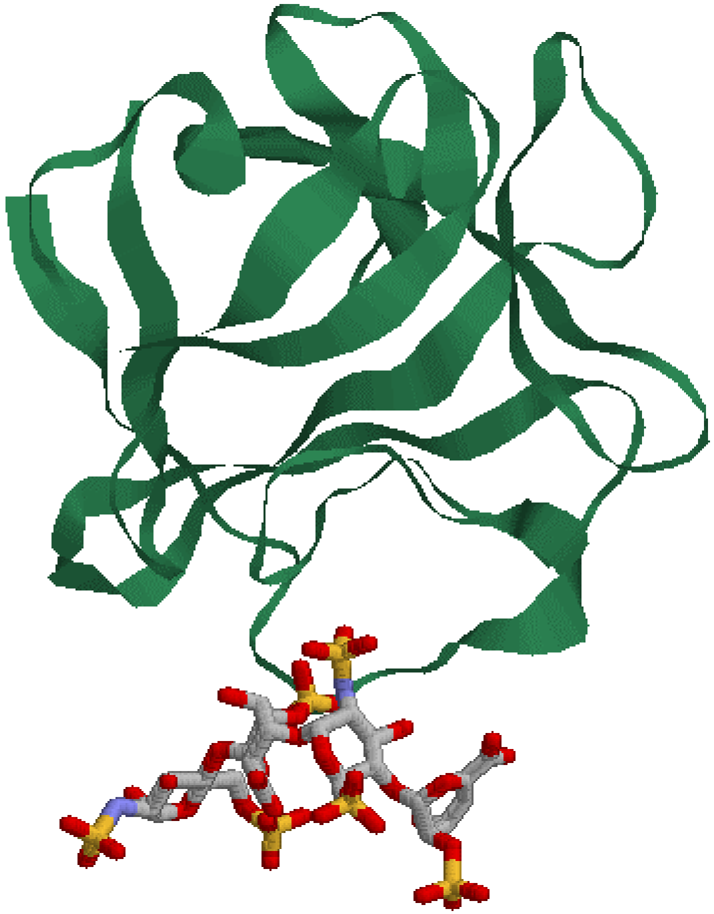
The conformation of carbohydrates

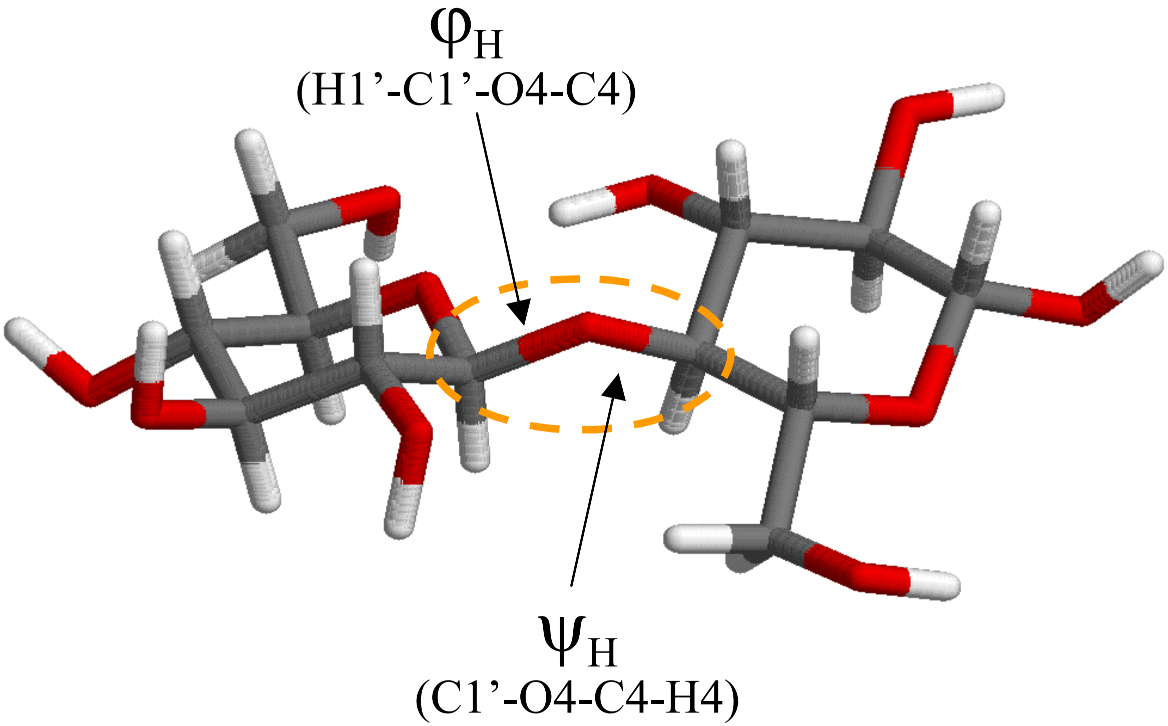
What can scalar coupling constants (^{n}J) tell us?

