Resonant optical rectification. Theory and application to bacteriorhodopsin

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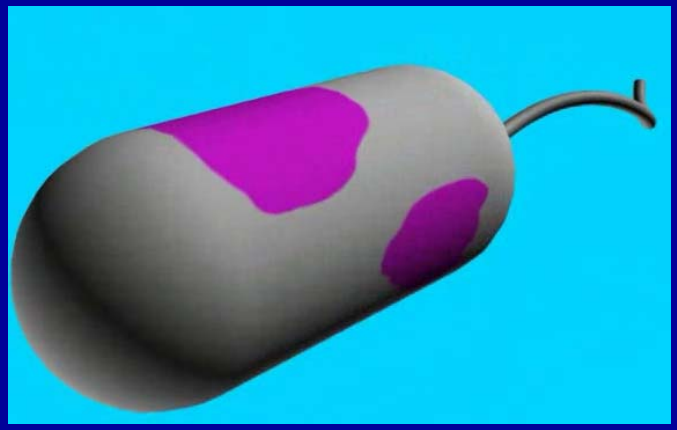
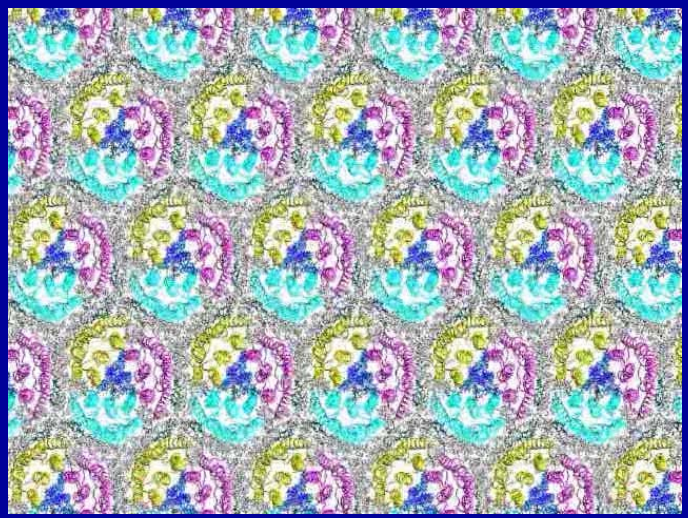
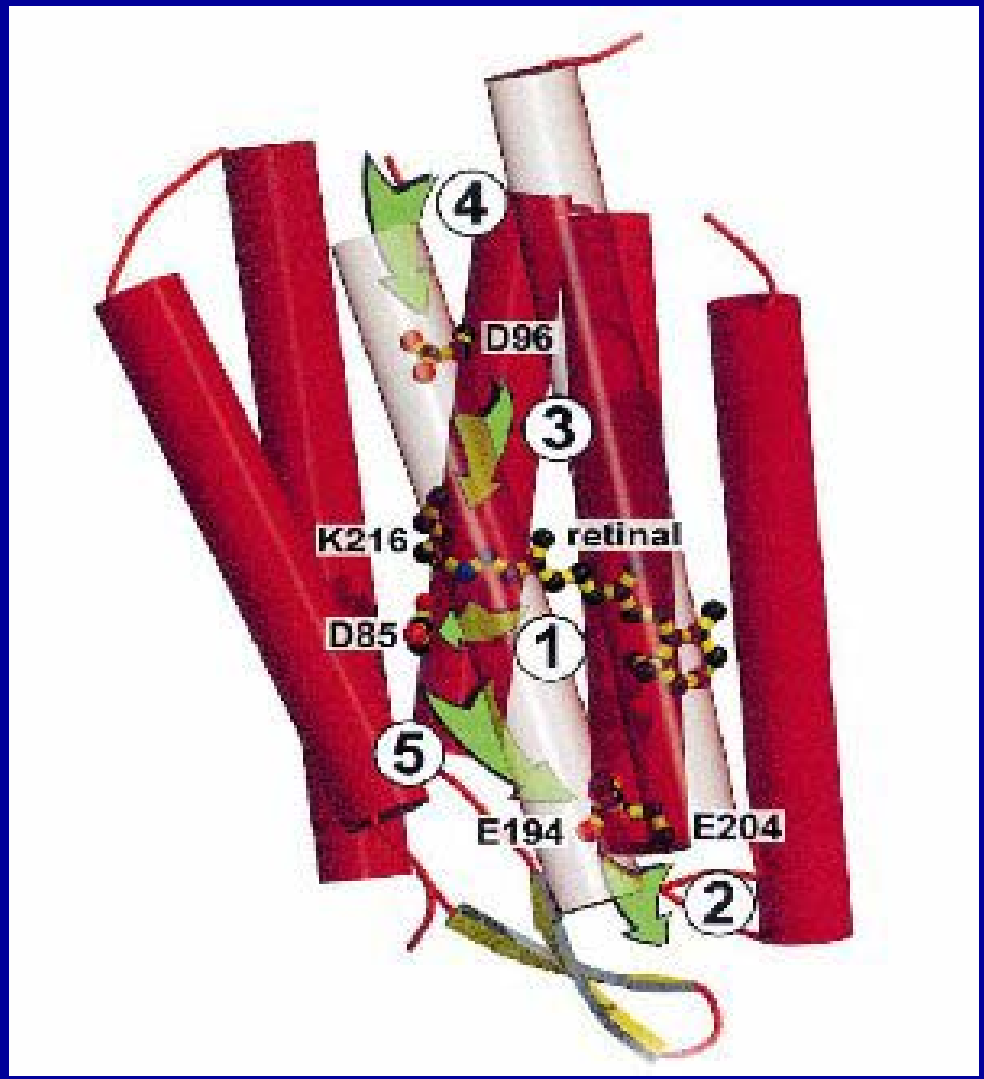
Bacteriorhodopsin



