Analytic Function for the H + CH₃ ⇆ CH₄ Potential Energy Surface

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An analytic function for the ground electronic state CH₄ = -CH₃ + -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 CH₄ = -CH₃ + -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 CH₄ = -CH₃ + -H is particularly important for the resolution of several fundamental questions. While the CH₄ → -CH₃ + -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.9-11

This study was initiated in an attempt to begin the clarification of some of these issues. We have reported previously12-14 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 CH₄ = -CH₃ + -H potential energy surface.

II. Method

The ab initio calculations were carried out with the GAUSSIAN 80 series of programs5 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 previously11 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 (1.08 Å), optimizing the pyramidal angle (the angle formed by the C–H* bond and the unchanged C–H bonds), and retaining Cₓ molecular symmetry. In this work, the effects of angular deformation on the potential energy were investigated by reducing the symmetry of the molecule. Figure 1 depicts the angular coordinates used for these calculations. The angles ϕ and μ are dihedral angles, while χ and γ are angles defined by a C–H bond and the former Cₓ 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 Vibrational harmonic 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


8 P. Roth, Forsch. Ingenieurwes., 46, 93 (1980).
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: \( f_{\text{stretch}} \), bond stretch constant; \( f_{\text{bond}} \), stretch-stretch interaction constant; \( f_{\text{angle}} \), angle bend constant; \( f_{\text{bond-angle}} \), bend-angle interaction constant; \( f_{\text{bend-bend}} \), bend-bend interaction constant; \( f_{\text{stretch-bend}} \), stretch-bend interaction constant; \( f_{\text{stretch-bend}} \), stretch-bend interaction constant. The interaction force constants contribute substantially less to the total potential than does either \( f_{\text{stretch}} \) or \( f_{\text{angle}} \). 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 \( f_{\text{stretch}} = f_{\text{angle}} = 0.0 \). The values of the remaining five force constants were then adjusted in the NCRDW program until the calculated harmonic frequencies were in good agreement with the experimental harmonic frequencies. This process was repeated with \( f_{\text{stretch}} = f_{\text{angle}} = 0.0 \). 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. Consequently, we chose to define a set of harmonic frequencies 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 \( f_{\text{stretch}} = f_{\text{angle}} = 0.0 \). The values of the remaining five force constants were then adjusted in the NCRDW program until the calculated harmonic frequencies were in good agreement with the experimental harmonic frequencies. This process was repeated with \( f_{\text{stretch}} = f_{\text{angle}} = 0.0 \). 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. 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

HF/6-31G** level, we computed a ratio (EXPERIMENT/GAUSSIAN) 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 \( f_{\text{stretch}} = f_{\text{angle}} = 0.0 \). Under this simplifying assumption the remaining three internal coordinate force constants \( (f_{\text{stretch}}, f_{\text{angle}}, f_{\text{bend-bend}}) \) were adjusted in the NCRDW program until the calculated harmonic frequencies showed good agreement with the reference set of harmonic frequencies. This process was repeated after assigning \( f_{\text{stretch}} = f_{\text{angle}} = f_{\text{bend-bend}} = 0.0 \). 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.

### Table I: Harmonic Frequencies and Force Fields

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<tr>
<th></th>
<th>Methane</th>
<th>Methyl Radical</th>
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<td><strong>analytic</strong></td>
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<td>( \omega_1 (A_1^g) )</td>
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<td>( \omega_2 (E) )</td>
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<td>( \omega_5 (T_3^g) )</td>
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<td>1423</td>
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<table>
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<th><strong>force constants</strong></th>
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<th><strong>f_2</strong></th>
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<td>( f_{\text{stretch}} )</td>
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<td>( f_{\text{bend-bend}} )</td>
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<tr>
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<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( f_{\text{stretch}} )</td>
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<td>0.183</td>
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<tr>
<td>( f_{\text{angle}} )</td>
<td>-0.186</td>
<td>-0.186</td>
</tr>
</tbody>
</table>

