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Can X-ray Data Distinguish Bonding Effects from Vibrational Smearing?

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The frequent practice of combining X-ray and neutron diffraction for distinguishing vibrational smearing from charge deformation due to chemical bonding is neither necessary nor completely satisfactory. The two effects occur principally in distinct regions of real and reciprocal space. They can be distinguished by X-ray data alone provided these extend to reciprocal radii $d^* > 2$ Å^{-1} and provided the refinement program allows explicitly for the bonding deformation. The success of this separation can be tested by comparison of the vibration ellipsoids of bonded atom pairs, which should have equal amplitudes in the bond direction. Application of this 'rigid-bond' test to four recent refinements using the charge deformation model shows the vibration parameters to be largely unbiased, as those from parallel spherical-atom refinements are not. Hydrogen vibration parameters cannot be derived from X-ray data because of large deformation densities at the nuclei; nor do they satisfy the rigid-bond postulate.

The correlation problem

It has long been recognized that in an X-ray diffraction experiment the effects on the charge distribution of chemical bonding and of vibrational smearing tend to be highly correlated (Dawson, 1964; Stewart, 1968, 1973*a*; Sakurai & Ito, 1969). The usual refinement program contains many adjustable parameters to describe the atomic vibrations but none for bonding effects. As a result the vibration parameters, and to a lesser degree the coordinates, do their best to allow for the neglected bonding effects and do not describe the true vibrational behaviour. These errors, in turn, cause the final difference density to present a distorted picture of the charge migration due to chemical bonding.

A widely adopted solution is to measure both X-ray and neutron data for the same structure. In the method pioneered by Coppens (1967) atomic coordinates and vibration parameters deduced from the neutron study are adopted for the calculation of X-ray structure factors; an X-ray difference synthesis ϱ_{X-N} is then computed for displaying the bonding density. Despite its many successes (*e.g.* Coppens, 1974 and references therein; Almlöf, Kvick & Thomas, 1973; O'Connor, 1973; Griffin & Coppens, 1975; Thomas, Tellgren & Almlöf, 1975) the method has severe shortcomings. It requires two complete sets of diffraction measurements and the final result is burdened with the experimental errors of both sets of data. Considerable uncertainty, exemplified by the study of cyanuric acid (Coppens & Vos, 1971), may arise from the difficulty of matching the crystal temperatures in the X-ray and neutron experiments. Finally, the ϱ_{X-N} map is smeared by thermal vibration and is thus not ideally suitable for comparison with other structures or with theoretical predictions.

A simpler alternative, needing X-ray data alone, relies on the firmly accepted generalization that charge deformation due to chemical bonding is virtually confined to the valence orbitals, which make little contribution to the charge density near the atomic nuclei. Reflexions at large reciprocal radii should therefore be almost free of bonding effects and properly reflect the vibrational smearing of the atomic cusp densities alone (Stewart, 1968; Groenewegen, Zeevalkink & Feil, 1971; Bentley & Stewart, 1974). Hence we can discard the inner reflexions and refine the vibration parameters, and possibly the coordinates as well, from the high-angle data (Jeffrey & Cruickshank, 1953; Ruysink & Vos, 1974). With these parameters thus established, we can then examine the low-angle intensities for evidence of the charge deformation.

Such a partitioning of the X-ray data is easily implemented and has in fact been used to produce refined atomic parameters that appear largely free of systematic error (Coppens & Vos, 1971; Hanson, Sieker & Jensen, 1973; Cromer & Larson, 1974; Von Dreele, 1975; Stevens & Hope, 1975). But it is far from elegant. There is no well defined reciprocal radius where bonding effects become abruptly inappreciable. The optimal lower limit in d^* for a high-angle refinement can be approximated only by crude qualitative arguments or by hit-or-miss experimentation and may well vary widely from atom to atom in the same structure. Clearly, we can do better.

