Table 1 presents a compilation of the standard deviations calculated using the two methods. We decided to redetermine the values reported by RWS since we found some inconsistencies in their original paper [for instance, the ratio $\sigma(\tau_m)/\sigma(P)$ for entry v was $1{\cdot}8\ \tau_m$ (rad) while it should be close to $1{\cdot}0\ \tau_m$ (rad)]. Since individual $\sigma(\theta_i)$'s are not available in the original references, we had to calculate them also. For the calculations we used the original positional parameters and their e.s.d.'s and the method of Shmueli (1974). From a comparison of the standard deviations calculated with the two methods, three cases can be distinguished (Table 1): (i) σ_{FS}'s and σ_{LS}'s are roughly the same (entry ii); (ii) low-precision observations fit the model very well (entry v); and (iii) precise observations give very poor fit (entry vii).

As discussed above, the σ^2_{LS}'s are a measure of the fit between the real and calculated worlds. Another measure of this agreement in the LS formalism is the conventional R factor. Entries vii and ix of Table 1 show that R is sensitive to both systematic and random errors. As pointed out by RWS, the departure of the A_0 and A_1 coefficients of their Fourier series [see (1) of RWS] from 0 furnishes the FS method with a measure of the deviation from the ideal pseudorotation description. Table 1 reports the A_0 and A_1 values for each entry. Although it is possible to trace a very poor fit by the large values of $|A_0|$ and $|A_1|$ (entry vii), it is in general not obvious how to establish the discrepancy between the observations and the model from individual $|A_0|$ and $|A_1|$ values, and how to compare the deviations for different systems. It seems that the R factor provides a more convenient measure of the deviation from the ideal pseudorotation description.

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Rules for Estimating the Values of Triplet Phase Invariants in Multiwavelength Anomalous Dispersion Experiments

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Abstract

Several simple rules, $R_{ano,4}$, $R_{ano,5}$, $R_{ano,6}$ and $R_{ano,7}$, have been derived on the basis of the mathematical and physical characteristics of anomalous dispersion experiments that permit the estimation of values for triplet phase invariants. They apply to two-wavelength experiments and concern a variety of values defined in terms of the real and imaginary corrections to atomic scattering factors. The rules apply to the case of a single type of predominant anomalous scatterer. The generalization to more than one type of predominant anomalous scatterer is also described. Test examples show that large numbers of invariants may be evaluated by these means with reliabilities that, in certain circumstances, are at a potentially useful level, but the ultimate applicability depends, of course, on the reliability of the experimental data. The only information required besides the measurements of the diffraction intensities is the chemical composition of the anomalously scattering atoms. If there is more than one type of predominant anomalous scatterer, information concerning the relative proportion of the different types is also required.

Introduction

In a previous article (Karle, 1984*b*), rules were presented for selecting triplet phase invariants whose values are close to certain anticipated values. The rules arise from considerations of a mathematical and physical

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nature that apply to the anomalous dispersion technique and concern anomalous dispersion data collected at a single wavelength. In this article, new rules will be developed that apply to anomalous dispersion data from a multiwavelength experiment. It will be seen that the same sort of mathematical and physical characteristics that provide the basis for the rules for single-wavelength experiments also provide the basis for the rules for multiwavelength experiments.

The characteristics of interest concern observations related to the differences of the magnitudes of selected types of structure factors and also the expected values of triplet phase invariants associated with the structure of the anomalous scatterers. In order to be able to estimate values for the triplet phase invariants in this approach, when there is only one predominant type of anomalous scatterer, it is only necessary to know the chemical nature of the predominant anomalous scatterers, not their number, the positions they occupy nor the occupancy of the positions that they occupy. If there is more than one predominant anomalous scatterer, an estimate of their number is needed.

The results to be obtained here for a multiple-wavelength experiment are simple rules for selecting triplet phase invariants whose values are near some particular predetermined values. The rules are similar to those for a single-wavelength experiment and are to be combined with them to enhance the usefulness of a multiple-wavelength experiment.

Conceptual basis

The concepts that form the basis for the rules of interest are illustrated in Fig. 1. This figure provided the basis for the formulation of three rules appropriate for a single-wavelength experiment (Karle, 1984*b*). For the multiwavelength experiment considered here, the symbolism represents four additonal cases ($m = 4$–7), listed in Table 1. The quantity $F_{\lambda_p \mathbf{h}}$ is the structure factor associated with a measured intensity at wavelength λ_p and includes the contribution from anomalous dispersion, $F^n_{\mathbf{h}}$ is the corresponding structure factor when the contribution from anomalous dispersion is omitted and $F^a_{\lambda_p \mathbf{h}}$ is the corresponding structure factor that represents only the contribution from anomalous dispersion at wavelength λ_p. The quantities are related by

$$F_{\lambda_p \mathbf{h}} = F^n_{\mathbf{h}} + F^a_{\lambda_p \mathbf{h}}. \tag{1}$$

It follows from (1) that for all the cases in Table 1

$${}_m\mathscr{F}_{1,\mathbf{h}} = {}_m\mathscr{F}_{2,\mathbf{h}} + {}_m\mathscr{F}_{3,\mathbf{h}}. \tag{2}$$

The atomic scattering factor for the qth atom that scatters anomalously is given by

$$f_{q,\mathbf{h}} = f^n_{q,\mathbf{h}} + f'_q + if''_q, \tag{3}$$

where $f^n_{q,\mathbf{h}}$ is the normal atomic scattering factor and f'_q and f''_q are the real and imaginary parts of the anomalous correction, respectively.

The insights provided by Fig. 1 have already provided the basis for the derivation of the rules for evaluating triplet phase invariants in a one-wavelength anomalous dispersion experiment (Karle, 1984*b*). The insights are also applicable to multiple-wavelength experiments. For convenience, the characteristics of Fig. 1 are repeated here.

The solid lines forming the closed triangle in Fig. 1 represent the vector equation (2), with the pre-subscript m omitted. Given, for example, the vector $\mathscr{F}_{1,\mathbf{h}}$ as in Fig. 1, the dotted line of radius $|\mathscr{F}_{2,\mathbf{h}}|$ could be a possible location for $\mathscr{F}_{2,\mathbf{h}}$, but not necessarily. It would not be possible if the dotted line connecting this vector with $\mathscr{F}_{1,\mathbf{h}}$ would have to have a magnitude that exceeds the maximum possible value for $|\mathscr{F}_{3,\mathbf{h}}|$. The implication of this observation is that if the largest differences $\|\mathscr{F}_{1,\mathbf{h}}| - |\mathscr{F}_{2,\mathbf{h}}\|$ are selected from a data set, they would be associated with the largest possible values of $|\mathscr{F}_{3,\mathbf{h}}|$ and $\mathscr{F}_{1,\mathbf{h}}$ and $\mathscr{F}_{2,\mathbf{h}}$ would have phases that do not differ greatly. We formalize these observations and their implications, as follows.

