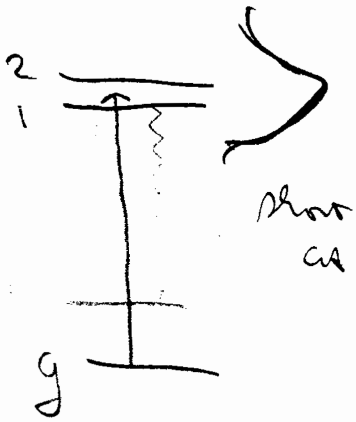
10.2.1

Quantum-Beat Spectroscopy

Motivation: You have a broadband light source but want to learn something about closely-lying levels

(this was the common situation before lasers came up)



$$|\psi(0)\rangle = \sum_{k=1,2} a_k \, |\phi_k(0)\rangle$$

short pulse at $t=0$

$$|\psi(t)\rangle = \sum a_k \, |\phi_k(0)\rangle \, e^{-iE_k t/\hbar} \underbrace{e^{-t/2\tau}}_{\text{spont. decay}}$$

Observe fluorescence to level f (could be g)

$$I(t) = C \, |\langle \phi_f | \hat{e}\,\vec{r} \, | \psi(t) \rangle|^2$$

Pol. of observed light

$$\Rightarrow \quad I(t) = C \, e^{-t/\tau} \Big(A + \underbrace{B_1 \cos\omega_{12} t + B_2 \sin\omega_{12} t}_{B} \Big)$$

$$A = a_1^2 \, |\langle \phi_f | \hat{e}\,\vec{r} \, | \phi_1 \rangle|^2 + a_2^2 \, |\langle \phi_f | \hat{e}\,\vec{r} \, | \phi_2 \rangle|^2$$

$$B = 2\,\mathrm{Re}\Big[a_1^* a_2 \, \langle \phi_f | \hat{e}\,\vec{r} \, | \phi_1 \rangle^* \langle \phi_f | \hat{e}\,\vec{r} \, | \phi_2 \rangle \, e^{-i(E_2-E_1)t/\hbar} \Big]$$

Wolfgang Demtröder

Laser Spectroscopy

Basic Concepts and Instrumentation

Second Enlarged Edition
With 644 Figures and 91 Problems

8.421

10.2.2. Quantum beats with delayed detection

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14.6 Spectral Resolution within the Natural Linewidth

Assume that all other line-broadening effects except the natural linewidth have been eliminated by one of the methods discussed in the previous chapters. The question that arises is whether the natural linewidth represents an insurmountable natural limit to spectral resolution. At first sight it might seem that Heisenberg's uncertainty relation does not allow any outwit of the natural linewidth (Sect.3.1). In order to demonstrate that this is not true we give in this section some examples of techniques which do allow observation of structures *within* the natural linewidth. It is, however, not obvious that all of these methods may really increase the amount of information about the molecular structure, since the inevitable loss in intensity may outweight the gain in resolution. We discuss under which conditions spectroscopy within the natural linewidth may be a tool which really helps to improve the quality of spectral information.

14.6.1 Time-Gated Coherent Spectroscopy

The first of these techniques is based on the selective detection of those excited atoms or molecules which have survived in the excited state for times $t \gg \tau$ long compared to the natural lifetime τ.

If molecules are excited into an upper level with the spontaneous lifetime $\tau = 1/\gamma$ by a light pulse ending at $t = 0$, the time-resolved fluorescence amplitude is given by

$$A(t) = A(0)\, e^{-(\gamma/2)t} \cos\omega_0 t \qquad (14.49)$$

If the observation time extends from $t = 0$ to $t = \infty$, a Fourier transformation of the measured intensity $I(t) \propto A^2(t)$ yields, for the line profile of the fluorescence emitted by atoms at rest, the Lorentzian profile (Sect.3.1)

$$I(\omega) = \frac{I_0}{(\omega-\omega_0)^2 + (\gamma/2)^2} \quad \text{with} \quad I_0 = \frac{\gamma}{2\pi}\int I(\omega)\, d\omega\, . \qquad (14.50)$$

