Structures and vibrational frequencies in the full configuration interaction limit: Predictions for four electronic states of methylene using a triple-zeta plus double polarization (TZ2P) basis

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Benchmark energies, geometries, dipole moments, and harmonic vibrational frequencies are determined for four states of methylene (CH_2) by solving the electronic Schrödinger equation exactly for a triple-ζ plus double polarization (TZ2P) basis with the restrictions that the core orbital remains doubly occupied and the highest-lying virtual orbital is deleted. Approximate models of electron correlation are evaluated based on their ability to match the exact, full configuration interaction results. Predictions from configuration interaction with all single, double, triple, and quadruple substitutions (CISDTQ) and coupled-cluster including singles, doubles, and triples (CCSDT) are virtually identical to the full CI results for all but the $\tilde{c}\ ^1A_1$ state, which is poorly described by a single-configuration reference. In agreement with previous work, the $\tilde{c}$ state remains slightly bent at the TZ2P full CI level of theory, with a bond angle of 170.1° and a barrier to linearity of only 25 cm^{-1}. © *1998 American Institute of Physics.* [S0021-9606(98)02103-5]

I. INTRODUCTION

In principle, exact solutions to the electronic Schrödinger equation can be obtained by a configuration interaction (CI) procedure which includes all configuration state functions (CSFs, $\hat{S}^2$-adapted combinations of Slater determinants) that can be formed from a complete set of orbitals. However, as a truly complete set of orbitals will be infinite, this procedure is of course impossible to implement, and it becomes necessary to truncate the orbital basis set; typically, only two or three basis functions are used to describe each atomic orbital (''double-ζ'' or ''triple-ζ'' basis sets). A CI procedure including all CSFs which can be formed for a fixed orbital basis is designated ''full CI.'' However, since the number of CSFs has a factorial dependence on the number of electrons and orbitals, it is rarely possible to solve the full CI eigenvalue equation; instead, one must also truncate the configuration space.

Approximate models of electron correlation can be evaluated according to their ability to predict results approaching the full CI limits for a fixed orbital basis set. The 1984 vectorized full CI program of Knowles and Handy[1] enabled Bauschlicher, Taylor, Langhoff, and others to perform a series of benchmark full CI computations on small molecules in the late 1980's.[2] These studies typically employed double-ζ plus polarization (DZP) basis sets, and the CI spaces spanned tens of millions of determinants. More recent full CI algorithms, which follow Olsen *et al.*[3] in sacrificing some degree of vectorization for reduced operation counts,[3–5] have allowed for CI spaces including up to one billion determinants.[6,7]

Due to their extreme computational requirements, full CI benchmark studies are generally limited to single-point energy calculations at a fixed geometry. Nevertheless, researchers have obtained exact full CI equilibrium geometries for a few polyatomic systems with a DZP basis: the linear transition state for the reaction $F+H_2 \rightarrow HF+H$;[8] the systems H_6, H_7^+ and $H_5^+ \cdot He$;[9,10] the $\tilde{X}\ ^2B_1$ and $\tilde{A}\ ^2A_1$ states of NH_2;[11] BH_3;[11,12] H_5^+;[13] and the four lowest-lying states of methylene.[11,14] For the latter three molecules, full CI dipole moments and harmonic vibrational frequencies were reported at the full CI equilibrium geometries.[12–14] Other studies of small molecules using highly accurate treatments of electron correlation (but short of full CI) in conjunction with a DZP basis have been reported by Lee *et al.*,[15] Scuseria *et al.*,[16,17] and Wulfov.[18]

Benchmark studies of methylene[11,14] clearly demonstrate that even full CI does not achieve perfect agreement with experiment when used in conjunction with a small orbital basis set: full CI predictions for the singlet-triplet energy gap[11,14,19] are at least 2.5 kcal mol^{-1} above the best (nonrelativistic, Born-Oppenheimer) experimental estimate[20–22] of 9.37 kcal mol^{-1}. A complementary approach to benchmarking is to expand the single-particle basis set for a fixed method of electron correlation. The second-order CI[23] (SOCI) method and multi-reference CI (MRCI) wavefunctions of similar quality are useful in such studies as they are nearly of full CI quality[2] at a substantially reduced computational cost. When used with very large single-particle basis sets, these methods give very good agreement with experiment.[2] Several workers have presented benchmark predictions for the spectroscopic constants of diatomics using these MRCI methods in conjunction with sequences of single-particle basis sets which systematically approach completeness. Bauschlicher, Partridge, Langhoff, Taylor, Almlöf, and others have carried out these studies[24–30] using atomic natural orbital (ANO) basis sets,[31] while Dunning and co-workers[32–38] have employed the correlation consistent ba-

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TABLE I. Equilibrium geometry, dipole moment and vibrational frequencies for the $\tilde{X}\ ^3B_1$ state of methylene.[a,b]

Method	Reference	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$
DZP CISD[c]	14	1.0853	131.79	0.254	3193	1167	3407
DZP CCSD(T)[c]	14	1.0875	132.15		3166	1146	3383
DZP CISDTQ[c,d]	14	1.0877	132.16	0.256	3162	1145	3380
DZP Full CI[c,e]	14	1.0878	132.16	0.256	3162	1144	3379
TZ2P SCF	This work	1.0693	129.49	0.229	3271	1299	3480
TZ2P CISD[f]	This work	1.0746	132.80	0.237	3172	1155	3393
TZ2P CCSD[f]	This work	1.0760	133.20		3154	1136	3375
TZ2P CCSD(T)[f]	This work	1.0772	133.28		3140	1131	3362
TZ2P CISDTQ[f]	This work	1.0774	133.29	0.237	3135	1127	3358
TZ2P Full CI[f]	This work	1.0775	133.29	0.237	3134	1127	3358
TZ3P (2 f,2d)+2diff CISD[f]	70	1.0747	132.94	0.236	3174	1134	3399
MORBID fit to $5s4p3d2f1g/3s2p1d$ ANO MRCI[c,g]	84	1.0794	133.58		3015	972	3236
est. complete basis CMRCI[h]	37	1.0749	133.72				
est. complete basis RCCSD(T)[h]	37	1.0750	133.82				
MORBID fit to experiment[i]	20	1.0753	133.93		2992		3213
experiment (IR) est.[j]	67						3190
experiment (diode laser)	78					963.1	

