

INFRARED INTENSITIES AND THE NATURE OF THE CHEMICAL BOND

PART I. VARIATION OF HYBRIDIZATION WITH BOND LENGTH IN SO₂, NH₃ AND PH₃

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(Communicated by R. S. Krishnan, F.N.I.)

(Received June 13 ; read December 6, 1957)

ABSTRACT

The differences in the $\frac{d\mu}{dr}$ values (μ = bond dipole moment, r = bond length) obtained from parallel and perpendicular infrared fundamental vibration bands SO₂, NH₃ and PH₃ are ascribed to changes in the hybridization of the pair orbitals which will contribute to the moment derivatives due to stretch in the parallel bands but may not influence the perpendicular bands on account of symmetry. By making use of the plausible assumption that when the bonds in these molecules are stretched (totally symmetric mode) the s character of the lone pair orbitals tends to increase, it has been possible to study the variation of hybridization due to bond stretch from infrared intensity data. A discussion on the method of ascertaining the sign of $\frac{d\mu}{dr}$ of bonds, using the case of H₂O for illustration, is also given.

1. INTRODUCTION

The importance of absolute infrared intensity measurements on fundamental vibration bands for the study of polar properties of bonds has come to be widely recognized. Although experimental data do not claim very high order of accuracy it is nevertheless possible with their aid to arrive at reasonably accurate values of $\frac{d\mu}{dr}$ and $\frac{d\mu}{d\alpha}$ (μ = bond dipole moment ; r = bond length and α = bond angle).

The quantity $\frac{d\mu}{dr}$ is of interest in the study of the polar behaviour of bonds due to stretch while the quantity $\frac{d\mu}{d\alpha}$ is related to the bond moment (Rollefson and Havens, 1940 ; Volkenstein, 1941 ; Thorndike, Wells and Wilson, 1947). In deducing the $\frac{d\mu}{dr}$ and μ values from the observed intensities one generally makes the assumption that the moment of a bond lies along its axis and originates from the asymmetric charge distribution of the bonding electrons. Of course, the assumption of the additivity of these bond moments (Thorndike, 1947) is implicitly made and usually inductive effects are neglected.

Valuable data on $\frac{d\mu}{dr}$ values for the S-O, N-H and P-H bonds in SO₂, NH₃ and PH₃ respectively have been recently obtained from infrared intensities by

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Eggers, Hisatsune and Van Alten (1955) and McKean and Schatz (1956). The $\frac{d\mu}{dr}$ values obtained from the parallel bands of these molecules differ significantly from those obtained from the perpendicular bands. Although the genuine nature of these differences seems to be well established the exact magnitudes are very much dependent on the correctness in the choice of the potential functions used in the vibrational analyses. Further, the $\frac{d\mu}{dr}$ values are obtained from $\frac{\partial M}{\partial Q}$ (M = molecular moment and Q = normal co-ordinate) and on this account the signs of $\frac{d\mu}{dr}$ are not

known since the experimentally observed intensities are proportional to $\left| \frac{\partial M}{\partial Q} \right|^2$.

When there are two or more normal co-ordinates in the same symmetry class then a linear combination of these has to be used and thus various combinations of signs result. It is sometimes possible in this manner to choose suitable combinations of $\frac{\partial M}{\partial Q}$ such that the $\frac{d\mu}{dr}$ values obtained for the same bond from bands of different symmetry are almost equal. More often this is not so. The validity of the procedure of choosing so-called 'self-consistent' signs for $\frac{\partial M}{\partial Q}$ has been recently questioned by Hornig and McKean (1955) and we shall content ourselves for the present to refer the reader to the paper by these authors.