If the detection probability for $I(t)$ is not constant, but follows the time dependence $f(t)$, the detected intensity $I_g(t)$ is determined by the *gate function* $f(t)$

$$I_g(t) = I(t)\, f(t)\, .$$

The Fourier transform of $I_g(t)$ now depends on the form of $f(t)$ and may no longer be a Lorentzian. Assume the detection is gated by a step function

$$f(t) = \begin{Bmatrix} 0 \text{ for } t < T \\ 1 \text{ for } t \geq T \end{Bmatrix}$$

which may simply be realised by a shutter in front of the detector, which opens only for times $t \geq T$ (Fig.14.44)

The Fourier transform of the amplitude $A(t)$ in (14.49) is now

$$A(\omega) = \int_T^{\infty} A(0)\,e^{-\gamma/2t}\cos(\omega_0 t)\,e^{-i\omega t}\,dt\,,$$

which yields in the approximation $\Omega = |\omega-\omega_0| \ll \omega_0$, with $\exp(-i\omega t) = \cos(\omega t) - i\sin(\omega t)$ the cosine and sine Fourier transforms:

$$A_c(\omega) = \frac{A_0}{2}\,\frac{e^{-\gamma/2T}}{\Omega^2 + (\gamma/2)^2}\left[\frac{\gamma}{2}\cos(\Omega T) - \Omega\sin(\Omega T)\right],$$

$$A_s(\omega) = \frac{A_0}{2}\,\frac{e^{-(\gamma/2)T}}{\Omega^2 + (\gamma/2)^2}\left[\frac{\gamma}{2}\sin(\Omega T) + \Omega\cos(\Omega T)\right]. \qquad (14.51)$$

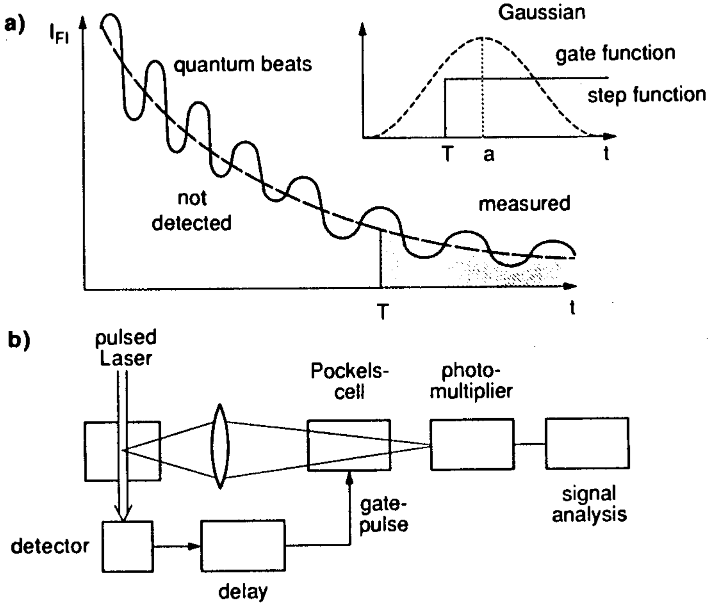

Fig.14.44a,b. Gated detection of exponentional fluorescence decay with a gate function f(t). (a) Schematic scheme and (b) experimental realization

If only the incoherent fluorescence intensity is observed without getting any information on the phases of the wave function of the excited state, we observe the intensity

$$I(\omega) \propto |A_c(\omega) - iA_s(\omega)|^2 = A_c^2 + A_s^2 = \frac{A_0^2}{2\cdot 2}\,\frac{e^{-\gamma T}}{\Omega^2 + (\gamma/2)^2}\,. \qquad (14.52)$$

This is again a Lorentzian with a halfwidth (FWHM) of $\gamma = 1/\tau$, that is independent of the gate time T! Because of the delayed detection one loses the factor $\exp(-T/\tau)$ in intensity, since all fluorescence events occurring for times $t < T$ are missing. *This shows that with incoherent techniques no narrowing of the natural linewidth can be achieved, even if only fluorescence photons from selected long-living atoms with $t > T \gg \tau$ are selected* [14.109].

