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The Prediction of Molecular Orbital Symmetries from Localized Pair Models

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One interpretation of localized electron pair models for molecular structure such as those proposed by Gillespie and by Bent is that the pair locations in these models are maxima of localized molecular orbitals. It is shown that under this assumption the symmetry species for all of the (conventional, nonlocalized) molecular orbitals can be predicted from a localized-pair model. Symmetries thus predicted agree in most cases with those of Walsh. This relationship should be useful whenever semiempirical models of the MO or the localized-pair type are applied to small inorganic molecules.

Barring a massive breakthrough in quantum chemistry, chemists will continue to rely upon a variety of conceptual models in discussing the broad and varied spectrum of bond geometries found in inorganic chemistry. Two of the most popular models are empirical and semiempirical molecular orbital approaches, including the monumental treatment by Walsh,[2] and localized electron pairs, as skillfully employed by Gillespie[3] and others. It is the intent of this paper to present a useful interconnection between these apparently very different models.

Since the proposals of Lewis,[4] localized electron pairs have played a major part in discussion of molecular structure and bonding. The concept of localized pairs underlies much of the structural intuition of chemists and is basic to a variety of treatments, from ball-and-spring models to the approaches of Gillespie and Bent.[5] These models correlate a broad spectrum of molecular geometry. Gillespie's formulation in particular has drawn interest owing to its ability to predict molecular symmetry and trends in bond lengths and angles. A singular recent success was the prediction[6] of a nonoctahedral structure[7] for XeF_6.

Localized electrons have often been linked to the valence bond approach to the quantum theory of molecules. However, their relationship to molecular orbitals may be examined profitably. While molecular orbital calculations are commonly carried out for orbitals delocalized over an entire molecule, it has long been known[8] that these orbitals could be transformed into more localized sets, which at least in some cases correspond in location to the electron pairs of chemical intuition. Gillespie has indeed suggested[3] that the electron pair locations in his model are localized molecular orbitals. On the other hand, the nature of theoretically derived localized orbitals has been studied recently by Edmiston and Ruedenberg.[9,10] These often do appear to coincide with chemical intuition and to exhibit some of the properties predicted by Gillespie. Peters[11] has also used the localized orbital approach to predict bond and atomic properties, including hybridization, dipole moments, electronegativity, and hyperconjugation.

It is the thesis of this paper that the process may be in part reversed. The chemist's picture of the electron pair locations may be used to predict properties of the (delocalized) molecular orbitals. In particular, the symmetries of the occupied molecular orbitals can often be predicted without elaborate calculation. These symmetries will be derived from a localized-pair model for a variety of molecular and ionic types. The results will be compared with those of Walsh,[2] who has predicted the ordering of molecular orbitals for several molecular types from a quite different basis and has shown that his orderings are generally in accord with spectroscopic information.

The Nature of Localized Orbitals

In the molecular orbital formulation, the wave function for a molecule with $2N$ electrons in N orbitals may be written as a Slater determinant.

$$\psi = \frac{1}{\sqrt{2N!}} \times \begin{vmatrix} \phi_1\alpha(1) & \phi_1\beta(1) & \phi_2\alpha(1) & \cdots & \phi_N\beta(1) \\ \phi_1\alpha(2) & \phi_1\beta(2) & \phi_2\alpha(2) & \cdots & \phi_N\beta(2) \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \phi_1\alpha(2N) & \phi_1\beta(2N) & \phi_2\alpha(2N) & \cdots & \phi_N\beta(2N) \end{vmatrix} \qquad (1)$$

However, the total wave function Ψ does not uniquely define the orbitals $\{\phi_i\}$. A second set of orbitals can be defined by taking linear combinations

$$\lambda_j = \sum_{i=1}^{N} T_{ij}\phi_i \qquad (2)$$

If the transformation $\{T\}$ is such that the λ_j are orthonormal, the Slater determinant formed from these orbitals is *identically* equal to Ψ. Thus the $\{\lambda_j\}$ are

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(2) A. D. Walsh, *J. Chem. Soc.*, 2260, 2266, 2288, 2296, 2301, 2306 (1953).

(3) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963); *J. Am. Chem. Soc.*, **82**, 5978 (1960); *J. Chem. Soc.*, 4672 (1963).

(4) G. N. Lewis, *J. Am. Chem. Soc.*, **38**, 762 (1916).

