AB INITIO MOLECULAR ORBITAL CALCULATIONS ON $F+H_2 \rightarrow HF+H$ AND $OH+H_2 \rightarrow H_2O+H$ USING UNRESTRICTED MØLLER–PLESSET PERTURBATION THEORY WITH SPIN PROJECTION

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Received 13 January 1988

The reactions of fluorine atom and hydroxyl radical with molecular hydrogen have been studied by molecular orbital methods using the 6-311G(d, p) and 6-311++G(2df, 2pd) basis sets with the unrestricted Hartree–Fock approach and with Møller–Plesset perturbation theory up to fourth order, with and without spin projection. The positions of transition states were optimized with a grid search at the MP*n* and PMP*n* levels using the 6-311G(d, p) basis. The projected MP2, MP3 and MP4 barriers are 1–1.5 kcal/mol lower and 0.03–0.05 Å closer to the reactants than the unprojected calculations. At the PMP4SDTQ/6-311++G(2df, 2pd) level, the classical barriers are 2.6 kcal/mol for $F+H_2$ and 5.7 kcal/mol for $OH+H_2$.

1. Introduction

The reactions of $F+H_2$ and $OH+H_2$ are isoelectronic and should entail similar computational difficulties. The barrier height for $F+H_2$ has been studied by almost all available quantum mechanical methods (for recent reviews see ref. [1]). Recent calculations include MBPT [1–4], MRCI [1–7], coupled clusters [8], quantum Monte Carlo [9] and CI [6]. Nevertheless, agreement between theory and experiment has been difficult to achieve [7]. The second reaction, $OH+H_2 \rightarrow H_2O+H$, is an important process in hydrogen–oxygen flames [10]. Although it is closely related to $F+H_2$, the calculation of the barrier height for $OH+H_2$ has received much less attention [11–15] and some differences between theory and experiment remain. The purpose of this note is to examine the effect of spin projection on the barrier heights and transition state geometries calculated by unrestricted fourth-order Møller–Plesset perturbation theory. Unrestricted Møller–Plesset perturbation theory is known to converge slowly when spin contamination is appreciable [16–18]. In previous studies [19–23], we have found that a simple, approximate spin projection scheme dramatically improves the heights of barriers and the shapes of potential energy curves.

2. Method

Ab initio molecular orbital calculations were performed with the GAUSSIAN 82 system of programs [24] using the 6-311G(d, p) and 6-311++G(2df, 2pd) basis sets [25]. For $F+H_2$, additional calculations were carried out with a [4s3p1d/2s1p] basis set for comparison with recent full CI calculations [6]. Electron correlation corrections were estimated by Møller–Plesset perturbation theory [26] [#1] up to fourth order (MP2, MP3, MP4SDTQ, frozen core). Unwanted spin contamination was removed using approximate spin projection methods (PMP2, PMP3, PMP4SDTQ, see refs. [19,23] for the definition of these levels of theory). A grid search was used to explore the region of the linear transition

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[#1] For a review of many-body perturbation theory and coupled cluster methods see ref. [27].

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(North-Holland Physics Publishing Division)

state at the MPn/6-311G(d, p) level with and without spin projection. For the $F+H_2$ transition state, the step sizes for the grid were 0.02 Å for R(H–F) and 0.005 for R(H–H). At the MP2 level, the results from the grid search for the collinear transition state (see table 2) are in excellent agreement with the geometry obtained earlier by direct optimization using gradients [2]. This suggests that an accuracy of ±0.002 Å will be obtained for the grid search with the other levels of theory. For the $HO+H_2$ transition state, the step sizes for the numerical gradient calculations were 0.02 Å for R(O–H) and R(H–H), 0.005 for R(HO), 2° for ∠HO–H and 5° for ∠O–H–H. An approximate Hessian was constructed by combining the Hartree–Fock analytical second derivative matrix calculated at the HF transition state with averaged O–H and H–H stretch and interaction force constants calculated numerically at the MPn and PMPn levels. By comparison with a direct transition state optimization with analytical gradients at the MP2/6-311G(d, p) level, the numerical uncertainties arising from the grid search are expected to be ±0.01 Å for R(O–H), ±0.005 Å for R(H–H), ±0.001 Å for R(HO) and ±1° for ∠HO–H and ∠O–H–H. For both reactions, the final estimates of the optimized geometry at each level of calculation (MPn and PMPn) are based on the gradients and Hessians at the grid points closest to the predicted transition structure at that level. The MP4SDTQ/6-311G(d, p)-optimized geometries were then used for single point calculations at the MP4SDTQ and PMP4SDTQ levels with t 6-311++G(2df, 2pd) basis set.

