# Electronic Supplementary Information (ESI) for:

# Density Functional Approximations for Charge Transfer Excitations with Intermediate Spatial Overlap

Ruifang Li, Jingjing Zheng, and Donald G. Truhlar

Prepared on July 14, 2010

The ESI accompanies an article in *PCCP*.

***Contents***

Cartesian coordinates (Å) for AE6 database

These structures are from "The Effectiveness of Diffuse Basis Functions for Calculating Relative Energies by Density Functional Theory," B. J. Lynch, Y. Zhao, and D. G. Truhlar, Journal of Physical Chemistry A **107**, 1384-1388 (2003).

**$C_2H_2O_2$**

| | | | |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 0.000000 |
| 6 | 0.000000 | 0.000000 | 1.520712 |
| 8 | 1.027828 | 0.000000 | -0.626472 |
| 1 | -0.996668 | 0.000000 | -0.467311 |
| 8 | -1.027828 | 0.000000 | 2.147184 |
| 1 | 0.996668 | 0.000000 | 1.988024 |

**$C_3H_4$**

| | | | |
|---|---|---|---|
| C | 0.000000 | 0.000000 | 0.219507 |
| C | 0.000000 | 0.000000 | 1.423958 |
| C | 0.000000 | 0.000000 | -1.243764 |
| H | 0.000000 | 0.000000 | 2.486256 |
| H | 0.000000 | 1.019009 | -1.628154 |
| H | 0.882487 | -0.509504 | -1.628154 |
| H | -0.882487 | -0.509504 | -1.628154 |

**$C_4H_8$**

| | | | |
|---|---|---|---|
| C | 0.000000 | 1.076294 | 0.142865 |
| C | 0.000000 | -1.076294 | 0.142865 |
| C | -1.076294 | 0.000000 | -0.142865 |
| C | 1.076294 | 0.000000 | -0.142865 |
| H | 0.000000 | 1.979204 | -0.465165 |
| H | 0.000000 | 1.359222 | 1.195822 |
| H | 0.000000 | -1.979204 | -0.465165 |
| H | 0.000000 | -1.359222 | 1.195822 |
| H | -1.979204 | 0.000000 | 0.465165 |
| H | -1.359222 | 0.000000 | -1.195822 |
| H | 1.979204 | 0.000000 | 0.465165 |
| H | 1.359222 | 0.000000 | -1.195822 |

**$S_2$**

| | | | |
|---|---|---|---|
| 16 | 0.000000 | 0.000000 | 0.000000 |
| 16 | 0.000000 | 0.000000 | 1.892594 |

**$SiH_4$**

| | | | |
|---|---|---|---|
| 14 | 0.000000 | 0.000000 | 0.000000 |
| 1 | 0.852576 | 0.852576 | 0.852576 |
| 1 | -0.852576 | -0.852576 | 0.852576 |
| 1 | -0.852576 | 0.852576 | -0.852576 |

| | | | |
|---|---|---|---|
| 1 | 0.852576 | -0.852576 | -0.852576 |

**SiO**

| | | | |
|---|---|---|---|
| 14 | 0.000000 | 0.000000 | 0.000000 |
| 8 | 0.000000 | 0.000000 | 1.512667 |

## Cartesian coordinates (Å) for structures of protonated Schiff bases

These structures are optimized in the present work.

### Protonated 11- *Z-cis*-retinal (1)

**CAM-B3LYP**

| | | | |
|---|---|---|---|
| 6 | 3.471415 | -1.316667 | 0.845529 |
| 6 | 4.977196 | -1.631570 | 0.823000 |
| 6 | 5.549777 | -1.672755 | -0.584854 |
| 6 | 5.365955 | -0.318011 | -1.256359 |
| 6 | 4.008034 | 0.308466 | -1.044289 |
| 6 | 3.155704 | -0.125993 | -0.081894 |
| 6 | 3.093289 | -0.976072 | 2.298334 |
| 6 | 3.722840 | 1.435926 | -2.002546 |
| 6 | 1.833646 | 0.460591 | 0.124211 |
| 6 | 1.494026 | 1.772022 | 0.100143 |
| 6 | 0.167260 | 2.301669 | 0.341187 |
| 6 | -0.962299 | 1.524947 | 0.177085 |
| 6 | 0.150440 | 3.746238 | 0.753525 |
| 6 | -2.274111 | 1.960735 | 0.467509 |
| 6 | -3.505937 | 1.336056 | 0.356311 |
| 6 | -3.859723 | 0.052540 | -0.120364 |
| 6 | -2.825308 | -0.901162 | -0.641722 |
| 6 | -5.224292 | -0.278082 | -0.085865 |
| 6 | -5.767349 | -1.481280 | -0.508254 |
| 7 | -7.057161 | -1.788683 | -0.468276 |
| 6 | -8.109615 | -0.911011 | 0.023926 |
| 6 | 2.669177 | -2.555802 | 0.403325 |
| 1 | 5.146272 | -2.582210 | 1.342169 |
| 1 | 5.508897 | -0.862645 | 1.399738 |
| 1 | 5.051842 | -2.449578 | -1.176412 |
| 1 | 6.612023 | -1.936279 | -0.559972 |
| 1 | 5.557436 | -0.395035 | -2.332870 |
| 1 | 6.118424 | 0.392250 | -0.879150 |
| 1 | 2.014298 | -0.847071 | 2.433808 |
| 1 | 3.586101 | -0.056121 | 2.630049 |
| 1 | 3.410089 | -1.785387 | 2.965084 |
| 1 | 2.659653 | 1.648008 | -2.121507 |
| 1 | 4.136049 | 1.202026 | -2.988635 |
| 1 | 4.214512 | 2.361103 | -1.673557 |

| | | | |
|---|---|---|---|
| 1 | 1.057329 | -0.248073 | 0.407793 |
| 1 | 2.279865 | 2.511999 | -0.019214 |
| 1 | -0.810780 | 0.526389 | -0.205572 |
| 1 | -0.842777 | 4.180612 | 0.852834 |
| 1 | 0.675830 | 3.865618 | 1.707980 |
| 1 | 0.702468 | 4.340737 | 0.017197 |
| 1 | -2.351048 | 2.970000 | 0.860356 |
| 1 | -4.346054 | 1.940047 | 0.688287 |
| 1 | -2.114074 | -1.156816 | 0.150089 |
| 1 | -2.261647 | -0.439311 | -1.457453 |
| 1 | -3.243273 | -1.832930 | -1.019246 |
| 1 | -5.900939 | 0.473824 | 0.306717 |
| 1 | -5.139212 | -2.268856 | -0.909563 |
| 1 | -7.332302 | -2.700837 | -0.806053 |
| 1 | -9.063448 | -1.430786 | -0.058393 |
| 1 | -7.936675 | -0.655153 | 1.073354 |
| 1 | -8.154879 | 0.005966 | -0.570968 |
| 1 | 1.589291 | -2.370351 | 0.418251 |
| 1 | 2.861748 | -3.392307 | 1.084164 |
| 1 | 2.934361 | -2.872774 | -0.609014 |

