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Does Methane Invert through Square Planar?

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Abstract: MCSCF calculations using a triple-ζ basis set augmented with diffuse and polarization functions are used to probe that part of the singlet methane potential energy surface that pertains to the inversion of CH_4 from one tetrahedral structure to another. The true inversion transition state is found to have a distorted C_s structure, quite different both geometrically and energetically from the previously *presumed* square planar saddle point. At the second-order configuration interaction level of theory, the barrier to inversion is predicted to be just 7–8 kcal/mol higher in energy than the bond dissociation energy for the first C–H bond cleavage in methane.

I. Introduction

The inversion of tetrahedral compounds, presumably through a square planar D_{4h} transition state, has been of considerable chemical interest for some time, as has been the possibility of stabilizing a square planar structure. Inversion of the quintessential prototype, methane, was at the center of a flurry of theoretical activity in the decade from 1970 to 1980. Based on a variety of theoretical approaches, the consensus by the end of this period was that, while various substitutions for the hydrogens or replacement of the central carbon can stabilize the square planar structure, the energy requirement for forcing the parent CH_4 from T_d through D_{4h} requires considerably more energy than is required to break a C–H bond.

Hoffmann et al.[1] considered the qualitative electronic structure of D_{4h} CH_4, noting that in this molecular arrangement the occupied valence space comprises the following: two "normal" C–H bonds formed from a combination of C sp^2 hybrids with H 1s orbitals; one three-center, two-electron bond formed from a C sp^2 hybrid and two hydrogens, using only electrons from H; and a nonbonding π MO on C. The latter MO is orthogonal to the molecular plane and has a_{2u} symmetry. The authors conclude from this description that (1) all CH bonds are weaker in planar than in tetrahedral CH_4, (2) considerable electron transfer occurs from H to C upon going from T_d to D_{4h}, (3) the transformation path can be either $T_d \rightarrow D_2 \rightarrow D_{4h}$ ("twisting" path) or $T_d \rightarrow D_{2d} \rightarrow D_{4h}$ ("squashing" path), and (4) the planar structure can be stabilized by forcing delocalization of the lone pair, by incorporating the lone pair into a $4n + 2$ π system, or by replacing hydrogens by more electropositive ligands (e.g., Li). Quantitative $T_d \rightarrow D_{4h}$ energy differences were estimated using extended Hückel theory[2] (126.8 kcal/mol), CNDO[3] (186.8 kcal/mol), and a limited *ab initio* calculation (249.1 kcal/mol).

Durmaz, Murrell, and Pedley[4] used an approximate *ab initio* method with a minimal basis set of Slater type orbitals (STO's) to demonstrate that the lowest square planar triplet state is 179.9 kcal/mol higher in energy than the tetrahedral structure and 73.7 kcal/mol *lower* than the square planar closed-shell singlet. This was apparently the first suggestion that the lowest energy state in the square planar arrangement might be open shell. These authors also predicted that the D_{4h} triplet is stable to distortions to lower symmetry. Firestone[5] used a qualitative topological analysis to predict a much smaller D_{4h}–T_d energy difference of 35–40 kcal/mol.

In a more recent paper, Collins et al.[6] noted that "Planar tetracoordinate carbon is a difficult problem to attack experimentally, but it is easy computationally." These authors used minimal basis (STO-3G)[7] restricted Hartree–Fock (RHF) geometry optimizations, followed by 6-31G(d,p)[8] single-point energies to obtain a D_{4h}–T_d energy difference of 168 kcal/mol. RMP2[9]/6-31G(d,p) single points give a barrier of 157 kcal/mol. It was also discovered that, as suggested earlier by Hoffmann and co-workers,[1] systematic substitution of Li for H lowers the inversion barrier, with CLi_4 predicted to be square planar. In a related paper, Krogh-Jespersen et al.[10] carried out *ab initio* calculations on a series of compounds which are valence isoelectronic with methane. Geometry optimizations were performed with restricted Hartree–Fock (RHF)/6-31G(d) calculations for second-period hydrides and with RHF/STO-3G* for their third-period analogs. It was predicted that closed-shell singlets are lower in energy than the lowest triplet states (obtained with unrestricted Hartree–Fock (UHF) calculations) in all species studied. These authors verified the earlier prediction by Hoffmann et al.[1] that the highest occupied molecular orbital (HOMO) in methane is a π (a_{2u}) orbital localized on carbon, while the lowest unoccupied molecular orbital (LUMO) is a hydrogen δ (b_{1g}) MO (with the x and y axes chosen to lie along the C–H bonds). This closed-shell electronic state is predicted to be 160 kcal/mol higher in energy than the tetrahedral structure at the MP2/6-31G(d) level of theory. These authors also noted that when the HOMO and LUMO are switched (forming what was termed a "lumomer"), the energy of the square planar species increases by 67 kcal/mol. However, it is important to note that such a closed-shell calculation is not variationally meaningful, since the "lumomer" is simply a poor approximation to the lower-energy closed-shell calculation. So, the latter result is meaningless. When the central carbon atom is replaced by a more electropositive element (e.g., Si), the HOMO (a_{2u}) and LUMO (b_{1g}) do switch their order.

