

# Theoretical study on the mechanism of $\text{CH}_4 + \text{C}_2\text{H}_2^+$ reaction: Mode-enhancement effect

Qiang Cui, Zhiwei Liu, and Keiji Morokuma

Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322

(Received 26 January 1998; accepted 26 March 1998)

High level *ab initio* calculations have been performed to investigate the mechanism of the ion-molecule reaction of  $\text{CH}_4 + \text{C}_2\text{H}_2^+$ . Except for some subtle differences, the profile for the H-abstraction channel obtained here at the G2M//B3PW91/6-311G(*d,p*) level is very similar to that found in a previous study at the G2//MP2/6-31G(*d*) level. For the complex formation channel, however, a different transition state has been located; the geometry and energetics of which are more consistent with experimental findings. Calculations of a few direct trajectories have been carried out to investigate the possible reason for the significant mode enhancement observed experimentally for the H-abstraction channel. Although none of them is reactive, a trajectory with an asymmetric  $\text{C}_2\text{H}$  bend excitation exhibits a clear signature for being more reactive than those without vibrational excitation or with a symmetric bend excitation. © 1998 American Institute of Physics. [S0021-9606(98)30125-7]

## I. INTRODUCTION

Controlling the outcome of a chemical reaction is the dream of chemists and a fascinating branch of modern chemistry. There are many approaches that attempt to take advantage of the power, frequency resolution, and coherence of lasers to achieve this task. Among them, two schemes are extremely appealing, i.e., “coherent control” and “mode-selective excitation.” The former approach utilizes phase and intensity properties of laser excitation to alter the character of the prepared states so that production of the desired outcome is enhanced. This method has proved to be quite promising<sup>1</sup> not only in controlling the nuclear motion of the system, but also in directing electronic motion in chemical systems.<sup>2</sup> The second approach of mode-selective excitation concentrates on local vibrational modes, and emphasizes selective excitation of the particular motion, which nudges the reaction toward the desired channel.<sup>3</sup> Many beautiful examples have accumulated over the years in the photodissociation process of vibrationally or rovibrationally selected small molecules including  $\text{H}_2\text{O}$ ,<sup>3(a)–3(d)</sup>  $\text{HNCO}$ ,<sup>3(e)–3(f)</sup> and  $\text{C}_2\text{H}_2$ .<sup>3(g)</sup> Despite the clear chemical picture, there are few *bimolecular* reactions where the effects of different reactant vibrational modes have been examined. This is largely due to the difficulty of preparing mode-selective excited reactants. In addition, the vibrational coupling in most molecules quickly redistributes the applied energy to a selected vibrational mode. Earlier studies have mostly concentrated on small system including various isotopic forms of water molecules. However, recent findings<sup>4</sup> provide us with some new examples in the case of more complex ion-molecular reactions which are vibrational selective. Zare *et al.* studied the reaction of ammonium ion and  $\text{ND}_3$ , and found that the umbrella mode of  $\text{NH}_3^+$  enhances charge transfer and deuterium abstraction significantly, while the isoenergetic excitation of the breathing mode does not induce any effect.<sup>4(c)</sup>

In another experiment, Anderson *et al.*<sup>4(a),4(b)</sup> have studied the effects of collision energy and mode-selective vibrational excitation on the reaction of  $\text{C}_2\text{H}_2^+$  with  $\text{CH}_4$  and  $\text{CD}_4$  with a guided-ion beam scattering instrument. Two distinct reaction mechanisms are active in the energy range below 5 eV. At low energies, a long-lived  $\text{C}_3\text{H}_6^+$  complex forms efficiently and then decomposes primarily to  $\text{C}_3\text{H}_5^+ + \text{H}$  and  $\text{C}_3\text{H}_4^+ + \text{H}_2$  (R1), (R2)



Competing with (R1) and (R2) is a hydrogen transfer reaction (R3), producing  $\text{C}_2\text{H}_3^+ + \text{CH}_3$  with little atom scrambling. The (R3) channel is strongly enhanced by collision energy and becomes dominant above 0.4 eV. One interesting feature of this channel is that, while CC stretching provides a weaker enhancement than collision energy, two quanta of a C–H bending modes ( $\sim 155$  meV) enhance the reaction at least  $\sim 10$  times! Based on the isotope study with  $\text{CD}_4$ , they concluded that there exist two possible reaction mechanisms for (R3):  $\text{CH}_3$  elimination from a long-lived  $\text{C}_3\text{H}_6^+$  complex and a direct H-atom abstraction through an intermediate, where the latter path is dominant by a factor of 5–10:1. They also predicted an early barrier of about  $150 \pm 50$  meV. The enhancement effect of C–H bending excitation on the reaction rate is explained by the necessity of carbon atom rehybridization from *sp* to *sp*<sup>2</sup> to reach a bent transition state during the process.

