

A teachable unit on molecular vibration and the greenhouse effect of earth's atmosphere

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This unit contains a student worksheet (page 2), a table of relevant IR vibration frequencies derived experimentally and computationally (page 3), and some materials for introducing the topic before students do the assignment and some materials for leading the discussion after students have done the assignment (page 4).

Greenhouse gases: molecule that absorb electromagnetic radiation in the infrared region

An interactive homework activity for students taking GenChem1

Your task is to explore the structure and properties of two molecules found in our atmosphere. One of your molecules is diatomic (choose between O₂ and N₂) and the other one is triatomic (choose between H₂O and CO₂). None of these molecules absorb visible light strongly – if they would, air would be colored and the sunlight would not reach earth. However, some of them absorb the infrared radiation emitted from the surface of the earth, and we call them greenhouse gases. Serving a role analogous to the glass walls of a greenhouse, these gases act as insulation to make our planetary climate habitable, distinguishing earth from other planets lacking an atmosphere. However, the concentration of these greenhouse gases has been increasing significantly since the start of the industrial age through burning of fossil fuels and other human activities, causing the earth's climate to warm up. This process, called climate change or global warming, is one of the largest challenges the world population faces in the next 100 years.

You can predict whether a molecule is a greenhouse gas by analyzing its structure.

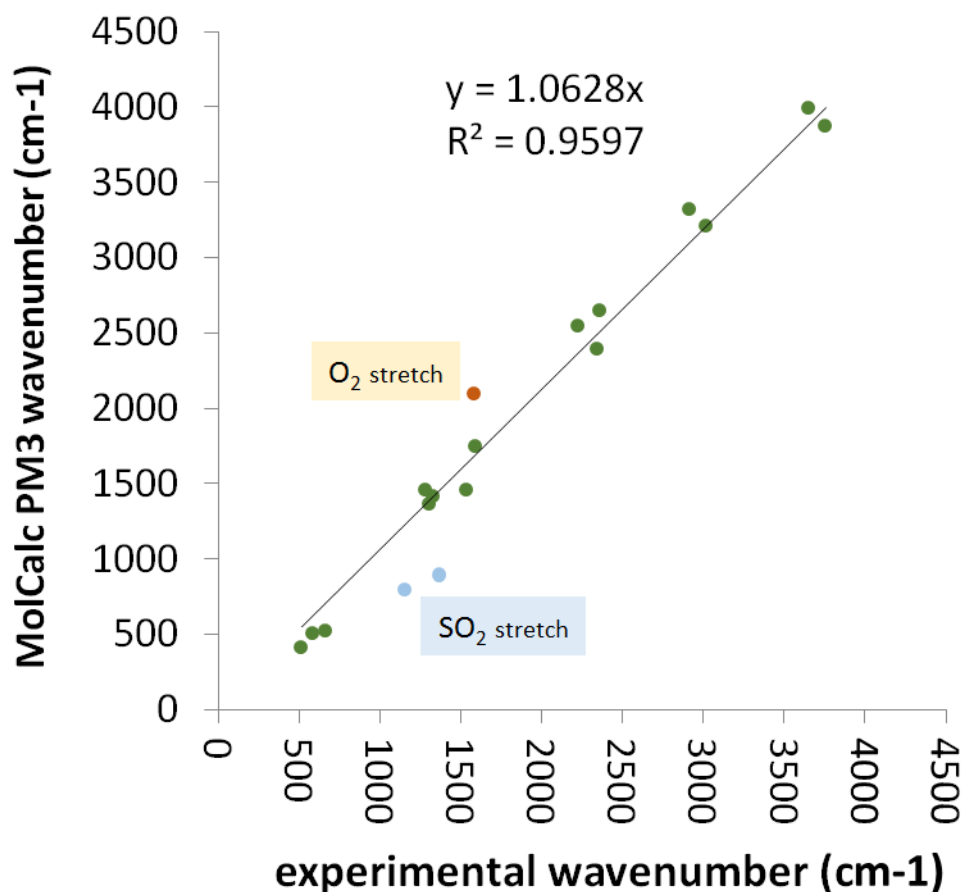
For each molecule:

- 1) Figure out the Lewis structure and the geometry.
- 2) Identify polar bonds and determine whether the molecule is polar or not.
- 3) Check your work and learn some more about your molecule by calculating its properties using molcalc.org (see the example video to learn how). This program does a quantum chemical calculation to estimate the electronic structure and the properties of your molecule.
 - a. Draw (build) the molecule in molcalc.
 - b. Optimize the geometry.
 - c. Calculate partial charges and note whether the molecule is polar (if it is, take a look at the direction of the dipole moment).
 - d. Calculate the vibrations (so-called normal modes).
 - e. Instead of giving the frequency of the vibration or the energy associated with it, the program outputs a so-called wavenumber w with units of cm^{-1} . Convert this into a wavelength λ and the oscillation period τ (how long it takes for one vibration). The wavelength tells you something about the energy ("color") of the light absorbed/emitted. Here are the relationships between wavenumber and wavelength and oscillation period:
$$\lambda = 1/w \qquad \tau = \lambda / c_0 \quad (\text{speed of light } c_0 = 299,792,458 \text{ m/s})$$
 - f. Make a table giving the wavenumber (in cm^{-1}), wavelength λ (in μm), oscillation period (in femtoseconds = 10^{-15} s) and a description of the motion (stretch, bend).
- 4) Decide whether your molecule is a greenhouse gas, i.e. whether it absorbs electromagnetic radiation in the infrared spectrum. Here are **two requirements for a molecule to be a greenhouse gas**:
 - a. It has to have vibration modes that are inside of the infrared region (in terms of wavelengths, the infrared is between $0.8 \mu\text{m}$ and $\sim 50 \mu\text{m}$)
 - b. The molecule needs to have polar bonds. The interaction between vibrations and electromagnetic radiation is based on a change of dipole moments during the vibration. If all bonds are nonpolar, no interaction will occur. (This rule is a special case of a more general rule you might learn in organic or physical chemistry courses: A vibration is said to be infrared inactive if the motion does not change the dipole moment of the molecule. Infrared inactive vibrations do not contribute to absorbing infrared light.)
- 5) Bring your work to class to check and discuss.

Comparison of vibration frequencies measured or calculated (the latter at different levels of theory).

Molecule	mode	experimental (1/cm)	IR active?	MolCalc and PM3	PM6	B3LYP 6-31G(d,p)
N ₂	stretch	2359	n	2640	2418	2457
O ₂	stretch	1580	n	2096	1602	1660
H ₂ O	asymm str	3756	y	3869	2529	3913
H ₂ O	symm str	3657	y	3989	2616	3800
H ₂ O	bend	1595	y	1742	1336	1665
CO ₂	asymm str	2349	y	2386	2321	2436
CO ₂	symm str	1333	n	1408	1377	1372
CO ₂	bend	667	y	521	538	640

Correlation of experimental and MolCalc frequencies for N₂, O₂, H₂O, CO₂, N₂O, CH₄, SO₂

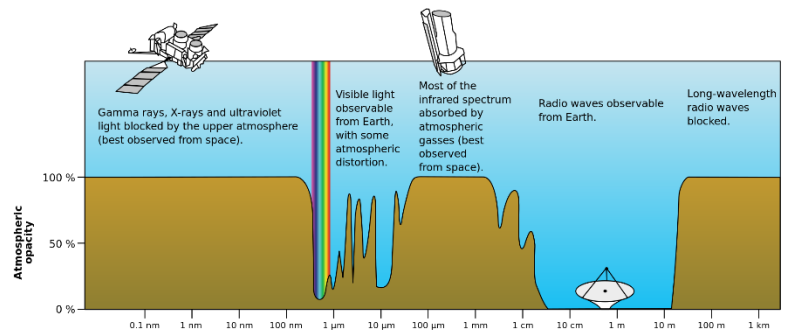


The earth's atmosphere (a layer of ~100 km thickness around the earth with a radius of ~6000 km) contains molecules that absorb (or reflect) electromagnetic radiation of most wavelengths. To clarify the dimensions, 99.9997% of the mass of the atmosphere is below 100 km from sea level, the ozone layer is at about 30 km - 50 km above sea level, and the mass concentration decreases exponentially with altitude, dropping by half every 5.6 km.

