NMR at Cryogenic Temperatures

Tony Horsewill

School of Physics & Astronomy

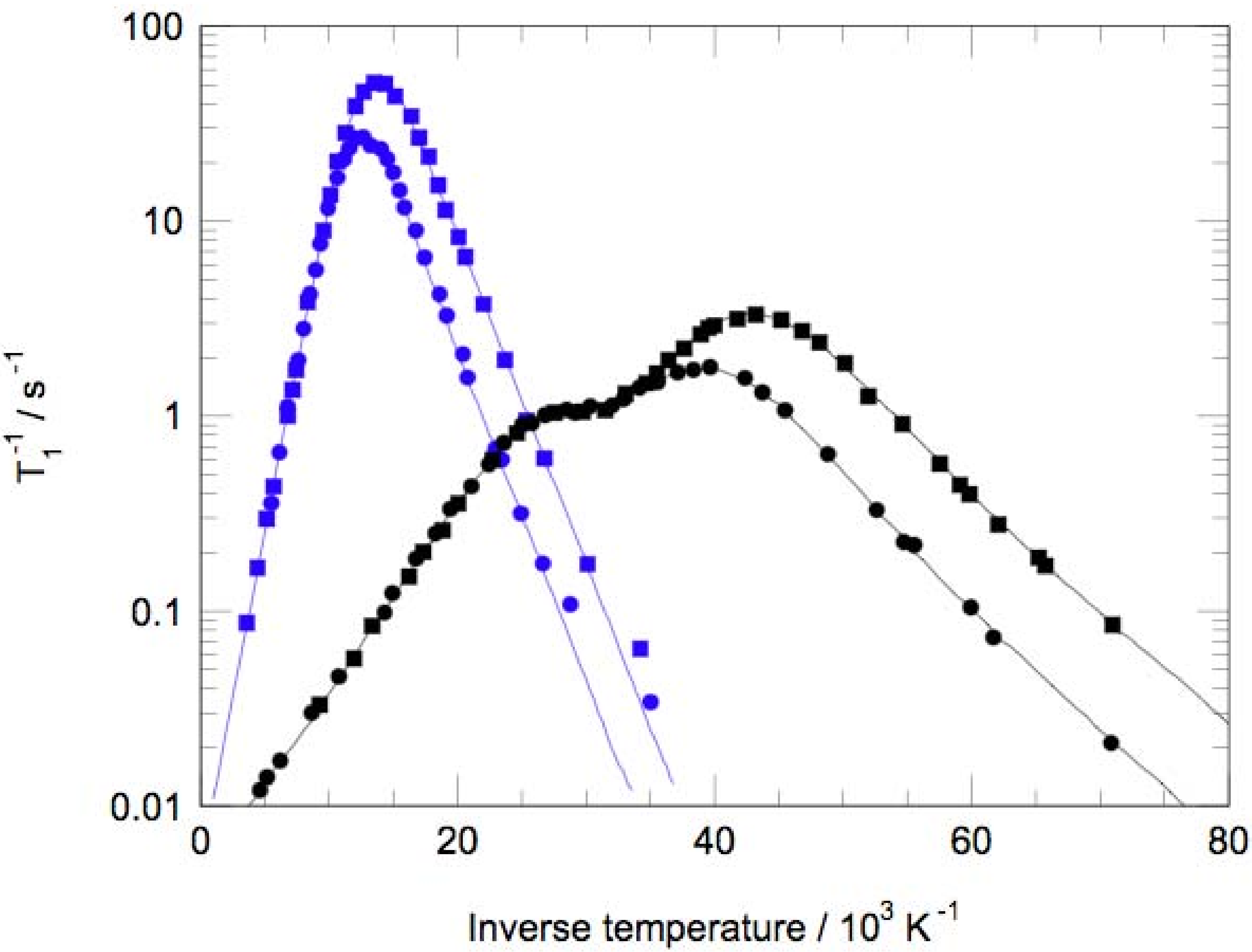
NMR at Cryogenic Temperatures

Typically liquid helium temperatures but including

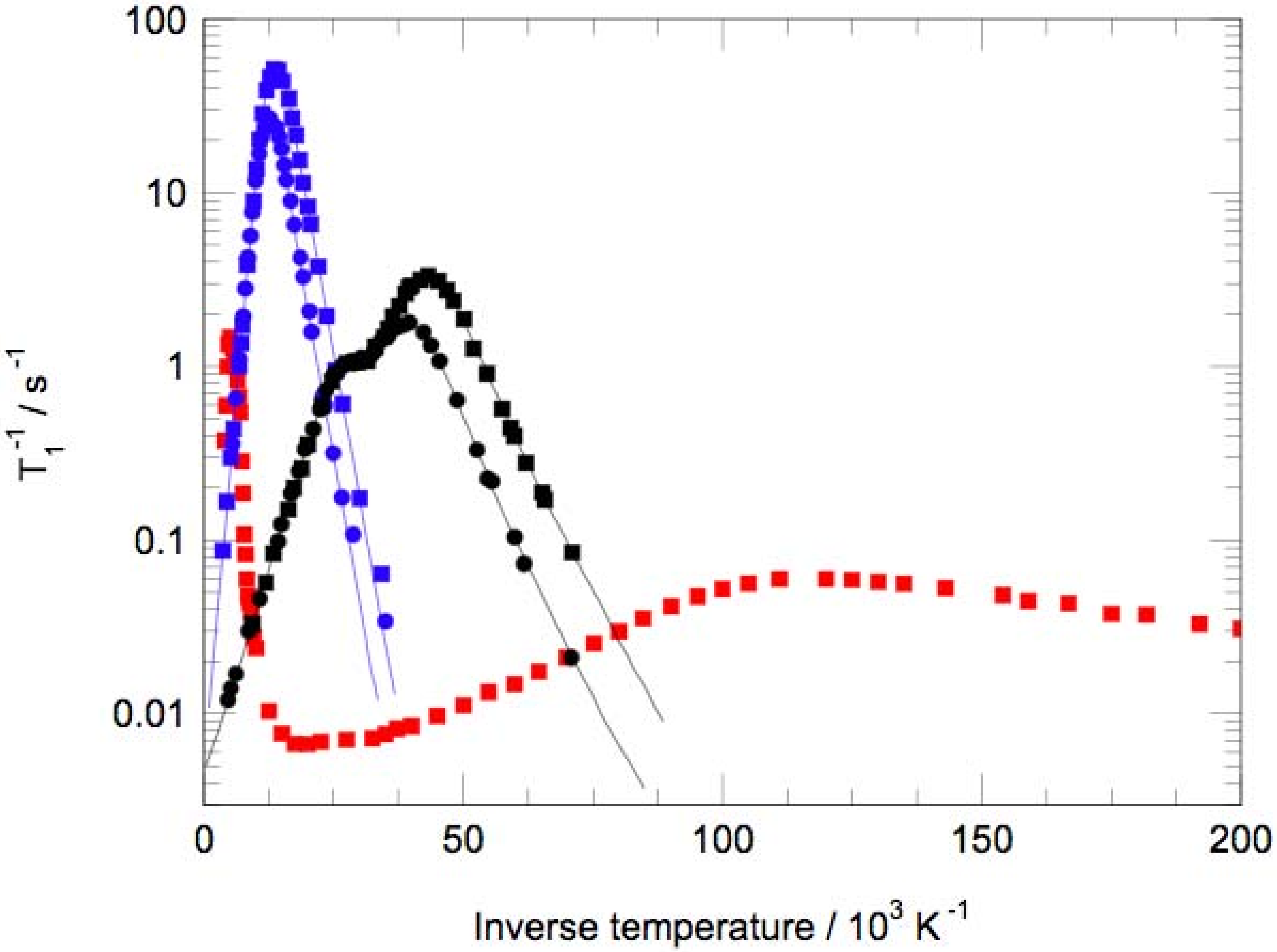
T < 100K

- *Quantum Tunnelling Dynamics*
- *Exploitation of magnetic field dependence*
- *'Novel' polarisation transfer effects*

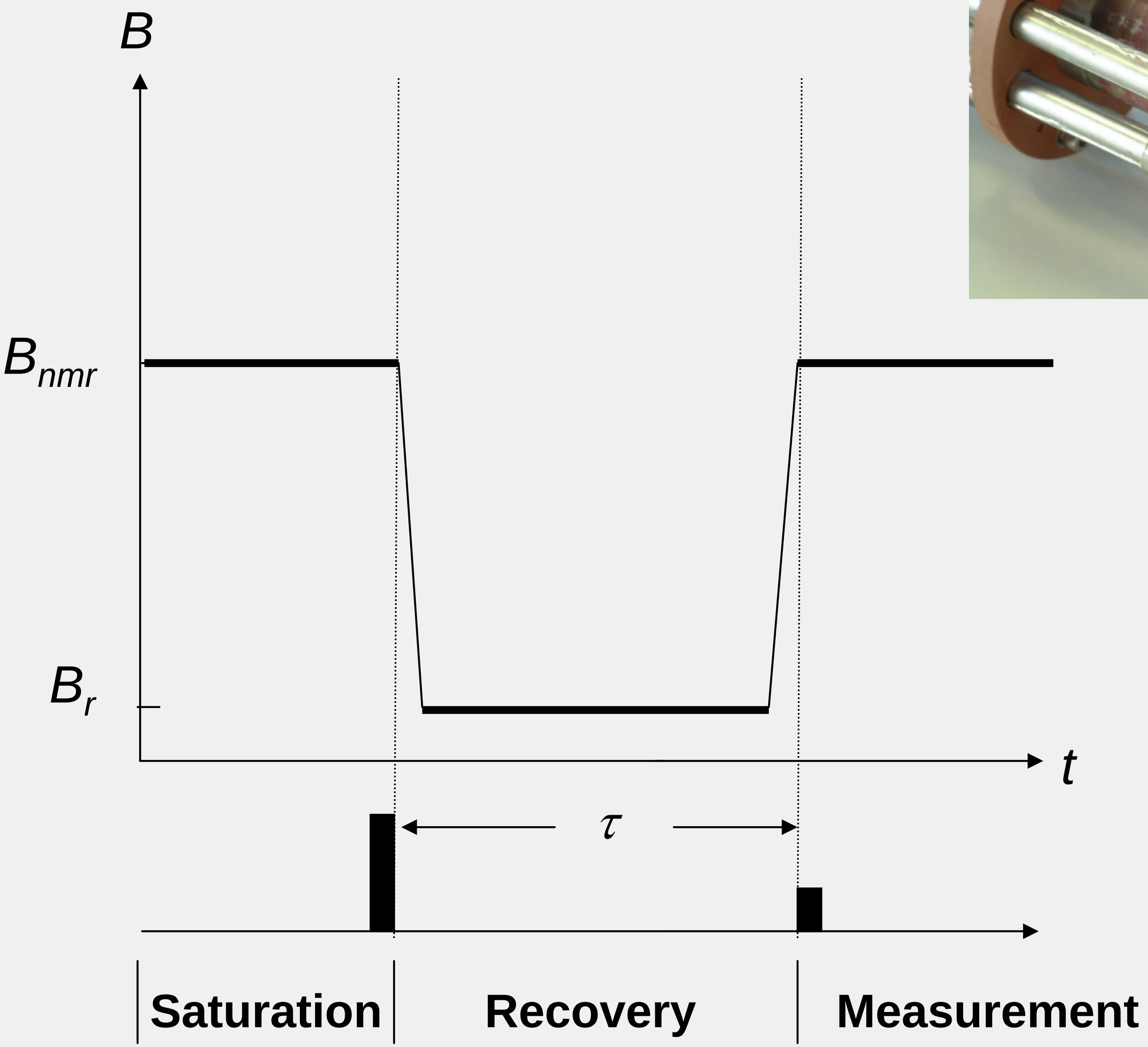
NMR Relaxometry

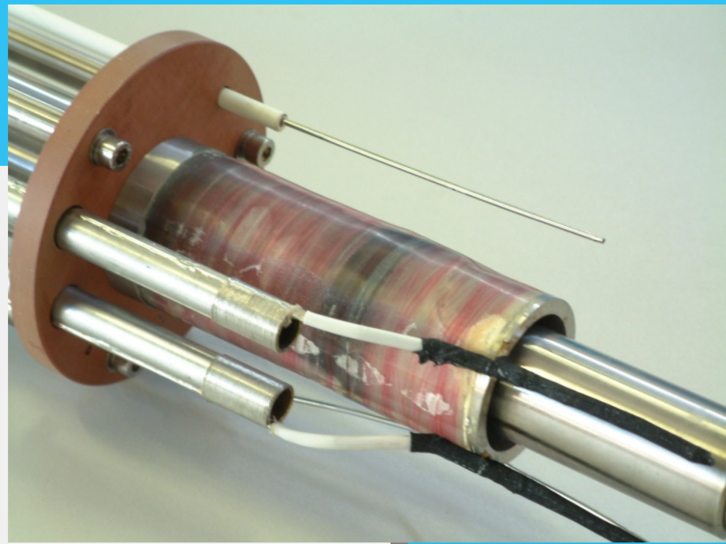


NMR Relaxometry



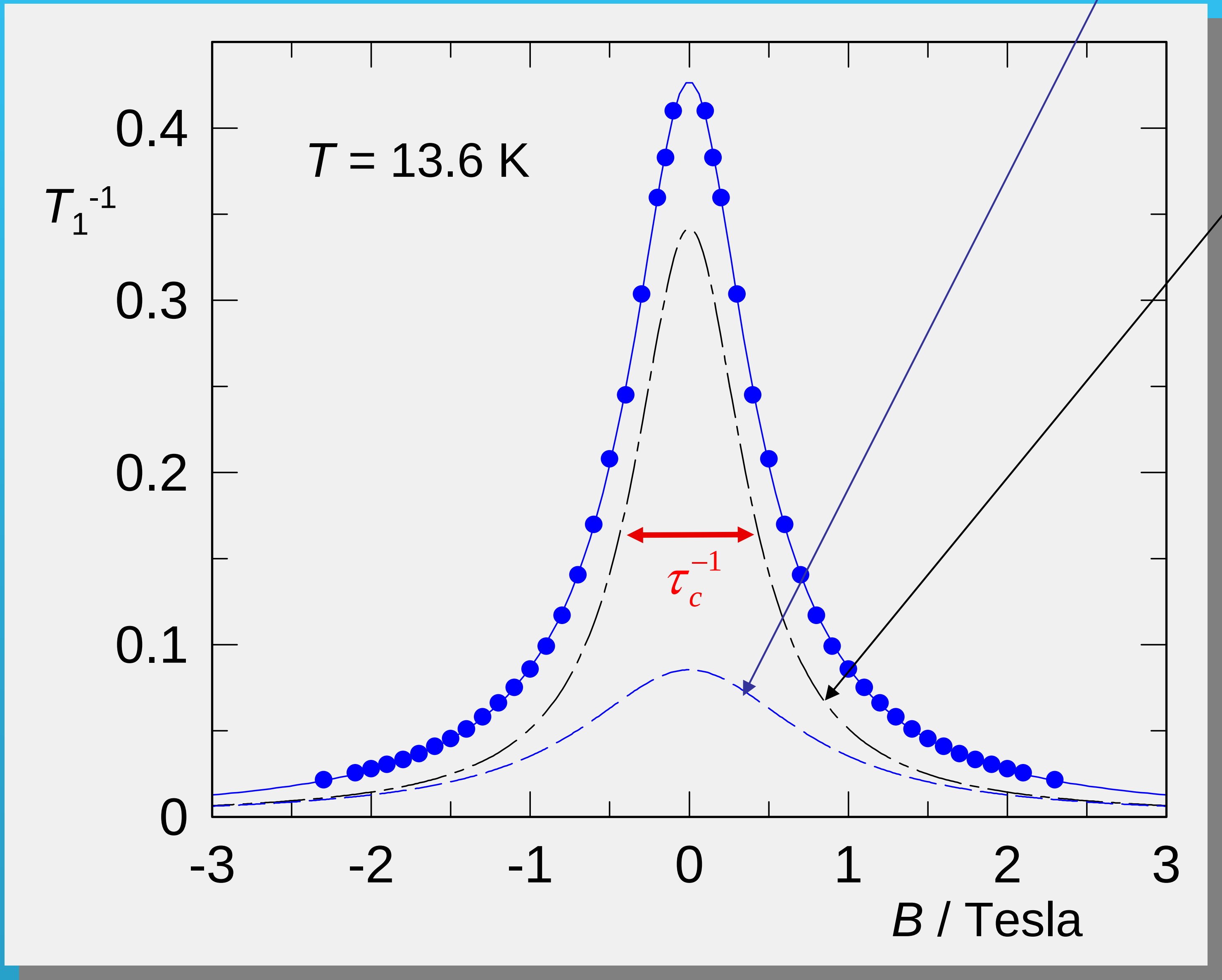
Field-Cycling NMR Relaxometry





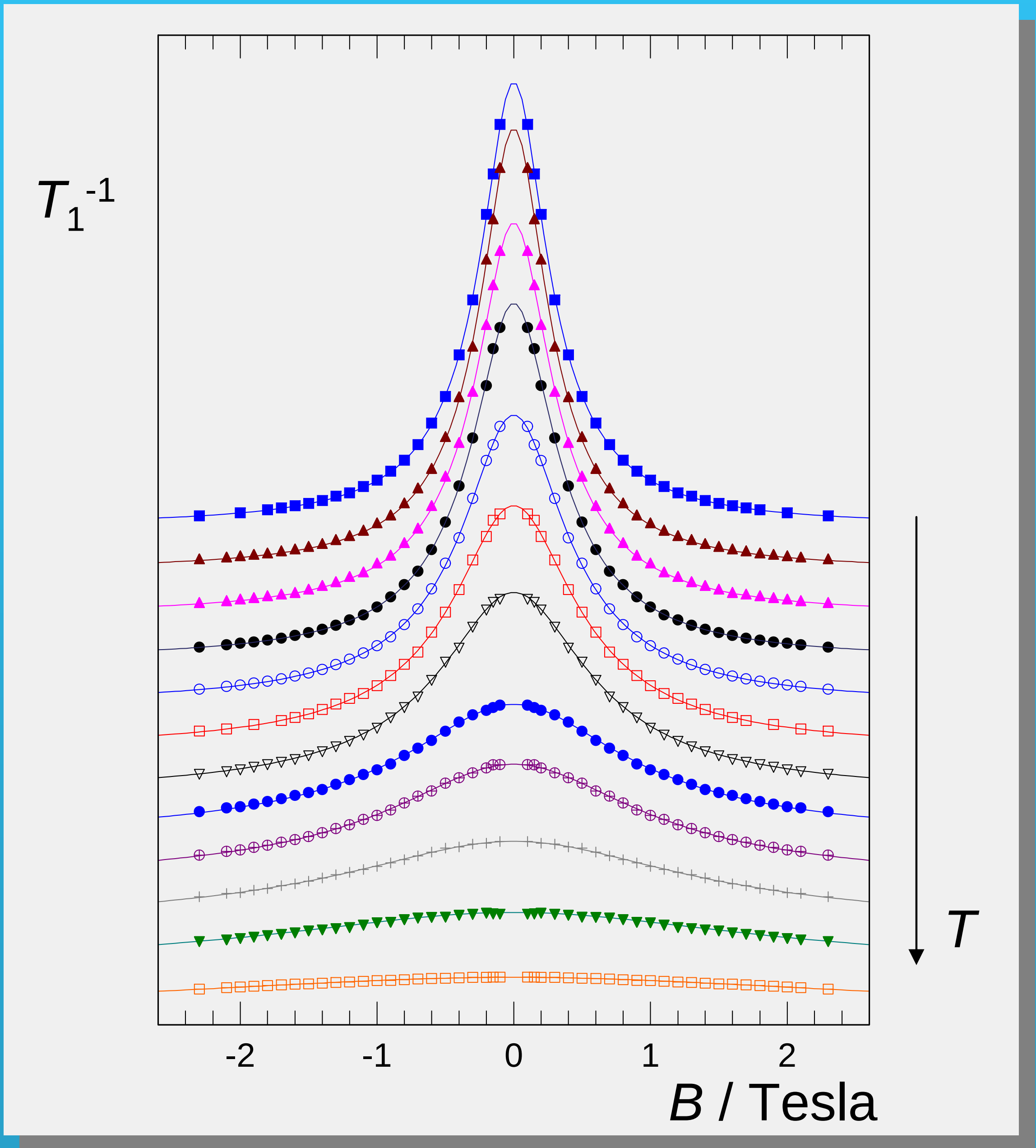
Spectral Density: T_1^{-1} vs B

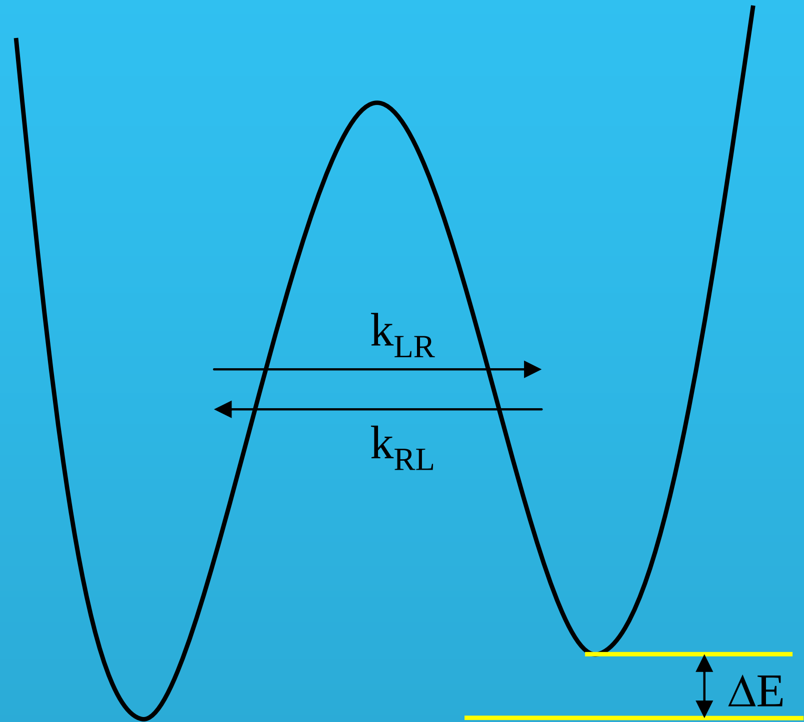
$$T_1^{-1} = C_D\left[\frac{\tau_c}{\left(1+\omega^2\tau_c^2\right)} + \frac{4\tau_c}{\left(1+(2\omega)^2\,\tau_c^2\right)}\right]$$

