The time scale for these lower energy abstraction reactions may be estimated from the velocity of the tritium atom itself: a 1-eV tritium atom has a velocity of 8×10^{13} Å/sec, and the reaction time scale must thus be $\geq 10^{-14}$ sec.

Specific HT Yields in Different Moderators. The relative values of the specific HT yields for abstraction from c-C_3H_6 in three moderators are given in Table III. The higher such a yield, the proportionally greater must have been the number of tritium atom collisions to which the c-C_3H_6 molecules were exposed. Consequently, the collision density of tritium atoms can be assumed to fall in the ratio 4.7 ± 0.2:2.2 ± 0.1:1.0 for Ar/N_2/c-C_4F_6, suitably averaged over the reaction range in which abstraction occurs with c-C_3H_6. The general observation of parallel relative yields in the different moderators further suggests that these relative collision densities may be suitable averages for a wide range of energies.

The three quantities which determine the relative collision densities in each moderator are (a) rate of loss of tritium by chemical reaction; (b) rate of energy loss of tritium in nonreactive collisions; and (c) the relative frequency of collision with each of the components of the mixture, *i.e.*, molecular size or collision cross section. Since all estimates of the molecular radii indicate N_2 and Ar to be very similar in size, and both are essentially inert moderators, the average energy loss in collisions with N_2 must be almost twice as large as in collision with Ar to account for the substantial differences in HT yield. The difference must arise from substantial energy losses in inelastic collisions with nitrogen.

Comparative collision densities can be stated quantitatively through the formalism of the kinetic theory of hot reactions.[4] In the case of a small amount of reacting compound (RH), a large excess of moderator gas (M), and a small quantity of scavenger molecule (O_2), the following limiting expression is obtained[11]

$$\frac{(I_{HT})(\sigma_{RH})}{(\alpha_M)(\sigma_M)} = \frac{P_{HT}(M)}{(RH)} \tag{3}$$

in which the σ_i's are collision cross sections, I_{HT} is the reactivity integral for HT from RH, P_{HT} is the measured yield of HT, and α_M is the logarithmic energy loss for collisions with M. The cross-product of cross-section and logarithmic energy loss for each moderator ($\sigma_M\alpha_M$) is thus the reciprocal of the HT yield and will have the values, normalized to argon, given in Table V.

Table V. Relative Specific HT Yields and Tritium Collision Densities from Various Moderator Systems

Moderator	$(HT)^0$	$\sigma_M\alpha_M$
Ar	4.7 ± 0.2	(1.0)
N_2	2.2 ± 0.1	2.2 ± 0.1
c-C_4F_6	(1.0)	4.7 ± 0.2

On the Possible Existence of Double Minima in Potential Energy Surfaces of AB_2-Type Molecules[1a]

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Abstract: Recently LCAO-SCF-MO calculations were reported for the low-lying $^1A_1$ states of NO_2^+ and O_3 for several bond angles. Some of these calculated zero-order energy curves were reported to cross. Here it is shown these crossings can be predicted on the basis of Walsh-type diagrams. Further it is suggested that the crossings of the zero-order $^1A_1$ curves lead to double minima in the ground-state potential energy surfaces of AB_2-type molecules with 14–18 valence electrons. On this basis the high-temperature isomer of SO_2 postulated by Norrish and Oldershaw is predicted to be a symmetrical form of SO_2 with a somewhat larger S–O bond distance and a bond angle of about 72°.

The potential energy surfaces of polyatomic molecules arising from changes in bond angle are difficult to investigate experimentally.[2] Recently molecular orbital calculations have been performed that approximate true Hartree–Fock solutions for the molecular energy and predict equilibrium bond angles within 1–2% of the accepted experimental values.[3] In general, however, it is necessary to extend the Hartree–Fock scheme (say by configuration interaction) in order to accurately determine potential energy surfaces.