[a]Bond lengths in angstroms, bond angles in degrees, dipole moments in atomic units, and vibrational frequencies in cm^{-1}.
[b]Unless otherwise noted, theoretical vibrational frequencies are determined in the harmonic approximation (ω), whereas experimentally derived frequencies are fundamentals (ν) which include anharmonicity.
[c]One frozen core orbital.
[d]Lee *et al.* (Ref. 15) also report DZP CISDTQ results, using a slightly different DZP basis.
[e]Anglada and Bofill (Ref. 11) also report DZP full CI geometries using a slightly different basis.
[f]One frozen core and one deleted virtual orbital.
[g]Predictions using the Morse oscillator-rigid bender internal dynamics (MORBID) Hamiltonian fit to *ab initio* data. Frequencies are fundamentals.
[h]Based on all-electron contracted MRCI or RCCSD(T) calculations employing the *cc-pCVXZ* basis sets up to $X=5$ (quintuple-ζ).
[i]Predictions using the MORBID Hamiltonian fit to experimental data.
[j]Estimate from perturbations in the IR spectrum of the $\tilde{a}$ state.

sis sets.[39,37] Woon and Dunning[37] have also used internally contracted multireference CI (CMRCI)[40] and a sequence of correlation consistent polarized valence basis sets to examine the singlet-triplet splitting in methylene.

Unfortunately, it is usually impossible to systematically increase the basis set size in conjunction with the full CI method due to the factorial growth of the computation time. This motivates the present study, in which we examine the effect on the full CI geometries, dipole moments, and harmonic vibrational frequencies for the $\tilde{X}\ ^3B_1$, $\tilde{a}\ ^1A_1$, $\tilde{b}\ ^1B_1$, and $\tilde{c}\ ^1A_1$ states of methylene when the relatively small DZP basis set is replaced by the more flexible TZ2P basis set. In addition, we consider whether various models of electron correlation become better or worse approximations to the full CI in the larger basis set. Of particular interest is the $\tilde{c}\ ^1A_1$ state, which is theoretically challenging because it is the second root of its spatial and spin symmetry and is not well described by a single-determinant reference. Hence, our benchmark results for this state in particular may be valuable for calibrating various excited-state methods. Furthermore, it has not been definitively established whether the equilibrium geometry of the $\tilde{c}$ state is linear or slightly bent; Bauschlicher has recently shown[41] that the bending potential is extremely flat. The full CI results presented here shed some additional light on this issue.

II. THEORETICAL APPROACH

The ground electronic state of methylene, $\tilde{X}\ ^3B_1$, may be qualitatively described by the electronic configuration

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1). \tag{1}$$

Promotion of an electron from the $1b_1$ to the $3a_1$ orbital gives the closed-shell configuration

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2, \tag{2}$$

which qualitatively describes the lowest-lying electronic excited state, $\tilde{a}\ ^1A_1$. However, this state has a second important configuration which becomes equally important at linear geometries; this can be accounted for by employing the two-configuration wave function

$$C_1(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2 + C_2(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2, \tag{3}$$

where the two CI coefficients C_1 and C_2 have opposite signs and $|C_1|\geqslant|C_2|$. The third electronic state ($\tilde{b}\ ^1B_1$) shares the same spatial orbital configuration (1) as the ground state, but the two open-shell electrons are singlet-coupled rather than triplet-coupled. The fourth electronic state considered here ($\tilde{c}\ ^1A_1$) is represented by the same two configurations as the $\tilde{a}$ state except that the two CI coefficients have the same sign and $|C_1|\leqslant|C_2|$.

TABLE II. Equilibrium geometry, dipole moment and vibrational frequencies for the $\tilde{a}\ ^1A_1$ state of methylene.[a,b]

Method	Reference	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$
DZP TCSCF-CISD[c]	14	1.1168	101.50	0.713	2966	1417	3046
DZP CCSD(T)[c]	14	1.1199	101.28	0.714	2930	1404	3014
DZP CCSDT[c]	14	1.1199	101.42		2929	1397	3014
DZP CISDTQ[c,d]	14	1.1198	101.43	0.710	2930	1397	3015
DZP Full CI[c,e]	14	1.1199	101.44	0.708	2928	1396	3013
TZ2P SCF	This work	1.0945	103.73	0.776	3105	1503	3169
TZ2P TCSCF	This work	1.0967	102.99	0.686	3085	1527	3140
TZ2P CISD[f]	This work	1.1122	101.80	0.707	2949	1441	3016
TZ2P TCSCF-CISD[f]	This work	1.1051	102.05	0.679	2944	1429	3013
TZ2P CCSD[f]	This work	1.1074	101.73	0.692	2919	1428	2988
TZ2P CCSD(T)[f]	This work	1.1089	101.72	0.679	2899	1414	2971
TZ2P CCSDT[f]	This work	1.1088	101.86		2899	1406	2972
TZ2P CISDTQ[f]	This work	1.1087	101.88	0.674	2900	1405	2973
TZ2P Full CI[f]	This work	1.1089	101.89	0.673	2899	1404	2971
TZ3P(2 f,2d)+2diff CISD[f]	70	1.1049	102.00	0.691	2968	1434	3036
TZ3P(2 f,2d)+2diff TCSCF-CISD[f]	70	1.1047	102.30	0.665	2965	1420	3035
MORBID fit to $5s4p3d2f1g/3s2p1d$ ANO MRCI[c,g]	84	1.1112	101.95		2787	1351	2839
Renner-Teller model fit to $7s5p3d2f1g/4s3p1d$ CMRCI[c,h]	79				2808	1356	2863
est. complete basis CMRCI[i]	37	1.1061	102.23				
est. complete basis RCCSD(T)[i]	37	1.1058	102.23				
experiment (IR)	67	1.107	102.4				
experiment (IR)	76, 77				2805.9	1352.6	2864.5
experiment (dispersed fluorescence)[j]	85				2846	1371.3	

