The Off-Resonance ROESY Experiments

Description

In an anisotropic molecule, the NOESY or ROESY based distances calculated using the *Isolated Spin Pair Approximation* using a single distance (and therefore a single correlation time) as reference are not accurate as they depend on the angle between the interprotonic vector and the molecular axis, that governs the correlation time of the vector. As an alternative method it was proposed to use several reference distances selected to cover the range of possible orientations with respect to the rotation axis (de Paz et al., 2001O â?? jeda et al., 2002 â?? Lucas et al., 2003 â?? de Paz et al., 2005). Thus, ranges for all the unknown distances could be obtained (de Paz et al., 2001 â?? Ojeda et al., 2002 â?? Lucas et al., 2003 â?? de Paz et al., 2005). However, in the carbohydrate field the accuracy needed to distinguish some of the characteristic features is usually lost (e.g. with heparin oligosaccharides). A more precise method is the *off-resonance* ROESY approach (Desvaux et al., 1994 â?? Berthault et al., 1996). This allows to calculate distances from relaxation data out from the *Isolated Spin Pair Approximation* (ISPA) by obtaining simultaneously the correlation time and the distance for each pair of protons. This method relies on calculating several *off-resonance* ROESY values by varying the tilted angle of the effective ROESY spin-lock field to achieve enough amounts of independent data as to extract the correlation time for each vector and from this to calculate the interprotonic distances. This procedure allows to extract simultaneously cross relaxation rates $Ï?_{NOE}$ and $Ï?_{ROE}$ and effective correlation times $Ï?_c$ by measuring a linear combination of NOE and ROE effects controlled by the spin lock offset. In order to quantify the distances, arrays of several series of *off-resonance* ROESY experiments at several mixing times are recorded at different tilted angles (6, 10, 20 and 30 kHz), and all growth curves for each proton and each tilted angle are linearly fitted. Then, by calculating the growth rate of several series of *off-resonance* ROESY experiments corresponding to different spin lock offsets, the values of $Ï?_{NOE}$, $Ï?_{ROE}$and $Ï?_c$ can be independently obtained for each proton pair.

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