Coherent two-dimensional electronic and infrared crystallography

Jasper J. van Thor$^{1}$

$^{1}$ Molecular Biophysics, Imperial College London. SW7 2AZ, London, UK

# Corresponding author. j.vanthor@imperial.ac.uk

Abstract

The two-dimensional electronic and infrared spectroscopy of oriented single crystals is sensitive to structure and point group symmetry. The third order response of crystals is generally different from measurements of isotropic solutions because each coherence path that contributes to the measured field scales to the ensemble average of the four-point correlation functions of the four field-dipole interactions involved in the respective Feynman paths. An analytical evaluation of 2D optical crystallography which depends on the crystal symmetry, laboratory orientation as well as the orientation in the crystallographic frame is presented. Applying a symmetry operator in the basis of the allowed polarised radiation modes provides a method for evaluation of non-zero fourth rank tensor elements alternative to direct inspection methods. Uniaxial and biaxial systems are distinguished and the contributions to the rephasing and non-rephasing directions are evaluated for isolated and coupled oscillators. By exploiting coordinate analysis the extension of non-linear electronic and infrared crystallography for coupled oscillators demonstrates the structural, directional and symmetry dependent selection of coherences to the four-wave mixing signal.

1. Introduction to 2D spectroscopy applications

Two-dimensional infrared (2DIR) and electronic (2DES) spectroscopy have emerged as very powerful techniques to probe molecular structure and dynamics on femtosecond and picosecond time scales since the 1990’s. 2D spectroscopy can be considered an optical analog of Nuclear Magnetic Resonance spectroscopy (NMR) as some formalisms of 2D and NMR can be compared. Of special interest are the many successful applications of 2DIR to interrogate protein structure and dynamics, particularly focussing on the amide I vibrations. The amide I vibration is known to be sensitive to protein secondary and tertiary structure, which is derived from the molecule-wide delocalisation. While linear FTIR spectroscopy reveals limited line-shape and frequency information, 2DIR spectroscopy disperses the spectral information in two dimensions to reveal two-dimensional line shapes and cross-peaks. Additionally, the non-linear signals scale with the fourth power of the transition dipole moment, which generally leads to more significant spectral structure as compared to linear spectroscopy. 2DIR
spectroscopy also carries ultrafast time information, providing access to rapid protein structural dynamics, and can be combined with actinic excitation (for TR-2DIR) \(^6\). An important approach to understanding and linking the 2DIR measurements with the protein structures makes use of an exciton model which many have shown is appropriate to construct the interaction Hamiltonian as the basis of the spectral simulations \(^6,10,11,12,13,14\). It is generally agreed that determining the precise site-energies of the individual oscillators provides the greatest uncertainty, whereas the resulting off-diagonal elements and subsequent calculation presents computational challenges for more than 200 oscillators which may be overcome with current computing technology \(^13,14\). Many examples and demonstrations have been reported and methodology and instrumentation has developed considerably \(^5,6,7,8,9,11,15,16\).

Coherent two-dimensional electronic spectroscopy (2D-ES) \(^3,17\) has been established as a prominent method to study photosynthetic exciton dynamics at room temperature and at cryogenic temperatures \(^18-21,22,23,24\). Benefiting from advances in instrument designs that provide phase stability that is necessary for the accurate frequency-frequency correlation that is retrieved, a major focus has been the assignment of oscillatory behaviour during the population time of interstate coherence that has been widely reported. Many recent discussions have revolved around methods to separate and assign pure electronic coherence and to distinguish signals from vibronic contributions, where interpretation and assignment has converged following the report by Tiwari et al (2013)\(^19\). For purely electronic coherences, it has been pointed out that cross-peaks should oscillate in phase, but that the absolute phase depends on excitation conditions, as it does in conventional pump-probe spectroscopy \(^20-22\). Since the original report of oscillatory features in 2D-ES at 77K of the FMO light harvesting complex in 2007 by the Fleming group \(^25\), many groups have addressed coherence measurements at ambient and cryogenic temperatures. Many now agree that oscillations observed experimentally during the population time have strong contributions from, or would be dominated by electronic-vibrational mixing\(^20,21,26\), with explicit assignment \(^19\). Different mechanisms have however been proposed; Plenio and co-workers argued that long-lived vibrational coherence enhances the electronic coherence lifetime \(^23\). Mančal and coworkers \(^21,27\) and others have discussed mechanisms that involve transition dipole borrowing in scenarios where vibronic levels match electronic energy level gaps. Jonas and coworkers demonstrated compelling evidence that quantum beating during the waiting time for 2DES measurements on photosynthetic materials arises from non-adiabatic electron-vibrational coupling rather than from pure electronic coherence \(^19\). Experimentally, it has also been pointed out that frequency selection in the 2D-ES measurement and the laser spectrum act as filters for the coherence pathways that contribute \(^28\). For the theoretical and experimental analysis of exciton dynamics in photosynthesis, the coupling strength between pigments should be evaluated with regard to the reorganisation energy and inhomogeneous distribution \(^29\).

The polarisation dependence of 2D spectroscopy, which is of particular interest for this contribution, has been described for 2DIR spectroscopy under isotropic conditions in detail for isolated and vibrationally coupled states, in the presence and absence of rotational diffusion. Robin Hochstrasser first wrote out explicit four-point correlation functions for these conditions \(^7\). Here, the established formalisms are used in order to quantify the four-wave mixing response for molecular crystals, with a
particular emphasis on structural analysis having knowledge of unique laboratory orientation, point
group symmetry and coordinates from X-ray crystallography.

The present contribution is arranged in the following way. Section 2 briefly summarises the
‘rules’ for relating crystal orientation to finding the allowed polarisation directions, known from general
non-linear optics and mineralogy. Section 3 discusses and reviews the ‘rules’ for the crystal symmetry
dependence of allowed polarisation combinations that contribute to the third-order response. An
analytical method to provide the non-zero tensor elements is demonstrated that is an alternative to
direct inspection methods. Section 4 presents calculation of four-point correlation functions of dipole-
field interaction in the response function formalism to four-wave mixing for uniaxial and biaxial crystal
systems, and includes calculation and simulation. Section 5 briefly discusses the phase matching
conditions for oriented single crystal measurements.

