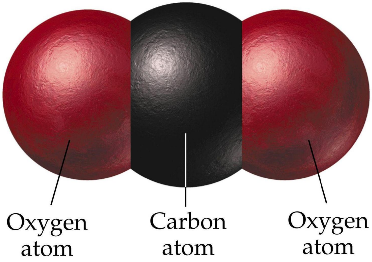
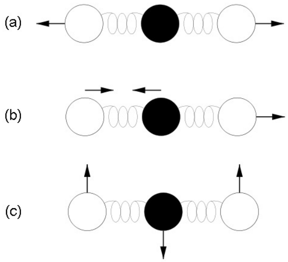
Why Is CO_2 a Greenhouse Gas?

The Earth is warming and the likely cause is the increase in greenhouse gases like carbon dioxide (CO_2) in the atmosphere. Carbon dioxide is a linear, tri-atomic molecule with a central carbon atom. The harmonic vibrations of CO_2 give it its absorption properties.



The vibrations of CO_2 can be described by a small set of 'normal modes' shown here. If a normal mode distorts the symmetry of the charge distribution of the molecule, then it will acquire an electric dipole moment and can absorb light in the infrared range - preventing that light from passing through the atmosphere.



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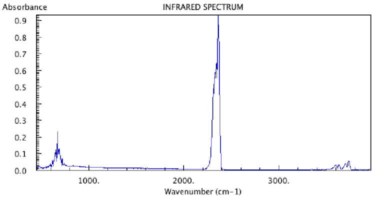
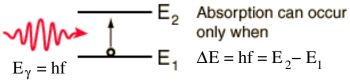
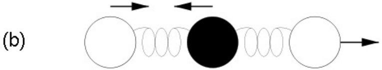
The peak is located at the frequency of light that is absorbed as the CO_2 molecule makes the transition from one quantized energy state to a higher one. The energy of the light is $E_\gamma = hf$ where h is Planck's constant.

The atoms vibrate in the asymmetric mode shown here. This particular mode gives CO_2 its greenhouse gas properties.







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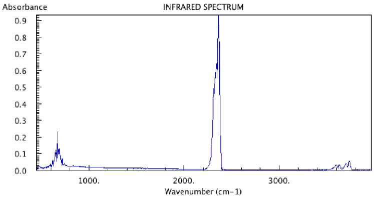

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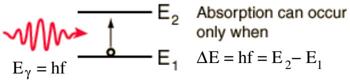

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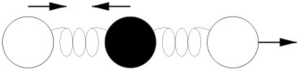
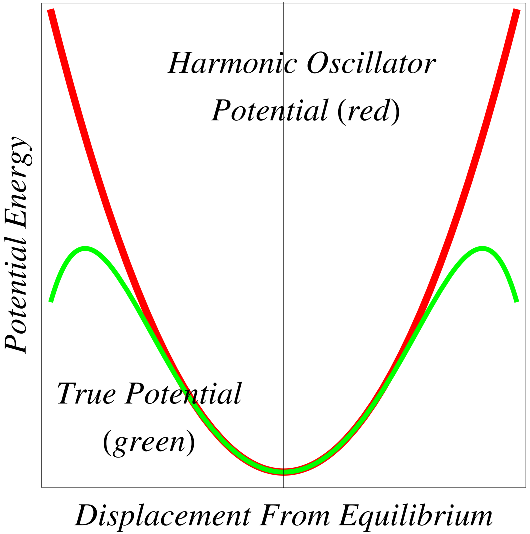
(b)



How hard do the atoms vibrate?

