

**Table 16. IBM RS/6000 591 Timings<sup>(a)</sup>**

Ethylene, 16 electrons,  $^1A_1$  ( $D_{2h}$ ), Basis Set=6-311++G\*\*  
 (74 functions, 6-term d's)<sup>(b)</sup>

| Method       | Gaussian 92/DFT (G) | Gaussian 94 (C)  |  |
|--------------|---------------------|------------------|--|
| Conv. RHF    | 1/11 (12)           | 1/13 (14)        |  |
| Direct RHF   | 3/28 (29)           | 3/31 (32)        |  |
| RHF Gradient | 6/17 (19)           | 10/23 (25)       |  |
| RHF Hessian  | 93/104 (108)        | 80/93 (96)       |  |
| UHF          | 1/12 (14)           | 1/16 (18)        |  |
| Conv. MP2    | 11/22 (23)          | 6/19 (20)        |  |
| Direct MP2   | 12/40 (42)          | 7/38 (38)        |  |
| MP2 Gradient | 48/70 (83)          | 95/114 (141)     |  |
| MP2 Hessian  | 511/533 (840)       | 1173/1186 (1323) |  |
| MP4(SDTQ)    | 322/334 (382)       | 310/323 (337)    |  |
| SDCI         | 24/251 (254)        | 15/149 (152)     |  |
| CCSD         | 36/407 (916)        | 29/303 (355)     |  |
| CCSD(T)      | 696/707 (1224)      | 595/608 (649)    |  |
| QCISD        | 29/296 (330)        | 21/225 (240)     |  |
| QCISD(T)     | 584/595 (648)       | 551/564 (594)    |  |
| CASSCF       | 10/203 (821)        | 8/176 (277)      |  |
| CAS-CI       | NA                  | NA               |  |
| SVWN (LSD)   | 3/18 (25)           | 10/77 (81)       |  |
| BLYP (NLSD)  | 3/16 (18)           | 14/110 (115)     |  |

  

| Method       | MOLPRO (94.8) | GAMESS-US 11/17/94 | HONDO (8.3) |
|--------------|---------------|--------------------|-------------|
| Conv. RHF    |               |                    |             |
| Direct RHF   | NA            |                    |             |
| RHF Gradient |               |                    |             |
| RHF Hessian  | NA            |                    |             |
| UHF          |               |                    |             |
| Conv. MP2    |               |                    |             |
| Direct MP2   | NA            | NA                 | NA          |
| MP2 Gradient | NA            | NA                 | NA          |
| MP2 Hessian  | NA            | NA                 |             |
| MP4(SDTQ)    |               | NA                 |             |
| SDCI         |               |                    |             |
| CCSD         |               | NA                 | NA          |
| CCSD(T)      |               | NA                 |             |
| QCISD        |               | NA                 | NA          |
| QCISD(T)     |               | NA                 |             |
| CASSCF       |               |                    |             |
| CAS-CI       |               | NA                 |             |
| SVWN (LSD)   |               | NA                 |             |
| BLYP (NLSD)  |               | NA                 |             |

**Table 16.** IBM RS/6000 591 Timings (cont.)

Ethylene, 16 electrons,  $^1A_g$  ( $D_{2h}$ ), Basis Set=cc-pVTZ  
 (116 basis functions, 5-term d's, 7-term f's)

| <u>Method</u> | <u>Gaussian 92/DFT (G)</u> | <u>Gaussian 94 (C)</u> |  |
|---------------|----------------------------|------------------------|--|
| Conv. RHF     |                            | 12/118 (126)           |  |
| Direct RHF    |                            | 17/173 (182)           |  |
| RHF Gradient  |                            | 61/179 (194)           |  |
| RHF Hessian   |                            | 445/563 (594)          |  |
| UHF           |                            | 11/132 (146)           |  |
| Conv. MP2     |                            | 340/458 (499)          |  |
| Direct MP2    |                            |                        |  |
| MP2 Gradient  |                            |                        |  |
| MP4(SDTQ)     |                            |                        |  |
| SDCI          |                            |                        |  |
| CCSD          |                            |                        |  |
| CCSD(T)       |                            |                        |  |
| QCISD         |                            |                        |  |
| QCISD(T)      |                            |                        |  |
| CASSCF        |                            |                        |  |
| SVWN (LSD)    | NA                         |                        |  |
| BLYP (NLSD)   | NA                         |                        |  |

