Chemistry 2000 Slide Set 6: Vibrational spectroscopy of polyatomic molecules

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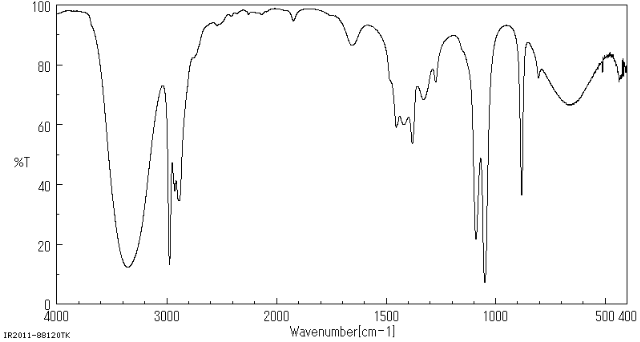
Example: IR spectrum of liquid ethanol

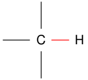
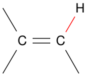


Source: Spectral Database of Organic Compounds, `http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi`, Jan. 16, 2013

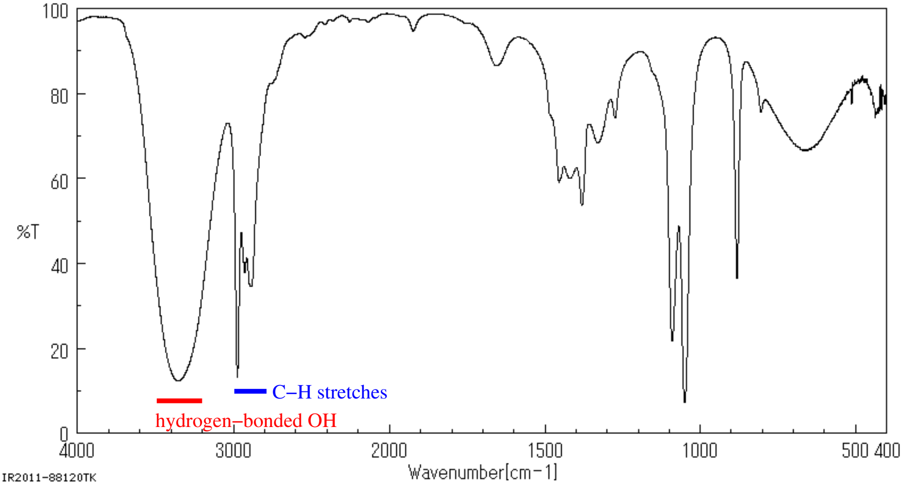
Note: The wavenumber axis often runs backward, as shown here.

Infrared spectroscopy and the identification of compounds

- One important application of spectroscopy (in general) is for the identification of unknown compounds.
- Certain bonds in organic molecules are associated with characteristic IR bands in specific spectral regions:

Bond	**Spectral region/cm^{-1}**
	2800–3000
 (including aromatic CH)	3000–3200
O—H (non-hydrogen-bonded)	3500–3700 (sharp)
O—H (hydrogen-bonded)	3200–3500 (broad)

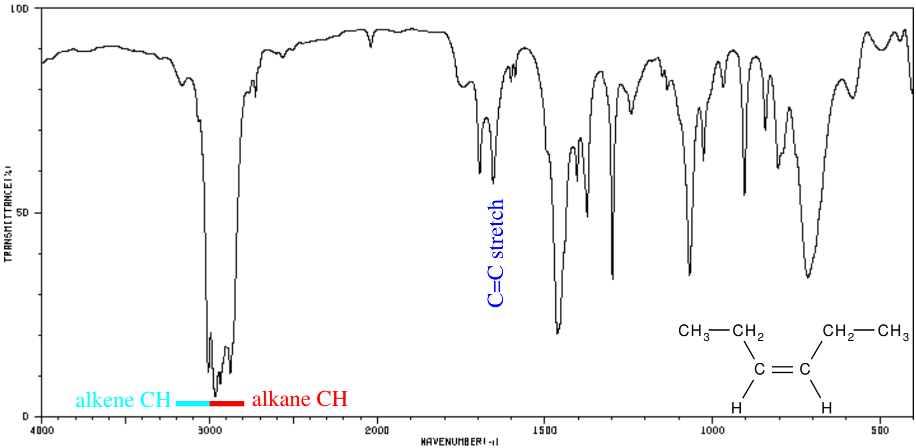
Example: The IR spectrum of ethanol



Alkene and alkyne carbon-carbon bond stretches

Bond	Spectral region/cm^{-1}
C=C	1640–1675 (sometimes)
C≡C	1950–2300 (sometimes)

