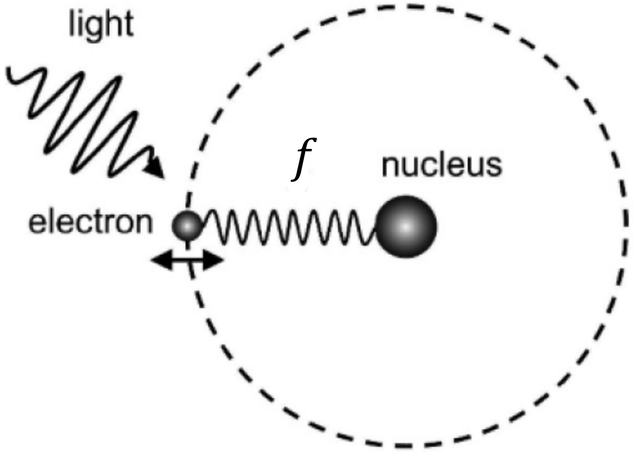
1.5 Absorption and Emission

The classical oscillator model

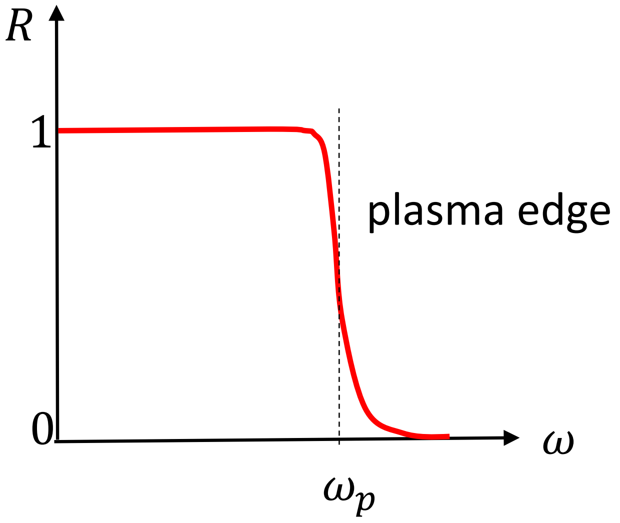


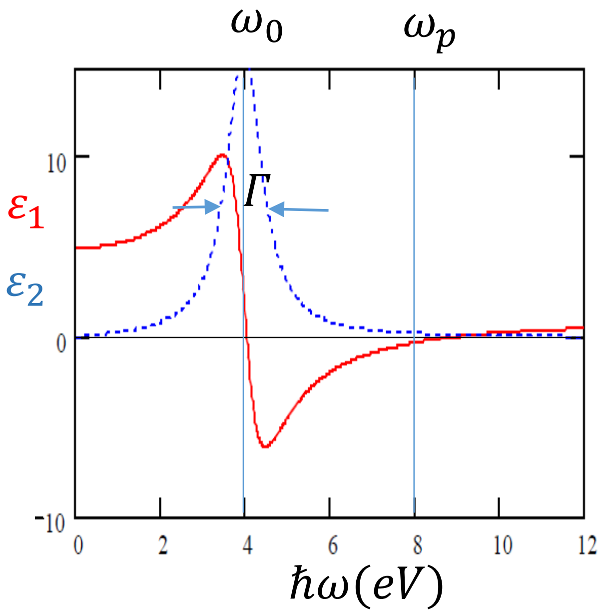
at resonance

$$\omega_0 = \sqrt{\frac{f}{m_e}}$$

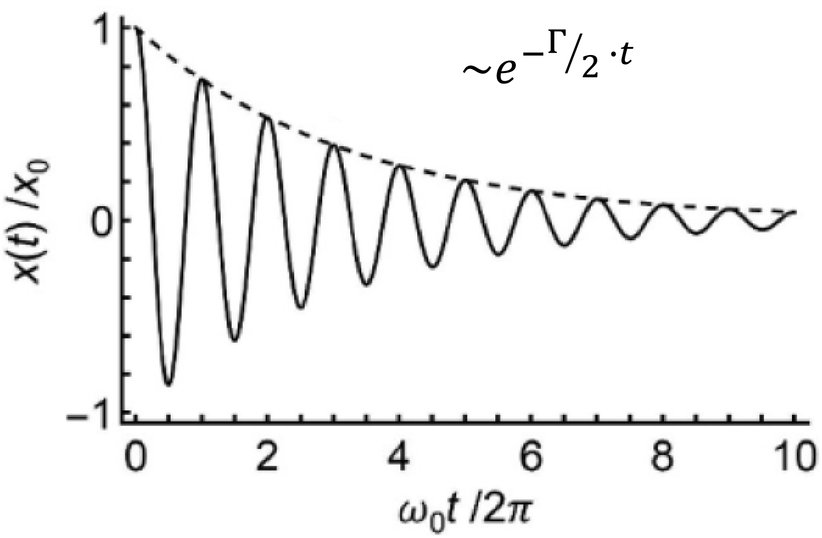
Many spectral features can very well be described by classical dispersion theory (for example the dispersion relation