

## INTENSITIES OF RAMAN SPECTRA AND ELECTROOPTICAL PARAMETERS OF MOLECULES

O.G. Bokov

*N.I. Vavilov Agricultural Institute, Saratov*

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*A review of the development of the Wolkenstein valence-optical (VO) theory of the integral characteristics of Raman spectra is given invariant expressions for the anisotropy of the molecular polarizability tensor and the anisotropy of the derived (in normal coordinates) polarizability tensor, which are independent of the choice of the coordinate system fixed in the molecule, are obtained. The most recent data for Raman intensities of methane and carbon tetrachloride are used and the electrooptical parameters of the C-H and C-Cl bonds are calculated. The consistency of the zeroth-order approximation of the VO theory is shown for the considered molecules. A critical analysis of attempts to introduce the first-order approximation into the VO theory is carried out.*

### INTRODUCTION

The creation of Raman lidars as an effective instruments of optical investigation of the Earth's atmosphere in recent years has stimulated interest in the possibilities of Raman spectroscopy in the study of the structure of matter.

The integral characteristics of Raman spectra, i.e., the intensities and depolarization ratios of the bands, contain information about such fundamental molecular properties as the electrooptical parameters (EOP). This information is deciphered by solving the inverse electrooptical problem of vibrational spectroscopy. However, after investigating a great number of molecules and molecular conformations, the vibrational spectroscopy begins to fulfill the functions of systematization only when a reasonable choice of the EOP is made, which can be transferred from one related molecule to another.

Taking this fact into account, it is necessary to relate vibrational spectroscopy with the fundamental structural units of these molecules. In chemistry such structural units are chemical bonds and the individual atomic groups. The concept of the chemical bond (which is the foundation of the valence scheme) gives some invariant properties to geometrical characteristics of the related molecules. This is confirmed by X-ray-structural data, according to which the bond lengths and valence angles between these bonds vary only slightly within a homologous series of molecules.

The above-mentioned "invariance" of chemical bonds points to one of the main features of valence chemistry, i.e., its additivity, which holds, at least, in the zeroth-order initial approximation.<sup>1</sup> The idea of additivity has become a guiding principle not only in valence chemistry, but also in molecular optics and spectroscopy, which study correspondingly equilibrium and dynamic properties of molecules and their structural

elements.<sup>1,2</sup> The classical experimental confirmation of additivity of optical effects is the well-known additivity of molecular refractions, which is observed for the majority of organic molecules with high accuracy.<sup>2-4</sup>

Modern molecular optics and vibrational spectroscopy are based on the valence-optical (VO) theory, which was formulated by M.V. Wolkenstein<sup>5</sup> by analogy with the valence scheme in chemistry. The VO theory was developed later in a series of papers,<sup>6-9</sup> and enables one to correctly introduce the EOF's of the molecules. These are the dipole electric moments of the bonds and their derivatives with respect to internal coordinates (they are determined by IR-spectroscopic methods) and the principal values of the bond polarizability tensors and their derivatives with respect to the internal coordinates, which are determined by the methods of molecular optics and Raman spectroscopy, respectively.

Molecular EOP's are considered in the Placzek's semiclassical theory<sup>10</sup> for the vibrational spectral intensities. The modern theory of vibrational spectroscopy, which is essentially based on the methods of quantum chemistry, does not use the concept of EOP. What is the reason for returning to the problem of EOP and a revision of the methods of VO theory?

There are some reasons for so doing. First, the problem of calculating molecular EOP is a classical one in the sciences dealing with the structure of matter, but up till now the problem has not been finally solved. Second, the VO theory, as it was shown in Refs. 1, 2, 8, and 9, works well in most cases, while quantum chemistry calculations of molecular parameters are often complicated by serious computational difficulties. Finally, the accuracy of semiempirical methods in the VO theory is usually considerably higher than those of quantum chemistry.

Taking all this into account, in this paper we work out a new method for calculating the intensities

of Raman light scattering by molecules in the electronic ground state. In our method the technique for calculating Raman intensities is considerably simplified in comparison with traditional methods.<sup>1,8,9</sup> All of the calculations are made in the additive scheme of the VO theory, i.e., in its zeroth-order approximation, in which the anharmonic vibrations are neglected. The question of the so-called first-order approximation of VO theory is discussed separately.

Recent experimental data on the Raman intensities in methane and carbon tetrachloride vapor are used to obtain more accurate values of the EOP of the C–H and C–Cl bonds, which are structural elements of a large number of organic molecules. The so-obtained values of the EOP of these bonds and the parameters for the O–H bond<sup>11</sup> make it possible to solve the direct and inverse electrooptical problems of Raman scattering for a large class of molecules, including those which define the normal and polluting components of the Earth's atmosphere.

### CALCULATION OF INVARIANTS OF MOLECULAR OPTICS IN VALENCE-OPTICAL THEORY

In order to demonstrate our method for calculating Raman Intensities, let us first consider a similar calculation for a molecule in the equilibrium state, i.e., under the conditions which are studied in molecular optics.

Stuart and Volkman<sup>12</sup> were the first to represent the molecular polarizability tensor  $a_{uv}$  ( $u, v = x, y, z$ ), written in the laboratory coordinate system ( $L$ -system), as a sum of the polarizability tensors  $\alpha_{uv}^{(n)}$  of the individual molecular chemical bonds:

$$\alpha_{uv} = \sum_n \alpha_{uv}^{(n)}. \quad (1)$$

Diagonalization of each of the tensors  $\alpha_{uv}^{(n)}$  is carried out in its own local coordinate system  $M^{(n)}$ , where the polarizability ellipsoid of the given bond is reduced to its principal axes. In the  $M^{(n)}$ -system the first principal axis ( $a = 1$ ) of the ellipsoid is directed along the bond, while the other two ( $a = 2, 3$ ), being mutually perpendicular, are found in the plane  $P^{(n)}$  orthogonal to the bond. We should emphasize that the additivity of the VO theory, represented in Eq. (1), makes it possible to carry out the diagonalizations of the tensors  $\alpha_{uv}^{(n)}$  simultaneously and independently for each bond by choosing for it its own coordinate system  $M^{(n)}$ . Consequently, the direction cosines in the well-known expression<sup>1,2</sup>

$$\alpha_{uv} = \sum_n \sum_{a=1}^3 \alpha_a^{(n)} \cos(nau) \cos(nav) \quad (u, v = x, y, z), \quad (2)$$

depend on the bond number  $n$ .

The values  $\alpha_{uv}^{(n)}$  — the principal (proper) values of the bond polarizability tensor, reduced to its principal axes, — are invariant relative to any coordinate transformation, which does not stretch or compress the bond polarizability ellipsoid, the lengths of whose semiaxes are these values.<sup>4</sup>

On the other hand, the direction cosines  $\cos(nau)$  of the angles between the coordinate axes of each local  $M^{(n)}$ -system and the axes of the  $L$ -system depend on the choice of the latter. Hence, for rather complex molecules, geometrical calculation of all the direction cosines takes on the character of a separate problem.<sup>4</sup> However, there is no need to perform these calculations, as will be shown below.

