The Abdus Salam International Centre for Theoretical Physics

IAEA International Atomic Energy Agency
Atoms for Peace

Molecular Spectroscopy 3

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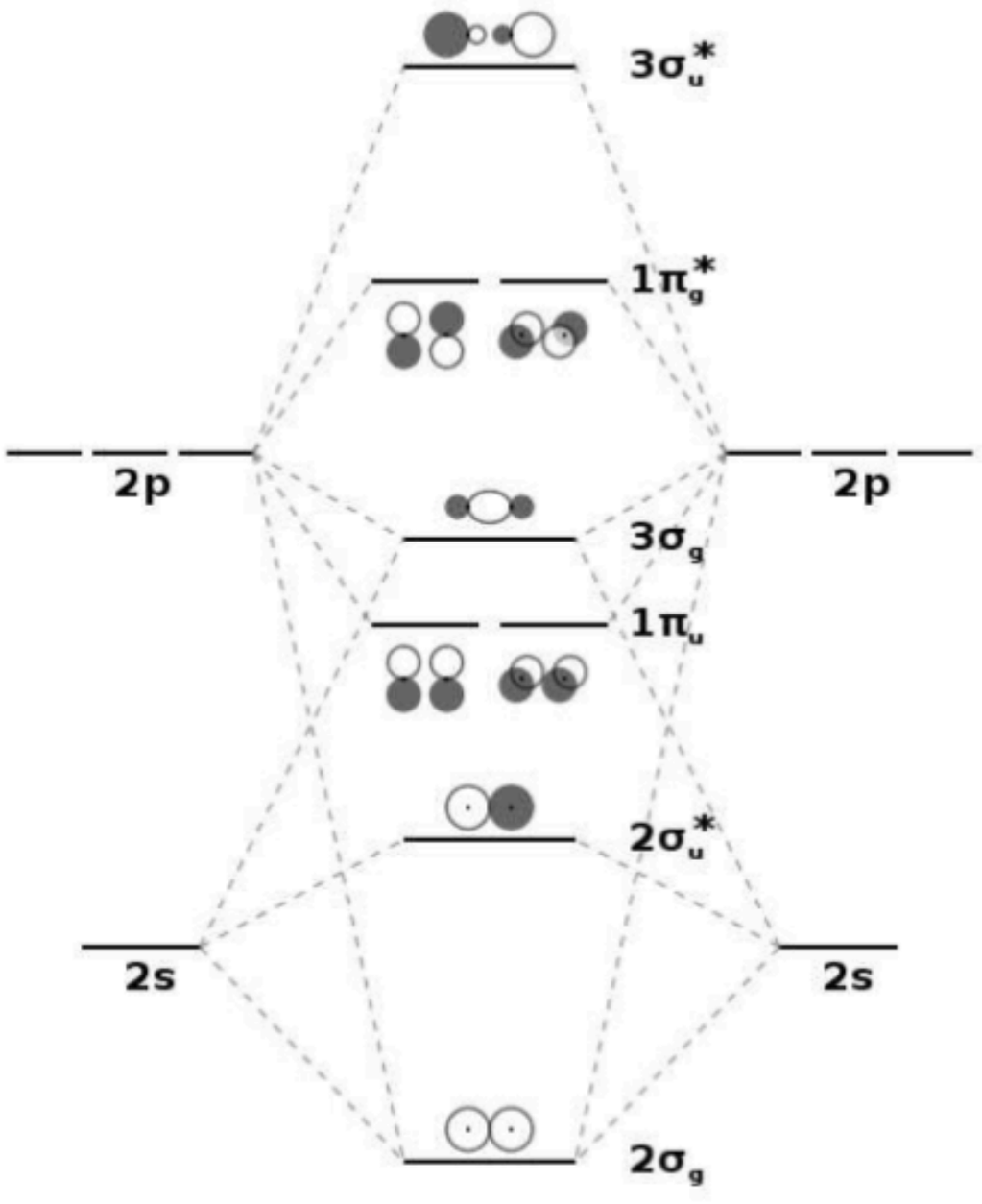
Joint ICTP-IAEA School on Atomic and Molecular Spectroscopy in Plasmas
6 – 10 May 2019
Trieste, Italy

Electronic spectroscopy

The electronic structure of diatomics

- A *molecular configuration* is a specification of the occupied molecular orbitals in a molecule



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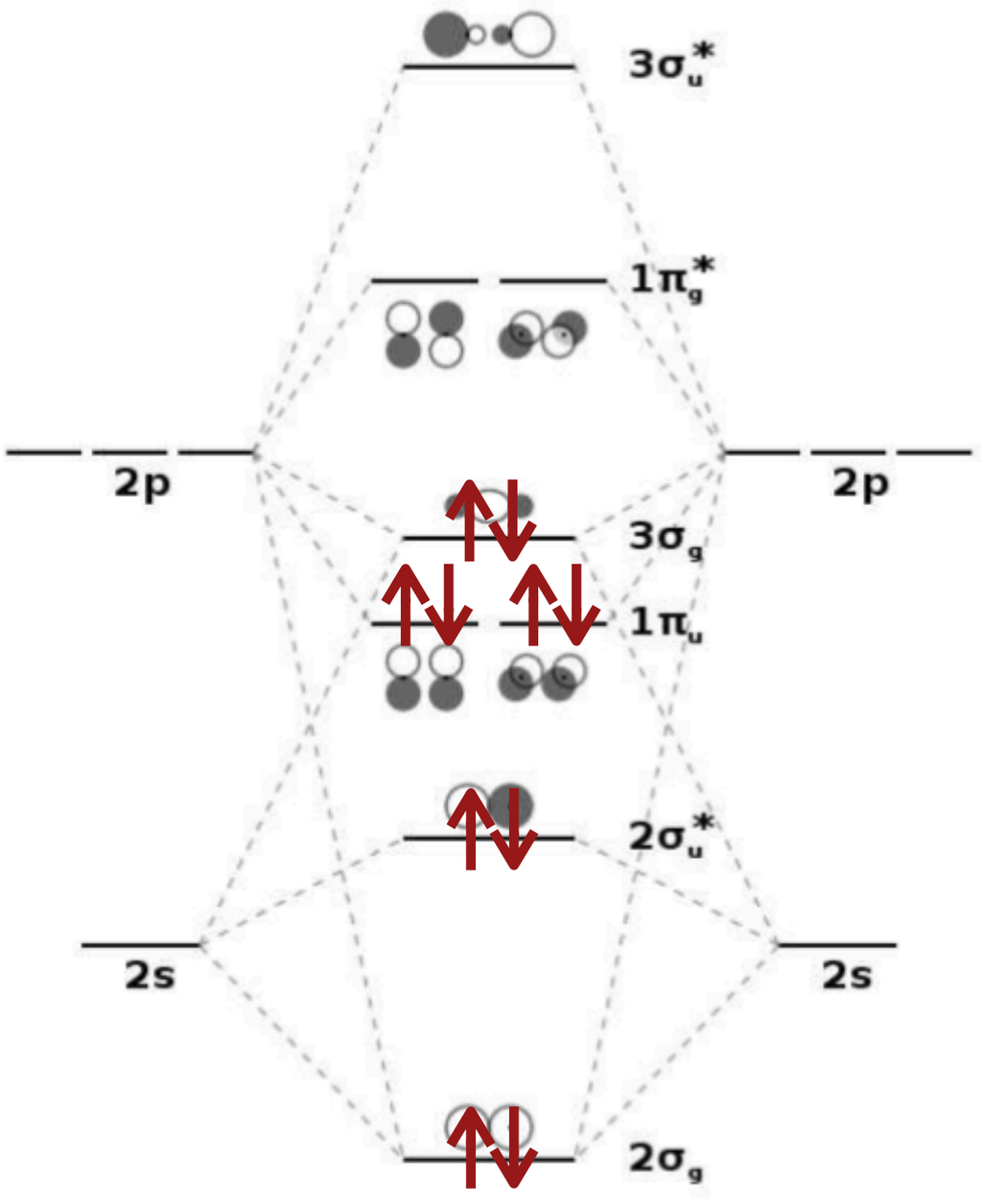

$$N_2 : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$$

The electronic structure of diatomics

- A configuration may have one or more states, labelled as *molecular term symbols*:

$$^{2S+1}|\Lambda|^{(+/-)}_{(g/u)}$$

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Total electronic spin angular momentum: $\underline{S} = \sum_i \underline{s}_i$

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The electronic structure of diatomics

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$$^{2S+1}|\Lambda|^{(+/-)}_{(g/u)}$$

Total electronic orbital angular momentum about internuclear axis:

$$|\Lambda| = \left|\sum_i \lambda_i\right| = 0,1,2,\cdots = \Sigma, \Pi, \Delta, \cdots$$

The electronic structure of diatomics

- A configuration may have one or more states, labelled as *molecular term symbols*:

Reflection symmetry of electronic wavefunction (for Σ states)

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The electronic structure of diatomics

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Inversion symmetry of electronic wavefunction (for homonuclear diatomics)

The electronic structure of diatomics

- Example 1: a closed-shell configuration

$$F_2 : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^4$$

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  - Easiest case: all electrons paired off in their orbitals
  - No net spin or orbital angular momentum: $S = \Lambda = 0$
  - Electronic wavefunction is totally symmetric:

$$^1\Sigma_g^+$$

The electronic structure of diatomics

- Example 2: one unpaired σ-electron

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The electronic structure of diatomics

