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CH_5^+: The never-ending story or the final word?

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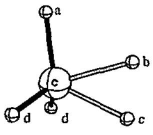
The closely related $C_s(1)$, $C_s(2)$, and $C_{2v}(3)$ structures of CH_5^+ have been reinvestigated with high level *ab initio* theory through the coupled cluster with single and double substitutions (CCSD), and CCSD with perturbatively included connected triple excitations [CCSD(T)] levels, employing a triple-ζ plus double polarization functions basis set, with f-functions on carbon as well as d-functions on the hydrogens [TZ2P(f,d)]. Vibrational frequencies have been computed up to TZ2P$+f$ CCSD; the inclusion of f-functions on carbon is critical for the configuration interaction with single and double excitations (CISD) and coupled cluster methods using the triple-ζ basis sets. The changes in geometries between the CISD and CCSD levels are very small, e.g., the C–H bond lengths vary by at most 0.005 Å. Thus, the optimizations are essentially converged within theoretical limits. The differences in energies of 1, 2, and 3 decrease and essentially vanish at the most sophisticated levels when the zero point vibrational energy corrections are applied. Hence, there is essentially *no barrier* to complete hydrogen scrambling.

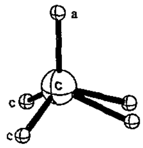
I. INTRODUCTION

As the CH_5^+ ion is the smallest pentacoordinate nonclassical carbonium ion,[1,2] it is of crucial importance to establish its structure and energy. CH_5^+ is a well known chemical ionization mass spectrometry source,[3] but the detailed geometry has not been determined. A recent study[4] of the vibrational spectrum of the $CH_5^+(H_2)$ complex provides some degree of experimental characterization of CH_5^+. In contrast, the structures of protonated methane have been computed theoretically for many years.[5–10] These studies revealed that while the extra hydrogen is attached to carbon, the molecule is best described as an H_2 subunit strongly bound to CH_3^+ (by 40–45 kcal mol^{-1} according both to experimental[11] and to theoretical data).[12]

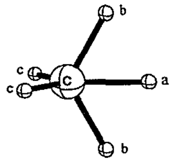
Although the C_s structure (1) has long been considered to be the global minimum, Schleyer and Carneiro[12] showed recently that this might not be entirely correct. At high levels of *ab initio* theory, not only the two C_s forms (1) and (2) but also the $C_{2v}(3)$ form are very close in energy. However, 2 and 3 both have an imaginary vibrational frequency and serve as transition states for hydrogen scrambling. The trigonal bipyramidal (D_{3h}) and the square pyramidal (C_{4v}) structures are a few kcal mol^{-1} higher in energy. The importance of the zero point vibrational energy corrections, which are responsible for equalizing the energies of the C_s and C_{2v} forms, was emphasized.



(1), C_s (I)



(2), C_s (II)



(3), C_{2v}

Since Klopper and Kutzelnigg[10] recently suggested that the stability order (C_s 1 lowest) might even be reversed at highly correlated levels, we have reinvestigated the problem by using configuration interaction and coupled cluster methods with large basis sets {triple-zeta plus double polarization (TZ2P), triple-zeta plus double polarization with f-functions (TZ2P$+f$), and triple-zeta plus double polarization with f-functions on carbon as well as d-functions on the hydrogens [TZ2P(f,d)]} for the geometry optimizations. Moreover, we determined the harmonic vibrational frequencies up to the coupled cluster with single and double substitutions (CCSD/TZ2P$+f$) level of theory to aid the experimental identification of this unique ion. Remarkably, to our knowledge, this is the first report on correlated frequencies beyond the MP2 method for the CH_5^+ ion. Since a primary goal of current experimental studies is the detection and assignment of the CH_5^+ infrared spectrum, the present research is timely.