Charge deformation models

The obvious answer is to retain all the measured reflexions and use a model for structure-factor calculations that allows explicitly for the bonding deformation. Several models are available: the expansion in atomic orbital products due to Stewart (1969), various forms of multipole expansion (Dawson, 1967; Kurki-Suonio, 1968; Stewart, 1973*b*), and the basically similar deformation model of the present author (Hirshfeld, 1971; Harel & Hirshfeld, 1975). Each of these models attempts to represent either the total density (rarely), the valence density (total minus atomic cores), or the deformation density (total minus spherical atoms) as a sum of localized density functions with adjustable coefficients. With such a model no arbitrary division of the X-ray reflexions into inner and outer regions is needed; the derivatives entering into the least-squares matrix ensure that the vibration parameters are primarily determined by the high-angle data, the charge-density coefficients by the low-angle data. This approximate separation, which is needed to assure convergence, rests on the exclusion from the density expansion of basis functions with excessively steep radial dependence at the atomic nuclei. With a least-squares program based on any of these models, a single refinement should provide an unbiased set of coordinates and vibration parameters together with a detailed description of the charge distribution (*e.g.* McConnell & Sanger, 1970; Cromer & Larson, 1974; Larson & Cromer, 1974; Harel & Hirshfeld, 1975). As an added benefit, the model is commonly defined so that the resulting density map refers to the non-vibrating molecule and can serve directly for theoretical interpretation and analysis.

It should be emphasized that the method advocated, while not requiring neutron-diffraction measurements, can be readily adapted to make use of neutron data if these have been measured and are deemed sufficiently reliable. The recommended procedure (Duckworth, Willis & Pawley, 1969) would be to combine X-ray and neutron data in a single refinement for the simultaneous determination of all parameters. An easier but less legitimate alternative is to refine the coordinates and vibration parameters against the neutron data alone and then constrain their values while deriving the charge density coefficients from the X-ray data (Jones, Pautler & Coppens, 1972; Matthews, Stucky & Coppens, 1972; O'Connor & Maslen, 1974).

The qualitative arguments outlined above cannot hope to win many adherents without the support of solid experimental results. It is therefore appropriate to summarize some recent data that demonstrate the practical utility of a suitably flexible refinement model.

To prove that a structure refinement has yielded an unbiased result, we need an objective standard against which to judge the parameters obtained. Such a standard for the charge distribution is not easily established; small molecules for which one might adduce *ab initio* calculations of Hartree–Fock quality or better rarely crystallize at convenient temperatures for precise crystallographic studies. But the vibration parameters should be more amenable to verification. If we can show that these have been correctly determined we can thereby acquit both the vibration parameters and the charge distribution of the suspicion that each is contaminated by a faulty description of the other.

Rigid-bond test

How, then, can we prove the correctness of a refined set of vibration parameters? To begin, it is well established that the intermolecular lattice vibrations contribute most of the vibrational motion in a molecular crystal. Of the intramolecular modes, the most important are those involving torsional and, to a smaller extent, angle-bending distortions. In comparison with these the bond-stretching vibrations are usually negligible in amplitude. Such reasoning leads us to the 'rigid-bond' postulate, which asserts (Harel & Hirshfeld, 1975) that the *relative* vibrational motion of a pair of bonded atoms has an effectively vanishing component in the direction of the bond. It follows that if $z^2_{A,B}$ denotes the radius of the vibration ellipsoid of atom A along the vector from A to B, we expect that for every covalently bonded pair of atoms A and B $z^2_{A,B}=z^2_{B,A}$, *i.e.* the two atoms have equal mean square vibration amplitudes along their mutual bond. For atoms at least as heavy as carbon, it can be estimated that this equality should normally hold to within well under 0·001 Å^2. Thus, if the vibration parameters from a given refinement satisfy this equation, within the expected tolerance, for every bond in the molecule, we have good objective evidence of the physical acceptability of the results. We can then fairly conclude that the deformation map obtained from the same refinement is at least free of bias from improperly derived vibration parameters. We may often argue further that a refinement giving true vibration parameters is unlikely to have severely falsified the other parameters.

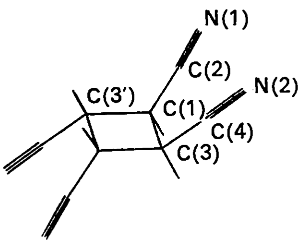
The proposed test is related to, but more widely applicable than, one based on the rigid-body model (Cruickshank, 1956; Schomaker & Trueblood, 1968), which has sometimes been invoked for a similar purpose (*e.g.* Sakurai & Ito, 1969). That more stringent test neglects *all* internal vibrations, often with less than compelling justification. Where the rigid-body model is applied it of course incorporates the rigid-bond postulate in an altered algebraic form. Thus a convenient check of the relevant computer routines is to verify that calculated atomic vibration parameters derived from a set of rigid-body molecular vibration tensors accurately satisfy the rigid-bond condition. Note, incidentally, that the required resolution of atomic mean square displacements into components parallel and perpendicular to each bond axis is often obtained as a by-product of bond-length corrections according to the riding model of Busing & Levy (1964). Algebraic details are given in the Appendix.

