

A New Refinement Technique for XRay Structure Analysis

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A tetragonal unit cell was then considered, and all of the Debye-Scherrer lines were indexable on the basis of a primitive tetragonal unit cell with $a=7.8\text{\AA}$, $c=10.7\text{\AA}$. The pseudo-cubic character of this cell is evident; $c \approx a(2)^{\frac{1}{2}}$.

TABLE I. Interplanar spacings and relative intensities of cyclooctatetraene from Debye-Scherrer powder diagrams.

d -A (obs.)	d -A (comp.)*	Intensity	$h\ k\ l$
5.34	5.33	m	0 0 2
4.88	4.88	s	1 1 1
3.87	3.89	m	0 2 0-2 0 0
3.49	3.49	m	1 2 0
3.30	3.30	m	2 1 1
3.14	3.14	m	2 0 2-0 2 2
2.98	2.98	m	1 1 3
2.91	2.91	$m-w$	1 2 2
2.65	2.66	$m-w$	0 0 4
2.48	2.48	w	2 1 3
2.39	2.39	$m-w$	3 1 1-1 3 1
2.19	2.19	$m-w$	2 0 4-0 2 4
2.16	2.15	w	3 2 0
2.13	2.12	w	2 3 1
2.02	2.02	mw	1 3 3-3 1 3
1.95	1.95	w	0 4 0-4 0 0
1.82	1.82	w	4 0 2-0 4 2
1.67	1.66	w	4 2 2-2 4 2

* In those cases where two sets of indices are given the computed spacing is an average.

At this stage it appeared desirable to employ single-crystal x-ray measurements. A study of the intensities of observed reflections showed that the tetragonal unit cell was untenable. This led to the choice of an orthorhombic pseudo-tetragonal cell where $a \approx b \approx 7.8\text{\AA}$ and $C=10.7\text{\AA}$. This revised cell permitted satisfactory indexing of all Debye-Scherrer lines (Table I) as well as of the single crystal reflections.

The lattice constants were then determined more exactly by a least-squares solution of those Debye-Scherrer lines which could be uniquely indexed. This gave $a=7.76\text{\AA}$, $b=7.80\text{\AA}$, $c=10.66\text{\AA}$. These values were used to calculate the spacings for the powder reflections (Table I). The agreement is good.

Systematic extinctions of the (hkl) reflections for ($k+1$) odd, of the (hol) reflections for h odd, and the (okl) reflections for k odd were found. Two orthorhombic space groups require these extinctions; $A b a$ and $A b a m$.

For four molecules per cell, the x-ray density is 1.06 which may be compared to the measured value of 1.04.

Inasmuch as the space group choice is limited to $A b a$ or $A b a m$, the molecular centers must be located at special locations in the unit cell. In either case, the centers of the molecules are located at the points of a face centered orthorhombic lattice, and the molecule must possess at least a twofold axis of symmetry. If the space groups were $A b a m$, in addition, the molecule would have to have a plane of symmetry. We now feel that this latter space group is the less likely of the two.

¹ This work represents part of a dissertation to be presented by H. S. Kaufman to the Graduate Faculty of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Willstätter and Waser, Ber. 44, 3423 (1911); Willstätter and Heideberger, Ber. 46, 517 (1913).

³ Report by Dr. Walter Reppe on Cyclopolyolefines (Ludwigshafen on Rhine, April 28, 1944).

A New Refinement Technique for X-Ray Structure Analysis

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May 5, 1947

THE standard technique of Fourier refinement, which has been used with such success in many simple structure analyses, is unfortunately reaching a state in which, despite technical improvements,¹⁻³ the time taken for a structure analysis is increasing to a prohibitive extent. Thus, in recent determinations (on geranylamine hydrochloride⁴ and penicillin⁵), times of the order of 3 years have been needed for completion.

At the root of this decline is the fact that, in order for the Fourier process to converge, a set of parameters must be found by trial and error, which are a reasonable approximation to the correct ones. Roughly speaking, the region of convergence of the Fourier method is the same as that of its differential variant.³

Patterson-Harker syntheses cannot be considered the complete solution to the problem of approximate structure determination since, in a wide range of cases, no useful information is obtainable from this technique; and this is especially true in complex organic structures. Similarly, molecular transforms are very difficult to apply in any but the simplest space groups.

It can be stated that the desirable features of any systematic form of structure determination are the following:

- (1) Starting from any arbitrary position, it should be possible to locate the position of a molecule considered as a rigid unit.
- (2) Having found the position of the molecule considered rigid, it should be possible to determine the individual atomic positions.
- (3) If necessary, the method should be applicable to density distributions. This is particularly true for macromolecules since here, although the general shape may be known, the details may be completely obscure.

A solution to these problems is to be found *via* the method of "steepest" descents" which, although in some ways a generalization of the least-squares refinement,⁶ is unlike the latter in that it can be applied to systems of any degree of complexity. In addition, it is possible to locate the position of a molecule considered either as a rigid whole or as a set of rigid parts, or to refine a density distribution given at lattice points over the unit cell.

Full details of the method in all its forms, will be published at a later date, but it is proposed to explain here the general philosophy of the attack and to give the equations for the simplest case.

In essence, the scheme is merely a procedure for minimizing either:

$$R_1 = \sum_{hkl} \|F_{\text{obs}} - F_{\text{calc}}\|$$

or

$$R_2 = \sum_{hkl} (F_{\text{obs}}^2 - F_{\text{calc}}^2)^2.$$

Now $R_n = \text{const.}$ represents a surface in the $3N$ dimensional space defined by the atomic parameters x_{rj} ($r=1 \dots N$; $j=1, 2, 3$). The method of minimization is to proceed in the direction of the normal to any given surface until the value of R_n no longer decreases. Having arrived at this

point, the procedure is repeated, and a little consideration shows that this technique leads to the minimization of R_n .

