Obtain vibrational energy levels and rotational temperatures for some small molecules from QM calculation (e.g. using Gaussian); calculate their Cv at various temperatures and compare with tabulated values

(Computational resources were provided by the e-INFRA CZ project (ID:90254), supported by the Ministry of Education, Youth and Sports of the Czech Republic. https://metavo.metacentrum.cz/)

Gaussian job setup for a frequency calculation using CCSD method and correlation-consistent polarized valence triple-zeta basis set:

```
%chk=l04_qmcalc.chk
#p opt freq ccsd/cc-pvtz

opt + freq on co2

0 1
C  0.0  0.0  0.0
O -1.0  0.0  0.0
O  1.0  0.0  0.0
```

Frequency information retrieved from the log file of the finished calculation:

```
 Harmonic frequencies (cm**-1), IR intensities (KM/Mole), 
Raman scattering
 activities (A**4/AMU), depolarization ratios for plane 
and unpolarized
 incident light, reduced masses (AMU), force constants 
(mDyne/A),
 and normal coordinates:
                      1                      2                      
3
                     PIU                    PIU                    
SGG
 Frequencies --    684.5137               684.5137              
1389.7091
 Red. masses --     12.8774                12.8774                
15.9949
 Frc consts  --      3.5550                 3.5550                
18.2004
 IR Inten    --     34.3245                34.3245                 
0.0000
  Atom  AN      X      Y      Z        X      Y      Z        
X      Y      Z
     1   6     0.00   0.88   0.00     0.88  -0.00   0.00     
0.00  -0.00  -0.00
     2   8    -0.00  -0.33   0.00    -0.33   0.00  -0.00    
-0.00   0.00   0.71
     3   8    -0.00  -0.33  -0.00    -0.33   0.00  -0.00     
0.00   0.00  -0.71
                      4
                     SGU
 Frequencies --   2434.6980
 Red. masses --     12.8774
 Frc consts  --     44.9746
 IR Inten    --    709.2532
  Atom  AN      X      Y      Z
     1   6    -0.00  -0.00   0.88
     2   8     0.00   0.00  -0.33
     3   8     0.00   0.00  -0.33
...
 -------------------
 - Thermochemistry -
 -------------------
 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
 Atom     1 has atomic number  6 and mass  12.00000
 Atom     2 has atomic number  8 and mass  15.99491
 Atom     3 has atomic number  8 and mass  15.99491
 Molecular mass:    43.98983 amu.
 Principal axes and moments of inertia in atomic units:
                           1         2         3
     Eigenvalues --     0.00000 153.49903 153.49903
           X           -0.00000   1.00000   0.00000
           Y           -0.00000   0.00000   1.00000
           Z            1.00000   0.00000   0.00000
 This molecule is a prolate symmetric top.
 Rotational symmetry number  2.
 Rotational temperature (Kelvin)      0.56426
 Rotational constant (GHZ):          11.757346
 Zero-point vibrational energy      31063.6 (Joules/Mol)
                                    7.42439 (Kcal/Mol)
 Vibrational temperatures:    984.86   984.86  1999.48
3502.99
          (Kelvin)

 Zero-point correction=                           0.011832
(Hartree/Particle)
 Thermal correction to Energy=                    0.014438
 Thermal correction to Enthalpy=                  0.015382
 Thermal correction to Gibbs Free Energy=        -0.008854
 Sum of electronic and zero-point Energies=
-188.286840
 Sum of electronic and thermal Energies=
-188.284234
 Sum of electronic and thermal Enthalpies=
-188.283290
 Sum of electronic and thermal Free Energies=
-188.307525

                     E (Thermal)            CV
S
                      KCal/Mol        Cal/Mol-Kelvin
Cal/Mol-Kelvin
 Total                    9.060              6.798
51.008
 Electronic               0.000              0.000
0.000
 Translational            0.889              2.981
```

```
37.270
 Rotational                0.592              1.987
13.069
 Vibrational               7.579              1.830
0.669
```

Analysing calculation results

We can see from the log above that CO2 has 4 vibrational modes:

- ($\nu_1 = 684(2)\ cm^{-1}$) => two degenerate bending modes
- ($\nu_2 = 1389\ cm^{-1}$) => symmetric strech
- ($\nu_3 = 2434\ cm^{-1}$) => antisymmetric strech

With the following associated vibrational temperatures:

- $\nu_1 :\ 984.86(2)\ K$
- $\nu_2 :\ 1999.48\ K$
- $\nu_3 :\ 3502.99\ K$

Rotational temperature for CO2 can be retrieved from the thermochemistry section of the log:

- $T_{rot} = 0.5643\ K$

Now let's calculate contributions of these modes to heat capacity of the molecule: Vibrational contribution to heat capacity $C_{V,vib}$ is given as:

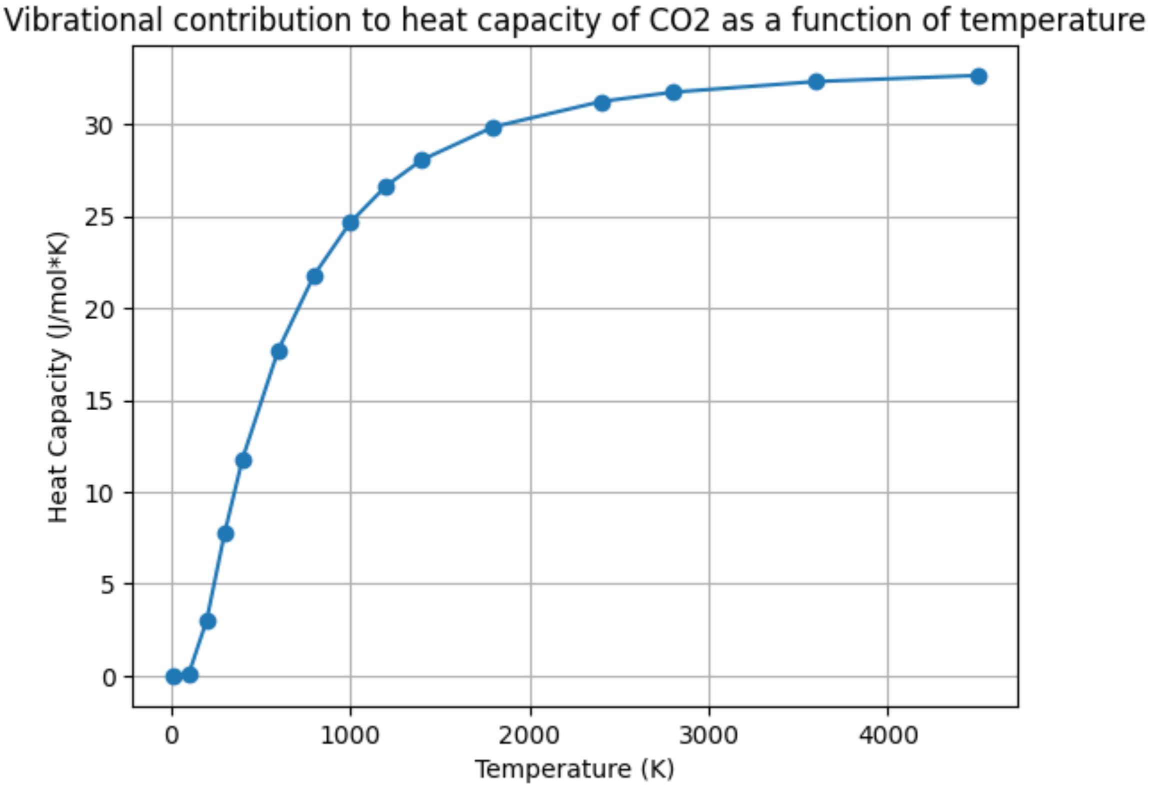
$$C_{V,vib} = N k_B \sum_{n=1}^{\alpha} \left[\left(\frac{\Theta_{V,n}}{T} \right)^2 \frac{e^{-\Theta_{V,n}/T}}{(e^{-\Theta_{V,n}/T} - 1)^2} \right]$$

- N is number of molecules
- $\Theta_{V,n}$ is the characteristic temperature for the n-th vibrational mode
- T is temperature
- α is the total number of normal modes

