A Comparison of the Molecular Structures of Ammonia and Deuteroammonia as Determined by Electron Diffraction

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The molecular structures of gaseous ammonia and deuteroammonia have been determined by the electron diffraction sector method and are compared. The lengths of the N—H and N—D bonds are found to be the same, but their vibrational amplitudes differ significantly, that for ammonia being the greatest. Anharmonicity of the stretching vibrations was not observed to any significant extent. The HNH angle in ammonia is found to be three degrees greater than the DND angle in deuteroammonia. The results are compared with those of Bartell, Kuchitsu and deNeui for methane and deuteromethane where both anharmonicity and a difference in the bond lengths were observed.

In a recent paper,[1] comparing the molecular structures of methane and deuteromethane, Bartell, Kuchitsu and deNeui showed that the electron diffraction sector method can be applied to detect differences which occur when hydrogen is replaced by deuterium in a molecule. These investigators found that the C—H bond in methane appears to be slightly longer than the C—D bond in deuteromethane, when $r_g(0)$ values are considered. They attributed the difference in length to the combined effect of anharmonicity of the C—D and C—H stretching vibrations and the greater amplitude of vibration of the lighter isotope. The present study was undertaken to ascertain whether the molecular structures of ammonia and deuteroammonia differ in a similar way.

DATA AND ANALYSIS

Ammonia itself has been studied before in this laboratory.[2] The diffraction photographs which were obtained at that time were subsequently carefully preserved and it was possible to use them again for the new study. Plates recording the diffraction pattern of deuteroammonia were also obtained at about the time of the earlier study, but until now, work with these has never

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been completed. Two complete sets of plates were in fact available for each compound; each set comprised eight to twelve plates, half of which had been exposed at a nozzle to plate distance of about 48 cm, the remainder having been exposed at about 19 cm. This gave an s range of 1.5 to 45 Å^{-1}, although the molecular diffraction patterns used extended only to $s = 30$ to 35 Å^{-1}.

New microphotometer curves for each plate were obtained and analysed much as in the previous structure determination.[2] Empirical background curves were constructed using the criteria that both the background itself and the envelope it is necessary to draw in on the radial distribution curve, must be smooth lines. The molecular intensity curves obtained after the background curves had finally been fixed are shown in Fig. 1, multiplied by
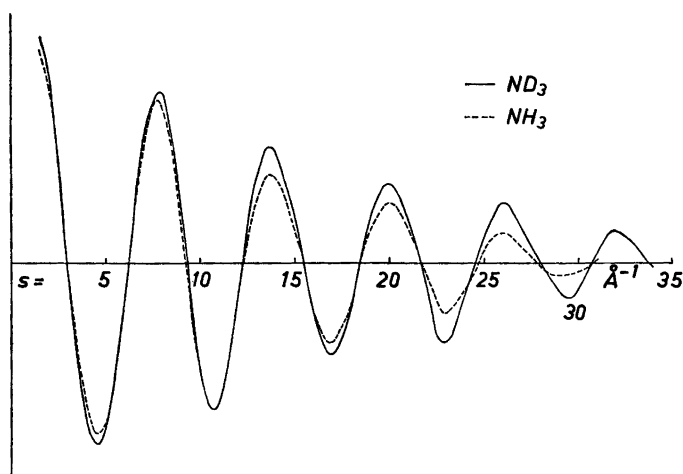

Fig. 1. Ammonia and deuteroammonia. Experimental molecular intensity curves.

$s/[(1-F_N/Z_N)(1-F_H/Z_H)]$. It was immediately apparent from the more rapid diminution of the curve for ammonia that the mean vibrational amplitude, u_{NH}, of the N—H bond in ammonia is greater than the mean vibrational amplitude, u_{ND}, of the N—D bond in deuteroammonia.

Assuming harmonic vibrations, these intensity curves are proportional to

$$3 \ Z_N Z_H [\exp(-\tfrac{1}{2} u_1^2 s^2) \sin r_1 s]/r_1$$

$$+ \ 3 \ Z_H^2 \ \frac{(1-F_H/Z_H)}{(1-F_N/Z_N)} \ [\exp(-\tfrac{1}{2} u_2^2 s^2) \sin r_2 s]/r_2$$

where r_1, u_1 are either r_{NH}, u_{NH} or r_{ND}, u_{ND} and r_2, u_2 are either r_{HH}, u_{HH} or r_{DD}, u_{DD}. Using an IBM 1620 computer and a least squares programme written by H. M. Seip, it was possible to fit this function to the experimental curves by refining the length and amplitude parameters and also the scale factor which relates observed and calculated molecular intensities. A weighting scheme was used which permitted unit weight to be applied to the data between $s = 10$ and 25 Å^{-1}. Outside these limits the weight was allowed to

decrease exponentially with s to 0.8 at $s = 1.5$ Å^{-1} and 0.5 at the maximum s-values used.