The point is that in molecular optics one compares with experiment not the components of the tensor  $a_{uv}$ , which obviously depend on the choice of coordinate system, but the invariants of this tensor, which are

$$b = \sum_{u=x,y,z} a_{uu} \quad (3)$$

and

$$g^2 = \frac{3}{2} \sum_{u,v} \alpha_{uv}^2 - \frac{1}{2} b^2, \quad (4)$$

which are independent of the choice of the  $L$ -system. Hence, such finite expressions should exist for the invariants  $b$  and  $g^2$ , which do not contain noninvariant values of the direction cosines.

Such an expression for the trace of the tensor  $b$  is well-known<sup>1</sup>:

$$b = \sum_u \alpha_{uu} = \sum_n \sum_{a=1}^3 \alpha_a^{(n)} \sum_u \cos^2(nau) = \sum_n \sum_{a=1}^3 \alpha_a^{(n)}. \quad (5)$$

As regards the anisotropy  $g^2$  of the tensor  $a_{uv}$ , it seems very strange, but no invariant expression for this value has been cited in the literature to date.

A method for obtaining this invariant expression has been indicated elsewhere.<sup>13</sup> Let us consider the formulation of this method, for we shall need it further.

Note that the direction cosines  $\cos(nau)$  in Eq. (2) are the elements  $R_{au}^{(n)}$  of the rotation matrix  $\tilde{R}^{(n)}$ , which realize all the rotations in three-dimensional space needed to align the orthogonal basis  $\{e_a^{(n)}\}$  ( $a = 1, 2, 3$ ) of the  $M^{(n)}$ -system with the orthogonal basis  $\{e_u\}$  ( $u = x, y, z$ ) of the  $L$ -system. Thus expression (2) can be written

$$\alpha_{uv} = \sum_n \sum_{a=1}^3 \alpha_a^{(n)} R_{au}^{(n)} R_{av}^{(n)}. \quad (6)$$

Now we calculate, using formula (6), the sum entering into expression (4):

$$\sum_{u,v} \alpha_{uv}^2 = \sum_n \left\{ \sum_{a=1}^3 \alpha_a^{(n)2} \sum_u R_{au}^{(n)2} \sum_v R_{av}^{(n)2} + \right.$$

$$\begin{aligned}
 & + \sum_{a=1}^3 \alpha_a^{(n)} \sum_{b \neq a} \sum_v R_{au}^{(n)} R_{bu}^{(n)} \sum_v R_{av}^{(n)} R_{bv}^{(n)} \} + \\
 & + \sum_m \sum_{a=1}^3 \alpha_a^{(m)} \sum_{n \neq m} \sum_{b=1}^3 \alpha_b^{(n)} \sum_u R_{au}^{(m)} R_{bu}^{(n)} \sum_v R_{av}^{(m)} R_{bv}^{(n)}. \tag{7}
 \end{aligned}$$

Since the values  $q^2$  and  $b^2$  in expression (4) are invariants, the sum  $\sum_{u,v} a_{uv}^2$  is also invariant. That is why

Eq. (7) consists only of the invariant terms, which are independent of the choice of the  $L$ -system. For example,

$$\sum_{u=x,y,z} R_{au}^{(n)} R_{bu}^{(n)} = \delta_{ab}, \tag{8}$$

which follows from the orthogonal properties of the rotation matrix  $\tilde{R}^{(n)}$ .

The sum

$$\sum_{u=x,y,z} R_{au}^{(m)} R_{bu}^{(n)} \quad (m \neq n), \tag{9}$$

which expresses the convolution of the matrices  $\tilde{R}^{(m)}$  and  $[\tilde{R}^{(n)}]^{-1}$  for different bonds  $m$  and  $n$  in a molecule, must also be invariant. As was shown in Ref. 13 on the basis of the properties of the three-dimensional rotation group, expression (9) is the matrix element of the matrix  $\tilde{R}^{(m,n)}$ , which aligns the two bases  $\{e_a^{(m)}\}$  and  $\{e_b^{(n)}\}$  ( $a, b = 1, 2, 3$ ) of the local coordinate systems  $M^{(m)}$  and  $M^{(n)}$ . Since the explicit form of the matrix  $\tilde{R}^{(m,n)}$  was not indicated,<sup>13</sup> we shall do it here.

Let the positions of two local bases  $\{e_a^{(m)}\}$  and  $\{e_b^{(n)}\}$  in the  $L$ -system be characterized respectively by two sets of angles  $\Omega_m$  and  $\Omega_n$  (e.g., the Euler angles) for each bond  $m$  and  $n$ . Since the group  $R(3)$  of three-dimensional rotations (in contrast to the group  $R(2)$  of rotations in a plane) is noncommutative, the rule of group addition states only that

$$\hat{R}^{(m)}(\Omega_m) \cdot \hat{R}^{(n)}(\Omega_n) = \hat{R}(\Omega_m, \Omega_n), \tag{10}$$

i.e., there is no rule of simple additivity of angles in the group  $R(3)$ , as for the group  $R(2)$ . Hence, expression (9), written in matrix form,

$$\begin{aligned}
 & \hat{R}^{(m)} \cdot [\hat{R}^{(n)}]^{-1} = \hat{R}^{(m,n)} \\
 & = \begin{bmatrix} e_1^{(m)} \cdot e_1^{(n)} & e_1^{(m)} \cdot e_2^{(n)} & e_1^{(m)} \cdot e_3^{(n)} \\ e_2^{(m)} \cdot e_1^{(n)} & e_2^{(m)} \cdot e_2^{(n)} & e_2^{(m)} \cdot e_3^{(n)} \\ e_3^{(m)} \cdot e_1^{(n)} & e_3^{(m)} \cdot e_2^{(n)} & e_3^{(m)} \cdot e_3^{(n)} \end{bmatrix}. \tag{11}
 \end{aligned}$$

has elements which cannot be calculated in practice.

The situation changes, however, if the vectors  $e_2^{(m)}$  and  $e_2^{(n)}$  are located in the common plane ( $m, n$ )

which contains the bonds  $m$  and  $n$ , if they intersect, or parallels to these bonds, if they do not. There is no loss of generality under such choice of the directions of these vectors, because expression (9) is invariant with respect to the choice of these directions. In the basic relation (2) of the VO theory the bond polarizability ellipsoids are reduced to their principal axes, but in the  $L$ -system only the directions of the vectors  $e_1^{(m)}$ , extending along the bonds themselves, are fixed. As regards the vectors  $e_2^{(m)}$ , one can only say that they are located in the planes  $P^{(m)}$ , which are perpendicular to the corresponding bonds. Within these planes  $P^{(m)}$  we can place the vectors  $e_2^{(m)}$  in any way we want, but the characteristics of the polarizability ellipsoids – the principal values of the bond polarizability  $\alpha_a^{(m)}$  – do not change in any case. So in the process of calculating the double sums  $\sum_m \sum_{n \neq m}$  entering into expression (7) for one and the same bond  $m$  and different bonds  $n$  and  $n'$  we can subsequently locate the vector  $e_2^{(m)}$  in the planes ( $m, n$ ) and ( $m, n'$ ), taking no care of how its orientation in the plane  $P^{(m)}$  changes, for the invariant expressions (9), (7), and (4) do not depend on the direction of this vector. This is all a consequence of the additivity of the VO theory, which excludes the mutual influence of bonds in the relation (2).

