we must be satisfied with the partial understanding of the structures themselves, which we think we have attained.

Acknowledgment. We are grateful to the members of our research group for useful discussions. We thank the Deutsche Forschungsgemeinschaft (DFG) and the Verband der Chemischen Industrie for postdoctoral and Habilitation fellowships to W.T. and the NSF for the support of this work under Research Grants CHE 84064119 and DMR 84722702 to the Materials Science Center. Computing equipment at the University of Münster was purchased through a grant by the Deutsche Forschungsgemeinschaft (DFG, Kr 406/9-1). We are grateful to Jane Jorgensen and Elisabeth Fields for their expert drawings.

Appendix

All the calculations were performed by using the extended Hückel method[33a,b] with weighted H_{ij}'s.[33c] Unless otherwise mentioned, the experimental bond lengths were used. The values for the H_{ii}'s and the orbital exponents are listed in Table III. The parameters for C and H are the standard ones.[33a,b]

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Dependence of Bond Angles upon Bond Distances in Simple Covalent Hydrides, Halides, and Oxides[1]

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Ab initio molecular orbital calculations for a variety of hydrides, fluorides, and oxides of first- and second-row elements show that the optimum bond angle subtended by a pair of ligands increases significantly as the internuclear separation between the ligand and the central atom is decreased. This dependence is interpreted in terms of a directed valence theory of bonding, with departures from ideal bond angles arising from steric clashes among ligands. Some of the apparent anomalies of bond angles in simple hydrides and halides are resolved by the discovery that the steric size of a ligand depends significantly upon the length of its bond to the central atom.

For many years, chemists have attempted to elucidate the principal factors that determine the three-dimensional arrangement of ligands X about a central atom A in common molecules. The most successful simple theory of structure is the well-known VSEPR (valence shell electron pair repulsion) method elaborated by Gillespie,[2] in which repulsion between electron pairs on A is considered to be the dominant factor. In VSEPR, the number of electron pairs at A determines the "ideal" geometry, and the electronegativity of the ligands controls minor deviations from this structure.

We wish to report *ab initio* molecular orbital calculations which indicate that the bond distance R_{AX} is a major factor in determining the optimum XAX bond angle in AX_n molecules, particularly if A is a first-row element.

The variation in HOH angle with changes to the OH bond distance in H_2O is illustrated in Figure 1.[3] The MO calculations here use the 6-31G* basis set,[4,5] i.e., one that includes d orbitals on oxygen, in which inner-shell atomic orbitals are expanded by a fixed linear combination of six Gaussian orbitals and the valence-shell atomic orbitals are expanded as a combination of two sets of Gaussians, one with three components and one with one. The HOH angle widens appreciably as the OH distance is reduced, becoming greater than the tetrahedral value (109.5°) for OH separations of 0.83 Å or less. As the bond is stretched, the angle closes down toward 90°.[6] Similar results are obtained[3] for NH_3 (not shown) and for the singlet state of CH_2 (Figure 1). Although the trend of increasing bond angle with decreasing XH atomic separation is also obtained when X is a second-row atom, the rate of change is only about one-third of that obtained when X is from the first row (see Figure 1 results for H_2S). Again the limiting angle is near 90° for long bond distances but stays well under the tetrahedral value even at short separations. This behavior is not related significantly to the ligand's electronegativity or to the number of lone pairs on A, as the variation for CH_2 is similar to that for H_2O and is very different from that for PH_3 (not shown).

The substantial dependence of bond angle upon interatomic separation and the limiting values of about 90° for bond angles at long separations for the hydrides are unanticipated by VSEPR theory. To explore this point further and to discover the actual reasons for bond angle variations, the ab initio MO calculations were extended to a variety of other molecules. For reasons of economy, smaller basis sets were employed.[7] The basis set used

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(1) Research supported by the Natural Sciences and Engineering Research Council of Canada.

(2) Gillespie, R. J., *Molecular Geometry*; Van Nostrand Reinhold: Company: London, 1972.

(3) The detailed values of the predicted bond angles and energies as a function of the varied separations are reported in Tables 1-4, available as supplementary data.

(4) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; Chapter 4.

