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Citation: The Journal of Chemical Physics **112**, 9375 (2000); doi: 10.1063/1.481602 View online: http://dx.doi.org/10.1063/1.481602 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/112/21?ver=pdfcov Published by the AIP Publishing

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Potential energy surface, thermal, and state-selected rate coefficients, and kinetic isotope effects for $CI+CH_4\rightarrow HCI+CH_3$

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(Received 25 October 1999; accepted 6 March 2000)

A new potential energy surface is reported for the gas-phase reaction $CI+CH_4\rightarrow HCI+CH_3$. It is based on the analytical function of Jordan and Gilbert for the analog reaction $H+CH_4\rightarrow H_2+CH_3$, and it is calibrated by using the experimental thermal rate coefficients and kinetic isotope effects. The forward and reverse thermal rate coefficients were calculated using variational transition state theory with semiclassical transmission coefficients over a wide temperature range, 200–2500 K. This surface is also used to analyze dynamical features, such as reaction-path curvature, the coupling between the reaction coordinate and vibrational modes, and the effect of vibrational excitation on the rate coefficients. We find that excitation of C–H stretching modes and Cl–H stretching modes enhances the rate of both the forward and the reverse reactions, and excitation of the lowest frequency bending mode in the CH_4 reactant also enhances the rate coefficient for the forward reaction. However, the vibrational excitation of the CH_3 umbrella mode (lowest frequency mode in products) slows the reaction at temperatures below 1000 K, while above 1000 K it also accelerates the reaction. © 2000 American Institute of Physics. [S0021-9606(00)00321-4]

I. INTRODUCTION

Chlorine atom chemistry is of great importance over a wide temperature range. At low temperatures (200-300 K), Cl plays an active role as ozone destroyer in the atmosphere, and at high temperatures (1000-2500 K) it is important for combustion. In recent years the reaction with methane, $Cl+CH_4 \rightarrow HCl+CH_3$, has been widely studied as a mechanism to eliminate chlorine atoms from the atmosphere by converting them into inactive HCl. This reaction is also prototypical for halogen-hydrocarbon combustion. Experimentally, this reaction has been the subject of a number of studies using various experimental techniques over a range of temperatures.¹⁻²² The rate coefficients determined by various experimental groups agree well with each other at room temperature, with a recommended value of $1.0 \times 10^{-13} \,\mathrm{cm}^3$ molecule⁻¹ s⁻¹ (Refs. 12, 14). In addition to rate constants, some experimental studies^{1,13,16,17,20} provide kinetic isotope effects (KIEs), which are ratios of rate coefficients for isotopologs or isotopomers and which are a sensitive test of the shape of the potential energy surface (PES), especially the barrier width and vibrational force constants near the dynamic bottleneck. The ${}^{12}C/{}^{13}C$ KIE is 1.066 ± 0.002 [Refs. 16(a) and 16(b)] at 298 K, the CH₄/CD₄ KIE has been determined to be 15±4 at 295-304 K (Refs. 1, 13, 20, 22), decreasing to 5 at 400 K (Ref. 1), and the CH₄/CH₃D KIE is 1.6 at 250 K [Ref. 16(c)], decreasing to 1.4–1.5 at 295–298 K [Refs. 13, 16(c), 22]. Note that the KIE is defined as the

ratio between two rate coefficients, with the one corresponding to the reaction involving the lighter isotopolog in the numerator.

Ab initio calculations²³⁻²⁸ have predicted potential energy barrier heights, V^{\neq} , ranging from 8.0 to 9.9 kcal/mol, and vibrationally adiabatic ground-state barrier heights, ΔV_a^{G} (i.e., zero-point-inclusive barrier heights), ranging from 3.6 to 5.5 kcal/mol. For a more complete study one needs to know more than just the properties of the saddle point. One example of a more complete study is the mapping of the reaction valley near all state-selected dynamical bottlenecks. Furthermore, the title reaction is an interesting system because it represents a heavy-light-heavy mass combination (H-L-H), which, a priori, is a good candidate for large "corner cutting" tunneling effects in which reaction-path curvature leads to internal centrifugal forces that tend to make the system leave the minimum energy path (MEP),²⁹ and tunneling paths on the concave side of the MEP are favored. It is possible that tunneling is enhanced when the system leaves the valley described by a quadratic expansion around the MEP to "cut the corner" of the potential energy surface to a large extent. To study these effects or to rule them out requires a description of the PES over a wider region than is required to only describe the zero-point vibrational valley around the MEP.²⁹ Rate coefficients for the title reaction have been calculated by several groups.^{24-27,30,31} Chen et al.²⁴ calculated rate coefficients for the reverse reac-

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tion based on RRKM theory³² with a tunneling correction evaluated using the simple Wigner factor,³³ and they obtained excellent agreement with experimental values. However, since the Wigner factor ignores variational effects on the location of the effective barrier for tunneling and since it includes only the lowest-order nonzero term in a power series in \hbar , this agreement may be fortuitous. Gonzalez-Lafont et al.²⁵ used ab initio information along the reaction path to calculate rate coefficients using canonical variational transition state theory (CVT) (Refs. 34,35) with small-curvature semiclassical adiabatic ground-state (SCSAG) (Ref. 35) tunneling contributions; their calculations agree with the experimental values within a factor of 5.5 at 300 K. Dobbs and Dixon²⁶ used conventional transition state theory to calculate the rate coefficients; they obtained values lower than experiment at low temperature but in good agreement with experiment for T>300 K. Duncan and Truong²⁷ calculated rate coefficients using CVT and centrifugal-dominant SCSAG tunneling (SCT),³⁶ based on *ab initio* information on the reaction path. Their rate coefficients are significantly lower than the experimental values by factors increasing from 2.2 to 11.2 as the temperature decreases from 500 to 200 K. In 1996, two of the present authors reported an analytical PES for this reaction³⁰ based on the CH₅ PES of Joseph *et al.*,³⁷ and they carried out rate coefficient calculations using CVT with large-curvature tunneling³⁸ (LCT) transmission coefficients including information about the corner cutting region of the potential energy surface. Although the rate coefficients were in good agreement with the experimental data, the CH₄/CD₄ KIEs were too high compared to the experimental ones. More recently, one of the authors and co-workers³¹ reported dual-level direct dynamics calculations of rate coefficients and deuterium and carbon-13 KIEs by CVT with microcanonical optimized multidimensional tunneling (μOMT) (Ref. 38) and obtained rate coefficients and KIEs in good agreement with experimental data, although the lowerlevel surface has a "deep" well in reactant valley.

In the present paper, to correct the deficiency of the earlier PES, we report the construction of a new analytical PES for the title reaction based on the PES for the H+CH₄ reaction by Jordan and Gilbert,³⁹ which has the advantage that is symmetric with respect to any permutation of the four CH₄ hydrogens. The previously reported surface³⁰ treats the hydrogen being abstracted differently than the remaining hydrogen atoms. (As pointed out by Jordan and Gilbert,³⁹ the asymmetric hydrogen treatment is an inconvenient feature when the analytical surface is used for trajectory calculations.) We then use this PES to perform variational transition state theory calculations of thermal and vibrational-stateselected rate coefficients and KIEs. For the thermal rate coefficients and KIEs we include multidimensional tunneling effects, by both the SCT (Ref. 36) and LCT (Ref. 38) methods.

II. METHODS AND CALCULATION DETAILS

A. Estimation of the barrier height

Dobbs and Dixon²⁶ noted that the classical barrier height is very sensitive to extension of the one-electron basis set.

For this reason and because of the difficulty of converging higher-order correlation effects, we believe that none of the unextrapolated theoretical calculations²³⁻²⁸ is entirely reliable. The first attempt to extrapolate the barrier height was carried out by Truong et al.23 who used the scaling all correlation-energy (SAC) (Ref. 40) method to extrapolate second-order Møller-Plesset perturbation theory (MP2) to the complete basis set and full configuration interaction level. Their calculation is, by construction, in good agreement with the experimental heat of reaction, and it yields a barrier height of 7.9 kcal/mol. Recently, one of us⁴¹ has proposed a new method, the "infinite-basis" (IB) method, for extrapolation to a complete one-electron basis set for correlated electronic structure calculations. This method is based on the extrapolation of energies obtained by using correlation-consistent polarized double- and triple-zeta basis sets,⁴² cc-pVDZ and cc-pVTZ (henceforth abbreviated pDZ and pTZ). The extrapolated energies are more accurate than even larger basis sets.41,43

The total energy for the basis set limit is written as^{41,43}

$$E_{\infty}^{\text{total}} = E_{\infty}^{\text{HF}} + E_{\infty}^{\text{corr}},\tag{1}$$

$$E_{\infty}^{\text{total}} = \frac{3^{\alpha}}{3^{\alpha} - 2^{\alpha}} E_{3}^{\text{HF}} - \frac{2^{\alpha}}{3^{\alpha} - 2^{\alpha}} E_{2}^{\text{HF}} + \frac{3^{\beta}}{3^{\beta} - 2^{\beta}} E_{3}^{\text{corr}} - \frac{2^{\beta}}{3^{\beta} - 2^{\beta}} E_{2}^{\text{corr}}, \qquad (2)$$

where "corr" is correlation energy, "HF" is Hartree–Fock energy, α and β are parameters, and the subscripts 2 and 3 denote use of the pDZ and pTZ basis sets. The values of α and β that are employed in this paper where taken from Ref. 43, where they were fitted in order to reproduce the experimental atomization energies of a series of test molecules. We will apply the IB method at two levels of electron correlation, namely, MP2 (Møller–Plesset second-order perturbation theory with correlation of only the valence electrons), and CCSD(T) (singles and doubles coupled-cluster approach including a quasiperturbative estimate of connected triple excitations, again correlating only valence electrons).

