Structure and Dynamics of Hydrogen-Bonded Systems

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The Evolution of Hydrogen Bonds in Molecular Materials under Changing External Conditions by Neutron Diffraction and Complementary Methods

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Structure and Dynamics of Hydrogen Bonded Systems, ICTP Trieste, October 2009
The Problem

- Even Excellent experiments can lead to ambiguous interpretation
- We use multi-condition X-ray and neutron diffraction (usually single crystal), including high resolution X-ray
- But we can still have ambiguities

Schmidtmann et al, CrystEngComm, 2007, 9, 743

- We also constrain our systems to be in the solid state
- Can modern computational chemistry methods help us to understand better our experiments?
One Concept: Evolving Molecules in the Hall of Mirrors

Structural Evolution
• Materials whose structure or properties change with external variables

Materials
• Molecules or molecular complexes with “tuneable” atoms – often protons

Our “Laboratory”
• We work in the solid-state – periodic crystalline arrays – The Hall of Mirrors

Techniques
• Crystallisation – self-assembly in the solid-state
• Variable condition diffraction – X & n
• Solid-state quantum chemical calculations
Pushing the Limits of Diffraction Techniques

- **X-ray single crystal diffraction**
  Strong focus on variable temperature for examining evolving structures

- **Neutron Single crystal diffraction**
  Multiple condition, shorter data collection times

- **High throughput X-ray diffraction**
  Powder and single crystal

- **High throughput neutron single crystal**
  Exploiting new instrumentation

- **Neutron powder diffraction**
  Just becoming possible for these materials
Motifs with Predictable (and tuneable?) HB Properties?

- Short, strong HB – Transfer, Migration
- Proton sponges – Proton Transfer
- COOH dimers – Disorder
- “bifurcated” motifs
An old favourite* - proton migration in urea-phosphoric acid

* But still not fully understood!

Wilson & Morrison,

Computational Chemistry of the short HB
Neutron, 15K  
O-H, 1.158Å  O...O, 2.41Å  H...O, 1.267Å
Isolated molecule  
O-H, 1.004Å  O...O, 2.65Å  H...O, 1.604Å
Plane-wave DFT  
O-H, 1.105Å  O...O, 2.42Å  H...O, 1.329Å

VT neutron diffraction
Raise the stakes, raise the Temperature (MD-DFT)

Morrison et al, JACS, 2005, 127, 4042
Joint X-n Analysis of proton/electron density evolution in hydrogen bonds

Migration can also be followed by XRD - and additional information obtained about the nature of the electron density in the HB.

Parkin, Harte, Goeta & Wilson
Designing Molecular Complexes for proton migration

Pentachlorophenol: Methylpyridines

Steiner, Majerz & Wilson, Chem Comm, 2000, 1231
Angewandte Chemie, 2001, 40, 2651

Position of proton in the short N-H…O HB tuned by chemistry and by temperature
First observed centred N-H-O HB obtained by thermal tuning at 95K

Steiner, Majerz & Wilson, Angewandte Chemie, 2001, 40, 2651
From proton disorder to proton migration?

A continuum in the hydrogen bond of a proton sponge complex

1,8-bis(dimethylamino)naphthalene and 4,5-dichlorophthalic acid
DMAN:DCP – only X-ray data so far – ambiguous!

Tempting, but unproven and unsubstantiated – VT neutron collected

Disorder/transfer?

and “migration”?
Picric acid forms charge transfer complexes with many organic compounds, some of which also exhibit thermochromism.