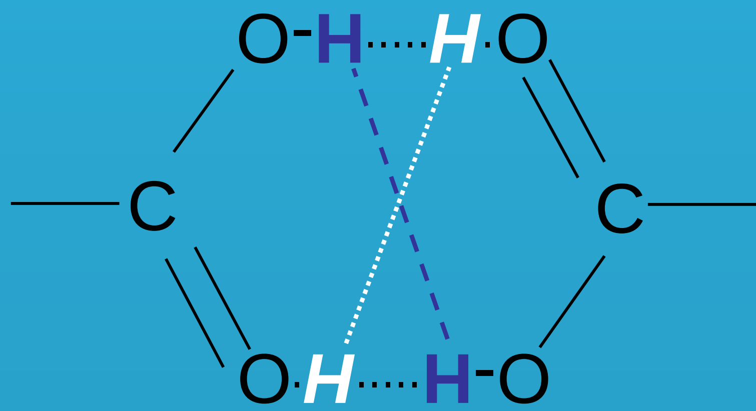


τ_c^{-1}=1.22×10^8 s^{-1}

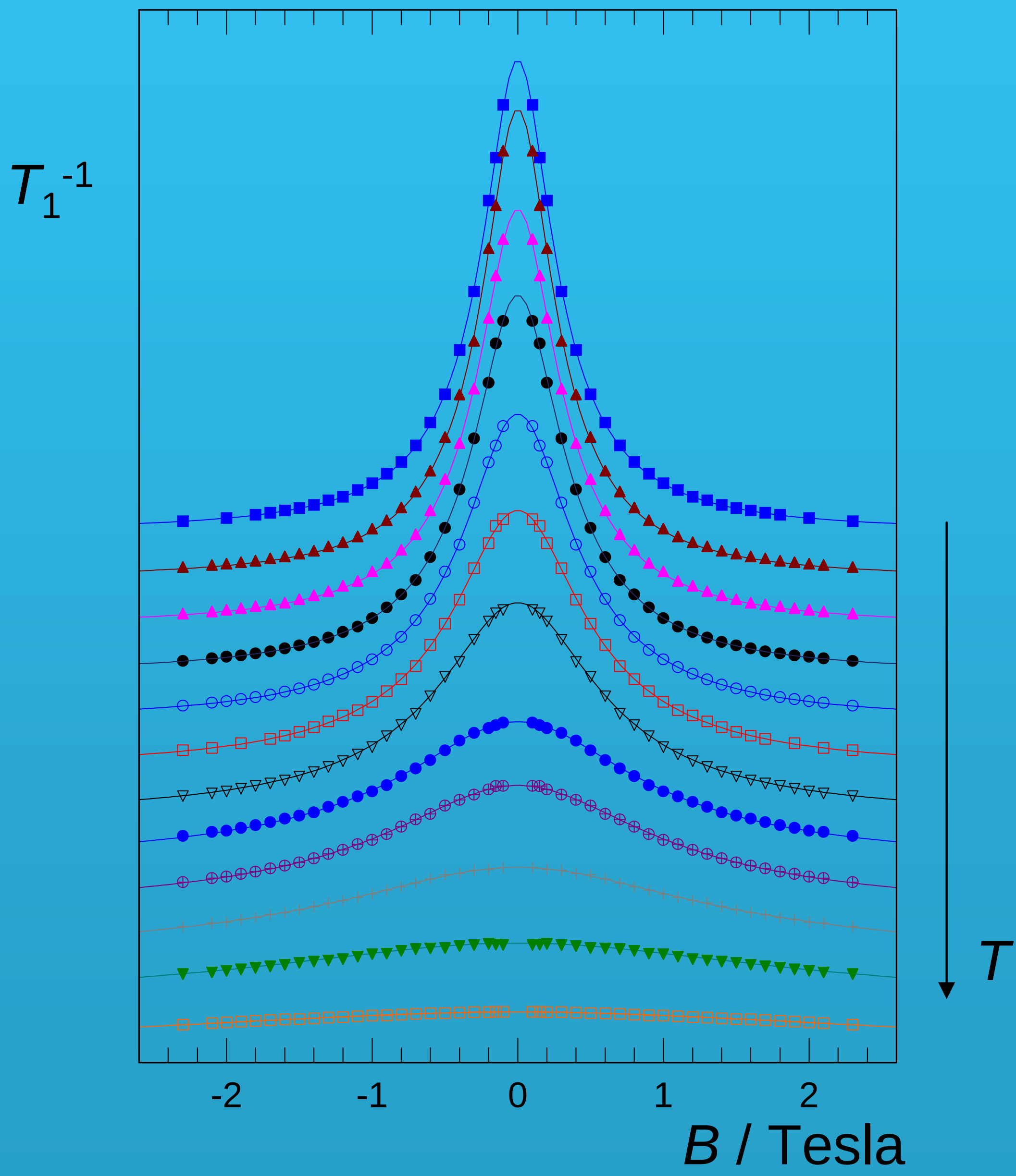
Proton transfer in the hydrogen bond: incoherent tunnelling

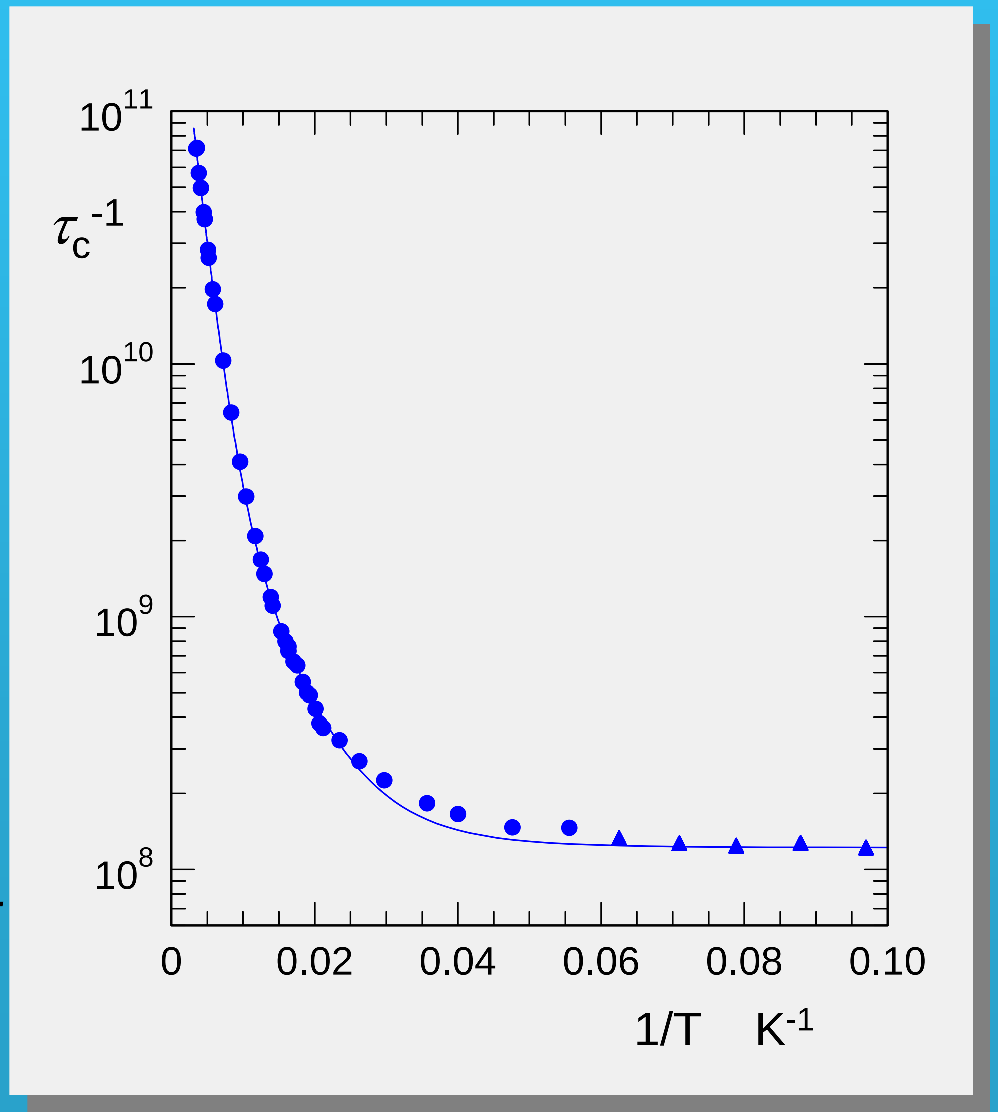




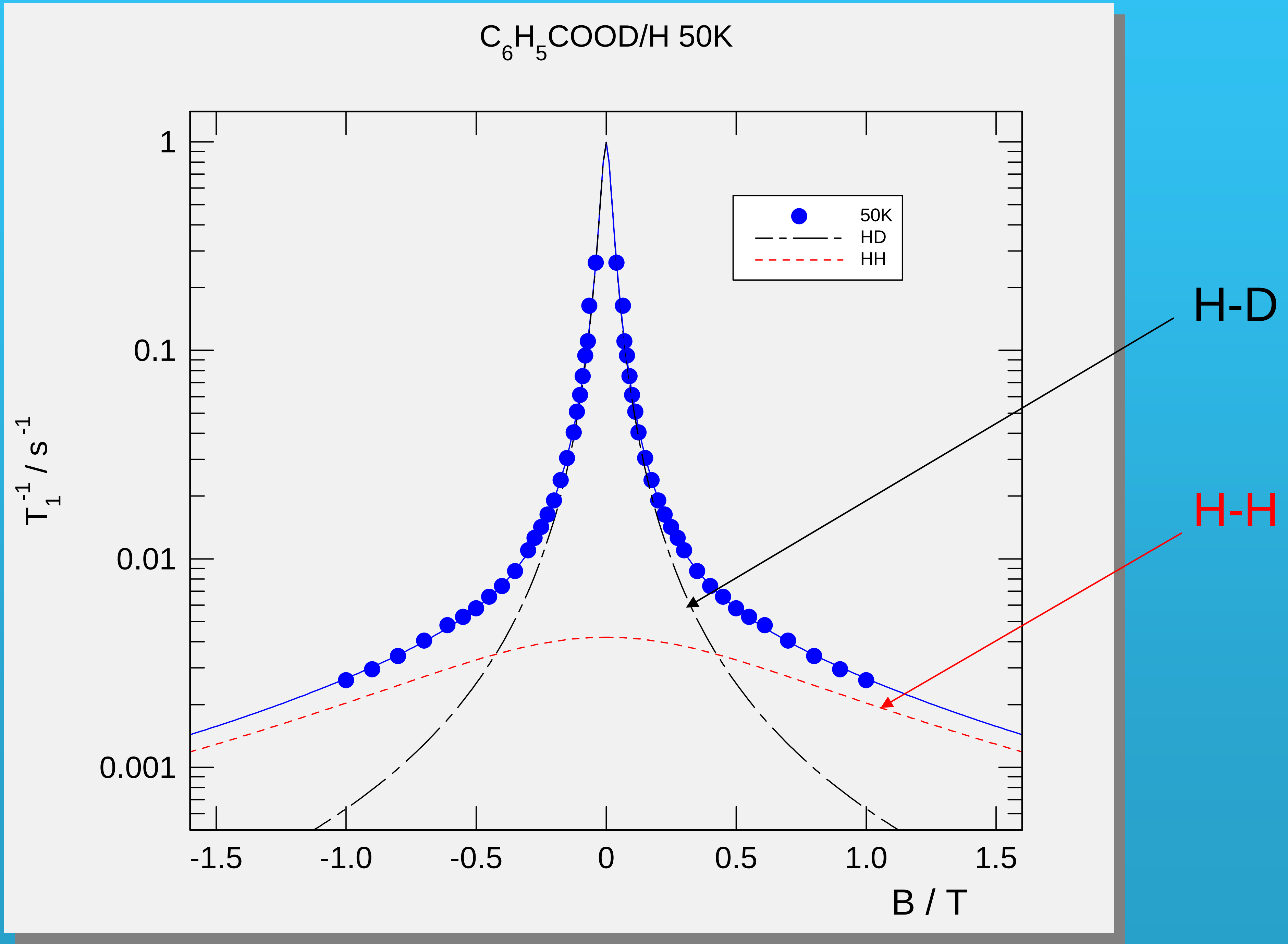


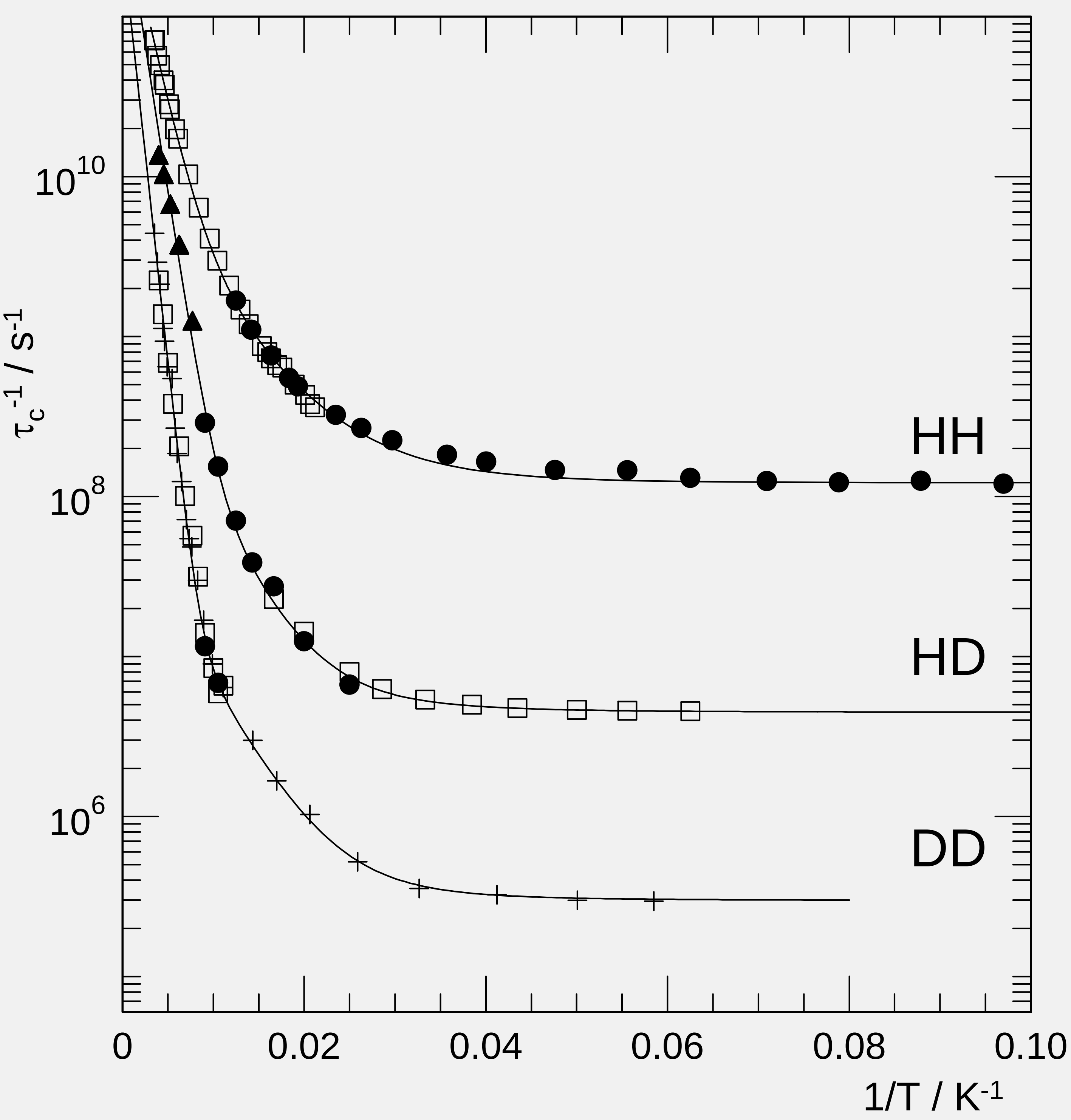
Proton transfer in the hydrogen bond: the quantum-to-classical transition