(5) Calculations were performed on a VAX 8600 using the GAUSSIAN 86 program (release C) from Carnegie-Mellon University, by M. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, R. Martin, J. J. P. Stewart, F. Bobrowicz, D. Defrees, R. Seeger, R. Whiteside, D. Fox, E. Fluder, and J. A. Pople.

(6) Calculations with the 6-31G* basis set which include correction for the more substantive effects of electron correlation have been performed by second-order Moller-Plesset perturbation theory. The bond angle-bond length curves are virtually identical with those without correlation when the distances are short. (This applies even to the results for CH_2, for which there is a doubly excited configuration that lies close to the lowest singlet state.) For long AX separations, the optimum XAX angles are smaller than those obtained by the Hartree-Fock calculations, due to incipient bonding between the ligands themselves that is introduced by incorporating doubly excited configurations into the wave function. For example, as the OH bond in H_2O becomes very long, the best electronic structure eventually becomes an oxygen atom separated from an H_2 molecule. To avoid these difficulties, and because there is no significant effect of correlation upon angle at short AX separations (the area of prime importance here), these 6-31G*/MP2 calculations are not discussed further herein.

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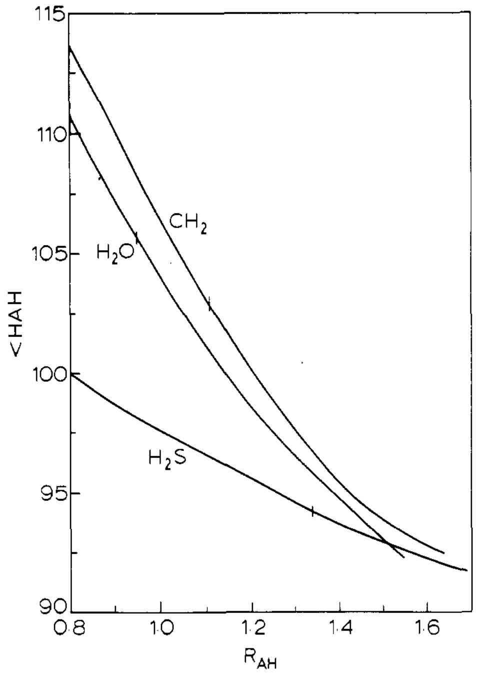

Figure 1. Bond angle (in deg) versus bond length (in Å) for H_2O, CH_2 (S_0 state), and H_2S calculated by use of the 6-31G* basis set. Vertical marks indicate equilibrium bond lengths.

was the STO-3G$^{(*)}$, where the superscript implies that d orbitals are included on second-row atoms (only) and STO-3G means that each Slater-type atomic orbital is expanded as a fixed linear combination of three Gaussian orbitals.[4]

The dependence of bond angle upon AX distance is compared for H_2O, F_2O, $(CH_3)_2O$, and Cl_2O in Figure 2. The curves all have the same shape but are displaced from one another by amounts that decrease somewhat as the distances become small. The simplest explanation for these results is that the optimum XAX angle is determined simply by the steric size of the ligands X. The ligands do not act completely as "hard spheres", since the XX distance is not constant. It is difficult to deduce exactly the effective potential function acting between the ligands that yields curves of the form of those in Figures 1 and 2.[8] However, if the optimum XX distance is plotted against the AX distance, an excellent straight line is obtained over a fairly wide range, at least in the cases discussed herein. The slopes of these lines range from 1.1 to 1.4, the larger values being associated with second-row atoms. Thus the ligands appear to be acting as spheres whose nonbonded radius decreases linearly with the reduction in the AX distance. This behavior is consistent with the known contraction in size of the hydrogen atoms in H_2 as the internuclear separation is reduced to zero that is presumed to occur in other atoms as well.[9]

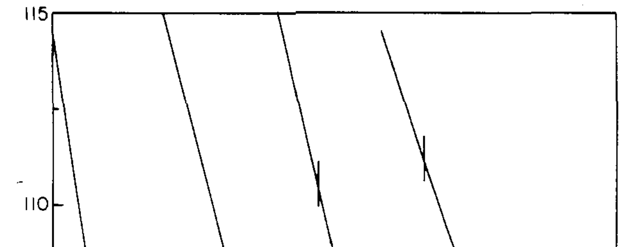

Figure 2. Bond angle (in deg) versus bond length (in Å) for H_2O, F_2O, Cl_2O, and $(CH_3)_2O$ calculated by use of the STO-3G basis set. Vertical marks indicate equilibrium bond lengths.

