

On R factors for dynamic structure crystallography

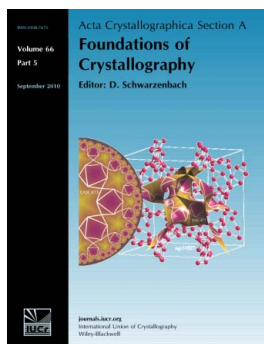
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In studies of dynamic changes in crystals in which induced metastable species may have lifetimes of microseconds or less, refinements are most sensitive if based on the changes induced in the measured intensities. Agreement factors appropriate for such refinements, based on the ratios of the intensities before and after the external perturbation is applied, are discussed and compared with R factors commonly applied in static structure crystallography.

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1. Introduction

As the field of dynamic structure crystallography including photocrystallography is rapidly developing (Coppens, 2009; Collet, 2010), the formulation of agreement indices sensitive to the photo-induced changes is desirable. Photocrystallography and, more generally, dynamical structure science have recently been the subject of special issues of scientific journals (Collet, 2010; Woike & Schaniel, 2008). In its broadest sense the field includes externally induced unidirectional reactions in crystals, photo-induced phase transitions and the establishment of photo-induced equilibria, and also the exploration of the nature of very short lived species with lifetimes of microseconds or less through use of pulsed laser and X-ray sources. Such species can be precursors in photochemical reactions, efficient light emitters and sources of electrons to be injected in underlying substrates. The following discussion is based on photocrystallographic examples, but is equally applicable to other changes in crystals induced by external perturbations.

The crystallographic experiment consists of the measurement of often large numbers of reflections both with and without laser exposure. It has been shown that a refinement based on the response of the diffraction pattern to light (*i.e.* on the intensity changes) is much more sensitive to the photo-induced changes than refinement of the light-ON structure factors in terms of a disordered structure (Coppens, 1992; Ozawa *et al.*, 1998). When the refinement is based on the intensity changes, definition of appropriate agreement factors becomes imperative.

2. Agreement factors for photocrystallography

The relative intensity change of a reflection on photo-excitation is defined by the response ratio η , defined as

$$\eta(\mathbf{H}) = \frac{I_{\text{ON}}(\mathbf{H}) - I_{\text{OFF}}(\mathbf{H})}{I(\mathbf{H})_{\text{OFF}}}, \quad (1)$$

in which I_{ON} and I_{OFF} are the light-ON and light-OFF intensities after appropriate background subtraction. Alternatively, the variation of intensity can be described by the ratio R of the ON and OFF intensities:

$$R(\mathbf{H}) = \frac{I_{\text{ON}}(\mathbf{H})}{I_{\text{OFF}}(\mathbf{H})}. \quad (2)$$

The two descriptors are related by

$$R = \eta + 1. \quad (3)$$

We note that whereas R is always positive, η is either positive or negative, depending on the direction of the response.

The agreement factors can be based either on η or on R . What is the relation between the two, and how do their values compare with R factors conventionally used in structure refinement? We have

$$R_\eta = \frac{\sum_{\mathbf{H}} |\eta_{\text{obs}}(\mathbf{H}) - \eta_{\text{calc}}(\mathbf{H})|}{\sum_{\mathbf{H}} |\eta_{\text{obs}}(\mathbf{H})|} = \frac{\sum_{\mathbf{H}} |\Delta\eta(\mathbf{H})|}{\sum_{\mathbf{H}} |\eta_{\text{obs}}(\mathbf{H})|}. \quad (4)$$

It follows from equation (3) that

$$R_R = \frac{\sum_{\mathbf{H}} |\Delta R(\mathbf{H})|}{\sum_{\mathbf{H}} R_{\text{obs}}(\mathbf{H})} = \frac{\sum_{\mathbf{H}} |\Delta\eta(\mathbf{H})|}{\sum_{\mathbf{H}} \eta_{\text{obs}}(\mathbf{H}) + N}, \quad (5)$$

where $\Delta R = R_{\text{obs}} - R_{\text{calc}}$ and N is the number of reflections common in the light-ON and light-OFF data sets. Thus, if $\langle \eta_{\text{obs}} \rangle = c$ and $\langle |\eta_{\text{obs}}| \rangle = c'$, we obtain for the ratio of the two agreement factors

$$\frac{R_R}{R_\eta} = \frac{\sum_{\mathbf{H}} |\eta_{\text{obs}}(\mathbf{H})|}{\sum_{\mathbf{H}} \eta_{\text{obs}}(\mathbf{H}) + N} = \frac{c'N}{cN + N} = \frac{c'}{c + 1}. \quad (6)$$

