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Origin of the second-order optical susceptibilities of crystalline substituted benzene

D. S. Chemla, J. L. Oudar, and J. Jerphagnon
Centre National d'Etudes des Télécommunications, 196 rue de Paris, 92220 Bagneux, France

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An analysis of the second-order optical nonlinearities of crystalline substituted benzene is presented. A new irreducible tensor formalism for the decomposition of a crystal tensor as the sum of the contributions of microscopic units is developed and applied to the study of the second-order susceptibility in four benzene derivatives with related structures and substituent radicals (*m*-dinitrobenzene, *m*-nitroaniline, *m*-aminophenol, and resorcinol). It is shown that an additivity approach can precisely account for the crystal nonlinearities and enables one to calculate the contributions of each radical to the nonlinearity of the molecule. these contributions are found to be strongly related to the donor or acceptor character of the radical. A very simple model is proposed to explain this relation.

I. INTRODUCTION

Recently, several theories have been proposed to explain the linear[1,3] and the nonlinear[4–14] optical susceptibilities of some families of inorganic crystals. The underlying principles of all these theories are the following: Under the hypothesis of additivity of microscopic polarizabilities a crystal is decomposed into an assembly of microscopic units (MU). These elementary building blocks are chosen according to the crystal structure as well as to the physico-chemical properties of the compounds. For example, biatomic bonds, regular and irregular tetrahedra, and distorted octahedra have been successfully used as MU to describe semiconductors and ferroelectric compounds. If no simple elementary building block can be found it is always possible to use as MU the primitive crystallographic cell. The crystal susceptibility tensors are written as the sum of the contributions of the various MU within the crystal,

$$\chi^{(1)}=\sum_s \alpha(s),\quad \chi^{(2)}=\sum_s \beta(s),\quad \chi^{(3)}=\sum_s \gamma(s)\ . \qquad (1)$$

In these equations $\chi^{(n)}$ is the nth-order crystal optical susceptibility; the subscript (s) covers all the MU within the crystal; and $\alpha(s)$, $\beta(s)$, $\gamma(s), \ldots$, are the linear, quadratic, cubic, etc., polarizability tensors of the MU with subscript (s). Such a decomposition raises difficult questions. In particular only very heavy quantum-mechanical self-consistent calculations can account for the local-field effects. Although a detailed formal scheme has been proposed[15] there have been to the best of our knowledge no full calculations performed to date. Several simple attempts have been made such as including the local-field effects in the definition of the microscopic polarizabilities,[1,3,8,12] using the experimental refractive index to calculate the local-field factor from the linear susceptibility expression[7] or using electrostatic cavity results for a "Lorentz"-type correction. None of these approaches is completely correct and they all indicate the difficulty of giving a simple account of these effects.

The next step is to find a model which correctly accounts for the microscopic properties of the building blocks. To be useful this model should apply to some family of related materials and hopefully predict the properties of unknown compounds. In addition, the models should be simple enough to indicate physico-chemical trends, in order to be a useful guide for material selection.

Theories developed along these lines have successfully explained the linear and nonlinear optical effects up to the third order in the family of tetrahedrally coordinated semiconductors, as well as the linear and nonlinear second-order effects in oxygen-octahedra ferroelectrics. It is worth noticing that successful modeling was possible in these two cases because the large amount of reliable experimental data on large groups of related compounds provided an invaluable guide to theorists.

The origins of the nonlinear optical properties of organic crystals are by far less well understood. Owing to the abundance of organic compounds systematic survey[16–19] only became possible with the powder technique developed by Kurtz and Perry.[16] Evaluation of the second-order nonlinearities shows that they are in some cases anomalously larger than would be predicted from their refractive indices and the Miller's rule.[20] Although the mechanical and optical qualities of most organic crystals make reliable experiments difficult to perform, several measurements on single crystals[21–26] have confirmed the results on powders. But up to the past few months no model in quantitative agreement with experiment has been proposed.

Recently, the situation has quickly changed. The experiments of Gott[21] and Hermann *et al*[27–29] on glasses and on liquids, and the theoretical analysis of Rustagi and Ducuing[30] undoubtfully stress the fundamental role played by electronic delocalization on third-order susceptibilities in unsaturated organic compounds. As for second-order susceptibilities there have been several measurements by dc-induced second-harmonic generation both on saturated[31,32,34] and unsaturated molecules,[33] which show that the second-order polarizabilities of saturated molecules are only a few percent of those of the unsaturated molecules. A typical example is the comparison of nitrobenzene ($C_6H_5-NO_2$) with nitromethane (CH_3-NO_2) performed by Levine and Bethea.[33] They found that while the static dipoles μ of the two molecules are of the same order of magnitude [$\mu(CH_3-NO_2) = 3.4$ D; $\mu(C_6H_5-NO_2) = 4.2$ D], the nonlinearity of the benzene substitutes is about 30 times larger than that of the methane substitute. While Miller's rule qualitatively agrees with the results for substituted aliphatic molecules it underestimates the quadratic polarizabilities of aromatic substitutes by at least an order of magnitude. All this experimental evidence indicates that the system of delocalized electrons is responsible for the anomalous behavior of these molecules. Molecular symmetry causes the π-electrons contribution to second-order polarizabilities to vanish for most of the nonsubstituted conjugated molecules, and one must therefore attribute the major part of the second-order nonlinearities of the substituted conjugated molecules to the distortion of the π-electrons system (π-ES) of the molecule by the interaction with the substituent group. This, together with the reliable experimental data on several related crystalline benzene substitutes[24,26] has led us to present a very simple model[35] relating the second-order polarizabilities of benzene substitutes to the deformation of the π-ES of the benzene ring induced by the substituent group and measured by its *mesomeric moment* $\Delta\mu$ (often called the electromeric dipole).

The mesomeric moment introduced in chemistry to explain the difference in dipole moment between aliphatic and aromatic molecules[36,37] characterizes the overall interaction of the substituent group with the π electrons of the molecule. In this interaction the π-ES looses its center of symmetry and thus gains a moment and a quadratic polarizability which are very likely to be related. To describe the nonlinearities of multisubstituted molecules we assumed the additivity of the second-order polarizabilities associated with radicals bound to a benzene ring.

In this paper we develop an analysis of the optical susceptibilities of benzene substitutes. We first present a theory of the decomposition of a molecular-crystal tensor into the sum of the contributions of microscopic units (Sec. II). Besides considering the local-field correction, we make extensive use of irreducible tensors and their relationships to Cartesian tensors. High-rank Cartesian tensors can always be decomposed into a direct sum of irreducible tensors, each with a specific physical meaning. By contrast with Cartesian components, the different-weight irreducible tensors (which transform as spherical harmonics) do not mix together in a transformation of reference frame from microscopic axes to crystal axes. This makes it possible to separate the microscopic contributions with different symmetries. In Sec. III we check the validity of the additivity scheme for the quadratic polarizabilities associated with a substituent group bound to a benzene molecule. Four crystalline substituted benzene with related crystal structures and substituent groups are considered; α-resorcinol (OH$-$Ph$-$OH), *m*-aminophenol (OH$-$Ph$-NH_2$), *m*-nitroaniline (NH_2-Ph$-NO_2$), and *m*-dinitrobenzene (NO_2-Ph$-NO_2$). In these compounds only three radicals R are involved, namely, OH, NH_2, NO_2. The geometrical analysis of the macroscopic nonlinear susceptibilities overdetermines the quadratic polarizabilities associated with the microscopic units $R-$Ph and thus provides a test of the validity of the additivity approach. In Sec. IV the results of the geometrical analysis are compared with the theoretical model both in respect of sign and magnitude. The vector parts of the MU quadratic polarizabilities are shown to be directly connected with the mesomeric moments of the substituent groups, the sign being directly linked to the nature (donor or acceptor) of the substituent.

