



## Review

# Theoretical foundation of electroabsorption spectroscopy: Self-contained derivation of the basic equations with the direction cosine method and the Euler angle method

Erko Jalviste<sup>a</sup>, Nobuhiro Ohta<sup>b,\*</sup><sup>a</sup> *Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia*<sup>b</sup> *Research Institute for Electronic Science (RIES), Hokkaido University, Sapporo 060-0812, Japan*

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**Abstract**

Self-contained derivation of the electroabsorption (E-A, Stark effect) equations of Liptay and Czekalla, which describe the external electric field effects on absorption spectra of a mobile ensemble of light-absorbing molecules at thermal equilibrium, is reported. Two mathematically different ways for obtaining the ensemble averages, the “direction cosine method” and the “Euler angle method”, are compared. Some examples illustrating the application of E-A equations in the analysis of electroabsorption spectra are presented.

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**Keywords:** Electroabsorption; Stark effect; Electric dipole moment; Molecular polarizability; Angular distribution; Orientation; Alignment; Euler angle; Direction cosine

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**Contents**

1. Introduction .....	31
2. Basic principles of the theory .....	32
3. Angular distribution of molecules under the electric field .....	32
4. Angular dependence of the Stark shift .....	34
5. Dipole- and polarization-induced contributions to the absorbance change .....	35
6. Averaging by the direction cosine method .....	36
6.1. The zeroth-derivative dipole term .....	36
6.2. The first-derivative dipole term .....	37
6.3. The second-derivative dipole term .....	37
6.4. The zeroth-derivative polarizability term .....	37
6.5. The first-derivative polarizability term .....	37
7. Averaging by the Euler angle method .....	37
7.1. The zeroth-derivative dipole term .....	38
7.2. The first-derivative dipole term .....	39
7.3. The second-derivative dipole term .....	40
7.4. The zeroth-derivative polarizability term .....	40
7.5. The first-derivative polarizability term .....	41

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\* Corresponding author. Tel.: +81 11 706 2594; fax: +81 11 706 4970.

E-mail address: [nohta@es.hokudai.ac.jp](mailto:nohta@es.hokudai.ac.jp) (N. Ohta).

8. The resulting set of equations and its physical background .....	41
9. Application to the electroabsorption spectra .....	42
10. Summary .....	44
Acknowledgment .....	45
References .....	45



**Erko Jalviste** was born in Tartu, Soviet Estonia, in 1962. He received his PhD degree from University of Tartu in 1994. Currently, he is a research scientist at Institute of Physics, University of Tartu, Estonia. He has been a visiting scientist at University of Nijmegen, Netherlands (1992–1993), Alexander von Humboldt Fellow at University of Kiel and at Max-Planck-Institute of Fluid Dynamics, Göttingen, Germany (1997–1998), and a JSPS Fellow at Hokkaido University, Japan (2002–2003). His research interest

is concerned with laser spectroscopy of jet-cooled molecules and complexes and electroabsorption spectroscopy of molecules embedded into a polymer film.



**Nobuhiro Ohta** was born in 1950 in Tendo, Yamagata Prefecture, Japan. He is currently a professor at Research Institute for Electronic Science, Hokkaido University. He graduated in Chemistry in the Faculty of Science, Tohoku University in 1977 and received a PhD under supervision of Prof. Mitsuo Ito. He was a post-doctoral Fellow at Marquette University in Milwaukee in 1972–1973 working with prof. Kazuo Nakamoto. He became a research associate in 1978 at Research Institute for Applied Electricity, Hokkaido University, where he worked with prof. Hiroaki Baba. He was

appointed as an associate professor at the faculty of engineering at the same university in 1992, where he worked with prof. Iwao Yamazaki, and appointed as a full professor in 1998 at the present Institute. He is interested in interaction between molecule(s) and photon and in relation among “Structure” and “Dynamics” of photoexcited species and photoinduced “Functionality”. Experimentally, emission measurements have been widely done in the absence and presence of electric fields and/or magnetic fields. Recently he has extended his research field to molecular photonics and biophotonics with special attention to the field effects on material property and on biological property.

## 1. Introduction

Electroabsorption (E-A) or Stark effect spectroscopy, which rests on the measurement of the spectrum of absorbance change,  $\Delta A(\nu) = A(\nu, F \neq 0) - A(\nu, F = 0)$ , induced by an externally applied electric field  $F$ , is a widely used method for the determination of molecular parameters (see, for example, the review papers [1–4]). The change in permanent dipole moment,  $\Delta\mu$ , and the change in polarizability,  $\Delta\alpha$ , on an electronic transition [4–54] as well as on vibrational transition [55–58] are typical quantities that can be obtained from the E-A spectrum of a solid film containing the absorbing molecules of interest. Through these effects, molecular aggregation or molecular complex formation which cannot be identified in usual absorption spectra may be detected [59,60]. For a liquid sample with dissolved polar molecules and even for some molecules doped in a polymer film, further, the field-induced orientation effects become actual [13,22,40,46,52,61–63].

For the determination of molecular parameters from the measured absorption and E-A spectra, a model-based fitting of the simulated spectra to the measured ones is needed. A theory describing the effect of an externally applied static electric field on the absorption of polarized light by an ensemble of mobile molecules at thermal equilibrium was developed by Liptay and Czekalla [64,65] in the early 1960s. The physical phenomena, on which the E-A theory is based, are the field-induced change in the angular distribution of molecules and the Stark shift of their absorption band(s). According to this theory the change in absorbance scales quadratically with the applied field strength. Furthermore, it was shown that the E-A spectrum and the absorption spectrum of a given electronic transition are related to each other so that the E-A spectrum can be expressed as a linear combination of the zeroth, the first, and the second derivatives of the absorption spectrum with respect to the frequency.

In spite of the extensive application of the Liptay’s equations in the interpretation of measured E-A data, as far as we know, full details of their rather cumbersome derivation are available only from a few original papers [64–66]. A most laborious step in obtaining these equations is the calculation of the ensemble averages of several different products of angle-dependent quantities. Recently Andrews [67] published an introductory overview explaining the mathematical and the physical principles of angular (rotational) averaging in the context of the E-A theory. The present work serves as an introduction to the E-A theory too, but with a more specific aim; to reproduce the derivation of a certain set of the E-A equations in a self-contained manner from the beginning rather than to provide a general guidance for doing this.

We shall confine the scope of this paper to the derivation of a basic (and therefore more widely used) set of E-A equations that is presented in Ref. [68]. These equations describe the absorbance change caused by the dipole-induced and the polarizability-induced contributions to the Stark shift and to the orientation/alignment. The hyperpolarizability effects [1], the transition moment polarizability and hyperpolarizability effects [1,2,69], the orientational saturation effects [70], and the higher order (scaling proportionally to the fourth and the sixth power of the field strength) Stark effects [71] will not be considered. It should also be noted that the change in absorbance which scales linearly with the applied field strength is feasible in oriented molecular systems such as Langmuir–Blodgett films [59,60,72,73], but we focus only to the randomly distributed system in this manuscript.

The E-A equations will be derived using two equivalent, but mathematically different ways for angular averaging, that we call the “direction cosine method” and the “Euler angle method”. In the case of the direction cosine method [67,74–76], by which

the E-A equations were originally deduced, the orientation of absorbing molecules in the laboratory frame is given by their direction cosines, and known formulas for the averaged products of direction cosines are applied. In the case of the Euler angle method, which is applied, e.g., in Ref. [77], the orientation of molecules is given by the Euler angles, and a convenient Legendre polynomial representation of the angle-dependent quantities is used.

## 2. Basic principles of the theory

In the so-called Liptay's theory of the Stark effect [1], a thermally equilibrated ensemble of molecules with unrestricted angular mobility is considered. In the context of this theory, the molecules are treated as a set of vectors (the permanent dipole moment,  $\mu$ , its change following the optical transition,  $\Delta\mu$ , and the transition dipole moment,  $d$ , and tensors (the polarizability,  $\tilde{\alpha}$ , and its change following the transition,  $\Delta\tilde{\alpha}$ ), whose relative configuration is fixed. A single electronic transition is assumed to be responsible for the light absorption.

It is assumed that the absorption band shifts in frequency, but does not change its shape under the external electric field,  $F$ . Mathematically, the band shape function in the presence of field,  $s(\nu)_F$ , is related to the same function in the absence of the field,  $s(\nu)$ , by

$$s(\nu)_F = s(\nu - \Delta\nu), \quad (1)$$

where  $\Delta\nu$  is the field-induced shift of the band shape (the Stark shift). For a small Stark shift in comparison with the spectral width of the features in the absorption band, the field-induced change of the shape function,  $\Delta s = s(\nu)_F - s(\nu)$ , can be expanded to the power series by the Stark shift, i.e.,

$$\Delta s = -\frac{ds}{d\nu}\Delta\nu + \frac{1}{2}\frac{d^2s}{d\nu^2}(\Delta\nu)^2, \quad (2)$$

where  $\Delta\nu$ , and consequently also  $\Delta s$ , depends on the field strength as well as on the orientation of the molecule with respect to the applied electric field direction (see Section 4).

In the absence of an external electric field, the absorbance,  $A$ , is given by

$$\frac{A}{\nu} = cs\langle\Phi_{Ed}^2\rangle = \frac{cs}{3}, \quad (3)$$

where  $c$  is a constant, which is related to the oscillator strength, and  $\Phi_{Ed} \equiv \cos(\mathbf{d}\angle\mathbf{E})$  is the cosine of the angle between the transition dipole moment,  $d$ , and the polarization direction of the absorbing light given by electric field vector,  $\mathbf{E}$ . The angular brackets denote the averaging over all possible orientations of a molecule in an ensemble. Here we used the equality  $\langle\Phi_{Ed}^2\rangle = 1/3$  that is valid for an isotropically distributed ensemble.

To describe the electric field induced orientation effect, the angular distribution function  $W(F)$ , which represents the probability for a molecule to have a given orientation, is introduced. In the case of an isotropic ensemble of molecules,  $W=1$ . Absorbance in the presence of external field,  $A_F$ , is then given

by

$$\frac{A_F}{\nu} = c\langle(s + \Delta s)\Phi_{Ed}^2 W\rangle = cs\langle\Phi_{Ed}^2 W\rangle + c\langle\Delta s\Phi_{Ed}^2 W\rangle, \quad (4)$$

where it was taken into account that the shape function,  $s$ , does not depend on, but its field-induced change,  $\Delta s$ , depends on the orientation of absorbing molecules through  $\Delta\nu$  according to Eq. (2).

Using the expression of  $\Delta s$  from Eq. (2), the field-induced change in absorbance can be written as follows:

$$\begin{aligned} \frac{\Delta A}{\nu} &= \frac{A_F}{\nu} - \frac{A}{\nu} = cs \left( \langle\Phi_{Ed}^2 W\rangle - \frac{1}{3} \right) - c \frac{ds}{d\nu} \langle\Delta\nu\Phi_{Ed}^2 W\rangle \\ &\quad + \frac{c}{2} \frac{d^2s}{d\nu^2} \langle(\Delta\nu)^2\Phi_{Ed}^2 W\rangle, \end{aligned} \quad (5)$$

Finally, by taking into account that  $cs=3A/\nu$  and consequently  $c ds/d\nu=3d(A/\nu)/d\nu$  and  $c d^2s/d\nu^2=3d^2(A/\nu)/d\nu^2$ , we find that

$$\begin{aligned} \frac{\Delta A}{\nu} &= \frac{A}{\nu} (3\langle\Phi_{Ed}^2 W\rangle - 1) + \frac{d(A/\nu)}{d\nu} (-3)\langle\Delta\nu\Phi_{Ed}^2 W\rangle \\ &\quad + \frac{d^2(A/\nu)}{d\nu^2} \frac{3}{2} \langle(\Delta\nu)^2\Phi_{Ed}^2 W\rangle, \end{aligned} \quad (6)$$

where the terms which represent the zeroth-, the first-, and the second-derivative of the bandshape function,  $A/\nu$ , with respect to frequency emerge in their raw form.

## 3. Angular distribution of molecules under the electric field

For a thermal ensemble of molecules at temperature  $T$  under an externally applied static electric field,  $F$ , the distribution of molecules by energy is given by the Boltzmann formula,

$$W = \frac{\exp(-E''/kT)}{\langle\exp(-E''/kT)\rangle}, \quad (7)$$

where  $E''$  is the interaction energy of the molecule with the electric field. More explicitly,  $E''$  is the sum of the energy given by the ground-state permanent dipole moment and the induced dipole moment in the presence of an electric field, i.e.,

$$E'' = -\mu \cdot F - \frac{1}{2} F \cdot \tilde{\alpha} \cdot F = -\mu F \Phi_{F\mu} - \frac{F^2}{2} \sum_{ij} \Phi_{Fi} \alpha_{ij} \Phi_{Fj}, \quad (8)$$

where  $\Phi_{F\mu} = \cos(\mu\angle F)$ , and  $\Phi_{Fi}$  and  $\Phi_{Fj}$  are the direction cosines of the angles between  $F$  and the axes in a molecular frame, and  $\alpha_{ij}$  are the components of the polarizability tensor,  $\tilde{\alpha}$ . Since Eq. (8) determines explicitly the dependence of the interaction energy on the orientation angle of a molecule, Eqs. (7) and (8) combined together determine the equilibrium angular distribution function (which gives probability to find the molecule at a given orientation angle) sought for. Note that the distribution function,  $W$ , in Eq. (7) is defined so that it obeys the normalization condition, i.e.,  $\langle W \rangle = 1$ .

