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Analysis of multicrystal pump–probe data sets. I. Expressions for the RATIO model

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The RATIO method in time-resolved crystallography [Coppens *et al.* (2009). *J. Synchrotron Rad.* **16**, 226–230] was developed for use with Laue pump–probe diffraction data to avoid complex corrections due to wavelength dependence of the intensities. The application of the RATIO method in processing/analysis prior to structure refinement requires an appropriate ratio model for modeling the light response. The assessment of the accuracy of pump–probe time-resolved structure refinements based on the observed ratios was discussed in a previous paper. In the current paper, a detailed ratio model is discussed, taking into account both geometric and thermal light-induced changes.

1. Introduction

The RATIO method in time-resolved crystallography (Coppens *et al.*, 2009) was developed specifically for pump–probe Laue data, but is applicable generally for use in pump–probe crystallography. The method is based on the ratio R of the intensities with and without light exposure $I^{\rm laserON}/I^{\rm laserOFF}$. It eliminates dependence on the wavelength when using the pink-Laue technique, the need for absorption corrections (Šrajer *et al.*, 2000; Ren & Moffat, 1995) and the effect of all but very short range fluctuations in the source intensity. In previous work, we have used photo-Wilson plots to estimate temperature increases on exposure (Schmøkel *et al.*, 2010) and ratio correlation plots between data sets to estimate reproducibility (Vorontsov *et al.*, 2009; Makal *et al.*, 2011). The assessment of the accuracy of pump–probe time-resolved results has been discussed in a previous paper (Fournier & Coppens, 2014). In the current paper we discuss specific aspects of application of the RATIO method in the processing/analysis of the data prior to the refinement based on the ratios, taking into account thermal changes and differences in response to light exposure. The analysis allows subsequent scaling of the different data sets, which will be discussed in a following paper.

2. Modeling of the intensity ratios

The ratio $R_{\rm model}(\mathbf{H})$ is obtained by dividing the laser-ON intensity, $I^{\rm laserON}_{\rm model}(\mathbf{H})$, by the corresponding laser-OFF one, $I^{\rm laserOFF}_{\rm model}(\mathbf{H})$:

$$R_{\rm model}(\mathbf{H}) = \frac{I^{\rm laserON}_{\rm model}(\mathbf{H})}{I^{\rm laserOFF}_{\rm model}(\mathbf{H})} = 1 + \eta_{\rm model}(\mathbf{H}), \qquad (1)$$

in which $\eta_{\rm model}$ is the calculated relative change of intensity under light exposure.

$I^{\rm laserOFF}_{\rm model}(\mathbf{H})$ is defined as

$$I^{\rm laserOFF}_{\rm model}(\mathbf{H}) = {\rm Lp}^{\rm laserOFF}(\theta) A^{\rm laserOFF}(\theta, \lambda, \mathbf{M}) K_I^{\rm laserOFF} \times |\mathbf{F}^{{\rm GS}^{\Delta T=0}}_{\rm model}(\mathbf{H})|^2, \qquad (2)$$

in which $A^{\rm laserOFF}$ and ${\rm Lp}^{\rm laserOFF}$ are, respectively, the absorption correction factor dependent on the θ angle, the λ wavelength and $\mathbf{M}$ the sample orientation, and the θ-angle-dependent Lorentz–polarization factor, $K_I^{\rm laserOFF}$ is the data scale factor, and $\mathbf{F}^{{\rm GS}^{\Delta T=0}}_{\rm model}(\mathbf{H})$ is the structure factor of the ground-state (GS) species without temperature increase as $I^{\rm laserOFF}_{\rm model}(\mathbf{H})$ is collected without light exposure.

Similarly, we have for the intensity $I^{\rm laserON}_{\rm model}(\mathbf{H})$:

$$I^{\rm laserON}_{\rm model}(\mathbf{H}) = {\rm Lp}^{\rm laserON}(\theta) A^{\rm laserON}(\theta, \lambda, \mathbf{M}) K_I^{\rm laserON} \times |\mathbf{F}^{\rm laserON}_{\rm model}(\mathbf{H})|^2, \qquad (3)$$

where $A^{\rm laserON}$, ${\rm Lp}^{\rm laserON}$, $K_I^{\rm laserON}$ are defined as previously but for the light-exposure case, and $\mathbf{F}^{\rm laserON}_{\rm model}(\mathbf{H})$ is the laser-ON structure factor of the reflection $\mathbf{H}$.