II. DECOMPOSITION OF A MOLECULAR CRYSTAL INTO AN ASSEMBLY OF MICROSCOPIC UNITS

In a molecular crystal the intermolecular forces are mostly owing to Van der Waals interactions, and are much weaker than the forces within a molecule. Consequently, a number of crystal properties can be accounted for by assuming that the molecules are almost independent. This is the case of their response to electromagnetic perturbations. Furthermore, in the special case of inorganic molecules the additivity of the linear bond polarizabilities is well established.[38] Some recent results both on molecules[29,34] and on crystals[39,40] indicate that the bond polarizability approach can be generalized to higher-order effects as, for instance, quadratic polarizabilities.

In relating the nonlinear polarization source term[41] to the sum of the contributions of all the MU in the crystal, one has to make local-field corrections. The exact values of these corrections are very difficult to evaluate in a closed form. For the organic crystals which we consider the refractive indices are not large (roughly around 1.6), and the local-field corrections are expected to be small. It has been sometimes stressed that

TABLE I. Crystallographic cell parameters and refractive indices of four crystalline substituted benzene: *m*-dinitrobenzene, *m*-nitroaniline, *m*-aminophenol, and *m*-resorcinol. The refractive indices are taken from Refs. 22–26.

	a	b	c	n_x^ω	n_y^ω	n_z^ω	$n_z^{2\omega}$
NO_2–Ph–NO_2	13.257	14.048	3.806	1.706	1.655	1.47	1.49
NO_2–Ph–NH_2	6.5	19.33	5.08	1.72	1.682	1.635	1.724
NH_2–Ph–OH	11.23	6.1	8.28	1.736	1.636	1.562	1.589
OH–Ph–OH	10.53	9.53	5.66	1.558	1.599	1.60	1.634

the π bonding is so spread out that the microscopic field seen by the π electron can be taken on average equal to the applied field. It seems to us that this is too crude a treatment, in particular in the sense that it does not at all account for the crystal symmetry. Nevertheless, it is true that the π electron wave function is rather extended and the field they probe on average smooths out the rapid local-field spatial variations at different points of the unit cell. It is therefore possible to approximate the true local-field effects by using an effective local field E^{loc}, which is assumed to be uniform over the primitive cell. Such an effective field is related to the applied electric field through the tensor f_{IJ}, which at least has the crystal symmetry. Then the macroscopic second-order susceptibility tensor d^{mac} can be written[41]

$$d_{IJK}^{\text{mac}} = f_{II} f_{JJ} f_{KK} d_{IJK} \; , \tag{2a}$$

with

$$E_I^{\text{loc}} = f_{IJ} E_J \tag{2b}$$

and

$$d = \sum_s \beta(s) \; . \tag{2c}$$

In these equations we assume the crystal symmetry to be high enough, so that the tensor f is diagonal in the crystallographic frame.

A well-known approximation to evaluate the local-field factor is to use the anisotropic Lorentz cavity correction (modified spherical) and to put $f_{II} = \frac{1}{3}(n_I^2 + 2)$, where n_I is the refractive index along the I axis. All the compounds that we consider are orthorhombic and the crystallographic cell parameters are too different to justify the use of a spherical cavity calculation as in the Lorentz correction (Table I). A better estimate of the local field may be found by using an ellipsoidal cavity whose axes are chosen proportional to the cell parameters a, b, and c. The ellipsoidal cavity is more consistent with the anisotropic shape of the crystallographic cell. The electric field inside a polarized dielectric ellipsoidal cavity may be found from the solution of the Maxwell equations and of the boundary conditions in electrostatics.[42] In this case the local-field factor along a crystallographic axis I can be written

$$f_{II} = 1 + (n_I^2 - 1) A_I \; . \tag{3}$$

A_I is an elliptic integral which has been extensively tabulated,[43]

$$A_I = \frac{abc}{2} \int_0^\infty [(u+a^2)(u+b^2)(u+c^2)]^{-1/2} \frac{du}{u+a_I^2} \; , \tag{4}$$

where $a_I = a, b,$ and c for $I = 1, 2,$ and 3. The values of the A_I's satisfy $\sum_I A_I = 1$. In the case of a cubic cell ($a = b = c$), $A_I = \frac{1}{3}$ and Eq. (4) yields the customary Lorentz correction. Table I gives the crystallographic cell parameters of the four compounds we analyze as well as the refractive indices for the corresponding directions, the two wavelengths chosen are those of the YAlG:Nd laser and its second harmonic, which were used for all the measurements. Table II compares the modified cavity and the ellipsoidal cavity corrections. In the latter case, the anisotropy of the f tensor is quite large and depends strongly on the cavity shape, i.e., on the crystallographic cell geometry. By contrast the mean values $\frac{1}{3}(f_1 + f_2 + f_3)$ are very

TABLE II. Local-field corrections calculated for a spherical cavity and for an ellipsoidal cavity.

	Modified ellipsoidal cavity				Modified spherical cavity			
	f_x^ω	f_y^ω	f_z^ω	$f_z^{2\omega}$	f_x^ω	f_y^ω	f_z^ω	$f_z^{2\omega}$
NO_2–Ph–NO_2	1.31	1.26	1.79	1.83	1.64	1.58	1.39	1.41
NO_2–Ph–NH_2	1.74	1.16	1.87	2.02	1.65	1.61	1.56	1.66
NH_2–Ph–OH	1.44	1.77	1.46	1.49	1.67	1.56	1.48	1.51
OH–Ph–OH	1.34	1.42	1.76	1.82	1.47	1.52	1.52	1.56

similar in the two cases and are moderately large. Although the ellipsoidal cavity correction may overestimate the magnitude of the actual local field field, it correctly accounts for the crystal anisotropy. For this reason we use the ellipsoidal cavity correction all through this paper, keeping in mind that it is an upper limit of the local-field factors.

The tensor d as well as other various crystal tensors are expressed as a sum of microscopic contributions over the MU which form the crystal. Let us consider a physical property of a crystal described by a tensor T. Usually, in order to use the selection rules owing to the crystal symmetry, the tensor T is expressed by its Cartesian components $T_{IJK\cdots M}$ in the crystallographic axes (X, Y, Z). Now suppose that for the property described by T, the crystal can be decomposed into an assembly of MU labeled by the index (s). Each individual MU has its own set of natural axes $[x^{(s)}, y^{(s)}, z^{(s)}]$, and a microscopic tensor $t(s)$ describing the physical property under analysis. In order to express the MU symmetry $t(s)$ is given in the natural microscopic frame. T must then be written

$$T_{IJK\cdots M}=\sum_{s}\sum_{ijk\cdots m}(\cos\theta_{Ii}^{(s)}\cos\theta_{Jj}^{(s)}$$

$$\times\cos\theta_{Kk}^{(s)}\cdots\cos\theta_{Mm}^{(s)})\,t_{ijk\cdots m}^{(s)}\,, \tag{5}$$

where $\theta_{Mm}^{(s)}$ is the angle between the macroscopic M axis and the microscopic $m^{(s)}$ axis. In an equation such as Eq. (5) *all* the components of $t(s)$ mix to give *one* component of T, and it is almost impossible to follow up to the macroscopic scale the consequences of an hypothesis made on the microscopic scale. It is therefore quite difficult to discuss different types of microscopic models. To keep track of the microscopic symmetry up to the crystal scale, it is necessary to use quantities which *do not mix together* in a change of coordinates frame, i.e., quantities which are *irreducible* with respect to the rotation group.