The most recent paper on square planar methane is that by Crans and Synder.[11] These authors noted that the lowest singlet state of "planarized methane" may be an open-shell singlet of $^1B_{2u}$ symmetry. MNDO[12] and PRDDO[13]–GVB[14] calculations

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predict this biradical to be 25–30 kcal/mol below the closed-shell state. These were the first calculations that to our knowledge made use of a multiconfigurational wave function to describe square planar CH_4.

A key point regarding all previous calculations on this subject is that none of them included an analysis of the Hessian (matrix of energy second derivatives) for either the tetrahedral or square planar structures, primarily because most of the studies cited in the previous paragraphs were performed prior to the availability of efficient Hessian evaluations. As a result, the nature of the stationary points is unknown. In particular, it is not clear from the previous work if there is a square planar electronic state of methane that correlates with the $^1A_1$ T_d closed-shell ground state and is a proper transition state (that is, with just one imaginary frequency leading downhill to the tetrahedral structure that is presumably the global minimum).

The studies by Hoffmann et al.,[1] Krogh-Jespersen and coworkers,[10] and Crans and Synder[11] are particularly poignant, since their collective description emphasizes that the electronic structure of methane really should be investigated with wave functions that are more complex than simple single-configuration descriptions. The motivation for the current work is to understand the nature of that part of the methane potential energy surface (PES) that relates to the possible inversion of this compound through a valid transition state.

II. Computational Approach

On the basis of previous investigations of this problem, the two key molecular orbitals at the square planar structure are the π (a_{2u}) and δ (b_{1g}) MO's, since they are apparently the HOMO and LUMO in D_{4h} symmetry. Double occupancy of either of these MO's leads to a totally symmetric (^1A_g) electronic state, while single occupancy of each can produce $^1B_{2u}$ and $^3B_{2u}$ states. Upon distortion from D_{4h} to D_{2d} symmetry, the "squashing" path noted by Hoffmann et al.,[1] A_g and B_{2u} both correlate with the totally symmetric representation A_1. So, there is a possibility that a conical intersection exists on the square planar part of the PES. This means that both ^1A_g and $^1B_{2u}$ electronic states must be considered for a proper analysis of the methane inversion process, if that process proceeds through a square planar arrangement. This in turn requires the use of a multiconfigurational description of the wave functions. All calculations described here are therefore based on a "full-valence" multiconfigurational (MC) SCF description, using the fully optimized reaction space (FORS)[15] model. According to this prescription, all electronic configurations (configuration state functions or CSF's) are included which arise from excitation of the eight valence electrons in methane into the four virtual (unoccupied) MO's used to correlate the four MO's which are doubly occupied in the closed-shell restricted Hartree–Fock description. The virtual MO's correspond to CH antibonding orbitals in the tetrahedral structure and to either CH antibonding or composite hydrogen (b_{1g}) MO's in D_{4h} symmetry.

All molecular structures have been determined at the full-valence MCSCF level of theory, using analytic gradients, and all stationary points so determined were characterized by calculating and diagonalizing the corresponding Hessian. The Hessian was obtained from finite differences of the analytically determined gradients. Double differencing was used throughout to ensure numerical accuracy. In several cases, intrinsic reaction coordinate (IRC) methods[16,17] have been used to track minimum energy paths from transition states to their connecting minima. To obtain refined energy comparisons, second-order configuration interaction (SOCI) calculations were performed, in which all single and double excitations from the MCSCF reference space are included in the wave function. This can lead to as many as 1 300 000 (uncontracted) CSF's.

Table I. Molecular and Electronic Structure of Square Planar Methane

	R (Å)		ΔE (kcal/mol)[a]	
	^1A_g	$^1B_{2u}$	^1A_g	$^1B_{2u}$
6-31G(d,p)	1.096 (4i)[b]	1.204 (1i)	11.3	0.0
6-31+G(d,p)	1.100 (4i)	1.205 (2i)	3.8	0.0
TZV++G(d,p)	1.098 (4i)	1.204 (2i)	3.9	0.0

[a] Energy difference between closed- and open-shell states. [b] Number of imaginary frequencies given in parentheses.

Three basis sets were used in the calculations described in this paper. The simplest basis set, used for initial probes of the PES, is the 6-31G(d,p)[8] split valence plus polarization basis set. Some calculations were also performed with a slightly larger 6-31+G-(d,p)[18] basis set, in which diffuse functions are included on the central atom to provide a better description of the carbon lone pair. Since the latter modification significantly improves the description of the planar closed-shell state, a much larger basis set, denoted TZV++G(d,p),[19] was used for the final probes of the potential energy surface. This is a triple-ζ plus polarization basis set, with diffuse functions on all atoms.