In the present work we have optimized all the stationary point geometries at the MP2/pTZ level and we carry out single-point calculations with the IB method. The geometric parameters of all the stationary points are listed in Table I, together with other *ab initio* calculations and experimental data, when available, for comparison. The optimum geometry predicted by all the calculation levels listed in Table I have a linear C–H'–Cl angle and a saddle point with C_{3v} symmetry.

The MP2/pTZ reactant and product geometries agree with the experimental data, and the MP2/pTZ transition structure (TS) agrees with other *ab initio* calculations (within a 0.01 Å range). Among the four high-level *ab initio* calculations compared in Table I, we note that the DFT calculations of Ref. 27 stand out for having a longer C–H' bond than the other three calculations. The situation is more complicated with respect to the barrier height because there is a significant basis set effect on the classical barrier height. This behavior agrees with the more general experience of many

TABLE I. Ab initio and SAC properties for reactant, product, and saddle point.

		MP2/p	TZ ^{a,b}					TS		
Parameter	$\mathrm{CH}_3\mathrm{H}'$	CH ₃	H'Cl	Cl	TTBGS ^c	DD^d	DT ^e	MP2/pTZ ^a	CCSD(T)/IB ^f	Best ^g
Geome	try ^h									
R(CH)	1.085	1.074			1.086	1.078	1.077	1.080		
R(CH')	1.085				1.388	1.375	1.443	1.359		
R(ClH')			1.273		1.431	1.452	1.431	1.451		
Energ	y ⁱ									
ΔE					6.7	6.8 ^j	8.9	6.2	6.0	6.8
ΔH_0					1.4	1.9	3.6	0.9 ^k	1.4	2.2
V^{\neq}					7.9	8.9	9.9	9.0	7.6	8.4
$\Delta V_a^{G\neq}$					3.7	4.9	5.5	4.8 ^k	3.7	4.5
Spin	l									
$\langle S^2 \rangle^1$		0.762		0.759				0.784		

^aThis work: optimized at the MP2/pTZ level.

^bReactants and products.

^cFrom Ref. 23. MP2-SAC/MC-311G(2d,d,p) energies and geometries with MP2/MC-311G(2d,d,p) frequencies.

^dFrom Ref. 26. MP2/TZ+2P level.

^eFrom Ref. 27. DFT/6-311G(*d*,*p*) level.

^fThis work: CCSD(T)/IB//MP2/pTZ with parameters from Ref. 43. See Table II.

^gSame as f and including +0.8 kcal/mol from the spin-orbit interaction.

^hH' is the hydrogen abstracted. Experimental values (Ref. 44): CH₄ (T_d): 1.091 Å, CH₃(D_{3h}): 1.079 Å, ClH (C_{xy}): 1.275 Å.

 ${}^{i}\Delta E$: zero-point-exclusive energy of reaction, also called classical energy of reaction; ΔH_0 : zero-point-inclusive energy of reaction, equal to enthalpy of reaction at 0 K; V^{\neq} : zero-point-exclusive barrier height; also called classical barrier height; $\Delta V_a^{G^{\neq}}$: vibrationally adiabatic ground-state barrier height evaluated at the saddle point, equal to the conventional transition state theory approximation to the enthalpy of activation at 0 K.

^jSingle-point CCSD(T)/cc-pVQZ energy calculations from Ref. 26.

^kZero-point energy at the MP2/MC-6311G(2d,d,p) level from Ref. 23.

¹Calculated at the MP2/pTZ level.

workers⁴⁵ that the truncation of the one-electron basis set is a major source of error in most *ab initio* calculations of molecular energies. Therefore, we have calculated the energy changes (reaction and activation) based on the IB basis-set extrapolation method^{41,43} to obtain the basis-set limit for the energy at this level. Tables I and II give the IB values for the energy of the product and the transition structure relative to reactants, together other theoretical and experimental values for comparison. Note that this is the first time that the IB method has been used to calculate barrier heights. The IB barrier height is in excellent agreement with the previous²³ SAC calculation, being only 0.3 kcal/mol lower.

The chlorine atom has two low-lying electronic states with a separation of $\Delta E = 882 \text{ cm}^{-1}$ (2.5 kcal/mol) (Ref. 44) due to spin–orbit coupling. In nonrelativistic calculations, such as the present *ab initio* calculations, both states would

TABLE II. Single-point energy calculations (kcal/mol).

	ΔE	$V^{ eq}$
MP2/pTZ	6.2	9.0
MP2/IB(orig.) ^a	4.6	7.0
MP2/IB ^b	4.3	6.6
CCSD(T)/pTZ	7.3	9.6
CCSD(T)/IB(orig.) ^a	6.2	8.1
CCSD(T)/IB ^b	6.0	7.6
CCSD(T)/IB ^{b,c}	6.8	8.4

^aExtrapolated to infinite basis with original parameters of Ref. 41. ^bExtrapolated to infinite basis with improved parameters of Ref. 43. ^cIncludes spin–orbit contributions of +0.8 kcal/mol. have the same energy. Including the spin-orbit effect would lower the energy of the lower state of the Cl atom to onethird of ΔE below its nonrelativistic energy (0.8 kcal/mol). As usual, we assume that at the saddle point the spin-orbit coupling is essentially fully quenched and the nonrelativistic treatment will give a good approximation to the correct energy. As discussed previously,³¹ the effect of the lowering in the reactants energy due to the spin-orbit coupling can be simulated in our nonrelativistic calculations by adding 0.8 kcal/mol to the barrier height and reaction enthalpy. Note that the quenching of the spin-orbit interaction energy of Cl has been usually ignored by other workers, and indeed the uncertainty in the usual ab initio calculations does not allow one to eliminate other sources of error of this magnitude. Nevertheless, the spin-orbit effect is systematic, and it should be included. With this contribution added, the MP2/ pTZ enthalpy of reaction at 0 K is 2.2 kcal/mol, only 1.2 kcal/mol higher than the experimental value⁴⁴ of 1.0 kcal/ mol.

B. Calibration of the analytical PES

The potential energy surface for the $Cl+CH_4$ \rightarrow HCl+CH₃ reaction is similar to that for the well-studied H+CH₄ \rightarrow H₂+CH₃ reaction. Both are hydrogen abstraction reactions from methane to yield the CH₃ radical, and there is a slow change in geometry of the CH₃ group from pyramidal to planar along the reaction path. With this similarity in mind, we have modified several parameters of the H+CH₄ \rightarrow H₂+CH₃ surface of Jordan and Gilbert³⁹ in order to get an analytical PES for the title reaction. The new surface consists of four London–Eyring–Polanyi⁴⁶ (LEP) functions augmented by bending terms as in the earlier CH_5 surface³⁷ on which it is based. This potential is written in terms of stretching (str), out-of-plane (op) bending, and valence (val) bending terms and has the form

$$V = V_{\rm str} + V_{\rm op} + V_{\rm val}, \tag{3}$$

where $V_{\rm str}$ is the stretching term given by

$$V_{\rm str} = \sum_{i=1}^{4} V_3(R_{\rm CH_i}, R_{\rm CCI}, R_{\rm CIH}),$$
(4)

and where V_3 represents the LEP functional form used by Joseph *et al.*,³⁷ V_{op} is the out-of-plane bending term, correlating with the out-of-plane motion of the methyl radical, and V_{val} is a harmonic term for valence bends. The latter terms are designed to be reasonable both for the methane molecule and the methyl radical. The mathematical expressions of the bending terms are given by Jordan and Gilbert,³⁹ and they are not repeated here. It is however critical to note that V_3 involves three singlet parameters (${}^{1}D_{X-Y}$, α_{X-Y} , and R_{X-Y}^0) and five triplet parameters (${}^{3}D_{X-Y}$, β_{X-Y} , c_{X-Y} , a_{X-Y} , and R_{X-Y}^*) for each bond X-Y.³⁷

The calibration process used in this work has several steps. In the first step, we changed the parameters (R_{CH}^0) , R_{CCI}^{0} , R_{CIH}^{0} , ${}^{1}D_{\text{CH}}$, ${}^{1}D_{\text{CCI}}$, ${}^{1}D_{\text{CIH}}$, α_{CH} , α_{CIH}) of the PES related to the geometric, energetic, and vibrational properties of the reactants and products, so that the geometries, endothermicity, and vibrational frequencies agreed reasonably with the available experimental values. In the second step, we refit some parameters $({}^{3}D_{CH}, {}^{3}D_{CCI}, {}^{3}D_{CIH}, \alpha_{CCI})$ in order to reproduce the characteristics of the ab initio calculated saddle point, in particular, the geometry, barrier height, and the vibrational frequencies. During this fitting, we exercised special care to insure that no artificially deep wells were introduced in the reactant or product valley. Finally, since a main objective in this work is to analyze the dynamical details of the rate process (importance of tunneling, temperature dependence, excited-state reactivity, etc.) and to calculate possible sources of the KIEs, as the third step of our recalibration, we refit some of the parameters of the analytical PES, in order to reproduce more accurately the experimental rate coefficients at 300 K and improve the agreement with experimental ${}^{13}C$ and deuterium (CD₄ vs CH₄) KIEs at 300 K. The final parameters that are different from the original³⁹ H+CH₄ parameters are given in Table III.

