

A new direct *ab initio* dynamics method for calculating thermal rate constants from density functional theory

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We present a new direct *ab initio* dynamics methodology for calculating thermal rate constants from density functional theory (DFT). Dynamical theory is based on a full variational transition state theory plus multidimensional semiclassical tunneling approximations. We have applied this approach to the $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$ abstraction reaction using the BH&H-LYP method which is the combination of the hybrid Becke's half-and-half (BH&H) method for nonlocal exchange and Lee-Yang-Parr (LYP) functional for nonlocal correlation. The 6-311G(*d,p*) basis set was used in these calculations. To obtain quantitative results, the classical potential energy along the minimum energy path (MEP) was corrected either by scaling to match a more accurate *ab initio* results for the barrier heights or by carrying out single point calculations at selected points along the MEP at a more accurate level of *ab initio* molecular orbital (MO) theory. By comparing with our previous QCISD results and experimental rate constants, we found that DFT particular the BH&H-LYP method can provide sufficient accurate potential energy surface information for rate calculations for this system. The present direct DFT dynamics method can be used for reactive dynamics studies of reactions involving large polyatomic molecules from first principles. More work however is still needed to test the accuracy of DFT methods for such calculations.

I. INTRODUCTION

Recent development in direct *ab initio* dynamics method¹ has opened up the possibility for detailed quantitative dynamical calculations of thermal rate constants and kinetic isotope effects of gas-phase chemical reactions from first principles. It was based on a variational transition state theory augmented by multidimensional semiclassical tunneling corrections²⁻⁶ where the potential energy information can be calculated directly from a sufficiently accurate *ab initio* molecular orbital (MO) theory without having to fit this information to an analytical function. However, in order to obtain accurate dynamical results, electron correlation often must be included in calculating the potential energy surface. Including electron correlation in the MO based method increases the computational demand substantially. As a consequence, this has limited the application of such direct dynamics method to small gas phase reactions. Note for accurate rate calculations, we not only need accurate minimum energy path (MEP) information, i.e., geometries and energies along the MEP but also the generalized frequencies as functions of the reaction coordinate. These frequencies describe the width of the MEP and are calculated by performing Hessian calculations at selected points along the MEP. This is in fact the most time consuming step in our previously introduced direct dynamics method.¹ Thus, developing alternative approach which can reduce the computational demand for this step but without sacrificing the accuracy of the rate calculations is of great interest.

Density functional theory⁷⁻¹³ (DFT) with the recent availability of more accurate treatments of nonlocal exchange-correlation functionals¹⁴⁻¹⁸ has offered an alternative approach for including electron correlation at a much

less computational cost. Particularly, DFT computation formally scales as the third power of the number of basis functions N , whereas the Hartree-Fock theory scales as N^4 . Numerous validity tests^{11,19-32} has been carried out for DFT, and the general conclusion was that the DFT with nonlocal exchange-correlation functionals is comparable to the second order Møller-Plesset perturbation theory (MP2) for predicting equilibrium properties and bond energies. In a separate report,³³ we have carried out systematic tests of DFT methods for calculating transition state properties for a series of hydrogen abstraction reactions and found that the general conclusion was quite different. More specifically, among different combinations of the nonlocal exchange and correlation functionals, only one namely the Becke's half-and-half method¹⁵ for the exchange and the Lee-Yang-Parr¹⁷ gradient-corrected correlation functional (BH&H-LYP) can predict the transition state properties with comparable accuracy to and sometimes better than the MP2 level. The other nonlocal DFT methods such as the B3-LYP or B3-P86 methods, which consist of Becke's three-parameter hybrid scheme¹⁶ for exchange and either LYP (Ref. 17) or Perdew's functional¹⁸ (P86) for correlation yield unacceptable results for transition state properties, although they can predict excellent equilibrium structure properties. This conclusion however may depend on a particular reaction type and the magnitude error due to spin contamination³⁴ has not yet been addressed for such properties.