All of the calculations described here, unless otherwise noted, were performed with the electronic structure code GAMESS.[20]

III. Results and Discussion

A. Square Planar Structures. The MCSCF-optimized bond lengths (R) for the closed- and open-shell states of square planar CH_4 are listed in Table I. The effect of basis set on the predicted bond length is small, with the open-shell distance consistently being about 0.1 Å longer than the closed-shell distance. This is consistent with the conclusion drawn by Hoffmann et al.[1] that the bonds in the square planar arrangement are expected to be weaker than those in the tetrahedral structure. However, R in the ^1A_g state is virtually the same as that predicted for the closed-shell T_d structure (1.102 Å).

The basis set has a larger effect on the relative energies of the two states. With the smallest basis set, 6-31G(d,p), the open-shell $^1B_{2u}$ state is predicted to be 11.3 kcal/mol below closed-shell CH_4. The addition of diffuse functions decreases this energy difference to 3.8 kcal/mol. Note that this difference is almost entirely due to the energy decrease in ^1A_g (0.021 hartree) when diffuse functions are added to the basis set. This is likely a result of zwitterionic ($C^-H_4^+$) nature of the square planar closed-shell state, resulting from the π lone pair nature of the highest occupied orbital. Further improvement of the basis set, to TZV++G-(d,p), has a negligible effect on the predicted energetics, so the MCSCF level of theory consistently predicts the $^1B_{2u}$ state of square planar methane to be the lowest singlet state.

A key point regarding these results on square planar methane is the determination of the nature of the stationary points listed in Table I. The number of imaginary frequencies for each structure is given in the table. The closed-shell state exhibits four imaginary frequencies, regardless of basis set. These

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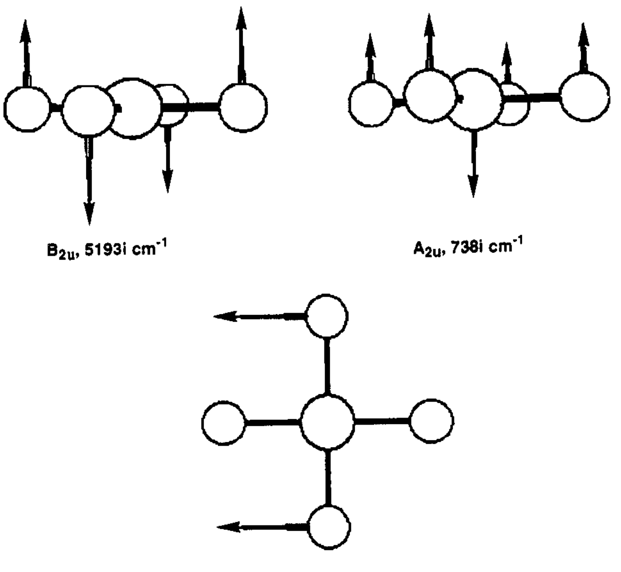
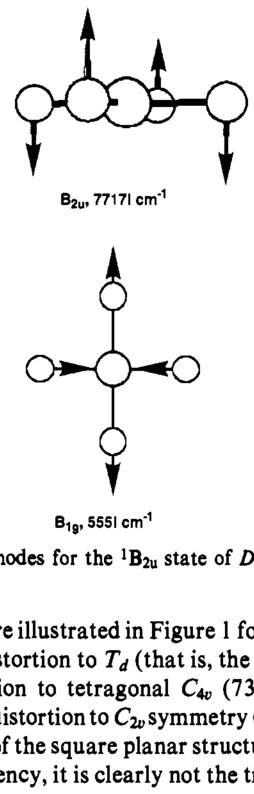


B_{2u}, 5193i cm^{-1}

A_{2u}, 738i cm^{-1}

E_u, 769i cm^{-1}

Figure 1. Imaginary modes for the ^1A_g state of D_{4h} CH$_4$. Each figure of this type gives the symmetry of the normal mode and its frequency calculated at the MCSCF/TZV++G(d,p) level of theory. Distances are given in angstroms and angles in degrees.



B_{2u}, 7717i cm^{-1}

B_{1g}, 555i cm^{-1}

Figure 2. Imaginary modes for the $^1B_{2u}$ state of D_{4h} CH$_4$.

frequencies, which are illustrated in Figure 1 for the largest basis set, correspond to distortion to T_d (that is, the inversion motion: 5193i cm^{-1}), distortion to tetragonal C_{4v} (738i cm^{-1}), and an in-plane degenerate distortion to C_{2v} symmetry (769i cm^{-1}). Since this electronic state of the square planar structure has more than one imaginary frequency, it is clearly not the transition state for inversion of methane.

