**Lab4. Electronic excited states**

*Due: December 11*

In this lab you will learn to perform and analyze excited statecalculations in Q-Chem. The task is to compare excited states in three molecules of relevance to atmospheric photochemistry: isoprene nitrooxy enal (O=CH-C(CH3)=CH-CH2-O-NO2), methacrolein (MACR, O=CH-C(CH3)=CH2) and n-butyl nitrate (CH3-CH2-CH2-CH2-O-NO2). The lab is based on computational work conducted in paper Atmos. Chem. Phys., 16, 5595–5610, 201; doi:10.5194/acp-16-5595-2016

**Lab Procedure:**

Repeat the following procedure for each molecule:

1. Build molecule in IQmol. Minimize its energy with “Minimize Energy” option.
2. Perform geometry optimization of each molecule at the **wB97X-D/6-31+G\*** level of theory. wB97X-D is dispersion-corrected and long-range corrected density functional.
3. At the optimized geometry, perform excited state calculations for each molecule, using time-dependent DFT (TD-DFT), with the same functional and basis set, i.e., wB97X-D/6-31+G\*. You will need at least two excited states to be computed for each molecule. Setup of these calculations is as follows:

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BASIS = 6-31+G\*

CIS\_N\_ROOTS = 4 🡨 number of excited states to be computed

CIS\_TRIPLETS = 0 🡨 triplet states will not be computed

EXCHANGE = omegaB97X-D 🡨 functional

GUI = 2

JOB\_TYPE = SP

SCF\_CONVERGENCE = 8

$end

1. For analysis of excited states, you need to inspect the output file and look at molecular orbitals. In the output, find section called “TDDFT/TDA Excitation Energies”, e.g.:

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TDDFT/TDA Excitation Energies

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Excited state 1: excitation energy (eV) = 3.7639

Total energy for state 1: -549.924470931891

Multiplicity: Singlet

Trans. Mom.: -0.0000 X -0.0000 Y -0.0327 Z

Strength : 0.0001 🡨 oscillator strength

D( 38) --> V( 1) amplitude = 0.9429 🡨 leading amplitude

D( 38) --> V( 2) amplitude = 0.2352

In the example above, electronic excitation is dominated by transition of an electron from doubly-occupied orbital #38 to virtual orbital #1. Orbital numbers correspond to those in IQmol (virtual #1 is LUMO).

**Lab report:**

Nitrooxy enal has two photoactive functional groups, NO3 and C=O, while two other molecules have only one of each. Thus, it is possible to compare excited states of nitrooxy enal to excited states of MACR and butyl nitrate. In a broader context, it is often possible to guess presence of specific functional groups in a molecule based on their characteristic absorption/emission spectra.

* Analyze the lowest singlet excited state of MACR and butyl nitrate. Report excitation energy in eV and nm, oscillator strength, figures of leading molecular orbitals involved in electronic transition. Describe type/character of these orbitals (sigma, pi, lone-pair, their location on specific atoms, etc).
* In the same way analyze first two excited states of nitrooxy enal.
* Find similar electronic transitions between nitrooxy enal and MACR, and between nitrooxy enal and butyl nitrate. Make conclusions how similar/different they are in terms of excitation energies, oscillator strength, localization of involved orbitals.