

From Pseudo-dynamics to Real Dynamics

H.B. Bürgi, S.C. Capelli, *Helv. Chim. Acta*, **86** (2003) 1625-1640,
'Getting More out of Crystal-Structure Analyses'

Results of a 'crystal structure' analysis

Atomic coordinates

x, y, z



Interatomic distances
and angles



Static structure

Atomic displacement

Parameters (ADPs)

$U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, U_{23}$



???

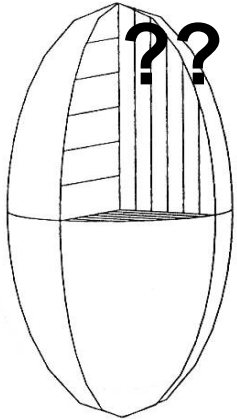


???

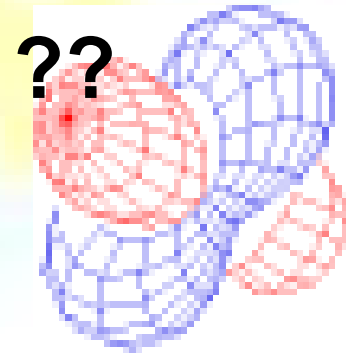
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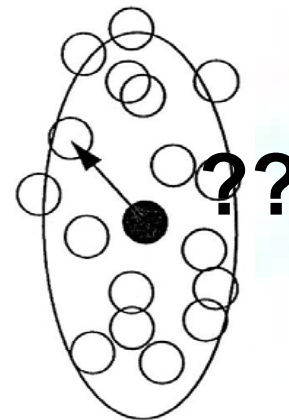
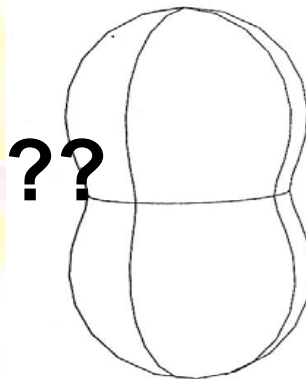
A few reminders about ADPs



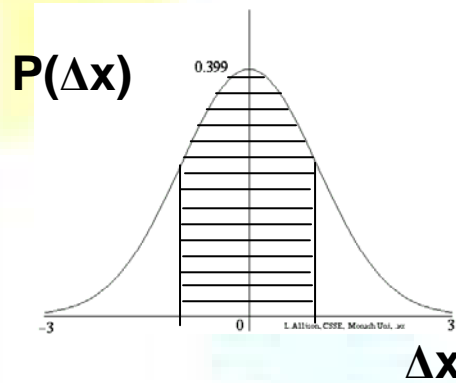
$$\mathbf{U} = \begin{bmatrix} U_{11} & U_{12} & U_{13} \\ U_{12} & U_{22} & U_{23} \\ U_{13} & U_{23} & U_{33} \end{bmatrix}$$



??



Instantaneous and mean-square displacements



- Distribution of instantaneous atomic displacements is Gaussian

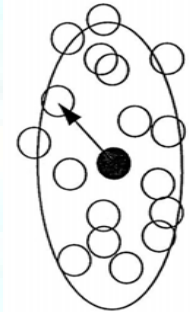
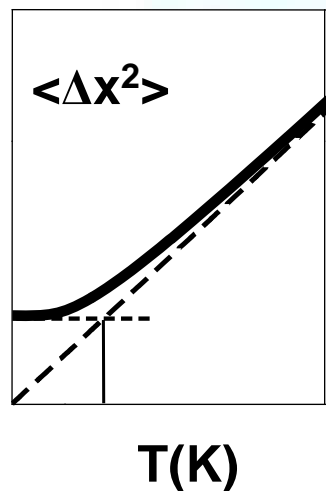
$$P(\Delta x, T) = (2\pi \langle \Delta x^2 \rangle)^{-1} \exp\{-\Delta x^2 / (2\langle \Delta x^2 \rangle)\}$$

- mean square displacement amplitude is the quadratic expectation value $\langle \Delta x^2 \rangle$

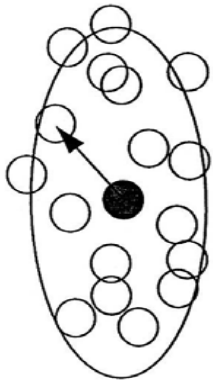
$$\langle \Delta x^2 \rangle = \int \Delta x^2 P(\Delta x, T) d\Delta x$$

- $\langle \Delta x^2 \rangle$ is temperature dependent: constant at very low T (zero point motion), proportional to T at high T

$$\langle \Delta x^2 \rangle = h / (8\pi^2 m \nu) * \coth(h\nu / 2k_B T)$$



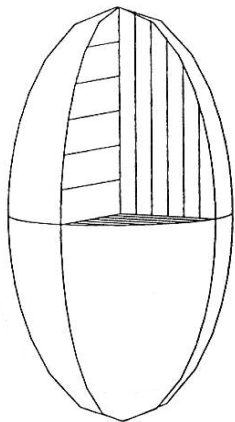
3-D anisotropic harmonic oscillator



$$\mathbf{v} = \Delta x \mathbf{a} + \Delta y \mathbf{b} + \Delta z \mathbf{c} = \zeta(\mathbf{a}^* \mathbf{a}) + \eta(\mathbf{b}^* \mathbf{b}) + \theta(\mathbf{c}^* \mathbf{c})$$

$$P(\mathbf{v}) = (2\pi)^{-3/2} (\det \mathbf{U}^{-1})^{1/2} \exp(-\mathbf{v}^T \mathbf{U}^{-1} \mathbf{v} / 2)$$

$$\mathbf{U} = \begin{bmatrix} U_{11} & U_{12} & U_{13} \\ U_{12} & U_{22} & U_{23} \\ U_{13} & U_{23} & U_{33} \end{bmatrix} = \begin{bmatrix} \langle \zeta \zeta \rangle & \langle \zeta \eta \rangle & \langle \zeta \theta \rangle \\ \langle \zeta \eta \rangle & \langle \eta \eta \rangle & \langle \eta \theta \rangle \\ \langle \zeta \theta \rangle & \langle \eta \theta \rangle & \langle \theta \theta \rangle \end{bmatrix}$$

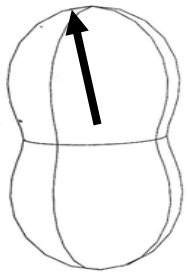


Equiprobability surface (ellipsoid)

$$-\ln P(\mathbf{v}) = \text{const} = (2\pi)^{-3/2} (\det \mathbf{U}^{-1})^{1/2} (\mathbf{v}^T \mathbf{U}^{-1} \mathbf{v})$$

Peanuts instead of ellipsoids

$\langle u^2(\mathbf{n}) \rangle$



Mean-square amplitude surface

$$\langle u^2(\mathbf{n}) \rangle = \mathbf{n}^T \mathbf{U} \mathbf{n}$$

rms amplitude surface (PEANUT)

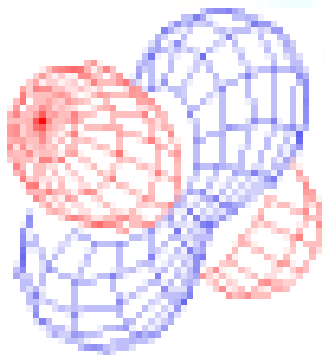
$$\langle u^2(\mathbf{n}) \rangle^{1/2} = (\mathbf{n}^T \mathbf{U} \mathbf{n})^{1/2}$$

Mean-square amplitude difference-surface

$$\langle \Delta u^2(\mathbf{n}) \rangle = \mathbf{n}^T (\mathbf{U}_{\text{obs}} - \mathbf{U}_{\text{model}}) \mathbf{n}$$

rms amplitude difference-surface (PEANUT)

$$\langle \Delta u^2(\mathbf{n}) \rangle^{1/2} = (\mathbf{n}^T (\mathbf{U}_{\text{obs}} - \mathbf{U}_{\text{model}}) \mathbf{n})^{1/2}$$



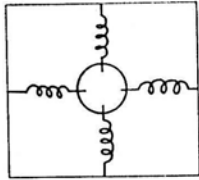
Why bother about ADPs?

- Proper correction of interatomic distances
- Discrimination between motion and disorder
- Low frequency vibration modes (including eigenvectors)
- Specific heat curves, enthalpies and entropies
- Basis of heat conduction, thermoelectric properties, etc.
- Physically sound and practically useful model of molecular dynamics in crystals (complement to charge density model)

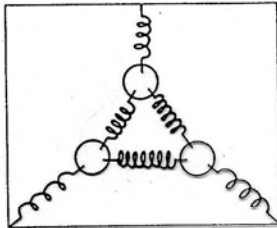
Correlated motion

- Atomic motion in crystals is highly correlated (phonons)
- Structure analysis provides no obvious information on this correlation!
- What can be done?
- Make assumptions!?

