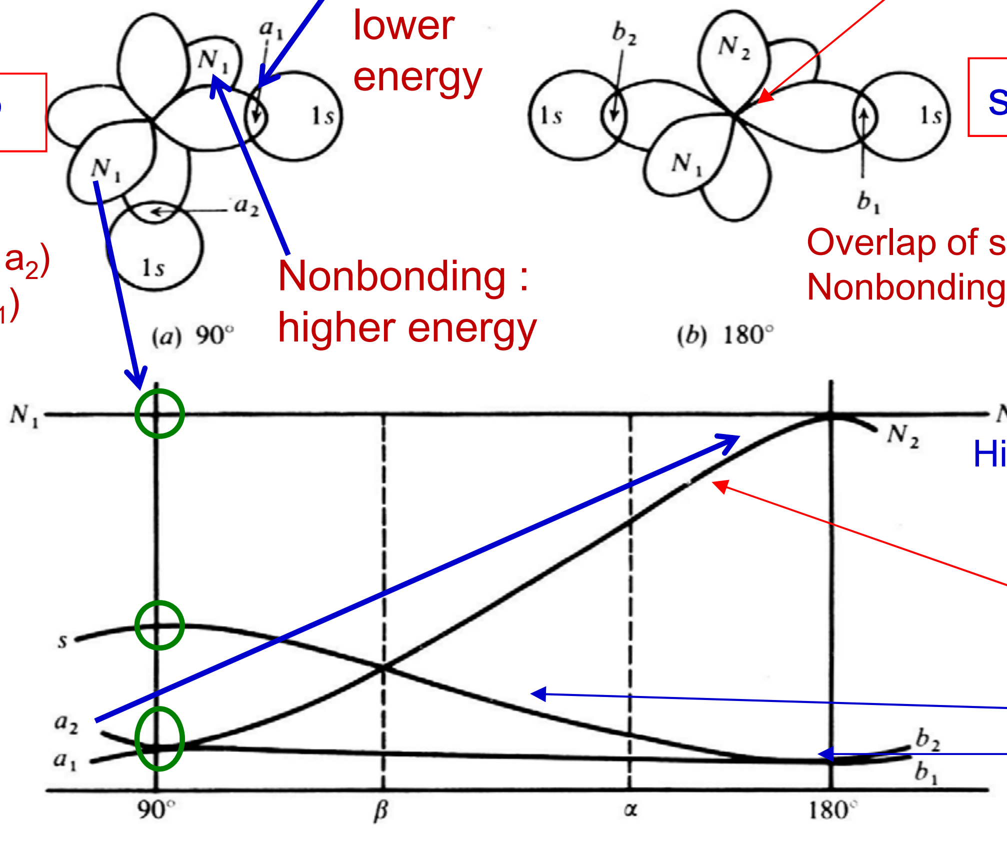
bonding : lower energy

sp hybridization : 180°

Overlap of p-1s (a_1, a_2)
Nonbonding of p (N_1)
2s of central atom

Nonbonding : higher energy

Overlap of sp-1s (b_1, b_2)
Nonbonding of p^2 (N_1 and N_2)



Stronger bonding

Higher energy

increase

decrease

The nature tries to get the minimum energy (the most stable one). The energy depends on the angle.

Occupy electrons from the lowest orbitals.

Figure 6.16 Orbital pictures for an AH_2 molecule where the AH bonds are (*a*) at 90° and (*b*) at 180°. In (*c*) is shown qualitatively the change in energy of the various orbitals as the bond angle changes from 90 to 180°. (*Adapted, with kind permission of the author, from A. D. Walsh,* J. Chem. Soc., *1953, p. 2262.*)

Remembering that a non-bonding orbital is higher in energy than a bonding orbital and that an *sp*-bonding orbital is stronger (hence *lower* in energy because the molecule is more stable) than a *p*-bonding orbital, we can plot the qualitative energy changes for a smooth transition from 90 to 180° bonding. This we do in Fig. 6.16(*c*), which is constructed as follows:

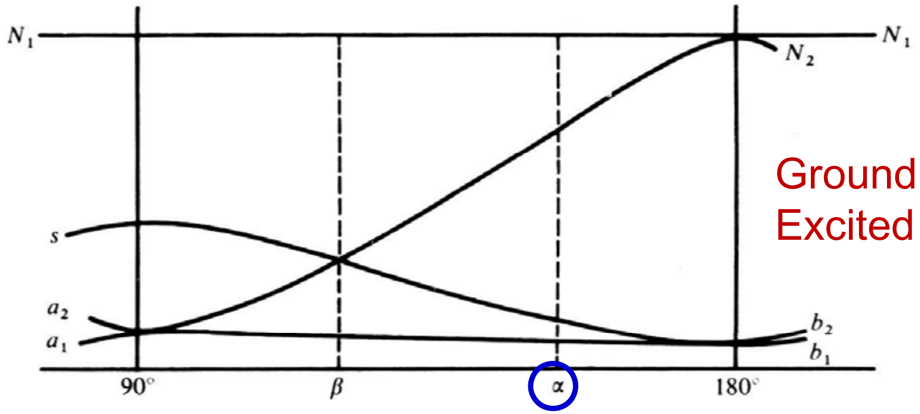
What is happening when changing from 90^0 to 180^0?

1. The non-bonding orbital N_1 remains unchanged throughout; hence its energy is constant.
2. The bonding orbital a_1 passes over into the stronger orbital b_1; hence its energy decreases.
3. The bonding orbital a_2 becomes the non-bonding N_2, thus increasing in energy; N_1 and N_2 are identical in energy at 180°.
4. The bonding orbitals b_1 and b_2 are formed by absorption of the non-bonding s into a_1.
5. If we increase the bond angle beyond 180° (or decrease it below 90°) the reverse changes begin to take place, so 180 and 90° represent maxima and minima on the energy curves as shown.

Applications

BeH_2 : $1s^2\,2s^2$: 2 electrons in bonding from Be and another 2 electrons from hydrogen.

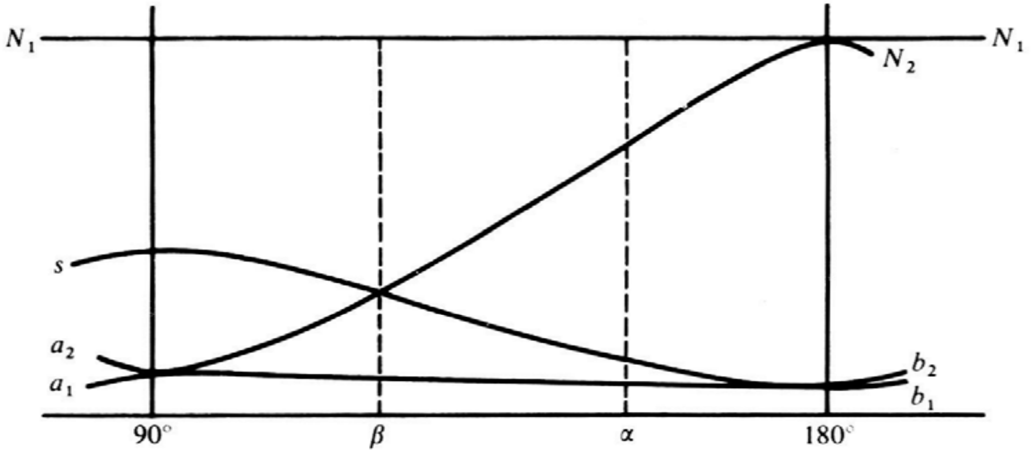
Two electrons per orbitals according to Pauli principle, so two electrons to go into b_1 and another two b_2, thus producing a linear molecule.



Ground : 180°
Excited : between 90° and 180°.

For the excited state, the configuration is $b_1^2\, b_2^1 N_2$ (or N_1)^1, the most stable state will be at a bond angle, α, somewhere between 90^0 and 180^0. The increase in the energies of b_1 and b_2 being more than compensated for by the decrease in N_2 until equilibrium occurs at an angle α.

