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Author's Review

Microwave Spectroscopic Investigations of Hydrogen-Bonded Dimers and the Directional Character of Hydrogen Bonds

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Microwave spectroscopic investigations can provide a wide variety of information about hydrogen-bonded dimers. Two particular types of information, namely geometry and bending force constants, are used here to explore the directional character of hydrogen bonds. It is found where such information is available that bending at the acceptor atom is relatively easy to bring about while resistance to bending at the hydrogen atom is appreciably greater.

Comparisons of geometries are made for a series of hydrogen bonded structures in the solid state and also for the gas-phase. For moderately strong hydrogen bonds it appears that the conventionally viewed lone-pair directions correlate closely with observed geometries of gas-phase dimers, but the energetic preference for such a geometry is sufficiently small that other factors frequently over-ride it for hydrogen-bonded structures found in the solid state. This behaviour can be understood in terms of the total electron density distribution at the acceptor atom.

INTRODUCTION

Microwave spectroscopy has provided a direct method for the determination of the geometries of a number of simple gas-phase hydrogen bonded dimers. In addition the technique offers the possibility of determining dissociation energies of dimers from intensity measurements and electric dipole moments from Stark effects. Investigation of spectra of dimers in vibrationally exited states and the study of vibration-rotation interaction can in addition afford a route to information about dimer potential energy functions. The present paper examines first, evidence about the directional character of hydrogen bonds in isolated gas-phase dimers, by considering both dimer geometries and the ease of angular distortion of the geometry as indicated by bending potential functions, and then considers structures in the solid state.

GEOMETRY AND BENDING FORCE CONSTANTS

The first heterodimer to be investigated by microwave spectroscopy,[1] $CH_3CN\ldots HF$, offers a convenient starting point for the discussion. Under low resolution a number of transitions have been observed in the microwave spectrum with a uniform spacing typical of a symmetric rotor. Under higher

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* Festschrift of Professor Dušan Hadži.

resolution each line is split into a sub-structure of several components as shown for the $J = 8 \leftarrow 7$ transition in Figure 1. The origin of the structure can be understood in terms of the new vibrational modes that arise on dimer formation[2], which are shown diagrammatically in Figure 2. There is a doubly degenerate low-frequency bending mode ν_β and a doubly degenerate higher-