The situation changes, however, if instead of the intensity (14.52), the amplitude (14.49) or an intensity representing a coherent superposition of amplitudes can be measured where the phase information and its development in time is preserved. Such measurements are possible with one of the coherent techniques discussed in Chap.12.

One example is the quantum-beat technique. According to (12.25a) the fluorescence signal at the time t after the coherent excitation at $t = 0$ of two closely spaced levels separated by $\Delta\omega$, with equal decay times $\tau = 1/\gamma$, is

$$I(t) = I(0)\,e^{-\gamma t}(1 + a\cos\Delta\omega t) \qquad (14.53)$$

where the term $\cos(\Delta\omega t)$ contains the wanted information on the phase difference

$$\Delta\varphi(t) = \Delta\omega t = (E_i - E_k)t/\hbar$$

between the wave functions $\psi_n(t) = \psi_n(0)\,e^{-iE_n t/\hbar}$ $(n = i,k)$ of the two levels $|i\rangle$ and $|k\rangle$.

For observations from $t = 0$ to $t = \infty$ the cosine Fourier transform of (14.53) is

$$I(\omega) = I_0\gamma\,\cancel{e^{t}}\left(\frac{1}{\omega^2 + \gamma^2} + \frac{a\;1}{(\Delta\omega+\omega)^2 + \gamma^2} + \frac{a\;1}{(\Delta\omega-\omega)^2 + \gamma^2}\right). \qquad (14.54)$$

For frequencies ω close to the difference $\Delta\omega$ (i.e., $\Delta\omega-\omega \ll \Delta\omega$) the first two terms can be neglected. The third term yields a Lorentzian profile centered at $\omega = \Delta\omega$ with the halfwidth 2γ which equals the sum of the two level widths $\gamma_a = \gamma_b = \gamma$ (Fig.12.7).

If now the detector is gated to receive fluorescence only for $t > T$, the Lorentzian term in the Fourier transform of (14.53) becomes

$$I_c(\omega) = \frac{I_0\,a}{2}\,\frac{e^{-\gamma T}}{(\Delta\omega-\omega)^2 + \gamma^2}\left[\gamma\cos(\Delta\omega-\omega)T - (\Delta\omega-\omega)\sin(\Delta\omega-\omega)T\right]. \qquad (14.55)$$

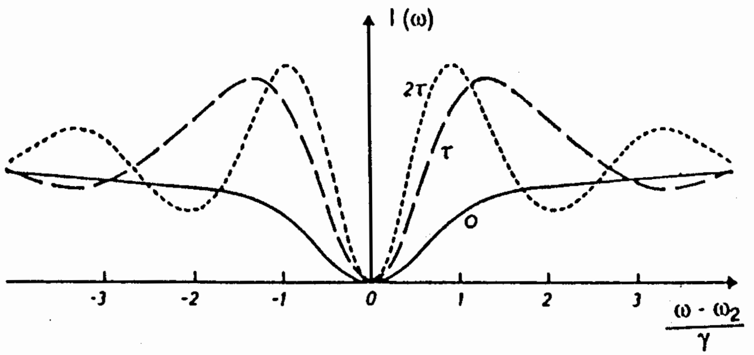

Fig.14.45. Oscillatory structure of the cosine Fourier transform with narrowed central maximum for increasing values of the gate delay time T = 0, τ and 2τ. The peak intensity has been always normalized

For T > 0 the intensity $I_c(\omega)$ exhibits an oscillatory structure (Fig.14.45) with a central maximum at $\omega \simeq \Delta\omega$ [because of the first two terms in (14.54) the center is not exactly at $\omega = \Delta\omega$] and the halfwidth

$$\Delta\omega_{12} = \frac{2\gamma}{\sqrt{1+\gamma^2 T^2}}. \tag{14.56}$$

Example 14.12

For $T = 5\tau = 5/\gamma$ the *halfwidth* of the central peak has decreased from γ to 0.4γ. The peak intensity, however, has drastically decreased by the factor $\exp(-\gamma T) = \exp(-5) \simeq 10^{-2}$ to less than 1% of its value for T = 0.

