

Analytic Function for the $\text{H} + \text{CH}_3 \rightleftharpoons \text{CH}_4$ Potential Energy Surface

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An analytic function for the ground electronic state $\text{CH}_4 \rightleftharpoons \cdot\text{CH}_3 + \cdot\text{H}$ potential energy surface is proposed. This model makes use of a switching-function formalism and is based on both spectroscopic data and ab initio calculations at the MP4/6-31G** level. The proposed general symmetric analytic potential is suitable for use in quasiclassical trajectory studies of the $\text{CH}_4 \rightleftharpoons \cdot\text{CH}_3 + \cdot\text{H}$ reaction.

I. Introduction

The construction of polyatomic potential energy surfaces presents a formidable challenge to the current state of chemical knowledge.¹⁻³ The development of quantitative energy surfaces is dependent upon both the availability of accurate experimental data and the ability to perform high-level ab initio calculations. In addition, the process is complicated by the lack of a generalized method of formulating these surfaces which is applicable to a wide range of polyatomic chemical systems. As a result, there are only a small number of potential energy surfaces which effectively model the dynamical behavior of these complex systems.

The determination of the potential energy surface for the reaction $\text{CH}_4 \rightleftharpoons \cdot\text{CH}_3 + \cdot\text{H}$ is particularly important for the resolution of several fundamental questions. While the $\text{CH}_4 \rightarrow \cdot\text{CH}_3 + \cdot\text{H}$ dissociation probably does not have a saddle point, variational activated complex theory⁴⁻⁶ indicates that the activated complex, and hence the bimolecular and unimolecular rate constants, will depend upon the shape of the potential energy surface. These rate constants have been measured experimentally,^{7,8} but they have not been successfully understood in terms of transition-state theory. In addition, the vibrational energy levels and anharmonic frequencies of bound methane are strongly dependent upon the potential energy surface. Finally, the shape of the potential energy surface will determine whether the classical motion is chaotic or quasiperiodic.⁹⁻¹³

This study was initiated in an attempt to begin the clarification of some of these issues. We have reported previously¹⁴ the results of ab initio calculations describing the dissociation of a single C-H bond in methane. In this work we present an analytic formulation of the $\text{CH}_4 \rightleftharpoons \cdot\text{CH}_3 + \cdot\text{H}$ potential energy surface.

II. Method

The ab initio calculations were carried out with the GAUSSIAN 80 series of programs¹⁵ using the 3-21G and 6-31G** bases.¹⁶ Both basis sets are extended bases of the split-valence type. In addition, the 6-31G** basis includes polarization functions: six Cartesian d orbitals on non-hydrogen atoms and three p orbitals on the hydrogen atoms. Energies were calculated at both the closed-shell restricted Hartree-Fock (RHF) and the open-shell unrestricted Hartree-Fock (UHF) levels. Correlation effects were estimated by means of Møller-Plesset perturbation theory. The perturbation calculations were carried out through complete fourth order with the 6-31G** basis; i.e., the final fourth-order energies were computed in the space of single, double, triple, and quadruple substitutions (MP4) with the perturbation theory applied to all the orbitals (valence and core) of the molecule.

The energy calculations were performed for various geometries in order to assess the changes in the molecular potential energy due to bond stretching and angle deformations. We have reported previously¹⁴ the effects of extending a single C-H bond (symbolized by C-H*) while simultaneously maintaining the remaining C-H bonds at their equilibrium bond length (1.086 Å), optimizing the pyramidal angle (the angle formed by the C-H* bond and the unchanged C-H bonds), and retaining C_{3v} molecular sym-

metry. In this work, the effects of angular deformation on the potential were investigated by reducing the symmetry of the molecule. Figure 1 depicts the angular coordinates used for these calculations. The angles ψ and μ are dihedral angles, while χ and γ are angles defined by a C-H bond and the former C_3 axis.

Ab initio force constants were computed from the ab initio molecular orbital calculations using an analytical second-derivative procedure at the Hartree-Fock level.¹⁷ Harmonic vibrational frequencies for methane and methyl radical were calculated from internal coordinate force constants by using the NCRDWC program.¹⁸ Finally, the parameters of the analytic model were fitted to the ab initio data by using a nonlinear least-squares procedure.

III. Spectroscopic Data

The vibrational spectrum of methane has been studied experimentally by a number of researchers.¹⁹⁻²³ We have chosen to use the recent work of Gray and Robiette²⁴ as a source of experimental harmonic frequencies. In their work, Gray and Robiette made a new determination of the quadratic and cubic potential constants of methane by fitting the available experimental

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*Fellow of the Alfred P. Sloan Foundation, 1981-1983.

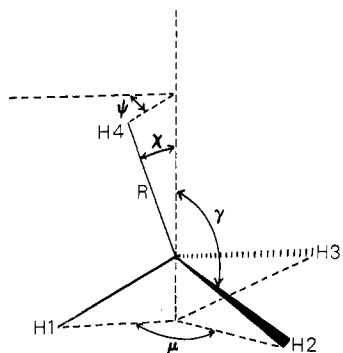


Figure 1. Definitions of the angular deformations used in the ab initio calculations. χ and γ are measured from the C_3 molecular axis to C-H bonds; ψ and μ are dihedral angles.

data. The harmonic frequencies of methane were then calculated with this new refinement of the potential constants.

In terms of a redundant set of internal coordinates (bond lengths and bond angles) seven constants are required to define the quadratic force field of methane: f_r , bond stretch constant; f_{rr} , stretch-stretch interaction constant; f_{α} , angle bend constant; $f_{\alpha\alpha}$, bend-bend interaction constant; $f_{\alpha\alpha'}$, bend-bend interaction constant; $f_{r\alpha}$, stretch-bend interaction constant; $f_{r\alpha'}$, stretch-bend interaction constant. The interaction force constants contribute substantially less to the total potential than does either f_r or f_{α} . Consequently, in order to simplify our model of the methane quadratic force field, we sought to use the redundancy in the coordinates to set one or more interaction forces to zero without limiting the force field's ability to reproduce the experimental harmonic frequencies. An analysis in terms of symmetry force constants suggested that we assign $f_{\alpha\alpha} = f_{\alpha\alpha'} = 0.0$. The values of the remaining five force constants were then adjusted in the NCRDWC program until the calculated harmonic frequencies were in good agreement with the experimental harmonic frequencies. This process was repeated with $f_{rr} = f_{\alpha\alpha} = f_{\alpha\alpha'} = 0.0$. Table I contains a summary of the experimental harmonic frequencies, the two sets of calculated ("best fit") harmonic frequencies, and the associated quadratic force fields for methane.

In contrast to methane, the vibrational spectrum of methyl radical has not been subjected to exhaustive experimental analysis. The great majority of studies have used matrix isolation or other techniques to examine only the out-of-plane bending frequency.³⁰⁻⁴¹ Consequently, we chose to define a set of harmonic frequencies for the in-plane vibrations of methyl radical by combining the experimental quadratic force field of methane with the theoretical harmonic frequencies for methane and methyl radical. Using the experimental harmonic frequencies of Gray and Robiette and ab initio harmonic frequencies calculated with GAUSSIAN 80 at the

TABLE I: Harmonic Frequencies and Force Fields

	expt ^{a,c}	best fit ^b		analytic potential ^b
Methane				
frequencies				
$\omega_1 (A_1)$	3025.5	3025.7	3023.6	3023
$\omega_2 (E)$	1582.7	1583.1	1583.1	1595
$\omega_3 (T_2)$	3156.8	3156.7	3158.9	3197
$\omega_4 (T_2)$	1367.4	1367.2	1367.3	1423
force constants				
f_r	<i>d</i>	5.422	5.426	5.496
f_{rr}		0.0038	0.0	-0.0234
f_{α}		0.5848	0.5848	0.5938
$f_{\alpha\alpha}$		0.0	0.0	0.0
$f_{\alpha\alpha'}$		0.0	0.0	0.0
$f_{r\alpha}$		0.183	0.183	0.0845
$f_{r\alpha'}$		-0.186	-0.186	-0.0823
Methyl Radical				
frequencies				
$\omega_1 (A_1')$	3026.7 ^f	3027.0	3015.0	3035
$\omega_2 (A_2')$	606.5 ^e			567.3 ^g
$\omega_3 (E')$	3192.5 ^f	3192.3	3204.5	3208
$\omega_4 (E')$	1445.0 ^f	1445.1	1445.2	1471
force constants				
f_r		5.382	5.395	5.462
f_{rr}		0.028	0.0	0.0090
f_{α}		0.4397	0.4397	0.4543
$f_{\alpha\alpha}$		0.0	0.0	0.0
$f_{r\alpha}$		0.0	0.0	0.0646
$f_{r\alpha'}$		0.0	0.0	-0.0630

^a Equilibrium bond length 1.0858 Å. ^b Equilibrium bond length 1.086 Å. Spirko and Bunker²⁵ in fitting experimental data with a nonrigid inverter anharmonic Hamiltonian report $R_e = 1.058$ Å for methyl radical. This value appears to be anomalously shorter than other values reported in the recent literature.²⁶⁻²⁹

^c Reference 20. ^d Gray and Robiette report the following symmetry force constants: $F_{11} = 5.435$ aJ/Å², $F_{22} = 0.584$ aJ, $F_{33} = 5.378$ aJ/Å², $F_{34} = 0.221$ aJ/Å, $F_{44} = 0.548$ aJ. ^e Experimental anharmonic frequency ref 30. ^f In-plane frequencies for CH₃ obtained by scaling ab initio frequencies (HF/6-31G**) by 0.96354 for the CH stretching modes and by 0.93294 for the bending modes. Scale factors were obtained by comparing experimental and theoretical harmonic frequencies for methane.

