Electronic Spectroscopy of molecules

Part II: Dissociation and Diatomic term symbols

B.Sc. (H) Chemistry

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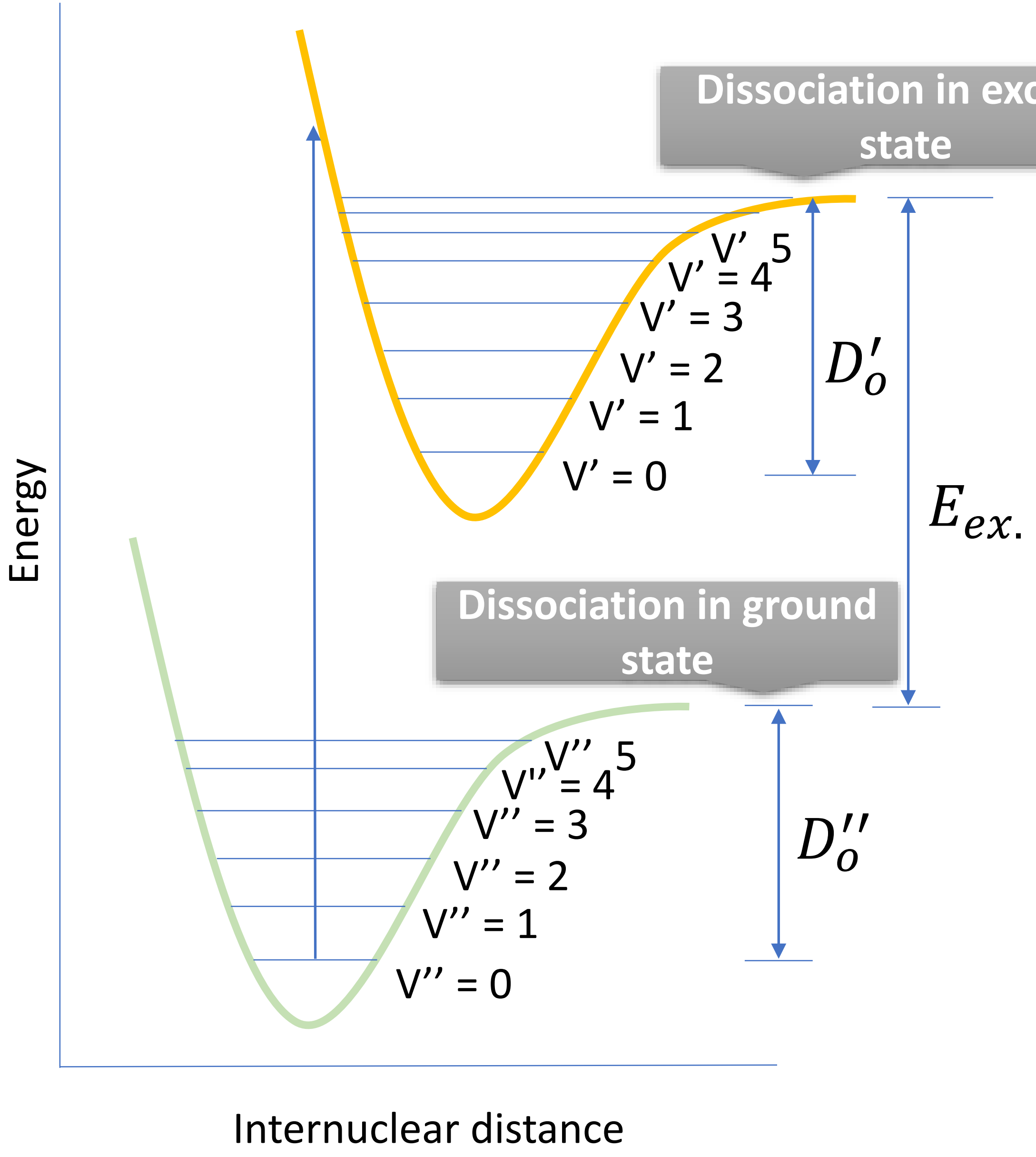
Dissociation Energy and Dissociation Products



Dissociation by excitation into a stable upper state

The total energy of the dissociation products (i.e. atoms) from the upper state is greater by an amount called **E_{ex}.** than that of the products of dissociation in the lower state. *This energy is the **excitation energy** of one (or rarely both) of the atoms produced on dissociation.*

The lower wavenumber limit of this continuum must represent just sufficient energy to cause dissociation and no more (i.e. the dissociation products separate with virtually zero kinetic energy) and thus we have

