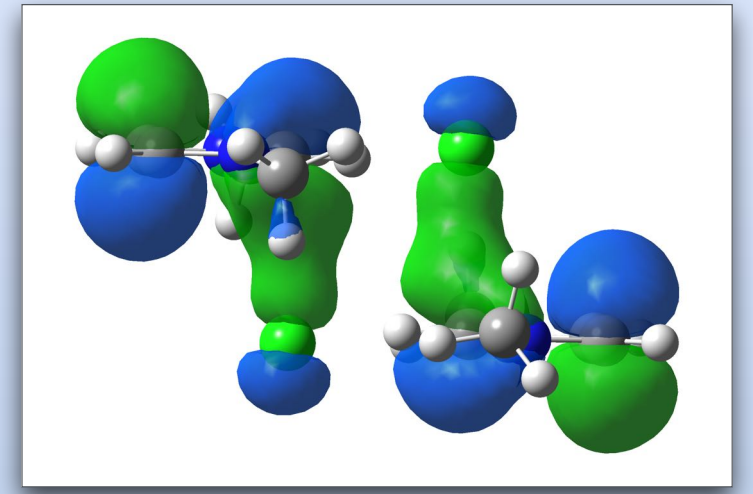
Chemistry with Computers (not Chemicals)

Prof. Patricia Hunt
Victoria University of Wellington



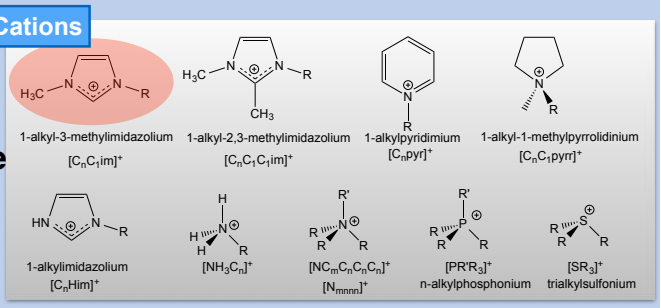
Outline

- what are Ionic liquids (ILs)?
- why are IL interesting?
- delving deeper!
- hydrogen bonding in ILs
- current research in my group

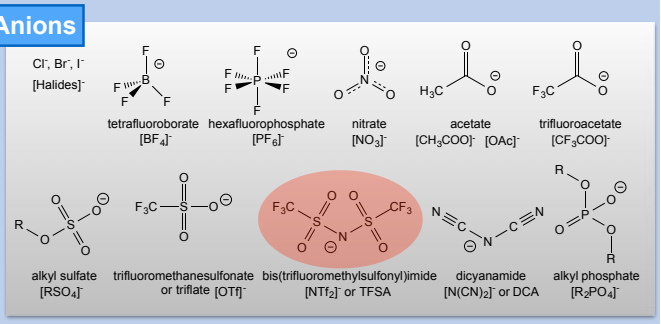
Room Temperature Ionic Liquids

- **composed of large ions**
  - large organic cation
  - inorganic anion
- **liquid at (or just above) room tempe**
  - unlike molten salts
    - eg NaCl melt ≈800 °C
  - melting point <100°C
    - eg $[C_4C_1im][NTf_2]$ -4 °C

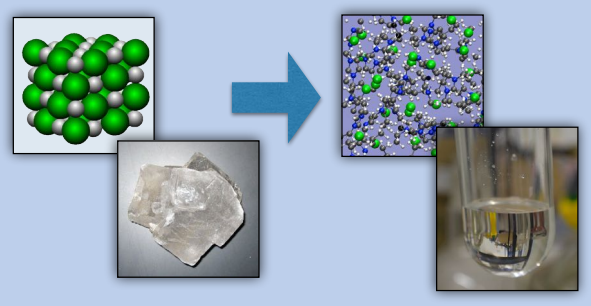
Cations



Anions



ionic solid → **ionic liquid**



Why are Ionic Liquids Interesting?

- **unusual combination physical and chemical properties**
- **significant advantages over other solvents**
- **can be GREEN, environmentally friendly**
- **new liquids, solvents, electrolytes, engineering materials**

substantial industrial, technological and environmental benefits

technological

- ✦ large liquidous range
- ✦ good ionic conductivity
- ✦ wide electrochemical window
- ✦ high thermal stability
- ✦ high energy density

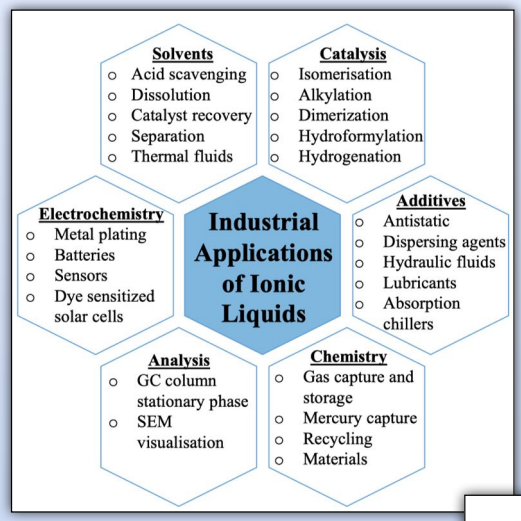
battery / fuel cell electrolytes
fuels / lubricants
industrial electrochemistry

chemical

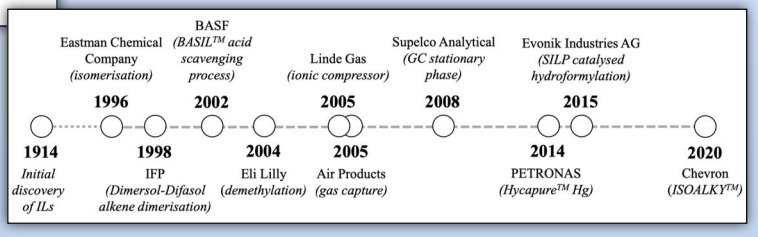
- ✦ hydrophobic/hydrophilic
- ✦ variable miscibility
- ✦ fantastic solvents
- ✦ vanishing vapor pressure
- ✦ task specific

biphasic mixtures for catalysis
recycling of solvents
bio-refining, analytics

Applications have Exploded



100 commerical applications
57 in open literature
19,000 patents (up-to 2019)



Greer, A.J.; Jacquemin, J.; Hardacre, C. Industrial Applications of Ionic Liquids. *Molecules* **2020**, *25*, 5207. https://doi.org/10.3390/molecules25215207

Who is Interested?

Scionic
Shell
Arkema
Airbus
SASOL
Eli Lilly
BASF
BCS
GSK
BP
Merck
Cheveron
Petrochina
AWE
IFP-France
Degussa
Creavix
American Dept Energy
Ciba
Eastman-Kodac
Rio Tinto
DuPont
Texaco/Cheveron

commercial industrial scale processes that employ ionic liquids as catalysts, performance additives, extractants, solvents or liquid supports

oil & gas
energy & bio-fuels
chemicals, paint
pulp & paper, textile
automotive, lubricant
battery & fuel cell
mining, metals
analytical / biochem
pharma, enzyme catalysis

http://cen.acs.org/articles/94/i39/Chevron-embraces-ionic-liquids.html
https://www.chemistryworld.com/news/mercury-grabbing-ionic-liquids-hit-the-gas/8363.article

Who is Interested?

https://cen.acs.org/materials/ionic-liquids/time-ionic-liquids/98/i5

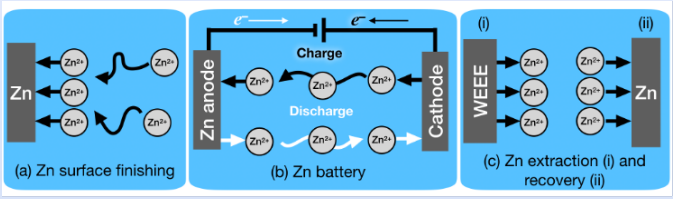
dress made from wood using new Ioncell process, worn by Finnish First Lady

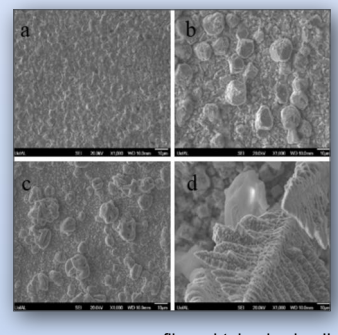
Photo: Vesa Moilanen/Lehtikuva
BBC 19 Dec 2018

- **Ioncell**
  - uses ILs to dissolve cellulose from wood pulp
  - natural polymer is spun into fibers
  - existing process for "viscose": harsh conditions, harsh chemicals
  - IL process is closed-loop, no chemical discharge
  - can use cardboard, discarded cotton textiles, newspaper …
- **Where is IL used in this process?**
  - to dissolve the wood-pulp
  - that is: to break up the H-bonding in the cellulose

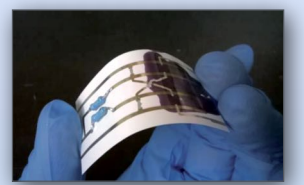
Who is Interested?

