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

Sept 2 2008
CHEM 5161
You heat up 252g of water in the microwave \( (\lambda = 1.55 \text{ cm}) \) 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

\[ H = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \]

<table>
<thead>
<tr>
<th>Quantum number</th>
<th>Description</th>
<th>Allowed values</th>
<th>Symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>Principal quantum number; determines energy (size of elliptical orbit)</td>
<td>1, 2, 3, 4, ...</td>
<td>1 = ( K ) shell  2 = ( L ) shell  3 = ( M ) shell etc.</td>
</tr>
<tr>
<td>( l )</td>
<td>Orbital (azimuthal) angular momentum quantum number; determines magnitude of orbital angular momentum (shape of orbital)</td>
<td>0, 1, 2, ..., ( n - 1 )</td>
<td>0 = ( s ) orbital  1 = ( p )  2 = ( d )  3 = ( f ) etc.</td>
</tr>
<tr>
<td>( m_l )</td>
<td>Orbital magnetic quantum number; describes orientation of angular momentum vector</td>
<td>( l, l-1, \ldots, 0, \ldots, -l )</td>
<td>( s )  ( p_x, p_y, p_z, d_{x^2-y^2}, d_{xz}, d_{xy}, d_{yz} )</td>
</tr>
<tr>
<td>( s )</td>
<td>Electron spin quantum number; determines magnitude of spin angular momentum</td>
<td>( +\frac{1}{2}, -\frac{1}{2} )</td>
<td>( \uparrow, \downarrow )</td>
</tr>
<tr>
<td>( m_s )</td>
<td>Spin magnetic quantum number; describes orientation of spin angular momentum vector</td>
<td>+( \frac{1}{2}, -\frac{1}{2} )</td>
<td>( \uparrow, \downarrow )</td>
</tr>
</tbody>
</table>
Molecules (but NOT atoms)

Rotational kinetic energy (rigid rotor):
- Rotational quantum number $J = 0, 1, 2, \ldots$
- 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 $v = 0, 1, 2, \ldots$
- $E_V = \hbar \nu (v + 1/2)$ (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:

\[ R_{nm} = \int \psi_n^* \mu \psi_m \, d\tau \]

\[ \mu = \sum_i q_i r_i \]

Energy density (Planck):

\[ \rho(\nu) = \frac{8\pi \hbar \nu^3}{\exp(hc\nu/kT) - 1} \]
Einstein coefficients

• Absorption: \[ B_{1\leftarrow 0} = \frac{1}{6\varepsilon_0 \hbar^2} \mu_{10}^2 = \frac{2\pi^2}{3\varepsilon_0 h^2} \mu_{10}^2 \]

• 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:

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

\[A_{nm} = 8\pi hc\tilde{v}^3 B_{nm}\]

*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:

\[ A = \log_{10} \left( \frac{I_0}{I} \right) = \alpha(\tilde{v}) c \ell \]

Hollas

Base e version:

\[ I = I_0 e^{-\sigma(N_0 - N_1)\ell} \]

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 Beer's 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