The results of the final fit are listed in Table IV for reactants and products and in Table V for the saddle point. In general, the experimental^{44,47} reactant and product properties are well reproduced, with the most significant difference being 0.02 Å for the C–H bond length in CH₃. With respect to the vibrational frequencies, small differences were obtained, although these small errors partially cancel between reactants and products, yielding an enthalpy of reaction at 0 K of 0.9 kcal/mol, in very good agreement with the experimental value of 1.0 kcal/mol.⁴⁴ Comparison of the properties of the saddle point of this surface with *ab initio* calculations shows that this surface reproduces, in general, the trends and values although the new surface has a shorter Cl–H' bond. At the

TABLE III. Fitted parameters for the analytical PES.

Parameter ^a	Value
$R_{\rm CH}^0$	1.0939 Å
${}^{1}D_{\rm CH}$	112.341 kcal/mol
${}^{3}D_{\rm CH}$	38.680 kcal/mol
a_{CH}	1.7030 Å ⁻¹
$b_{ m CH}$	0.1350 Å^{-1}
c _{CH}	6.6140 Å^{-1}
$R_{\rm CCI}^0$	1.7811 Å
${}^{1}D_{CCI}$	87.149 kcal/mol
$^{3}D_{\rm CCl}$	23.583 kcal/mol
$\alpha_{\rm CCl}$	0.8650 Å^{-1}
R^0_{CIH}	1.2745 Å
${}^{1}D_{\text{CIH}}$	106.266 kcal/mol
${}^{3}D_{\text{CIH}}$	36.664 kcal/mol
$lpha_{ m ClH}$	1.8700 Å^{-1}
a_1	$0.413\ 952\ \text{\AA}^{-2}$
a_2	$2.099 \ \text{A}^{-2}$
<i>a</i> ₃	$2.865 95 \text{ Å}^{-2}$

^aFor a complete definition of the parameters and the analytical form of the PES, see Ref. 39.

saddle point the length of the bond that is broken (C-H')increases by 27%, and the length of the bond that is formed (Cl-H') is only 6% larger than at products. This indicates that the reaction of the Cl atom with methane proceeds via a "late" transition state, i.e., it is a productlike transition state. The saddle point has one imaginary frequency. The absolute value of the imaginary part of this frequency is lower in our calculations than the ab initio values, although it is well known that sometimes ab initio calculations overestimate this value.⁴⁵ Moreover, as noted above, our objective was to reproduce experimental KIEs, and the value of this imaginary frequency actually rose during this adjustment. The combined effect of potential energy and zero-point energy at the saddle point is embodied in, ΔH_0^{\neq} , the conventional transition-state enthalpy of activation at 0 K, and this agrees within 1.5 kcal/mol with the ab initio calculations and with the IB calculations performed in this work.

C. Dynamical calculations

With the new surface calibrated as described in the previous section, the reaction path was calculated starting from the saddle point geometry and going downhill to both reac-

TABLE IV. Reactant and product properties^a calculated using the analytical surface.

System	R(C-H)	R(Cl-H)	Frequencies
CH4 ^b	1.094		3037 (t), 2871,
			1501 (e), 1339 (t)
CH ₃ ^c	1.094		3165 (e), 2994,
			1240 (e), 580
ClH ^d		1.274	2993

^aDistances in Å, frequencies in cm⁻¹, energies in kcal/mol.

^bExperimental values (Ref. 44): CH₄(*T_d*): 1.091 Å, 3019(t), 2917, 1534(e), 1306(t).

^cExperimental values (Ref. 44): CH₃(D_{3h}): 1.079 Å, 3184(e), 3002, 1383(e), 580.

^dExperimental values: ClH(C_{xv}): 1.275 Å (Ref. 44), 2991 cm⁻¹ (Ref. 47).

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TABLE V. Saddle point properties^a calculated using the analytical surface.

				Electronic struct	ture calculations	
Parameter m	SPES ^b	APES ^c	TTBGS ^d	DD ^e	DT^{f}	Best ^g
$R^{\neq}(CH)$	1.098	1.096	1.086	1.078	1.077	1.080
$R^{\neq}(CH')$	1.389	1.377	1.388	1.375	1.443	1.359
$R^{\neq}(\text{ClH}')$	1.356	1.386	1.431	1.452	1.431	1.451
ΔE	6.1	6.1	7.5 ^h	$7.6^{h,i}$	$9.7^{\rm h}$	6.8 ^h
ΔH_0	0.9	0.9	2.2^{h}	$2.7^{\rm h}$	4.4 ^h	2.2^{h}
ΔE^{\neq}	7.7	8.1	$8.8^{\rm h}$	$9.7^{\rm h}$	10.7 ^h	8.4 ^h
$\Delta H^{\neq}(0 \text{ K})$	3.1	4.4	4.4 ^h	5.7 ^h	6.3 ^h	4.5 ^h
Frequencies						
1,2	3039 (e)	3022 (e)	3295 (e)	3305 (e)	3328 (e)	3303 (e)
3	2910	2960	3118	3132	3162	3131
4,5	1372 (e)	1419 (e)	1449 (e)	1448 (e)	1468 (e)	1457 (e)
6	1126	1190	1227	1213	1211	1223
7,8	782 (e)	1102 (e)	874 (e)	958 (e)	920 (e)	923 (e)
9	732	543	572	511	541	519
10,11	312 (e)	344 (e)	324 (e)	378 (e)	385 (e)	337 (e)
F	760 <i>i</i>	1196 <i>i</i>	949 <i>i</i>	1262 <i>i</i>	996i	1136i

^aDistances in Å, frequencies in cm^{-1} , energies in kcal/mol. H' is the hydrogen abstracted. Symmetry C_{3v} . ^bSymmetric PES. This work.

^cAsymmetric PES, from Ref. 30.

^dFrom Ref. 23. MP2-SAC/MC-311G(2*d*,*d*,*p*) energies and geometries with MP2/MC-311G(2*d*,*d*,*p*) frequencies. ^eFrom Ref. 26. MP2/TZ+2P level.

^fFrom Ref. 27. DFT/6-311G(d,p) level.

^gCCSD(T)/IB//MP2/pTZ from present work with scaled MP2/MC-311G(2*d*,*d*,*p*) frequencies for the saddle point (scale factor 0.96) and experimental frequencies for the reactants and products.

 h We added the +0.8 kcal/mol contribution from the spin–orbit interaction to all energies in this table to provide a consistent comparison.

ⁱSingle-point CCSD(T)/cc-pVQZ energy calculations from Ref. 26.

tants and products in mass-weighted Cartesian coordinates, using Euler's single-step method⁴⁸ with step-size of 0.0005 $\operatorname{amu}^{1/2} a_0$, where $1 a_0 \equiv 1$ bohr $\equiv 0.529$ Å. The Hessian matrix was evaluated every 30 points along this reaction-path. Along this minimum energy path (MEP), the reaction coordinate, s, is defined as the signed distance from the saddle point, with s > 0 referring to the product side. In the rest of paper, the units of s are a_0 , and all calculations are carried out in mass-scaled coordinates with a reduced mass μ equal to 1 amu. Thus, distances through the mass-scaled coordinates in a_0 are equivalent to distances through massweighted coordinates in $amu^{1/2}a_0$. We calculate the reaction-path between $s = -3.0 a_0$ and $s = +3.0 a_0$; all the rate coefficients are well converged with respect to the gradient step-size, distance between Hessian matrices (0.015 a_0), and extent of reaction-path calculated. Along the MEP a generalized normal-mode analysis was performed using a redundant curvilinear projection operator⁴⁹ formalism. With this information, we calculated the ground-state vibrationally adiabatic potential curve

$$V_a^G(s) = V_{\text{MEP}}(s) + \varepsilon_{\text{int}}^G(s), \tag{5}$$

where $V_{\text{MEP}}(s)$ is the classical energy along the MEP with its zero of energy at the reactants $(s = -\infty)$, and $\epsilon_{\text{int}}^G(s)$ is the zero-point energy at *s* from the generalized normal-mode vibrations orthogonal to the reaction coordinate. We also calculated the coupling terms,⁴⁹ $B_{mF}(s)$, measuring the coupling between normal mode *m* and the motion along the reaction coordinate, mode *F*, and the Coriolis-type terms,⁵⁰ $B_{mm'}(s)$, measuring the coupling between generalized normal modes *m* and *m'* induced by motion of the system along the reaction path. The $B_{mF}(s)$ coupling terms are the components of the reaction path curvature, $\kappa(s)$, defined as

$$\kappa(s) = \left(\sum_{k=1}^{F-1} \left[B_{mF}(s)\right]^2\right)^{1/2}$$
(6)

and they control the nonadiabatic flow of energy between these modes and the reaction coordinate.⁵¹ These coupling terms are used in the calculation of transmission coefficients that include the effects of the reaction path curvature. They also allow us to give a qualitative explanation of the effects of vibrational excitation of reactants and/or products.