With the smallest basis set, the $^1B_{2u}$ state is found to have just one imaginary frequency, corresponding to the inversion motion connecting two equivalent tetrahedral structures. This suggests that this open-shell structure is the correct transition state for the inversion of methane. Indeed, one may follow the intrinsic reaction coordinate (IRC) from $^1B_{2u}$ CH$_4$ in D_{4h} symmetry smoothly to closed-shell ^1A T_d methane, since (as noted in section II) the open- and closed-shell states have the same symmetry in the intermediate D_{2d} point group. However, when the basis set is improved to either of the larger ones used, a second imaginary frequency appears. This mode, illustrated for the largest basis set in Figure 2, corresponds to a distortion from square planar (D_{4h}) to rectangular (D_{2h}) symmetry. So, neither electronic state is found to be a true transition state when an adequate basis set is used.

As noted by previous authors, the square planar–tetrahedral CH$_4$ energy difference is quite large. At the MCSCF/6-31G(d,p) level of theory, this energy difference is calculated to be 161.6 kcal/mol for the open-shell state. Use of the largest basis set only reduces this value to 159.7 kcal/mol. The MCSCF level of theory only accounts for part of the correlation error introduced by the orbital approximation. One may improve the predicted energetics by incorporating into the wave function additional electronic configurations corresponding to excitations from the MCSCF reference space. Such calculations have been performed for the 6-31G(d,p) basis set, in which all single and double excitations from the MCSCF space are included (referred to as SOCI). Since there is only one geometric parameter in D_{4h} symmetry, it is possible to numerically determine the optimal geometry at the SOCI level of theory. At this level of theory, the open- and closed-shell bond lengths in D_{4h} symmetry are predicted to be 1.18 and 1.08 Å, respectively. At this level of theory, the closed-shell electronic state is actually found to be lower in energy than the open-shell $^1B_{2u}$ state by 4.6 kcal/mol, and the T_d structure is 158.5 kcal/mol below the closed-shell state (^1A_g) in D_{4h} symmetry.

So, at all levels of theory used here, the energy required to access singlet square planar methane is predicted to be much (about 60 kcal/mol) larger than that required to break a C–H bond. This is consistent with most of the earlier papers on this subject. It also appears that the square planar arrangement does not correspond to an inversion transition state for methane. It is possible that all but one of the imaginary frequencies of square planar methane disappear at the SOCI level of theory, but this is unlikely in light of the discussion in the next subsection.

The existence of a conical intersection involving the two singlet electronic states of square planar methane may be illustrated by following the energy as a function of the bond length R for the two states. This is illustrated in Figure 3, where it is seen that the conical intersection occurs at R = 1.10, 1.13, and 1.15 Å for MCSCF/6-31G(d,p), MCSCF/6-31+G(d,p), and SOCI/6-31G(d,p), respectively.

The optimal bond length for the $^3B_{2u}$ state of square planar methane was determined (at the MCSCF level of theory) to be 1.193 Å with both the 6-31G(d,p) and TZV++G(d,p) basis sets. At the MCSCF level of theory, the 6-31G(d,p) (TZV++G(d,p)) triplet is found to be 8.2 (7.1) kcal/mol higher in energy than the $^1B_{2u}$ state. For both basis sets, the square planar triplet state is found to have one imaginary frequency (1098i and 1356i cm^{-1} for the smaller and larger basis set, respectively), corresponding to an in-plane distortion to D_{2h} symmetry. At the SOCI/6-31G(d,p) level of theory, the lowest of the three states of interest is the ^1A_g state, with the $^1B_{2u}$ and $^3B_{2u}$ states 4.9 and 8.1 kcal/mol, respectively, higher in energy. It is possible that higher levels of theory and larger basis sets will reverse the order of the latter two states.

B. Distortions from Square Planar. Since both the open- and closed-shell square planar singlet electronic states have more than one imaginary frequency, distortions in both states from D_{4h} have been probed at the MCSCF/TZV++G(d,p) level of theory. These distortions were carried out systematically by following the directions indicated by the calculated imaginary frequencies. At the square planar structure, the largest imaginary frequency for both electronic states corresponds to distortion to D_{2d} symmetry, leading to the T_d global minimum.

First, consider the open-shell $^1B_{2u}$ state, summarized in Scheme I. The second imaginary frequency corresponds to an in-plane distortion to D_{2h} symmetry. Optimization in D_{2h} symmetry indeed leads to a lower energy structure, with two bond lengths (1.144, 1.283 Å) which differ from each other by more than 0.1 Å. As