II. COMPUTATIONAL METHODS

Geometries for all stationary points were optimized using self-consistent-field (SCF)[13] configuration interaction (CI),[14] coupled cluster including all single and double excitations (CCSD)[15] analytic gradient methods, and the CCSD method with the effect of connected triple excitations included perturbatively [CCSD(T)].[16] Residual Car-

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TABLE I. Absolute (in a.u.) and relative energies (in kcal mol^{-1}) of CH_5^+, C_s(I) (1), at different levels of theory.

	SCF	CISD	CISD(+Q)	CCSD	CCSD(T)
TZ2P	40.421 93	40.616 57	40.629 21	40.625 38	40.631 08
ZPVE	31.26	31.19	31.19	30.87	30.87[a]
Relative energy	0.00	0.00	0.00	0.00	0.00
Relative energy+ZPVE	0.00	0.00	0.00	0.00	0.00
TZ2P+f	40.422 60	40.628 99	40.642 65	40.638 47	40.644 84
ZPVE	31.23	31.02	31.02	31.07	31.07[b]
Relative energy	0.00	0.00	0.00	0.00	0.00
Relative energy+ZPVE	0.00	0.00	0.00	0.00	0.00
TZ2P(f,d)	40.423 09	40.634 90	40.648 98	40.644 66[c]	40.651 31[d]
ZPVE	31.20	31.02	31.02	31.07[e]	31.07[e]
Relative energy	0.00	0.00	0.00	0.00	0.00
Relative energy+ZPVE	0.00	0.00	0.00	0.00	0.00

[a] ZPVE from the CCSD/TZ2P level.

[b] ZPVE from the CCSD/TZ2P+f level.

[c] Single point at the CCSD/TZ2P+f optimized geometry.

[d] Single point at the CCSD(T)/TZ2P+f optimized geometry.

[e] ZPVE from the CCSD/TZ2P+f level.

tesian and internal coordinate gradients were always $< 10^{-6}$ atomic units. At the SCF level of theory, harmonic vibrational frequencies were obtained from analytic second derivative methods[17] whereas at correlated levels of theory they were determined by finite central differences of analytic gradients. SCF level zero-point vibrational energies (ZPVE) and vibrational frequencies were scaled by a factor of 0.91 to account for anharmonicity and electron correlation.[18] At the CISD and CCSD levels, the scaling factor was 0.95 to correct primarily for anharmonicity.[19] The configurations in the CI expansion included single and double substitutions with respect to the Hartree–Fock reference determinant (CISD). In the CISD, CCSD, and CCSD(T) energy calculations the core orbitals were kept frozen. The effect of unlinked quadruple excitations on the CISD energies was estimated by incorporating the Davidson correction,[20] and the corresponding energies are denoted CISD+Q.

The smallest basis set employed was the Huzinaga–Dunning triple zeta basis set[21]—designated C(10s6p/5s3p) and H(5s/3s)—with two sets of polarization functions (TZ2P) on all the nuclei. The polarization function exponents for orbitals of $l = l_v + 1$ (where l_v represents the l angular momentum value for the outermost valence shell) were $\alpha_p(\mathrm{H}) = 1.50$, 0.375 and $\alpha_d(\mathrm{C}) = 1.50$, 0.375. The exponents for the $l_v + 2$ functions were $\alpha_d(\mathrm{H}) = 1.00$ and $\alpha_f(\mathrm{C}) = 0.80$. The C(10$s6p2d1f$/5$s3p2d1f$) and H(5$s2p$/3$s2p$) basis set will be referred to as TZ2P+f, whereas TZ2P(f,d) corresponds to a C(10s6p2d1f/5s3p2d1f) and H(5s2p1d/3s2p1d) basis.

The d functions in the augmented basis sets were the six-component spherical harmonic functions, and the f functions in the TZ2P+f and TZ2P(f,d) calculations were the ten-component spherical harmonics.