Finally, the energies, vibrational frequencies, geometries, and gradients along the MEP were used to estimate rate coefficients and kinetic isotope effects (KIEs) by using variational transition state theory (VTST) with semiclassical multidimensional tunneling. We calculated thermal rates using canonical variational theory^{34,35} (CVT), which locates the dividing surface between reactants and products at a point $s_*^{\text{CVT}}(T)$ along the reaction path that minimizes the generalized TST rate coefficients, $k^{\text{GT}}(T,s)$, for a given temperature *T*. Thermodynamically, this is equivalent to locating the transition state at the maximum $\Delta G^{\text{GT},0}[T,s_*^{\text{CVT}}(T)]$, of the standard-state free energy of activation profile $\Delta G^{\text{GT},0}(T,s)$.^{34,35} Thus, the thermal rate coefficient will be given by

$$k^{\text{CVT}}(T) = \sigma \frac{k_{\text{B}}T}{h} K^0 \exp[-\Delta G^{\text{GT},0}(T, s_*^{\text{CVT}})/k_{\text{B}}T], \quad (7)$$

with k_B being Boltzmann's constant, *h* being Planck's constant, σ being the symmetry factor (the number of equivalent reaction paths, which were assumed to be 4 and 2 for the forward and reverse nonsubstituted reactions, respectively), and K^0 being the reciprocal of the standard-state concentration, taken as 1 molecule cm⁻³.

In the present work, we used the general polyatomic rate coefficient code POLYRATE.⁵² We correctly⁵³ included the ${}^{2}P_{1/2}$ excited state of Cl (with excitation energy⁴⁴ 882 cm⁻¹) in the reactant electronic partition function. The rotational partition functions were calculated classically, and vibrations are treated as quantum mechanical separable harmonic oscillators, with the generalized normal-modes defined in curvilinear coordinates.^{49,54} The chosen curvilinear coordinates were all the possible bond lengths and bond angles. The advantage of curvilinear coordinates^{49,54} (nonlinear functions of Cartesian coordinates) is that all the vibrational frequencies were real over the whole of the reaction path, while with rectilinear coordinates^{50,55} (linear functions of Cartesian coordinates), we found that the lowest bending frequencies had unphysical imaginary values over a wide range of the reaction coordinate. The appearance of imaginary frequencies along the reaction path is a consequence of the inadequacy of the Cartesian coordinates for describing vibrational motions, and this behavior has also been found in other hydrogen abstraction reactions.49,54,56,57

The vibrational-state-selected rate coefficients were calculated using a vibrationally adiabatic version of generalized transition state theory.^{58,59} The adiabatic expression differs from the form of the thermal rate only in the vibrational partition function for the state-selected mode, which is replaced by

$$Q_m(n,T) = \exp\left[-\left(\frac{1}{2}+n\right)\frac{\hbar\,\omega_m}{k_{\rm B}T}\right],\tag{8}$$

where *n* is the vibrational state of mode *m*. Substituting Eq. (8) for the usual canonical partition function of mode *n* yields a state-selected free energy of activation profile called $\Delta G^{\text{GT},0}(n,T,s)$. This adiabatic model assumes that vibrational modes preserve their character along the reaction path. This approximation is most likely to be fulfilled for excited-state reactions involving excitation of high-frequency modes in reactants and in thermoneutral or exothermic reactions where the dynamical bottleneck is located early along the reaction path. The adiabatic approximation may be poor for excited-state reactions with vibrational excitation of the low-frequency modes.⁵⁸

Since the assumption of vibrational adiabaticity all along the reaction path may not hold for this reaction, we also used the partial-reaction-path adiabaticity approximation (PRP).⁶⁰ In this method, we assume that the adiabaticity of the stateselected high-frequency mode transverse to the reaction path is conserved until a point where the generalized normal modes become strongly coupled. We identify this point with the first point on the way from reactants to products where the reaction-path curvature peaks. Beyond that point, the energy in the state-selected high-frequency mode is transferred freely to all the other motions, and, as a result, that particular mode can find itself in its ground state. The operational way of implementing this method is the following: We start by locating the first point, s_+ , where the reaction-path curvature shows a peak. The region before that point will be taken as adiabatic, and the free energy of activation along that portion of the reaction path will be taken as the state-selected free energy of activation, $\Delta G^{\text{GT},0}(n,T,s)$. After that point, the free energy of activation will be taken as the one for the ground state, $\Delta G^{\text{GT},0}(n=0,T,s)$. Thus, the rate coefficient can be written as⁶⁰

$$k^{\text{PRP-CVT}}(n,T) = \sigma \frac{k_B T}{h} K^0 \exp \left[-\max \left\{ \begin{array}{c} \max_{-\infty \leqslant s \leqslant s_+} \Delta G^{\text{GT},0}(n,T,s)/k_B T \\ \max_{s_+ \leqslant s \leqslant +\infty} \Delta G^{\text{GT},0}(n=0,T,s)/k_B T \\ \end{array} \right\} \right].$$
(9)

Note that, as discussed in previous work,⁶⁰ the rates calculated using this method will probably underestimate the rates of the vibrationally excited reactions and the true value will lie between the fully adiabatic and PRP rate coefficients.

Finally, we added the tunneling contributions. The Cl+CH₄ reaction has a heavy–light–heavy mass combination, and, therefore, a large curvature tunneling (LCT) calculation should be performed.^{29,61} We used the microcanonical optimized multidimensional tunneling (μ OMT) approach³⁸ in which, at each total energy, the larger of the SCT and LCT tunneling probabilities is accepted as the best estimate. In the LCT calculations we allowed the system to reach all the energetically accessible vibrational excited states of the mode that receives the transferred atom.⁶¹ All transmission coefficients also include the classical adiabatic ground-state (CAG) transmission coefficient⁶² that adjusts the quantal correction for the difference between V_a^G at its maximum and at the CVT transition state.

III. RESULTS AND DISCUSSION

A. Reaction path and curvature terms

Figure 1 shows the classical potential energy, V_{MEP} , the ground state vibrationally adiabatic potential energy relative to reactants, ΔV_a^G , and the change of the local zero-point energy (ΔZPE), as functions of *s* over the range from s=-2.0 to s=+2.0 a_0 , i.e., from a geometry with a C-H



FIG. 1. Classical potential energy curve, V_{MEP} , zero-point energy, ΔZPE , and vibrationally adiabatic potential energy curve, ΔV_a^G , as a function of s for the unsubstituted reaction. All quantities are with respect to the reactants.

distance of 1.090 Å and a Cl-H distance of 1.871 Å to a geometry with a C-H distance of 1.805 Å and a Cl-H distance of 1.274 Å. Note that ΔV_a^G and ΔZPE are defined as the difference between V_a^G at *s* or ZPE at *s* and their values for reactants.

Figure 1 shows that the maximum of ΔV_a^G is shifted with respect to the saddle point (s=0); in particular it occurs at s = +0.29 bohr. Therefore, large variational effects may be expected for this reaction (a "variational effect" is a difference between a prediction of variational transition state theory and a prediction of conventional transition state theory).

To analyze the origin of the variational shift in the maximum of ΔV_a^G , in Fig. 2 we show the variation of the generalized normal mode frequencies along the reaction path. The lowest curve in Fig. 2 tends to zero in the reactant limit (s $=\infty$), i.e., it is a transitional mode, and in that limit there are nine frequencies corresponding to CH_4 . The lowestfrequency C–H stretching mode numbered m=4 transforms adiabatically into the stretching frequency of the bond that breaks during the reaction; thus it is called the reactive mode, and it correlates adiabatically with the mode numbered m=9at the saddle point, where the modes are numbered in order of decreasing frequency and degenerate modes are counted twice. However, in the rest of this paper we will label the modes by the way that they correlate adiabatically. Thus the mode that we call the reactive mode at the saddle point is m=6. At about $s=-0.5 a_0$ and again at $s=+0.2 a_0$, the reactive mode exhibits an avoided crossing with a methyl umbrella mode (m=7, which correlates adiabatically to m=9at the saddle point). The transitional modes have a maximum close to the minimum of the reactive and umbrella modes in the saddle point region, although their frequencies increase less than the other ones decrease. As a result, the ZPE shows



3500

FIG. 2. Generalized normal-mode vibrational frequencies as a function of reaction coordinate s. Doubly degenerate modes are dashed curves, and nondegenerate modes are solid curves. These vibrational frequencies were calculated by a curvilinear vibrational analysis and were used to generate the Δ ZPE curve of Fig. 1.

a minimum near s=0 with a reasonable steep rise immediately thereafter (Fig. 1), and, therefore, variational effects may be expected for this reaction. Large variational effects are the expected behavior for a nearly thermoneutral reaction with a heavy-light-heavy mass combination.^{29(a),35} The reason for this is that the dip in the reactive mode frequency is most pronounced in such cases.34