^g Anharmonic frequency calculated with a semiclassical formalism. Units: frequencies in cm⁻¹; f_r, f_{rr} in mdyn/Å, f_{α} in mdyn Å/rad². $f_{r\alpha}, f_{r\alpha'}$ in mdyn/rad.

HF/6-31G** level, we computed a ratio (EXPERIMENT/GAUSSIAN 80) for each of the four vibrational frequencies of methane. The mean value of the high (3000-3200 cm⁻¹) frequency ratios together with the mean value of low (1300-1600 cm⁻¹) frequency ratios then constituted two adjustment factors which were applied to the ab initio frequency calculations for methyl radical. The resulting values form a reference set of harmonic frequencies for the in-plane vibrations of methyl radical and are listed in Table I.

To determine a quadratic force field for the in-plane frequencies of methyl radical we assigned $f_{\alpha\alpha} = f_{r\alpha} = f_{r\alpha'} = 0.0$. Under this simplifying assumption the remaining three internal coordinate force constants (f_r, f_{rr}, f_{α}) were adjusted in the NCRDWC program until the calculated harmonic frequencies showed good agreement with the reference set of harmonic frequencies. This process was repeated after assigning $f_{rr} = f_{\alpha\alpha} = f_{r\alpha} = f_{r\alpha'} = 0.0$. A summary of the two sets of calculated (best fit) harmonic frequencies and the associated quadratic force fields is contained in Table I.

Finally, the out-of-plane bending frequency of methyl radical is known to be quite anharmonic. Very recently, Yamada et al.³⁰ have made detailed measurements of the out-of-plane bending frequency in the gas phase using an infrared tunable diode laser. This determination, reported in Table I, is in good agreement with previous matrix isolation and flash photolysis studies.

IV. Ab Initio and Numerical Fitting Results

Methane. A series of calculations was carried out at the restricted Hartree-Fock level with the 3-21G basis and at the re-

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TABLE II: Methane Energy Calculations^a

γ	μ	ψ	χ	MP4/6-31G**	fitted ^b			
109.47	120.0	0.0	0.0	-40.393 863	-40.393 863			
			10.0	-40.390 753	-40.390 767			
			30.0	-40.366 085	-40.366 271			
			50.0	-40.317 221	-40.317 297			
			30.0	10.0	-40.390 754	-40.390 754		
				30.0	-40.366 084	-40.366 088		
				50.0	-40.317 841	-40.318 886		
				60.0	10.0	-40.390 756	-40.390 740	
			60.0	30.0	0.0	10.0	-40.366 056	-40.365 741
						50.0	-40.317 770	-40.316 744
						100.0	0.0	0.0
			90.0	120.0	0.0	80.0	-40.350 386	-40.350 576
60.0	-40.297 523	-40.298 990						
99.0				-40.355 831	-40.357 607			
108.47				-40.381 744	-40.381 836			
110.47				-40.393 743	-40.393 739			
119.0				-40.393 741	-40.393 738			
129.0				-40.382 113	-40.381 705			
				-40.341 064	-40.340 607			

^a Energy in hartrees; 1 hartree = 627.51 kcal/mol. Angles in degrees; see Figure 1 for definition of angles. Equilibrium bond length = 1.086 Å. ^b Calculated with eq 15 by using methane equilibrium parameters.

stricted MP4 level with the 6-31G** basis to investigate the angular dependence of the methane potential. In these calculations, the four C-H bonds were held fixed at their equilibrium bond length (1.086 Å) while the angular coordinates (defined in Figure 1) were varied. The results of the MP4 calculations at various angular geometries are summarized in Table II.

It should be noted that the data in Table II are divided into three subgroups. The first subgroup involves variations in the χ and ψ angles. These angular deformations define the spatial orientation of the C-H* bond and, hence, the values of the three bond angles formed by the C-H* bond and the CH₃ moiety. These three angles are identified as ϕ_{14} , ϕ_{24} , ϕ_{34} and the angular variations are designated "φ-type" motions. The second subgroup of data was generated by varying the μ angle while holding one of the three dihedral angles of the CH₃ moiety fixed at its nominal value of 120.0°. This process defines the values of the three bond angles, θ_{12} , θ_{13} , θ_{23} , of the CH₃ fragment. These "θ-type" motions are the precursors of the in-plane angle bending motions of the methyl radical. Finally, the third subgroup of data was produced by a symmetric umbrella-like motion of the CH₃ moiety which is defined by the angle γ . This angular variation will be known as "Δ-type" motion and it will become the out-of-plane motion in methyl radical.

To begin the construction of an analytic representation of the potential surface, we performed a nonlinear least-squares analysis of the various levels of ab initio calculations. This analysis included only data for φ-type and θ-type motions and utilized a function of the form

$$V = V_0(R) + \frac{1}{2}f_\phi \sum_{i=1}^3 (\phi_{i4} - \phi_0(R))^2 + g_\phi \sum_{i=1}^3 (\phi_{i4} - \phi_0(R))^3 + h_\phi \sum_{i=1}^3 (\phi_{i4} - \phi_0(R))^4 + \frac{1}{2}f_\theta \sum_{i=1}^2 \sum_{j>i}^3 (\theta_{ij} - \theta_0(R))^2 + g_\theta \sum_{i=1}^2 \sum_{j>i}^3 (\theta_{ij} - \theta_0(R))^3 + h_\theta \sum_{i=1}^2 \sum_{j>i}^3 (\theta_{ij} - \theta_0(R))^4 \quad (1)$$

where $V_0(R)$ is the energy minimum and $\phi_0(R)$ and $\theta_0(R)$ are the equilibrium values of the ϕ_{i4} and θ_{ij} angles for a given C-H* bond length. The angle $\phi_0(R)$ is the optimized pyramidal angle for a given extension of the C-H* bond and is trigonometrically related to $\theta_0(R)$ by the expression

$$\theta_0(R) = \cos^{-1} [\frac{1}{2}(3 \cos^2 \phi_0(R) - 1)] \quad (2)$$

Since methane possesses tetrahedral symmetry at equilibrium (R

= 1.086 Å), we require $f_\phi = f_\theta$, $g_\phi = g_\theta$, $h_\phi = h_\theta$ for the diagonal quadratic, cubic, and quartic force constants, respectively.

This analysis was accomplished in a two-step process. First, eq 1 was fitted to the ab initio data, yielding diagonal quadratic, cubic, and quartic force constants. Secondly, in order to ensure that the cubic terms of eq 1 behave properly at large angular deformations, an augmented data set was constructed by quadratically extrapolating the ab initio data to large angular displacements. These displacements represent very high-energy regions of the potential energy surface. Their inclusion only ensures that the behavior of the function is qualitatively correct at large angular deformations and is not intended to represent accurately the potential energy surface in these regions. Equation 1 was then refitted to the enlarged data set by retaining the values of the quadratic and quartic force constants from the first step and allowing only the cubic force constant to vary in the fitting procedure. The results of fitting these diagonal force constants are summarized in Table III ($R = 1.086$ Å).

