# Supplementary Material

## Methyl internal rotation in fruit esters: Chain-length effect observed in the microwave spectrum of methyl hexanoate

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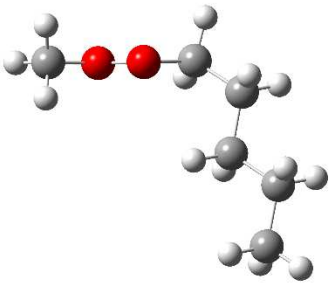
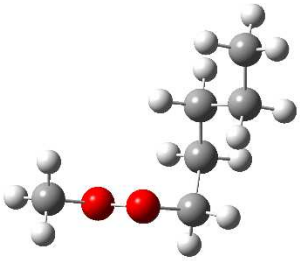
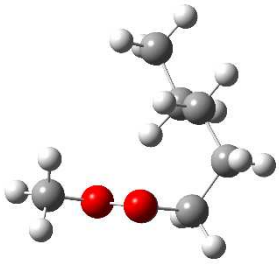
**Figure S-1.** The 14 most stable conformers of MHO obtained at the MP2/6-311++G(d,p) level of theory.



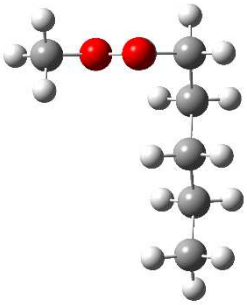
Conformer I



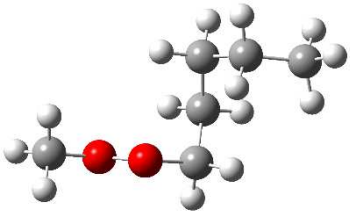
Conformer II



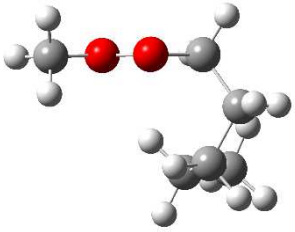
Conformer III



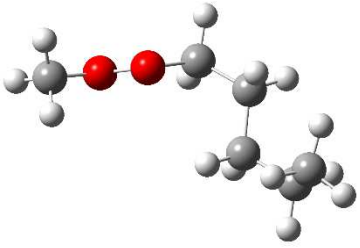
Conformer IV



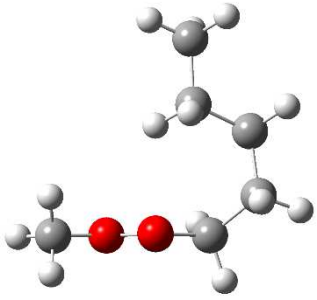
Conformer V



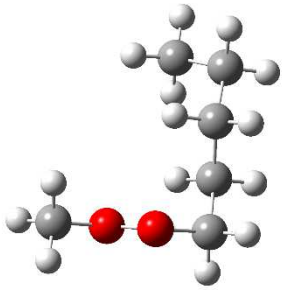
Conformer VI



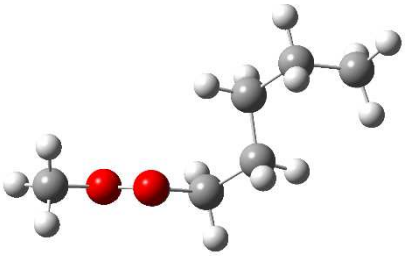
Conformer VII



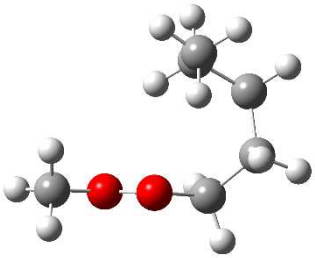
Conformer VIII



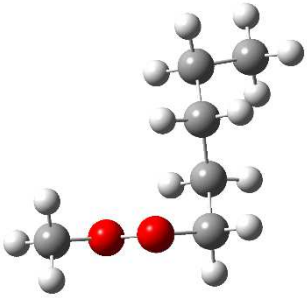
Conformer IX



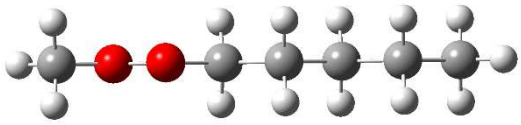
Conformer X



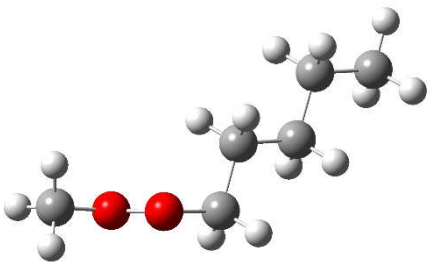
Conformer XI



Conformer XII



Conformer XIII



Conformer XIV

**Table S-1.** Rotational constants (in GHz), dipole moment components (in Debye), dihedral angles (in degress), and energies relative to that of the lowest energy conformer I ($E$ = –424.5296788 Hartree) of 25 conformers of MHO obtained at the MP2/6-311++G(d,p) level of theory with an energy cut-off at 5 kJ/mol.

| Conf. | $A$ | $B$ | $C$ | $\mu_a$ | $\mu_b$ | $\mu_c$ | $\vartheta_1$ | $\vartheta_2$ | $\vartheta_3$ | $\vartheta_4$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3101.3 | 664.2 | 616.4 | –0.37 | 0.33 | –1.62 | –146.54 | 66.52 | 179.98 | 179.95 | 0.00 |
| 2 | 2533.0 | 867.0 | 793.1 | –0.33 | –1.38 | –1.40 | 64.85 | 52.86 | 59.20 | 175.13 | 0.05 |
| 3 | 2142.4 | 1010.1 | 790.5 | –1.08 | 0.91 | 1.33 | 113.48 | –57.71 | –60.27 | –175.71 | 0.07 |
| 4 | 2548.4 | 748.8 | 691.4 | 0.70 | –0.06 | –2.07 | –57.48 | –57.45 | –177.92 | –179.22 | 0.74 |
| 5 | 3159.0 | 833.2 | 799.8 | 0.13 | 1.92 | –0.45 | 63.23 | 53.71 | 56.28 | 57.98 | 1.09 |
| 6 | 2614.4 | 921.0 | 802.2 | –0.85 | –1.47 | 0.83 | –120.81 | 58.82 | 56.34 | 57.94 | 1.13 |
| 7 | 3341.2 | 695.7 | 662.8 | –0.55 | 1.28 | –1.02 | –144.95 | 66.90 | 176.74 | 63.39 | 1.67 |
| 8 | 2149.9 | 997.5 | 797.2 | 0.01 | –0.18 | –1.67 | 141.46 | –79.74 | 59.80 | 174.62 | 2.06 |
| 9 | 2510.6 | 836.2 | 734.9 | 1.12 | –0.97 | 1.54 | 58.23 | 58.34 | 175.31 | 63.15 | 2.22 |
| 10 | 4206.1 | 629.8 | 610.9 | –0.34 | 0.85 | 1.40 | 147.98 | –67.60 | 174.07 | 62.01 | 2.24 |
| 11 | 2219.7 | 1091.5 | 922.5 | –0.27 | 0.61 | 1.62 | 137.60 | –80.52 | 64.57 | 65.42 | 2.32 |
| 12 | 3142.2 | 720.1 | 674.5 | 0.94 | 0.97 | –1.70 | 56.36 | 58.38 | –176.77 | –62.90 | 3.11 |
| 13 | 6990.7 | 483.4 | 459.9 | 0.07 | –1.72 | 0.00 | 180.00 | 180.00 | 180.00 | 180.00 | 3.25 |
| 14 | 4745.5 | 519.6 | 500.5 | –0.87 | 1.71 | 0.89 | 86.46 | 178.77 | –179.79 | 179.94 | 3.26 |
| 15 | 2061.0 | 1027.6 | 859.5 | 0.43 | 0.40 | –2.07 | –49.41 | – 70.53 | 67.61 | 173.81 | 4.09 |
| 16 | 1989.6 | 1258.0 | 980.4 | 0.86 | –0.50 | –1.85 | –51.87 | – 69.31 | 71.33 | 173.81 | 4.20 |
| 17 | 3090.0 | 734.3 | 642.0 | 1.34 | –1.72 | –0.16 | 82.16 | 175.58 | 58.21 | 56.90 | 4.40 |
| 18 | 3894.4 | 667.6 | 611.3 | –0.29 | –2.03 | 0.20 | – 90.15 | 177.67 | 57.98 | 56.99 | 4.61 |
| 19 | 4969.4 | 544.2 | 513.2 | 0.30 | –1.68 | 0.55 | –167.74 | 176.04 | 62.93 | 173.77 | 4.66 |
| 20 | 5129.8 | 550.1 | 512.0 | –0.27 | –1.74 | 0.19 | 164.28 | 177.30 | 174.67 | 62.30 | 4.68 |
| 21 | 4277.3 | 576.6 | 544.6 | 1.11 | –1.86 | 0.31 | –81.94 | –174.38 | –62.56 | –174.00 | 4.71 |
| 22 | 3816.2 | 623.1 | 621.2 | –0.15 | –0.09 | 1.80 | 161.29 | –177.25 | –58.70 | –57.08 | 4.75 |
| 23 | 5085.2 | 554.7 | 529.3 | –0.57 | –1.89 | –0.54 | 88.37 | –176.57 | –62.27 | –174.05 | 4.86 |
| 24 | 3368.3 | 617.1 | 569.0 | 1.01 | 1.28 | 1.33 | –87.38 | –179.43 | 174.83 | 62.55 | 4.91 |
| 25 | 3589.3 | 584.1 | 580.7 | 0.72 | –0.64 | –1.92 | 87.47 | 178.13 | 174.95 | 62.44 | 4.93 |

