Resonant optical rectification. Theory and application to bacteriorhodopsin

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Although optical rectification (OR) is well known as a fundamental second-order phenomenon and widely used e.g. in generation of THz or mid-IR radiation, its theoretical description is surprisingly restricted to the nonresonant case. Under this condition if an OR signal is induced by an ultrafast laser pulse, the time evolution of its electric field follows the derivative of the intensity envelope corresponding to the generating pulse[1]. Here we show that under resonant condition the OR response is markedly different, holding information also on the population dynamics of the excited material.

Using the method of Liouville-space pathways[2] we derived the second-order response function for a simple two-level system to calculate the $P^{(2)}$ polarization created by a laser pulse. (An experimentally detectable second-order optical signal is proportional to the second or first derivative of $P^{(2)}$, corresponding to the point-source or the plane-wave approximation, respectively.) Unlike in earlier approaches we applied a complete (nondiagonal) T_1 relaxation matrix to describe population dynamics. This was crucial to avoid singularity in the formula of the OR signal at resonance, and resulted in an expression for $P^{(2)}$ proportional to $\Delta\mu$, the difference of the dipole moment in the two states. Partitioning $P^{(2)}$ into second harmonic generation (SHG) and OR term, at off-resonance both terms reproduce the conventional results. Contrary to this, at full resonance the OR term follows the population dynamics of the excited state decaying with the T_1 relaxation time. This corresponds to a simple classical view expecting Hertzian dipole radiation during population change if $\Delta\mu$ is nonzero.

It is well known that retinal chromophores have a large $\Delta\mu$ resulting in a high second-order susceptibility of retinal proteins such as bacteriorhodopsin, detected previously by SHG measurements. Recently we demonstrated resonant OR radiation from this protein measured by coherent IR emission technique[3]. Numerical simulations show the existence of a non-instantaneous component in the observed OR signal in good accordance with the above theory. The OR part of the signal was accompanied by a complex set of coherent vibrations analyzed by multimodal fitting and windowed Fourier transformation.

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[1] A. Bonvalet and M. Joffre, "Terahertz femtosecond pulses", in Femtosecond laser pulses, ed. C. Rullière, Springer, Berlin, **1998**, pp. 285-305

[2] S. Mukamel, Principles of nonlinear optical spectroscopy, Oxford Univ. Press, Oxford, **1995**

[3] G.I. Groma, A. Colonna, J.-C. Lambry, J.W. Petrich, G. Váró, M. Joffre, M.H. Vos and J.-L Martin, "Resonant optical rectification in bacteriorhodopsin", Proceedings of the National Academy of Siences, USA, **2004**, 101, 7971-7975