1. The largest magnitude differences, $\|\mathscr{F}_{1,\mathbf{h}}| - |\mathscr{F}_{2,\mathbf{h}}\|$, are associated with the largest values of the magnitudes $|\mathscr{F}_{3,\mathbf{h}}|$.

2. Triplet phase invariants associated with the largest $|\mathscr{F}_{3,\mathbf{h}}\mathscr{F}_{3,\mathbf{k}}\mathscr{F}_{3,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ can be expected to have values close to zero, especially for simple 'heavy-atom' structures. [The triplet phase invariants refer to the nonanomalous portion of the scattering, $(\varphi^n_{j,\mathbf{h}} + \varphi^n_{j,\mathbf{k}} + \varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})$; additional phase functions arise from the anomalous portion of the scattering and can be readily evaluated from appropriate tables.]

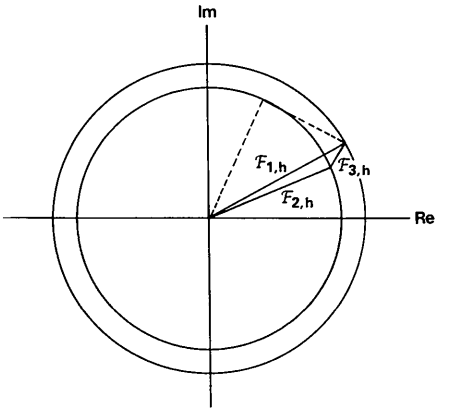

Fig. 1. An illustration of the vector equation $\mathscr{F}_{1,\mathbf{h}} = \mathscr{F}_{2,\mathbf{h}} + \mathscr{F}_{3,\mathbf{h}}$. The largest magnitude differences, $\|\mathscr{F}_{1,\mathbf{h}}| - |\mathscr{F}_{2,\mathbf{h}}\|$, are associated with the largest possible values of $|\mathscr{F}_{3,\mathbf{h}}|$. This case is represented by the triangle formed from the solid lines. The placement of the dotted line representing alternative position for $\mathscr{F}_{2,\mathbf{h}}$ would not be possible if the magnitude of the dotted line connecting it to $\mathscr{F}_{1,\mathbf{h}}$ would exceed the maximum possible value. This implies that, for the largest magnitude differences, the phase angles for $\mathscr{F}_{1,\mathbf{h}}$ and $\mathscr{F}_{2,\mathbf{h}}$ do not differ by much.

Table 1. *Quantities involved in the four cases leading to rules for selecting triplet phase invariants in multi-wavelength experiments*

The first three cases, which apply to a single-wavelength experiment, were considered in an earlier paper (Karle, 1984*b*). The quantities ${}_m\mathscr{F}_{1,\mathbf{h}}$, ${}_m\mathscr{F}_{2,\mathbf{h}}$ and ${}_m\mathscr{F}_{3,\mathbf{h}}$ are defined by the corresponding entries in colums 2, 3, 4, respectively, for $m = 4, 5, 6, 7$.

Case m	${}_m\mathscr{F}_{1,\mathbf{h}}$	${}_m\mathscr{F}_{2,\mathbf{h}}$	${}_m\mathscr{F}_{3,\mathbf{h}}$	Estimates†	Defining equation
4	$F_{\lambda_1\mathbf{h}}$	$F_{\lambda_2\mathbf{h}}$	$F^a_{\lambda_1\mathbf{h}} - F^a_{\lambda_2\mathbf{h}}$	$\delta^{-,-}_{\lambda_1\lambda_2}$ or $\delta^{-,-}_{\lambda_1\lambda_2} + \pi$	(15)
5	$F_{\lambda_1\mathbf{h}} + F_{\lambda_2\mathbf{h}}$	$2F^n_{\mathbf{h}}$	$F^a_{\lambda_1\mathbf{h}} + F^a_{\lambda_2\mathbf{h}}$	$\delta^{+,+}_{\lambda_1\lambda_2}$ or $\delta^{+,+}_{\lambda_1\lambda_2} + \pi$	(23)
6	$F_{\lambda_1\mathbf{h}}$	$F^*_{\lambda_2\bar{\mathbf{h}}}$	$F^a_{\lambda_1\mathbf{h}} - F^{a*}_{\lambda_2\bar{\mathbf{h}}}$	$\delta^{+,-}_{\lambda_1\lambda_2}$ or $\delta^{+,-}_{\lambda_1\lambda_2} + \pi$	(32)
7	$F_{\lambda_1\mathbf{h}} + F^*_{\lambda_2\bar{\mathbf{h}}}$‡	$2F^n_{\mathbf{h}}$	$F^a_{\lambda_1\mathbf{h}} + F^{a*}_{\lambda_2\bar{\mathbf{h}}}$	$\delta^{-,+}_{\lambda_1\lambda_2}$ or $\delta^{-,+}_{\lambda_1\lambda_2} + \pi$	(40)

† These estimates are appropriate when only one type of predominant anomalous scatterer is present. Otherwise, the estimates would involve functions of several δ, one for each type of anomalous scatterer, as discussed in the text.

‡ The asterisk denotes complex conjugate.

3. For the larger values of $\|\mathscr{F}_{1,\mathbf{h}}| - |\mathscr{F}_{2,\mathbf{h}}\|$, the phase of $\mathscr{F}_{1,\mathbf{h}}$ will differ little in value from the phase of $\mathscr{F}_{2,\mathbf{h}}$.

Theory

The analyses to be carried out all depend upon the triplet product that follows from (2),

$$({}_m\mathscr{F}_{1,\mathbf{h}} - {}_m\mathscr{F}_{2,\mathbf{h}})({}_m\mathscr{F}_{1,\mathbf{k}} - {}_m\mathscr{F}_{2,\mathbf{k}})({}_m\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})} - {}_m\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}) = ({}_m\mathscr{F}_{3,\mathbf{h}})({}_m\mathscr{F}_{3,\mathbf{k}})({}_m\mathscr{F}_{3,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}), \quad (4)$$

where $m = 4, 5, 6, 7$, as defined in Table 1. The left side of (4) may be rewritten

