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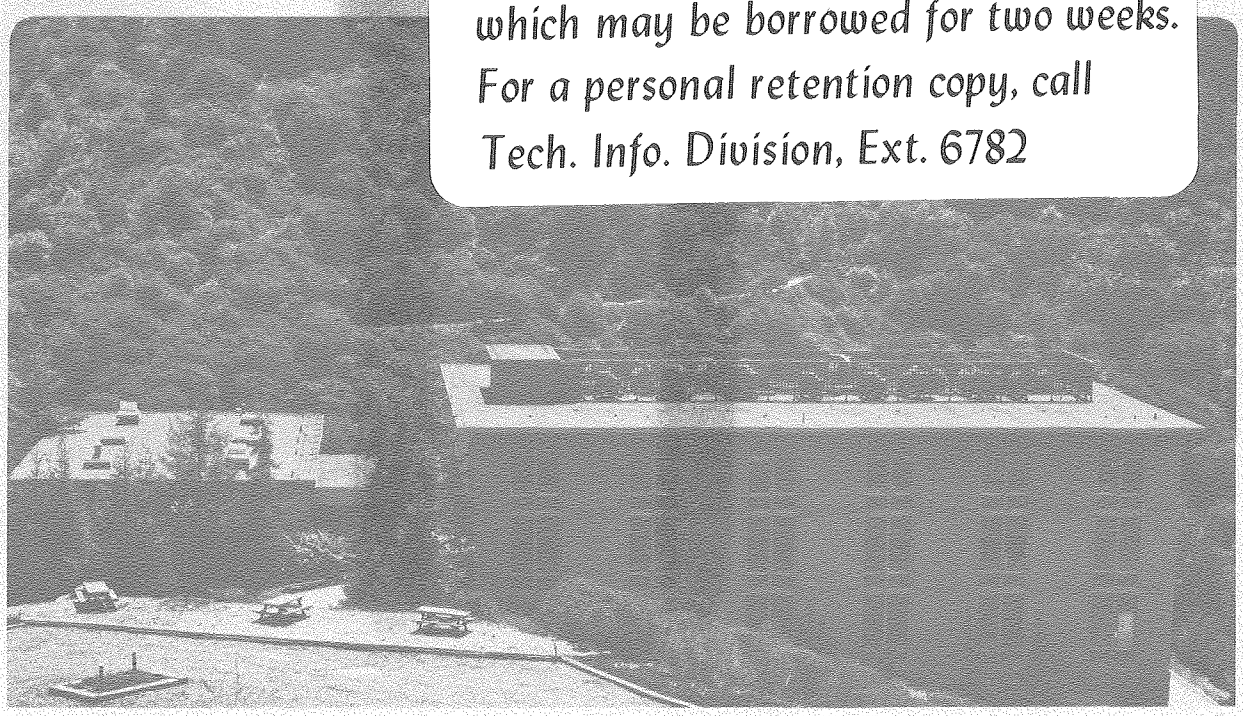

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# Mechanism of the $H + O_3$ Reaction

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## Abstract

The $H + O_3$ reaction has played an important role in the evolution of modern chemical kinetics. Here certain aspects of the $HO_3$ potential energy hypersurface have been investigated using nonempirical molecular electronic structure theory. For the qualitative purposes of the present study, most wave functions were of the self-consistent-field (SCF) variety, constructed from a double zeta basis set of contracted gaussian functions. Two low energy pathways were established for the reaction. The first involves a coplanar transition state with a nearly linear H-O-O arrangement. The second possible mechanism allows the hydrogen atom to descend perpendicularly upon the ozone molecule. The two mechanisms are evaluated in light of the current experimental understanding of the $H + O_3$ reaction.

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## Introduction

Studies of the near infrared spectra of night-day radiation[1-3] led Bates, Nicolet,[2] Meinel[3] and Herzberg[4] to attribute their origin to the radiation of vibrationally excited hydroxyl radicals in the $^2\Pi$ ground state. It was further suggested by Herzberg that these radicals were a product of the reaction of atomic hydrogen with ozone.[4,5]

$$H + O_3 \rightarrow OH^{\dagger} + O_2 \qquad \Delta G = -77 \text{ kcal/mole} \quad (1)$$

This explanation was verified when McKinley, Garvin and Boudart[6] were able to reproduce these Meinel bands in the laboratory by mixing H atoms with ozone. Since then, reaction (1) has been carefully studied by kineticists.[7-18] There have been several determinations of its rate constant[11,15-17] and various estimates of the energy partitioning in the products.[10,12-14] The most recent experimental value for the rate constant was 2.79 (±0.18) × $10^{-11}$ $cm^{-3}$ $molecule^{-1}$ $sec^{-1}$,[17] and the Arrhenius activation energy was found to be approximately 1 kcal/mole.[15-17]

From the mechanistic perspective, the research of Polanyi and co-workers,[12-14] using the "arrested relaxation" variant of the infrared chemiluminescence method, is the most informative. They found that the large exothermicity of (1) was primarily channeled (90%) into vibrational activation of the OH product, only ∿ 3% into OH rotation, and 7% into translation and internal energy of $O_2$. Due to the extreme inversion of the vibrational distribution in the $OH^{\dagger}$ product, only the highest accessible state ($v'=9$) showed sufficient emission intensity for reliable analysis. In essence, this means that for the $H + O_3$ reaction, energy release is converted into vibration in the new bond with a higher efficiency than for any other reaction analysed in this manner to date.

Polanyi and Sloan[14] then compared their $H + O_3$ experimental results with classical trajectory studies on a London-Eyring-Polanyi-Sato (LEPS)[19,20] potential surfaces for model <u>triatomic</u> systems of the type light-atom plus heavy-diatom (abbreviated $L + H\,H$). The underlying assumption behind this tetra-atomic/triatomic analogy was that since the fraction of internal energy

taken up by $O_2$ ($f_I''$) was very small (< 7%), it could be reasonably approximated by a single heavy atom. They concluded that the potential energy hypersurface of this reaction was a strongly attractive one. Moreover, they also discovered that the ratios of rotational energy ($f'_R$) to vibrational energy ($f'_v$) in OH was much smaller than the usual ratio found in the products of their LEPS model surfaces. This led them to suggest that the potential energy surface favors collinearity of the HOO approach and is restricted to a narrow range of impact parameters. Lee, Michael, Payne and Stief[16] have also studied this reaction and were in agreement with that conclusion, adding that the collinear approach should be even more enhanced if their measured activation energy (0.892 ± 0.115 kcal/mole) could be associated with a barrier on the surface.

To date the only specific theoretical study of the $H + O_3$ system is that of Blint and Newton.[21] Using a 4-31G basis, they optimized the SCF structure of $HO_3$, and found a local minimum when the hydrogen sat approximately one Å above one of the terminal oxygens of a somewhat distorted ozone. This structure was about 15 kcal/mole unstable with

respect to $O_2$ + OH and since the reaction is extremely exothermic they did not consider it to be a viable intermediate for this reaction. It is also clear from the energetics that this structure corresponds to a point on the hypersurface that is already past the transition state.

