The Role of Relaxation in NMR Signal Detection

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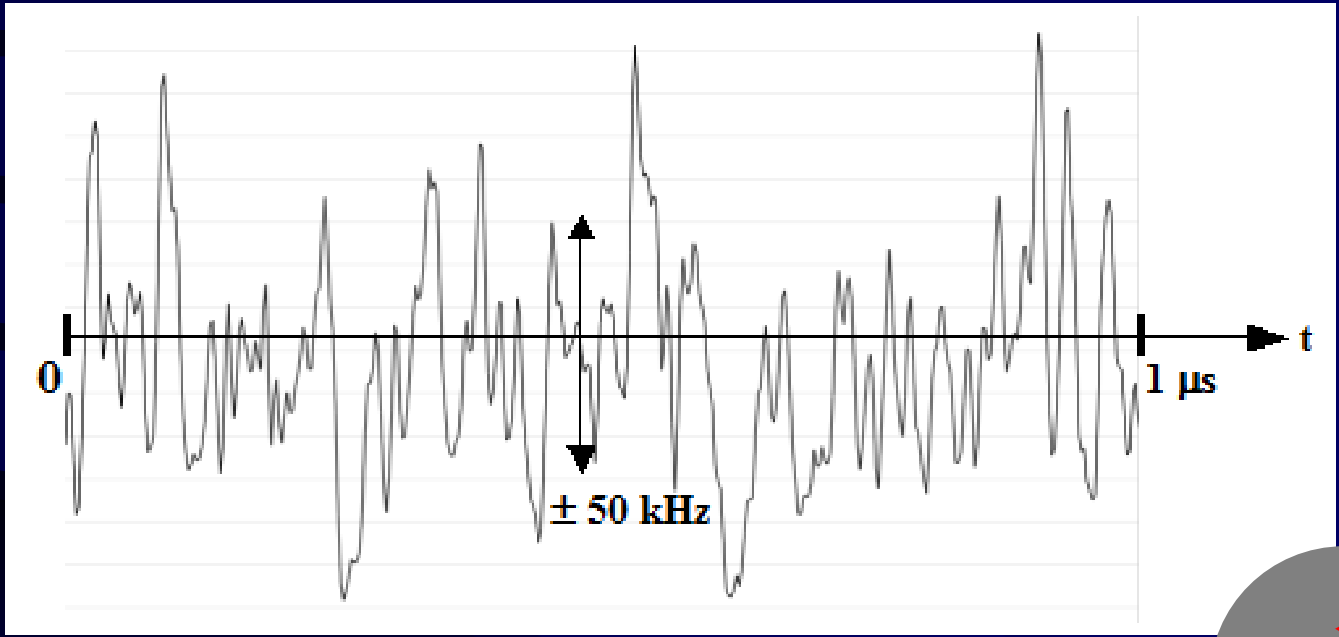