The Harmonic Oscillator Approximation



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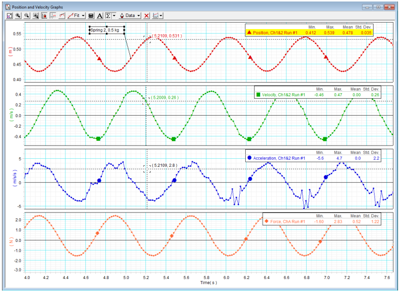

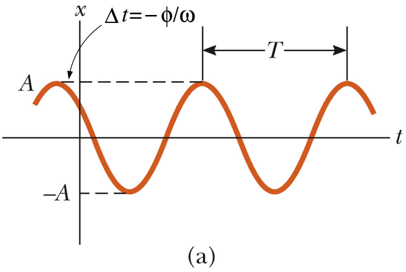

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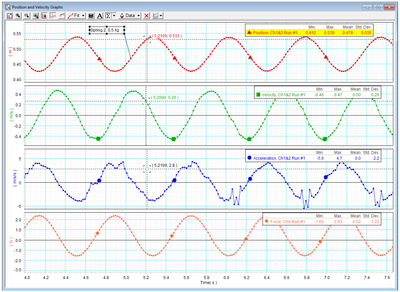

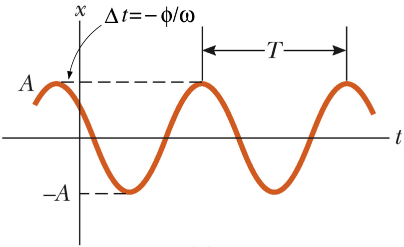

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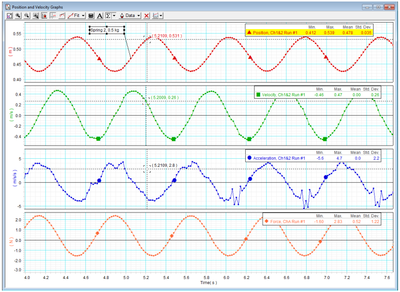
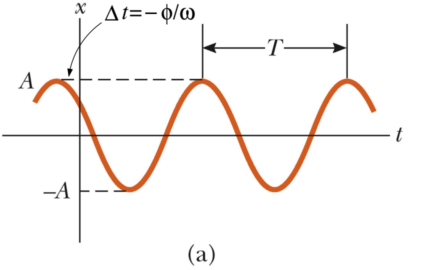




4. The Solution: $x(t) = A\cos(\omega t + \phi)$
5. Parameters:

$$\omega = \sqrt{\frac{k}{m}} \qquad T = \frac{2\pi}{\omega} \qquad f = \frac{1}{T}$$

A and ϕ are initial conditions.

How Do you Weigh a Weightless Person?

To weigh astronauts on the International Space Station NASA uses a chair of mass m_c mounted on a spring of spring constant $k_c = 605.6\ N/m$ that is anchored to the spacecraft. The period of the oscillation of the empty chair is $T_c = 0.90149\ s$. When an astronaut is sitting in the chair the new period is $T_a = 2.12151\ s$. What is the mass of the astronaut?

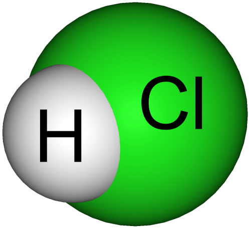
Atomic Vibrations

The force law describing the interaction between hydrogen and chlorine atoms is HCl is

$$F_h = -a\left[\left(\frac{b}{r}\right)^2 - \left(\frac{c}{r}\right)^3\right]$$

where F_h is the force acting on the hydrogen atom, a is a constant with units of force, b and c are constants with units of length, and r is the distance of the hydrogen atom from the chlorine. Chlorine is much heavier than hydrogen so we can consider it fixed.

1. What is the equilibrium position r_0 for the hydrogen atom in HCl?
2. Let $x \equiv r - r_0$ and show that for small x the force resembles the harmonic oscillator force.
3. What is the frequency of small oscillations of the hydrogen atom in terms of its mass m, and the constants a, b, and c.