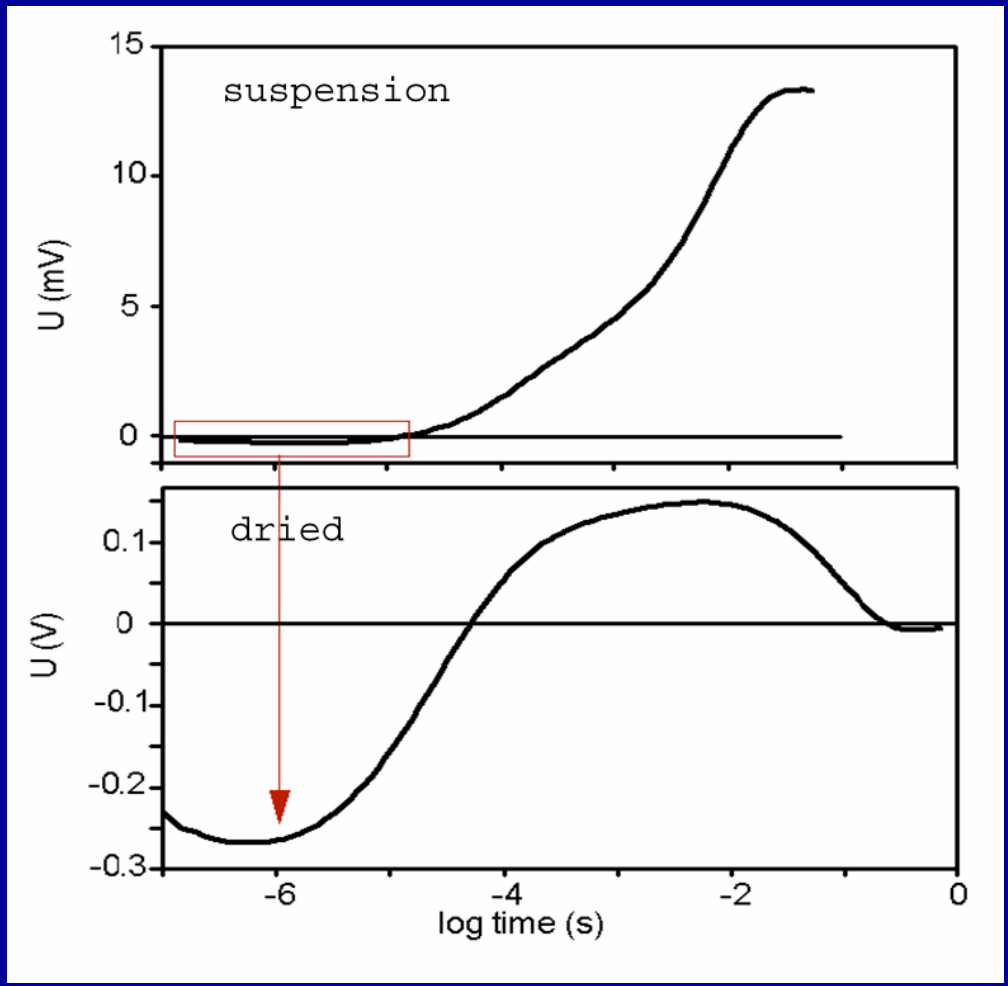
Single protein in the purple membrane of *Halobactrium salinarium*

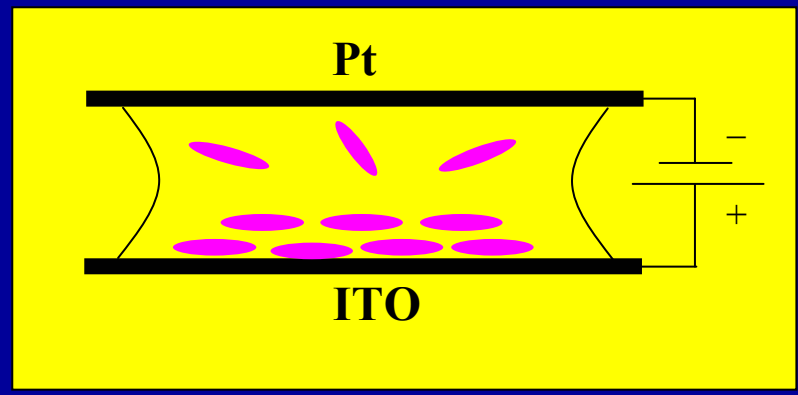


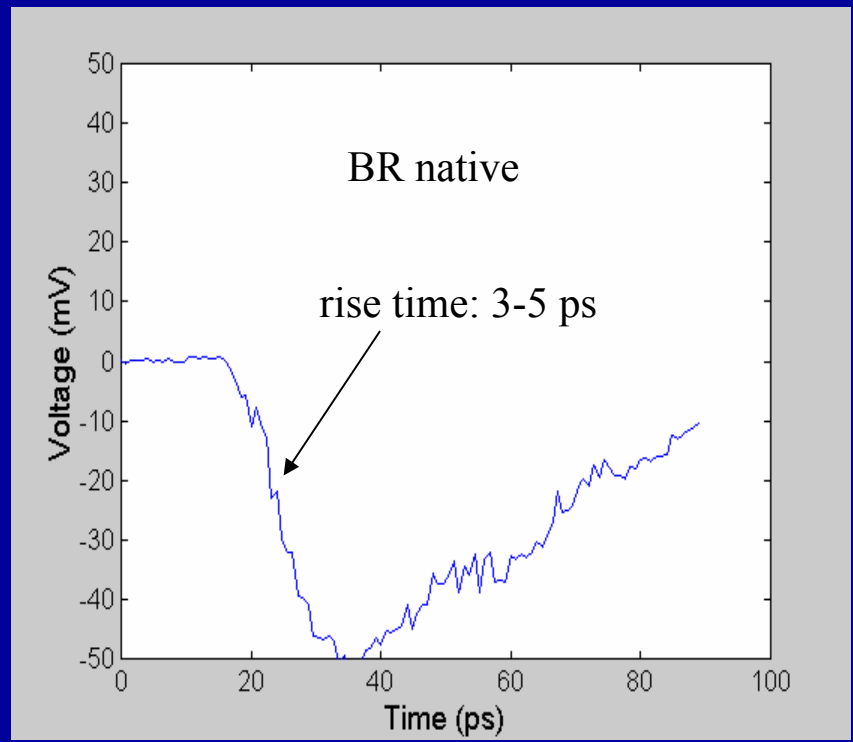
Forms hexagonal 2D crystal in the membrane



