**Vibrational and Rotational Spectra of HCl-DCl Python**

# Import necessary modules  
**import** psi4  
**import** numpy **as** np  
  
# Set memory and output  
psi4.set\_memory('500 MB')  
psi4.core.set\_output\_file('vibration\_rotation\_spectrum\_output.dat', False)  
  
# Define the molecular geometries of HCl and DCl  
hcl\_geometry = """  
0 1  
H 0.000000 0.000000 0.000000  
Cl 0.000000 0.000000 1.274000  
"""  
  
dcl\_geometry = """  
0 1  
D 0.000000 0.000000 0.000000  
Cl 0.000000 0.000000 1.274000  
"""  
  
# Set computational options  
psi4.set\_options({  
 'basis': 'cc-pvdz',  
 'scf\_type': 'df', # Use density fitting for efficiency  
 'reference': 'rhf', # Restricted Hartree-Fock  
 'freeze\_core': True # Freeze core electrons in post-HF calculations  
})  
  
# Function to calculate vibrational frequencies and rotational constants  
**def** **calculate\_spectrum**(geometry, molecule\_name):  
 # Create the molecule  
 mol = psi4.geometry(geometry)  
   
 # Optimize the geometry  
 psi4.optimize('scf/cc-pvdz', molecule=mol)  
  
 # Calculate harmonic vibrational frequencies  
 frequencies, wfn = psi4.frequency('scf/cc-pvdz', molecule=mol, return\_wfn=True)  
   
 # Extract rotational constant (Be) in cm^-1  
 rotational\_constants = wfn.molecule().rotational\_constants()  
 B\_e = rotational\_constants['B'] # cm^-1  
  
 # Extract vibrational frequencies in cm^-1  
 vibrational\_frequencies = wfn.frequency\_analysis['omega'][2] # Harmonic frequencies  
   
 print(f"Results for {molecule\_name}:")  
 print(f"Rotational Constant (B\_e): {B\_e} cm^-1")  
 print(f"Vibrational Frequencies (cm^-1): {vibrational\_frequencies}")  
   
 **return** B\_e, vibrational\_frequencies  
  
# Perform the calculations for HCl and DCl  
B\_e\_hcl, vib\_freqs\_hcl = calculate\_spectrum(hcl\_geometry, "HCl")  
B\_e\_dcl, vib\_freqs\_dcl = calculate\_spectrum(dcl\_geometry, "DCl")  
  
# Anharmonic correction: Calculate vibrational-rotational coupling constant alpha\_e  
# Assuming a harmonic approximation for the coupling  
**def** **calculate\_alpha\_e**(B\_e\_hcl, B\_e\_dcl):  
 alpha\_e = B\_e\_hcl - B\_e\_dcl # Approximation based on isotopic substitution  
 **return** alpha\_e  
  
alpha\_e = calculate\_alpha\_e(B\_e\_hcl, B\_e\_dcl)  
print(f"Vibrational-Rotational Coupling Constant (alpha\_e): {alpha\_e} cm^-1")  
  
# Plotting the P and R branch lines (optional, using matplotlib)  
**import** matplotlib.pyplot **as** plt  
  
**def** **plot\_spectrum**(vib\_freqs, molecule\_name):  
 plt.figure(figsize=(8,6))  
 plt.stem(vib\_freqs, use\_line\_collection=True)  
 plt.title(f'Vibration-Rotation Spectrum of {molecule\_name}')  
 plt.xlabel('Rotational Line (m)')  
 plt.ylabel('Wavenumber (cm^-1)')  
 plt.grid(True)  
 plt.show()  
  
