

Transitions in atoms and molecules

A: green is higher energy ?

B: red has the longer wavelength ?

C: green has higher frequency ?

D: green higher wavenumber ?

E: all of the above

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CHEM 5161



You heat up 252g of water in the microwave
($\lambda=1.55$ cm) from 20 to 98 C.

- How many photons were absorbed by the water ?
- A: $x < 10^{10}$
- B: $10^{10} < x < 10^{20}$
- C: $10^{20} < x < 10^{30}$
- D: $10^{30} < x < 10^{40}$
- E: $10^{40} < x$



Schroedinger Equation and quantum numbers for atoms

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

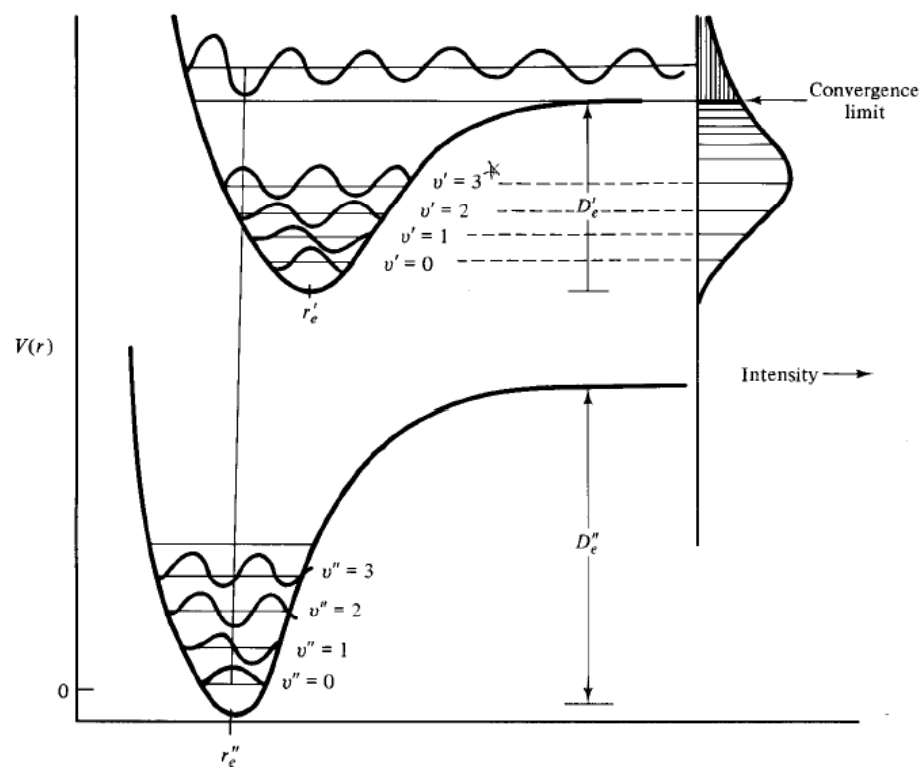
TABLE 7-1

Summary of quantum numbers for individual electrons

of Atoms

Quantum number	Description	Allowed values	Symbols
n	Principal quantum number; determines energy (size of elliptical orbit)	1, 2, 3, 4, . . .	1 = K shell 2 = L shell 3 = M shell etc.
l	Orbital (azimuthal) angular momentum quantum number; determines magnitude of orbital angular momentum (shape of orbital)	0, 1, 2, . . . , $n - 1$	0 = s orbital 1 = p 2 = d 3 = f etc.
m_l	Orbital magnetic quantum number; describes orientation of angular momentum vector	$l, l - 1, . . . , 0, . . . , -l$	s p_x, p_z, p_y $d_{x^2-y^2}, d_{xz}, d_{z^2}, d_{yz}, d_{xy}$
s	Electron spin quantum number; determines magnitude of spin angular momentum	$+\frac{1}{2}$	
m_s	Spin magnetic quantum number; describes orientation of spin angular momentum vector	$+\frac{1}{2}, -\frac{1}{2}$	\uparrow, \downarrow

