APPENDIX 1

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Extended Active Space CASSCF/MRSD CI Calculations of the Barrier Height for the Reaction: $O + H_2 \rightarrow OH + H$

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Abstract

The convergence of the barrier height for the $O + H_2 \rightarrow OH + H$ reaction has been studied as a function of the size of the active space and basis set completeness. The barrier height is rapidly convergent with respect to expansion of the active space. Addition of $2p \rightarrow 2p'$ correlation terms to the active space lowers the barrier to the $O + H_2$ reaction by about 2.0 kcal/mole, but addition of 3d and other terms has little additional effect. Multireference singles and doubles contracted CI plus Davidson's correction calculations using a [5s5p3d2f1g/4s3p2d1f] basis set with a $5\sigma 2\pi$ active space lead to a barrier height of 12.7 kcal/mole. Including an estimate of the CI contraction error and basis set superposition error leads to 12.4 kcal/mole as the best estimate of the barrier height.

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I. Introduction

The national aerospace plane(NASP) will be an air breathing hypersonic flight vehicle capable of achieving velocities as high as Mach 25.0. It will utilize supersonic combustion ramjet(scramjet) engines and burn hydrogen for fuel. The high flow velocities introduce design difficulties, since the flame propagation speed may not be as large as the flow velocity i.e. the flame may blow out. This has resulted in considerable interest in the kinetics of reactions involving H, O, and N. Recently a research program has been started to compute from first principles the rates of selected reactions important in SCRAM jets. The computation of the rate of these reactions first entails the computation of the potential energy surfaces for the reactions of interest.

In order to assess the accuracy of potential energy surfaces involving oxygen, a systematic study was carried out of the convergence of the barrier height for the $O + H_2 \rightarrow OH + H$ reaction as a function of both the size of the active space in the CASSCF calculation and the size of the basis set. This reaction was selected for study since a number of dynamics studies[1-4] have been carried out based on the POL-CI surface of Walch et al.[5]. The agreement between the computed and the experimental thermal rate constants establish that the barrier height of 12.5 kcal/mole from the POL-CI surface is accurate to better than 1.0 kcal/mole. We also note here that a similar study by Howard et al.[6] using a first order CI iterative natural orbital procedure led to a barrier height of 14.0 kcal/mole.

Although the POL-CI barrier height is believed to be quite accurate, the computed endoergicity(ΔE_{rx}) on the other hand is -0.1 kcal/mole compared to an experimental value of +2.9 kcal/mole. Thus, one has to assume that the good result for the computed barrier height is somewhat fortuitous. As discussed in Section III., attempts to improve upon the POL-CI result by using multireference singles

and doubles CI methods (MRSD CI) lead to a barrier of 16.0 kcal/mole using the same three reference configurations and a comparable basis set to that used in the POL-CI study. Similarly, for the F + H_2 reaction a first order CI calculation by Bender and coworkers[7] gave a barrier height of 1.66 kcal/mole, but more recent calculations using MRSD CI and perturbation theory methods have lead to barriers greater than 3.2 kcal/mole even when very large basis sets are used[8].

In the present paper we examine the source of the differences between the POL-CI and MRSD-CI calculations. For both of these reactions, ionic terms are expected to be important in the saddle point and products regions but not in the reactants region. Thus, the problem of describing the barrier height for these reactions is closely related to the problem of dscribing the electron affinity of the O and F atoms. Botch and Dunning[9] found that 2p→2p′ terms were important in describing the O and F atom electron affinities. For example, with the largest basis set used in the present studies, the computed electron affinity for O is 1.27 eV for a MRSD-CI calculation based on a CASSCF including 2p → 2p′ correlation. This number may be compared to 1.46 eV for experiment[10] and 1.04 eV for SCF plus singles and doubles CI with a very large basis set[11]. Thus, it is seen that 2p → 2p′ correlation is very important in describing the electron affinity of O atom, and these terms were added to the active space in these calculations.

Section II describes the basis sets and the computational approach. Section III presents the results of calculations using an expanded active space and extended basis sets, while the conclusions are presented in Section IV.

