Accurate coupled cluster reaction enthalpies and activation energies for $X+H_2 \rightarrow XH+H$ (X=F, OH, NH_2, and CH_3)

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Coupled cluster calculations at the CCSD(T)/[5s4p3d/4s3p] and CCSD(T)/[5s4p3d2 f1g/4s3p2d] level of theory are reported for reactions $X+H_2 \rightarrow XH+H$ [X=F (1a), OH (1b), NH_2 (1c), and CH_3 (1d)] utilizing analytical energy gradients for geometry, frequency, charge distribution, and dipole moment calculations of reactants, transition states, and products. A careful analysis of vibrational corrections leads to reaction enthalpies at 300 K, which are within 0.04, 0.15, 0.62, and 0.89 kcal/mol of experimental values. For reaction (1a) a bent transition state and for reactions (1b) and (1c) transition states with a *cis* arrangement of the reactants are calculated. The *cis* forms of transition states (1b) and (1c) are energetically favored because of electrostatic interactions, in particular dipole–dipole attraction as is revealed by calculated charge distributions. For reactions (1a)–(1d), the CCSD(T)/[5s4p3d2 f1g/4s3p2d] activation energies at 300 K are 1.1, 5.4, 10.8, and 12.7 kcal/mol which differ by just 0.1, 1.4, 2.3, and 1.8 kcal/mol, respectively, from the corresponding experimental values of 1 ± 0.1, 4 ± 0.5, 8.5 ± 0.5, and 10.9 ± 0.5 kcal/mol. For reactions (1), this is the best agreement between experiment and theory that has been obtained from *ab initio* calculations not including any empirically based corrections. Agreement is achieved after considering basis set effects, basis set superposition errors, spin contamination, tunneling effect and, in particular, zero-point energies as well as temperature corrections. Net corrections for the four activation energies are -1.05, -0.2, 1.25, and 0.89 kcal/mol, which shows that for high accuracy calculations a direct comparison of classical barriers and activation energies is misleading.

I. INTRODUCTION

The prediction of reaction energies and activation barriers from first principles is a major goal in quantum chemistry. Since reactions mostly involve the breaking and forming of a chemical bond and since multireference methods provide a reasonable starting wave function for such a process, high accuracy results have mostly been obtained with multireference configuration interaction (MRCI) methods.[1] Nevertheless, attempts have been continued to get also accurate results from a single determinant approach which includes major correlation effects. Such an approach, if not too costly, is appealing since it allows routine calculations without definition of appropriate reference configurations. Also, the routine calculation of response properties by analytical energy derivative methods is straightforward for single determinant methods.[2,3] Most promising in this regard have been coupled cluster (CC) methods[4] and, in particular, the CCSD(T) approach,[5] which includes single (S) and double (D) excitations together with a perturbative treatment of triple excitations (T). CC methods are size-extensive and contain infinite order effects. CCSD(T) has already proven to lead to reasonable results in cases with some multireference character.[6] Therefore, it should be well suited to describe potential energy surfaces (PES) or at least important parts of

them. This will be investigated in this and some following papers. Here, we will examine CCSD(T) reaction energies and barriers for reactions of the type

$$X+H_2 \rightarrow XH+H \qquad (1)$$

$$X=F(1a), OH(1b), NH_2(1c), and CH_3(1d),$$

which are perfect test targets because of two reasons. First, the H abstraction reactions (1) have been intensively studied with experimental means and, therefore, sufficient data are available to assess the accuracy of CCSD(T) results. Second, reactions (1) represents examples of strongly exoergic, weakly exoergic, and thermoneutral reactions with either an early or normal transition state (TS). Accordingly, calculations will show whether CCSD(T) describes different types of reactions on an equal footing. An investigation of reactions (1) will reveal whether CCSD(T) is suitable to explore PES along reaction paths in order to get a more detailed description of chemical reactions.

II. THEORETICAL APPROACH

CCSD(T) calculations have been performed with Dunning's correlation consistent valence quadruple zeta (VQZ) basis set [5s4p3d/4s3p],[7] which includes three sets of polarization functions and which, henceforth, will be called basis A. Geometries and frequencies were determined utilizing analytical energy gradients at the RHF- and UHF-CCSD(T) level.[9] Single point calculations at optimized geometries were performed with a [5s4p3d2 f1g/

$4s3p2d1f$] basis (basis B, identical with Dunning's cc-PVQZ basis[7]) which adds pure spherical harmonic components of d-, f-, and g-type basis functions to basis A.[7] In some cases, basis B was also used with Cartesian d-, f-, and g-type basis functions (basis C). All electrons were correlated to avoid errors resulting from frozen core approximation. Calculations were performed with the ACES II program,[8] which has been especially designed for large scale correlated energy and energy gradient calculations using CC/MBPT (many-body perturbation theory) methods.

CCSD(T) reaction enthalpies $\Delta H_R(0)$ and $\Delta H_R(300)$ were obtained from reaction energies ΔE_R by adding the difference in zero-point energies, $\Delta E_{\text{zero}} = E_{\text{zero}}(\text{products}) - E_{\text{zero}}(\text{reactants})$ and appropriate vibrational corrections. Experimental reaction enthalpies were evaluated from available heats of formation $\Delta H_f^0(300)$ of reactants and products.[10] Classical barrier heights ΔE_b given by the energy difference between TS and reactants at 0 K were also adjusted to 300 K by adding vibrational corrections so that a direct comparison with experimental activation energies ΔE_a at 300 K is possible.[11] Tunneling was estimated by applying the Wigner correction,[12] which has proven to lead to remarkably accurate activation energies in case of reactions involving diatomic molecules.[13] For polyatomic reaction systems, the value of the Wigner approximation is less known and, therefore, it cannot be excluded that tunneling corrections are somewhat too low in these cases. In addition to zero-point energy, temperature, and tunneling corrections, basis set superposition errors (BSSE) were investigated in some cases using the counterpoise method by Boys and Bernardi.[14]

III. RESULTS AND DISCUSSION

CCSD(T) geometries and harmonic frequencies of all molecules and TSs are summarized in Table I. Table II gives absolute energies, zero-point energies E_{zero}, and experimental heats of formation $\Delta H_f^0(300)$.[10] Finally, in Table III, calculated and experimental reaction enthalpies and activation energies are compared. Figure 1 depicts some properties of the investigated TSs.