**M06-2X**

| | | | |
|---|---|---|---|
| 6 | 3.092927 | -1.625565 | 0.263032 |
| 6 | 4.479935 | -2.128295 | 0.693360 |
| 6 | 5.577325 | -1.718391 | -0.277712 |
| 6 | 5.661639 | -0.197674 | -0.348331 |
| 6 | 4.321974 | 0.499078 | -0.422827 |
| 6 | 3.163067 | -0.135694 | -0.117211 |
| 6 | 2.136440 | -1.827371 | 1.451093 |
| 6 | 4.421653 | 1.936235 | -0.870000 |
| 6 | 1.854245 | 0.519995 | -0.160419 |
| 6 | 1.545431 | 1.753612 | 0.303747 |
| 6 | 0.221377 | 2.354077 | 0.282450 |
| 6 | -0.915939 | 1.581108 | 0.166055 |
| 6 | 0.222160 | 3.848513 | 0.438844 |
| 6 | -2.226980 | 2.107666 | 0.078420 |
| 6 | -3.464117 | 1.488347 | -0.001107 |
| 6 | -3.813640 | 0.114947 | 0.027193 |
| 6 | -2.768362 | -0.952119 | 0.184677 |
| 6 | -5.178064 | -0.189661 | -0.088072 |
| 6 | -5.710097 | -1.474912 | -0.090017 |
| 7 | -6.999815 | -1.750932 | -0.207259 |
| 6 | -8.047829 | -0.748226 | -0.347092 |
| 6 | 2.576406 | -2.445421 | -0.932653 |
| 1 | 4.439394 | -3.219251 | 0.803322 |
| 1 | 4.711240 | -1.717180 | 1.686560 |
| 1 | 5.373584 | -2.124544 | -1.275541 |

| | | | |
|---|---|---|---|
| 1 | 6.541157 | -2.131354 | 0.036536 |
| 1 | 6.271157 | 0.112744 | -1.205200 |
| 1 | 6.184363 | 0.191044 | 0.540376 |
| 1 | 1.094350 | -1.607149 | 1.188605 |
| 1 | 2.415066 | -1.187044 | 2.295266 |
| 1 | 2.176690 | -2.870139 | 1.786218 |
| 1 | 3.483866 | 2.331706 | -1.263857 |
| 1 | 5.184678 | 2.028562 | -1.649163 |
| 1 | 4.744239 | 2.580119 | -0.040878 |
| 1 | 1.045661 | -0.086792 | -0.570781 |
| 1 | 2.339628 | 2.371371 | 0.717890 |
| 1 | -0.772419 | 0.510127 | 0.150106 |
| 1 | -0.764511 | 4.296555 | 0.541905 |
| 1 | 0.806470 | 4.115635 | 1.326376 |
| 1 | 0.726891 | 4.307739 | -0.419375 |
| 1 | -2.294722 | 3.192345 | 0.055346 |
| 1 | -4.306810 | 2.169347 | -0.091646 |
| 1 | -2.176858 | -0.763977 | 1.086093 |
| 1 | -2.088086 | -0.939063 | -0.673727 |
| 1 | -3.181255 | -1.956275 | 0.265337 |
| 1 | -5.865381 | 0.645112 | -0.189657 |
| 1 | -5.074374 | -2.349633 | 0.002728 |
| 1 | -7.278900 | -2.723468 | -0.198523 |
| 1 | -9.007314 | -1.256213 | -0.430244 |
| 1 | -8.064261 | -0.093783 | 0.529317 |
| 1 | -7.880748 | -0.150656 | -1.248168 |
| 1 | 1.584547 | -2.108533 | -1.256706 |
| 1 | 2.488818 | -3.502077 | -0.653721 |
| 1 | 3.245242 | -2.370254 | -1.794551 |

**M08-HX**

| | | | |
|---|---|---|---|
| 6 | 4.857727 | 1.867236 | -1.149631 |
| 6 | 3.625216 | 0.997502 | -1.105984 |
| 6 | 3.473137 | 0.005152 | -0.187356 |
| 6 | 4.579966 | -0.396683 | 0.804550 |
| 6 | 5.903782 | 0.311809 | 0.467119 |
| 6 | 5.704821 | 1.780761 | 0.113381 |
| 1 | 5.457058 | 1.575782 | -2.032648 |
| 1 | 6.592815 | 0.194751 | 1.319140 |
| 1 | 5.202347 | 2.310800 | 0.938957 |
| 6 | 4.127729 | -0.033680 | 2.231091 |
| 1 | 3.986173 | 1.050198 | 2.352727 |
| 1 | 3.170833 | -0.521369 | 2.477216 |
| 1 | 4.874193 | -0.368422 | 2.967904 |
| 6 | 4.842642 | -1.914350 | 0.748048 |
| 1 | 5.759544 | -2.145088 | 1.311183 |
| 1 | 4.036460 | -2.507490 | 1.205490 |

| | | | |
|---|---|---|---|
| 1 | 4.989325 | -2.260426 | -0.286469 |
| 6 | 2.647271 | 1.314559 | -2.209720 |
| 1 | 2.044278 | 2.204703 | -1.964109 |
| 1 | 3.205537 | 1.567187 | -3.124287 |
| 1 | 1.964033 | 0.488854 | -2.441999 |
| 6 | 2.239840 | -0.775786 | -0.091122 |
| 6 | -1.437286 | -0.455830 | -0.244468 |
| 1 | -1.415321 | 0.629597 | -0.384409 |
| 6 | -2.713232 | -1.066713 | -0.209630 |
| 1 | -2.769418 | -2.152383 | -0.094664 |
| 6 | -3.898048 | -0.363110 | -0.303206 |
| 1 | -3.825150 | 0.720190 | -0.435674 |
| 6 | -5.180188 | -0.977506 | -0.364521 |
| 6 | -6.380835 | -0.265086 | -0.315918 |
| 1 | -7.291005 | -0.790084 | -0.602721 |
| 6 | -5.274123 | -2.470855 | -0.551903 |
| 1 | -6.310724 | -2.787997 | -0.710946 |
| 1 | -4.670770 | -2.809525 | -1.405096 |
| 1 | -4.906790 | -2.991524 | 0.345930 |
| 6 | -6.595531 | 1.055585 | 0.113346 |
| 1 | -7.593240 | 1.478752 | -0.038726 |
| 7 | -5.763821 | 1.856647 | 0.747325 |
| 1 | 2.358320 | -1.833028 | 0.169135 |
| 1 | -4.857000 | 1.489864 | 1.022033 |
| 6 | -6.099095 | 3.198313 | 1.204754 |
| 1 | -6.019264 | 3.256138 | 2.297683 |
| 1 | -5.421462 | 3.933843 | 0.753175 |
| 1 | -7.126948 | 3.432452 | 0.907580 |
| 6 | -0.081869 | -2.583454 | 0.075354 |
| 1 | -1.040769 | -3.108456 | 0.114644 |
| 1 | 0.513017 | -3.031048 | -0.733414 |
| 1 | 0.444658 | -2.787763 | 1.019282 |
| 1 | 6.671761 | 2.280632 | -0.039989 |
| 1 | 4.538381 | 2.905364 | -1.347044 |
| 6 | -0.220031 | -1.100207 | -0.133170 |
| 6 | 0.975165 | -0.294133 | -0.225622 |
| 1 | 0.828680 | 0.776561 | -0.391012 |
| 1 | 6.374843 | -0.198733 | -0.392492 |