In [ ]:

```
import numpy as np
from scipy import constants
import matplotlib.pyplot as plt

def vibrational_heat_capacity(Theta, T):
    cv_sum = 0
    for theta in Theta:
        cv_sum += (theta / T)**2 * np.exp(- theta / T) / (np.exp(- theta

    #print(constants.Boltzmann * cv_sum)
    cv = constants.Avogadro * constants.Boltzmann * cv_sum
    return cv

Theta = [
    984.86,
    984.86,
    1999.48,
    3502.99
```

```
]

Temps = [
    10,
    100,
    200,
    300,
    400,
    600,
    800,
    1000,
    1200,
    1400,
    1800,
    2400,
    2800,
    3600,
    4500,
]

c_vib_plot = []

for temp in Temps:
    c_vib = vibrational_heat_capacity(Theta, temp)
    #print('Temperature: %s; C_vib: %s' % (temp, c_vib))
    c_vib_plot.append(c_vib)

plt.plot(Temps, c_vib_plot, marker='o')
plt.xlabel('Temperature (K)')
plt.ylabel('Heat Capacity (J/mol*K)')
plt.title('Vibrational contribution to heat capacity of CO2 as a function
plt.grid(True)
plt.show()
```



Now we can do the same for some additional small molecules

(Curly brackets contain the tabulated value)

Molecule	Normal Mode Frequencies $[cm^{-1}]$	Characteristic Temperatures	Rotational Temperature(s) $[K]$
CO_2	684(2) 1389 2434	984.86(2) 1999.48 3502.99	0.56 {0.56}

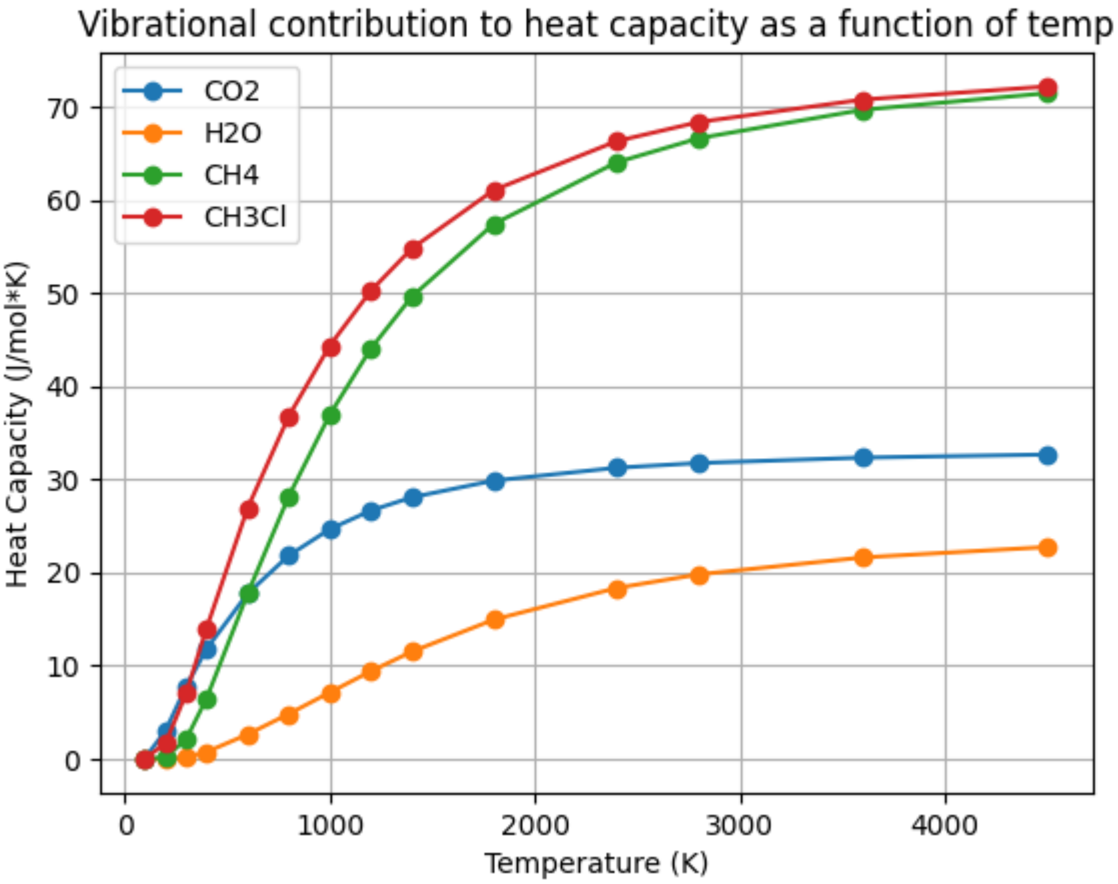
H_2O	1678
	3875
	3979
		2414.60
		5575.90
		5724.61
			38.96 {40.10}
			21.17 {20.90}
			13.72 {13.40}

