

The cover represents a simulation of solvated ions (gold). Fluoride prefers the bulk and iodide the surface, as reported by Vrbka and Jungwirth (p. 1211).

# AUSTRALIAN JOURNAL OF CHEMISTRY

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## Foreword

### Computational Chemistry and Spectroscopy

Brian F. Yates

*Aust. J. Chem.* **2004**, 57, 1117–1118.

This issue of the *Australian Journal of Chemistry* focusses on a diverse range of topics in physical chemistry, from fundamental structural studies of small molecules to the complicated phenomena of proteins.

## Current Chemistry

### Fluctuations Relations for Nonequilibrium Systems

Debra J. Searles, Denis J. Evans

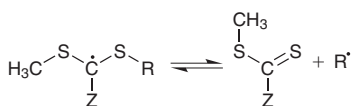
*Aust. J. Chem.* **2004**, 57, 1119–1123.

At the micro-scale both forward and reverse courses are equally likely, yet at the macro-scale thermodynamic irreversibility dominates. The overlap of these domains, at the size range of interest for nanotechnology and molecular modelling of biological systems, is the province of the fluctuation theorem.

### A Quantum-Chemical Approach to Understanding Reversible Addition Fragmentation Chain-Transfer Polymerization

Michelle L. Coote

*Aust. J. Chem.* **2004**, 57, 1125–1132.

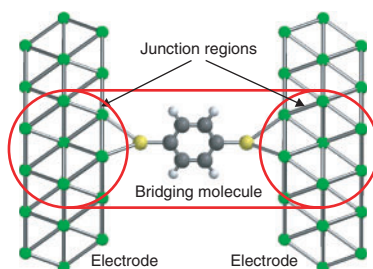


The RAFT polymerization process is a technique for controlling the molecular weight and architecture in free-radical polymerization. Quantum-chemical calculations of model fragmentation reactions (shown here) are helping to clarify the reaction mechanism and interpret the effects of substituents on the process. This article highlights these recent theoretical investigations.

### Molecular Electronics: From Basic Chemical Principles to Photosynthesis to Steady-State Through-Molecule Conductivity to Computer Architectures

Jeffrey R. Reimers, Ante Bilić,  
Zheng-Li Cai, Mats Dahlbom,  
Nicholas A. Lambropoulos,  
Gemma C. Solomon,  
Maxwell J. Crossley, Noel S. Hush

*Aust. J. Chem.* **2004**, 57, 1133–1138.



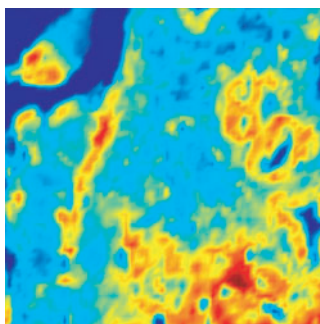
Advances in molecular electronics are essentially advances in the control and manipulation of electrons, for which issues of localization and delocalization come to the fore. Ab initio molecular dynamics simulations of electrode–molecule–electrode systems (as shown), and the localization of electrons thereon, are becoming a reliable guide for nanotechnology.

## Rapid Communications

## Fourier Transform Infrared Imaging and Unsupervised Hierarchical Clustering Applied to Cervical Biopsies

Keith R. Bamberg, Bayden R. Wood,  
Michael A. Quinn, Don McNaughton

*Aust. J. Chem.* **2004**, 57, 1139–1143.

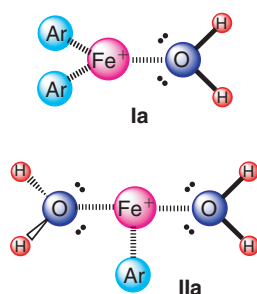


The advent of FTIR imaging spectrometers that are rapidly able to collect large arrays of spectra has opened up their use as potential pathological tools. Here the authors used IR microspectroscopy to investigate the chemical changes that occur upon the development of cervical cancer. In particular, they were able to demonstrate that the technique allows anatomical and histopathological features to be clearly resolved.

Infrared Spectroscopy of Solvation and Isomers in  $\text{Fe}^+(\text{H}_2\text{O})_{1,2}\text{Ar}_m$  Complexes

Richard S. Walters, Michael A. Duncan

*Aust. J. Chem.* **2004**, 57, 1145–1148.



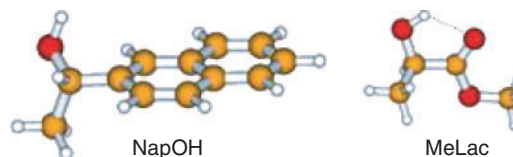
Throughout chemistry and biology, the solvation of metal cations by water is a vital process but one in which the finest details are still missing. Cluster studies engaged with the argon tagging method provide this detail, through perturbing the measured spectra in a small but significant way. This paper reports on the arrangement of lightly solvated iron, but suggests the argon tag may not perturb the spectra regularly.