$$\begin{aligned}
&|{}_m\mathscr{F}_{1,\mathbf{h}}\, {}_m\mathscr{F}_{1,\mathbf{k}}\, {}_m\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad \times \exp[i({}_m\varphi_{1,\mathbf{h}} + {}_m\varphi_{1,\mathbf{k}} + {}_m\varphi_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad - |{}_m\mathscr{F}_{1,\mathbf{h}}\, {}_m\mathscr{F}_{1,\mathbf{k}}\, {}_m\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad \times \exp[i({}_m\varphi_{1,\mathbf{h}} + {}_m\varphi_{1,\mathbf{k}} + {}_m\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad - |{}_m\mathscr{F}_{1,\mathbf{h}}\, {}_m\mathscr{F}_{2,\mathbf{k}}\, {}_m\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad \times \exp[i({}_m\varphi_{1,\mathbf{h}} + {}_m\varphi_{2,\mathbf{k}} + {}_m\varphi_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad + |{}_m\mathscr{F}_{1,\mathbf{h}}\, {}_m\mathscr{F}_{2,\mathbf{k}}\, {}_m\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad \times \exp[i({}_m\varphi_{1,\mathbf{h}} + {}_m\varphi_{2,\mathbf{k}} + {}_m\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad - |{}_m\mathscr{F}_{2,\mathbf{h}}\, {}_m\mathscr{F}_{1,\mathbf{k}}\, {}_m\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad \times \exp[i({}_m\varphi_{2,\mathbf{h}} + {}_m\varphi_{1,\mathbf{k}} + {}_m\varphi_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad + |{}_m\mathscr{F}_{2,\mathbf{h}}\, {}_m\mathscr{F}_{1,\mathbf{k}}\, {}_m\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad \times \exp[i({}_m\varphi_{2,\mathbf{h}} + {}_m\varphi_{1,\mathbf{k}} + {}_m\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad + |{}_m\mathscr{F}_{2,\mathbf{h}}\, {}_m\mathscr{F}_{2,\mathbf{k}}\, {}_m\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad \times \exp[i({}_m\varphi_{2,\mathbf{h}} + {}_m\varphi_{2,\mathbf{k}} + {}_m\varphi_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \\
&\quad - |{}_m\mathscr{F}_{2,\mathbf{h}}\, {}_m\mathscr{F}_{2,\mathbf{k}}\, {}_m\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \\
&\quad \times \exp[i({}_m\varphi_{2,\mathbf{h}} + {}_m\varphi_{2,\mathbf{k}} + {}_m\varphi_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})]. \qquad (5)
\end{aligned}$$

On the basis of observation 3 above, when the appropriate magnitude differences are large, the triplet phase invariants in (5) may be replaced by some average value, $\langle {}_m\Phi_{\mathbf{hk}} \rangle$, and then (5) may be rewritten

$$(|{}_m\mathscr{F}_{1,\mathbf{h}}| - |{}_m\mathscr{F}_{2,\mathbf{h}}|)(|{}_m\mathscr{F}_{1,\mathbf{k}}| - |{}_m\mathscr{F}_{2,\mathbf{k}}|) \times (|{}_m\mathscr{F}_{1,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| - |{}_m\mathscr{F}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|) \exp(i\langle {}_m\Phi_{\mathbf{hk}} \rangle). \quad (6)$$

By comparing (6) with the right side of (4) and making use of observations 1 and 2, the opportunity for evaluating $\langle {}_m\Phi_{\mathbf{hk}} \rangle$ for the four cases listed in Table 1 will ensue. If desired, the evaluation may be applied to those triplet phase invariants in (5) that are associated only with the largest products of $\mathscr{F}$ magnitudes. Previous calculations (Karle, 1983) have indicated that an increase in accuracy may be achieved in this way, although it may not be of any great practical significance to do so.

When there is a single predominant type of anomalous scatterer, simple rules for evaluating the triplet phase invariants will be obtained. Otherwise somewhat more complicated and somewhat approximate calculations are involved unless the structure of the anomalous scatterers is known.

Derivation of $R_{\text{ano},4}$

We are concerned here with case 4 of Table 1. The right side of (4) is now developed for this case. According to (1),

$$F_{\lambda_1\mathbf{h}} - F_{\lambda_2\mathbf{h}} = F^a_{\lambda_1\mathbf{h}} - F^a_{\lambda_2\mathbf{h}}. \quad (7)$$

We have

$$F^a_{\lambda_1\mathbf{h}} = \sum_{j=1}^{N_{\text{ano}}} f^a_{\lambda_1 j} \exp(i\delta_{\lambda_1 j}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j), \quad (8)$$

where N_{ano} is the number of anomalously scattering atoms in the unit cell,

$$f^a_{\lambda_1 j} = (f'^2_{\lambda_1 j} + f''^2_{\lambda_1 j})^{1/2} \quad (9)$$

$$\delta_{\lambda_1 j} = \tan^{-1}(f''^2_{\lambda_1 j}/f'^2_{\lambda_1 j}) \quad (10)$$

and λ_1 specifies some particular wavelength.

Equation (8) can be rewritten in terms of the number of types of anomalous scatterers, q (the subscript, $j = 1$, is reserved for atoms that essentially do not scatter anomalously):

$$F^a_{\lambda_1\mathbf{h}} = \sum_{j=2}^{q+1} (f^a_{\lambda_1 j}/f^n_{j,\mathbf{h}}) \exp(i\delta_{\lambda_1 j}) F^n_{j,\mathbf{h}}, \quad (11)$$

where $f^n_{j,\mathbf{h}}$ is the normal atomic scattering factor and the $F^n_{j,\mathbf{h}}$ are the structure factors for each type of anomalously scattering atom. We express (7) in terms of (11),

$$F^a_{\lambda_1\mathbf{h}} - F^a_{\lambda_2\mathbf{h}} = \sum_{j=2}^{q+1} (1/f^n_{j,\mathbf{h}}) \times [f^a_{\lambda_1 j} \exp(i\delta_{\lambda_1 j}) - f^a_{\lambda_2 j} \exp(i\delta_{\lambda_2 j})] F^n_{j,\mathbf{h}}. \quad (12)$$

Expression (12) can be rewritten as

$$F^a_{\lambda_1\mathbf{h}} - F^a_{\lambda_2\mathbf{h}} = \sum_{j=2}^{q+1} (f^{a\,-,-}_{\lambda_1\lambda_2 j}/f^n_{j,\mathbf{h}}) \exp(i\delta^{-,-}_{\lambda_1\lambda_2 j}) F^n_{j,\mathbf{h}}, \quad (13)$$

where

$$f^{a\,-,-}_{\lambda_1\lambda_2 j} = [(f''_{\lambda_1 j} - f''_{\lambda_2 j})^2 + (f'_{\lambda_1 j} - f'_{\lambda_2 j})^2]^{1/2} \quad (14)$$

and

$$\delta^{-,-}_{\lambda_1\lambda_2 j} = \tan^{-1}[(f''_{\lambda_1 j} - f''_{\lambda_2 j})/(f'_{\lambda_1 j} - f'_{\lambda_2 j})]. \quad (15)$$

The product on the right side of (4) can now be given in terms of the product of three sums obtainable from the right side of (13). As an approximation, the neglect of cross terms in the latter product gives

$$\sum_{j=2}^{q+1} [(f^{a\,-,-}_{\lambda_1\lambda_2 j})^3/f^n_{j,\mathbf{h}} f^n_{j,\mathbf{k}} f^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}] \times \exp(i3\delta^{-,-}_{\lambda_1\lambda_2 j}) |F^n_{j,\mathbf{h}} F^n_{j,\mathbf{k}} F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp[i(\varphi^n_{j,\mathbf{h}} + \varphi^n_{j,\mathbf{k}} + \varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})], \quad (16)$$

where it is expected that, for large values of $|F^n_{j,\mathbf{h}} F^n_{j,\mathbf{k}} F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$, the triplet phase invariants $(\varphi^n_{j,\mathbf{h}} + \varphi^n_{j,\mathbf{k}} + \varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})$ will have a value close to zero (observations 1 and 2). A test of the appropriateness of the type of approximation used in (16) has been carried out (Karle, 1984*b*). There is often only one type of predominant anomalous scatterer. We proceed with this assumption.

