LS, *JK*, and *jj* Atomic Spectroscopic Terms and Spectroscopic Terms for small molecules

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Spectral Terms for Molecules

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References

Basic books on symmetry

Any book on inorganic chemistry

- Weller, M.; Overton, T.; Rourke, J.; Armstrong, F. *Inorganic Chemistry*, 6th ed., Oxford University Press, 2014.

- Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, 4th ed., Prentice-Hall, 2010.

- Douglas, B. E.; McDaniel, D. H.; Alexander, J. J. *Concepts and Models of Inorganic Chemistry*, 3rd. ed., John Wiley & Sons, Inc, 1994.

Basic books on symmetry

Any book on inorganic chemistry

- Pfennig, B. W. *Principles of Inorganic Chemistry*, Wiley, 2015.

Advanced books on symmetry

- COTTON, F. A. Chemical Applications of Group Theory, 3rd. ed., New York: John Wiley & Sons, 1990

- CARTER, R; L. Molecular Symmetry and Group Theory, New York: John Wiley & Sons, 1998

- KETTLE, S. F. A. Symmetry and Structure -Readable Group Theory for Chemists, 3rd. ed., New York: John Wiley & Sons, 2007

Books
Spectroscopic Terms for Molecules

- Harris, D. C.; Bertolucci, M. D. *Symmetry and Spectroscopy*, Oxford, 1978

- Bernath, P. F. *Spectra of Atoms and Molecules*, 3rd, ed., Oxford University Press, 2016.

Spectroscopic Terms for Molecules

They are based on the

- Molecular Orbital Theory
- Symmetry labels of molecular orbitals
- They depend on the partially filled molecular orbitals
- It is necessary to know the molecular orbital diagram for the molecule being considered

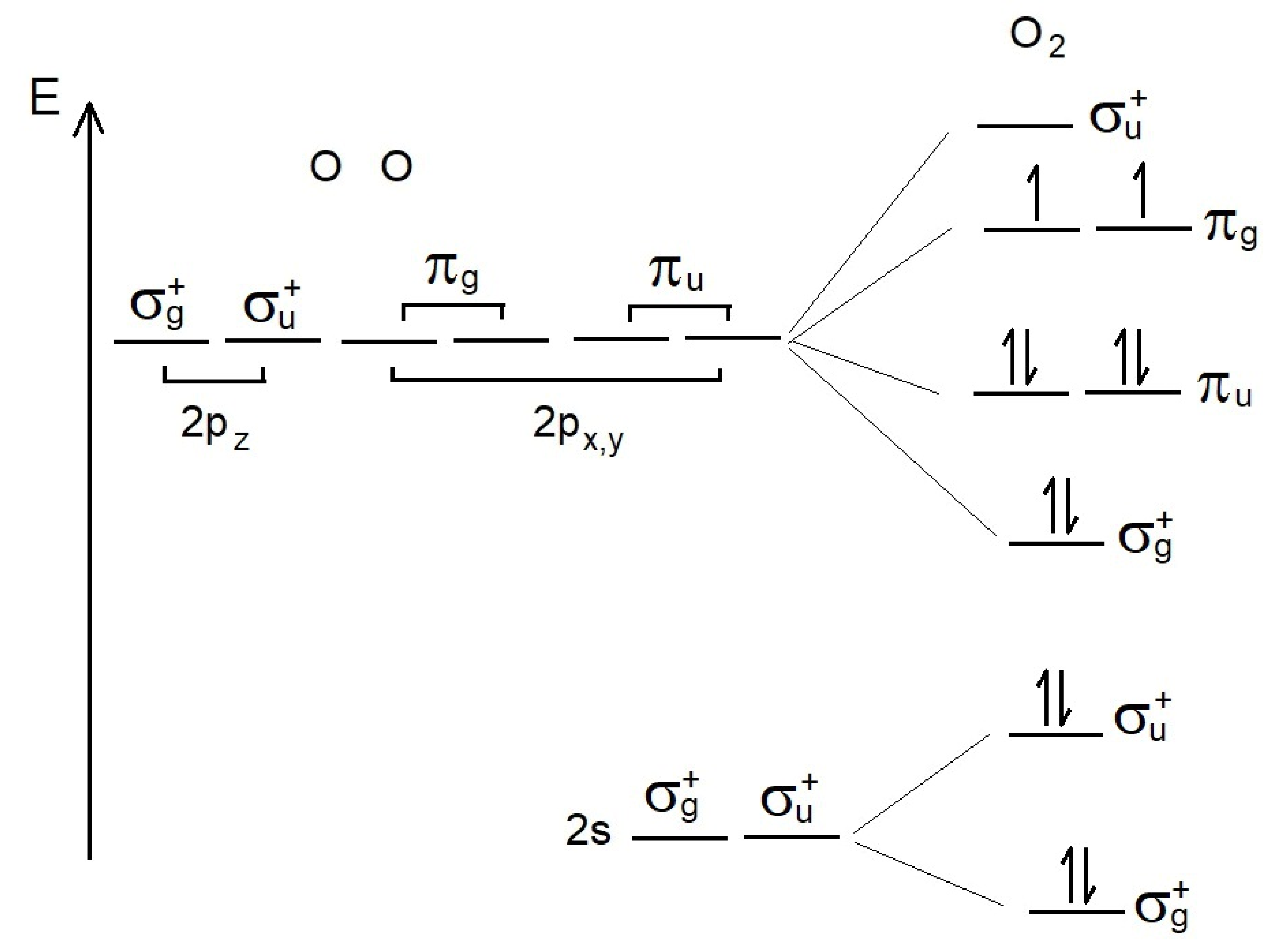
Homonuclear Diatomic Molecules
$D_{\infty h}$

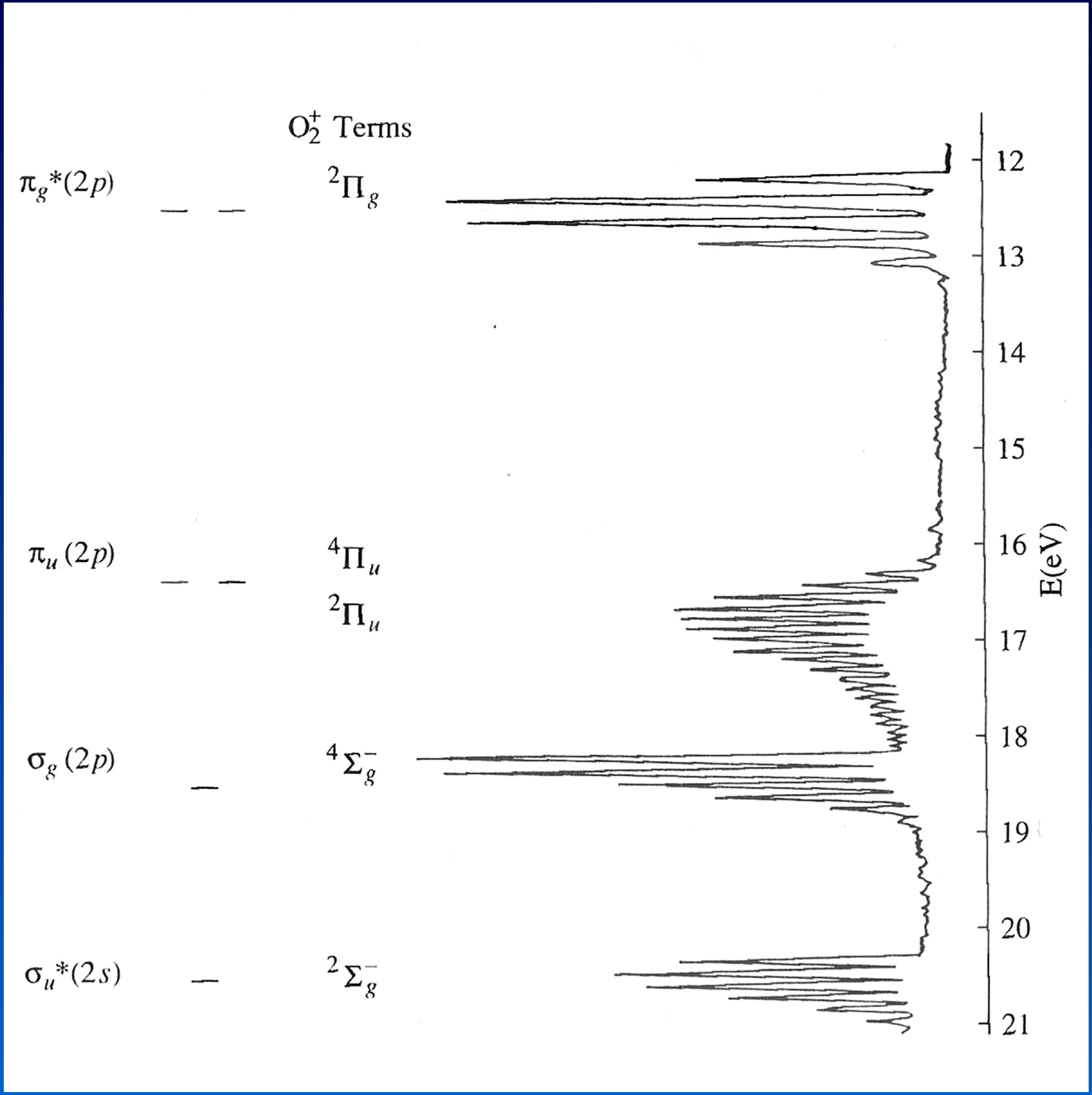
$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_g^+	1	1	1	1	1	1
Σ_g^-	1	1	-1	1	1	-1
Π_g	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0
Δ_g	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
Σ_u^+	1	1	1	-1	-1	-1
Σ_u^-	1	1	-1	-1	-1	1
Π_u	2	$2\cos\varphi$	0	-2	$2\cos\varphi$	0
Δ_u	2	$2\cos 2\varphi$	0	-2	$-2\cos 2\varphi$	0

Dioxigen - O_2

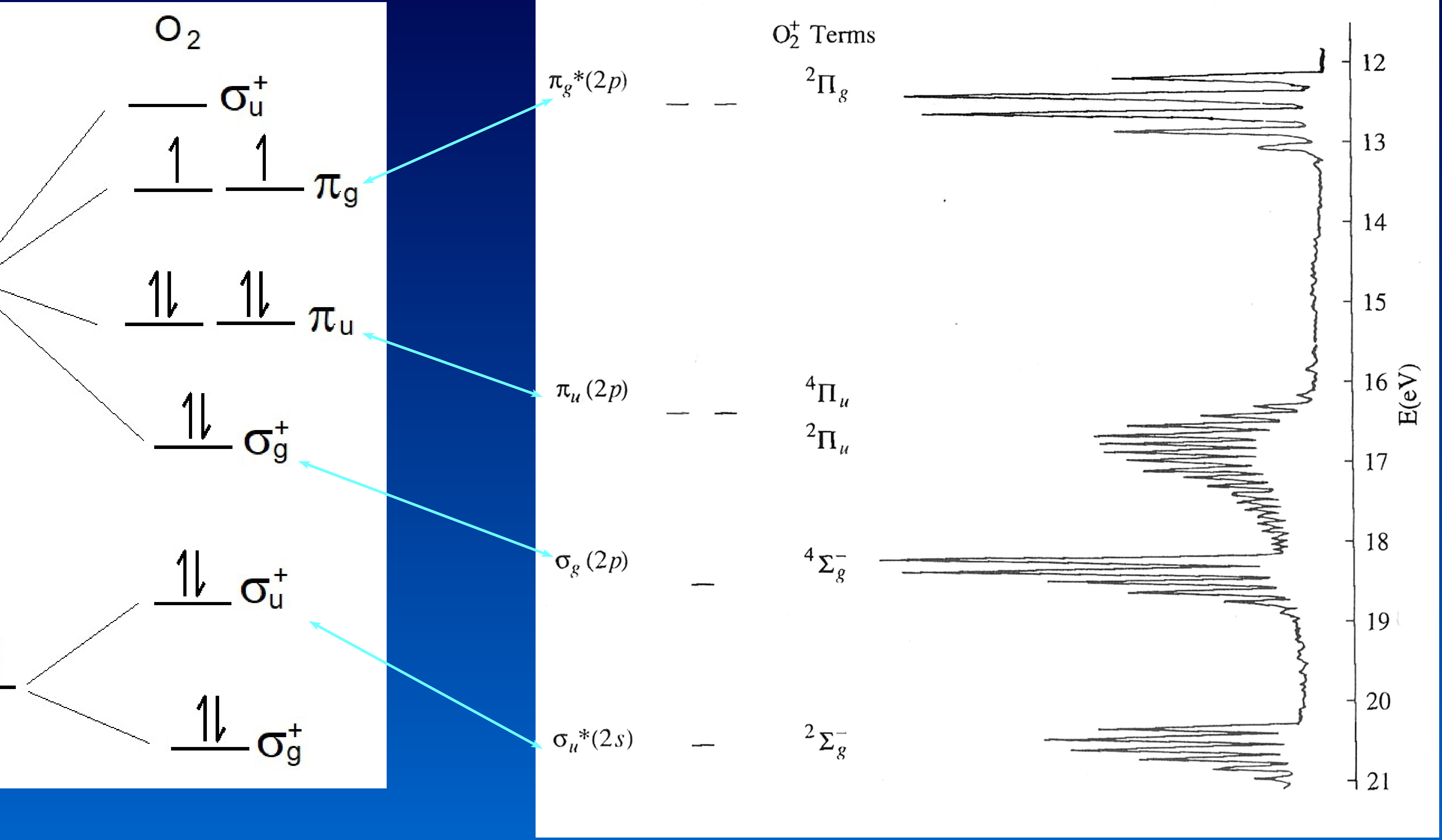
O_2 - $D_{\infty h}$


E
O O
O_2
σ_g^+
σ_u^+
π_g
π_u
2p$_z$
2p$_{x,y}$
2s
σ_g^+
σ_u^+
σ_u^+
π_g
π_u
σ_g^+
σ_u^+
σ_g^+



Photoelectron spectra O_2

Eland, J. H. *Photoelectron Spectroscopy*, Butterworths, 1974


O_2
σ_u^+
π_g
π_u
σ_g^+
σ_u^+
σ_g^+
O_2^+ Terms
$\pi_g^*(2p)$
$^2\Pi_g$
$\pi_u(2p)$
$^4\Pi_u$
$^2\Pi_u$
$\sigma_g(2p)$
$^4\Sigma_g^-$
$\sigma_u^*(2s)$
$^2\Sigma_g^-$
12
13
14
15
16
17
18
19
20
21
E(eV)

$\mathbf{D}_{\infty \mathbf{h}}$

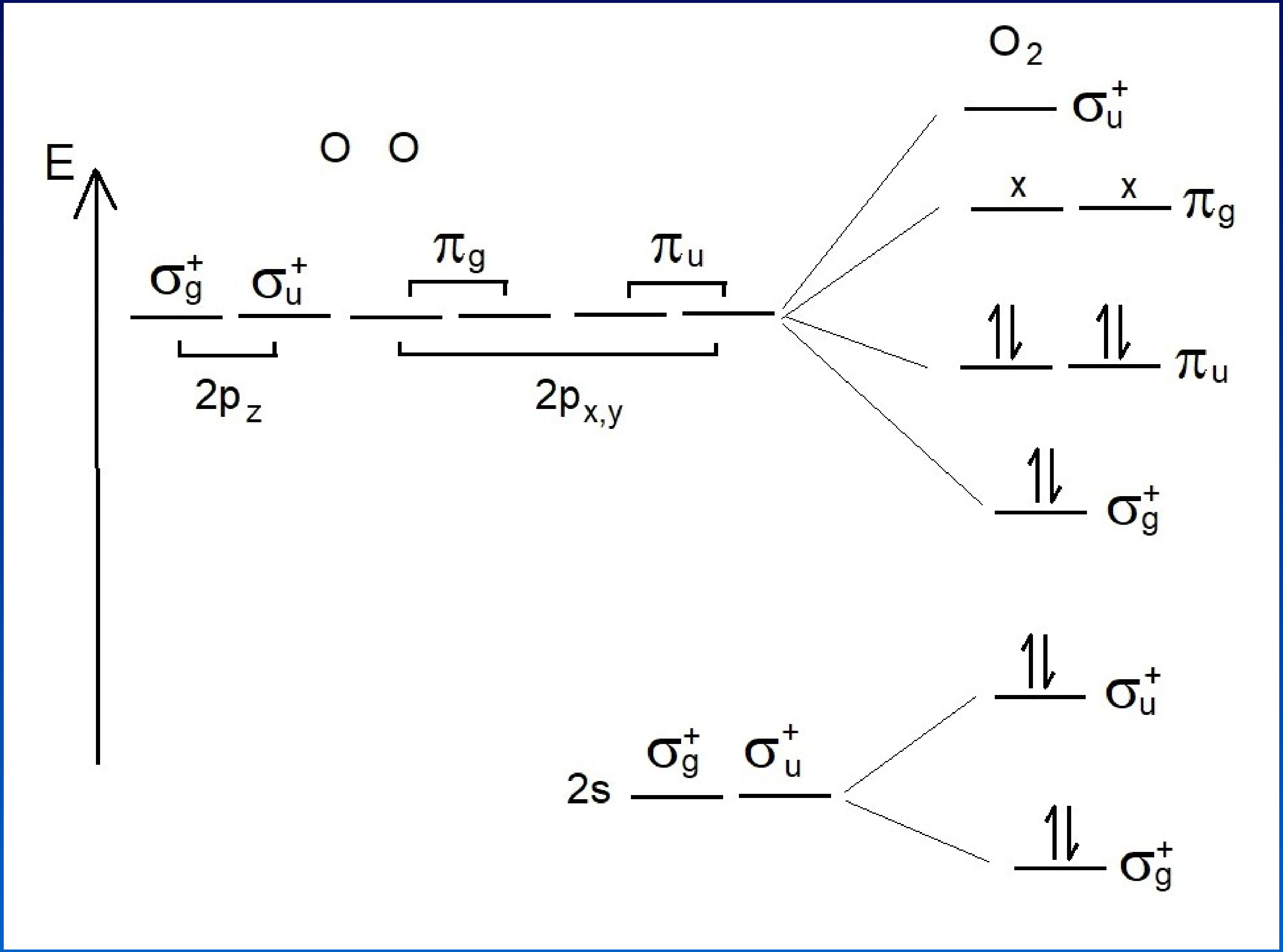
$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_g^+	1	1	1	1	1	1
Σ_g^-	1	1	-1	1	1	-1
Π_g	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0
Δ_g	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
Σ_u^+	1	1	1	-1	-1	-1
Σ_u^-	1	1	-1	-1	-1	1
Π_u	2	$2\cos\varphi$	0	-2	$2\cos\varphi$	0
Δ_u	2	$2\cos 2\varphi$	0	-2	$-2\cos 2\varphi$	0