This amazing experimental results certainly attracted the attention of theoreticians. A combined quantum and transition state theory (TST) study has been carried out by Klippenstein to unravel the detailed reaction mechanism and the observed mode-enhancement effect.<sup>5</sup> Based on the structure

and frequencies of several intermediates obtained at the level of MP2/6-31G(*d*) and Gaussian-2(G2)<sup>6</sup> energetics, TST was found to yield a qualitatively correct cross section for the direct channel (R3), but not to be so satisfactory for the complex channels, (R1) and (R2). It was found that if the energetics of the transition state involved in the complex channels was lowered by 4.5 kcal/mol, the magnitude of the cross section for the complex channel could be qualitatively reproduced. Most importantly, no entrance or exit channel barrier was found for the H-abstraction channel (R3). However, it was found that the enhancement of the H-abstraction cross section by the H-C-C bending excitation in  $C_2H_2^+$  was qualitatively reproduced if the two quanta of H-C-C bending were assumed to be totally randomized.

It might look as if all the issues have been resolved by the work of Klippenstein. However, the necessity of artificially lowering the energy of the transition state involved in the complex channel looks somewhat questionable. Judging from the structure of the transition state presented in Ref. 5, we suspect that there may be a lower saddle point with a totally different structure involved in the complex channel. This will be examined in the present work. In addition, this might be the ideal system to test the capability of the direct trajectory method,<sup>7</sup> which has become popular due to the advantage that no analytical potential energy functions have to be constructed. In application of the methodology without approximations<sup>7(c)</sup> in the electronic structure part, it is usually too expensive to run a large number of trajectories for a meaningful statistical average. It is hoped that the interesting features of the reaction dynamics can be captured by few limited trajectories with wisely chosen initial conditions.

In Sec. II, we shall discuss the method of computation. Results of electronic structure calculation and direct trajectory calculations will be discussed in Sec. III. Finally, we draw some conclusions in Sec. IV.

## II. COMPUTATIONAL METHOD

In order to find the most appropriate method to investigate the structure of the important intermediates and transition states involved in the titled reaction, we have carried out a series of test calculations at a variety of levels including B3LYP,<sup>8</sup> B3PW91,<sup>9</sup> and second-order Møller-Plesset perturbation theory (MP2), together with the 6-31G(*d,p*)<sup>10</sup> or 6-311G(*d,p*)<sup>11</sup> basis sets. Preliminary calculations clearly indicated that polarization *p* function on the bridged H atoms is rather important even for geometries, and therefore at least a 6-31G(*d,p*) basis set should be used. At first, we examine the relative stability of the two conformations of the H-abstraction reaction product  $C_2H_3^+$ . It is well known from numerous experimental<sup>12</sup> as well as theoretical calculations<sup>13</sup> that the nonclassical (nc) structure with a bridging H atom,  $C_2H_3^+(nc)$  in Fig. 1, is more stable than the classical structure,  $C_2H_3^+(c)$ . The energy difference is as small as several kcal/mol and depends sensitively<sup>13(a)</sup> on the level of calculations. In the three methods we have tested, B3LYP/6-311G(*d,p*), B3PW91/6-311G(*d,p*) and MP2/6-311G(*d,p*), only the B3LYP results gave the wrong trend, namely, it predicted the classical structure to be the global

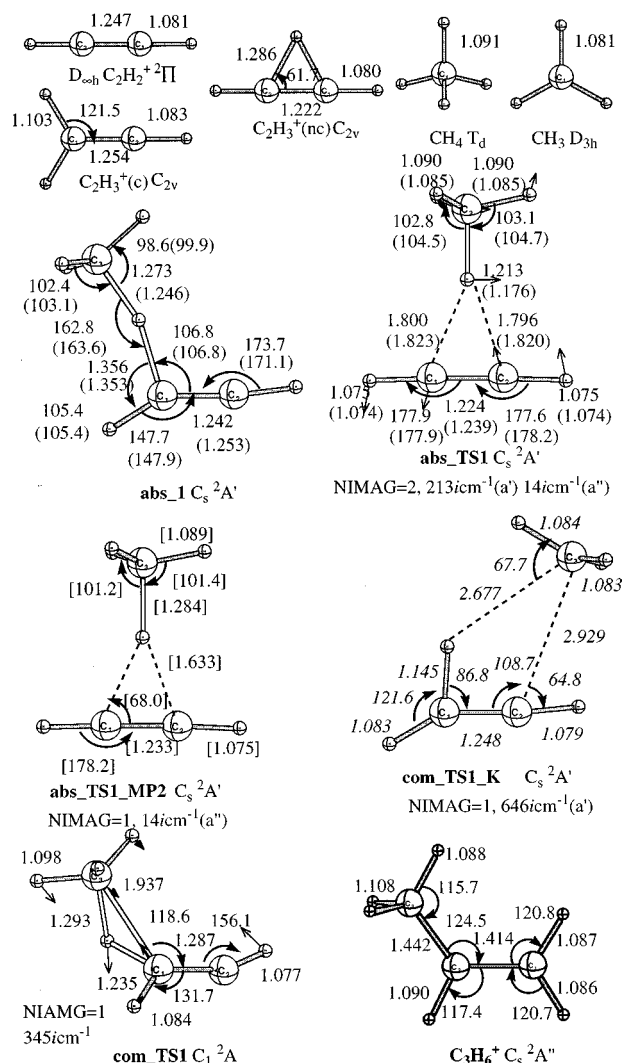


FIG. 1. Geometries (in Å and deg) of reactants, products, intermediates, and transition states involved in the reaction of  $CH_4 + C_2H_2^+$ . Plain numbers are obtained at the B3PW91/6-311G(*d,p*) level. Numbers in parentheses are from UCCSD/6-31G(*d,p*) calculations. Numbers in brackets are from MP2/6-311G(*d,p*) calculations. Italic numbers are taken from Ref. 5. The number of imaginary frequencies (NIMAG) at the B3PW91/6-311G(*d,p*) level, with corresponding imaginary frequencies, are shown for the systems with NIMAG > 0.