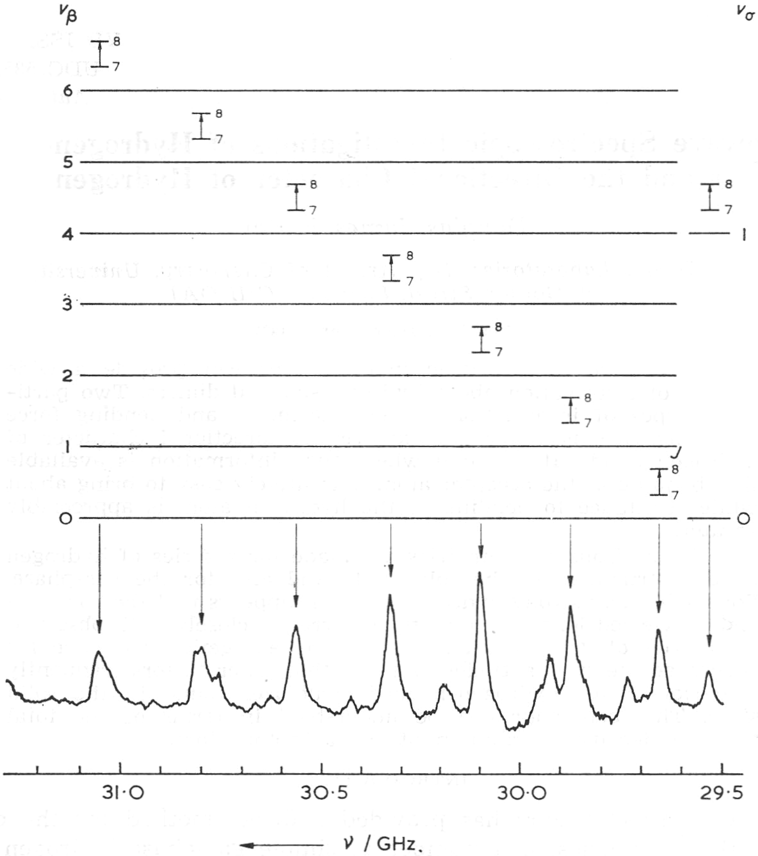


Figure 1. Origin of rotational satellites for the rotational transition $J = 8 \leftarrow 7$ in the microwave spectrum of $CH_3CN \ldots HF$

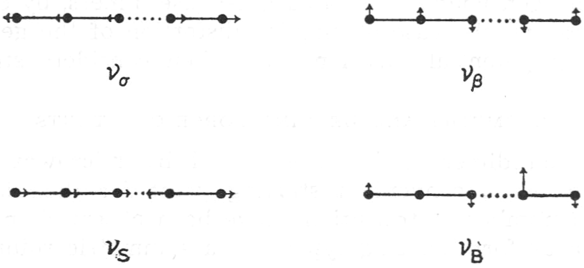


Figure 2. Diagrammatic representation of the vibrational modes associated with the hydrogen bond for $RCN \ldots HF$.

-frequency bending mode ν_B, in which the motion is largely that of the hydrogen atom of the hydrogen fluoride molecule. There is also a low-frequency stretching mode denoted as ν_σ, while the modified hydrogen fluoride stretching mode will be denoted as ν_S. Several excited vibrational states of the bending mode are populated at the temperature of the experiment and, as Figure 1 shows, a separate rotational transition arises for each such state, the rotational constant increasing with the vibration quantum number v_β. In addition, a satellite rotational transition can also be seen which corresponds to a decrease in rotational constant and this has been assigned to $v_\sigma = 1$. Such satellite rotational spectra can give information about the potential function, since relative intensity measurements lead through the Boltzmann equation to the vibrational spacings $v_\beta = 1 \leftarrow 0$ and $v_\sigma = 1 \leftarrow 0$. These are compared in Table I with values obtained from an infrared spectroscopic study[3] of $CH_3CN \ldots HF$ in the gas phase.

TABLE I

Vibrational Energy Separations for $CH_3CN \ldots HF/cm^{-1}$

vibrational spacing	microwave[2]	infrared[3]
$v_\beta = 1 \leftarrow 0$	45 ± 15	40 ± 14
$v_\sigma = 1 \leftarrow 0$	181 ± 20	168 ± 3
$v_B = 1 \leftarrow 0$	—	620 ± 3
$v_S = 1 \leftarrow 0$	—	3627 ± 2

Typical symmetric rotor characteristics of the spectrum of $CH_3CN \ldots HF$ indicate that the dimer has a linear heavy atom geometry, and the rotational constants of several isotopic species lead to $r_0(N \ldots F) = 2.795$ Å. Having established the geometry we can turn to consider the ease of angular distortion of the geometry by seeking the bending potential constants. The appropriate angles are defined in Figure 3. The bending frequencies ν_B and ν_β provide by themselves insufficient information to determine the bending force constants, f_θ, f_φ and $f_{\theta\varphi}$. However, a third piece of information is available in the form of the centrifugal distortion constant D_{JK} which has also been obtained from the analysis of the rotational spectrum. In this vay the following values $f_\theta = 2.4 \pm 0.2) \times 10^{-20}$, $f_\varphi = (8.0 \pm 0.7) \times 10^{-20}$ and $f_{\theta\varphi} = 0 \pm 1) \times$ $\times 10^{-20}$ J rad^{-2} have been obtained with only the very reasonable assumption that the cross terms $f_{\omega\theta}$ and $f_{\omega\varphi}$ are zero. The zero value, within experimental error, obtained for $f_{\theta\varphi}$ is in accord with such an assumption.

