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both corundum and diaspore the shift of the Al−O distances from 1.90A, the sum of the radii concerned, is evidence of the effect of Al−Al repulsion.

The formula for diaspore we have written $AlHO_2$, the HO_2 group so indicated being taken as representing hydrogen-bonded oxygens. The formula $HAlO_2$ would be equally correct as indicating that both H and Al cations formed coordinated structures with the oxygen cations, and the chemical inference in this latter formula that diaspore is meta-aluminic acid is borne out

by the existence of meta-aluminate salts such as the spinels. Either formula would be more correctly written in the polymerized form $(AlHO_2)_n$ or $(HAlO_2)_n$ to admit the known coordination number of 6 for Al. The usual formulas for diaspore, $Al_2O_3 \cdot H_2O$, $Al_2O_2(OH)_2$, or $AlO(OH)$ are wrong in indicating a distinct existence of water or OH^- ions.

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On the Normal Vibration Frequencies of NH3, PH3 and AsH3

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It is shown that the assumption of valence forces for NH_3, PH_3 and AsH_3 leads to the conclusion that the high frequency, degenerate normal vibration, although theoretically active, does not appear as a fundamental in the infrared spectra of these compounds. This conclusion follows from the fact that the remaining three fundamentals, all of which have been observed, can be accounted for satisfactorily with proper values of the two constants of the potential function for valence forces. The values calculated for this absent frequency with the same force-constants are 3450 cm^{-1}, 2340 cm^{-1} and 2125 cm^{-1} for NH_3, PH_3 and AsH_3, respectively. The frequency for NH_3 may be fixed more precisely at 3470 cm^{-1} if we interpret the 4417 cm^{-1} band as a combination band involving this frequency and the 950 cm^{-1} frequency. Other evidence is given in support of a value for the frequency in the neighborhood of 3450 cm^{-1}. There is, however, the difficulty of explaining why the predicted frequencies are not observed. The 4417 cm^{-1} band is probably to be ascribed to the fourth fundamental in case this fundamental does actually appear. If this is the case, then there is an extreme departure from valence forces in NH_3 and probably likewise in PH_3 and AsH_3. Frequencies are computed for NH_2D, ND_2H and ND_3 to provide a means of testing the value predicted upon the assumption of valence forces for the fourth fundamental in NH_3.

THE justification for using the concept of valence forces in treating NH_3 is based upon its reasonably successful application to H_2O and CH_4. J. H. Van Vleck and P. C. Cross[1] have shown that the fundamental frequencies of H_2O can be computed with fair accuracy using a valence-type potential function. Jenny E. Rosenthal[2] has found that the frequencies of CH_4 are consistent with such a potential function to within six percent. It is therefore justifiable to make the assumption that a similar kind of forces exists in NH_3 and

that the valence-type potential function is probably a good first approximation to the general quadratic expression. Any large deviation from this approximation would, on this assumption, then be considered a consequence of the anharmonic terms introduced by the passing of the nitrogen atom through the plane of the hydrogen atoms. Consequently, to afford a comparison with the results obtained for NH_3, we have also considered PH_3 and AsH_3, in which the bonds are doubtless similar to those of NH_3 and in which this so-called tunnel effect is thought to be of less consequence.[3]

[1] J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).
[2] Jenny E. Rosenthal, Phys. Rev. **46**, 730 (1934).

[3] See for example D. M. Yost and T. F. Anderson, J. Chem. Phys. **2**, 624 (1934).

CALCULATION OF FREQUENCIES

Under the assumption of valence forces the potential function of the symmetrical pyramidal molecule YX_3 is

$$V = 1/2K(\Delta R_1^2 + \Delta R_2^2 + \Delta R_3^2) + 1/2HR_0^2(\Delta\alpha_{12}^2 + \Delta\alpha_{23}^2 + \Delta\alpha_{31}^2).$$

Here K and H are force constants, ΔR_i is the departure of the distance $Y-X_i$ from its equilibrium value R_0 and $\Delta\alpha_{ij}$ is the departure of the angle X_i-Y-X_j from its equilibrium value α_0. This molecule has four distinct frequencies: ν_1 and ν_3, in the notation of Dennison,[4] denote the high and low frequencies, respectively, of vibrations with change of electric moment parallel to the figure axis. Likewise ν_2 and ν_4 correspond to the high and low frequency vibrations, respectively, with change of electric moment perpendicular to this axis, the latter vibrations being doubly degenerate. All four frequencies are theoretically active in both the Raman and infrared spectra.