[a]Bond lengths in angstroms, bond angles in degrees, dipole moments in atomic units, and vibrational frequencies in cm^{-1}.
[b]Unless otherwise noted, theoretical vibrational frequencies are determined in the harmonic approximation (ω), whereas experimentally derived frequencies are fundamentals (ν) which include anharmonicity.
[c]One frozen core orbital.
[d]Lee *et al.* (Ref. 15) also report DZP CISDTQ results, using a slightly different DZP basis.
[e]Anglada and Bofill (Ref. 11) also report DZP full CI geometries using a slightly different basis.
[f]One frozen core and one deleted virtual orbital.
[g]Predictions using the Morse oscillator-rigid bender internal dynamics (MORBID) Hamiltonian fit to *ab initio* data. Frequencies are fundamentals.
[h]Fundamental frequencies.
[i]Based on all-electron contracted MRCI or RCCSD(T) calculations employing the cc-$pCVXZ$ basis sets up to $X=5$ (quintuple-ζ).
[j]Harmonic frequencies.

While the first three electronic states ($\tilde{X}\ ^1A_1, \tilde{a}\ ^1A_1, \tilde{b}\ ^1B_1$) may be described in zeroth order by restricted Hartree-Fock (RHF) or restricted open-shell Hartree-Fock (ROHF) wave functions, a minimal description of the $\tilde{c}\ ^1A_1$ state requires a two-configuration self-consistent-field (TCSCF) treatment. Using these reference wave functions, the effects of electron correlation were treated using the configuration interaction and coupled-cluster methods. The least accurate models used were configuration interaction with single and double substitutions (CISD) and, where possible, coupled-cluster singles and doubles (CCSD)[42–45] (our ground state coupled-cluster program, like others, is incapable of describing the $\tilde{b}\ ^1B_1$ open-shell singlet or of using multi-configurational references). For the CISD procedures based on two-configuration references (TCSCF-CISD), the CI space included all single and double substitutions for each reference configuration. The $\tilde{c}\ ^1A_1$ state is represented by the second root of the TCSCF or CI secular equations.

Several more complete treatments of electron correlation were also considered. The additional effects of connected triple excitations on the CCSD model were estimated perturbatively according to the CCSD(T) method,[46–48] and for the $\tilde{a}\ ^1A_1$ state, the connected triples are also fully included by the CCSDT model.[16,49,50] We have further employed configuration interaction wave functions incorporating all singles, doubles, triples, and quadruples (CISDTQ). For these wave functions, only a single-configuration reference was used for each state. This is already a good approximation for the $\tilde{a}\ ^1A_1$ state and would seem justified for the $\tilde{c}\ ^1A_1$ state also because of the decreasing importance of the zeroth-order wave function in a correlation procedure as complete as CISDTQ. For the $\tilde{a}\ ^1A_1$ state, the SCF reference wave function is based on the leading configuration, $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2$. For the $\tilde{c}$ state, the configuration $(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2$ is slightly more important; we therefore considered CISDTQ wave functions based on *each* of these configurations, denoted CISDTQ I and II, respectively. In C_{2v} symmetry, the number of CSFs for the CISDTQ wave functions for the $\tilde{X}$, $\tilde{a}$, $\tilde{b}$, and $\tilde{c}$ states were, respectively, 752 367, 450 449, 664 437, and 450 449 (ref I) or 439 695 (ref II). For the high-spin open-shell $\tilde{X}\ ^3B_1$ ground state, spin flips are counted as excitations. For CISD, this restricts the CI space to the first-order interacting space;[51–53] for CISDTQ, this reduces the number of CSFs by 380 925.

TABLE III. Equilibrium geometry, dipole moment and vibrational frequencies for the $\tilde{b}\ ^1B_1$ state of methylene.[a,b]

Method	Reference	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$
DZP CISD[c]	14	1.0817	141.35	0.316	3199	1011	3478
DZP CISDTQ[c]	14	1.0845	140.97	0.319	3163	1012	3444
DZP Full CI[c,d]	14	1.0845	140.97	0.319	3163	1011	3444
TZ2P SCF	This work	1.0644	141.30	0.268	3301	1081	3579
TZ2P CISD[e]	This work	1.0716	141.74	0.277	3178	1016	3455
TZ2P CISDTQ[e]	This work	1.0747	141.55	0.277	3137	1006	3415
TZ2P Full CI[e]	This work	1.0748	141.56	0.277	3136	1006	3414
TZ3P(2 f,2d)+2diff CISD[e]	70	1.0713	142.94	0.263	3184	967	3470
experiment (vis. abs.)[f]	68	1.05	140				
Renner model fit to experiment[f]	69	1.086	139.3				

[a]Bond lengths in angstroms, bond angles in degrees, dipole moments in atomic units, and vibrational frequencies in cm^{-1}.
[b]Theoretical vibrational frequencies are determined in the harmonic approximation.
[c]One frozen core orbital.
[d]Anglada and Bofill (Ref. 11) also report DZP full CI geometries using a slightly different basis.
[e]One frozen core and one deleted virtual orbital.
[f]Zero-point geometry (r_0, θ_0).