(5) H. A. Bent, *Inorg. Chem.*, **2**, 747 (1963); *J. Chem. Educ.*, **40**, 446, 523 (1963).

(6) R. J. Gillespie in "Noble Gas Compounds," University of Chicago Press, Chicago, Ill., 1963, p 333. See also footnote 11 to ref 7.

(7) L. S. Bartell, R. M. Gavin, Jr., H. B. Thompson, and C. L. Chernick, *J. Chem. Phys.*, **43**, 2547 (1965); K. Hedberg, S. H. Peterson, R. R. Ryan, and B. Weinstock, *ibid.*, **44**, 1726 (1966).

(8) J. E. Lennard-Jones, *Proc. Roy. Soc.* (London), **A198**, 1, 14 (1949); J. E. Lennard-Jones and J. A. Pople, *ibid.*, **A202**, 166 (1950).

(9) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963); *J. Chem. Phys.*, **43**, S97 (1965).

(10) K. Ruedenberg in "Modern Quantum Chemistry," Vol. 1, Academic Press Inc., New York, N. Y., 1965, p 85.

(11) D. Peters, *J. Chem. Soc.*, 2003, 2015, 4017 (1963); 2901, 2908, 2916 (1964); 3026 (1965), 644, 652, 656 (1966).

an alternative orbital description of the same total wave function.[12] As there is an infinity of unitary transformations $\{T\}$, there is an infinity of alternative orbital descriptions $\{\lambda_i\}$ for any molecular orbital description $\{\phi_i\}$. Among the sets $\{\lambda_i\}$ some will be more localized than others. The sp, sp^2, and sp^3 hybrids in atoms are familiar examples—by most criteria these are more localized descriptions than s and p orbitals. The degree of localization can be defined in various ways.[13] One useful definition is in terms of the interorbital repulsion sum

$$\sum_{i} \sum_{j<i} \int\int \lambda_i^2(1)\lambda_j^2(2)\frac{1}{r_{12}}\, \mathrm{d}V_1 \mathrm{d}V_2 \qquad (3)$$

Edmiston and Ruedenberg[9] have shown how to obtain a set of *energy localized molecular orbitals* (ELMO's) for which this sum is a minimum. From the work to date, the ELMO's appear to coincide in many ways with the more qualitative electron-pair descriptions. Nitrogen has one lone pair on each atom and three bond orbitals, trigonally disposed about the N–N axis as in a spring or "banana-bond" model. Fluorine and hydrogen fluoride have a bonding orbital between the nuclei and three lone-pair orbitals centered trigonally behind each fluorine. Examination of the fluorine and hydrogen fluoride results shows two features of the Gillespie model: the angle between the axis of a bond-pair orbital and that of a lone pair is smaller than the angle between two lone-pair axes; furthermore, this difference in angle is greater in F_2 than in HF, thus showing the proper trend with respect to electronegativity.

It should perhaps be emphasized that the ELMO's are not the only localized orbitals to which the arguments in the remainder of this paper apply—indeed, it may well be that the intuitive electron pairs coincide better with orbitals obtained using some other localization criterion. At present, data on the ELMO's are available on more molecules than is the case for other localization paths. They thus form the best present basis for discussion.[14]

Localized Orbitals, Molecular Orbitals, and Symmetry

It is here proposed that a localized-pair model, corresponding to chemical intuition and agreeing in most respects with the models of Bent and Gillespie, can be devised that will serve as a guide to the probable distribution of a highly localized basis such as the ELMO's. If this be true, then it is (at least usually) possible without elaborate calculation to predict the symmetries of the occupied molecular orbitals. For, if the intuitive pairs form a localized basis λ, they must be related to the molecular orbitals ϕ by some unitary transformation T. By the inverse transformation T' one could then obtain ϕ from λ. If a transformation T_1' can be found such that the set of orbitals $\eta = T_1' \cdot \lambda$ transform as *irreducible* representations of the molecular symmetry group, then the transformation T_2', defined by $\phi = T_2'\eta$ or equivalently $T' = T_2'T_1'$, merely mixes orbitals within each symmetry type and does not change the number of filled orbitals of each symmetry. To find the transformation matrix T' (or T_2') may be involved and tedious and may require a knowledge of the exact form of the localized orbitals. T_1' is much easier to find, provided the symmetry of the localized pair model is closely related to the molecular symmetry.