**Table S-2a.** Geometry parameters in the principal axes of inertia of conformer I ($C_1$) and conformer XIII ($C_s$) of MHO calculated at the MP2/6-311++G(d,p) level of theory. The atoms are numbered according to Figure 1.

| | Conformer I | | | Conformer XIII | | |
|---|---|---|---|---|---|---|
| | ***a*** **/Å** | ***b*** **/Å** | ***c*** **/Å** | ***a*** **/Å** | ***b*** **/Å** | ***c*** **/Å** |
| C1 | –1.440017 | 0.271433 | 0.170154 | –1.793418 | 0.120542 | –0.000002 |
| O2 | –1.349420 | –0.127303 | 1.312377 | –1.942101 | 1.323858 | 0.000012 |
| O3 | –2.355283 | –0.193967 | –0.710353 | –2.824248 | –0.757881 | –0.000008 |
| C4 | –3.238542 | –1.191265 | –0.171502 | –4.123607 | –0.146083 | –0.000003 |
| H5 | –3.908161 | –1.454758 | –0.988029 | –4.831841 | –0.972573 | –0.000015 |
| H6 | –2.671713 | –2.063446 | 0.158975 | –4.254410 | 0.472937 | 0.889419 |
| H7 | –3.799877 | –0.787740 | 0.673085 | –4.254406 | 0.472959 | –0.889410 |
| C8 | –0.583281 | 1.354522 | –0.444403 | –0.469999 | –0.608490 | 0.000008 |
| H9 | –0.598886 | 1.250842 | –1.533263 | –0.450793 | –1.267327 | 0.876450 |
| H10 | –1.065686 | 2.309626 | –0.200924 | –0.450796 | –1.267360 | –0.876409 |
| C11 | 0.844808 | 1.320921 | 0.101071 | 0.727660 | 0.335591 | –0.000010 |
| H12 | 0.810463 | 1.384076 | 1.194256 | 0.672346 | 0.990072 | 0.877324 |
| H13 | 1.383809 | 2.204296 | –0.262526 | 0.672348 | 0.990038 | –0.877369 |
| C14 | 1.600719 | 0.058574 | –0.314318 | 2.056707 | –0.418990 | 0.000005 |
| H15 | 1.625125 | –0.004444 | –1.411585 | 2.104531 | –1.074485 | –0.880860 |
| H16 | 1.057172 | –0.825312 | 0.044690 | 2.104530 | –1.074452 | 0.880895 |
| C17 | 3.030452 | 0.014011 | 0.224978 | 3.270855 | 0.510277 | –0.000011 |
| H18 | 3.575577 | 0.898719 | –0.128325 | 3.220118 | 1.164009 | –0.879766 |
| H19 | 2.999453 | 0.079229 | 1.319741 | 3.220116 | 1.164041 | 0.879721 |
| C20 | 3.775370 | –1.253276 | –0.196073 | 4.595374 | –0.253753 | 0.000004 |
| H21 | 3.834264 | –1.323039 | –1.287328 | 4.673103 | –0.893921 | –0.884959 |
| H22 | 4.795566 | –1.269348 | 0.199008 | 5.451423 | 0.427567 | –0.000007 |
| H23 | 3.256830 | –2.145399 | 0.170082 | 4.673101 | –0.893889 | 0.884992 |

**Table S-2b.** Geometry parameters in the principal axes of inertia of conformer I ($C_1$) and conformer XIII ($C_s$) of MHO calculated at the MP2/cc-pVDZ level of theory. The atoms are numbered according to Figure 1.

| | Conformer I | | | Conformer XIII | | |
|---|---|---|---|---|---|---|
| | ***a*** **/Å** | ***b*** **/Å** | ***c*** **/Å** | ***a*** **/Å** | ***b*** **/Å** | ***c*** **/Å** |
| C1 | –1.436275 | 0.146521 | 0.161188 | 1.700610 | 0.103457 | 0.000391 |
| O2 | –1.185656 | –0.659136 | 1.037927 | 1.840015 | 1.311577 | 0.000017 |
| O3 | –2.566262 | 0.110624 | –0.588771 | 2.737282 | –0.773260 | –0.000001 |
| C4 | –3.456202 | –0.962861 | –0.241342 | 4.027704 | –0.141692 | –0.000408 |
| H5 | –4.311771 | –0.868571 | –0.921934 | 4.757244 | –0.961389 | –0.000696 |
| H6 | –2.962693 | –1.937741 | –0.374582 | 4.155084 | 0.487985 | –0.894353 |
| H7 | –3.784731 | –0.875530 | 0.805720 | 4.155684 | 0.487895 | 0.893515 |
| C8 | –0.573065 | 1.329560 | –0.229600 | 0.378884 | –0.635331 | 0.000254 |
| H9 | –0.571233 | 1.411385 | –1.330159 | 0.365645 | –1.302619 | –0.880452 |
| H10 | –1.087669 | 2.233616 | 0.144282 | 0.365498 | –1.302610 | 0.880963 |
| C11 | 0.844640 | 1.230265 | 0.334373 | –0.821048 | 0.308473 | 0.000142 |
| H12 | 0.782979 | 1.056642 | 1.423184 | –0.760153 | 0.971228 | –0.881595 |
| H13 | 1.357746 | 2.197870 | 0.186257 | –0.760314 | 0.971226 | 0.881891 |
| C14 | 1.669966 | 0.113718 | –0.311049 | –2.156053 | –0.438590 | 0.000020 |
| H15 | 1.717809 | 0.280132 | –1.405614 | –2.208262 | –1.101740 | 0.885781 |
| H16 | 1.158341 | –0.853383 | –0.154830 | –2.208103 | –1.101734 | –0.885754 |
| C17 | 3.092403 | 0.024345 | 0.247593 | –3.366353 | 0.498973 | –0.000085 |
| H18 | 3.604724 | 0.993987 | 0.099805 | –3.311119 | 1.160354 | 0.884829 |
| H19 | 3.040271 | –0.137074 | 1.340609 | –3.310962 | 1.160359 | –0.884984 |
| C20 | 3.910454 | –1.095055 | –0.400246 | –4.698575 | –0.253944 | –0.000205 |
| H21 | 3.998210 | –0.938563 | –1.489352 | –4.785466 | –0.899699 | 0.890639 |
| H22 | 4.929795 | –1.147249 | 0.016827 | –5.556310 | 0.438738 | –0.000279 |
| H23 | 3.428376 | –2.074850 | –0.240557 | –4.785308 | –0.899694 | –0.891068 |

**Table S-3a.** The rotational constants *A*, *B*, *C* (in MHz) of conformer I of MHO calculated at different levels of theory and their deviations to the experimental values (calc.−exp.) Δ*A*, Δ*B*, and Δ*C*, respectively (in MHz).