In the case of the weak electric field limit where  $\mu F/kT \ll 1$  and  $\bar{\alpha}F^2/2kT \ll 1$ , the molecular system is far from the orientational saturation; the deviation from isotropy is small. Then the numerator and the denominator in the expression of  $W$  given by Eq. (7) can be approximated by their series expansions up to the second order:

$$\exp\left(\frac{-E''}{kT}\right) = 1 + \frac{\mu F}{kT} \Phi_{F\mu} + \frac{\mu^2 F^2}{2k^2 T^2} \Phi_{F\mu}^2 + \frac{F^2}{2kT} \sum_{ij} \Phi_{Fi} \alpha_{ij} \Phi_{Fj}. \quad (9)$$

$$\left\langle \exp\left(\frac{-E''}{kT}\right) \right\rangle = 1 + \frac{\mu^2 F^2}{6k^2 T^2} + \frac{F^2 \bar{\alpha}}{2kT}. \quad (10)$$

where  $\bar{\alpha} \equiv (1/3) \sum_i \alpha_{ii} = (1/3)(\alpha_{11} + \alpha_{22} + \alpha_{33})$  is the average polarizability. In Eq. (10), it was taken into account that  $\langle \Phi_{F\mu} \rangle = 0$ ,  $\langle \Phi_{F\mu}^2 \rangle = 1/3$ , and  $\langle \Phi_{Fi} \Phi_{Fj} \rangle = (1/3) \delta_{ij}$ . Marking the last two terms in Eq. (10) by  $x$  and considering that  $x \ll 1$ , we realize that the expression of  $W$  can be simplified by using the approximate relation  $1/(1+x) \approx 1-x$ .

The approximated distribution function can then be written in the form

$$W = 1 + W_{d1} + W_{d2} + W_p, \quad (11)$$

where its dipole and polarizability contributions are given by

$$W_{d1} = \frac{\mu F}{kT} \Phi_{F\mu} = \frac{\mu F}{kT} P_1(\Phi_{F\mu}), \quad (12)$$

$$W_{d2} = \frac{\mu^2 F^2}{2k^2 T^2} \Phi_{F\mu}^2 - \frac{\mu^2 F^2}{6k^2 T^2} = \frac{\mu^2 F^2}{3k^2 T^2} P_2(\Phi_{F\mu}), \quad (13)$$

$$W_p = \frac{F^2}{2kT} \sum_{ij} \Phi_{Fi} \alpha_{ij} \Phi_{Fj} - \frac{F^2 \bar{\alpha}}{2kT} = \frac{F^2 \alpha_0}{3kT} P_2(\Phi_{F\alpha}) + \frac{F^2 \alpha_x}{2kT} \Psi_{F\alpha}^2 \cos 2\psi'. \quad (14)$$

The formulas of  $W_{d1}$ ,  $W_{d2}$ , and  $W_p$  are also expressed via the Legendre polynomials, where  $P_1(\cos\theta) \equiv \cos\theta$  and  $P_2(\cos\theta) \equiv (3/2)\cos^2\theta - 1/2$ .  $\Phi_{F\alpha}$  and  $\Psi_{F\alpha}$  are the cosine and sine, respectively, of the angle between the electric field vector  $F$  and the long (first) principal axis of the polarizability tensor  $\tilde{\alpha}$ , and  $\psi'$  is the azimuthal (dihedral) angle about the long principal axis of  $\tilde{\alpha}$  between  $F$  and the intermediate (second) principal axis of  $\tilde{\alpha}$  (see Fig. 1). The polarizability anisotropy parameters  $\alpha_0$  and  $\alpha_x$  in Eq. (14) are related to the diagonal components of the polarizability tensor in its principal axes frame ( $\alpha_{11}$ ,  $\alpha_{22}$ ,  $\alpha_{33}$ ) by  $\alpha_0 = \alpha_{11} - (1/2)(\alpha_{22} + \alpha_{33})$  and  $\alpha_x = (1/2)(\alpha_{22} - \alpha_{33})$ . For an axially symmetric polarizability tensor, where  $\alpha_{11} = \alpha_{11}$  and  $\alpha_{22} = \alpha_{33} = \alpha_{\perp}$ , the expressions of  $\alpha_0$  and  $\alpha_x$  are reduced to  $\alpha_0 = \alpha_{11} - \alpha_{\perp}$  and  $\alpha_x = 0$ . Note that the condition  $\langle W \rangle = 1$  is followed in a natural way from the Legendre polynomials representation since  $\langle P_n(\theta) \rangle = (1/2) \int_{-1}^1 P_n(\theta) d \cos \theta = 0$  for every  $n \neq 0$  and  $\langle \cos 2\psi' \rangle = 0$ .

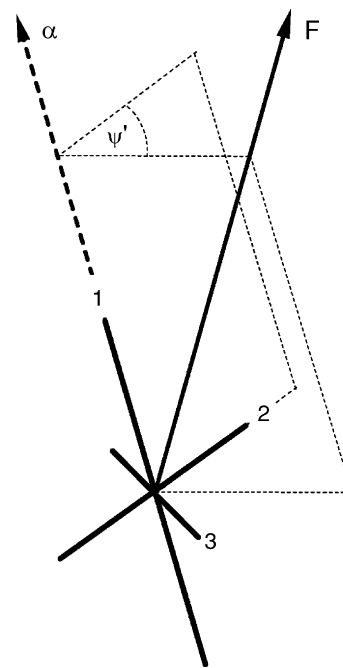


Fig. 1. Definition of the azimuthal dihedral angles  $\psi'$ ,  $\psi''$ ,  $\phi'$  and  $\phi''$ . Only the case of  $\psi'$  is illustrated. The angles  $\psi'$  and  $\psi''$  are given by a rotation about the long axis of the polarizability tensor  $\tilde{\alpha}$ , but the angles  $\phi'$  and  $\phi''$  are given by a rotation about the long axis of the polarizability difference tensor  $\Delta\tilde{\alpha}$ .  $\psi'$  and  $\phi'$  are the angles between the electric field vector  $F$  and the intermediate axis of  $\tilde{\alpha}$  and  $\Delta\tilde{\alpha}$ , respectively.  $\psi''$  and  $\phi''$  are the angles between the transition dipole moment vector  $d$  and the intermediate axis of  $\tilde{\alpha}$  and  $\Delta\tilde{\alpha}$ , respectively. The long, the intermediate, and the short principal axes of the  $\tilde{\alpha}$  tensor are denoted by the numbered bars, whose lengths correspond to the diagonal components  $\alpha_{11}$ ,  $\alpha_{22}$  and  $\alpha_{33}$  ( $\alpha_{11} > \alpha_{22} > \alpha_{33}$ ), respectively.

The equivalence between the direction cosines and the Legendre polynomial expressions of  $W_{d1}$  and  $W_{d2}$  is straightforward. To verify the equivalence of the corresponding expressions of  $W_p$ , we first note that if the indices  $i$  and  $j$  denote the principal axes of the polarizability tensor  $\tilde{\alpha}$ , the sum in Eq. (14) can be written as

$$\sum_{ij} \Phi_{Fi} \alpha_{ij} \Phi_{Fj} = \sum_i \Phi_{Fi}^2 \alpha_{ii} = \alpha_{11} \Phi_{F\alpha}^2 + \alpha_{22} \Psi_{F\alpha}^2 \cos^2 \psi' + \alpha_{33} \Psi_{F\alpha}^2 \sin^2 \psi'. \quad (15)$$

Transforming the last two terms of this expression into the form of  $\Psi_{F\alpha}^2 [(\alpha_{22} + \alpha_{33})/2 + (\cos^2 \psi' - \sin^2 \psi')(\alpha_{22} - \alpha_{33})/2]$  and introducing the parameters  $\alpha_0$ ,  $\alpha_x$ , and  $\bar{\alpha}$  according to their definitions, we find that

$$\sum_{ij} \Phi_{Fi} \alpha_{ij} \Phi_{Fj} = \bar{\alpha} + \frac{2}{3} \alpha_0 P_2(\Phi_{F\alpha}) + \alpha_x \Psi_{F\alpha}^2 \cos 2\psi'. \quad (16)$$

The  $W_{d1}$ ,  $W_{d2}$ , and  $W_p$  components of the distribution function are illustrated in the polar plots in Figs. 2–4, respectively. Actually, the functions  $1 + W_{d1}$ ,  $1 + W_{d2}$ , and  $1 + W_p$ , which represent the sum of the isotropic and the field induced distribution components, are shown, in order to avoid negative values of the plotted function. Note that only the weak field case distributions obeying  $\mu F/kT \ll 1$  are relevant for the present theory.

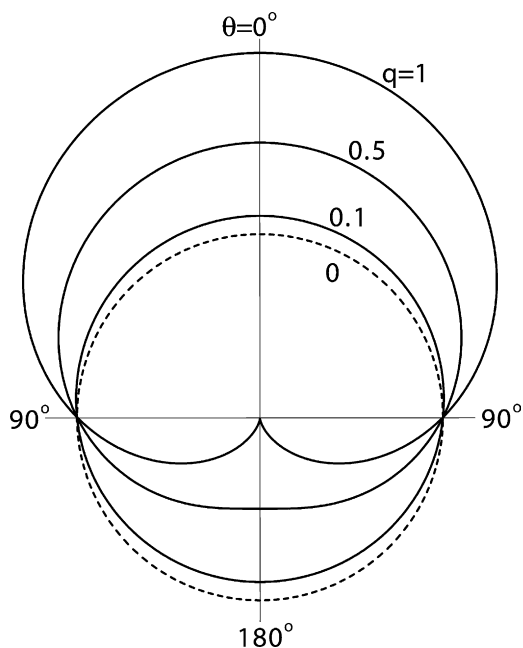


Fig. 2. Illustration of the electric field induced *orientation* of an ensemble of polar molecules. Cross section of the 3D angular distribution of the molecular dipoles, given by a polar plot of  $r(\theta) = 1 + W_{d1}(\theta) = 1 + q\cos\theta$ , is shown at zero field case ( $q \equiv \mu F/kT = 0$ , the dotted circle) and at three different field strength ( $q = 0.1, 0.5, 1$ ).  $\cos\theta \equiv \Phi_{F\mu}$ . The 3D distribution is symmetric about the electric field direction (the vertical axis of the plot). The maximum and the minimum of the distribution function correspond to the orientation of a dipole towards the field direction ( $\theta = 0^\circ$ ) and against the field direction ( $\theta = 180^\circ$ ), respectively. For perpendicular orientation of a dipole ( $\theta = 90^\circ$ ), the distribution function is not changed.

Physically, the first term (unity) in Eq. (11) describes an isotropic angular distribution of the orientations of molecules in an ensemble. This realizes in the absence of an applied electric field. The remaining terms describe the resultant effect on the angular distribution induced by the applied electric field, which tends to orient the molecules, and of the thermal motion, which tends to restore the isotropy. The  $W_{d1}$  term describes the *orientation* of the dipole moments towards the field direction, and the  $W_{d2}$  term describes the *alignment* of the dipoles parallel to the field. The orientational polarization of an ensemble of dipoles is often characterized by the “average cosine theta”, given by  $\langle W\cos\theta \rangle \equiv \langle W\Phi_{F\mu} \rangle = \langle W_{d1}\Phi_{F\mu} \rangle = (1/3)(\mu F)/(kT)$ .

The first term in the  $W_p$  expression of Eq. (14) describes the *alignment* of the maximum polarizability axis along the field, and the second term describes the alignment of the intermediate polarizability axis parallel to the field for a given direction of the maximum polarizability axes. We note that the polarizability contributions to the alignment are caused solely by the polarizability anisotropy, because the dipole moment induced by the isotropic component of polarizability is always in the field direction irrespective of the orientation of a molecule.