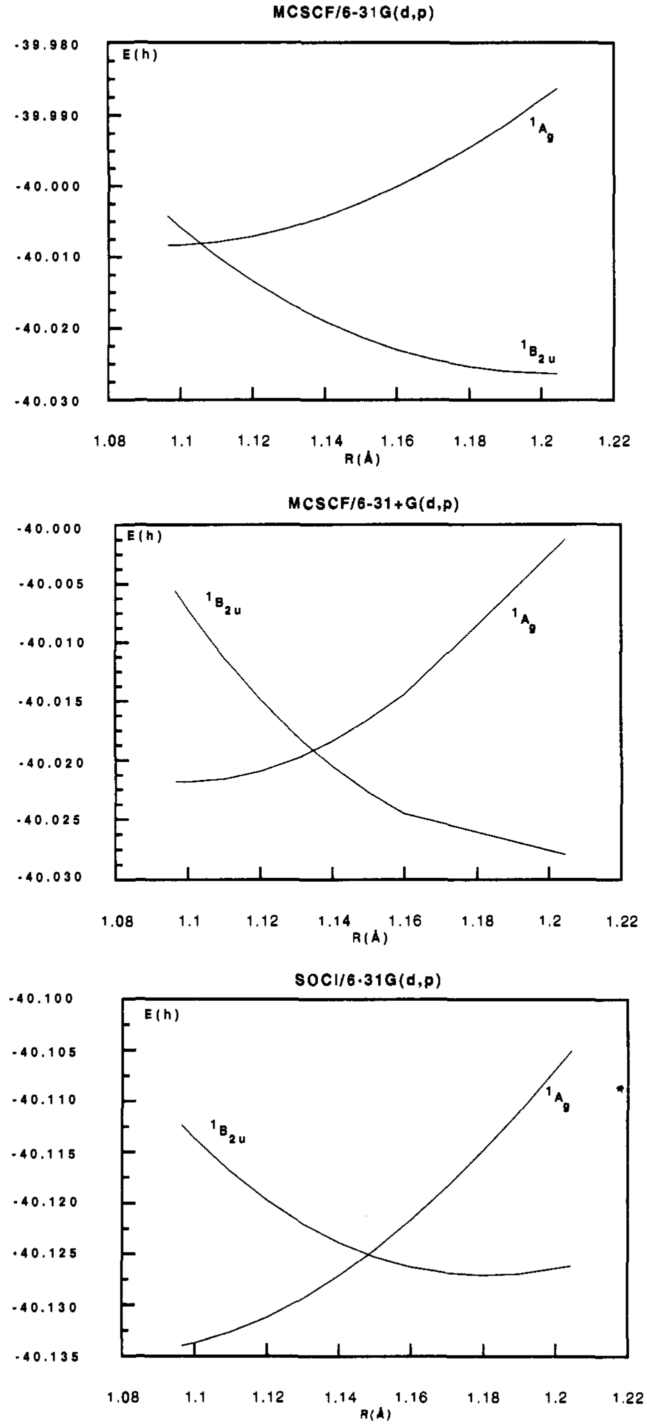
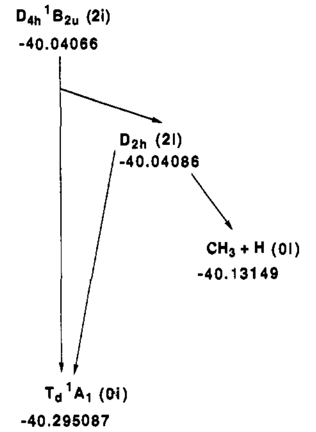


Figure 3. Plot of ^1A_g and $^1B_{2u}$ (D_{4h}) energies (hartrees) as a function of C–H distance (Å): (a) MCSCF/6-31G(d,p); (b) MCSCF/6-31+G(d,p); (c) SOCI/6-31G(d,p). Note that 1 hartree = 627.517 kcal/mol.

illustrated in Figure 4, this structure also has two imaginary modes. One of these (B_{1u}, 6107i cm^{-1}) again clearly leads to the global minimum, while the other (1360i cm^{-1}) is an in-plane distortion to C_s symmetry. In C_s, the open-shell electronic state correlates with A″ symmetry. A small distortion in the direction indicated by the imaginary mode, followed by geometry optimization, leads smoothly downhill to the $^2A''$ ground state of CH_3 + H. So, despite the importance of the open-shell state to the correct description of the electronic structure of methane in the square planar geometry, this state does not appear to be directly involved in the minimum energy inversion path.

Scheme I. Structures and Energies (hartrees) Starting from D_{4h} $^1B_{2u}$[a]



[a] Number of imaginary frequencies given in parentheses.

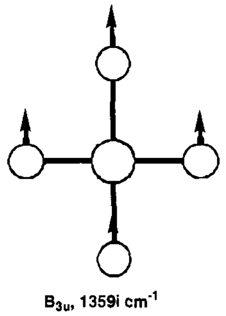
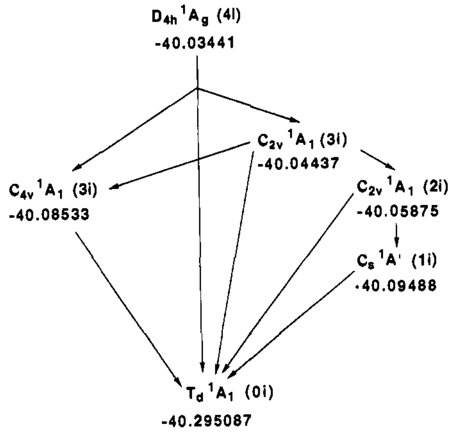


Figure 4. Second imaginary frequency for the open-shell state in D_{2h} symmetry.