II. Computational Details.

Table I gives the O basis sets which were used in this study. The O sp basis set is a [5s3p] segmented contraction of the van Duijneveldt (11s6p) primitive set[12]. The inner nine primitive functions were contracted (63) based on the 1s orbital, while

the outer five s functions were contracted (311) based on the 2s orbital. (Note that this contraction uses three functions twice.) In order to describe O^- character, the basis set was augmented by a single set of 2p functions with the exponent selected using an even tempered criterion leading to a [5s4p] sp basis set. The polarization function basis sets were developed from the gaussian fits to Slater type orbitals given by Stewart[13]. In each case the effective Slater exponent was optimized at the CI level using a two term GTO fit[13] to a Slater. The exponent for the O3d function was optimized at the CI level for the ground state of the O atom, while the exponents for the O4f and O5g were optimized at the CI level for the OH molecule.

The H basis set is given in Table II. The hydrogen s basis set used the van Duijneveldt 6s set[12] contracted to [3s] plus one diffuse function selected in an even tempered fashion. The [2p] basis set was selected as a four term fit[13] to a 2p STO with exponent of 1.0. This primitive basis was contracted (211) and the most diffuse function was discarded leading to a [4s2p] basis set, which was used for the smallest basis set for O + H_2. The scale factor of the H p function was subsequently optimized at the SDCI level for H_2 using a [4s1p] basis set. This lead to an effective 2p Slater exponent of 1.84. The [4p] basis was generated from this Slater exponent as a 211 contraction of a 4 term STO[13] plus one diffuse 2p function selected by an even tempered criterion. A [3p] set was also used which consisted of the [4p] set minus the most diffuse exponent. The 3d and 4f exponents used here were optimized at the CI level for OH. From these s, p, d, and f basis functions five different basis sets were generated: [4s2p], [4s3p1d], [4s4p1d], [4s4p2d], and [4s4p2d1f].

During the course of this work, Almlöf and Taylor implemented a new version of the molecule integral program which permits general contractions. These authors also developed basis sets for use with this program in which the occupied and virtual orbitals are generally contracted based on the natural orbitals

from an atomic CI calculation[14]. These basis sets are optimal for describing the atomic correlation and thus have very small basis set superposition errors. In addition the basis sets are found to be sufficiently flexible to be used in molecular calculations at both the SCF and CI level. In the present studies a (13s9p6d4f2g/8s6p4d3f)/[5s5p3d2f1g/4s3p2d1f] basis set[14] was used. Here the fifth O2p function was a diffuse function to describe O^- character. This last function was selected using an even tempered criterion. This basis set is referred to as the atomic natural orbital (ANO) basis set.

Most of the calculations were carried out on the CRAY XMP-48 with the MOLECULE[15]-SWEDEN[16] system of programs. Some of the basis set tests were carried out on the Cyber-205 using the Karlsruhe adaptation[17] of the COLUMBUS[18] codes. These calculations used the Coupled Pair Functional(CPF) method of Ahlrichs[19].

Since the CI calculations reported here use a limited set of reference configurations, the CI energy is not invariant to a unitary transformation of the CASSSCF orbitals among themselves. The CASSCF active orbitals are uniquely defined by a natural orbital transformation of the converged active orbitals, followed by a CASSCF CI in the natural orbital basis to define the important reference configurations.

Most of the CI calculations presented here were uncontracted; however, some calculations were carried out with the externally contracted CI of Siegbahn[20]. Calculations which use the contracted CI are denoted by CCI while the uncontracted calculations are denoted by CI. In all cases the multireference analog of Davidson's correction[21] was computed and results are reported both with and without Davidson's correction. The correction used in the CCI is $\Delta E\ (1 - C_0^2)/C_0^2$ which differs slightly from the original Davidson's correction, used in the uncontracted CI, which

is $\Delta E\ (1 - C_0^2)$, where ΔE is the CI energy minus the reference energy and C_0^2 is the square of the coefficient of the reference configuration or the sum of the squares of the coefficients of the reference configurations in the multireference case. The results where Davidson's correction has been applied are denoted by CI + Q or CCI + Q for the uncontracted and contracted CI, respectively. All of the calculations were performed for collinear geometries using C_{2v} symmetry.