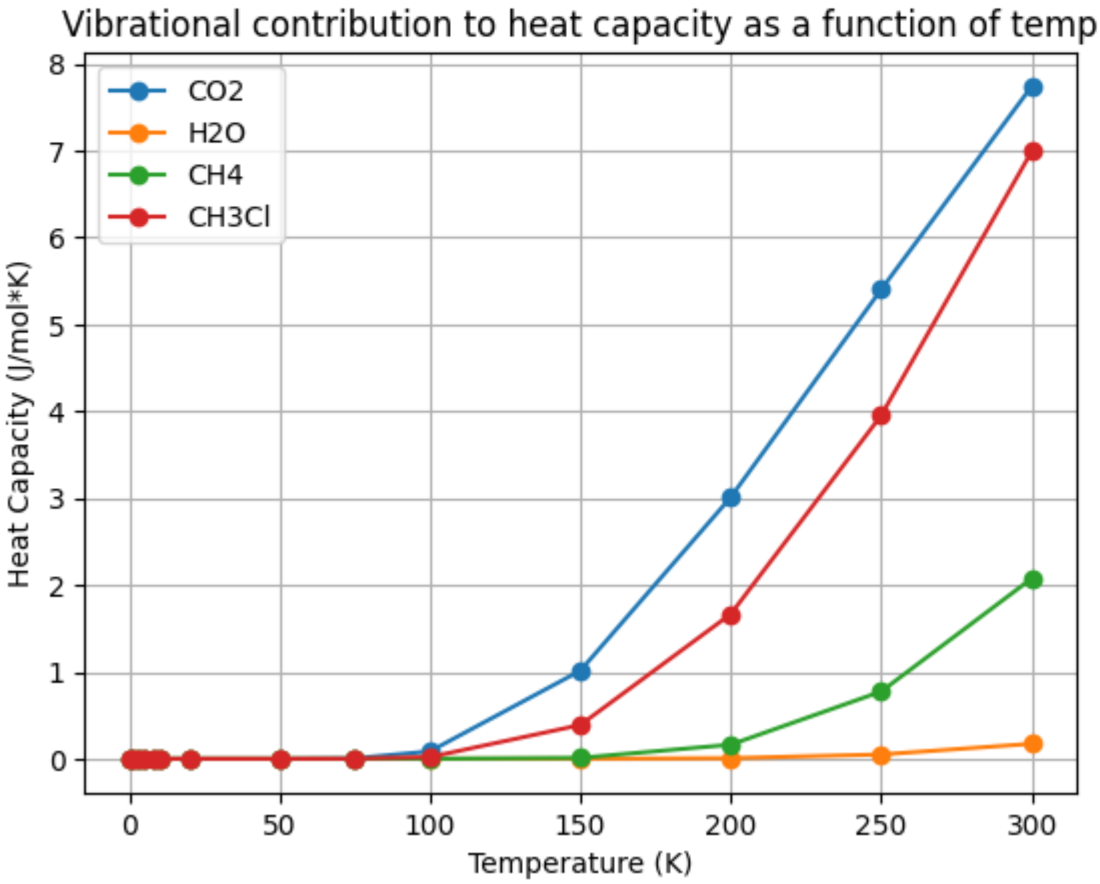
CH_4	1356(3)
	1581(2)
	3052
	3169(3)
		1950.58
		1951.06
		1951.40
		2274.77
		2274.86
		4391.22
		4559.39
		4559.87
		4560.12
			7.63(3) {7.54(3)}