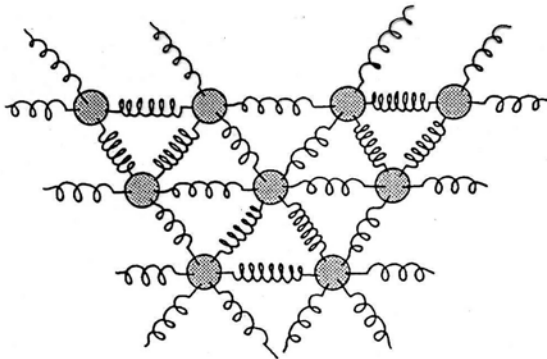
Models of motion



Atomic Einstein or
mean-field model



Generalized Einstein
or molecular
mean-field model



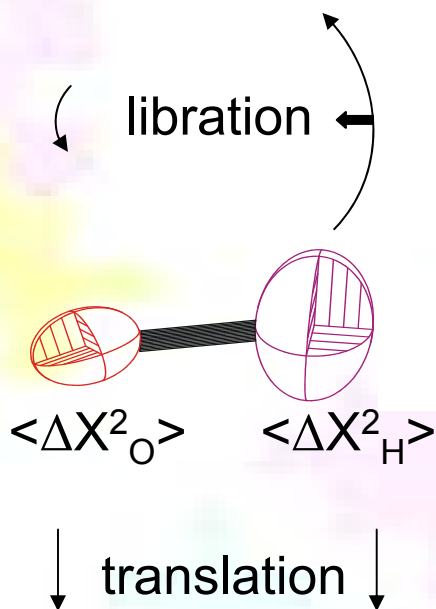
Lattice-dynamical model

An old problem first!

... one that people have been thinking about already
50 years ago

Interatomic distance in
a diatomic fragment

Bond Length Corrections



$$\Delta d = \langle \Delta X^2 \rangle / (2d_{\text{obs}})$$

W.R. Busing, H.A. Levy,
Acta Cryst **17** (1964) 142

$\langle \Delta X^2 \rangle$ [Å ²]	$= \langle \Delta X^2_H \rangle + \langle \Delta X^2_O \rangle - 2\langle \Delta X_O \Delta X_H \rangle$
Upper Limit	$\langle \Delta X^2_H \rangle + \langle \Delta X^2_O \rangle + 2\{\langle \Delta X^2_O \rangle \langle \Delta X^2_H \rangle\}^{1/2}$
Independent Motion	$\langle \Delta X^2_H \rangle + \langle \Delta X^2_O \rangle + 0$
H riding on O	$\langle \Delta X^2_H \rangle - \langle \Delta X^2_O \rangle$
Lower Limit	$\langle \Delta X^2_H \rangle + \langle \Delta X^2_O \rangle - 2\{\langle \Delta X^2_O \rangle \langle \Delta X^2_H \rangle\}^{1/2}$

Diatomic, coupling of atomic motions



$$\begin{bmatrix} \langle \Delta \mathbf{x}_O^2(T) \rangle & \langle \Delta \mathbf{x}_O \Delta \mathbf{x}_H(T) \rangle \\ \langle \Delta \mathbf{x}_O \Delta \mathbf{x}_H(T) \rangle & \langle \Delta \mathbf{x}_H^2(T) \rangle \end{bmatrix} = \mathbf{m}^{-1/2} \mathbf{V} \begin{bmatrix} \delta(\omega_1^{-1}, T) & 0 \\ 0 & \delta(\omega_2^{-1}, T) \end{bmatrix} \mathbf{V}' \mathbf{m}^{-1/2}$$

ADPs

Generalized Einstein Model

ADPs, determined
at several T 's

LSQ \rightarrow

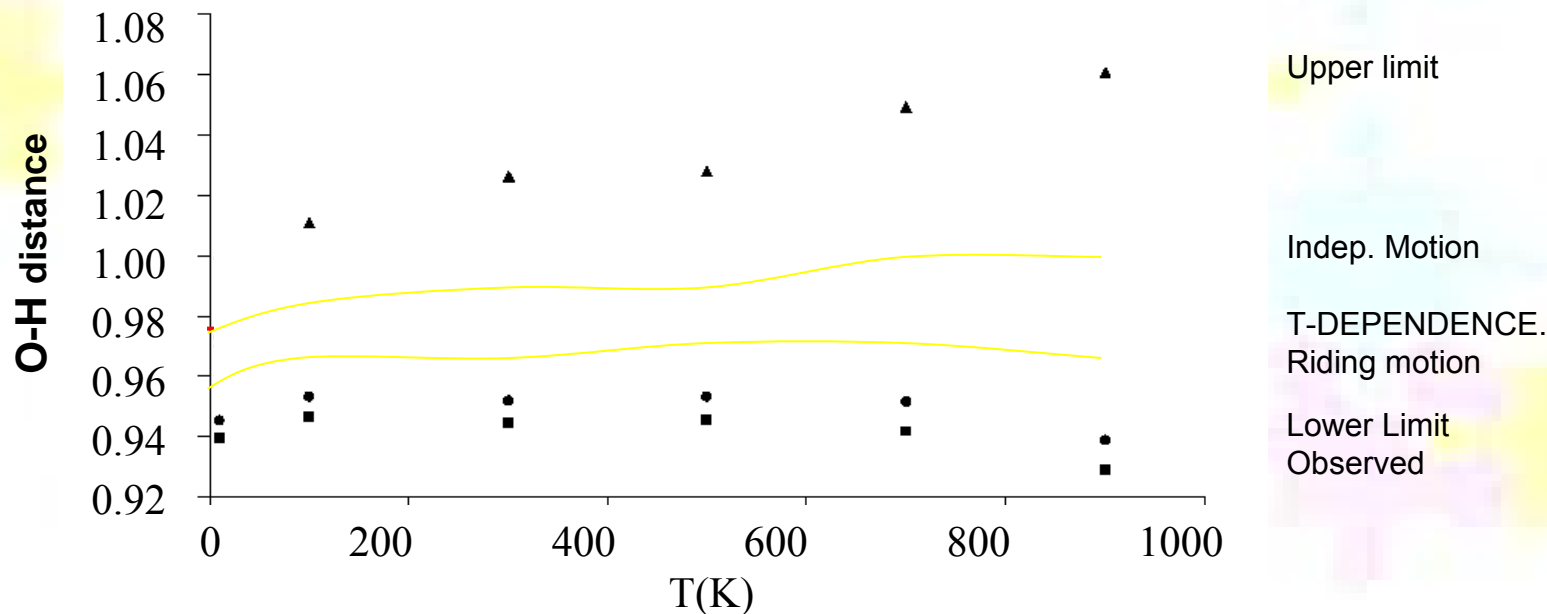
Normal modes:
Frequencies ω ,
eigenvectors \mathbf{V}
(Mix of libration
And translation)

Correlation ADPs
 $\langle \Delta \mathbf{x}_O \Delta \mathbf{x}_H(T) \rangle$
from model

\leftarrow

Comparison of Corrections

$$\langle \Delta x^2 \rangle = \langle \Delta x^2_{\text{O}} \rangle + \langle \Delta x^2_{\text{H}} \rangle - \text{cross term } [\text{\AA}^2]$$



Average O-H distance

0.976 Å

Vibration frequencies \perp to O-H bond

888, 338 cm^{-1}

Vibration frequencies \parallel to O-H bond

3514, 263 cm^{-1}

An evergreen

- Schomaker-Trueblood or Rigid body or TLS analysis:
- Schomaker V. & Trueblood K. N., *Acta Crystallogr. B* **24** (1968) 63-76
- > 2000 citations
- Assumption: rigid molecule without intramolecular motion!