As an example, consider the ball-and-stick model of OF_2 in Figure 1. The numbers identify the localized orbitals λ_i to be assigned to each location. An appropriate transformation T_2' is

$$\begin{array}{lll}
\eta_1 & = {}^1/_2(\lambda_1 + \lambda_2) & a_1' \\
\eta_2 & = {}^1/_2(\lambda_1 - \lambda_2) & b_2' \\
\eta_3 & = {}^1/_2(\lambda_3 + \lambda_4) & a_1' \\
\eta_4 & = {}^1/_2(\lambda_3 - \lambda_4) & b_2' \\
\eta_5 & = {}^1/_2(\lambda_5 + \lambda_6) & a_1' \\
\eta_6 & = {}^1/_2(\lambda_5 - \lambda_6) & b_1'' \\
\eta_7 & = {}^1/_2(\lambda_7 + \lambda_8 + \lambda_9 + \lambda_{10}) & a_1' \\
\eta_8 & = {}^1/_2(\lambda_7 + \lambda_8 - \lambda_9 - \lambda_{10}) & b_2' \\
\eta_9 & = {}^1/_2(\lambda_7 - \lambda_8 - \lambda_9 + \lambda_{10}) & b_1'' \\
\eta_{10} & = {}^1/_2(\lambda_7 - \lambda_8 + \lambda_9 - \lambda_{10}) & a_2''
\end{array}$$

Since the molecular orbitals must be made from these by linear combination *within each symmetry type*, the number of orbitals of each type can be compared with those given by Walsh[2] for molecules of the type AB_2 with symmetry C_{2v}. For the lowest ten orbitals[15] Walsh gives four of type a_1', three b_2', two b_1'', and one a_2''. This agrees with the symmetries given for the $\{\eta_i\}$ above. (Alternatively, these symmetries might in this case have been obtained from the original localized-orbital basis by use of the group character table in a manner analogous to that often employed using an atomic orbital basis. This procedure will suffice and is totally equivalent to that in the preceding example whenever the symmetry group of the stick model is identically that of the molecule.)

In Figure 2, localized-pair representations are given for a number of molecular types falling within the classes discussed by Walsh. These models are drawn following the rules below. It should be noted that the specific rules adopted have no bearing on the validity of the symmetry-prediction process. No great merit is claimed for the following—they merely constitute a straightforward recipe for localized-pair arrangements generally in accord with those of Gillespie or Bent.

(I) The geometry around each atomic kernel is

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[12] V. Fock, *Z. Physik*, **61**, 126 (1930). A proof of the equivalence of the two determinants can be found in J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1963, Appendix 8.

[13] Ruedenberg has discussed several localization criteria.[9] See also S. F. Boys, *Rev. Mod. Phys.*, **32**, 296 (1960).

[14] Dr. Ruedenberg has kindly made available to the author very excellent detailed contour maps of many of his ELMO's (K. Ruedenberg and L. S. Salmon, unpublished results). While these maps contain no information not present in the published literature, they have greatly simplified the examination of the properties of these orbitals.

[15] Walsh does not use the s valence orbitals on atoms B in making his molecular orbitals and indicates these on his diagrams merely as S. For comparison with the treatment here, the antisymmetric and symmetric combinations of these, types a_1' and b_2', must be taken. All symmetry designations herein accord with the conventions used by Walsh.

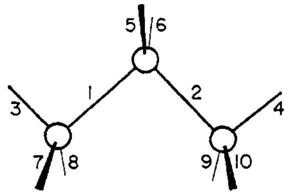

Figure 1.—Localized-pair model for AB_2 with 10 valence elctron pairs.