- **electrochemical applications**
  - access novel coating morphologies
  - nanoporous/nanostructured metals
  - microelectronics: printing circuts
  - batteries and supercapacitors
  - industrial electrochemistry

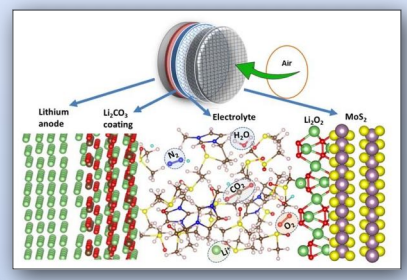




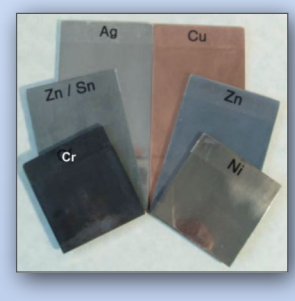
nanoporous copper films obtained using IL
PCCP, 17(22), **2015**, p14702



printed circut using IL
ChemPhysChem, 16(6), **2015**, p1286



Li-oxygen battery
Nature, 555, **2018**, p502

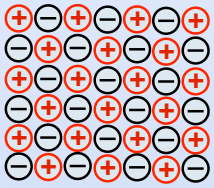


metals deposited on brass using ILs
PCCP, 8(37), **2006**, p4265

Interactions within ILs

- primary interaction is ionic
  - point charges interacting

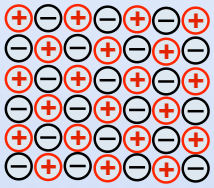
point charges



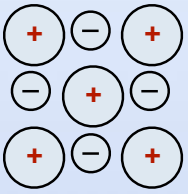
Interactions within ILs

- primary interaction is ionic
  - point charges interacting
  - large ions weaken Coulomb forces
  - change size of ions frustrates packing

point charges

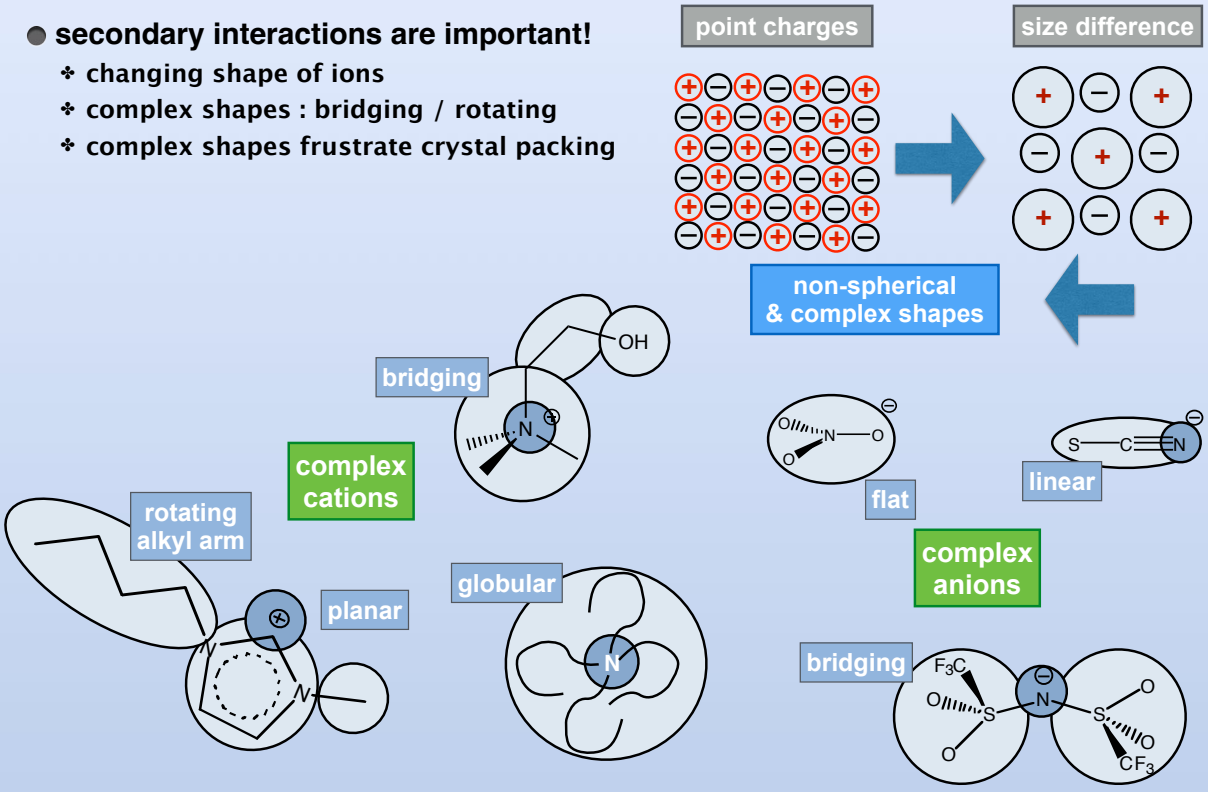


size difference



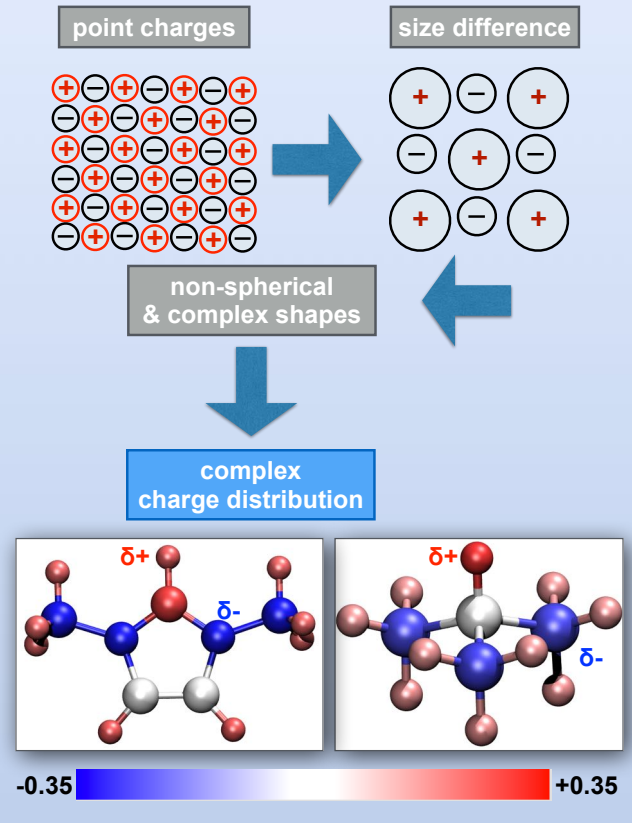
Interactions within ILs

- **secondary interactions are important!**
  - changing shape of ions
  - complex shapes : bridging / rotating
  - complex shapes frustrate crystal packing



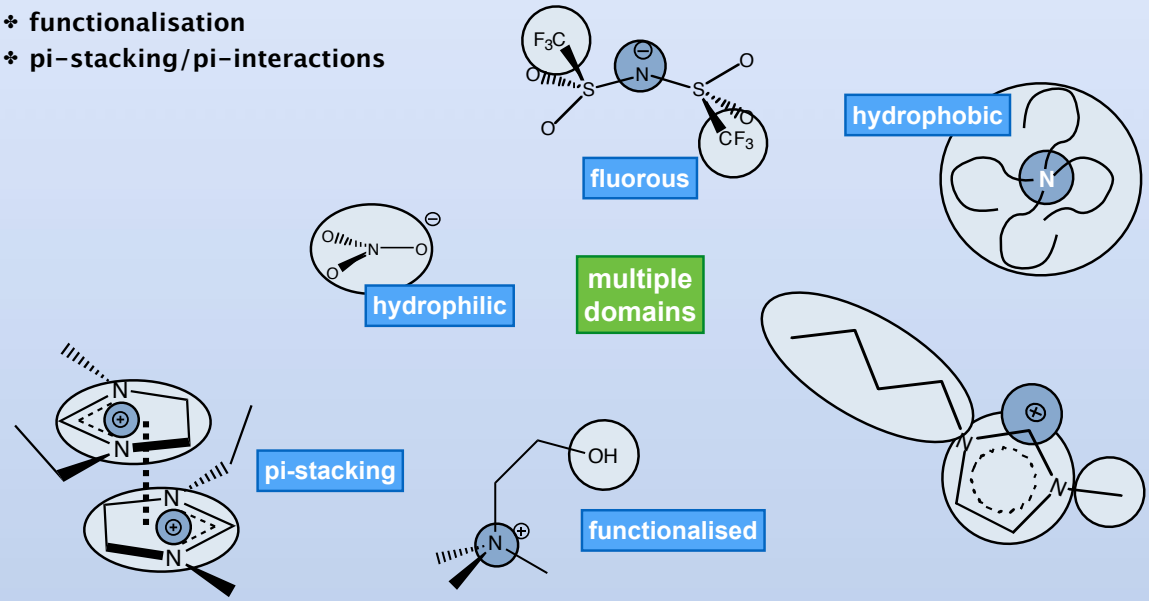
Interactions within ILs

- **secondary interactions are important!**
  - changing shape of ions
  - complex shapes : bridging / rotating
  - complex shapes frustrate crystal packing
  - complex shapes are not "point" charges