$$\bar{V}_{continuum\ limit} = D''_0 + E_{ex.}\ cm^{-1}$$

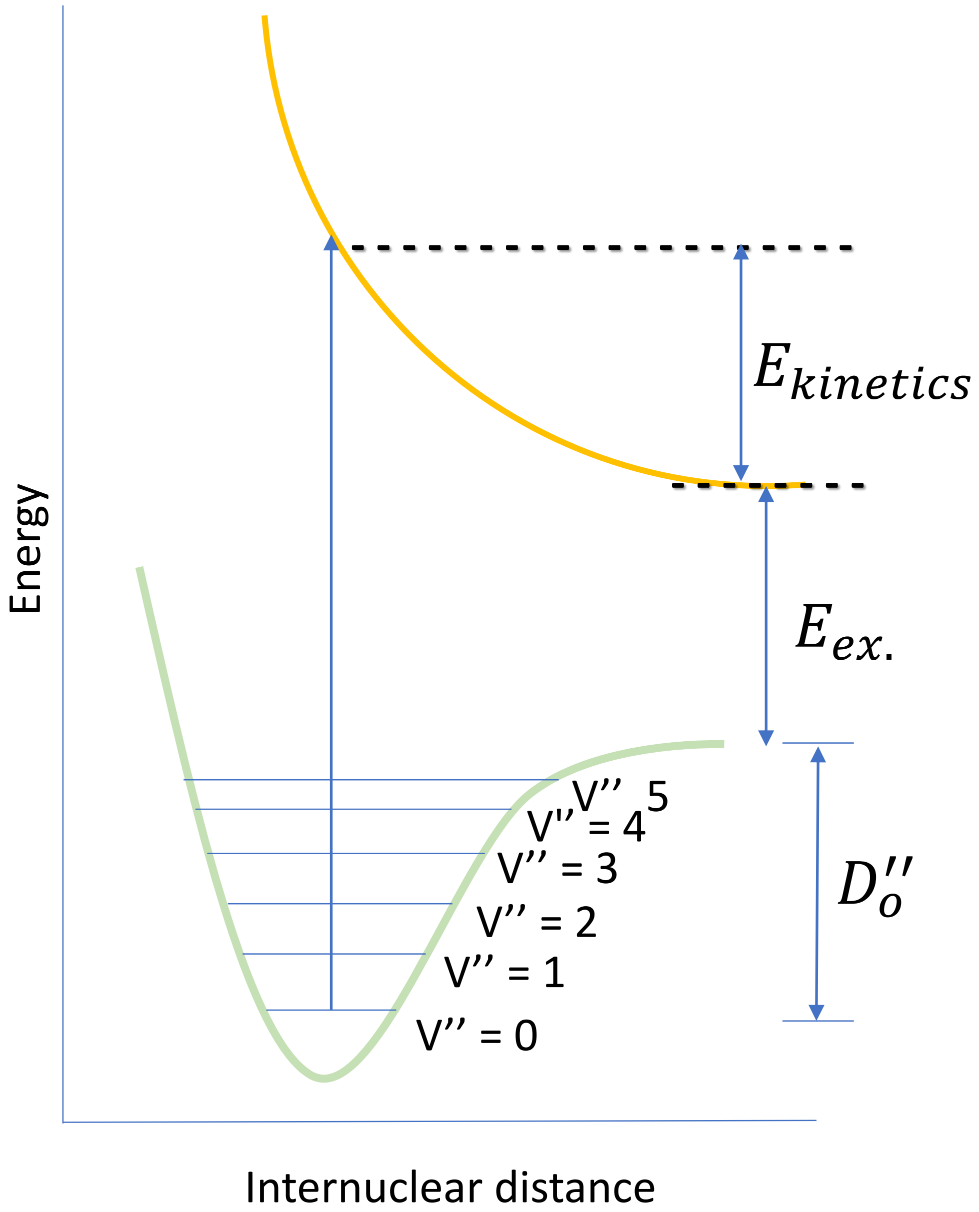
Measurement of D_0'' and $E_{ex.}$

- We can measure D_0'' , the dissociation energy, if we know $E_{ex.}$, the excitation energy of the products.

- The excitation energy of atoms to various electronic states is readily measurable by atomic spectroscopy.

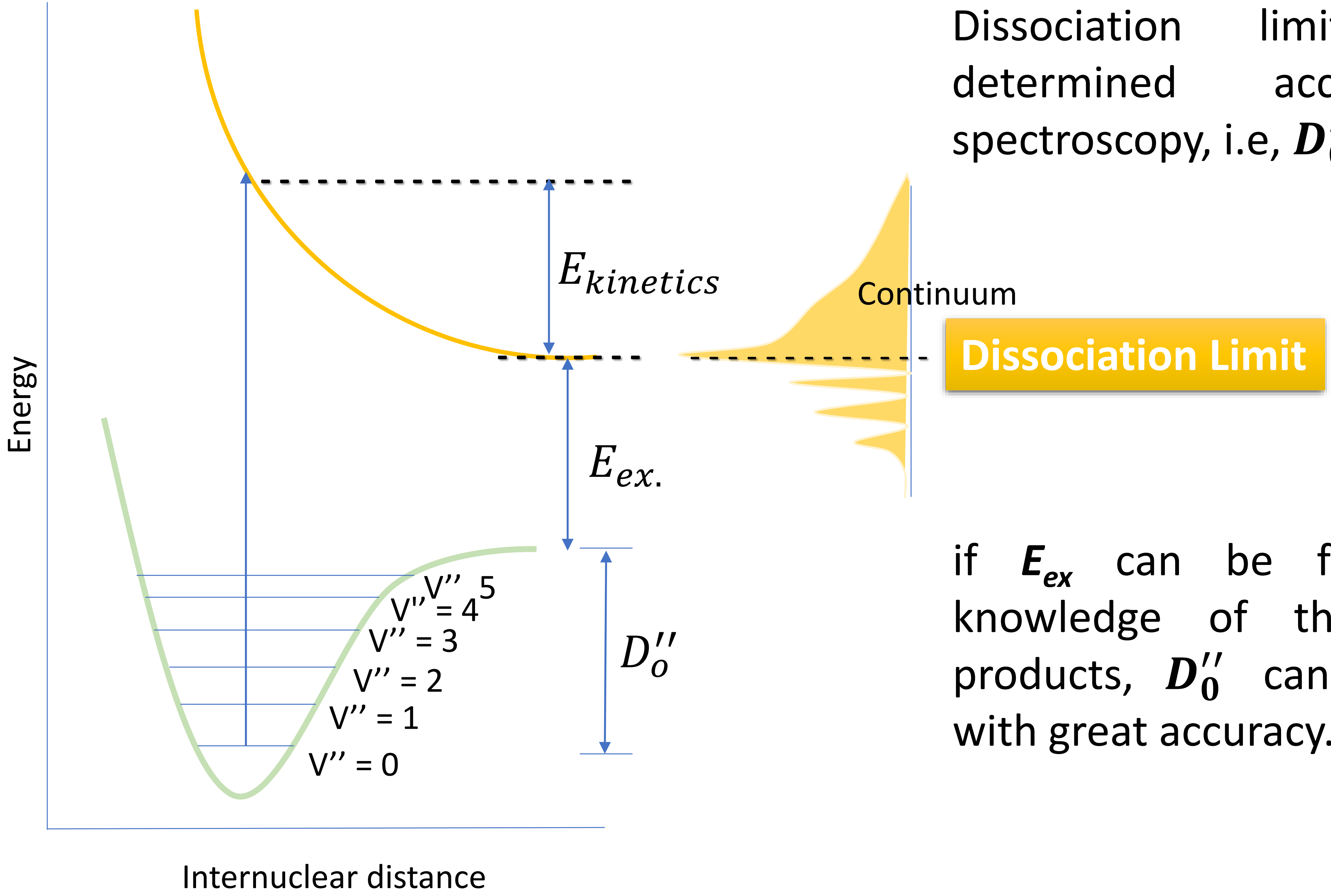
- The thermochemical studies can lead to measurement of approx. value of D_0'' and by spectroscopic methods we can measure the accurate value of $D_0'' + E_{ex}$, we can measure approx. value of $E_{ex.}$

