A simple approach to estimate isotropic displacement parameters for hydrogen atoms

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A simple combination of riding motion and an additive term is sufficient to estimate the temperature-dependent isotropic displacement parameters of hydrogen atoms, for use in X-ray structure refinements. The approach is validated against neutron diffraction data, and gives reasonable estimates in a very large temperature range (10–300 K). The model can be readily implemented in common structure refinement programs without auxiliary software.

1. Introduction

It is common practice to estimate the thermal motion of hydrogen atoms using a riding-atom approach, as *e.g.* embedded in the *SHELXL* (Sheldrick, 2008) program. The riding-atom approach estimates the isotropic displacement parameter of hydrogen atom H, bound to the heavier atom X (typically C, N or O) by $U_{iso}(H) = A \times U_{eq}(X)$, where $U_{eq}(X)$ is the so-called equivalent isotropic displacement parameter, which is the arithmetic mean value of the eigenvalues of the mean-square displacement (MSD) matrix of atom X (which is refined anisotropically), and A is a factor that depends on the atom type X, but is traditionally set to 1.2 or 1.5 in *SHELXL*. As noted in a recent paper by Lübben *et al.* (2014), by which we were inspired, the A factors used in the *SHELXL* program are based on observations made at room temperature, and at lower temperatures (*e.g.* the commonly used 100 K), these factors have to be modified. Lübben and co-workers demonstrate that the ratio is large at low temperatures (larger than 3) and decreases with temperature (to less than 2).

In the present work we propose a simple scheme to estimate isotropic hydrogen-atom motion based on a riding-model approach and an additive term, which takes the internal motion of the hydrogen atom into account. This scheme can be readily used in structure-refinement programs without the use of external software.

Before embarking on the analysis of isotropic displacement parameters, we want to emphasize the following: whereas the use of isotropic displacement parameters for hydrogen atoms may be sufficient for refinement data with the independent-atom model (IAM), it is not recommended for accurate high-resolution studies, charge-density investigations and studies using database aspherical scattering factors (Dittrich *et al.*, 2006; Jarzembska & Dominiak, 2012; Domagała *et al.*, 2012). The consequences of neglecting an anisotropic model have been demonstrated in many cases (Madsen *et al.*, 2004; Roversi & Destro, 2004; Hoser *et al.*, 2009). The use of anisotropic displacement parameters in accurate studies is becoming standard, as witnessed by many recent studies as

$U_{iso}H$
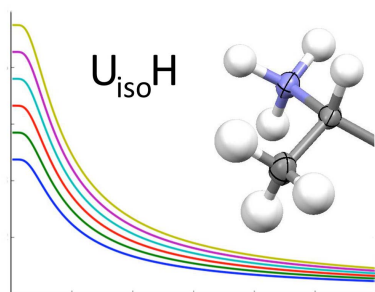
recently reviewed (Madsen, 2012). Estimating hydrogen anisotropic displacement parameters (ADPs) is an extra step in model building, which usually involves the use of a TLS analysis, and the imposition of internal motion for the hydrogen atoms. The most used approaches are TLS+ONIOM (Whitten & Spackman, 2006) and *SHADE* (Madsen *et al.*, 2004; Roversi & Destro, 2004; Madsen, 2006; Hoser *et al.*, 2009).

2. The proposed model

The temperature dependence of the ratio $U_{iso}(H)$ to $U_{eq}(X)$, as observed by Lübben and co-workers, is due to the fact that the thermal motion of atoms depends both on the atomic mass and the temperature. The *internal* molecular motion $\langle u^2 \rangle^{int}$, which is almost temperature independent, dominates at low temperatures, where the *external* molecular concerted vibrations of molecules (phonons) are small. Because of the differences in atomic mass the intramolecular motion, $\langle u^2 \rangle^{int}$, is large for hydrogen and smaller for heavier atoms (Madsen, 2012; Madsen *et al.*, 2013). As the temperature increases, the external molecular motion dominates. The external motion of hydrogen and heavier atoms is proportional, and it is this combination of a temperature-dependent and temperature-independent atomic motion which causes the ratio $U_{iso}(H):U_{eq}(X)$ to change with temperature.

