

Multi-dimensional spectroscopy



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Shakespeare - Hamlet - 1600



2D or not 2D???



Outline

*Why do multi-dimensional spectroscopy?
Examples from the real world.*

Phenomena:

Spectral diffusion

Rotation

Population transfer

Structure:

Peptides/Proteins

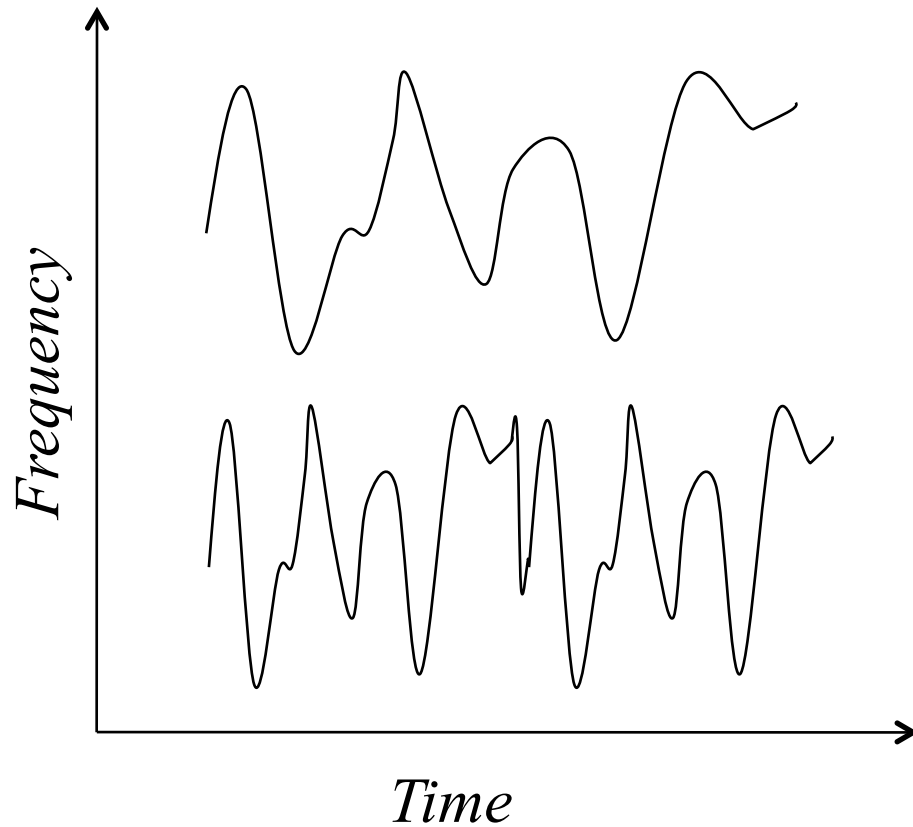
Dynamics:

Chemical exchange

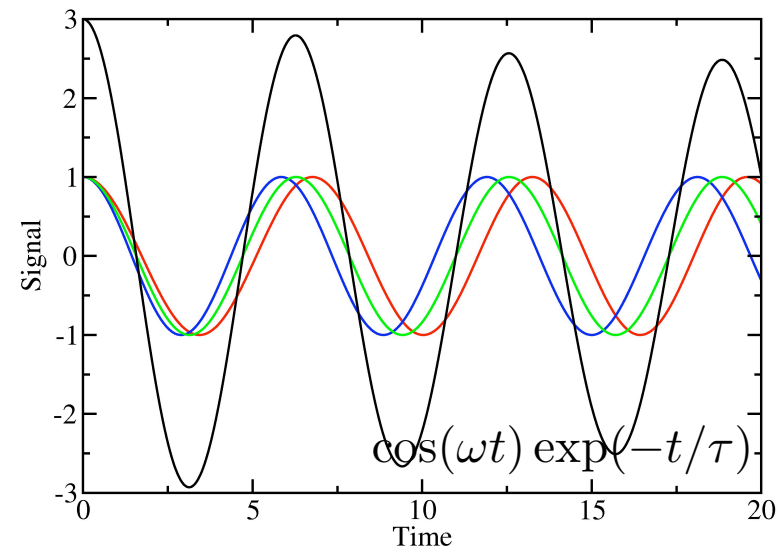
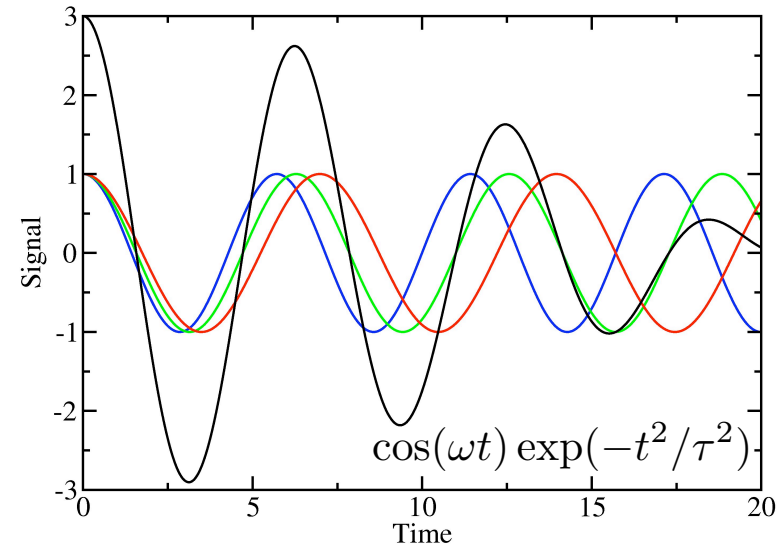
Water