**Protonated 11-*Z-cis*-7,8-dihydro (2)**

**CAM-B3LYP**

| | | | |
|---|---|---|---|
| 6 | -3.481320 | -1.471814 | 0.455010 |
| 6 | -4.578942 | -2.212926 | -0.331042 |
| 6 | -5.923899 | -1.502931 | -0.282768 |
| 6 | -5.790026 | -0.118715 | -0.903032 |
| 6 | -4.558004 | 0.631272 | -0.447359 |

| | | | |
|---|---|---|---|
| 6 | -3.514187 | 0.034236 | 0.154170 |
| 6 | -2.134533 | -2.101097 | 0.054728 |
| 6 | -4.641884 | 2.108050 | -0.743557 |
| 6 | -2.316027 | 0.843132 | 0.626235 |
| 6 | -1.296947 | 1.141111 | -0.502434 |
| 6 | -0.058756 | 1.833649 | -0.011270 |
| 6 | 1.146851 | 1.204806 | -0.125774 |
| 6 | -0.272060 | 3.183592 | 0.604132 |
| 6 | 2.385729 | 1.757416 | 0.319596 |
| 6 | 3.671351 | 1.270491 | 0.308229 |
| 6 | 4.198538 | 0.026111 | -0.145675 |
| 6 | 3.310113 | -1.033567 | -0.725024 |
| 6 | 5.578873 | -0.144971 | -0.018194 |
| 6 | 6.282020 | -1.282217 | -0.405655 |
| 7 | 7.588458 | -1.438686 | -0.288074 |
| 6 | 8.508892 | -0.451589 | 0.264422 |
| 6 | -3.684232 | -1.695532 | 1.967539 |
| 1 | -4.662208 | -3.236247 | 0.054577 |
| 1 | -4.266647 | -2.298776 | -1.381197 |
| 1 | -6.269570 | -1.413601 | 0.753696 |
| 1 | -6.683650 | -2.085300 | -0.814835 |
| 1 | -6.676871 | 0.487872 | -0.679515 |
| 1 | -5.762250 | -0.200614 | -2.000320 |
| 1 | -1.292470 | -1.689227 | 0.621695 |
| 1 | -1.934254 | -1.967276 | -1.014159 |
| 1 | -2.159399 | -3.178541 | 0.252529 |
| 1 | -3.738797 | 2.671208 | -0.504805 |
| 1 | -5.471549 | 2.560421 | -0.186013 |
| 1 | -4.861839 | 2.268552 | -1.806516 |
| 1 | -1.795166 | 0.306043 | 1.425134 |
| 1 | -2.648714 | 1.785457 | 1.069956 |
| 1 | -1.783584 | 1.779916 | -1.250116 |
| 1 | -1.030195 | 0.209925 | -1.007370 |
| 1 | 1.136537 | 0.227035 | -0.587831 |
| 1 | 0.632673 | 3.784228 | 0.698223 |
| 1 | -0.997547 | 3.753359 | 0.014819 |
| 1 | -0.703536 | 3.071292 | 1.606170 |
| 1 | 2.313518 | 2.752196 | 0.749791 |
| 1 | 4.416339 | 1.948273 | 0.716182 |
| 1 | 2.810240 | -0.656752 | -1.622473 |
| 1 | 2.533624 | -1.309666 | -0.005917 |
| 1 | 3.839212 | -1.943859 | -1.001866 |
| 1 | 6.141956 | 0.675664 | 0.413630 |
| 1 | 5.771262 | -2.132897 | -0.843108 |
| 1 | 7.985055 | -2.313208 | -0.606763 |
| 1 | 9.517942 | -0.860095 | 0.228240 |
| 1 | 8.479114 | 0.469932 | -0.323510 |

| | | | |
|---|---|---|---|
| 1 | 8.253843 | -0.230881 | 1.304613 |
| 1 | -2.913998 | -1.191928 | 2.561351 |
| 1 | -3.633639 | -2.764347 | 2.205354 |
| 1 | -4.653936 | -1.318405 | 2.303213 |

**M06-2X**

| | | | |
|---|---|---|---|
| 6 | -3.353277 | -1.496434 | 0.402096 |
| 6 | -4.464132 | -2.242945 | -0.357340 |
| 6 | -5.829244 | -1.589279 | -0.189412 |
| 6 | -5.784708 | -0.180239 | -0.768610 |
| 6 | -4.556800 | 0.598214 | -0.349212 |
| 6 | -3.463647 | 0.015352 | 0.177395 |
| 6 | -2.006967 | -2.042412 | -0.105842 |
| 6 | -4.698287 | 2.082032 | -0.585050 |
| 6 | -2.270860 | 0.846882 | 0.615000 |
| 6 | -1.345590 | 1.218109 | -0.573936 |
| 6 | -0.099392 | 1.901123 | -0.101955 |
| 6 | 1.102356 | 1.262154 | -0.223087 |
| 6 | -0.299696 | 3.237119 | 0.554895 |
| 6 | 2.332138 | 1.806730 | 0.261643 |
| 6 | 3.616418 | 1.312875 | 0.286887 |
| 6 | 4.133001 | 0.054292 | -0.144782 |
| 6 | 3.229161 | -0.997482 | -0.717557 |
| 6 | 5.508015 | -0.137395 | 0.001978 |
| 6 | 6.190823 | -1.297247 | -0.370309 |
| 7 | 7.491749 | -1.470960 | -0.237348 |
| 6 | 8.411024 | -0.482090 | 0.316001 |
| 6 | -3.456835 | -1.795489 | 1.910079 |
| 1 | -4.482523 | -3.287755 | -0.022209 |
| 1 | -4.213057 | -2.256688 | -1.428199 |
| 1 | -6.101249 | -1.545654 | 0.872169 |
| 1 | -6.603089 | -2.181055 | -0.689305 |
| 1 | -6.678553 | 0.385748 | -0.475732 |
| 1 | -5.810405 | -0.225650 | -1.868501 |
| 1 | -1.150509 | -1.606070 | 0.423349 |
| 1 | -1.886391 | -1.859012 | -1.179926 |
| 1 | -1.969375 | -3.126492 | 0.052877 |
| 1 | -3.802496 | 2.663811 | -0.359493 |
| 1 | -5.519370 | 2.484294 | 0.021236 |
| 1 | -4.964483 | 2.270132 | -1.633002 |
| 1 | -1.675848 | 0.296117 | 1.352419 |
| 1 | -2.602186 | 1.761655 | 1.117625 |
| 1 | -1.897263 | 1.884938 | -1.249423 |
| 1 | -1.097456 | 0.315747 | -1.139156 |
| 1 | 1.087769 | 0.295645 | -0.710874 |
| 1 | 0.559297 | 3.904252 | 0.465460 |
| 1 | -1.169057 | 3.741622 | 0.123118 |

| | | | |
|---|---|---|---|
| 1 | -0.507881 | 3.098345 | 1.623786 |
| 1 | 2.246999 | 2.801334 | 0.694612 |
| 1 | 4.358822 | 1.986077 | 0.708363 |
| 1 | 2.774532 | -0.632246 | -1.644179 |
| 1 | 2.421774 | -1.218440 | -0.012820 |
| 1 | 3.736789 | -1.933809 | -0.943014 |
| 1 | 6.084219 | 0.677233 | 0.430791 |
| 1 | 5.668715 | -2.142955 | -0.806398 |
| 1 | 7.883845 | -2.353238 | -0.542958 |
| 1 | 9.417619 | -0.896671 | 0.297066 |
| 1 | 8.388613 | 0.430888 | -0.285535 |
| 1 | 8.138845 | -0.250463 | 1.349509 |
| 1 | -2.660888 | -1.298416 | 2.475934 |
| 1 | -3.366410 | -2.873242 | 2.090580 |
| 1 | -4.412584 | -1.456489 | 2.319973 |