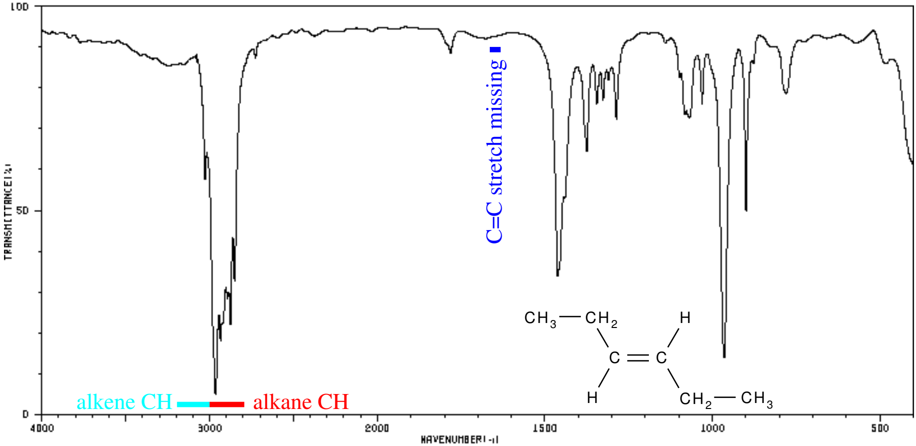
Example: IR spectrum of liquid *cis*-3-hexene



Spectrum source: Spectral Database of Organic Compounds,

`http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi`, Jan. 20, 2013

Example: IR spectrum of liquid *trans*-3-hexene



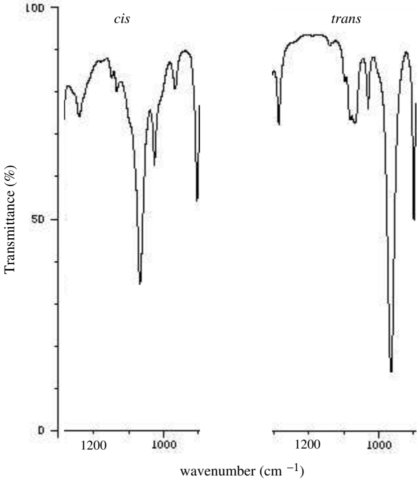
Spectrum source: Spectral Database of Organic Compounds,

`http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi`, Jan. 20, 2013

The fingerprint region of the spectrum

- The region from 900 to 1300 cm^{-1} is called the fingerprint region of the IR spectrum.
- In this region, we typically find many peaks arising from various low-energy stretching and bending motions of the molecules.
- Very difficult to assign peaks in this region but they are very different even for closely related compounds
- Used for confirmation that a particular (known) compound has been isolated

Example: Fingerprint regions of *cis*- and *trans*-3-hexene compared



Review: Molecular dipole moments

- A bond dipole is a slight separation of charge between two non-identical atoms connected by a bond.
- The size of the bond dipole is proportional to the amount of charge separation and to the bond length.
- The dipole moment of a molecule is the vector sum of the bond dipoles.
- A polar molecule has a non-zero dipole moment.
- Examples: CO_2, H_2O

Normal modes

- Except in diatomics, molecular vibrations generally involve motions of several atoms, i.e. more than one bond is deformed at a time.
- The vibrational modes must conserve overall molecular momentum.
- We can choose vibrational modes that are independent motions, called normal modes.

Number of normal modes

- A molecule made up of N atoms can move in $3N$ different ways (one direction of motion per atom per Cartesian axis).
- 3 of these motions are associated with the translational motion of the molecule as a whole.