^2H Isotope Effect





k_0

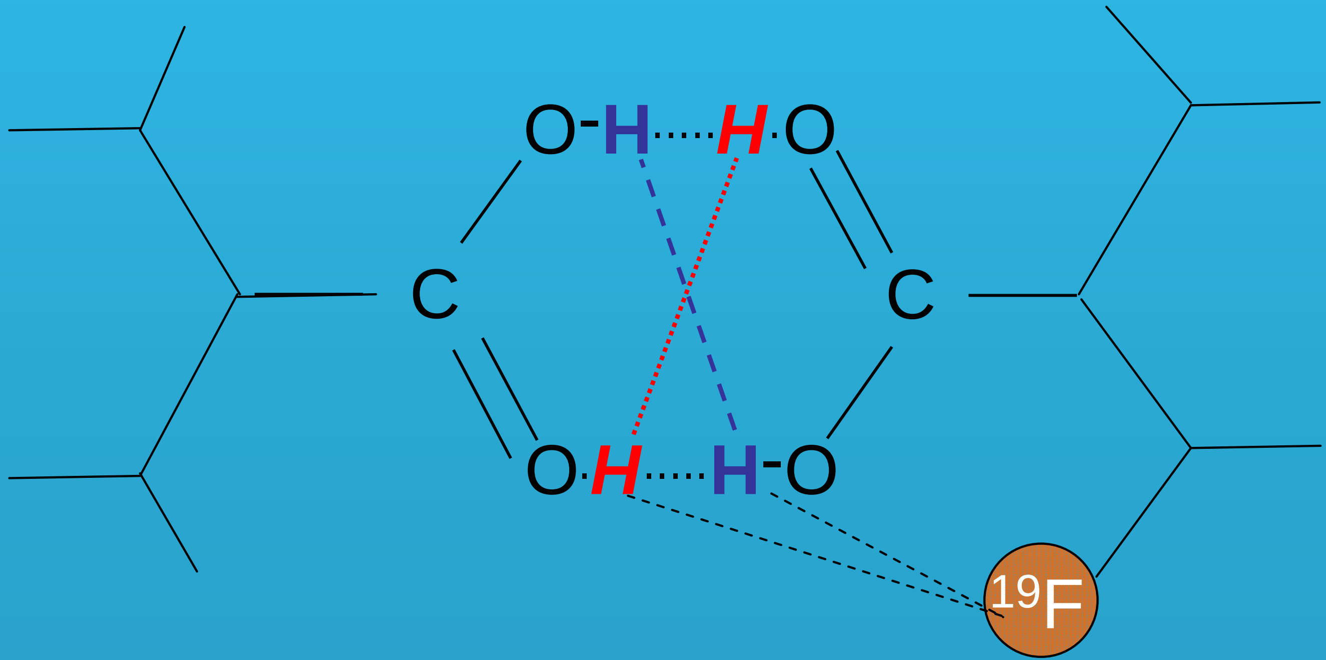
1.22×10^8 s^{-1}

4.5×10^6 s^{-1}

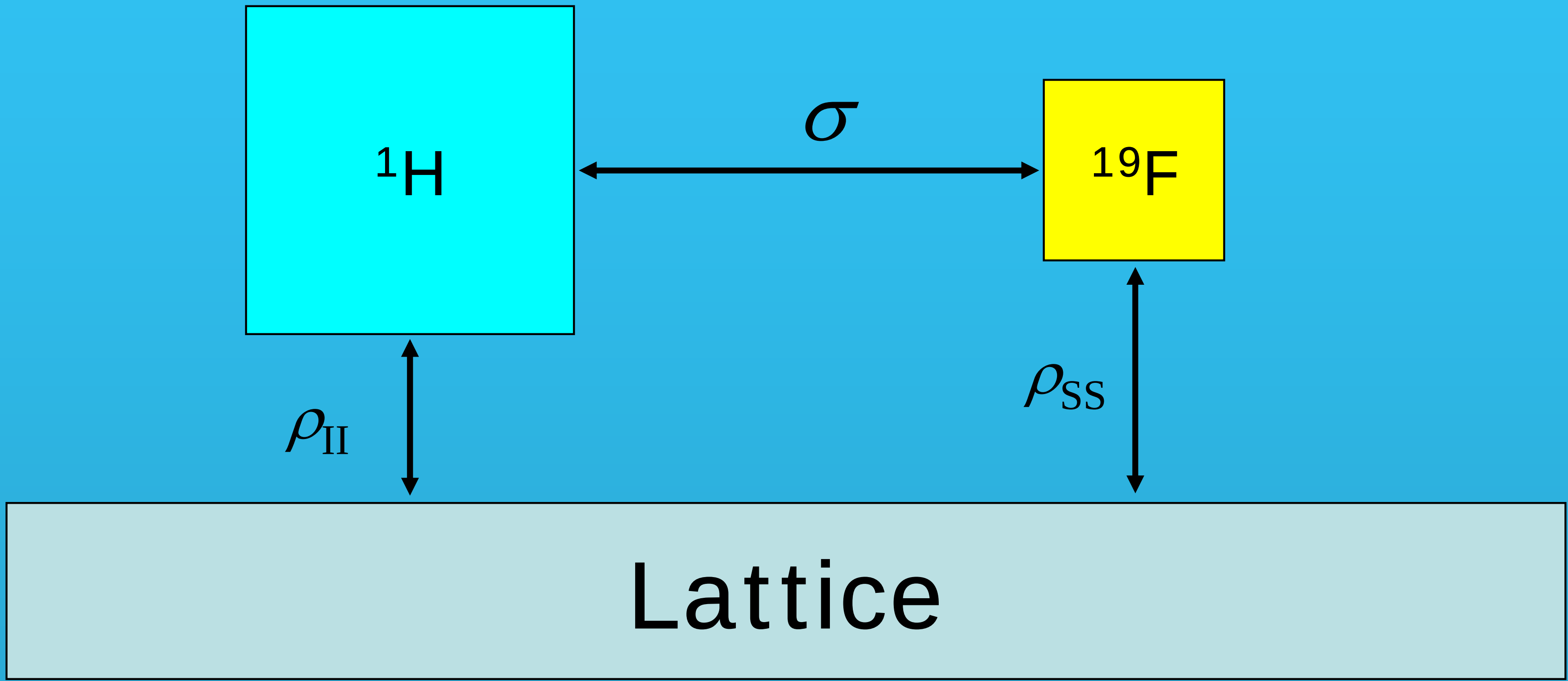
$\approx3\times10^5$ s^{-1}

Heteronuclear Interactions: polarisation transfer etc

Tetrafluoroterephthalic acid

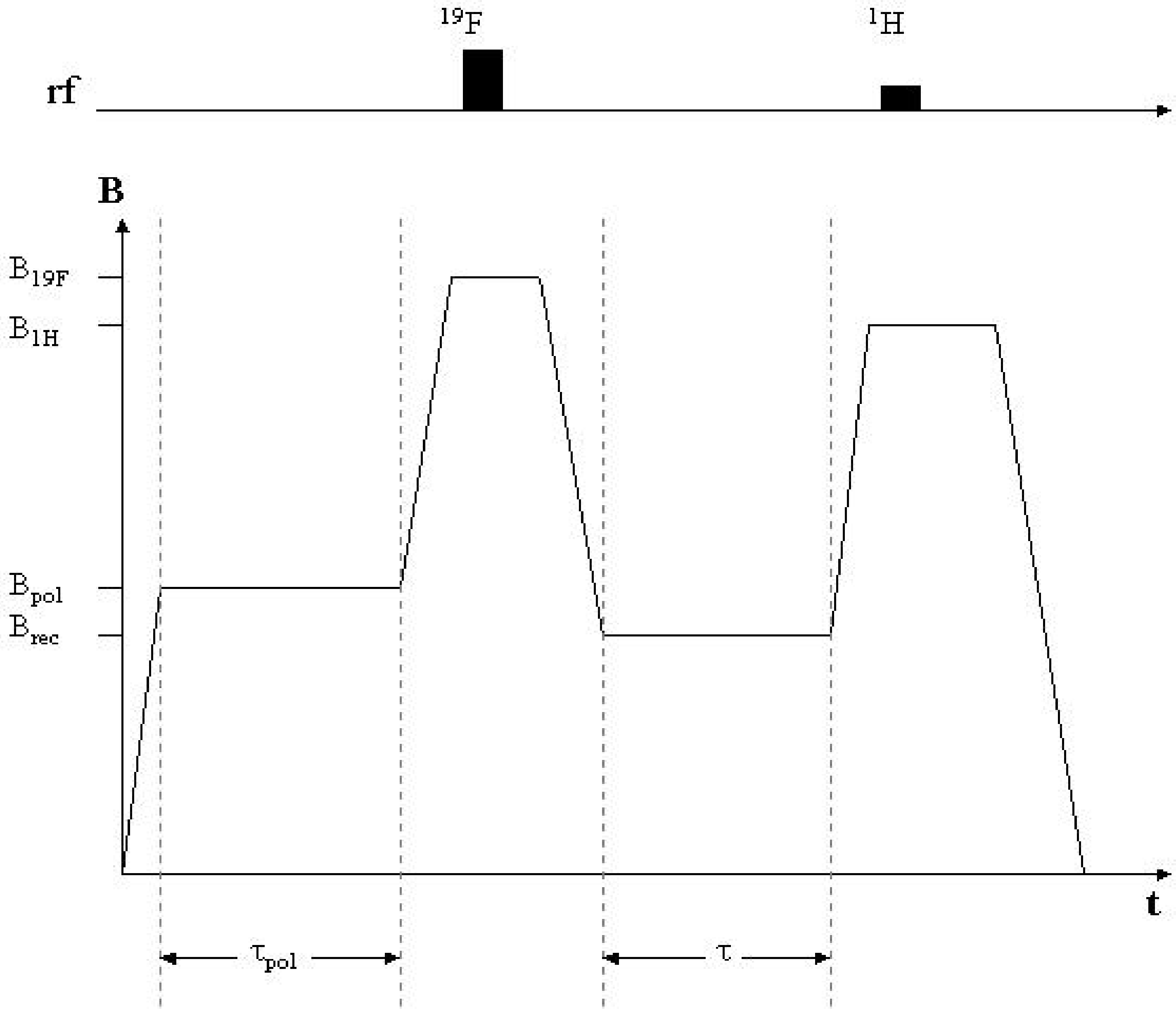


Heteronuclear spin system: cross-relaxation



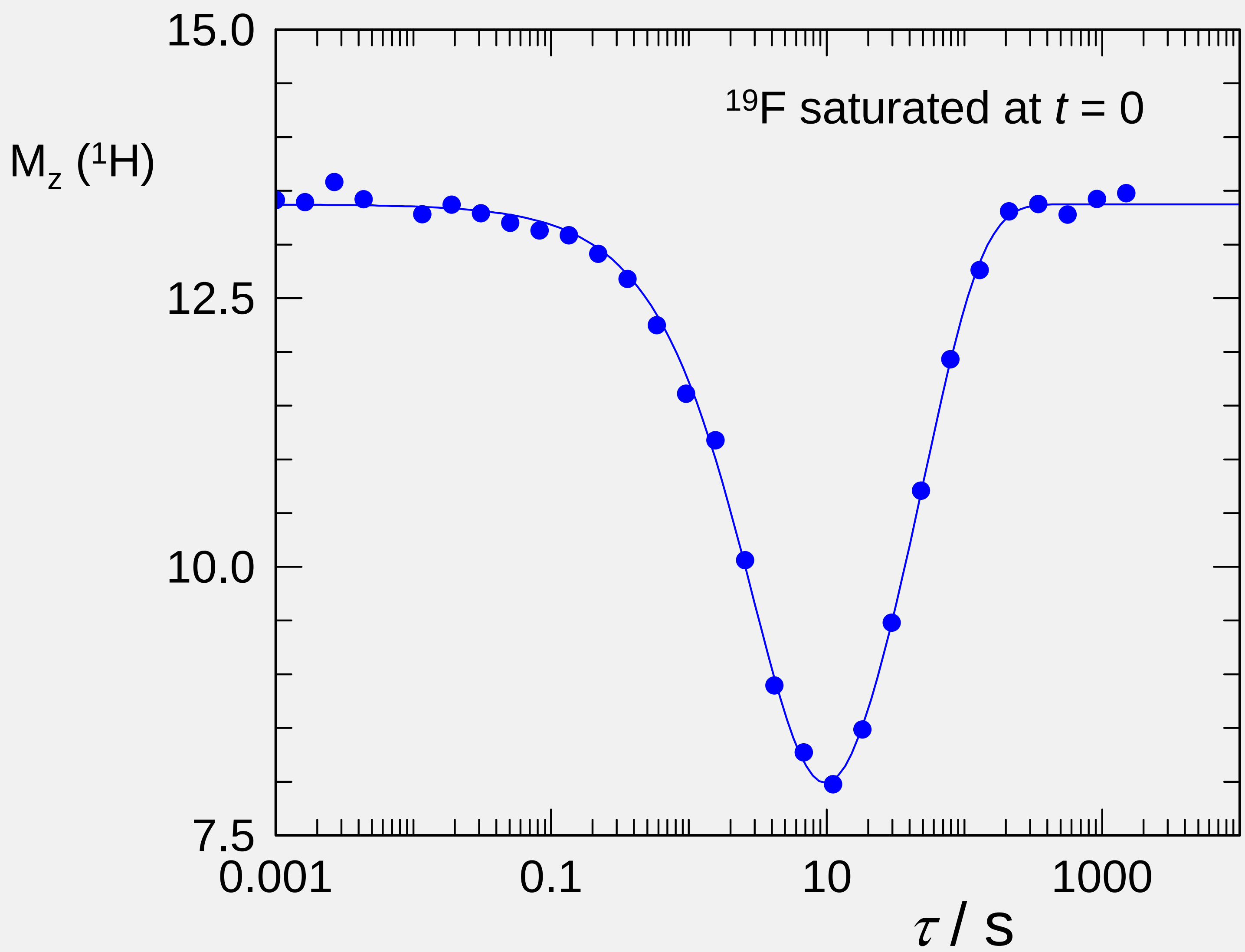
Off-diagonal:

$$\sigma \propto \left(-L\left(\omega_I - \omega_S\right) + 6L\left(\omega_I + \omega_S\right)\right)$$

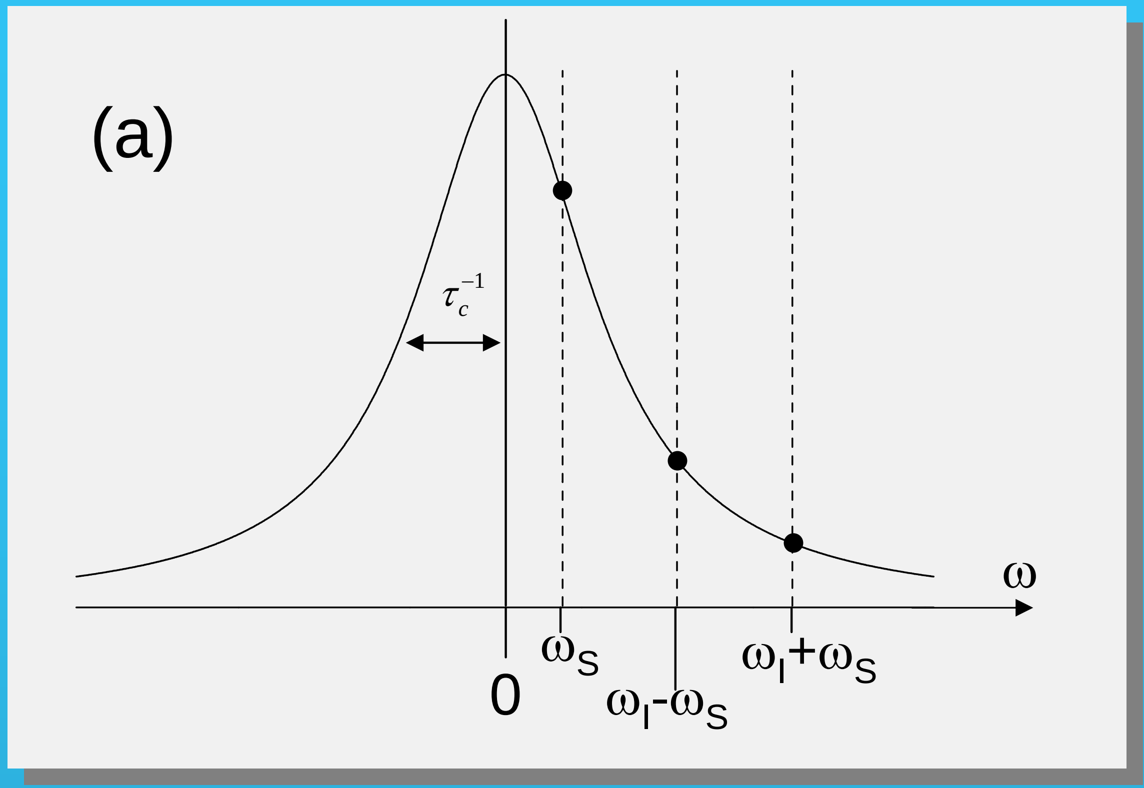


19F
1H
rf
B
B19F
B1H
Bpol
Brec
t
τpol
τ

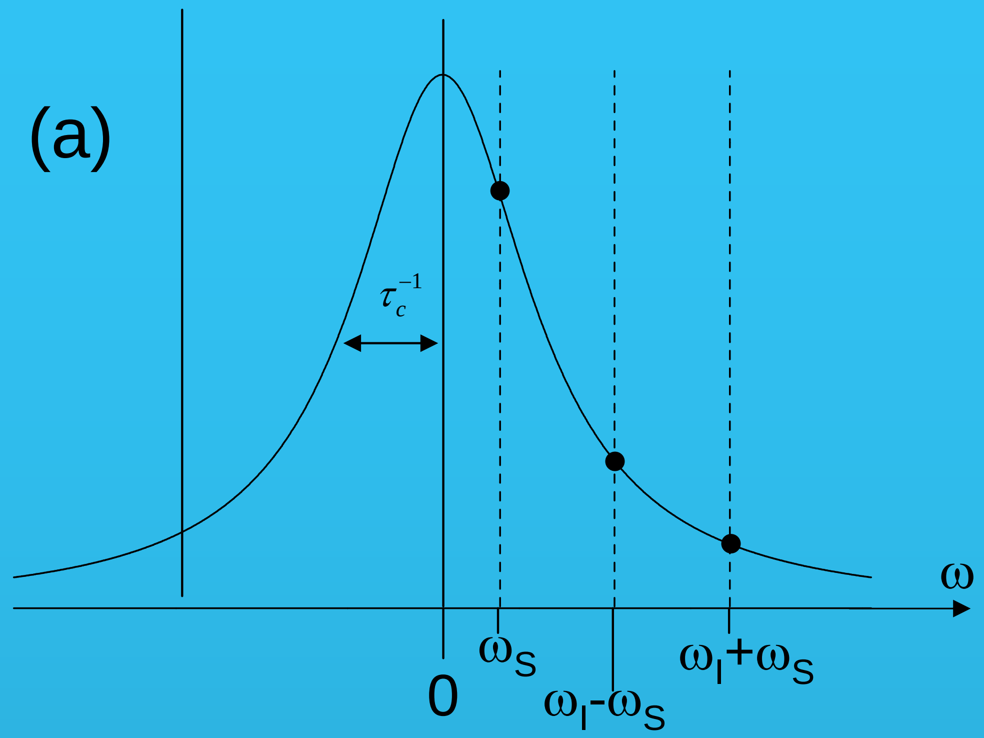
Cross-relaxation: ^{19}F - ^{1}H

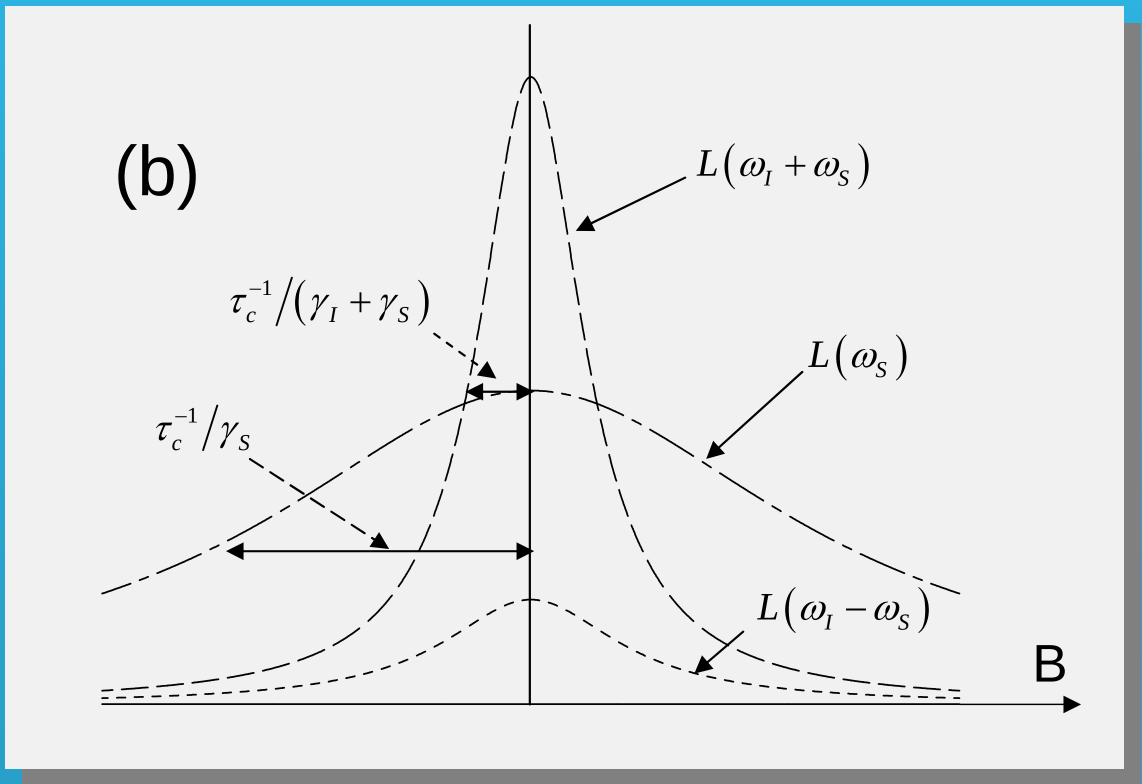


vs. frequency



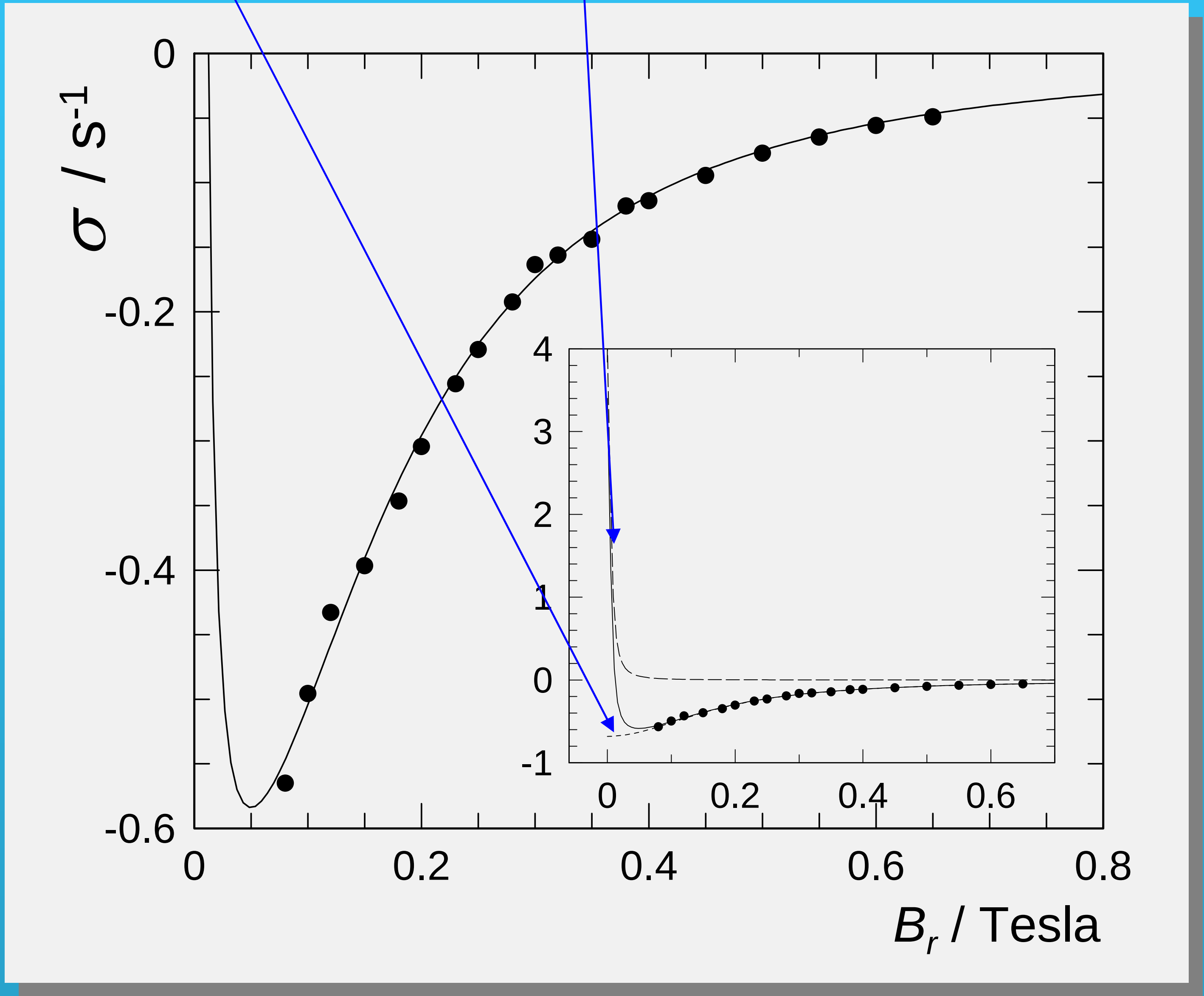
vs. frequency





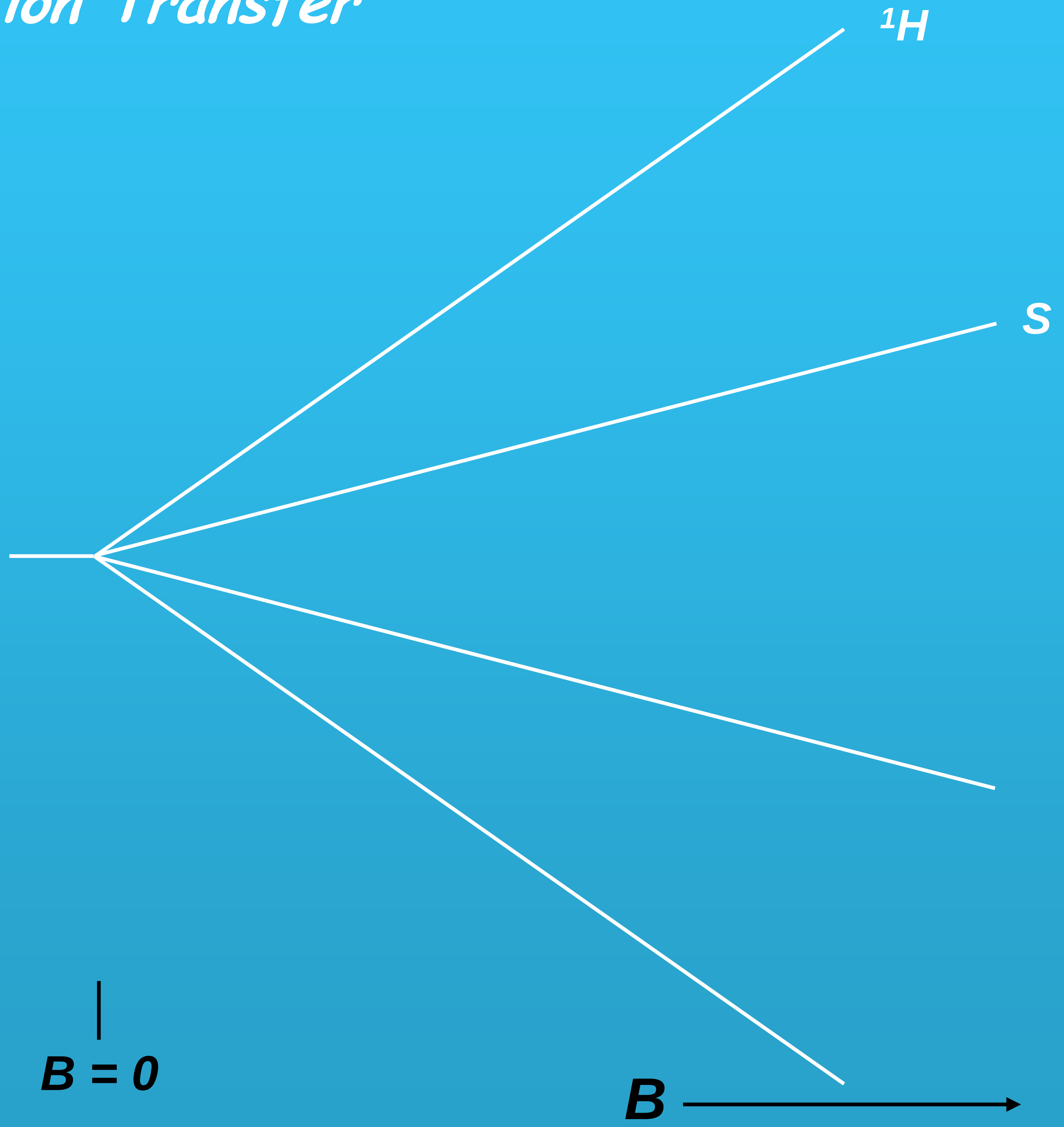
vs. field

$$\sigma \propto \left(-L(\omega_I - \omega_S) + 6L(\omega_I + \omega_S)\right)$$

