

ELECTROOPTICAL PARAMETERS OF MOLECULES: POLARIZABILITIES OF CHEMICAL BONDS

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A review of the methods for solving the inverse electrooptical problem of molecular optics is presented. The reasons for the uncertainty in semiempirical determination of the principal values of the molecular polarizability tensor are analyzed and the necessity of solving the inverse problem based on the use of the valence–optical (VO) theory is shown. Based on the invariant expression for the molecular polarizability anisotropy (O.G. Bokov, Atm. Opt. 3 No. 9, 827–839 (1990)) invariant equations have been derived for calculating the electrooptical parameters (EOP's), i.e., of the chemical bond polarizabilities of diatomic and hexatomic molecules. The EOP's of the twenty five molecules presented in the atmosphere as their main components or pollutants have been calculated.

INTRODUCTION

It is impossible to investigate experimentally and theoretically the effects in the atmosphere by optical methods without making use of the reliable information on the structure and the electrooptical parameters (EOP's) of the atmospheric molecules.

It was shown in Ref. 1 for simplest (in structure) molecules, such as methane and carbon tetrachloride, that the greater the number of authors who have studied the given molecule in optical and spectroscopical experiments, the more ambiguous is the information about its EOP.

The paradoxicality of this problem is explained by the fact that there exists the large number of the experimental data of different authors on molecules most "popular" for the experimental investigations (see, for example, Refs. 2–4) although the parameters being measured were the same. As a result, "experimental uncertainty" arises in scientific literature with respect to the parameters, which are fundamental for the problem under investigation.^{3,4} This uncertainty seriously impedes both the comparison of the theoretical values of the EOP with experimental data and the use of these parameters in the semiempirical theories of the other phenomena.

It follows from the above said that to eliminate the uncertainties in choosing the experimental EOP's of molecules must be an important problem of the sciences dealing with the structure of matter both in the applied and fundamental aspects.

The paper studies the methods of solving the inverse electrooptical problem of molecular optics, which enable us to choose the consistent experimental data and to determine the reliable values of the EOP's, that is, the polarizabilities of the chemical bonds of molecules of Earth's atmosphere.

INVERSE PROBLEM OF THE MOLECULAR OPTICS

Electrical structure of molecules and the intramolecule interaction determine the important physical characteristics such as the polarizability and the dipole moments of molecules and their structural components, that is, chemical bonds. The problem of the dipole moments was examined in detail in Ref. 5. We will study here the problem of the polarizability of molecules and bonds in the modern molecular optics.

The polarizability of an anisotropic molecule is known to be described completely (see, for instance, Refs. 3 and 6) by the three principal (proper) values a_p ($p = 1, 2, 3$) of polarizability tensor a_{uv} of molecule which is reduced to its principal axes being the axes of the molecular polarizability ellipsoid. Invariant (relative to the translation and rotation of the laboratory system coordinate) values of a_p are determined by solving the inverse electrooptical problem based on the three independent experiments of the molecular optics, i.e., on the measurements of the refraction coefficient n , the Kerr optical effect (or anisotropic portion of Rayleigh scattering of light), and the Kerr static effect.

It should be noted that in order to avoid the distortions of the components a_{uv} of the polarizability tensor caused by the intermolecular interaction, these values should be measured in not very dense gases. However, the accuracy is usually low when we measure the integral parameters of the optical and spectroscopic effects in gases. Therefore, the more accurate measurements of these parameters can be performed by an experimenter in pure liquids and solutions.

In the last case the well-known difficulties has arisen on correct accounting of the effect of the interaction between molecules in liquid on their proper parameters, including the molecular polarizability. Many authors could not overcome these difficulties, when they interpreted their own results. The number of values of the anisotropy g^2 of the polarizability tensor a_{uv} of molecules, which were calculated on the basis of the measurements performed mainly in liquids, amounts to 25 (for instance, for carbon bisulphide molecule) in the reference book,⁴ that is indicative of the above-mentioned fact.

However, the situation is the same for the polarizabilities a_p measured in gases. The reason is that we retrieve the trace b of the tensor a_{uv} from the measurements of the refraction of light

$$b = \sum_{p=1}^3 a_p. \quad (1)$$

The Kerr optical effect or the anisotropic scattering of light provides the information on the anisotropy of this tensor

$$g^2 = \frac{1}{2} [(a_1 - a_2)^2 + (a_2 - a_3)^2 + (a_3 - a_1)^2] \quad (2)$$

(it is denoted by γ^2 in Refs. 3 and 4).

It is clear that the third relation is required to relate the values of a_p to the experimental data for molecules without axial symmetry (that is, when $a_1 \neq a_2 = a_3$). One can obtain this relation by measuring the parameter of the Kerr static effect. Here the first difficulty has arisen. As was shown by Stuart,⁷ the most common case, which can be completely studied and the three different values of a_p can be found is the case of molecule, which has dipole moment μ_p directed along one of the principal axes of the molecular polarizability ellipsoid.

However, generally it is difficult to determine the direction of the principal axes of the polarizability ellipsoid for the molecules with the symmetry being not higher than C_s . In addition the direction of the dipole moment μ_0 may coincide with none of the principal axes of the tensor a_{uv} , neither this direction may be known in the coordinate system affixed to the principal axes of the molecular ellipsoid (which was called M -system in Ref. 1). In this case the third relation similar to Eqs. (1) and (2) and relating the values a_p and μ_0 to the Kerr static parameter appears to be useless as the third equation for determining a_p because the functions of unknown angles enter into it.

In other cases (few in number), when the direction of the dipole moment in the M -system is well known, the other principal difficulty has arisen in calculating the value a_p due to the fact that μ_0 enters as the parameter into the expression for a_p . To choose the single value of μ_0 for a given molecule from the variety of the values published by different authors (see, for instance, Refs. 2 and 8) is practically impossible because all of these values have been approved experimentally.

Thus, it follows from the above discussion that the above described method for solving the inverse electrooptical problem on the basis of the experiments of the molecular optics is not reliable. The validity of the data on the principal values a_p of the molecular polarizability, obtained in such a way, may be questioned.