### References

H + CH3 ≜ CH4 Potential Energy Surface

| TABLE II: Methane Energy Calculationsd |
|-----------------|-------|--------|
| \( \gamma \) | \( \mu \) | \( \psi \) | \( \chi \) | \( \text{MP4/6-31G}^{**} \) |
| 109.47 | 120.0 | 0.0 | 0.0 | -40.393 863 |
| 100.0 | 0.0 | 0.0 | 0.0 | -40.390 753 |
| 30.0 | 0.0 | 0.0 | 0.0 | -40.366 085 |
| 30.0 | 50.0 | 0.0 | 0.0 | -40.317 221 |
| 30.0 | 50.0 | 10.0 | 0.0 | -40.317 754 |
| 30.0 | 50.0 | 10.0 | 50.0 | -40.366 084 |
| 30.0 | 50.0 | 10.0 | 50.0 | -40.317 841 |
| 30.0 | 60.0 | 10.0 | 0.0 | -40.390 756 |
| 30.0 | 60.0 | 10.0 | 50.0 | -40.366 088 |
| 30.0 | 60.0 | 10.0 | 50.0 | -40.318 886 |
| 100.0 | 0.0 | 0.0 | 0.0 | -40.382 845 |
| 100.0 | 50.0 | 0.0 | 0.0 | -40.382 856 |
| 80.0 | 0.0 | 0.0 | 0.0 | -40.350 386 |
| 60.0 | 0.0 | 0.0 | 0.0 | -40.297 523 |
| 60.0 | 0.0 | 0.0 | 0.0 | -40.298 990 |
| 90.0 | 120.0 | 0.0 | 0.0 | -40.355 831 |
| 90.0 | 120.0 | 0.0 | 0.0 | -40.357 607 |
| 108.47 | 120.0 | 0.0 | 0.0 | -40.381 744 |
| 108.47 | 120.0 | 0.0 | 0.0 | -40.381 836 |
| 110.47 | 120.0 | 0.0 | 0.0 | -40.370 741 |
| 119.0 | 120.0 | 0.0 | 0.0 | -40.341 113 |
| 129.0 | 120.0 | 0.0 | 0.0 | -40.341 064 |

\( \text{fitted} \)

\( \text{a} \) 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. \( \text{b} \) 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 \( \chi \) and \( \psi \) 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 \( \psi_{14}, \psi_{23}, \) and \( \psi_{34} \) and the angular variations are designated "\( \phi \)-type" motions. The second subgroup of data was generated by varying the \( \mu \) 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, \( \theta_{12}, \theta_{34}, \theta_{23}, \) of the CH3 fragment. These "\( \theta \)-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 \( \gamma \). This angular variation will be known as "\( \Lambda \)-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 \( \phi \)-type and \( \theta \)-type motions and utilized a function of the form

\[
V = V_0(R) + \frac{1}{2} \sum_{1=1}^{3} \frac{1}{2} \left( \phi_{14} - \phi_0(R) \right)^2 + h_0 \sum_{1=1}^{3} \left( \phi_1 - \phi_0(R) \right)^2
\]

where \( V_0(R) \) is the energy minimum and \( \phi_0(R) \) and \( \theta_0(R) \) are the equilibrium values of the \( \phi_{14} \) and \( \theta_{12} \) angles for a given C-H* bond length. The angle \( \theta_{12} \) 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

\[
\theta_0(R) = \cos^{-1} \left[ \frac{1}{2} \left( \frac{2}{3} m^2 \phi_0(R) \right) \right]
\]

Since methane possesses tetrahedral symmetry at equilibrium (\( R = 1.086 \) Å), we require \( f_0 = f_0 \), \( g_0 = g_0 \), \( h_0 = h_0 \) 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 \( \Lambda \)-type deformations were allowed. It became necessary to include nondiagonal cubic terms (in \( \phi_{14} \) and \( \theta_{12} \)) 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 symmetry.

\[
C_1 = \left( \phi_{14} - \phi_0 \right)^2 \left( \theta_{12} - \theta_0 \right) + \left( \phi_{24} - \phi_0 \right)^2 \left( \theta_{34} - \theta_0 \right) + \left( \phi_{34} - \phi_0 \right)^2 \left( \theta_{23} - \theta_0 \right)
\]

\[
C_2 = \left( \theta_{12} - \theta_0 \right)^2 \left( \phi_{14} - \phi_0 \right) + \left( \theta_{12} - \theta_0 \right)^2 \left( \phi_{24} - \phi_0 \right) + \left( \theta_{12} - \theta_0 \right)^2 \left( \phi_{34} - \phi_0 \right)
\]