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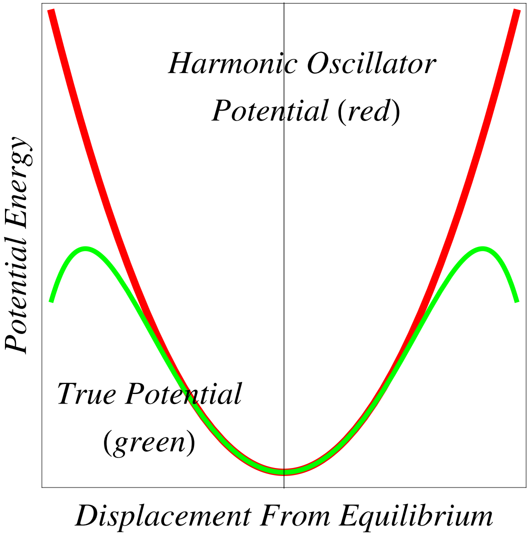


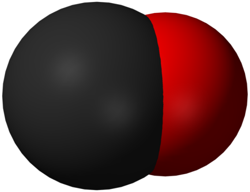
More Atomic Vibrations

The force law describing the interaction between the carbon and oxygen atoms in CO is the Lennard-Jones form

$$F_{CO} = \frac{\alpha}{r^{13}} - \frac{\beta}{r^7}$$

where F_{CO} is the force acting between the carbon and oxygen, α and β are adjustable constants, and r is the distance between the atoms. Carbon and oxygen are similar in mass so we cannot consider one of them fixed.

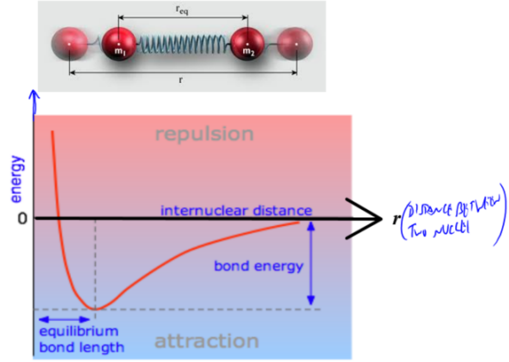
1. What mass goes in the harmonic oscillator expressions?
2. What is the equilibrium separation r_0 for the atoms in CO in terms of α and β?
3. How are α and β related to k?
4. The effective spring constant of the CO bond is $k_{CO} = 1860\ N/m$. What is the frequency of small oscillations of the CO molecule?



The Center of Mass Frame of Reference

An Application: Potential Energy of Diatomic Molecules

Molecular vibration video



4

$\mathrm{CO_2}$ Absorption Spectrum

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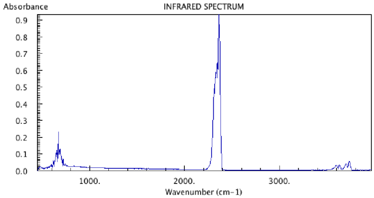

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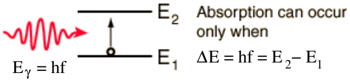

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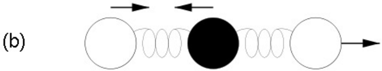

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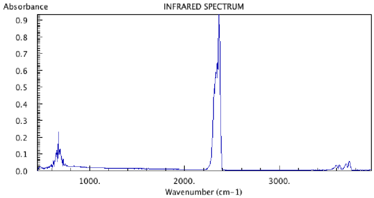
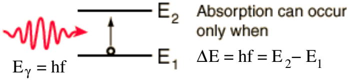


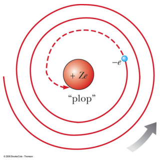


WHY ARE THE ENERGIES QUANTIZED?

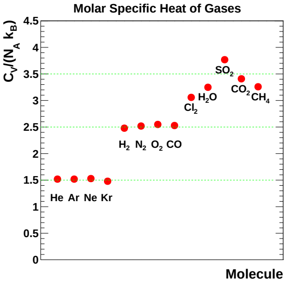
How hard do the atoms vibrate?

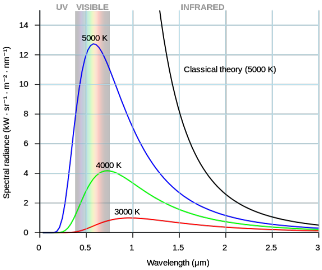
Clouds Over Classical Physics

- Mini solar system model - Moving charges radiate energy so electrons death spiral into nucleus.