Tetrasaccharide + Protein

Heparin + Basic Fibroblast Growth Factor



Conformation of the glycosidic linkage



Properties of the glycosidic linkage

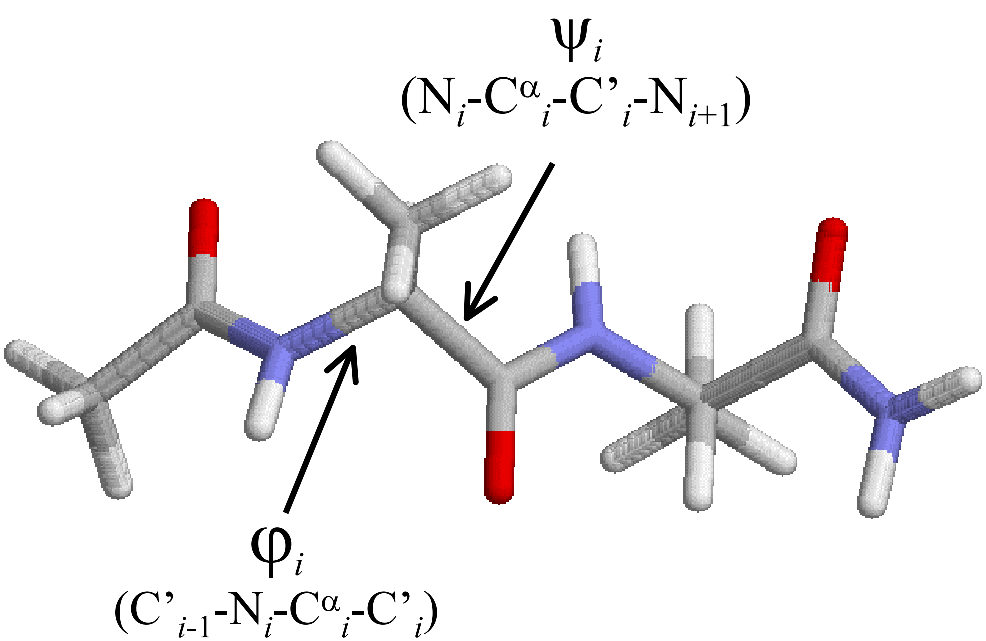
- Stereoelectronic (*exo*-anomeric-) effects influence the φ_H torsion
- The ψ_H torsion is determined by steric factors
- Both φ_H and ψ_H are known to prefer a single conformation with varying flexibility

Difficulties

- Two consecutive torsion angles are needed to define the conformation
- No $^3J_{HH}$ values related to the glycosidic torsion
- NOE distances depend on both torsion angles

Not a unique problem!

A similar situation exists in peptides



Solution: Heteronuclear *J*:s

φ_i

- $^3J_{C'i\text{-}1,H\alpha i}$
- $^3J_{C'i\text{-}1,C'i}$
- $^3J_{C'i\text{-}1,C\beta i}$
- $^3J_{HNi,H\alpha i}$
- $^3J_{HNi,C'i}$
- $^3J_{HNi,C\beta i}$