For ionized state, BeH_2^+, the three remaining electrons will all be at b_1 and b_2 orbitals and hence the most stable configuration will again be linear

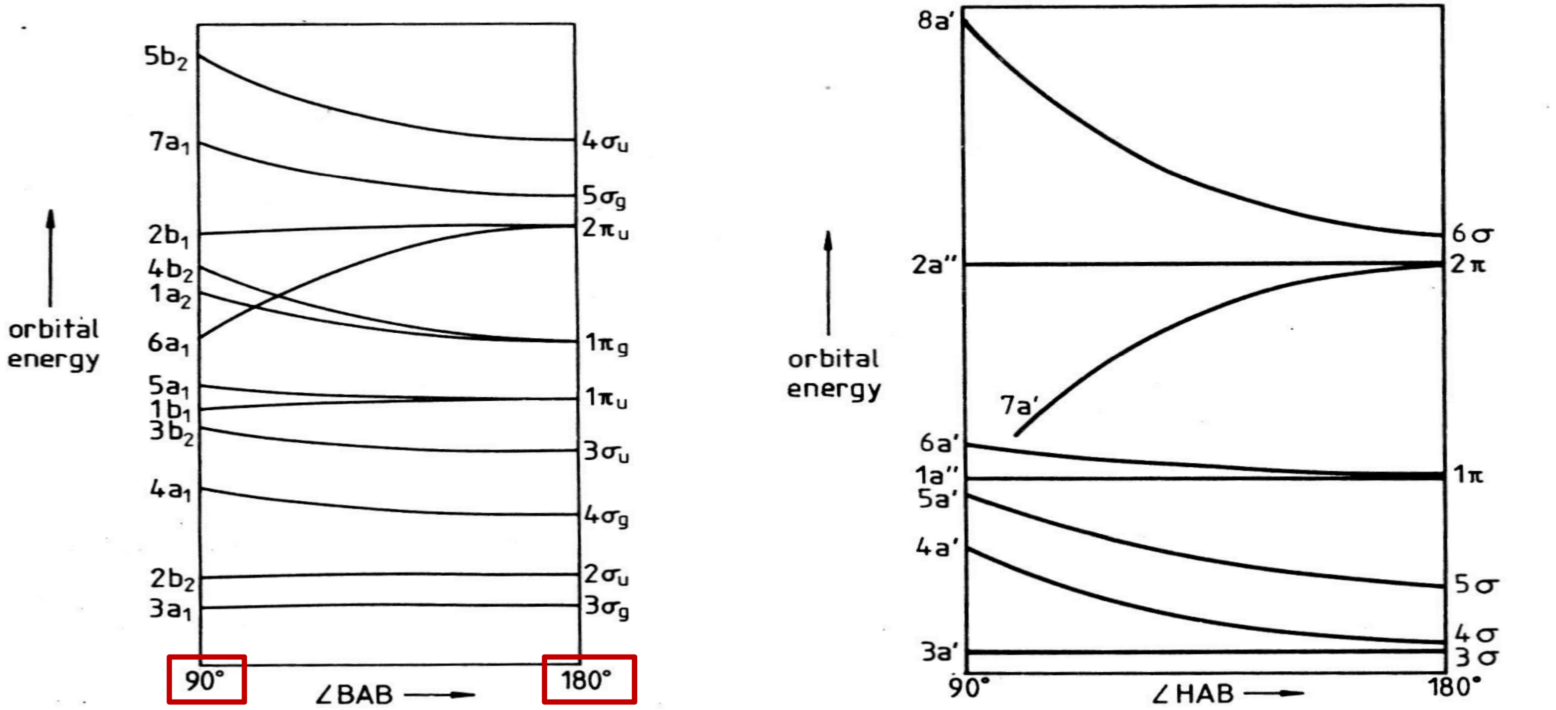


For H_2O, in which the oxygen atom has an outer electron configuration $2s^2\ 2p^4$, and has 6 electrons into molecular orbitals. two electrons from H. The lowest energy state is the angle β(=104.5°) in the figure. The bent structure has a configuration of $a_1^2a_2^2s^2N_1^2$, which is not far away from 90°.

For the H_2O^+ ?

Shift of orbital energies

The energy of each electronic level is changed with the angle. The electrons try to occupy the lowest levels as possible, eventually making new structure.



(a) (b)

(a) Walsh MO diagram for AB_2 molecules. The *z*-axis is the C_2 axis in bent AB_2 and the C_∞ axis in linear AB_2. In bent AB_2 the *x*-axis is perpendicular to the plane of the molecule. (b) Walsh MO diagram for HAB molecules

CO_2 : linear at ground state, bent at excited state

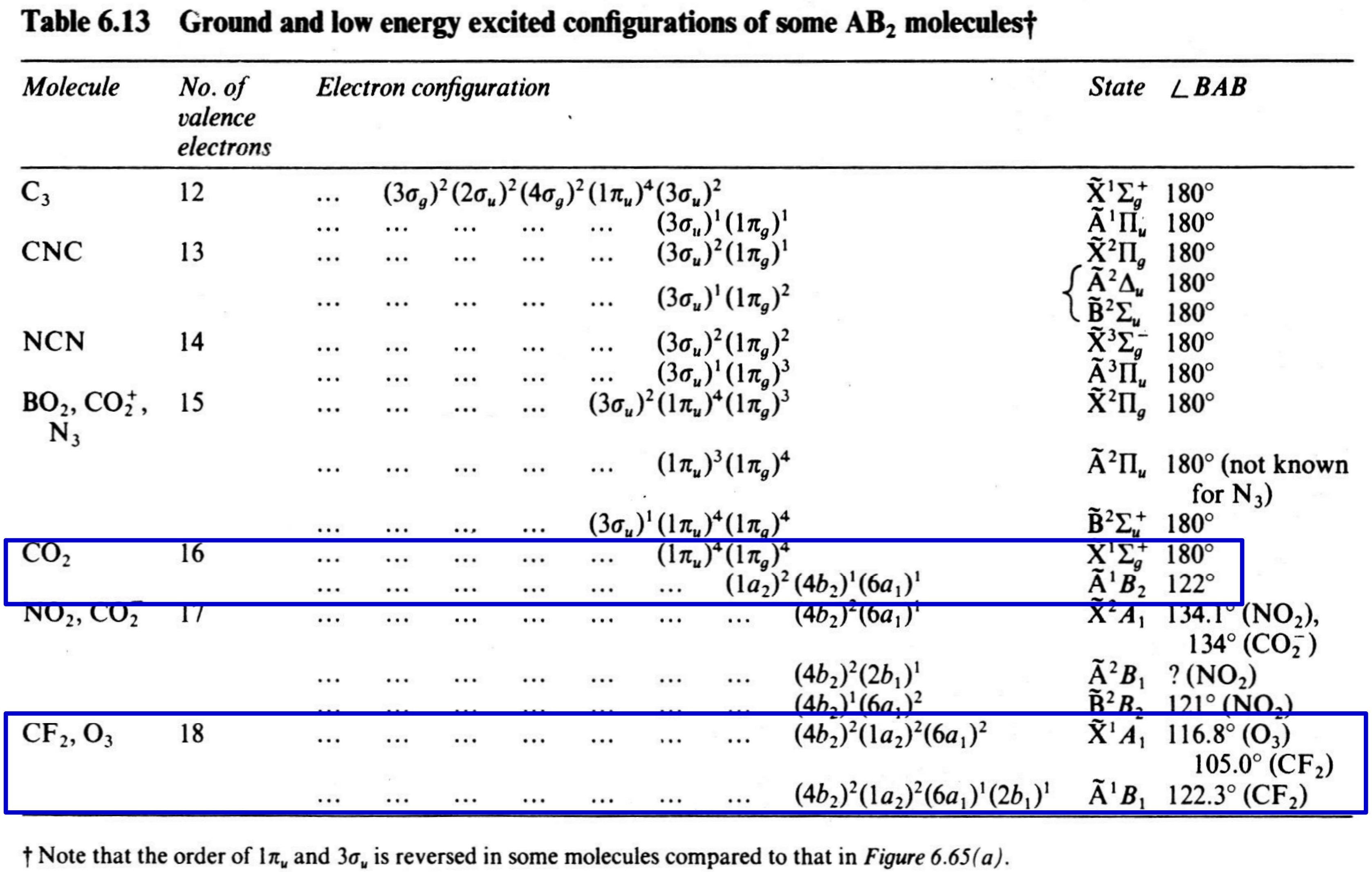


Table 6.13 Ground and low energy excited configurations of some AB_2 molecules†

Molecule	*No. of valence electrons*	*Electron configuration*	*State*	*∠BAB*
C_3	12	… $(3\sigma_g)^2(2\sigma_u)^2(4\sigma_g)^2(1\pi_u)^4(3\sigma_u)^2$	$\tilde{X}\,^1\Sigma_g^+$	180°
		… … … … … $(3\sigma_u)^1(1\pi_g)^1$	$\tilde{A}\,^1\Pi_u$	180°
CNC	13	… … … … … $(3\sigma_u)^2(1\pi_g)^1$	$\tilde{X}\,^2\Pi_g$	180°
		… … … … … $(3\sigma_u)^1(1\pi_g)^2$	$\left\{\begin{matrix}\tilde{A}\,^2\Delta_u \\ \tilde{B}\,^2\Sigma_u\end{matrix}\right.$	180° 180°
NCN	14	… … … … … $(3\sigma_u)^2(1\pi_g)^2$	$\tilde{X}\,^3\Sigma_g^-$	180°
		… … … … … $(3\sigma_u)^1(1\pi_g)^3$	$\tilde{A}\,^3\Pi_u$	180°
BO_2, CO_2^+, N_3	15	… … … … $(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^3$	$\tilde{X}\,^2\Pi_g$	180°
		… … … … … $(1\pi_u)^3(1\pi_g)^4$	$\tilde{A}\,^2\Pi_u$	180° (not known for N_3)
		… … … … $(3\sigma_u)^1(1\pi_u)^4(1\pi_g)^4$	$\tilde{B}\,^2\Sigma_u^+$	180°
CO_2	16	… … … … … $(1\pi_u)^4(1\pi_g)^4$	$\tilde{X}\,^1\Sigma_g^+$	180°
		… … … … … … $(1a_2)^2(4b_2)^1(6a_1)^1$	$\tilde{A}\,^1B_2$	122°
NO_2, CO_2^-	17	… … … … … … … $(4b_2)^2(6a_1)^1$	$\tilde{X}\,^2A_1$	134.1° (NO_2), 134° (CO_2^-)
		… … … … … … … $(4b_2)^2(2b_1)^1$	$\tilde{A}\,^2B_1$	? (NO_2)
		… … … … … … … $(4b_2)^1(6a_1)^2$	$\tilde{B}\,^2B_2$	121° (NO_2)
CF_2, O_3	18	… … … … … … … $(4b_2)^2(1a_2)^2(6a_1)^2$	$\tilde{X}\,^1A_1$	116.8° (O_3) 105.0° (CF_2)
		… … … … … … … $(4b_2)^2(1a_2)^2(6a_1)^1(2b_1)^1$	$\tilde{A}\,^1B_1$	122.3° (CF_2)

† Note that the order of $1\pi_u$ and $3\sigma_u$ is reversed in some molecules compared to that in *Figure 6.65(a)*.

