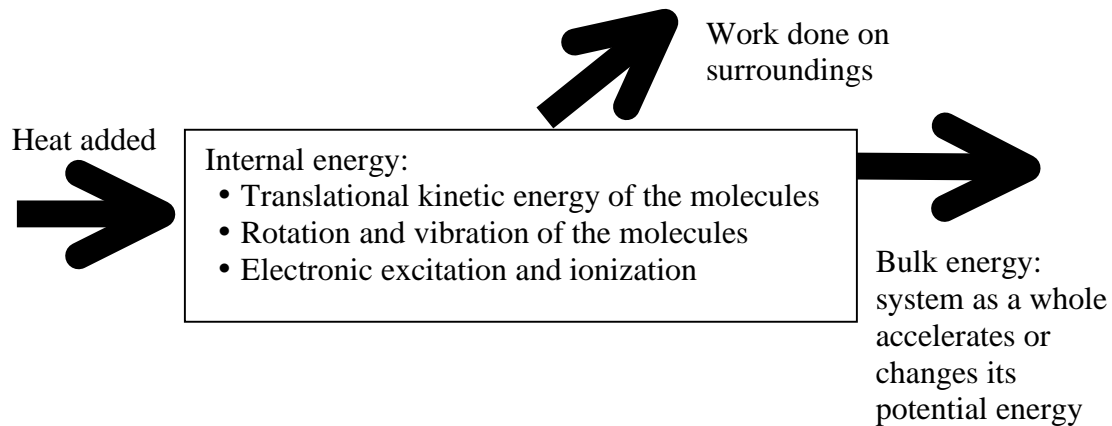**Specific Heat or Heat Capacity**

When energy is added to a material, it can be divided in various ways (see figure below).
- Some may go into the bulk energy of the substance like the acceleration of a rocket's exhaust gas.
- Some may go into doing work on the surroundings if the material expands.
- Some may go into internal energy.

Of the internal energy,
- Some goes into translational kinetic energy which results in a rise in temperature
- Some goes into the excitation of the atoms and molecules of the material

Excitation includes molecular rotation, molecular vibration and at high enough temperatures, dissociation of molecules and ionization.

Definition: The specific heat of a material is the amount of heat that must be added to a unit mass of material to raise its temperature by 1 degree.

The symbol for specific heat is C. It is either at constant volume, C_V, or constant pressure, C_P. We will learn about the distinction between these two shortly. In mks, the units of specific heat are joules per kg per Kelvin, $J \, kg^{-1} \, K^{-1}$.

$$\Delta Q = C \, M \, \Delta T$$

The amount of heat required to raise the temperature of a mass, M, through a temperature interval, ΔT, is equal to the product of at the specific heat of the material, its mass and the temperature interval.

At normal temperatures, the specific heat of water is 1 calorie/gram °C = 4.186 joule/gram °C = 4,186 J/kg/K which is higher than any other common substance. As a result, water plays a very important role in temperature regulation. In fact the oceans are the heat sink that will take a long time to heat up because of global warming due to the imbalance in radiation de to increased greenhouse gases (GHG) in Earth's atmosphere. Once the oceans are heated up it will also take a long time to cool them off if the original GHG concentrations were ever achieved again.

Raising 1 kg of water by 1°C requires 4,186 joules of heat (energy) to be added to the water. Using a 100 watt heat source, it would take about 42 seconds to increase the temperature of the 1 kg of water by 1°C.

Molar specific heat

Molar specific heat is defined as the heat required to raise the temperature of 1 mole of a substance by 1K. Its units are J/mole/K. We will use the designation, *C'*, to refer to molar specific heat. From a units analysis

$$C' = C\,m$$

where *m* is the molar weight or mass in kg (or grams) per mole.

It is easier to understand the physics of specific heats using molar specific heats. In practice, since the mass of an object is an easier quantity to determine than the number of moles in an object, the mass form of the specific heat is typically used when performing actual calculations.

Equipartition Theorem and Modes of excitation

When an object or substance is in equilibrium, its internal energy is distributed ***equally*** between its different modes of storing energy. These are also called degrees of freedom. The minimum number of degrees of freedom of an atom or molecule is 3, one for each direction of its translational motion: *x*, *y*, and *z* in Cartesian coordinates.

Additional modes of energy storage of molecules are the rotational, vibrational and electronic modes of excitation.
- Electronic: Electron transition between different electron orbits
- Vibrational: Transitions between different vibrational modes of the molecule.
- Rotational: Rotation of the molecule around different axes of rotation.

Each mode or degree of freedom receives or is allocated $k_B T/2$ of energy.
So when heat is added to an object, the object distributes the energy equally to all of the available degrees of freedom. The temperature only refers to the translational or kinetic energy.

So a high molar specific heat means the material has many modes of storing energy beyond just translational or kinetic energy.

