

The Anisotropic Polarizability of a few Aromatic Hydrocarbons

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For sufficiently symmetric molecules without a permanent electric dipole moment, it is shown that refractive indices, Kerr constants and electrooptical absorption measurements in suitable non-polar solvents can be utilized to determine the components α_{gx} , α_{gy} , α_{gz} of the polarizability tensor of solute molecules in the electronic ground state. Since the required quantities are available for anthracene, tetracene, perylene and bianthryl, an evaluation of the polarizability tensor components is made possible.

In solutions where the solvent molecules possess a permanent electric dipole moment or a sufficiently large quadrupole moment, as for example benzene, the fluctuations of the reaction field cause a contribution to the Kerr constant which may be an essential reason for its solvent dependence.

For molecules with a permanent electric dipole moment the components α_{gx} , α_{gy} and α_{gz} of the polarizability tensor (in the electronic ground state) parallel to its principal axes may generally be determined from refractive indices, Kerr constants and the degree of depolarization of scattered light¹. To these three quantities correspond three independent equations which may be solved for the three components α_{gx} , α_{gy} , and α_{gz} . For molecules without a permanent electric dipole moment, these equations are no longer independent of one another, and therefore, an evaluation of α_{gx} , α_{gy} and α_{gz} is possible only if an additional and appropriate quantity is known. For this purpose refractive measurements on crystals^{2,3} or empirical estimations based on the measurements on substituted molecules⁴ with a permanent electric dipole moment have been used. Alternatively, one could also obtain a suitable quantity from electrooptical absorption measurements, i.e., from the change of the optical absorption of molecules due to an applied electric field⁵. Electrooptical measurements for anthracene, tetracene, perylene and bianthryl have been recently carried out⁶. With the results from these measurements, supplemented by the experimental results from Kerr measurements and refractive and dielectric measurements by LE FEVRE et al.^{4,7,8} and by KUBALL and GÖB⁹, the components α_{gx} , α_{gy} , α_{gz} of the polarizability of these molecules in the electronic ground state have been estimated.

The components of the polarizabilities determined from experimental data are rather strongly dependent

on the theoretical model used, as has been shown by KUBALL and GÖB^{3,9,10}. Similar difficulties, which are essentially due to the difference of the magnitude of the external applied electric field and the local field acting on a molecule in a dense medium, occur also in the evaluation of data of electrooptical absorption measurements. For the joint evaluation of the results of dielectric and refractive measurements, of Kerr measurements and of electrooptical absorption measurements, all relations between the experimental quantities and the interesting molecular quantities have to be based on the same model. The model used in the following is based on the concepts introduced by ONSAGER¹¹ and modified by SCHOLTE¹². The evaluation of results of dielectric and refractive measurements has been described¹³ and that of electrooptical absorption measurements also⁶. The relations for Kerr effect measurements, based on the Onsager-Scholte model but with neglect of fluctuation effects were developed by KUBALL and GÖB^{9,14}; they correspond, with minor modifications, to the following equations, when the fluctuation dependent terms are neglected.

I. Theory

The quantity K ,

$$K = (n_3 - n_2)/n_0 E_a^2, \quad (1)$$

as well as the quantity B ,

$$B = (n_3 - n_2) \bar{v}/E_a^2, \quad (2)$$

are usually called Kerr constant, where E_a is the magnitude of the external applied electric field, n_0 is the refractive index of the homogeneous and iso-

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tropic system for light with the wavenumber $\bar{\nu}$ in absence of an applied field, n_2 and n_3 are the refractive indices in presence of an applied electric field for linearly polarized light with the electric field vector perpendicular and parallel to the direction of the applied field, respectively.

A light wave causes an electric polarization \mathbf{P}_0 of a medium; the components P_{02} and P_{03} perpendicular and parallel, respectively, to the applied electric field \mathbf{E}_a are *

$$P_{0\alpha} = \epsilon_0(n_\alpha^2 - 1) L_{a\alpha} = \sum_B N_B \langle \mu_{0B\alpha} \rangle, (\alpha = 2, 3), \quad (3)$$

where $L_{a\alpha}$ is a component of the external electric field vector of the light wave, $\epsilon_0 = 8.854 \cdot 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ is the permittivity of vacuum, N_B is the number density of molecules of the kind B , and $\langle \mu_{0B\alpha} \rangle$ is the average of a component of the electric dipole moment induced by the light wave in molecules of the kind B . For wavenumbers outside of the absorption range, hyperpolarizabilities may be neglected^{14, 15, 16}. Then, the induced dipole moment μ_0 becomes,

$$\mu_0 = \Pi \mathbf{L}_s, \quad (4)$$

$$\bar{w} = \frac{1}{8\pi^2} \left\{ 1 + \frac{1}{kT} \tilde{\mathbf{E}}_a \mathbf{f}_e \tilde{\mu} + \frac{1}{6kT} \tilde{\mathbf{E}}_a \left[\frac{3}{kT} \mathbf{f}_e \tilde{\mu} \tilde{\mu} \mathbf{f} - \frac{1}{kT} \tilde{\mu} \mathbf{f}_e^2 \tilde{\mu} + 3 \mathbf{f}_e^2 \alpha - \text{tr}(\mathbf{f}_e^2 \alpha) \right] \mathbf{E}_a \right\}, \quad (9)$$

where

$$\tilde{\mu} = \mu + (\mathbf{1} - \mathbf{f}' \alpha_g) \alpha_g \mathbf{E}_{Ag}, \quad (10)$$

$$\mu = (\mathbf{1} - \mathbf{f} \alpha_g)^{-1} \mu_g, \quad (11)$$

$$\alpha = (\mathbf{1} - \mathbf{f} \alpha_g)^{-1} \alpha_g, \quad (12)$$

and where μ_g is the permanent electric dipole moment and α_g is the static polarizability of the molecule and k is the Boltzmann constant and T the temperature. The second term on the right-hand side of Eq. (10) takes into consideration the fluctuation of the reaction field⁵.