$\mathbf{D_{\infty h}}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_g^+	1	1	1	1	1	1
Σ_g^-	1	1	-1	1	1	-1
Π_g	2	0	0	2	0	0
Δ_g	2	-2	0	2	-2	0
Σ_u^+	1	1	1	-1	-1	-1
Σ_u^-	1	1	-1	-1	-1	1
Π_u	2	0	0	-2	0	0
Δ_u	2	-2	0	-2	2	0

Considering $\varphi = 90°$ $\cos\varphi = 0$ $\cos 2\varphi = -1$

O_2 - $D_{\infty h}$



E
O O
σ_g^+
σ_u^+
π_g
π_u
$2p_z$
$2p_{x,y}$
2s
σ_g^+
σ_u^+
O_2
σ_u^+
x
x
π_g
π_u
σ_g^+
σ_u^+
σ_g^+

$D_{\infty h}$

$D_{\infty h}$	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2
Σ_g^+	1	1	1	1	1	1
Σ_g^-	1	1	-1	1	1	-1
Π_g	2	0	0	2	0	0
Δ_g	2	-2	0	2	-2	0
Σ_u^+	1	1	1	-1	-1	-1
Σ_u^-	1	1	-1	-1	-1	1
Π_u	2	0	0	-2	0	0
Δ_u	2	-2	0	-2	2	0
$\Pi_g \otimes \Pi_g$	4	0	0	4	0	0

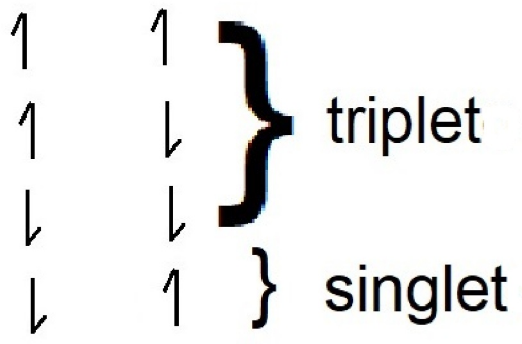
$\Sigma_g^+ \oplus \Sigma_g^- \oplus \Delta_g$

O_2 - $D_{\infty h}$

Determining the spin multiplicity

Building the microstates

Π_g		Σ_{ms}
x	x	1, 0, 0, -1
xx		0
	xx	0



triplet = 1, 0, -1
singlet = 0

O_2 - $D_{\infty h}$

Determining the spin multiplicity

Building the microstates

Π_g		Σ_{ms}
$\underline{x\quad}$	$\underline{x\quad}$	1, 0, 0, -1
$\underline{xx}$	$\underline{\quad\quad}$	0
$\underline{\quad\quad}$	$\underline{xx}$	0

triplet = 1, 0, -1

singlet = 0

six microstates

$\Pi_g \otimes \Pi_g = {}^a\Sigma_g^+ + {}^b\Sigma_g^- + {}^c\Delta_g$

$a + b + 2c = 6$

(a, b, c) can be 1 or 3

Possible solutions:

$(3, 1, 1) = {}^3\Sigma_g^+ + {}^1\Sigma_g^- + {}^1\Delta_g$

or

$(1, 3, 1) = {}^1\Sigma_g^+ + {}^3\Sigma_g^- + {}^1\Delta_g$

O_2 - $D_{\infty h}$

Determining the spin multiplicity

To decide between these solutions

$$^3\Sigma_g^+ + {}^1\Sigma_g^- + {}^1\Delta_g \quad \text{or} \quad {}^1\Sigma_g^+ + {}^3\Sigma_g^- + {}^1\Delta_g$$

we need to know which terms are symmetric and antisymmetric

The total wavefunction, $\psi_{\text{orbital}}\psi_{\text{spin}}$, must be antisymmetric on exchanging of two electrons.

O_2 - $D_{\infty h}$

Determining the spin multiplicity

In the case of the direct product of two equal irreducible representations ($\Pi_g \otimes \Pi_g$), the characters of symmetric (χ^+) and antisymmetric (χ^-) are given by:

$$\text{characters } \chi^+ = (\tfrac{1}{2})\ \{[\chi(R)]^2 + \chi(R^2)\}$$

$$\text{characters } \chi^- = (\tfrac{1}{2})\ \{[\chi(R)]^2 - \chi(R^2)\}$$

R^2 is the result when applying two times the same symmetry operation. For $D_{\infty h}$ we will have:

R	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2
R^2	E	–	E	E	–	E

O_2 - $D_{\infty h}$

Determining the spin multiplicity

$$\text{characters } \chi^{+} = (½)\ \{[\chi(R)]^2 + \chi(R^2)\}$$
$$\text{characters } \chi^{-} = (½)\ \{[\chi(R)]^2 - \chi(R^2)\}$$

$\chi(R^2)$ is the character of the resulting symmetry operation. In the irreducible representation Π_g, the character for the symmetry operation E is equal 2. Then $\chi(E) = \chi(R) = 2 \quad \Rightarrow \quad \chi(R^2) = \chi(E) = 2$

R	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2
R^2	E	–	E	E	–	E
$\chi(R^2)$	2	–	2	2	–	2

O_2 - $D_{\infty h}$

Determining the spin multiplicity

caracteres $\chi^+ = (½)\ \{[\chi(R)]^2 + \chi(R^2)\}$
caracteres $\chi^- = (½)\ \{[\chi(R)]^2 - \chi(R^2)\}$

$[\chi(R)]^2$ is the square of the character of each symmetry operation. For the Π_g we have:

	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2
Π_g	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0
$[\chi(R)]^2$	4	–	0	4	–	0

O_2 - $D_{\infty h}$

Determining the spin multiplicity

$$\text{characters } \chi^{+} = (½)\ \{[\chi(R)]^2 + \chi(R^2)\}$$
$$\text{characters } \chi^{-} = (½)\ \{[\chi(R)]^2 - \chi(R^2)\}$$

Then we have:

	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2
$[\chi(R)]^2$	4	–	0	4	–	0
$\chi(R^2)$	2	–	2	2	–	2
χ^{+} =	3	–	1	3	–	1
χ^{-} =	1	–	-1	1	–	-1

O_2 - $D_{\infty h}$

Determining the spin multiplicity

$D_{\infty h}$	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2
Σ_g^+	1	1	1	1	1	1
Δ_g	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
$\chi^+ =$	3	–	1	3	–	1
Σ_g^-	1	1	-1	1	1	-1
$\chi^- =$	1	–	-1	1	–	-1

Symmetric irreducible representations

Antisymmetric irreducible representations

Harris, D. C.; Bertolucci, M. D. ; *Symmetry and Spectroscopy* , Dover: Nova Iorque, 1978. pg 327

O_2 - $D_{\infty h}$

Determining the spin multiplicity

- Electrons have a half-odd-integer spin. They are fermions.

- The total wavefunction, $\psi_{orbital}\psi_{spin}$, must be antisymmetric on exchange of two electrons.

Σ_g^+ (symmetric) × ψ_{spin} (antisymmetric)
Σ_g^- (antisymmetric) × ψ_{spin} (symmetric)
Δ_g (symmetric) × ψ_{spin} (antisymmetric)

O_2 - $D_{\infty h}$

Determining the spin multiplicity

- ➢ Electrons have a half-odd-integer spin. They are fermions.

- ➢ The total wavefunction, $\psi_{\text{orbital}}\psi_{\text{spin}}$, must be antisymmetric on exchange of two electrons.

Σ_g^+ (symmetric) × $[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$
Σ_g^- (antisymmetric) × ψ_{spin} (symmetric)
Δ_g (symmetric) × $[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

O_2 - $D_{\infty h}$

Determining the spin multiplicity

- As the antisymmetric spin function

$$[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

corresponds to only one arrangement of the electrons, it is a singlet state.

Σ_g^+ (symmetric) × singlet
Σ_g^- (antisymmetric) × ψ_{spin} (symmetric)
Δ_g (symmetric) × singlet

O_2 - $D_{\infty h}$

Determining the spin multiplicity

$$\begin{aligned}\psi_{\text{spin}}\ (\text{symmetric}) = {} & [\alpha(1)\alpha(2)] + \\ & [\beta(1)\beta(2)] + \\ & [\alpha(1)\beta(2) + \alpha(2)\beta(1)]\end{aligned}$$

TRIPLET

- ➢ As the symmetric spin function is the sum of three arrangements of the electrons, it is a triplet state.

O_2 - $D_{\infty h}$

Determining the spin multiplicity

Σ_g^+ (symmetric) × singlet = $^1\Sigma_g^+$

Σ_g^- (antisymmetric) × triplet = $^3\Sigma_g^-$

Δ_g (symmetric) × singlet = $^1\Delta_g$

O_2 - $D_{\infty h}$

Determining the spin multiplicity

Then, after consider the two possible solutions

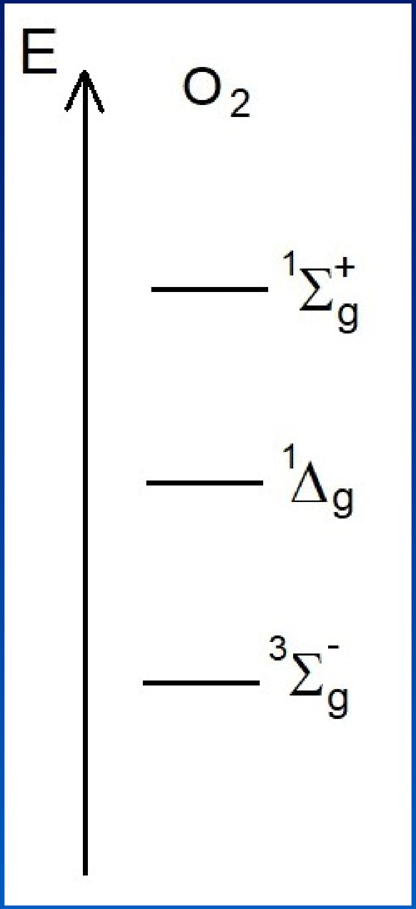
$$^3\Sigma_g^+ + {}^1\Sigma_g^- + {}^1\Delta_g \quad \text{or} \quad {}^1\Sigma_g^+ + {}^3\Sigma_g^- + {}^1\Delta_g$$

the correct solution is

$$^1\Sigma_g^+ + {}^3\Sigma_g^- + {}^1\Delta_g$$

O_2 - $D_{\infty h}$

Molecular Energy Levels



Hund’s Rule

Triplets are more stable than singlets

O_2 - $D_{\infty h}$

UV-Vis spectra at 150 atm

$2[^1\Sigma_g^+]$ $2[^1\Delta_g]$

$^3\Sigma_u^+$ $[^1\Sigma_g^+ + {}^1\Delta_g]$ $^1\Sigma_g^+$ $^1\Delta_g$

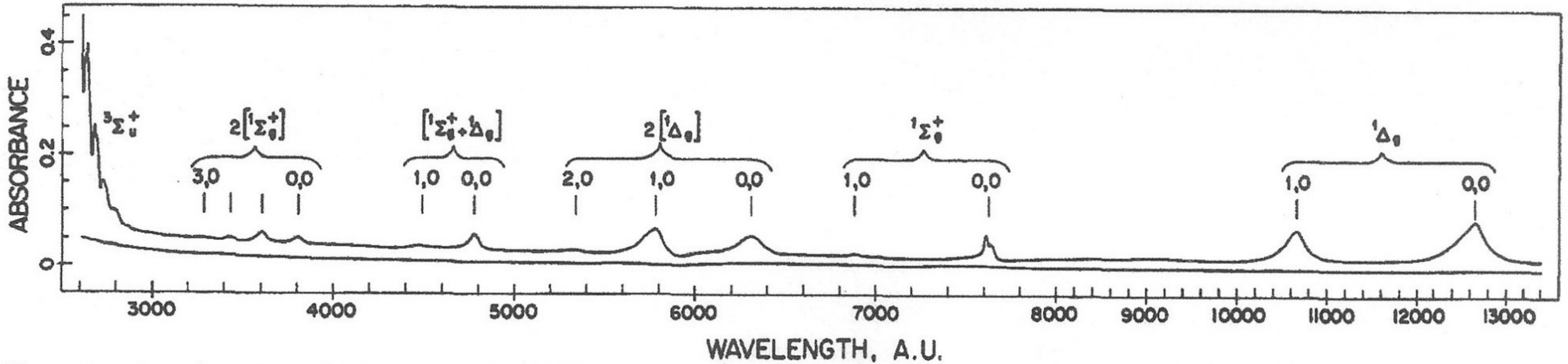
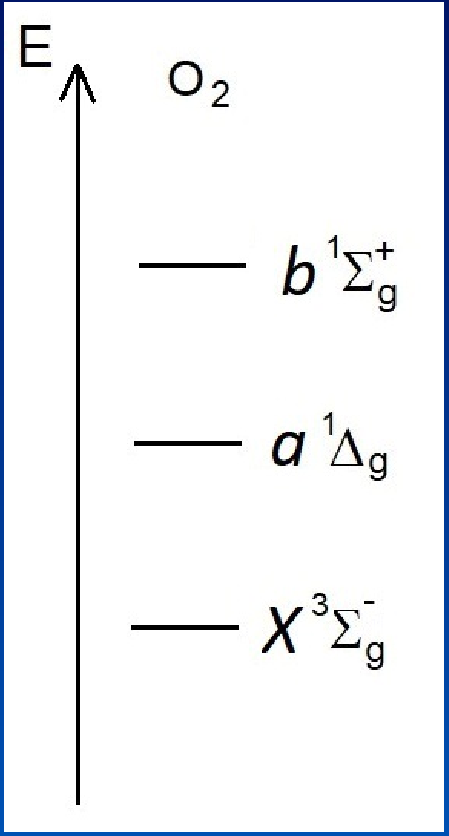


Figure 7. Complete absorption spectrum from 2600 to 13,400 Å of gaseous molecular oxygen at 150 atm in a 6.5-cm cell at 20°. Bands labeled according to upper electronic state by energy convention, with vibronic components.

Khan, A. U.; Kasha, *M. J. Amer. Chem. Soc. 92* :3293 (1970).

O_2 - $D_{\infty h}$



Molecular Energy Levels

Energy of the transition 0-0

cm^{-1}	nm	
13120	762	$b\,^1\Sigma_g^+$
7882	1268	$a\,^1\Delta_g$
0	0	$X\,^3\Sigma_g^-$

Khan, A. U.; Kasha, *M. J. Amer. Chem. Soc. 92* :3293 (1970).

Rules to name the energy levels[1,2]

➢ The ground state is indicated by X

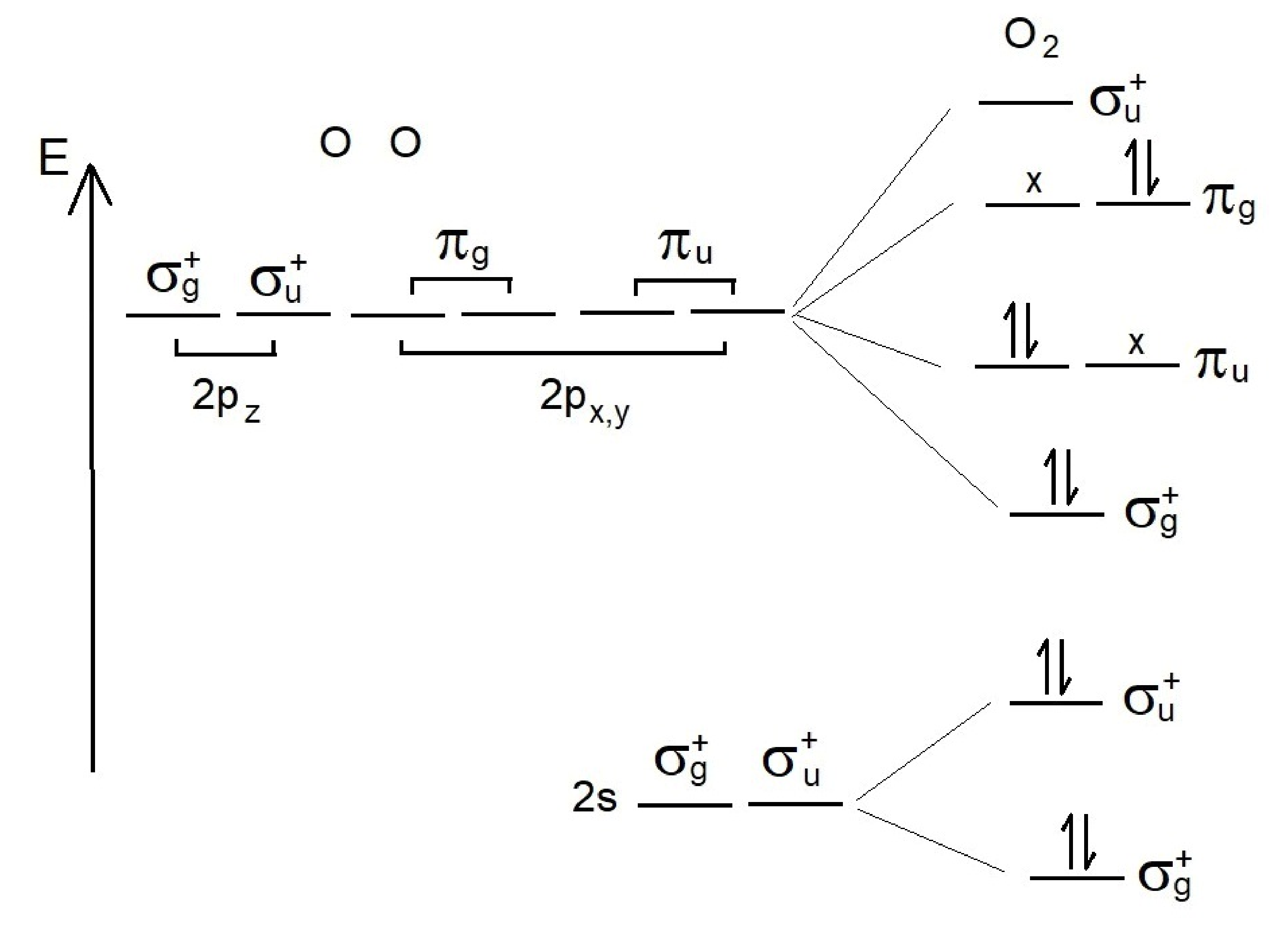
➢ Capital letters A, B, C ... are used to indicate excited states with the same spin multiplicity of the ground state.