We now present the irreducible tensor formalism well suited for relating macroscopic tensor properties to the microscopic contribution. Irreducible tensors are widely used in atomic and nuclear physics but are scarcely used in crystal physics. Their introduction in nonlinear optics is owing independently to Maker[44] and to Jerphagnon.[45] An irreducible Cartesian tensor of rank n and weight l has 3^n components, only $2l+1$ of which are independent. They can be chosen so that they transform like the spherical harmonics Y_l^m.[46] A tensor of rank n is generally reducible and can be written as a direct sum of irreducible tensors of weight $l\leq n$; $T=\sum_l T^{(l)}$. The decomposition of reducible tensors of rank two and three can be found in Refs. 45 and 46. The general decomposition scheme as well as the use of irreducible tensors for studying physical properties of crystals are discussed elsewhere.[47] For practical convenience irreducible components of symmetric second- and third-rank tensors are explicitly written in the Appendix.

Since irreducible subspaces are disconnected each irreducible component of the crystal tensor depends only on the microscopic tensors components with same weight, and

$$\left.\begin{aligned}T&=\sum_{s}t^{(s)}\\ T&=\sum_{l}T^{(l)}\end{aligned}\right\}\rightarrow T^{(l)}=\sum_{s}t_{(s)}^{(l)}\,. \tag{6}$$

It will be shown later that each irreducible component has a very specific physical meaning. The fundamental equation (6) expresses the remarkable possibility of separating the microscopic contributions associated with the different irreducible components. As already noted we may choose the $2l+1$ components of $T^{(l)}$ so that they transform like the spherical harmonics. Consequently the equivalent of Eq. (5) for each irreducible component of T is

$$T_l^m=\sum_{s}\sum_{m'}R_{m'm}^{(l)}(\psi^{(s)},\theta^{(s)},\phi^{(s)})\,t_l^{m'}(s)\,,$$

where $R_{m'm}^{(l)}$ is the Wigner matrix associated with the change of a coordinates frame. The Euler angles of the natural axes of the MU labeled (s) are $\psi^{(s)}$, $\theta^{(s)}$, and $\phi^{(s)}$.

It has to be noted in fact that the practical use of the expression of T_l^m is very simple. It is well known that the Wigner matrix can be written $R_{m'm}^{(l)}=e^{-im'\psi}r_{m'm}^{(l)}(\theta)\,e^{-im\phi}$. The matrices $r_{m'm}^{(l)}(\theta)$ are tabulated up to $l=7$ in Ref. 48. Furthermore, owing to crystal symmetry for each MU in the crystallographic unit cell there must be number of identical MU obtained by simple geometric operations. Let us call V the volume of the unit cell and use the label (s) to characterize the groups of nonequivalent MU, and the index (r) to distinguish among the equivalent MU within a group. All the MU within a group, i.e., with same (s) index have the same microscopic tensor $t(s)$ so that T_l^m can be rewritten

$$T_l^m=\frac{1}{V}\sum_{s}\sum_{m'}t_l^{m'}(s)\left(\sum_{r}R_{m'm}^{(l)}(\psi^{(r)},\theta^{(r)},\phi^{(r)})\right)\,. \tag{7}$$

In almost all practical cases the sum in large parenthesis is straightforward to calculate. We illustrate this with an example, which will be useful later on. Consider a crystal whose point group is $mm2$, built up of MU whose microscopic point group is also $mm2$. In general there are four identical MU of each type in the unit cell. Therefore if one MU has the set of Euler angles (ψ, θ, ϕ), there are in the cell three other identical MU whose sets of Euler angles are: $(\psi, \theta, \phi + \pi)$, $(-\psi, \theta, -\phi)$, and $(-\psi, \theta, \pi - \phi)$. Using these values in the sum into curly brackets of Eq. (7) we obtain

$$T_l^m = \frac{1}{V} \sum_{s, m'} t_l^{m'}(s)\{2[1 + (-1)^{m'}] \times [\cos(m'\psi^{(s)} + m\phi^{(s)})] r_{m'm}^{(l)}(\theta^{(s)})\} . \tag{8}$$

To apply this theory to the optical susceptibility tensors, we must discuss the form and meaning of their irreducible components.

The general decomposition of the linear and of the second-order susceptibility tensor has been given in Ref. 45. The linear case is well known. For a nonabsorbing crystal it is a symmetric second-rank tensor (six independent components), which is the direct sum of a scalar ($l = 0$, one component) and a deviator ($l = 2$, five components). The scalar describes the average susceptibility, for example, as measured in liquid phase. The deviator describes the anisotropy of the susceptibility and is therefore directly connected with the birefringence. The case of the second-order susceptibility is less well known. In the most general configuration[45] it involves seven irreducible parts. One pseudoscalar ($l = 0$), three vectors ($l = 1$), two pseudodeviators ($l = 2$), and one septor ($l = 3$), which all together correspond to the number of independent Cartesian components ($3^3 = 27 = 1 \times 1 + 3 \times 3 + 2 \times 5 + 1 \times 7$).

The pseudoscalar and the pseudodeviators always contain differences of Cartesian components with identical indices but arranged in different orders. For example, the only component of the pseudoscalar is $d_0^0 \simeq \frac{1}{6}(d_{123} - d_{132} + d_{231} - d_{213} + d_{312} - d_{321})$. They therefore characterize how far the spatial indices and the frequency indices are independent. The pseudoscalar has the same symmetry as the rotatory power in liquid phase and describes frequency mixing in a noncentered isotropic medium.[49] It vanishes for second-harmonic generation or more generally when two of the frequencies involved are equal. The pseudodeviators have the same symmetry as the structural part of the rotatory power.[50] They describe the dispersion of the susceptibility tensor in the crystalline state. The two pseudodeviators become equal when two frequencies become equal, for example, in the case of second-harmonic generation or the static electro-optic effect. They vanish if the system exhibits no dispersion, i.e., if the so-called Kleinman symmetry[51] holds. The three vectors are the traces of the susceptibility tensor ($\sum_J d_{IJJ}$, $\sum_J d_{JIJ}$, and $\sum_J d_{JJI}$). Two of them are equal when two frequencies are equal, and they are all equal if the system exhibits no dispersion. Finally, the septor involves differences of Cartesian components having different indices such as $(2d_{333} - 3d_{322} - 3d_{311})$. It describes a deviation from isotropy (for an isotropic system $d_{333} = 3d_{322} = 3d_{311}$).

Selection rules owing to crystal symmetry can result in a vanishing vector or septor. The vector only exists in the ten polar crystal classes, whereas the septor exists alone in the eight classes 222, 23, 32, $\bar{4}$, $\bar{4}2m$, $\bar{4}3m$, $\bar{6}$, and $\bar{6}m2$.