The quantities \mathbf{f}_e , \mathbf{f} , \mathbf{f}' , \mathbf{g}_{e0} , \mathbf{g}_{e1} , \mathbf{g}_{e2} and \mathbf{g} are second-order tensors. Usually it is assumed that the solvent can be represented by a homogeneous and isotropic dielectric where the solute molecules are localized in cavities with a definite shape. In the most simple approximation the shape of the cavities is assumed to be spherical; consequently, the tensor \mathbf{f}_e is reduced to a scalar

$$\mathbf{f}_e = f_e \cdot \mathbf{1} = \frac{3\epsilon_r}{2\epsilon_r + 1} \cdot \mathbf{1}, \quad (13)$$

where Π is the tensor of the optical polarizability and \mathbf{L}_s is the effective field strength of the light wave. According to ONSAGER¹¹ the quantity \mathbf{L}_s may be represented as a sum of the cavity field \mathbf{L}_h and of the reaction field \mathbf{L}_R :

$$\mathbf{L}_s = \mathbf{L}_h + \mathbf{L}_R, \quad (5)$$

where

$$\mathbf{L}_R = \mathbf{g} \mu_0 \quad (6)$$

and

$$\mathbf{L}_h = \mathbf{g}_{e2} \mathbf{L}_{a2} + \mathbf{g}_{e3} \mathbf{L}_{a3}. \quad (7)$$

The vectors \mathbf{L}_{a2} and \mathbf{L}_{a3} result from partitioning of the external field vector \mathbf{L}_a of the light wave into a vector \mathbf{L}_{a2} perpendicular and a vector \mathbf{L}_{a3} parallel to the applied electric field \mathbf{E}_a . The tensors \mathbf{g} , \mathbf{g}_{e2} and \mathbf{g}_{e3} are defined in Eqs. (18) and (19). From Eqs. (4) to (7) one obtains

$$\mathbf{L}_s = (\mathbf{1} - \mathbf{g} \Pi)^{-1} (\mathbf{g}_{e2} \mathbf{L}_{a2} + \mathbf{g}_{e3} \mathbf{L}_{a3}). \quad (8)$$

For molecules with permanent electric dipole moments or with anisotropic polarizabilities, their distribution becomes anisotropic in the presence of an applied electric field. The probability \bar{w} for a molecule to have a definite orientation described, for example, by Eulerian angles ϑ , φ and ψ is (Eq. (98)⁵]

where ϵ_r is the relative permittivity of the solution. If furthermore the electric dipole moment of the solute molecule is approximated by a point dipole localized at the center of the sphere, then

$$\mathbf{f} = f \cdot \mathbf{1} = \frac{2(\epsilon_r - 1)}{4\pi\epsilon_0 a_w^3 (2\epsilon_r + 1)} \cdot \mathbf{1}, \quad (14)$$

where a_w is the radius of the sphere (interaction radius). If the shape of the cavity is assumed to be ellipsoidal with axes $2a_x$, $2a_y$ and $2a_z$, then the principal components of the tensors become¹³

$$f_{e\lambda} = \frac{\epsilon_r}{\epsilon_r - \kappa_\lambda(\epsilon_r - 1)} (\lambda = x, y, z), \quad (15)$$

and

$$f_\lambda = \frac{3}{4\pi\epsilon_0 a_x a_y a_z} \frac{\kappa_\lambda(1 - \kappa_\lambda)(\epsilon_r - 1)}{(1 - \kappa_\lambda)\epsilon_r - \kappa_\lambda}, \quad (16)$$

where

$$\kappa_\lambda = \frac{a_x a_y a_z}{2} \int_0^\infty \frac{ds}{(s + a_\lambda^2) \{(s + a_x^2)(s + a_y^2)(s + a_z^2)\}^{1/2}}. \quad (17)$$

The tensors \mathbf{g}_{e0} , \mathbf{g}_{e2} and \mathbf{g}_{e3} are similar to \mathbf{f}_e , only ε_r has to be substituted by the square of the refractive indices n_0^2 (for the wavenumber $\bar{\nu}$ of the incident light wave in absence of an applied field), n_2^2 (in presence of an applied electric field perpendicular to the field vector of the light wave), and n_3^2 (in presence of an applied electric field parallel to the field vector of the light wave), respectively. Hence

$$\begin{aligned} \mathbf{f}_e &= \psi(\varepsilon_r), \quad \mathbf{g}_{e0} = \psi(n_0^2), \quad \mathbf{g}_{e2} = \psi(n_2^2), \\ \mathbf{g}_{e3} &= \psi(n_3^2). \end{aligned} \quad (18)$$

The tensors \mathbf{f}' and \mathbf{g} are related similarly to \mathbf{f} :

$$\mathbf{f} = \chi(\varepsilon_r), \quad \mathbf{f}' = \chi(n^2), \quad \mathbf{g} = \chi(n_0^2), \quad (19)$$

where n is the refractive index of the solution for $\bar{\nu} \rightarrow 0$ in absence of an applied field. It is assumed that the principal axes of all tensors coincide. This is necessarily true for sufficiently symmetric molecules and assures that all products of two or more tensors are commutative.

Equations (4) to (9) lead to the following average values for the components of the optical induced dipole moments

$$\begin{aligned} \langle \mu_{0B2} \rangle &= \frac{L_{a2}}{3} \left\{ \left[1 + \frac{E_a^2}{30 k T} \left\{ \frac{1}{k T} \overline{\tilde{\mu} \mathbf{f}_e^2 \tilde{\mu}^*} + \text{tr}(\mathbf{f}_e^2 \alpha) \right\} \right] \text{tr} \{ \mathbf{g}_{e2} (\mathbf{1} - \mathbf{g} \Pi)^{-1} \Pi \} - \right. \\ &\quad \left. - \frac{E_a^2}{10 k T} \left[\frac{1}{k T} \overline{\tilde{\mu} \mathbf{f}_e^2 \mathbf{g}_{e2} (\mathbf{1} - \mathbf{g} \Pi)^{-1} \Pi \tilde{\mu}^*} + \text{tr} \{ \mathbf{f}_e^2 \mathbf{g}_{e2} (\mathbf{1} - \mathbf{g} \Pi)^{-1} \Pi \alpha \} \right] \right\}_B, \end{aligned} \quad (20)$$

$$\begin{aligned} \langle \mu_{0B3} \rangle &= \frac{L_{a3}}{3} \left\{ \left[1 - \frac{E_a^2}{15 k T} \left\{ \frac{1}{k T} \overline{\tilde{\mu} \mathbf{f}_e^2 \tilde{\mu}^*} + \text{tr}(\mathbf{f}_e^2 \alpha) \right\} \right] \text{tr} \{ \mathbf{g}_{e3} (\mathbf{1} - \mathbf{g} \Pi)^{-1} \Pi \} \right. \\ &\quad \left. + \frac{E_a^2}{5 k T} \left[\frac{1}{k T} \overline{\tilde{\mu} \mathbf{f}_e^2 \mathbf{g}_{e3} (\mathbf{1} - \mathbf{g} \Pi)^{-1} \Pi \tilde{\mu}^*} + \text{tr} \{ \mathbf{f}_e^2 \mathbf{g}_{e3} (\mathbf{1} - \mathbf{g} \Pi)^{-1} \Pi \alpha \} \right] \right\}_B. \end{aligned} \quad (21)$$

The subscripts B to the sides of the brackets designate that the molecular quantities in the brackets are those of the molecule B in the solution. The barred quantities are the values averaged over the fluctuation of the reaction field⁵.