This expression can be rewritten as follows:

$$I^{\rm laserON}_{\rm model}(\mathbf{H}) = {\rm Lp}^{\rm laserON}(\theta) A^{\rm laserON}(\theta, \lambda, \mathbf{M}) K_I^{\rm laserON} \times |\mathbf{F}^{{\rm laserON}^{\Delta T=0}}_{\rm model}(\mathbf{H})|^2 \times T_{\rm model}(\mathbf{H}) \qquad (4)$$

with the thermal function $T_{\rm model}(\mathbf{H})$ given by

$$T_{\rm model}(\mathbf{H}) = \frac{|\mathbf{F}^{\rm laserON}_{\rm model}(\mathbf{H})|^2}{|\mathbf{F}^{{\rm laserON}^{\Delta T=0}}_{\rm model}(\mathbf{H})|^2}, \qquad (5)$$

where $\mathbf{F}^{{\rm laserON}^{\Delta T=0}}_{\rm model}(\mathbf{H})$ is the laser-ON modeled structure factor without temperature increase ($\Delta T = 0$).

The expression of the general modeled ratio of the reflection $\mathbf{H}$ can be deduced from the expressions (2) and (4):

$$R_{\rm model}(\mathbf{H}) = K_{\rm ratio} S_{\rm model}(\mathbf{H}) T_{\rm model}(\mathbf{H}), \qquad (6)$$

in which the structure-change function $S_{\rm model}(\mathbf{H})$ is defined as

$$S_{\rm model}(\mathbf{H}) = \frac{|\mathbf{F}_{\rm model}^{{\rm laserON}^{\Delta T=0}}(\mathbf{H})|^2}{|\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})|^2} \tag{7}$$

and

$$K_{\rm ratio} = \frac{{\rm Lp}^{\rm laserON}(\theta)A^{\rm laserON}(\theta, \lambda, \mathbf{M})K_I^{\rm laserON}}{{\rm Lp}^{\rm laserOFF}(\theta)A^{\rm laserOFF}(\theta, \lambda, \mathbf{M})K_I^{\rm laserOFF}}. \tag{8}$$

In pump–probe experiments, the laser-ON and laser-OFF frames can be collected alternatively on the same sample. For each goniometer orientation, the laser-ON and laser-OFF intensities share the same Lorentz–polarization, absorption correction and scale factors, and in that case $K_{\rm ratio} = 1$. In the case of RATIO data sets deduced from intensity data sets with and without light exposure collected separately, their intensities do not share the same absorption and Lorentz–polarization factors. Thus, appropriate corrections must be performed prior to the ratio calculations to simplify the global scale factor $K_{\rm ratio}$ [equation (8)], which thus becomes $K_{\rm ratio} = {K_I}^{\rm laserON}/{K_I}^{\rm laserOFF}$, independent of the θ angle, the λ wavelength and $\mathbf{M}$ the sample orientation, after the corrections have been made.

3. Dependence on the structure changes

3.1. Different distribution models of the excited-state species

Two different models have been defined. In the cluster formation model (CF), the excited-state (ES) species are clustered and form separate domains in the crystal. In the random distribution model (RD), domain formation does not occur and the distribution is essentially random (Vorontsov & Coppens, 2005).

In the case of CF,

$$|\mathbf{F}_{\rm model}^{{\rm laserON}^{\Delta T=0}}(\mathbf{H})|^2 = \Big[P|\mathbf{F}_{\rm model}^{{\rm ES}^{\Delta T=0}}(\mathbf{H})|^2 + (1-P)|\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})|^2\Big]. \tag{9}$$

Here $\mathbf{F}_{\rm model}^{{\rm ES}^{\Delta T=0}}(\mathbf{H})$ is the laser-ON structure factor without temperature increase of ES species, and P the ES species population, also known as the conversion fraction.

