CHEMISTRY C1404
Spring 2003

- Professors: FINE and VALENTINI
- Preceptor: Melissa MORLOK
- Webmaster: Michael CLAYTON
- Undergraduate Office:
  - Socky LUGO
  - Daisy MELENDEZ

Nota Bene

LECTURES are MW or TR, 11:00-12:15 P.M.

OFFICE HOURS are immediately after class and from 2-4 PM on most Friday afternoons.

RECITATION SECTIONS begin next week. There are 16 of them. Register for one.

LABORATORY COURSES begin next week. Note that C1500 is independent of the C1404 lecture.

SEMINARS IN RESEARCH begin on this Friday.

Syllabus for the Course Professor FINE

- Spectroscopy and Atmospheric Chemistry
- The Gaseous State
- Condensed Phases and Phase Transitions
- Chemical Equilibrium
- Acid-Base Equilibria
- Dissolution and Preciptiation Equilibria

- Structure and Bonding in Solids

Syllabus for the Course
Professor VALENTINI

- Thermochemistry
- Spontaneous Change and Equilibrium
- Redox Reactions and Electrochemistry
- Electrochemistry and Cell Voltage
- Chemical Kinetics

- Silicon and Solid State Materials

Exam Schedule

- Three Term-time Exams:
  - EXAM 1 February 18 7:30 P.M.
  - EXAM 2 March 25 7:30 P.M.
  - EXAM 3 April 22 7:30 P.M.
- Comprehensive FINAL Exam:
  - EXAM 4 May 9 9:00 A.M.

ChemWrite

- Philip BALL: Life's Matrix
- Rachel CARSON/Albert GORE: Silent Spring
- Kenneth DEFFEYES: Hubbert's Peak-The Impending World Oil Shortage
- Eric KLINENBERG: Heat Wave
- Tom SCHACHTMAN: Absolute Zero
- Vaclav SMAIL: Enriching the Earth - Fritz Haber, Carl Bosch, and the Transformation of World Food
- Kurt VONNEGUT: Cat's Cradle

Grading

- Three Term-time Exams (16% each)
- Comprehensive Final Exam (26%)
- CHEMWrite (16%)
- QUIZZES (10%)
- Total of 157 points=100%
- Online evaluation (up to 3-point bonus)

COURSE Policy

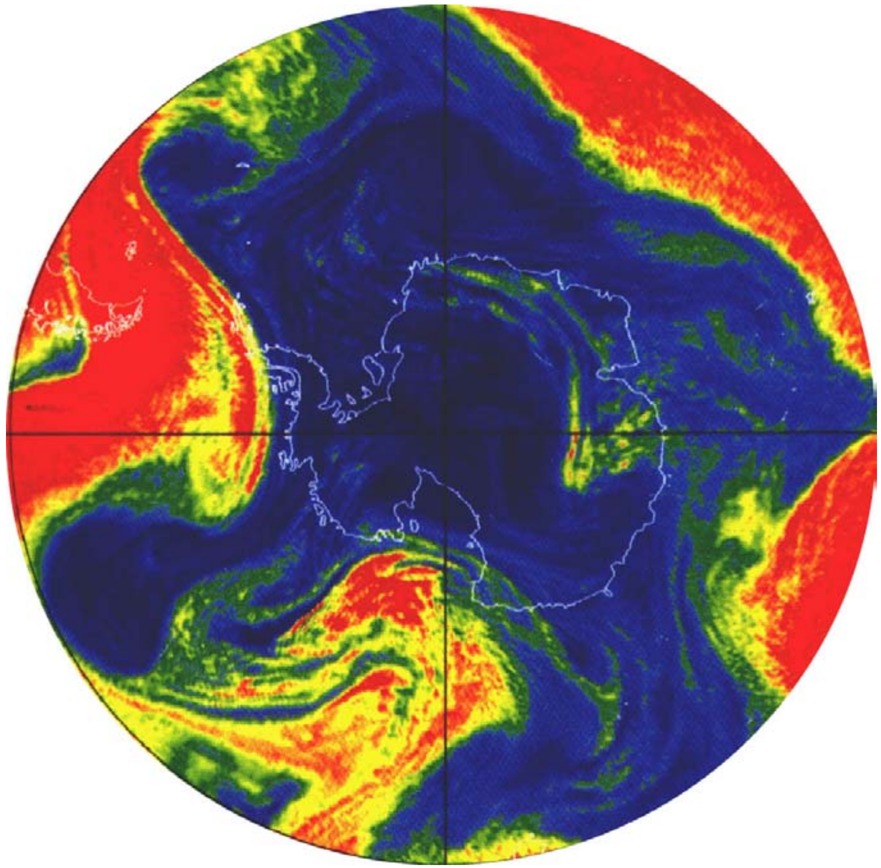
- MAKE-UP EXAMS. NONE! No Kidding!
- EXCUSED ABSENCES. In advance and for just cause, you may be excused from one of the three term-time exams.
- CONFLICT RESOLUTION with regard to the three Tuesday evening exams:
  - must be done in advance
  - with the UNDERGRADUTE OFFICE,
  - the week before the exam
  - for genuine, irreconcilable conflicts

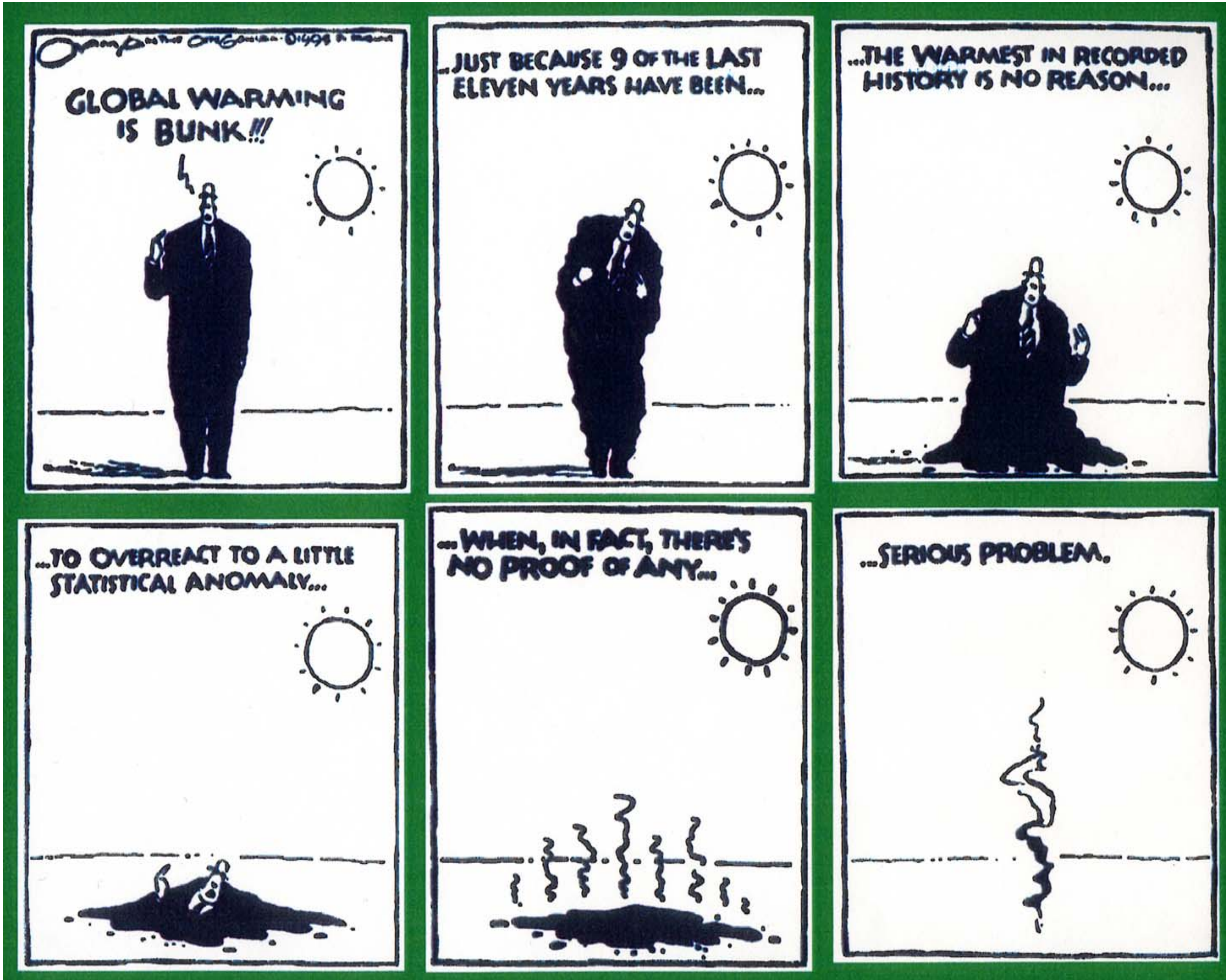
Chemistry is the Science of Molecules and Bonds

- Spectroscopy
- Atmospheric Chemistry
- Properties of Gases State

GASES
Extremely Important!

- The air that is our atmosphere supports life as we know it:
  - 80% Nitrogen (N_2) and 20% Oxygen (O_2)
- Other constituents, because they are present in trace quantities, cannot be ignored:
  - They establish a delicate balance:
    - Ozone (and the real ultraviolet catastrophe)
    - Carbon dioxide (and global warming)




GLOBAL WARMING IS BUNK!!!
...JUST BECAUSE 9 OF THE LAST ELEVEN YEARS HAVE BEEN...
...THE WARMEST IN RECORDED HISTORY IS NO REASON...
...TO OVERREACT TO A LITTLE STATISTICAL ANOMALY...
...WHEN, IN FACT, THERE'S NO PROOF OF ANY...
...SERIOUS PROBLEM.