2. Optical propagation in crystals, the linear response and laboratory orientation

Propagation of light in anisotropic media has been described many times, starting with the Fresnel
equations over two centuries ago. The consequence of birefringence and its dependence on
crystal symmetry is well known. For the purpose of this contribution it is necessary and also sufficient to
briefly consider the relationship between laboratory orientation and the directions of the allowed
polarised radiation modes. This summary provides a general description for the linear optical response,
that will be extended to non-linear optical response. Throughout, equations are given for non-
absorbing, opaque crystals which is generally valid for weak attenuation which is the case for protein
crystals in particular. Consequently, the conduction term does not appear in the equation (1) Ellipticity
caused by attenuation is neglected. In contrast, under conditions of absorption, considering metals, the
conduction term accounts for the physical behavior of the free electrons. A principal result in this case is
that polarisation is generally elliptical, and can be strongly so. Furthermore, although it is possible to
write expressions for the linear and non-linear response for any k-vector and polarisation direction, it is
most useful to review the general rules for finding the allowed principal polarisation directions, so that
the optical response can be expressed in this basis. Briefly, the general case seeks solutions to Maxwell’s
polarised wave equation

\[ \nabla \times (\nabla \times E) + \frac{1}{c^2} \frac{\delta^2 E}{\delta t^2} = -\frac{1}{c^2} \chi \frac{\delta^2 E}{\delta t^2} \]  \hspace{1cm} (1)

Where \( \chi \) is the susceptibility tensor proportional to the Polarisation,

\[ P = \epsilon_0 \chi E \]  \hspace{1cm} (2)

There are generally two solutions for Maxwell’s polarised wave equation (eq 1) in anisotropic media,
which are given as two wave vector surfaces that represent the magnitude of two wave-vectors \( k= n_{1,2,3} \omega/c \) for the allowed orthogonally polarised radiation modes, where \( n_{1,2,3} \) are the three principal indices
of refraction.
The principal dielectric susceptibility tensor $\chi$ is symmetric and thus has no off-diagonal components in the absence of optical activity, and determines the polarisation direction of the allowed polarised radiation modes. That is, there is always a condition where a coordinate system exists such that off-diagonal elements are zero:

$$\chi = \begin{pmatrix} \chi_{11} & 0 & 0 \\ 0 & \chi_{22} & 0 \\ 0 & 0 & \chi_{33} \end{pmatrix}$$

(4)

Alternatively a linear susceptibility tensor may be given which uses Cartesian indices, in which case triclinic and monoclinic crystals have off-diagonal elements. For the principal dielectric susceptibility tensor $\chi$ (equation 4), point group symmetry determines the number of independent elements and their inter-dependency. Isotropic and cubic materials show a single linear susceptibility such that $\chi_{11}=\chi_{22}=\chi_{33}$. Uniaxial crystals through rotational symmetry have two independent susceptibilities such that $\chi_{11}=\chi_{22} \neq \chi_{33}$. Biaxial crystals have three independent susceptibilities such that $\chi_{11} \neq \chi_{22} \neq \chi_{33}$. Crystal symmetry, and notably the presence of two-fold symmetry operators, determines whether the directions of the principle susceptibility is wavelength dependent and the relationship to crystallographic directions. Generally, their directions is modified by anomalous dispersion near resonance conditions, unless a two-fold rotation, screw axis or mirror symmetry forces the symmetric form of the wavevector surfaces. As a result the dielectric constant is the tensor, which is the medium equation

$$\mathbf{D} = \varepsilon \mathbf{E} = \varepsilon_0 \chi \mathbf{E}$$

(5)

In order to find the directions of the allowed polarised waves that correspond to the two wave-vector solutions, it is common to write Maxwell’s equations for non-conducting, nonmagnetic crystal which results in the expression for the dielectric ‘indicatrix’ ellipsoid of wave normals, also referred to as the quadratic representation

$$\frac{x^2}{n_1^2} + \frac{y^2}{n_2^2} + \frac{z^2}{n_3^2} = 1$$

(6)

Expressed in the orthogonal coordinates $x,y,z$ corresponding to the directions of the principal refractive indices $n_1 = (1+ \chi_{11})^{1/2}$, $n_2 = (1+ \chi_{22})^{1/2}$, $n_3 = (1+ \chi_{33})^{1/2}$.

With the exception of cubic symmetry, which are crystals that have point groups 432, -43m, 23, m-3 or m-3m, all 27 other point group symmetries are doubly refracting. These are further separated in biaxial and uniaxial crystal classes that have three or two unique principal indices of refraction respectively. As a consequence, their indicatrices are triaxial ellipsoids, or ellipsoids of revolution respectively. For weakly absorbing crystals, the two classes are trichroic and dichroic in nature.

The indicatrix ellipsoid may be used to find the allowed polarisation directions for any direction of $k$, by finding the wave-normal surface intersection of the indicatrix ellipsoid which either corresponds to a
circle (in the case of an optic axis direction or for isotropic samples where \( n_1 = n_2 = n_3 \)) or an ellipse. For the latter case the ellipse major and minor axes correspond to the slow and fast directions. Alternative to a geometric construction that uses the ellipsoid of wave normals (eq 6), a general solution to finding the directions of the two normal modes for Displacement for any ray direction involves solving the dispersion relation. The procedure involves use of Maxwell’s equations and the medium equation (equation 5). These are commonly given in textbook literature and not further considered here.

For uniaxial crystals \( n_1 = n_2 \neq n_3 \) the indicatrix is an ellipsoid of revolution, either oblate (uniaxial negative) or prolate (uniaxial positive) and the material is birefringent, having one optic axis. Uniaxial crystals are those that have rotational symmetry larger than two-fold and include trigonal, tetragonal and hexagonal systems (Figure 1). For these systems there are two directions for which the susceptibility tensor elements must be identical and are freely rotatable; e.g. \( \chi_{11} = \chi_{22} \). In uniaxial crystals the wave-vector construction involves a sphere and a spheroid and are classed negative uniaxial or positive uniaxial if for \( k \) vectors other than the ordinary direction the spheroid \( k \) vector is smaller or larger than the sphere \( k \) vector, respectively. The ordinary index \( n_o \) is defined by the direction for which both \( k \) vectors have the same value, the spheroid being the extraordinary index \( n_e \). The allowed polarised wave direction for the ordinary wave is independent of the \( k \)-vector direction and is perpendicular to the optic axis. The polarisation direction of the orthogonal extraordinary wave does depend on the direction of \( k \), but we restrict the discussion to the experimental geometry shown in Figure 1 where the \( k \)-vector is normal to the optic axis, in which case the extraordinary polarisation direction is parallel to the optic axis.

For the geometry shown in Figure 1, the molecular ordering allows a simple coordinate system determined by the polar angle \( \Phi \) made between the transition dipole moment \( \mu \) and the optic axis alone. Orientational averaging for three-fold, four-fold or six-fold rotational symmetry axis results in an absence of polarisation dependence for \( k \) vectors parallel to \( u \), while the polarisation dependence for \( k \) vectors orthogonal to \( u \) depend only on the angle \( \Phi \) of \( \mu \) with \( c \).

For biaxial crystals \( n_1 \neq n_2 \neq n_3 \) the indicatrix is a tri-axial ellipsoid and has two circular sections, corresponding to the optic axes wave-vector normals of two optic axes. The wave-vector constructions involve two general spheroids that intersect twice to define the optic axes directions. Crystal symmetry of biaxial systems determines the orientation of the principle dielectric axes relative to the crystallographic directions.

In triclinic crystals the absence of symmetry generally means that there is no relationship between the two coordinate systems, unless by accident (Figure 2A). Furthermore, the directions of the principal dielectric axes are wavelength dependent, especially close in frequency to each resonance due to anomalous dispersion. The directions of the allowed polarised waves will therefore be different and must be experimentally determined in principle for each wavelength. The Figure 2, left does not indicate directions of polarisation but can be found in the usual way for each \( k \)-vector at each frequency by evaluating the indicatrix.