- Example 2: one unpaired σ-electron

$$N_2^+ : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^1$$

  - Only contribution is from the partially-filled orbital
  - $\Lambda = 0$ and $S = ½$, so $2S+1 = 2$ (a doublet state):

$$^2\Sigma_g^+$$

The electronic structure of diatomics

- Example 3: one or three unpaired π-electrons

$$B_2^+ : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^1$$

  - $\Lambda = \pm 1$ and $S = ½$, so $2S+1 = 2$ (a doublet state):

$$^2\Pi_u$$

The electronic structure of diatomics

- Example 4: two identical π-electrons

$$O_2 : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$$

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- Label the valence orbitals π_- and π_+. Consider some possible spatial wavefunctions:

$$\left.\begin{aligned} \psi_{\text{spatial}}^{(a_1)} &= \pi_+(1)\pi_+(2) \\ \psi_{\text{spatial}}^{(a_2)} &= \pi_-(1)\pi_-(2) \end{aligned}\right\} \Lambda = 2 \quad \Rightarrow \boxed{\Delta}$$

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The electronic structure of diatomics

- Example 4: two identical π-electrons
- Combine with suitable spin wavefunctions:

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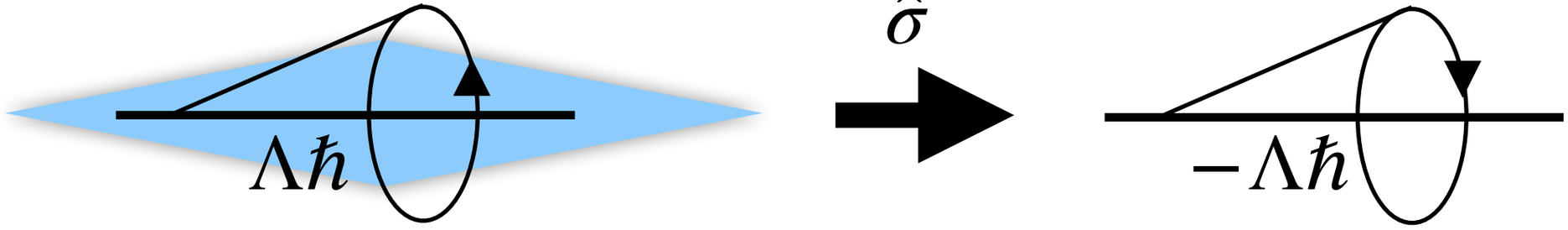
The electronic structure of diatomics

- Example 4: two identical π-electrons
- ± -reflection symmetry (molecular axis system):

$$\hat{\sigma} e^{i\Lambda\hbar\phi} = e^{-i\Lambda\hbar\phi} \Rightarrow \hat{\sigma}\pi_{\pm}(i) = \pi_{\mp}(i)$$



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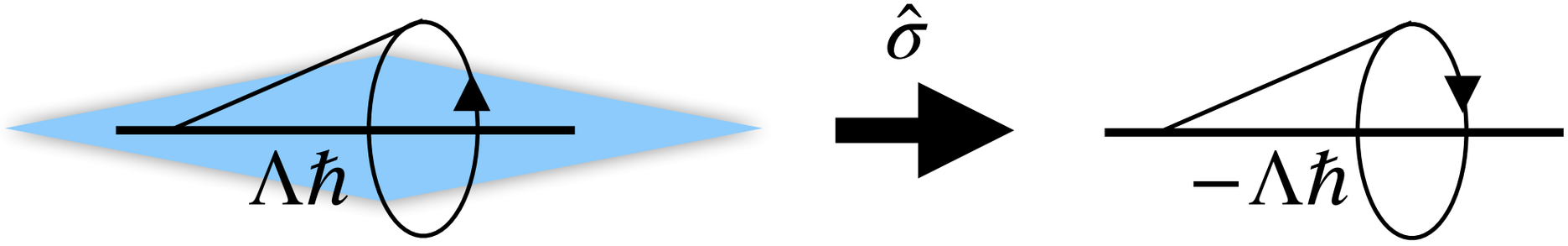

- e.g.

$$\begin{aligned}\hat{\sigma}\psi^{(c)}_{\text{spatial}} &= \hat{\sigma}\frac{1}{\sqrt{2}}[\pi_+(1)\pi_-(2) - \pi_-(1)\pi_+(2)] \\ &= \frac{1}{\sqrt{2}}[\pi_-(1)\pi_+(2) - \pi_+(1)\pi_-(2)] \\ &= -\psi^{(c)}_{\text{spatial}}\end{aligned}$$

$^3\Sigma^-$

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$$X^3\Sigma_g^-, \quad a^1\Delta_g, \quad b^1\Sigma_g^+$$

The electronic structure of diatomics

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- NB Hund's rules predict energy ordering
- Labelling:
  - X = ground state
  - A, B, C, ...= excited states with the *same* spin multiplicity
  - a, b, c, ...= excited states with *different* spin multiplicity

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- Labelling:
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  - a, b, c, ...= excited states with *different* spin multiplicity
  - No ± label for states with $|\Lambda| > 0$

The electronic structure of diatomics

- *Hund's rules* predict energy ordering

$$O_2 : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$$

$$X^3\Sigma_g^- < a^1\Delta_g, \quad b^1\Sigma_g^+$$

- State with *highest multiplicity* is lowest in energy:
  - "Fermi hole":

$$\psi^{(c)} = \frac{1}{\sqrt{2}}\left[\pi_+(1)\pi_-(2) - \pi_-(1)\pi_+(2)\right] \; \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]$$

$^3\Sigma$

The electronic structure of diatomics

- *Hund's rules* predict energy ordering

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- Then, state with highest electronic orbital angular momentum, $|\Lambda|$