We found, however, that the utilization of only the diagonal force constants through fourth order was not sufficient to represent accurately the methane potential energy surface when large Δ-type deformations were allowed. It became necessary to include nondiagonal cubic terms (in ϕ_{i4} and θ_{ij}) in the analytic expression. For methane there are 50 such nondiagonal cubic terms which can be grouped into the five distinct sets of eq 3 based on sym-

$$C_1 = (\phi_{14} - \phi_0)^2(\theta_{23} - \theta_0) + (\phi_{24} - \phi_0)^2(\theta_{13} - \theta_0) + (\phi_{34} - \phi_0)^2(\theta_{12} - \theta_0) + (\theta_{12} - \theta_0)^2(\phi_{34} - \phi_0) + (\theta_{13} - \theta_0)^2(\phi_{24} - \phi_0) + (\theta_{23} - \theta_0)^2(\phi_{14} - \phi_0)$$

$$C_2 = (\theta_{12} - \theta_0)^2(\theta_{13} - \theta_0) + (\theta_{12} - \theta_0)^2(\theta_{23} - \theta_0) + (\theta_{13} - \theta_0)^2(\theta_{12} - \theta_0) + (\theta_{13} - \theta_0)^2(\theta_{23} - \theta_0) + (\theta_{23} - \theta_0)^2(\theta_{12} - \theta_0) + (\theta_{23} - \theta_0)^2(\theta_{13} - \theta_0) + (\phi_{14} - \phi_0)^2(\theta_{12} - \theta_0) + (\phi_{14} - \phi_0)^2(\theta_{13} - \theta_0) + (\phi_{14} - \phi_0)^2(\phi_{24} - \phi_0) + (\phi_{14} - \phi_0)^2(\phi_{34} - \phi_0) + (\phi_{24} - \phi_0)^2(\theta_{12} - \theta_0) + (\phi_{24} - \phi_0)^2(\theta_{23} - \theta_0) + (\phi_{24} - \phi_0)^2(\phi_{14} - \phi_0) + (\phi_{24} - \phi_0)^2(\phi_{34} - \phi_0) + (\phi_{34} - \phi_0)^2(\theta_{13} - \theta_0) + (\phi_{34} - \phi_0)^2(\theta_{23} - \theta_0) + (\phi_{34} - \phi_0)^2(\phi_{14} - \phi_0) + (\phi_{34} - \phi_0)^2(\phi_{24} - \phi_0) + (\theta_{12} - \theta_0)^2(\phi_{14} - \phi_0) + (\theta_{12} - \theta_0)^2(\phi_{24} - \phi_0) + (\theta_{13} - \theta_0)^2(\phi_{14} - \phi_0) + (\theta_{13} - \theta_0)^2(\phi_{34} - \phi_0) + (\theta_{23} - \theta_0)^2(\phi_{24} - \phi_0) + (\theta_{23} - \theta_0)^2(\phi_{34} - \phi_0)$$

$$C_3 = (\phi_{14} - \phi_0)(\theta_{12} - \theta_0)(\theta_{13} - \theta_0) + (\phi_{14} - \phi_0)(\phi_{24} - \phi_0)(\phi_{34} - \phi_0) + (\phi_{24} - \phi_0)(\theta_{12} - \theta_0)(\theta_{23} - \theta_0) + (\phi_{34} - \phi_0)(\theta_{13} - \theta_0)(\theta_{23} - \theta_0)$$

$$C_4 = (\theta_{12} - \theta_0)(\theta_{13} - \theta_0)(\theta_{23} - \theta_0) + (\phi_{14} - \phi_0)(\theta_{12} - \theta_0)(\phi_{24} - \phi_0) + (\phi_{14} - \phi_0)(\theta_{13} - \theta_0)(\phi_{34} - \phi_0) + (\phi_{24} - \phi_0)(\theta_{23} - \theta_0)(\phi_{34} - \phi_0)$$

$$C_5 = (\phi_{14} - \phi_0)(\theta_{12} - \theta_0)(\phi_{34} - \phi_0) + (\phi_{14} - \phi_0)(\theta_{13} - \theta_0)(\phi_{24} - \phi_0) + (\phi_{14} - \phi_0)(\theta_{23} - \theta_0)(\theta_{12} - \theta_0) + (\phi_{14} - \phi_0)(\theta_{23} - \theta_0)(\theta_{13} - \theta_0) + (\phi_{14} - \phi_0)(\theta_{23} - \theta_0)(\phi_{24} - \phi_0) + (\phi_{14} - \phi_0)(\theta_{23} - \theta_0)(\phi_{34} - \phi_0) + (\phi_{24} - \phi_0)(\theta_{12} - \theta_0)(\phi_{34} - \phi_0) + (\phi_{24} - \phi_0)(\theta_{13} - \theta_0)(\theta_{12} - \theta_0) + (\phi_{24} - \phi_0)(\theta_{13} - \theta_0)(\theta_{23} - \theta_0) + (\phi_{24} - \phi_0)(\theta_{13} - \theta_0)(\phi_{34} - \phi_0) + (\phi_{34} - \phi_0)(\theta_{12} - \theta_0)(\theta_{13} - \theta_0) + (\phi_{34} - \phi_0)(\theta_{12} - \theta_0)(\theta_{23} - \theta_0) \quad (3)$$

metry. An augmented data set (based on all the MP4/6-31G** data, i.e., φ-type, θ-type, and Δ-type motions) was fitted by including these nondiagonal cubic terms. The diagonal quadratic, cubic, and quartic force constants were assigned the values determined by the initial two-step fit described above. We found that only the C_4 set of nondiagonal cubic terms, with a force constant $g_{n4} = 0.2242$ mdyn Å/rad³, is required to be nonzero to attain an excellent fit to the data. These results are contained in Table III.

For comparison with the calculated MP4 methane energies, Table II lists the energies predicted by the complete analytic

TABLE III: Force Constants

ϕ and θ Diagonal Force Constants							
R	calculation	f_ϕ	g_ϕ	h_ϕ	f_θ	g_θ	h_θ
1.086	HF/3-21G	0.7020	-0.1243	0.0030	0.7020	-0.1243	0.0030
	HF/6-32G**	0.6507	-0.1068	0.0045	0.6507	-0.1068	0.0045
	MP4/6-31G**	0.5938	-0.0903	0.0120	0.5938	-0.0903	0.0120
	SWITCH	0.5938	-0.0903	0.0120	0.5938	-0.0903	0.0120
1.5	HF/3-21G	0.5892	-0.1057	0.0287	0.6172	-0.0129	0.0954
	HF/6-31G**	0.5727	-0.0845	0.0182	0.5891	-0.0846	0.0258
	MP4/6-31G**	0.4958	-0.0758	0.0196	0.5454	-0.1213	-0.0021
	SWITCH	0.5152	-0.0784	0.0104	0.5534	-0.0998	0.0056
2.0	HF/3-21G	0.4084	-0.0520	0.0240	0.5509	-0.0954	0.0323
	HF/6-31G**	0.4027	-0.0469	0.0193	0.5319	-0.1132	0.0040
	MP4/6-31G**	0.2902	-0.0420	0.0169	0.4940	-0.1219	-0.0031
	SWITCH	0.2975	-0.0452	0.0060	0.5001	-0.1124	-0.0028
2.5 ^a	UHF/3-21G	0.0490	-0.0126	0.0011	0.5088	-0.1209	0.0157
	UHF/6-31G**	0.0490	-0.0121	-0.0015			
	UMP4/6-31G**	0.0560	-0.0105	-0.0022			
	SWITCH	0.0551	-0.0084	0.0011	0.4664	-0.1203	-0.0082
∞^a	UHF/3-21G	0.0	0.0	0.0			
	UHF/6-31G**	0.0	0.0	0.0	0.4819	0.0	-0.0100
	UMP4/6-31G**	0.0	0.0	0.0	0.4543	-0.1232	-0.0101
	SWITCH	0.0	0.0	0.0	0.4543	-0.1232	-0.0101
Δ Diagonal Quadratic and Quartic and Nondiagonal Cubic Force Constants							
R	calculation	f_Δ	h_Δ	g_{n_4}			
1.086	MP4/6-31G**	0.0	0.0	0.2242			
	SWITCH	0.0	0.0	0.2242			
2.0	MP4/6-31G**	0.0261	0.0511	0.0901			
	SWITCH	0.0261	0.0511	0.0901			
∞^a	UMP4/6-31G**	0.0436	0.0854	0.0			
	SWITCH	0.0436	0.0854	0.0			

^a UHF data. ^b R in angstroms; $f_\phi, f_\theta, f_\Delta$ in mdyne $\text{\AA}/\text{rad}^2$; $g_\phi, g_\theta, g_{n_4}$ in mdyne $\text{\AA}/\text{rad}^3$; $h_\phi, h_\theta, h_\Delta$ in mdyne $\text{\AA}/\text{rad}^4$.

function for each angle deformation. The maximum difference between the MP4 values and the predicted values is 1.11 kcal/mol with a mean for all the data of 0.23 kcal/mol. As a percent of the MP4 energy above equilibrium, the mean difference for the entire data set is 1.21%. Finally, using the MP4 data, the analytic function predicts a quadratic bending force constant of 0.5938 mdyne $\text{\AA}/\text{rad}^2$ (Table III) which compares very favorably with the value of 0.5848 mdyne $\text{\AA}/\text{rad}^2$ (Table I) from the harmonic quadratic force field which is based on spectroscopic data.

