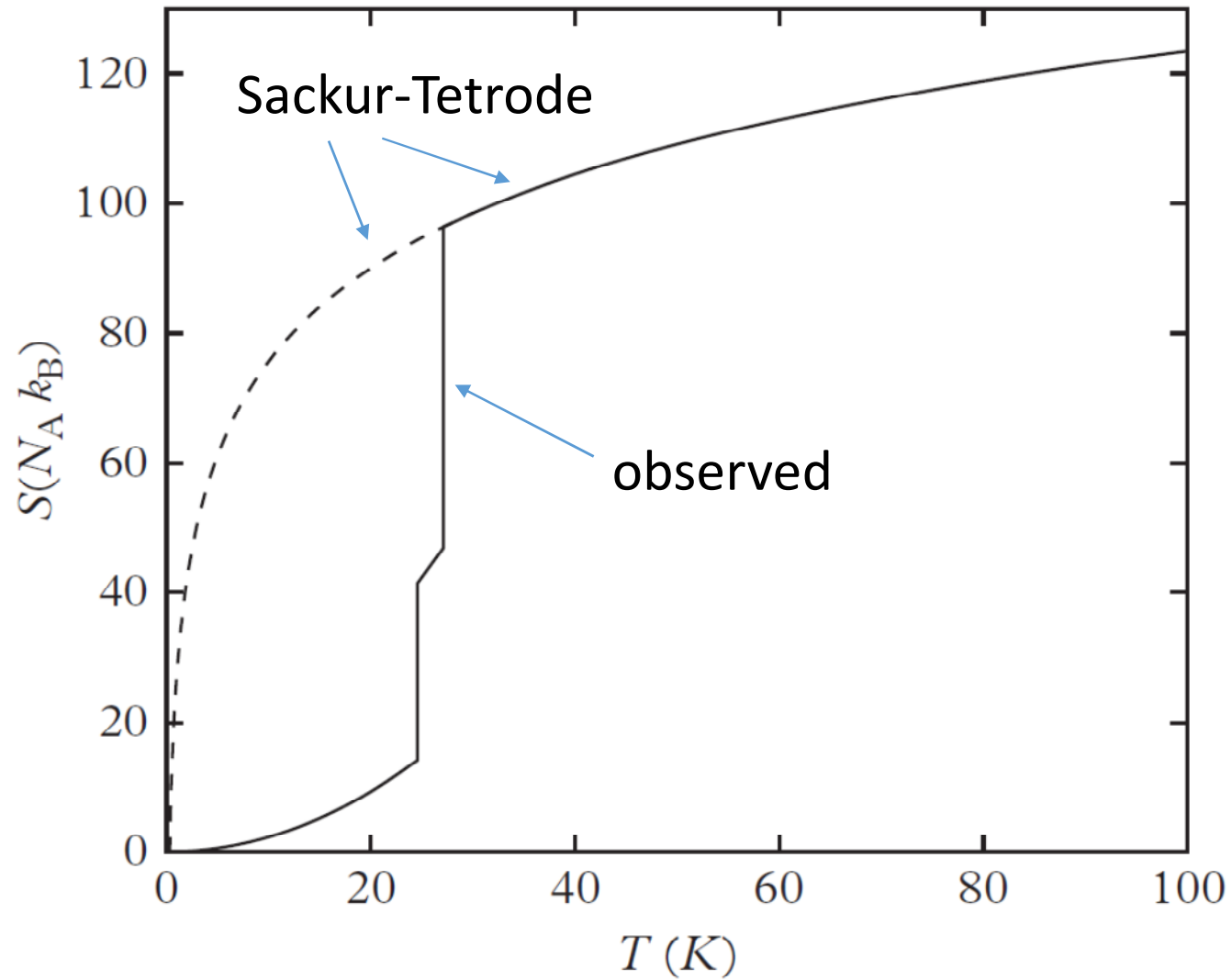


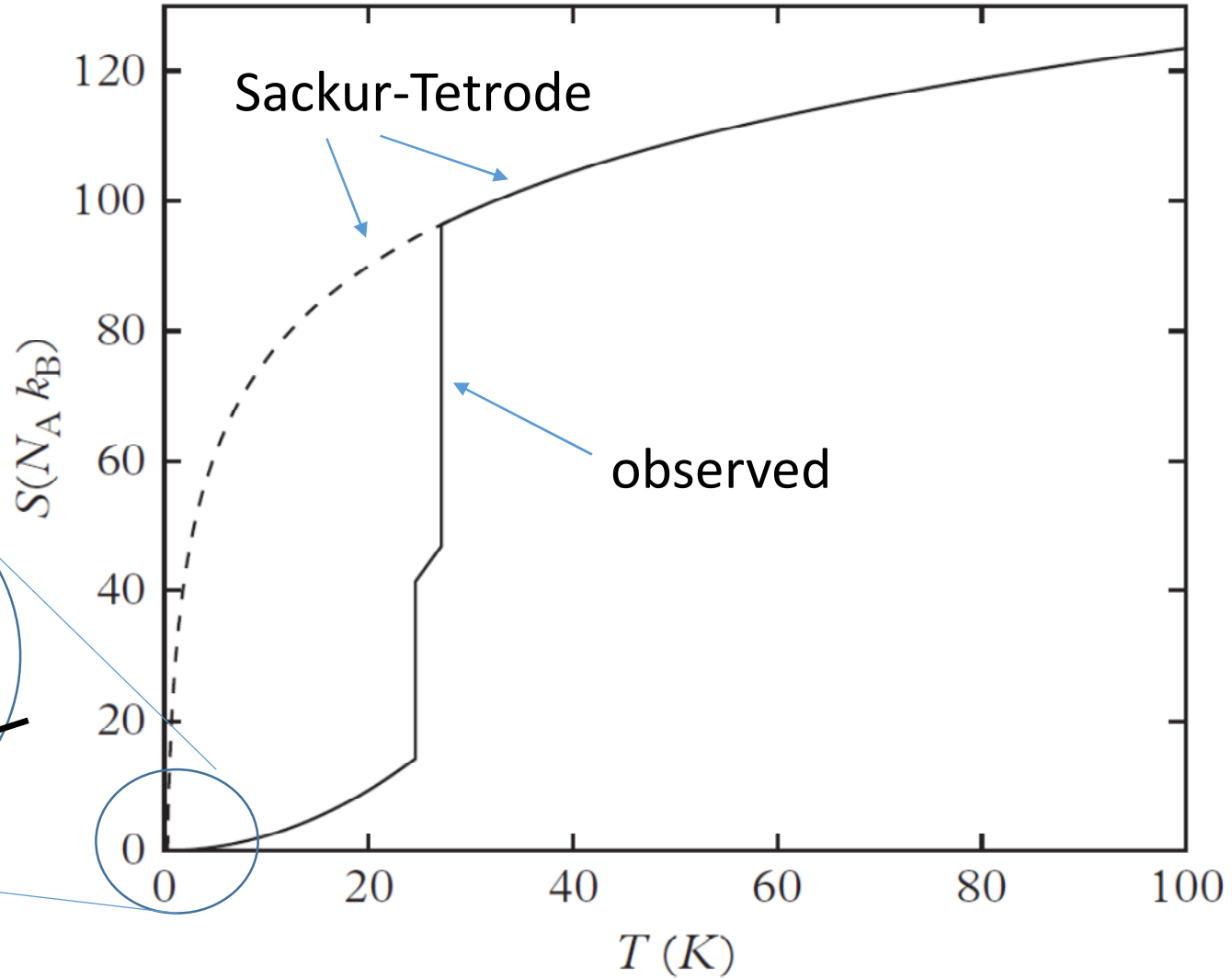
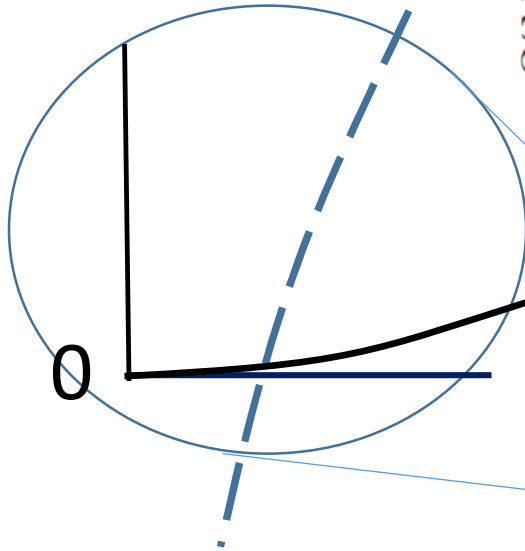
# Statistical mechanics of a gas at high temperature

