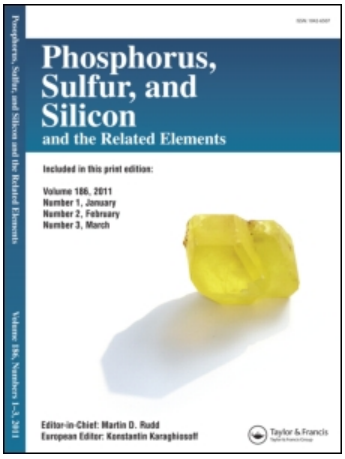

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Theory of ^{31}P Chemical Shifts

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Theory of ^{31}P Chemical Shifts

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The IGLO (individual gauge for localized orbitals) method[1], has been applied successfully to organic molecules.[2] The application to phosphorous compounds is more laborious, mainly since larger basis sets are required. By the IGLO method one obtains the chemical shielding as a sum of contributions of localized orbitals. For ^{31}P the dominant contributions come from the K-shell (well transferable), the L-shell (depending somewhat on the bonding situation), the bonds attached to P (large differences between single and multiple bonds), and the lone pair on P (large variations), the contributions of distant bonds and lone pairs being small, but often not negligible. We find good agreement with experiments for those molecules for which experimental data are available (e.g. PH_3, P_2H_4, P_4, CH_3PH_2, OPF_3) and we can make predictions for others (e.g. P_2, P_2H_2, HSiP). The interpretation of the variation of is more complicated than in the case of hydrocarbons, since bond contributions are usually not transferable between different molecules,and it is hard to justify an increment system. An interesting example is the dependence of the ^{31}P-shift in RC≡P on R.

The IGLO calculations furnish directly all tensor components of σ. So far we have more information on anisotropies from theory than from experiment.

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