Experimental evidence

Tables 1, 2, 3, and 4 show the application of this test to four structures recently refined in this laboratory: tetracyanocyclobutane, diketopiperazine, *p*-nitropyridine-*N*-oxide, and 2-cyanoguanidine (Harel, Hecht & Hirshfeld, 1975). The first two are based on X-ray data measured by Harel (1975) at a temperature near 160K, the third is based on data at 30K kindly supplied by Professor P. Coppens of S.U.N.Y. at Buffalo (Wang, Blessing, Ross & Coppens, 1976), and the last is a room-temperature structure for which highly accurate

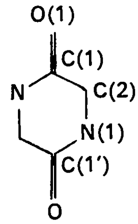
X-ray intensities were obtained from Professor H. Hope of the University of California at Davis. Each table lists the values of $z^2_{A,B}$ and $z^2_{B,A}$ for all bonded pairs of first-row atoms in the corresponding structure. Values from a spherical-atom refinement are listed for comparison alongside those from the deformation model. The estimated standard deviations of the vibration parameters, deduced from the least-squares matrix, were in all cases roughly isotropic and approximately equal for the several atoms. Accordingly, only an average value of $\sigma(u^2)$ is tabulated for each refinement. Inspection of the Tables shows that the use of the deformation model has generally yielded vibration parameters in almost as good accord with the rigid-bond postulate as the estimated random errors permit. By contrast, the spherical-atom refinements have produced systematic errors that are often many times larger than the random errors.

Table 1. *Tetracyanocyclobutane near* 160K. 1781 *independent reflexions to* $d^*_{\max}=2{\cdot}09$ Å^{-1}



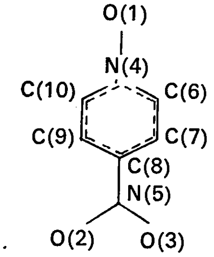
		Spherical-atom refinement $\sigma(u^2)\sim 0{\cdot}0004$ Å^2		Deformation model $\sigma(u^2)\sim 0{\cdot}0003$ Å^2	
A	*B*	$10^4z^2_{A,B}$	$10^4z^2_{B,A}$	$10^4z^2_{A,B}$	$10^4z^2_{B,A}$
C(1)	C(3)	138 Å^2	142 Å^2	135 Å^2	138 Å^2
C(1)	C(3')	124	128	118	121
C(1)	C(2)	146	190	138	141
C(3)	C(4)	119	164	117	121
C(2)	N(1)	194	204	146	158
C(4)	N(2)	166	175	123	136
r.m.s. discrepancy		26		8	

Table 2. *Diketopiperazine near* 160K. 1311 *independent reflexions to* $d^*_{\max}=2{\cdot}15$ Å^{-1}



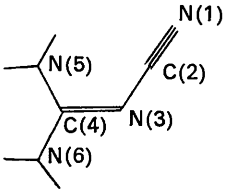
		Spherical-atom refinement $\sigma(u^2)\sim 0{\cdot}0003$ Å^2		Deformation model $\sigma(u^2)\sim 0{\cdot}0004$ Å^2	
A	*B*	$10^4z^2_{A,B}$	$10^4z^2_{B,A}$	$10^4z^2_{A,B}$	$10^4z^2_{B,A}$
C(1)	C(2)	129 Å^2	127 Å^2	118 Å^2	115 Å^2
C(2)	N(1)	131	131	132	130
N(1)	C(1')	111	129	109	118
C(1)	O(1)	136	120	120	118
r.m.s. discrepancy		12		5	

Table 3. *p-Nitropyridine-N-oxide at* 30K. 2201 *independent reflexions to* $d^*_{\max}=2{\cdot}07$ Å^{-1}