A study of a related reaction is that of Farantos and Murrell[22] for

$$C\ell + O_3 \rightarrow C\ell O + O_2 \qquad (2)$$

They derived an explicit functional form for the ground state potential energy surface of $C\ell O_3$, using the six interatomic distances as variables. In this way Farantos and Murrell[22] (MF) initially predicted a minimum energy pathway with a small barrier (∿ 7 kcal) for collinear approach along one OO bond, maintaining an OOO angle of 117°. However kinetic studies of reaction (2) indicate a lower barrier, and accordingly, MF utilized a four-body term to reduce the barrier to 0.3 kcal. Classical trajectory studies on this final surface then yielded good agreement with experimental rate constants. Finally,

Murrell[23] has suggested that the $HO_3$ potential energy surface might be similar to that for $C\ell O_3$ with the qualification that a stable $C_{3v}$ structure is not expected for the former.

With the above background in mind, it was decided to pursue *ab initio* theoretical studies of the $HO_3$ potential energy surface. The primary goal was to check and characterize the transition state, presumed to lie early in the collinear approach. In particular, we wished to ascertain whether the surface was attractive and if the transition state was collinear. It was expected that the $H + O_3$ surface might be quite similar to that for the $H + F_2$ reaction[24] in the sense that electron correlation in the latter case was shown to significantly flatten the very repulsive self-consistent-field (SCF) potential surface. Therefore, in the present $HO_3$ study, configuration interaction (CI) wavefunctions could be later determined at a number of critical points, to lessen the possibility of erroneous conclusions based upon the SCF surface(s).

## Theoretical Method

The basis set used in all calculations consisted of the Dunning-Huzinaga[25] 9s5p set of primitive Gaussians contracted to 4s2p on the oxygen atoms and the comparable 4s set of primitives contracted to 2s for the hydrogen. This basis is of double zeta (DZ) quality and expected to provide a moderately good description of the limiting species on the surface, while retaining some flexibility to adjust to changes in bonding in the intermediate regions. A more adequate basis would require diffuse and/or Rydberg functions to describe long range interactions leading up to the region of the transition state; and polarization functions to provide improved flexibility for uniformity in the description of the various states with notably different character.

The inadequacies of the Hartree-Fock (HF) single determinant description of the ozone molecule have been previously noted by Hay and Dunning.[26] For example the $^3B_2$ state is erroneously placed 3 eV below the $^1A_1$ ground state, and (even with a DZ plus polarization basis set) $O_3$ is

unbound relative to three $O(^3P)$ atoms.[27] Nevertheless Hay and Dunning[26] also found that the HF optimized structure of $O_3$ by Blint and Newton[21] showed much better agreement with the experimental structure than their configuratio interaction (CI) results. Since the aim of this study was basically qualitative, it was felt that single-determinant SCF calculations would suffice for an exploratory attack on the problem.

## Coplanar Approaches

Before considering the in-plane approaches it was considered prudent to check that the reactants in their ground state do indeed correlate with the products. When all four atoms are constrained within a plane, the reactants $O_3(^1A_1)$ and $H(^2S)$ will resolve to a single $^2A'$ state, while the products $O_2(^3\Sigma_g^-)$ and $OH(^2\Pi)$ can form the $^4A' + {}^4A''$ and the $^2A' + {}^2A''$ states. The quartet states should be spin inaccessible to the reactants as long as spin-orbit couplings are weak, so they can be ignored. Of the remaining doublets, only the $^2A'$ is accessible as the hydrogen approaches in the plane of ozone.

A. Frozen Ozone Approximation--Collinear Approach

As noted above, reaction (1) is highly exothermic. Therefore it is expected that if Hammond's postulate is valid,[28] then the transition state should be "early" and will strongly resemble the reactants. Hence "freezing" the ozone in its equilibrium geometry whilst the reactants are being brought together should be a reasonable approximation when searching for the transition state.[29] Furthermore because hydrogen is relatively much lighter than oxygen, this approximation should also be dynamically reasonable. The preliminary excursions into the full six dimensional hypersurface of $HO_3$ were carried out with the fixed ozone geometry of O-O bond lengths 1.28 Å and OOO angle of 116.8°. Relative to the ozone, the position of hydrogen was described by the O-H bond length, the OOH angle ($\theta$) and the OOOH dihedral angle ($\alpha$). (See Figure 1.)

The changing energy as hydrogen was brought in collinearly towards O(3) of the frozen ozone is shown in Figure 2 where zero on the energy scale corresponds to the energy of $O_3$ and H at infinite separation (this energy is -224.70471 Hartrees). Contrary to our expectations,

the energy of the $^2A'$ state rises monotonically without a trace of a turning point[30] even when the OH distance is reduced to 0.8 Å. From this it would be inappropriate to conclude that the transition state is not collinear, but one can safely say that if it is, then the surface is unlikely to be an attractive one. An attractive surface[31] should release a major part of the reaction exothermicity as the reactants are brought together, and so far we have not seen any sign of release.

The electronic configuration of this state is:

$$\ldots\ 4a'^2\ 5a'^2\ 6a'^2\ 7a'^2\ 8a'^2\ 1a''^2\ 9a'^2\ 10a'^2\ 2a''^2\ 11a' \qquad (2)$$

and we shall refer to this configuration as the $^2A'$ $(4\pi)$ state, since there are four electrons in orbitals which are antisymmetric with respect to the plane of symmetry. The reason for discussing the electronic configuration is because an excited state was found which started out higher in energy at large OH distances, but gradually become more stable than the $4\pi$ as the hydrogen drew closer. The crossing point (see Figure 2) takes place at r(OH) $\simeq$ 1.55 Å and E $\approx$ 18 Kcal/mole.

This state was generated by promoting one electron from the singly-occupied symmetric orbital into the lowest unoccupied antisymmetric orbital, and its electronic configuration is:

$$\ldots\ 4a'^2\ 5a'^2\ 6a'^2\ 7a'^2\ 8a'^2\ 1a''^2\ 9a'^2\ 10a'^2\ 2a''^2\ 3a'' \qquad (3)$$

Since there are now 5 electrons in antisymmetric orbitals, we shall refer to this configuration as $^2A''$ ($5\pi$). The behavior of the energy of this state is what one would expect of an attractive surface, but as mentioned in the previous section, it is symmetry inaccessible from the ground state reactants when they are co-planar.