Utilizes light energy by pumping protons across the membrane







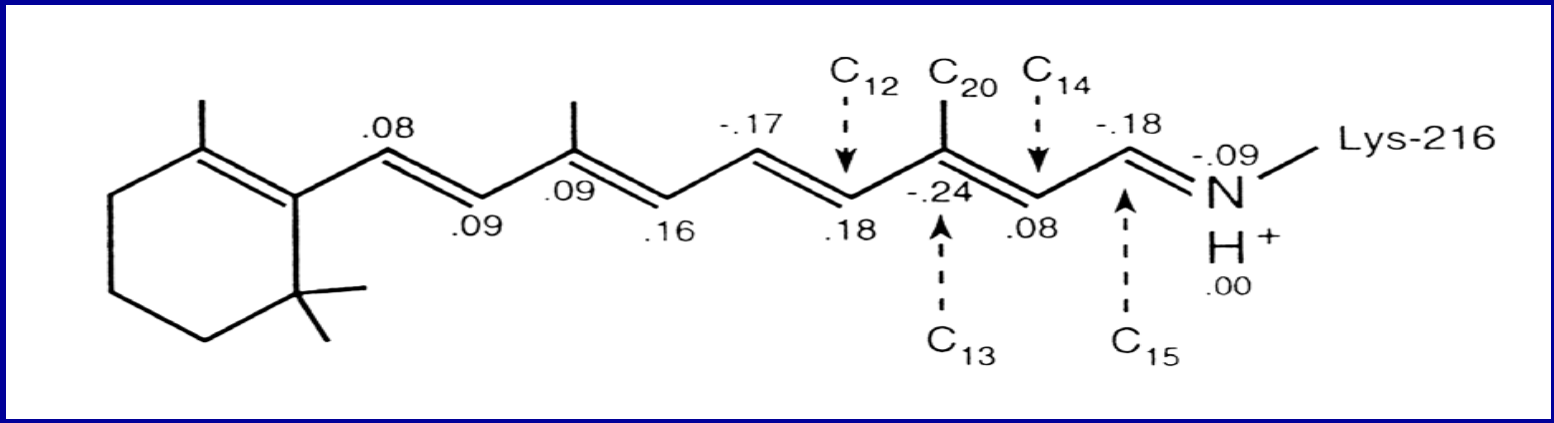
Light-induced electric response signal of oriented purple membrane sample

What is the real primary charge separation process?

Traditional idea: charge separation by all-trans → 13-cis isomerization of the retinal chromophore

still popular

questioned by studies on artificial pigments of locked isomerization



μ_{11}

excited state

μ_{00}

ground state

$\mu_{11} - \mu_{00} = 12\,\mathrm{D}$

Mathies & Stryer, PNAS 73, 2169 (1976)

Upon excitation a huge change of dipole moment takes place.

According to the Maxwell theory this is a source of electromagnetic radiation.

What kind of optical phenomenon could describe this radiation?

The expected radiation

- rises instantaneously with absorption
- decays with excited state = aperiodic, no carrier freqency
- observable only on oriented (noncentrosymmetric) sample

- can not be a first order optical process
- resonant
- dominated by T_1 relaxation

fundemental 2nd order processes

~~second harmonic generation~~

optical rectification

no resonant theory!

(popular χ^2 expressions are singular)

Theory of resonant optical rectification

(based on Mukamel's method)

$$P^{(2)}(\mathbf{r},t)=\int_0^\infty dt_2\int_0^\infty dt_1 S^{(2)}(t_2,t_1)E(\mathbf{r},t-t_2)E(\mathbf{r},t-t_2-t_1)$$ second-order polarisation

$$S^{(2)}(t_2,t_1)=\left(\frac{i}{\hbar}\right)^2 <<V|G(t_2)VG(t_1)V|\rho(-\infty)>>$$ two-point transfer function

$$G(t)A\equiv\theta(t)\exp\left(-\frac{i}{\hbar}[H,A]t\right)$$ Liouville-space Green function

$$V=\sum_{a,b}\mu_{ab}\,|a><b| \qquad \mu_{ab}=<a|V|b>$$ Hilbert-space dipole operator

$$V\,A=[V,A]$$ Liouville-space dipole operator

$$\chi^{(2)}(-\omega_s;\omega_1,\omega_2)=\frac{1}{2}\rho_0\sum_p S^{(2)}(\omega_1+\omega_2,\omega_1)$$ second-order susceptibility

Specification of the (tetradic) relaxation matrix:

$$\Gamma_{aa,bb\ (a\neq b)} \equiv \gamma_{ab}$$

$$\Gamma_{aa,aa} \equiv -\gamma_a \equiv -\sum_{b(\neq a)} \Gamma_{bb,aa}$$

$$\Gamma_{ab,ab} = -\frac{1}{2}\left(\gamma_a + \gamma_b\right) - \hat{\Gamma}_{ab} \equiv -\Gamma_{ab}$$