In an earlier paper,[4] a method was discussed which predicted the additional configurations most likely to alter the energy curves obtained from Hartree–Fock or "best molecular orbital" calculations. It is the purpose

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[1] (a) Research supported by the Directorate of Chemical Sciences of the Air Force Office of Scientific Research, Contract No. AF 49 (638)-1625; (b) AFOSR Postdoctoral Fellow, 1967–1968; Princeton University; (c) Ohio University.

[2] See, for instance, M. A. Pariseau, I. Suzuki, and J. Overend, *J. Chem. Phys.*, **42**, 2335 (1965); J. Pliva, V. Spirko, and D. Papousek, *J. Mol. Spectrosc.*, **23**, 331 (1967).

[3] L. C. Allen, "Quantum Theory of Atoms, Molecules, and the Solid State," P. O. Löwdin, Ed., Academic Press Inc., New York, N. Y., 1966, pp 39–80.

[4] E. F. Hayes and G. V. Pfeiffer, *J. Chem. Phys.*, **47**, 5168 (1967).

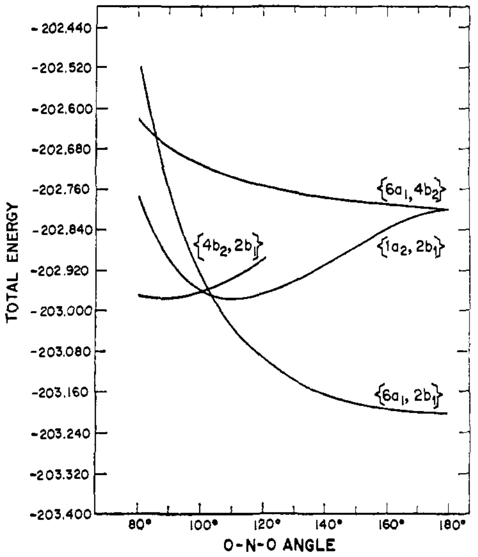

Figure 1. Total energy as a function of bond angle for low-lying $^1A_1$ states of NO_2^+, calculated by the SCF-LCAO-MO method using Gaussian lobe functions. The labels indicate the symmetry orbitals which are not occupied. This figure is reproduced from ref 16; energy in hartrees.

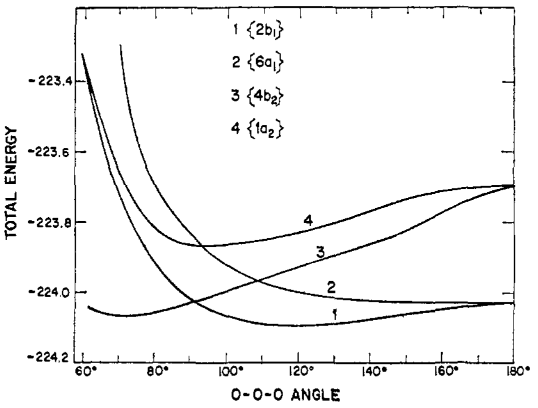

Figure 2. Total energy as a function of bond angle for low-lying $^1A_1$ states of O_3, calculated by the SCF-LCAO-MO method using Gaussian lobe functions. The labels indicate the symmetry orbital which is not occupied. This figure is reproduced from ref 17; energy in hartrees.