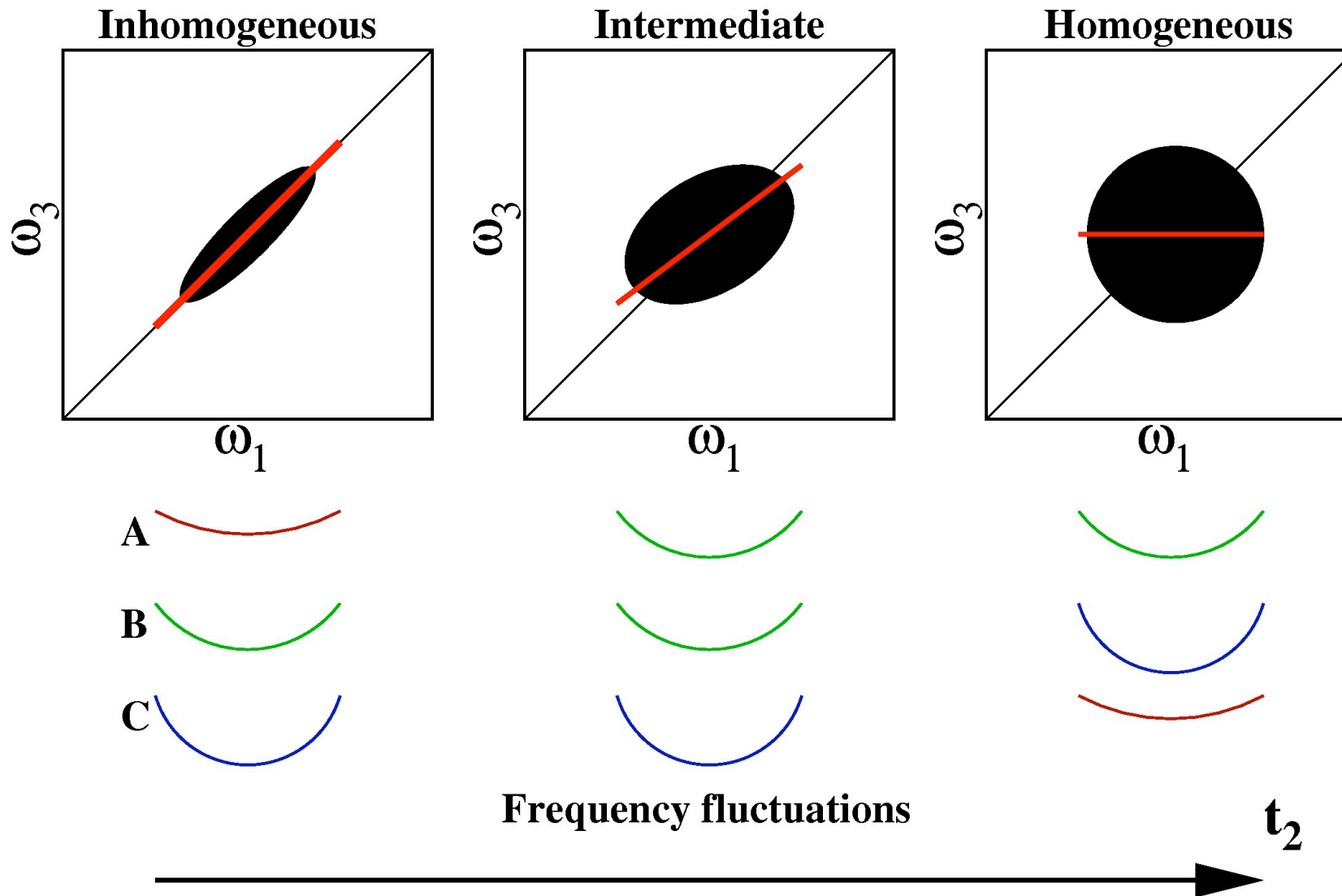
Motional narrowing



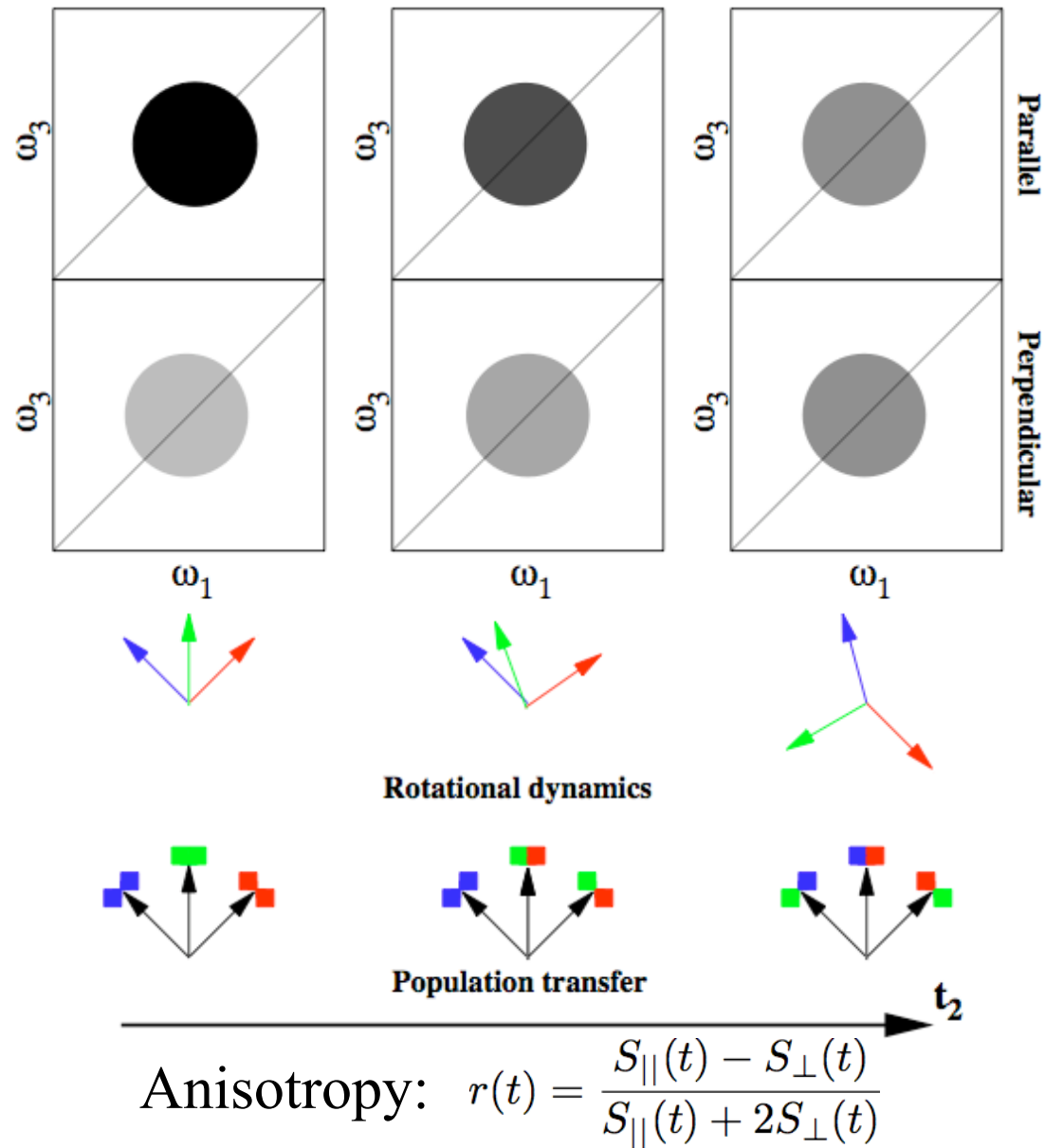
Kubo, J. Math. Phys., 4:174 (1963)



