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A mayor obstacle for the prediction of the crystal structures of organic molecules is the discrepancy between the small size of typical lattice energy differences and the limited accuracy of force fields or pure density functional theory (DFT) calculations. We present a hybrid method for the calculation of accurate lattice energy differences that combines DFT calculations using the VASP program with empirical Van der Waals (VdW) potentials.

The key to success is the careful adjustment of the empirical potentials, in particular in the region of intermediate interatomic distances, where both the DFT component and the VdW component yield a significant contribution to the total interaction energy. We have fitted the empirical parameters for H, B, C, N, O, S, F, Cl and Br to molecular  $C_6$  coefficients and to the unit cells of low temperature crystal structures. The unit cell volumes and the cell lengths are typically reproduced to within 1%.

Energy ranking studies have been conducted for a variety of molecules, including acetylene, ethylene, ethane, methane, acetic acid, urea, paracetamol and several molecules from the first two CCDC blind tests on polymorph prediction. The experimental low temperature crystal structures are generally found as the most stable predicted crystal structures. In several cases, the most stable packing motif is expressed in more than one space group, giving rise to tiny energy differences of less than 1kcal/mol per molecule.

**Keywords:** polymorphs, lattice energy, modeling

### MS76.29.3

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#### Exploring Polymorphism: the Case of Benzene

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Crystal structure prediction is one of the most challenging problems in theoretical chemistry. The standard approaches focus on the minimization at  $T=0$  of lattice energies. Here instead we concentrate on the finite temperature, finite pressure Gibbs free energy, thus fully accounting for entropic effects. This is achieved by combining the Parrinello-Rahman variable cell approach with metadynamics[1], a novel powerful sampling method. We apply this scheme to an old and difficult problem, the prediction of benzene polymorphs[2]. Only the knowledge of the molecular structure and a reasonable intermolecular potential are necessary. We find seven stable crystalline structures of benzene. Comparison with the experimental data shows an unambiguous correspondence between our structures and those revealed by Raman spectroscopy and X-ray diffraction, so that for the first time the benzene phase diagram appears to be completely accessible. These results demonstrate that metadynamics is a powerful tool that shows definite promise for solving the problems of crystal structure prediction or search for polymorphs and suggest that the smoothness of the free energy surface, as compared to the enthalpy surface, may facilitate the task even when using extremely accurate force fields.

[1] Laio A., Parrinello M., *PNAS*, 2002, **99**, 12562-12566. [2] Raiteri P., Martoňák R., Parrinello M., *Angew. Chem. Int.Ed.*, in press.

**Keywords:** molecular dynamics, free energy, crystal structure prediction

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#### Progress in Crystal Structure Prediction for Diastereomeric Salts

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The development of a methodology that will allow the prediction of the structure and relative stability of diastereomeric salt pairs could have an immense impact in the manufacture of chemical entities in optically pure form as it will assist the design of separation processes based on diastereomeric resolution. The solubility differences of the diastereomeric pair is an important determinant for the resolution

efficiency of the resolving agent and can be estimated *via* lattice (free) energy calculations.

This paper develops an approach to the crystal structure prediction of such systems based on global lattice energy optimisation. To alleviate the mathematical complexity of the solution space due to the presence of two entities in the asymmetric unit, the search is guided by a statistical analysis of the Cambridge Structural Database for common coordination environments. A distributed multipole model for the dominant electrostatic interactions and high level *ab initio* calculations for the intramolecular contributions allow the quantitative calculation of the relative stabilities of the p- and n-salt for a given resolving agent.

The methodology is successfully applied in the case of 1-phenylethylammonium-2-phenylpropanoate. All experimentally determined known forms and their relative stabilities are predicted.

**Keywords:** diastereomeric, resolution, prediction

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#### Inorganic Structure Prediction with GRINSP

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The computer program GRINSP (Geometrically Restrained INorganic Structure Prediction) [1], allows to explore the possibilities of occurrence of 3, 4, 5 and 6-connected 3D networks. Hypothetical binary models (as well as known frameworks) are produced with exclusive connections of polyhedra by corners, such as  $[MX_3]$  triangles in  $M_2X_3$  formulation,  $[MX_4]$  tetrahedra in  $MX_2$  (zeolites or dense  $SiO_2$  polymorphs),  $[MX_5]$  polyhedra in  $M_2X_5$  and finally  $[MX_6]$  octahedra in  $MX_3$  polymorphs. Moreover, hypothetical ternary  $M_aM'_bX_c$  compounds are built up by combinations of either two different polyhedra or two different cations adopting the same coordination but with two different radii. The cost function is based on the agreement of the model interatomic distances with ideal distances provided by the user. The Monte Carlo algorithm explores randomly a range of cell parameters. First are found rough structure candidates, selected after the verification of the expected geometry, and then are optimized the cell parameters and the atomic coordinates. A satellite software (GRINS) can use the predicted models and produces the characteristics of isostructural compounds which would be obtained by cationic substitutions. CIF files (>1000) of hypothetical boron oxyde polymorphs (including nanotubes), zeolites, fluoroaluminates, borosilicates, titanosilicates, gallophosphates, are available at the PCOD (Predicted Crystallography Open Database) [2].

[1] a) Le Bail A., *J. Appl. Cryst.*, submitted; b) <http://www.cristal.org/grinps/>  
[2] <http://www.crystallography.net/pcod/>

**Keywords:** structure prediction, inorganic compounds, Monte Carlo treatment

### MS77 PERSPECTIVE OF NEUTRON CRYSTALLOGRAPHY AT HIGH POWER SOURCES

**Chairpersons:** Masatoshi Arai, Ian Anderson

### MS77.29.1

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#### Prospects for Neutron Diffraction under Extreme Pressure Conditions

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The Spallation Neutron Source currently under construction at Oak Ridge National Laboratory in the United States is due to receive first neutrons in the spring of 2006. In this talk the current state of the