Formulas for calculating the fundamental frequencies of vibration have been derived by Lechner[5] and others for the above potential function. In Table I are given the values of K and H which make the calculated values of ν_1 and ν_4 agree with the experimental values we have assigned to these frequencies. The values computed for ν_2 and ν_3 with these force constants are likewise given; in the case of NH_3 this calculated value of ν_3 is the unstarred frequency. It is seen that the difference between the calculated value of ν_3 and the observed frequency in its neighborhood, which we have assigned to ν_3, is rather large for NH_3 but is smaller for PH_3 and AsH_3.

The large discrepancy in the case of NH_3 can be explained as a consequence of anharmonic terms in the potential function and does not otherwise, invalidate the assumption of valence forces. These terms principally affect the ν_3 (950) frequency and necessitate a large correction in obtaining the observed frequency, which corresponds to a vibration with finite amplitude, from the frequency for infinitesimal amplitude of vibration, called the mechanical frequency. Mr.

TABLE I. *Bond angle α_0,[6] observed infrared frequencies[7] and calculated frequencies in cm^{-1}, and calculated force constants in dynes/cm for NH_3, PH_3 and AsH_3.*

α_0	NH_3 109°		PH_3 96°		AsH_3 94°	
	obs.	calc.	obs.	calc.	obs.	calc.
ν_3 ($\parallel$)	950	$\begin{cases}1110 \\ 1010*\end{cases}$	990	1050	906	960
ν_4 ($\perp$)	1631	(1631)	1121	(1121)	1005	(1005)
ν_1 ($\parallel$)	3335	(3335)	2327	(2327)	2122	(2122)
ν_2 ($\perp$)		3450		2340		2125
	4417		3428		3091	
	5059					
$K \times 10^{-5}$		6.35		3.09		2.60
$H \times 10^{-5}$		0.59		0.34		0.28

* Corrected for anharmonic term.

M. F. Manning has kindly consented to calculate the mechanical frequency directly from his symmetric double-minima potential function[8] for NH_3. He finds it to be 1050 cm^{-1}, in contrast to the experimental frequency of 950 cm^{-1}. The value 1110 cm^{-1}, calculated for ν_3 upon the assumption of valence forces, does not, of course, allow for the anharmonic correction. It will resemble the mechanical frequency since the anharmonic corrections for the other frequencies are no doubt much smaller than that for ν_3. Applying Manning's correction to the computed value of ν_3 we obtain a final calculated frequency of 1010 cm^{-1}, which is to be compared with the experimental frequency, 950 cm^{-1}. Thus the agreement between the observed frequency ν_3 and the frequency calculated upon the basis of valence forces is as good for NH_3 as for PH_3 and AsH_3, in which there is probably no large anharmonic correction necessary. Furthermore the agreement is to within about six percent. This gives one a certain amount of confidence in the valence-force approximation.

No frequencies have been observed in the infrared, however, in the neighborhoods of the values calculated for ν_2, excepting those assigned to ν_1.

[4] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).
[5] F. Lechner, Wien. Berichte **141**, 633 (1932).

[6] The angle for NH_3 is known from spectroscopic data. The angles for PH_3 and AsH_3 were chosen on the basis of theoretical considerations and evidence from crystal structure given by Pauling, J. Am. Chem. Soc. **53**, 1367 (1931). No appreciable change is produced in the force constants by a change of a few degrees in the angles.
[7] Source of frequencies: NH_3—Schaefer and Matossi, *Das Ultrarote Spektrum*, p. 250. PH_3—Fung and Barker, Phys. Rev. **45**, 238 (1934). AsH_3—Robertson and Fox, Proc. Roy. Soc. **A120**, 149 (1928).
[8] M. F. Manning, J. Chem. Phys. **3**, 136 (1935).

