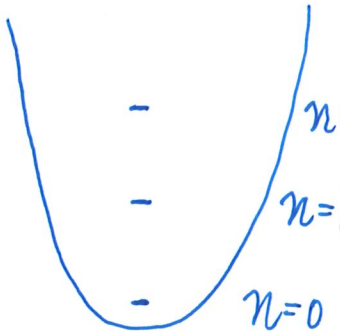
I. Transitions involving different vibrational levels



$\hbar\omega = \hbar\sqrt{\frac{k}{\mu}}$ (IR)

involving $n=0$ only

[c.f. rotational spectrum (microwave)]

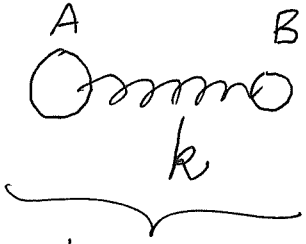
Q: What will happen when molecules interact with IR light?

Q: Any condition on the molecular property for absorption?

- Depending on resolution, spectrum shows different details
- $n=0 \rightarrow n=1$ oscillator state typical [room temp ~ 1/40 eV]

under what condition would this happen?
How to use spectrum to extract k ("spring constant")?

Diatomic Molecules



$$\omega = \sqrt{\frac{k}{\mu}}, \quad f = \frac{\omega}{2\pi}$$

only one normal mode [not counting freely moving CM]

Fundamental Vibrational Frequencies and Effective Force Constants for Some Diatomic Molecules

Molecule	Frequency (Hz), $n = 0$ to $n = 1$	Force Constant (N/m)
HF	8.72×10^{13}	970
HCl	8.66×10^{13}	480
HBr	7.68×10^{13}	410
HI	6.69×10^{13}	320
CO	6.42×10^{13}	1860
NO	5.63×10^{13}	1530

diatomic molecules

0.2 - 0.4 eV

From G. M. Barrows, *The Structure of Molecules*, New York, W. A. Benjamin, 1963.

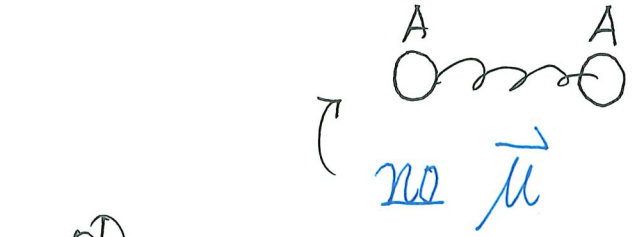
Units: 5×10^{13} Hz = 50 THz ; 0.207 eV; ~6000 nm (wavelength); 1668 cm^{-1} (wave number)

6 μm

- Why do we show $\nu(\omega)$ for AB molecules with $A \neq B$?

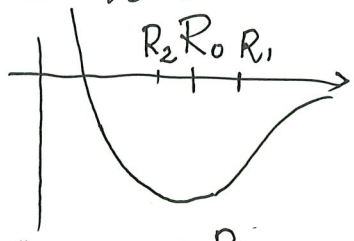
Electric dipole mechanism

molecule should carry an electric dipole moment



"$\nu\nu\nu$" due to electrons and electrons will not bias any side

Is that all?



$\mu = qR_0$ (constant)

$\mu = qR_1$

$\mu = qR_2$

Need this to have vibrational spectrum!

μ changes as atoms vibrate!

Aside: Transitions involving $n' \leftrightarrow n$ involve [e.g. $n=0$, $n'=1$]

$$\int \underbrace{\phi_{n'}^{*}(r-R_0)}_{\text{oscillator state } n'} \left[-\vec{\mu}\cdot\vec{\mathcal{E}}_0\right] \underbrace{\phi_n(r-R_0)}_{\text{oscillator state } n} dr \cdot \underbrace{[\text{integral for } \textcircled{H}, \textcircled{E}]}_{\text{related to } \Delta l \text{ (after taking care of } \Delta n)}$$

if $\vec{\mu}$ = constant (permanent dipole), $\int \phi_{n'}^{*}\phi_n dr = \underline{0}$ $(n \neq n')$ oscillator physics

Need $\vec{\mu} \approx \underbrace{\vec{\mu}(R=R_0)}_{\text{constant}} + \underbrace{\left.\frac{d\vec{\mu}}{dR}\right|_{R=R_0}}_{\text{electric dipole changes as } R \text{ vibrates about } R_0 \neq 0} \cdot (R-R_0)$

then $\left.\frac{d\vec{\mu}}{dR}\right|_{R=R_0} \int \phi_{n'}^{*}(r-R_0)\,(R-R_0)\,\phi_n(r-R_0)\,dr$

$$\propto \int \phi_{n'}^{*}(x)\cdot x \cdot \phi_n(x)\,dx \neq 0 \text{ only for } \Delta n = \pm 1$$