In the transparency domain of the system where dispersion is negligible, the frequency dependence of the susceptibility tensor is irrelevant d_{IJK} becomes fully symmetric in the exchange of its Cartesian indices and depends on ten independent parameters. The three components of the unique vector left provide three parameters and the septor the seven others. In this case the susceptibility tensor and its irreducible parts describe the geometrical properties of the system. For a system having a center of symmetry, the second-order susceptibility tensor vanishes. This tensor therefore measures how far a system is from having a center of symmetry. Consider a highly symmetric system which is isotropic and centered. Under an axial perturbation it loses its symmetry center and gains a third-rank tensor, with only a vector part. An octupolar perturbation also eliminates the symmetry center but in this case the system gains a third-rank tensor with only a septor part.

The decomposition of the susceptibility tensor into two irreducible parts means that as far as third-rank tensors are concerned the most general noncentered system can be obtained from an isotropic and centered system by application of two independent perturbations, one with dipole symmetry and the other with octupole symmetry. This geometrical interpretation of the susceptibility tensor and its irreducible components will be used throughout this paper.

Coming back to our example of a system with point group $mm2$, there is one component for the vector part (along the polar axis) and two components for the septor part,

$$T_1^0 = \sqrt{\tfrac{3}{5}}(T_{333} + T_{322} + T_{311}) , \tag{9a}$$

$$T_3^0 = (1/\sqrt{10})(2T_{333} - 3T_{322} - 3T_{311}) , \tag{9b}$$

$$T_3^{\pm 2} = \sqrt{\tfrac{3}{4}}(T_{311} - T_{322}) . \tag{9c}$$

These can be expressed as the sum of the contributions of the MU for which we also assume the point group $mm2$. According to Eq. (6),

$$T_1^0 = \frac{1}{V} \sum_s 4(\cos\theta)\, t_1^0 , \tag{10a}$$

$$T_3^0 = \frac{1}{V} \sum_s 2(5\cos^3\theta - 3\cos\theta)\, t_3^0$$

$$+2(\sqrt{30}\cos 2\psi\cos\theta\sin^2\theta)\,t_3^2\,, \qquad (10b)$$

$$T_3^2=\frac{1}{V}\sum_s(\sqrt{30}\cos 2\phi\cos\theta\sin^2\theta)\,t_3^0$$
$$+[2\cos 2\psi\cos 2\phi\cos\theta(3\cos^2\theta-1)$$
$$+4\sin 2\psi\sin 2\phi(1-2\cos^2\theta)]\,t_3^2\,, \qquad (10c)$$

where the index (s) in the expressions under the summation sign has been dropped for simplicity.

Finally, let us consider another useful example, the case of the linear susceptibility tensor of an uniaxial system built up from uniaxial MU. χ is the susceptibility tensor of the system, and α is that of the MU. In the transparency domain χ and α are symmetric tensors having two irreducible parts, a scalar and a deviator, which can be written in terms of the Cartesian components $\chi_{ZZ}=\chi_\parallel$, and $\chi_{XX}=\chi_{YY}=\chi_\perp$,

$$\chi=(\chi_\parallel+2\chi_\perp)/\sqrt{3}, \quad \delta\chi=\sqrt{\tfrac{2}{3}}(\chi_\parallel-\chi_\perp)\ . \qquad (11)$$

Equivalent expressions hold for α. The additivity scheme is simply written

$$\chi=\sum_s\alpha, \quad \delta\chi=\sum_s\frac{3\cos^2\theta-1}{2}\delta\alpha\ , \qquad (12)$$

where θ is the angle between the system optic axis and the MU optic axis. These forms do not include local-field factor, they apply as they are to molecules considered as the sum of uniaxial building blocks such as biatomic bonds. In the case of crystals, the local-field factors have to be written explicitly[52] or should be included in the definition of the polarizabilities.[3]

III. ADDITIVITY APPROACH FOR SUBSTITUTED BENZENE

The molecules constituting the considered crystals are substituted benzene. The benzene molecule is an hexagonal centered system whose point group is $6/mmm$. It exhibits no second-order optical effects. The second-order optical susceptibilities of the substituted benzene are consequences of the change of symmetry owing to the substitution, and it is necessary to analyze the effect of the substituent group on the benzene molecule. This molecule is formed by six σ(C–C) bonds, six σ(C–H) bonds and a system of six delocalized π-electrons. The individual C–H bonds are accentric, but their overall contribution vanishes because of the symmetric positions of the six bonds. The C–C bonds and the π-ES are individually centered and give no contribution. The replacement of a hydrogen atom by a radical R has three effects. First, one of the C–H bonds is replaced by the C–R group and the geometrical cancellation of the C–H bonds is eliminated. The symmetry of the σ(C–C) is destroyed by the so-called inductive effect of the radical,[53] which is a short-range effect that also appears in the saturated molecules. Finally, the radical has a "nonclassical inductive effect[54]" on the π electrons and may also contribute to the π bonding by the mesomeric effect.[54]

The first two consequences of the substitution are the same in aliphatic and aromatic molecules, and should, therefore, induce second-order nonlinearities of the same magnitude. For example, one can expect the substitution and the inductive effect on the sigma bonds in nitrobenzene to be of the same order of magnitude as they are in nitromethane. Some recent measurements on substituted saturated molecules by Hauchecorne *et al.*,[32] Levine and Bethea,[33] and Ward and Bigio[34] show that the second-order polarizabilities of aliphatic molecules are only a few per cent different from those of aromatic molecules. Thus we attribute the nonlinear susceptibilities of substituted benzene almost entirely to the distortion of the delocalized π electrons.

To describe the nonlinear susceptibility of disubstituted benzene we make the hypothesis of the additivity of the nonlinear susceptibilities associated with a radical bound to a benzene ring. This type of additivity approach seems to be very different to that usually admitted and may at first glance be surprising. But if we consider the geometrical interpretation of the second-order susceptibility tensor developed in Sec. II we see that we are indeed assuming the additivity of the distortions of a centered system under application of two perturbations. From this point of view our hypothesis is more reasonable and should at least be a sensible starting point. It is possible to gain an idea of the accuracy of this hypothesis by looking at the difference between the observed dipole of disubstituted benzene and the dipole calculated from the additivity hypothesis.[55] For the *meta*-disubstitutes the agreement is better than 6%, but for *ortho*- and *para*-disubstitutes the agreement is in some cases not better than 20%. Luckily all the disubstituted benzene for which we have reliable experimental data have radicals in *meta* positions.

The crystal structures of the four compounds considered are given in Refs. 56–58. They all belong to the crystallographic point group $mm2$. In each cell there are four identical molecules. Since the MU are chosen as a radical bound to a benzene ring, there are three different MU to consider; (Ph–NO_2), (Ph–OH), and (Ph–NH_2) which correspond, respectively, to the values 1, 2, and 3 of the superscript (s). The point group symmetry of the MU is very close to $mm2$ so that Eqs. (10a)–(10c) directly apply to the four crystals.

It is necessary to define the microscopic axes of the MU in the crystals. According to the x-ray data the centers of the six carbon atoms are not strictly speaking in a plane, but are found within a small dihedral angle (< 5° for all four compounds). By a mean-square program we calculate a "mean plane" for the benzene ring that we choose as the yz plane. The normal to this plane at the center of the ring is the x axis. The line joining the center of the ring to the first atom of the substituent group generally makes a small angle (<1°) with the yz plane. We take the projection of this line on the "mean ring plane" as the z axis. y is taken perpendicular to the other two axes. For each MU the microscopic axes *in situ* are defined according to these lines, they determinate the Euler angles (Fig. 1) and therefore the geometrical factors appearing in Eqs. (10a)–(10c).