The electronic structure of diatomics

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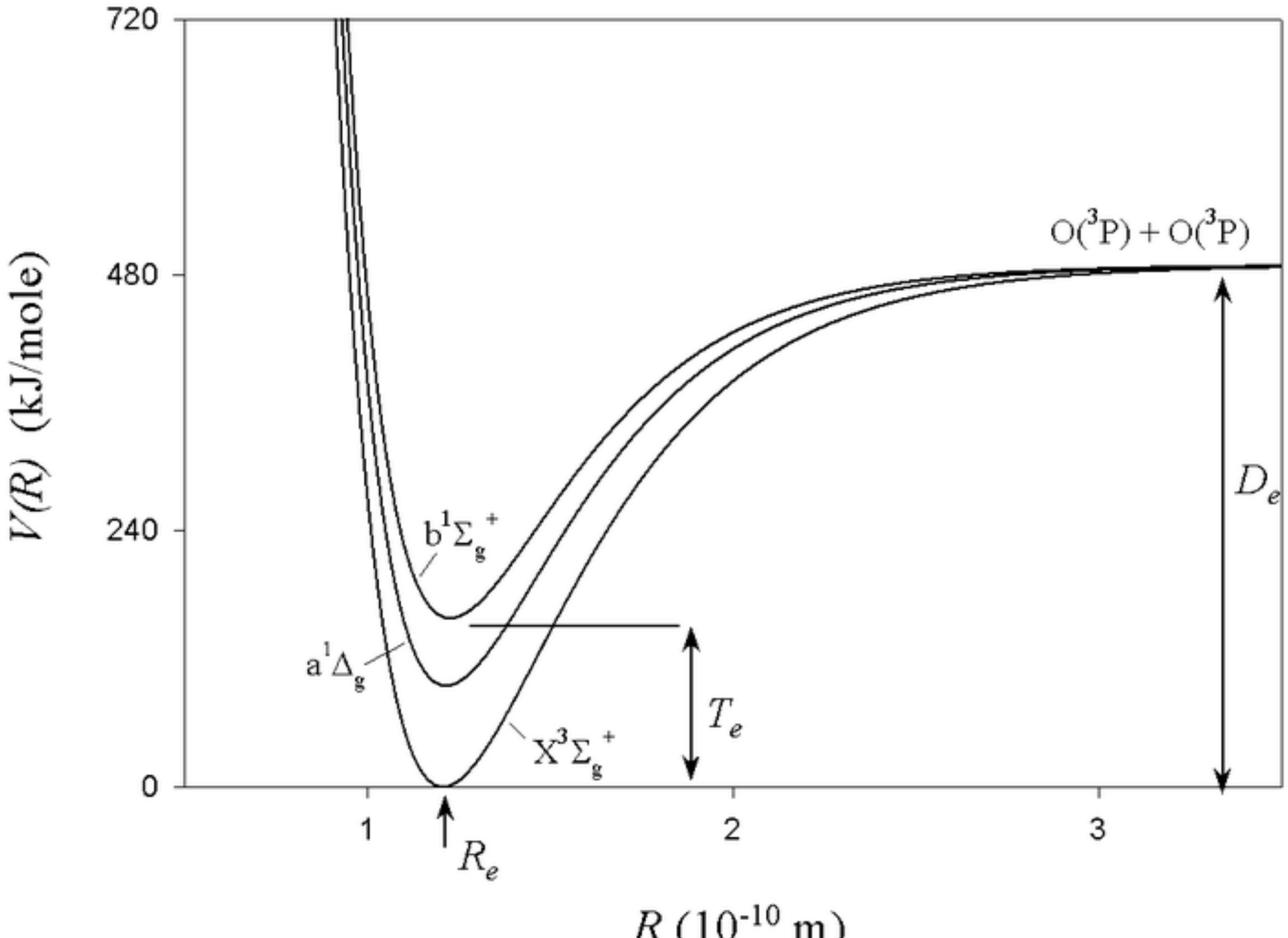
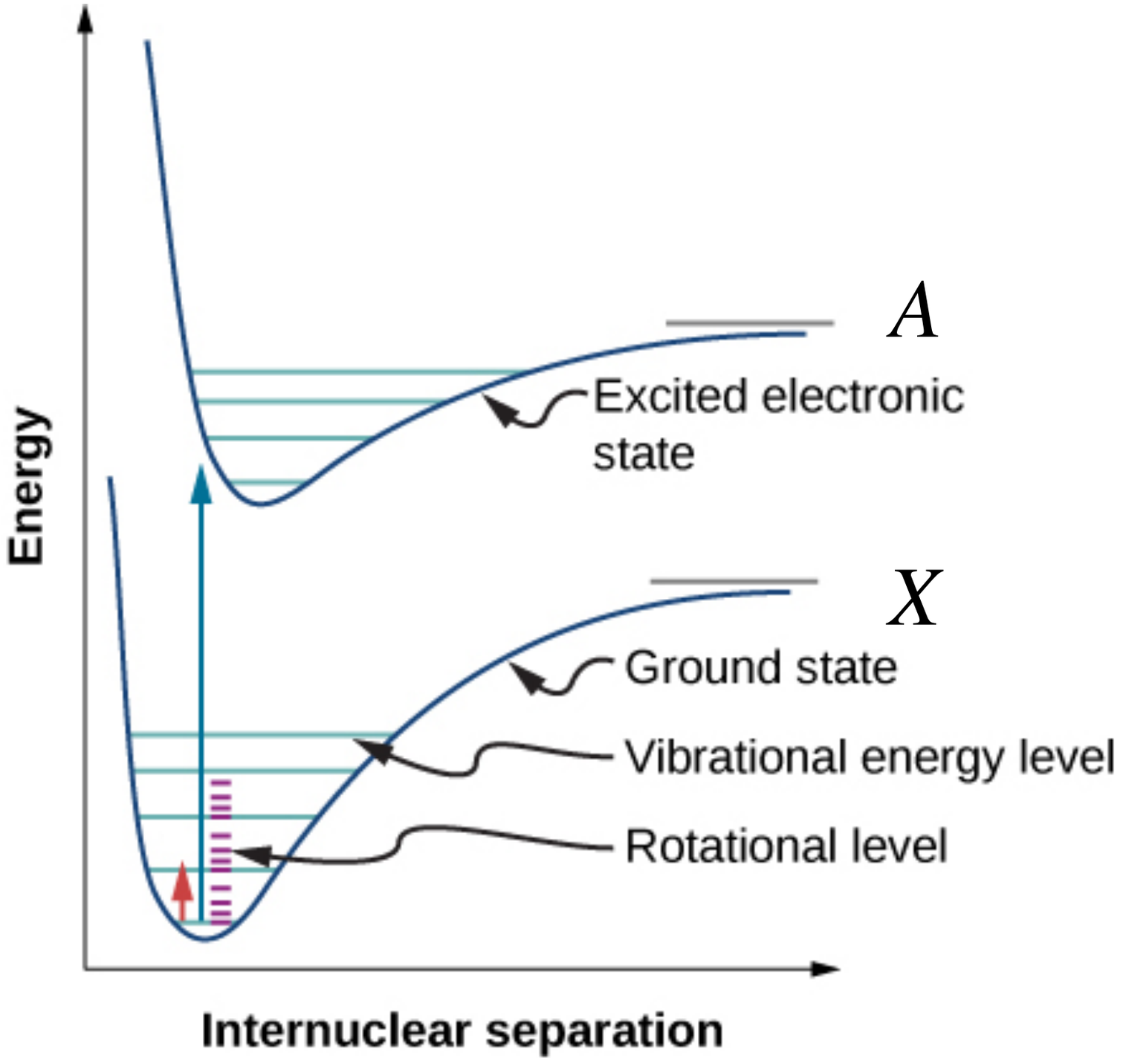


Electronic transitions for diatomics



Electronic transitions for diatomics

- Transition probability

$$
\begin{aligned}
I_{fi} &\propto |\langle \psi_f | \hat{\boldsymbol{\mu}} | \psi_i \rangle|^2 \\
&= |\langle \chi_{f,m} \phi_{f,n} | \hat{\boldsymbol{\mu}} | \chi_{i,m} \phi_{i,n} \rangle|^2 \\
&\approx |\langle \chi_{f,m} | \chi_{i,m} \rangle|^2 |\langle \phi_{f,n} | \hat{\boldsymbol{\mu}} | \phi_{i,n} \rangle|^2
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Electronic transitions for diatomics

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Electronic selection rules

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

$$g \leftrightarrow u$$

$$\Sigma^+ \leftrightarrow \Sigma^+, \quad \Sigma^- \leftrightarrow \Sigma^-$$

Electronic transitions for diatomics

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Franck-Condon Factor

$\Delta v = \text{unrestricted}$

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Electronic transitions for diatomics

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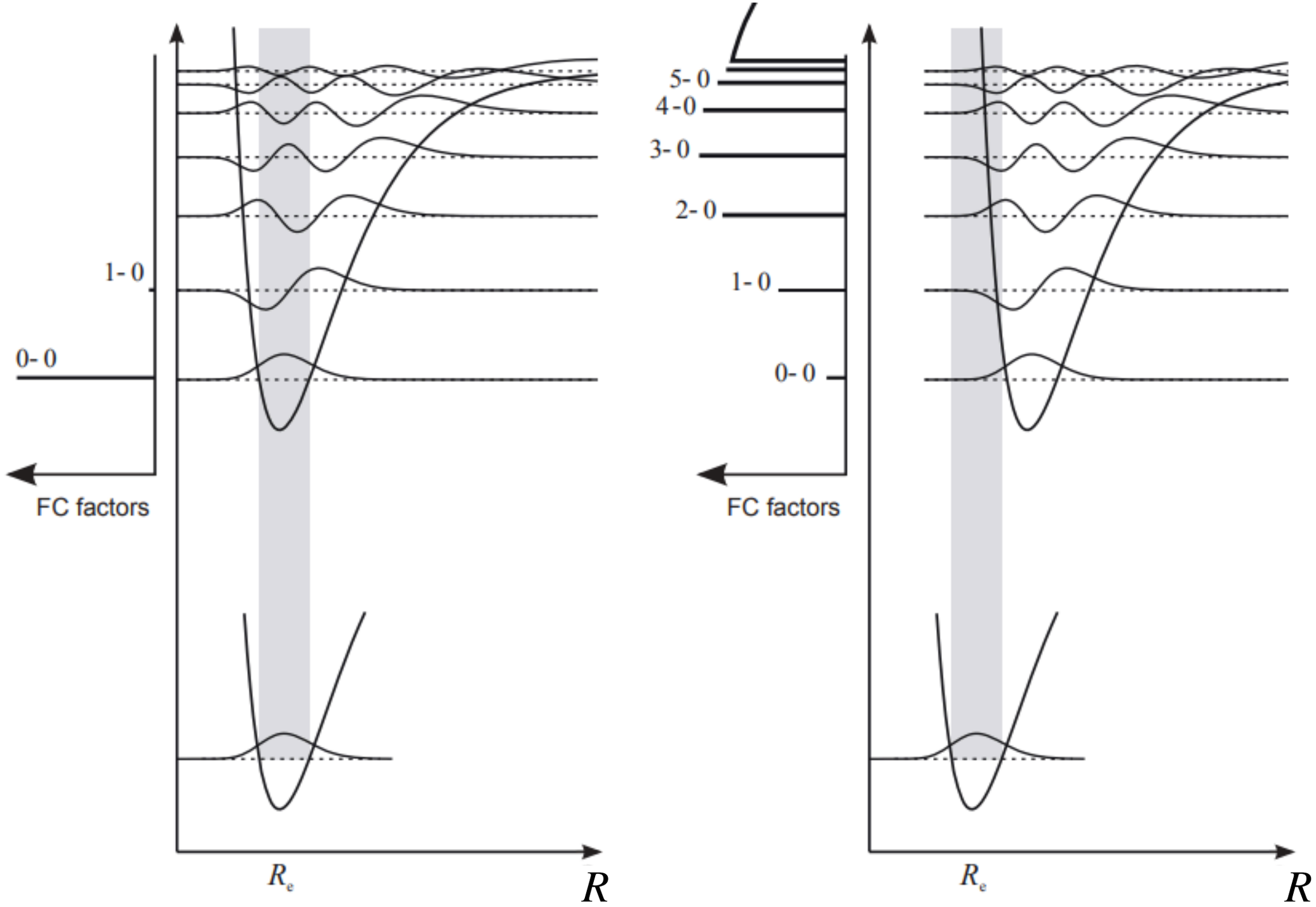
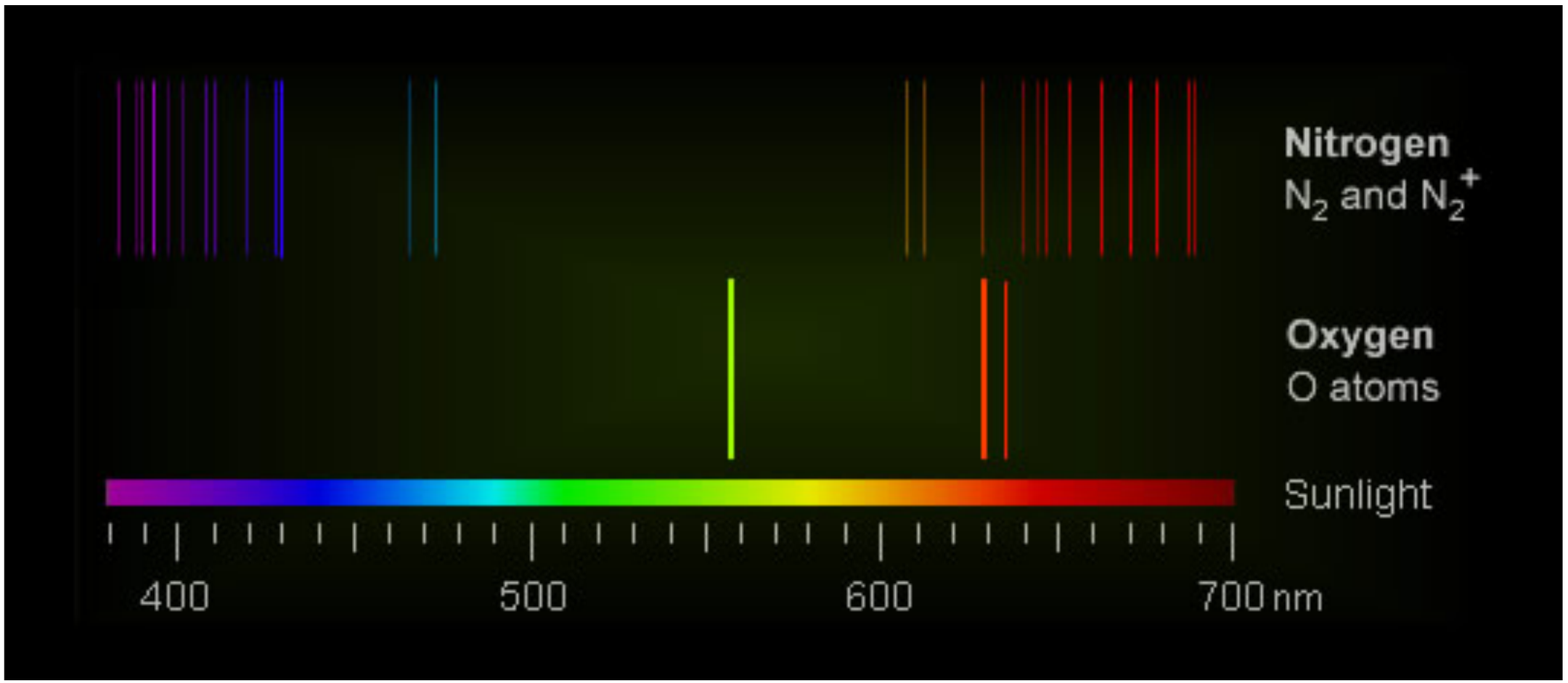


