Investigation of Hydration Water Induced Dynamic Transitions in Lysozyme

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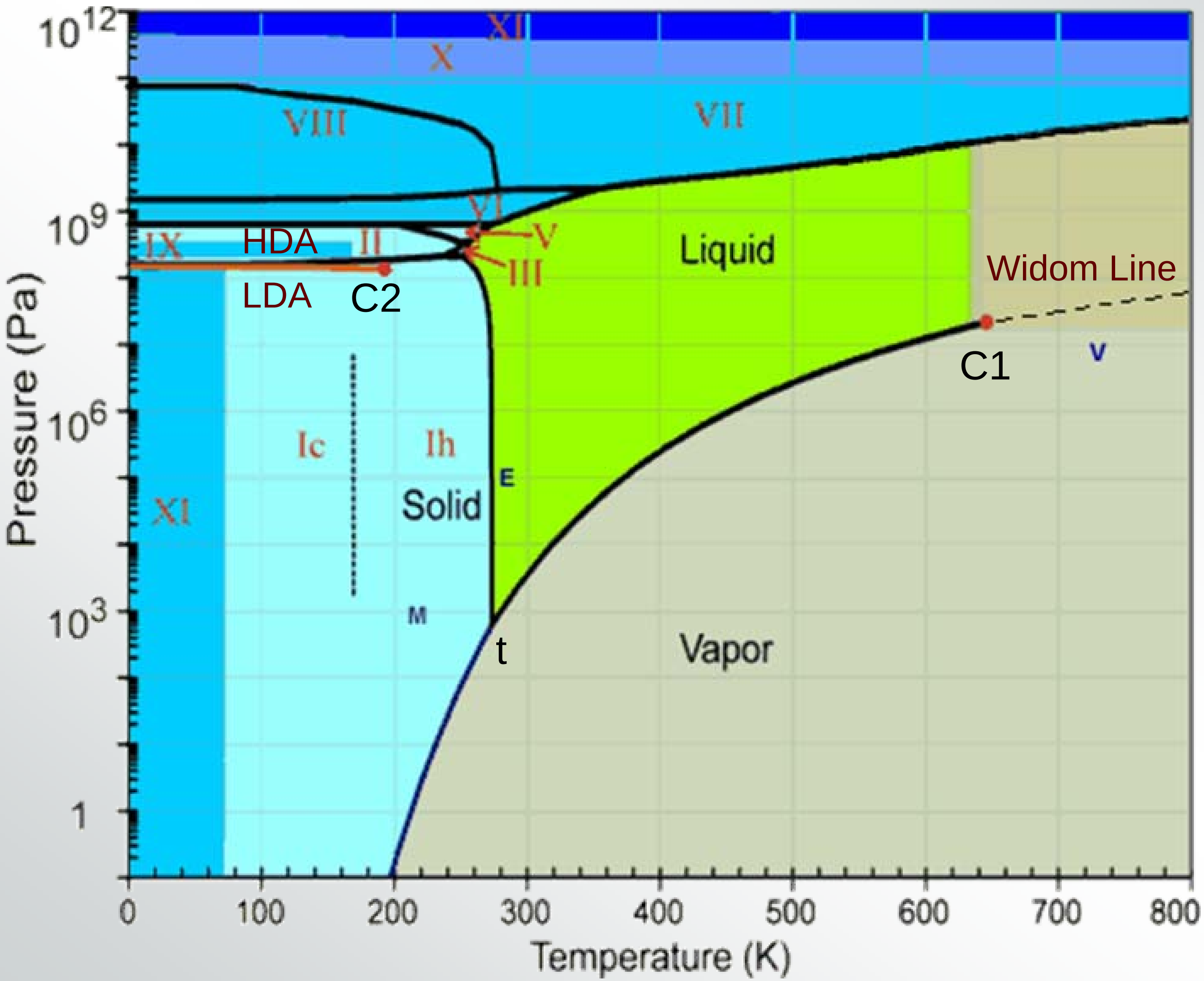
A talk presented at *the SNS/HFIR User Meeting*, ORNL, October 8-10, 2007

Phase Diagram of Water and Ice



15 Ice Polymorphs

2 Amorphous Ices

LDA & HDA,VHDA

ρ(HDA)=1.17 g/cm^3

ρ(VHDA)=1.25

ρ(LDA)=0.94

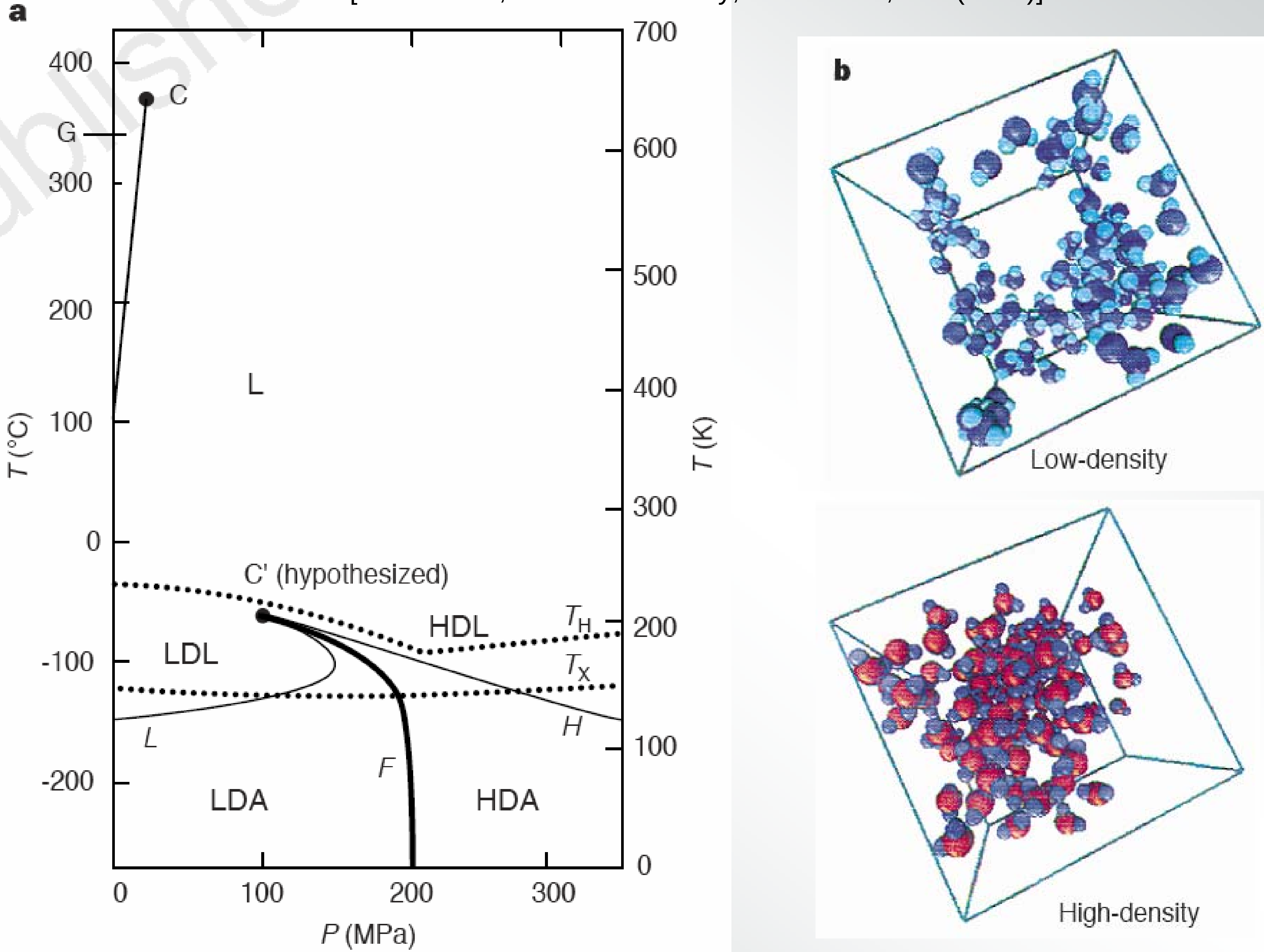
ρ(Ih)=0.92

ρ(Ic)=0.92

ρ(C1)=0.322

The Two Critical Points Scenario in Water

[O. Mishima, and H. E. Stanley, Nature 396, 331 (1998)]



Study of Dynamic Crossover Phenomena by Neutron Scattering

Confined water in MCM-41-S--its relation to the existence of the second critical point in supercooled water

↓

Mean Square Fluctuation, <x^2>: by Elastic Scan

Fragile-to-Strong Crossover, <τ_T>: by QENS

Appearance of Boson Peak : by INS

The dynamic crossover in hydration water on protein, DNA and RNA

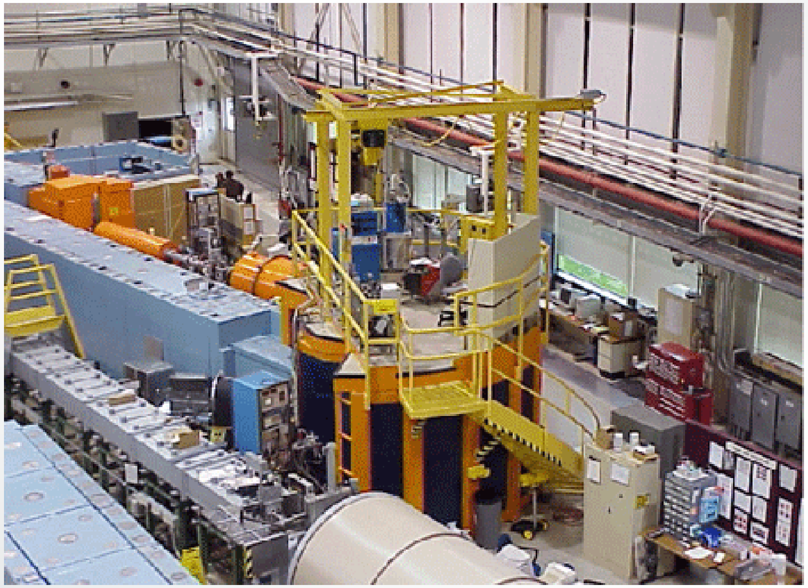
↓

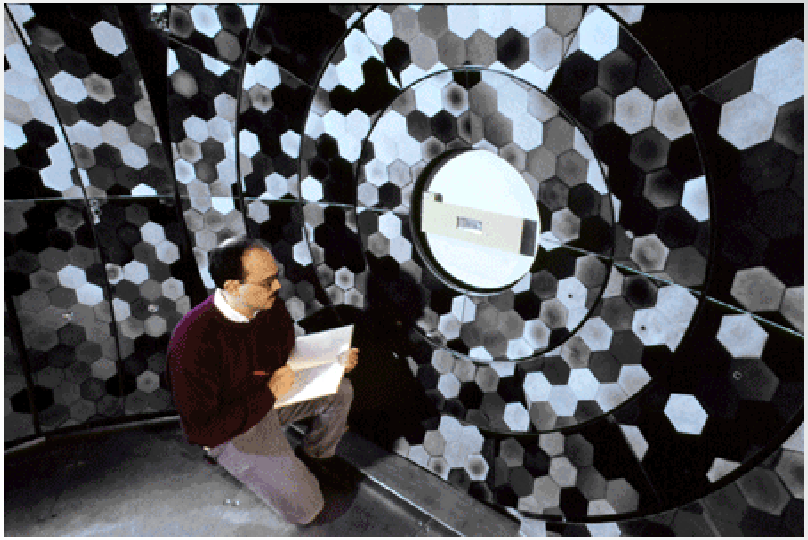
The crossover triggers the so-called Glass Transition in biomolecules