In the case of monoclinic crystals, the presence of a two-fold operation in the possible point groups has the result that the crystallographic b-axis must correspond to one of the principle dielectric axes and is
thus wavelength independent, while the other two are wavelength-dependent and have no relationship to crystal symmetry (Figure 2B). The practical implication is that for a k-vector orthogonal to the crystallographic b-axis the two allowed polarised waves have directions that are parallel and perpendicular to the b-axis, independent of wave-length. In orthorhombic crystals the highest symmetry operations involve two-fold rotations, the consequence of which is that all crystallographic directions correspond to the principal dielectric axes and are wavelength independent (Figure 2C). This provides a convenient coordinate system where the allowed polarised directions for k-vectors normal to any two of the crystallographic directions always correspond to the same crystallographic axes.

Orthorhombic crystals offer an additional advantage within the class of biaxial systems in that the three two-fold or mirror symmetries (point groups 222, mm2, mmm) force a wavelength independence for all three principle directions. Because the wave-vector surfaces must survive the two-fold symmetry operations, the directions of the principal dielectric axes (εₓ ≠ εᵧ ≠ εz) of orthorhombic crystals correspond to the crystallographic symmetry axes (a,b,c) and are wavelength independent.

Crystal orientation has been discussed in detail elsewhere ⁴³,⁴⁴. For practical considerations single crystals with uniaxial symmetry may be oriented if the crystal morphology allows identification of the crystallographic c-axis visually. For instance, long needles may be formed for hexagonal space groups, where the long dimension corresponds to the C-axis. Alternatively, such crystals may form flat plates where the spectroscopically accessible surface forces the k-vector to be parallel to the optic axis. For this orientation, measurements have a polarisation dependence that is the same as isotropic samples, although the magnitude of the linear or non-linear response optical response depends on the polar angle. Birefringence analysis should therefore allow unique orientation of uniaxial crystals.

X-ray crystallographic face-indexing should normally be used in cases where birefringence analysis provides ambiguous results in the case of biaxial systems. However, a wavelength dependent analysis of birefringence may identify the presence and direction of twofold symmetry axes, which in the case of monoclinic symmetry can provide sufficient information. Further, in order to verify the crystallographic directions and assign the indices of the accessible surfaces, explicit coordinate analysis may be included.

The direction of the optic axis can be verified using cross-polarisers. Extinction is seen if the optic axis is in the plane of the sight path and one of the polariser directions, as well as at every 90 degrees. Optical identification of the optic axis direction is achieved from observing interference generated from divergent light with the optic axis direction matching the polariser direction. The presence of two optical axes in biaxial crystals is detected similarly. Such methods are well known and described in many mineralogy and optics texts ⁴⁵. This present contribution focuses on exploiting coordinate analysis in combination with non-linear optical spectroscopy, which results in the specific application of two-dimensional optical crystallography. It is also pertinent to define the term infrared crystallography, or generally optical crystallography, independent from this coordinate analysis. Optical crystallography is the study of optical properties of crystals and the classification of crystals according to their properties and the connection between optical and other physical properties of crystals, in particular their symmetry. Pleochromism is a branch of optical crystallography and was first reported by Babinet in 1838 ⁴⁶ and described by theory by Voigt in 1885 ⁴⁷. The directions of vibration are principally found in
coordinates relative to the principal dielectric axes. In order to also perform a coordinate analysis from an X-ray crystallographic structure solution and refinement, the laboratory orientation should be determined. A real-space rotation matrix will then transform the optical coordinates to the X-ray crystallographic coordinates. While optical measurements should in most cases be sufficient to find the laboratory orientation of uniaxial crystals, X-ray crystallographic face-indexing may be necessary for biaxial symmetry. Crystal morphology may guide this process particularly for crystals of small molecules, but protein crystals generally do not follow similar morphology relationships. In the case of biaxial crystals, the primary concern for the use of optical crystallography is to consider whether the optical directions are wavelength-dependent or -independent and whether one or all three optical directions correspond to crystallographic axes. The Figures 2 and 4 summarise the practicality of experimental trichroism measurements for different classifications of biaxial systems. Thus, the definition of optical crystallography is unconnected with the use of X-ray crystallography for additional analysis.

Figure 1. Experimental geometry discussed for uniaxial crystals. The k-vector is directed normal to the crystallographic c-axis which corresponds to the high symmetry axis for trigonal, tetragonal and hexagonal crystals and defines the optic axis. For a dipole \( \mu \), the polar angle \( \Theta \) with the optic axis and azimuthal angle \( \Phi \) with the ordinary direction.
Figure 2. Three classes of biaxial systems, indicating the wavelength-independent experimental orientation for optical measurement. The orientation of the biaxial indicatrix (principal refractive axes in red) is shown relative to the unit cell and crystallographic axes (blue). A) Triclinic crystals. There is no correspondence between dielectric and crystallographic axes systems and the dielectric directions are wavelength independent. B) Monoclinic crystals. The dielectric axis \( n_2 \) always corresponds to the crystallographic \( b \)-axis by convention. The consequence is that allowed polarisation directions (green and red waves) are wavelength independent for orientations perpendicular and parallel to the \( b \)-axis. C) Orthorhombic crystals. Because of 2-fold symmetry in all three directions, dielectric and crystallographic axes must correspond and are wavelength independent. The resulting allowed polarisation directions thus always correspond to the crystallographic symmetry directions. Directions of polarised optical pulses are shown for conditions as discussed.

The Figure 2 illustrates the use of the optical indicatrix (equation 6) to indicate the directions of the principle susceptibility axes relative to the crystallographic directions. It is generally convenient to
perform measurements as indicated in Figure 2 to be orthogonal to two-fold symmetry axis, but in principle an explicit analysis for any k-vector direction is possible. In order to find the normal modes corresponding to the orthogonal directions of the allowed polarised radiation modes, a graphical contraction that uses the indicatrix ellipsoid can be made. The normal plane of any k-vector intersects the indicatrix such that the direction of the extrema correspond with the normal mode directions \(^{30,34}\). In order to solve this problem it is generally necessary to know the precise values of the intrinsic birefringence in order to construct the indicatrix (equation 6) accurately, which is challenging. Instead, it is more convenient to restrict optical analysis in the directions that are indicated in Figure 1 and Figure 2.

The consequence of birefringence is that for a given direction of wave-vector k any polarisation direction is a linear combination of the two allowed polarised radiation modes, e1 and e2. For weakly absorbing crystals corresponding attenuation constants must therefore be specified that results in the phenomenon called ‘pleochromism’ \(^{30}\). Uniaxial crystals are dichroic as a result of the rotationally symmetric ellipsoid of revolution form of the indicatrix, whereas biaxial crystals are trichroic and have three unique directional attenuation coefficients. In the case of a resonant interaction, thus for the linear response, it has been pointed out \(^{33}\) that for a polarised wave having an angle alpha with respect to the electric field direction of e1, the absorbance

\[
A(\alpha) = -\log[T_1 10^{-A_1 \cos^2 \alpha} + T_2 10^{-A_2 \sin^2 \alpha}]
\] (7)

Where \(T_1\) and \(T_2\) are the transmission coefficients and \(A_1\) and \(A_2\) the absorbances in the e1 and e2 directions.