Electronic transitions for diatomics

- Aurorae



Electronic transitions for diatomics

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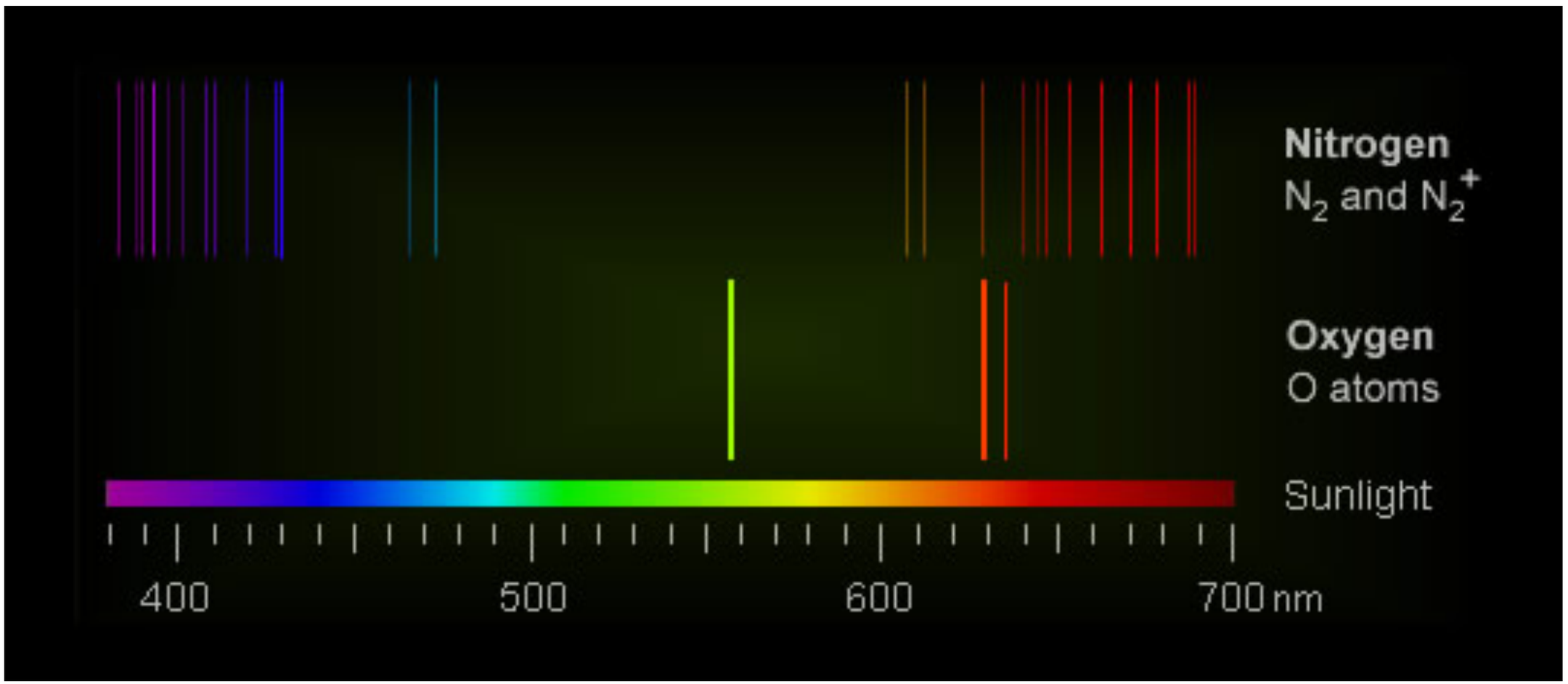
$$\mathrm{N}_2 : B(^3\Pi_g) - A(^3\Sigma_u^+)$$



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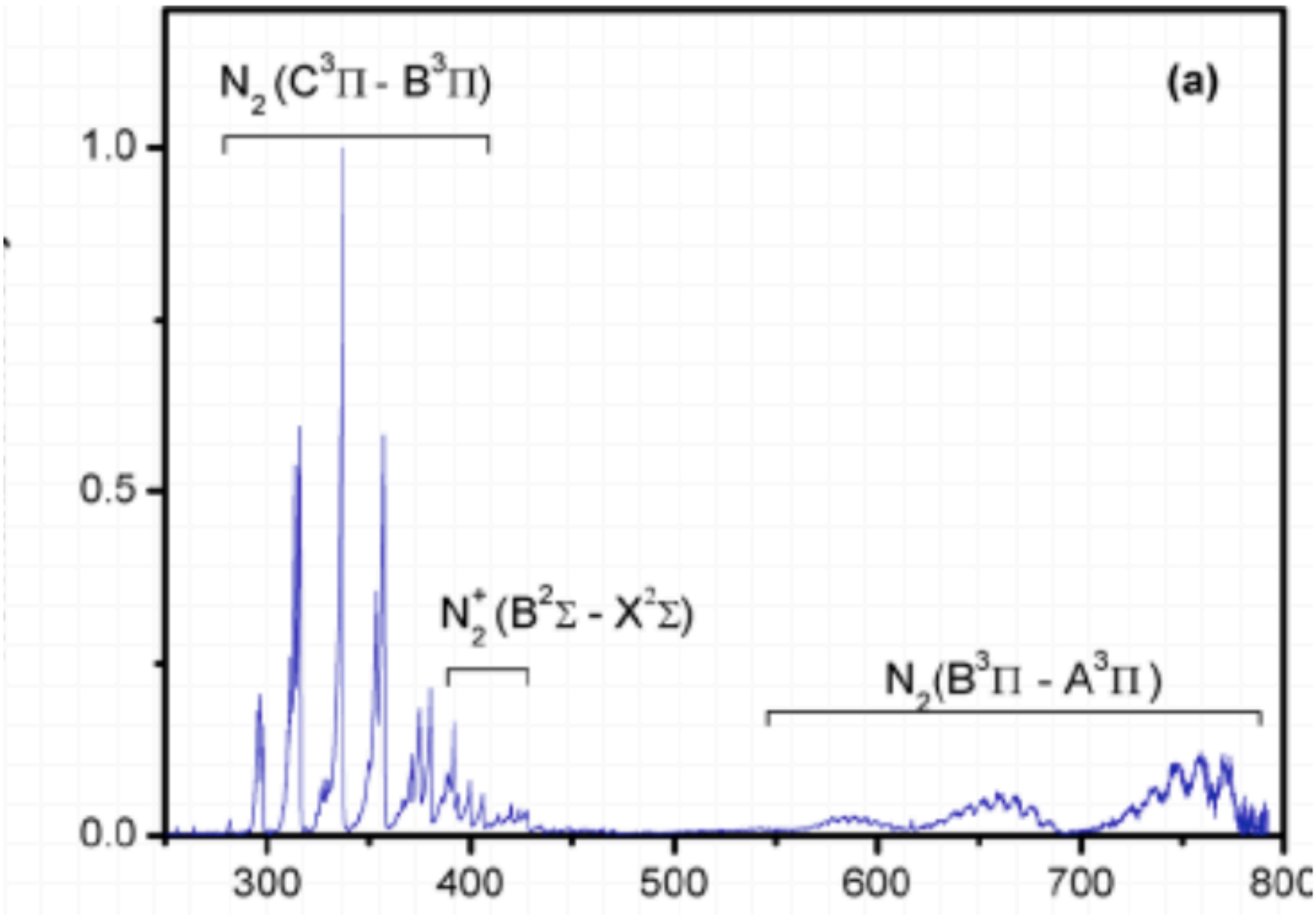