DISCUSSION OF ν_2

NH$_3$

With the value of ν_2 calculated on the assumption of valence forces it is possible to explain the 4417 cm^{-1} infrared band as the combination $\nu_2 (3450) + \nu_3 (950) = 4400$ cm^{-1} and, indeed, it is difficult to account for the band with any other combination of frequencies. The structure of the band is very irregular and does not admit a simple analysis.[9] Because of this complexity it is probably not a parallel-type band. Such bands have, in general, a relatively simple structure and are free of the distortions resulting from rotation-vibration interaction. Hence we must account for what is probably either a perpendicular-type structure or an overlapping of several bands. There appear to be only four alternative explanations. (a) The assignment $\nu_1 (3335) + \nu_3 (950) = 4285$ cm^{-1} suggested by Badger and Mecke[10] leads to a parallel-type band and would not alone explain the structure. Now it is possible that the second overtone of $\nu_4 (1631)$, *viz.*, $3\nu_4 = 4893$ cm^{-1} (minus the anharmonic terms), is stronger than the first overtone and accordingly might badly distort the parallel-type structure of this combination band. This alternative is improbable, however, because of the wide separation of the two frequencies involved. (b) There is the possibility that the second overtone of ν_4 gives rise by itself to the 4417 cm^{-1} band although this is doubtful since the band is almost as intense as the fundamental at 3335 cm^{-1}. (c) The combination $\nu_2 (3450) + \nu_3 (950) = 4400$ cm^{-1} involving the valence-force value of ν_2 does, on the other hand, account for the frequency and intensity of the band, and leads to a perpendicular-type structure, the complexity of which would be increased by the doublet character introduced by the 950 cm^{-1} component. (d) The possibility that the 4417 cm^{-1} frequency is itself ν_2 is considered below.

In the Raman spectrum of gaseous NH$_3$ Lewis and Houston[11] have observed a line at a shift of 3219 cm^{-1} which they suggest may be ν_2. The difference between this frequency and the valence-force value calculated for ν_2 might conceivably be ascribed to the presence of cross terms of moderate size in the potential function. There are two bits of evidence, however, which conflict with the allotment of this line to ν_2. Firstly, Bhagavantam[12] finds that the corresponding line with 3208 cm^{-1} shift in the Raman spectrum of the liquid is very well polarized, a result which is incompatible with the assignment of this line to a degenerate vibration. Secondly, the combination $\nu_2 (3219) + \nu_3 (950) = 4169$ cm^{-1} gives too low a frequency for the 4417 cm^{-1} band which is difficult to account for by another assignment.

Further support of the valence-force assignment for ν_2 is given by the frequencies of the CH$_3$ group in the methyl halides. The CH$_3$X molecule has two more frequencies than the NH$_3$-type molecule as a result of the additional atom X. If we allow the bond between C and X to vanish, however, these two frequencies will go to zero and, simultaneously, the vibrations of CH$_3$X will pass over into the vibrations of a free CH$_3$ molecule. In the spectra[13] of the methyl halides the four frequencies characteristic of the CH$_3$ group are readily identified. The strength of the C – X bond in each halide can be estimated from the observed frequency of vibration of the CH$_3$ group against X by using the diatomic model (CH$_3$) – X. For X equal to F, Cl, Br and I, the force constant for stretching of the C – X bond assumes the values 5.3×10^5, 3.3×10^5, 2.8×10^5 and 2.2×10^5 dynes/cm, respectively. Plotting these values against the observed frequencies of the CH$_3$X molecules and extrapolating to zero force-constant, we obtain the following approximate frequencies of vibration of a free CH$_3$ molecule: $\nu_3 = 900$ cm^{-1}, $\bar{\nu}_4 = 1420$ cm^{-1}, $\nu_1 = 2985$ cm^{-1} and $\nu_2 = 3120$ cm^{-1}. These values are similar to the frequencies calculated for NH$_3$ upon the assumption of valence forces. The extrapolation does not, of course, take into account the consequences of the tunnel effect.

