Analysis of the linear and non-linear optics of crystals of CHI 3, S 8 and their 1:3 complex

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Analysis of the linear and non-linear optics of crystals of CHI_3, S_8 and their 1:3 complex

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Abstract

The molecules CHI_3 (iodoform) and S_8 (octasulfur) form not only their own homomolecular crystals but also a complex of formula $CHI_3 \cdot 3S_8$. Molecular polarizabilities are deduced for the molecules in their homomolecular crystals from the crystal linear susceptibilities. These polarizabilities, treated as transferable between crystal environments, are then used to calculate the refractive indices of the complex, but the results do not agree well with experiment. Approximate local fields deduced at the different molecules in the complex using the crystal susceptibilities directly yield better agreement. These local fields also indicate that to reproduce the experimental refractive indices of the complex requires an iodoform polarizability increased perpendicular to the molecular axis, which could occur through charge transfer from octasulfur. Theoretical hyperpolarizabilities for the two molecules combined with the same local fields are used to calculate the quadratic non-linear optical susceptibility $\chi^{(2)}$ of the complex, yielding only moderate agreement with experiment. Distortions of the octasulfur molecular framework in the crystal structure of the complex are important because they induce sizeable hyperpolarizability components, absent in the free molecule, which determine the sign of the major components of $\chi^{(2)}$. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

One strategy for developing useful molecular non-linear optical materials is to combine two components. NLO-active molecules may be incorporated in layered inorganic materials, in polymer matrices, in channels in molecular crystals, in inclusion compounds, or in van der Waals or charge-transfer complexes. Among crystalline complexes, iodoform (CHI_3: tri-iodomethane) forms NLO-active complexes [1–3] with hexamine [$(CH_2)_6N_4$: hexamethylene tetramine or urotropine; 1:1 complex], quinoline (C_9H_7N; 1:3 complex), and octasulfur (S_8; 1:3 complex). Complexes isomorphous to $CHI_3 \cdot 3S_8$ are also formed by octasulfur with the arsenic and antimony tri-iodides AsI_3 and SbI_3. These complexes crystallize in the trigonal space group R3m preserving the C_{3v} point group symmetry of the tri-iodide molecule. They therefore offer favourable conditions

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for understanding how the molecular linear and non-linear optical responses contribute to the overall crystal response [4], especially since the tri-iodide molecule is expected to dominate.

In the present paper we analyse the linear and non-linear optical response of the iodoform-octasulfur complex. Not only is it representative of these various crystalline complexes, being common to both groups mentioned, but it also has the advantage that the linear optics of iodoform [5] and octasulfur [6] have been studied previously in their homomolecular crystals. In attempting to understand how the properties of the complex arise from those of the constituent molecules, information on how the molecules behave separately is a valuable adjunct. However, the theory of optics of molecular materials requires the behaviour of the molecules in the material environment. Analysing experimental data on the material gives the *effective* molecular response in this environment, which can differ markedly from the free molecular response. Moreover, among the three crystals, each molecule experiences two different environments, in its homomolecular crystal and in the complex, so that its effective responses may well be different. Although this somewhat complicates the analysis of the crystal optics, it also offers an opportunity to obtain insight into such environmental effects. (Studying polymorphic crystal forms of the same molecule would be a more direct alternative, but suitable data are not readily available.)

Calculations for ions in an environment that simulates an ionic crystal show how markedly the environment may affect polarizabilities [7,8] and less extensive evidence confirms that there are similar changes in molecular crystals [9,10]. Environment affects molecular response in several ways.

1.1. Molecular distortion

Synthetic chemists may take the molecular structure from the crystal structure. Theoretical chemists may take it from the energy-minimized isolated molecule. Spectroscopists may take it from the gas phase, solution phase or neat liquid. These can all differ (e.g. biphenyl by gas-phase electron diffraction and in the crystal – see Fig. 1). Hence their properties will necessarily differ.

1.2. Permanent electric field

In a condensed phase the permanent charge distributions produce permanent electric local fields. In the crystal of the polar molecule HCN this field was calculated to be 17 GV/m and in p-nitroaniline it was 4 GV/m [16], while at the surface of the crystal of the quadrupolar anthracene molecule the field was calculated to be 5 GV/m [17]. In linear and non-linear optics the molecule responds to an optical local field F additional to the permanent local field F_0. So the polarizability and hyperpolarizability required are those that refer to field F_0, not zero field [18].

1.3. Orbital or valence compression

Polarizing a free molecule encounters no external resistance, but polarizing an array of molecules encounters resistance where orbitals overlap – see Fig. 2. So the intrinsic response is modified by the surroundings [19].

Fig. 1. Structures of biphenyl: twisted form observed in the gas [11,12] and in solution [13,14] and co-planar form observed in the crystal above 40 K [15].
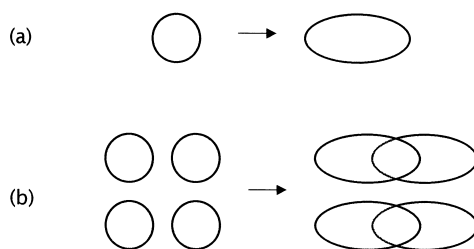
Fig. 2. (a) Polarizing a free molecule encounters no external resistance, but (b) polarizing an array of molecules encounters resistance where orbitals overlap.

1.4. Distributed response

Molecules are not points, and so we may expect their response to vary over the molecule, e.g. as group polarizabilities. This even affects what we mean by the total polarizability or hyperpolarizability. For a free molecule it gives the total response in a uniform field, but in a crystal the local fields are not uniform even if the macroscopic field is. So how the same total response is distributed affects the average response, and this average depends on the local fields due to the molecular environment. Work on Langmuir–Blodgett molecular thin films [20] illustrates this point. Molecules can have different polarizability distributions that yield the same total polarizability for a uniform field but yield somewhat different refractive indices for the film – see Fig. 3.