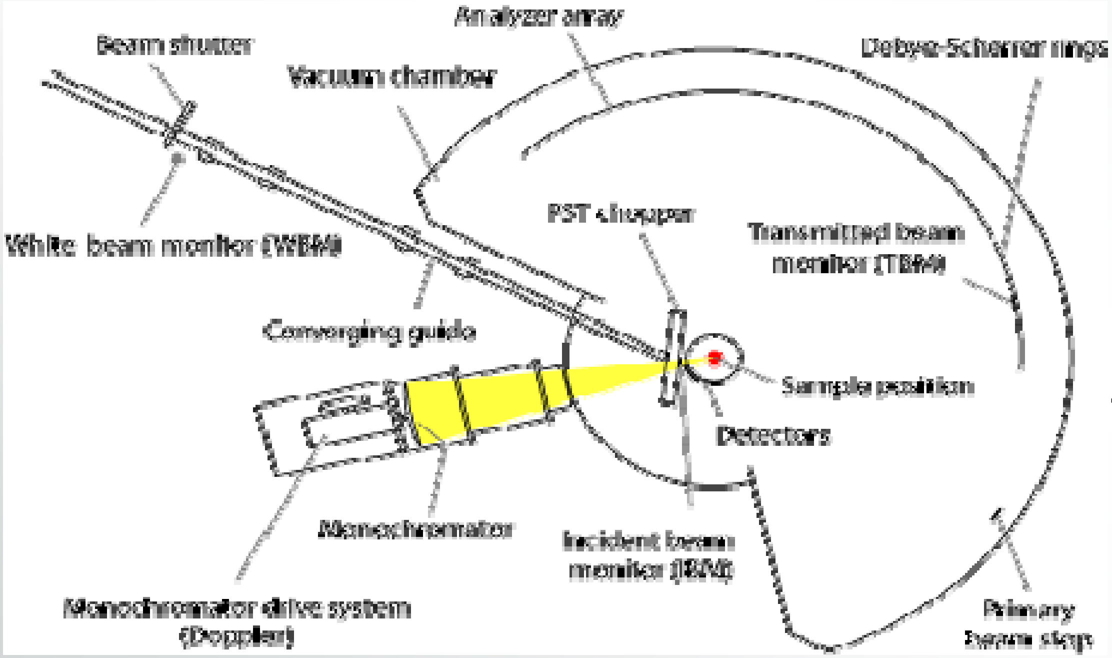
MOTIVATION

- At low T globular proteins exist in a glassy state having no conformational flexibility and show hardly any biological activities.
- For hydrated proteins above about 200 K, the flexibility is restored, able to sample more conformational sub-states, thus becoming biologically active.
- This “dynamical transition” is universal to all biopolymers. Believe to be triggered by their strong coupling with their hydration water, which shows a similar “dynamical transition” at approximately the same temperature.
- We show experimentally that this sudden switch in dynamical behavior of hydration water on Lysozyme, B-DNA and RNA occurs precisely at 220 K and can be described as a Fragile-to-Strong dynamic crossover (FSC).
- At FSC, the structure of hydration water makes a transition from predominantly high density form (HDL), a more fluid state, to predominantly low density form (LDL), a less fluid state, derived from the existence of a second critical point at an elevated pressure.

High-Flux Backscattering Spectrometer







Energy resolution

0.8 μV

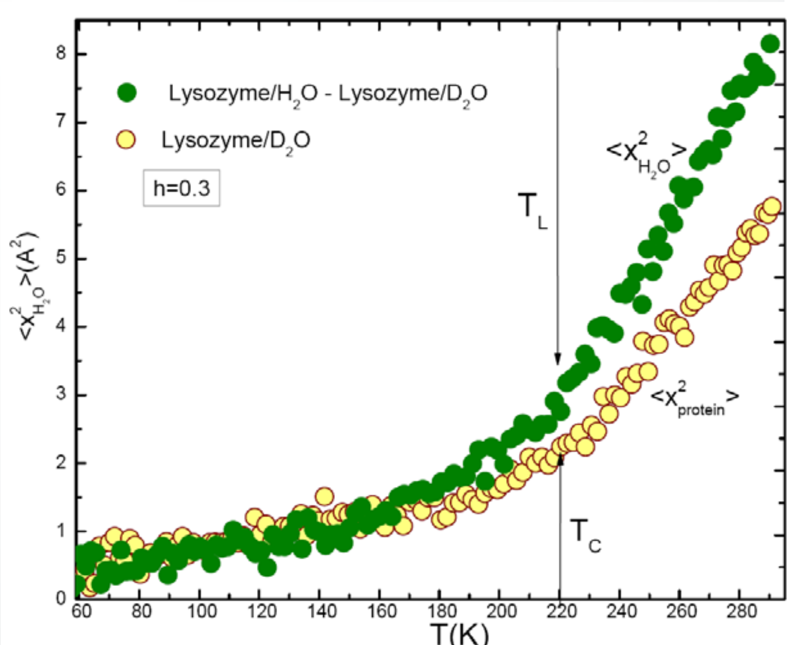
Dynamic range

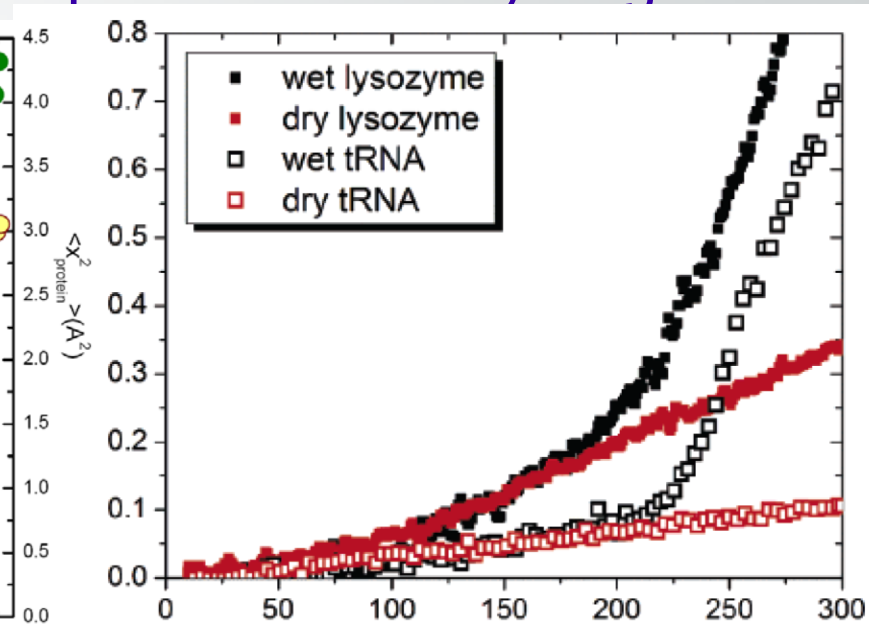
11 μV

Time range covered

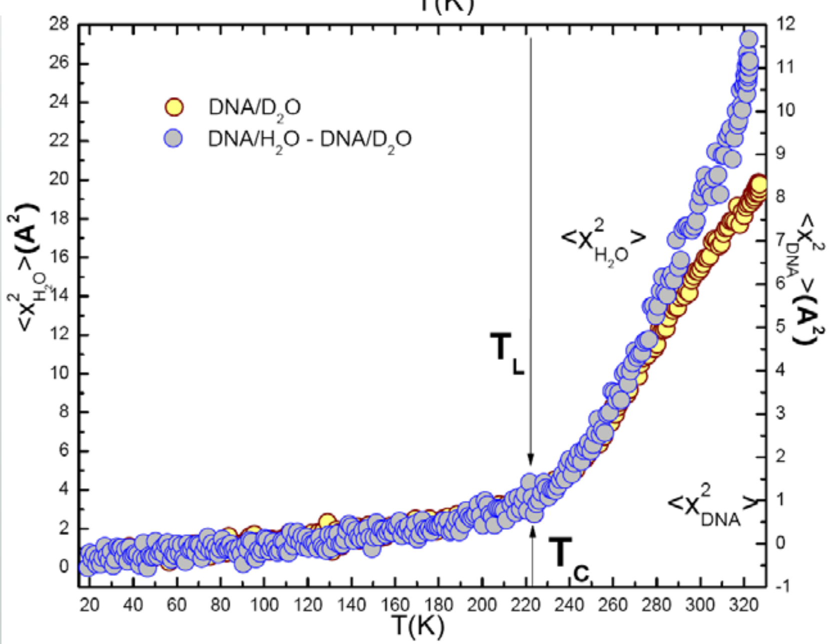
60 ps to 20 ns

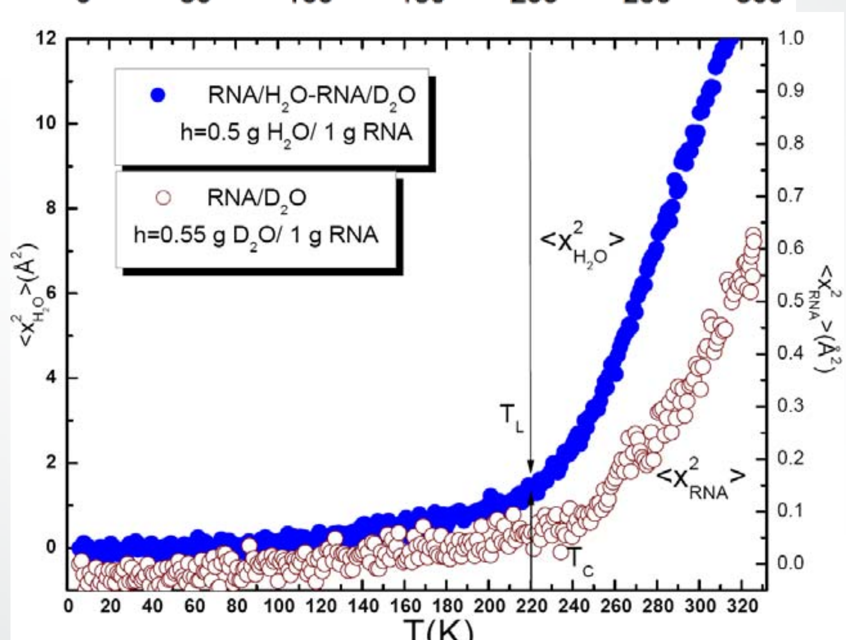
Mean-Square Atomic Displacement of Hydrogen Atoms





