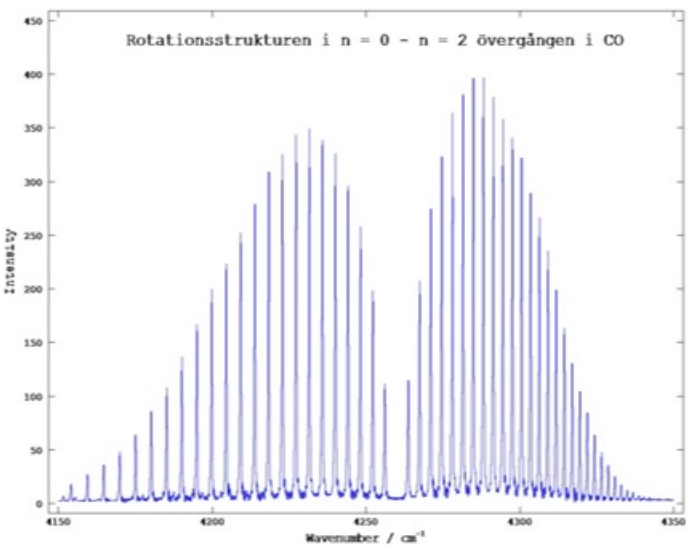
Structure and Spectra of Diatomic Molecules

Spectrophysics Ch 5 and 6. Exercises: 41, 42 and H43.
Focus on the vibration and rotation, that is unique to molecules.

- **Energy = electronic + vibrational + rotational**

- Bonding and anti-bonding electronic states
- Photodissociation (Ozon)

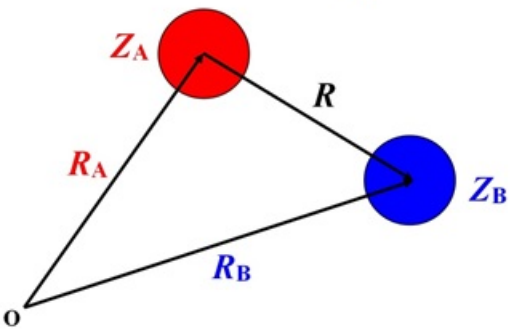
- Vibration: $E_{\text{vib}} = \hbar\omega_0(\nu + \frac{1}{2})$
- Rotation: $E_{\text{rot}} = \frac{\hbar^2}{2\mu r^2} \cdot \ell(\ell+1)$
- Roto-vibrational transitions:

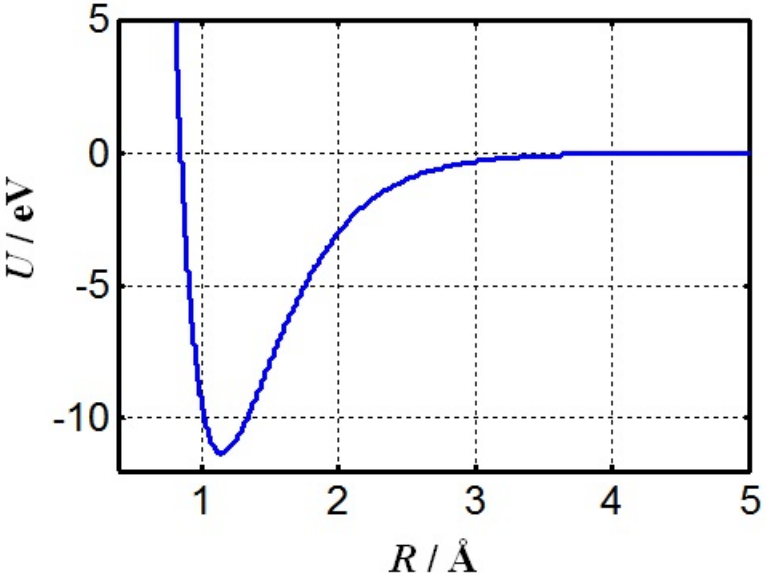


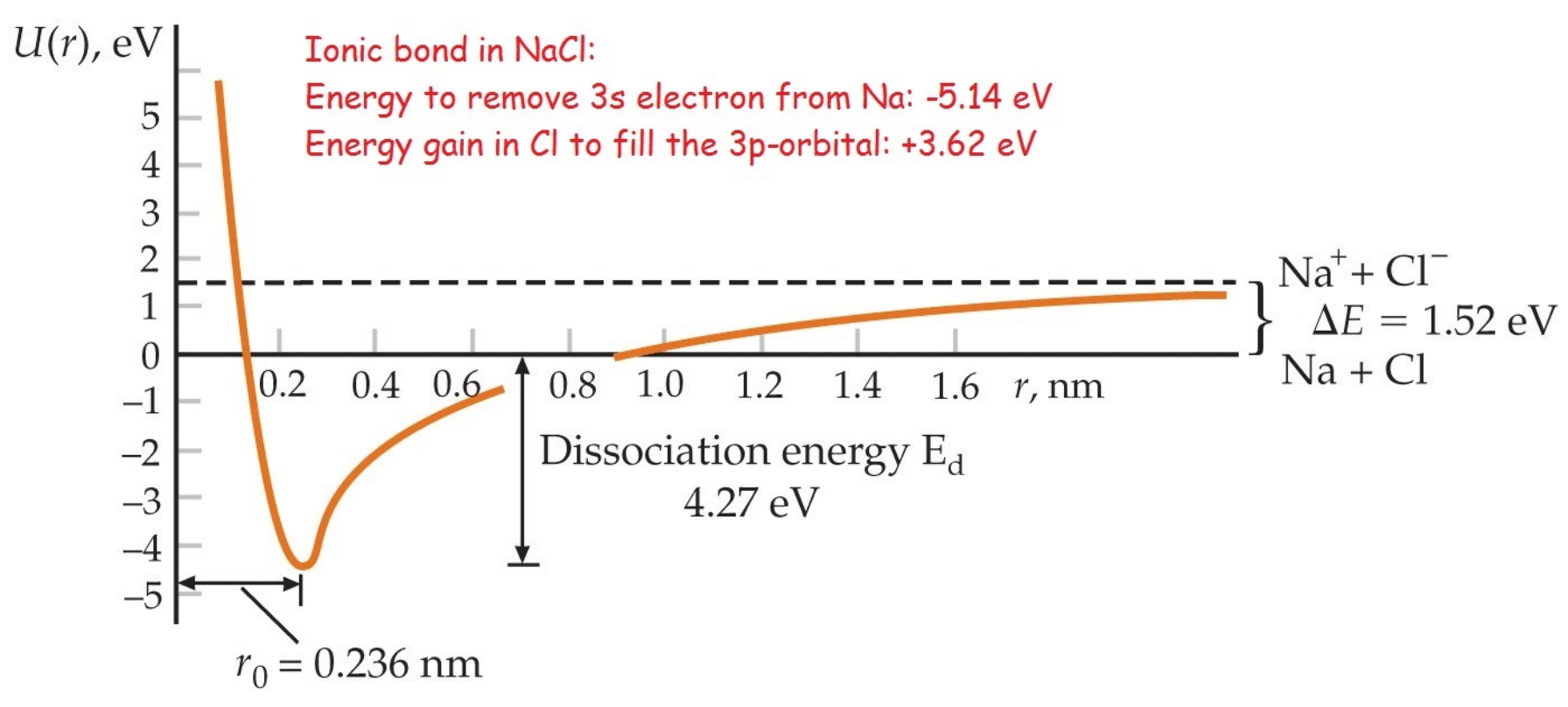
- Basic physics regarding the green house effect