U of atom k in terms of mean square libration, translation and screw coupling motion

$$U(k) = \begin{bmatrix} U_{k,11} & U_{k,12} & U_{k,13} \\ U_{k,12} & U_{k,22} & U_{k,23} \\ U_{k,13} & U_{k,23} & U_{k,33} \end{bmatrix}$$

to be represented in terms of $\langle t_i t_j \rangle = T_{ij}$ $\langle l_i l_j \rangle = L_{ij}$ $\langle l_i t_j \rangle = S_{ij}$

$$U_{calc}(k) = \begin{bmatrix} 1 & 0 & 0 & 0 & r_{k3} & -r_{k2} \\ 0 & 1 & 0 & -r_{k3} & 0 & r_{k1} \\ 0 & 0 & 1 & r_{k2} & -r_{k1} & 0 \end{bmatrix} \begin{bmatrix} T_{11} & T_{12} & T_{13} & S_{11} & S_{12} & S_{13} \\ T_{12} & T_{22} & T_{23} & S_{21} & S_{22} & S_{23} \\ T_{13} & T_{23} & T_{33} & S_{31} & S_{32} & S_{33} \\ S_{11} & S_{21} & S_{31} & L_{11} & L_{12} & L_{13} \\ S_{12} & S_{22} & S_{32} & L_{12} & L_{22} & L_{23} \\ S_{13} & S_{23} & S_{33} & L_{13} & L_{23} & L_{33} \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & -r_{k3} & r_{k2} \\ r_{k3} & 0 & -r_{k1} \\ -r_{k1} & r_{k1} & 0 \end{bmatrix}$$

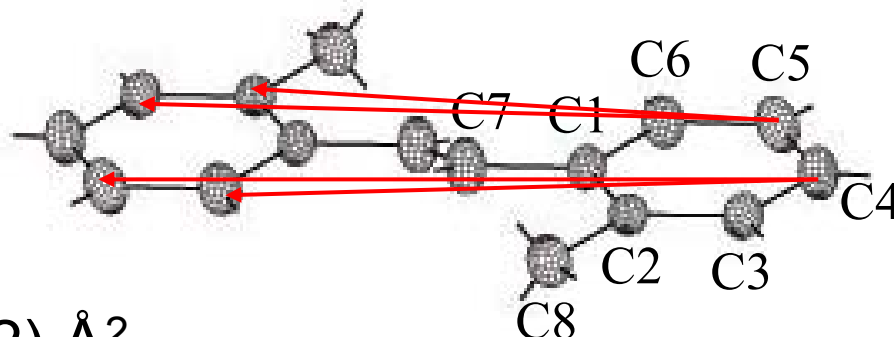
Test your assumption: Rigid-bond and rigid-body tests

- calculate U_A in the direction of atom B and U_B in the direction of atom A and take the difference

$$\Delta U_{AB} = \mathbf{n}_{AB}^T (\mathbf{U}_A - \mathbf{U}_B) \mathbf{n}_{AB} \quad (|\mathbf{n}_{AB}| = 1)$$

- If A and B are connected through a covalent bond, ΔU_{AB} is expected to be $< 0.001 \text{ \AA}^2$, for atoms at least as heavy as carbon (so called 'Hirshfeld test')
- If the ΔU_{IJ} -values for an entire group of atoms $\{A, B, C, \dots, Z\}$ fulfill the Hirshfeld test, $\{A, B, C, \dots, Z\}$ may be considered to form a rigid body.

Example 2: 2,2'-dimethylstilben (symmetry: 1bar)



$$\langle \Delta U(\text{bonds}) \rangle = 0.0010(2) \text{ \AA}^2$$

$$\langle \Delta U(\text{ring...ring}) \rangle = 0.0105(2) \text{ \AA}^2$$

ATOM->	C8	C4	C7	C5	C6	C3	C2	C1	C8	C4	C7	C5	C6	C3	C2
POSN->	2	2	2	2	2	2	2	2	1	1	1	1	1	1	1
C1	68	8	20	94	97	7	14	0	2	-1	18	8	12	5	1
C2	54	8	4	110	74	-10	0	-14	14	-3	4	-19	-17	11	
C3	68	8	14	105	78	0	10	-7	-13	-11	10	-15	-17		
C6	22	-103	-76	-34	0	-78	-74	-97	18	-8	-64	4			
C5	-62	-101	-72	0	34	-105	-110	-94	33	-17	-28				
C7	39	-8	0	72	76	-14	-4	-20	30	-19					
C4	35	0	8	101	103	-8	-8	-8	10						
C8	0	-35	-39	62	-22	-68	-54	-68							

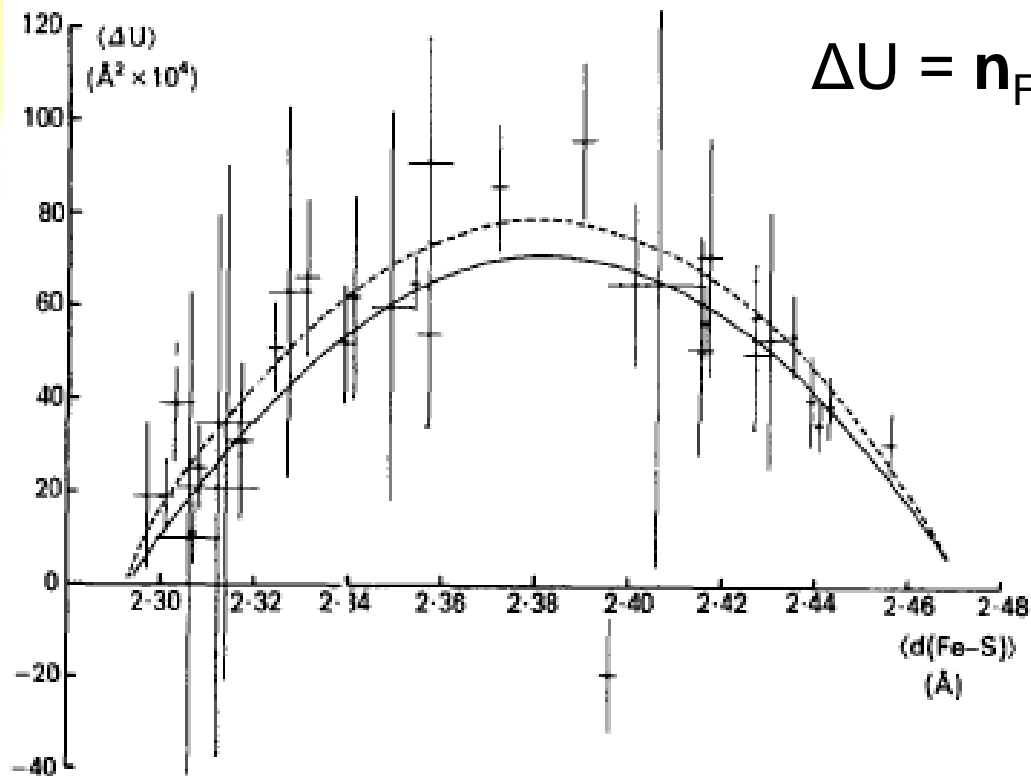
AVE. DIFF = 0.0035

R.M.S. DIFF = 0.0049

Remarks on rigid body models

- used mostly for correction of interatomic distances.
- quality of corrections depends on the degree of rigidity and on the condition that contributions of internal molecular motion and disorder are negligibly small compared to libration and translation. Problem at low T and in disordered structures!
- the indeterminacy in $\text{Tr}(\mathbf{S})$ does not affect these corrections, but vibrational frequencies from TLS are unreliable. No corrections of *intermolecular* distances.
- could the multi-temperature approach illustrated for diatomics be useful here?

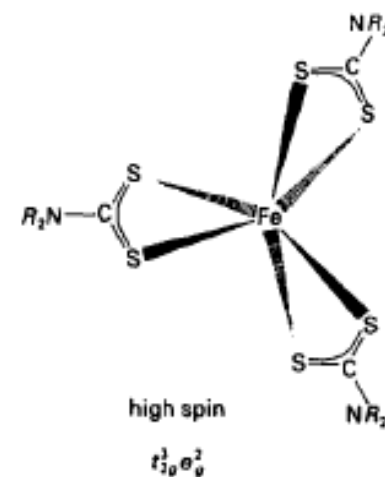
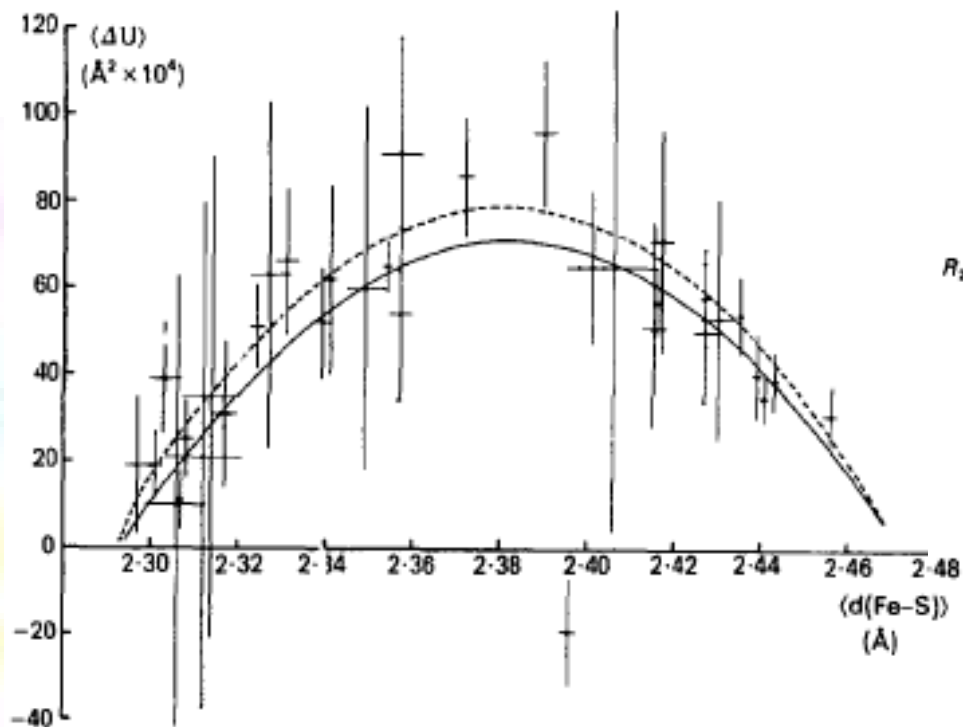
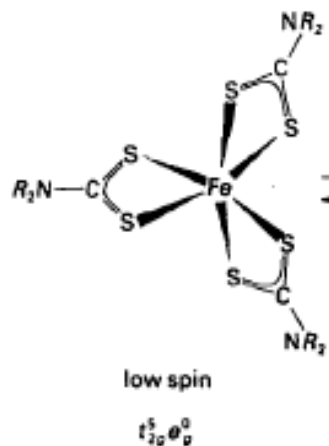
Pathological ΔU 's from 33 iron tris-dithiocarbamates