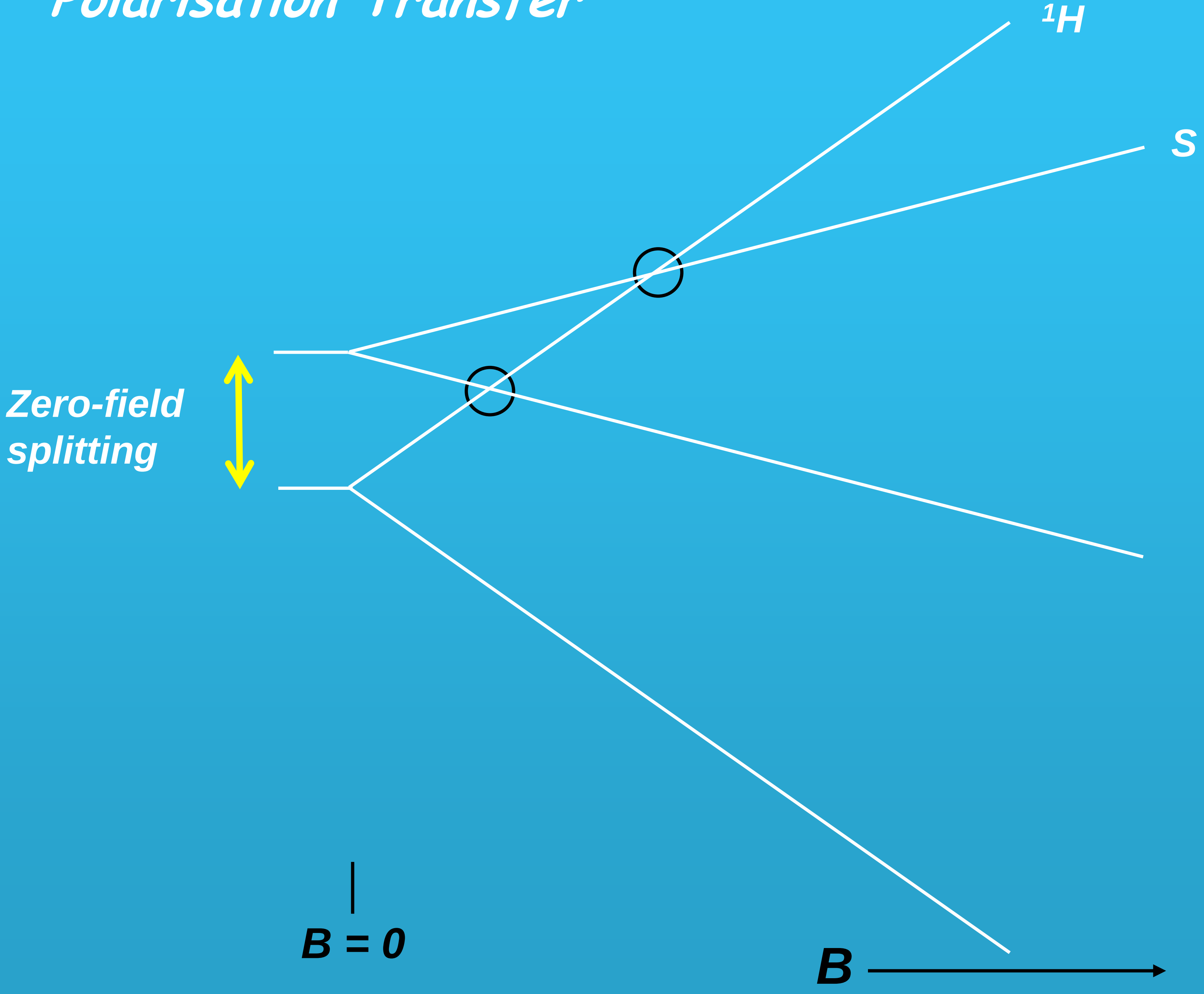


$$\Rightarrow \qquad \tau_c^{-1} = (2.66 \pm 0.08) \times 10^6\, s^{-1}$$

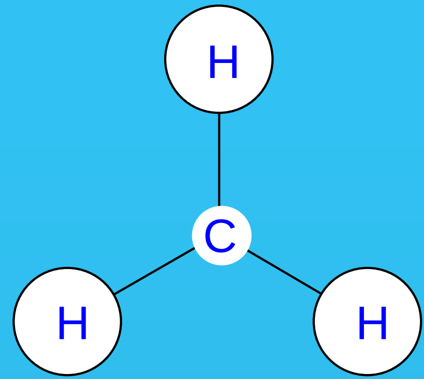
Polarisation Transfer

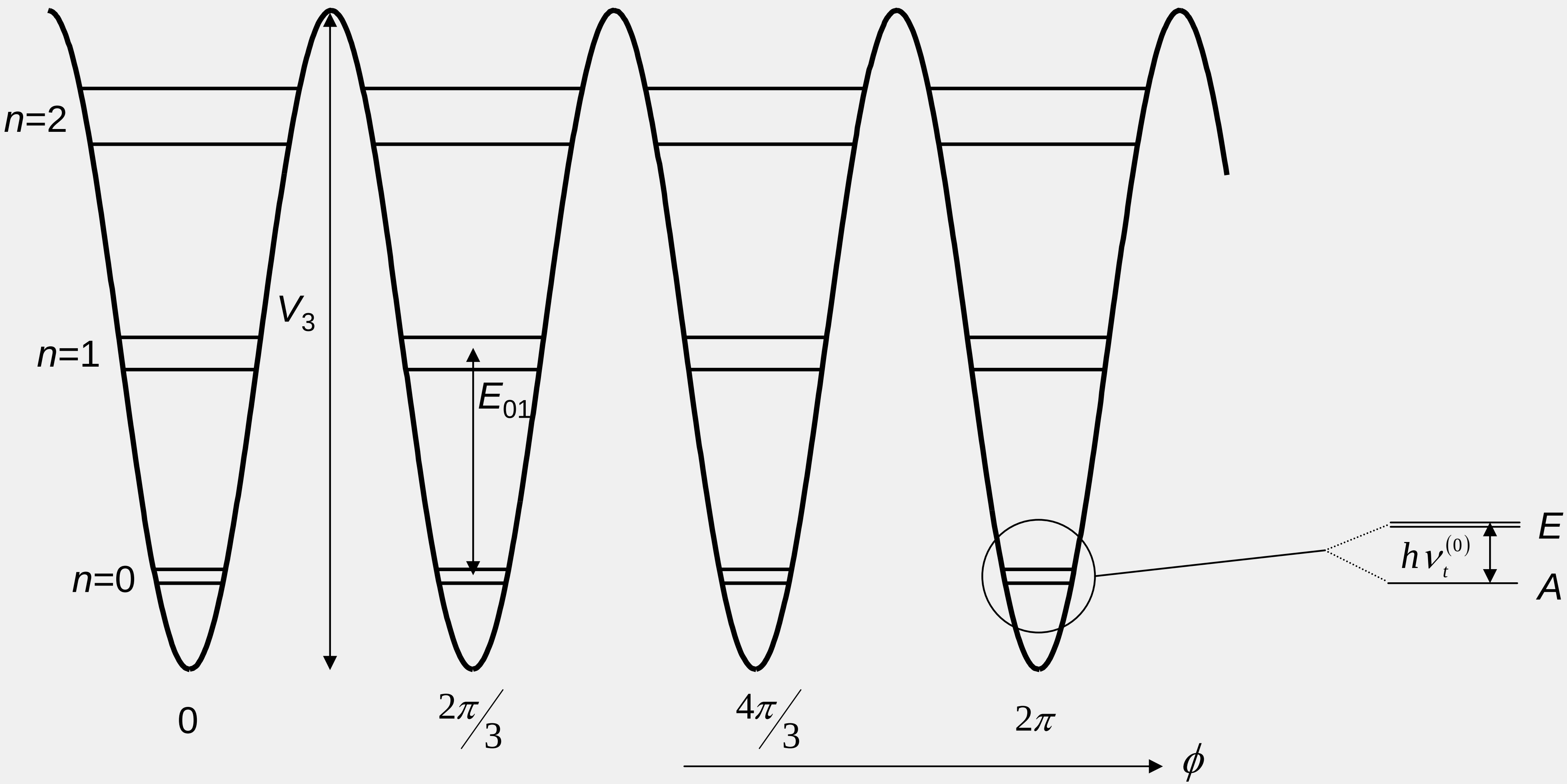


Polarisation Transfer

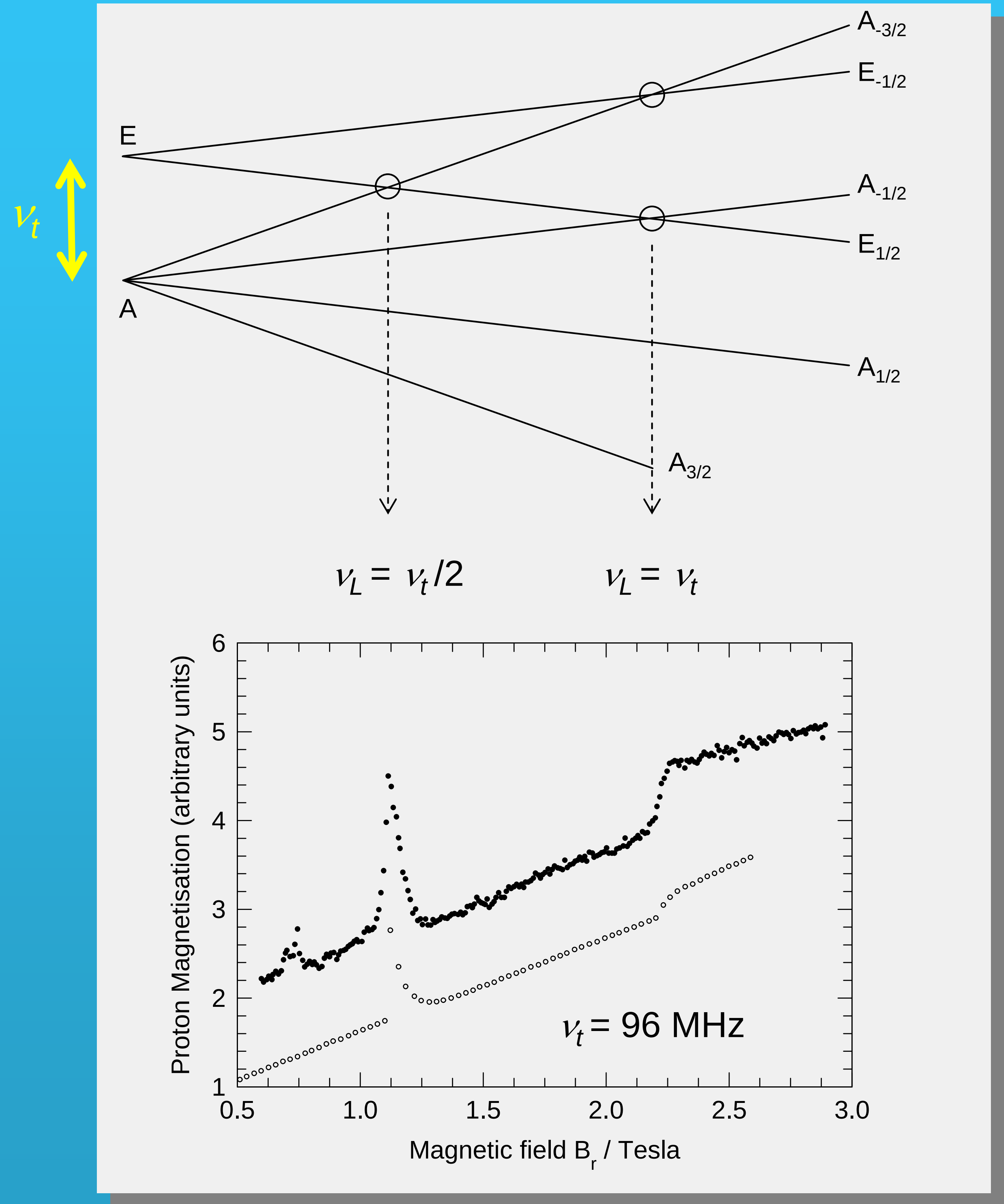


Methyl Tunnelling

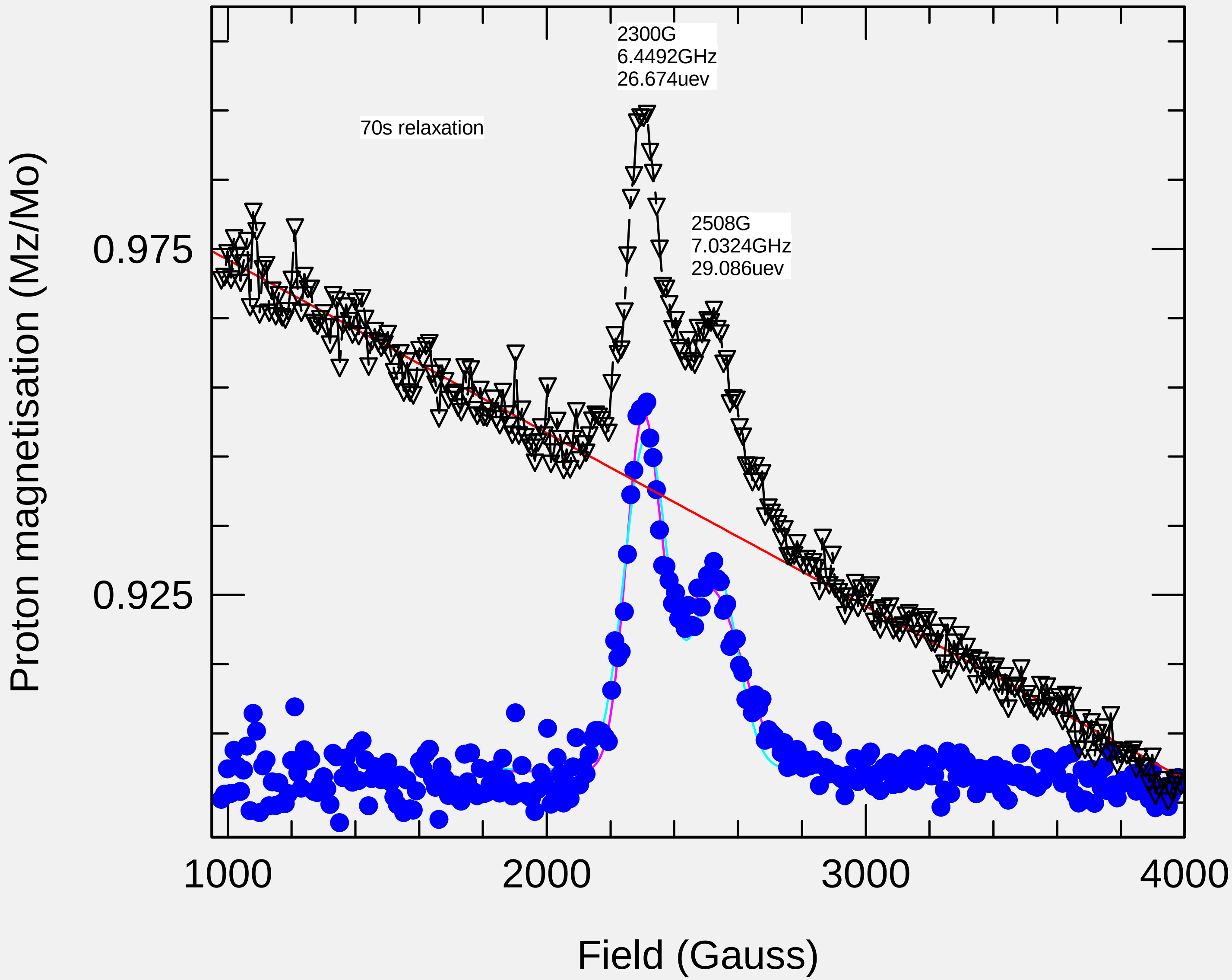




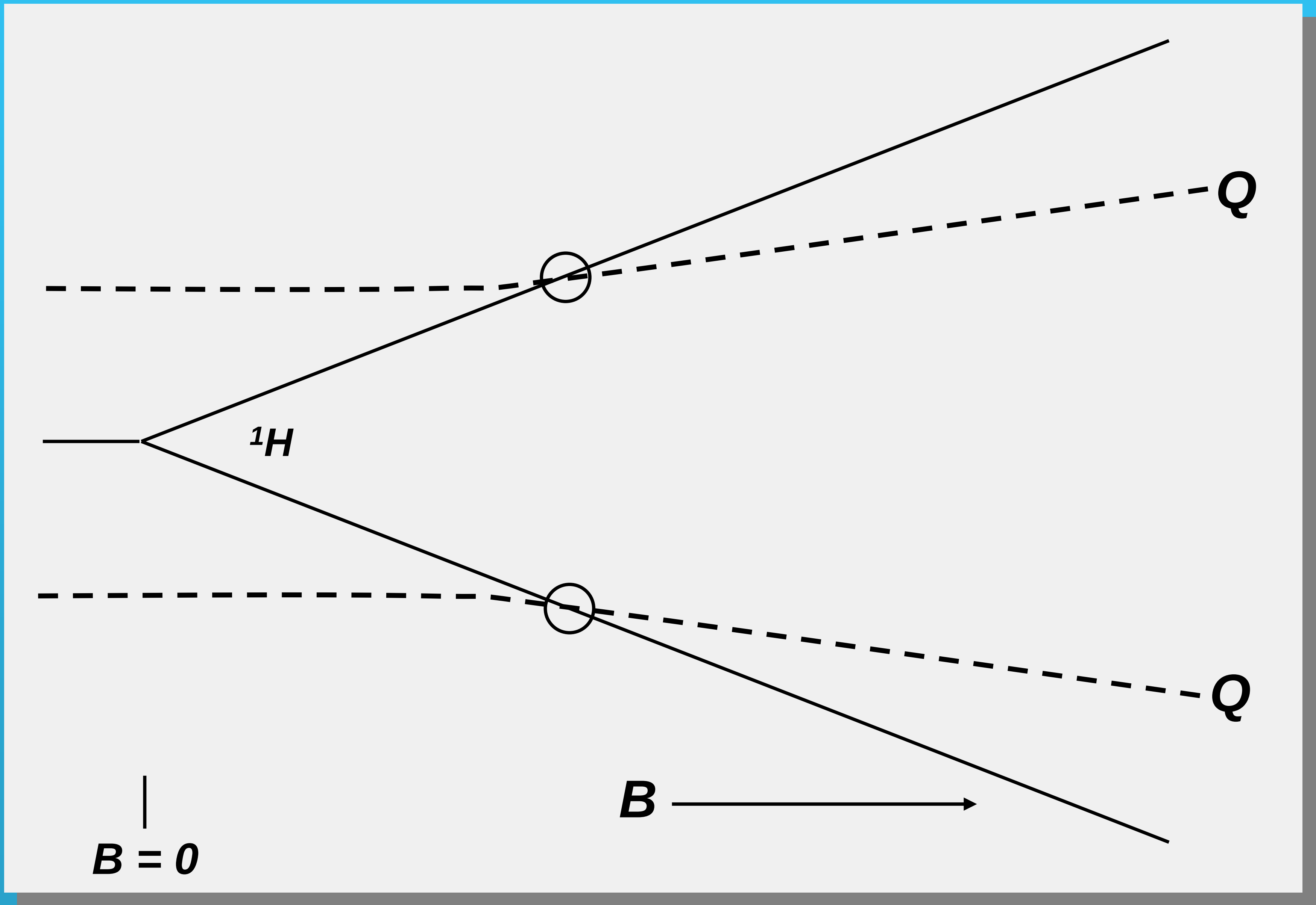