1.5. Non-local response

The foregoing arguments assume that molecules respond at any point only to the local field there. But in general molecules respond at any point to the fields at all other points, i.e. their response is *non-local* [21–23]. The linear change in charge density caused by an external potential can be written in terms of a charge-density susceptibility. Expanding over basins centred on atoms gives an expression for the polarizability as a sum of local atomic polarizabilities plus terms that describe charge flow between atoms [24]. Non-local response functions can be calculated using standard programs, given a choice of the atomic basins, and one suggestion [25] is that for this purpose the topological atoms-in-molecules method is particularly appropriate. Non-local response naturally extends to non-linear response, leading to a non-linear charge-density susceptibility [26].

Behaviour of human beings is often discussed in terms of 'Nature versus Nurture', that is, whether people behave the way they do because of their nature – what they inherited through their genes – or their nurture – what they acquired through the family environment in which they were brought up. One approach to this question is to study identical twins, who are expected to have identical nature, who experienced different nurture through being separated accidentally when they were babies and hence being brought up apart. The present paper can be regarded as adopting a comparable empirical approach to linear and non-linear optical behaviour of
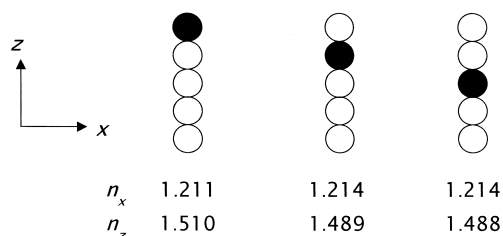

n_x	1.211	1.214	1.214
n_z	1.510	1.489	1.488

Fig. 3. Calculated refractive indices n_x and n_z parallel and perpendicular to a model Langmuir–Blodgett thin film composed of molecules with the same average polarizability in a uniform electric field but different distributions of the polarizability; the polarizability represented by the solid circle is six times that represented by the open circles.

molecules, namely studying the same molecules (the same nature) in different crystal environments (different nurture).

We first describe the structure of the three crystals and the optical properties that we shall analyse and interpret. We then summarize the basic theory of linear optical response in molecular crystals. We use this theory to deduce the effective polarizabilities of CHI_3 and S_8 in their homomolecular crystals, and to show that when used unchanged for the complex crystal they do not reproduce satisfactorily the linear optical response. We present an alternative way of using the linear response of the homomolecular crystals, to determine the local electric fields in the complex crystal, which does reproduce satisfactorily the linear optical response. We show that these local fields also afford a reasonable prediction of the non-linear optical response of the complex crystal from theoretical calculations of the molecular hyperpolarizabilities, whereas usual approximate approaches to local fields are clearly unsatisfactory for complexes because they cannot yield different fields at the different molecules. Finally, we discuss the insights gained into this and similar complexes and into environmental effects on molecular response.

2. Crystal properties

2.1. Iodoform

Iodoform crystallizes in a hexagonal structure with the polar molecular axis parallel to the hexagonal axis, so that the molecular symmetry is preserved. Early work [27,28] reported a polar crystal structure, but later work [29] suggested a non-polar disordered structure, supported by measurements [30,31] that detected no piezoelectricity and pyroelectricity. The refractive indices [32] were used previously [5] to deduce the effective polarizability, but with the incorrect polar crystal structure. Corrected results are presented below.

2.2. Octasulfur

Octasulfur crystallizes at room temperature in the orthorhombic structure Fddd with sixteen molecules per conventional unit cell [33]. The crown-shaped molecules lie with their mean planes parallel to the crystal c axis, making angles $\tan^{-1}(\pm b/a)$ with the a axis [34]. Static relative permittivities [35] were used previously [6] to deduce the effective polarizability.

2.3. $CHI_3 \cdot 3S_8$ complex

The complex crystallizes in the R3m space group [36], as already noted. The iodoform molecule aligns parallel to the trigonal axis, with the molecular symmetry preserved, surrounded by three octasulfur molecules with their mean planes normal to the trigonal axis. Refractive indices, static dielectric constants, linear electro-optic coefficients and second-harmonic generation coefficients have been reported [1–3].

3. Basic theory for linear optics

Consider a crystal composed of Z molecules (which need not be chemically equivalent) labelled k in a unit cell of volume v. The molecules have an effective polarizability $\boldsymbol{\alpha}_k$ in the crystal environment. The linear electric susceptibility $\boldsymbol{\chi}^{(1)}$ is given by [37]

$$\boldsymbol{\chi}^{(1)} = \sum_k \boldsymbol{a}_k \cdot \boldsymbol{d}_k , \tag{1}$$

where $a_k = \alpha_k / \varepsilon_0 v$ is a dimensionless reduced polarizability (equivalent to $4\pi\alpha_k / v$ in the c.g.s. system). The quantity d_k is the local-field tensor that relates the local polarizing electric field F_k at molecule k to the macroscopic field E for linear response:

$$F_k = d_k \cdot E. \tag{2}$$

It is given by

$$d_k = \sum_{k'} (I - L \cdot a)_{kk'}^{-1}, \tag{3}$$

where I is the unit matrix of dimension $3Z$ with 3×3 sub-matrices $\mathbf{1}\delta_{kk'}$ and a is a polarizability matrix of dimension $3Z$ with 3×3 sub-matrices $a_k \delta_{kk'}$. The quantity L is a Lorentz-factor matrix of dimension $3Z$ with 3×3 sub-matrices $L_{kk'}$ which are the Lorentz-factor tensors. These are lattice dipole tensor sums, obtained from the crystal structure, that relate the electric field at a molecule of type k to the dipole on all molecules of type k' in the crystal. In all these expressions, a particular frequency is implied. Substituting Eq. (3) in Eq. (1) yields

$$\chi^{(1)} = \sum_{kk'} (a^{-1} - L)_{kk'}^{-1}, \tag{4}$$

which confirms that $\chi^{(1)}$ is symmetric because each term is a symmetric matrix.