CH_3Cl	756
	1043(2)
	1402
	1506(2)
	3100(3)
		1088.10
		1500.74
		1501.37
		2016.70
		2167.14
		2167.86
		4460.76
		4604.56
		4605.03
			7.59 {7.32}
			0.64(2) {0.64(2)}

In [ ]:

```python
import time
import numpy as np
from scipy import constants
import matplotlib.pyplot as plt

start = time.time()


def vibrational_heat_capacity(Theta, T):
    cv_sum = 0
    for theta in Theta:
        cv_sum += (theta / T)**2 * np.exp(-theta / T) / (np.exp(-theta /
    cv = constants.Avogadro * constants.Boltzmann * cv_sum
    return cv

def plot_vibrational_heat_capacity(molecule_data, temperatures):
    heat_capacity_data = {}

    for molecule_name, theta in molecule_data.items():
        c_vib_plot = []
        for temp in temperatures:
            c_vib = vibrational_heat_capacity(theta, temp)
            c_vib_plot.append(c_vib)
        heat_capacity_data[molecule_name] = c_vib_plot

    for molecule_name, c_vib_values in heat_capacity_data.items():
        plt.plot(temperatures, c_vib_values, marker='o', label=molecule_n

    plt.legend()
    plt.grid(True)
    plt.xlabel('Temperature (K)')
    plt.ylabel('Heat Capacity (J/mol*K)')
    plt.title('Vibrational contribution to heat capacity as a function of
    plt.show()

molecules = {
    "CO2": [984.86, 984.86, 1999.48, 3502.99],
    "H2O": [2414.6, 5575.9, 5724.61],
    "CH4": [1950.58, 1951.06, 1951.4, 2274.77, 2274.86, 4391.22, 4559.39,
    "CH3Cl": [1088.10, 1500.74, 1501.37, 2016.70, 2167.14, 2167.86, 4460.
}

high_temperatures = [
    100, 200, 300, 400, 600, 800, 1000, 1200, 1400,
    1800, 2400, 2800, 3600, 4500
]

low_temperatures = [ 0.1, 1, 3, 5, 8, 10, 20, 50, 75, 100, 150, 200, 250,

plot_vibrational_heat_capacity(molecules, high_temperatures)
plot_vibrational_heat_capacity(molecules, low_temperatures)

print("Exec. Time [s]: ", time.time() - start)
```





```
Exec. Time [s]:  0.4659726619720459
```

With the vibrational contribution solved, we now have to calculate other contributions to total heat capacity C_V:
(source slides 3,9 and 12 of C05_23_polyatomic_gas_equilibrium)

$$C_V = C_{V,trans} + C_{V,rot} + C_{V,vib}$$

Translational Contribution
Translational contribution to molar heat capacity at constant volume is quite straightforward as each degree of translational freedom contributes $R/2$:

$$C_{V,trans} = \frac{3}{2}R$$

Rotational Contribution
Similarly for rotational contribution. Each degree of freedom contributes $R/2$ with the distinction that the total rotational contribution depends on the linearity of the studied molecule, as linear molecules have only two (footnote: or one?) rotational degrees of freedom.

For linear molecules: $C_{V,rot} = R$
For non-linear molecules: $C_{V,rot} = \frac{3}{2}R$

Electronic Contribution
I neglected it for gas. Usually only noticeable in metals with large amounts of free electrons (Heat capacity of metals => Sommerfeld theory of metals)

Plotted below (**USING kJ NOW**)