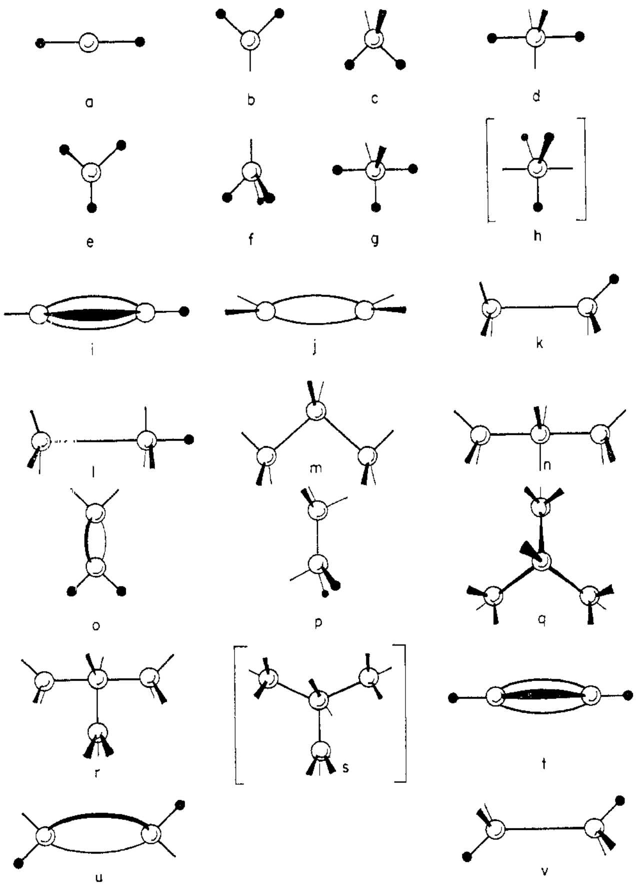

Figure 2.—Localized-pair models. Brackets enclose models which violate Gillespie's rule regarding the relative sizes of bond pairs and lone pairs. See text.

that proposed by Gillespie: linear for two pair, planar-trigonal for three pair, tetrahedral for four pair, trigonal-bipyramidal for five pair, octahedral for six pair.

(II) Octets are completed around each kernel where possible by use of multiple bonds.

(III) Multiple bonds are represented as "banana bonds" rather than as four- (or six-) electron orbitals.[16]

(IV) Where a choice exists corresponding to "rotation" about a single bond, the lone pairs have been oriented so as to match the symmetry of the model to that of the molecular framework.[17]

(V) Gillespie's principle that a lone pair tends to preempt more solid angle around a kernel than a bonding pair has been applied where appropriate. Thus in Figures 2d, 2g, 2n, and 2r, bond pairs rather than lone pairs occupy the apex positions of the pentagonal bipyramid around the central atom. In 2n, 2r, and 2s a fifth pair has been placed on the atom having three bond pairs rather than on an atom having one bond pair.

The molecular orbital symmetries predicted from these models are given in Table I. These are in good accord with Walsh's symmetries. The only disagreement is in the 10-electron AH_3 and 28-electron AB_3 structures. The accepted structures for ClF_3[18] and BrF_3 and the prediction from Gillespie's approach indicate that Walsh is in error[19] in this case. It is worth noting that, by violation of rule V above, Figures 2h and 2s can be drawn, which then do give molecular orbitals agreeing in symmetry with Walsh.

TABLE I

PREDICTED SYMMETRIES OF FILLED MOLECULAR ORBITALS

Type	Symmetry	Valence electrons	Model (from Figure 2)	Symmetries of MO's predicted
AH_2	$D_{\infty h}$	4	a	σ_g, σ_u
		10^b	d	$2\sigma_g$, σ_u, $2\pi_u$
	C_{2v}	6	b	$2a_1'$, b_2'
		8	c	$2a_1'$, b_2', b_1''
AH_3	D_{3h}	6	e	a_1', $2e'$
		[10	h	$2a_1'$, a_2'', $2e']^a$
	$C_{2v}{}^b$	10	g	$3a_1'$, b_1'', b_2'
	3_{3v}	8	f	$2a_1$, $2e$
HAB	$C_{\infty v}$	10	i	3σ, 2π
		16	l	4σ, 4π
	C_s	12	j	$5a'$, a''
		14	k	$5a'$, $2a''$
AB_2	C_{2v}	20	m	$4a_1'$, a_2'', $2b_1''$, $3b_2'$
	$D_{\infty h}$	22	n	$3\sigma_g$, $2\sigma_u$, $2\pi_g$, $4\pi_u$
H_2AB	C_{2v}	12	o	$3a_1'$, b_1'', $2b_2'$
	C_s	14	p	$5a'$, $2a''$
AB_3	C_{3v}	26	q	$4a_1$, a_2, $8e$
	$C_{2v}{}^b$	28	r	$7a_1'$, a_2'', $2b_1''$, $4b_2'$
	D_{3h}	[28	s	$3a_1'$, a_2', $2a_2''$, $6e'$, $2e'']^a$
HAAH	C_{2h}	12	u	$3a_g$, a_u, $2b_u$
		14	v	$3a_g$, a_u, b_g, $2b_u$
$D_{\infty h}$		10	t	$2\sigma_g$, σ_u, $2\pi_u$

[a] Cases enclosed in brackets here and in Figure 2 are models in which rule V (see text) was violated in order to check agreement with Walsh. [b] Cases not covered by Walsh.