3. Results and discussion

3.1. $F+H_2 \rightarrow HF+H$

The results for the [4s3p1d/2s1p] basis set w seven and nine electrons correlated are collected table 1; the 6-31G(d, p) and 6-311++G(2df, 2p results are presented in table 2. Although the m recent calculations indicate that a bent transiti structure is ≈0.1 kcal/mol more stable [5,7], t present calculations are restricted to the colline structure to facilitate comparison with earlier c culations. For each of the three different sets of c culations given in tables 1 and 2, the MP4-optimiz collinear transition state is similar to the MP2-o timized structure, but both are more reactant-li than the MP3 structure. Even though the spin co tamination is small ($\langle S^2 \rangle = 0.77$ at the UHF leve spin projection pushes the transition state further in the entrance channel by ≈0.05 Å. Since the effect spin projection on the geometry is very similar the [5s3p1d/2s1p] and 6-311G(d, p) basis sets, a since the effect on the energy is nearly the same 6-311++G(2df, 2pd), a reasonable estimate of t optimized collinear transition state at the PMP4, 311++G(3df, 3pd) level is R(HF) = 1.49 Å a R(HH) = 0.76 Å (based on R(HF) = 1.44 Å a R(HH) = 0.77 Å for the MP4/6-311++

Table 1
Optimized transition state geometries and classical barrier heights for $F+H_2 \rightarrow HF+H$ [a] with a [5s3p1d/2s1p] basis set

Level	Seven electrons correlated			Nine electrons correlated		
	R(H–F)	R(H–H)	$\Delta E^{\ddagger}$	R(H–F)	R(H–H)	$\Delta E^{\ddagger}$
MP2	1.363	0.781	7.3	1.388	0.777	6.8
MP3	1.337	0.787	8.4	1.344	0.787	8.2
MP4	1.370	0.784	6.9	1.384	0.782	6.4
PMP2	1.422	0.776	6.2	1.442	0.774	5.2
PMP3	1.382	0.784	6.9	1.382	0.785	6.7
PMP4	1.414	0.780	5.9	1.426	0.780	5.2
MRCI+Q [b]	1.467	0.775	4.4	1.471	0.774	3.6
full CI [b]	1.461	0.776	4.5			

[a] Bond lengths in Å, energies in kcal/mol, zero-point energies *not* included.
[b] From ref. [6].

Table 2
Optimized transition state geometries, classical barrier heights and energies of reaction for $F+H_2 \rightarrow HF+H$ [a] with 6-311G(d, p) and 6-311++G(2df, 2pd) basis sets

Level	6-311G(d, p)				6-311++G(2df, 2pd) [b]	
	R(H–F)	R(H–H)	$\Delta E^{\ddagger}$	ΔE	$\Delta E^{\ddagger}$	ΔE
MP2	1.359	0.781	8.1	−41.1	4.8	−40.2
MP3	1.301	0.794	9.8	−33.9	6.2	−29.8
MP4	1.354	0.786	7.7	−33.4	3.9	−32.6
PMP2	1.416	0.778	6.2	−38.6	3.0	−39.2
PMP3	1.348	0.792	8.1	−31.9	4.9	−29.3
PMP4	1.396	0.785	6.3	−31.7	2.6	−32.1

[a] Bond lengths in Å, energies in kcal/mol, zero-point energies *not* included.
[b] At the PMP4/6-311G(d, p) geometry.