Also Needs molecule to have <u>varying $\vec{\mu}$ as it vibrates</u>

Two results follow: (a) Need $\left.\frac{d\vec{\mu}}{dR}\right|_{R=R_0} \neq 0$ (43)

changing electric dipole moment as molecule vibrates

Important for science of global warming

(b) $\Delta n = \pm 1$ (44)

selection rule on transitions between vibrational levels

[there is an angular integral determining Δl after taking care of Δn]

Results applicable to polyatomic molecules.

CO_2 linear molecule

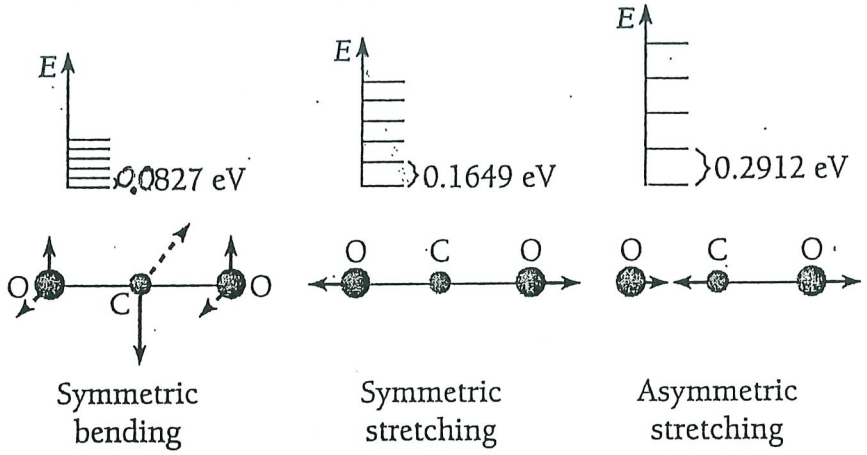
c.f. 

Normal modes, each with characteristic normal mode frequency

⇒ several independent oscillators

0.0827 eV ↕ 667 cm^{-1} ⇝

2 degenerate ⇝ modes



(different normal mode frequencies)

(4 vibrational modes)

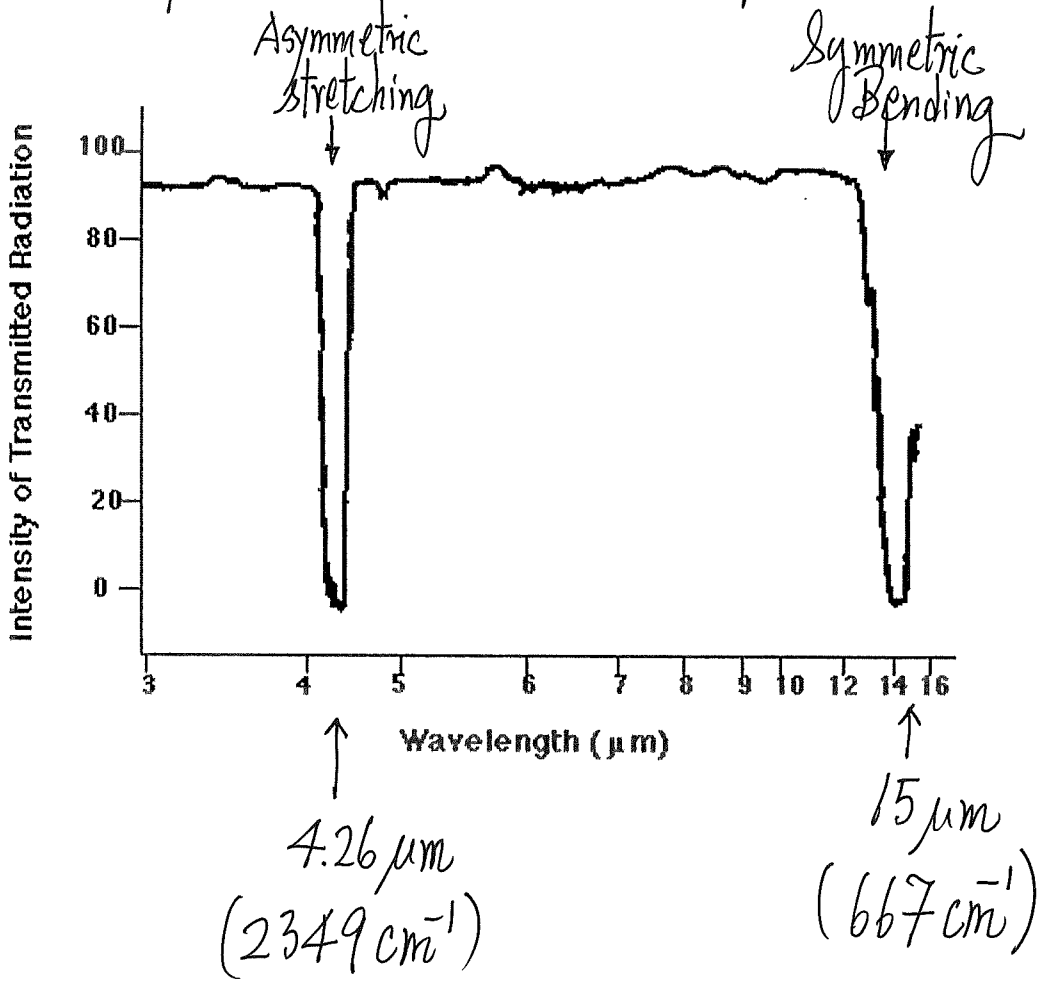
The normal modes of vibration of the CO_2 molecule and the energy levels of each mode. The symmetric bending mode can occur in two perpendicular planes.