$$\Delta U = \mathbf{n}_{\text{Fe-S}}^T (\mathbf{U}_{\text{S}} - \mathbf{U}_{\text{Fe}}) \mathbf{n}_{\text{Fe-S}}$$



Spin equilibrium in iron tris-dithiocarbamates

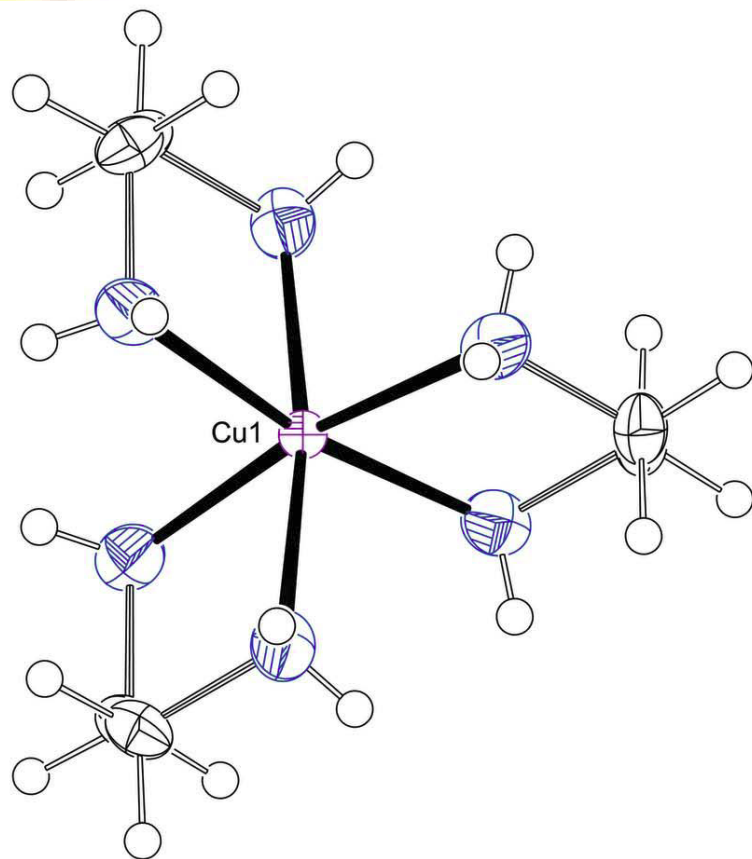


Low spin:
 $d(\text{Fe-S})$ short

Two half S-atoms
 $\sim 0.16 \text{ \AA}$ apart

High spin:
 $d(\text{Fe-S})$ long

Cu(II)en₃ SO₄



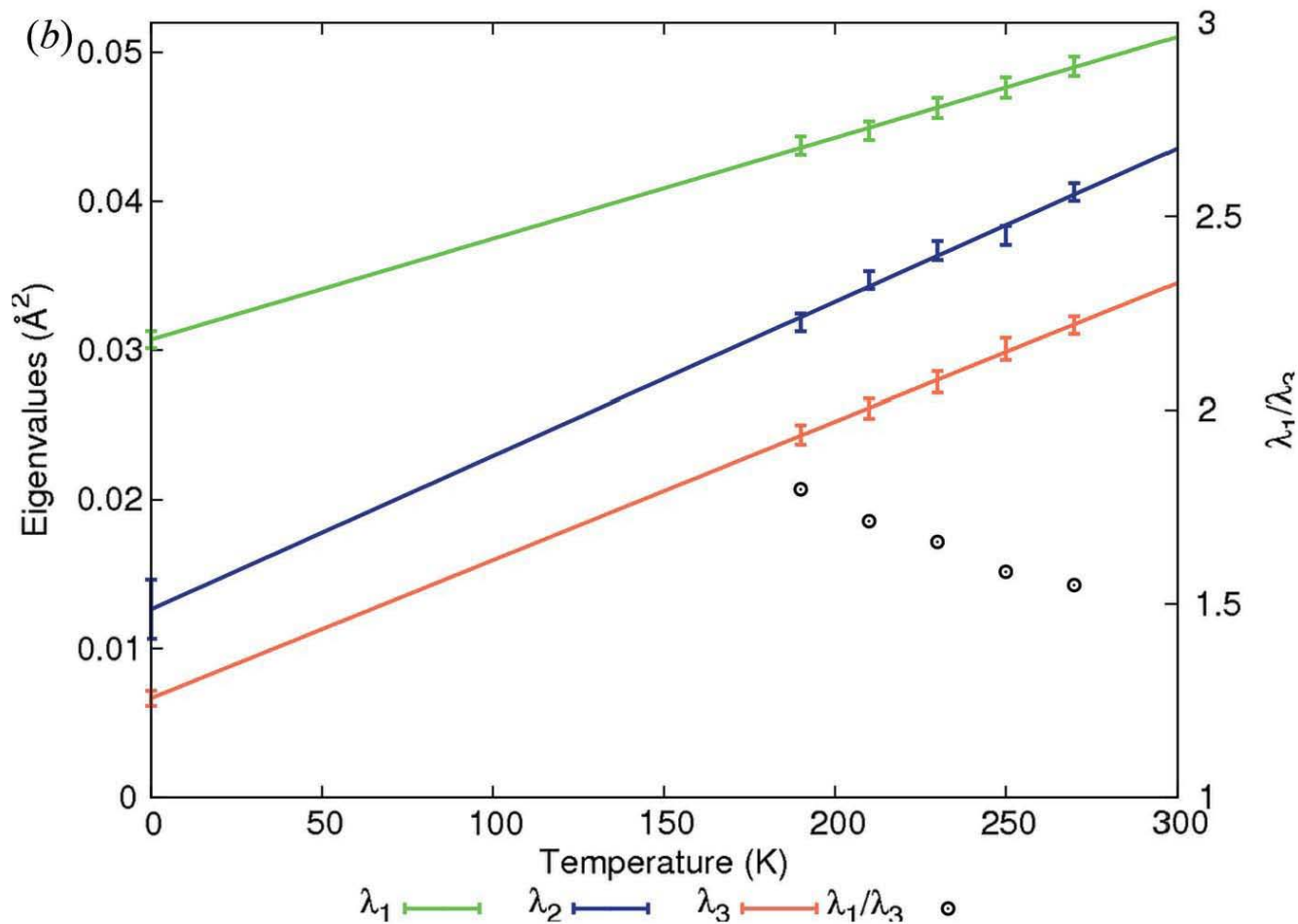
Observed:

Six identical, symmetry equivalent Cu(II)-N distances of length 2.15 Å

Expected:

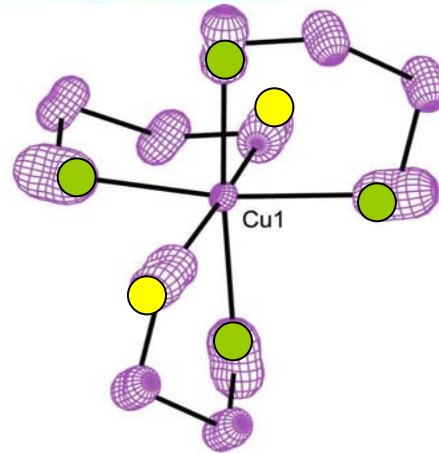
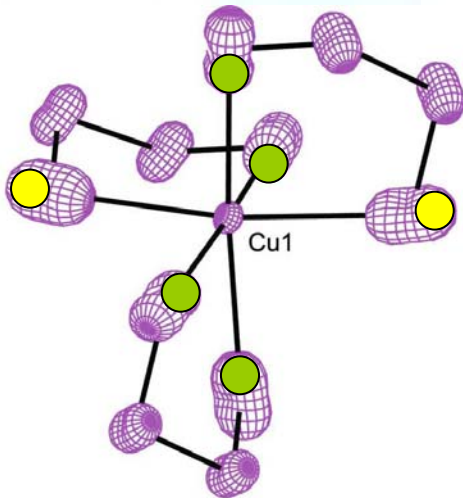
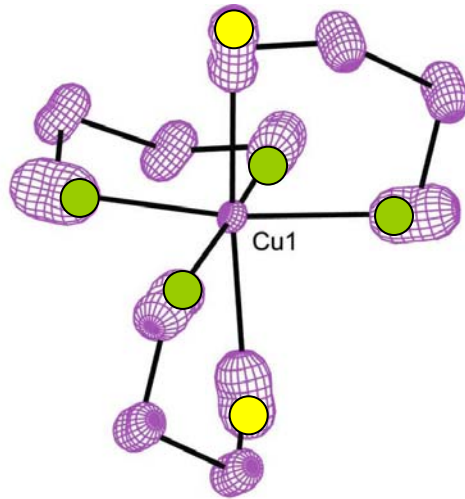
Jahn-Teller distorted coordination with four short and two long Cu(II)-N distances

Principal values of $U(N)$ as function of T



$\text{Cu(II)en}_3 \text{SO}_4$

- Three ways of distorting the Cu(II)en_3 ion,
- Each one occupies 1/3 of the unit cells in the crystal randomly
- Each one occupies a unit cell only during 1/3 of the observation time



Effects absorbed by ADPs

Average over time of experiment (= time average):
Atomic displacements arising from dynamic processes faster than hours, e.g. molecular vibrations, conformational equilibria, etc.

Average over entire crystal (= space average):
Differences in atomic positions smaller than the resolution limit (ca. 0.5 Å) due to positional and orientational disorder

A cautionary remark

Crystal structure analysis

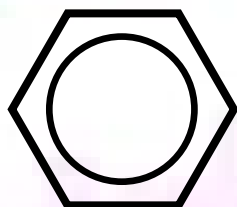
- **does not measure** the chemically interesting **bond lengths and angles**, but mean atomic positions, mean square dynamic and static displacements.
- **does not provide** 'crystal structures', but a unit cell showing the distribution of atoms averaged over the time of the experiment and the space occupied by the crystal.

Some caveats

Cases in which any interpretation of ADPs has to be taken with a grain of salt (or better: two!)

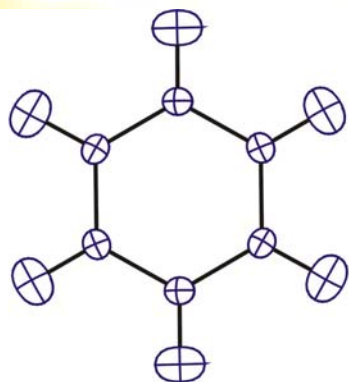
- Molecules with low-energy vibrations, e.g. torsions and angle-bends (i.e. nonrigid molecules!!!)
- Disorder with a good chemical explanation, e.g.
 - High spin/low spin mixtures in spin crossover compounds
 - Molecules with dynamic Jahn-Teller effects
 - Fluxional molecules in general
- Anharmonic motion: potentials are no longer quadratic, ADPs are Gaussian fits to non-Gaussian probability density functions.
- Absorption and (pseudo-)extinction, incomplete data

**What is the experimental evidence for
the D_{6h} symmetry of benzene?**



Concerning the structure of benzene

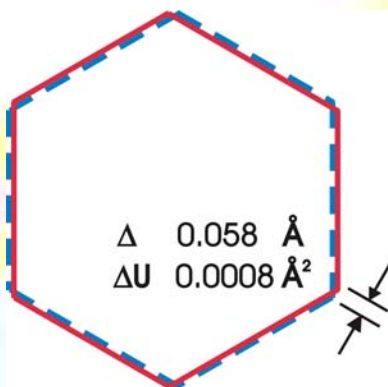
Rms displacements U of C_6D_6 from neutron diffraction



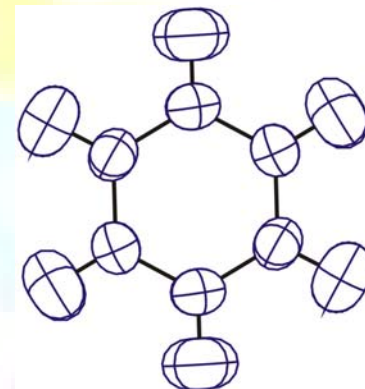
15 K

$$U_{\text{iso}}(\text{C}) \sim 0.008 \text{ \AA}^2$$

(shown: * 2.5)



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



123 K

$$U_{\text{iso}}(\text{C}) \sim 0.023 \text{ \AA}^2$$

(shown: * 2.5)

G.A. Jeffrey, J.R. Ruble, R.K. Mullan, J.A. Pople, *Proc. R. Soc. London*, **A414** (1987) 47

O. Ermer, *Angew. Chem., Int. Edit.*, **26** (1987) 782

Temperature dependence of ADPs

Vibrations of a molecule in its crystal field

$$\Sigma^x(T) = \mathbf{A} * \mathbf{g} * \mathbf{V} * \delta(1/\omega, T) * \mathbf{V}' * \mathbf{g}' * \mathbf{A}' + \epsilon^x$$

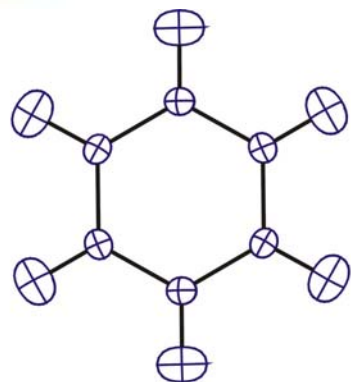
ADPs (blue) determine parameters of model (red)

ADPs,
determined
experimentally
at several
temperatures

Low frequency,
soft vibrations (ω),
e.g. librations,
translations and
deformations (\mathbf{V})

Intramolecular,
hard vibrations
and disorder (ϵ)
(~temperature
independent),

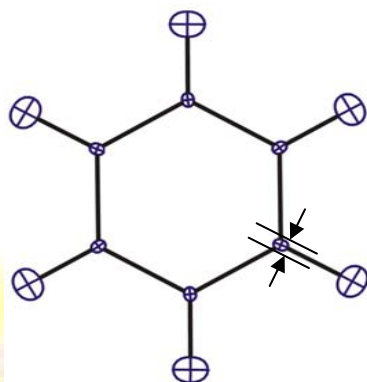
Results for Benzene, C₆D₆



15 K

$$U_{\text{iso}}(\text{C}) \sim 0.008 \text{ \AA}^2$$

(shown: *2.5)



123 K

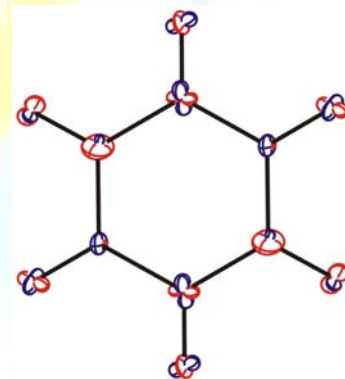
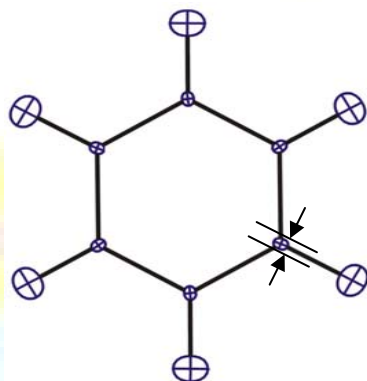
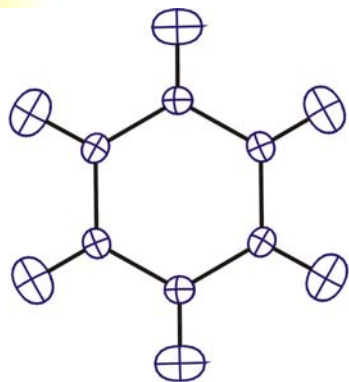
$$U_{\text{iso}}(\text{C}) \sim 0.023 \text{ \AA}^2$$

(shown: * 2.5)

	Along C-H	in plane	out-of-plane)
ϵ_{C}	0.0014(1)	0.0007(1)	0.0015(1) \text{ \AA}^2