CCSD(T)/A geometries and harmonic frequencies are in excellent agreement with experimental values (Table I), in particular in those cases where experimentally derived r_e geometries and harmonic frequencies are available.[15,16] We infer from these results that the same accuracy can be expected for calculated TS geometries and frequencies. In the following, we will discuss each of the four reactions separately.

A. Reaction (1a): F+H$_2$→FH+H

Since the F+H$_2$ reaction (1a) is a prototype for gas phase reactions, it has been extensively studied by both experimental and theoretical means during the past 20 years.[17] The experimental $\Delta H_R(300)$ value of reaction (1a) is −29.27 kcal/mol (Table III). According to the Hammond Postulate, reaction (1a) should possess a small

energy barrier located early in the reaction channel. The experimentally determined activation energy at 300 K, $\Delta E_a(300)$, is 1.0±0.1 kcal/mol.[18]

The calculation of such a small barrier is challenging because of two reasons. First, in order to describe the reaction barrier of reaction (1a) relative ab initio energies have to be more accurate than ±1 kcal/mol. Second, possible energy errors due to basis set deficiencies, electron correlation, spin contamination in case of UHF calculations, size-extensivity problems, and multireference character of the wave function have effectively the same sign for reaction (1a) and, therefore, one cannot benefit from a fortuitous cancellation of some of these errors.

Early ab initio calculations predict a classical barrier ΔE_b of 3–4 kcal/mol for reaction (1a).[17] More recent ab initio investigations with improved methods report smaller barriers. For example, Bauschlicher and co-workers[19] calculated a MRCI+Q (including Davidson correction) classical barrier of 1.4±0.4 kcal/mol. Werner and Knowles reported a MRCI+Q barrier of 1.93 kcal/mol for a collinear TS and 1.53 kcal/mol for a bent TS[20] while Scuseria obtained a CCSD(T) barrier of 2.05 kcal/mol for the linear TS.[21] According to these and other recent results the classical barrier should be in the range of 1.4–2.3 kcal/mol.[17(b)]

Although agreement between experimental and theoretical barrier values seems to be satisfactory, a caveat is appropriate. The experimental $\Delta E_a(300)$ cannot directly be compared with the classical barrier because of important vibrational corrections not considered in most of the more advanced ab initio calculations cited above. In this work, we calculate a zero-point correction E_{zero} for the activation energy of reaction (1a), which is almost as large as $\Delta E_a(300)$ itself (~ 1 kcal/mol, Table III) and, therefore, cannot be neglected.

The CCSD(T)/A TS of reaction (1a), (F...H$_2$), is characterized by a bent rather than a linear arrangement of the three atoms (Fig. 1). For the linear TS we obtain two imaginary frequencies (Table I), identifying the linear form as a second-order TS. The calculated TS geometry differs with a FH′ distance of 1.477 Å, a H′H″ distance of 0.774 Å and a bending angle of 140° significantly from the geometry of the linear TS (1.485, 0.770 Å, and 180°), but since the bending potential is rather flat the corresponding difference in the energy is just 0.1 kcal/mol [0.2 kcal/mol with CCSD(T)/B]. Most of the high accuracy ab initio investigations of reaction (1a) reported so far describe just the collinear TS form with H′H″ and FH′ distances of 0.76–0.78 and 1.47–1.56 Å, respectively.[17–21] The large variation in the later value reflects the fact that the TS region is also rather flat in the direction of the FH′ coordinate. We calculate a low imaginary frequency of 869i cm^{-1} (Table II), which means that even a FH′ variation of 0.1 Å not necessarily implies a similarly large change in ΔE_b.

In the bent TS, the H′H″ distance is only 4% longer than in H$_2$, while the FH′ distance is 61% longer than in FH. The dipole moment at the TS is 0.678 D, which is still less than half the value of the FH dipole moment [1.809 D,

TABLE I. CCSD(T)/[5s4p3d/4s3p] geometries and harmonic frequencies.[a]

Molecule	Geometry			Harmonic frequencies		
H$_2$, $D_{\infty h}$	r_{HH}	0.741	(0.741)	ω_1	4409	(4405)
FH, $C_{\infty v}$	r_{FH}	0.916	(0.917)	ω_1	4132	(4139)
H$_2$O, C_{2v}	r_{OH}	0.957	(0.958)	ω_1	3938	(3943)
	$\angle_{HOH}$	104.3	(104.5)	ω_2	3830	(3832)
				ω_3	1662	(1648)
OH, $C_{\infty v}$	r_{OH}	0.969	(0.971)	ω_1	3729	(3735)
NH$_3$, C_{3v}	r_{NH}	1.011	(1.012)	ω_1	3602	(3577)
	$\angle_{HNH}$	106.3	(106.7)	ω_2	3506	(3476)
				ω_3	1702	(1691)
				ω_4	1095	(1022)
NH$_2$, C_{2v}	r_{NH}	1.024	(1.024)	ω_1	3457	(3301)[b]
	$\angle_{HNH}$	102.7	(103.4)	ω_2	3364	(3219)[b]
				ω_3	1560	(1497)[b]
CH$_4$, T_d	r_{CH}	1.086	(1.086)	ω_1	3153	(3158)
				ω_2	3037	(3137)
				ω_3	1592	(1567)
				ω_4	1366	(1357)
CH$_3$, D_{3h}	r_{CH}	1.076	(1.079)	ω_1	3307	(3161)[b]
				ω_2	3125	(3002)[b]
				ω_3	1445	(1396)[b]
				ω_4	492	(606)[b]
F...H$_2$, $C_{\infty v}$[c]	$r_{FH'}$	1.485		ω_1	3513	
	$r_{H'H''}$	0.770		$\omega_{i,1}$	758i	
				$\omega_{i,2}$	283i	
F...H$_2$, C_s	$r_{FH'}$	1.477		ω_1	3558	
	$r_{H'H''}$	0.774		ω_1	263	
	$\angle_{FH'H''}$	139.9		ω_i	869i	
HO...H$_2$, C_s	$r_{OH'}$	1.329		ω_1	3741	
	$r_{H'H''}$	0.829		ω_2	2449	
	r_{OH}	0.968		ω_3	1102	
	$\angle_{OH'H''}$	162.8		ω_4	616	
	$\angle_{HOH'}$	97.1		ω_5	403	
				ω_i	1333i	
H$_2$N...H$_2$, C_s	$r_{NH'}$	1.307		ω_1	3485	
	$r_{H'H''}$	0.890		ω_2	3390	
	r_{NH}	1.022		ω_3	1908	
	$\angle_{NH'H''}$	158.7		ω_4	1576	
	$\angle_{HNH'}$	98.5		ω_5	1277	
	$\angle_{HNH}$	103.7		ω_6	1125	
				ω_7	704	
				ω_8	672	
				ω_i	1624i	
H$_3$C...H$_2$, C_{3v}	$r_{CH'}$	1.393		$\omega_{1,2}$	3229	
	$r_{H'H''}$	0.897		ω_3	3083	
	r_{CH}	1.082		ω_4	1763	
	$\angle_{HCH'}$	103.2		$\omega_{5,6}$	1458	
				$\omega_{7,8}$	1124	
				ω_9	1093	
				$\omega_{10,11}$	518	
				ω_i	1500i	