**M08-HX**

| | | | |
|---|---|---|---|
| 6 | -3.510457 | -1.500440 | 0.390401 |
| 6 | -4.685615 | -2.156291 | -0.358404 |
| 6 | -5.992120 | -1.393286 | -0.170682 |
| 6 | -5.842292 | 0.003568 | -0.763605 |
| 6 | -4.554538 | 0.684848 | -0.350208 |
| 6 | -3.508070 | 0.017729 | 0.174698 |
| 6 | -2.213148 | -2.137388 | -0.139934 |
| 6 | -4.580167 | 2.177418 | -0.577948 |
| 6 | -2.255199 | 0.757307 | 0.615216 |
| 6 | -1.304419 | 1.074925 | -0.569331 |
| 6 | -0.062746 | 1.768338 | -0.095060 |
| 6 | 1.148263 | 1.140932 | -0.199155 |
| 6 | -0.275011 | 3.116508 | 0.538669 |
| 6 | 2.362102 | 1.711091 | 0.302256 |
| 6 | 3.661604 | 1.255207 | 0.327274 |
| 6 | 4.224709 | 0.034775 | -0.160316 |
| 6 | 3.366315 | -1.001115 | -0.825704 |
| 6 | 5.600812 | -0.128680 | 0.016155 |
| 6 | 6.326303 | -1.250765 | -0.399149 |
| 7 | 7.625207 | -1.396880 | -0.236939 |
| 6 | 8.496324 | -0.414714 | 0.394647 |
| 6 | -3.616265 | -1.803744 | 1.898410 |
| 1 | -4.781795 | -3.203019 | -0.025417 |
| 1 | -4.448007 | -2.188069 | -1.437624 |
| 1 | -6.241244 | -1.318435 | 0.900367 |
| 1 | -6.826116 | -1.926344 | -0.650191 |
| 1 | -6.691776 | 0.643458 | -0.471349 |
| 1 | -5.878771 | -0.047882 | -1.867995 |
| 1 | -1.317290 | -1.775573 | 0.390775 |
| 1 | -2.086019 | -1.944386 | -1.216727 |

| | | | |
|---|---|---|---|
| 1 | -2.252887 | -3.229039 | -0.000398 |
| 1 | -3.634084 | 2.688829 | -0.360983 |
| 1 | -5.360687 | 2.645959 | 0.042710 |
| 1 | -4.844481 | 2.396153 | -1.625223 |
| 1 | -1.697733 | 0.158225 | 1.352738 |
| 1 | -2.521600 | 1.692353 | 1.131809 |
| 1 | -1.838181 | 1.727049 | -1.282237 |
| 1 | -1.053903 | 0.148036 | -1.104270 |
| 1 | 1.149753 | 0.163317 | -0.676100 |
| 1 | 0.550410 | 3.817345 | 0.365558 |
| 1 | -1.194215 | 3.578118 | 0.152273 |
| 1 | -0.404208 | 3.010407 | 1.628295 |
| 1 | 2.242455 | 2.695694 | 0.764042 |
| 1 | 4.380810 | 1.933314 | 0.791892 |
| 1 | 2.879680 | -0.571918 | -1.713104 |
| 1 | 2.575893 | -1.333712 | -0.137877 |
| 1 | 3.915938 | -1.889662 | -1.148948 |
| 1 | 6.142939 | 0.678583 | 0.510690 |
| 1 | 5.836472 | -2.089286 | -0.895672 |
| 1 | 8.051873 | -2.251900 | -0.574051 |
| 1 | 9.521028 | -0.795458 | 0.385352 |
| 1 | 8.463828 | 0.534343 | -0.157881 |
| 1 | 8.188850 | -0.244728 | 1.435670 |
| 1 | -2.780973 | -1.363130 | 2.464256 |
| 1 | -3.593260 | -2.890905 | 2.072806 |
| 1 | -4.547461 | -1.406919 | 2.326003 |

## Details of the calculations on which Table 3 is based

BO denotes Born-Oppenheimer energy without spin-orbit coupling.

1 $E_h$ ≡ 1 hartree ≈ 627.5095 kcal/mol

### 1. AE6 database

| | E(BO) | E(spin-orbit) | E(BO)+E(spin-orbit) |
|---|---|---|---|
| | $E_h$ | kcal/mol | kcal/mol |
| **M06-2X** | | | |
| $SiH_4$ | -291.8556012 | 0.00 | -183142.162 |
| SiO | -364.7155865 | 0.00 | -228862.495 |
| $S_2$ | -796.3612514 | 0.00 | -499724.251 |
| $C_3H_4$ | -116.6380982 | 0.00 | -73191.515 |
| $C_2H_2O_2$ | -227.8108396 | 0.00 | -142953.466 |
| $C_4H_8$ | -157.1771300 | 0.00 | -98630.142 |
| H | -0.4981341 | 0.00 | -312.584 |
| C | -37.8407451 | -0.09 | -23745.517 |
| O | -75.0618945 | -0.23 | -47102.282 |
| S | -398.0975649 | -0.56 | -249810.56 |
| Si | -289.3506556 | -0.430 | -181570.702 |
| **M08-HX** | | | |
| $SiH_4$ | -291.8696042 | 0.00 | -183150.949 |
| SiO | -364.7013911 | 0.00 | -228853.588 |
| $S_2$ | -796.3571549 | 0.00 | -499721.681 |
| $C_3H_4$ | -116.6628351 | 0.00 | -73207.037 |
| $C_2H_2O_2$ | -227.8119000 | 0.00 | -142954.131 |
| $C_4H_8$ | -157.2245502 | 0.00 | -98659.899 |
| H | -0.5018647 | 0.00 | -314.925 |
| C | -37.8448910 | -0.09 | -23748.119 |
| O | -75.0552786 | -0.23 | -47098.130 |
| S | -398.0936236 | -0.56 | -249808.091 |
| Si | -289.350047 | -0.43 | -181570.333 |
| **CAM-B3LYP** | | | |
| $SiH_4$ | -291.8932564 | 0.00 | -183165.791 |
| SiO | -364.7482972 | 0.00 | -228883.022 |
| $S_2$ | -796.4184826 | 0.00 | -499760.164 |
| $C_3H_4$ | -116.6237968 | 0.00 | -73182.540 |
| $C_2H_2O_2$ | -227.8145110 | 0.00 | -142955.770 |
| $C_4H_8$ | -157.1632526 | 0.00 | -98621.434 |
| H | -0.4988128 | 0.00 | -313.010 |
| C | -37.8349933 | -0.09 | -23741.908 |
| O | -75.0679572 | -0.23 | -47106.086 |
| S | -398.1294913 | -0.56 | -249830.598 |
| Si | -289.3793922 | -0.430 | -181588.748 |

SE is signed error.

UE is unsigned error (absolute error).

