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An extended rigid-body model for molecular crystals.

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The rigid body model for molecular motion in crystals assumes a negligible amplitude for internal vibrational modes. This results in too small a value for the displacements of the hydrogen atoms as these are the lightest and are generally peripheral. This is shown to be important for neutron scattering by extending the rigid-body model. Each hydrogen atom is given an extra anisotropic displacement, all determined by three parameters. The values of these parameters for three examples, naphthalene, anthracene and pyrene, agree very well with that expected. Comparison is made with a calculation on benzene.

Ever since the work of Cruickshank (1956) authors have been examining the anisotropic temperature factors of atoms in molecular crystals for rigid body motion. We must make the assumption that all the thermal displacement of each atom is determined by two or at most three tensors, **T**, **L**, and **S** (Schomaker & Trueblood, 1968). These are respectively the mean-square translational displacement, the mean-square rotational displacement and a screw tensor for the molecule.

Most authors analyse their anisotropic temperature factors at the end of refinement, but if the model is good it is worth applying a constraint to the refinement so that the temperature factors always agree strictly with **T**, **L**, and **S**. This requires in general 20 parameters instead of 6 parameters per atom. This has proved most successful (Pawley, 1966, 1971), but the later refinements have shown that the model is weaker for neutron diffraction results.

The neutron scattering effect of hydrogen and deuterium is comparable with that of most atoms, whereas with X-ray scattering their effect is only of minor importance. These atoms, being of small mass, suffer the greatest displacements in internal modes of vibration, and this is further increased by the fact that these atoms usually occupy a peripheral place in the molecule. The rigid body model of molecular motion necessitates the assumption that the internal modes of vibration produce a negligible displacement. We are thus assuming that the larger amplitudes that the hydrogen atoms must have are unimportant. Although good enough for X-ray diffraction results this assumption becomes rather poor when using neutron data.

The simplest way of improving the rigid body model is to give all hydrogen atoms the same variable extra isotropic temperature factor. This has been tried successfully by Pawley (1971) with the following result.

	Extra isotropic temperature factor, Å^2	
	Observed	Expected
Naphthalene-d$_8$	0·0063 (9)	0·0063
Anthracene-d$_{10}$	0·0063 (3)	0·0063
Pyrene-h$_{10}$	0·0139 (7)	0·0126

The 'expected' value comes from a calculation on benzene in the free state (see Johnson, 1970). From Johnson's figure (Fig. 1) we have

mean-square displacement of C = 0·0013 Å^2
mean-square displacement of H = 0·0139 Å^2

and the difference gives the value tabulated above opposite pyrene-h$_{10}$. The corresponding value for the deuterated molecules is roughly half this value.

The success of this analysis and the striking anisotropy of Johnson's figure prompted the author to extend the model further. All hydrogen atoms are now given the same extra anisotropic temperature factor, requiring three extra parameters rather than one. These three are the extra squared displacement along the C–H bond, then that across the bond and in the molecular plane, and then that out of the molecular plane. The expected values of these parameters are, from the Figure

I	along the bond	$0{\cdot}077^2 - 0{\cdot}036^2 = 0{\cdot}005$ Å^2, (0·002)
II	across the bond in plane	$0{\cdot}116^2 - 0{\cdot}029^2 = 0{\cdot}013$ Å^2, (0·006)
III	out of plane	$0{\cdot}150^2 - 0{\cdot}041^2 = 0{\cdot}021$ Å^2, (0·010)

The numbers in parentheses are those expected for the deuterated molecules.

Refinement for the same three examples as above gives values

	I	II	III
Naphthalene-d$_8$	0·005 (1)	0·008 (2)	0·021 (3)
Anthracene-d$_{10}$	0·0024 (5)	0·0093 (7)	0·0178 (11)
Pyrene-h$_{10}$	0·005 (1)	0·016 (2)	0·029 (2)

The closeness of agreement between theory and experiment suggests that these three parameters have a high physical significance. Let us now investigate statistical significance.