1. Obtain partition function for the translational motion of particles in a box
2. Hence obtain energy, heat capacity, **and entropy**
- 3. The idea of k space and density of states**
4. Bring in rotation and vibration



Entropy of neon as a function of temperature, with prediction of Sackur-Tetrode equation.

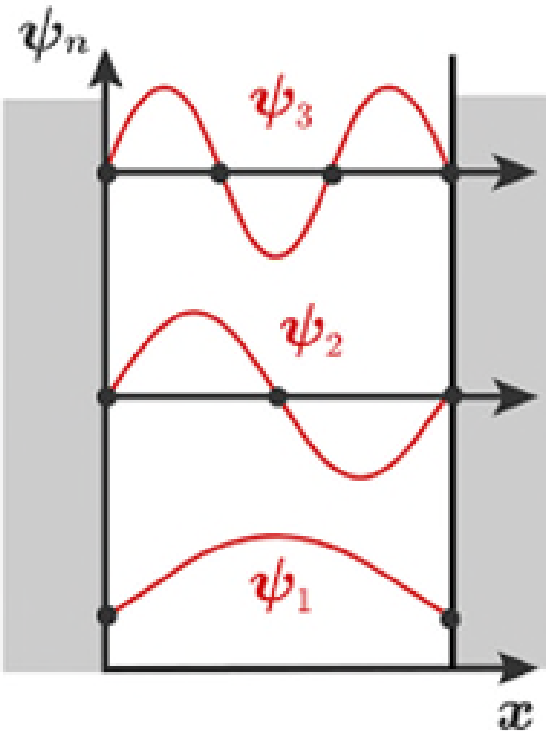
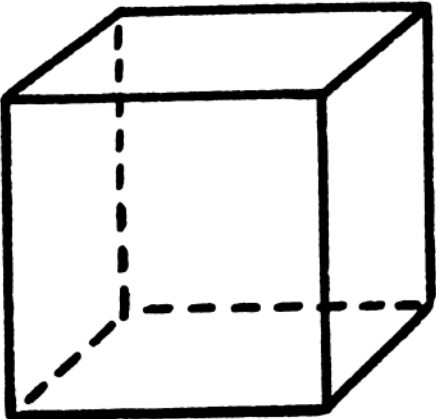
Entropy prediction  
WRONG at low T



At low T we have to take **indistinguishability** into account, which we have NOT done here.