2-iodoanilinium picrate: colour change at ~320K

Only obvious structural change on thermochromic PT is an apparent H migration...
Look for disorder, find migration – isonicotinamidium formate

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Type</th>
<th>A-H (Å)</th>
<th>H…D (Å)</th>
<th>A…H…D (°)</th>
<th>angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40K</td>
<td>N1-H...O1</td>
<td>1.213</td>
<td>1.344</td>
<td>2.555</td>
<td>175.35</td>
</tr>
<tr>
<td>50K</td>
<td>N41-H...O2</td>
<td>1.011</td>
<td>1.845</td>
<td>2.831</td>
<td>164.08</td>
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<td>100K</td>
<td>N1-H...O1</td>
<td>1.264</td>
<td>1.298</td>
<td>2.551</td>
<td>175.21</td>
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<tr>
<td>150K</td>
<td>N41-H...O2</td>
<td>1.029</td>
<td>1.841</td>
<td>2.842</td>
<td>163.53</td>
</tr>
<tr>
<td>200K</td>
<td>N41-H...O4</td>
<td>1.033</td>
<td>1.887</td>
<td>2.919</td>
<td>175.07</td>
</tr>
</tbody>
</table>

Isonicotinamidium Formate
Potassium hydrogen maleate – centred HB

• COOH dimers; carboxylic acids

• Bifurcated HB
• HB-matching – Etter, Aakeroy
• [Short, strong HB]
• Metal-mediated
• Supramolecular synthons
Designing Molecular Complexes for HB proton transfer

Chloranilic acid:Methylpyridines (lutidines, picolines)

- Supramolecular motifs
  (different in 1:1 & 2:1 complexes)

Adam et al, CrystEngComm, in press
Chloranilic acid:n.Methylpyridine complexes

Hydrogen bonded hydrogen almost always transferred – charge/resonance assisted HB

Adam et al,
CrystEngComm, in press
Designing Molecular Complexes: pKa matching?

Pentachlorophenol:Lutidine

- pKa matching to “predict proton transfer?
- Pattern difficult to discern in solid-state

Schmidtmann & Wilson
CrystEngComm, 2008, 10, 177
Tuning proton disorder

- 4-dimethylaminobenzoic acid (4DMBA)

- Proton disorder in native structure

Parkin et al
Cryst Growth Design
2007, 7, 531
4-dimethylaminobenzoic acid (4DMBA)

Different disorder patterns in molecular complexes 4DMBA-4DMBA:35DNB-35DNB

with 3,5-dinitrobenzoic acid
4DMBA NO disorder

BUT the 3,5-dinitrobenzoic acid DOES show disorder
Asymmetry only introduced in the solid state - in the local crystalline environment

H disorder/transfer in solid-state HB dimers
Modelling Disordered Protons: from T dependence to $\Delta E$

Modelling of HB H atom in carboxylic acid dimers clearly breaks down at higher T—second (disordered, tautomeric) site

Clearly a split site
Site occupancies can be modelled in simple Van’t Hoff model and Energy Asymmetry extracted. This allows us to establish a Tautomerism energy scale in HB carboxylic acid dimers. Experimentally, and...

VT XRD: 2,4,6-trimethylbenzoic acid

Wilson & Goeta
Angew Chemie, 2004, 43, 2095

tmba, $\Delta H = -2.5(3)$ kJ.mol$^{-1}$
Computing the Asymmetry in H-transfer tautomerisation

Can solid state, periodic computation do the same?

Benzoic Acid
Computed asymmetry = 0.46 kJ.mol\(^{-1}\)
cf NMR 0.4-0.65; neutron diffraction 0.50 kJ.mol\(^{-1}\)

Middlemiss et al, CrystEngComm, 2007, 9, 777
A second example of promising agreement

\( p\)-chloro-benzoic acid
Computed asymmetry = 1.15 kJ.mol\(^{-1}\)
\( cf \) NMR 1.5;
neutron diffraction 1.60 kJ.mol\(^{-1}\)

Middlemiss et al, CrystEngComm, 2007, 9, 777
Co-operative hydrogen bonding?

Relative Energies of tautomeric forms

Form I
0 kJ.mol⁻¹

Form II
~+50 kJ.mol⁻¹

Form III
+8.6 kJ.mol⁻¹

Parkin et al, Acta Cryst, 2007, B63, 303
Neutron diffraction supports the computational conclusion that only one tautomer should be expected in these T ranges.