\[
C_3 = \left( \phi_{14} - \phi_0 \right) \left( \theta_{12} - \theta_0 \right) + \left( \phi_{24} - \phi_0 \right) \left( \theta_{23} - \theta_0 \right) + \left( \phi_{34} - \phi_0 \right) \left( \theta_{34} - \theta_0 \right)
\]

\[
C_4 = \left( \phi_{14} - \phi_0 \right) \left( \theta_{12} - \theta_0 \right) + \left( \phi_{24} - \phi_0 \right) \left( \theta_{23} - \theta_0 \right) + \left( \phi_{34} - \phi_0 \right) \left( \theta_{34} - \theta_0 \right)
\]

\[
C_5 = \left( \phi_{14} - \phi_0 \right) \left( \theta_{12} - \theta_0 \right) + \left( \phi_{24} - \phi_0 \right) \left( \theta_{23} - \theta_0 \right)
\]

For comparison with the calculated MP4 methane energies, Table II lists the energies predicted by the complete analytic expression.
function for each angle deformation. The maximum difference between the MP4 energies 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 mdyn Å/rad² (Table III) which compares very favorably with the value of 0.5848 mdyn Å/rad² (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 CH₄ radical. In the case of methane, a two-step fitting process was utilized. 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 = ∞). 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 mdyn Å/rad², Table III) and the harmonic quadratic force constant (0.4397 mdyn Å/rad², 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 (Riveros²⁴) 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

\[ J \, p_4 \, dq = (n + \frac{1}{2})h \]

where the appropriate mass term is given by

\[ M = 3m_2m_3/(3m_2 + m_3) \]

with \( m_2 = \text{mass of } ^1\text{H}_2 \) and \( m_3 = \text{mass of } ^2\text{C}_2 \). 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,
H + CH₃ = CH₄ Potential Energy Surface

TABLE IV: Methyl Radical Energy Calculations

<table>
<thead>
<tr>
<th>γ</th>
<th>μ</th>
<th>MP4/6-31G**</th>
<th>Fitted (^b)</th>
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<tr>
<td>90.0</td>
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<tr>
<td>109.47</td>
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\(^a\) 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.

Viswanath and Goddard \(^11\) have calculated this frequency \(\nu_{\text{b}}\) obtaining a value of 585 cm\(^{-1}\) by numerically solving for the vibrational wave functions using the complete analytic potential for methyl radical 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 \(\phi\)-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 Johnston \(^{45}\) which represents the bending force constant by the expression

\[
f_{\phi} = f_{\phi}^0 n_1 n_2
\]

where \(f_{\phi}^0\) is the force constant for angle \(\phi\) 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:

\[
R = R_0 - a \ln n_2
\]

where \(R_0\) is the equilibrium bond length. In his original work Pauling \(^{46}\) 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.


