Vibrational-coherence measurement of nonequilibrium quantum systems by four-wave mixing

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Within a four wave mixing set up, coherences in non-equilibrium quantum systems are shown to lead to signal emission in directions opposite to the ones usually considered. Since this emission is generated uniquely by the coherences, a background-free measurement should be possible by placing the detectors in specific, unconventional directions.

We show theoretically that a quantum system in a nonequilibrium state interacting with a set of laser pulses in a four-wave-mixing setup leads to signal emission in directions opposite to the ones usually considered. When combined with a pump mechanism which sets a time origin for the nonequilibrium state creation, this particular optical response can be utilized to directly follow decoherence processes in real time. By varying the time delays within the probe sequence, signals in these unconventional directions can also be used to detect two-dimensional spectra determined by the dynamics of up to three-quantum coherences, revealing energetical anharmonicities and environmental influences. As a numerical example, these findings are demonstrated by considering a model of vibrational decoherence of carbon monoxide after photolysis from a hemeprotein. [1]

FIG. 1. (a) In transient 2D-IR spectroscopy, a pump pulse (k_0) generates a nonequilibrium state $\rho(\tau_0)$, followed by a three-pulse probe sequence (k_1, k_2, k_3) inducing a third-order polarization $P^3(t)$, which leads to radiative emission in directions ks according to the phase-matching condition. The presence of coherences causes emissions opposite to directions usually used in conventional detection schemes. (b) Simulated 2D spectra $|\sigma_I(\omega,\Omega)|^2$ in k_I direction (left) and $|\sigma_V(\omega,\Omega)|^2$ in $k_V = -k_I$ direction (right) of the out-of-equilibrium CO vibration after photolysis of a CO-heme protein. The spectra are represented for different UV-IR delay times (0, 1, and 2ps). In k_V direction, the signal is proportional to $\rho_{n+2,n}$ coherences, and thus follows their decay as a function of the delay UV-IR delay.
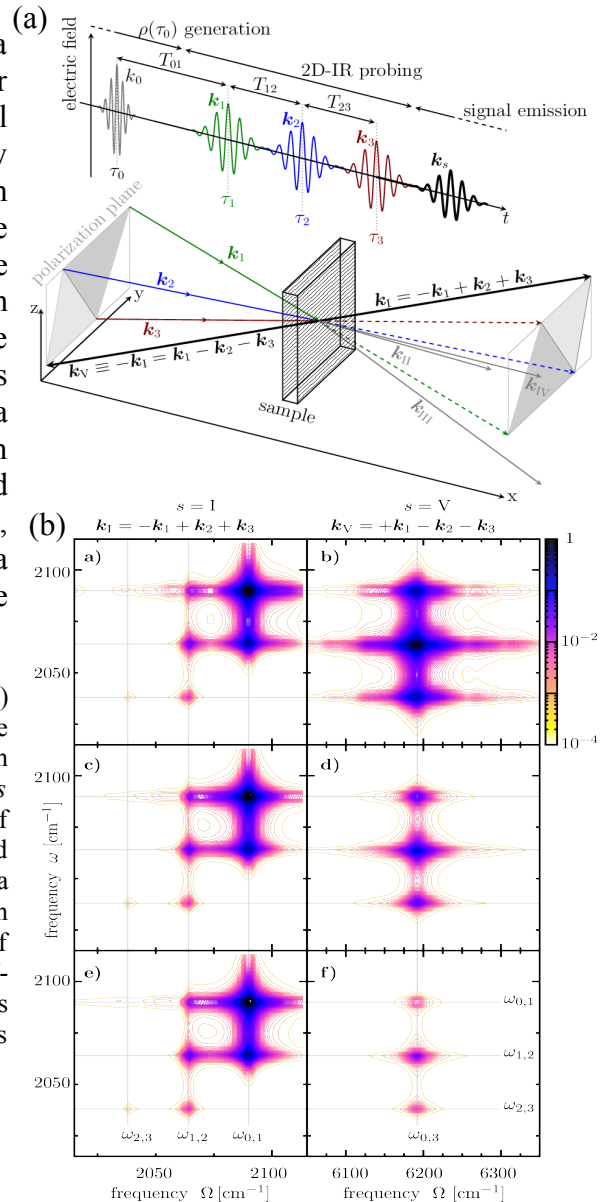
[1] A. Schubert, C. Falvo, C. Meier, Phys. Rev. A **92** (2015).