An analysis of the data so far obtained forces us to note the genuine nature of the differences in $\frac{d\mu}{dr}$ values obtained from the different symmetry types of bands in several molecules and in this paper an attempt has been made to relate the observed differences between parallel and perpendicular bands in SO_2 , NH_3 and PH_3 to the changes in the hybridization of the lone pair orbitals with bond stretch in these molecules. The variation of the hybridization of bond orbitals due to stretch has thus been studied. It has been pointed out here that it would be possible to get at the sign of $\frac{d\mu}{dr}$ in some cases from a consideration of the nature of the hybridization changes in the lone pair orbitals due to bond stretch. A discussion of the effect of lone pair orbital hybridization variation on the infrared intensity of the carbon monoxide molecule has been given by Moffitt (1949). Hitherto the effect of hybridization changes of lone pair orbitals on $\frac{d\mu}{dr}$ values in polyatomic molecules has been generally neglected and it appears worth while to go into this matter in greater detail.

2. NORMAL CO-ORDINATES, SYMMETRY CO-ORDINATES AND $\frac{d\mu}{dr}$

Infrared intensity data already obtained for several molecules have been hitherto discussed as follows. The absolute intensity A_k of the k th normal mode can be expressed as

$$A_k = \int_{\nu \text{ band}} \frac{I_0}{I} d\nu = \frac{N\pi}{3c} \left\{ \left| \frac{\partial M_x}{\partial Q_k} \right|^2 + \left| \frac{\partial M_y}{\partial Q_k} \right|^2 + \left| \frac{\partial M_z}{\partial Q_k} \right|^2 \right\} \quad \dots \quad (1)$$

I_0 and I are the intensities of the incident and transmitted beams, N is the number of molecules per unit volume and c is the velocity of light. The integration is over the entire band and M_x , M_y and M_z are the components of the molecular moment during vibration along chosen mutually perpendicular axes in the molecule. Using

the symmetry of the molecule under consideration it is then possible to relate $\frac{\partial M}{\partial Q}$ values to $\frac{\partial M}{\partial S}$, S being the symmetry co-ordinate (Wilson, Decius and Cross, 1955). Thus

$$\frac{\partial M}{\partial S_i} = \sum \frac{\partial M}{\partial Q_k} \frac{\partial Q_k}{\partial S_i} = \sum (L^{-1})_{ki} \frac{\partial M}{\partial Q_k} \quad \dots \quad (2)$$

where (L^{-1}) is the transformation matrix. The $\frac{\partial M}{\partial S_i}$'s are then expressed as functions of $\frac{d\mu}{dr}$ and μ according to the symmetry of the vibration. While doing so, only bonded orbitals, i.e. chemical bonds, are considered and the quantitative analysis of the effect of lone pair orbitals on $\frac{d\mu}{dr}$ values is generally neglected. The effect of lone pair orbitals on $\frac{d\mu}{d\alpha}$ in NH_3 and PH_3 has been considered by McKean and Schatz (1956) while the case of the 'umbrella mode' of NH_3 has been discussed recently by Cohan and Coulson (1956). In this paper, however, we shall limit ourselves to a consideration of the $\frac{d\mu}{dr}$ values alone.

It will be now advantageous to focus our attention on the details of the usual normal co-ordinate analysis for non-linear triatomic molecules of type AB_2 (see Herzberg, 1945, p. 66). The symmetry co-ordinates for this class (C_{2v}) of molecules are given below.

$$S_1 = \frac{1}{\sqrt{2}} (\Delta r_1 + \Delta r_2) \quad \dots \quad (3)$$

$$S_2 = r \Delta \alpha \quad \dots \quad (4)$$

$$S_3 = \frac{1}{\sqrt{2}} (\Delta r_1 - \Delta r_2) \quad \dots \quad (5)$$

S_1 and S_2 belong to the A_1 species and S_3 belongs to B_1 . Equation (2) therefore gives the following relations.

$$\frac{\partial M_s}{\partial S_1} = (L^{-1})_{11} \frac{\partial M_s}{\partial Q_1} + (L^{-1})_{12} \frac{\partial M_s}{\partial Q_2} \quad \dots \quad (6)$$

$$\frac{\partial M_s}{\partial S_2} = (L^{-1})_{21} \frac{\partial M_s}{\partial Q_1} + (L^{-1})_{22} \frac{\partial M_s}{\partial Q_2} \quad \dots \quad (7)$$

$$\frac{\partial M_s}{\partial S_3} = (L^{-1})_{33} \frac{\partial M_s}{\partial Q_3} \quad \dots \quad (8)$$