  

| <u>Method</u> | <u>MOLPRO (94.8)</u> | <u>GAMESS-US 7/17/93</u> | <u>HONDO (8.3)</u> |
|---------------|----------------------|--------------------------|--------------------|
| Conv. RHF     |                      |                          |                    |
| Direct RHF    | NA                   |                          |                    |
| RHF Gradient  | NA                   |                          |                    |
| RHF Hessian   | NA                   |                          |                    |
| UHF           |                      |                          |                    |
| Conv. MP2     |                      |                          |                    |
| Direct MP2    | NA                   | NA                       | NA                 |
| MP2 Gradient  | NA                   | NA                       | NA                 |
| MP4(SDTQ)     |                      | NA                       |                    |
| SDCI          |                      |                          |                    |
| CCSD          |                      | NA                       | NA                 |
| CCSD(T)       |                      |                          |                    |
| QCISD         |                      | NA                       | NA                 |
| QCISD(T)      |                      |                          |                    |
| CASSCF        |                      |                          |                    |
| SVWN (LSD)    |                      |                          |                    |
| BLYP (NLSD)   |                      |                          |                    |

**Table 16.** IBM RS/6000 591 Timings (cont.)

18-crown-6, C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>, 144 electrons, C<sub>i</sub>, Basis Set=3-21G  
(210 functions)

| <u>Method</u> | <u>Gaussian 92/DFT (G)</u> | <u>Gaussian 94 (C)</u> |  |
|---------------|----------------------------|------------------------|--|
| Direct RHF    | 42/539 (558)               |                        |  |
| RHF Gradient  | 216/755 (774)              |                        |  |
| RHF Hessian   | 12790/13326 (13611)        |                        |  |
| Conv. RHF     |                            |                        |  |
| Conv. MP2     |                            |                        |  |
| Direct MP2    |                            |                        |  |
| MP2 Gradient  |                            |                        |  |
| MP4(SDTQ)     |                            |                        |  |
| SDCI          |                            |                        |  |
| CCSD          |                            |                        |  |
| QCISD         |                            |                        |  |
| CASSCF        |                            |                        |  |

  

| <u>Method</u> | <u>GAMESS-US 6/17/92</u> | <u>HONDO (8.1)</u> | <u>MOLPRO (92.3)</u> |
|---------------|--------------------------|--------------------|----------------------|
| Direct RHF    |                          |                    |                      |
| RHF Gradient  |                          |                    |                      |
| RHF Hessian   |                          |                    | NA                   |
| Conv. RHF     |                          |                    |                      |
| Conv. MP2     |                          |                    |                      |
| Direct MP2    |                          |                    | NA                   |
| MP2 Gradient  |                          |                    |                      |
| MP4(SDTQ)     |                          |                    |                      |
| SDCI          |                          |                    |                      |
| CCSD          |                          |                    |                      |
| QCISD         |                          |                    |                      |
| CASSCF        |                          |                    |                      |

**Table 16.** IBM RS/6000 591 Timings (cont.)

18-crown-6, C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>, 144 electrons, C<sub>i</sub>, Basis Set=6-31G\*\*  
(390 functions)

| <u>Method</u> | <u>Gaussian 92/DFT (G)</u> | <u>Gaussian 94 (C)</u> | <u>MOLPRO (92.3)</u> |
|---------------|----------------------------|------------------------|----------------------|
| Direct RHF    | 225/2925 (2940)            |                        |                      |
| RHF Gradient  |                            |                        |                      |
| RHF Hessian   |                            |                        | NA                   |
| Conv. RHF     |                            |                        |                      |
| Conv. MP2     |                            |                        |                      |
| Direct MP2    |                            |                        | NA                   |
| MP2 Gradient  |                            |                        |                      |
| MP4(SDTQ)     |                            |                        |                      |
| SDCI          |                            |                        |                      |
| CCSD          |                            |                        |                      |
| QCISD         |                            |                        |                      |
| CASSCF        |                            |                        |                      |

  

| <u>Method</u> | <u>GAMESS-US 6/17/92</u> | <u>HONDO (8.1)</u> | <u>GAMESS-UK (2)</u> |
|---------------|--------------------------|--------------------|----------------------|
| Direct RHF    |                          |                    |                      |
| RHF Gradient  |                          |                    |                      |
| RHF Hessian   |                          |                    |                      |
| Conv. RHF     |                          |                    |                      |
| Conv. MP2     |                          |                    |                      |
| Direct MP2    |                          |                    |                      |
| MP2 Gradient  |                          |                    |                      |
| MP4(SDTQ)     |                          |                    |                      |
| SDCI          |                          |                    |                      |
| CCSD          |                          |                    |                      |
| QCISD         |                          |                    |                      |
| CASSCF        |                          |                    |                      |