Two expressions are available for the change ϵ_{rj} in any coordinate x_{rj} :

$$\epsilon_{rj} = -2R_n(\partial R_n/\partial x_{rj})/(\sum_{rj} \partial R_n/\partial x_{rj})^2$$

or:

$$\epsilon_{rj} = -[\sum_{rj} (\partial R_n/\partial x_{rj})^2](\partial R_n/\partial x_{rj})/ \sum_{rj, r'j'} (\partial^2 R_n/\partial x_{rj} \partial x_{r'j'}) (\partial R_n/\partial x_{rj}) (\partial R_n/\partial x_{r'j'}).$$

The first expression should be used only so long as the coordinates are far from their final values and is particularly simple to compute; whilst the second equation applies up to the minimum itself.

A particularly interesting variant of the method is available when a sufficiently large number of planes of zero observed intensity is available (excluding zeros due to symmetry elements). In this case the expressions:

$$O_1 = \sum_{hkl} |F_{\text{calc}}|$$

$$O_2 = \sum_{hkl} F_{\text{calc}}^2$$

taken over all planes of zero observed intensity can be minimized, and the resulting calculations are much simplified.

Simple extensions enable the position of a fixed molecular shape to be found such that R_n is minimized. This is done either by referring the molecule to an axial system, whose orientation and origin are then varied, or by taking three atoms of the molecule as standards and minimizing R_n in such a way that all inter-atomic distances remain fixed. When a molecule contains known groupings related to one another by free rotations, a slightly more general approach enables the same methods to be applied.

Finally, it is possible to use the technique to obtain density distributions which minimize R_n , although there, particular care has to be taken to obtain a stereo-chemically plausible starting distribution.

¹ Booth, *Trans. Faraday Soc.* **41**, 434 (1945).

² Booth, *Trans. Faraday Soc.* **42**, 444 (1946).

³ Booth, *Trans. Faraday Soc.* **42**, 617 (1946).

⁴ Jeffrey, *Proc. Roy. Soc. A* **183**, 388 (1945).

⁵ Crowfoot (to be published).

⁶ Hughes, *J. Am. Chem. Soc.* **63**, 1737 (1941).

Upper Limit to the Tritium Content of Ordinary Water

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April 23, 1947

IN 1938 Sherr, Smith, and Bleakney¹ concluded from mass spectrographic measurements, using deuterium gas, that the tritium content of ordinary water is less than one part in 10^{12} . It has been established by the experiments described below that the tritium atom fraction in ordinary water is less than one part in 10^{17} . An extension of this technique should lead to a smaller upper limit to the abundance of this isotope.

22-mm partial pressure of deuterium gas, having a D content greater than 95 percent,² was added to a glass envelope copper gauze cathode Geiger-counter tube having a diameter of 42 mm, an effective counting volume of 200 cc and containing 23-mm partial pressure each of argon and ethyl alcohol. The normal background count, employing a $\frac{3}{8}$ " lead shield was 2.85 counts per second. The addition of the deuterium gas did not change the counting rate within the precision of the measurements. The average deviation of this measurement (based upon four independent experiments) was 0.03 counts per second. The latter value was used in calculating the upper limit to tritium abundance.

Using the above data and a tritium half-life of 31 years,³ the tritium atom fraction in ordinary water is less than $1.5 \times 10^{-13} (T^\circ/T)$, where (T/T°) is the factor by which the tritium was enriched in the electrolysis of normal water from 99.98 percent H to the final D content. Using 95 percent for the latter, the initial-volume/final-volume water ratio was calculated from the $H-D$ cathodic separation factor. The ratio (T/T°) was calculated from this volume ratio and the $H-T$ separation factor.⁴ For $H-D$ and $H-T$ separation factors of 5 and 10, respectively, (T/T°) equals 2.0×10^4 . For corresponding factors 6.5 and 13, respectively, (T/T°) equals 1.3×10^4 . Taking (T/T°) as 1.5×10^4 , the tritium atom fraction in ordinary water is less than one part in 10^{17} . By exhaustive electrolysis of heavy water, it will be possible to decrease the magnitude of this upper limit. The latter is of interest, inasmuch as tritium is a possible reaction product in nuclear processes taking place in the earth's atmosphere.⁵

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¹ R. Sherr, L. G. Smith, and W. Bleakney, *Phys. Rev.* **54**, 388 (1938).

² From Stuart Oxygen Company, San Francisco, California.

³ R. D. O'Neal and M. Goldhaber, *Phys. Rev.* **58**, 574 (1940).

⁴ M. L. Eidinoff, *J. Am. Chem. Soc.* **69**, 977 (1947).

⁵ E.g., W. F. Libby, *Phys. Rev.* **69**, 671 (1946).

Patterson-Harker Maps of Molecular Crystals

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THE interpretation of the x-ray data obtained from megamolecular crystals presents a new and difficult problem in cases where the structure and even the composition of the molecular units are unknown. If an attack be attempted by way of Patterson and Patterson-Harker maps, computed from the experimental data, a useful, even necessary preliminary is the study of the Patterson maps of various structure types.¹ A fundamental difficulty, however, arises at the outset owing to the overlapping in Patterson space S_2 of the Pattersons of individual molecules in the crystal in atomic space S_1 .² The purpose of this note is to draw attention to and indicate some of the implications of the fact that there is always a region about the