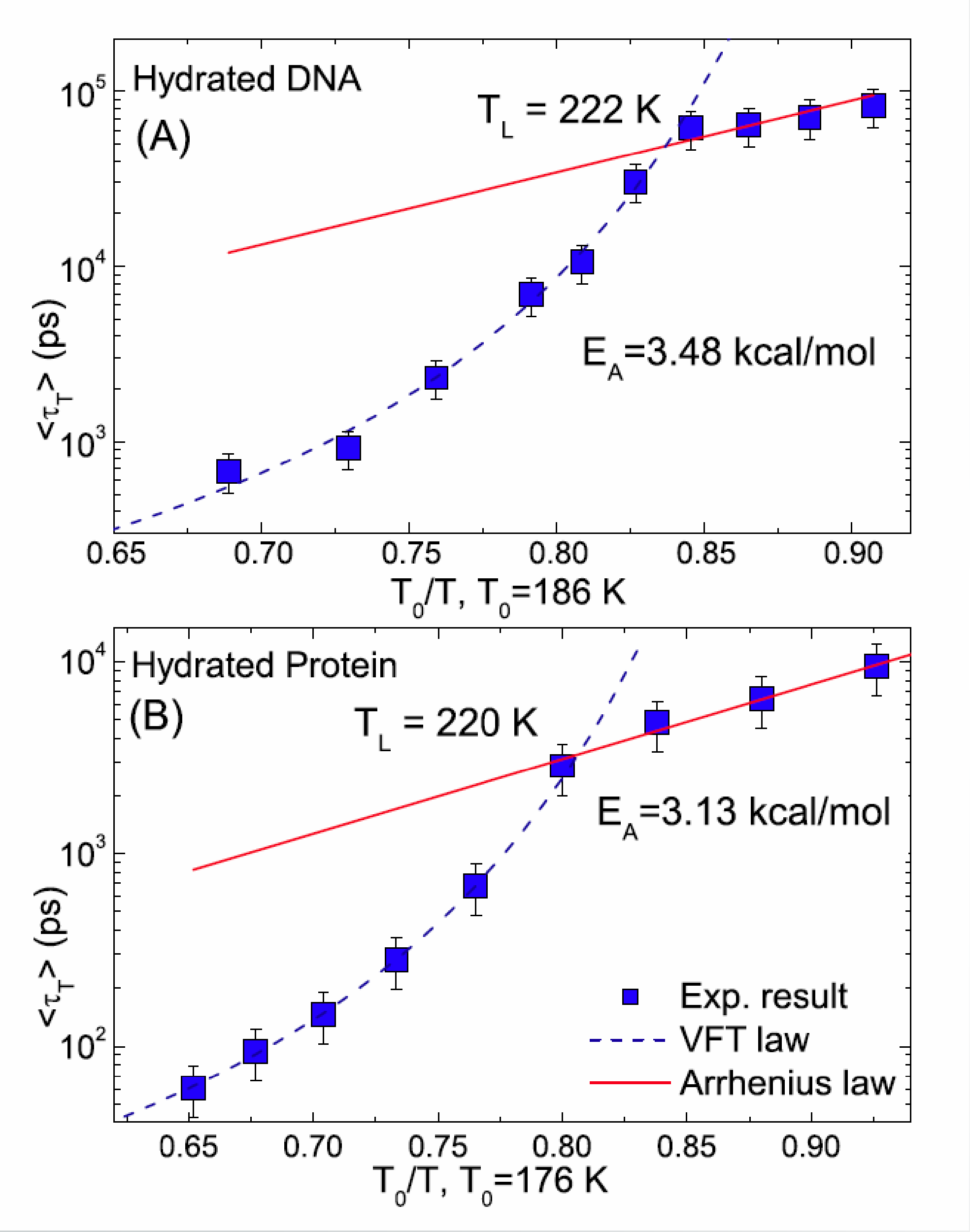
G. Caliskan *et al.*, ***JACS*** 128, 32-33 (2006).





Chen SH, Liu L, Chu X, Zhang Y, Fratini E, Baglioni P, Faraone A, Mamontov E, JCP **125**, 171103, 2006

Comparison of FSC in DNA and Protein hydration water



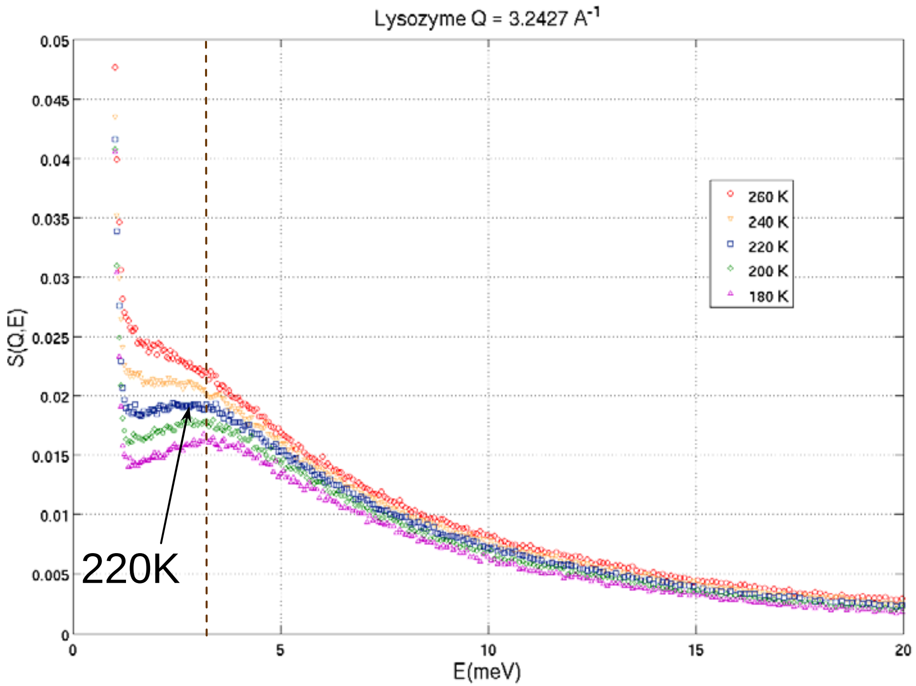
Comparison of the temperature dependence of the average translational relaxation times of hydration water:

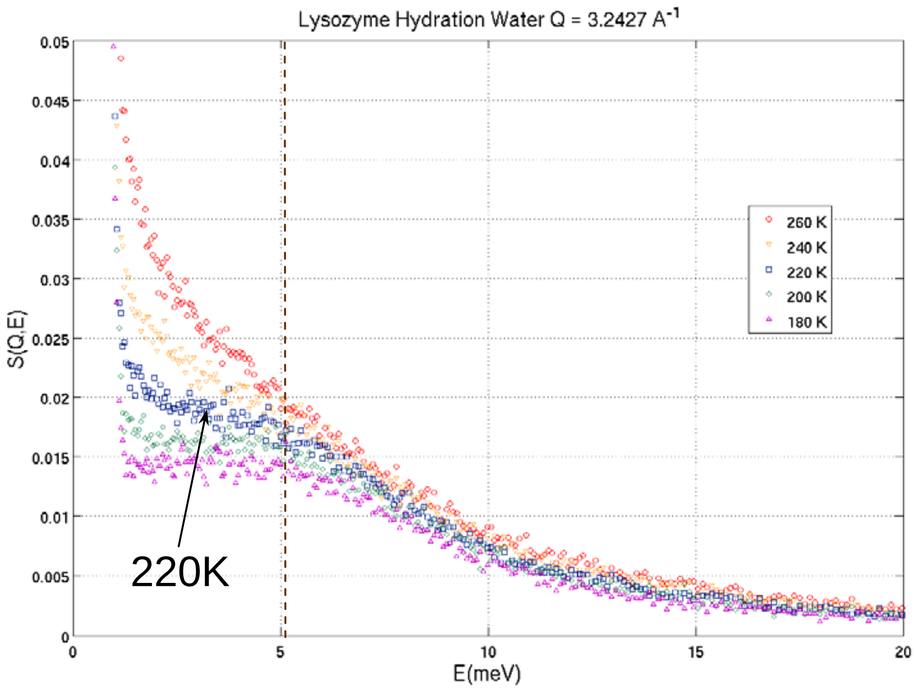
(A) in hydrated DNA

(B) in hydrated Protein.

They both show a cusp-like dynamic crossover phenomenon at temperatures around 220 K. Dash line and solid line are a VFT law and an Arrehnius law fits respectively.

S.-H. Chen et al., "Experimental Evidence of Fragile-to-Strong Dynamic Crossover in DNA Hydration Water," JCP **125**, 171103 (2006).





Appearance of a Well-defined Boson Peak at and below 220K

Protein lysozyme

$E_B = 3$ meV

$T_C = T_L = 220$K

T_C : protein “glass transition” temp.

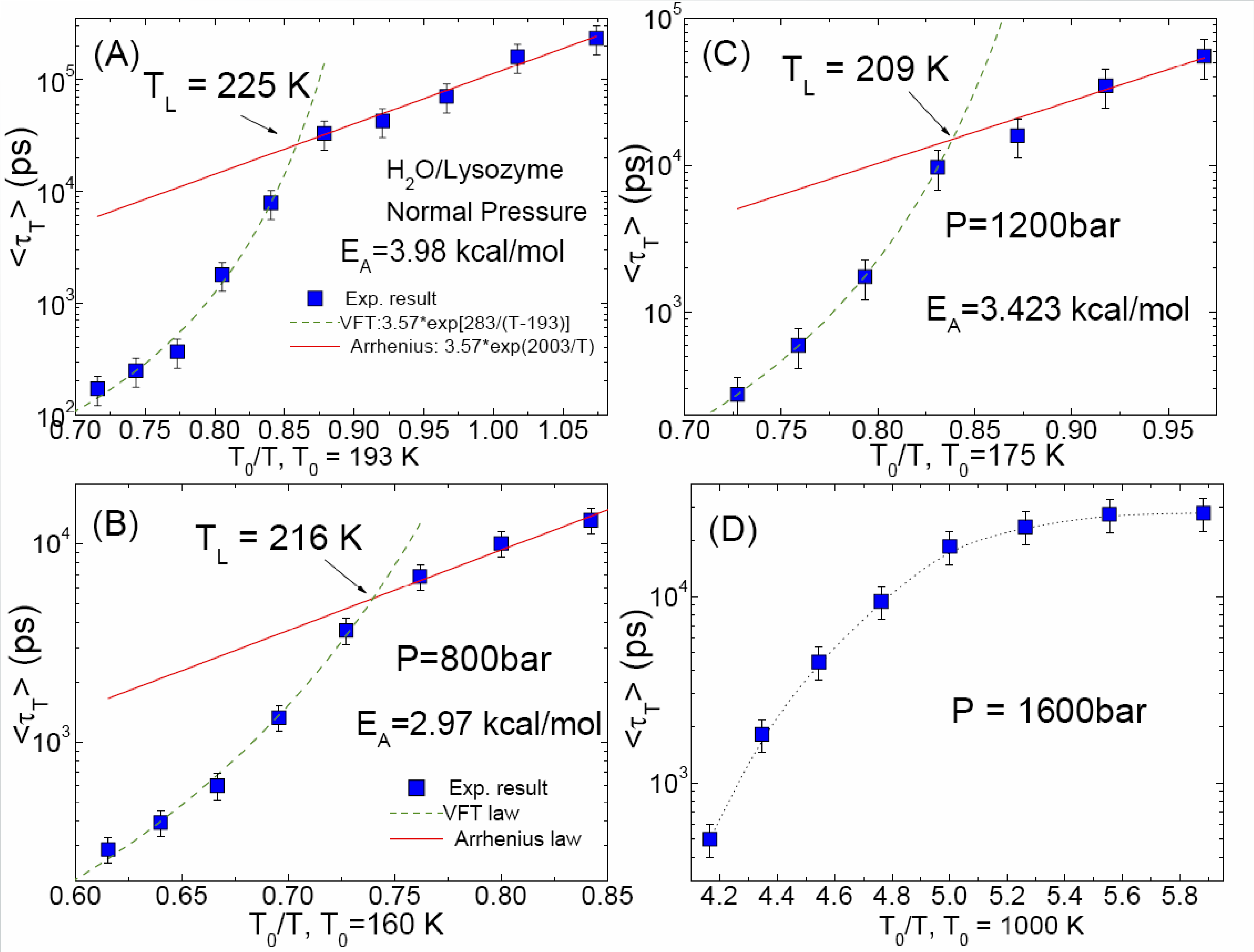
T_L : dynamic crossover temp.

