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CONDITIONAL DYNAMICS: REFINEMENT AND PHASING BY N-PARTICLE OPTIMIZATION

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Exploiting the prior knowledge of standard protein geometry in structure refinement is common practice. The prior geometrical data is a wealthy source of phase information. However, the application of these data requires assignment of the protein structure. This is typically achieved by model building in an experimentally phased map. We have developed an N-particle formalism that allows a rigorous treatment of stereo-chemical information without the need of prior assignments. In effect, the optimization works on loose atoms and the topology is developed in the optimization process. Our method, called Conditional Dynamics, enhances the radius of convergence in refinement and may, in principle, be applied to random starting models for ab initio phasing. Calculations using a simplified test case, consisting of a poly-alanine four helical bundle, showed i. a large radius of convergence even when the resolution is limited to 3.5 Å, and ii. successful *ab initio* optimization against 2.0 Å resolution data. Recently, we have developed a conditional dynamics-force field containing stereo-chemical restraints for all prevalent configurations in protein structures. We are now testing our method against real protein-diffraction data with respect to map improvement and ab initio phasing, i.e. modeling starting from random models.

Keywords: PROTEIN CRYSTALLOGRAPHY, PHASING, REFINEMENT

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CRYO-CRYSTALLOGRAPHY. THE LOWER THE TEMPERATURE, THE BETTER?

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Cryo-crystallography offers well-documented advantages for solving and describing crystal structures. Radiation damage is reduced at low temperature. Cooled crystals last longer in the X-ray beam, which is particularly important in biocrystallography working with huge fragile molecular structures. Flash cooling of crystals prior to data collection at very low temperatures is the rule more than the exception nowadays. Thermal motion is reduced at low temperature. This is the basis for collecting data to better resolution, data, which is less influenced by thermal diffuse scattering and anharmonicity. At low data collection temperature one can obtain more data, better data and use a simpler model for describing the thermal motion. The colder the data collection temperature, the better the least squares modeling, a prerequisite for accurate and detailed charge density studies. Cold nitrogen-gas-stream cooling, which allows a minimum temperature close to the boiling point of nitrogen, 77 K is in widespread use. Many reports have appeared on advantages of going to even lower data collection temperature. Recent developments of cooling equipment allowing data collection below 77K will be mentioned and examples will be given of necessity and pitfalls of very-low-temperature measurements aiming for charge density studies. Variable-temperature data collection is a valuable tool for characterizing phase transitions by powder diffraction studies. The use of area detectors in single crystal diffractometry and the resulting increased data collection speed has allowed wider use of variable-temperature studies with interesting implications. Analysis of multi-temperature atomic displacement amplitudes allows insight into the molecular dynamics and improved description of the crystal structure.

Keywords: CRYO CRYSTALLOGRAPHY, VARIABLE TEMPERATURE STUDIES, CHARGE DENSITY STUDIES

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LOW TEMPERATURE METASTABLE MAGNETIC STATES IN IRON(II) COMPLEXES

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The transition from a low spin diamagnetic state to a high spin paramagnetic state in iron (II) molecular complexes may be induced by warming the sample, by pressure effects or by a light irradiation at very low temperature. On the way to obtain electronic devices based on such phenomenon, one of the first steps is to understand the correlation between the structural properties and the magnetic transition features. To this end, X-ray diffraction at very low temperature represents a powerful tool. Indeed, on the basis of the temperature dependence from 10 K to 300 K of the crystal structures of a large number of iron (II) complexes, we were able to show direct correlations between structural aspects (intramolecular distortion, hydrogen bonds...) and spin transition features (abruptness, critical temperature ...) (1). Moreover, very low temperature X-ray diffraction allowed us to determine the crystal structures of an iron (II) complex in the photoinduced metastable high spin state at 30 K (2). As well, more recently, the crystal structure of an iron (II) complex in a metastable quenched high spin state at very low temperature has been determined using an open flow He gas cryostat.

References
(1) P. Guionneau, C. Brigouleix, Y. Barrans, A. E. Goeta, J-F. Letard, J.A.K. Howard, J. Gaultier, D. Chasseau, C.R. Acad. Sci. Paris, Chemistry, 4, 161-171 (2001)
(2) M. Marchivie, P. Guionneau, J.A.K. Howard, G. Chastanet, J.F. Letard, A.E. Goeta, D. Chasseau, J. Am. Chem. Soc., 124(2), 194-195 (2002).

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HIGH RESOLUTION POWDER DIFFRACTION STUDIES AT LOW TEMPERATURE

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On the high-resolution powder diffraction beam line at the european synchrotron radiation facility we can investigate spinning capillary or flat-plate samples at temperatures down 2.5 k using a liquid-helium-cooled flow cryostat. Capillary samples can also be cooled via cold nitrogen or helium gas blowers, which are mounted coaxially with the capillary to ensure a laminar flow of gas and hence reduce turbulence and icing. The high-resolution data available using synchrotron radiation is well suited to studying a range of low-temperature phenomena, such as phase transitions, thermal expansion, magnetostriction effects, etc. For example, camphor transforms from an orientationally disordered hexagonal plastic phase ii to a more-ordered phase iii on cooling. The ordering induces a large change in volume so single crystals fragment. We have solved and refined the structures of phase iii for the pure enantiomer (S-camphor), and for the racemic solid solution (RS-camphor), from powder diffraction data. The former is fully ordered whereas the latter has residual fourfold disorder. We have also built gas-condensation cells to study the low-temperature phases of volatile molecular compounds. The gases are condensed in situ as liquid in the capillary, then the temperature is lowered to solidify the sample. We have studied a number of hydrofluorocarbon and hydrochlorofluorocarbon refrigerant molecules, such as hfc 134a (1,1,1,2-tetrafluoroethane) and hfc 152a (1,1-difluoroethane). We have found order-disorder phase transitions, and solved the structures of the low-temperature phases. These reveal details of the intermolecular interactions, which are important in defining the thermodynamic and heat-transporting properties of the fluids.

Keywords: SYNCHROTRON RADIATION PHASE TRANSITIONS POWDER DIFFRACTION