Scheme II. Structures and Energies (hartrees) Starting from D_{4h} ^1A_g[a]



[a] Number of imaginary frequencies given in parentheses.

Now consider the behavior of the closed-shell electronic state upon distortions from D_{4h} symmetry, summarized in Scheme II. This is more complex, since there are more downhill directions from this state. As noted above, the largest imaginary frequency is the inversion motion that leads to the tetrahedral structure (see Figure 1). The other nondegenerate imaginary mode leads to the C_{4v} tetragonal structure illustrated in Figure 5. In this geometric arrangement, methane has the three imaginary frequencies shown in Figure 5. One of these (974i cm^{-1}) is clearly the inversion motion that leads to the tetrahedral global minimum. The other two imaginary frequencies are a degenerate pair (760i cm^{-1}) which distort the molecule into C_s symmetry. A small distortion along the direction indicated by this mode, followed by full geometry optimization, leads directly to the global minimum. So, there are apparently three routes to T_d methane from the tetragonal structure, directly via a distortion through C_{2v} symmetry or indirectly through a pair of degenerate distortions into C_s

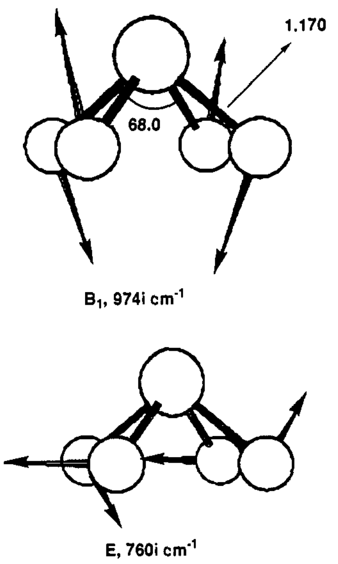


Figure 5. Tetragonal (C_{4v}) structure ($^1A_1$) and imaginary modes.

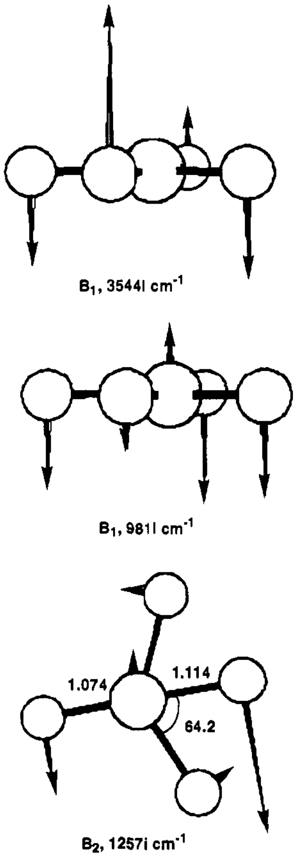


Figure 6. Structure and imaginary modes for $^1A_1$ C_{2v} CH_4.

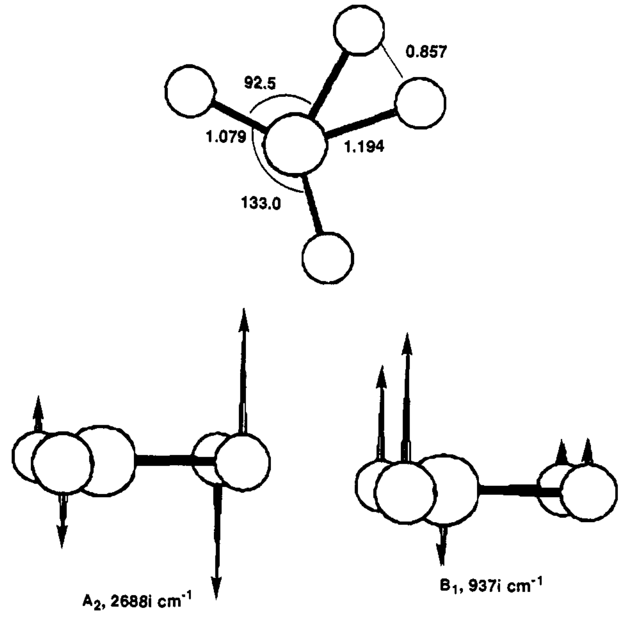


Figure 7. Structure and imaginary modes for $^1A'$ C_s ($^1A_1$ C_{2v}) CH_4.

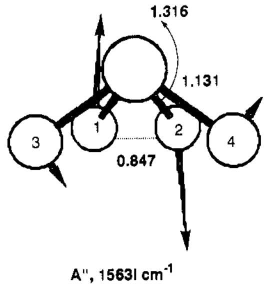


Figure 8. Structure and imaginary mode for the $^1A'$ C_s CH_4 inversion transition state. The bond angles in this structure are H_2–C–H_3 (105.9°), H_2–C–H_4 (77.8°), H_4–C–H_3 (98.0°).

symmetry. With three imaginary frequencies, this is a rather high energy pathway and not a true transition state.