ψ_i

- $^3J_{H\alpha,Ni+1}$
- $^3J_{C\beta i,Ni+1}$

Couplings across glycosidic linkage

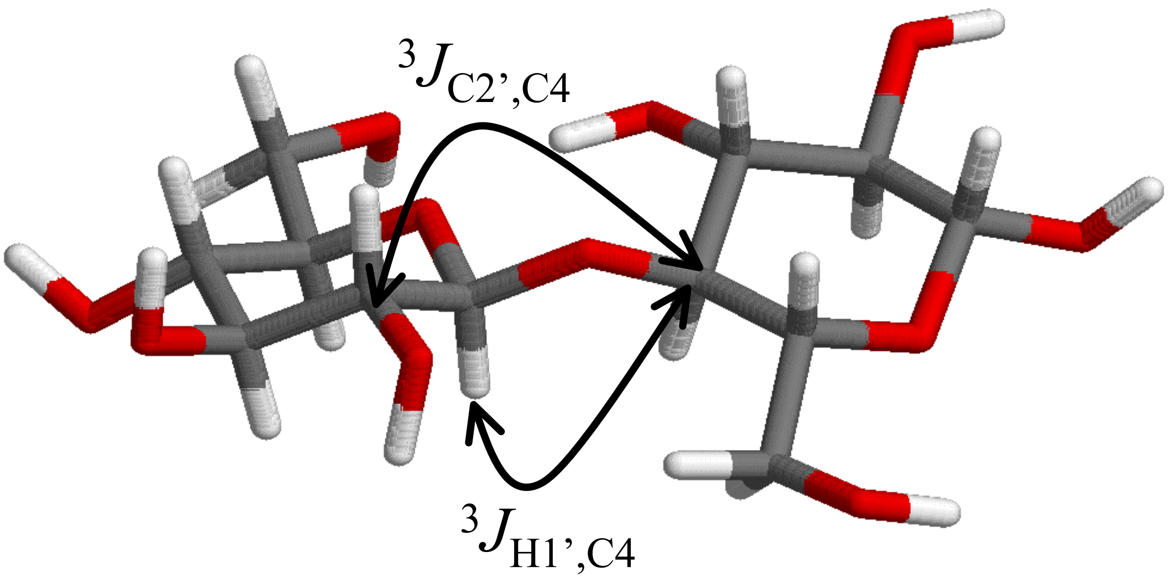
φ_H