III. RESULTS AND DISCUSSION

A. Energies

The previously reported[12] approximate energy equivalence [$E_{\mathrm{rel}}(3) = 0.02$ kcal mol^{-1}] of 1 and 3 at the QCISD(T)/cc-pVTZ//MP2(fu)/6-311++G(2df,2pd) level of theory, including the ZPVE from the frequencies at the MP2(fu)/6-31G** level, was confirmed by our studies at even higher levels of theory. In going from the SCF/TZ2P to the CCSD(T)/TZ2P(f,d) levels, the relative energy of 3 decreases from 2.39 to -0.20 kcal mol^{-1}. Obviously, the large imaginary frequency of 3 of, e.g., 747 i at the CCSD/TZ2P+f level, is a major contributor to the rather large differences in the zero-point vibrational energies of 2 vs 3. Even without inclusion of the zero-point vibrational energy correction, the relative energy difference is only 0.9 kcal mol^{-1} our highest level. Our detailed results are summarized in Tables I, II, and III. Group theoretical arguments imply that 240 nearly degenerate minima exist for CH_5^+, if one considers 1, 2, and 3 to be very similar in energy.[22] These minima also may interchange through tunneling.

The energies obtained with the fully optimized geometries at the TZ2P(f,d)/CCSD level do not differ(within 10^{-6} a.u.) from the TZ2P(f,d)/CCSD single point energies on the TZ2P+f optimized geometries. Hence, optimization with even larger basis sets should not alter the energies of the CH_5^+ isomers to any significant extent. The same argument applies to the zero-point vibrational energies, which differ by at most 0.20 kcal mol^{-1} at all levels of theory.

B. Geometries

Although the energies are not very different at the correlated optimization levels, the geometries of the H–H moieties do change significantly (Tables IV, V, and VI). While the C–H bond lengths do not vary by more than 0.005 Å from CISD to CCSD(T), the H–H distances in 1 and 2 increase by over 0.02 Å from the CISD/TZ2P to the CCSD(T)/TZ2P+f level. This is another illustration that correlated methods tend to favor nonclassically bound structures, i.e., CH_3^+–H_2, with extensions of the basis set.[8]

TABLE II. Absolute (in a.u.) and relative energies (in kcal mol^{-1}) of CH_5^+, C_s(II) (2), at different levels of theory.

	SCF	CISD	CISD(+*Q*)	CCSD	CCSD(T)
TZ2P	40.421 87	40.616 55	40.629 21	40.625 38	40.631 08
ZPVE	31.10	31.26	31.26	30.95	30.95[a]
Relative energy	0.04	0.01	0.00	0.00	0.00
Relative energy+ZPVE	−0.12	0.08	0.07	0.08	0.08
TZ2P+*f*	40.422 54	40.628 91	40.642 58	40.638 40	40.644 76
ZPVE	31.07	31.11	31.11	30.97	30.97[b]
Relative energy	1.29	0.05	0.04	0.04	0.05
Relative energy+ZPVE	1.13	0.14	0.13	−0.06	−0.05
TZ2P(*f*,*d*)	40.423 02	40.634 77	40.648 84	40.644 54[c]	40.651 17[d]
ZPVE	31.03	31.11	31.11	30.97[e]	30.97[e]
Relative energy	0.04	0.08	0.09	0.08	0.09
Relative energy+ZPVE	−0.13	0.17	0.18	−0.02	−0.01

[a] ZPVE from the CCSD/TZ2P level.

[b] ZPVE from the CCSD/TZ2P+*f* level.

[c] Single point at the CCSD/TZ2P+*f* optimized geometry.

[d] Single point at the CCSD(T)/TZ2P+*f* optimized geometry.

[e] ZPVE from the CCSD/TZ2P+*f* level.

TABLE III. Absolute (in a.u.) and relative energies (in kcal mol^{-1}) of CH_5^+, C_{2v} (3), at different levels of theory.