The electronic configurations of these states also enable us to understand the general shape of their energy curves in Figure 2. Molecular orbital 11a' is basically just the 1s on hydrogen, so the $4\pi$ state corresponds to the covalent interaction of two neutral species. Hence it is not surprising that its energy should be unchanged until the overlaps between the frontier orbitals have built up significantly (at around 2 Å). A drastically simplified way of viewing the $5\pi$ state is that it corresponds to $O_3^- + H^+$, and so should show evidence of the long range electrostatic ($\frac{1}{R}$) attraction. The

single-determinant SCF description of this state is expected to be poor at large OH separation, and thus relatively little confidence should be placed on the Mulliken charge variations from our calculations.

B. Frozen Ozone Approximation--Non-Collinear Approaches

The coplanar variations of the $4\pi$ and $5\pi$ potential energies as a function of OOH angle $\theta$ were studied next at 3 different r(OH) distances [r(OH) = 1.6, 1.8, 2.0 Å] and the results are illustrated in Figure 3. There it is clear that the $4\pi$ surface is destabilized whether $\theta$ increases or decreases from around 180°; so there is even less likelihood of finding a coplanar and attractive pathway to the product away from collinearity.

A rationalization of the angular behavior of the $4\pi$ and $5\pi$ surfaces (also plotted in Figure 3) is not difficult to obtain if one looks at the frontier orbitals of ozone.[32] The in-plane HOMO 10a' (Figure 4a) and LUMO 11a' (Figure 4b) are displayed in Figure 4 with an angular scale superimposed to suggest the range swept out by the hydrogen as $\theta$ varies from 90° to 270°.

On the 4π surface, the incoming hydrogen atom with its half-filled 1s orbital will seek to maximize overlap with the LUMO and minimize overlap with the HOMO, because interaction with the former is a filled/unfilled interaction while the latter is a filled/partially-filled interaction. Though the latter may not be as unfavorable as a two orbital, four electron interaction, it is still repulsive (see Figure 2) in this case. Only at $\theta \sim 180°$ when the hydrogen 1s lies on the node of the HOMO and faces an outwardly directed lobe of the LUMO are both above-mentioned tendencies satisfied, and this is why the bottom of the 4π valley is situated around that angle.

Now consider the 5π surface, where that electron in the 1s orbital has been promoted into a π orbital on ozone. The in-plane HOMO of ozone is still 10a' but the LUMO with which it interacts is now the hydrogen 1s, so of course the angular trends are now the converse of the previous case.

In fact, from a visual comparison of the relative HOMO/LUMO

overlap when the hydrogen is cis versus the overlap when it is trans, one can also explain the asymmetry of the potential curves in Figure 3. However the frontier orbitals can only facilitate qualitative understanding of the shapes of potential curves--a more detailed analysis will require examination of the role of other orbitals as well.

C. Fully Optimized In-Plane Approach

Having found no trace of exothermicity in all of the frozen reactant coplanar approaches, it was decided to allow the ozone to relax within the plane to check whether there is any low energy pathway on the $^2A'$ surface that could lead to the products. In order to locate this constrained co-planar saddle point, it was assumed that the O(1)-O(3) and O(3)-H bond lengths were the crucial components of the reaction coordinate. A grid of points generated by the independent variation of O(1)-O(3) and O(3)-H distances was generated.[33] It indicated the presence of a saddle point separating the reactants from products, justifying the simplifying assumption made above. It also revealed that at short O(3)-H distances (around 1 Å), the energy drops rapidly only when the O(1)-O(3) bond is stretched.

In other words, the surface would appear to be repulsive.[31] However if the O(1)-O(3) is first stretched to 1.8 Å, then contraction of O(3)-H distance is accompanied by a drop in energy. Taking the saddle point on the grid as a starting guess, we proceeded to optimize the coplanar structure with the aid of open shell analytic gradient techniques.[34] This approach obtains directly the forces acting on the internal coordinates of a molecule. After six sets of these forces were determined in the neighborhood of the saddle, they were fit to a quadratic surface[35] which was used to provide an improved guess of the saddle geometry. The forces at this new point were then included in the fit and the whole process was iterated until all forces were less than 0.001 mdynes.

The result, illustrated in Figure 5 appears to be "intermediate" rather than "early" as both the O(1)-O(3) and O(3)-H distances are rather long. Collinearity is essentially preserved while the O(1)-O(2) bond is reduced, in anticipation of the dioxygen product. The energy at this saddle point is -224.693304 Hartrees which is

$\sim$ 7.2 Kcal/mole above the infinitely separated reactants at equilibrium.[36] In view of the diminishing adequacy of the single determinant SCF representation as the O(1)-O(3) bond elongates, this energy is probably too high.[24]

## Out-of-Plane Approach

Thus far our study of the coplanar hypersurface has shown that reaction is possible on the $^2A'$ ($4\pi$) surface, but the exothermicity is released repulsively unless the ozone is vibrationally activated, so that one of the O-O bonds is stretched while the hydrogen approaches. In order to explore the topography of the hypersurface for an out-of-plane approach it was decided to calculate the energy as a function of r(OH) distance as the hydrogen descends vertically upon a terminal oxygen of the frozen ozone molecule.

### A. Frozen Ozone Approximation--Vertical Descent Upon $O_3$

The surface in this case (Figure 6) bears a resemblance to the collinear approach surface where the repulsive $^2A'(4\pi)$ state intersected

a strongly attractive $^2A''(5\pi)$ state (Figure 2). The critical difference is the loss of the plane of symmetry, as a result of which all states are permitted to mix and an avoided crossing occurs.[37] The O(3)-H distance at this point is 1.92 Å and the barrier height is ≈ 8 kcal/mole. This topographical similarity is but a manifestation of the same underlying electronic factors previously discussed. The neutral reactants approach the avoided crossing where major electronic rearrangements take place, involving the transfer of electron density from hydrogen to ozone, after which the surface becomes strongly attractive. In contrast to the coplanar approaches, the geometry at this saddle point is "early" and reactant-like, and the surface is attractive.

B. Out-of-Plane Perturbations of the Coplanar Saddle Point Geometry

In order to determine whether the planar saddle point geometry is a true transition state, further calculations of the structure shown in Figure 5 with each of the atoms successively displaced 0.002 Å out-of-plane were carried out. In all cases the energy went up, indicating that the planar geometry is a true transition state geometry.

## Discussion and Conclusion

An overall summary of the characteristics of the $HO_3$ SCF hypersurface is presented in this section with a discussion of their dynamical implications. This theoretically derived picture is then compared with the one which experimentalists have deduced from their data.

Of all the coplanar approaches of hydrogen to ozone, the collinear one is the least repulsive. It leads to a collinear transition geometry which is predicted to lie 7 kcal/mole above the separated reactants at equilibrium. Contrary to expectations based upon the large exothermicity and Hammond's postulate, the structure of the planar transition state appears to be[38] intermediate rather than early, as the O(1)-O(3) is stretched to 1.83 Å (at equilibrium the O-O bond length is 1.26 Å). This structure implies that the ozone may have to be vibrationally excited to pass through the transition state. The O(3)-H bond length of 1.79 Å is also far from its expected equilibrium value, and since the heat of reaction will most likely be released by a

combination of O(1)-O(3) expansion concurrent with O(3)-H contraction, it is expected that reactants which pass through the planar transition state will channel substantial energy into translational and rotational energy of the $O_2$ product.

