

Table S1. Phosphorous Acid Vibrational Frequencies^a

| Assignment | RHF/ | | MM3 | ? ^c |
|---------------------------|---------|---------------------|------|----------------|
| | 6-31G** | scaled ^b | | |
| O-H symmetric stretching | 4162 | 3746 | 3735 | -11 |
| O-H asymmetric stretching | 4158 | 3742 | 3735 | -7 |
| P-H stretching | 2780 | 2502 | 2388 | -114 |
| P=O stretching | 1420 | 1278 | 1277 | -1 |
| P-H wag (in-plane) | 1184 | 1065 | 1116 | 51 |
| P-H wag (out-of-plane) | 1178 | 1060 | 1003 | -57 |
| O-H asymmetric wag | 1080 | 972 | 961 | -12 |
| O-H symmetric wag | 1050 | 945 | 938 | -7 |
| P-O asymmetric stretching | 1000 | 900 | 919 | 19 |
| P-O symmetric stretching | 949 | 854 | 819 | -35 |
| O=P-O asymmetric bending | 521 | 469 | 427 | -42 |
| | 443 | 398 | 427 | 29 |
| O-P-O bending | 376 | 339 | 361 | 22 |
| O-H torsion | 300 | 270 | 169 | -101 |
| | 26 | 24 | 112 | 88 |
| RMS | | | | 53 |

^aAll vibrational frequencies in this table are expressed in cm⁻¹.^bRHF/6-31G** vibrational frequencies are scaled by 0.90.^cMM3- scaled RHF/6-31G** differenceTable S2. Phosphoric Acid Vibrational Frequencies^a

| Assignment | IR ^b | RHF/ | | MM3 | ? RHF ^d |
|--|-----------------|---------|---------------------|------|--------------------|
| | | 6-31G** | scaled ^c | | |
| O-H stretching | 2700-3000 | 4176 | 3759 | 3743 | -17 |
| O-H stretching | 2370 | 4171 | 3754 | 3743 | -12 |
| Combination (O-H stretching) | 1780 | 4171 | 3754 | 3742 | -12 |
| P-O-H in-plane deformation | 1250 | 1432 | | | |
| P=O stretching | 1165 | 1432 | 1289 | 1277 | -12 |
| P(OH) ₃ degenerate stretching | 1066-1074 | 1132 | 1018 | 1045 | 27 |
| | | 1132 | 1018 | 1045 | 27 |
| | | 1124 | 1011 | 956 | -55 |
| P-O stretching | 1007 | 1017 | 916 | 916 | 0 |
| | | 1017 | 915 | 916 | 1 |
| | | 916 | 824 | 788 | -36 |
| OPO bending mode (F2 mode) | 500 | 507 | 456 | 444 | -12 |
| | | 507 | 456 | 444 | -12 |
| OPO bending mode (E mode) | 390 | 494 | 444 | 434 | -10 |
| OPO bending mode (E mode) | 345 | 404 | 363 | 342 | -21 |

| | | | | |
|-----------------|-----|-----|-----|-----------|
| | 404 | 363 | 342 | -21 |
| Torsional modes | 294 | 264 | 218 | -46 |
| | 172 | 155 | 213 | 58 |
| | 172 | 154 | 213 | 59 |
| RMS | | | | 31 |

^aAll vibrational frequencies in this table are expressed in cm⁻¹.

^bExperimental aqueous phase IR is taken from reference 38.

^cRHF/6-31G** vibrational frequencies are scaled by 0.90.