Methyl Radical. We now turn our attention to methyl radical, the other asymptotic limit of the $\text{CH}_4 \rightleftharpoons \cdot\text{CH}_3 + \cdot\text{H}$ potential surface. Since the C-H* bond has been ruptured, only θ -type (in-plane) and Δ -type (out-of-plane) angular motions remain to be investigated. Open-shell unrestricted MP4 calculations using the 6-31G** basis were performed for various angle deformations of the methyl radical. The resulting MP4 energies are summarized in Table IV, where the angular coordinates are those of Figure 1. Using the nonlinear least-squares procedure, we fitted these data with a function of the form

$$V = V_0(R) + \frac{1}{2}f_\theta \sum_{i=1}^2 \sum_{j>i}^3 (\theta_{ij} - \theta_0(R))^2 + g_\theta \sum_{i=1}^2 \sum_{j>i}^3 (\theta_{ij} - \theta_0(R))^3 + h_\theta \sum_{i=1}^2 \sum_{j>i}^3 (\theta_{ij} - \theta_0(R))^4 + f_\Delta \sum_{i=1}^3 \Delta_i^2 + h_\Delta \sum_{i=1}^3 \Delta_i^4 \quad (4)$$

where $V_0(R)$ and $\theta_0(R)$ are defined as in eq 1, $f_\theta, g_\theta,$ and h_θ are the in-plane diagonal quadratic, cubic, and quartic force constants, respectively, f_Δ and h_Δ are the out-of-plane quadratic and quartic force constants, and $\Delta_i = \gamma - 90.0^\circ$ for $i = 1, 2, 3$. Note that the functional form allows the possibility of an unsymmetric out-of-plane motion even though we have included only symmetric out-of-plane bends in this analysis.

As in the case of methane, a two-step fitting process was utilized. First, eq 4 was fitted to the ab initio data, yielding the diagonal quadratic, cubic, quartic, and the out-of-plane quadratic and quartic force constants. After augmenting the data set as described above, we refitted eq 4 to the enlarged data set, retaining the values of the diagonal quadratic and quartic force constants determined in the first step, and allowing only the diagonal cubic and the

out-of-plane quadratic and quartic force constants to vary in the fitting procedure. The values of the force constants determined by the fitting are contained in Table III ($R = \infty$).

The energies predicted by the analytic function for various geometries are also included in Table IV for comparison with the calculated MP4 energies. The maximum difference between the MP4 energies and the predicted values is 0.052 kcal/mol with a mean of 0.016 kcal/mol for the entire data set. As a percent of the MP4 energy above equilibrium, the mean difference is 2.49%. There is also good agreement between the in-plane quadratic force constant of the analytic function (0.4543 mdyne $\text{\AA}/\text{rad}^2$, Table III) and the harmonic quadratic force constant (0.4397 mdyne $\text{\AA}/\text{rad}^2$, Table I) calculated from spectroscopic data.

As indicated above, the out-of-plane bending motion of the methyl radical is very anharmonic. Previous investigators have proposed both quartic (Riveros³⁴) and sextic (Yamada et al.) polynomials as models of this bending motion. In this study we have chosen to represent the out-of-plane frequency by a quartic polynomial and we have used a semiclassical procedure to evaluate the ability of the analytic methyl potential to reproduce the anharmonic out-of-plane bending frequency. The methyl radical was treated as if it were a classical mechanical system oscillating symmetrically such that the center of mass remains stationary. By applying the quantization formalism first proposed by Einstein⁴²

$$\oint p_q dq = (n + \frac{1}{2})h \quad (5)$$

where the appropriate mass term is given by

$$M = 3m_{\text{H}}m_{\text{C}}/(3m_{\text{H}} + m_{\text{C}}) \quad (6)$$

with m_{H} = mass of ^1H , and m_{C} = mass of ^{12}C , we are able to determine the energy levels corresponding to the quantum numbers $n = 0$ and $n = 1$ and, consequently, the lowest vibrational frequency of the methyl radical.

This semiclassical formalism was used to evaluate the out-of-plane bending frequency predicted by the sextic polynomial of Yamada et al. It yielded a value of 606.10 cm^{-1} . However,

TABLE IV: Methyl Radical Energy Calculations^a

γ	μ	MP4/6-31G**	fitted ^b
90.0	120.0	-40.217 592	-40.217 592
	110.0	-40.214 456	-40.214 422
	100.0	-40.205 047	-40.204 965
	90.0	-40.189 432	-40.189 375
	80.0	-40.167 877	-40.167 910
	70.0	-40.140 880	-40.140 934
	60.0	-40.108 940	-40.108 912
70.0	120.0	-40.206 657	-40.206 639
	80.0	-40.216 201	-40.216 198
89.0		-40.217 584	-40.217 583
91.0		-40.217 584	-40.217 583
100.0		-40.216 201	-40.216 198
109.47		-40.207 532	-40.207 552

^a Energy in hartrees; 1 hartree = 627.51 kcal/mol. Angles in degrees; see Figure 1 for definition of angles. Equilibrium bond length = 1.086 Å. ^b Calculated with eq 15 by using methyl radical equilibrium parameters.

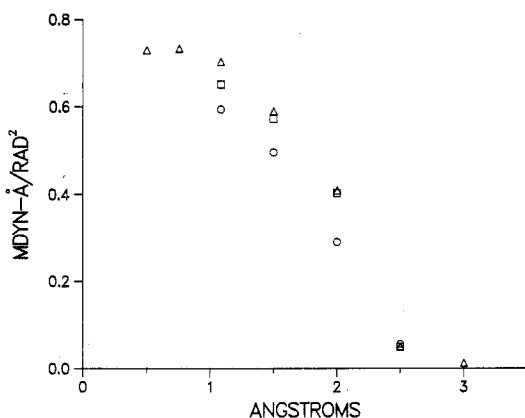


Figure 2. Quadratic force constants for the ϕ angles as a function of the C-H* bond length at various levels of calculation: (Δ) HF/3-21G; (\square) HF/6-31G**; (\circ) MP4/6-31G**.

Chipman⁴³ has corrected an error in the masses used by Yamada et al. in their calculations and has offered a revised set of potential parameters. With this new set of parameters, the semiclassical calculation predicts a frequency of 608.11 cm⁻¹. This value is in good agreement with Chipman's own calculation of 606 cm⁻¹, which is also based on the revised parameters, confirming the suitability of our semiclassical formalism.

Using the complete analytic potential for methyl radical proposed in this work, we have calculated an out-of-plane frequency of 567.34 cm⁻¹. This result differs from the experimental value of 606.453 cm⁻¹ by 39.11 cm⁻¹ or 6.45%. Surrat and Goddard⁴⁴ have also calculated this frequency obtaining a value of 585 cm⁻¹ by numerically solving for the vibrational wave functions using a CI potential curve. The harmonic frequency calculated with GAUSSIAN 80 using the 6-31G** basis at the Hartree-Fock level is 487.37 cm⁻¹.

C-H Bond Rupture Minimum-Energy Path. We have now examined the asymptotic limits of the CH₄ ⇌ ·CH₃ + ·H potential surface, proposing analytic functions which describe the angular deformations of both methane and methyl radical. The remaining task is to describe the potential energy surface as a function of the C-H* bond length. We have previously¹⁴ reported MP4 energies along the dissociation path which were calculated by optimizing the pyramidal angle at each step while maintaining C_{3v} molecular symmetry. This path, defined by the optimized pyramidal geometry with C_{3v} molecular symmetry, will be designated the minimum-energy path (MEP).

Additional calculations at the Hartree-Fock level with the 3-21G basis and at the MP4 level with the 6-31G** basis have been completed in order to explore angular deformations along

(43) D. M. Chipman, *J. Chem. Phys.*, in press.

(44) G. T. Surrat and W. A. Goddard III, *Chem. Phys.*, **27**, 39 (1977).

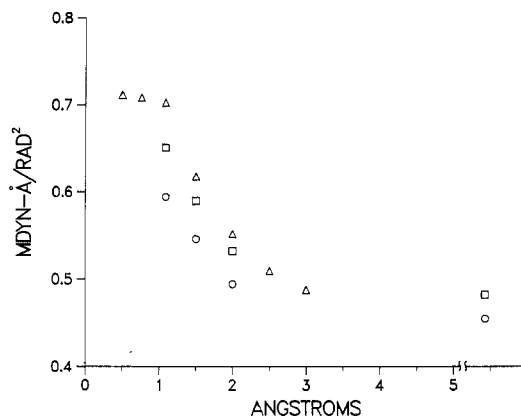


Figure 3. Quadratic force constants for the θ angles as a function of the C-H* bond length at various levels of calculation: (Δ) HF/3-21G; (\square) HF/6-31G**; (\circ) MP4/6-31G**.