	SCF	CISD	CISD(+*Q*)	CCSD	CCSD(T)
TZ2P	40.416 38	40.613 96	40.626 92	40.622 96	40.629 00
ZPVE	30.17	30.18	30.18	29.88	29.88[a]
Relative energy	3.48	1.64	1.44	1.51	1.30
Relative energy+ZPVE	2.39	0.63	0.33	0.56	0.31
TZ2P+*f*	40.416 94	40.626 62	40.640 62	40.636 31	40.643 04
ZPVE	30.13	30.11	30.11	29.97	29.97[b]
Relative energy	3.55	1.49	1.27	1.35	1.13
Relative energy+ZPVE	2.45	0.58	0.36	0.25	0.03
TZ2P(*f*,*d*)	40.417 65	40.632 89	40.647 30	40.642 86[c]	40.649 87[d]
ZPVE	30.13	30.11	30.11	29.97[e]	29.97[e]
Relative energy	3.41	1.26	1.05	1.13	0.90
Relative energy+ZPVE	2.34	0.35	0.14	0.03	0.20

[a] ZPVE from the CCSD/TZ2P level.

[b] ZPVE from the CCSD/TZ2P+*f* level.

[c] Single point at the CCSD/TZ2P+*f* optimized geometry.

[d] Single point at the CCSD(T)/TZ2P+*f* optimized geometry.

[e] ZPVE from the CCSD/TZ2P+*f* level.

TABLE IV. Geometrical parameters of CH_5^+, C_s(I) (1) at various levels of theory.

SCF			CISD			CCSD		CCSD(T)		
TZ2P	TZ2P+*f*	TZ2P(*f*,*d*)	TZ2P	TZ2P+*f*	TZ2P(*f*,*d*)	TZ2P	TZ2P+*f*	TZ2P	TZ2P+*f*	Parameter
1.090	1.090	1.090	1.099	1.101	1.101	1.101	1.104	1.104	1.106	$C–H_a$
1.230	1.223	1.232	1.200	1.199	1.197	1.202	1.200	1.200	1.198	$C–H_b$
1.230	1.232	1.231	1.200	1.199	1.197	1.201	1.199	1.200	1.197	$C–H_c$
1.078	1.078	1.078	1.082	1.083	1.083	1.085	1.086	1.086	1.088	$C–H_d$
0.872	0.870	0.872	0.921	0.927	0.932	0.927	0.934	0.936	0.945	$H_b–H_c$

TABLE V. Geometrical parameters of CH_5^+, C_s(II) (2) at various levels of theory.

SCF			CISD			CCSD		CCSD(T)		
TZ2P	TZ2P+*f*	TZ2P(*f*,*d*)	TZ2P	TZ2P+*f*	TZ2P(*f*,*d*)	TZ2P	TZ2P+*f*	TZ2P	TZ2P+*f*	Parameter
1.075	1.075	1.075	1.078	1.080	1.080	1.081	1.083	1.082	1.084	$C–H_a$
1.232	1.234	1.233	1.202	1.201	1.201	1.202	1.201	1.201	1.199	$C–H_b$
1.085	1.085	1.085	1.092	1.094	1.201	1.095	1.096	1.096	1.098	$C–H_c$
0.870	0.869	0.870	0.918	0.923	0.923	0.924	0.929	0.933	0.940	$H_b–H_c$

TABLE VI. Geometrical parameters of CH_5^+, C_{2v} (3) at various levels of theory.

SCF			CISD			CCSD		CCSD(T)		
TZ2P	TZ2P+*f*	TZ2P(*f*,*d*)	TZ2P	TZ2P+*f*	TZ2P(*f*,*d*)	TZ2P	TZ2P+*f*	TZ2P	TZ2P+*f*	Parameter
1.159	1.159	1.159	1.157	1.158	1.158	1.159	1.161	1.161	1.162	$C–H_a$
1.135	1.136	1.136	1.135	1.137	1.136	1.137	1.139	1.139	1.140	$C–H_b$
1.076	1.077	1.077	1.081	1.083	1.082	1.083	1.085	1.085	1.087	$C–H_c$

TABLE VII. Vibrational frequencies (cm^{-1}) of CH_5^+, C_s(I) (1) at different levels of theory (SCF frequencies scaled by 0.91; correlated frequencies scaled by 0.95).