Interactions within ILs

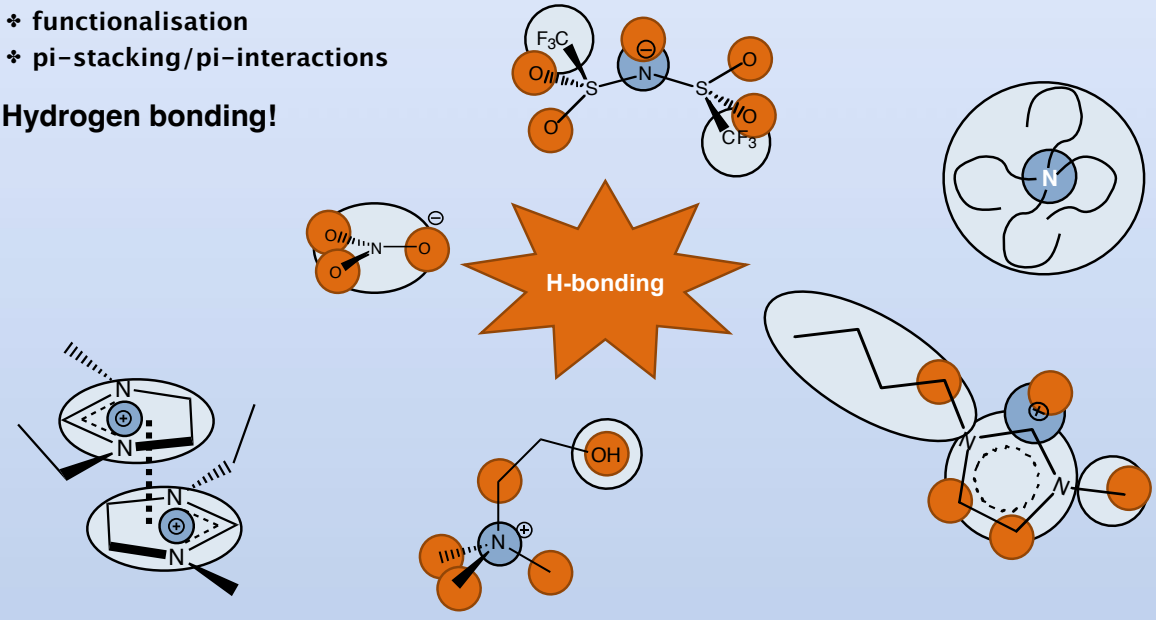
- **secondary interactions are important!**
  - fluorous
  - alkyl tails –hydrophobic
  - hydrophilic anions
  - functionalisation
  - pi–stacking/pi–interactions



Interactions within ILs

- **secondary interactions are important!**
  - fluorous
  - alkyl tails –hydrophobic
  - hydrophilic anions
  - functionalisation
  - pi–stacking/pi–interactions
- **Hydrogen bonding!**

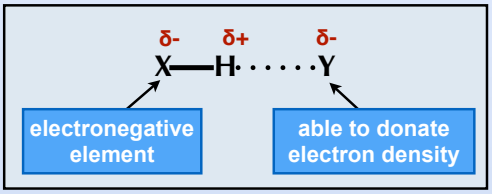
multiple H-bond donor and acceptor sites => complex picture!



P. Hunt, C. Ashworth, R.P. Matthews, *Chem Soc Rev.* **2015**, 44, 1257

Back to Basics: H-Bond Definition

- **OLD definition**
  - predominantly ionic interaction where 2 electronegative atoms share a H-atom



X= O, N
Y= lone pair O, N, halide, S

  - dominance has impeded further development for decades[1]

- **Still not precisely defined**
  - IUPAC updated in 2011[2]
  - set of criteria, not all of which need to be fulfilled
  - experimental (bond distance, angle, pK_a/pK_b, IR, NMR)
  - theoretical (E, G, charge transfer, topological properties of ρ(r))

- **WORKING definition**
  - a mildly polar bond interacts via the H-atom with an area of concentrated electron density

X=O, N, C, S, Se, Si, halogen
Y=lone pair O, N, halide, S, π-bond, aromatic, metal, main group element, multiple bond, carbene

1. T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48.
2. Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. G.; Legon, A. C.; Mennucci, B.; Nesbitt, D. J. *Pure Appl. Chem.* **2011**, *83*, 1637.

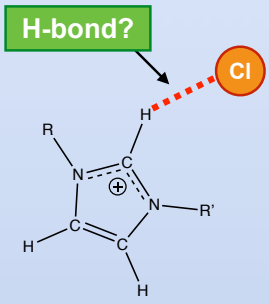
Computational Chemistry

- **Established model**
  - H-bonds form only between N & O species

O-H···N | N-H···O | N-H···N | O-H···O

H-bond

- **Can ILs form H-bonds??**
  - would have to involve C-H "donor"
  - and Cl "acceptor"
  - conventional wisdom says NO



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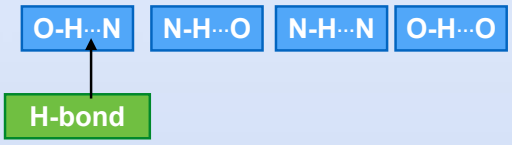
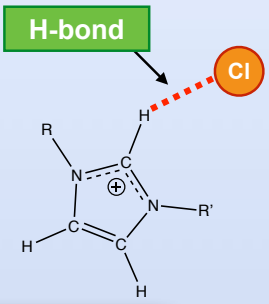
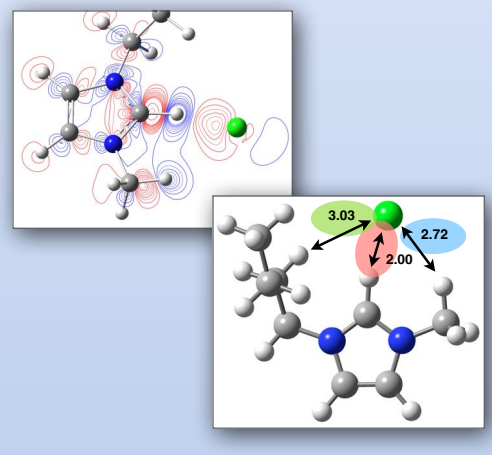


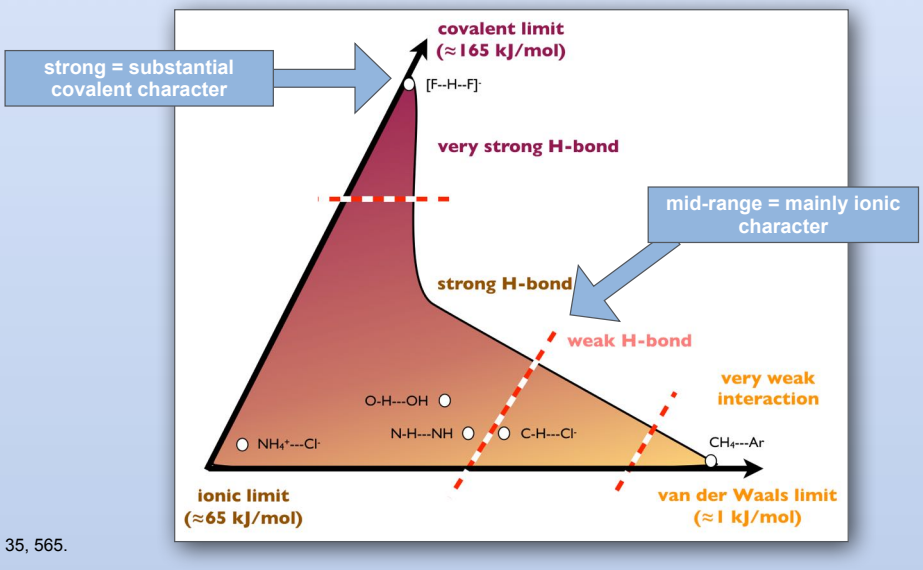
- **Can ILs form H-bonds??**
  - would have to involve C-H "donor"
  - and Cl "acceptor"
  - conventional wisdom says NO
- **We used computational chemistry to prove that**
  - YES ionic liquids can form H-bonds!
  - identified a critical point in the electron density
  - identified H-bonding in structure
  - identified H-bonding in IR vibrations & spectrum





Doubly Ionic H-bond

- **dispersive, ionic and covalent components**
  - variable contributions
  - well summarised in diagram by Desiraju[1]
  - strongest H-bonds have large covalent component
  - weakest H-bonds are essentially van der Waals
  - mid-range H-bonds are primarily ionic with covalent and dispersive contribution



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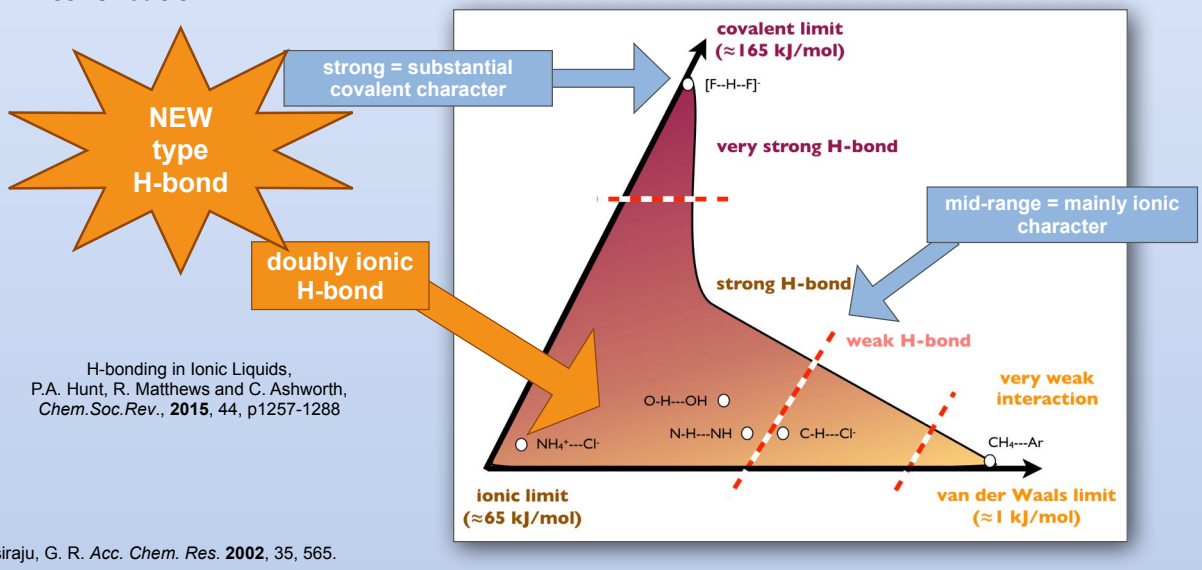