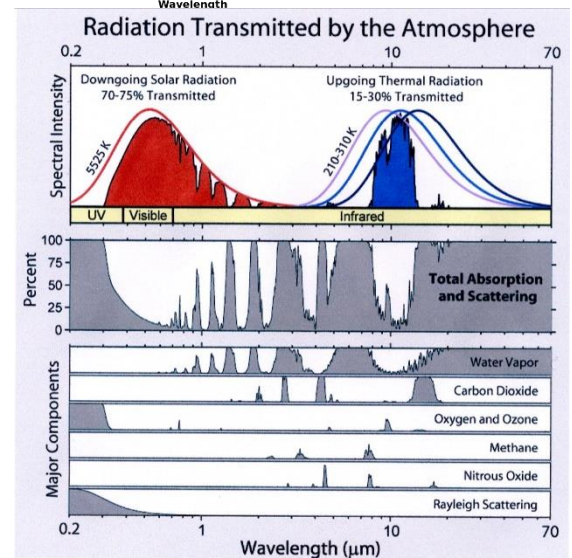
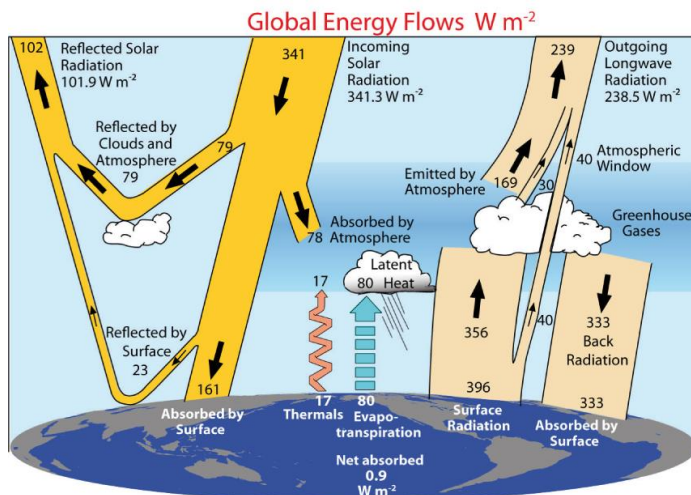
The pictures show (from left to right) infrared emission, visible emission and UV emission (taken with an Apollo camera stationed on the



moon – the sun is shining its UV light from the right, and the ozone layer reflects it). The pictures show that the atmosphere is transparent to visible light (except for the clouds, i.e. scattering effect), whereas it is less transparent to infrared light. The diagram on the right shows transmission at different wavelengths.



In a nut shell, electromagnetic radiation comes in as visible light, warms up the atmosphere and the earth's surface, which then emits infrared light (cf. black body radiation), much of which is trapped by the atmosphere (i.e. molecules absorb energy coming from the surface and emit it in all directions, see main contributors on the right). Below is a schematic of the energy balance sheet:



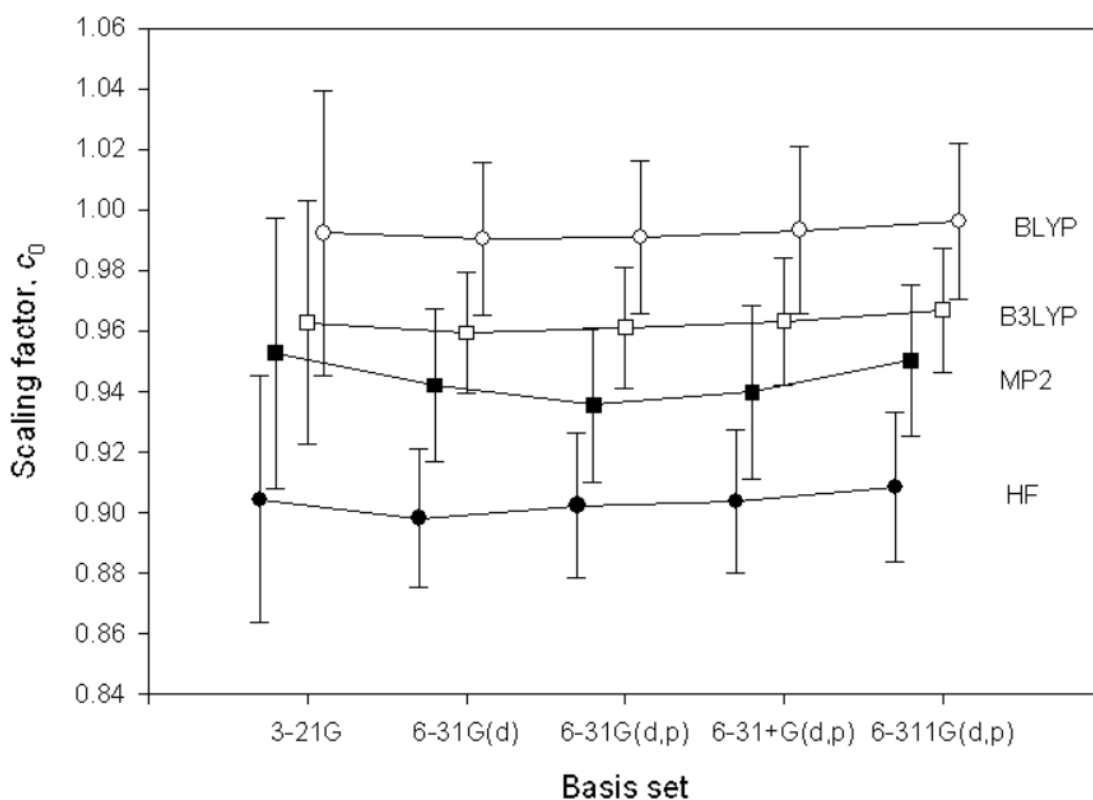
Calculating vibrational frequencies:

Frequencies are typically calculated using a harmonic oscillator model as an approximation. This introduces systematic errors into the calculation which can be partially addressed through a scaling factor. Here are some examples of scaling factors for a given collection of molecules for which vibration frequencies were calculated with different levels of theory and different basis sets and then fit to experimental values using a single scaling factor for the entire collection of molecules (but separate for different level of theory and basis sets).

How much do the factors change with basis set?

The following figure shows several scaling factors and their uncertainties. The figure is from: K. K. Irikura, R. D. Johnson III 8437.

Filled circles = HF, filled squares = MP2, open circles = BLYP, open squares = B3LYP.



Sites for images:

<http://orbitingfrog.com/2008/06/25/earth-and-friends-in-multiple-wavelengths/>

http://earthguide.ucsd.edu/eoc/special_topics/teach/sp_climate_change/p_atmospheric_window.htm
|

https://commons.wikimedia.org/wiki/File:Atmospheric_Transmission.png

http://www.climate.be/textbook/chapter2_node8.xml

Citation for MolCalc:

Jan H. Jensen and Jimmy C. Kromann,

The Molecule Calculator: A Web Application for Fast Quantum Mechanics-Based Estimation of Molecular Properties,

Journal of Chemical Education, 2013, [DOI: 10.1021/ed400164n](https://doi.org/10.1021/ed400164n)

Very basic video at EPA:

<http://www.epa.gov/climatestudents/basics/today/greenhouse-effect.html>

Tutorial of a slightly older version of MolCalc by the first author:

<https://www.youtube.com/watch?v=ODdGGrzNp9Y>

Describing vibration modes:

<https://www.youtube.com/watch?v=xITzGUjongU>