Assignment	TZ2P SCF	TZ2P+*f* SCF	TZ2P CISD	TZ2P+*f* CISD	TZ2P CCSD	TZ2P+*f* CCSD
Asymmetric CH_3 stretch (A'')	3062.7	3055.0	3108.1	3107.1	3080.7	3079.0
Symmetric CH_3 stretch (A')	2991.5	2985.9	3024.2	3021.3	2996.1	2992.6
Symmetric CH_3 breath (A')	2923.4	2924.9	2922.5	2920.8	2892.8	2890.5
H_2 stretch (A')	2773.9	2783.9	2667.1	2666.6	2633.3	2632.5
H_2 rock (A')	2103.9	2103.6	2280.3	2307.5	2266.1	2295.0
H_2 center-of-mass motion (A')	1513.6	1511.9	1560.6	1563.2	1545.7	1547.2
Asymmetric CH_3 bend (A'')	1450.9	1444.7	1447.5	1439.9	1434.6	1426.8
CH_3 rock/bend (A')	1436.6	1431.5	1422.1	1414.7	1408.1	1400.5
CH_3 bend/rock (A')	1257.9	1255.1	1253.8	1251.6	1238.8	1236.0
Asymmetric CH_3 rock (A'')	1248.6	1243.4	1239.1	1244.8	1228.1	1234.4
CH_3 bend/rock (A')	967.9	969.4	886.6	874.5	870.0	855.7
Torsional twist (A'')	137.8	137.7	12.4	147.0	45.5*i*	144.9

TABLE VIII. Vibrational frequencies (cm^{-1}) of CH_5^+, C_s(II) (2) at different levels of theory (SCF frequencies scaled by 0.91; correlated frequencies scaled by 0.95).

Assignment	TZ2P SCF	TZ2P+*f* SCF	TZ2P CISD	TZ2P+*f* CISD	TZ2P CCSD	TZ2P+*f* CCSD
CH_3 symmetric stretch (A')	3068.6	3067.0	3116.0	3113.5	3088.2	3085.2
Asymmetric CH_3 stretch (A'')	2978.1	2972.7	2999.2	2997.5	2970.7	2968.3
Symmetric CH_3 breath (A')	2930.3	2931.4	2943.3	2942.7	2914.5	2913.6
H_2 stretch (A')	2790.8	2800.8	2681.9	2684.5	2647.9	2649.8
H_2 rock (A'')	2096.3	2095.9	2275.5	2296.7	2261.8	2284.3
CH_3 bend (A')	1581.5	1579.1	1572.0	1575.9	1558.2	1561.1
CH_3 bend/rock (A')	1450.4	1444.5	1447.8	1440.5	1434.4	1427.0
Asymmetric HCH bend (A'')	1440.4	1435.1	1426.5	1420.3	1412.8	1406.4
CH_3 bend/rock (A')	1348.3	1344.2	1291.1	1287.4	1277.8	1273.9
Asymmetric CH_3 rock (A'')	1150.0	1146.5	1113.6	1117.3	1101.4	1105.4
CH_3 rock/bend (A')	1092.6	1094.8	1002.6	1001.0	985.4	982.5
Torsional twist (A'')	134.2*i*	134.2*i*	65.9*i*	139.6*i*	53.0*i*	138.0*i*

TABLE IX. Vibrational frequencies (cm^{-1}) of CH_5^+, C_{2v} (3) at different levels of theory (SCF frequencies scaled by 0.91; correlated frequencies scaled by 0.95).

