What we can learn about fast chemical processes
from slow diffraction experiments

*Faraday Discuss.* 122 (2002) 41

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T. Lüthi Nyffeler  
A. Raselli  
K. W. Törnroos  

H.B. Bürgi
Universität Bern, Switzerland

Universität Heidelberg, July 2, 2003
Energy profiles, time scales and observation

Process: Vibrations | Reactions
---|---
Time scale: fs, individual microscopic events rare
'Slow' mean square rate constants
Observation amplitudes events/sec
Inferring features of energy surfaces from crystal structure data

**Single-minimum process** (Vibrations)
- Mapping deformation patterns of molecular vibrations (SS, from structural data bases)
- Ground state structures (S)
- Estimating energy differences between different molecular states from occupancy (T)

**Multiple-minimum process** (Chemical reactions)
- Mapping reaction coordinates (SS, from structural data bases)
- Structure-reactivity correlations (E)
- Resolving structures of different molecular states (S), (e.g. ground and excited state)
- Estimating energy differences between different molecular states from occupancy (T)
- Bond breaking-bond making reactions, conformational interconversions, etc.

**Single structures (S) or Series of Structures (SS)** (The same molecular fragment in different environments)
- Structures as a function of temperature (T).
- Structures and activation energies (E).
Vibrations of molecular zeolite fragments

Least-squares superposition of Si-atoms from 40 $\text{Si}_{10}\text{O}_{15}$ fragments observed in three structures ($\text{H, CH}_3, \text{C}_6\text{H}_5$) and Rms displacements of $\text{Si}_{10}\text{O}_{15}$-fragment after subtraction of translation and libration motion of Si-atoms.

Conclusion: static displacements from symmetric reference structure give clear indications of low frequency motion.

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Intramolecular vibrations from mean square displacements

<table>
<thead>
<tr>
<th>Mode</th>
<th>100 K</th>
<th>10 K*</th>
<th>IR/Raman†</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$ (cm$^{-1}$)</td>
<td>49</td>
<td>(49)</td>
<td>57</td>
</tr>
<tr>
<td>$E_g$ (cm$^{-1}$)</td>
<td>75</td>
<td>(75)</td>
<td>84</td>
</tr>
<tr>
<td>$T_u$ (cm$^{-1}$)</td>
<td>62</td>
<td>(62)</td>
<td>68</td>
</tr>
<tr>
<td>$L(T_g)$ (cm$^{-1}$)</td>
<td>47,47,48</td>
<td>45,45,37</td>
<td>—</td>
</tr>
<tr>
<td>$T(T_u)$ (cm$^{-1}$)</td>
<td>32,32,32</td>
<td>19,19,17</td>
<td>—</td>
</tr>
<tr>
<td>$f$(Si—O—Si) (mdyn Å)</td>
<td>0.077</td>
<td></td>
<td>0.091</td>
</tr>
<tr>
<td>$f$ (SiO–SiO) (mdyn Å)</td>
<td>0.0034</td>
<td></td>
<td>0.0040</td>
</tr>
</tbody>
</table>

After accounting for translational and librational motion

Concerning the structure of benzene

G.A. Jeffrey, J.R. Ruble, R.K. Mullan, J.A. Pople,  


**15 K**  
$U_{\text{iso}}(C) \sim 0.008 \, \text{Å}^2$  
(shown: * 2.5)

Centrosymmetric superposition of two cyclo-hexatriene molecules?  
(1.35 and 1.45 Å)

**123 K**  
$U_{\text{iso}}(C) \sim 0.023 \, \text{Å}^2$  
(shown: * 2.5)

Rms displacements $U$ of C$_6$D$_6$ from neutron diffraction
Temperature dependence of mean square amplitudes

\[ \langle u^2 \rangle = k_B T / (\omega^2 \mu) + \varepsilon \]

- high T

\[ \langle u^2 \rangle = h / (2\omega \mu) \coth (h\omega / 2k_B T) + \varepsilon \]

- general

\[ \langle u^2 \rangle = h / (2\omega \mu) + \varepsilon \]