These expressions show that, given the crystal structure (to calculate the $L_{kk'}$) and the effective polarizabilities, one can calculate the linear and quadratic susceptibilities. However, the analysis of $\chi^{(1)}$ is complicated by the fact that in general a given $\chi^{(1)}$ does not suffice to determine completely the polarizabilities and local fields [38,39], and we need to explore how to circumvent this problem. The problem has been discussed and exemplified on a number of occasions. Since $\chi^{(1)}$ is symmetrical, it is determined by six components relative to a given set of axes, or by three principal components and three angles that relate the principal axes to the original axes. However, Eq. (1) is a sum of Z terms each of which is a symmetrical tensor determined by six components, the symmetry of the terms following from Eq. (4). Hence $\chi^{(1)}$ cannot determine all the separate terms, and thereby all the separate polarizabilities, unless all the terms are the same. For $Z = 1$ this is trivial: the site symmetry and the crystal point group symmetry coincide, and the polarizability is directly determined. For homomolecular crystals with $Z \geq 2$, the extent to which the polarizabilities can be determined depends on the extent to which symmetry forces them to coincide, for example if two sites are related by inversion. For complex crystals, Z is necessarily 2 or more, and the polarizabilities of the chemically different components are necessarily different.

In molecular crystals, three approaches to determining polarizabilities despite the arbitrariness have been adopted. One is to solve the problem algebraically for a given crystal in terms of one or more arbitrary parameters and thereby to define the range over which the polarizabilities may vary [6,38–40]. Another is to construct a non-linear equation for one polarizability and solve it for a suitable starting polarizability, such as the free-molecule polarizability [41,42]. This process can be seen as a numerical emulation of the physical process that occurs when the molecules come together in the crystal, but the outcome naturally depends on the choice of starting value. As the equation is non-linear, multiple roots also have to be eliminated, for example by comparison with other experimental data. Thirdly, some arbitrary but plausible choice may be made that fixes the relationship between the polarizabilities, or equivalently between the terms in Eq. (1); this choice has been used on several previous calculations on NLO materials [43–45]. It should also be noted that the polarizabilities can be determined, at least in principle, if other suitable experimental data are available, such as measurements of the Stark effect [46], lattice Raman intensities [47] or lattice infra-red intensities [48].

Since these problems arise because the different molecules in the unit cell do not necessarily all give the same contribution to $\chi^{(1)}$, a convenient procedure is to introduce matrices that relate the contributions of the different molecules [38,43]. Thus $\chi^{(1)}$ is written as

$$\chi^{(1)} = (1 + \rho_2 + \rho_3 + \ldots + \rho_Z) \cdot a_1 \cdot d_1, \tag{5}$$

where the ρ matrices are defined by

$$\rho_k = (a_k \cdot d_k) \cdot (a_1 \cdot d_1)^{-1}. \tag{6}$$

Symmetry determines the relations (if any) between the ρ_k, and the algebraic solution referred to earlier then determines the ρ_k, usually in terms of one or more arbitrary parameters [6,39]. Given the ρ matrices, the combination $a_1 \cdot d_1$ follows from $\chi^{(1)}$, and hence the polarizabilities can be obtained. On the other hand, the arbitrary choice $\rho_k = 1$ for all k (which implies that all molecules in the unit cell contribute equally to the linear susceptibility) always yields an explicit solution and has frequently been adopted for its simplicity. This choice is adopted for orthorhombic sulfur in the following section.

The foregoing is expressed in terms of a single label for each molecule. As discussed in the Introduction, we need to take account of the size and shape of the molecules, and of their orientation. This has usually been done by choosing suitable sets of sub-molecules to represent the molecules. Lorentz-factor tensors are then calculated not just between a particular molecule of type k and all molecules in the crystal of type k', but between a particular sub-molecule of type j on a particular molecule of type k and all sub-molecules of type j' on molecules of type k' in the crystal. The required Lorentz-factor tensors between different molecules k and k' are then calculated as averages over the sets of sub-molecules [40,49].

4. Analysis of linear optics

4.1. Iodoform

As already noted, the refractive indices of iodoform were analysed previously [5], but using an ordered polar structure rather than the correct disordered one. No general method of analysing the linear optics of disordered crystals has been developed. However, in iodoform the disorder affects only the orientation of the polar molecular axis relative to the crystal c axis, and inverting a molecule does not change its polarizability relative to that axis. Moreover, the large iodine atoms are expected to dominate both the structure and the polarizability. Hence the disordered crystal has been represented as an average ordered structure by calculating the Lorentz-factor tensor averaged over just the iodine atoms, thereby omitting the C–H group and its disordered orientation. (A given local arrangement of C–H groups will also influence the iodine atom positions, but this is ignored as a secondary effect.)

Under the crystal hexagonal symmetry of the average ordered structure, with $Z = 2$ molecules in the unit cell, there are two Lorentz-factor tensors L_{11} and L_{12}. Each is diagonal, with components $L_{aa} = L_{bb}$ perpendicular to the axis and L_{cc} parallel to it, where (as for all Lorentz-factor tensors) $L_{aa} + L_{bb} + L_{cc} = 1$. For the disordered crystal we calculate the components of L_{11} as $L_{aa} = 0.5656$ and $L_{cc} = -0.1312$, and those of L_{12} as $L_{aa} = 0.0253$ and $L_{cc} = 0.9493$. These do not differ greatly from the values calculated previously [5] for the ordered structure including the C–H group, which were 0.5164 and -0.0328 for L_{11}, and 0.0599 and 0.8802 for L_{12}.

