

Lesson 6: Frequency calculations and IR spectra

Frequency calculations

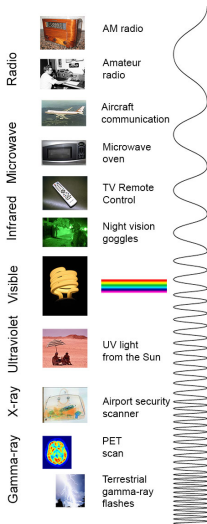
- Hessian matrix eigenvalues
- Second derivatives with respect to molecular geometry
- All positive values (curvature) - local minimum
- Imaginary (negative) values - “ n^{th} order saddle point”

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

- If optimizer finds saddle point instead of a minimum, 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

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

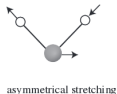
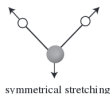
$$E = h\nu = \frac{hc}{\lambda} \quad (1)$$

$$\tilde{\nu} = \frac{1}{\lambda} \quad (2)$$

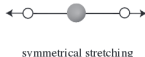
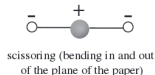
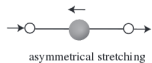
$$\tilde{\nu} = \frac{E}{hc} \quad (3)$$

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:



• CO₂



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

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

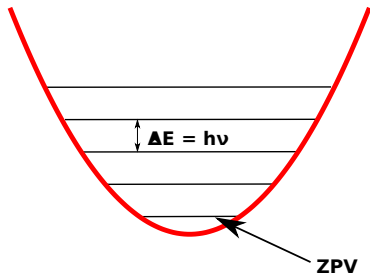
$$E = \frac{1}{2} kx^2 \quad (5)$$

- Energy is quantized

$$E = (n + 1/2)h\nu \quad (6)$$

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 oscillator

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

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

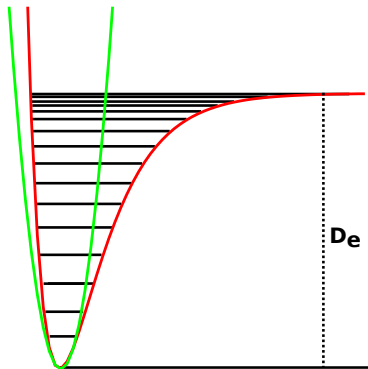
- where
 - f is the force constant of the bond

Task:

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

Harmonic vs. Anharmonic oscillator

- 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 , $\text{CH}_3^{79}\text{Br}$ and, $\text{CH}_3^{81}\text{Br}$
 - Harmonic and anharmonic frequency calculations
 - Use Def2-SVPD basis set
 - Run the calculations in serial
- Run everything using batch system

- 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

- 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.

- %chk=checkpoint.chk
- %nprocshared=ncpu
- %mem=memory
- How to find out available resources:
 - pnodes