| **Level** | ***A*** | **Δ*A*** | ***B*** | **Δ*B*** | ***C*** | **Δ*C*** |
|---|---|---|---|---|---|---|
| B3LYP-D3/6-311G(3df,3pd) | 3747.1 | 148.1 | 617.8 | –7.6 | 577.3 | –8.5 |
| B3LYP-D3/6-311+G(3df,3pd) | 3591.1 | –7.9 | 622.7 | –2.7 | 583.6 | –2.2 |
| B3LYP-D3/6-311++G(3df,3pd) | 3588.1 | –10.9 | 622.8 | –2.6 | 583.8 | –2.0 |
| B3LYP-D3/6-311G(2d,2p) | 3751.7 | 152.7 | 617.1 | –8.3 | 576.3 | –9.5 |
| B3LYP-D3/6-311+G(2d,2p) | 3584.4 | –14.6 | 621.7 | –3.7 | 582.7 | –3.1 |
| B3LYP-D3/6-311++G(2d,2p) | 3580.5 | –18.5 | 622.0 | –3.4 | 583.0 | –2.8 |
| B3LYP-D3/6-311G(2df,2pd) | 3776.9 | 177.9 | 616.7 | –8.7 | 576.0 | –9.8 |
| B3LYP-D3/6-311+G(2df,2pd) | 3602.1 | 3.1 | 621.6 | –3.8 | 582.7 | –3.1 |
| B3LYP-D3/6-311++G(2df,2pd) | 3596.7 | –2.3 | 621.9 | –3.5 | 583.0 | –2.8 |
| B3LYP-D3/6-311G(df,pd) | 3748.7 | 149.7 | 617.4 | –8.0 | 576.4 | –9.4 |
| B3LYP-D3/6-311+G(df,pd) | 3556.7 | –42.3 | 623.1 | –2.3 | 584.1 | –1.7 |
| B3LYP-D3/6-311++G(df,pd) | 3549.5 | –49.5 | 623.6 | –1.8 | 584.5 | –1.3 |
| B3LYP-D3/6-311G(d,p) | 3749.2 | 150.2 | 615.1 | –10.3 | 574.2 | –11.6 |
| B3LYP-D3/6-311+G(d,p) | 3555.1 | –43.9 | 621.0 | –4.4 | 582.1 | –3.7 |
| B3LYP-D3/6-311++G(d,p) | 3552.6 | –46.4 | 621.2 | –4.2 | 582.2 | –3.6 |
| B3LYP-D3/6-31G(d,p) | 3658.4 | 59.4 | 620.1 | –5.3 | 578.5 | –7.3 |
| B3LYP-D3/6-31+G(d,p) | 3508.5 | –90.5 | 621.3 | –4.1 | 582.4 | –3.4 |
| B3LYP-D3/6-31++G(d,p) | 3508.6 | –90.4 | 621.3 | –4.1 | 582.4 | –3.4 |
| B3LYP-D3/cc-pVDZ | 3762.4 | 163.4 | 614.9 | –10.5 | 573.1 | –12.7 |
| B3LYP-D3/cc-pVTZ | 3687.4 | 88.4 | 618.3 | –7.1 | 579.0 | –6.8 |
| B3LYP-D3/aug-cc-pVDZ | 3568.7 | –30.3 | 620.0 | –5.4 | 580.9 | –4.9 |
| B3LYP-D3/aug-cc-pVTZ | 3598.6 | –0.4 | 621.5 | –3.9 | 582.7 | –3.1 |
| B3LYP-D3BJ/6-311G(3df,3pd) | 3691.3 | 92.3 | 620.5 | –4.9 | 581.0 | –4.8 |
| B3LYP-D3BJ/6-311+G(3df,3pd) | 3499.6 | –99.4 | 627.7 | 2.3 | 589.2 | 3.4 |
| B3LYP-D3BJ/6-311++G(3df,3pd) | 3496.0 | –103.0 | 627.9 | 2.5 | 589.4 | 3.6 |
| B3LYP-D3BJ/6-311G(2d,2p) | 3699.7 | 100.7 | 619.7 | –5.7 | 579.8 | –6.0 |
| B3LYP-D3BJ/6-311+G(2d,2p) | 3500.2 | –98.8 | 626.5 | 1.1 | 588.0 | 2.2 |
| B3LYP-D3BJ/6-311++G(2d,2p) | 3494.6 | –104.4 | 626.8 | 1.4 | 588.3 | 2.5 |
| B3LYP-D3BJ/6-311G(2df,2pd) | 3730.9 | 131.9 | 618.9 | –6.5 | 579.1 | –6.7 |
| B3LYP-D3BJ/6-311+G(2df,2pd) | 3515.5 | –83.5 | 626.4 | 1.0 | 588.0 | 2.2 |
| B3LYP-D3BJ/6-311++G(2df,2pd) | 3510.8 | –88.2 | 626.7 | 1.3 | 588.3 | 2.5 |
| B3LYP-D3BJ/6-311G(df,pd) | 3685.0 | 86.0 | 620.3 | –5.1 | 580.4 | –5.4 |
| B3LYP-D3BJ/6-311+G(df,pd) | 3462.0 | –137.0 | 628.5 | 3.1 | 589.9 | 4.1 |
| B3LYP-D3BJ/6-311++G(df,pd) | 3454.7 | –144.3 | 629.1 | 3.7 | 590.3 | 4.5 |
| B3LYP-D3BJ/6-311G(d,p) | 3687.9 | 88.9 | 617.9 | –7.5 | 578.1 | –7.7 |
| B3LYP-D3BJ/6-311+G(d,p) | 3461.8 | –137.2 | 626.1 | 0.7 | 587.7 | 1.9 |
| B3LYP-D3BJ/6-311++G(d,p) | 3461.6 | –137.4 | 626.2 | 0.8 | 587.7 | 1.9 |
| B3LYP-D3BJ/6-31G(d,p) | 3588.6 | –10.4 | 623.8 | –1.6 | 582.9 | –2.9 |
| B3LYP-D3BJ/6-31+G(d,p) | 3404.1 | –194.9 | 627.4 | 2.0 | 588.7 | 2.9 |
| B3LYP-D3BJ/6-31++G(d,p) | 3402.0 | –197.0 | 627.5 | 2.1 | 588.8 | 3.0 |
| B3LYP-D3BJ/aug-cc-pVDZ | 3483.6 | –115.4 | 624.7 | –0.7 | 586.2 | 0.4 |
| B3LYP-D3BJ/aug-cc-pVTZ | 3508.2 | –90.8 | 626.4 | 1.0 | 588.2 | 2.4 |
| B3LYP-D3BJ/cc-pVDZ | 3711.7 | 112.7 | 617.3 | –8.1 | 576.5 | –9.3 |
| B3LYP-D3BJ/cc-pVTZ | 3611.4 | 12.4 | 622.0 | –3.4 | 583.6 | –2.2 |
| CAM-B3LYP-D3BJ/6-311G(d,p) | 3780.0 | 181.0 | 620.7 | –4.7 | 580.0 | –5.8 |
| CAM-B3LYP-D3BJ/6-311+G(d,p) | 3590.7 | –8.3 | 626.3 | 0.9 | 587.5 | 1.7 |
| CAM-B3LYP-D3BJ/6-311++G(d,p) | 3587.4 | –11.6 | 626.5 | 1.1 | 587.7 | 1.9 |
| CAM-B3LYP-D3BJ/aug-cc-pVDZ | 3600.6 | 1.6 | 625.3 | –0.1 | 586.4 | 0.6 |
| CAM-B3LYP-D3BJ/aug-cc-pVTZ | 3620.7 | 21.7 | 627.6 | 2.2 | 588.9 | 3.1 |

| | | | | | | |
|---|---|---|---|---|---|---|
| CAM-B3LYP-D3BJ/cc-pVDZ | 3793.9 | 194.9 | 620.6 | –4.8 | 578.7 | –7.1 |
| CAM-B3LYP-D3BJ/cc-pVTZ | 3716.4 | 117.4 | 623.9 | –1.5 | 584.8 | –1.0 |
| M06-2X/6-311G(3df,3pd) | 3776.9 | 177.9 | 626.9 | 1.5 | 584.6 | –1.2 |
| M06-2X/6-311+G(3df,3pd) | 3695.5 | 96.5 | 629.2 | 3.8 | 587.7 | 1.9 |
| M06-2X/6-311++G(3df,3pd) | 3691.7 | 92.7 | 629.4 | 4.0 | 587.9 | 2.1 |
| M06-2X/6-311G(df,pd) | 3772.9 | 173.9 | 626.5 | 1.1 | 584.0 | –1.8 |
| M06-2X/6-311+G(df,pd) | 3659.4 | 60.4 | 630.0 | 4.6 | 588.5 | 2.7 |
| M06-2X/6-311++G(df,pd) | 3647.5 | 48.5 | 630.7 | 5.3 | 589.2 | 3.4 |
| M06-2X/6-311G(d,p) | 3773.9 | 174.9 | 624.7 | –0.7 | 582.3 | –3.5 |
| M06-2X/6-311+G(d,p) | 3660.8 | 61.8 | 628.1 | 2.7 | 586.8 | 1.0 |
| M06-2X/6-311++G(d,p) | 3653.5 | 54.5 | 628.5 | 3.1 | 587.2 | 1.4 |
| M06-2X/6-31G(d,p) | 3716.0 | 117.0 | 628.4 | 3.0 | 585.1 | –0.7 |
| M06-2X/6-31+G(d,p) | 3641.5 | 42.5 | 627.7 | 2.3 | 586.2 | 0.4 |
| M06-2X/6-31++G(d,p) | 3639.5 | 40.5 | 627.8 | 2.4 | 586.3 | 0.5 |
| M06-2X-aug-cc-pVDZ | 3664.9 | 65.9 | 628.2 | 2.8 | 586.5 | 0.7 |
| M06-2X-aug-cc-pVTZ | 3691.6 | 92.6 | 628.7 | 3.3 | 587.6 | 1.8 |
| M06-2X-cc-pVDZ | 3778.3 | 179.3 | 625.6 | 0.2 | 582.1 | –3.7 |
| M06-2X-cc-pVTZ | 3744.4 | 145.4 | 626.7 | 1.3 | 585.3 | –0.5 |
| MP2/6-311G(3df,3pd) | 3590.8 | –8.2 | 639.0 | 13.6 | 595.7 | 9.9 |
| MP2/6-311G(2d,2p) | 3620.2 | 21.2 | 634.0 | 8.6 | 591.1 | 5.3 |
| MP2/6-311+G(2d,2p) | 3361.9 | –237.1 | 646.7 | 21.3 | 603.7 | 17.9 |
| MP2/6-311++G(2d,2p) | 3353.2 | –245.8 | 647.2 | 21.8 | 604.1 | 18.3 |
| MP2/6-311G(2df,2pd) | 3659.8 | 60.8 | 636.1 | 10.7 | 592.9 | 7.1 |
| MP2/6-311+G(2df,2pd) | 3397.5 | –201.5 | 648.5 | 23.1 | 605.4 | 19.6 |
| MP2/6-311++G(2df,2pd) | 3387.9 | –211.1 | 649.0 | 23.6 | 605.9 | 20.1 |
| MP2/6-311G(df,pd) | 3458.9 | –140.1 | 644.4 | 19.0 | 601.7 | 15.9 |
| MP2/6-311+G(df,pd) | 3120.6 | –478.4 | 669.4 | 44.0 | 621.0 | 35.2 |
| MP2/6-311++G(df,pd) | 3117.7 | –481.3 | 669.7 | 44.3 | 621.1 | 35.3 |
| MP2/6-311G(d,p) | 3445.3 | –153.7 | 638.7 | 13.3 | 596.7 | 10.9 |
| MP2/6-311+G(d,p) | 3105.8 | –493.2 | 663.7 | 38.3 | 616.1 | 30.3 |
| ***MP2/6-311++G(d,p)*** | ***3101.3*** | ***–497.7*** | ***664.2*** | ***38.8*** | ***616.4*** | ***30.6*** |
| MP2/6-31G(d,p) | 3524.1 | –74.9 | 635.0 | 9.6 | 592.7 | 6.9 |
| MP2/6-31+G(d,p) | 3135.3 | –463.7 | 659.0 | 33.6 | 613.0 | 27.2 |
| MP2/6-31++G(d,p) | 3050.4 | –548.6 | 666.9 | 41.5 | 618.3 | 32.5 |
| MP2/aug-cc-pVDZ | 3095.3 | –503.7 | 661.3 | 35.9 | 613.1 | 27.3 |
| **MP2/cc-pVDZ** | **3598.9** | **–0.1** | **626.6** | **1.2** | **584.6** | **–1.2** |
| MP2/cc-pVTZ | 3503.5 | –95.5 | 640.5 | 15.1 | 598.5 | 12.7 |
| ωB97X-D/6-311G(d,p) | 3552.3 | –46.7 | 625.6 | 0.2 | 587.5 | 1.7 |
| ωB97X-D/6-311+G(d,p) | 3549.4 | –49.6 | 625.8 | 0.4 | 587.7 | 1.9 |
| ωB97X-D/6-311++G(d,p) | 3730.9 | 131.9 | 619.7 | –5.7 | 580.2 | –5.6 |
| ωB97X-D/aug-cc-pVDZ | 3573.1 | –25.9 | 623.5 | –1.9 | 585.4 | –0.4 |
| ωB97X-D/aug-cc-pVTZ | 3597.1 | –1.9 | 625.2 | –0.2 | 587.7 | 1.9 |
| ωB97X-D/cc-pVDZ | 3749.1 | 150.1 | 618.1 | –7.3 | 578.0 | –7.8 |
| ωB97X-D/cc-pVTZ | 3685.0 | 86.0 | 621.4 | –4.0 | 583.6 | –2.2 |
| **Expt.** | **3599.0** | | **625.4** | | **585.8** | |