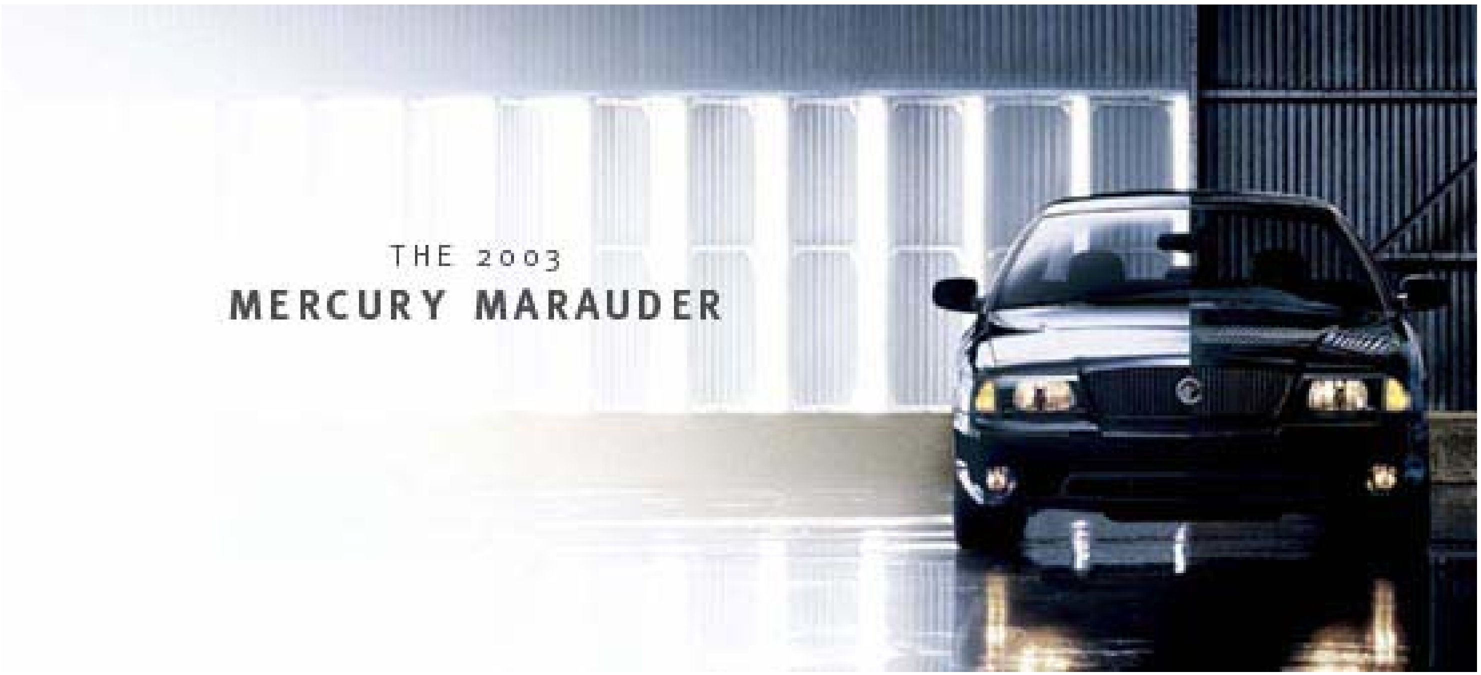
Atmospheric Gases Control Earth's Temperature

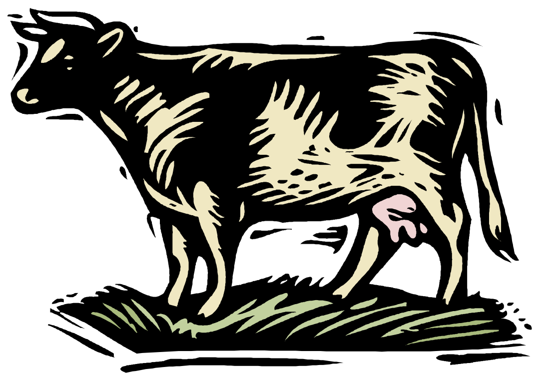
- Radiation from the Sun is converted to heat at the Earth's surface.
- Earth reradiates a fraction of the heat at longer wavelengths which cannot penetrate the atmosphere and are retained.
- As a result, an ambient temperature is established that determines life on Earth.
- The balance is critical.

GREENHOUSE GASES

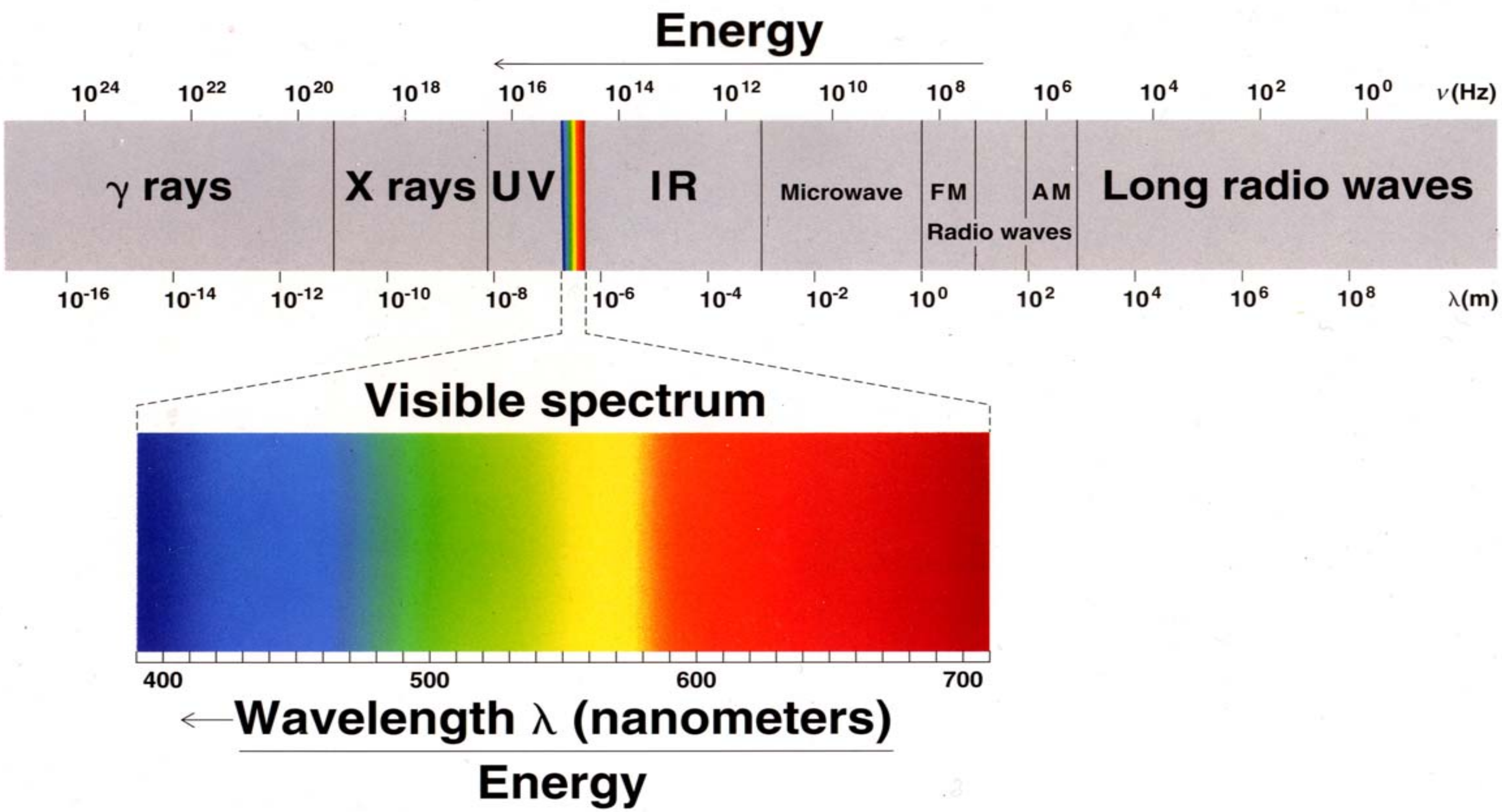
- Naturally occurring Greenhouse Gases that have been on the increase, largely from anthropogenic sources:
  - Methane (CH_4)
  - Carbon Dioxide (CO_2)
  - Dinitrogen Oxide (N_2O)