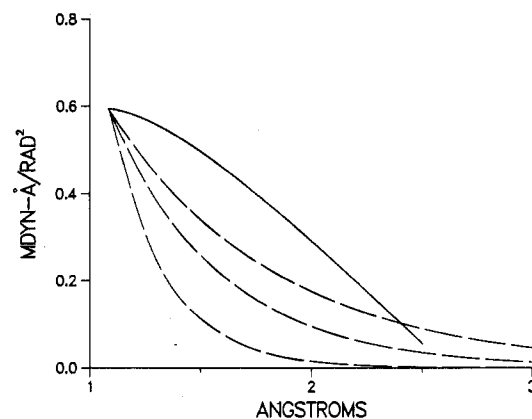


Figure 4. Quadratic bending force constant (mdyn Å/rad²) for ϕ -type motions. Solid curve: spline fit to MP4/6-31G** data. Dashed curves: BEBO calculations in which $a = 0.25$ Å (lower), $a = 0.50$ Å (middle), $a = 0.75$ Å (upper).

the MEP. The behavior of the diagonal quadratic, cubic, and quartic force constants was delineated by fitting the ab initio data for only ϕ -type and θ -type motions with eq 1. The results of this least-squares analysis are summarized in Table III for various extensions of the C-H* bond. Selected data from Table III are portrayed in Figures 2 and 3 and demonstrate the behavior of the quadratic force constants as a function of the C-H* bond length.

It is of some interest to contrast the behavior of the quadratic force constant for ϕ -type motions with the prediction of a bond-energy-bond-order (BEBO) analysis. Although the BEBO approximation was developed initially to describe the stretching force constant, an extension has been postulated by Johnston⁴⁵ which represents the bending force constant by the expression

$$f_{\alpha} = f_{\alpha}^0 n_1 n_2 \quad (7)$$

where f_{α}^0 is the force constant for angle α at equilibrium, and n_1 and n_2 are the bond orders of the two bonds which define the angle. In this study, since only one bond is extended, we set $n_1 = 1$ and represent n_2 as follows:

$$R = R_0 - a \ln n_2 \quad (8)$$

where R_0 is the equilibrium bond length. In his original work Pauling⁴⁶ found $a = 0.26$ Å while more recent studies^{47,48} in which rate constant data were fitted by using eq 8 and treating a as a parameter yield values which cluster around 0.50 Å.

(45) H. S. Johnston, "Gas Phase Reaction Rate Theory", Ronald Press, New York, 1966.

(46) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, NY, 1960.

(47) W. L. Hase, *J. Chem. Phys.*, **57**, 730 (1972); **64**, 2442 (1976).

(48) J. Troe, *J. Phys. Chem.*, **83**, 114 (1979); M. Quack, *ibid.*, **83**, 150 (1979); *Chem. Phys.*, **51**, 353 (1980).

Figure 4 depicts four curves which describe the quadratic force constant, f_ϕ , as a function of the C-H* bond length. One curve is a spline fit to the MP4/6-31G** ab initio data, while the remaining three are the results of BEBO calculations in which α is assigned the values 0.25, 0.50, and 0.75 Å, successively. The figure clearly shows both a quantitative and a qualitative difference between the MP4 curve and the three BEBO curves. These observations suggest that a BEBO approximation does not provide an adequate description of the quadratic bending force constant as a function of bond length.

In order to determine the behavior of the nondiagonal cubic and out-of-plane quadratic and quartic force constants in the intermediate region, a set of MP4/6-31G** calculations which include ϕ -type, θ -type, and Δ -type motions was completed at $R = 2.0$ Å. Rather than allow these force constants to vary independently in a least-squares analysis of the data, we chose to control their behavior with a single parameter. In this analysis the force constants were represented by expressions of the form

$$\begin{aligned} f_\Delta(R) &= (1 - Z)f_\Delta^{\text{CH}_3} \\ h_\Delta(R) &= (1 - Z)h_\Delta^{\text{CH}_3} \\ g_{n4}(R) &= Zg_{n4}^{\text{CH}_4} \end{aligned} \quad (9)$$

where $g_{n4}^{\text{CH}_4}$ is the value of the nondiagonal cubic force constant in the methane asymptotic limit, $f_\Delta^{\text{CH}_3}$ and $h_\Delta^{\text{CH}_3}$ are the values of the out-of-plane force constants in the methyl radical asymptotic limit, and Z is the parameter whose value was determined by the least-squares analysis. Since $g_{n1} = g_{n2} = g_{n3} = g_{n5} = 0.0$ in both asymptotic limits, we chose to set $g_{n1} = g_{n2} = g_{n3} = g_{n5} = 0.0$ for all extensions of the C-H* bond. The value of Z was determined to be 0.4019. The resulting force constants are reported in Table III.

V. Analytic Model Potential

All the information necessary to formulate a model potential energy surface for the $\text{CH}_4 \rightleftharpoons \cdot\text{CH}_3 + \cdot\text{H}$ reaction has now been assembled. The model potential proposed here initially will be mathematically unsymmetric in that the analytic expression is written as a function of a single C-H bond. In reality, the four C-H bonds of methane are identical and the model potential should, more generally, be expressed as a function of all four bonds. In this general form, the potential function would be invariant (or symmetric) with respect to permutations of the four C-H bond lengths. In section VI we will present a symmetric analytic potential which is an extension and generalization of this initial model.

Bond stretches will be represented as simple Morse functions:

$$V(R) = D_e[1 - e^{-\beta(R-R_0)}]^2 \quad (10)$$

where R_0 is the equilibrium bond length and the β parameter is chosen to reproduce the methane spectroscopy. Specifically, $\beta = (f_s/2D_e)^{1/2}$ where $f_s = 5.426$ mdyne/Å and $D_e = 110.60$ kcal/mol is the methane well depth calculated at the MP4 level. The use of the Morse function is probably the simplest choice for a model which possesses realistic properties of bond stretching. The actual methane potential for bond extensions probably lies between the MP4 calculated potential and the Morse potential. Intermediate forms of the bond stretch can be modeled by making the β term in the Morse function dependent on the C-H* bond length.

As noted above, the pyramidal angle is a function of the C-H* bond length. We have found that the pyramidal angle is well represented by the function

$$\phi_0(R) = \phi_0^{\text{CH}_4} + (\phi_0^{\text{CH}_4} - 90.0)[S_\phi(R) - 1.0] \quad (11)$$

with $S_\phi(R)$, a switching function, given by

$$S_\phi(R) = 1.0 - \tanh[A_\phi(R - R_0)e^{B_\phi(R - C_\phi)^3}] \quad (12)$$

The parameters in eq 11 and 12 are as follows: $\phi_0^{\text{CH}_4} = 109.47^\circ$, $A_\phi = 5.2879029 \times 10^{-1} \text{ \AA}^{-1}$, $B_\phi = 4.0066377 \times 10^{-1} \text{ \AA}^{-3}$, $C_\phi = 1.9209937 \text{ \AA}$, $R = \text{C-H}^*$ bond length in angstroms, and $\phi_0(R)$ is in degrees. While eq 11 can be used in conjunction with eq

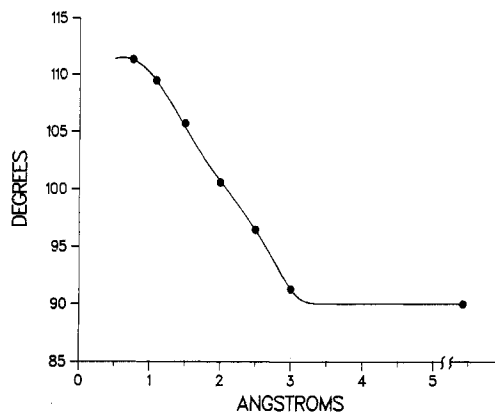


Figure 5. ϕ angle as a function of the C-H* bond length: (●) least-squares fit to MP4/6-31G** data; (solid curve) graph of the analytic function for ϕ -type angles.

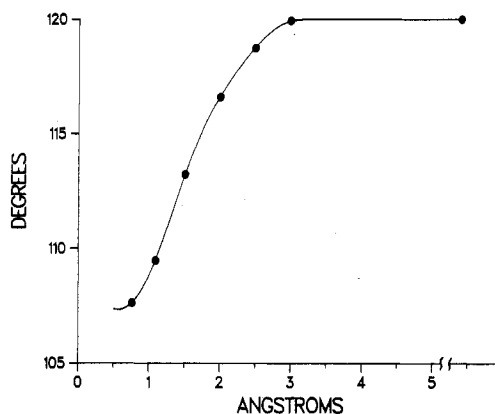


Figure 6. θ angle as a function of the C-H* bond length: (●) values calculated from the analytic function for the ϕ -type angles; (solid curve) graph of the analytic function for θ -type angles.

2 to determine the optimized values of the ϕ and θ bond angles along the MEP, it is computationally advantageous to represent the θ bond angles by a separate function:

$$\theta_0(R) = \theta_0^{\text{CH}_4} + (\theta_0^{\text{CH}_4} - 120.00)[S_\theta(R) - 1.0] \quad (13)$$

$$S_\theta(R) = 1.0 - \tanh[A_\theta(R - R_0)e^{B_\theta(R - C_\theta)^3}] \quad (14)$$

where $\theta_0^{\text{CH}_4} = 109.47^\circ$, $A_\theta = 9.0787142 \times 10^{-1} \text{ \AA}^{-1}$, $B_\theta = 3.5488587 \times 10^{-1} \text{ \AA}^{-3}$, $C_\theta = 1.8915497 \text{ \AA}$, $R = \text{C-H}^*$ bond length in angstroms, and $\theta_0(R)$ is in degrees. In order to ensure geometric consistency, the switching function $S_\theta(R)$ was fitted to a set of data derived from eq 11. Equations 11 and 13 are plotted in Figures 5 and 6, demonstrating both the variation of $\phi_0(R)$ and $\theta_0(R)$ as a function of the C-H* bond length, and the ability of these analytic functions to represent this angular variation.

