Analytical fittings for the global potential energy surface of the ground state of methylene

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The global potential energy surface (PES) corresponding to the dissociation reaction of the ground state of methylene (CH₂) is studied with the coupled-cluster method with single, double and perturbative triplet excitations, CCSD(T), in conjunction with the correlation-consistent cc-pVTZ basis set, and fitted by three analytical potential functions in terms of the Simons–Parr–Finlan (SPF) polynomial, Jensen function and the Sorbie–Murrell (SM) function. Ab initio single-point calculations over a distributed range of grids are performed first, and totally 12 085 converged points are fed into these functions. The fitting of each analytical PES function is done with an unconstrained minimization of the difference between the evaluations of the analytical function and the ab initio results, solved by a modified Levenberg–Marquardt algorithm with a finite-difference Jacobian in the IMSL package. The SPF polynomial is found to have the best global description, while the SM function behaves superior in the dissociation region forming three atoms. The spline function is potentially feasible to interpolate the computationally divergent points in the ab initio calculations. © 2003 American Institute of Physics. [DOI: 10.1063/1.1523906]

I. INTRODUCTION

Potential energy surfaces (PES) are essential in chemical process studies. The actual reaction path of molecules in terms of encounter depends on their total energies, which are the sum of the kinetic and the potential energies. However, PES alone provides primary insights of possible pathways, which correspond to the minimal potential energy that are the most important. Experimentally, the task considering how the molecules move through their PES when they as well possess kinetic energy can be explored by molecular beam studies. Dynamical calculations, namely the calculations for cross sections, rate constants, transition probabilities, or dynamical attributes such as threshold energies, require analytical PES functions. Chemical dynamics produces results comparable to experimental measurements while highly accurate potential energy functions as well as extra details from the theoretical outputs are available. For example, theoretical investigations may either generate information about the dependence of cross sections on the initial vibrational states if only the initial translational energy is experimentally varied, or yield rotational distributions of products provided the experimental product-state resolution is merely sufficient to distinguish vibrational structure. In other cases, theoretical rate calculation for systems that no experiments have been performed is possible. Moreover, dynamical theories can provide opacity functions, which are transition probabilities as a function of the impact parameter and are absolutely unattainable by experiments. The disadvantages over potential energy surfaces are that for many systems the PES lacks of either chemical accuracy or demonstrated reliability, and on the other hand additional errors are possibly introduced by the dynamical calculations. Thus further improvements are required in this field of potential energy surfaces combined with dynamics calculations.

Methylene radical, CH₂, is the simplest polyatomic molecule of which the ground state is a triplet state and having a very low-lying singlet excited state. The electronic characteristics make methylene rather unusual chemical and physical properties. Depending on its multiplicity, the radical adds differently to olefins. Methylene is also the simplest carbene, which is an important intermediate in various organic reactions. In addition, methylene is a product of the photolysis reaction of diazomethane (CH₂N₂), or ketene (CH₂CO). Carbenes share the common isoelectronic property with the two generally accessible electronic singlet and triplet states. The singlet electronic state appears as an electrophile and/or a nucleophile whereas the triplet electronic state possesses radical properties. Therefore, carbenes are related to “the reactive intermediate” and are simultaneously classically stable species. In the interstellar space, although not firmly identified, CH₂ is the direct precursor of the widely observed CH radical and other carbon-bearing molecules. Nevertheless, CH₂ is in addition considered as an important link in the Lyman α-band photodissociation sequence of cometary methane. The CH₃ photodissociates into CH₂, and further dissociates to form CH+H or C+H₂ photochemically. In the aforementioned sequence, CH is the only observable species. Studies on CH and CH₄ have been done in detail and the largest uncertainty lies on the photodissociation rate of CH₂ as well as the branching ratio to form CH or C.

Many theoretical studies have been done for the PES of methylene. The most accurate result to date has been done by Comeau et al. using the multireference configuration-interaction (MRCI) method with a large basis

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set of \([5s4p3d2f1g3s2p1d]\). Totally 45 points were reported, focusing on the region close to the minimum. Those points were then fitted by Morse-oscillator rigid bender internal dynamics (MORBID) procedure\(^ {20,21}\) to get the rotational-vibrational energy levels. The semiempirical potential by Jensen and Bunker\(^ {15}\) is probably very accurate description in the region near the minimum. They adjusted nine out of the 24 parameters in the same \textit{ab initio} potential used by Comeau \textit{et al.} to improve the agreement between the predicted and the observed rotational-vibrational energy levels. As for the global potential, Knowles, Handy, and Carter\(^ {12}\) reported complete active-space self-consistent field (CASSCF) calculations employing the \([5s3p2d2s1p]\) basis set on the two lowest \(3\Delta^\nu\) states. These data points have been scaled to match the experimental dissociation energy prior to fit a potential function, which is in the form of a diagonalized 2 by 2 matrix and describes well around the conical intersections between the two lowest triplet surfaces that occur at linear geometries.

Recently Harding, Guadagnini, and Schatz\(^ {18}\) carried out calculations of about 6000 points on the ground state potential surface of methylene by MRCI/\([4s3p2d1f/3s2p1d]\) level of theory. Four stationary points were reported with \(3B_1, 3A_2, 3\Pi,\) and \(3\Sigma^-\) symmetries, respectively. The resultant energies were fit to a many-body expansion and conical insertions between the \(3B_1, 3A_2\) states for \(C_{2v}\) geometries and between the \(3\Pi\) and \(3\Sigma^-\) states for linear geometries are also included. No barrier is predicted for either \(\text{C}+\text{H}_2\) addition or \(\text{C}+\text{H}_2\) insertion reactions. The entrance channel of \(\text{C}+\text{H}_2\) addition reaction is very broadly attractive and the long-range approaching force becomes repulsive only when geometries are close to linear. On the \(3A_2\) surface the repulsion increases at shorter distances and the energy is minimum at long range. Furthermore, no barrier exists and a loosely bound complex is formed for the \(\text{C}+\text{H}_2\) addition. The \(C_{2v}\) conical insertion between \(3B_1\) and \(3A_2\) surfaces is predicted to be important in determining the topology of the surface in the neighborhood of \(\text{C}+\text{H}_2\) insertion reaction path.

It is aimed for obtaining the global potential energy surface of the triplet ground state methylene in this study. According to the correlation diagram,\(^ {15}\) CH\(_2\) dissociates via two possible channels: \(C(\Sigma^\pi)+\text{H}_2(\Sigma^\pi_x)\) and \(\text{CH}(^2\Pi)+\text{H}(^2\Sigma)\). The global potential energy surface functions are deduced by the following procedure. High level \textit{ab initio} calculations at more than ten thousand of molecular geometries are carried out, followed by the fitting of the parameters of the analytical potential energy functions.