In the most commonly encountered case of RD,

$$|\mathbf{F}_{\rm model}^{{\rm laserON}^{\Delta T=0}}(\mathbf{H})|^2 = \Big|P\mathbf{F}_{\rm model}^{{\rm ES}^{\Delta T=0}}(\mathbf{H}) + (1-P)\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})\Big|^2, \tag{10}$$

which can be rewritten as

$$\begin{aligned}|\mathbf{F}_{\rm model}^{{\rm laserON}^{\Delta T=0}}(\mathbf{H})|^2 = {}& |\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})|^2 \\ & \times\left[1 + 2\frac{\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})}{|\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})|}\Delta\mathbf{F}_{\rm model}^{{\rm relative}^{\Delta T=0}}(\mathbf{H}) \right.\\ & \left. + |\Delta\mathbf{F}_{\rm model}^{{\rm relative}^{\Delta T=0}}(\mathbf{H})|^2\right]\end{aligned} \tag{11}$$

with

$$\Delta\mathbf{F}_{\rm model}^{{\rm relative}^{\Delta T=0}}(\mathbf{H}) = \frac{P\Big[\mathbf{F}_{\rm model}^{{\rm ES}^{\Delta T=0}}(\mathbf{H}) - \mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})\Big]}{|\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})|}.$$

For $\Delta\mathbf{F}_{\rm model}^{{\rm relative}^{\Delta T=0}}$ with small amplitudes and the same directions in complex space as the corresponding $\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})$, a first-order expansion with respect to $\Delta\mathbf{F}_{\rm model}^{{\rm relative}^{\Delta T=0}}(\mathbf{H})$ is a reasonable approximation, which gives

$$\begin{aligned}|\mathbf{F}_{\rm model}^{{\rm laserON}^{\Delta T=0}}(\mathbf{H})|^2 \simeq {}& |\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})|^2 \\ & + 2P\Big[\mathbf{F}_{\rm model}^{{\rm ES}^{\Delta T=0}}(\mathbf{H}) - \mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})\Big] \\ & \times \mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H}).\end{aligned} \tag{12}$$

This assumption is most appropriate for centrosymmetric structures when conversion percentages are low.

3.2. Expressions for the structure change

The expression of the structure-change function [equation (7)] in the modeled ratio [equation (6)] of the reflection $\mathbf{H}$ can be written using the expressions (9) or (12) as

$$S_{\rm model}(\mathbf{H}) = \big[PL_{\rm model}(\mathbf{H}) + 1\big] \tag{13}$$

with $L_{\rm model}(\mathbf{H})$ the relative intensity change for full conversion to the ES:

$$L_{\rm model}(\mathbf{H}) = \begin{cases} \text{in the CF case} \\ \dfrac{\Big[|\mathbf{F}_{\rm model}^{{\rm ES}^{\Delta T=0}}(\mathbf{H})|^2 - |\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})|^2\Big]}{|\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})|^2}, \\ \text{in the RD case with small population [expression (12)]} \\ \dfrac{2\Big[\mathbf{F}_{\rm model}^{{\rm ES}^{\Delta T=0}}(\mathbf{H}) - \mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})\Big]\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})}{|\mathbf{F}_{\rm model}^{{\rm GS}^{\Delta T=0}}(\mathbf{H})|^2}. \end{cases}$$

We note that the factor $L_{\rm model}(\mathbf{H})$, a characteristic of $\mathbf{H}$, can be positive or negative.

Analysis tools such as ratio correlation plots (Vorontsov *et al.*, 2009; Makal *et al.*, 2011) are used prior to structure refinements to compare different data sets. They do not provide information about the absolute light-induced system response for each data set, but can estimate the relative light-induced system response in different data sets. Let us consider $N_{\rm sets}$ RATIO data sets. Each data set $i \in \{\rm sets\}$ is characterized, under the assumptions of the RATIO model [equation (6)], by a thermal function $T^i_{\rm model}$ (discussed in §4), an ES population P^i (variable in the structure-change function $S^i_{\rm model}$) and a RATIO scale factor $K^i_{\rm ratio}$ if the laser-ON and laser-OFF reflections are collected separately rather than alternatively.