## Chiral Recognition in Jet-Cooled Complexes

Nathalie Seurre, Katia Le Barbu-Debus,  
Françoise Lahmani, Nicole Borho,  
Martin A. Suhm, Anne Zehnacker

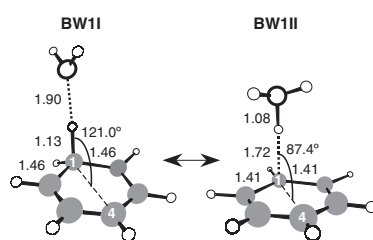
*Aust. J. Chem.* **2004**, 57, 1149–1152.

Understanding the nature of short-lived contact pairs, and, in particular, the role of multiple hydrogen bonds in chiral recognition is of great importance. In investigations into ( $\pm$ )-methyl lactate and the fluorescent probe 2-naphthylethanol (shown), a definite chiral discrimination in which a chirality-dependent competition arose between intramolecular and intermolecular hydrogen bonds is observed.

Comparative Studies of  $\text{H}^+(\text{C}_6\text{H}_6)(\text{H}_2\text{O})_{1,2}$  and  $\text{H}^+(\text{C}_5\text{H}_5\text{N})(\text{H}_2\text{O})_{1,2}$  by DFT Calculations and IR Spectroscopy

Chanchal Chaudhuri, Chih-Che Wu,  
Jyh Chiang Jiang, Huan-Cheng Chang

*Aust. J. Chem.* **2004**, 57, 1153–1156.

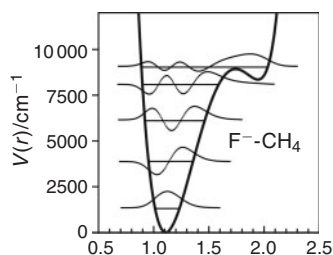


The  $\pi$ -electron clouds of aromatic compounds play an important role in intermolecular stacking. Using benzene–water clusters as a model and probed with both spectroscopic and computational methods, the change in  $\pi$ -electron clouds upon protonation of benzene is shown to directly affect the cluster organization, as shown in the graphic.

Structures of  $\text{F}^-(\text{CH}_4)_n$  and  $\text{Cl}^-(\text{CH}_4)_n$  ( $n = 1-2$ ) Anion Clusters Elucidated through Ab Initio Calculations and Infrared Spectra

Zoë M. Loh, Rosemary L. Wilson,  
Duncan A. Wild, Evan J. Bieske,  
Mark S. Gordon

*Aust. J. Chem.* **2004**, 57, 1157–1160.



Infrared spectra and ab initio calculations for the  $\text{F}^-(\text{CH}_4)_n$  and  $\text{Cl}^-(\text{CH}_4)_n$  anion complexes show that methane establishes a single linear hydrogen bond with halide anions. The potential energy curve for stretching motion of the intermediate proton can be extremely anharmonic, reflecting the proton's tendency to move towards the halide. Correspondence between the measured IR spectrum of  $\text{F}^-(\text{CH}_4)_n$  and theoretical predictions improves markedly when anharmonicity is taken into account.

### Photodissociation Dynamics of Vinyl Chloride Investigated with a Pulsed Slit-Jet and Time-Resolved Fourier-Transform Spectroscopy

Mohammed Bahou, Yuan-Pern Lee

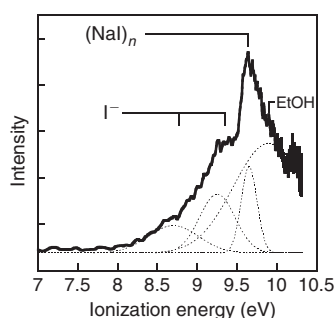
*Aust. J. Chem.* **2004**, 57, 1161–1164.

During dissociation of vinyl chloride, three- and four-centre HCl elimination processes compete; the products are identical but their energies reflect the dissociation pathway. The energies measured in this study agree well with trajectory calculations, and residual energy differences in previous experiments can be attributed to quenching.

### Solvation Structure of NaI on the Surface of Ethanol Solution

Fumitaka Mafuné, Tamotsu Kondow

*Aust. J. Chem.* **2004**, 57, 1165–1167.

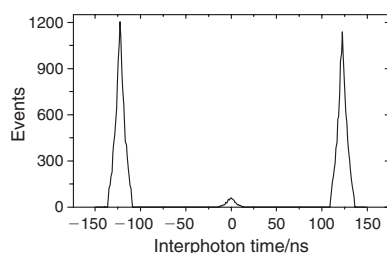


Photoelectron spectra arising from within 1 nm of the surface of a continuously renewed, clean solution of NaI in ethanol were generated by irradiation with a laser at 118 nm wavelength. Covalent, solvated  $(\text{NaI})_n$  clusters remain on the surface, and the clusters are in equilibrium with  $(\text{Na}^+ - \text{I}^-)$  ion pairs in the bulk of the solution.