H-bonding in Ionic Liquids,
P.A. Hunt, R. Matthews and C. Ashworth,
Chem.Soc.Rev., **2015**, 44, p1257-1288

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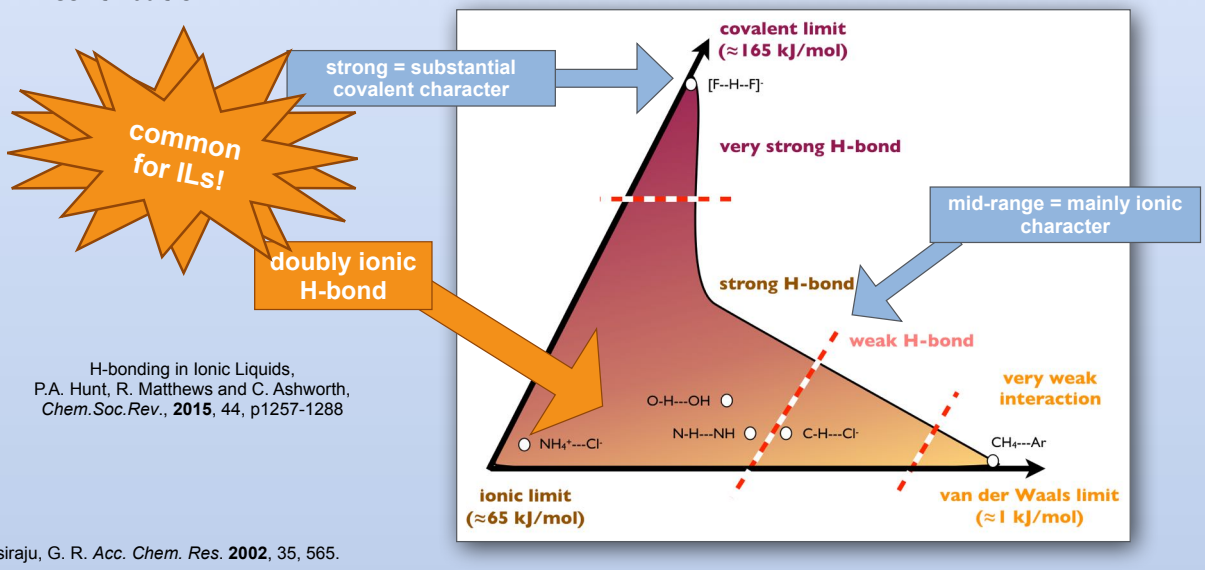

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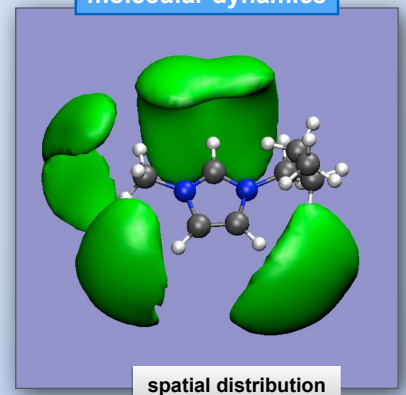
- **Anion**
  - identify 7 stable positions for the anion
  - reality is an extended network
- **Relative energy**
  - gives preferred position
  - dynamics: probability that positions are populated over time

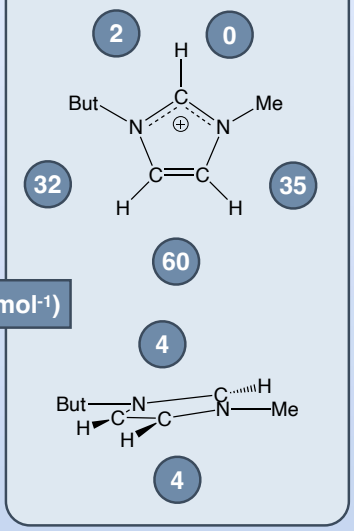
molecular dynamics



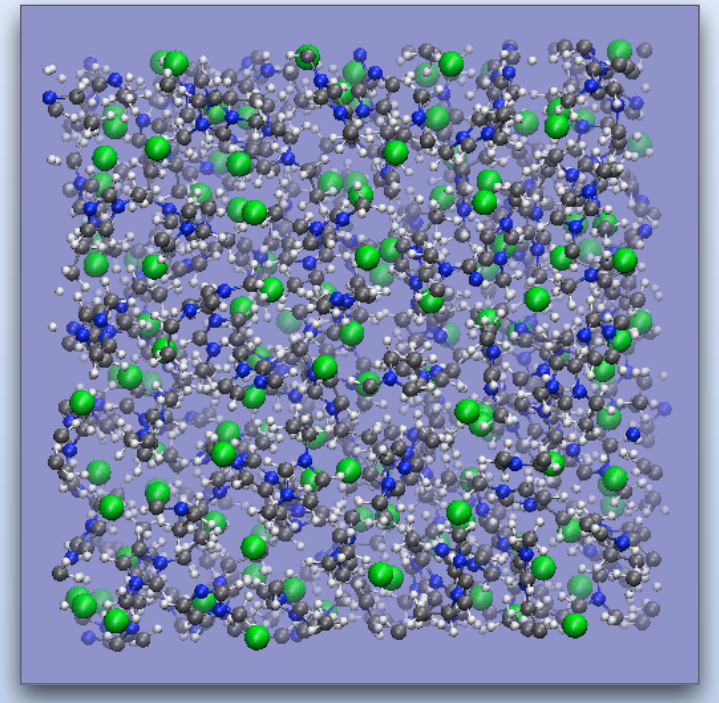
spatial distribution of Cl anions

quantum mechanics

energy ($kJmol^{-1}$)



Basic Interactions within ILs



classical MD

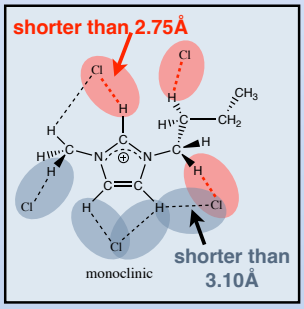
H-Bonding in ILs

- **Distance**
  - used predominantly (because it is easy)
  - use Van der Waals radius
  - "biological" typical O–H···N $r_{H-bond} \approx 2$Å
  - BUT "inorganic" C–H···Cl $r_{H-bond} \approx 3$Å

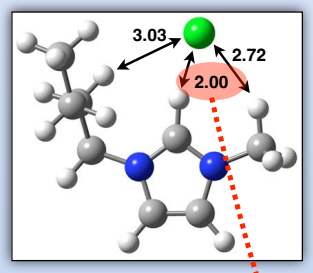
H-bonds are longer (than typical "bio" H-bonds)

Evidence from:

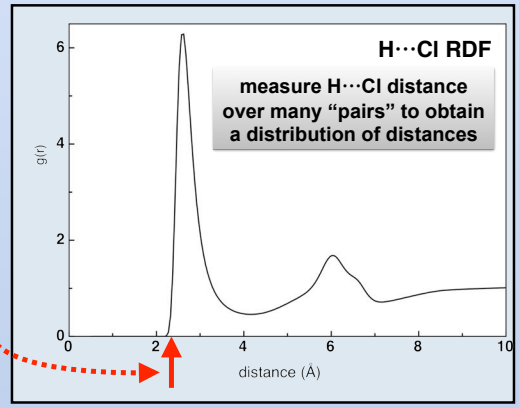
crystal structures



quantum chemistry



molecular dynamics



I. Skarmoutsos, T. Welton and P. A. Hunt, Phys. Chem. Chem. Phys., 2014, 16, 3675–3685.

H-Bond Distance

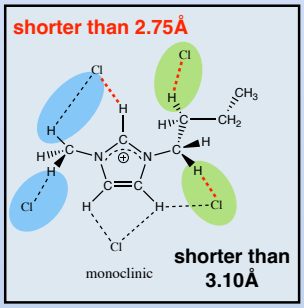
- **Distance**
  - BUT "inorganic" C–H···Cl $r_{H-bond} \approx 3$Å
  - ALSO weaker secondary H–bonds

Me H-bonds | But H-bonds

H-bonds to alkyl chains are important

Evidence from:

crystal structures



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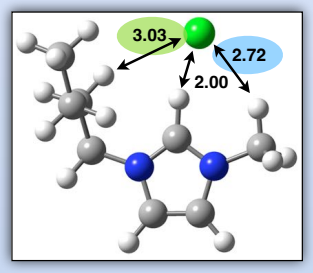

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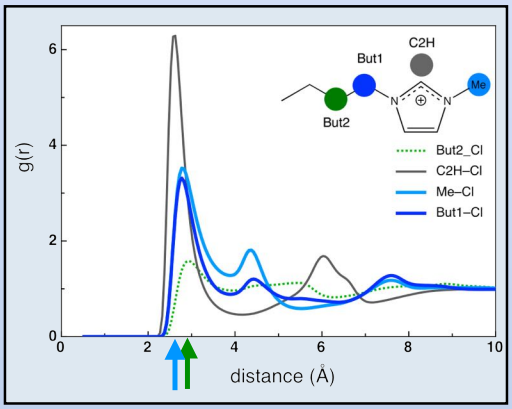

