What is Nonlinear Spectroscopy?

Linear spectroscopy commonly refers to light-matter interaction with one primary incident radiation field which is weak, and can be treated as a linear response between the incident light and the matter. From a quantum mechanical view of the light field, it is often conceived as a "one photon in/one photon out" measurement. Nonlinear spectroscopy is used to refer to cases that fall outside this view, including:

1. Watching the response of matter subjected to interactions with two or more independent incident fields, and
2. the case where linear response theory is inadequate for treating how the material behaves, as in the case of very intense incident radiation.

If we work within the electric dipole Hamiltonian, nonlinear experiments can be expressed in terms of three or more transition matrix elements. The response of the matter in linear experiments will scale as $|\mu_{ab}|^2$ or $\mu_{ab}\mu_{ab}$, whereas in nonlinear experiments will take a form such as $\mu_{ab}\mu_{bc}\mu_{ca}$. Our approach to describing nonlinear spectroscopy will use the electric dipole Hamiltonian and a perturbation theory expansion of the dipole operator.