### Single Photon Emission from a Dendrimer Containing Eight Perylene Diimide Chromophores

Toby D. M. Bell, Satoshi Habuchi, Sadahiro Masuo, Ingo Österling, Klaus Müllen, Phillip Tinnefeld, Markus Sauer, Mark van der Auweraer, Johan Hofkens, Frans C. De Schryver

*Aust. J. Chem.* **2004**, 57, 1169–1173.

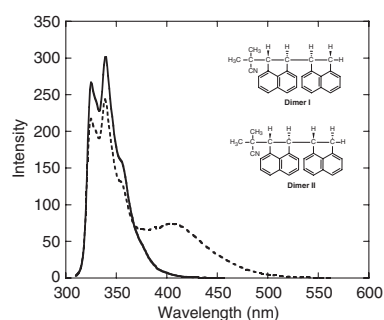


Materials able to emit a single photon on demand are core to many technologies such as quantum cryptography. The title dendrimer is one such material; the coincidence plot shown displays strong photon anti-bunching behaviour. This arises from efficient singlet–singlet annihilation in the dendrimer.

### Mechanisms of Excimer Formation in Poly(acenaphthylene)

Ming Chen, Kenneth P. Ghiggino, Trevor A. Smith, San H. Thang, Gerard J. Wilson

*Aust. J. Chem.* **2004**, 57, 1175–1177.

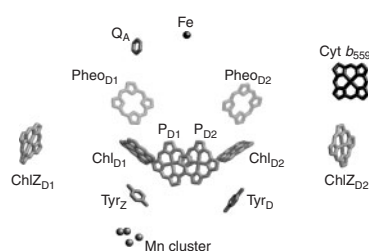


The photochemistry of chromophores is modified significantly when they are incorporated into macromolecules, since the close proximity of groups in a polymer can lead to energy transfer and excimer formation. For poly(acenaphthylene), excimer fluorescence is both tacticity and chain length dependent, revealing the role of nearest-neighbour and long-range chromophore interactions.

### The Native Reaction Centre of Photosystem II: A New Paradigm for P680

Joseph L. Hughes, Barry J. Prince, Sindra Peterson Årsköld, Paul J. Smith, Ron J. Pace, Hans Riesen, Elmars Krausz

*Aust. J. Chem.* **2004**, 57, 1179–1183.

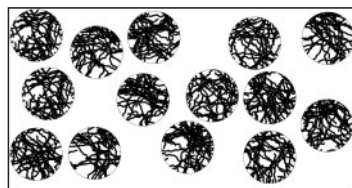


The engineroom of photosynthesis in plants and cyanobacteria is the PSII reaction centre (shown), a finely tuned collection of redox-active chlorophylls' pheophytins and other charge-carrying components. The charge separation mechanism driving this machine has been widely disputed. Laser selective excitation of PSII at low temperatures has revealed that the charge-separating state lies at far lower energy than previously thought and also that excitation transfer from inner antenna is remarkably slow.

## NMR Studies of Nanoscale Organization and Dynamics in Polymer Electrolytes

William S. Price, Yuichi Aihara,  
Kikuko Hayamizu

*Aust. J. Chem.* **2004**, 57, 1185–1190.



The dynamics of the species present in a lithium ion–polymer electrolyte system are studied using multinuclear NMR relaxation and NMR diffusion measurements. The system underwent significant structural relaxation from a fluid porous model to one containing more discrete hyperstructures (indicated by the graphic). The results may provide understanding into the long-term conductivity changes in battery electrolytes.

## Chemical Bonding in Octahedral $\text{XeF}_6$ and $\text{SF}_6$

Matthias Lein, Gernot Frenking

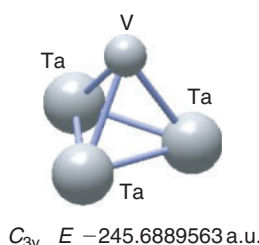
*Aust. J. Chem.* **2004**, 57, 1191–1195.

The Xe–F and S–F bonds are predominantly composed of  $\sigma$ -orbitals of  $t_{1u}$  symmetry, but S–F bonds have a greater  $a_{1g}$  contribution. DFT calculations with relativistic effects included reveal that for both molecules the overall stability depends on quasiclassical electrostatic interactions.

