Spectroscopy, Global Warming and the Ozone Layer

Chemistry 35

Fall 2000

Spectroscopy: Probing Atoms and Molecules

- Atomic emission spectroscopy was a critical link to the structure of *electrons* inside the atom

Can we learn <u>more</u> about these systems with spectroscopy?

Let's take a look . . .

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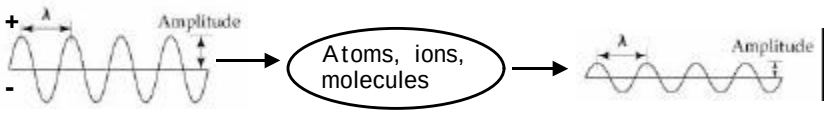
One View of EMR/Matter Interactions

- **Resonance**

  -EMR as *oscillating electric field* propagating through space

  -if the *frequency* of oscillation matches a *natural* oscillation frequency of the system, the system can ***absorb*** energy from the EMR, reducing its amplitude:



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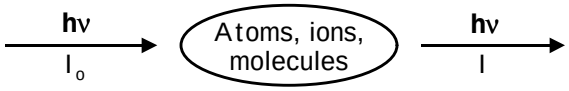
Another View

- **Quantum**

  -EMR as a stream of photons propagating through space

  -if the *energy* of a photon *matches the energy of a* ***transition*** between two energy states of the system, *the photon can be absorbed by the system*, raising it to the excited state:



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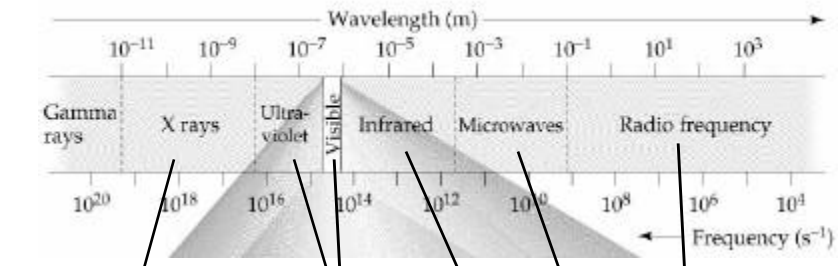
What can we "see" with Spectroscopy?



Inner shell *electrons*
(core *electron energies*)

Outer shell *electrons*
(*electron configurations*)

Molecular *vibrations*
(*bond lengths/angles*)

Molecular *rotations*
(*bond strengths*)

Nuclear spin states
(*electron density near nucleus*)

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Infrared Absorption

- Probes the *vibrational modes* of a molecule
- *Resonance* view works well here:
  -in order for a molecule to absorb IR EMR, there must be a *change in the dipole moment* during the vibration

  -**Why?**
  - If dipole moment *changes* during a vibration, then the molecule has an *electric field* oscillating at the frequency of the vibration
  - If IR EMR is at the same freq as the molecular vibration, then the two oscillating electric fields can interact and exchange energy (molecule *absorbs* IR EMR)

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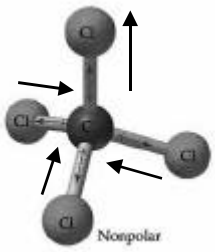
What Molecules Absorb IR?

- Almost ***all*** molecules have at least *one* vibrational mode which results in a changing dipole
- Even molecules with no dipole moment? Yes!



CCl_4

✓Not all vibrational modes will be symmetrical

BUT: All *homonuclear diatomic* molecules are **IR INACTIVE**

(all vibrational modes are symmetrical)

So: N_2, O_2, H_2, F_2, etc. do not absorb in the IR

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Environmental Aspects of IR Absorption

- Although N_2 and O_2 *don't* absorb IR, molecules such as *CO_2 and H_2O* ***DO***
- So:
  - Light from the sun enters the atmosphere and reaches the surface of the Earth
  - The surface of the Earth *absorbs* the EMR, and *reradiates it as IR* (**blackbody radiation**)
  - Molecules such as CO_2 and H_2O in the atmosphere *absorb* some of the IR, preventing it from leaving the atmosphere (**radiation trapping**)