The average ES population $\langle P\rangle = \langle P^i\rangle_{i\in\{\rm sets\}}$ over all different data sets can be defined and a relative ES population Q^i introduced as follows:

$$Q^i = \frac{P^i}{\langle P\rangle}. \tag{14}$$

For each reflection $\mathbf{H}$, the averaged η with no temperature increase is defined as

$$\eta_{\rm model}^{\Delta T=0}(\mathbf{H}) = \langle P^i\rangle_{\{i\in{\rm sets}\}}L_{\rm model}(\mathbf{H}). \tag{15}$$

Therefore, the structure-change function (13) in the modeled ratio [equation (6)] of the reflection **H** in the RATIO data set i can be expressed using expressions (14) and (15) as

$$S^{i}_{\rm model}(\mathbf{H}) = \left[Q^{i}\eta^{\Delta T=0}_{\rm model}(\mathbf{H}) + 1\right]. \tag{16}$$

4. The effect of the light-induced temperature increase

If the thermal function $T_{\rm model}(\mathbf{H})$ [equation (5)] is assumed to be independent of the structure changes, it can be written for any P as

$$T_{\rm model}(\mathbf{H}) = T_{\rm model}(\mathbf{H}, P). \tag{17}$$

It can then be modeled in different ways. Assuming that the laser exposure results in a global and isotropic increase of the B factor ΔB, the thermal function can be modeled as an exponential factor and referred to, in this case, as $T^{\Delta B}_{\rm model}$:

$$T^{\Delta B}_{\rm model}(\mathbf{H}) = \exp\left[-2\Delta B^{i} s^{2}(\mathbf{H})\right] \tag{18}$$

with $s^{2}(\mathbf{H}) = (\sin\theta/\lambda)^{2}$ for the reflection **H**.

A more accurate model can be defined based on the known laser-OFF structure model used as a reference model in the ratio-based refinement. In the laser software (Vorontsov *et al.*, 2010), the temperature increase is modeled assuming for each atom a proportional increase of the atomic displacement parameters such $U_{ij} = k_{\rm B} U^{\Delta T=0}_{ij}$. If the GS conformation coordinates of the non-converted fraction in the laser-ON structure are assumed not affected by the light exposure, $\mathbf{F}^{\rm laserON}_{\rm model}(\mathbf{H}, k_{\rm B}, P=0) = \mathbf{F}^{\rm reference}_{\rm model}(\mathbf{H}, k_{\rm B})$, this gives

$$\begin{aligned} T^{k_{\rm B}}_{\rm model}(\mathbf{H}, k_{\rm B}) &= \frac{|\mathbf{F}^{\rm laserON}_{\rm model}(\mathbf{H}, k_{\rm B}, P=0)|^{2}}{|\mathbf{F}^{\rm laserON^{\Delta T=0}}_{\rm model}(\mathbf{H}, P=0)|^{2}} \\ &= \frac{|\mathbf{F}^{\rm reference}_{\rm model}(\mathbf{H}, k_{\rm B})|^{2}}{|\mathbf{F}^{\rm reference^{\Delta T=0}}_{\rm model}(\mathbf{H})|^{2}}. \end{aligned} \tag{19}$$

5. Approximated RATIO model assuming small geometric and thermal responses

In the expression of the modeled ratio [equation (6)], the thermal function $T_{\rm model}(\mathbf{H})$ [equation (5)] can be approximated by assuming a small temperature increase. In the case of the global and isotropic increase ΔB model, the thermal function, $T^{\Delta B}_{\rm model}(\mathbf{H})$ [equation (18)], can be approximated by a first-order Taylor expansion with respect to ΔB^{i} which gives, for each reflection **H**,

$$T^{\Delta B}_{\rm model}(\mathbf{H}) \simeq 1 - 2\Delta B^{i} s^{2}(\mathbf{H}), \tag{20}$$

in which $s(\mathbf{H}) = \sin\theta/\lambda$.

Assuming that ΔB^{i} and P^{i} share the same asymptotic order when the light-induced response tends to zero, the first-order Taylor expansion of the modeled ratio [equation (6)] with respect to ΔB^{i} and P^{i} for small values, using expression (13), is

$$R^{\Delta B^{i}}_{\rm model}(\mathbf{H}) \simeq K^{i}_{\rm ratio}\left[1 + P^{i} L_{\rm model}(\mathbf{H}) - 2\Delta B^{i} s^{2}(\mathbf{H})\right], \tag{21}$$

where $L_{\rm model}(\mathbf{H})$ is the intensity change at full conversion defined in expression (13) and approximated for small photo-induced changes in the case of the RD model. The mixed term $\Delta B^{i} s^{2}(\mathbf{H}) P^{i} L_{\rm model}(\mathbf{H})$ is not a term of this Taylor expansion because it is a second-order term considering ΔB^{i} and P^{i} share the same asymptotic order near the zero-change limit.