**Table S-3b.** The rotational constants *A*, *B*, *C* (in MHz) of conformer XIII of MHO calculated at different levels of theory and their deviations to the experimental values (calc.−exp.) Δ*A*, Δ*B*, and Δ*C*, respectively (in MHz).

| **Level** | ***A*** | **Δ*A*** | ***B*** | **Δ*B*** | ***C*** | **Δ*C*** |
|---|---|---|---|---|---|---|
| B3LYP-D3/6-311G(3df,3pd) | 7057.8 | 70.4 | 482.2 | –1.5 | 458.9 | –1.5 |
| B3LYP-D3/6-311+G(3df,3pd) | 7047.3 | 59.9 | 481.4 | –2.3 | 458.2 | –2.2 |
| B3LYP-D3/6-311++G(3df,3pd) | 7047.4 | 60.0 | 481.4 | –2.3 | 458.2 | –2.2 |
| B3LYP-D3/6-311G(2d,2p) | 7056.6 | 69.2 | 481.6 | –2.1 | 458.4 | –2.0 |
| B3LYP-D3/6-311+G(2d,2p) | 7037.7 | 50.3 | 480.8 | –2.9 | 457.6 | –2.8 |
| B3LYP-D3/6-311++G(2d,2p) | 7037.7 | 50.3 | 480.8 | –2.9 | 457.6 | –2.8 |
| B3LYP-D3/6-311G(2df,2pd) | 7060.1 | 72.7 | 482.1 | –1.6 | 458.9 | –1.5 |
| B3LYP-D3/6-311+G(2df,2pd) | 7042.6 | 55.2 | 481.3 | –2.4 | 458.1 | –2.3 |
| B3LYP-D3/6-311++G(2df,2pd) | 7042.7 | 55.3 | 481.3 | –2.4 | 458.1 | –2.3 |
| B3LYP-D3/6-311G(df,pd) | 7040.5 | 53.1 | 481.5 | –2.2 | 458.2 | –2.2 |
| B3LYP-D3/6-311+G(df,pd) | 7026.0 | 38.6 | 480.7 | –3.0 | 457.5 | –2.9 |
| B3LYP-D3/6-311++G(df,pd) | 7026.1 | 38.7 | 480.7 | –3.0 | 457.5 | –2.9 |
| B3LYP-D3/6-311G(d,p) | 7022.0 | 34.6 | 480.1 | –3.6 | 457.0 | –3.4 |
| B3LYP-D3/6-311+G(d,p) | 7005.7 | 18.3 | 479.4 | –4.3 | 456.2 | –4.2 |
| B3LYP-D3/6-311++G(d,p) | 7005.7 | 18.3 | 479.4 | –4.3 | 456.2 | –4.2 |
| B3LYP-D3/6-31G(d,p) | 6996.4 | 9.0 | 480.1 | –3.6 | 456.9 | –3.5 |
| B3LYP-D3/6-31+G(d,p) | 6974.1 | –13.3 | 478.4 | –5.3 | 455.2 | –5.2 |
| B3LYP-D3/6-31++G(d,p) | 6973.9 | –13.5 | 478.4 | –5.3 | 455.2 | –5.2 |
| B3LYP-D3/cc-pVDZ | 6983.7 | –3.7 | 480.2 | –3.5 | 457.0 | –3.4 |
| B3LYP-D3/cc-pVTZ | 7039.5 | 52.1 | 481.6 | –2.1 | 458.4 | –2.0 |
| B3LYP-D3/aug-cc-pVDZ | 6972.7 | –14.7 | 479.3 | –4.4 | 456.1 | –4.3 |
| B3LYP-D3/aug-cc-pVTZ | 7035.7 | 48.3 | 481.3 | –2.4 | 458.0 | –2.4 |
| B3LYP-D3BJ/6-311G(3df,3pd) | 7065.6 | 78.2 | 482.9 | –0.8 | 459.7 | –0.7 |
| B3LYP-D3BJ/6-311+G(3df,3pd) | 7054.3 | 66.9 | 482.2 | –1.5 | 459.0 | –1.4 |
| B3LYP-D3BJ/6-311++G(3df,3pd) | 7054.4 | 67.0 | 482.2 | –1.5 | 459.0 | –1.4 |
| B3LYP-D3BJ/6-311G(2d,2p) | 7064.6 | 77.2 | 482.4 | –1.3 | 459.2 | –1.2 |
| B3LYP-D3BJ/6-311+G(2d,2p) | 7045.0 | 57.6 | 481.6 | –2.1 | 458.3 | –2.1 |
| B3LYP-D3BJ/6-311++G(2d,2p) | 7044.9 | 57.5 | 481.6 | –2.1 | 458.3 | –2.1 |
| B3LYP-D3BJ/6-311G(2df,2pd) | 7067.9 | 80.5 | 482.9 | –0.8 | 459.7 | –0.7 |
| B3LYP-D3BJ/6-311+G(2df,2pd) | 7049.6 | 62.2 | 482.1 | –1.6 | 458.8 | –1.6 |
| B3LYP-D3BJ/6-311++G(2df,2pd) | 7049.7 | 62.3 | 482.1 | –1.6 | 458.8 | –1.6 |
| B3LYP-D3BJ/6-311G(df,pd) | 7048.2 | 60.8 | 482.2 | –1.5 | 459.0 | –1.4 |
| B3LYP-D3BJ/6-311+G(df,pd) | 7033.0 | 45.6 | 481.4 | –2.3 | 458.2 | –2.2 |
| B3LYP-D3BJ/6-311++G(df,pd) | 7033.0 | 45.6 | 481.4 | –2.3 | 458.2 | –2.2 |
| B3LYP-D3BJ/6-311G(d,p) | 7029.5 | 42.1 | 480.9 | –2.8 | 457.7 | –2.7 |
| B3LYP-D3BJ/6-311+G(d,p) | 7012.7 | 25.3 | 480.1 | –3.6 | 457.0 | –3.4 |
| B3LYP-D3BJ/6-311++G(d,p) | 7012.7 | 25.3 | 480.1 | –3.6 | 457.0 | –3.4 |
| B3LYP-D3BJ/6-31G(d,p) | 7004.6 | 17.2 | 480.9 | –2.8 | 457.6 | –2.8 |
| B3LYP-D3BJ/6-31+G(d,p) | 6981.5 | –5.9 | 479.2 | –4.5 | 456.0 | –4.4 |
| B3LYP-D3BJ/6-31++G(d,p) | 6981.2 | –6.2 | 479.2 | –4.5 | 456.0 | –4.4 |
| B3LYP-D3BJ/aug-cc-pVDZ | 6980.0 | –7.4 | 480.0 | –3.7 | 456.8 | –3.6 |
| B3LYP-D3BJ/aug-cc-pVTZ | 7042.6 | 55.2 | 482.1 | –1.6 | 458.8 | –1.6 |
| B3LYP-D3BJ/cc-pVDZ | 6991.3 | 3.9 | 480.9 | –2.8 | 457.7 | –2.7 |
| B3LYP-D3BJ/cc-pVTZ | 7046.6 | 59.2 | 482.4 | –1.3 | 459.1 | –1.3 |
| CAM-B3LYP-D3BJ/6-311G(d,p) | 7094.9 | 107.5 | 484.9 | 1.2 | 461.6 | 1.2 |
| CAM-B3LYP-D3BJ/6-311+G(d,p) | 7078.7 | 91.3 | 484.1 | 0.4 | 460.8 | 0.4 |
| CAM-B3LYP-D3BJ/6-311++G(d,p) | 7078.5 | 91.1 | 484.1 | 0.4 | 460.8 | 0.4 |
| CAM-B3LYP-D3BJ/aug-cc-pVDZ | 7049.4 | 62.0 | 483.9 | 0.2 | 460.6 | 0.2 |
| CAM-B3LYP-D3BJ/aug-cc-pVTZ | 7107.8 | 120.4 | 486.1 | 2.4 | 462.7 | 2.3 |