We will talk about specific heat at constant ***volume*** first and then discuss the modification to understand the constant pressure version by applying the work concept

Monatomic gas

The easiest specific heat to understand is that of the monatomic gas. Monatomic gases are gases made up of single atoms that don't bond easily with other atoms of the same kind. The obvious examples are the noble gases, He, Ne, Ar, Kr, Xe and Rn. Their internal energy at Earth's temperatures is distributed as follows
- A monatomic gas has the 3 kinetic energy modes associated with translational motion in the *x*, *y* and *z* directions.
- A monatomic gas has no vibrational modes.
- Because of its very small moment of inertia, its rotational modes have very high energies, much higher than the thermal energies of Earth temperatures. Therefore, except for the ground state, these rotational energy levels are not populated.

So the only energy modes that are populated are the 3 translational modes. The molar specific heat at constant volume of atomic gases is therefore $C_V' = C_{V,m} = 3/2\ R^*$ and the mass specific heat of atomic gases is $C_V = 3/2\ R^*/m$ where m is the molar mass in kg/mole. The following table shows values of specific heats at constant volume for monatomic gases.

Monatomic gas	$C_{V,m}$ (J/K/mol)	$C_{V,m}$ /(R/2)	C_V (J/K/kg)
He	12.5	3.00	3,125
Ne	12.5	3.00	619
Ar	12.5	3.00	313
Kr	12.5	3.00	149
Xe	12.5	3.00	95

Note that when looking up specific heats, one must be careful whether one is looking at a C_V or a C_p. Most gases are given in terms of C_p which we have not yet discussed.

Clearly the simple theory of energy equal to $k_B T/2$ per degree of freedom per molecule works very well in this case.

Specific Heat of Molecules

    Molecules (which to state the obvious have at least 2 atoms) are clearly more complicated than atoms because they have both rotational and vibrational modes. Therefore, the molar specific heats of gases of molecules will be systematically higher than those of monatomic gases and more heat will be required per mole to raise their temperature than for monatomic gases.

    A key point before going farther is the accessibility of these energy modes given the magnitude of thermal energies available as defined by the temperature. This has to do with the Boltzmann distribution which states the probability that a given energy level of a system is populated at a temperature, T.

Boltzmann Distribution

    The Boltzmann distribution defines how the various energy states of a system are populated given that the system has a well defined temperature, T. According to the Boltzmann distribution, given a total number of particles, N, occupying a set of states, the number of particles N_i occupying the states with energy $= E_i$ or equivalently having an energy, E_i, is given by

$$\frac{N_i}{N} = \frac{g_i e^{E_i/k_B T}}{Z(T)}$$

where g_i is the degeneracy which is the number of states having energy E_i, and N is the total number of particles

$$N = \sum_i N_i$$

and $Z(T)$ is called the partition function, which is equal to

$$Z(T) = \sum g_i e^{E_i/k_B T}$$

For a given single system, this fraction, N_i/N, gives the probability that the system is in the specified state. The Boltzmann distribution applies only to particles at a high enough temperature and low enough density that quantum effects can be ignored, and the particles are obeying Maxwell–Boltzmann statistics.