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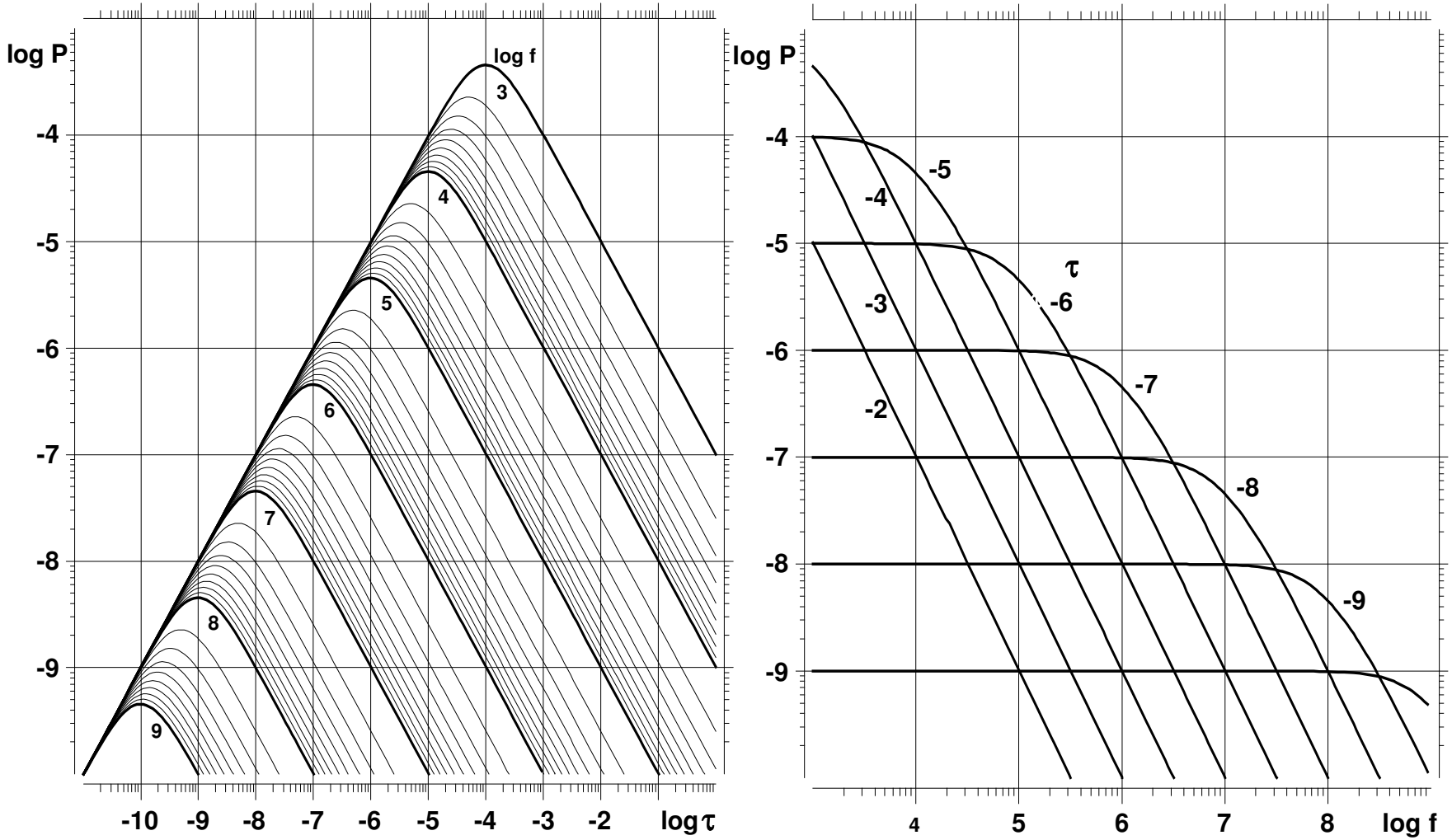
The purpose of this talk is …
to raise doubts ☹ so we can discuss them

Topics to be discussed:

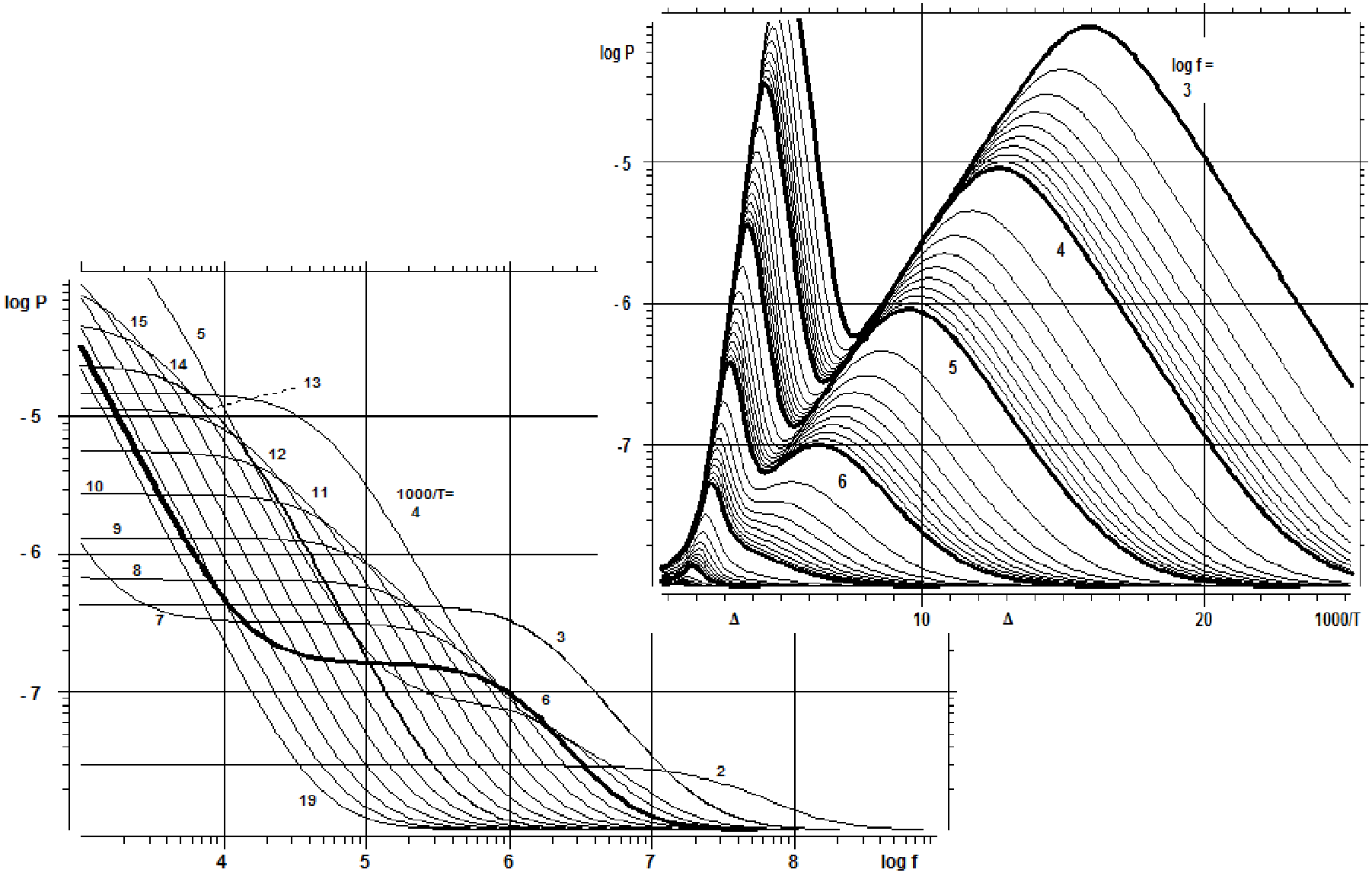
- Relaxation as an ensemble-enabling process (thermo-dynamics)
- The role of relaxation in establishing nuclear magnetic [thermal] polarization
- Relaxation and phase coherence of quantum spin states
- Relaxation and the feasibility of a single-spin experiment
- Relaxation and the concept of "spontaneous" emission
- **Time-dependent Hamiltonians, averaging, and the nature of quantum transitions**
- **Is an FID a superposition of *instantaneous* transitions or of *lengthy* ones?**
- Comparing CW and pulsed NMR in the limit of very long relaxation times
- Relaxation via coil-induced magnetic field fluctuations Relaxation and S/N ratio

What I am not going to talk about: BPP formula

Function $P(\tau,f) = J_\tau(\omega)+4\,J_\tau(2\omega)$, where $J_\tau(\omega) = 2\tau/[1+(\omega\tau)^2]$ and $\omega = 2\pi f$



What I will skip: BPP+Arrhenius processes



What I will also barely mention:
Relaxation Mechanisms (heat & entropy "pumps")

Spin interactions:

- Nucleus - Nucleus Dipole-Dipole
- Nuclear - Electron Dipole-Dipole
- Chemical spin anisotropy
- Quadrupole
- Spin-Rotation
- …

N different types

Molecular dynamics:

- Rotational diffusion
- Translational diffusion
- Internal rotations
- Librations
- Reptations
- …

M different types

Total: N*x*M principal formulas
plus (N*x*M) (N*x*M - 1)/2 cross-relaxation ones

Example: for N = 5, M = 5 we have 25 principal and 300 cross "kinds of pumps"

For what I want to say

we just need to keep in mind that relaxations
reflect large numbers of interactions *among* spins,
as well as *between spins and the rest of the world*,
which

(a) are time-dependent,
(b) fluctuate too fast for the system to follow,
(c) and time-average to zero

Let us call them simply ***relaxation interactions***

They do not appear in the static Hamiltonian,
yet they are paramount to understanding
the NMR phenomenon

Relaxation – like interactions as an ensemble-enabling process

Thermodynamics is ***enabled*** by relaxations

Without relaxation there would be **NO thermal equilibrium,**

… and **NO thermal polarization**

… and **NO signal !**

(or not ?)