| | | | | | | |
|---|---|---|---|---|---|---|
| CAM-B3LYP-D3BJ/cc-pVDZ | 7059.4 | 72.0 | 484.8 | 1.1 | 461.5 | 1.1 |
| CAM-B3LYP-D3BJ/cc-pVTZ | 7111.7 | 124.3 | 486.5 | 2.8 | 463.1 | 2.7 |
| M06-2X/6-311G(3df,3pd) | 7130.0 | 142.6 | 487.3 | 3.6 | 463.9 | 3.5 |
| M06-2X/6-311+G(3df,3pd) | 7121.6 | 134.2 | 486.7 | 3.0 | 463.3 | 2.9 |
| M06-2X/6-311++G(3df,3pd) | 7121.6 | 134.2 | 486.7 | 3.0 | 463.3 | 2.9 |
| M06-2X/6-311G(df,pd) | 7110.2 | 122.8 | 486.6 | 2.9 | 463.2 | 2.8 |
| M06-2X/6-311+G(df,pd) | 7099.0 | 111.6 | 486.0 | 2.3 | 462.6 | 2.2 |
| M06-2X/6-311++G(df,pd) | 7098.9 | 111.5 | 486.0 | 2.3 | 462.6 | 2.2 |
| M06-2X/6-311G(d,p) | 7096.4 | 109.0 | 485.6 | 1.9 | 462.3 | 1.9 |
| M06-2X/6-311+G(d,p) | 7084.1 | 96.7 | 485.1 | 1.4 | 461.7 | 1.3 |
| M06-2X/6-311++G(d,p) | 7083.9 | 96.5 | 485.1 | 1.4 | 461.7 | 1.3 |
| M06-2X/6-31G(d,p) | 7073.7 | 86.3 | 485.6 | 1.9 | 462.2 | 1.8 |
| M06-2X/6-31+G(d,p) | 7055.4 | 68.0 | 484.2 | 0.5 | 460.9 | 0.5 |
| M06-2X/6-31++G(d,p) | 7055.1 | 67.7 | 484.2 | 0.5 | 460.9 | 0.5 |
| M06-2X-aug-cc-pVDZ | 7060.6 | 73.2 | 485.1 | 1.4 | 461.8 | 1.4 |
| M06-2X-aug-cc-pVTZ | 7109.6 | 122.2 | 486.7 | 3.0 | 463.3 | 2.9 |
| M06-2X-cc-pVDZ | 7071.0 | 83.6 | 485.9 | 2.2 | 462.5 | 2.1 |
| M06-2X-cc-pVTZ | 7111.4 | 124.0 | 486.9 | 3.2 | 463.5 | 3.1 |
| MP2/6-311G(3df,3pd) | 7060.1 | 72.7 | 488.4 | 4.7 | 464.6 | 4.2 |
| MP2/6-311G+(3df,3pd) | 7048.6 | 61.2 | 487.5 | 3.8 | 463.8 | 3.4 |
| MP2/6-311G++(3df,3pd) | 7048.6 | 61.2 | 487.5 | 3.8 | 463.8 | 3.4 |
| MP2/6-311G(2d,2p) | 7051.6 | 64.2 | 486.3 | 2.6 | 462.6 | 2.2 |
| MP2/ 6-311+G(2d,2p) | 7033.2 | 45.8 | 485.4 | 1.7 | 461.7 | 1.3 |
| MP2/6-311++G(2d,2p) | 7032.6 | 45.2 | 485.4 | 1.7 | 461.8 | 1.4 |
| MP2/6-311G(2df,2pd) | 7069.3 | 81.9 | 488.8 | 5.1 | 465.0 | 4.6 |
| MP2/6-311+G(2df,2pd) | 7051.0 | 63.6 | 487.9 | 4.2 | 464.1 | 3.7 |
| MP2/6-311++G(2df,2pd) | 7050.4 | 63.0 | 487.9 | 4.2 | 464.1 | 3.7 |
| MP2/6-311G(df,pd) | 7060.3 | 72.9 | 487.5 | 3.8 | 463.8 | 3.4 |
| MP2/6-311+G(df,pd) | 7045.0 | 57.6 | 486.5 | 2.8 | 462.9 | 2.5 |
| MP2/6-311++G(df,pd) | 7043.7 | 56.3 | 486.6 | 2.9 | 462.9 | 2.5 |
| MP2/6-311G(d,p) | 7008.4 | 21.0 | 484.1 | 0.4 | 460.6 | 0.2 |
| MP2/6-311+G(d,p) | 6993.0 | 5.6 | 483.4 | –0.3 | 459.8 | –0.6 |
| ***MP2/6-311++G(d,p)*** | ***6990.7*** | ***3.3*** | ***483.4*** | ***–0.3*** | ***459.9*** | ***–0.5*** |
| MP2/6-31G(d,p) | 6988.2 | 0.8 | 484.7 | 1.0 | 461.0 | 0.6 |
| MP2/6-31+G(d,p) | 6959.2 | –28.2 | 483.3 | –0.4 | 459.6 | –0.8 |
| MP2/6-31++G(d,p) | 6954.4 | –33.0 | 483.3 | –0.4 | 459.5 | –0.9 |
| MP2/aug-cc-pVDZ | 6913.6 | –73.8 | 480.7 | –3.0 | 457.2 | –3.2 |
| MP2/cc-pVDZ | 6949.3 | –38.1 | 482.4 | –1.3 | 458.9 | –1.5 |
| MP2/cc-pVTZ | 7039.5 | 52.1 | 487.5 | 3.8 | 463.7 | 3.3 |
| ωB97X-D/6-311G(d,p) | 7051.5 | 64.1 | 483.2 | –0.5 | 459.9 | –0.5 |
| ωB97X-D/6-311+G(d,p) | 7051.3 | 63.9 | 483.2 | –0.5 | 459.9 | –0.5 |
| ωB97X-D/6-311++G(d,p) | 7065.0 | 77.6 | 483.8 | 0.1 | 460.5 | 0.1 |
| ωB97X-D/aug-cc-pVDZ | 7021.2 | 33.8 | 482.7 | –1.0 | 459.4 | –1.0 |
| ωB97X-D/aug-cc-pVTZ | 7075.9 | 88.5 | 484.9 | 1.2 | 461.5 | 1.1 |
| ωB97X-D/cc-pVDZ | 7030.7 | 43.3 | 483.3 | –0.4 | 460.0 | –0.4 |
| ωB97X-D/cc-pVTZ | 7078.8 | 91.4 | 485.2 | 1.5 | 461.7 | 1.3 |
| **Expt.** | **3599.0** | | **625.4** | | **585.8** | |

**Table S-4.** Observed 100 A and 80 E species frequencies ($\nu_{Obs.}$) of conformer I of MHO. $\nu_{Obs.} - \nu_{Calc.}$ values as obtained with the program *XIAM*.