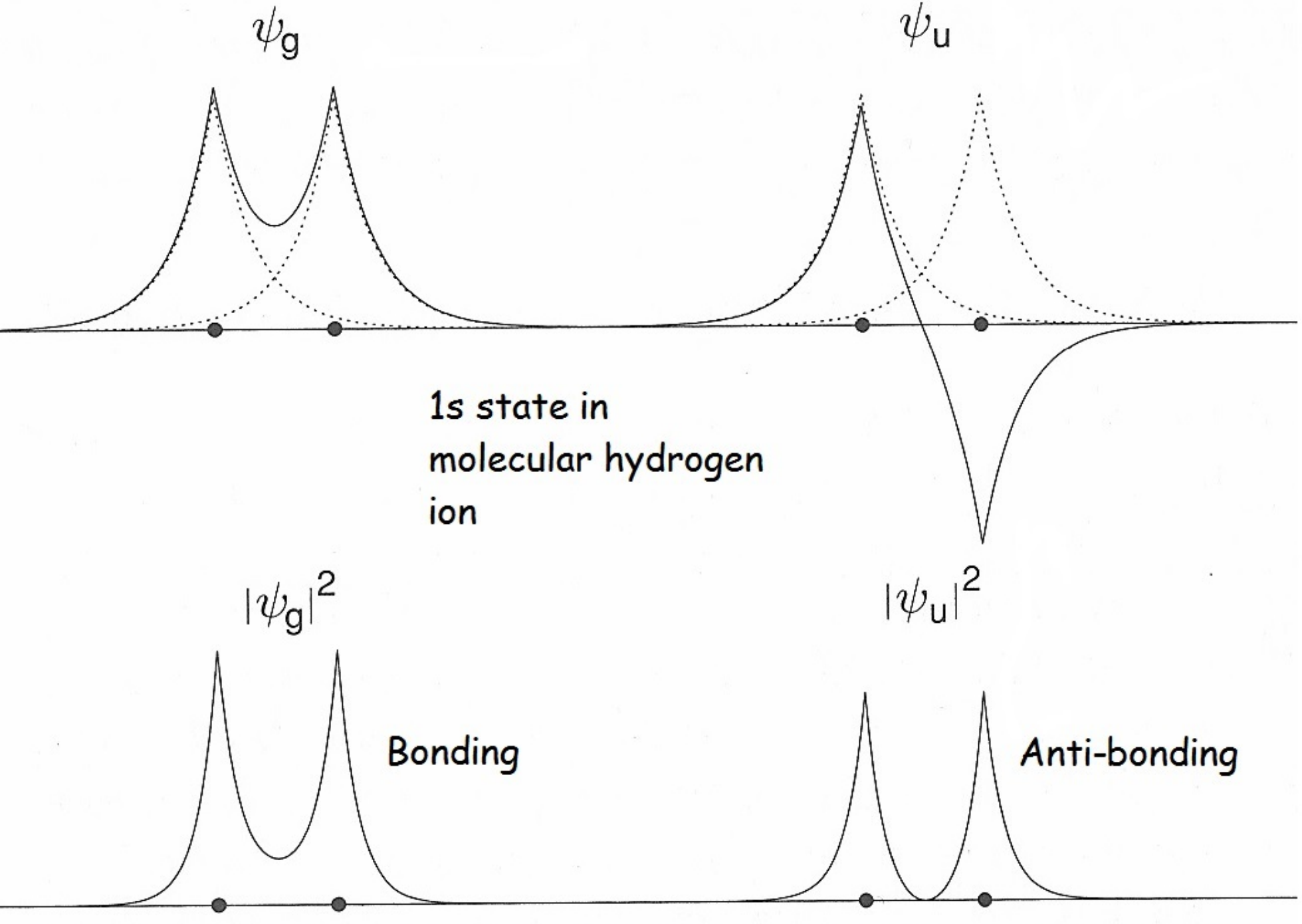
Potential in a diatomic molecule with N electrons

$$V(\bar{R},\bar{r}_1,\bar{r}_2,\ldots,\bar{r}_N) = -\sum_{i=1}^{N}\frac{Z_A e^2}{4\pi\varepsilon_0\left|\bar{r}_i-\bar{R}_A\right|} - \sum_{i=1}^{N}\frac{Z_B e^2}{4\pi\varepsilon_0\left|\bar{r}_i-\bar{R}_B\right|} + \sum_{\substack{i,j=1\\ i>j}}^{N}\frac{e^2}{4\pi\varepsilon_0\left|\bar{r}_i-\bar{r}_j\right|} + \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R}$$