If the reagents approach via a non-planar pathway such as the vertical descent upon a terminal oxygen, then reaction can also occur over a barrier of comparable height but with a geometry that resembles closely the frozen reactants. Hence translational energy alone would suffice for overcoming the barrier. Most of the reaction enthalpy is released as O(3)-H contracts to ≃ 1 Å, so energy in this case will be channeled more specifically into $E_{vib}$ of OH.

The attractive nature of the calculated potential surface is due to a crossing from the covalent to an ionic surface during which an "electron jump" takes place. This process is suggestively reminescent of the alkali-atom/halogen reactions[39] where the reaction surfaces are extremely attractive. One's sense of deja-vu is all the more intensified when one recalls that 90% of the exothermicity in those

reactions were also liberated as vibrational energy of a single bond. The electron jump may be the common factor behind all reactions involving neutral reactants that give rise to selectively excited products.

As mentioned before in the Introduction, experimentalists have compared their measured product energy distribution of $H + O_3$ with dynamical studies of triatomics on model LEPS surfaces. This tetra-atomic/triatomic analogy was drawn post-hoc when the experimental results showed that there was very little internal energy in $O_2$. From that comparison they deduced three conclusions about the hypersurface: (i) the surface is attractive, (ii) the transition state should be collinear, and (iii) only a narrow range of impact parameters will lead to reaction.

Our limited exploration of the $HO_3$ hypersurface leads us to agreement with the first conclusion, but we are faced with a dilemma with respect to the second. Although we do find a collinear transition state geometry, its "intermediate" structure

suggests a need for prior vibrational excitation of the $O_3$ and a product energy distribution that was not necessarily concentrated into the OH bond alone, which is at variance with the experimental facts. In contrast, the out-of-plane approach (not fully optimized) has a barrier structure that is more consistent with the notions of "early" reaction and of high bond specificity in the product energy.

It is worth mentioning here that the experimentally deduced picture is not without its problems too, for if the transition geometry is collinear, it is difficult to explain why the violently oscillating OH molecule does not have secondary collisions with $O_2$, thereby dissipating part of its energy into translational and rotational energy. If the transition state geometry were not collinear, then this would be less of a problem as the $O_2$ molecule could then be out of the path of the vibrating OH.

Clearly a better theoretical study of this fascinating problem is called for, especially since the reaction appears to proceed with far

less activation energy than predicted by SCF calculations.[40] A more systematic mapping (at a substantially higher level of theory) of the out-of-plane approaches would be useful for obtaining a better idea of the range of impact parameters that could lead to reaction. There is also the interesting possibility that the collinear transition state though energetically the most accessible, may be dramatically disfavored as the ozone is effectively frozen on the time scale of the light and rapid hydrogen, and cannot stretch its O-O bond sufficiently during a collisional encounter.

## Acknowledgments

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29. The alternative approach of optimizing at six degrees of freedom is of course feasible, but could leave us without any feel for the shape of the hypersurface.

30. There was however a fluctuation in the gradient around OH = 0.9 Å.

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32. Frontier orbital reference 8.

33. All other internal coordinates were fixed as before: O(1)-O(2) = 1.28 Å, ∢ OOO = 116.8° and ∢ OOH = 180°.

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36. The optimized ozone geometry is: O-O = 1.258 Å ∢ OOO = 120°. Energy of the reactants at equilibrium ($H + O_3$) is -224.7061 Hartrees. This is the only case not being compared to the ozone fixed at its experimental geometry, O-O = 1.28 Å and ∢ OOO = 116.8°.

37. Readers may be interested to know how the excited state energies were obtained, since symmetry is no longer available as an aid to prevent the calculations from collapsing to the ground state. It was found that if the eigenvectors obtained at r(OH) ≤ 1.8 Å were used for calculations with r(OH) ≤ 2.0 Å, they were sufficiently isomorphic to the excited state vectors that the calculations would converge smoothly to the excited state. The procedure could also be reversed to get the excited state at r(OH) < 1.8 Å.

38. A word of caution must be sounded here, inasmuch as the SCF approximation is known in several well-studied cases to artifically predict saddle point geometries significantly "later" than when correlation is incorporated. In the classic case of $F + H_2$ the SCF transition state is r(F-H) = 1.18 Å, r(H-H) = 0.84 Å, while the CI saddle point geometry is much different, r(F-H) = 1.54 Å, r(H-H) = 0.77 Å. See C. F. Bender, S. V. O'Neil, P. K. Pearson, and H. F. Schaefer, Science 176, 1412 (1972). The same trend is observed for $H + F_2$ in reference 24.

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40. This of course is hardly an unprecedented result. For example, for the $H + F_2$ system using a comparable DZ basis set, the SCF barrier height of 12.2 kcal is reduced to 1.0 kcal when correlation effects are taken into account. See reference 24.

## Figure Captions

Figure 1. For the H + $O_3$ system, the relative position of hydrogen is specified in terms of a bond length r(OH), the OOH $\measuredangle$ θ, and the dihedral $\measuredangle$ α. The dihedral angle is defined relative to the O(1)-O(2) bond when viewed down the O(3)-O(1) bond axis.

Figure 2. Energy of the $^2A'(4\pi)$ and $^2A''(5\pi)$ states as a function of r(OH) as hydrogen approaches the frozen ozone collinearly (θ = 180°). Zero on the energy scale is the energy of the infinitely separated reactants.

