Practical X-ray Diffraction

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Outline

Practical X-ray Crystallography:

- Single crystal X-ray diffraction
  From crystals to structures (for small molecules)

- Polycrystalline X-ray diffraction
  Instruments calibration;
  Sample preparation;
  Data acquisition;
  All kinds of applications.
  XRD of polymers (Prof. BRISSON)

- Solutions, Resources, Books, …etc.

No: Neutron, Electron, SAXS, Macromolecule.

Preamble

1. Why bother to determine the structure of a chemical compound?

2. Why we need X-rays?

Two intuitive questions

Carbon

Example:

Diamond
Graphite

> 1.3 million ATM
Features of X-Rays

Suitable Wavelength (Å):

- Max von Laue, Paul P. Ewald

Applications of X-Rays

One of the Most Important Inventions

Part 1: Single Crystal X-Ray Diffraction

Physical X-Ray Crystallography

- Select/prepare sample;
- Mount the sample;
- Collect enough diffractions efficiently;
- Make corrections;
- Refine the structural model against data;
- Evaluate the results of refinement;
- Write log and plot figures.

Learned by experience
General Procedure of SXRD

1. Grow Single Crystal
2. Select and Mount the Sample
3. Determine Crystallinity
4. Determine Unit Cell and Lattice Symmetry
5. Compose Data Collection Strategy
6. Collect Data
7. Reduce and Correct Data
8. Solve and Refine the Structure
9. Evaluate the Structural Model
10. Document Files and Plot Figures

N.B.: No Rules Cannot Be Broken

Why We Need A Single Crystal?

Structure
Motif and Lattice

Search the Database

Consult extra information

Nice Crystals

Size, shape, surface, polarizes light...

Useless Crystals

Parallel growing, interpenetration of two compounds, bubbles, fibers, balls, branches...

Patience

Intuition
Craft
Science
Art

Huge and Flexible Molecules

If you have problems getting a crystal, visit the lab of structural biologist...
It can take years before they get a protein crystals!
Modern Single Crystal Diffractometer

Basic Configuration:

- Platform and Cooling System;
- Controlling PC(s);
- Monochromator and Collimator;
- Area Detector(s);
- X-Ray Source(s);
- Goniometer;

Variable

N.B: Diffractometer after CAD4, or with area detector.

Bruker SMART APEX II 1K CCD single crystal X-ray diffractometer

APeX II CCD and Fixed Chi Goniometer

Chi fixed at 54.7°

Kappa Goniometer

Full functional 4-circle goniometer

Euler Goniometer

Rigaku Mercury CCD Diffractometer
Fine-Focus X-Ray Tube

1.5 – 3 kW, ~1%, weak but long-life, cheap (5000$ USA).

Collimator

Fraunhofer diffraction (Far field) Different collimators

Collimator in different sizes and styles, severe intensity loss

Rotating Anode

~ 100 times stronger than fine-focus X-ray tube, needs a lot of maintenance

Micro-Focus X-Ray Source

Micro MAX 003 Oxford Supernova

~ 1.5 times stronger than rotating anodes, only 50 W.

Synchrotron

Kyoto, Japan

Time-resolving XRD, $10^{10-12}$ times more brilliant than a X-ray tube (3G).

CCD Detector

CCD in Small (Standard) Size
Large CCD Detector

Bruker Proteum, Oxford Titan, Atlas, Mar 165, etc.

CCD vs CMOS


The Best One for Chemical Lab

Powerful, professional, and maintenance free.

Bench-Top Diffractometer

Select the Most Suitable Diffractometer

Absorption effect and diffraction damage

<table>
<thead>
<tr>
<th></th>
<th>Mo</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.71073</td>
<td>1.5401</td>
</tr>
<tr>
<td>Ti</td>
<td>24.2</td>
<td>208</td>
</tr>
<tr>
<td>V</td>
<td>27.5</td>
<td>235</td>
</tr>
<tr>
<td>Cr</td>
<td>31.1</td>
<td>280</td>
</tr>
<tr>
<td>Mn</td>
<td>24.7</td>
<td>285</td>
</tr>
<tr>
<td>Fe</td>
<td>38.5</td>
<td>308</td>
</tr>
<tr>
<td>Co</td>
<td>42.5</td>
<td>313</td>
</tr>
</tbody>
</table>
Select and Mount the Best Crystal

Mount the Sample

Research Conditions in Our Lab
- Microscopy
- Cryoloops
- 90 s glue
- Paratone-N
- Vacuum grease

Crystal Size (X-Ray Tube)
- 0.1-0.3mm for samples with heavy elements
- 0.3-0.5mm for samples without heavy elements

Center the crystal, ~10 microns for ImuS

Crystallinity
- 360 phi rotation, diffraction during 1 minute

Crystal Quality
- Structural model from Cu Kα radiation:
  - Disordered Cu⁺ group;
  - No H on the μ₂-O atoms.
- Structural model from Mo Kα radiation:
  - No disorder group;
  - H atoms on the μ₂-O atoms.

If you don’t have a good crystal, you will have nothing!!!
Unit Cell and Lattice Type

\[ \begin{align*}
    a &= 5.9513(3) \text{ Å} \\
    b &= 9.0205(5) \text{ Å} \\
    c &= 18.3614(10) \text{ Å} \\
    \alpha &= 90^\circ \\
    \beta &= 90^\circ \\
    \gamma &= 90^\circ \\
    V &= 985.708(6) \text{ Å}^3 \\
    P &= 2, 2, 2_1,
\end{align*} \]

3 Scans of 20 frames; Rule of 18 Å³/non-H Atom.

Profile of Spots

Experimental profile of the diffractometer.

Orientation

Databases

- CSD
- ICSD
- NIST
- COD
- PDB
- ...

Personal, Commercial or Free Databases

Formulate Strategy for Data Acquisition

Formulate strategy for data acquisition

Fix all kinds of parameters and optimize the strategy.
Supervise the Data Collection

Fight against all kinds of problems:

- Trouble from instruments;
  Power-off, collision, leakage,... etc.
- Problems due to sample;
  Decay, decomposition, loss,... etc.
- Other problems.
  Ice, shift,... etc.

Solving and Refining Two Structures

1. Ylid: 2-Dimethylsulfuranylidene-indan 1,3 dione

2. Vanadium(IV) oxide sulfate hydrate:
   \( \text{VOSO}_4 \cdot X(\text{H}_2\text{O}) \)

Evaluate the Structure Model

http://checkcif.iucr.org/

Understand the structure

Values of Bond Lengths (s.u.)

s.u. : standard uncertainty
Summary

- With 100 years of development, the SXRD technique is very sophisticated;
- Abundant structural information can be obtained with great precision (including absolute configuration);
- In some cases, information about disorder within the crystal structure;
- It's indispensable in certain cases.

Deficiency of SXRD

- Only accepts nice, large single crystals;
- Difficult to get structures at high T and P;
- No information about defects, texture, ...;
- Only time and space averaged results;
- Comparatively time-consuming;
- ...

Many thanks for your attention!

We will talk about the polycrystalline X-ray diffraction after the break!