As already noted, the two molecular orientations have identical polarizability, which can therefore be determined uniquely. The Lorentz-factor tensors then yield effective polarizability volume components (defined as $\alpha/4\pi\varepsilon_0$) of 15.4 Å^3 perpendicular to the molecular axis and 14.1 Å^3 parallel to it. The previous values were 15.6 Å^3 and 13.9 Å^3 [5]. As expected, the polarizability is rather larger in the plane where the iodine atoms are extended. The corresponding components of the local field tensor d are 1.606 perpendicular to the crystal axis

and 1.918 parallel to it (previously 1.595 and 1.942). The components parallel to the axis are rather large compared with most molecular crystals, owing to the high polarizability per unit volume and the details of the molecular packing. It can be seen that taking account of the disordered crystal in this way produces only modest changes from the previous results for an ordered structure.

4.2. Orthorhombic sulfur

The static dielectric constants of orthorhombic sulfur were analysed previously [6], but no polarizabilities were quoted. The results depend on one arbitrary parameter, but this degree of freedom is eliminated here by the choice $\rho_k = 1$ for all k, which avoids extremes of anisotropy. The Lorentz-factor tensors are averaged over all sulfur atoms.

The effective polarizabilities are expressed relative to molecular axes. The x and y molecular axes are taken in the mean molecular plane, which would be the plane perpendicular to the fourfold axis in the free molecule, with the x axis parallel to the crystal c axis. The calculated polarizability volume components are then

$$\alpha / 4\pi\varepsilon_0 (\text{Å}^3) = \begin{pmatrix} 32.87 & 0.08 & -0.18 \\ 0.08 & 28.54 & 0.64 \\ -0.18 & 0.64 & 20.10 \end{pmatrix}.$$

As expected, the polarizability is significantly larger in the molecular plane than out of it. The site symmetry in the crystal does not preserve the free molecular symmetry, so that the polarizability tensor is not diagonal, and the diagonal components in the plane are not equal. Later we use the symmetrized diagonal polarizability volume with a mean in-plane component of 30.70 Å^3 and an out-of-plane component of 20.10 Å^3.

The local-field tensor components are calculated to be

$$d = \begin{pmatrix} 2.149 & (\pm)0.371 & (\pm)0.018 \\ (\pm)0.331 & 2.118 & -0.006 \\ (\pm)0.013 & -0.005 & 2.087 \end{pmatrix}.$$

Here $(\pm)$ denotes that the sign of this component varies among the four independent molecules in the primitive unit cell, but with different combinations of sign that are not correlated. The local-field tensor is not required to be symmetric, but deviations from symmetry here are small. The diagonal elements are large and very close in magnitude, reflecting the high polarizability of the sulfur atoms and the effective packing of the molecules in the crystal.

4.3. $CHI_3 \cdot 3S_8$ complex

We calculate the refractive indices of the complex via Eq. (4). The complex contains one formula unit in the primitive unit cell, whereas the conventional hexagonal cell contains three formula units. As before, the label k takes the value I for iodoform and $S1$, $S2$ and $S3$ for the three octasulfur molecules.

The Lorentz-factor tensors are again taken as averages over sub-molecules. However, in the complex the iodoform molecules are ordered, and so the carbon atom is now included as a sub-molecule with the iodine atoms. The components of the distinct tensors are calculated to be as follows.

$$
\boldsymbol{L}_{I,I} = \begin{pmatrix} -0.475 & 0 & 0 \\ 0 & -0.475 & 0 \\ 0 & 0 & 1.950 \end{pmatrix}, \quad
\boldsymbol{L}_{I,S1} = \begin{pmatrix} 0.876 & -0.691 & 0.018 \\ -0.691 & 0.078 & -0.010 \\ 0.018 & -0.010 & 0.045 \end{pmatrix},
$$

$$
\boldsymbol{L}_{I,S2} = \begin{pmatrix} -0.321 & 0 & 0 \\ 0 & 1.275 & 0.021 \\ 0 & 0.021 & 0.045 \end{pmatrix}, \quad
\boldsymbol{L}_{I,S3} = \begin{pmatrix} 0.876 & 0.691 & -0.018 \\ 0.691 & 0.078 & -0.010 \\ -0.018 & -0.010 & 0.045 \end{pmatrix},
$$

$$
\boldsymbol{L}_{S1,S1} = \begin{pmatrix} -0.254 & 0 & -0.017 \\ 0 & -0.254 & 0.010 \\ -0.017 & 0.010 & 1.508 \end{pmatrix}, \quad
\boldsymbol{L}_{S1,S2} = \begin{pmatrix} 0.784 & 0.547 & -0.056 \\ 0.547 & 0.153 & -0.032 \\ -0.056 & -0.032 & 0.063 \end{pmatrix},
$$

$$
\boldsymbol{L}_{S1,S3} = \begin{pmatrix} -0.163 & 0 & 0 \\ 0 & 1.100 & 0 \\ 0 & 0.064 & 0.063 \end{pmatrix}, \quad
\boldsymbol{L}_{S2,S2} = \begin{pmatrix} -0.254 & 0 & 0 \\ 0 & -0.254 & -0.019 \\ 0 & -0.019 & 1.508 \end{pmatrix},
$$

$$
\boldsymbol{L}_{S2,S3} = \begin{pmatrix} 0.784 & -0.547 & -0.056 \\ -0.547 & 0.153 & -0.032 \\ -0.056 & -0.032 & 0.063 \end{pmatrix}, \quad
\boldsymbol{L}_{S3,S3} = \begin{pmatrix} -0.254 & 0 & 0.017 \\ 0 & -0.254 & 0.010 \\ 0.017 & 0.010 & 1.508 \end{pmatrix}.
$$

The symmetry of the individual tensors is affected by the choice of molecule 3 to lie on the crystal a axis, with molecules 2 and 3 therefore symmetrically disposed about this axis. Adding a set of three corresponding tensors that involve the three octasulfur molecules gives a tensor with the requisite axial symmetry, showing the effect of the rotation about the trigonal axis that relates the three molecules. For example, $\boldsymbol{L}_{I,S1}$ has zeros where $\boldsymbol{L}_{I,S2}$ and $\boldsymbol{L}_{I,S3}$ have equal and opposite components, and it has off-diagonal components that are equal and opposite to the sum of their corresponding components.

