Introduction to Computational Quantum Chemistry

Lesson 6: Frequency calculations and IR spectra

Frequency calculations

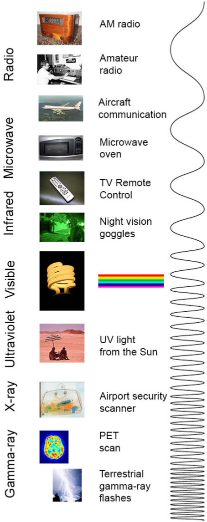
- Hessian matrix eigenvalues
- Second derivatives with respect to molecular geometry
- All positive values (curvature) - local minimum
- Imaginary (negative) values - “n^{th} order saddle point”

$$H(f) = \begin{bmatrix} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_1 \partial x_n} \\ \frac{\partial^2 f}{\partial x_1 \partial x_2} & \frac{\partial^2 f}{\partial x_2^2} & \cdots & \frac{\partial^2 f}{\partial x_2 \partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 f}{\partial x_n \partial x_1} & \frac{\partial^2 f}{\partial x_n \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_n^2} \end{bmatrix}$$

- If optimizer finds saddle point move atoms “in vibration’s direction”

IR spectroscopy

- Uses infrared electromagnetic radiation
- Excites vibrational states
- Molecular dipole must change during excitation
- Energy reported in cm^{-1} (wavenumbers)
- Typical range of experiment is 400-4000 cm^{-1}



Wavenumber

- Wavenuber states how many waves (amplitudes) of the radiation is in one centimeter
- Therefore higher wavenumber equals to higher energy radiation

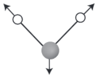
$$E = h\nu = \frac{hc}{\lambda} \tag{1}$$

$$\tilde{\nu} = \frac{1}{\lambda} \tag{2}$$

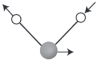
$$\tilde{\nu} = \frac{E}{hc} \tag{3}$$

Normal modes of vibrations

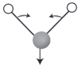
- Two types of molecular vibrations:
  - Stretching
  - Bending
- Molecule of N-atoms has
  - $3N - 6$ degrees of freedom (non-linear)
  - $3N - 5$ degrees of freedom (linear)
- Water:



symmetrical stretching

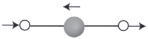


asymmetrical stretching

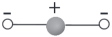


scissoring (bending)

- CO_2



asymmetrical stretching



scissoring (bending in and out of the plane of the paper)

symmetrical stretching

scissoring (bending in the plane of the paper)

Characteristic frequencies

- Bending is less demanding than stretching

Group	Type	Value	Intensity
-O-H (HB)	Stretch	3200-3600	Strong, broad
-O-H (Free)	Stretch	3500-3700	Strong, sharp
-C-H	Stretch	2850-3000	Strong
-C-H	Bend	1350-1480	Variable
=C-H	Stretch	3010-3100	Medium
=C-H	Bend	675-1000	Strong
C=O	Stretch	1670-1820	Strong
C=C (alkene)	Stretch	1620-1680	Variable
C=C (aromatic)	Stretch	1400-1600	Medium-Weak

Stretching vibrations

- Simplest approximation: Atoms connected with springs
- Hook's law: Frequency of vibration is given by mass and force constant

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{m}} \tag{4}$$

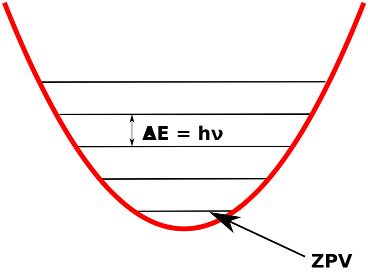
$$E = \frac{1}{2}kx^2 \tag{5}$$

- Energy is quantized

$$E = (n + 1/2)h\nu \tag{6}$$

Selection rules

- Photon has energy $h\nu$
- Transitions to next energy levels
- Overtones: Transitions to further levels (less intensive)
- Combination bands: 2 or more simultaneous excitations



Beyond harmonic oscilator

- Bonded atoms behave as anharmonic oscilators
- This causes the higher energy levels to be closer
- For diatomic oscilator:

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{f(m_1 + m_2)}{m_1 m_2}} \tag{7}$$

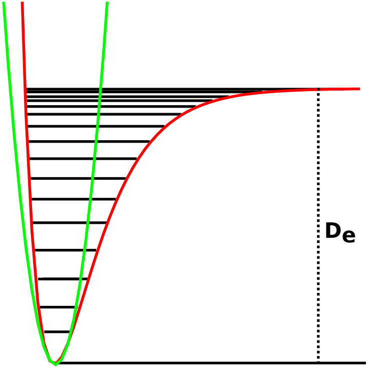
- where
    - *f* is the force constant of the bond

Task:

- Calculate the absorption energy (in wavenumbers) for following groups:
    - C-H, C=O and C≡N
- Use these force constants:
    - Single bond: $f = 5 \cdot 10^5 dyn \cdot cm^{-1}$
    - Double bond: $f = 10 \cdot 10^5 dyn \cdot cm^{-1}$
    - Triple bond: $f = 15 \cdot 10^5 dyn \cdot cm^{-1}$
    - $1dyn = 1g \cdot cm \cdot s^{-2}$
- Compare them to typical experimental values:
    - C-H: 2850-3000
    - C=O: 1670-1820
    - C≡N: 2000-2300

Harmonic vs. Anharmonic oscilator

- Harmonic: Quadratic potential:
  - $V(r) = k(r - r_0)^2$
- Anharmonic: Morse potential:
  - $V(r) = D_e(1 - e^{-a(r-r_0)})^2$
- Scaling factors for various levels of theory available in literature
- Merrick, J.P. et al. *J. Phys. Chem. A* **2007**, *111*, 11683.



Tasks:

- Perform following calculations:
  - Use Gaussian for optimization of CH_3F, $CH_3\ {}^{79}$Br and, $CH_3\ {}^{81}$Br
  - Harmonic and anharmonic frequency calculations
  - Use Def2-SVPD basis set
  - Run the calculations in serial
- Run everything in /scratch/username or using infinity

Custom basis sets

- Keyword *gen* instead of basis set specification
- EMSL Basis Set Exchange: `https://bse.pnl.gov/bse/portal`
- Select desired atoms and basis set
- Specify “Gaussian94” format
- Put the basis set after molecular specification
- BE AWARE
  - Missing atomic basis set → WARNING
  - Extra atomic basis set → ERROR

Serial Gaussian jobs

- Use this syntax:
  job1
  blank line
  - -link1- -
  job2
  blank line
- Logfiles are *appended* into 1 huge file
- Everything goes well:
  Normal termination of Gaussian 09 at Tue Jul 1 04:34:16 2014.

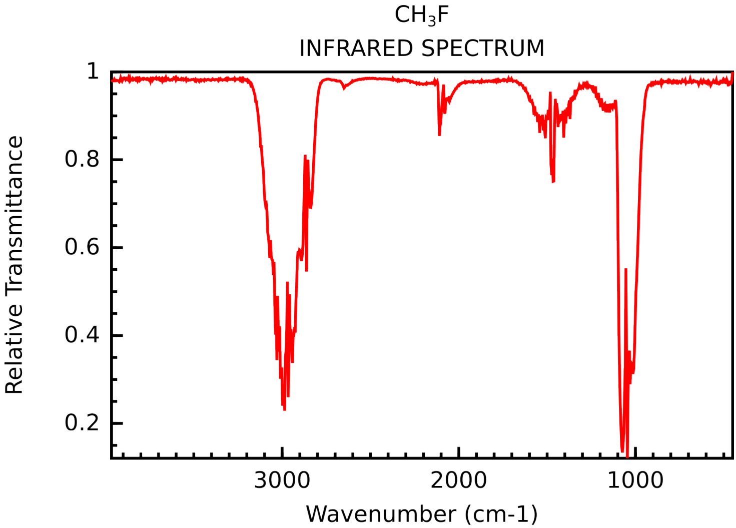
Gaussian resources

- %chk=checkpoint.chk
- %nprocshared=ncpu
- %mem=memory
- How to find out available resources:
  - System monitor
  - *cat* /proc/cpuinfo # Prints all available cores
  - *top* # Available memory