Figure 2 is intended to include all the chemically important cases for the molecular types listed, provided only that a single picture following rules I–V corresponds to the symmetry of the molecular frame-

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(16) Gillespie's multi-pair orbitals[2] are clearly inappropriate here, since the symmetry properties of the orbitals are of primary importance. In this respect the author's usage corresponds more closely with that of Bent. For the predictions to be made, there is of course no difference between a banana-bond description and a σ–π description of an isolated multiple bond.

(17) In Figures 2d, l, and n (symmetries $C_{\infty v}$ and $D_{\infty h}$ for the molecules) this symmetry match is not strictly correct. This creates no major complication, since (a) the commonly used real π orbitals do not have an infinitefold symmetry axis except in proper combination and (b) each set of orbitals trigonally disposed about the axis is degenerate in exactly the sense that three sp^2 hybrids are degenerate and can be resolved into a σ orbital and two π orbitals. In Figure 2s there is no reason to prefer one rotational orientation of the lone pairs about each B-type atom over another orientation, so the same degeneracy applies: these pairs can thus similarly be resolved into σ and π components. The same argument can be applied to the lower B atom in Figure 2r.

(18) D. F. Smith, *J. Chem. Phys.*, **21**, 609 (1953).

(19) As Walsh did not consider the T shape as a possibility, it cannot be said that the ClF_3 geometry shows a flaw in his approach. It is not obvious to the author how the T geometry would be treated in the Walsh formulation.

work.[20] As is well known, many cases occur where a number of equally valid localized pictures can be drawn. An example is 24-electron AB_3 (sulfur trioxide, for instance). Three equally valid structures are shown in Figure 3a. Only a subgroup of the full-symmetry group of the molecule applies to each structure. This is, of course, a case in which single-bond–double-bond resonance is invoked in valence-bond discussions, and an extended π-bond system occurs in molecular orbital treatments. Edmiston and Ruedenberg[21] discovered that in such systems the locations of the ELMO's can be ill defined and may not match the molecular symmetry. In the π-bond system in benzene[22] three localized orbitals can be found, located symmetrically around the ring, but there is an infinity of such possible sets, the exact orientation of the entire localized-orbital system with respect to the ring atoms being undefined. In the molecule C_2 they found that again the ELMO distribution did not match the molecular symmetry and that sizable changes (10^{-2}) in the coefficients for atomic orbital contributions to the ELMO's produce very small changes (10^{-8}) in the localization sum.

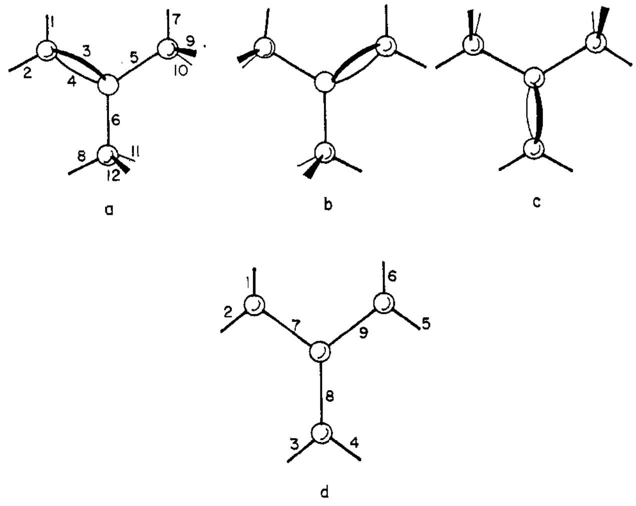

Figure 3.—Localized-pair model for 12-pair AB_3. Figure 3d shows a model of the σ pairs only.

Pople[23] has emphasized that these systems are best discussed in terms of localized σ-bond systems and delocalized π electrons. This procedure follows easily in our case. We will equate the σ-bond system to an optimally localized set of σ orbitals[22] and take as the π-bond molecular orbital symmetries those that would result from any simple (say, Hückel-type) treatment.