Along the MEP, the coupling terms, $B_{mF}(s)$, between the reaction coordinate and the orthogonal bound modes control the nonadiabatic flow of energy between these modes and the reaction coordinate.^{50,51,63-70} Figure 3 shows the curvature (κ) of the reaction path as a function of s. There are two sharp peaks, one on the reactant side and one on the product side of the saddle point, as usual for most thermoneutral reactions. The first is due to strong coupling of the reaction path to the CH_4 reactive stretch (which is m=6 at this peak) which has $B_{mF} = 15.6 a_0^{-1}$ at the maximum of κ at $s = -0.53 a_0$ and to the umbrella bend mode (which is m = 7at this location) which contributes to a lesser extent (B_{mF}) = 5.6 a_0^{-1} at $s = -0.48 a_0$). Therefore, a priori, excitation of these modes might be expected to enhance the rate. The second peak is in the exit channel $(s = +0.02 a_0)$, and it is lower than the first. It is due to the coupling of the reaction path to the Cl-H stretch (which is m=6 at $s=+0.05 a_0$), which has $B_{\rm mF} = 3.3_{a_0}^{-1}$ and to the CH₃ bend (which is m = 9at this location), which has $B_{\rm mF} = 4.2 a_0^{-1}$. This might be an indication that these product modes could appear vibrationally excited. However, if we examine ΔV_a^G curve (Fig. 1) we note that the energy difference between the maximum of the ΔV_a^G at s=0.29 and the products is only 2.89 kcal/mol and therefore, there is not enough available energy to excite quanta the Cl-H stretch mode (2993 cm^{-1}) one \approx 8.5 kcal/mol) if the system passes through the transition

16 - 12 - 1 - 1 - 1 - 1 - 1 - 1 - 2

FIG. 3. Reaction path curvature, κ , as a function of reaction coordinate s.

state region in the ground vibrational state, although there is enough energy to excite one quanta the CH₃ umbrella mode (550 cm⁻¹ \approx 1.6 kcal/mol). Therefore, for thermal reactions the Cl–H stretch mode will appear vibrationally unexcited, while the CH₃ umbrella mode can appear vibrationally excited. This situation would be typical of a reaction with a 'late'' transition state where the reagent vibrational energy is more effective than the translational energy for enhancing the reaction rate, while the products are formed with small vibrational excitation.^{64,68–70} The present analytical PES does have a 'late'' transition state. These qualitative conclusions on the population of the vibrational states agree with the experimentally observed populations of Zare *et al.*^{15,17,21} and with the results of the theoretical study of Duncan and Truong.²⁷

In order to shed more light on the dynamical features of this reaction, we also calculated the coupling between the vibrational modes, B_{mm} (Fig. 4). Although several modes seem to be coupled, one particular B_{mm} term is especially large; the one that measures the coupling between the reactive mode and the CH₃ umbrella mode. These are the two modes that are responsible for the peaks in $\kappa(s)$ in the two avoided crossing zones as seen in Fig. 2 and as discussed above.

The coupling of the vibrational modes and the reaction coordinate has an important effect on tunneling.^{29,35,71} Our analysis of this coupling shows that the reaction-path curvature peaks at a point close to the variational transition state, which is the region where tunneling is most likely to take place. This makes it necessary to take into account the reaction path curvature in order to correctly describe the tunneling effect.

FIG. 4. Coriolis coupling term, $B_{mm'}$, between the reactive mode and the umbrella mode of CH₃ as a function of reaction coordinate *s*.

IV. RATE COEFFICIENTS FOR THE ISOTOPICALLY UNSUBSTITUTED REACTION

In canonical variational transition state theory the location of the generalized transition state dividing surface is optimized along the reaction path for each temperature in order to minimize the rate coefficients.^{34,35} The value of the reaction coordinate, *s*, where the canonical variational transition state occurs is denoted as $s_*^{\text{CVT}}(T)$. In the present case, bottleneck properties of the thermally averaged reaction, based on this CVT approach, show significant dependence on such optimization, and the value of $s_*^{\text{CVT}}(T)$ ranges from $+0.29 a_0$ at 0 K to $-0.57 a_0$ at 2500 K. Comparison of columns 2 and 3 of Table VI shows the variational effect on the thermal rate coefficients, decreasing from a factor of 5.2 at 200 K to a factor of 1.4 at 1000 K, then increasing again to a factor of 3.1 at 2500 K.

The shifting of the transition state as we increase the temperature occurs suddenly. For temperatures below 967 K the variational transition state is located in the product chan-

TABLE VI. Rate coefficients without tunneling (*k*) and transmission coefficients (κ) for the CH₄+Cl reaction.

T(K)	k(TST)	k(CVT)	k(CUS)	$\kappa(\text{ZCT})$	$\kappa(SCT)$	$\kappa(\mu \text{OMT})^{a}$
200	$6.2(-15)^{b}$	1.2(-15)	1.1(-15)	1.80	2.30	12.8
250	3.1(-14)	8.6(-15)	7.9(-15)	1.45	1.69	5.48
300	9.5(-14)	3.4(-14)	3.0(-14)	1.29	1.43	3.33
400	4.4(-13)	2.1(-13)	1.7(-13)	1.15	1.22	1.98
600	2.8(-12)	1.8(-12)	1.2(-12)	1.06	1.09	1.35
800	8.8(-12)	6.2(-12)	3.9(-12)	1.04	1.05	1.18
1000	2.0(-11)	1.4(-11)	8.3(-12)	1.02	1.03	1.11
1500	7.7(-11)	3.7(-11)	2.7(-11)	1.01	1.01	1.05
2000	1.8(-10)	6.9(-11)	5.6(-11)	1.00	1.00	1.03
2500	3.3(-10)	1.1(-10)	9.2(-11)	1.00	1.00	1.02

^aIn all cases κ (LCT)= κ (μ OMT) to at least three significant figures. ^b6.2(-15) stands for 6.2×10⁻¹⁵, in cm³ molecule⁻¹ s⁻¹.

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TABLE VII. Forward rate coefficients for the Cl+CH₄→HCl+CH₃ reaction.

	Theory					Expe	riment	
$T(\mathbf{K})$	CVT/µOMT	CUS/µOMT	RCT ^a	APES ^b	Ref. 4	Ref. 11	Ref. 12	Ref. 21
200 250 300 400 500 600 800 1000 1500 2000 2500	$\begin{array}{c} 1.5(-14)^{\rm c}\\ 4.7(-14)\\ 1.1(-14)\\ 4.1(-13)\\ 1.1(-12)\\ 2.3(-12)\\ 7.0(-12)\\ 8.5(-12)\\ 2.6(-11)\\ 5.2(-11)\\ 8.6(-11)\\ \end{array}$	$\begin{array}{c} 1.4(-14) \\ 4.3(-14) \\ 9.9(-14) \\ 3.4(-13) \\ 8.1(-13) \\ 1.6(-12) \\ 4.3(-12) \\ 4.9(-12) \\ 1.9(-11) \\ 4.2(-11) \\ 7.3(-11) \end{array}$	$\begin{array}{c} 5.6(-15)\\ 2.4(-14)\\ 6.9(-14)\\ 3.1(-13)\\ 8.6(-13)\\ 1.9(-12)\\ 6.2(-12)\\ 1.4(-11)\\ 5.6(-11)\\ 1.3(-10)\\ 2.4(-10) \end{array}$	$\begin{array}{c} 1.5(-14)\\ 4.2(-14)\\ 8.8(-14)\\ 2.7(-13)\\ 6.4(-13)\\ 1.3(-12)\\ 3.7(-12)\\ 8.2(-12)\\ 3.1(-11)\\ 7.2(-11)\\ 1.3(-10) \end{array}$	$\begin{array}{c} 1.1(-14) \\ 4.1(-14) \\ 1.0(-13) \\ 3.5(-13) \\ 8.8(-13) \end{array}$	9.4(-14) 3.4(-13) 7.5(-13)	$\begin{array}{c} 1.1(-14) \\ 4.3(-14) \\ 1.0(-13) \\ 3.1(-13) \\ 8.2(-13) \end{array}$	9.3(-14) 3.0(-13) 6.5(-13) 1.3(-12) 3.0(-12)

^aRoberto-Neto, Coitiño, and Truhlar (Ref. 31). CVT/µOMT calculations based on a dual-level direct dynamic calculation.

^bOur earlier asymmetric PES (Ref. 30). CVT/LCT calculations.

^c1.5(-14) stands for 1.5×10^{-14} , in cm³ molecule⁻¹ s⁻¹.

nel, while for temperatures over 967 K it is located on the reactant side of the reaction path. The reason is that $\Delta G^{GT,0}(T,s)$ presents a double-peaked shape, as does the ΔV_a^G curve plotted in Fig. 1. For temperatures below 967 K, the higher $\Delta G^{GT,0}(T,s)$ peak is found on the product side $[s_*^{\text{CVT}}(966 \text{ K})=0.14]$, while at temperatures higher than 967 K, $\Delta G^{\text{GT},0}(T,s)$ has its higher peak on the reactant side $[s_{\perp}^{\text{CVT}}(968 \text{ K}) = -0.57 a_0]$. At 967 K both peaks are equally high. This sudden change in the location of the transition state leads to a discontinuity in the activation energy (and in an Arrhenius plot) around 967 K. We will avoid this problem by using the canonical unified statistical theory (CUS).^{35,72} This approach takes account of both maxima (global and local maxima) in $\Delta G^{\text{GT},0}(T,s)$ by using a canonical version of the branching analyses of Hirschfelder and Wigner and Miller.⁷³ Thus the CUS rate coefficient has a continuous temperature derivatives even where the variational transition state undergoes a sudden switch.