➢ Lowercase letters a, b, c ... are used for the excited states with a spin multiplicity different than the ground state.

➢ A tilde (~) is used above the terms for nonlinear poliatomic molecules, to distinguish them from the symmetry labels.

1. Bernath, P. F., *Spectra of Atoms and Molecules* , 3ª ed., Oxford University Press, 2016. pg. 344.
2. Cohen, E. R. *et al*., eds., *Grandezas, Unidades de Símbolos em Físico-Química* , 3ª ed., IUPAC-SBQ, 2018. pg. 35.

O_2 - $D_{\infty h}$ (upper excited states)



$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_g^+	1	1	1	1	1	1
Σ_g^-	1	1	-1	1	1	-1
Π_g	2	0	0	2	0	0
Δ_g	2	-2	0	2	-2	0
Σ_u^+	1	1	1	-1	-1	-1
Σ_u^-	1	1	-1	-1	-1	1
Π_u	2	0	0	-2	0	0
Δ_u	2	-2	0	-2	2	0
$\Pi_g \otimes \Pi_u$	4	0	0	-4	0	0

$$\Sigma_u^+ \oplus \Sigma_u^- \oplus \Delta_u$$

O_2 - $D_{\infty h}$

Determining the spin multiplicity

Is this case, as the unpaired electrons are in different orbitals, all terms can be singlet and triplet.

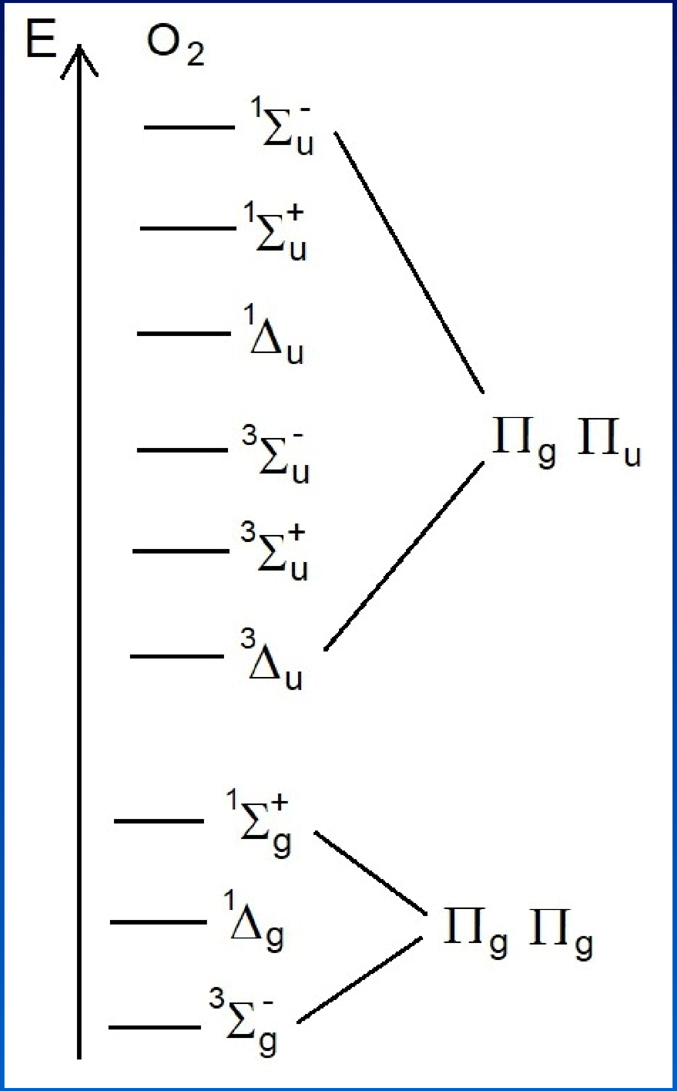
$^1\Sigma_u^+$ $^1\Sigma_u^-$ $^1\Delta_u$

$^3\Sigma_u^+$ $^3\Sigma_u^-$ $^3\Delta_u$

Harris, D. C.; Bertolucci, M. D. ; *Symmetry and Spectroscopy* , Dover: New York 1978. pg 324

O_2 - $D_{\infty h}$

Energy levels, including the upper excited states

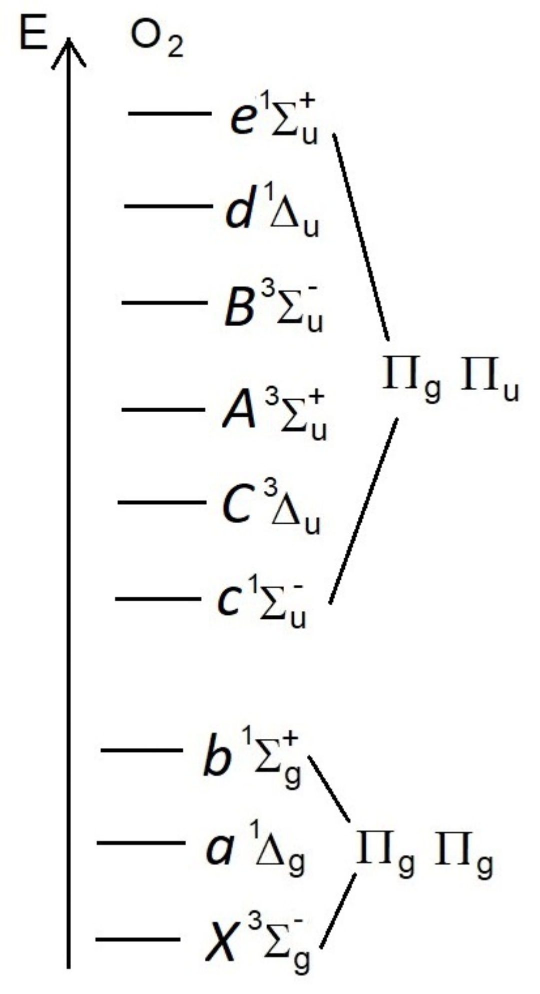


Hund’s Rules do not apply strictly to excited states.

This is a preliminar ordering.

O_2 - $D_{\infty h}$

Energy levels, including the upper excited states



Energy for the 0-0 transition

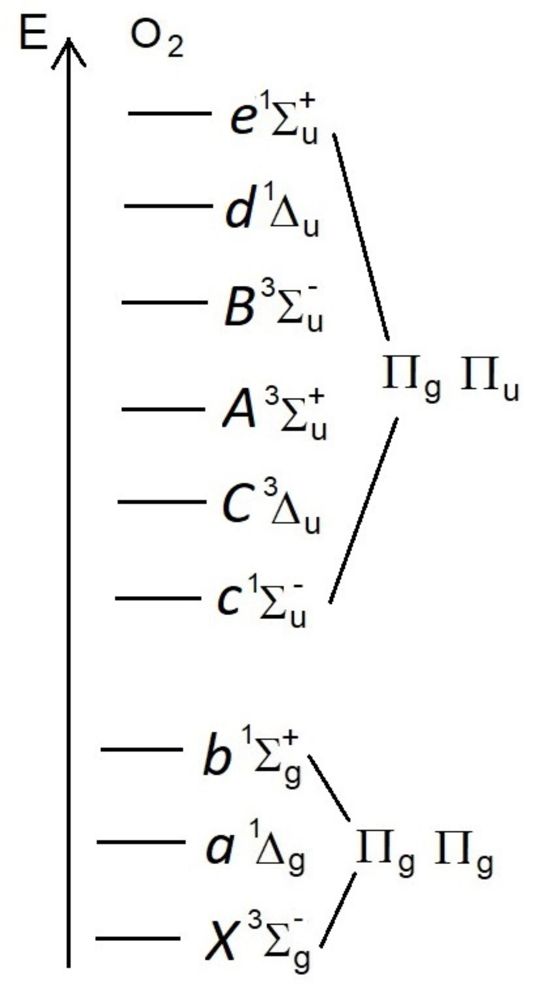
cm^{-1}	nm	
49358	203	$B\ ^3\Sigma_u^-$
35007	285	$A\ ^3\Sigma_u^+$
34319	291	$C\ ^3\Delta_u$
32664	306	$c\ ^1\Sigma_u^-$
13120	762	$b\ ^1\Sigma_g^+$
7882	1268	$a\ ^1\Delta_g$
0	0	$X\ ^3\Sigma_g^-$

It does not follow the sequence of the letters because it was discovered after the *A* and *B* transitions

Krupenie, P. H.; *J. Phys. Chem. Ref. Data 1* :423 (1972). Table 1, pg. 456-457.

O_2 - $D_{\infty h}$

Energy levels, including the upper excited states



Energy for the 0-0 transition

cm^{-1}	nm		
49358	203	$B\,^3\Sigma_u^-$	(Schumann-Runge system)
35007	285	$A\,^3\Sigma_u^+$	(Herzberg I system)
34319	291	$C\,^3\Delta_u$	(Herzberg III system)
32664	306	$c\,^1\Sigma_u^-$	(Herzberg II system)
13120	762	$b\,^1\Sigma_g^+$	(Atmospheric System)
7882	1268	$a\,^1\Delta_g$	(Infrared Atmospheric System)
0	0	$X\,^3\Sigma_g^-$	

Krupenie, P. H.; *J. Phys. Chem. Ref. Data 1* :423 (1972). Table 1, pg. 456-457.

O_2 - $D_{\infty h}$

UV-Vis spectra at 150 atm

$2[^1\Sigma_g^+]$ $2[^1\Delta_g]$

$A^3\Sigma_u^+$ $[^1\Sigma_g^+ + {}^1\Delta_g]$ $b^1\Sigma_g^+$ $a^1\Delta_g$

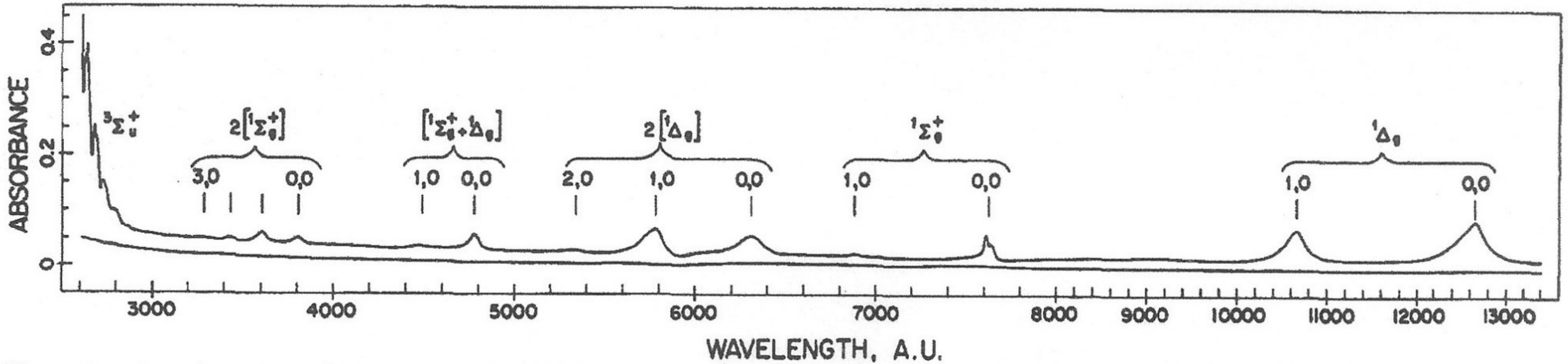


Figure 7. Complete absorption spectrum from 2600 to 13,400 Å of gaseous molecular oxygen at 150 atm in a 6.5-cm cell at 20°. Bands labeled according to upper electronic state by energy convention, with vibronic components.

Khan, A. U.; Kasha, *M. J. Amer. Chem. Soc. 92* :3293 (1970).

O_2 - $D_{\infty h}$

UV-Vis spectra at 150 atm

$2[^1\Sigma_g^+]$ $2[^1\Delta_g]$

$A^3\Sigma_u^+$ $[^1\Sigma_g^+ + {}^1\Delta_g]$ $b^1\Sigma_g^+$ $a^1\Delta_g$

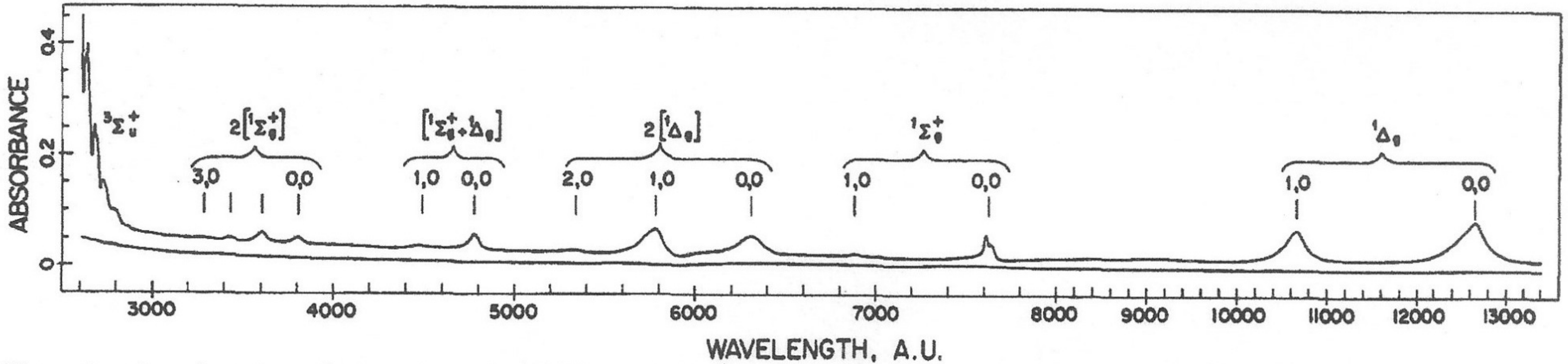


Figure 7. Complete absorption spectrum from 2600 to 13,400 Å of gaseous molecular oxygen at 150 atm in a 6.5-cm cell at 20°. Bands labeled according to upper electronic state by energy convention, with vibronic components.

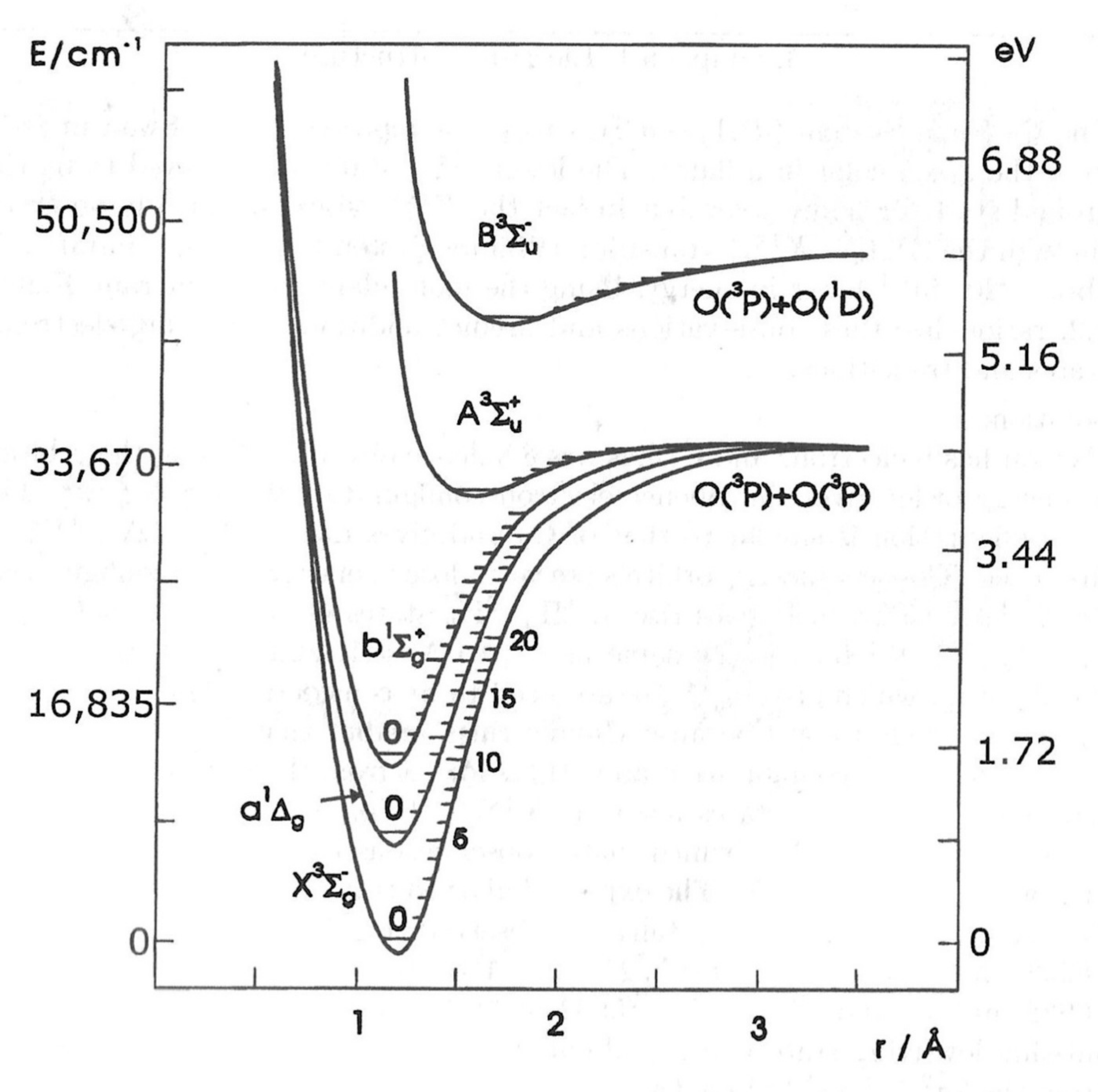
Bands related with the $(O_2)_2$ Collision Complex or O_4 Stable Dimmer of O_2