[a]Bond distances in Å, angles in deg, frequencies in cm^{-1}. Experimental values taken from Refs. 15 (geometries) and 16 (frequencies) are given in parentheses. For a distinction of H' and H", see Fig. 1.
[b]Fundamental (anharmonic) frequencies.
[c]Saddle point of second order.

CCSD(T)/A]. These data confirm a very early TS as suggested by the Hammond postulate.

With basis A, we get $\Delta H_R(300) = -29.27$ which is 2.75 kcal/mol above the experimental value of -32.01 kcal/mol (Table III). Basis B and basis C lead to $\Delta H_R(300) = -31.69$ and -32.05 kcal/mol in excellent agreement with experiment. The addition of higher polarization functions (f and g for F, d for H) leads to an improvement of 2.4 kcal/mol which clearly shows the importance of these functions for the determination of accurate energies. This is also reflected by the calculated activation energies.

Basis A leads to a classical barrier of 3.22 kcal/mol and a $\Delta E_a(300)$ of 2.67 kcal/mol. With basis B the classical barrier is 2.17, $\Delta E_a(0) = 1.33$ kcal/mol and $\Delta E_a(300) = 1.63$ kcal/mol (Table III). If one takes into

TABLE II. CCSD(T) energies, calculated and experimental zero-point energies, and experimental heat of formation.[a]

Molecule/ atom	[5s4p3d/ 4s3p]	Energy [5s4p3d2 f1g/ 4s3p2d1f][e]	[5s4p3d2 f1g/ 4s3p2d1f][f]	E_{zero}[b]	E_{zero} (expt)[c]	$\Delta H_f^0(300)$[d]
H₂	−1.171 89	−1.173 80	1.173 84	6.30	5.94	0
H	−0.499 95	−0.499 95	−0.499 95	···	···	52.10
FH	−100.366 34	−100.405 24	−100.413 06	5.91	5.66	−65.14
F	−99.648 44	−99.681 57	−99.688 79	···	···	18.97
H₂O	−76.356 67	−76.391 09	−76.401 15	13.48	12.88	−57.80
OH	−75.662 73	−75.692 02	−75.700 72	5.33	5.10	9.32
NH₃	−56.496 15	−56.524 21	−56.535 73	21.70	20.63	−10.97
NH₂	−55.817 32	−55.840 98	−55.851 65	11.98	11.46	44.0±2
CH₄	−40.459 75	−40.481 15	−40.492 02	28.27	27.11	−17.89
CH₃	−39.783 36	−39.801 79	−39.811 74	18.76	18.25	34.80
F...H₂(linear)	−100.815 01	−100.851 62		5.03		
F...H₂(bent)	−100.815 20	−100.851 91		5.46		
HO...H₂	−76.823 34	−76.856 87		11.88		
H₂N...H₂	−56.972 02	−56.999 62		20.21		
H₃C...H₂	−40.935 16	−40.956 77		26.59		

[a]Absolute energies in hartree obtained with CCSD(T)/[5s4p3d/4s3p] geometries. All other energies in kcal/mol.
[b]Calculated from CCSD(T)/[5s4p3d/4s3p] harmonic frequencies.
[c]From experimental fundamental frequencies, see Ref. 16.
[d]From JANAF Tables, Ref. 10. $\Delta H_f^0(300)$ for NH₂ from Ref. 32.
[e]Polarization functions are spherical Gaussian functions.
[f]Polarization functions are Cartesian Gaussian functions.

account that the zero-point correction is 40% of the magnitude of the classical barrier, then it becomes obvious that a direct comparison of calculated barriers and the experimental activation energy is not meaningful at all. On the contrary, agreement between ΔE_b and $\Delta E_a(300)$ values indicates deficiencies of the theory since in view of a −0.84 kcal/mol zero-point correction ΔE_b has to be larger than 2 kcal/mol.

In order to make a fair judgement on the accuracy of our calculated barrier we have to consider possible sources of error which may lead to fortuitous error cancellation. As noted already above this should not be the case with regard to basis set deficiencies and correlation errors. However, BSSEs would artificially lower the barrier of reaction (1a). Bauschlicher and co-workers[19] calculated a BSSE of 0.15 kcal/mol for the classical barrier using an ANO (atomic natural orbital) basis set that is comparable in size to basis B and the counterpoise method with the full space of the ghost basis.[14] However, these authors argued against including BSSE corrections since the remaining basis set incompleteness effects are probably of the same magnitude and of opposite sign. In this work, we follow the argument of Bauschlicher and co-workers and consider the various basis set errors to cancel each other.

