Nauwkeurige bepaling van de electronenverdeling in kristallen en onderzoek naar de invloed van thermisch diffuse verstrooiing
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SUMMARY

The aim of the investigation described in this thesis is to study the changes in the electron density distribution due to chemical bonding. This work is part of the research being done in the laboratory of structural chemistry in Groningen on the accurate determination and interpretation of electron density distributions in crystals. The experimental electron density distributions are obtained by X-ray diffraction. The changes due to chemical bonding ('bonding effects') are studied by means of difference Fourier syntheses displaying the difference between the actual electron density distribution in the crystal and that corresponding to a model of non-bonded atoms. The positions and vibrations of the atoms of the model should be equal to those in the crystal. In the absence of structural information from other sources, such as neutron diffraction, the best picture of the bonding effects is obtained by deriving the structural parameters from X-ray reflections with high sinθ/λ values and by using low order reflections for the calculation of the map (sections 7.7.2 and 7.9.1).

In the first, more theoretical, part of the thesis we discuss the errors in the structural parameters and in the difference densities due to thermal diffuse scattering (TDS). Chapter 2 starts from formulae given in the literature and gives a description of the thermal vibrations
in the crystal and their influence on the scattering of X-rays. The vibrations are assumed to be harmonic. Formulae for the zero order (Bragg) scattering and the first order TDS are derived (see 2-38 and 2-53). As the distribution \( I_1^1(S) \) of the TDS in reciprocal space appears to be peaked at the reciprocal lattice points, the integrated X-ray intensities contain, in addition to the integrated Bragg intensity, the TDS intensity \( I(TDS) \). The intensity \( I(TDS) \) is equal to the total TDS intensity minus the contribution of TDS to the background. For intensities measured by a diffractometer the total TDS intensity is obtained by integration of \( I_1^1(S) \) over \( S \) for the volume of reciprocal space from which scattered radiation is detected by the counter during the scan. The computer programmes used for the integration are described in chapter 3.

The most fundamental assumption made in the derivation of the formulae given for the TDS scattering in chapters 2 and 3, is that only first order thermal diffuse scattering from acoustic branches is considered and that these branches are approximated by the linear relation

\[
\omega_j(\hat{g}) = 2\pi v_j(\hat{\omega}) g \quad \text{with} \quad \hat{\omega} = \omega / g, \quad \omega_j(\hat{\omega}) = \text{angular frequency},
\]

\[
v_j(\hat{\omega}) = \text{velocity and} \ g = \text{wave vector of the lattice mode} (j, g), \ j = 1-3 \text{for the acoustic modes}. \]

The neglect of dispersion implies that the complex amplitude vectors \( \Psi_j(\kappa, g) \) in formula 2-6 are equal for all atoms \( \kappa \) and that \( I(TDS) \) is proportional to \( |F(H)|^2 \), \( F(H) \) being the structure factor of reflection \( H \).

The Fourier transforms \( Q \) depend on the order to the reciprocal lattice points, and the measurements, cubic in form, for quantities above 5.42 and of \( H \) and \( NH_4 \) made to eliminate these in the computation, are from chapter (1965). From these...
The formula obtained reads
\[ I(TDS, H) = T|H|^2 |F(H)|^2 Q(C, H, T) \]
where \( Q \) depends in a complicated way on the anisotropic fourth order elastic tensor \( C \) of the crystal (which is related to the velocities \( v_j(\mathbf{R}) \)), on the reflection \( H \) considered and the diffraction geometry used during the intensity measurement, and on the temperature \( T \). Contrary to earlier authors we have worked out the formulae for non-cubic as well as for cubic crystals and have accounted for quantum effects. It appeared, however, that for diffraction geometries used for accurate intensity measurements, quantum effects can be neglected for temperatures above 5 K. In that case \( Q \) does not depend on \( T \). In figs. 4.2 and 4.3 \( a(H) = I(TDS, H)/|F(H)|^2 \) is given as a function of \( H \) and of \( T \) for some reflections of \( \text{C}_6\text{H}_5\text{COCOC}_6\text{H}_5(\text{DBZ}) \) and \( \text{NH}_4\text{H}_2\text{O}_4\cdot\text{H}_2\text{O}(\text{AHO}) \). In section 3.5.4 an attempt is made to estimate the errors in \( I(TDS) \) resulting from the above mentioned assumptions.

