substituted benzenes. This also confirms the results of our calculations. The details will be published elsewhere.

The writer wishes to express his sincere thanks to Professor S. Mizushima and Dr. T. Shimanouchi at Tokyo University for their kind guidance.

1 Young, DuVall, and Wright, Anal. Chem. 23, 709 (1951).
4 American Chemical Society, Research Project 44, catalog of infra-red and ultra-violet absorption spectra (1951).

Assignment of the OH In-Plane Deformation Frequency

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(Received August 3, 1956)

THE assignment of the OH in-plane deformation frequency, \( \delta(\text{OH}) \), in which the hydrogen atom moves in the COH plane and essentially perpendicular to the OH bond, has been controversial for some time. On the basis of a study of the spectrum of methyl alcohol, some authors\(^9\) have favored a value near 1110 cm\(^{-1}\) for this vibration, whereas others\(^9\) have assigned it to a band at 1340 cm\(^{-1}\). It has also been suggested that this vibration occurs in the 1030 to 1080 cm\(^{-1}\) region.\(^6,7\) and near 1020 cm\(^{-1}\).\(^8\)

In a recent detailed study of a series of alcohols, Stuart and Sutherland\(^9\) found that on dilution a broad doublet with peaks at 1330 and 1410 cm\(^{-1}\) was replaced by a single band near 1250 cm\(^{-1}\), and that a band near 1110 cm\(^{-1}\) shifted to about 1080 cm\(^{-1}\). On deuteration, a band appeared near 900 cm\(^{-1}\) which shifted to 900 cm\(^{-1}\) on dilution. They concluded from these and other results that the \( \delta(\text{OH}) \) vibration in the associated alcohols should be assigned to the 1410 to 1330 cm\(^{-1}\) doublet, although no satisfactory explanation could be given for the doublet structure of this band. We wish to report some results of a study of the spectrum of polyvinyl alcohol\(^9\) which bear on the assignment of the \( \delta(\text{OH}) \) frequency.

We have obtained the infrared spectra of normal and of deuterated polyvinyl alcohol\(^9\) and have found that on deuteration the \( \delta(\text{OH}) \) frequency decreases from about 1080 cm\(^{-1}\) for normal polyvinyl alcohol to about 900 cm\(^{-1}\) for deuterated polyvinyl alcohol.\(^9,10,11\) The significant changes on deuteration are the disappearance of bands at 1446 cm\(^{-1}\), 1326 cm\(^{-1}\), and 1096 cm\(^{-1}\), and the appearance of bands at 1384 cm\(^{-1}\), 1052 cm\(^{-1}\), and 985 cm\(^{-1}\), all of these bands being of comparable intensity. It seems fairly certain\(^9\) that the 1096 cm\(^{-1}\) band, and its counterpart at 1052 cm\(^{-1}\), is related to a \( \nu(\text{CO}) \) vibration, and that the 985 cm\(^{-1}\) band is a \( \delta(\text{OD}) \) vibration. There is also good evidence\(^9,10\) that the 1384 cm\(^{-1}\) band is to be assigned to a CH bending mode, \( \delta(\text{CH}) \). We therefore suggest that the \( \delta(\text{OH}) \) mode of the associated molecule interacts with the \( \delta(\text{OD}) \) mode, giving rise to two mixed vibrations \( \delta(\text{OH}+\text{CH}) \), whose frequencies are close to 1330 cm\(^{-1}\) and 1410 cm\(^{-1}\) (or 1446 cm\(^{-1}\) in polyvinyl alcohol). In the monomeric state of the alcohols this interaction disappears, leaving a single \( \delta(\text{OH}) \) frequency at about 1250 cm\(^{-1}\). The same happens on deuteration, giving a single \( \delta(\text{OD}) \) frequency at about 950 cm\(^{-1}\).