Our conclusion can be confirmed by the following. Since Stuart had no doubts about the reliability of the results of his calculations of a_p at first for more than thirty molecules⁷ and then for almost fifty molecules,⁹ the unique values of a_p have been listed in his tables. As for more recent monograph by Vereshchagin³ where the data on a_p for almost one hundred and seventy molecules have been presented, the number of different values of a_p varied from 2–3 to 11 for certain molecules (benzol). Six or seven values of a_p can be found in Ref. 3 for chloroform and carbon bisulphide molecules, and we see again that the more measurements have been performed for the given molecule the wider is the spread of values of a_p . The experimental errors of different authors (which, generally speaking, may be small) are added to much greater errors which were committed by the authors when they extracted the molecular invariant g^2 from their own data.

The spread in the experimental data obtained by different authors under various conditions and with the use of different methods is the common problem for any area of research. Therefore, to solve the inverse problem, the universal procedure is required in order to sort the experimental data on the invariant g^2 , which would be

consistent and thereby would ensure the unambiguous solution of the inverse problem.

It is possible only when the electrooptical problem is formulated in terms of fundamental quantities, which are stable practically within a homologous series of molecules. As was mentioned in Ref. 1, only the EOP's of molecule may be such fundamental quantities, in our case they are the polarizabilities of the chemical bonds. The principal values of the molecular polarizability a_p despite they are invariant (and, as a result, are measurable) may not be used as fundamental because the authors published different values of a_p for one and the same molecule.

In conclusion of the section it should be emphasized once more, that the need for values of a_p expressed in terms of molecular dipole moment μ_0 is one of the main reasons of the fact that the value of the molecular polarizability retrieved from the experimental data become not reliable. As was mentioned above, both the polarizability and the dipole moment have the same electrical nature, but they are considered to be independent parameters of molecule when studied phenomenologically. Therefore, to construct the semiempirical theory it is desirable to obtain the relations, in which the polarizability would not be expressed in terms of μ_0 as a parameter.

ADDITIVE SCHEME OF THE MOLECULAR OPTICS

As the analysis of the possible ways of solving the inverse electrooptical problem given in the foregoing section has shown, the difficulties here are associated mainly with the nonfundamental character of the molecular polarizability a_p ($p = 1, 2, 3$), which for this reason cannot be used as the EOP's of molecules. Only the polarizability of the chemical bonds, which can be inferred from one related molecule to another, can be considered the EOP's of molecules.^{1,6}

The above-mentioned inference of the bonds of the EOP's is based on the approximate additive scheme well applicable in molecular optics which was formulated by Wolkenshtein⁶ and is well known as the valence optical theory. The additive scheme is based on the relation for the polarizability tensor of molecule a_{uv} , which can be written in the arbitrary laboratory coordinate system (L -system) in the form

$$a_{uv} = \sum_m \sum_{a=1}^3 \alpha_a^{(m)} R_{au}^{(m)} R_{av}^{(m)} (u, v = x, y, z), \quad (3)$$

where m is the bond number in molecule, $\alpha_a^{(m)}$ ($a = 1, 2, 3$) are the principal values of the polarizability tensor of the m th bond and $R_{au}^{(m)}$ are the direction cosines of the principal axes of the polarizability ellipsoid of the m th bond in the L -system (in notation of Ref. 1).

It is the additivity of the polarizability ellipsoids of the bonds in the molecule, that is expressed by relation (3) and can be called as microadditivity in molecular optics. The idea of microadditivity is used within the framework of the approximation in which we neglect the intramolecular interaction of action between the chemical bonds. Its use is quite justified until the conception of the chemical bond is applicable as a structural unit of molecule.¹ It is the microadditivity that guarantee the inference of the EOP's from one related molecule to another.

The microadditivity (3) is the theoretical conception within the framework of the valency scheme in chemistry.⁶

Experimentally the macroadditivity is manifested mainly in the additivity of the molar refractions in solutions and liquid mixtures.^{3,6,7,10} Stuart and Volkman¹¹ were the first to assume that the observed macroadditivity is based on relation (3), which serves its theoretical argument.

In fact it is not entirely so. The additivity of the molar refraction in gaseous mixtures means that we may add the average polarizabilities \bar{a} of the noninteracting molecules in gases. Therefore, under assumption (3) the average polarizabilities $\bar{\alpha}^{(m)}$ of the individual noninteracting chemical bonds are also additive in not dense gases.

In the condensed state (dense gases, pure liquids and solutions) the average polarizabilities a of molecules are no longer additive due to the interaction between molecules. Here we can only say about the additivity of the average effective polarizabilities, which describe the noninteracting quasi-molecules, that is, the molecules "clothed by the interactions" with their nearest surroundings.¹²⁻¹⁴

Therefore, generally speaking, the fact that the refraction in solutions and liquid mixtures is found to be nearly additive does not imply the additivity of the average polarizability of bonds and atomic groups which are usually assumed in solving the inverse problem of molecular optics (see, for instance, Refs. 3 and 15 and the literature cited there). Such conclusion can be made only if we neglect the intramolecular and intermolecular interactions.

Nevertheless, understanding clearly the approximate nature of the additive scheme, we do not see at present the other experimental and theoretical basis for solving the inverse electrooptical problem in molecular optics and for calculating the EOP's of molecules. We go over to the discussion of new approach in solving this problem in the next section.

INVARIANTS OF THE MOLECULAR OPTICS AND EQUATIONS FOR THE EOP'S OF MOLECULES

Within the framework of additive scheme (3) only two invariants of the molecular polarizability tensor, i.e., the trace b and the anisotropy g defined by relations (1) and (2), may be used for solving the general electrooptical problem, because the third invariant $\det(a_{uv})$ is not related directly to the experiment.

The relation for the invariant b , obtained on the basis of additive scheme (3), is well known:^{3,6,7}

$$b = \sum_{u=xyz} a_{uu} = \sum_{p=1}^3 a_p = \sum_m \sum_{a=1}^3 \alpha_a^{(m)}. \quad (4)$$

The direction cosines $R_{au}^{(m)}$, which are noninvariant relative to the coordinate transformation, do not enter in this relation, therefore, we consider the right side of Eq. (4) to be the invariant expression for b .

