X-Rays snap molecules: Chemists love to do it

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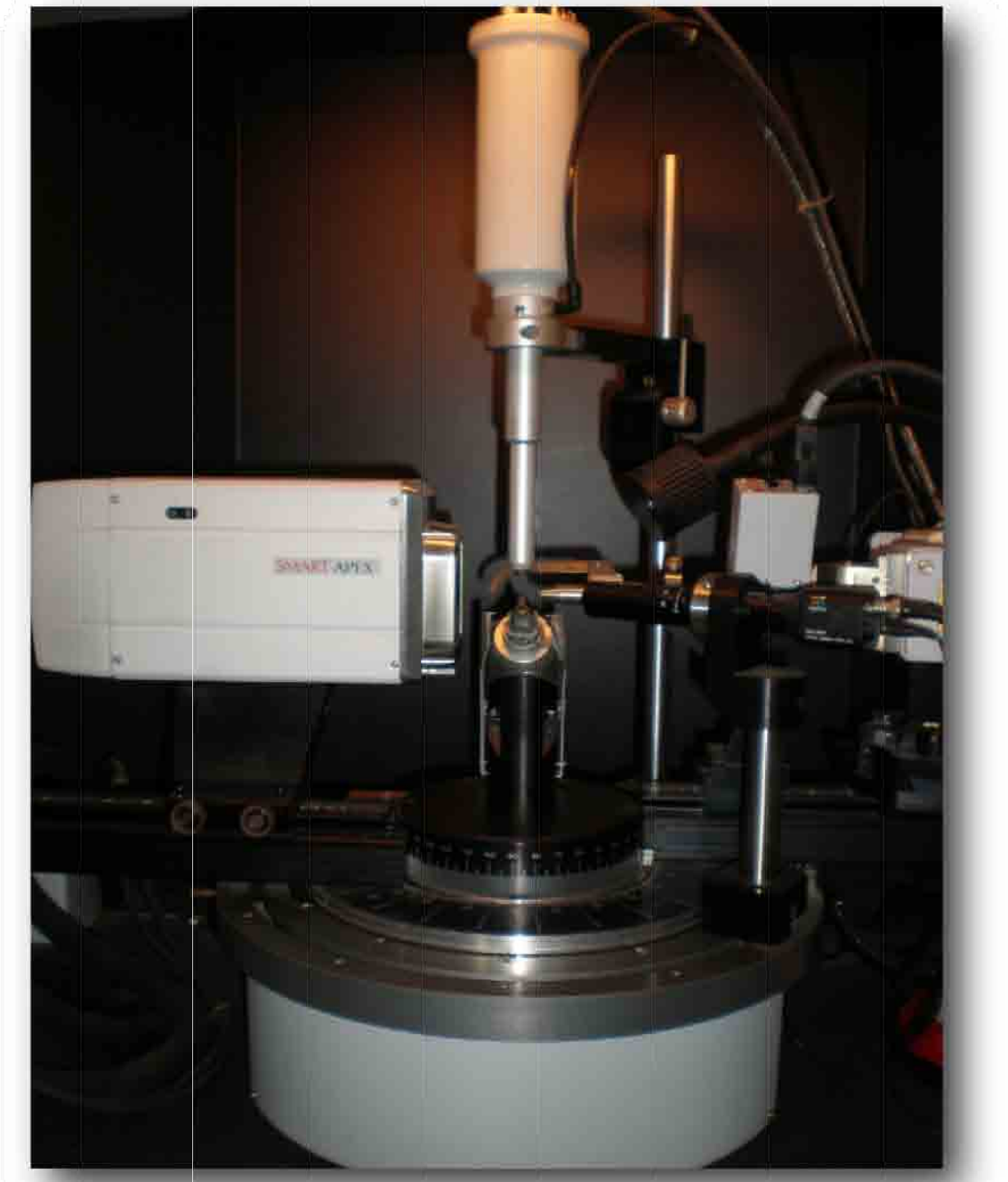
SCIENTIFIC VERSES

Visualizing molecules in 3-dimensions has always been an enthralling charm for chemists, it helps in understanding the structure-reactivity and -property relationships, which are occasionally prone to be unpredictable. In addition, geometrical parameters such as bond length, bond angle and torsion angle further assist in understanding the complex structural details of multifaceted materials like naturally occurring crystals, crystalline inorganic, organic, hybrid and biological molecules. Although crystal structure provides molecular insight about solids, visualizing it at the atomic level (an atom is 10^{-8} th of a centimeter) was a challenge owing to the limited resolution of the conventional optical and electron microscopes. It was X-rays that made it feasible to probe the structures at the atomic scale. It readily found applications in various fields such as chemistry, biology, physics & materials science. It was possible to deduce the structures ranging from complex biomolecules to pure organic, hybrid or organometallic solids using X-ray crystallography. This technique is now often considered to be a 'routine' analytical method.