As noted above, while it was necessary to include nondiagonal cubic terms in the definition of the CH_4 asymptotic limit, only one set, C_4 , contributes significantly to the angular deformation potential. We propose the following functional form to represent this potential:

$$\begin{aligned} V_{\text{angle}} &= V_0(R) + \frac{1}{2}f_\phi(R) \sum_{i=1}^3 (\phi_{i4} - \phi_0(R))^2 + \\ &g_\phi(R) \sum_{i=1}^3 (\phi_{i4} - \phi_0(R))^3 + h_\phi(R) \sum_{i=1}^3 (\phi_{i4} - \phi_0(R))^4 + \\ &\frac{1}{2}f_\theta(R) \sum_{i=1}^3 \sum_{j>i}^3 (\theta_{ij} - \theta_0(R))^2 + \\ &g_\theta(R) \sum_{i=1}^3 \sum_{j>i}^3 (\theta_{ij} - \theta_0(R))^3 + h_\theta(R) \sum_{i=1}^3 \sum_{j>i}^3 (\theta_{ij} - \theta_0(R))^4 + \\ &f_\Delta(R) \sum_{i=1}^3 \Delta_i^2 + h_\Delta(R) \sum_{i=1}^3 \Delta_i^4 + g_{n4}(R)C_4 \end{aligned} \quad (15)$$

where

$$\Delta_i = \cos^{-1} \left[\frac{(\vec{r}_2 - \vec{r}_1) \times (\vec{r}_3 - \vec{r}_1) \cdot \vec{r}_i}{|(\vec{r}_2 - \vec{r}_1) \times (\vec{r}_3 - \vec{r}_1)| |\vec{r}_i|} \right] - \phi_0(R) \quad i = 1, 2, 3$$

The vectors \vec{r}_1 , \vec{r}_2 , and \vec{r}_3 are associated with the bonds, r_1 , r_2 , and r_3 of the CH₃ moiety. All the remaining symbols in eq 15 have been previously defined. The reader will note that with $f_\Delta = h_\Delta = 0.0$ eq 15 reduces to the asymptotic expression for methane. Similarly, with $f_\phi = g_\phi = h_\phi = 0.0$ and $g_{n4} = 0.0$ eq 15 assumes the asymptotic form of the potential for methyl radical. Rather than constructing separate functions to describe each of the nine nonzero force constants in eq 15, we chose a conceptually simpler route which ensures that the diagonal cubic and quartic forces, and the nondiagonal cubic forces remain well-behaved. Generalizing the scheme used in eq 9, we expressed the force constants in the form of eq 16, where $f_\phi^{\text{CH}_4}$, $g_\phi^{\text{CH}_4}$, $h_\phi^{\text{CH}_4}$, $f_\theta^{\text{CH}_4}$, $g_\theta^{\text{CH}_4}$, $h_\theta^{\text{CH}_4}$,

$$\begin{aligned} f_\phi(R) &= S_1(R) f_\phi^{\text{CH}_4} \\ g_\phi(R) &= S_1(R) g_\phi^{\text{CH}_4} \\ h_\phi(R) &= S_1(R) h_\phi^{\text{CH}_4} \\ f_\theta(R) &= (f_\theta^{\text{CH}_4} - f_\theta^{\text{CH}_3}) S_2(R) + f_\theta^{\text{CH}_3} \\ g_\theta(R) &= (g_\theta^{\text{CH}_4} - g_\theta^{\text{CH}_3}) S_2(R) + g_\theta^{\text{CH}_3} \\ h_\theta(R) &= (h_\theta^{\text{CH}_4} - h_\theta^{\text{CH}_3}) S_2(R) + h_\theta^{\text{CH}_3} \\ f_\Delta(R) &= (1 - S_3(R)) f_\Delta^{\text{CH}_3} \\ h_\Delta(R) &= (1 - S_3(R)) h_\Delta^{\text{CH}_3} \\ g_{n4}(R) &= S_3(R) g_{n4}^{\text{CH}_4} \end{aligned} \quad (16)$$

and $g_{n4}^{\text{CH}_4}$ are the values of the respective force constants in the methane asymptotic limit; $f_\theta^{\text{CH}_3}$, $g_\theta^{\text{CH}_3}$, $h_\theta^{\text{CH}_3}$, $f_\Delta^{\text{CH}_3}$, and $h_\Delta^{\text{CH}_3}$ are the values of the respective force constants in the methyl radical asymptotic limit; and $S_1(R)$, $S_2(R)$, and $S_3(R)$ are continuous functions whose values are 1.0 in the methane limit and 0.0 in the methyl radical limit. Hence, only three switching functions, $S_1(R)$, $S_2(R)$, and $S_3(R)$, must be constructed which have the correct asymptotic behavior and which are well-behaved along the MEP between methane and methyl radical.

The three functional forms of eq 17 were constructed by a

$$\begin{aligned} S_1(R) &= 1.0 - \tanh(\alpha_1(R - R_0)(R - \beta_1)^8) \\ \alpha_1 &= 1.5313681 \times 10^{-7} \text{ \AA}^{-9} \\ \beta_1 &= -4.6696246 \text{ \AA} \\ S_2(R) &= 1.0 - \tanh(\alpha_2(R - R_0)(R - \beta_2)^6) \\ \alpha_2 &= 1.0147402 \times 10^{-7} \text{ \AA}^{-7} \\ \beta_2 &= -1.2362798 \times 10^1 \text{ \AA} \\ S_3(R) &= 1.0 - \tanh(\alpha_3(R - R_0)(R - \beta_3)^2) \\ \alpha_3 &= 1.4191474 \times 10^{-1} \text{ \AA}^{-3} \\ \beta_3 &= -3.0684503 \times 10^{-1} \text{ \AA} \end{aligned} \quad (17)$$

nonlinear least-squares analysis of the MP4/6-31G** data along the MEP. Figures 7–9 display the graphs of the three analytic switching functions and their agreement with the parameters derived from the least-squares analysis of the ab initio data. The effectiveness of the switching-function formalism is further demonstrated by calculating force constants along the MEP. Table III displays the agreement between the force constants calculated by using the analytic switching functions and the values obtained by a least-squares analysis of the MP4 data.

The complete analytic expression for the CH₄ ⇌ ·CH₃ + ·H potential energy surface can now be written:

$$V_{\text{total}} = \sum_{i=1}^3 D_e [1 - e^{-\beta(r_i - R_0)}]^2 + D_e [1 - e^{-\beta(R - R_0)}]^2 + V_{\text{angle}} \quad (18)$$

where R is the C–H* bond length and the r_i are the three bond

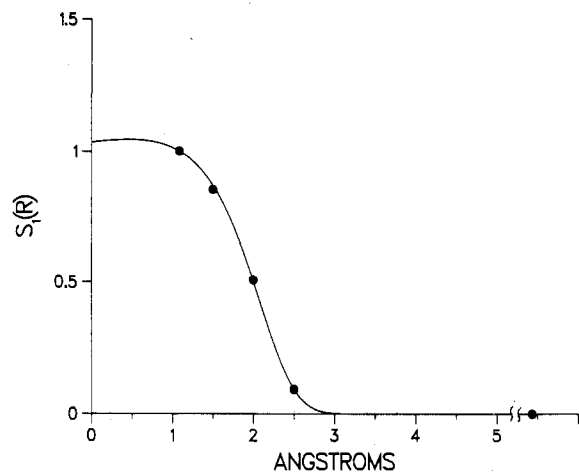


Figure 7. Switching function $S_1(R)$: (●) least-squares fit to MP4/6-31G** data; (solid curve) graph of the analytic switching function.

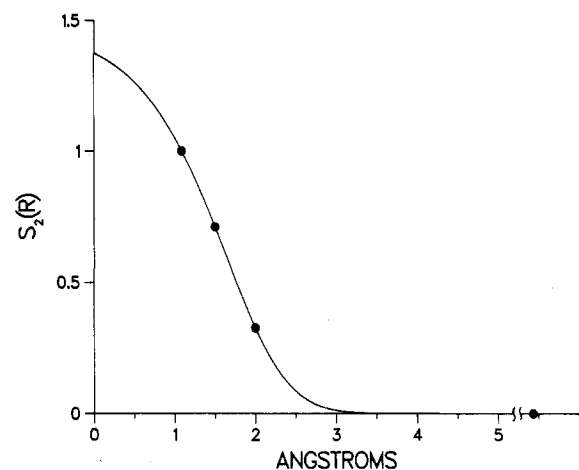


Figure 8. Switching function $S_2(R)$: (●) least-squares fit to MP4/6-31G** data; (solid curve) graph of the analytic switching function.

