A general method for fully homodecoupled 1H-13C HSQC spectra

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Résumé

Pure shift experiments deliver homodecoupled 1H NMR spectra, boosting spectral resolution by an order of magnitude.[1] Several methods have been proposed (BASH/HOBS, Zangger-Sterk, BIRD, PSYCHE), each with specific advantages and restrictions in terms of sensitivity or broadband character. Pure shift methods are easily integrated in 2D correlation experiments. For 1H-13C HSQC experiments at natural isotope abundance, the combination with the BIRD (Bilinear Rotation Decoupling)[2] method is very attractive.[3] BIRD applies a 180◦ inversion to protons only when they are bound to a 13C nucleus, effectively decoupling them from all protons not attached to 13C. The sensitivity cost for BIRD thus comes from the 13C natural isotope abundance, paid by default in the HSQC experiment. Unfortunately, couplings between geminal protons are not removed, as such protons are by definition attached to the same 13C nucleus. This severely reduces the usefulness of BIRD pure shift HSQC experiments for compounds rich in methylene groups. Solutions based on constant-time or perfect echo pulse sequence elements have been proposed [4,5], but these require either prior knowledge and near-uniformity of the geminal couplings or cause a doubling of the natural line width, which are important shortcomings when working under molecular alignment conditions or with medium to large size molecules.
Here, we present CYBORG (CYcling through Bilinear rotation Operators to Regulate Geminal couplings), a generally applicable pure shift method compatible with 1H-13C HSQC experiments that circumvents all aforementioned shortcomings at a reasonable price in sensitivity relative to the parent HSQC experiment. The method, inspired by the concept of time-reversal,[6] allows maximum pure shift resolution for 1H-13C HSQC experiments, and holds promise for the study of larger compounds, such as peptides or protein side-chains.

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*Intervenant