The first-order Taylor expansion of the modeled ratio of the reflection **H** [equation (21)] in the RATIO data set i can be expressed using expressions (14) and (15) as

$$\begin{aligned} R^{\Delta B^{i}}_{\rm model}(\mathbf{H}) &\simeq K^{i}_{\rm ratio}\left[1 + Q^{i}\eta^{\Delta T=0}_{\rm model}(\mathbf{H}) - 2\Delta B^{i} s^{2}(\mathbf{H})\right] \\ &\simeq K^{i}_{\rm ratio}\left\{1 + Q^{i}\left[\eta^{\Delta T=0}_{\rm model}(\mathbf{H}) - 2\frac{\Delta B^{i}}{Q^{i}} s^{2}(\mathbf{H})\right]\right\}. \end{aligned} \tag{22}$$

We define $A_{\Delta B_Q}$ as the average ratio of the thermal factor increase ΔB and the relative population Q over the different data sets:

$$A_{\Delta B_Q} = \left\langle \frac{\Delta B^{i}}{Q^{i}} \right\rangle_{\rm sets}. \tag{23}$$

For each data set i, $\delta\Delta B^{i}_{Q}$, the shift of the ratio of the thermal factor increase ΔB^{i} and the relative population Q^{i} from their average $A_{\Delta B_Q}$ becomes

$$\delta\Delta B^{i}_{Q} = \frac{\Delta B^{i}}{Q^{i}} - A_{\Delta B_Q}, \tag{24}$$

which implies that

$$\langle \delta\Delta B^{i}_{Q} \rangle_{\rm sets} = 0. \tag{25}$$

The calculated η for a unique reflection **H** averaged over all sets, $\eta^{\Delta B}_{\rm model}$, is defined as

$$\eta^{\Delta B}_{\rm model}(\mathbf{H}) = \eta^{\Delta T=0}_{\rm model}(\mathbf{H}) - 2A_{\Delta B_Q} s^{2}(\mathbf{H}), \tag{26}$$

which gives for the first-order Taylor expansion of the modeled ratio [equation (22)] of the reflection **H** using the expressions (24), (26)

$$\begin{aligned} R^{\Delta B^{i}}_{\rm model}(\mathbf{H}) &\simeq K^{i}_{\rm ratio}\left\{1 + Q^{i}\left[\eta^{\Delta T=0}_{\rm model}(\mathbf{H}) - 2\frac{\Delta B^{i}}{Q^{i}} s^{2}(\mathbf{H})\right]\right\} \\ &\simeq K^{i}_{\rm ratio}\left\{1 + Q^{i}\left[\eta^{\Delta T=0}_{\rm model}(\mathbf{H}) - 2\left(\delta\Delta B^{i}_{Q} + A_{\Delta B_Q}\right) s^{2}(\mathbf{H})\right]\right\} \\ &\simeq K^{i}_{\rm ratio}\left\{1 + Q^{i}\left[\eta^{\Delta B}_{\rm model}(\mathbf{H}) - 2\delta\Delta B^{i}_{Q} s^{2}(\mathbf{H})\right]\right\}. \end{aligned} \tag{27}$$

A similar approximation can be obtained in the case of the accurate thermal function, $T^{k_{\rm B}}_{\rm model}(\mathbf{H})$ [equation (19)], of the reflection **H**. Assuming small $k_{\rm B}$ thermal factor increase with $\Delta k_{\rm B} = k_{\rm B} - 1$,

$$T^{k_{\rm B}}_{\rm model}(\mathbf{H}) \simeq 1 + \Delta k_{\rm B} \frac{\partial T^{k_{\rm B}}_{\rm model}}{\partial k_{\rm B}}(\mathbf{H}). \tag{28}$$

Assuming $\Delta k^{i}_{\rm B}$ and P^{i} share the same asymptotic order when the light-induced response tends to zero, the first-order Taylor expansion of expression (6) with respect to $\Delta k^{i}_{\rm B}$ and P^{i} for small values, using expression (13), is

$$R^{k_{\rm B}^i}_{\rm model}(\mathbf{H}) \simeq K^i_{\rm ratio}\left[1 + P^i L_{\rm model}(\mathbf{H}) + \Delta k_{\rm B}\frac{\partial T^{k_{\rm B}}_{\rm model}}{\partial k_{\rm B}}(\mathbf{H})\right]. \quad (29)$$