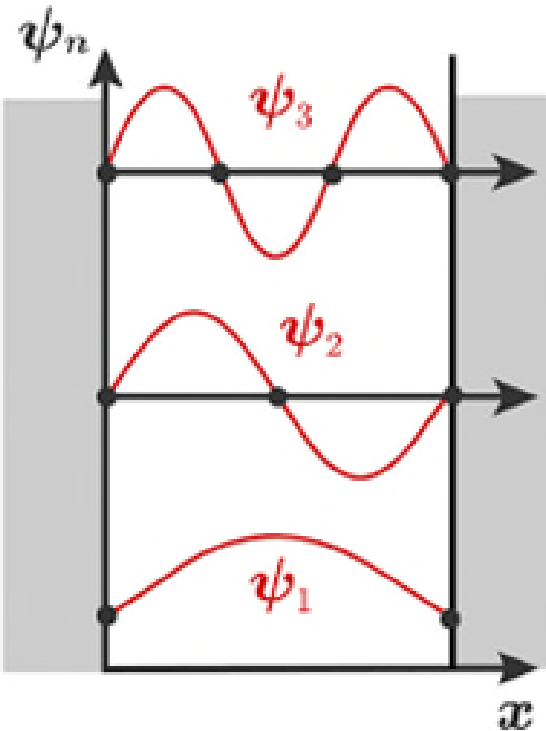
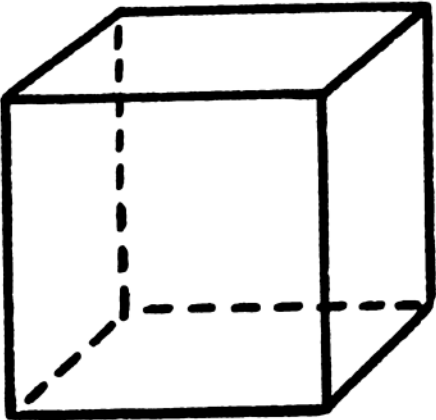
Entropy of neon as a function of temperature, with prediction of Sackur-Tetrode equation.

# Gas in a box

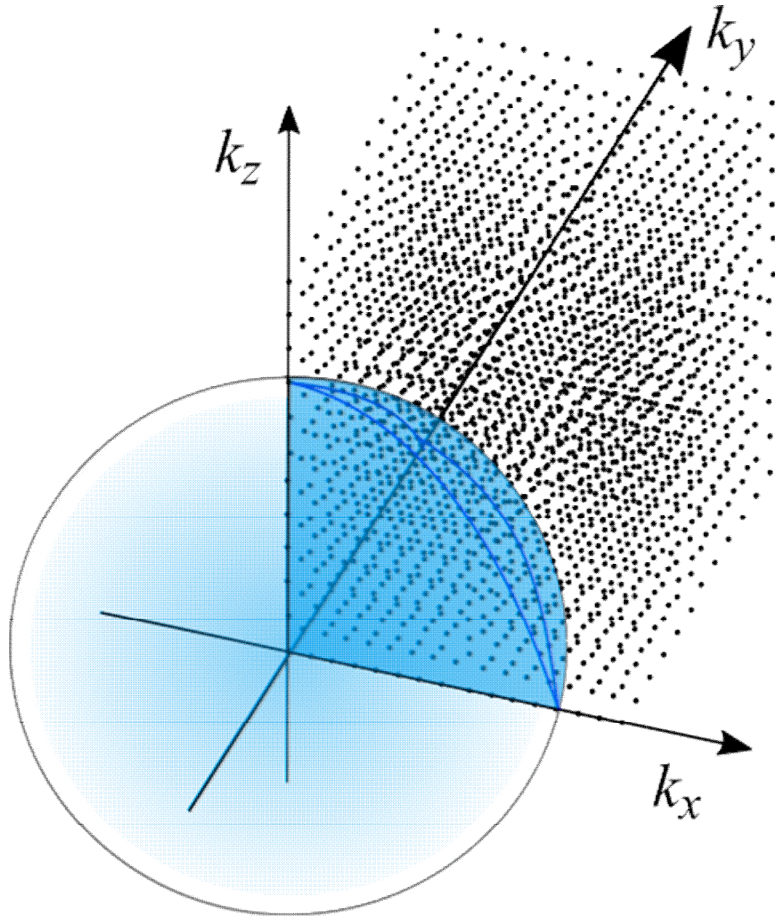


Potential well with  
energy  
eigenstates  
(in one dimension)

# Gas in a box



Potential well with energy eigenstates (in one dimension)



States in k space

The quantity

$$\frac{1}{\Delta k_x \Delta k_y \Delta k_z} = \frac{V}{\pi^3}$$

is called the **density of states in  $k$ -space**.

The quantity

$$\frac{dN}{dk}$$

is also a **density of states**, but now a density with respect to the magnitude of  $k$ .