To discover the appropriate σ–π separation, we note that in each structure in Figure 3a–c, the plane containing the nuclei is a reflection plane. Indeed, this is the only symmetry element (other than the identity element) common to all three structures. For each electron pair above this plane and its partner below, we can by linear combination obtain a σ pair in the plane and a π pair antisymmetric to the plane. For each structure in Figure 3a–c, the total σ-bond pattern will resemble Figure 3d, differing in minor respects. Since the combination of structures in Figure 3a–c corresponds to symmetry D_{3h}, Figure 3d will be taken to have this symmetry. This will be identified with the σ-bond structure. The π-bond system contains three electron pairs and clearly cannot as easily be reduced to a single average structure, although this approach is by no means impossible. However, chemists are used to the idea that these electrons are delocalized, so a straightforward approach is to obtain the orbital symmetries by the simplest of Hückel-type treatments.[23]

In addition to the 24-electron AB_3 structure, the 16- and 18-electron AB_2 structures were not included in Table I. These can be treated in similar fashion, and all three cases are summarized in Table II. As is apparent, no disagreement between this treatment and Walsh's appears at this stage.

TABLE II

PREDICTED SYMMETRIES OF FILLED MOLECULAR ORBITALS FOR MOLECULES WITH EXTENDED π SYSTEMS

Type	Symmetry	Valence electrons	System	Symmetries of MO's predicted
AB_3	D_{3h}	24	σ ($18e^-$)	$2a_1'$, a_2'', $6e'$
			π ($6e^-$)	a_2'', $2e''$
AB_2	C_{2v}	18	σ ($14e^-$)	$4a_1'$, $3b_2'$
			π ($4e^-$)	a_2'', b_1''
	$D_{\infty h}$	16	σ ($8e^-$)	$2\sigma_g$, $2\sigma_u$
			π ($8e^-$)	$2\pi_u$, $2\pi_g$

Discussion

The success of the above comparison of orbital symmetries would seem to lend considerable support to the proposition that localized-electron models, as the chemist has conventionally used them and as made more precise by recent treatments, have a close relationship to localized molecular orbitals and thus to molecular orbitals in general. This can be a useful hypothesis in a number of ways. Clearly, it provides a test for localized models in cases where the molecular orbital symmetries are available and provides a channel for examination and improvement of these models and for closer calibration of our chemical intuition. Further, a localized-orbital basis might serve as an interesting starting point for parameterized, semiempirical molecular orbital treatments analogous to extended Hückel theory.[24] Some thought will be required as to the nature and magnitude of off-diagonal matrix elements in the secular equation, since their estimation from overlap integrals is not applicable. One might reasonably expect these ele-

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(20) Except for the trivial difficulties noted in footnote 17.

(21) C. Edmiston and K. Ruedenberg, to be published.

(22) Using the procedure of Edmiston and Ruedenberg it is feasible to localize only a subset of the filled molecular orbitals, so that one can discuss localized σ or localized π orbitals if desired.

(23) J. A. Pople, *Quart. Rev.* (London), **11**, 273 (1957).

(24) For example, R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963). One treatment starting with localized orbitals is the line combination of bond orbitals approach: G. G. Hall, *Proc. Roy. Soc.* (London), **A205**, 541 (1951); R. D. Brown and F. A. Matsen, *J. Chem. Phys.*, **21**, 1298 (1953).

ments to be smaller and their estimation less critical than in other approaches.

One immediate result of an identification of intuitive localized pairs with ELMO's might be the estimation of the nature of the repulsive potential for use in Gillespie's model. In this model the pair distributions (rule I above) were arrived at by considering the stable distribution of mutually repulsive points on the surface of a sphere. The repulsive potential was given the form $1/r^n$, where n was positive. The best value for n has not been clear from the empirical evidence, since for up to six points (electron pairs) the stable geometry is independent of n. However, if the position of the point represents the center of a localized orbital, two estimates of n might be made: (1) the interorbital interaction may be largely a Coulomb repulsion, in which case the appropriate value is $n = 1$; (2) a change in r could be thought to be a change in a dimension of each orbital, and, by simple analogy to a particle in a potential well, $n = 2$. In the case of seven-coordination a value between 1 and 2 corresponds to a pentagonal bipyramid (D_{5h}),[25] while higher powers of r require a C_{3v} or C_{2v} symmetry. This conclusion agrees with the known structure of IF_7.[26]

Acknowledgments.—The author wishes to express his gratitude to the numerous colleagues who have aided this work by their interest, suggestions, and valuable discussion; special thanks are due Professors Klaus Ruedenberg, T. M. Dunn, and L. S. Bartell.