The macroscopic nonlinear susceptibilities are available from the experimental data, the microscopic hyperpolarizabilities are unknown. Let the superscript (u) cover the four compounds under analysis. Equations (10) can be written for the vector and the septor parts of the four crystals as a set of linear equations

$$d_1^0(u) = A_{00}^{(1)}(u, s)\beta_1^0(s) \ , \tag{13a}$$

$$d_3^0(u) = A_{00}^{(3)}(u, s)\beta_3^0(s) + A_{02}^{(3)}(u, s)\beta_3^2(s) \ , \tag{13b}$$

$$d_3^2(u) = A_{20}^{(3)}(u, s)\beta_3^0(s) + A_{22}^{(3)}(u, s)\beta_3^2(s) \ . \tag{13c}$$

The numerical factors $A_{mm'}^{(l)}$ are calculated from the x-ray data on the four crystal structures. The 12 $d_l^m(u)$ are known, and the nine $\beta_l^m(s)$ are overdetermined. To obtain a best fit we use a multiple regression program to minimize the standard deviation as described in Ref. 39. In the regression various weights can be attributed to the experimental data; if the weight is the same for all equations then the fit tends to optimize the larger observed constants. We have used a weight giving equal importance to all experimental observations ($\omega_i = 1/d_i^2$ with the notations of Ref. 39). This is more consistent with the fact that the relative accuracy claimed by the experimentalists is roughly the same (≃ 20%). The best fit gives a mean relative deviation $N^{-1}\sum_s^N (d_{\text{cal}} - d_{\text{exp}})/d_{\text{exp}}$ of 10%, which compares well with the experimental accuracy and indicates that the additivity approach gives correct results. When an equal weight is given to all the equations, then the average mean deviation is larger but the values of the $\beta(s)$ remain remarkably constant. The Cartesian components of the macroscopic nonlinear susceptibilities are listed in Table III. Experimentally it has been verified for each crystal that the three nonlinear coefficients have the same sign, but there is no absolute sign determination at the moment. The fit for the vector part ($\simeq d_{311} + d_{322} + d_{333}$) is only possible with a set of signs, which are indicated between brackets in Table III. Our analysis, therefore, provides a direct and simple method discriminating among the possible absolute signs for all the nonlinear

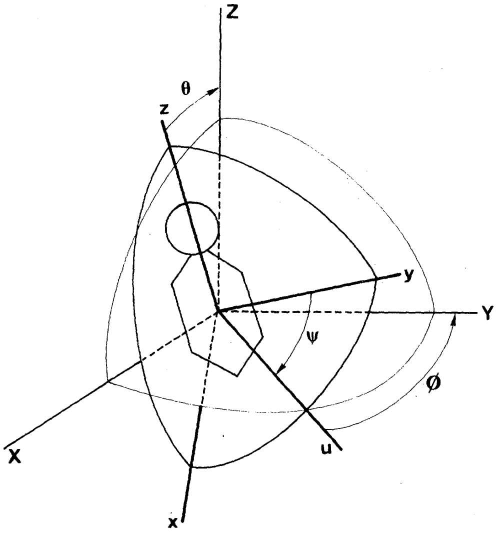

FIG. 1. Definition of the Euler angles of the microscopic units.

TABLE III. Experimental nonlinear susceptibilities relative to d_{11} (SiO_2) of the four crystalline substituted benzene. The signs in parenthesis are those which correspond to the best fit.

	d_{31}	d_{32}	d_{33}
NO_2–Ph–NO_2[a]	(+) 1.5	(+) 5.9	(+) 1.4
NO_2–Ph–NH_2[b]	(+) 27	(+) 3	(+) 32
NH_2–Ph–OH[c]	(–) 4.7	(–) 1.5	(–) 6.6
OH–Ph–OH[b]	(–) 1.8	(–) 4.5	(–) 3.7

[a] See Ref. 26.
[b] See Ref. 24.
[c] See Ref. 25.

TABLE IV. Experimental and calculated spherical components of the crystal nonlinear susceptibilities (in 10^{-9} esu). Best fit for the spherical components of the microscopic quadratic polarizabilities (in 10^{-30} esu).

		d_1^0	d_3^0	d_3^2
NO_2–Ph–NO_2	experimental	2.6	−2.7	−1.6
	calculated	2.9	−3.4	−1.4
NO_2–Ph–NH_2	experimental	9.3	−2.8	3.4
	calculated	7.0	−2.2	3.1
NH_2–Ph–OH	experimental	−3.6	0.5	−1.3
	calculated	−3.7	0.5	−1.3
OH–Ph–OH	experimental	−2.3	1.5	0.7
	calculated	−2.3	1.6	0.6

	β_1^0	β_3^0	β_3^2
Ph–NO_2	−1.42	−1.35	−0.03
Ph–NH_2	1	0.43	0.07
Ph–OH	0.37	0.17	0.18

coefficients. In Table IV we give the experimental spherical components of the *d* tensors, the best fit for the $\beta(s)$, and the calculated spherical components of the *d* tensors using the best fit.

We have also performed the same calculation with the modified Lorentz local-field factors, in order to check the effect of this the correction. In this case the average mean deviation is not better than 20% but again the values of the $\beta(s)$ giving the best fit do not vary drastically.

The accuracy of the best fit is better than the experimental uncertainty. This result provides a good confirmation of the first step of our analysis. It shows that the nonlinear susceptibilities of substituted benzene can be accounted for by the additivity of the nonlinearities associated with substituent groups bound to a benzene ring. We now examine in Sec. IV how the microscopic nonlinearities can be explained.

IV. ORIGINS OF THE SECOND-ORDER NONLINEARITIES OF SUBSTITUTED AROMATIC MOLECULES

The interactions of substituent groups with unsaturated molecules have been studied extensively by Sutton and his co-workers.[36,37,54] They may be analyzed in the following way. First the electric field of the substituent group may polarize the σ bonds of the aromatic molecule giving rise to the *inductive effect* similar to that in saturated molecules. This effect falls steadily with distance from the inducing group and dies down rapidly.[59] The substituent group also interacts with the π electrons of the molecule. This is because of the delocalization of the π-ES is a long-range effect and it can be decomposed into two parts. The substituent may participate in the π orbitals giving rise to the *mesomeric effect,* it can also through *nonclassical inductive effect* so much affect the conjugated system in the molecule that the π-bond order is changed.[54] The last two effects occur through the same medium. They are therefore not independent, and both result in a drift of electrons to or from the substituent group. Chemists have sought for a quantity to characterize the overall interactions of the various substituent groups with the conjugated electrons of aromatic molecules. This quantity is the *mesomeric moment* $\Delta\mu$ originally introduced by Sutton.[36] It is defined as the moment resulting from the substitution of the π-ES alone. The sign of $\Delta\mu$ yields to the well-known classification of substituents into donor and acceptor groups, which successfully explains the directed chemical activity of substituted benzene molecules. In practice $\Delta\mu$ can be measured by the difference in dipole moment between the substituted aromatic molecule and a suitable aliphatic molecule with the same substituent group. This aliphatic molecule must be such that its dipole reproduces as far as possible the moment of the σ bonds of the aromatic molecule. This results in some discrepancy among the values quoted in the literature, even in the case of the most common radicals[36,53,54,60–62] [NH_2, OH, NO_2, CN, $N(CH_3)_2$, CHO, ...]. In fact, only the over-all dipole of the molecule can be directly measured and several corrections have to be considered to isolate the moment of the π electrons, such as, for instance, the change in moment of the σ bonds from the aliphatic molecules to the aromatic molecules. These corrections vary slightly according to the various authors, and this has some important bearing on the values of $\Delta\mu$ which appear as the difference of two moments of the same order of magnitude. Nevertheless the *sign* of the mesomeric moment is well established and the absolute values are consistently defined within a factor of 2. The chemists were interested in explaining the directed chemical activation of the benzene substitutes and only considered dipole moments. The approach is, however, more general and along these lines we can consider the relevance of this analysis to high-order multipoles, which can now be observed using the techniques of nonlinear optics.[6]