In the current context, the Boltzmann distribution is important because it tells us the likelihood that a given rotational or vibrational or electronic state is occupied. If the energy of a particular state is very high in comparison to available thermal energies, such that the probability or likelihood that a given state is occupied is very low according to the Boltzmann distribution, then that state will not contribute to the specific heat of the material and can be ignored. We now need to estimate the energies of the rotational and vibrational modes and compare them with the thermal energies to determine which sets of states need to be counted in the degrees of freedom.
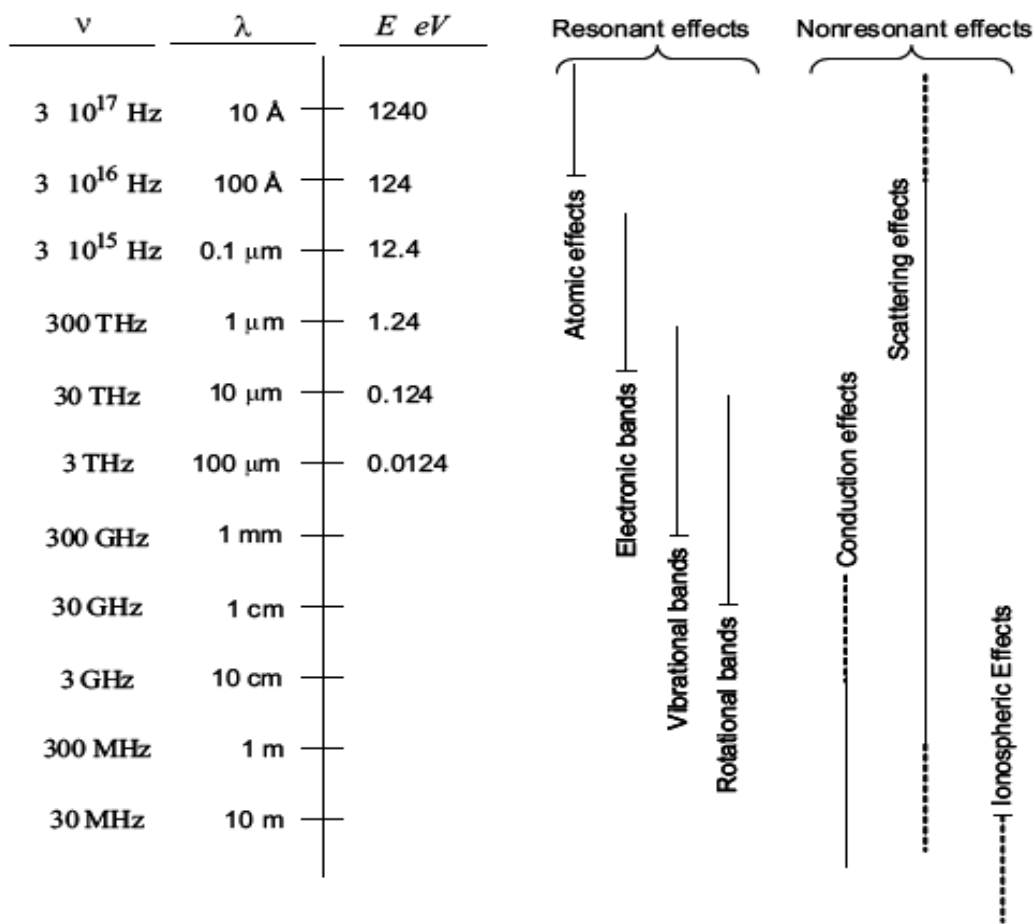
Figure 2-15. Correspondence of spectral bands, photon energy, and range of different wave–matter interaction mechanisms of importance in remote sensing. The photon energy in electron volts is given by $E(eV) = 1.24/\lambda$, where λ is in μm.

Note: 1 eV = 1.60219 J
        k_B = 1.3806e-23 J/K = 8.617e-5 eV/K

So, for scale, T= 300 K => $k_B T$ = 0.0258 eV. This corresponds to wavelengths of 50 microns in the figure above.

Diatomic gases (the next easiest case)

Diatomic molecules are the easiest gas particles after the monatomic gas. The typical value given for the molar specific heat at constant *volume* for a diatomic molecule is approximately 5/2 *R**, the rationale for which we will now try to understand.

Consider the rotational and vibrational modes of a diatomic molecule thinking in terms of a simple dumbbell model.
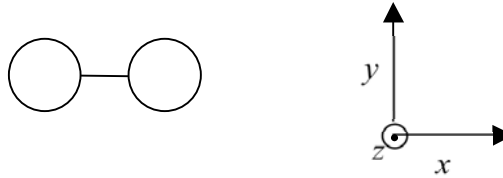
Define the *x* direction as along the line between the molecules in the figure, the *y* direction as up in the plane of the paper and the *z* direction as being out of the paper. There are 3 rotational modes defined as rotation about each of the 3 axes: *x*, *y* and *z*. Rotation around the y and z axes are very similar and have the same moments of inertia, $I=mr^2$. Rotation about the x-axis differs from the other two because the moment of inertia is much smaller because the distance from the mass to the spin axis is much smaller. This distinction is very important because the quantum rotational energy levels of a dumbbell are inversely proportional to *I*.

Rotational energy levels

In the simple 2 atom dumbbell molecule, the rotational energy levels are

$$E_j = \frac{h^2}{8\pi^2 I} j(j+1)$$

where *h* is Planck's constant, 6.6×10^{-34} J s, *j* is the rotational quantum number, 0, 1, 2,… and *I* is the moment of inertia:

$$I = \int r^2 \rho dV$$

where ρ is the mass density, *V* is volume and *r* is distance of the mass element from the spin axis. [Units check: $J^2 s^2/(kg\ m^2) = J^2/J = J$ OK]
In the simple dumbbell model, for the rotation around the *y* and *z* axes, the two atoms can be considered as 2 point masses so the moment of inertia is straight forward to calculate.