O_2 - $D_{\infty h}$

Energy levels, including the upper excited states

Energy for the 0-0 transition

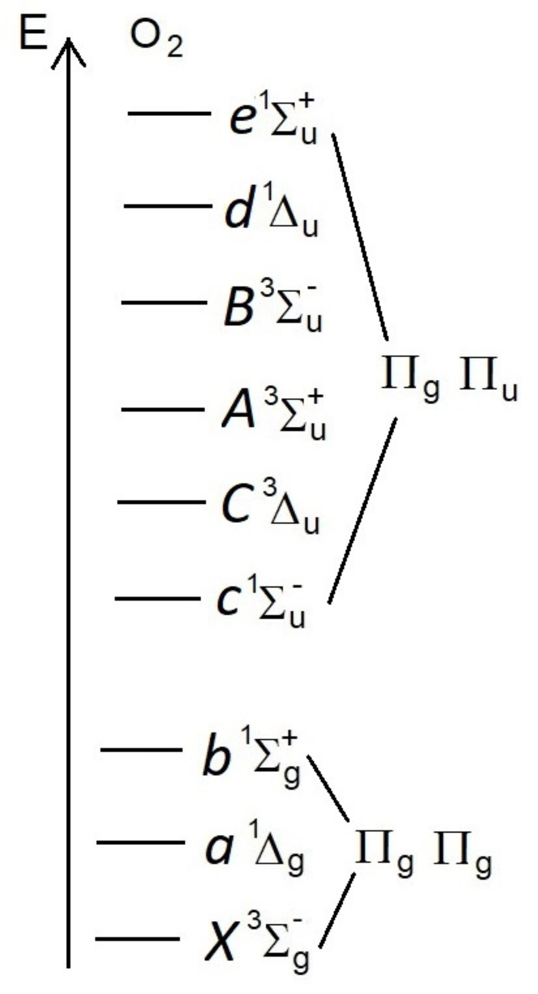
cm^{-1}	nm	
49358	203	$B\ {}^3\Sigma_u^-$
35007	285	$A\ {}^3\Sigma_u^+$
34319	291	$C\ {}^3\Delta_u$
32664	306	$c\ {}^1\Sigma_u^-$
13120	762	$b\ {}^1\Sigma_g^+$
7882	1268	$a\ {}^1\Delta_g$
0	0	$X\ {}^3\Sigma_g^-$

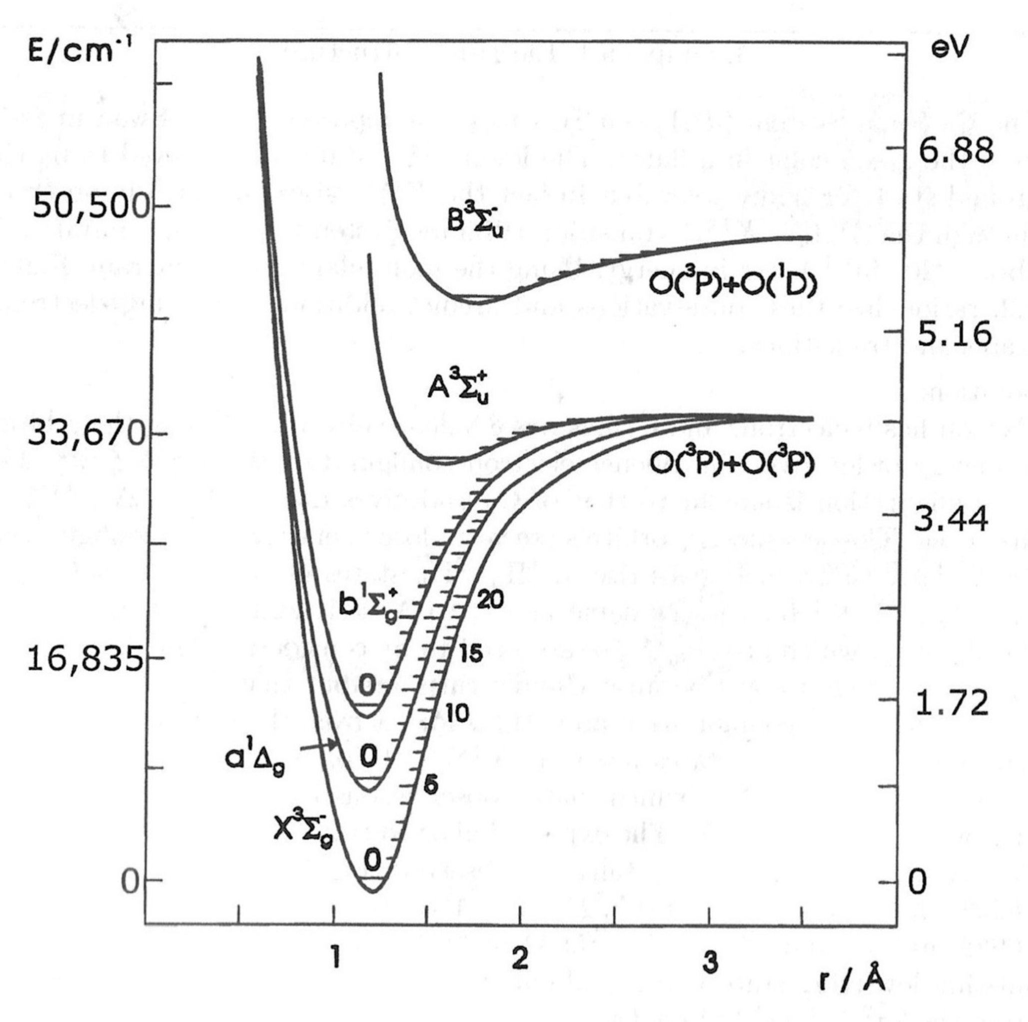


Bernath, P. F. *Spectra of Atoms and Molecules,* 3rd ed.,Oxford University Press, 2016. pg 345

O_2 - $D_{\infty h}$

Energy levels, including the upper excited states





O_2 - $D_{\infty h}$

Symmetry Selections Rules for linear molecules *

1) $\Delta\Lambda = 0, \pm 1$

	Σ	Π	Δ	Φ	
$\Lambda =$	0	1	2	3	...

It means that the allowed transions are

$\Sigma \leftrightarrow \Sigma$ $\quad \Pi \leftrightarrow \Pi$ $\quad \Delta \leftrightarrow \Delta$ $\quad \Phi \leftrightarrow \Phi$ $\quad (\Delta\Lambda = 0)$

$\Sigma \leftrightarrow \Pi$ $\quad \Pi \leftrightarrow \Delta$ $\quad \Delta \leftrightarrow \Phi$ $\quad (\Delta\Lambda = \pm 1)$

*Bernath, P. F. *Spectra of Atoms and Molecules,* 3rd ed.,Oxford University Press, 2016. pg 344

O_2 - $D_{\infty h}$

Symmetry Selections Rules for linear molecules

2) Because the *z* coordinate and consequently the electric dipole moment (μ_z) belongs to the Σ_u^+ irreducible representation of the $D_{\infty h}$ point group, droping the g subscript we have,

Allowed transitions

$\Sigma^+ \leftrightarrow \Sigma^+$ $\Sigma^- \leftrightarrow \Sigma^-$

$\Sigma^+ \leftrightarrow \Pi$ $\Sigma^- \leftrightarrow \Pi$

Forbidden transitions

$\Sigma^+ \leftrightarrow \Sigma^-$

O_2 - $D_{\infty h}$

Spin Selection Rule

3) $\Delta S = 0$ (S = spin multiplicity)

It means that the allowed transions are

singlet ↔ singlet doublet ↔ double triplet ↔ triplet ...

When the molecule contains heavier atoms this rule is sometimes violated.

O_2 - $D_{\infty h}$

Symmetry Selections Rules

4) Parity rule   g ↔ u

It is equivalent to the rule T° ↔ T for atoms

O_2 - $D_{\infty h}$

Spin and Symmetry Selections Rules

Allowed (yes) and forbidden (no) bands

cm^{-1}	nm		$\Delta S = 0$	$g \leftrightarrow u$	$\Delta\Lambda = 0, \pm 1$	$\Sigma^+ \xleftarrow{} \text{no} \xrightarrow{} \Sigma^-$
49358	203	$B\ ^3\Sigma_u^-$	yes	yes	yes	yes
35007	285	$A\ ^3\Sigma_u^+$	yes	yes	yes	no
34319	291	$C\ ^3\Delta_u$	yes	yes	no	–
32664	306	$c\ ^1\Sigma_u^-$	no	yes	yes	yes
13120	762	$b\ ^1\Sigma_g^+$	no	no	yes	no
7882	1268	$a\ ^1\Delta_g$	no	no	no	–
0	0	$X\ ^3\Sigma_g^-$				

Although forbidden, Band A is observed in the spectra by Khan and Kasha. Band B is responsible for the absorption of UV light with $\lambda < 200$ nm in the high atmosphere.

O_2 - $D_{\infty h}$

UV-Vis spectra at 150 atm

$2[^1\Sigma_g^+]$ $2[^1\Delta_g]$

$A^3\Sigma_u^+$ $[^1\Sigma_g^+ + {}^1\Delta_g]$ $b^1\Sigma_g^+$ $a^1\Delta_g$

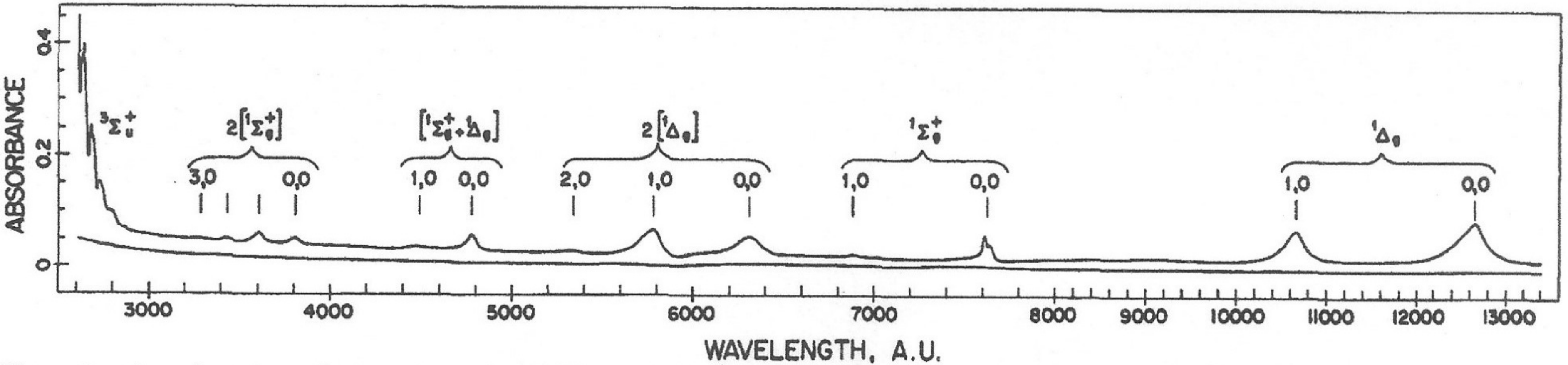


Figure 7. Complete absorption spectrum from 2600 to 13,400 Å of gaseous molecular oxygen at 150 atm in a 6.5-cm cell at 20°. Bands labeled according to upper electronic state by energy convention, with vibronic components.

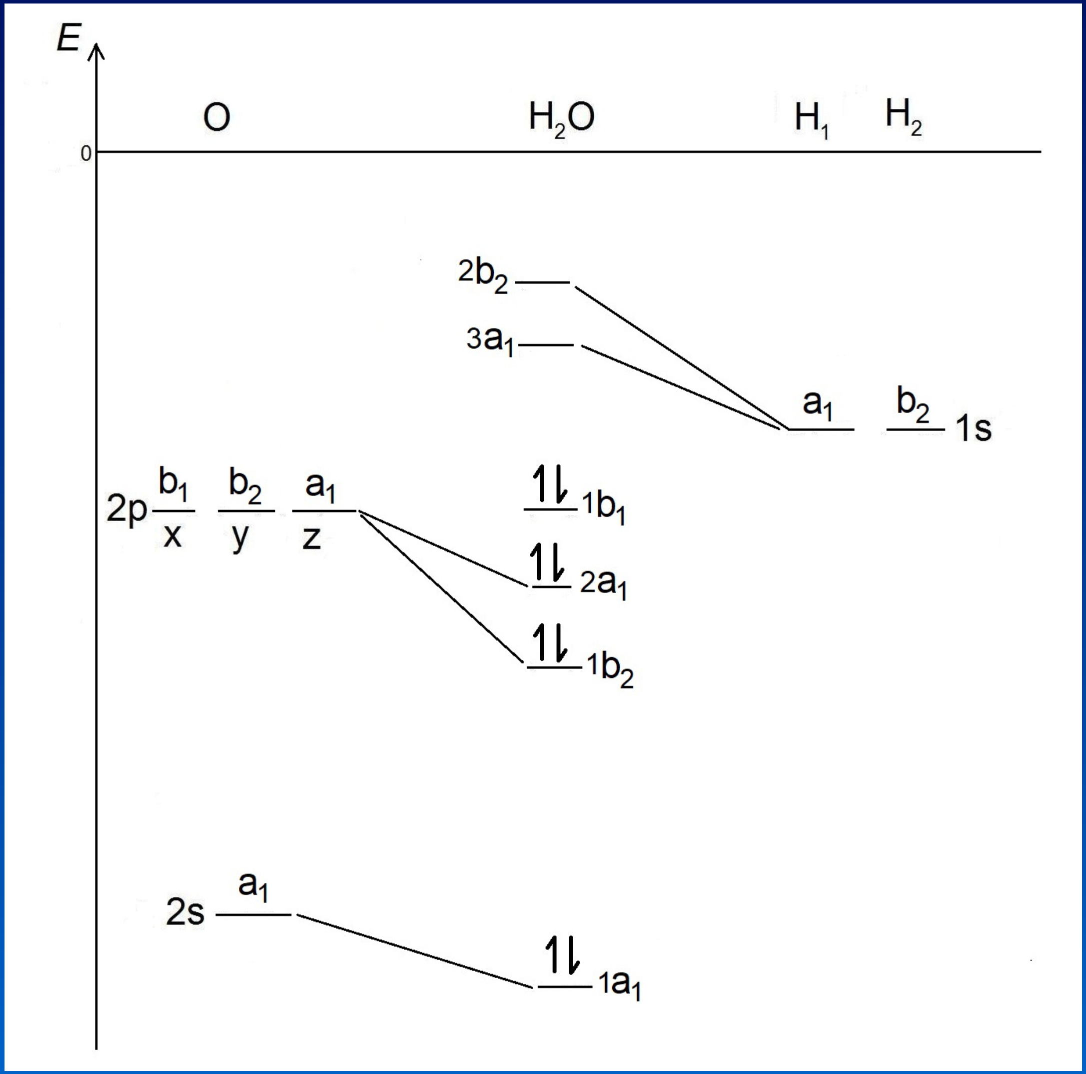
Khan, A. U.; Kasha, *M. J. Amer. Chem. Soc. 92* :3293 (1970).

Spectral Terms for Molecules

Water

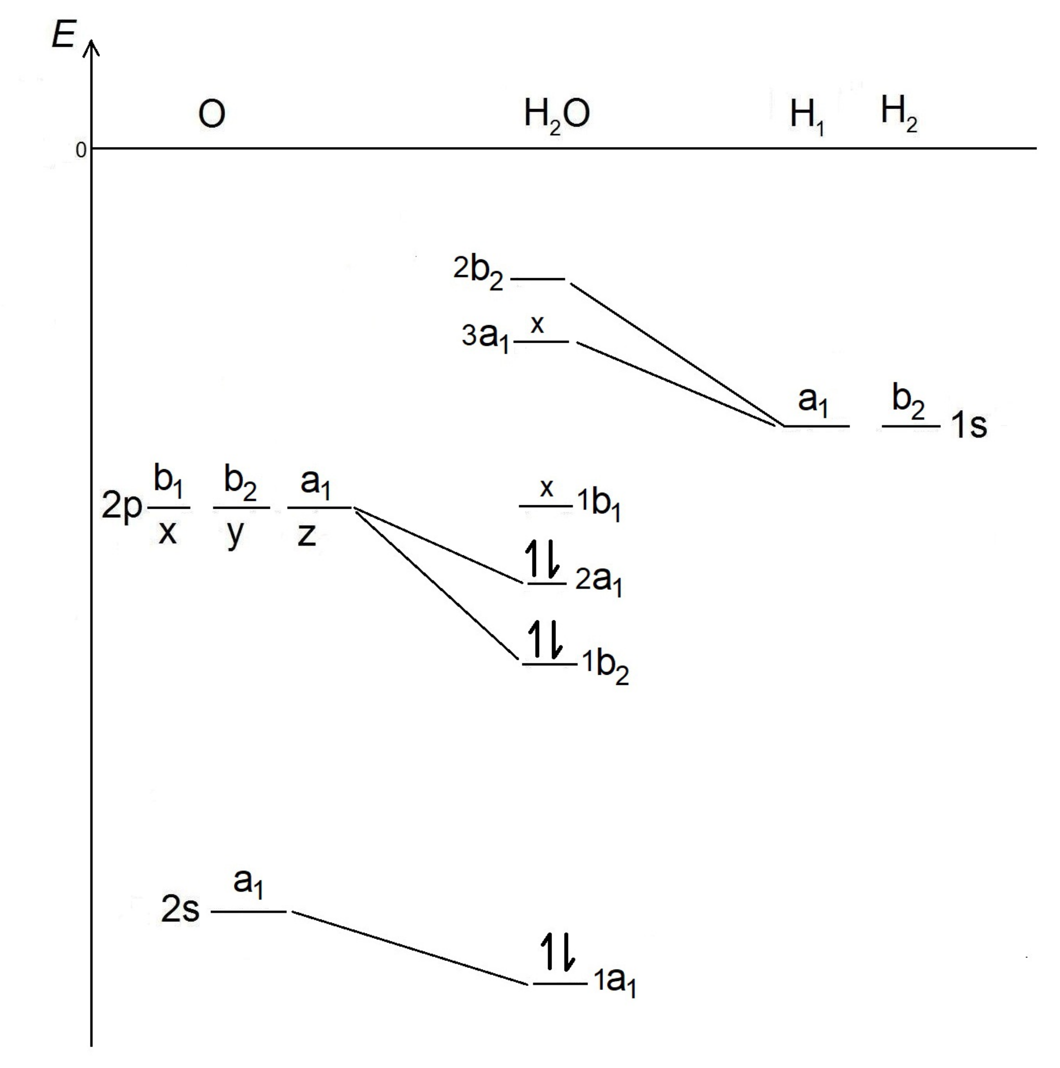
H_2O - C_{2v}

Molecular orbital diagram



H_2O - C_{2v}

Spectroscopic terms for excited states



H_2O - C_{2v}

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	
$B_1 \otimes A_1$	1	-1	1	-1	B_1

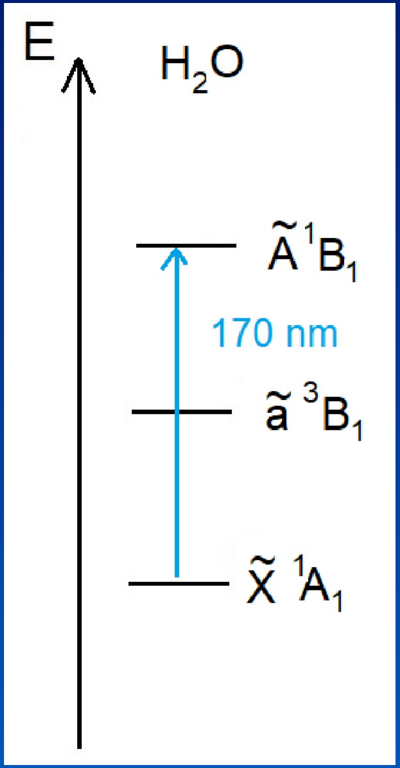
As the unpaired electrons are in different orbitals, the terms can be singlet and triplet.