minima. At the B3PW91/6-311G(*d,p*) and the MP2/6-311G(*d,p*) levels, the nonclassical structure has been calculated to be more stable by 0.06 eV (1.4 kcal/mol) and 0.33 eV (7.8 kcal/mol), respectively. Therefore, we did not use the B3LYP method to further investigate the potential energy surface of this particular system of  $CH_4 + C_2H_2^+$ . As will be discussed further in Sec. III, we found that B3PW91/6-311G(*d,p*) seems to produce the most reliable structures on the sensitive potential energy surface of the  $CH_4 + C_2H_2^+$  system. Therefore, we shall use the B3PW91/6-311G(*d,p*) structures in most of the discussions. As to the energetics, we have carried out G2M<sup>14</sup> calculations based on the B3PW91/6-311G(*d,p*) optimized geometries and vibrational frequencies. Note that although the RCCSD(T)<sup>15</sup> theory has been used in the original scheme of G2M,<sup>14</sup> we used UCCSD(T) with unrestricted Hartree-Fock

TABLE I. Energetics of intermediates, transition states in the reaction of  $\text{CH}_4 + \text{C}_2\text{H}_2^+$ .<sup>a</sup>

Structure	State	B3PW91/I	PMP4/I	UCCSD(T)/I	PMP4/II	PMP4/III	MP2/IV	G2M	G2M+ZPE
$\text{CH}_4$	$^1A_1$	-40.517 12	-40.405 05	-40.405 84	-40.405 35	-40.424 67	-40.405 63	...	...
$\text{C}_2\text{H}_2^+$	$^2\Pi_g$	-76.903 66	-76.729 98	-76.731 15	-76.730 87	-76.763 91	-76.734 90	0.00	0.00
$\text{CH}_3 + \text{C}_2\text{H}_3^+(\text{nc})^b$		0.30	0.27	0.32	0.25	0.24	0.14	0.24	0.06
$\text{CH}_3 + \text{C}_2\text{H}_3^+(\text{c})^b$		0.36	0.47	0.44	0.45	0.45	0.52	0.41	0.23
<b>abs_1</b>	$^2A'$	-0.86	-0.64	-0.58	-0.65	-0.68	-0.45	-0.61	-0.66
<b>abs_TS1</b>	$^2A'$	-0.71	-0.46	-0.41	-0.46	-0.52	-0.49	-0.47	-0.55
<b>Com_TS</b>	$^2A'$	-0.64	-0.40	-0.37	-0.40	-0.43	-0.27	-0.41	-0.38
$\text{C}_3\text{H}_6^+$	$^2A''$	-3.41	-3.04	-3.04	-3.04	-3.09	-2.94	-2.89	-2.74

<sup>a</sup>Optimized at the B3PW91/6-311G(*d,p*) level. Total energies in hartree are shown in italics for the reactants, and relative energetics respective to  $\text{CH}_4 + \text{C}_2\text{H}_2^+$  in eV are shown for the other structures. Basis notations are I: 6-311G(*d,p*), II: 6-311+G(*d,p*), III: 6-311G(2*df,p*), IV: 6-311+G(3*df,2p*). No ZPE included in the relative energetics unless specified. ZPEs are calculated at B3PW91/6-311G(*d,p*) level.

<sup>b</sup> $\text{C}_2\text{H}_3^+(\text{nc})$  denotes the nonclassical H-bridged structure, while  $\text{C}_2\text{H}_3^+(\text{c})$  denotes the classical structure.

references in the current G2M calculations because of the small spin contamination even at the UHF level.<sup>16</sup> All the calculations have been carried out using the GAUSSIAN94 package.<sup>17</sup>

In the direct trajectory calculations, a less computationally demanding method has to be employed. According to our preliminary calculations, the B3PW91/6-31G(*d,p*) method can predict the structures and energetics of the intermediates and transition states rather well. Therefore, we have carried out trajectory calculations with the energy and gradients obtained at the level of B3PW91/6-31G(*d,p*) on the fly.

The structures of the intermediates and transition states involved are shown in Fig. 1. Their energetics calculated at varieties of levels are summarized in Table I. The schematic

reaction profile is shown in Fig. 2. Some results from limited direct trajectory calculations are presented in Fig. 3.