In-plane disorder contribution was estimated at 0.0008 \text{ \AA}^2

Results for Benzene, C₆D₆



Zero point motion from neutron diffraction and
From a benchmark force field (*10⁴ Å²)

	C(bond)	C(ip)	C(oop)	D(bond)	D(ip)	D(oop)
Diffraction	14(1)	7(1)	15(1)	52(1)	83(1)	110(2)
Force Field	13	8	16	44	89	133

Isotope effect: from ADP(D) to ADP(H)

$$\Sigma_D^x = A * g_D * V_D * \delta(1/\omega_D, T1) * V_D' * g_D' * A' + \epsilon_D^x$$

Neutron diffraction
C₆D₆, 15 and 123 K

$$\omega_D^2 = g_D * V_D * F * V_D' * g_D'$$

$$\omega_H^2 = g_H * V_H * F * V_H' * g_H'$$

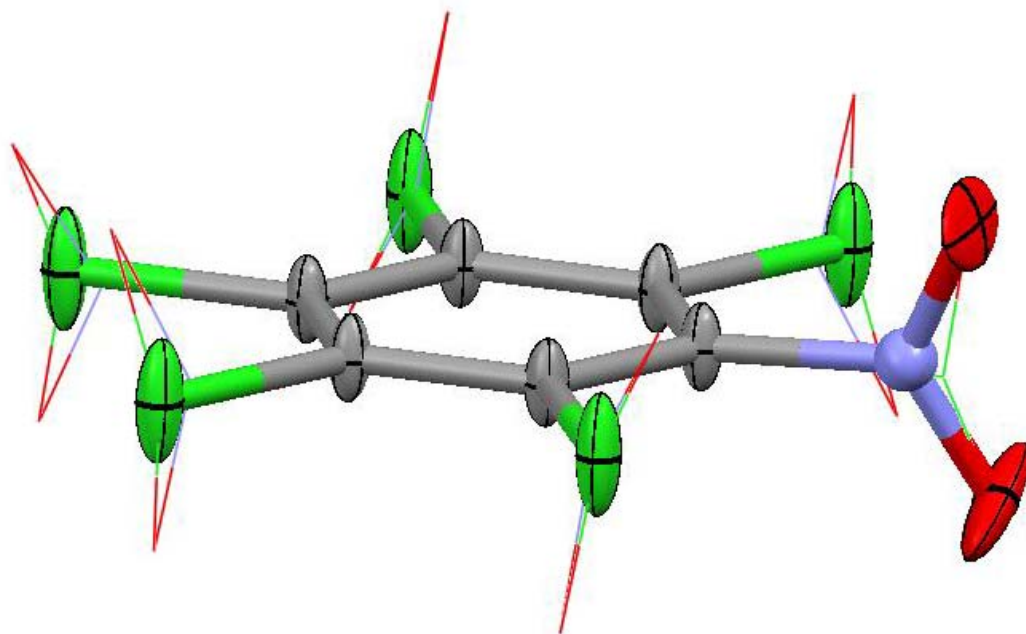


Theory of normal vibrations

$$\Sigma_H^x = A * g_H * V_H * \delta(1/\omega_H, T2) * V_H' * g_H' * A' + \epsilon_H^x$$

Predict ADP(C, H)
C₆H₆, 110 K
X-Ray diffraction

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1, predicted	211	186	240	13	-7	-9
obs-pred ($\times 10^4 \text{ \AA}^2$)	1	5	-4	-1	-5	-1
C2, predicted	195	236	222	13	27	-17
obs-pred ($\times 10^4 \text{ \AA}^2$)	2	1	-1	0	2	-1
C3, predicted	206	215	217	-17	11	18
obs-pred ($\times 10^4 \text{ \AA}^2$)	5	0	-3	-4	-1	2



$C_6Cl_5NO_2$, motion vs. disorder

Site symmetry
3bar

Sixfold disorder

Neutron diffraction data at 5, 100, 200, 295 K ^a

Strong diffuse scattering ^b

a) J.M. Cole, H.B. Bürgi, G.J. McIntyre, Phys. Rev. B (2011) **83**, 224202

b) L. H. Thomas, T. R. Welberry, D. J. Goossens, A. P. Heerdegen, M. J. Gutmann, S. J. Teat, P. L. Lee, C. C. Wilson, J. M. Cole, Acta Cryst. (2007). **B63**, 663–673

Static and dynamic contributions to ADPs

	$C_6Cl_5NO_2$ (5 K)	C_6D_6 (15 K)
$U_{\perp}(C)$	0.039 Å ²	0.0100 Å ²
$\varepsilon(C)$	0.037 (disorder)	0.0015 (oop)
dynamic	0.002	0.0085
$U_{\perp}(Cl/D)$	0.078 Å ²	0.028 Å ²
$\varepsilon(Cl/D)$	0.071 (disorder)	0.0110 (oop)
dynamic	0.007	0.0170

J.M. Cole, H.B. Bürgi, G.J. McIntyre, Phys. Rev. B (2011) **83**, 224202
L. H. Thomas, T. R. Welberry, D. J. Goossens, A. P. Heerdegen, M. J. Gutmann, S. J. Teat,
P. L. Lee, C. C. Wilson, J. M. Cole, Acta Cryst. (2007). **B63**, 663–673

Origin of dynamic contributions to ADPs

	$C_6Cl_5NO_2$ (5 K)	C_6D_6 (15 K)
$\omega_{\text{translation}}$	32, 35, 35 cm^{-1}	43, 45, 51 cm^{-1}
$\omega_{\text{libration}}$	44, 44, 44 cm^{-1}	70, 84, 60 cm^{-1}

Terahertz spectroscopy $C_6Cl_5NO_2$: band at $\sim 40\text{ cm}^{-1}$
 ' ... attributed to molecular librations'

C. Reid, G. J. Evans, and M.W. Evans, Spectrochim. Acta A **35**, 679 (1979).

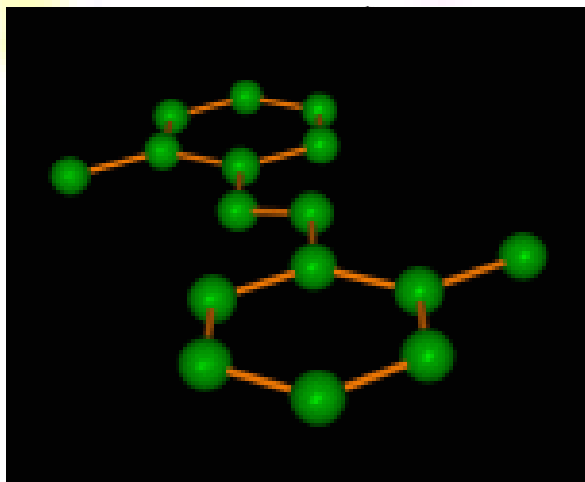
$$\frac{f_{\text{trans}}(C_6Cl_5NO_2)}{f_{\text{trans}}(C_6D_6)} = \frac{\omega^2(C_6Cl_5NO_2)}{\omega^2(C_6D_6)} \frac{M(C_6Cl_5NO_2)}{M(C_6D_6)} \approx 2$$

J.M. Cole, H.B. Bürgi, G.J. McIntyre, Phys. Rev. B (2011) **83**, 224202

Cranckshaft motion in dimethylstilbene

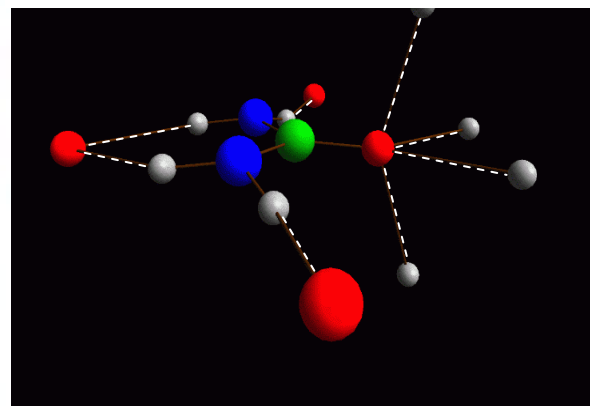
S.C.Capelli, M. Förtsch,
H.B. Bürgi, *Acta Cryst.*
A56 (2000) 413