Another possible error source results from spin contamination of the UHF starting wave functions. In case of UMP2 (unrestricted Møller–Plesset second order) calculations of reactions (1a) and (1b) Schlegel and Sosa have estimated the errors due to spin contamination to be 1–1.5 kcal/mol.[22] However, CC theory significantly improves the results obtained with UHF wave functions. For example, CCSD benefits from annihilation of the principal UHF contaminant as shown by Schlegel[23] and confirmed by a

number of investigations.[24] Nevertheless, we have directly determined possible errors because of spin contamination by carrying out CCSD(T) using a ROHF (restricted open-shell Hartree Fock) reference function.[25] Results are identical with the UHF-CCSD(T) energies within 0.1 kcal/ mol.

We have also considered the possibility of barrier lowering by tunneling. Using the Wigner formula[12] and the imaginary frequency of 869i cm⁻¹ (Table I), we obtain an energy correction of −0.50 kcal/mol. Hence, our final CCSD(T)/B $\Delta E_a(300)$ value of 1.13 kcal/mol gives the most accurate theoretical activation energy for reaction (1a) directly obtained from *ab initio* calculations without including any empirically based corrections.

B. Reaction (1b): OH+H₂→H₂O+H

Reaction (1b) is an important reaction in hydrogen–oxygen flames and, therefore, it has attracted the attention of both theoreticians and experimentalists.[26–29] The experimental $\Delta_R H(300)$ is −15.01 kcal/mol (Table III). Since it is less exothermic than the isoelectronic reaction (1a), a somewhat higher and later barrier can be expected according to the Hammond postulate. An experimental activation energy of 6 kcal/mol has been measured for 1700–2500 K.[26(a)] But for the temperature range 250–396 K $\Delta E_a=4.0 \pm 0.5$ kcal/mol has been obtained.[26(b)]

Extensive dynamic studies[27] on reaction (1b) have been published most of them using the Schatz–Elgersma–Walch–Dunning (SEWD) PES,[28] which is based on POL-CI/DZ+P calculations. Kraka and Dunning calculated a GVB-CI/TZ+P reaction energy of −15.5 and a barrier of 6.0 kcal/mol.[29] Schlegel and Sosa obtained $\Delta E_R=−16.3$

TABLE III. CCSD(T) reaction energies, enthalpies, classical barriers, and activation energies.[a]

Basis[b]	Energy	$F+H_2 \to$ $FH+H$ (1a)	$OH+H_2 \to$ H_2O+H (1b)	$NH_2+H_2 \to$ NH_3+H (1c)	$CH_3+H_2 \to$ CH_4+H (1d)
Reaction energies ΔE_R and reaction enthalpies ΔH_R					
[5s4p3d/	ΔE_{zero}	−0.39	1.85	3.42	3.21
4s3p]	ΔE_R	−28.83	−13.80	−4.32	−2.79
(Basis A)	$\Delta H_R(0)$	−29.22	−11.95	−0.90	0.42
	$\Delta H_R(300)$	−29.27	−12.31	−1.42	−0.26
[5s4p3d2 f1g/	ΔE_R	−31.25	−15.83	−5.89	−3.46
4s3p2d1f]	$\Delta H_R(0)$	−31.64	−13.98	−2.47	−0.25
(Basis B)	$\Delta H_R(300)$	−31.69	−14.34	−2.99	−0.93
[5s4p3d2 f1g/	ΔE_R	−31.61	−16.65	−6.39	−4.01
4s3p2d1f]	$\Delta H_R(0)$	−32.00	−14.80	−2.97	−0.80
(Basis C)	$\Delta H_R(300)$	−32.05	−15.16	−3.49	−1.48
Expt[c]	$\Delta H_R(300)$	−32.01	−15.01	−2.87±2.0	−0.59
Classical barriers ΔE_b and activation energies ΔE_a					
[5s4p3d/	ΔE_{zero}	−0.84	0.25	1.93	1.53
4s3p]	ΔE_b	3.22	7.08	10.78	12.60
(Basis A)	$\Delta E_a(300)$	2.67	7.63	12.88	14.30
	ΔE_{tunnel}	−0.50	−0.75	−0.85	−0.81
	final $\Delta E_a(300)$[e]	2.17	6.88	12.03	13.49
[5s4p3d2 f1g/	ΔE_b	2.17	5.62	9.51	11.81
4s3p2d1f]	$\Delta E_a(300)$	1.63	6.17	11.61	13.51
(Basis B)	final $\Delta E_a(300)$[e]	1.13	5.42	10.76	12.70
Expt[d]	$\Delta E_a(300)$	1±0.1	4±0.5	8.5±0.5	10.9±0.5

[a]All values in kcal/mol. ΔE_{zero} is the correction due to difference in zero-point energies (see Table II). $\Delta H_R(0)$ and $\Delta H_R(300)$ are reaction enthalpies at 0 and 300 K. ΔE_b denotes the classical barrier. ΔE_a is the classical barrier corrected by ΔE_{zero} and vibrational corrections at 300 K. The tunneling correction ΔE_{tunnel} has been evaluated from the Wigner formula (Ref. 12) with the imaginary frequencies given in Table I.
[b]Basis B includes f- and g-type polarization functions (d- at H) in form of spherical, basis C in form of Cartesian Gaussian functions.
[c]Experimental values derived from $\Delta H_f^0(300)$ (Ref. 10). The $\Delta H_f^0(300)$ value for NH₂ (44.0±2.0 kcal/mol) has been taken from Ref. 32.
[d]Experimental ΔE_a values from Refs. 18, 26, 33, 36.
[e]Final activation energies at 300 K are obtained by subtracting tunneling corrections ΔE_{tunnel} calculated with basis A from $\Delta E_a(300)$ values.

kcal/mol and a classical barrier height of 5.7 kcal/mol at the PMP4/TZ+P level of theory.[22]

The CCSD(T) geometry of TS (1b) (Fig. 1) suggests a *cis* arrangement of H′H″ and OH bond. The OH bond length differs only by 0.02 Å from that of the OH molecule, indicating that the OH bond is a spectator bond, not being involved in the reaction. The H′H″ distance is 12% longer than that in H₂ and the OH′ distance (1.329 Å) 37% longer than that in H₂O. The dipole moment of the TS (1.639 D) is closer to the OH dipole moment (1.661 D) than that of H₂O (1.895 D) at the CCSD(T)/A level.