Electronic transitions for diatomics

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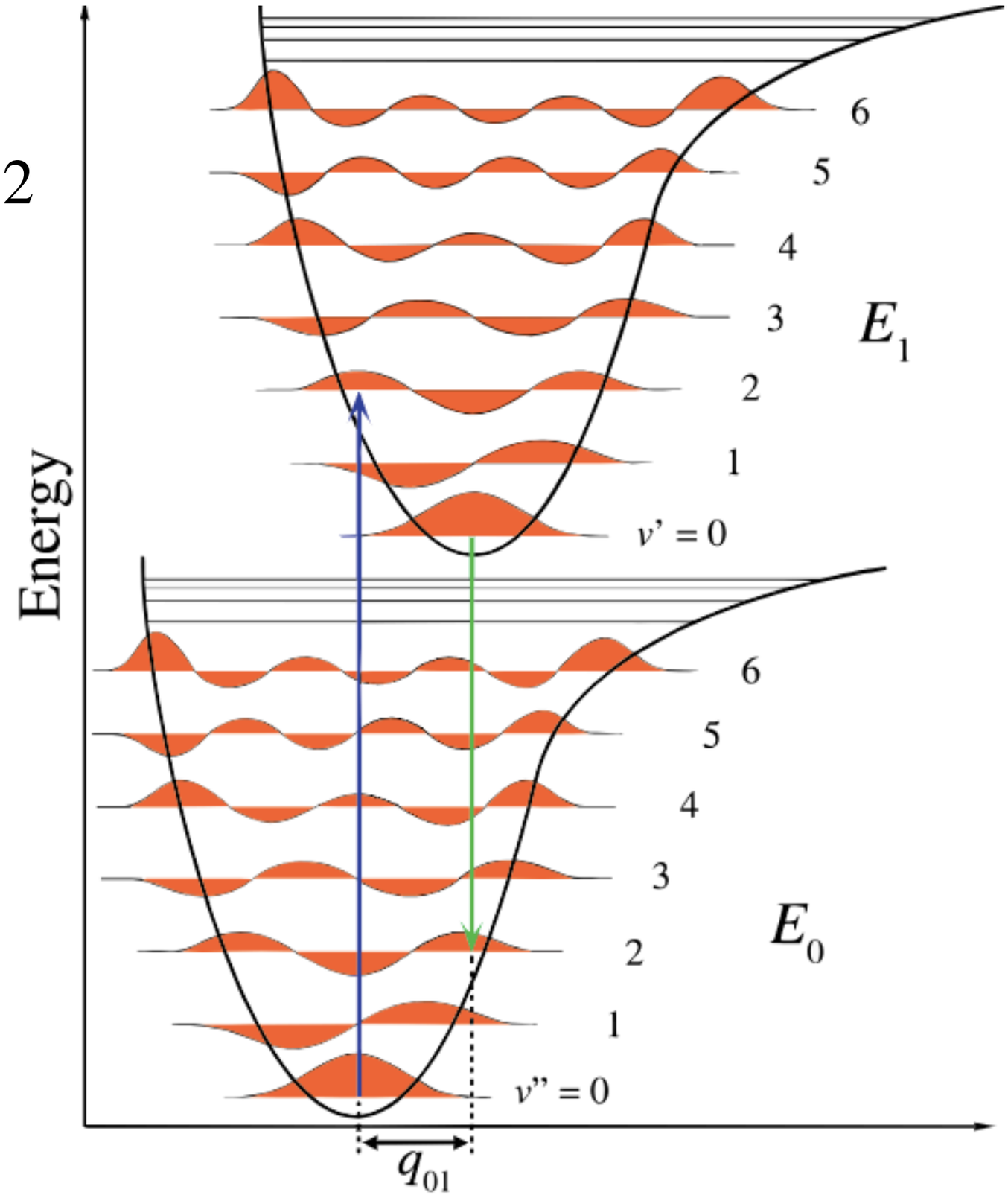
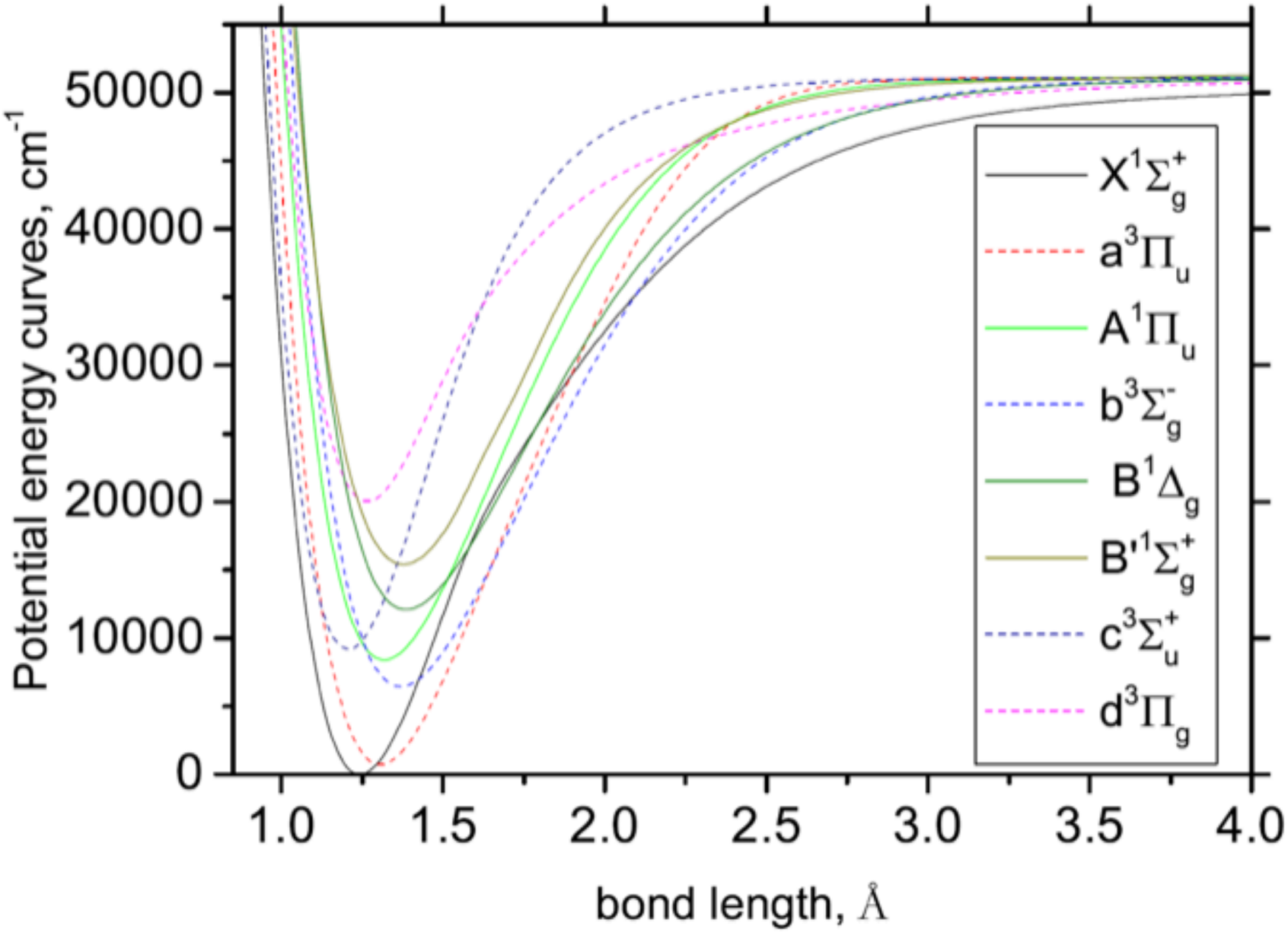
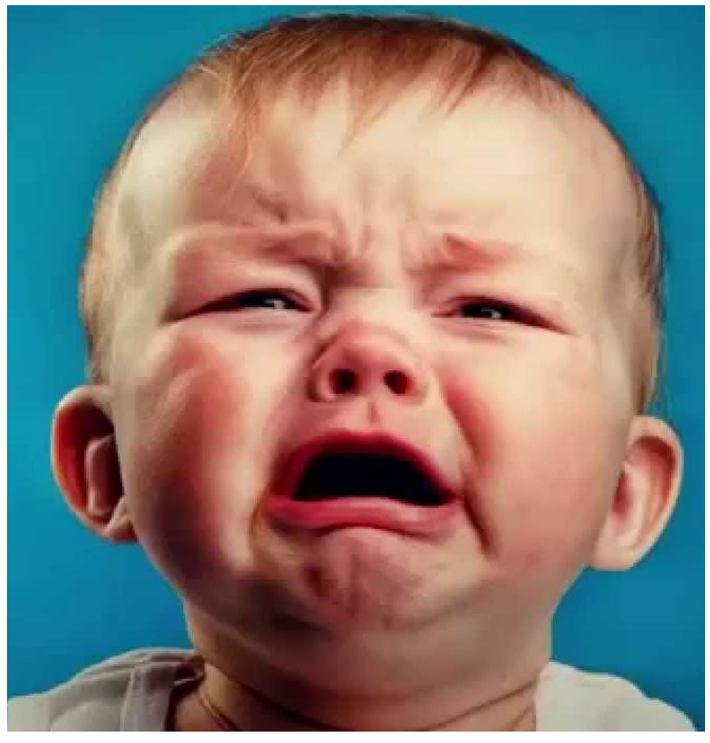
$$I_{\text{em}} \propto |\langle \chi_{f,v'} | \chi_{i,v''} \rangle|^2$$