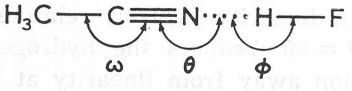


Figure 3. Bending co-ordinates for RCN . . . HF.

DISTORTION ENERGIES

The availability of bending force constants makes it possible to examine the energetics of angular distortion[2] of the hydrogen bond for each of the distortions shown in Figure 4. Values of the energy ΔE required to produce

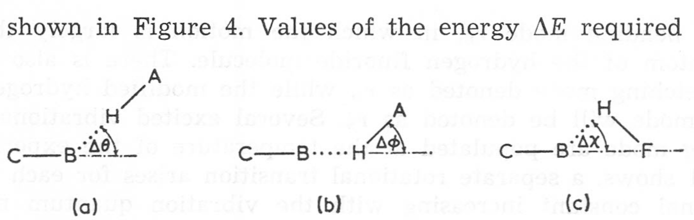


Figure 4. Angular distortion of hydrogen bonds.

angular distortions of $\Delta\varphi$ in the range 0 — 30° are given in Table II. The calculations are based on the harmonic force constants and although it has not been established that the force field is harmonic over that range, the nearly uniform spacings observed in the satellite progression for several quanta of the bending mode v_β, illustrated in Figure 1, suggests that for this mode at least the harmonic assumption may well be a good approximation. Table II also gives distortion energies as a percentage of the dissociation energy based on the value of D_e, for HCN ... HF[4], since that for CH_3CN ... HF is not available. The value of D_e for the latter is probably somewhat larger and so percentages in Table II are likely to be a little overestimated. It is

TABLE II

Hydrogen Bond Distortion Energies for CH_3CN ... HF

Distortion angle	$\Delta\theta$ ΔE/kJ mol^{-1}	$\Delta E/D_e$	$\Delta\phi$ ΔE/kJ mol^{-1}	$\Delta E/D_e$	$\Delta\chi$ ΔE/kJ mol^{-1}	$\Delta E/D_e$
10°	0.4	2%	1.5	6%	1.5	6%
20°	1.7	7%	5.9	22%	6.1	23%
30°	3.8	15%	13.8	53%	14.2	54%

seen that distortion from linearity at B is relatively easy to bring about; even a distortion of $\Delta\vartheta = 30°$ reduces the hydrogen bond energy by only 15%. By contrast distortion away from linearity at H leads to a more rapid reduction in binding energy. Thus for $\Delta\varphi = 30°$ the result is a reduction in binding energy of 53%, while for a bent hydrogen bond with $\Delta\chi = 30°$ the loss in binding energy is slightly greater. It is a striking result that bending the hydrogen bonded dimer so that the H — A axis is turned away from the lone-pair direction is relatively easy to bring about. The result draws attention to the question of what importance lone-pairs have in determining the directional character of hydrogen bonds. The question is most conveniently examined by turning to examples where the lone-pair directions are not symmetry axes, and hydrogen bonds to groups through an oxygen atom provide particularly useful examples of this kind. Numerous examples have been examined in the solid state and these will be considered first, and then attention will be turned to gas-phase dimers.

GEOMETRIES OF O...H—O HYDROGEN BONDS IN CRYSTALS

A survey[5] of O—H...O configuration has been made by statistical analysis for 196 hydrogen bonds taken from 45 crystal structures of polyalcohols, saccharides, and related compounds, determined by X-ray crystallography. The results have been presented in detail but for the purposes of the present discussion the scatter diagrams reproduced in Figure 5 (Kroon et al.) offer direct visualization of the main relevant features. Figure 5(a) shows the projections of all the H atoms on the C—O—H plane, while Figure 5(b) presents the projections of the H atoms on the bisector plane of the C—O—H angle, where because of the C_s symmetry of the C—O—H group all positions have been transferred to one-half of the diagram. It will be seen that Figure 5(a) indicates there is some preference for hydrogen bonding within or near the plane containing the lone pair-axes, while Figure 5(b) which refers to directions within this plane illustrates very clearly one of the main conclusions reached about directional properties of hydrogen bonds in these crystals,