The choice of directions of the vectors  $e_3^{(m)}$  and  $e_3^{(n)}$  now causes no difficulties. As is commonly accepted in the vibrational spectroscopy,<sup>1,8,9</sup> for the noncollinear molecule  $Y_mXY_n$  the vectors  $e_2^{(m)}$  and  $e_2^{(n)}$  are arranged in the plane ( $m, n$ ) in such a way that both are directed inside valence angle between the bonds. Hence, since the bases  $\{e_a^{(m)}\}$  and  $\{e_b^{(n)}\}$  are both orthogonal and right-handed, it follows that it is necessary to set  $e_3^{(n)} = -e_3^{(m)}$ , so that both vectors remain perpendicular to the plane ( $m, n$ ).

Taking the above remarks into account, one can now easily calculate the elements of the matrix  $\hat{R}^{(m,n)}$  in expression (11):

$$\hat{R}^{(m,n)} = \begin{bmatrix} \cos \varphi_{mn} & \sin \varphi_{mn} & 0 \\ \sin \varphi_{mn} & -\cos \varphi_{mn} & 0 \\ 0 & 0 & -1 \end{bmatrix}. \tag{12}$$

The matrix  $\hat{R}^{(m,n)}$  describes the rotation by the angle  $\varphi_{mn}$  in the plane ( $m, n$ ), which brings in the bond  $m$  in line with the bond  $n$ , simultaneously the reflection of the vector  $e_3^{(m)}$  takes place in this plane and, as a result of these transformations, the vector  $e_3^{(m)}$  turns into the vector  $e_3^{(n)}$ .

Thus, the invariant sum in expression (9) is equal to

$$\sum_{u=x,y,z} R_{au}^{(m)} R_{bu}^{(n)} = R_{ab}^{(m,n)}(\varphi_{mn}), \tag{13}$$

where, as follows from expression (12), the matrix  $\hat{R}^{(m,n)}$  does not depend on the choice of the L-system, but is determined only by the value of the valence angle  $\varphi_{mm}$  between the bonds. On the basis of expression (7), (8), and (13) we find an invariant expression for the anisotropy of the molecular polarizability:

$$g^2 = \frac{3}{2} \sum_m \sum_{a=1}^3 \left[ \alpha_a^{(m)2} + \sum_{n \neq m} \sum_{b=1}^3 \alpha_a^{(m)} R_{ab}^{(m,n)2} \alpha_b^{(n)2} \right] - \frac{1}{2} \left[ \sum_m \sum_{a=1}^3 \alpha_a^{(m)} \right]^2. \quad (14)$$

This expression for  $g^2$  takes the main idea (the idea of additivity) of the VO theory in molecular optics to its logical conclusion. It substantially simplifies the procedure of calculating the EOP  $\alpha_a^{(m)}$  based on the experimental data, as will be demonstrated in subsequent papers.

### INTENSITIES OF RAMAN LIGHT SCATTERING

An invariant expression of the type (14) can also be derived for the invariant  $(g')^2$  of Raman spectroscopy, which together with  $(b')^2$  enters into the definition of the absolute intensity or scattering power (SP) of a molecule:

$$I_1^v = 5(b'_1)^2 + 7(g'_1)^2, \quad (15)$$

where  $l$  is the number of the normal molecular vibration active in Raman scattering. The parameters  $b'_l$  and  $(g'_l)^2$  are defined by analogy with expressions (3) and (4) for the tensor

$$\alpha'_{uv(1)} = \left[ \frac{\partial \alpha_{uv}}{\partial Q_1} \right]_0 \quad (16)$$

of the derivative of the polarizability of the molecule with respect to the normal coordinate  $Q_1$ .

Raman electrooptical parameters include in addition to the parameters  $\alpha_a^{(m)}$  the derivatives

$$\alpha_a^{(m)'} = \left[ \frac{\partial \alpha_a^{(m)}}{\partial q_m} \right]_0 \quad (\alpha = 1, 2, 3) \quad (17)$$

of the principal values of the bond polarizabilities with respect to the internal coordinates  $q_m$  (changes in the bond lengths), which together with the coordinates  $\gamma_{mm}$  (changes in the valence angles) form the system of valence-force vibrational coordinates.<sup>1</sup> The electrooptical parameters  $\alpha_a^{(m)'}$  are sufficient for the description of valence molecular vibrations; as for deformational and valence-deformational vibrations, it is necessary to differentiate the molecular polarizability tensor  $a_{uv}$  with respect to the angle coordinates  $\gamma$ , on which, according

to relation (2), the direction cosines of the bonds which vary during the indicated vibrations depend.

The main problem of VO theory consists in calculating the derivatives with respect to  $\gamma$  of the direction cosines, since (as was remarked by the author of this theory, Wolkenstein) "in the general case the calculation of the derivatives of these cosines by valence-force coordinates  $\gamma$  can be very difficult".<sup>1</sup> For solving this problem two methods have been worked out in literature.

Wolkenstein and Eliashevich<sup>6</sup> introduced the valence-optical angular coordinates  $\beta$ , which are changes in the angles between the bonds and the coordinate axes. In this method the transformation from the valence-optical coordinates to the symmetry coordinates is very cumbersome, because it is necessary to consider, in addition, the condition of vanishing the components of the molecular angular momentum vector during the vibrations. Suffice it to say that for a simple noncollinear molecule  $XY_2$  calculation of the invariants  $(b')^2$  and  $(g')^2$  occupies seven pages in Ref. 1, while the components of the tensor  $a'_{uv}$  are listed in a two-page table.

Another way of calculating the derivatives of the direction cosines was proposed by Long,<sup>7</sup> Ferigle and Weber,<sup>14</sup> and Gribov.<sup>15</sup> According to this method, in order to differentiate the cosines, one should, first, turn to the derivatives with respect to the atomic displacements  $r_1$ . As a result, the gradients of the direction cosines now appear in the theory, and are calculated in Refs. 14 and 16. Calculations of invariants by this method remain as cumbersome as before.<sup>8,9</sup> Besides, in the technique for calculating the invariants  $(b')^2$  and  $(g')^2$  (i.e., in the electrooptical problem) there appear matrices which enter into the solution of the mechanical problem; the latter, however, is independent of the electrooptical one.

In both methods one must first define the direction angles between the axes of the bond polarizability ellipsoids and the axes of the L-system, when the molecule is in the nonequilibrium position in the process of vibrations. It is clear that this problem may have no solution for molecules, having a sufficiently complex space structure. Therefore in these methods the question about solving the electrooptical problem becomes dependent on the possibility of determining the direction cosines and calculating their derivatives.

In this connection another question arises: why is it necessary to develop a sophisticated technique of differentiation of the direction cosines with respect to  $\gamma$  and then to carry out cumbersome calculations of the Raman invariants  $(b')^2$  and  $(g')^2$  if the latter, by definition, are independent of the cosines and their derivatives? The situation becomes paradoxical and it is quite natural to attempt to develop a method, analogous to that demonstrated for the case of molecular optics in the previous paragraph, which should enable one to find an invariant expression for  $(g')^2$  (such an expression for the invariant  $(b')^2$  is known<sup>1</sup>), which is independent of the noninvariant direction cosines and their derivatives.