Distortion along either of the pair of degenerate in-plane imaginary modes at the ^1A_g square planar geometry, followed by a geometry optimization, leads to the C_{2v} structure illustrated in Figure 6. As may be seen in the figure, this structure has three imaginary frequencies. One of these (3544i cm^{-1}) corresponds to a somewhat distorted, but quite discernible, inversion motion to the tetrahedral minimum. Another imaginary mode (981i cm^{-1}) clearly corresponds to a distortion toward the tetragonal structure discussed in the previous paragraph. The third imaginary mode (1257i cm^{-1}) in this unusual C_{2v} arrangement is a further in-plane distortion. Optimization via a distortion into C_s symmetry in the direction suggested by this mode leads to a new C_{2v} structure shown in Figure 7. This structure has an interesting geometry, with two pairs of equivalent CH bonds. The pair of hydrogens that are somewhat stretched from the usual CH bond length (to 1.194 Å) are separated by a distance of 0.857 Å. This is only about 0.15 Å longer than the equilibrium H–H distance in H_2.

The C_{2v} structure in Figure 7 has two remaining imaginary frequencies. The larger of these (2688i cm^{-1}) leads once again to the tetrahedral minimum. The other (937i cm^{-1}) appears to lead to a distorted version of the tetragonal C_{4v} structure; however, distortion of the geometry along the direction indicated by this mode, followed by optimization of the geometry in C_s symmetry, leads to the unusual C_s geometry shown in Figure 8. All four of the hydrogens in this structure are in the same hemisphere, and two of these H's are still separated by the very small distance of 0.847 Å. The C–H distances to these two hydrogens have now stretched to 1.316 Å. The *structure* in Figure 8 looks suspiciously like a transition state for H_2 elimination to give methylene. This structure does indeed have just one imaginary mode (1563i cm^{-1}), but the (a″) mode illustrated in Figure 8 looks more like a scissor motion into C_1 symmetry, and it will clearly connect to the same minimum in both the forward and reverse directions. To determine just what those minima connected to the transition state in Figure 8 are, an intrinsic reaction path (IRC) was traced, using the Gonzalez–Schlegel algorithm,[17] with a step size of 0.15 $amu^{1/2}$ bohr. This IRC smoothly leads to the global T_d minimum, as illustrated in Figure 9. Thus, the transition state in Figure 8 is in fact the true transition state for the inversion of methane. This transition state is 125.6 kcal/mol higher in energy than the global minimum at the MCSCF/TZV++G(d,p) level of theory.

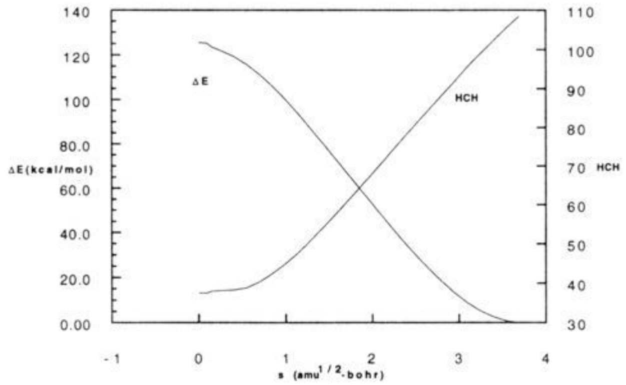


Figure 9. MCSCF/TZV++G(d,p) intrinsic reaction coordinate for methane inversion. Energy (kcal/mol), relative to the T_d structure, is plotted on the left as ΔE; HCH bond angle (degrees) is plotted on the right, vs reaction coordinate s (amu$^{1/2}$ bohr).

This is about 30 kcal/mol lower in energy than the lowest previous estimates of the inversion barrier, but still larger than the value of the C–H bond energy.

To obtain a better estimate of the barrier height for the methane inversion, SOCI calculations were performed at the transition state and global minimum, using the largest basis set. Since this results in well over 1 million (uncontracted) configurations, the MOLPRO[21] suite of programs was used for this final set of calculations. The number of contracted configurations is just over 80 000, and the SOCI/TZV++G(d,p) barrier height is 117.9 kcal/mol. Applying the multireference Davidson correction[22] to both the minimum and the transition state reduces the barrier further to 117.0 kcal/mol. This should be considered an upper limit for the barrier height, since additional improvements in the basis set are likely to reduce this value a bit further.