These equations yield the following relations for $\frac{d\mu}{dr}$ and μ .

$$\frac{d\mu}{dr} = \frac{\partial M_s}{\partial S_1} \frac{1}{\sqrt{2}} \frac{1}{\cos \frac{\alpha}{2}} \quad \dots \quad (9)$$

$$\mu = - \frac{\partial M_s}{\partial S_2} \frac{r}{2 \sin \frac{\alpha}{2}} \quad \dots \quad (10)$$

$$\frac{d\mu}{dr} = \frac{\partial M_z}{\partial S_3} \frac{1}{\sqrt{2} \sin \frac{\alpha}{2}} \dots \dots \dots (11)$$

We note that equations (9) and (11) both give an expression for $\frac{d\mu}{dr}$ and on the basis of the assumptions mentioned earlier these equations should lead to identical values. Since experimental data do not confirm this identity in several cases it appears that we are neglecting certain important factors. We have also reasons to expect that these factors might affect the values of $\frac{d\mu}{dr}$ in a varying manner according to the symmetry of the vibrations. In fact, on the basis of our present quantum mechanical picture of the electron density distribution in a molecule it is possible to evaluate these factors quantitatively also. We shall now consider this matter in greater detail.

3. ORBITAL HYBRIDIZATION, LONE PAIR ORBITALS AND INFRARED INTENSITIES

The work of Coulson (1942), Robinson (1949), Moffitt (1949), Pople (1950; 1953) and others (Duncan and Pople, 1953) has shown that when orbital hybridization takes place the lone pair orbitals make a significant contribution to the dipole moment of the molecule. Thus, in the case of H₂O Coulson, Pople and Duncan and Pople have shown that the *s-p* hybridized lone pair orbitals of the oxygen atom contribute a fairly large moment, the magnitude of which depends on the ratio of *s* and *p* in the hybrid. The direction of this lone pair moment is such that it points away from the O-H bonds (i.e. along the *z* axis, taken as negative). Thus in addition to the so-called 'bond moment' we have the lone pair moment also. With this picture in mind let us now consider, as an example, the normal co-ordinate analysis of H₂O by means of equations 1 to 11.

In the totally symmetric stretching (*S*₁) mode of vibration the O-H bonds are simultaneously subjected to a stretch along their lengths. Such a stretch will lead to a readjustment of the electron cloud in the molecule and hence to a change in its dipole moment. We can picture to ourselves the change in the dipole moment with stretch as due to four factors. These are (a) change in the overlap of the bonding orbitals, (b) change in the ionic character of the bond, (c) change in the hybridization of the bonding orbitals and (d) change in the hybridization of the lone pair orbital (s) consequent upon a change in the hybridization of the bonding orbitals. It should be pointed out here that we have neglected the effect of (b) on the lone pair orbital moment in the present discussion. The nature of such an effect does not seem to be well established although it is probable. Factors (a), (b), and (c) produce a change in the 'bond moment' while (d) affects the lone pair moment. The origin of (d) is as follows: When, for example, a *s-p* hybrid bond between two atoms is stretched the bond partakes more *p* character than *s* (Coulson, 1948). Owing to the normalization condition, however, the bond stretch leads to more *s* character of the lone pair orbital and thus changes its dipole moment. The infrared absolute intensity of the totally symmetric stretching mode of the vibration band (parallel band) is proportional to the quantity $\sum \left| \frac{\partial M_z}{\partial Q} \right|^2$ or, in other words, to the square of the derivative of the *z* component of the total moment of the molecule with respect to the normal co-ordinate. Since the lone pair moment has a non-vanishing component μ_l along the *z* axis the $\frac{d\mu}{dr}$ value obtained from this mode (equation 9) will include the contribution from the lone pair orbital (s) also if $\frac{d\mu_l}{dr} \neq 0$. We speak of the lone pair orbital or orbitals depending on the

hybridization scheme, as for example, whether we use sp^2 or sp^3 hybridization scheme for oxygen in H_2O .