This treatment neglects the ellipticity of the vibrations, which results from attenuation. Formally, in absorbing anisotropic media the refractive index should be written as a complex property. The two allowed radiation modes that result from Maxwell’s wave equations become elliptical in the presence of extinction.

It has been shown that dichroic extinction in uniaxial crystals, that includes all spacegroup symmetries that are trigonal, tetragonal and hexagonal, the attenuation for any polarisation direction depends only on the polar angle \(\Theta\) with the optic axis \(^{33}\) (Figure 1). For a k-vector in Figure 1, the absorbances \(A_0\) and \(A_e\) for the ordinary and extraordinary polarisations, which are normalised by 1/3\(\varepsilon_{cd}\), are given as

\[
A_1 = A_0 = \langle (\hat{\mathbf{\mu}} \cdot \hat{\mathbf{e}_1})^2 \rangle = \frac{1}{2} (1 - (\hat{\mathbf{\mu}} \cdot \hat{\mathbf{u}})^2) = \frac{1}{2} \sin^2 \Theta
\] (8)

\[
A_2 = A_E = \langle (\hat{\mathbf{\mu}} \cdot \hat{\mathbf{e}_2})^2 \rangle = (\hat{\mathbf{\mu}} \cdot \hat{\mathbf{u}})^2 = \cos^2 \Theta
\] (9)

For e vectors \(e_1||u\) and \(e_2\perp u\) with the optic axis u (Figure 1). The equations are given for a single transition dipole moment in the asymmetric unit, but in case multiple copies are present the absorbances arising from them must be summed, which is not included here. For biaxial crystals, for each wavelength there exist three orthogonal directions, corresponding to the k-vector aligning with one of the dielectric axes shown in figure 2, so that the two absorbances \(A_2\) and \(A_3\) (or \(A_1\) and \(A_2\), or \(A_1\) and \(A_3\)) for the e2 and e3 fields (Figure 3) are
\[ A_2 = \langle \hat{\mu} \cdot e_2 \rangle^2 = (\sin \delta \cdot \sin \Psi)^2 \]  
\[ A_3 = \langle \hat{\mu} \cdot e_3 \rangle^2 = (\sin \delta \cdot \cos \Psi)^2 \]

Figure 3. The two angles \( \delta \) and \( \Psi \) for the transition dipole moment \( \mu \) in biaxial crystals determine the dichroic measurements of \( A_2 \) and \( A_3 \) in the direction of the \( k \)-vector shown, while a measurement in a second direction parallel to \( n_2 \) or \( n_3 \) retrieves the trichroic measurement.

In the presence of two-fold rotational symmetry in monoclinic and orthorhombic crystals the linear response is unchanged and the analysis of a single transition dipole vector suffices.

The figure 4 shows the resulting dichroic absorbances relative to polarisation direction for uniaxial and biaxial crystals. Of course, for any other \( k \)-vector the resulting absorbance is found by linear combination from the contributing amplitudes in Figure 4 according to scaling the transmitted intensities to the squared directional cosines and sines with the principal dielectric axes. The general classification described here is a useful simplification of the five major classes for the linear susceptibility tensors \( \chi_{jk} \) that group the 32 point groups, where each tensor contains 9 tensor elements. The above compact summary of well known and previously described linear optical crystallography is included as it serves as a necessary reference to describe the non-linear optical crystallography, below in sections 3, 4 and 5.
Figure 4. Polarisation dependence of the linear response for uniaxial crystals (left) shown for a k-vector perpendicular to the optic axis and biaxial crystals (right), shown for a k-vector parallel to one of the principal optical directions. The absorbances A1 and A2 are shown as polar plots for rotation of $\theta$. For uniaxial crystals dichroic information provides information only on the polar angle $\Theta$ with the optic axis. For biaxial crystals equivalent graphs for A1, A3 and A2, A3 together provide trichroic information.

3. Third-order non-linear susceptibility tensor elements

The symmetry dependence of non-linear optical susceptibility is described in standard texts. Mostly, tabulation of the non-zero non-linear tensor elements are given for the second order and third order response that is fundamental to non-linear optics. Commonly, direct inspection methods that involves coordinate transformation has been used to identify the specific Cartesian indices that survive as non-zero tensor elements. Furthermore, it is known that non-linear susceptibility tensor elements may be expressed as linear combinations of selected lower order tensor elements. Details are collected and presented in Boyd \(^{38}\) and also Zernike and Midwinter \(^{34}\). Butcher first calculated the tensor elements \(^{39}\) for the second order and third order response, and Zernike and Midwinter Zernike presented a graphical representation of the classification of Kleinman’s symmetry matrix elements for the non-centrosymmetric crystal classes \(^{34}\). A correction was published for the third order by Shang and Hsu (1987) \(^{40}\) and Boyd tabulates the corrected elements \(^{38}\). In the absence of symmetry, in triclinic crystals, it is seen that for dipole allowed conditions there must exist 81 non-zero third order susceptibility tensor elements. Experimentally, this has the interesting consequence that for a photon echo measurement three pulses may be launched in for example the x-direction, so that the emitted signal is measured in any of the X-, Y- and Z-directions. A point of interest in considering the various classes of non-zero third order tensor elements is the occurrence of exclusively pairs of Cartesian indices (as is the case for isotropic materials) or the possibility that also single and thus also triple indices are symmetry allowed. The results by Butcher \(^{39}\), Zernike and Midwinter \(^{34}\), Shang and Hsu \(^{40}\), Yang and Xu \(^{41}\) and Boyd \(^{38}\) have given well understood relationships for the third order response in Cartesian coordinates. An alternative
treatment in the basis of the principal susceptibility coordinates may evaluate the non-zero tensor elements and in addition calculate the magnitude of the third order response is given below. In order to evaluate the number of indices that can contribute to non-zero tensor elements, the point correlation function can be written in general form

$$\langle (\hat{\mu} \cdot \hat{e})^h \rangle = \frac{1}{n} \sum_{k=1}^{n} (O_k \cdot \hat{\mu} \cdot \hat{e})^h$$

(12)

Which applies the symmetry operator $O_k$ with $n$-fold symmetry and a rank of $h$ for the number of interactions. The resulting linear response for $h=2$ is given in section 2 above. For the first, second, third and fourth order correlation (or rank) this expression evaluates the result relative to each rotation, screw operation or inversion symmetry. Thus, for a uniaxial crystal and a wave in the extraordinary direction

$$\langle (\hat{\mu} \cdot \hat{e})^2 \rangle = (\mu \cdot h)^2 = \cos^2 \Theta$$

(13)

It is seen that for all values of $h$ the ranked correlations are nonzero for trigonal, tetragonal and hexagonal crystals, allowing in principle any number of Cartesian indices that include $z$, the $z$ direction by convention corresponding to the rotational symmetry axis and optic axes $u$.