#### 4. Angular dependence of the Stark shift

In the presence of external electric fields, the energy levels of a molecule are shifted by the Stark effect. For a given

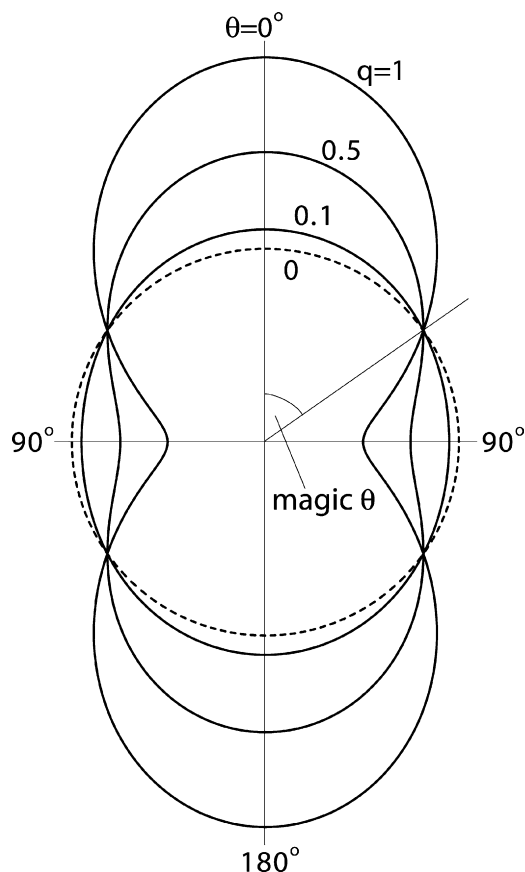


Fig. 3. Illustration of the electric field induced *alignment* of an ensemble of polar molecules. Cross section of the 3D angular distribution of the molecular dipoles, given by a polar plot of  $r(\theta) = 1 + W_{d2}(\theta) = 1 + qP_2(\theta)$ , is shown at zero field case ( $q \equiv \mu^2 F^2/3k^2 T^2 = 0$ , the dotted circle) at three different field strength ( $q = 0.1, 0.5, 1$ ).  $\cos\theta \equiv \Phi_{F\mu}$ . The 3D distribution is symmetric about the electric field direction (the vertical axis of the plot). Magic angle direction, for which the probability to find a dipole is not changed by the field induced alignment, is indicated. The maximum of the distribution function correspond to the parallel orientation of a dipole ( $\theta = 0^\circ$  or  $\theta = 180^\circ$ ) and its minimum corresponds to the perpendicular orientation of a dipole ( $\theta = 90^\circ$ ) with respect to the field.

non-degenerate electronic level, the Stark shift is determined by the interaction energy between the effective dipole moment and the applied electric field [1]. The effective dipole moment for a given molecular electronic state is the sum of permanent and polarization-induced dipole moments in this state. Hence, the field-induced shifts in energy of the ground and excited electronic states,  $\Delta E''$  and  $\Delta E'$ , respectively, are given by

$$\Delta E'' = E''(F) - E''(0) = -\boldsymbol{\mu} \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot \tilde{\boldsymbol{\alpha}} \cdot \mathbf{F}, \quad (17)$$

$$\Delta E' = E'(F) - E'(0) = -\boldsymbol{\mu}' \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot \tilde{\boldsymbol{\alpha}}' \cdot \mathbf{F}, \quad (18)$$

where  $\boldsymbol{\mu}$  and  $\boldsymbol{\mu}'$  are the permanent dipole moment vectors, and  $\tilde{\boldsymbol{\alpha}}$  and  $\tilde{\boldsymbol{\alpha}}'$  are the polarizability tensors of the ground state and the excited state, respectively. The field induced Stark shift in the transition frequency,  $\Delta\nu$ , is therefore given by

$$\Delta\nu = \frac{\Delta E' - \Delta E''}{h} = -\frac{1}{h} \Delta\boldsymbol{\mu} \cdot \mathbf{F} - \frac{1}{2h} \mathbf{F} \cdot \Delta\tilde{\boldsymbol{\alpha}} \cdot \mathbf{F}, \quad (19)$$

where  $\Delta\boldsymbol{\mu} = \boldsymbol{\mu}' - \boldsymbol{\mu}$  and  $\Delta\tilde{\boldsymbol{\alpha}} = \tilde{\boldsymbol{\alpha}}' - \tilde{\boldsymbol{\alpha}}$ .

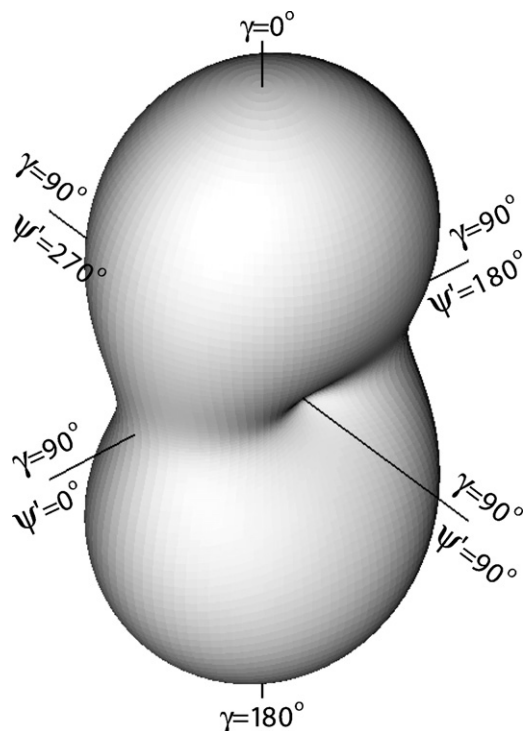


Fig. 4. Illustration of the electric field induced alignment of a molecular ensemble caused by the polarizability anisotropy of molecules. A 3D plot of the angular distribution function, given by  $r(\gamma, \psi') = 1 + W_p(\gamma, \psi') = 1 + (1/3)\alpha_0 P_2(\gamma) + (1/2)\alpha_x \sin^2 \gamma \cos^2 \psi'$ , where  $\alpha_0 = 2.5$  and  $\alpha_x = 0.5$  (corresponding to  $\alpha_{11}:\alpha_{22}:\alpha_{33} = 4:2:1$ ), is shown.  $\cos \gamma \equiv \Phi_{F\alpha}$ . Note that  $\psi'$  is defined not as a rotation about  $F$ , but about the  $\alpha$  axis, i.e., the axis of maximal polarizability (see Fig. 1). The distribution is still symmetric with respect to the electric field direction, since  $W_p(\gamma, \psi')$  does not depend on the other azimuthal angle which specifies the rotation about  $F$ . The maximum, the saddle point, and the minimum of the function correspond to the orientation of the molecule, where the long ( $\gamma = 0^\circ$ ), the intermediate ( $\gamma = 90^\circ, \psi' = 0^\circ$ ), and the short ( $\gamma = 90^\circ, \psi' = 90^\circ$ ) principal axis of its polarizability tensor is parallel to the electric field, respectively.

For the convenience in further calculations, it is useful to distinguish the dipole-induced and the polarizability-induced contributions to the Stark shift as follows:

$$\Delta v = \Delta v_d + \Delta v_p, \quad (20)$$

where

$$\Delta v_d = -\frac{F\Delta\mu}{h} \Phi_{F\Delta\mu} = -\frac{F\Delta\mu}{h} P_1(\Phi_{F\Delta\mu}), \quad (21)$$

$$\begin{aligned} \Delta v_p = & -\frac{F^2}{2h} \sum_{ij} \Phi_{Fi} \Delta\alpha_{ij} \Phi_{Fj} = -\frac{F^2 \overline{\Delta\alpha}}{2h} \\ & -\frac{F^2 \Delta\alpha_0}{3h} P_2(\Phi_{F\Delta\alpha}) - \frac{F^2 \Delta\alpha_x}{2h} \Psi_{F\Delta\alpha}^2 \cos 2\phi'. \end{aligned} \quad (22)$$

Here  $\Phi_{F\Delta\alpha}$  and  $\Psi_{F\Delta\alpha}$  are the cosine and sine, respectively, of the angle between the field direction and the long (first) axis of the difference in polarizability tensor,  $\Delta\tilde{\alpha}$ , between the ground and excited states,  $\phi'$  is the azimuthal (dihedral) angle about the long axis of  $\Delta\tilde{\alpha}$  between  $F$  and the intermediate (second)

axis of  $\Delta\tilde{\alpha}$ . The parameters  $\overline{\Delta\alpha}$ ,  $\Delta\alpha_0$ , and  $\Delta\alpha_x$  are related to the principal components of  $\Delta\tilde{\alpha}$  by  $\overline{\Delta\alpha} = (1/3)(\Delta\alpha_{11} + \Delta\alpha_{22} + \Delta\alpha_{33})$ ,  $\Delta\alpha_0 = \Delta\alpha_{11} - (1/2)(\Delta\alpha_{22} + \Delta\alpha_{33})$  and  $\Delta\alpha_x = (1/2)(\Delta\alpha_{22} - \Delta\alpha_{33})$ .

In Eq. (22), the sum  $\sum_{ij} \Phi_{Fi} \Delta\alpha_{ij} \Phi_{Fj}$  is expressed analogically to Eq. (16) so that the difference in isotropic polarizability and the difference in polarizability anisotropy are given by separate terms. It is noteworthy that the angle-independent isotropic polarizability difference contribution to the Stark shift remains in effect even without a change in polarizability anisotropy.

A comparison of Eq. (21) with Eq. (12) indicates that the angular dependence of  $\Delta v_d$  and  $W_{d1}$  is governed by the same expression in the mathematical sense (see Fig. 2), though the parameters are different. A comparison of Eq. (22) with Eq. (14) also reveals the same kind of angular dependence for the anisotropic part of  $\Delta v_p$  and  $W_p$  (see Fig. 4). For further use, we present here also the expression of squared dipole-induced Stark shift. Squaring Eq. (21), we get

$$\begin{aligned} (\Delta v_d)^2 = & \frac{F^2(\Delta\mu)^2}{h^2} \Phi_{F\Delta\mu}^2 \\ = & \frac{2F^2(\Delta\mu)^2}{3h^2} P_2(\Phi_{F\Delta\mu}) + \frac{F^2(\Delta\mu)^2}{3h^2}. \end{aligned} \quad (23)$$

## 5. Dipole- and polarization-induced contributions to the absorbance change

As an intermediate step, it is reasonable to express the absorbance change  $\Delta A$  given by Eq. (6) in terms of the  $W_{d1}(F)$ ,  $W_{d2}(F^2)$  and  $W_p(F^2)$  components of the distribution function and in terms of the  $\Delta v_d(F)$  and  $\Delta v_p(F^2)$  components of the Stark shift. Replacing  $W$  and  $\Delta v$  in Eq. (6) with their expression taken from Eqs. (11) and (20), respectively, and omitting all the resulting products that scale more than quadratically with the field strength, we obtain that

$$\begin{aligned} \frac{\Delta A}{\nu} = & \frac{A}{\nu} 3\langle \Phi_{Ed}^2 W_{d2} \rangle + \frac{d(A/\nu)}{d\nu} (-3)\langle \Phi_{Ed}^2 \Delta v_d W_{d1} \rangle \\ & + \frac{d^2(A/\nu)}{d\nu^2} \frac{3}{2} \langle \Phi_{Ed}^2 (\Delta v_d)^2 \rangle + \frac{A}{\nu} 3\langle \Phi_{Ed}^2 W_p \rangle \\ & + \frac{d(A/\nu)}{d\nu} (-3)\langle \Phi_{Ed}^2 \Delta v_p \rangle. \end{aligned} \quad (24)$$

Thus, the field-induced change in absorbance is given by a sum of five terms; the zeroth-, the first-, and the second-derivative dipole terms, and the zeroth- and the first-derivative polarizability terms.

The terms that ought to be in Eq. (24),  $3\langle \Phi_{Ed}^2 W_{d1} \rangle$  and  $-3\langle \Phi_{Ed}^2 \Delta v_d \rangle$ , which are linear to the field strength, vanish to zero on angular averaging because of the odd number of cosines in their expressions. Note that  $W_{d1} \propto \Phi_{F\mu}$  and  $\Delta v_d \propto \Phi_{F\Delta\mu}$ . Physically, the equality  $3\langle \Phi_{Ed}^2 W_{d1} \rangle = 0$  means that the absorption is unaffected by a dipolar orientation, because an increase in the number of transition dipoles in some direction is compensated by the decrease in their number in the opposite direction.

The equality,  $-3\langle\Phi_{Ed}^2\Delta\nu_d\rangle = 0$  means that there is no net shift of the absorption band owing to equal number of red-shifted and blue-shifted molecules in the isotropic distribution of electric dipoles. Thus, the averaged change in absorbance cannot scale linearly with the applied field strength in the case where the initial distribution of molecules is isotropic.

Hence, only the quadratic terms with respect to the field strength can contribute to the field-induced change in absorbance. It is noteworthy that Eq. (24) does not contain cross terms between polarization-induced and dipole-induced factors. This means that the absorbance change caused by the dipole-induced orientation/alignment can be separated from the Stark shift induced by a change in polarizability. This separation implies that the dipolar alignment does not affect the absorbance change induced by a change in polarizability on excitation. It is also noted that neither the field induced alignment nor the field-induced orientation does not contribute to the second derivative dipole term and to the first derivative polarizability term, i.e., only the isotropic part of the distribution function has to be considered for these terms.

Next two sections are devoted to the calculation of the five averages given by the angular brackets in Eq. (24).

## 6. Averaging by the direction cosine method

Traditionally and in the original works of Liptay and Czekalla [64–66], the angular averaging over an ensemble of molecules is performed by the direction cosine method, where the orientation of molecules in space is defined by the direction cosines. The bracketed terms in Eq. (24) consist of the products of physical quantities, which depend on the cosine of the angle between laboratory-fixed and molecule-fixed quantities ( $\Phi_{Ed}$ ,  $\Phi_{F\mu}$ ,  $\Phi_{F\Delta\mu}$ ,  $\Phi_{F\alpha}$ , or  $\Phi_{F\Delta\alpha}$ ). The idea is to express these quantities in terms of direction cosines that are defined by the axes of two suitably selected frames, a laboratory frame and a molecule frame. Then the averaging over the orientations of molecules reduces to the application of known formulas for the averages of the products of direction cosines between the axes of two orthogonal Cartesian frames. The expressions which result from the angular averaging depend on the cosines of the angles between the vectors or between a vector and a tensor axis, both of which belong to the same frame;  $\Phi_{EF}$ ,  $\Phi_{d\mu}$ ,  $\Phi_{d\Delta\mu}$ ,  $\Phi_{\mu\Delta\mu}$ ,  $\Phi_{d\alpha}$ , and  $\Phi_{d\Delta\alpha}$ .