Figure 4 depicts four curves which describe the quadratic force constant, \( f_a \), 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 \( \alpha \) is assigned the values 0.25, 0.50, and 0.75 Å, successively. The figure clearly shows both a qualitative and a quantitative 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 \( \phi \)-type, \( \theta \)-type, and \( \Delta \)-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
\[
\begin{align*}
  f_a(R) &= (1 - Z)f_a^{\text{CH}_4} \\
  h_a(R) &= (1 - Z)h_a^{\text{CH}_4} \\
  g_a(R) &= Zg_a^{\text{CH}_4}
\end{align*}
\]
where \( g_a^{\text{CH}_4} \) is the value of the nondiagonal cubic force constant in the methane asymptotic limit; \( f_a^{\text{CH}_4} \) and \( h_a^{\text{CH}_4} \) 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 \( g_a = g_a = g_a = g_a = 0.0 \) in both asymptotic limits, we chose to set \( g_a = g_a = g_a = g_a = 0.0 \) for all extensions of the C–H* bond. The value of \( Z \) was determined to be 0.4091. 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 \( \text{CH}_4 \rightarrow \text{CH}_3^+ + \cdot \text{H} \) 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:
\[
V(R) = D_e [1 - e^{-\beta(R-R_0)}]^2
\]
where \( R_0 \) is the equilibrium bond length and the \( \beta \) parameter is chosen to reproduce the methane spectroscopy. Specifically, \( \beta = (f_a/2D_e)^{1/2} \) where \( f_a = 5.426 \text{ mdyn/Å} \) and \( D_e = 110.60 \text{ kcal/mol} \) 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 \( \beta \) 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
\[
\phi(R) = \phi_0^{\text{CH}_4} + (\phi_0^{\text{CH}_4} - 90.0)[S_0(R) - 1.0]
\]
with \( S_0(R) \), a switching function, given by
\[
S_0(R) = 1.0 - \tanh [A_s(R - R_0_e) e^{B_s(R - R_0_e)}]
\]
The parameters in eq 11 and 12 are as follows: \( \phi_0^{\text{CH}_4} = 109.47^\circ \), \( A_s = 5.2879029 \times 10^{-1} \text{ Å}^{-1} \), \( B_s = 4.0066377 \times 10^{-1} \text{ Å}^{-3} \), \( C_s = 1.9209937 \text{ Å} \), \( R = \text{C–H* bond length in angstroms} \), and \( \phi_0(R) \) is in degrees. While eq 11 can be used in conjunction with eq 9 to determine the optimized values of the \( \phi \) and \( \theta \) bond angles along the MEP, it is computationally advantageous to represent the \( \theta \) bond angles by a separate function:
\[
\theta_0(R) = \theta_0^{\text{CH}_4} + (\theta_0^{\text{CH}_4} - 120.00)[S_0(R) - 1.0]
\]
where \( \theta_0^{\text{CH}_4} = 109.47^\circ \), \( A_s = 9.0787142 \times 10^{-1} \text{ Å}^{-1} \), \( B_s = 3.5485587 \times 10^{-1} \text{ Å}^{-3} \), \( C_s = 1.8915497 \text{ Å} \), \( R = \text{C–H* bond length in angstroms} \), and \( \theta_0(R) \) is in degrees. In order to ensure geometric consistency, the switching function \( S_0(R) \) 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 \( \phi_0(R) \) as a function of the C–H* bond length, and the ability of these analytic functions to represent this angular variation.

As noted above, it was necessary to include nondiagonal cubic terms in the definition of the \( \text{CH}_4 \) asymptotic limit, only one set, \( C_s \), contributes significantly to the angular deformation potential. We propose the following functional form to represent this potential:
\[
V_{\alpha}(R) = V_0(R) + \frac{1}{2} \sum_{i=1}^{3} (\phi_{\alpha i} - \phi_{\alpha 0}(R))^2 + \sum_{i=1}^{3} (\phi_{\alpha i} - \phi_{\alpha 0}(R))^2 + \sum_{i=1}^{3} (\theta_{\alpha i} - \theta_{\alpha 0}(R))^2 + \sum_{i=1}^{3} (\Delta_{\alpha i} - \Delta_{\alpha 0}(R))^2 + \sum_{i=1}^{3} (\phi_{\alpha 0}(R) - \phi_{\alpha i}(R))^2 + \sum_{i=1}^{3} (\theta_{\alpha 0}(R) - \theta_{\alpha i}(R))^2 + \sum_{i=1}^{3} (\Delta_{\alpha 0}(R) - \Delta_{\alpha i}(R))^2 + \sum_{i=1}^{3} (\phi_{\alpha 0}(R) - \phi_{\alpha 0}(R))^2 + \sum_{i=1}^{3} (\theta_{\alpha 0}(R) - \theta_{\alpha 0}(R))^2 + \sum_{i=1}^{3} (\Delta_{\alpha 0}(R) - \Delta_{\alpha 0}(R))^2 \]

Figure 5. \( \phi \) 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 \( \phi \)-type angles.