Protein hydration water

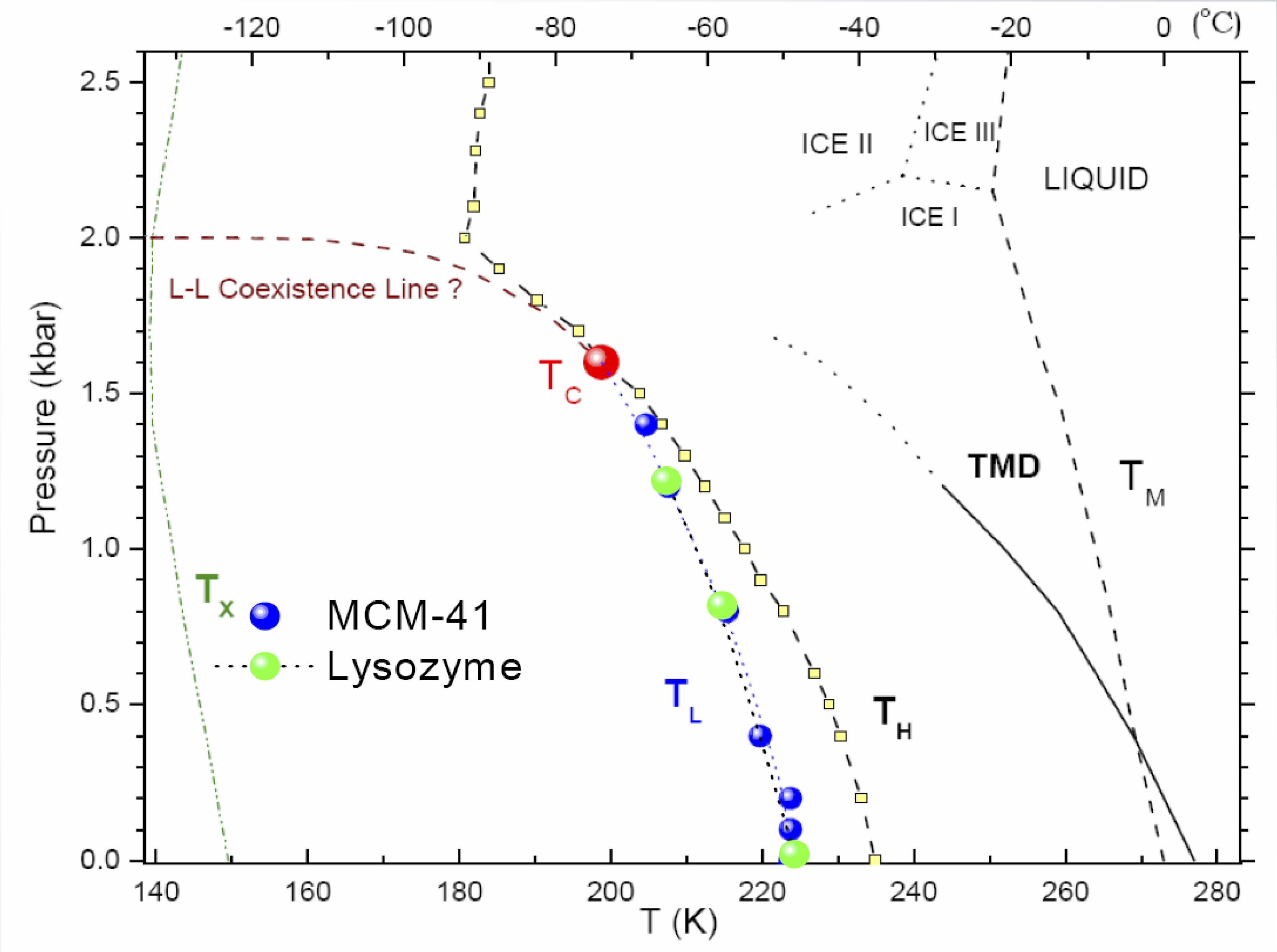
$E_B = 5$ meV

Y. Zhang, S.-H. Chen, et al. (to be published)

Measured Crossover Temperature T_L as a Function of Pressure



Tracking of T_L in Hydration Water of Lysozyme Along the Widom Line Emanating from the Second Critical Point of Water (to be published)



Conclusions

1. **We show that hydration water in Lysozyme [4], DNA and RNA all exhibit FSC at 220 K at ambient pressure. This result is supported by a recent MD simulation [5].**

2. **Protein Lysozyme and its hydration water were shown to have a well-defined Boson peak at and below 220 K at ambient pressure.**

3. **Upon applying pressure, the protein hydration water shows the crossover phenomenon which tracks the Widom line emanating from the second (liquid-liquid) critical point.**

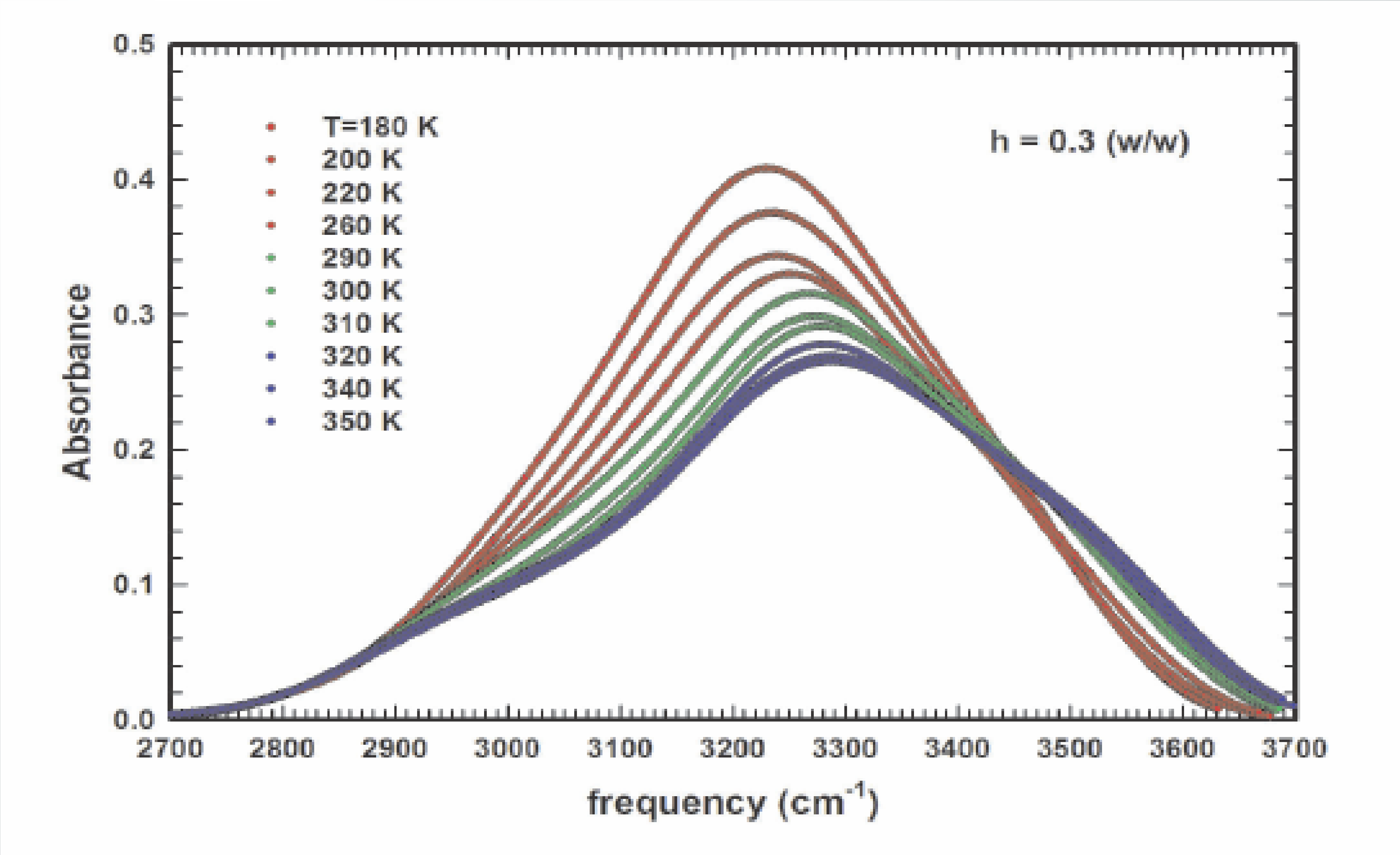
[1] A. Faraone and S.H. Chen et al., JCP **121**, 10843 (2004). [2] L. Liu and S.H. Chen et al.,PRL **95**,117802 (2005).

[3] L. Xu, P. Kumar, S.V. Buldyrev, S.H. Chen, P.H. Poole, F. Sciortino, H.E. Stanley, PNAS **102**,16558 (2005).

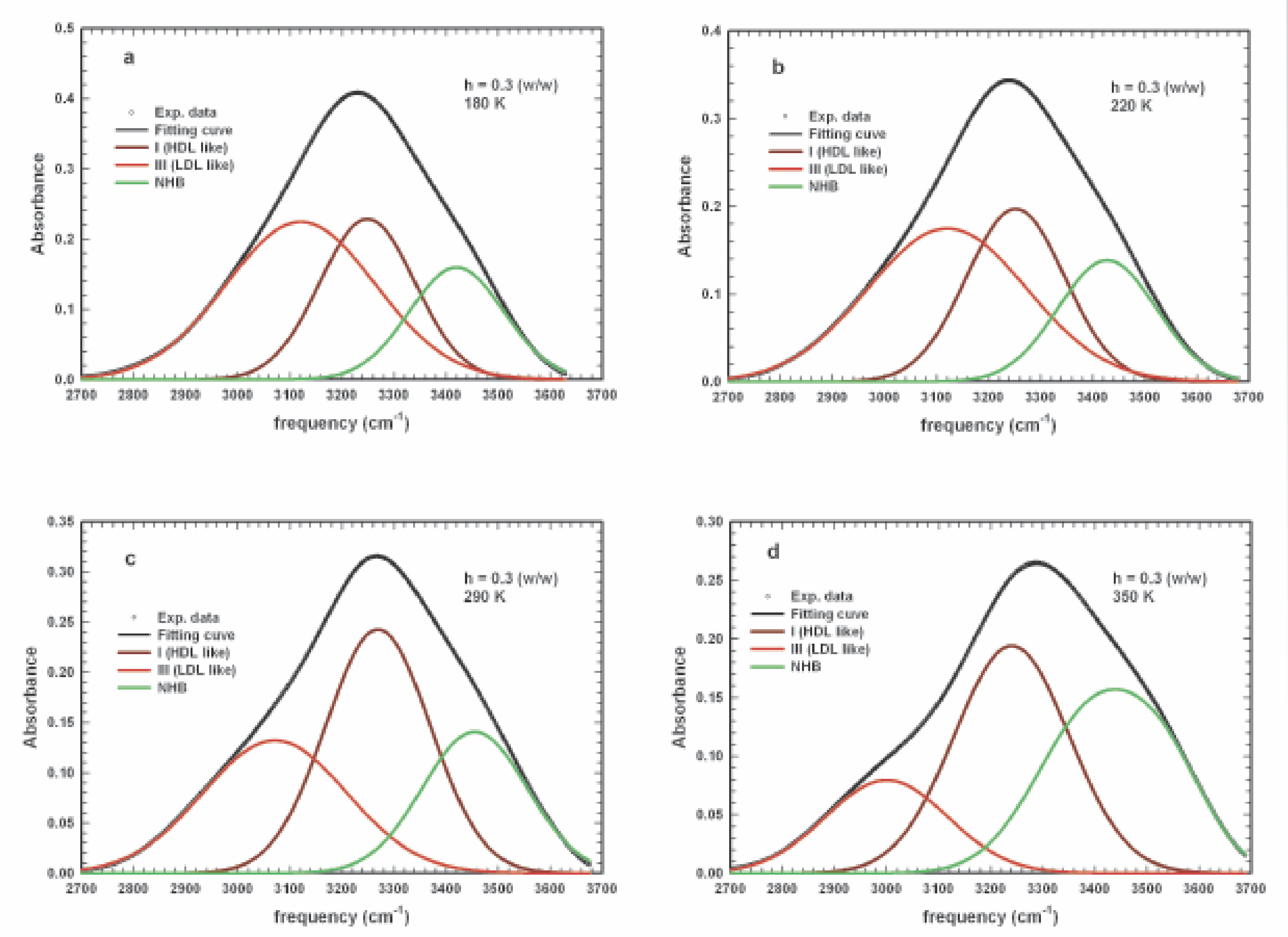
[4] S.-H. Chen, L.Liu, E. Fratini, P. Baglioni, A. Faraone and E. Mamontov, PNAS **103**, 9012-9016 (2006).