In earlier work the offdiagonal elements were neglected $\Gamma_{aa,bb\ (a\neq b)} = 0$

- simpler formula
- lack of conservation of the probability
- singularity in $\chi^{(2)}\left(-\omega_s;\omega_1,\omega_2\right)$ for $\omega_1 = -\omega_2$

For a two-level system with complete T_1 relaxation matrix:

$$S^{(2)}(t_2,t_1)=\left(\frac{1}{\hbar}\right)^2\left(P(0)-P(1)\right)\mu_{10}^2\left(\mu_{11}-\mu_{00}\right)\theta(t_2)\theta(t_1)\left\{-2\,\mathrm{e}^{-\frac{t_1+t_2}{T_2}}\cos\left[\omega_{10}(t_1+t_2)\right]\right.$$
$$\left.+2\,\mathrm{e}^{-\frac{t_2}{T_1}}\mathrm{e}^{-\frac{t_1}{T_2}}\cos(\omega_{10}t_1)\right\}$$

ω_{10} transition frequency

T_1 population relaxation time

T_2 coherence relaxation time

$$0<T_2<=2T_1$$

incident light:

$$E(t) = Env(t)\cos(\omega_0 t)$$

polarisation:

$$P^{(2)}(t) = \int_0^\infty dt_2 \int_0^\infty dt_1 S^{(2)}(t_2, t_1)\, Env(t - t_2)\cos\left[\omega_0 (t - t_2)\right] Env(t - t_2 - t_1)\cos\left[\omega_0 (t - t_2 - t_1)\right]$$

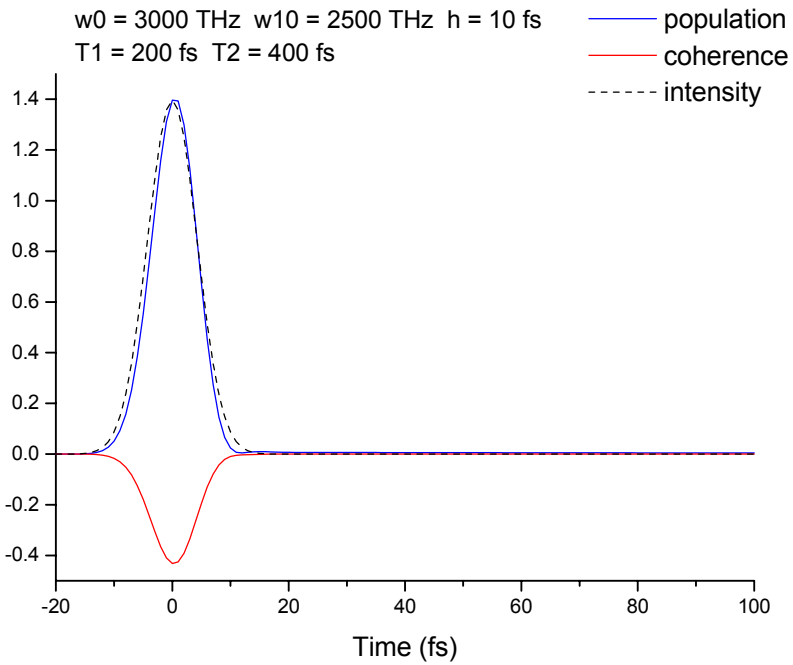
$$P^{(2)}(t) = P^{(2)}_{OR}(t) + P^{(2)}_{SH}(t)$$

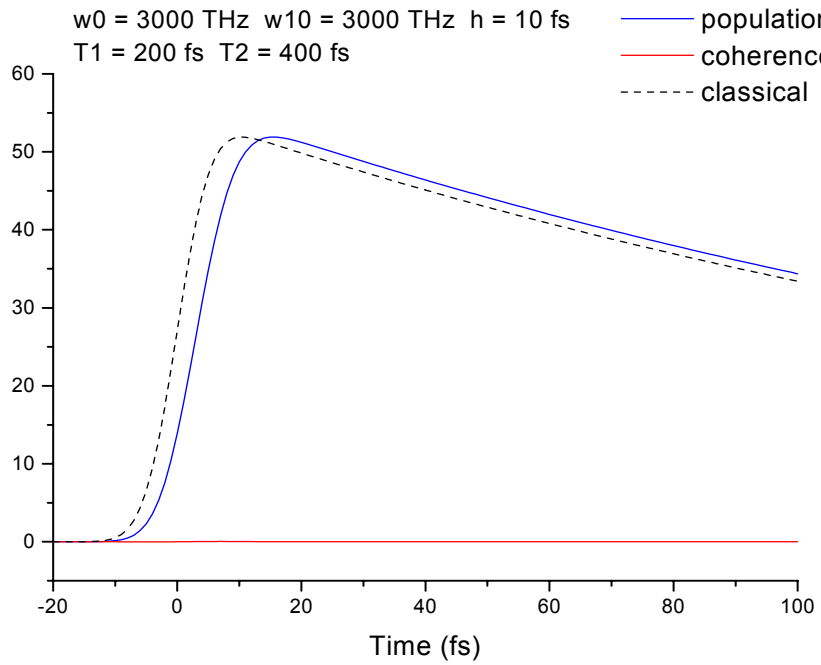
optical rectification:

$$P^{(2)}_{OR}(t) = \int_0^\infty dt_2 \int_0^\infty dt_1 S^{(2)}_0(t_2, t_1)\, Env(t - t_2)\, Env(t - t_2 - t_1)$$