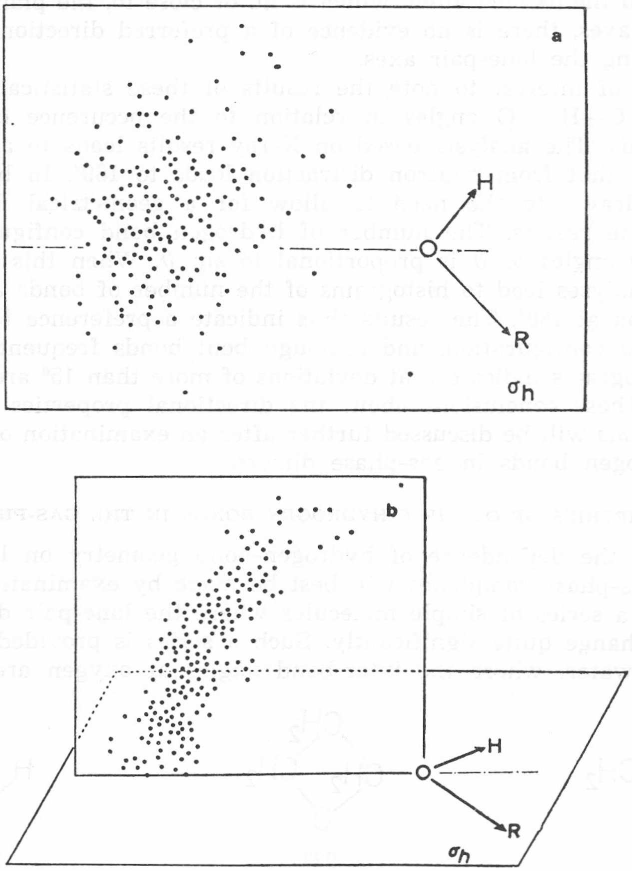


Figure 5. (a) Projections of the observed hydrogen-atom positions on the plane of the C—O—H acceptor group;
(b) Projections of the observed hydrogen atom positions on the plane bisecting the C—O—H acceptor group.

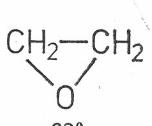
namely that there is no distinct preference for hydrogen bond formation along the lone-pair directions.

An analysis has also been made of the geometries of O—H...O hydrogen bonds determined by neutron diffraction in 24 crystal structures.[6] Bifurcated hydrogen bonds where the geometry is related to two acceptor oxygen atoms were eliminated from the total of 100 O—H...O hydrogen bonds leaving 74 in the survey. The analysis of the geometries of these hydrogen bonds, within the experimental accuracy afforded by neutron diffraction, supports the conclusion that while there is a preferred direction of hydrogen bonding with respect to the oxygen atom, which is in, or close to, the plane containing the lone-pair axes, there is no evidence of a preferred direction within that plane containing the lone-pair axes.

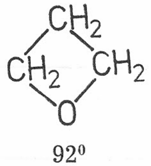
It is also of interest to note the results of these statistical analyses of the observed O—H...O angles in relation to the occurence of non-linear hydrogen bonds. The analysis based on X-ray results leads to a mean value of ~160° and that from neutron diffraction leads to 169°. In both analyses attention is drawn to the need to allow for a geometrical factor before interpreting the results. The number of hydrogen bond configurations with an O—H...O angles of ϑ is proportional to sin ϑ. When this correction is made, both analyses lead to histograms of the number of bonds against angle having maxima at 180°. The results thus indicate a preference for the linear hydrogen bond configuration, and although bent bonds frequently occur the corrected histograms indicate that deviations of more than 15° are proportionately small. These conclusions about the directional properties of hydrogen bonds in crystals will be discussed further after an examination of the geometries of hydrogen bonds in gas-phase dimers.