II. COMPUTATIONAL DETAILS

Many-body methods for electron correlation are used due to the size consistent requirement in considering the dissociation channels. Coupled-cluster method with single, double and perturbative triplet excitations, CCSD(T),\(^ {22}\) are used in conjunction with Dunning’s correlation-consistent cc-pVTZ basis set. The CCSD(T) calculations are performed with the ACES II program.\(^ {23}\)

The most efficient strategy to proceed with electronic structure calculations on numerous points over the extension of a global potential energy surface is to scan the surface stepwise starting from the equilibrium geometry. The initial guess of the molecular orbitals (MOs) of one certain geometry is the converged molecular orbitals of the preceding point. For CH\(_2\) molecule, the single-point calculations are done with separate groups of computations, in terms of the \(C_{2v}\) symmetry and those with \(C_s\) symmetry in order to take the advantage of molecular symmetry with proper initial MO guesses.

In order to cover the complete dissociation routes, grids over a large range of bond length and bond angle are used. The coordinates initially chosen to perform high level \textit{ab initio} calculations are shown in Table I. It generates 28 101 points \((57 \times 29 \times 17)\). Nevertheless, denser grids are aimed at the region near the equilibrium structure, while sparser grids are chosen for large bond lengths and small bond angles in order to save computational resources. Three empirically derived analytical potential energy functions, in terms of the Simons–Parr–Finlan (SPF) polynomial, Jensen function and the Sorbie–Murrell (SM) function, plus the bivariate spline function which is one of the most frequently employed all-numerical fitting among the numerical methods, are employed to fit to the results by \textit{ab initio} calculations. The mathematical form and algorithms of each analytical function is described in detail in the Appendix.

The fitting of each analytical PES function is an unconstrained minimization of a continuous many-variable function. This nonlinear least-square problem can be solved by a modified Levenberg–Marquardt algorithm with a finite-difference Jacobian, implemented by the subroutines UNLSF/DUNLSF within the IMSL\(^ {24}\) package. The bivariate spline interpolation is done by the SURF/DSURF subroutine in the identical IMSL package.

III. RESULTS AND DISCUSSIONS

Table II contains the equilibrium properties of C, H, CH, H\(_2\) in their ground states calculated by the same CCSD(T)/cc-pVTZ level used in CH\(_2\) calculations. In Table II, the results by CCSD(T)/TZ2P and CCSD(T)/cc-pVTZ together with those of literatures are listed. The computation by Comeau \textit{et al.}\(^ {16}\) is regarded the historically most accurate \textit{ab initio} calculation. Their optimized C–H bond distance was 1.071 \(\text{\AA}\), \(\angle\text{HCH}\) angle was 132.9° and energy was \(-39.087\) 452 hartree, and our calculated energy at CCSD(T)/cc-pVTZ is lower by 0.006 652 4 hartree. Experimentally,\(^ {14}\) the bond distance is 1.0748 \pm 0.0004 \(\text{\AA}\), and the bond angle is 133.84° \pm 0.05°. The geometry at the level of CCSD(T)/TZ2P is very close to the experimental values; however, due to its poor level of theory and small basis set, this match is regarded as a coincidence. For the vibrational spectrum of CH\(_2\), only the fundamental bending frequency\(^ {5}\) has been measured\(^ {25}\) to be 963.10 cm\(^{-1}\). The frequency of this mode is 1128 cm\(^{-1}\) according to CCSD(T)/TZ2P. The fundamental frequencies of the two stretching modes, 1 and 3 are still not clear for their very weak intensity. The calculation done by Comeau \textit{et al.} yielded these two modes at 3013 and 3235 cm\(^{-1}\), while our study reports 3173 and 3395 cm\(^{-1}\) by
CCSD/TZ2P. The algorithm to calculate vibrational frequencies with CCSD(T) method is not yet available in ACES II, and therefore the values are not listed.

The ground state of CH$_2$ correlates with the ground states of CH+H and C+H$_2$. From \textit{ab initio} results at the level of CCSD(T)/cc-pVTZ, the sums of energy of separate atoms are $-38.791\,636\,43$ hartree for C+H+H, $-38.923\,471\,19$ hartree for CH+H and $-38.964\,470\,52$ hartree for C+H$_2$, respectively. Figure 1 shows the relative energy levels. Results of \textit{ab initio} calculation featuring unreasonable energies are omitted according to the following examination. Points with energies higher than $-38.791\,636\,43$ hartree, which is the sum of energies of three separate atoms, are deleted. The number of data points is reduced to 12,085 out of the original computationally converged 12,448 points by the filtration.

In our initial test using the SPF polynomial, only terms up to quartic expansions were considered, however, the DUNLSF subroutine of IMSL package failed to minimize due to insufficient number of parameters. Thus the terms of the fifth order are taken into consideration. The SM function has the most complex form comparing with the other two for the reason that several Taylor series transformations are necessary to generate the coefficients in the polynomial $P(s_1,s_2,s_3)$. The zero of energy of the SM function is defined as the ground state of the three separate atoms (C+H+H). Although there are only five explicit parameters ($c_0, A_1, \gamma_1, \gamma_2, \gamma_3$) in the SM function, those force constants in Eq. (14) must be also included as parameters for optimization in order to yield satisfactory results. Thus the number of parameters to be optimized therefore increases from 5 to 21.

Table III reports the fitted values of parameters determined in each analytical potential function. Both of the SPF polynomial and Jensen functions behave satisfying in regenerating the exact equilibrium geometry and energy of the \textit{ab initio} data. Since the zero of the fitted SM function is defined as the three separate atoms, its failure to reproduce the optimized structure of CCSD(T)/cc-pVTZ is within expectation. The relative energy evaluated by the SM function at the equilibrium geometry is $-2.313$ kcal/mol.

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**TABLE I.** The combination of coordinate grids for the global PES calculation of CH$_2$ with CCSD(T)/cc-pVTZ method. The numbers in bold face are of the equilibrium structure.