For $L_{a2} = L_{a3}$ (a condition usually true for Kerr effect measurements) and with the approximation $n_2 + n_3 = 2 n_0$ Eqs. (1)–(3), (20) and (21) yield for a mixture

$$K = \frac{B}{n_0} = \frac{n_3^2 - n_2^2}{2 n_0^2 E_a^2} = \frac{N_A}{60 \varepsilon_0 k T \bar{V}} \frac{(2 n_0^2 + 1)}{(2 n_0^4 + 1)} \sum_B x_B \Phi_B \quad (22)$$

where

$$\begin{aligned} \Phi_B &= \left[\frac{3}{k T} \overline{\tilde{\mu} \mathbf{f}_e^2 \mathbf{g}_{e0} (\mathbf{1} - \mathbf{g} \Pi)^{-1} \Pi \tilde{\mu}^*} \right. \\ &\quad \left. + 3 \text{tr} \{ \mathbf{f}_e^2 \mathbf{g}_{e0} (\mathbf{1} - \mathbf{g} \Pi)^{-1} \Pi \alpha \} \right. \\ &\quad \left. - \left\{ \frac{1}{k T} \overline{\tilde{\mu} \mathbf{f}_e^2 \tilde{\mu}^*} + \text{tr}(\mathbf{f}_e^2 \alpha) \right\} \right. \\ &\quad \left. \text{tr} \{ \mathbf{g}_{e0} (\mathbf{1} - \mathbf{g} \Pi)^{-1} \Pi \} \right]_B, \end{aligned} \quad (23)$$

and where x_B is the mole fraction of substance B , $\bar{V} = V / \sum n_B$ is the average molar volume of the mixture, and N_A is the Avogadro constant.

For a solution of solute molecules ($B = 2$) in a solvent ($B = 1$) at sufficiently small mole fractions x_2 the relative permittivities ε_r , the squares n_0^2 of

the refractive indices, the densities ρ as well as the differences $n_3^2 - n_2^2$ and the Kerr constants B and K are linear functions of the mole fractions x_2 (and also of the weight fractions w_2) of the solute molecules to a very good approximation, hence

$$\varepsilon_r = \varepsilon_{rs} + \left(\frac{d\varepsilon_r}{dx_2} \right)_{x_2 \rightarrow 0} x_2 = \varepsilon_{rs} + \left(\frac{d\varepsilon_r}{dw_2} \right)_{w_2 \rightarrow 0} w_2, \quad (24)$$

$$n_0^2 = n_{0s}^2 + \left(\frac{dn_0^2}{dx_2} \right)_{x_2 \rightarrow 0} x_2 = n_{0s}^2 + \left(\frac{dn_0^2}{dw_2} \right)_{w_2 \rightarrow 0} w_2, \quad (25)$$

$$\rho = \rho_s + \left(\frac{d\rho}{dx_2} \right)_{x_2 \rightarrow 0} x_2 = \rho_s + \left(\frac{d\rho}{dw_2} \right)_{w_2 \rightarrow 0} w_2, \quad (26)$$

$$B = B_s + \left(\frac{dB}{dx_2} \right)_{x_2 \rightarrow 0} x_2 = B_s + \left(\frac{dB}{dw_2} \right)_{w_2 \rightarrow 0} w_2, \quad (27)$$

where

$$\left(\frac{d\varepsilon_r}{dx_2} \right) = \frac{M_2}{M_1} \left(\frac{d\varepsilon_r}{dw_2} \right)_{w_2 \rightarrow 0}, \quad \text{etc.} \quad (28)$$

ε_{rs} , n_{0s}^2 , ρ_s and B_s are the corresponding quantities of the pure solvent. M_1 and M_2 are the molar masses of solvent and solute molecules, respectively. The quantities $(d\varepsilon_r/dx_2)_{x_2 \rightarrow 0}$ etc. [or $(d\varepsilon_r/dw_2)_{w_2 \rightarrow 0}$ etc.] may easily be determined, hence the further evaluation will advantageously be based on the limit $x_2 \rightarrow 0$. For a non-polar solvent [$(\mu_g)_1 = 0$] and with the assumption of spherical cavities for the solvent molecules Eq. (22) yields for the limit $x_2 \rightarrow 0$:

$$\begin{aligned}
(\Phi_2)_{x_2 \rightarrow 0} = & \frac{60 \varepsilon_0 k T M_1 B_s (2 n_{0s}^4 + 1)}{N_A \varrho_s (2 n_{0s}^4 + 1)} \left\{ \frac{1}{B_s} \left(\frac{dB}{dx_2} \right)_{x_2 \rightarrow 0} + \frac{M_2}{M_1} - \frac{1}{\varrho_s} \left(\frac{d\varrho}{dx_2} \right)_{x_2 \rightarrow 0} \right. \\
& - \left[2 + \frac{3 \varepsilon_{rs} f_{1s} (1 - f_{1s} \bar{\alpha}_{g1})^{-1} \bar{\alpha}_{g1}}{\varepsilon_{rs} - 1} \right] \frac{1}{(2 \varepsilon_{rs} + 1) \varepsilon_{rs}} \left(\frac{d\varepsilon_r}{dx_2} \right)_{x_2 \rightarrow 0} \\
& \left. - \left[\frac{(2 n_{0s}^2 + 1) (3 - 2 n_{0s}^4)}{2 (2 n_{0s}^4 + 1)} + \frac{3 n_{0s}^2 g_{1s} (1 - g_{1s} \bar{\Pi}_1) \bar{\Pi}_1}{n_{0s}^2 - 1} \right] \frac{1}{(2 n_{0s}^2 + 1) n_{0s}^2} \left(\frac{dn_0^2}{dx_2} \right)_{x_2 \rightarrow 0} \right\}, \quad (29)
\end{aligned}$$

where f_{1s} and g_{1s} are the values of f and g for a solvent molecule in the pure solvent and $\bar{\alpha}_{g1}$ and $\bar{\Pi}_1$ are the average static and optical polarizabilities of a solvent molecule, respectively ($\bar{\alpha}_{g1} = \text{tr } \alpha_{g1}/3$, $\bar{\Pi}_1 = \text{tr } \Pi_1/3$).