The most obvious difficulty with the valence-force value of 3450 cm^{-1} for ν_2 is that such a frequency does not appear in the infrared whereas

[9] E. F. Barker, private communication.
[10] R. M. Badger and R. Mecke, Zeits. f. physik. Chemie B5, 333 (1929).
[11] C. M. Lewis and W. V. Houston, Phys. Rev. 44, 903 (1933).

[12] S. Bhagavantam, Ind. J. Phys. 5, 49 (1930). For a discussion of the significance of the polarization of Raman lines see G. Placzek, Leipziger Vorträge, p. 71 (1931).
[13] The frequencies of the methyl halides are given by A. Adel and E. F. Barker, J. Chem. Phys. 2, 627 (1934).

ν_2 is a theoretically active frequency. Very little is known, however, regarding the change of electric moment during vibration in such molecules as NH_3 and it cannot be said how serious a difficulty this is. The failure to appear in the Raman spectrum of the gas may be due merely to insufficient intensity; ν_4 (1631) is likewise not observed. It is commonly true that theoretically active, degenerate frequencies appear less intense in Raman spectra than frequencies of completely symmetric vibrations and in the case of compounds containing hydrogen are frequently not observed.

Another possible difficulty has been pointed out to the author by Professor Dennison. From the complete expressions derived by Salant and Rosenthal[14] for the symmetrical tetratomic molecule $Y^{(M)}X_3^{(m)}$ we obtain for two such molecules (denoted by single and double primes) the relation $(m\nu_2\nu_4)'^2/(m\nu_2\nu_4)''^2 = (b/\mu)'/(b/\mu)''$, where $b = 6_B(c^2/a^2) + 1$ and $\mu = M/(3m + M)$. Here c and a are the altitude of the pyramid and the side of the base, respectively. This relation must be satisfied rigorously as long as the potential functions of the two molecules remain purely quadratic. Assuming that the 4417 cm^{-1} band of NH_3 and the 3287 cm^{-1} band of ND_3[15] arise from the combination $\nu_2 + \nu_3$, we obtain 3470 cm^{-1} and 2520 cm^{-1} as the values of ν_2 for NH_3 and ND_3, respectively. These frequencies, when substituted in the above relation together with the observed values of ν_4, lead to a ratio of 0.94 instead of 0.87 which is the value of the ratio of the (b/μ) term for NH_3 to that for ND_3. This difficulty is serious only if the centers ascribed to the observed bands for $\nu_2 + \nu_3$ and ν_4 are correct and if our method of obtaining values for ν_2 is valid. It does not require a large change in the values used to yield a ratio 0.87. Thus the values $\nu_2 = 2565$ cm^{-1} and $\nu_4 = 1180$ cm^{-1} calculated below for ND_3 assuming valence

forces give the correct ratio (since they are obtained from the NH_3 frequencies by using the formulas from which the above comparison relation is derived).

The 4417 cm^{-1} and 3287 cm^{-1} frequencies, on the other hand, give (as was pointed out by Professor Dennison) a ratio of 0.89, in closer agreement. A check of this sort does not, of course, imply that the frequencies used are the correct ones since only the ratios of the frequencies are tested. Nevertheless, this bit of evidence, together with the difficulty of explaining the 4417 cm^{-1} band as a combination other than ν_2 (3470) + ν_3 (950) = 4420 cm^{-1}, indicates that if the assumption of valence forces does not give the correct value of ν_2, this frequency of 4417 cm^{-1} is probably the fourth fundamental. If such is the case then there is a very large departure from valence forces in passing from CH_4 or H_2O to NH_3.

PH_3 and AsH_3

No evidence is available regarding the valence-force interpretation of ν_2 in PH_3 and AsH_3. It seems probable from structural considerations, however, that the values of ν_2 in Table I, calculated using valence forces, will be equally good for these molecules and for NH_3.

