^{19}F Spin-rotation Constants and Chemical Shifts of Unstable Molecules from their Microwave Spectra

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The inherently high resolution of the pulsed molecular beam-microwave Fourier transform (MWFT) technique allows spin-rotation coupling constants to be routinely determined from small hyperfine splittings in rotational transitions. The relationship between the spin-rotation coupling constants and the chemical shielding of a given nucleus has been well established[b]; these constants can be used to calculate the individual components of the chemical shielding tensor as well as the average chemical shift. Thus, shielding data for unstable and semi-stable molecules, which are relatively easily studied by MWFT, can be obtained.

Several ^{19}F containing species have been prepared using an electric discharge. Their microwave spectra have been measured in the 4-26 GHz frequency range and the determined diagonal components of the nuclear spin-rotation tensors have been used to calculate the chemical shielding tensors. One such molecule that is of particular interest is sulphur difluoride. Two of its spin-rotation coupling constants were found to be negative. Negative fluorine spin-rotation coupling constants are very unusual, and have been seen before only for the interhalogens[c] ClF, BrF, and IF. These findings are consistent with previous *ab initio* calculations[d] and an NMR experiment[e].

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