

## Theoretical Molecular Spectroscopy on Carbon Monoxide

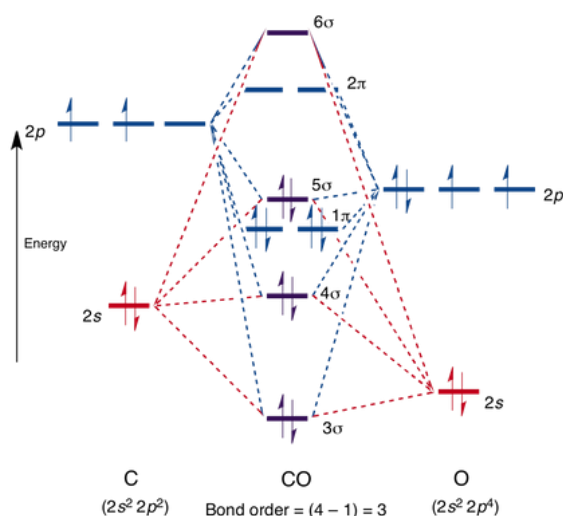


Figure 1: MO diagram of carbon monoxide

The aim of this exercise is to introduce students to the [MOLPRO](#) quantum chemistry package, which is a particularly useful tool for the calculation of electronically excited states of a molecule with multi-reference methods such as [CASSCF](#) or [MRCI](#). We focus on carbon monoxide or CO and investigate its vibronic (= vibrational and electronic) spectra in greater detail.

Carbon monoxide is an odorless, colorless and toxic gas consisting of a carbon and an oxygen atom, connected by two covalent bonds as well as one dative covalent bond. Its molecular

orbital diagram is given in Figure 1. Carbon monoxide is the second-most common molecule in the interstellar medium after molecular hydrogen, and the standard tracer for molecular gases in space.

### Preparative Tasks

- A. Optimize the geometry of CO in its electronic ground state with the aug-cc-pCVQZ basis set taken from the [EMSL basis set library](#) at the HF level of theory. Use Koopman's theorem to estimate the ionization energy of the molecule, and let MOLPRO calculate the [vibrational frequency](#) of CO in its electronic ground state.
- B. Repeat the optimization and the frequency calculation at the [CCSD\(T\)](#) level of theory. Use these results as a reference and compare them to the HF results above.
- C. With the same method (CCSD(T)), [scan](#) over the energy as a function of the C-O distance to obtain the potential energy surface (PES) for the molecule in its electronic ground state. Determine the dissociation energy for the CO molecule.
- D. Write a short script (Python, Matlab, Mathematica or C) which solves the Schrödinger equation for the nuclei in the given PES via e.g. a finite differences method. Compare the spacings between your eigenenergies to the frequency calculated in A and explain the deviations in particular for spacings between higher vibrational quantum numbers.
- E. Next, remove one electron from the system to obtain  $\text{CO}^+$ , and proceed as in steps B and C.
- F. Calculate the first 5 electronically excited states of  $\text{CO}^+$  via a combination of CASSCF and MRCI. As an active space, choose all MOs than can be built from atomic orbitals up to an angular momentum quantum number  $d$ , i.e.  $l=2$ . Scan over the PES as a function of the C-O distance.

## Final Tasks

In [UV photoelectron spectroscopy](#), we measure the kinetic energies of electrons emitted after photoexcitation to learn about the electronic structure of a system, i.e. its molecular orbital energies. For CO, we obtain the following spectrum:

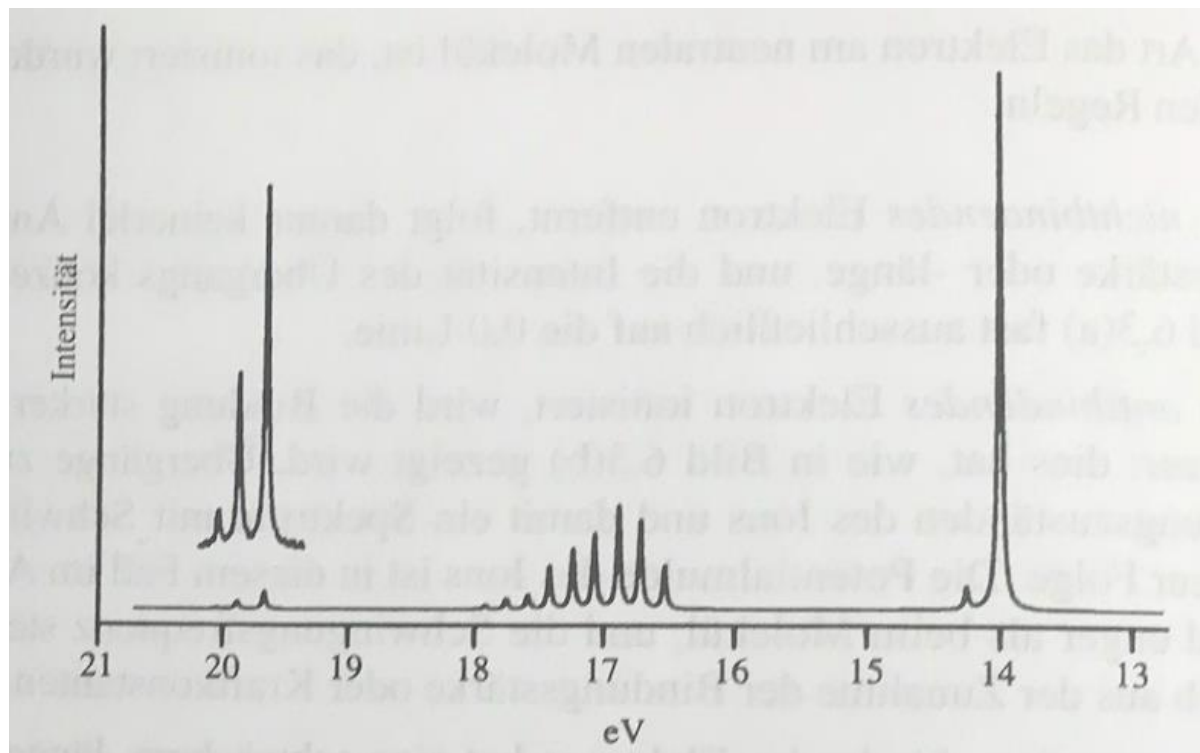


Figure 2: Photoelectron spectrum of carbon monoxide

Use the potential curves obtained in B, E and F to interpret the spectrum in the figure. How close are your excitation energies to the peak positions in the experiment? How good was Koopman's approach (task A) in comparison?

Finally, use the script you wrote for task D to reproduce the vibrational structure of the peak at 17 eV. Which PES is involved here?

BONUS: What has the "Franck-Condon-principle" to do with the distribution of intensities in this molecular "band" at 17 eV? How can you calculate the distribution of relative intensities within the band from your data?

## Literature

Banwell / McCash : *Molekülspektroskopie*. Oldenbourg, Wien 1999.

Haken / Wolf: *Molekülphysik und Quantenchemie*. Springer, Berlin 1992.

Hertel / Schulz: *Atome, Moleküle und optische Physik 2*, Springer, Berlin 2010.