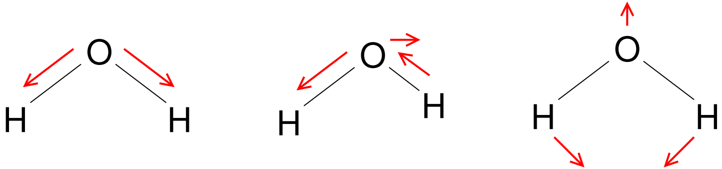
- A nonlinear molecule has 3 modes associated with rotation of the molecule as a whole.
- The remaining $3N - 6$ modes of a nonlinear molecule are the normal modes of vibration.

- A linear molecule only has 2 rotational modes.
- The remaining $3N - 5$ modes of a linear molecule are the vibrational normal modes.

Normal modes of H_2O

- $N = 3$ atoms, nonlinear molecule

$\Longrightarrow$ 3 normal modes



Symmetric stretch   Asymmetric stretch   Bend

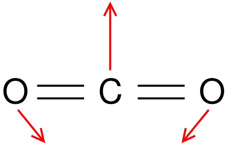
Normal modes of CO_2

- $N = 3$ atoms, linear molecule

$\Longrightarrow$ 4 normal modes

Symmetric stretch

Asymmetric stretch



Bend ($\times 2$)

Selection rule

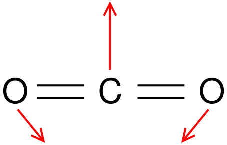
- A selection rule is a rule that tells us when a particular kind of spectroscopic event can occur.
- In IR absorption spectroscopy, the key selection rule is that the dipole moment of the molecule has to change during the vibration.
- A normal mode that can absorb an IR photon is said to be IR active.

Normal modes of CO_2 in IR spectroscopy

Which of these modes are IR active?

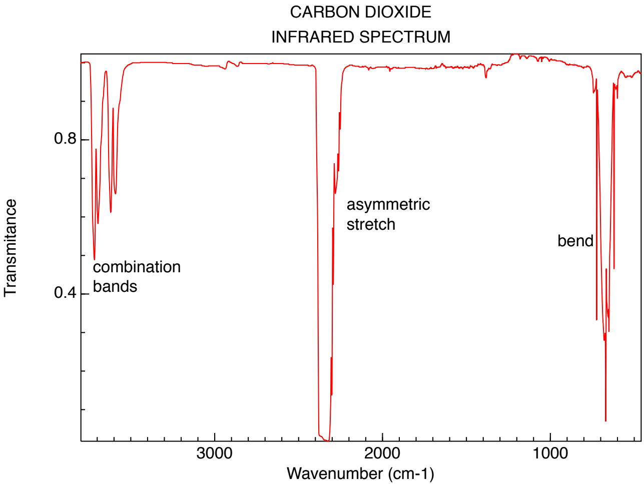
Symmetric stretch

Asymmetric stretch



Bend (×2)

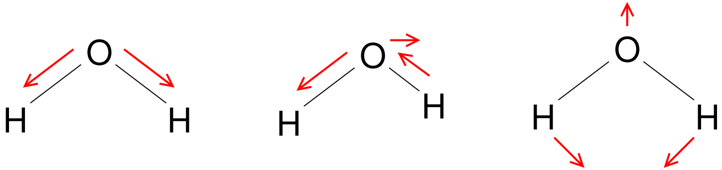
IR spectrum of CO_2



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

Normal modes of H_2O in IR spectroscopy

Which of these modes are IR active?



Symmetric stretch   Asymmetric stretch   Bend

Application: Earth's heat balance

- Energy from the Sun mostly arrives at the Earth in the form of visible light.
  Note that the atmosphere is essentially transparent at optical wavelengths.
- The Earth reflects some of that energy (esp. snow and ice at poles), but absorbs a lot of it.
  Averaged over the whole planet, about 30% of the light coming in is just reflected back to space.
- The planet radiates mostly in the infrared (blackbody radiation).
- The atmosphere contains many gases that absorb in the infrared, so some of the radiation from the Earth is absorbed in the atmosphere, but then what happens to the energy captured by the atmosphere?