III. Discussion.

For collinear geometries, the SCF configuration of the reactants O + H_2 on the $^3\Pi$ surface is:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi_x^2 1\pi_y^1 \tag{1}$$

Here 1σ and 2σ are O1s and O2s like orbitals. The 3σ orbital is the H_2 bonding orbital ($1\sigma_g$) and the 4σ and 1π orbitals are the O2p orbitals. As described elsewhere[5], the 3σ and 4σ orbitals map into the OHσ bonding orbital and a H1s orbital for the products. In order to describe the spin recoupling process it is necessary to also include the configurations.

$$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 5\sigma^1 1\pi_x^2 1\pi_y^1 \tag{2}$$

$$1\sigma^2 2\sigma^2 4\sigma^1 5\sigma^2 1\pi_x^2 1\pi_y^1 \tag{3}$$

where the 5σ orbital corresponds to the $H_2 1\sigma_u$ orbital. The three configurations above were the reference configurations in the POL-CI calculations of Walch et al.[5].

Table III shows the calculated barrier height and endoergicity obtained using CASSCF orbitals for a $3\sigma 1\pi$ active space and a CCI with eqn. 1-3 as reference configurations ([5s4p2d1f/4s2p] basis set). Looking first at the results correlating eight electrons, it is seen that the computed barrier height and endoergicity are both

too large. Since the saddle point and products regions both contain an O^- term that is not present for reactants, this problem is probably related to the difficulty in calculating the electron affinity of O atom at the SCF level. For both saddle point and products regions, quadruple excitations, which arise as products of correlation terms needed to describe the transfer of the H_2 bond pair and correlation terms for describing O^- character, are important. These terms may be somewhat less important for the products region, since the bond pair has relocalized. As will be seen later, this hypothesis is supported by the lowering of the barrier height when these higher excitations are explicitly included by expanding the reference space in the expanded active space CI calculations.

From Table III it is also seen that, at this level of calculation, a better endoergicity is obtained if the O2s electrons are not correlated. This is in accord with calculated D_e's for the O_2 molecule where better results are obtained, when the O2s electrons are inactive in the CASSCF calculation, if the O2s levels are not correlated in the CI calculation[22]. As will be seen later, with larger basis sets and a more complete correlation treatment, the eight electron endoergicicity is in better agreement with the experimental value. For the [5s4p2d1f/4s2p] basis set, the calculated barrier height is the same at the CI + Q level whether six electrons or eight electrons are correlated. Thus, the calculations to determine the size of the active space, which used this basis set, were carried out with only six electrons correlated.

Since O^--like terms are expected to be important in the saddle point region, the CASSCF active space was expanded to include the most important of these terms. In the present studies the active space was expanded by addition of the O2p′ natural orbitals, where the 2p′ is a tight-diffuse correlating orbital (i.e. it has an extra radial node like a 3p orbital but is of the same radial extent as a 2p orbital), the O3d natural orbitals, and the H_2 $2\sigma_g$ and $1\pi_u$ natural orbitals, where

the orbital notation refers to the reactant geometry. For the σ orbitals, the order of these natural orbitals (in order of decreasing natural orbital occupation numbers) is the same for both the reactants and saddle point geometries:

$H_2 1\sigma_g > O2p\sigma > H_2 1\sigma_u > H_2 2\sigma_g > O2p\sigma' > O3d$

For the π orbitals on the other hand the order is different for reactants and saddle point geometries. The order for reactants is:

$O2p\pi > O2p\pi' > H_2 1\pi_u > O3d$

while for the saddle point region the order is:

$O2p\pi > O2p\pi' > O3d > H_2 1\pi_u$

From the above one sees that in order to include the O2p$'$ shell consistently it is necessary to use a $5\sigma 2\pi$ active space. To consistently add the O3d shell would require a $6\sigma 4\pi 1\delta$ active space.