Relaxation and phase-coherence of spin states

Relaxation destroys induced phase coherence …

(decay of an FID in even a perfectly homogeneous field)

… but it also …

induces a degree of **spontaneous** phase coherence

(consider the spin noise phenomenon)

Relaxation phenomena in quantum systems

The density matrix of the spin system is a *projection* of a density matrix defined in a much larger Liouville-space onto a subspace thereof

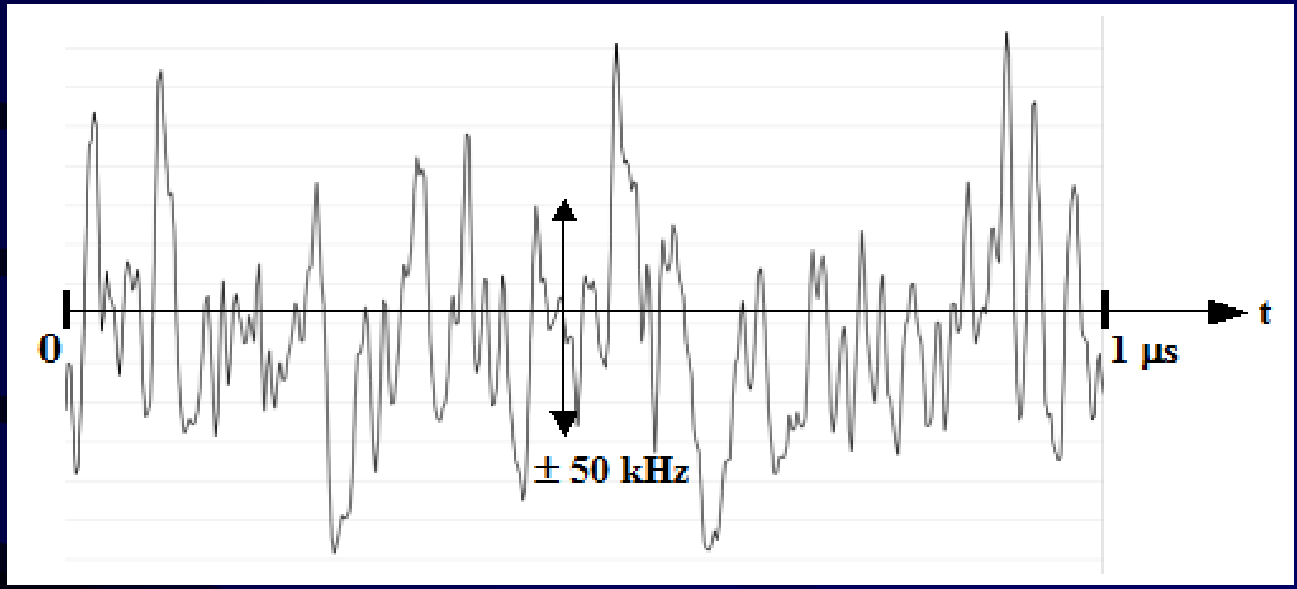
Principal effects of relaxation interactions:

- ✓ Broadening of quantum energy levels
- ✓ Finite lifetimes of quantum eigenstates
- ✓ Appearance of 'spontaneous' emissions
- ✓ Broadening of spectral lines
- ✓ 'Forbidden' coherences

None of these concepts is applicable to an 'isolated spin system'

But let us have a look at one such interaction

Dipolar interaction between vicinal protons of a methylene group under typical conditions of a small-molecule liquid-state NMR:

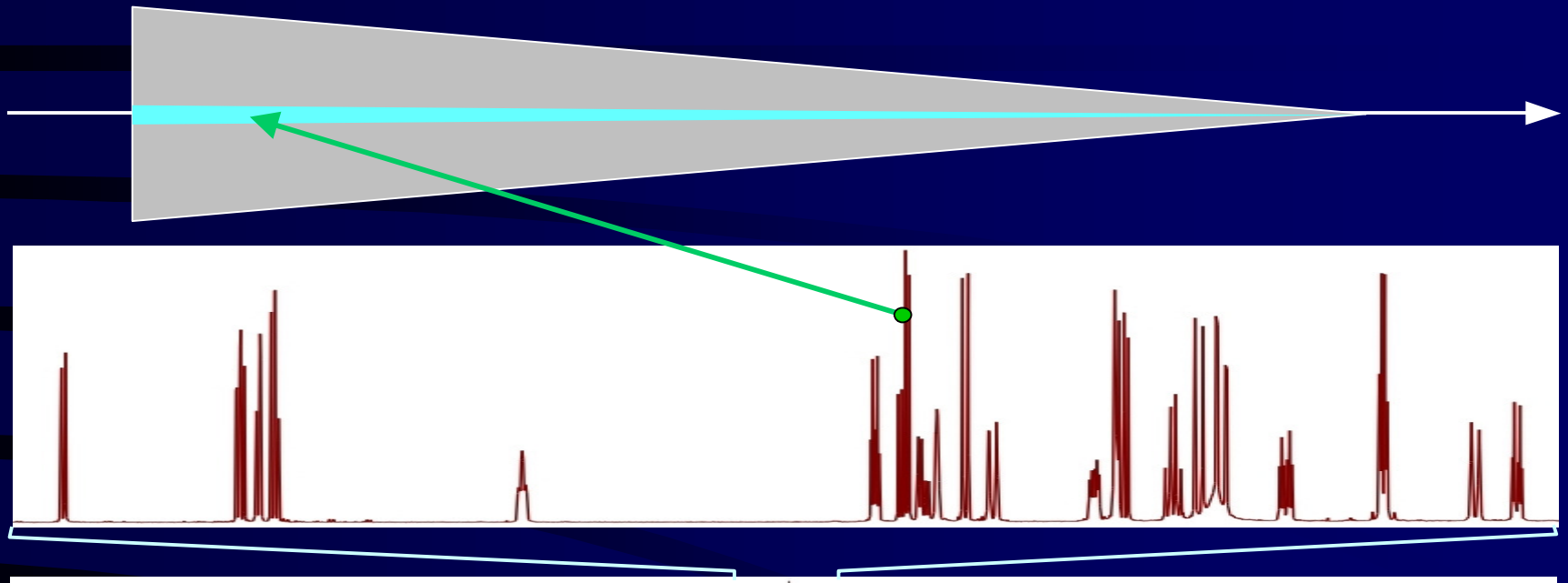


The molecular tumbling avarages it out to about 0.01 Hz

To achieve this, a random walk brownian motion needs hundreds of seconds – the whole duration of an FID !

FID's of time-averaged quantum systems:

a mind-boggling puzzle



Dipolar couplings average out and only 'mean photons' get emitted ?

So what really IS an FID?

? A *swarm* of *brief, pulse-like* quantum transitions

? A *sum* of many *long* quantum transitions

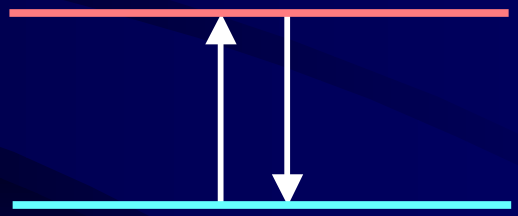
? Something else altogether

Transitions in Quantum Physics?