Refinement of the bond parameters proceeded satisfactorily, but satisfactory refinement of the parameters for the non-bonded interatomic distances was not achieved. Refinement of the latter was prejudiced by errors in the data at medium and large values of s, which were of the same order of magnitude as the true H$\cdots$H and D$\cdots$D contributions at lower s-values. The scale factors which the refinement produced were used to normalise to each other the two molecular intensity curves shown in Fig. 1.

Other attempts were made to obtain accurate H$\cdots$H and D$\cdots$D parameters. The radial distribution curves, which are the Fourier transforms of the intensity curves shown in Fig. 1, cannot of course be expected to have H$\cdots$H or D$\cdots$D peaks which are exactly Gaussian in form even if the vibrations are harmonic, because of the nearness of the larger N—H or N—D peaks and the $(1-F_{\mathrm{H}}/Z_{\mathrm{H}})/(1-F_{\mathrm{N}}/Z_{\mathrm{N}})$ factor in the intensity expression. Distorted peaks were indeed obtained and in consequence it was difficult to determine accurate parameters from them. By subtracting the theoretical contribution of the N—D or N—H bonds from the experimental intensity curves and multiplying by $(1-F_{\mathrm{N}}/Z_{\mathrm{N}})/(1-F_{\mathrm{H}}/Z_{\mathrm{H}})$ the theoretical expression for the remaining intensity becomes

$$3\ Z_{\mathrm{H}}^2[\exp(-\tfrac{1}{2}u_2^2s^2)\sin r_2s]/r_2$$

When difference Fourier transforms for the two substances were calculated with this set of data and suitable envelopes had been subtracted, H$\cdots$H and D$\cdots$D peaks were obtained which were less distorted than the ones obtained by the method described above, and parameters could be determined from them more readily. The H$\cdots$H and D$\cdots$D peaks obtained by both methods

Table 1. Final length and amplitude parameters.

	NH$_3$ (X = H) (Å)	ND$_3$ (X = D) (Å)	Probable error [e] (Å)
r_{NX} [a]	1.019$_1$	1.020$_2$	0.002$_4$
u_{NX} [a]	0.078$_9$	0.066$_7$	0.002$_7$
r_{XX} [d]	1.66	1.63	0.02
u_{XX} [b]	0.11	0.10⎫	0.02
u_{XX} [c]	0.09	0.08⎭	
	(°)	(°)	(°)
∠ XNX	109.1	106.1	1.0

a From least squares analyses.
b From difference Fourier transforms.
c From Fourier transforms of intensity curves shown in Fig. 1.
d Obtained by both methods (*i.e.*, b and c).
e Owing to the fact that old data were used it is possible that a systematic scaling error exists in addition to the probable error quoted. Such an error would affect all parameters in a similar way and would thus have only a very minor effect on the difference between the two r_{NX} values.

showed signs of anharmonicity, but is was not possible to estimate the extent of it owing to the level of the experimental error.

The final length and amplitude parameters are given in Table 1 together with an estimate of the probable error in each of them. For the bond parameters, a value of three times the estimated standard deviation produced by the least squares treatment is given as the probable error.

DISCUSSION

The lengths of the N—H and N—D bonds are the same within the limits of error of the structure determination. The most significant difference between the two substances occurs in the vibrational amplitudes of the bonds, as was observed from the intensity curves. Of lesser significance is the difference between the two r_{XX} distances which results in the HNH angle being three degrees larger than the DND angle, although this is in agreement with the suggestion of Bartell that hydrogen atoms, because they have greater amplitudes of vibration, exert stronger repulsions on neighbours.[3]

The tetrahedral nature of methane precludes the possibility of observing a difference between the corresponding angles in methane and deuteromethane,[1] but the pyramidal nature of ammonia appears to permit such an expansion to occur.

The lengths quoted in the table are, using the notation of Ref.[1], $r_g(1)$ values. On convertion to $r_g(0)$ values by adding u^2/r, r_{NH} and r_{ND} both become 1.025 Å. The difference between the $r_g(0)$ values for methane and deuteromethane was found by Bartell, Kuchitsu and deNeui to be 0.004 Å and attributed to the combined effect of anharmonicity of the C—D and C—H stretching vibrations and the greater amplitude of vibration of the lighter isotope.[1] These workers were able to observe the effects of anharmonicity both in the experimental intensity curves and in the radial distribution curves, but such effects were not observable to any significant extent in the present study of ammonia and deuteroammonia. In both pairs of compounds the amplitude of vibration of the lighter isotope is greater, but this difference does not lead to a difference in the $r_g(0)$ values unless anharmonicity is present also.

The results for methane and deuteromethane and those for ammonia and deuteroammonia both therefore support the theoretical approach to anharmonicity which is referred to in Ref.[1], although the vibrational properties of the two pairs of compounds appear to be different.

REFERENCES

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