The effect of adding additional active orbitals was tested at the CCI level by systematically expanding the CASSCF active space while adding corresponding reference configurations. The smallest active space is $3\sigma 1\pi$ which corresponds to the configurations given in eqn. 1-3. The $4\sigma 2\pi$ active space adds the O2pσ' and O2pπ' orbitals. The $5\sigma 3\pi$ active space adds the H_2 $2\sigma_g$ like and O3dπ like natural orbitals. Finally, the $6\sigma 3\pi$ active space had the same π space as the $5\sigma 3\pi$ case, but the 3dσ like natural orbital was added to the σ active space.

The reference configurations for the MRSD CCI calculations included 1-3 and added 4-7.

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 2\pi_x^2 1\pi_y^1 \tag{4}$$

$$1\sigma^2 2\sigma^2 3\sigma^1 5\sigma^1 n\sigma^1 1\pi_x^2 1\pi_y^1 \tag{5}$$

$$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 5\sigma^1 1\pi_x^1 l\pi_x^1 1\pi_y^1 \tag{6}$$

$$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 5\sigma^1 1\pi_x^2 m\pi_y^1 \tag{7}$$

In 5-7 n runs from 6 to the total number of σ orbitals and l and m run from 2 to the total number of π orbitals. Eqn. 4 corresponds to the diagonal double 2p→2p′ excitation, while 5-7 are interpair terms between the H_2 bond pair and the 2p→2p′ excitations. This choice of reference configurations includes all configurations with CI coefficients greater than 0.05 in the CASSCF wavefunction. The barrier height was computed in each case with and without Davidson's correction[21] with the reactants limit referenced to the $6\sigma 3\pi$ reactants energy. The energy reference was chosen in this way since the reactants energy was relatively insensitive to expansion of the active space (the effect of expanding the active space is only 0.3 kcal/mole at the reactants geometry) and the resulting values of the barrier height, ΔE_b, then reflect the convergence of the total energy at the saddle point geometry.

Table IV shows the effect of expanding the active space in the CASSCF calculation. Adding the 2p′ shell has a large differential effect on the barrier height, but addition of further active orbitals has only a relatively small effect. This is consistent with the idea that configurations involving the 2p′ shell are the most important correlation terms needed to describe O^-. Based on these calculations a $5\sigma 2\pi$ active space was used in subsequent calculations to determine the saddle point properties for O + H_2. The reference configurations that were used in these calculations are given in Table V. The configurations in Table V include a diagonal double $3\sigma^2 \rightarrow 6\sigma^2$ which is the H_2 $1\sigma_g^2 \rightarrow 2\sigma_u^2$ and which was not included in the set of configurations given above. In addition, the configuration given in eqn(5) for n=6 is found to be unimportant and is omitted.

A grid of points was computed about the expected saddle point and the actual saddle point geometry was determined by fitting these data to a function of the form:

$$F(r_1, r_2) = c_0 + c_1 r_1 + c_2 r_2 + c_3 r_1 r_2 + c_4 r_1^2 + c_5 r_2^2 \qquad (8)$$

Here the saddle point was determined both for CI and CI + Q. At the reactants geometry, the H_2 distance was optimized for an O + H_2 supermolecule calculation.

Table VI shows the results of MRSD CI calculations for O + H_2 using the [5s4p2d1f/4s2p] basis set and a $5\sigma 2\pi$ active space as described above. The saddle point geometry obtained here has r_{OH} 0.01 a_0 shorter and r_{HH} 0.06 a_0 shorter than the values determined for the POL-CI calculations. The present studies also show a larger curvature in the direction along the reaction coordinate. Based on a Wigner correction[23] for tunneling, the larger curvature would indicate tunneling is more important on the CI surface than on the POL-CI surface. The barrier height obtained for the $5\sigma 2\pi$ active space is 2.1 kcal/mole lower than obtained with the $3\sigma 1\pi$ active space(see table III). This is a very significant effect strongly suggesting that O^--like terms are very important for the O + H_2 reaction.