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

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

\( i = 1, 2, 3 \)

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 CH\(_3\) moiety. All the remaining symbols in eq 15 have been previously defined. The reader will note that with \( f_2 = h_\Delta = 0.0 \) eq 15 reduces to the asymptotic expression for methane. Similarly, with \( f_2 = g_\Delta = 0.0 \) and \( g_\Delta = 0.0 \) 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 \( f_{CH_a}, g_{CH_a}, h_{CH_a}, f_{SC_a}, g_{SC_a}, h_{SC_a}, \)

\[ f_0(R) = S_1(R)f_{CH_a} \]

\[ g_0(R) = S_1(R)g_{CH_a} \]

\[ h_0(R) = S_1(R)h_{CH_a} \]

\[ f_2(R) = (f_{CH_a} - f_{SC_a})S_2(R) + f_{SC_a} \]

\[ g_2(R) = (g_{CH_a} - g_{SC_a})S_2(R) + g_{SC_a} \]

\[ h_2(R) = (h_{CH_a} - h_{SC_a})S_2(R) + h_{SC_a} \]

\[ f_3(R) = (1 - S_3(R))f_{SC_b} \]

\[ g_3(R) = (1 - S_3(R))g_{SC_b} \]

\[ h_3(R) = (1 - S_3(R))h_{SC_b} \]

\[ g_{as}(R) = S_3(R)g_{as} \]

(16)

and \( g_{as} \) are the values of the respective force constants in the methane asymptotic limit; \( f_{SC_a}, g_{SC_a}, h_{SC_a}, f_{SC_b}, g_{SC_b}, h_{SC_b} \) 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 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 CH\(_4\) = -CH\(_3\) + H potential energy surface can now be written:

\[ V_{total} = \sum_{i=1}^{3} D_1[1 - e^{-a(R-R_0)}]^2 + D_2[1 - e^{-b(R-R_0)}]^2 + V_{angle} \]

where \( R \) is the C–H* bond length and the \( r_i \) are the three bond lengths of the CH\(_3\) moiety. Using this potential, we are able to calculate the stretch–bend interaction force constants for methane from the following expressions:

\[ \frac{\partial^2 V_{total}}{\partial R \partial \theta} \]

\[ = f_{R \theta} = -f_{\theta R} \]

\[ \frac{\partial^2 V_{total}}{\partial \theta \partial \phi} \]

\[ = f_{\theta \phi} = -f_{\phi \theta} \]

\[ \frac{\partial^2 V_{total}}{\partial \phi R} \]

\[ = f_{\phi R} = -f_{R \phi} \]

where \( f_0 = f_{R0} \) 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 $f_{\beta A} = 0.845$ mdyr/deg and $f_{\beta A} = -0.0823$ mdyr/deg.

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 CH$_4$ 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

$$V(r_i) = D_i [1 - e^{\beta_i (r_i - r_{0i})}]^2$$

where $r_{0i}$ is the equilibrium bond length of the $i$-th bond. The two Morse parameters, $\beta_i$ and $D_i$, are written as functions of the other three bond lengths:

$$\beta_i = \beta_0 + (\beta_1 - \beta_0) [S_0(r_i) S_0(r_j) S_0(r_k) - 1]$$

where $\beta_0$ and $\beta_1$ are the equilibrium values of the parameters and $\beta_1$ and $D_1$ are their asymptotic values as $r_i \to \infty$. Again, the switching functions $S_0(r_i)$ and $S_0(r_j)$ are designed to represent the properties of the system of interest, monotonically assuming values between 1.0 and 0.0. For our methane potential, $\beta_0 = \beta_1$ and $D_0 = D_1$.

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

$$\theta_{ij} = \theta^0_{ij} + (\theta_{ij} - \theta^0_{ij}) [S_1(r_i) S_1(r_j) - 1]$$

where $\theta^0_{ij}$ is the equilibrium value of $\theta_{ij}$ at the undistorted tetrahedral center, $\theta^0_{ij}$ is the asymptotic value of $\theta_{ij}$ as either $r_i \to \infty$ or $r_j \to \infty$. The expression is the asymptotic value of $\theta_{ij}$ as either $r_i \to \infty$ or $r_j \to \infty$. Again, the switching functions, $S_1(r_i)$ and $S_1(r_j)$, are chosen to represent the properties of the system of interest, monotonically assuming values between 1.0 and 0.0. Specifically, for the CH$_4$ $\rightleftharpoons$ CH$_3$ + H reaction, $\theta^0_{ij} = 109.47^\circ$, $\theta^0_{ij} = 120.0^\circ$, and, using earlier notation, $S_1(r_i) = S_0(r_i)$ and $S_1(r_j) = S_0(r_j)$ (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

$$f_{\theta ij} = f_{\theta ij}^0 + f_{\theta ij}^1 [S_1(r_i) S_1(r_j) - 1] + (g_{\theta ij}^0 - f_{\theta ij}^0) [S_2^0(r_i) S_2^0(r_j) - 1]$$