One might argue that because of bond staggering a *trans* arrangement of OH and H′H″ bonds in TS (1b) is energetically more favorable. Indeed, such a configuration has been suggested by the SEWD surface.[28(b)] However, from calculated charge distributions and dipole moments (Fig. 1) it becomes obvious that a *cis* TS must be energetically more favorable than a *trans* TS. In the *cis* form, the OH bond dipole and the induced H′H″ bond dipole attract each other as do the positively charged H and the negatively charged H″ atoms. This has been overlooked in previous investigations of reaction (1b), mainly because appropriate response densities and properties have not been calculated.

For reaction (1b), a much larger imaginary frequency (1333*i* cm⁻¹, Table I) is obtained than that of reaction (1a), which suggests a much steeper reaction valley in line with the increase of ΔE_a from reaction (1a) to (1b). Ac-

cordingly, the classical barrier should be sensitive to changes in the OH′ distance and the possibility for tunneling should increase.

The CCSD(T)/A reaction enthalpy $\Delta H_R(300)$ (−12.31 kcal/mol, Table III) is 2.7 kcal/mol higher than the experimental value of −15.01 kcal/mol. Basis B improves the calculated $\Delta H_R(300)$ value by 2 kcal/mol and basis C predicts a reaction enthalpy being as close as 0.15 kcal/mol to the experimental value. The CCSD(T)/A classical barrier is 7.08 kcal/mol and the corresponding $\Delta E_a(300)$ (7.63 kcal/mol, Table III) differs just by 0.55 kcal/mol from this value since vibrational corrections are less important for reaction (1b) than for (1a). After correcting for tunneling (−0.75 kcal/mol, Wigner correction based on 1333*i* cm⁻¹, Table III), a final activation energy $\Delta E_a(300)$ of 7.1 kcal/mol is obtained, which is 3 kcal/mol higher than the experimental $\Delta E_a(300)$ of 4 kcal/mol.

CCSD(T)/B leads to a 1.5 kcal/mol improvement of the classical barrier (5.62 kcal/mol, Table III), which clearly demonstrates the importance of f- and g-type polarization functions in the basis. When adding to ΔE_b vibrational and tunneling corrections, a final $\Delta E_a(300)$ of 5.42 kcal/mol (Table III) is obtained. This value can be further improved by replacing the Wigner tunneling correction by a more realistic tunneling correction of 1.07 kcal/mol (see Sec. III E) thus leading to $\Delta E_a(300)=5.12$ kcal/mol. Although this value is still 1.1 kcal/mol larger
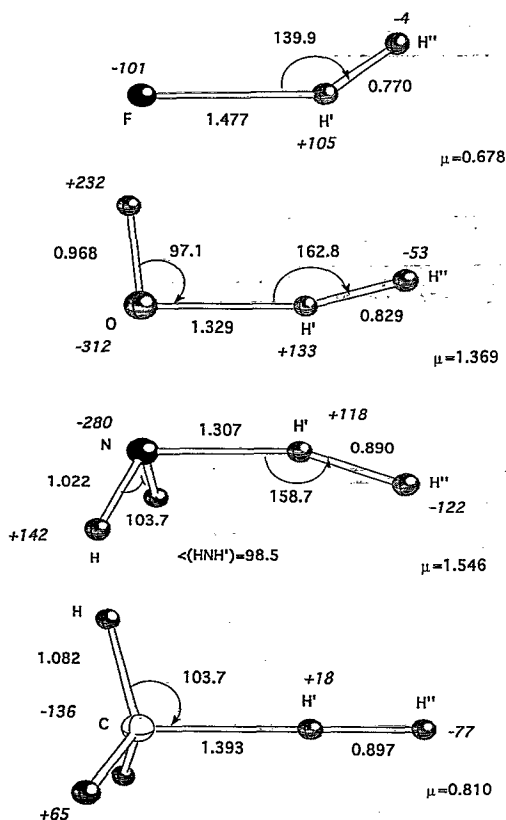
FIG. 1. CCSD(T)/[5s4p3d/4s3p] geometries, atomic charges, and dipole moments of transition states (1a)–(1d). Interatomic distances are given in Å, angles in deg, charges in melectron (in italics), dipole moments μ in Debye.

than the experimental $\Delta E_a(300)$ of 4 kcal/mol, the CCSD(T)/B activation energy is clearly the best value that has been predicted so far from *ab initio* calculations not including any empirically based corrections.

It is likely that a further improvement of $\Delta E_a(300)$ can be achieved by reoptimizing the TS geometry at the CCSD(T)/B level of theory. The reaction path of (1b) is much steeper than that of reaction (1a), and, therefore, a barrier decrease of 1.5 kcal/mol probably indicates that the OH...H$_2$ TS is located earlier in the entrance channel of the reaction thus making a reoptimization of the TS geometry desirable.

It is interesting to note that vibrational corrections and tunneling correction do have the same magnitude, but possess different signs so that their net effect vanishes or is at least rather small (see Sec. III E). This explains why previous investigations of reaction (1b) that did not include these corrections reported ΔE_b values that come within 1 kcal/mol of our best prediction of $\Delta E_a(300)$.