GREENHOUSE GASES





Electromagnetic Spectrum



Spectroscopic Properties

$$E(nergy) = h\nu = h\frac{c}{\lambda} = hc\bar{\nu}$$

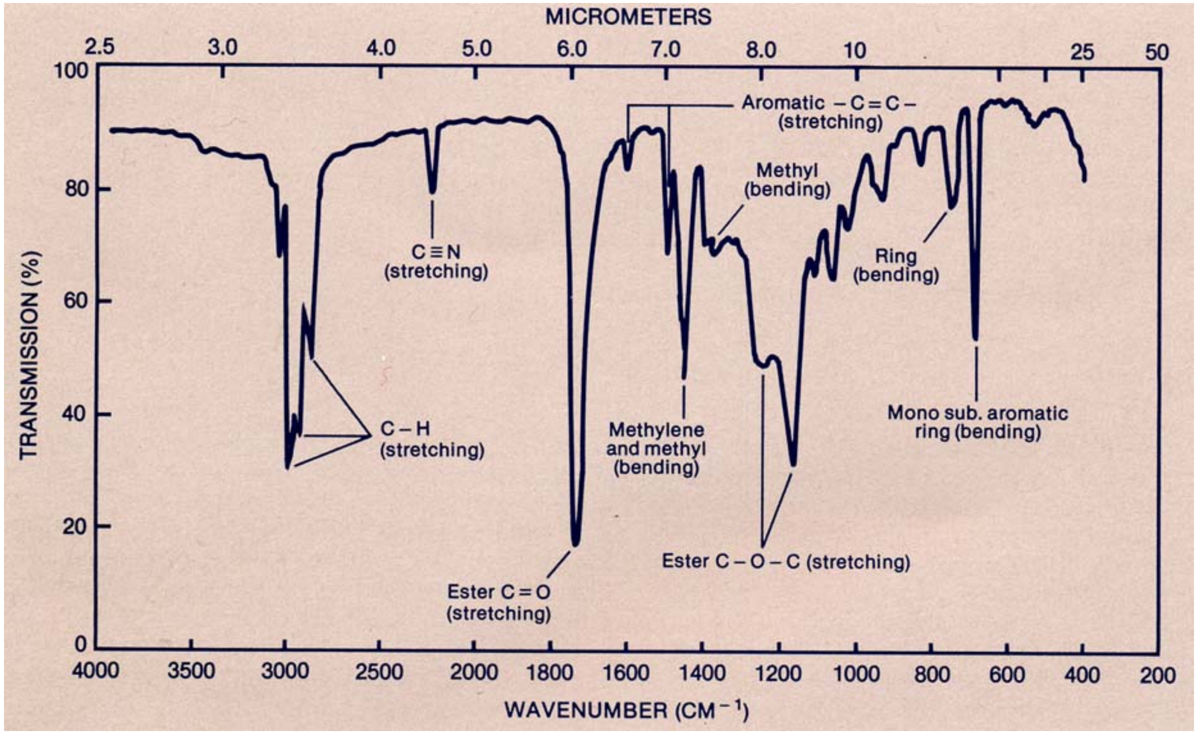
$$Frequency(\nu) = \frac{c}{\lambda}$$

$$Wavenumber(\bar{\nu}) = \frac{1}{\lambda}$$

Spectroscopic Properties

- UV
  - 200 to 400 nm
- VIS
  - 400 to 800 nm
- IR
  - 2500 - 25,000 nm
  - 2.5 - 25 um
  - 4000 - 400 cm^{-1}

Spectroscopic Properties



Infrared (IR) Spectroscopy is primarily used for qualitative and quantitative analysis of molecules in/as gases, liquids, solids, or solutions, based on the unique “fingerprint” provided by interaction with radiation in the range of 2.5-25 microns.

Spectroscopic Properties

- Plot fraction of incident energy passing through a sample versus some measure of wavelength or frequency:

$$\frac{I(transmitted)}{I_0(incident)}$$

- Hooke's Law:

$$F = -kx$$

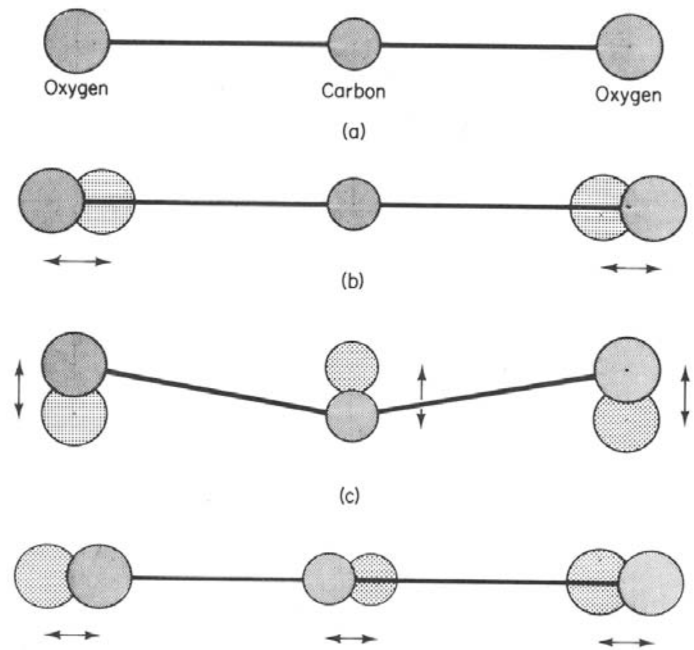
Some Conclusions

- Frequency scales directly with bond strength (as measured by the force constant):
  - Triple bonds > double bonds > single bonds
  - 2150cm^{-1} > 1650cm^{-1} > 1200 cm^{-1}
- Frequency scales inversely with masses atoms:
  - The heavier the atom,the lower the frequency:
  - CO vs CS (1700cm^{-1} vs 1350cm^{-1})
  - CH vs CD (3000cm^{-1} vs 2200cm^{-1})

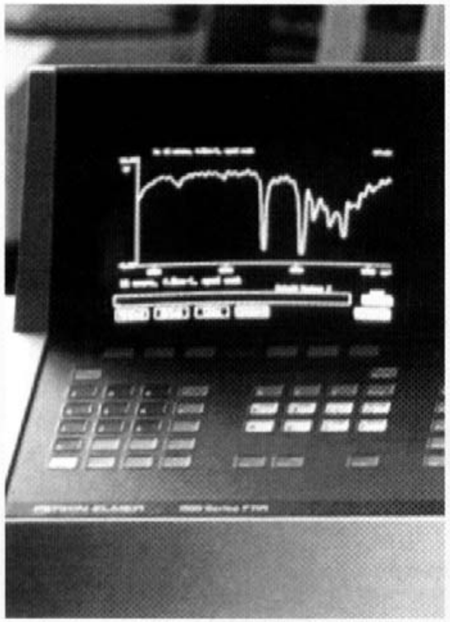
Other Features

- Coupled frequencies: Antisymmetric stretching modes at higher frequencies (wave numbers) than symmetric stretching modes.
- Overtones: Excitations energies beyond first excited state.
- Bending, wagging, scissoring, rocking at typically at lower frequencies (than stretching modes).

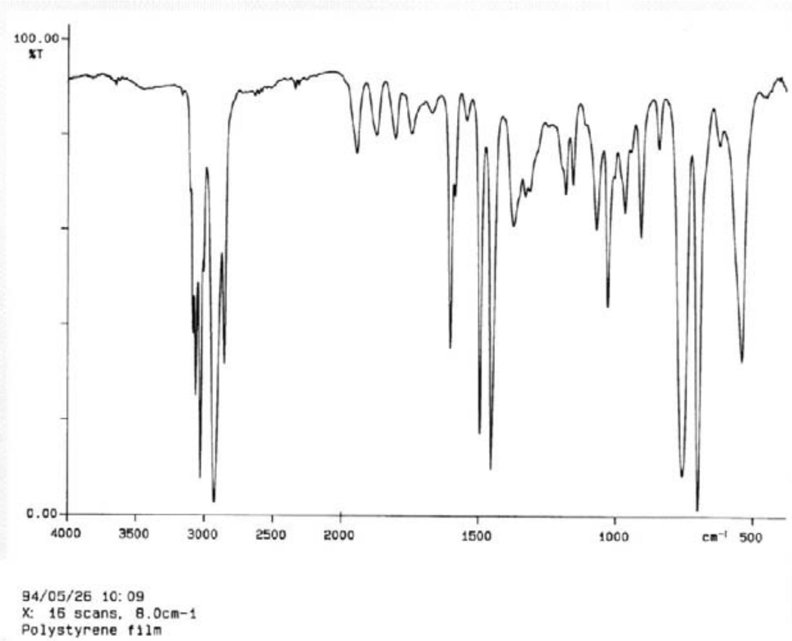
CO_2 Vibrational Modes



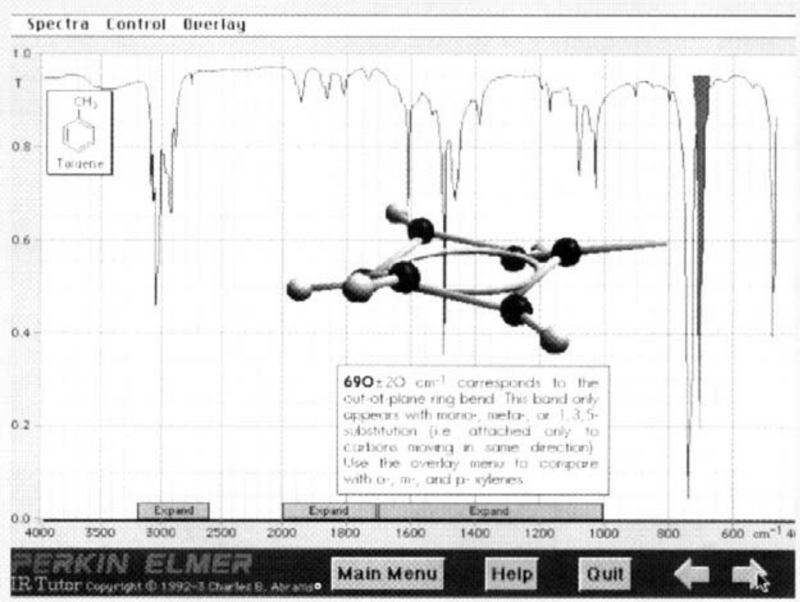
IR spectroscopy



(a)

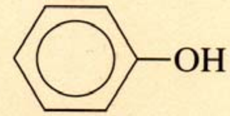


(b)