- $^3J_{H1',Cn}$
- $^3J_{C2',Cn}$

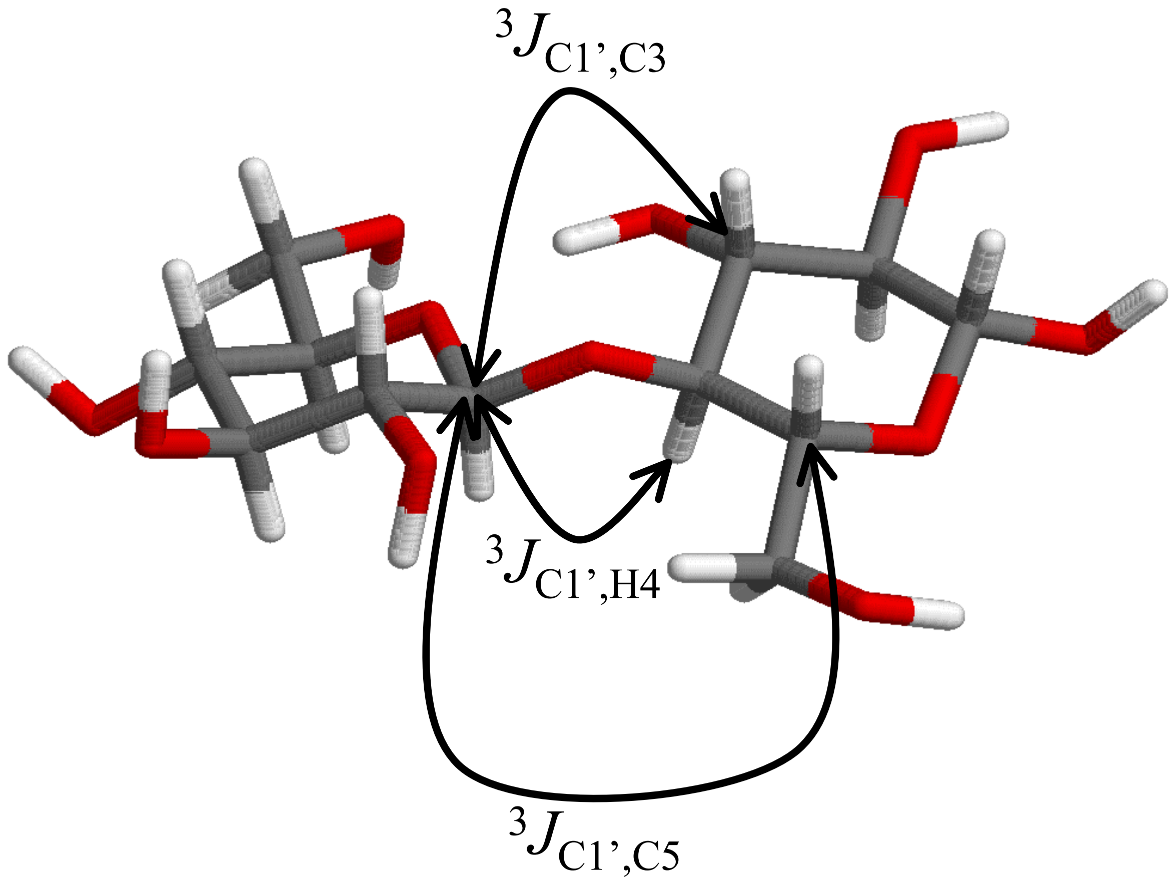
ψ_H

- $^3J_{C1',Hn}$
- $^3J_{C1',Cn-1}$
- $^3J_{C1',Cn+1}$