As to the anisotropy g^2 , up to date this invariant was calculated based on its definition in the L -system

$$g^2 = \frac{3}{2} \sum_{u,v} a_{uv}^2 - \frac{1}{2} b^2 \quad (5)$$

and additive scheme (3), with the use of the noninvariant expressions which contained the direction cosines of the principal axes of the ellipsoids of the bond polarizabilities in the coordinate system suitable for each type of molecules. As has been noted in Ref. 3 (see p. 73), "the angles between

the principal axes of the bond tensors and the axes of the laboratory coordinate system must be known for the calculation of g^2 ... The problem is reduced to the transformation of the bond polarizability tensor from the local coordinate system affixed to its principal axes to the laboratory coordinate system, chosen for it".

In such a way the components of the polarizability tensor for each bond are calculated, and then they are summed up over the bonds of molecule. The summation technique proposed by Smith and Mortensen¹⁶ was called general in Ref. 3 (see p. 73); however, it was written there below that "in fact the techniques employed for calculating the projections of the principal vectors and contribution of bonds to the components of the polarizability tensor of molecules are few in number when we perform the structural investigations" (see p. 75). It is not surprising because, as was mentioned in Ref. 1, it is impossible to determine all required angles between the axes of the ellipsoids of bond polarizabilities and that of the chosen L -system for any noninvariant method of calculation of g^2 for molecule, which has sufficiently complicated spatial structure.

General relation for g^2 , which is valid for molecule irrespective of its spatial structure, was obtained in Ref. 1

$$g^2 = \frac{3}{2} \sum_m \sum_{a=1}^3 \left[\alpha_a^{(m)2} + \sum_{n \neq m} \sum_{b=1}^3 \alpha_a^{(m)} \times \right. \\ \left. \times (R_{ab}^{(m,n)}(\varphi_{mn})^2) \alpha_b^{(n)} \right] - \frac{1}{2} \left[\sum_m \sum_{a=1}^3 \alpha_a^{(m)} \right]^2, \quad (6)$$

where the matrix

$$\hat{R}^{(m,n)}(\varphi_{mn}) = \begin{pmatrix} \cos \varphi_{mn} & \sin \varphi_{mn} & 0 \\ \sin \varphi_{mn} & -\cos \varphi_{mn} & 0 \\ 0 & 0 & -1 \end{pmatrix} (m \neq n) \quad (7)$$

depends only on the angle φ_{mn} between the bonds m and n of a molecule.

Thus, two equations (4) and (6) with the left sides containing the measurable values b and g^2 and with the right sides containing the EOP's $\alpha_a^{(m)}$ are available for each type of a molecule. These are the equations that represent the basis for solving the inverse electrooptical problem by the additive scheme of the molecular optics. The number of the quantities $\alpha_a^{(m)}$ being calculated is generally greater than that of the measurable values b and g^2 for a given molecule. However the inference of the EOP's from one related molecule to another enables one to increase the number of equations of the inverse problem by using the pairs of equations (4) and (6) for different molecules with the chemical bonds of the same nature and to increase the number of corresponding measurements of b and g^2 for each molecule within a homologous series.

Before proceeding to the specific examples we note that for double chemical bonds (π -bonds) all the three EOP's $\alpha_a^{(m)}$ ($a = 1, 2, 3$) are different because these bonds are not axially symmetrical. Therefore, the number of equations of the inverse problem should be substantially increased for calculation of the parameters of such bonds. Below we will consider mainly the molecules with the single bonds (σ -bonds) for which $\alpha_1^{(m)} \neq \alpha_2^{(m)} = \alpha_3^{(m)}$, because we want to present and to demonstrate the new method of solving

the electrooptical problem of molecular optics with the help of simple examples, but not to calculate the EOP's for the extremely large number of molecules.

Note also, that it is necessary to account for the variance of polarizability of molecules and the EOP's. In examples considered below we will use as often as possible the data obtained in the visible range¹⁷ where the variance does not exceed 1,5–2%, for retrieval of b and g^2 .

We will consider below some simple molecules with no more than five bonds. Because of the simple structure of such molecules containing the small number of atoms, the corresponding substances are volatile, and therefore they are of great interest in the study of Earth's atmosphere.

The relations for g^2 of certain molecule types, derived from general formula (6) and presented below are published mostly for the first time. The noninvariant direction cosines of the principal axes of the bond polarizability ellipsoids do not enter in these formulas, only the trigonometric functions of the structural angles between the molecular bonds, which are invariant relative to the coordinate transformation, enter in them. It is the main novelty of the proposed method of obtaining the equations for electrooptical problem of molecular optics (the electrooptical problem of the spectroscopy of Raman scattering has been considered in Ref. 1). A new approach to solve the inverse problem and to calculate the EOP's $\alpha_a^{(m)}$ will be discussed below.

DIATOMIC MOLECULES

The molecules of the types X_2 or XY have one chemical bond, therefore, the relations for the invariants b and g^2 are trivial for these molecules:

$$b(X_2, XY) = \alpha_1 + 2\alpha_2, \quad (8)$$

$$g^2(X_2; XY) = (\alpha_1 - \alpha_2)^2, \quad (9)$$

The fact that "the electron cloud of individual bond – the diatomic molecule – is always axially symmetrical irrespective of the nature of this bond" (see Ref. 18, p. 92) is taken into consideration here. Therefore, $\alpha_2 = \alpha_3$ for these molecules (in the bond polarizability ellipsoid α_1 is assumed to be directed along the bond).

Solving equations (8) and (9) for α_1 and α_2 we find

$$\alpha_1 = \frac{1}{3}(b + 2g), \quad \alpha_2 = \alpha_3 = \frac{1}{3}(b - g). \quad (10)$$

The EOP's of others atmospheric diatomic gaze molecules are presented in Table I.

