

Comments on Recent Work on Hydrogen Atom Location and Thermal Motion Determination by Neutron Diffraction*

WALTER C. HAMILTON

*Chemistry Department, Brookhaven National Laboratory
Upton, New York, U.S.A.*

In the fifteen years since the inception of the neutron diffraction technique, some fifty compounds containing hydrogen atoms have been studied. Although the approximate location of hydrogen atoms by neutron diffraction is, for well-known reasons, in most cases a fairly simple task, much of the work in this field has been somewhat disappointing because of the lack of accuracy in the determination of bond lengths and angles involving hydrogen atoms. In only a handful of the investigations has a C-H or O-H bond length been determined to better than 0.01-0.02 Å. There are a number of reasons why additional accuracy in these determinations should be sought.

First of all, an important question is whether the internuclear distance in bonds involving hydrogen as determined by neutron diffraction is the same as the bond length determined by X-ray diffraction, where the electronic cloud is the agent responsible for the scattering, i.e., is there a detectible difference between the nuclear position and the centroid of the electron cloud? Accurate neutron and X-ray work on the same compound would help to resolve this question.

Second, the correlations between O-H bond length and O...O distance or O-H stretching frequency in hydrogen bonded systems could be made much more precise if the accuracy of the bond distances as determined by neutron diffraction could be improved by a factor of four or more.

Finally, if anything significant is to be said about the amplitudes of intramolecular thermal vibrations, the accuracy of the diffraction results must be considerably better than those giving rise to errors of more than 0.01 Å in the bond lengths.

A survey of the work in the field would seem to indicate that it is important to carry out these investigations at low temperatures in order to minimize the effects of thermal vibrations. Furthermore, extreme care must be taken in selection and orientation of the crystal, correction for absorption and extinction effects, and intensity measurement, particularly in the elimination of double Bragg reflections and overlapping peaks caused by the relatively poor resolution in many neutron diffraction single crystal diffractometers. The neutron diffraction technique can lead to extremely useful and accurate results, but, due in part to the relative paucity of data as compared with the usual X-ray diffraction study, more care must be taken to fully realize the potentialities of the method.

Some of the most interesting neutron diffraction studies have been on hydrogen bonded compounds. One of the striking features of this field of study has been that the hydrogen bond in the crystal is frequently not the linear bond commonly assumed. If one omits the half dozen hydrogen bonds with very short (2.5 Å) O...O distances, the average X-H...X angle for about fifteen compounds is 167° with a root mean square deviation of 9°. Although this is not a large departure from linearity, it does indicate that intermolecular forces, packing considerations, and perhaps other effects partially outweigh any inherent tendency for a hydrogen bond to be linear. Recent work at Brookhaven National Laboratory on hydrogen-atom location includes studies of the following hydrogen bonded systems: FeSiF₆·6H₂O,¹ *o*-nitrobenzaldehyde,² and HCrO₂.³

The determination of thermal motion by neutron and X-ray diffraction has become of increasing importance in recent years as the

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accuracy of these investigations has increased. In crystals containing molecular groups or complex ions, the thermal motion can frequently be broken down into group translations, group oscillations, and intramolecular vibrations. Although many of the recent investigations have been of sufficient quality to determine the group motions with reasonable accuracy, the intramolecular vibrations contribute such a relatively small amount to the thermal motion that in only a very few studies has it been possible to say anything very significant about them. This is again a problem where careful investigations at low temperature may bear much fruit.

One of the most significant advances in the study of thermal motion has come in the

measurement of total neutron cross-sections of hydrogenous materials, where a simple relation has been found between the slope of the cross-section per hydrogen vs. wavelength curve and the freedom of motion of ammonium ions.^{4) -5) -6)}

References

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- 3 W. C. Hamilton and J. A. Ibers: In this Volume, p. 383.
- 4 J. J. Rush, T. I. Taylor and W. W. Havens, Jr.: *Phys. Rev. Letters* **5** (1960) 507.
- 5 *Ibid.*: *Bull. Am. Phys. Soc.* **6** (1961) 261.
- 6 *Ibid.*: *J. Chem. Phys.*, in press.

DISCUSSION

G. E. BACON: I am sure that all of us who have worked on these problems will agree with Dr. Hamilton's remarks: we are very humbly conscious of the limited accuracy which has been achieved.

W. C. HAMILTON: I should have mentioned that Dr. Bacon in his opening paper has discussed most of the points which I have raised. I am sure that we are all in agreement on the need for all work in this field to be of the high quality characterized by the work at Harwell.