GEOMETRIES OF O...H—F HYDROGEN BONDS IN THE GAS-PHASE

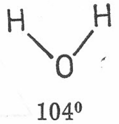
A test of the dependence of hydrogen-bond geometry on lome-pair direction for gas-phase complexes will best be made by examination of hydrogen bonds to a series of simple molecules where the lone-pair directions are expected to change quite significantly. Such a series is provided by oxirane, oxetane and water, where the inter-bond angles at oxygen are as follows:



62°



92°



104°

Correspondingly the angle between the lone-pair directions is expected to decrease markedly along the series and so this series should provide a clear test of the model. Microwave spectra have been obtained for hydrogen bonded complexes formed by each member of the series with hydrogen fluoride. Geometries have been obtained for the complexes formed by oxirane[7] and oxetane[8] with hydrogen fluoride from rotational constants, on the basis of the now well justified assumption of unchanged monomer geometries. For the dimer $H_2O...HF$ the structural problem proves more difficult[9], but a recent analysis[10] of the out-of-plane bending potential for the dimer leads to the infor-

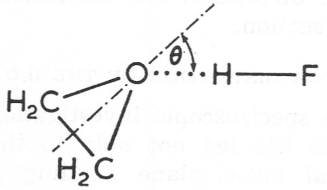


Figure 6. The angle θ defined as the angle between the O ... H—F direction and the bisector of the $\overset{\text{O}}{\diagup\diagdown}$ angle of the acceptor molecule.

mation required and allows comparison to be made for the three dimers. The geometrical parameter of interest for the present purpose is ϑ the angle between the O ... H—F direction and the bisector of the interbond angle, as illustrated in Figure 6 for the oxirane hydrogen fluoride dimer. Values of ϑ are tabulated in Table III for dimers formed by hydrogen fluoride with each acceptor. It is immediately evident from Table III that ϑ decreases as the interbond angle increases for the three members of the series. For the water hydrogen fluoride dimer[9] ϑ equals 46 ± 8^0, close to the value of 54^0 expected for a regular tetrahedral configuration at oxygen, while for the oxirane hydrogen fluoride dimer $\vartheta = 71.8^0$, a strikingly greater value than the regular tetrahedral one. It has been pointed out that the result can be understood if it is assumed that the O ... H—F axis coincides in these dimers with direction of the conventionally pictured lone-pairs, the angle between which is expected to decrease as the interbond angle is increased.[8].

TABLE III

Angles in Hydrogen bonded Dimers Formed by Hydrogen Fluoride

Acceptor molecule	Molecular angle at oxygen	Hydrogen bond angle ϑ
$(CH_2)_2O$	$61^0 38'$	72^0
$(CH_2)_3O$	$91^0 44'$	58^0
H_2O	$104^0 31'$	46^0

A further result which fits the general pattern is that for $H_2O \ldots HOH$ where a value of ϑ equals 58 ± 6^0, not far removed from tetrahedral, has been reported.[11] Two other gas phase dimers involving hydrogen bonding to oxygen should be mentioned. For $N_2O \ldots HF$ the angle between the N_2O and HF axes has been reported[12] to be 47^0 while for $CO_2 \ldots HF$ a linear geometry has been reported.[13] These dimers are presumably relatively weakly bonded by comparison with the others considered here, being so far detected only at low temperatures, and it may well be that the balance of factors determining geometry is rather different for weak dimers than for the moderately strong ones discussed here. Whatever the position about relatively weak dimers may be, it appears that for moderately strongly bound hydrogen bonded gas-phase dimers lone pairs have a determining influence on hydrogen bond direction while for crystals statistical analyses of results for many hydrogen bonds reveal no such correlation between hydrogen bond directions and the supposed lone-pair directions. The resolution of this apparent conflict is considered in the next section.