In the harmonic approximation the internal and external vibrations can be summed to give the total atomic vibration. For hydrogen we have

$$U_{iso}(H) = \langle u^2 \rangle_H^{total} = \langle u^2 \rangle_H^{int} + \langle u^2 \rangle_H^{ext}, \qquad (1)$$
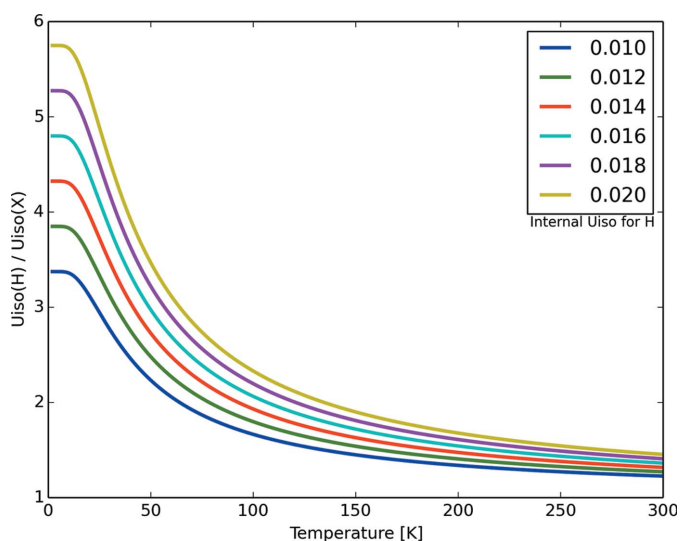
and for the heavy atom X,

Figure 1
The plot shows the ratio $U_{iso}(H)/U_{iso}(X)$ as a function of temperature [calculated using equation (3)], using different values for the internal displacement of hydrogen (in units of Å^2). The overall molecular motion was estimated using equation (4) for a molecule with a mass of 100 Da and a vibrational frequency of 40 cm^{-1}.

$$U_{eq}(X) = \langle u^2 \rangle_X^{total} = \langle u^2 \rangle_X^{int} + \langle u^2 \rangle_X^{ext}. \qquad (2)$$

For molecular compounds the external vibrations of the molecules give rise to very similar contributions to $\langle u^2 \rangle_H^{ext}$ and $\langle u^2 \rangle_X^{ext}$. In the riding-atom approximation $\langle u^2 \rangle_H^{ext} = A \langle u^2 \rangle_X^{ext}$. If we furthermore assume that $\langle u^2 \rangle_H^{int}$ is negligible (it is normally less than 10% of $\langle u^2 \rangle_H^{int}$), we obtain the ratio between the isotropic motion of hydrogen atom H and heavy atom X:

$$\frac{\langle u^2 \rangle_H^{total}}{\langle u^2 \rangle_X^{total}} \simeq \frac{\langle u^2 \rangle_H^{int}}{\langle u^2 \rangle_X^{ext}} + A. \qquad (3)$$

The ratio depends on the temperature *via* $\langle u^2 \rangle_X^{ext}$ which is dominated by the low-frequency concerted vibrations (phonons) of molecules in the crystal.

2.1. An example

As an example, we may consider the internal vibration of a hydrogen atom H to be constant at all temperatures. H is bound to X, which has got negligible internal motion because of its larger mass. The external vibration of both atoms is considered to be the same (*i.e.* $A = 1$ in the riding-atom approximation) and corresponds to the vibration of the whole molecule. The external motion is temperature dependent. The amplitude of motion may be roughly approximated by the mean-square amplitude of a single (quantum-mechanical) harmonic oscillator:

$$\langle u^2 \rangle_X^{ext} = \frac{\hbar}{2\omega m} \coth\left(\frac{\hbar\omega}{2k_B T}\right). \qquad (4)$$

We use a mass of 100 Da and a frequency of the oscillator of 40 cm^{-1}. The ratio in equation (3) has been plotted as a function of temperature in Fig. 1 using a range of values for $\langle u^2 \rangle_H^{int}$, the internal motion of hydrogen. Notice the similarity to the experimental findings by Lübben and co-workers.