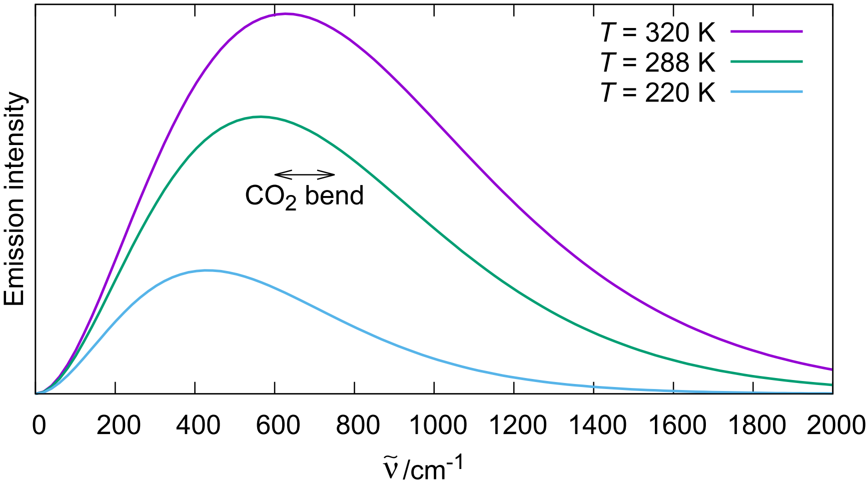
Application: Earth's heat balance

Greenhouse gases

- When a gaseous molecule becomes vibrationally excited by absorbing infrared radiation, the excess vibrational energy can be converted to translational kinetic energy during collisions.
- Energy is constantly redistributed in collisions and other energy-transfer processes.
- A gas at temperature T also emits "blackbody" radiation.

Application: Earth's heat balance

Blackbody curves



Application: Earth's heat balance

Greenhouse gases

- N_2, O_2 and Ar, the major components of the atmosphere, don't absorb in the IR. (Why?)
- The next two most common components of the atmosphere, water and carbon dioxide do absorb in the IR.
- Gases that absorb in the IR are called greenhouse gases.
- The atmospheric water content is set by the balance of evaporation and precipitation, which depends on the atmospheric temperature. It is a responding variable.
- We worry a lot about CO_2 because we are adding a lot of it to the atmosphere, which affects energy transfer through the atmosphere.

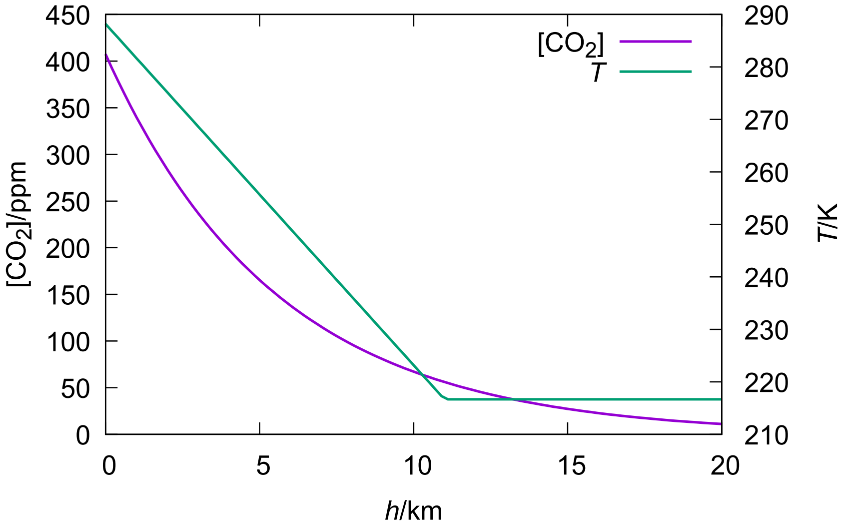
Application: Earth's heat balance

Photons reabsorbed vs lost to space

- At lower altitudes, photons emitted at wavelengths that CO_2 can absorb travel only a short distance (a few meters) before they are in fact absorbed by a CO_2 molecule.
  Similar statements could be made about other greenhouse gases in their respective absorption ranges.
- Absorption of IR photons slows the migration of heat through the atmosphere.
- Near the top of the atmosphere, where the pressure of CO_2 is low, there is a much larger probability that a photon emitted toward space will actually escape without being reabsorbed.
- Important fact: At those altitudes, the atmosphere is a lot cooler.