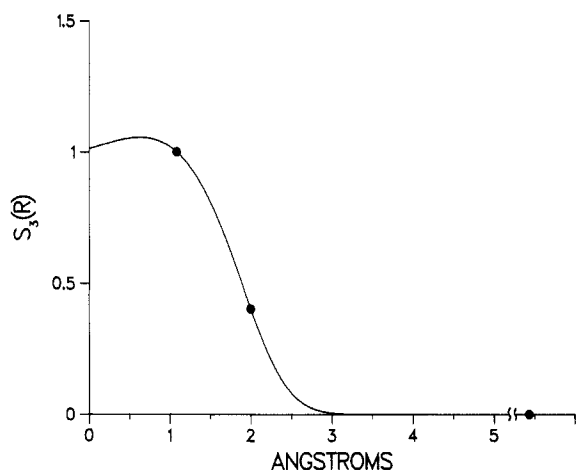


Figure 9. Switching function $S_3(R)$: (●) least-squares fit to MP4/6-31G** data; (solid curve) graph of the analytic switching function.

lengths of the CH₃ moiety. Using this potential, we are able to calculate the stretch–bend interaction force constants for methane from the following expressions:

$$\begin{aligned} \frac{\partial^2 V_{\text{total}}}{\partial R \partial \phi} \Big|_{\text{eq}} &\equiv f_{R\phi} = -f_\phi \frac{\partial \phi_0}{\partial R} \Big|_{\text{eq}} \\ \frac{\partial^2 V_{\text{total}}}{\partial R \partial \theta} \Big|_{\text{eq}} &\equiv f_{R\theta} = -f_\theta \frac{\partial \theta_0}{\partial R} \Big|_{\text{eq}} \end{aligned} \quad (19)$$

where $f_\phi = f_\theta$ is the diagonal quadratic force constant for the

equilibrium geometry of methane. Both partial derivatives can be computed analytically from eq 11 and 13. Evaluating the expression in eq 19 yields the values $f_{R\phi} = 0.845$ mdyn/rad and $f_{R\theta} = -0.0823$ mdyn/rad.

VI. General Symmetric Analytic Potential

There are several chemically significant reasons for developing a model potential which is a function of all four CH bonds. In methane all the bonds are equivalent. Hence, a potential function must reflect this symmetry in order to represent properly the unimolecular decomposition of the CH₄ molecule. Further, the various substituted-methane systems or, more generally, tetrahedral carbon centers are candidates for potentially significant studies of molecular reaction dynamics. Such investigations will require potential energy surfaces which incorporate the complete symmetry of the tetrahedral carbon center. We now propose a generalized symmetric analytic potential which describes the rupture of one bond of a tetrahedral carbon center.

The i -th bond is represented by a Morse function of the form

$$V(r_i) = D_i [1 - e^{-\beta(r-r_i^0)}]^2 \quad (20)$$

where r_i^0 is the equilibrium bond length of the i -th bond. The two Morse parameters, β , and D_i , are written as functions of the other three bond lengths:

$$\beta_i = \beta_i^0 + (\beta_i^1 - \beta_i^0) [S_\beta(r_j) S_\beta(r_k) S_\beta(r_l) - 1] \quad (21)$$

$$D_i = D_i^0 + (D_i^1 - D_i^0) [S_D(r_j) S_D(r_k) S_D(r_l) - 1] \quad (22)$$

where β_i^0 and D_i^0 are the equilibrium values of the parameters and β_i^1 and D_i^1 are their asymptotic values as $r_i \rightarrow \infty$. The switching functions $S_\beta(r_j)$ and $S_D(r_j)$ are designed to represent the properties of the system of interest, monotonically assuming values between 1.0 and 0.0. For our methane potential, $\beta_i^0 = \beta_i^1$ and $D_i^0 = D_i^1$.

The equilibrium value of the angle defined by the i -th and j -th bonds, θ_{ij}^0 , is modeled as a function of the rupturing bond by the expression

$$\theta_{ij}^0 = \theta_{ij}^1 + (\theta_{ij}^2 - \theta_{ij}^1) [S_\theta^1(r_i) S_\theta^1(r_j) - 1] + (\theta_{ij}^3 - \theta_{ij}^2) [S_\theta^2(r_k) S_\theta^2(r_l) - 1] \quad (23)$$

where θ_{ij}^1 is the equilibrium value of θ_{ij} at the undistorted tetrahedral center, θ_{ij}^2 is the asymptotic value of θ_{ij} as either $r_i \rightarrow \infty$ or $r_j \rightarrow \infty$, and θ_{ij}^3 is the asymptotic value of θ_{ij} as either $r_k \rightarrow \infty$ or $r_l \rightarrow \infty$. Again, the switching functions, $S_\theta^1(r_i)$ and $S_\theta^2(r_k)$, are chosen to represent the properties of the system of interest, monotonically assuming values between 1.0 and 0.0. Specifically, for the CH₄ \rightleftharpoons \cdot CH₃ + \cdot H reaction, $\theta_{ij}^1 = 109.47^\circ$, $\theta_{ij}^2 = 90.0^\circ$, $\theta_{ij}^3 = 120.0^\circ$ and, using earlier notation, $S_\theta^1(r_i) \equiv S_\phi(r_i)$ and $S_\theta^2(r_k) \equiv S_\phi(r_k)$ (see eq 11-14).

Because the equilibrium value of each bond angle is written as a function of all four bond lengths, it can be shown analytically that the general symmetric potential exhibits several nonzero interaction force constants. In particular, the stretch-stretch force constants and the stretch-bend force constants for both methane and methyl radical are nonzero. Hence, the general symmetric potential proposed here includes coupling both between the individual stretching degrees of freedom and between the stretching and bending degrees of freedom. The values of the interaction force constants are listed in Table I.

In the same spirit, the diagonal quadratic, cubic, and quartic force constants for the angle defined by the i -th and j -th bonds are described by the functions

$$f_{ij} = f_{ij}^0 + f_{ij}^1 [S_f^1(r_i) S_f^1(r_j) - 1] + (f_{ij}^2 - f_{ij}^1) [S_f^2(r_k) S_f^2(r_l) - 1] \quad (24)$$

$$g_{ij} = g_{ij}^0 + g_{ij}^1 [S_g^1(r_i) S_g^1(r_j) - 1] + (g_{ij}^2 - g_{ij}^1) [S_g^2(r_k) S_g^2(r_l) - 1] \quad (25)$$

$$h_{ij} = h_{ij}^0 + h_{ij}^1 [S_h^1(r_i) S_h^1(r_j) - 1] + (h_{ij}^2 - h_{ij}^1) [S_h^2(r_k) S_h^2(r_l) - 1] \quad (26)$$

where f_{ij}^0 , g_{ij}^0 , and h_{ij}^0 are the equilibrium values of the quadratic, cubic, and quartic force constants, respectively, and f_{ij}^1 , g_{ij}^1 , and h_{ij}^1 are the asymptotic values of these constants as $r_k \rightarrow \infty$ or $r_l \rightarrow \infty$. The reader should note that f_{ij}^1 , g_{ij}^1 , h_{ij}^1 , the asymptotic values of the constants as $r_i \rightarrow \infty$ or $r_j \rightarrow \infty$, are identically zero since the angle θ_{ij} is no longer defined when either bond i or bond j is ruptured. The functions $S_f^1(r_i)$, $S_g^1(r_i)$, $S_h^1(r_i)$, $S_f^2(r_k)$, $S_g^2(r_k)$, and $S_h^2(r_k)$ must be suitably defined, monotonically taking the values between 1.0 and 0.0. For the methane system, $S_f^1(r_i) = S_g^1(r_i) = S_h^1(r_i) \equiv S_1(r_i)$ and $S_f^2(r_k) = S_g^2(r_k) = S_h^2(r_k) \equiv S_2(r_k)$, where $S_1(r_i)$ and $S_2(r_k)$ are defined in eq 17.

The out-of-plane quadratic and quartic force constants are represented as

$$f_{\Delta i} = (1 - S_\Delta(r_i)) S_\Delta(r_j) S_\Delta(r_k) S_\Delta(R_i) f_{\Delta i}^1 \quad (27)$$

$$h_{\Delta i} = (1 - S_\Delta(r_i)) S_\Delta(r_j) S_\Delta(r_k) S_\Delta(R_i) h_{\Delta i}^1 \quad (28)$$

where $f_{\Delta i}^1$ and $h_{\Delta i}^1$ are the asymptotic limits of the quadratic and quartic force constants as bond i is broken, and $S_\Delta(r_i)$ is a suitably chosen switching function with values ranging monotonically from 1.0 to 0.0. Finally, the nondiagonal cubic force constants are described by the following functional form:

$$g_{ni} = \sum_{j=1}^4 (S_g^n(r_j) - 1) (g_{ni}^0 - g_{nj}^1) + g_{ni}^0 \quad (29)$$

where g_{ni}^0 is the equilibrium value of the i -th nondiagonal cubic force constant, g_{nj}^1 is the asymptotic limit of the i -th constant when the j -th bond is broken, and $S_g^n(r_j)$ is a suitably chosen switching function whose values range monotonically between 1.0 and 0.0.