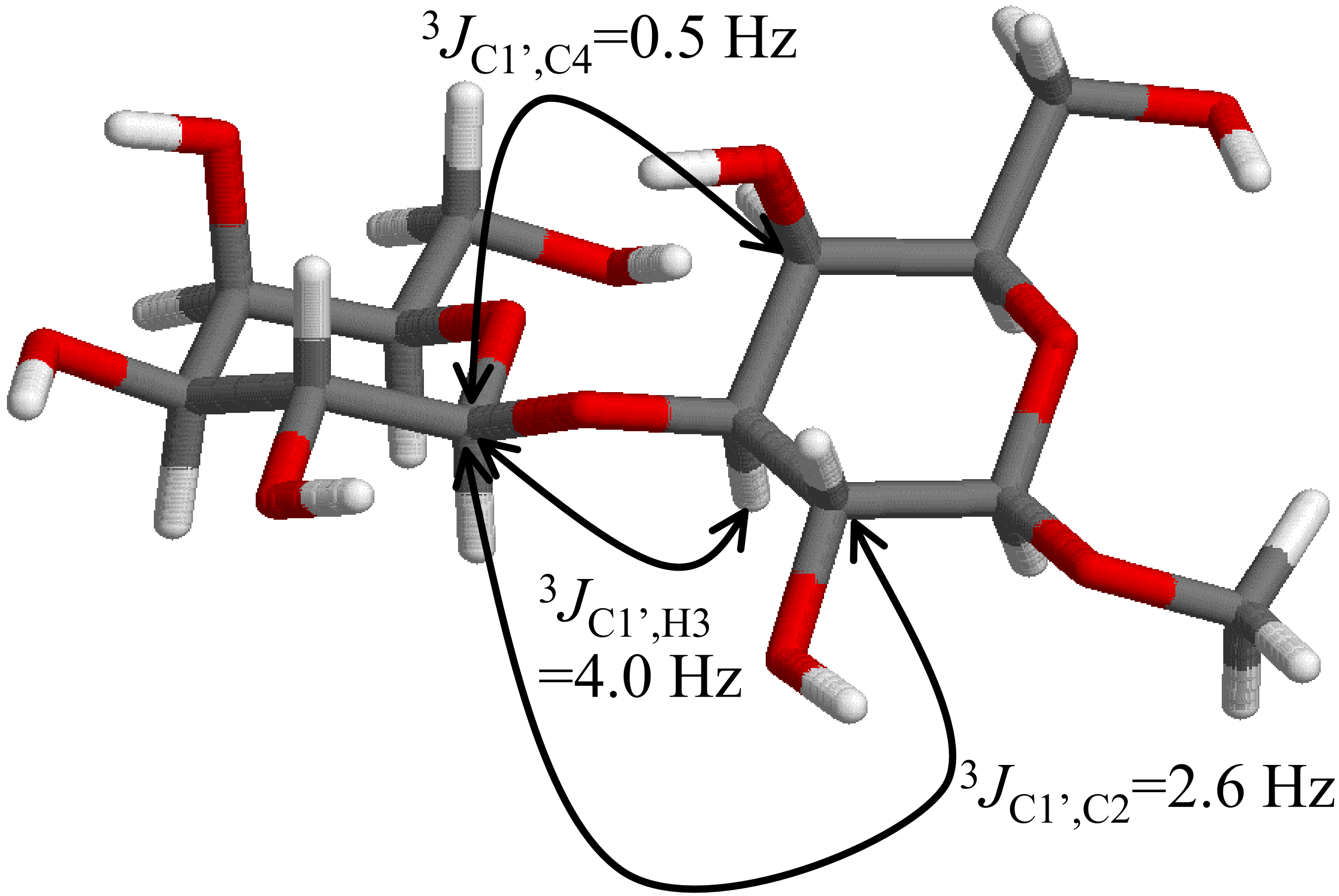
Couplings related to φ_H



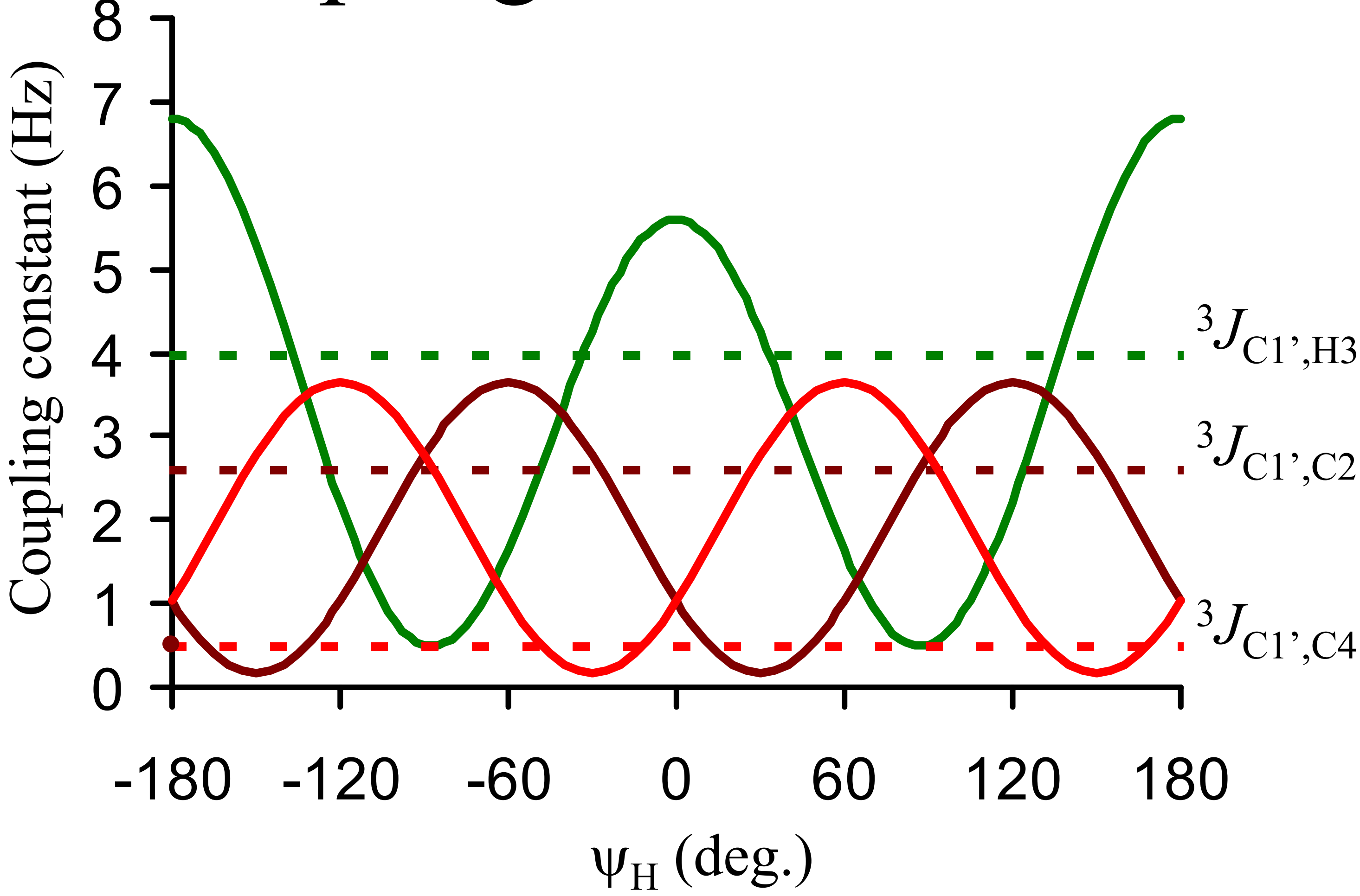
Couplings related to ψ_H



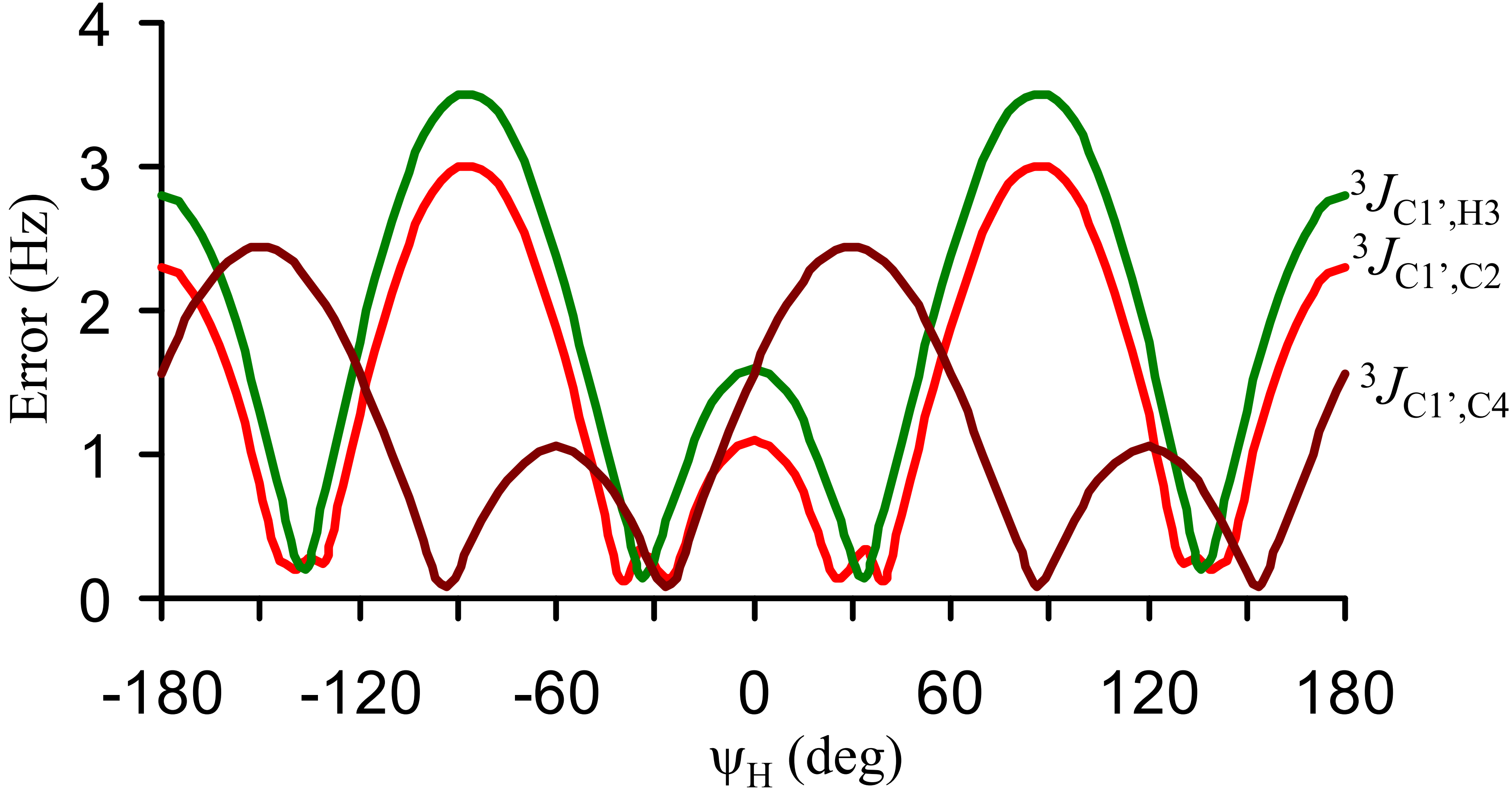
