

Density functional theory and ab initio studies on hyperfine coupling constants of phosphinyl radicals.

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Streszczenie

The ^{31}P hyperfine coupling constants for various phosphinyl radicals were calculated using density functional theory (DFT) as well as the ab initio orbital-optimized spin-component-scaled MP2 (OO-SCS-MP2) and coupled cluster methods (with relaxed and unrelaxed density). However before that, electron correlation in phosphinyl radicals was investigated by means of the fractional occupation number weighted electron density (FOD). The isotropic hyperfine coupling constants for phosphinyl radicals posed a considerable challenge to DFT; among other issues, the well-known functional B3LYP substantially underperformed, but TPSS0 provided highly accurate results. Two tested double hybrid functionals, namely B2PLYP and mPW2PLYP, and OO-SCS-MP2 were found to be reasonably accurate. The unbalanced description of spin polarization in the valence region was identified as the root of the problems of DFT methods with correct prediction of the isotropic hyperfine coupling constants. In calculations at the coupled cluster level, relaxed and unrelaxed density matrices were tested and both were proved to provide highly satisfactory results for phosphinyl radicals. This was confirmed for a set of small paramagnetic species.

Słowa kluczowe

ab initio calculations, density functional calculations, EPR spectroscopy, hyperfine coupling constants, radicals

Adres publiczny

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