### III. AB INITIO AND DIRECT TRAJECTORY CALCULATIONS

In this section, we shall discuss our findings concerning the mechanism of the reaction  $\text{CH}_4 + \text{C}_2\text{H}_2^+$ . Two different channels are distinguished, the H-abstraction channel (R3) and the complex channel (R1), (R2). The structures involved in the reaction will be labeled after the channel in bold face, e.g., **abs\_1** and **com\_TS1** in Fig. 1 denotes intermediate involved in the abstraction channel, and transition state involved in the complex channel, respectively. We note that although the reactant is actually doubly degenerate due to the

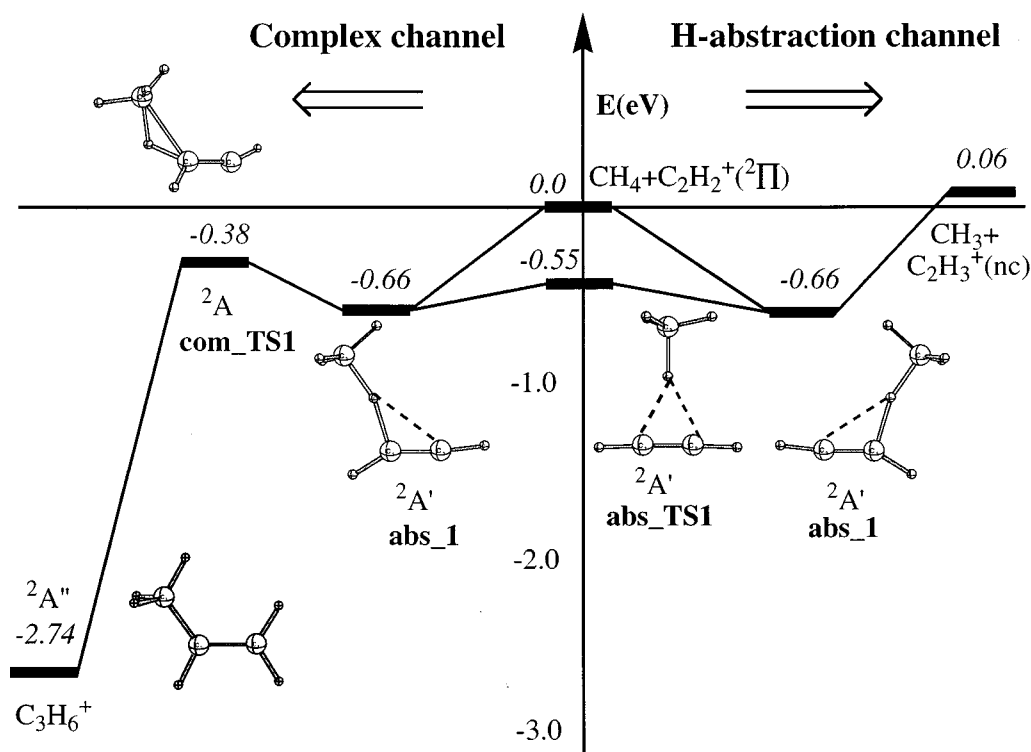


FIG. 2. Schematic profile for the reaction of  $\text{CH}_4 + \text{C}_2\text{H}_2^+$ . Energies (in eV) are obtained from G2M/B3PW91/6-311G(*d,p*) level including ZPE.

