

This article was downloaded by:

On: 28 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Assignments of Hyperfine Splittings by DFT Methods of Radicals Containing ^{33}S ($I = 3/2$), ^{31}P ($I = 1/2$), and ^{29}Si ($I = 1/2$) Nuclei

L. Hermosilla^a; P. Calle^a; C. Sieiro^a

^a Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid, Spain

To cite this Article Hermosilla, L. , Calle, P. and Sieiro, C.(2005) 'Assignments of Hyperfine Splittings by DFT Methods of Radicals Containing ^{33}S ($I = 3/2$), ^{31}P ($I = 1/2$), and ^{29}Si ($I = 1/2$) Nuclei', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 180: 5, 1421 – 1422

To link to this Article: DOI: 10.1080/10426500590912808

URL: <http://dx.doi.org/10.1080/10426500590912808>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Assignments of Hyperfine Splittings by DFT Methods of Radicals Containing ^{33}S ($I = 3/2$), ^{31}P ($I = 1/2$), and ^{29}Si ($I = 1/2$) Nuclei

L. Hermosilla
P. Calle
C. Sieiro

Departamento de Química Física Aplicada, Facultad de Ciencias,
Universidad Autónoma de Madrid, Madrid, Spain

INTRODUCTION

The assignment of the hyperfine coupling constants (hfccs), obtained by analysis of EPR (electron paramagnetic resonance) spectra, is a basic task in this magnetic spectroscopy. Density functional theory (DFT) methodology gives accurate values of spin densities, leading to good assignments of experimental hfccs.¹ DFT methods allow us to carry out calculations with lower CPU time cost using the same basis with respect to other post-HF methods. The basic aim of the present work is to perform an analysis of the power of the combination B3LYP/TZVP/B3LYP/6-31G* in predicting the isotropic hyperfine coupling constants of radicals containing ^{29}Si , ^{31}P , and ^{33}S nuclei. Neutral, anions, and cations radicals are analyzed, ranging from small triatomic molecules to medium- and large-size systems.

RESULTS

155 hfccs from 55 radicals containing ^{29}Si , ^{31}P , or ^{33}S nuclei have been analyzed. To compare the obtained theoretical values of hfccs with the available experimental data, a regression analysis has been employed. From this analysis we can conclude that DFT predictions of the hfccs of radicals containing the above nuclei are reliable for the B3LYP/TZVP/B3LYP/6-31G* combination. We obtain the same result if we consider all nuclei (^1H , ^{13}C , ^{14}N , ^{17}O , ^{29}Si , ^{31}P , and ^{33}S) or only ^{29}Si ,

Received July 9, 2004; accepted October 5, 2004.

This work has been supported by Grant BQU2002-00582 (DGICyT).

Address correspondence to C. Sieiro, Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain. E-mail: carlos.sieiro@uam.es

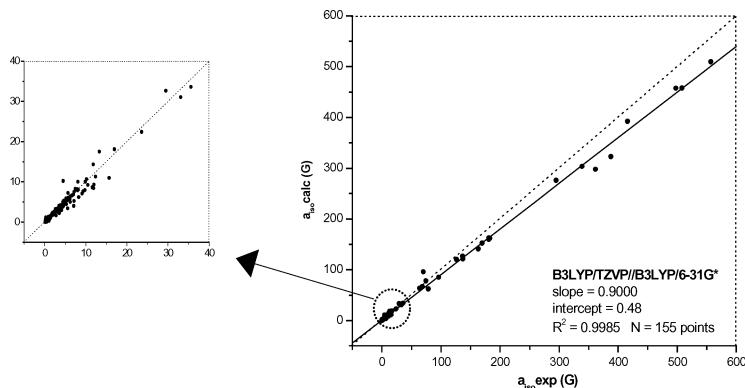


FIGURE 1 Regression analysis of the calculated and experimental hfccs of all nuclei.

^{31}P , and ^{33}S ones. Therefore, the above combination has good behavior in describing not only the first and second row but the third as well.

REFERENCE

- [1] R. Batra, B. Giese, M. Spichty, G. Gescheidt, and K. N. Houk, *J. Phys. Chem.*, **100**, 18371 (1996); M. T. Nguyen, S. Creve, L. A. Eriksson, and L. G. Vanquickenborne, *Mol. Phys.*, **91**, 537 (1997); R. Janoschek, *Pure Appl. Chem.*, **73**, 1521 (2001); L. Hermosilla, P. Calle, J. M. García de la Vega, and C. Sieiro, in press.