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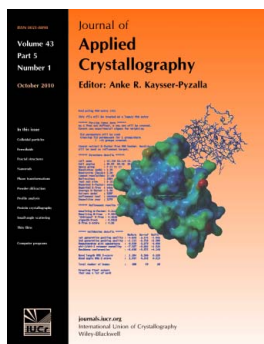
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J. Appl. Cryst. (2010). **43**, 1129–1130

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LASER – a program for response-ratio refinement of time-resolved diffraction data

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Received 29 June 2010
Accepted 27 July 2010

The program *LASER2010* is described. It is specifically designed for the refinement of externally induced structural changes in crystalline solids, including time-resolved laser-pump X-ray probe experiments. The refinement is based on the measured relative intensity changes rather than on the integrated reflection intensities.

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1. Introduction

Recent advances in time-resolved photocrystallographic techniques allow the measurement of light-induced excited states and the monitoring of chemical reactions. As limitations including insufficient laser light penetration and temperature increases due to exposure are being alleviated by rapid technical advances, it is necessary to devise refinement algorithms optimized for the analysis of observed changes in the diffraction pattern. A first step in this direction was implemented by Ozawa *et al.* (1998) with the program *LASER96*. The program has since been greatly expanded with new features. The program *LASER2010* is described in the following. It is a Fortran77 code composed of a main program and a series of small subroutines.

2. Program description

The program is based on refinement of the response ratios defined as

$$\eta_{\text{ON/OFF}}(\mathbf{h}) = \frac{F_{\text{ON}}^2(\mathbf{h}) - F_{\text{OFF}}^2(\mathbf{h})}{F_{\text{OFF}}^2(\mathbf{h})} = \frac{I_{\text{ON}}(\mathbf{h}) - I_{\text{OFF}}(\mathbf{h})}{I_{\text{OFF}}(\mathbf{h})} = R_{\text{ON/OFF}}(\mathbf{h}) - 1 \quad (1)$$

in which F and I denote structure factors and intensities, respectively, the subscripts ON and OFF indicate light-ON and light-OFF quantities, and R is the respective ratio of the two values. The corresponding least-squares error function to be minimized is

$$S_\eta = \sum_{\mathbf{h}} w(\mathbf{h}) |\eta_o(\mathbf{h}) - \eta_c(\mathbf{h})|^2 \quad (2)$$

where η_o and η_c are the observed and calculated response ratios, respectively, and w is the appropriate weight for reciprocal vector $\mathbf{h}$.

Features introduced in *LASER2010* include the following:

- (1) Calculation of the fractional coordinates of the ground-state structure molecules, counter-ions, solvate molecules and framework components, if present, in the light-ON unit cell.
- (2) Refinement of the position and orientation of the ground- and excited-state molecules, and other species present in the light-ON structure.
- (3) Capability of rigid-body or segmented-rigid-body refinement of any of the species present.
- (4) Application of a riding model to any of the fragments.
- (5) Refinement of a central atom–ligand distance for the excited-state molecules.

(6) Constrained refinement of the orientation of the ligand along a specified vector.

(7) Separate refinement of the population for up to four independent entities.

(8) Simultaneous refinement of up to six data sets on the same system.

(9) Refinement of temperature scale factors (k_B) for each of the data sets included.

(10) Calculation of photocrystallography-specific agreement factors (Coppens *et al.*, 2010).

2.1. Refinement formalism

The refinement, based on the response-ratio formalism, assumes a random distribution of excited molecules, leading to the structure factor equation

$$F_{\text{ON}}(\mathbf{h}) = (1 - P)F_{\text{ON}}^{\text{GS}}(\mathbf{h}) + PF_{\text{ON}}^{\text{ES}}(\mathbf{h}) + F_r(\mathbf{h}) \quad (3)$$

and

$$F_{\text{OFF}}(\mathbf{h}) = F_{\text{OFF}}^{\text{GS}}(\mathbf{h}), \quad (4)$$

where P is the population of excited-state molecules ($0 < P < 1$), and $F_{\text{OFF}}^{\text{GS}}$, $F_{\text{ON}}^{\text{GS}}$ and $F_{\text{ON}}^{\text{ES}}$ are the structure factors corresponding to the ground-state (GS) and excited-state (ES) species in light-OFF and light-ON structures. F_r represents the scattering of the photochemically inert part of the structure. A possible change in the unit-cell parameters, positions and orientations of all species present, as well as an increase of the thermal motion parameters under laser exposure in the light-ON unit cell, can be taken into account in the calculation of $F_{\text{ON}}^{\text{GS}}(\mathbf{h})$. All structure factors are computed using the independent atom model (IAM).

The general expression for derivatives based on the error function defined in expression (2) is

$$\frac{\partial \eta}{\partial u} = \frac{\partial}{\partial u} \left(\frac{F_{\text{ON}}^2}{F_{\text{OFF}}^2} \right) = 2 \left(\frac{1}{F_{\text{OFF}}^2} \right) \left(A_{\text{ON}} \frac{\partial A_{\text{ON}}}{\partial u} + B_{\text{ON}} \frac{\partial B_{\text{ON}}}{\partial u} \right), \quad (5)$$

where A_{ON} and B_{ON} are real and imaginary parts of F_{ON} , and u represents the variables of the refinement.