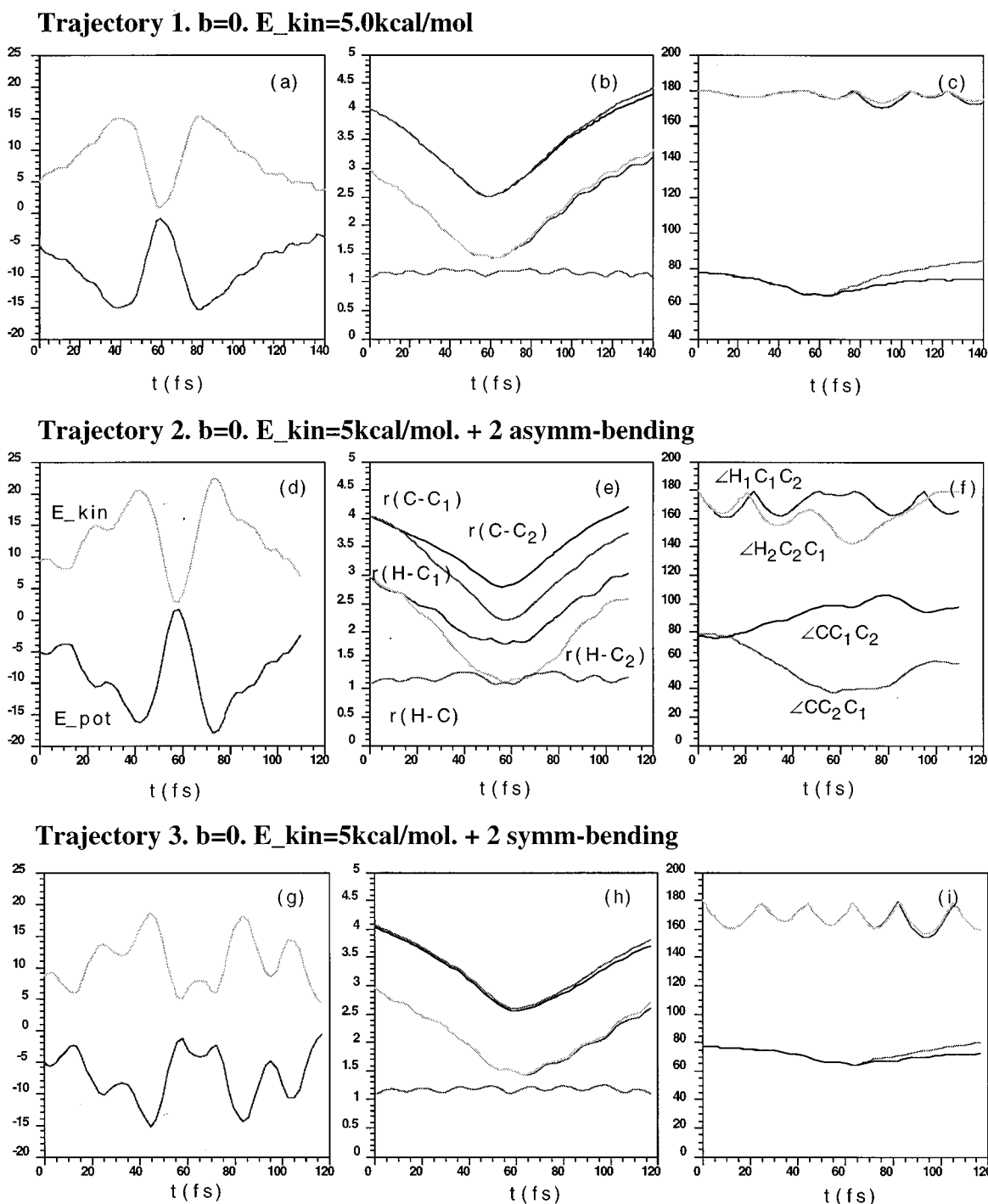


FIG. 3. Results from three direct trajectory calculations. The figures in the first column are kinetic and potential energies in kcal/mol. Those in the second column are essential bond distances (in Å) as indicated in the figure. The plots in the third column are important bond angles (in deg) as indicated in the figures.

$^2\Pi$  state of  $\text{C}_2\text{H}_2^+$ , we only need to consider the lowest electronic state during the reaction, which is  $^2A'$  if  $C_s$  symmetry is maintained. This is because the interaction between the  $\text{CH}_4$  and the  $^2A''$  component of  $\text{C}_2\text{H}_2^+$  is expected to be repulsive.

#### A. The H-abstraction channel: MP2 vs DFT, which is correct?

According to the previous study<sup>5</sup> at the level of UMP2/6-31G(*d*), the H-abstraction channel proceeds with-

out entrance or exit barriers. Two minima with very similar energetics ( $\sim -13$  kcal/mol) were found on the potential energy surfaces, which resemble the structure of **abs\_1**, and **abs\_TS1** shown in Fig. 1, respectively. A saddle point connecting the two minima was also found, and the barrier was calculated to be as small as 0.5 kcal/mol. Therefore, the so-called “direct” H-abstraction channel actually can be viewed as proceeding with a moderately bound intermediate complex.

At the level of B3PW91/6-311G(*d,p*), the overall pro-

file of the reaction remains the same. Namely, no entrance or exit channel barrier was found, and the structure of **abs\_1** from the current work and the so-called classical  $\text{CH}_4 \cdots \text{C}_2\text{H}_2^+$  minimum in Ref. 5 are rather similar as well. However, there are a few subtle differences between the so-called bridged  $\text{CH}_4 \cdots \text{C}_2\text{H}_2^+$  geometry found by Klippenstein,<sup>5</sup> and the similar structure we have obtained as **abs\_TS1** in Fig. 1. According to Ref. 5, this structure is a *minimum* at the MP2/6-31G(*d*) level. At the B3PW91/6-311G(*d,p*) level, however, **abs\_TS1** is actually a second-order *saddle point*, which, according to the *a'* normal mode ( $213i \text{ cm}^{-1}$ ) shown in Fig. 1, connects **abs\_1** and its pseudomirror image **abs\_1'** (not shown). In other words, through **abs\_TS1**, the  $\text{CH}_4$  group migrates from one carbon atom of  $\text{C}_2\text{H}_2^+$  in **abs\_1**, to the other carbon atom in **abs\_1'**. We use the word pseudomirror image because **abs\_1** and **abs\_1'** are not exactly a mirror image, since the  $\text{CH}_3$  group has different orientations in the two structures. In fact, **abs\_1'** has to have one low *a''* imaginary frequency corresponding to  $\text{CH}_3$  rotation. Since **abs\_TS1** connects a minima (**abs\_1**) and a saddle point (**abs\_1'**), it can have two imaginary frequencies, which is exactly what we find. Since the  $\text{CH}_3$  rotation is nearly free, the *a''* imaginary frequency is found to be as low as  $14i \text{ cm}^{-1}$ . Therefore, we did not try to look for a first-order saddle point in  $C_1$  symmetry connecting **abs\_1** and its equivalent structure.

Where does the difference between **abs\_TS1** and the bridged  $\text{CH}_4 \cdots \text{C}_2\text{H}_2^+$  structure in Ref. 5 come from? Since both the basis set and the method employed are different in the two calculations, we have reoptimized the structure of bridged  $\text{CH}_4 \cdots \text{C}_2\text{H}_2^+$  as a minimum with UMP2/6-311G(*d,p*) to have a fair comparison. The resultant structure is shown in Fig. 1 as **abs\_TS1\_MP2**. It has one small *a''* imaginary frequency of  $14i \text{ cm}^{-1}$  and all real *a'* frequencies. Clearly, the different results obtained here and Ref. 5 mainly originate from the difference in method, not in basis set. The basis set does have some influence on the geometrical parameters involving the bridging-H atom. For instance, the distance between the bridging-H and carbon atom in  $\text{C}_2\text{H}_2^+$  is seen to decrease from  $1.718 \text{ \AA}$  at the UMP2/6-31G(*d*) level to  $1.633 \text{ \AA}$  at the UMP2/6-311G(*d,p*) level.