$^1B_1$ $^3B_1$

H_2O - C_{2v}

Energy levels

For closed shell molecules, the ground state is the totally symmetric irreducible representation, in this case, A_1



Hund’s Rule

Triplets are more stable than singlets

H_2O - C_{2v}

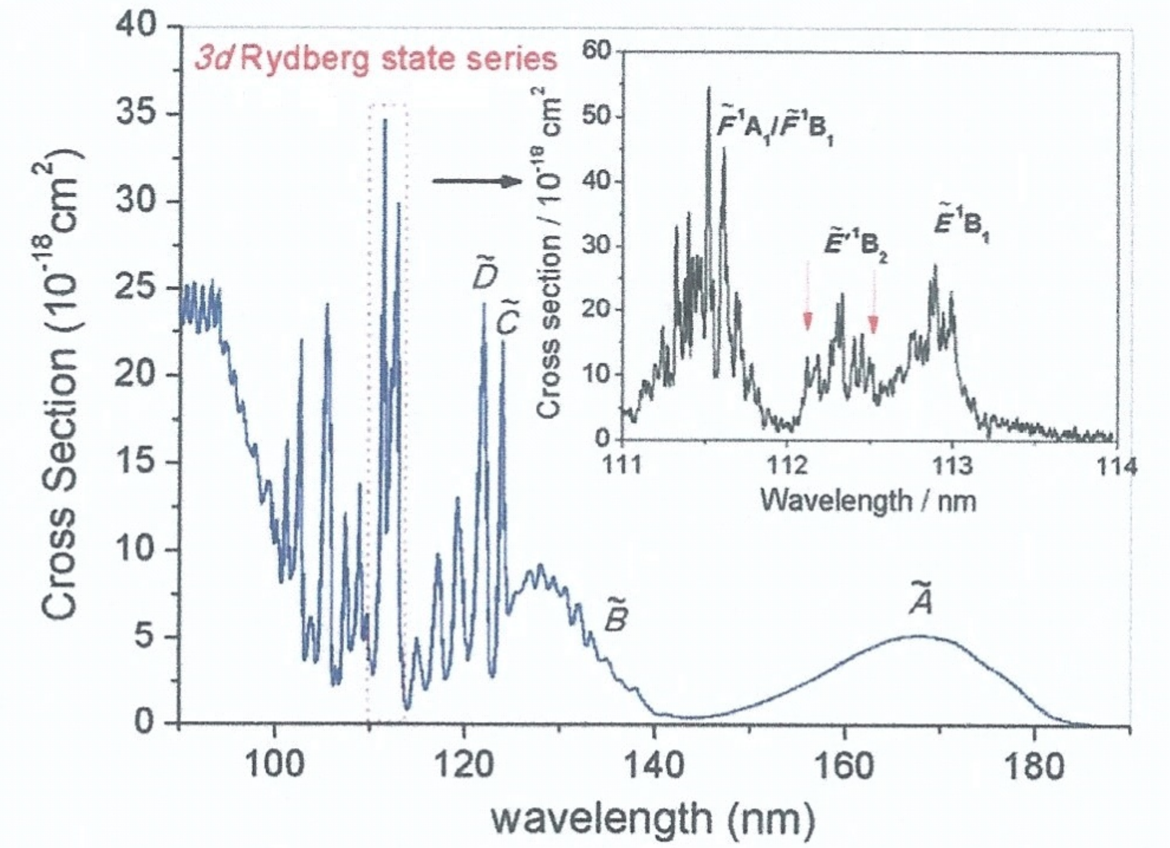
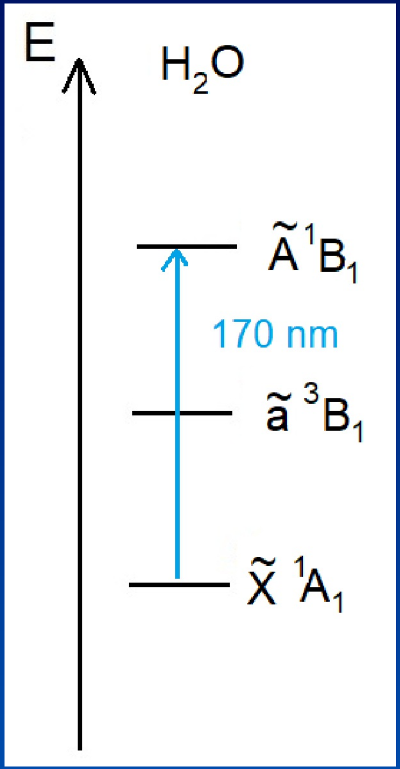


Figure 1. Absorption spectrum of a room temperature sample of H_2O vapor (adapted from ref 4). The spectrum around 114−111 nm with high resolution is adapted from ref 54. The excited electronic states have been marked in the figures. The photolysis wavelengths applied in this work are marked by red arrows.



Luo *et al. J. Phys. Chem. A* *125*:3622 (2021)

Electric Dipole Moment Selections Rules

Transition moment integral

$$M = \int \psi' |\mu| \psi d\tau$$

$|\mu|$ = electric dipole moment operator
ψ = ground state electronic wave function
ψ' = excited state electronic wave function

➢The electronic transition is allowed if $M \neq 0$

➢M will be non zero if $\psi'|\mu|\psi$ belongs or contains the totally symmetric irreducible representation (in this case, A_1)

Electric Dipole Moment Selections Rules

As the electric dipole moment operator can be |x|, |y|, or |z|, we have three possibilities for the transition moment integral.

$$\mathrm{M_x} = \int \psi' |\mathrm{x}| \psi d\tau$$

$$\mathrm{M_y} = \int \psi' |\mathrm{y}| \psi d\tau$$

$$\mathrm{M_z} = \int \psi' |\mathrm{z}| \psi d\tau$$

H_2O - C_{2v}

C_{2v}	E	C_2	$\sigma_v^{(xz)}$	$\sigma'_v{}^{(yz)}$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

For a closed shell molecule, the ground state belongs to the totally symmetric irreducible representation, in this case, A_1.

Electric Dipole Moment Selections Rules

Substituting for the irreducible representations, we have

$$M_x = \int \psi'|x|\psi d\tau = \int \psi'|B_1|A_1 d\tau$$

$$M_y = \int \psi'|y|\psi d\tau = \int \psi'|B_2|A_1 d\tau$$

$$M_z = \int \psi'|z|\psi d\tau = \int \psi'|A_1|A_1 d\tau$$

C_{2v}	E	C_2	$\sigma_v^{(xz)}$	$\sigma'_v{}^{(yz)}$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

Electric Dipole Moment Selections Rules

As A_1 is the totally symmetric irreducible representation, we have the results

$$B_1 \otimes A_1 = B_1$$
$$B_2 \otimes A_1 = B_2$$
$$A_1 \otimes A_1 = A_1$$

then,

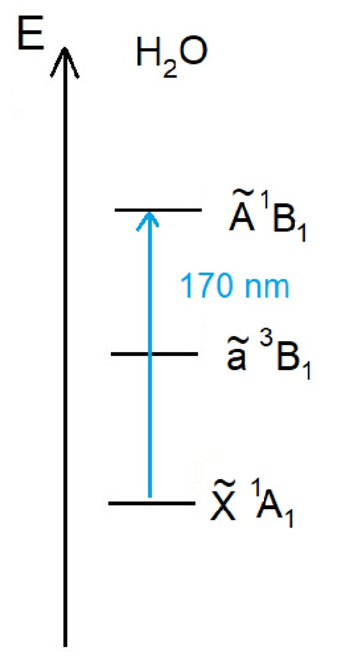
$$M_x = \int \psi' |x| \psi d\tau = \int \psi' |B_1| A_1 d\tau = \int \psi' \otimes B_1 d\tau$$

$$M_y = \int \psi' |y| \psi d\tau = \int \psi' |B_2| A_1 d\tau = \int \psi' \otimes B_2 d\tau$$

$$M_z = \int \psi' |z| \psi d\tau = \int \psi' |A_1| A_1 d\tau = \int \psi' \otimes A_1 d\tau$$

Electric Dipole Moment Selections Rules

Now we can consider the irreducible representation of the excited states. Both of them belongs to B_1



$$M_x = \int \psi' | x | \psi d\tau = \int \psi' | B_1 | A_1 d\tau = \int \psi' \otimes B_1 d\tau = \int B_1 \otimes B_1 d\tau$$

$$M_y = \int \psi' | y | \psi d\tau = \int \psi' | B_2 | A_1 d\tau = \int \psi' \otimes B_2 d\tau = \int B_1 \otimes B_2 d\tau$$

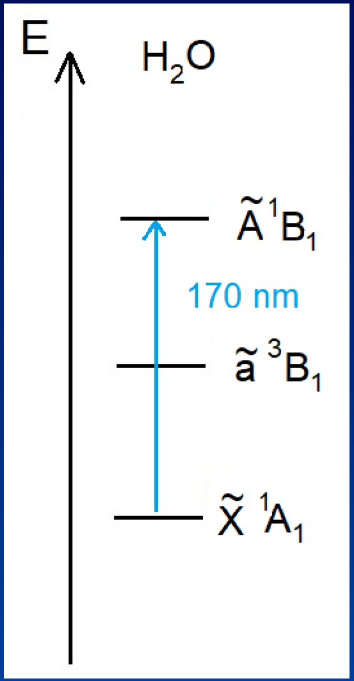
$$M_z = \int \psi' | z | \psi d\tau = \int \psi' | A_1 | A_1 d\tau = \int \psi' \otimes A_1 d\tau = \int B_1 \otimes A_1 d\tau$$

Electric Dipole Moment Selections Rules

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

$B_1 \otimes B_1$	1	1	1	1	A_1
$B_1 \otimes B_2$	1	1	-1	-1	A_2
$B_1 \otimes A_1$	1	1	1	1	B_1

Electric Dipole Moment Selections Rules



In this case, both electronic transitions

$$\tilde{A}\,^1\mathrm{B}_1 \leftrightarrow \tilde{X}\,^1\mathrm{A}_1$$

$$\tilde{a}\,^3\mathrm{B}_1 \leftrightarrow \tilde{X}\,^1\mathrm{A}_1$$

are electric dipole allowed in x.

$$\mathrm{M_x} = \int \psi' |\mathrm{x}| \psi d\tau = \int \psi' |\mathrm{B_1}| \mathrm{A_1} d\tau = \int \psi' \otimes \mathrm{B_1} d\tau = \int \mathrm{B_1} \otimes \mathrm{B_1} d\tau = \mathrm{A_1}$$

$$\mathrm{M_y} = \int \psi' |\mathrm{y}| \psi d\tau = \int \psi' |\mathrm{B_2}| \mathrm{A_1} d\tau = \int \psi' \otimes \mathrm{B_2} d\tau = \int \mathrm{B_1} \otimes \mathrm{B_2} d\tau = \mathrm{A_2}$$

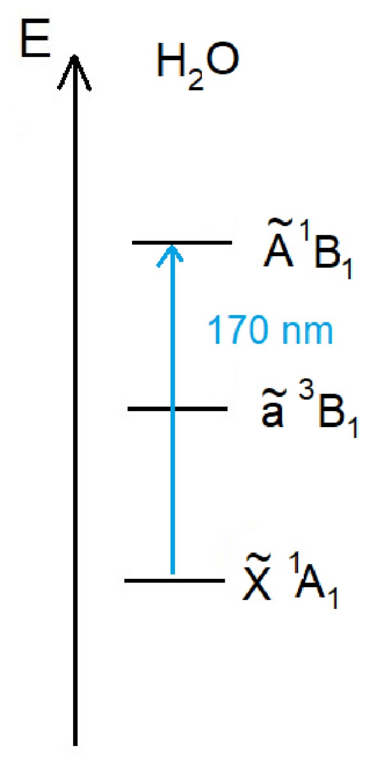
$$\mathrm{M_z} = \int \psi' |\mathrm{z}| \psi d\tau = \int \psi' |\mathrm{A_1}| \mathrm{A_1} d\tau = \int \psi' \otimes \mathrm{A_1} d\tau = \int \mathrm{B_1} \otimes \mathrm{A_1} d\tau = \mathrm{B_1}$$

Selections Rules

However, the spin multiplicity selection rule

$$\Delta S = 0$$

do not allow the transition to the ã triplet state.



H_2O - C_{2v}

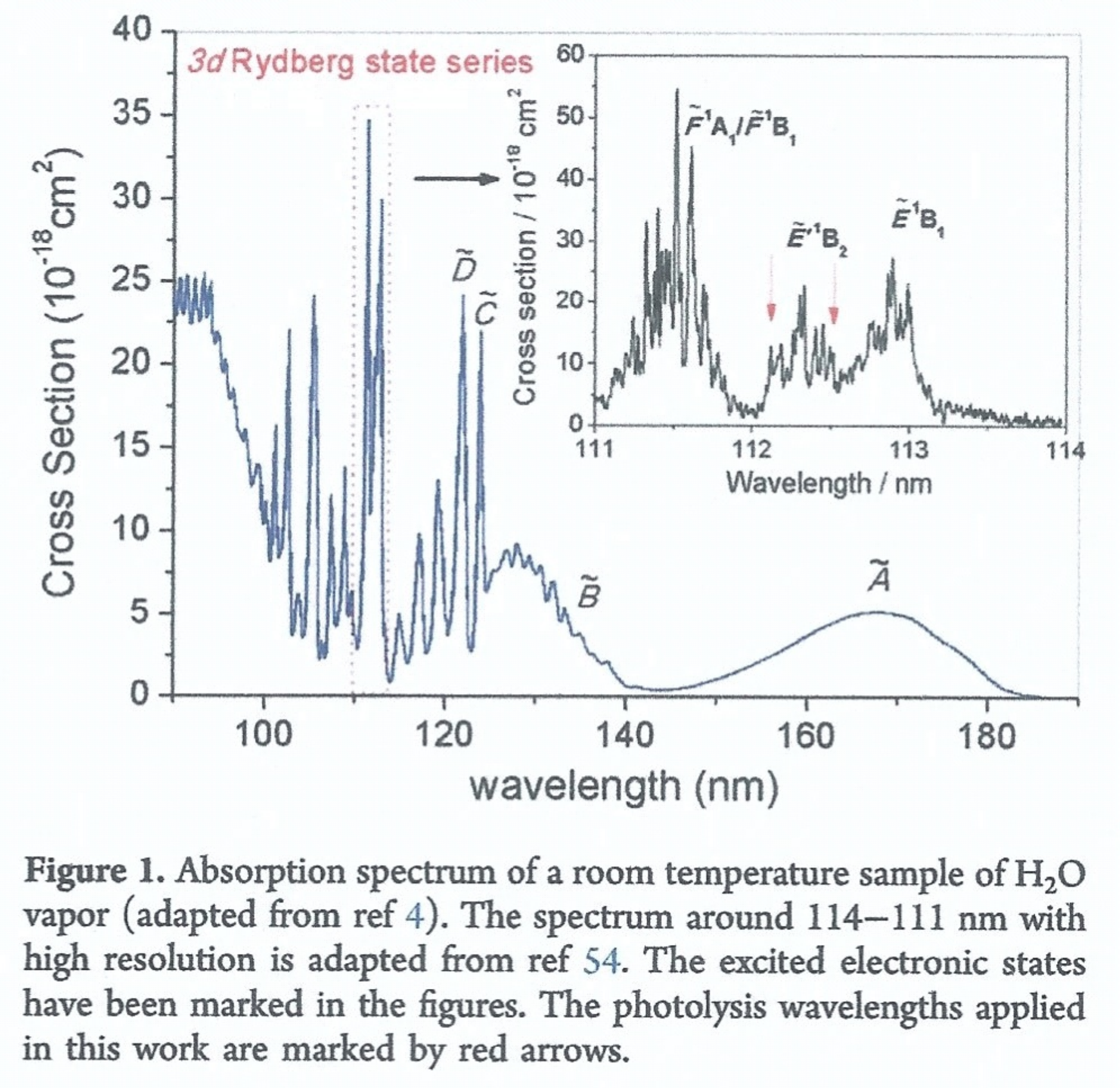
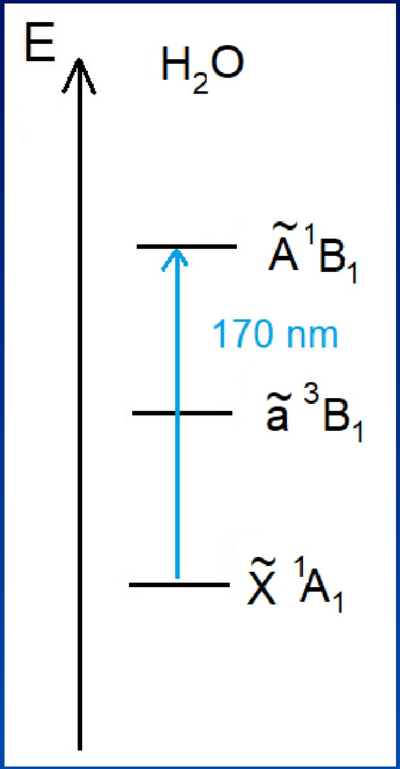


Figure 1. Absorption spectrum of a room temperature sample of H_2O vapor (adapted from ref 4). The spectrum around 114−111 nm with high resolution is adapted from ref 54. The excited electronic states have been marked in the figures. The photolysis wavelengths applied in this work are marked by red arrows.