- low T

Harmonic oscillator only


Temperature dependence of rms displacements
(=atomic displacement parameters, ADPs)

Vibrations of a molecule in its crystal field

$$\sum^x(T) = A \ast g \ast V \ast \delta(1/\omega, T) \ast V' \ast g' \ast A' + \varepsilon^x$$

ADPs (blue) determine parameters of model (red)

ADPs, determined experimentally at several temperatures

Low frequency, soft vibrations ($\omega$), e.g. librations, translations and deformations ($V$)

Intramolecular, hard vibrations (~temperature independent), and disorder ($\varepsilon$)

Results for Benzene, C₆D₆

15 K
U_{iso}(C) \sim 0.008 \text{ Å}^2
(shown: *2.5)

\varepsilon_C \sim 0.0007 \text{ Å}^2
zero-point motion or disorder?
(shown: *2.5)

(ADP_{obs} – ADP_{calc})^{1/2}
av \langle \text{diff} \rangle \sim 0.0002 \text{ Å}^2
(shown: *2.5*5)

Zero point motion from neutron diffraction and a benchmark force field (*10^4 \text{ Å}^2)

<table>
<thead>
<tr>
<th></th>
<th>C_{(bond)}</th>
<th>C_{(ip)}</th>
<th>C_{(oop)}</th>
<th>D_{(bond)}</th>
<th>D_{(ip)}</th>
<th>D_{(oop)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffraction</td>
<td>14(1)</td>
<td>7(1)</td>
<td>15(1)</td>
<td>52(1)</td>
<td>83(1)</td>
<td>110(2)</td>
</tr>
<tr>
<td>Force Field</td>
<td>13</td>
<td>8</td>
<td>16</td>
<td>44</td>
<td>89</td>
<td>133</td>
</tr>
</tbody>
</table>
Isotope effect on ADPs

\[ \Sigma_D^x = A * g_D * V_D * \delta(1/\omega_D, T) * V_D' * g_D' * A' + \varepsilon_D^x \]

\[ \lambda_D(\omega_D^2) = \begin{array}{c} g_D * V_D * F * V_D' * g_D' \\ \end{array} \]

\[ \lambda_H(\omega_H^2) = \begin{array}{c} g_H * V_H * F * V_H' * g_H' \\ \end{array} \]

\[ \Sigma_H^x = A * g_H * V_H * \delta(1/\omega_H, T) * V_H' * g_H' * A' + \varepsilon_H^x \]

Neutron diffraction
\( \text{C}_6\text{D}_6 \), 15 and 123 K

Theory of
normal
vibrations

X-ray diffraction
\( \text{C}_6\text{H}_6 \), 110 K

<table>
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<tr>
<th></th>
<th>( U_{11} )</th>
<th>( U_{22} )</th>
<th>( U_{33} )</th>
<th>( U_{12} )</th>
<th>( U_{13} )</th>
<th>( U_{23} )</th>
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<td>C1, X-ray</td>
<td>predict 212</td>
<td>181</td>
<td>236</td>
<td>12</td>
<td>-12</td>
<td>-10</td>
</tr>
<tr>
<td>C2, X-ray</td>
<td>predict 197</td>
<td>237</td>
<td>221</td>
<td>13</td>
<td>29</td>
<td>-18</td>
</tr>
<tr>
<td>C3, X-ray</td>
<td>predict 211</td>
<td>214</td>
<td>-21</td>
<td>10</td>
<td>20</td>
<td></td>
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Crankshaft motion in dimethylstilbene

S.C. Capelli, M. Förtsch, H.B. Bürgi

Frequency 54(2) cm\(^{-1}\)

Libration and out-of-plane vibration of urea

T. Lüthi Nyffeler, H.B. Bürgi,
unpublished

Frequency 45(5) cm\(^{-1}\)
## Inferring features of energy surfaces from crystal structure data

### Single-minimum process
(Vibrations)

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| multiple molecular states present in the same crystal (disordered structures) | Resolution of structures of different molecular states (S), (e.g. ground and excited state) | Estimating energy differences between different molecular states from occupancy (T) |
Nucleophile-electrophile contacts to carbonyl groups from the CSD