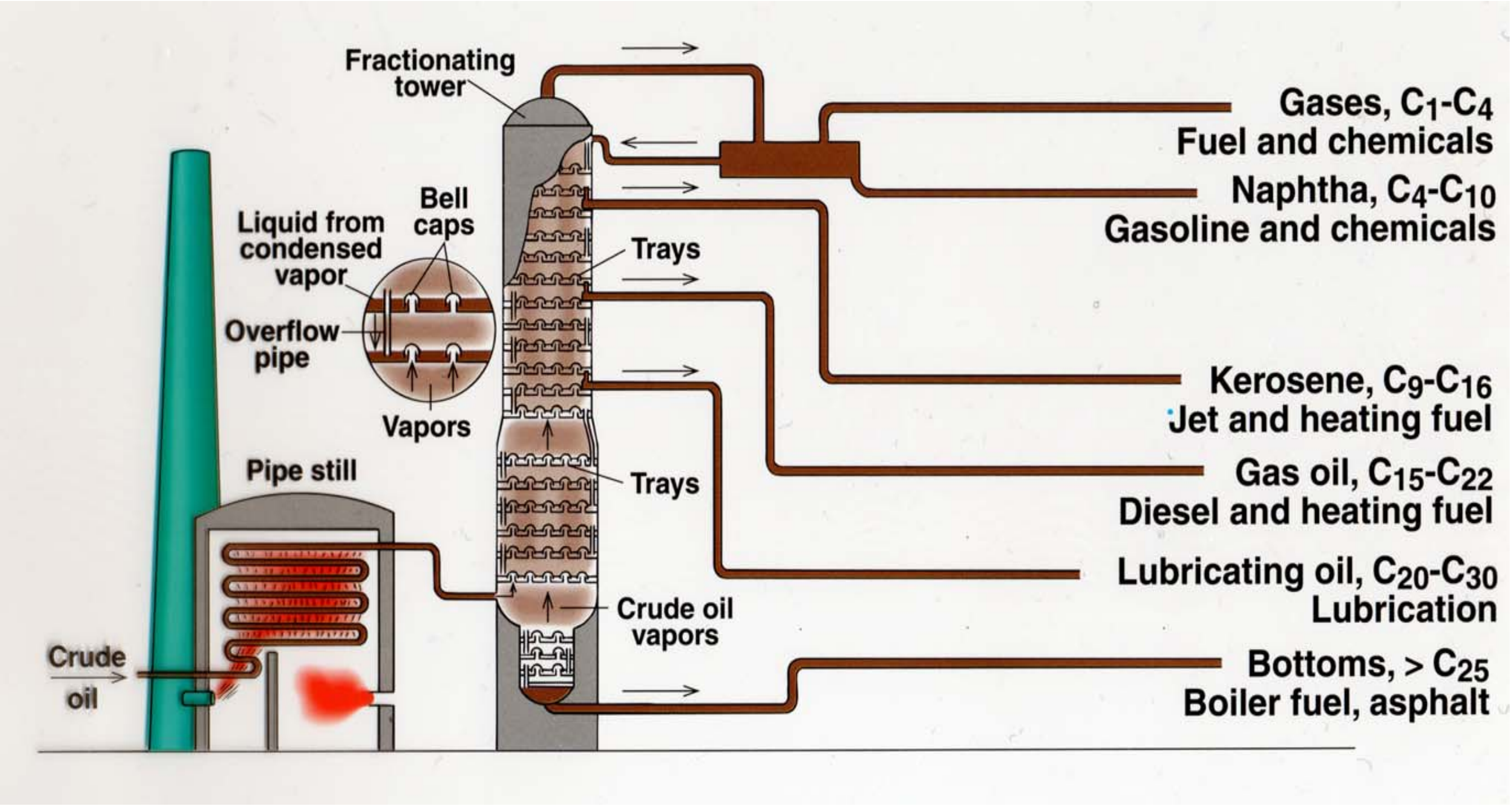
(c)

Figure 6-6
(a) A machine used to record the infrared sprectrum of a molecule. Shown here are the characteristic infrared sprectra of polystyrene (b) and toluene (c)

Functional Group†	Type of Compound	Examples
$R-F$, $-Cl$, $-Br$, $-I$	Alkyl or aryl halide	CH_3CH_2Br (bromoethane)
$R-OH$	Alcohol	CH_3CH_2OH (ethanol)
	Phenol	 (phenol)
$R-O-R''$	Ether	CH_3-O-CH_3 (dimethyl ether)
$R-C(=O)H$	Aldehyde	$CH_3CH_2CH_2-C(=O)-H$ (butyraldehyde, or butanal)
$R(R')C=O$	Ketone	$CH_3-C(=O)-CH_3$ (propanone, or acetone)
$R-C(=O)OH$	Carboxylic acid	CH_3COOH (acetic acid, or ethanoic acid)
$R-C(=O)O-R'$	Ester	$CH_3-C(=O)O-CH_3$ (methyl acetate)
$R-NH_2$	Amine	CH_3NH_2 (methylamine)
$R-C(=O)N(R')R''$	Amide	$CH_3-C(=O)NH_2$ (acetamide)

Pumping Oil

Petroleum Distillation



Natural Gases and Gasolines

- Methane CH_4
- Ethane CH_3CH_3
- Propane $CH_3CH_2CH_3$
- Butane $CH_3CH_2CH_2CH_3$
- Pentane $CH_3CH_2CH_2CH_2CH_3$
- Hexane $CH_3CH_2CH_2CH_2CH_2CH_3$
- Heptane $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
- Octane $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
  - n-octane 0-octane (straight-chain)
  - iso-octane 100-octane (branch-chain)

Homework Problem

COMBUSTION is central to the consumption of most power.

Significant Exceptions:
- **Nuclear**
- **Geothermal**
- **Solar.**

Natural gas can be burned for home heating or electric lighting and the chemistry looks like this:

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$$

Direct conversion (home heating)

Indirect conversion, via steam to turbine electricity (lighting)

About 5-6 ounces of methane are required to provide enough heat for a comfortable bath for an average-sized adult in a tub appropriate in size for containing 20 gallons of water.

Do a Best Estimate/Good guess/Back-of-the-envelope approximate calculation to validate that assumption.

You will need to know....

- Specific heat of the bath water
  - Joules (or calories) per gram per degree
- Heats of combustion of the fuel
  - Joules (or calories) per mole
- Conversion factors
  - Ounces of methane
  - Gallons of water