Level-crossing NMR



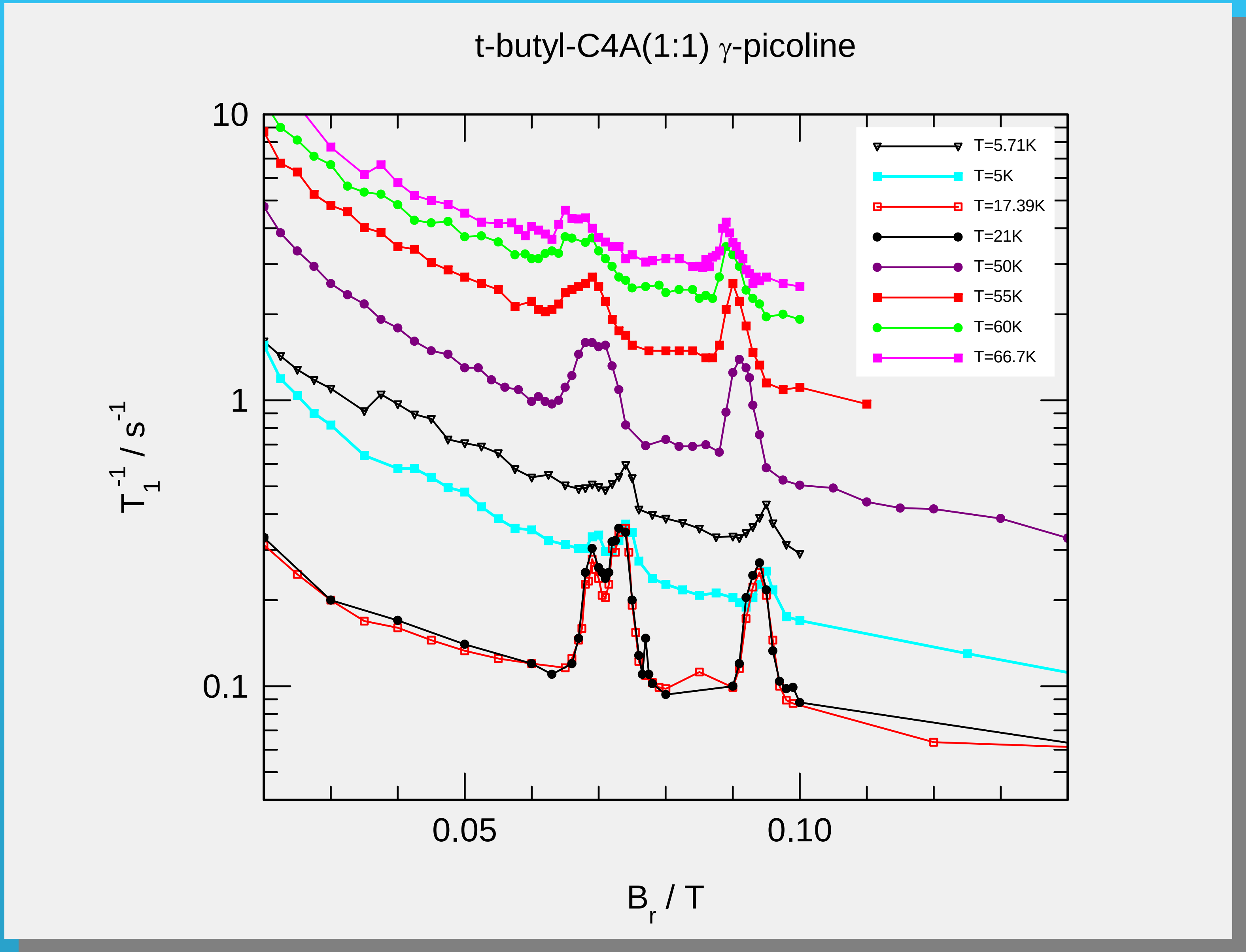
Methyl Tunnel resonance in Toluene/DPPH



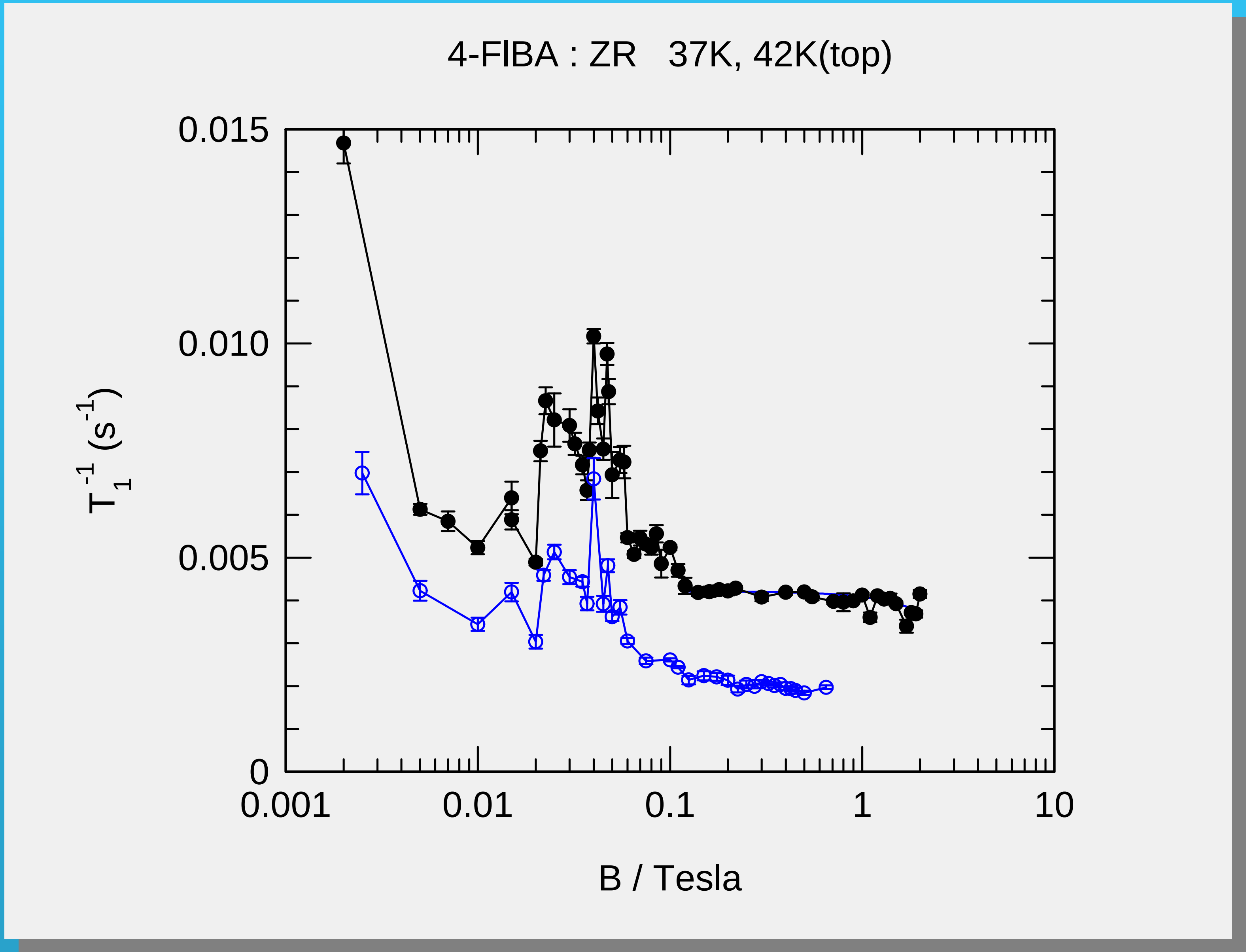
Quadrupolar nuclei



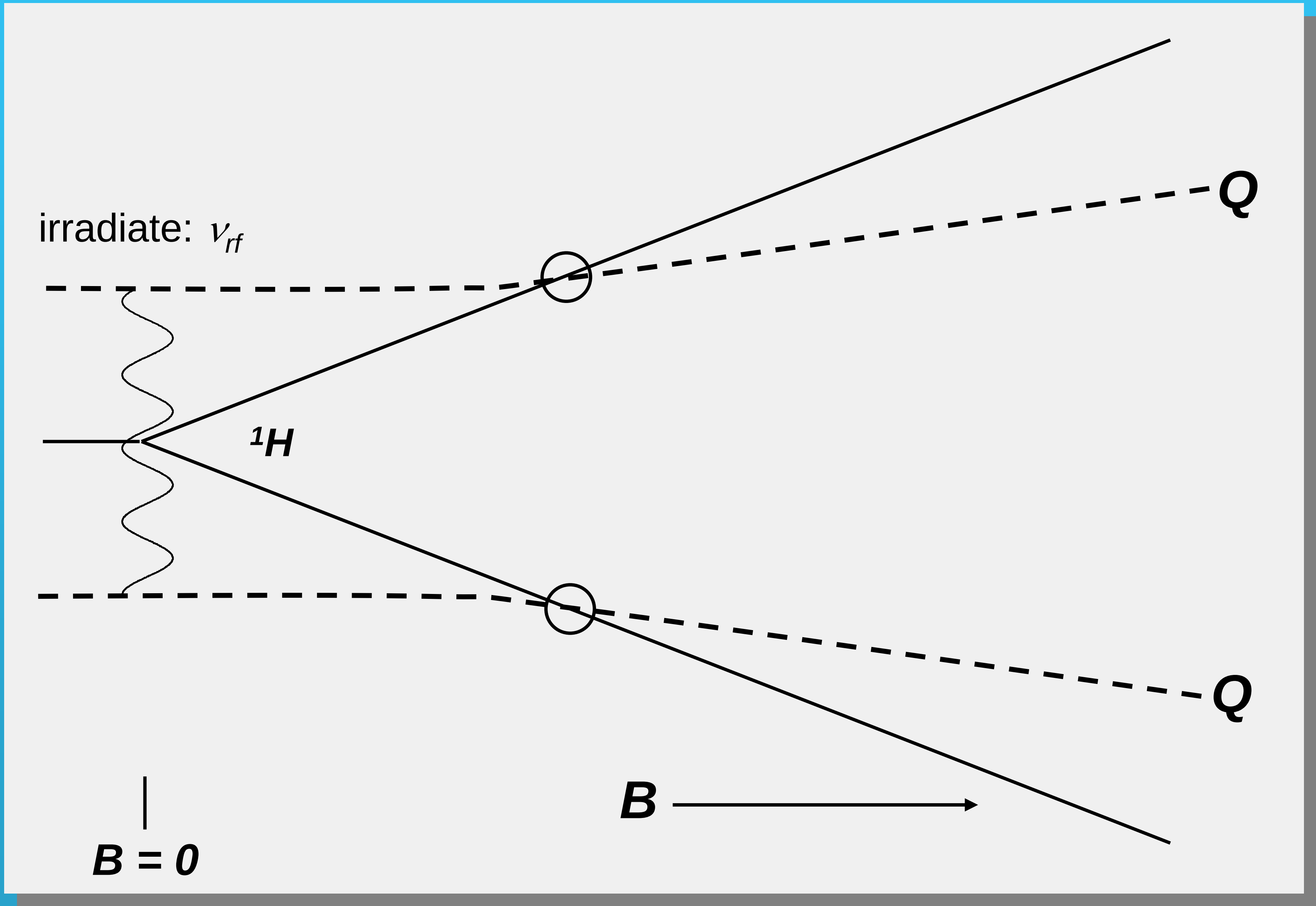
Quadrupole dips: ^{14}N



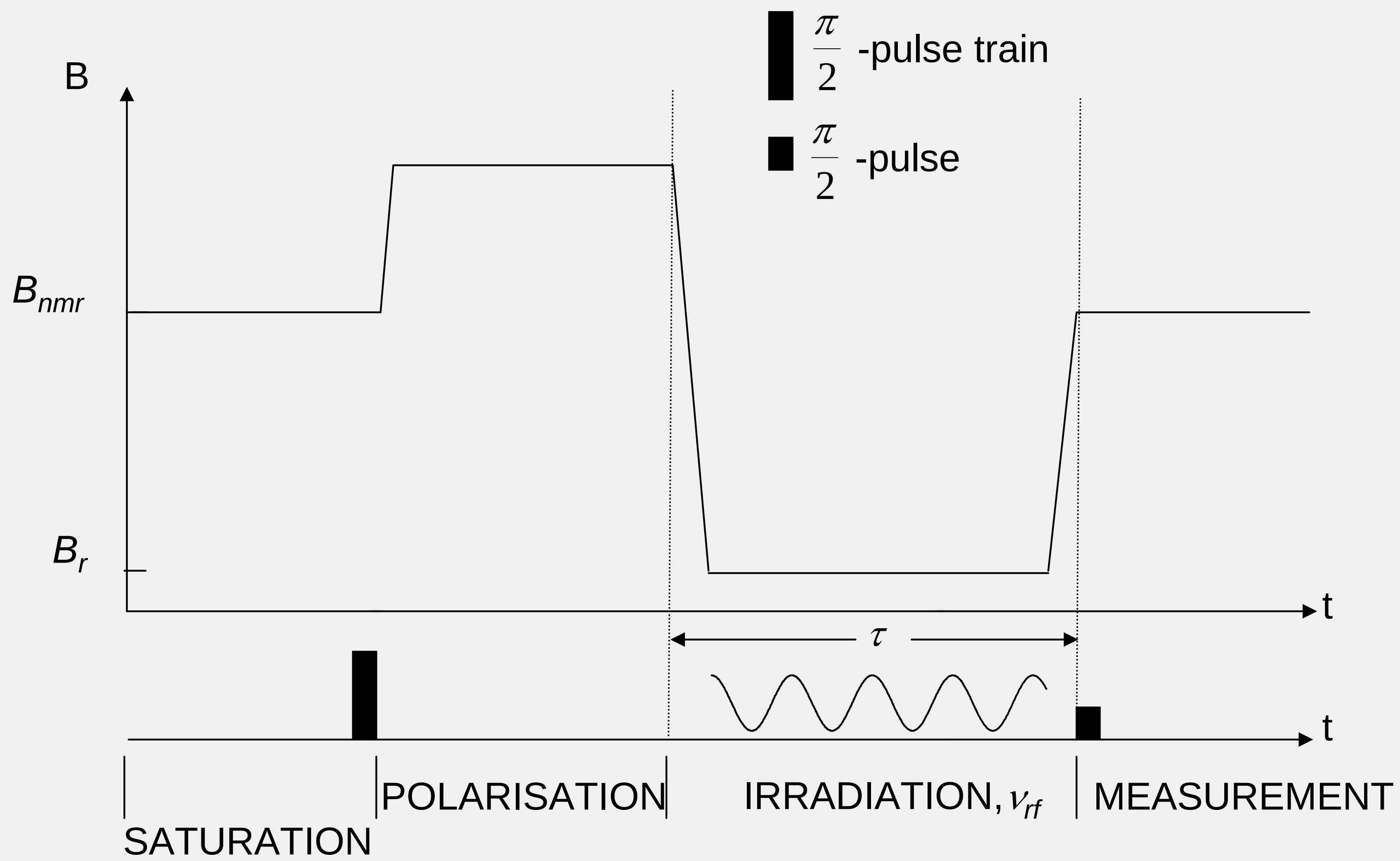
Quadrupole dips: ^{17}O



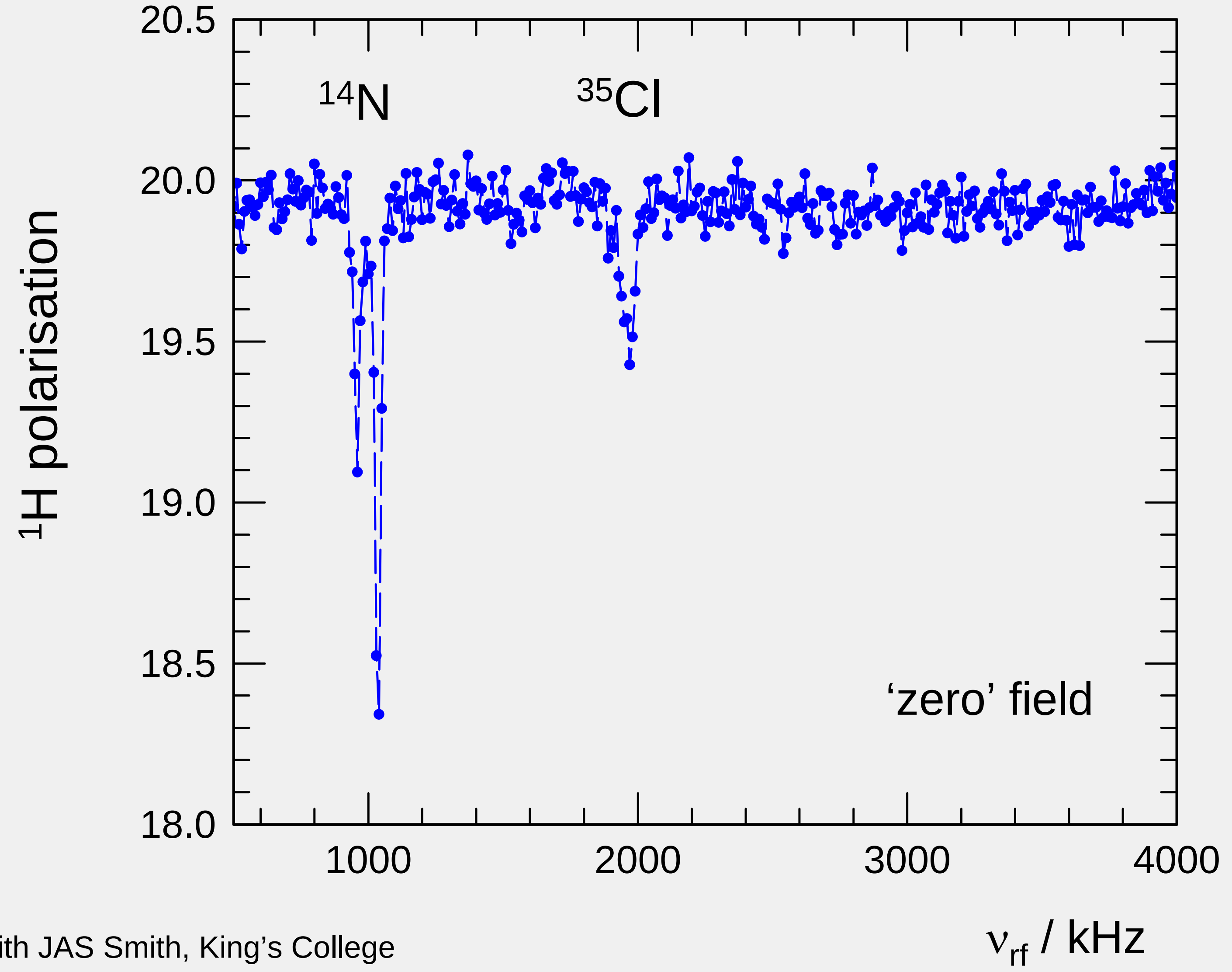
DRLC: Double Resonance by Level Crossing