The first point to be noted in the vector part of the MU in Table IV is that the sign of $\beta_1^0(\text{Ph–NO}_2)$ is opposite to those of $\beta_1^0(\text{Ph–OH})$ and $\beta_1^0(\text{Ph–NH}_2)$. NO_2 is an acceptor group (*meta*-directing), while NH_2 and OH are donor groups (*ortho-para*-directing). The vector part of the MU second-order polarizabilities has no obvious connection with the total moment of the molecule, but has the same sign as the moment of the π-ES. This tends to confirm our attribution of the major part of the nonlinear response of the molecule to the delocalized electrons. As in inorganic crystals the vector part of the second-order polarizabilities seems to be strongly correlated with the permanent dipole moment of the system[45] *responsible* for the nonlinear susceptibility.

The benzene molecule π-ES is centered and the dipole induced on it by an intense electric field E is given by

$$p = \alpha E + \gamma E^3 \ . \tag{14}$$

In this equation α and γ are the linear and cubic π-ES polarizability tensors. According to the choice of axes defined in Sec. II and Fig. 2, the nonvanishing elements of the polarizability tensors are $\alpha_\parallel = \alpha_{11}$, $\alpha_\perp = \alpha_{22} = \alpha_{33}$; $\gamma_\parallel = \gamma_{1111}$, $\gamma_\perp = \gamma_{2222} = \gamma_{3333} = 3\gamma_{3322}$, and $\gamma_{\parallel\perp} = \gamma_{1122} = \gamma_{1133}$. Here again we only consider the transparency domain and neglect the dispersion so that α and γ are symmetric under permutations of their Cartesian indices.

The mesomeric and nonclassical inductive effects are quantum mechanical. Their overall con-

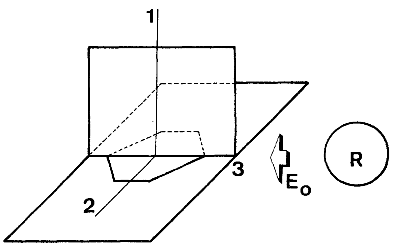

FIG. 2. Definition of the axes of the perturbated and unperturbated systems.

sequence is the appearance of the mesomeric dipole $\Delta\mu$. The mesomeric dipole arises from the action of the substituent group along the axis (3), Fig. 2. It is possible to interpret the interaction of the substituent group with the π-ES as equivalent to a certain field E_0 such as $\Delta\mu = \alpha E_0$. According to this interpretation the mesomeric and nonclassical inductive effects not only create a permanent dipole, but they distort the electronic distribution modifying the polarizabilities and creating multipole moments. When an external field is applied to a substituted benzene molecule, the π-ES dipole is equal to the dipole of the π-ES of the benzene molecule under the total field $E_T = E + E_0$. Then according to Eq. (14) we have

$$p = \alpha E_0 + \gamma E_0^3 + (\alpha + 3\gamma E_0^2)E + 3\gamma E_0 E^2 + \gamma E^3 + \cdots$$

$$= \Delta\mu + \alpha' E + \beta E^2 + \gamma E^3 + \cdots \ . \tag{15}$$

In addition to the creation of the mesomeric moment $\Delta\mu = \alpha E_0 + \gamma E_0^3 \simeq \alpha E_0$, the substitution results in a modification of the linear susceptibility related to the optical exaltation, and in the appearance of a second-order susceptibility $\beta = 3\gamma E_0$. The linear polarizability becomes $\alpha + 3\gamma E_0^2$. We do not consider the effect of the substitution on the linear susceptibility in the present paper, but concentrate on the second-order susceptibility. A full calculation, keeping track of the tensor nature of the quantities involved in Eq. (15) as well as the transformation from static field to periodic field responses, has been given in Ref. 35. The elements of the second-order polarizability tensor measured in second-harmonic generation can be expressed in terms of the third-order polarizability tensor elements measured in third-harmonic generation by the following relations[35]:

$$\beta_{33} = 3\beta_{32} = 6(\gamma_\perp/\alpha_\perp)\Delta\mu \ , \tag{16a}$$

$$\beta_{31} = 6(\gamma_{\parallel\perp}/\alpha_\perp)\Delta\mu \ . \tag{16b}$$

The original system belongs to the point group $6/mmm$. Owing to the axial symmetry along the z axis of the perturbation, the perturbed π-ES now belongs to the orthorhombic point group $mm2$. The unperturbed system has a sixfold axis along x, and is isotropic in the plane (yz) for tensors up to the fifth rank. This particular symmetry results in the relation $\beta_{33} = 3\beta_{32}$. According to the linear combinations of Cartesian components indicated in Eqs. (10a)–(10c), the spherical components of the β tensor are

$$\beta_1^0 = 2\sqrt{\tfrac{3}{5}}[(4\gamma_\perp + 3\gamma_{\parallel\perp})/\alpha_\perp]\Delta\mu \ , \tag{17a}$$

$$\beta_3^0 = (6/\sqrt{10})[(\gamma_\perp - 3\gamma_{\parallel\perp})/\alpha_\perp]\Delta\mu \ , \tag{17b}$$

$$\beta_3^{\pm 2} = \sqrt{3}[(3\gamma_{\parallel\perp} - \gamma_\perp)/\alpha_\perp]\Delta\mu \ . \tag{17c}$$

This form can be explained by use of the parentage scheme of irreducible tensors[46] as follows. The cubic polarizability tensor has three components in the dispersionless configuration, a scalar $(j=0)$, a deviator $(j=2)$, and a nonor $(j=4)$. For the benzene π-ES the sixfold axis is equivalent to axial symmetry for γ and only its $m=0$ spherical components do not vanish. They are $\gamma_0 = \frac{1}{15}(3\gamma_\parallel + 8\gamma_\perp + 15\gamma_{\parallel\perp})$, $\gamma_2^0 = \frac{1}{21}(3\gamma_\parallel - 4\gamma_\perp + 3\gamma_{\parallel\perp})$, and $\gamma_4^0 = \frac{1}{35}(\gamma_\parallel + \gamma_\perp - 6\gamma_{\parallel\perp})$. The equivalent field E_0 is a tensor with weight $j=1$. According to the rules of composition of spherical tensors, when E_0 is multiplied by a tensor of weight j it gives three tensors of weight $j-1$, j, and $j+1$. The vector part of β, therefore, comes from the multiplication of E_0 by the scalar and the deviator, whereas the septor part comes from the multiplication by the deviator and the nonor,

$$\beta_1^0 = 2\sqrt{\tfrac{3}{5}}(5\gamma_0 - 7\gamma_2^0)(\Delta\mu/\alpha_\perp) \ , \tag{18a}$$

$$\beta_3^0 = (9/\sqrt{10})(5\gamma_4^0 - \gamma_2^0)(\Delta\mu/\alpha_\perp) \ , \tag{18b}$$

$$\beta_3^{\pm 2} = 3\sqrt{3}(\gamma_2^0 - 5\gamma_4^0)(\Delta\mu/\alpha_\perp) \ . \tag{18c}$$

