Table I. Energy Differences[a] ($E_{\text{eclipsed}} - E_{\text{staggered}}$) for Ethane SCF Calculations

	Pitzer and Lipscomb[b]	Stevens[c]
	Energy Components	
Kinetic	0.02014	0.00994
Nuclear repulsion	0.00749	−0.11848
Nuclear attraction	−0.04898	0.20113
Electron repulsion (2-electron)	0.02657	−0.08736
	Canonical MO's[d]	
$1a_{2u}(1a_2'')$	0.00223	0.00187
$1a_{1g}(1a_1')$	0.00224	0.00182
$2a_{1g}(2a_1')$	0.00099	0.00413
$2a_{2u}(2a_2'')$	0.00106	−0.00137
$1e_u(1e')$	−0.00032	0.00215
$3a_{1g}(3a_1')$	0.00115	0.00218
$1e_g(1e'')$	0.00256	0.00265
	Localized MO's[e]	
CH		6(0.00736) = 0.04416
CC		0.04160
C inner shell		2(0.01898) = 0.03796
Scaling factors[f]	1.00659, 1.00643	1.00022, 1.00012
Barrier	0.00522 = 3.3 kcal/mol	0.00523 = 3.3 kcal/mol
Exptl, kcal/mol	2.875 ± 0.125[g] 3.030 ± 0.300[h] 2.928 ± 0.025[i]	

[a] Atomic units. [b] Reference 3. [c] Reference 7. [d] Symmetry notation for MO's is that of ref 3. First MO is the staggered conformation. MO in parentheses is the eclipsed conformation. The reader is reminded that the SCF total energy is not equal to the sum of the individual MO energies. [e] Values given are the electronic energy differences between localized MO's, analogous to the canonical MO eigenvalues given above. [f] Reference 8. First number refers to staggered configuration second to eclipsed. [g] K. S. Pitzer, *Discuss. Faraday Soc.*, **10**, 66 (1951). [h] D. R. Lide, *J. Chem. Phys.*, **29**, 1426 (1958). [i] S. Weiss and G. E. Leroi, *ibid.*, **48**, 962 (1968).

contributions of the nuclear repulsion, nuclear attraction, and electron repulsion all have different signs in the two calculations, yet the calculated total barriers are within 10^{-5} au of one another. Both calculations show a positive kinetic energy barrier and a smaller negative potential energy barrier. However, if we scale the coordinates so that they satisfy the virial theorem,[8] even this small change in geometry reverses the situation, making kinetic energy contributions negative and potential energy terms positive. Finally, the "invariants" suggested by Fink and Allen[9] show no invariance between these two calculations.

An analysis of the Stevens wave function[7] in terms of localized orbitals[10] shows that the C–C, C–H, and C inner-shell orbitals make roughly equal contributions to the electronic part of the barrier. This result and the well-known importance of inner shells (as normally constituted) in the total energy make it unlikely that valence-electron-only calculations can give a complete explanation of the barrier.

In summary, we find marked discrepancies in the various contributions to the barrier between two very similar calculations. Even more surprising is the fact that SCF calculations employing vastly different basis sets have all produced barriers ranging only from 2.5 to 3.6 kcal/mol.[3,7,9,11–14] Thus, it seems that the only presently known near invariant in ethane barrier calculations is *the height of the barrier itself.* Further analysis is required to reveal other and more illuminating invariants, which may be useful in any "explanation" of the source of the barrier in ethane. Consideration of the overlap (exclusion principle) repulsion between filled C–H bond orbitals[15] may unveil one such invariant.

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Structure of the $^3B_1$ State of Sulfur Dioxide[1]

Sir:

Recent interest in the formation[2] and lifetime[3] of the lowest triplet state of sulfur dioxide prompts us to report the physical constants of that state, determined by rotational analysis of the 3880-Å triplet ← singlet absorption band. In outline, the results of the analysis are that (i) the coupling scheme in the triplet state is close to case b, *i.e.*, the magnetic interactions produce splittings which are small compared with the rotational intervals; (ii) the rotational structure together with the identity of levels "missing" on account of the zero spin

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Table I. Molecular Constants of the $^3B_1$ State (cm^{-1})

Term value (band origin)	Rotational constants	Centrifugal constants	Spin-rotation constants	Spin-spin constants
25765.79	A_{000} 2.3129	$10^4 D_N$ 0.0044	a_0 −0.005	α 0.115
	B_{000} 0.2970	$10^4 D_{NK}$ −0.080	a −0.008	β (0.03)
	C_{000} 0.2624	$10^4 D_K$ 2.84	b (0)	
		$10^8 H_K$ 7.9		

of ^{16}O nuclei *prove* that the electronic symmetry is $^3B_1$; and (iii) the electric-dipole-active spin function is $|b\rangle$; thus the transition gains its intensity by spin-orbit coupling of $^3B_1$ with a singlet state of B_2 orbital symmetry. The electronic symmetry and spin-orbit coupling mechanism are the same as those recently established for the isovalent molecule NO_2^-.[4,5] Some of the results described here are foreshadowed in the excellent work of Merer, who, however, was not successful in analyzing the spin splittings.[6]