M denotes mean

PB denotes "per bond". To put the results of the AE6 database on a per bond basis, we divide the mean error per molecule by the average number of bonds in a molecule, which is 4.83.

| **kcal/mol** | **$SiH_4$** | **SiO** | **$S_2$** | **$C_3H_4$** | **$C_2H_2O_2$** | **$C_4H_8$** |
|---|---|---|---|---|---|---|
| **Experiment** | 322.40[a] | 192.08[a] | 101.67[a] | 704.79[b] | 633.35[b] | 1149.01[b] |
| | | | | | | |
| **M06-2X** | 321.112 | 189.498 | 103.123 | 704.628 | 632.700 | 1147.403 |
| SE | -1.288 | -2.582 | 1.453 | -0.162 | -0.650 | -1.607 |
| UE | 1.288 | 2.5818 | 1.453 | 0.162 | 0.650 | 1.607 |
| MSEPB | -0.167 | | | | | |
| MUEPB | 0.267 | | | | | |
| | | | | | | |
| **M08-HX** | 320.917 | 185.124 | 105.499 | 702.982 | 631.784 | 1148.025 |
| SE | -1.483 | -6.956 | 3.829 | -1.808 | -1.566 | -0.985 |
| UE | 1.483 | 6.9561 | 3.829 | 1.808 | 1.566 | 0.985 |
| MSEPB | -0.310 | | | | | |
| MUEPB | 0.574 | | | | | |
| | | | | | | |
| **CAM-B3LYP** | 325.005 | 188.188 | 98.968 | 704.778 | 633.762 | 1149.725 |
| SE | 2.605 | -3.892 | -2.702 | -0.012 | 0.412 | 0.715 |
| UE | 2.605 | 3.892 | 2.702 | 0.012 | 0.412 | 0.715 |
| MSEPB | -0.10 | | | | | |
| MUEPB | 0.357 | | | | | |

[a] from the tabulation in "Optimized Parameters for Scaling Correlation Energy," P. L. Fast, J. Corchado, M. L. Sanchez, and D. G. Truhlar, Journal of Physical Chemistry A **103**, 3139-3143 (1999).

[b] from the tabulation in "Small Representative Benchmarks for Thermochemical Calculations," B. J. Lynch and D. G. Truhlar, Journal of Physical Chemistry A **107**, 8996-8999 (2003); erratum: **108**, 1460 (2003).

## 2. ABDE4 database

| Unit: a.u. | $C_2H_6$ | $C_2H_6O$ | $C_4H_{10}$ | $C_4H_{10}O$ | $CH_3$ | $CH_3O$ | *i*-Pr |
|---|---|---|---|---|---|---|---|
| **M06-2X** | -79.8340046 | -155.0062433 | -158.4154472 | -233.6257087 | -39.8231203 | -115.0372714 | -118.4424147 |
| **M08-HX** | -79.8017933 | -155.0289020 | -158.4715129 | -233.6724047 | -39.8395373 | -115.0457509 | -118.4822882 |
| **CAM-B3LYP** | -79.8016994 | -155.0093313 | -158.4066137 | -233.6209615 | -39.8262034 | -115.0465436 | -118.4399270 |

| | **Experiment**[a] | **Calculated** | **SE** | **UE** |
|---|---|---|---|---|
| | **kcal/mol** | **kcal/mol** | **kcal/mol** | **kcal/mol** |
| $H_3C$-$CH_3$ | | | | |
| **M06-2X** | 97.39 | 97.220 | -0.170 | 0.170 |
| **M08-HX** | 97.39 | 97.611 | 0.221 | 0.221 |
| **CAM-B3LYP** | 97.39 | 93.683 | -3.707 | 3.707 |
| $H_3C$-$CH(CH_3)_2$ | | | | |
| **M06-2X** | 95.00 | 93.930 | -1.070 | 1.070 |
| **M08-HX** | 95.00 | 94.071 | -0.929 | 0.929 |
| **CAM-B3LYP** | 95.00 | 88.155 | -6.845 | 6.845 |
| $H_3CO$-$CH_3$ | | | | |
| **M06-2X** | 89.79 | 90.119 | 0.329 | 0.329 |
| **M08-HX** | 89.79 | 91.523 | 1.733 | 1.733 |
| **CAM-B3LYP** | 89.79 | 85.708 | -4.08 | 4.082 |
| $H_3CO$-$CH(CH_3)_2$ | | | | |
| **M06-2X** | 91.51 | 90.591 | -0.919 | 0.919 |
| **M08-HX** | 91.51 | 91.631 | 0.121 | 0.121 |
| **CAM-B3LYP** | 91.51 | 84.394 | -7.116 | 7.116 |
| | | | | |
| | | | **MSE** | **MUE** |
| **M06-2X** | | | 0.286 | 0.751 |
| **M08-HX** | | | -0.457 | 0.622 |
| **CAM-B3LYP** | | | -5.438 | 5.438 |

[a] from the tabulation in "A New Local Density Functional for Main Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions," Y. Zhao and D. G. Truhlar, Journal of Chemical Physics **125**, 194101/1-18 (2006).

**Details of the calculations on which Table 4 is based**

CpC denotes counterpoise correction

1. **With CpC (units: kcal/mol)**

| **M06-2X/ def2-TZVP** | | Best estimate | calc. | Signed error | Unsigned error |
|---|---|---|---|---|---|
| **HB7A** | **Hydrogen bonded** | | | | |
| | $(NH_3)_2$ ($C_{2h}$) | -3.17 | -3.49 | -0.32 | 0.32 |
| | $(H_2O)_2$ ($C_s$) | -5.02 | -5.40 | -0.38 | 0.38 |
| | Formic acid dimer | -18.80 | -18.77 | 0.03 | 0.03 |
| | formamide dimer | -16.12 | -15.51 | 0.61 | 0.61 |
| | uracil dimer | -20.69 | -19.29 | 1.40 | 1.40 |
| | 2-pyridoxine-2-amino-pyridine | -17.00 | -15.44 | 1.56 | 1.56 |
| | adenine_thymine (WC) | -16.74 | -14.88 | 1.86 | 1.86 |
| **D8A** | **Dispersion-dominated** | | | | |
| | $(CH_4)_2$ | -0.53 | -0.41 | 0.12 | 0.12 |
| | $(C_2H_4)_2$ | -1.50 | -1.38 | 0.12 | 0.12 |
| | benzene-$CH_4$ | -1.45 | -1.30 | 0.15 | 0.15 |
| | benzene dimer (stacked) | -2.62 | -2.28 | 0.34 | 0.34 |
| | pyrazine dimer | -4.20 | -3.76 | 0.44 | 0.44 |
| | indole-benzene (stacked) | -4.59 | -4.14 | 0.45 | 0.45 |
| | uracil dimer ($C_2$) | -9.74 | -9.52 | 0.22 | 0.22 |
| | adenine-thymine (stacked) | -11.66 | -11.82 | -0.16 | 0.16 |
| **M7A** | **Mixed** | | | | |
| | Ethylene–acetylene | -1.51 | -1.31 | 0.19 | 0.19 |
| | benzene-water | -3.29 | -3.55 | -0.26 | 0.26 |
| | benzene-$NH_3$ | -2.32 | -2.29 | 0.03 | 0.03 |
| | benzene-HCN | -4.55 | -4.80 | -0.25 | 0.25 |
| | benzene dimer (T-shaped) | -2.71 | -2.16 | 0.55 | 0.55 |
| | indole-benzene (T-shaped) | -5.62 | -4.84 | 0.78 | 0.78 |
| | phenol dimer | -7.09 | -6.48 | 0.61 | 0.61 |

.