With one type of predominant anomalous scatterer, we may replace (16), and avoid the need to make any approximation, with

$$[(f^{a\,-,-}_{\lambda_1\lambda_2})^3/f^n_{2,\mathbf{h}} f^n_{2,\mathbf{k}} f^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}] \times \exp(i3\delta^{-,-}_{\lambda_1\lambda_2}) |F^n_{2,\mathbf{h}} F^n_{2,\mathbf{k}} F^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|. \quad (17)$$

From Table 1, (6) may be rewritten, when $m = 4$,

$$(|F_{\lambda_1\mathbf{h}}| - |F_{\lambda_2\mathbf{h}}|)(|F_{\lambda_1\mathbf{k}}| - |F_{\lambda_2\mathbf{k}}|) \times (|F_{\lambda_1(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| - |F_{\lambda_2(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|) \exp(i\langle {}_4\Phi_{\mathbf{hk}}\rangle. \quad (18)$$

We now compare (18) with (17) representing the left and right sides of (4), respectively, when $m = 4$. In order for (17) and (18) to be approximately equal, the average of the triplet phase invariants, $\langle {}_4\Phi_{\mathbf{hk}}\rangle$, should have a value close to $3\delta^{-,-}_{\lambda_1\lambda_2 2}$ or $3\delta^{-,-}_{\lambda_1\lambda_2 2} + \pi$, depending upon the sign of the triplet product of magnitude differences in (18). This leads to the following rule for the largest triple products of magnitude differences.

$R_{\text{ano},4}$: *If the sign of the product of the largest magnitude differences,* $(|F_{\lambda_1\mathbf{h}}| - |F_{\lambda_2\mathbf{h}}|)(|F_{\lambda_1\mathbf{k}}| - |F_{\lambda_2\mathbf{k}}|) \times (|F_{\lambda_1(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| - |F_{\lambda_2(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|)$, *is plus, the value of the associated average triplet phase invariant is close to* $3\delta^{-,-}_{\lambda_1\lambda_2 2}$ *and, when it is minus, the value of the average triplet phase invariant is close to* $3\delta^{-,-}_{\lambda_1\lambda_2 2} + \pi$.

This rule, in effect, assigns the estimate to all eight triplet phase invariants in (5) (when $m = 4$). As a modification to $R_{\text{ano},4}$, the estimates may be assigned only to those triplet phase invariants that are associated with the larger products of structure-factor magnitudes among the eight possibilities given in (5), instead of to all eight of them. Improved accuracy may be obtained this way.

If there is more than one type of predominant anomalous scatterer, (16) may be used instead of (17) and compared with (18). In order to use (16), at least the chemical composition of the anomalously scattering atoms would have to be known. From it, the values of the $|F^n_{j,\mathbf{h}} F^n_{j,\mathbf{k}} F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ could be evaluated approximately. If the anomalously scattering structure were known, the exact product on the right side of (4) could be computed from the product of three sums obtainable from the right side of (13).

Derivation of $R_{\text{ano},5}$

We are concerned here with case 5 on Table 1. The right side of (4) is now developed for this case. According to (1),

$$F_{\lambda_1\mathbf{h}} + F_{\lambda_2\mathbf{h}} - 2F^n_{\mathbf{h}} = F^a_{\lambda_1\mathbf{h}} + F^a_{\lambda_2\mathbf{h}}. \quad (19)$$

The right side of (19) is now expressed in terms of (11);

$$F^a_{\lambda_1\mathbf{h}} + F^a_{\lambda_2\mathbf{h}} = \sum_{j=2}^{q+1} (1/f^n_{j,\mathbf{h}})[f^a_{\lambda_1 j} \exp(i\delta_{\lambda_1 j}) + f^a_{\lambda_2 j} \exp(i\delta_{\lambda_2 j})] F^n_{j,\mathbf{h}}. \quad (20)$$

Expression (20) may be rewritten as

$$F^a_{\lambda_1\mathbf{h}} + F^a_{\lambda_2\mathbf{h}} = \sum_{j=2}^{q+1} (f^{a\,+,+}_{\lambda_1\lambda_2 j}/f^n_{j,\mathbf{h}}) \exp(i\delta^{+,+}_{\lambda_1\lambda_2 j}) F^n_{j,\mathbf{h}}, \quad (21)$$

where

$$f^{a\,+,+}_{\lambda_1\lambda_2 j} = [(f''_{\lambda_1 j} + f''_{\lambda_2 j})^2 + (f'_{\lambda_1 j} + f'_{\lambda_2 j})^2]^{1/2} \quad (22)$$

and

$$\delta^{+,+}_{\lambda_1\lambda_2 j} = \tan^{-1}[(f''_{\lambda_1 j} + f''_{\lambda_2 j})/(f'_{\lambda_1 j} + f'_{\lambda_2 j})]. \quad (23)$$

This case proceeds similarly to case 4 with (16) and (17) replaced by (24) and (25), respectively,

$$\sum_{j=2}^{q+1} [(f^{a\,+,+}_{\lambda_1\lambda_2 j})^3/f^n_{j,\mathbf{h}} f^n_{j,\mathbf{k}} f^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}] \times \exp(i3\delta^{+,+}_{\lambda_1\lambda_2 j}) |F^n_{j,\mathbf{h}} F^n_{j,\mathbf{k}} F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp[i(\varphi^n_{j,\mathbf{h}} + \varphi^n_{j,\mathbf{k}} + \varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \quad (24)$$

and

$$[(f^{a\,+,+}_{\lambda_1\lambda_2 2})^3/f^n_{2,\mathbf{h}} f^n_{2,\mathbf{k}} f^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}] \times \exp(i3\delta^{+,+}_{\lambda_1\lambda_2 2}) |F^n_{2,\mathbf{h}} F^n_{2,\mathbf{k}} F^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|. \quad (25)$$

From Table 1, (6) may be rewritten when $m = 5$.