Based on these arguments, we propose that to scale $U_{eq}(X)$ to obtain $U_{iso}(H)$ is not (only) a multiplicative factor, but also an *additive factor* which corresponds to the internal motion of the hydrogen atom. This factor is temperature independent because the temperature dependence is embedded in the variation of $U_{eq}(X)$ with temperature. The factor depends on the bonding environment, *i.e.* it is different for hydrogen atoms in O—H, C—H, CH$_2$ *etc.*, as previously shown (Madsen *et al.*, 2003; Whitten & Spackman, 2006; Munshi *et al.*, 2008).

2.2. Internal vibrations from library of neutron experiments

We propose to derive the isotropic internal motion $U_{iso}^{int}(H)$ from the library of anisotropic internal motion as implemented in the *SHADE2* server (Munshi *et al.*, 2008). This library is reproduced in Table 1. In the column named 'Neutron least-squares estimate' we report the equivalent isotropic displacements corresponding to the internal motion from the *SHADE2* library. These are the values that we propose to use as an additive factor in the riding-atom model. For the hydrogen atom H bound covalently to the heavier atom X we estimate the isotropic displacement parameter as

Table 1
Library of internal motion of hydrogen atoms derived from neutron diffraction experiments (taken from Munshi *et al.*, 2008).

The right-most column reports different estimates of isotropic motion based on the anisotropic values, as discussed by Stewart (1976). All values given in units of 10^{-4} Å^2.

Group	Population	Stretch	Out-of-plane	In-plane	Arithmetic mean	Geometric mean	Neutron least-squares estimate
—C—H aliphatic	67	48 (26)	148 (33)		115	102	113
—C—H aromatic	14	47 (32)	232 (55)	146 (36)	142	116	139
—CH—H	142	58 (40)	153 (35)	238 (75)	150	128	147
—CH$_2$—H	53	57 (39)	367 (73)	182 (33)	202	156	193
—N—H	7	52 (12)	235 (86)	122 (23)	136	114	133
—NH—H	22	51 (19)	200 (104)	138 (29)	130	112	128
—NH$_2$—H	12	34 (20)	172 (61)	135 (19)	114	92	112
—O—H	23	55 (44)	165(53)	108 (38)	109	99	108

Table 2
The structures used to test the model.

Compound	Label in Fig. 2	Measurement temperature (K)	Abbreviation	Reference
Benzidine dihydrochloride	(*a*)	100	BD^{2+}×2Cl$^-$	Hoser *et al.* (2012)
Protonated *N,N,N-peri*(dimethylamino)naphthalene with pyromellitic acid	(*b*)	100	DMANH$^+$×tCA$^-$	Mallinson *et al.* (2003)
Protonated *N,N,N-peri*(dimethylamino)naphthalene with saccharin	(*c*)	100	DMANH$^+$×SAC$^-$	Mallinson *et al.* (2003)
Protonated *N,N,N-peri*(dimethylamino)naphthalene with 4,5-dichlorophthalic acid	(*d*)	100	DMANH$^+$×dCldCA$^-$	Mallinson *et al.* (2003)
Hydrated and protonated *N,N,N-peri*(dimethylamino)-(dimethylamino)naphthalene chloride	(*e*)	100	DMANH$^+$×H$_5$O$_2$$^+$×2Cl$^-$	Hoser *et al.* (2010)
L-Alanine	(*f*)	60	l-ala_60 K	Wilson *et al.* (2005)
L-Alanine	(*g*)	295	l-ala_rt	Wilson *et al.* (2005)
D-Alanine	(*h*)	60	d-ala_60 K	Wilson *et al.* (2005)
D-Alanine	(*i*)	295	d-ala_rt	Wilson *et al.* (2005)
Triptycene	(*j*)	100	T	Sanjuan-Szklarz *et al.* (2015)
Xylitol	(*k*)	122	xylitol	Madsen *et al.* (2003)
1-Methyluracil	(*l*)	15	Muracil	McMullan & Craven (1989)
2-Methyl-4-nitroaniline	(*m*)	100	MNA	Whitten & Spackman (2006)
Decamethylferrocene	(*n*)	100	Fc*	Sanjuan-Szklarz *et al.* (2015)

$$U_{\mathrm{iso}}(\mathrm{H}) \simeq \langle u^2 \rangle_{\mathrm{H}}^{\mathrm{int}} + \langle u^2 \rangle_X^{\mathrm{ext}} \simeq U_{\mathrm{iso}}^{\mathrm{int}}(\mathrm{H}) + M \times U_{\mathrm{eq}}(X). \quad (5)$$