| $J$ | $K_a$ | $K_c$ | $J$ | $K_a$ | $K_c$ | | $\nu_{Obs.}$ | $\nu_{Obs.} - \nu_{Calc.}$ |
|---|---|---|---|---|---|---|---|---|
| upper level | | | lower level | | | | GHz | kHz |
| 8 | 0 | 8 | 7 | 0 | 7 | A | 9656.6451 | –1.9 |
| 8 | 0 | 8 | 7 | 0 | 7 | E | 9656.6180 | 2.3 |
| 8 | 1 | 7 | 7 | 1 | 6 | A | 9839.2242 | –2.3 |
| 8 | 1 | 7 | 7 | 1 | 6 | E | 9839.1749 | 2.0 |
| 8 | 2 | 6 | 7 | 2 | 5 | A | 9717.2734 | –2.6 |
| 8 | 2 | 7 | 7 | 2 | 6 | A | 9684.7185 | –2.6 |
| 9 | 0 | 9 | 8 | 0 | 8 | A | 10854.0067 | –2.7 |
| 9 | 0 | 9 | 8 | 0 | 8 | E | 10853.9786 | 2.9 |
| 9 | 1 | 8 | 8 | 1 | 7 | A | 11066.2934 | –2.6 |
| 9 | 1 | 8 | 8 | 1 | 7 | E | 11066.2397 | 1.8 |
| 9 | 1 | 9 | 8 | 1 | 8 | A | 10711.7442 | –0.8 |
| 9 | 1 | 9 | 8 | 1 | 8 | E | 10711.7294 | 1.5 |
| 9 | 2 | 7 | 8 | 2 | 6 | A | 10939.7688 | –2.4 |
| 9 | 2 | 7 | 8 | 2 | 6 | E | 10939.3282 | 2.8 |
| 9 | 2 | 8 | 8 | 2 | 7 | A | 10893.5377 | –3.3 |
| 9 | 2 | 8 | 8 | 2 | 7 | E | 10893.9038 | 0.2 |
| 10 | 0 | 10 | 9 | 0 | 9 | A | 12048.1819 | –2.3 |
| 10 | 0 | 10 | 9 | 0 | 9 | E | 12048.1521 | 3.5 |
| 10 | 1 | 9 | 9 | 1 | 8 | A | 12292.2924 | –3.1 |
| 10 | 1 | 9 | 9 | 1 | 8 | E | 12292.2346 | 2.1 |
| 10 | 1 | 10 | 9 | 1 | 9 | A | 11899.0506 | –0.1 |
| 10 | 1 | 10 | 9 | 1 | 9 | E | 11899.0328 | 1.9 |
| 10 | 2 | 8 | 9 | 2 | 7 | A | 12164.7854 | –2.6 |
| 10 | 2 | 8 | 9 | 2 | 7 | E | 12164.5020 | 2.8 |
| 10 | 2 | 9 | 9 | 2 | 8 | A | 12101.7351 | –3.3 |
| 10 | 2 | 9 | 9 | 2 | 8 | E | 12101.9349 | 1.1 |
| 10 | 3 | 8 | 9 | 3 | 7 | A | 12119.9612 | –3.9 |
| 10 | 3 | 8 | 9 | 3 | 7 | E | 12120.7803 | 1.4 |
| 1 | 1 | 1 | 0 | 0 | 0 | A | 4184.9260 | –1.0 |
| 1 | 1 | 1 | 0 | 0 | 0 | E | 4184.2045 | –1.2 |
| 1 | 1 | 0 | 1 | 0 | 1 | A | 3013.2520 | –11.3 |
| 1 | 1 | 0 | 1 | 0 | 1 | E | 3013.7037 | –2.9 |
| 2 | 2 | 0 | 1 | 1 | 1 | A | 11422.5699 | 1.2 |
| 2 | 2 | 0 | 1 | 1 | 1 | E | 11432.1877 | –3.3 |
| 2 | 2 | 1 | 1 | 1 | 0 | A | 11382.6439 | –2.0 |
| 2 | 2 | 1 | 1 | 1 | 0 | E | 11372.1825 | –1.2 |
| 2 | 1 | 1 | 2 | 0 | 2 | A | 3053.2148 | 10.2 |
| 2 | 1 | 1 | 2 | 0 | 2 | E | 3053.2582 | –1.3 |
| 2 | 2 | 1 | 2 | 1 | 2 | A | 9039.3035 | 0.4 |
| 2 | 2 | 0 | 2 | 1 | 2 | A | 9039.6940 | –0.7 |
| 2 | 2 | 0 | 2 | 1 | 2 | E | 9048.9341 | –2.5 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 2 | 2 | 0 | 2 | 1 | 1 | A | 8921.1008 | –1.3 |
| 2 | 2 | 0 | 2 | 1 | 1 | E | 8929.9740 | 11.9 |
| 3 | 1 | 3 | 2 | 0 | 2 | A | 6508.6694 | –0.6 |
| 3 | 1 | 3 | 2 | 0 | 2 | E | 6508.4321 | –1.5 |
| 3 | 2 | 1 | 2 | 1 | 2 | A | 12674.9394 | –3.6 |
| 3 | 2 | 1 | 2 | 1 | 2 | E | 12683.4258 | –9.2 |
| 3 | 2 | 2 | 2 | 1 | 1 | A | 12554.3920 | –0.7 |
| 3 | 2 | 2 | 2 | 1 | 1 | E | 12545.0422 | –9.5 |
| 3 | 3 | 0 | 2 | 2 | 1 | A | 18598.9372 | –0.6 |
| 3 | 3 | 1 | 2 | 2 | 0 | A | 18598.5501 | 6.3 |
| 3 | 2 | 2 | 3 | 1 | 3 | A | 9098.9254 | –2.0 |
| 3 | 2 | 2 | 3 | 1 | 3 | E | 9089.8709 | –6.6 |
| 3 | 2 | 1 | 3 | 1 | 3 | A | 9100.8827 | –2.3 |
| 3 | 2 | 1 | 3 | 1 | 3 | E | 9109.2811 | –5.2 |
| 3 | 2 | 1 | 3 | 1 | 2 | A | 8863.7064 | 1.4 |
| 3 | 2 | 1 | 3 | 1 | 2 | E | 8871.9317 | 0.0 |
| 3 | 3 | 1 | 3 | 2 | 2 | A | 14965.2499 | –3.2 |
| 3 | 3 | 1 | 3 | 2 | 2 | E | 14958.8231 | –1.5 |
| 3 | 3 | 0 | 3 | 2 | 2 | A | 14965.2499 | –5.6 |
| 3 | 3 | 0 | 3 | 2 | 1 | A | 14963.3018 | 3.9 |
| 3 | 3 | 0 | 3 | 2 | 1 | E | 14968.3592 | 2.0 |
| 4 | 1 | 4 | 3 | 0 | 3 | A | 7641.6074 | –2.4 |
| 4 | 1 | 4 | 3 | 0 | 3 | E | 7641.4181 | 1.5 |
| 4 | 2 | 2 | 3 | 1 | 3 | A | 13949.3751 | –8.1 |
| 4 | 2 | 2 | 3 | 1 | 3 | E | 13956.1974 | 2.5 |
| 4 | 2 | 3 | 3 | 1 | 2 | A | 13706.3299 | –2.5 |
| 4 | 2 | 3 | 3 | 1 | 2 | E | 13698.6623 | 0.2 |
| 4 | 2 | 3 | 4 | 1 | 4 | A | 9178.5725 | 1.8 |
| 4 | 2 | 3 | 4 | 1 | 4 | E | 9171.0394 | –6.0 |
| 4 | 2 | 2 | 4 | 1 | 4 | A | 9184.4391 | –2.4 |
| 4 | 2 | 2 | 4 | 1 | 4 | E | 9191.2192 | –4.4 |
| 5 | 1 | 5 | 4 | 0 | 4 | A | 8756.2152 | –1.0 |
| 5 | 1 | 5 | 4 | 0 | 4 | E | 8756.0486 | 0.1 |
| 5 | 2 | 3 | 4 | 1 | 4 | A | 15247.4663 | –3.5 |
| 5 | 2 | 3 | 4 | 1 | 4 | E | 15252.0692 | 8.4 |
| 5 | 2 | 4 | 4 | 1 | 3 | A | 14838.5000 | 0.6 |
| 5 | 2 | 4 | 4 | 1 | 3 | E | 14833.0378 | –1.8 |
| 5 | 2 | 4 | 5 | 1 | 5 | A | 9278.3515 | 2.1 |
| 5 | 2 | 4 | 5 | 1 | 5 | E | 9272.9601 | –2.9 |
| 5 | 2 | 3 | 5 | 1 | 5 | A | 9292.0412 | 2.4 |
| 5 | 2 | 3 | 5 | 1 | 5 | E | 9296.6221 | –0.2 |
| 5 | 2 | 3 | 5 | 1 | 4 | A | 8699.1702 | –1.5 |
| 5 | 2 | 3 | 5 | 1 | 4 | E | 8703.7324 | 0.4 |
| 5 | 3 | 3 | 5 | 2 | 4 | A | 14968.9518 | –3.2 |
| 5 | 3 | 3 | 5 | 2 | 4 | E | 14958.8231 | 1.1 |
| 5 | 3 | 2 | 5 | 2 | 4 | A | 14969.0230 | 0.1 |
| 6 | 1 | 6 | 5 | 0 | 5 | A | 9853.5771 | –3.3 |