- Specific heat freeze-out - Where did the other degrees of freedom go?





- Black-body radiation - the ultraviolet catastrophe.

Postulates of Quantum Mechanics

1. The quantum state of a particle is characterized by a wave function $\Psi(\vec{r}, t)$, which contains all the information about the system an observer can possibly obtain.
2. The square of the magnitude of the wave function $|\Psi(\vec{r}, t)|^2$ is the probability or probability density for the particle's position.
3. The things we measure (*e.g.* energy, momentum) are called observables. Each observable has a corresponding mathematical object called an operator that does 'something' to the wave function $\Psi(\vec{r}, t)$ to generate the value of the observable.
4. The x dependence of the wave function in one dimension $\psi(x)$ is governed by the energy operator which generates the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$

where $\hbar$ is Planck's constant, m is the mass of the particle, and V is the potential energy of the particle.

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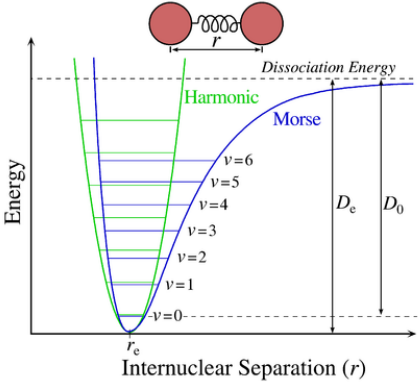
3. For many molecules (and atoms and nuclei) they're potential energies are, sometimes, well described by the harmonic oscillator.



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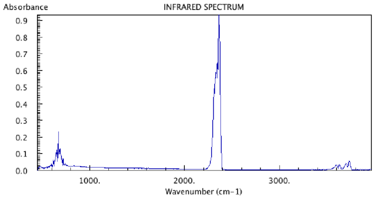

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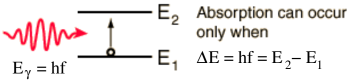

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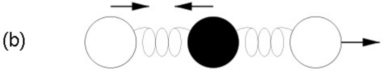

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3. What is the energy of the ground state of the $\mathrm{CO_2}$ molecule in terms of the separation between successive energy states (Hint: Recall lab results.)?
4. The relationship among the frequency f, the spring constant k, and the masses for the simple harmonic oscillator is

$$f = \frac{1}{2\pi}\omega = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad .$$

   For the $\mathrm{CO_2}$ molecule it is

$$f = \sqrt{\frac{2m_o + m_C}{m_O m_C}k}$$

   where m_O and m_C are the oxygen and carbon masses respectively. What is the spring constant of the $\mathrm{CO_2}$ oscillator in this mode?

How hard do CO_2 atoms vibrate? - 2

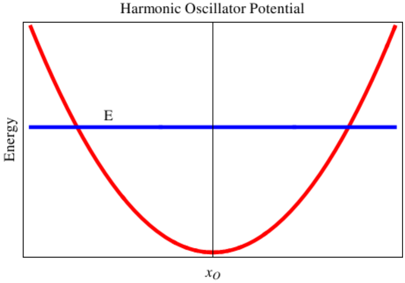
5. The relationship among the potential energy, the positions of the atoms in CO_2 and the spring constant is also more complex here than for the simple harmonic oscillator. The potential energy is

$$V(x_O) = \frac{2m_O + m_C}{2m_C} 4kx_O^2$$

where x_O is the displacement of the oxygen atoms from equilibrium. What is the classical turning point of the oxygen atoms when the CO_2 molecule is in the ground state?

6. How does your answer compare with the $\mathrm{C-O}$ bond length in carbon dioxide of 1.16 Å?

7. What is the maximum acceleration of the oxygen?



Periodic Chart

B = Solids   Hg = Liquids   Kr = Gases   Pm = Not found in nature

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	71 Lu 174.967	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	103 Lr (262)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (269)	111 Rg (272)	112 Cn (277)	113 Uut (277)	114 Uuq (277)	115 Uup (277)	116 Uuh (277)		118 Uuo (277)

57 La 138.9055	58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04
89 Ac 232.0381	90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)