Notes on CSA Tensor Parameters

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Methods

Calculation of CSA

In studies on the structure of phage fd (Marvin et al., 2006), we used the program FX-PLOR (Wang & Stubbs, 1993) to refine models against the X-ray fibre diffraction data and stereochemical constraints, followed by the program CNS-SS02 (Bertram et al., 2000; 2003) to refine the X-ray model further against the solid-state NMR data of Zeri et al. (2003). Simultaneous refinement is clearly preferable to such sequential refinement, and since the refinement against fibre diffraction data and the refinement against solid-state NMR data are now both implemented in the program Xplor-NIH (Schwieters et al., 2003; 2006), we use Xplor-NIH for simultaneous refinement in our current studies.

A few considerations are important to ensure that the refinement against CSA data is the same for Xplor-NIH as for CNS-SS02. First, in CNS-SS02 the plane of the peptide is defined by the atoms N, C, CA. According to convention, the torsion angle ω about the C-N bond is defined in terms of CA-N-C-CA (IUPAC, 1970). To be consistent with the IUPAC definition of ω, one should use the C, N, CA atoms to define the x-y plane of the CSA molecular frame. This is important because the ω torsion angle is known to be not precisely 180.0°, although it is within a few degrees of 180°, as found by theoretical studies (Nambudripad et al., 1981), by analysis of experimental data (MacArthur & Thornton,1996), and by more recent studies by Priestle (2002) and Esposito et al. (2005) among others. Therefore the plane defined by atoms N, C, HN (as used by some authors and in earlier versions of Xplor-NIH) will not be identical to the plane defined by atoms N, C, CA. We edited csaPotTools.py in Xplor-NIH version 2.20 to a new file, csaPotToolsCA3.py, which includes a new name, NCA, mimicking N, but with atom names C, N, and CA, mimicking C, N, and HN. We used this to calculate CSA, with the bond order N, C, CA; the angle $\beta = 103.3°$ for non-glycine residues; and Da = 10.862. The scale factor Da can be calculated in Xplor-NIH with the python routine calcDaRh.

Further potential confusion arises from the existence of different notations for defining the chemical shift tensor. There are two main sets of notations for the principal components of the chemical shift tensors.

See, for instance, http://anorganik.uni-tuebingen.de/klaus/nmr/index.php?p=conventions/csa/csa

These notations are:

σ_{xx}, σ_{yy}, σ_{zz} : the Haeberlen convention (Haeberlen, 1976)

or σ_{11}, σ_{22}, σ_{33} : the IUPAC or "standard" convention (Mason, 1993)

The isotropic chemical shift, σ_{iso}, is

$$\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$$

The σ_{xx}, σ_{yy}, σ_{zz} notation is defined by:

$$| \sigma_{zz} - \sigma_{iso}| \geq | \sigma_{xx} - \sigma_{iso}| \geq |\sigma_{yy} - \sigma_{iso}|$$

The σ_{11}, σ_{22}, σ_{33} notation is defined for ^{15}N by:

$$\sigma_{11} < \sigma_{22} < \sigma_{33}$$

The relationship between the two notations is:

$$\sigma_{xx} = \sigma_{iso} - \sigma_{11}$$

$\sigma_{yy} = \sigma_{iso} - \sigma_{22}$
$\sigma_{zz} = \sigma_{iso} - \sigma_{33}$

and thus,
$\sigma_{xx} + \sigma_{yy} + \sigma_{zz} = 0$

Straus et al. (2003), Bertram et al. (2000; 2003) (in CNS-SS02), and the Opella group (Zeri et al., 2003; Thiriot et al., 2005) use the σ_{11}, σ_{22}, σ_{33} notation, with σ_{11} directed from N along the N-C bond, and θ measuring the angle from the NH bond to σ_{33}. The value of β corresponds to $120 - \theta$.