Spectral diffusion

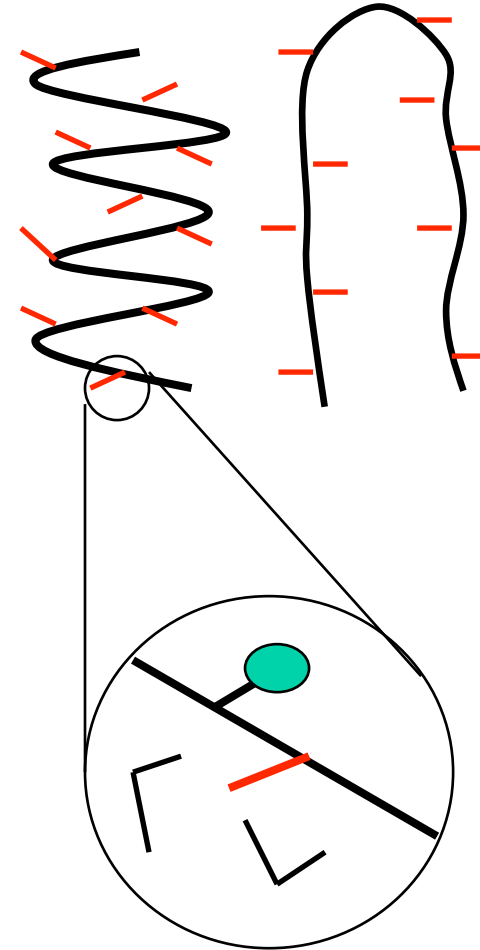


Rotational dynamics

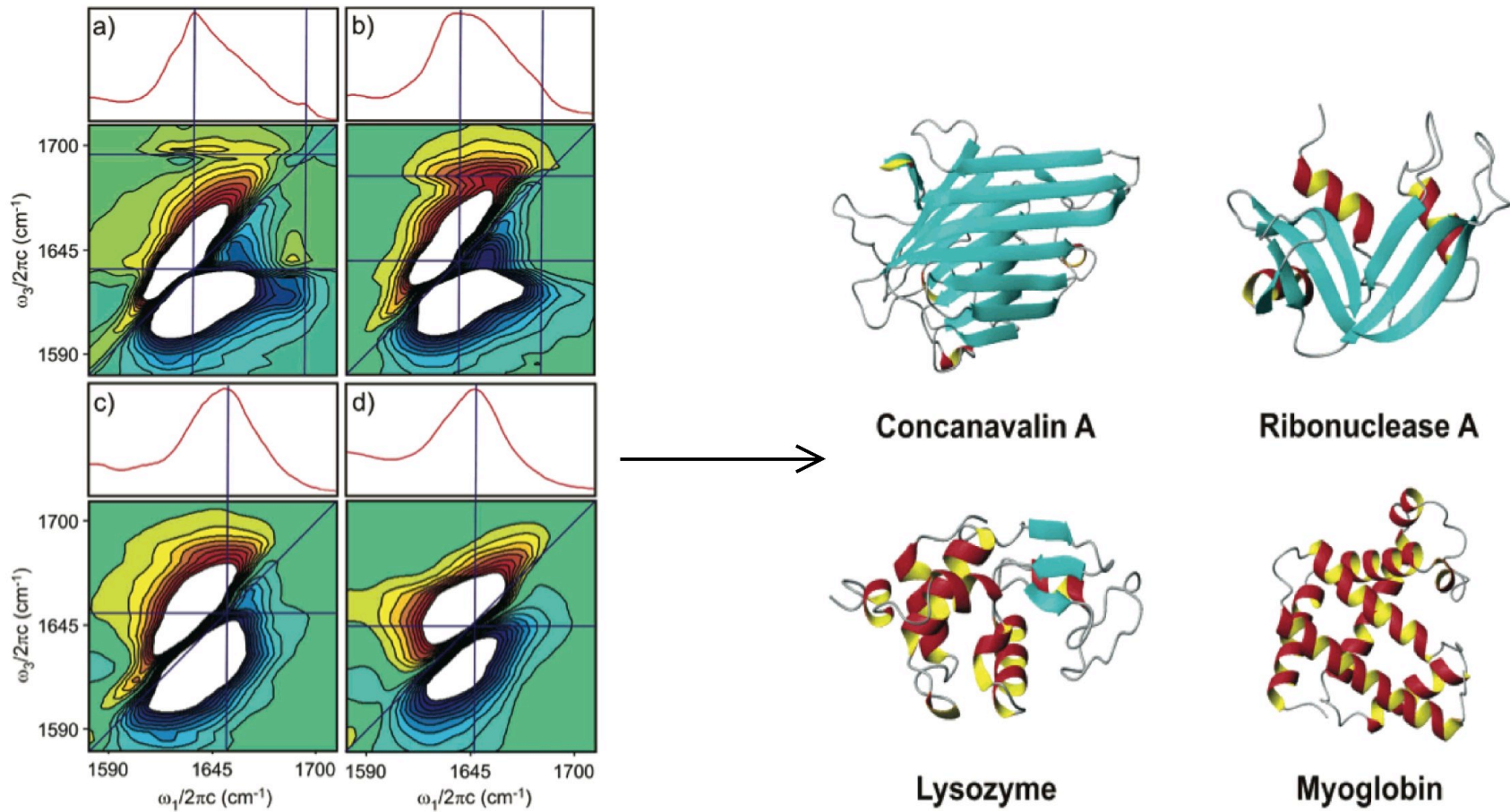


Peptides/Proteins

- Amide CO stretch in every peptide unit.
- Coupling depends on the conformation
- Probe global structure and it's dynamics.
- Require treatment of the local environment