In this model, the temperature dependence is embedded in $U_{\mathrm{eq}}(X)$. This corresponds to the rigid-molecule (TLS) motion in the TLS+ONIOM and *SHADE* approaches for ADP estimation. The M factor takes into account that the hydrogen atom H is typically further away from the centre of mass than atom X. Librational molecular motion will therefore cause a larger amplitude of vibration for H than for X. This extra amplitude will depend on the distance of atoms X and H to the centre of libration, and will therefore be structure dependent, although we propose to use a common factor for all structures (see below).

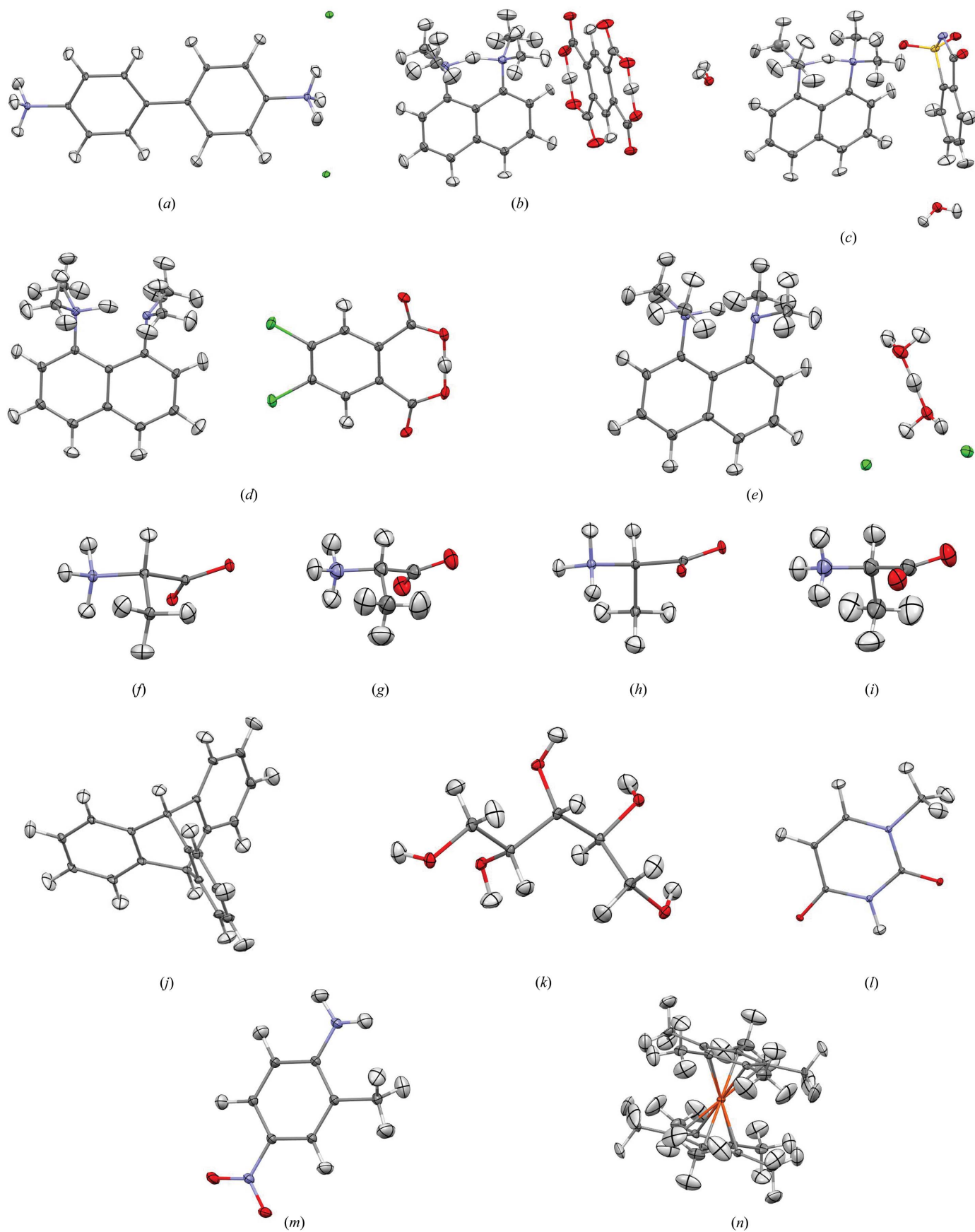## 3. Validation and estimation of the multiplicative factor M