$$(|F_{\lambda_1\mathbf{h}} + F_{\lambda_2\mathbf{h}}| - 2|F^n_{\mathbf{h}}|)(|F_{\lambda_1\mathbf{k}} + F_{\lambda_2\mathbf{k}}| - 2|F^n_{\mathbf{k}}|) \times (|F_{\lambda_1(\bar{\mathbf{h}}+\bar{\mathbf{k}})} + F_{\lambda_2(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| - 2|F^n_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}|) \exp(i\langle {}_5\Phi_{\mathbf{hk}}\rangle). \quad (26)$$

A comparison is now made of (26) and (25) and, in order for them to be approximately equal, the average of the triplet phase invariants, $\langle {}_5\Phi_{\mathbf{hk}}\rangle$, should have a value close to $3\delta^{+,+}_{\lambda_1\lambda_2 2}$ or $3\delta^{+,+}_{\lambda_1\lambda_2 2}+\pi$, depending upon the sign of the triplet product of magnitude differences in (26). Since $|F_{\lambda_1\mathbf{h}}+F_{\lambda_2\mathbf{h}}|$ is not directly measurable from experiment, in application we use the approximation

$$|F_{\lambda_1\mathbf{h}}+F_{\lambda_2\mathbf{h}}|\sim|F_{\lambda_1\mathbf{h}}|+|F_{\lambda_2\mathbf{h}}| \tag{27}$$

with insignificant error since, in the cases of interest, the phase of $F_{\lambda_1\mathbf{h}}$ differs little from that of $F_{\lambda_2\mathbf{h}}$. We have now the following rule for the largest triple products of magnitude differences.

$R_{\text{ano},5}$: *If the sign of the product of the largest magnitude differences,* $(|F_{\lambda_1\mathbf{h}}|+|F_{\lambda_2\mathbf{h}}|-2|F^n_{\mathbf{h}}|)\times(|F_{\lambda_1\mathbf{k}}|+|F_{\lambda_2\mathbf{k}}|-2|F^n_{\mathbf{k}}|)\times(|F_{\lambda_1(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|+|F_{\lambda_2(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|-2|F^n_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}|)$, *is plus, the value of the associated average triplet phase invariant is close to* $3\delta^{+,+}_{\lambda_1\lambda_2 2}$ *and, when it is minus, the value of the average triplet phase invariant is close to* $3\delta^{+,+}_{\lambda_1\lambda_2 2}+\pi$.

The same type of discussion that follows $R_{\text{ano},4}$ applies to $R_{\text{ano},5}$. It is only necessary to change some of the equation numbers. For example, if there is more than one type of predominant anomalous scatterer, (24) may be used instead of (25) and compared with (26). In order to use (24), at least the chemical composition of the anomalously scattering atoms would have to be known. From it, the values of the $|F^n_{j,\mathbf{h}}F^n_{j,\mathbf{k}}F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ could be evaluated approximately. If the anomalously scattering structure were known, the exact product on the right side of (4) could be computed from the product of the three sums obtainable from the right side of (21).

Derivation of $R_{\text{ano},6}$

We are concerned here with case 6 of Table 1. The right side of (4) is now developed for this case. According to (1),

$$F_{\lambda_1\mathbf{h}}-F^*_{\lambda_2\bar{\mathbf{h}}}=F^a_{\lambda_1\mathbf{h}}-F^{a*}_{\lambda_2\bar{\mathbf{h}}}. \tag{28}$$

The right side of (28) is now expressed in terms of (11),

$$F^a_{\lambda_1\mathbf{h}}-F^{a*}_{\lambda_2\bar{\mathbf{h}}}=\sum_{j=2}^{q+1}(1/f^n_{j,\mathbf{h}})[f^a_{\lambda_1 j}\exp(i\delta_{\lambda_1 j})-f^a_{\lambda_2 j}\exp(-i\delta_{\lambda_2 j})]F^n_{j,\mathbf{h}}. \tag{29}$$

Expression (29) may be rewritten as

$$F^a_{\lambda_1\mathbf{h}}-F^{a*}_{\lambda_2\bar{\mathbf{h}}}=\sum_{j=2}^{q+1}(f^{a+,-}_{\lambda_1\lambda_2 j}/f^n_{j,\mathbf{h}})\exp(i\delta^{+,-}_{\lambda_1\lambda_2 j})F^n_{j,\mathbf{h}}, \tag{30}$$

where

$$f^{a+,-}_{\lambda_1\lambda_2 j}=[(f''_{\lambda_1 j}+f''_{\lambda_2 j})^2+(f'_{\lambda_1 j}-f'_{\lambda_2 j})^2]^{1/2} \tag{31}$$

and

$$\delta^{+,-}_{\lambda_1\lambda_2 j}=\tan^{-1}[(f''_{\lambda_1 j}+f''_{\lambda_2 j})/(f'_{\lambda_1 j}-f'_{\lambda_2 j})]. \tag{32}$$

This case proceeds similarly to cases 4 and 5 with (16) and (17) replaced by (33) and (34), respectively,

$$\sum_{j=2}^{q+1}[(f^{a+,-}_{\lambda_1\lambda_2 j})^3/f^n_{j,\mathbf{h}}f^n_{j,\mathbf{k}}f^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}]\times\exp(i3\delta^{+,-}_{\lambda_1\lambda_2 j})|F^n_{j,\mathbf{h}}F^n_{j,\mathbf{k}}F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|\times\exp[i(\varphi^n_{j,\mathbf{h}}+\varphi^n_{j,\mathbf{k}}+\varphi^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \tag{33}$$

and

$$[(f^{a+,-}_{\lambda_1\lambda_2 2})^3/f^n_{2,\mathbf{h}}f^n_{2,\mathbf{k}}f^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}]\times\exp(i3\delta^{+,-}_{\lambda_1\lambda_2 2})|F^n_{2,\mathbf{h}}F^n_{2,\mathbf{k}}F^n_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|. \tag{34}$$

From Table 1, (6) may be rewritten, when $m=6$,

$$(|F_{\lambda_1\mathbf{h}}|-|F_{\lambda_2\bar{\mathbf{h}}}|)(|F_{\lambda\mathbf{k}}|-|F_{\lambda_2\bar{\mathbf{k}}}|)(|F_{\lambda_1(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|-|F_{\lambda_2(\mathbf{h}+\mathbf{k})}|)\exp(i\langle {}_6\Phi_{\mathbf{hk}}\rangle). \tag{35}$$

A comparison is now made of (35) and (34) and, in order for them to be approximately equal, the average of the triplet phase invariants, $\langle {}_6\Phi_{\mathbf{hk}}\rangle$, should have a value close to $3\delta^{+,-}_{\lambda_1\lambda_2 2}$ or $3\delta^{+,-}_{\lambda_1\lambda_2 2}+\pi$, depending upon the sign of the triple product of magnitude differences in (35). We have now the following rule for the largest triple products of magnitude differences.