Dissociation by excitation into a unstable upper state/continuous upper state



In this case, the upper electronic state is unstable: there is no minimum in the energy curve and, as soon as a molecule is raised to this state by excitation, the molecule dissociates into products with total excitation energy $\boldsymbol{E_{ex}}$ **.**

The products fly apart with kinetic energy $E_{kinetic}$ which represents (as shown on the figure) the excess energy in the final state above that needed just to dissociate the molecule. Since $E_{kinetic}$ not quantized the whole spectrum for this system will exhibit a continuum, the lower limit of which (if observable) will be precisely the energy $\boldsymbol{D''_0} + \boldsymbol{E_{ex}}$. As before, if $\boldsymbol{E_{ex}}$ can be found from a knowledge of the dissociation products, $\boldsymbol{D''_0}$ can be measured with great accuracy.



Dissociation limit can be determined accurately by spectroscopy, i.e, $\boldsymbol{D_0''}$ + $\boldsymbol{E_{ex.}}$

if $\boldsymbol{E_{ex}}$ can be found from a knowledge of the dissociation products, $\boldsymbol{D_0''}$ can be measured with great accuracy.

How to calculate when continua doesn't appear in spectra???

It is possible to derive a value for the dissociation energy by noting how the vibrational lines converge.

We know that, $\varepsilon_v = \left(\mathrm{v} + \frac{1}{2}\right)\bar{\omega}_e - x_e\left(\mathrm{v} + \frac{1}{2}\right)^2 \bar{\omega}_e \quad cm^{-1}$

So the separation between the energy sates will be,

$$\Delta\varepsilon_v = \varepsilon_{v+1} - \varepsilon_v$$

$$= \bar{\omega}_e\{1 - 2x_e(v+1)\} \quad cm^{-1}$$

As the value of v increases, $\Delta\varepsilon_v$ tends to be zero, i.e, $\Delta\varepsilon_v \rightarrow 0$