CO_2 Crystals

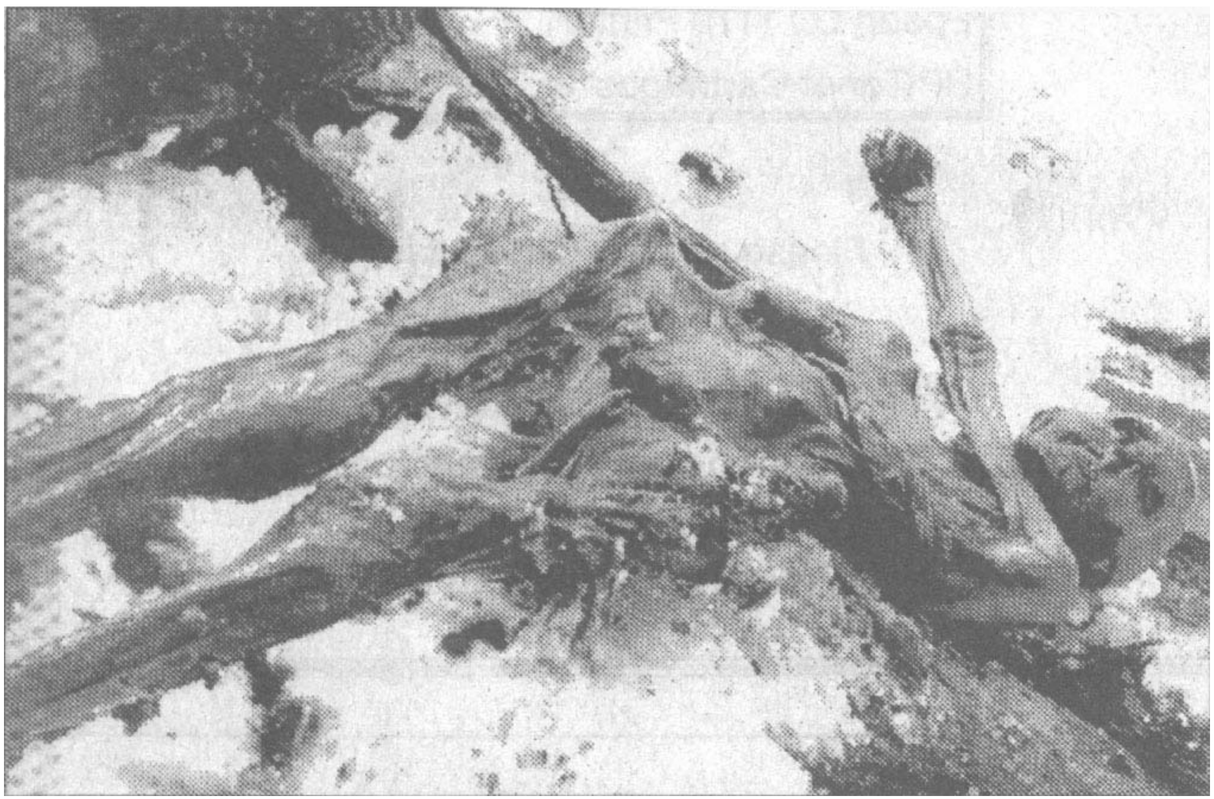
Mount ETNA emits CO_2

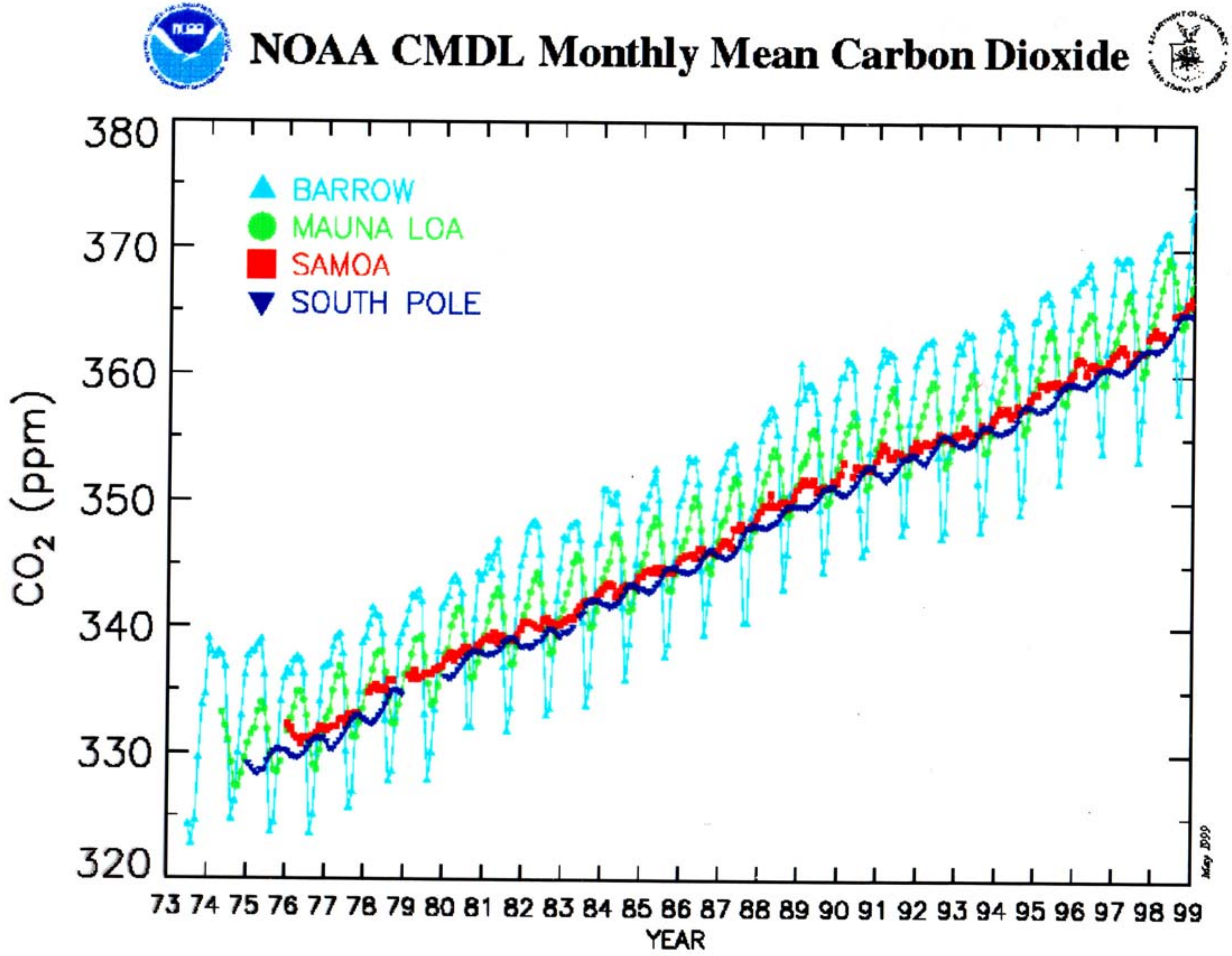
Lake NYOS Eruption in the Cameroon

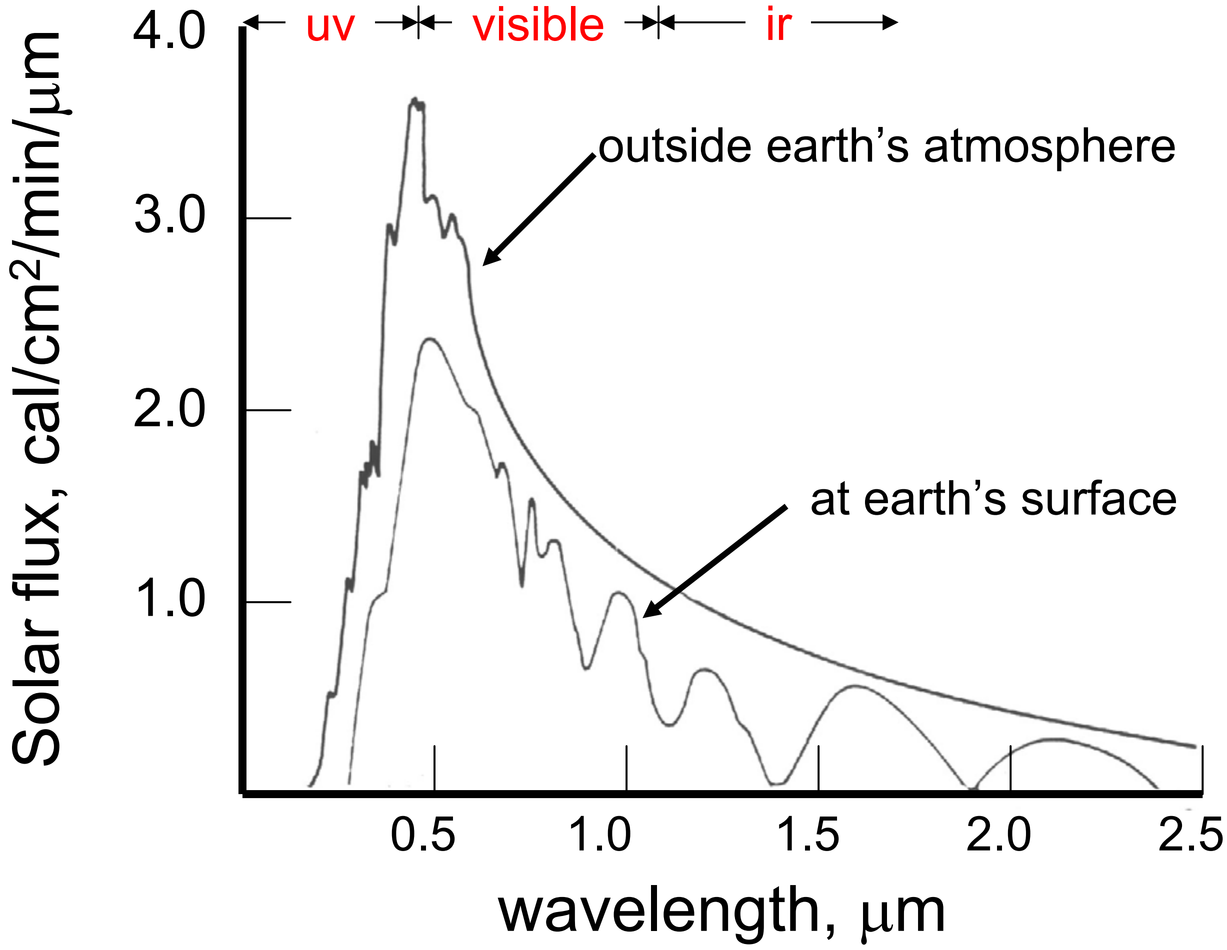
Iron deposits brought up from the bottom caused Lake Nyos to turn red after the gas explosion.

[Animation of lake explosion]

