Lab 5: NMR and IR spectra & vibrational analysis

A brief theoretical background[1]

Some of the available chemical quantum methods for calculating NMR chemical shifts are based on the Hartree-Fock self-consistent field (HF-SCF) approximation and, therefore, neglect electron correlation effects. The latter have been shown to be important for accurate theoretical determination of equilibrium geometries, vibrational frequencies, and electrical properties. While NMR shift calculations at the HF-SCF level are suitable for a wide range of chemical applications, there are cases where no satisfactory agreement between theory and experiment is obtained at this level of approximation and explicit consideration of electron correlation effects is required.

IR spectra

The harmonic vibrational frequencies of a molecule are calculated as follows:

- Solve the electronic Schrödinger equation:

$$\left(H_{el} + V_{NN}\right)\psi_{el} = U\psi_{el}$$

  where $\hat{H}_{el}$ is the one-electron Hamiltonian and V_{NN} is the operator of the potential energy between the nuclei of the molecular system, for several molecular geometries to find the equilibrium geometry of the molecule (geometry optimization).

- Calculate the set of second derivatives of the molecular energy *U* with respect to the 3*N* nuclear Cartesian coordinates of a coordinate system with origin at the center of mass, where these derivatives are evaluated at the equilibrium geometry.

$$\left(\frac{\partial^2 U}{\partial X_i \partial X_j}\right)_{eq} \qquad i, j = 1, 2, ..., 3N$$

[1] This theoretical background is based on the following references:

1. Gauss, J. (1993). Effects of Electron Correlation in the Calculation of Nuclear Magnetic Resonance Chemical Shifts. *Journal of Chemical Physics.* 99 (5), 3629-3643.
2. Levin, I. N. (2000). *Quantum Chemistry*, Fifth Edition. New Jersey: Prentice-Hall, Inc.

- From the *mass-weighted force constant matrix elements*, we get:

$$F_{ij} = \frac{1}{\left(m_i m_j\right)^{1/2}} \left(\frac{\partial^2 U}{\partial X_i \partial X_j} \right)_{eq}$$

where m_i is the mass of the nucleus corresponding to coordinate X_i.

- Solve the following set of 3*N* linear equations in 3*N* unknowns:

$$\sum_{j=1}^{3N} \left(F_{ij} - \delta_{ij} \lambda_k \right) l_{jk} = 0, \qquad i, j = 1, 2, ..., 3N$$

This set of homogenous equations has a nontrivial solution if the coefficient determinant vanishes:

$$\det\left(F_{ij} - \delta_{ij} \lambda_k \right) = 0$$

This determinant is of order 3*N* and when expanded gives a polynomial whose highest power of λ_k is λ_k^{3N}, so the determinantal (secular) equation will yield 3*N* roots (some of which may be the same) for λ_k. The molecular harmonic vibrational frequencies are then calculated from:

$$\nu_k = \lambda_k^{1/2} / 2\pi$$

Six of the λ_k values found by solving (5) will be zero, yielding six frequencies with value zero, corresponding to the three translational and three rotational degrees of freedom of the molecule. (In practice, because the equilibrium geometry is never found with infinite accuracy, one may find six vibrational frequencies with values close to zero). The remaining $3N-6$ vibrational frequencies are the molecular harmonic vibrational frequencies.

Note that a vibrational-frequency calculation must be preceded by a geometry optimization using the same method and basis set as used for the frequency calculation.

NMR spectra

To calculate NMR chemical shielding (screening) constants, the applied magnetic field $\vec{B}$ is treated as a perturbation, and one solves a set of equations called coupled perturbed equations. Just as the electric field is minus the gradient of the electric potential, the magnetic induction $\vec{B}$ is given by:

$$\vec{B} = \nabla \times \vec{A}$$

where $\vec{A}$ is the magnetic vector. Many different choices of $\vec{A}$ give the same $\vec{B}$. Several methods have been proposed to give calculated quantum-mechanical results that are independent of the choice of $\vec{A}$. The most widely used of these is the *gauge-including atomic orbital* (GIAO) method, in which each basis AO includes an exponential factor that contains $\vec{B}$. This method is the default while using the NMR option in the Gaussian input file. Chemical shifts are reported as parts per million (ppm) and are the difference between screening constants in the molecule and that in a reference molecule such as tetramethylsilane for proton and ^{13}C NMR spectra. To calculate chemical shifts theoretically, one calculates the shielding constants for the molecule of interest and the reference molecule and takes the differences.