The structure changes upon electronic excitation.

Region of electronic spectrum

Bonding(σ,π), Nonbonding(n), Antibonding electrons (σ*,π*)

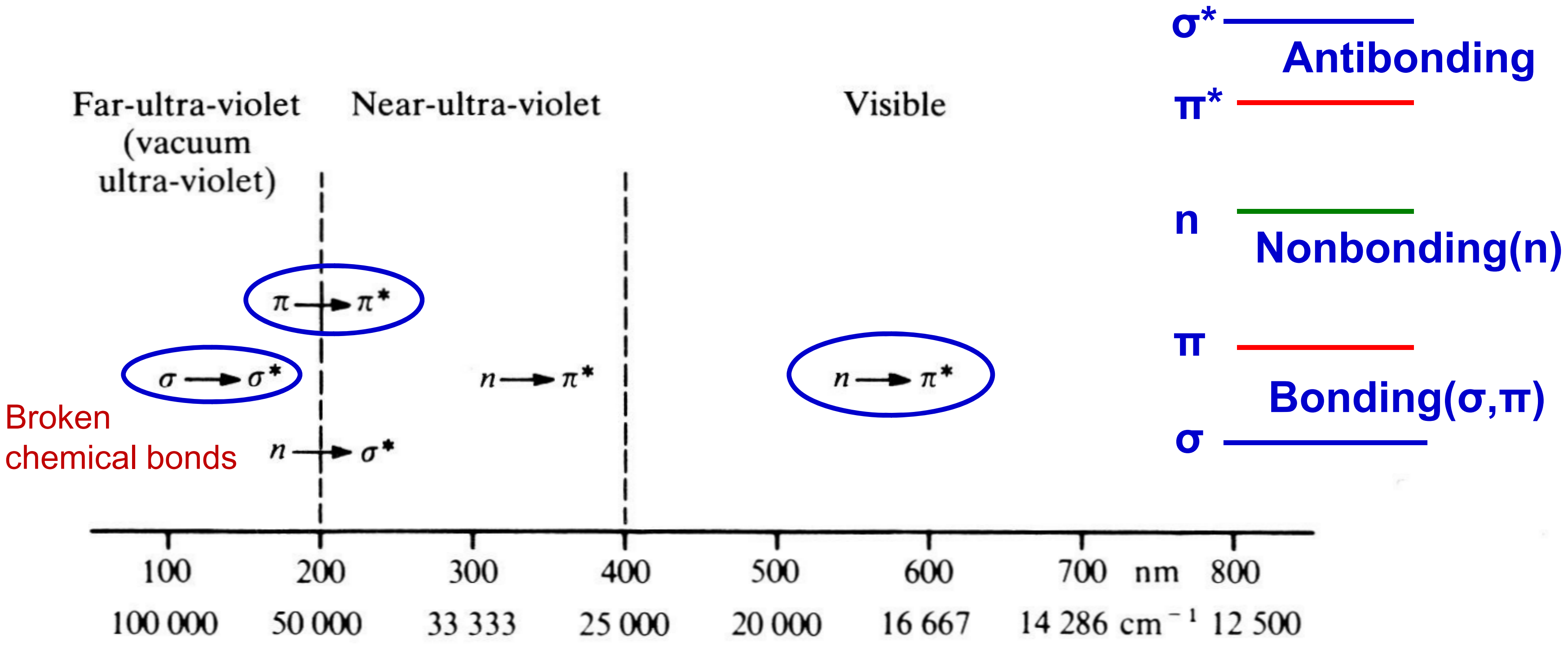


Figure 6.17 The regions of the electronic spectrum and the type of transition which occurs in each.

We can classify the orbitals into bonding, antibonding, and nonbonding.

	$\pi \rightarrow \pi^*$ (strong) (nm)	$n \rightarrow \pi^*$ (weak) (nm)
$>C=C<$	170	—
$-C\equiv C-$	170	—
$>C=O$	166	280
$>C=N-$	190	300
$-N=N-$	?	350
$>C=S$	?	500

Nonbonding electrons

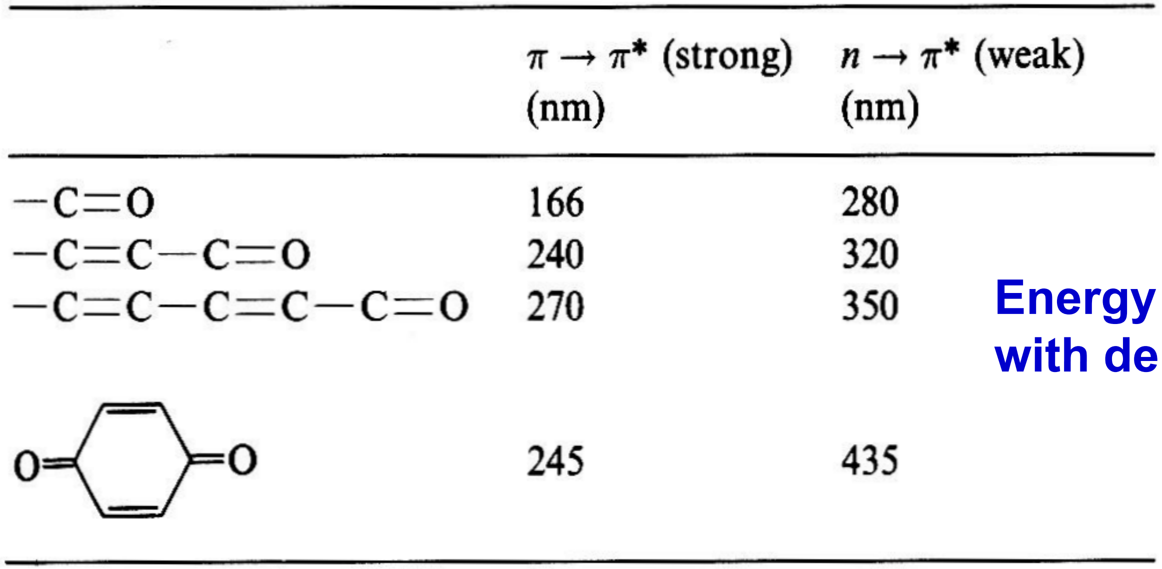
We studied this equation in QC class.

$$E_n = \frac{n^2h^2}{8mL^2}$$

	$\lambda_{\text{max.}}$ (nm)	ε
$-C=C-$	170	16 000
$-C=C-C=C-$	220	21 000
$-C=C-C=C-C=C-$	260	35 000

Energy decreases with delocalization

Quantum Chemistry: Particles in one-dimensional box



	$\pi \rightarrow \pi^*$ (strong) (nm)	$n \rightarrow \pi^*$ (weak) (nm)
$-C=O$	166	280
$-C=C-C=O$	240	320
$-C=C-C=C-C=O$	270	350
	245	435