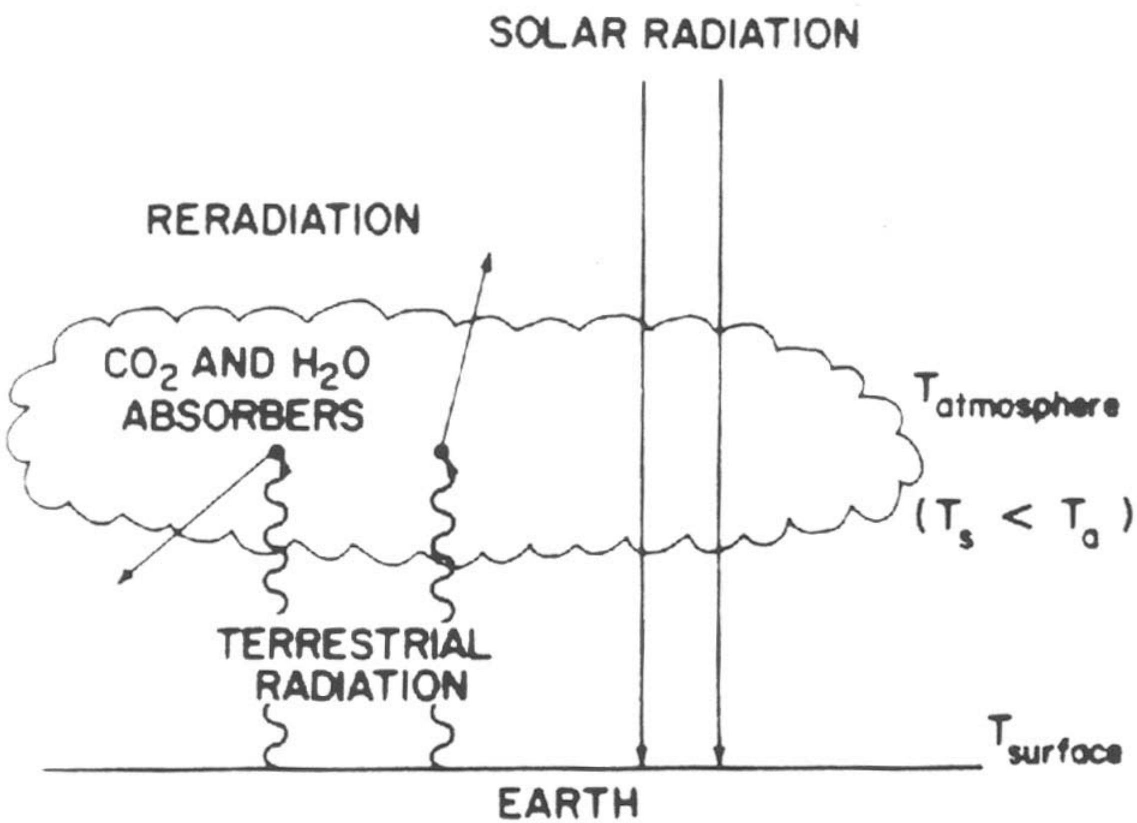
ICEMAN



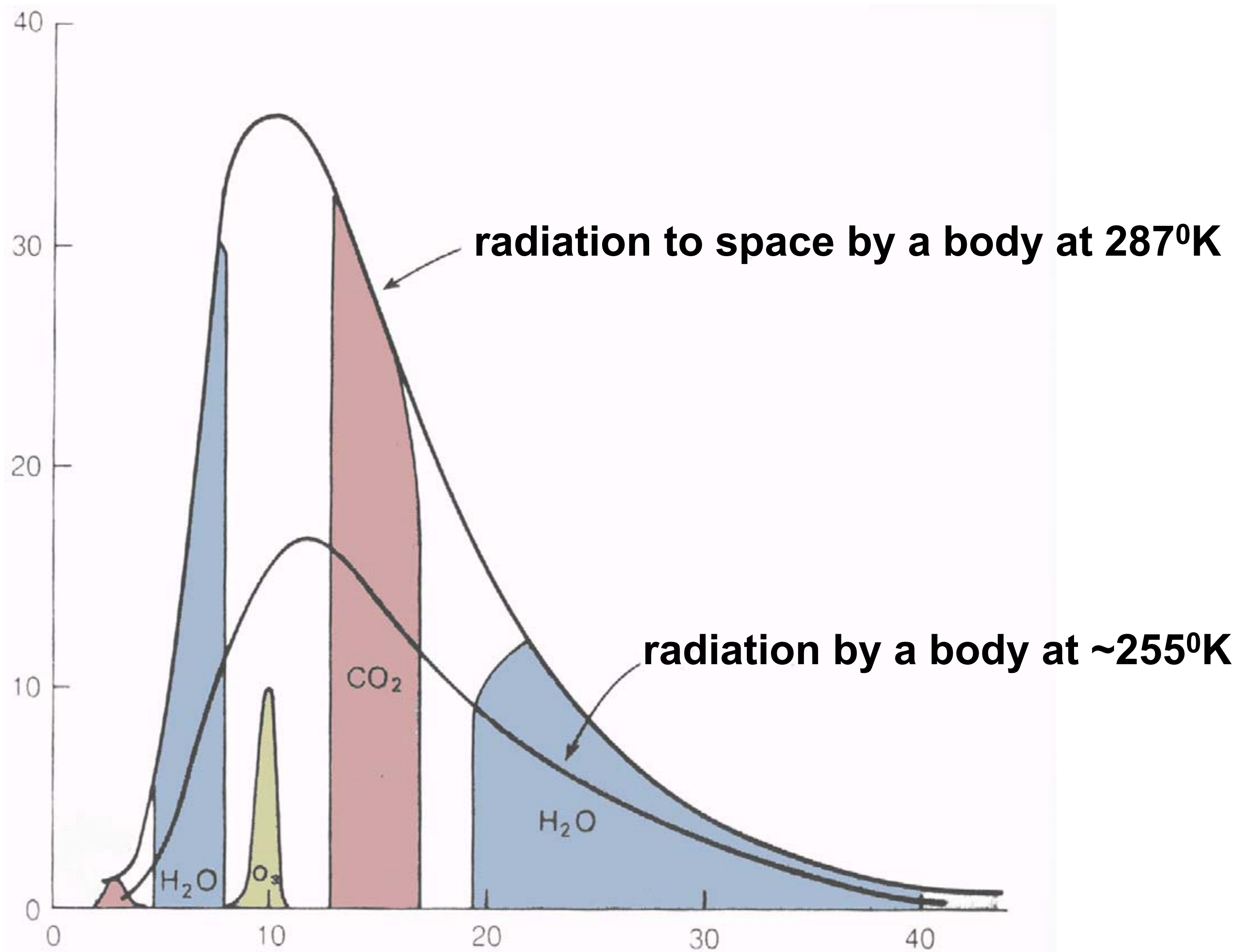

NOAA CMDL Monthly Mean Carbon Dioxide
BARROW
MAUNA LOA
SAMOA
SOUTH POLE
380
370
360
350
340
330
320
CO2 (ppm)
73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99
YEAR
May 1999



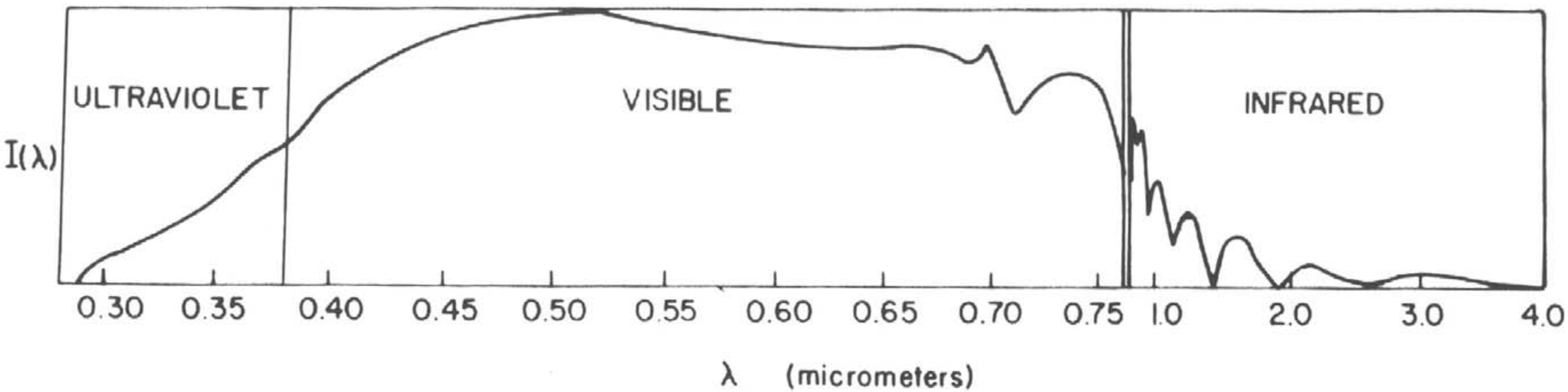
uv
visible
ir
4.0
3.0
2.0
1.0
Solar flux, cal/cm2/min/μm
outside earth's atmosphere
at earth's surface
0.5
1.0
1.5
2.0
2.5
wavelength, μm

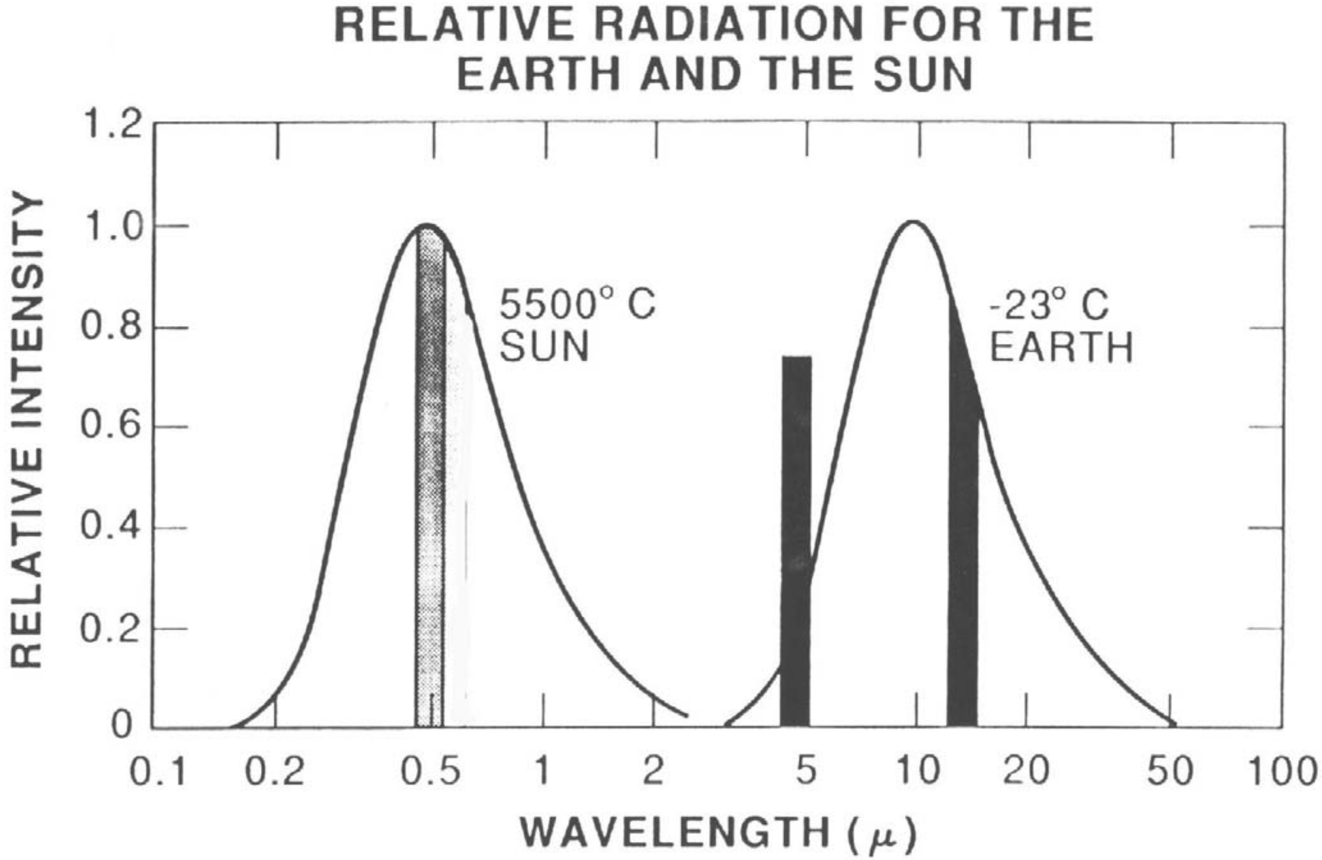

SOLAR RADIATION
RERADIATION
CO2 AND H2O
ABSORBERS
T atmosphere
(T s < T a)
TERRESTRIAL
RADIATION
T surface
EARTH