Notwithstanding the difficulty of establishing precisely the exact potential function involved, all of the calculations are consistent with the hypothesis that XAX bond angle departures from their "ideal" value are due primarily to steric clashes between the ligands and that this ideal angle is 90° for AX_n systems in which the number of ligands equals the number of singly occupied orbitals present on the (unpromoted) central atom. This viewpoint is very similar to the concept of directed valence advanced long ago by Pauling[10] on the basis of valence-bond theory, which has been discussed recently by Goddard and Harding[11a] and by Hall.[11b] The greater dependence of bond angle upon AX distance for first-row atoms X is consistent with the very small size of first-row atoms,[11,12] though this cannot be the whole explanation since for the same separation R the optimum angle is greater around first-row elements A. This lesser tendency to depart from 90° angles arises in part from the poorer ability of 3s orbitals to bond

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(7) We refrain from discussing calculations using the 3-21G and 6-31G basis sets, as they are known to predict bond angles in AX_n molecules, containing lone pairs on A, that are too large, even though they often give superior energetics. However the curves obtained from such calculations and from the 3-21G$^{(*)}$ basis do parallel the STO-3G$^{(*)}$ and 6-31G* results. See Tables 1 and 2 for details.[3] Similarly, the curves are not changed significantly when 2p orbitals are added to the hydrogen atoms, i.e., in the 6-31G** basis set.

(8) Many of the curves are fit by equations of the type

$$\theta - \theta_0 = ke^{-aR}$$

The angles θ_0, which would be optimum for molecules in which the ligands do not repel each other, are close to 90°. For example, the H_2O and NH_3 curves follow this equation with $a = 3$ and 4, respectively, and give θ_0 values of 90.0 and 92.6°, respectively. The fit to an exponential should not necessarily be taken as indicating van der Waals forces are involved, however, since other functions fit almost as well. For example, many of the optimum θ versus R curves, and E versus θ curves for a fixed R_{AX}, are well fit by appropriate derivatives of potential energy functions of the type

$$E = k(\theta - \theta_0) - K/d$$

where d is the distance separating the ligand nuclei. The physical significance of the $1/d$ dependence is that of electrostatic repulsion. However this dependence probably could be replaced by many other forms that also increase sharply as d decreases, so one cannot conclude that the repulsions are due to partial charges on the ligands. A considerable amount of experience has been amassed in the fitting of intramolecular potential energy surfaces by more sophisticated functions. For details, see: Truhlar, D. G.; Steckler, R.; Gordon, M. S. *Chem. Rev.* **1987**, *87*, 217.

(9) See: Baird, N. C. *J. Chem. Educ.* **1986**, *63*, 660. Ruedenberg, K.; *Rev. Mod. Phys.* **1962**, *34*, 326.

(10) See: Pauling, L. *The Nature of the Chemical Bond*, 3rd ed: Cornell University Press: Ithaca, NY, 1960; Chapter 4. Pauling, L., *J. Am. Chem. Soc.* **1981**, *53*, 1367.

(11) (a) Goddard, W. A.; Harding, L. B. *Annu. Rev. Phys. Chem.* **1970**, *29*, 363. (b) Hall, M. B. *J. Am. Chem. Soc.* **1978**, *100*, 6333.

(12) See, for example: Gillespie, R. J.; Humphreys, D. A.; Baird, N. C.; Robinson, E. A. *Chemistry*; Allyn and Bacon: Boston, MA, 1986; pp 134 and 477.

to ligands as compared to the ability of 2s orbitals to bond, in both cases relative to bonding by the corresponding p orbitals.[11] As a further test of this point, the energies of both H_2O and H_2S have been calculated with XH separations of 1.20 Å. The energy required to increase the HSH angle by 5° beyond its optimum value (95.5°) for this distance is found to be 2.2 kcal mol^{-1}, which is almost 3 times that of the 0.8 kcal mol^{-1} required to widen the HOH angle (from its optimum 98.7°). Forcing the s orbital to pick up the slack in bonding therefore is much easier for a first-row atom than it is for one from the second row.