The ratio therefore depends on the values of c and c' . Since there will in general be both positive and negative responses to exposure, c will be smaller than c' . Therefore, the relation that $R_R < R_\eta$ is always true. If we take the case in which c is close to zero (*i.e.* a small average response) we arrive at the approximation

$$\frac{R_R}{R_\eta} = c'. \quad (7)$$

It follows that for small induced changes the ratio of the two agreement factors is approximately equal to the average absolute fractional change in the intensities. Thus, for small conversion percentages R_R can easily be ten times smaller than R_η .

3. Practical examples

The use of expressions (6) and (7) is illustrated with the results of three experimental runs. They are summarized in Table 1. The first is a small synchrotron pump-probe experiment conducted at 100 K on tetrakis[(μ_3 -iodo)-(piperidine)copper(I)] using a ps Ti:sapphire laser (Benedict *et al.*, 2010; Kamiński *et al.*, 2010). Results were analyzed

Table 1

Selected numerical descriptors for three measurements and refinements.

Notes: Copper(I) complex: $T = 100$ K, synchrotron data, RATIO method. Zinc(II) complex at a laser repetition rate of 20 kHz and laser power of 118 mW: $T = 30$ K, $\min[I/\sigma(I)] = 2.0$, $\min[\eta/\sigma(\eta)] = 1.0$. Zinc(II) complex at a laser repetition rate of 100 kHz and laser power of 7 mW: $T = 35$ K, $\min[I/\sigma(I)] = 2.0$, $\min[\eta/\sigma(\eta)] = 1.0$.

| Parameter | Copper(I) complex | Zinc(II) complex (20 kHz) | Zinc(II) complex (100 kHz) |
|----------------------------------|-------------------|---------------------------|----------------------------|
| N | 187 | 1438 | 1056 |
| R_η | 54.93% | 59.29% | 61.84% |
| R_R | 4.29% | 17.24% | 18.04% |
| c | -0.0666 | -0.1522 | -0.1269 |
| c' | 0.0730 | 0.2466 | 0.2546 |
| R_R/R_η from expression (6) | 0.078 | 0.291 | 0.292 |
| R_R/R_η from expression (7) | 0.073 | 0.247 | 0.255 |
| Conversion percentage | ~1% | 12.6% | 5.1% |

with the RATIO method (Coppens *et al.*, 2009), in which the ratios R recorded with synchrotron radiation are combined with data from a monochromatic experiment to obtain the light-ON structure factors.

The second and third data sets were measured at a monochromatic rotating-anode source on [bis(4-chlorobenzenethiolato)-1,10-phenanthroline]zinc(II) (Schmøkel *et al.*, 2010) at 30 and 35 K, respectively. A high repetition rate ns pulse length Nd:vanadate laser was used with two different pulse separations (10 and 50 μ s) comparable to the low-temperature lifetime of the complex. Different laser powers were used in the two experiments. Conversion percentages reached in these experiments are considerably larger than in the synchrotron pump-probe measurements.

The results in Table 1 confirm the validity of expression (6) and indicate that for small c (column 2) expression (7) gives a result within a few % of the exact value but that it is not valid for larger responses.

4. Discussion

It is of interest to examine what R factors may be expected from a successful photocrystallographic refinement. Even though R_η is larger than R_R , it follows from expression (3) that $\sigma(\eta)$ is equal to $\sigma(R)$.