at the transition frequency, the behavior of free electrons, plasmons, absorption and potentially emission. (We could add phonons, that we have not discussed here).

However, we were not able to make any prediction about the strength of the absorption. Also we are not sure about the lifetime of an excited state:



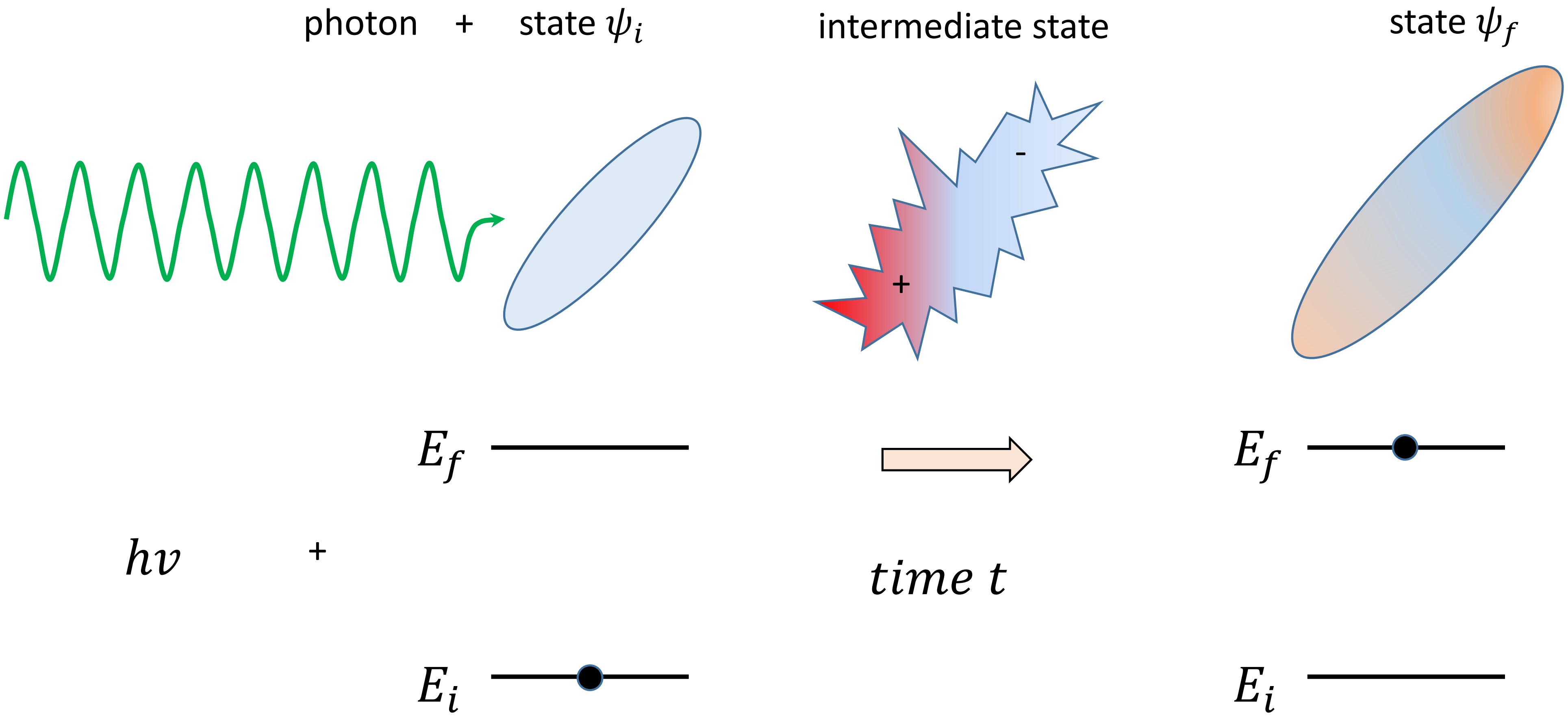


For a damped harmonic oscillator:



Absorption from a quantum mechanical point of view:

Example of a two level system:



photon + state ψ_i

intermediate state

state ψ_f

$h\nu$ +

E_f

E_i

$time\ t$

E_f

E_i

The quantum mechanical approach

The strongest interaction of a photon with an atom, molecule or solid is the interaction of the photon electric field $\vec{E}$ with the electric dipole moment of the object. The energy of this interaction is given by $\widehat{\mathrm{H}}' = \vec{\mu}\vec{E}$, the potential energy of an electric dipole in the electric field $\vec{E}$.

To calculate the transition probability of a simple two level system from an initial state with energy E_i to a final state with energy E_f the Schrödinger equation is solved using perturbation theory.

$$i\hbar\frac{\partial}{\partial t}\Psi = \widehat{H}_{total}\Psi \qquad \text{with} \qquad \widehat{H}_{total} = \widehat{H}_0 + \widehat{H}' \qquad \text{and} \qquad \widehat{H}' = \vec{\mu}\cdot\vec{E}(\omega, t)$$

Ansatz: $\Psi = a_i\Psi_i + a_f\Psi_f$

The probability to find the system in the final state Ψ_f after a time *t* is proportional to $\left|a_f\right|^2$

As a result, we obtain the transition probability *P* which can be listed as follows:

P has its maximum at resonance, i.e. when $\omega_{if} = \frac{1}{\hbar}\left(E_f - E_i\right)$, meaning that energy is conserved.

$$P \sim \left|\vec{E}\right|^2 \cdot \left|\vec{\mu}_{if}\right|^2$$

$\vec{\mu}_{if}$ **is the transition dipole moment**:

$$\vec{\mu}_{if} = \int \psi_f^*\ e\cdot\vec{r}\ \psi_i\ d^3\vec{r}$$

ψ_i and ψ_f are the wave functions of the initial and final state, respectively. The wave functions include the spatial, vibrational and spin function.

The transition dipole moment

We see that $\vec{\mu}_{if}$ contains the pertinent physical information about the transition, which could not be extracted from the classical model:

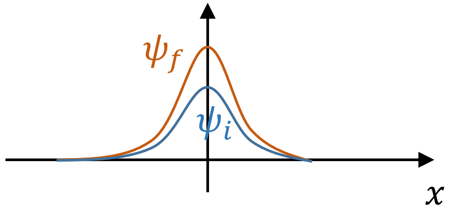
- ☐ Strength of the transition
- ☐ Polarization dependence
- ☐ Rate of the transition
- ☐ Selection rules: Symmetry, angular momentum, Franck Condon overlap, spin

The selection rules for a single electron system are:

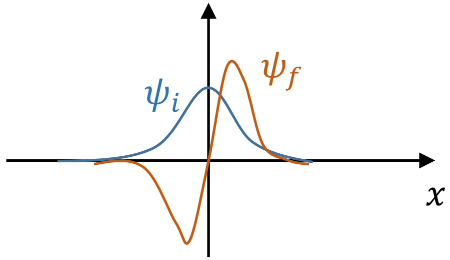
Angular momentum: $\Delta l = \pm 1$
Magnetic quantum number: $\Delta m = 0,\ \pm 1$
Spin: $\Delta s = 0$

An illustration of zero and non-zero transition dipole moment (only the spatial wave function is considered):