Example: βDGal(1→3)βDGalOMe



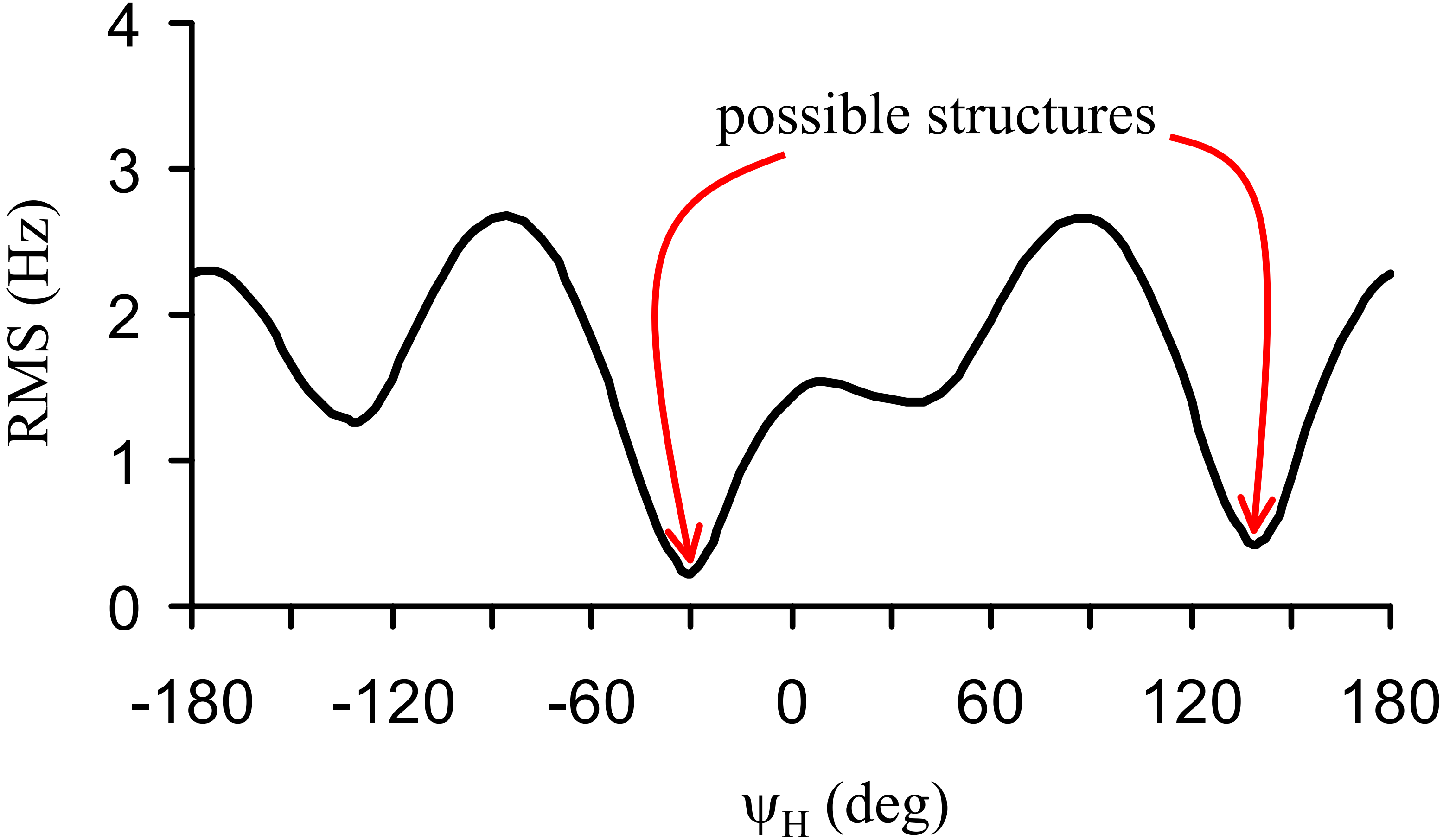
Torsion angle dependence of couplings across O3-C3