Exact solutions of the electronic Schrödinger equation within the TZ2P basis, subject to one frozen core orbital and one deleted virtual orbital, were obtained using the full CI procedure, where the CI space includes all possible configuration state functions (CSFs) of the proper spatial and spin symmetry. Although the loop-driven graphical unitary group approach (GUGA) CI program[54,55] can be used to obtain these full CI wave functions, we found it more efficient to employ our Slater determinant based program, DETCI.[56,57] For the $\tilde{X}\ ^3B_1$, $\tilde{a}\ ^1A_1$, $\tilde{b}\ ^1B_1$, and $\tilde{c}\ ^1A_1$ states, the full CI wave function in C_{2v} symmetry included 17 770 124, 24 500 738, 24 309 054, and 24 500 738 determinants. For the evaluation of harmonic vibrational frequencies, it was necessary to consider displacements in to C_s symmetry; these full CI wave functions included 48 616 238, 48 998 162, 48 616 238, and 48 998 162 determinants, respectively. In all correlated procedures, the core orbital (carbon $1s$-like) was constrained to remain doubly occupied, and the corresponding virtual orbital was deleted; the TZ2P atomic orbital basis used here was not designed to describe core–core or core-valence correlation effects.

This study employs the standard Huzinaga-Dunning[58,59] triple-ζ basis augmented with two sets of five d-type polarization functions on carbon $[\alpha_d(\mathrm{C})=1.50, 0.375]$ and two sets of p polarization functions on each hydrogen $[\alpha_p(\mathrm{H})=1.50, 0.375]$, denoted TZ2P. The contraction scheme for this basis is $\mathrm{C}(10s6p2d/5s3p2d)$, $\mathrm{H}(5s2p/3s2p)$, and it consists of 42 contracted Gaussian functions. In our previous methylene benchmark study,[14] we employed a smaller DZP basis with only one set of d-type functions on carbon. The orbital exponent used there, $\alpha_d(C)=0.75$, was not optimal for the $\tilde{a}$ and $\tilde{c}$ states, which prefer a more diffuse set of d orbitals;[60] this contributed to the overestimation of the excitation energies of these two states. We expect that the larger TZ2P basis used in the present study should provide a more balanced description of the four electronic states. Theoretical results were obtained using the PSI package of *ab initio* electronic structure programs.[61] Optimized geometries and harmonic vibrational frequencies were obtained using the procedures of Ref. 14.

III. RESULTS AND DISCUSSION

A. Geometries

Geometries, dipole moments, and harmonic vibrational frequencies are presented in Tables I–IV; additional theoretical and experimental data for these four states of methylene have been given in a recent review.[14] From the tables, one can see that the DZP full CI geometries from our previous study[14] are not in especially good agreement with experiment. More complete treatments of electron correlation introduce more antibonding configurations into the wave function, so that the DZP full CI level of theory substantially overestimates bond lengths. The trend for basis sets is just the opposite: larger single-particle basis sets tend to give shorter bond lengths for a fixed correlation method. Systematic studies of small molecules suggest that the SCF and CISD methods provide a good balance for double-ζ quality basis sets,[62] whereas CCSD and CCSD(T) may overestimate bond lengths in this basis[63] and are better paired with a triple-ζ or better basis.[64] Of course, molecules with substantial nondynamical correlation, such as the $\tilde{c}\ ^1A_1$ state of methylene, may require more accurate treatments of electron correlation to balance a given basis set.

The most balanced partner to the full CI method would be an infinite basis, so we generally expect full CI to overestimate bond lengths for any truncated basis, including the present TZ2P basis. Indeed, comparison to experiment for the $\tilde{X}$ and $\tilde{a}$ states (Tables I and II) shows this to be the case. The experimentally-derived[20] equilibrium geometry of the ground state is (1.0753 Å, 133.93°), indicating that the TZ2P full CI method overestimates the bond length by 0.0022 Å and underestimates the bond angle by 0.64°. This is a substantial improvement over the DZP full CI predictions, which overestimate the bond length by 0.0125 Å and underestimate the bond angle by 1.77°. Better agreement with ex-

TABLE IV. Equilibrium geometry, dipole moment and vibrational frequencies for the $\tilde{c}\ ^1A_1$ state of methylene.[a,b]

Method	Reference	r_e	θ_e	μ_e	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$
DZP TCSCF-CISD[c]	14	1.0719	170.00	0.116	3285	663	3630
DZP CISDTQ I[c,d]	14	1.0740	171.49	0.099	3257	578	3605
DZP CISDTQ II[c,d]	14	1.0749	168.16	0.137	3248	788	3594
DZP Full CI[c,e]	14	1.0749	169.68	0.119	3246	695	3593
TZ2P TCSCF	This work	1.0556	176.20	0.041	3381	240	3732
TZ2P TCSCF-CISD[f]	This work	1.0640	170.47	0.099	3249	634	3580
TZ2P CISDTQ I[d,f]	This work	1.0667	172.51	0.077	3214	511	3545
TZ2P CISDTQ II[d,f]	This work	1.0676	168.36	0.118	3204	774	3533
TZ2P Full CI[f]	This work	1.0678	170.08	0.101	3200	666	3531
TZ3P $(2f,2d)+2$diff TCSCF-CISD[f]	70	1.064	171.6	0.081	3254	552	3597

[a]Bond lengths in angstroms, bond angles in degrees, dipole moments in atomic units, and vibrational frequencies in cm^{-1}.
[b]Theoretical vibrational frequencies are determined in the harmonic approximation.
[c]One frozen core orbital.
[d]Roman numeral I (II) signifies that the SCF reference for the $\tilde{c}$ state is the first (second) configuration in eq. 3 (see text).
[e]Anglada and Bofill (Ref. 11) also report DZP full CI geometries using a slightly different basis.
[f]One frozen core and one deleted virtual orbital.