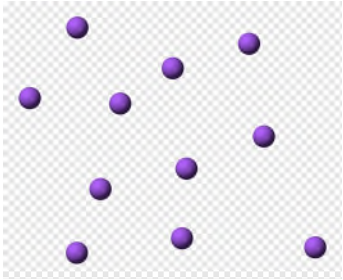
This is often written  $g(k) \equiv \frac{dN}{dk}$  and so we have:

(number of states between  $k$  and  $k + dk$ ) =  $g(k)dk$

and

$$g(k)dk = \frac{V}{(2\pi)^3} 4\pi k^2 dk$$

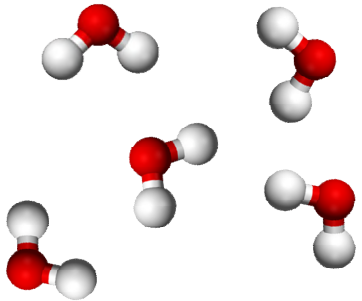
So far, we have treated translational motion.



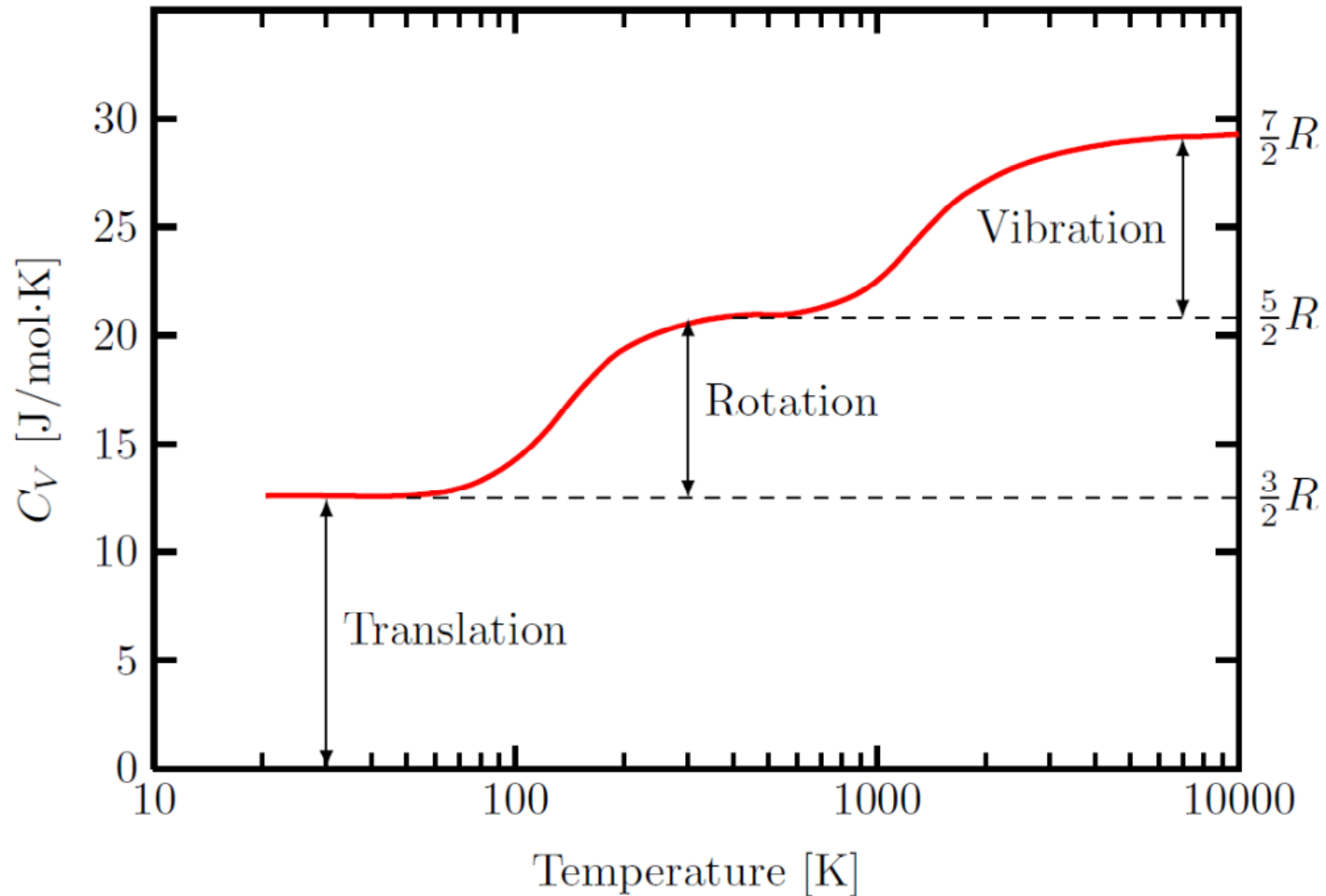
For MONATOMIC gas that's the whole story  
(except there can be fine structure in the internal electronic energy levels ... see notes)