TRIATOMIC MOLECULES

We restrict our consideration with molecules of YXZ type with axially symmetrical XY and XZ bonds. For nonlinear molecule YXZ from (4) and (6) we find

$$b(YXZ) = \alpha_1(XY) + 2\alpha_2(XY) + \alpha_1(XZ) + 2\alpha_2(XZ); \quad (11)$$

$$g^2(YXZ)_{nl} = [g(XY) + g(XZ)]^2 - 3g(XY)g(XZ)(1 - \cos^2\varphi), \quad (12)$$

where φ is the structural angle of the molecule. The following notation has been introduced here:

$$g(XY) = \alpha_1(XY) - \alpha_2(XY), \quad g(XZ) = \alpha_1(XZ) - \alpha_2(XZ) \quad (13)$$

for the polarizability anisotropy of the molecular bond.

The HNO and FNO molecules are classified as nonlinear triatomic molecules of YXZ type with symmetry C_s . For the linear molecules of YXZ type (HCN , FCN , $ClCN$, OCS) $\varphi = 180^\circ$ and Eq. (12) takes the form

$$g^2(YXZ)_l = [g(XY) + g(XZ)]^2, \quad (14)$$

The molecules of XY_2 type are the particular case of triatomic molecules and, in addition, for nonlinear molecules (H_2O , Cl_2O , and H_2S) we have

$$b(XY_2) = 2(\alpha_1 + 2\alpha_2); \quad (15)$$

$$g^2(XY_2)_{nl} = (\alpha_1 - \alpha_2)^2(1 + 3\cos^2\varphi), \quad (16)$$

while for linear molecules (CO_2 , CS_2 , CN_2)

$$g^2(XY_2)_l = 4(\alpha_1 - \alpha_2)^2. \quad (17)$$

Here $\alpha_1 - \alpha_2 = g(XY)$ is the anisotropy of the polarizability of one of the equivalent molecular bonds. Formulas (15)–(17) are valid for $\alpha_3 = \alpha_2$.

The nitrous oxide molecule N_2O is linear and the anisotropy of its polarizability is given by the formula¹⁴

$$g^2(XXY)_l = [g(XX) + g(XY)]^2. \quad (18)$$

Some examples of calculations of the EOP's of triatomic molecules are presented in Table I.

TABLE I. The calculated polarizabilities of the chemical bonds of certain molecules.

Molecule	$b_{exp}, \text{ \AA}^3$	$g_{exp}^2, \text{ \AA}^6$	Bond polarizabilities, \AA^3	
H_2	2.301 Ref. 19	0.098 Ref. 4	$\alpha_1(H-H) = 0.976;$	$\alpha_2(H-H) = 0.663$
D_2	2.40 Ref. 19	0.09 Ref. 4	$\alpha_1(D-D) = 1.00$	$\alpha_2(D-D) = 0.70$
N_2	5.220 Ref. 19	0.48 Ref. 4	$\alpha_1(N\equiv N) = 2.20$	$\alpha_2(N\equiv N) = 1.51$
O_2	4.713 Ref. 19	0.712 Ref. 4	$\alpha_1(O=O) = 2.134$	$\alpha_2(O=O) = 1.290$
Cl_2	13.83 Ref. 19	6.75 Ref. 4	$\alpha_1(Cl-Cl) = 6.34$	$\alpha_2(Cl-Cl) = 3.74$
CO	5.85 Ref. 19	0.28 Ref. 4	$\alpha_1(C=O) = 2.30$	$\alpha_2(C=O) = 1.77$
NO	5.10 Ref. 19	0.712 Ref. 4	$\alpha_1(N=O) = 2.26$	$\alpha_2(N=O) = 1.42$
HCl	7.74 Ref. 19	0.55 Ref. 3	$\alpha_1(N-\chi\lambda) = 3.07$	$\alpha_2(N-\chi\lambda) = 2.33$
HBr	10.56 Ref. 19	0.83 Ref. 3	$\alpha_1(H-Br) = 4.13$	$\alpha_2(H-Br) = 3.22$

TABLE I. (continued).

Molecule	$b_{\text{exp}}, \text{Å}^3$	$g_{\text{exp}}^2, \text{Å}^6$	Bond polarizabilities, Å^3	
HI	15.69 Ref. 19	2.82 Ref. 3	$\alpha_1(\text{H-J}) = 6.35$	$\alpha_2(\text{H-J}) = 4.67$
H ₂ O	4.365 Ref. 19	0.14 Ref. 4	$\alpha_1(\text{O-H}) = 0.965$	$\alpha_2(\text{O-H}) = 0.622$
H ₂ S	11.01 Ref. 19	0.144 Ref. 4	$\alpha_1(\text{S-H}) = 2.09$	$\alpha_2(\text{S-H}) = 2.51$
NH ₃	6.78 Ref. 3	0.058 Ref. 3	$\alpha_1(\text{N H}) = 0.94$	$\alpha_2(\text{N H}) = 0.66$
PCl ₃	30.12 Ref. 3	1.82 Ref. 3	$\alpha_1(\text{P-Cl}) = 5.06$	$\alpha_2(\text{P-Cl}) = 2.49$
AsCl ₃	32.44 Ref. 3	0.689 Ref. 3	$\alpha_1(\text{As-Cl}) = 4.42$	$\alpha_2(\text{As-Cl}) = 3.19$
BCl ₃	23.97 Ref. 3	9.00 Ref. 3	$\alpha_1(\text{B-Cl}) = 4.00$	$\alpha_2(\text{B-Cl}) = 2.00$
BBr ₃	34.14 Ref. 3	26.01 Ref. 3	$\alpha_1(\text{B-Br}) = 6.06$	$\alpha_2(\text{B-Br}) = 2.66$
NO ₃ ⁻	11.90 Ref. 3	5.954 Ref. 3	$\alpha_1(\text{N=O}) = 2.41$	$\alpha_2(\text{N=O}) = 0.78$
CO ₃ ²⁻	12.02 Ref. 3	2.372 Ref. 3	$\alpha_1(\text{C=O}) = 2.02$	$\alpha_2(\text{C=O}) = 0.99$
CHF ₃	8.31 Ref. 3	0.084 Ref. 4	$\alpha_1(\text{C-F}) = 0.74$	$\alpha_2(\text{C-F}) = 0.70$
CH ₃ F	7.80 Ref. 3	0.09 Ref. 4	$\alpha_1(\text{C-H}) = 0.80$	$\alpha_2(\text{C-H}) = 0.54$
CHCl ₃	25.30 Ref. 3	2.89 Ref. 3	$\alpha_1(\text{C-Cl}) = 3.82$	$\alpha_2(\text{C-Cl}) = 1.98$
CH ₃ Cl	13.70 Ref. 3	2.56 Ref. 4	$\alpha_1(\text{C-H}) = 0.81$	$\alpha_2(\text{C-H}) = 0.58$
CHI ₃	51.60 Ref. 3	3.80 Ref. 3	$\alpha_1(\text{C-J}) = 6.19$	$\alpha_2(\text{C-J}) = 5.20$
CH ₃ I	22.0 Ref. 3	3.72 Ref. 3	$\alpha_1(\text{C-H}) = 1.16$	$\alpha_2(\text{C-H}) = 0.32$