<table>
<thead>
<tr>
<th>$R_{	ext{CH}}^{(1)}$ (Å)</th>
<th>$R_{	ext{CH}}^{(1)}$ cont.</th>
<th>$R_{	ext{CH}}^{(2)}$ (Å)</th>
<th>$\angle \text{HCH}$ (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.023 519</td>
<td>1.666 469</td>
<td>1.018 227</td>
<td>24.126 806</td>
</tr>
<tr>
<td>1.028 810</td>
<td>1.732 616</td>
<td>1.028 810</td>
<td>44.126 806</td>
</tr>
<tr>
<td>1.036 748</td>
<td>1.798 763</td>
<td>10.44 686</td>
<td>64.126 806</td>
</tr>
<tr>
<td>1.044 686</td>
<td>1.864 910</td>
<td>1.055 269</td>
<td>84.126 806</td>
</tr>
<tr>
<td>1.049 977</td>
<td>1.931 057</td>
<td>1.065 853</td>
<td>104.126 806</td>
</tr>
<tr>
<td>1.055 269</td>
<td>1.997 204</td>
<td>1.071 145</td>
<td>124.126 806</td>
</tr>
<tr>
<td>1.060 561</td>
<td>2.063 351</td>
<td>1.097 603</td>
<td>144.126 806</td>
</tr>
<tr>
<td>1.065 853</td>
<td>2.129 499</td>
<td>1.113 479</td>
<td>164.126 806</td>
</tr>
<tr>
<td><strong>1.071 145</strong></td>
<td><strong>2.195 646</strong></td>
<td><strong>1.124 062</strong></td>
<td><strong>129.126 806</strong></td>
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<td>2.261 793</td>
<td>1.150 521</td>
<td><strong>134.126 806</strong></td>
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<td>1.092 312</td>
<td>2.327 940</td>
<td>1.176 980</td>
<td>139.126 806</td>
</tr>
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<td>1.203 439</td>
<td>144.126 806</td>
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<td>2.460 234</td>
<td>1.335 733</td>
<td>149.126 806</td>
</tr>
<tr>
<td>1.108 187</td>
<td>2.526 381</td>
<td>1.468 027</td>
<td>154.126 806</td>
</tr>
<tr>
<td>1.113 479</td>
<td>2.658 676</td>
<td>1.600 322</td>
<td>159.126 806</td>
</tr>
<tr>
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<td>2.790 970</td>
<td>1.732 616</td>
<td>164.126 806</td>
</tr>
<tr>
<td>1.124 062</td>
<td>2.989 411</td>
<td>1.864 910</td>
<td>174.126 806</td>
</tr>
<tr>
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<tr>
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<td>3.452 441</td>
<td>2.129 499</td>
<td>174.126 806</td>
</tr>
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<td>2.361 793</td>
<td>174.126 806</td>
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<tr>
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<td>4.444 648</td>
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<td>174.126 806</td>
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<tr>
<td>1.190 209</td>
<td>5.172 266</td>
<td>2.526 381</td>
<td>174.126 806</td>
</tr>
<tr>
<td>1.203 439</td>
<td>6.495 209</td>
<td>2.790 970</td>
<td>174.126 806</td>
</tr>
<tr>
<td>1.269 586</td>
<td>7.818 151</td>
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<td>174.126 806</td>
</tr>
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<td>1.335 733</td>
<td>9.141 094</td>
<td>3.717 030</td>
<td>174.126 806</td>
</tr>
<tr>
<td>1.401 880</td>
<td>10.464 036</td>
<td>5.172 266</td>
<td>174.126 806</td>
</tr>
<tr>
<td>1.468 027</td>
<td>11.786 979</td>
<td>7.818 151</td>
<td>174.126 806</td>
</tr>
<tr>
<td>1.534 174</td>
<td>13.109 921</td>
<td>10.464 036</td>
<td>174.126 806</td>
</tr>
<tr>
<td>1.600 322</td>
<td>13.109 921</td>
<td></td>
<td></td>
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</table>

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**TABLE II.** The optimized structures, energies, and harmonic frequencies of all the species involved in the CH$_2$ dissociation reaction at various levels of theories.

<table>
<thead>
<tr>
<th></th>
<th>CCSD(T)/TZ2P</th>
<th>CCSD(T)/cc-pVTZ</th>
<th>MRCI$^{[5s4p3d2f1g3s2p1d]}$</th>
<th>Experimental value</th>
</tr>
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<tr>
<td>$R_{\text{CH}}$ (Å)</td>
<td>1.075</td>
<td>1.071</td>
<td>1.078</td>
<td>1.0748±0.0004</td>
</tr>
<tr>
<td>$\angle \text{HCH}$ (°)</td>
<td>133.3</td>
<td>134.1</td>
<td>132.9</td>
<td>133.84±0.05</td>
</tr>
<tr>
<td>Energy (a.u.)</td>
<td>$-39.082,891,0$</td>
<td>$-39.094,104,4$</td>
<td>$-39.087,452$</td>
<td></td>
</tr>
<tr>
<td>$v_1$ (cm$^{-1}$)</td>
<td>1128</td>
<td>1085</td>
<td>969$^a$</td>
<td>963.10$^b$</td>
</tr>
<tr>
<td>$v_2$ (cm$^{-1}$)</td>
<td>3173</td>
<td>3167</td>
<td>3013$^c$</td>
<td></td>
</tr>
<tr>
<td>$v_3$ (cm$^{-1}$)</td>
<td>3395</td>
<td>3369</td>
<td>3235$^c$</td>
<td></td>
</tr>
<tr>
<td>ZPE (kcal/mol)</td>
<td>11.00</td>
<td>10.90</td>
<td>10.61</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference 16. The frequencies are fitted by the MORBID procedure.

$^b$Reference 25.

$^c$Reference 25.
A summary of fitting error is given in Table IV: The calculated points are sorted by the energy relative to the CH₃ minimum and grouped into ranges with the interval of 10 kcal/mol. Two statistical factors are used to illustrate the fitting error: the standard deviation (STDEV) and the root mean square (rms). Near the equilibrium geometry where the energy range is between 0 and 30 kcal/mol, the SPF polynomial and the Jensen function reproduce well with an rms error of less than 1.773 kcal/mol. Within the range of 40–60 kcal/mol above the ground state of CH₂, the fitting results of these two functions are also superior with STDEV less than 0.963 kcal/mol and rms error less than 1.641 kcal/mol. At the energy range of 160–170 kcal/mol above the minimum, the SPF polynomial and Jensen function behave the worst. The SM function acts relatively inferior at the energy of 170–180 kcal/mol, but has the best description around the range of 100–120 kcal/mol. For the global PES, the SPF polynomial has the smallest STDEV as well as the smallest rms error. In Table V, the SPF polynomial, Jensen function, and the SM function yield 86%, 62%, and 66% respectively, out of the
total 12 085 points with an error within ±5% of energy deviation from the corresponding ab initio result. The SPF polynomial has the highest accuracy for reproducing ab initio values while the SM function is less accurate.

Figures 2 and 3 illustrate the energy curves of computed ab initio energies and corresponding fitted energies as functions of bond distances of C–H with constant $\angle$HCH angles of 39° and 134.1°. The PES curve drawn in Fig. 2 are those with one C–H bond being fixed at its equilibrium value of 1.071 Å as well as the $\angle$HCH angles being constrained at 134.1°. The energy curves distribute from 0 to 100 kcal/mol relative to the ground state CH$_2$ while the other C–H bond lies between 1 and 3 Å. All energy curves have similar shape: Curves move upward with minima located around the equilibrium bond length of 1.071 Å. In this region all three potential functions show this tendency; however, the SPF polynomial and Jensen function are more accurate. For very small bond length (<0.8 Å), the SPF polynomial expansion presents incorrect energetic tendency due to its polynomial nature without empirical terms [Fig. 2(a)]; Jensen function and the SM function have correct descriptions for their Morse-like shape. This disadvantage of the SPF polynomial still exists even the constraint of the first C–H bond increases to 10.71 Å [Figs. 3(a) and 3(b)]. The minima of energy curves in Fig. 3 should reside around 110 kcal/mol, which is slightly higher than the relative energy of CH+H in the correlation diagram in Fig. 1. Jensen function and the SM function have successful fitting results [Figs. 3(c)–3(f)]. Therefore, ab initio data points for very short C–H bonds are required for the SPF polynomial to behave correctly if this region is of interest.