Solar flux, cal/cm^2/min/μm

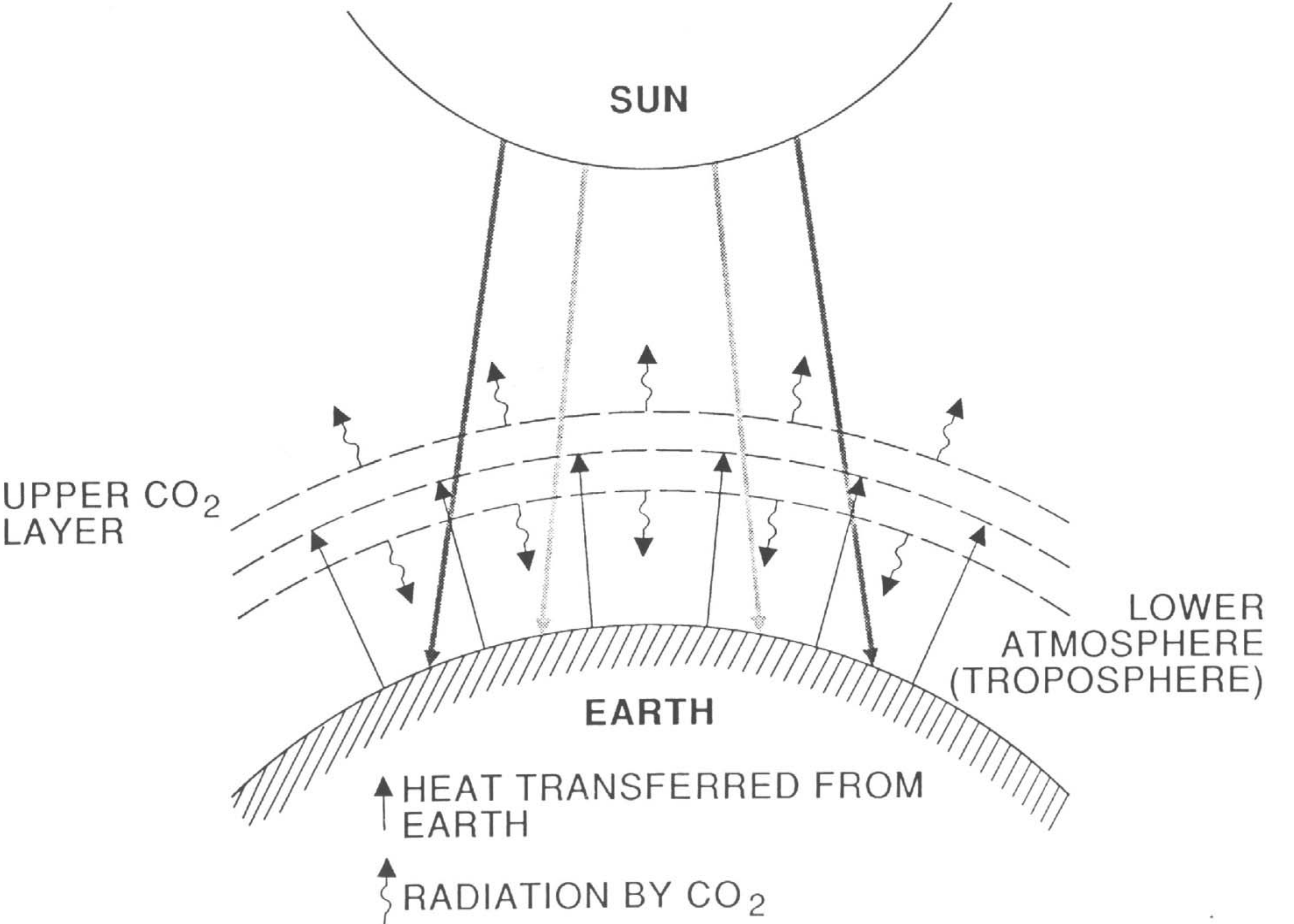


wavelength, μm


ULTRAVIOLET
VISIBLE
INFRARED
I(λ)
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
1.0
2.0
3.0
4.0
λ (micrometers)


RELATIVE RADIATION FOR THE
EARTH AND THE SUN
RELATIVE INTENSITY
1.2
1.0
0.8
0.6
0.4
0.2
0
5500° C
SUN
-23° C
EARTH
0.1
0.2
0.5
1
2
5
10
20
50
100
WAVELENGTH (μ)

THE CARBON DIOXIDE GREENHOUSE EFFECT



Homework

Homework Problem

COMBUSTION is central to the consumption of most power.

Significant Exceptions:
- **Nuclear**
- **Geothermal**
- **Solar.**

Natural gas can be burned for home heating or electric lighting and the chemistry looks like this:

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$$

Direct conversion (home heating)

Indirect conversion, via steam to turbine electricity (lighting)

About 5-6 ounces of methane are required to provide enough heat for a comfortable bath for an average-sized adult in a tub appropriate in size for containing 20 gallons of water.

Do a Best Estimate/Good guess/Back-of-the-envelope approximate calculation to validate that assumption.

(1) To take 20 gallons of water

from say 15°C $\rightarrow$ 45°C

20 gal = 80 qt = 80 L = 80 kg = 80,000 g

sp. ht of water = 4.184 J/g/deg

heat = mass X sp. ht X ΔT

$$= (80,000\ \text{g})\left(\frac{4.184\ \text{J}}{\text{g deg}}\right)(45 - 15)\text{deg}$$

= 10,041,600 J

(2) Methane required to do that job:

$$(10{,}041{,}600\ \text{J})\left(\frac{1\ \text{mol}}{890\ \text{kJ}}\right)\left(\frac{1\ \text{kJ}}{1000\text{J}}\right) = 11.28\ \text{mol}$$

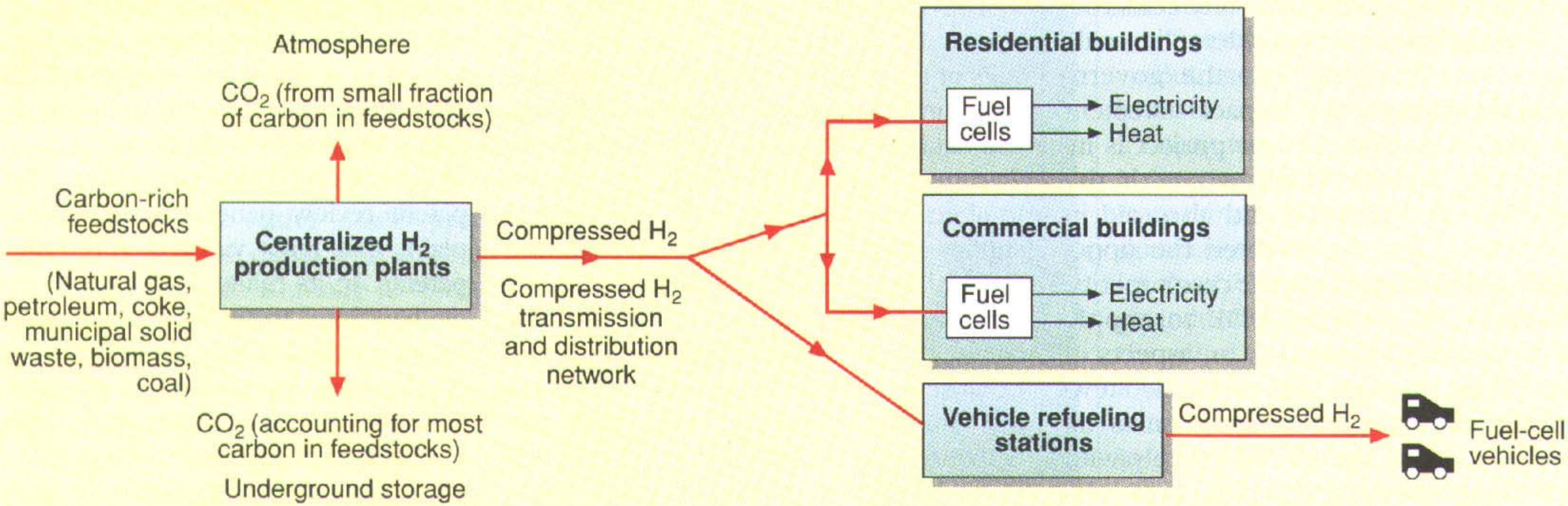
$$(11.3\ \text{mol})\left(\frac{16\ \text{g}}{1\ \text{mol}}\right)\left(\frac{1\ \text{lb}}{454\ \text{g}}\right)\left(\frac{16\ \text{oz}}{1\ \text{lb}}\right) = 6\ \text{oz}$$

.... or about 0.4 lb

.... or if propane (C_3H_8) is combusted, then about 2.5 ounces of fuel..... which means the heat of combustion of propane must differ from methane by a factor of .....

