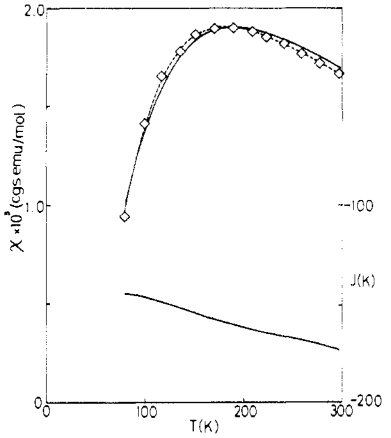

Figure 3. Magnetic susceptibility behavior of spin $^1/_2$ dimers with Ising-Heisenberg coupling. The upper solid curve shows the powder susceptibility calculated by the use of eq 6 and 8 with $J/k = -345.50$ K, $\gamma = 0.217$, and $g = g_x = 2.02$, and the dashed curve shows the parallel susceptibility, eq 6, with $J/k = -213.50$ K and $\gamma = 0.282$. Both curves are compared with the experimental data on Cu(n-C_3H_7-nso)NO_3 given by Mikuriya et al. The lower solid curve shows the temperature dependence of the exchange integral J estimated from the comparison of the Bleaney-Bowers formula, eq 2, with the experimental data.

interactions into account, the system necessarily becomes that of many spins interacting among themselves. However, the exact solution for such a many-spin system of the Heisenberg exchange is not yet known, and we have to be satisfied by an approximate solution such as the mean-field theory. As can easily be shown, the mean-field approximation modifies the magnetic susceptibility χ_0 for the system of isolated dimers as

$$\chi = \chi_0 \bigg/ \left[1 - \frac{2zJ'}{Ng^2\mu_B{}^2}\chi_0 \right] \qquad (9)$$

where J' denotes the exchange coupling constant of the interdimer interaction and z is the number of nearest dimers. Apparently, the effect of this type of correction is an upward ($J' > 0$) or downward ($J' < 0$) shift of the suceptibility curve and is different from that of the anisotropic exchange proposed in the present note. Therefore, the susceptibility behavior of the present example cannot be explained solely by the interdimer interactions. An extension of the present analysis including the interdimer interactions will be able to give an overall fitting with a more resonable anisotropy parameter γ, which is usually of the order of a few percent.

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Trigonal-Bipyramidal Molecular Structures and the VSEPR Model

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The compatibility of a molecular structure with the VSEPR model[1] has to be judged by examining *all* angles characterizing the configuration of all electron pairs in the valence shell of the central atom. Usually, only the variations of the bond angles are considered as they are determined directly from experiment while the angles made by the lone pairs of electrons are not always attainable from the experimental data. For example, the E-P-F angle of PF_3, where E is the lone pair, can be calculated from the F-P-F bond angle by virture of C_{3v} symmetry; on the other hand, the angles of E-S-E and E-S-F of the C_{2v} symmetry SF_2 molecule cannot be calculated from the F-S-F bond angle.

For some time a series of tetrahedral structures has seemed to provide incompatible variations with the VSEPR model. While originally it has been stated[1] that in the series CH_4, NH_3, and H_2O the bond angles decrease as the number of nonbonding pairs increases, for several analogous series this was not entirely the case.[2] While it was invariably observed that in going from AX_4 to BX_3E, with E being a lone pair of electrons, the bond angles decreased, the replacement of yet another bond by a second lone pair did not lead to further decrease of the bond angle in CX_2E_2, except for the hydride molecules.

As the "bond angles" made by the lone pairs of electrons in the tetrahedral systems under consideration were not available from experimental data, ab initio molecular orbital calculations have been carried out[3] for a series of molecules. The structural variations in the resulting geometries showed complete agreement with the predictions of the VSEPR model when *all* angles have been considered. In the series SiF_4, PF_3, SF_2, for example, these angles were[4]

SiF_4		PF_3		SF_2	
F-Si-F	109.5°	F-P-F	96.9°	F-S-F	98.1°
		E-P-F	120.2°	E-S-F	104.3°
				E-S-E	135.8°

While the F-S-F bond angle is indeed smaller than the F-P-F bond angle, the E-P-F angle is much larger than the E-S-F angle, and the origin of this difference is decisive as the relative strength of the repulsive interactions decrease in the order

$$E/E > E/b > b/b$$

where b is a bonding pair.

It appeared to be particularly useful to characterize the general space requirements of various bonds and lone pairs by the so-called triple-average angles[5] that were shown to be rather constant for single bonds and double bonds as well as for lone pairs of electrons.[3]

Following the success of this approach, the so-called quadruple-average angle[6] $\bar{\alpha}_Y$ was introduced by Hargittai[7] to characterize the general space requirements of bonds, lone pairs, and double bonds in YAX_4 trigonal-bipyramidal molecules. The consideration of the relatively constant values of the quadruple-average angles for lone pairs and double bonds has facilitated the selection of one or two of the four models of $O{=}SF_4$ that had been reported from experimental studies displaying considerable differences in the bond angles.[8] The results of ab initio calculations[9] and further experimental

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(4) The position of the lone pair was characterized by the center of its charge distribution.

(5) The triple-average angle is the mean of the three angles made by a bond or a lone pair in a tetrahedral configuration.[3]

(6) The quadruple-average angle, $\bar{\alpha}_Y$, is the mean of the four angles made by A-Y in YAX_4, where Y may be a ligand or a lone pair and the X ligands may be the same or may be different.

