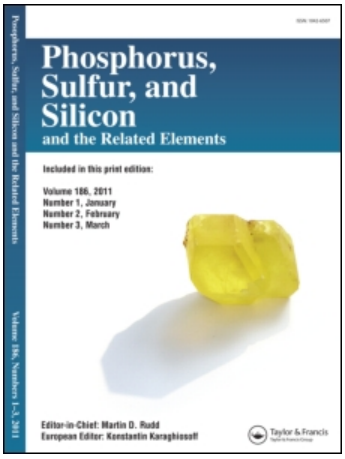

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Assignments of Hyperfine Splittings by DFT Methods of Radicals Containing ^{33}S (I = 3/2), ^{31}P(I = 1/2), and ^{29}Si (I = 1/2) Nuclei

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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 (^{1}H, ^{13}C, ^{14}N, ^{17}O, ^{29}Si, ^{31}P, and ^{33}S) or only ^{29}Si,

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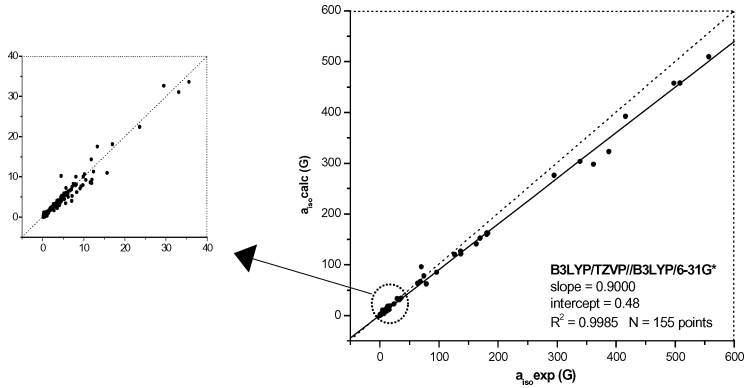

FIGURE 1 Regression analysis of the calculated and experimental hfccs of all nuclei.

^{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.

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