The Lorentz-factor tensors are now used with the effective polarizabilities for iodoform and octasulfur deduced in their homomolecular crystals to calculate $\boldsymbol{\chi}^{(1)}$ for the complex crystal. The result is $\chi_{aa} = \chi_{bb} = 3.558$, $\chi_{cc} = 2.719$, and the refractive indices given by $n_i^2 = \chi_{ii} + 1$ are $n_a = 2.135$ and $n_c = 1.929$. The experimental refractive indices at a wavelength of 632.8 nm are $n_a = 2.236$ and $n_c = 1.789$. Although broadly satisfactory, the calculated values markedly under-estimate the anisotropy $n_a - n_c$, which at 0.206 is less than half the experimental value of 0.447. This discrepancy can be regarded as an indication of the difference in environmental effects on the polarizabilities between the complex and the homomolecular crystals.

5. Local fields in the complex

The same Lorentz-factor tensors and effective polarizabilities are also used to give local-field tensors in the complex, which are as follows.

$$
\boldsymbol{d}_I = \begin{pmatrix} 1.567 & 0 & 0 \\ 0 & 1.567 & 0 \\ 0 & 0 & 1.967 \end{pmatrix}, \quad
\boldsymbol{d}_{S1} = \begin{pmatrix} 2.120 & 0.034 & -0.090 \\ 0.034 & 2.160 & 0.052 \\ -0.084 & 0.048 & 2.265 \end{pmatrix},
$$

$$
\boldsymbol{d}_{S2} = \begin{pmatrix} 2.179 & 0 & 0 \\ 0 & 2.101 & -0.104 \\ 0 & -0.096 & 2.265 \end{pmatrix}, \quad
\boldsymbol{d}_{S3} = \begin{pmatrix} 2.120 & -0.034 & 0.090 \\ -0.034 & 2.160 & 0.052 \\ 0.084 & 0.048 & 2.265 \end{pmatrix}.
$$

The tensors for the octasulfur molecules show the symmetry features noted previously in the Lorentz-factor tensors, with the local-field tensor at octasulfur exhibiting axial symmetry only in the average. For each molecule, the local-field tensor resembles quite closely that in its homomolecular crystal, but this implies that the local fields at iodoform and octasulfur in the complex are markedly different. Hence any attempt to predict the linear or non-linear optical response of the crystal from a single average local field (for example, using the Lorentz local fields obtained from the refractive indices of the complex) must be regarded as questionable. However, since using the effective polarizabilities from the homomolecular crystals gives a poor prediction of the birefringence, a more direct approach to the local fields themselves might be more profitable.

For complex crystals such as that of interest here, the assumption that all molecules contribute equally to $\chi^{(1)}$, which is what $\rho_k = 1$ implies, is clearly much less plausible than in a homomolecular crystal. In work on weak charge-transfer complexes of anthracene, a non-linear numerical approach was adopted, starting from various plausible input values which involved the polarizabilities of the parent molecules and their ions; preferred values of the polarizabilities were selected by comparison with electrical data on the complexes [42]. For the present complexes, evidence for charge transfer is less clear-cut and comparable electrical data are not available. However, the information available on $\chi^{(1)}$ and the polarizabilities in the homomolecular crystals of the parent compounds suggests a rather direct way of fixing the ρ_k by assuming that each molecule contributes to $\chi^{(1)}$ in the complex in the same way as it does in its homomolecular crystal.

To explore this assumption, we write Eq. (1) in a form specific to the present complexes, i.e.

$$\chi^{(1)} = a_I \cdot d_I + \sum_{k=1}^{3} a_{Sk} \cdot d_{Sk}, \tag{7}$$

where I denotes the iodoform molecule, and $S1$, $S2$ and $S3$ the three octasulfur molecules. Since there is only one iodoform molecule, which enjoys a higher site symmetry, we relate the contributions of the octasulfur molecules to its contribution, so that

$$\chi^{(1)} = \left(1 + \sum_{k=1}^{3} \rho_{Sk} \right) \cdot a_I \cdot d_I, \tag{8}$$

where

$$\rho_{Sk} = (a_{Sk} \cdot d_{Sk}) \cdot (a_I \cdot d_I)^{-1}. \tag{9}$$

Now for orthorhombic sulfur crystals $\chi^{(1)}$ is given by a sum of terms $a_{Sk} \cdot d_{Sk}$ and for iodoform crystals $\chi^{(1)}$ is given by the single term $a_I \cdot d_I$. These relate to the orientations of the molecules in the homomolecular crystals, which for the octasulfur molecules do not map onto those in the complexes, so that it is difficult to transfer directional information from $\chi^{(1)}$ for the orthorhombic sulfur crystal to the complex crystal. A simple plausible assumption that circumvents this problem is then to set

$$\rho_{Sk} = (\chi_S/\chi_I)\mathbf{1} \text{ for all } k, \tag{10}$$

where χ_S and χ_I are the mean linear susceptibilities of the orthorhombic sulfur and iodoform homomolecular crystals given by $(\chi_{aa} + \chi_{bb} + \chi_{cc})/3$, so that $\chi_S = 3.66$ and $\chi_I = 2.12$. This assumption immediately yields the separate contributions to $\chi^{(1)}$ for the complex from Eq. (1) as

$$a_I \cdot d_I = \left(\frac{\chi_I}{\chi_I + 3\chi_S} \right) \chi^{(1)}, \tag{11}$$

$$a_{Sk} \cdot d_{Sk} = \left(\frac{\chi_S}{\chi_I + 3\chi_S} \right) \chi^{(1)} \text{ for all } k. \tag{12}$$

The local-field tensors in the complex satisfy the set of equations [39]

$$\boldsymbol{d}_k = \sum_{k'} \boldsymbol{L}_{kk'} \cdot \boldsymbol{a}_{k'} \cdot \boldsymbol{d}_{k'} . \tag{13}$$