Thus the maximum value of ***v*** is given by ***v**_{max}*

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

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

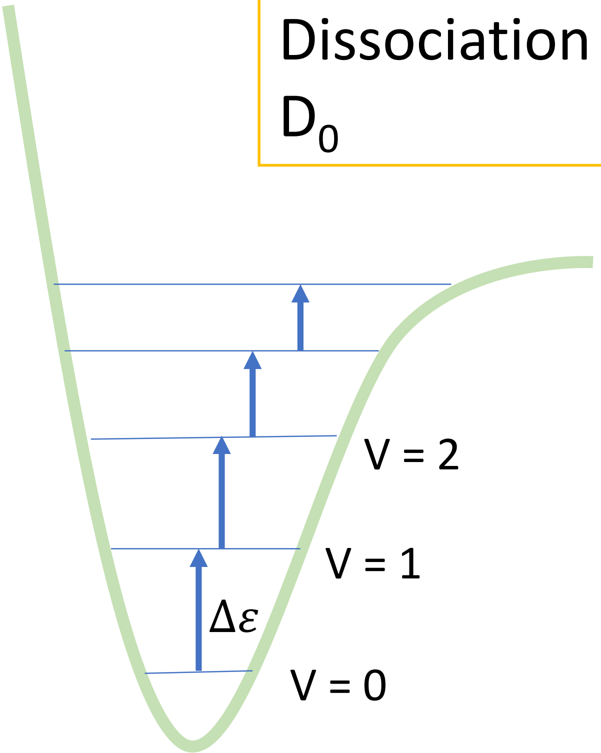
So, $v_{max.} = 50$

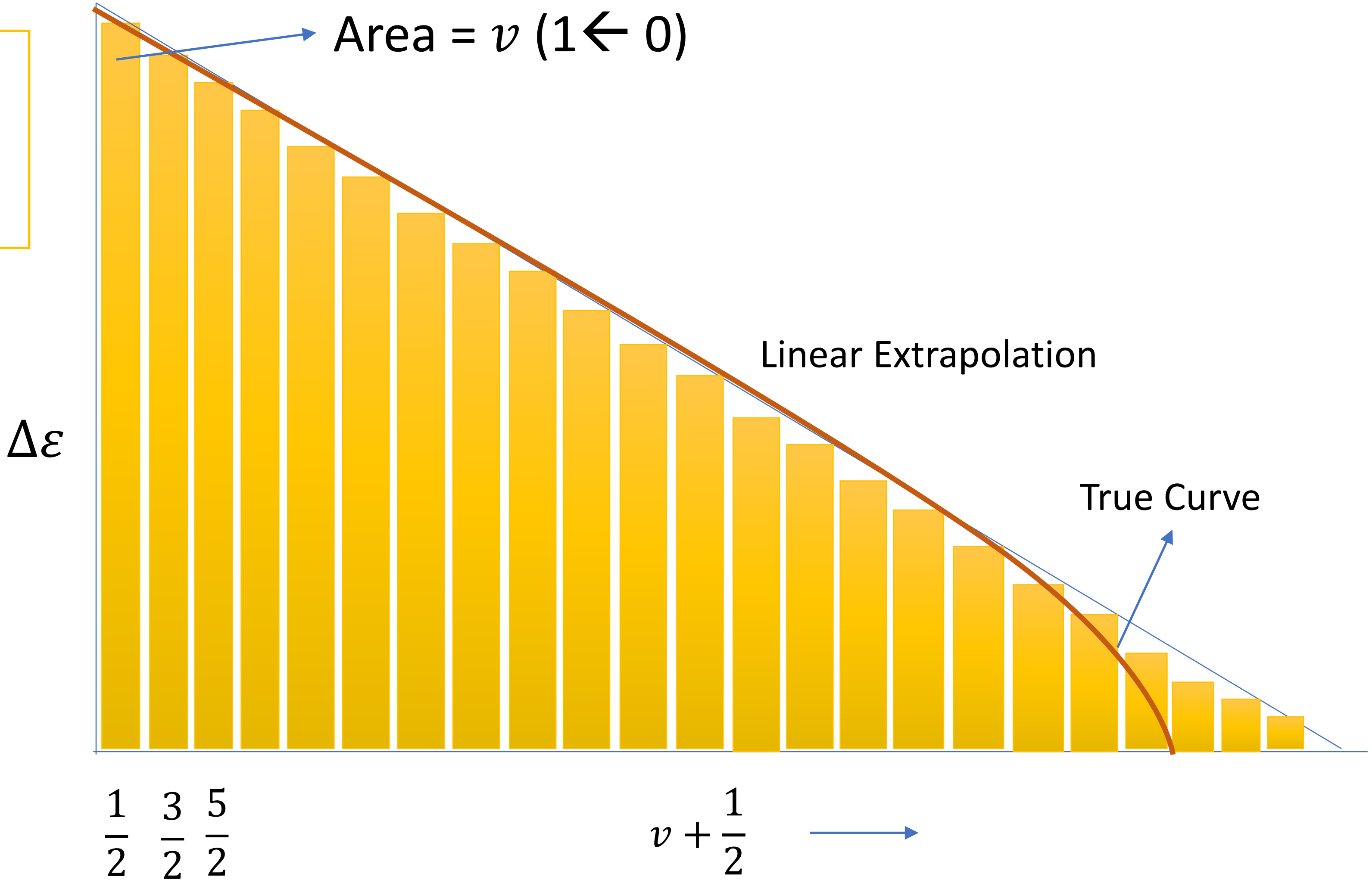
We recall that the anharmonicity constant, x_e is of the order of 10^{-2} hence, $V_{max.}$ is about 50.