MOLECULES OF XY₃ TYPE

Two modifications of molecules of this type, i.e., pyramidal (NH₃, PF₃, PCl₃, and AsCl₃) and planar (BCl₃, BBr₃, NO₃⁻, and CO₃²⁻), are described by the formulas

$$b(\text{XY}_3) = 3(\alpha_1 + 2\alpha_2), \quad (19)$$

$$g^2(\text{XY}_3) = 9(\alpha_1 - \alpha_2)^2 \cos^2 \varphi, \quad (20)$$

where for planar modification ($\varphi = 120^\circ$) the second relation takes the form

$$g^2(\text{XY}_3)_p = \frac{9}{4}(\alpha_1 - \alpha_2)^2. \quad (21)$$

MOLECULES OF XY₄ TYPE

The relations for invariants of molecules of this type

$$b(\text{XY}_4) = 4(\alpha_1 + 2\alpha_2), \quad (22)$$

$$g^2(\text{XY}_4) = 2(\alpha_1 - \alpha_2)^2(9\cos^2 \varphi - 1) \quad (23)$$

make it impossible to calculate both parameters α_1 and α_2 because for the tetrahedral angle $\cos^2 \varphi = 1/9$ and $g^2(\text{XY}_4) = 0$, which corresponds to the well-known fact that the anisotropy of polarizability of molecules with symmetry T_d is equal to zero. Therefore, the experimental data both for initial tetrahedral molecules, for example, CH₄ and CCl₄, and for pyramidal molecules CHCl₃ and CH₃Cl with C_{3v} symmetry should be employed. We begin the consideration of these molecules below.

MOLECULES OF XYZ₃ TYPE

The molecules of this type are formed by replacing three atoms Y, located in the apexes of tetrahedron, by

atoms Z in the molecule of XY₄ type, that does not change the pyramidal structure of the molecule, but reduces its symmetry, and as a result, the anisotropy of polarizability $g^2(\text{XYZ}_3) \neq 0$ for such a molecule.

All molecular bonds of this type are σ -bonds that enables us to consider simultaneously the pairs of homologically related molecules (CHF₃ and CH₃F, CHCl₃ and CH₃Cl, CHBr₃ and CH₃Br, and CHI₃ and CH₃I) which have the bonds of two types, i.e., X-Y and X-Z in solving the inverse electrooptical problem. In so doing, there are two measurable quantities, namely, b_1 and g_1^2 and b_2 and g_2^2 , for each molecule of any pair. Therefore, we can obtain four equations of the inverse problem and calculate the four EOP's, namely, $\alpha_1(X-Y)$, $\alpha_1(X-Z)$, $\alpha_2(X-Z)$, and $\alpha_2(X-Y)$, that is, to solve completely the inverse electrooptical problem for this type of molecules, provided, certainly, that the postulate is valid on the inference of the parameters from one related molecule to another, which is the basis of the additive scheme of molecular optics.

By considering, by way of example, the above-mentioned molecules we not only examine the feasibility of the postulate, but also develop a new approach to solving of the inverse problem, which makes the obtained values of the EOP's to be reliable. Preliminary we introduce some notations for the equations of the inverse problem to be convenient for writing.

In all molecules XYZ₃ under consideration the atom X represents the atom of carbon C, which is inside the pyramid. In the molecule CHHal₃ the atom Y represents the atom of hydrogen H, the atom Z represents the atom of halogen. In the molecule CHalH₃, on the contrary, the atom Y represents the atom of halogen, while Z represents the atom of H. The structural angles in the molecules are denoted as follows:

$$\varphi(\text{H al CH al}) = \varphi_1^{(1)}, \quad \varphi(\text{H al CH}) = \varphi_2^{(1)},$$

$$\varphi(\text{HCH}) = \varphi_1^{(2)}, \quad \varphi(\text{HCH al}) = \varphi_2^{(2)}.$$

The polarizabilities of bonds can be written as

$$\alpha_1(\text{C}-\text{H } al) = \alpha_1, \quad \alpha_2(\text{C}-\text{H } al) = \alpha_2,$$

$$\alpha_1(\text{C}-\text{H}) = \beta_1, \quad \alpha_2(\text{C}-\text{H}) = \beta_2.$$

We denote the invariants by b_1 and g_1^2 for the molecule CHHal_3 while for the molecule CHalH – by b_2 and g_2^2 .

In this notation, we obtain the following four equations:

$$b_1 = 3(\alpha_1 + 2\alpha_2) + \beta_1 + 2\beta_2, \quad (24)$$

$$b_2 = 3(\beta_1 + 2\beta_2) + \alpha_1 + 2\alpha_2, \quad (25)$$

$$g_1^2 = (\beta_1 - \beta_2)^2 + 9(\alpha_1 - \alpha_2)^2 \cos^2 \varphi_1^{(1)} + 3(\alpha_1 - \alpha_2)(\beta_1 - \beta_2)(3\cos^2 \varphi_2^{(1)} - 1), \quad (26)$$

$$g_2^2 = (\alpha_1 - \alpha_2)^2 + 9(\beta_1 - \beta_2)^2 \cos^2 \varphi_1^{(2)} + 3(\beta_1 - \beta_2)(\alpha_1 - \alpha_2)(3\cos^2 \varphi_2^{(2)} - 1), \quad (27)$$

which in principle enable one to calculate the four unknown parameters α_1 , α_2 , β_1 and β_2 .