Energy decreases with delocalization

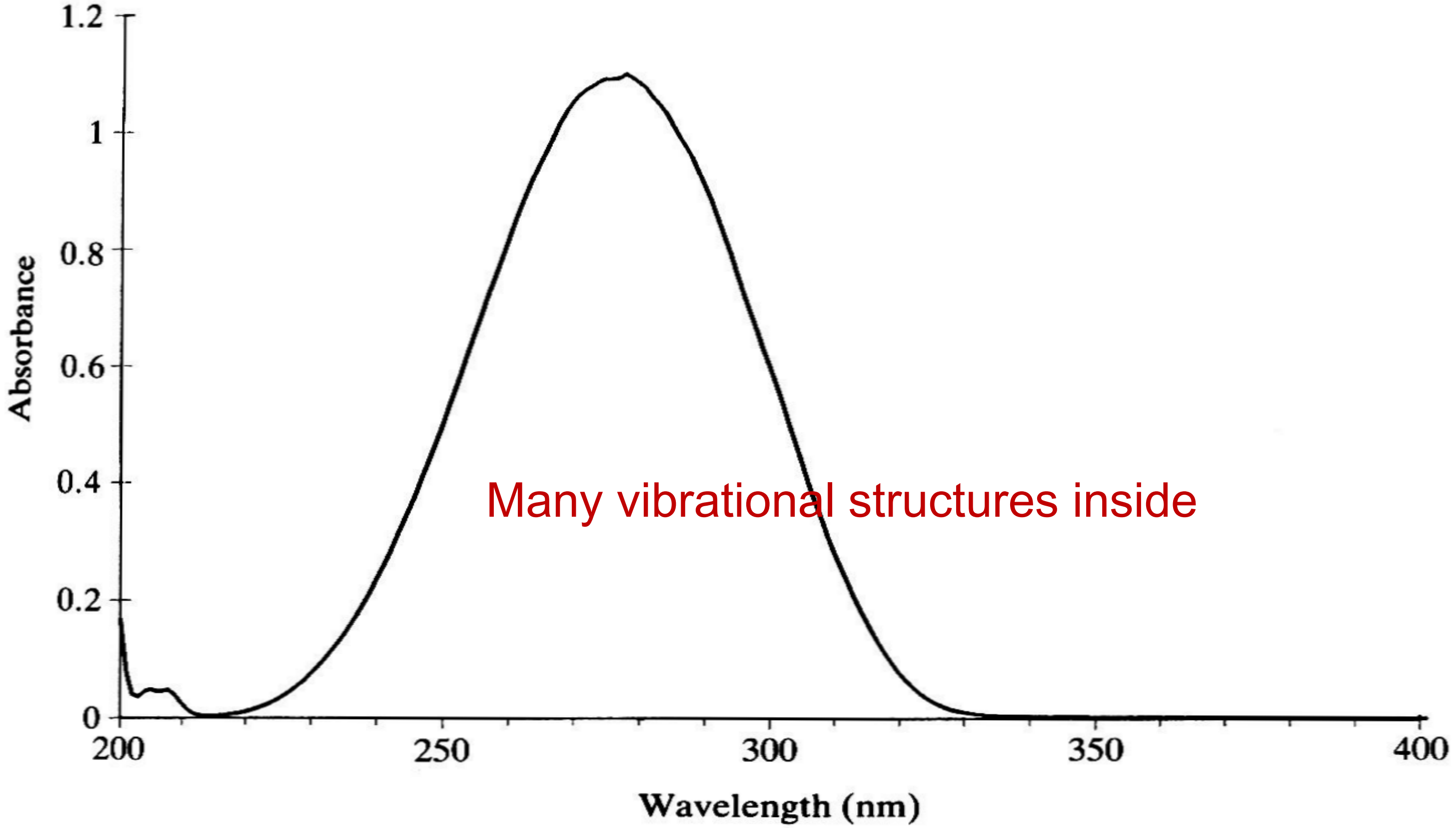
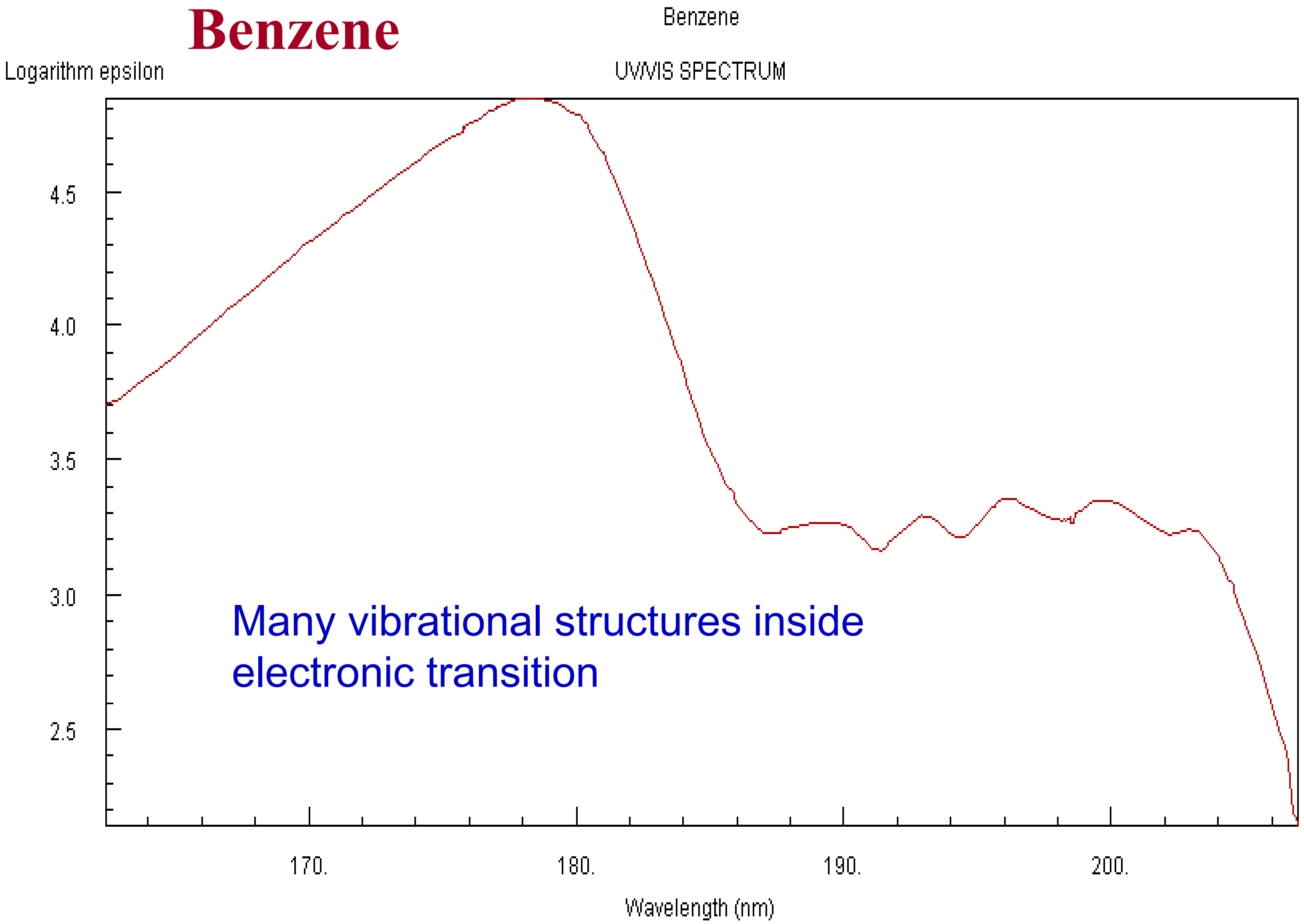


Figure 6.18 The ultra-violet spectrum of propanone.