$$\left(\frac{6}{2.5}\right)(890\ \text{kJ/mol}) = 2250\ \text{kJ/mol.}$$

Hydrogen energy system would release little carbon dioxide to the atmosphere

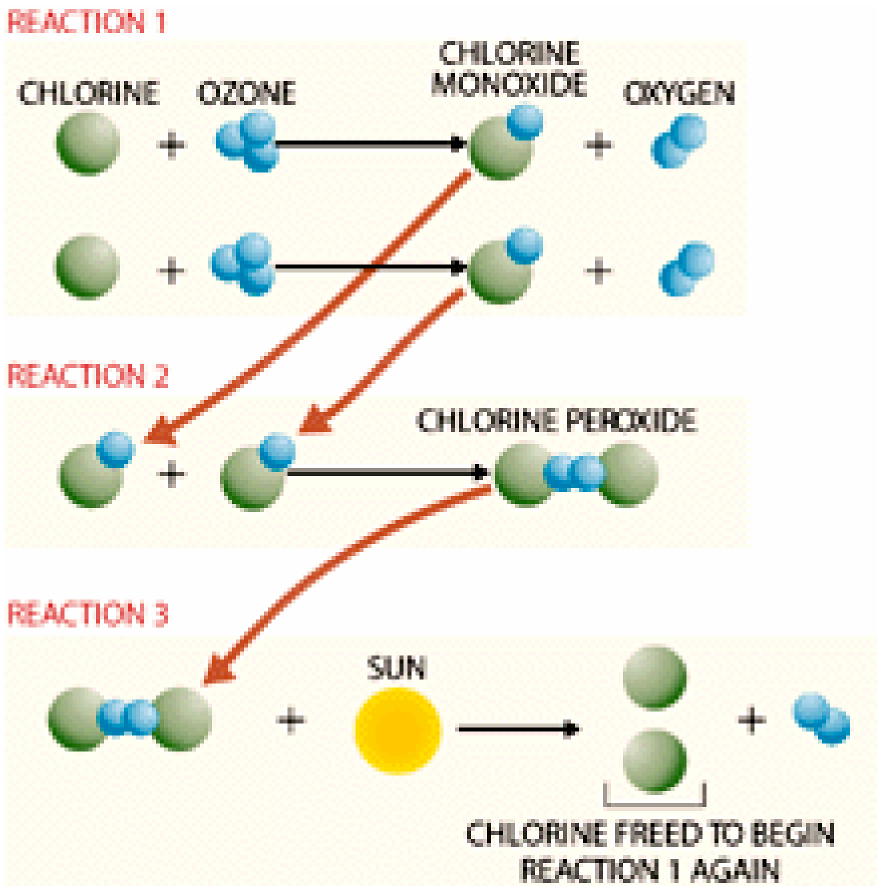


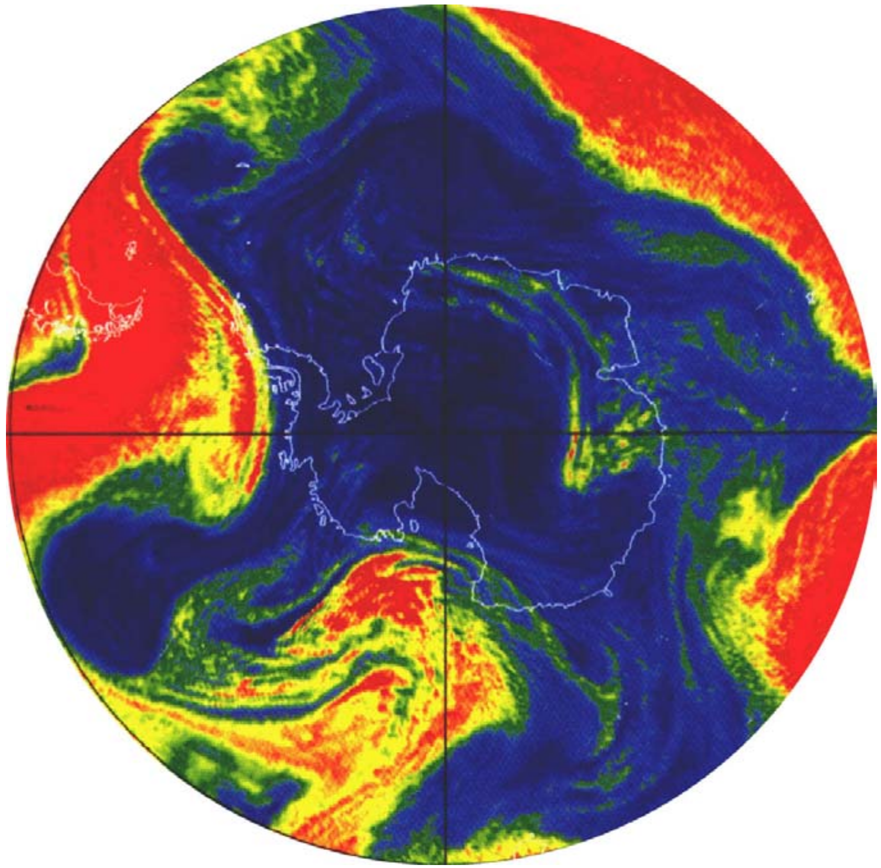
Source: Robert H. Williams

Chrysler Smart Car
Hybrid Vehicle

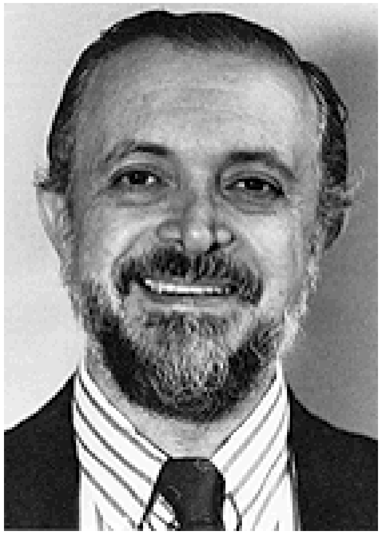
Chlorine Destroys Ozone

but is not consumed in the process





Crutzen



Molina

Rowland

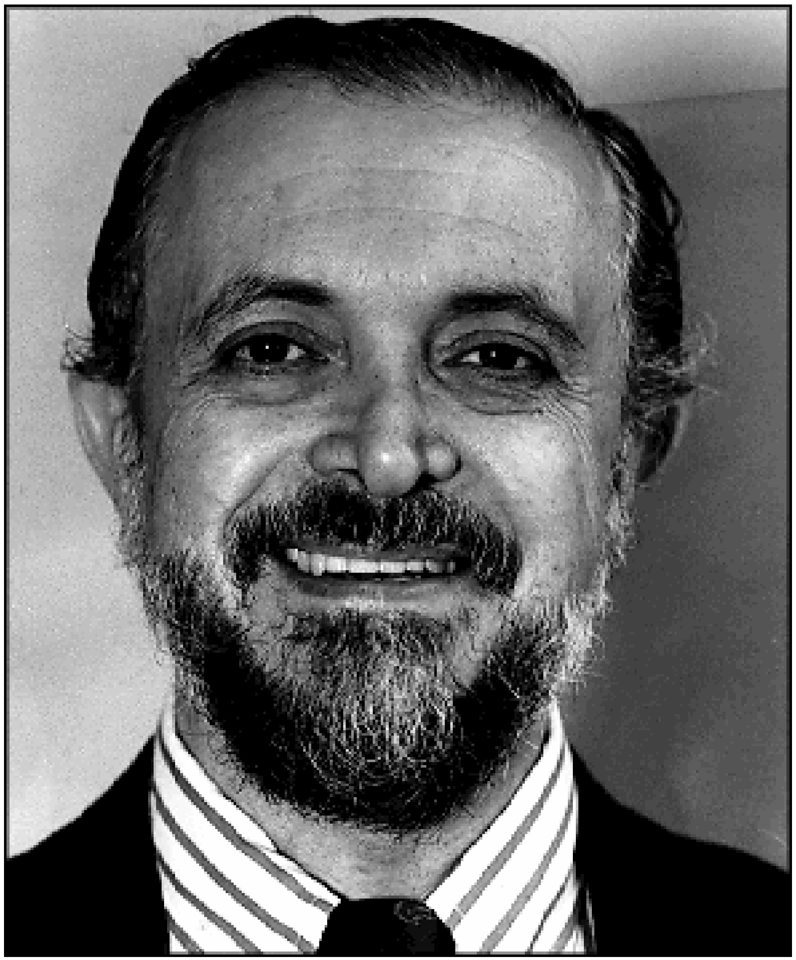
Paul Crutzen

Holland (The Netherlands)

Max-Planck-Institute for Chemistry
Mainz, Germany

1933 -

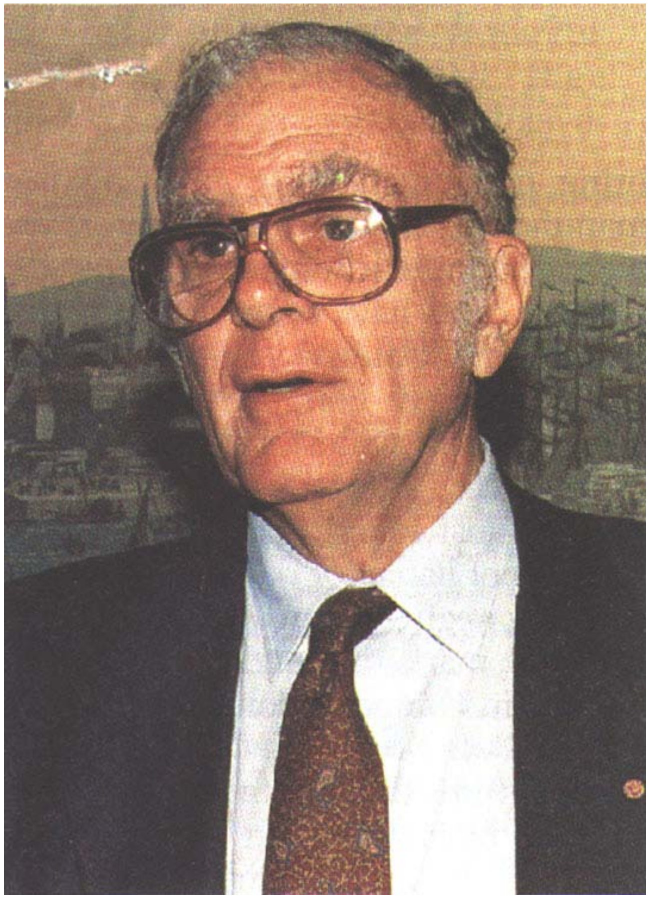
Mario Molina



USA (Mexico)

Department of Earth, Atmospheric and Planetary Sciences and Department of Chemistry, MIT
Cambridge, MA, USA
1943 -

F. Sherwood Rowland



USA

Department of Chemistry,
University of California
Irvine, CA, USA

1927 -

Monday, November 3, 1997

Nearly a third of U.S. bridges rated deficient

But the money to fix them just isn't there, state officials say.

WASHINGTON -- Almost a third of the nation's bridges are dilapidated or too narrow or too weak to carry the traffic crossing them, federal records show.

By JONATHAN D. SALANT
The Associated Press