In this study, we propose a new methodology for direct dynamics calculations of thermal rate constants using density functional theory. The computational advantage of DFT would allow applications of such direct reactive dynamics method to study reactions involving larger polyatomic molecules. Furthermore, the feedback from dynamical results would provide far more information on the potential surface than just at the stationary points. Such information can be

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TABLE I. Theoretical and experimental geometries (distances in Å, angle in deg) and harmonic frequencies (cm^{-1}).

		Geometry			Harmonic frequencies		
		BH&H-LYP	QCISD ^a	Expt. ^b	BH&H-LYP	QCISD ^a	Expt. ^b
H ₂	R_{HH}	0.7384	0.743	0.741	4518	4422	4401
CH ₃	R_{CH}	1.0733	1.083	1.076	3187	3128	3002
					500	432	580
					3370	3310	3184
					1453	1436	1383
CH ₄	R_{HH}	1.0837	1.093	1.086	3107	3047	2917
					1609	1573	1534
					3217	3167	3019
					1389	1367	1306
CH ₃ ...H'...H''	R_{CH}	1.3874	1.390		3151	3090	
	$R_{\text{CH}'}$	1.0789	1.089		1807	1764	
	$R_{\text{H}'\text{H}''}$	0.8962	0.899		1127	1111	
	$\angle\text{HCH}'$	103.4	103.7		3297	3236	
					1482	1459	
				1177	1152		
				558	534		
				1411i	1529i		

^aFrom Ref. 1.^bExperimental geometries and harmonic frequencies are from Refs. 69 and 70, respectively.

used for further assessing the accuracy of the DFT functionals. To test the feasibility and accuracy of the new method, we have applied it to the $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$ abstraction reaction. The present results were then compared with previous calculations using the QCISD method¹ or the J3 analytical potential energy function,³⁵ and with experimental data.³⁶⁻⁶³

II. METHODOLOGY

Dynamical calculations were based on a full canonical variational transition state theory (CVT) plus multidimensional semiclassical tunneling methods, particularly the zero-curvature and centrifugal-dominant small curvature adiabatic ground-state approximations, denoted as ZCT and SCT, respectively. The detailed methodology had been discussed elsewhere.¹ The potential energy information needed for rate calculations, i.e., the energy, gradients, and Hessians, is calculated from the nonlocal BH&H-LYP functionals using the 6-311G(*d,p*) (Ref. 64) basis set.

The minimum energy path was calculated in the mass-weighted internal coordinate using the Gonzalez-Schlegel method⁶⁵ with the step size of 0.05 amu^{1/2} bohr. Unstructured Hessian grids along the minimum energy path were determined using the focusing technique as proposed in our earlier study. Other computational details are the same as in our previous direct *ab initio* dynamics calculations of rate constants for this reaction using the QCISD method. All electronic structure calculations were done using the GAUSSIAN 92/DFT program⁶⁶ and rate calculations were done using our new DIRATE program.⁶⁷

III. RESULTS AND DISCUSSION

In our previous study¹ of the $\text{H} + \text{CH}_4 \leftrightarrow \text{CH}_3 + \text{H}_2$ reaction, we had found that the QCISD/6-311G(*d,p*) level of theory is able to predict structure and vibrational frequency information at the stationary points as accurate as the more

expensive CCSD(T)/cc-VQZ level where cc-VQZ (Ref. 68) denotes Dunning's correlated consistent [5s4p3d/4s3p] basis set. The QCISD forward and reverse classical barriers however are about 1 kcal/mol too high. In order to obtain quantitative rate constants, the potential energy along the QCISD MEP was scaled by a factor of 0.86 to reproduce the previously calculated classical barrier from single point CCSD(T)/cc-pVQZ calculations,⁶⁹ where cc-pVQZ (Ref. 68) denotes Dunning's correlation consistent [5s4p3d2f1g/4s3p2d1f] basis set, at the CCSD(T)/cc-VQZ geometries. Thus, in discussion on the accuracy of the BH&H-LYP method below, we can compare the DFT predictions to the QCISD results for the geometry and vibrational frequencies. However, for energetics information such as the classical barrier heights and reaction energy, it is more informative

TABLE II. Heat of reaction and barrier heights^a (kcal/mol) for the $\text{CH}_4 + \text{H} \leftrightarrow \text{CH}_3 + \text{H}_2$ reaction.

