

Work plan: Complexes of electronically excited O₂ molecules and atmospherically relevant collision partners

Tijs Karman, Piotr S. Żuchowski, Roman Ciuryło, Ad van der Avoird

August 1, 2016

During this visit, we will theoretically study complexes of electronically excited $^1\Sigma_g^+$ and $^1\Delta_g$ O₂ molecules and atmospherically relevant collision partners, such as argon atoms and N₂ molecules. Such systems exhibit strong non-adiabatic couplings between nearly-degenerate electronic states, which we will treat using two complementary approaches: Computing adiabatic potential energy surfaces with traditional methods followed by a transformation to a diabatic representation, and directly computing diabatic potential energy surfaces using symmetry-adapted perturbation theory (SAPT).

The first part of the work plan is to set up electronic structure calculations for collision complexes of experimental interest. Most relevant is the N₂–O₂ system, with the oxygen molecule in an electronically excited state. If necessary, we will consider the simpler triatomic O₂–Ar system as a first step. We will initially focus on implementing property-based diabatization for these systems[J. Chem. Phys., **144**, 121101 (2016)], which can be done using fast low-level electronic structure calculations, in particular SCF or CASSCF. In the period directly after the STSM, such calculations can be repeated using more sophisticated but computer-intensive calculations, in particular coupled-cluster or configuration-interaction methods.

The second part of the plan for this STSM is to work on generalized multi-state symmetry-adapted perturbation theory (SAPT). The aim is to extend the applicability of SAPT, which is currently used for closed-shell systems and systems with spin degeneracies, to also treat systems with spatial degeneracies. This should allow to directly compute diagonal and off-diagonal diabatic potentials. The SAPT 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.