

# Motivation: Complexes of electronically excited O<sub>2</sub> molecules and atmospherically relevant collision partners

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The goal of the visit is to theoretically study potential energy surfaces and dynamics of complexes of electronically excited  $^1\Sigma_g^+$  and  $^1\Delta_g$  O<sub>2</sub> molecules and atmospherically relevant collision partners, such as argon atoms and N<sub>2</sub> molecules. These studies are motivated by on-going experiments on N<sub>2</sub>-O<sub>2</sub>( $^1\Sigma_g^+$ ) complexes in the group of Roman Ciuryło, in Torun.

The theoretical treatment of such systems is complicated by non-adiabatic couplings between electronic states, such as the states correlating to the two degenerate components of the  $^1\Delta_g$  excited state of O<sub>2</sub>. Dynamical calculations for these coupled states require diabatic potential energy surfaces, rather than the adiabatic potentials which are calculated using standard electronic structure approaches. During this visit, we will work on this using two complementary approaches: The first approach will be to apply a diabatization algorithm developed in the Nijmegen theory group specifically for van der Waals molecules. The second approach is to generalize symmetry-adapted perturbation theory (SAPT), an expertise of the Torun theory group, to directly compute the diabatic potentials.

The Nijmegen group has recently developed a property-based diabatization algorithm which is generally applicable to open-shell van der Waals molecules.[J. Chem. Phys., **144**, 121101 (2016)] The first application has been to seven coupled low-lying triplet states of O<sub>2</sub>-O<sub>2</sub>. These states correlate to O<sub>2</sub> monomers in either the  $X\ ^3\Sigma_g^-$  electronic ground state, or the  $a\ ^1\Delta_g$  or  $b\ ^1\Sigma_g^+$  excited states. Currently diabatic potential energy surfaces for this system are employed in quantum dynamical studies of the collision-induced absorption spectra of the O<sub>2</sub>-O<sub>2</sub> system, which is relevant for atmospheric applications, such as the calibration of satellite instruments. Further on-going work employing the newly developed diabatization algorithm is directed at computing potentials for systems involving open-shell radicals, such as NO-H<sub>2</sub> and NO-O<sub>2</sub>.

The weak interactions in van der Waals molecules can conveniently be calculated using symmetry-adapted perturbation theory (SAPT). This approach has several advantages including accurate treatment of long-range interactions, clear physical interpretation of the different contributions, and SAPT enables computation of BSSE-free interaction energies (i.e., without basis-set superposition error). SAPT has frequently been applied to compute the interaction between closed-shell fragments. The Torun group has developed SAPT approaches also for interacting open-shell fragments in the spin-stretched state and, more recently, to obtain the splittings between different spin states. However, these methods have so far remained limited to a single state per symmetry, and are not yet applicable to the two coupled states of the O<sub>2</sub>( $^1\Delta_g$ )-N<sub>2</sub> system.