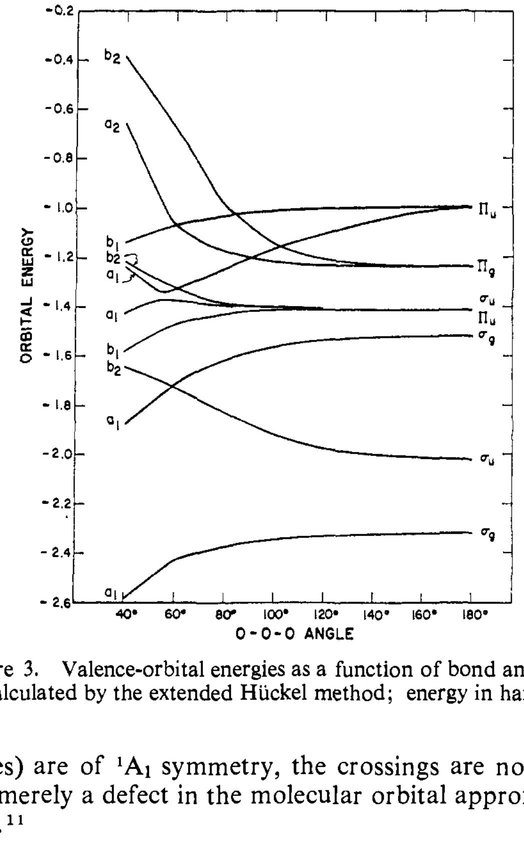

Figure 3. Valence-orbital energies as a function of bond angle for O_3 calculated by the extended Hückel method; energy in hartrees.

of this paper to present evidence for the existence of double minima[5] in the potential energy surfaces of AB_2-type molecules.

Molecular Orbital Calculations of AB_2-Type Molecules

The electronic structure of AB_2-type molecules has been extensively investigated in recent studies.[6-8] Potential energy curves for these molecules were obtained using the LCAO-SCF-MO method of Roothaan[9] with orbitals constructed from Gaussian lobe functions[10a] which give atomic energies of approximately the same quality as double-ζ calculations.[10b] The resulting SCF molecular orbitals are reasonable approximations to the true Hartree-Fock orbitals.

The molecules NO_2^+, O_3, and F_2O represent AB_2-type molecules with 16, 18, and 20 valence electrons, respectively. For NO_2^+ [6] and O_3[7] $^1A_1$ configurations with different occupancies of the valence orbitals,[8] $1a_2$, $4b_2$, $6a_1$, and $2b_1$ have been studied. In Figures 1 and 2 potential energy curves for four, single determinant, $^1A_1$ configurations of NO_2^+ and O_3, respectively, are presented. The notation used to label the configurations refers to unoccupied orbitals in the set of orbitals given previously. For example, in the configuration $\{1a_2, 2b_1\}$ the $4b_2$ and $6a_1$ orbitals are occupied and the $1a_2$ and $2b_1$ orbitals are unoccupied.

For our discussion, the important feature of these curves is the existence of the crossing points. Since all of these single determinant configurations (zero-order states) are of $^1A_1$ symmetry, the crossings are not real but merely a defect in the molecular orbital approximation.[11]

Prediction of *Ab Initio* Results Using Walsh Diagrams

It has been known for many years that diagrams such as those of Walsh[12] and Mulliken[13] in which the valence molecular orbital energies are plotted as a function of bond angle exhibit the same general features for similar types of molecules. Figure 3 is a Walsh diagram for O_3 constructed by extended Hückel theory.[14,15]

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[5] The term double minima may be confusing when both minima occur for bond angles of less than 180°, since if one plots the total energy curve from 90 to 180 to 90° there will actually be four minima in the curve. We hope that this note will be sufficient to eliminate the confusion.

[6] G. V. Pfeiffer, R. J. Buenker, S. D. Peyerimhoff, and L. C. Allen, "Linear Combination of Gaussian Orbitals Self-Consistent Field Calculations for NO_2^+ and NO_2^-," paper in preparation.

[7] S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **47**, 1953 (1967).

[8] R. J. Buenker and S. D. Peyerimhoff, *ibid.*, **45**, 3682 (1966).

[9] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[10] (a) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966); (b) E. Clementi, *ibid.*, **40**, 1944 (1964).

[11] In ref 7 the authors did not point out that the crossings of the zero-order potential energy curves for these states are just a defect in the molecular orbital approximation. Unless one keeps this in mind, an incorrect interpretation of Figures 4a and 5a of ref 7 might result.

[12] A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

[13] R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 204 (1942).

[14] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962); R. Hoffmann, *ibid.*, **39**, 1397 (1963).