Consider this simple fact:

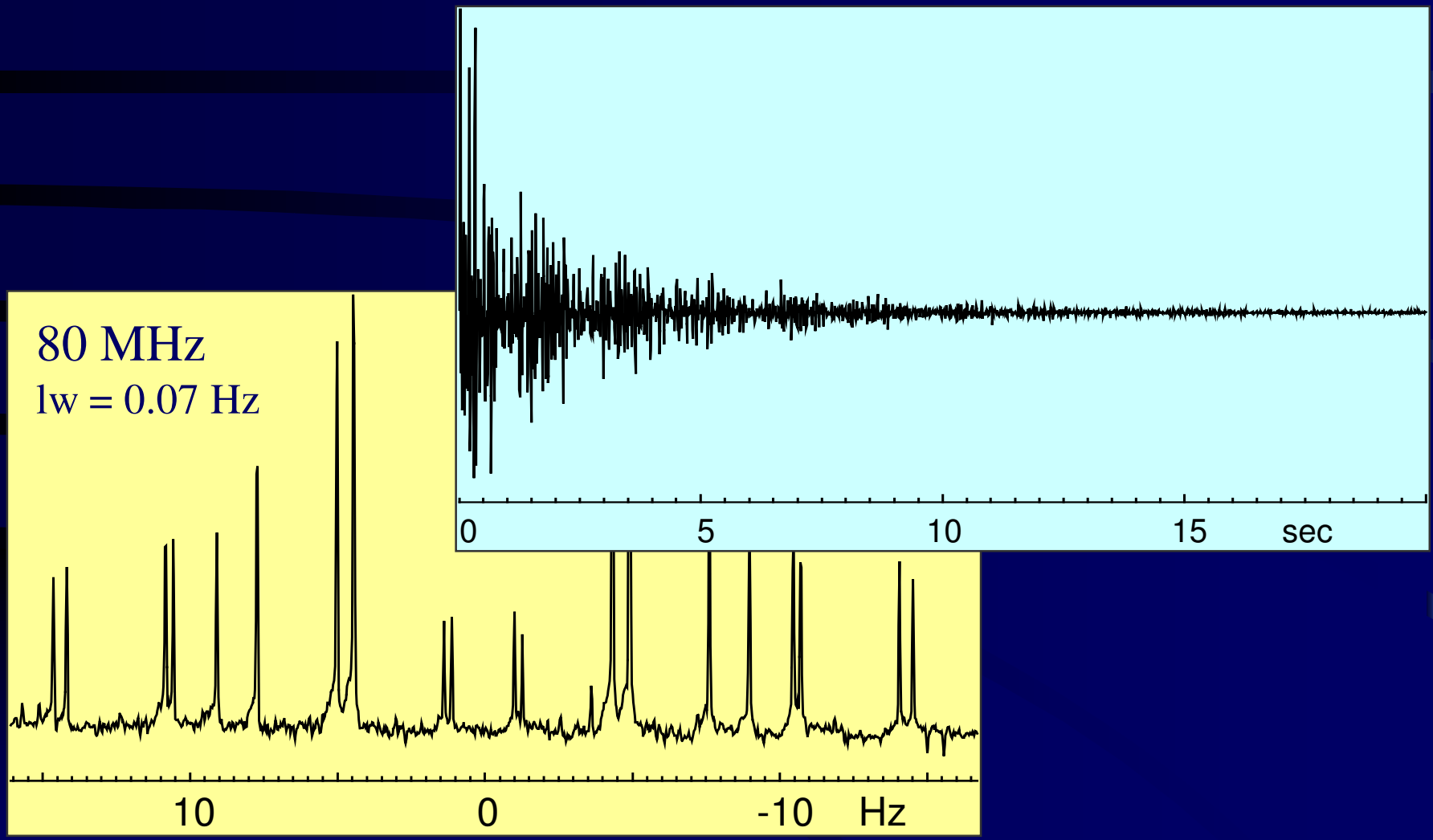
Quantum Physics has NO *apparatus* to tell us what happens *during* a Quantum Transition!

By *convention*, and *convention* only, transitions are assumed to be instantaneous.



Quantum transitions lasting 15 seconds !?

Why not! Quantum Physics can't contradict it



So how can we describe an FID?

I presently believe that it is best done (at least for practical purposes) as a smooth, transition-less evolution in the Liouville-space of the combined {spin-system-cum-coil} under the effect of its time-averaged Hamiltonian (including the spins-coil coupling) and the relaxation interactions with their second-order secular effects.

Nothing less can do it!

Alas, it still does not cover the radiation component
(if really present)

Thank you – and let's Discuss!