DRLC: Double Resonance by Level Crossing

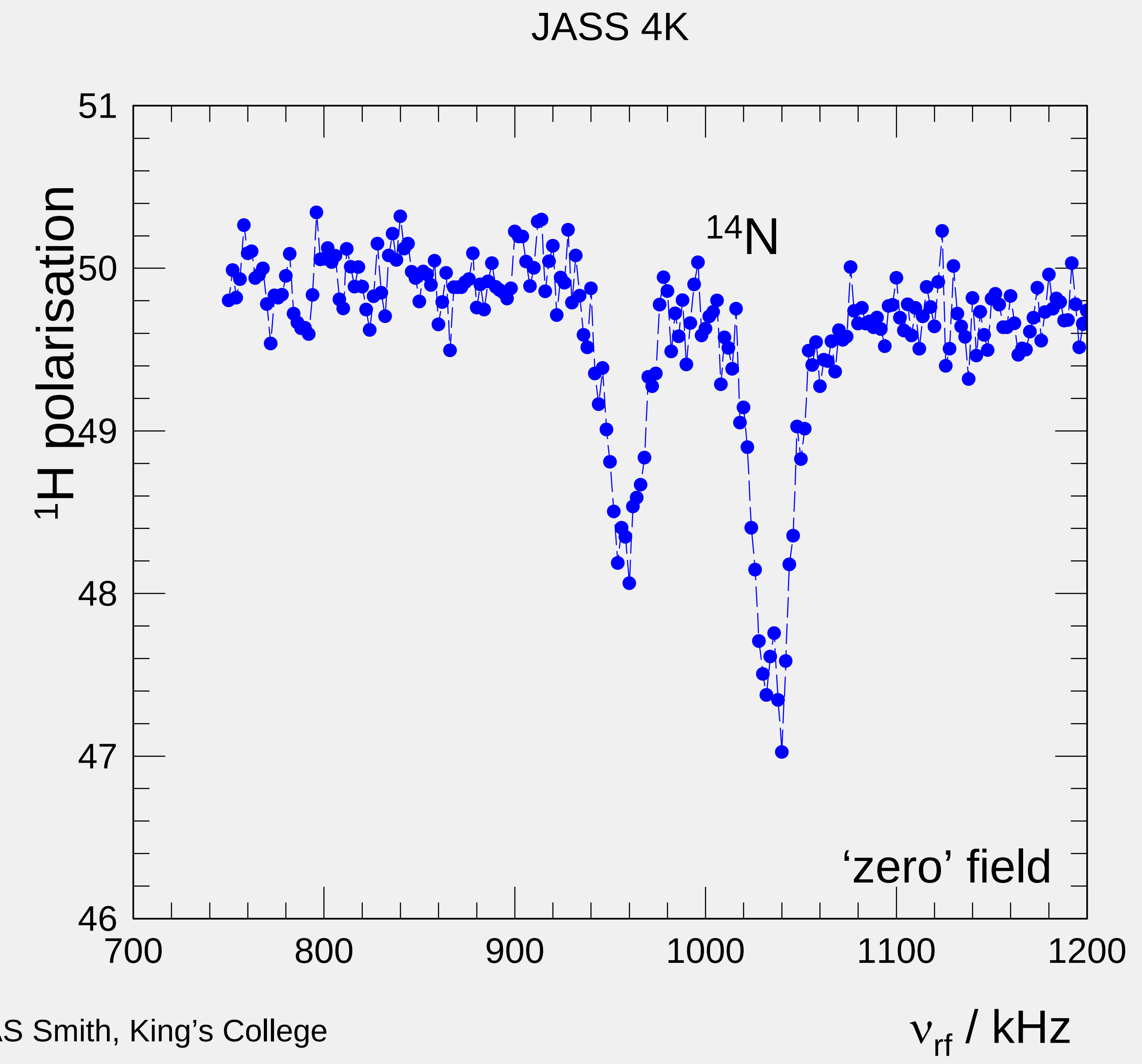


DRLC: Double Resonance by Level Crossing



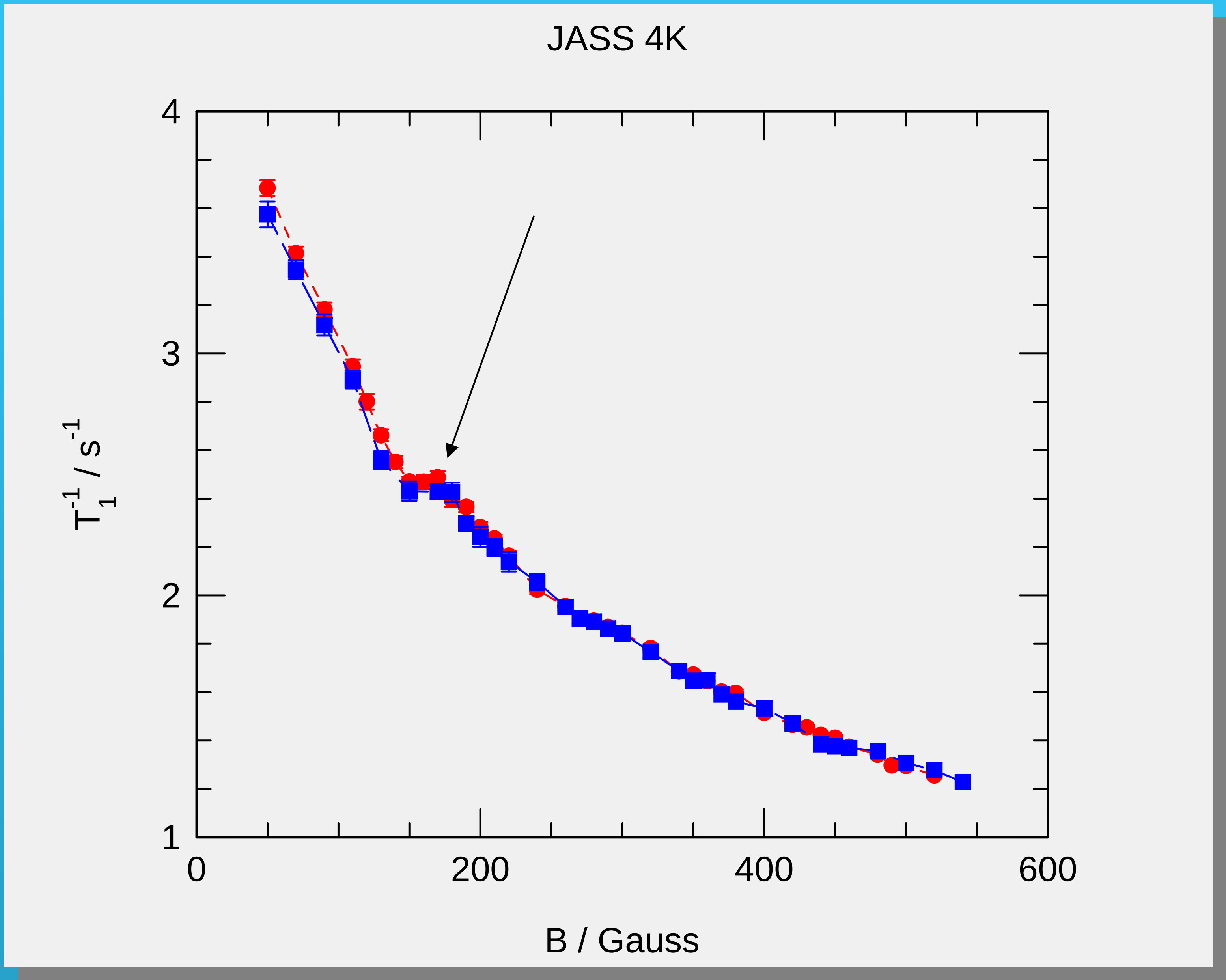
With JAS Smith, King's College

DRLC: ^{14}N in heroin hydrochloride monohydrate

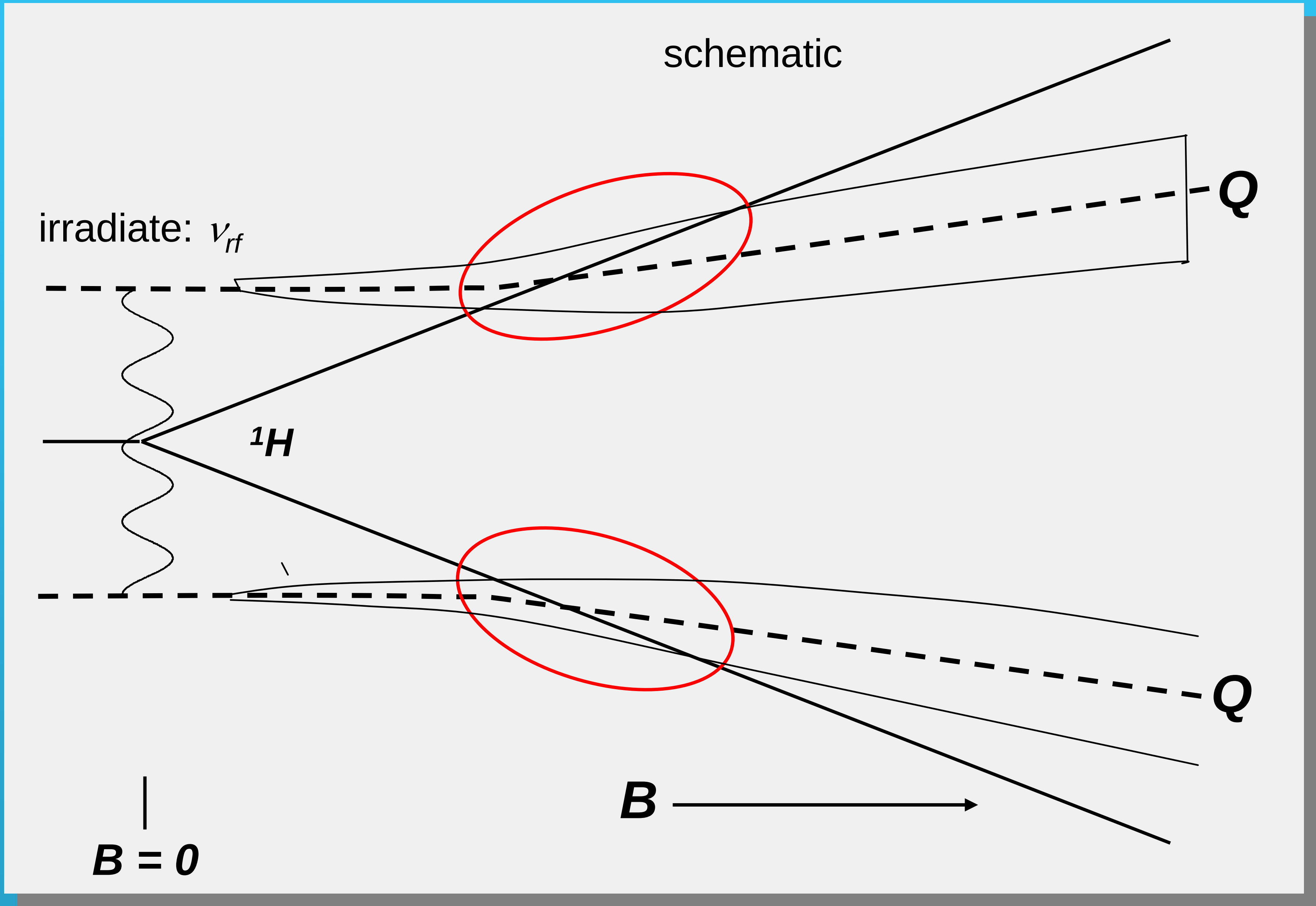


With JAS Smith, King's College

Quadrupole dips: heroin hydrochloride monohydrate



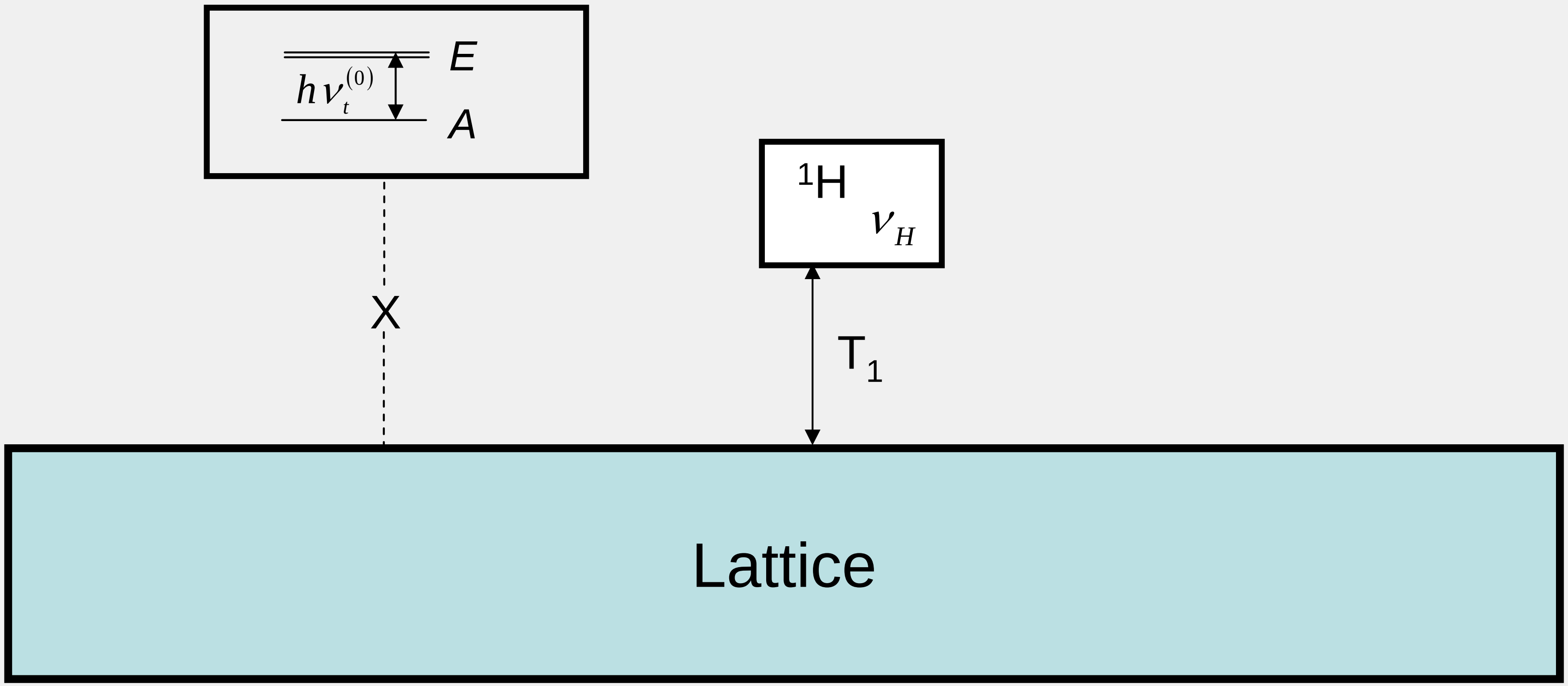
DRLC vs. Quadrupole dips:



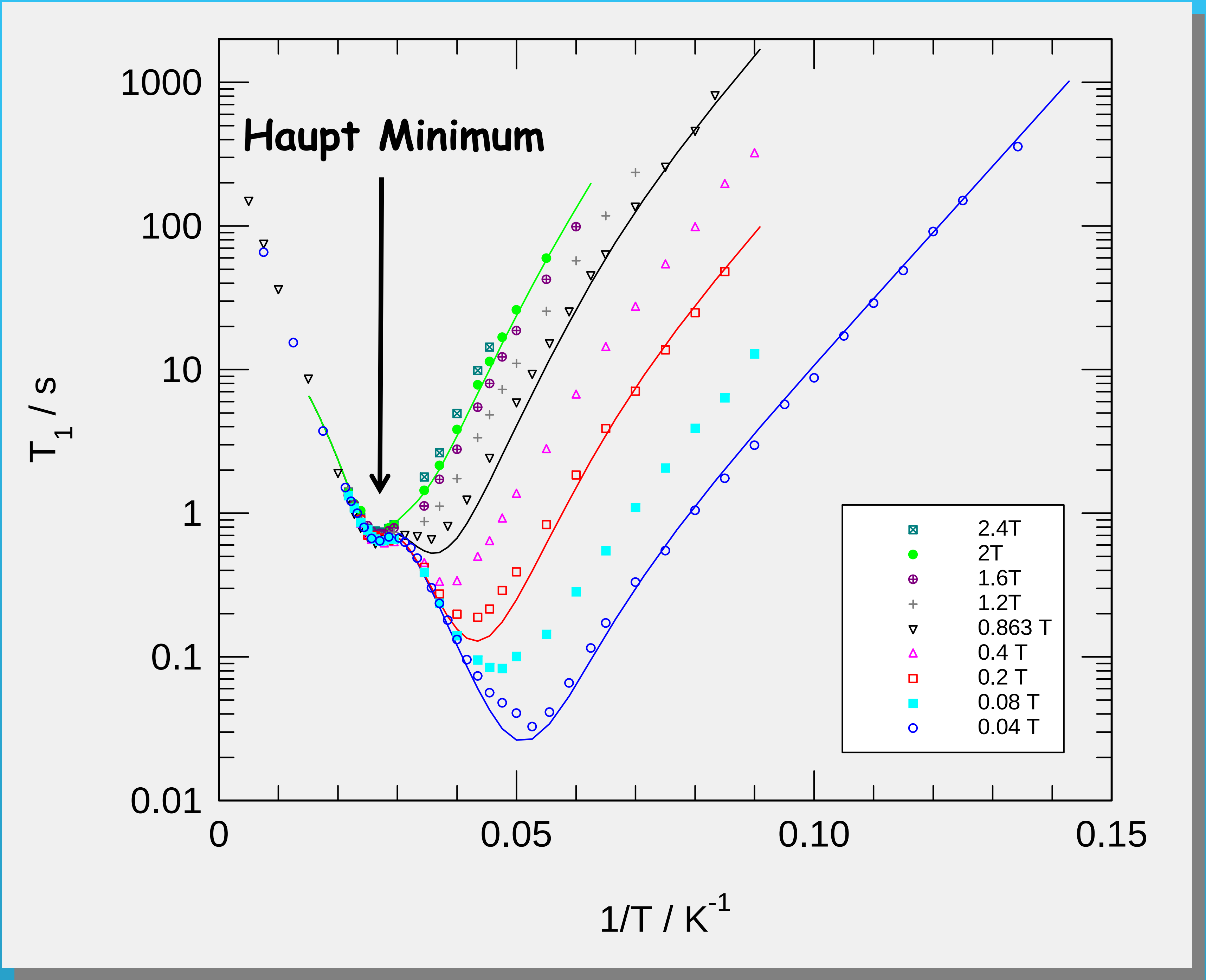
Tunnelling, the Pauli Exclusion Principle:

and the entanglement of space and spin

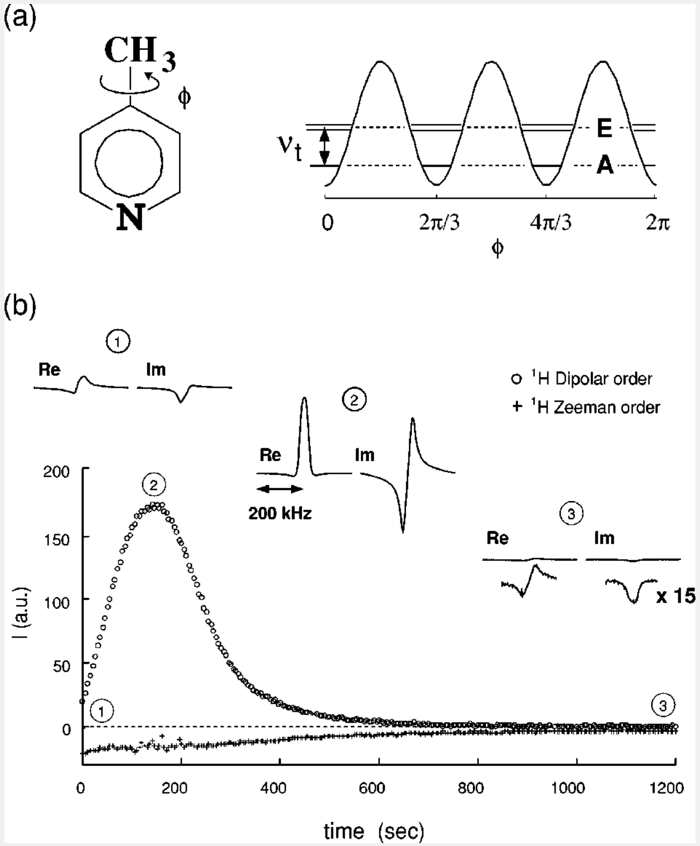
Spin-symmetry species:

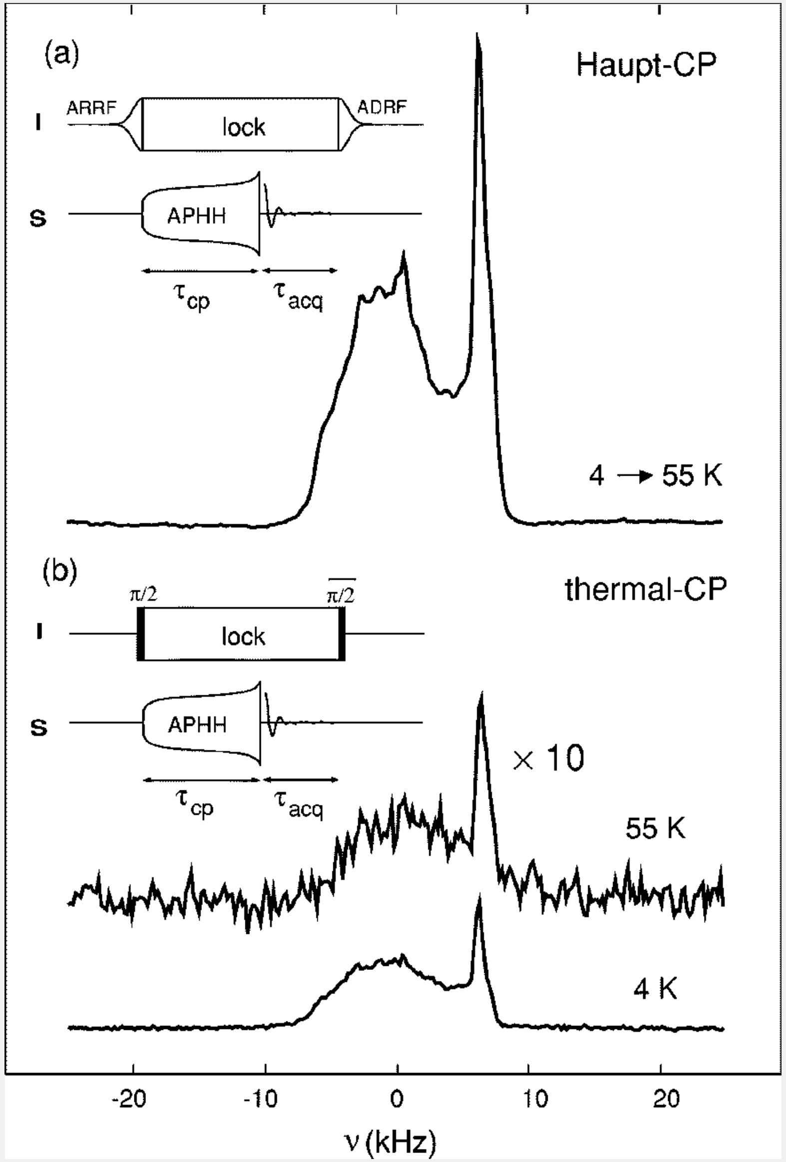


Methyl Tunnelling : Sodium Acetate



Methyl Tunnelling: Haupt Effect





Haupt magnetic double resonance

M. Tomaselli,* C. Degen, and B. H. Meier

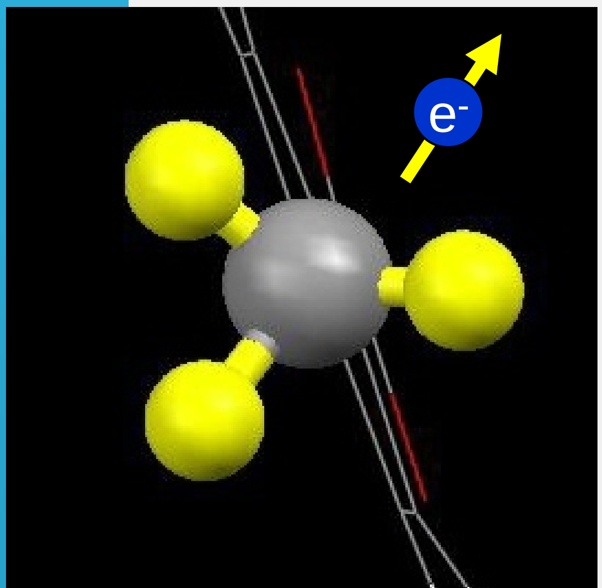
Physical Chemistry, ETH-Zürich, CH-8093 Zürich, Switzerland

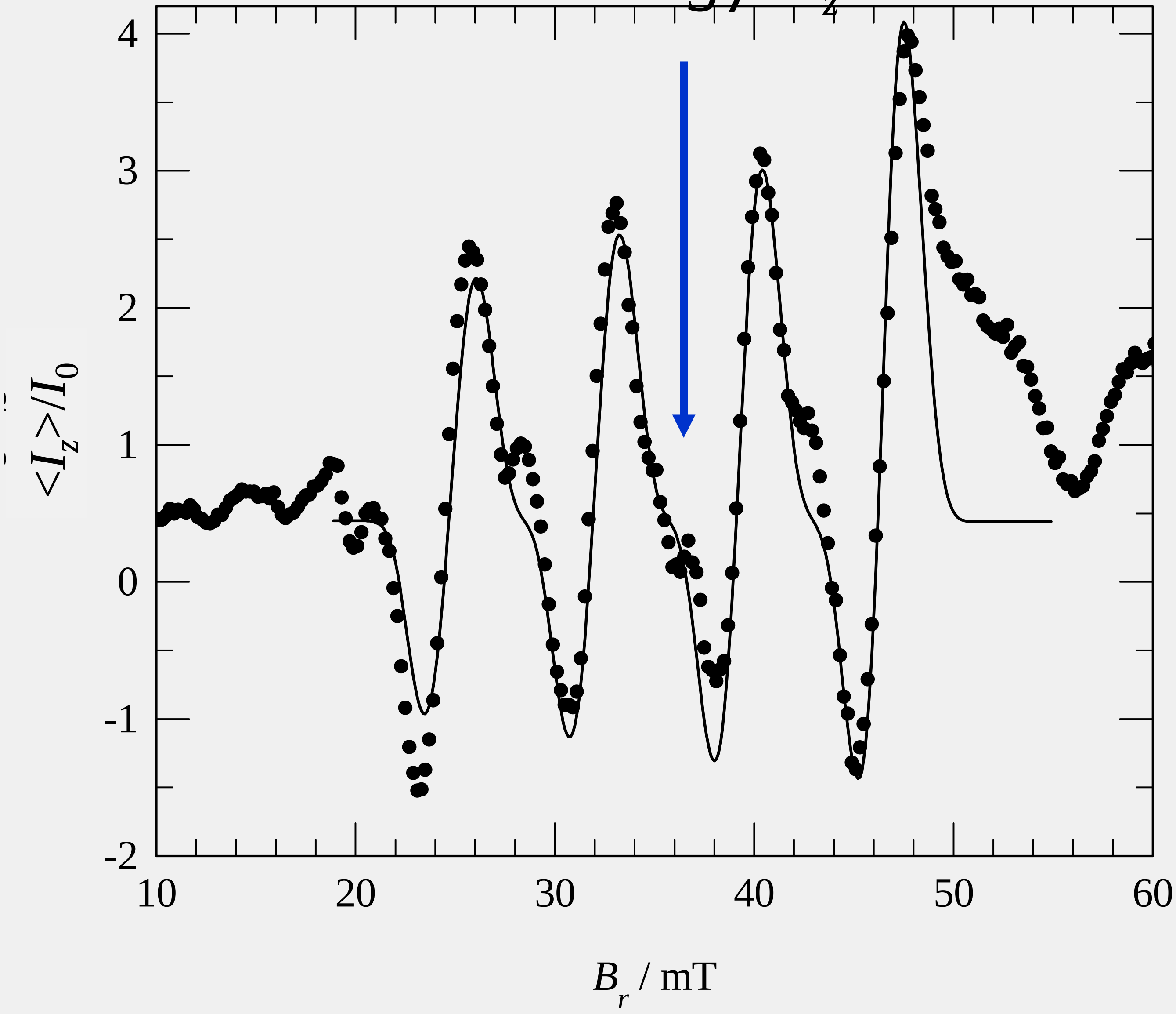
J. Chem. Phys.,118, (2003) 8559- 8562 Tomaselli, Degen, and Meier

Tunnel resonance : (Cu,Zn) acetate dihydrate (Xtl)