$$S^{(2)}_0(t_2, t_1) = \frac{1}{2} S^{(2)}(t_2, t_1)\cos(\omega_0 t_1)$$

Simulations

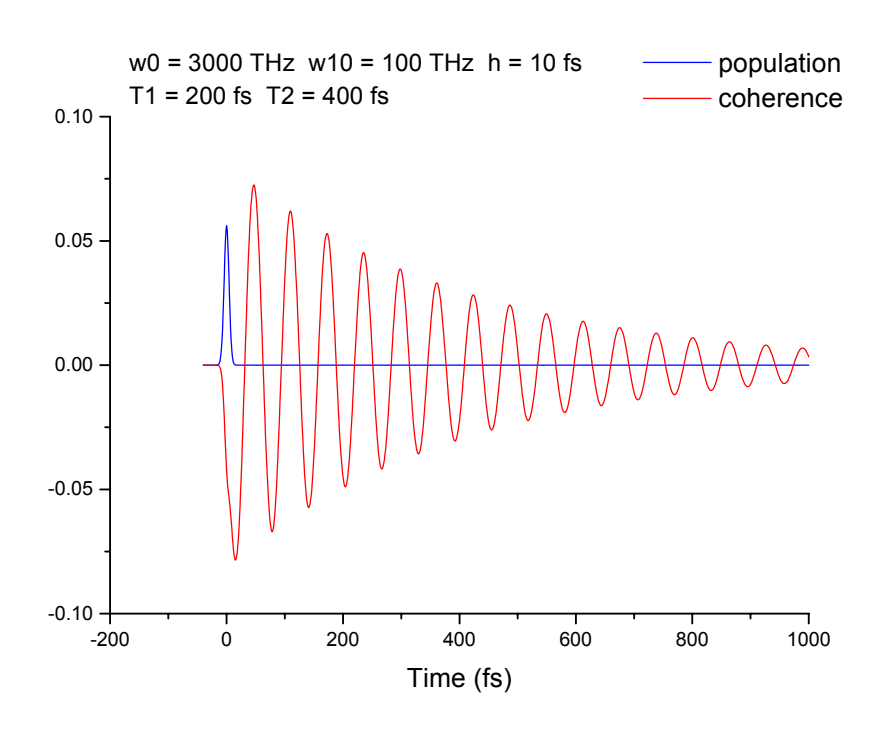