The GIAO assumption for calculating NMR chemical shifts utilizes the following explicitly field-dependent basis functions:

$$\chi_\mu(\vec{\mathrm{B}}) = \exp\left[-\frac{i}{2c}(\vec{\mathrm{B}} \times \vec{\mathrm{R}}_\mu) \cdot \vec{r}\right] \chi_\mu(0)$$

where $\chi_\mu(0)$ denotes the usual field-independent atomic orbitals, $\vec{\mathrm{R}}_\mu$ their center and c is the speed of light. At the SCF level the expression for the chemical shielding tensor of the nucleus *N* is given as:

$$\sigma_{kl}^N = \left[\frac{d^2E}{d\mathrm{B}_k dm_{N_l}}\right]_{\mathrm{B}=0} \qquad k,l = x,y,z$$

with $\vec{\mathrm{B}}$ as the external magnetic field and m_N as the magnetic moment of the nucleus *N*. Equation (8) for the shielding tensor can be more explicitly written as:

$$\sigma_{kl}^N = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial B_k \partial m_{N_l}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_k} \frac{\partial h_{\mu\nu}}{\partial m_{N_l}} \qquad k,l = x,y,z$$

with $D_{\mu\nu}$ as the density matrix, $h_{\mu\nu}$ as the one-electron Hamiltonian in the atomic orbitals representation and $\mu,\nu,\cdots$ label atomic orbitals.

Exercises

Consult your lab-instructor regarding which of the following calculations should you perform:

Molecule	Method	Basis sets	NMR calc. (solvent)	IR calc.	SCF=Tight
cis-2-Butene	HF, B3LYP	6-31G(d), 6-311+G(2d, p)	√ (none)		√
trans-2-Butene	HF, B3LYP	6-31G(d), 6-311+G(2d, p)	√ (none)		√
CH_3CH_2Cl	HF, B3LYP	6-31G(d) 6-311+G(2d, p)	√ (CCl_4)		√
CH_3CH_2CN	HF, B3LYP	6-31G(d), 6-311+G(2d, p)	√ (chloroform)	√	√
H_2O	HF, B3LYP	6-31G(d)		√	√
NH_3 (pyramidal)	HF, B3LYP	6-31G(d), 6-31G(d, p), 6-311G(d, p)		√	√
$AlCl_3$	HF, B3LYP	6-31G(d)		√	√
O=C=C=C=O	HF, B3LYP	6-31G(d), 6-31G(d, p), 6-311G(d, p)		√	√

Very important note:

The job type Opt+Freq in GaussView stands for a geometry optimization calculation followed by a vibrational spectrum calculation (one step). However, in the case of an NMR spectrum calculation, you need to perform a geometry optimization calculation and then use the optimized structure to perform an NMR spectrum calculation of the same method and basis set (two steps).

Steps of IR spectrum calculation:

- Predict the number of vibrational modes of your assigned molecules, and the regions where their frequencies will be found.
  - Build the molecule in GaussView and press the 'Clean' button.
  - Press the Calculate button in the GaussView toolbar and select Gaussian.
  - In the Job Type dialog box, select Opt+Freq, optimize to a 'Minimum' Calculate Force Constants – 'Never', Compute Raman – 'Default', deselect any other option.
  - In the Method dialog box:
    Select ground state, (Hartree-Fock, Restricted or DFT Restricted and B3LYP according to your calculation), select a basis set, Charge – 0 and Spin – Singlet.
  - Insert a convenient title in the Title section.
  - Deselect any option in the General dialog box.
  - Insert SCF=Tight in the Additional Keywords section.
  - If your calculation is in vacuo, select 'None' in the Solvation dialog box.
  - Submit the calculation. If you encounter the GaussView message regarding improper angle, ignore it.
  - Open the output file of the optimized structure in GaussView, verify the structure (does it make sense?).
  - Open the output file as a text file by pressing the 'View File' button on the GaussView toolbar. Verify that the optimization calculation has converged by checking that the maximum force, RMS force, maximum displacement and RMS displacement parameters are all converged.
  - Press the 'Results' button and select the 'Vibrations' option.
  - View the IR spectrum by pressing the 'Spectrum' button (does the number of vibrational modes make sense?).

1. Visualize each vibrational mode by highlighting it in the 'Display Vibrations' table and pressing the 'Start' button (to stop the visualization press the 'Stop' button).