The Ordinary direction $e_1=eO$ of uniaxial crystals

$$\langle (\hat{\mu} \cdot \hat{e}_O)^h \rangle = \frac{1}{n} \sin^h \theta \sum_{k=1}^{n} \cos^h (\phi + \frac{2\pi k}{n})$$

(14)

For $h=1$ the first order correlation must be zero for $n \geq 3$, from multiplication with a term that becomes the General Identity of which Euler’s identity is a special case. Therefore tensor elements with indices $xzzz=yzzz$ or any other index combining three interactions in $z$ with one in either $x$ or $y$ are zero in all uniaxial crystals.

When $h=2$ the expression already retrieved for the linear response are found, which are in principle non-zero for any pair of $z$, or any pair $xx$, $xy$, $yx$, $yy$ for $n \geq 3$.

A special case concerns $h=3$ for the ordinary direction.

$$\langle (\hat{\mu} \cdot \hat{e}_O)^3 \rangle = \frac{1}{4n} \sin^3 \theta [3 \cos \phi \sum_{k=1}^{n} \cos \frac{2\pi k}{n} - 3 \sin \phi \sum_{k=1}^{n} \sin \frac{2\pi k}{n} + \cos 3\phi \sum_{k=1}^{n} \cos \frac{6\pi k}{n} - \sin 3\phi \sum_{k=1}^{n} \sin \frac{6\pi k}{n}]$$

(15)

The sums remaining are sums of de Moivre numbers and are all zero for $n=4$ or $n=6$. However for trigonal symmetry, $n=3$, it is seen that one summation survives to give

$$\langle (\hat{\mu} \cdot \hat{e}_O)^3 \rangle = \frac{3}{4n} \sin^3 \theta \cos 3\phi = \frac{1}{4} \sin^3 \theta \cos 3\phi$$

(16)
Thus, trigonal crystals in the classes 3 and \(-3\), allow indices such as \(y^3 y^2 z\) or \(x^3 z^2 x\), or any combination of three \(x\) and/or \(y\) indices together with a single \(z\) index, whereas these are not allowed for tetragonal or hexagonal symmetry.

Figure 5. A real-space plot of the third order response of an isolated oscillator with combination of three interactions in the ordinary directions (left) and a single interaction in the extraordinary direction (right) in the presence of trigonal symmetry, corresponding to a dipole-allowed \(<OOOE>\) interaction.

Finally, for the fourth rank of interaction in the ordinary direction the general expression becomes

\[
\langle (\hat{\mu} \cdot \hat{e}_O)^4 \rangle = \frac{1}{n} \sin^4 \theta \left[ \frac{9}{8} + \frac{1}{2} \cos 2\phi \right] + \frac{1}{2} \sin 2\phi \sum_{k=1}^{n} \cos \frac{4\pi k}{n} - \frac{1}{2} \sin 2\phi \sum_{k=1}^{n} \sin^4 \theta \frac{\sin^4 \theta}{n} + \frac{1}{8} \cos 4\phi \sum_{k=1}^{n} \cos \frac{8\pi k}{n} -
\]

\[
\frac{1}{8} \sin 4\phi \sum_{k=1}^{n} \sin \frac{8\pi k}{n}
\]

The fourth rank in the ordinary direction is non-zero for all uniaxial crystals, however has a unique solution for tetragonal symmetry, \(n=4\), that depend on both polar and azimuthal angles \(\theta\) and \(\Phi\).

\[
\langle (\hat{\mu} \cdot \hat{e}_O)^4 \rangle = \frac{3}{8} \sin^4 \theta + \frac{1}{8} \sin^4 \theta \cos 4\phi
\]

Whereas for trigonal and hexagonal crystals the fourth order response depends only on the polar angle \(\theta\).
\[
\langle (\mu \cdot e_o)^4 \rangle = \frac{3}{8} \sin^4 \theta
\]  

(19)

Therefore any combination of x and/or y making up four interactions are allowed for all uniaxial symmetries as well. Tetragonal and hexagonal crystals have fewer non-zero tensor elements than trigonal crystals allowing only h=2 and h=4 for the ordinary direction.

In the above, the lowest symmetry point groups have been represented for the uniaxial systems, considering only the single three-, four- or six-fold rotation axis. Point groups with higher symmetry generally reduce the number of allowed tensor elements for the third order interaction.

For example, for classes 3 and -3 there are 73 non-zero tensor elements of which 27 are independent, while the presence of additional two-fold symmetry in classes 3m, -3m and 32 do not allow tensor elements with two z-indices combined with single x- and single y-indices. The additional two-fold symmetry causes a variant response for x and y cartesian directions, such that single interactions in either x or y become zero. As a consequence the xyzz tensor element and all others with permutations of these indices, are disallowed in trigonal point groups with two-fold symmetry in addition to the three-fold rotation. The 3m, -3m and 32 point groups have 37 nonzero elements of which 14 are independent. This demonstrates the mechanism by which additional, lower symmetry, elements in the point group reduce the number of non-zero tensor elements.

Similarly, tetragonal and hexagonal crystals that have two additional two-fold symmetry elements (classes 622, 6mm, -6m2, 422, 4mm, 4/mmm and -4m) have fewer non-zero tensor elements than the corresponding crystal classes without or with single two-fold symmetry elements for similar reasons.

For biaxial crystals, non-zero tensor elements are found from the general validity of equation 12. Monoclinic and orthorhombic crystal systems have two-fold rotations as the highest symmetry element. Thus, for a k-vector such as drawn in Figure 3, this finds the interactions for rank h in the e2 and e3 directions with respective n-fold and m-fold symmetry as

\[
\langle (\mu \cdot e_2)^h \rangle = \frac{1}{nm} \sum_{k=1}^{n} \sin^h (\delta + \frac{2\pi k}{n}) \sum_{k=1}^{m} \sin^h (\Psi + \frac{2\pi k}{m})
\]  

(20)

\[
\langle (\mu \cdot e_3)^h \rangle = \frac{1}{nm} \sum_{k=1}^{n} \sin^h (\delta + \frac{2\pi k}{n}) \sum_{k=1}^{n} \cos^h (\Psi + \frac{2\pi k}{n})
\]  

(21)

Triclinic crystals are biaxial and have no symmetry except for centrosymmetric point inversion in spacegroup P-1. Unless by coincidence, the optical directions should not correspond to the crystallographic axes. As the sums above will contain only a single term, each rank will be non-zero for each direction and therefore each possible combination of Cartesian indices is allowed and there exist \(3^3 = 81\) third order susceptibility tensor elements.

Monoclinic crystals either have a single two-fold rotation axis or a two-fold mirror plane. By convention the symmetry axis in monoclinic systems corresponds to the b-axis. The effect of the two-fold symmetry is then that for polarisation directions parallel to the symmetry axis (The e2 direction in Figures 3 and 2) that the ranks of h=1 and h=3 are zero. Only ranks of two and four survive. Thus, for monoclinic crystals
\[ \langle \mu \cdot e_2 \rangle^2 = \sin^2 \delta \sin^2 \Psi \]  
(22)

\[ \langle \mu \cdot e_2 \rangle^4 = \sin^4 \delta \sin^4 \Psi \]  
(23)

And for \( e_3 \), similarly the first and third rank are zero, while the second and fourth rank survives

\[ \langle \mu \cdot e_3 \rangle^2 = \cos^2 \Psi \sin^2 \delta \]  
(24)

\[ \langle \mu \cdot e_3 \rangle^4 = \cos^4 \Psi \sin^4 \delta \]  
(25)

Figure 6. The general case for the second rank (left) and fourth rank (right) dipole allowed response for an isolated oscillator in biaxial crystals, with \( k \) orthogonal to the \( e_1-e_2 \) plane. The components in two orthogonal dielectric axes (labelled here \( A1 \) and \( A2 \)) are plotted for values of \( \Psi \) in the geometry shown in Figure 3 with a direction \( k \).