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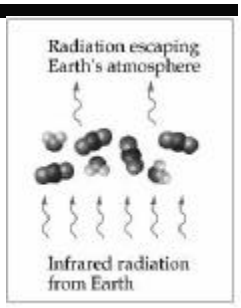
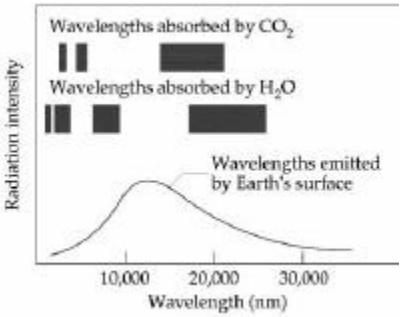
The Greenhouse Effect





- The greenhouse effect is responsible for life on this planet:

  -the avg temp of the Earth is ***30 - 35º higher*** than it would be without the greenhouse effect

  -without the greenhouse effect, *the oceans would be frozen year 'round*

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So, the Greenhouse Effect is good?

- Yes . . . and no . . .
- *What if the amount of "greenhouse gases" began to increase?*

  -increased temperature
  -increased H_2O vaporized into atmosphere
  -more IR absorption

  RUNAWAY GREENHOUSE EFFECT

Example: Venus

-Surface temp: ~450ºC (would be 100ºC w/o GHE)

-Atmosphere is *96% CO_2* (clouds are made of H_2SO_4)

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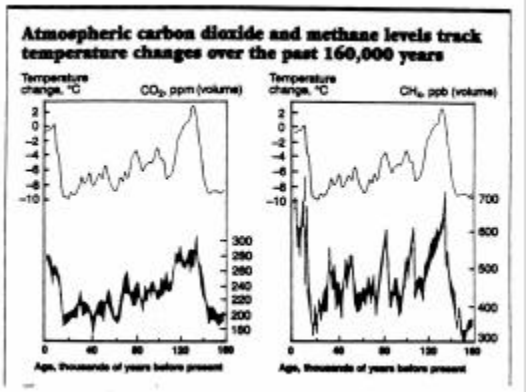
"Global Warming"?

- Atmospheric CO_2 and CH_4 levels correlate well with global temperatures over the past 160,000 years:



CO_2 and CH_4 values: meas. in air bubbles from 1 mile deep Antartic ice core

Temperature values: inferred from *deuterium* levels in the ice core (deuterium is enriched at higher temperatures)

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Why is the Earth's Temp Increasing?

- Hypothesis: *increased* CO_2 in atmosphere
- Arrhenius Model (1900): **doubling CO_2** in atmosphere will increase temps by **5-6 degrees**

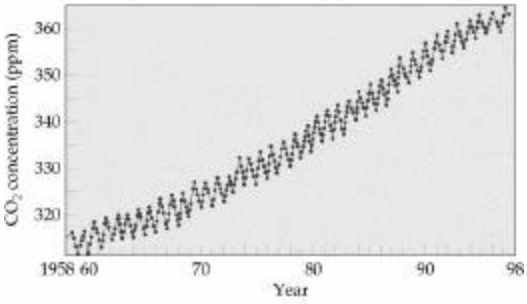
CO_2 levels:

-constant (280 ppm) until early 1800's

-steadily increasing

-about *25% increase* over the past 100 years

-about *0.7°C temp increase* over the past 100 years



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The Carbon Cycle

"Natural" Emission of CO_2:

-25% from respiration

-25% from plant/animal decomposition

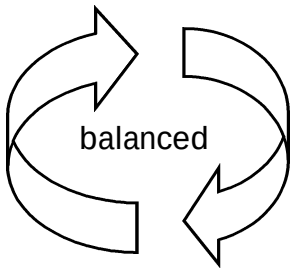
-50% from rock ($CaCO_3$) decomposition

"Natural" Uptake of CO_2

-50% from photosynthesis

-50% dissolves in oceans: $CO_2 + H_2O \rightarrow 2H^+ + CO_3^{2-}$

$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3(s)$



- burning fossil fuels *increases CO_2 emission* by about 3 billion tons/year (out of more than 200 billions tons emitted "naturally").