2.2. Temperature changes

One of the important features of *LASER2010* is the possibility of using both the light-ON and light-OFF unit cells, which allows one to

take into account the effect of geometry and temperature changes of the unit cell as a result of both molecular excitation and heating of the crystal (Vorontsov & Coppens, 2005). The effect on the thermal parameters is approximated by the overall temperature scale factor k_B defined by

$$U_{\text{ON},ij} = k_B U_{\text{OFF},ij} \quad (6)$$

where $U_{\text{ON},ij}$ and $U_{\text{OFF},ij}$ are displacement parameters of the atoms in the light-ON and light-OFF structures. In the observational equations k_B is included as

$$F_{\text{ON}}^{\text{GS}}(\mathbf{h}) = \sum_k f_k \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_k) \exp\left(-\sum_{lm} k_B U_{klm} h_l h_m a_l^* a_m^*\right) \quad (7)$$

in which the index k runs over all atoms of the ground-state species in the partially excited crystal and $F_{\text{ON}}^{\text{ES}}(\mathbf{h})$ is defined by the analogous expression for the excited-state species. Comparison with photo-Wilson plots in which $F_{\text{ON}}^2/F_{\text{OFF}}^2$ for all reflections is plotted against $(\sin\theta/\lambda)^2$ shows that this simple isotropic description is a reasonable approximation for the treatment of thermal motion in molecular crystals of coordination complexes (Schmøkel *et al.*, 2010).

2.3. Rigid-body refinement

The program allows refinement of the orientation of rigid bodies. The orientation is described by three angles, which can be arbitrarily defined. This makes it possible to refine photo-induced ligand wagging or rocking distortions. It is possible to use dummy atoms as anchoring sites.

2.4. Discrepancy descriptors

The convergence of the refinement procedure is judged by photocrystallography-specific R factors (Coppens *et al.*, 2010) as well as goodness-of-fit (GooF), defined as follows:

$$\mathbf{R}_\eta = \frac{\sum_{\mathbf{h}} |\eta_o(\mathbf{h}) - \eta_c(\mathbf{h})|}{\sum_{\mathbf{h}} |\eta_o(\mathbf{h})|}, \quad (8a)$$

$$\mathbf{R}_R = \frac{\sum_{\mathbf{h}} |R_o(\mathbf{h}) - R_c(\mathbf{h})|}{\sum_{\mathbf{h}} |R_o(\mathbf{h})|}, \quad (8b)$$

$$w\mathbf{R}_\eta = \left[\frac{\sum_{\mathbf{h}} w(\mathbf{h}) |\eta_o(\mathbf{h}) - \eta_c(\mathbf{h})|^2}{\sum_{\mathbf{h}} w(\mathbf{h}) |\eta_o(\mathbf{h})|^2} \right]^{1/2}, \quad (8c)$$

$$\text{GooF} = \left[\frac{\sum_{\mathbf{h}} w(\mathbf{h}) |\eta_o(\mathbf{h}) - \eta_c(\mathbf{h})|^2}{n - m} \right]^{1/2}, \quad (8d)$$

where n is the number of observations and m is the number of variables. In the case of joint refinement on several data sets all the convergence factors are also calculated individually for every data set.

3. Literature examples

Application of the *LASER2010* program shows the response-ratio refinement to be efficient and sensitive to geometric and temperature changes. Among the examples reported in the literature are the following:

(1) Laser-induced structural changes in the $\text{Cu}(\text{dmp})(\text{dppe})^+$ ion [dmp is 2,9-dimethyl-1,10-phenanthroline; dppe is 1,2-bis(diphenylphosphino)ethane; Vorontsov *et al.*, 2009]. A monochromatic pump-probe study using synchrotron radiation followed with *LASER2010* refinement yielded a population of excited molecules around 7–10% and a k_B parameter in the range 1.50–2.10, depending on the data set.

(2) Excited-state geometry of the dinuclear $[\text{Rh}_2(1,8\text{-diisocyano-}p\text{-menthane})]_4^{2+}$ ion (Coppens *et al.*, 2004). The population of excited-state molecules was estimated to be about 2%. The most striking feature is the shortening of the $\text{Rh} \cdots \text{Rh}$ distance of 0.85 (6) Å, which is the largest structural change observed so far by time-resolved X-ray diffraction methods.

(3) Excited state of trimeric $\{[3,5\text{-(CF}_3)_2\text{Pz}]\text{Cu}\}_3$ molecules (Pz is pyrazolate), studied by monochromatic X-ray synchrotron radiation in the pump-probe mode (Vorontsov *et al.*, 2005). Refinement of structural changes indicates an intermolecular $\text{Cu} \cdots \text{Cu}$ distance shortening of about 0.56 Å.

(4) Photocrystallographic analysis of dimeric $[\text{Cu}(\text{NH}_3)_2]_2^{2+}$ ions stabilized by hydrogen bonds with the H_2THPE^- [THPE is tris(4-hydroxyphenyl)ethane] anionic host framework (Coppens *et al.*, 2006). The $\text{Cu} \cdots \text{Cu}$ bond shortening on excitation was determined as 0.31 Å. The molecular excitation is accompanied by a 7° rotation of the cationic species.

4. Conclusions and final remarks

LASER2010 is a robust program for response-ratio refinement of externally induced structural changes. Its file format is partially based on *JANA* (Petříček *et al.*, 2006), which facilitates importation of data from other sources. Future developments include incorporation of a more sophisticated thermal motion description. At the moment visualization of results is possible by use of programs such as *SHELX* (Sheldrick, 2008), *XD* (Volkov *et al.*, 2006) and *JANA*, for which input files are produced. The program is available on request from the authors.

Support of this work by the National Science Foundation (grant No. CHE0843922) is gratefully acknowledged. RK would like to thank the Foundation for Polish Science for financial support within the 'International PhD Projects' program. MSS is grateful to the Danish National Research Foundation and the Danish Strategic Research Council for financial support.

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