

***Ab-Initio* Calculation of the Virial Coefficients of Water**

Giovanni Garberoglio^{C, S}

ECT, Fondazione Bruno Kessler, Trento, Italy*
garberoglio@ectstar.eu

Piotr Jankowski

Faculty of Chemistry, Nicolaus Copernicus University, Torun, Poland

Krzysztof Szalewicz

Department of Physics and Astronomy, University of Delaware, Newark, DE, U.S.A.

Allan Harvey

Applied Chemicals and Materials Division, NIST, Boulder, CO, U.S.A.

The availability of fast computers has enabled the calculation of pair and three-body intermolecular potentials with considerable accuracy, paving the way for a completely *ab-initio* calculation of the thermophysical properties of gases. In this talk, I will present recent results regarding the calculation of the second and third virial coefficients of water, which are the first two terms in a systematic expansion of the equation of state in powers of the density. For this molecule, quantum mechanical effects cannot be neglected, even under common operating conditions. The principal sources of uncertainty – rigid vs. flexible molecular models, accuracy of the intermolecular potentials, statistical uncertainty of the virial calculations – will be discussed and analyzed in detail. The results show that the second virial coefficient is in very good agreement with experimental data for light water (H₂O). This finding validates the accuracy of the state-of-the-art intermolecular potential – which includes flexibility effects –, and enables theoretical results to be used to extend the knowledge of second virial coefficient for other isotopologues, such as HDO and D₂O, at those temperatures where experimental data are lacking. In the case of the third virial coefficient, the existing rigid-molecule potentials provide a very good description, and the investigation of flexibility effects is the current frontier.