XIX SBQT
Simpósio Brasileiro de Química Teórica 2017
12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

Theoretical Study of the Xenon NMR Chemical Shift in Supercritical Condition: many-body, electron-correlation and relativistic effects

Evanildo G. Lacerda Jr. [a,b] , Stephan P. A. Sauer [a] ,

Kaline Coutinho [b] , Sylvio Canuto [b]

[a] *Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen , Denmark*
[b] *Instituto de Física da Universidade de São Paulo, CP 66318, 05314-970 São Paulo, SP, Brazil*

Abstract: Xenon in a supercritical condition is an important solvent to investigate various chemical systems. Xe is lipophilic and soluble in many substances. With its highly sensitive NMR chemical shift Xenon serves as a probe used to characterize solids, proteins and biomembranes, nanosystems, polymers, clathrates, mixtures, and even to detect radiations of interest in astrophysics [1]. Consequently, gaseous, liquid and supercritical Xe have been the subject of experimental investigation as well as theoretical calculations [2-4].

In this work we study how the NMR chemical shift of the ^{129}Xe in a supercritical condition depends on the solvation and on many-body and relativistic effects. Solvation effects are included using a sequential QM/MM methodology. Relativistic analysis is made using 4-component Hartree-Fock calculations (4c-HF) and electron correlation effects are considered using second order Møller-Plesset perturbation theory (MP2). To simplify the calculations of the relativistic and electron correlation effects we decompose the chemical shift in various contributions. Calculations are made at the non-relativistic Hartree-Fock (HF) level as an average over selected configurations generated by Monte Carlo simulation and then the contributions due to electron correlation and relativistic effects are added in a two-body approximation. Our results are in agreement with the experimental data and show that the chemical shifts for Xe are very well described at the HF level, with small contributions from relativistic and electron correlation effects.

Key-words: Supercritical condition, Xenon, QM/MM, NMR magnetic shielding.
Support: This work has been supported by the Science without Borders program and CAPES/Brazil.

References:

[1] Aprile, E. and Doke, T. “Liquid xenon detectors for particle physics and astrophysics”. Reviews of Modern Physics, vol. 82, pp. 2053, 2010.

[2] Fulton, L. “Fluid Structure in Supercritical Xenon by Nuclear Magnetic Resonance Spectroscopy and Small Angle X-ray Scattering”. Journal of Physical Chemistry, vol. 98, pp.11846, 1994.

[3] Yuan, H., Murad, S., Jameson, C.J. and Olson, J.D. “Molecular dynamics simulations of Xe chemical shifts and solubility in n-alkanes”. Journal of Physical Chemistry C , vol. 111, pp. 15771, 2007.