(3df, 3pd) calculations in ref. [3]). Comparison with the MRCI+Q and full CI calculations [6] listed in table 1 indicates that spin projection recovers only about half of the difference between the UMP4 and the full CI or MRCI+Q calculations. If this is taken into account in correcting MP4/6-311++G(3df, 3pd) results [3], R(HF) is estimated to be ≈1.54 Å, in good agreement with R(HF) = 1.56 Å obtained by MRCI+Q calculations with very large basis sets [7].

Full CI calculations by Bauschlicher and Taylor [6] predict a barrier of 4.5 kcal/mol with a [5s3p1d/2s1p] basis set and seven electrons correlated; the MRCI+Q (multi-reference CI with quadruples correction) result is nearly identical. With the same basis set and seven electrons correlated, the MP4 level gives a barrier of 6.9 kcal/mol, 2.4 kcal/mol higher than the full CI result. Spin projection lowers the barrier by 1.0 kcal/mol to 5.9 kcal/mol. Similar results are obtained when all nine valence electrons are correlated. Test calculations with a smaller basis set and full spin projection [23] suggest that the remaining 1.4 kcal/mol difference between the PMP4 calculations and the full CI result (table 1) is probably due to dynamic correlation corrections not adequately treated by fourth-order perturbation theory rather than approximations in the spin projection. With the much larger 6-311++G(2df, 2pd) basis set, the MP4 barrier is 3.9 kcal/mol (at the PMP4/6-311G(d, p)-optimized geometry) and spin projection lowers it by 1.3 kcal/mol. This suggests that even with large basis sets the UMP4 barrier will be lowered by 1–1.3 kcal/mol by spin projection. When the corrections for spin contamination (1–1.3 kcal/mol) and residual dynamic correlation (≈1.5 kcal/mol) are combined with the optimized MP4/6-311++G(3df, 3pd) barrier height [3] (3.64 kcal/mol), an estimate of 1.8–2.1 kcal/mol is obtained. However, further expansion of the basis set changes the barrier by up to ±0.4 kcal/mol and basis set superposition corrections raise the barrier by 0.2–0.6 kcal/mol [3,5–7]. The best calculations of Bauschlicher and Taylor [7] predict a classical barrier of 1.4±0.4 kcal/mol for the collinear transition state.

Spin projection improves the calculated ΔE for the reaction slightly, making it 0.5 kcal/mol less exothermic than the MP4/6-311++G(2df, 2pd) level (experimental $\Delta E = -31.8$ kcal/mol). However, the remaining basis set deficiencies and basis set superposition effects may both be in the range of ±0.5 kcal/mol [2,3,5–7].

3.2. $OH+H_2 \rightarrow H_2O+H$

Since the reaction $OH+H_2 \rightarrow H_2O+H$ is less exothermic than $F+H_2$, the barrier is expected to be somewhat later than the $F+H_2$ barrier. The calculations at all levels support this prediction, as can be judged from the H–H distances. The optimized transition structure at the PMP4 level is comparable with the one obtained using POL-CI calculations with a similar basis set [12]. Like $F+H_2$, extra diffuse and polarization functions will probably move the transition state toward the reactants. Since the barrier is higher and not as early in the entrance channel as

$F+H_2$, the position of the transition state is not shifted as much by spin projection (ΔR(O–H) $=0.034$ Å). Similarly, the barrier position may not be quite as sensitive to basis set expansion and correlation corrections. Comparison with $F+H_2$ suggests that further expansion of the basis set and improvement in the treatment of electron correlation may yield a transition state with R(O–H) as large as 1.40 to 1.45 Å.