For the \( z \) or \( x \) directions no symmetry exists, such that all ranks are in principle allowed. Since the \( y \) direction corresponds to the allowed polarisation in the \( e_2 \) direction by convention, pairs of \( y \) or two pairs of \( y \) are allowed, combines with combinations of \( z \) or \( x \).

Orthorhombic crystal systems generally provide the most convenient coordinate system for polarised optical crystallography measurements. Firstly, as described in section 2, due to molecular symmetry the principle susceptibility axes must correspond to the crystallographic directions and the optical crystallography coordinates are expressed directly also in the crystallographic coordinates. Furthermore, this must be wavelength independent, as the two wavevector surfaces must survive the two-fold symmetry operations for each wavelength. The presence of molecular symmetry then restrict the allowed combinations of indices, the single and triple cases being all zero. Therefore, for the three classes with point groups 222, mm2 and mmm, there are only 3 tensor elements with all indices equal,
and 18 further elements with indices equal in pairs, where the second order and fourth order response is found as in equations 22-25.

In the approach demonstrated above it is thus possible to evaluate the allowed tensor elements for all crystal systems. While these results are in principle equivalent to those derived by Butcher and others, they are derived in the basis of the allowed polarised radiation modes. This leads to a significant simplification. Moreover the explicit field dipole correlation functions allow a quantitative calculation of coherence contributions in 2D measurements of crystals (Table 1, Table 2).

4. Two-dimensional optical crystallography of coupled oscillators

The preceding sections served as a basis to introduce a geometrical analysis of the third order response of coupled oscillators in crystals, which is of general interest for two-dimensional electronic and vibrational spectroscopy. The formalisms of the third order response is presented in many texts, and in the following the conventions as written by Hamm, Zanni, Hochstrasser and Tokmakoff are used in particular.

2D spectroscopy measures the full complex valued third-order polarisation which by definition is the convolution of the system response functions by the electric fields. Experimental measurements can separate response belonging to rephasing and non-rephasing pathways either by phase-matching or phase-cycling techniques, in non-collinear or collinear geometries respectively. Both vibronic and electronic pathways belong to four general types of rephasing and four general types of non-rephasing Liouville-space pathways.

Briefly, it is well known that the polarisation to third order response is given

\[ P^{(3)}(t) = -\frac{i}{\hbar^3} \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 E_3(t - t_3)E_2(t - t_3 - t_2)E_1(t - t_3 - t_2 - t_1)R^{(3)}(t_3, t_2, t_1) \] (26)

With the third order Response functions \( R^{(3)} \):

\[ R^{(3)}(t_3, t_2, t_1) \propto -i(\hat{\mu}(t_3, t_2, t_1)[\hat{\mu}(t_2 + t_1), [\hat{\mu}(t_1), [\hat{\rho}(-\infty)]]]) \] (27)

The third order Response function includes many terms, which have been given. Depending on the number of oscillators involved and the inclusion of anharmonicity, the terms contributing to the third order response function \( R(3) \) are often separated in general types of Response Functions. The rephasing and non-rephasing Liouville pathways are often represented with Feynman diagrams for the general types \( R_1, R_2, R_3 \) and \( R_4, R_5, R_6 \) response functions, respectively. For an isolated anharmonic oscillator, these are shown in Figure 7 together with the corresponding four-point correlation functions that determine their contributing amplitude. These correlation functions contain the optical crystallographic selection through the inclusion of the ensemble average. In isotropic samples, the resulting ensemble average of the four-point correlations can be found either through application of Legendre polynomials, or by using a Tensor approach as shown by Hochstrasser in 2001. The latter
result provided a single relationship that is valid for any combination of dipole and electric field polarisation direction, and provides the known relationships and magnitudes for third order signals for individual Feynman pathways and polarisation combination. It is of interest to note that this equation is expressed solely by combinations of trigonometric amplitudes taken from both internal coordinates, e.g., angles between coupled transition dipoles, as well as angles between incident polarisation of electric fields. Thus, polarisation control of 2D measurements in the case of isotropic samples is sensitive to internal coordinates only. The ensemble averaging of the four-point correlation function removes any dependence of the laboratory-frame orientation in isotropic samples. It should also be noted that the derived expressions of the polarisation on the internal angle is valid only for weak pulses. With significant transfer of population, a ‘finite bleach’ will generate an angular dependence proportional to the square of the direction cosine for the electric field direction that is neglected in the present form of the four-point correlation function. Previously, analysis of propagation of finite bleach in multi-pulse experiments has been shown explicitly for two-pulse interactions, and are not further considered here. The focus of this work is to analyse the optical crystallographic application of 2D measurements via the explicit calculation of the symmetry progressions of the corresponding four-point correlation functions when measurements are made on single crystals in transmission geometry and are oriented in the laboratory frame.

Figure 7. Feynman diagrams for the third order Response Functions for an isolated anharmonic oscillator. The response functions R1, R2 and R3 contribute to the Rephasing phase matching condition, and the Response functions R4, R5 and R6 for the non-rephasing condition. The density matrix elements

\[
\begin{align*}
R_1 & : 
\langle (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) \rangle \\
R_2 & : 
\langle (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) \rangle \\
R_3 & : 
\langle (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) \rangle \\
R_4 & : 
\langle (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) \rangle \\
R_5 & : 
\langle (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) \rangle \\
R_6 & : 
\langle (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) (\mu_0 \cdot \hat{E}_3) \rangle
\end{align*}
\]
are given in Dirac notation, and the corresponding four-point correlation functions correspond to the selected Feynman path after interaction with the electric fields \(a, b, c\) and \(d\).

In the case of two coupled oscillators, the resulting Response Functions for the third order polarisation fall in general categories that take a similar form to those seen in Figure 7. Hochstrasser\(^7\) used a simplified notation to denote the Feynman paths that contribute to the third order response, which is illustrated in the Figure 8. Coupling and exciton levels are not indicated in the figure, and the formalisms are taken for the case of weak coupling, where the coupling constant \(|\beta_{12}| \ll |\hbar\nu_2 - \hbar\nu_1|\)\(^7\).

\[
\begin{align*}
|0\rangle & \quad \begin{array}{c} \frac{2\kappa}{\nu + \kappa} \end{array} \\
|1\rangle & \quad \begin{array}{c} \frac{\kappa}{\nu} \end{array} \\
|0\rangle & \quad \begin{array}{c} \frac{2\nu}{\nu + \kappa} \end{array} \\
|1\rangle & \quad \begin{array}{c} \frac{\nu}{\kappa} \end{array} \\
|0\rangle & \quad 0
\end{align*}
\]

Figure 8. A shorthand notation to denote dipole allowed transitions in a system of two coupled oscillators \(\nu\) and \(\kappa\) (right) corresponding to the Dirac notation also shown (left). The possible doubly excited states are taken together as the \(\lambda\) character as represented in the figure 8.