Level	ΔE	ΔH_0^\ddagger	ΔV_f^\ddagger	ΔV_r^\ddagger
BH&H-LYP/6-311G(<i>d,p</i>)	1.4	-1.9	12.6(11.1) ^a	11.2(13.0) ^a
PMP4/6-311+G(2df,2pd)	2.9	-0.4	14.6(13.1)	11.7(13.5)
//BH&H-LYP/6-311G(<i>d,p</i>)				
PMP4/6-311G(<i>d,p</i>)	3.23		15.45	12.22
//BH&H-LYP/6-311G(<i>d,p</i>)				
PMP4/6-311G(<i>d,p</i>)	3.25		15.46	12.20
//QCISD/6-311G(<i>d,p</i>)				
QCISD/6-311G(<i>d,p</i>) ^b	2.5	-0.7	16.3(14.8)	13.8(15.5)
CCSD(T)/cc-pVQZ	3.5	-0.3	15.3(13.1)	11.8(13.3)
//CCSD(T)/cc-VQZ ^c				
J3 ^d	2.8	-0.02	12.9(11.8)	10.1(11.9)
Expt. ^e	2.6	-1.3	(13.3±0.5)	(14.6±0.4)

^aZero-point energy corrected barriers are given in the parentheses.^bReference 1.^cReference 72.^dReference 35.^eReference 71.

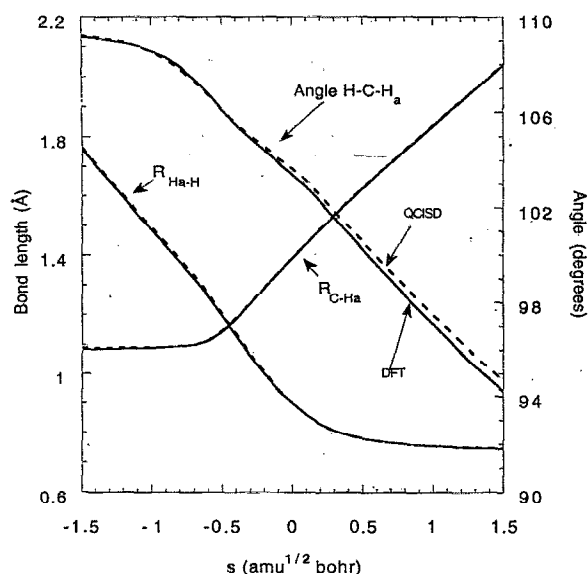


FIG. 1. Geometries along minimum energy path for the $\text{CH}_4 + \text{H} \leftrightarrow \text{CH}_3 + \text{H}_2$ reaction plotted vs the reaction coordinate s in the mass-weighted internal coordinates. Solid curves are from the present BH&H-LYP/6-311G(d,p) calculations, and dashed curves are from the previous QCISD/6-311G(d,p) calculations (Ref. 1).

and consistent with our previous study to compare the DFT results to the most accurate predictions to date, namely the CCSD(T)/cc-pVQZ results.⁶⁹

In a separate report,³³ we have discussed in more details the performance of different DFT methods for predicting transition state properties for a set of hydrogen abstraction reactions. For completeness, the geometries and vibrational frequencies at the stationary points for the $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$ reaction calculated at the BH&H-LYP level are given in Table I along with the previous QCISD/6-311G(d,p) results¹ and experimental data.^{70,71} As mentioned previously, the BH&H-LYP method underestimates the equilibrium bond lengths slightly while overestimates the equilibrium vibrational frequencies by about 4%. For the $\text{H}_3\text{C}\dots\text{H}\dots\text{H}$ transition state geometry and vibrational frequencies, the BH&H-LYP method yields excellent agreement with the previous QCISD results. In particular, the maximum differences are 0.01 Å in the bond length, 0.3 degrees in the angle, and 61 cm^{-1} in the bound mode frequencies.