| **M08-HX/ def2-TZVP** | | Best estimate | calc. | Signed error | Unsigned error |
|---|---|---|---|---|---|
| **HB7A** | **Hydrogen bonded** | | | | |
| | $(NH_3)_2$ ($C_{2h}$) | -3.17 | -3.70 | -0.53 | 0.53 |
| | $(H_2O)_2$ ($C_s$) | -5.02 | -5.49 | -0.47 | 0.47 |
| | Formic acid dimer | -18.80 | -18.27 | 0.53 | 0.53 |
| | formamide dimer | -16.12 | -15.68 | 0.44 | 0.44 |
| | uracil dimer | -20.69 | -19.52 | 1.17 | 1.17 |
| | 2-pyridoxine-2-amino-pyridine | -17.00 | -15.59 | 1.41 | 1.41 |
| | adenine_thymine (WC) | -16.74 | -15.03 | 1.71 | 1.71 |
| **D8A** | **Dispersion-dominated** | | | | |
| | $(CH_4)_2$ | -0.53 | -0.15 | 0.38 | 0.38 |
| | $(C_2H_4)_2$ | -1.50 | -1.44 | 0.06 | 0.06 |
| | benzene-$CH_4$ | -1.45 | -1.46 | -0.01 | 0.01 |
| | benzene dimer (stacked) | -2.62 | -2.01 | 0.61 | 0.61 |
| | pyrazine dimer | -4.20 | -3.35 | 0.85 | 0.85 |
| | indole-benzene (stacked) | -4.59 | -3.82 | 0.77 | 0.77 |
| | uracil dimer ($C_2$) | -9.74 | -8.68 | 1.06 | 1.06 |
| | adenine-thymine (stacked) | -11.66 | -11.10 | 0.56 | 0.56 |
| **M7A** | **Mixed** | | | | |
| | Ethylene–acetylene | -1.51 | -1.46 | 0.05 | 0.05 |
| | benzene-water | -3.29 | -3.49 | -0.20 | 0.20 |
| | benzene-$NH_3$ | -2.32 | -2.35 | -0.03 | 0.03 |
| | benzene-HCN | -4.55 | -5.04 | -0.49 | 0.49 |
| | benzene dimer (T-shaped) | -2.71 | -2.06 | 0.65 | 0.65 |
| | indole-benzene (T-shaped) | -5.62 | -4.77 | 0.85 | 0.85 |
| | phenol dimer | -7.09 | -6.33 | 0.76 | 0.76 |

| **CAM-B3LYP/ def2-TZVP** | | Best estimate | calc. | Signed error | Unsigned error |
|---|---|---|---|---|---|
| **HB7A** | **Hydrogen bonded** | | | | |
| | $(NH_3)_2$ ($C_{2h}$) | -3.17 | -3.10 | 0.07 | 0.07 |
| | $(H_2O)_2$ ($C_s$) | -5.02 | -5.60 | -0.58 | 0.58 |
| | Formic acid dimer | -18.80 | -19.12 | -0.32 | 0.32 |
| | formamide dimer | -16.12 | -15.43 | 0.69 | 0.69 |
| | uracil dimer | -20.69 | -19.41 | 1.28 | 1.28 |
| | 2-pyridoxine-2-amino-pyridine | -17.00 | -15.12 | 1.88 | 1.88 |
| | adenine_thymine (WC) | -16.74 | -14.33 | 2.41 | 2.41 |
| **D8A** | **Dispersion-dominated** | | | | |
| | $(CH_4)_2$ | -0.53 | 0.06 | 0.59 | 0.59 |
| | $(C_2H_4)_2$ | -1.50 | -0.21 | 1.29 | 1.29 |
| | benzene-$CH_4$ | -1.45 | 0.06 | 1.51 | 1.51 |
| | benzene dimer (stacked) | -2.62 | 2.31 | 4.93 | 4.93 |
| | pyrazine dimer | -4.20 | 0.87 | 5.07 | 5.07 |
| | indole-benzene (stacked) | -4.59 | 2.66 | 7.25 | 7.25 |
| | uracil dimer ($C_2$) | -9.74 | -3.41 | 6.33 | 6.33 |
| | adenine-thymine (stacked) | -11.66 | -2.07 | 9.59 | 9.59 |
| **M7A** | **Mixed** | | | | |
| | Ethylene–acetylene | -1.51 | -0.98 | 0.53 | 0.53 |
| | benzene-water | -3.29 | -2.10 | 1.19 | 1.19 |
| | benzene-$NH_3$ | -2.32 | -0.89 | 1.43 | 1.43 |
| | benzene-HCN | -4.55 | -3.06 | 1.49 | 1.49 |
| | benzene dimer (T-shaped) | -2.71 | -0.02 | 2.69 | 2.69 |
| | indole-benzene (T-shaped) | -5.62 | -1.95 | 3.67 | 3.67 |

**Details of the calculations on which Table 4 is based (continued)**

**2. Without CpC (units: kcal/mol)**

| **M06-2X/ def2-TZVP** | | Best estimate | calc. | Signed error | Unsigned error |
|---|---|---|---|---|---|
| **HB7A** | **Hydrogen bonded** | | | | |
| | $(NH_3)_2$ ($C_{2h}$) | -3.17 | -3.79 | -0.62 | 0.62 |
| | $(H_2O)_2$ ($C_s$) | -5.02 | -5.90 | -0.88 | 0.88 |
| | Formic acid dimer | -18.80 | -19.30 | -0.50 | 0.50 |
| | formamide dimer | -16.12 | -15.98 | 0.14 | 0.14 |
| | uracil dimer | -20.69 | -19.66 | 1.03 | 1.03 |
| | 2-pyridoxine-2-amino-pyridine | -17.00 | -15.92 | 1.08 | 1.08 |
| | adenine_thymine (WC) | -16.74 | -15.34 | 1.40 | 1.40 |
| **D8A** | **Dispersion-dominated** | | | | |
| | $(CH_4)_2$ | -0.53 | -0.45 | 0.08 | 0.08 |
| | $(C_2H_4)_2$ | -1.50 | -1.44 | 0.06 | 0.06 |
| | benzene-$CH_4$ | -1.45 | -1.37 | 0.08 | 0.08 |
| | benzene dimer (stacked) | -2.62 | -2.55 | 0.07 | 0.07 |
| | pyrazine dimer | -4.20 | -4.03 | 0.17 | 0.17 |
| | indole-benzene (stacked) | -4.59 | -4.59 | 0.00 | 0.00 |
| | uracil dimer ($C_2$) | -9.74 | -10.15 | -0.41 | 0.41 |
| | adenine-thymine (stacked) | -11.66 | -12.64 | -0.98 | 0.98 |
| **M7A** | **Mixed** | | | | |
| | Ethylene–acetylene | -1.51 | -1.40 | 0.11 | 0.11 |
| | benzene-water | -3.29 | -4.19 | -0.90 | 0.90 |
| | benzene-$NH_3$ | -2.32 | -2.59 | -0.27 | 0.27 |
| | benzene-HCN | -4.55 | -4.90 | -0.35 | 0.35 |
| | benzene dimer (T-shaped) | -2.71 | -2.31 | 0.40 | 0.40 |
| | indole-benzene (T-shaped) | -5.62 | -5.19 | 0.43 | 0.43 |
| | phenol dimer | -7.09 | -7.03 | 0.06 | 0.06 |