Although the difference between B3PW91/6-311G(*d,p*) and UMP2/6-31(*d*) results are rather small and may not have a major effect on the overall dynamics, it is interesting to learn which method gives results that are closer to reality. To investigate this point, we have carried out optimization for both the minimum and the transition state starting from the structure of **abs\_TS1** at the CCSD(T)/6-31G(*d,p*) level. The minimum search leads to a structure very similar to **abs\_1**, and the TS search leads to a structure similar to **abs\_TS1**. The optimized parameters are also shown in Fig. 1 in parentheses. Therefore, the CCSD(T)/6-31G(*d,p*) results agree with the B3PW91/6-311G(*d,p*) results, which strongly suggests that B3PW91/6-311G(*d,p*) results are closer to reality than the MP2 ones.

The relative energetics of **abs\_1** and **abs\_TS1** does not depend on the method of calculation very much, as illustrated in Table I. At the G2M level including the zero-point

energy corrections, **abs\_1** lies  $0.66 \text{ eV}$  ( $15.2 \text{ kcal/mol}$ ) below the reactants, which is rather close to the G2 result of  $12.9 \text{ kcal/mol}$  from Ref. 5. The **abs\_TS1** structure lies  $0.55 \text{ eV}$  ( $12.7 \text{ kcal/mol}$ ) below the reactants, i.e., the barrier relative to **abs\_1** is predicted to be  $0.11 \text{ eV}$  ( $2.5 \text{ kcal/mol}$ ).

As a short summary, the overall mechanism of the H-abstraction channel as shown in Fig. 2, remains the same as predicted by Klippenstein,<sup>5</sup> despite some small differences. The so-called "direct" abstraction channel actually proceeds through a moderately bound ( $\sim 15 \text{ kcal/mol}$ ) complex, and without entrance or exit barrier.

## B. The complex channel: A new transition state at lower energy

In Ref. 5 the complex channel (R1), (R2) leading to  $\text{C}_3\text{H}_6^+$  has been shown to proceed, starting from the so-called classical  $\text{CH}_4 \cdots \text{C}_2\text{H}_2^+$  geometry, through a saddle point, **com\_TS1\_K**, which is also included in Fig. 1. However, as mentioned above, with the energetics for this transition state, one cannot obtain the cross section for this channel even qualitatively. In Ref. 5, the qualitatively correct cross section was obtained by lowering the energy of **com\_TS1\_K** by  $4.5 \text{ kcal/mol}$ . However, we suspect that the reason for the disagreement is that another transition state with a different structure exists at lower energy. Indeed, the structure of **com\_TS1\_K** does not look like a transition state for C-H activation of  $\text{CH}_4$  by  $\text{C}_2\text{H}_2^+$ , but more like a  $\text{C}_2\text{H}_3^+$  isomerization transition state between its two conformations perturbed by a  $\text{CH}_3$  fragment. Since two bonds, C-C and C-H, have to be formed starting from the **abs\_1**, the transition state has to break the symmetry and resemble the transition state found in the similar reaction of  $\text{H}_2 + \text{C}_2\text{H}_2^+$ .<sup>18</sup> Bearing these in mind, we have successfully located the  $C_1$  transition state **com\_TS1** shown in Fig. 1. The length of the forming C-C and H-C bonds and that of the breaking H-C bond are quite reasonable. The normal mode vector, shown on the structure in Fig. 1, also clearly manifests the character of the transition state. The IRC<sup>19</sup> calculations verify that it does connect **abs\_1** at one end. Towards the other side of the barrier, geometry optimization starting from the structure obtained after 24 steps of IRC leads to  $\text{C}_3\text{H}_6^+$ , which indicates that no other significant wells exist on the path. Therefore, in the schematic reaction mechanism presented in Fig. 2, the transition state **com\_TS1** is directly connected to the final product  $\text{C}_3\text{H}_6^+$ . The situation is rather similar to the case of  $\text{H}_2 + \text{C}_2\text{H}_2^+$ , where the deep  $\text{C}_2\text{H}_4^+$  minimum can be reached nearly directly after overcoming a barrier similar to **com\_TS1** with only few negligible bumps on the reaction path.<sup>18</sup>

At the G2M level, the energy of **com\_TS1** is  $0.38 \text{ eV}$  ( $8.7 \text{ kcal/mol}$ ) below the reactants, and the barrier height measured from **abs\_1** is  $0.28 \text{ eV}$  ( $6.5 \text{ kcal/mol}$ ). In the previous study of Klippenstein,<sup>5</sup> it was found that qualitatively correct cross sections for the complex channel can be obtained if the barrier height is artificially modified to  $7.2$  from  $11.7 \text{ kcal/mol}$  calculated with **com\_TS1\_K**. Therefore, we are confident that with the present results reasonable cross sections comparable to the experimentally measured value can be obtained.