Reaction energies and barrier heights are listed in Table II. The BH&H-LYP classical barriers were found to be too low by 2.7 and 0.6 kcal/mol for the forward and reverse reactions, respectively, as compared to the CCSD(T)/cc-pVQZ results. Single point spin projected fourth-order Møller-Plesset perturbation theory (PMP4) calculations with the larger 6-311+G($2df,2pd$) basis set at the BH&H-LYP/6-311G(d,p) geometries bring the differences in the classical barriers to less than 0.7 kcal/mol and also yield the reaction enthalpy at 0 K to be -0.36 kcal/mol as compared to the CCSD(T)/cc-pVQZ value of -0.3 kcal/mol and experimental value from JANAF tables of -0.02 kcal/mol. Using the BH&H-LYP zero-point energy correction, the PMP4//

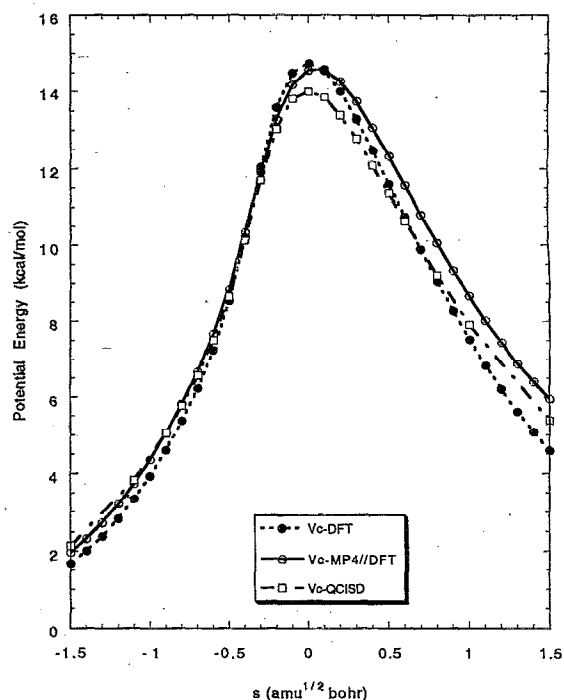


FIG. 2. The classical potential $V_{\text{MEP}}(s)$ energy along the MEP as functions of the reaction coordinate s , (—) is from PMP4/6-311+G($2df,2pd$) single point calculations along the BH&H-LYP/6-311G(d,p) MEP, (---) is from BH&H-LYP/6-311G(d,p) calculations with V_{MEP} scaled by a factor of 1.174, (---) is from the previous QCISD/6-311G(d,p) calculations with V_{MEP} scaled by a factor of 0.86 (Ref. 1). Circles and squares are points on the MEP where Hessian information is available.

BH&H-LYP zero-point energy corrected barriers for both forward and reverse directions are within 0.2 kcal/mol to the CCSD(T)/cc-pVQZ values and are also in good agreement with experimental data.⁷² Note there is a difference of about 2 kcal/mol in the PMP4/6-311+G($2df,2pd$)/BH&H-LYP/6-311G(d,p) and QCISD/6-311G(d,p) barriers. This difference can be due to the differences in geometries, basis sets, and/or levels of theory. To sort this out, we have carried two additional PMP4 single point calculations using the same 6-311G(d,p) basis set but at the BH&H-LYP and QCISD optimized geometries and the results were also listed in Table II. First, the differences in the reaction energy and the classical barrier heights between the PMP4/6-311G(d,p)/BH&H-LYP/6-311G(d,p) and PMP4/6-311G(d,p)/QCISD/6-311G(d,p) are of order 0.02 kcal/mol, thus the contribution from the differences in the DFT and QCISD geometries are quite small. Second, comparing the PMP4/6-311G(d,p)/QCISD/6-311G(d,p) and QCISD/6-311G(d,p) results yields contribution from the differences in the methodology, i.e., PMP4 vs QCISD. More specifically, PMP4 predicts the reaction energy higher by 0.7 kcal/mol while yields the classical barrier heights lower by at most 1.6 kcal/mol from the QCISD results. Finally, comparing the PMP4/6-311+G($2df,2pd$)/BH&H-LYP/6-311G(d,p) and PMP4/6-311G(d,p)/BH&H-LYP/6-311G(d,p) results yields contribution from the difference in the basis set at the PMP4 level. In fact, using the larger basis set lowers the reaction energy