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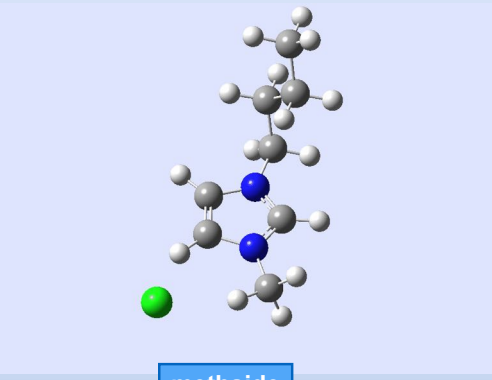
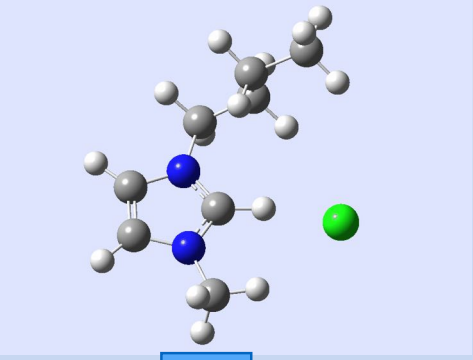
Computational Chemistry

- Computed vibrations & spectrum
  - shows changes
  - evidence of effect of H-bonding

Computed Vibrations



methside



front

Computational Chemistry

- Computed vibrations & spectrum
  - shows changes
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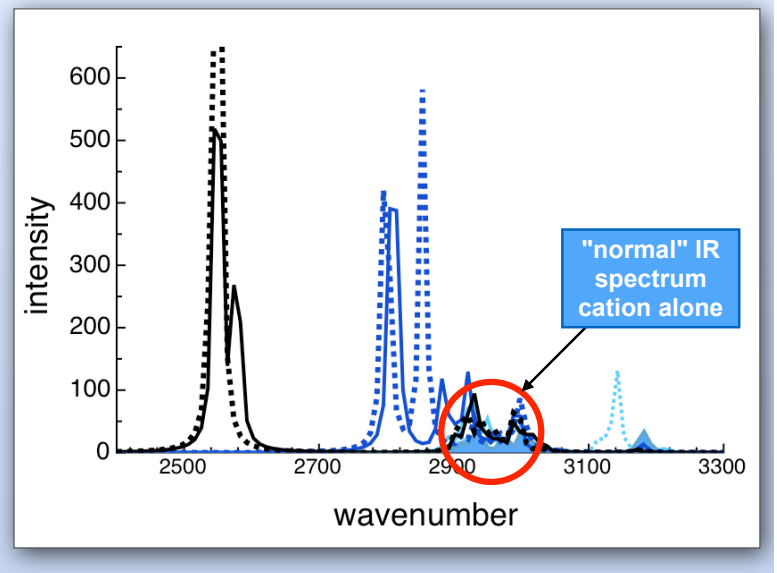
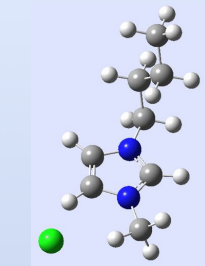
Computed Spectrum



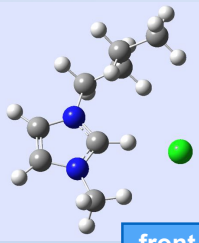
	redshift	intensity
cation	0	29

Computational Chemistry

- **Computed vibrations & spectrum**
  - shows changes
  - evidence of effect of H-bonding



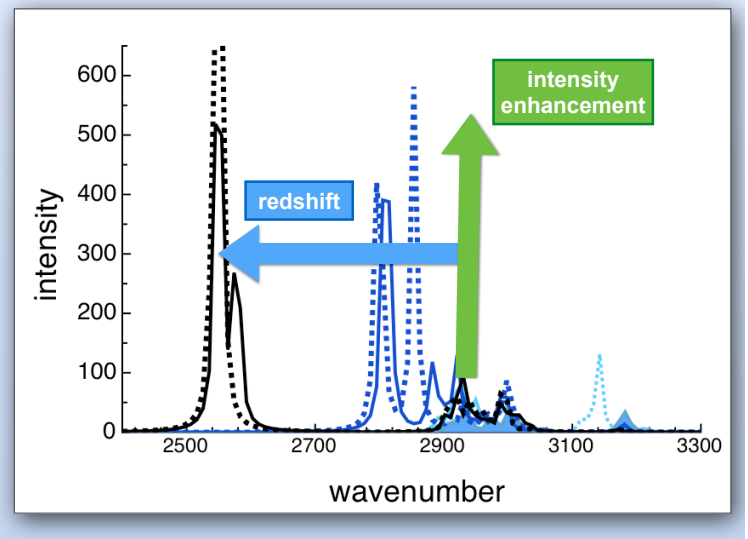
methside



front

	redshift	intensity
cation	0	29
front	-643	1354
butside	-384	664
methside	-338	649

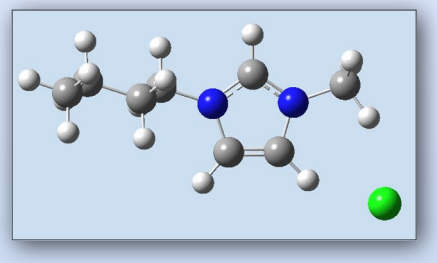
Computed Spectrum

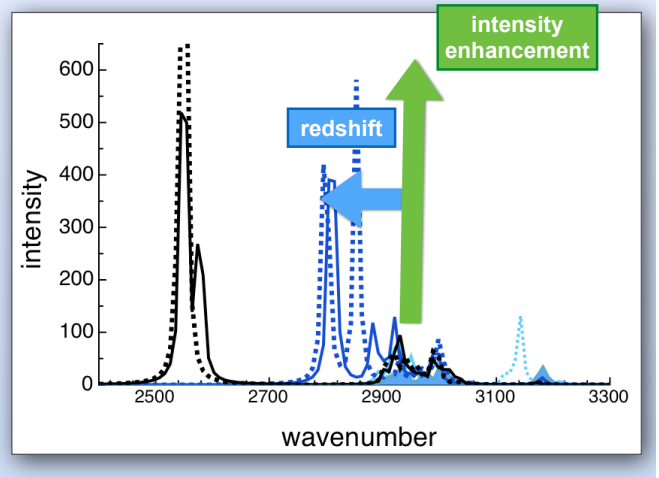


ionic liquids do form H-bonds!

H-Bonding in ILs

- **Red-shift and intensity enhancement**
  - evidence of effect of H-bonding
  - primary (ring) H-bond
  - secondary (alkyl) H-bond





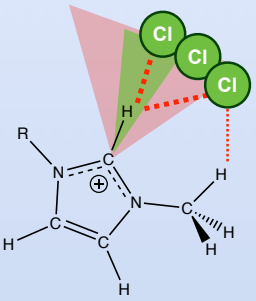
alkyl C^n-H

	C-H···Cl	redshift	intensity
cation	3184	0	0
front	3041	-143	80
butside	2989	-195	343
methside	2960	-224	605

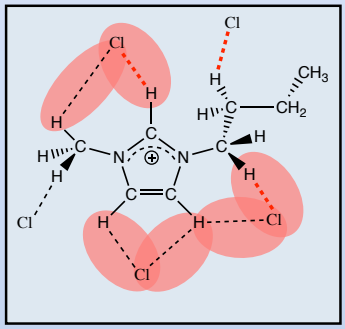
Hydrogen Bond Angle

- **H-Bonds in ILs are not linear!**
  - traditional definition is that H-bonds can only be "linear"
  - BUT original criteria based on water! a highly structured liquid
  - in ILs we have non-linear H-bonding
  - C-H groups in SAME cation pull anion “off-center”

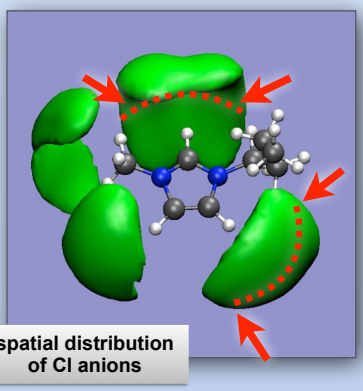
secondary H-bonds are important



crystal structures

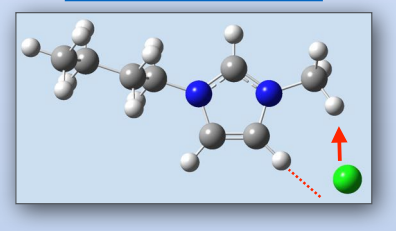


molecular dynamics



spatial distribution of Cl anions

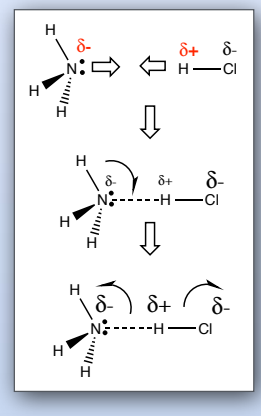
quantum chemistry



“Inside” a Hydrogen Bond

typical exemplar: $H_3N\cdots H\text{-}Cl$

simplistic description



ionic attraction

lone pair donation

closed shell lone pair / Cl-H bond repulsion

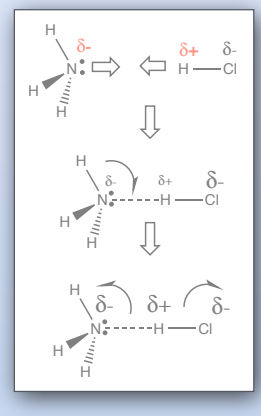
electron density reorganisation plays a key role in forming H-bonds

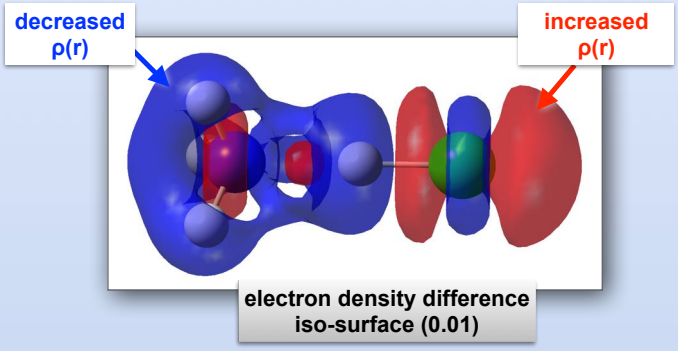
“Inside” a Hydrogen Bond

typical exemplar: $H_3N\cdots H\text{-}Cl$

simplistic description

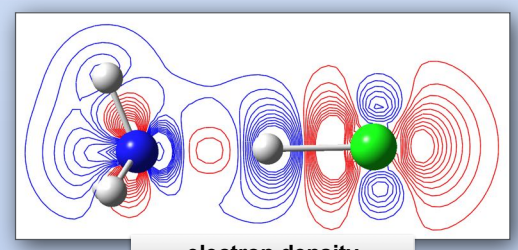
reality more complex!