Tables VII and VIII list the CUS/µOMT rate coefficients, along with experimental^{4,11,12,21,74} and other theoretical^{30,31} rate coefficients for the temperature range 200-2500 K for both the forward and reverse reactions, respectively. In both cases, with the new parametrization of the surface, the calculated rates agree better than the previously reported surface³⁰ with the experimental data in the temperature range that has been studied experimentally. Since the experimental data were used in the parametrization, this represents simply a check on the consistency of the parametrization. It is encouraging though that the new results are more consistent with direct dynamics calculations³¹ than were the earlier results based on the previous analytic surface. For the forward reaction, with our earlier asymmetric PES (Ref. 30) we obtained a transmission coefficient of 106 and a CVT rate coefficient of $1.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 200 K, while in this work we obtain values of 12.8 and 1.2 $\times 10^{-15}$ cm³ molecule⁻¹ s⁻¹, respectively; the latter value is in better agreement with previous direct dynamics μ OMT transmission coefficient calculations,³¹ which range from 4.3 to 7.4 at 200 K. This discrepancy between the present result and the earlier one is not due to the form of the analytical expression used to describe the surface (asymmetric vs symmetric) but rather to the different criteria used to calibrate it. In our first paper, the calibration was based on the stationary point properties (geometries, frequencies, and energies), while in the present paper, the calibration is designed to reproduce the rate coefficients and the KIEs. With these new criteria, the tunneling effect is considered in the calibration.

Table IX lists phenomenological activation energies computed as local two-point slopes of Arrhenius plots for the forward and reverse reactions, in order to provide the most appropriate comparison to experiment. Our theoretical results show excellent agreement with experimental values in various temperature ranges up to 500 K.

Our activation energies at 298 K (from slopes of Arrhenius plots from 293 K to 303 K) are 2.63 and 1.07 kcal/mol for the forward and reverse reactions, respectively. Using these theoretical activation energies a value of 1.56 kcal/mol is obtained for the enthalpy of reaction at 298 K, in agreement with the experimental value from enthalpies of formation, $\Delta H_r^{298 \text{ K}} = 1.65 \text{ kcal/mol}$ (Ref. 44). This result is encouraging, although of course all transition state properties cancel out, as does the barrier shape. This comparison confirms that we have a reasonable ΔH_{298}^0 by means of the well known relation⁷⁵ between the overall enthalpy of reaction and the difference of the forward and reverse enthalpy of activation.

A. Kinetic isotope effects

The ${}^{12}C/{}^{13}C$ KIEs are listed in Table X in the temperature range 200–2500 K. Our results slightly overestimate these KIEs, especially at low temperatures, as compared to previous experimental 16 and theoretical 31 values. To analyze this behavior in more detail, in the same Table X we also give a factor analysis. This factorization of the KIEs involves writing them as a product, where each factor in the product arises from the ratio, for the two isotopologs or isotopomers, of a particular subset of partition coefficients or of some other factor in the overall rate expression. For the sake of clarity, the factorization of partition functions is based on conventional transition state theory, and the variational and

TABLE VIII. Reverse rate coefficients for the $Cl+CH_4 \rightarrow HCl+CH_3$ reaction.

		Theory		Expe	riment	
$T(\mathbf{K})$	CVT/µOMT	CUS/µOMT	RCT ^a	APES ^b	Ref. 11	Ref. 74
200	$3.8(-14)^{c}$	3.6(-14)	3.3(-14)	2.3(-14)		
250	5.8(-14)	5.4(-14)	5.1(-14)	3.0(-14)		
300	8.4(-14)	7.5(-14)	7.0(-14)	3.8(-14)	4.8(-14)	6.6(-14)
400	1.5(-13)	1.3(-13)	1.1(-13)	5.6(-14)	8.6(-14)	1.6(-13)
500	2.5(-13)	1.9(-13)	1.7(-13)	8.1(-14)	1.2(-13)	2.8(-13)
600	3.7(-12)	2.6(-12)	2.3(-13)	1.1(-13)		
800	7.1(-13)	4.4(-13)	4.5(-13)	2.1(-13)		
1000	6.6(-13)	3.8(-13)	6.5(-13)	3.6(-13)		
1500	1.4(-12)	1.1(-12)	1.8(-12)	9.9(-13)		
2000	2.6(-12)	2.1(-12)	3.6(-12)	2.1(-12)		
2500	4.2(-12)	3.6(-12)	6.2(-12)	3.8(-12)		

^aRoberto-Neto, Coitiño, and Truhlar (Ref. 31). CVT/µOMT calculations based on a dual-level direct dynamic calculation.

^bCVT/LCT results obtained using the earlier asymmetric PES from Ref. 30.

 $^{\circ}3.8(-14)$ stands for 3.8×10^{-14} , in cm³ molecule⁻¹ s⁻¹.

tunneling effects are introduced in additional factors. This factorization can be useful for understanding the chemical nature of the KIEs. Thus, we write^{37,76}

$$\text{KIE} = \frac{k(^{12}\text{CH}_4)}{k(^{13}\text{CH}_4)} = \eta_{\text{trans}} \eta_{\text{rot}}^{\neq} \eta_{\text{vib}}^{\neq} \eta_{\text{tun}} \eta_{\text{var}} \eta_{\text{CUS}}, \qquad (10)$$

where η_{trans} is the ratio of the relative translational partition functions, η_{rot}^{\neq} is from rotational partition functions as evaluated at the saddle point, η_{vib}^{\neq} is from vibration (including zero-point energy) at the saddle point, η_{tun} is the ratio of tunneling factors $[\kappa^{\mu \text{ OMT}}(^{12}\text{CH}_4)/\kappa^{\mu \text{OMT}}(^{13}\text{CH}_4)]$, η_{var} =KIE^{CVT}/KIE^{TST}, i.e., the ratio of KIEs calculated using variational and conventional transition state theories, and η_{CUS} =KIE^{CUS}/KIE^{CVT}, i.e., the ratio of KIEs calculated using the CVT and CUS methods. Table X indicates that for temperatures where experimental values are available, the single most important factor in the KIEs is the tunneling factor.

The CH₄/CD₄ KIEs are listed in Table XI in the same temperature range. The theoretical KIEs are in good agreement with the available experimental data. Note that the new surface corrects a major deficiency of our previous surface,³⁰ which was the poor description of the deuterium KIEs. For example, at 300 K, the KIE was 41.8 with our previous surface, but now is 14.0, i.e., a factor of 3 lower, in closer agreement with the experimental values (~11–18). To explain this reduction, we performed another factor analysis. This is also given in Table XI. We find that the reduction is due, mainly, to variational effects, η_{var} =KIE^{CVT}/KIE^{TST}, i.e., the ratio of KIEs calculated using variational and conventional transition state theory, which at 300 K decreases from 0.91 (Ref. 30) to 0.52 for the new surface. Table XI also allows us to explain the origin of the experimentally

TABLE IX. Activation energies (kcal/mol).

			Expe	riment
T(K)	CVT/µOMT	CUS/µOMT	Ref. 4	Ref. 11
	Forv	vard reaction		
200-300	2.38	2.29	2.6 ± 0.4	
300-500	3.38	3.14	3.5 ± 0.5	3.1 ± 0.3
500-600	4.46	4.04		
600-967	5.67	5.01		
968-1000	5.74	7.19		
1000-1500	6.59	7.97		
1500-2000	8.36	9.55		
	Rev	verse reaction		
200-300	0.96	0.87		
300-500	1.61	1.37		1.4 ^a
500-600	2.38	1.96		
600-967	3.47	2.80		
968-1000	3.58	5.02		
1000-1500	4.65	6.03		
1500-2000	7.12	8.32		

TABLE X. $^{12}\mathrm{C}/^{13}\mathrm{C}$ kinetic isotope effects for the forward reaction and factor analysis.

		KIE			SPES f	factors ^a	
$T(\mathbf{K})$	SPES ^b	RCT ^c	Expt.	$\eta_{ m vib}^{ eq}$	$\eta_{ m var}{}^{ m d}$	$\eta_{ m CUS}$	$\eta_{ ext{tun}}$
200	1.216	1.094		1.02	1.03	1.00	1.13
250	1.173	1.070	1.069 ^e	1.01	1.03	1.00	1.10
300	1.141	1.057	1.066 ^{e,f}	1.01	1.02	0.99	1.08
400	1.099	1.042		1.00	1.02	0.99	1.06
500	1.074	1.034		1.00	1.02	0.99	1.04
600	1.060	1.030		1.00	1.01	0.99	1.03
800	1.043	1.025		1.00	1.01	0.99	1.02
1000	1.051	1.022		1.00	1.01	1.01	1.01
1500	1.038	1.020		1.00	1.01	1.01	1.00
2000	1.034	1.019		1.00	1.00	1.01	1.00
2500	1.031	1.019		1.00	1.00	1.01	1.00

^a η_{trans} and η_{tot}^{\neq} are independent of temperature, and their values are 1.06 and 0.96, respectively.

^bThis work, CUS/µOMT results for SPES analytic surface.

^cThis work: CVT/μOMT using the AM1-SRP4[MP2]-IC direct dynamics level of Roberto-Neto, Coitiño, and Truhlar (Ref. 31).