Because the third and the fourth equations are nonlinear, their preliminary simplification is required for the system to be solved analytically. In this connection it should be noted that all of the structural angles entering in Eqs. (26) and (27) "originate from" tetrahedral angle and therefore their values are close enough for all the molecules under consideration.^{20–22} For instance, for the molecule of chloroform CHCl_3 the angle $\varphi_1^{(1)} = \varphi(\text{CICCl}) = 110.4^\circ$, while for the molecule of methyl chloride CClH_3 the angle $\varphi_1^{(2)} = \varphi(\text{HCH}) = 110.5^\circ$. The situation is the same for other molecules. Therefore with high enough accuracy one can set

$$\varphi_1^{(1)} = \varphi_1^{(2)} = \varphi_1; \quad \varphi_2^{(1)} = \varphi_2^{(2)} = \varphi_2. \quad (28)$$

Using approximation (28), we obtain easily from Eqs. (26) and (27) the following relations:

$$(A-1)[(\alpha_1 - \alpha_2)^2 + (\beta_1 - \beta_2)^2] + 2B(\alpha_1 - \alpha_2)(\beta_1 - \beta_2) = g_1^2 + g_2^2, \quad (29)$$

$$(A-1)[(\alpha_1 - \alpha_2)^2 - (\beta_1 - \beta_2)^2] = g_1^2 - g_2^2, \quad (30)$$

which are completed by Eqs. (24) and (25) without modifications. Systems (24), (25), (29), and (30) may be solved rigorously without further approximations

$$\alpha_1 = \frac{1}{24}(3b_1 - b_2 + 16C_1), \quad \alpha_2 = \frac{1}{24}(3b_1 - b_2 - 8C_1),$$

$$\beta_1 = \frac{1}{24}(3b_2 - b_1 + 16C_2), \quad \beta_2 = \frac{1}{24}(3b_2 - b_1 - 8C_2). \quad (31)$$

Following notation has been employed here:

$$A = 9\cos^2 \varphi_1, \quad B = 3(\cos^2 \varphi_2 - 1), \quad D = \frac{2B}{A+1},$$

$$C_1 = \sqrt{C_2^2 + Q}, \quad C_2 = \sqrt{\frac{p}{2} - \sqrt{\left(\frac{p}{2}\right)^2 - q}},$$

$$p = \frac{4(P-Q) + D^2Q}{4-D^2}, \quad q = \frac{(P-Q)^2}{4-D^2},$$

$$P = \frac{g_1^2 + g_2^2}{A+1}, \quad Q = \frac{g_1^2 - g_2^2}{A-1}. \quad (32)$$

In so obtained relations (31) and (32) we omit unnecessary roots, which arise when solving the biquadratic equation for the difference $\beta_1 - \beta_2$. These roots yield unreal values of the EOP's, namely, imaginary and negative values of bond polarizabilities.

However, as the direct calculations showed, the rest of the roots also may yield the unreal values of the EOP's. It may be explained by the fact that the values of the invariants g_1^2 for the molecule CHHal_3 and g_2^2 for the molecule CHalH_3 employed in the calculation of the EOP's as the experimental data, may be contradictory.

As an example, which confirms this not completely usual statement, we consider the pair of molecules CHCl_3 and CH_3Cl . The experimental values $b_1(\text{CHCl}_3) = 25.30 \text{ \AA}^3$ and $b_2(\text{CH}_3\text{Cl}) = 13.70 \text{ \AA}^3$ (see Ref. 3, p. 49). The values of structural angles:²² $\varphi_1(\text{CHCl}_3) = 110.4^\circ$, $\varphi_2(\text{CHCl}_3) = 108.6^\circ$, $\varphi_1(\text{CH}_3\text{Cl}) = 110.5^\circ$, and $\varphi_2(\text{CH}_3\text{Cl}) = 108^\circ$. Determining the values of A and B entering in Eq. (32) in the form of average values

$$A = \frac{1}{2}[A(\text{CHH } al_3) + A(\text{CH } al \text{ H}_3)];$$

$$B = \frac{1}{2}[B(\text{CHH } al_3) + B(\text{CH } al \text{ H}_3)],$$

we obtain using the above-mentioned data $A = 1.0994$ and $B = -2.0859$. As for g_1^2 and g_2^2 , fifteen different values have been given in Ref. 4 for the molecule CHCl_3 and nine for the molecule CH_3Cl . In addition, a series of values of the invariants g_1^2 and g_2^2 may be estimated from formula (2) with the use of the experimental data on the principal polarizabilities of these molecules published in Ref. 3.

In this situation all of the pairs g_1^2 and g_2^2 seem to be useful for calculations based on formulas (31) and (32). In fact it is not so.

Let us take, for instance, $g_1^2(\text{CHCl}_3) = 7.585$ and $g_2^2(\text{CH}_3\text{Cl}) = 2.427 \text{ \AA}^6$ cited in Ref. 4 (see pp. 30 and 34) from the data of Ref. 23 obtain from the measurements for both the molecules at a wavelength of 514 nm. In this case the term $\sqrt{(p/2)^2 - q}$ in Eq. (32) becomes imaginary, that makes the bond polarizabilities in Eq. (31) unreal. On the other hand, if we employ $g_1^2 = 5.43$ and $g_2^2 = 2.43 \text{ \AA}^6$, which are obtained from formula (2) on the basis of the data on the molecular polarizabilities a_p published in Ref. 3 (see Table II.II), then imaginary terms disappear, but the bond polarizabilities α_2 and β_2 become negative, what is unreal too.