Benzene



Many vibrational structures inside electronic transition

Benzene

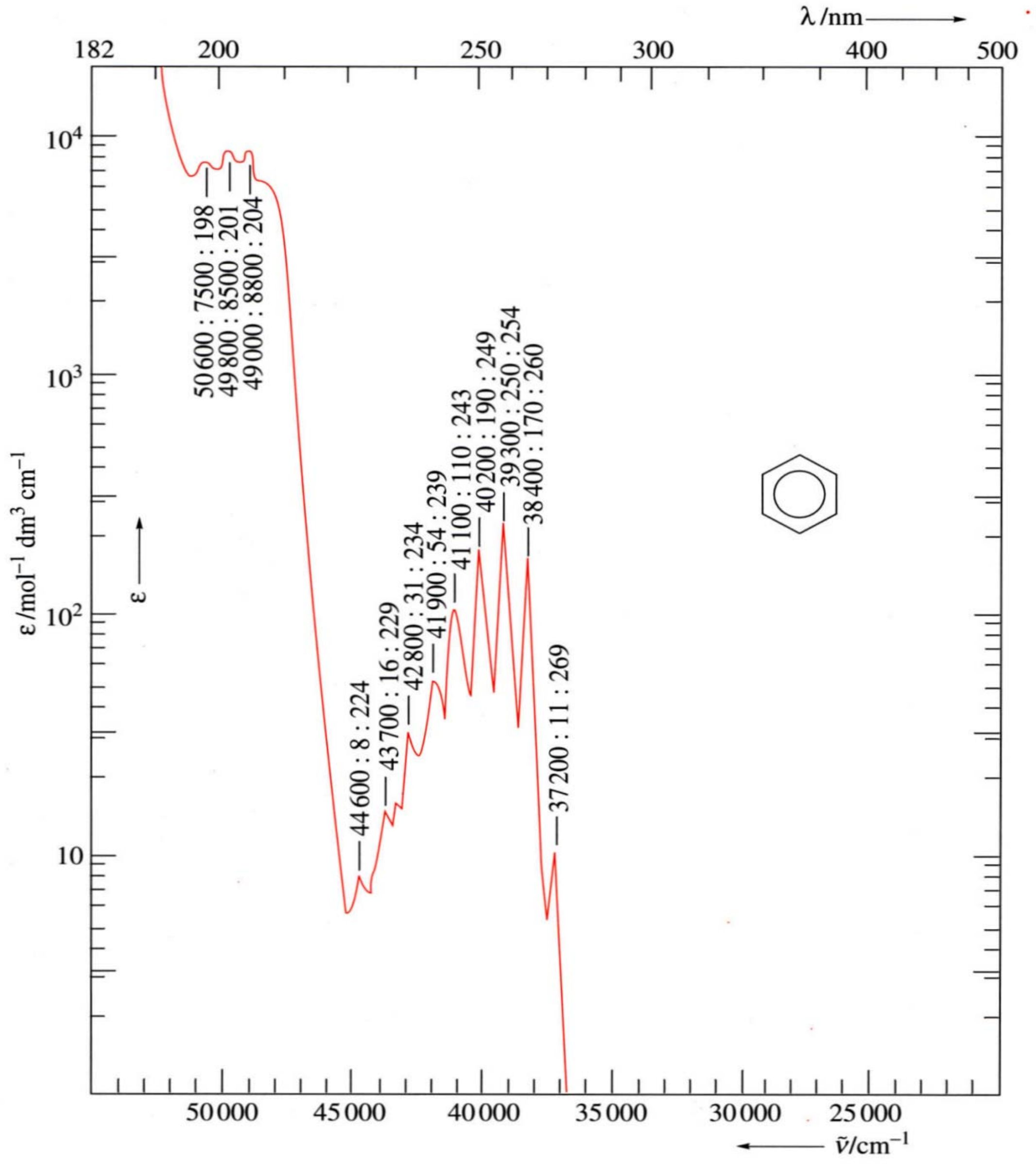


Figure 11.10 Near-ultraviolet absorption spectrum of benzene in solution in hexane (after H.-H. Perkampus and G. Kassebeer, in *UV Atlas of Organic Compounds*, Butterworths, London, 1966, p. D1/1)

Vibronic Spectrum of Benzene

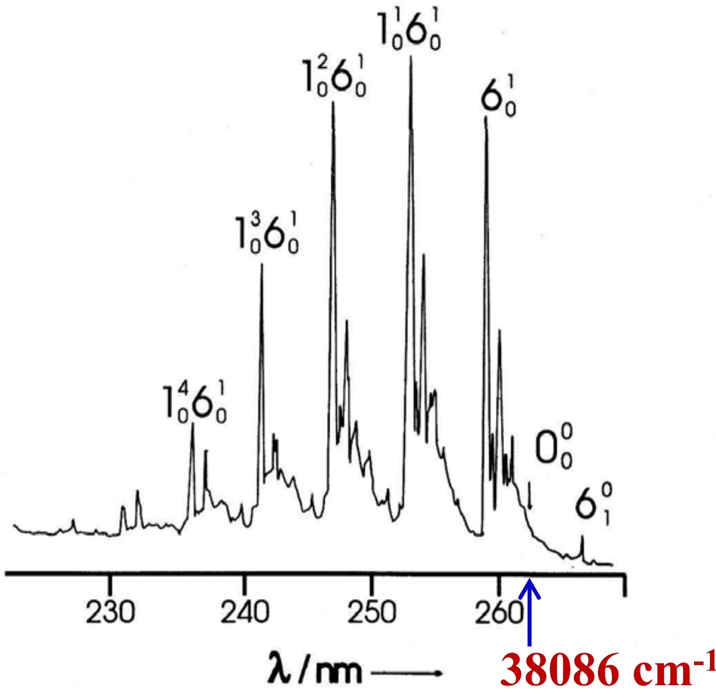
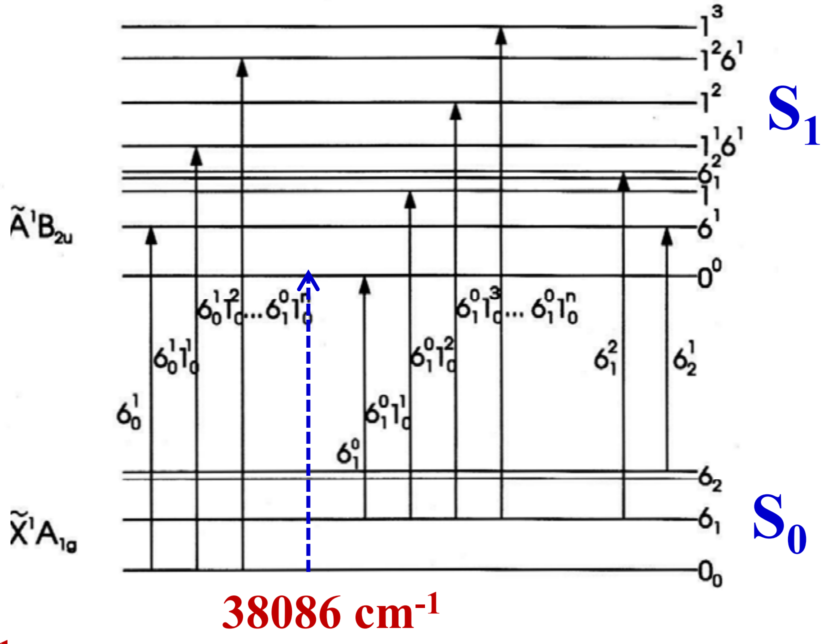
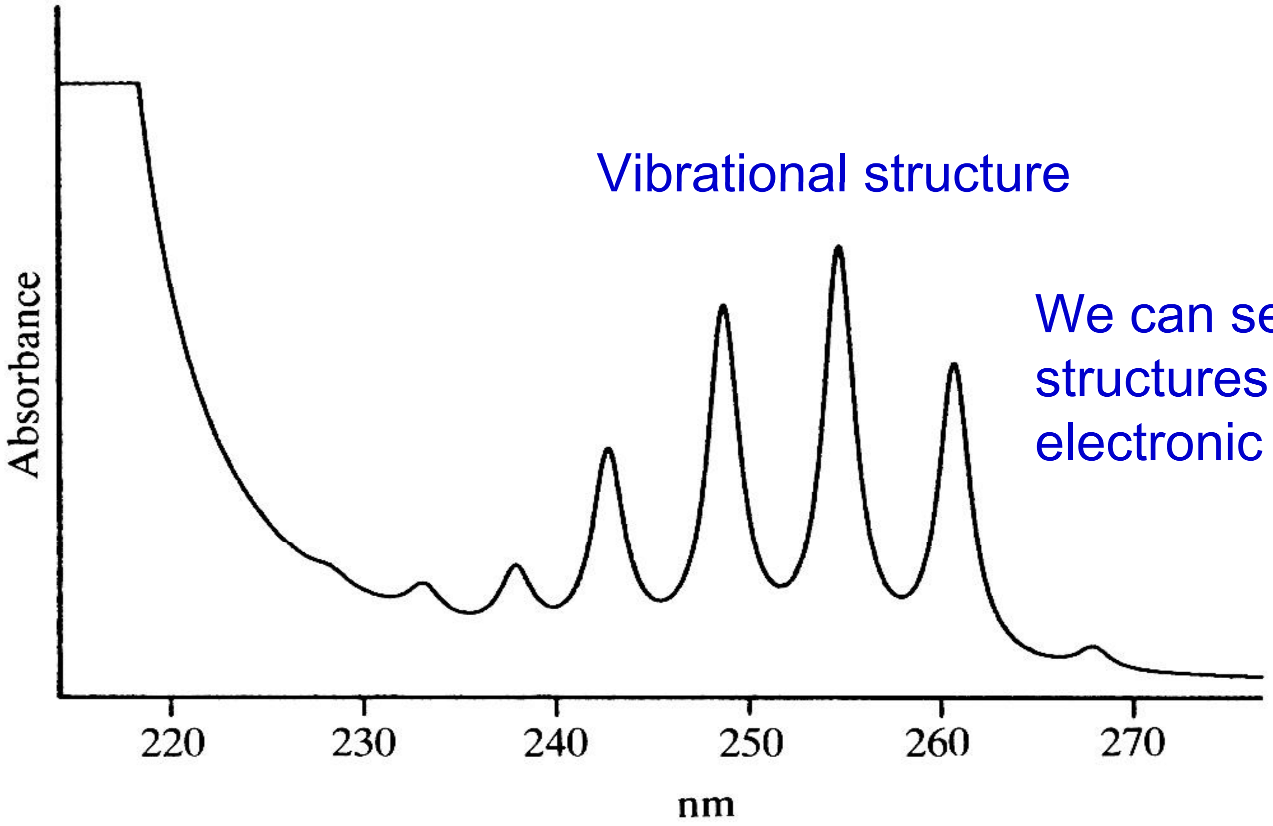


Figure 10.12. The $\tilde{A}\ ^1B_{2u}$–$\tilde{X}\ ^1A_{1g}$ transition of benzene near 260 nm.



Benzene



Vibrational structure

We can see vibrational structures inside the electronic transition.

Figure 6.19 Part of the ultra-violet spectrum of benzene showing vibrational fine structure.