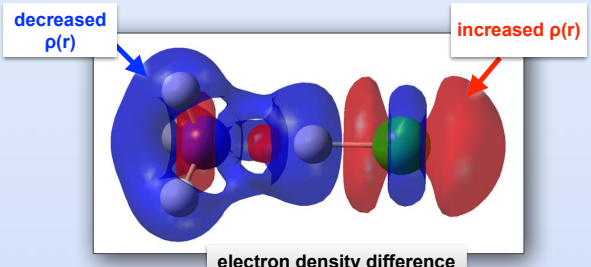
electron density difference iso-surface (0.01)

electron density reorganisation plays a key role in forming H-bonds

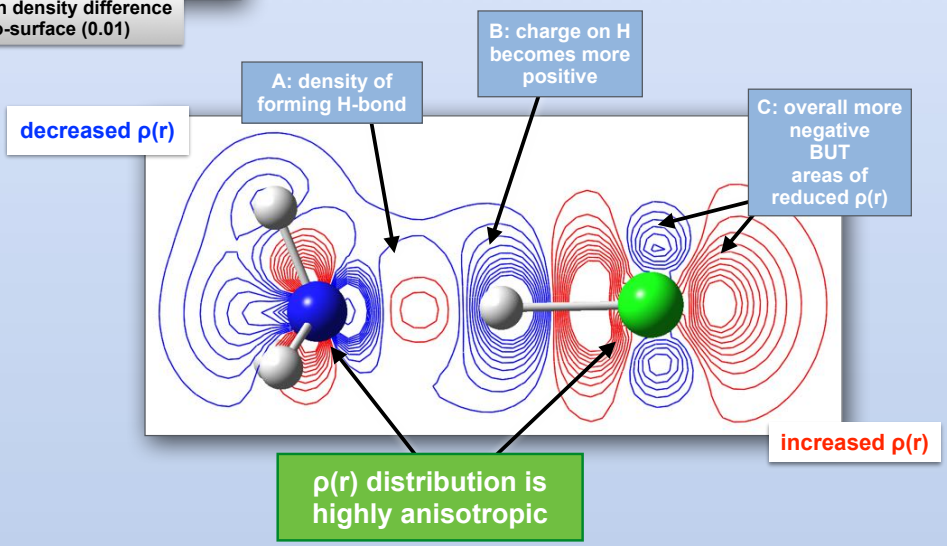


electron density difference contour plot

“Inside” a Hydrogen Bond



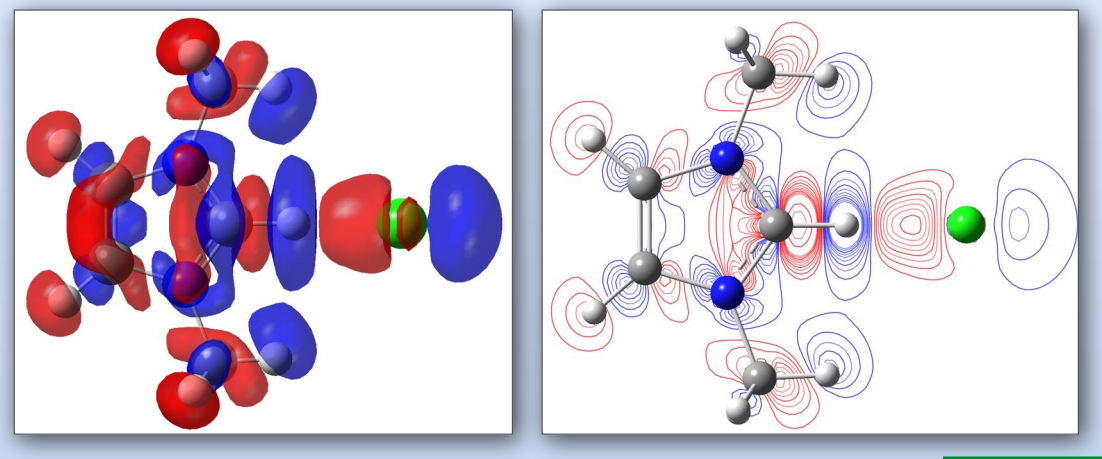
electron density difference iso-surface (0.01)



ρ(r) distribution is highly anisotropic

“Inside” a Hydrogen Bond

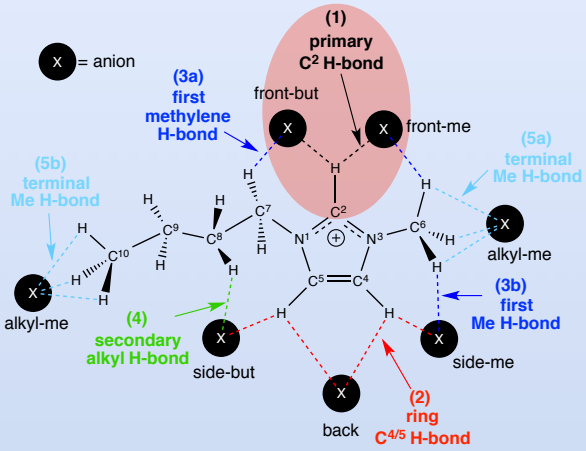
increased ρ(r) | decreased ρ(r)



C_1C_1imCl N-C-H plane

H-Bonding in ILs

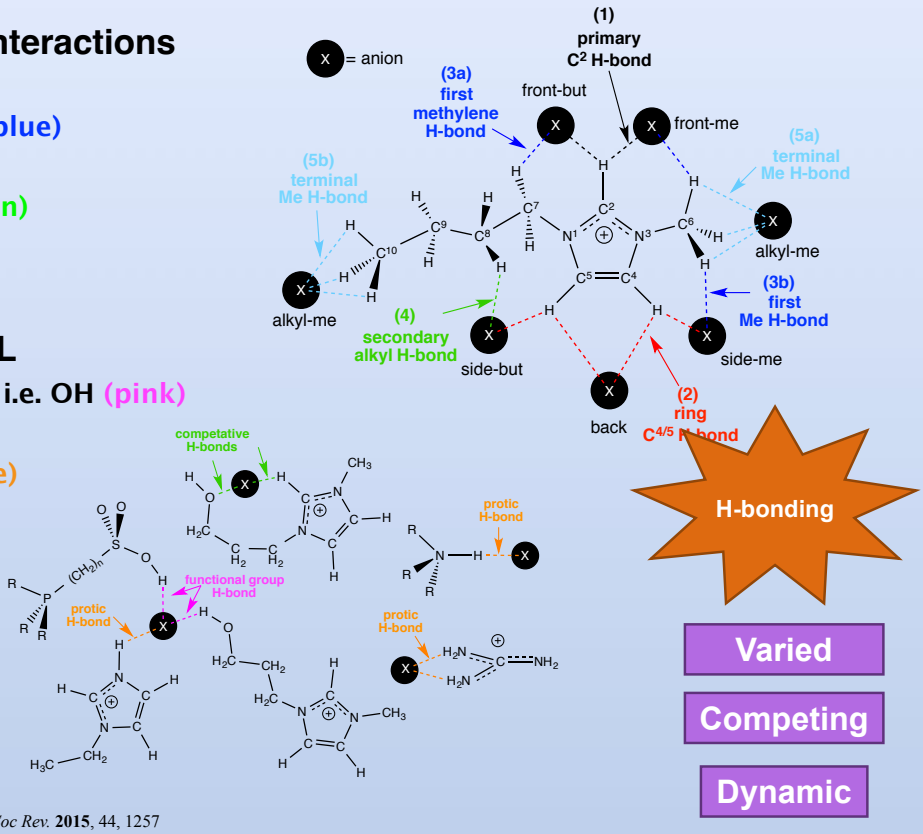
- **Many different interactions**
  - primary
  - first methylene (blue)
  - alkyl-me (cyan)
  - alkyl-chain (green)
  - ring (red)



P. Hunt, C. Ashworth, R.P. Matthews, *Chem Soc Rev.* **2015**, 44, 1257

H-Bonding in ILs

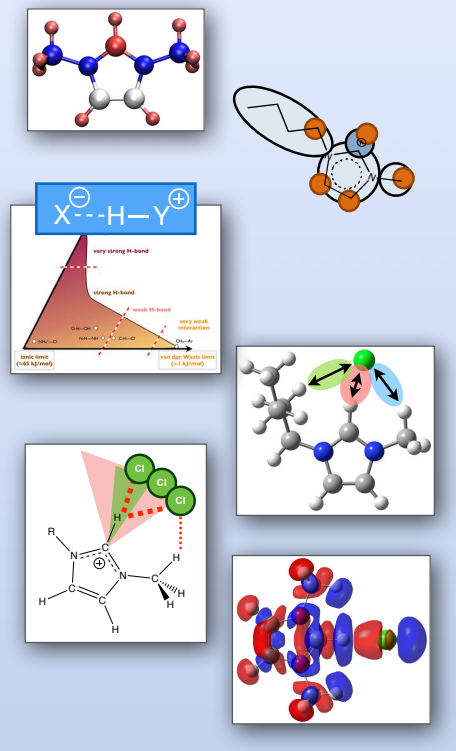
- **Many different interactions**
  - primary
  - first methylene (blue)
  - alkyl-me (cyan)
  - alkyl-chain (green)
  - ring (red)
- **Functionalised IL**
  - functional group i.e. OH (pink)
  - N-H imine
  - protic ILs (orange)