[15] For details of extended Hückel calculations in O_3, see Appendix A.

The quantitative similarity between Walsh diagrams produced by many-electron, *ab initio* molecular orbital theory and extended Hückel theory has been established by Allen and Russell[16] for molecules containing no highly ionic bonds. The Walsh diagrams for NO_2^+ and F_2O are essentially the same as the O_3 diagrams and are not reported here.[17]

For a molecule with 16 valence electrons the eight molecular orbitals of lowest energy will be doubly occupied. In Figure 3 we note that the eight molecular orbitals of lowest energy will vary with bond angle. Since the $6a_1$ orbital crosses both the $4b_2$ and $1a_2$ orbitals near 100° we would expect that the zero-order curves for electronic configurations differing only in the occupancy of the $6a_1$, $4b_2$, or $1a_2$ orbital would also exhibit crossings at about the same bond angle. These latter crossings are evident in Figure 1 for NO_2^+ in the intersection of the zero-order curves for the configurations $\{6a_1, 2b_1\}$, $\{1a_2, 2b_1\}$, and $\{4b_2, 2b_1\}$ near 100°. Again from Figure 3 we note that the $2b_1$ and $4b_2$ curves cross at a bond angle slightly less than 90°. This crossing also appears in Figure 1 as the intersection of the zero-order curves for the $\{6a_1, 2b_1\}$ and $\{6a_1, 4b_2\}$ configurations near 85°.

In the case of O_3 the nine molecular orbitals of lowest energy will be doubly occupied in the ground state. In Figure 3 we see that the nine molecular orbitals of lowest energy again depend upon bond angle. The crossing of the $2b_1$ and $4b_2$ orbital energy curves is responsible for the crossing of the zero-order potential energy curves 1 and 3, $\{2b_1\}$ and $\{4b_2\}$, in Figure 2. Similarly, the crossings of the $\{6a_1\}$ and $\{4b_2\}$ curves near 110° and the $\{6a_1\}$ and $\{1a_2\}$ curves near 95° are predicted by the crossings of the corresponding orbital energy curves in Figure 3.

Figure 4 displays the sum of extended Hückel theory molecular orbital energies *vs.* bond angle in O_3 for four singlet states. Comparison with Figure 2 shows that in this particular case the extended Hückel orbital energy sum parallels the *ab initio* total energy well for all angles. It is an empirical observation from the results of Allen and Russell[16] that this parallelism holds for at least some covalent species (*e.g.*, F_2O). However, this parallelism is not implied by the inequality relation established by Peyerimhoff, Buenker, and Allen[18] which relates only to equilibrium bond angle predictions.

In the case of the F_2O molecule the ten valence molecular orbitals of lowest energy will be doubly occupied. Since there are no unoccupied low-lying orbitals, there are no crossings of the occupied and unoccupied orbitals in the Walsh diagram.[8] Thus we would not expect the F_2O molecule to have crossings associated with its ground-state potential energy curve. Indeed, this is consistent with the *ab initio* results of Buenker and Peyerimhoff.[8]

This correspondence between the NO_2^+, O_3, and F_2O correlation diagrams and their zero-order potential energy curves suggests that one might be able to predict crossing and noncrossing of these curves from Walsh-type diagrams without any further calculations. It should be borne in mind, however, that the sum of the orbital energies in Hartree–Fock theory does not add up to the total energy so there is no guarantee that a crossing of occupied and unoccupied orbital energy curves will lead to a crossing of the total energy curves. This is the case for NO_2^+ and O_3, but without further *ab initio* results one cannot be certain that this will always be true.

