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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 $\boldsymbol{P} = \boldsymbol{D} - \varepsilon_0 \boldsymbol{E}$, where $\boldsymbol{D}$ is the electric displacement, ε_0 the electric constant (vacuum permittivity) , and $\boldsymbol{E}$ the strength of the radiation electric field. A dielectric medium is characterized by the constitutive relation $\boldsymbol{D} = \varepsilon_0 \chi^{(1)}$ where $\chi^{(1)} = \varepsilon_\mathrm{r} - 1$ 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 $\boldsymbol{D}$, 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 nth-order in the field is denoted as $\boldsymbol{P}^{(\mathrm{n})}$ Thus, the following equations apply,

   $\boldsymbol{P} = \boldsymbol{P}^{(1)} + \boldsymbol{P}_\mathrm{NL}$ and $\boldsymbol{P}_\mathrm{NL} = \boldsymbol{P}^{(2)} + \boldsymbol{P}^{(3)} + \ldots$

   $\boldsymbol{P} = \varepsilon_0 [\chi_\mathrm{e}^{(1)} \boldsymbol{E} + (1/2)\, \chi_\mathrm{e}^{(2)} \boldsymbol{E}^2 + (1/6)\, \chi_\mathrm{e}^{(3)} \boldsymbol{E}^3 + \ldots] = \boldsymbol{P}^{(1)} + \boldsymbol{P}^{(2)} + \boldsymbol{P}^{(3)} + \ldots$

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

   In an anisotropic medium, $\chi_\mathrm{e}^{(1)}$, $\chi_\mathrm{e}^{(2)}$ and $\chi_\mathrm{e}^{(3)}$ 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 $\boldsymbol{P}^{(1)}$. Non-linear techniques are connected to the non-linear polarization $\boldsymbol{P}_\mathrm{NL}$. Low order non-linear techniques, such as three-wave mixing, are related to the second order optical polarization $\boldsymbol{P}^{(2)}$. For a random isotropic medium (such as a liquid) or for a crystal with a centrosymmetric unit cell, $\chi_\mathrm{e}^{(2)}$ 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, $\boldsymbol{P}^{(3)}$, and the corresponding hyper-susceptibility.

Source:

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