It is important to compare the predicted barrier height for inversion with the experimental C–H bond energy in methane. There are two ways this can be done. The experimental CH_3–H bond dissociation energy (or D_e) can be estimated[23] by combining the experimental D_0[24] with the experimental vibrational zero point energy (ZPE) corrections.[25] This gives an experimental D_e of 110.3 kcal/mol for the methane C–H D_e. Alternatively, a theoretical D_0 may be estimated by adding the calculated MCSCF/TZV++G(d,p) harmonic Δ(ZPE) to the 117.0 kcal/mol SOCI barrier height. This results in a calculated E_a of 111.1 kcal/mol, compared with the experimental D_0(C–H) of 103.3 kcal/mol. So, we predict that the estimated upper limit required for the inversion of CH_4 is approximately 7–8 kcal/mol greater than the C–H dissociation energy.

Some insight into the nature of the electronic structure of the methane inversion transition state is provided by the plot of the total electron density shown in Figure 10. As is implied by the long distances from C to H_2 and H_3, the C–H_2–H_3 interaction is best described by a weak π complex between C and a stretched H_2 molecule. As the molecule proceeds along the minimum energy path from transition state to tetrahedral, the H_2–H_3 moiety initially remains essentially intact while one of these hydrogens closes toward C (see Chart I). Only then does the other H move away from its partner and closer to C, in a rather asynchronous motion.[26]

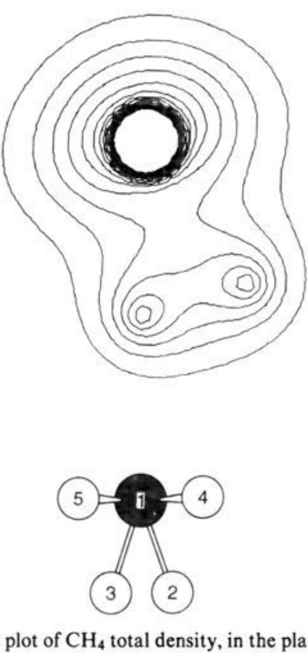
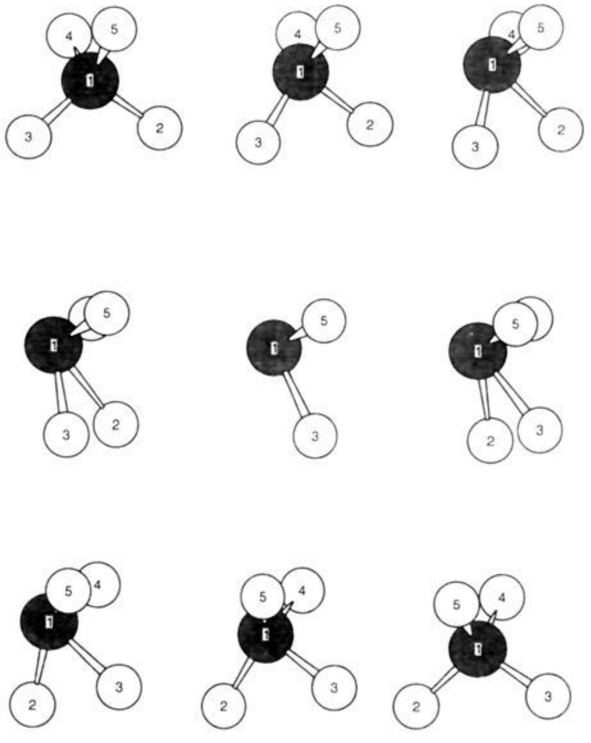


Figure 10. Contour plot of CH_4 total density, in the plane of C–H_2–H_3.

Chart I. Structures along the CH_4 IRC



The MCSCF/TZV++G(d,p) wave function at the (C_s) transition state has its primary contribution from the closed-shell (RHF) configuration ...$(4a')^2(5a')^0$ with CI coefficient = 0.92. However, the open-shell configuration ...$(4a')^1(5a')^1$ has a nontrivial coefficient of –0.29. The HOMO (4a′) and LUMO (5a′) have little contribution from the pivoting H's (H_2, H_3 in Chart I). Instead, these orbitals correspond to $CH_{4,5}$ bonding and antibonding, respectively.

IV. Conclusions

The calculations presented here show that there is indeed a mechanism for inversion of methane but that this inversion proceeds through a distorted C_s structure rather than through the square planar geometry. The use of MCSCF wave functions

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(26) A Chem 3D movie of this IRC (that runs on a Macintosh) is available upon request from mark@si.fi.ameslab.gov.

and characterization of stationary points with Hessians have been critical in unraveling the complex potential energy surface.

The actual transition state is nearly 40 kcal/mol lower in energy than the square planar geometry. The predicted barrier height for the inversion is 117.0 kcal/mol. This is 7 kcal/mol more energy than that required to break a C–H bond. However, this does not necessarily prevent the inversion process from taking place, since bond dissociation will occur only if most of the available energy is concentrated in one C–H bond. This will depend, among other things, on the coupling between the reaction path and the transverse vibrational modes (especially those modes which lead to C–H dissociation) as the molecule proceeds along the minimum energy path. To determine if this will occur will require a study of the reaction dynamics.

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