Dodecahedral Octacovalent Bond Orbitals

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TABLE III. A comparison of the experimental and theoretical second virial coefficients for ammonia on the basis of the hard sphere model.

Temp. °K	Classical virial cm³/mole	Quantum correction cm³/mole	Theoretical virial cm³/mole	Experimental virial cm³/mole	Percent difference
300	−282	6	−276	−270	−2.2
400	−119	1	−118	−119	−0.8
500	− 64.1	0.5	− 63.6	− 66.6	4.5
600	− 37.3	0.2	− 37.1	− 40.6	8.6

TABLE IV. A comparison of the experimental and theoretical second virial coefficients for ammonia on the basis of the exponential repulsion.

Temp. °K	Classical virial cm³/mole	Quantum correction cm³/mole	Theoretical virial cm³/mole	Experimental virial cm³/mole	Percent difference
300	−261	8	−253	−270	6.3
400	−122	2	−120	−119	0.8
500	− 72.8	0.8	− 72.0	− 66.6	− 8.1
600	− 46.0	0.4	− 45.6	− 40.6	−12.3

was used:

$$V = 5.00 \cdot 10^{-9} \exp(-R/0.28) - (74.4 \cdot 10^{-12}R^{-6} + 221 \cdot 10^{-12}R^{-8}) - (2.07 \cdot 10^{-12}R^{-3} + 2.07 \cdot 10^{-12}R^{-5})f(\theta_1, \theta_2, \phi) \text{ erg. } \quad (15)$$

It is seen in Table IV that the repulsion term counteracts the increasing effect of the polar forces at lower temperatures and reverses the trend of the calculated values given in Table III.

The critical temperature of NH_3 is 405°K so dimerization may occur below this temperature. The value of B at 300°K is therefore somewhat uncertain. The author wishes to thank Mr. Andrew Skumanich for performing most of the numerical work.

Dodecahedral Octacovalent Bond Orbitals

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Dodecahedral octacovalent bond orbitals of D_{2d} symmetry are considered. The bond orbitals are divided into two groups which may differ widely in composition, the over-all composition remaining sp^3d^4. When the average orbital strength is greatest, it equals 2.981 and the orbitals of group one and group two differ in composition and strength. The concept of orbital strength does not allow us to exclude either the dodecahedral or the tetragonal antiprism structure in AB_8 when A employs the sp^3d^4 configuration.

IN a recent paper[1] the author considered hybrid orbitals of tetragonal antiprism symmetry. Since covalent molecules or ions of type AB_8 may also possess a dodecahedral arrangement (an arrangement which $Mo(CN)_8^{-4}$ can assume), it is of interest to consider hybrid orbitals of this symmetry. For a figure illustrating this structure see the paper of Hoard and Nordsieck.[2]

When eight spd hybrid orbitals of D_{2d} symmetry are set up, one obtains the following functions:

$$\psi_1 = [(1/2)\cos\alpha]s + [(1/2)\cos\beta]p_z + [(1/\sqrt{2})\cos\gamma]p_x + [(1/2)\sin\alpha]d_z + [(1/2)\sin\beta]d_{xy} + [(1/\sqrt{2})\sin\gamma]d_{x+z}, \quad (1)$$

$$\psi_2 = [(1/2)\sin\alpha]s + [(1/2)\sin\beta]p_z + [(1/\sqrt{2})\sin\gamma]p_y - [(1/2)\cos\alpha]d_z - [(1/2)\cos\beta]d_{xy} + [(1/\sqrt{2})\cos\gamma]d_{y+z}, \quad (2)$$

$$\psi_3 = [(1/2)\cos\alpha]s + [(1/2)\cos\beta]p_z - [(1/\sqrt{2})\cos\gamma]p_x + [(1/2)\sin\alpha]d_z + [(1/2)\sin\beta]d_{xy} - [(1/\sqrt{2})\sin\gamma]d_{x+z}, \quad (3)$$

$$\psi_4 = [(1/2)\sin\alpha]s + [(1/2)\sin\beta]p_z - [(1/\sqrt{2})\sin\gamma]p_y - [(1/2)\cos\alpha]d_z - [(1/2)\cos\beta]d_{xy} - [(1/\sqrt{2})\cos\gamma]d_{y+z}, \quad (4)$$

$$\psi_5 = [(1/2)\sin\alpha]s - [(1/2)\sin\beta]p_z + [(1/\sqrt{2})\sin\gamma]p_x - [(1/2)\cos\alpha]d_z + [(1/2)\cos\beta]d_{xy} - [(1/\sqrt{2})\cos\gamma]d_{x+z}, \quad (5)$$

$$\psi_6 = [(1/2)\cos\alpha]s - [(1/2)\cos\beta]p_z + [(1/\sqrt{2})\cos\gamma]p_y + [(1/2)\sin\alpha]d_z - [(1/2)\sin\beta]d_{xy} - [(1/\sqrt{2})\sin\gamma]d_{y+z}, \quad (6)$$

$$\psi_7 = [(1/2)\sin\alpha]s - [(1/2)\sin\beta]p_z - [(1/\sqrt{2})\sin\gamma]p_x - [(1/2)\cos\alpha]d_z + [(1/2)\cos\beta]d_{xy} + [(1/\sqrt{2})\cos\gamma]d_{x+z}, \quad (7)$$

$$\psi_8 = [(1/2)\cos\alpha]s - [(1/2)\cos\beta]p_z - [(1/\sqrt{2})\cos\gamma]p_y + [(1/2)\sin\alpha]d_z - [(1/2)\sin\beta]d_{xy} + [(1/\sqrt{2})\sin\gamma]d_{y+z}. \quad (8)$$

The s, p, and d functions are defined in the same way as in previous papers[1] by the author. The z axis coincides with the fourfold rotation-reflection axis (S_4). The numbering of the bonds is the same as the numbering of the ψ_i. Thus bonds one, three, five, and seven

[1] G. H. Duffey, J. Chem. Phys. 18, 746 (1950).
[2] J. L. Hoard and H. H. Nordsieck, J. Am. Chem. Soc. 61, 2853 (1939).

lie in the xz plane, bonds two, four, six, and eight in the yz plane.