A complete list of non-vanishing averages up to the fourth order over the orientations of the movable frame relative to a fixed frame for the products of direction cosines are given by the following well-known formulas [74–76]:

$$\langle\Phi_{Ai}^2\rangle = \frac{1}{3}, \quad \langle\Phi_{Ai}^4\rangle = \frac{1}{5}, \quad \langle\Phi_{Ai}^2\Phi_{Aj}^2\rangle = \frac{1}{15}, \quad (25)$$

$$\langle\Phi_{Ai}^2\Phi_{Bi}^2\rangle = \frac{1}{15}, \quad \langle\Phi_{Ai}^2\Phi_{Bj}^2\rangle = \frac{2}{15},$$

$$\langle\Phi_{Ai}\Phi_{Aj}\Phi_{Bi}\Phi_{Bj}\rangle = -\frac{1}{30}, \quad (26)$$

where the axes in movable (molecule-fixed) frame are marked by small-letter indices and the axes of the fixed (laboratory-fixed) frame are marked by capital-letter indices. The first two

formulas in Eq. (25) can be obtained by direct integration. The remaining equalities can be derived from the orthogonality and the completeness properties of the direction cosines, i.e.,

$$\sum_i \Phi_{Ai}^2 = 1, \quad \sum_i \Phi_{Ai}\Phi_{Bi} = 0,$$

$$\sum_A \Phi_{Ai}^2 = 1, \quad \sum_A \Phi_{Ai}\Phi_{Aj} = 0, \quad (27)$$

through their squaring and the averaging of the resulting terms [74–76]. The last two formulas in Eqs. (25) and the first two formulas in Eqs. (26) can be concatenated to a single expression,

$$\langle\Phi_{Ai}^2\Phi_{Bj}^2\rangle = \frac{1}{5}\delta_{AB}\delta_{ij} - \frac{1}{15}\delta_{AB} - \frac{1}{15}\delta_{ij} + \frac{2}{15}. \quad (28)$$

It will be shown in the following subsections that a certain direction cosine product, i.e.,  $\langle\Phi_{Ei}^2\Phi_{Fk}\Phi_{Fl}\rangle$ , appears in the calculation of the averages of Eq. (24). Therefore, it is useful to know its averaged value in advance. Note that the indices  $E$  and  $F$  mark the directions of corresponding laboratory frame vectors (the electric field of the absorbing light and the applied static field) and the indices  $i$ ,  $k$ , and  $l$  mark the molecular frame axes. The angle  $\mathbf{E}\angle\mathbf{F}$  can have any given value, but the axes  $i$ ,  $k$ , and  $l$  are orthogonal.

Substituting  $\Phi_{Fk}$  and  $\Phi_{Fl}$  with their expansions to the set of orthogonal laboratory frame axes  $E$ ,  $E'$ , and  $E''$  of the  $\mathbf{E}$  vector, i.e., with  $\Phi_{Fk} = \Phi_{FE}\Phi_{Ek} + \Phi_{FE'}\Phi_{E'k} + \Phi_{FE''}\Phi_{E''k}$ , omitting the terms which give zero on averaging, taking into account that  $\langle\Phi_{Ei}^2\Phi_{E'k}\Phi_{E'l}\rangle = \langle\Phi_{Ei}^2\Phi_{E''k}\Phi_{E''l}\rangle$ , and finally applying the completeness condition in the form  $\Phi_{FE}^2 + \Phi_{FE'}^2 + \Phi_{FE''}^2 = 1$ , we find that

$$\langle\Phi_{Ei}^2\Phi_{Fk}\Phi_{Fl}\rangle = \langle\Phi_{Ei}^2\Phi_{Ek}\Phi_{El}\rangle\Phi_{FE}^2 + \langle\Phi_{Ei}^2\Phi_{E'k}\Phi_{E'l}\rangle(1 - \Phi_{FE}^2). \quad (29)$$

From Eq. (28) and from the equality  $\delta_{ik}\delta_{kl} = \delta_{ik}\delta_{il}$ , the following equations are hold:

$$\langle\Phi_{Ei}^2\Phi_{Ek}\Phi_{El}\rangle = \frac{1}{15}\delta_{kl} + \frac{2}{15}\delta_{ik}\delta_{il}, \quad (30)$$

$$\langle\Phi_{Ei}^2\Phi_{E'k}\Phi_{E'l}\rangle = \frac{2}{15}\delta_{kl} - \frac{1}{15}\delta_{ik}\delta_{il}. \quad (31)$$

By applying these expressions to Eq. (29), we obtain that

$$\langle\Phi_{Ei}^2\Phi_{Fk}\Phi_{Fl}\rangle = \frac{1}{45}(-\delta_{kl} + 3\delta_{ik}\delta_{il})(3\Phi_{FE}^2 - 1) + \frac{1}{9}\delta_{kl}. \quad (32)$$

### 6.1. The zeroth-derivative dipole term

By substituting  $W_{d2}$  with its expression from Eq. (13), the following is obtained for the first term of Eq. (24):

$$3\langle\Phi_{Ed}^2W_{d2}\rangle = \frac{3\mu^2F^2}{2k^2T^2}\langle\Phi_{Ed}^2\Phi_{F\mu}^2\rangle - \frac{\mu^2F^2}{2k^2T^2}. \quad (33)$$

It is not possible to apply Eq. (32) directly to the evaluation of  $\langle\Phi_{Ed}^2\Phi_{F\mu}^2\rangle$ , because the axes defined by  $d$  and  $\mu$  indexes are in general not orthogonal, i.e., the angle between the transition dipole,  $\mathbf{d}$ , and the ground state dipole,  $\boldsymbol{\mu}$ , depends on the molecule. This problem can be solved by expressing  $\Phi_{F\mu}^2$  with the direction cosines in a molecule-fixed frame, where one of the

three axes ( $\mathbf{a}$ ,  $\mathbf{b}$  or  $\mathbf{c}$ ) is parallel but the other two are perpendicular to the axis defined by the  $\mathbf{d}$  vector so that

$$\Phi_{F\mu}^2 = \sum_{ab} \Phi_{Fa} \Phi_{a\mu} \Phi_{Fb} \Phi_{b\mu}. \quad (34)$$

Since  $\Phi_{a\mu}$  and  $\Phi_{b\mu}$  are constants, they can be left out from the averaging. Note that the indexes of  $a$ ,  $b$  and  $\mu$  are defined in the molecular frame. By inserting the above expression into Eq. (33), then by substituting  $\langle \Phi_{Ed}^2 \Phi_{Fa} \Phi_{Fb} \rangle$  according to (32), and further by applying the completeness condition, i.e.,  $\sum_a \Phi_{a\mu}^2 = 1$ , we obtain that

$$3\langle \Phi_{Ed}^2 W_{d2} \rangle = \frac{1}{30} \frac{\mu^2 F^2}{k^2 T^2} (3\Phi_{FE}^2 - 1)(3\Phi_{d\mu}^2 - 1), \quad (35)$$

where  $\Phi_{d\mu} \equiv \cos(\mathbf{d} \angle \boldsymbol{\mu})$ .

### 6.2. The first-derivative dipole term

$W_{d1}$  and  $\Delta v_d$  in the second term of Eq. (24) are replaced with their expressions given in Eq. (12) and Eq. (21), respectively. Then,

$$-3\langle \Phi_{Ed}^2 \Delta v_d W_{d1} \rangle = \frac{3\mu \Delta \mu F^2}{hkT} \langle \Phi_{Ed}^2 \Phi_{F\Delta\mu} \Phi_{F\mu} \rangle. \quad (36)$$

Expressing  $\Phi_{F\Delta\mu} \Phi_{F\mu}$  through the frame defined by the  $\mathbf{d}$  vector,

$$\Phi_{F\Delta\mu} \Phi_{F\mu} = \sum_{ab} \Phi_{Fa} \Phi_{a\Delta\mu} \Phi_{Fb} \Phi_{b\mu}, \quad (37)$$

and substituting  $\langle \Phi_{Ed}^2 \Phi_{Fa} \Phi_{Fb} \rangle$  according to Eq. (32), we find after some transformation that

$$\begin{aligned} -3\langle \Phi_{Ed}^2 \Delta v_d W_{d1} \rangle &= \frac{\mu \Delta \mu F^2}{15hkT} (3\Phi_{FE} - 1)(3\Phi_{d\Delta\mu} \Phi_{d\mu} - \Phi_{\mu\Delta\mu}) \\ &+ \frac{\mu \Delta \mu F^2}{3hkT} \Phi_{\mu\Delta\mu}, \end{aligned} \quad (38)$$

where  $\sum_a \Phi_{a\Delta\mu} \Phi_{a\mu}$  was replaced with  $\Phi_{\mu\Delta\mu} (\equiv \cos(\boldsymbol{\mu} \angle \Delta \boldsymbol{\mu}))$ .

### 6.3. The second-derivative dipole term

$(\Delta v_d)^2$  in the third term of Eq. (24) is replaced with its expression given in Eq. (23). Then,

$$\frac{3}{2} \langle \Phi_{Ed}^2 (\Delta v_d)^2 \rangle = \frac{3(\Delta\mu)^2 F^2}{2h^2} \langle \Phi_{Ed}^2 \Phi_{F\Delta\mu}^2 \rangle. \quad (39)$$

By processing analogously to the zeroth-derivative term, we find that

$$\begin{aligned} \frac{3}{2} \langle \Phi_{Ed}^2 (\Delta v_d)^2 \rangle &= \frac{(\Delta\mu)^2 F^2}{30h^2} (3\Phi_{d\Delta\mu}^2 - 1)(3\Phi_{FE}^2 - 1) + \frac{(\Delta\mu)^2 F^2}{6h^2}. \end{aligned} \quad (40)$$

where  $\Phi_{d\Delta\mu} \equiv \cos(\mathbf{d} \angle \Delta \boldsymbol{\mu})$ .

### 6.4. The zeroth-derivative polarizability term

$W_p$  in the fourth term of Eq. (24) is replaced with its formula given in Eq. (14). Then,

$$\begin{aligned} 3\langle \Phi_{Ed}^2 W_p \rangle &= \frac{3F^2}{2kT} \left\langle \Phi_{Ed}^2 \sum_{ij} \Phi_{Fi} \alpha_{ij} \Phi_{Fj} \right\rangle - \frac{3F^2 \bar{\alpha}}{2kT} \langle \Phi_{Ed}^2 \rangle \\ &= \frac{3F^2}{2kT} \sum_{ab} \langle \Phi_{Ed}^2 \Phi_{Fa} \Phi_{Fb} \rangle \sum_{ij} \Phi_{ai} \alpha_{ij} \Phi_{bj} - \frac{F^2 \bar{\alpha}}{2kT} \\ &= \frac{F^2}{10kT} (3\Phi_{FE}^2 - 1) \left( \sum_{ij} \Phi_{di} \alpha_{ij} \Phi_{dj} - \bar{\alpha} \right), \end{aligned} \quad (41)$$

where  $\sum_a \Phi_{ai} \Phi_{aj} = \delta_{ij}$  and  $\sum_i \alpha_{ii} = 3\bar{\alpha}$  were used. The expression  $\sum_{ij} \Phi_{di} \alpha_{ij} \Phi_{dj} = \mathbf{d} \cdot \bar{\boldsymbol{\alpha}} \cdot \mathbf{d} / |\mathbf{d}|^2$  gives the value of the ground state polarizability along the direction of the transition dipole moment. For an isotropic polarizability tensor satisfying  $\alpha_{ij} = \bar{\alpha} \delta_{ij}$ , the zeroth-derivative polarizability term vanishes since  $\sum_{ij} \Phi_{di} \alpha_{ij} \Phi_{dj} = \bar{\alpha}$ .

### 6.5. The first-derivative polarizability term

If  $\Delta v_p$  in the last term of Eq. (24) is replaced with its formula given in Eq. (22), we obtain that

$$\begin{aligned} -3\langle \Phi_{Ed}^2 \Delta v_p \rangle &= \frac{3F^2}{2h} \left\langle \Phi_{Ed}^2 \sum_{ij} \Phi_{Fi} \Delta \alpha_{ij} \Phi_{Fj} \right\rangle \\ &= \frac{F^2}{10h} (3\Phi_{FE}^2 - 1) \left( \sum_{ij} \Phi_{di} \Delta \alpha_{ij} \Phi_{dj} - \overline{\Delta \alpha} \right) \\ &+ \frac{F^2 \overline{\Delta \alpha}}{2h}, \end{aligned} \quad (42)$$

where  $\sum_n \Phi_{di} \Delta \alpha_{ij} \Phi_{dj} = \mathbf{d} \cdot \Delta \bar{\boldsymbol{\alpha}} \cdot \mathbf{d}$  gives the value of the excited and the ground state polarizability difference along the transition dipole moment direction. If the ground and the excited state polarizabilities are isotropic, the non-vanishing contribution comes only from the angle-independent term  $F^2 \overline{\Delta \alpha} / 2h$ .