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What do we *know?*

- Two things that most agree on:
  1. Increases in CO_2 (and other greenhouse gases) can result in global warming
  2. CO_2 levels are rising AND global temperatures are rising
- Two things that are *hotly disputed:*
  1. The *magnitude* of the temperature increases
  2. The *impact* of such temp increases on life on Earth

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What about the "Ozone Layer"?

- Another *spectroscopy-related* issue

  -ozone (O_3) is produced in the upper atmosphere (stratosphere) by *photolytic decomposition of oxygen:*

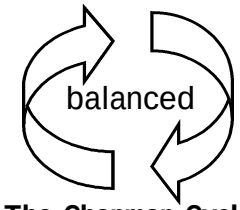
  $O_2 + hn\ (< 242\ nm) \rightarrow 2\ O\bullet$

  $O\bullet + O_2 \rightarrow O_3$

  -ozone is also *destroyed* photolytically:

  $O_3 + hn\ (< 320\ nm) \rightarrow O_2 + O\bullet$

  $O_3 + O\bullet \rightarrow 2\ O_2$



The Chapman Cycle

- 300 million tons of ozone created and destroyed each day
- Typical ozone molecule survives 100 - 200 secs

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Environmental Implications

- Photolytic ozone creation and depletion shields the surface of the Earth from ***95 - 99% of UV*** light from the Sun
- Other (naturally occurring) compounds can also participate in the Chapman Cycle:

  $N_2O + O\bullet \rightarrow 2\ NO\bullet$

  $NO\bullet + O_3 \rightarrow NO_2 + O_2$

  $NO_2 + O\bullet \rightarrow NO\bullet + O_2$

  -this reduces the amount of ozone in the stratosphere

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Chlorofluorocarbons (CFC's)

- Developed in the 1930's by Dupont as a safe refrigerant to replace ***toxic and corrosive*** NH_3 and SO_2

  Example: CFC-12 (CF_2Cl_2)

  -very unreactive -noncorrosive

  -non-flammable

  -a gas at room temperature (B.P. ~30 ^oC)

  -a chemistry success story!

- Very popular (850,000 tons produced/year by 1985)

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Where do CFC's go?

- **Unforeseen problem:** CFC's are so *unreactive* that they do not decompose in the lower atmosphere
- After 2-5 years, CFC's drift into the stratosphere (upper atmosphere) where they *photodissociate:*

$$CCl_3F + hn\ (UV) \rightarrow CCl_2F\bullet + Cl\bullet$$

- $Cl\bullet$ reacts with O_3:

$$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$$
$$ClO\bullet + O\bullet \rightarrow O_2 + Cl\bullet$$

-this cycle can repeat as many as 100,000 times before terminating and forming HCl or $ClONO_2$

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Environmental Implications

- As CFC levels have increased, O_3 levels have decreased (with the expected time delay)
- Effect is not disputed (scientifically)
  - resulted in a Nobel Prize for the scientists (Rowland and Mollina) who first proposed this
- Decreased O_3 levels allows more UV to reach the Earth's surface
  - 10% increase in UV causes about 10% increase in skin cancer (equiv. to living 200 km closer to the equator)

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Solutions?

- CFC use has been phased out
- New "ozone layer friendly" compounds (HFC's - ***hydro***fluorocarbons) have been developed which perform similarly but do not have the same reactive properties which result in O_3 destruction
- <u>BUT:</u> it will be about a ***century*** before CFC levels drop back to levels which do not have a significant impact on the ozone layer

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Is there a "Global Warming" and "Ozone Depletion" connection?

- Commonly used *interchangeably* by the media, there ***are*** some connections:

  -CFC's *also* contribute to the "greenhouse effect" by effectively trapping IR

    -CO_2 accounts for a little more than half of global warming effects (CFC's contribute about 25%)

  -increased UV levels inhibits plant growth

    -could result in decreased CO_2 uptake by plants, increasing CO_2 levels

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