^dMM3 – scaled RHF/6-31G** difference

Table S3. Dimethylphosphinic Acid Vibrational Frequencies^a

| Assignment | RHF/ 6-31G** | scaled ^b | MM3 | ? ^c |
|---------------------------------------|-----------------|---------------------|------|----------------|
| O-H stretching | 4162 | 3746 | 3730 | -16 |
| CH ₃ asymmetric stretching | 3290 | 2961 | 3003 | 42 |
| | 3289 | 2960 | 3003 | 43 |
| | 3287 | 2958 | 3003 | 45 |
| | 3283 | 2954 | 3002 | 48 |
| CH ₃ symmetric stretching | 3201 | 2881 | 2902 | 21 |
| | 3197 | 2878 | 2902 | 24 |
| CH ₃ asymmetric bending | 1593 | 1433 | 1434 | 1 |
| | 1587 | 1428 | 1432 | 4 |
| | 1579 | 1421 | 1432 | 11 |
| | 1577 | 1419 | 1430 | 11 |
| CH ₃ symmetric bending | 1492 | 1343 | 1296 | -48 |
| | 1482 | 1334 | 1293 | -41 |
| P = O stretching | 1371 | 1234 | 1234 | 0 |
| P - O - H bending | 1115 | 1003 | 969 | -34 |
| CH ₃ rock | 1054 | 949 | 939 | -10 |
| | 1018 | 917 | 898 | -19 |
| CH ₃ wag | 968 | 871 | 895 | 24 |
| | 947 | 852 | 885 | 33 |
| P - O stretching | 921 | 829 | 842 | 13 |
| P - C asymmetric stretching | 808 | 728 | 747 | 19 |
| P - C symmetric stretching | 732 | 658 | 647 | -11 |
| O = P - C asymmetric bending | 427 | 385 | 426 | 41 |
| O = P - O bending | 420 | 378 | 377 | -1 |
| O - P - C asymmetric bending | 337 | 303 | 320 | 17 |
| | 308 | 277 | 280 | 3 |
| C - P - C bending | 265 | 238 | 238 | 0 |
| CH ₃ torsions | 209 | 188 | 216 | 28 |
| | 191 | 172 | 195 | 23 |
| O - H torsion | 174 | 156 | 191 | 35 |
| RMS | | | | 27 |

^a All vibrational frequencies in this table are expressed in cm^{-1} .

^b RHF/6-31G** vibrational frequencies are scaled by 0.90.

^c MM3- scaled RHF/6-31G** difference

Table S4. Dimethylphosphonate Vibrational Frequencies^a

| Assignment | IR ^b | RHF/ | | MM3 | ? RHF ^d | ? IR ^e |
|---------------------------------------|-----------------|---------|---------------------|------|--------------------|-------------------|
| | | 6-31G** | scaled ^c | | | |
| CH ₃ asymmetric stretching | 3008 | 3327 | 2994 | 3007 | 13 | -1 |
| | 3008 | 3325 | 2993 | 3007 | 14 | -1 |
| | 3008 | 3302 | 2972 | 3002 | 30 | -6 |
| | 3008 | 3296 | 2966 | 3002 | 36 | -6 |
| CH ₃ symmetric stretching | 2938 | 3218 | 2896 | 2902 | 6 | -36 |
| | 2938 | 3211 | 2890 | 2902 | 12 | -36 |
| P - H stretching | 2438 | 2747 | 2472 | 2381 | -91 | -57 |
| CH ₃ asymmetric bending | 1462 | 1640 | 1476 | 1514 | 38 | 52 |
| | 1462 | 1638 | 1475 | 1508 | 33 | 46 |
| | 1462 | 1635 | 1471 | 1472 | 1 | 10 |
| | 1462 | 1631 | 1468 | 1471 | 3 | 9 |
| CH ₃ symmetric bending | 1449 | 1619 | 1457 | 1448 | -9 | -1 |
| | 1449 | 1614 | 1453 | 1447 | -6 | -2 |
| P = O stretching | 1275 | 1400 | 1260 | 1279 | 19 | 4 |
| CH ₃ rock/wag | 1174 | 1318 | 1186 | 1194 | 8 | 20 |
| | 1174 | 1317 | 1185 | 1174 | -11 | 0 |
| | 1174 | 1291 | 1162 | 1160 | -2 | -14 |
| | 1174 | 1287 | 1158 | 1158 | 0 | -16 |
| | 1081 | 1243 | 1119 | 1131 | 12 | 50 |
| C - O asymmetric bending | 1055 | 1200 | 1080 | 1088 | 8 | 33 |
| | 1055 | 1132 | 1019 | 1048 | 29 | -7 |
| | 1055 | 1099 | 989 | 975 | -14 | -80 |
| PO ₂ asymmetric stretching | 820 | 890 | 801 | 815 | 14 | -5 |
| PO ₂ symmetric stretching | 765 | 833 | 750 | 758 | 8 | -7 |
| P - O - C symmetric bending | 526 | 606 | 545 | 514 | -31 | -12 |
| P - O - C asymmetric bending | 526 | 506 | 455 | 472 | 17 | -54 |
| PO ₃ deformation | 402 | 412 | 371 | 373 | 2 | -29 |
| | 402 | 248 | 223 | 295 | 72 | -107 |
| | 402 | 217 | 195 | 224 | 29 | -178 |
| CH ₃ torsion | 228 | 116 | 105 | 168 | 63 | -60 |
| | 228 | 104 | 94 | 150 | 56 | -78 |
| P - O - C torsion | 80 | 84 | 75 | 89 | 14 | 9 |
| | | 61 | 55 | 65 | 10 | |
| RMS | | | | | 30 | 50 |