## 7. Averaging by the Euler angle method

In the Euler angle method, the orientation of a molecule is given by the three Euler angles instead of the direction cosines. Again, as a result of averaging over an ensemble, the expressions containing the cosines, which define the orientation of individual molecules in the laboratory frame ( $\Phi_{Ed}$ ,  $\Phi_{F\mu}$ ,  $\Phi_{F\Delta\mu}$ ,  $\Phi_{F\alpha}$ ,  $\Phi_{F\Delta\alpha}$ ,  $\psi'$ ,  $\phi'$ ), are transformed to the expressions containing the cosines of fixed molecular angles ( $\Phi_{d\mu}$ ,  $\Phi_{d\Delta\mu}$ ,  $\Phi_{\mu\Delta\mu}$ ,  $\Phi_{d\alpha}$ ,  $\Phi_{d\Delta\alpha}$ ,  $\psi''$ ,  $\phi''$ ) and a cosine between the two laboratory frame vectors, e.g.,  $\cos \chi = \Phi_{EF}$  (see Fig. 1 for the definitions of the angles  $\psi'$ ,  $\phi'$ ,  $\psi''$ ,  $\phi''$ ).

Let  $\theta$  be a (polar) angle between a selected molecule-fixed vector and a selected laboratory-fixed vector, which we call the



reference vectors. The remaining two angles,  $\varphi$  and  $\psi$ , define the azimuthal rotations about the molecular reference vector (axis) and the laboratory reference vector (axis), respectively. The average of an angle-dependent function,  $X(\theta, \varphi, \psi)$ , can be then calculated as

$$\langle\langle X(\theta, \varphi, \psi) \rangle_{\psi} \rangle_{\varphi} \rangle_{\theta} = \frac{1}{8\pi^2} \int_{-1}^1 \int_0^{2\pi} \int_0^{2\pi} X(\theta, \varphi, \psi) d\psi d\varphi d\cos\theta, \quad (43)$$

where the normalization factor,  $1/8\pi^2$ , comes from  $\int \int \int d\psi d\varphi d\cos\theta = 8\pi^2$ .

In order to calculate the averages of the products of cosines between the molecule-fixed and the laboratory-fixed vectors in Eq. (24), they have first to be expressed through a selected set of the three Euler angles. Then the angular averages can be calculated via the integration according to Eq. (43). As shown in the appendix of Ref. [77], however, much easier procedure is to obtain the azimuthal averages using the relations presented below. Only the integration over the polar angle is to be carried out explicitly.

According to the cosine law of spherical trigonometry for an arbitrary three vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ , the (polar) angles  $\mathbf{b}\angle\mathbf{c}$ ,  $\mathbf{b}\angle\mathbf{a}$ , and  $\mathbf{a}\angle\mathbf{c}$  are related to each other by

$$\Phi_{bc} = \Phi_{ba}\Phi_{ac} + \Psi_{ba}\Psi_{ac} \cos\varphi, \quad (44)$$

where  $\Phi$  and  $\Psi$  denote the cosine and sine, respectively, of the polar angles between vectors given by the indices [ $\Phi_{ba} \equiv \cos(\mathbf{b}\angle\mathbf{a})$ ,  $\Psi_{ba} \equiv \sin(\mathbf{b}\angle\mathbf{a})$ ], and  $\varphi$  is the azimuthal angle between the vectors  $\mathbf{b}$  and  $\mathbf{c}$  about the axis defined by the vector  $\mathbf{a}$  (see Fig. 5). This angle can also be regarded as a dihedral angle between the plane where the vectors  $\mathbf{a}$  and  $\mathbf{b}$  are lying and the plane where the vectors  $\mathbf{a}$  and  $\mathbf{c}$  are lying.

By squaring Eq. (44), we see that

$$\Phi_{bc}^2 = \Phi_{ba}^2 \Phi_{ac}^2 + 2\Phi_{ba}\Phi_{ac}\Psi_{ba}\Psi_{ac} \cos\varphi + \Psi_{ba}^2 \Psi_{ac}^2 \cos^2\varphi. \quad (45)$$

By averaging Eq. (45) over the angle  $\varphi$  using  $\langle \cos^2\varphi \rangle = 1/2$  and  $\langle \cos\varphi \rangle = 0$ , and by expressing the cosines of polar angles via the second order Legendre polynomials, we find that

$$\langle \Phi_{bc}^2 \rangle_{\varphi} = \frac{2}{3} P_2(\Phi_{ba}) P_2(\Phi_{ac}) + \frac{1}{3}, \quad (46)$$

where the index  $\varphi$  marks the azimuthal average over this angle. The same relation can be also written in the form

$$\langle P_2(\Phi_{bc}) \rangle_{\varphi} = P_2(\Phi_{ba}) P_2(\Phi_{ac}). \quad (47)$$

It is noted that this equation follows directly from the spherical harmonic addition theorem. Obviously, Eqs. (44)–(47) remain valid on permuting the angles  $\mathbf{b}\angle\mathbf{c}$ ,  $\mathbf{b}\angle\mathbf{a}$ , and  $\mathbf{a}\angle\mathbf{c}$ , and redefining the angle  $\varphi$  about the axis, that is conjugate to the angle, whose averaged squared cosine is to be expressed.

### 7.1. The zeroth-derivative dipole term

Using the expression of  $W_{d2}$  given in Eq. (13), then applying the equality  $\Phi_{Ed}^2 = (2/3) P_2(\Phi_{Ed}) + 1/3$ , and further consid-

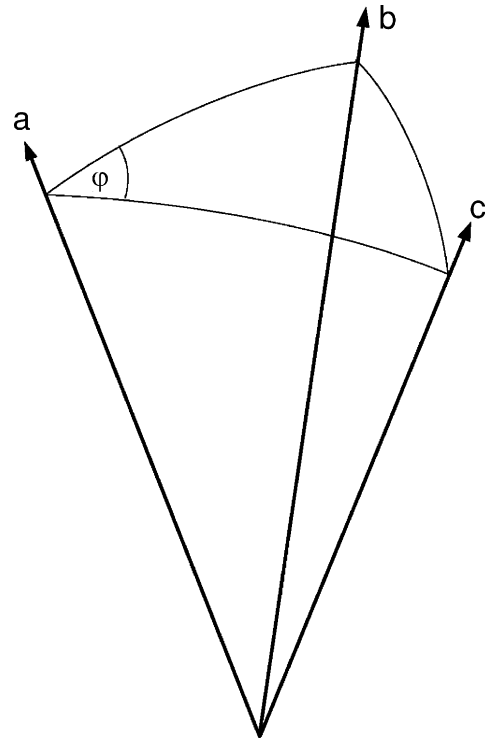


Fig. 5. For the explanation of the spherical trigonometry cosine law relation,  $\Phi_{bc} = \Phi_{ba}\Phi_{ac} + \Psi_{ba}\Psi_{ac} \cos\varphi$ , between the angles formed by the three crossing vectors. The symbols  $\Phi$  and  $\Psi$  mark cosine and sine, respectively, of the angle between the vectors given by the indices.

ering that  $\langle P_2(\Phi_{F\mu}) \rangle = 0$ , the first term in Eq. (24) can be written as

$$3\langle \Phi_{Ed}^2 W_{d2} \rangle = \frac{2\mu^2 F^2}{3k^2 T^2} \langle P_2(\Phi_{Ed}) P_2(\Phi_{F\mu}) \rangle. \quad (48)$$

If the vectors  $\mathbf{F}$  and  $\mathbf{d}$  are chosen to define the reference axes, the corresponding Euler angles are  $\delta (\equiv \mathbf{F}\angle\mathbf{d})$ ,  $\varphi$ , and  $\psi$ , where  $\varphi$  is the azimuthal angle about  $\mathbf{F}$  between  $\mathbf{E}$  and  $\mathbf{d}$  and  $\psi$  is the azimuthal angle about  $\mathbf{d}$  between  $\mathbf{F}$  and  $\mu$  (see Fig. 6). In terms of these angles, the average in Eq. (48) can be specified into the form  $\langle\langle P_2(\Phi_{Ed}) \rangle_{\varphi} \rangle_{\psi} \rangle_{\delta}$ . According to Eq. (45), we can write that

$$\langle P_2(\Phi_{Ed}) \rangle_{\varphi} = P_2(\Phi_{EF}) P_2(\Phi_{Fd}), \quad (49)$$

$$\langle P_2(\Phi_{F\mu}) \rangle_{\psi} = P_2(\Phi_{Fd}) P_2(\Phi_{d\mu}), \quad (50)$$

where  $P_2(\Phi_{EF})$  and  $P_2(\Phi_{d\mu})$  are constant factors. Since the averaging over  $\varphi$  and  $\psi$  is accomplished in Eqs. (49) and (50), only the averaging over the polar angle  $\delta \equiv \mathbf{F}\angle\mathbf{d}$  is to be done.

The relations in Eqs. (49) and (50) are applied, and the resulting squared Legendre polynomial  $[P_2(\Phi_{Fd})]^2$  is averaged over the angle  $\delta$  using the following:

$$\langle [P_2(\delta)]^2 \rangle_{\delta} = \left( \int_{-1}^1 d\cos\delta \right)^{-1} \int_{-1}^1 [P_2(\cos\delta)]^2 d\cos\delta = \frac{1}{5}. \quad (51)$$

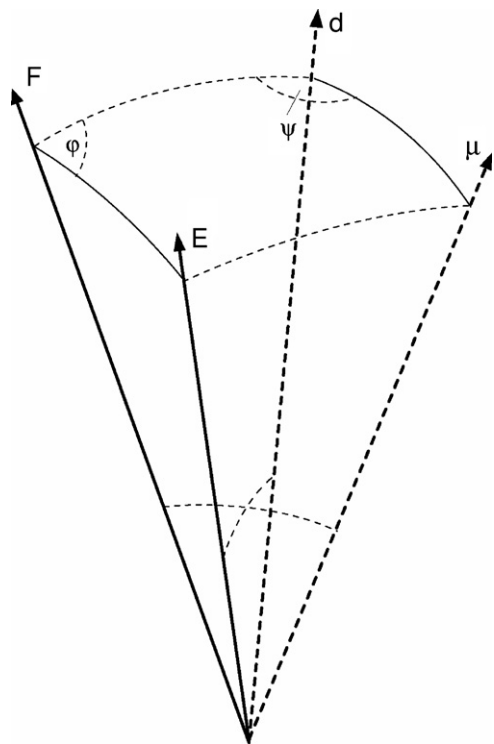


Fig. 6. The vectors and angles related to the derivation of the zeroth-derivative dipole term by the Euler angle method. Fixed vectors (angles) are marked by solid arrows (curves). Molecule-orientation-dependent vectors (angles) are marked by dashed arrows (curves). The average of the product  $P_2(\Phi_{Ed})P_2(\Phi_{F\mu})$  over all possible orientations can be calculated, for instance, by averaging (integrating) over the polar angle between  $F$  and  $d$  and over the two azimuthal angles  $\varphi$  and  $\psi$ .

Then, the following result, which is equivalent to Eq. (35), is obtained:

$$\begin{aligned} 3\langle\Phi_{Ed}^2 W_{d2}\rangle &= \frac{2\mu^2 F^2}{3k^2 T^2} \langle\langle P_2(\Phi_{Ed})\rangle_\varphi \langle P_2(\Phi_{F\mu})\rangle_\psi\rangle_\delta \\ &= \frac{2\mu^2 F^2}{15k^2 T^2} P_2(\Phi_{EF})P_2(\Phi_{d\mu}). \end{aligned} \quad (52)$$

The above equation is independent of the choice of the pair of reference vectors; the selection of the  $\mu$  and  $F$  pair, the  $\mu$  and  $E$  pair, or the  $d$  and  $E$  pair as the reference vectors leads to the same equation. In the case of the  $\mu$  and  $F$  pair, for instance, the orientation of a molecule is given by the angles  $\theta$  ( $\equiv F \angle \mu$ ),  $\varphi$ , and  $\psi$ , where  $\varphi$  is the azimuthal angle about  $F$  between  $E$  and  $d$  as before, but  $\psi$  is the azimuthal angle about  $\mu$  between  $F$  and  $d$ . Now  $\Phi_{Ed}$  has to be expressed via  $\Phi_{F\mu}$ . Eq. (47) is applied twice to  $\langle\langle P_2(\Phi_{Ed})\rangle_\varphi\rangle_\psi$  gives

$$\begin{aligned} \langle\langle P_2(\Phi_{Ed})\rangle_\varphi\rangle_\psi &= P_2(\Phi_{EF})\langle P_2(\Phi_{Fd})\rangle_\psi \\ &= P_2(\Phi_{EF})P_2(\Phi_{F\mu})P_2(\Phi_{\mu d}). \end{aligned} \quad (53)$$

Proceeding as before, we obtain the same result:

$$\begin{aligned} 3\langle\Phi_{Ed}^2 W_{d2}\rangle &= \frac{2\mu^2 F^2}{3k^2 T^2} \langle\langle\langle P_2(\Phi_{Ed})\rangle_\varphi\rangle_\psi P_2(\Phi_{F\mu})\rangle_\theta \\ &= \frac{2\mu^2 F^2}{15k^2 T^2} P_2(\Phi_{EF})P_2(\Phi_{d\mu}). \end{aligned} \quad (54)$$