In usual X-ray diffraction studies \( I(TDS) \) is not eliminated from the measured X-ray intensities, so that these intensities contain systematic errors. The resulting errors in the coordinates, thermal parameters and difference densities have been calculated for DBZ and AHO in chapter 4. The structure determined by Brown and Sadanaga (1965) and by Küppers (1973) respectively have been used. From these structure models \( M \), consisting of vibrating...
spherically symmetric atoms, structure factors \( F(u,H) \) have been calculated and transformed to 'experimental' intensities by accounting for the TDS contribution:
\[
|F(\text{exp},H)|^2 = |F(u,H)|^2 + I(TDS) \].
Least squares refinements based on \( |F(\text{exp},H)| \) have been done. The differences between final structural parameters and model \( M \) parameters are considered as 'TDS-errors'. The calculations have been performed for temperatures of 293, 110 and 150 K; four \( \sin(\theta)/\lambda \) ranges were considered during the refinement. The results are given in tables 4-4 and 4-5.

The errors in the coordinates are very small, but those in the thermal parameters are appreciable at room temperature as expected from fig. 4.2. To check the influence of \( I(TDS) \) on the difference density various difference maps, differing e.g. in the \( \sin(\theta)/\lambda \) range used to derive the parameters or to compute the map, have been calculated. The resulting difference densities can be considered as 'TDS density errors'. The map of fig. 4-5 is computed with all \( [F(\text{exp},H) - F(u,H)] \) terms. Further results are given in table 4-6 for the centres of the bonds and for the positions of the atoms. Map c for AHO at \( T=110^\circ K \), corresponds best with the maps calculated for the study of bonding effects in chapter 7. Within the theoretical approximations made, we have estimated errors for these maps ranging from 0.00-0.03 e\( A^{-3} \) at the centres of the bonds and from 0.05-0.08 e\( A^{-3} \) at the atomic positions.
From table 4-6 it is seen that the 'TDS density errors' decrease with decreasing temperature. The best procedure to avoid these errors is to measure the intensities at low temperatures, say 150K. Exact calculation of I(TDS) and thus the possibility of making good theoretical corrections has to await the availability of good models for intermolecular interactions in crystals.

The second, more experimental, part of the thesis contributes to the study of electron density distributions on single, double and triple C-C bonds (see also Ruysink, 1973). For this study we have chosen compounds derived from 2,5-dimethylhexane-2,5-diol

\[
\text{CH}_3\quad \text{C-CH}_p\quad \text{CH}_3
\]

\[
\text{CH}_3\quad \text{C-CH}_3\quad \text{CH}_3\quad \text{C-CH}_3
\]

with \( p=1 \) for the single bond (compound called I), \( p=2 \) for the double bond (II-cis and II-trans) and \( p=3 \) for the triple bond (III). Structure determinations of I and III at 1100K, based on intensities collected without special precautions, are described in sections 6.1 to 6.4. The space groups of I and III are \( P2_1/c \) and \( P\overline{1} \) respectively, for lattice dimensions see table 6-1. For each compound the unit cell contains one independent molecule at a general position and one (a half independent) molecule around an inversion centre. For a picture of the molecules and the numbering of the atoms see fig. 6.6.
The group C(4)[(OH)(CH$_3$)$_3$] in III shows disorder and is not considered in the discussion of the electron densities in chapter 7. In section 6.5 the crystal packing of I and III is discussed and in section 6.6 the molecules of I and III are compared with those of II-cis and II-trans as determined by Ruysink (1973).