| **M08-HX/ def2-TZVP** | | Best estimate | calc. | Signed error | Unsigned error |
|---|---|---|---|---|---|
| **HB7A** | **Hydrogen bonded** | | | | |
| | $(NH_3)_2$ ($C_{2h}$) | -3.17 | -4.06 | -0.89 | 0.89 |
| | $(H_2O)_2$ ($C_s$) | -5.02 | -6.09 | -1.07 | 1.07 |
| | Formic acid dimer | -18.80 | -18.97 | -0.17 | 0.17 |
| | formamide dimer | -16.12 | -16.32 | -0.20 | 0.20 |
| | uracil dimer | -20.69 | -20.09 | 0.60 | 0.60 |
| | 2-pyridoxine-2-amino-pyridine | -17.00 | -16.28 | 0.72 | 0.72 |
| | adenine_thymine (WC) | -16.74 | -15.72 | 1.02 | 1.02 |
| **D8A** | **Dispersion-dominated** | | | | |
| | $(CH_4)_2$ | -0.53 | -0.18 | 0.35 | 0.35 |
| | $(C_2H_4)_2$ | -1.50 | -1.56 | -0.06 | 0.06 |
| | benzene-$CH_4$ | -1.45 | -1.54 | -0.09 | 0.09 |
| | benzene dimer (stacked) | -2.62 | -2.40 | 0.22 | 0.22 |
| | pyrazine dimer | -4.20 | -3.72 | 0.48 | 0.48 |
| | indole-benzene (stacked) | -4.59 | -4.46 | 0.13 | 0.13 |
| | uracil dimer ($C_2$) | -9.74 | -9.55 | 0.19 | 0.19 |
| | adenine-thymine (stacked) | -11.66 | -12.18 | -0.52 | 0.52 |
| **M7A** | **Mixed** | | | | |
| | Ethylene–acetylene | -1.51 | -1.60 | -0.09 | 0.09 |
| | benzene-water | -3.29 | -4.24 | -0.95 | 0.95 |
| | benzene-$NH_3$ | -2.32 | -2.73 | -0.41 | 0.41 |
| | benzene-HCN | -4.55 | -5.18 | -0.63 | 0.63 |
| | benzene dimer (T-shaped) | -2.71 | -2.31 | 0.40 | 0.40 |
| | indole-benzene (T-shaped) | -5.62 | -5.27 | 0.35 | 0.35 |
| | phenol dimer | -7.09 | -7.02 | 0.07 | 0.07 |

| **CAM-B3LYP/ def2-TZVP** | | Best estimate | calc. | Signed error | Unsigned error |
|---|---|---|---|---|---|
| **HB7A** | **Hydrogen bonded** | | | | |
| | $(NH_3)_2$ ($C_{2h}$) | -3.17 | -3.50 | -0.33 | 0.33 |
| | $(H_2O)_2$ ($C_s$) | -5.02 | -6.22 | -1.20 | 1.20 |
| | Formic acid dimer | -18.80 | -19.83 | -1.03 | 1.03 |
| | formamide dimer | -16.12 | -16.07 | 0.05 | 0.05 |
| | uracil dimer | -20.69 | -19.89 | 0.80 | 0.80 |
| | 2-pyridoxine-2-amino-pyridine | -17.00 | -15.73 | 1.27 | 1.27 |
| | adenine_thymine (WC) | -16.74 | -14.92 | 1.82 | 1.82 |
| **D8A** | **Dispersion-dominated** | | | | |
| | $(CH_4)_2$ | -0.53 | 0.01 | 0.54 | 0.54 |
| | $(C_2H_4)_2$ | -1.50 | -0.29 | 1.21 | 1.21 |
| | benzene-$CH_4$ | -1.45 | -0.03 | 1.42 | 1.42 |
| | benzene dimer (stacked) | -2.62 | 1.97 | 4.59 | 4.59 |
| | pyrazine dimer | -4.20 | 0.54 | 4.74 | 4.74 |
| | indole-benzene (stacked) | -4.59 | 2.11 | 6.70 | 6.70 |
| | uracil dimer ($C_2$) | -9.74 | -4.14 | 5.60 | 5.60 |
| | adenine-thymine (stacked) | -11.66 | -3.01 | 8.65 | 8.65 |
| **M7A** | **Mixed** | | | | |
| | Ethylene–acetylene | -1.51 | -1.09 | 0.42 | 0.42 |
| | benzene-water | -3.29 | -2.94 | 0.35 | 0.35 |
| | benzene-$NH_3$ | -2.32 | -1.27 | 1.05 | 1.05 |
| | benzene-HCN | -4.55 | -3.19 | 1.36 | 1.36 |
| | benzene dimer (T-shaped) | -2.71 | -0.23 | 2.48 | 2.48 |
| | indole-benzene (T-shaped) | -5.62 | -2.40 | 3.22 | 3.22 |
| | phenol dimer | | | | |

**Details of the calculations on which Table 4 is based (continued)**

**3. Mean signed errors and mean unsigned errors (kcal/mol) in noncovalent interaction database (S22A) with def2-TZVP basis set**

| Method | HB7A | | D8A | | Mixed7A | | S22A | |
|---|---|---|---|---|---|---|---|---|
| | MSE | MUE | MSE | MUE | MSE | MUE | MSE | MUE |
| Not Counterpoise Corrected | | | | | | | | |
| **M06-2X** | 0.24 | 0.81 | -0.12 | 0.23 | -0.08 | 0.36 | 0.01 | 0.46 |
| **M08-HX** | 0.00 | 0.67 | 0.09 | 0.25 | -0.18 | 0.42 | -0.03 | 0.44 |
| **CAM-B3LYP** | 0.20 | 0.93 | 4.18 | 4.18 | 1.54 | 1.54 | 2.07 | 2.30 |
| Counterpoise Corrected | | | | | | | | |
| **M06-2X** | 0.68 | 0.88 | 0.21 | 0.25 | 0.24 | 0.38 | 0.37 | 0.49 |
| **M08-HX** | 0.61 | 0.90 | 0.54 | 0.54 | 0.23 | 0.43 | 0.46 | 0.62 |
| **CAM-B3LYP** | 0.78 | 1.03 | 4.57 | 4.57 | 1.94 | 1.94 | 2.52 | 2.61 |

**Details of the calculations on which Table 5 is based**

| **M06-2X/MG3S** | | | | | |
|---|---|---|---|---|---|
| | | Best Est. | Calc. | SE | UE |
| **Heavy atom transfer** | | | | | |
| $H\cdot + N_2O \rightarrow OH\cdot + N_2$ | forward | 17.13 | 17.60 | 0.47 | 0.47 |
| | reverse | 82.47 | 82.26 | -0.21 | 0.21 |
| $H\cdot + ClH \rightarrow HCl + H\cdot$ | forward | 18.00 | 18.55 | 0.55 | 0.55 |
| | reverse | 18.00 | 18.55 | 0.55 | 0.55 |
| $CH_3 + FCl \rightarrow CH_3F + Cl$ | forward | 6.75 | 4.71 | -2.04 | 2.04 |
| | reverse | 60.00 | 60.55 | 0.55 | 0.55 |
| **$S_N2$** | | | | | |
| $Cl^-\cdots CH_3Cl \rightarrow ClCH_3\cdots Cl^-$ | forward | 13.41 | 13.54 | 0.13 | 0.13 |
| | reverse | 13.41 | 13.54 | 0.13 | 0.13 |
| $F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$ | forward | 3.44 | 3.24 | -0.20 | 0.20 |
| | reverse | 29.42 | 33.54 | 4.12 | 4.12 |
| $OH^- + CH_3F \rightarrow HOCH_3 + F^-$ | forward | -2.44 | -2.87 | -0.43 | 0.43 |
| | reverse | 17.66 | 17.53 | -0.13 | 0.13 |
| **Unimolecular and association reactions** | | | | | |
| $H\cdot + N_2 \rightarrow HN_2\cdot$ | forward | 14.36 | 14.11 | -0.25 | 0.25 |
| | reverse | 10.61 | 11.34 | 0.73 | 0.73 |
| $H\cdot + C_2H_4 \rightarrow CH_3CH_2\cdot$ | forward | 1.72 | 2.94 | 1.22 | 1.22 |
| | reverse | 41.75 | 43.65 | 1.90 | 1.90 |
| $HCN \rightarrow HNC$ | forward | 48.07 | 46.17 | -1.90 | 1.90 |
| | reverse | 32.82 | 33.34 | 0.52 | 0.52 |
| **Hydrogen atom transfer reactions** | | | | | |
| $OH + CH_4 \rightarrow CH_3 + H_2O$ | forward | 6.70 | 5.63 | -1.07 | 1.07 |
| | reverse | 19.60 | 17.48 | -2.12 | 2.12 |
| $H + OH \rightarrow O + H_2$ | forward | 10.70 | 9.80 | -0.90 | 0.90 |
| | reverse | 13.10 | 12.02 | -1.08 | 1.08 |
| $H + H_2S \rightarrow H_2 + HS$ | forward | 3.60 | 4.43 | 0.83 | 0.83 |
| | reverse | 17.30 | 18.71 | 1.41 | 1.41 |