## 7.2. The first-derivative dipole term

The first derivative dipole term involves three molecule-fixed vectors, i.e.,  $\mu$ ,  $\Delta\mu$ , and  $d$ . If the directions of  $F$  and  $d$  are selected as reference vectors, the averages in Eq. (36) can be specified as follows:

$$-3\langle\Phi_{Ed}^2 \Delta v_d W_{d1}\rangle = \frac{3\mu\Delta\mu F^2}{hkT} \langle\langle\Phi_{Ed}^2\rangle_\varphi \langle\Phi_{F\Delta\mu}\Phi_{F\mu}\rangle_\psi\rangle_\delta, \quad (55)$$

where  $\delta \equiv F \angle d$ ,  $\varphi$  is the azimuthal angle about  $F$  between  $E$  and  $d$ , and  $\psi$  is the azimuthal angle about  $d$  between  $F$  and  $\mu$ . Analogously to Eq. (46), the  $\varphi$  average of  $\Phi_{Ed}^2$  is given by

$$\langle\Phi_{Ed}^2\rangle_\varphi = \frac{2}{3} P_2(\Phi_{EF})P_2(\Phi_{Fd}) + \frac{1}{3}. \quad (56)$$

In order to calculate the average of  $\langle\Phi_{F\Delta\mu}\Phi_{F\mu}\rangle_\psi$ , the following relations can be used:

$$\Phi_{F\mu} = \Phi_{Fd}\Phi_{d\mu} + \Psi_{Fd}\Psi_{d\mu} \cos \psi, \quad (57)$$

$$\Phi_{F\Delta\mu} = \Phi_{Fd}\Phi_{d\Delta\mu} + \Psi_{Fd}\Psi_{d\Delta\mu} \cos \psi^*, \quad (58)$$

$$\Phi_{\mu\Delta\mu} = \Phi_{\mu d}\Phi_{d\Delta\mu} + \Psi_{\mu d}\Psi_{d\Delta\mu} \cos \Delta\psi, \quad (59)$$

where  $\psi^*$  is the azimuthal angle about  $d$  between  $F$  and  $\Delta\mu$ , and  $\Delta\psi = \psi^* - \psi$  is the azimuthal angle about  $d$  between  $\mu$  and  $\Delta\mu$ . Note that  $\Delta\psi$  is independent of the orientation of molecule. From Eqs. (57) and (58), it follows that

$$\begin{aligned} \langle\Phi_{F\Delta\mu}\Phi_{F\mu}\rangle_\psi &= \Phi_{d\mu}\Phi_{d\Delta\mu}\Phi_{Fd}^2 + \Psi_{d\mu}\Psi_{d\Delta\mu}(1 - \Phi_{Fd}^2)\langle\cos \psi \cos \psi^*\rangle_\psi. \end{aligned} \quad (60)$$

Here the factor  $\langle\cos \psi \cos \psi^*\rangle_\psi$  can be calculated via the direct integration as follows:

$$\begin{aligned} \langle\cos \psi \cos \psi^*\rangle_\psi &= \frac{1}{2\pi} \int_0^{2\pi} \cos \psi \cos(\psi + \Delta\psi) d\psi \\ &= \frac{1}{2} \cos \Delta\psi. \end{aligned} \quad (61)$$

Further,  $\cos \Delta\psi$  can be replaced with its expression deduced from Eq. (59). Then Eq. (60) takes the form

$$\langle\Phi_{F\Delta\mu}\Phi_{F\mu}\rangle_\psi = \frac{2}{3} P_2(\Phi_{Fd}) \left( \frac{3}{2} \Phi_{d\mu}\Phi_{d\Delta\mu} - \frac{1}{2} \Phi_{\mu\Delta\mu} \right) + \frac{1}{3} \Phi_{\mu\Delta\mu}. \quad (62)$$

Inserting the expressions of  $\langle\Phi_{F\Delta\mu}\Phi_{F\mu}\rangle_\psi$  and  $\langle\Phi_{Ed}^2\rangle_\varphi$  into Eq. (55), and integrating the result over ( $\delta \equiv F \angle d$ ), the first-derivative term is given by

$$\begin{aligned} -3\langle\Phi_{Ed}^2 \Delta v_d W_{d1}\rangle &= \frac{2\mu\Delta\mu F^2}{15hkT} P_2(\Phi_{EF}) (3\Phi_{d\mu}\Phi_{d\Delta\mu} - \Phi_{\mu\Delta\mu}) \\ &\quad + \frac{\mu\Delta\mu F^2}{3hkT} \Phi_{\mu\Delta\mu}, \end{aligned} \quad (63)$$

which is equivalent to Eq. (38).

The same result is obtained, though more laboriously, if the reference axes are given by  $F$  and  $\mu$ ,  $F$  and  $\Delta\mu$ ,  $E$  and  $d$ ,  $E$  and  $\mu$ , or  $E$  and  $\Delta\mu$ . In the case of the  $F$  and  $\mu$  pair, for example, the starting expression is given by

$$-3\langle\Phi_{Ed}^2\Delta v_d W_{d1}\rangle = \frac{3\mu\Delta\mu F^2}{hkT} \langle\langle\Phi_{Ed}^2\rangle_\varphi \Phi_{F\Delta\mu}\rangle_\psi \Phi_{F\mu}\rangle_\theta, \quad (64)$$

and the relations for its transformation are

$$\Phi_{Fd} = \Phi_{F\mu}\Phi_{\mu d} + \Psi_{F\mu}\Psi_{\mu d} \cos\psi, \quad (65)$$

$$\Phi_{F\Delta\mu} = \Phi_{F\mu}\Phi_{\mu\Delta\mu} + \Psi_{F\mu}\Psi_{\mu\Delta\mu} \cos\psi^*, \quad (66)$$

$$\Phi_{d\Delta\mu} = \Phi_{d\mu}\Phi_{\mu\Delta\mu} + \Psi_{d\mu}\Psi_{\mu\Delta\mu} \cos\Delta\psi, \quad (67)$$

where  $\theta \equiv F\angle\mu$ ,  $\varphi$  is the azimuthal angle about  $F$  between  $E$  and  $d$ ,  $\psi$  is the azimuthal angle about  $\mu$  between  $F$  and  $d$ ,  $\psi^*$  is the azimuthal angle about  $\mu$  between  $F$  and  $\Delta\mu$ , and  $\Delta\psi = \psi^* - \psi$ .

### 7.3. The second-derivative dipole term

For the reference axes given by  $F$  and  $d$ , the averages in equation of Eq. (39) can be specified as follows:

$$\frac{3}{2}\langle\Phi_{Ed}^2(\Delta v_d)^2\rangle = \frac{3(\Delta\mu)^2 F^2}{2h^2} \langle\langle\Phi_{Ed}^2\rangle_\varphi \langle\Phi_{F\Delta\mu}^2\rangle_\psi\rangle_\delta, \quad (68)$$

where  $\delta \equiv F\angle d$ ,  $\varphi$  is the azimuthal angle about  $F$  between  $E$  and  $d$ , and  $\psi$  is the azimuthal angle about  $d$  between  $F$  and  $\Delta\mu$ . Based on Eq. (46), we can write that

$$\langle\Phi_{F\Delta\mu}^2\rangle_\psi = \frac{2}{3}P_2(\Phi_{Fd})P_2(\Phi_{d\Delta\mu}) + \frac{1}{3}. \quad (69)$$

Using Eqs. (56) and (69) in Eq. (68), and taking into account that  $\langle P_2(\Phi_{Fd})\rangle_\delta = 0$  and  $\langle [P_2(\Phi_{Fd})]^2\rangle_\delta = 1/5$ , the following equation can be obtained:

$$\frac{3}{2}\langle\Phi_{Ed}^2(\Delta v_d)^2\rangle = \frac{2(\Delta\mu)^2 F^2}{15h^2} P_2(\Phi_{FE})P_2(\Phi_{d\Delta\mu}) + \frac{(\Delta\mu)^2 F^2}{6h^2}, \quad (70)$$

which is equivalent to Eq. (40). The same result is obtained, if  $F$  and  $\Delta\mu$ ,  $E$  and  $d$ , or  $E$  and  $\Delta\mu$  define the reference axes.

### 7.4. The zeroth-derivative polarizability term

Let the direction of the electric field, given by  $F$ , and the long (first) principal axis of the polarizability tensor  $\tilde{\alpha}$  (the  $\alpha$  axis) be the reference axes. Thus, the corresponding Euler angles are the polar angles marked by  $\gamma$  between  $F$  and the  $\alpha$  axis, the angle  $\varphi$  about  $F$  between the light polarization vector  $E$  and the  $\alpha$  axis, and the angle  $\psi$  about the  $\alpha$  axis between  $F$  and the transition dipole moment  $d$ .

With the expression of  $W_p$  in Eq. (14), the fourth term in Eq. (24) can be then written as

$$3\langle\Phi_{Ed}^2 W_p\rangle = \frac{\alpha_0 F^2}{kT} \langle\langle\Phi_{Ed}^2\rangle_\varphi\rangle_\psi P_2(\Phi_{F\alpha})\rangle_\gamma + \frac{3\alpha_x F^2}{2kT} \langle\langle\Phi_{Ed}^2\rangle_\varphi \cos 2\psi'\rangle_\psi \Psi_{F\alpha}^2\rangle_\gamma. \quad (71)$$

Analogously to Eq. (53),

$$\begin{aligned} \langle\langle\Phi_{Ed}^2\rangle_\varphi\rangle_\psi &= \frac{2}{3}\langle\langle P_2(\Phi_{Ed})\rangle_\varphi\rangle_\psi + \frac{1}{3} \\ &= \frac{2}{3}P_2(\Phi_{EF})P_2(\Phi_{F\alpha})P_2(\Phi_{\alpha d}) + \frac{1}{3}. \end{aligned} \quad (72)$$

Applying the relation of Eq. (46) and considering that  $\langle\cos 2\psi'\rangle_\psi = 0$ , then, we find that

$$\langle\langle\Phi_{Ed}^2\rangle_\varphi \cos 2\psi'\rangle_\psi = P_2(\Phi_{EF})\langle\Phi_{Fd}^2 \cos 2\psi'\rangle_\psi. \quad (73)$$

Here the complication is that the product of two  $\psi$ -dependent functions is to be averaged. The dependence of  $\Phi_{Fd}^2$  on  $\psi$  becomes evident in its expression as follows:

$$\Phi_{Fd}^2 = \Phi_{F\alpha}^2 \Phi_{\alpha d}^2 + 2\Phi_{F\alpha}\Phi_{\alpha d}\Psi_{F\alpha}\Psi_{\alpha d} \cos\psi + \Psi_{F\alpha}^2 \Psi_{\alpha d}^2 \cos^2\psi, \quad (74)$$

in analogy with Eq. (45). By introducing this result into Eq. (73), and by considering that  $\langle\cos 2\psi'\rangle_\psi = \langle\cos\psi \cos 2\psi'\rangle_\psi = 0$ , we obtain that

$$\langle\langle\Phi_{Ed}^2\rangle_\varphi \cos 2\psi'\rangle_\psi = P_2(\Phi_{EF})\Psi_{F\alpha}^2 \Psi_{\alpha d}^2 \langle\cos^2\psi \cos 2\psi'\rangle_\psi. \quad (75)$$

From the definition of the azimuthal angles  $\psi$  and  $\psi'$  (see Fig. 1), which are both about the long axis of the polarizability tensor (the  $\alpha$  axis), it follows immediately that their difference, i.e.,  $\psi'' = \psi' - \psi$  is a molecule-fixed dihedral angle about the  $\alpha$  axis between the transition dipole moment and the intermediate (second) principal axis of the polarizability tensor. By substituting  $\psi$  in Eq. (75) with  $\psi' - \psi''$ , and by averaging the resulting expression over  $\psi'$ , which is equivalent to the average over  $\psi$ , we find that

$$\begin{aligned} \langle\cos^2\psi \cos 2\psi'\rangle_{\psi'} &= \langle\cos^2(\psi' - \psi'')(\cos^2\psi' - \sin^2\psi'')\rangle_{\psi'} = \frac{1}{4} \cos 2\psi''. \end{aligned} \quad (76)$$

In the calculation, the following relations were used:  $\langle\cos^4\psi\rangle_\psi = \langle\sin^4\psi\rangle_\psi = 3/8$ ,  $\langle\cos^2\psi \sin^2\psi\rangle_\psi = 1/8$ ,  $\langle\cos^3\psi \sin\psi\rangle_\psi = \langle\cos\psi \sin^3\psi\rangle_\psi = 0$ .

Finally, by combing the intermediate results and by averaging over the polar angle  $\gamma$  with  $\langle [P_2(\Phi_{F\alpha})]^2\rangle_\gamma = 1/5$  and  $\langle\Phi_{F\alpha}^4\rangle_\gamma = (1/2) \int_0^\pi \sin^4\gamma d\cos\gamma = (1/2) \int_{-1}^1 (1-x^2)^2 dx = 8/15$ , we obtain that

$$3\langle\Phi_{Ed}^2 W_p\rangle = \frac{2\alpha_0 F^2}{15kT} P_2(\Phi_{EF})P_2(\Phi_{\alpha d}) + \frac{\alpha_x F^2}{5kT} P_2(\Phi_{EF})\Psi_{\alpha d}^2 \cos 2\psi''. \quad (77)$$

According to Eq. (16), it is obvious that Eq. (77) is equivalent to Eq. (41).