Therefore once the individual contributions $\boldsymbol{a}_k \cdot \boldsymbol{d}_k$ to the linear susceptibility are known, the local fields can be obtained directly. With the results (11) and (12), the local fields are found to be

$$\boldsymbol{d}_I = \boldsymbol{1} + \boldsymbol{L}_I \cdot \boldsymbol{\chi}^{(1)} , \tag{14}$$

$$\boldsymbol{d}_{Sk} = \boldsymbol{1} + \boldsymbol{L}_{Sk} \cdot \boldsymbol{\chi}^{(1)} , \tag{15}$$

where the new quantities are averages of Lorentz-factor tensors weighted by the susceptibilities of the homomolecular crystals:

$$\boldsymbol{L}_I = \frac{\chi_I \boldsymbol{L}_{I,I} + \chi_S \sum_{k=1}^{3} \boldsymbol{L}_{I,Sk}}{\chi_I + 3\chi_S} , \tag{16}$$

$$\boldsymbol{L}_{Sk} = \frac{\chi_I \boldsymbol{L}_{Sk,I} + \chi_S \sum_{k'=1}^{3} \boldsymbol{L}_{Sk,Sk'}}{\chi_I + 3\chi_S} . \tag{17}$$

Hence by this approach the local fields in the complex are obtainable from the linear susceptibility tensor of the complex crystal, the structure of the complex crystal (for the Lorentz-factor tensors), and the mean linear susceptibilities of the homomolecular crystals of the separate components.

An assessment of the reliability of this approach can be obtained by calculating these local fields and then using them with the effective polarizabilities from the homomolecular crystals as before to calculate the refractive indices for the complex. The averaged Lorentz-factor tensors are found to be

$$\boldsymbol{L}_I = \begin{pmatrix} 0.298 & 0 & 0 \\ 0 & 0.298 & 0 \\ 0 & 0 & 0.404 \end{pmatrix}, \qquad \boldsymbol{L}_{S1} = \begin{pmatrix} 0.264 & 0.018 & -0.016 \\ 0.018 & 0.285 & 0.009 \\ -0.016 & 0.009 & 0.450 \end{pmatrix},$$

$$\boldsymbol{L}_{S2} = \begin{pmatrix} 0.295 & 0 & 0 \\ 0 & 0.254 & -0.018 \\ 0 & -0.018 & 0.450 \end{pmatrix}, \quad \boldsymbol{L}_{S3} = \begin{pmatrix} 0.264 & -0.018 & 0.016 \\ -0.018 & 0.285 & 0.009 \\ 0.016 & 0.009 & 0.450 \end{pmatrix}.$$

The local-field tensors then follow as

$$\boldsymbol{d}_I = \begin{pmatrix} 2.192 & 0 & 0 \\ 0 & 2.192 & 0 \\ 0 & 0 & 1.889 \end{pmatrix}, \qquad \boldsymbol{d}_{S1} = \begin{pmatrix} 2.058 & 0.072 & -0.036 \\ 0.072 & 2.141 & 0.021 \\ -0.065 & 0.037 & 1.991 \end{pmatrix},$$

$$\boldsymbol{d}_{S2} = \begin{pmatrix} 2.182 & 0 & 0 \\ 0 & 2.017 & -0.041 \\ 0 & -0.074 & 1.991 \end{pmatrix}, \quad \boldsymbol{d}_{S3} = \begin{pmatrix} 2.058 & -0.072 & 0.036 \\ -0.072 & 2.141 & 0.021 \\ 0.065 & 0.037 & 1.991 \end{pmatrix}.$$

Like the Lorentz-factor tensors, these show the symmetry already observed in the previous calculations, with the average tensor at octasulfur exhibiting axial symmetry. They are slightly smaller in magnitude than those calculated in Section 4.3, and show the opposite anisotropy, with the cc component the smallest rather than the largest diagonal component.

The local-field tensors are now used with the effective polarizabilities for iodoform and octasulfur deduced in their homomolecular crystals in Sections 4.1 and 4.2 to calculate $\boldsymbol{\chi}^{(1)}$ for the complex crystal. The result is

$\chi_{aa} = \chi_{bb} = 3.764$ and $\chi_{cc} = 2.432$, leading to refractive indices $n_a = 2.183$ and $n_c = 1.852$, compared with the experimental values $n_a = 2.236$ and $n_c = 1.789$. The calculated values are closer to the experimental ones than those calculated in Section 4.3, and give an anisotropy $n_a - n_c$ of 0.330 that is much closer to the experimental value of 0.447 than the value of 0.206 calculated in Section 4.3.

If this approach to the local fields were entirely self-consistent, it would return the same crystal $\chi^{(1)}$ that was used as input, but use of the effective molecular polarizabilities from the homomolecular crystals precludes this. One ought also to expect to reproduce $\chi^{(1)}$ for the complex better when using $\chi^{(1)}$ as input than when using just the Lorentz-factor tensors for the complex with the effective molecular polarizabilities from the homomolecular crystals as done in Section 4.3. Nevertheless, the approach in the present section does afford local fields that give a reasonable prediction of $\chi^{(1)}$ in conjunction with effective molecular polarizabilities deduced quite independently of the linear optical properties of the complex crystal. This encourages the hope that the same local fields might give a reasonable prediction of $\chi^{(2)}$ in conjunction with molecular hyperpolarizabilities deduced independently. Before exploring this, we examine one further aspect of the present approach.