We have

$$R_R = \frac{\sum_{\mathbf{H}} |\Delta R(\mathbf{H})|}{\sum_{\mathbf{H}} R_{\text{obs}}(\mathbf{H})} = \frac{\sum_{\mathbf{H}} |\Delta F^2(\mathbf{H})/F_{\text{OFF}}^2(\mathbf{H})|}{\sum_{\mathbf{H}} F_{\text{ON}}^2(\mathbf{H})/F_{\text{OFF}}^2(\mathbf{H})}, \quad (8)$$

in which ΔF^2 and F^2 are the change in the squared structure factor and the squared structure factor, respectively. For the limiting case in which all structure factors are equal, R_R becomes essentially similar to the agreement factor R_F used in static structure crystallography. It may therefore be selected as the preferred agreement factor in photocrystallographic studies.

We have from the theory of propagation of errors (Coppens, 1992)

$$\sigma^2(R) = \sigma^2(I_{\text{ON}}/I_{\text{OFF}}) = \frac{1}{I_{\text{OFF}}^2} \sigma^2(I_{\text{ON}}) + \frac{I_{\text{ON}}^2}{I_{\text{OFF}}^4} \sigma^2(I_{\text{OFF}}). \quad (9)$$

With standard deviations based on counting statistics only: $\sigma^2(I) = I$. Using the approximation $I_{\text{ON}} \simeq I_{\text{OFF}}$, this leads to

$$\sigma^2(R) = 2/I_{\text{OFF}} \quad (10a)$$

or

$$\sigma(R) = (2/I_{\text{OFF}})^{1/2}. \quad (10b)$$

In other words, the standard deviation in the ratio is smaller for the stronger reflections. It follows that to reach a standard deviation of

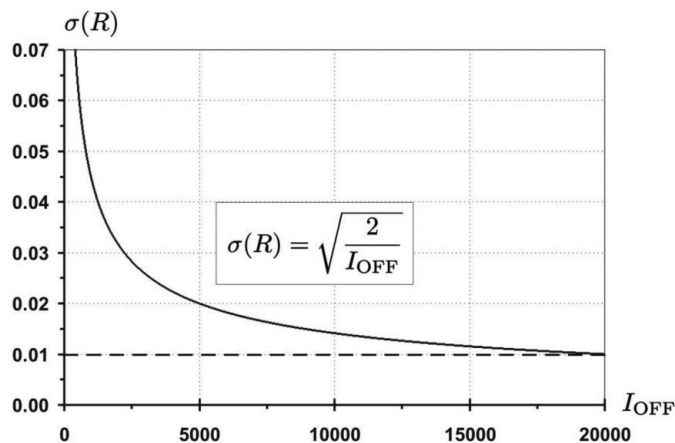


Figure 1

The standard deviation in the $I_{\text{ON}}/I_{\text{OFF}}$ ratio based on counting statistics as a function of I_{OFF} .

0.01 in R we would need an integrated intensity of 20 000. Equation (10b) may be compared with the counting statistical standard deviations in the intensity, which are $\sigma(I) = I^{1/2}$. This gives $\sigma(I)/I = (1/I)^{1/2}$. Since $R \simeq 1$, $\sigma(R)/R = (2/I)^{1/2}$ or $2^{1/2}$ times larger than $\sigma(I)/I$. Thus R factors based on the intensity ratios R may be expected to be larger than conventional R factors. In photocrystallographic experiments the difference is enhanced by the need to use very small crystals to ensure sufficient penetration of the laser beam. This obviously leads to weaker intensities and thus to a further increase in the standard deviations of the $I_{\text{ON}}/I_{\text{OFF}}$ ratios, as illustrated in Fig. 1.

5. Conclusions

R factors that are widely used in structure determination should be modified for studies of dynamic processes in crystals. This is in particular the case for photocrystallographic studies in which molecular changes or chemical reactions are induced by exposure of small samples to intense laser beams. As a result of the inherently larger uncertainties in the ratio of two intensities and the need to minimize sample size, R factors based on the ratio of intensities after and before exposure will tend to be larger than conventional R factors used in static structure determination.

We note that the treatment outlined above can not be applied to extra reflections which may appear due to symmetry breaking. As R and η can not be defined for these reflections, conventional R factors should be applied to this subset.

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