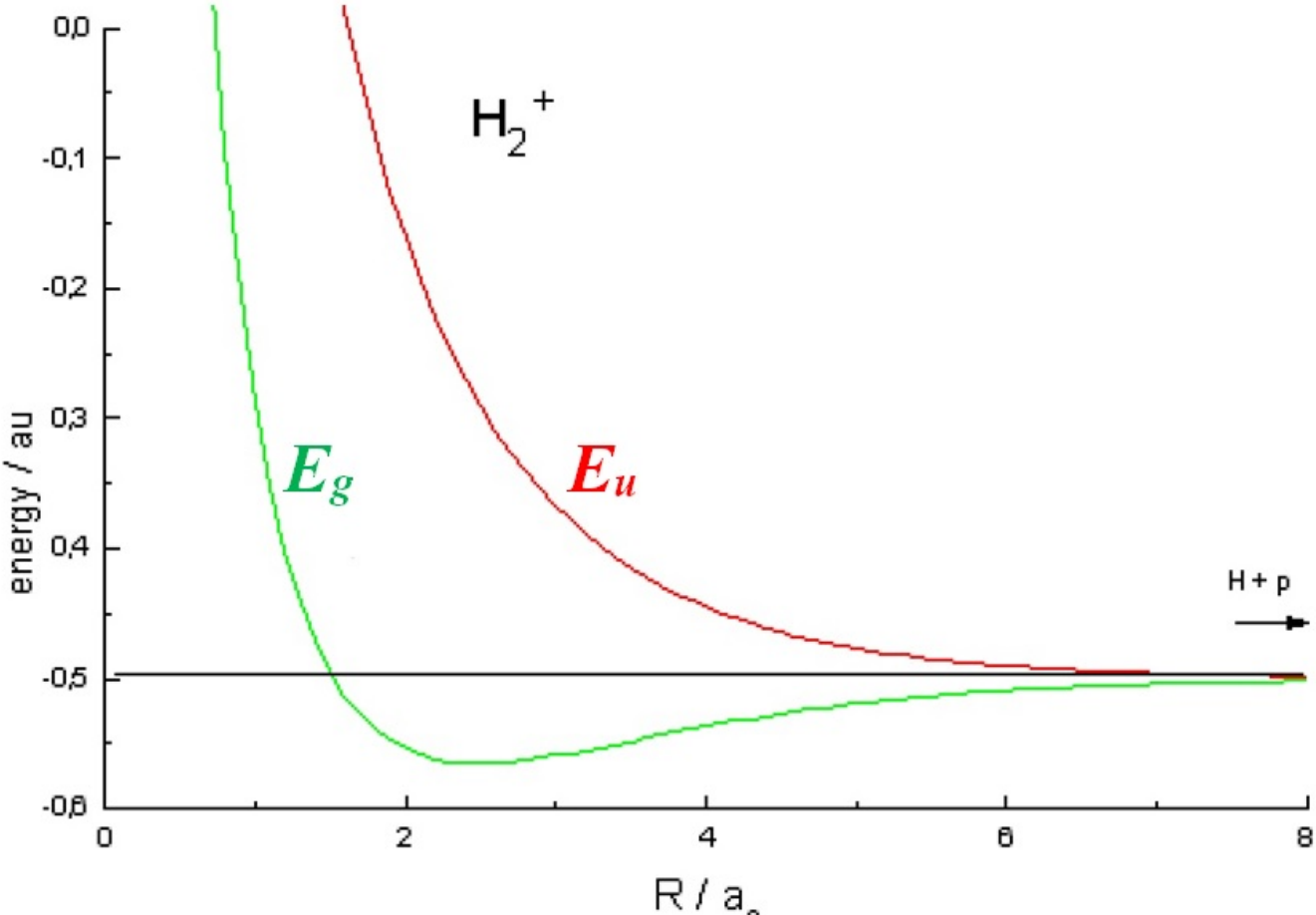




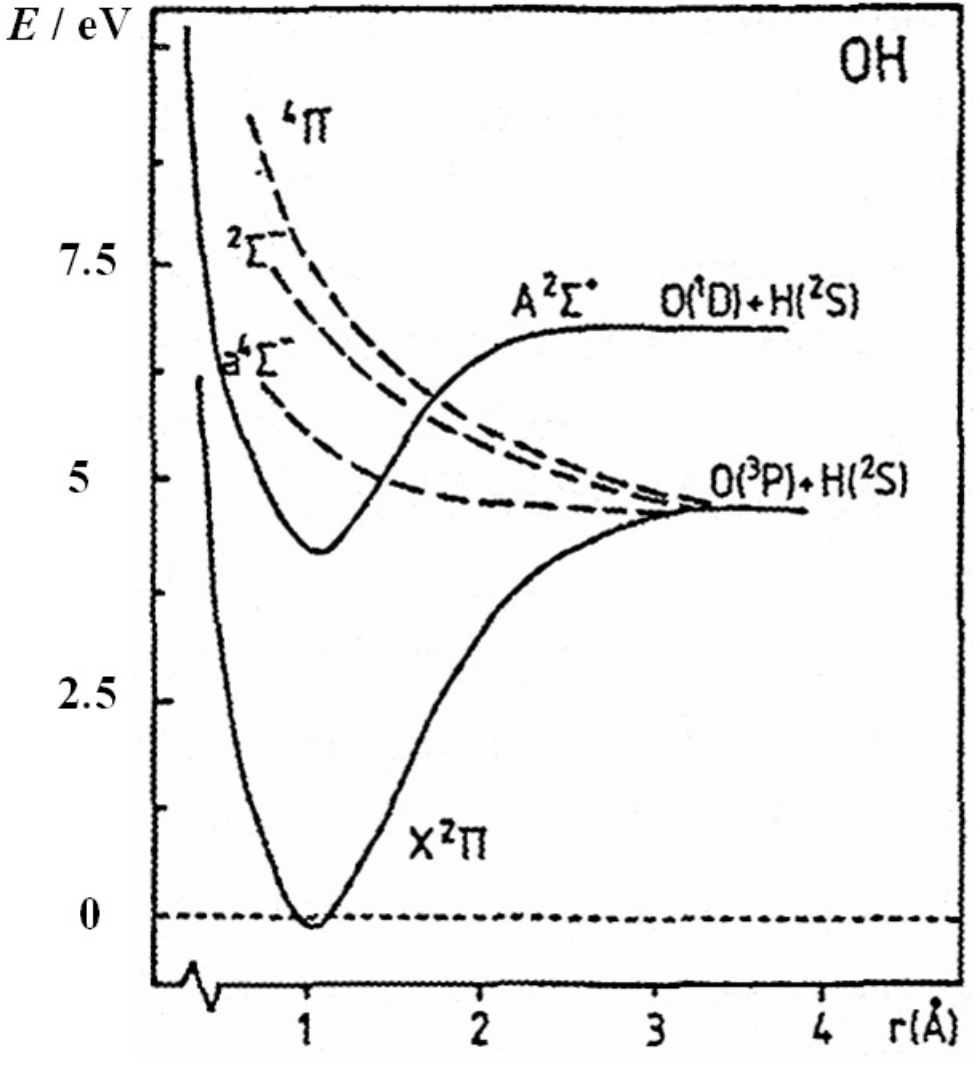

U(r), eV
Ionic bond in NaCl:
Energy to remove 3s electron from Na: -5.14 eV
Energy gain in Cl to fill the 3p-orbital: +3.62 eV
5
4
3
2
1
0
–1
–2
–3
–4
–5
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
r, nm
Na+ + Cl−
ΔE = 1.52 eV
Na + Cl
Dissociation energy Ed
4.27 eV
r0 = 0.236 nm

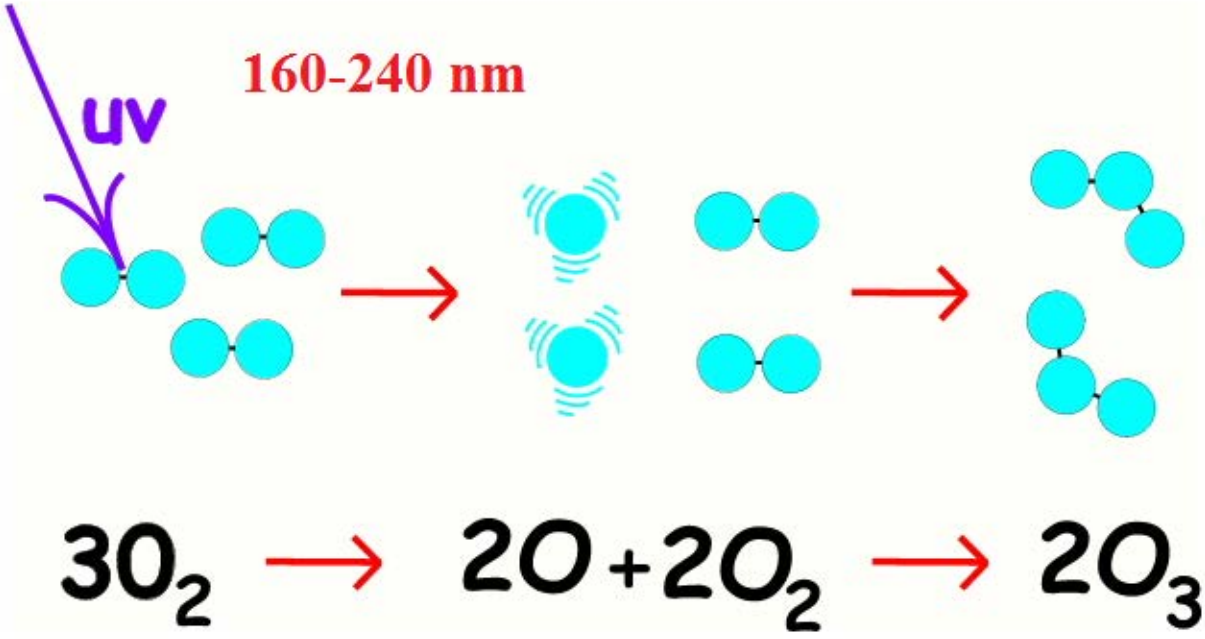


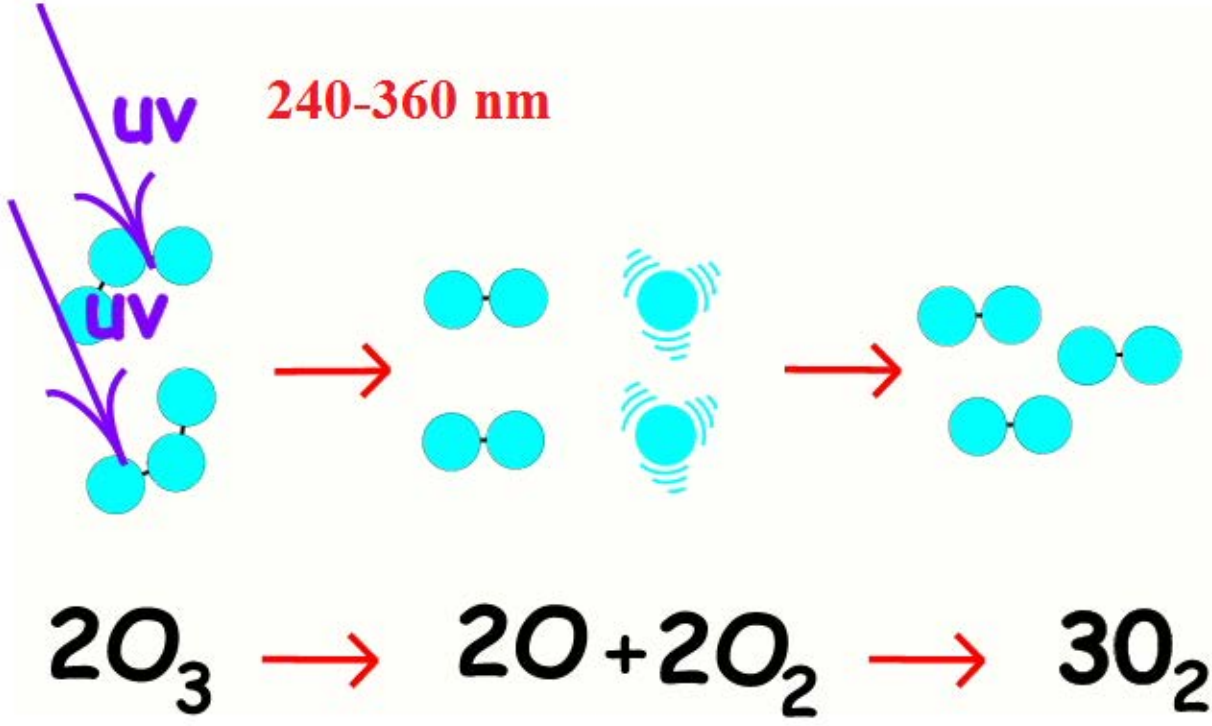
https://chem.libretexts.org/LibreTexts/New_York_University/CHEM-UA_127%3A_Advanced_General_Chemistry_I/14%3A_Linear_combination_of_atomic_orbitals


H_2^+
E_g
E_u
H + p
energy / au
0,0
-0,1
-0,2
-0,3
-0,4
-0,5
-0,6
0
2
4
6
8
R / a_o