The steric theory nicely explains a phenomenon that cannot be understood by VSEPR theory—namely the fact that PX_3 and SX_2 bond angles are significantly larger when X = F than when X = H, whereas for the analogous NX_3 and OX_2 systems the angles are a little larger with hydrogen ligands.[2] (In other words, the bond angles in H_2S and PH_3 are anomalously low from the VSEPR viewpoint.[2]) Consider, however, that the covalent radius of P is 0.40 Å greater than that of N and that of S is 0.38 Å greater than that of O.[13] (Indeed, the experimental bond length in PH_3 is 0.41 Å greater than that in NH_3 and that of H_2S is 0.38 Å greater than that in H_2O.[13]) However the bond in NF_3 is only 0.19 Å shorter than that in PF_3, which is similar to that observed in F_2O compared to that observed in F_2S.[13] According to STO-$3G^{(*)}$ calculations, if the bond lengths in the first-row fluorides were indeed 0.39 Å rather than 0.19 Å shorter than they are in the second-row analogues, the FNF and FOF bond angles would exceed the HNH and HOH angles by 4.2 and 7.2°, respectively, i.e., by amounts that are similar to those observed for second-row systems (e.g. 4.4° for PX_3 and 6.1° for SX_2). Thus according to the present picture, the bond angles in the second-row compounds are "normal" and reflect the behavior expected from the larger van der Waals radius of fluorine compared to that of hydrogen.[12] The angles in the first-row fluorides are small because of anomalously long N–F and O–F bonds, which have the effect of reducing the steric requirement of fluorine. The viewpoint that the second-row hydrides are "normal" is supported also by the differences observed experimentally in the bond angle at the central atom when the hydrogen atoms in water or hydrogen sulfide are replaced by methyl groups; the bond angle increase at sulfur of 6.9° is almost identical with that of 7.3° at oxygen.

STO-3G calculations have been performed on propane, $(CH_3)_2CH_2$. Here the "natural" angles are expected to be tetrahedral (109.47°), since the 2s orbital of carbon must be involved in bonding in order to raise the valence of carbon to four. The CCC angle increases substantially, and the HCH angle decreases by almost the same amount, when the CC bond distances are reduced; for example, reduction of R(CC) from 1.65 to 1.35 Å increases the CCC angle by 5° and decreases the HCH angle by 6°. Alternatively, when the CC distances are held at 1.55 Å, then as the CH separations in the methylene group are reduced, eventually the steric repulsion of hydrogens becomes greater than that between methyl groups, and the optimum CCH angle rises above tetrahedral. (The crossover occurs at R_{CH} = 0.88 Å, according to STO-3G calculations.)

The ab initio calculations for the $CH_4 \rightarrow CH_3 + H$ potential energy reaction surface reported by Hase and co-workers[14] are also relevant to the present study. They found that when the length of the unique C–H* bond in CH_4 was less than that for the other three, the optimum H*CH angles exceeded the tetrahedral value (109.47°) and the other HCH angles became less than tetrahedral. This result is consistent with our steric interpretation of bond angle. As the C–H* bond was lengthened, they found that the H*CH angles converged to 90° and the HCH angles to 120°, owing to changes in hybridization from sp^3 in CH_4 to sp^2 in CH_3.

Some years ago, Bartell noted that the experimental bond angles about carbon in substituted ethylene and formaldehyde could be interpreted entirely on the basis of steric effects.[15] The XCX angles in such molecules are slightly less than the "ideal" value of 120° for sp^2 hybridization due to the large steric size of the carbon or oxygen, which lies at a relatively short distance from the carbon in question. Indeed the idea that the steric size of a group is dependent upon the length of its bond is implicit in that analysis. We have performed ab initio STO-3G calculations on ethylene at a variety of C=C distances to test this point. The HCH angle increases as the C=C distance increases and exceeds 120° for CC separations of 1.6 Å or more. Calculations also have been performed as a function of the CX distances on a series of derivatives $X_2C{=}CH_2$, where X = H, F, Cl, and CH_3. At the normal C=C separation of 1.34 Å and the optimum CX distances, all of these X groups are smaller than $=CH_2$ and thus all XCX angles are smaller than 120°. However, for small CX separations the X–X steric interaction should be sufficient to dominate over C–X ones and the XCX angle should become greater than 120°. This behavior is indeed found for the disubstituted ethylenes—see Figure 3 for plots of XCX angle against CX distance. For example, the FCF angle will exceed 120° for CF distances less than 1.0 Å.