An additional calculation was carried out at the saddle point geometry from Table VI using the $5\sigma 2\pi$ active space CASSCF but with additional reference configurations. The new reference configurations included: i) selected triple and quadruple excitations which arise as products of the diagonal double excitation $3\sigma^2 \rightarrow 5\sigma^2$ and 2p $\rightarrow$ 2p′ single and double excitations and ii) atomic interpair terms which are double 2p $\rightarrow$ 2p′ excitations. Inclusion of these addition reference configurations increases the barrier height very slightly (0.1 kcal/mole). This result indicates that the calculation is essentially converged with respect to the list of reference configurations.

Table VII shows two important effects on the barrier height for the O + H_2 reaction as a result of expanding the basis set. The first is that correlating the O2s lowers the barrier by only 0.1 kcal/mole with the [5s4p2d1f/4s2p] basis set, but by 0.5 kcal/mole for the [5s4p3d2f1g/4s3p1d] basis set. The second effect illustrated in Table VII is the importance of higher angular momentum functions for these CPF

wave functions. For the case of correlating eight electrons one sees a 1.1 kcal/mole lowering of the barrier height for the [5s4p3d2f1g/4s4p2d1f] basis set compared to the [5s4p2d1f/4s2p] basis set. For the largest basis set the CPF barrier height is 13.6 kcal/mole when eight electrons are correlated (Table VII). Correcting for the basis set superposition error leads to a CPF barrier height of 14.3 kcal/mole.

Table VIII shows the results of CCI calculations with the ANO basis set. Here it is seen that the barrier height is 14.7 kcal/mole for CCI and 12.7 kcal/mole for CCI + Q when eight electrons are correlated. For these calculations it was necessary to use the contracted CI, since the calculation involves about 1.2 million configurations (uncontracted). For the calculation with the [5s4p2d1f/4s2p] basis set and $5\sigma 2\pi$ active space the contraction error is found to be 0.5 kcal/mole when six electrons are correlated. The superposition error for the ANO basis set is calculated by the counterpoise method to be 0.15 kcal/mole when eight electrons are correlated. Combining these numbers leads to an estimate of 14.4 kcal/mole and 12.4 kcal/mole for CI and CI + Q, respectively. Since the multireference Davidson's correction may be an overestimate, we can only say with confidence that the computed barrier height is within 2.0 kcal/mole of the currently accepted value of 12.5 kcal/mole; although, the true error is probably about half that large. Table VIII also shows the computed endoergicity. Here it is seen that the error is 0.9 kcal/mole for CCI and 1.6 kcal/mole for CCI + Q. These errors are seen to be of the same order of magnitude as the estimated error in the barrier height.

Table VIII also shows the computed barrier height with respect to the OH + H products. The result for CCI + Q correlating eight electrons is 8.2 kcal/mole as compared to the experimentally derived value of 9.6 kcal/mole (the 12.5 kcal/mole barrier height minus the experimental endoergicity). This result indicates that the multireference Davidson's correction must be overshooting to some extent, since the

CCI + Q barrier height is 0.1 kcal/mole and 1.4 kcal/mole lower than "experiment" for the forward and reverse directions, respectively. It should be noted that the barrier height for the reverse reaction is not corrected for superposition error or the CCI contraction error.

A remarkable result of these studies is that the present calculations which involve more than 1.2 million configurations are finally converging toward the barrier height obtained in the POL-CI calculations which involved only a few thousand configurations. It is clear from the present studies that the POL-CI calculations, which allow only one electron outside the $3\sigma 1\pi$ active space, cannot properly describe the O^- character in the wavefunction at the saddle point geometry, since these studies show that a larger active space ($5\sigma 2\pi$) is needed for that purpose. Thus, one might have expected that the POL-CI method would result in too large a barrier height as was obtained in the CCI studies using a $3\sigma 1\pi$ active space. The POL-CI treatment neglects the angular and radial correlation of the H_2 molecule which is expected be more important for reactants than for the saddle point region. However, the neglected ionic terms are less important for the reactants than for the saddle point region. Thus, it appears that an accidental cancellation of these opposing effects acounts for the good barrier height obtained in the POL-CI. Adding additional correlation to this wavefunction by allowing single and double excitations from the POL-CI reference set leads to a higher barrier, since angular and radial correlation is easy to describe, but a larger active space and extended basis set treatment is necesssary to properly describe O^- character. It is only after inclusion of extended basis sets and active spaces that a balanced description and lower barrier height are obtained, as in the present calculation.