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

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

$$f_{\theta ij} = (1 - S_2^0(r_i)) S_2^0(r_j) S_2^0(r_k) S_2^0(r_l) f_{\theta ij}^0$$

where $f_{\theta ij}^0$ is the equilibrium value of the $i$-th non diagonal cubic force constant, $g_{\theta ij}^0$ is the asymptotic limit of the $i$-th constant when the $j$-th bond is broken, and $S_2^0(r_i)$ is a suitably chosen switching function whose values range monotonically from 1.0 to 0.0.

Finally, the nondiagonal cubic force constants are described by the following functional form:

$$g_{\theta ij} = \sum_{\mu, \nu} (S^0_\mu(r_i) - 1) (g_{\theta ij}^0 - g_{\theta ij}^0) + g_{\theta ij}^0$$

where $g_{\theta ij}^0$ is the equilibrium value of the $i$-th non diagonal cubic force constant, $g_{\theta ij}^0$ is the asymptotic limit of the $i$-th constant when the $j$-th bond is broken, and $S^0_\mu(r_i)$ is a suitably chosen switching function whose values range monotonically from 1.0 to 0.0.

In describing the CH$_4$ $\rightleftharpoons$ CH$_3$ + H reaction, we have chosen $S_2^0(r_i) = S_2^0(r_l) = S_2^0(r_k)$ where $S_2^0(r_j)$ is defined by eq 17 and $g_{\theta ij}^0 = 0.0$ for all five nondiagonal cubic force constants. The out-of-plane angles, $\Delta_\theta$, associated with the breaking of the $i$-th bond are defined by the expression

$$\Delta_\theta = \cos^{-1} (\vec{N}_t \times \vec{r}_j)$$

where $\vec{N}_t$ is a unit vector normal to the plane defined by the three hydrogen atoms of the CH$_3$ moiety, and $\theta^0_\theta$ is defined in eq 23. The vector $\vec{N}_t$ is given by

$$\vec{N}_t = \left( \frac{\vec{r}_j - \vec{r}_i}{|\vec{r}_j - \vec{r}_i|} \right) \times \left( \frac{\vec{r}_i - \vec{r}_k}{|\vec{r}_i - \vec{r}_k|} \right)$$

The vectors $\vec{r}_i$, $\vec{r}_j$, $\vec{r}_k$ are those associated with the three unruptured bonds of the CH$_3$ fragment. Lastly, the $G_i$ set of nondiagonal cubic force constants is written in terms of the symmetric notation:

$$C_{\theta ij} = g_{\theta ij}^0 \sum_{\mu, \nu} (\theta_{ij} - \mu \theta_{ij}) (\theta_{ij} - \nu \theta_{ij}) +$$

$$g_{\theta ij}^0 \sum_{\mu, \nu} (\theta_{ij} - \mu \theta_{ij}) (\theta_{ij} - \nu \theta_{ij}) + g_{\theta ij}^0 \sum_{\mu, \nu} (\theta_{ij} - \mu \theta_{ij}) (\theta_{ij} - \nu \theta_{ij})$$

Using the above definitions we now write a general symmetric analytic potential describing the CH$_4$ $\rightleftharpoons$ CH$_3$ + H reaction:

$$V_{\text{total}} = \sum_{i=1}^{4} D_i (1 - e^{\beta_i (r_i - r_{0i})})^2 + \frac{1}{2} \sum_{i,j} f_{\theta ij}^0 (\theta_{ij} - \theta_{ij}^0)^2 +$$

$$\sum_{i=1}^{4} g_{\theta ij}^0 (\theta_{ij} - \theta_{ij}^0)^3 + \sum_{i,j} h_{\theta ij}^0 (\theta_{ij} - \theta_{ij}^0)^4 + \sum_{i,j} f_{\theta ij}^0 \sum_{k} \Delta_\theta +$$

$$\sum_{i,j} h_{\theta ij}^0 \sum_{k} \Delta_\theta^4 + g_{\theta ij}^0$$

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 CH$_4$...
Kinetic Parameters for Hydrogen Bonding to an Anion Radical

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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–solvant 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 polarization 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