

# In memoriam Shi Shavitt: Application of MR-CI methods to describe the potential energy surfaces of O<sub>3</sub> and the dimer of O<sub>2</sub>

Péter G. Szalay<sup>1</sup>, Attila Tajti<sup>1</sup>, Vladimir G. Tyuterev<sup>2</sup>, Thomas Müller<sup>3</sup>

<sup>1</sup> Laboratory of Theoretical Chemistry, Institute of Chemistry, Eötvös Loránd University, Budapest, Hungary

<sup>2</sup> Groupe de Spectrométrie Moléculaire et Atmosphérique, Reims University, Reims Cedex 2, France

<sup>3</sup> Institute of Advanced Simulation, Jülich Supercomputer Centre, Research Centre Jülich, Jülich, Germany

szalay@chem.elte.hu

The contribution by Isaiah Shavitt to the development of MR-CI method is certainly dominating, as well represented by his early book [1]. For a recent review on MR-CI method see Ref. [2]. As a tribute to him, in this paper we will present some recent results obtained with MR-CISD method and its corrected versions on systems formed by oxygen atoms.

An accurate description of the complicated shape of the potential energy surface (PES) of ozone and the characterization of the highly excited vibration states is of crucial importance for dealing with various unsolved issues in its spectroscopy and dynamics. Well designed MR-CISD and MR-AQCC surfaces are presented which describe the important features of the surface, in particular for large variations of nuclear displacements along the minimum energy path (MEP). We discuss typical problems we face when performing MR-CI type calculations. The resulting new analytical representation of PES is the most accurate available today and allows accurate theoretical predictions for ozone vibrational band centres at the energy range near the dissociation threshold.

The other example deals with chemiluminescence of oxygen molecule: it is perhaps the most widely known of such processes, even used as demonstration experiment in high school. The currently accepted interpretation predicts the dimer of two singlet oxygen molecules to be responsible for the red light emission, however, no theoretical study could fully support this mechanism so far. In this study, the potential energy surfaces of the singlet oxygen dimer were investigated using the highest level MCSCF and multi-reference CI approaches, to locate excited state minima and structures corresponding to experimentally observed transition energies. However, no such minima could be found. Performing therefore collision simulations on these repulsive surfaces, it was indeed possible to reproduce the observed red emission.

[1] Shavitt, I, in *Methods of Electronic Structure Theory*, ed. Schaefer, H.F., pg. 189, Plenum Press, New York, 1977.

[2] Szalay, P. G., Mueller, T., Gidofalvi, G., Lischka, H., and Shepard, R., *Chemical Reviews*, 112:108–181, 2013.