Selected three-dimensional graphs of the three potential energy functions are shown in Fig. 4 with either the bond angle fixed at 134.1° or one bond length fixed at 1.071 Å. Each surface is plotted using the analytical forms of corresponding fitted functions. Figures 4(a), 4(c), and 4(e) show how CH$_2$ dissociates into CH and H at a fixed bond distance of C–H. The surfaces are flat with various $\angle$HCH angles when the length of the C–H bond is 1.071 Å. With very long C–H bond, the SM function successfully reproduces this behavior [Fig. 4(e)]. Jensen function generates higher energies at small bond angles. The existence of a small exit channel barrier around 2.2 Å has been reproduced by all of the three functions. When the $\angle$HCH angle is fixed, the surfaces are symmetric with respect to the two C–H bonds. The surfaces are flat in the vicinity of three separate atoms, and the local minima appear around the region of CH+H [Figs. 4(b), 4(d), and 4(f)]. If $\angle$HCH angle is constrained at 134.1°, the surfaces of the SPF polynomial and Jensen function are correct in shape but the energy values are not constant in the dissociation region [Figs. 4(b) and 4(d)].

Our potential energy surfaces are based on ab initio calculations except those parameters introduced by the Morse potentials [Eqs. (9)–(11)], which are experimentally determined values. This work is a complete scanning of potential energy surface from the ground state of CH$_2$ to the...
ground states of the three separate atoms (C+H+H). For a given geometry we can get the approximate energy and a full concept of continuity over the entire system without other considerations such as crossing. No information will be obtained about the stationary points. A contour plot of the potential energy surface with fixed $\angle \text{HCH}$ angle of 134.1° for the ground state had been presented by Beärda et al. (Fig. 1 of Ref. 26) and no barrier was displayed on the surface. Their energy for dissociation into CH+H is 4.57 eV (105.39 kcal/mol), which is 1.68 kcal/mol lower than our value. Better experimental values are not available for comparison. The analytical potential function fitted by Harding et al. is quite accurate with enough points (~6000 points) and has very low rms errors (from 0.01 kcal/mol around the equilibrium to 0.82 kcal/mol at the region of CH+H). Their potential energy surfaces are classified according to four different term symbols and details are discussed on the crossing of $^3B_1$, $^3A_2$, $^3\Pi$, and $^3\Sigma^-$ states, respectively, and are well described along these high-symmetry reaction coordinates. Their system focused on the CH$_2$ dissociation into CH+H and C+H$_2$, while this study also covers the dissociation region into three separate atoms.

The SPF polynomial and Jensen function are good at the description when the $\angle \text{HCH}$ angle is fixed and close to the equilibrium value 134.1°. These two functions are proper if the regions of interest are near the equilibrium geometry of CH$_2$ or in the calculations of vibrational spectrums. Unsatisfactory results are obtained from the SPF polynomial and Jensen function on the course of C+H$_2$ insertion reaction because this reaction exists only when the $\angle \text{HCH}$ angle is small. Although energy values are not perfectly accurate, the SM function will give a satisfactory description on the CH+H addition reaction. For further scattering studies, the SM function is predicted to be a better choice among the three analytical potential energy functions for that it gives a correct profile in the dissociation regions while the other two functions report too high energies at small $\angle \text{HCH}$ angle. Thus the SM function will generate correct descriptions both in the region near the equilibrium geometry of CH$_2$ and the dissociation regions of CH+H as well as C+H+H.

The three-dimensional potential energy surfaces are re-
constructed by the spline fitting on the grids in Table I. The surfaces with respect to the bond angles are shown in Fig. 5, with $\angle \text{HCH}$ angles being 94.1°, 114.1°, 134.1°, and 174.1°. The spline fitting reproduces the exact value offered by the \textit{ab initio} calculations, and can interpolate rather smoothly the data points that are not converged in the theoretical calculations. Even with small $\angle \text{HCH}$ angle, the smoothness of the surface is still retained. With very large bond lengths, i.e., the frontier regions on the potential energy surfaces, the spline-fitted data points become very unreasonable as shown in Fig. 5(b). The energy rises to over 1000 kcal/mol for several points, which indicates the incapability of extrapolation by the spline fitting. It should only be applied to the regions near the equilibrium structures.

FIG. 4. The 3D graphs of fitted analytical functions: the SPF polynomial with (a) one C–H bond fixed at 1.071 Å, (b) $\angle \text{HCH}$ fixed at 134.1°; Jensen function with (c) one C–H bond fixed at 1.071 Å, (d) $\angle \text{HCH}$ fixed at 134.1°; as well as the SM function with (e) one C–H bond fixed at 1.071 Å, (f) $\angle \text{HCH}$ fixed at 134.1°. All energies are relative to CH$_2$(^3$B_1$).
IV. CONCLUSION

The fitting strategies do not have any consideration about symmetry factors and provide a full description of continuity over the entire region, from the ground state of CH$_2$ to the ground states of three separate atoms. From *ab initio* results, the bond lengths can be divided into three approximate ranges: near the equilibrium bond length, medium range, and very long distance from the equilibrium. Thus there are six combinations considering the relative energy with respect to the bond angle. Each region has its own properties. Near equilibrium, all three functions reproduce potential energy curves (relative to the minimum) upward with a local minimum as functions of bond angles with fixed bond lengths. When one of the C–H bonds is approximately at the equilibrium length and the other is slightly away from the equilibrium length, *ab initio* calculations are rather unstable. Fitting results are the poorest in this region. The variations in bond angle do not severely affect the shape of energy curves as functions of bond lengths according to *ab initio* calculations. The SM function yields invariant energy when one or both C–H bonds are sufficiently longer than the equilibrium bond length and agrees quite well with *ab initio* outputs. As shown in the 3D surface plots, the SPF produces very unreliable energetic values at very short C–H bond length. The SM function generates the features well in dissociation regions of CH+H and C+H+H. The global fit approximately produces a rms deviation of approximately 5.53 to 7.13 kcal/mol for all three potential functions. The spline fitting procedure is feasible of interpolation for the computationally divergent points within the range of *ab initio* calculations, while extrapolation can be contentious.

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APPENDIX: THE FUNCTIONS TO FIT THE POTENTIAL ENERGY SURFACES

For triatomic molecules, three types of empirical potential energy functions with the Born–Oppenheimer approximation are utilized, namely the Simons–Parr–Finlan polynomial, Jensen function and the Sorbie–Murrell function. The spline function featured by the algorithm of bivariate quintic polynomials is additionally employed to fit the PESs numerically.