Molecules (but NOT atoms)



Rotational kinetic energy (rigid rotor):

- Rotational quantum number $J = 0, 1, 2, \dots$
- Space Quantization $-J < M_J < J$
- $E_R = c J (J+1)$ (diverge with J)
- each rotational level is $(2J+1)$ fold degenerate

• Potential energy (harmonic oscillator):

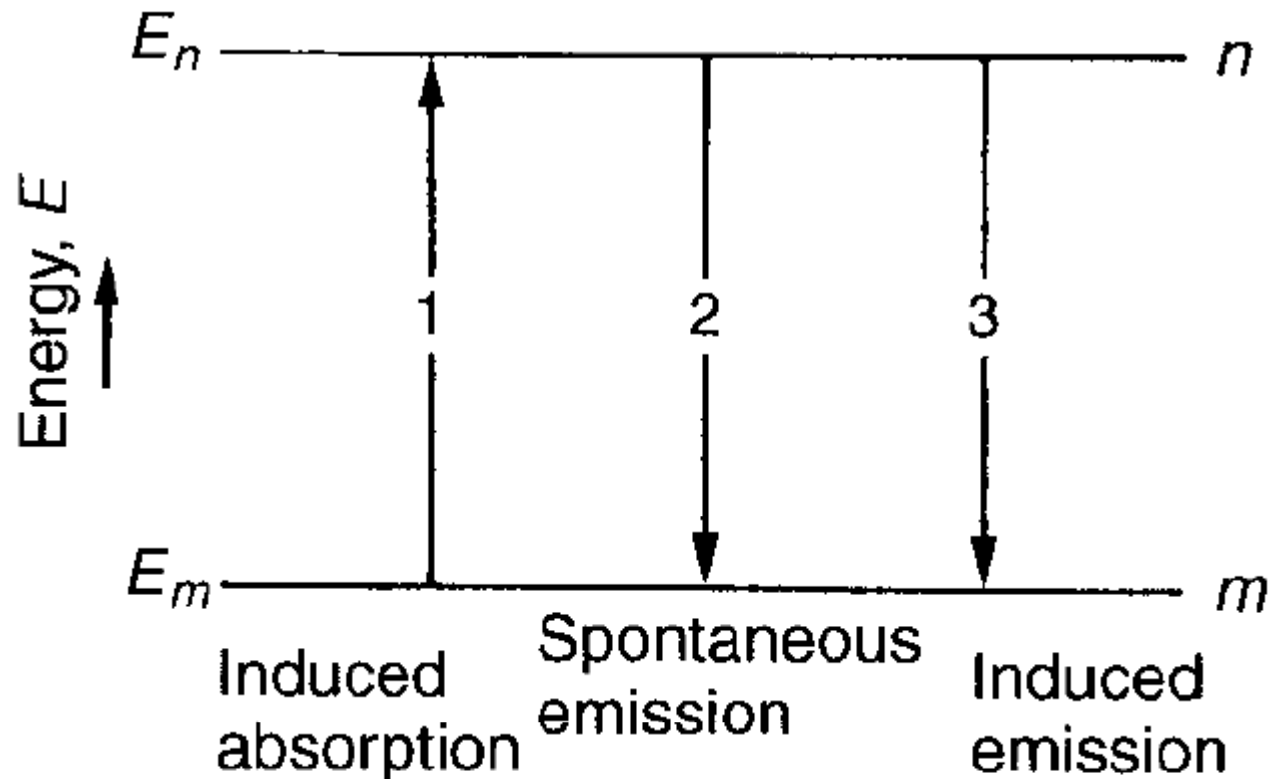
- Vibrational quantum number $v = 0, 1, 2, \dots$
- $E_V = h\nu (v + 1/2)$ (equally spaced)
- Non-zero “zero point energy”

• Born Oppenheimer approximation:

- way to simplify Schroedinger Equation
- factorize wavefunction into an electronic and nuclear component

• Overall Energy: $E = E_E + E_V + E_R$

How does quantum mechanics relate to observable absorption and emission rates ?