periment is achieved by the complete basis set estimates of Woon and Dunning[37] for the CMRCI[40] and RCCSD(T)[65,66] methods. For the $\tilde{a}$ state, if we use the experimental geometry of Petek *et al.*[67] (1.107 Å, 102.4°), we find that TZ2P full CI overestimates the bond length by 0.002 Å and underestimates the bond angle by 0.5°, representing an improvement of 0.011 Å and 0.5° over the DZP full CI results. The errors in the TZ2P full CI geometries thus appear to be roughly equal for the $\tilde{X}$ and $\tilde{a}$ states. Once again, even better agreement with experiment is obtained by the complete basis set extrapolations of Woon and Dunning.[37]

Replacing the DZP basis with a TZ2P basis causes roughly equal changes in the full CI geometries of the $\tilde{b}$ and $\tilde{c}$ states as it does for the $\tilde{a}$ state: bond lengths decrease by about 0.01 Å, and bond angles increase by about 0.5°. Unfortunately, no experimental data are available for the geometry of the $\tilde{c}$ state, and experimental estimates of the $\tilde{b}$ state geometry are not very precise. The experimental geometry for the $\tilde{b}$ state deduced from visible absorption spectroscopy by Herzberg and Johns[68] is not in particularly good agreement with the Renner-Teller model of Duxbury and Jungen.[69] These geometries are zero-point geometries (r_0,θ_0) and as such are not strictly comparable to the equilibrium geometries (r_e,θ_e) reported here; however, the TZ2P full CI geometry does not appear to be particularly close to either estimate. Given the overestimation of bond lengths by the full CI method, the TZ2P full CI results appear to be in reasonable agreement with the larger basis set CISD geometries of Yamaguchi *et al.*[70]

Tables I–IV also contain theoretical geometries for various approximate models of electron correlation so that one can evaluate their ability to approach the full CI limits in the same basis set. Convergence of the equilibrium bond lengths with respect to improved treatments of electron correlation is very similar to that seen in our previous study using the DZP basis set,[14] and the interested reader is referred to that work for a more detailed analysis. Electronic correlation has a pronounced effect on the HCH bond angle; compared to the SCF method (or TCSCF for the $\tilde{a}$ and $\tilde{c}$ states), CISD (or TCSCF-CISD) changes the bond angle by $+3.31$, -0.94, $+0.44$, and -5.73 degrees for the $\tilde{X}$, $\tilde{a}$, $\tilde{b}$, and $\tilde{c}$ states, respectively. These changes are generally in qualitative but not quantitative agreement with those seen for the DZP basis set.[14] The large change in bond angle for the $\tilde{c}$ state is actually much smaller than that seen with the DZP basis, for which the optimum structure is linear for TCSCF and bent (170°) for TCSCF-CISD.[14] Bauschlicher and Yarkony[71] have previously suggested that the bent structure predicted at the DZP TCSCF-CISD level of theory may be due to artifactual symmetry breaking of the wavefunction. However, all of our TZ2P results support a slightly bent structure, including the TZ2P full CI, which should be virtually immune to symmetry breaking.[72] The TZ2P full CI bond angle is 170.08°, only slightly larger than the DZP full CI prediction[14] of 169.69°. Bauschlicher's most recent study on the $\tilde{c}$ state employs extensive MRCI with large single-particle basis sets; his data support a slightly bent minimum with a very small ($\sim 10\ cm^{-1}$) barrier to linearity.[41] We have determined the barrier at the TZ2P full CI level of theory by optimizing the geometry of the $\tilde{c}$ state with the constraint that the molecule remain linear; this yields a bond length of 1.0668 Å and an energy of $-38.968\ 356$ hartree, making the barrier only $25\ cm^{-1}$.

Compared to CISD (or TCSCF-CISD), the triple and quadruple substitutions in CISDTQ change the bond angle for the $\tilde{X}$, $\tilde{a}$, and $\tilde{b}$ states by about $\pm 0.5°$, which is slightly larger than the comparable changes for the DZP basis. For the $\tilde{c}$ state, triples and quadruples have a much larger effect $(\pm 2°)$ which changes sign depending on which of the two nearly degenerate electron configurations in eq. (3) is used as the reference (see introduction). The effect on the bond angle of quintuples and sextuples in the full CI wave function is remarkably large and nearly cancels the effect of triples and quadruples, giving a final bond angle (170.08°) rather similar to that predicted (170.47°) by the TCSCF-CISD method,

TABLE V. Total energies in hartrees for the four lowest-lying electronic states of methylene.

Method	Reference	$\tilde{X}\ ^3B_1$	$\tilde{a}\ ^1A_1$	$\tilde{b}\ ^1B_1$	$\tilde{c}\ ^1A_1$
DZP Full CI[a,b]	14	-39.046 816	-39.026 635	-38.985 569	-38.942 663
TZ2P SCF	This work	-38.932 879	-38.892 826	-38.868 934	
TZ2P TCSCF	This work		-38.914 802		-38.813 319
TZ2P CISD[c]	This work	-39.059 810	-39.037 949	-39.002 655	
TZ2P TCSCF-CISD[c]	This work		-39.042 236		-38.959 535
TZ2P CISDTQ I[c,d]	This work	-39.066 634	-39.048 735	-39.009 964	-38.967 346
TZ2P CISDTQ II[c,d]	This work				-38.967 527
TZ2P CCSD[c]	This work	-39.063 316	-39.043 794		
TZ2P CCSD(T)[c]	This work	-39.066 184	-39.048 005		
TZ2P CCSDT[c]	This work		-39.048 776		
TZ2P Full CI[c]	This work	-39.066 738	-39.048 984	-39.010 059	-38.968 471
TZ3P(2 f,2d)+2diff SOCI// TZ3P(2 f,2d)+2diff (TC)CISD[c,e,f]	70	-39.080 444	-39.065 406	-39.027 300	-38.985 605
est. complete basis CMRCI[g]	37	-39.141 93	-39.127 28		
est. complete basis RCCSD(T)[g]	37	-39.148 03	-37.132 93		
MORBID fit to 5s4p3d2f1g/3s2p1d ANO MRCI[b]	84	-39.083 084	-39.068 308		
13s10p8d1f/3s2p1d ANO MRCI+Q// TZ2P SOCI[b,f,h]	86	-39.099 050	-39.083 854		