What is the reason for such unexpected results? It is because the employed values of g_1^2 and g_2^2 are incompatible. Indeed, all above-considered angles employed in Eqs. (26) and (27) suggests that if all the structural angles in the pyramidal molecules under investigation were exactly tetrahedral, then the invariants g_1^2 and g_2^2 in this equations would be identical

$$g_{1T}^2 = g_{2T}^2 = [(\alpha_1 - \alpha_2) - (\beta_1 - \beta_2)]^2 \quad (33)$$

(since $\cos^2\varphi = 1/9$). However because the structural angles differ slightly from that of the tetrahedron, which equal to $109^\circ 28'$, in fact g_1^2 differs from g_2^2 , but this difference must be small.

In the above-considered case the difference between g_1^2 and g_2^2 is substantial and as a result, equations (26) and (27) either become incompatible (the imaginary roots appear) or lead to the unreal (negative) solutions. Thus, in solving the inverse problem for the pyramidal molecules of XYZ_3 type it is necessary to choose g_1^2 and g_2^2 very close in values from the experimental data available. At the same time, such a procedure of choice seems to be the criterion for estimating the reliability of the experimental data on the invariant g_2^2 for this type of molecules.

It should be noticed that such a problem of choice has not arisen for the invariant β . It is because this value is determined with the use of refraction of a substance which, first, may be measured with very high accuracy in gas and liquid and, secondly, during the phase change the refraction remains practically unchanged for almost all substances.

Why there are no unambiguous experimental data on the invariant g^2 ? As has been already mentioned above, it is impossible to measure the molecular anisotropy itself. Usually the depolarization degree for the Rayleigh scattering Δ or the Kerr factor K is measured. These in turn are expressed in terms of invariant g^2 , but the rigorous relation between Δ and g^2 or between K and g^2 is well known only for gases. In addition as has been already mentioned above, for polar molecules the factor of the Kerr static effect K_{stat} depends not only on g^2 but also on the molecular dipole moment μ_0 . Therefore, the errors in measurements of μ_0 introduce significant errors in the results of calculation of g^2 even in gases. The results of calculation of g based on the values of Δ and K measured in liquids and solutions (that is the most typical situation) are still more unreliable.

When the data on g^2 published by many authors, are unreliable, the solution of the inverse electrooptical problem on the basis of our equations is the only criterion for the choice of the reliable data on this invariant. Such a criterion is obtaining the calculated values of the EOP's, which do not contradict to their physical meaning.

The results of numerical calculation of the EOP's of pyramidal molecules $\text{CHF}_3\text{-CH}_3\text{F}$, $\text{CHCl}_3\text{-CHCl}$, and $\text{CHI}_3\text{-CH}_3\text{I}$ are presented in Table I. As for the pair of molecules $\text{CHBr}_3\text{-CH}_3\text{Br}$ from a series of molecules being considered their structural angles seems to be calculated insufficiently accurate.²² The fact is that the parameter D in Eq. (32) for these two molecules overshoots of the set of this parameter for the pair of the above-mentioned molecules. Since the results of calculation of the EOP's are very sensitive to this parameter, they are hardly reliable and are not presented here.

In the derivation of Eqs. (24), (25), (26), and (27) the polarizability of C-H bond (that is, β_1 and $\beta_2 = \beta_3$) as well as the bonds C-Hal (that is, α_1 and $\alpha_2 = \alpha_3$) were assumed to be identical for both molecules of the pair $\text{CHHal}_3\text{-CH}_3\text{Hal}$. At the same time, as can be seen from Table I, the polarizabilities of C-H bond vary slowly within the homological series of molecules under consideration in going on from molecules in which methane is substituted by fluorine to the molecules in

which methane is substituted by iodine. This result becomes clear if we take into account that intramolecular interactions deform the C-H bond in different ways depending on the surroundings of this bond in the given molecule.

MOLECULES OF XYZ_3 TYPE

For calculation of the invariants b and g^2 with the help of general formulas (4) and (6) we take the following numbers for the bonds: the three equivalent X-Z bonds we will number by $m = 1, 2, 3$, the X-Y bonds we will number by $m = 4$ and the Y-V bonds - by $m = 5$. The following notations have been used for the bond polarizabilities:

$$\begin{aligned} \alpha_1^{(1)} &= \alpha_1^{(2)} = \alpha_1^{(3)} = \alpha_1; \\ \alpha_2^{(1)} &= \alpha_3^{(1)} = \alpha_2^{(2)} = \alpha_3^{(2)} = \alpha_2^{(3)} = \alpha_3^{(3)} = \alpha_2; \\ \alpha_4^{(4)} &= \beta_1; \alpha_5^{(4)} = \alpha_3^{(4)} = \beta_2; \end{aligned} \quad (34)$$

The notations for the angles are as follows:

$$\begin{aligned} \varphi^{(1,2)} &= \varphi^{(1,3)} = \varphi^{(2,3)} = \varphi_1; \quad \varphi^{(1,4)} = \varphi^{(2,4)} = \varphi^{(3,4)} = \varphi_2; \\ \varphi^{(4,5)} &= \varphi_3; \quad \varphi^{(1,5)} = \varphi^{(2,5)} = \varphi_4; \quad \varphi^{(3,5)} = \varphi_5. \end{aligned} \quad (35)$$

With the use of these notations we find

$$b(XYZ_3V) = 3(\alpha_1 + 2\alpha_2) + (\beta_1 + 2\beta_2) + (\gamma_1 + 2\gamma_2), \quad (36)$$

$$\begin{aligned} g^2(XYZ_3V) &= 9(\alpha_1 - \alpha_2)^2 \cos^2\varphi_1 + 3(\alpha_1 - \alpha_2) \times \\ &\times (\beta_1 - \beta_2)(3\cos^2\varphi_2 - 1) + 3(\alpha_1 - \alpha_2)(\gamma_1 - \gamma_2) \times \\ &\times (2\cos^2\varphi_4 + \cos^2\varphi_5 - 1) + (\beta_1 - \beta_2)(\gamma_1 - \gamma_2) \times \\ &\times (3\cos^2\varphi_3 - 1) + (\beta_1 - \beta_2)^2 + (\gamma_1 - \gamma_2)^2. \end{aligned} \quad (37)$$