↑ IR active
667 cm^{-1}
(15 μm)

↑ IR inactive
[$\vec{\mu}$ doesn't change]
1388 cm^{-1}
(7.2 μm)

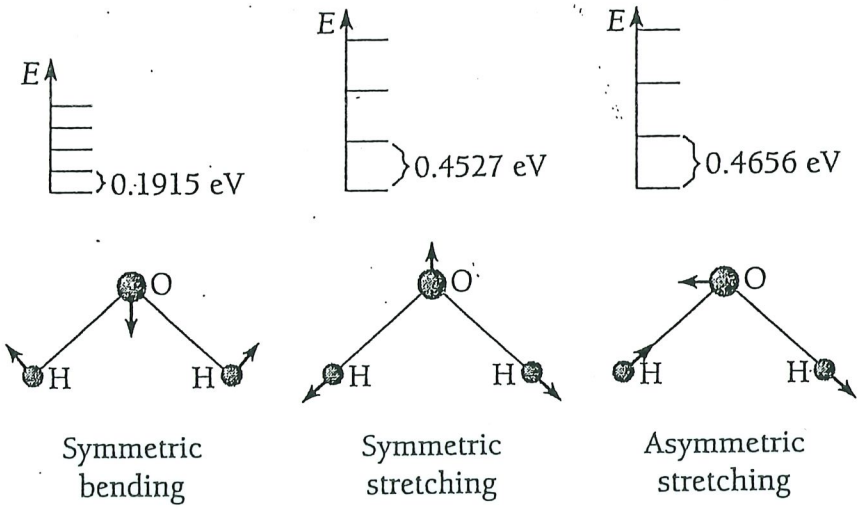
↑ IR active
2349 cm^{-1}
(4.26 μm)

CO_2 spectrum in IR [absorption due to IR active modes]



H_2O : Normal Modes (H_2O is not a linear molecule)