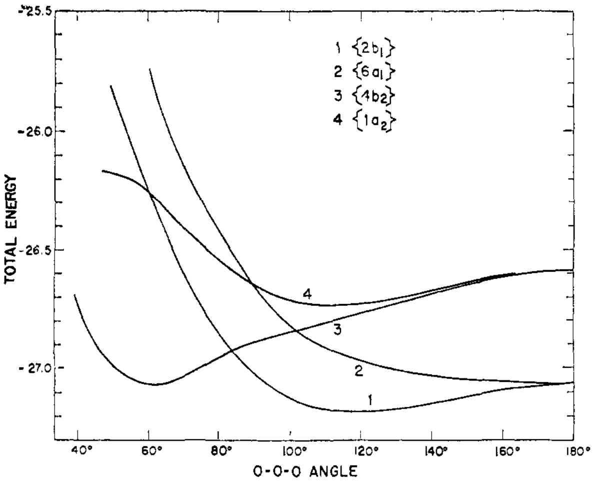

Figure 4. Sum of valence orbital energies from an extended Hückel calculation as a function of bond angle for O_3. Labels indicate the symmetry orbital which is not occupied; energy in hartrees.

Possibility of Double Minima

The central question is how do the zero-order energy curves change when configuration interaction is taken into account. For several years it has been recognized that the crossing of zero-order potential energy curves leads to double minima in the first excited ${}^1\Sigma_g^+$ state of H_2.[19] If the first excited ${}^1\Sigma_g^+$ state of the hydrogen molecule is taken as the model of how configuration interaction affects the zero-order curves, we would expect double minima would remain even after configuration interaction is taken into account.

The determining factor for the presence or absence of double minima will be the magnitude of the interaction terms between configurations. If the interaction term is relatively small, as in the case of the first ${}^1\Sigma_g^+$ excited state of H_2, then the resultant curve might have a double minimum; if, however, large interaction terms are present, a single minimum is strongly suggested. In the case of O_3 the minimum in the $\{2b_1\}$ curve is at 118.5° (Figure 2). The fact that this value is close to the experimental bond angle, 116.8°, may be an indication that configuration interaction terms may be small. A reliable estimate of the magnitude of the interaction terms must await detailed *ab initio* configuration interaction studies.

The existence of double minima has been suggested for the excited states of AB_2-type molecules, but these

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(16) L. C. Allen and J. D. Russell, *J. Chem. Phys.*, **46**, 1029 (1967).

(17) There are, of course, 12 valence molecular orbitals that may be constructed from s and p orbitals on each of the atoms. The two highest molecular orbitals are not shown on Figure 4 since they are at such high energies that they will not be important for our considerations.

(18) S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966).

(19) E. R. Davidson, *ibid.*, **35**, 1189 (1961). Similar double minima have been noted for excited states of C_2 (P. F. Fougere and R. K. Nesbet, *ibid.*, **44**, 285 (1966)) and B_2 (C. F. Bender and E. Davidson, *ibid.*, **46**, 3313 (1967)).

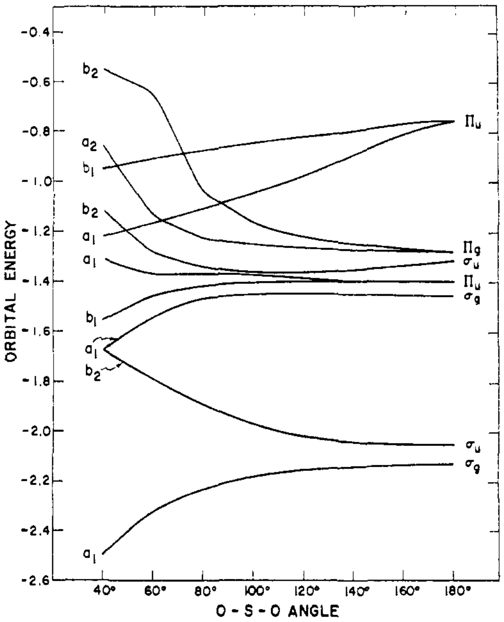

Figure 5. Valence orbital energies as a function of bond angle for SO_2 calculated by the extended Hückel method; energy in hartrees.

minima were associated with A–B bond stretches.[20] To our knowledge no one has considered the existence of double minima associated with bond angle changes in the ground state of an AB_2-type molecule.