Assignment	TZ2P SCF	TZ2P+*f* SCF	TZ2P CISD	TZ2P+*f* CISD	TZ2P CCSD	TZ2P+*f* CCSD
Asymmetric $CH_2(c)$ stretch (B_1)	3078.4	3070.9	3124.6	3123.1	3096.1	3094.4
Symmetric $CH_2(c)$ stretch (A_1)	2971.1	2965.6	3017.5	3015.7	2989.5	2987.4
Asymmetric $CH_2(b)$ stretch (B_2)	2683.3	2680.9	2743.0	2756.0	2717.9	2731.5
Symmetric $CH_2(b)$ stretch (A_1)	2547.1	2545.2	2594.1	2608.3	2568.8	2583.9
$CH(a)$ stretch (A_1)	2472.9	2477.1	2535.0	2551.5	2512.9	2529.9
$H_2(b)$ vs $H_2(c)$ twist (A_2)	1428.7	1420.9	1425.8	1418.4	1413.5	1406.1
Symmetric $CH_2(c)$ bend (A_1)	1414.8	1411.2	1397.6	1391.0	1383.8	1376.7
$H_2(c)$ out-of-plane (B_2)	1347.2	1346.1	1343.6	1345.3	1332.2	1334.2
CH_3 out-of-plane (B_1)	1272.5	1271.9	1255.5	1262.0	1244.1	1251.2
Symmetric $CH_2(b)$ bend (A_1)	1268.8	1260.8	1201.8	1198.9	1181.4	1178.2
Wagging $CH_2(b)$ and $CH_2(c)$ (B_1)	617.7	622.7	480.2	505.2	461.2	487.7
$CH(c)$ out-of-plane (B_2)	962.3*i*	966.7*i*	789.5*i*	772.3*i*	767.7*i*	747.1*i*

C. Vibrational frequencies

The trends in the vibrational frequencies from the SCF to the correlated levels (Tables VII, VIII, and IX) also reflect the increased stabilization of such species due to correlation. The most direct measure is the reaction $CH_3^+ + H_2 \rightarrow CH_5^+$, where the reaction enthalpy only agrees with experiment[11] at correlated levels.[8,10,12] The hydrogen stretching frequency for the H_2 subunit of, e.g., 1 decreases from 2774 cm^{-1} at SCF/TZ2P to 2633 cm^{-1} at the CCSD/TZ2P+f level of theory, indicating a H–H bond weakening of 0.4 kcal mol^{-1}.

The "floppiness" of CH_5^+ with respect to hydrogen scrambling is revealed by the small values for the lowest vibrational frequencies for 1 and 2 at all levels of theory. While 2 is the transition state for the internal rotation of the H_2 moiety, leading to the exchange of those two hydrogens, the C_{2v} transition structure 3 serves to interconvert these H's with the remaining hydrogens. The very flat potential energy surface makes the experimental determination and interpretation of the vibrational spectrum of CH_5^+ extremely difficult, if not impossible.

The inclusion of carbon f-functions changes the values for the lowest frequencies of 1 and 2 at the correlated levels appreciably. Apparently, the f-functions serve as important polarization functions at the correlated levels of theory, and are necessary for the proper balance between basis set and theoretical method.[23] The addition of d-functions on the hydrogen atoms did not influence the vibrational frequencies significantly, perhaps in part due to the larger $\alpha_d(H)$ exponent $[\alpha_f(C)=0.80$ and $\alpha_d(H)=1.00]$. The variation in frequency for the torsional twist of the H_2 subunit of 1 shows this effect drastically; at the CCSD/TZ2P level, 1 even has a small imaginary vibrational frequency. We confirmed the correctness of our method for determining the vibrational frequencies by using a different set of coordinates to exclude a systematic error in the method employed. The deviations were in the range of 0.1 cm^{-1}. However, it is known that small errors do arise in the numerical procedures, and they are of greater relative importance for small vibrational frequencies.

IV. CONCLUSIONS

The usual representation of CH_5^+, $C_s(1)$ with three center–two electron bonding, is misleading. In fact, CH_5^+ is a highly fluxional molecule without a definite structure. The latest gas phase experiments showing very rapid H–D scrambling,[24] may be reinterpreted on this basis. All five C–H bonds are effectively equivalent and exchange dynamically very rapidly.

Rather than serving as the nonclassical carbocation prototype, CH_5^+ is unique.

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