6.5 MOLECULAR PHOTOELECTRON SPECTROSCOPY

6.5.1 Ultra-violet Photoelectron Spectroscopy

1. If a *non-bonding* electron is removed, there is virtually no change in bond strength or length and, as shown in Fig. 6.3(*a*), the intensity of the transition is concentrated almost entirely into the 0,0 line.
2. If an *antibonding* electron is ionized, the bond becomes stronger and hence shorter; this, as shown in Fig. 6.3(*b*), results in transitions to several vibrational states in the ion, and consequently a spectrum showing vibrational fine structure. In this case, too, the potential well for the ion is generally rather deeper and narrower than that of the molecule, and the vibrational frequency increases; this is a consequence of the increase in bond strength or force constant.
3. The removal of a *bonding* electron gives a weaker, longer bond (Fig. 6.4(*c*)), with a spectrum otherwise similar to that of 2 above. Here, however, the decrease in bond strength results in a wider and shallower potential well, with a lower vibrational frequency than that of the neutral molecule.

Energy sequence: bonding < antibonding < nonbonding

Removing electrons from photoelectron spectroscopy

What to expect from removing electrons from the following orbitals?

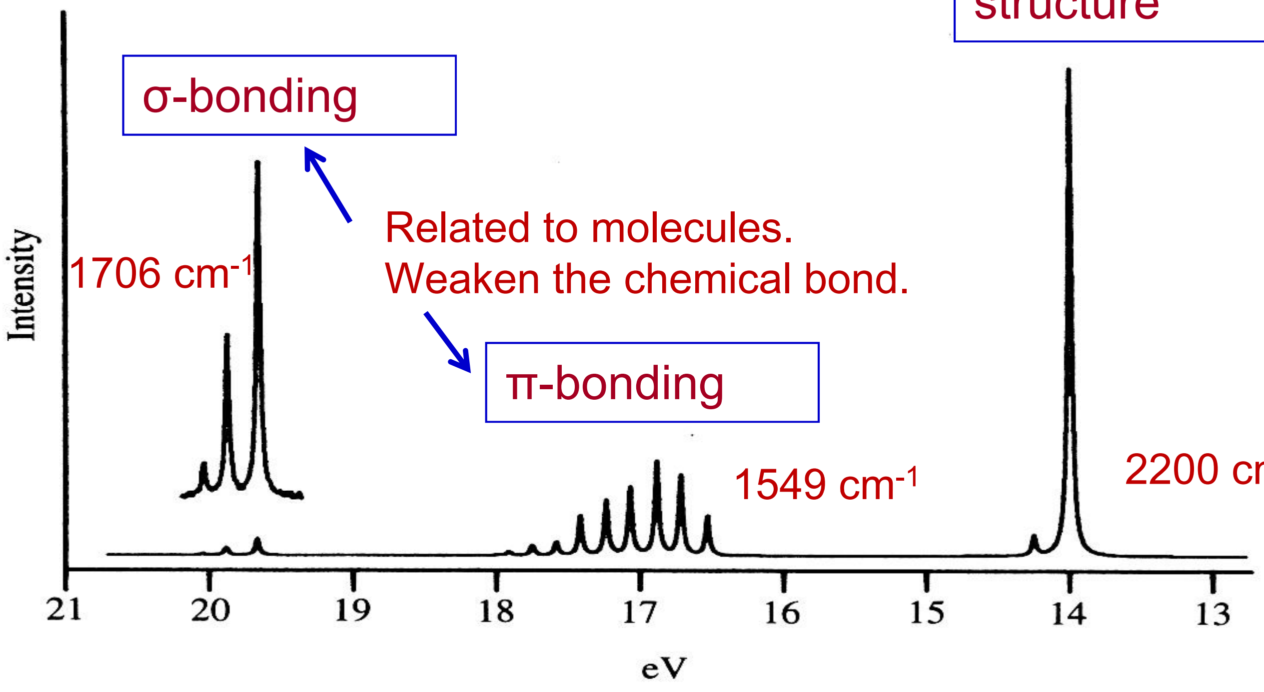
- Nonbonding orbitals : No change in bond strength and length (atomic orbitals)
- Antibonding orbitals : Bonds become stronger and shorter.
- Bonding orbitals : Bonds become weaker and longer.

Bond order = ½ (number of electrons in bonding orbitals
– number of electrons in antibonding orbitals)

Photoelectron spectrum of CO

A total of 10 electrons, 4 from C and 6 from O. Of them, 8 electrons go to molecular orbitals $2\sigma^2\ 2\pi^4\ 2n^2$ (triple bond)

Very similar to UPS, XPS



Nonbonding : no fine structure

σ-bonding

Related to molecules.
Weaken the chemical bond.

π-bonding

1706 cm^{-1}

1549 cm^{-1}

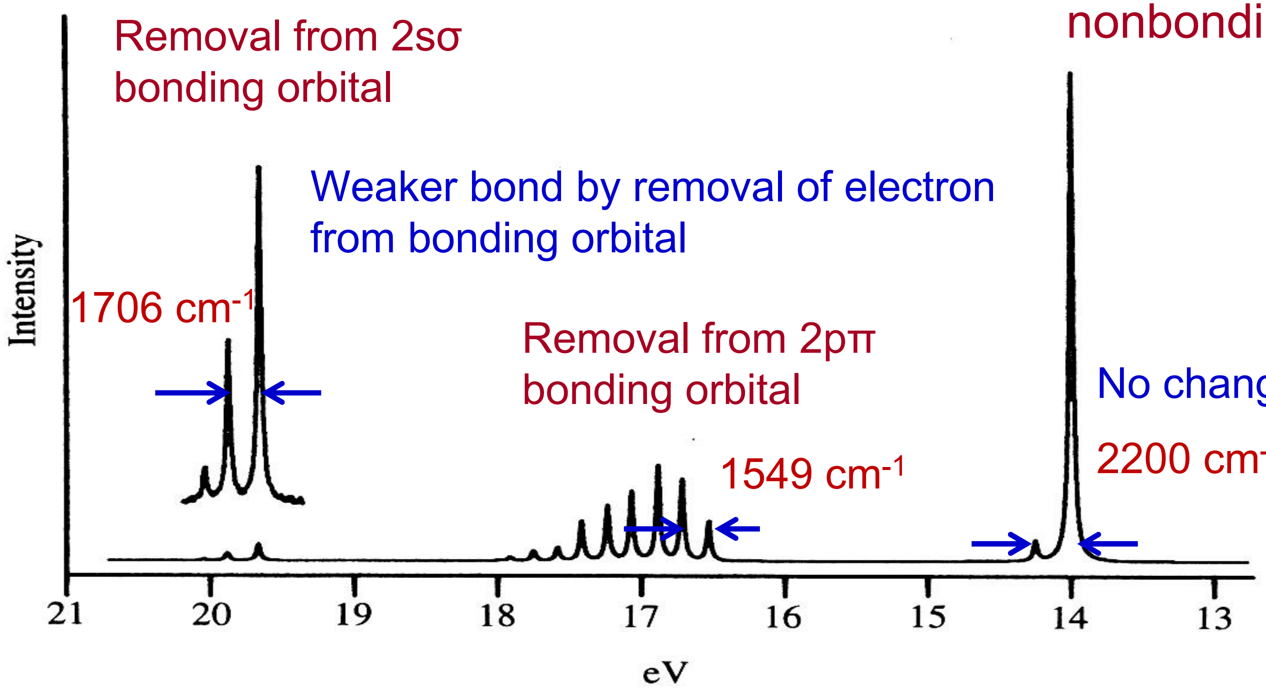
2200 cm^{-1}

Figure 6.21 The photoelectron spectrum of carbon monoxide.

This is a spectrum of CO^+ ion because an electron was removed from CO.

$2\sigma^2\ 2\pi^4\ 2n^2$ (triple bond)

Vibrational frequency of CO : 2157 cm^{-1}



Removal from 2sσ bonding orbital

Weaker bond by removal of electron from bonding orbital

1706 cm^{-1}

Removal from 2pπ bonding orbital

1549 cm^{-1}

Removal from nonbonding

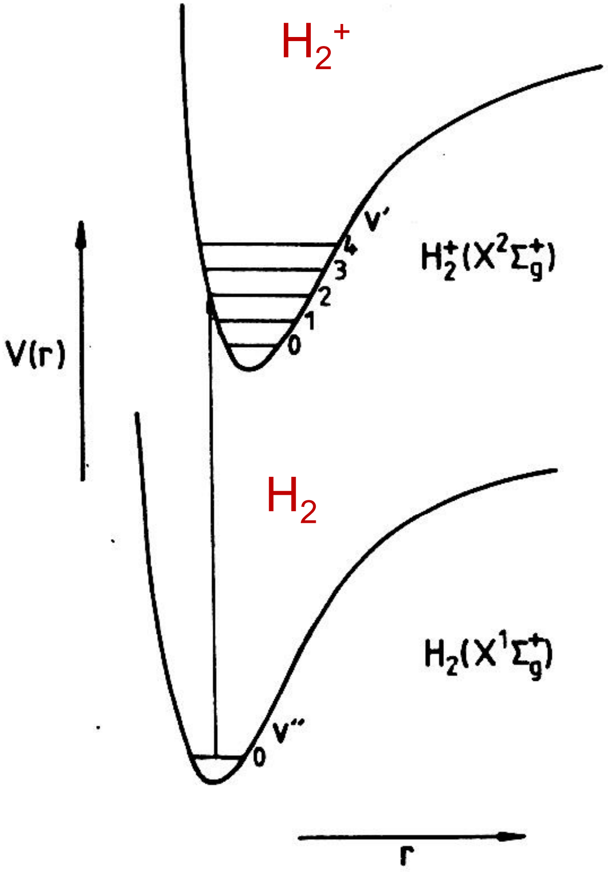
No change from CO

2200 cm^{-1}

Figure 6.21 The photoelectron spectrum of carbon monoxide.