3.1. Test data

In order to validate the proposed riding-atom model, we have picked out accurate neutron structures from the litera-ture. We chose a range of systems that fulfil the rigid-bond test (Hirshfeld, 1976). The structures and references to the original papers are given in Table 2 and Fig. 2. In all we include 182 hydrogen atoms from 14 different data sets, representing a large variety of different H-atom types. For each hydrogen atom we have estimated $U_{\mathrm{iso}}(H)$ by using equation (5) with $U_{\mathrm{iso}}^{\mathrm{int}}(H)$ based on the library values in Table 1 ['Neutron least-squares estimate' column, obtained by using the best least-squares estimate of $U_{\mathrm{iso}}(H)$ (Stewart, 1976)].

3.2. The M factor

The optimal multiplicative factor M was found by least-squares refinement to minimize the difference between $U_{\mathrm{iso}}(H)$ and the reference values $U_{\mathrm{eq}}(H)$, taken from the neutron experiments at different temperatures (from 15 to 300 K). Our best value of M is approximately 1.3.

In this fit $U_{\mathrm{eq}}(H)$ was as above obtained by using Stewart's best least-squares estimate of $U_{\mathrm{iso}}(H)$, but very similar results were obtained by using the arithmetic mean of the eigenvalues of the mean-square displacement matrices.

Figure 2
The structures used to test the model. Names, abbreviations and measurement temperatures are given in Table 2.
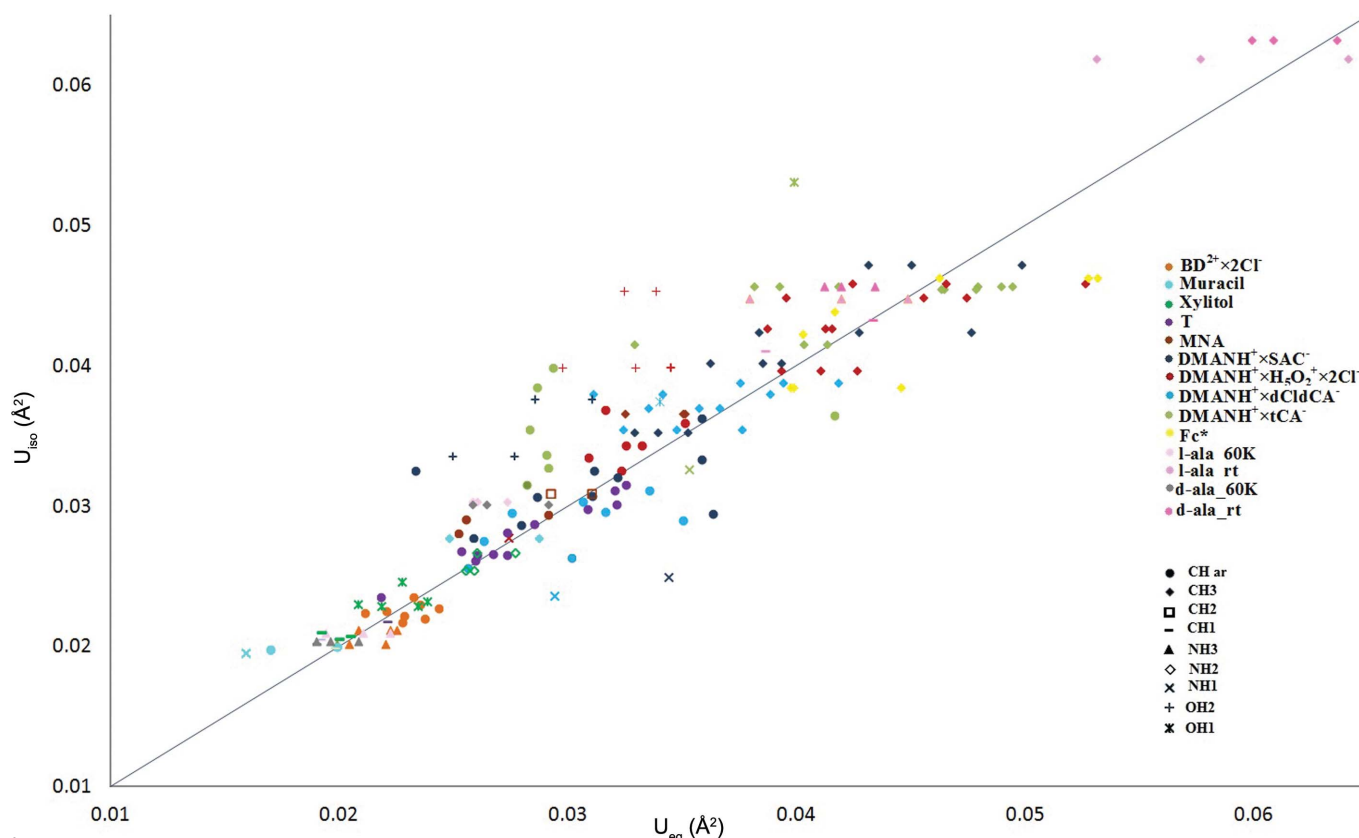
Figure 3
The estimated isotropic displacement of hydrogen atoms (U_{iso}) against the corresponding equivalent displacement U_{eq}, as obtained from the anisotropic MSD matrices from neutron diffraction experiments. The data points are colour coded according to the structures they belong to, and the symbols used signify the type of hydrogen atom.