Similarly from Eq. (23) one obtains for the limit $x_2 \rightarrow 0$:

$$\begin{aligned}
(\Phi_2)_{x_2 \rightarrow 0} = & \frac{1}{k T} \{ 3 \tilde{\mu}_g f_e^2 g_{e0} (1 - f \alpha_g)^{-2} (1 - g \Pi)^{-1} \Pi \mu_g - \tilde{\mu}_g f_e^2 (1 - f \alpha_g)^{-2} \mu_g \text{tr} \{ g_{e0} (1 - g \Pi)^{-1} \Pi \} \\
& + \overline{(E_A)}_1^2 [3 \text{tr} \{ f_e^2 g_{e0} (1 - f' \alpha_g)^2 (1 - f \alpha_g)^{-4} (1 - g \Pi)^{-1} \alpha_g^2 \Pi \} \\
& - \text{tr} \{ f_e^2 (1 - f' \alpha_g)^2 (1 - f \alpha_g)^{-4} \alpha_g^2 \} \text{tr} \{ g_{e0} (1 - g \Pi)^{-1} \Pi \}]_{2, x_2 \rightarrow 0} \\
& + 3 \text{tr} \{ f_e^2 g_{e0} (1 - f \alpha_g)^{-1} (1 - g \Pi)^{-1} \alpha_g \Pi \}_{2, x_2 \rightarrow 0} \\
& - \text{tr} \{ f_e^2 (1 - f \alpha_g)^{-1} \alpha_g \}_{2, x_2 \rightarrow 0} \text{tr} \{ g_{e0} (1 - g \Pi)^{-1} \Pi \}_{2, x_2 \rightarrow 0} \}. \quad (30)
\end{aligned}$$

Under similar conditions the following equations hold¹²:

$$\begin{aligned}
\text{tr} \{ g_{e0} (1 - g \Pi)^{-1} \Pi \}_{2, x_2 \rightarrow 0} = & \frac{3 M_1 \varepsilon_0}{N_A \varrho_s} \left\{ (n_{0s}^2 - 1) \left[\frac{M_2}{M_1} - \frac{1}{\varrho_s} \left(\frac{d\varrho_s}{dx_2} \right)_{x_2 \rightarrow 0} \right] \right. \\
& \left. + \left[2 n_{0s}^4 + 1 - \frac{3 n_{0s}^2 (n_{0s}^2 - 1)}{(2 n_{0s}^2 + 1)} \frac{2 \text{tr} \{ (1 - g_{1s} \Pi_1)^{-2} \Pi_1^2 \}}{\alpha_{w1}^3 \text{tr} \{ (1 - g_{1s} \Pi_1)^{-1} \Pi_1 \}} \right] \frac{1}{(2 n_{0s}^2 + 1) n_{0s}^2} \left(\frac{dn_0^2}{dx_2} \right)_{x_2 \rightarrow 0} \right\}, \quad (31)
\end{aligned}$$

$$\begin{aligned}
& \left[\frac{1}{k T} \tilde{\mu}_g f_e (1 - f \alpha_g)^{-2} \mu_g + \text{tr} \{ f_e (1 - f \alpha_g)^{-1} \alpha_g \} \right]_{2, x_2 \rightarrow 0} \\
& = \frac{3 M_1 \varepsilon_0}{N_A \varrho_s} \left\{ (\varepsilon_{rs} - 1) \left[\frac{M_2}{M_1} - \frac{1}{\varrho_s} \left(\frac{d\varrho}{dx_2} \right)_{x_2 \rightarrow 0} \right] \right. \\
& \quad \left. + \left[2 \varepsilon_{rs}^2 + 1 - \frac{3 \varepsilon_{rs} (\varepsilon_{rs} - 1)}{(2 \varepsilon_{rs} + 1)} \frac{2 \text{tr} \{ (1 - f_{1s} \alpha_{g1})^{-2} \alpha_{g1}^2 \}}{\alpha_{w1}^3 \text{tr} \{ (1 - f_{1s} \alpha_{g1})^{-1} \alpha_{g1} \}} \right] \frac{1}{(2 \varepsilon_{rs} + 1) \varepsilon_{rs}} \left(\frac{d\varepsilon_r}{dx_2} \right)_{x_2 \rightarrow 0} \right\}. \quad (32)
\end{aligned}$$

With Eq. (28) and similar equations for n_0^2 , ϱ and B the Eqs. (29)–(32) may be transformed into the corresponding equations for the limit $w_2 \rightarrow 0$.

By means of electrooptical absorption measurements the following quantity may be determined, if for example aliphatic hydrocarbons are used as solvents⁶:

$$\begin{aligned}
\frac{1}{k T} \{ 3 [\tilde{m} f_e (1 - f \alpha_g)^{-1} \mu_g]^2 - \tilde{\mu}_g f_e^2 (1 - f \alpha_g)^{-2} \mu_g \} + 3 \tilde{m} f_e^2 (1 - f \alpha_g)^{-1} \alpha_g m - \text{tr} \{ f_e^2 (1 - f \alpha_g)^{-1} \alpha_g \} \\
= k T (E + 2 f_e^2 S^{(1)} - 3 f_e^2 S^{(2)}) + (2 \tilde{R}^{(1)} - 3 \tilde{R}^{(2)}) f_e^2 (1 - f \alpha_g)^{-1} \mu_g, \quad (33)
\end{aligned}$$

where the quantity E may be obtained from the effect of an applied electric field on the absorption spectra of solute molecules, m is a unit vector in direction of the transition moment of the considered absorption band, and where the quantities $R^{(1)}$, $R^{(2)}$, $S^{(1)}$ and $S^{(2)}$ describe the first- and second-order electric field dependence of the transition moment⁵.