[5] P. Kumar, Z.Yan, L. Xu, M.Z. Mazza, S.V. Buldyrev, S.H. Chen, S. Sastry and H.E. Stanley, PRL 97, 177802 (2006).

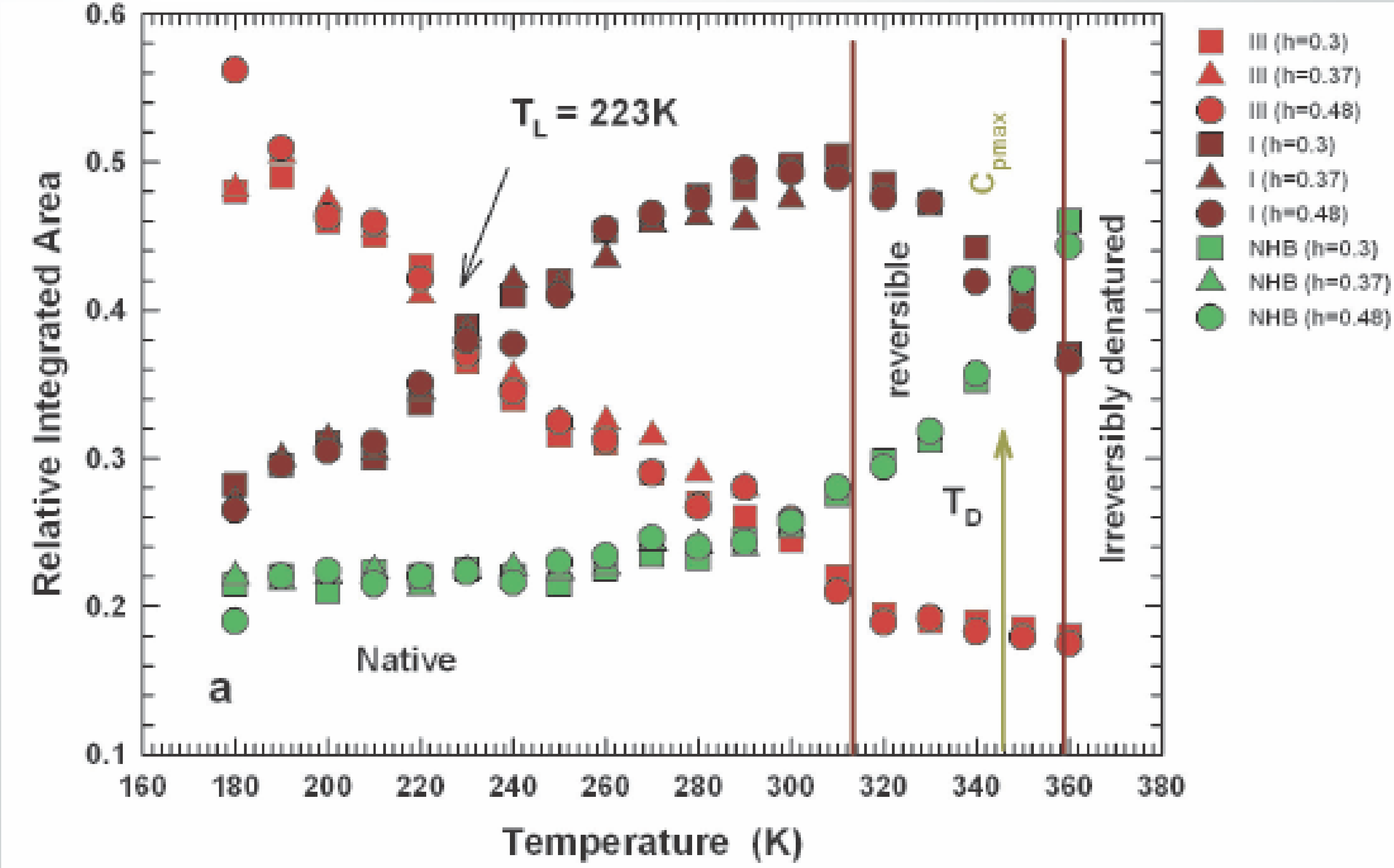
FTIR Absorption Band of Lysozyme Hydration Water in the O-H Stretch Vibration Range of 2700-3800 cm^{-1}



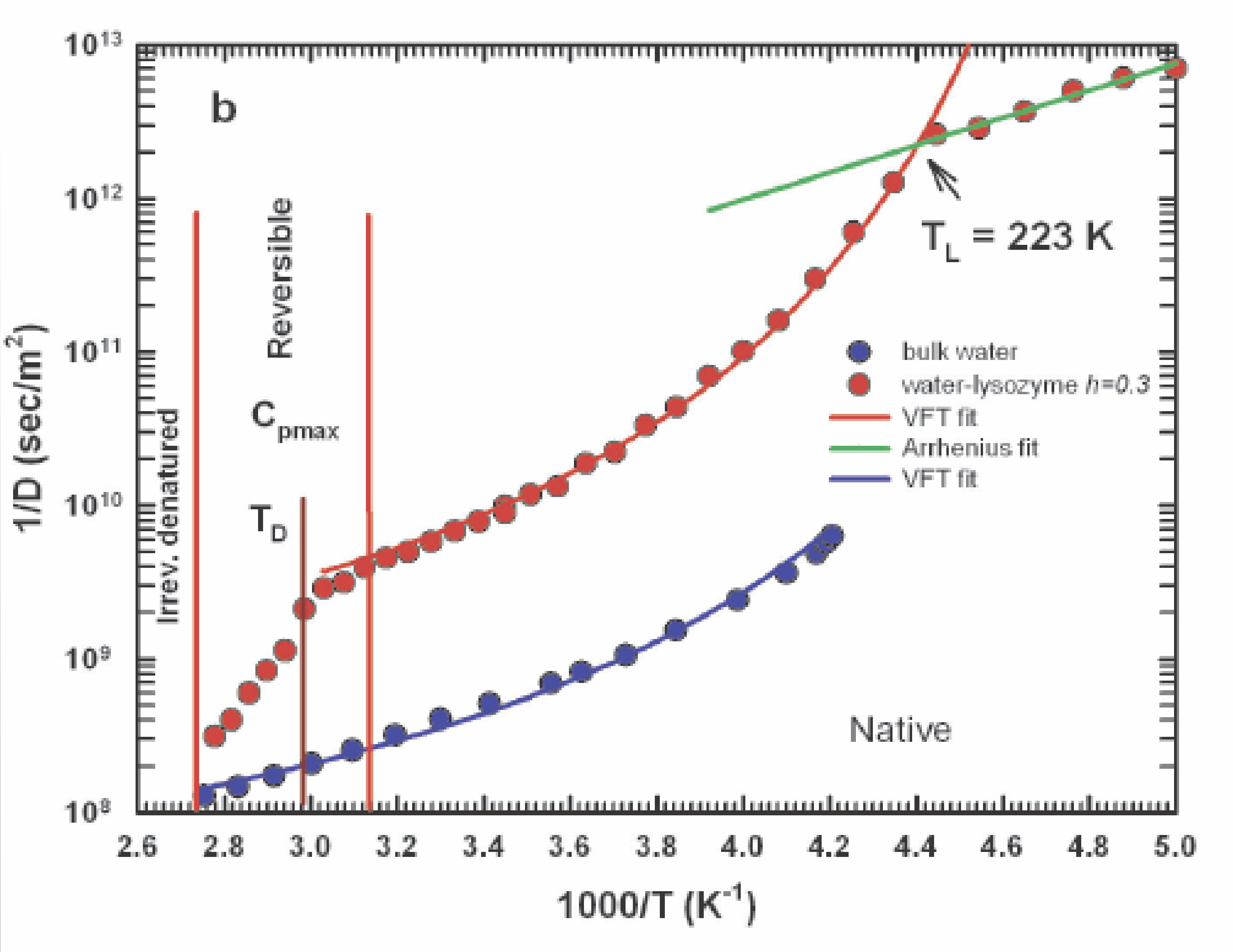
Spectral Decomposition of O-H Vibration Band in Terms of Three Species of Water