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|---|---|---|---|---|---|---|---|---|
| 6 | 1 | 6 | 5 | 0 | 5 | E | 9853.4323 | 0.9 |
| 6 | 2 | 4 | 5 | 1 | 5 | A | 16571.1871 | 2.5 |
| 6 | 2 | 4 | 5 | 1 | 5 | E | 16573.8163 | 3.6 |
| 6 | 3 | 3 | 5 | 2 | 4 | A | 22238.7905 | 10.6 |
| 6 | 2 | 5 | 6 | 1 | 6 | A | 9398.4001 | 0.1 |
| 6 | 2 | 5 | 6 | 1 | 6 | E | 9394.9157 | –2.5 |
| 6 | 2 | 4 | 6 | 1 | 6 | A | 9425.7504 | 1.8 |
| 6 | 2 | 4 | 6 | 1 | 6 | E | 9428.3810 | 1.2 |
| 6 | 2 | 4 | 6 | 1 | 5 | A | 8595.8650 | 2.1 |
| 6 | 2 | 4 | 6 | 1 | 5 | E | 8598.5163 | 0.3 |
| 6 | 3 | 3 | 6 | 2 | 5 | A | 14973.3004 | 7.0 |
| 6 | 3 | 3 | 6 | 2 | 4 | A | 14945.9508 | 6.1 |
| 6 | 3 | 3 | 6 | 2 | 4 | E | 14956.5684 | 0.4 |
| 6 | 4 | 3 | 6 | 3 | 4 | A | 20946.2859 | –6.2 |
| 6 | 4 | 2 | 6 | 3 | 4 | A | 20946.2859 | –6.8 |
| 7 | 3 | 4 | 7 | 2 | 6 | A | 14980.0850 | 4.1 |
| 8 | 1 | 8 | 7 | 0 | 7 | A | 12002.4189 | –4.4 |
| 8 | 1 | 8 | 7 | 0 | 7 | E | 12002.3096 | 4.6 |
| 8 | 3 | 6 | 8 | 2 | 7 | A | 14989.1209 | –12.3 |
| 8 | 3 | 6 | 8 | 2 | 7 | E | 14975.6545 | –0.3 |
| 8 | 3 | 5 | 8 | 2 | 6 | A | 14908.5553 | 1.0 |
| 8 | 3 | 5 | 8 | 2 | 6 | E | 14920.6681 | –0.5 |
| 9 | 1 | 9 | 8 | 0 | 8 | A | 13057.5214 | 0.2 |
| 9 | 1 | 9 | 8 | 0 | 8 | E | 13057.4205 | 3.3 |
| 9 | 3 | 6 | 9 | 2 | 8 | A | 15004.8229 | 1.6 |
| 9 | 3 | 6 | 9 | 2 | 8 | E | 15018.2241 | –0.4 |
| 9 | 3 | 6 | 9 | 2 | 7 | A | 14876.8936 | 0.2 |
| 10 | 1 | 10 | 9 | 0 | 9 | A | 14102.5587 | –3.8 |
| 10 | 1 | 10 | 9 | 0 | 9 | E | 14102.4754 | 3.1 |
| 10 | 3 | 7 | 10 | 2 | 9 | A | 15024.9603 | 0.1 |
| 10 | 3 | 7 | 10 | 2 | 9 | E | 15037.2655 | 1.0 |
| 1 | 1 | 0 | 0 | 0 | 0 | A | 4224.4583 | 0.1 |
| 1 | 1 | 0 | 0 | 0 | 0 | E | 4224.8959 | –1.0 |
| 2 | 1 | 1 | 1 | 0 | 1 | A | 5475.2001 | 1.4 |
| 2 | 1 | 1 | 1 | 0 | 1 | E | 5475.2428 | –1.5 |
| 2 | 2 | 1 | 1 | 1 | 1 | A | 11422.1727 | –4.4 |
| 2 | 2 | 1 | 1 | 1 | 1 | E | 11412.8867 | 11.8 |
| 2 | 2 | 0 | 1 | 1 | 0 | A | 11383.0386 | 1.1 |
| 2 | 2 | 0 | 1 | 1 | 0 | E | 11391.4993 | –0.5 |
| 2 | 2 | 1 | 2 | 1 | 1 | A | 8920.7068 | –3.7 |
| 2 | 2 | 1 | 2 | 1 | 1 | E | 8910.6402 | –5.7 |
| 3 | 1 | 2 | 2 | 0 | 2 | A | 6745.8465 | –3.5 |
| 3 | 1 | 2 | 2 | 0 | 2 | E | 6745.7888 | 0.6 |
| 3 | 2 | 2 | 2 | 1 | 2 | A | 12672.9917 | 6.3 |
| 3 | 2 | 1 | 2 | 1 | 1 | A | 12556.3500 | –0.4 |
| 3 | 2 | 1 | 2 | 1 | 1 | E | 12564.4557 | –4.8 |
| 3 | 3 | 1 | 2 | 2 | 1 | A | 18598.9370 | 1.7 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 3 | 3 | 1 | 2 | 2 | 1 | E | 18593.2345 | 4.2 |
| 3 | 3 | 0 | 2 | 2 | 0 | A | 18598.5501 | 3.9 |
| 3 | 3 | 0 | 2 | 2 | 0 | E | 18602.8554 | –0.2 |
| 3 | 2 | 2 | 3 | 1 | 2 | A | 8861.7479 | 0.5 |
| 3 | 2 | 2 | 3 | 1 | 2 | E | 8852.5325 | 9.6 |
| 3 | 3 | 1 | 3 | 2 | 1 | A | 14963.3018 | 6.3 |
| 4 | 1 | 3 | 3 | 0 | 3 | A | 8036.8856 | –5.0 |
| 4 | 1 | 3 | 3 | 0 | 3 | E | 8036.7813 | 2.7 |
| 4 | 2 | 3 | 3 | 1 | 3 | A | 13943.5147 | 2.3 |
| 4 | 2 | 3 | 3 | 1 | 3 | E | 13936.0125 | –4.2 |
| 4 | 2 | 2 | 3 | 1 | 2 | A | 13712.2033 | 0.1 |
| 4 | 2 | 2 | 3 | 1 | 2 | E | 13718.8381 | –2.2 |
| 4 | 3 | 2 | 3 | 2 | 2 | A | 19811.1100 | 0.0 |
| 4 | 3 | 2 | 3 | 2 | 2 | E | 19804.6768 | 4.3 |
| 4 | 3 | 1 | 3 | 2 | 1 | A | 19809.1740 | 4.7 |
| 4 | 3 | 1 | 3 | 2 | 1 | E | 19814.2021 | –0.4 |
| 5 | 1 | 4 | 4 | 0 | 4 | A | 9349.0822 | –1.1 |
| 5 | 1 | 4 | 4 | 0 | 4 | E | 9348.9405 | 1.8 |
| 5 | 2 | 4 | 4 | 1 | 4 | A | 15233.7794 | –0.9 |
| 5 | 2 | 3 | 4 | 1 | 3 | A | 14852.1876 | –1.3 |
| 5 | 3 | 3 | 4 | 2 | 3 | A | 21024.1687 | 4.2 |
| 5 | 3 | 3 | 4 | 2 | 3 | E | 21016.1813 | 3.1 |
| 5 | 3 | 2 | 4 | 2 | 2 | A | 21018.3628 | 1.2 |
| 5 | 3 | 2 | 4 | 2 | 2 | E | 21024.9348 | –0.3 |
| 5 | 2 | 4 | 5 | 1 | 4 | A | 8685.4811 | –1.1 |
| 5 | 2 | 4 | 5 | 1 | 4 | E | 8680.0719 | –0.9 |
| 5 | 3 | 3 | 5 | 2 | 3 | A | 14955.2693 | 3.8 |
| 6 | 1 | 5 | 5 | 0 | 5 | A | 10683.4638 | –2.3 |
| 6 | 1 | 5 | 5 | 0 | 5 | E | 10683.2963 | 1.1 |
| 6 | 2 | 5 | 5 | 1 | 5 | A | 16543.8352 | –0.7 |
| 6 | 2 | 5 | 5 | 1 | 5 | E | 16540.3528 | 1.7 |
| 6 | 3 | 4 | 5 | 2 | 4 | A | 22238.5642 | –12.1 |
| 6 | 3 | 4 | 5 | 2 | 4 | E | 22228.4905 | 3.4 |
| 6 | 2 | 5 | 6 | 1 | 5 | A | 8568.5138 | –0.5 |
| 6 | 2 | 5 | 6 | 1 | 5 | E | 8565.0541 | –0.3 |
| 6 | 3 | 4 | 6 | 2 | 4 | A | 14945.7369 | –4.2 |
| 6 | 3 | 4 | 6 | 2 | 4 | E | 14927.6380 | 0.6 |
| 7 | 1 | 6 | 6 | 0 | 6 | A | 12041.3361 | –1.0 |
| 7 | 1 | 6 | 6 | 0 | 6 | E | 12041.1429 | 1.3 |
| 8 | 1 | 7 | 7 | 0 | 7 | A | 13424.2261 | –4.2 |
| 8 | 1 | 7 | 7 | 0 | 7 | E | 13424.0128 | 3.0 |
| 8 | 3 | 6 | 8 | 2 | 6 | A | 14907.4368 | 1.3 |
| 9 | 1 | 8 | 8 | 0 | 8 | A | 14833.8796 | 0.3 |
| 9 | 1 | 8 | 8 | 0 | 8 | E | 14833.6366 | 4.6 |
| 10 | 3 | 8 | 10 | 2 | 8 | A | 14829.8353 | 0.7 |

**Table S-5a.** Molecular constants in the rho axis system of conformer $C_1$ of MHO obtained by a fit using the program *BELGI-C$_1$*.

| **Operator**[a] | **Constant**[b] | **Units** | **Values**[c] |
|---|---|---|---|
| $\mathbf{P_a^2}$ | $A$ | MHz | 3507.798(86) |
| $\mathbf{P_b^2}$ | $B$ | MHz | 715.01(23) |
| $\mathbf{P_c^2}$ | $C$ | MHz | 587.42(32) |
| $\{\mathbf{P_a}, \mathbf{P_b}\}$ | $D_{ab}$ | GHz | –0.53[d] |
| $-\mathbf{P^4}$ | $\Delta_J$ | kHz | 0.33723(76) |
| $-\mathbf{P^2 P_a^2}$ | $\Delta_{JK}$ | kHz | –10.195(10) |
| $-\mathbf{P_a^4}$ | $\Delta_K$ | kHz | 53.514(27) |
| $-\mathbf{2P^2}\left(\mathbf{P_b^2} - \mathbf{P_c^2}\right)$ | $\delta_J$ | kHz | 0.09894(50) |
| $-\left\{\mathbf{P_a^2}, \left(\mathbf{P_b^2} - \mathbf{P_c^2}\right)\right\}^2$ | $\delta_K$ | kHz | –1.012(31) |
| $\mathbf{P_\alpha^2}$ | $F$ | cm$^{-1}$ | 5.268[e] |
| $(1/2)[1 - \cos(3\alpha)]$ | $V_3$ | cm$^{-1}$ | 408.35(11) |
| $\mathbf{P_a P_\alpha}$ | $\rho$ | unitless | 0.016138(23) |
| $\{\mathbf{P_a}, \mathbf{P_c}\}$ | $D_{acI}$ | GHz | 0.0378(37) |
| | $N_A/N_E$ | | 100/80 |
| | *rms* | kHz | 4.3/5.1 |

[a] All constants refer to a rho-axis system, therefore the inertia tensor is not diagonal and the constants cannot be directly compared to those of a principal axis system given in Table 2. $\mathbf{P_a}$, $\mathbf{P_b}$, $\mathbf{P_c}$ are the components of the overall rotation angular momentum, $\mathbf{P_\alpha}$ is the angular momentum of the internal rotor rotating around the internal rotor axis by an angle $\alpha$. {u,v} is the anti commutator uv + vu.