The electronic structure of diatomics

- Example 5: C_2

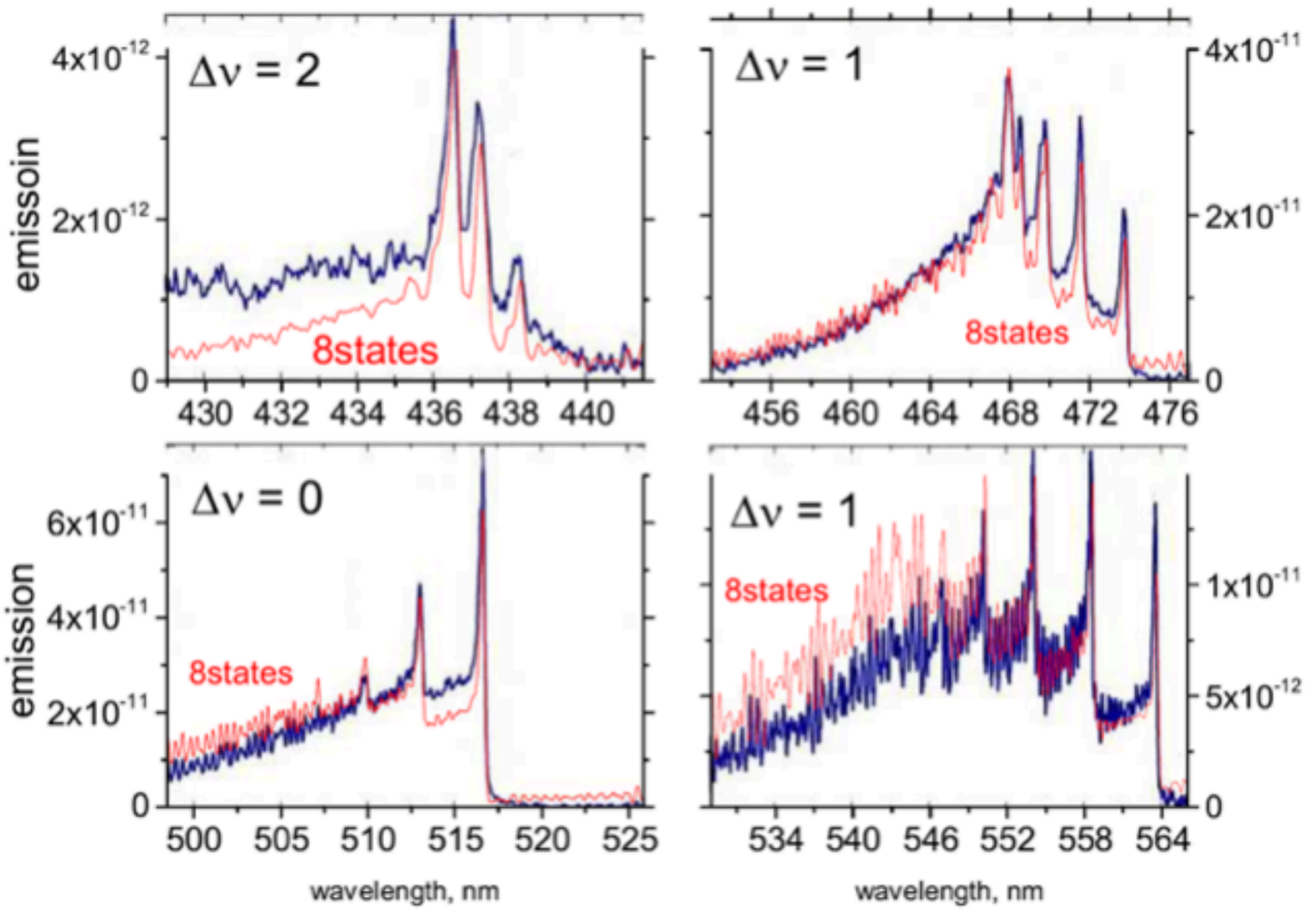




Electronic Structure of C_2: 8 coupled electronic states

The electronic structure of diatomics

- Example 5: C_2
- Nonetheless: Swan bands $d(^3\Pi_g) - a(^3\Pi_u)$
- *ab initio* calcualtions of hot line lists (e.g. exomol.com)



Nuclear spin statistics

- There are two kinds of H_2 molecule.

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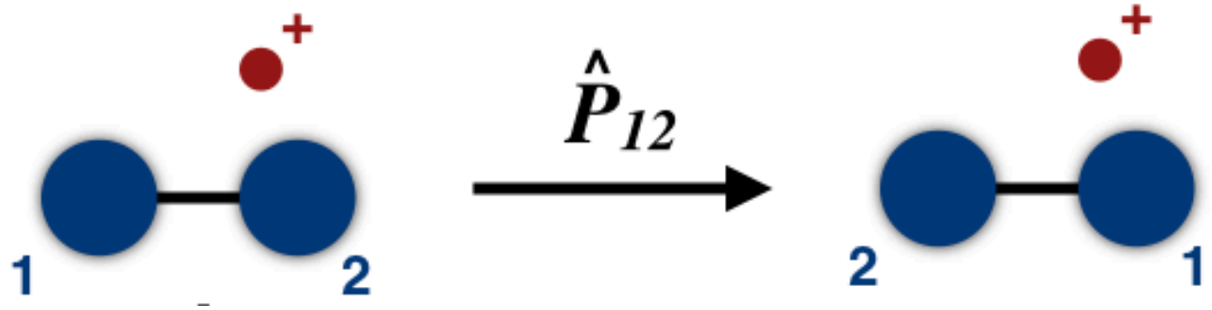
- There are two kinds of H_2 molecule.
- ^1H has a nuclear spin; quantum number $I = \frac{1}{2}$
- Just as for identical electrons, the nuclear angular momentum couples:

$$\psi_{\text{ns;ortho}} = \begin{cases} \alpha_1\alpha_2 \\ \frac{1}{\sqrt{2}}[\alpha_1\beta_2 + \beta_1\alpha_2] \\ \beta_1\beta_2 \end{cases} \qquad I = 1$$

$$\psi_{\text{ns;para}} = \frac{1}{\sqrt{2}}[\alpha_1\beta_2 - \beta_1\alpha_2] \qquad I = 0$$

Nuclear spin statistics

- Consequence on population distribution of rotational states
- ^{1}H nuclei are a *fermions*: antisymmetric w.r.t. exchange