For this purpose we shall transform in Eq. (16) from the derivative with respect to the normal coordinate  $Q$  to the derivatives with respect to the internal coordinates  $q$  and  $\gamma$  by introducing the corresponding form coefficients  $L_q$  and  $L_\gamma$  of the vibration:

$$\alpha'_{uv} = \left[ \frac{\partial \alpha_{uv}}{\partial q} \right]_0 \left[ \frac{dq}{dQ} \right]_0 + \left[ \frac{\partial \alpha_{uv}}{\partial \gamma} \right]_0 \left[ \frac{d\gamma}{dQ} \right]_0 = \alpha'_{uv(q)} L_q + \alpha'_{uv(\gamma)} L_\gamma \quad (18)$$

In the zeroth-order approximation of the VO theory the invariant  $b'_1$  (if we do not transform to the symmetry coordinates) is equal<sup>1</sup> to

$$b'_1 = \sum_{u=x,y,z} \left[ \frac{\partial \alpha_{uu}}{\partial Q_1} \right]_0 = \sum_m \sum_{a=1}^3 \alpha_a^{(m)'} L_{q1}^{(m)}, \quad (19)$$

where  $L_{q1}^{(m)} = (\partial q_m / \partial Q_1)_0$  is the form of the valence vibration.

The anisotropy  $(g')^2$  of the tensor  $a'_{uv}$  is defined on the basis of an expression analogous to expression (4):

$$(g')^2 = \frac{3}{2} \sum_{u,v} \left[ \frac{\partial \alpha_{uv}}{\partial Q} \right]_0^2 - \frac{1}{2} (b')^2 \quad (20)$$

so that the problem is reduced to the calculation of the sum entering into expression (20), which, according to expression (18) can be represented in the form

$$\sum_{u,v} (\alpha'_{uv})^2 = \sum_{u,v} (\alpha'_{uv(q)})^2 L_q^2 + \sum_{u,v} (\alpha'_{uv(\gamma)})^2 L_\gamma^2 + 2 \sum_{u,v} \alpha'_{uv(q)} \alpha'_{uv(\gamma)} L_q L_\gamma \quad (21)$$

The terms on the right-hand side of expression (21) represent the valence, deformational, and valence-deformational contributions to the anisotropy  $(g')^2$ , respectively (we do not consider here nonplanar vibrations, which require special consideration).

The essence of our method consists in calculating invariant constructions, which appear in expression (21) when we substitute definition (6) for the tensor  $a_{uv}$ , without calculating the derivatives  $a'_{uv(q,\gamma)}$  directly. In particular, the second term on the right-hand side of Eq. (21) after the indicated substitution reads

$$\begin{aligned} \sum_{u,v} (\alpha'_{uv(\gamma)})^2 &= \sum_{u,v} \left\{ \sum_m \sum_{a=1}^3 \alpha_a^{(m)} \left[ R_{au}^{(m)} R_{av}^{(m)} \right]'_{(\gamma)} \right\}^2 = \\ &= \sum_m \sum_{a,b=1}^3 \alpha_a^{(m)} \alpha_b^{(m)} \sum_{u,v} \left[ R_{au}^{(m)} R_{av}^{(m)} \right]'_{(\gamma)} \left[ R_{bu}^{(m)} R_{bv}^{(m)} \right]'_{(\gamma)} + \\ &+ \sum_m \sum_{n \neq m} \sum_{a,b=1}^3 \alpha_a^{(m)} \alpha_b^{(n)} \sum_{u,v} \left[ R_{au}^{(m)} R_{av}^{(m)} \right]'_{(\gamma)} \left[ R_{bu}^{(n)} R_{bv}^{(n)} \right]'_{(\gamma)}. \end{aligned} \quad (22)$$

After differentiating the product of the matrices  $\hat{R}^{(m)}$  with respect to  $\gamma$ , according to relation (8), there appears the invariant construction in Eq. (22)

$$\sum_u R_{au}^{(m)'} R_{bu}^{(m)'} = - \sum_u R_{bu}^{(m)} R_{au}^{(m)'} = A_{ab}^{(m)} \quad (\alpha, \beta = 1, 2, 3), \quad (23)$$

which is an antisymmetric tensor:  $A_{ab}^{(m)} = -A_{ba}^{(m)}$ , and consequently its diagonal components  $A_{aa}^{(m)}$  equal zero (the latter fact for the components  $A_{22}^{(m)}$  and  $A_{33}^{(m)}$  was mentioned in Ref. 9). Taking relation (8) and these properties of the tensor  $A_{ab}^{(m)}$  into account, one can reduce the sum on the right-hand side of Eq. (22) to the form

$$\begin{aligned} \sum_m &= 2 \sum_m \left\{ \sum_{a=1}^3 \alpha_a^{(m)2} \sum_{u=x,y,z} \left[ R_{au}^{(m)'} \right]^2 - \right. \\ &\left. - \sum_{a,b} \alpha_a^{(m)} \alpha_b^{(m)} A_{ab}^{(m)2} \right\}. \end{aligned} \quad (24)$$

The double sum over,  $m$  and  $n \neq m$  in Eq. (22) is equal to

$$\begin{aligned} \sum_m \sum_{n \neq m} &= 2 \sum_m \sum_{n \neq m} \sum_{a,b} \alpha_a^{(m)} \alpha_b^{(n)} \left[ R_{ab}^{(m,n)} \sum_u R_{au}^{(m)'} R_{bu}^{(n)'} + \right. \\ &\left. + \sum_u R_{au}^{(m)} R_{bu}^{(n)'} \sum_v R_{bv}^{(n)} R_{av}^{(m)'} \right]. \end{aligned} \quad (25)$$

if one takes into account relation (13), which was deduced in the previous argument. The matrix products  $\hat{R}^{(m)} \cdot \hat{R}^{(n)}$  entering into expression (25) can be calculated by differentiating expression (13) with respect to  $\gamma$ , if we consider the  $\gamma_{\min}$ -dependence of the valence angle  $\varphi_{uv}$ , which changes during the deformational vibrations. As is customary in vibrational spectroscopy, the internal coordinate  $\gamma$  is equal to the change in the valence angle, taken with the opposite sign,<sup>1,17</sup> i.e.,

$$\gamma_{mn} = -\Delta\varphi_{mn} = -(\varphi_{mn} - \varphi_{mn}^0), \quad (26)$$

where  $\varphi_{mn}^0$  is the equilibrium value of the angle. Hence,

$$\frac{\partial}{\partial \gamma_{mn}} = - \frac{\partial}{\partial \varphi_{mn}}. \quad (27)$$

Thus, we have

$$\sum_m \sum_{n \neq m} \sum_u R_{au}^{(m)} R_{bu}^{(n)'} = \frac{1}{2} \sum_m \sum_{n \neq m} R_{ab}^{(m,n)'} \quad (28)$$

where, according to Eqs. (13) and (27),

$$\hat{R}^{(m,n)} (\varphi_{mn}')_{(\gamma)} = -\hat{R}^{(m,n)} (\varphi_{mn}')_{(\varphi)} =$$

$$= \begin{pmatrix} \sin \varphi_{mn} & -\cos \varphi_{mn} & 0 \\ -\cos \varphi_{mn} & -\sin \varphi_{mn} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (29)$$

Using the models of noncollinear triatomic molecules of the types  $Y_mXY_m$  and  $Y_mXY_n$ , one can find an explicit form for the tensor  $A_{ab}^{(m)}$  and the invariant sums over  $u$  and  $v$  remaining in Eqs. (24) and (25), which contain the direction cosines  $R_{au}^{(m)}$  or their derivatives  $R_{au(\gamma)}^{(m)}$ . In this case there is no loss of generality in our treatment, since expressions (22), (24) and (25) contain sums over  $m$  and  $n$ , i.e., they are additive in these triatomic fragments.