As noted in Section 3, once the $\boldsymbol{\rho}$ matrices are known, then the polarizabilities follow. We have seen that the present direct determination of the local fields leads to a better representation of the linear susceptibility $\chi^{(1)}$ in the complex when combined with the polarizabilities from the homomolecular crystals than using these polarizabilities directly in Eq. (4). Hence it may be instructive to compare the homomolecular polarizabilities with those obtained from the present approach to the $\boldsymbol{\rho}$ matrices. The new polarizabilities follow directly by combining Eq. (11) and (12) with (14) and (15) to obtain

$$a_I = \left(\frac{\chi_I}{\chi_I + 3\chi_S} \right) \left[\left(\chi^{(1)} \right)^{-1} + L_I \right]^{-1}, \tag{18}$$

$$a_{Sk} = \left(\frac{\chi_S}{\chi_I + 3\chi_S} \right) \left[\left(\chi^{(1)} \right)^{-1} + L_{Sk} \right]^{-1}. \tag{19}$$

From these equations, the iodoform polarizability is found to be 13.2 Å^3 parallel to the molecular axis and 20.7 Å^3 perpendicular to the axis, while the octasulfur polarizability is found to be 18.1 Å^3 parallel to the molecular axis (perpendicular to the mean molecular plane) with an average of 31.2 Å^3 in the mean molecular plane. The mean iodoform polarizability is increased by over 20% from that in the homomolecular crystal, decreasing slightly parallel to the molecular axis but increasing by over 30% perpendicular to the axis. The mean octasulfur polarizability is marginally smaller than in the homomolecular crystal, being slightly decreased perpendicular to the mean molecular plane and slightly increased in the plane. With the given choice of $\boldsymbol{\rho}$ and the local fields that this choice implies, these changes in the polarizabilities are required to increase the calculated refractive index n_a and decrease n_c to agree with the experimental values. Significant changes perpendicular to the molecular axes in the complex crystal are consistent with the existence of a short nearest-neighbour I–S distance suggestive of charge transfer in the crystal symmetry plane [36].

6. Non-linear optics

The quadratic susceptibility is given by [43]

$$\chi^{(2)}(-\omega_3; \omega_1, \omega_2) = \sum_k d_k^T(\omega_3) \cdot \mathbf{b}_k(-\omega_3; \omega_1, \omega_2) : d_k(\omega_1) d_k(\omega_2), \tag{20}$$

where $\mathbf{b}_k = \boldsymbol{\beta}_k / \varepsilon_0 v$ is a reduced first hyperpolarizability, with $\boldsymbol{\beta}_k$ the effective hyperpolarizability of molecule k in the crystal environment, and the superscript T denotes the transpose. Energy conservation requires $\omega_3 = \omega_1 + \omega_2$, where ω_3 is the output frequency and ω_1 and ω_2 are the two input frequencies. Compared with the expression for the linear susceptibility, this has two additional local-field factors: one because the response

Table 1
Static hyperpolarizability components β_{ijk} /a.u. for iodoform calculated using in-crystal geometries

ijk		
aaa	*aac*	*ccc*
86	3.5	1.7

1 a.u. = 8.639 418×10^{-33} esu = 3.206 361×10^{-53} F m^3 V^{-1}.

to the local field is quadratic and the other because the local field itself contains non-linear contributions. We use the local fields from the preceding section, and hence we now require the hyperpolarizabilities.

Much effort has been put into calculating molecular hyperpolarizabilities. Semi-empirical calculations have been widely used to assess the potential of molecules for use in NLO materials. Used judiciously, such calculations can give useful predictions of relative values, especially in series of related molecules. However, they do not normally give quantitatively reliable predictions. Moreover, iodoform and octasulfur are significantly different from the conjugated molecules most commonly treated by semi-empirical techniques, and so for present purposes ab initio techniques are preferable. The reliability of the predicted hyperpolarizabilities depends mainly on the quality of the basis set, and although reliable approaches are available for small molecules, for molecules as large as iodoform and octasulfur the prospects are less encouraging and relatively little work has been reported. Iodoform has been studied by the coupled perturbed Hartree–Fock (CPHF) approach, using an effective core potential for the iodine atom [50], first in the static limit [51] and subsequently at optical frequencies [52,53]. In each case, agreement with experimental results in solution was disappointing. As far as we are aware, there are no previous calculations on octasulfur. In its free state it is arguably an ideal octupolar molecule, unlike some of those first studied, which were hexapolar in structural terms although octupolar in irreducible tensor terms.

We have performed calculations for iodoform and octasulfur using the Gaussian94® package, which is restricted to static hyperpolarizabilities. Evidence from calculations on conventional organic octupolar molecules suggests that including correlation is especially important to obtain reliable results [54]. The largest basis set used was 6-311 + + G(2df, 2pd) with D95 + (df) for iodine, so including the diffuse functions indicated by the + signs and the polarization functions specified in parentheses. Correlation was treated at the MP2 level. In accordance with the discussion earlier, environmental effects were partially accounted for by using the observed molecular structures in the complex crystal. For iodoform, this makes a modest quantitative difference compared with using the SCF optimized geometry. For octasulfur it makes a qualitative difference: the D$_{4d}$ symmetry of the free molecule makes the first hyperpolarizability zero in the zero-frequency limit, but the lowering of the molecular symmetry in the complex crystal induces non-zero components.

The calculated hyperpolarizability components for iodoform are shown in Table 1. The component β_{aaa} varies little with basis set once two d and two p polarization functions are included, at which stage β_{aac} also settles down. The purely axial component β_{ccc} settles down only when a diffuse function is also added for iodine, before which it may exceed β_{aaa}. The final calculated dipole moment is 0.73 D (2.4 × 10^{-30} C m: experiment 0.74 D). The calculated hyperpolarizability components for octasulfur are shown in Table 2, where

Table 2
Static hyperpolarizability components β_{ijk} /a.u. for octasulfur calculated using in-crystal geometries

ijk		
aaa	*aac*	*ccc*
− 46	0	− 22.5

1 a.u. = 8.639 418×10^{-33} esu = 3.206 361×10^{-53} F m^3 V^{-1}.