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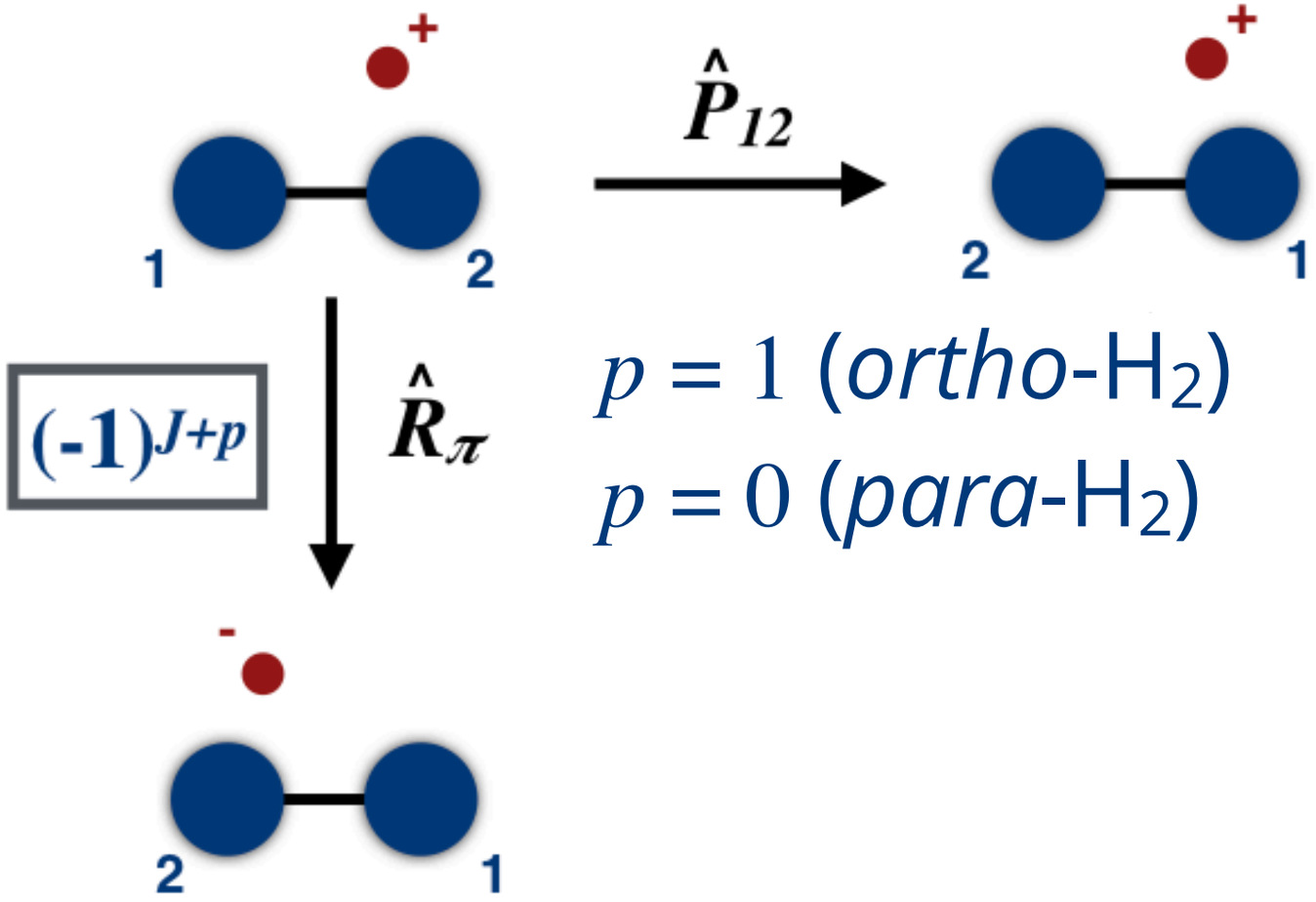

$p = 1$ (*ortho*-H_2)

$p = 0$ (*para*-H_2)

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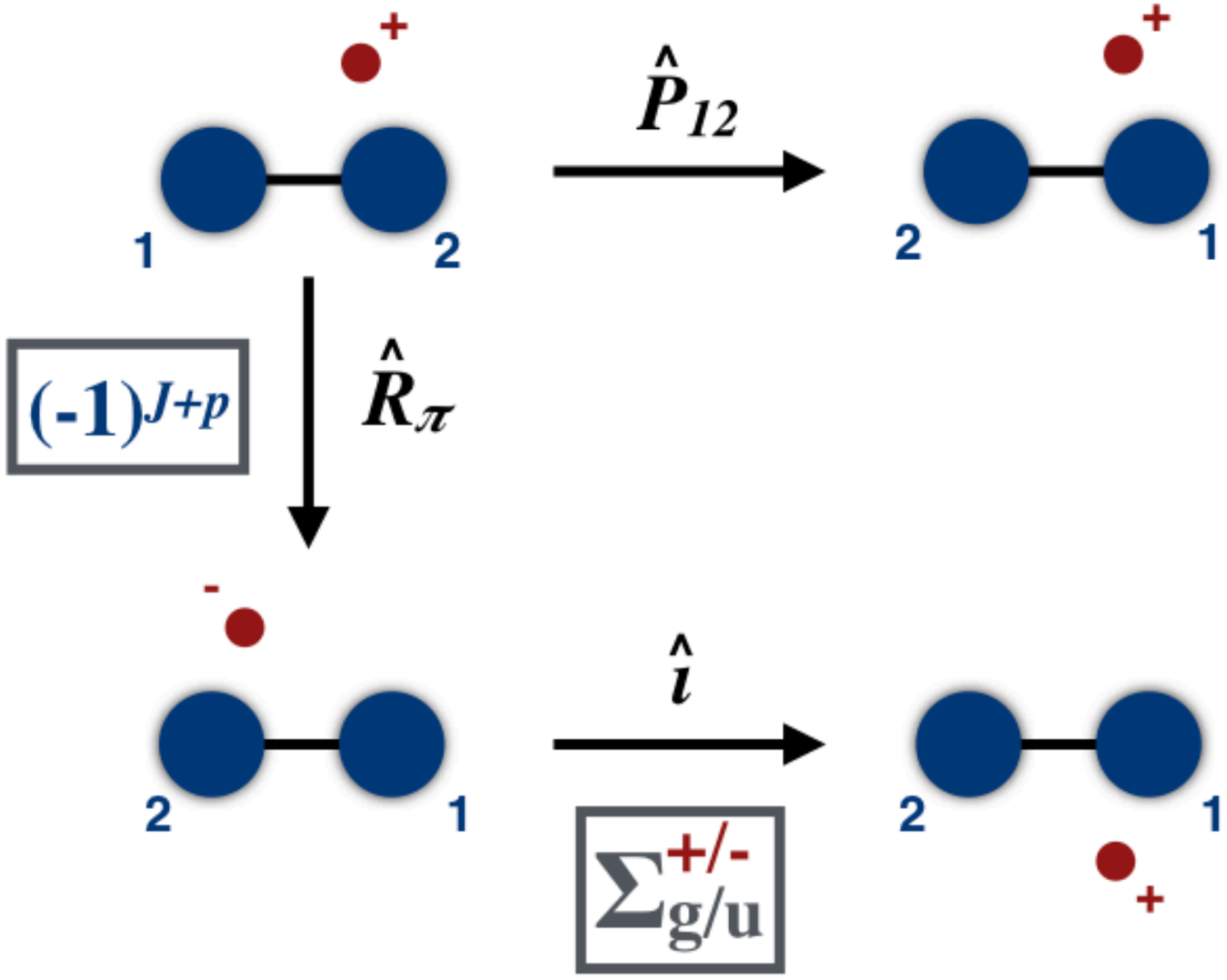

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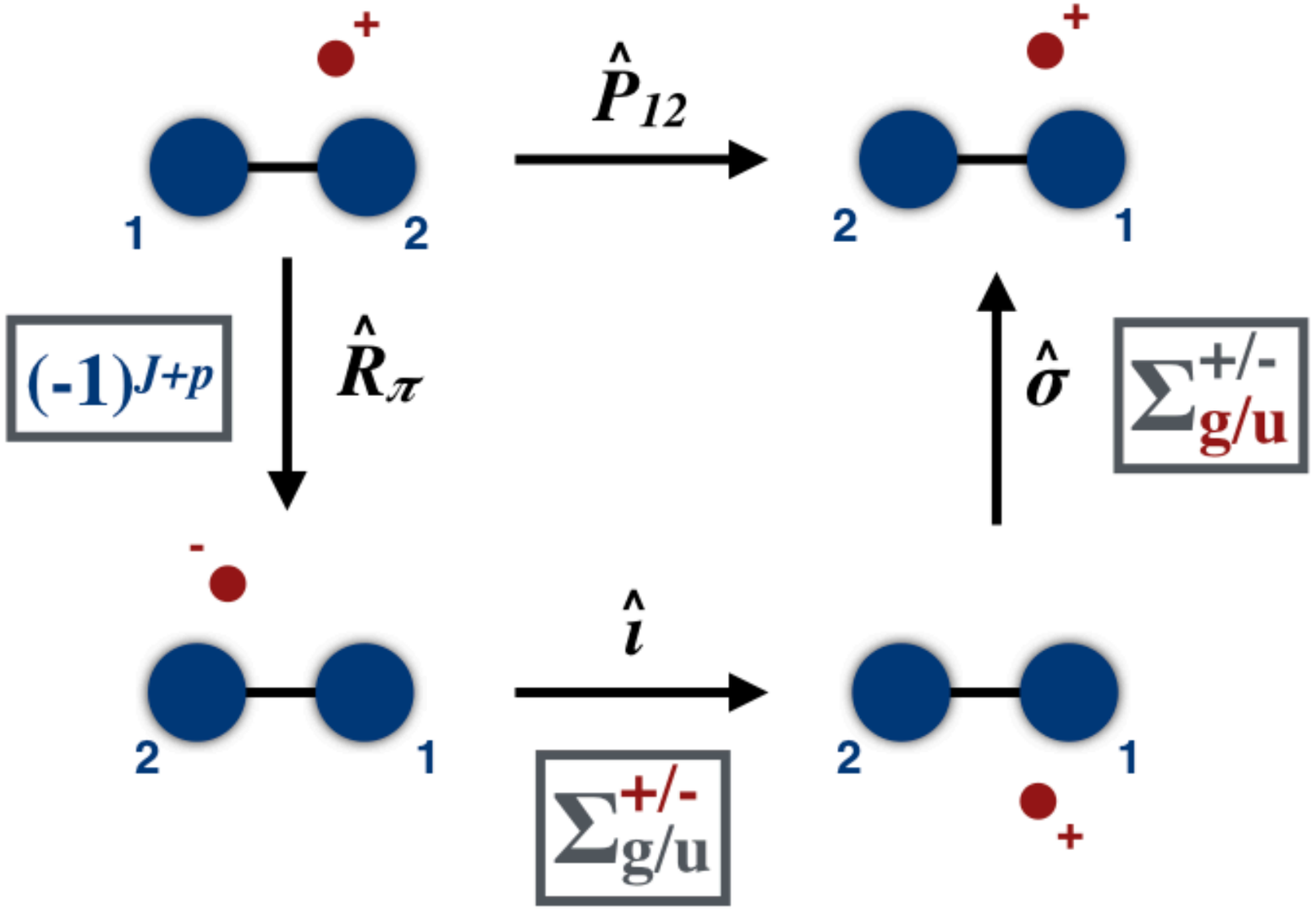