Most suitable for the description of triatomic molecules is the coordinate system<sup>1,2,8,9</sup> in which both bonds are located in the plane ( $x, y$ ), so that the negative direction of the  $Oy$  axis serves as the bisector of the valence angle  $\varphi$  between the bonds. In the chosen coordinate system (the  $L$ -system) the matrices of the direction cosines for the bonds have the form<sup>8</sup>

$$\hat{R}^{(m)} = \begin{pmatrix} -\sin \frac{\varphi}{2} & -\cos \frac{\varphi}{2} & 0 \\ \cos \frac{\varphi}{2} & -\sin \frac{\varphi}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\hat{R}^{(n)} = \begin{pmatrix} \sin \frac{\varphi}{2} & -\cos \frac{\varphi}{2} & 0 \\ -\cos \frac{\varphi}{2} & -\sin \frac{\varphi}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}. \quad (30)$$

Note that matrices (30) are defined solely for the sake of convenience. The invariant constructions, obtained below, do not depend on the choice of the  $L$ -system and, as one can easily verify, these constructions will retain their form in other coordinate systems. On the other hand, the components of the tensor  $a_{uv}$ , as shown in Refs. 1, 8, and 9, will change; obviously, their form in different coordinate systems for the tensor components are not invariant relative to the choice of coordinate system.

Differentiating the matrices (30) with respect to  $\gamma$  with the help of relation (27) and calculating the sums over  $u$  one can obtain the following relations:

$$A_{ab}^{(m)2} = \left[ \sum_{u=x,y,z} R_{au}^{(m)} R_{bu(\gamma)}^{(m)'} \right]^2 = \frac{1}{4} (\delta_{ab} - 1) \times$$

$$\times (\delta_{a3} - 1) (\delta_{b3} - 1) \quad (\alpha, \beta = 1, 2, 3); \quad (31)$$

$$\sum_{u=x,y,z} \left[ R_{au(\gamma)}^{(m)'} \right]^2 = \frac{1}{4} (1 - \delta_{a3}); \quad (32)$$

$$\sum_{u=x,y,z} R_{au(\gamma)}^{(m)'} R_{bu(\gamma)}^{(n)'} = \frac{1}{4} R_{ab}^{(m,n)} (\delta_{a3} \delta_{b3} - 1). \quad (33)$$

It is not difficult to carry out remaining calculations with the help of the obtained equations (23), (28) and (31)–(33). As a result we find (according to the definition (20) and taking into account Eq. (19))

$$(\mathcal{E}'_1)^2 = \left[ \mathcal{E}'_{1_{\text{val}}} \right]^2 + \left[ \mathcal{E}'_{1_{\text{def}}} \right]^2 + \left[ \mathcal{E}'_{1_{\text{val-def}}} \right]^2 =$$

$$= \frac{1}{2} \left\{ \sum_m \left[ \sum_{a=1}^3 3 (\alpha_a^{(m)'})^2 - \sum_{a,b=1}^3 \alpha_a^{(m)'} \alpha_b^{(m)'} \right] L_{q1}^{(m)2} + \right.$$

$$+ \sum_m \sum_{n \neq m} \sum_{a,b=1}^3 \alpha_a^{(m)'} \left[ 3 (R_{ab_0}^{(m,n)})^2 - 1 \right] \alpha_b^{(n)'} L_{q1}^{(m)} L_{q1}^{(n)} \left. \right\} +$$

$$+ \frac{3}{4} \sum_m \sum_{n \neq m} \left[ (\alpha_1^{(m)} - \alpha_2^{(m)})^2 - (\alpha_1^{(n)} - \alpha_2^{(n)}) \times \right.$$

$$\times (\alpha_1^{(n)} - \alpha_2^{(n)}) \cos 2\varphi_{mn}^0 \left. \right] L_{\gamma 1}^{(m,n)2} +$$

$$+ 3 \sum_m \sum_{n \neq m} \sum_{a,b=1}^3 \alpha_a^{(m)'} \times$$

$$\times R_{ab_0}^{(m,n)} \left[ \frac{\partial R_{ab}^{(m,n)}}{\partial \gamma_{mn}} \right] \alpha_b^{(n)'} L_{q1}^{(m)} L_{\gamma 1}^{(m,n)}, \quad (34)$$

where  $L_{\gamma 1}^{(m)} = (\partial \gamma_m / \partial Q_1)_0$  is the form of the deformational vibration. Expression (34) is written in terms of the internal coordinates. One must transform to the symmetry coordinates according to the known rules,<sup>1,8,9</sup> when the electrooptical problem for the specific vibrations of definite molecules is solved.

The obtained expression (34) for the Raman invariant  $(g')^2$  allows one to bypass the cumbersome technique of the preliminary calculation of the components of the derivative of the molecular polarizability tensor  $a'_{uv}$ . No care one should take of the convenient choice of the  $L$ -coordinate system. As an example, we shall consider the Raman invariants, given in Eqs. (19) and (31), for the vibrations of the  $XY_2$  molecules (which were obtained earlier<sup>11</sup> by means of the standard technique<sup>8</sup> of calculating the tensor  $a'_{uv}$  components). Now, transforming to the symmetry coordinates, we obtain automatically:

– for the symmetrical valence vibration  $\nu_1$

$$b'_1 = \sqrt{2} (\alpha'_1 + 2\alpha'_2) \left[ \frac{\partial q^A}{\partial Q_1} \right]_0, \quad (35)$$

$$(\mathcal{E}'_1) = \frac{1}{2} (\alpha'_1 - \alpha'_2)^2 (1 + 3\cos^2 \varphi_0) \left[ \frac{\partial q^A}{\partial Q_1} \right]_0^2; \quad (36)$$

– for the antisymmetrical valence vibration  $\nu_3$

$$b'_3 = 0, \quad (\mathcal{E}'_3)^2 = \frac{3}{2} (\alpha'_1 - \alpha'_2)^2 \sin^2 \varphi_0 \left[ \frac{\partial q^B}{\partial Q_3} \right]_0^2; \quad (37)$$

– for the symmetrical deformational vibration  $\nu_2$

$$b'_2 = 0, \quad (\mathcal{E}'_2)^3 = 3 (\alpha'_1 - \alpha'_2)^2 \sin^2 \varphi_0 \left[ \frac{\partial \gamma^A}{\partial Q_2} \right]_0^2. \quad (38)$$

The case of  $\sigma$ –bonds, for which  $\alpha_3 = \alpha_2$  and  $\alpha'_3 = \alpha'_2$ , is considered here.