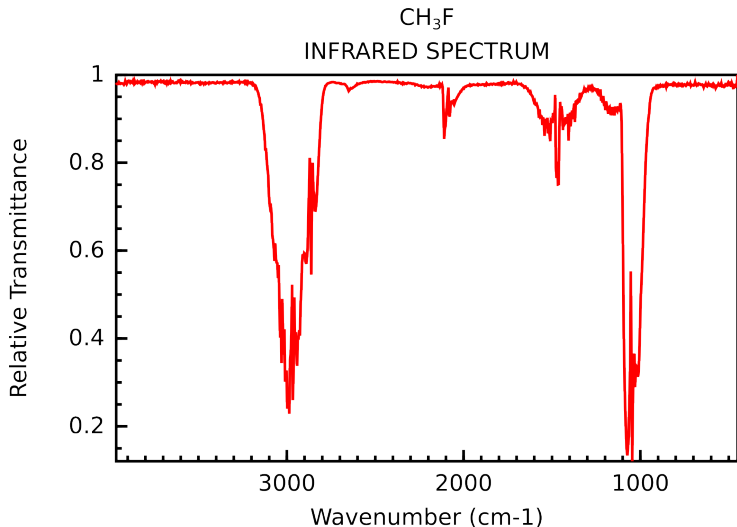
Gaussian resources

```
[mnovak@wolf ~]$ snodes
#
# Site name      : wolf
# Batch servers  : ...
# -> * w wolf.ncbr.muni.cz
#
# Node Group    : student
#
# Common properties: R18 cgroups gr_student
#
# Node name  S  CPUs  GPUs  Memory  Local Share  SSD  Extra properties
# ---
# wolf02    F  3/  3  0/  0   5G/   5G  805G  OK  OK
# wolf03    F  3/  3  0/  0   5G/   5G  805G  OK  OK
# wolf04    F  3/  3  1/  1   7G/   7G  371G  OK  OK
# wolf05    F  3/  3  1/  1   7G/   7G  370G  OK  OK
# wolf06    F  3/  3  1/  1   7G/   7G  371G  OK  OK
# wolf07    F  3/  3  1/  1   7G/   7G  371G  OK  OK
# wolf08    F  3/  3  1/  1   7G/   7G  371G  OK  OK
# wolf09    F  3/  3  1/  1   7G/   7G  371G  OK  OK
# wolf10    F  3/  3  1/  1   7G/   7G  371G  OK  OK
# wolf11    F  3/  3  1/  1   7G/   7G  371G  OK  OK
# wolf12    F  3/  3  1/  1   7G/   7G  371G  OK  OK
# wolf13    F  3/  3  0/  0  15G/  15G  806G  OK  OK
# wolf14    F  3/  3  0/  0   5G/   5G   1T  OK  OK
# wolf15    F  3/  3  1/  1  15G/  15G  806G  OK  OK
# wolf16    F  3/  3  1/  1  15G/  15G  806G  OK  OK
# wolf17    F  3/  3  1/  1  15G/  15G  806G  OK  OK
# wolf18    F  1/  1  1/  1   1G/   1G   5G  OK  OK
# wolf19    F  1/  1  1/  1   1G/   1G   4C  OK  OK
# wolf20    F  1/  1  1/  1   1G/   1G  110G  OK  OK
# wolf21    F  1/  1  1/  1   1G/   1G  371G  OK  OK
# wolf22    F  3/  3  1/  1   5G/   5G   5G  OK  OK
# wolf23    F  3/  3  0/  0   7G/   7G  792G  OK  OK
#
# Total number of nodes: 22
# Total number of CPUs : 58      Total number of GPUs : 17
# Free CPUs           : 58      Free GPUs           : 17
#
# Node Group    : compnode
#
# Common properties: R018 cgroups gr_compnode
#
# Node name  S  CPUs  GPUs  Memory  Local Share  SSD  Extra properties
# ---
# wolf30    O  1/  8  0/  0   16G/  23G  356G  OK  OK  hyperthreading
# wolf31    O  4/  8  0/  0   19G/  23G  350G  OK  OK  hyperthreading
# wolf32    E  0/  8  0/  0   15G/  23G  319G  OK  OK  hyperthreading
# wolf33    E  8/  8  0/  0   15G/  23G  350G  OK  OK  hyperthreading
# wolf34    F  8/  8  0/  0   23G/  23G  352G  OK  OK  hyperthreading
# wolf35    F  8/  8  0/  0   23G/  23G  370G  OK  OK  hyperthreading
# wolf36    F  8/  8  0/  0   23G/  23G  369G  OK  OK  hyperthreading
# wolf37    F  8/  8  0/  0   23G/  23G  354G  OK  OK  hyperthreading
# wolf38    F  8/  8  0/  0   23G/  23G  369G  OK  OK  hyperthreading
# wolf39    F  8/  8  0/  0   23G/  23G  346G  OK  OK  hyperthreading
# wolf40    F  8/  8  2/  2   15G/  15G  366G  OK  OK
#
# Total number of nodes: 11
# Total number of CPUs : 88      Total number of GPUs : 2
```


Evaluation of results

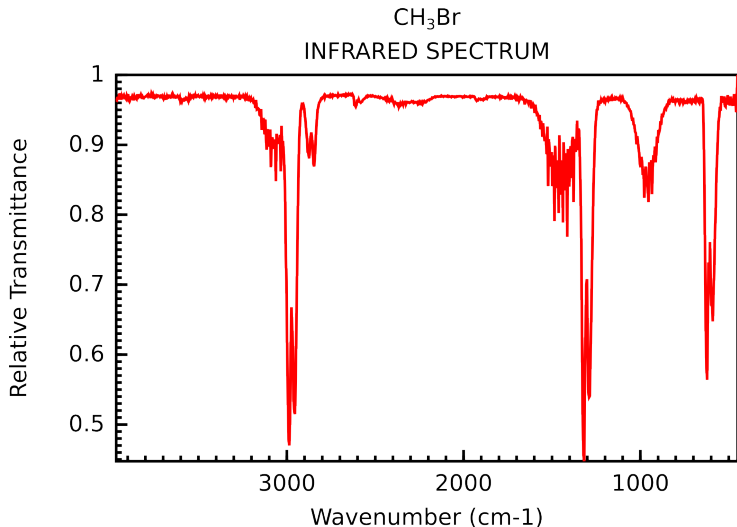
- Thermodynamic corrections to electronic energy
- Frequencies can be visualized from logfile in GaussView
- Anharmonic vibrations are generally closer to experiment but require much more resources
- Calculate the RMSD of vibrations using the prepared scripts
- Structure of result.dat:
 - Sort the frequencies from lowest to highest wavenumber
 - One number per line
 - Group the degenerate modes together (calculate average)
 - Average the CH₃ ⁷⁹Br and CH₃ ⁸¹Br results
- *awk -f script.awk result.dat*

Experimental spectra of CH₃F



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

Experimental spectra of CH₃Br



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

- 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)

- 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

- 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*

- 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:7.02:x86_64:para*
- Infinity selects it by default if `ncpu > 1`

`mnovak@wolf`

```
#!/usr/bin/env infinity-env  
module add turbomole:7.02  
jobex -ri -c 1024 > dft.out  
aoforce > freq.out
```


Turbomole output

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