The investigated molecules do not possess a permanent electric dipole moment, i.e. $\mu_g = 0$. The components of the tensors ($f \alpha_g$) etc. are smaller than 0.1, hence the following equations hold to a sufficient approximation

$$(1 - f \alpha_g) = (1 - f \bar{\alpha}_g) \cdot 1, \quad (1 - f' \alpha_g) = (1 - g \Pi) = (1 - f' \bar{\alpha}_g) \cdot 1,$$

where $\bar{\alpha}_g = \text{tr } \alpha_g/3$. The following quantities, dependent on the polarizabilities and the interaction radii a_{w1} of the solvent molecules, are nearly equal to each other for non-polar solvents and therefore will be approximated by η_s :

$$\begin{aligned}
\frac{2 \text{tr} \{ (1 - g_{1s} \Pi_1)^{-2} \Pi_1^2 \}}{a_{w1}^3 \text{tr} \{ (1 - g_{1s} \Pi_1)^{-1} \Pi_1 \}} &= \frac{2 \text{tr} \{ (1 - f_{1s} \alpha_{g1})^{-2} \alpha_{g1}^2 \}}{a_{w1}^3 \text{tr} \{ (1 - f_{1s} \alpha_{g1})^{-1} \alpha_{g1} \}} \\
&= \frac{(2 n_{0s}^2 + 1)}{(n_{0s}^2 - 1)} (1 - g_{1s} \bar{\Pi}_1)^{-1} g_{1s} \bar{\Pi}_1 = \frac{(2 \varepsilon_{rs} + 1)}{(\varepsilon_{rs} - 1)} (1 - f_{1s} \bar{\alpha}_{g1}) f_{1s} \bar{\alpha}_{g1} = \eta_s. \quad (34)
\end{aligned}$$

With these approximations Eqs. (31), (32) and (29) are simplified to

$$W = (1 - f' \bar{\alpha}_g) \frac{3 M_1 \varepsilon_0}{N_A \varrho_s} \left\{ (n_{0s}^2 - 1) \left[\frac{M_2}{M_1} - \frac{1}{\varrho_s} \left(\frac{d\rho}{dx_2} \right)_{x_2 \rightarrow 0} \right] + \left[\frac{2 n_{0s}^4 + 1}{2 n_{0s}^2 + 1} - \frac{3 n_{0s}^2 (n_{0s}^2 - 1) \eta_s}{(2 n_{0s}^2 + 1)^2} \right] \frac{1}{n_{0s}^2} \left(\frac{dn_0^2}{dx_2} \right)_{x_2 \rightarrow 0} \right\}, \quad (35)$$

$$X = (1 - f' \bar{\alpha}_g) \frac{3 M_1 \varepsilon_0}{N_A \varrho_s} \left\{ (\varepsilon_{rs} - 1) \left[\frac{M_2}{M_1} - \frac{1}{\varrho_s} \left(\frac{d\rho}{dx_2} \right)_{x_2 \rightarrow 0} \right] + \left[\frac{2 \varepsilon_{rs}^2 + 1}{2 \varepsilon_{rs} + 1} - \frac{3 \varepsilon_{rs} (\varepsilon_{rs} - 1) \eta_s}{(2 \varepsilon_{rs} + 1)^2} \right] \frac{1}{\varepsilon_{rs}} \left(\frac{d\varepsilon_r}{dx_2} \right)_{x_2 \rightarrow 0} \right\}, \quad (36)$$

$$Y = (1 - f' \bar{\alpha}_g) (1 - f' \bar{\alpha}_g) \frac{60 \varepsilon_0 k T M_1 B_s (2 n_{0s}^4 + 1)}{N_A \varrho_s \tilde{\nu} n_{0s} (2 n_{0s}^2 + 1)} \left\{ \frac{1}{B_s} \left(\frac{dB}{dx_2} \right)_{x_2 \rightarrow 0} + \frac{M_2}{M_1} - \frac{1}{\varrho_s} \left(\frac{d\rho}{dx_2} \right)_{x_2 \rightarrow 0} - \left[\frac{2}{2 \varepsilon_{rs} + 1} + \frac{3 \varepsilon_{rs} \eta_s}{(2 \varepsilon_{rs} + 1)^2} \right] \frac{1}{\varepsilon_{rs}} \left(\frac{d\varepsilon_r}{dx_2} \right)_{x_2 \rightarrow 0} - \left[\frac{3 - 2 n_{0s}^4}{2 (2 n_{0s}^4 + 1)} + \frac{3 n_{0s}^2 \eta_s}{(2 n_{0s}^2 + 1)^2} \right] \frac{1}{n_{0s}^2} \left(\frac{dn_0^2}{dx_2} \right)_{x_2 \rightarrow 0} \right\}, \quad (37)$$

where

$$W = \text{tr}\{\mathbf{g}_{e0} \mathbf{\Pi}\}_{2, x_2 \rightarrow 0} \quad (38), \quad X = \text{tr}\{\mathbf{f}_e \boldsymbol{\alpha}_g\}_{2, x_2 \rightarrow 0}, \quad (39)$$

$$Y = 3 \text{tr}\{\mathbf{f}_e^2 \mathbf{g}_{e0} \boldsymbol{\alpha}_g \mathbf{\Pi}\}_{2, x_2 \rightarrow 0} - \text{tr}\{\mathbf{f}_e^2 \boldsymbol{\alpha}_g\}_{2, x_2 \rightarrow 0} \text{tr}\{\mathbf{g}_{e0} \mathbf{\Pi}\}_{2, x_2 \rightarrow 0} + Y', \quad (40)$$

where

$$Y' = \frac{(\overline{E_d})_i^2}{k T} (1 - f' \bar{\alpha}_g) (1 - f \bar{\alpha}_g)^{-4} [3 \text{tr}\{\mathbf{f}_e^2 \mathbf{g}_{e0} \boldsymbol{\alpha}_g^2 \mathbf{\Pi}\} - \text{tr}\{\mathbf{f}_e^2 \boldsymbol{\alpha}_g^2\} \text{tr}\{\mathbf{g}_{e0} \mathbf{\Pi}\}]_{2, x_2 \rightarrow 0}. \quad (41)$$