ENERGETICS FOR DISTORTION OF THE H_2O . . . HF DIMER

A detailed microwave spectroscopic investigation has been made for the H_2O . . . HF dimer and this has led not only to the geometry but has also enabled a one-dimensional out-of-plane bending potential function to be determined.[10] Three types of information from the spectrum have been combined to this end. First the vibrational spacings for the out-of-plane bending motion have been determined from the relative intensities of satellite transitions. Such spacings provide a direct route to the potential function, but because they are obtained from intensity measurements they are less accurately determined than is desirable. The second source of information, namely dependence of rotational constants on vibrational states, can be obtained from frequency measurements with high accuracy and the constants are very sensitive to the potential function, though in a less direct way than vibrational spacings. The third source of information about the potential function is the dependence of molecular electric dipole moment on vibrational state, which has been obtained by a study of Stark effects in the microwave spectrum of the dimer.

An optimum potential energy function for out-of-plane bending has been obtained by combining the three types of measurement. The form of the one-dimensional potential energy function is found to be a double minimum one as illustrated in Figure 7, which shows the dependence of the potential energy on the angle ϑ defined as in Figure 6. The height of the barrier

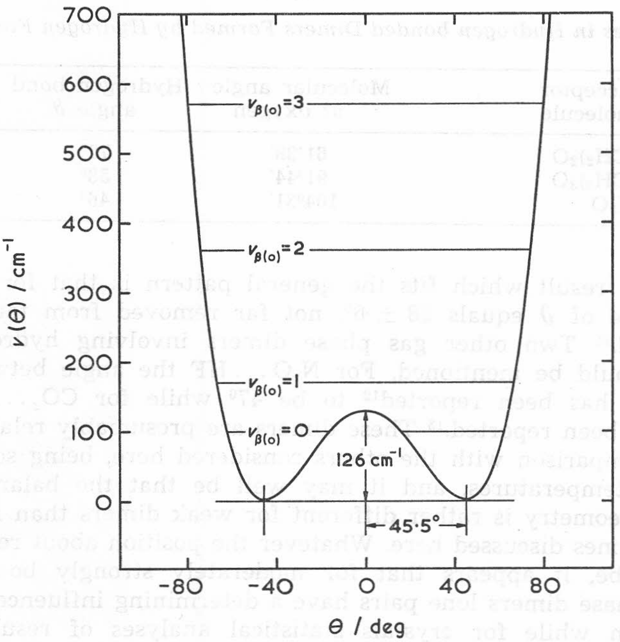


Figure 7. Out-of-plane bending potential energy function for H_2O . . . HF.

between the two pyramidal configurations is found to be 1.5 ± 0.8 kJ mol^{-1}. As already noted the equilibrium structure is a non-planar one with $\vartheta = 46^0$. However, it is seen from the Figure that the planar structure is only slightly less stable than the equilibrium nonplanar structure. Indeed, out-of-plane distortion of the structure over a wide angle costs relatively little energy. For example the whole range of ϑ changing from -60^0 to $+60^0$ is encompassed by 1.5 kJ mol^{-1}. It is seen that large amplitude bending distortions lead to a relatively small decrease in the bonding energy, for which a value $D_e = 30$ kJ mol^{-1} has been reported.[14] A similar conclusion was noted earlier for bending distortions in $CH_3CN \ldots HF$, which again lead to relatively little loss of binding energy.

The quite different observations on directional properties of hydrogen bonds made for solid-state and gas-phase studies, referred to previously, may now be interpreted in a straightforward way. It appears that the lone pair directions have an important influence on geometries of isolated hydrogen bonded dimers in the gas-phase. In fact it has been suggested that the hydrogen bond may provide a good probe of the direction of the axis of lone-pair electrons.[8] Nevertheless it is found that the energy required to distort the direction of hydrogen bonding is relatively small, a 5% change in binding energy covering range of ϑ from -60^0 to $+60^0$ for the $H_2O \ldots HF$ dimer. If this is generally true for hydrogen bonding to oxygen it is understandable that large variations in angle may be found for hydrogen bonds in crystals, since such distortions may be achieved for relatively little cost in energy at the demand of other factors contributing to the total packing energy of the crystal, depending on a number of properties including size, shape and polar character of the molecules or ions involved, and so understandably a wide range of angle have been reported for hydrogen bonds to oxygen in crystals containing $O \ldots H—O$ hydrogen bonds[5,6].

