



Computational Chemistry Workshop

Example of an Experiment and Calculation
Synchronously Working Together
Calculation of NMR, UV and IR Spectra

Angelo R. Rossi
Department of Chemistry
The University of Connecticut
angelo.rossi@uconn.edu

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The Experiment

Mixing $\text{Ag}(\text{CN})_2$ and $\text{Ni}(\text{CO})_4$ in chloroform under a CO atmosphere, you isolate a solid precipitate that microanalysis and mass spectroscopy indicate to be $\text{NiC}_4\text{N}_2\text{O}_2$. A ^{13}C NMR spectrum of the precipitate in chloroform with $\text{Ni}(\text{CO})_4$ added as an internal standard shows a strong peak 6.6 ppm upfield from $\text{Ni}(\text{CO})_4$ and a much smaller peak 8.4 ppm upfield from $\text{Ni}(\text{CO})_4$. There is also a very strong peak 84 ppm upfield from $\text{Ni}(\text{CO})_4$.

An IR spectrum of the precipitate in a KBr pellet shows a strong absorption at 2154 cm^{-1} and very weak absorptions/shoulders at 2143, 2170, and 2188 cm^{-1} . After three recrystallizations from diisopropyl ether, your solid is composed of beautifully twinned light orange crystals. NMR and IR spectra of the recrystallized solid show only the strong peaks noted above, and none of the weak ones. An ultraviolet spectrum of the recrystallized solid in freon shows absorptions at 310 and 333 nm.

Explanation of the Experiment

After performing the calculations below on spectroscopic observables from the above experiment, discuss in a narrative fashion, and describe in some detail how you came to your conclusion.

- Use the results from the calculations to substantiate the experimental NMR, IR, and UV electronic absorption spectra of the molecules in this experiment with the species proposed to be present.
- What are the structures of the molecules in the recrystallized solid?

NMR Spectra

- Calculate the NMR spectra for all species proposed to be present.
- Compare the experimental ^{13}C isotropic NMR shieldings of all structures with the calculated results.
- Discuss the upfield shifts of all species present relative to $\text{Ni}(\text{CO})_4$, which is added as an internal standard.

Electronic Spectra

- Visualize the molecular orbitals for each species proposed to be present.
- Characterize the MOs by $\sigma, \sigma^*, \pi, \pi^*, n, d_{z^2}, d_{xy}, \dots$, bonding, antibonding, and non-bonding.
- Provide molecular orbital interaction diagrams for each species, showing MOs and energy levels along with the symmetry representations.
- Calculate the vertical excitation spectra for all species present, and provide a plot of the spectra for these species.
- Characterize the excitations for the first few excited states as MCT (metal charge transfer), MLCT (metal-ligand charge transfer), LMCT (ligand-metal charge transfer), or LLCT (ligand-ligand charge transfer).

What part of the electromagnetic spectrum do the transitions lie? Explain.

- Compare the spectrum of calculated excitation energies with the experimental spectrum.

Based on the calculated spectra, indicate which compound is orange and why?

What electronic transitions do the two peaks in the spectrum correspond? Are they the absorptions at 310 nm and 330 nm in freon? Explain.

- Based the nature of molecular orbitals involved in the electronic transitions, how might you expect the geometries of the first and second excited states to differ from the ground state?

Comment on UV Calculations

It is not always the case that TD-DFT calculations agree with experiment, and there is every reason to be critical about the calculational results. Very carefully compare the TD-DFT calculations with experiment. In many cases, artifacts will arise: charge transfer states tend to appear much too low in the spectrum; double excitations are entirely missing; neutral-to-ionic transitions are poorly predicted; and spin-flip transitions cannot be predicted.

The calculations requested here represent one of the cases where TD-DFT with normal GGA functionals like BP86 fails badly, and predict LMCT states where there should be d-d excitations (in the region below $\sim 15000 \text{ cm}^{-1}$). The calculation should, instead, be performed with a functional that includes more HF exchange. A functional is recommended which introduces some HF exchange. It may also be necessary to calculate more than the desired four ligand field states in order to capture the states of interest, since they may not come in order of increasing orbital energy difference. To be on the safe side, a calculation requesting more excited states should be performed

Infrared and Raman Spectra

- Optimize all structures that are proposed to be present, perform a vibrational analysis, and visualize the normal modes.
- Assign the character of each normal mode, e.g. stretching, in-plane bending, out-of-plane bending, and other deformation.
- Assign a symmetry representation for each calculated normal mode vibration, and indicate which is allowed or forbidden.

Also indicate whether it is infrared active, Raman active, or both active. For Raman transitions, indicate whether they are polarized or unpolarized.

- Compare the bands in the experimental IR/Raman spectra with the calculated spectra, by providing graphs and discussing similarities or differences.

Comment on IR Calculations

When vibrational frequencies are calculated by electronic structure theory, they can often be improved by scaling, and it is useful to have scale factors for doing this. Such scale factors depend on the level of electronic structure theory and the one-electron basis set, the combination of which we denote as an electronic model chemistry. Frequencies can be scaled using scale factors in [Database of Frequency Scale Factors](#) to improve agreement with experimental values (H). the observed vibrational fundamental frequencies (F), or the vibrational zero-point energy (ZPE).