Stronger bonds have higher vibrational frequencies.

Intensity distribution

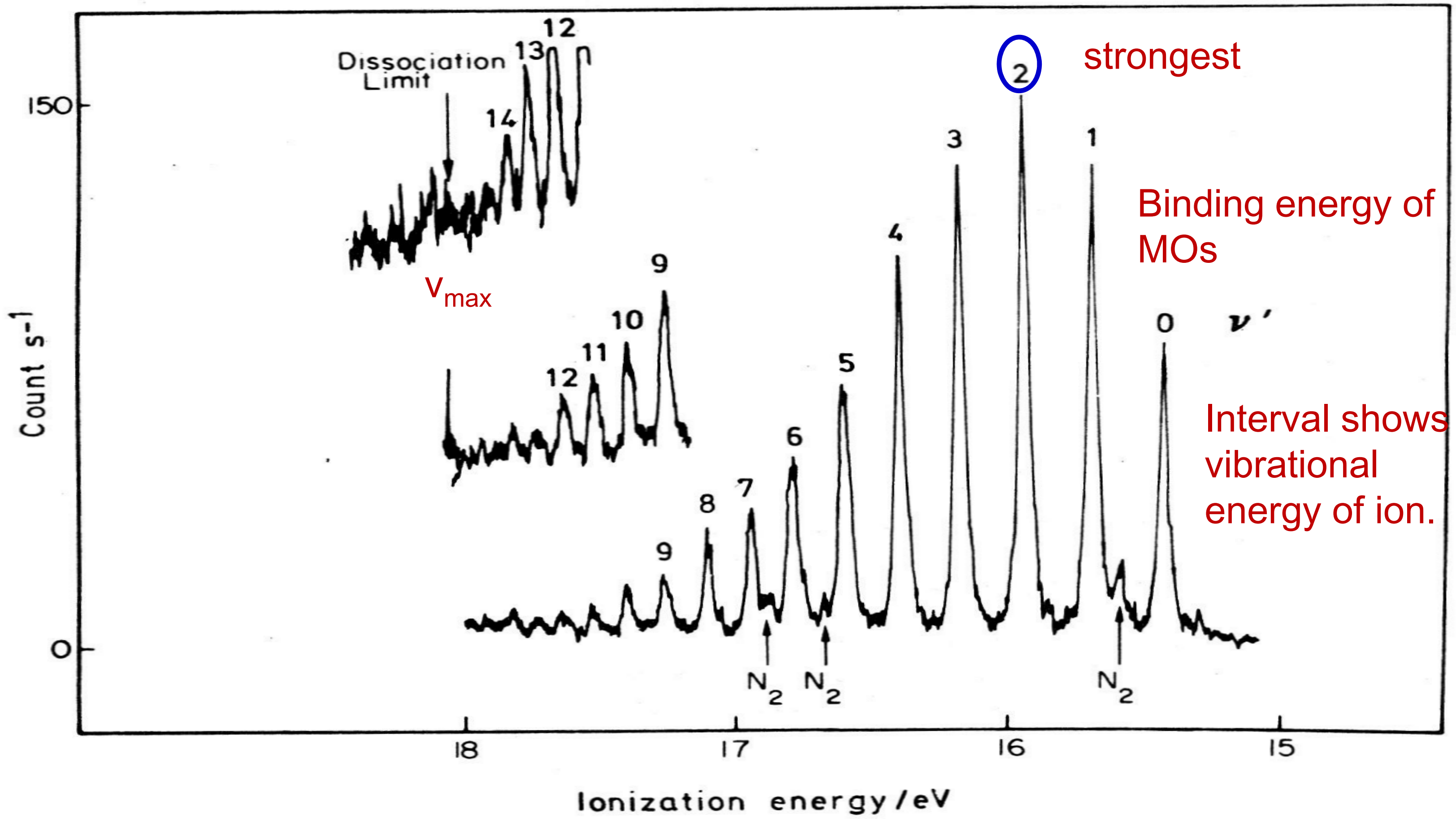


Hydrogen molecular ion can be obtained by removing an electron from hydrogen molecule.

We can see the potential energy of each species in the ground state. In transition from molecule to molecular ions, we can see the transition intensity of vibronic bands by Franck-Condon factor.

The Franck–Condon principle applied to the $H_2^+(X^2\Sigma_g^+) \leftarrow H_2(X^1\Sigma_g^+)$ ionization process

Intensity distribution by Franck-Condon factor



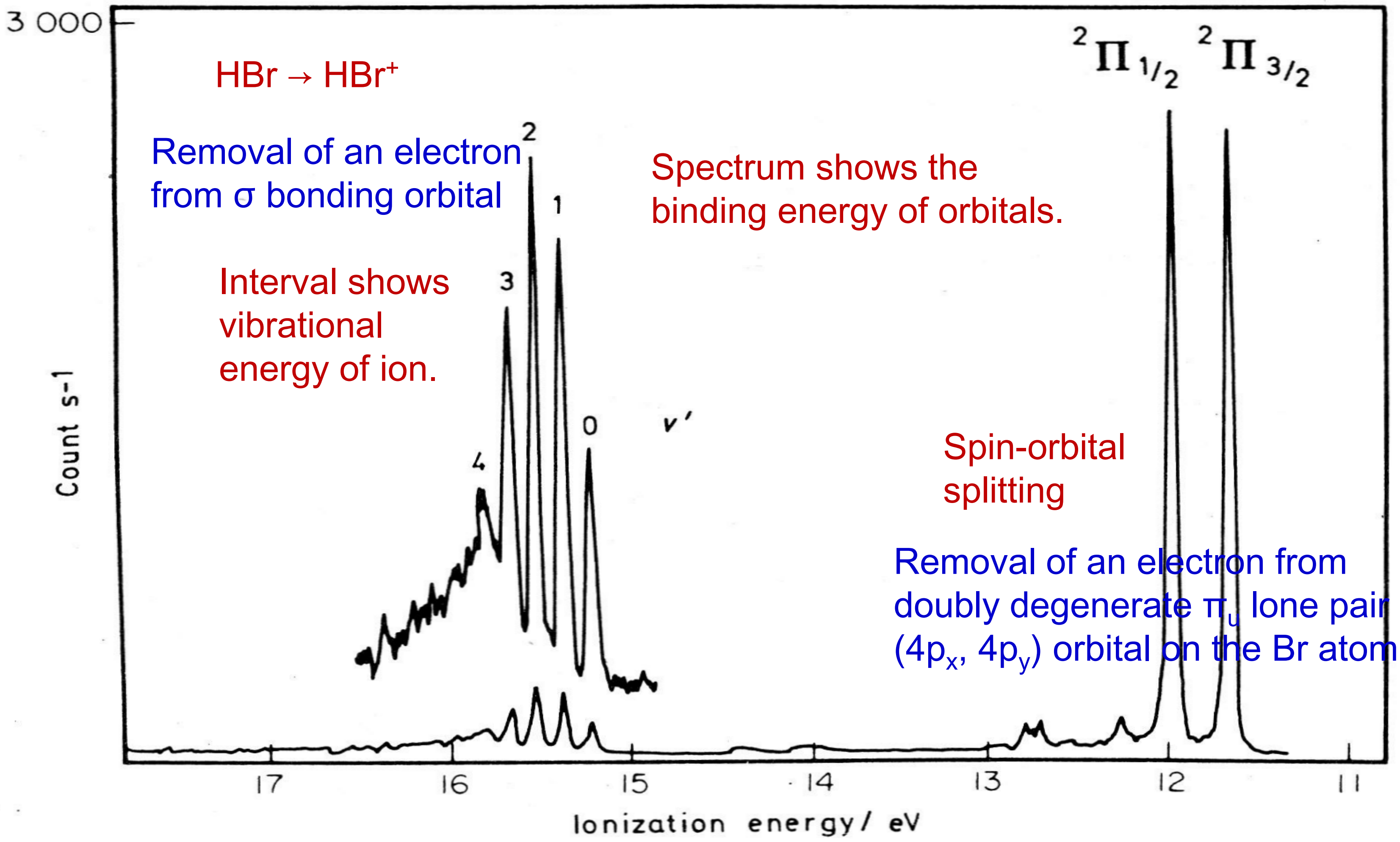
strongest

Binding energy of MOs

v_{max}

Interval shows vibrational energy of ion.

Figure 7.13 The HeI UPS spectrum of the hydrogen molecule (Reproduced, with permission, from Turner, D. W., Baker, C., Baker, A. D. and Brundle, C. R. (1970). *Molecular Photoelectron Spectroscopy*, p. 44, Wiley, London)



HBr → HBr^+

Removal of an electron from σ bonding orbital

Spectrum shows the binding energy of orbitals.