For DIATOMIC gas we have also rotation and vibration.



For POLYATOMIC gas there is even more rotation and vibration.



Heat capacity of a typical diatomic gas as a function of temperature.  
Most gases have rotation but not vibration excited at room temperature.



# Total heat capacity when rotation is fully excited

$$C_V = C_V^{(t)} + C_V^{(r)} + C_V^{(v)}$$
$$= \frac{3}{2}Nk_B + \begin{cases} Nk_B & \text{(linear molecule)} \\ \frac{3}{2}Nk_B & \text{(non-linear molecule)} \end{cases} + Nk_B \sum_{i=1}^{q_v} \frac{(T_{v,i}/(2T))^2}{\sinh^2(T_{v,i}/(2T))}$$

↑  
Translational

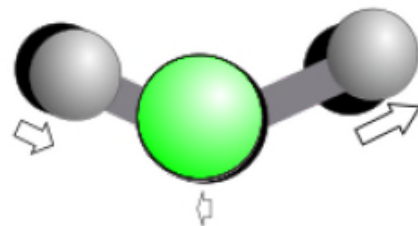
↑  
rotational

↑  
Vibrational  
(simple harmonic motion  
for each normal mode)

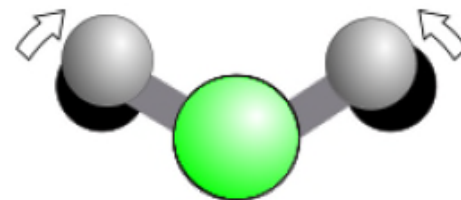
H<sub>2</sub>O



Symmetric stretch

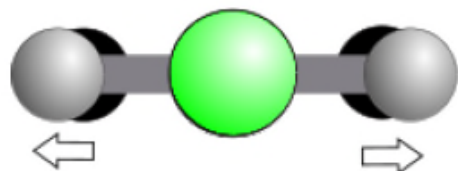


Asymmetric stretch

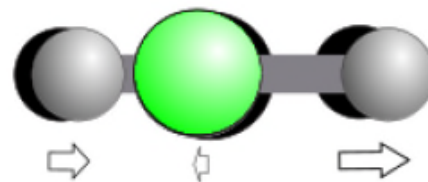


Bending

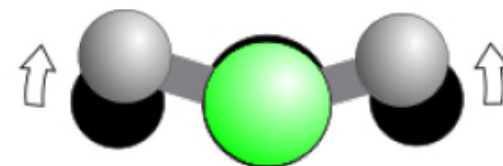
CO<sub>2</sub>



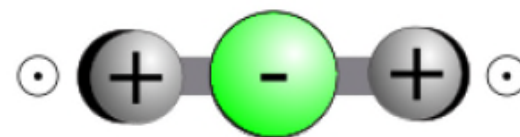
Symmetric stretch



Asymmetric stretch



Bending



**Fig. E.1** Normal modes of H<sub>2</sub>O and CO<sub>2</sub> molecules. The arrows indicate the motion during one half of any given oscillation. The second bending mode for CO<sub>2</sub> is in the direction perpendicular to the plane of the diagram.