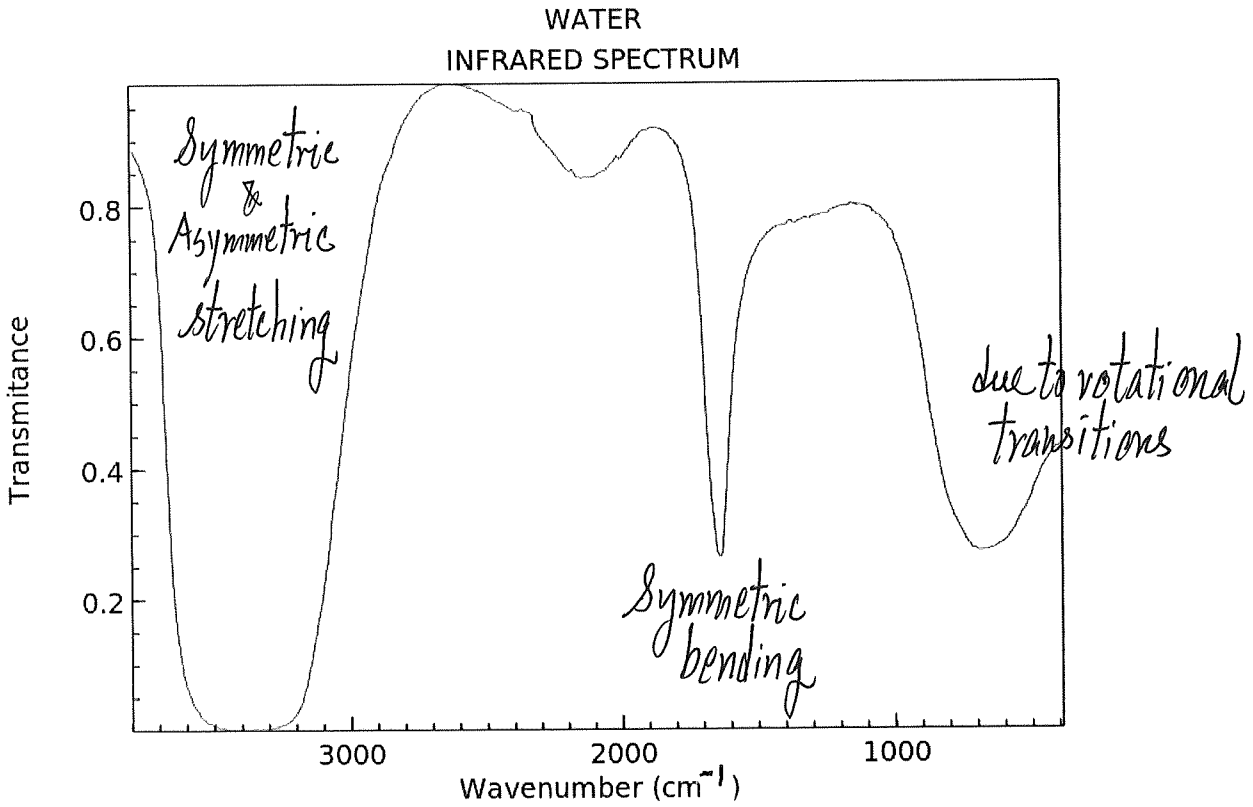
0.1915 eV
⇕
~1540 cm^{-1}



∴ 3 normal modes

↑ ALL are IR active ↑ ($\vec{\mu}$ changes as molecule vibrates)

↑	↑	↑
1595 cm^{-1}	3657 cm^{-1}	3756 cm^{-1}
(6.27 μm)	(2.74 μm)	(2.66 μm)

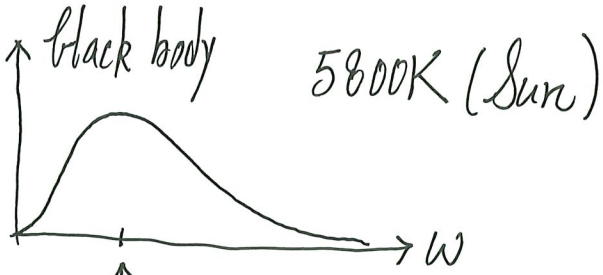


NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

CO_2 and H_2O (vapour) are Greenhouse Gases

Sun $T \sim 5800K$

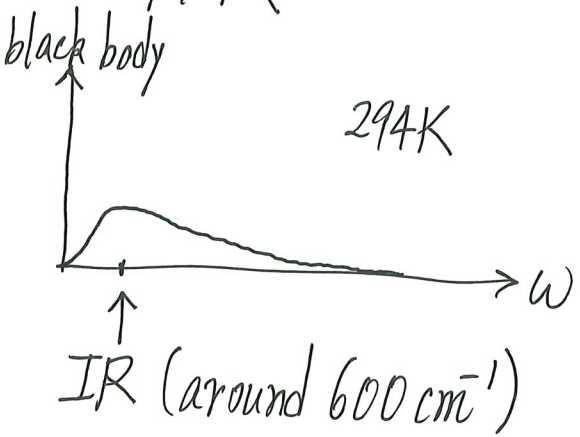
gives us $\sim 1360\ KW/m^2$
(solar constant)