### 7.5. The first-derivative polarizability term

The direction of the electric field and the long (first) principal axis ( $\Delta\alpha$  axis) of the excited and ground state polarizability difference tensor  $\Delta\tilde{\alpha}$  are taken as the reference axes. The relevant Euler angles are the polar angle  $\beta$  between  $\mathbf{F}$  and the  $\Delta\alpha$  axis, the angle  $\varphi$  about  $\mathbf{F}$  between the light polarization vector  $\mathbf{E}$  and the  $\Delta\alpha$  axis, and the angle  $\phi$  about the  $\Delta\alpha$  axis between  $\mathbf{F}$  and the transition dipole moment  $\mathbf{d}$ . By using the expression of  $\Delta\nu_p$  of Eq. (22), the last term of Eq. (24) can be expressed as

$$\begin{aligned} & -3\langle\Phi_{Ed}^2\Delta\nu_p\rangle \\ &= \frac{3F^2\overline{\Delta\alpha}}{2h}\langle\Phi_{Ed}^2\rangle + \frac{F^2\Delta\alpha_0}{h}\langle\langle\Phi_{Ed}^2\rangle_\varphi\rangle_\phi P_2(\Phi_{F\Delta\alpha})_\beta \\ &+ \frac{3F^2\Delta\alpha_x}{2h}\langle\langle\Phi_{Ed}^2\rangle_\varphi \cos 2\phi'\rangle_\phi \Psi_{F\Delta\alpha}^2_\beta, \end{aligned} \quad (78)$$

where  $\cos\beta$  is  $\Phi_{F\Delta\alpha}$ . In analogy with the derivation of the zeroth-derivative polarizability term, we obtain that

$$\begin{aligned} -3\langle\Phi_{Ed}^2\Delta\nu_p\rangle &= \frac{F^2\overline{\Delta\alpha}}{2h} + \frac{2F^2\Delta\alpha_0}{15h}P_2(\Phi_{EF})P_2(\Phi_{d\Delta\alpha}) \\ &+ \frac{F^2\Delta\alpha_x}{5h}P_2(\Phi_{EF})\Psi_{d\Delta\alpha}^2 \cos 2\phi'', \end{aligned} \quad (79)$$

where  $\phi''$  is a molecule-fixed dihedral angle about the  $\Delta\alpha$  axis between the transition dipole moment  $\mathbf{d}$  and the intermediate (second) principal axes of the  $\Delta\tilde{\alpha}$  tensor.

## 8. The resulting set of equations and its physical background

Replacing the averages in Eq. (24) with their expressions obtained in Sections 6 and 7 and taking into account the local enhancement in the electric field by a dimensionless factor  $f$ , [1,68] we get the equations for the absorbance change in their traditional form as a linear combination of the zeroth-, the first- and the second-derivative contributions:

$$\frac{\Delta A}{\nu} = (fF)^2 \left[ a \left( \frac{A}{\nu} \right) + b \frac{d(A/\nu)}{d\nu} + c \frac{d^2(A/\nu)}{d\nu^2} \right], \quad (80)$$

where the coefficients  $a$ ,  $b$ , and  $c$  are given by

$$\begin{aligned} a &= \frac{\mu^2}{30k^2T^2}(3\Phi_{FE}^2 - 1)(3\Phi_{d\mu}^2 - 1) + \frac{1}{10kT}(3\Phi_{FE}^2 - 1) \\ &\times \left( \sum_{ij} \Phi_{di}\alpha_{ij}\Phi_{dj} - \bar{\alpha} \right), \end{aligned} \quad (81)$$

$$\begin{aligned} b &= \frac{\mu\Delta\mu}{3hkT}\Phi_{\mu\Delta\mu} + \frac{\mu\Delta\mu}{15hkT}(3\Phi_{FE}^2 - 1)(3\Phi_{d\mu}\Phi_{d\Delta\mu} - \Phi_{\mu\Delta\mu}) \\ &+ \frac{\overline{\Delta\alpha}}{2h} + \frac{1}{10h}(3\Phi_{FE}^2 - 1) \left( \sum_{ij} \Phi_{di}\Delta\alpha_{ij}\Phi_{dj} - \overline{\Delta\alpha} \right), \end{aligned} \quad (82)$$

$$c = \frac{(\Delta\mu)^2}{6h^2} + \frac{(\Delta\mu)^2}{30h^2}(3\Phi_{FE}^2 - 1)(3\Phi_{d\Delta\mu}^2 - 1). \quad (83)$$

Alternatively, the polarizability dependent terms in Eqs. (81) and (82) can be written as:

$$\frac{\alpha_0}{30kT}(3\Phi_{FE}^2 - 1)(3\Phi_{d\alpha}^2 - 1) + \frac{\alpha_x}{10kT}(3\Phi_{FE}^2 - 1)\Psi_{d\alpha}^2 \cos 2\psi'', \quad (84)$$

$$\begin{aligned} \frac{\overline{\Delta\alpha}}{2h} &+ \frac{\Delta\alpha_0}{30h}(3\Phi_{FE}^2 - 1)(3\Phi_{d\Delta\alpha}^2 - 1) \\ &+ \frac{\Delta\alpha_x}{10h}(3\Phi_{FE}^2 - 1)\Psi_{d\Delta\alpha}^2 \cos 2\phi'', \end{aligned} \quad (85)$$

respectively. Traditionally [1–3,64,65], the angle between the electric vector of the applied static field,  $\mathbf{F}$ , and the electric vector of absorbing light,  $\mathbf{E}$ , is marked by  $\chi$  so that  $\Phi_{FE} \equiv \cos \chi$ .

When the band shape function,  $A(\nu)/\nu$ , is a smooth positive valued function of frequency that approaches to zero on both sides farther away from the center frequency (like Gaussian or Lorentzian, for example), the first derivative with respect to frequency,  $d(A(\nu)/\nu)/d\nu$ , describes a shift of the band, and its second derivative,  $d^2(A(\nu)/\nu)/d\nu^2$ , describes a broadening of the band [2]. In other words, the difference between the original band shape and the shifted one (for a small shift compared to the bandwidth) results in the first derivative curve, and the difference between the original band shape and the broadened one (for a small broadening compared to the bandwidth) results in the second derivative curve.

Eqs. (80)–(83) describe the effect of external electric field on the absorption of polarized light by a thermal ensemble of molecules caused by the Stark shift of their electronic transition frequency and by the field-induced alignment/orientation of the ensemble. The same set of electroabsorption (E-A) equations, though with different notations, is presented in Ref. [68]. A practical importance of these equations is that they provide a link between the macroscopic quantities measured in an experiment, i.e.,  $A(\nu)$ ,  $\Delta A(\nu)$ ,  $F$ ,  $T$ , and  $\chi \equiv \arccos \Phi_{FE}$ , and the microscopic constants characterizing the molecule, i.e.,  $\mu$ ,  $\Delta\mu$ ,  $\alpha$ ,  $\alpha_0$ ,  $\alpha_x$ ,  $\Delta\alpha$ ,  $\Delta\alpha_0$ ,  $\Delta\alpha_x$ ,  $\Phi_{d\mu}$ ,  $\Phi_{d\Delta\mu}$ ,  $\Phi_{d\alpha}$ ,  $\Phi_{d\Delta\alpha}$ ,  $\psi''$ , and  $\phi''$ . For overlapping electronic transitions, the change in absorbance is a sum of the contributions from each transition.

The zeroth-derivative dipole contribution to the absorption change (called also the linear dichroism) arises from the deviation of the distribution of the ensemble of transition dipoles from isotropy owing to the alignment of the ground state dipoles along the direction of the applied electric field. Stark shift is not relevant to this contribution. In molecules whose ground state permanent dipole moment and transition dipole moment are parallel to each other, the absorbance is larger for a light polarized parallel with the applied electric field direction, the absorbance is smaller for a light polarized perpendicularly to the field direction, and the absorbance is not altered for a light whose polarization direction forms magic angle with the field direction. The orientation component of the distribution function,  $W_{d1}$ , cannot cause a change in absorbance, because the

increase in a number of dipoles in the vicinity of a selected direction is compensated with equal decrease in the vicinity of the opposite direction.

The first-derivative dipole contribution to the absorption change arises from the concerted effect of the orientation of the molecular dipoles towards the field and the linear Stark shift caused by a change in the dipole moment accompanying the absorption. This effect can be regarded as a detection of the field-induced orientation through the observation of the average Stark shift. For an orientated ensemble where the number of molecules with a red-shifted absorption band is larger than the number of molecules with a blue-shifted band, the ensemble average results in an effective red-shift. The first-derivative dipole contribution can be also regarded as an orientational polarizability since it appears in the same way as the first-derivative polarizability contribution. The resulting quadratic dependence comes from the orientation component of the distribution function and the dipole induced Stark shift, both of which scale linearly with the electric field.

The second-derivative dipole contribution arises from the effective field-induced broadening of the absorption band resulting from the squared linear (dipole-induced) Stark shift. This broadening results from the average over an ensemble containing equal number of molecules with blue-shifted and red-shifted absorption band. Indeed, according to Eq. (21),  $\langle \Delta v_d \rangle = 0$ , indicating the absence of a resultant shift, but according to Eq. (23),  $\langle (\Delta v_d)^2 \rangle = F^2 (\Delta \mu)^2 / (3h^2)$ , indicating the presence of a broadening. However, such a rationalization does not explain the existence of the second term, which is proportional to  $3\Phi_{FE}^2 - 1 = 2P_2(\chi)$ . Actually, the angular dependence of the absorbance change comes from  $\langle \Phi_{Ed}^2 (\Delta v_d)^2 \rangle$ , which gives rise to both  $\chi$ -dependent and  $\chi$ -independent components on averaging. The quadratic dependence on the field strength follows directly from the expression of squared linear Stark shift (see Eq. (23)). The orientation/alignment is not relevant to this contribution. The inclusion of orientation/alignment factors gives rise to higher order contributions ( $\propto F^4$ , for instance).

The zeroth-derivative polarizability anisotropy contribution for an ensemble of axially symmetric molecules reflects the alignment of their maximum polarizability axes along the electric field vector. For molecules whose polarizability is non-axially symmetric additional alignment of the intermediate polarizability axes along the electric field takes place. This is most evident for molecules whose maximum polarizability axes are oriented perpendicularly to the field. Non-polar molecules with isotropic polarizability will not be aligned, since the energy of a molecule in electric field is then independent of its orientation. No  $\chi$ -independent component exists for this contribution.

The first-derivative polarizability contribution comes from the Stark shift of the absorption band. The Stark shift as well as the resulting change in absorbance has the isotropic component owing to the change in average polarizability and the  $\chi$ -dependent component owing to the change in polarizability anisotropy on electronic transition. Angular dependence of the polarizability anisotropy difference contribution is governed by the same expression as the polarizability anisotropy contribution for the zeroth-derivative term (cf. Eqs. (84) and (85)), but

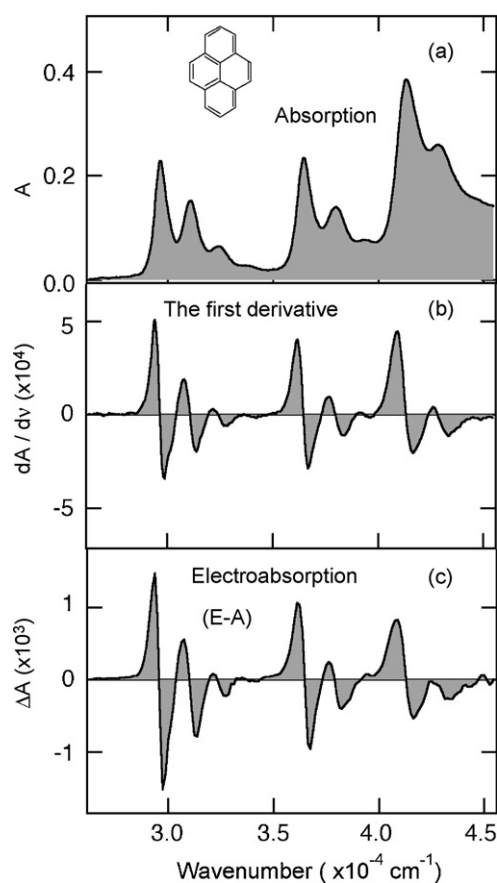


Fig. 7. Absorption spectrum (a), its first derivative spectrum (b), and E-A spectrum (c) of pyrene doped in a PMMA film at a concentration of 1.0 mol%. The applied field strength was  $1.0 \text{ MV cm}^{-1}$ , and  $\chi$  was  $90^\circ$ .

with the components of polarizability difference tensor,  $\Delta\alpha_0$  and  $\Delta\alpha_x$ , instead of the components of ground state polarizability tensor,  $\alpha_0$  and  $\alpha_x$ .

In Eqs. (81)–(85), it is important to note that the terms proportional to  $3\Phi_{ab}^2 - 1$ , which depend on some angle  $a \angle b$ , vanish in the case of the magic value for this angle, i.e., if  $a \angle b = \arccos \sqrt{1/3} \approx 54.7^\circ$ . This is illustrated graphically in Fig. 3. In order to simplify the data treatment of an electroabsorption experiment, the angle  $\chi$  between the direction of the applied electric field and the light polarization is often intentionally set to the magic value.