Finally, with considerations about bending potential constants in mind, we may consider bent hydrogen bonds. It will be recalled that for $CH_3CN \ldots HF$ where the relevant information is available (Table II) the energy to produce a distortion leading to a bent hydrogen bond rises rather rapidly with the angle of the bent bond. Thus for an angle of 10^0 the energy required is approximately 6% of the binding energy while by 30^0 it has reached approximately 54%, a quite different situation from that for those bending distortions where the hydrogen bond remains linear. If this situation is general, then significantly bent hydrogen bonds are energetically improbable. This accords well with results obtained from the analyses[5,6], of $O \ldots H—O$ hydrogen bonds where only a relatively low proportion of the examples were found to show bent hydrogen bonds with an angle greater than 15^0.

LONE-PAIR MODELS FOR HYDROGEN BONDING

The results available at the present time for reasonably strong hydrogen bonds indicate that the direction of the hydrogen bond formed by HA at B to give a gas-phase dimer $B \ldots H—A$ is dependent on the lone-pair direction on B, while distortions in which H—A is bent away from the lone pair direction, as shown in Figure 4a, lead to relatively little loss of binding energy. This finding that lone-pair directions are important in determining geometries of gas-phase hydrogen bonded dimers, and yet that such hydrogen bonds are relatively easily distorted away from lone-pair directions calls for comment on lone-pair models of hydrogen bonding.

Olovsson[15] has already drawn attention to the finding that total electron density in a lone-pair region is very close to spherical and to correlation of this with observations, for hydrogen-bonded crystals, that the entire non--bonded region seems to be equally accessible for hydrogen bonding.

It might be supposed for a simple lone-pair model, of $CH_3CN \ldots HF$ for example, that distortion of type (a), in Figure 4 which turns the HF axis away from the lone-pair direction might lead to significant loss of binding energy while a similar bending distortion of type (b) which leaves the position of the electropositive hydrogen unchanged with respect to the lone-pair might be accomplished with a smaller expenditure of energy. The bending force constants show in fact that the contrary is true.

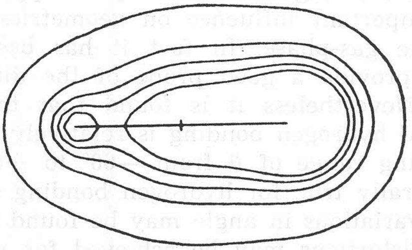


Figure 8. Contours of total electron density in the molecular plane for HCN, at 0.01, 0.07, 0.13, 0.19 and 0.25 $e\text{Å}^{-3}$.

The result emphasises how representations frequently used for lone pairs can be misleading. If the total electron density for HCN as obtained by *ab initio* calculations[16] is considered it is found, as the contour diagram in Figure 8 (Streitweisser and Owens) for total electron density in the molecular plane shows, that while the electron density at the lone-pair end of the molecule falls off less steeply than at the other end of the molecule the angular distribution at nitrogen is quite smooth. A low resistance to the bending motion being considered is readily understandable.

These considerations may be extended to the case where there are two lone-pairs available for hydrogen bonding. Figure 9 (Van Wazer and Absar) reproduces total electron density shape plots for the water molecule[17]. The O—H bonding regions are marked by relatively high directional electron density, but, as has beeen pointed out[16], in the total electron density picture the rabbit ears commonly used to represent lone-pairs do not appear. Instead as the Figure shows there is a smooth electron density distribution and attention has already been drawn to dangers of taking symbolic representations too seriously[16]. Again the total electron density distribution makes it understandable that in the dimer $H_2O \ldots HF$ the H—F axis is readily bent away from a conventional lone-pair axis. Indeed as already pointed out an amplitude of $\pm 60^0$ is encompassed by an energy expenditure of about 1.5 kJ mol^{-1} which is a relatively small fraction of the binding energy of approximately 30 kJ mol^{-1}.