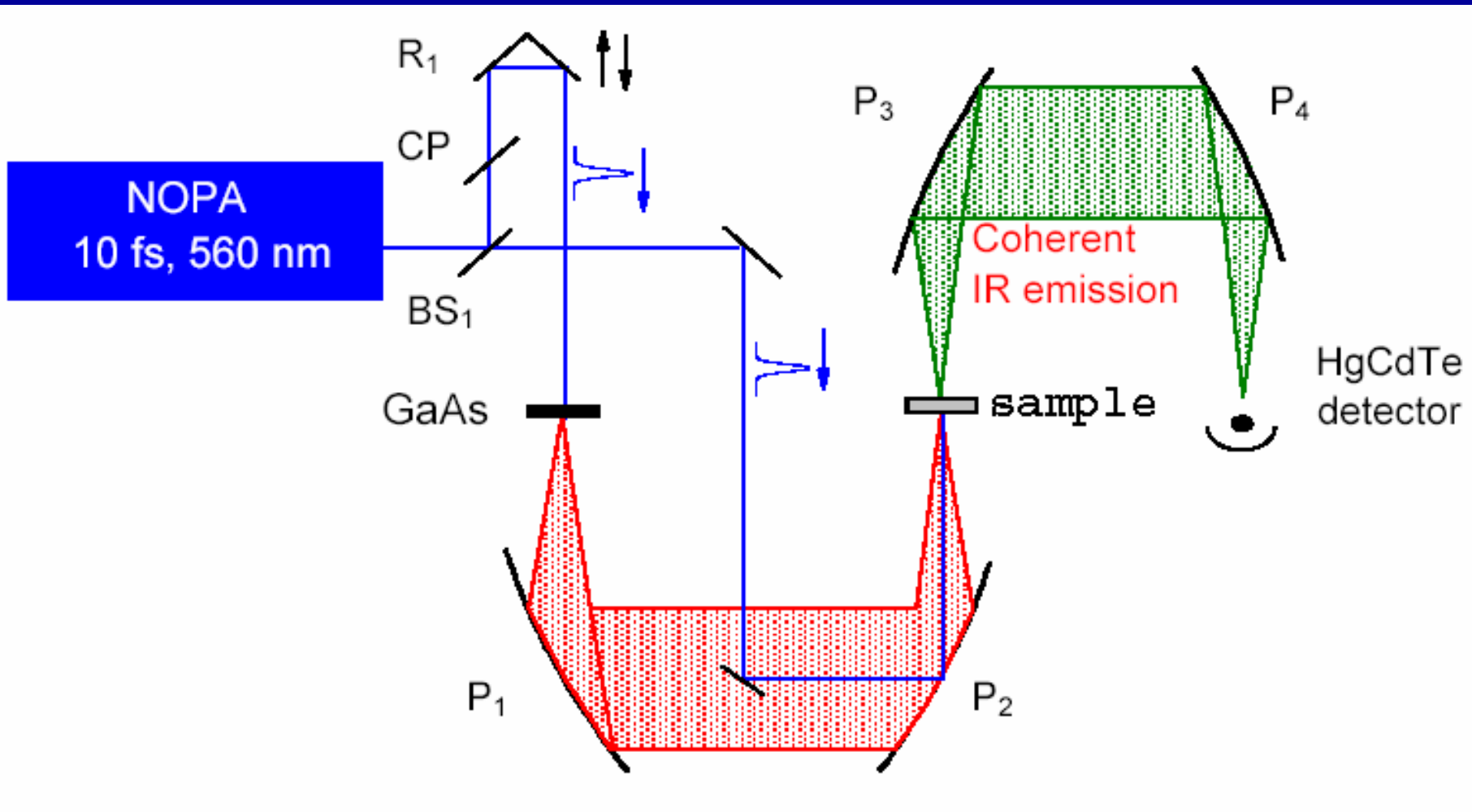
off-resonant excitation

resonant excitation

Simulations

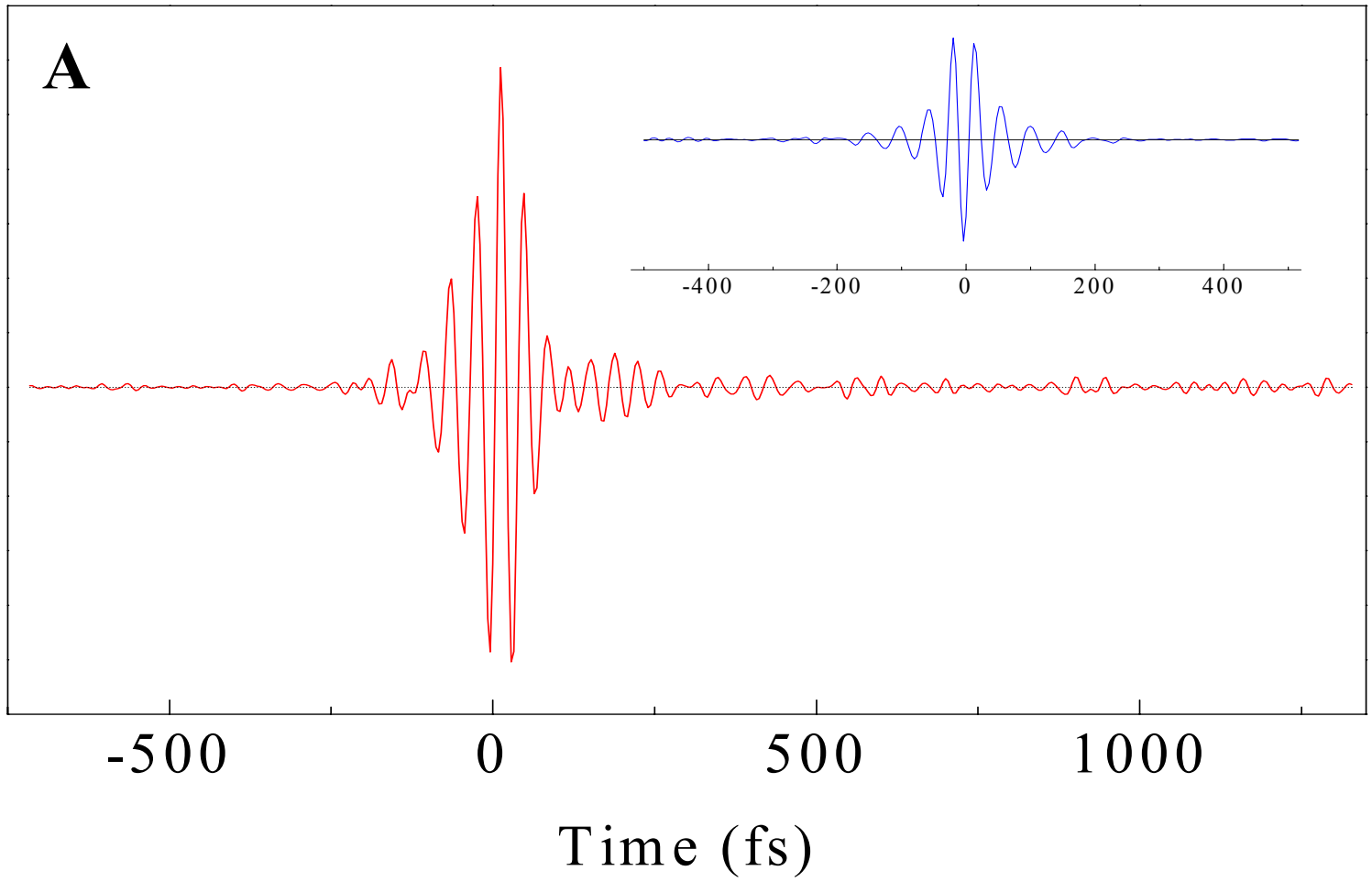


‘envelope resonance’