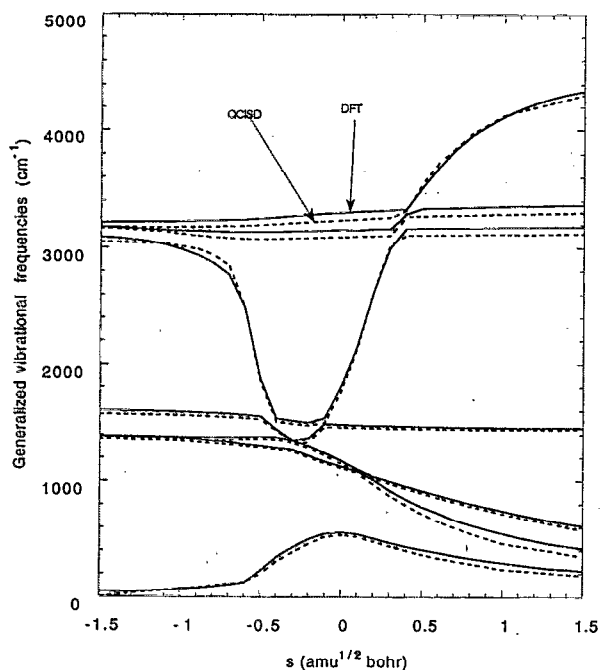


FIG. 3. Harmonic vibrational frequencies along the reaction coordinate s . Solid curves are the BH&H-LYP/6-311G(d,p) results and dashed curves are the previous QCISD/6-311G(d,p) results.

by 0.3 kcal/mol and the classical barrier heights by at most 0.9 kcal/mol. Consequently, the differences of the order 2 kcal/mol in the classical barrier heights between the PMP4/6-3311+G(2df,2pd)//BH&H-LYP/6-311G(d,p) and QCISD/6-311G(d,p) levels are due mostly to the combination of the differences in the levels and basis sets used, i.e., the PMP4 vs QCISD level and the 6-311+G(2df,2pd) vs 6-311G(d,p) basis set, and not so much on the differences in the DFT and QCISD geometries.

The geometries along the minimum energy path calculated by both the BH&H-LYP are shown in Fig. 1 with our previous QCISD results. We found that the BH&H-LYP method yields the active C-H_a and H_a-H bond lengths and H-C-H_a angle as functions of the reaction coordinate in excellent agreement with the QCISD results. More specifically, Fig. 1 shows an unnoticeable difference in the active bond lengths and a difference of less than 1 deg in the H-C-H_a angle between the two methods.

The above result has an important implication that one can further improve the accuracy of the potential energy along the MEP by carrying out single point calculations at selected points along the DFT MEP using a more accurate *ab initio* method. In fact, we have employed such approach as well as our previous approach of scaling the potential energy along the MEP by a single factor to match the classical barrier calculated from a more accurate method. In particular, in one approach the BH&H-LYP classical potential energy curve was scaled by a factor of 1.175, which is the average of the two scaling factors for reproducing the forward and reverse classical barriers calculated at the CCSD(T)/cc-pVQZ level of theory by Kraka *et al.*⁶⁹ In the other ap-