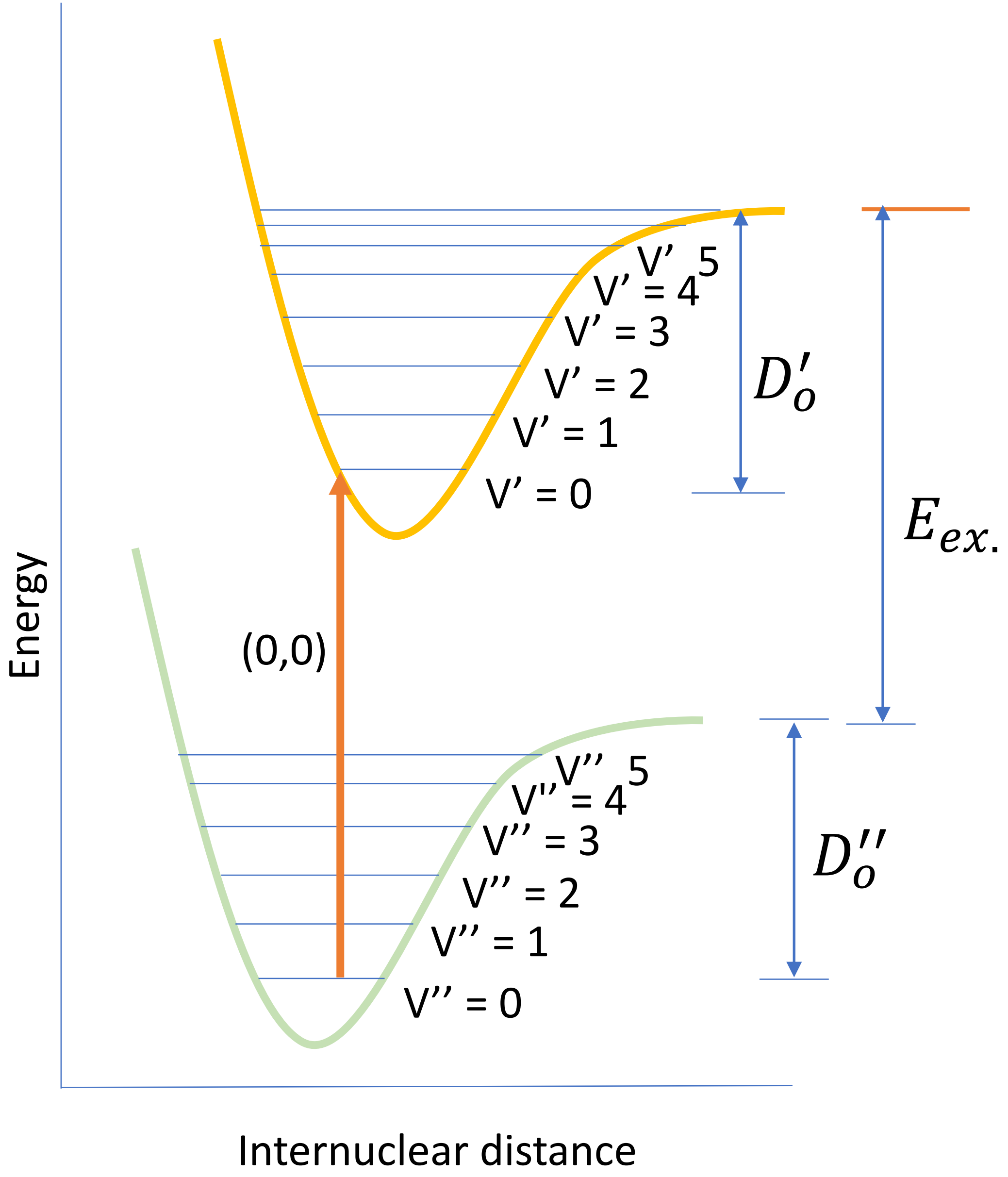
Birge–Sponer plot- Calculation D_o

When several vibrational transitions are detectable, a graphical technique called a **Birge–Sponer** plot may be used to determine the dissociation energy, D_0, of the bond. The basis of the Birge–Sponer plot is that the sum of successive intervals $\Delta\varepsilon$ from the zero-point level to the dissociation limit is the dissociation energy.

Sum of Area = Dissociation Energy, D_0







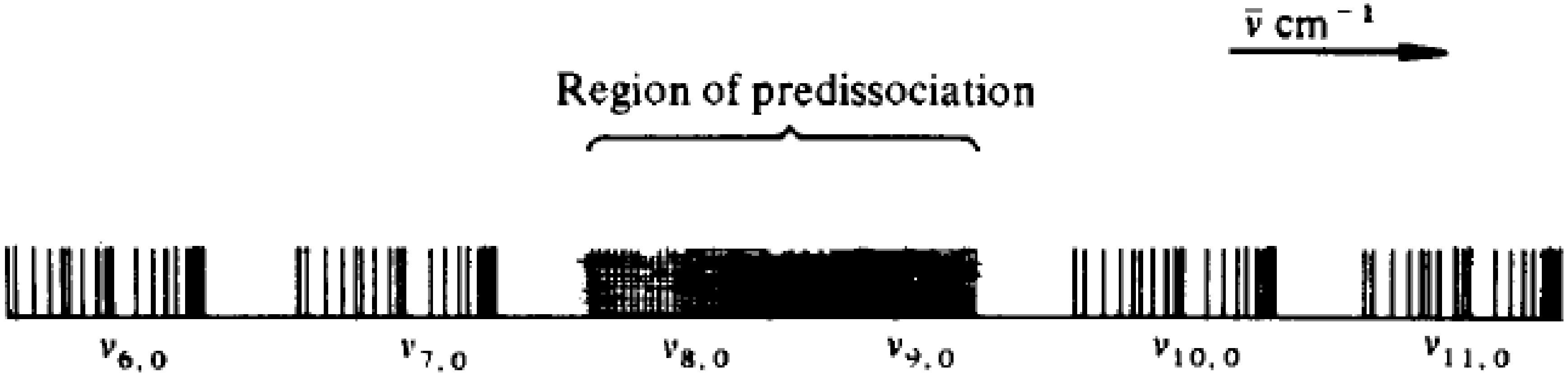
- In absorption spectra it is normally the series of lines originating at v''= 0 which is observed. Thus the convergence of the levels in the upper state and hence the dissociation energy of that state is normally found.

- If we know $E_{ex.}$ (from atomic spectroscopy) and D_0' (from Birge-Sponer extrapolation), and if we can measure the energy of the (0,0) transition either directly or by calculation from the observed energy levels, we have:

D_o''= energy of (0,0) + D_o' $-$ $E_{ex.}$ cm^{-1}

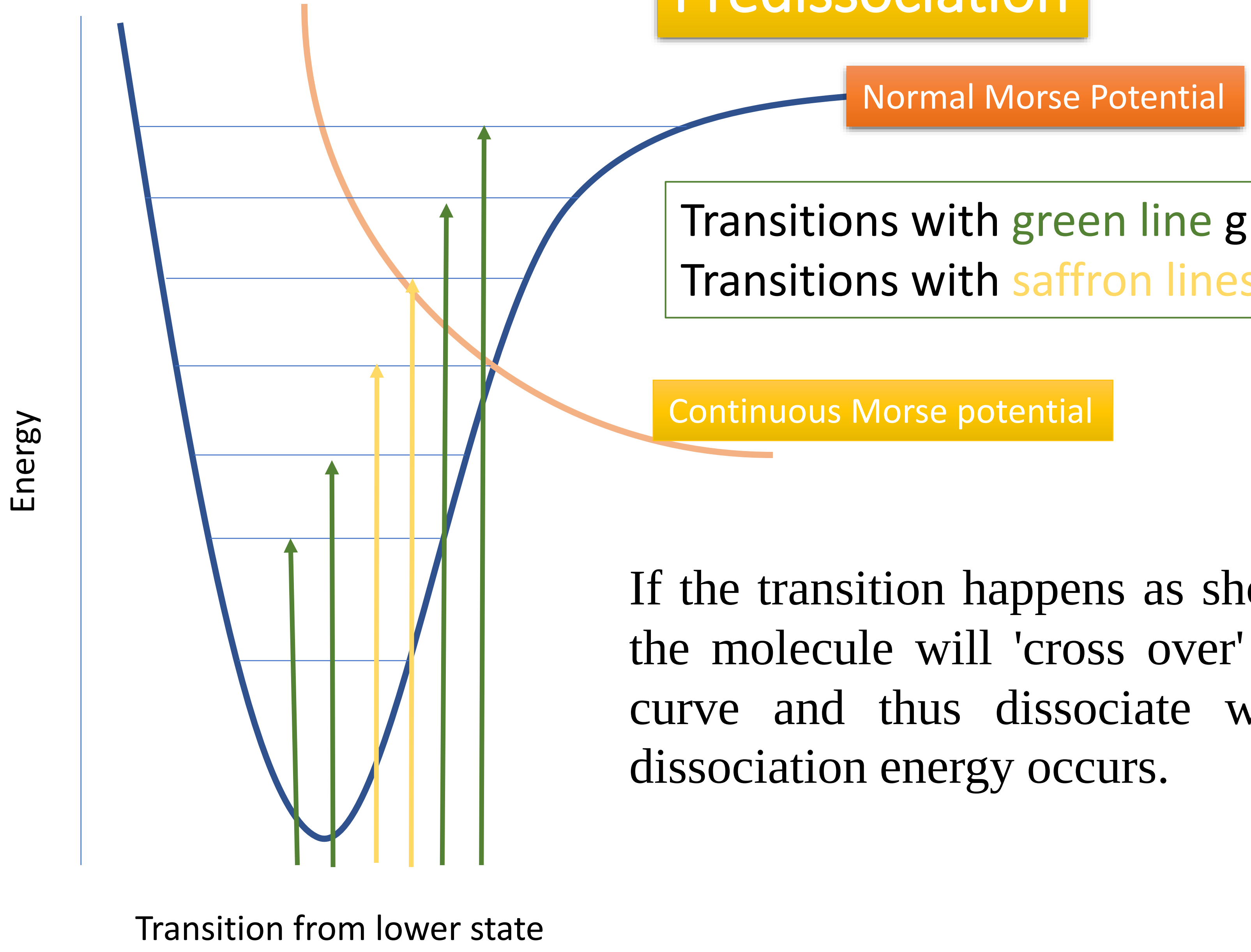
Predissociation

A continuum at high wavenumber would correspond to ordinary but the central continuum, occurring at energies well below the true dissociation limit, is referred to as predissociation.



Predissociation can arise when the Morse curves of a particular molecule in two different excited states intersect. One of the excited states is stable, since it has a minimum in the curve, and the other is continuous.

Predissociation



Transitions with green line give normal spectral line
Transitions with saffron lines give predissociation case

If the transition happens as shown with saffron then the molecule will 'cross over' on to the continuous curve and thus dissociate without achieving the dissociation energy occurs.

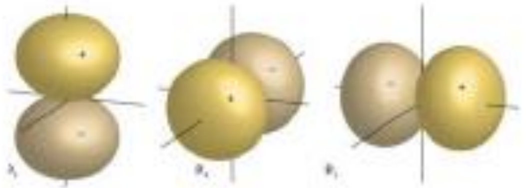
Diatomic Molecules

Diatomic Term Symbols:

Classify according to angular momentum around the internuclear axis, λ.

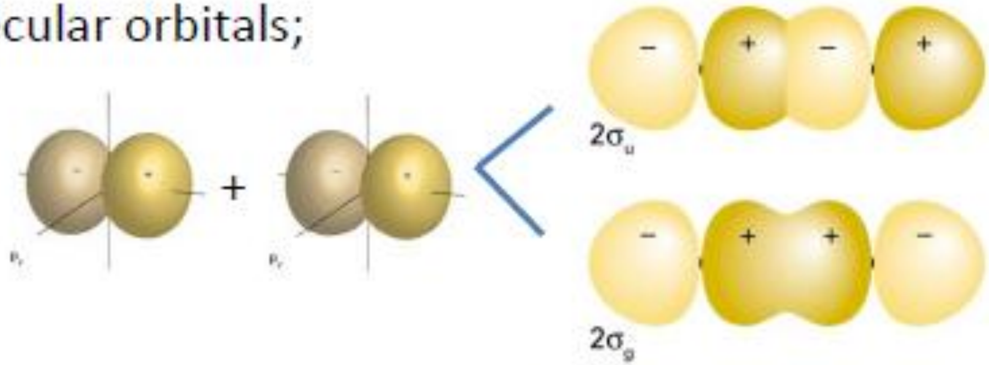
λ is analogous to m_l in atoms:

e.g., a *p* orbital has $l = 1$, $m_l = 0, \pm 1$

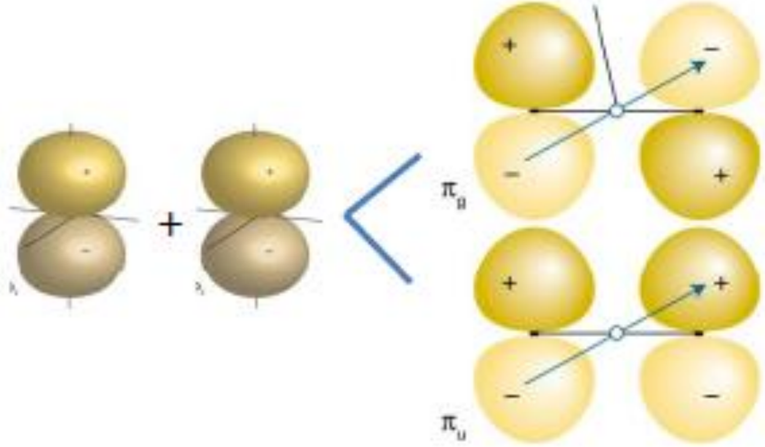


Two p-orbital systems yield σ and π molecular orbitals;

p_z (m_l=0) combine to yield σ, σ^* (λ=0)

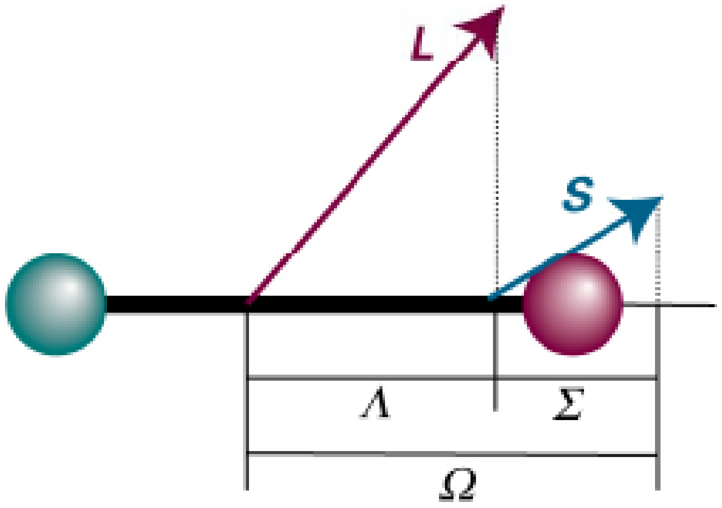


$p_{x,y}$ (m_l= ±1) combine to yield π, π^* (λ=±1)



Electronic terms are classified according to their overall angular momentum on the internuclear axis, Λ:

$$\Lambda = \sum_i \lambda_i = \lambda_1 + \lambda_2 + \lambda_3 + \ldots$$



By analogy with atoms we use term symbols:

“Spin multiplicity”= $2S+1$
(S is the total spin quantum number for the molecule)

$$^{2}\Pi_{3/2}$$

Gives Λ, according to:

Σ for $\Lambda = 0$
Π for $\Lambda = \pm 1$
Δ for $\Lambda = \pm 2$

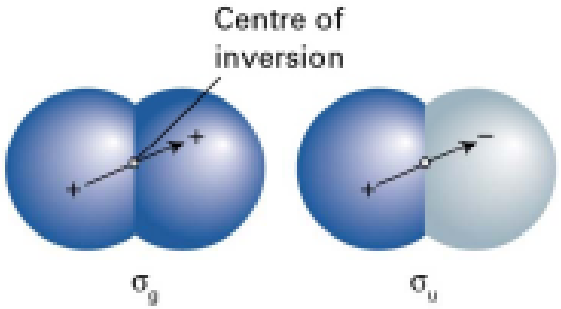
Spin-orbit levels
$\Omega = |\Lambda + \Sigma|$

Projection of S on internuclear axis

For homonuclear diatomics (or symmetric linear molecules, e.g., CO_2) it is convenient to label molecular orbitals and terms according to symmetry (g,u) with respect to inversion through the centre of symmetry.

Ungerade: u Anti-symmetric

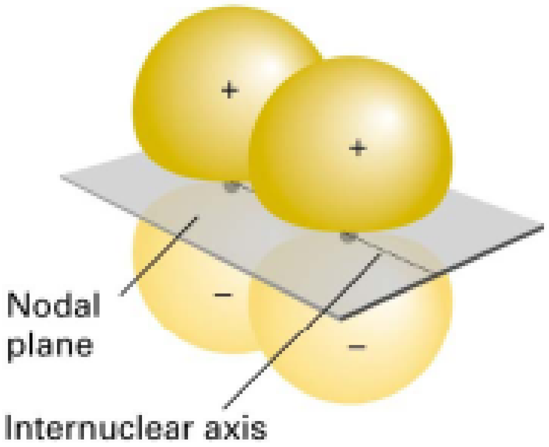
Gerade: g symmetric

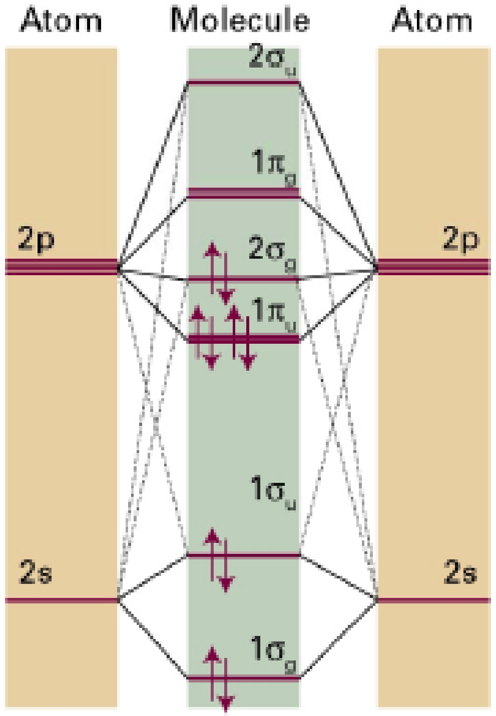


n.b.:

$$g \otimes g = g$$
$$u \otimes u = g$$
$$g \otimes u = u \otimes g = u$$

For Sigma terms we denote the symmetry (+/-) with respect to reflection in a plane containing the internuclear axis.