In [ ]:

```
import time
import numpy as np
from scipy import constants
import matplotlib.pyplot as plt

start = time.time()


def heat_capacity(Theta, T, linearity):
    cv_vib = 0
    if linearity:
        cv_rot = constants.gas_constant/2
    else:
        cv_rot = constants.gas_constant

    for theta in Theta:
        cv_vib += (theta / T)**2 * np.exp(-theta / T) / (np.exp(-theta /
    cv = ((3 * constants.gas_constant)/2) * cv_rot * (constants.Avogadro
    return cv/1000

def plot_heat_capacity(molecule_data, temperatures):
    heat_capacity_data = {}

    for molecule_name, theta in molecule_data.items():
        if "CO2" or "H2" or "N2" in molecule_name:
            linearity = True
        else:
            linearity = False
        c_vib_plot = []
        for temp in temperatures:
            c_vib = heat_capacity(theta, temp, linearity)
            c_vib_plot.append(c_vib)
        heat_capacity_data[molecule_name] = c_vib_plot

    for molecule_name, c_vib_values in heat_capacity_data.items():
        plt.plot(temperatures, c_vib_values, marker='o', label=molecule_n

    plt.legend()
    plt.grid(True)
    plt.xlabel('Temperature (K)')
    plt.ylabel('Heat Capacity (kJ/mol*K)')
    plt.title('Vibrational contribution to heat capacity as a function of
    plt.show()

molecules = {
    "CO2": [984.86, 984.86, 1999.48, 3502.99],
    "H2O": [2414.6, 5575.9, 5724.61],
    "CH4": [1950.58, 1951.06, 1951.4, 2274.77, 2274.86, 4391.22, 4559.39,
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high_temperatures = [
    100, 200, 300, 400, 600, 800, 1000, 1200, 1400,
    1800, 2400, 2800, 3600, 4500
]

low_temperatures = [ 0.1, 1, 3, 5, 8, 10, 20, 50, 75, 100, 150, 200, 250,

plot_heat_capacity(molecules, high_temperatures)
plot_heat_capacity(molecules, low_temperatures)

print("Exec. Time [s]: ", time.time() - start)
```