Transition dipole moment:

$$R^{nm} = \int \psi_n^* \boldsymbol{\mu} \psi_m \, d\tau \quad \boldsymbol{\mu} = \sum_i q_i \mathbf{r}_i$$

Energy density (Planck):

$$\rho(\tilde{\nu}) = \frac{8\pi h c \tilde{\nu}^3}{\exp(hc\tilde{\nu}/kT) - 1}$$

Einstein coefficients

- Absorption: $B_{1\leftarrow 0} = \frac{1}{6\varepsilon_0\hbar^2}\mu_{10}^2 = \frac{2\pi^2}{3\varepsilon_0\hbar^2}\mu_{10}^2$
- Stimulated Emission: $B_{1\leftarrow 0} = B_{1\rightarrow 0}$
- Spontaneous Emission: $A_{1\rightarrow 0} = \frac{8\pi h\nu_{10}^3}{c^3}B_{1\leftarrow 0}$
- Absorption cross-section: $\sigma = \frac{2\pi^2\mu_{10}^2}{3\varepsilon_0\hbar c}\nu$

They are all related quantities. That means,
if you know one, you can derive all the others !!

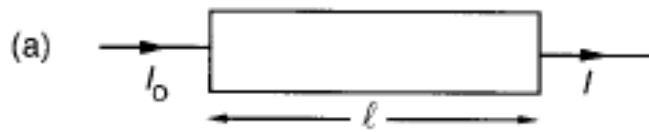
In equilibrium:

$$\frac{N_n}{N_m} = \frac{g_n}{g_m} \exp\left(-\frac{\Delta E}{kT}\right) = \exp\left(-\frac{\Delta E}{kT}\right)$$

$$A_{nm} = 8\pi hc\tilde{\nu}^3 B_{nm}$$

Question. For temperatures of 25 °C and 1000 °C, calculate the ratio of molecules in a typical excited rotational, vibrational and electronic energy level to that in the lowest energy level, assuming that the levels are 30 cm⁻¹, 1000 cm⁻¹ and 40 000 cm⁻¹, respectively, above the lowest energy level. [Three significant figures are sufficient. Assume that, for the excited rotational level, the rotational quantum number J is 4, and remember that each level is $(2J + 1)$ -fold degenerate. Assume that the vibrational and electronic energy levels are non-degenerate.]

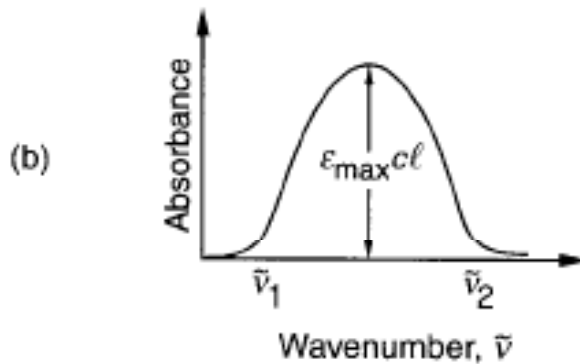
Lambert Beer's law



Decadic (base 10) version:

$$A = \log_{10} \left(\frac{I_0}{I} \right) = \epsilon(\tilde{\nu}) c \ell$$

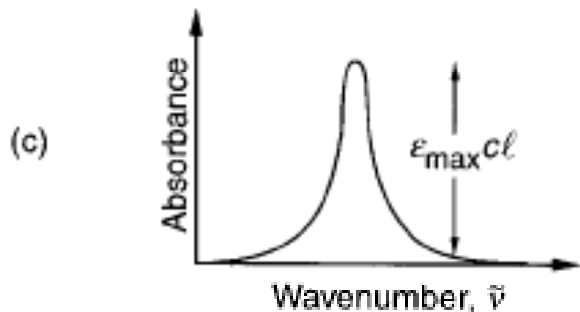
Hollas



Base e version:

$$I = I_0 e^{-\sigma(N_0 - N_1)l}$$

Bernath



Units:

Cross section [cm^2]

Number density [molecules / cm^3]

Length [cm]

Or

Concentration [moles/l]

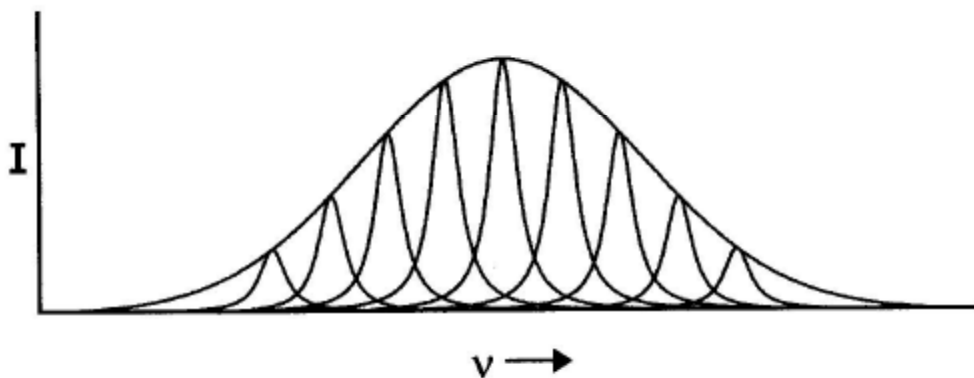
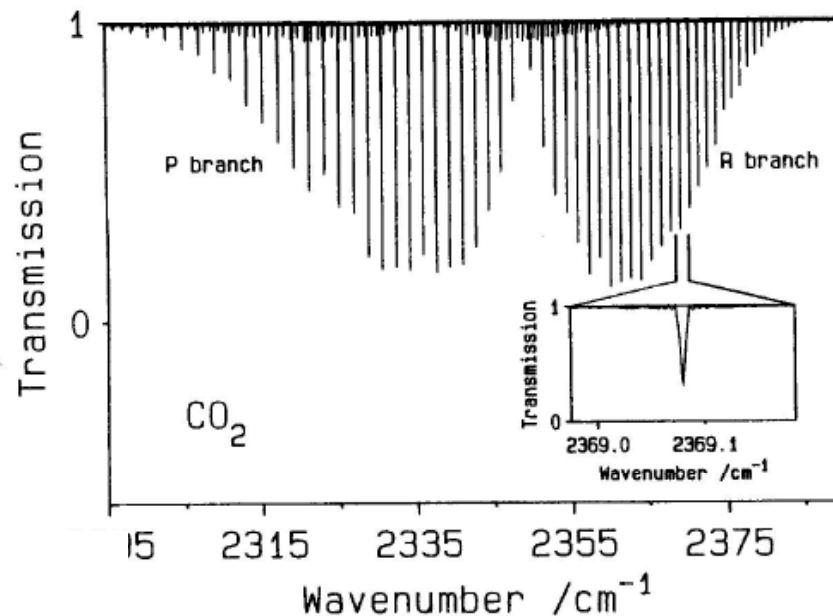
Molar absorption coefficient [l/mole/cm]

Length [cm]

What are limitations to Lambert Beers law ?

Limitations to Lambert Beer's law

- Saturation effects
- Resolution effects



- The global mean OH free radical concentration is about 10^6 molecules cm^{-3} . OH has a UV absorption band near 308nm, with a peak absorption cross-section of 10^{-16} cm^2 molecule $^{-1}$. What absorption path is needed to obtain a 1/10000 change in the atmospheric transmission ($1-I/I_0$) at 308nm due to OH?
- A: 10 m
- B: 500 m
- C: 2 km
- D: 10 km
- E: > 10 km

