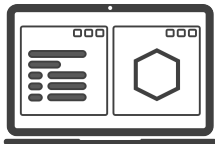


# Introduction to Computational Chemistry

## Part 6: Spectroscopy

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- Part 1: Takeoff
- Part 2: Reaction pathways from scratch
- Part 3: Preparing structures
- Part 4: Density Functional Theory
- Part 5: Organometallics
- **Part 6: Spectroscopy**
- Part 7: Chemical concepts

# What you should know from previous sessions



- Run simple DFT jobs with ORCA
  - Geometry optimization
  - Frequency analysis
- Visualize the results
- Read relevant data from the output



- Calculate and visualize spectra
  - IR
  - UV/Vis
  - NMR



From the foreword in the ORCA 2.9 manual (2012):

“However, with all developments in improved wavefunctions, speed *und* user friendliness, a major focus of the program will remain theoretical spectroscopy.”

Explosive development (also of non-spectroscopy methods) from there on.

| Year | Version | Pages (manual) |
|------|---------|----------------|
| 2012 | 2.9     | 534            |
| 2014 | 3.0.3   | 595            |
| 2017 | 4.0.1   | 827            |
| 2019 | 4.2.1   | 1048           |
| 2023 | 5.0.3   | 1329           |

# Energy scales in spectroscopy



|                 | γ-ray      | X-ray          | UV/Vis      | IR             | Microwave         | Radiowave         |
|-----------------|------------|----------------|-------------|----------------|-------------------|-------------------|
| Energy (eV)     | $>10^5$    | $10^5-10^2$    | $10^0$      | $10^0-10^{-3}$ | $10^{-3}-10^{-6}$ | $10^{-6}-10^{-9}$ |
| Wavelength (nm) | $<10^{-2}$ | $10^{-1}-10^1$ | $10^2$      | $10^2-10^6$    | $10^6-10^9$       | $10^9-10^{12}$    |
| Methods         | Mössbauer  | XAS            | Abs.,<br>CD | Abs.,<br>Raman | EPR               | NMR               |

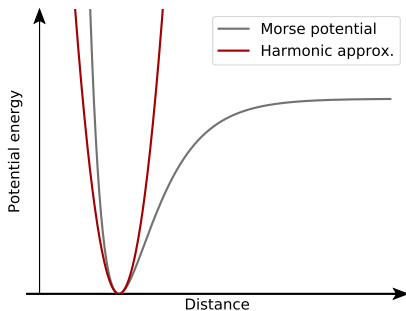
ORCA can be used to calculate all of these.

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ORCA can be used to calculate all of these.  
We will introduce three of them.



Common approximation: uncoupled harmonic oscillators (normal modes)

- No overtones, combination bands, or resonances
- Usually blue-shifted frequencies
  - Scaling factors are often used to “correct for anharmonicity”
  - BP86 often has good error cancellation

*J. Chem. Phys.* **2003**, *118*, 7215.





Invoked by the already familiar Freq (or NumFreq) keyword:

! Keywords Freq

- Should only be used on an optimized geometry
  - Use *exactly* the same method as was used for the optimization
  - Freq is more costly than Opt – consider splitting up the calculations
- !PrintThermoChem for isotope effects on the spectra
  - See Part 4 for details



Common approach: apply a time-dependent potential (an oscillating electric field)

Several options of different cost/accuracy:

- Time-dependent DFT (TD-DFT) – workhorse
- STEOM-DLPNO-CCSD – similar usage to TD-DFT, good accuracy
- (CASSCF/NEVPT2 – a whole different thing for special cases when you're desperate)



- Invoked by adding the respective module block to the input:

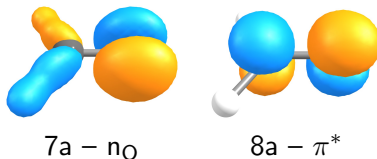
```
%tddft
```

```
nroots 5 # number of states
```

```
end
```

- The states “are made of” orbital excitations (printed in the output).  
For example, formaldehyde:

```
STATE 1: E= 0.149939 au      4.080 eV      32907.7 cm**-1  
7a -> 8a : 0.996757 (c= 0.99837704)
```



- Not all excitations have significant intensity (e.g.,  $n \rightarrow \pi^*$ )



- No vibronic structure
- Missing double excitations
- Missing spin-flip excitations
  - But there are ways (e.g., ORCA 5.0.3 manual Section 9.26.5)
- Gives vertical transitions
- Most transition energies are too high
- Charge-transfer excitation energies are too low (up to several eV)



Common approach: the magnetic field is incorporated into the basis functions (so-called GIAO or London orbitals).

You can calculate:

- Chemical shift tensors and absolute isotropic shieldings (default)
  - Need to correct the shifts with respect to a standard (see the Exercises)
- $J$ -coupling constants
- Hyperfine coupling
- Quadrupole coupling



Invoked by adding the keyword !NMR:

! Keywords NMR

- Sensitive to basis set:
  - Use at least def2-TZVP basis set
  - Special basis sets are available for higher accuracy (e.g., pcSseg)
- Extra options can be controlled via the module block:

```
%eprnmr
```

```
Extra options; see the Exercises
```

```
end
```

This block has to appear *after* the xyz coordinates.

See ORCA 5.0.3 manual Sections 8.9.7 and 9.42.3 for more info.



- The calculations give “stick”-spectra – peak positions and intensities.  
For broadened spectra:
  - External software: Chemcraft, Avogadro, ...
  - `orca_mapspc` tool
- Input coordinates:
  - IR/Raman – optimized with exactly the same method
  - Other spectroscopy – any structure is fine
- A non-exhaustive list of additional methods:

| Method             | Manual section    |
|--------------------|-------------------|
| Raman              | 8.9.3.3           |
| Fluorescence       | 8.9.2             |
| X-Ray spectroscopy | 9.29.2 / 9.36.2.8 |
| EPR                | 9.42.3            |
| Mössbauer          | 8.9.10            |