An accurate determination of the electron density has been done for the compound III-D in which the CH$_3$ groups of III are replaced by CD$_3$ groups. The deuterated compounds has been chosen in view of a possible future elastic and/or inelastic neutron scattering study. The synthesis and crystallization of the compound is described in chapter 5. The X-ray diffraction intensities have been measured at 90$^\circ$K on an accurately aligned Nonius CAD4 diffractometer, with the $\theta/2\theta$ scan technique and Mo radiation (chapter 7). The background corrections (and thus the random errors associated with it) were kept as small as possible by recording the complete reflection profiles and determining the peak width as accurately as possible. Dispersion of the X-rays was kept small by use of a graphite monochromator ($\Delta\lambda/\lambda = 0.03$, care was taken to obtain an incident beam with homogeneous intensity distribution). Each reflection was measured three times with different reflection geometry. Checks were made on the occurrence of multiple diffraction and intensities which were shown to be in error were eliminated from the list.

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disorder and is electron density. The molecules I-cis and II-cis were kept as small as possible during the refinement study. The structural parameters were obtained from full angle and from a high order \((0.7<\sin \theta/\lambda<1.0 \text{ \AA}^{-1})\) least squares refinement (see tables 7.4 till 7.9). The occurrence of correlation between structural parameters of the model of spherically symmetric atoms and bonding effects during the full angle refinement is, for instance, shown by the fact that in the high order refinement the C=C bond is 0.004 \text{ \AA} longer than in the full angle refinement (for a comparison of bond lengths, see table 7-10). For the high order refinement the correlation is expected to be small, but finite.

The standard deviation of the difference density (parameters from high order refinement, reflections up to \(\sin \theta/\lambda= 0.65 \text{ \AA}^{-1}\) used for the map) is estimated at 0.025 e\text{\AA}^{-3}. It is noteworthy that in comparison with this, small, standard deviation the spread in difference densities on the centres of the bonds is small. Observed values are 0.57-0.59 for C=C, 0.36-0.37 for C(sp)-C(sp\(^3\)) and 0.32-0.36 e\text{\AA}^{-3} for C-CH\(_3\). Sections of the map are shown in figs. 7-5 till 7-8. For sections perpendicular to the various C-C bonds and through the centres of the bonds the difference density \(D\) is given as a function...
of the distance $r$ to the bond in fig. 7-9, the deviation of the parameter $A_s$ from 1 gives the deviation from radial symmetry in these sections (formula 7-18). In all cases there is a surplus of electrons on the bonds, this surplus was calculated at 0.275 e for C=C, at 0.069 e for C(sp)-C(sp$^3$) and at 0.070 e for C-CH$_3$. At the positions of the atoms a negative difference density is observed. For the lone pairs (at the right hand side of fig. 7-6) it is noteworthy that the maximum in the difference density lies close to the hydrogen bond for which the oxygen atom is acceptor. In table 7-11 the C(sp)-C(sp$^3$) and C-CH$_3$ densities are compared with those in other compounds (mind that the sucrose values are not accurate as the structure is acentric; multiplication by $V$ accounts for differences in thermal motion).

A theoretical calculation of the dynamic difference density has been performed for the model compound III-4H in which the four CH$_3$ groups of III are replaced by H (section 7.9.4). A small (6,3/3) GTO basis set was used for the ab initio calculations. A section of the theoretical difference density is shown in fig. 7-10a. For C-O and the lone pair region the experimental and theoretical maps show quite large differences. For C=C and C(sp)-C(sp$^3$) no large differences are observed between theory and experiment, but the experimental difference between the maxima on the two bonds, 0.21 eÅ$^{-3}$, is small.
the deviation from
the theoretical difference, 0.27 eÅ⁻³. This may be due to a small correlation between structural parameters and bonding effects during the high order refinement, which correlation tends to equalize the bonding maxima. It should be stressed that the theoretical maxima on C≡C and C(sp)-C(sp³) are appr. 10 per cent too low due to the use of the small basis set, whereas the experimental values are too low due to correlation (appr. 10 per cent on the average, but more for the C≡C than for the C(sp)-C(sp³) bond). Further research to improve the quantum mechanical calculations and the experimental work, especially in connection with the correlation problem, is planned for the near future.