Tab. 1. Data of refractometric and dielectric measurements and

Molecule	Anthracene			
Solvent *	CH	CH	CT	B
T/K	293.1	298.1	293.1	298.1
$M_1 \cdot 10^3/\text{kg} \cdot \text{mol}^{-1}$	84.2	84.2	153.8	78.1
$M_2 \cdot 10^3/\text{kg} \cdot \text{mol}^{-1}$	178.2	178.2	178.2	178.2
$\varrho_s \cdot 10^3/\text{kg} \cdot \text{m}^{-3}$	0.779	0.774	1.595	0.874
ε_{rs}	2.023	2.015	2.238	2.273
n_{0s}^2	2.039	2.027	2.139	2.250
$B_s \cdot 10^{16}/\text{V}^{-2} \text{m}^2 \text{cm}^{-1}$	0.0626		0.0945	0.41
$(d\rho/dw)_{w \rightarrow 0} \cdot 10^3/\text{kg} \cdot \text{m}^{-3}$	0.071 ± 0.08		-0.6 ± 0.08	0.186 ± 0.002
$(d\varepsilon_r/dw)_{w \rightarrow 0}$	0.418 ± 0.09		0.85 ± 0.18	0.616 ± 0.01
$(dn_0^2/dw)_{w \rightarrow 0}$	0.559 ± 0.09		1.08 ± 0.1	0.598 ± 0.01
$(dB/dw)_{w \rightarrow 0} \cdot 10^{16}/\text{V}^{-2} \text{m}^2 \text{cm}^{-1}$	3.2 ± 0.6		7.6 ± 0.7	4.45 ± 0.07
$\tilde{\nu}/\text{cm}^{-1}$	17730	26600	17730	16970
$E \cdot 10^{33}/\text{V}^{-2} \text{m}^2$		-0.7 ± 3.9		
$a_w \cdot 10^{10}/\text{m}$	7	7	7	7
$\alpha_g \cdot 10^{40}/\text{CV}^{-1} \text{m}^2$	34	34	34	34
$(1 - f' \bar{\alpha}_g)$	0.966	0.966	0.960	0.960
$(1 - f' \bar{\alpha}_g)$	0.966	0.966	0.963	0.960
$W \cdot 10^{40}/\text{CV}^{-1} \text{m}^2$	135 ± 12		116 ± 6	125 ± 2
$X \cdot 10^{40}/\text{CV}^{-1} \text{m}^2$	122 ± 12		113 ± 8	128 ± 2
$Y \cdot 10^{78}/\text{C}^2 \text{V}^{-2} \text{m}^4$	17.3 ± 5		20.6 ± 2.1	28.3 ± 0.5
$(Y - Y') \cdot 10^{78}/\text{C}^2 \text{V}^{-2} \text{m}^4$				21 ± 3.7
$Z \cdot 10^{40}/\text{CV}^{-1} \text{m}^2$		-2.2 ± 16		
$a_x : a_y : a_z$	3.6 : 7.5 : 5.4	3.6 : 7.5 : 5.4	3.6 : 7.5 : 5.4	3.6 : 7.5 : 5.4
$\kappa_x : \kappa_y : \kappa_z$	0.485 : 0.204 : 0.314	0.485 : 0.204 : 0.314	0.485 : 0.204 : 0.314	0.485 : 0.204 : 0.314
f_e	1.20	1.20	1.23	1.23
f_{ex}	1.33	1.33	1.37	1.37
f_{ey}	1.12	1.12	1.13	1.13
f_{ez}	1.19	1.19	1.21	1.21
g_{eo}	1.20	1.20	1.22	1.23
g_{eox}	1.33	1.33	1.35	1.37
g_{eoy}	1.12	1.12	1.12	1.13
g_{eoz}	1.19	1.19	1.20	1.21

* CH = cyclohexane, B = benzene, CT = carbon tetrachloride.

The quantity Y' describes the effects caused by the fluctuation of the reaction field. $\overline{(E_A)_i^2}$ is the average of the square of one component of the fluctuation of the electric field. For solvents, where all electric multipole moments but the dipole moment are negligible, $\overline{(E_A)_i^2}$ may be estimated by the equation⁵

$$\overline{(E_A)_i^2} = \frac{1}{18\pi\epsilon_0\alpha_w^2} \left[\frac{(\epsilon_{rs} - 1)(2\epsilon_{rs} + 1)}{\epsilon_{rs}} - \frac{(n_s^2 - 1)(2n_s^2 + 1)}{n_s^2} \right]. \quad (42)$$

According to Eq. (42), $\overline{(E_A)_i^2}$ vanishes in non-polar solvents where $\epsilon_{rs} \approx n_s^2$. Actually this is true for aliphatic hydrocarbons but not for dioxane or benzene as solvents. In view of the fact that the quadrupole moments of the latter molecules are relatively large, Eq. (42) cannot be applied⁶.

Furthermore, for the molecules under investigation, \mathbf{m} is parallel to the z -axis of the molecules and the quantities $S^{(1)}$ and $S^{(2)}$ are negligible, hence Eq. (33) is simplified to

$$Z = (1 - f\alpha_g) k T E = [3f_{ez}^2\alpha_{gz} - \text{tr}\{f_c^2\alpha_g\}]_{2,x_2 \rightarrow 0}. \quad (43)$$

According to Eqs. (35) to (37) and (43) the quantities W , X , Y and Z may be determined from refractometric and dielectric measurements, from the Kerr effect and from electrooptical measurements. If light with a wavenumber $\bar{\nu}$ in sufficient distance from an absorption band is used for the refractometric and Kerr measurements the tensor Π may be substituted by the tensor α_g to a sufficient approximation. Then Eqs. (38) to (40) and (43) are reduced to

$$W = g_{e0x}\alpha_{gx} + g_{e0y}\alpha_{gy} + g_{e0z}\alpha_{gz}, \quad (44)$$

$$X = f_{ex}\alpha_{gx} + f_{ey}\alpha_{gy} + f_{ez}\alpha_{gz}, \quad (45)$$

Kerr effect and electrooptical absorption measurements.