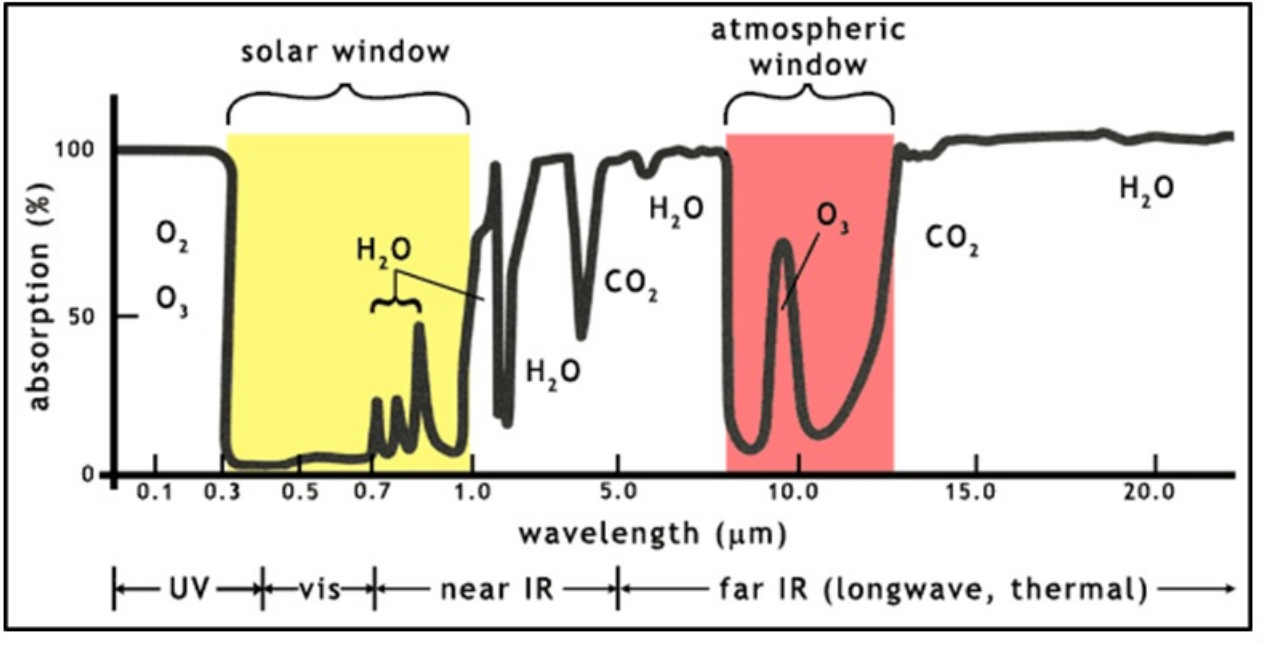
Potential curves in OH




160-240 nm
uv
$3O_2 \rightarrow 2O + 2O_2 \rightarrow 2O_3$


240-360 nm
uv
uv
$2O_3 \rightarrow 2O + 2O_2 \rightarrow 3O_2$

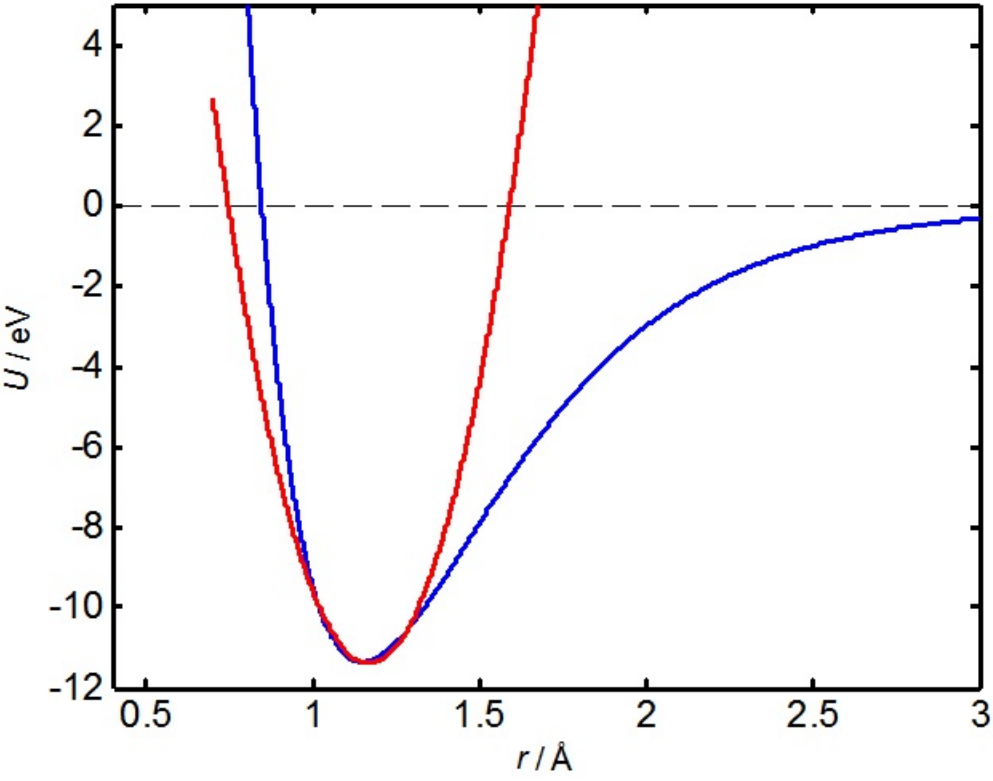
Absorption of Sunlight in the Atmosphere



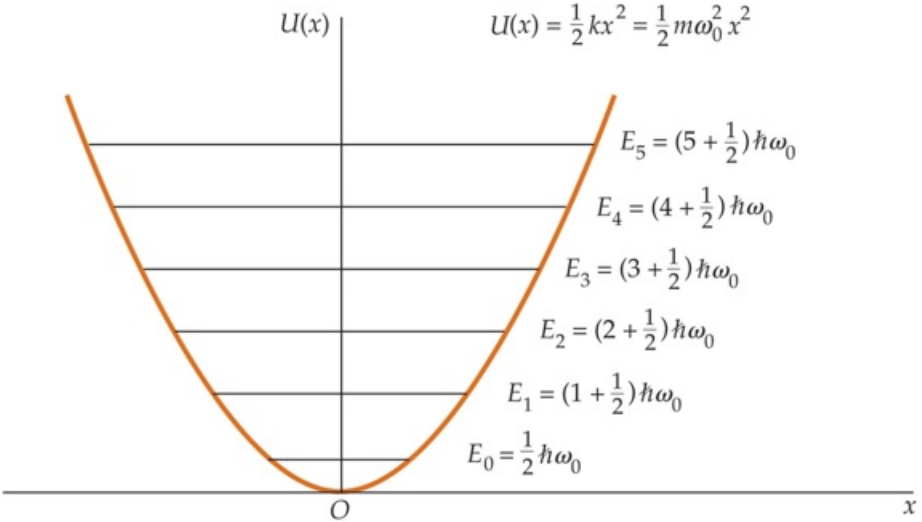
Atoms	Molecules
Energy <u>levels</u>	Energy <u>curves</u> (function of R)
Infinite number, converging to ionization limit	Limited number
$E \sim$ eV, $\lambda \sim$ UV, Visible	$E \sim$ eV, $\lambda \sim$ UV, Visible
Ionized up to Z	1, 2 times
-	Photo dissociation (ozone)
-	Vibration
-	Rotation