If the foregoing explanation is correct, we would expect that upon dilution of a secondary alcohol a band near 1380 cm\(^{-1}\) should become more intense, representing the uncoupled \( \delta(\text{CH}) \) mode. This has indeed been found\(^9\) in dilution studies on pentanol-3. Similarly, we would predict that the \( \delta(\text{OH}) \) frequency of associated tertiary alcohols should be single, and this again is in accord with the observations.\(^9\) The experimental evidence is less clear in the case of primary alcohols, where we would expect the doubling to arise from coupling between the \( \delta(\text{OH}) \) and \( \delta(\text{CH}_2) \) vibrations. However, there do seem to be some apparently anomalous frequency and intensity changes in this region on dilution.\(^8\) The situation in polyvinyl alcohol is more clear-cut because of the absence of CH\(_2\) group absorption, and because of simplifications introduced by the repeating chain. In order to clarify the problem in the case of the primary alcohols, more observations are needed on alcohols in which the CH\(_3\) and OH groups have been deuteroned, both individually and simultaneously.

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‡ G. B. B. M. Sutherland, Discussions Faraday Soc. 9, 274 (1950).
• Krimm, Liang, and Sutherland, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June, 1956; J. Polymer Sci. (to be published).
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Millimeter-Wave Lines of Heavy Water

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(Received August 13, 1956)

FROM the rotational and centrifugal distortion constants of HDO given by Posener\(^2\) the 1,1-1,1 line of HDO is predicted to 80 606 Mc. The constants given by Weisbaum et al.\(^4,5\) give 80 545 Mc for the same line. The corresponding predictions for the 2,2-2,2, line are 241 699 Mc and 241 436 Mc, respectively. These lines have been observed here at frequencies, which are about intermediate between the two predictions, namely 80 578.15 Mc and 241 561.3 Mc. The first line has been identified by means of its Stark effect whereas the identification of the latter is still a matter of probability.

Since the rigid rotor frequency of the 2, line is exactly three times that of the 1, line, this pair gives directly some information about the centrifugal distortion. Neglecting the \( (K, K \pm 1) \) off diagonal elements in the energy matrix one gets

\[
\begin{align*}
\{\nu(1) &= \nu(1) - 3\delta J + 3\delta S \\
\nu(2) &= 3\nu(1) - 72\delta J + 24\delta S
\end{align*}
\]

where \( \nu(1) \) is the rigid rotor frequency. (The same relations may be derived from the Kivelson-Wilson approximation formula for Q-branch lines.) Eliminating \( \nu(2) + 3\nu(1) \) one obtains \( \delta J = 3.61 \pm 0.04 \) Mc, which is somewhat closer to Posener's theoretical value 3.333 Mc than to Weisbaum's empirical 4.168 Mc.

In addition to the above lines a number of other lines of HDO and D\(_2\)O have been observed in the millimeter region. The identification of these has been greatly facilitated by the infrared results of Benedict et al.\(^8\) In two cases (HDO and D\(_2\)O, 5,4-6,4) the lines were found as a result of searching at the frequencies predicted by them (138.5 and 90.5 kMc). The observed lines and their assignments are given in Table I. The somewhat tedious task

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Transition</th>
<th>Frequency Mc</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDO</td>
<td>1,1-1,1</td>
<td>80 578.15</td>
</tr>
<tr>
<td></td>
<td>2,2-2,2</td>
<td>241 699.3</td>
</tr>
<tr>
<td></td>
<td>3,3-3,3</td>
<td>50 236.30</td>
</tr>
<tr>
<td></td>
<td>4,4-4,4</td>
<td>143 727.2</td>
</tr>
<tr>
<td></td>
<td>5,5-5,5</td>
<td>120 173.2</td>
</tr>
<tr>
<td></td>
<td>6,6-6,6</td>
<td>138 530.4</td>
</tr>
<tr>
<td>D(_2)O</td>
<td>3,3-4,4</td>
<td>43 414.57</td>
</tr>
<tr>
<td></td>
<td>4,4-5,4</td>
<td>154 483.32</td>
</tr>
<tr>
<td></td>
<td>5,5-6,5</td>
<td>90 916.8</td>
</tr>
</tbody>
</table>

of refining the constants for HDO to fit the new data has hitherto only been started. It is hoped that it can be put up to an electronic computer later on.

We are grateful to Professor Walter Gordy for suggesting this work and for helpful discussions.

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Dipole Moment of NF₃

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(Received July 6, 1956)

In a recent letter,1 Masmia presented calculations intended to show that the dipole moment of NF₃ can be satisfactorily explained assuming directed single bonds with the amount of singlet–triplet hybridization of the N orbitals required by the observed bond angle. The present author has contended2 that this interpretation can be reasonably explained only by abandoning the simple single bond model and adopting a multiple bonded structure in which the singlet–triplet hybridization is a function of the bond angle.