tracene	CH	Perylene	CH	Bianthryl	CH	Refer-
		B		B		ences
1	298.1	298.1	298.1	298.1	298.1	
1	84.2	78.1	84.2	78.1	84.2	
3	228.3	252.3	252.3	354.4	354.4	
.874	0.774	0.874	0.774	0.874	0.774	
.273	2.015	2.273	2.015	2.273	2.015	
.250	2.027	2.250	2.027	2.250	2.027	
.41	—	0.41	—	0.41	—	4, 8, 9
.266 ± 0.02	—	0.240 ± 0.002	—	0.22 ± 0.01	—	7, 8, 9
.76 ± 0.1	—	0.65 ± 0.03	—	—	—	7, 8, 9
.79 ± 0.07	—	0.66 ± 0.01	—	0.52 ± 0.1	—	7, 8, 9
.5 ± 0.2	—	6.5 ± 0.2	—	1.2 ± 0.1	—	4, 8, 9
.70	21200	16970	23000	16970	25700	
	—5.6 ± 4.5	—	8.9 ± 4.5	—	—12.2 ± 13.3	6
	8	7	7	8	8	6
	46	47	47	63	63	
.963	0.968	0.942	0.953	0.950	0.956	
.963	0.967	0.942	0.953	0.950	0.956	
± 8	—	171 ± 2	—	229 ± 3	—	
± 9.5	—	172 ± 3	—	—	—	
± 1.5	—	56 ± 1.9	—	15.7 ± 1.2	—	
± 4.3	—	37 ± 5	—	7 ± 5	—	
	—22 ± 18	—	34 ± 18	—	50 ± 52	
8.8:5.4	3.6:8.8:5.4	3.6:6.3:7.5	3.6:6.3:7.5	7.5:7.5:7.5	7.5:7.5:7.5	6
:0.166:0.329	0.51:0.166:0.329	0.511:0.274:0.215	0.511:0.274:0.215	0.333:0.333:0.333	0.333:0.333:0.333	6
	1.20	1.23	1.2	1.23	1.20	
	1.35	1.40	1.35	1.23	1.20	
	1.09	1.18	1.16	1.23	1.20	
	1.20	1.14	1.12	1.23	1.20	
	1.20	1.23	1.2	1.23	1.20	
	1.35	1.40	1.35	1.23	1.20	
	1.09	1.18	1.16	1.23	1.20	
	1.20	1.14	1.12	1.23	1.20	

$$Y = 3(f_{ex}^2 g_{e0x} \alpha_{gx}^2 + f_{ey}^2 g_{e0y} \alpha_{gy}^2 + f_{ez}^2 g_{e0z} \alpha_{gz}^2) - (f_{ex}^2 \alpha_{gx} + f_{ey}^2 \alpha_{gy} + f_{ez}^2 \alpha_{gz}) (g_{e0x} \alpha_{gx} + g_{e0y} \alpha_{gy} + g_{e0z} \alpha_{gz}) + Y', \quad (46)$$

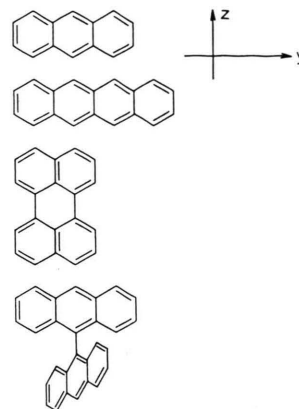
$$Z = 3f_{ez}^2 \alpha_{gz} - (f_{ex}^2 \alpha_{gx} + f_{ey}^2 \alpha_{gy} + f_{ez}^2 \alpha_{gz}), \quad (47)$$

where $\alpha_{g\lambda}$, $f_{e\lambda}$ and $g_{e0\lambda}$ ($\lambda = x, y, z$) are the components of the tensors α_g , f_e and g_{e0} , respectively, parallel to the principal axes of the molecule. The quantities $f_{e\lambda}$ and $g_{e0\lambda}$ may be determined using Eq. (13) or Eq. (15) and Eq. (18) with the relative permittivity ϵ_{rs} and the square n_{0s}^2 of the refractive index of the pure solvent. For Kerr measurements in solvents as aliphatic hydrocarbons, for example, the quantity Y' is negligible, then the Eqs. (44) to (47) may be solved for the components α_{gx} , α_{gy} and α_{gz} of the polarizability. For Kerr measurements in other solvents the quantity Y' has to be estimated from independent measurements or with the help of Eq. (42), if this relation is appropriate.

According to Eq. (47) α_{gz} (or generally the component of the polarizability parallel to the transition moment of the electronic band investigated by electrooptical absorption measurements) may be determined uniquely. The axes of the other two components must be chosen on basis of other arguments. In the case of planar aromatic molecules it may be assumed that the smallest component of the polarizability is perpendicular to the plane of the molecule. It should be mentioned, that for sufficiently symmetric molecules, where electrooptical absorption measurements could also be made on a further absorption band with a transition moment perpendicular to the transition moment of the other investigated absorption band, a unique determination of a second component of the polarizability would be possible. In such a case all components $\alpha_{g\lambda}$ could be determined without using Kerr effect measurements.

II. Results

The data necessary for the determination of W , X , Y and Z according to Eqs. (35) to (37) and (43) are available for the molecules anthracene (I), tetracene (II), perylene (III) and bianthryl (IV) and are collected in Table 1. The molecules and the coordinate system used are given in the following figure. The values of $(dQ/dw)_{w \rightarrow 0}$ etc. are determined from



published data using Eqs. (24) to (27). The values of the interaction radii a_w , needed for the calculation of f and f' , and the ratios $a_x/a_y/a_z$, needed for the calculation of $f_{e\lambda}$ and $g_{e0\lambda}$ are chosen from our recent work⁶. The estimated value of $\eta_s = 0.85 \pm 0.2$ was used for all solvents¹⁷. The calculated value of W , X , Y and Z are listed in Table 1. For Kerr effect measurements in the solvents cyclohexane and carbon tetrachloride the quantity Y' may be neglected, hence in these cases from the quantities W to Z the values of α_{gx} , α_{gy} and α_{gz} may be calculated according to Eqs. (44) to (47). For Kerr measurements in benzene as solvent the value of Y' is comparable to the value of Y due to the rather large quadrupole moment of the benzene molecule. From fluctuation effects in electrooptical absorption measurements⁶ and also from the solvent dependence of spectra a maximal value of $(\overline{E_A})_1^2 = 18 \cdot 10^{16} \text{ V}^2 \text{ m}^{-2}$ was estimated for the average of the square of one component of the fluctuation of the electric field at the location of the solute molecules in benzene as the solvent. With this value, $(Y - Y')$ was evaluated (Tab. 1), which is for anthracene almost identical to the values of Y obtained from Kerr effect measurements in cyclohexane and carbon tetrachloride as should be expected. The value of $(Y - Y')$ together with the values of W , X and Z yield, then, the components $\alpha_{g\lambda}$ of the polarizability. In spite of Y' being of the same magnitude as Y the neglect of Y' does not have an essential effect on the calculated values of $\alpha_{g\lambda}$ as may be seen from the data listed in Table 2. The reason is, that for these molecules the value of Y is rather small compared to the other values needed for the calculation of the components of the polarizability. Hence, in such cases, even a large error in