[b] The product of the parameter and operator from a given row yields the term actually used in the rotation-torsion Hamiltonian, except for $F$, $\rho$, and $A$, which occur in the Hamiltonian in the form $F(\mathbf{P_\alpha} - \rho\mathbf{P_a^2}) + A\mathbf{P_a^2}$.

[c] Values of the parameters from the present fit. Statistical uncertainties are shown as one standard uncertainty in the last digit.

[d] Fixed to the value from a previous fit.

[e] Fixed to the *XIAM* value.

**Table S-5b.** Molecular constants in the rho axis system of conformer $C_s$ of MHO obtained by a fit using the program *BELGI-$C_s$*.

| **Operator**[a] | **Constant**[b] | **Units** | **Values**[c] |
|---|---|---|---|
| $\mathbf{P_a^2}$ | $A$ | MHz | 6809(14) |
| $\mathbf{P_b^2}$ | $B$ | MHz | 511.0(21) |
| $\mathbf{P_c^2}$ | $C$ | MHz | 472.9(18) |
| $\{\mathbf{P_a}, \mathbf{P_b}\}$ | $D_{ab}$ | GHz | –0.48[d] |
| $\mathbf{P_\alpha^2}$ | $F$ | $cm^{-1}$ | 5.268[e] |
| $(1/2)[1-\cos(3\alpha)]$ | $V_3$ | $cm^{-1}$ | 395.5(33) |
| $\mathbf{P_a P_\alpha}$ | $\rho$ | unitless | 0.0322(13) |
| $[1-\cos(3\alpha)]\mathbf{P_a^2}$ | $k_5$ | MHz | 4.086(42) |
| $[1-\cos(3\alpha)]\mathbf{P^2}$ | $F_v$ | MHz | –12.08(22) |
| $\mathbf{P_a P_\alpha P^2}$ | $L_v$ | kHz | –5.9(18) |
| $[1-\cos(3\alpha)]\left(\mathbf{P_b^2}-\mathbf{P_c^2}\right)$ | $c_2$ | MHz | 29.1(63) |
| $\mathbf{P_\alpha^2}\left(\mathbf{P_b^2}-\mathbf{P_c^2}\right)$ | $c_1$ | MHz | 0.447(69) |
| | $N_A/N_E$ | | 21/21 |

[a] All constants refer to a rho-axis system, therefore the inertia tensor is not diagonal and the constants cannot be directly compared to those of a principal axis system given in Table 2. $\mathbf{P_a}$, $\mathbf{P_b}$, $\mathbf{P_c}$ are the components of the overall rotation angular momentum, $\mathbf{P_\alpha}$ is the angular momentum of the internal rotor rotating around the internal rotor axis by an angle $\alpha$. {u,v} is the anti commutator uv + vu.

[b] The product of the parameter and operator from a given row yields the term actually used in the rotation-torsion Hamiltonian, except for $F$, $\rho$, and $A$, which occur in the Hamiltonian in the form $F(\mathbf{P_\alpha}-\rho\mathbf{P_a^2})+A\mathbf{P_a^2}$.

[c] Values of the parameters from the present fit. Statistical uncertainties are shown as one standard uncertainty in the last digit.

[d] Fixed to the *ab initio* value.

[e] Fixed to the *XIAM* value.

**Table S-6.** Observed 21 A and 21 E species frequencies ($\nu_{Obs.}$) of conformer XIII of MHO. $\nu_{Obs.} - \nu_{Calc.}$ values as obtained with the program *XIAM*.

| $J$ | $K_a$ | $K_c$ | $J$ | $K_a$ | $K_c$ | | $\nu_{Obs.}$ | $\nu_{Obs.} - \nu_{Calc.}$ |
|---|---|---|---|---|---|---|---|---|
| upper level | | | lower level | | | | GHz | kHz |
| 2 | 1 | 2 | 1 | 0 | 1 | A | 8369.3315 | –4.7 |
| 2 | 1 | 2 | 1 | 0 | 1 | E | 8365.3963 | –10.3 |
| 3 | 1 | 3 | 2 | 0 | 2 | A | 9278.6122 | –0.6 |
| 3 | 1 | 3 | 2 | 0 | 2 | E | 9276.0759 | 7.9 |
| 4 | 1 | 4 | 3 | 0 | 3 | A | 10176.4023 | 0.3 |
| 4 | 1 | 4 | 3 | 0 | 3 | E | 10174.4447 | 4.4 |
| 5 | 1 | 5 | 4 | 0 | 4 | A | 11062.8250 | –2.7 |
| 5 | 1 | 5 | 4 | 0 | 4 | E | 11061.1631 | 1.1 |
| 6 | 1 | 6 | 5 | 0 | 5 | A | 11938.0615 | 0.8 |
| 6 | 1 | 6 | 5 | 0 | 5 | E | 11936.5696 | 3.7 |
| 7 | 1 | 7 | 6 | 0 | 6 | A | 12802.3215 | 2.7 |
| 7 | 1 | 7 | 6 | 0 | 6 | E | 12800.9365 | 4.3 |
| 8 | 1 | 8 | 7 | 0 | 7 | A | 13655.8640 | –3.0 |
| 8 | 1 | 8 | 7 | 0 | 7 | E | 13654.5511 | –2.8 |
| 9 | 1 | 9 | 8 | 0 | 8 | A | 14499.0170 | –0.3 |
| 9 | 1 | 9 | 8 | 0 | 8 | E | 14497.7560 | –0.9 |
| 10 | 1 | 10 | 9 | 0 | 9 | A | 15332.1275 | –1.2 |
| 10 | 1 | 10 | 9 | 0 | 9 | E | 15330.9106 | 2.5 |
| 11 | 1 | 11 | 10 | 0 | 10 | A | 16155.6055 | –1.2 |
| 11 | 1 | 11 | 10 | 0 | 10 | E | 16154.4169 | –0.6 |
| 12 | 1 | 12 | 11 | 0 | 11 | A | 16969.9042 | 1.4 |
| 12 | 1 | 12 | 11 | 0 | 11 | E | 16968.7378 | –1.7 |
| 13 | 1 | 13 | 12 | 0 | 12 | A | 17775.5145 | 0.7 |
| 13 | 1 | 13 | 12 | 0 | 12 | E | 17774.3726 | 0.1 |
| 14 | 1 | 14 | 13 | 0 | 13 | A | 18572.9758 | –4.1 |
| 14 | 1 | 14 | 13 | 0 | 13 | E | 18571.8593 | 1.2 |
| 15 | 1 | 15 | 14 | 0 | 14 | A | 19362.8827 | –0.6 |
| 15 | 1 | 15 | 14 | 0 | 14 | E | 19361.7827 | 3.4 |
| 16 | 1 | 16 | 15 | 0 | 15 | A | 20145.8441 | –1.4 |
| 16 | 1 | 16 | 15 | 0 | 15 | E | 20144.7595 | 1.2 |
| 4 | 1 | 3 | 4 | 0 | 4 | A | 6632.6961 | –2.1 |
| 4 | 1 | 3 | 4 | 0 | 4 | E | 6632.5107 | 2.6 |
| 4 | 2 | 3 | 4 | 1 | 4 | A | 19664.1047 | 5.5 |
| 5 | 2 | 4 | 5 | 1 | 5 | A | 19722.1582 | –9.2 |
| 5 | 2 | 4 | 5 | 1 | 5 | E | 19691.9458 | –6.6 |
| 6 | 2 | 5 | 6 | 1 | 6 | A | 19791.9125 | 5.9 |
| 6 | 2 | 5 | 6 | 1 | 6 | E | 19762.5366 | 3.6 |
| 7 | 2 | 6 | 7 | 1 | 7 | A | 19873.3488 | 1.2 |
| 2 | 2 | 0 | 1 | 1 | 0 | E | 21443.1443 | 4.6 |
| 3 | 2 | 1 | 2 | 1 | 1 | E | 22368.1196 | –3.1 |
| 4 | 2 | 2 | 3 | 1 | 2 | E | 23279.0544 | –4.6 |
| 5 | 2 | 3 | 5 | 1 | 4 | A | 19376.7035 | 2.8 |