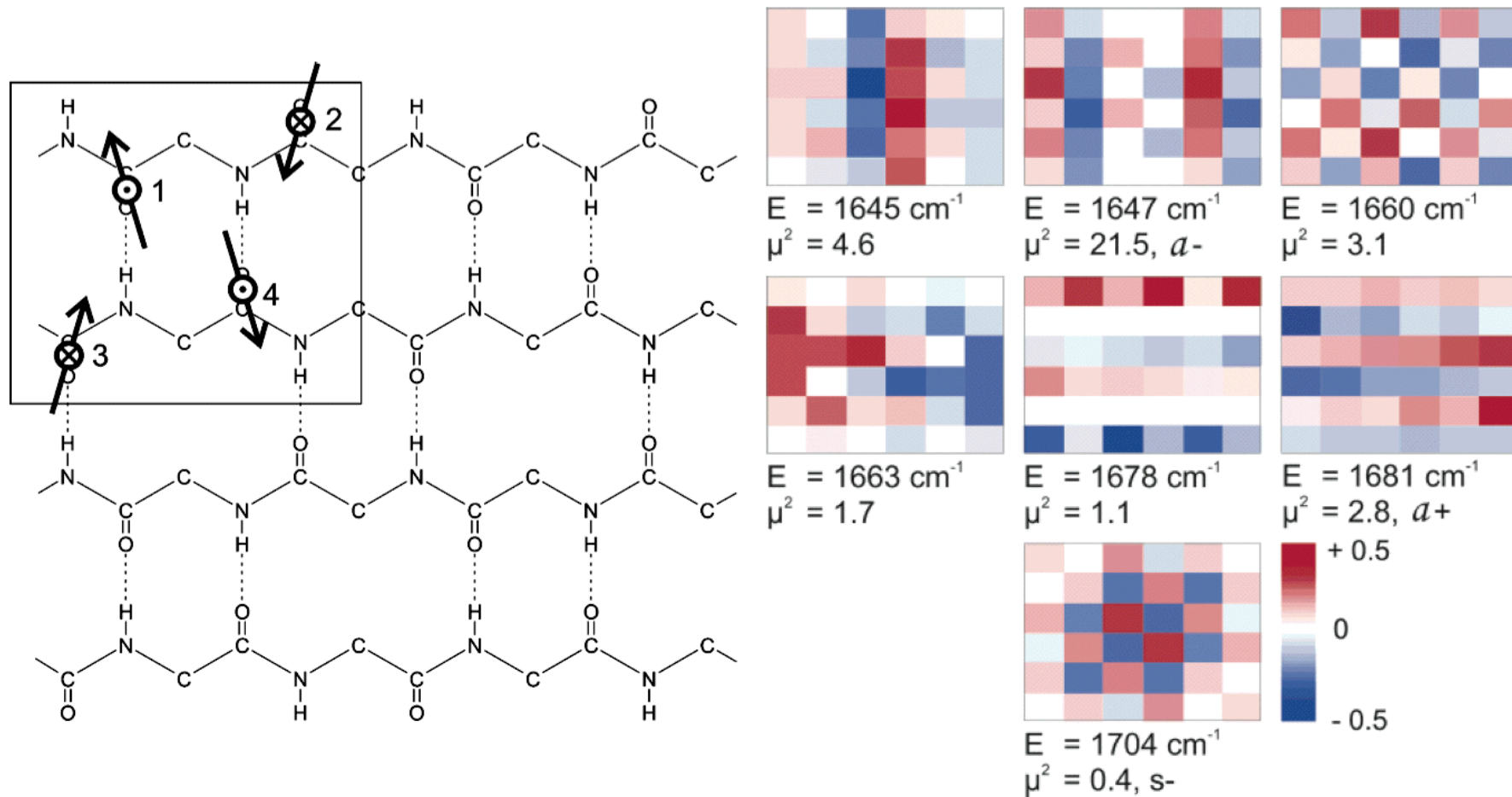
Proteins/Peptides



Tokmakoff et al. J. Am. Chem. Soc. 126:7981 (2004)