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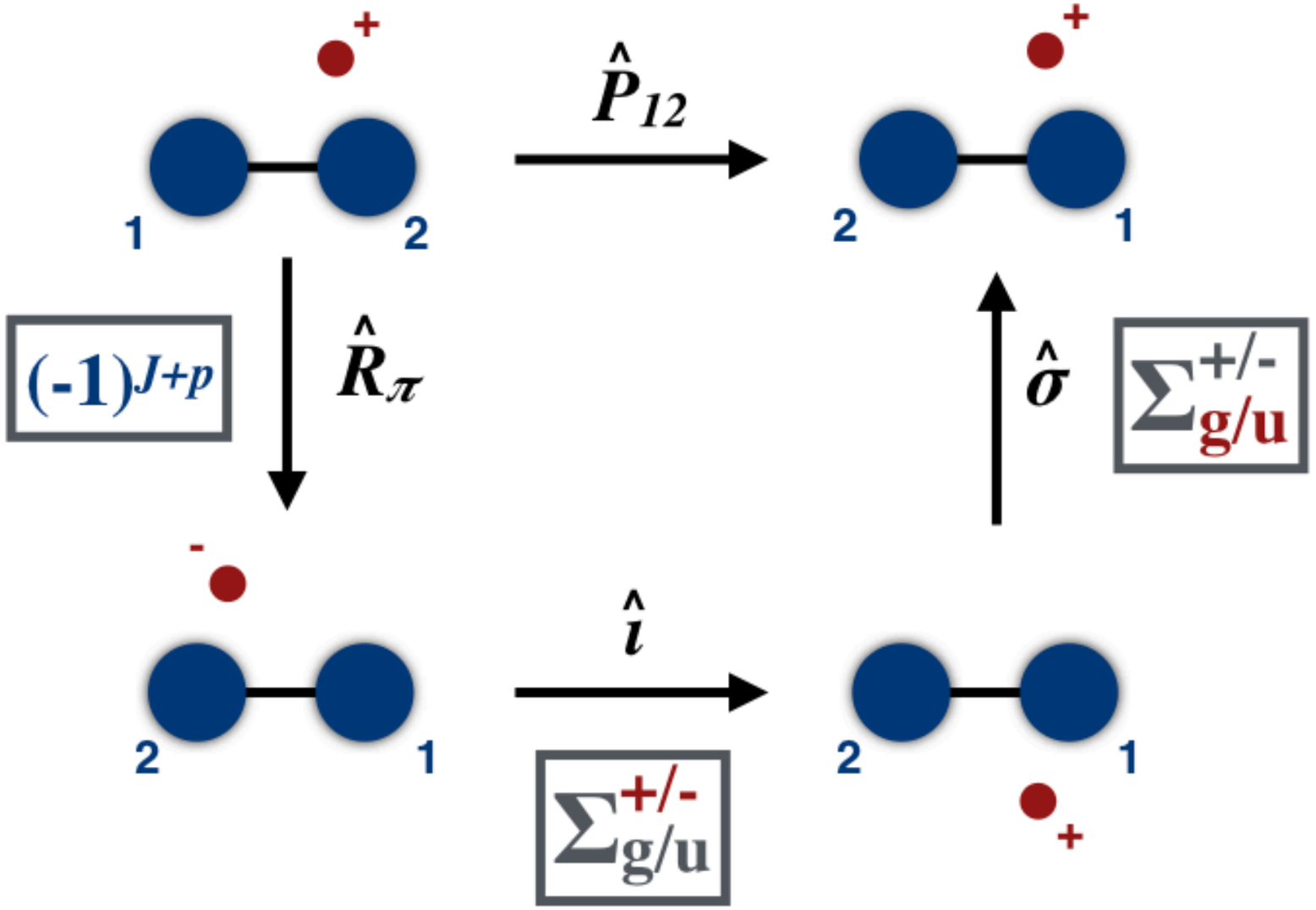

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- *ortho*-H_2 molecule: only odd-J levels exist
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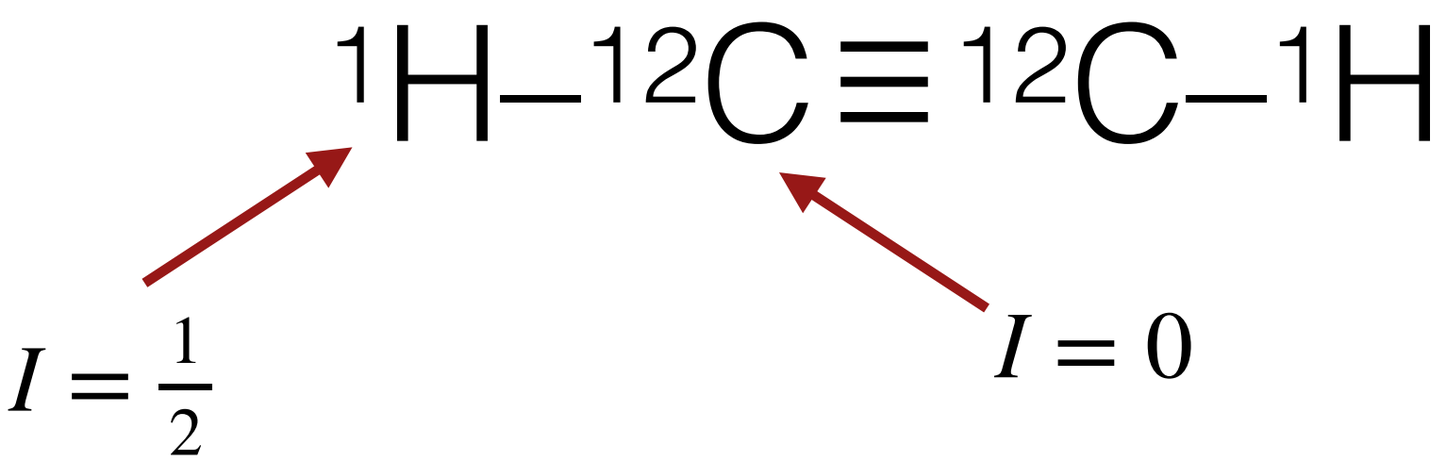
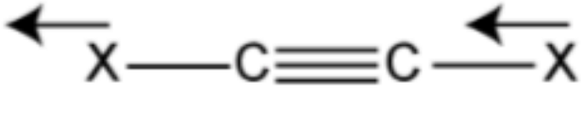
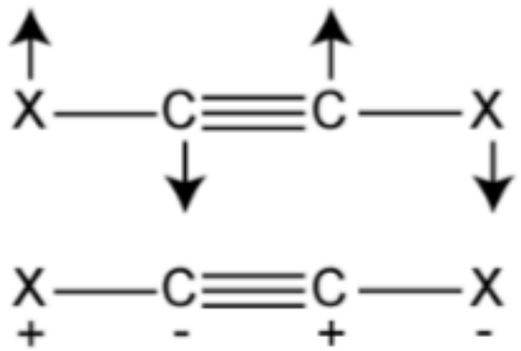
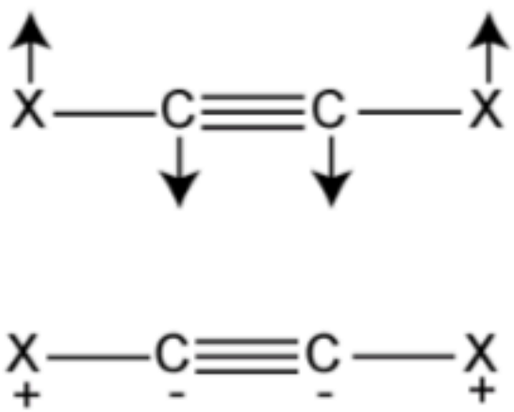
Nuclear spin statistics

- *ortho*-H_2 molecule: only odd-J levels exist
- *para*-H_2 molecule: only even-J levels exist
- *ortho* : *para* ratio is 3:1
- … but H_2 doesn't have an (electric dipole-allowed) IR spectrum, so we'll look at $^{12}C_2{}^{1}H_2$



Same nuclear spin statistics as H_2

Nuclear spin statistics: C_2H_2

Mode	Description	Normal Mode	Band (cm^{-1})
ν_1	Symmetric C-X stretch		X=H, 3373.7 X=D, 2700.5
ν_2	Symmetric CC stretch		X=H, 1973.8 X=D, 1762.4
ν_3	Asymmetric C-X stretch		X=H, 3281.9 X=D, 2439.3
ν_4	Symmetric bend		X=H, 612.9 X=D, 505
ν_5	Asymmetric bend		X=H, 730.3 X=D, 536.9

Nuclear spin statistics: C_2H_2

- *e.g.* ν_3 *asymmetric stretching mode* $\left(\Sigma_u^+\right)$