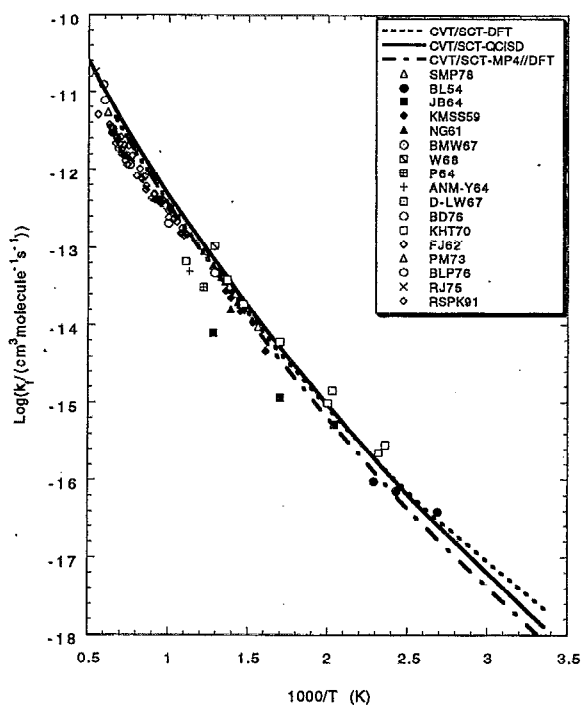


FIG. 4. Arrhenius plot of the forward rate constants vs $1/T$. The (---) and (-.-) curves are the present CVT/SCT results from the scaled BH&H-LYP/6-311G(d,p) and PMP4/6-311+G(2df,2pd)//BH&H-LYP/6-311G(d,p) methods, respectively. The solid curve is from the previous CVT/SCT-QCISD/6-311G(d,p) results (Ref. 1); SMP78, Ref. 53; BL54, Ref. 37; JB64, Ref. 38; KMSS59, Ref. 39; NG61, Ref. 40; BMW67, Ref. 41; W68, Ref. 42; P64, Ref. 43; ANM-Y64, Ref. 44; D-LW67, Ref. 45; BD76, Ref. 46; KHT70, Ref. 47; FJ62, Ref. 48; PM73, Ref. 49; BLP76, Ref. 50; RJ75, Ref. 51; RSPK91, Ref. 52.

proach, single point calculations were performed at selected points along the BH&H-LYP MEP using the spin projected fourth-order Møller-Plesset perturbation theory with the 6-311+G(2df,2pd) basis set, and are denoted as PMP4//BH&H-LYP. The improved (scaled) classical potential energy curves along the BH&H-LYP MEP are plotted in Fig. 2 with the previous QCISD classical potential curve, which was also scaled by a factor of 0.86 to reproduce the same previous CCSD(T) results. Note that both the scaled DFT as well as the PMP4//BH&H-LYP classical potential curves have about the same width compared to the scaled QCISD curves, though the forward barrier heights are higher by about 1 kcal/mol.

Generalized frequencies calculated at the BH&H-LYP/6-311G(d,p) level vs the reaction coordinate are plotted in Fig. 3 along with the previous QCISD/6-311G(d,p) results. Note that excellent agreement was found between the BH&H-LYP and QCISD results, though the former are slightly larger.

The Arrhenius plots of the calculated and experimental forward and reverse rate constants are shown in Figs. 4 and 5, respectively. Note that our present BH&H-LYP results for the forward and reverse rate constants are in excellent agreement with the experimental data over the wide range of temperature from 300 to 1500 K. The agreement is even slightly