| M08-HX/MG3S | | | | | |
|---|---|---|---|---|---|
| | | Best Est. | Calc. | SE | UE |
| **Heavy atom transfer** | | | | | |
| $H\cdot + N_2O \rightarrow OH\cdot + N_2$ | forward | 17.13 | 17.88 | 0.75 | 0.75 |
| | reverse | 82.47 | 82.53 | 0.06 | 0.06 |
| $H\cdot + ClH \rightarrow HCl + H\cdot$ | forward | 18.00 | 19.39 | 1.39 | 1.39 |
| | reverse | 18.00 | 19.39 | 1.39 | 1.39 |
| $CH_3 + FCl \rightarrow CH_3F + Cl$ | forward | 6.75 | 5.54 | -1.21 | 1.21 |
| | reverse | 60.00 | 58.02 | -1.98 | 1.98 |
| **$S_N2$** | | | | | |
| $Cl^-\cdots CH_3Cl \rightarrow ClCH_3\cdots Cl^-$ | forward | 13.41 | 15.24 | 1.83 | 1.83 |
| | reverse | 13.41 | 15.24 | 1.83 | 1.83 |
| $F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$ | forward | 3.44 | 4.55 | 1.11 | 1.11 |
| | reverse | 29.42 | 30.37 | 0.95 | 0.95 |
| $OH^- + CH_3F \rightarrow HOCH_3 + F^-$ | forward | -2.44 | -4.33 | -1.89 | 1.89 |
| | reverse | 17.66 | 18.27 | 0.61 | 0.61 |
| **Unimolecular and association reactions** | | | | | |
| $H\cdot + N_2 \rightarrow HN_2\cdot$ | forward | 14.36 | 14.03 | -0.33 | 0.33 |
| | reverse | 10.61 | 11.80 | 1.19 | 1.19 |
| $H\cdot + C_2H_4 \rightarrow CH_3CH_2\cdot$ | forward | 1.72 | 2.25 | 0.53 | 0.53 |
| | reverse | 41.75 | 44.07 | 2.32 | 2.32 |
| $HCN \rightarrow HNC$ | forward | 48.07 | 46.70 | -1.37 | 1.37 |
| | reverse | 32.82 | 34.85 | 2.03 | 2.03 |
| **Hydrogen atom transfer reactions** | | | | | |
| $OH + CH_4 \rightarrow CH_3 + H_2O$ | forward | 6.70 | 6.41 | -0.29 | 0.29 |
| | reverse | 19.60 | 19.17 | -0.43 | 0.43 |
| $H + OH \rightarrow O + H_2$ | forward | 10.70 | 10.00 | -0.70 | 0.70 |
| | reverse | 13.10 | 11.37 | -1.73 | 1.73 |
| $H + H_2S \rightarrow H_2 + HS$ | forward | 3.60 | 4.15 | 0.55 | 0.55 |
| | reverse | 17.30 | 16.96 | -0.34 | 0.34 |

| CAM-B3lYP/MG3S | | | | | |
|---|---|---|---|---|---|
| | | Best Est. | Calc. | SE | UE |
| **Heavy atom transfer** | | | | | |
| $H\cdot + N_2O \rightarrow OH\cdot + N_2$ | forward | 17.13 | 13.19 | -3.94 | 3.94 |
| | reverse | 82.47 | 77.23 | -5.24 | 5.24 |
| $H\cdot + ClH \rightarrow HCl + H\cdot$ | forward | 18.00 | 15.05 | -2.95 | 2.95 |
| | reverse | 18.00 | 15.05 | -2.95 | 2.95 |
| $CH_3 + FCl \rightarrow CH_3F + Cl$ | forward | 6.75 | 2.63 | -4.12 | 4.12 |
| | reverse | 60.00 | 57.96 | -2.04 | 2.04 |
| **$S_N2$** | | | | | |
| $Cl^-\cdots CH_3Cl \rightarrow ClCH_3\cdots Cl^-$ | forward | 13.41 | 12.57 | -0.84 | 0.84 |
| | reverse | 13.41 | 12.57 | -0.84 | 0.84 |
| $F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$ | forward | 3.44 | 2.04 | -1.40 | 1.40 |
| | reverse | 29.42 | 29.27 | -0.15 | 0.15 |
| $OH^- + CH_3F \rightarrow HOCH_3 + F^-$ | forward | -2.44 | -4.43 | -1.99 | 1.99 |
| | reverse | 17.66 | 16.74 | -0.92 | 0.92 |
| **Unimolecular and association reactions** | | | | | |
| $H\cdot + N_2 \rightarrow HN_2\cdot$ | forward | 14.36 | 9.25 | -5.11 | 5.11 |
| | reverse | 10.61 | 11.95 | 1.34 | 1.34 |
| $H\cdot + C_2H_4 \rightarrow CH_3CH_2\cdot$ | forward | 1.72 | 0.28 | -1.44 | 1.44 |
| | reverse | 41.75 | 43.56 | 1.81 | 1.81 |
| $HCN \rightarrow HNC$ | forward | 48.07 | 47.39 | -0.68 | 0.68 |
| | reverse | 32.82 | 34.27 | 1.45 | 1.45 |
| **Hydrogen atom transfer reactions** | | | | | |
| $OH + CH_4 \rightarrow CH_3 + H_2O$ | forward | 6.70 | 3.53 | -3.17 | 3.17 |
| | reverse | 19.60 | 15.26 | -4.34 | 4.34 |
| $H + OH \rightarrow O + H_2$ | forward | 10.70 | 5.79 | -4.91 | 4.91 |
| | reverse | 13.10 | 6.85 | -6.25 | 6.25 |
| $H + H_2S \rightarrow H_2 + HS$ | forward | 3.60 | 0.73 | -2.87 | 2.87 |
| | reverse | 17.30 | 16.46 | -0.84 | 0.84 |

**Mean signed errors and mean unsigned errors (kcal/mol) in barrier heights of DBH24/08 database as calculated with the MG3S basis set**

| Method[a] | HATBH6 | | NSBH6 | | UABH6 | | HTBH6 | | DBH24/08 |
|---|---|---|---|---|---|---|---|---|---|
| | MSE | MUE | MSE | MUE | MSE | MUE | MSE | MUE | MUE |
| **M06-2X** | -0.02 | 0.73 | 0.60 | 0.86 | 0.37 | 1.09 | -0.49 | 1.24 | 0.98 |
| **M08-HX** | 0.07 | 1.13 | 0.74 | 1.37 | 0.73 | 1.30 | -0.49 | 0.67 | 1.12 |
| **CAM-B3LYP** | -3.54 | 3.54 | -1.02 | 1.02 | -0.44 | 1.97 | -3.73 | 3.73 | 2.57 |