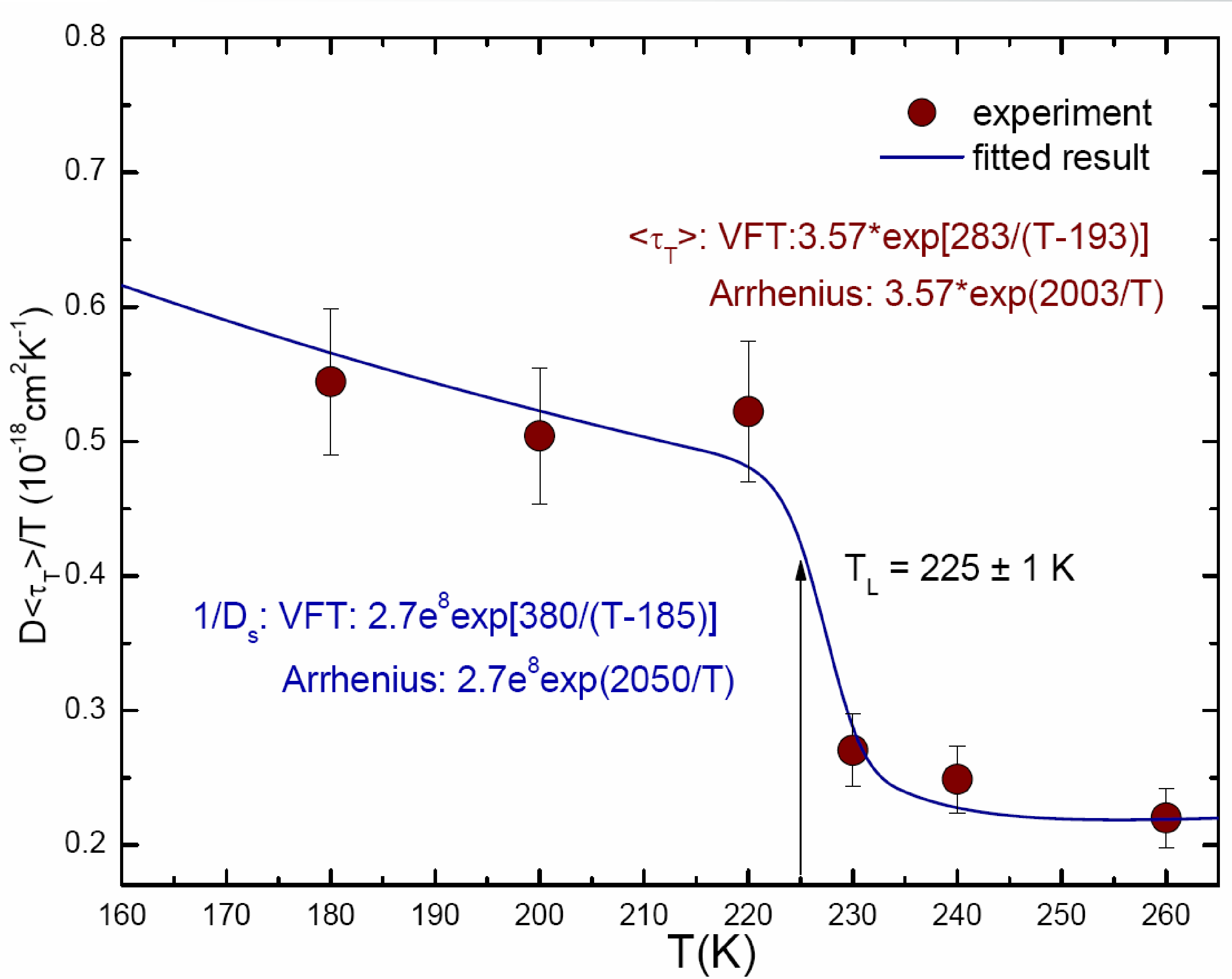
Fractional Population of Three Species of Water

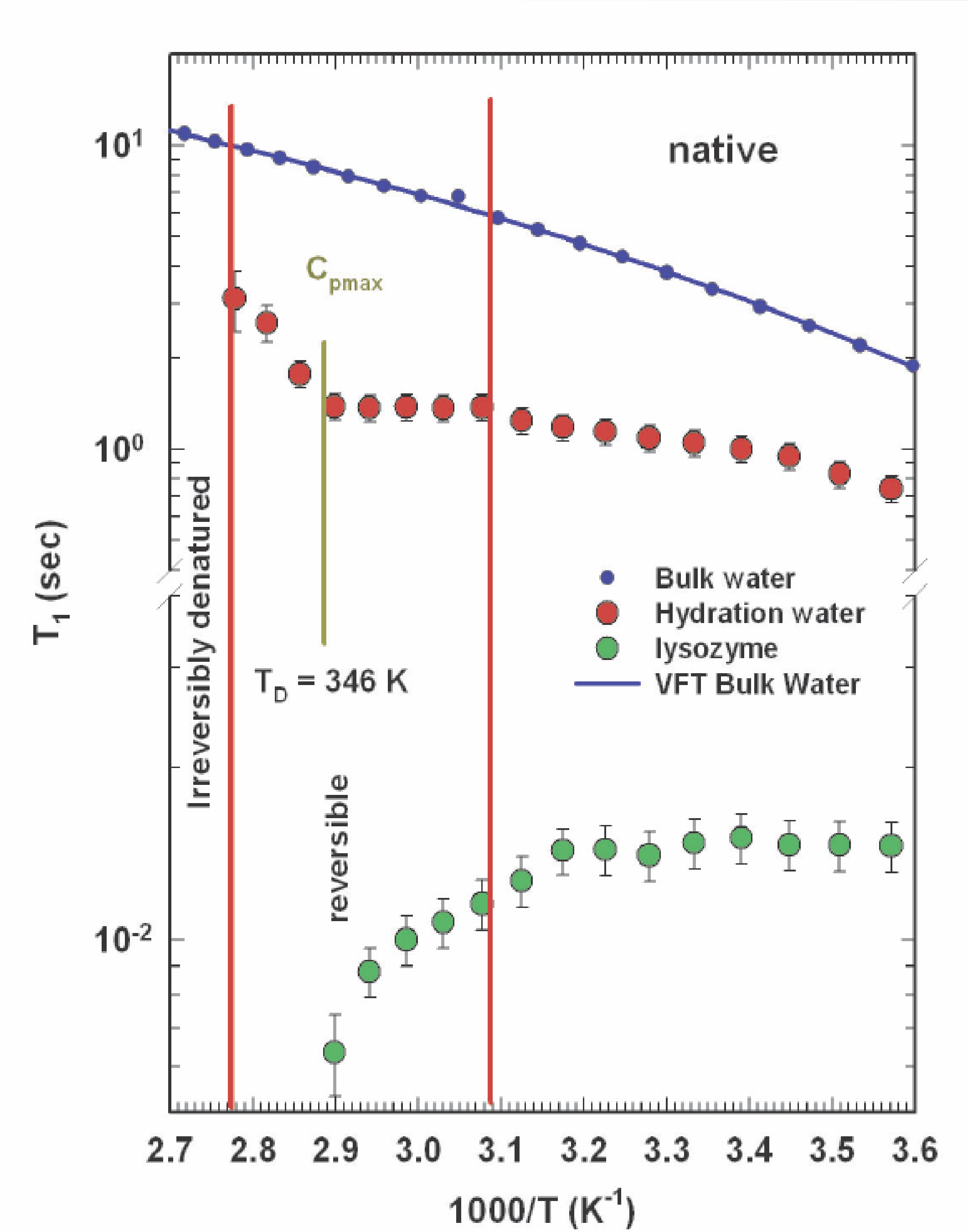


Evidence of the Low- and High-Temperature Dynamic Crossovers in Lysozyme Hydration Water



Violation of Stokes-Einstein Relation At and Below the Crossover Temperature

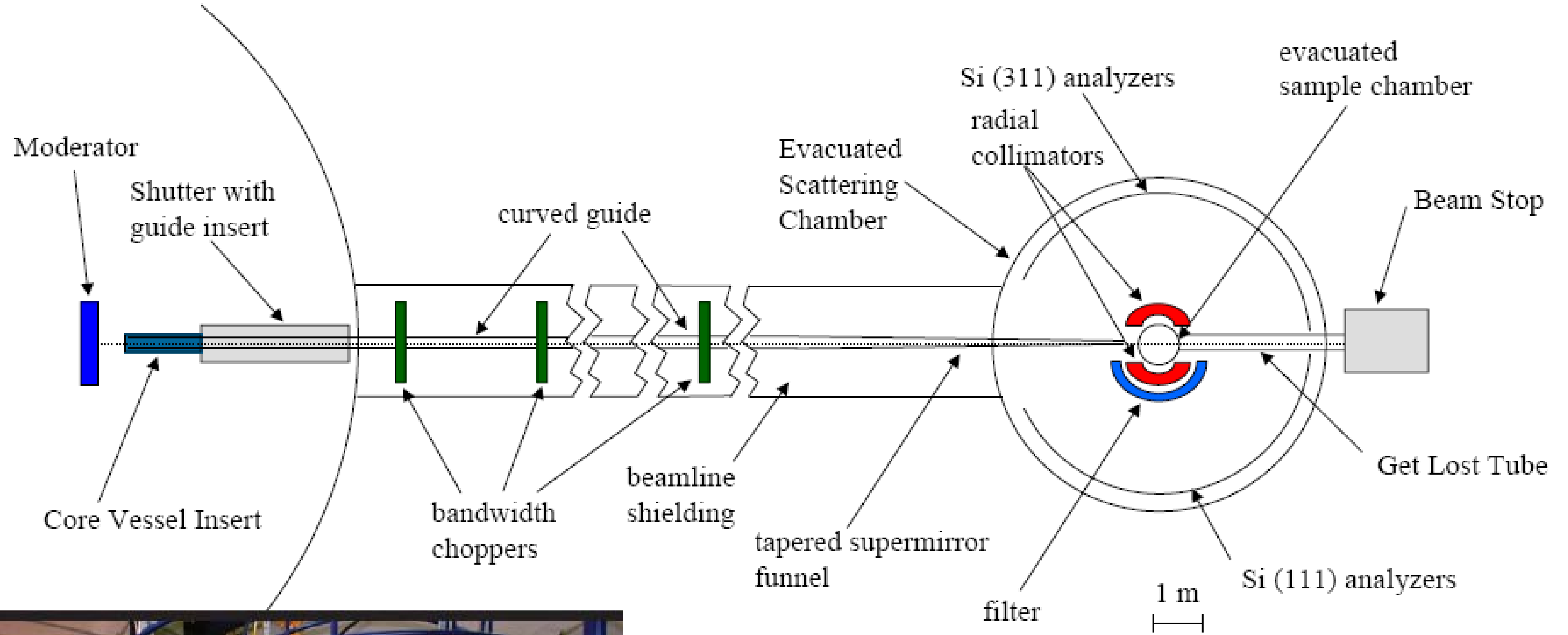




NMR T1 relaxation time as a function of 1/T, for protons in bluk water, lysozyme hydration water and lysozyme.