On the basis of the Walsh-type diagram given in Figure 3 and assuming that the interaction between ${}^1A_1$ configurations is small, we predict that AB_2-type molecules with 14–18 valence electrons have double minima in their ground-state potential energy surfaces. In this group we include molecules such as NO_2^+, CO_2, NO_2, CF_2, SiF_2, CCl_2, $SiCl_2$, O_3, SO_2, and CS_2.

Some Evidence Supporting the Existence of Double Minima in the Ground State of SO_2

In 1959 Norrish and Oldershaw[21] suggested the existence of a high-temperature isomer of SO_2. The existence of such an isomer was postulated as a reasonable explanation for their flash-photolysis experiments on SO_2.

We have carried out extended Hückel calculations on SO_2 using s, p, and d orbitals on the sulfur atom and s and p orbitals on the oxygen atom.[22] The valence molecular orbital energy curves are given in Figure 5. Note that the crossing of the highest b_2 and b_1 curves is the same as reported for O_3 in Figure 3.

This crossing of the $4b_2$ and $2b_1$ orbital energy curves is easily rationalized. In the linear case the $2b_1$ orbital becomes the $2\pi_u$ orbital which is antibonding between the S and O atoms by virtue of out-of-phase pπ orbitals on these nuclear centers. The $4b_2$ orbital becomes the $1\pi_g$ orbital in the linear case and is predominantly two out-of-phase pπ orbitals on the oxygen atoms. The absence of antibonding character between the S and O atoms in the $1\pi_g$ orbital accounts for this orbital being lower in energy that the $2\pi_u$ orbital for linear conformations. This ordering will not be changed by including d orbitals in the basis set since there are no d orbitals of π_u symmetry to interact with the $2\pi_u$ orbital and possibly lower its energy. Upon bending, the $4b_2$ orbital is strongly antibonding between the approaching oxygen atoms, while the $2b_1$ orbital allows a bonding environment between these two atoms. These different environments account for the rapid increase in energy for the $4b_2$ orbital upon bending and for the decrease in energy of the $2b_1$ orbital. The crossing of these levels is therefore expected for bond angles between 60 and 100°.

We would like to suggest therefore that the high-temperature isomer postulated by Norrish and Oldershaw is a form of SO_2 with C_{2v} symmetry and a bond angle of about 72°. A larger SO bond distance is likely since the $2b_1$ $(2\pi_u)$ orbital, which is occupied in the isomer, is antibonding in the SO bond whereas the formerly occupied $4b_2$ $(1\pi_g)$ orbital is almost nonbonding in the SO bond.

Conclusions

In view of the theoretical and experimental results presented above, it appears that nonionic AB_2-type molecules with 14–18 valence electrons may have double minima in their ground-state potential energy surfaces. We believe that further investigation of the spectra of these AB_2 molecules is needed in order to settle the question of whether double minima really exist in the ground-state potential energy surfaces of these molecules.

Acknowledgments. The authors are pleased to acknowledge extensive discussions with Leland C. Allen, Stephen Rothenberg, and Maurice Schwartz. We wish to thank Roald Hoffmann for making available to us a copy of his extended Hückel theory computer program. The services and computer time made available to us by the Princeton University Computation Center have been invaluable for this study. The Computation Center is supported in part by National Science Foundation Grant NSF-GP579.

Appendix. Extended Hückel Calculations on O_3 and SO_2

In these calculations the normal form of the extended Hückel theory was used. Only valence electrons were included and the off-diagonal matrix elements, H_{ij}, were evaluated by the Ballhausen-Gray form[23] of the Mulliken proposal.[24]

$$H_{ij} = KS_{ij}(H_{ii}H_{jj})^{1/2}$$

The overlap integrals, S_{ij}, were calculated using orbitals of the single exponential type with free atom optimized exponents.[25] Similar results were obtained using Slater orbital exponents. The diagonal matrix elements, H_{ii} were taken as the valence-state ionization potentials. The results reported here are for $K = -2.00$, but similar results were obtained using $K = -1.75$. The AO_2 molecule (A = O or S) was situated with A at the origin and the oxygens at $X = 0$, $Y = \pm R \sin {}^1/_2\Theta$, and $Z = R \cos {}^1/_2\Theta$, where R is the A–O bond distance and Θ is the OAO angle.