Table 3
Calculated and experimental quadratic susceptibility components $\chi_{ijk}/\text{pm V}^{-1}$ for the $CHI_3 \cdot 3S_8$ complex

	ijk		
	aaa	*aac*	*ccc*
Calculated	−1.8	0.2	−2.5
Experimental	42	5	4.6

The *aaa* and *ccc* components come from SHG measurements that do not determine the absolute sign; the *aac* component comes from the electro-optic coefficient.

it can be seen that the distortion in the crystal induces components comparable in magnitude with those in iodoform, but of opposite sign. Hence the plausible assumption from the free-molecule geometries that the quadratic susceptibility $\chi^{(2)}$ of the complex can be determined from the first hyperpolarizability β for iodoform alone is surprisingly far from the truth.

The quadratic susceptibility components calculated for the complex from the local fields and hyperpolarizabilities are shown in Table 3, together with experimental values [1–3]. As can be seen, the calculated results fall short of the experimental ones by factors of some $2-20$, and the 'diagonal' *aaa* and *ccc* components are of opposite sign to the experimental ones. However, absolute signs are not usually determined experimentally, so that the disagreement in sign is not problematic in itself. Since the octasulfur hyperpolarizabilities are negative, and there are three of them, it is evident that their contribution to $\chi^{(2)}$ determines the sign. To this extent, relying on the iodoform contribution alone to predict $\chi^{(2)}$ is completely misleading.

The serious under-estimate of the components of $\chi^{(2)}$ that involve the *a* direction is disappointing. However, it is consistent with the earlier deductions about the shortcomings of the effective polarizabilities that were deduced from the homomolecular crystal refractive indices. There, the response perpendicular to the axis appeared to be about 30% lower than required to give agreement with experiment for the complex, and the discrepancy was ascribed to charge transfer between iodoform and octasulfur. Similarly one would expect that the hyperpolarizabilities calculated here would be deficient because they take no account of the crystal environment apart from using the molecular structure in the crystal. They certainly take no account of any charge transfer, or of the permanent electric fields in the complex crystal. Such effects would affect hyperpolarizabilities more strongly than polarizabilities, for example because they involve three rather than two transition dipole moments. This could certainly make the calculated components a factor of two too low, even before any inadequacies in the calculations themselves, most importantly the exclusion of frequency dependence that could lead to pre-resonant enhancement of $\chi^{(2)}$. Thus all the known weaknesses might be expected to increase the magnitude of the calculated susceptibility components and hence improve the agreement with experiment.

7. Discussion

In this paper we have considered in detail the problem of calculating and interpreting the linear and non-linear optical properties of a crystalline molecular complex. Our approach has been to make use of information from the homomolecular crystals of the separate constituents, with the idea that this should account partially for the influence of *a* crystal environment on the molecular response, if not exactly that of *the* crystal environment of the complex. This has proved instructive but not definitive.

The molecular polarizabilities deduced from the linear susceptibility of the homomolecular crystals do not give an adequate representation of the linear susceptibility of the complex crystal. Using the same polarizabilities with an alternative method for obtaining the local fields in the complex gives an improved representation. The alternative approach to the local fields can also yield molecular polarizabilities that reproduce exactly the

linear susceptibility of the complex crystal. The main feature of these polarizabilities is that the iodoform polarizability perpendicular to the molecular axis is over 30% larger than in the homomolecular crystal. It has been suggested that charge transfer between molecules contributes to the binding in the complex crystal, and this suggestion is supported by a short I–S nearest-neighbour distance in the crystal ab plane [36]. In a simple sum-over-states picture of the iodoform polarizability in the complex, such charge transfer adds three equivalent excited-state configurations that contribute transition dipole moments polarized perpendicular to the molecular axis and hence enhance the polarizability in that direction. Attempts have been made to rationalize in more detail the effect of charge transfer on polarizabilities and dielectric response in weak charge-transfer crystals [42,55] and in homomolecular crystals [56,57]. Charge transfer not only modifies the local molecular polarizability but also introduces a non-local polarizability [23] such that the field at one molecule contributes to the dipole induced at another. However, including the charge-transfer contribution to the local fields as well as to the polarizability [57] confirms that charge transfer enhances the susceptibility.

The quadratic susceptibility of the complex crystal requires the first hyperpolarizabilities of the constituent molecules. This information is not available from the homomolecular crystals, and so the static hyperpolarizabilities have been calculated at a reasonably high ab initio level. The immediate effect of the complex crystal environment is included by using the observed molecular geometries. This has the important consequence that it induces hyperpolarizabilities in the octasulfur molecules that make a significant contribution to the net susceptibility, to the extent of changing the sign of the largest components from that predicted from iodoform hyperpolarizability components alone. The calculated susceptibility components are still a factor of 2–20 below those observed experimentally. This could be attributable to the use here of static hyperpolarizabilities that ignore the enhancement expected at optical frequencies; to inadequacies in the level of calculation of the hyperpolarizabilities; and to the approximate local fields used. However, it is likely that there are also specific environmental effects. As already noted, the linear polarizability in the complex appears to be enhanced perpendicular to its axis, possibly through charge-transfer interactions. Permanent local electric fields have been shown to have a significant effect on the hyperpolarizability in urea [58] and could well do so here too. When allowance is made for such effects, the residual difference between the calculated and experimental components would probably be comparable with discrepancies obtained in earlier calculations of $\chi^{(2)}$ [44,45].

In conclusion, we have derived useful local fields in the complex crystal $CHI_3 \cdot 3S_8$ from experimental information about the homomolecular crystals of its constituent molecules. We have provided evidence that charge transfer, inferred previously from the structure of the complex, may enhance the polarizability of iodoform in the complex. We have shown that the distortion of the octasulfur molecules in the environment of the complex induces hyperpolarizabilities that make a dominant contribution to the quadratic susceptibility. The final calculated susceptibility is still significantly smaller than observed, implying additional environmental effects, presumably from charge transfer and from the permanent local fields in the complex.

Acknowledgements

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