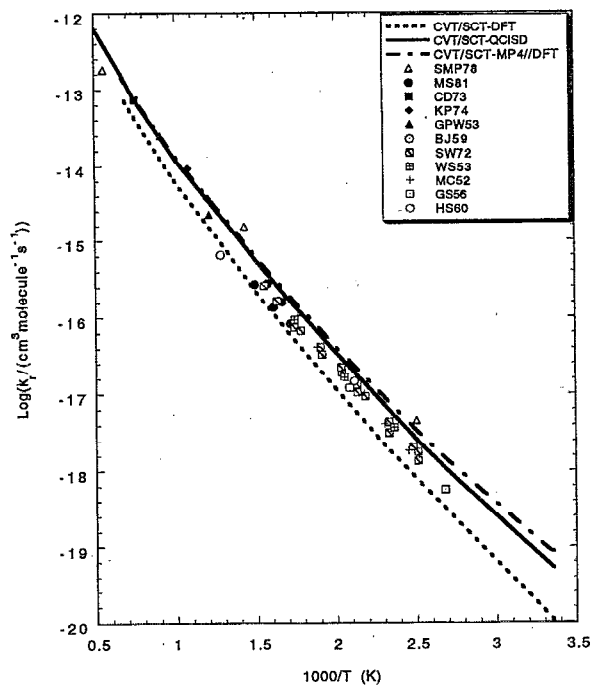


FIG. 5. Arrhenius plot of the reverse rate constants vs $1/T$. The (---) and (—) curves are the present CVT/SCT results from the scaled BH&H-LYP/6-311G(*d,p*) and PMP4/6-311+G(2*df*,2*pd*)//BH&H-LYP/6-311G(*d,p*) methods, respectively. The solid curve is from the previous CVT/SCT-QCISD/6-311G(*d,p*) results (Ref. 1). SMP78, Ref. 53; MS81, Ref. 54; CD73, Ref. 55; KP74, Ref. 36; GPW53, Ref. 56; BJ59, Ref. 57; SW72, Ref. 58; WS53, Ref. 59; MC52, Ref. 60; GS56, Ref. 61; HS60, Ref. 62.

better than the previous QCISD results for the forward reaction (see Fig. 4) though not as good for the reverse rate constants. The PMP4//BH&H-LYP calculations predict both the forward and reverse rate constants in excellent agreement with the experimental data and with our previous QCISD results.

The calculated forward and reverse rate constants are listed in Tables III and IV, respectively, along with the most

recently recommended values from the Arrhenius fit to experimental data by Baulch *et al.*⁶³ and previous calculated values from the J3 analytical potential energy function (PEF). For the forward $\text{CH}_4 + \text{H}$ reaction, notice that above 600 K, both the BH&H-LYP and PMP4//BH&H-LYP yield excellent agreement with the experimental recommended data though slightly smaller rate constants by at most 20%. Below 500 K, the BH&H-LYP rate constants are larger than the Baulch *et al.*'s⁶³ recommended values by up to a factor of 1.5 at 372 K whereas the PMP4//BH&H-LYP rate constants are slightly smaller with a maximum deviation factor of 0.8 at 372 K. Since only extrapolations of Baulch *et al.*'s⁶³ recommended values are available for temperature below 372 K, quantitative comparisons are not given here. The BH&H-LYP and PMP4//BH&H-LYP results also yield excellent quantitative agreement with rate constants previously calculated from the J3 PEF and from the QCISD method, though the PMP4//BH&H-LYP rate constants are slightly smaller for temperature below 600 K. For the reverse $\text{CH}_3 + \text{H}_2$ reaction, the calculated BH&H-LYP rate constants are slightly smaller than Baulch *et al.*'s⁶³ recommended values with the deviation factor increases to 2.76 as the temperature increases to 1500 K. The PMP4//BH&H-LYP results on the other hand give generally better agreement with previous QCISD and J3 PEF calculations, though they are slightly too large compared to the experimental recommended data for temperature below 1000 K. As mentioned in our earlier study¹ that there are large variations among different recommended experimental rate constants. Our present results are in fact within such uncertainty. It is also important to point out that in the present study the vibrational partition functions were calculated quantum mechanically within the harmonic approximation. Previous study³⁵ had shown that including anharmonicity lowers the rate constants thus it would improve the agreement of the present PMP4//BH&H-LYP results with the experimental data while worsen the agreement for BH&H-LYP results.

TABLE III. Rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reaction $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$.^a

<i>T</i> (K)	MP4 ^c				
	BH&H-LYP ^b	//BH&H-LYP	QCISD ^d	J3 ^e	Baulch <i>et al.</i> ^f
298	2.1E-18	8.4E-19	1.3E-18	9.9E-19	[7.4E-19]
300	2.3E-18	9.2E-19	1.4E-18	1.1E-18	[8.2E-19]
372	3.1E-17	1.7E-17	2.6E-17	2.3E-17	2.1E-17
400	7.1E-17	4.3E-17	6.6E-17	6.0E-17	5.7E-17
424	1.4E-16	9.0E-17	1.4E-16	1.2E-16	1.2E-16
500	8.4E-16	6.3E-16	9.3E-16	8.0E-16	8.4E-16
600	5.3E-15	4.4E-15	6.3E-15	5.0E-15	5.6E-15
667	1.4E-14	1.2E-14	1.7E-14	1.3E-14	1.5E-14
1000	3.6E-13	3.6E-13	4.7E-13	2.9E-13	3.8E-13
1340	2.4E-12	2.5E-12	3.1E-12	1.8E-12	2.6E-12
1500	4.5E-12	4.7E-12	5.9E-12	3.2E-12	5.0E-12

^aValues in brackets are extrapolations.