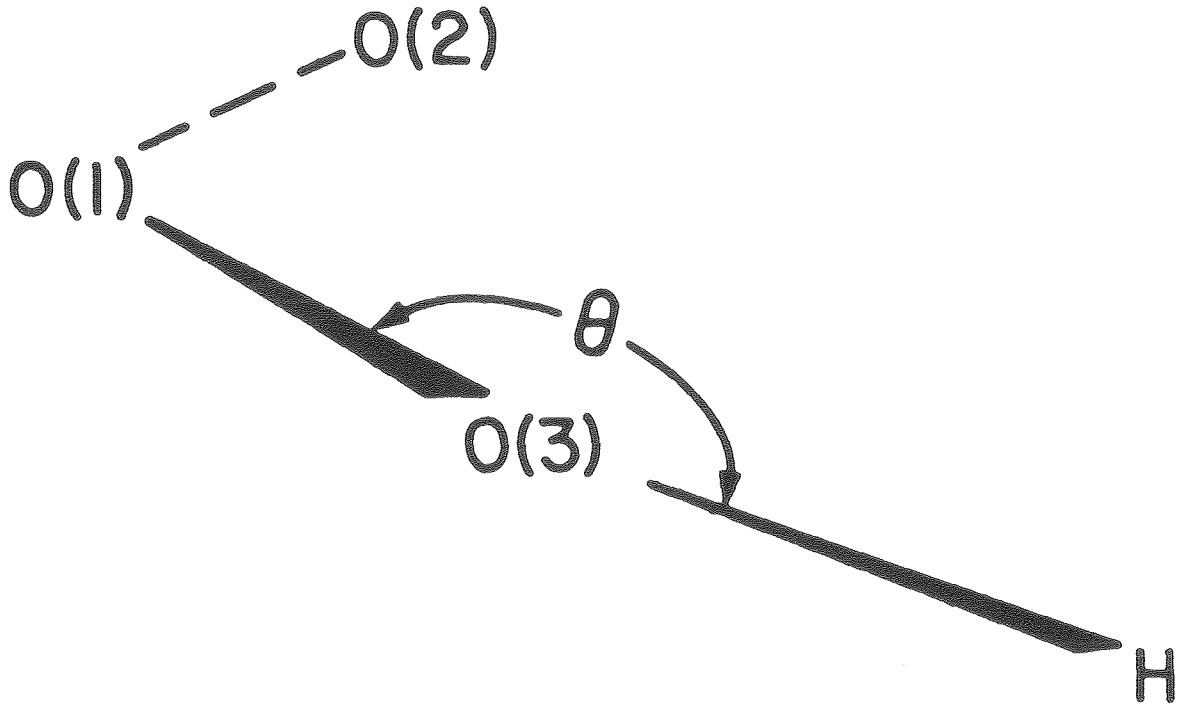
Figure 3. Energy of the $^2A'(4\pi)$ and $^2A''(5\pi)$ states as a function of θ (see Figure 1 for definition) at r(OH) = 1.6 Å, 1.8 Å and 2.0 Å. Zero is the energy of the infinitely separated reactants.

Figure 4. a) Contour map of the in-plane ozone HOMO. Scale on sides are in Angstroms and the superimposed angular scale at r(OH) = 1.6 Å shows the variation of the hydrogen position as a function of θ.

b) Contour map of the in-plane LUMO.

Figure 5. Constrained coplanar saddle point geometry for the H + $O_3$ reaction.

Figure 6. Energy as a function of r(OH) for an out-of-plane approach ($\theta$ = 90° and $\alpha$ = 99°) of H to $O_3$. Zero is the energy of the infinitely separated reactants.



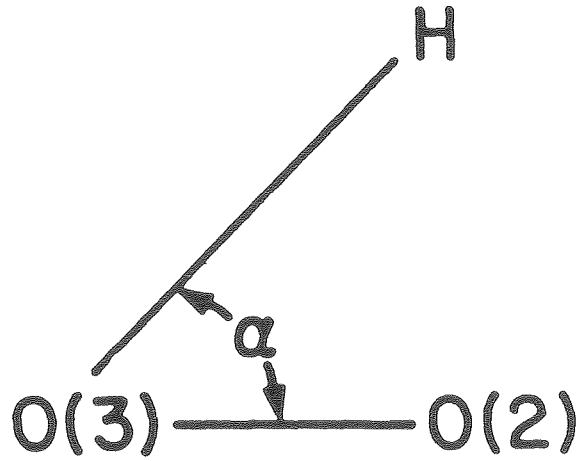




Figure 1

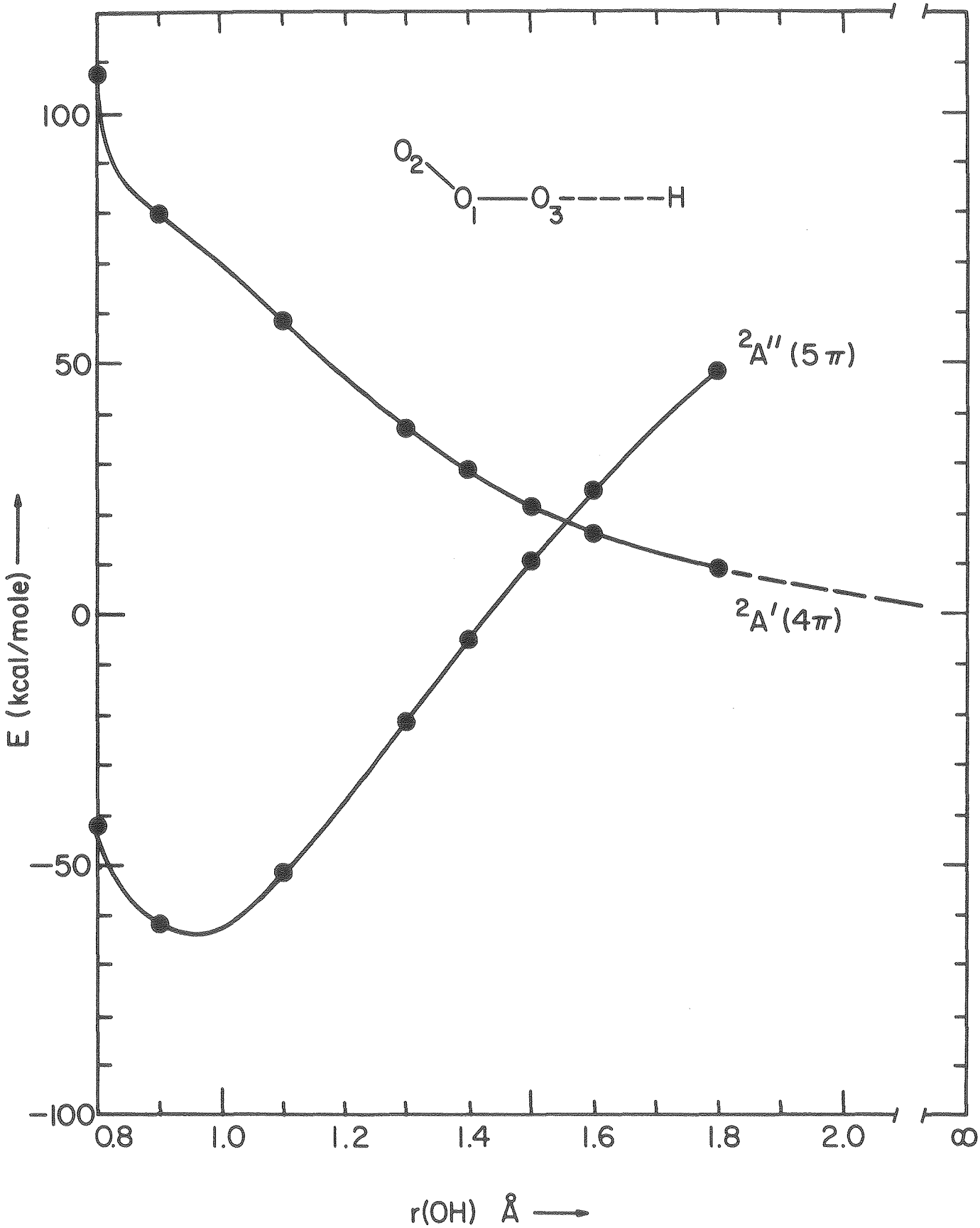

100
50
0
−50
−100
E (kcal/mole)
0.8
1.0
1.2
1.4
1.6
1.8
2.0
∞
r(OH) Å
$O_2$
$O_1$
$O_3$
H
$^2A''$ (5π)
$^2A'$ (4π)