IV. Conclusions.

The convergence of the barrier height for the $O + H_2 \rightarrow OH + H$ reaction has

been studied as a function of the size of the active space and basis set completeness. The barrier height is found to be rapidly convergent with respect to expansion of the active space. Addition of 2p→2p′ correlation terms to the active space lowers the barrier to the O + H_2 reaction by about 2.0 kcal/mole, but addition of 3d and other terms has little additional effect. Since the saddle point region of this reaction is expected to have a significant O^- component which will not be important for the reactants, these results suggest that the difficulty in accurately computing the barrier height for the O + H_2 reaction parallels the problem of describing the electron affinity of oxygen. Multireference singles and doubles contracted CI plus Davidson's correction calculations using a [5s5p3d2f1g/4s3p2d1f] basis set with a $5\sigma 2\pi$ active space lead to a barrier height of 12.7 kcal/mole. Including an estimate of the CI contraction error and basis set superposition error leads to 12.4 kcal/mole as the best estimate of the barrier height. The latter result is in good agreement with the current estimate of 12.5 kcal/mole.

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Table I. Basis Sets for Oxygen.

O [5s4p] valence basis

function	s	p
1	31195.560(0.00021)	64.7719(0.00584)
2	4669.3800(0.00163)	14.9727(0.04058)
3	1062.2600(0.00845)	4.55440(0.15754)
4	301.42600(0.03419)	1.56370(0.35300)
5	98.515300(0.11031)	0.54107(1.00000)
6	35.460900(0.26949)	0.17776(1.00000)
7	13.617900(0.42355)	0.05840(1.00000)
8	5.3862000(0.28304)	
9	1.5387000(0.02748)	
7	13.617900(-.14601)	
8	5.3862000(-.14788)	
9	1.5387000(0.23867)	
10	0.605500(1.00000)	
11	0.220500(1.00000)	

[3d2f1g] polarization basis

function	d	f	g
1	7.5130(0.05799)	5.4860(0.173786)	2.5880(0.484830)
2	2.3890(0.30456)	1.9670(0.597338)	0.9750(0.653938)
3	0.9713(1.00000)	0.8418(1.000000)	
4	0.4324(1.00000)		

[2d1f] polarization basis

function	d	f
1	4.2770(0.16866)	1.806(0.47694
2	1.3410(0.58480)	0.618(0.65874)
3	0.5220(1.00000)	

Table II. Basis Sets for Hydrogen.

[4s4p2d1f] Hydrogen basis

function	s	p	d	f
1	82.63637(0.006172)	6.0760(0.05713)	3.535(0.168660)	1.204(0.476935)
2	12.40960(0.047210)	1.5750(0.28575)	1.108(0.584798)	0.412(0.658738)
3	2.823850(0.232530)	0.5554(1.00000)	0.432(1.000000)	
4	0.797670(0.790500)	0.2211(1.00000)		
5	0.258100(1.000000)	0.0880(1.00000)		
6	0.089890(1.000000)			
7	0.030000(1.000000)			

[2p1d] polarization basis

function	p	d
1	1.7983(0.17705)	1.827(0.46662
2	0.4663(0.88560)	0.548(0.66447)
3	0.1644(1.00000)	

Table III. Calculations for $O + H_2 \rightarrow OH + H$
[5s4p2d1f/4s2p] basis set
$3\sigma 1\pi$ active space

	CCI[a,b], kcal/mole		
Geometry	6 electrons	8 electrons	expt.
products	3.6(3.3)	6.7(6.6)	2.9
saddle point[c]	17.0(16.0)	17.5(16.0)	12.5
reactants	0.0	0.0	0.0
$D_e(H_2)$	4.62	4.62	4.75
$D_e(OH)$	4.48	4.33	4.62