The values are (Straus et al., 2003):

For non-glycine residues:

σ_{11}=56.3 ppm, σ_{22}=79.0 ppm, σ_{33}=224.0 ppm, $\theta = 16.7^o$

$\sigma_{iso} = 119.77$

For glycine residues:

σ_{11}=45.6 ppm, σ_{22}=66.3 ppm, σ_{33}=211.6 ppm, $\theta = 21.6^o$

σ_{iso}=107.83

Cornilescu & Bax (2000) and Schwieters et al. (2006) (in Xplor-NIH) use the σ_{xx}, σ_{yy}, σ_{zz} notation, so for non-Gly

σ_{xx}= 63.5 σ_{yy}=40.8 σ_{zz}= -104.2, $\beta = 103.3^o$

and for Gly

σ_{xx}= 62.2 σ_{yy}=41.5 σ_{zz}= -103.8, $\beta = 98.4^o$

The latest version of Xplor-NIH uses the order

63.5, -104.2, 40.8, $\beta = 103.3^o$

for non-Gly, that is σ_{xx}, σ_{zz}, σ_{yy} , and the analogous order for Gly. This is due to the choice of bond order in csaPotToolsCA3.py.

Differences between CSA tensor values

It is found experimentally that the tensor values for Gly residues are significantly different from the values for other residues, as shown above.

Also, Thiriot et al. (2005) found that the experimentally measured values of σ_{33} for 6 residues in Pf1^L phage (namely residues 13, 18, 28, 32, 39, 42) are higher than the usual maximum σ_{33} = 224.0 ppm, although slightly high values have been found in some other systems (Hall & Fushman, 2006). This might be a function of the low temperature at which these values are measured (Cordier et al., 2002). Note that residue 28 of Pf1^L (Thiriot et al., 2005) is Gly, but since it has a high measured σ_{33} (234.0 ppm), we group it with the anomalous non-Gly residues in the CSA calculations. We use for these 6 anomalous residues

σ_{11}=56.3 ppm, σ_{22}=79.0 ppm, σ_{33}=234.0 ppm

σ_{iso}=123.1

so in Xplor-NIH we use

66.8, -110.9, 44.1, β = 103.3º

References

Bertram, R., Asbury, T., Fabiola, F., Quine, J. R., Cross, T. A. & Chapman, M. S. (2003). Atomic refinement with correlated solid-state NMR restraints. J. Magn. Reson. 163, 300-309.

Bertram, R., Quine, J. R., Chapman, M. S. & Cross, T. A. (2000). Atomic refinement using orientational restraints from solid-state NMR. J. Magn.Reson. 147, 9-16

Cordier et al. (2002) JMB, 715:739

Cornilescu & Bax (2000) JACS 122: 10143.

Esposito et al (2005). J. Mol. Biol. 347: 483

Haeberlen (1976) Advances in Magnetic Resonance, Suppl. 1, ed. J.S. Waugh

Hall & Fushman (2006) JACS 128: 7855

IUPAC (1970) J Biol Chem 245: 6489.

MacArthur & Thornton (1996). J. Mol. Biol. 264: 1180.

Marvin DA, Welsh LC, Symmons MF, Scott WRP, Straus SK (2006) Molecular structure of fd (f1, M13) filamentous bacteriophage refined with respect to X-ray fibre diffraction and solid-state NMR data supports specific models of phage assembly at the bacterial membrane. J Mol Biol 355:294–309

Mason (1993) Solid State NMR 2, 285.

Nambudripad et al (1981). Int. J. Peptide Protein Res. 18: 374.

Priestle (2003). J. Appl. Cryst. 36: 34.

Schwieters CD, Kuszewski JJ, Clore GM (2006) Using Xplor-NIH for NMR molecular structure determination. Prog NMR Spectrosc 48:47–62

Schwieters CD, Kuszewski JJ, Tjandra N, Clore GM (2003) The Xplor-NIH NMR molecular structure determination package. J Magn Reson 160:65–73

Straus, S. K., Scott, W. R. P. & Watts, A. (2003). Assessing the effects of time and spatial averaging in 15N chemical shift/15N-1H dipolar correlation solid state NMR experiments. J. Biomol. NMR, 26, 283–295.

Thiriot, D. S., Nevzorov, A. A. & Opella, S. J. (2005). Structural basis of the temperature transition of Pf1 bacteriophage. Protein Sci. 14, 1064-1070

Wang, H. & Stubbs, G. (1993). Molecular dynamics in refinement against fiber diffraction data. Acta Crystallog. sect. A, 49, 504-513.

Zeri, A. C., Mesleh, M. F., Nevzorov, A. A. & Opella, S. J. (2003). Structure of the coat protein in fd filamentous bacteriophage particles determined by solid-state NMR spectroscopy. Proc. Natl. Acad. Sci. USA, 100, 6458-6463.