^dThis factor includes the CAG transmission coefficient (see Ref. 62) as well as the Boltzmann factor of the potential energy difference at the two isotopic variational transition states.

^eSaueressig *et al.* [Ref. 16(a)]. ^fCrowley *et al.* [Ref. 16(b)].

TABLE XI. CH_4/CD_4 kinetic isotope effects for the forward reaction and factor analysis.

	KIE				SPES f	actors ^a		
<i>T</i> (K)	SPES ^b	RCT ^c	APES ^d	Expt.	$\eta_{ m vib}^{ eq}$	$\eta_{\mathrm{var}}^{\ \ \mathrm{e}}$	η_{CUS}	$\eta_{ ext{tun}}$
200	87.7	18.9	267.8		22.4	0.37	0.96	5.20
250	29.3	11.4	92.0		10.3	0.45	0.94	3.15
295	14.9	8.0	44.2	16.4 ^f	6.4	0.51	0.92	2.35
298	14.3	7.9	42.3	18.5, ^g 12.2 ^h	6.2	0.52	0.92	2.30
300	14.0	7.8	41.8		6.1	0.52	0.92	2.28
304	13.3	7.6	38.9	10.9 ⁱ	5.9	0.53	0.92	2.23
400	5.6	4.6	13.4	5.2 ⁱ	3.1	0.63	0.89	1.60
500	3.3	3.3	7.2		1.95	0.69	0.86	1.35
600	2.4	2.6	4.7		1.48	0.74	0.85	1.23
800	1.6	1.9	2.9		1.05	0.78	0.85	1.12
1000	0.8	1.6	2.3		0.87	0.44	0.89	1.08
1500	1.4	1.3	1.8		0.67	1.00	0.92	1.03
2000	1.3	1.2	1.6		0.64	0.99	0.92	1.02
2500	1.2	1.2	1.5		0.60	0.98	0.92	1.01

^a η_{trans} and η_{rot}^{\neq} are independent of temperature, and their values are 1.25 and 1.69, respectively.

^bThis work, CUS/ μ OMT results for the SPES analytic surface.

^cThis work, CVT/ μ OMT using the AM1-SRP4[MP2]-IC direct dynamics method of Roberto-Neto, Coitiño, and Truhlar (Ref 31).

^dCVT/LCT results obtained using the earlier asymmetric PES from Ref. 30. ^eThis factor includes the CAG transmission coefficient (see Ref. 62) as well as the Boltzmann factor of the potential energy difference at the two isotopic variational transition states.

^fWallington and Hurley (Ref. 13).

^gBoone *et al.* (Ref. 22). This value is based on $k(CH_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^hMatsumi et al. (Ref. 19), at "room temperature."

ⁱChiltz et al. (Ref. 1).

measured KIEs; in particular we find that the differences in the vibrational frequencies introduced by the isotopic substitution.

We also have calculated the CH_4/CH_3D KIEs (Table XII). For the Cl+CH₃D, two reactions must be considered,

TABLE XII. CH₄/CH₃D kinetic isotope effects for the forward reaction.

	SPI			
$T(\mathbf{K})$	CVT/µOMT	CUS/µOMT	RCT ^b	Expt.
200	2.63	2.61	1.49	
250	2.22	2.20	1.41	1.58 ^c
295	1.97	1.94	1.36	1.36 ^d
296	1.96	1.94	1.36	1.51 ^c
298	1.95	1.93	1.35	1.54 ^e
300	1.94	1.92	1.35	
400	1.61	1.58	1.27	
500	1.43	1.40	1.22	
600	1.32	1.29	1.18	
800	1.20	1.16	1.12	
1000	0.99	0.95	1.10	
1500	1.12	1.09	1.05	
2000	1.09	1.06	1.03	
2500	1.07	1.05	1.02	

^aThis work.

^bThis work, CVT/μOMT using the AM1-SRP4[MP2]-IC direct dynamics method of Roberto-Neto, Coitiño, and Truhlar (Ref. 31).

^cSaueressig *et al.* [Ref. 16(c)]. ^dWallington and Hurley (Ref. 13).

^eBoone *et al.* (Ref. 22). This KIE is based on $k(CH_4) = 1.0 \times 10^{-13} \text{ cm}^3$ molecule⁻¹ s⁻¹.

TABLE XIII. CH₄/CH₂D₂ kinetic isotope effects for the forward reaction.

	SP		
$T(\mathbf{K})$	CVT/µOMT	CUS/µOMT	Expt. ^b
200	4.61	4.56	
250	3.63	3.56	
298	3.01	2.93	1.43
300	2.98	2.91	
400	2.24	2.16	
500	1.85	1.76	
600	1.63	1.53	
800	1.38	1.29	
1000	0.95	0.87	
1500	1.23	1.19	
2000	1.17	1.12	
2500	1.14	1.10	

^aThis work.

^bMatsumi et al. (Ref. 19).

$$Cl + CH_3D \rightarrow DCl + CH_3$$
,
 $Cl + CH_3D \rightarrow HCl + CH_2D$,

the first with symmetry factors 1 and 2, for the forward and reverse reactions, respectively, and the second with symmetry factors of 3 and 2, respectively. The total rate coefficient corresponds to the sum of these two partial reactions. Table XII shows that our results agree better with the results obtained by Roberto-Neto *et al.*³¹ for their direct dynamics implicit surface at high temperature than at low temperature. Our values are larger than the experimental measurements.

Finally, we calculated the CH_4/CH_2D_2 KIEs (Table XIII), which consists of two reactions,

 $Cl + CH_2D_2 \rightarrow DCl + CH_2D$, $Cl + CH_2D_2 \rightarrow HCl + CHD_2$,

both with symmetry factors of 2 for the forward and reverse reactions. The agreement with the only experimental measurement¹⁹ is poor, with our CUS/ μ OMT value being almost twice the experimental value.

The nonsmooth behavior of the KIEs near 1000 K is due to the transition state switch discussed in Sec. III B (which occurs at 967 K for the perprotio case). Even without considering temperatures close to this switch, the KIEs from the various theoretical treatments differ by disturbingly large amounts. Clearly the KIEs are very sensitive to the potential energy surface and the assumptions of the dynamical treatment.

B. Vibrational-state selected rate coefficients

The effect of umbrella motions on reactions of the form $X+CH_4\rightarrow XH+CH_3$ [where $X=O(^{3}P)$ or Cl] has recently been studied by approximate quantum mechanical scattering calculations.^{77,78} For example, it was found that the reverse reaction, $CH_3+HCl\rightarrow CH_4+Cl$, is impeded by excitation of the CH_3 umbrella mode, in agreement with the state-selected variational transition state theory results by Duncan and Truong.²⁷ However, Duncan and Truong also predicted that the umbrella mode enhances the forward reaction, and stretch excitation enhances the reaction in both directions.

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Nyman *et al.*⁷⁹ predicted considerably larger rate coefficients for stretch-excited CH_4 than for ground-state CH_4 .

The above analysis of the B_{mF} coupling terms showed that excitation of the reactants (C–H symmetric stretching and the lowest frequency mode in CH₄) may enhance the forward reaction rates. In a similar fashion, it is possible that the excitation of some vibrational modes of the products (for example, the Cl–H stretching and CH₃ umbrella modes) enhances the reverse reaction. In the present section we will present VTST calculations (including multidimensional tunneling contributions) on vibrational state-selected rate coefficients in order to shed more light on this subject.

We will start analyzing the vibrationally adiabatic potential energy curves of the ground state and two excited states [Figs. 5(a) and 5(b)]. In particular we consider the reactive mode and the CH₃ umbrella mode. We use the convention of numbering the modes in order of decreasing frequency, and we correlate the modes adiabatically. Thus, in this section, the reactive mode is the one that starts as m=4, becomes m=6 near the saddle point, and ends as m=4 (see Fig. 2). Thus it transforms from a CH₄ symmetric stretch to an HCl stretch. The CH₃ umbrella mode starts as m=7, becomes m=9 near the saddle point, and then becomes m=7 again. To be sure that there is no misunderstanding, we note explicitly that in spectroscopic notation (where one gives the lowest numbers to totally symmetric modes), the "reactive mode'' transforms from ν_2 of CH₄ to ν of HCl, and the "umbrella mode" transforms from ν_3 of CH₄ to ν_3 of CH₃. The excitation of the reactive mode by one quantum lowers the vibrationally adiabatic barrier to 2.17 kcal/mol and the reverse one to 0.94 kcal/mol as compared to 3.78 kcal/mol⁻¹ and 2.89 kcal/mol for the forward and reverse ground-state barriers. Thus, vibrational excitation of this mode is expected to enhance both the forward and reverse reactions. This excitation shifts the maximum of the vibrationally adiabatic barrier from $s = +0.29 a_0$ for the ground state to s $= +0.96 a_0$ for the excited-state. Thus the variational transition state is in the exit channel. The local maximum of the vibrationally adiabatic potential curve in the entrance channel is called a supernumerary transition state,⁸⁰ and its analog for the Cl+H₂ reaction has recently been discussed in detail.81

Excitation of the CH₃ umbrella mode by one quantum lowers the vibrationally adiabatic barrier height with respect to reactants from 3.78 kcal/mol (at $s = 0.25 a_0$) to 2.52 kcal/ mol (at $s = 0.29 a_0$), but it raises the vibrationally adiabatic barrier height with respect to products to 3.80 kcal/mol from 2.89 kcal/mol. These results agree well with the theoretical estimation of Duncan and Truong²⁷ for the reverse reaction. If this mode were to remain adiabatic from each asymptote to the respective dynamical bottleneck, we would expect that the excitation of this mode in methyl accelerates the forward reaction but retards the reverse reaction.