^bBH&H-LYP/6-311G(*d,p*) level with the V_{MEP} scaled by a factor of 1.174.

^cPMP4/6-311+G(2*df*,2*pd*)//BH&H-LYP/6-311G(*d,p*).

^dPrevious CVT/SCT results at the QCISD/6-311(*d,p*) level with the V_{MEP} scaled by a factor of 0.86 (Ref. 1).

^ePrevious ICVT/SCSAG results from the J3 semiempirical PEF (Ref. 35).

^fMost recently recommended values from the Arrhenius fit of Baulch *et al.* (Ref. 63).

TABLE IV. Rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reaction $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$.^a

T (K)	BH&H-LYP ^b	MP4 ^c //BH&H-LYP	QCISD ^d	J3 ^e	Baulch <i>et al.</i> ^f
298	1.5E-20	8.2E-20	5.2E-20	1.7E-19	[8.5E-21]
300	1.7E-20	9.0E-20	5.7E-20	1.9E-19	[9.6E-21]
372	3.1E-19	1.4E-18	1.1E-18	3.2E-18	3.7E-19
400	7.9E-19	3.4E-18	2.6E-18	7.4E-18	1.1E-18
424	1.6E-18	6.7E-18	5.3E-18	1.4E-17	2.5E-18
500	1.1E-17	4.1E-17	3.4E-17	7.6E-17	2.2E-17
600	7.9E-17	2.4E-16	2.1E-16	3.9E-16	1.7E-16
667	2.2E-16	6.1E-16	5.4E-16	9.1E-16	5.1E-16
1000	6.1E-15	1.3E-14	1.2E-14	1.4E-14	1.7E-14
1340	4.3E-14	8.0E-14	7.6E-14	7.5E-14	1.2E-13
1500	8.7E-14	1.5E-13	1.4E-13	1.4E-13	2.4E-13

^aValues in brackets are extrapolations.

^bBH&H-LYP/6-311G(*d,p*) level with the V_{MEP} scaled by a factor of 1.174.

^cPMP4/6-311+G(2*df*,2*pd*)//BH&H-LYP/6-311G(*d,p*).

^dPrevious CVT/SCT results at the QCISD/6-311G(*d,p*) level with the V_{MEP} scaled by a factor of 0.86 (Ref. 1).

^ePrevious ICVT/SCSAG results from the semiempirical J3 PEF (Ref. 35).

^fMost recently recommended values from the Arrhenius fit of Baulch *et al.* (Ref. 63).

IV. CONCLUSION

We have presented a new methodology for calculating thermal rate constants from first principles. It is based on a full variational transition state theory plus multidimensional semiclassical tunneling corrections with the potential energy surface information calculated directly from a density functional theory. We have applied the new method to calculate rate constants of the $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$ reaction. The combination of a hybrid Becke half-and-half exchange and Lee-Yang-Parr correlation (BH&H-LYP) functionals was used to calculate the potential energy surface using the 6-311G(*d,p*) basis set. We found that the BH&H-LYP generalized frequencies and transition state geometries as functions of the reaction coordinate agree very well our previous QCISD calculations. To improve the energetics information along the MEP, we have either scaled the potential energy along the MEP to match the more accurate classical barrier or performed series of single point calculations at selected points along the MEP at a higher level of *ab initio* theory. Both approaches yield rate constants in excellent agreement with experimental data and with our previous QCISD results.

We conclude that the proposed direct *ab initio* dynamics method provides a powerful and practical dynamical simulation tool by combining the computational advantages of variational transition state theory and density functional theory. With the new tool, it is now feasible to carry out detailed dynamics and mechanism studies of large and more complex chemical reactions from first principles. Much work however still needs to be done to assess the accuracy and range of applicability of the proposed method. Progress so far in our lab in dynamical studies of other types of chemical reactions using the present tool is quite encouraging.

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