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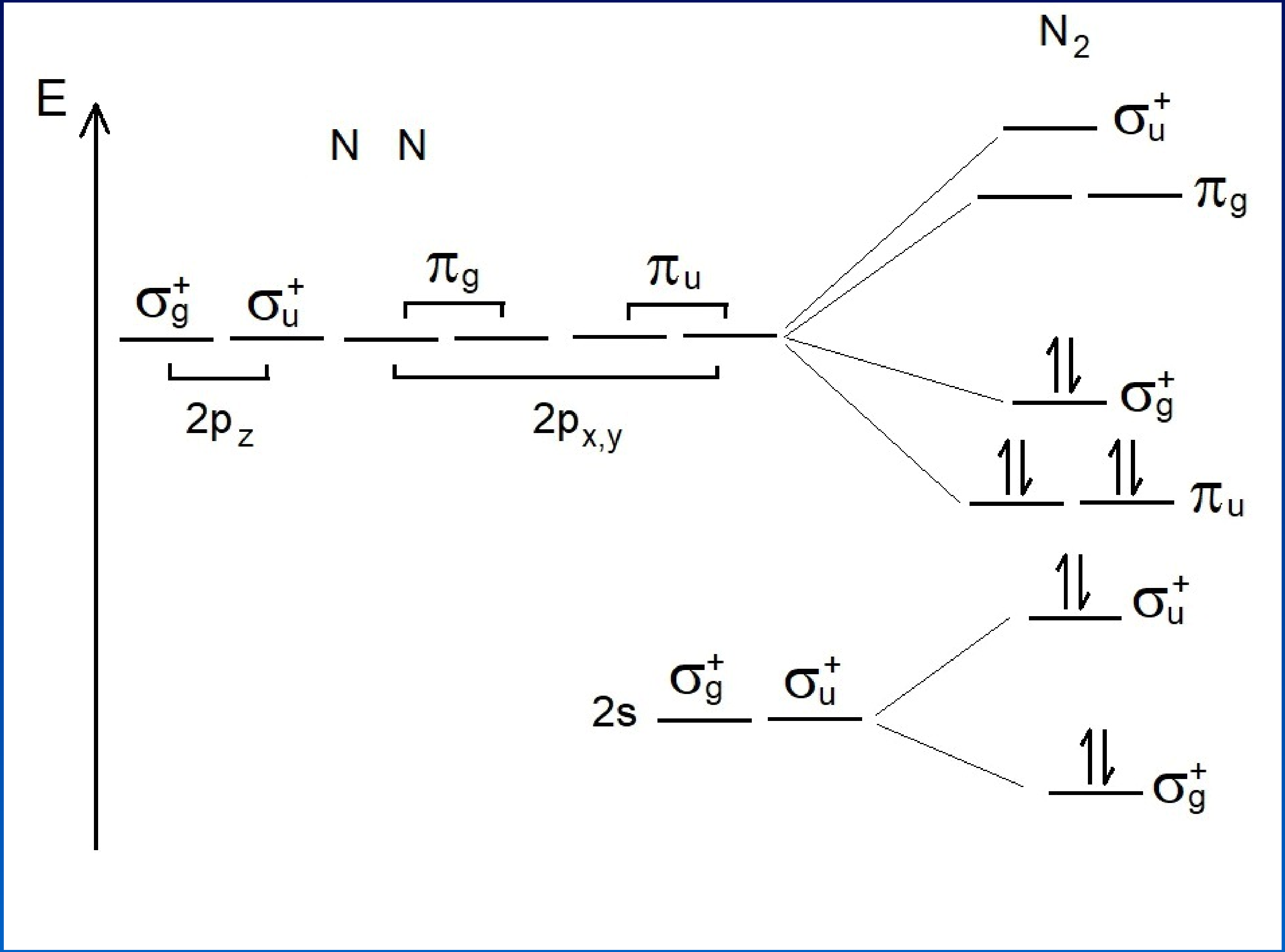
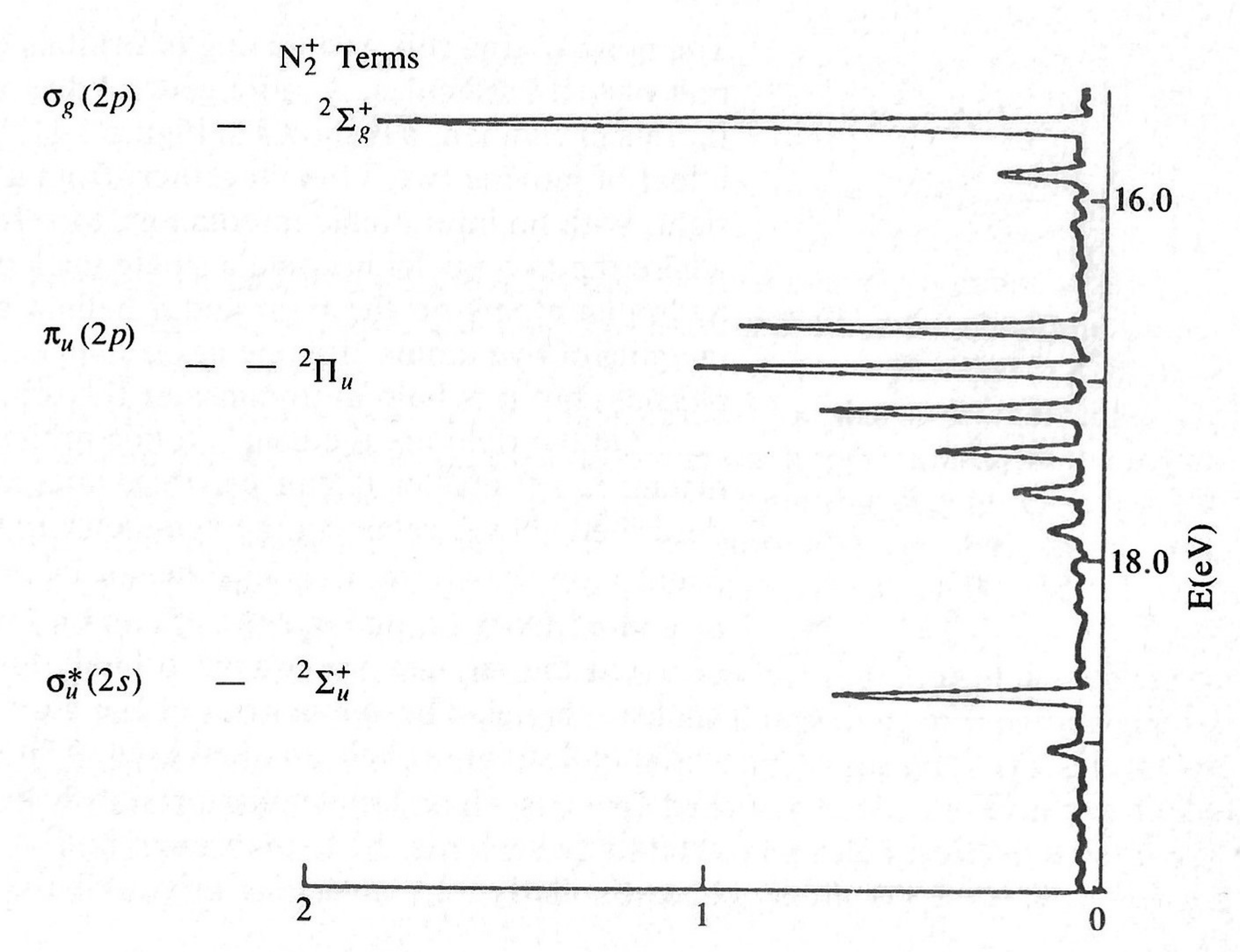
Dinitrogen - N_2

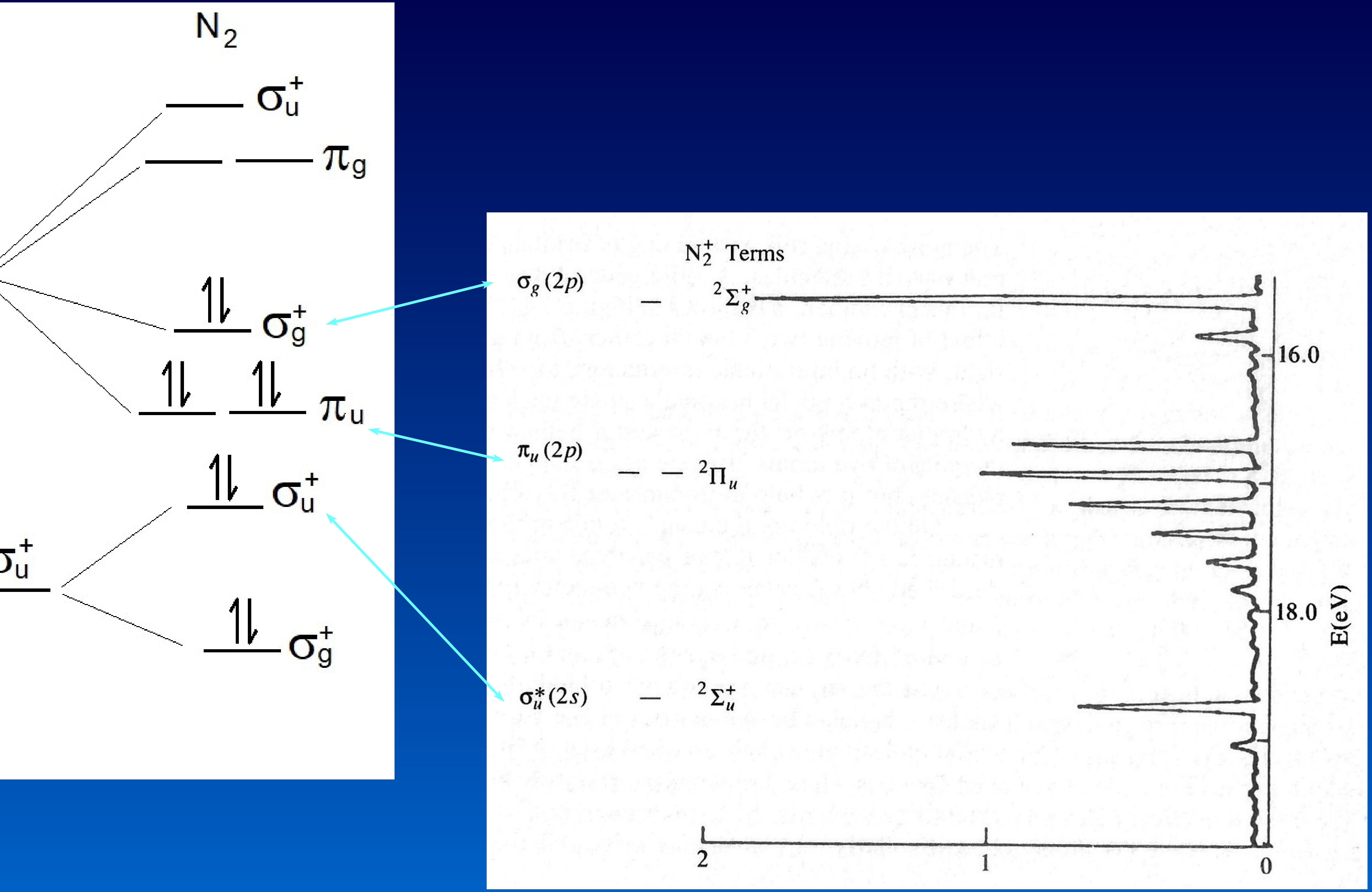
N_2 - $D_{\infty h}$


E
N N
σ_g^+ σ_u^+
π_g
π_u
$2p_z$
$2p_{x,y}$
2s σ_g^+ σ_u^+
N_2
σ_u^+
π_g
σ_g^+
π_u
σ_u^+
σ_g^+



Photoelectron spectra N_2

Gardner, J. L.; Samson, J. A. R. *J. Chem. Phys. 62*:1447 (1975).


N$_2$
σ_u^+
π_g
σ_g^+
π_u
σ_u^+
σ_u^+
σ_g^+
N$_2^+$ Terms
$\sigma_g(2p)$
$^2\Sigma_g^+$
$\pi_u(2p)$
$^2\Pi_u$
$\sigma_u^*(2s)$
$^2\Sigma_u^+$
16.0
18.0
E(eV)
2
1
0

$\mathbf{D}_{\infty \mathbf{h}}$

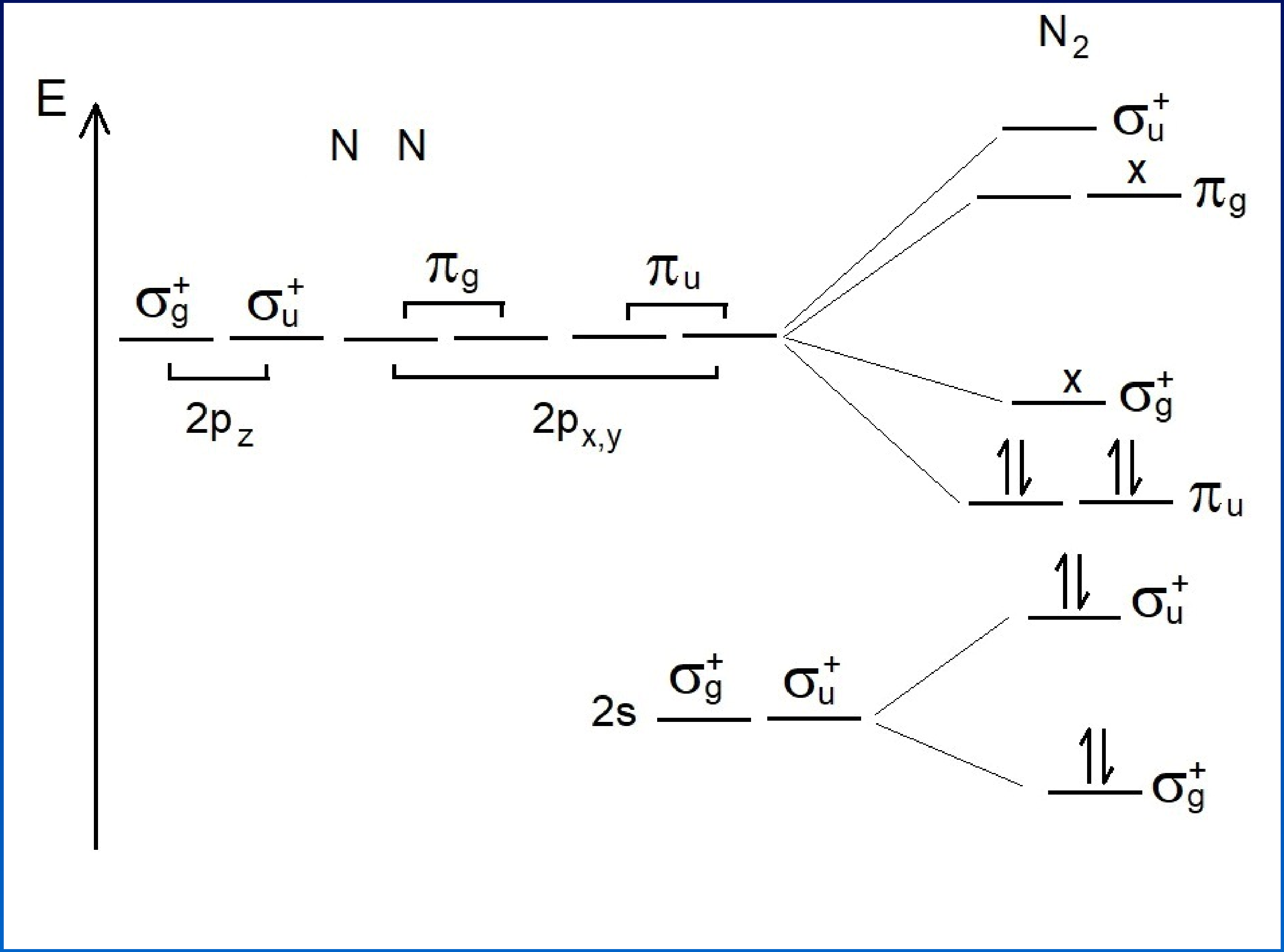
$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_g^+	1	1	1	1	1	1
Σ_g^-	1	1	-1	1	1	-1
Π_g	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0
Δ_g	2	$2\cos2\varphi$	0	2	$2\cos2\varphi$	0
Σ_u^+	1	1	1	-1	-1	-1
Σ_u^-	1	1	-1	-1	-1	1
Π_u	2	$2\cos\varphi$	0	-2	$2\cos\varphi$	0
Δ_u	2	$2\cos2\varphi$	0	-2	$-2\cos2\varphi$	0

$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_g^+	1	1	1	1	1	1
Σ_g^-	1	1	-1	1	1	-1
Π_g	2	0	0	2	0	0
Δ_g	2	-2	0	2	-2	0
Σ_u^+	1	1	1	-1	-1	-1
Σ_u^-	1	1	-1	-1	-1	1
Π_u	2	0	0	-2	0	0
Δ_u	2	-2	0	-2	2	0

Considering $\varphi = 90°$ $\cos\varphi = 0$ $\cos 2\varphi = -1$

N_2 - $D_{\infty h}$



$D_{\infty h}$

$D_{\infty h}$	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2	
Σ_g^+	1	1	1	1	1	1	
Σ_g^-	1	1	-1	1	1	-1	
Π_g	2	0	0	2	0	0	
Δ_g	2	-2	0	2	-2	0	
Σ_u^+	1	1	1	-1	-1	-1	
Σ_u^-	1	1	-1	-1	-1	1	
Π_u	2	0	0	-2	0	0	
Δ_u	2	-2	0	-2	2	0	
$\Pi_g\otimes\Sigma_g^+$	2	0	0	2	0	0	Π_g

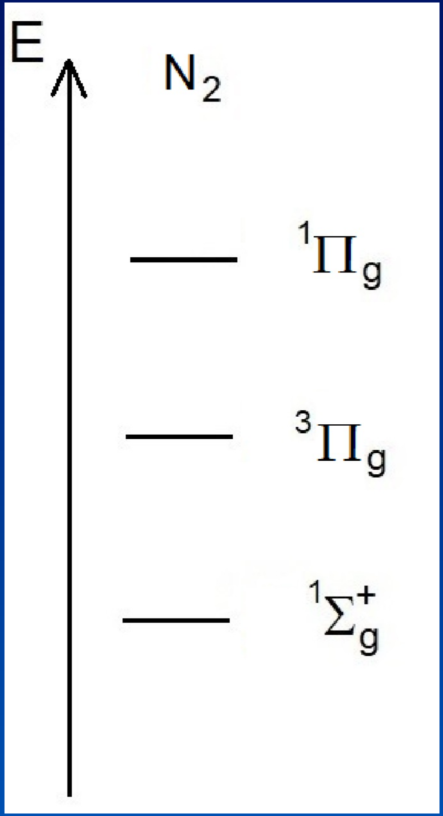
N_2 - $D_{\infty h}$

Determining the spin multiplicity

As the unpaired electrons are in different orbitals, all terms can be singlet and triplet.