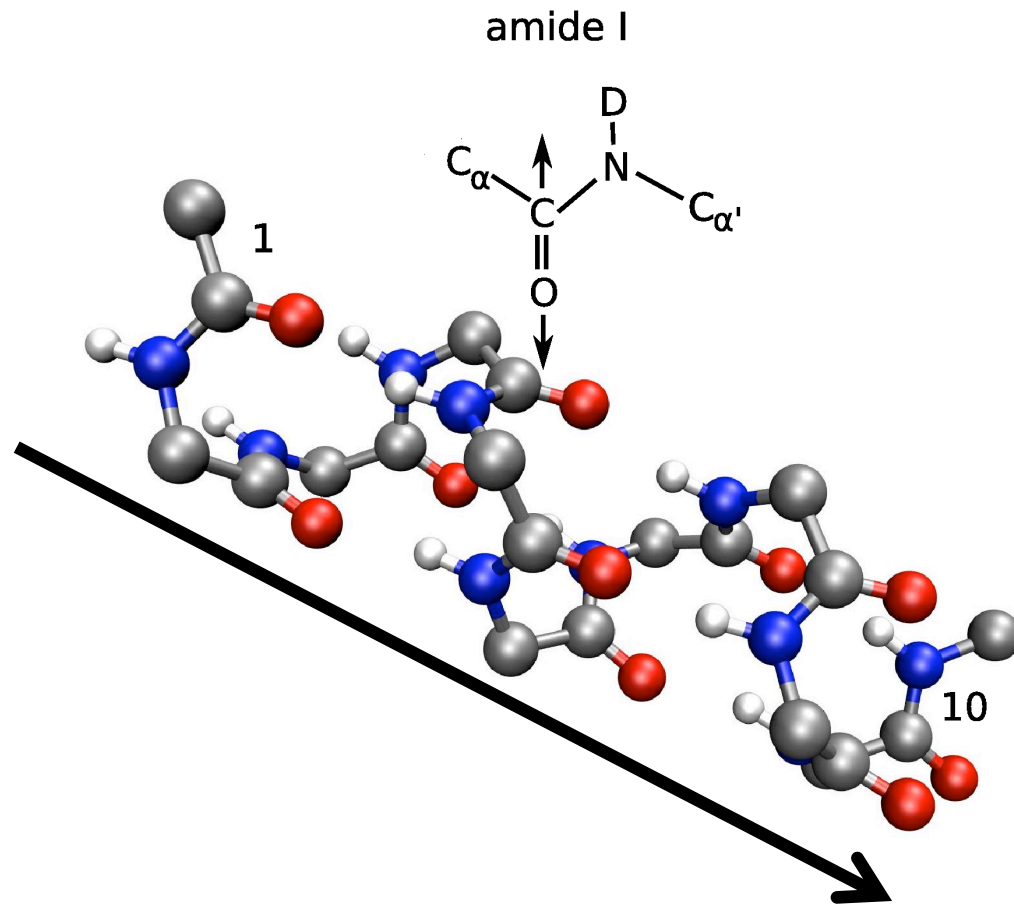
Proteins/Peptides



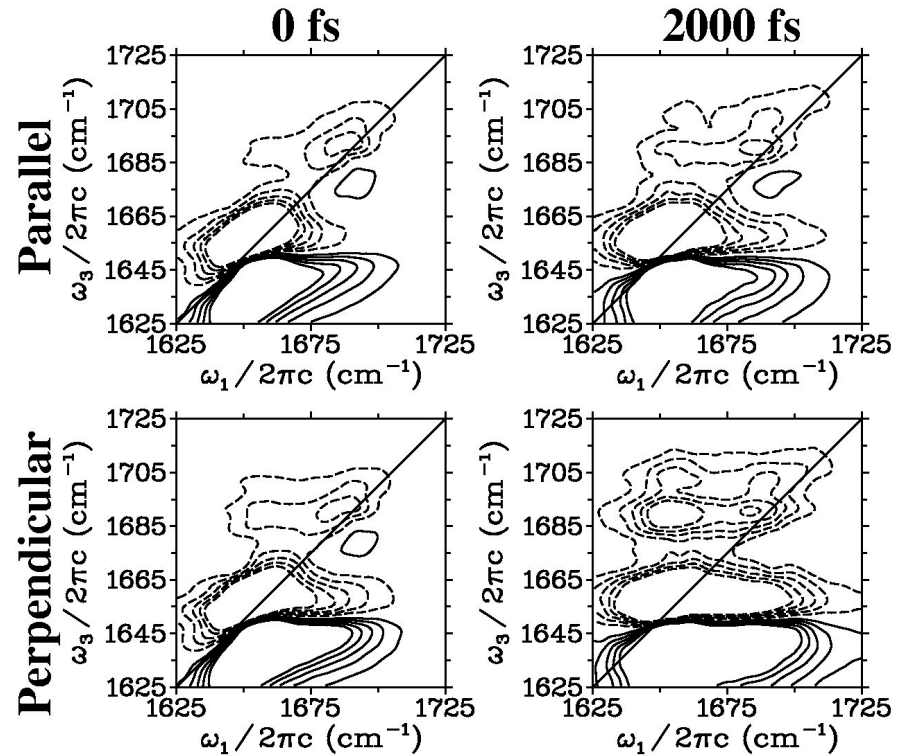
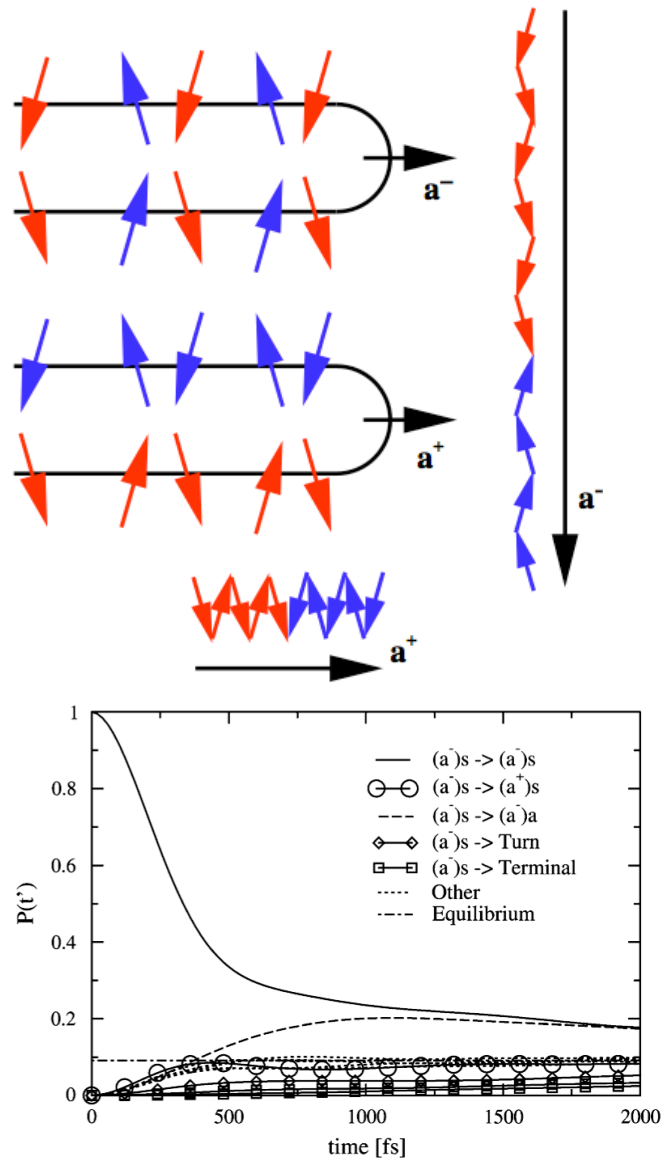
Dijkstra and Knoester, J. Phys. Chem. B 109:9787 (2005)



Peptides/Proteins



Peptides/Proteins

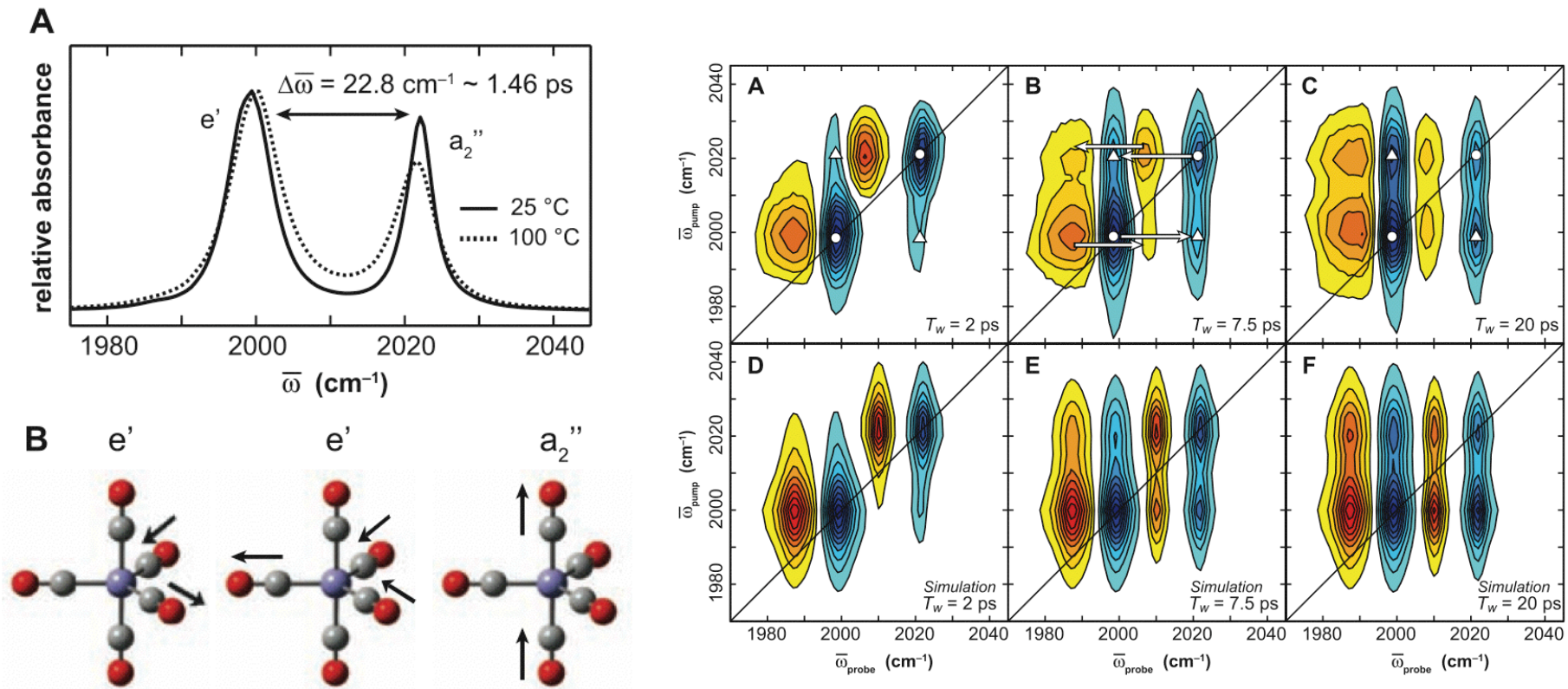


Jansen and Knoester, Biophys. J. 94:1818 (2008)