A. The Simons–Parr–Finlan (SPF) polynomial

First introduced by G. Simons, R. G. Parr, and J. M. Finlan$^{27}$ in 1973, it was applied to diatomic molecules. Later
in 1974, G. Simons\textsuperscript{28} slightly modified that to be employed to triatomic molecules $\text{CS}_2$, $\text{CO}_2$, etc. Having a similar form as a Taylor series, up to the quintic terms were expanded and SPF polynomial was expressed as follows with the coordinates defined in Fig. 6:

$$V = \sum_{i<j} L_{ij} \rho_i \rho_j + \sum_{i<j<k} L_{ijk} \rho_i \rho_j \rho_k + \sum_{i<j<k<l} L_{ijkl} \rho_i \rho_j \rho_k \rho_l$$

$$+ \sum_{i<j<k<l=m} L_{ijklm} \rho_i \rho_j \rho_k \rho_m,$$

where $\rho_1 = \frac{r_1 - \bar{r}_1}{r_1}$, $\rho_2 = \frac{r_2 - \bar{r}_2}{r_2}$, and $\rho_3 = \frac{\alpha - \alpha^e}{\alpha}$. The indices $i, j, k, l,$ and $m$ are of the numbers 1, 2, and 3. The geometric data $r_1^e$, $r_2^e$ and $\alpha^e$ are the bond-length and bond angle values of the equilibrium geometry, and $L_{ijkl} \ldots$ are the parameters required for fitting to \textit{ab initio} values $(r_1, r_2, \alpha, W(r_1, r_2, \alpha))$. If the molecule belongs to the $C_{2v}$ point group instead of $C_3$, the number of parameters would be reduced from 52 to 36. The definition of zero-energy level is the equilibrium level of the triatomic CH$_2$ molecule.

This potential function includes terms that are effectively hexic in normal coordinates displacements without introducing extra coefficients. The variables $\rho_1 = (r_1 - \bar{r}_1)/r_1$ and $\rho_2 = (r_2 - \bar{r}_2)/r_2$ have the correct asymmetry for a bond-stretch and behaved well as the bond lengths approach to infinity, and $\rho_3 = (\alpha - \alpha^e)/\alpha$ reflects the asymmetry property of nonlinear molecules.

B. Jensen function

In 1988, P. Jensen introduced this potential function for internal-dynamics purposes.\textsuperscript{20,21} It was expected to be sufficiently flexible for representing the PES over a wide range of triatomic molecules. In 1989, Comeau \textit{et al.}\textsuperscript{16} used it to get the methylene potential surface focusing on the part close to the minimum. This Jensen function has the following form where the coordinates are defined as given in Fig. 7:

$$V(\Delta r_{12}, \Delta r_{32}, \bar{\rho}) = V_0(\bar{\rho}) + \sum_j F_j(\bar{\rho}) y_j + \sum_{j<k} F_{jk}(\bar{\rho}) y_j y_k$$

$$+ \sum_{j<k<l} F_{jkl}(\bar{\rho}) y_j y_k y_l + \sum_{j<k<l<m} F_{jklm}(\bar{\rho}) y_j y_k y_l y_m,$$

where $\Delta r_{12}$ and $\Delta r_{32}$ were two stretching coordinates that $\Delta r_{12} = r_{12} - r_{12}^e$ for $j = 1$ or 3, and the so-called Morse oscillator-type functions $y_j = 1 - \exp(-a_j \Delta r_{j2})$ for $j = 1$ or 3 with $a_j$ being molecule constants to be determined. The indices $j, k, m,$ and $n$ are of the values of 1 or 3. The $F_{jkm} \ldots$ expansion coefficients are functions of $\bar{\rho}$, the instantaneous value of the supplement of the bond angle $\rho$, i.e., $\bar{\rho} = 180 - \rho$:\textsuperscript{29}

$$F_j(\bar{\rho}) = \sum_{i=1}^{4} f_j^{(i)}(\cos \rho_e - \cos \bar{\rho})^i,$$

$$F_{jk}(\bar{\rho}) = \sum_{i=1}^{3} f_{jk}^{(i)}(\cos \rho_e - \cos \bar{\rho})^i,$$

$$F_{jkm}(\bar{\rho}) = \sum_{i=1}^{2} f_{jkm}^{(i)}(\cos \rho_e - \cos \bar{\rho})^i,$$

$$F_{jklm}(\bar{\rho}) = \sum_{i=1}^{1} f_{jklm}^{(i)}(\cos \rho_e - \cos \bar{\rho}).$$

$\rho_e$ is the equilibrium of $\bar{\rho}$. Those $f_{jkm} \ldots$ are the parameters which to be optimized by fitted to \textit{ab initio} values during the surface fitting process.

The pure bending potential energy function, the one for the molecular bending with the bond lengths fixed at their equilibrium values and denoted as $V_0(\bar{\rho})$, is parametrized as

$$V_0(\bar{\rho}) = \sum_{i=1}^{8} f_0^{(i)}(\cos \rho_e - \cos \bar{\rho})^i.$$

Similarly, $f_0^{(i)} \ldots$ are the parameters. The expression for this potential function, which constitutes rapidly converging power series, is to have a physically reasonable asymptotic behavior at all coordinate boundaries. For $\bar{\rho} = 0$ and 180 with any values of $r_{12}$ and $r_{32}$, the first derivative of the potential function is zero. For large values of $r_{12}$ and $r_{32}$, it approaches to a constant for any value of $\bar{\rho}$, and for small $r_{12}$ and $r_{32}$, it approaches to a very large value, but not infinite.

The total number of parameters is 51. For a molecule of $C_{2v}$ point group, $a_1$ equals to $a_3$, and symmetry relations exists between the parameters so that $V$ is totally symmetric under the exchange of $y_1$ and $y_3$. Thus the number of parameters is reduced to 36. In addition, the zero of the potential energy is set to where the triatomic molecule resides at its equilibrium geometry.

C. The Sorbie–Murrell (SM) function

K. S. Sorbie and J. N. Murrell constructed this analytical function\textsuperscript{30} in 1975 for the ground states of stable triatomic
molecules from spectroscopic data, aiming to reproduce both the equilibrium and asymptotic properties of the molecule. It was first applied to water molecule. Later, this potential function was used for CH$_2$ \cite{31}, H + CO \cite{32-34}, and HCO \cite{35,36}.

This SM function $V(R_1, R_2, R_3)$ is only applicable for molecules which have nonlinear equilibrium geometry. Three out of the four terms of the SM function are for diatomic potentials and the other term is a three-body term. The mathematical expression is as follows shown in Fig. 8:

$$V(R_1, R_2, R_3) = V_{AB}(R_1) + V_{AC}(R_2) + V_{BC}(R_3) + V_I(R_1, R_2, R_3),$$  \hspace{1cm} (A8)

where $V_{AB}$, $V_{AC}$, and $V_{BC}$ are Morse potentials, where $R_{AB}$, $R_{AC}$, and $R_{BC}$ are the diatomic equilibrium bond lengths of AB, AC, and BC, respectively. The zero-energy level of the Morse potentials are set at where two atoms are in their individual ground states.