Frequency 54(2) cm^{-1}



Frequency 45(5) cm^{-1}

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



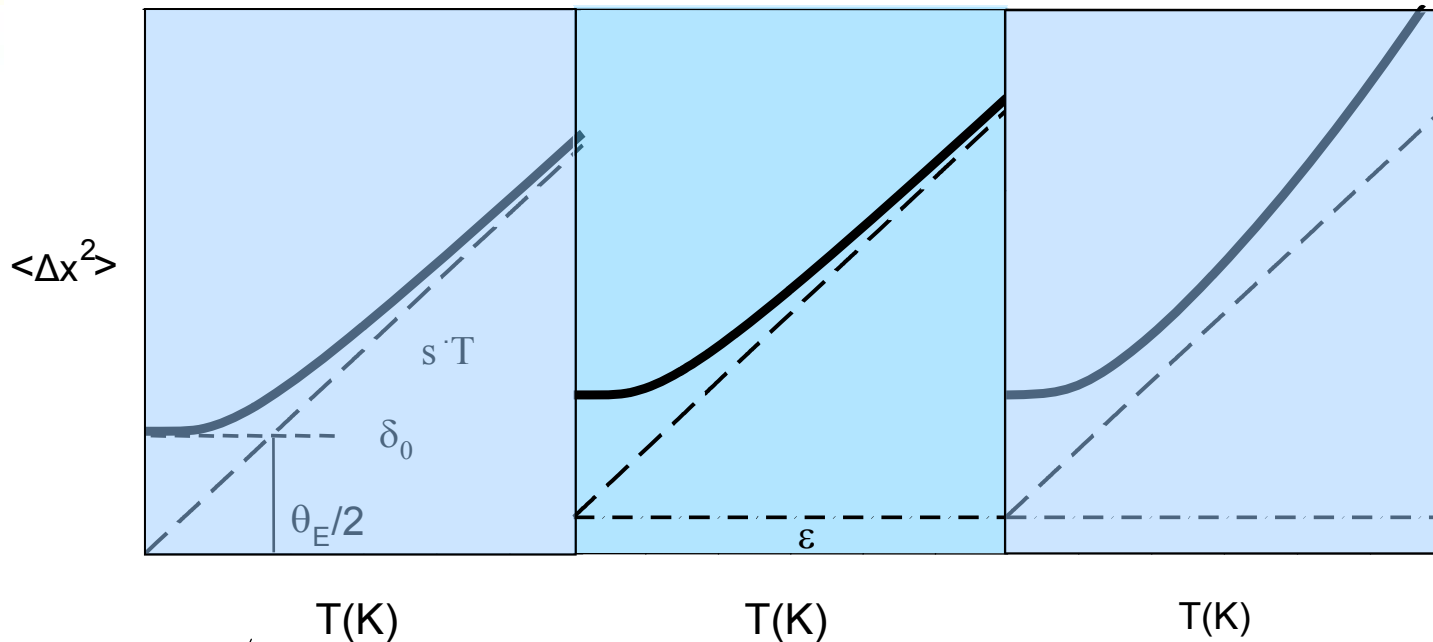
(c)

Libration and out-of-plane vibration of urea

Temperature dependence of ADPs

$$\langle \Delta x^2 \rangle = \hbar / (2\omega_{\text{eff}}) \coth (\hbar\omega_{\text{eff}} / 2k_B T) + \varepsilon$$

$$\omega_{\text{eff}}(T) = \omega_0 [1 - \gamma_G \Delta V(T) / V_0]$$

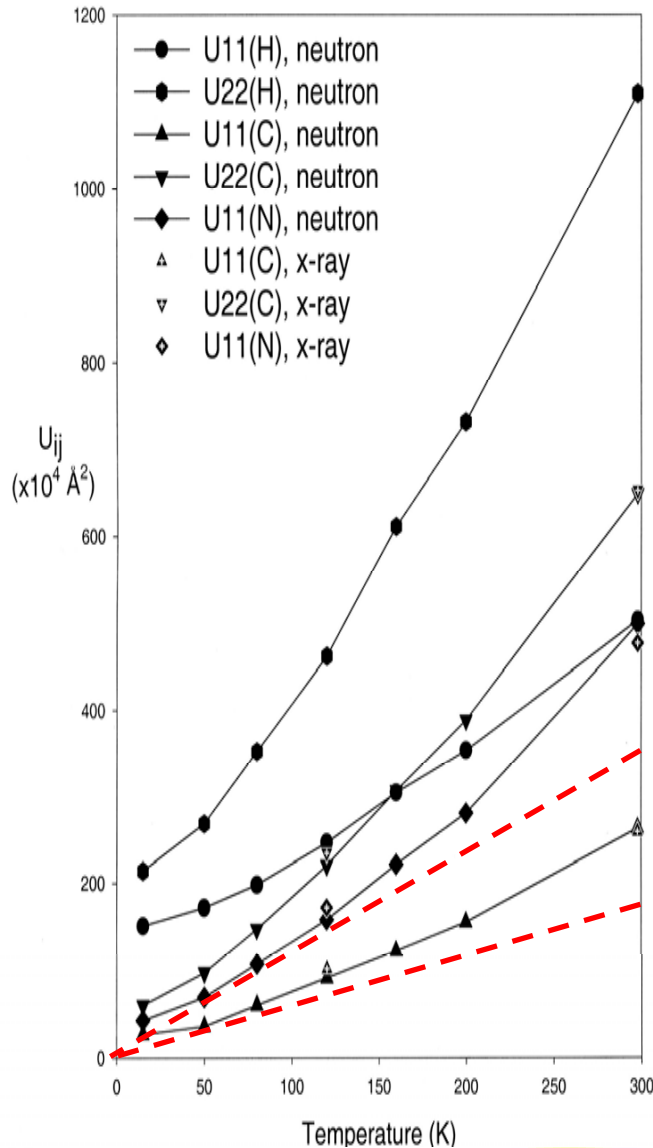


Harmonic
oscillator only

Harm. Osc. with
T-indep. Contrib.

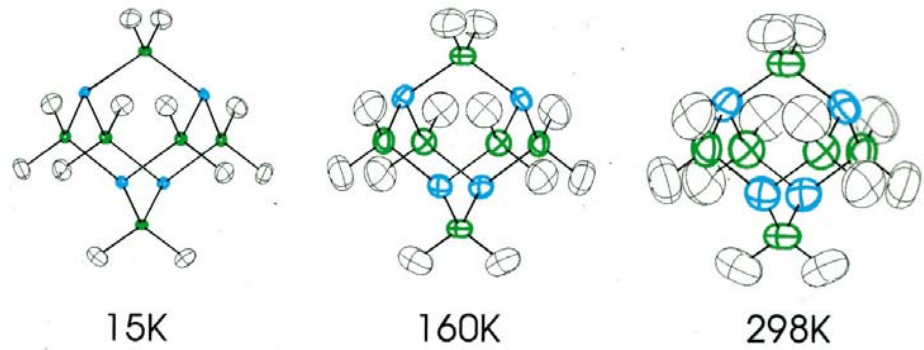
Anharm. Osc. and
T-indep. Contrib.

Hexamethylenetetramine (neutron data)



Note the nonlinear
increase of ADPs at
higher temperatures

Anharmonicity!



Temperature dependence of ADPs

Quasi-harmonic model

Vibrations of a molecule in its crystal field

$$\Sigma^x(T) = \mathbf{A} * \mathbf{g} * \mathbf{V} * \delta(1/\omega(T), T) * \mathbf{V}' * \mathbf{g}' * \mathbf{A}' + \epsilon^x$$

ADPs (blue) determine parameters of model (red)

ADPs,
determined
experimentally
at several
temperatures

Low frequency,
soft vibrations (ω),
e.g. librations,
translations and
deformations (\mathbf{V})