[a]Anglada and Bofill (Ref. 11) also report DZP full CI energies using a slightly different basis.
[b]One frozen core orbital.
[c]One frozen core and one deleted virtual orbital.
[d]Roman numeral I (II) signifies that the SCF reference for the $\tilde{c}$ state is the first (second) configuration in eq. 3 (see text).
[e](TC) designates a two-configuration reference for the $\tilde{a}$ and $\tilde{c}$ states; otherwise a one-configuration reference.
[f]Second order configuration interaction (SOCI) includes all configurations having no more than two electrons in external orbitals (see Ref. 23).
[g]Based on all-electron contracted MRCI or RCCSD(T) calculations employing the cc-$pCVXZ$ basis sets up to $X=5$ (quintuple-ζ). Note that the energies in Ref. 37 are all 2 hartrees too high due to misprints.
[h]$+Q$ denotes the multireference Davidson correction for disconnected quadruple substitutions (see Ref. 87).

which provides a balanced treatment of the two different electron configurations.

B. Dipole moments

Equilibrium dipole moments (μ_e, in atomic units) are presented in Tables I–IV. The $\tilde{c}$ state is nearly linear and thus has the smallest dipole moment ($\sim$0.10 a.u.). The $\tilde{X}\ ^3B_1$ and $\tilde{b}\ ^1B_1$ states have nearly equal dipole moments due to their similar geometries and electron configurations; the theoretical predictions show little variation with correlation method and are 0.24 and 0.28 a.u., respectively, with the TZ2P basis. The $\tilde{a}$ state has the largest dipole moment (0.67 a.u. for TZ2P full CI) because it places an additional electron in the in-plane $3a_1$ orbital. The most accurate dipole moments for these four states are probably the large basis set CISD and TCSCF-CISD predictions of Yamaguchi *et al.*[70]

C. Vibrational frequencies

Theoretical and available experimental vibrational frequencies are presented in Tables I–IV. Our theoretical frequencies are evaluated in the harmonic approximation and are thus not strictly comparable to the experimentally determined fundamental frequencies, which contain anharmonic contributions that typically reduce vibrational frequencies by a few percent. However, in the case of methylene, substantial anharmonicity is expected for the bending modes of the states which are not strongly bent: i.e., the $\tilde{X}$, $\tilde{b}$, and $\tilde{c}$ states. Indeed, the harmonic approximation is not really applicable to the $\tilde{c}$ state, which is quasilinear with a very small barrier to linearity.[41] Nevertheless, the harmonic frequency provides some additional information about the shape of the bending potential. Clabo *et al.*[73] have presented a theoretical investigation of anharmonic effects in the $\tilde{X}$, $\tilde{a}$, and $\tilde{b}$ states of methylene.

The harmonic vibrational frequency predictions for these four states of methylene follow Badger's rule[74,75] that larger frequencies are associated with smaller bond lengths. Thus, the bond lengths are in the order $r_e(\tilde{a}\ ^1A_1)>r_e(\tilde{X}\ ^3B_1)>r_e(\tilde{b}\ ^1B_1)>r_e(\tilde{c}\ ^1A_1)$, whereas the harmonic stretching frequencies ω_1 (symmetric stretch) and ω_3 (antisymmetric stretch) are in the opposite order. A similar trend is often seen for bond angles in which larger bond angles are associated with smaller bending frequencies, and indeed the bond angles for methylene are in the order $\theta_e(\tilde{c}\ ^1A_1)>\theta_e(\tilde{b}\ ^1B_1)>\theta_e(\tilde{X}\ ^3B_1)>\theta_e(\tilde{a}\ ^1A_1)$ while the bending frequencies ω_2 are in the opposite order.

Experimental frequencies are available only for the $\tilde{X}$ and $\tilde{a}$ states. Harmonic vibrational frequency predictions are generally lower with the TZ2P basis than with the DZP basis[14] for the same level of theory, and they appear to be in better agreement with experiment. For the $\tilde{a}$ state, Hartland[85] *et al.* have actually reported experimentally derived *harmonic* frequencies of $\omega_1=2846$ and $\omega_2=1371$ cm^{-1}, and our TZ2P full CI frequencies ($\omega_1=2899$ and $\omega_2=1404$) are

TABLE VI. Relative energies T_e in kcal mol^{-1} for the three lowest-lying electronic excited states of methylene. Zero-point corrected values T_0 are in parentheses.