Vibrational Energy in a Diatomic Molecule

HO approximation (red) of the exact potential (blue) in CO



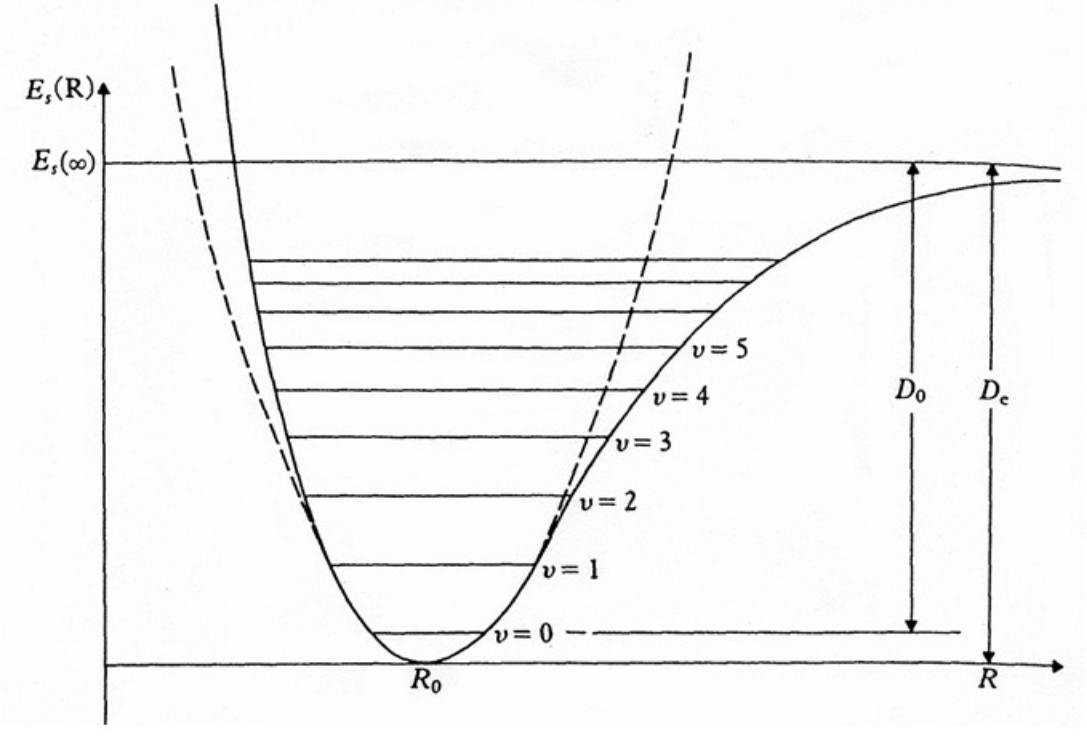
Quantized harmonic oscillator



$$E = (\nu + \frac{1}{2}) \cdot \hbar\omega_0, \ \ \nu = 0,1,2....$$

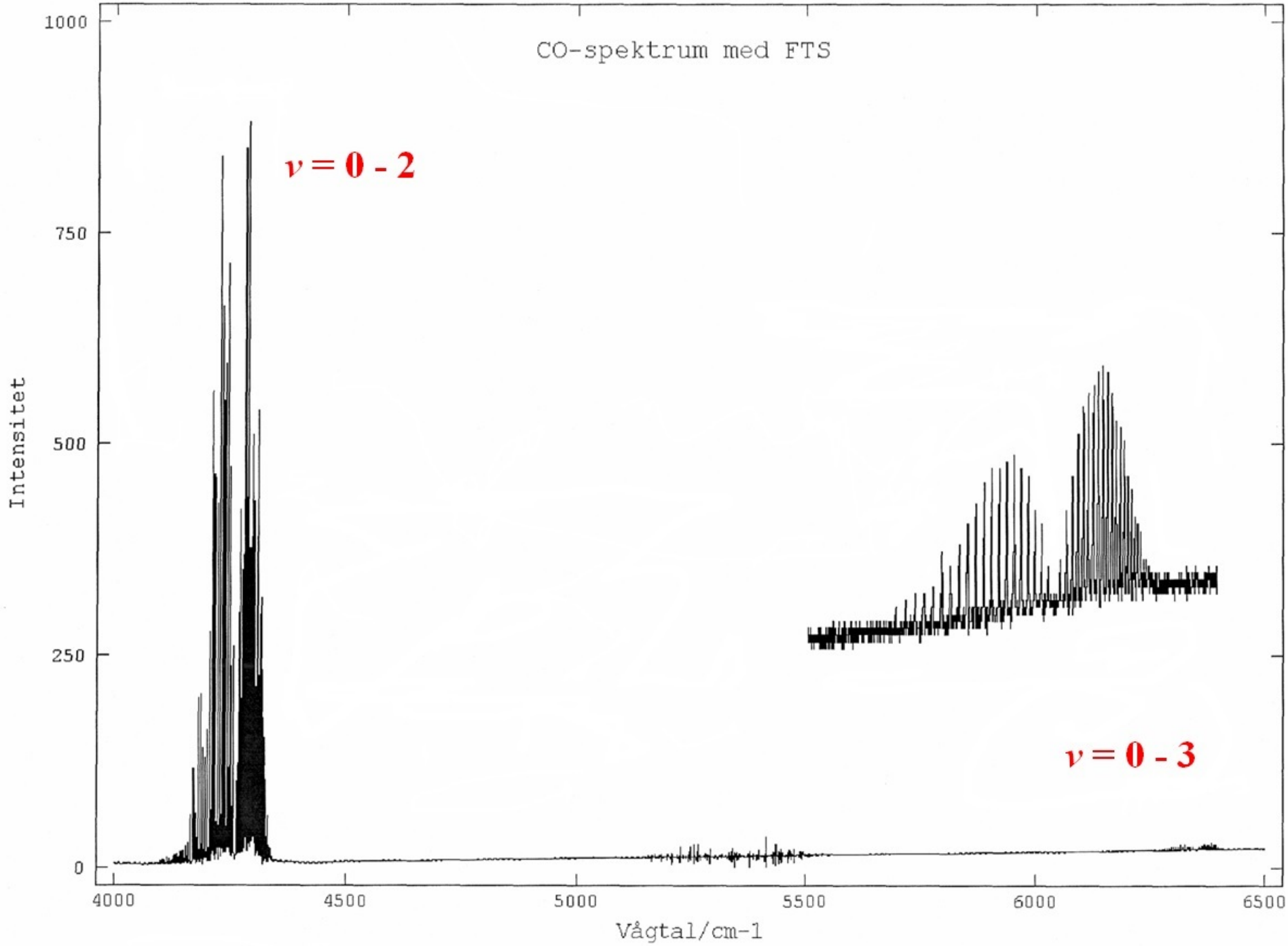
$$\Delta E = \hbar\omega_0$$

Comparison of vibrational energies in the HO approximation and in the real potential



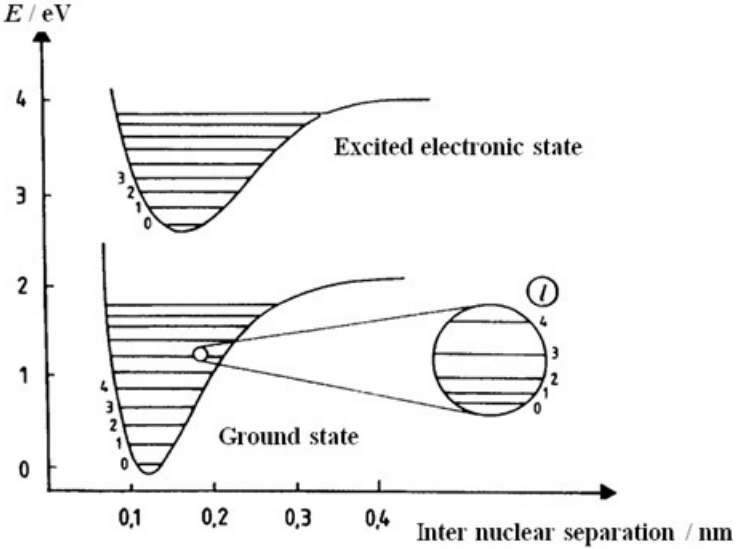
Selection rules: **HO:** $\Delta v = 1$

Real: $\Delta v = 1, 2, 3$ (>1 weak)


CO-spektrum med FTS
v = 0 - 2
v = 0 - 3
Intensitet
1000
750
500
250
0
4000
4500
5000
5500
6000
6500
Vågtal/cm-1

Energies in a Diatomic Molecule - Summary.

$$E = E_{elektron} + E_{vib} + E_{rot} = E_{elektron} + \hbar\omega_0(\nu + \frac{1}{2}) + \frac{\hbar^2}{2\mu r^2} \cdot \ell(\ell+1)$$