Evaluation of results

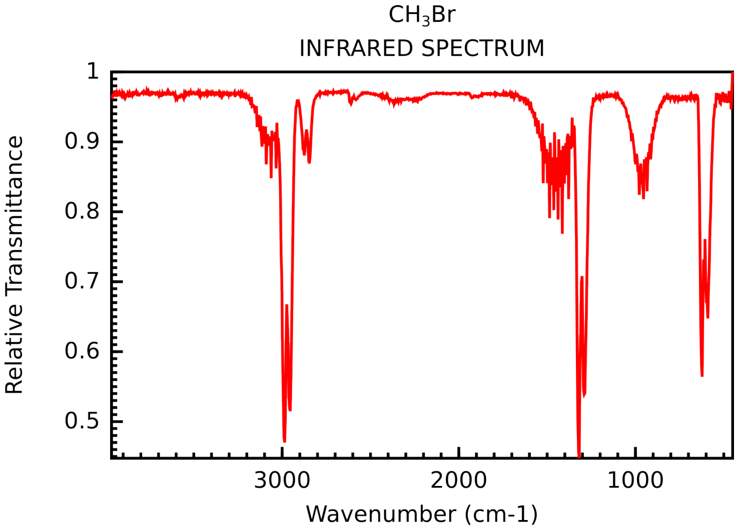
- Thermodynamic corrections to electronic energy
- Frequencies can be visualized from logfile in GaussView
- Anharmonic vibrations are generally closer to experiment but require much more resources
- Calculate the RMSD of vibrations using the prepared scripts
- Structure of result.dat:
  - Sort the frequencies from lowest to highest wavenumber
  - One number per line
  - Group the degenerate modes together (calculate average)
  - Average the $CH_3\ ^{79}Br$ and $CH_3\ ^{81}Br$ results
- *awk -f script.awk result.dat*

Experimental spectra of CH_3F



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Experimental spectra of CH_3Br



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Turbomole

- Developed at University of Karlsruhe and Forschungszentrum Karlsruhe GmbH
- More UNIX-like approach to solve problems:
  - Several independent modules
  - *x2t* and *t2x*
  - *define*
  - *dscf*
  - *jobex*
  - *aoforce*
- RI and MARIJ approximations of Coulombic terms in DFT → insanely fast code (not for hybrids)

Workflow

- Build a molecule and save it in xyz format
- *x2t* molecule.xyz > coord
- *define*
  - Interactive program
  - Prepares the *control* file containing all job specifications
  - Basis sets and initial guess
- *jobex*
  - Performs optimization of geometry
- *aoforce*
  - Runs frequency calculations
  - Cannot do anharmonic frequencies

define

- First two items can be skipped
- Molecular geometry:
  - a coord Reads in the geometry
  - ired Generates internal coordinates
  - * Proceed to next stage
- Basis set:
  - b all def2-SVP Assign this basis set to all atoms
  - * Proceed to next stage
- Method
  - eht Perform initial guess from Extended Hückel Theory
  - *Accept all defaults*

define - cont.

- Method
  - dft Enter the DFT submenu
    - on Use DFT
    - func b-lyp Select the functional
    - grid m5 Increase the gridsize to m5
    - * Exit the submenu
  - ri Enter the RI submenu
    - m Assign memory for RI
    - 2000 As much as possible
    - on Use RI
    - * Exit the submenu
  - dsp Use dispersion correction
    - on Use Grimme D3 correction
    - * Exit the submenu
  - marij Multipole-Accelerated RI-J
- * End the define session

Turbomole job

- For running TM in parallel mode use the parallel build
- *module add turbomole:6.05:x86_64:para*
- Infinity selects it by default if ncpu > 1

mnovak@wolf

```
#!/bin/bash
module add turbomole:6.05
jobex -ri -c 1024 > dft.out
aoforce > freq.out
```

Turbomole output

File	Contens
dft.out	Optimization procedure
energy	Energies of steps
gradient	Gradients of steps
mos	Molecular orbitals
freq.out	Output from aoforce program