F. Mallamace, S.-H. Chen, et al, *JCP* **127**, 045104 (2007)

Backscattering Spectrometer (BASIS) of SNS



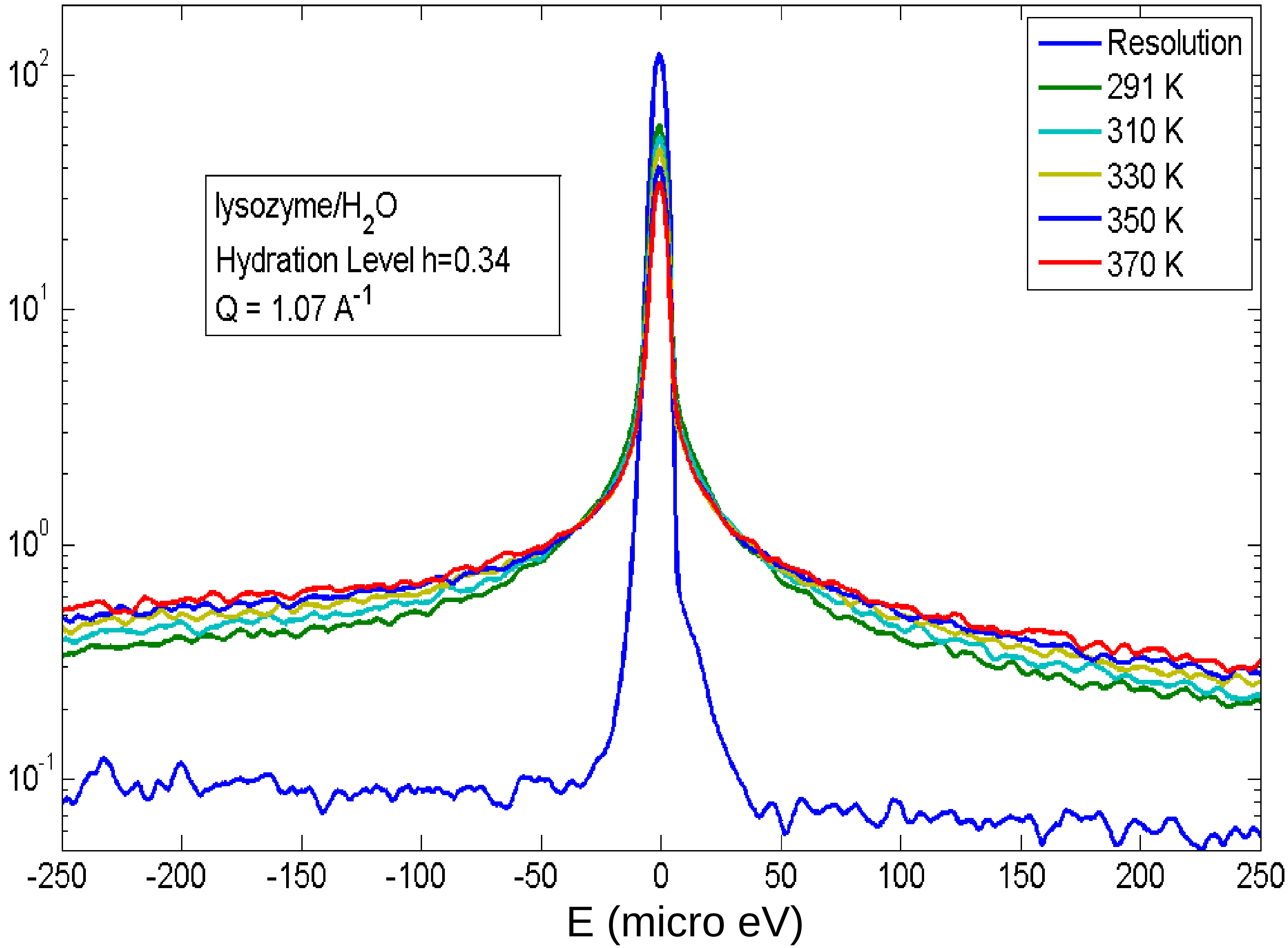
Si 111	
Elastic energy	2.08 meV
Bandwidth	±258 μeV
Resolution (elastic)	3 μeV
Q range (elastic)	0.17 $Å^{-1}$ < Q < 2.0 $Å^{-1}$
Solid angle	2.0 sr 4.0 sr (upgrade)

Si 311 (upgrade)	
Elastic energy	7.64 meV
Bandwidth	±1700 μeV
Resolution (elastic)	10 μeV
Q range (elastic)	0.35 $Å^{-1}$ < Q < 3.8 $Å^{-1}$
Solid angle	4.0 sr

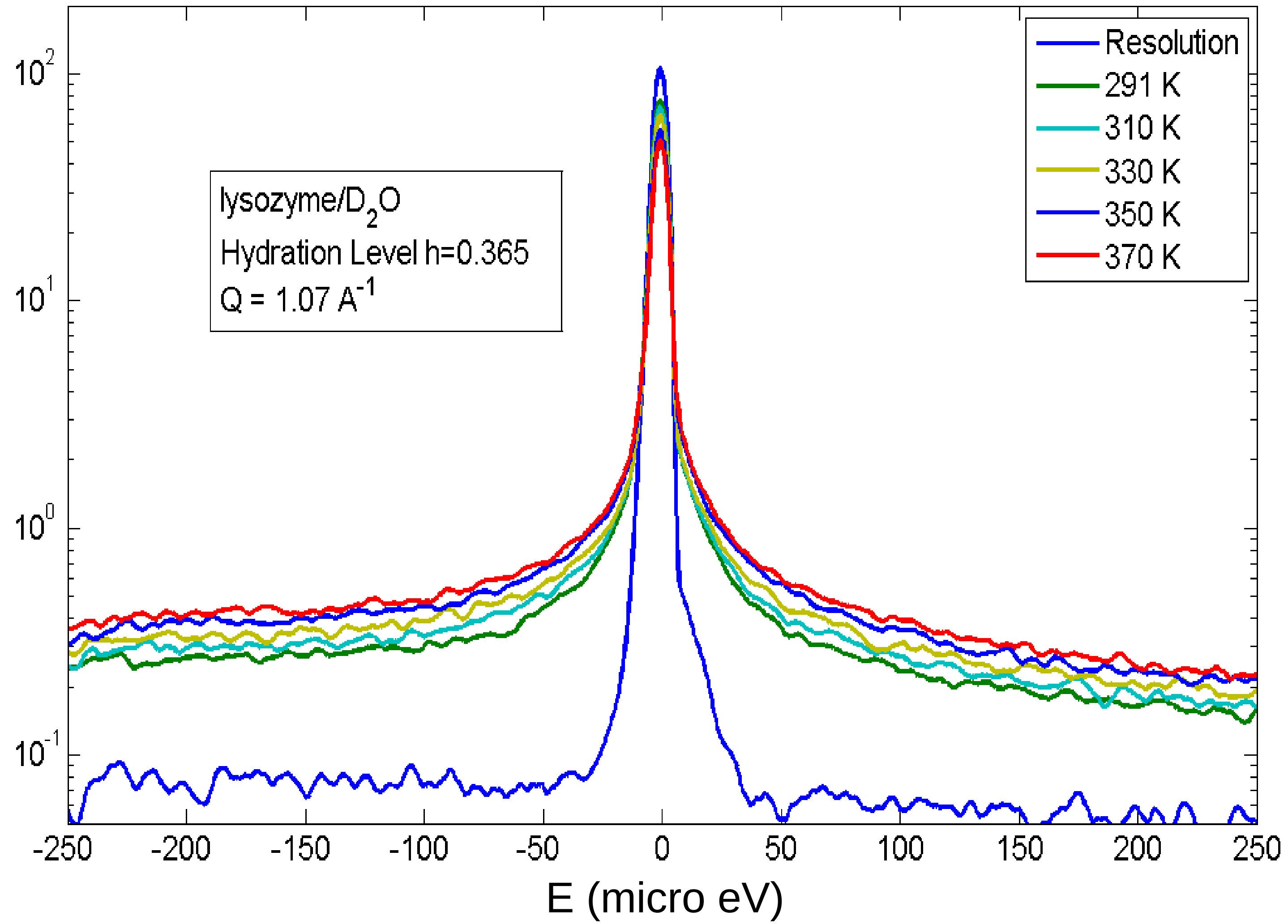
Available Q and Energy Resolution

Q ($Å^{-1}$)	Measured Resolution HWHM (μeV)
0.37	1.35
0.73	1.32
1.07	1.34
1.37	1.41
1.62	1.53
1.82	1.70
1.94	1.78