[a] Values in parenthesis include Davidson's correction.
[b] All quantities are in kcal/mole except the D_e values which are in eV.
[c] The saddle point geometry is r_{OH}=2.293 and r_{HH}=1.764 which is very close to the POL-CI saddle point geometry. The OH and H_2 bond lengths are r_{OH}=1.868 and r_{HH} = 1.431

Table IV. Calculations for $O + H_2 \rightarrow OH + H$
[5s4p2d1f/4s2p] basis set
Effect of expanded active space

	ΔE_b [a], kcal/mole	
active space	CCI	CCI + Q
$3\sigma 1\pi$	17.3	15.9
$4\sigma 2\pi$	15.2	14.4
$5\sigma 3\pi$	15.1	14.3
$6\sigma 3\pi$	15.0	14.2

[a] Using the reactants and saddle point geometry as in Table III.

Table V. Reference Configurations for $O + H_2$.

$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi_x^2 1\pi_y^1$

$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 5\sigma^1 1\pi_x^2 1\pi_y^1$

$1\sigma^2 2\sigma^2 4\sigma^1 5\sigma^2 1\pi_x^2 1\pi_y^1$

$1\sigma^2 2\sigma^2 4\sigma^1 6\sigma^2 1\pi_x^2 1\pi_y^1$

$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 2\pi_x^2 1\pi_y^1$

$1\sigma^2 2\sigma^2 3\sigma^1 5\sigma^1 7\sigma^1 1\pi_x^2 1\pi_y^1$

$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 5\sigma^1 1\pi_x^1 2\pi_x^1 1\pi_y^1$

$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 5\sigma^1 1\pi_x^2 2\pi_y^1$

Table VI. Computed Saddle Point Properties for O + H_2. [a]

property	POL-CI	CI	CI + Q
ΔE_b, kcal/mole	12.5	14.9	13.9
r_{OH}, a_0	2.320	2.313	2.314
r_{HH}, a_0	1.747	1.690	1.688
curvature [b]	-0.057	-0.083	-0.078

[a] Multireference SDCI calculations with a $5\sigma 2\pi$ active space and a [5s4p2d1f/4s2p] basis set.

[b] Negative eigenvalue of the Hessian matrix.

Table VII. Calculations for $O + H_2 \rightarrow OH + H$
Effect of Basis Set

	ΔE_b [a], kcal/mole	
Basis set	6 electrons	8 electrons
[5s4p2d1f/4s2p]	14.83	14.72
[5s4p3d2f1g/4s3p1d]	14.73	14.20
[5s4p3d2f1g/4s4p1d]		14.09
[5s4p3d2f1g/4s4p2d]		13.87
[5s4p3d2f1g/4s4p2d1f]		13.60(14.3[b])

[a] CPF calculations using the saddle point and reactants geometries from the multireference SDCI calculations using a $5\sigma 2\pi$ active space and the [5s4p2d1f/4s2p] basis set.

[b] Including an estimate of basis set superposition error.

Table VIII. Computed Barrier Height and Endoergicity for $O + H_2$.[a]

property	CCI(6 electrons)	CCI(8 electrons)	expt.
ΔE_b [b], kcal/mole	15.1(14.0)	14.7(12.7)	
contraction error	0.5	0.5	
superposition error	(0.0)	0.15	
ΔE_b(corr.)	14.8(13.7)	14.4(12.4)	(12.5)
ΔE_{rx}, kcal/mole	1.7(1.9)	3.8(4.5)	2.9

[a] Multireference CCI calculations with a $5\sigma 2\pi$ active space and a [5s5p3d2f1g/4s3p2d1f] ANO basis set.

[b] The computed barrier height viewed from the OH + H direction is 13.5(12.1) and 11.0(8.2) kcal/mole for correlating six electrons and eight electrons, respectively. This may be compared to 9.6 kcal/mole for "experiment".