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The Use of the Electron Diffraction Sector Method for Location of Hydrogen in Gas Molecules

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Molecular structure determination of gaseous ammonia and ethane has been carried out with the aid of the electron diffraction sector method. The structure parameters found are the following: Ammonia, N—H = 1.015 Å and ∠H—N—H = 106.6° ± 4.0°. Ethane, C—H = 1.107 Å, C—C = 1.536 Å and ∠C—C—H = 109.54°. The ethane molecule shows the *trans* form.

Structural chemists have tried in recent years to improve the various methods for determination of the position of hydrogen atoms in crystal lattices and in free gas molecules [1]. To investigate the possibilities of the electron diffraction sector method for this kind of study we have chosen two rather simple and structurally well-known molecules, namely ammonia and ethane.

The electron diffraction apparatus used has been described earlier [2].

Ammonia was obtained from ammonium chloride and dry slaked lime. The pictures were taken using an ordinary liquid-air trap. Better results might have been obtained by the procedure described below for ethane. Intensity data for large s values were not obtained, the data extend only to about $s = 30$ Å^{-1}. The following general procedure is applied to obtain the best intensity and radial-distribution curves: The microphotometer curves are read off in a logarithmic scale, correction for the deviation from linearity of the density values is carried through, and the resulting curve is multiplied by the factor

$$c \frac{s^4}{\alpha \cos^3 2\Theta}$$

where α is the sector-screening factor and $\cos^3 2\Theta$ takes care of the correction necessary because of the use of plane photographic plates. The constant c is chosen to make the resulting curve (I_E) fit the scale of the background

$$B_T = \sum_i [(Z_i - F_i)^2 + S_i]$$

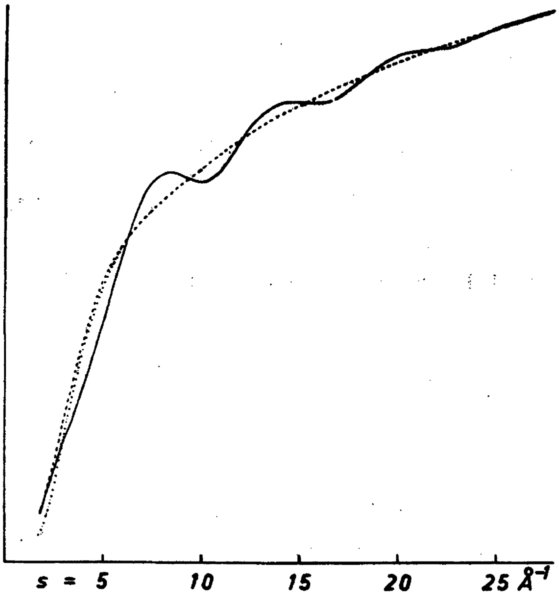

Fig. 1. The I_E *curve of ammonia with background drawn in.*

Though this procedure in most cases gives a fairly good fit of the intensity curve to the background, it is usually necessary to draw an empirical background for at least some parts of the *s* range. In Fig. 1 the fully-drawn curve is the inner part of the I_E curve. The dashed curve is the background as drawn in. The background is subtracted from the I_E curve and the difference is multiplied by the factor

$$\frac{s}{\left(1-\frac{F}{Z}\right)^2} e^{-ks^2}$$

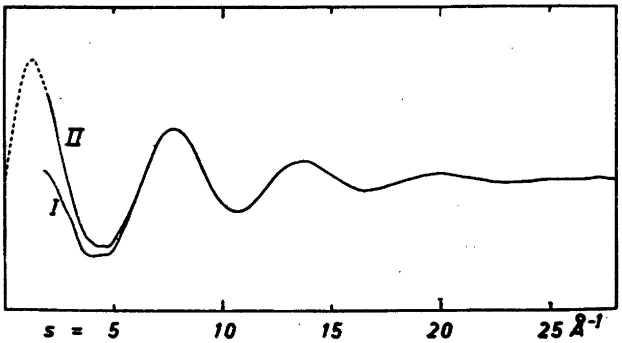

Fig. 2. Intensity curve of ammonia.