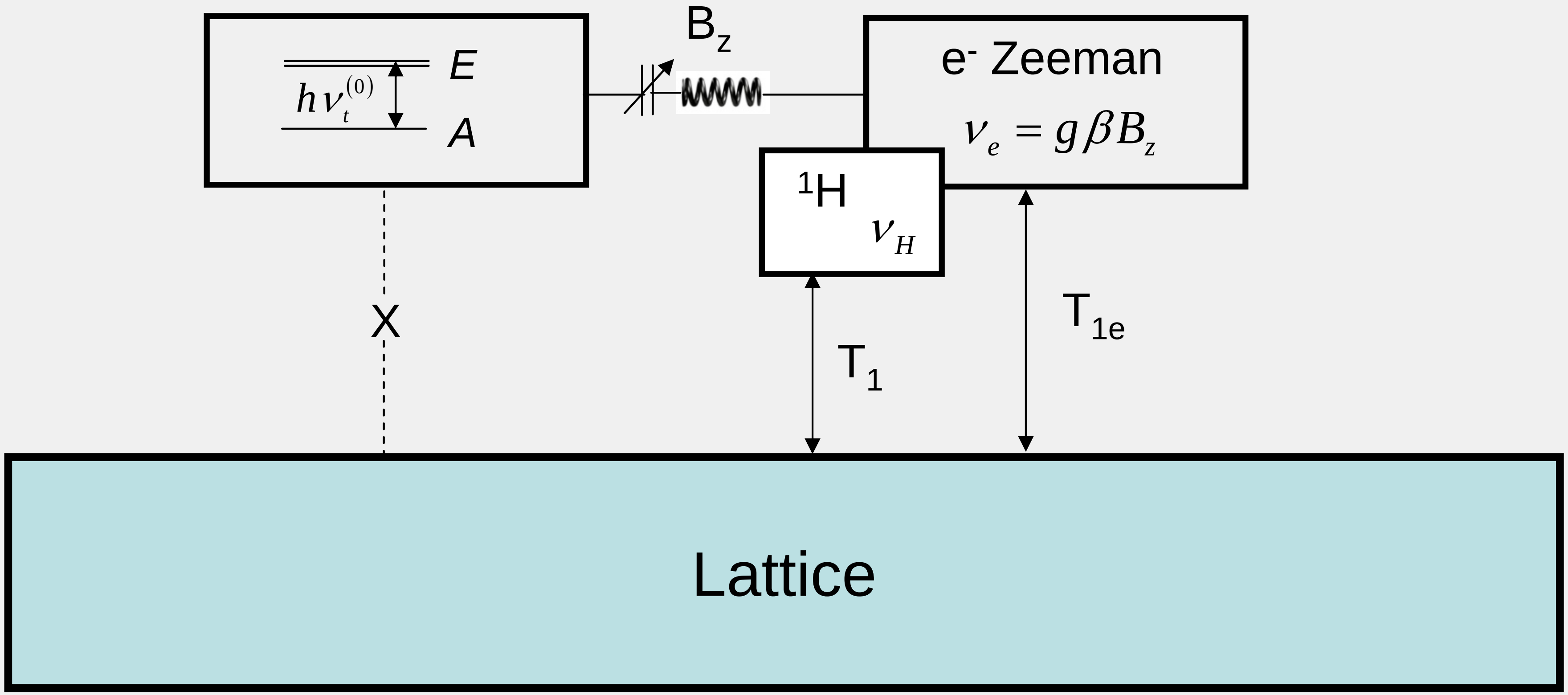
$$\nu_t = \nu_e$$

$$= g\beta B_z$$

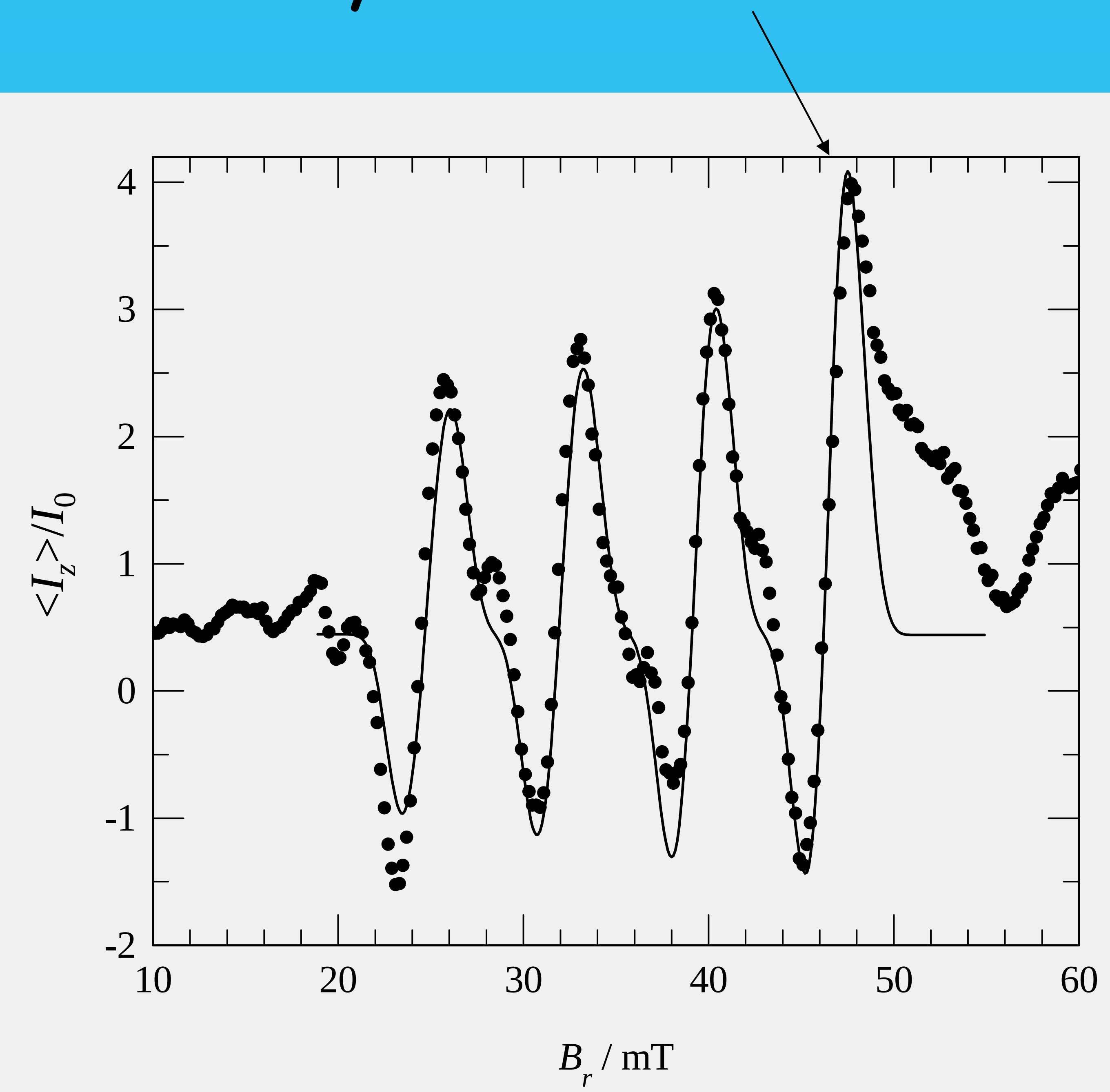




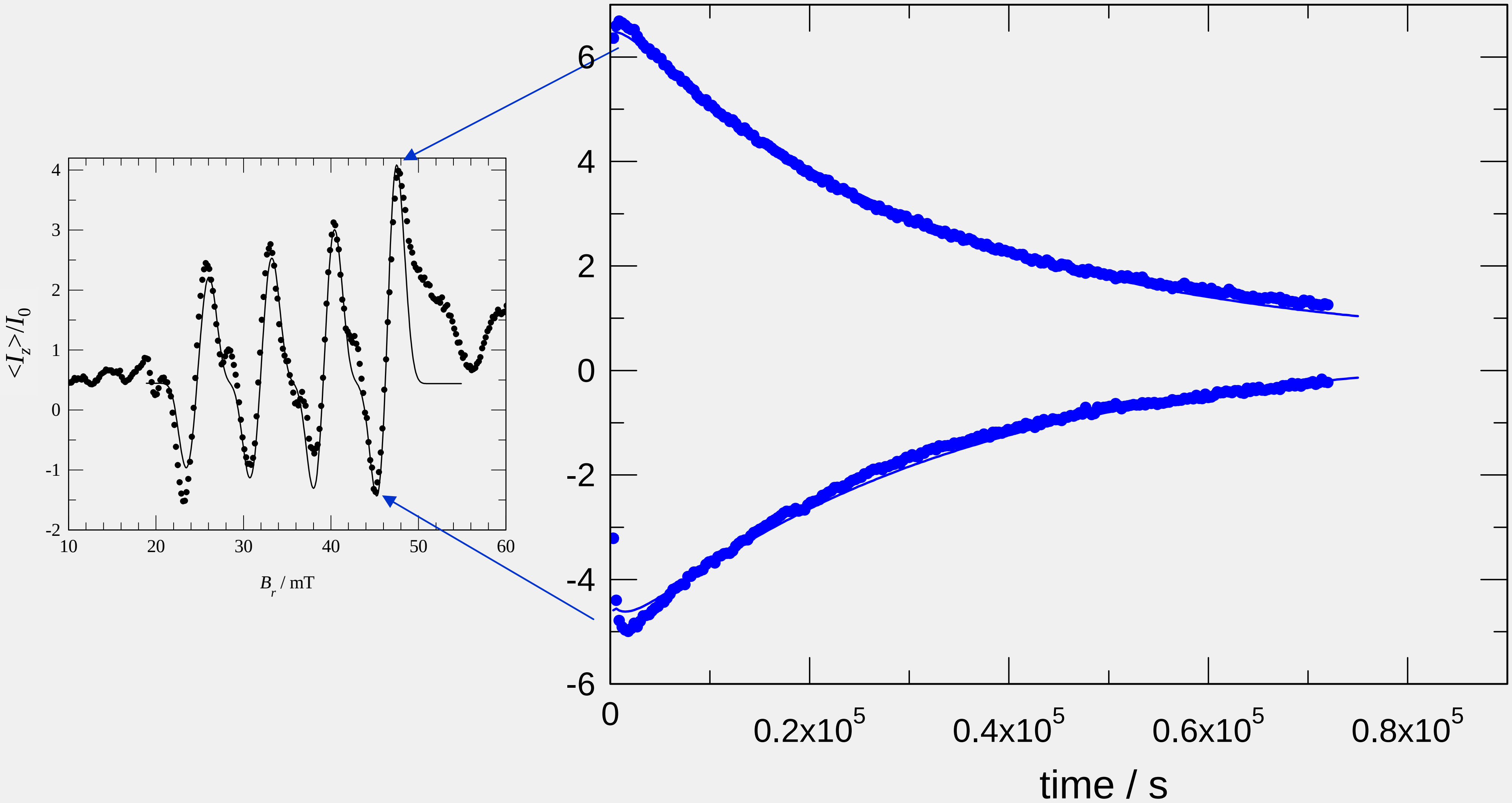
Spin-symmetry species: Pauli Exclusion Principle



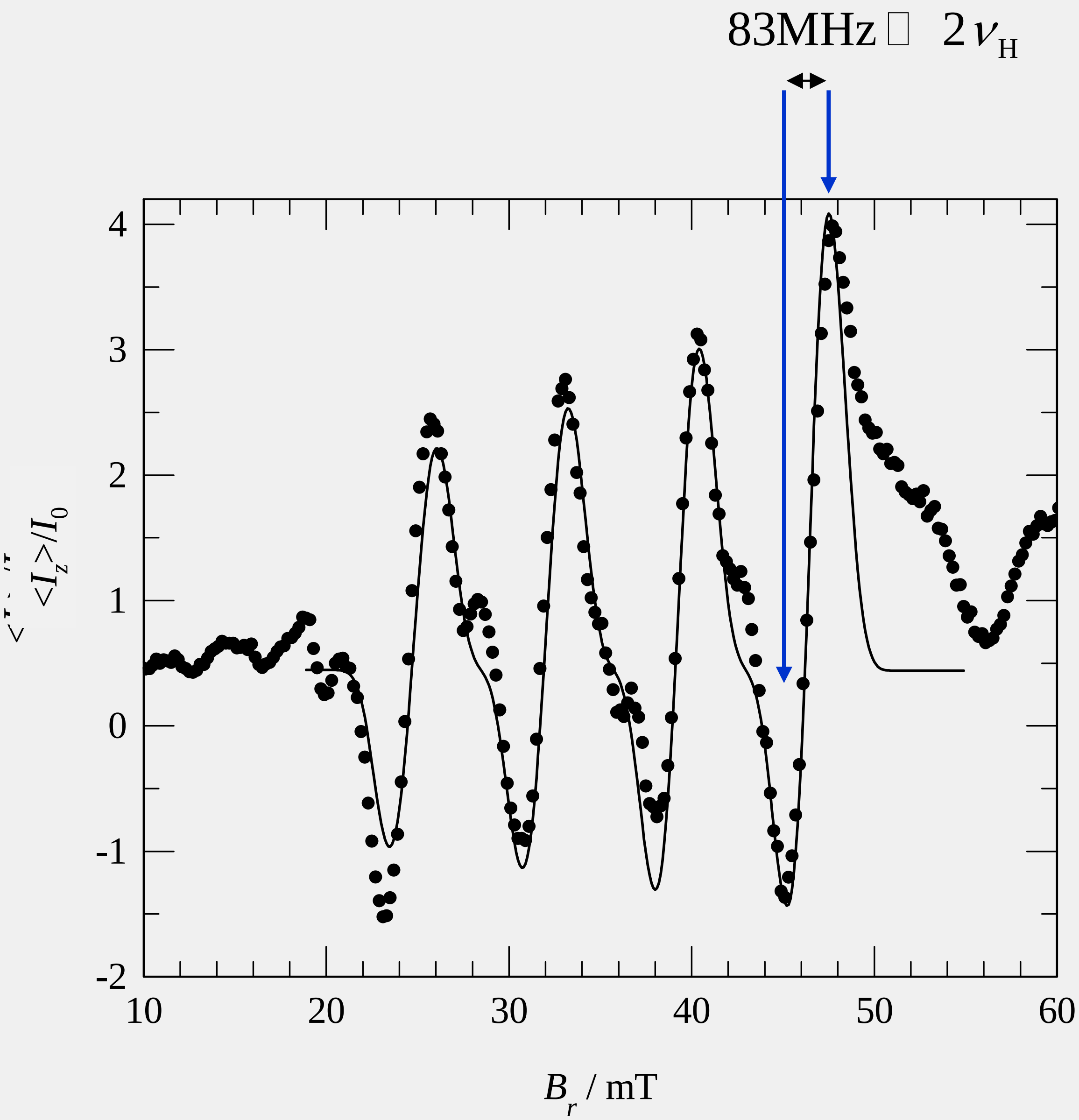
Observations:



The Tunnel Reservoir



Tunnel Resonance Lineshapes

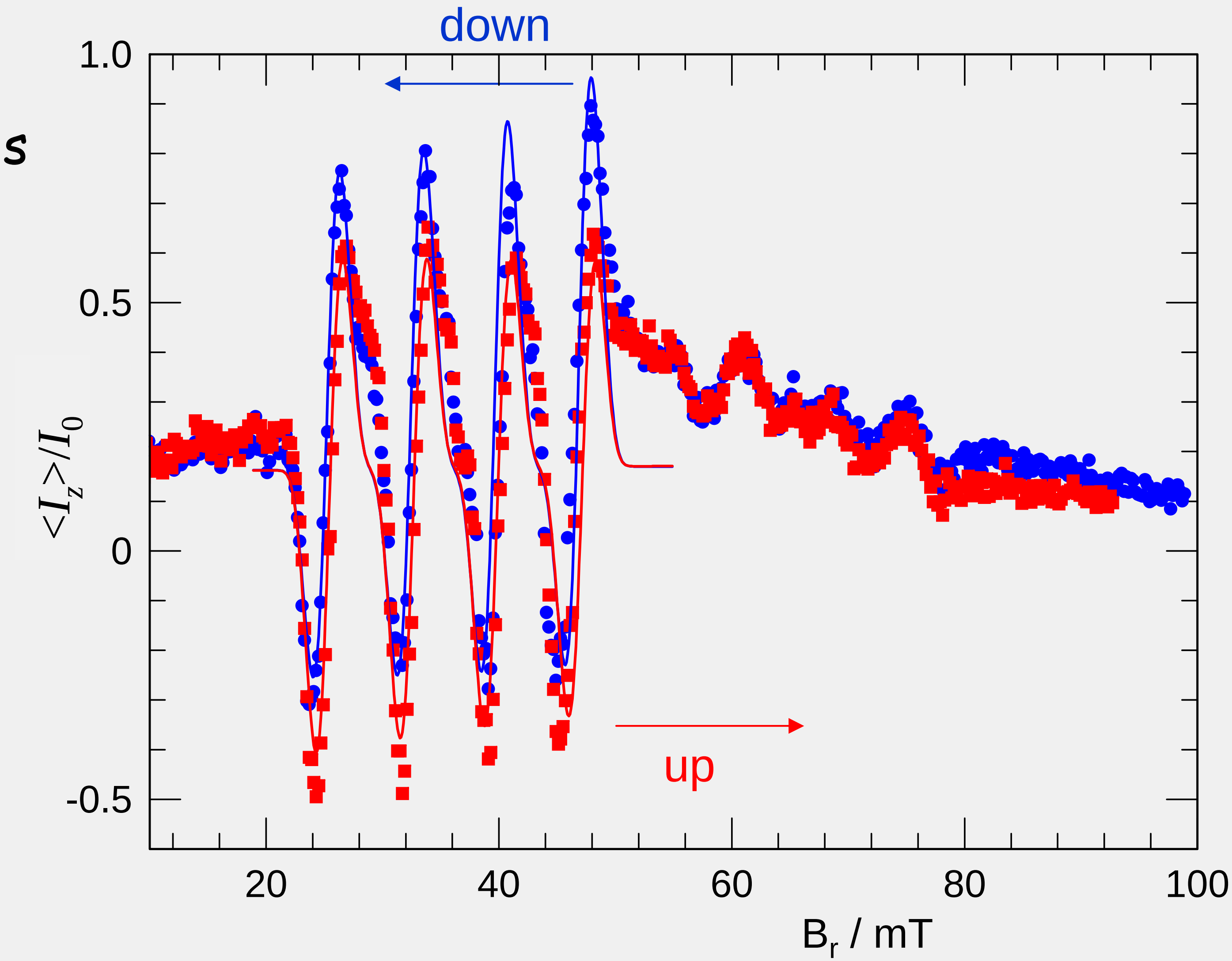


Distribution of Tunnelling Frequencies:

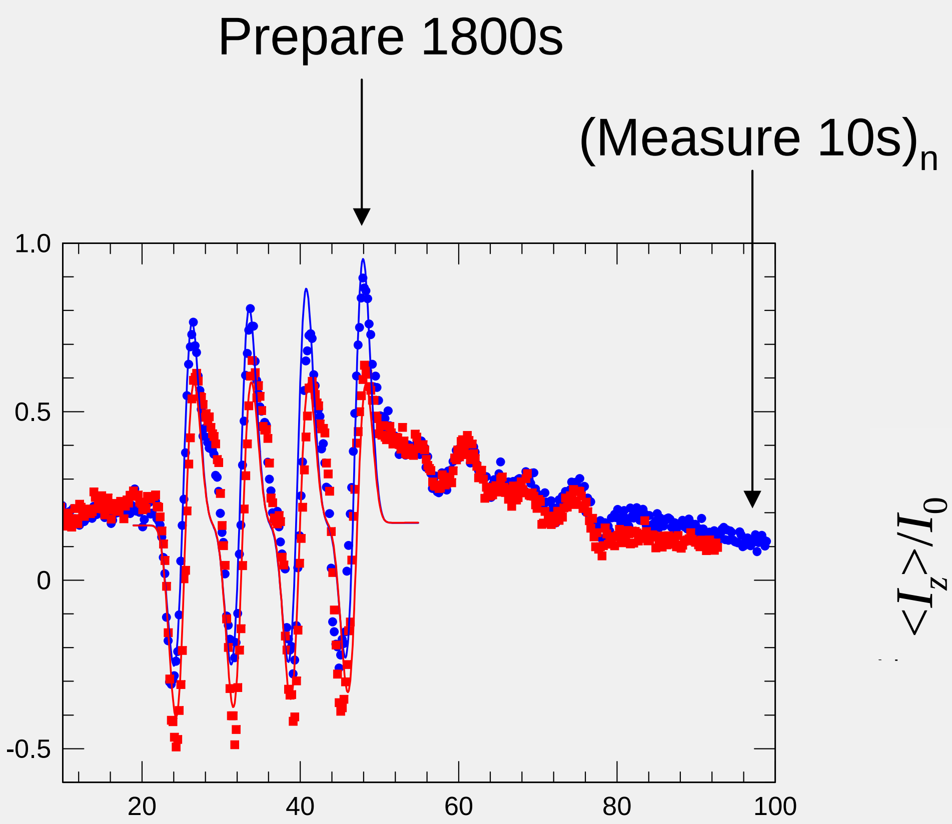
Tunnel Resonance Mechanism

Distribution of Tunnelling Frequencies:

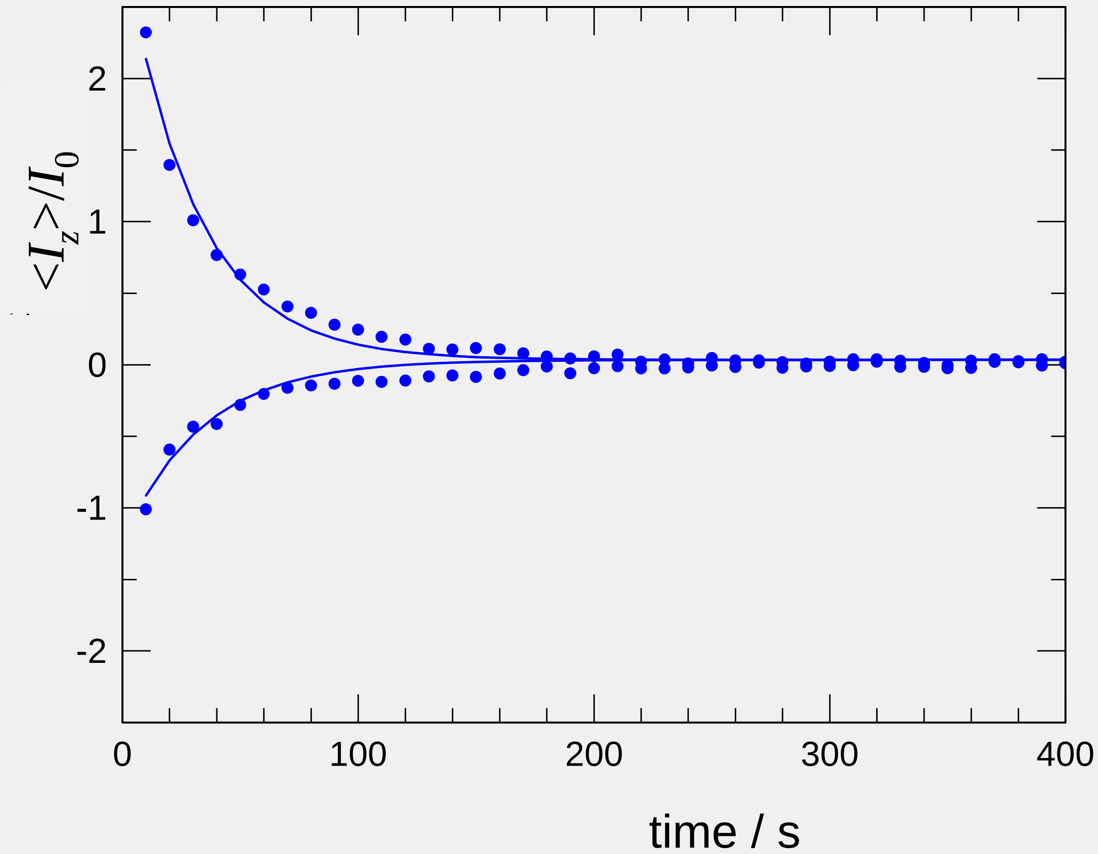
- no hole-burning
- observe hysteresis



Tunnel Resonance Mechanism

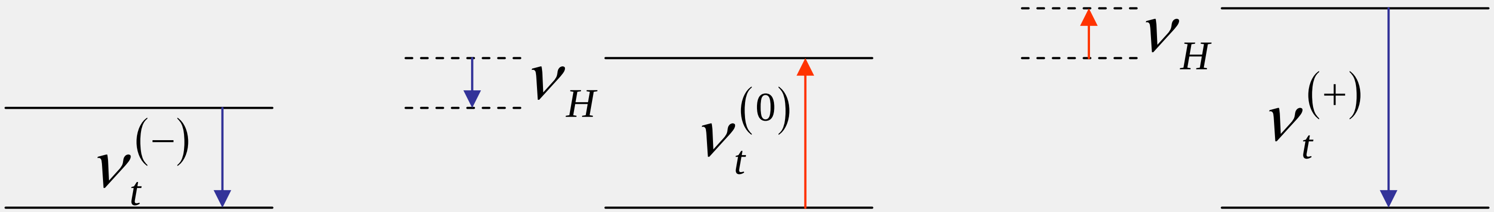


Tunnel Diffusion



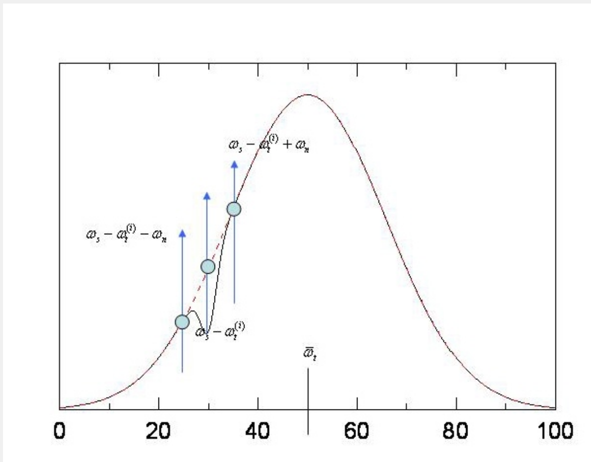
Tunnel Resonance Mechanism

- **spatial and spectral diffusion of tunnelling energy**



proton
cooling

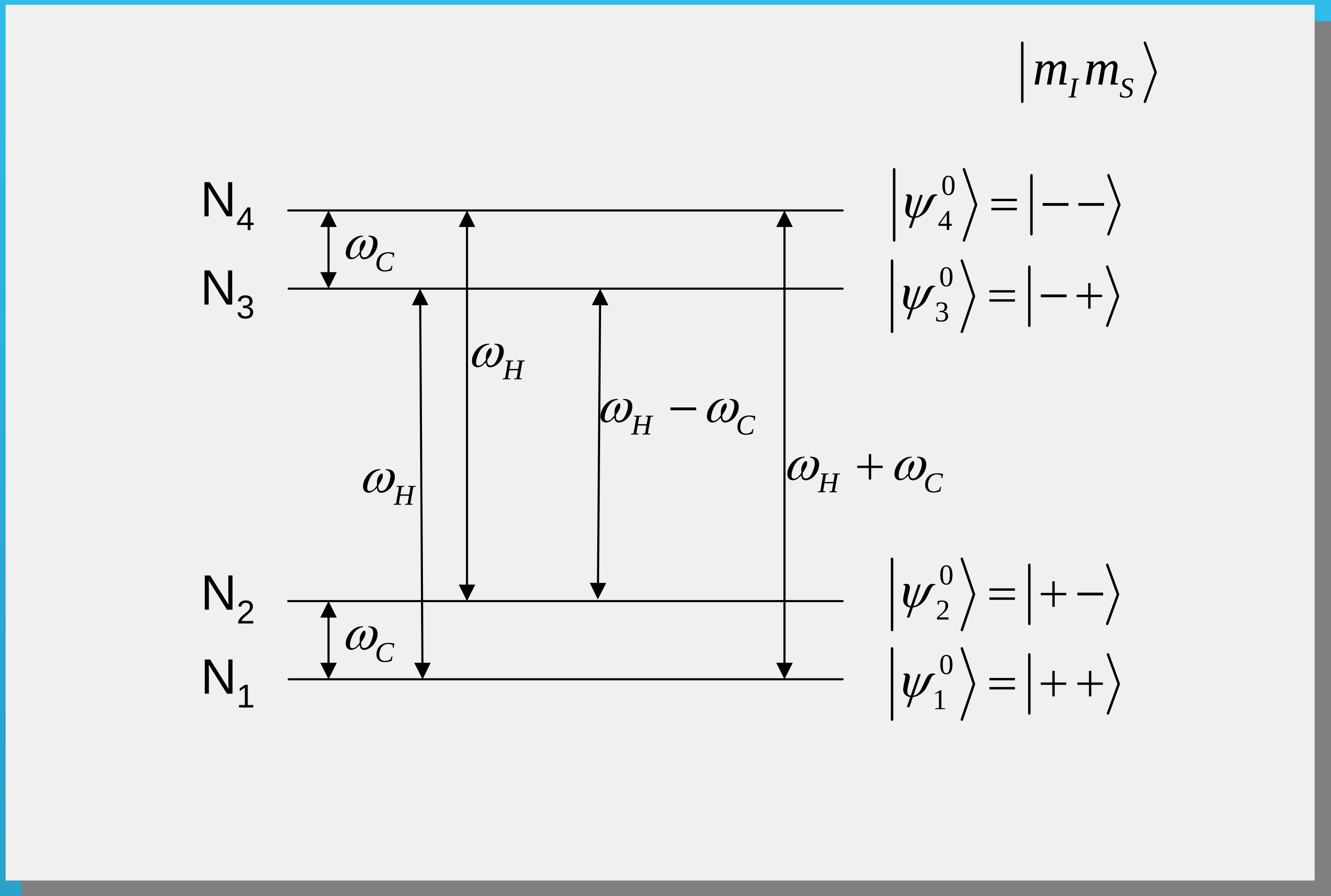
proton
warming

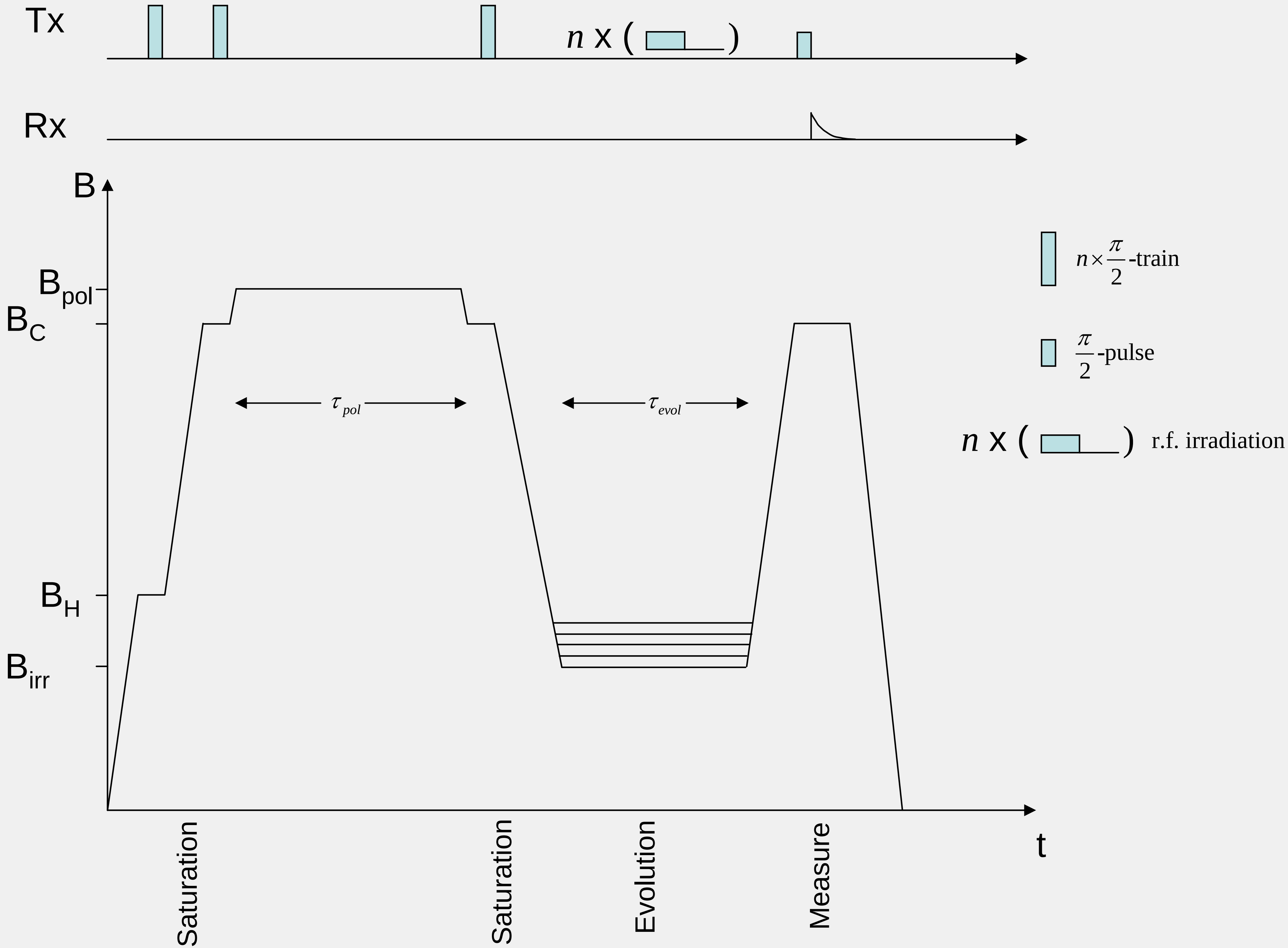


- **resulting in dynamic nuclear polarisation of ^1H**

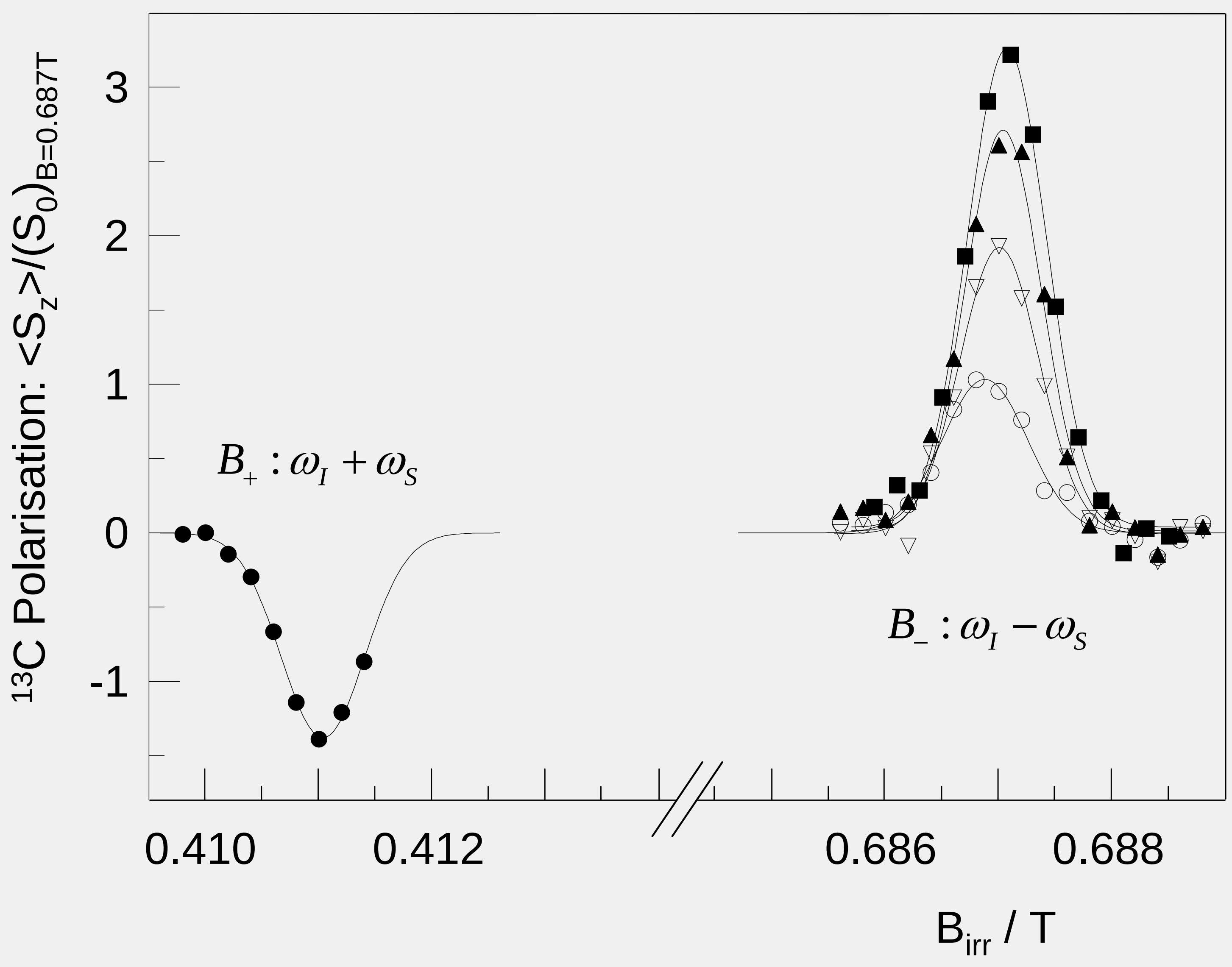
Nuclear Solid Effect:

Dynamic Nuclear Polarisation

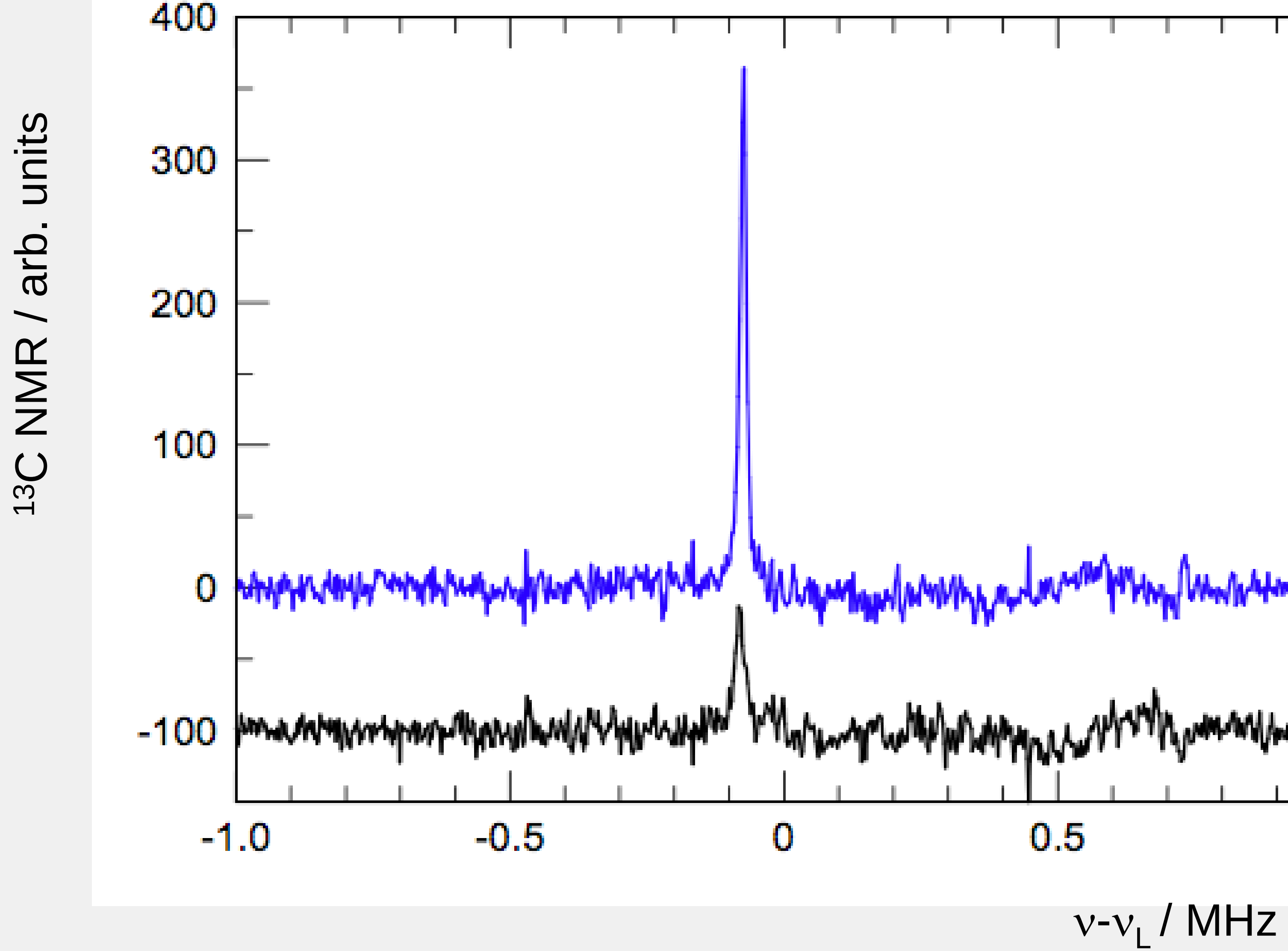



Tx
n x ( )
Rx
B
B
pol
B
C
B
H
B
irr
τ pol
τ evol
n × π/2 -train
π/2 -pulse
n x ( ) r.f. irradiation
t
Saturation
Saturation
Evolution
Measure

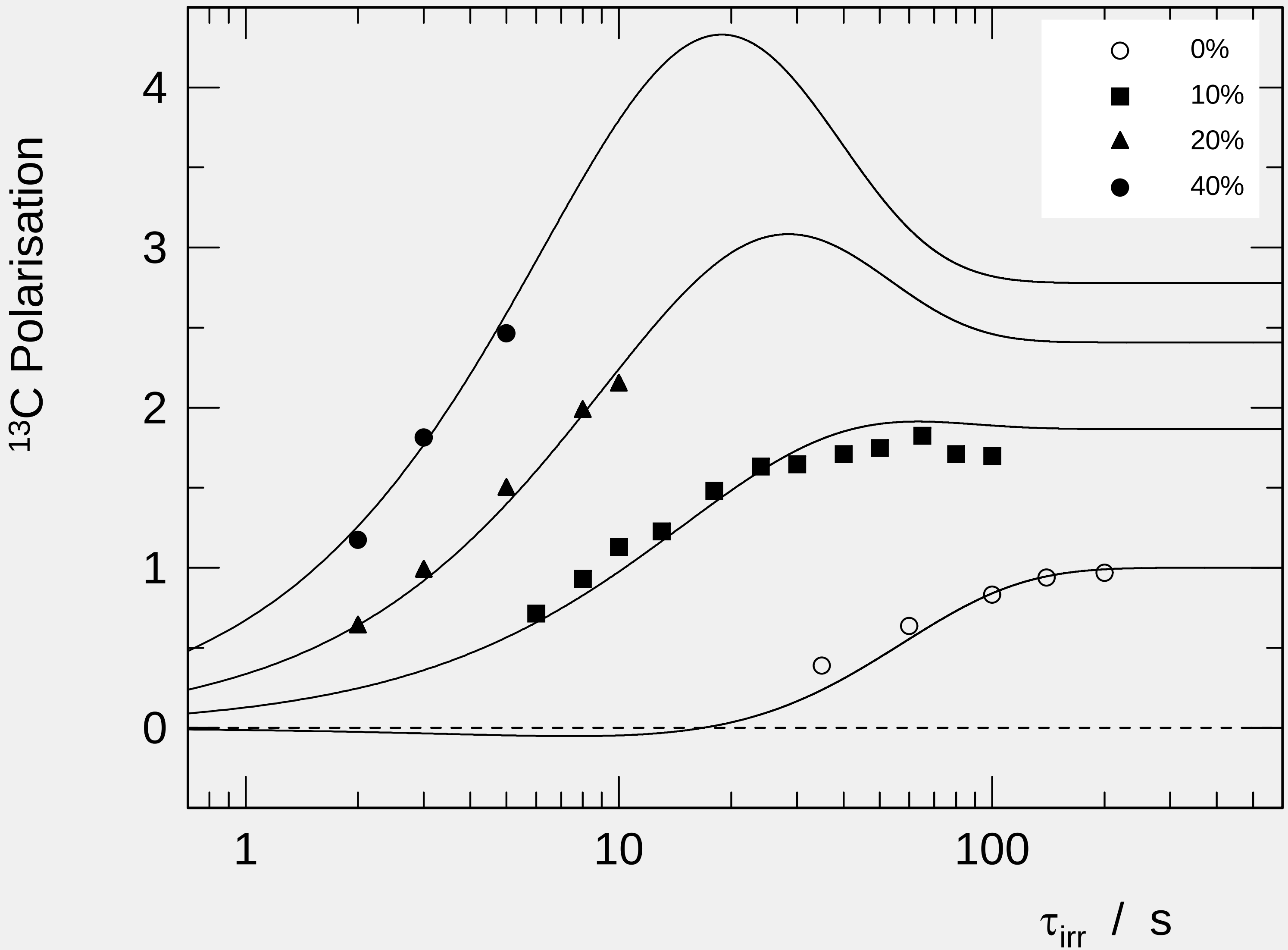
Nuclear Solid Effect:



Nuclear Solid Effect:



Nuclear Solid Effect:



Concluding remarks

- Molecular Dynamics influences the low temperature nuclear relaxation
- Combining magnetic field dependence with low temperature enables one to explore and exploit a wide variety of magnetic resonance behaviour
- Thermal reservoirs and the Pauli Exclusion Principle
- Facilitates investigation of both the quantised states and the transfer of energy between thermally isolated reservoirs

Acknowledgements

Nottingham: Cheng Sun, Daniel Noble, Qiang Xu, Weimin Wu,

Kuldeep Panesar, Ilya Frantsuzov, Dermot Brougham,

Richard Jenkinson

DRLC Quadrupolar Nuclei: John Smith, King's College