In the asymmetric stretching mode (S_3) of vibration (perpendicular band) the infrared absolute intensity is proportional to the quantity $\left| \frac{\partial M_z}{\partial Q_3} \right|^2$. If we assume that the lone pair orbital moment continues to lie along the z axis during this mode of vibration then we can say that the value of $\frac{d\mu}{dr}$ obtained from equation (11) represents the 'true' value since it will have no contribution from the lone pair orbitals (s) unlike the $\frac{d\mu}{dr}$ value obtained from equation (9). As long as we are dealing with identical symmetrically bonding orbitals and very small displacements the above assumption seems to be reasonable. Now, the moment of the lone pair orbital along the z axis being μ_l , we can calculate this moment according to the sp^2 hybridization scheme as follows:

$$\mu_l = -4e \cos \chi_l \sin \chi_l \int \psi_{2s} z \psi_{2p} d\tau \quad \dots \quad (12)$$

(e = electronic charge). Here χ_l denotes the hybridization parameter ($0 < \chi < \frac{\pi}{2}$) in the wave function ψ_l of the lone pair orbital, i.e.

$$\psi_l = \cos \chi_l \psi_{2s} + \sin \chi_l \psi_{2p} \quad \dots \quad (13)$$

Now χ_l is related to χ_b , the bond hybridization parameter, by the normalization condition

$$\cos^2 \chi_l + 2 \cos^2 \chi_b = 1 \quad \dots \quad (14)$$

In the totally symmetric stretching mode, as has been pointed out earlier, χ_b will vary with stretch, i.e. $\frac{d\chi_b}{dr} \neq 0$ and hence we expect $\frac{d\chi_l}{dr} \neq 0$. It follows therefore that $\frac{d\mu_l}{dr} \neq 0$. Thus we find

$$\frac{d\mu_l}{dr} = -4e \cos 2\chi_l \frac{d\chi_l}{dr} \int \psi_{2s} z \psi_{2p} d\tau \quad \dots \quad (15)$$

Incidentally for H_2O the value of χ_b and hence χ_l may be obtained from the equation

$$\cos^2 \chi_b = \frac{\cos \alpha}{\cos \alpha - 1} \quad \dots \quad (16)$$

where α is the bond angle. From equations (3) and (15) we can write $\frac{d\mu_l}{dS_1}$ as follows:

$$\frac{d\mu_l}{dS_1} = \frac{1}{\sqrt{2}} \frac{d\mu_l}{dr} = -2\sqrt{2}e \cos 2\chi_l \frac{d\chi_l}{dr} \int \psi_{2s} z \psi_{2p} d\tau \quad \dots \quad (17)$$

The total moment of the molecule along the z axis is

$$-M_z = 2\mu \cos \frac{\alpha}{2} - \mu_l \quad \dots \quad (18)$$

the sign being given from considerations of the magnitude and direction of the lone

pair moment and the value of the total molecular moment. From (3) and (18) we have

$$-\left(\frac{\partial M_x}{\partial S_1}\right) = \sqrt{2} \left(\frac{d\mu}{dr}\right) \cos \frac{\alpha}{2} - \frac{1}{\sqrt{2}} \left(\frac{d\mu_1}{dr}\right) \quad \dots \quad (19)$$

It should be pointed out here that we do not know as yet the signs of the quantities in brackets. Substituting expression (11) for $\frac{d\mu}{dr}$ in (19) and using equation (17) we get on rearranging

$$\left(\frac{d\mu_1}{dr}\right) = \sqrt{2} \left\{ \left(\frac{\partial M_x}{\partial S_3}\right) \frac{1}{\tan \frac{\alpha}{2}} + \left(\frac{\partial M_x}{\partial S_1}\right) \right\} \quad \dots \quad (20)$$