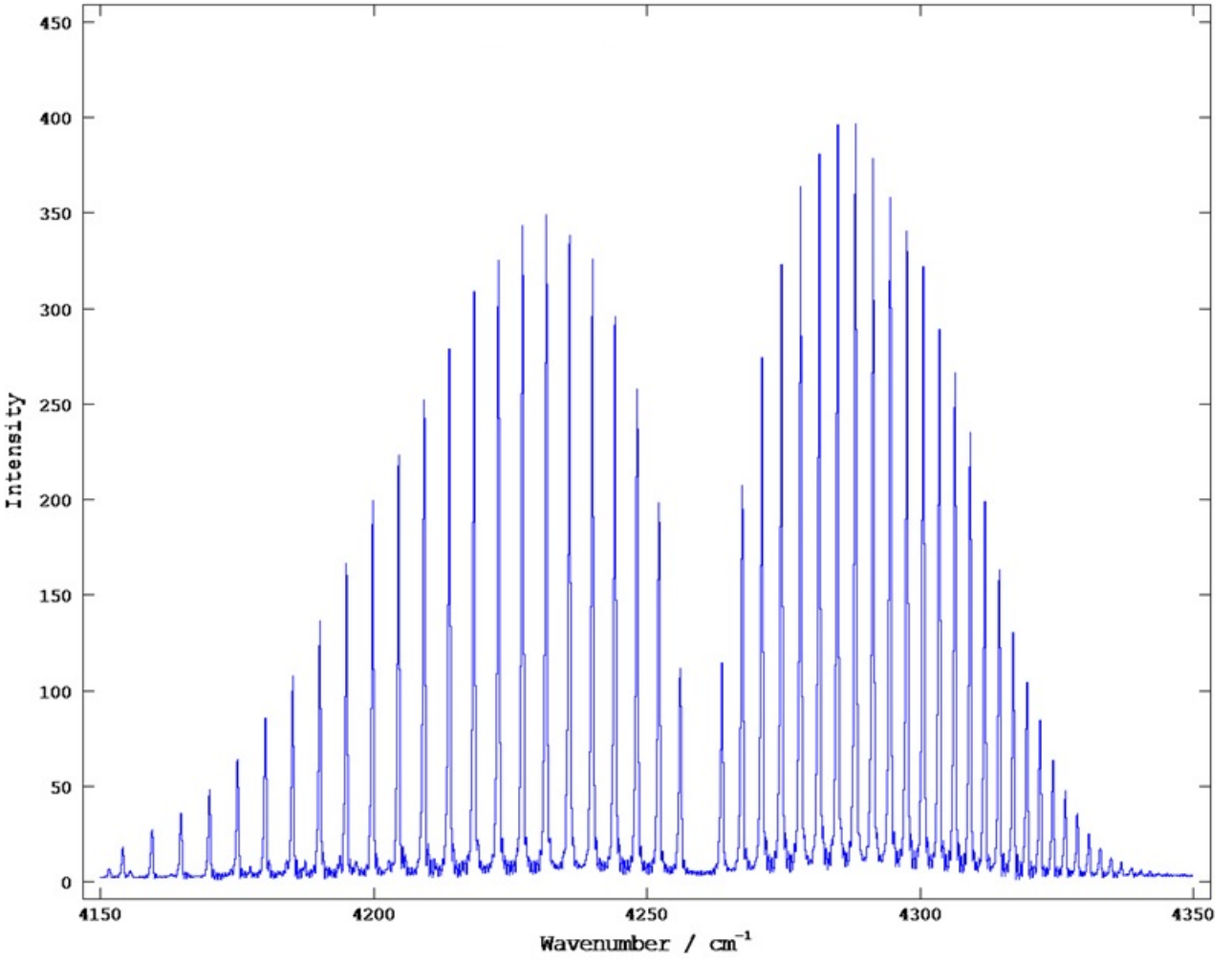


Orders of magnitude

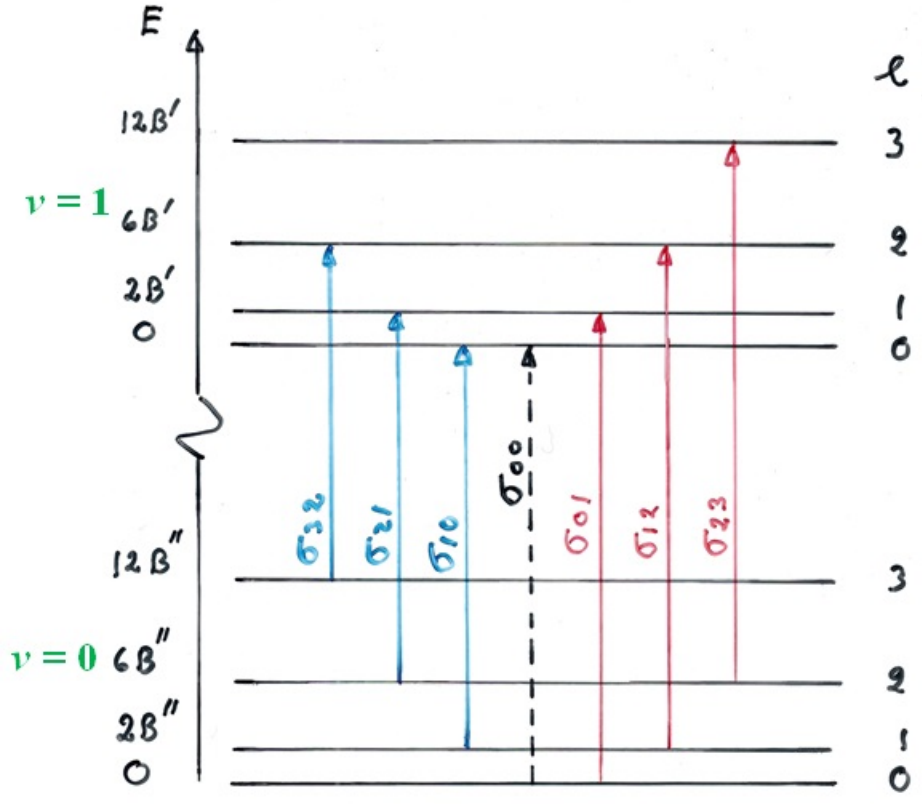
	Electron	Vibration	Rotation
E / cm^{-1}	40000	1500	10
E / eV	5	0.2	0.001
λ / µm	0.3	6	1000
T / K	40000	1500	10

(Note the coincidence that energies expressed in cm^{-1} and as a temperature in K has almost the same numerical value, i.e. $1/(100 \cdot h \cdot c) = 5.035 \cdot 10^{22} \approx 2/(3 \cdot k) = 4.83 \cdot 10^{22}$!)

Rotational Fine Structure in the 0 – 2 Vibrational Transition in CO



Rotational fine structure in a vibrational transition.



$$E_{rot} = \frac{\hbar^2}{2\mu R_0^2} \cdot \ell \cdot (\ell + 1) \equiv B \cdot \ell \cdot (\ell + 1)$$

Selection rule for rotation: $\Delta\ell = \pm 1$.

$\Delta\ell = +1$ is called R-branch $\Delta\ell = -1$ is called P-branch

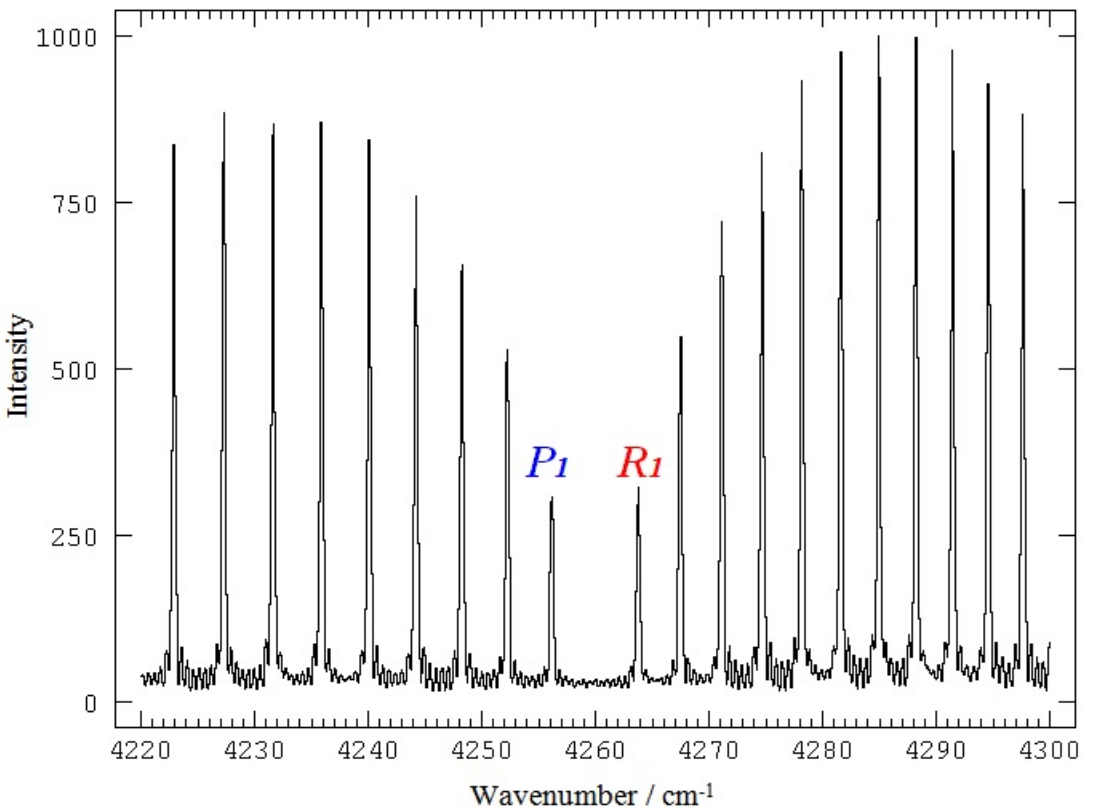
The figure shows part of an absorption spectrum for CO, in the 0 – 2 vibrational transition, registered using a Fourier-Transform spectrometer (in the figure the absorption spectrum is inverted so that it looks like an emission spectrum)

Using a Gaussian line profile we obtain the wavenumbers:

P_1, i.e. $\ell = 1 \rightarrow \ell = 0$: 4256,1248 cm^{-1}

R_1, i.e. $\ell = 0 \rightarrow \ell = 1$: 4263,7566 cm^{-1}.

Use this to determine the equilibrium distance between the C and O atoms assuming the moment of inertia is the same in the 2 vibrational levels



Molecular spectra – selection rules. (SP Ch.6)

For light to be emitted or absorbed the total angular momentum of the molecule has to change since the photon that is emitted/absorbed in a transition carries one unit of angular momentum. Since the vibrational states are not associated with any angular momentum, this implies that the rotational state and/or the electronic state must change. To state selection rules we therefore have to separate three cases.

