polarization, $P$

The relevant material property that couples with the radiation field. May be called optical or dielectric polarization. Optical spectroscopies may be classified according to the dielectric polarization power-law dependence on the external electric field.

Notes:
1. Mathematically it is defined as the electric dipole moment change per volume resulting from absorption of radiation of optical frequencies, defined as $P = D - \varepsilon_0 E$, where $D$ is the electric displacement, $\varepsilon_0$ the electric constant (vacuum permittivity), and $E$ the strength of the radiation electric field. A dielectric medium is characterized by the constitutive relation $D = \varepsilon_0 \chi^{(1)}$ where $\chi^{(1)} = \varepsilon_i - 1$ is the linear 'susceptibility' for a transparent singly refracting medium. Depending on the molecular or atomic restoring force on the electron with respect to the displacement $D$, the field-induced motion of the electron can introduce other frequency components on the electron motion, and this in turn leads to non-linear optical effects.

2. The polarization component to the $n$th-order in the field is denoted as $P^{(n)}$. Thus, the following equations apply,

$$ P = P^{(1)} + P_{NL} $$

$$ P_{NL} = P^{(2)} + P^{(3)} + \ldots $$

$$ P = \varepsilon_0 \left[ \chi_e^{(1)} E + \frac{1}{2} \chi_e^{(2)} E^2 + \frac{1}{6} \chi_e^{(3)} E^3 + \ldots \right] = P^{(1)} + P^{(2)} + P^{(3)} + \ldots $$

where $E^i$ is the $i$-th component of the electric field strength and $\chi_e^{(n)}$ is the usual 'susceptibility' $\chi^{(1)} = \varepsilon_i - 1$ in the absence of higher terms and $P^{(n)}$ is the order of the field-induced polarization in the material.

In an anisotropic medium, $\chi_e^{(1)}$, $\chi_e^{(2)}$, and $\chi_e^{(3)}$ are the medium 'hyper-susceptibilities'; they are tensors of rank 2, 3, and 4, respectively.

Linear optical responses such as absorption, light propagation, reflection, and refraction, involving a weak incoming field, are related to $P^{(1)}$. Non-linear techniques are connected to the non-linear polarization $P_{NL}$. Low order non-linear techniques, such as three-wave mixing, are related to the second order optical polarization $P^{(2)}$. For a random isotropic medium (such as a liquid) or for a crystal with a centrosymmetric unit cell, $\chi_e^{(2)}$ is zero by symmetry and then the lowest order non-linear techniques, as well as the higher order, are related to the third-order optical polarization, $P^{(3)}$, and the corresponding hyper-susceptibility.

**Source:**
PAC, 2007, 79, 293 (Glossary of terms used in photochemistry, 3rd edition (IUPAC Recommendations 2006)) on page 402