## DFT Calculations on Group 5 Mixed Metal Tetramers: $\text{Ta}_x\text{Nb}_y\text{V}_z$ ( $x + y + z = 4$ )

Magdalene A. Addicoat, Mark A. Buntine,  
Gregory F. Metha

*Aust. J. Chem.* **2004**, 57, 1197–1203.



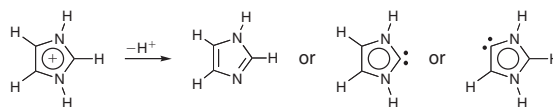
The physical and chemical properties of transition metal clusters can vary dramatically with size, and it is important to understand how these properties evolve. There still remains a paucity of structural information regarding the effect of substituting one or more heteroatoms into a metal cluster. This paper outlines the use of DFT in exploring the structure and bonding of the title clusters, an example of which is shown.

## An Assessment of Theoretical Protocols for Calculation of the $\text{pK}_a$ Values of the Prototype Imidazolium Cation

Alison M. Magill, Brian F. Yates

*Aust. J. Chem.* **2004**, 57, 1205–1210.

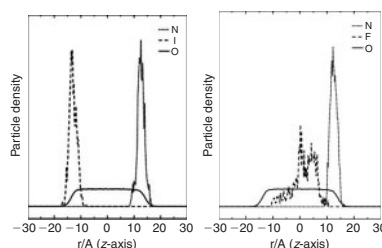
$\text{pK}_a$  values for the three different hydrogen atoms in the imidazolium cation have been calculated with highly accurate theoretical methods. Excellent agreement was obtained with the available experimental values. A discussion of the models used is provided, along with their levels of theory and their accuracy.



## Counter-Ion Effects and Interfacial Properties of Aqueous Tetrabutylammonium Halide Solutions

Luboř Vrbka, Pavel Jungwirth

*Aust. J. Chem.* **2004**, 57, 1211–1217.

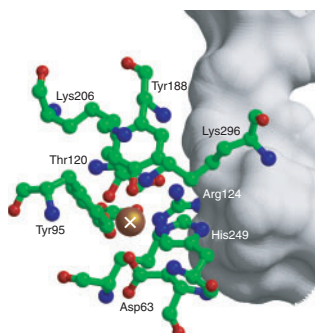


The behaviour of tetrabutylammonium fluoride and iodide in aqueous solution (in particular at the air/water interface) was studied by molecular dynamics simulations. The behaviour of the counter ions depended upon ionic size and polarizability: fluoride resided in the bulk whereas iodide was surface active. The cation behaved as a typical surfactant.

## A Density Functional Theory Study of the Iron-Binding Site of Human Serum Transferrin

David Rinaldo, Martin J. Field

*Aust. J. Chem.* **2004**, 57, 1219–1222.



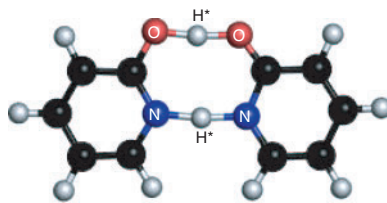
How the transferrins capture, hold, and release (ferric) iron is unclear, but the protein's conformation and protonation state are factors. Applying electronic structure calculations to this biochemical problem reveals Tyr188 is protonated, His249 is not, and Tyr188 is involved with the iron atom directly (marked with a  $\times$  in the graphic).



## Double Proton Transfer using Dissociable Force Fields

Sven Lammers, Markus Meuwly

*Aust. J. Chem.* **2004**, 57, 1223–1228.



Classical force fields enable the theoretical study of complex chemical processes, but limited with regard to molecular rearrangements. Dissociable force fields overcome this limitation, exemplified in this paper with a 2-pyridone/2-hydroxypyridine complex. The method is also fast; a 10 ps simulation with ab initio methods took 11 h CPU time but a 1 ns simulation with this method took just 5 min.

## Quantum Monte Carlo Study of Water Molecule: A Preliminary Investigation

Nicole A. Benedek, Irene Yarovsky,  
Kay Latham, Ian K. Snook

*Aust. J. Chem.* **2004**, 57, 1229–1232.

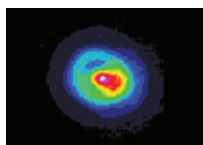
Many common computational methods (Hartree–Fock, DFT, Møller–Plesset, coupled cluster) handle chemical bonding well but describe weaker physical interactions poorly. Using water as a model, the QMC method is shown to provide good results with a smaller basis set.

## Focus

### Feasibility Study of Direct Measurement of Two-Photon Absorption Cross-Sections

Craig Richmond

*Aust. J. Chem.* **2004**, 57, 1233.



Current methods to measure two-photon absorption cross-sections require focussed laser beams or indirect methods. This article shows that they can be measured directly, in a manner similar to one-photon absorption cross-sections, for solutes in a non-hydrogen bonding solvents.

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