Chemical Exchange

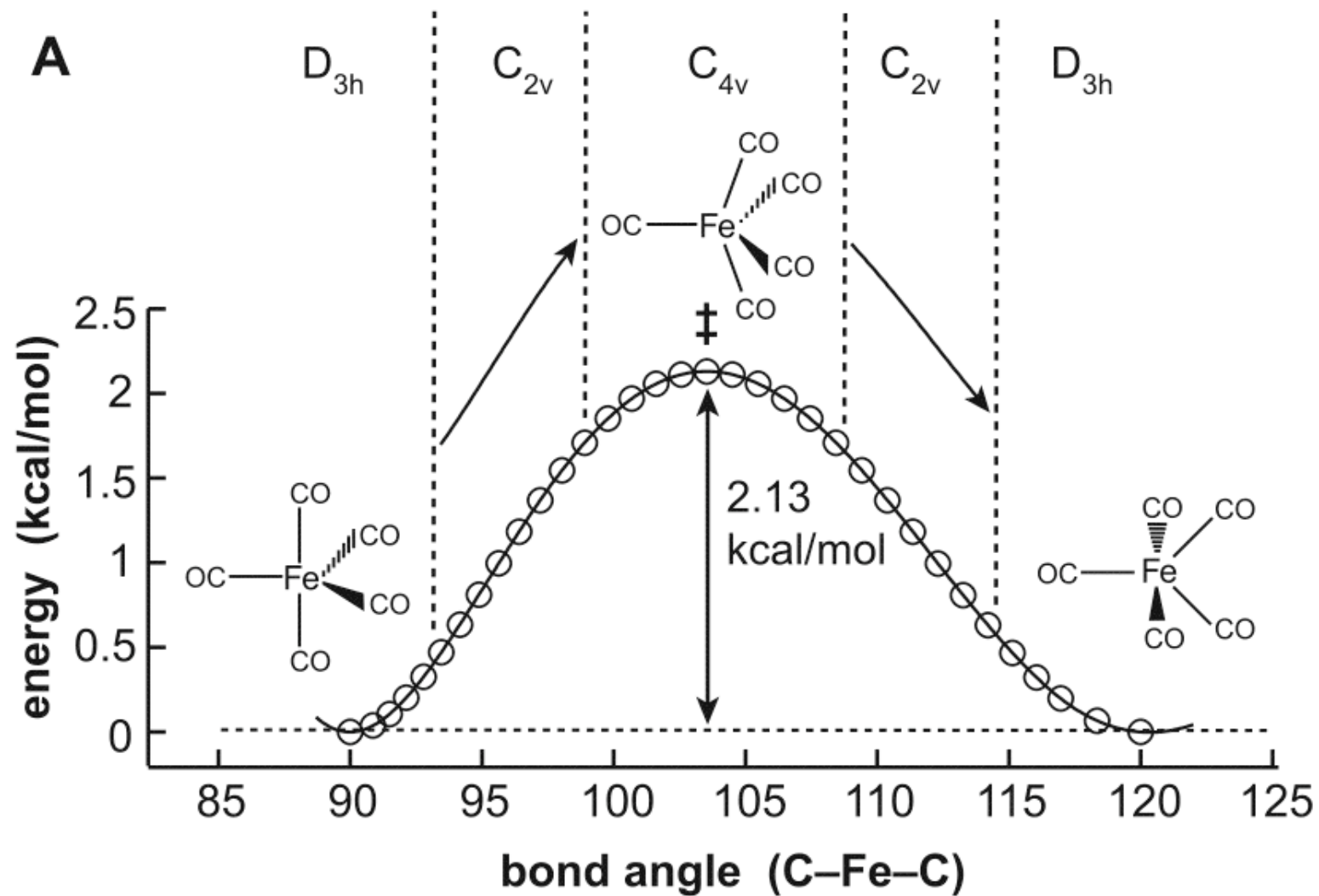
Structural rearrangement in $Fe(CO)_5$



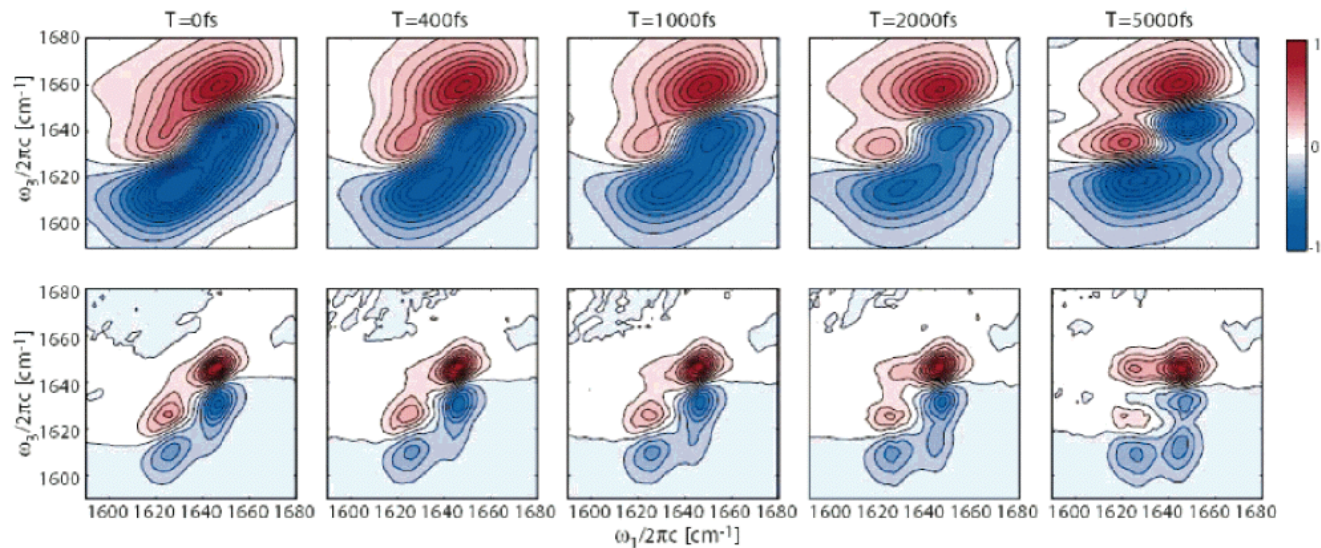
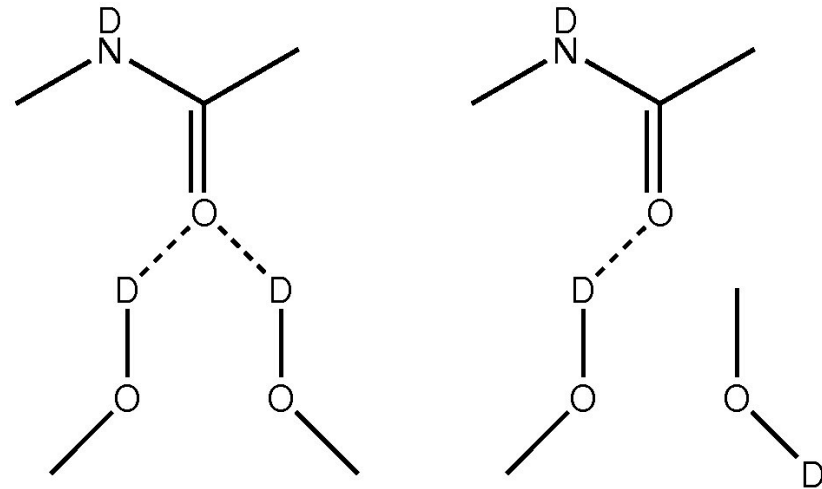
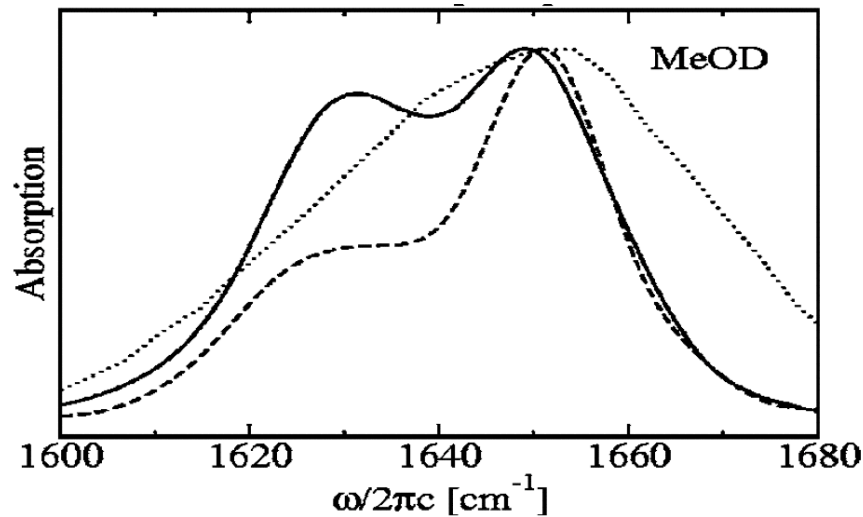
Harris et al. *Science* **319**:1820 (2008)