Figure 2

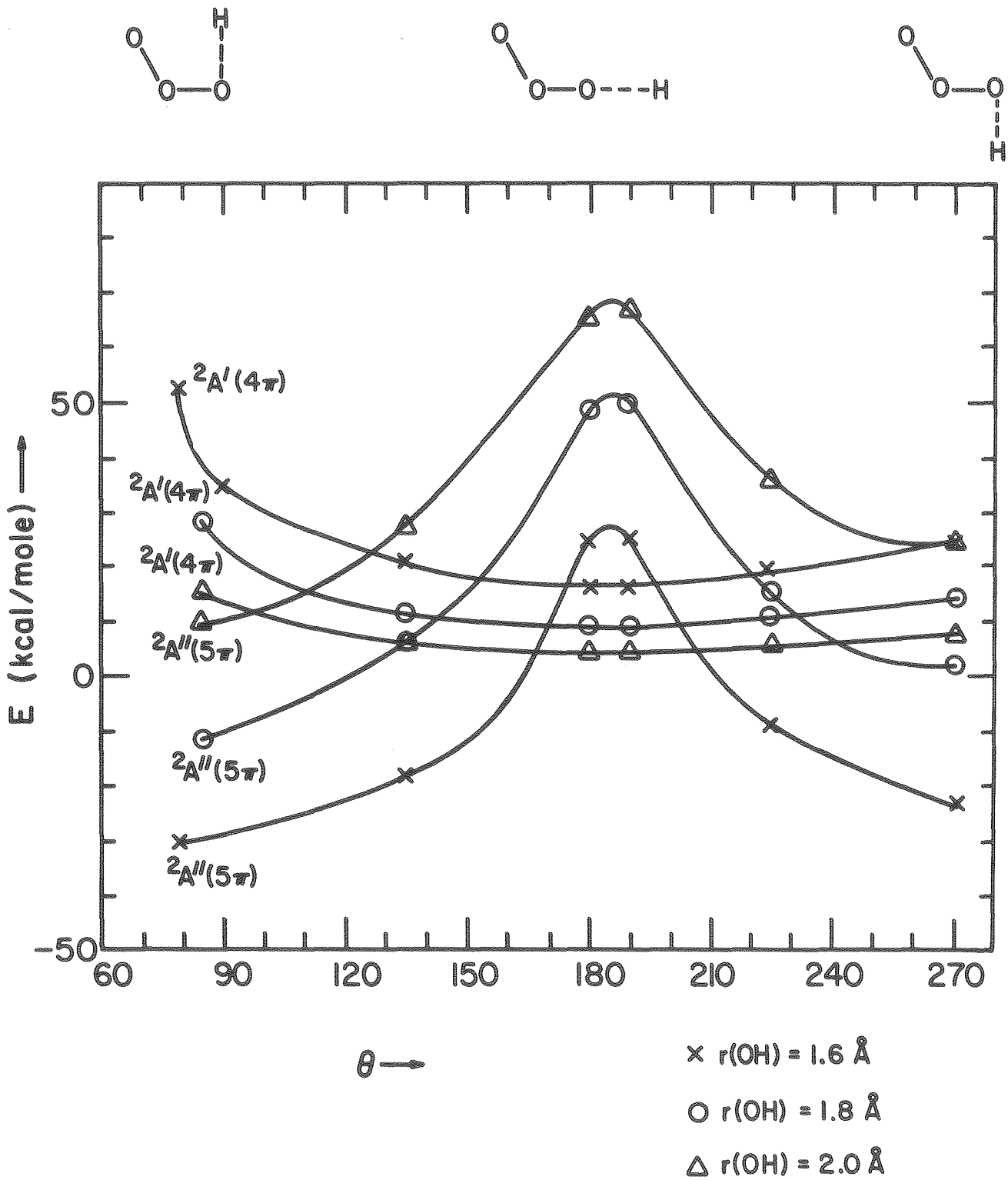

O
H
O—O
O
O—O---H
O
O—O
H
50
0
-50
E (kcal/mole)
$^2A'(4\pi)$
$^2A'(4\pi)$
$^2A'(4\pi)$
$^2A''(5\pi)$
$^2A''(5\pi)$
$^2A''(5\pi)$
60
90
120
150
180
210
240
270
θ
× r(OH) = 1.6 Å
○ r(OH) = 1.8 Å
△ r(OH) = 2.0 Å