In describing the CH₄ \rightleftharpoons \cdot CH₃ + \cdot H reaction, we have chosen $S_\Delta(r_i) = S_g^n(r_i) \equiv S_3(r_i)$ where $S_3(r_i)$ is defined by eq 17 and $g_{ni}^1 = 0.0$ for all five nondiagonal cubic force constants. The out-of-plane angles, Δ_{ij} , associated with the breaking of the i -th bond are defined by the expression

$$\Delta_{ij} = \cos^{-1} [\tilde{N}_i \tilde{r}_j / |\tilde{r}_j|] - \theta_{ij}^0 \quad (30)$$

where \tilde{N}_i is a unit vector normal to the plane defined by the three hydrogen atoms of the CH₃ moiety, and θ_{ij}^0 is defined in eq 23. The vector \tilde{N}_i is given by

$$\tilde{N}_i = \frac{(\tilde{r}_k - \tilde{r}_j) \times (\tilde{r}_l - \tilde{r}_j)}{|(\tilde{r}_k - \tilde{r}_j) \times (\tilde{r}_l - \tilde{r}_j)|} \quad i = 1, 2, 3, 4 \quad (31)$$

The vectors \tilde{r}_j , \tilde{r}_k , \tilde{r}_l are those associated with the three unruptured bonds of the CH₃ fragment. Lastly, the C₄ set of nondiagonal cubic force constants is written in terms of the symmetric notation:

$$C_4 = (\theta_{12} - \theta_{12}^0)(\theta_{13} - \theta_{13}^0)(\theta_{23} - \theta_{23}^0) + (\theta_{14} - \theta_{14}^0)(\theta_{12} - \theta_{12}^0)(\theta_{24} - \theta_{24}^0) + (\theta_{14} - \theta_{14}^0)(\theta_{13} - \theta_{13}^0)(\theta_{34} - \theta_{34}^0) + (\theta_{24} - \theta_{24}^0)(\theta_{23} - \theta_{23}^0)(\theta_{34} - \theta_{34}^0) \quad (32)$$

Using the above definitions we now write a general symmetric analytic potential describing the CH₄ \rightleftharpoons \cdot CH₃ + \cdot H reaction:

$$V_{\text{total}} = \sum_{i=1}^4 D_i (1 - e^{\beta(r-r_i^0)})^2 + \frac{1}{2} \sum_{i=1}^3 \sum_{j>i}^4 f_{ij} (\theta_{ij} - \theta_{ij}^0)^2 + \sum_{i=1}^3 \sum_{j>i}^4 g_{ij} (\theta_{ij} - \theta_{ij}^0)^3 + \sum_{i=1}^3 \sum_{j>i}^4 h_{ij} (\theta_{ij} - \theta_{ij}^0)^4 + \sum_{i=1}^4 f_{\Delta i} \sum_{j=1}^4 \Delta_{ij}^2 + \sum_{i=1}^4 h_{\Delta i} \sum_{j=1}^4 \Delta_{ij}^4 + g_{n4} C_4 \quad (33)$$

where all the symbols have been previously defined. Equation 33 is the symmetric analogue of eq 18. It allows one to treat all four bonds of a tetrahedral carbon center in a symmetric and uniform manner. Table I contains a summary of the frequencies calculated with the general symmetric potential and the corresponding force fields for both methane and methyl radical.

VII. Summary

In this work we have presented a model molecular anharmonic potential based on a switching-function formalism for the CH₄

$\rightleftharpoons \cdot\text{CH}_3 + \cdot\text{H}$ reactive pathway (MAPS/ $\text{CH}_4\text{-I}$). In constructing this model potential we used the available spectroscopic data in conjunction with ab initio calculations to define the asymptotic limits of methane and methyl radical. These limits were then joined by using a set of switching functions based on ab initio calculations performed along the dissociation path.

This switching-function formalism confers a great deal of flexibility on the analytic model of the potential energy surface. One may, for example, use either ab initio or spectroscopic force constants in the two asymptotic limits. Further, as more detailed and sophisticated ab initio information describing the reaction pathway becomes available, it can be incorporated into this model by refitting the parameters of the switching functions. In effect, the construction and modification of a model potential energy surface has been divided into two more tractable steps: (1) determination of each asymptotic limit; (2) connection of these limits by physically realistic analytic functions.

The general symmetric potential proposed in this paper only addresses the $\text{CH}_4 \rightleftharpoons \cdot\text{CH}_3 + \cdot\text{H}$ channel. There is another allowed reaction channel, namely, $\text{CH}_4 \rightleftharpoons \text{H}_2 + \text{CH}_2(^1\text{A}_1)$. However, the available thermochemical data⁴⁹⁻⁵¹ indicates that

its threshold is approximately 15 kcal/mol higher than that for the former channel. Even the symmetry-forbidden reaction $\text{CH}_4 \rightleftharpoons \text{H}_2 + \text{CH}_2(^3\text{B}_1)$ has an endothermicity which is approximately 7 kcal/mol higher than that for the $\text{CH}_4 \rightleftharpoons \cdot\text{CH}_3 + \cdot\text{H}$ reaction pathway. Triplet methylene undergoes an abstraction reaction with H_2 to form hydrogen atoms and methyl radicals.⁵²

The model potential proposed here can be used, following Miller,⁵³ to find the $\cdot\text{CH}_3 + \cdot\text{H} \rightarrow \text{CH}$ reaction path. Variational criteria can then be applied to locate the critical configuration as a function of energy and the activated complex as a function of temperature. Finally, this model potential can be used in quasiclassical trajectory calculations of the $\text{CH}_4 \rightleftharpoons \cdot\text{CH}_3 + \cdot\text{H}$ unimolecular and bimolecular rate constants at energies where these are the only open reaction channels on the potential energy surface.

Acknowledgment. We express our gratitude to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for their support of this research. We also thank the Wayne State University Computing Center for providing the facilities which were used to carry out our calculations. Special thanks to Dr. K. N. Swamy for his helpful conversations.

Registry No. CH_4 , 74-82-8; CH_3 , 15194-58-8; H, 12385-13-6.

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Kinetic Parameters for Hydrogen Bonding to an Anion Radical

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Electron spin resonance and relaxation theory have been utilized to measure the rate constant and its temperature dependence of hydrogen-bond formation to the *p*-cyanonitrobenzene anion radical ($\text{PCNB}^{\cdot-}$). The rate constant (k_f) for hydrogen-bond exchange from the solvent to the unassociated anion radical ($\text{PCNB}^{\cdot-} + \text{HMPA} \cdots \text{H-OEt} \rightarrow \text{PCNB}^{\cdot-} \cdots \text{H-OEt} + \text{HMPA}$) is $(7.0 \pm 1.0) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C where the solvent is hexamethylphosphoramide (HMPA) and the hydrogen-bond donor is ethanol. The negative entropy of activation and entropy of reaction are interpreted in terms of an activated complex that consists of an ethanol molecule having a partial hydrogen bond to a solvent and anion radical molecule. This is the first report of activation parameters controlling the rate of hydrogen-bond formation to an anionic species.

In protic solvents, the most important phenomenon incorporated into the free energy of solvation of anions is hydrogen bonding. However, there are very few reports of thermodynamic parameters controlling hydrogen-bond formation to solvated anions due to experimental difficulties and complexities that arise from competing interactions such as ion association and solvent-solvent hydrogen-bonding interactions. These problems have been discussed by Benoit and co-workers.¹ For a few systems these difficulties have been overcome, and free energies of hydrogen-bond formation to ion associated halide ions have been determined by using IR spectroscopy.² For several systems, the presence of hydrogen-bonded anions in solution has been noted by their effect upon IR and NMR spectra.³⁻⁵ The difficulties of studying the

formation of hydrogen bonds to anions are greatly enhanced when one tries to study the kinetics of these processes. Thus, other than a single report from our laboratory,⁶ the literature is devoid of reports of the kinetics of hydrogen bonding to anions. Further, there are no reports of activation parameters for hydrogen-bond formation to anions in solution. Here we wish to report the first enthalpy and entropy of activation for hydrogen-bond formation to a solvated anion.

This kinetic study is carried out with an anion system that is paramagnetic so that relaxation theory can be applied. The anion radical must be generated free from association with the cation and must be polarizable enough so that the formation of anion radical-proton donor hydrogen bonds will perturb the spin density in the anion radical. Also, the interpretation of the data, in this

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