2. Tabulate the IR spectra of your assigned molecules, calculated using different methods and basis sets and the experimental results. Compare the obtained results with the experimental data.
    - Compare your predictions for the number of vibrational modes with the obtained results. Explain the criterion you used to decide what signals to consider as peaks and which others simply do not show up. Other spectroscopic methods may give signals where "regular" (Rayleigh) IR scattering does not. Why?
    - Discuss the effect of the size of the basis set and the method on the obtained results of each molecule. If different modes behave differently under change of calculation method or basis set, attribute each of these vibrations a symmetry group and discuss the relevance that this might have. For each calculation, compare the differences between each calculated frequency and the experimentally known one (use multiple-data series or 3-D bar graphs to visualize this). Which signals are most susceptible to a change in method or basis? Which method and basis give the best overall agreement with experiment?

Steps of NMR spectrum calculation:

- How many types of protons are there in your molecule, and which are they (via their program-assigned serial #)?
- How many NMR signals do you expect to see and in which regions?

Pay attention: In the case of an NMR spectrum calculation, you need to perform a geometry optimization calculation and then use the optimized structure to perform an NMR spectrum calculation of the same method and basis set.

- Build the molecule in GaussView and press the 'Clean' button.
- Press the Calculate button in the GaussView toolbar and select Gaussian.
- In the Job Type dialog box, select 'Optimization', optimize to a minimum' Calculate Force Constants – 'Never' and deselect any other option.
- In the Method dialog box:
  Select ground state, (Hartree-Fock, Restricted or DFT Restricted and B3LYP according to your desired calculation), select a basis set, Charge – 0 and Spin – Singlet.
- Insert a convenient title in the Title section.
- Deselect any option in the General dialog box.
- Insert SCF=Tight in the Additional Keywords section.
- In the Solvation dialog box select either 'None' or ‘Default’ and the proper solvent.
- Submit the calculation.
- Open the output file of the optimized structure in GaussView, verify the structure (does it make sense?).
- Open the output file as a text file by pressing the 'View File' button on the GaussView toolbar. Verify that the optimization calculation has converged by checking that the maximum force, RMS force, maximum displacement and RMS displacement parameters are all converged. (If not, perform another optimization calculation).

Use the following steps to perform an HNMR spectrum calculation of the optimized structure with the same method and basis set:

- Press the Calculate button in the GaussView toolbar and select Gaussian.
- In the Job Type dialog box, select 'NMR' and 'GIAO method'.
  In the Method dialog check that all parameters are the same as on geometry optimization.
- Insert a convenient title in the Title section.
- Deselect any option in the General dialog box.
- Check SCF=Tight in the Additional Keywords section.
- In the Solvation dialog box check that all parameters are the same as on geometry optimization.
- Submit the calculation.
- Open the output file in GaussView.
- Press the Results button and the select the NMR option.
- In the 'SCF GIAO magnetic shielding' dialog box select 'H' option in the Element drop down list, and in the Reference list select the calculation method you used. Why can't we always use one of the given reference values?
- How many peaks of magnetic shielding do you see? Explain the calculated spectrum and compare it with your expectations. Also, discuss the following questions:
  - What is the multiplicity of the peaks? Explain.
  - What is the temperature at which this NMR experiment is simulated? What is the width of the NMR peaks? Explain.
- Open the log file and search for or scroll to the line "SCF GIAO Magnetic Shielding tensor (ppm)". For simple NMR experiments, the signals are found at the chemical shifts which appear after the heading "isotropic". All other numbers relate to the directionality of the NMR signals.

3. The chemical shift is the difference between screening constants of the molecule and that of a reference molecule such as Tetramethylsilane. We will compare the calculated and experimental differences of chemical shifts.
    - Tabulate the differences between the chemical shifts of each group of hydrogen atoms of your assigned molecules as obtained using different methods and basis set and the experimental data[2].
    - Compare the results obtained using different methods and basis sets to the experimental differences in chemical shifts, what is relative error between calculated differences and the experimental differences? Is there a difference in agreement with the experimental data between higher and lower shift regions?
    - Discuss the effect of the size of the basis set and the method on the obtained results of each molecule.
    - Analyze the obtained H-NMR spectra (explain the number of peaks and their heights).

[2] Experimental values of IR spectra can be found at the http://webbook.nist.gov/chemistry/ website (enter the desired chemical formula and select the 'Vibrational & electronic energy levels' option). Experimental values of IR and NMR spectra can be found at the http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng website (enter the Compound Name/ Formula/ Molecular Weight and select 'HNMR' or 'IR' in the Spectrum dialog box).

4. What are the advantages and the disadvantages of the use of theoretical IR and NMR spectra in chemistry?