The Feynman diagrams for the Response Functions, given in many places in the literature, can be presented using the short-hand notation used in Figure 8. These diagrams are general and explicit calculation must include a summation of the respective pathways. For \(R_1\), this includes the Feynman paths \(\nu\nu\nu\nu, \kappa\kappa\kappa\kappa, \nu\nu\kappa\kappa\kappa\kappa\) and \(\nu\kappa\kappa\nu\nu\kappa\kappa\kappa\kappa\). For \(R_2\) this includes the paths \(\nu\nu\nu\nu, \kappa\kappa\kappa\kappa, \nu\nu\kappa\kappa\nu\nu\kappa\kappa\). For \(R_3\), this includes the paths \(\nu\nu\nu\nu, \kappa\kappa\kappa\kappa, \nu\kappa\kappa\nu\nu\kappa\kappa\kappa\kappa\). For \(R_4\), this includes \(\nu\nu\nu\nu, \kappa\kappa\kappa\kappa, \nu\kappa\kappa\nu\nu\kappa\kappa\kappa\kappa\) and \(\nu\kappa\kappa\nu\nu\kappa\kappa\kappa\kappa\kappa\). For \(R_5\) this includes \(\nu\nu\nu\nu, \kappa\kappa\kappa\kappa, \nu\kappa\kappa\kappa\nu\kappa\kappa\kappa\kappa\kappa\). For \(R_6\), this includes \(\nu\nu\nu\nu, \kappa\kappa\kappa\kappa, \nu\kappa\kappa\nu\nu\kappa\kappa\kappa\kappa\) and \(\nu\kappa\kappa\nu\nu\kappa\kappa\kappa\kappa\kappa\).

Figure 9. General classes of Feynman diagrams for the rephasing \((-k_1+k_2+k_3)\) and non-rephasing \((k_1-k_2+k_3)\) conditions for two coupled oscillators using the notation in Figure 8. The corresponding four-point correlation functions are given for each general type.
In order to explicitly calculate the third order response functions for the Feynman paths shown in Figure 9, the following equations include the ensemble average of the relevant four-point correlation functions and write the appropriate phasors. In these equation T2 is the homogenous dephasing time.

\[ R_1 = i(\hat{\mu}_{0y} \cdot \hat{E}_1)(\hat{\mu}_{0k} \cdot \hat{E}_2)(\hat{\mu}_{0v} \cdot \hat{E}_3)(\hat{\mu}_{0k} \cdot \hat{E}_4))e^{+i\omega_e t_1+i(\omega_{v}-\omega_{k})t_2-i\omega_{k}t_3 e^{-(t_1+t_3)/T2}} \]  

(28)

\[ R_2 = i(\hat{\mu}_{0y} \cdot \hat{E}_1)(\hat{\mu}_{0v} \cdot \hat{E}_2)(\hat{\mu}_{0k} \cdot \hat{E}_3)(\hat{\mu}_{0k} \cdot \hat{E}_4))e^{+i\omega_{v}t_1-i\omega_{k}t_3 e^{-(t_1+t_3)/T2}} \]  

(29)

\[ R_3 = i(\hat{\mu}_{0y} \cdot \hat{E}_1)(\hat{\mu}_{0k} \cdot \hat{E}_2)(\hat{\mu}_{0k} \cdot \hat{E}_3)(\hat{\mu}_{0k} \cdot \hat{E}_4))e^{+i\omega_{v}t_1+i(\omega_{v}-\omega_{k})t_2-i(\omega_{k}-\omega_{v})t_3 e^{-(t_1+t_3)/T2}} \]  

(30)

\[ R_4 = i(\hat{\mu}_{0y} \cdot \hat{E}_1)(\hat{\mu}_{0k} \cdot \hat{E}_2)(\hat{\mu}_{0k} \cdot \hat{E}_3)(\hat{\mu}_{0k} \cdot \hat{E}_4))e^{-i\omega_{v}t_1-i(\omega_{v}-\omega_{k})t_2-i\omega_{k}t_3 e^{-(t_1+t_3)/T2}} \]  

(31)

\[ R_5 = i(\hat{\mu}_{0y} \cdot \hat{E}_1)(\hat{\mu}_{0v} \cdot \hat{E}_2)(\hat{\mu}_{0k} \cdot \hat{E}_3)(\hat{\mu}_{0k} \cdot \hat{E}_4))e^{-i\omega_{v}t_1-i(\omega_{v}-\omega_{k})t_2-i\omega_{k}t_3 e^{-(t_1+t_3)/T2}} \]  

(32)

\[ R_6 = i(\hat{\mu}_{0y} \cdot \hat{E}_1)(\hat{\mu}_{0k} \cdot \hat{E}_2)(\hat{\mu}_{0k} \cdot \hat{E}_3)(\hat{\mu}_{0k} \cdot \hat{E}_4))e^{-i\omega_{v}t_1-i(\omega_{v}-\omega_{k})t_2-i(\omega_{k}-\omega_{v})t_3 e^{-(t_1+t_3)/T2}} \]  

(33)

2D spectra can thus be calculated for the crystallographic case by explicitly evaluating the four-point correlation functions for each of the response function contributions in equations 28-33. Using similar approach to the calculation included in section 3, the following evaluates the magnitude for each type of Feynman path. Table 1 shows calculation for uniaxial symmetry, listing separately the trigonal, tetragonal and hexagonal cases. Table 2 lists the results for the general biaxial case. Both tables are expressed in the basis of the allowed polarised radiation modes, so section 2 must be considered for experimental usage, frequency dependence, crystal orientation and potential ambiguity.

For example, considering the rephasing response function ‘R1’ involving density matrix elements gg->ag- >ab->ag->gg (with exciton states a, b), for isotropic samples the ratio of orientational factors for ZZZZ/XZXZ polarisations is known to yield 1.1 and 3 for electronic and nuclear coherence, respectively. For oriented single crystals these relationships no longer hold: Instead, the response function will contribute to the rephasing signal weighted by their four-point correlation dipole terms for the corresponding Liouville pathways. For example, the off-diagonal matrix element \( \rho_{ab} \), with creation of a coherence involving the exciton state a after the interaction -k\_s, contributes to the total four-point correlation via its single-point correlation which is a symmetry dependent (point-group) progression for the inner product of the exciton transition dipole and the electric field E\_1.
Figure 10. Example simulation of 2D spectra with population time $t_2=0\text{fs}$ of coupled oscillators with orthogonal transition dipole directions (Top: $(0,0,1)$ and $(0,1,0)$; Bottom: $(0.30,-0.90,0.30)$ and $(0.04,0.33,0.94)$) in the asymmetric unit (left) in the example of tetragonal symmetry and all-Ordinary $<OOOO>$ measurement. The c-axis carries by definition the four-fold rotational symmetry. Simulated spectra are shown separately for the rephasing condition ($-k_1+k_2+k_3$) involving $R_1+R_2+R_3$ and non-rephasing condition ($k_1-k_2+k_3$) involving $R_4+R_5+R_6$ in addition to absorptive spectra (sum of rephasing and non-rephasing response).