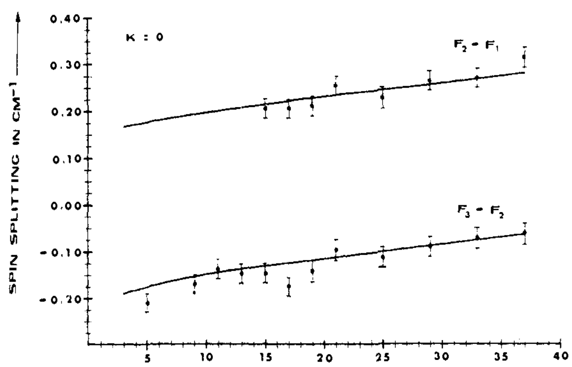

Figure 1. Spin splittings $F_2 - F_1$ and $F_3 - F_2$ for $K' = 0$. The vertical lines represent the standard deviation in the fit (see text).

In the triplet state, except when $N - K$ is small, the spin sublevels in order of decreasing energy are F_2 ($J = N$) > F_3 ($J = N - 1$) > F_1 ($J = N + 1$), the splittings being typically 0.1–0.2 cm^{-1}. Splittings observed for the $K' = 0$ manifold are shown in Figure 1, the curves being calculated by diagonalization of the complete energy matrices for the asymmetric rotor in a triplet state,[7] using values of the spin-spin and spin-rotation constants given in Table I. The sequence $F_2 > F_3 > F_1$ indicates a positive value for the dominant spin-spin constant α,[8] combined with relatively small constants for spin-rotation coupling. Zero-field splittings are not resolved in the triplet-singlet crystal spectrum of SO_2,[9] possibly by a narrow margin.

In the low K subbands, where the effects of asymmetry are greatest, the intense rotational branches are $^rS_3$, $^pS_3$, $^rQ_3$, $^rR_2$, $^pP_2$, $^pQ_1$, $^pO_1$, and $^rO_1$.[10] Except for small values of N, the $^rS_3$ and $^pS_3$ branches run together and generate (about 9 cm^{-1} to high frequency of the band origin) the prominent "spike" characteristic of the triplet-singlet bands of SO_2 as seen under low resolution: its mechanism of formation is then similar to that which produces the Q branch of ordinary C-type infrared transitions. The intensity distribution in the subbands is characteristic of singlet-triplet mixing induced by a spin function of a_2 symmetry, *i.e.*, the active function $|b\rangle$.[11,12] The fact that the branches all conform to the rule $\Delta K_{\text{prolate}} = \pm 1$ means that the triplet-state symmetry must be $^3A_1$ or $^3B_1$, but does not of itself distinguish between these possibilities. However, owing to the zero spin of ^{16}O nuclei, one-half the rotational levels are missing in each state of the transition: in the triplet state the missing levels have even values of τ and are compatible only with the assignments $^3B_1$ or $^3B_2$,[6,11,12] so that the observations jointly prove that the symmetry is $^3B_1$. This confirms the identification, current for many years, with the triplet state of the first excited electronic configuration, $\ldots(6a_1)^1(2b_1)^1$; $^{1,3}B_1$.

As the spin greatly increases the core requirement for least-squares procedures, the constants in Table I are fitted to the frequencies of about 250 selected transitions only (standard deviation <0.02 cm^{-1}) and are considered reliable to the extent indicated. The r_0 structure calculated without regard to effects of vibrational amplitude is

$$r(\mathrm{SO}) = 1.493\ \text{Å} \qquad \angle\mathrm{OSO} = 126.2°$$

with probable error of about 1 part in 10^3. The corresponding ground-state constants are 1.432 Å and 119.5°;[13] thus the bond distance and angle both increase in the transition. The identity of the $^1B_2$ state which shares in the large matrix element for spin-orbit coupling is uncertain, though it may occur in the 3000-Å band system(s).[14] It is tempting to consider that this coupling is responsible also for the strong magnetic rotation spectrum known in that region.[15]

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Addition of Hydrogen Atoms to Glutathione Disulfide in Aqueous Solution

Sir:

The inactivation of enzymes by hydrogen atoms in aqueous solution has been successfully correlated with the selective attack of H atoms at the disulfide bridges