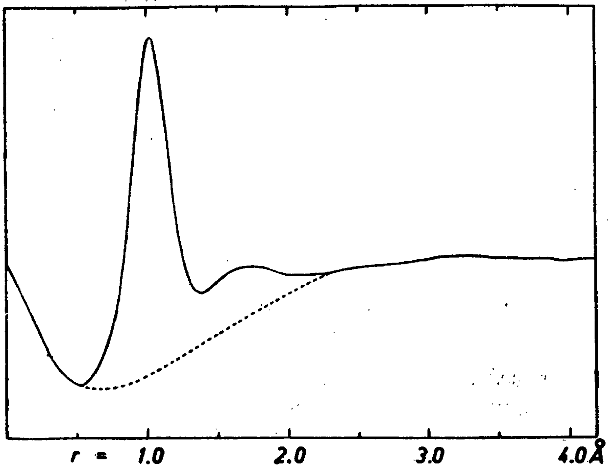

Fig. 3. Radial distribution curve of ammonia with "envelope".

k being in this case 0.0036, and $\left(1-\frac{F}{Z}\right)^2 = \left(1-\frac{F_N}{Z_N}\right)\left(1-\frac{F_H}{Z_H}\right)$. The curve thus obtained is given as curve I in Fig. 2. The Fourier transform of this curve is shown in Fig. 3.

Because of experimental limitations we cannot obtain the intensity values of the first ring from $s = 0$ to about $s = 1.5$ Å^{-1}. Further, the empirical background introduces uncertainties in the subtracted intensity curve, particularly in the inner part of the curve. To allow for these defects we draw in an "envelope" in the radial distribution curve; dashed curve in Fig. 3. This envelope coincides with the radial distribution curve in the areas $0 < r < 0.6$ and $2.2 < r$. The difference between the original radial distribution curve and the envelope is shown in Fig. 4 (fully-drawn curve). The Fourier transform of the

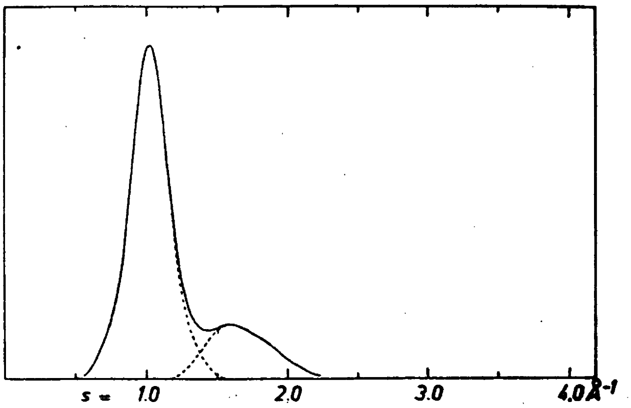

Fig. 4. Radial distribution curve of ammonia. Envelope subtracted.

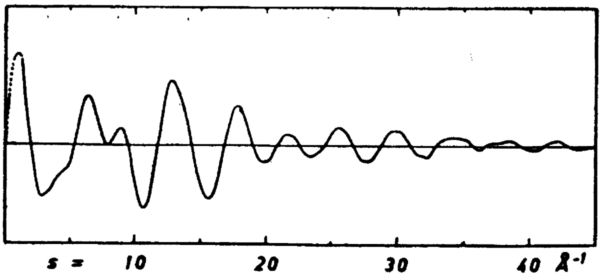

Fig. 5. Intensity curve of ethane.

envelope has also been calculated and added to the intensity curve I of Fig. 2, giving curve II of the same figure. This curve now, of course, shows the inner peak which could not be determined directly from the experiments. It has also been corrected somewhat in the area from $s = 1.5$ to $s = 6$ Å^{-1}. This correction corresponds to only a slight change in the background. The new background is shown as the dotted curve in Fig. 1.

Two more radial distribution curves have been calculated using different k values in the exponential factor e^{-ks^2} ($k = 0$ and $k = 0.0015$). The maximum of the main peak corresponding to the N—H distance ($k = 0$) occurs at 1.015 Å, in excellent agreement with the spectroscopically obtained value[3] of 1.014 Å.