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[20] F. P. Huberman, F. A. Cesani, and J. B. Coon, 22nd Symposium on Molecular Structure and Spectroscopy, Ohio State University, 1967.

[21] R. G. W. Norrish and G. A. Oldershaw, *Proc. Roy. Soc.* (London), **A249**, 498 (1959); see in particular the first full paragraph on p 508.

[22] For details of extended Hückel calculations on SO_2 see Appendix B.

[23] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

[24] R. S. Mulliken, *J. Chim. Phys.*, **46**, 497 (1949).

[25] E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

A. Results for O_3. The O–O distance was taken as 2.50 bohr. The experimental value is 2.413 bohr,[26] but 2.50 bohr was used in order to be consistent with the *ab initio* work of Peyerimhoff and Buenker.[6] The valence-state ionization potentials and orbital exponents for the oxygen atom are

$$(\mathrm{O,2s}) = 2.25,\ H_{ii}(\mathrm{O,2s}) = -50.00\ \mathrm{eV}$$

$$(\mathrm{O,2p}) = 2.23,\ H_{ii}(\mathrm{O,2p}) = -33.60\ \mathrm{eV}$$

Note that the energy scale is relative to $H_{ii}(\mathrm{O,2s}) = -50.00$ eV.

In Table I we report the wave functions and orbital energies (in hartrees) for the calculation at a bond angle of 120°. Similar tables for bond angles at 180, 160, 140, 100, 80, 60, and 40° are to be deposited with ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C.

Table I. O_3 Wave Function: Bond Angle 120°

		Symmetry				
		a_1	b_2	a_1	b_1	a_1
Orbital energy		−2.3722	−1.9683	−1.5932	−1.4119	−1.4006
I[a]	II[b]					
1	2s	−0.4026	0.5634	0.4400	0.0	−0.1714
1	$2p_z$	0.0488	−0.0458	0.2906	0.0	0.2252
1	$2p_x$	0.0	0.0	0.0	0.4676	0.0
1	$2p_y$	−0.0946	0.0238	−0.2725	0.0	0.4354
2	2s	−0.5812	0.0	−0.4147	0.0	−0.1196
2	$2p_z$	−0.0718	0.0	0.3118	0.0	0.5702
2	$2p_x$	0.0	0.0	0.0	0.6475	0.0
2	$2p_y$	0.0	−0.3895	0.0	0.0	0.0

		Symmetry				
		b_2	a_2	b_2	a_1	b_1
Orbital energy		−1.4074	−1.2262	−1.2047	−1.1028	−0.9989
I[a]	II[b]					
1	2s	−0.3052	0.0	0.0080	−0.0111	0.0
1	$2p_z$	−0.3726	0.0	0.5291	0.5737	0.0
1	$2p_x$	0.0	0.7096	0.0	0.0	0.5399
1	$2p_y$	0.3944	0.0	0.4805	0.1258	0.0
2	2s	0.0	0.0	0.0	0.2657	0.0
2	$2p_z$	0.0	0.0	0.0	−0.5978	0.0
2	$2p_x$	0.0	0.0	0.0	0.0	−0.7798
2	$2p_y$	−0.3650	0.0	−0.0518	0.0	0.0

[a] I = Atom. [b] II = Orbital.