P. Hunt, C. Ashworth, R.P. Matthews, *Chem Soc Rev.* **2015**, 44, 1257

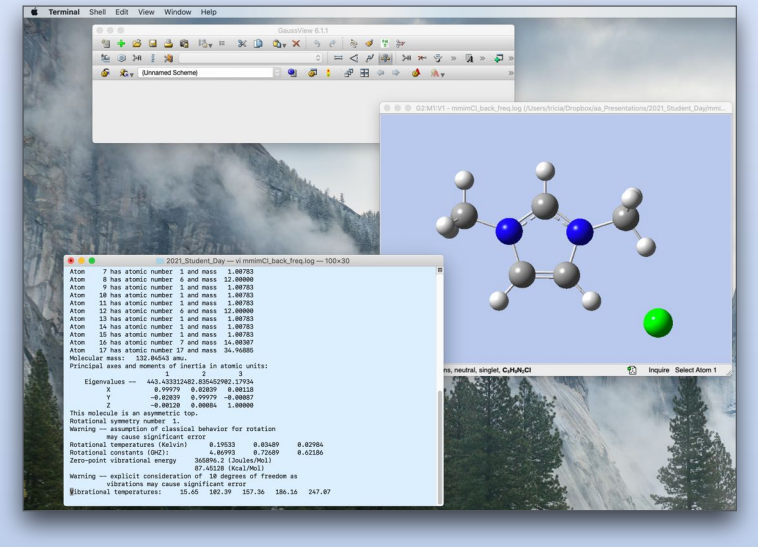
Summary

- IL are not just spherical balls of charge
- Complex chemical species: shape, interactions
- H-bonding is a secondary structuring factor that differentiates ILs
- doubly ionic H-bonds common in ILs!
- "inorganic" H-bonds are longer than "bio H-bonds"
- secondary H-bonds to alkyl chains are important
- numerous H-bonds pull H-bond "off linear"
- ILs form many types of H-bond
- H-bonds involve complex reorganisation of ρ(r)



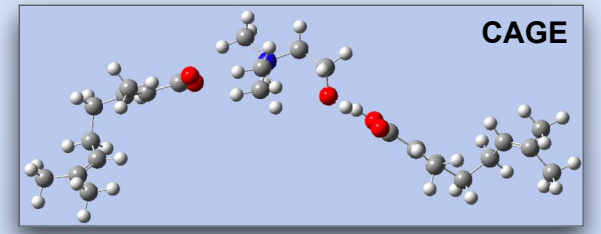
Computational Chemistry

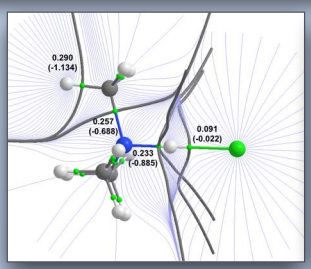
- build a molecule
- “optimise” the molecule into its most stable state
- analyse the results!
  - stability
  - shape (conformation)
  - electronic structure (molecular orbitals, partial charges)
  - vibrations & spectra
- BSc students learn
  - underpinning theory
  - how to "run" programs
  - how to interpret the results

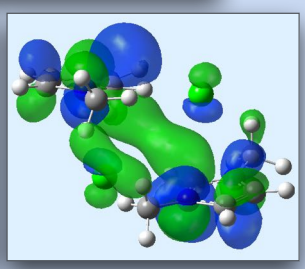


My Group Projects in Chemistry

- developing novel IL fuels for space-craft
- super heavy ionic liquids: F1 Lubricants
- a new IL anti-biotic agent (CAGE)
- new forms of bonding in ILs
- designer solvents as Green replacements in industry



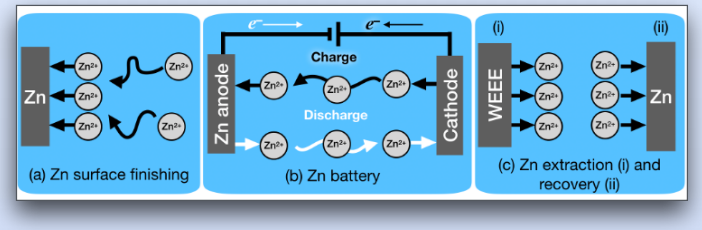


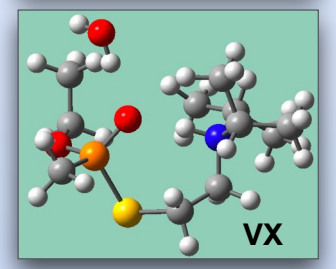


https://en.wikipedia.org/wiki/File:Soyuz_TMA-7_spacecraft2edit1.jpg
Image: Formula One 2012 Rd.2 Malaysian GP, Morio,
https://commons.wikimedia.org/wiki/File:Nico_Rosberg_2012_Malaysia_FP3.jpg
BASF SE, Ludwigshafen site,

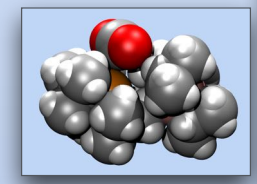
My Group Projects in Chemistry

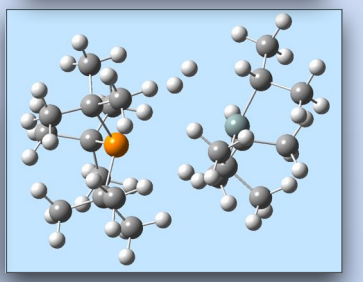
- understanding and developing electrolytes for batteries
- Zn batteries, Zn recycling, Zn plating (galvanising)





- extracting heavy metals from mining waste
- new solvents for extracting metals from electronics
- decomposition of chemical warfare agents
- carbon (CO_2) capture and utilisation



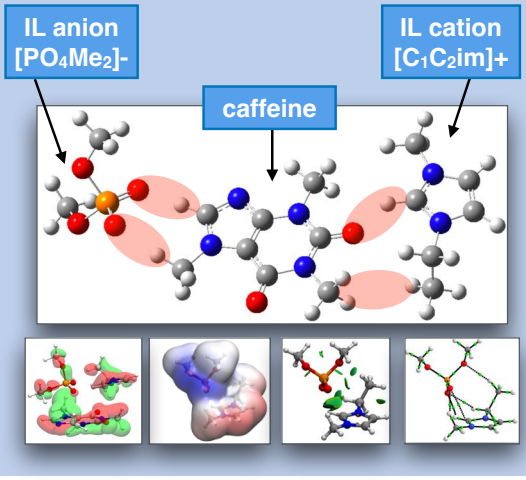


https://commons.wikimedia.org/wiki/File:Rio_tinto_river_CarolStoker_NASA_Ames_Research_Center.jpg

Industrial Projects

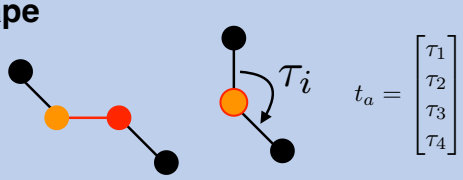
- **DSTL -CWA solvation/extraction/detection, IL based wearable sensor technology**
- **Concept**
  - toxin/drug absorbs into the IL
  - an electrical circuit is formed
  - electrochemical signal (current vs voltage) obtained which is unique to that chemical
  - chemical is identified as present
- **Solubility of toxins: fentanyl**
  - IL are fantastic solvents and can be tailored
  - can ILs be used to absorb the toxin?
  - solubility not as expected -> redirect project
- **Computational chemistry**
  - study chemical interactions between functional groups and IL solvent
  - select non-toxic target: caffine!
  - enables experiment/computational overlap
  - use range methods to investigate types of interaction: ionic, H-bonding, dispersion, anion-π
  - goal: design a better IL for solubility

ionic liquid interacting with caffeine



Genetic Algorithm: Example

- **molecule for which we want to know the shape**
  - 4 key torsion angles
  - that can take on different minima at 0°=0 or 180°=1
- **we form a vector, t_a**
  - each vector represents a different conformer
- **create initial population**
  - randomly setting bits to 0 or 1
- **use QC to evaluate the energy**
  - the more negative the energy the better the conformer
  - keep only the best
- **form a new population**
  - select pairs of "best" vectors
  - mutation is when random bits are inverted eg 0→1
  - cross-over is when random portions of vectors are swapped, formed "children"
- **use QC to evaluate the energy**
  - reduce the population,
  - vectors "compete" to "survive"
  - discard "poor" configurations



$t_1 = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 1 \end{bmatrix}$ $t_2 = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 1 \end{bmatrix}$

$t_1 = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 1 \end{bmatrix}$ mutate 1→0 $t_3 = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$

swap components

$t_1 = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 1 \end{bmatrix}$ $t_2 = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 1 \end{bmatrix}$ $t_4 = \begin{bmatrix} 0 \\ 1 \\ 1 \\ 1 \end{bmatrix}$ $t_5 = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$