The H—H distance shows up as a well-resolved peak both in Fig. 3 and in Fig. 4. In Fig. 4 the contribution of the N—H peak is subtracted to give the shape of the H—H peak. This does not have the usual symmetric form of radial distribution peaks. This might be due either to experimental imperfections or to the conversion mechanism of the ammonia molecule. The maximum of the H—H peak occurs at $r = 1.584$ Å, corresponding to an H—N—H angle of 102.6°. The average r value found from the "center of gravity" of the peak is 1.668 Å, corresponding to an angle of 110.5°. It is a reasonable assumption to believe that the equilibrium distance is somewhere between these values. Our determination should, accordingly, lead to an angle of 106.6° ± 4°, which is in good agreement with the spectroscopically obtained value of 106.8° [3].

Ethane was prepared by electrolysis of sodium acetate dissolved in glacial acetic acid. The cold trap of the electron diffraction apparatus was cooled by liquid air evaporated under reduced pressure. Under these circumstances, we obtained a temperature on the liquid-air trap of approximately —210°, at which temperature the vapour pressure of ethane was low enough not to destroy the vacuum in the electron diffraction apparatus.

Fig. 5 is the final undamped intensity curve corrected in the same way as described for ammonia. Since the outer part of the intensity curve contributes very little to the non-bonded distances of special interest in this work, no particular effort was done to obtain intensity data for the very large s values. On the other hand, our diagrams which extend to $s = 45$ Å^{-1} do not give any indication of diffraction rings much beyond this point. Four radial distribution curves were calculated. One of them was based upon an undamped intensity curve, the other ones were based upon intensity curves multiplied by e^{-ks^2},

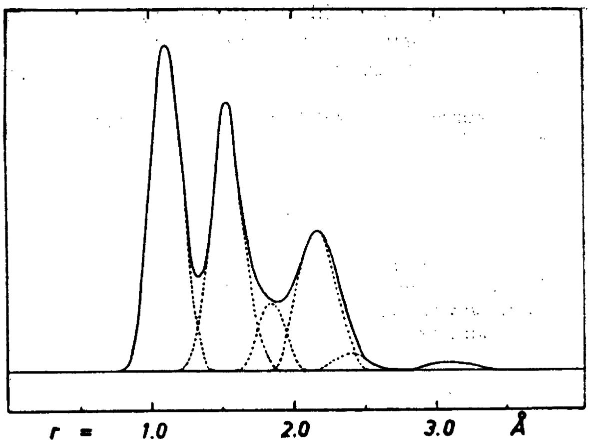

Fig. 6. Radial distribution curve of ethane.

k ranging from 0.0015 to 0.003. (For Fig. 6, $k = 0.003$). The three predominant peaks of the radial distribution curves correspond to the C—H bond, the C—C bond, and the long C···H distance. The best values obtained for these three distances are 1.107, 1.536, and 2.173 Å, respectively. This leads to $\angle$ C—C—H = 109.54° and $\angle$ H—C—H = 109.40°. These values are in fair agreement with the values obtained from spectroscopic measurements by Hansen and Dennison[4] who find C—H = 1.102 Å, C—C = 1.543 Å, and $\angle$ C—C—H = 109.62°.

If we assume the *trans* form for the ethane molecule, we find that three different H—H distances should exist. One of them, the *trans* distance, is easily determined as the corresponding peak occurs at an r value well beyond the region of the peaks of the three predominant distances. The two other H—H distances, however, must be determined indirectly. This is done by assuming the peaks from each distance to be symmetrical. In this way the right side of the first peak is easily constructed and subtracted from the radial distribution curve. Then the left side of the second peak is constructed. By continuing this procedure the two remaining H—H peaks are found. The first H—H peak, corresponding to the H···H distance through one angle, can be determined quite accurately. The correct shape of the second H···H peak corresponding to the *gauche* distance, however, is more difficult to find in this simple manner, because the various necessary corrections introduce uncertainties. A closer analysis of these corrections, however, seem to establish beyond doubt the existence of the *gauche* H—H contribution. In the final determination of the *gauche* peak, the C···H peak has been given the proper weight before subtraction, *i. e.* the area of the C···H peak is made equal to that of the first C—H peak multiplied by 1.107/2.173.

The three H—H distances thus obtained are the following: the H—H distance through one angle 1.83 Å, the *gauche* distance 2.44 Å, and the *trans* distance 3.09 Å. The corresponding distances calculated using the parameters

given above are 1.81, 2.50, and 3.09, respectively. Thus, even if the *gauche* distance is not determined very accurately we may consider the present studies as a direct proof for a predominating *trans* form in the gaseous ethane molecule.

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