An illustration of the resulting real-space and symmetry response is seen in a simulation in Figure 10 using equations 28–33. The example is based on Hamm and Zanni’s simulation of the 2DIR spectrum of the two $\text{–C=O}$ stretch vibrations of dicarbonylacetylacetonato rhodium ($\text{Rh(CO)}_2\text{C}_5\text{H}_7\text{O}_2$) (RDC), using fundamental and overtone frequencies as given in their Table 10.1. Using these parameters, equations 28–33 were used for the tetragonal symmetry progression calculation for two explicit orientations in the asymmetric unit. For two orthogonal coupled dipoles in a tetragonal (uniaxial) symmetry, with selection of all-ordinary, $<\text{OOOO}>$ polarisation direction, in the unique case that the dipoles are oriented in the crystallographic b- and c-directions (Top), then all $\kappa\kappa\kappa\kappa$, $\kappa\kappa\nu\kappa$, $\nu\kappa\kappa\kappa$, $\kappa\nu\kappa\kappa$, $\kappa\kappa\kappa\nu$, and $\nu\nu\kappa\kappa$ single and double quantum pathways are zero having no component in the ordinary direction for $\mu\kappa$, selecting only the $\nu\nu\nu$ signals (Fig. 10). This demonstrates a specific filtering of coherence signals which is not possible in isotropic samples, as the spectra appear not to show coupling while it is physically present. Other orientations of the same dipoles (Bottom) do show cross-peaks and may result in line-shape distortions in absorptive spectra from the unbalanced amplitudes of the rephasing and non-rephasing contributions thus adding portions of their differing ‘phase twists’. In both uniaxial and biaxial cases, specific combinations of polarisation and Feynman path orderings are disallowed depending on the symmetry.
elements present (Tables I and II). For instance, for the ⟨OEOE⟩ directions cross-peaks can only result from κνκν and νκνκ pathways for all uniaxial classes, which can additionally be set to zero through the dipole angles θν or θκ values of 0 and π or π/2 and 3π/2 respectively.

5. Phase matching conditions

The objective outlined in section 4 above is the analysis of the four-wave mixing signals in two-dimensional spectroscopy for aligned single crystals. The phase matching conditions have been presented only for the k-vector combinations of the rephasing and non-rephasing signals (Figs. 8,9,10). Furthermore, the analysis included a polarisation response for the normal mode directions of polarisation. A number of experimental considerations must be taken into account for a practical application of 2D optical crystallography. Firstly, both the linear and non-linear response representations in sections 2,3 and 4 ignore reflection from the surface of the crystal. Second, the description of the optical indicatrix is valid for k-vector analysis inside the anisotropic crystals medium, and refraction is not yet included in the orientational analysis. In order to do so, knowledge of refractive indices and geometrical knowledge of crystal morphology must be included. In practise however, a normal incidence is recommended to avoid error caused by calculation or estimation of the angle of refraction. Consequently the Figures 1 and 2 indicate experimental directions that avoid large angles of refraction. Third, the intrinsic birefringence will cause a phase difference between the orthogonal normal modes of radiation. As is the case for frequency conversion geometry, formally there should be a requirement to conduct experiments in phase-matching direction. Furthermore, this direction is wavelength dependent which adds further complication. Also, in the absence of double diffraction the above analysis which separates the response from the orthogonal normal modes in the presence of birefringence is invalidated. For experimental conditions needed to perform a 2D measurement in transmission, previous calculations have indicated that the few-micron optical pathlength causes negligible phase difference, and can therefore be ignored 50. The Figure 11 indicates a possible experimental geometry for 2D measurements on oriented single crystals that uses achromatic Schwarzschild objectives that have high numerical aperture, also commonly used for mid-infrared measurements on single crystals 29,33,51. The advantages of the Schwarzschild optics for such applications include the achromaticity, the large numerical aperture, near-diffraction limited performance and long working distance generally needed for crystal manipulation and mounting. A well known disadvantage is that diffraction may be significant and the throughput with Gaussian beams can be reduced due to obscuration. In practice, throughput is often acceptable using Gaussian beams with very small misalignment that should not impact phase-matching geometry much 51. With appropriate visual alignment of single crystals (Figs 1,2) that have suitable optical density, including an output mask the rephasing and non-rephasing signals can be collected in the same direction using the conventional pump-probe geometry. With appropriate optical alignment however, there should be possibility to achieve traditional boxcar geometry as well.
6. Conclusions

The field of optical crystallography, which includes pleochroism, was first established in the 19th century. Traditionally, the linear response applications are mostly done in mineralogy, while frequency conversion applications of optical crystallography are fundamental to non-linear optics. Demonstration of pleochroism is well established with examples in mineralogy, THz spectroscopy and coherent infrared emission. However, the pleochroism sub-area has received surprisingly little attention for the explicit structural analysis of molecular response, but has been well demonstrated. As briefly reviewed, the symmetry dependence of third-rank and fourth-rank Tensor elements are well known and previously reported some decades ago. The section 2 and introduction to section 3 is meant to provide a summary and overview of the conclusions that are relevant to the analysis of 2D optical measurements on crystals. Section 3 continues to provide an analytical method of calculation of non-zero third order tensor elements, which is an alternative to ‘direct inspection’ methods that typically involves transformation of Cartesian indices in the evaluation of the symmetry dependence. In section 4 an explicit calculation of the relevant four-point correlation functions for the field-dipole interactions for the traditional response function formalism is given for uniaxial and biaxial crystal systems. The
simulations show that lineshape distortion and selective amplitude modification for coherence contributions can be understood from the symmetry progression solutions of the four-point correlation functions. In essence, the oriented single crystal in the presence of birefringence acts as a structural ‘filter’ that selects and weighs the coherence contributions to the frequency-frequency correlation signals that are measured by 2D spectroscopy. The 2D measurements are shown to be explicitly and quantifiably sensitive to crystal symmetry, crystal orientation, polarization direction, molecular structure and associated transition dipole directions, and orientation of the molecular structure in the asymmetric unit. These results connect the X-ray structural coordinate analysis with a two-dimensional spectroscopy measurements under conditions of defined geometry. Explicit analysis of the separate contributions of the frequency-frequency correlation provides a new method for visualizing structural dynamics and the coherences directly in real-space of the molecular structure.
Selected field combinations are given for the four major types of Feynman pathways. The point group symmetry is given as reduced point group thus accounting only for the high symmetry rotational operator, thus may only be applied to third order tensor elements that survive the higher symmetry elements.

### Table 1

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Acknowledgements

JvT acknowledges support from The Leverhulme Trust via award RPG-2014-126 and the Engineering and Physical Sciences Research Council (EPSRC) via award EP/R020574/1.

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