The eight orthogonal bond orbitals fall into two groups. Group one includes ψ_1, ψ_3, ψ_6, and ψ_8, which represent four equivalent bond orbitals with the over-all composition $s^n p^{3m} d^{4-n-3m}$. Group two includes ψ_2, ψ_4, ψ_5, and ψ_7, which represent four equivalent bond orbitals with the over-all composition $s^{1-n} p^{3-3m} d^{n+3m}$. The parameters n and m are related to the parameters α, β, and γ by the two equations

$$n = \cos^2\alpha, \tag{9}$$

$$m = \tfrac{1}{3}(\cos^2\beta + 2\cos^2\gamma). \tag{10}$$

The tetrahedral orbitals and the tetragonal plane orbitals discussed by Kuhn[3] are special cases of group one and group two orbitals.

A function orthogonal to $\psi_1, \cdots \psi_8$ is given by

$$\psi_9 = d_{x+y}. \tag{11}$$

Let ϑ_1 be the angle between the z axis and the maximum in ψ_1 (approximately the angle between the axis and bond one), and ϑ_2 the angle between the z axis and the maximum in ψ_2 (approximately the angle between the axis and bond two). Let the maximum value of ψ_1 be called S_1, and the maximum value of ψ_2, S_2. Assume the energy of each bond is given by Eq. (13) of "Hexacovalent bond orbitals III."[4] Assume that the sum of the W's and the sum of the R's over all bonds are independent of the variation of the parameters. This assumption is reasonable if the degrees of ionic character of all bonds are equal and constant. Then in dodecahedral AB_8 the values of the parameters giving the largest sum of the bond energies are found by maximizing $4S_1 + 4S_2$. The results are given in the second row of Table I.

The average strength of the best dodecahedral orbitals equals 2.981. The $sp^3 d^4$ configuration may also yield the tetragonal antiprism structure where the strength of each orbital is[1] 2.979. Thus the concept of orbital strength does not allow us to exclude either structure when the $sp^3 d^4$ configuration is used and one might expect that some molecules or ions of type AB_8 could be prepared in both the dodecahedral and the tetragonal antiprism forms. It is probable that a con-

[3] H. Kuhn, J. Chem. Phys. **16**, 727 (1948).
[4] G. H. Duffey, J. Chem. Phys. **18**, 510 (1950).

TABLE I. Properties of three sets of dodecahedral octacovalent bond orbitals.

Function maximized	$\cos\alpha$[a]	$\cos\beta$[a]	$\cos\gamma$[a]	S_1[b]	ϑ_1[c]	S_2[d]	ϑ_2[b]
S_1	0.6760	0.9048	0.4827	2.999	35°46'	2.954	72°53'
$S_1 + S_2$	0.6457	0.9422	0.5144	2.995	34°33'	2.968	72°47'
S_2	0.5990	0.9485	0.5962	2.979	34°5'	2.971	70°36'

[a] The orbitals of group one have the over-all composition $s^n p^{3m} d^{4-n-3m}$; the orbitals of group two $s^{1-n} p^{3-3m} d^{n+3m}$, where $n = \cos^2\alpha$, $m = \tfrac{1}{3}(\cos^2\beta + 2\cos^2\gamma)$.

[b] Maximum value of an orbital of group one.

[c] Acute angle between the rotation-reflection axis and the maximum in an orbital of group one.

[d] Maximum value of an orbital of group two.

[e] Acute angle between the rotation-reflection axis and the maximum in an orbital of group two.

siderable potential barrier restricts the conversion of one form into the other.

In the "best" dodecahedral structure the s content, the p content, and the d content of an orbital of group one equal 0.1042, 0.3542, and 0.5416, respectively; the s content, the p content, and the d content of an orbital of group two equal 0.1458, 0.3958, and 0.4584, respectively.

Consider dodecahedral $Mo(CN)_8^{-4}$. In molybdenum[5] the $4d$ orbitals are more stable than the $5s$ or $5p$ orbitals. However, the high $5s$ and $5p$ content and the low strength of an orbital of group two in the "best" structure are not extreme enough to make the energy of a bond in group two very much less than the energy of a bond in group one. Hence one would expect the $Mo-C$ bonds of group two to be only slightly longer than the $Mo-C$ bonds of group one. In the ideal structure postulated by Pauling[6] and Hoard and Nordsieck,[2] all bonds were taken of equal length, the angle between the z axis and bond one was set equal to 36°51', and the angle between the z axis and bond two was set equal to 69°28'. The experimental data[2] do not seem accurate enough to distinguish between this ideal structure and the structure obtained here. One should note that the bond angles, and consequently the effective strength and the composition of the orbitals, may be altered by the repulsion between the attached groups and by the environment of the ion in the crystal state.

[5] In Mo the state $4d^4 5s^2$ $^5D_0$ is 31 kcal./mole less stable than the state $4d^5 5s$ $^7S_3$. See F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

[6] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940).