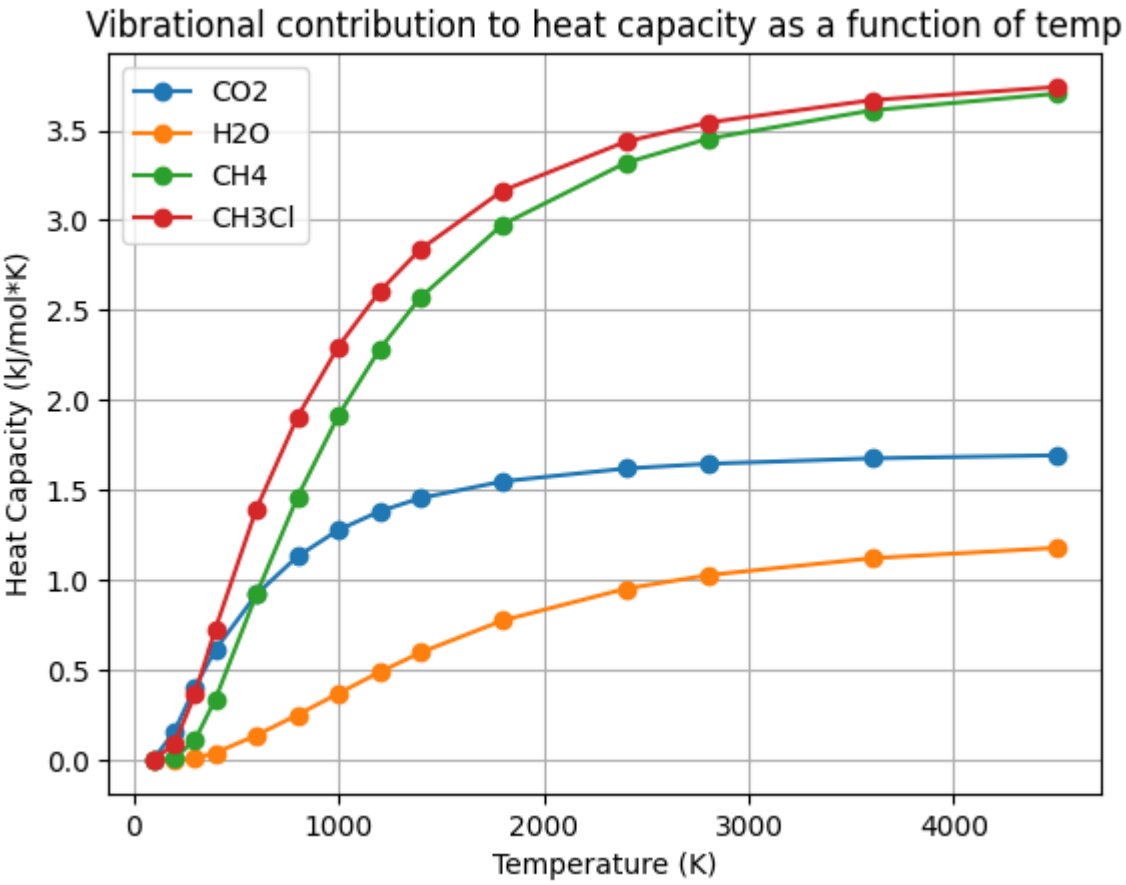

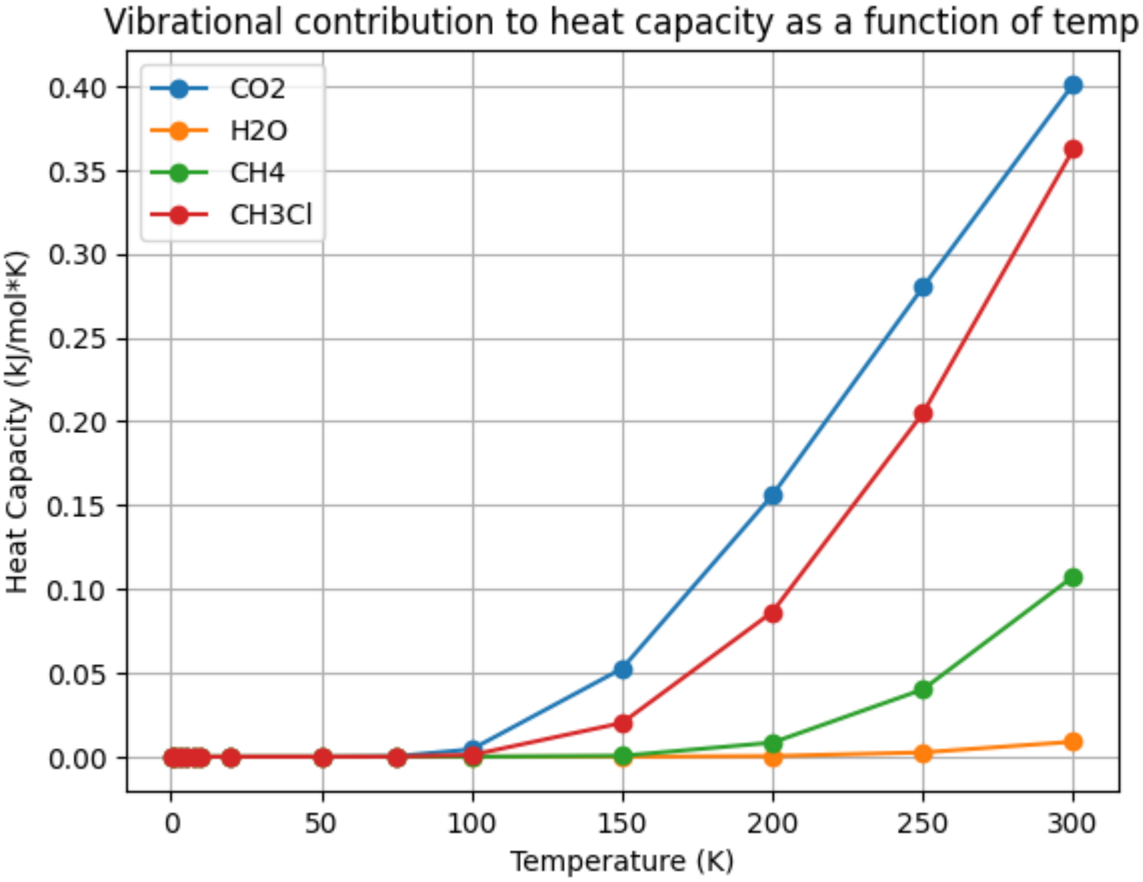

```
Exec. Time [s]:  0.4270014762878418
```