Chemical Exchange



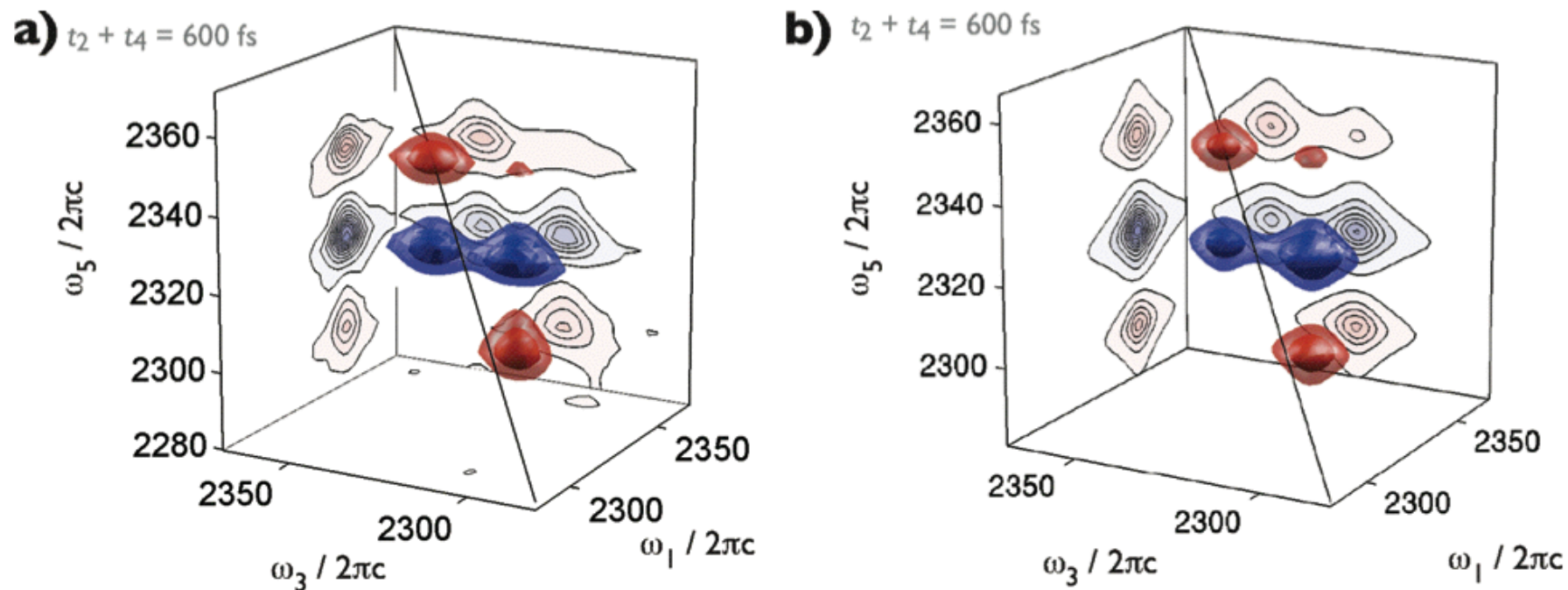
Chemical Exchange



Tokmakoff, Cho et al. *J. Phys. Chem. B* **109**:11016 (2005)