It should be mentioned that, as one can see directly from expressions (19) and (34), the Raman intensity for the valence vibrations is determined by the values of all three EOP's  $\alpha'_a$  ( $a = 1, 2, 3$ ) for each band. That is why the SP of molecules for the valence vibrations of  $\sigma$ -bonds and  $\pi$ -bonds (for which  $\alpha_3 \neq \alpha_2$  and  $\alpha'_3 \neq \alpha'_2$ ), having the same chemical composition (e.g., for the bonds C–O and C = O), must be different. For deformational and valence-deformational vibrations this is not the case. In the corresponding terms of the expression (34) only the EOP's  $\alpha_1$ ,  $\alpha_2$  and  $\alpha'_1$ ,  $\alpha'_2$  make a contribution (for the last term in expression (34) this follows from the expression for the matrix (29), the elements of the third row and third column of which are equal to zero). Hence, the parameters  $\alpha_3$  and  $\alpha'_3$  have no influence on the absolute Raman intensities for the vibrations which take place in the plane perpendicular to the vectors  $e_3^{(m)}$  and  $e_3^{(n)}$  during which the valence angles between the bonds change. So the intensities of the deformational and valence-deformational vibrations for fragments containing  $\sigma$ - and  $\pi$ -bonds of the same chemical nature must be equal. Experimental verification of this prediction would have, no doubt, great interest for both Raman spectroscopy and quantum chemistry.

#### ON THE FIRST APPROXIMATION OF THE VALENCE-OPTICAL THEORY

The idea of additivity of dipole moments and polarizability of valence bonds in a molecule, which was transplanted by Wolkenstein from molecular optics to vibrational spectroscopy, proved to be very constructive in investigating the electrooptics of molecular vibrations. The success of the additivity concept in molecular optics and spectroscopy is explained by its adequacy to the principle of valence chemistry, according to which a molecule is considered as a totality of chemical bonds, which play the role of its structural elements.

However, in chemistry a valence scheme is approximation, since in the quantum system the primary building blocks are the nuclei of atoms and electron densities, while their interactions lead, in particular, to the formation of chemical bonds. It is clear that the bonds also interact, but the bond interaction is weaker than that of the atoms, forming an individual bond. The interaction between the bonds manifests the nonadditivity effect in valence chemistry, but in most cases the nonadditivity is a small correction to the additive properties.

However, there are some molecules which Wolkenstein called "nonadditive." In these molecules "the electron clouds cannot be located on separate bonds, but rather belong to the whole molecule. In this case physical meaning vanishes not only for the valence-optical scheme, but for the very idea of the valence bond itself."<sup>1</sup> Thus, the author of the VO theory sees the limit of validity of his theory in the nonadditivity, which, first of all, manifests itself in

the interaction of the bonds, and in the utmost case it deprives of physical meaning the chemical bond itself.

In this situation it would be logical to speak of the approximate character of the VO theory, in which the additivity property enters as a principal component of its construction. So the rejection of additivity should be recognized as the rejection of the VO theory, itself. Nevertheless, historically the further development of the VO theory followed another path: the corrections for nonadditivity were included in the theory as a first-order approximation. In this connection, we shall analyze how contradictory the inclusion of the first-order approximation in the VO theory is to the logic of the construction of the theory.

Relation (1), in which the bond polarizabilities are additive, is basic for the VO theory which describes Raman scattering. Hence, the VO theory supposes that in the equilibrium state of the molecule the chemical bonds do not interact. During the vibrations changes in the bond lengths and the valence angles remain almost two orders of magnitude less than their equilibrium values. The bond interactions due to the vibrations, therefore, cannot grow rapidly in comparison with the initial interaction of the bonds in the equilibrium state of the molecule. If the latter was neglected in the initial relation (1), there is no reason to include it for small molecular vibrations.

Formally, the bond interaction during molecular vibrations is accounted for within the framework of the VO theory by taking into account the bond polarizability derivatives with respect to changes in the lengths of the other bonds, which are obviously equal to zero in the zeroth-order approximation. They also consider the polarizability derivatives with respect to changes of the valence angles, which are not equal to zero in the first-order approximation. Thus, the introduction of the derivatives  $\partial\alpha_a^{(n)} / \partial q_t$  ( $t \neq n$ )  $\partial\alpha_a^{(n)} / \partial \gamma_{lm}$  into the theory is the basis of the first-order approximation in the VO theory for Raman scattering.

Originally, all the calculations of the electrooptics of molecular vibrations were made in the zeroth-order approximation of the VO theory.<sup>1</sup> Why did other scientists later use the first-order approximation in their work? The answer was given in Ref. 8: "the zeroth-order approximation of the VO theory is unsuitable for calculating the electrooptical parameters of polyatomic molecules." However, only a few examples are given in Ref. 8 of the unsuitability of the zeroth-order approximation – the basic example being the molecules CH<sub>4</sub> and CCl<sub>4</sub>. We shall examine these cases. According to Ref. 8, within the zeroth-order approximation one cannot extract such information about the value of the difference of the principal bond polarizabilities  $\Delta\alpha = \alpha_1 - \alpha_2$  from the experimental data on Raman cross sections of the *E* and *F* types of vibrations of the mentioned molecules. Thus, in methane for the C–H bond from the data on the *E*-type vibration one finds the value  $\Delta\alpha(\text{C–H}) = 0.313 \text{ \AA}^3$ , while for the *F*-type vibration  $\Delta\alpha = 0.086 \text{ \AA}^3$ . Correspondingly, for the CCl<sub>4</sub>

molecule we have the values  $\Delta\alpha(\text{C-Cl}) = 2.96 \text{ \AA}^3$  (from the  $E$ -type) and  $\Delta\alpha = 4.14 \text{ \AA}^3$  (from the  $F$ -type).

Regarding this point, we should note that if the corrections of the first-order approximation enable one to remove the differences in the value of  $\Delta\alpha$ , which reach 40% for the C-Cl bond and 260% for the C-H bond, then one cannot call them corrections in the usual sense of the word. In this case the hierarchy of the introduced approximations loses its meaning, because the EOP's, calculated in the first-order approximation, differ by hundreds of percents from the values of the same parameters obtained in the zeroth-order approximation. Hence, the VO theory ceases to be self-consistent after incorporating the first-order approximation. In other words, rejection of the zeroth-order approximation is tantamount to rejection of the VO theory itself. However, as will be demonstrated below, the examples of the molecules  $\text{CH}_4$  and  $\text{CCl}_4$  leave no grounds for doubt as to the validity of the zeroth-order approximation for the VO theory describing the electrooptics of Raman scattering. In this connection we shall consider a more detailed comparison of the theory with experiment for these molecules.

Transforming in Eqs. (19) and (34) from the internal coordinates to the symmetry coordinates for vibrations of  $XY_4$ -type molecules, we obtain the well-known<sup>1,7,8</sup> expression for the Raman invariants: for the full symmetrical valence vibration  $\nu_1$  of  $A_1$ -type symmetry:

$$b'_1 = 2(\alpha'_1 + 2\alpha'_2) L_{q_1}^1, \quad (q'_1)^2 = 0; \quad (39)$$

for the doubly-degenerate deformational vibration  $\nu_2$  of  $E$ -type symmetry:

$$b'_2 = 0, \quad (g'_2)^2 = 3(\alpha_1 - \alpha_2)^2 \sin^2 \varphi_0 (L_{\gamma_2}^E)^2; \quad (40)$$

for the two triply-degenerate valence-deformational vibrations  $\nu_3$  and  $\nu_4$  of  $F_2$ -type symmetry:

$$b'_l = 0, \quad (g'_l)^2 = \frac{4}{3} \left[ (\alpha'_1 - \alpha'_2) L_{q_1}^{F_2} + (\alpha_1 - \alpha_2) L_{\gamma_1}^{F_2} \right]^2 \quad (l = 3, 4) \quad (41)$$

The fact that the C-H and C-Cl bonds are  $\sigma$ -bonds is taken into account here.