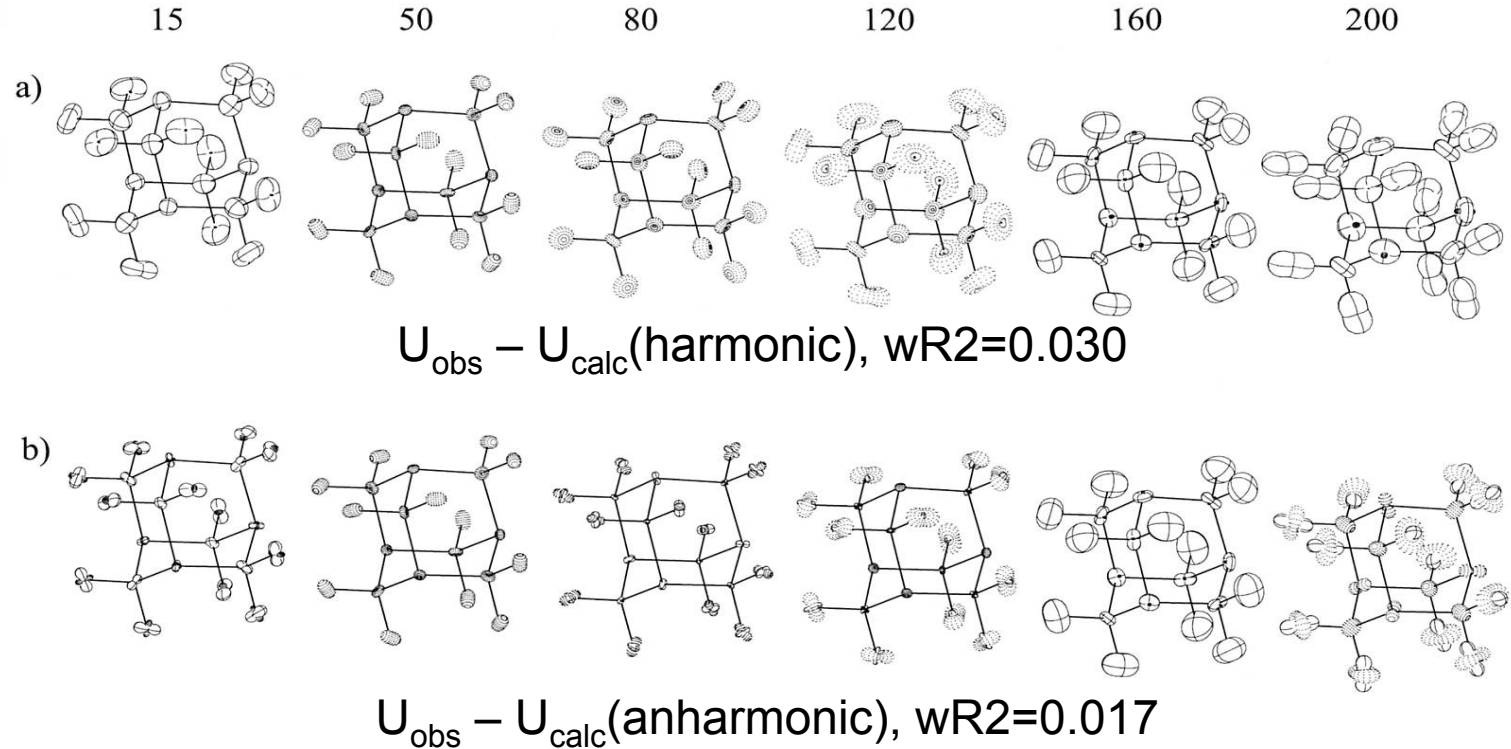
Intramolecular,
hard vibrations
and disorder (ϵ)
(~temperature
independent),

Anharmonic motion

Quasi-harmonic model:

$$\omega_{\text{eff}}(T) = \omega_0 [1 - \gamma_G \Delta V(T) / V_0]$$

γ_G : Grüneisen constant
 $\gamma_G = 2.3$, elastic n-diffraction
 $\gamma_G = 2.2 - 2.5$, inelastic n-scattering



C_V , C_P of hexamethylenetetramine

$$C_v(T) = \sum_{i=1}^3 3R \left(\frac{T}{1.437\bar{\nu}_{D,i}} \right)^3 \int_0^{1.437\bar{\nu}_{D,i}/T} \frac{x^4 e^x}{(e^x - 1)^2} dx +$$

$$\sum_{i=4}^6 R \left(\frac{1.437\bar{\nu}_{E,i}}{T} \right)^2 \frac{e^{1.437\bar{\nu}_{E,i}/T}}{(e^{1.437\bar{\nu}_{E,i}/T} - 1)^2} +$$

$$\sum_{i=7}^{3n} R \left(\frac{1.437\bar{\nu}_{int,i}}{T} \right)^2 \frac{e^{1.437\bar{\nu}_{int,i}/T}}{(e^{1.437\bar{\nu}_{int,i}/T} - 1)^2}$$

$$C_p(T) - C_v(T) = T \chi^2(T) V(T) / \kappa(T)$$

$$C_p(T) - C_v(T) = \gamma_G T \chi(T) C_v(T)$$

$$C_p(T) - C_v(T) = 3 R A_0 T C_v(T) / T_m$$

Translation

$$\nu_D = 1.5-1.732 \nu_E$$

Libration

Internal vibrations

B3LYP

6-311+G(2d,p)

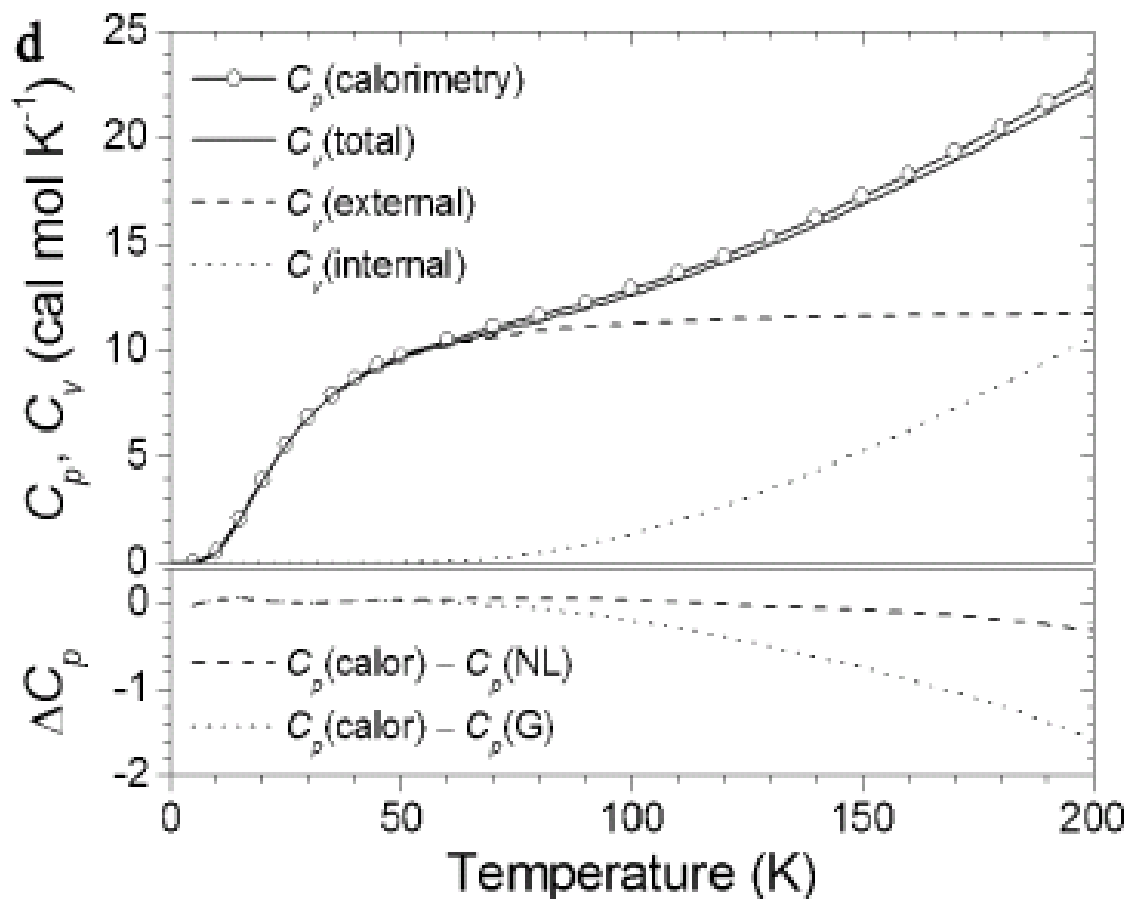
Thermodynamics

Approximations

$$A_0 = 0.0163 \text{ K mol cal}^{-1}$$

T_m : melting point

C_V , C_P of hexamethylenetetramine



Good agreement between calorimetric and diffraction results

Nernst-Lindemann relation is a better approximation to $C_p - C_v$ than Grüneisen relation

Possibility to measure compressibility $\kappa(T)$ by diffraction

Comparing the stability of polymorphs

- $\Delta H = \int c_p dT$ $\Delta S = \int c_p/T dT$
- $\Delta G = \Delta H - T\Delta S$
- Dynamics and Thermodynamics of Crystalline Polymorphs: α -Glycine, Analysis of Variable-Temperature Atomic Displacement Parameters
J. Phys. Chem. A, **116** (2012) 8092–8099
- Dynamics and Thermodynamics of Crystalline Polymorphs. 2. β -Glycine, Analysis of Variable-Temperature Atomic Displacement Parameters
J. Phys. Chem. A **117** (2013) 8001–8009
- γ -Glycine, in preparation

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Some conclusions

- the lack of information on correlation of atomic motion can be overcome by analysing the temperature dependence of the ADPs with a normal mode approach
- more founded distance correction
- $\text{Tr}(\mathbf{S})$ can be determined
- Internal rotation can be distinguished from overall rotation
- low frequencies modes can be obtained (still difficult to calculate ab initio)
- in combination with information on internal vibrations crystal thermodynamic function can be calculated



Another puzzle!