In his calculation Masmia has ignored the exact ionic character of the N–F bond. Using a recently published tabulation,3 the electronegativity difference X(N)-X(F) is 0.95. This would correspond, according to estimates by various authors,4 to between 42% and 51% ionic character for a corresponding diatomic molecule, so that one might estimate each N–F bond in NF₃ to be roughly 16% ionic. This is sufficient to severely influence a calculation of the dipole moment.

Evidence of partial multiple bonding arises from the observation that the N–F bond distance in NF₃ (1.37 Å) is significantly less than that in NH₃ (1.46 Å).5 Inclusion of partial multiple bonding would presumably affect the computed bond angle and dipole moment.

Even if one accepts a model without partial ionic or multiple character, agreement with the observed dipole moment is difficult with the observed bond angle and dipole moment can be obtained by a suitable choice of two adjustable parameters, would be of enhanced interest if further understanding of the bond energy, bond length, or nuclear quadrupole coupling followed from the orbitals so obtained.

7. Reference 7, p. 231.

Electrostatic Interpretation of Directed Valence

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(Received July 19, 1956)

Since the early 1930's, it has been common to discuss bond angles in terms of directional properties of atomic orbitals. It is clear, however, that there is no causal relationship between the mathematical convenience of the orbital approximation and the occurrence of directed valences. We will take the two molecules BeH₂ and H₂O as typifying the problem of directed valence and show that their difference in shape can be understood qualitatively in terms of an electrostatic model.

First, consider the symmetrical approach of two protons P to a hydrogen-like atom M: the energy of repulsion between the two nuclei will be a minimum when they are in a straight line $P-M-P$, but the energy of attraction between the electron and the nucleus is a maximum when the two P nuclei are superimposed, i.e., $[2P-M]$ (compare the H₂⁺ molecule, where approximate electronic attraction energies for 4a₄ separation are $1; \theta = 180^\circ$, $E = -2.62\mu$; $\theta = 60^\circ$, $E = -3.31\mu$; $\theta = 0$, $E = -4.51\mu$). For any given $M-P$ distance, the expected bond angle will depend on the absolute magnitudes of these two energy terms and the way in which they vary with the $P-M-P$ angle. The equilibrium molecular configuration arises from a compromise between these considerations and the way in which the two energy terms vary with internuclear separation.

The compounds $MH₄$ may be divided into two classes, (1) where the nuclear repulsion term dominates and (2) where the net electronic attraction term dominates. Consider the approach of

Dipole Moment of NF₃

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(Received July 26, 1956)

It is pertinent to add to the Letter of P. Kisliuk,1 under the above title, the following remarks. In a previous Letter,2 the author has indicated that the observed dipole moment of NF₃ can be satisfactorily explained assuming $s-\pi$ hybridization of the N and F bonds of the bonding wave function.

Kisliuk3 points out that the $s$ hybridization (53%) of the F bond orbital is unusually large. According to the author's calculation, 33.4% $s$ character is required for maximum overlap, and agreement with the observed dipole moment is obtained for 51.5% or 55.8% $s$ character. Thus, it may be said that the principle of maximum overlapping is nearly satisfied.

For another example, PCl₅, we can see that maximum overlap is attained at 45.2% $s$ character of the Cl bond orbital, and agreement with the observed dipole moment is obtained at 40.5% $s$ character. It is clear that similar character of the bond orbitals in these molecules is reasonable, since the electronegativity4 difference in NF₃ and PCl₅ are 0.95 and 0.9, respectively.

For PF₅ (with the electronegativity difference $X(F)-X(P)=1.85$), there is a striking difference in that the observed dipole moment is larger than the maximum value calculated by the same type of assumption as NF₃. Thus, the observed dipole moment cannot be explained merely in terms of hybridization, but the ionic terms must be added to the bonding wave function.

It is of interest to see that with regard to HCl (with $X(Cl)-X(H) = 0.9$) and HF ($X(F)-X(H) = 1.4$), similar circumstances have been indicated by Warhurst and Whittle.4 Of course, further checks of the simple model with experiment are needed before it may be used with confidence.