The result for pyrene comes from a refinement where the molecule is constrained to retain the free state *mmm* symmetry, and where the temperature factors agree with the three tensors **T**, **L** and **S**. Without these extra parameters for the hydrogen atoms, that is with their values at zero, the conventional R index was 5·6%. With one extra isotropic temperature parameter this fell to 4·8%, finally

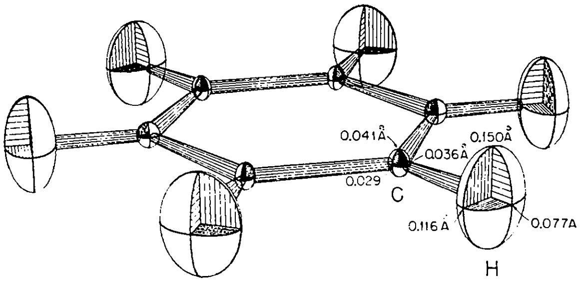

Fig. 1. Benzene internal vibration.

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reaching 4·5 % with the three extra parameters. Clearly the single parameter gave an enormous improvement, so let us simply test whether the introduction of two more parameters gives a significant improvement. The R index ratio is $4{\cdot}8/4{\cdot}5 = 1{\cdot}067$, there are 1008 observations and 44 parameters in the better fitting model. We now calculate the percentage points of the appropriate distribution as described by Hamilton (1965), with the use of the approximation of Pawley (1970). At the 1 % level we get 1·007, which shows the improvement to be highly significant. Strictly, the weighted sum of squares of the deviations should be used for this test but the simple ratio suffices at this level of significance. A completely unconstrained refinement for pyrene gave $R = 3{\cdot}4$ %, (Hazell, Larsen & Lehmann, 1970).

The R indices for the refinements of naphthalene and anthracene (Lehmann & Pawley, 1970) are

	Model: **T, L** plus anisotropic deuterium contribution	Unconstrained	Number of observations
Naphthalene-d_8	3·3	3·3	330
Anthracene-d_{10}	4·0 (9300)	3·4 (6980)	951

The values in parentheses are the weighted sums of squares of deviations.

The conclusion of this paper is simple: it is considered that the rigid body model is greatly improved by allowing an anisotropic internal mode contribution to the temperature factors of the hydrogen or deuterium atoms.

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Absorptionsfaktor für ebene Pulverproben unter Berücksichtigung der Primärstrahldivergenz.

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Following the calculations of Kunze an expression for the absorption factor of flat powder samples in Bragg–Brentano arrangement is given with regard to any intensity distribution in the primary beam. The primary beam is characterized by the 1st and the 2nd moment of the intensity distribution.

Für den Absorptionsfaktor an ebenen Pulverproben im symmetrischen Braggfall erhält man unter der Voraussetzung eines einfallenden Parallelstrahlbündels $\sin\theta/2\mu$. Für Intensitätsmessungen, die nicht genauer als 1% sein sollen, sind diese Voraussetzungen in den üblichen Diffraktometeranordnungen genügend gut erfüllt. Für genauere Intensitätsmessungen muss man neben anderen Faktoren den Einfluss der Intensitätsverteilung im Primärstrahl berücksichtigen. Dazu kann man der von Kunze (1964) durchgeführten Berechnung des Absorptionsfaktors folgen, wenn man zusätzlich im Primärstrahl eine beliebige Intensitätsverteilung $i(\omega)$ zulässt und die Integration über den gesamten Divergenzbereich des Primärstrahls erstreckt. Belässt man $i(\omega)$ weiterhin unter dem Integralzeichen und führt diese Rechnung durch, erhält man im Ergebnis für den Absorptionsfaktor

$$\frac{\sin\theta}{2\mu} \,.\, [1 + 3\,\mathrm{ctg}\,\theta \,.\, \Omega_s + \tfrac{1}{2}\,(15\,\mathrm{ctg}^2\,\theta - 2\,\csc^2\theta)\Omega_t^2]\,,$$

wobei Ω_s bzw. Ω_t^2 das 1. bzw. 2. Moment der Intensitätsverteilung $i(\omega)$ im Primärstrahl und θ der Braggsche Winkel ist.

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