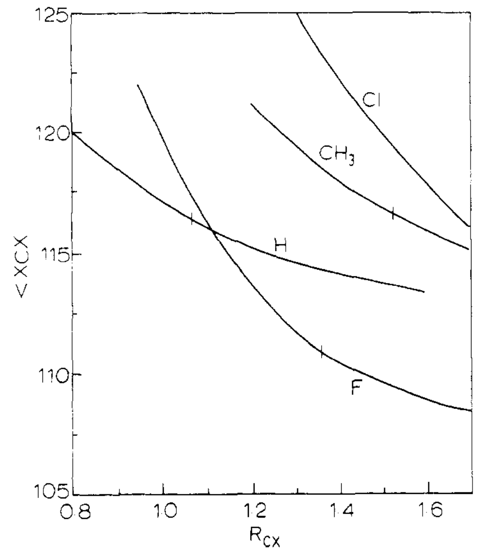

Figure 3. XCX bond angle (in deg) versus CX bond length (in Å) for 1,1-disubstituted ethylenes, calculated by use of the STO-3G basis set. Vertical marks indicate equilibrium bond lengths.

If the present picture of steric determination of bond angle is correct, there is no reason that bond angles greater than tetrahedral (109.5°) should not occur in systems isoelectronic with water and ammonia. Indeed, H_2F^+ and H_3O^+ are known experimentally to possess bond angles of 113.9 and 111.3°, respectively.[13] Our calculations for H_2Cl^+ as well as the available experimental data for cations indicate that positive charge produces almost no change in the AX_2 bond angle for second-row elements A but usually gives a significant increase for first-row atoms. This result applies also upon double ionization of SF_2 and OF_2. When all bond distances are held at 1.4 Å, the increase calculated by STO-$3G^{(*)}$ due to loss of two electrons in SF_2 amounts to only 2.3° whereas that for doubly ionizing OF_2 amounts to 14.1°, the angle increasing from 101.3 to 115.4°. Overall, the trends seem to indicate that positive ionization improves the ability of 2s orbitals (relative to 2p) to participate effectively in bonding—whereas this does not apply to atoms from the second row (and beyond)—and that relief from the electrostatic repulsion of the partially positive ligands in these ions is a major driving force in widening the angles.

The substantial dependence of XAX angle upon AX length also accounts in large measure for the observed variations in angles observed when group 5–8 atoms are bonded to oxygen and/or halogens. Characteristically, OAO angles formed by unicoordinate oxygen atoms are much larger than expected from "ideal" values

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(13) All experimental structures are from: Calloman, J. H.; Hirota, E.; Iijima, T.; Kuchitsu, K.; Lafferty, W. J. *Structure Data of Free Polyatomic Molecules*; Springer-Verlag: Berlin, 1987.

(14) Duchovic, R. J.; Hase, W. L.; Schlegel, H. B. *J. Phys. Chem.* **1984**, *88*, 1339. Duchovic, R. J.; Hase, W. L.; Schlegel, H. B.; Frisch, M. J.; Raghavachari, K. *Chem. Phys. Lett.* **1982**, *89*, 120.

(15) Bartell, L. S. *J. Chem. Phys.* **1960**, *32*, 827; *Inorg. Chem.* **1966**, *5*, 1635; *J. Chem. Educ.* **1968**, *45*, 754.