Now, in H₂O hybridization considerations have shown that $\frac{d\chi_1}{dr}$ in equation (15) is negative and hence $\frac{d\mu_1}{dr}$ is positive. Hence, this restricts further the choice of $\frac{\partial M_x}{\partial S_1}$ and $\frac{\partial M_x}{\partial S_3}$. If we could calculate *a priori* the value of $\frac{d\chi_1}{dr}$ from other considerations then we can find the sign and magnitude of $\frac{d\mu_1}{dr}$ from equation (17) and thus equation (20) will enable us to make the correct choice of $\frac{\partial M_x}{\partial S_1}$ and $\frac{\partial M_x}{\partial S_3}$. The sign and magnitude of $\frac{d\mu}{dr}$ can therefore be obtained from equation (11). The extension of this method to other types of molecules is also obvious. Unfortunately, it is not possible at present to calculate theoretically or obtain otherwise the value of $\frac{d\chi_1}{dr}$ and consequently we shall reverse the procedure by calculating the value of $\frac{d\chi_1}{dr}$ from the observed intensity data of SO₂, NH₃ and PH₃. It may be remarked here that accurate infrared intensity data for H₂O are lacking.

4. SULPHUR DIOXIDE

The electronic structure of sulphur dioxide has been discussed by Moffitt (1950). Although we will not be directly interested in the detailed description of the electronic structure of the S-O bond it is necessary for us to know the hybridization characteristics of the central sulphur atom in order to enable us to calculate the lone pair moment derivative. For our present calculations we shall take the lone pair orbital to be a *sp*² hybrid and neglect *d*. This procedure may be justified on account of the very small *d*-character of the S-O bond in sulphur dioxide and also in view of the approximate nature of the wave functions to be used in the present calculations. Thus, using Slater-type wave functions for sulphur with *Z* = 5.45 we get the following relation (distances are in Bohr radii):

$$\frac{d\mu_1}{dr} = -4e \cos 2\chi_1 \frac{d\chi_1}{dr} \int \psi_{3s} z \psi_{3p} dr = 2.965e \frac{d\chi_1}{dr} \quad \dots \quad (21)$$

The infrared intensity data for SO₂ have been obtained by Eggers, Hisatsune and

Van Alten (1955) who give the following values:— $\frac{\partial M_x}{\partial S_3} = \pm 1.064e$; $\frac{\partial M_x}{\partial S_1} = \pm 0.300e$ or $\pm 0.633e$. On account of the ambiguity in the sign and magnitude of these quantities we get a large number of possible values for $\frac{d\chi_i}{dr}$ as shown in Table I. A value of $\alpha = 120^\circ$ has been used in the calculations. The method is similar to that outlined for H_2O in the previous section.

5. AMMONIA AND PHOSPHINE

In these molecules the totally symmetric stretch mode (ν_1) of symmetry A_1 will have the lone pair contribution according to our previous considerations while the asymmetric stretch mode (ν_3) of symmetry (E) (see Herzberg, 1945, p. 155) will have no contribution from the lone pair orbital. For ammonia, McKean and Schatz (1956) give the following data:— $\frac{\partial M_x}{\partial S_3} = \pm 0.037e$ and $\frac{\partial M_x}{\partial S_1} = \pm 0.082e$. From the symmetry co-ordinates of this molecule (C_{3v}) and its known geometry we have

$$\frac{d\mu_i}{dr} = \sqrt{3} \left\{ 0.572 \left(\frac{\partial M_x}{\partial S_3} \right) + \left(\frac{\partial M_x}{\partial S_1} \right) \right\} \quad \dots \quad (22)$$

Using Slater-type s and p wave functions for nitrogen atom with $Z = 3.90$ we get

$$\frac{d\mu_i}{dr} = -4e \cos 2\chi_i \frac{d\chi_i}{dr} \int \psi_{2s} z \psi_{2p} d\tau = 1.02e \frac{d\chi_i}{dr} \quad \dots \quad (23)$$

Table II gives the values of $\frac{d\mu_i}{dr}$ and $\frac{d\chi_i}{dr}$ for NH_3 obtained from equations (22) and (23).