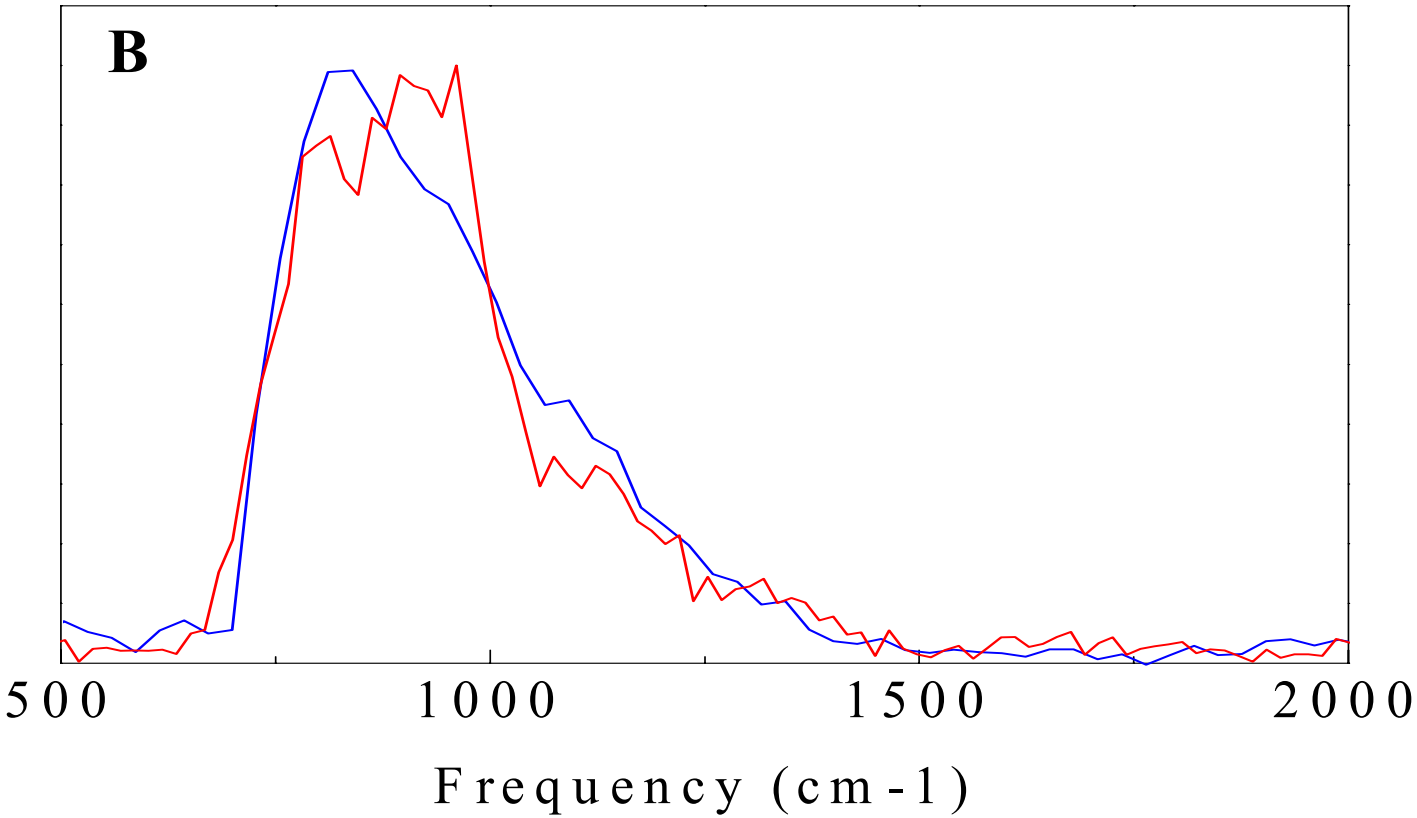
Scheme of the setup for coherent IR emission measurement

700-1500 cm^{-1}
(Ecole Polytechnique, Palaiseau)