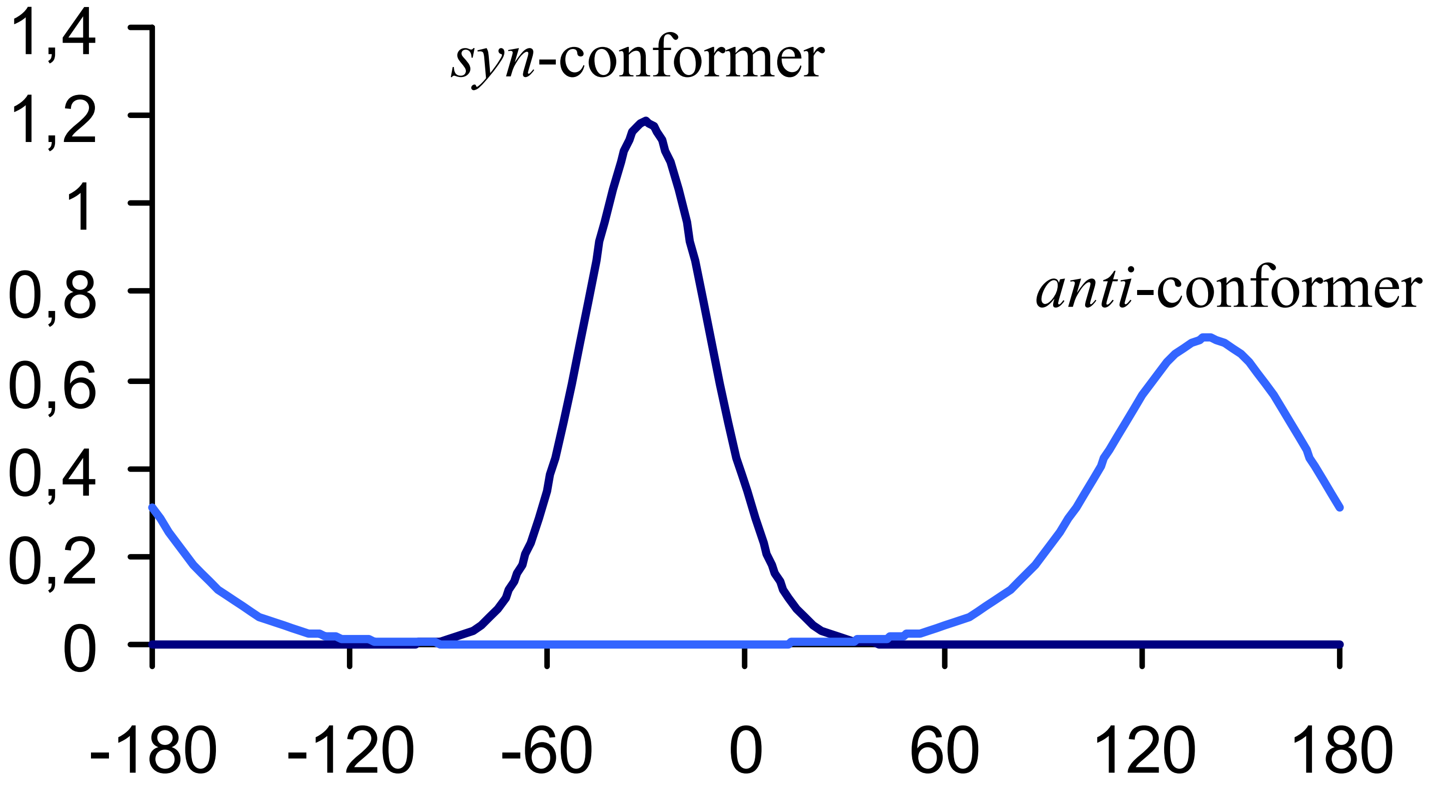
Deviation between calculated and experimental *vs* ψ_H