		Spherical-atom refinement $\sigma(u^2)\sim 0{\cdot}0003$ Å^2		Deformation model $\sigma(u^2)\sim 0{\cdot}0002$ Å^2	
A	*B*	$10^4z^2_{A,B}$	$10^4z^2_{B,A}$	$10^4z^2_{A,B}$	$10^4z^2_{B,A}$
N(4)	C(6)	60 Å^2	48 Å^2	52 Å^2	52 Å^2
C(6)	C(7)	66	65	56	53
C(7)	C(8)	55	66	52	58
C(8)	C(9)	57	53	51	45
C(9)	C(10)	62	69	55	57
C(10)	N(4)	64	70	64	65
N(4)	O(1)	46	28	41	38
C(8)	N(5)	40	56	42	47
N(5)	O(2)	72	51	63	56
N(5)	O(3)	66	42	58	50
r.m.s. discrepancy		14		5	

Table 4. 2-*Cyanoguanidine at room temperature.* 1853 *independent reflexions to* $d^*_{\max}=2{\cdot}28$ Å^{-1}



		Spherical-atom refinement $\sigma(u^2)\sim 0{\cdot}0004$ Å^2		Deformation model $\sigma(u^2)\sim 0{\cdot}0003$ Å^2	
A	*B*	$10^4z^2_{A,B}$	$10^4z^2_{B,A}$	$10^4z^2_{A,B}$	$10^4z^2_{B,A}$
C(4)	N(5)	334 Å^2	320 Å^2	301 Å^2	295 Å^2
C(4)	N(6)	280	269	261	250
C(4)	N(3)	271	253	240	239
N(3)	C(2)	292	349	273	279
C(2)	N(1)	335	316	266	264
r.m.s. discrepancy		29		6	

Most instructive is the way gross violations of the rigid-bond postulate in the spherical refinements can be correlated with specific features in the corresponding deformation density maps. A clear example is provided by the digonally bonded carbon atoms C(2) and C(4) in tetracyanocyclobutane and C(2) in cyanoguanidine. Each of these atoms is flanked by a pair of prominent bond peaks (Harel, Hecht & Hirshfeld, 1975). In the spherical refinement, this elongation of the atomic charge cloud is necessarily interpreted as implying an extra vibrational motion of the atom in the bonding direction. The spuriousness of this interpretation is obvious when the apparent motion of this atom is compared with that of its neighbour in a different bonding configuration. Thus we find exceptionally large discrepancies for bonds C(1)–C(2) and C(3)–C(4) in Table 1 and bond N(3)–C(2) in Table 4. No such discrepancy arises, in each case, for the C≡N bond, which appears to satisfy the rigid-bond postulate quite well since both its atoms have similarly elevated vibration amplitudes in the bond direction. For the nitrogen atom this excess apparent motion, in the spherical refinement, reflects the neglected triple-bond peak on one side and the compact lone-pair peak on the other.

In nitropyridine-*N*-oxide the spherical refinement has produced z^2 values that are systematically large for nitrogen and small for oxygen (Table 3). In fact the lowering of the oxygen amplitudes in the bond direction is accompanied by an increase in the perpendicular directions. The deformation map (Harel, Hecht & Hirshfeld, 1975) shows that both nitrogen atoms have lost appreciable charge to the surrounding bonds and to their oxygen ligands, leaving the nitrogen with an apparent net positive charge. The extra charge on oxygen is concentrated in a pair of compact lone-pair lobes extending nearly perpendicular to the N–O bond with their maxima straddling the molecular plane. In this structure the major shortcomings of the spherical refinement, as revealed by the rigid-bond test, are evidently associated with the neglected polarity of the N–O bonds.