# Plot the spectra for HCl and DCl  
plot\_spectrum(vib\_freqs\_hcl, "HCl")  
plot\_spectrum(vib\_freqs\_dcl, "DCl")

### Key Components of the Code:

1. **Geometry Definition**:  
   The geometries of HCl and DCl are defined in the hcl\_geometry and dcl\_geometry strings. This assumes the bond length between H/D and Cl is approximately 1.274 Å.
2. **Quantum Chemistry Setup**:  
   The script uses the **cc-pVDZ** basis set and Restricted Hartree-Fock (RHF) method. Geometry optimization and vibrational frequency calculations are performed.
3. **Rotational Constant**:  
   The rotational constants ​ are extracted from the optimized geometry and displayed in units of cm⁻¹.
4. **Vibrational Frequencies**:  
   The script computes harmonic vibrational frequencies for both HCl and DCl. These are printed as wavenumbers (cm⁻¹).
5. **Anharmonic Correction**:  
   A simple approximation for the vibrational-rotational coupling constant αe\alpha\_eαe​ is calculated as the difference between the rotational constants of HCl and DCl.
6. **Optional Plotting**:  
   Using matplotlib, the spectra of HCl and DCl can be plotted, highlighting the vibrational frequencies.

### How to Run the Code:

1. Install PSI4 on your machine from the official website ([PSI4 Installation Guide](http://www.psicode.org/)).
2. Install Python and the required libraries (numpy, matplotlib, and psi4).
3. Run the script in your Python environment, and it will output the rotational constants, vibrational frequencies, and αe\alpha\_eαe​ for both HCl and DCl.

**Questions**

1. What is the significance of the optimized geometry in the PSI4 calculation, and how does it compare to the bond lengths assumed in the experiment?
   * PSI4 optimizes the geometry of HCl and DCl. How do the calculated bond lengths compare to the experimental bond lengths assumed in the lab (1.274 Å)? How do bond lengths affect the rotational constants?
2. How do the rotational constants ​ calculated using PSI4 compare to the experimentally determined values?
   * Using the spectral data, you derived ​ experimentally. How do these values compare to the ones calculated from the PSI4 output? What might account for any differences between theory and experiment?
3. How accurate are the vibrational frequencies ​ calculated by PSI4 compared to those observed in the FTIR spectra?
   * PSI4 provides harmonic vibrational frequencies for both HCl and DCl. Compare these theoretical values to the experimental vibrational frequencies you obtained from the FTIR spectra. What are possible reasons for any discrepancies?
4. What is the role of anharmonicity in both the PSI4 and experimental results?
   * PSI4 calculates harmonic frequencies, but experimental frequencies are often slightly lower due to anharmonicity. How does the difference between these two highlight the role of anharmonic corrections in molecular spectra?
5. How does the calculated vibrational-rotational coupling constant ​ from PSI4 compare to the one derived experimentally?
   * In both the theoretical and experimental components, you can calculate as the difference between the rotational constants of HCl and DCl. How do these two results compare, and what factors could cause deviations?
6. Why is it important to compare theoretical rotational constants with experimental ones, and what does this tell you about the molecular structure of HCl and DCl?
   * What information can you derive about the molecular structure of HCl and DCl by comparing the theoretical and experimental values of ? How do these constants relate to bond lengths and molecular moments of inertia?
7. How does PSI4 handle the isotopic substitution (H → D) when calculating the spectra, and how does this affect the rotational and vibrational constants?
   * Compare how the isotopic substitution affects the theoretical values of and ​ in PSI4. How do these theoretical effects compare to your experimental findings?
8. What are the differences between the harmonic vibrational frequencies calculated by PSI4 and the experimentally observed anharmonic frequencies?
   * PSI4 calculates harmonic frequencies, but real molecules exhibit anharmonic behavior. How much do the experimental frequencies for HCl and DCl deviate from the harmonic frequencies, and why is it important to account for anharmonicity?
9. In what ways does the PSI4 theoretical model simplify the molecular system, and how do these simplifications compare to the real experimental conditions?
   * PSI4 uses an idealized model (harmonic oscillators, perfect vacuum, etc.). Compare these assumptions with the real experimental conditions. How do real-world factors (e.g., impurities, temperature fluctuations) affect the experimental results?
10. How do the P and R branch peaks observed in the FTIR spectra compare to the peaks predicted by the PSI4 calculations?
    * Plot the P and R branches from the experimental spectra and compare them to the predicted rotational energy levels from the PSI4 data. How well does the theoretical model predict the structure and spacing of the peaks in these branches?