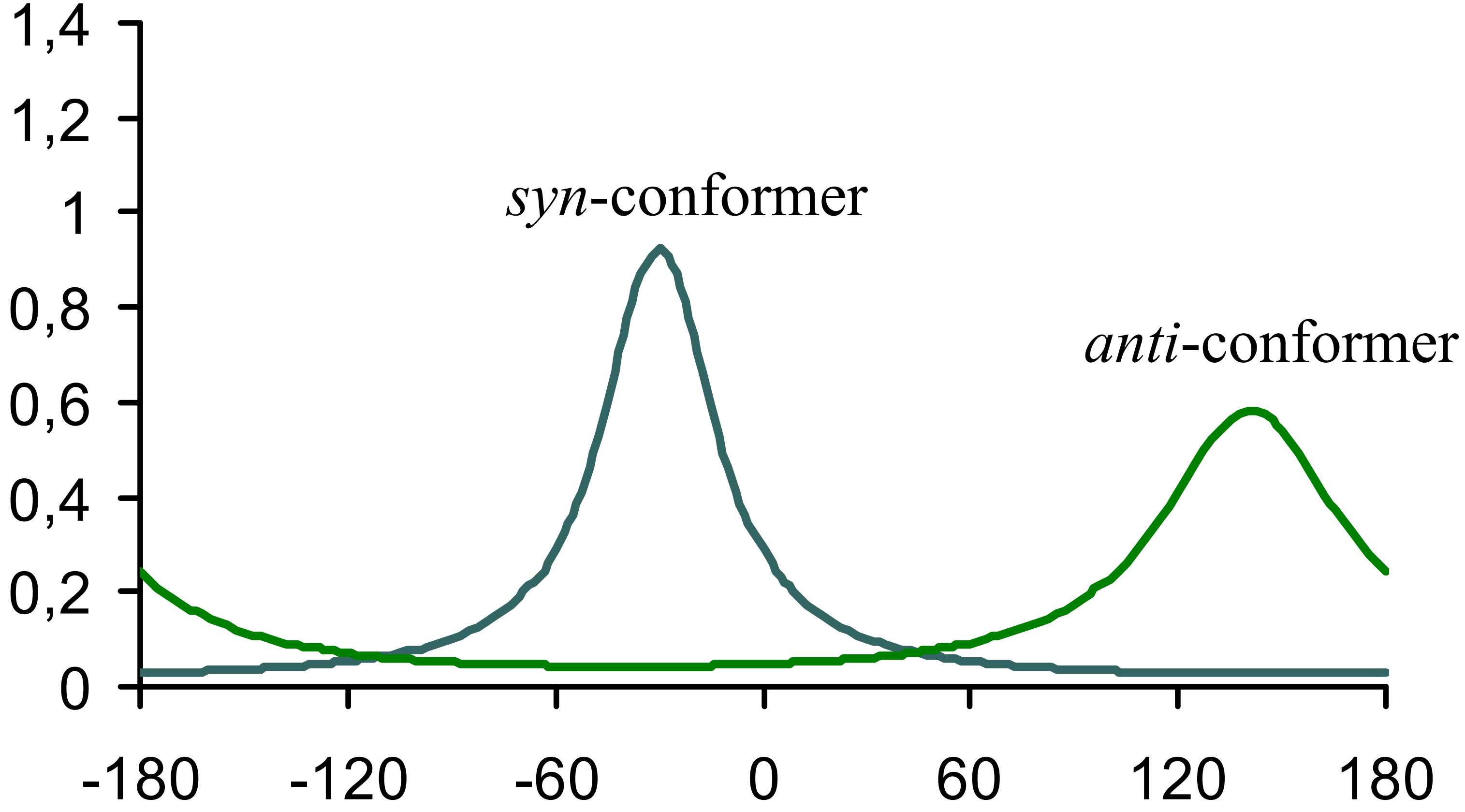
RMS deviation *vs* ψ_H



Gaussian distribution



Lorentzian distribution



Conclusion

- Using two or more ${}^{3}J$ values a much more detailed picture of the conformation of disaccharides emerges
- Some ambiguities (*e.g. syn*↔*anti*) can not be resolved by ${}^{3}J$ values alone

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