C. Reaction (1c): NH$_2$+H$_2$→NH$_3$+H

Although the NH$_2$ radical is a key intermediate in most chemical reactions involving ammonia, especially in atmospheric chemistry, experimental and theoretical data on reaction (1c) are sparse.[30,31] The experimental $\Delta H_R(300)$ for this reaction is -2.87 ± 2.0 kcal/mol (Ta-

ble III) where the relatively large uncertainty of 2.0 kcal/mol results from the heat of formation of NH$_2$.[32] Since the exoergicity of reaction (1c) is further reduced in comparison with reactions (1a) and (1b), a higher barrier, being located further down the reaction channel can be expected. This is confirmed by an experimental ΔE_a at 300 K of 8.5 ± 0.5 kcal/mol.[33]

The CCSD(T)/A TS (Fig. 1) also adopts a *cis* arrangement of H$_2$ and NH$_2$, i.e., the bond H'H'' is eclipsed with the bisector of NH$_2$. This is contrary to previous results obtained at lower levels of theory,[31] but in line with what we find for TS (1b). Again, the *cis* conformation is energetically favored because of attractive electrostatic interactions, in particular dipole–dipole attractions as can be seen from calculated CCSD(T) charges. The NH' distance of 1.307 Å is 30% longer than the NH bond length in NH$_3$ while the H'H'' distance is 0.06 and 0.12 Å longer than in the TS of reaction (1b) and (1a), respectively. This indicates that for reaction (1c) the TS is moved further down the reaction channel. Additional indication for the position of the TS is given by its dipole moment (1.546 D, Fig. 1) which is closer to the NH$_3$ dipole moment of 1.573 D than the NH$_2$ dipole moment of 1.808 D. On the other hand, the NH distance of 1.022 Å is still close to that of NH$_2$, which suggests that the adjustment of the NH distance to that in NH$_3$ must occur further out in the exit channel.

With basis A we calculate $\Delta E_R = -4.32$ and $\Delta H_R(300) = -1.42$ kcal/mol (Table III), which shows that vibrational corrections are as much as 3 kcal/mol where ΔE_{zero} makes the largest part. Obviously, a comparison of *ab initio* reaction energies with experimental enthalpies is inappropriate as long as vibrational corrections are not considered. The CCSD(T)/A value of $\Delta H_R(300)$ is 1.4 kcal/mol higher than the experimental $\Delta H_R(300)$. With basis B we get -2.99 and with basis C -3.49 kcal/mol, both $\Delta H_R(300)$ values being slightly more negative than the experimental value. Considering the relatively high uncertainty of the experimental $\Delta H_f^0(300)$ for NH$_2$,[32] it is interesting to determine $\Delta H_f^0(300)_{NH_2}$ with the CCSD(T)/C reaction enthalpy. We obtain -44.6 kcal/mol, which is within the error margin of the experimental estimate (-44.0 ± 2.0) of DeFrees and co-workers.[32] However, a critical analysis of all our calculated CCSD(T) energies (see below) suggests that our reaction enthalpy for reaction (1c) is slightly too negative and that, therefore, the experimental $\Delta H_f^0(300)_{NH_2}$ is well confirmed by our calculations.

For the TS (1c) an imaginary frequency as large as $2834i$ cm^{-1} (Ref. 30) has been suggested on the basis of HF/4-31G calculations and some empirical corrections. Our CCSD(T)/A value ($1624i$, Table I) is clearly smaller, but still larger than any of the other imaginary frequencies obtained for reaction (1). Hence, a relatively steep reaction path can be expected, which is in line with the experimental $\Delta E_a(300)$ of 8.5 kcal/mol. The steepness of the reaction path will make it more difficult to calculate an accurate activation energy since relatively small changes in the distance between X and H$_2$ will lead to relatively large changes in the energy. Also, tunneling becomes more likely

which is reflected by a calculated tunneling correction of −0.85 kcal/mol (Table III).

The CCSD(T)/A classical barrier of reaction (1c) is 10.78 kcal/mol, which together with vibrational corrections (1.93 and 0.17 kcal/mol) and tunneling correction leads to a final $\Delta E_a(300)$ of 12.0 kcal/mol. However, a considerably improved $\Delta E_a(300)$ of 10.8 kcal/mol (ΔE_b =9.51 kcal/mol, Table III) is obtained at the CCSD(T)/B level of theory, which again demonstrates the importance of additional polarization functions. Nevertheless, the agreement between CCSD(T) and experimental activation energies (2.3 kcal/mol difference, Table III) is poorer for reaction (1c) than for reactions (1a) or (1b). Improvements of the TS geometry, calculation of zero-point energy corrections with anharmonically corrected frequencies, and a more sophisticated treatment of tunneling will reduce the difference between experimental and theoretical $\Delta E_a(300)$ values. However, the size of this difference indicates that even basis B is not sufficient to give a balanced description of reactants and products in the case of reaction (1c) (see Sec. III E).

D. Reaction (1d): CH₃+H₂→CH₄+H

Reaction (1d) can be considered as a prototype for polyatomic chemical reactions involving tetrahedral carbon. Both semiempirical and *ab initio* PESs for this reaction have been reported.[34,35] The experimental $\Delta H_R(300)$ is −0.59 kcal/mol. According to the Hammond postulate, the barrier of reaction (1d) should be higher than in reactions (1a), (1b), or (1c). This is in line with an experimental $\Delta E_a(300)$ of 10.9 kcal/mol.[36]

The TS of reaction (1d) has C_{3v} symmetry with the H₂ molecule approaching the CH₃ radical along the C_3 axis (Fig. 1). The CH' distance is 1.393 Å which is only 28% longer than the CH distance in CH₄. All other CH bond lengths (1.082 Å, Fig. 1) have almost adjusted to the methane value of 1.086 Å, which is 0.01 Å longer than the CH₃ value (1.076 Å). The H'H" distance (0.897 Å) is longer than in any of the other TSs investigated in this work. All parameters suggest a later TS compared to that of reaction (1c).

With basis A, B, and C, ΔE_R values of −2.71, −3.46, and −4.01 kcal/mol are calculated, which because of vibrational corrections of 2.5 kcal/mol increase to $\Delta H_R(300) = −0.26$, −0.93, and −1.48 kcal/mol. Again, CCSD(T)/C leads to a reasonable agreement (error, −0.89 kcal/mol) with the experimental value, but contrary to reactions (1a)–(1c), both basis A and B values for $\Delta H_R(300)$ are closer to the observed $\Delta H_R(300)$ (Table III). The calculated reaction energies and enthalpies for reaction (1d) reveal that because of small basis set and correlation errors an accuracy of 0.1 kcal/mol cannot be reached even at the CCSD(T)/C level of theory. We will have to analyze in the next section why such an accuracy seems to be reached in the case of reactions (1a) and (1b), but is lost for reactions (1c) and (1d).