^a All vibrational frequencies in this table are expressed in cm^{-1} .

^b Experimental liquid phase IR is taken from reference 39.

^c RHF/6-31G** vibrational frequencies are scaled by 0.90.

^d MM3 - scaled RHF/6-31G** difference

°MM3 – IR difference

Table S5. Methyl dimethylphosphinate Vibrational Frequencies^a

| Assignments | IR ^b | RHF/ | | MM3 | ? RHF ^d | ? IR ^e |
|--------------------------------------|-----------------|---------|---------------------|------|--------------------|-------------------|
| | | 6-31G** | scaled ^c | | | |
| CH ₃ O asymmetric stretch | 3005 | 3320 | 2988 | 3008 | 20 | 3 |
| CH ₃ P asymmetric stretch | 3005 | 3293 | 2964 | 3005 | 41 | 0 |
| | 3005 | 3288 | 2959 | 2993 | 34 | -12 |
| | 3005 | 3287 | 2958 | 2992 | 34 | -13 |
| CH ₃ O asymmetric stretch | 3005 | 3284 | 2955 | 2992 | 37 | -13 |
| CH ₃ P asymmetric stretch | 3005 | 3281 | 2953 | 2991 | 38 | -14 |
| CH ₃ O symmetric stretch | 2960 | 3204 | 2883 | 2904 | 21 | -56 |
| CH ₃ P symmetric stretch | 2920 | 3201 | 2881 | 2892 | 11 | -28 |
| | 2920 | 3196 | 2877 | 2891 | 14 | -29 |
| CH ₃ O asymmetric stretch | 1430 | 1640 | 1476 | 1513 | 37 | 83 |
| | 1430 | 1634 | 1471 | 1476 | 5 | 46 |
| CH ₃ O symmetric stretch | 1430 | 1617 | 1455 | 1450 | -5 | 20 |
| CH ₃ P asymmetric stretch | 1430 | 1593 | 1434 | 1436 | 2 | 6 |
| | 1430 | 1588 | 1429 | 1431 | 2 | 1 |
| | 1430 | 1580 | 1422 | 1430 | 8 | 0 |
| | 1430 | 1578 | 1420 | 1428 | 8 | -2 |
| | 1430 | 1578 | 1420 | 1428 | 8 | -2 |
| CH ₃ P symmetric stretch | 1310 | 1490 | 1341 | 1296 | -45 | -14 |
| | 1310 | 1480 | 1332 | 1293 | -39 | -17 |
| P = O stretch | 1260 | 1361 | 1225 | 1237 | 12 | -23 |
| CH ₃ O wag/rock | 1187 | 1315 | 1184 | 1175 | -9 | -13 |
| | 1187 | 1290 | 1161 | 1160 | -1 | -27 |
| C - O stretch | 1058 | 1192 | 1072 | 1061 | -11 | 3 |
| CH ₃ P wag/rock | 935 | 1049 | 944 | 910 | -34 | -25 |
| | 935 | 1026 | 923 | 898 | -25 | -37 |
| CH ₃ P wag/rock | 869 | 966 | 869 | 894 | 25 | 25 |
| | 869 | 947 | 853 | 884 | 31 | 15 |
| P - O stretch | 765 | 834 | 751 | 786 | 35 | 21 |
| PC ₂ asymmetric stretch | 743 | 808 | 727 | 747 | 20 | 4 |
| PC ₂ symmetric stretch | 680 | 729 | 656 | 657 | 1 | -23 |
| P - O - C bend | 462 | 505 | 454 | 474 | 20 | 12 |
| C - P - O asymmetric bend | 407 | 433 | 390 | 380 | -10 | -27 |
| C - P - O symmetric bend | | 334 | 300 | 324 | 24 | |
| C - P - C asymmetric bend | | 288 | 259 | 316 | 57 | |
| C - P - C symmetric bend | | 263 | 237 | 242 | 5 | |
| CH ₃ P methyl torsion | | 214 | 193 | 207 | 14 | |
| | | 199 | 179 | 198 | 19 | |
| | | 179 | 161 | 191 | 30 | |
| CH ₃ O methyl torsion | | 109 | 98 | 159 | 61 | |
| CH ₃ O torsion | | 75 | 68 | 79 | 11 | |
| RMS | | | | | 27 | 26 |