Interval shows vibrational energy of ion.

Spin-orbital splitting

Removal of an electron from doubly degenerate π_u lone pair ($4p_x$, $4p_y$) orbital on the Br atom

Figure 7.20 The HeI UPS spectrum of the HBr molecule (Reproduced, with permission, from Turner, D. W., Baker, C., Baker, A. D. and Brundle, C. R. (1970). *Molecular Photoelectron Spectroscopy*, p. 57, Wiley, London)

$H_2O : (2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2 \rightarrow H_2O^+$

Removal of an electron from

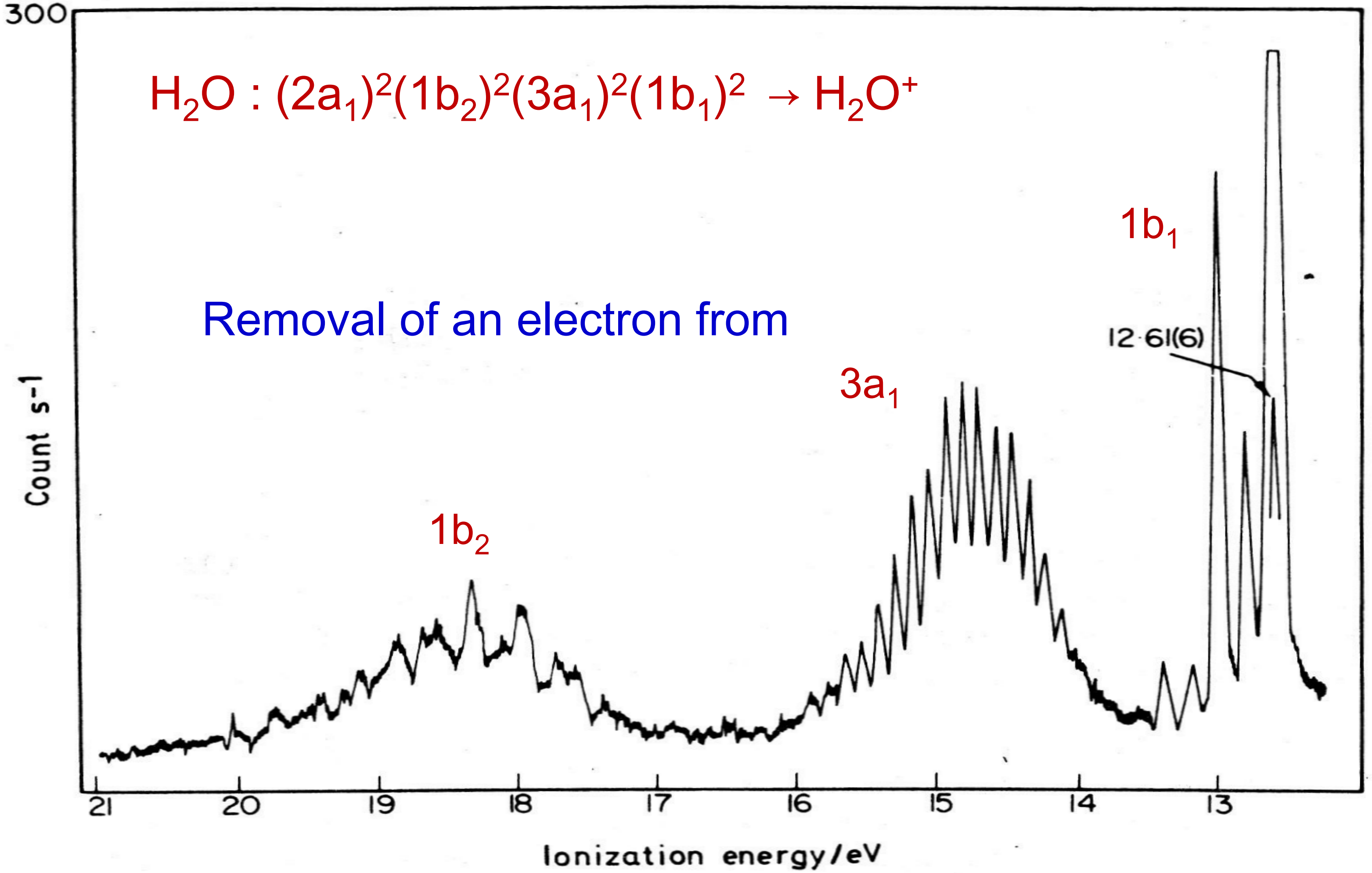


Figure 7.21 The HeI UPS spectrum of the H_2O molecule (Reproduced, with permission, from Turner, D. W., Baker, C., Baker, A. D. and Brundle, C. R. (1970). *Molecular Photoelectron Spectroscopy*, p. 113, Wiley, London)

6.5.2 X-ray Photoelectron Spectroscopy (XPES)

Removal of core electrons

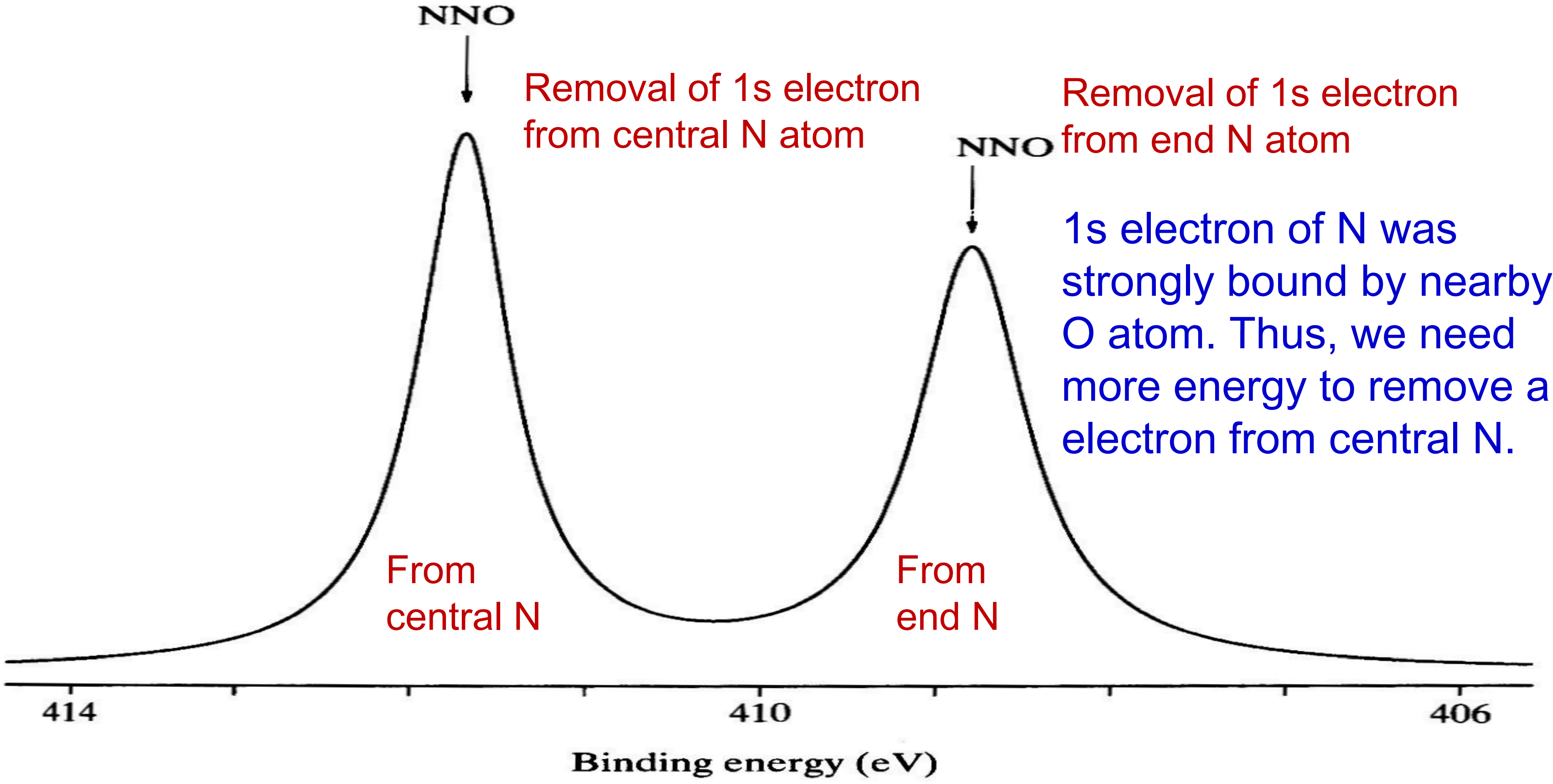


Figure 6.22 The photoelectron spectrum of N_2O.

Removal of 1s electron from central N atom

Removal of 1s electron from end N atom

From central N

From end N

1s electron of N was strongly bound by nearby O atom. Thus, we need more energy to remove an electron from central N.