The three-body term $V_I$ has the following form:

$$V_I(R_1, R_2, R_3) = AP(s_1, s_2, s_3)[1 - \tanh(g_1s_1/2)] \times [1 - \tanh(g_2s_2/2)][1 - \tanh(g_3s_3/2)],$$  \hspace{1cm} (A12)

where $s_1$, $s_2$, $s_3$ defined as $s_i = R_i - R_{eq}$ with $i = 1$, 2, and 3 being displacements from the triatomic equilibrium distances, $R_{eq}$, $R_{2e}$, and $R_{3e}$ and $g_1$, $g_2$, and $g_3$, are parameters.

$P(s_1, s_2, s_3)$ in Eq. (A12) is a polynomial up to the cubic terms

$$P(s_1, s_2, s_3) = c_0 + c_1 s_1 + c_2 s_2 + c_3 s_3 (c_{11}s_1^2 + c_{22}s_2^2 + c_{33}s_3^2) + c_{12}s_1 s_2 + c_{13}s_1 s_3 + c_{23}s_2 s_3 + \frac{1}{2}(c_{111}s_1^3 + c_{122}s_2^3 + c_{133}s_3^3 + c_{222}s_2^3 + c_{333}s_3^3 + c_{233}s_2 s_3^2 + c_{323}s_3 s_2^2 + c_{123}s_1 s_2 s_3),$$  \hspace{1cm} (A13)

where $c_0$ is a parameter and $c_1$, $c_{ij}$, and $c_{ijk}$ are constants and to be derived later.

The zero of energy of this SM function is the ground state of three separate atoms. The condition is imposed that $V_I$ becomes zero at all dissociation limits and this is controlled by $[1 - \tanh(g_1s_1/2)][1 - \tanh(g_2s_2/2)][1 - \tanh(g_3s_3/2)]$. The term $[1 - \tanh(g_2s_2/2)]$ has the property of being zero as $s_i$ approaches to positive infinity and being a constant of 2 as $s_i$ gets close to negative infinity. The Morse potentials are then the potentials of appropriate electronic states of the diatomic dissociation products.

There is no cusp on the potential energy surface in this study. In order to get the values of coefficients in $P(s_1, s_2, s_3)$, the first step is to use the ab initio values to get the derivatives and force constants in the Taylor polynomial. With internal coordinates $(R_1, R_2, \alpha)$ being used and up to the cubic terms being expanded, the Taylor polynomial is

$$W(R_1, R_2, \alpha) = W(R_{1e}, R_{2e}, \alpha_e) + \frac{1}{2} \left[ f_{11}(R_1 - R_{1e})^2 + f_{22}(R_2 - R_{2e})^2 + f_{aa}(\alpha - \alpha_e)^2 \right] f_{12}(R_1 - R_{1e})(R_2 - R_{2e})$$

$$+ f_{1a}(R_1 - R_{1e})(\alpha - \alpha_e) + f_{2a}(R_2 - R_{2e})(\alpha - \alpha_e) + \frac{1}{6} \left[ f_{111}(R_1 - R_{1e})^3 + f_{222}(R_2 - R_{2e})^3 \right]$$

$$+ f_{aao}(\alpha_3 - \alpha_e^3) + \frac{1}{2} \left[ f_{112}(R_1 - R_{1e})^2(R_2 - R_{2e}) + f_{221}(R_2 - R_{2e})^2(R_1 - R_{1e})^2 + f_{111}(R_1 - R_{1e})^2(\alpha - \alpha_e) \right]$$

$$+ f_{1a0}(R_1 - R_{1e})(\alpha - \alpha_e)^2 + f_{2a0}(R_2 - R_{2e})(\alpha - \alpha_e)^2 + f_{aa0}(R_2 - R_{2e})(\alpha - \alpha_e)^2$$

$$+ f_{12a}(R_1 - R_{1e})(R_2 - R_{2e})(\alpha - \alpha_e).$$  \hspace{1cm} (A14)

The first-order derivatives are not appeared above because at the equilibrium geometry, the potential is a minimum and thus those terms are all zero.

The force constants that are represented in the coordinate set $(R_1, R_2, \alpha)$ must be converted to those in the set $(R_1, R_2, R_3)$. The relevant transformations start from the derivatives of $\alpha$ with respect to $R_1$, $R_2$, and $R_3$, which are related by the law of cosine,

$$\alpha = a \cos \left( \frac{R_1^2 + R_2^2 - R_3^2}{2R_1R_2} \right),$$  \hspace{1cm} (A15)
\[
Z = -R_{1e}^4 + 2R_{1e}^2(R_{2e}^2 + R_{3e}^2) - R_{2e}^4 + R_{3e}^2(2R_{2e}^2 - R_{3e}^2).
\]

(A16)

The following listed all the expressions of the derivatives \(\alpha_{ij} \ldots\) calculated at the equilibrium geometry \((R_{1e}, R_{2e}, R_{3e})\):

\[\alpha_1 = -\frac{R_{1e}^4 + R_{2e}^2 - R_{3e}^2}{R_{1e}^4 \sqrt{Z}},\]

(A17)

\[\alpha_2 = \frac{R_{1e}^4 - R_{2e}^2 - R_{3e}^2}{R_{2e}^4 \sqrt{Z}},\]

(A18)

\[\alpha_3 = \frac{2R_{3e}^2}{\sqrt{Z}},\]

(A19)

\[\alpha_{11} = -\frac{1}{2R_{1e}^2 Z \sqrt{Z}}[R_{1e}^6 + 3R_{1e}^4(R_{3e}^2 - R_{2e}^2)\]

\[+ R_{1e}^2(3R_{4e}^4 + 2R_{2e}^2R_{3e}^2 - 5R_{1e}^4)\]

\[+ (R_{3e}^2 - R_{2e}^2)(R_{1e}^2 - 2R_{2e}R_{3e}^3 + R_{1e}^4),\]

\[+ (R_{2e}^2 - R_{3e}^2)(R_{1e}^2 - 2R_{2e}R_{3e}^3 + R_{1e}^4),\]

(A20)

\[\alpha_{22} = \frac{2}{R_{2e}^2 Z \sqrt{Z}}[R_{1e}^6 - 3R_{1e}^4(2R_{2e}^2 + R_{1e}^2)\]

\[+ R_{1e}^2(3R_{4e}^4 - 2R_{2e}^2R_{3e}^2 + 3R_{1e}^4)\]

\[+ (R_{3e}^2 - R_{2e}^2)(R_{1e}^2 - 2R_{2e}R_{3e}^3 + R_{1e}^4),\]

\[+ (R_{2e}^2 - R_{3e}^2)(R_{1e}^2 - 2R_{2e}R_{3e}^3 + R_{1e}^4),\]