Pure rotational transitions, i.e. within a vibrational level in a given electronic state. Wavelengths in the microwave range.

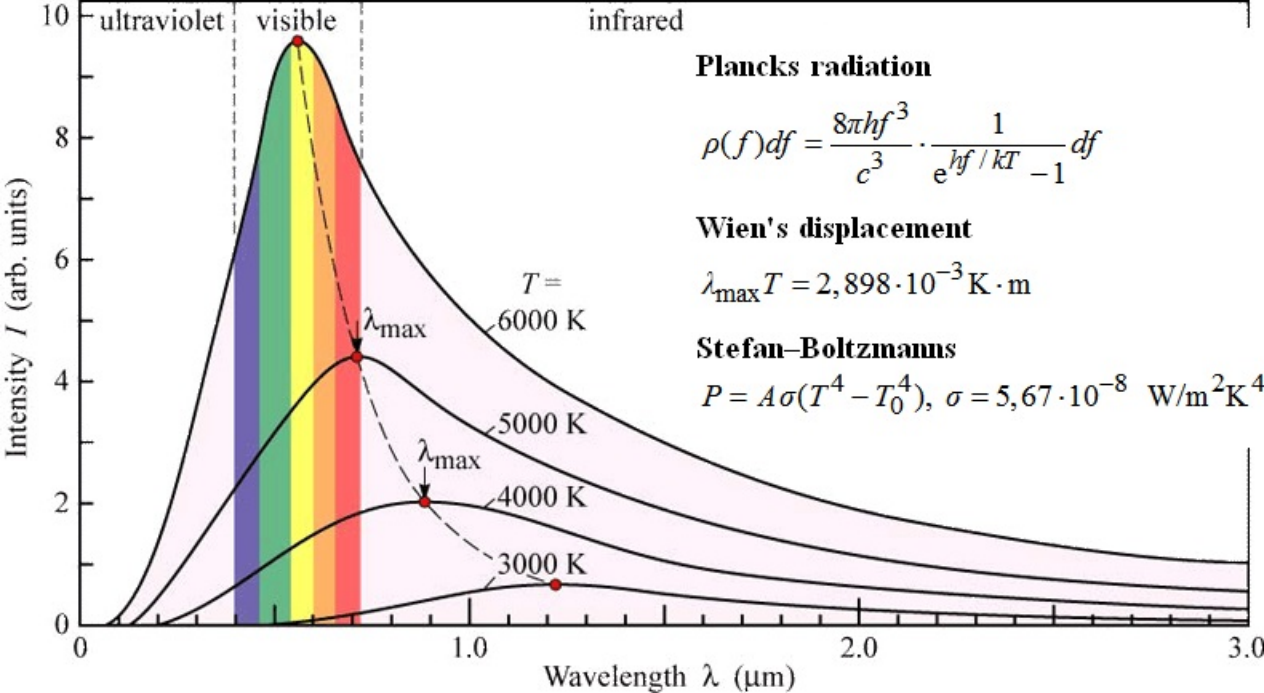
a. Homonuclear molecules (e.g. O_2, N_2), that lack permanent dipole moment, do not have rotational spectra since their rotation cannot interact with electromagnetic radiation.
b. $\Delta\ell = \pm 1$

Rotational-vibrational transitions, i.e. within a given electronic state. Wavelengths in IR.

a. Homonuclear molecules, that lack a permanent dipole moment, do not have rotational-vibrational spectra since their vibration cannot interact with the light.
b. $\Delta v = \pm 1$ (harmonic-oscillator approximation), ± 2, ± 3,...
c. $\Delta\ell = \pm 1$ (+1 yield R-branch, -1 yield P-branch)

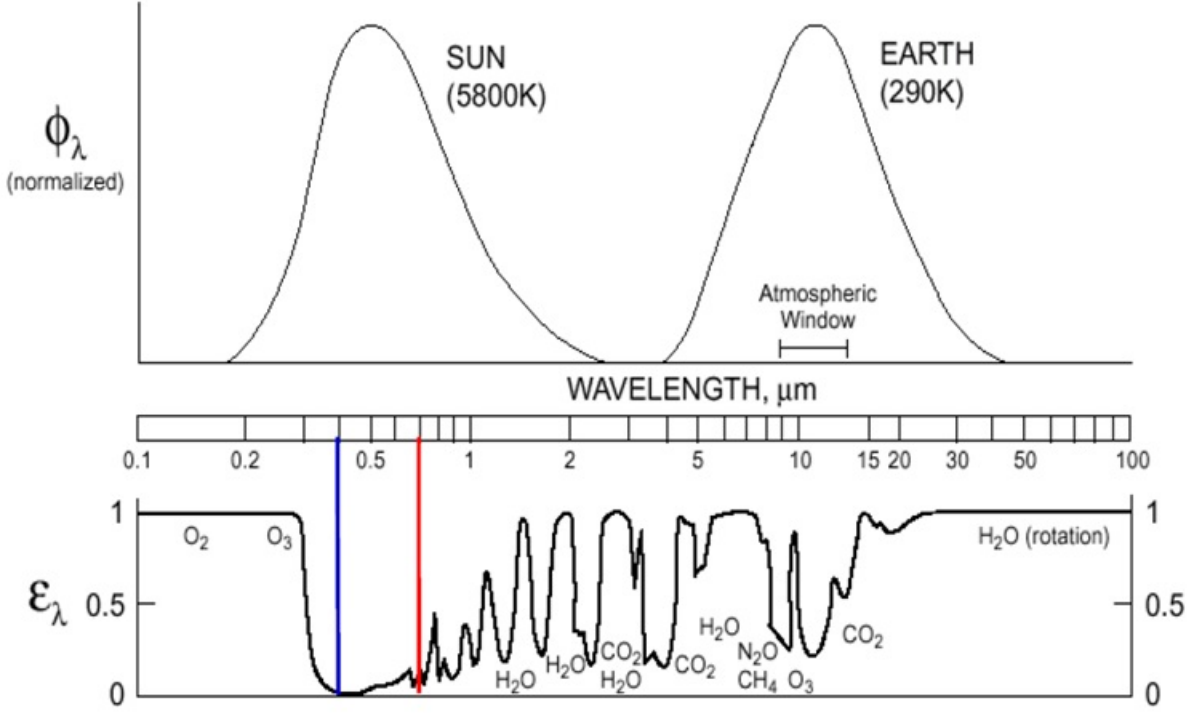
Transitions between electronic states. Wavelengths in visible or UV.

a. Analogous with the situation in atoms, selection rules can be stated for electronic transitions in molecules, utilizing the total eletron angular momentum and spin.
b. $\Delta v = 0, \pm 1, \pm 2, \pm 3,...$
c. $\Delta\ell = 0, \pm 1$ ($\Delta\ell = 0$ is called the Q-branch)
   $\Delta\ell = 0$ is forbidden in a pure rotational-vibrational transition, i.e. within an electronic state but permitted in conjunction with electronic transitions since the total angular momentum of the molecule might be different in the lower and upper electronic state respectively.

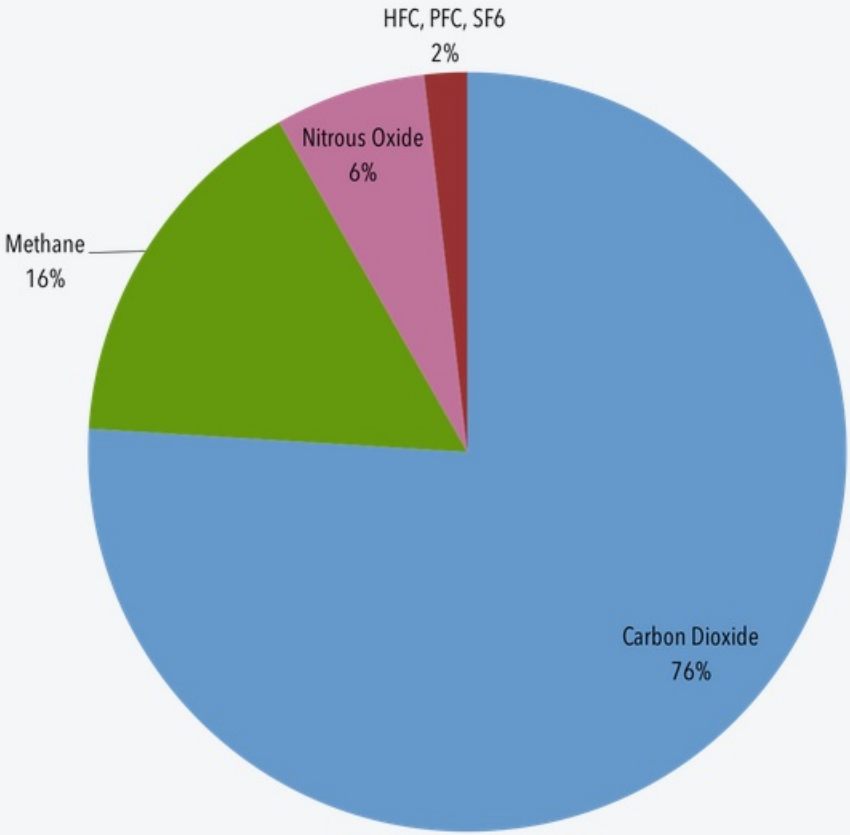

ultraviolet
visible
infrared
Plancks radiation
$\rho(f)df = \frac{8\pi hf^3}{c^3} \cdot \frac{1}{e^{hf/kT} - 1} df$
Wien's displacement
$\lambda_{max} T = 2,898 \cdot 10^{-3}\,\mathrm{K \cdot m}$
Stefan–Boltzmanns
$P = A\sigma(T^4 - T_0^4),\ \sigma = 5,67 \cdot 10^{-8}\ \mathrm{W/m^2K^4}$
T =
6000 K
5000 K
4000 K
3000 K
λ_{max}
λ_{max}
Intensity I (arb. units)
Wavelength λ (μm)
0
2
4
6
8
10
0
1.0
2.0
3.0

The Greenhouse Effect.