Tab. 2. Polarizabilities α_g of some aromatic hydrocarbons in the electronic ground state

Molecule	Anthracene												
Solvent *	CH			CT		B			Pol. acc. to ref.				
Approximation **	E(NF)	S(NF)		E(NF)	S(NF)	E(WF)	E(NF)	S(NF)	2	3	4	7	18
$\alpha_{gx} \cdot 10^{40}/CV^{-1} \text{ m}^2$	21 ± 4.5	24.5 ± 4.5		16 ± 2	18 ± 2	18 ± 2.2	16.6 ± 1.8	18 ± 1.8	13.2	10.9	17.8	14.5	16
$\alpha_{gy} \cdot 10^{40}/CV^{-1} \text{ m}^2$	43 ± 4.5	50 ± 4.5		39 ± 2	46 ± 2	41 ± 2.2	42 ± 1.8	50 ± 1.8	44.8	49.7	40.0	37.8	49
$\alpha_{gz} \cdot 10^{40}/CV^{-1} \text{ m}^2$	38 ± 5	36.7 ± 5		32 ± 4	31 ± 4	34 ± 3.7	34 ± 3.6	33 ± 3.6	28.7	28.7	27.0	32.3	32
tr $\alpha_g 10^{40}/CV^{-1} \text{ m}^2$	102 ± 11	111 ± 11		87 ± 2	95 ± 2	93 ± 1.3	92 ± 1.3	101 ± 1.3	86.7	89.3	84.8	84.6	97
Molecule	Tetracene				Perylene				Bianthryl				
Solvent	B			Pol. acc.	B			Pol. acc.	B				
Approximation	E(WF)	E(NF)	S(NF)	to ref. ⁷	E(WF)	E(NF)	S(NF)	to ref. ⁷	E(WF)	E(NF)	S(NF)		
$\alpha_{gx} \cdot 10^{40}/CV^{-1} \text{ m}^2$	21 ± 2.7	18 ± 2	22 ± 2	17.3	21 ± 3	18 ± 3	22 ± 3	19.2	68 ± 10	74 ± 10	74 ± 10		
$\alpha_{gy} \cdot 10^{40}/CV^{-1} \text{ m}^2$	58 ± 2.7	61 ± 2	73 ± 2	53.6	48 ± 3	51 ± 3	63 ± 3	(49)	68 ± 10	61 ± 10	61 ± 10		
$\alpha_{gz} \cdot 10^{40}/CV^{-1} \text{ m}^2$	40 ± 4.7	41 ± 4.5	40 ± 4.5	38.6	62 ± 4.5	63 ± 4.5	55 ± 4.5	(49)	50 ± 12	50 ± 12	50 ± 12		
tr $\alpha_g 10^{40}/CV^{-1} \text{ m}^2$	119 ± 6	120 ± 6	135 ± 6	109.5	131 ± 3	132 ± 3	140 ± 3	117.2	186 ± 11	185 ± 11	185 ± 11		

* Solvents used for refractometric and Kerr effect measurements: CH = cyclohexane, B = benzene, CT = carbon tetrachloride.

** Approximation used for evaluation of data:

E(WF): Ellipsoidal cavity and taking fluctuation effects into account $[(\overline{EA})_1^2 = 18 \cdot 10^{16} V^2 m^{-2}]$,

E(NF): Ellipsoidal cavity and neglect of fluctuation effects ($Y' = 0$),

S(NF): Spherical cavity and neglect of fluctuation effects ($Y' = 0$).

the determined quantity Y or in the estimated quantity Y' will cause only a minor effect on the calculated values of $\alpha_{g\lambda}$.

The evaluation of the components $\alpha_{g\lambda}$ of the polarizability are based on the assumption of spherical cavities for the solute molecules as well as on the assumption of ellipsoidal cavities. The values obtained are listed in Tab. 2. For anthracene there are refractometric and Kerr effect measurements in three solvents; the values of $\alpha_{g\lambda}$ obtained from these measurements are in rather good agreement. In Tab. 1 are also given the components $\alpha_{g\lambda}$ determined by LE FÈVRE et al.^{4,7}, VUKS² and KUBALL and GÖB³. The components α_{gx} and α_{gy} are in rather good agreement with the values of LE FÈVRE et al.⁴, however the component α_{gz} obtained in this paper is a little larger than their value. Furthermore the components α_{gx} and α_{gz} calculated by AMOS and BURROWS¹⁸ are in very good agreement with experimental values, only the component α_{gy} is a little larger.

The values of $\alpha_{g\lambda}$ for tetracene compare quite well with those for anthracene. The main increase of the polarizability is parallel to the y -axis as may be expected. The same holds for perylene, where in the estimation based on ellipsoidal cavities the lar-

gest polarizability is along the z -axis. In bianthryl the value of α_{gz} is too small compared with the value of α_{gz} of anthracene. Also one should expect (nearly) equal values of α_{gx} and α_{gy} . However for this molecule the values of the components $\alpha_{g\lambda}$ may be rather erroneous due to a poor value of Z , i.e. to rather poor electrooptical absorption measurements.

The difference between the values of the components $\alpha_{g\lambda}$ obtained with the assumption of ellipsoidal cavities and the values obtained on the basis of spherical cavities are never too large, however, they are significant. In case of perylene there is even an exchange of the largest component resulting in the two models. Probably the most reliable data are those obtained with the assumption of ellipsoidal cavities.

Since the component of the polarizability parallel to the transition moment of the absorption band, investigated using electrooptical absorption measurements, is obtained uniquely, the relative values of the components α_{gx} , α_{gy} and α_{gz} confirm that the transition moment of the first singlet-singlet transition of the molecules I–IV is parallel to the z -axis.

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* Vectors are represented by bold-faced italic type letters, tensors by bold-faced sanserif type letters. Thus for example μ is a column vector, $\bar{\mu}$ is the corresponding row vector and α a tensor; hence $\bar{\mu}\mu$ is the scalar product and $\mu\bar{\mu}$ the second-order tensor product. The physical quantities are given in SI units. The conversion factor for the polarizability α in cgs units is $[\alpha]_{\text{SI}}/\text{CV}^{-1}\text{m}^2 = 1.11265 \cdot 10^{-16} [\alpha]_{\text{cgs}}/\text{cm}^3$.

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