$R_{\text{ano},6}$: *If the sign of the product of the largest magnitude differences,* $(|F_{\lambda_1\mathbf{h}}|-|F_{\lambda_2\bar{\mathbf{h}}}|)(|F_{\lambda_1\mathbf{k}}|-|F_{\lambda_2\bar{\mathbf{k}}}|)\times(|F_{\lambda_1\bar{\mathbf{h}}+\bar{\mathbf{k}})}|-|F_{\lambda_2(\mathbf{h}+\mathbf{k})}|)$, *is plus, the value of the associated average triplet phase invariant is close to* $3\delta^{+,-}_{\lambda_1\lambda_2 2}$ *and, when it is minus, the value of the average triplet phase invariant is close to* $3\delta^{+,-}_{\lambda_1\lambda_2 2}+\pi$.

The same type of discussion as that for $R_{\text{ano},4}$ and $R_{\text{ano},5}$ ensues. If there is more than one type of predominant anomalous scatterer, (33) may be used instead of (34) and compared with (35). In order to use (33), at least the chemical composition of the anomalously scattering atoms would have to be known. From it, the values of the $|F^n_{j,\mathbf{h}}F^n_{j,\mathbf{k}}F^n_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ could be evaluated approximately. If the anomalously scattering structure were known, the exact product on the right side of (4) could be computed from the product of the three sums obtainable from the right side of (30).

Derivation of $R_{\text{ano},7}$

We are concerned here with case 7 of Table 1. The right side of (4) is now developed for this case. According to (1),

$$F_{\lambda_1\mathbf{h}}+F^*_{\lambda_2\bar{\mathbf{h}}}-2F^n_{\mathbf{h}}=F^a_{\lambda_1\mathbf{h}}+F^{a*}_{\lambda_2\bar{\mathbf{h}}}. \tag{36}$$

The right side of (36) is now expressed in terms of (11),

$$F^a_{\lambda_1\mathbf{h}}+F^{a*}_{\lambda_2\bar{\mathbf{h}}}=\sum_{j=2}^{q+1}(1/f^n_{j,\mathbf{h}})[f^a_{\lambda_1 j}\exp(i\delta_{\lambda_1 j})+f^a_{\lambda_2 j}\exp(-i\delta_{\lambda_2 j})]F^n_{j,\mathbf{h}}. \tag{37}$$

Expression (36) may be rewritten as

$$F^{a}_{\lambda_1\mathbf{h}} + F^{a*}_{\lambda_2\bar{\mathbf{h}}} = \sum_{j=2}^{q+1} (f^{a-,+}_{\lambda_1\lambda_2 j}/f^{n}_{j,\mathbf{h}}) \exp(i\delta^{-,+}_{\lambda_1\lambda_2 j}) F^{n}_{j\mathbf{h}}, \quad (38)$$

where

$$f^{a-,+}_{\lambda_1\lambda_2 j} = [(f''_{\lambda_1 j} - f''_{\lambda_2 j})^2 + (f'_{\lambda_1 j} + f'_{\lambda_2 j})^2]^{1/2} \quad (39)$$

and

$$\delta^{-,+}_{\lambda_1\lambda_2 j} = \tan^{-1}[(f''_{\lambda_1 j} - f''_{\lambda_2 j})/(f'_{\lambda_1 j} + f'_{\lambda_2 j})]. \quad (40)$$

This case proceeds similarly to cases 4–6 with (16) and (17) replaced by (41) and (42), respectively,

$$\sum_{j=2}^{q+1} [(f^{a-,+}_{\lambda_1\lambda_2 j})^3 / f^{n}_{j,\mathbf{h}} f^{n}_{j,\mathbf{k}} f^{n}_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}] \times \exp(i3\delta^{-,+}_{\lambda_1\lambda_2 j}) |F^{n}_{j,\mathbf{h}} F^{n}_{j,\mathbf{k}} F^{n}_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| \times \exp[i(\varphi^{n}_{j,\mathbf{h}} + \varphi^{n}_{j,\mathbf{k}} + \varphi^{n}_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})})] \quad (41)$$

and

$$[(f^{a-,+}_{\lambda_1\lambda_2 2})^3 / f^{n}_{2,\mathbf{h}} f^{n}_{2,\mathbf{k}} f^{n}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}] \times \exp(i3\delta^{-,+}_{\lambda_1\lambda_2 2}) |F^{n}_{2,\mathbf{h}} F^{n}_{2,\mathbf{k}} F^{n}_{2,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|. \quad (42)$$

From Table 1, (6) may be rewritten when $m = 7$,

$$(|F_{\lambda_1\mathbf{h}} + F^{*}_{\lambda_2\bar{\mathbf{h}}}| - 2|F^{n}_{\mathbf{h}}|)(|F_{\lambda_1\mathbf{k}} + F^{*}_{\lambda_2\bar{\mathbf{k}}}| - 2|F^{n}_{\mathbf{k}}|) \times (|F_{\lambda_1(\bar{\mathbf{h}}+\bar{\mathbf{k}})} + F^{*}_{\lambda_2(\mathbf{h}+\mathbf{k})}| - 2|F^{n}_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}|) \exp(i\langle_7\Phi_{\mathbf{hk}}\rangle). \quad (43)$$

A comparison is now made of (43) and (42), and, in order for them to be approximately equal, the average of the triplet phase invariants, $\langle_7\Phi_{\mathbf{hk}}\rangle$, should have a value close to $3\delta^{-,+}_{\lambda_1\lambda_2 2}$ or $3\delta^{-,+}_{\lambda_1\lambda_2 2} + \pi$, depending upon the sign of the triplet product of magnitude differences in (43). Since $|F_{\lambda_1\mathbf{h}} + F^{*}_{\lambda_2\bar{\mathbf{h}}}|$ is not directly measurable from experiment, in application we use the approximation

$$|F_{\lambda_1\mathbf{h}} + F^{*}_{\lambda_2\bar{\mathbf{h}}}| \sim |F_{\lambda_1\mathbf{h}}| + |F_{\lambda_2\bar{\mathbf{h}}}| \quad (44)$$

with insignificant error since, in the cases of interest, the phase of $F_{\lambda_1\mathbf{h}}$ differs little from that of $F^{*}_{\lambda_2\bar{\mathbf{h}}}$. We have now the following rule for the largest triple products of magnitude differences:

$R_{\text{ano},7}$: *If the sign of the product of the largest magnitude differences,* $(|F_{\lambda_1\mathbf{h}}| + |F_{\lambda_2\bar{\mathbf{h}}}| - 2|F^{n}_{\mathbf{h}}|) \times (|F_{\lambda_1\mathbf{k}}| + |F_{\lambda_2\bar{\mathbf{k}}}| - 2|F^{n}_{\mathbf{k}}|)(|F_{\lambda_1(\bar{\mathbf{h}}+\bar{\mathbf{k}})}| + |F_{\lambda_2(\mathbf{h}+\mathbf{k})}| - 2|F^{n}_{\bar{\mathbf{h}}+\bar{\mathbf{k}}}|)$, *is plus, the value of the associated average triplet phase invariant is close to* $3\delta^{-,+}_{\lambda_1\lambda_2 2}$ *and, when it is minus, the value of the average triplet phase invariant is close to* $3\delta^{-,+}_{\lambda_1\lambda_2 2} + \pi$.

