Computer Program Abstracts

PSL + SEARCHER and DIRECTER – automatic structure analysis of organic compounds using a PC. By KENJI OKADA, *Research and Development Center, Ricoh Co. Ltd, Kouhoku-ku, Yokohama 223, Japan*

The crystallographic problem: *PSL* selects one heavy-atom solving Patterson function and *SEARCHER* determines the positions of all the remaining atoms automatically. *DIRECTER* is based on the symbolic-addition method and automatically determines most atoms. In a single PC run, the user can determine the molecular fragments by inputting the atom symbols with no chemical assumptions or human intervention.

Method of solution: *PSL* and *SEARCHER* are used for organic compounds that include sulfur or a heavier atom. The *PSL* procedure is as follows: (i) read the cell constants, heavy-atom symbol, reflection data and Harker sets; (ii) calculate the Patterson function for all Harker sets or an asymmetric unit and store the peaks and heights (u, v, w, H); (iii) convert all peaks into coordinates, combine these coordinates and store them as atoms (x, y, z, H); (iv) remove the centers of symmetry $[(0, 0, 0), (\frac{1}{2}, 0, 0), \ldots, (1, 1, 1)]$ and equivalent positions; (v) calculate the structure factors and refine each parameter (x, y, z, B) with full-matrix least squares; (vi) sort the final R factors so that heavy atoms are located with the lower R factor.

SEARCHER proceeds as follows: (i) read the cell constants, the number of input (NSF), total (NLS) and additional (NLH) atoms, the heavy-atom parameters, the reflection data and a maximum temperature factor (BCUT); (ii) calculate the structure factors and Fourier synthesis using the controlled reflection data by the combination of NSF and (sin θ)/λ; (iii) select the peaks (x, y, z, H), check for 'reasonable' interatomic distances between input atoms and peaks and add the NLH peaks to NSF atoms. If NSF is less than NLS, repeat step (ii); (iv) refine the parameters until ghost atoms are removed $(B > \text{BCUT})$; (v) draw 2D projections of the molecules.

DIRECTER proceeds as follows: (i) read the cell constants, atom symbols, reflection data with $|F_o(h)|$; (ii) select three kinds of origin sets including enantiomorphs and Σ_1 reflections for which $P_+ [E(2h)]$ are greater than 0.95; (iii) choose several potential members that can generate phases for more than 95% of the data; (iv) generate new phases by the tangent formula. The process is repeated to cover all combinations (run sets) of phases; (v) select the 'best five' run sets using the figures of merit R_{Karle}, Q_{Drew}, $\langle \alpha \rangle$ and $\langle t \rangle$ (Drew, Larson & Motherwell, 1971); (vi) calculate the 'best five' E maps, select 1.1 times peaks of one molecule and calculate the structure factors; (vii) draw 2D projections. If some fragments are obtained by *DIRECTER*, *SEARCHER* is a powerful tool to find the remaining atoms.

Software and hardware environments: These programs are written in standard Fortran77 and fully tested under MS-DOS™ 3.x. Only the standard option has been applied. These programs need 520 kbyte of memory and 2 Mbyte of disk space. A laser printer with HPGL emulation is needed for drawing.

Program specifications: These programs are part of the *DS*SYSTEM* (Okada & Koyama, 1991). Each program consists of a main segment plus *DS*SYSTEM* libraries totaling about 29 000 source-code lines. Run times are usually less than 30 min (*PSL* + *SEARCHER* and *DIRECTER*) and 1–7 h (*DIRECTER*) for a small structure by i486 + ODP (25MHz). The PC 1993 version is improved from 1991 by a change to the algorithms of peak summation in Fourier synthesis, which decreases calculation time.

References

Drew, M., Larson, A. & Motherwell, S. (1971). *TANTWO: Generation and Refinement of Phases by the Tangent Formula*. Univ. of Cambridge, England.

Okada, K. & Koyama, H. (1991). *J. Appl. Cryst.* **24**, 1067–1070.

International Union of Crystallography

Restructuring of the IUCr editorial office

Following the promotion of Mr Michael Dacombe from Technical Editor to Executive Secretary, it was considered an opportune time to restructure the editorial office to reflect better the greater variety of work now carried out and to clarify the responsibilities of the staff.

Mr Peter Strickland has been appointed as Managing Editor with overall responsibility for both the technical editing and the centralized checking. Mrs Sue King has been appointed as Technical Editor. Dr Amanda Berry has been appointed as Assistant Technical Editor with special responsibility for the centralized checking. There are three Senior Editorial Assistants and six Editorial Assistants. Mr Brian McMahon is the Research and Development Officer and his assistant is Dr M. Hoyland. The total number of graduate staff in the editorial office is 14.

Book Reviews

Structure of electrified interfaces. Edited by *J. Lipkowski* and *P. N. Ross.* Pp. x + 406. Weinheim: VCH Verlagsgesellschaft mbH, 1993. Price DM 196, £80.00. ISBN 3-527-28787-6.