Other lessons to be drawn from these refinements are somewhat less optimistic. Comparing the last two columns of Table 1 with corresponding figures for the same structure that were listed in Table 3 of Harel & Hirshfeld (1975), we find the two sets of results to differ in a very systematic manner. The mean square amplitudes of all atoms have consistently increased, compared with the earlier values, by about 0·0006 Å^2 isotropically for the carbon atoms, and by 0·0022 Å^2 in the bond direction, 0·0009 Å^2 in the perpendicular directions for nitrogen. Two separate effects are apparent here, attributable to specific differences between the latest refinement and that reported previously. We find, first, a general increase of about 5% in all vibration parameters and, in addition, an extra increase in the apparent motion of the nitrogen atoms, especially in the C≡N bond direction. The former effect is evidently due to an isotropic extinction correction that was applied to all reflexions before the latest refinement was completed. Although not severe, raising the largest F_o by only 4%, this correction seems to have increased all the refined vibration parameters uniformly by more than their estimated standard deviations. What is disturbing is that the rigid-bond test, applied to the output of each refinement separately, gives no indication that one of the data sets suffers from extinction error. Because all vibration parameters are similarly affected there is no anomaly in the relative amplitudes of neighbouring atoms to sound the alarm. This experience contains an obvious warning: not all systematic errors in the vibration parameters will be detected by the rigid-bond test. The possibility must be recognized that other kinds of experimental error as well, such as those arising from thermal diffuse scattering, from imperfect monochromatization, or from instrumental or scanning deficiencies, may similarly lead to errors in the vibration parameters of a sort not readily detected by such a test. The strength of this test may, therefore, lie more in its sensitivity to defects in the model or in the refinement procedure than in its ability to uncover unsuspected systematic errors in the intensity data. With respect to the latter problem, it may be comforting to surmise that to the extent that systematic experimental errors are absorbed in the vibration parameters they are that much less likely to falsify the charge deformation. This is not a persuasive argument for tolerating avoidable errors in the measured intensities.

The specific differences noted above in the nitrogen vibration parameters are probably related to changes in the deformation model, which was modified since the earlier refinement by the inclusion of basis functions with a $\cos^4\theta$ angular dependence, by the elimination of two spherical terms on each atom, and by the explicit refinement of the breadth parameters γ (Harel, Hecht & Hirshfeld, 1975). The latest vibration parameters satisfy the rigid-bond postulate for the C≡N bonds much less closely (Table 1) than did those from the earlier refinement (Harel & Hirshfeld, 1975). This behaviour reinforces other indications that the supposed improvement in the deformation model may actually have worsened the description of the charge distribution around nitrogen, especially in the lone-pair region. For example, the new deformation map shows a much reduced lone-pair peak, in far poorer agreement with the Hartree–Fock difference densities for HCN and NCCN (Hirshfeld, 1971). The precise source of the difficulty remains obscure, however, and is not obviously illuminated by the observation that the apparently similar C(2)≡N(1) bond in cyanoguanidine, which also shows a small lone-pair peak, easily passes the rigid-bond test (Table 4). While the results on tetracyanocyclobutane thus raise some question about the details of the deformation model, they also illustrate the sensitivity of the rigid-bond test to such details.

Are these results general?

The wider relevance of the results presented above must be judged in the light of certain common features shared by all four structures studied. All consist of atoms no heavier than oxygen, all were refined with the same deformation model, and all used X-ray data extending to a reciprocal radius $d^*_{\max}$ exceeding 2 Å^{-1}. The first limitation is of scant pertinence to the present context; for atoms beyond the first row, charge deformation features will be even less important relative to the total density and will overlap less with the vibrational effects. Where heavy atoms are present it is the larger random errors, not systematic correlations among parameters, that are likely to hamper charge deformation studies. The second limitation is probably also of little import. Other bonding-density models would likely succeed as well or better, though it would perhaps be reassuring to have the relevant evidence on the performance of alternative models currently employed. The third restriction is essential. With X-ray data confined to reciprocal radii much under 2 Å^{-1}, correlation between the vibration parameters and the coefficients of the charge-deformation expansion becomes quite troublesome and may prevent stable convergence. Often, judicious constraints on the vibration parameters may save such a refinement from failure, but then we forfeit the benefits of the *a posteriori* verification of these parameters by the rigid-bond test. In the absence of adequate high-angle data, the optimal strategy must be tailored to the circumstances of each particular structure. But in any case the explicit demonstration of large parameter correlations, by the use of an appropriate deformation model, is always preferable to a spherical-atom refinement whose underestimated standard deviations merely conceal large systematic errors in the parameters.