It is very important to emphasize that the forms of vibration entering into expressions (39)–(41) are calculated approximately in the solution of the mechanical vibrational problem. That is why the calculated values of these forms introduce a substantial error in the determination of the EOP from the experimental data on Raman cross sections. In connection with this, an indirect check of the values of the vibrational form coefficients, which are used in the solution of the electrooptical problem, is always necessary.

According to Eq. (40), only the value  $L_{\gamma_2}^E$  of the form can be verified directly, because the po-

larizability difference  $\Delta\alpha$  is measured with rather good accuracy in molecular optics experiments<sup>4</sup>:  $\Delta\alpha(\text{C-H}) = 0.24 \text{ \AA}^3$  and  $\Delta\alpha(\text{C-Cl}) = 1.6 \text{ \AA}^3$ . The values of the form  $L_{\gamma_2}^E = 1.23 \cdot 10^{20} \text{ g}^{-1/2} \cdot \text{cm}^{-1}$  for the  $\text{CH}_4$  molecule<sup>8</sup> and  $L_{\gamma_2}^E = 0.133 \cdot 10^{20} \text{ g}^{-1/2} \cdot \text{cm}^{-1}$  for the  $\text{CCl}_4$  molecule.<sup>18</sup> Using these values of  $L_{\gamma_2}^E$  we obtain the following values of the SP for these molecules:  $I_2^v(\text{CH}_4) = 1.63 \cdot 10^{-8} \text{ g}^{-1} \cdot \text{cm}^4 \cdot \text{molec}^{-1}$  and  $I_2^v(\text{CCl}_4) = 0.845 \cdot 10^{-8} \text{ g}^{-1} \cdot \text{cm}^4 \cdot \text{molec}^{-1}$ , whereas the corresponding experimental values of the SP are  $1.67 \cdot 10^{-8}$  ( $\text{CH}_4$ ) (Ref. 19) and  $0.99 \cdot 10^{-8}$  ( $\text{CCl}_4$ ) (Ref. 20). Thus, the theory is in good agreement with experiment for the  $\nu_2$  band, and we can trust the values of the form  $L_{\gamma_2}^E$  cited in Refs. 8 and 18.

More complicated is the case of the other form coefficients of the vibrations. They are also given in Refs. 8 and 18 (in units of  $10^{-12} \text{ g}^{-1/2}$ ) for the  $\text{CH}_4$  molecule:  $L_{q_1}^{A_1} = 0.77$ ,  $L_{q_3}^{F_2} = 0.81$ ,  $L_{q_4}^{F_2} = -0.03$ ,  $L_{\alpha_3}^{F_2} = r_{\text{CH}} \cdot L_{\gamma_3}^{F_2} = -0.11$ ,  $L_{\alpha_4}^{F_2} = 1.2$ ; for the  $\text{CCl}_4$  molecule  $L_{q_1}^{A_1} = 0.136$ ,  $L_{q_3}^{F_2} = -0.29$ ,  $L_{q_4}^{F_2} = 0.29$ ,  $L_{\alpha_3}^{F_2} = 0.204$ ,  $L_{\alpha_4}^{F_2} = -0.00155$ . These values can be verified if we calculate the mean square amplitudes of the atomic vibrations according to relation (21):

$$\langle Q_1^2 \rangle = \sum L_{i1}^2 \langle Q_i^2 \rangle, \quad (42)$$

where

$$\langle Q_1^2 \rangle = \frac{\hbar\hbar}{2\omega_1} \text{cth} \frac{\hbar\omega_1}{2kT}, \quad (43)$$

and compare them with the results of the electron scattering measurements given in Ref. 21.

For  $XY_4$ -type molecules, the mean square amplitude of the vibrations of the X-Y bond (taking into account the symmetry coefficients relating the vibrational forms  $L_{i1}$  and  $L_{i1}^s$ ) is equal to

$$l_{X-Y} = \sqrt{\langle Q_{X-Y}^2 \rangle} = \frac{1}{2} \left[ \delta_1 (L_{q_1}^{A_1})^2 + \delta_3 (L_{q_3}^{F_2})^2 + \delta_4 (L_{q_4}^{F_2})^2 \right]^{1/2}, \quad (44)$$

where  $\delta_1 = \langle Q_1^2 \rangle$ . Correspondingly, the mean square amplitude of the vibrations of the atoms  $Y \dots Y$  is equal to

$$l_{Y \dots Y} = \sqrt{\langle Q_{Y \dots Y}^2 \rangle} = \frac{1}{2} \left[ \delta_2 (L_{\alpha_2}^E)^2 + 2\delta_3 (L_{\alpha_3}^{F_2})^2 + 2\delta_4 (L_{\alpha_4}^{F_2})^2 \right]^{1/2}. \quad (45)$$

According to these formulas and the above values of the vibrational forms we obtain for the C-H bond in the  $\text{CH}_4$  molecule  $l_{\text{C-H}} = 0.0543 \text{ \AA}$ , while experiment<sup>21</sup> gives

$l_{C-H} = 0.0764 \text{ \AA}$ , which is 40.7% higher than the theoretical value. Correspondingly, for  $l_{H-H}$  we obtain 0.154 Å (theory) while experiment gives 0.119 Å, i.e., the theoretical value is 29.4% higher than the experimental one. Note that the same results are also obtained for the molecules  $CD_4$  and  $CT_4$ , for which the vibrational form coefficients are also given in Ref. 8. We arrive at the necessity of introducing the correction factor  $k_q$  on the basis of the purely empirical relation

$$\left[ L_{q1}^S \right]_{\text{exp}} = k_q \left[ L_{q1}^S \right]_{\text{theo}} \quad (l = 1, 3, 4), \quad (46)$$

Comparison of the theoretical and experimental values of  $l_{C-H}$  shows that  $k_q = 1.407$ . Consequently, we find  $(L_{q1}^A)_{\text{exp}} = 1.083$ ,  $(L_{q3}^{F_2})_{\text{exp}} = 1.14$ ;  $(L_{q4}^{F_2})_{\text{exp}} = -0.0422$ . From Eq. (45) and the empirical value  $k_\alpha = 0.62$  we find  $(L_{\alpha 3}^{F_2})_{\text{exp}} = -0.068$ ;  $(L_{\alpha 4}^{F_2})_{\text{exp}} = 0.74$ , while keeping the value of  $L_{\alpha 2}^E$  fixed in accordance with the above-made conclusion about the deformational form coefficients.

The above method of "recounting" the vibrational forms is, of course, an empirical one. But in situations in which the form coefficients are calculated approximately, one may speak only of the consistency of the latter with two different kinds of experimental data: 1) electron scattering measurements of the mean square amplitudes and 2) the Raman cross sections of the spectral lines that are determined by these coefficients.