### C. Direct trajectory calculations: Any hints on the mode enhancement?

According to our *ab initio* calculations presented above, it is seen that H–C–C bending is clearly strongly coupled to the reaction path. Therefore, one can imagine that additional energy in this mode may contribute to the reaction rate effectively unlike the C–C stretch, which is nearly inert during the whole reaction.

One wonders if anything additional can be learned with the direct trajectory calculations. Since no statistical average can be made to obtain the cross section as a function of the bending excitation levels, one hopes that some characteristics of the dynamical process can be captured by *wisely* selecting the initial conditions. In Fig. 3, we present the results from three trajectory calculations as our first attempt.

In all three trajectories, the impact parameter  $b$  is taken to be zero, the initial velocity is along the line that joins the centers of mass of  $\text{CH}_4$  and  $\text{C}_2\text{H}_2^+$ , and is perpendicular to the CC triple bond in  $\text{C}_2\text{H}_2^+$ . All the trajectories start with the center of mass separation of 4.0 Å. In the first trajectory, the initial velocity in the center of mass frame has been scaled so that the total initial kinetic energy is 5.0 kcal/mol. In the second and third trajectories, the initial velocities of the two H atoms in  $\text{C}_2\text{H}_2^+$  have been modified so that approximately two modes of asymmetric and symmetric H–C–C bending, respectively, are excited. To be more specific, we assume that all the vibrational energy (excluding the zero-point energy) went into kinetic energy, and we project the velocity (momentum) in normal mode coordinate back to the Cartesian space according to the well-known relationship

$$\sqrt{m_k} \dot{X}_k(0) = \sum_{i=1}^{3N-6} P_i(0) \cdot L_{ik} = \sum_{i=1}^{3N-6} \sqrt{E_i(0)} \cdot L_{ik}, \quad (1)$$

where the summation over the normal modes in Eq. (1) becomes a single term in such cases where only one mode is excited and no zero-point energy is considered. In all the trajectory calculations, a step size of 0.2 fs has been used. To save CPU time, we have run all the trajectories with the  $C_s$  symmetry constraint.

Unfortunately, all the three trajectories with the initial conditions selected here are *nonreactive*! The  $\text{CH}_4$  molecule comes close to  $\text{C}_2\text{H}_2^+$ , dances for a while, and then flies away. Nevertheless, we may make some observations on the dynamical processes based on these results. First of all, by comparing the results of the third and the first trajectory, we see that the symmetric H–C–C bending does not have much of an effect on the “reaction” process. The H–C–C bending is nearly adiabatic in the whole process. This may not be very surprising considering the *symmetry* of this trajectory. We expect a larger effect for cases with nonzero impact parameters.

Second, we see that the second trajectory with the initial asymmetric bending excitation reveals interesting features of the process. Although the trajectory starts with a nearly symmetric configuration,  $\text{CH}_4$  favors one carbon atom in  $\text{C}_2\text{H}_2^+$  as the trajectory propagates, and forms the configuration that resembles **abs\_1**. Clearly the H–C–C asymmetric bending mode is far from being adiabatic and actively participates in

the “reaction” process. It is also noted that the C–H bond that needs to be broken for the reaction has been significantly stretched compared to the other two trajectories, and becomes as long as 1.3 Å. At the same time, the C–H bond that needs to be formed becomes as short as 1.15 Å, whereas in the other trajectories the closest contact was only 1.45 Å. In other words, the second trajectory is nearly reactive.

In conclusion, although our initial attempt at direct trajectory calculations fails to produce any reactive event, we do observe the significant effect of the asymmetric bending during the collision process. Clearly, the initial excitation of the asymmetric bending in  $\text{C}_2\text{H}_2^+$  makes it easier to form the highly asymmetric classical complex **abs\_1** which is a critical step in the H-abstraction channel.

### IV. CONCLUSIONS

High quality *ab initio* calculations have been carried out to study the mechanism of the ion–molecule reaction of  $\text{CH}_4 + \text{C}_2\text{H}_2^+$ . Compared to the previous work of Klippenstein,<sup>5</sup> a very similar profile of the H-abstraction channel (R3) is obtained despite some subtle differences. No entrance or exit barrier was found, and the reaction proceeds through a moderately bound ( $\sim 15$  kcal/mol) intermediate complex. For the complex channel (R1), (R2), a new transition state, **com\_TS1**, with a  $C_1$  structure has been located. The geometry and energetics of this structure seem to be more consistent with experimental findings, and it is expected that a qualitatively correct cross section can be derived using the results in the current work.

Our initial attempt at direct trajectory calculation in the current system is not very satisfactory, since no reactive events have been observed. Nevertheless, we do notice that asymmetric H–C–C bending participates in the reaction actively, and nearly induced reaction in one of the trajectories we have propagated. Clearly, one has to choose the initial conditions wisely to gain any insights into the reaction process due to the limited number of calculations that one can afford in direct trajectory study. In the future, it would be of great interest if one can combine surface interpolation schemes and direct dynamics, so that larger number of trajectories can be carried out. Furthermore, more efficient propagation methods such as adaptive integrator should also be considered to achieve savings in CPU time requirement.