- First one finds the location of the center of mass (which is the spin axis):

$$r = \frac{\int \rho(r) r dV}{\int \rho(r) dV} = \frac{\sum m_i r_i}{\sum m_i}$$

  where the first form is for continuously distributed mass and the second is the discrete form when there are a finite number of masses.
- Then one calculates the moment of inertia (where r is now defined relative to the center of mass)

$$I = \int r^2 \rho dV = \sum m_i r_i^2$$

Then one plugs this value of the moment of inertia into the rotational energy equation above and finds the rotational energy levels, E_j. The following table shows the first few energy levels (in eV) for several diatomic molecules.

j	H$_2$	N$_2$	O$_2$	Br$_2$
0	0	0	0	0
1	1.53E-02	1.09E-03	9.54E-04	1.91E-04
2	4.58E-02	3.27E-03	2.86E-03	5.73E-04
3	9.16E-02	6.54E-03	5.73E-03	1.15E-03
4	1.53E-01	1.09E-02	9.54E-03	1.91E-03
5	2.29E-01	1.64E-02	1.43E-02	2.87E-03

The next table shows the same information converted to temperatures by dividing by k$_B$ in eV/K

j	H$_2$	N$_2$	O$_2$	Br$_2$
0	0	0	0	0
1	177.18	12.66	11.07	2.22
2	531.55	37.97	33.22	6.65
3	1063.10	75.94	66.44	13.31
4	1771.83	126.56	110.74	22.18
5	2657.74	189.84	166.11	33.26

- What this shows is for typical temperatures encountered on Earth, many rotational states will be populated according to the Boltzmann distribution (which assumes the system has a well defined temperature).
- It also shows that the heavier diatomic molecules have lower energy rotational states because the moment of inertia is larger because the mass of the atoms involved is higher.

Vibrational energy modes and levels
     The vibrational energy modes are thought of involving springs between the atoms. In the diatomic case, simplistically there is one spring between the two atoms. This is a simple harmonic oscillator defined as

$$F = -kx = \mu \frac{d^2 x}{dt^2}$$

The solution is of the form

$$x = a \sin\left(\sqrt{\frac{k}{\mu}} t + \phi\right) = a e^{i\left(\sqrt{\frac{k}{\mu}} t + \phi\right)}$$

Combining this concept with quantum mechanics leads to a discrete set of energy levels defined as

$$E_n = \left(n + \frac{1}{2}\right) \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where μ is the reduced mass:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

and m_1 and m_2 are the masses of the atoms at the ends of the spring. Note that the stronger the spring, the higher the spring constant, k, and the higher the energy levels. The more massive the atoms, the lower the energy levels.

		H2	CO	NO	N2	HI	Cl2	HCl	Br2	O2	
k		1000	1860	1530	1695	320	1000	1000	1000	930	N/m
m		0.50	6.86	7.47	7.47	0.99	17.73	0.97	39.95	8	amu
m		8.33E-28	1.14E-26	1.24E-26	1.24E-26	1.65E-27	2.95E-26	1.62E-27	6.66E-26	1.33E-26	kg
freq		1.74E+14	6.42E+13	5.58E+13	5.87E+13	7.00E+13	2.93E+13	1.25E+14	1.95E+13	4.20E+13	Hz
DE		1.16E-19	4.25E-20	3.70E-20	3.89E-20	4.64E-20	1.94E-20	8.28E-20	1.29E-20	2.79E-20	J
DT1	1	16743	6166	5359	5641	6723	2812	12005	1873	4037	K
DT2	2	50228	18498	16077	16922	20170	8436	36014	5619	12110	K
DT3	3	83714	30829	26796	28203	33617	14060	60024	9365	20183	K
		1	1	1	1	1	1	1	1	1	
		6.76E-59	3.78E-22	2.40E-19	2.52E-20	4.37E-24	**1.70E-10**	1.96E-42	**3.11E-07**	9.46E-15	
		4.6E-117	1.43E-43	5.77E-38	6.37E-40	1.91E-47	2.89E-20	3.83E-84	9.65E-14	8.94E-29	

The last 3 columns show the Boltzmann distribution probabilities

The point is that the vibrational energy levels are significantly higher than the rotational energuy levels and not nearly as populated as the rotational levels. Therefore, for a given molecule, the specific heat may not include the contribution of the vibrational energy levels.

	H_2	N_2	O_2	Cl_2	Br_2
$C_{p,m}$	28.84	29.12	29.38	34.03	
$C_{p,m}/(R^*/2)$	6.94	7.005	7.07	8.19	
$C_{V,m}$	20.18	19.9	21.07	24.1	32
$C_{V,m}/(R^*/2)$	4.85	4.79	5.07	5.80	7.70

Notice that Br_2 & Cl_2 have the lowest & 2nd lowest vibrational energy levels and have the highest molar specific heats consistent with the idea that their vibrational levels are populated

SUMMARY
   To understand which of these modes get excited at commonly experienced temperatures, we need to compare the thermal energy range to the range of energies of the rotational and vibrational modes.
   So thermal energies typically encountered on Earth are comparable to rotational energy levels and the lower portion of vibrational energy levels of many molecules but well below electronic energy levels. So for typical conditions found on Earth, the specific heat will depend on the rotational and vibrational energy levels of the molecules but not their electronic energy levels or modes.