To obtain numerical results the π-ES linear and cubic polarizabilities have to be evaluated. The linear polarizabilities of the benzene molecule,[38] and those of the σ(C–C) bonds,[63] and σ(C–H) bonds[63] are well known. All the electron systems in the benzene molecule being uniaxial, Eq. (12) applies directly. They can be written

$$\delta\alpha_{C_6H_6} = -\tfrac{1}{2}(6\delta\alpha_{CC} + 6\delta\alpha_{CH}) + \delta\alpha_{\pi\text{-ES}} \ , \tag{19}$$

$$\alpha_{C_6H_6} = 6\alpha_{CC} + 6\alpha_{CH} + \alpha_{\pi\text{-ES}} \ .$$

The resolution of these equations gives[35] $\alpha_\parallel(\pi\text{-ES}) = 2.34\times10^{-24}$ esu and $\alpha_\perp(\pi\text{-ES}) = 3.45\times10^{-24}$ esu. This last result is in agreement with the two theoretical calculations by Bolton[64]; $\alpha_\parallel(\pi\text{-ES}) = 3.3\times10^{-24}$ esu and $\alpha_\perp(\pi\text{-ES}) = 4\times10^{-24}$ esu.

The cubic polarizability has recently been measured by Hermann[28] using third-harmonic generation in liquid benzene. He found $\Gamma_{C_6H_6} = (1.74 \pm 0.58)\times10^4[d_{11}(\text{SiO}_2)]^2 = 2.5\times10^{-14}$ esu. In liquid phase the molecules are oriented at random, the contribution of all the irreducible components with nonzero weight vanishes by geometrical average and $\Gamma_{C_6H_6} = Nf^4\gamma_0^B$, where N is the number of molecules per unit volume and f is the Lorentz local-field factor. This gives $\gamma_0^B = 9\times10^{-37}$ esu with an accuracy of 30%.

It is now necessary to isolate the π-ES contribution. Hermann and Ducuing[29] have experimentally proved the validity of the additivity scheme for the scalar part of the polarizability of saturated molecules involving only $\sigma(C-C)$ and $\sigma(C-H)$ bonds (see Fig. 1 of Ref. 29). The contribution of the σ bonds of the benzene molecule can therefore be calculated according to

$$\gamma_0^\sigma = 6\gamma_0^{CC} + 6\gamma_0^{CH}$$
$$= \gamma_0(C_6H_{14}) - 2\gamma_0(CH_4) = 0.13\times10^{-36} \text{ esu} ,$$

so that we can take $\gamma_0^{\pi\text{-ES}} = 0.77\times10^{-36}$ esu. It is apparent from Eq. (18) that a full calculation also requires knowledge of the deviator and the nonor. Unfortunately, this information is not at present available and so we have to use approximations to get numerical results. From the geometry of the π-ES in the benzene molecule we can expect the polarizability component in the plane perpendicular to the ring to be quite small compared with that in the ring plane. Calculations by Schweig[65] tend to support this hypothesis, he also points out that $\gamma_\perp^{\pi\text{-ES}} \gg \gamma_\parallel^{\pi\text{-ES}}, \gamma_{\parallel\perp}^{\pi\text{-ES}}$. Thus, finally, we can take for our numerical calculations

$$\gamma_\perp^{\pi\text{-ES}} = 1.44\times10^{-36} \text{ esu}, \quad \gamma_{\parallel\perp}^{\pi\text{-ES}} \simeq 0 .$$

We are now left with only one independent quantity, i.e., $(\gamma_\perp/\alpha_\perp)\Delta\mu$, and the vector and septor parts of β are dependent,

$$\beta_3^0 = \tfrac{1}{4}\sqrt{\tfrac{3}{2}}\,\beta_1^0, \quad \beta_3^2 = -\sqrt{\tfrac{5}{8}}\,\beta_1^0 . \tag{20}$$

This relation is certainly owing to the oversimplified model, which results from our lack of information about the cubic polarizability. In fact, since the mesomeric moment is equivalent to a static field, the true tensor to use should be $\gamma(2\omega = \omega + \omega + 0)$, which is not symmetric. Unfortunately, at the present time we have reliable data only on the third-harmonic generation tensor. We should not be surprised if the numerical calculations are not very accurate.

TABLE V. Vector part of the quadratic polarizabilities calculated from the model and determinated from the best fit. ($\Delta\mu$ is in 10^{-18} esu and is β_l in 10^{-30} esu.)

Substituent group	$\Delta\mu$	Reference	β_1^0 (calculated)	β_1^0 (best fit)
OH	+0.12	60	+0.3	+0.37
	+0.25	62	+0.65	
NH_2	+0.32	53	+0.83	+1
	+1	54	+2.6	
NO_2	−0.88	36	−2.3	−1.42
	−0.79	62	−2	
	−0.76	54	−1.9	
	−0.3	60	−0.8	
	−0.3	61	−0.8	

In Table V we compare for the three substituent groups OH, NH_2, and NO_2, the vector part β_1^0 calculated from Eq. (17a), and the various values of the mesomeric moments, which can be found in literature, with the value obtained from the best fit in Sec. II. As can be seen the sign agrees very well showing that the sense of the electronic flow to or from the substituent groups is directly linked to the vector part. Moreover, the magnitude of the best fit lies within the range of values calculated from the various mesomeric moments and is rather close to their average value. The model correctly accounts for the vector part of the microscopic units. For the two septor components in Table VI, we compare their ratio to β_1^0, as given by the best fit to the theoretical ratio obtained from Eq. (20). In the case of the $m = 0$ component the sign is correct and the magnitude although inaccurate is in satisfactory agreement for OH and NH_2. It is worth noting that these are the two radicals for which the hypothesis of an axially symmetric perturbation is most likely to be a sensible one, whereas for NO_2 the size of the two oxygen atoms may result in more complicated interactions. For the $m = 2$ component the sign is reversed. There are several reasons which may explain this discrepancy. First, within the content of the model we have neglected $\gamma_{\parallel\perp}$; this quantity is suspected to be small but so far there are no experimental data on it to support this assumption. Another questionable point is the validity of Kleinman symmetry. The relevant tensor is $\gamma(2\omega = \omega + \omega + 0)$ for which the hexagonal symmetry implies that

$$\gamma_{3}^{2\omega}{}_{3}^{\omega}{}_{3}^{\omega}{}_{3}^{0} = \gamma_{3}^{2\omega}{}_{2}^{\omega}{}_{2}^{\omega}{}_{3}^{0} + 2\gamma_{2}^{2\omega}{}_{3}^{\omega}{}_{2}^{\omega}{}_{3}^{0} ,$$

but

$$\gamma_{3}^{2\omega}{}_{2}^{\omega}{}_{2}^{\omega}{}_{3}^{0} \neq \gamma_{2}^{2\omega}{}_{3}^{\omega}{}_{2}^{\omega}{}_{3}^{0} .$$

We have no indication how far these two components are different and this may have some consequences for the value predicted by the model. The only experimental data available upon the breaking of Kleinman symmetry in this type of molecule are those of Levenson and Bloembergen on liquid benzene.[66] For visible frequencies, they measured $\Gamma_{2323} = 1.2\Gamma_{3223}$ for the process $\omega_1 + \omega_1 - \omega_2 \rightarrow \omega_3$ far from any vibrational resonance.