The black-body radiation from the Sun (5500 °C) and the Earth (18 °C) and the absorption in the atmosphere in different wavelength regions



Global Manmade Greenhouse Gas Emissions by Gas, 2015



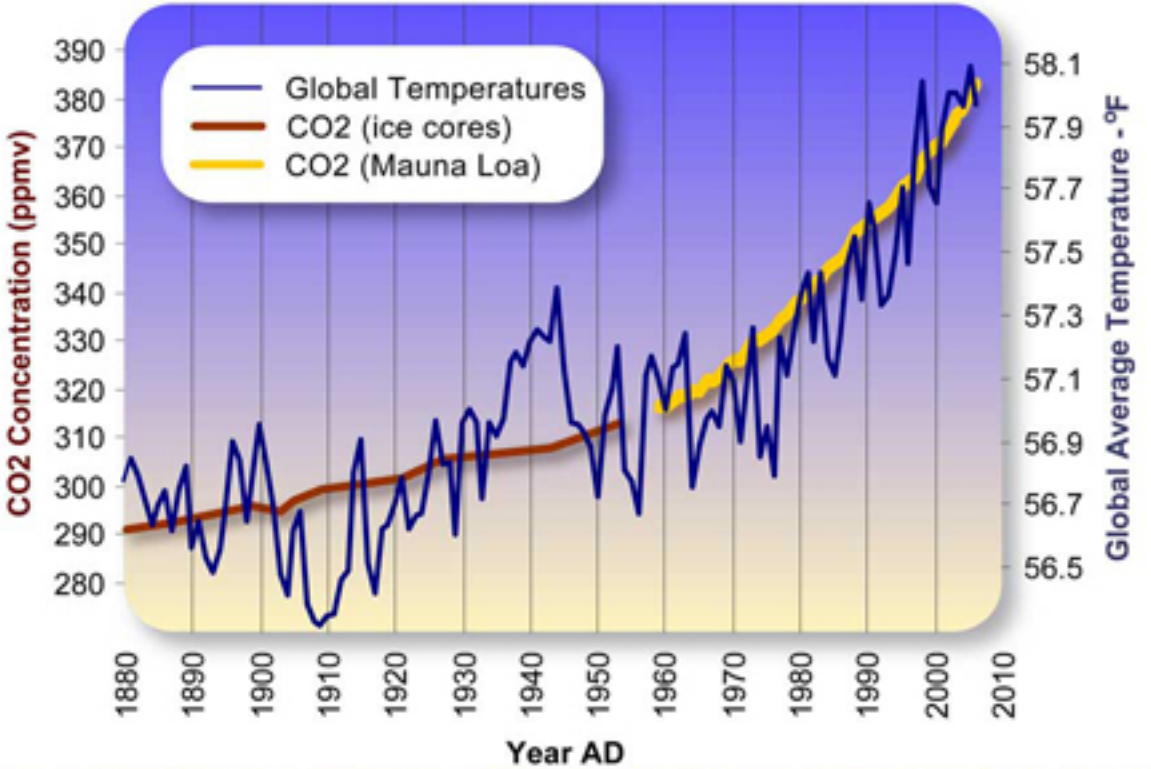
NOTES

CO2 accounts for about 76 percent of total greenhouse gas emissions. Methane, primarily from agriculture, contributes 16 percent of greenhouse gas emissions and nitrous oxide, mostly from industry and agriculture, contributes 6 percent to global emissions. All figures here are expressed in CO2-equivalents.

SOURCE

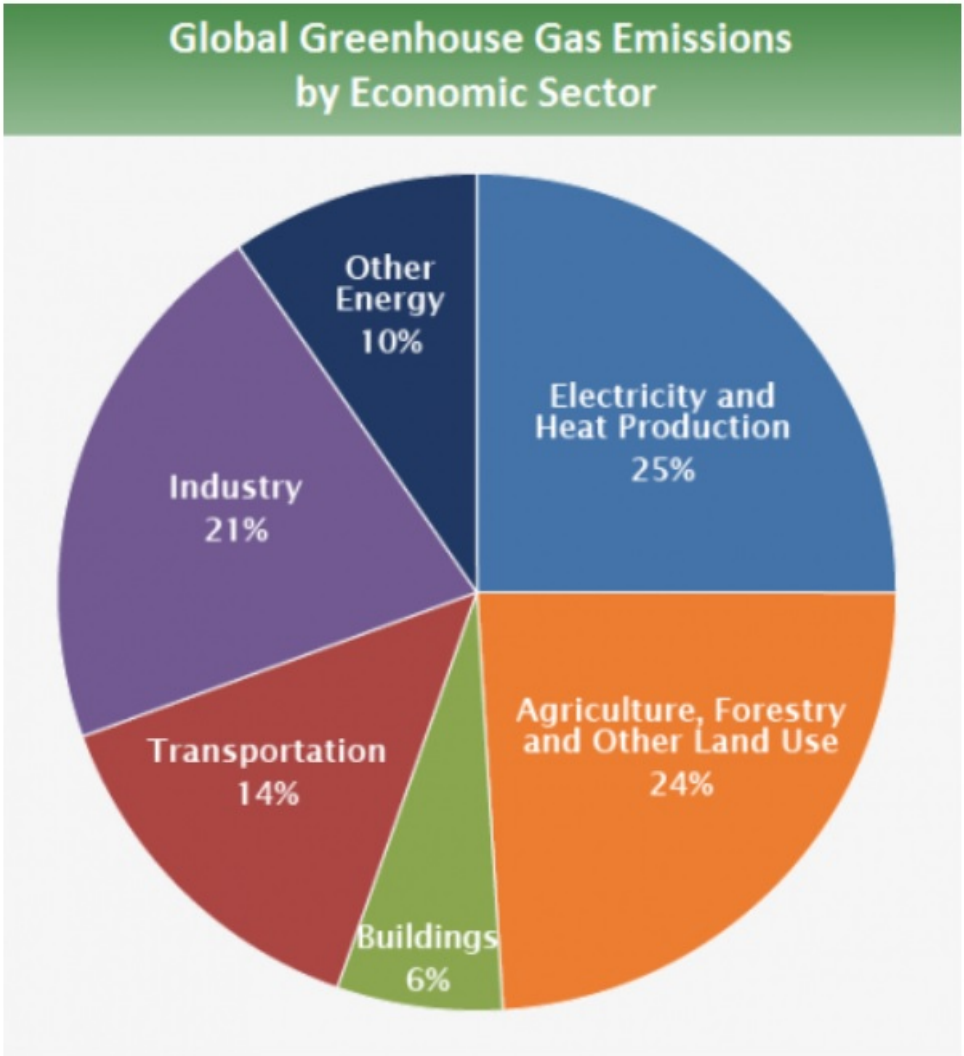
Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990-2015 (EPA, 2017)

Global Average Temperature and Carbon Dioxide Concentrations, 1880 - 2006



Data Source Temperature: ftp://ftp.ncdc.noaa.gov/pub/data/anomalies/annual.land_and_ocean.90S.90N.df_1901-2000mean.dat
Data Source CO2 (Siple Ice Cores): http://cdiac.esd.ornl.gov/ftp/trends/co2/siple2.013
Data Source CO2 (Mauna Loa): http://cdiac.esd.ornl.gov/ftp/trends/co2/maunaloa.co2
& http://www.esrl.noaa.gov/gmd/webdata/ccgg/trends/co2_mm_mlo.dat

Graphic Design: Michael Ernst, The Woods Hole Research Center



Source: IPCC (2014); EXIT based on global emissions from 2010. Details about the sources included in these estimates can be found in the *Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. EXIT