CALCULATION OF THE ISOTOPE EFFECT

If the valence-force frequency, $\nu_2 = 3450$ cm^{-1}, for NH_3 is approximately correct the assumption of valence forces should be sufficient to calculate the fundamental frequencies of the isotopic molecules NH_2D, ND_2H and ND_3. In making this calculation we have used the complete formulas derived by J. E. Rosenthal[14] for the vibrational frequencies of the symmetric tetratomic molecule YX_2X^*. Values of the force-constants, $K = 6.42 \times 10^5$ and $H = 0.59 \times 10^5$, were chosen so as to give the calculated frequencies $\nu_2 = 3470$ cm^{-1} and $\nu_4 = 1631$ cm^{-1} for NH_3. This value of ν_2 satisfies the relation $\nu_2 + 950$ cm$^{-1} = 4420$ cm^{-1}. Table II gives the results of the calculations. The letter A after a frequency of NH_2D or ND_2H indicates that it corresponds to a vibration which is antisymmetric with respect to reflection through a plane passing through the figure axis and the hydrogen isotope which differs from the other two. The other frequencies of NH_2D and ND_2H are symmetric with respect

[14] J. E. Rosenthal, Phys. Rev. **45**, 426 (1934); **47**, 235 (1935). These formulas are given in terms of the force constants of the general potential function. In making the calculation, the general constants were evaluated in terms of K and H by means of the expressions for the former given by E. O. Salant and J. E. Rosenthal, Phys. Rev. **42**, 812 (1932) on p. 819. To obtain agreement with the valence-force formulas[6] for YX_3 it was found necessary to change the negative sign before K_6 in the expression for D to a positive sign.
[15] Observed ND_3 frequencies taken from Silverman and Sanderson, Phys. Rev. **44**, 1032 (1933).

TABLE II. *Observed[15] and calculated fundamental frequencies in cm^{-1} of NH_3 and isotopic molecules.*

NH$_3$	obs.	950	1631	3335	?		
	calc.	$\begin{cases} 1010^* \\ 1110 \end{cases}$	(1631)	3355	(3470)		
NH$_2$D	obs.	1025	1385A 1600	3400	2510	3470A	
ND$_2$H	calc.	925	1230 1460A	2455	2565A	3435	
ND$_3$	obs.	770	1158	2421	?		
	calc.	840	1180	2405	2565		

* Corrected for anharmonic term. All other calculated values in the first column are frequencies for vibrations of infinitesimal amplitude.

to this plane. The computed values of ν_3 will lie above the observed frequencies, as is found to be the case for NH$_3$, and will more closely resemble the frequencies of vibrations with infinitesimal amplitude.

The agreement between the frequencies calculated for ND$_3$ and the three observed frequencies is satisfactory. As we have noted above the band reported at 3287 cm^{-1} may be used to determine ν_2 and gives the value $\nu_2 = 2520$ cm^{-1}, in rough agreement with the calculated value.

OVERTONE-COMBINATION BANDS

The proximity of ν_1 and ν_2 in all three molecules would explain the fair success of efforts to interpret the spectra using only the three fundamentals which appear. An attempt to obtain further evidence regarding the valence-force value of ν_2 from overtone-combination bands is rather inconclusive as long as the structures of these bands or the actual appearance of the bands to be expected from certain combinations of fundamentals are not better known. Thus, for example, we have two possible explanations of the 5059 cm^{-1} band of NH$_3$. The assignment given by Badger and Mecke[10] is ν_1 (3335) $+\nu_4$ (1631) = 4966 cm^{-1}. The alternative assignment is ν_2 (3470) $+\nu_4$ (1631) = 5101 cm^{-1}. The former combination leads to a perpendicular-type band, the latter to a band with both perpendicular and parallel components. The structure of the band has been analyzed as perpendicular by Stinchcomb and Barker[16] but it is possible that the presence of a parallel component would be masked by the more complex perpendicular component.

[16] Stinchcomb and Barker, Phys. Rev. **33**, 305 (1929).