### ACKNOWLEDGMENTS

The authors would like to acknowledge Dr. S. D. Klippenstein and Dr. S. L. Anderson for stimulating discussions, and Dr. H. Basch for correcting the English. QC and ZL acknowledge a graduate fellowship from the Phillips Petroleum Co. for 1994–7 and 1997–8, respectively. The use of computational facilities and software at the Emerson Center is acknowledged. This work was in part supported by Grants F49620-95-1-0182 and F49620-98-1-0063 from the Air Force Office of Scientific Research.

- <sup>1</sup>See, for example (a) P. Brumer and M. Shapiro, *Annu. Rev. Phys. Chem.* **43**, 257 (1992); (b) *Acc. Chem. Res.* **22**, 407 (1989), and reference there in.
- <sup>2</sup>See, for example, A. D. Bandrauk and E. E. Aubanel, *Chem. Phys.* **198**, 159 (1995).
- <sup>3</sup>See, for example (a) A. Singa, M. C. Hsiao, and F. F. Crim, *J. Chem. Phys.* **92**, 6333 (1990); (b) A. Singa, M. C. Hsiao, and F. F. Crim, *ibid.* **94**, 4928 (1991); (c) M. J. Bronikowski, W. R. Simpson, B. Girard, and R. N. Zare, *ibid.* **95**, 8647 (1991); (d) A. Sinha, J. D. Thoemke, and F. F. Crim, *ibid.* **96**, 372 (1992); (e) S. S. Brown, R. B. Metz, H. L. Berghout, and F. F. Crim, *J. Chem. Phys.* **105**, 6293 (1996); (f) **105**, 8103 (1996); (g) R. P. Schmid, T. Arusi-Parpar, R.-J. Li, I. Bar, and S. Rosenwaks, *ibid.* **107**, 385 (1997), and references there in.
- <sup>4</sup>(a) Y. Chiu, H. Fu, J. Huang, and S. L. Anderson, *J. Chem. Phys.* **102**, 1119 (1995); (b) Y. Chiu, H. Fu, J. Huang, and S. L. Anderson, *ibid.* **101**, 5410 (1994); (c) R. D. Guettler, G. C. Jones, Jr., L. A. Posey, and R. N. Zare, *Science* **266**, 259 (1994).
- <sup>5</sup>S. J. Klippenstein, *J. Chem. Phys.* **104**, 5437 (1996).
- <sup>6</sup>L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).
- <sup>7</sup>See, for example (a) R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985); (b) B. Harktko and E. A. Carter, *J. Chem. Phys.* **97**, 6596 (1992); (c) V. Keshari and Y. Ishikawa, *Chem. Phys. Lett.* **218**, 406 (1994); (d) A. I. Krylov and R. B. Gerber, *J. Chem. Phys.* **106**, 6574 (1997); (e) M. S. Gordon, G. C. Chaban, and T. Taketsugu, *J. Phys. Chem.* **100**, 11512 (1996).
- <sup>8</sup>(a) A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988); (b) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988); (c) A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- <sup>9</sup>(a) J. P. Perdew and Y. Wang, *Phys. Rev. B* **34**, 13244 (1992); (b) A. D. Becke, *J. Chem. Phys.* **97**, 9173 (1992).
- <sup>10</sup>P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* **28**, 213 (1973).
- <sup>11</sup>R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).
- <sup>12</sup>(a) M. W. Crofton, M. Jagod, B. D. Rehfuss, and T. Oka, *J. Chem. Phys.* **91**, 5139 (1989); (b) E. P. Kanter, Z. Vager, G. Both, and D. Zajfman, *J. Chem. Phys.* **85**, 7487 (1986).
- <sup>13</sup>See, for example, (a) C. Liang, T. P. Hamilton, and H. F. Schaefer III, *J. Chem. Phys.* **92**, 3653 (1990); (b) L. A. Curtiss and J. A. Pople, *ibid.* **88**, 7405 (1988).
- <sup>14</sup>A. M. Mebel, K. Morokuma, and M. C. Lin, *J. Chem. Phys.* **103**, 7414 (1995).
- <sup>15</sup>P. J. Knowles, C. Hampel, and H.-J. Werner, *J. Chem. Phys.* **99**, 5219 (1993).
- <sup>16</sup>J. F. Stanton, *J. Chem. Phys.* **101**, 371 (1994).
- <sup>17</sup>GAUSSIAN 94, Revision D.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. B. Cioslowski, B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople (Gaussian, Inc., Pittsburgh, PA, 1995).
- <sup>18</sup>(a) S. A. Maluendes, A. D. McLean, and E. Herbst, *Chem. Phys. Lett.* **217**, 571 (1994); (b) K. Yamashita and E. Herbst, *J. Chem. Phys.* **96**, 5801 (1992); (c) E. Herbst and K. Yamashita, *J. Chem. Soc., Faraday Trans.* **89**, 2175 (1993).
- <sup>19</sup>K. Fukui, *J. Phys. Chem.* **74**, 23 (1970); (b) K. Fukui, S. Kato, and H. Fujimoto, *J. Am. Chem. Soc.* **97**, 1 (1974); (c) K. Fukui, *Acc. Chem. Res.* **14**, 363 (1981).