^aAll vibrational frequencies in this table are expressed in cm^{-1} .

^bExperimental gas phase IR is taken from reference 40.

^cRHF/6-31G** vibrational frequencies are scaled by 0.90.

^dMM3 – scaled RHF/6-31G** difference

^eMM3 – IR difference

Table S6. Trimethylphosphine Oxide Vibrational Frequencies^a

| Assignment | RHF/ | | MM3 | ? ^c |
|---|---------|---------------------|------|----------------|
| | 6-31G** | scaled ^b | | |
| CH ₃ asymmetric stretching | 3282 | 2952 | 2982 | 30 |
| | 3282 | 2954 | 2982 | 28 |
| | 3280 | 2954 | 2982 | 28 |
| | 3279 | 2951 | 2981 | 30 |
| | 3273 | 2946 | 2981 | 35 |
| | 3273 | 2946 | 2980 | 34 |
| CH ₃ symmetric stretching | 3195 | 2875 | 2881 | 6 |
| | 3190 | 2871 | 2881 | 10 |
| | 3190 | 2871 | 2881 | 10 |
| CH ₃ asymmetric bending | 1604 | 1444 | 1431 | -13 |
| | 1588 | 1430 | 1429 | -1 |
| | 1588 | 1430 | 1429 | -1 |
| | 1583 | 1424 | 1427 | 3 |
| | 1583 | 1424 | 1427 | 3 |
| CH ₃ asymmetric bending + CH ₃ asymmetric bending (inact) | 1572 | 1415 | 1426 | 11 |
| CH ₃ asymmetric bending | 1492 | 1342 | 1291 | -51 |
| | 1474 | 1327 | 1288 | -39 |
| | 1474 | 1327 | 1288 | -39 |
| P = O stretching | 1331 | 1198 | 1212 | 14 |
| CH ₃ rock | 1047 | 943 | 911 | -32 |
| | 1047 | 943 | 911 | -32 |
| CH ₃ wag | 1042 | 938 | 896 | -43 |
| | 952 | 856 | 884 | 28 |
| | 952 | 856 | 884 | 28 |
| CH ₃ in-plane wag (inactive) | 854 | 769 | 877 | 108 |
| P - C asymmetric stretching | 787 | 708 | 729 | 21 |
| | 787 | 708 | 729 | 21 |
| P - C symmetric stretching | 697 | 627 | 623 | -4 |
| C - P - C asymmetric bending | 380 | 342 | 376 | 34 |
| | 380 | 342 | 376 | 34 |
| C - P - O symmetric bending | 314 | 282 | 305 | 23 |
| O - P - C asymmetric bending | 252 | 227 | 236 | 9 |
| | 252 | 227 | 236 | 9 |
| CH ₃ torsions | 211 | 190 | 196 | 6 |

| | | | | |
|------------|-----|-----|-----|-----------|
| | 211 | 190 | 196 | 6 |
| | 173 | 155 | 187 | 32 |
| RMS | | | | 31 |

^aAll vibrational frequencies in this table are expressed in cm^{-1} .

^bRHF/6-31G** vibrational frequencies are scaled by 0.90.