Figure 3

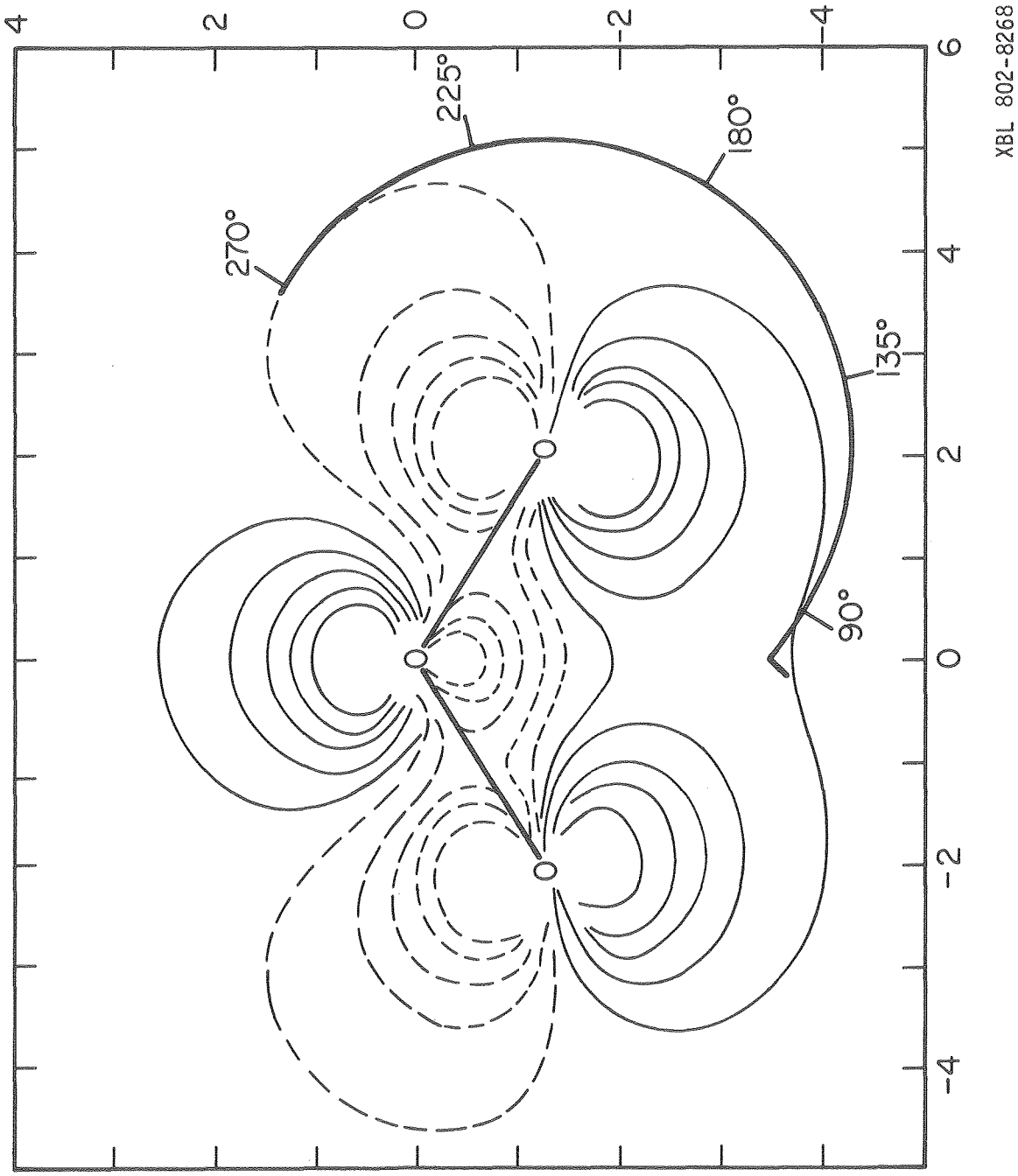



Figure 4 a

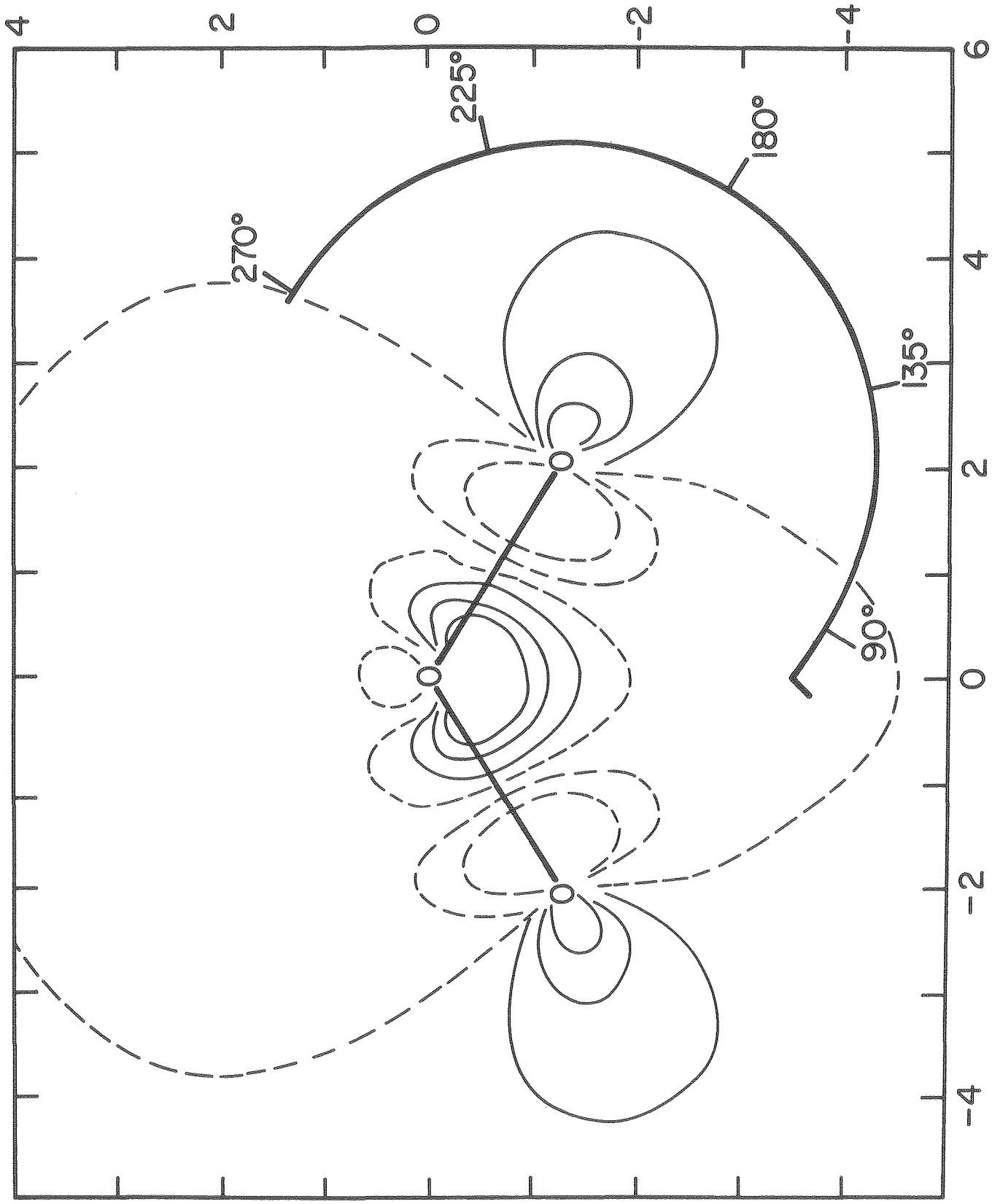



Figure 4 b

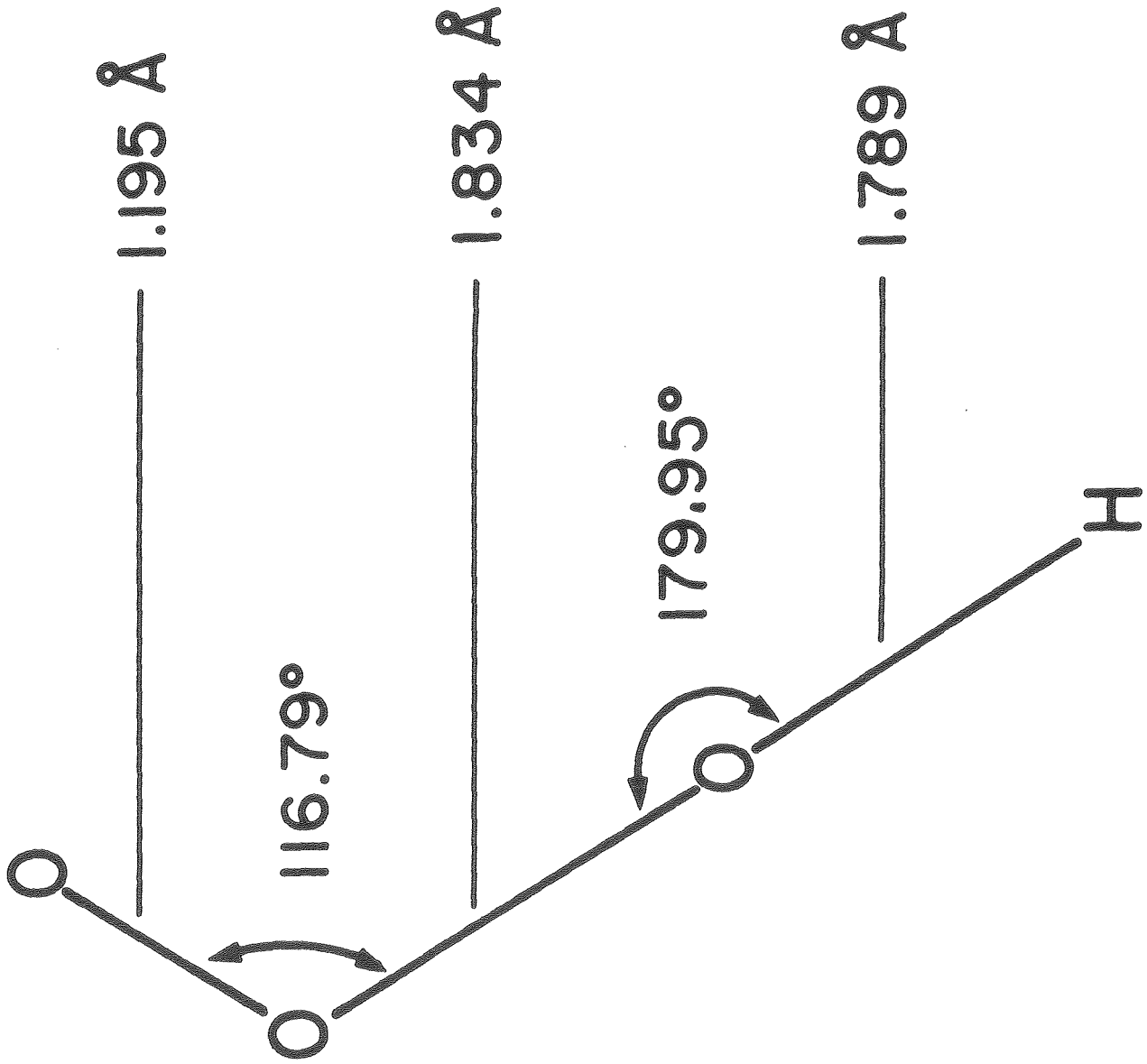