$^1\Pi_g$ $^3\Pi_g$

N_2 - $D_{\infty h}$



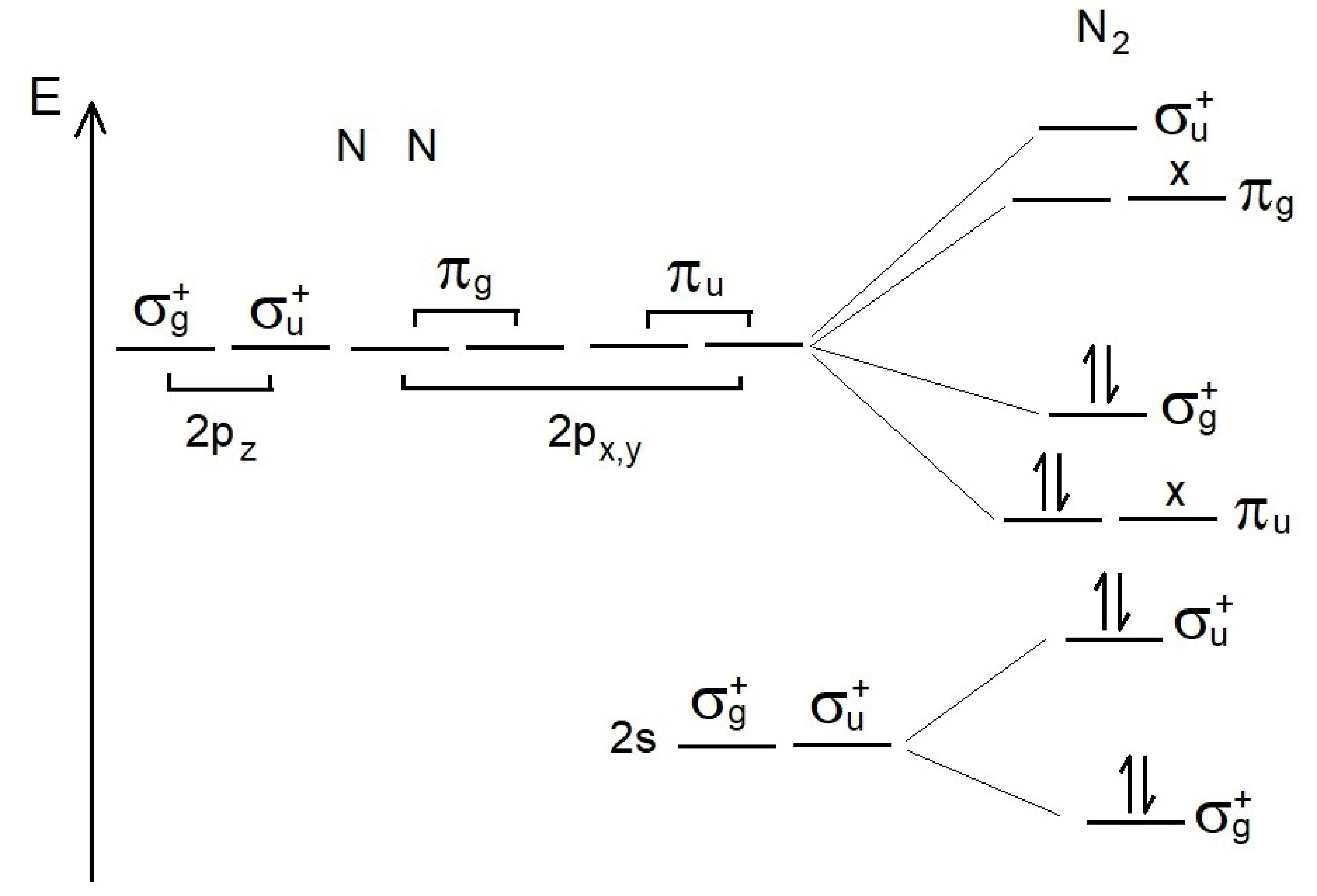
Molecular Energy Levels

Energy of the transition 0-0

cm^{-1}	nm	
69290	144	$^1\Pi_g$ (Lyman-Birge-Hopfield)
59626	168	$^3\Pi_g$
0	0	$^1\Sigma_g^+$

Herzberg, G. *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* , 2nd ed., Krieger Pub. Co., 1989. pg. 552

N_2 - $D_{\infty h}$


E
N N
N$_2$
σ_u^+
x
π_g
σ_g^+ σ_u^+
π_g
π_u
2p$_z$
2p$_{x,y}$
σ_g^+
x
π_u
σ_u^+
2s σ_g^+ σ_u^+
σ_g^+

$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_g^+	1	1	1	1	1	1
Σ_g^-	1	1	-1	1	1	-1
Π_g	2	0	0	2	0	0
Δ_g	2	-2	0	2	-2	0
Σ_u^+	1	1	1	-1	-1	-1
Σ_u^-	1	1	-1	-1	-1	1
Π_u	2	0	0	-2	0	0
Δ_u	2	-2	0	-2	2	0
$\Pi_g \otimes \Pi_u$	4	0	0	-4	0	0

$\Sigma_u^+ \oplus \Sigma_u^- \oplus \Delta_u$

N_2 - $D_{\infty h}$

Determining the spin multiplicity

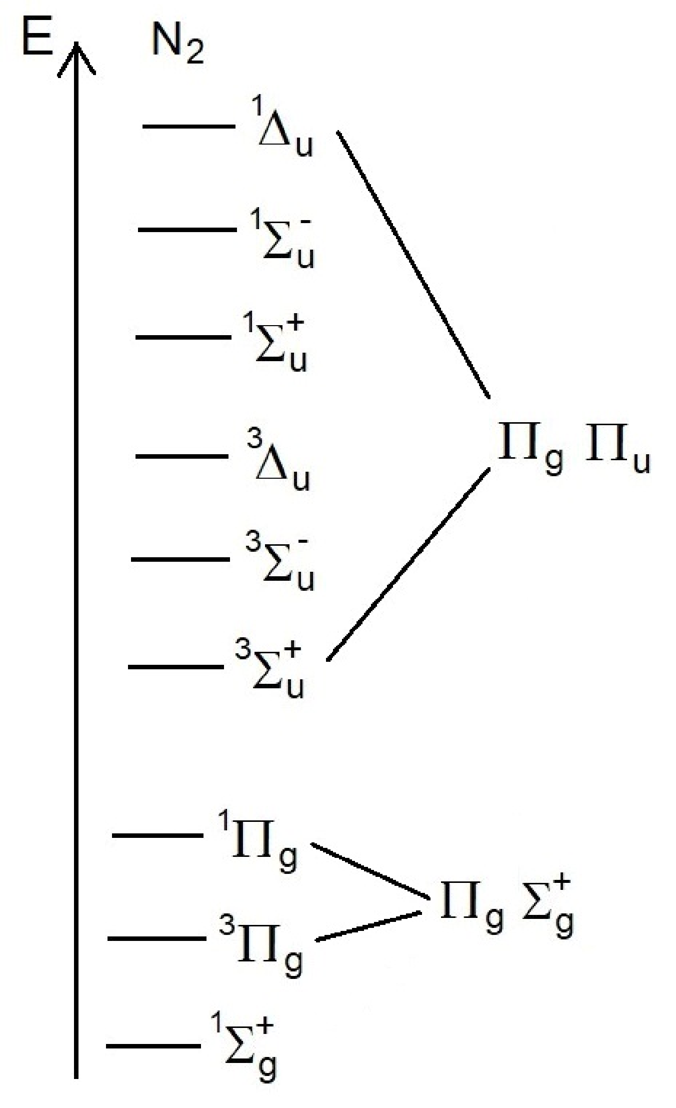
As the unpaired electrons are in different orbitals, all terms can be singlet and triplet.

$^1\Sigma_u^+$ $^1\Sigma_u^-$ $^1\Delta_u$

$^3\Sigma_u^+$ $^3\Sigma_u^-$ $^3\Delta_u$

Harris, D. C.; Bertolucci, M. D. ; *Symmetry and Spectroscopy* , Dover: New York 1978. pg 324

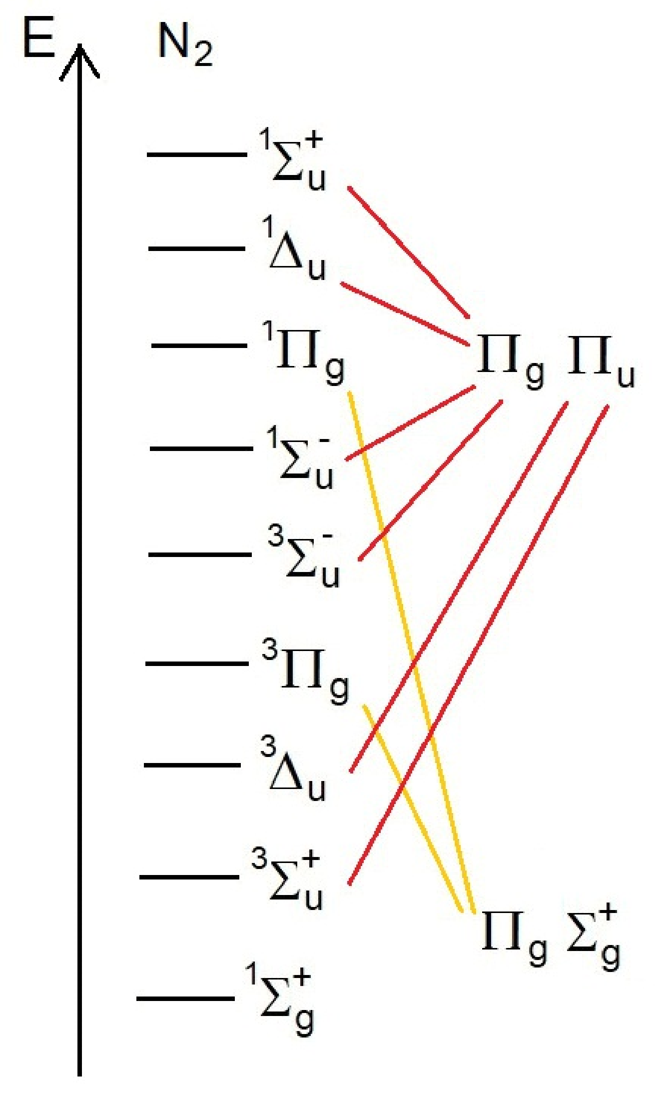
N_2 - $D_{\infty h}$



Hund’s Rules do not apply strictly to excited states.

This is a preliminar ordering.

N_2 - $D_{\infty h}$

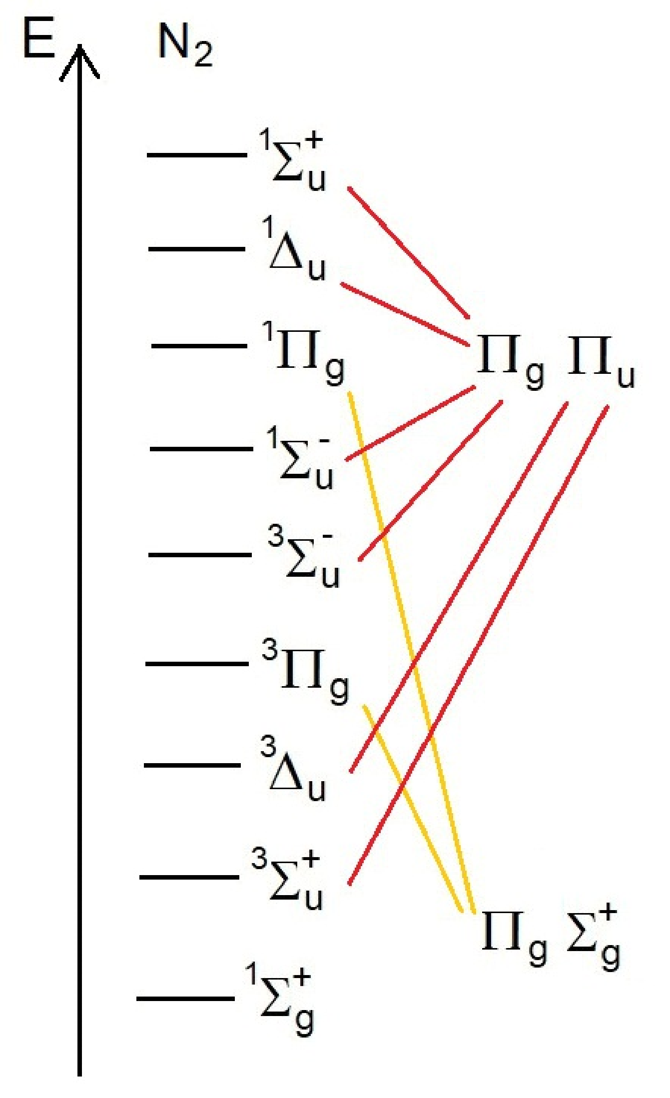


Energy of the transition 0-0

cm^{-1}	nm	
69290	144	$^1\Pi_g$
67568	148	$^1\Sigma_u^-$
65789	152	$^3\Sigma_u^-$
59626	168	$^3\Pi_g$
56818	176	$^3\Delta_u$
50206	199	$^3\Sigma_u^+$
0	0	$^1\Sigma_g^+$

Gilmore, F. R. *J. Quant. Spectrosc. Radiat. Transfer* 5:36-389 (1965)

N_2 - $D_{\infty h}$



Energy of the transition 0-0

cm^{-1}	nm	
69290	144	$a\ ^1\Pi_g$
67568	148	$a'\ ^1\Sigma_u^-$
65789	152	$B'\ ^3\Sigma_u^-$
59626	168	$B\ ^3\Pi_g$
56818	176	– $^3\Delta_u$
50206	199	$A\ ^3\Sigma_u^+$
0	0	$X\ ^1\Sigma_g^+$

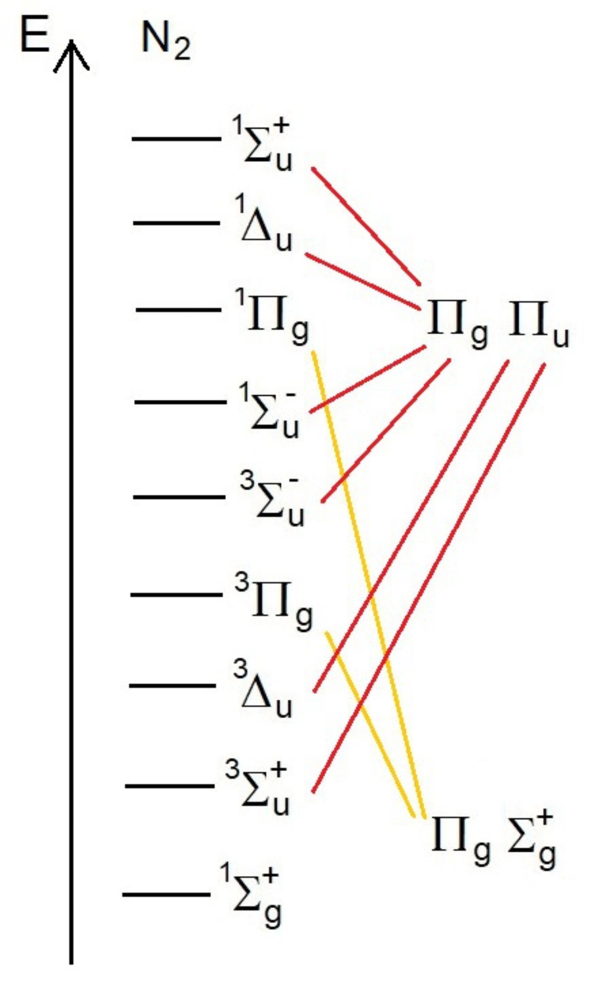
Gilmore, F. R. *J. Quant. Spectrosc. Radiat. Transfer* 5:36-389 (1965)

Rules to name the energy levels
Only for nitrogen[1,2,3]

- The ground state is indicated by *X*
- Lowercase letters *a*, *b*, *c* ... are used to indicate excited states with the same spin multiplicity of the ground state.
- Capital letters *A*, *B*, *C* ... are used for the excited states with a spin multiplicity different than the ground state.
- A tilde (~) is used above the terms for nonlinear poliatomic molecules, to distinguish them from the symmetry labels.

1. Bernath, P. F., *Spectra of Atoms and Molecules*, 3ª ed., Oxford University Press, 2016. pg. 344.
2. Cohen, E. R. *et al*., eds., *Grandezas, Unidades de Símbolos em Físico-Química*, 3ª ed., IUPAC-SBQ, 2018. pg. 35.
3. Herzberg, G. *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*, 2nd ed., Krieger Pub. Co., 1989. pg. 552

N_2 - $D_{\infty h}$



Energy of the transition 0-0

cm^{-1}	nm		
69290	144	$a\ ^1\Pi_g$	(Lyman-Birge-Hopfield)
67568	148	$a'\ ^1\Sigma_u^-$	(Wilkinson-Ogawa-Tanaka II)
65789	152	$B'\ ^3\Sigma_u^-$	(Wilkinson-Ogawa-Tanaka I)
59626	168	$B\ ^3\Pi_g$	
56818	176	– $^3\Delta_u$	
50206	199	$A\ ^3\Sigma_u^+$	(Vegard-Kaplan)
0	0	$X\ ^1\Sigma_g^+$	

Gilmore, F. R. *J. Quant. Spectrosc. Radiat. Transfer* 5:36-389 (1965)

Spin and Symmetry Selections Rules

Allowed (yes) and forbidden (no) bands

cm^{-1}	nm		$\Delta S = 0$	g ↔ u	$\Delta\Lambda = 0, \pm 1$	$\Sigma^+ \leftarrow$no$\rightarrow \Sigma^-$
69290	144	$a\ ^1\Pi_g$	yes	no	yes	yes
67568	148	$a'\ ^1\Sigma_u^-$	yes	yes	yes	no
65789	152	$B'\ ^3\Sigma_u^-$	no	yes	no	no
59626	168	$B\ ^3\Pi_g$	no	no	yes	yes
56818	176	– $^3\Delta_u$	no	yes	no	–
50206	199	$A\ ^3\Sigma_u^+$	no	yes	yes	yes
0	0	$X\ ^1\Sigma_g^+$				

As a conclusion, all transitions starting from the ground state are forbiden.