Finally, we must concede that our entire discussion suffers from a serious deliberate omission; nothing has been said about hydrogen atoms. In fact the hydrogen atom is an exception to most of the conclusions presented above in consequence of its two unique characteristics: its light weight and its lack of core electrons. The former typically leads to zero-point mean square bond-stretching amplitudes of ~0·0050 Å^2, in violation of the rigid-bond postulate. The latter deprives the atom of a chemically invariant cusp density whose observed smearing would unambiguously define its vibration amplitudes. On the contrary, the charge deformation in hydrogen is most pronounced at the nucleus, where the electron density is sharply elevated relative to that of the isolated atom (Stewart, Davidson & Simpson, 1965; Hirshfeld & Rzotkiewicz, 1974). Consequently *there is no possibility* of deriving hydrogen vibration parameters from the X-ray intensities. Our usual treatment is to augment the charge deformation model by assigning to hydrogen an effective charge in the range 1·2 to 1·3 and to fix the hydrogen vibration parameters on external evidence. Such evidence may come from neutron diffraction, if the data are available and sufficiently accurate, or from an appropriate set of infrared frequencies for the particular molecule under study or for a number of related molecules. With the internal vibrations approximated from such spectroscopic evidence, the lattice vibrations may be deduced from a constrained rigid-body refinement on the entire molecule or on suitable fragments bearing the hydrogen atoms. The total vibration tensor for each hydrogen atom is then obtained by algebraic summation of these two contributions.

Conclusions

The central implication of the evidence recorded above is that deformation densities can indeed be extracted from an X-ray experiment alone. To overcome the obstacle of excessive correlation with the vibration parameters we need intensity measurements, preferably at low temperature, spanning an adequate range of reciprocal radii and a refinement program that allows explicitly for the charge deformation. Stability of convergence then depends on the fact that the charge deformation and the vibrational smearing have their principal expressions in largely distinct regions of real and, correspondingly, of reciprocal space. The successful separation of the two effects can be verified by the physical acceptability of the vibration parameters, as proven by the rigid-bond test.

Special measures are required only for hydrogen atoms, which are doubly exceptional, undergoing characteristically large bond-stretching vibrations and having their largest deformation densities at the nuclear positions. The latter effect rules out the derivation of hydrogen vibration parameters from X-ray measurements alone.

Incidentally we have found that the rigid-bond test is often capable of distinguishing between a biased and an unbiased set of vibration parameters. It thus merits wider use in proving the correctness of the parameters from a crystallographic investigation. It may be suspected that such general testing of published crystal structures might not afford universal gratification.

I am most grateful to Professors P. Coppens and H. Hope for supplying unpublished X-ray intensity data of unusually high quality.

APPENDIX

An algebraic expression for $z^2_{A,B}$ is given by Busing & Levy (1964) in a non-standard notation that shuns the useful conventions of tensor arithmetic. In a more familiar notation, we assume that the vibration ellipsoid of atom A is defined by its contravariant tensor components β^{ij} with respect to the crystal axes $\mathbf{a}_i$ (=$\mathbf{a},\mathbf{b},\mathbf{c}$); *i.e.* the Debye–Waller factor has the form

$$q(\mathbf{h})=\exp\left(-2\pi^2 h_i h_j \beta^{ij}\right),$$

(with implied summation over the repeated indices i and j). Let the vector $\mathbf{l}_{AB}$ from A to B have the contravariant fractional components

$$l^j = x^j_{(B)} - x^j_{(A)},$$

i.e. $\mathbf{l}_{AB}=l^j\mathbf{a}_j$.

Its covariant components are then given by the transformation

$$l_i = g_{ij} l^j,$$

in which g_{ij} is the metric tensor defined by

$$g_{ij}=\mathbf{a}_i\cdot\mathbf{a}_j\,.$$

The required expression for the mean square displacement of atom A along the vector to B is

$$z^2_{A,B}=l_il_j\beta^{ij}/l_il^i\,,$$

where the denominator is simply the square of the distance l_{AB}.

If the Debye–Waller factor is chosen in the alternative form

$$q(\mathbf{h})=\exp\left(-2\pi^2h_ih_ja^ia^jU^{ij}\right)\,,$$

where a^i $(=a^*,b^*,c^*)$ are the lengths of the reciprocal axes (Hirshfeld & Rabinovich, 1966), we have only to substitute

$$\beta^{ij}=U^{ij}/a^ia^j$$

in the equation for $z^2_{A,B}$ above.

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