Similarly, for PH_3 we can write $\frac{d\mu_i}{dr}$ as below.

$$\frac{d\mu_i}{dr} = \sqrt{3} \left\{ 0.910 \left(\frac{\partial M_x}{\partial S_3} \right) + \left(\frac{\partial M_x}{\partial S_1} \right) \right\} \quad \dots \quad (24)$$

Considering for the sake of simplicity, only s - p hybridization and using Slater functions with $Z = 5.0$ for the P atom we get the following relation for $\frac{d\mu_i}{dr}$.

$$\frac{d\mu_i}{dr} = -4e \cos 2\chi_i \frac{d\chi_i}{dr} \int \psi_{3s} z \psi_{3p} d\tau = -6.351e \frac{d\chi_i}{dr} \quad \dots \quad (25)$$

Table III gives the values of $\frac{d\mu_i}{dr}$ and $\frac{d\chi_i}{dr}$ for PH_3 obtained from equations (24) and (25). The data for $\frac{\partial M_x}{\partial S_1}$ and $\frac{\partial M_x}{\partial S_3}$ are those given by McKean and Schatz.

6. DISCUSSION

The values of $\frac{d\chi_i}{dr}$ obtained in Tables I, II and III can be related to $\frac{d\chi_b}{dr}$ of the respective bonds by differentiation of equations similar to (14). Thus we have

$$\frac{d\chi_b}{dr} = -\frac{\cos \chi_i \sin \chi_i}{2 \cos \chi_b \sin \chi_b} \cdot \frac{d\chi_i}{dr} = -0.5 \frac{d\chi_i}{dr} \text{ for S-O, } \quad \dots \quad (26)$$

TABLE I
 $\frac{d\chi_i}{dr}$ values of sulphur dioxide

	$\frac{\partial M_x}{\partial S_3}$	$\frac{\partial M_x}{\partial S_1}$	$\frac{d\mu_i}{dr}$	$\frac{d\chi_i}{dr}$
(1a)	+1.064e	+0.300e	+1.293e	+0.436
(2a)	+1.064,,	-0.300,,	+0.445,,	+0.150
(3a)	-1.064,,	+0.300,,	-0.445,,	-0.150
(4a)	-1.064,,	-0.300,,	-1.293,,	-0.436
(1b)	+1.064e	+0.633e	+1.764e	+0.595
(2b)	+1.064,,	-0.633,,	-0.026,,	-0.009
(3b)	-1.064,,	+0.633,,	+0.026,,	+0.009
(4b)	-1.064,,	-0.633,,	-1.764,,	-0.595

TABLE II
 $\frac{d\chi_i}{dr}$ values of ammonia

	$\frac{\partial M_x}{\partial S_3}$	$\frac{\partial M_x}{\partial S_1}$	$\frac{d\mu_i}{dr}$	$\frac{d\chi_i}{dr}$
(1)	+0.037e	+0.082e	+0.178e	+0.175
(2)	+0.037,,	-0.082,,	-0.106,,	-0.104
(3)	-0.037,,	+0.082,,	+0.106,,	+0.104
(4)	-0.037,,	-0.082,,	-0.178,,	-0.175

TABLE III
 $\frac{d\chi_i}{dr}$ values of phosphine

	$\frac{\partial M_x}{\partial S_3}$	$\frac{\partial M_x}{\partial S_1}$	$\frac{d\mu_i}{dr}$	$\frac{d\chi_i}{dr}$
(1)	+0.148e	+0.233e	+0.637e	-0.100
(2)	+0.148,,	-0.233,,	-0.170,,	+0.027
(3)	-0.148,,	+0.233,,	+0.170,,	-0.027
(4)	-0.148,,	-0.233,,	-0.637,,	+0.100

and

$$\frac{d\chi_b}{dr} = -\frac{\cos \chi_i \sin \chi_i}{3 \cos \chi_b \sin \chi_b} \cdot \frac{d\chi_i}{dr} = -0.2167 \frac{d\chi_i}{dr} \text{ for N-H, } \dots \dots (27a)$$