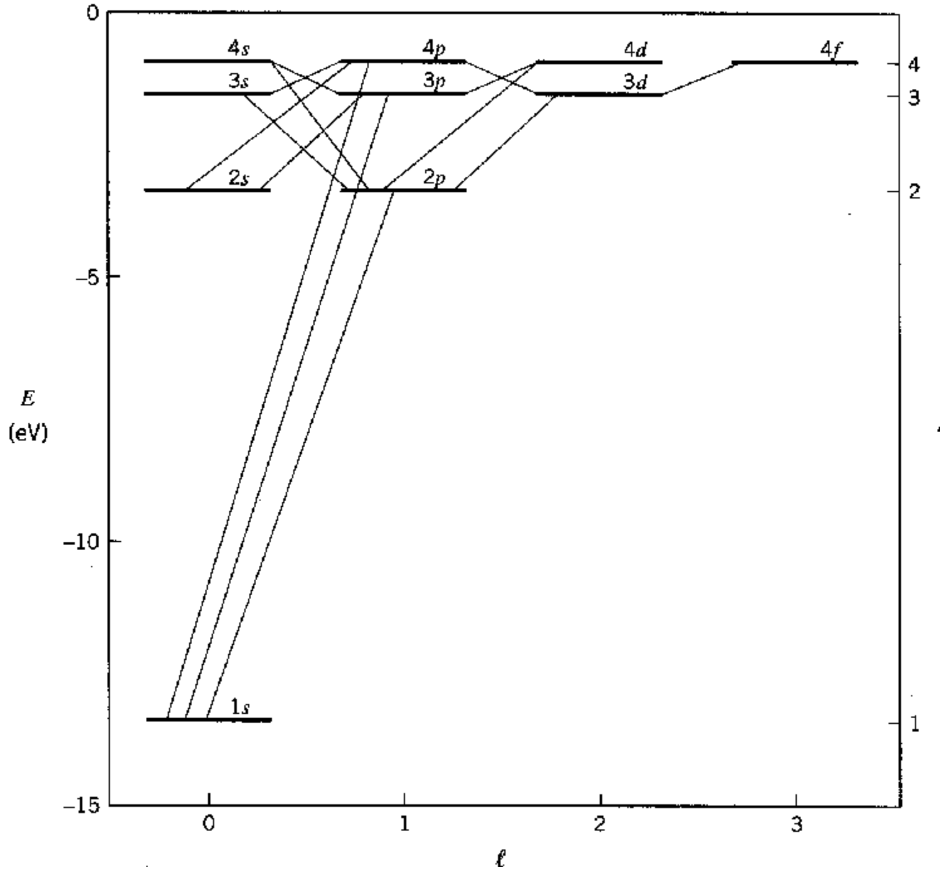
$$\vec{\mu}_{if} = \int \psi_f \, e \cdot x \, \psi_i \, dx = 0$$



$$\vec{\mu}_{if} = \int \psi_f \, e \cdot x \, \psi_i \, dx \neq 0$$



Allowed transitions for the hydrogen atom

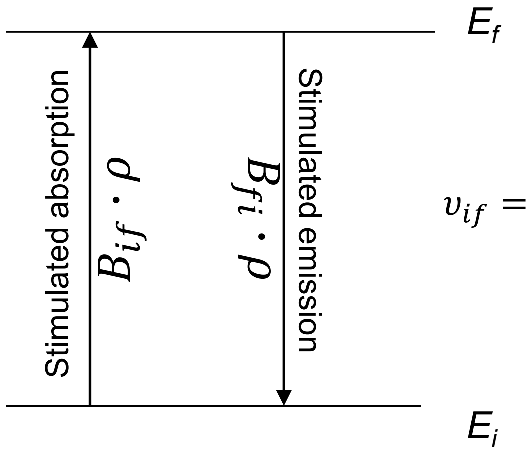


Final note: since the total angular momentum L must be conserved, the photon must carry an angular momentum of $\pm 1 \cdot \hbar$ (this can be understood as right handed and left handed polarization).

The laws of radiation – Einstein coefficients

In the following we will follow arguments in a non-chronological way. From the previous discussion, we have been able to describe the strength of the absorption transition by the transition dipole moment $\left|\vec{\mu}_{if}\right|^2$. By simple arguments, we see that the transition from the excited state to the ground state is governed by precisely the same transition dipole moment $\left|\vec{\mu}_{fi}\right|^2 = \left|\vec{\mu}_{if}\right|^2$. This also means that the "downwards" transition (=stimulated emission) is as likely as the upward transition (absorption) if we start from the excited state.