The CCSD(T)/A classical barrier is 12.60 kcal/mol, which after vibrational corrections leads to a $\Delta E_a(300)$ of 14.30 kcal/mol. The imaginary frequency is with 1500*i*

cm⁻¹ smaller than that for reaction (1c), but considerably larger than those for reactions (1a) and (1b). In the literature, values between 950*i* [Ref. 34(b)] and 1920*i* cm⁻¹ [Ref. 34(c)] have been reported, but none of these values was obtained with a sufficiently large basis and a method that includes higher correlation effects. Therefore, our value presents the most accurate prediction of the imaginary frequency. It leads to a tunneling correction of −0.81 kcal/mol and, thus, to a final $\Delta E_a(300)$ of 13.49 kcal/mol (Table III).

With basis B, the CCSD(T) classical barrier is 11.81 kcal/mol and the corresponding activation energy at 300 K, 12.70 kcal/mol which suggests a 1.8 kcal/mol improvement because of basis set enlargement. The CCSD(T)/B value of $\Delta E_a(300)$ is still 1.8 kcal/mol above the experimental value, which again seems to be too much to result just from errors in the TS geometry or the tunneling correction. Further improvement of the basis set seems to be of most importance in the case of reaction (1d).

Since the net effect of vibrational and tunneling corrections leads to an increase of the barrier by 0.9 kcal/mol, one has to criticize those investigations which report an excellent agreement between experimental and computed activation energies but compare ΔE_b with $\Delta E_a(300)$.[34,35] If $\Delta E_a(300)$ is correctly derived from a calculated ΔE_b, then the necessity of improved calculations becomes immediately obvious.

E. Discussion

Our CCSD(T) calculations reveal some general trends with regard to both reaction energies and classical barriers that we will analyze in the following in order to get a basis for improved calculations in the future.

Calculated CCSD(T)/A reaction energies are between 0.33 [reaction (1d)] and 2.74 [reaction (1a)] too endothermic while CCSD(T)/C values are between 0.04 [reaction (1a)] and 0.89 kcal/mol [reaction (1d)] too exothermic. These values change by 0.11 [reaction (1a)], −0.01 [reaction (1b)], −0.19 [reaction (1c)], and −0.29 kcal/mol [reaction (1d)] if the difference between calculated and experimental $\Delta E_{zero} = E_{zero}(\text{products}) − E_{zero}(\text{reactants})$ values is considered (calculated E_{zero} values are on the average 4.6% too large because of the use of harmonic frequencies, Table II), which means that agreement between experimental and our best CCSD(T) reaction enthalpies is slightly deteriorated. Close inspection of calculated ΔE_R values in dependence of method and basis set reveals the following.

(1) With basis A, radicals X are better described than molecules XH. This has to do with the fact that the introduction of an additional bond in reaction (1) leads to a larger anisotropy of the electron density distribution in XH which is more difficult to describe with a given basis set. The basis set description of reactants and products is not balanced and, therefore, calculated reaction energies are too endothermic.

(2) The basis set error decreases from reaction (1a) to (1d) and from basis A to basis C. Future calculations have to show whether basis C is already sufficient for an accu-

rate description of reaction (1) or whether the promising energy values obtained in this work are still a result of fortuitous error cancellation.

(3) The correlation error seems to be larger for the reactants than the products. Actually, one should expect the contrary since the correlation error should increase with the number of electrons and, in particular, with the number of electron pairs. Therefore, the CCSD(T) description of the products XH should be poorer than that for the reactants X thus increasing errors caused by the basis set. As a result, reaction energies should become too positive. In view of the opposite trend in the reaction energies, CCSD(T) seems to be slightly unbalanced for reaction (1) describing, e.g., FH better than F where we estimate the error being close to 0.1 kcal/mol in this case.

(4) At the CCSD(T)/C level basis set and correlation errors seem to have the same absolute magnitude for reactions (1a) and (1b), but because of opposite signs they cancel each other. In the case of reactions (1c) and (1d), the basis set errors seem to be almost negligible (see point 2) and, therefore, the CCSD(T) errors become obvious by too negative reaction energies.

(5) Charge distributions in the TS are much more anisotropic because of polarization of X (H₂) by H₂ (X). This leads not only to the problem of finding a basis set that is equally suitable for both reactants and TS, but also to the problem of a balanced account of correlation effects for both reactants and TS. Definitely, any polarization of the electron density distribution will complicate correlation of electrons and, therefore, will require a more sophisticated treatment of correlation effects. Accordingly, an insufficient basis set and an insufficient correlation method both will lead to barrier values that are too high. Obviously, this is still the case at the CCSD(T)/A level of theory but use of basis B reduces this problem considerably (see Table III).

In summary, our results suggest that CCSD(T)/C is the right level to describe reaction energies of reaction (1) with an accuracy of 1 kcal/mol or better. For an accuracy of 0.5 kcal/mol or better, both additional polarization functions and perhaps additional correlation effects have to be considered. On the other hand, it is obvious that highest accuracy (±0.1 kcal/mol) will only be possible if all vibrational corrections are determined with vibrational frequencies that contain anharmonic corrections. Our CCSD(T)/B calculations demonstrate that promising accuracy better than in any previous *ab initio* calculation can also be achieved in the case of the activation energies for reaction (1). Higher accuracy can only be obtained if better basis sets than B are used for reaction (1) and geometries, vibrational corrections, and tunneling effects are determined with B rather than A. Future work with increased computational resources has to prove these predictions.