The experimental thermal activation energy of $OH+H_2$ is 5.0 kcal/mol [28,30]. With the 6-311G(d, p) basis set, the classical barrier is 9.9 kcal/mol at the MP4 level and spin projection lowers the barrier by 1.5 kcal/mol. Expansion of the basis set from 6-311G(d, p) to 6-311++G(2df, 2pd) lowers the MP4 barrier to 7.1 kcal/mol at the MP4 level (using PMP4/6-311G(d, p)-optimized geometries). Spin projection decreases the barrier by 1.4 kcal/mol, giving 5.7 kcal/mol for the classical barrier height at the PMP4/6-311++G(2df, 2pd) level. This is in good agreement with the barrier height calculated by Dunning et al. (6.2 kcal/mol [12]). Zero-point energy correction decreases the barrier by ≈ 0.2 kcal/mol [12]. Comparison with $F+H_2$ suggests that further expansion of the basis set, more complete treatment of electron correlation and correction for basis set superposition error may have the combined effect of lowering the barrier by an additional 0.5–1.5 kcal/mol. This would lead to an estimate of 4.2–5.2 kcal/mol for the classical barrier. More extensive calculations of the barrier height will be carried out using the coupled clusters approach [31]. The classical energy difference between products and reactants is computed to be -16.3 kcal/mol, also in good agreement with experiment and with previous calculations [12].

4. Conclusions

In our previous applications of PMPn calculations, spin contamination was quite large and spin projection reduced barrier heights by 5–15 kcal/mol [20–22] or recovered a large fraction of the difference between the UMP4 and full CI calculations [19,23]. For both $F+H_2$ and $HO+H_2$, the spin contamination is quite small ($\langle S^2 \rangle = 0.77$–$0.78$). Nevertheless, spin projection lowers the UMP4 barriers by 1–1.5 kcal/mol and shift the transition states by 0.03 to 0.05 Å toward the reactants. However, compared to full CI calculations, the $F+H_2$ barrier is still 1.4 kcal/mol too high. The $F+H_2$ system is known to require a very extensive treatment of electron correlation. Thus, the difference between the PMP4 and the full CI calculations may reflect the shortcomings of the fourth-order treatment rather than approximations in the spin projection. For larger basis set calculations, the lowering due to spin projection is also ≈ 1.3 kcal/mol. If an additional correction of ≈ 1.5 kcal/mol is made for the electron correlation not recovered by fourth-order perturbation theory, the corrected PMP4 barrier is in the same range as the MRCI+Q barrier [7]. The $HO+H_2$ system is isoelectronic to $F+H_2$ and shows similar improvement on spin projection. The dynamic electron correlation not recovered at the MP4 level may be similar in magnitude to the $F+H_2$ system. This would lead to an estimated classical barrier of 4.2–5.2

Table 3
Optimized transition state geometries, classical barrier heights and energies of reaction for $OH+H_2 \rightarrow H_2O+H$ [a]

Level	6-311G(d, p)							6-311++G(2df, 2pd) [b]	
	R(HO)	∠HOH	∠OHH	R(O–H)	R(H–H)	$\Delta E^{\ddagger}$	ΔE	$\Delta E^{\ddagger}$	ΔE
MP2	0.967	96.9	161.5	1.310	0.820	9.9	−19.2	7.5	−23.9
MP3	0.965	97.2	162.2	1.251	0.843	12.4	−11.4	9.8	−14.8
MP4	0.970	96.7	162.1	1.292	0.832	9.9	−12.6	7.1.	−16.9
PMP2	0.968	96.0	162.8	1.362	0.813	7.8	−18.3	5.2	−22.7
PMP3	0.966	96.6	163.0	1.281	0.840	10.9	−10.9	8.4	−14.1
PMP4	0.970	96.0	162.8	1.326	0.828	8.4	−12.1	5.7	−16.3

[a] ∠HO–H–H $=0°$, bond lengths in Å, angles in deg., energies in kcal/mol, zero-point energies *not* included.
[b] At the PMP4/6-311G(d, p) geometry.

kcal/mol for $HO+H_2$ and a transition structure with an estimated R(O–H) of 1.40–1.45 Å.

Acknowledgement

This work was supported by a grant from the National Science Foundation (CHE-83-12505).

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