^cMM3 – scaled RHF/6-31G** difference

Table S7. Trimethylphosphate Vibrational Frequencies^a

| Assignment | RHF/ | | | MM3 | ? RHF ^d | ? IR ^e |
|---------------------------------------|-----------------|---------|---------------------|------|--------------------|-------------------|
| | IR ^b | 6-31G** | scaled ^c | | | |
| CH ₃ asymmetric stretching | 3017 | 3323 | 2991 | 3007 | 16 | -10 |
| | 3017 | 3323 | 2990 | 3007 | 17 | -10 |
| | 3017 | 3323 | 2990 | 3007 | 17 | -10 |
| | 2964 | 3301 | 2971 | 3003 | 32 | 39 |
| | 2964 | 3301 | 2971 | 3003 | 32 | 39 |
| | 2964 | 3301 | 2971 | 3003 | 32 | 39 |
| CH ₃ symmetric stretching | 2861 | 3218 | 2896 | 2902 | 6 | 41 |
| | 2861 | 3216 | 2895 | 2902 | 7 | 41 |
| | 2861 | 3216 | 2895 | 2902 | 7 | 41 |
| CH ₃ asymmetric bending | 1465 | 1641 | 1477 | 1514 | 37 | 49 |
| | 1465 | 1641 | 1477 | 1514 | 37 | 49 |
| | 1465 | 1640 | 1476 | 1513 | 37 | 48 |
| | 1465 | 1632 | 1469 | 1476 | 7 | 11 |
| | 1465 | 1631 | 1468 | 1476 | 8 | 11 |
| | 1465 | 1631 | 1468 | 1476 | 8 | 11 |
| CH ₃ symmetric bending | 1456 | 1620 | 1458 | 1451 | -7 | -5 |
| | 1456 | 1615 | 1453 | 1451 | -2 | -5 |
| | 1456 | 1615 | 1453 | 1451 | -2 | -5 |
| P = O stretching | 1284 | 1401 | 1261 | 1275 | 14 | -9 |
| CH ₃ rock | 1192 | 1321 | 1190 | 1196 | 6 | 4 |
| | 1192 | 1321 | 1189 | 1196 | 7 | 4 |
| | 1192 | 1321 | 1189 | 1168 | -21 | -24 |
| CH ₃ wag | 1192 | 1290 | 1161 | 1161 | 0 | -31 |
| | 1192 | 1290 | 1161 | 1161 | 0 | -31 |
| | 1192 | 1290 | 1161 | 1161 | 0 | -31 |
| C - O stretching | 1077 | 1231 | 1108 | 1092 | -16 | 15 |
| | 1048 | 1186 | 1067 | 1092 | 25 | 44 |
| | 1040 | 1186 | 1067 | 1027 | -40 | -13 |
| P - O asymmetric stretching | 851 | 936 | 842 | 847 | 5 | -5 |
| | 851 | 936 | 842 | 847 | 5 | -5 |
| P - O symmetric stretching | 747 | 823 | 741 | 745 | 4 | -3 |
| PO ₃ symmetric bending | 503 | 563 | 506 | 509 | 3 | 6 |
| | 503 | 563 | 506 | 509 | 3 | 6 |
| | 503 | 483 | 434 | 409 | -25 | -94 |
| PO ₃ asymmetric bending | 374 | 389 | 350 | 370 | 20 | -4 |

| | | | | | | |
|--------------------------|-----|-----|-----|-----|-----------|-----------|
| | 374 | 389 | 350 | 370 | 20 | -4 |
| P - O - C bending | 374 | 252 | 227 | 303 | 76 | -71 |
| | 242 | 211 | 190 | 214 | 24 | -28 |
| | 192 | 211 | 190 | 214 | 24 | 22 |
| CH ₃ torsions | | 124 | 111 | 155 | 44 | |
| | | 114 | 102 | 149 | 47 | |
| | | 114 | 102 | 149 | 47 | |
| O = P - O - C torsions | | 90 | 81 | 83 | 2 | |
| | | 60 | 54 | 76 | 22 | |
| | | 60 | 54 | 76 | 22 | |
| RMS | | | | | 25 | 31 |

^aAll vibrational frequencies in this table are expressed in cm⁻¹.

^bExperimental liquid phase IR is taken from reference 41.

^cRHF/6-31G** vibrational frequencies are scaled by 0.90.