$$= -0.3123 \frac{d\chi_i}{dr} \text{ for P-H. } \dots \dots (27b)$$

For the case of sulphur dioxide, lone pair $s-p$ hybridization considerations show that $\frac{d\chi_i}{dr}$ must be negative, as in the case of H_2O . Amongst the first set of values in Table I (1a to 4a) we note that 3a and 4a lead to this sign while 1a and 2a do not agree. Thus we may be justified in selecting 3a or 4a and these sets point to a negative sign for $\frac{\partial M_s}{\partial S_3}$ and thus for $\frac{d\mu}{dr}$. However, this clear-cut choice of sign for $\frac{\partial M_s}{\partial S_3}$ is not possible from the (b) sets since the two negative $\frac{d\chi_i}{dr}$ values are possible for both + and - signs for $\frac{\partial M_s}{\partial S_3}$ (see 2b and 4b in Table I). But it is worth while noting that these two $\frac{d\chi_i}{dr}$ values point to the negative sign for $\frac{\partial M_s}{\partial S_1}$. Thus it appears that with a knowledge of the sign of $\frac{d\chi_i}{dr}$ it is possible to assign the sign for at least one of the $\frac{\partial M}{\partial Q}$'s. Further assignment of signs will be possible when we can calculate *a priori* the value of $\frac{d\chi_i}{dr}$. In SO_2 the experimental data indicate that $\frac{d\chi_i}{dr} > -0.6$ and thus we can expect from equation (26) that $\frac{d\chi_b}{dr} < +0.3$. It must be remembered, however, that this value refers only to the σ -part of the S-O bond in sulphur dioxide. Moffitt (1949) has calculated from infrared intensity data the value of $\frac{d\chi_b}{dr} = +2.7$ for carbon monoxide. We may therefore conclude that our present approach is essentially correct and it may not be unreasonable to hope that infrared intensity data will in future be of great help in the study of the hybridization characteristics of bonds.

In PH_3 and NH_3 from hybridization considerations we again find $\frac{d\chi_i}{dr}$ to be negative. The two $\frac{\partial M_s}{\partial S_1}$ values corresponding to the negative $\frac{d\chi_i}{dr}$ values in NH_3 are both negative and thus $\frac{\partial M_s}{\partial S_1}$ can be taken to be negative. However, the sign of $\frac{\partial M_s}{\partial S_3}$ is not certain and hence the sign of $\frac{d\mu}{dr}$ can be found only when an accurate *a priori* calculation of $\frac{d\chi_i}{dr}$ is possible. In the case of PH_3 we may conclude by arguments similar to above that $\frac{\partial M_s}{\partial S_1}$ is positive. Using equations (27a) and (27b) we find that for NH_3 $\frac{d\chi_b}{dr} < +0.04$ while for PH_3 it is $< +0.03$. Needless to say

that these values are only approximate ones. However, it may be noted that the small magnitude of these values and the closeness of the range for NH_3 and PH_3 is in line with the similarity of the N-H and P-H bonds in several other respects. Comparison of these values for NH_3 and PH_3 with that for the σ -part of S-O bond indicates that the $\frac{dX_b}{dr}$ for the latter is nearly ten times larger. It is probable that this is due to the π character of the S-O bond. It is also probable that this fact could be accounted for on the basis of the ionic character of the bonds under consideration. There is need for more work along these lines. The calculated values of $\frac{dX_b}{dr}$ depend on the form of the wave functions used. But the very small magnitude of the $\frac{dX_i}{dr}$ values obtained here show that small changes in the hybridization character of bonds lead to fairly large changes in the dipole moment of the lone pair orbitals and thus affect the infrared intensities. It should be emphasized here that we have assumed in the present formulation that the dipole moments of the bonds are directed along their length (atomic orbital approximation). However, on the basis of the equivalent orbital (m.o.) approximation it can be shown that the component of the bond moment at right angles to the bond is in many cases not equal to zero. In such cases, then, these terms and their derivatives will have to be included. It is thus clear that a study of the infrared intensities will lead to more information concerning the nature of the chemical bond.

ACKNOWLEDGEMENTS

The author's grateful thanks are due to Professor R. S. Krishnan for his kind interest and valuable help in the progress of this work. The author's thanks are also due to the National Institute of Sciences of India for the award of an I.C.I. Research Fellowship which enabled him to carry out the work reported here.

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Issued March 14, 1958.