However, comparison of the $B_{mm'}$ Coriolis coupling terms to the state-selected vibrationally adiabatic potential curves indicates that the energy can flow between modes in the entrance valley and, therefore, the symmetric stretch and the umbrella modes do not preserve their character along the reaction path all the way from reactants to the transition



FIG. 5. Vibrationally adiabatic ground-state potential energy curve (dotted line), vibrationally adiabatic curve for exciting by one quantum the mode that transforms into the CIH stretch mode (mode m=6 at s=0 a_0 ; solid line), and vibrationally adiabatic curve for exciting by one quantum the mode that transforms adiabatically into the CH₃ umbrella mode (mode m=9 at s=0 a_0 ; dashed line), each as a function of reaction coordinate *s*. Each curve in (a) is relative to the value *for that state* at reactants, while in (b) they are relative to the value *for that state* at products.

state. This situation does not allow a more quantitative analysis for the forward reaction with a fully adiabatic approximation; instead, we will use the PRP (Ref. 60) adiabatic approximation.

The value of s_+ for the forward reaction is taken as $s_- = -0.53 a_0$, while for the reverse reaction it is taken as $s_+ = 0.02 a_0$; these are the values where the curvature of the reaction path shows its first peak in each direction (see Sec. III A).

TABLE XIV. Ratio between excited-state and thermal rate coefficients for the reactive mode excitation in the forward and reverse reactions.

	CH	$CH_4{+}Cl{\rightarrow}CH_3{+}HCl$			$CH_3+HCl \rightarrow CH_4+Cl$	
$T(\mathbf{K})$	CVT	CVT/SCT	Ref. 79	CVT	CVT/SCT	
200	406.0	489.0	43.0	180.0	97.0	
250	119.0	138.0	20.0	73.0	48.0	
300	52.0	58.0	12.0	40.0	30.0	
400	17.2	18.9	6.0	19.4	15.6	
600	5.2	5.6	2.8	9.3	7.6	
800	2.7	2.8	1.7	6.2	5.0	
1000	1.79	3.4		4.8	6.6	
1500	1.44	2.2		4.6	4.8	
2000	1.28	1.75		4.3	4.0	
2500	1.19	1.52		4.0	3.5	

CI+CH₄ reaction 9387

TABLE XV. Ratio between excited-state and thermal rate coefficients for the excitation of the m=9 mode for the forward and reverse reactions.

	$\rm CH_4{+}\rm Cl{\rightarrow}\rm CH_3{+}\rm HCl$		$CH_3+HCl \rightarrow CH_4+Cl$	
$T(\mathbf{K})$	CVT	CVT/SCT	CVT	CVT/SCT
200	56.8	235.0	0.10	0.16
250	24.6	68.5	0.16	0.21
300	13.8	29.9	0.22	0.27
400	6.37	10.4	0.34	0.38
600	2.65	3.46	0.54	0.57
800	1.58	1.89	0.69	0.72
1000	1.17	2.36	0.84	1.52
1500	1.08	1.69	1.61	2.36
2000	1.03	1.44	2.31	3.06
2500	1.01	1.31	2.90	3.63

We calculated the PRP rate coefficients for the reaction with the reactive mode excited for both the forward and reverse reaction. The ratios of these results to the ground-state rate coefficients are given in Table XIV. Each ratio is obtained from rate coefficients calculated at the same level of theory, i.e., CVT or CVT/SCT. These ratios measure the enhancement of the reaction rate when the reactive C-H stretching mode is excited for the forward reaction and the enhancement when the Cl-H stretching mode is excited in the reverse reaction. Unfortunately, a theory for performing this kind of calculation with the LCT tunneling approximation has not been developed yet, and therefore we will carry out our analysis based on CVT and CVT/SCT rate coefficients. Although LCT tunneling dominates in the groundstate calculations, the analysis of the CVT and CVT/SCT results will be valuable for carrying out at least a qualitative analysis.

The first conclusion we can draw from these results is that excitation of the reactive mode increases the rate coefficient significantly for both the forward and reverse reactions. It is encouraging that the CVT and CVT/SCT ratios are reasonably close (within a factor of 2) for the entire temperature range.

According to the CVT/SCT values, the forward rates are enhanced by a factor ranging from 489 at 200 K to 58 at 300 K and to 1.52 at 2500 K. The reverse rates show a lower enhancement at temperatures below 600 K (97 at 200 K and 30 at 300 K), but the ratio between excited-state and thermal rates is larger than for the forward reaction for temperatures above 600 K (3.5 at 2500 K).

It is interesting to point out that the dynamical bottleneck was always located before the s_+ value for the forward reaction, and after it for the reverse reaction (i.e., the dynamical bottleneck occurs in the region where n=1).

The enhancements we calculated for the forward reaction are compared to those of Nyman *et al.*⁷⁹ in Table XIV. Nyman *et al.* employed reduced-dimensionality scattering calculations, treating CH_4 as a pseudo-atom. We might expect that this reduced-dimensionality method is less accurate than our calculations because they do not take account of all the degrees of freedom. Duncan and Truong also obtained larger enhancements than the reduced-dimensionality calculations.²⁷ However, one cannot rule out that the differences are due to the differences in the dynamical methods, and not to the reduced dimensionality.

A similar set of ratios was calculated for the case of excitation of the umbrella mode, and they are listed in Table XV. In this case, the vibrational excitation of the umbrella mode in CH_4 causes an acceleration of the forward reaction rate that ranges between 235 and 1.3 at 200 K and 2500 K, respectively. The reverse reaction, however, has a different behavior. Thus, for temperatures below 800 K, the thermal reverse rate coefficient is larger when either the umbrella motion of CH_3 or the stretch of HCl is excited. Excitation of the CH_3 umbrella mode reduces the reverse rate coefficient by as much as a factor of 6.2 at 200 K. However, for temperatures above 800 K, excitation of the umbrella vibrational mode speeds up the reverse reaction, and the factor is as large as 3.6 (at 2500 K).

It is also interesting to note that tunneling has more effect on the rate coefficient ratios for the umbrella-mode case than for the stretch-mode case.

Once again, the PRP bottlenecks were found to be in the reaction-path regions where the vibrational mode is in its excited state.

C. Comparison with the earlier asymmetric PES

The largest differences between the earlier PES (asymmetric)³⁰ and this new PES (symmetric) are due to the different calibration criteria used in the two cases. While in the earlier PES the criterion was to reproduce the properties of experimental measurements and electronic structure calculations of the stationary points (geometry, frequency and changes of energy, reaction and activation), in this new PES the criterion is to reproduce the experimental rate coefficients and kinetic isotope effects. The most important effect of the calibration is that the shape of the adiabatic curve is greatly modified. We note especially that it has a wider barrier, which is correlated with the lowering of the absolute value of the imaginary frequency, from 1196i to 760i cm⁻¹, at the saddle point. This behavior leads a reduction of the CH₄/CD₄ KIEs from 41.8 to 14.0 at 300 K, and the latter value is in good agreement with the experimental values.

V. CONCLUSIONS

In this work we have constructed a new potential energy surface for the $Cl+CH_4 \rightarrow HCl+CH_3$ reaction based on the symmetric analytical potential energy function for the $H+CH_4 \rightarrow H_2+CH_3$ reaction. The new potential energy surface is semiempirical and is based on using the experimental rate coefficients and kinetic isotope effects as calibration criteria. This new surface is a repulsive surface, i.e., it has a "late" transition state (productlike transition state).

The forward and reverse rate coefficients were calculated over the temperature range 200–2500 K using the CVT/ μ OMT method. With this new reparametrization, the agreement of theory with experiment for the magnitudes of the thermal rate coefficients is excellent at all temperatures for which experiments are available (200–800 K). This is not surprising since experimental thermal rate coefficients were employed in the parameter fitting, but it lends confidence to the PES constructed in this work. This agreement between our calculations and the experimental measurements encouraged us to perform an analysis of the kinetic isotope effects. These KIEs are a very sensitive test of features of the new surface, such as barrier width. We find moderate agreement with the available experimental data.

The analysis of selected-state rate coefficients indicates that vibrational excitation of the C–H stretching and CH₄ lowest frequency bending accelerates the forward reaction rates, and excitation of HCl is predicted to accelerate the back reaction, whereas excitation of the CH₃ umbrella mode is predicted to slow down the reverse reaction for temperatures below 800 K and to accelerate it for temperatures above 900 K.

ACKNOWLEDGMENTS

J.E.G. would like to thank the Dirección General de Investigación Científica y Técnica del Ministerio de Educación y Cultura of Spain (Project PB97-0368) and Junta de Extremadura (Project IPR98-C033) for partial support of this work. J.C.C. would like to thank the Ministerio de Educación y Cultura (Spain) for a researcher reincorporating contract (Project PB96-0977). This work was supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences.

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