^dMM3 - scaled RHF/6-31G** difference

^eMM3 - IR difference

Table S8. Dimethylmethylphosphonate Vibrational Frequencies^a

| Assignment | RHF/ | | MM3 | ? IR ^d | ? RHF ^e | |
|--------------------------------------|-----------------|---------|------|-------------------|--------------------|---------------------|
| | IR ^b | 6-31G** | | | | scaled ^c |
| CH ₃ O asymmetric stretch | 3017 | 3324 | 2992 | 3008 | -9 | 16 |
| | 3017 | 3319 | 2987 | 3007 | -10 | 20 |
| | 3017 | 3303 | 2973 | 3004 | -13 | 31 |
| | 3017 | 3298 | 2968 | 3003 | -14 | 34 |
| CH ₃ P asymmetric stretch | 3000 | 3292 | 2963 | 2999 | -1 | 37 |
| | 3000 | 3290 | 2961 | 2998 | -2 | 37 |
| CH ₃ O symmetric stretch | 2963 | 3215 | 2894 | 2903 | -60 | 10 |
| | 2963 | 3209 | 2888 | 2902 | -61 | 15 |
| CH ₃ P symmetric stretch | 2924 | 3207 | 2886 | 2898 | -26 | 12 |
| CH ₃ O asymmetric bend | 1472 | 1641 | 1477 | 1513 | 41 | 36 |
| | 1472 | 1640 | 1476 | 1513 | 41 | 37 |
| | 1472 | 1635 | 1471 | 1476 | 4 | 5 |
| | 1472 | 1631 | 1468 | 1476 | 4 | 8 |
| CH ₃ O symmetric bend | 1454 | 1618 | 1456 | 1451 | -3 | -5 |
| | 1454 | 1614 | 1452 | 1450 | -4 | -2 |
| CH ₃ P asymmetric bend | 1424 | 1586 | 1427 | 1436 | 12 | 9 |
| | 1424 | 1583 | 1424 | 1430 | 6 | 5 |
| CH ₃ P symmetric bend | 1313 | 1493 | 1344 | 1298 | -15 | -46 |
| P=O stretch | 1276 | 1384 | 1246 | 1257 | -19 | 12 |
| CH ₃ O rock | 1189 | 1318 | 1186 | 1192 | 3 | 6 |
| | 1189 | 1316 | 1184 | 1171 | -18 | -14 |
| | 1189 | 1291 | 1162 | 1162 | -28 | 0 |
| | 1189 | 1288 | 1159 | 1160 | -29 | 0 |
| C-O asymmetric stretch | 1075 | 1180 | 1062 | 1087 | 12 | 25 |
| C-O symmetric stretch | 1050 | 1210 | 1089 | 1043 | -7 | -46 |

| | | | | | | |
|-----------------------------|-----|------|-----|-----|-----------|-----------|
| CH ₃ P rock | 918 | 1023 | 920 | 905 | -14 | -16 |
| | 894 | 1007 | 906 | 896 | 2 | -10 |
| P-O asymmetric stretch | 818 | 863 | 777 | 816 | -2 | 39 |
| P-O symmetric stretch | 786 | 886 | 798 | 798 | 12 | 0 |
| P-C stretch | 714 | 772 | 695 | 694 | -20 | -1 |
| P-O-C bend | 498 | 539 | 485 | 506 | 8 | 21 |
| | 498 | 518 | 466 | 447 | -52 | -20 |
| CPO ₃ bend | 397 | 432 | 388 | 378 | -19 | -11 |
| | 397 | 320 | 288 | 323 | -74 | 35 |
| O=P-O-C torsion | | 283 | 255 | 310 | | 55 |
| | | 244 | 219 | 239 | | 19 |
| O=P-CH ₃ torsion | | 196 | 177 | 200 | | 24 |
| | | 190 | 171 | 193 | | 22 |
| P-O-CH ₃ torsion | | 119 | 107 | 162 | | 55 |
| | | 95 | 86 | 149 | | 63 |
| | | 78 | 70 | 89 | | 18 |
| | | 62 | 56 | 64 | | 8 |
| RMS | | | | | 27 | 27 |

^a All vibrational frequencies in this table are expressed in cm⁻¹.

^b Experimental gas phase IR is taken from reference 45.

^c RHF/6-31G** vibrational frequencies are scaled by 0.90.

^d MM3 - IR difference

^e MM3 - scaled RHF/6-31G** difference