Einstein (1917) used both a quantum mechanical and thermodynamical argument to derive the laws of radiation. For this purpose a two level system is placed in equilibrium with the radiation field of a black body ρ ($\rho(\upsilon)d\upsilon$ is the radiation density in the range υ to υ+ $d\upsilon$).



$$\upsilon_{if} = \frac{\omega_{if}}{2\pi} = \frac{1}{h}\left(E_f - E_i\right)$$

First let us define the transition rate w for (stimulated) absorption: $w_{if} = B_{if} \cdot \rho(\upsilon_{if})$

As indicated in the figure to the right, we can similarly express the rate for stimulated emission: $w_{fi} = B_{fi} \cdot \rho(\upsilon_{if})$

To invoke a thermodynamical (equilibrium) argument, we need to look at the population N_i and N_f of the states with energies E_i and E_f, respectively. The rate W of change of the populations then is:

$W_{if} = B_{if} \cdot \rho(\upsilon_{if}) \cdot N_i$ and $W_{fi} = B_{fi} \cdot \rho(\upsilon_{if}) \cdot N_f$

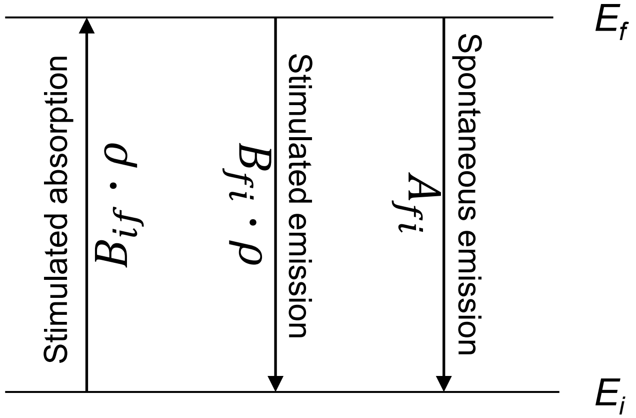
When only these two processes (see figure to the right) are in equilibrium, the following condition must hold:

$W_{if} = W_{fi}$ or $B_{if} \cdot \rho(\upsilon_{if}) \cdot N_i = B_{fi} \cdot \rho(\upsilon_{if}) \cdot N_f$ and therefore:

$\frac{B_{if}}{B_{fi}} = \frac{N_f}{N_i} \left(= e^{-\frac{(E_f - E_i)}{kT}} = e^{-\frac{h\upsilon_{if}}{kT}}\right)$ according to the Boltzmann distribution. Since B_{if} and B_{fi} are rate constants, this leads to a contradiction.

To resolve this inconsistency, a third process is introduced to the equilibrium of radiation: spontaneous emission with rate constant A_{fi}:

B_{if}…Einstein coefficient of stimulated absorption
B_{fi}…Einstein coefficient of stimulated emission
A_{fi}…Einstein coefficient of spontaneous emission



$$\upsilon_{if} = \frac{\omega_{if}}{2\pi} = \frac{1}{h}\left(E_f - E_i\right)$$

Therefore $w_{fi} = B_{fi} \cdot \rho(\upsilon_{if}) + A_{fi}$ and $W_{fi} = N_f[B_{fi} \cdot \rho(\upsilon_{if}) + A_{fi}]$. Again we can write the condition for thermodynamical equilibrium:

$B_{if} \cdot \rho(\upsilon_{if}) \cdot N_i = (B_{fi} \cdot \rho(\upsilon_{if}) + A_{fi}) \cdot N_f$. Solving for the radiation density $\rho(\upsilon_{if})$, we obtain:

$$\rho(\upsilon_{if}) = \frac{A_{fi}}{B_{if}} \cdot \frac{1}{\left(\frac{N_i}{N_f} - \frac{B_{fi}}{B_{if}}\right)} = \frac{A_{fi}}{B_{if}} \cdot \frac{1}{\left(e^{\frac{h\upsilon_{if}}{kT}} - \frac{B_{fi}}{B_{if}}\right)}$$

This relation must correspond to the Planck distribution:

$$\rho(\upsilon_{if}) = \frac{8\pi h {\upsilon_{if}}^3}{c^3} \cdot \frac{1}{\left(e^{\frac{h\upsilon_{if}}{kT}} - 1\right)}$$

Comparison of the above two expressions show that $B_{if} = B_{fi}$ (which confirms the arguments invoking $\left|\vec{\mu}_{fi}\right|^2 = \left|\vec{\mu}_{if}\right|^2$). Furthermore we obtain a relation between the coefficients of stimulated and spontaneous emission:

$$A_{fi} = \frac{8\pi h {\upsilon_{if}}^3}{c^3} \cdot B_{if} \qquad (1)$$

The relative importance of spontaneous emission grows as the cube of the transition frequency. Spontaneous emission is actually what we call fluorescence.