B. Results for SO_2. The S–O distance was taken to be 2.71 bohr.[27] The valence-state ionization potentials and orbital exponents for the sulfur atom are

$$(\mathrm{S,3s}) = 2.12,\ H_{ii}(\mathrm{S,3s}) = -38.40\ \mathrm{eV}$$

$$(\mathrm{S,3p}) = 1.83,\ H_{ii}(\mathrm{S,3p}) = -29.30\ \mathrm{eV}$$

$$(\mathrm{S,3d}) = 0.73,^{28}\ H_{ii}(\mathrm{S,3d}) = -17.10\ \mathrm{eV}$$

Note that the energy scale is relative to $H_{ii}(\mathrm{O,2s}) = -50.00$ eV.

In addition to these calculations we carried out calculations using just s and p orbitals on the sulfur atom. Since the valence orbital energy curves are qualitatively the same as those obtained using s, p, and d orbitals on the sulfur atom, we do not report the wave functions here. It also should be noted that, since we were mainly interested in establishing the crossing or noncrossing of b_1 (π_u) and b_2 (π_g) orbital energy curves, we have not attempted to find the best possible radial function for the sulfur d orbital, since the crossing of b_1 (π_u) and b_2 (π_g) orbital energy curves is determined by the p orbitals on the oxygen atom.

In Table II we report the wave functions and orbital energies (in hartrees) for the calculation at a bond angle of 120°. Similar tables for bond angles at 180, 160, 140, 100, 80, 60, and 40° are to be deposited with ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C.

Table II. SO_2 Wave Function: Bond Angle 120°

		Symmetry				
		a_1	b_2	a_1	b_1	a_1
Orbital energy		−2.1570	−2.0178	−1.4472	−1.4026	−1.3828
I[a]	II[b]					
1	2s	0.4841	−0.5342	0.2891	0.0	0.1119
1	$2p_z$	−0.0278	0.0278	0.3424	0.0	−0.3458
1	$2p_x$	0.0	0.0	0.0	0.5161	0.0
1	$2p_y$	0.0637	−0.0107	−0.3542	0.0	−0.4054
2	3s	0.4159	0.0	−0.3952	0.0	0.1124
2	$3p_z$	0.1329	0.0	0.2245	0.0	−0.3967
2	$3p_x$	0.0	0.0	0.0	0.5091	0.0
2	$3p_y$	0.0	0.3497	0.0	0.0	0.0
2	$3d_{z^2}$	−0.0009	0.0	−0.0087	0.0	−0.1074
2	$3d_{xz}$	0.0	0.0	0.0	0.0603	0.0
2	$3d_{x^2-y^2}$	−0.0014	0.0	−0.1255	0.0	−0.1178
2	$3d_{yz}$	0.0	0.0283	0.0	0.0	0.0
2	$3d_{xy}$	0.0	0.0	0.0	0.0	0.0

		Symmetry				
		b_2	a_2	b_2	a_1	b_1
Orbital energy		−1.3578	−1.2668	−1.2191	−0.9789	−0.8269
I[a]	II[b]					
1	2s	0.2011	0.0	−0.0422	−0.0284	0.0
1	$2p_z$	0.4711	0.0	0.3849	−0.4289	0.0
1	$2p_x$	0.0	−0.6452	0.0	0.0	0.3794
1	$2p_y$	−0.3195	0.0	0.5989	0.0444	0.0
2	3s	0.0	0.0	0.0	−0.4364	0.0
2	$3p_z$	0.0	0.0	0.0	0.6692	0.0
2	$2p_x$	0.0	0.0	0.0	0.0	−0.7987
2	$3p_y$	0.2521	0.0	−0.0434	0.0	0.0
2	$3d_{z^2}$	0.0	0.0	0.0	−0.2737	0.0
2	$3d_{xz}$	0.0	0.0	0.0	0.0	0.4502
2	$3d_{x^2-y^2}$	0.0	0.0	0.0	−0.0609	0.0
2	$3d_{yz}$	−0.1892	0.0	−0.0708	0.0	0.0
2	$3d_{xy}$	0.0	0.2182	0.0	0.0	0.0

[a] I = Atom. [b] II = Orbital.

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