A Single Crystal X-ray Diffractometer at IIT Delhi

X-ray crystallography relies on the ability of a compound to form crystals (regular and periodic arrangement of atoms or molecules as planes in three dimensions). The crystals therefore behave like a three-dimensional diffraction grating when exposed to X-rays. The crystals thus induce both constructive as well as destructive interference effects similar to the diffraction patterns, which appears as a series of spots called reflections (collected on a suitable detector). These reflections represent all possible planes that provide an image of the reciprocal lattice which is mathematically related to the parameters of crystal unit-cell in real space. The diffraction experiment produces a list of ***h***, ***k***, **ℓ**, **I** and **σ(I)**, where the indices **h**, ***k***, and **ℓ** define the position of a reflection in the reciprocal lattice; **I** corresponds to intensity and **σ(I)** to the estimated standard deviation. Respective positions of the reflections enable the dimensions of the reciprocal cell to be calculated, from which the dimensions of the real cell can be derived. The intensities of the reflections are corresponding to the contents of the unit-cell, i.e. the positions and nature of the atoms; hence unit-cell parameters and the intensities of the

reflections provide sufficient information to determine the structure.

Intense, highly focused X-ray beams from integrated synchrotron radiation lines, combined with fast desktop computers are now an integral part of the modern crystallographic techniques. Today, X-ray crystallography has enabled the structure determination of a myriad of solids. This has led to the establishment of structural databases. The repository of structures in the database has made computational processing simpler and fueled significant developments in the field of crystal engineering. In fact, the structural database of biomolecules was instrumental in initiating and prolific development of 'bioinformatics'. Some of the popular international database centers, along with their approximate respective datasets as of October 2007 (provided in brackets) are given alongside.

Out of these only the PDB is freely accessible via World Wide Web (http://www.rcsb.org). The number of structures deposited in the Protein Data Bank has doubled in the last five years and is growing rapidly ever since its inception in October 1971. At the current rate, it is expected to exceed the Cambridge Structural Database in terms of number of structures by 2035. However, an interesting observation is that since the PDB is solely dedicated to macromolecules, the PDB is already leading if the number of atoms is considered as the criterion.

A systematic study of these databases shall allow future crystallographers to direct experiments towards desired structures rather than a trial and error approach. This will be instrumental in laying the foundations for rational experimental design in the field of crystal engineering.

With the discovery of quasicrystals and the correlation between apparently disconnected phenomena like maximum enzyme efficiency of most symmetric conformation of enzyme active sites, a new era is ushering in the field of crystallography. As is evident, the role of diffraction based experiments cannot be overemphasized at this juncture.

In the references section, I have attempted to cite a number of representative books in the field of structure, diffraction & crystallography, which could be inspiring and useful for the interested readers.

STRUCTURE DATABASES

ICSD (Inorganic Crystal Structure Database: http://icsdweb.fiz-karlsruhe.de) for inorganic crystal structures (100,500).

CSD (The Cambridge Structural Database: http://www.ccdc.cam.ac.uk/products/csd) for organic, metal organic and organometallic structures (approximately 401, 000).

ICDD (The International Centre for Diffraction Data: http://www.icdd.com) for powder X-ray diagrams (approximately 256, 000).

CRYSTMET (Crystallographic and derived databases for intermetallic compounds http://www.tothcanada.com) for Metals and intermetallic compounds (approximately 110, 000 single crystal and powder).

PDB (Protein Data Bank www.pdb.org) for proteins, DNA, RNA etc., also NMR structures (approximately 47, 000).

NDB (Nucleic Acid Database) (http://ndbserver.rutgers.edu) – DNA and RNA (approximately 3, 500).

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