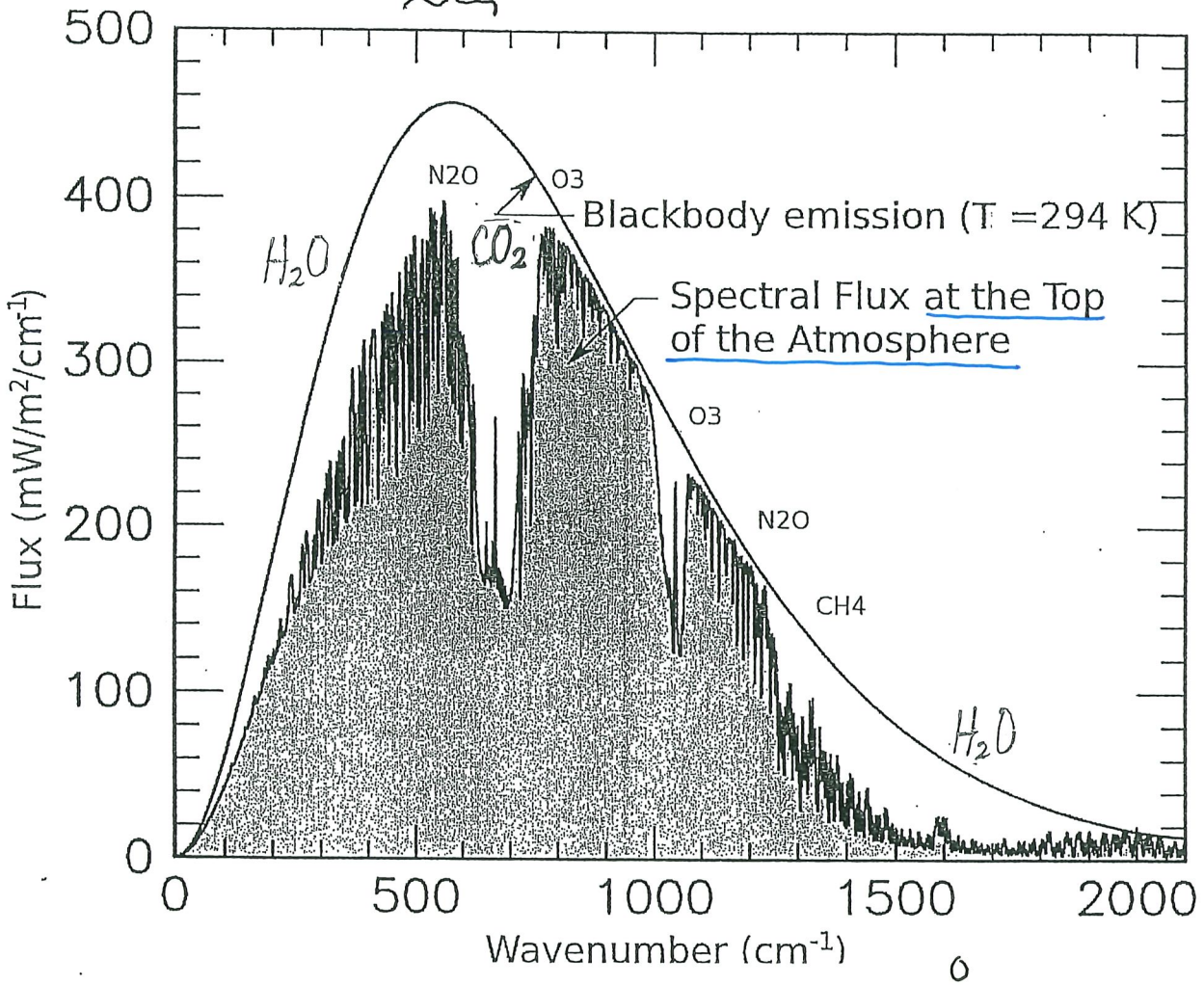
[our eyes evolve to fit to Sun's spectrum]

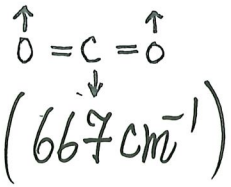
- Short wavelengths in and Long wavelengths out

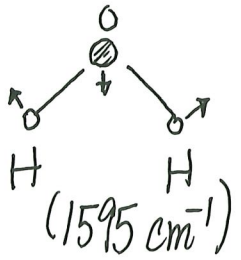
Earth $T \sim 20°C$ (average) $\sim 294K$



peak ($\sim 600\,cm^{-1}$) of Earth's radiations







"Greenhouse Effect"

- CO_2 suppresses heat (IR) loss (keeps us warm)†
- But we don't want to be too warm

† It is QM that keeps us warm!

- Earth's atmosphere:
  ~78% nitrogen†, ~20% oxygen†, ~0.9% argon
  ~0.038% CO_2 (~2010)

Records: ~1832: 0.028%
~1960: 0.032%
~1970: 0.033%
~1980: 0.034%
~1990: 0.035%
~2000: 0.037%

[Do human activities matter?]

Ways out?

- Reduce CO_2 production
- Reduce CO_2 emission
- Let CO_2 be produced

collect & store CO_2
Much research is on going!

[From Fayer, "Absolutely Small"]

† How lucky we are that O_2 and N_2 are not IR active!