This book aims to describe, to a broad audience, the current understanding of the metal–solution interface of electrochemistry. The clear objective in this field of interfacial electrochemistry is to replace or augment the thermodynamic continuum models of the classic electrochemical double layer with microscopic models that explicitly incorporate the roles and structures of individual atoms and molecules. The evolution of perspective from macroscopic to microscopic is clearly work in progress and the book provides an excellent overview of current theory and recent experimental advances.

The use of single-crystal electrodes, a host of new surface probes and the ability to analyze a working electrochemical interface *in situ* and then *ex situ* using ultra-high-vacuum (UHV) techniques have led to rapid experimental advances. The first three chapters of the book provide an introduction to structural characterization and behavior of single-crystal metal-electrode surfaces. The tools of surface crystallography as applied in UHV are expertly reviewed by Michel Van Hove. Phillip Ross and Dieter Kolb go on to describe *in situ* methods of characterizing working 'wet' electrodes by such techniques as surface extended X-ray absorption fine structure (SEXAFS), grazing-incidence X-ray scattering (GIXS), scanning tunneling microscopy (STM), atomic-force microscopy (AFM) and surface second-harmonic generation (SHG). Coupled wet electrochemistry and *ex situ* UHV-analysis studies are described, in which low-energy electron diffraction (LEED) and other electron spectroscopies are employed for structural analysis in UHV. These tools, coupled with cyclic voltammetry, are used to understand and discuss the structure of underpotentially deposited metal overlayers and potential-induced reconstruction of electrode surfaces.

The precise structure of directly adsorbed ions and diffusely ordered solvated ions that make up the electrochemical double layer at the electrochemical interface is difficult to characterize using any of the techniques above. In order to begin to understand the issues involved, Manuel Soriaga reviews molecular adsorption at single-crystal electrodes. Vibrational spectroscopy, *via* high-resolution electron energy-loss spectroscopy (HREELS) and infrared absorption spectroscopy (IRAS), is used to provide structural information on adsorbate bonding geometries through surface selection rules and analogies to inorganic cluster compounds. (It should be noted that recent dynamical LEED and SEXAFS studies have repudiated

several nitric oxide site assignments based on vibrational spectroscopy, and this has diminished the enthusiasm for extrapolating the structures of cluster compounds to surfaces.) A metal electrode tempered by co-adsorbed ions and water defines an inner electrochemical layer, and Gerhard Pirug and Hans Bonzel discuss the simulation of such layers in UHV by co-adsorption of alkali metals and water. Wolfgang Schmickler and Karl Heinzinger provide analytical and molecular-dynamics-based theoretical chapters on the electrochemical interface. The final experimental chapters of the book, by Zofia Borkowska and Ulrich Stimming and by Fred Wagner, examine the relationship between UHV simulations of electrochemical layers at cryogenic temperatures and 'wet' electrochemistry. Water typically desorbs from metal electrodes at temperatures below 200 K. Nevertheless, the consensus of the authors is that diffusion and conductivity in favorable acid/water systems can be sufficient for purposes of electrochemical simulations at temperatures as low as 150 K. The chapter by Wagner is truly delightful as he thoughtfully catalogs the difficulties of connecting cryogenic UHV surface science with wet electrochemistry from experimental and theoretical points of view. Impressive results from UHV simulations of the electrochemical interface include the ability to count water molecules of ion hydration by thermal desorption and the spectroscopic identification of the hydronium ion (H_3O^+) by HREELS when HF or HCl is co-adsorbed with H_2O on Pt(111).

The text provides a fine introduction to the field of interfacial electrochemistry. Its emphasis on current research and the many references to the primary literature suggest it will be much appreciated by the electrochemical community. Crystallographers will be particularly interested in the important role that diffraction techniques (LEED, GIXS and SEXAFS) have played in structural determinations of the inner electrochemi-

cal layer. At the same time, they may pause to reflect on how difficult it is to characterize the structure of the outer Helmholtz, or diffuse Gouy–Chapman, layer of solvated ions. Despite the difficulties of microscopically characterizing the electrochemical double layer, the text clearly indicates that rapid progress is being made in the emerging field of interfacial electrochemistry. Excellent accounts of the recent advances in and future prospects of the field are provided.

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Books Received

The following books have been received by the Editor. Brief and generally uncritical notices are given of works of marginal crystallographic interest; occasionally, a book of fundamental interest is included under this heading because of difficulty in finding a suitable reviewer without great delay.

Infrared transmission spectra of carbonate minerals. By *G. C. Jones* and *B. Jackson*. Pp. xv + 222. London: Chapman & Hall, 1993. Price £75.00. ISBN 0-412-54650-7. The stated purpose of this compilation is 'to make available recently acquired spectra of as many well-characterized carbonate minerals as possible in order to further the use of infrared spectroscopy in mineralogy.' Fourier-transform IR spectra and relevant physical and chemical data are presented on facing pages for over 100 minerals arranged in alphabetical order. In a few cases, expanded spectra are provided on an additional page. Cross references are provided, where available, for specimens that have been examined by X-ray powder diffraction.