I. **N$_2$ ground state** $(2s\sigma_g)^2(2s\sigma_u)^2(2p\pi_u)^4(2p\sigma_g)^2$

$\Lambda = 0$ therefore a Σ term

$S = 0$ (all electrons paired), hence a singlet term

$$^1\Sigma_g^+$$

For Heteronuclear molecules no u and g notation is used

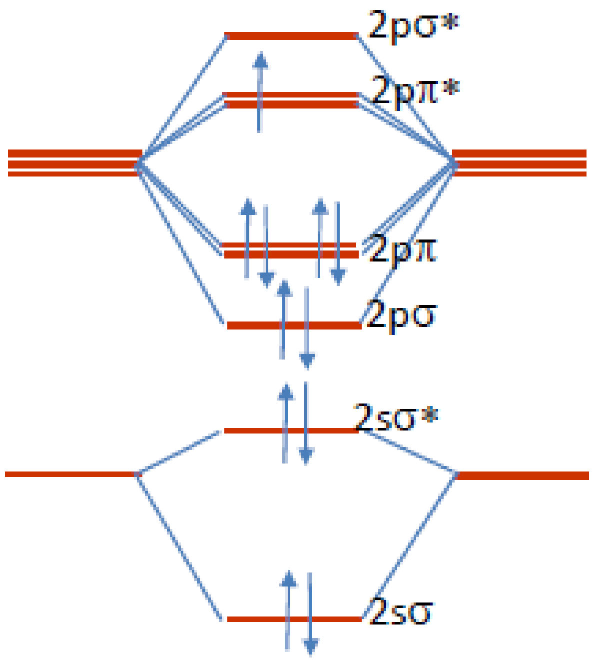
II. **NO ground state** $(2s\sigma)^2(2s\sigma*)^2(2p\sigma)^2\,(2p\pi)^4(2p\pi*)^1$

n.b. No g, u symmetry because non-symmetrical

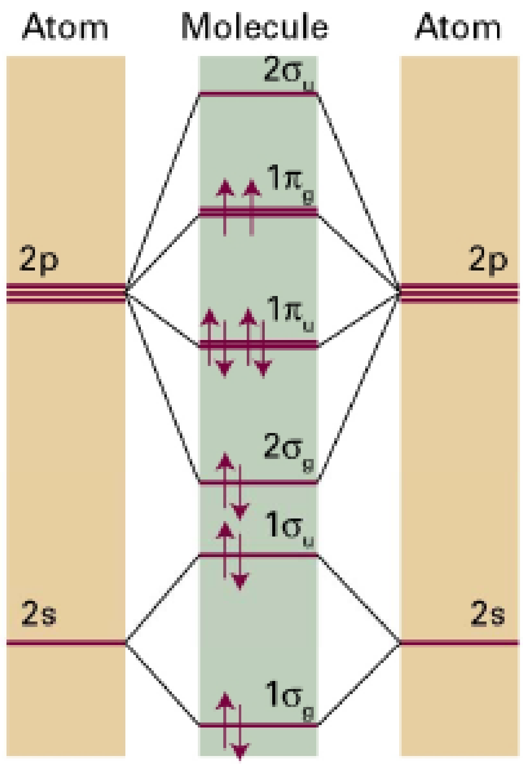
$\Lambda = \pm 1$ therefore a Π term

$S = 1/2$ (one unpaired electron), hence a doublet term

$^2\Pi$ Giving rise to $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$



Example molecular term symbols



III. O_2 ground state $(2s\sigma_g)^2(2s\sigma_u)^2(2p\sigma_g)^2(2p\pi_u)^4(2p\pi_g)^2$

$\Lambda = 0$, or ±2 therefore Σ, Δ terms arise
$S = 0$, or 1 singlets and triplets
$g \otimes g = g$ all terms gerade

$$\therefore expect \quad {}^1\Sigma_g^+ \quad {}^1\Sigma_g^- \quad {}^3\Sigma_g^+ \quad {}^3\Sigma_g^- \quad {}^1\Delta_g \quad {}^3\Delta_g$$

<u>But</u> this neglects the **Pauli Principle**.

In singlet states, ψ_{spin} is antisymmetric. Hence these can only be paired with symmetric ψ_{space} , *i.e.*, g, + states. Likewise triplet states must be paired with g, – states.

${}^1\Sigma_g^- \quad {}^3\Sigma_g^+ \quad {}^3\Delta_g$ all violate Pauli and thus do not exist

${}^1\Sigma_g^+ \quad {}^3\Sigma_g^- \quad {}^1\Delta_g$ Do exist, of which the triplet state is the lowest in energy (spin correlation)

Again, this is only a consideration for multiply occupied (but not full) orbitals

Self assessment

1. What is the full term symbol of the ground electronic state of Li_2^+ ?
2. What are the levels of the term for the ground electronic state of O_2^-?

REFERENCES:

1. Fundamentals of Molecular Spectroscopy, 4th Ed. By Colin N. Banwell and Elaine M. McCash.
2. PHYSICAL CHEMISTRY, Thermodynamics, Structure, and Change, 10th Edition By Peter Atkins and Julio de Paula, W. H. Freeman and Company New York.
3. Physical Chemistry by D. W. Ball.
4. Internet.

Thank You