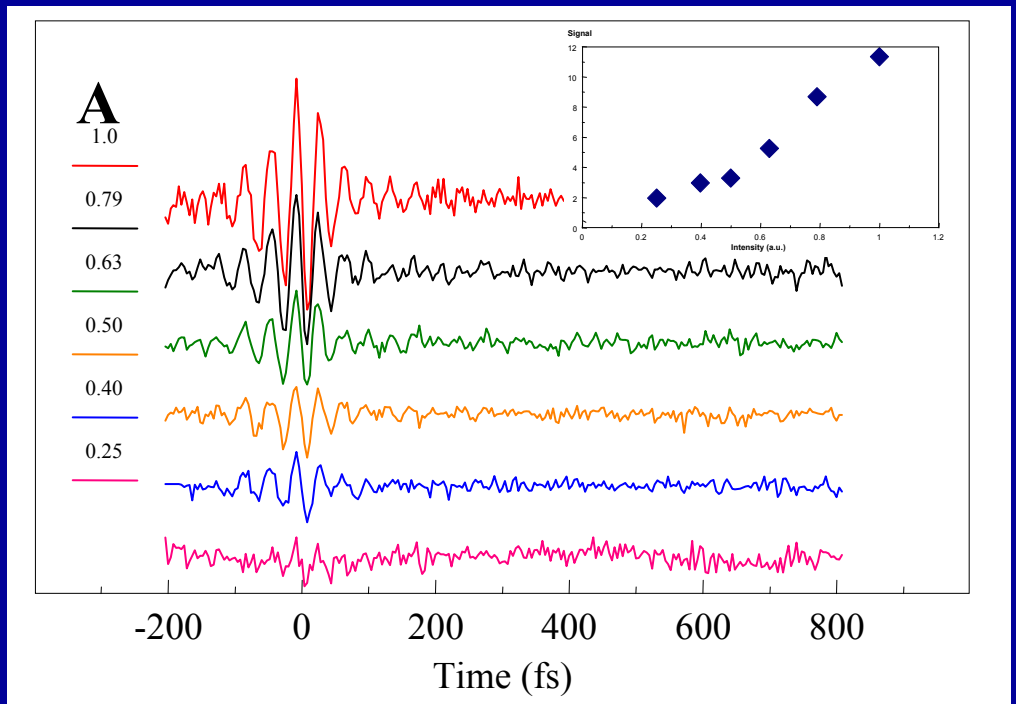


Coherent infrared emission signal from bR and GaAs

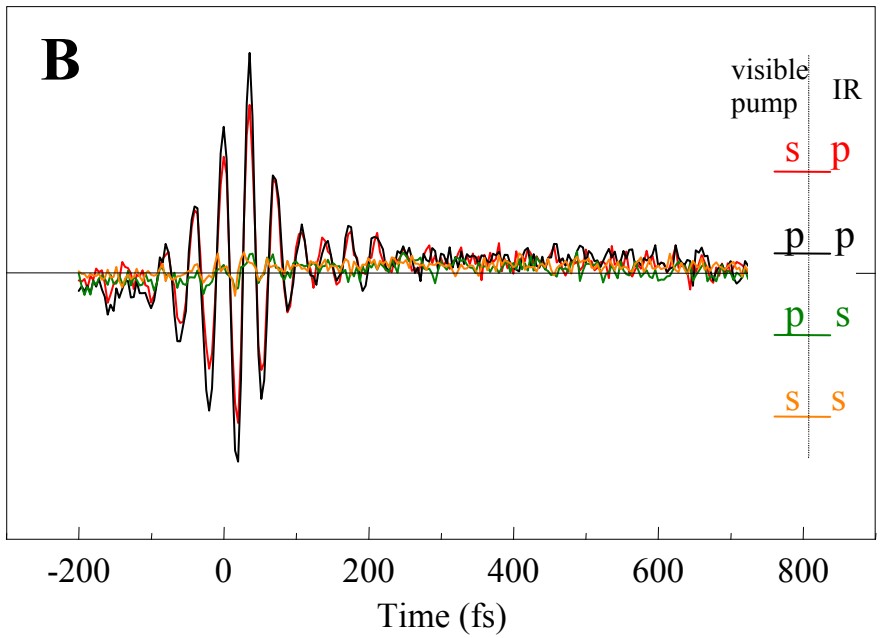
Groma et al. PNAS **101**: 7971 (2004)



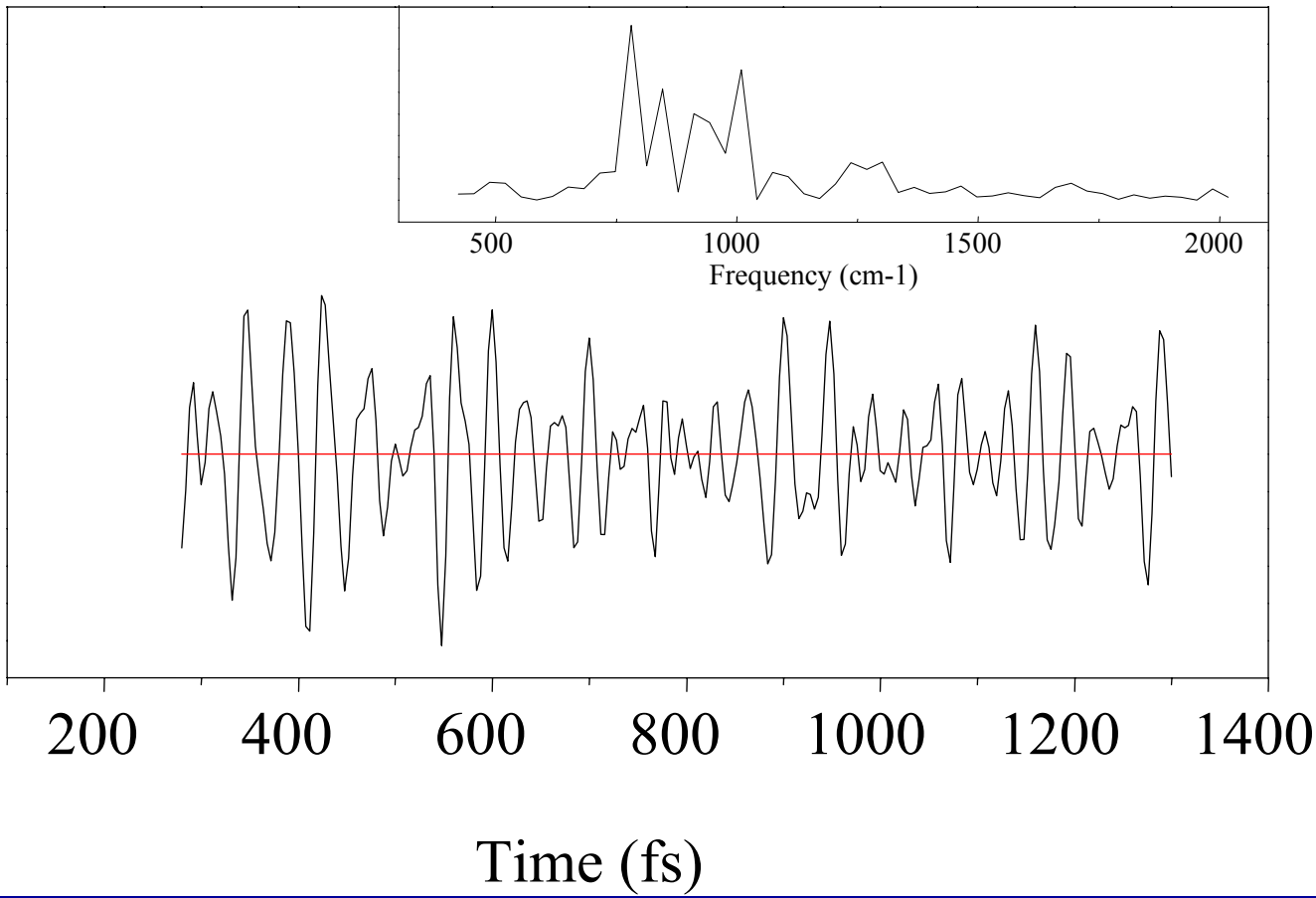
Power spectrum of bR and GaAs coherent infrared emission signal



intensity dependence



polarisation dependence



Power spectrum of the oscillation region.

Conclusions

- The theory of optical rectification was extended to the resonant case with complete relaxation matrix.

- The existence of the optical rectification process in bactriorhodopsin was experimentally confirmed.

- We assume that this second order process is the primary reason of the further proton motions, that is the 'functional motor' of the protein.

$$P = \chi^{(2)} E^2$$ the function is linear in light intensity

- The optical rectification process is accompanied by multimodal coherent vibration.

causal relation?
functionally important vibrations?