Potential tautomerism / cooperative hydrogen bonding in dihydroxybenzoic acids

Adam et al, New J Chem, in press
Neutron and Theoretical Deformation

Adam et al, New J Chem, in press
An energy scale for polymorphism

Polymorphism in molecular complexes of isonicotinamide and oxalic acid

“cis”

“trans”

Serious ambiguity in “good” SX X-ray


CRystal03
B3PW91, 6-31G**
Energy difference, Form I favoured over form II by 3.41 kJ.mol⁻¹
Conclusions – Next Steps

• Modern computational methods can underpin our careful multi-condition X-ray, neutron, etc experiments
• Interrogating both experiment and calculations allows questions not accessible by each alone to be asked

So… it’s all solved - No
• Still must benchmark any models through reproducing experimental findings
• Still “semi-empirical” choice of theoretical method, functional, etc
• Some answers still “wrong”, some models inconsistent between good theoretical methods
• Eventual aim – towards prediction of property in the molecular solid-state from structure – proton transfer, conduction, optical activity, colour, etc.
The Team

The Glasgow Group
Martin Adam, Suzanne Harte, Lorretta Lawton, Alan Martin, Craig Martin, Derek Middlemiss, Andy O’Neill, Andy Parkin, Marc Schmidtmann, Lynne Thomas, Craig Wales and the rest!

Visiting students (school, undergraduate)
Adam Jibson, Jennifer Kennedy, Bobby McTaggart, Caitlin Newlands

And many others
Colleagues in Glasgow, U. Western Australia, Natural History Museum, CCDC, CPOSS, Edinburgh, Bradford, Durham, TU Munich, Wroclaw, Warsaw, etc

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Ferromagnetism and spin transitions in Prussian Blue

Previous ferromagnetic coupling model based on $J_2$, ignores $J_1$

Middlemiss & Wilson, Phys Rev B, 2008, 77, 155129
Calculation of spin densities

CRYSTAL03

Hybrid functionals

\[ f^{xc} = \frac{100 - F_0}{100} \left( f_{\text{LSDA}}^{xc} + 0.9 \Delta f_{\text{B88}}^{xc} \right) + \frac{F_0}{100} f_{\text{UHF}}^{xc} + 0.81 f_{\text{LYP}}^{xc} + 0.19 f_{\text{VWN}}^{xc} \]

Varying HF content
– vary \( F_0 \) from 30 to 100%

Middlemiss & Wilson, Phys Rev B, 2008, 77, 155129
Critical Temperatures and Coupling Constants

Table VII. The variation with lattice constant, $a_0$ (Å), in the FM band gap, $\Delta E_g$ (eV), exchange interaction strengths, $J_1$ and $J_2$ (K), ratio $x = J_1/J_2$, and estimated critical temperature, $T_C$ (K), in PB at $F_0 = 35\%$.

<table>
<thead>
<tr>
<th>$a_0$</th>
<th>State</th>
<th>$\Delta E_g$</th>
<th>$J_1$</th>
<th>$J_2$</th>
<th>$x$</th>
<th>$T_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.35</td>
<td>FM</td>
<td>3.823</td>
<td>0.1980</td>
<td>0.1045</td>
<td>1.89</td>
<td>5.28</td>
</tr>
<tr>
<td>10.28</td>
<td>FM</td>
<td>3.870</td>
<td>0.2241</td>
<td>0.1190</td>
<td>1.88</td>
<td>5.98</td>
</tr>
<tr>
<td>10.20</td>
<td>FM</td>
<td>3.951</td>
<td>0.2566</td>
<td>0.1342</td>
<td>1.91</td>
<td>6.83</td>
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<tr>
<td>10.13</td>
<td>FM</td>
<td>4.037</td>
<td>0.2853</td>
<td>0.1509</td>
<td>1.89</td>
<td>7.61</td>
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<tr>
<td>10.06</td>
<td>FM</td>
<td>4.158</td>
<td>0.3169</td>
<td>0.1671</td>
<td>1.90</td>
<td>8.45</td>
</tr>
</tbody>
</table>

$J_1$, more significant contribution to FM coupling than $J_2$. 

Middlemiss & Wilson, Phys Rev B, 2008, 77, 155129
Hydrogen-bonded copper pyrazine coordination polymer

$[\text{Cu}^{II}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$ (pyz = pyrazine)