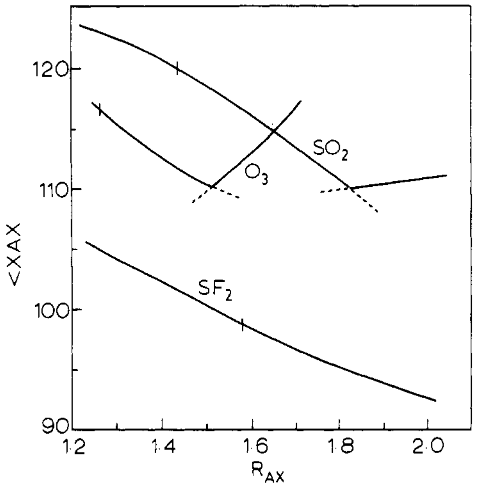
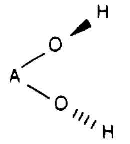


Figure 4. Bond angle (in deg) versus bond length (in Å) for O_3, SO_2, and SF_2 calculated by use of the STO-3G$^{(*)}$ basis set. Vertical marks indicate equilibrium bond lengths.

predicted by simple VSEPR or hybridization theories. (These deviations are explained in VSEPR theory as arising from the large effective size of two electron pairs forming a double bond to oxygen.[2]) For example, the experimental OAO angles in O_3, SO_2, and SO_2F_2 are 117.8°, 119.5°, and 122.6°, respectively, compared to the FAF angles of 103.1°, 98.0°, and 96.7° in F_2O, SF_2, and SO_2F_2, respectively.[13] To investigate these differences, ab initio calculations using the STO-3G$^{(*)}$ basis set have been performed. As illustrated in Figure 4, the OOO angle in ozone and the OSO angle in sulfur dioxide depend significantly upon the chosen bonded distances.[16] The curves for OF_2 (Figure 2) and for SF_2 (Figure 4) also display this dependence, although for a given OX or SX distance, the angle in O_3 is much greater than that in F_2O (e.g., 113 versus 101° at 1.4-Å bond lengths) and that in SO_2 is much greater than that in SF_2 (121 versus 102° at 1.4 Å). Thus the steric size of unicoordinate oxygen exceeds that of unicoordinate fluorine by a substantial amount. The effect of π bonding per se is relatively small according to calculations we have performed for OF_2^{2+} and SF_2^{2+}, which are isoelectronic with O_3 and SO_2 respectively. Notwithstanding the formal π bonding and positive charge in these ions, the FAF angles are about 2.8° greater and 13.6° less, respectively, than in ozone and sulfur dioxide for bond distances of 1.4 Å.

Inspection of the density and overlap population matrices indicate that much of the steric repulsion between the oxygen atoms is due to residual antibonding[17] associated with the p orbitals perpendicular to the AO bonds—both between electrons in p orbitals in the π system and between p lone pairs that lie in the OAO plane. To investigate the relative importance of these interactions, we have performed STO-3G calculations on $O(OH)_2$ and $S(OH)_2$. The interaction of π lone pairs in these systems is eliminated in the nonplanar geometry I in which the hydrogens



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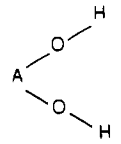

II

lie on opposite sides of the OAO plane, whereas in conformation II it is the in-plane repulsions that are minimized. For AO distances of 1.4 Å, the optimum OOO angles in I and II are 105 and 100°, and the optimum OSO angles are 104 and 98°, respectively. We conclude that the in-plane interactions are the more important but that both contribute to the overall steric repulsion of oxygens. (Note that the interactions between oxygens atoms in the 6-electron system in $O(OH)_2$ and $S(OH)_2$ are less than for the 4-electron systems in O_3 and SO_2 since the extra electron pair enters an MO that is OO bonding.)

Registry No. H_2O, 7732-18-5; CH_2, 2465-56-7; H_2S, 7783-06-4; F_2O, 7783-41-7; Cl_2O, 7791-21-1; $(CH_3)_2O$, 115-10-6.

Supplementary Material Available: Listings of data from ab initio calculations that were used to construct Figures 1–4 and from the calculations on propane mentioned in the text, giving bond angles as a function of bond distance for first- (Table 1) and second-row (Table 2) AX_2 molecules, including those from basis sets other than those discussed in the text in some cases, data for the STO-3G calculations on propane (Table 3), and data for the substituted ethylenes (Table 4) (6 pages). Ordering information is given on any current masthead page.

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(16) The curves in Figure 4 for ozone and sulfur dioxide both change slope at long bond distances due to a significant change in their electron distribution arising from avoided crossings of states.

(17) Residual antibonding is the net destabilization that occurs when two lone-pair orbitals overlap strongly and originates from the greater destabilization of the antibonding combination of the orbitals compared to the stabilization of the bonding combination.