Figure 5

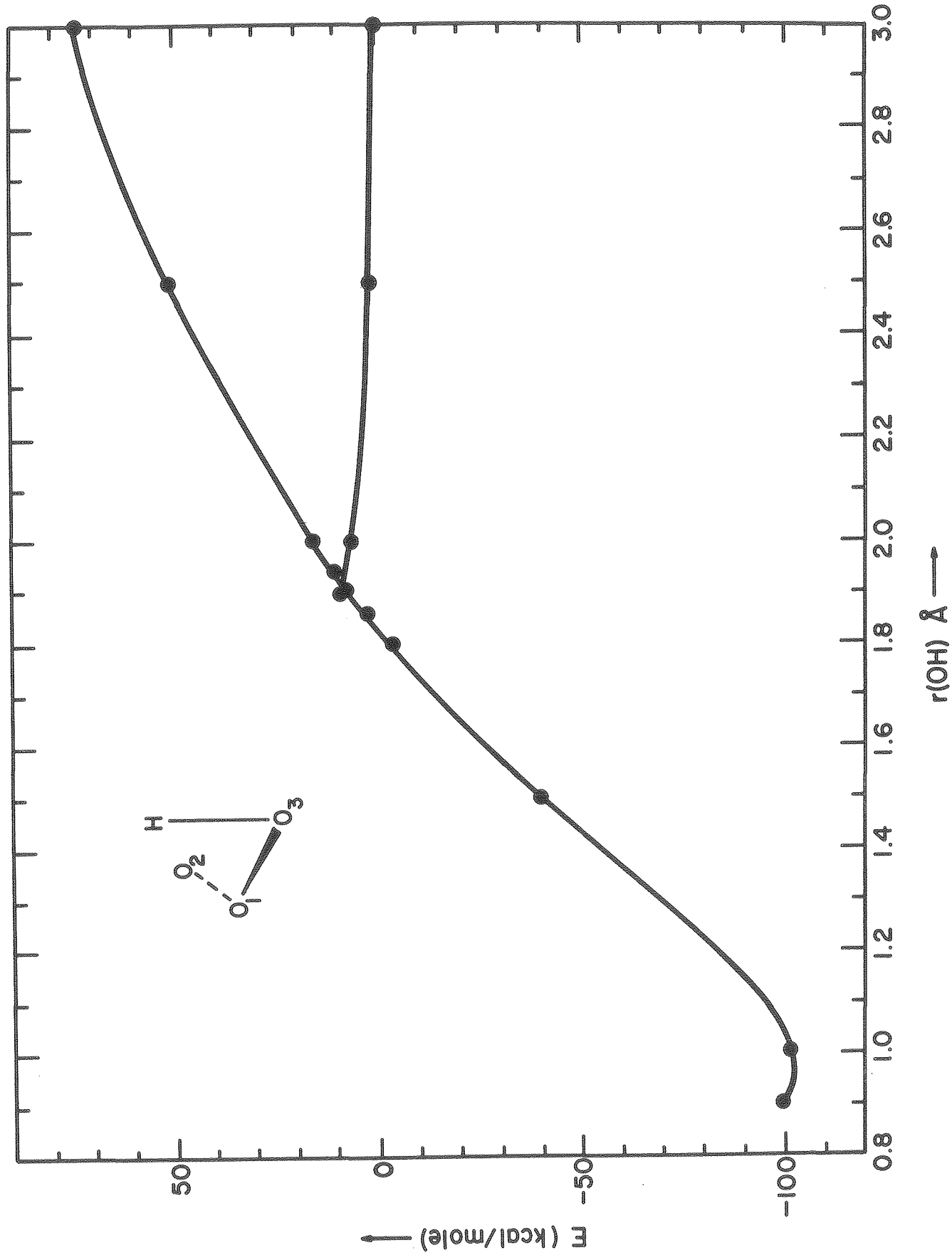

50
0
-50
-100
E (kcal/mole)
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
r(OH) Å
H
$O_3$
$O_2$
$O_1$

Figure 6