If there is more than one type of predominant anomalous scatterer, (41) may be used instead of (42) and compared with (43). In order to use (41), at least the chemical composition of the anomalously scattering atoms would have to be known. From it, the values of the $|F^{n}_{j,\mathbf{h}} F^{n}_{j,\mathbf{k}} F^{n}_{j,(\bar{\mathbf{h}}+\bar{\mathbf{k}})}|$ could be evaluated approximately. If the anomalously scattering structure were known, the exact product on the right side of (4) could be computed from the product of the three sums obtainable from the right side of (38).

Table 2. *Estimates of values of triplet phase invariants from anomalous dispersion by sulfur in quinidine sulfate at two wavelengths,* Cr $K\alpha$ *and* Cu $K\alpha$ ($m = 4, 5, 6, 7$)

Errors and averages are based on the correct values of the average triplet phase invariants (6). Phases, $\varphi_{\mathbf{h}}$, for which $|F_{\mathbf{h}}| < 10$ were not included in the calculations.

Number of data	Number of invariants	Case m	Estimate	Actual average value	Average error (rad)
4280	50	4	−1·85	−1·85	0·35
4280	50	4	1·29	1·21	0·34
670	45	4	−1·85	−1·89	0·67
670	55	4	1·29	1·02	0·59
4280	52	5	−2·73	−2·78	0·35
4280	48	5	0·41	0·44	0·35
670	47	5	−2·73	−2·91	0·77
670	53	5	0·41	0·36	0·57
4280	52	6	−1·67	−1·69	0·37
4280	48	6	1·47	1·41	0·36
670	49	6	−1·67	−1·61	0·67
670	51	6	1·47	1·32	0·53
4280	96	7	2·10	1·77	0·39
4280	4	7	−1·04	−1·32	0·28
670	75	7	2·10	1·64	0·63
670	25	7	−1·04	−1·01	0·54

Test calculations

Model calculations were performed on exact data computed from the coordinates of quinidine sulfate, $(C_{20}H_{25}N_2O_2)_2SO_4.2H_2O$, (Karle & Karle, 1981) which crystallizes in space group $P2_1$ and on exact data for cytochrome c550.$PtCl_4^{2-}$ from *Paracoccus denitrificans* (Timkovich & Dickerson, 1976). In the test calculations on quinidine sulfate, the source of anomalous dispersion was considered to be solely the sulfur atom. Products of magnitude differences, as appear in (18), (26), (35) and (43), were generally composed from the 300 largest magnitude differences and ordered with the largest product first. In Table 3, when 500 invariants were computed, the 800 largest magnitude differences were used. The values of hundreds of triplet phase invariants were estimated for cases 4, 5, 6 and 7 and the results are shown in Tables 2 and 3. The tables include the number of independent data used in the calculations. For acentric reflections, the value of $|F_{\mathbf{h}}|$ is independent of that for $|F_{\bar{\mathbf{h}}}|$ when anomalous dispersion is taken into account. In the evaluation of the average magnitude of error, the estimated values as obtained from the appropriate angles listed in Table 1, for example, were compared with computed values of the average of the eight invariants occurring in the general expression (5), $\langle_m\Phi_{\mathbf{hk}}\rangle$. The two wavelengths used in the calculations were Cr $K\alpha$ and Cu $K\alpha$.

For Table 2, the $|F^{n}_{\mathbf{h}}|$ required for cases 5 and 7 were computed exactly. In contrast, for Table 3, the

Table 3. *Estimates of values of triplet phase invariants from anomalous dispersion by sulfur in quinidine sulfate at two wavelengths,* Cr $K\alpha$ *and* Cu $K\alpha$ ($m = 5, 7$)

The calculations concern cases $m = 5$ and 7 and differ from those in Table 2 because the $|F_{\mathbf{h}}^n|$ required for cases $m = 5$ and 7 were computed here from (45). Errors and averages are based on the correct values of the average triplet phase invariants (6). Phases, $\varphi_{\mathbf{h}}$, for which $|F_{\mathbf{h}}| < 10$ were not included in the calculations.

Number of data	Number of invariants	Case, m	λ for computation of $\|F_{\mathbf{h}}^n\|$	Estimate	Actual average value	Average error (rad)
4280	65	5	Mo $K\alpha$	−2·73	−2·55	0·35
4280	35	5	Mo $K\alpha$	0·41	0·75	0·43
4280	82	5	Cu $K\alpha$	−2·73	−2·03	0·74
4280	18	5	Cu $K\alpha$	0·41	1·25	0·85
4280	90	5	Cr $K\alpha$	−2·73	−1·92	0·85
4280	10	5	Cr $K\alpha$	0·41	1·25	0·85
4280	36	7	Mo $K\alpha$	−1·04	−0·84	0·44
4280	464	7	Mo $K\alpha$	2·10	1·96	0·56
4280	500	7	Cu $K\alpha$	2·10	3·41	1·41
4280	500	7	Cr $K\alpha$	2·10	3·46	1·84

Table 4. *Estimates of values of triplet phase invariants from multiple-wavelength anomalous dispersion data at* 2·5 Å *resolution for cytochrome* $c550.PtCl_4^{2-}$

Errors and average values are based on the correct values of the average triplet phase invariants (6).

Rule	Number of invariants	λ_1	λ_2	Source of $\|F_{\mathbf{h}}^n\|$*	Estimate	Actual average value	Error (rad)
$R_{\text{ano},4}$	238	Cu $K\alpha$	Mo $K\alpha$	—	−1·73	−1·53	0·81
$R_{\text{ano},4}$	243	Cu $K\alpha$	Mo $K\alpha$	—	1·41	1·71	0·79
$R_{\text{ano},4}$	244	Cr $K\alpha$	Cu $K\alpha$	—	−1·90	−1·61	0·76
$R_{\text{ano},4}$	256	Cr $K\alpha$	Cu $K\alpha$	—	1·24	1·59	0·82
$R_{\text{ano},5}$	178	Cu $K\alpha$	Mo $K\alpha$	Ag $K\alpha$	−0·19	−0·55	0·69
$R_{\text{ano},5}$	204	Cu $K\alpha$	Mo $K\alpha$	Ag $K\alpha$	2·95	2·50	0·75
$R_{\text{ano},5}$	216	Cr $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	−0·18	−0·57	0·72
$R_{\text{ano},5}$	277	Cr $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	2·96	2·61	0·85
$R_{\text{ano},6}$	237	Cu $K\alpha$	Mo $K\alpha$	—	−1·01	−0·74	0·61
$R_{\text{ano},6}$	263	Cu $K\alpha$	Mo $K\alpha$	—	2·13	2·59	0·75
$R_{\text{ano},6}$	257	Cr $K\alpha$	Cu $K\alpha$	—	−1·67	−1·70	0·83
$R_{\text{ano},6}$	243	Cr $K\alpha$	Cu $K\alpha$	—	1·47	1·35	0·77
$R_{\text{ano},7}$	175	Cu $K\alpha$	Mo $K\alpha$	Ag $K\alpha$	−2·57	−2·43	0·55
$R_{\text{ano},7}$	325	Cu $K\alpha$	Mo $K\alpha$	Ag $K\alpha$	0·57	0·74	0·62
$R_{\text{ano},7}$	300	Cr $K\alpha$	Cu $K\alpha$	Ag $K\alpha$	−1·61	−1·56	0·60
$R_{\text{ano},7}$	200	Cr $K\alpha$	Cu $K\alpha$	Ag $K\alpha$	1·53	1·62	0·70
$R_{\text{ano},7}$	359	Cr $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	−1·61	−1·99	0·83
$R_{\text{ano},7}$	141	Cr $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	1·53	0·69	1·17