H. B. Bürgi  
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Acetal hydrolysis: structure correlation

Principal component analysis shows correlated changes of structural parameters


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Acetal hydrolysis: structure-energy correlation

\[ E = k_2 \cdot q^2 / 2 - k_3 \cdot q^3 - k_1 \cdot q \]

\[ \Delta E^\ddagger / \Delta q = -(6 \cdot E_0^\ddagger \cdot k_2)^{1/2} \]

Calc: 320 kcal (mol Å)^{-1}

Exp: 300 kcal (mol Å)^{-1}

Acetal hydrolysis: transition state structure

\[ E = k_2 \cdot \frac{q^2}{2} - k_3 \cdot q^3 - k_1 \cdot q \]

\[ q^\ddagger = \left( \frac{6 \cdot E_0^\ddagger}{k_2} \right)^{1/2} \]

\[ E = k_2 \cdot \frac{q^2}{2} - k_3 \cdot q^3 \]

\[ \Delta(C1-O1) \quad \Delta(C1-O5) \]

\[ q^\ddagger = \left( \frac{6 \cdot E_0^\ddagger}{k_2} \right)^{1/2} \]

0.55 Å  -0.15 Å

Ab initio:

OC(OH)$_2$.H$_2$O  0.17  -0.07
CH$_2$C(OH)$_2$.H$_2$O  0.34  -0.11
H$_2$C(OH)$_2$.H$_2$O  0.38  -0.16
Acetal hydrolysis: model of enzymatic catalysis

Structural data from 1:

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<th>No COOH</th>
<th>with COOH</th>
</tr>
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<tr>
<td>C-OCH$_3$</td>
<td>1.398</td>
<td>1.383 Å</td>
</tr>
<tr>
<td>C-OR$_3$</td>
<td>1.408</td>
<td>1.424 Å</td>
</tr>
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Relative rates of hydrolysis from 2

1  $10^{10}$


Bowl depth and inversion barrier in corannulenes

\[ E = x^4 - a \cdot x^2 \]

\[ x_{eq} = \pm \left( \frac{a}{2} \right)^{1/2} \]

\[ \Delta E = -x_{eq}^4 \]

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Trapping unstable species at low temperatures

Light induced excited high spin-state trapping in [FeL₂](BF₄)₂ (L = 2,6-di(pyrazol-1-yl)pyridine)

Victoria A. Money, a Ivana Radosavljevic Evans, a Malcolm A. Halcrow, b Andrés E. Goeta a and Judith A. K. Howard a

<table>
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<tr>
<th>Spin state</th>
<th>T/K</th>
<th>V/Å³</th>
<th>β°</th>
<th>Mean Fe–N/Å</th>
<th>Bite angle</th>
<th>BF₄⁻</th>
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<tr>
<td>HS-1</td>
<td>290</td>
<td>1373.3(5)</td>
<td>95.67(3)</td>
<td>2.166(6)</td>
<td>73.4(2)</td>
<td>Disordered</td>
</tr>
<tr>
<td>LS</td>
<td>120</td>
<td>1308.6(5)</td>
<td>98.37(3)</td>
<td>1.953(2)</td>
<td>80.09(8)</td>
<td>Ordered</td>
</tr>
<tr>
<td>LS</td>
<td>30</td>
<td>1288.8(1)</td>
<td>98.575(1)</td>
<td>1.950(2)</td>
<td>80.08(8)</td>
<td>Ordered</td>
</tr>
<tr>
<td>HS-2</td>
<td>30</td>
<td>1318.1(5)</td>
<td>97.15(1)</td>
<td>2.165(2)</td>
<td>73.52(7)</td>
<td>Ordered</td>
</tr>
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CHEM. COMMUN., 2003, 158–159
Excited-state structure by time-resolved X-ray diffraction


\[ \text{Pt}_2 (\text{H}_2\text{P}_2\text{O}_5)_4 \]

\[ \Delta d(\text{Pt-Pt}) = -0.28(9) \text{ Å} \]
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