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Table I[a]

ESF_4		$E(CF_3)_2SF_2$		comments
$E{-}S{-}F_a$	93.4_5	$E{-}S{-}F_a$	93.0_5	equal within exptl error
$E{-}S{-}F_e$	129.2_5	$E{-}S{-}C$	131.3_5	$\Delta_1 = 2.1°$; sign in agreement with the prediction of VSEPR model, 2 such interactions
$F_e{-}S{-}F_e$	101.5	$C{-}S{-}C$	97.3	$\Delta_2 = -4.2°$; sign in disagreement with the prediction of VSEPR model, 1 such interaction
$F_a{-}S{-}F_e$	87.8	$F_a{-}S{-}C$	88.0	equal within exptl error

[a] All angles given in degrees.

work[10] have been in agreement with the prediction from this simple approach indeed.

The consideration of the quadruple-average angles has also shown[7] the series of SF_4, OSF_4, and $H_2C{=}SF_4$ molecules to have structural consistency in spite of rather differing bond angles. The special advantage of utilizing quadruple-average angles in these trigonal-bipyramidal systems is that they can be simply calculated from the bond angles by virture of symmetry.

Recently the molecular geometry of $(CF_3)_2SF_2$ has been reported by Oberhammer et al.[11] from electron diffraction. The structure is characterized by a trigonal-bipyramidal configuration with the fluorine ligands in axial positions. The following bond angles described the geometry: $C{-}S{-}C = 97.3\ (8)°$ and $F_a{-}S{-}F_a = 173.9\ (8)°$. The values cited in parentheses were given as error limits representing 3σ from a least-squares analysis. Comparing the structures of SF_4[12] and $(CF_3)_2SF_2$, Oberhammer et al. noted that the bond angles involving the axial ligands were equal in the two molecules within experimental error. They also stated the following: "The decrease of the equatorial bond angle from 101.5 (5)° in SF_4 to 97.3 (8)° in $(CF_3)_2SF_2$ is incompatible ith the VSEPR model."[11]

When considering, however, the variations of *all* angles around the sulfur atom, as is shown below, they appear to be fully compatible with the VSEPR model. Indeed, the SF_4 and $(CF_3)_2SF_2$ structures provide an excellent example for the applicability of this model.

In both molecules there are two kinds of interactions that have to be taken into account, viz., E/b and b/b. The only difference in the two systems is that the two ligands in the equatorial positions are less electronegative[13] in $(CF_3)_2SF_2$ than the corresponding ones in SF_4.

Consider now first the quadruple-average angles of the lone pairs of electrons:

	SF_4	$(CF_3)_2SF_2$
$\tilde{\alpha}_Y$	$111.3_5°$	$112.2°$

Although the difference in the two quadruple-average angles is small, its direction is in complete agreement with the prediction of the VSEPR model postulating the E/b repulsions to be greater when involving bonds to less electronegative ligands.[1] Here the $E/S{-}F_a$ repulsions in the two molecules are assumed to be equal.

Consider now the individual bond angles given in Table I. It is obvious that $2|\Delta_1|$ and $|\Delta_2|$ are equal. It is also obvious that there are two competing effects acting in the equatorial plane of $(CF_3)_2SF_2$ as compared with the case for SF_4. One of them is that the $E/S{-}CF_3$ repulsion is greater than the $E/S{-}F_e$ repulsion, thus tending to increase the E-S-C angles. The other effect is that the $S{-}CF_3/S{-}CF_3$ repulsion is greater than the $S{-}F_e/S{-}F_e$ one, thus tending to increase the C-S-C bond angle.

All angles being in the equatorial plane, either the E-S-C angles or the C-S-C angle can increase and can do so only at the expense of the other. The relative magnitude of the two competing effects decides which of them prevails. The experimentally observed decrease of the C-S-C angle in $(CF_3)_2SF_2$ as compared with the $F_e{-}S{-}F_e$ angle in SF_4 unambiguously indicates the $E/S{-}CF_3$ repulsions to prevail, in complete agreement with the VSEPR model.

Registry No. SF_4, 7783-60-0; $(CF_3)_2SF_2$, 30341-38-9.

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Communications

Photochemical Fragmentation Kinetics of Triruthenium Dodecacarbonyl

Sir:

The photochemical fragmentation reaction (1) is known to

$$\mathrm{Ru_3(CO)_{12}} \xrightarrow[\mathrm{CO}]{h\nu} \mathrm{Ru(CO)_5} \tag{1}$$

proceed smoothly, without detectable side reactions.[1] In spite of the considerable current interest in photofragmentation of metal-metal-bonded carbonyls,[2,3] no detailed investigation of reaction 1 has been reported. We have studied it as a function of [CO], irradiation wavelength (λ), solvent, and the intensity, I_a, of absorbed light. Some of the results are reported in Table I.

Studies of reactions in deoxygenated cyclohexane and isooctane under $CO{-}N_2$ mixtures containing from 5 to 100% CO invariably showed a pronounced dependence of the quantum yield, ϕ_{obsd}, on [CO]. Plots of ϕ_{obsd} against [CO][4] always showed quite appreciable curvature (Figure 1), suggesting that ϕ_{obsd} would tend to a limiting value, ϕ_l, at sufficiently high values of [CO]. Plots of $1/\phi_{obsd}$ against $1/[CO]$ are closely

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