Method	Reference	$\tilde{a}\ ^1A_1$		$\tilde{b}\ ^1B_1$		$\tilde{c}\ ^1A_1$	
DZP Full CI[a]	14	12.664	(12.167)	38.433	(38.337)	65.357	(65.141)
DZP′ Full CI[a,b]	11	11.965		38.491		65.219	
TZ2P SCF	This work	25.134	(24.744)	40.126	(39.999)		
TZ2P (TC)SCF[c]	This work	11.343	(10.917)			75.025	(74.029)
TZ2P CISD[d]	This work	13.718	(13.269)	35.865	(35.764)		
TZ2P (TC)CISD[c,d]	This work	11.028	(10.551)			62.924	(62.557)
TZ2P CISDTQ I[d,f]	This work	11.232	(10.743)	35.561	(35.473)	62.304	(61.804)
TZ2P CISDTQ II[d,f]	This work					62.191	(62.036)
TZ2P CCSD[d]	This work	12.250	(11.778)				
TZ2P CCSD(T)[d]	This work	11.407	(10.908)				
TZ2P Full CI[d]	This work	11.141	(10.648)	35.567	(35.477)	61.663	(61.346)
TZ3P $(2f,2d)+2$diff SOCI// TZ3P $(2f,2d)+2$diff (TC)CISD[c,d,e]	70	9.436	(9.025)	33.348	(33.224)	59.512	(59.077)
$9s7p2d1f/5s2p$ MBPT4SDTQ//CMRCI	83	11.46					
$9s7p2d1f/5s2p$ CCSDT-1//CMRCI	83	10.10					
est. complete basis CMRCI[g]	37	9.19					
est. complete basis RCCSD(T)[g]	37	9.48					
$5s4p3d2f1g/4s3p2d$ ANO SOCI// TZ2P SOCI[a,e]	24	9.13[h]					
MORBID fit to $5s4p3d2f1g/3s2p1d$ ANO MRCI[a]	84	9.272	(8.909)				
$13s10p8d1f/3s2p1d$ ANO MRCI+Q// TZ2P SOCI[a,e,i,j]	86	9.536[h]					
Best experiment. (non rel., BO)[k]	20–22	9.372	(9.155)				
Renner/SO model fit to experiment.[l]	20 and 81				(32.546)		
Renner/SO MORBID MRCI model[a,l]	20 and 80				(33.804)		

[a]One frozen core orbital.
[b]The prime emphasizes that the DZP′ basis differs from the one used in this work.
[c](TC) designates a two-configuration reference for the $\tilde{a}$ and $\tilde{c}$ states, otherwise a one-configuration reference.
[d]One frozen core and one deleted virtual orbital.
[e]Second order configuration interaction (SOCI) includes all configurations having no more than two electrons in external orbitals (Ref. 23).
[f]Roman numeral I (II) signifies that the SCF reference for the $\tilde{c}$ state is the first (second) configuration in eq. 3 (see text).
[g]Based on all-electron contracted MRCI or RCCSD(T) calculations employing the *cc-pCVXZ* basis sets up to $X=5$ (quintuple-ζ).
[h]The authors' best estimate can be obtained by subtracting a 0.06 kcal mol^{-1} relativistic correction.
[i]Includes estimates of core-valence correlation which increase the splitting by 0.35 kcal mol^{-1}.
[j]$+Q$ denotes the multireference Davidson correction for disconnected quadruple substitutions (see Ref. 87).
[k]This estimate adds to the values of Ref. 20 a relativistic correction of 15 cm^{-1} (Ref. 21) and a Born-Oppenheimer diagonal correction of 40 cm^{-1} (Ref. 22).
[l]Using $T_0(\tilde{a}^1A_1)=3147$ cm^{-1} from Ref. 20.

in good agreement, with errors of about 2%. The TZ2P full CI prediction for the remaining frequency is $\omega_3=2971$ cm^{-1}, which seems to be in satisfactory agreement with the experimental[76,77] fundamental frequency 2864 cm^{-1}.

For the ground electronic state, the TZ2P full CI harmonic frequencies are reasonably close to the experimental fundamental frequencies for the two stretching modes, but for the bending mode the harmonic frequency (1127 cm^{-1}) is much larger than the fundamental[78] (963 cm^{-1}). This is probably due to a large anharmonic contribution to the bending mode. Note that the current TZ2P full CI frequencies appear to be in better agreement with experiment than the TZ3P(2 f,2d)+2diff CISD and TCSCF-CISD results of Yamaguchi *et al.*[70] This may be attributable to the CISD method not providing a sufficiently complete treatment of electron correlation to balance the extensive basis set used in that study.

Although none of the vibrational frequencies for the $\tilde{b}$ or $\tilde{c}$ states have been measured directly, estimates of the bending frequency for the $\tilde{b}$ state can be deduced from some of the rovibrational Hamiltonian models, as explained in Ref. 70. Green *et al.*[79] obtained 1183 cm^{-1}, and the MORBID fit[80] to Green's *ab initio* surface yields a very similar 1182 cm^{-1}. Alternatively, the Renner-Teller/spin-orbit model of Alijah and Duxbury[81] predicts 1257 cm^{-1}. The theoretical harmonic frequencies in Table III are substantially smaller, suggesting that the anharmonic contribution *increases* the fundamental frequency in this case.

For a given basis, more complete treatments of electron correlation tend to decrease the harmonic vibrational frequencies; for the stretching modes, the decreasing frequencies correlate with increased bond lengths. The effects of improved treatments of electron correlation are similar to those found in our previous DZP full CI benchmark study.[14] Note that quintuple and sextuple substitutions strongly affect the bending frequency of the $\tilde{c}$ state, so that the full CI value

falls roughly in between the two CISDTQ predictions and differs from each of them by more than 100 cm^{-1}. For all other vibrational modes, the CISDTQ frequencies are virtually identical to the full CI frequencies.

D. Energetics

Total energies are presented in Table V along with some energies from previous theoretical studies. All energies in the present study were determined at equilibrium geometries, whereas some previous studies have used non-equilibrium geometries; for the latter, we denote a single-point energy computed with method A at a geometry optimized using method B as $A//B$. To obtain the lowest total energy, increasing the basis set size is more effective than improving the description of electron correlation. The lowest energies are those of Woon and Dunning,[37] who give complete basis set estimates for the internally contracted multireference CI (CMRCI)[40] and restricted coupled-cluster [RCCSD(T)][65,66] methods. However, note that Woon and Dunning's energies would be somewhat higher if they had frozen core electrons as in the other studies listed.