Three-dimensional infrared spectroscopy

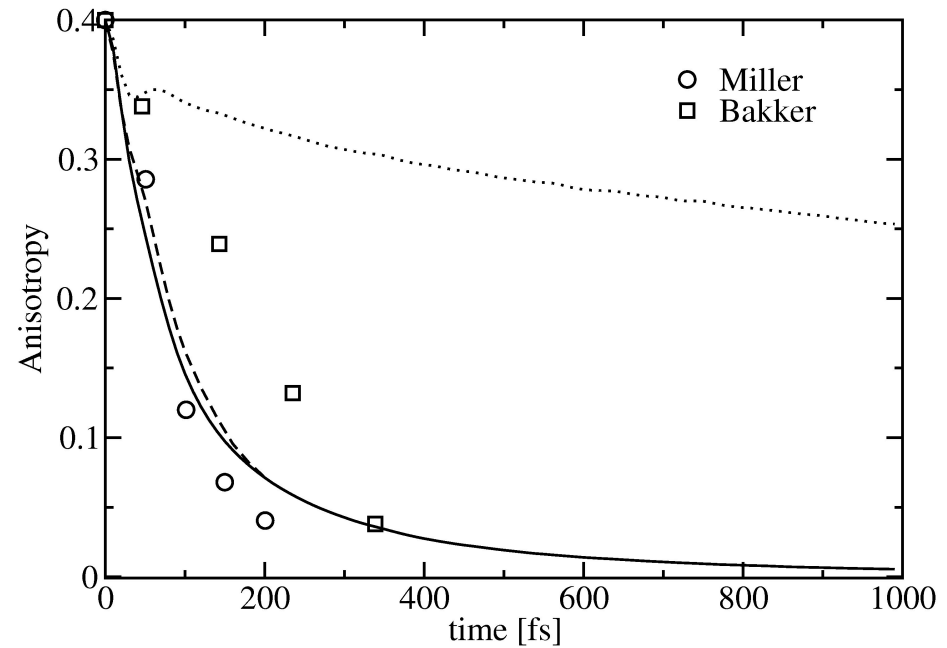
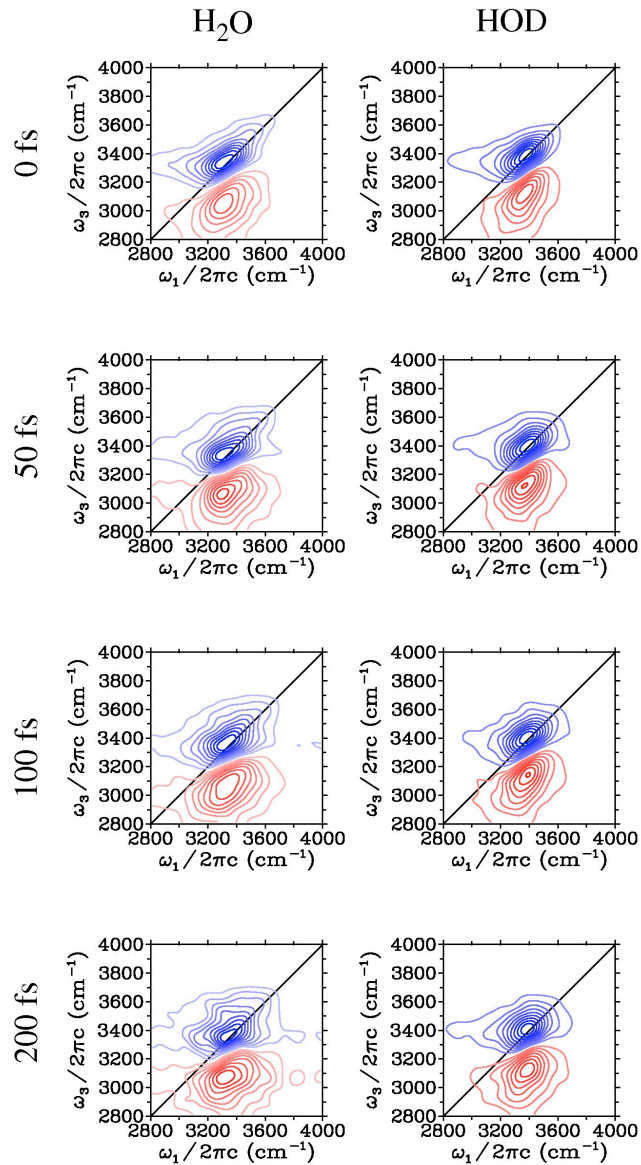


CO₂ dissolved in water

S. Garrett-Roe and P. Hamm, Acc. Chem. Res. 42:1412 (2009)



Bulk water

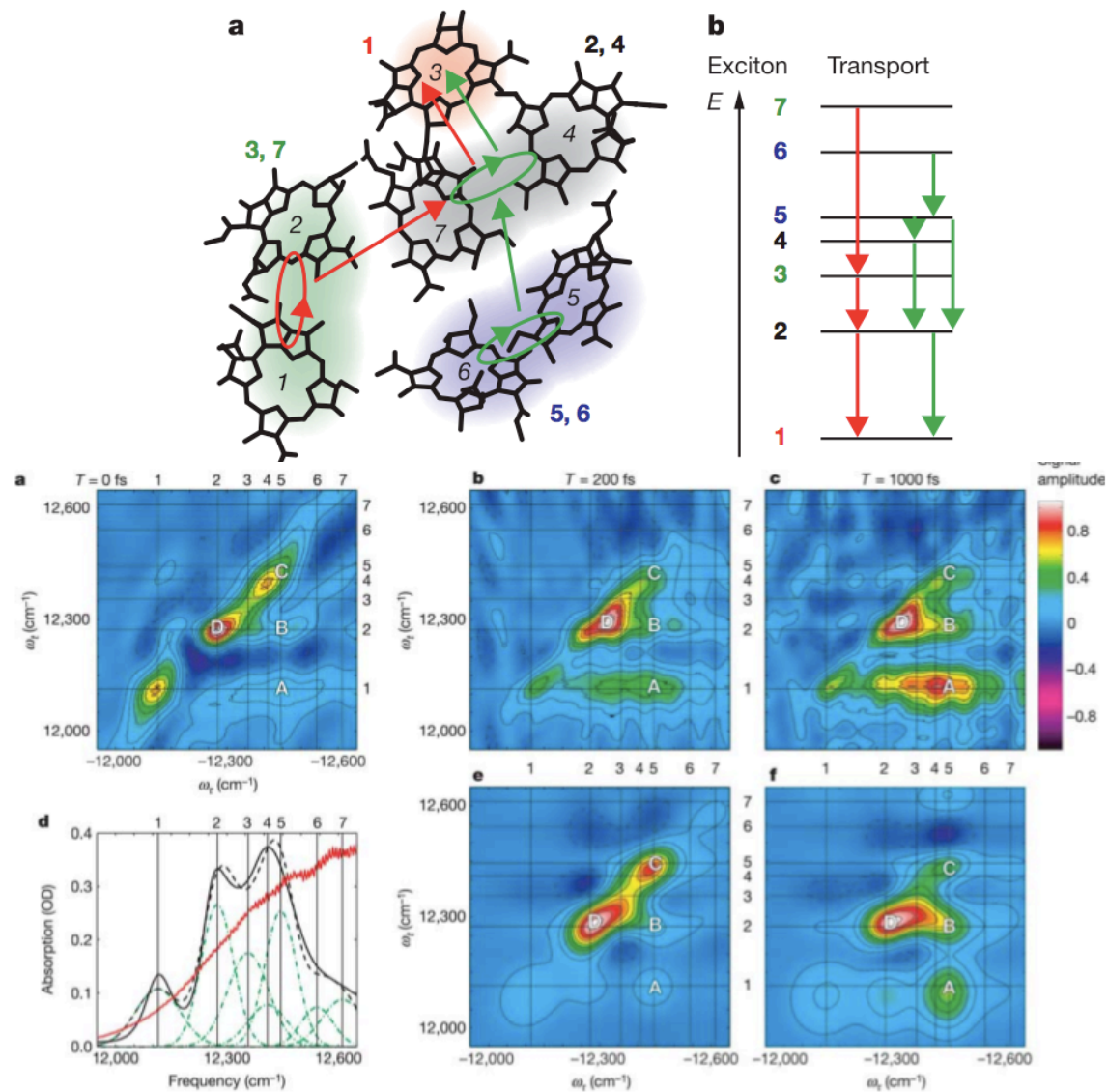


Miller et al., Nature, 434:199 (2005)

Woutersen and Bakker, Nature, 402:507 (1999)



Electronic spectroscopy



Freeming, Cho et al. Nature 434:625 (2005)