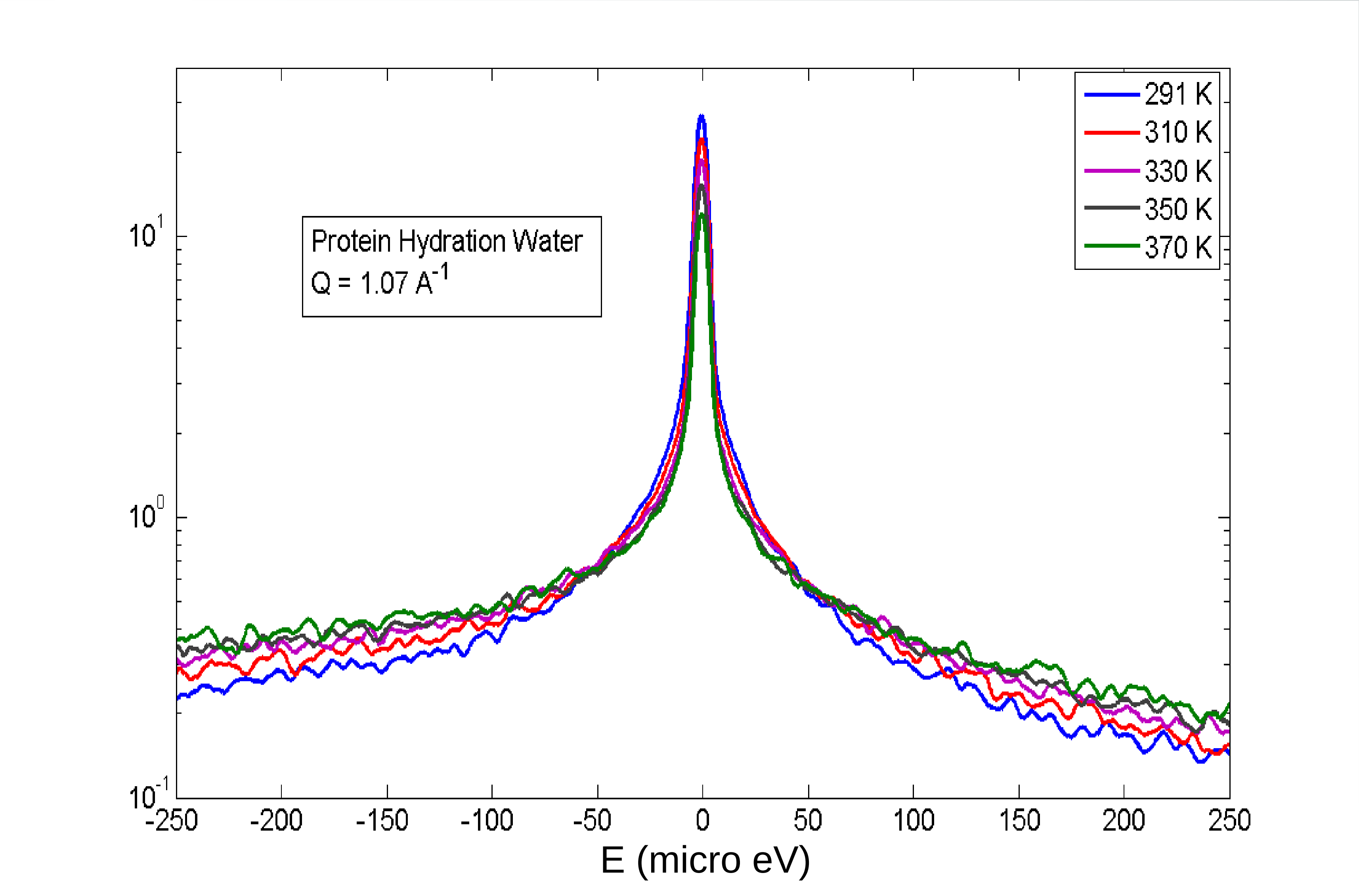
QENS Spectra of H_2O Hydrated Lysozyme



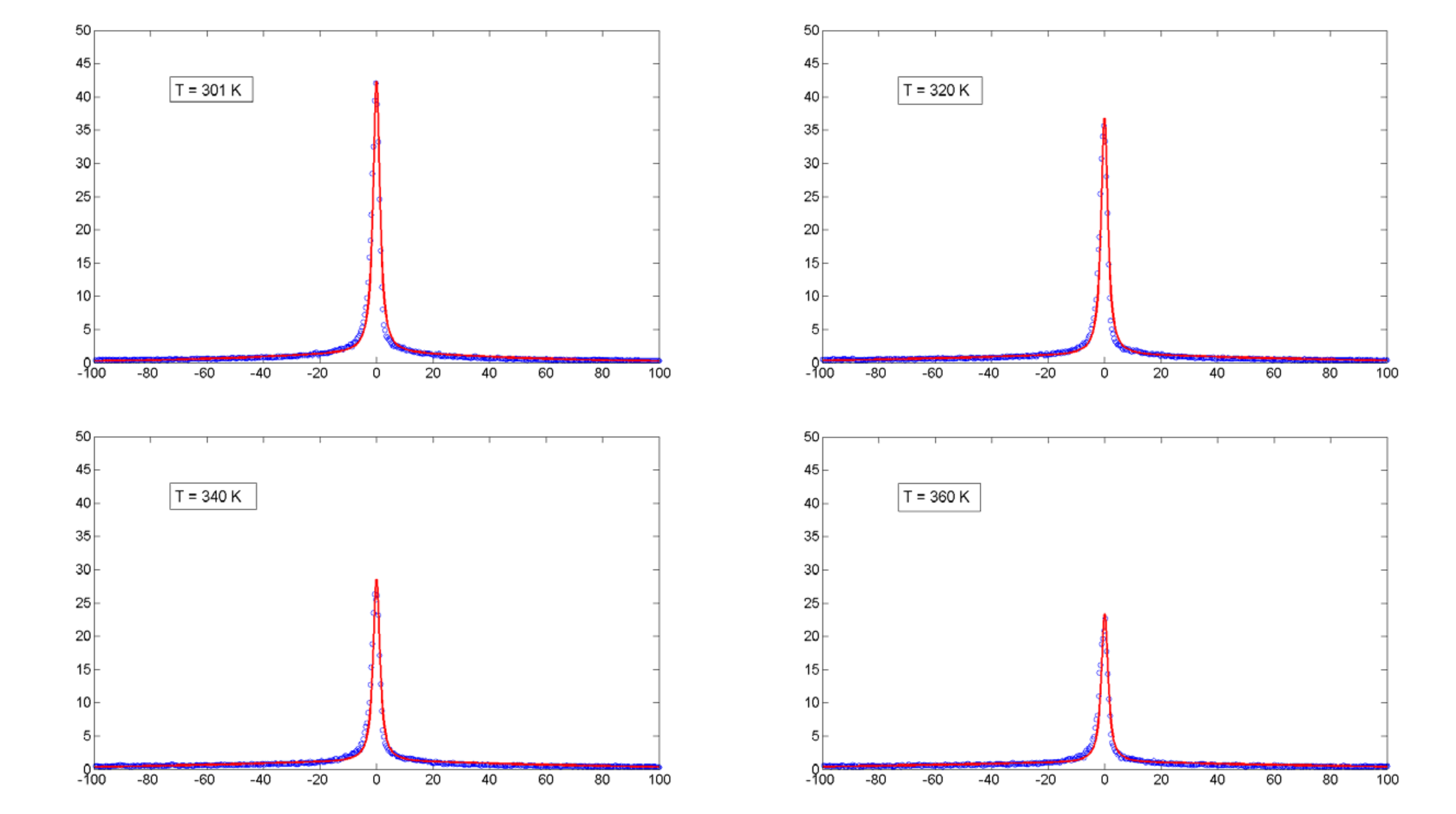
QENS Spectra of D_2O Hydrated Lysozyme



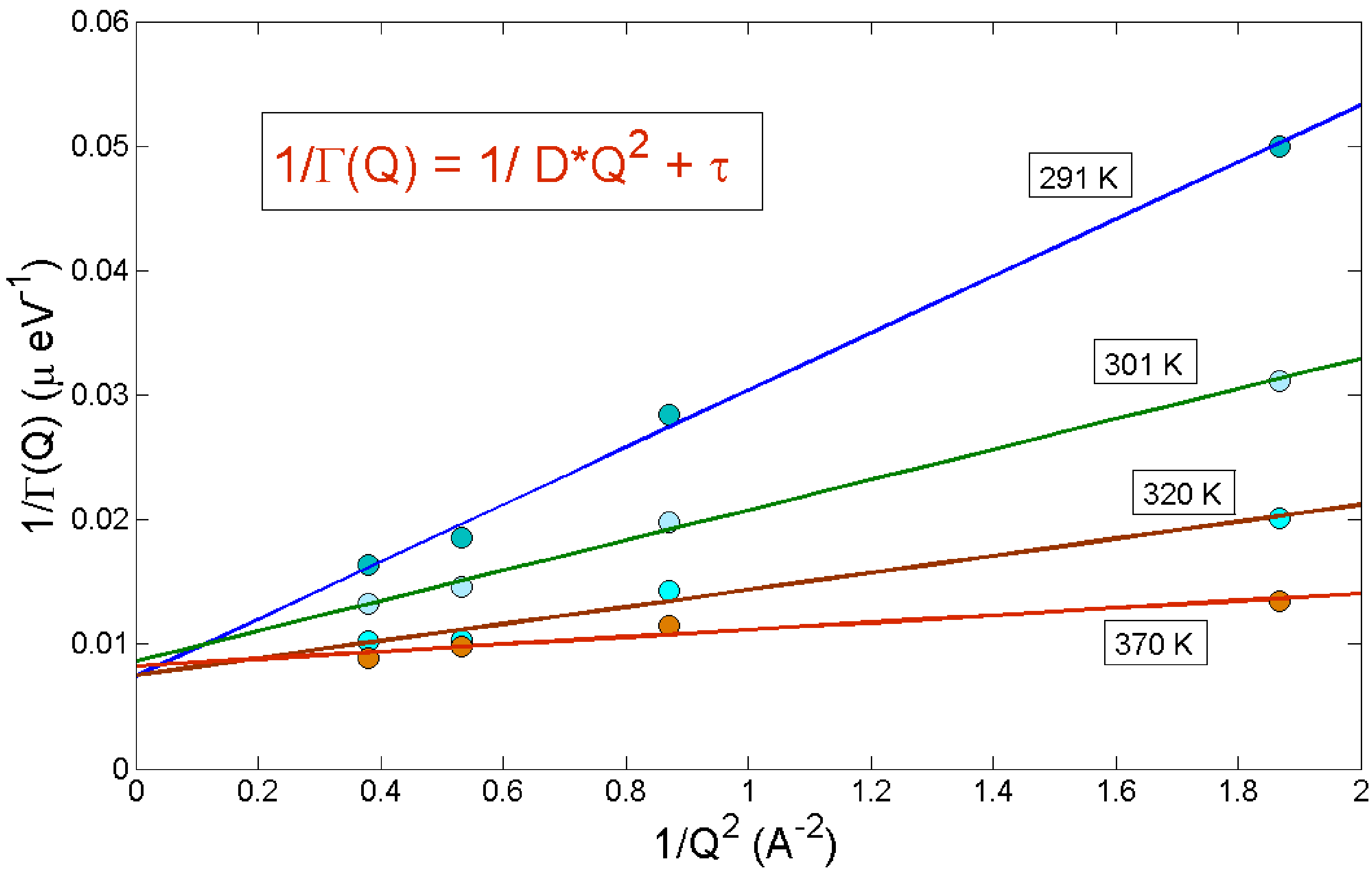
QENS Difference Spectra of H_2O and D_2O Hydrated Lysozyme



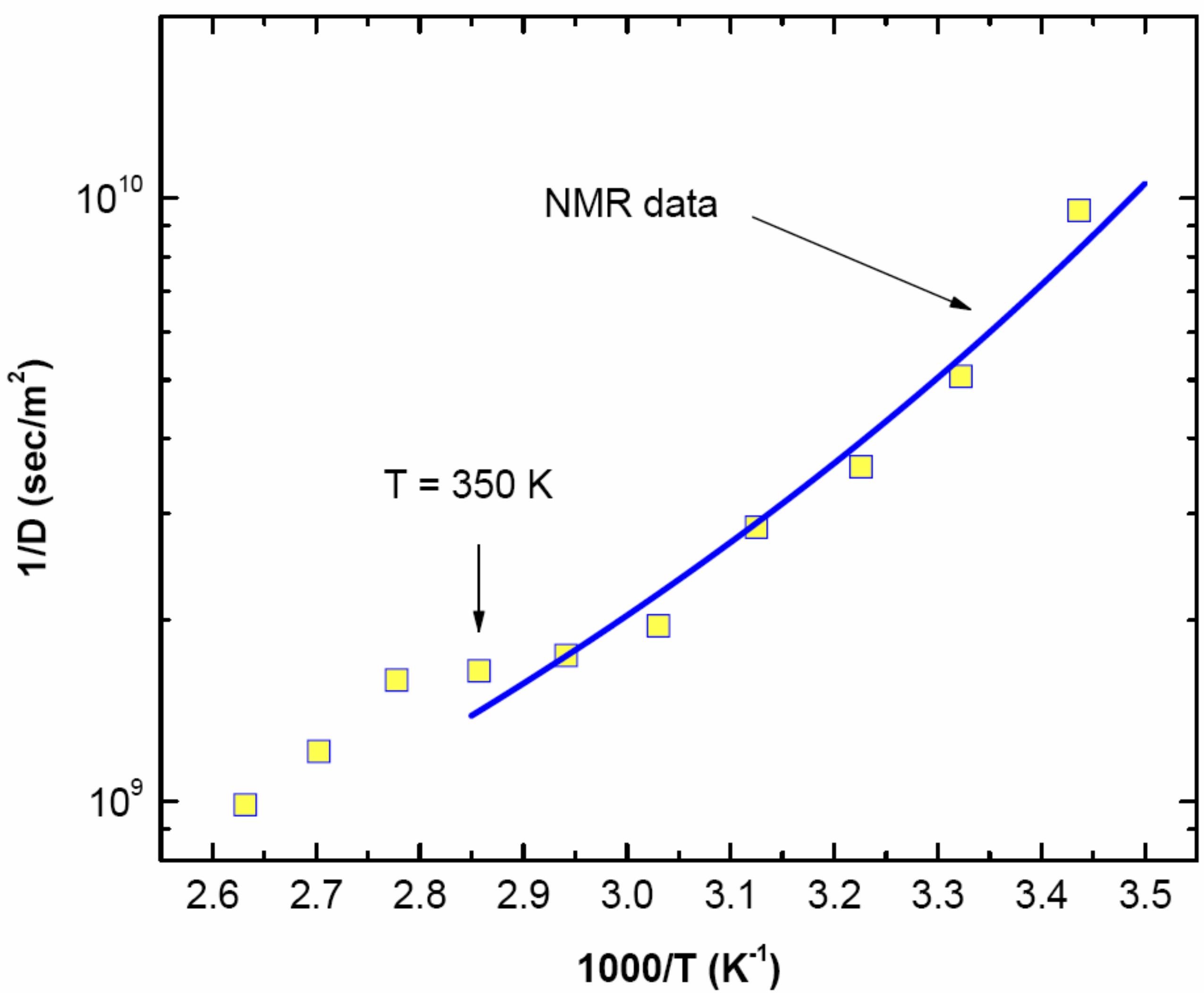
Two Lorentzian Fit of the Spectra



Analysis of Linewidth Based on Jump Diffusion Model



High-T Dynamic Crossover Phenomenon in Lysozyme Hydration Water



Conclusions

1. FTIR and NMR studies of lysozyme hydration water show the existence of two dynamic crossovers in the protein hydration water.
2. Below the low-temperature crossover, at about 220 K, the hydration water displays a fragile-to-strong dynamic crossover, resulting in the loss of the protein conformational flexibility.
3. Above the high-temperature crossover, at about 346 K, where the protein unfolds, the dynamics of the hydration water appears to be dominated by the non-hydrogen-bonded fraction of water molecules.
4. Our recent experiment done in BASIS confirms the existence of the high temperature dynamic crossover in protein hydration water.