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(25) H. B. Thompson and L. S. Bartell, *Inorg. Chem.*, **7**, 488 (1968).

(26) H. B. Thompson and L. S. Bartell, *Trans. Am. Cryst. Assoc.*, **2**, 190 (1966).

Notes

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Formation of Polymeric $(GeF_2)_n$ in the Vapor Phase over GeF_2

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Recently the formation of gaseous dimers and trimers of SnF_2 has been reported.[1] There is evidence also for the formation of polyperfluorosilanes and possibly $(SiF_2)_n$ molecules.[2] One might therefore expect a similar behavior for GeF_2.

Gaseous GeF_2 has been formed only at high temperatures and in the presence of excess Ge metal.[3] In this work solid GeF_2, prepared by the reaction of GeF_4 + Ge at 300°,[4] was evaporated under Knudsen conditions (Cu cell) in a mass spectrometer[1] and ions corresponding to $(GeF_2)_n^+$, where $n = 1$–4, were observed over the temperature range 361–403°K. Temperatures were measured using a Pt—Pt-10% Rh thermocouple and could be controlled to ±1°. During the initial heating of the salt $GeOF_3^+$ and $GeOF_4^+$ ions were observed, and the appearance potentials of 15.6 and 13.6 ± 0.5 eV, respectively, suggest the presence of $GeOF_4$ as an impurity. Other oxyfluorides have been found to have high appearance potentials. At higher temperatures GeF_2 showed an increasing tendency to disproportionate to GeF_4(g), Ge(s), and also to GeF(g).

The following appearance potentials (in eV) were recorded: Ge^+, 18.8 ± 0.3; GeF^+, <9.1 ± 0.2 and 14.0 ± 0.3; GeF_2^+, 11.8 ± 0.1; $Ge_2F_4^+$, 10.6 ± 0.3; and $Ge_3F_5^+$, 15.6 ± 0.5. The critical-slope method was used to obtain the GeF_2 ionization potential.

Heats of sublimation and vaporization for GeF_2 and $(GeF_2)_2$ were obtained from Clausius–Clapeyron plots (Figure 1) over the temperature range 335–365°K. Pressures were calculated from the usual relation $P = kI^+T$, where I^+ is the ion intensity signal in arbitrary units and k was determined by a silver calibration. No estimation of relative ionization cross section or multiplier efficiencies was made, so the calculated pressures are considered accurate only to within a factor of 2. At 361°K the following pressures (in mm) were found: GeF_2, 4.4×10^{-4}; $(GeF_2)_2$, 4.0×10^{-5}; $(GeF_2)_3$, 1.6×10^{-6}; and $(GeF_2)_4$, $\lesssim 2.7 \times 10^{-7}$. Table I presents a summary of the thermodynamic properties of these molecules.

The entropy decrease of 51 ± 2 eu for the dimerization of GeF_2 is comparable with a value of 45.5 ± 2 eu found for the SnF_2 case.[1] The entropy change for reaction 4 (Table I) was estimated from that for the analogous SnF_2 reaction and the enthalpy change was then calculated using the measured free energy change. This enthalpy is not significantly different from the value found for SnF_2 association processes.

Several possible structures may be postulated for the polymers, *e.g.*, by analogy with the tetrafluoroethylene structure, $F_2C{=}CF_2$ for dimers with cyclic trimers and tetramers, or by analogy with the halogen-bridged $(BeF_2)_2$ or $(MgF_2)_2$ structures.[5,6] However the former

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(1) K. Zmbov, J. W. Hastie, and J. L. Margrave, in press.

(2) (a) A. S. Kana'an and J. L. Margrave, *Inorg. Chem.*, **3**, 1037 (1964); (b) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.*, **87**, 2824 (1965).

(3) T. C. Ehlert and J. L. Margrave, *J. Chem. Phys.*, **41**, 1066 (1964).

(4) N. Bartlett and K. C. Yu, *Can. J. Chem.*, **39**, 80 (1961).

(5) D. R. Stull, Ed., "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1964, No. PB-168-370.

(6) A. Snelson, Report No. IITTRI-U6001-13, "Optical Spectra of Some Low Molecular Weight Compounds Using the Matrix Isolation Technique," U. S. Army Research Office, 1966.