It is interesting to consider the use of the *ab initio* results obtained in this work for reaction dynamics investigations. Such investigations have already been carried out for reactions (1a) to (1d), but they have been based on *ab initio* data of lower accuracy or *ab initio* data that have

been empirically improved. For example, Steckler and co-workers[37] have determined a relatively high classical barrier of 3.7 kcal/mol for the linear TS of reaction (1a) by MR CISD/[8s5p3d1f/3s1p1d] calculations, but were able to improve this value to 1.6 kcal/mol by scaling the external correlation (SEC) energy. The same authors[38] obtained a barrier value of 1.3 kcal/mol for an assumed bent transition state (bending angle 130°) with the SEC approximation (MR CISD result, 2.7 kcal/mol). Using these SEC results in connection with experimental predictions, Lynch and co-workers[39] were able to describe the PES of reaction (1a) in the TS region as well as the entrance and exit channels with promising accuracy. Using this PES, the authors were able to accurately describe the dynamics of reaction (1a) and to investigate the effects of a small, early barrier with a wide flat bend potential on thermal rate constants and kinetic isotope effects.

Several reaction dynamics investigations have also been carried for reaction (1b) using canonical variational transition state theory.[28(b),28(c),40,41] Most of these investigations were based on either POL-CI *ab initio* data of Walch and Dunning[28(a)] or the GVB-CISD results of Dunning, Harding, and Kraka,[29] which suggest $\Delta E_a(300)$ values somewhat larger than 6 kcal/mol. Nevertheless, rate constant calculations with a properly adjusted PES for reaction (1b) lead to values in good agreement with experiment.[41] In these investigations, tunneling corrections between 1 and 1.2 kcal/mol were found with a more sophisticated tunneling model than that used in this work.[40,41] Of course, the larger values result partially from an overestimation of the imaginary frequency for the TS of reaction (1b) by previous *ab initio* calculations (1526–1655i cm⁻¹, see Ref. 41). However, even when this effect is considered, the tunneling effect on $\Delta E_a(300)$ is predicted to be −1.07 rather than −0.75 kcal/mol (Table III) thus leading to a final $\Delta E_a(300)$ of 5.10 kcal/mol in better agreement with experiment [experimental $\Delta E_a(300) = 4 \pm 0.5$ kcal/mol, Table III].

Reaction (1c) has been investigated by Garrett and co-workers[42] who used MP4/VDZ in connection with thermochemically based bond additivity corrections (BAC-MP4). While such a method can lead to rather accurate reaction energies because of the adjustment of MP4 energies to experimental heats of formations, the description of the TS region suffers from method dependent shortcomings. However, in the case of reaction (1c) BAC-MP4 predicts a reaction energy of −7.7 kcal/mol, which is clearly too exothermic, and a classical barrier [9.0 kcal/mol (Ref. 42)] in good agreement with our results. The imaginary frequency used by Garrett and co-workers is clearly too high [2833i, HF/6-31G(d)] leading to a tunneling correction of 1.17 kcal/mol. Therefore, it seems just a fortuitous cancellation of errors that BAC-MP4 data on reaction (1c) lead to reasonable thermal rate constants.

Since the CCSD(T) results presented in this work provide a significantly better description of the TS region and since they are not based on any empirical data, scaling of energies or assumptions on geometry or frequencies, their use in future reaction dynamics investigations of reaction

(1) should lead to more accurate and new insights of the reaction mechanism.

IV. CONCLUSIONS

(1) CCSD(T) is a very promising method to describe reactions of the general type $X+H_2 \rightarrow XH+H$ (X=F, OH, NH$_2$, and CH$_3$). While geometries, vibrational frequencies, atomic charges, and dipole moments of the molecules involved are accurately determined already with a VQZ+P(d,p) basis set, polarization functions of f- and g-type at heavy atoms and d-type at H atoms are needed to get accurate energy differences. This is in line with the general observation that correlation corrected energies of high accuracy require higher polarization functions with additional nodal planes. If CCSD(T)/[5s4p3d2 f1g/ 4s3p2d1f] calculations are performed, results are as good as from any multireference based calculation.

(2) The results presented in this work clearly demonstrate that accurate reaction enthalpies $\Delta H_R(300)$ and activation energies $\Delta E_a(300)$ can only be obtained from *ab initio* calculations if zero-point energies and other vibrational corrections are calculated. These are −0.4, 1.5, 3, and 2.5 kcal/mol for reaction energies (1a)–(1d) and −0.6, 0.6, 2.1, 1.7 kcal/mol for the corresponding activation energies. In view of these corrections, previous attempts to adjust *ab initio* energies to experimental reaction enthalpies and activation energies without calculating vibrational corrections are highly misleading as for the quality of the methods used.

(3) CCSD(T) can routinely provide harmonic frequencies via analytical energy gradients and, therefore, it is superior to methods that only allow calculation of frequencies by numerical methods. CCSD(T) harmonic frequencies are reported for the first time for TSs of reactions (1a)–(1d).

(4) The TSs of both the OH+H$_2$ and the NH$_2$+H$_2$ reaction are characterized by a *cis* arrangement of the reactants contrary to common chemical assumptions or previous calculations. Analysis of the charge distribution reveals that the *cis* form is stabilized because of attractive electrostatic interactions, in particular dipole–dipole attraction. Also for the first time, the bent TS of the F+H$_2$ reaction is described in detail.

(5) For the first time, accurate imaginary frequencies for reactions (1) are reported. They reveal that the PES becomes increasingly steeper when going from reaction (1a) to (1b), (1d), and (1c). Tunneling corrections calculated with the Wigner approximation are −0.50, −0.75, −0.85, and −0.81 kcal/mol for reactions (1a)–(1d), where these values are probably somewhat underestimated because of the limitations of the Wigner approximation. For high accuracy determinations of $\Delta E_a(300)$, tunneling corrections cannot be excluded as has been done in most of the previous investigations.

(6) The $\Delta E_a(300)$ values of 1.1 kcal/mol for reaction (1a) and 5.4 (5.1 with a better tunneling correction) kcal/ mol for reaction (1b) calculated in this work are the most accurate activation energies ever reported. The corresponding values for reactions (1c) and (1d) are less accu-

rate, but they also agree with experimental values within 2 kcal/mol. We note that in previous work a seemingly better agreement between *ab initio* and experimental activation energies has been reported, but this is partly due to the fact that vibrational and tunneling corrections have not been considered, partially due to the fact that *ab initio* data have been calibrated with the help of empirical data.

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