(A21)

\[\alpha_{33} = \frac{2}{Z \sqrt{Z}} \frac{2R_{3e}^2(R_{1e}^2 + R_{2e}^2 - R_{3e}^2)}{Z \sqrt{Z}}\]

\[\alpha_{12} = -\frac{8R_{1e}R_{2e}R_{3e}^2}{Z \sqrt{Z}},\]

(A22)

\[\alpha_{13} = \frac{4R_{1e}R_{3e}(R_{1e}^2 - R_{2e}^2 - R_{3e}^2)}{Z \sqrt{Z}}\]

\[\alpha_{23} = \frac{4R_{2e}R_{3e}(R_{2e}^2 - R_{1e}^2 - R_{3e}^2)}{Z \sqrt{Z}}\]

\[\alpha_{111} = \frac{2(R_{2e}^2 - R_{3e}^2)}{R_{1e}^4 \sqrt{Z}}\]

\[\alpha_{222} = \frac{2(R_{2e}^2 - R_{3e}^2)}{R_{2e}^4 \sqrt{Z}}\]

\[\alpha_{333} = \frac{4R_{3e}^2}{Z^2 \sqrt{Z}} \frac{3R_{1e}^6 - R_{3e}^4(3R_{2e}^4 + 5R_{1e}^4)\}

\[- R_{1e}^2(3R_{4e}^4 - 10R_{2e}^2R_{3e}^2 - 3R_{1e}^4)\]

\[+ (3R_{2e}^4 + R_{3e}^2)(R_{1e}^2 - 2R_{2e}R_{3e}^3 + 3R_{3e}^4),\]

(A23)

\[\alpha_{112} = \frac{8R_{2e}^2 R_{3e}^2 [5R_{1e}^4 - 4R_{1e}^2(R_{2e}^2 - R_{3e}^2) - R_{2e}^4 + 2R_{2e}^2R_{3e}^2 - R_{1e}^4]}{Z^2 \sqrt{Z}},\]

(A24)

\[\alpha_{122} = -\frac{8R_{1e}R_{3e}^2 [R_{1e}^4 + 2R_{1e}^2(2R_{2e}^2 - R_{3e}^2) - 5R_{2e}^4 + R_{3e}^4(4R_{2e}^2 + R_{3e}^2)]}{Z^2 \sqrt{Z}},\]

(A25)

\[\alpha_{113} = -\frac{4R_{1e}^4}{Z^2 \sqrt{Z}} [R_{1e}^6 + R_{1e}^4(R_{3e}^2 - 3R_{2e}^2) + R_{1e}^2(3R_{4e}^4 + 6R_{2e}^2R_{3e}^2 - 5R_{1e}^4) - R_{2e}^4 - R_{3e}^2(7R_{2e}^2 - 5R_{2e}^2R_{3e}^2 - 3R_{1e}^4),\]

(A26)

\[\alpha_{223} = -\frac{4R_{2e}^4}{Z^2 \sqrt{Z}} [R_{1e}^6 + R_{1e}^4(R_{3e}^2 - 3R_{2e}^2) + R_{1e}^2(3R_{4e}^4 + 6R_{2e}^2R_{3e}^2 - 5R_{1e}^4) - R_{2e}^4 - R_{3e}^2(7R_{2e}^2 - 5R_{2e}^2R_{3e}^2 - 3R_{1e}^4),\]

(A27)

\[\alpha_{133} = -\frac{4R_{1e}^4}{Z^2 \sqrt{Z}} [R_{1e}^6 + R_{1e}^4(R_{3e}^2 - 3R_{2e}^2) + R_{1e}^2(3R_{4e}^4 + 6R_{2e}^2R_{3e}^2 - 5R_{1e}^4) - R_{2e}^4 - R_{3e}^2(7R_{2e}^2 - 5R_{2e}^2R_{3e}^2 - 3R_{1e}^4),\]

(A28)

\[\alpha_{223} = -\frac{2R_{3e}^2}{Z \sqrt{Z}} + \frac{2R_{3e}^2[R_{1e}^4 + 2R_{1e}^2(R_{2e}^2 - R_{3e}^2) + R_{2e}^4 + 2R_{2e}^2R_{3e}^2 + R_{3e}^4]}{Z \sqrt{Z}},\]

(A29)

\[\alpha_{333} = \frac{2R_{3e}^2}{Z \sqrt{Z}} \frac{2R_{3e}^2[R_{1e}^4 + 2R_{1e}^2(R_{2e}^2 - R_{3e}^2) + R_{2e}^4 + 2R_{2e}^2R_{3e}^2 + R_{3e}^4]}{Z \sqrt{Z}},\]

(A30)

\[\alpha_{111} = \frac{2R_{3e}^2}{Z \sqrt{Z}} \frac{2R_{3e}^2[R_{1e}^4 + 2R_{1e}^2(R_{2e}^2 - R_{3e}^2) + R_{2e}^4 + 2R_{2e}^2R_{3e}^2 + R_{3e}^4]}{Z \sqrt{Z}},\]

(A31)

\[\alpha_{113} = -\frac{4R_{1e}^4}{Z^2 \sqrt{Z}} [R_{1e}^6 + R_{1e}^4(R_{3e}^2 - 3R_{2e}^2) + R_{1e}^2(3R_{4e}^4 + 6R_{2e}^2R_{3e}^2 - 5R_{1e}^4) - R_{2e}^4 - R_{3e}^2(7R_{2e}^2 - 5R_{2e}^2R_{3e}^2 - 3R_{1e}^4),\]

(A32)

\[\alpha_{223} = -\frac{2R_{3e}^2}{Z \sqrt{Z}} + \frac{2R_{3e}^2[R_{1e}^4 + 2R_{1e}^2(R_{2e}^2 - R_{3e}^2) + R_{2e}^4 + 2R_{2e}^2R_{3e}^2 + R_{3e}^4]}{Z \sqrt{Z}},\]

(A33)
\[
\alpha_{233} = -\frac{4R^2_e}{Z^2 \sqrt{Z}} \left[ R^6_e + R^4_e(7R^2_e - 3R^2_{2e}) + R^2_e(3R^4_e - 6R^2_eR^2_{2e} - 5R^2_{3e}) - R^6_{2e} + R^4_{2e}(-R^4_{2e} + 5R^2_{2e}R^2_{3e} - 3R^2_{4e}) \right],
\]
(A34)

\[
\alpha_{123} = -\frac{16R^4_eR^2_e(2R^2_{2e} - R^2_{3e}) + R^2_eR^2_{2e} - 2R^2_{3e})}{Z^2 \sqrt{Z}}.
\]
(A35)

The formula of force constants in \( V(R_1, R_2, R_3) \) are in terms of \( \alpha_{ijk} \ldots \) and \( f_{ijk} \ldots \). The exact forms are not shown here; they are accompanied to appear instead in the expressions for the force constants in \( V_f(R_1, R_2, R_3) \).