The first-order Taylor expansion of the modeled ratio (29) of the reflection $\mathbf{H}$ in the RATIO data set i can be expressed using expressions (14) and (15) as

$$\begin{aligned} R^{k_{\rm B}^i}_{\rm model}(\mathbf{H}) &\simeq K^i_{\rm ratio}\left[1 + Q^i \eta^{\Delta T=0}_{\rm model}(\mathbf{H}) + \Delta k_{\rm B}\frac{\partial T^{k_{\rm B}}_{\rm model}}{\partial k_{\rm B}}(\mathbf{H})\right] \\ &\simeq K^i_{\rm ratio}\left\{1 + Q^i\left[\eta^{\Delta T=0}_{\rm model}(\mathbf{H}) + \frac{\Delta k^i_{\rm B}}{Q^i}\frac{\partial T^{k_{\rm B}}_{\rm model}}{\partial k_{\rm B}}(\mathbf{H})\right]\right\}. \end{aligned} \quad (30)$$

We define $A_{k_{{\rm B}_Q}}$ as the average ratio of the thermal factor increase $\Delta k_{\rm B}$ and the relative population Q over the different data sets and, for each data set i, $\delta k^i_{{\rm B}_Q}$

$$A_{k_{{\rm B}_Q}} = \left\langle \frac{\Delta k^i_{\rm B}}{Q^i} \right\rangle_{\rm sets} \quad (31)$$

$$\delta k^i_{{\rm B}_Q} = \frac{\Delta k^i_{\rm B}}{Q^i} - A_{k_{{\rm B}_Q}}. \quad (32)$$

The calculated average η over all sets, $\eta^{k_{\rm B}}_{\rm model}$, can be defined for each unique reflection $\mathbf{H}$ as

$$\eta^{k_{\rm B}}_{\rm model}(\mathbf{H}) = \eta^{\Delta T=0}_{\rm model}(\mathbf{H}) + A_{k_{{\rm B}_Q}}\frac{\partial T^{k_{\rm B}}_{\rm model}}{\partial k_{\rm B}}(\mathbf{H}) \quad (33)$$

and the first-order Taylor expansion of the modeled ratio [equation (30)] of the reflection $\mathbf{H}$ rewritten using the expressions (32), (33) becomes

$$\begin{aligned} R^{k_{\rm B}^i}_{\rm model}(\mathbf{H}) &\simeq K^i_{\rm ratio}\left\{1 + Q^i\left[\eta^{\Delta T=0}_{\rm model}(\mathbf{H}) + \frac{\Delta k^i_{\rm B}}{Q^i}\frac{\partial T^{k_{\rm B}}_{\rm model}}{\partial k_{\rm B}}(\mathbf{H})\right]\right\} \\ &\simeq K^i_{\rm ratio}\left\{1 + Q^i\left[\eta^{\Delta T=0}_{\rm model}(\mathbf{H}) + (\delta k^i_{{\rm B}_Q} + A_{k_{{\rm B}_Q}})\frac{\partial T^{k_{\rm B}}_{\rm model}}{\partial k_{\rm B}}(\mathbf{H})\right]\right\} \\ &\simeq K^i_{\rm ratio}\left\{1 + Q^i\left[\eta^{k_{\rm B}}_{\rm model}(\mathbf{H}) + \delta k^i_{{\rm B}_Q}\frac{\partial T^{k_{\rm B}}_{\rm model}}{\partial k_{\rm B}}(\mathbf{H})\right]\right\}. \end{aligned} \quad (34)$$

6. Conclusion

Expressions for the structure-change models in the case of either a random distribution or formation of clusters of excited-state molecules have been defined. Two thermal models are considered and their simplification in the case of small light-induced conversion percentages is discussed. Combining the structure-change and thermal models, a generalized RATIO model suitable for analysis of multi-crystal data sets has been developed. The scaling and merging of different data sets will be discussed in a following paper, together with the application of the two proposed thermal models. The corresponding software will be described there and made freely available.

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