The consistency of the recounted form coefficients for the  $CH_4$  molecule are confirmed by calculation of the theoretical values of the SP of the molecule for  $\nu_3$  and  $\nu_4$  bands and subsequent comparison with experiment, which according to the experimental value of the SP (Refs. 22 and 23) for the  $\nu_3$  band is  $I_3^v(CH_4) = 26.98 \cdot 10^{-8}$ ; hence, using the corrected values of  $(L_{q3}^{F_2})_{\text{exp}}$  and  $(L_{\alpha 3}^{F_2})_{\text{exp}}$  we find according to Eqs. (41) that  $\Delta\alpha' = 1.505 \text{ \AA}^2$ . Using these values of  $\Delta\alpha'$  and  $\Delta\alpha$ , we arrive at a theoretical value of the SP of the molecule for the  $\nu_4$  band  $I_4^v(CH_4)_{\text{theo}} = 0.0937 \cdot 10^{-8}$ , which with 12.5% accuracy coincides with the upper bound  $0.0833 \cdot 10^{-8}$  of the experimental value.<sup>22</sup>

Using the experimental value for the SP of the  $\nu_1$  band  $I_1^v(CH_4)_{\text{theo}} = 130.167 \cdot 10^{-8}$  (Ref. 23), on the basis of Eqs. (39) we find that  $\alpha'_1 + \alpha'_2 = 2.3555 \text{ \AA}^2$ , which together with the above-found value of the linear combination  $\alpha'_1 - \alpha'_2 = 1.505 \text{ \AA}^2$  gives the following values for the EOP's for the C-H bond:

$$\begin{aligned} \alpha'_1(C-H) &= 1.788 \text{ \AA}^2, \\ \alpha'_2(C-H) &= \alpha'_3(C-H) = 0.283 \text{ \AA}^2. \end{aligned} \quad (47)$$

The principal bond polarizabilities used here are  $\alpha_1(C-H) = 0.81 \text{ \AA}^3$  and  $\alpha_2(C-H) = \alpha_3(C-H) = 0.57 \text{ \AA}^3$

(Ref. 4). The values of the EOP, obtained in Eqs. (47), are close enough to those given in Ref. 1, which were also calculated in the zeroth-order approximation of VO theory.

The mean square amplitude for the  $CCl_4$  molecule, calculated on the basis of Eq. (44),  $l_{C-Cl} = 0.063 \text{ \AA}$ , exceeds the experimental value 0.054 Å by 16.7%. Thus, the recounting coefficient  $k_q = 0.855$ , i.e.,  $(L_{q1}^A)_{\text{exp}} = 116$ ,  $(L_{q3}^{F_2})_{\text{exp}} = -0.248$ , and  $(L_{q4}^{F_2})_{\text{exp}} = 0.248$ . The theoretical value of the amplitude  $l_{Cl...Cl} = 0.046 \text{ \AA}$  is 1.5 times less than the experimental value 0.069 Å. If one introduces a correction coefficient  $k_\alpha$  to the values of the vibrational forms, the set of experimental data for the mean square amplitudes should disagree with the data for the Raman cross sections. Thus, noting that in contrast to the molecules  $CH_4$ ,  $CD_4$ , and  $CT_4$  the form coefficient  $L_{\alpha 4}^{F_2}$  for  $CCl_4$  molecule is anomalously small,<sup>18</sup> we introduce an empirical correction factor (on the basis of the experimental value  $l_{Cl...Cl}$ ) only in the theoretical value of this form, leaving the remaining forms  $L_{\alpha 2}^{F_2}$  and  $L_{\alpha 3}^{F_2}$  in Eq. (45) unchanged. In this way we find  $(L_{\alpha 4}^{F_2})_{\text{exp}} = -0.196$ .

The remaining calculations for the  $CCl_4$  molecule are analogous to the case of methane. From the experimental data on the Raman cross sections for the  $\nu_1$  and  $\nu_3$  bands<sup>20</sup> we find two combinations of the EOP's:  $\alpha'_1 + 2\alpha'_2 = 7.32 \text{ \AA}_1$  and  $\alpha'_1 - \alpha'_2 = 3.76 \text{ \AA}$ , from which we obtain the EOP's for the C-Cl bond:

$$\begin{aligned} \alpha'_1(C-Cl) &= 4.95 \text{ \AA}^2, \\ \alpha'_2(C-Cl) &= \alpha'_3(C-Cl) = 1.19 \text{ \AA}^2. \end{aligned} \quad (48)$$

The bond polarizabilities are  $\alpha'_1(C-Cl) = 3.59 \text{ \AA}^3$  and  $\alpha'_2(C-Cl) = \alpha'_3(C-Cl) = 1.09 \text{ \AA}^3$  (Ref. 4). We can confirm the obtained values of the EOP's and of the form  $L_{\alpha 4}^{F_2}$  by comparing the theoretical value of the SP for the  $\nu_4$  band  $I_1^v(CCl_4)_{\text{theo}} = 2.914 \cdot 10^{-8}$  with experiment. It turns out that it coincides with the experimental value  $2.944 \cdot 10^{-8}$  (Ref. 24) with 1% accuracy.

Thus, we conclude that the zeroth-order (additive) approximation of the VO theory is in full agreement with the experimental data of molecular optics and Raman spectroscopy for the  $CH_4$  and  $CCl_4$  molecules. The contrary conclusion for these molecules, made in Ref. 8, is evidently based on the use of unreliable form coefficients, which were calculated approximately and which, as has been demonstrated, disagree with the electron scattering experiments for the mean square amplitudes.

The first-order approximation, incorporated in the theory to "correct for" the predictions of the zeroth-order technique, leads the VO theory up a blind alley. First of all,  $\sigma$ -bonds cannot exist in the first-order theory, for the interaction of the po-

larizability bond ellipsoids of different bonds deprives them of axial symmetry.<sup>1</sup> But such a conclusion of the first-order theory contradicts to the principles of quantum chemistry concerning the nature of ordinary chemical bonds. Besides, in a strict consideration of the problem in the first-order approximation the derivatives  $\partial\alpha_1^{(1)}/\partial q_2$  and  $\partial\alpha_2^{(1)}/\partial q_2$ , as well as combinations of the type  $\partial\alpha_1^{(1)}/\partial\gamma_{34} - \partial\alpha_2^{(1)}/\partial\gamma_{34}$  must contribute to the SP of molecules of the type  $XY_4$ , which have the highest symmetry. These rather strange EOP combinations cannot be determined from experiment in the semiempirical theory, and it was apparently for this reason that they were omitted in Ref. 8, though the theory cannot properly be called a first-order approximation without them.

IN complex molecules, which have low symmetry, the number of parameters of the first-order approximation, which it is fundamentally impossible to calculate or determine from experiment, increases so strongly that the VO theory ceases to be a theory in the full sense of the word, capable of quantitatively explaining the integral characteristics of Raman scattering.

The VO theory is based on physically clear ideas of additivity, which serve as a good approximation for the description of the electrooptics of molecular vibrations. This approximation, which has historically been called the zeroth-order approximation, can describe the Raman experiment with greater or lesser accuracy. But it is in principle impossible to refine the predictions of the VO theory by inserting so-called first-order corrections into it.

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