* Entries indicate the wavelength at which (45) was used to compute $|F_{\mathbf{h}}^n|$.

$|F_{\mathbf{h}}^n|$ were computed at a variety of wavelengths from (Karle, 1984*a*)

$$|F_{\mathbf{h}}^n| \simeq 0{\cdot}5\ W_{\lambda_p \mathbf{h}}(|F_{\lambda_p \mathbf{h}}| + |F_{\lambda_p \bar{\mathbf{h}}}|), \qquad (45)$$

where λ_p represents any particular wavelength, and

$$W_{\lambda_p \mathbf{h}} = \left\{ \frac{\sum_{j=1}^{N_{\text{non}}} f_{j\mathbf{h}}^2 + \sum_{j=1}^{N_{\text{ano}}} f_{j\mathbf{h}}^{n\,2}}{\sum_{j=1}^{N_{\text{non}}} f_{j\mathbf{h}}^2 + \sum_{j=1}^{N_{\text{ano}}} [(f_{j\mathbf{h}}^n + f_j')^2 + f_j''^2]} \right\}^{1/2}. \qquad (46)$$

As would be expected, the errors increase appreciably as the wavelength for computing (45) increases from that of Mo $K\alpha$ to that of Cr $K\alpha$. The calculations are seen to be quite poor for this example in case 7 when the $|F_{\mathbf{h}}^n|$ are computed with Cu $K\alpha$ or Cr $K\alpha$ radiation. The good results with Mo $K\alpha$ radiation are expected because of the smallness of the anomalous dispersion correction for S at the wavelength of Mo $K\alpha$ radiation.

Estimates of the values of triplet phase invariants and their average errors for cytochrome $c550.PtCl_4^{2-}$ for cases 4, 5, 6 and 7 are shown in Table 4. The estimates concern data at 2·5 Å resolution. The Pt atom is the predominant anomalous scatterer and its real and imaginary corrections to the atomic scattering factor were used for determining the values of the triplet phase invariants. The anomalous contributions from the Fe, S and Cl atoms were neglected. Estimated values were obtained from the appropriate angles listed in Table 1. Errors and average values were obtained from the correct values of the average triplet phase invariants, $\langle {}_m\Phi_{\mathbf{hk}} \rangle$.

As would be expected, Table 4 shows that improved accuracy is obtained when $|F_{\mathbf{h}}^n|$ is computed at the shorter wavelength, Ag $K\alpha$ rather than Mo $K\alpha$.

Additional calculations that do not appear in Table 4 indicated that for cytochrome c550.$PtCl_4^{2-}$ errors are smaller for a smaller spread between λ_1 and λ_2. Specifically, larger errors than those shown for $R_{ano,4}$ and $R_{ano,7}$ were obtained in calculations in which λ_1 was Cr $K\alpha$ and λ_2 was Mo $K\alpha$.

The experimental sensitivity, however, depends on the size of the magnitude differences. Calculations with cytochrome c550.$PtCl_4^{2-}$, having λ_1 and λ_2 Cu $K\alpha$ and Mo $K\alpha$, respectively, instead of Cr $K\alpha$ and Mo $K\alpha$, respectively, gave a range of values for the largest magnitude differences, generated by the former pair of wavelengths, approximately 0 to 50% smaller than those generated by the latter pair of wavelengths. Typical numbers for application of $R_{ano,7}$ are 200–1800 for the magnitudes of the structure factors and 20–40 for the largest differences.

Concluding remarks

Calculations have been performed to test the rules $R_{ano,4}$, $R_{ano,5}$, $R_{ano,6}$ and $R_{ano,7}$, rules that permit the estimation of the values of triplet phase invariants in a two-wavelength anomalous dispersion experiment. However, the rules have been applied only to exact data and this gives rise to questions concerning possible applicability. Evidently much depends upon the accuracy of the experimental data, a matter for detailed study.

There are a number of ways of using anomalous dispersion data to obtain phase information. These include the many established procedures that have been used for years (Ramaseshan & Abrahams, 1975), recent developments in extending the range of applications (Hendrickson & Teeter, 1981) and new ones essentially untested with respect to experimental data that derive from an exact algebraic analysis (Karle, 1980), applications in probability theory (Heinerman, Krabbendam, Kroon & Spek, 1978; Hauptman, 1982; Giacovazzo, 1983) and analyses of single-wavelength experiments (Karle, 1984*b*). Optimal strategies for the use of the various techniques await future investigations.

In order to apply the results of this paper to the case of one predominant type of anomalous scatterer, it is only necessary to know the chemical identity of the anomalous scatterer. In the case of more than one type of predominant anomalous scatterer, it is also necessary to have an estimate of the amount of each anomalous scatterer.

A probabilistic approach to the development of formulas for evaluating triplet phase invariants composed of a mixture of phases defined for anomalous dispersion data at two different wavelengths or for isomorphous substitution has been given recently by Pontenagel, Krabbendam, Peerdeman & Kroon (1983). This is somewhat different from the way triplet phase invariants are generated here, although there is some comparison since the phase associated with $|F_{\lambda_1\mathbf{h}}|+|F_{\lambda_2\mathbf{h}}|$, for example, derives from quantities generated in a two-wavelength experiment, whereas the phase associated with $|F_{\mathbf{h}}^n|$ derives from a quantity that is independent of wavelength. The probabilistic approach of Pontenagel *et al.* is, however, more closely akin to a method for developing formulas for estimating triplet phase invariants that combines the results for isomorphous replacement (Karle, 1983) and for anomalous dispersion (Karle, 1984*b*) with the ones in this paper. The combinations lead to a very large number of formulas for estimating triplet phase invariants. A paper on this subject is in preparation.

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