The decrease of the peak intensity results in a severe decrease of the signal-to-noise ratio. This may, in turn, lead to a larger uncertainty in determining the line center.

The oscillatory structure can be avoided if the gate function f(t) is not a step function but a Gaussian $f(t) = \exp[-(t-T)^2/b^2]$ with $b = (2T/\gamma)^{1/2}$ [4.110].

Another coherent technique which can be combined with gated detection is the level-crossing spectroscopy (Sect.12.1). If the upper atomic levels are excited by a pulsed laser and the fluorescence intensity $I_{Fl}(B, t \geq \tau)$ as a function of the magnetic field is observed with increasing delay times T for the opening of the detector gate, the central maximum of the Hanle signal becomes narrower with increasing T. This is illustrated by Fig.14.46 which shows a comparison of measured and calculated line profiles for different gate delay times T for Hanle measurements of the $Ba(6s6p\,^1P_1)$ level [14.111]. Similar measurements have been performed for the Na(3P) level [14.112].

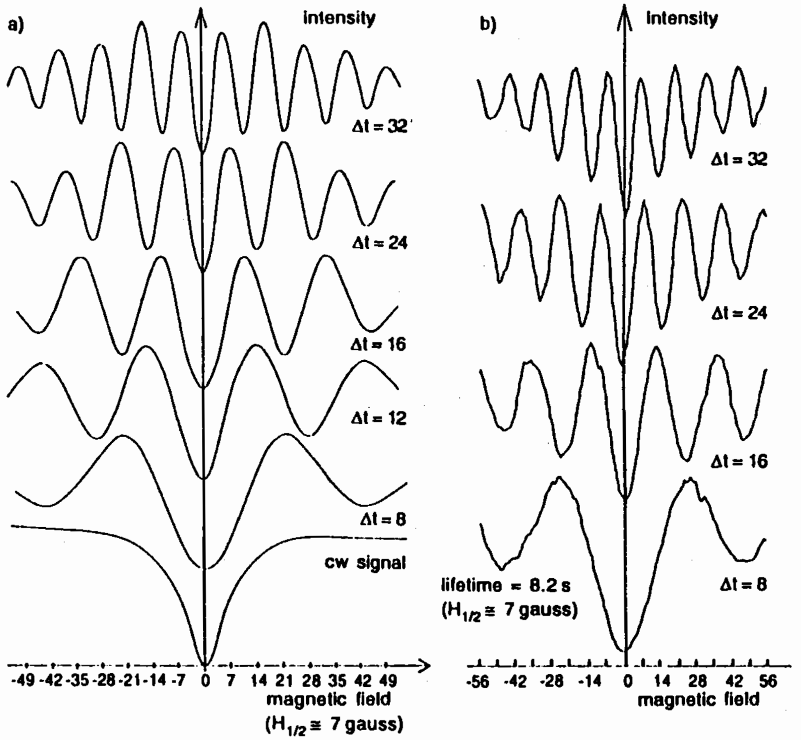

Fig.14.46. Comparison of calculated (a) and measured (b) line profiles of level crossing signals under observation with different gate delay times. The different curves have been renormalized to equals centered peak intensities [14.112]

It should be emphasized that line narrowing is only observed if the time development of the phase of the upper-state wave function can be measured. This is the case for all methods which utilize interference effects caused by the superposition of different spectral components of the fluorescence. Therefore, an interferometer with a spectral resolution better than the natural linewidth can be used, too. However, a narrowing of the observed fluorescence linewidth with increasing gate delay time T is only observed if the gating device is placed between the interferometer and the detector; it is *not* observed if the gate is placed between emitting source and interferometer [14.109]

Instead of a gated switch in the fluorescence detector for pulsed excitation one may also use excitation by a CW laser that is phase-modulated with a modulation amplitude of π (Fig.14.47). The fluorescence generated under sub-Doppler excitation in a collimated atomic beam is observed during a short time interval Δt which is shifted by the variable delay T against the time t_0 of the phase jump. If the fluorescence intensity $I_{Fl}(\omega, T)$ is monitored as a function of the laser frequency ω a narrowing of the line profile is found with increasing T [14.113].