As an example of molecules with symmetry C_s let us consider the molecule of methyl alcohol CH_3OH . The plane of symmetry passes through the C-O ($m = 4$) and O-H ($m = 5$) bonds and through one of the equivalent C-H bonds ($m = 3$). The structural angles (see Ref. 21, p. 426) are $\varphi_1 = \varphi(\text{HCH}) = 109.3^\circ$, $\varphi_2 = \varphi(\text{HCO}) = 111^\circ 52'$, and $\varphi_3 = \varphi(\text{COH}) = 108^\circ 52'$. Therefore, to within 3° the O-H and C-H bonds ($m = 3$) can be considered parallel, that is, $\varphi_5 \approx 0$. We find the angle between the O-H bond and one of the C-H bonds ($m = 1, 2$) as that between the crossed straight lines: $\varphi_4 \approx 180^\circ - \varphi_1 = 70.7^\circ$.

Under these conditions equation (37) simplifies and can be reduced to quadratic equation for the parameter $\beta_1 - \beta_2 = \alpha_1(\text{C-O}) - \alpha_2(\text{C-O})$:

$$\begin{aligned} &(\beta_1 - \beta_2)^2 + [3(\alpha_1 - \alpha_2)(3\cos^2\varphi_2 - 1) + \\ &+ (\gamma_1 - \gamma_2)(3\cos^2\varphi_3 - 1)](\beta_1 - \beta_2) + \\ &+ [9(\alpha_1 - \alpha_2)^2 + 6(\alpha_1 - \alpha_2)(\gamma_1 - \gamma_2)]\cos^2\varphi_1 + \\ &+ (\gamma_1 - \gamma_2)^2 - g_{\text{exp}}^2 = 0, \end{aligned} \quad (38)$$

which simultaneously with Eq. (36) enables us to determine the polarizabilities of the C-O bond when the polarizabilities of the C-H and O-H bonds are assumed to be known. For

the C–H bond we choose the values of the EOP's following the so-called Botorel approach (see Ref. 3, p. 89): $\alpha_1 = \alpha_1(\text{C–H}) = 0.81$ and $\alpha_2 = \alpha_2(\text{C–H}) = 0.59 \text{ \AA}^3$, which nearly coincide not only with the corresponding values obtained with the use of the Vux scheme¹⁵ but also with the corresponding values calculated by us (see Table I) for the pair of molecules CHCl_3 – CH_3Cl (both molecules of methyl chloride CH_3Cl and methanol CH_3OH contain the methyl group. Le Fevre (see Ref. 3, p. 97) has determined the polarizabilities of the O–H bond specially for methanol: $\gamma_1 = \alpha_1(\text{O–H}) = 0.95$ and $\gamma_2 = \alpha_2(\text{O–H}) = 0.49 \text{ \AA}^3$.

The experimental values of the invariants b_{exp} are equal to 9.68 \AA^3 (see Ref. 6, p. 52) based on the measurements in gases and $g_{\text{exp}}^2 = 0.38 \text{ \AA}^6$ based on the measurements of the Kerr optical factor²⁴ and of the depolarization degree from Rayleigh scattering of laser radiation in gases.¹⁵ Using these data we find $b_1 = \alpha_1(\text{C–O}) = 1.108$ and $\beta_2 = \alpha_2(\text{C–O}) = 0.336 \text{ \AA}^3$. The values of the EOP's of the C–O bond of the molecule of methanol are in a good agreement with that presented by Vux in Ref. 15 (see p. 52) which were calculated for the same molecule: $\beta_1 = 1.31$ and $\beta_2 = 0.21 \text{ \AA}^3$.

It should be noted that the molecule of methanol CH_3OH supports the above conclusion that the values of the main polarizabilities of polar molecules a_p obtained by solving the inverse problem often seem to be unreliable. Really, employing the values $a_1 = 4.0$, $a_2 = 2.56$ and $a_3 = 3.14 \text{ \AA}^3$ calculated by Stuart⁷ upon substituting into formulas (1) and (2) yield the invariant b which is in a good agreement with the experiment ($b_{\text{exp}} = 9.7 \text{ \AA}^3$) but the invariant $g_{\text{calc}}^2 = 1.575 \text{ \AA}^6$ which is by a factor of 5 larger than the above-considered experimental value.^{15,24} This contradiction is well known: the polarizabilities of the methanol molecule obtained by Stuart were published neither by Le Fevre,¹⁷ nor by Vereshagin,³ who collected most exhaustive data on the ellipsoids of the polarizabilities of a molecule. It is significant that Vux¹⁵ obtained $g^2 = 0.397 \text{ \AA}^6$, which is in a good agreement with the experimental data, assuming the tensor a_{uv} to be axially symmetrical, that is, $a_1 = 3.69$ and $a_2 = a_3 = 3.06 \text{ \AA}^3$. However it contradicts to the case of the symmetry C_s according to which all three polarizabilities of a molecule must be different.

The principal values a_p of the polarizability tensor a_{uv} of a molecule may be calculated on the basis of valence–optical theory if all the EOP's of the chemical bonds of molecules are known. In order to do this it is necessary preliminary to determine the coordinate system in which the diagonalization of the tensor a_{uv} is possible and subsequently to calculate all direction cosines of the angles between the axes of the system and axes of the polarizabilities ellipsoid for all the molecule bonds.

In conclusion it should be noted that the valence–optical theory is applicable only for analytical calculation of the EOP's of simple enough molecules with σ –bonds. However the possibilities of computer calculations of systems (4) and

(6), in which the unknown values of the EOP's enter, are practically unlimited. In this sense the great experience is acquired in solving the problems of quantum chemistry on a computer, when the unknown coefficients of the basis orbits which determine the shape of the wave function of the quantum system under consideration are varied. In principle the situation is the same for computation of the unknown EOP's, which are the fundamental parameters in describing the electrical structure of molecules and the electrooptical effects in optics and spectroscopy.

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