Electric Dipole Moment Selection Rule

As the dipole moment operator can be |x|, |y|, or |z|, we have three possibilities for the transition moment integral.

$$\mathrm{M_x} = \int \psi' |\mathrm{x}| \psi d\tau$$

$$\mathrm{M_y} = \int \psi' |\mathrm{y}| \psi d\tau$$

$$\mathrm{M_z} = \int \psi' |\mathrm{z}| \psi d\tau$$

$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2	
Σ_g^+	1	1	1	1	1	1	
Σ_g^-	1	1	-1	1	1	-1	
Π_g	2	0	0	2	0	0	
Δ_g	2	-2	0	2	-2	0	
Σ_u^+	1	1	1	-1	-1	-1	z
Σ_u^-	1	1	-1	-1	-1	1	
Π_u	2	0	0	-2	0	0	(x,y)
Δ_u	2	-2	0	-2	2	0	

Considering $\varphi = 90°$ $\cos\varphi = 0$ $\cos 2\varphi = -1$

Electric Dipole Moment Selection Rule

Substituting |x|, |y|, and |z| by their irreducible representations, we have,

$$\mathrm{M_x} = \int \psi' |\mathrm{x}| \psi d\tau = \int \psi' |\Pi_\mathrm{u}| \psi d\tau$$

$$\mathrm{M_y} = \int \psi' |\mathrm{y}| \psi d\tau = \int \psi' |\Pi_\mathrm{u}| \psi d\tau$$

$$\mathrm{M_z} = \int \psi' |\mathrm{z}| \psi d\tau = \int \psi' |\Sigma_\mathrm{u}{}^{+}| \psi d\tau$$

Electric Dipole Moment Selection Rule

As the ground state is Σ_g^+ we have

$$M_x = \int \psi' |x| \psi d\tau = \int \psi' |\Pi_u| \psi d\tau = \int \psi' |\Pi_u| \Sigma_g^+ d\tau$$

$$M_y = \int \psi' |y| \psi d\tau = \int \psi' |\Pi_u| \psi d\tau = \int \psi' |\Pi_u| \Sigma_g^+ d\tau$$

$$M_z = \int \psi' |z| \psi d\tau = \int \psi' |\Sigma_u^+| \psi d\tau = \int \psi' |\Sigma_u^+| \Sigma_g^+ d\tau$$

Electric Dipole Moment Selection Rule

As the Σ_g^+ irreducible representation is the totally simmetric, we have

$$M_x = \int \psi' |x| \psi d\tau = \int \psi' |\Pi_u| \psi d\tau = \int \psi' |\Pi_u| \Sigma_g^+ d\tau = \int \psi' \Pi_u d\tau$$

$$M_y = \int \psi' |y| \psi d\tau = \int \psi' |\Pi_u| \psi d\tau = \int \psi' |\Pi_u| \Sigma_g^+ d\tau = \int \psi' \Pi_u d\tau$$

$$M_z = \int \psi' |z| \psi d\tau = \int \psi' |\Sigma_u^+| \psi d\tau = \int \psi' |\Sigma_u^+| \Sigma_g^+ d\tau = \int \psi' \Sigma_u^+ d\tau$$

Electric Dipole Moment Selection Rule

Considering the Lyman-Birge- Hopfield transition

$$a\ {}^1\Pi_g \leftrightarrow X\,\Sigma_g^+$$

the excited state is Π_g , and we have

$$M_x = \int \psi' |x| \psi d\tau = \int \psi' |\Pi_u| \psi d\tau = \int \psi' |\Pi_u| \Sigma_g^+ d\tau = \int \psi' \Pi_u d\tau = \int \Pi_g \otimes \Pi_u d\tau$$

$$M_y = \int \psi' |y| \psi d\tau = \int \psi' |\Pi_u| \psi d\tau = \int \psi' |\Pi_u| \Sigma_g^+ d\tau = \int \psi' \Pi_u d\tau = \int \Pi_g \otimes \Pi_u d\tau$$

$$M_z = \int \psi' |z| \psi d\tau = \int \psi' |\Sigma_u^+| \psi d\tau = \int \psi' |\Sigma_u^+| \Sigma_g^+ d\tau = \int \psi' \Sigma_u^+ d\tau = \int \Pi_g \otimes \Sigma_u^+ d\tau$$

$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_g^+	1	1	1	1	1	1
Σ_g^-	1	1	-1	1	1	-1
Π_g	2	0	0	2	0	0
Δ_g	2	-2	0	2	-2	0
Σ_u^+	1	1	1	-1	-1	-1
Σ_u^-	1	1	-1	-1	-1	1
Π_u	2	0	0	-2	0	0
Δ_u	2	-2	0	-2	2	0
$\Pi_g \otimes \Pi_u$	4	0	0	-4	0	0

$$\Sigma_u^+ \oplus \Sigma_u^- \oplus \Delta_u$$

Electric Dipole Moment Selection Rule

As can be seen,

$$M_x = 0 \qquad M_y = 0$$

because they do not contain Σ_g^+ (totally symmetric irreducible representation)

$$M_x = \int \Pi_g \otimes \Pi_u d\tau = \int (\Sigma_u^+ \oplus \Sigma_u^- \oplus \Delta_u) d\tau = 0$$

$$M_y = \int \Pi_g \otimes \Pi_u d\tau = \int (\Sigma_u^+ \oplus \Sigma_u^- \oplus \Delta_u) d\tau = 0$$

$$M_z = \int \psi' |\mathrm{z}| \psi d\tau = \int \psi' |\Sigma_u^+| \psi d\tau = \int \psi' |\Sigma_u^+| \Sigma_g^+ d\tau = \int \psi' \Sigma_u^+ d\tau = \int \Pi_g \otimes \Sigma_u^+ d\tau$$

$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2	
Σ_g^+	1	1	1	1	1	1	
Σ_g^-	1	1	-1	1	1	-1	
Π_g	2	0	0	2	0	0	
Δ_g	2	-2	0	2	-2	0	
Σ_u^+	1	1	1	-1	-1	-1	
Σ_u^-	1	1	-1	-1	-1	1	
Π_u	2	0	0	-2	0	0	
Δ_u	2	-2	0	-2	2	0	
$\Pi_g \otimes \Sigma_u^+$	2	0	0	-2	0	0	Π_u

Electric Dipole Moment Selection Rule

As can be seen,

$$M_z = 0$$

because it does not contain Σ_g^+ (totally symmetric irreducible representation)

$$M_x = \int \Pi_g \otimes \Pi_u d\tau = \int (\Sigma_u^+ \oplus \Sigma_u^- \oplus \Delta_u) d\tau = 0$$

$$M_y = \int \Pi_g \otimes \Pi_u d\tau = \int (\Sigma_u^+ \oplus \Sigma_u^- \oplus \Delta_u) d\tau = 0$$

$$M_z = \int \Pi_g \otimes \Sigma_u^+ d\tau = \int \Pi_u d\tau = 0$$

Electric Dipole Moment Selection Rule

In this way, the transition

$$a\,{}^1\Pi_g - X\,{}^1\Sigma_g^+ \text{ (Lyman-Birge-Hopfield)}$$

is not allowed by electric dipole moment, confirming our previous conclusion.

Dioxigen - O_2

Electric Dipole Moment Selection Rule

O_2 - $D_{\infty h}$

Spin and Symmetry Selections Rules

Allowed (yes) and forbidden (no) bands

cm^{-1}	nm		$\Delta S = 0$	$g \leftrightarrow u$	$\Delta\Lambda = 0, \pm 1$	$\Sigma^+ \leftarrow \text{no} \rightarrow \Sigma^-$
49358	203	$B\ {}^3\Sigma_u^-$	yes	yes	yes	yes
35007	285	$A\ {}^3\Sigma_u^+$	yes	yes	yes	no
34319	291	$C\ {}^3\Delta_u$	yes	yes	no	–
32664	306	$c\ {}^1\Sigma_u^-$	no	yes	yes	yes
13120	762	$b\ {}^1\Sigma_g^+$	no	no	yes	no
7882	1268	$a\ {}^1\Delta_g$	no	no	no	–
0	0	$X\ {}^3\Sigma_g^-$				

Although forbidden, Band A is observed in the spectra by Khan and Kasha. Band B is responsible for the absorption of UV light with λ < 200 nm in the high atmosphere.

$D_{\infty h}$

$D_{\infty h}$	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2	
Σ_g^+	1	1	1	1	1	1	
Σ_g^-	1	1	-1	1	1	-1	
Π_g	2	0	0	2	0	0	
Δ_g	2	-2	0	2	-2	0	
Σ_u^+	1	1	1	-1	-1	-1	z
Σ_u^-	1	1	-1	-1	-1	1	
Π_u	2	0	0	-2	0	0	(x,y)
Δ_u	2	-2	0	-2	2	0	

Considering $\varphi = 90°$ $\cos\varphi = 0$ $\cos 2\varphi = -1$

Electric Dipole Moment Selection Rule

As the electric dipole moment operator can be |x|, |y|, or |z|, we have three possibilities for the transition moment integral.

$$\mathrm{M_x} = \int \psi' |\mathrm{x}| \psi d\tau = \int \psi' |\Pi_\mathrm{u}| \psi d\tau$$

$$\mathrm{M_y} = \int \psi' |\mathrm{y}| \psi d\tau = \int \psi' |\Pi_\mathrm{u}| \psi d\tau$$

$$\mathrm{M_z} = \int \psi' |\mathrm{z}| \psi d\tau = \int \psi' |\Sigma_\mathrm{u}{}^{+}| \psi d\tau$$

Electric Dipole Moment Selection Rule

As the O_2 ground state is Σ_g^-, we have

$$M_x = \int \psi' |x| \psi d\tau = \int \psi' |\Pi_u| \psi d\tau = \int \psi' |\Pi_u| \Sigma_g^- d\tau$$

$$M_y = \int \psi' |y| \psi d\tau = \int \psi' |\Pi_u| \psi d\tau = \int \psi' |\Pi_u| \Sigma_g^- d\tau$$

$$M_z = \int \psi' |z| \psi d\tau = \int \psi' |\Sigma_u^+| \psi d\tau = \int \psi' |\Sigma_u^+| \Sigma_g^- d\tau$$

$D_{\infty h}$

$D_{\infty h}$	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2	
Σ_g^+	1	1	1	1	1	1	
Σ_g^-	1	1	-1	1	1	-1	
Π_g	2	0	0	2	0	0	
Δ_g	2	-2	0	2	-2	0	
Σ_u^+	1	1	1	-1	-1	-1	
Σ_u^-	1	1	-1	-1	-1	1	
Π_u	2	0	0	-2	0	0	
Δ_u	2	-2	0	-2	2	0	
$\Pi_u \otimes \Sigma_g^-$	2	0	0	-2	0	0	Π_u

Electric Dipole Moment Selection Rule

$$\mathrm{M_x} = \int \psi' |\mathrm{x}| \psi d\tau = \int \psi' |\Pi_\mathrm{u}| \psi d\tau = \int \psi' |\Pi_\mathrm{u}| \Sigma_g^{-} d\tau = \int \psi' |\Pi_\mathrm{u}| d\tau$$

$$\mathrm{M_y} = \int \psi' |\mathrm{y}| \psi d\tau = \int \psi' |\Pi_\mathrm{u}| \psi d\tau = \int \psi' |\Pi_\mathrm{u}| \Sigma_g^{-} d\tau = \int \psi' |\Pi_\mathrm{u}| d\tau$$

$$\mathrm{M_z} = \int \psi' |\mathrm{z}| \psi d\tau = \int \psi' |\Sigma_\mathrm{u}^{+}| \psi d\tau = \int \psi' |\Sigma_\mathrm{u}^{+}| \Sigma_g^{-} d\tau$$

$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2	
Σ_g^+	1	1	1	1	1	1	
Σ_g^-	1	1	-1	1	1	-1	
Π_g	2	0	0	2	0	0	
Δ_g	2	-2	0	2	-2	0	
Σ_u^+	1	1	1	-1	-1	-1	
Σ_u^-	1	1	-1	-1	-1	1	
Π_u	2	0	0	-2	0	0	
Δ_u	2	-2	0	-2	2	0	
$\Sigma_u^+ \otimes \Sigma_g^-$	1	1	-1	-1	-1	1	Σ_u^-

Electric Dipole Moment Selection Rule

$$\mathrm{M_x} = \int \psi'|\mathrm{x}|\psi d\tau = \int \psi'|\Pi_\mathrm{u}|\psi d\tau = \int \psi'|\Pi_\mathrm{u}|\Sigma_\mathrm{g}^{-} d\tau = \int \psi'|\Pi_\mathrm{u}| d\tau$$

$$\mathrm{M_y} = \int \psi'|\mathrm{y}|\psi d\tau = \int \psi'|\Pi_\mathrm{u}|\psi d\tau = \int \psi'|\Pi_\mathrm{u}|\Sigma_\mathrm{g}^{-} d\tau = \int \psi'|\Pi_\mathrm{u}| d\tau$$

$$\mathrm{M_z} = \int \psi'|\mathrm{z}|\psi d\tau = \int \psi'|\Sigma_\mathrm{u}^{+}|\psi d\tau = \int \psi'|\Sigma_\mathrm{u}^{+}|\Sigma_\mathrm{g}^{-} d\tau = \int \psi'|\Sigma_\mathrm{u}^{-}| d\tau$$

Electric Dipole Moment Selection Rule

Considering the transition

$$B\,{}^3\Sigma_u^- \leftrightarrow X\,{}^3\Sigma_g^- \text{ (Schumann-Runge system)}$$

the excited state is Σ_u^-. Substituting, we have

$$M_x = \int \psi' |x| \psi d\tau = \int \psi' |\Pi_u| \psi d\tau = \int \psi' |\Pi_u| \Sigma_g^- d\tau = \int \psi' |\Pi_u| d\tau = \int \Sigma_u^- \otimes \Pi_u d\tau$$

$$M_y = \int \psi' |y| \psi d\tau = \int \psi' |\Pi_u| \psi d\tau = \int \psi' |\Pi_u| \Sigma_g^- d\tau = \int \psi' |\Pi_u| d\tau = \int \Sigma_u^- \otimes \Pi_u d\tau$$

$$M_z = \int \psi' |z| \psi d\tau = \int \psi' |\Sigma_u^+| \psi d\tau = \int \psi' |\Sigma_u^+| \Sigma_g^- d\tau = \int \psi' |\Sigma_u^-| d\tau = \int \Sigma_u^- \otimes \Sigma_u^- d\tau$$

$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2	
Σ_g^+	1	1	1	1	1	1	
Σ_g^-	1	1	-1	1	1	-1	
Π_g	2	0	0	2	0	0	
Δ_g	2	-2	0	2	-2	0	
Σ_u^+	1	1	1	-1	-1	-1	
Σ_u^-	1	1	-1	-1	-1	1	
Π_u	2	0	0	-2	0	0	
Δ_u	2	-2	0	-2	2	0	
$\Sigma_u^- \otimes \Pi_u$	2	0	0	2	0	0	Π_g

Electric Dipole Moment Selection Rule

Considering the transition

$$B\ {}^3\Sigma_u^- \leftrightarrow X\ {}^3\Sigma_g^-\ \text{(Schumann-Runge system)}$$

$$\mathrm{M_x} = \int \psi' |\mathrm{x}| \psi d\tau = \int \Sigma_u^- \otimes \Pi_u d\tau = \int \Pi_g d\tau = 0$$

$$\mathrm{M_y} = \int \psi' |\mathrm{y}| \psi d\tau = \int \Sigma_u^- \otimes \Pi_u d\tau = \int \Pi_g d\tau = 0$$

$$\mathrm{M_z} = \int \psi' |\mathrm{z}| \psi d\tau = \int \psi' |\Sigma_u^+| \psi d\tau = \int \psi' |\Sigma_u^+| \Sigma_g^- d\tau = \int \psi' |\Sigma_u^-| d\tau = \int \Sigma_u^- \otimes \Sigma_u^- d\tau$$

$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2	
Σ_g^+	1	1	1	1	1	1	
Σ_g^-	1	1	-1	1	1	-1	
Π_g	2	0	0	2	0	0	
Δ_g	2	-2	0	2	-2	0	
Σ_u^+	1	1	1	-1	-1	-1	
Σ_u^-	1	1	-1	-1	-1	1	
Π_u	2	0	0	-2	0	0	
Δ_u	2	-2	0	-2	2	0	
$\Sigma_u^- \otimes \Sigma_u^-$	1	1	1	1	1	1	Σ_g^+

Electric Dipole Moment Selection Rule

Considering the transition

$$B\ {}^3\Sigma_u^- \leftrightarrow X\ {}^3\Sigma_g^-\ \text{(Schumann-Runge system)}$$

$$\mathrm{M_x} = \int \psi' |\mathrm{x}| \psi d\tau = \int \Sigma_u^- \otimes \Pi_u d\tau = \int \Pi_g d\tau = 0$$

$$\mathrm{M_y} = \int \psi' |\mathrm{y}| \psi d\tau = \int \Sigma_u^- \otimes \Pi_u d\tau = \int \Pi_g d\tau = 0$$

$$\mathrm{M_z} = \int \psi' |\mathrm{z}| \psi d\tau = \int \Sigma_u^- \otimes \Sigma_u^- d\tau = \int \Sigma_g^+ d\tau \neq 0$$

Electric Dipole Moment Selection Rule

As $M_z = \Sigma_g^+$ (the totally symmetric irreducible representation) it is non zero.

$$M_z \neq 0$$

and the O_2 transition

$$B\,{}^3\Sigma_u^- \leftrightarrow X\,{}^3\Sigma_g^- \text{ (Schumann-Runge system)}$$

is allowed by electric dipole moment, confirming our previous conclusion.

$$M_x = \int \psi' |x| \psi d\tau = \int \Sigma_u^- \otimes \Pi_u d\tau = \int \Pi_g d\tau = 0$$

$$M_y = \int \psi' |y| \psi d\tau = \int \Sigma_u^- \otimes \Pi_u d\tau = \int \Pi_g d\tau = 0$$

$$M_z = \int \psi' |z| \psi d\tau = \int \Sigma_u^- \otimes \Sigma_u^- d\tau = \int \Sigma_g^+ d\tau \neq 0$$

THE END