For moderately strong hydrogen bonds it appears that the conventionally viewed lone-pair directions correlate closely with the observed geometries of gas-phase dimers,[18] but the energetic preference for such geometry is sufficiently small that other factors frequently over-ride it for hydrogen bonded structures found in the solid state.

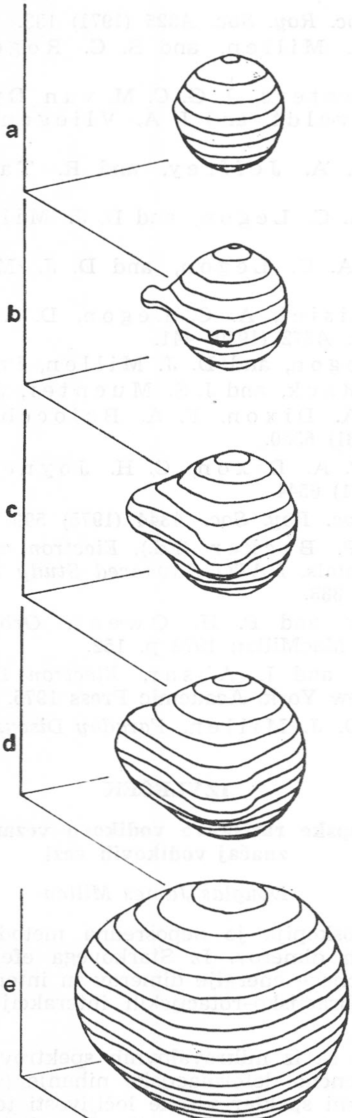


Figure 9. Three-dimensional electron density shape plots for all the electrons of the water molecule. The contour surfaces in the shape plots correspond (a) to 2.0 (b) to 1.7 (c) to 1.0 (d) to 0.6 and (e) to 0.07 $e\text{Å}^{-3}$.

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IZVLEČEK

Mikrovalovne spektroskopske raziskave vodikovo vezanih dimerov in usmerjeni značaj vodikovih vezi

Douglas James Millen

Mikrovalovna spektroskopija je neposredna metoda za določanje geometrije z vodikovo vezjo vezanih dimerov. Iz Starkovega efekta lahko dobimo dodatno dipolne momente, disociacijske energije dimerov in intenzitet, iz študija vibracijsko vzbujenih stanj in iz vibracijsko-rotacijskih interakcij pa potencialne energijske funkcije.

Članek opisuje, kako se iz mikrovalovnih spektrov določi geometrija in konstanta sile za nizkofrekvenčno deformacijsko nihanje (ν_β) vodikove vezi v dimeru $CH_3CN \ldots HF$. Mikrovalovni spekter visoke ločljivosti te spojine namreč kaže prehode med rotacijskimi kvantnimi stanji $J = 8 \leftarrow 7$, za katere je odgovorno nihanje ν_β. Poznavanje konstante sil f_θ, f_ϕ in $f_{\phi\theta}$ pove, da je mnogo laže upogniti vez $C \equiv \ldots N$ ($\Delta\theta$), kot vez $N \ldots H—F$ ($\Delta\phi$). Pri spremembi obeh kotov za 30^0 se v prvem primeru zmanjša energija vezi za 15%, v drugem pa celo za 53%.

Tudi znani podatki o strukturi vodikovo vezanih dimerov v kristalih, ki jih dobimo s sipanjem nevtronov, kažejo, da obstaja težnja po tvorbi vodikove vezi v ravnini ali blizu ravnine, v kateri leži samski elektronski par, medtem ko ni nobene takšne smeri v smeri samskega elektronskega para.

Pri dimerih s srednje močnimi vodikovimi vezmi v plinski fazi določa usmerjenost vezi AH glede na B smer samskega elektronskega para glede na B, medtem ko odklon vezi H—A od te smeri le malo vpliva na vezavno energijo vezi. Pri dimerih, ki se nahajajo v kristalih, pa se zaradi drugih vplivom tak usmerjeni značaj vodikove veze zgubi.