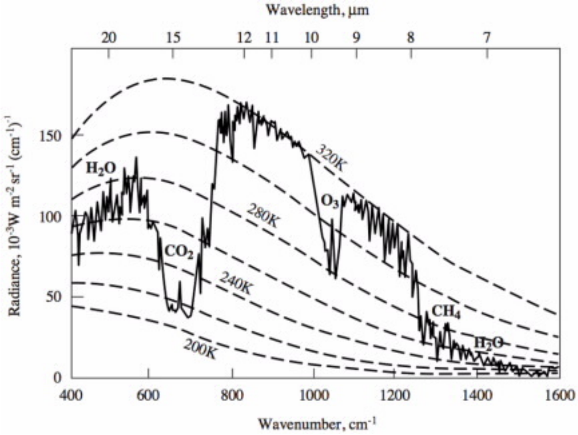
Application: Earth's heat balance

CO_2 concentration and temperature vs altitude



Application: Earth's heat balance

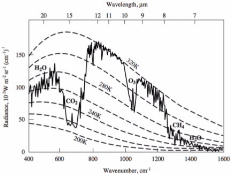
Earth emission spectrum (taken over North Africa)



Hanel et al., *J. Geophys. Res.* **77**, 2829 (1972)

Application: Earth's heat balance

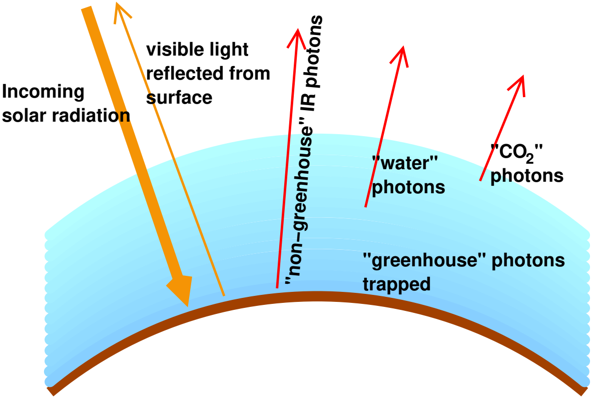
Interpretation of Earth's emission spectrum



- Emission from CO_2 comes from high in the atmosphere (where it's cool and there isn't much CO_2 to block the outgoing IR photons).
- Emission from water comes from lower down (where it's not quite as cool, since condensation of water prevents it from getting too high in the atmosphere).

Application: Earth's heat balance

Interpretation of Earth's emission spectrum



The wrap-up

- Greenhouse gases like CO_2 slow the escape of heat from the atmosphere to space.
- A simple analogy is that the atmosphere acts like a blanket.
- This is not inherently a bad thing. The planet would be a lot colder (average surface temperature of about 255 K, or $-18\,^\circ$C) if there were no greenhouse effect.
- Adding greenhouse gases to the atmosphere is analogous to making the blanket denser, resulting in a higher temperature under the blanket.

Application: Earth's heat balance

Carbon dioxide

- From 1959 to 2019, the CO_2 concentration in the atmosphere measured at the Mauna Loa observatory has risen from an annual average value of 316 ppm to 411 ppm, an increase of 30%.
- The rate of increase in the CO_2 concentration is also rising, from about 0.6 ppm y^{-1} in the early 1960s to about 2.6 ppm y^{-1} now.
- Warming induced by greenhouse gas emissions is a self-reinforcing problem:
  - It increases the amount of water vapor in the atmosphere.
  - On average, less of the planet is covered with ice.
  - Melting permafrost releases methane, a very powerful greenhouse gas.
  - ...
- There is no escaping the physics: adding greenhouse gases to the atmosphere heats up the planet.