  

| <u>Method</u> | <u>DISCO (1.82)</u> | <u>ACES II</u> |
|---------------|---------------------|----------------|
| Direct UHF    |                     | NA             |
| RHF Gradient  |                     |                |
| RHF Hessian   | NA                  |                |
| Direct RHF    |                     |                |
| Conv. MP2     | NA                  |                |
| Direct MP2    |                     | NA             |
| MP2 Gradient  | NA                  |                |
| MP4(SDTQ)     | NA                  |                |
| SDCI          | NA                  |                |
| CCSD          | NA                  |                |
| QCISD         | NA                  |                |
| CASSCF        | NA                  | NA             |

**Table 16.** IBM RS/6000 591 Timings (cont.)

18-crown-6, C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>, 144 electrons, C<sub>i</sub>, Basis Set=aug-cc-pVDZ  
(606 functions)

| <u>Method</u> | <u>Gaussian 92/DFT (G)</u> | <u>Gaussian 94 (C)</u> | <u>MOLPRO (92.3)</u> |
|---------------|----------------------------|------------------------|----------------------|
| Direct RHF    | 9607/144105 (144820)       | 8474/127124 (127577)   |                      |
| RHF Gradient  |                            |                        |                      |
| RHF Hessian   |                            |                        | NA                   |
| Conv. RHF     |                            |                        |                      |
| Conv. MP2     |                            |                        |                      |
| Direct MP2    |                            |                        | NA                   |
| MP2 Gradient  |                            |                        |                      |
| MP4(SDTQ)     |                            |                        |                      |
| SDCI          |                            |                        |                      |
| CCSD          |                            |                        |                      |
| QCISD         |                            |                        |                      |
| CASSCF        |                            |                        |                      |

s18-crown-6, C<sub>34</sub>H<sub>56</sub>O<sub>8</sub>, 324 electrons, C<sub>2</sub>, Basis Set=6-31G\*\*  
(910 functions)

| <u>Method</u> | <u>Gaussian 94 (C)</u> | <u>MOLPRO (92.3)</u> |
|---------------|------------------------|----------------------|
| Direct RHF    | 2666/34659 (34862)     |                      |
| RHF Gradient  | 14158/48817 (49108)    |                      |
| RHF Hessian   |                        | NA                   |
| Conv. RHF     |                        |                      |
| Conv. MP2     |                        |                      |
| Direct MP2    |                        | NA                   |
| MP2 Gradient  |                        |                      |
| MP4(SDTQ)     |                        |                      |

**Table 16. IBM RS/6000 591 Timings (cont.)**

- (a) All times are in seconds. CPU times are the sum of the "user + system" contributions. Wall clock times are given in parentheses. For the iterative methods (RHF, UHF, SD-CI, QCISD and CASSCF) each entry consists of a trio of numbers: "CPU-time-per-iteration/total-CPU (total-wall-clock)". The "CPU-time-per-iteration" for the conventional SCF methods was defined as the total run time (integrals + SCF) divided by the number of iterations. These values are intended to facilitate comparison with direct HF methods. For other methods the leftmost entry corresponds to the incremental time for the method. For example, the MP2 entry preceding the slash is the total run time minus the time needed for the HF step. Calculations were performed on a machine with 256 MB of memory and two 4.5 GB IBM F/W SCSI 2 disk running under AIX 4.1 with disk striping enabled. Release 4.1 of XLF Fortran was used for applications which had to be recompiled. Runs were made on an otherwise quiet system.
- NA:** not available with this program.  
**FTC-ND:** Failed to complete - not enough disk space.  
**FTC-unknown:** Failed to complete for unknown reasons.  
SCF calculations were converged to approximately 15 digits after the decimal point (8 digits in the density).
- (b) The ethylene UHF calculation treated the  $\pi \rightarrow \pi^*$  ( ${}^3B_{1u}$ ) state. The ethylene ground state is  ${}^1A_g$ . MP2, MP4, CISD and QCISD calculations involved all electrons, i.e., there were no "core" electrons. The CAS configuration list contains 8 CSF's in  $D_{2h}$  symmetry and was generated with 4 electrons in 4 orbitals ( $3a_g, 1b_{3u}, 1b_{2g}, 2b_{1u}$ ). This configuration list is sufficient to allow ethylene to dissociate into two singlet methylenes. The time reported includes the time required to compute the integrals and solve the CAS equations using the canonical RHF orbitals as the starting guess. The default INDO initial guess used by Gaussian for ethylene's open shell calculations did not pick up the  $\pi \rightarrow \pi^*$   ${}^3B_{1u}$  state. If the ordering of the initial guess orbitals was corrected using an ALTER command the calculation with Gaussian 90 died with a complaint that symmetry was being broken. Thus, it was necessary to run these calculations with the NOSYMM option, which ignored the available  $D_{2h}$  symmetry. Gaussian 92 fixed this problem with the UHF benchmark and it was run in full  $D_{2h}$  symmetry.