By making a Taylor series of the right-hand side of the equation listed below, Eq. (A36), there is a one-to-one correspondence between the derivatives and the coefficients of \( P(s_1, s_2, s_3) \).

\[
P(s_1, s_2, s_3) = AV_f(R_1, R_2, R_3)[1 - \tanh(\gamma_1 s_1/2)]^{-1} \times [1 - \tanh(\gamma_2 s_2/2)]^{-1} [1 - \tanh(\gamma_3 s_3/2)]^{-1}.
\]
(A36)

The force constants in the Taylor series of \( V_f \) around the equilibrium geometry are not directly obtained, but are derived from the equality \( V_f = V - V_{AA} - V_{AC} - V_{BC} \). Since the force constants in \( V \) are known and it is not difficult to get those force constants in Morse potentials:

\[
g_1 = \frac{\gamma_1}{2},
\]
(A37)

\[
g_2 = \frac{\gamma_2}{2},
\]
(A38)

\[
g_3 = \frac{\gamma_3}{2},
\]
(A39)

\[
G_{ij} = \frac{1}{A} \left( \frac{\partial^2 V_f}{\partial s_i \partial s_j} \right)_{s_i = 0, s_j = 0},
\]

\[
G_{11} = \frac{1}{A} [f_{11} + 2\alpha_1 f_{1a} + \alpha_1^2 f_{aa} - 2\beta e_1^2 D_1],
\]
(A40)

\[
G_{22} = \frac{1}{A} [f_{22} + 2\alpha_2 f_{2a} + \alpha_2^2 f_{aa} - 2\beta e_2^2 D_2],
\]
(A41)

\[
G_{33} = \frac{1}{A} [\alpha_3^2 f_{aa} - 2\beta e_3^2 D_3],
\]
(A42)

\[
G_{12} = \frac{1}{A} [f_{12} + 2\alpha_2 f_{1a} + \alpha_1 f_{2a} + \alpha_1 \alpha_2 f_{aa}],
\]
(A43)

\[
G_{13} = \frac{1}{A} [\alpha_3 f_{1a} + \alpha_1 \alpha_3 f_{aa}],
\]
(A44)

\[
G_{23} = \frac{1}{A} [\alpha_3 f_{2a} + \alpha_2 \alpha_3 f_{aa}],
\]
(A45)

\[
G_{111} = \frac{1}{A} [f_{111} + 3\alpha_1 f_{11a} + \alpha_1 f_{1aa}] + \alpha_3^3 f_{aaa} + 3\alpha_1 f_{1a} + \alpha_1 f_{aa}],
\]
(A46)

\[
G_{222} = \frac{1}{A} [f_{222} + 3\alpha_2 f_{22a} + \alpha_2 f_{2aa}] + \alpha_3^3 f_{aaa} + 3\alpha_2 f_{2a} + \alpha_2 f_{aa}],
\]
(A47)

\[
G_{333} = \frac{1}{A} [\alpha_3^3 f_{aaa} + 3\alpha_3 f_{aa} + 6\beta e_3^2 D_2],
\]
(A48)

In the above formula, only in \( G_{11}, G_{22}, G_{33}, G_{111}, G_{222}, \) and \( G_{333} \) appear in the \( \beta e \) and \( D_e \) terms. They are contributed from Morse potentials. Finally the coefficients in \( P(s_1, s_2, s_3) \) can be expressed in terms of \( g_1, G_{ij}, \) etc.:
c_1 = g_1,
\begin{align*}
c_2 &= g_2, \\
c_3 &= g_3, \\
c_{11} &= g_1^2 + \frac{1}{2} G_{11}, \\
c_{22} &= g_2^2 + \frac{1}{2} G_{22}, \\
c_{33} &= g_3^2 + \frac{1}{2} G_{33}, \\
c_{12} &= g_1 g_2 + G_{12}, \\
c_{13} &= g_1 g_3 + G_{13}, \\
c_{23} &= g_2 g_3 + G_{23}, \\
c_{111} &= \frac{1}{2} g_1^3 + \frac{1}{2} g_1 G_{11} + \frac{1}{6} G_{111}, \\
c_{222} &= \frac{1}{2} g_2^3 + \frac{1}{2} g_2 G_{22} + \frac{1}{6} G_{222}, \\
c_{333} &= \frac{1}{2} g_3^3 + \frac{1}{2} g_3 G_{33} + \frac{1}{6} G_{333}, \\
c_{112} &= g_1 g_2 g_1 + \frac{1}{2} g_2 G_{11} + \frac{1}{6} G_{112}, \\
c_{113} &= g_1 g_3 g_1 + \frac{1}{2} g_3 G_{11} + \frac{1}{6} G_{113}, \\
c_{122} &= g_1 g_2 g_2 + \frac{1}{2} g_2 G_{12} + \frac{1}{6} G_{122}, \\
c_{133} &= g_1 g_3 g_3 + \frac{1}{2} g_3 G_{13} + \frac{1}{6} G_{133}, \\
c_{223} &= g_2 g_3 g_2 + \frac{1}{2} g_2 G_{23} + \frac{1}{6} G_{223}, \\
c_{233} &= g_2 g_3 g_3 + \frac{1}{2} g_3 G_{23} + \frac{1}{6} G_{233}, \\
c_{123} &= g_1 g_2 g_3 + g_2 G_{12} + g_3 G_{13} + g_1 G_{12} + G_{123}.
\end{align*}

After substituting the coefficients into the polynomial, the analytical potential function is completed and the five parameters (\( \gamma_1, \gamma_2, \gamma_3, c_0, A \)) are to be optimized.

**D. The bivariate spline fitting**

The bivariate spline fitting aims to calculate a \( C^1 \) interpolant to scattered data in a plane. For the data points \( \{(x_i, y_i, V_i)\}_{i=1}^N \) in \( R^3 \), the interpolant \( s \) is computed by firstly the Delaunay triangulation of the points \( \{(x_i, y_i)\}_{i=1}^N \). In this triangulation on each triangle \( T \), the \( s \) has the form

\[
s(x, y) = \sum_{m+n \leq 5} c_{mn} x^m y^n \forall x, y \in T.
\]

Therefore on each triangle of this triangulation, \( s \) is a bivariate quintic polynomial. Additionally, \( s(x_i, y_i) = V_i \) for \( i = 1, 2, \ldots, N \), and \( s \) is continuously differentiable across the boundaries of nearby triangles.

The output points by our *ab initio* results are grouped into separate data sets of identical bond angles. Each data set with the fixed constant bond angle is then fitted using the preceding bivariate quintic polynomial with \( x_i \) and \( y_i \) being the two bond lengths.