## 9. Application to the electroabsorption spectra

To demonstrate the significance of the above equations, some experimental results of the electroabsorption (E-A) spectra are described. Fig. 7 shows the E-A spectrum of pyrene doped in a PMMA film, together with the absorption spectrum and its first derivative spectrum in the region of the  $S_0 \rightarrow S_2$ ,  $S_0 \rightarrow S_3$  and  $S_0 \rightarrow S_4$  transitions [5]. The observed E-A spectrum is essentially the same in shape as the first derivative of the absorption spectrum in each transition, indicating that the E-A spectrum results from the change in molecular polarizability between the ground state and the excited state (see Eq. (82)). The magnitudes of the E-A spectrum of the  $S_0 \rightarrow S_2$ ,  $S_0 \rightarrow S_3$  and  $S_0 \rightarrow S_4$

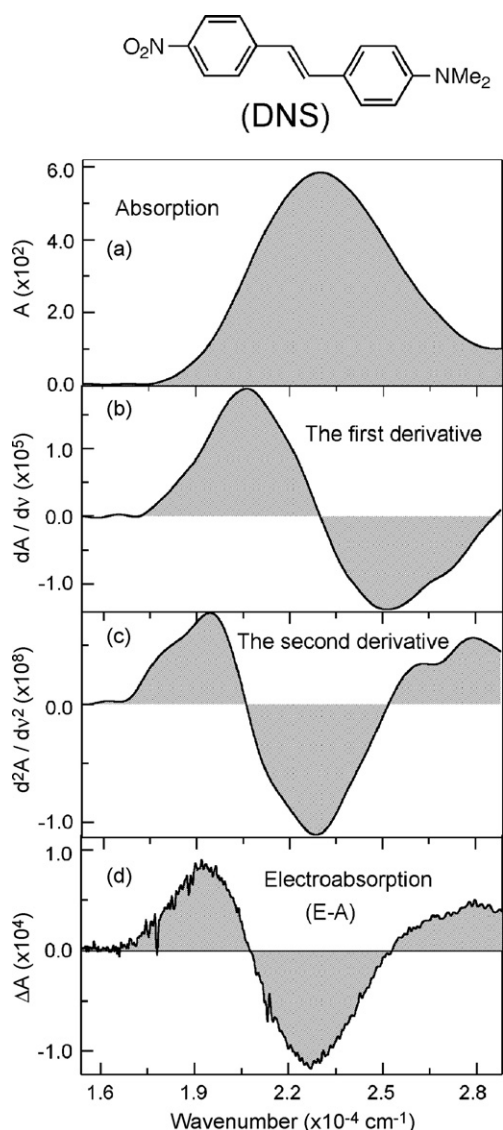


Fig. 8. Absorption spectrum (a), its first derivative spectrum (b), the second derivative spectrum (c), and E-A spectrum (d) of 4-dimethylamino-4'-nitrostilbene (DNS) doped in a PMMA film at a concentration of 0.15 mol%. The absorption spectrum was smoothed by taking the average, and then the derivative spectra were obtained. The applied field strength was 0.4 MV cm<sup>-1</sup>, and  $\chi$  was 90°.

transitions relative to the first derivative of the corresponding absorption spectrum of each transition are different from each other, indicating that the magnitudes of the molecular polarizability at the S<sub>2</sub>, S<sub>3</sub> and S<sub>4</sub> states are different from each other. The magnitude of  $\overline{\Delta\alpha}$  was evaluated to be 17.5, 15.5 and 13.2 in units of Å<sup>3</sup> for the excitation into S<sub>2</sub>, S<sub>3</sub> and S<sub>4</sub>, respectively [5]. Pyrene has no electric dipole moment because of the presence of the inversion symmetry. As a result, the second derivative component of the absorption spectrum was not observed in the E-A spectrum. The zeroth derivative component was not observed in the E-A spectrum either, indicating that pyrene is not oriented/aligned by an electric field in PMMA.

Fig. 8 shows the E-A spectrum of 4-dimethylamino-4'-nitrostilbene (DNS) doped in a PMMA film, together with the absorption spectrum and its first and second derivative spectra

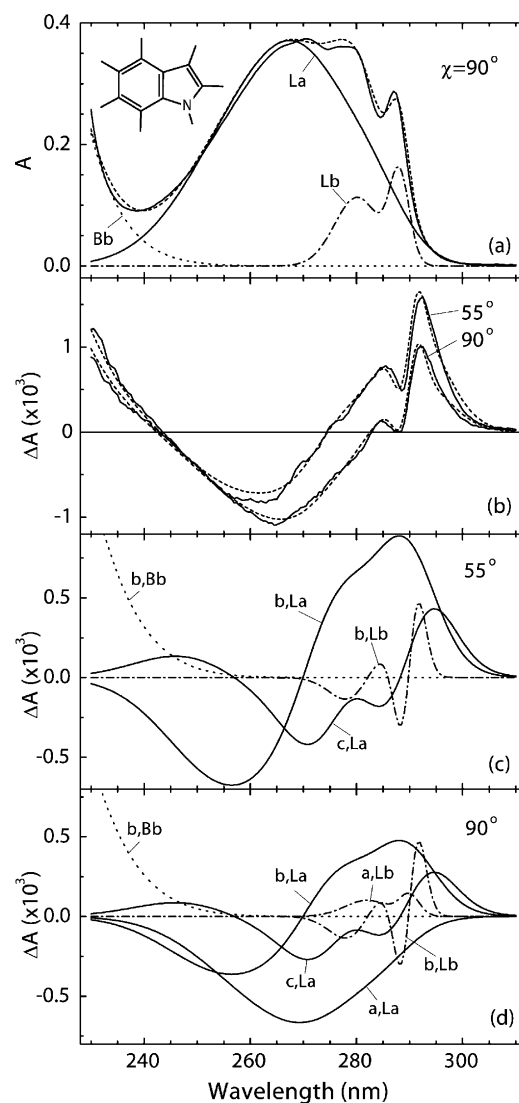


Fig. 9. (a) Absorption spectrum and its decomposition into the L<sub>b</sub>, L<sub>a</sub> and B<sub>b</sub> bands, (b) polarized E-A spectra observed at  $\chi = 90^\circ$  (normal incidence) and at  $\chi = 54.7^\circ$  (magic angle), respectively, and the simulated spectra (broken line), (c) the first and the second derivative components of the L<sub>b</sub>, L<sub>a</sub> and B<sub>b</sub> bands are required for the simulation of the E-A spectrum at  $\chi = 55^\circ$ , (d) the zeroth, the first and the second derivative components of the L<sub>b</sub>, L<sub>a</sub> and B<sub>b</sub> bands are required for the simulation of the E-A spectrum at  $\chi = 90^\circ$  (from top to bottom). The applied field strength was 1.0 MV cm<sup>-1</sup>. The letters a, b and c in the figures designate the zeroth, the first, and the second derivative contributions of the absorption to the state behind the letter, respectively.

in the S<sub>0</sub> → S<sub>1</sub> transition [45]. In contrast with pyrene, the E-A spectrum is very similar in shape to the second derivative spectrum, indicating that the E-A spectrum mainly results from the change in electric dipole moment between the ground state and the excited state (see Eq. (83)). The magnitude of  $\Delta\mu$  was evaluated to be 10.9 Debye [45]. The E-A spectrum of DNS does not show the zeroth derivative component even when the E-A spectrum was observed at  $\chi = 90^\circ$ , where  $\chi$  is the angle between the direction of the electric field and the polarization direction of the excitation light. These results indicate that DNS is not reoriented along the field direction in a PMMA film, though DNS has an electric dipole moment in the ground state, probably because

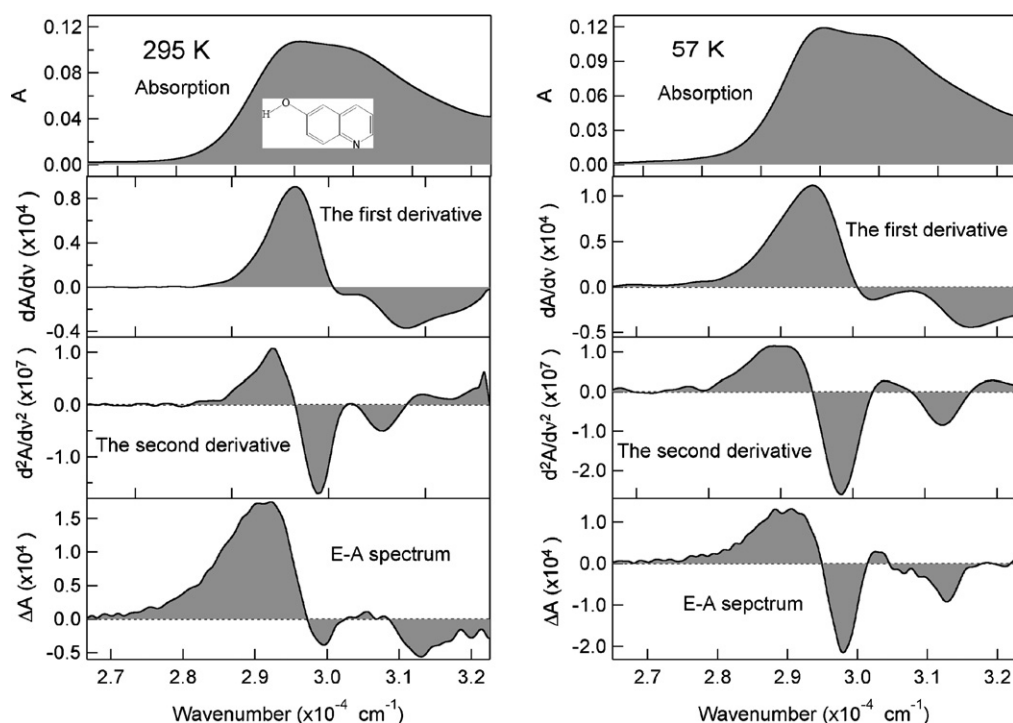


Fig. 10. E-A spectra of 6-hydroxyquinoline (bottom) doped in a PMMA film at 2.0 mol% observed with  $\chi=90^\circ$  at 295 K (left) and at 57 K (right), respectively, together with the absorption and its first and second derivative spectra. The field strength was  $1.0 \text{ MV cm}^{-1}$ .

DNS is confined in a small cavity of PMMA where the space is too small for DNS to reorient.

Fig. 9 shows the E-A spectra of indole doped in a PMMA film [40,46]. In this case, significant polarization dependence was observed in the E-A spectra. The absorption spectrum in the region from 230 to 310 nm is an overlap of the so-called  $L_b$ ,  $L_a$  and  $B_b$  bands. These three bands were separated, and the first and the second derivatives of each band were obtained. At the magic angle of  $\chi$ , E-A spectra are reproduced by a linear combination of only the derivative spectra of these three absorption bands, and the zeroth component is negligible. On the other hand, the zeroth derivative component of the  $L_a$  and  $L_b$  bands is very significant in the E-A spectrum observed at  $\chi=90^\circ$ , as shown in Fig. 9. These results indicate that indole can rotate in a cavity of PMMA and orient along the field direction to some extent (see Eq. (81)).

Another example of the molecular orientation along the field direction is shown in Fig. 10, where E-A spectra of 6-hydroxyquinoline (6-HQ) doped in a PMMA film are shown [52]. These E-A spectra were obtained at  $\chi=90^\circ$  both at room temperature (295 K) and at 57 K. At room temperature, the E-A spectra are given by a linear combination of the zeroth, first and second derivative components of the absorption spectrum. The presence of the zeroth derivative component indicates that 6-HQ is reoriented along the electric field direction in PMMA at room temperature. On the contrary, E-A spectrum of 6-HQ observed at 57 K is very similar in shape to the second derivative of the absorption spectrum. Negligible zeroth-derivative contribution indicates the absence of field-induced reorientation. This means that 6-HQ molecules are immobilized in a cavity of PMMA at low temperatures.

According to Eqs. (81) and (82), the orientation/alignment terms are larger at low temperatures, i.e., cooling the sample is expected to promote the reorientation effects. In the theory presented above, however, the light-absorbing molecules are assumed to be able to freely reorient, i.e., only the balance of their thermal kinetic energy and their potential energy in externally applied electric field is taken into account. The assumption of unrestricted mobility may be approximately valid for room-temperature solutions as well as for gaseous molecules, but not for a polymer matrix, especially at low temperatures. The lower the temperature, the less is the content of rotational-librational energy of a molecule in comparison with the potential barriers of its local surrounding. As a result, the embedded molecules are almost fixed in a cavity of the host matrix by local electrostatic barriers at cryogenic temperatures. At room temperature in PMMA matrix, on the other hand, some molecules, like pyrene [5] and DNS [45], are immobilized, but some molecules, like indole [40] and 6-HQ [52], are partially reoriented by the applied electric field.

As demonstrated above, the equations shown in the present paper enable us to analyze polarization absorption and E-A spectra of a mobile ensemble of light absorbing polar molecules, to elucidate the role of the Stark and orientational/alignment effects, and to obtain several important molecular parameters, like the change in dipole moment and the change in polarizability on photoexcitation.

## 10. Summary

A simple derivation of the electroabsorption equations, which model the absorption change for a mobile ensemble of molecules

at thermal equilibrium, is reported. Two physical effects, the field-induced reorientation of the molecules and the Stark shift of their electronic absorption band, are described by these equations. Both the direction cosine method and the Euler angle method are shown to be suitable for calculating the necessary orientational averages over the ensemble of molecules. In our opinion, the Euler angle method provides somewhat deeper physical insight although the mathematical transformations are easier to be carried out by the direction cosine method. The derived equations are essential to analyze the E-A spectra and to examine the molecular parameters as well as molecular orientation/alignment in the presence of an electric field.

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