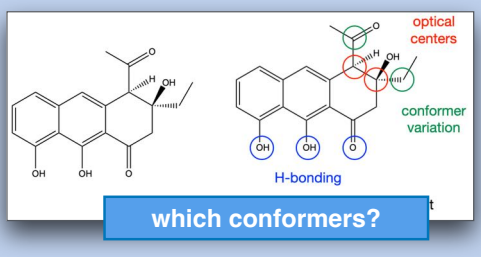
obtain final "optimised" geometry

through random variation

Research Example

- **extracted new natural product from sea sponge =JB10-81B**
- **only have VERY small amount,**
  - not enough to fully characterise
  - have some information on atomic structure (NMR)
  - do have ECD-spectrum

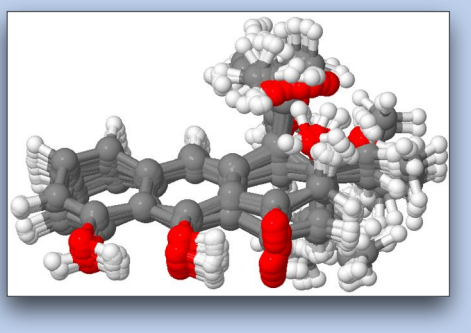
but not exact conformer

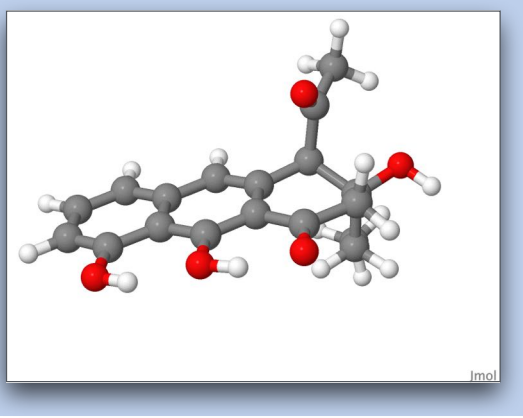


which conformers?

- **run MD and ANN program**
  - generates possible conformers
  - low level QM method to assess energies
  - obtain 52 strucutres, of which 45 are unique

oxygen **carbon** **hydrogen**



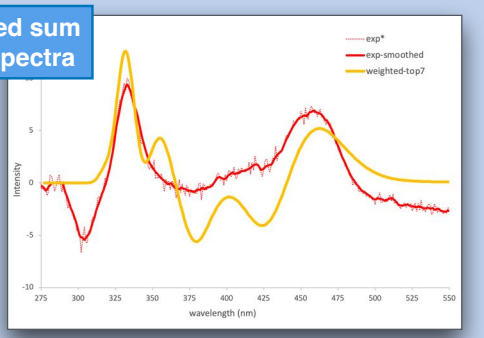


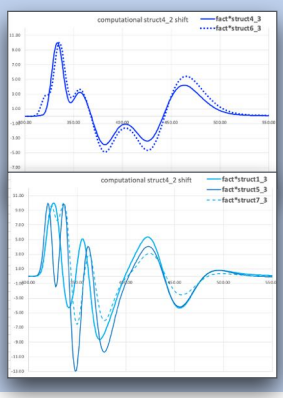
Research Example

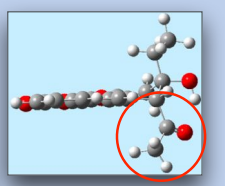
- **Quantum Chemistry**
  - use high level QC on 45 structures
  - python scripting to prepare jobs & extract key information
  - identify top 7 conformers as contributing!
  - compute spectra and combine weighted by probability
  - information "back" from the spectrum
  - find 2 major conformer groupings

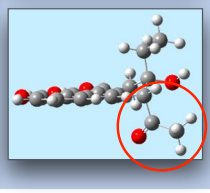
no.	energy kJ/mol	exp(-ΔE$_i$/RT)	compute prob
4	0.00	1.00	0.48
6	2.56	0.36	0.17
1	3.80	0.22	0.10
5	5.77	0.10	0.05
7	6.38	0.08	0.04
11	6.76	0.07	0.03
2	6.80	0.06	0.03
12	7.71	0.04	0.02
14	7.94	0.04	0.02
3	8.43	0.03	0.02
16	8.77	0.03	0.01
8	9.42	0.02	0.01
10	9.42	0.02	0.01

weighted sum top 7 spectra







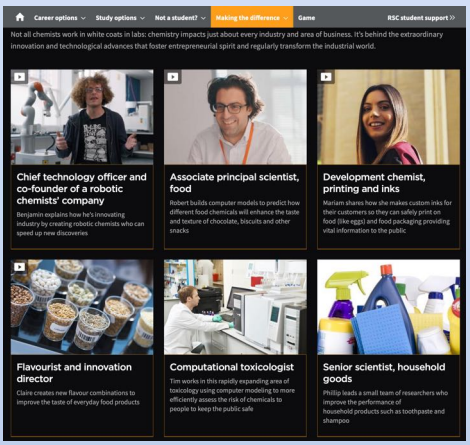


main difference is rotation of ketone

Chemistry

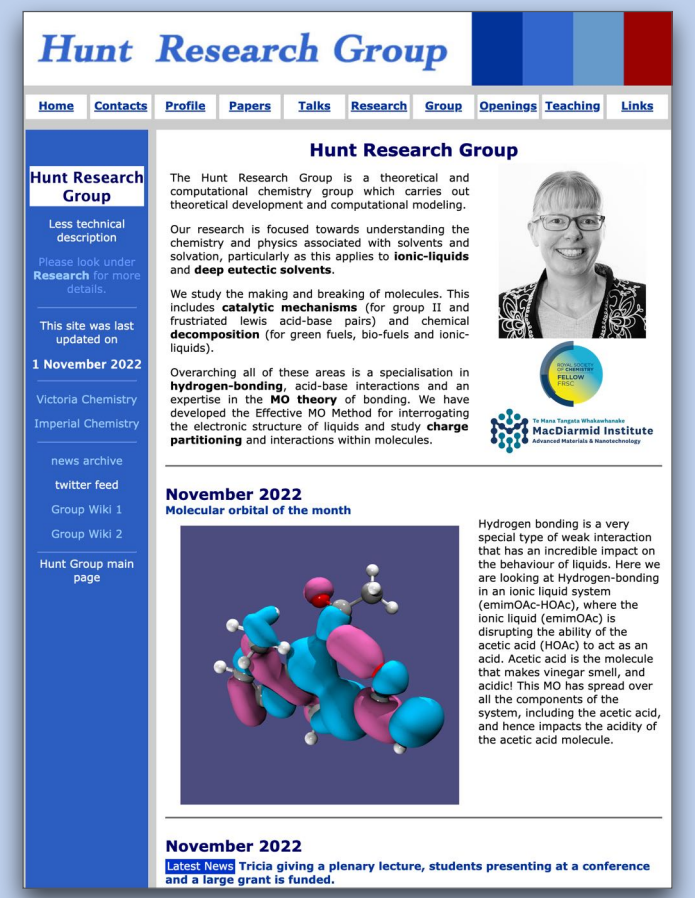
A career in Chemistry ranges from what we touch, wear and use, to developing life-changing medicines or finding solutions for the pressures on energy, food, and water to help us to live more sustainably. Be inspired by chemists who are making the difference!

- **Careers**
  - Environmental chemist
  - Water chemist
  - Atmospheric chemist
  - E scientific publishing
  - Consumer products development
  - Senior scientist, household goods
  - Research innovations manager
  - Radioactive waste consultant
  - Computational toxicologist
  - Computational medicinal chemist
  - Flavourist, innovation director
  - Sustainability manager
  - Project manager
  - Finance manager
  - Astrochemist
  - Development chemist
  - Drug control chemist
  - Analytical technician
  - Forensic toxicologist
  - Marine biogeochemist
  - Smart food team leader
  - Museum scientist
  - Science communicator
  - Policy researcher
  - Sports scientist
  - Medicinal chemist
  - Programmer
  - Patent attorney
  - Investor relations manager
  - Senior picture editor
  - Project leader oil & gas
  - Chief technology officer
  - Policy adviser, government



- **find out more:**
  - Royal Society of Chemistry excellent resources
  - https://edu.rsc.org/future-in-chemistry

The End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twitter feed
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Group Wiki 2
Hunt Group main page
Hunt Research Group
The Hunt Research Group is a theoretical and computational chemistry group which carries out theoretical development and computational modeling.
Our research is focused towards understanding the chemistry and physics associated with solvents and solvation, particularly as this applies to ionic-liquids and deep eutectic solvents.
We study the making and breaking of molecules. This includes catalytic mechanisms (for group II and frustriated lewis acid-base pairs) and chemical decomposition (for green fuels, bio-fuels and ionic-liquids).
Overarching all of these areas is a specialisation in hydrogen-bonding, acid-base interactions and an expertise in the MO theory of bonding. We have developed the Effective MO Method for interrogating the electronic structure of liquids and study charge partitioning and interactions within molecules.
Te Mana Tangata Whakawhanake
MacDiarmid Institute
Advanced Materials & Nanotechnology
November 2022
Molecular orbital of the month
Hydrogen bonding is a very special type of weak interaction that has an incredible impact on the behaviour of liquids. Here we are looking at Hydrogen-bonding in an ionic liquid system (emimOAc-HOAc), where the ionic liquid (emimOAc) is disrupting the ability of the acetic acid (HOAc) to act as an acid. Acetic acid is the molecule that makes vinegar smell, and acidic! This MO has spread over all the components of the system, including the acetic acid, and hence impacts the acidity of the acetic acid molecule.
November 2022
Latest News Tricia giving a plenary lecture, students presenting at a conference and a large grant is funded.