More important are the adiabatic relative energies, T_e, which are given in Table VI in kcal mol^{-1}. Excitation energies corrected for zero-point vibrational energy (ZPVE) are denoted T_0 and are given in parentheses. Most studies have focused on the singlet-triplet gap, ΔE ($\tilde{a}\ ^1A_1-\tilde{X}\ ^3B_1$), which is now accurately known but was formerly a subject of dispute.[82] For comparison to theory, we use a nonrelativistic Born-Oppenheimer value of $T_e(T_0)=9.372$ (9.155) kcal mol^{-1}, which is obtained from Jensen and Bunker's fit of experimental data using the MORBID Hamiltonian,[20] $T_e(T_0)=9.215$ (8.998 ± 0.014) kcal mol^{-1}, by adding a relativistic correction[21] of 15 cm^{-1} and a Born-Oppenheimer diagonal correction[22] of 40 cm^{-1}.

An experimentally derived estimate of T_0 ($\tilde{b}\ ^1B_1$) has been presented by Alijah and Duxbury,[81] who fitted a Renner-Teller/spin-orbit model of the first three electronic states to experimental data to obtain energy separations of 3162 cm^{-1} between the $\tilde{X}$ and $\tilde{a}$ states and 8326 cm^{-1} between the $\tilde{a}$ and $\tilde{b}$ states, yielding T_0 ($\tilde{b}\ ^1B_1$) $=11\,398$ cm^{-1} (32.589 kcal mol^{-1}). Alternatively, using Jensen and Bunker's singlet-triplet splitting of 3147 cm^{-1} (8.998 kcal mol^{-1}) together with Alijah and Duxbury's energy gap for the $\tilde{a}$ and $\tilde{b}$ states yields T_0 ($\tilde{b}\ ^1B_1$) $=11\,383$ cm^{-1} (32.546 kcal mol^{-1}). Reliable estimates of the energy difference between the $\tilde{a}$ and $\tilde{b}$ states are also available from rovibrational models fit to MRCI potential energy surfaces provided by Green *et al.*[79] Fitting this data to a Renner-Teller/spin-orbit MORBID model, Jensen *et al.*[80] found an energy difference of 8676 cm^{-1}, which, when combined with the singlet-triplet splitting of Jensen and Bunker[20] yields T_0 ($\tilde{b}\ ^1B_1$)$=11\,823$ cm^{-1} (33.804 kcal mol^{-1}).

The singlet-triplet splitting of methylene has been the subject of a large number of theoretical studies; indeed, this quantity has often been used to calibrate new theoretical methods. A few of the many high-quality theoretical estimates of this quantity are presented in Table VI; a more comprehensive review of previous work is given in Ref. 14. The table indicates that large basis set MRCI and CCSD(T) methods yield accurate singlet-triplet splittings, while the full fourth-order many-body perturbation theory (MBPT4SDTQ) with a $9s7p2d1f/5s2p$ basis set substantially overestimates the singlet-triplet gap,[83] yielding a value of 11.46 kcal mol^{-1}. The error can be reduced by 1.36 kcal mol^{-1} by adding the infinite-order contributions present in CCSDT-1,[83] and the remaining error is probably due to the lack of d functions on the hydrogens. There are few theoretical estimates of the $\tilde{b}$ state excitation energy aside from the studies of Green *et al.*[79] and Jensen *et al.*[80] discussed above, and even less work has been performed on the $\tilde{c}$ state. The large basis set [TZ3P(2 f,2d)+2diff] second-order CI results of Yamaguchi *et al.*[70] are within a few tenths of a kcal mol^{-1} for the excitation energies of the $\tilde{a}$ and $\tilde{b}$ states, suggesting that their prediction for the $\tilde{c}$ state may have similar accuracy.

When compared to full CI, the errors in excitation energies for approximate methods of electron correlation are slightly larger than those observed for the smaller DZP basis set;[14] however, when compared to experiment or large basis set SOCI results,[70] the present TZ2P excitation energies are much better than those determined using a DZP basis. The TZ2P full CI level of theory yields T_e ($\tilde{a}\ ^1A_1$) $=11.141$ kcal mol^{-1}, which overestimates the nonrelativistic Born-Oppenheimer estimate by 1.77 kcal mol^{-1}. Most of this error is probably due to the lack of f-type functions on carbon and d-type functions on the hydrogens. Nevertheless, this estimate is much improved over the DZP full CI estimate of 12.664 kcal mol^{-1}. Comparing to experiment and to the more reliable large basis set SOCI results of Yamaguchi *et al.*,[70] TZ2P full CI seems to overestimate the excitation energies for the $\tilde{b}$ and $\tilde{c}$ states by roughly 2 kcal mol^{-1}.

IV. CONCLUSIONS

We have reported optimized geometries, harmonic vibrational frequencies, dipole moments, and energies for the $\tilde{X}\ ^3B_1$, $\tilde{a}\ ^1A_1$, $\tilde{b}\ ^1B_1$, and $\tilde{c}\ ^1A_1$ states of methylene with the full CI method using a TZ2P basis set. These full CI benchmarks allow one to examine the effects on molecular property predictions caused by various approximations in the treatment of electron correlation. Predictions from the CISDTQ method match those of the full CI very well for all but the $\tilde{c}$ state, which must be described in zeroth-order by a two-configuration reference function and which features a very flat bending potential. The differences between CISDTQ and full CI predictions for this state suggest that even very highly correlated wave functions can remain sensitive to the choice of the zeroth-order reference function. The CCSD(T) method is not as accurate for this system as CISDTQ, but it yields predictions in good agreement with full CI for the $\tilde{X}$ and $\tilde{a}$ states where we were able to apply it. The present results are much improved over those obtained in a similar benchmark study using the smaller DZP basis set,[14]

while the effects of electron correlation are only slightly larger in the TZ2P basis. The full CI results for the $\tilde{c}$ state should be helpful in calibrating methods meant to describe excited electronic states.

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