TABLE VI. Theoretical and experimental ratio of the septor component to the vector component.

		β_3^0/β_1^0	β_3^2/β_1^0
Model		+0.31	−0.28
Experimental	Ph–OH	+0.46	0.48
	Ph–NH_2	+0.43	0.07
	Ph–NO_2	+0.95	0.02

A much more serious point is that which is connected with the symmetry of the perturbation. We have shown in Sec. II that the most general perturbation should have a part with dipole symmetry (angular dependency Y_1^m), and a part with octupole symmetry (angular dependency Y_3^m). By symmetry the equivalent field E_0 can only account for the first part of the perturbation. Therefore it can be expected that the vector part β_1^0 is well described. For the septor part several terms should be considered. A contribution which comes from the anisotropy of the unperturbed system [a dipole perturbation can give a septor through the coupling with the deviator Y_2^m and the nonor Y_4^m part of the cubic polarizability, see Eq. (18)]. Another contribution is due to the octupole coupling of the radical to the benzene ring. This might be the major contribution, but lack of information about this part of the perturbation prevents us from taking it into account. We think that this is the reason for the discrepancy between β_3^0 and β_3^2. In fact, no measurement by linear optical techniques can give information on the octupole coupling of the radical to the benzene ring. This coupling could be quite large especially for NO_2 because the oxygen atoms are large and polarizable and can therefore interact with the π-ES. We may look at the problem the other way around, and consider that nonlinear optics combined with irreducible tensor analysis gives direct access to parameters not measurable by other means. The geometrical analysis of Sec. III supports the additivity approach and should provide us with tables of physico-chemical parameters as useful as the mesomeric moments and which might be used to explain the chemical properties of substituted aromatic molecules.

CONCLUSIONS

We have developed a theory well suited to proceed to the geometrical analysis of crystal tensors in terms of the contributions from microscopic units. It is based on the decomposition of Cartesian tensors into irreducible Cartesian tensors, and their relationships to the spherical tensors. Its most interesting result is the separation of the contributions of microscopic tensors with different weights. We have applied the theory to the second-order susceptibility tensors of four molecular crystals with related structures and involving related aromatic molecules. The geometrical analysis shows that it is possible to account for the crystal nonlinearities by attributing definite microscopic quadratic polarizability tensors to substituent groups bound to a benzene ring. This type of additivity may seem different from the usual bond additivity, but the quadratic polarizability is indeed connected with the distortion of a centered system such as the π electrons of benzene. Our approach shows that the distortions of benzene disubstitutes are the sum of the distortion owing to the two substituents and that the crystal may be described as the geometrical sum of the molecules. We also presented a simple model explaining the microscopic polarizability as arising from the mesomeric and nonclassical inductive effects of the substituent groups on the delocalized electrons. This model correctly accounts for the vector part of the second-order polarizability tensor as well as for the $m=0$ component of the septor part. There are some discrepancies between the prediction of the model and the microscopic $m=2$ components determined by the additivity approach. Several reasons can be put forward to explain these discrepancies; the most likely is that the interaction of the substituent with the radical not only produces a distortion with dipole symmetry for the mesomeric moment, but may also produce an octupolar perturbation. This type of interaction induces modifications of the electronic distribution of the π-electron system, which cannot be reached by linear optical techniques. Reversing the point of view we can consider the microscopic septors resulting from the geometrical analysis as a measurement of the octupolar perturbation of the substituent groups. The additivity of the septor parts shows that these quantities can be attributed specifically to the substituent groups. It therefore appears to us that nonlinear optics and irreducible tensor analysis provide new information on molecular electronic distributions, which is complementary to that ususally considered in physical chemistry and may be useful as, say, the dipole moments.

A last comment can be put forward concerning our approach. In Equation (16) quantities which characterize the unperturbed system are isolated in parenthesis, whereas the mesomeric moment is specific to the substituent group, i.e., the perturbation. Although the exact value to be assigned to γ in this equation may be a matter for discussion, the form of this equation is likely to be valid for many substituted conjugated molecules, It is therefore possible to optimize the π-ES and the substituent group independently. On the other hand, the linear polarizability and the absorption bands of numerous organic radicals are well known. A molecular engineering approach to design *a priori* the linear and nonlinear optical susceptibility as well as the transparency domain of organic compounds is very likely to be developed soon.

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APPENDIX: IRREDUCIBLE COMPONENTS OF SECOND- AND THIRD-RANK CARTESIAN TENSORS.

To form the irreducible components with weight (l) of a symmetric Cartesian tensor, one can express the spherical harmonics Y_l^m as a function of the three components of a unit vector, $x = \sin\theta\cos\phi$, $y = \sin\theta\sin\phi$, and $z = \cos\theta$, and build up the linear combination of tensor components whose indices reproduce the expressions of the Y_l^m. In addition if the rules of spherical tensor algebra are to be used such as in the transformation of reference frames, these linear combinations must be normalized according to the rules used for spherical harmonics.

It is possible to define the norm of a Cartesian tensor as the sum of the square of all the components. This definition is such that the norm of the tensor is equal to the sum of the norms of the irreducible parts in their Cartesian form. We therefore adopt the following normalization conventions:

$$|t|^2 = \sum_{i,j,\ldots,m} (t_{ij\cdots m})^2$$

$$= \sum_{l} \sum_{ij\cdots m} (t^{(l)}_{ij\cdots m})^2 = \sum_{l} \sum_{m} (t_l^m)(t_l^m)^* \; .$$

A symmetric second-rank tensor t has six independent components and can be written as the direct sum of a scalar and a deviator, $t = t^{(0)} + t^{(2)}$. The spherical components are

$$t_0^0 = (t_{11} + t_{22} + t_{33})/\sqrt{3}, \quad t_2^0 = (2t_{33} - t_{11} - t_{22})/\sqrt{6} \; ,$$

$$t_2^{\pm 1} = t_{31} \pm i t_{32}, \quad t_2^{\pm 2} = \tfrac{1}{2}(t_{11} - t_{22} - i2t_{12}) \; .$$

A symmetric third-rank tensor has 10 independent components and can be written as the direct sum of a vector and a septor $t = t^{(1)} + t^{(3)}$,

$$t_1^0 = \sqrt{\tfrac{3}{5}}(t_{333} + t_{322} + t_{311}) \; ,$$

$$t_1^{\pm 1} = \mp \sqrt{\tfrac{3}{10}}[(t_{111} + t_{122} + t_{133}) \pm i(t_{222} + t_{211} + t_{233})] \; ,$$

$$t_3^0 = (1/\sqrt{10})(2t_{333} - 3t_{311} - 3t_{322}) \; ,$$

$$t_3^{\pm 1} = \mp \sqrt{\tfrac{3}{40}}[(4t_{133} - t_{122} - t_{111}) \pm i(4t_{233} - t_{222} - t_{211})] \; ,$$

$$t_3^{\pm 2} = \sqrt{\tfrac{3}{4}}(t_{311} - t_{322} \pm 2i\, t_{123}) \; ,$$

$$t_3^{\pm 3} = \pm(1/2\sqrt{2})[(t_{111} - 3t_{122}) \mp i(3t_{211} - t_{222})] \; .$$

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