3.3. Results

By using $M = 1.3$ and the internal motion from Table 1 we obtain the results depicted in Fig. 3. In spite of the very simple model we obtain quite satisfactory agreement of the $U_{iso}(H)$ with the $U_{eq}(H)$ obtained from the neutron ADPs. The mean absolute difference between $U_{eq}(H)$ and $U_{iso}(H)$ is 0.0025, whereas the calculated root-mean-square deviation equals 0.0035. The largest deviations are found for the hydrogen atoms from the proton sponge compounds (DMANH$^+$×tCA$^-$). $U_{iso}(H)$ estimated for hydrogen atoms involved in strong and moderate hydrogen bonds, $e.g.$ for hydrogen atoms from water molecules, are in slightly worse agreement with calculated $U_{eq}(H)$ than $U_{iso}(H)$ obtained for aromatic and methyl hydrogen atoms. The test structures represent temperatures from 15 K through to 100 K to room temperature, and our results indicate that the model can be used at all temperatures.

4. Conclusions

We have developed a model to estimate isotropic displacement parameters[1] for hydrogen atoms. The model is a riding-atom approximation, where the isotropic displacement of hydrogen atom H bound to atom X is

$$U_{iso}(H) \simeq U_{iso}^{int}(H) + 1.3 U_{eq}(X). \qquad (6)$$

The internal motion $U_{iso}^{int}(H)$ is derived from the *SHADE* database and given in the column 'Neutron least-squares estimate' of Table 1. The equivalent isotropic displacement $U_{eq}(X)$ of atom X is either the normally used arithmetic mean of the eigenvalues of the atomic mean-square displacement matrix or Stewarts 'least-squares estimate'.

Our model gives fairly good estimates of the test data, and provides an approach that can be easily implemented in structure-refinement programs.

Acknowledgements

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[1] We note that approximate anisotropic displacement parameters can be estimated using the same approach, simply by replacing $U_{eq}(X)$ in equation (6) with the anisotropic displacement matrix and using the *SHADE2* library to create internal motion. This approach would also be straightforward to implement in structure-refinement programs.

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