Relating the Einstein coefficients to the transition dipole moment

It can be sown that the coefficient of stimulated absorption B_{if} can be related to $\left|\vec{\mu}_{if}\right|^2$:

$$B_{if} = \frac{\left|\vec{\mu}_{if}\right|^2}{6\varepsilon_0 \hbar^2} \qquad (2) \qquad \text{and with (1), we obtain:} \quad A_{fi} = \frac{8\pi^2 \nu_{if}{}^3}{3\varepsilon_0 \hbar c^3} \left|\vec{\mu}_{if}\right|^2$$

Summarizin,g we can state for absorption: $\alpha = \frac{4\pi}{\lambda} k \sim B_{if} \sim \left|\vec{\mu}_{if}\right|^2$ and for the fluorescence Quantum yield : $\phi_f \sim A_{fi} \sim B_{if} \sim \left|\vec{\mu}_{if}\right|^2$

Final remarks on the line shape

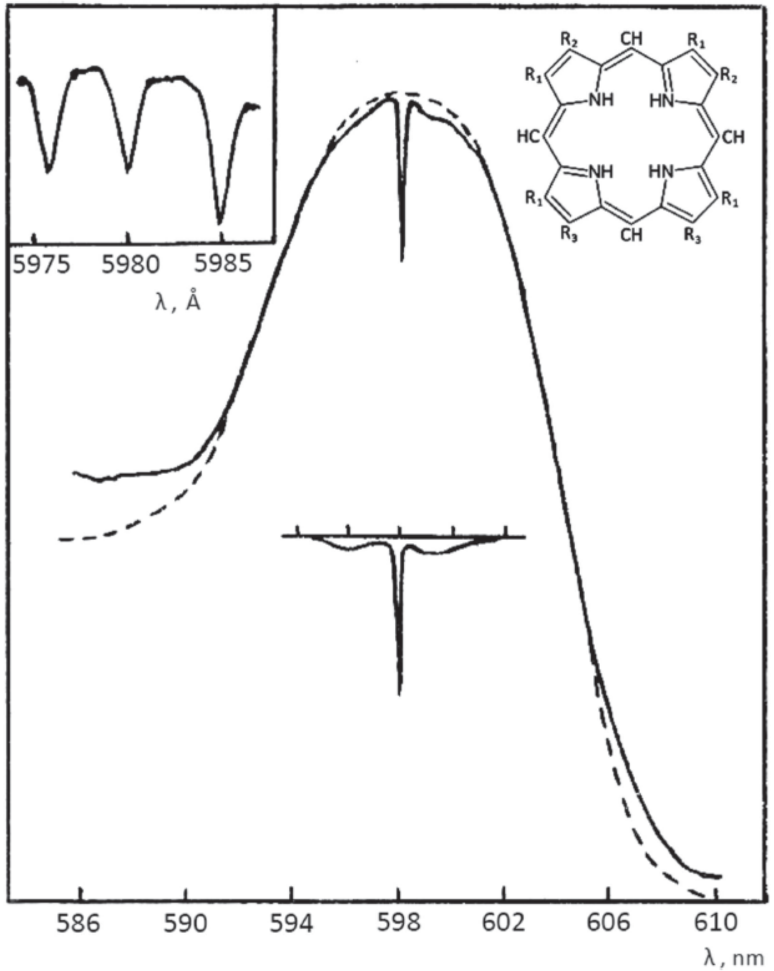
In quantum mechanics the natural linewidth (smallest possible) of a system is related by the Heisenberg uncertainty principle: $\Delta E \cdot \Delta t \geq {}^{\hbar}/_{2}$. Taking the lifetime $\Delta t = \tau$ (the lifetime of the resonance) we can relate the transition linewidth as follows:

$\Delta\omega \cdot \tau \geq {}^{1}/_{2}$ or $\Delta\omega = {}^{1}/_{2\tau}$ and with $\tau = {}^{1}/_{A_{fi}}$ one obtains $\Delta\omega = {}^{A_{fi}}/_{2}$

For a typical natural radiative lifetime of $10^{-9} s$ one would obtain a natural line width of $\Delta\omega = 5 \cdot 10^{8}$ Hz, which is extremely narrow compared to the resonance frequency (ω_0 or ν_{if}).
Let us compare this result to the classical Lorentz oscillator. Here we have $\Delta\omega = \Gamma$. For metals, typical values of $\Gamma = 10^{13}$ to 10^{14} Hz one obtains a linewidth of $\Delta\omega \approx 10^{14}$ Hz which is much broader and requires some interpretation. However, we can conclude that the analogy between classical damped harmonic oscillators and lifetime of an excited state indeed holds for optical transitions. As we find from the Heisenberg uncertainty principle, $\tau = {}^{1}/_{2\Gamma}$ holds, which is of the similar order of magnitude as for classical damped oscillators.

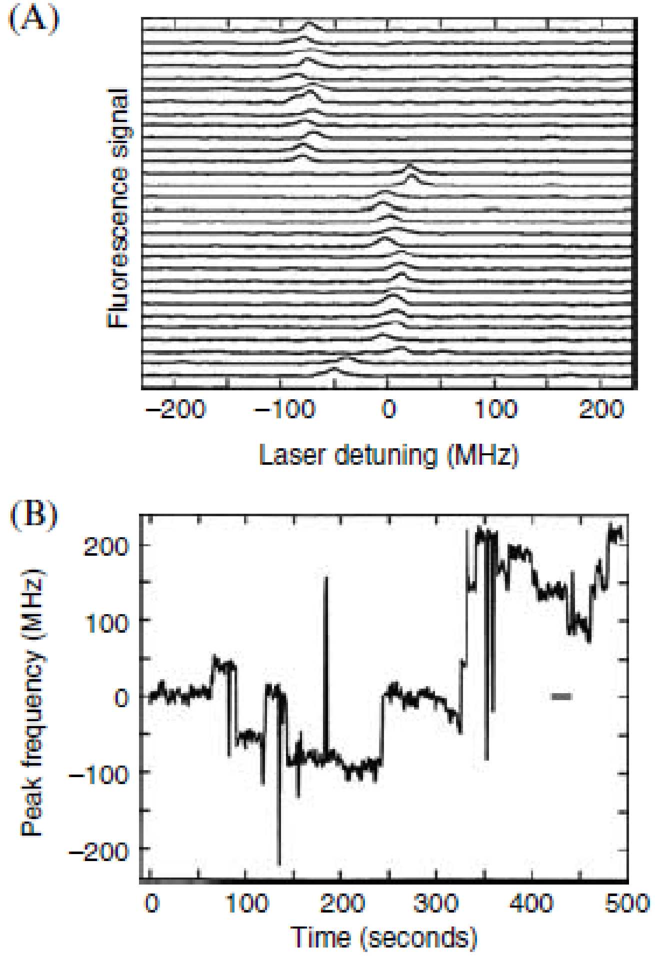
Note: The line shape of a transition or an absorption band is always significantly broadened, be it in the gas phase, in solution or even more in the solid. The broadening is due to collisions and to the Doppler effect. In solution and in the solid we get a substantial inhomogeneous broadening due to the different environments of the oscillator (chromophore) as well as from interatomic/intermolecular interactions. The width of the spectra actually could be fitted by a single Lorentz oscillator (or multiple oscillators), but in this case the obtained relaxation time no longer corresponds to the natural lifetime τ.

Spectral hole burning in the inhomogeneous 0–0 absorption band of protoporphyrin IX acid dication in 1 N HCl solution in ethanol at 5 K



M. Sapozhnikov *Phys. Scr.* **93** 033002 (2018)

Single molecule fluorescence excitation spectrum of pentacene in *p*-terphenyl at 1.5K *(zero detuning = 592.546 nm)*



W.P. Ambrose, W.E. Moerner, *Nature* 349, 225–227 (1991)