Supporting Information:

Infrared Multiple Photon Dissociation Spectroscopy Confirms Reversible Water Activation in Mn\(^+\)(H\(_2\)O)\(_n\), n ≤ 8

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Experimental Details

All experimental measurements were performed on a modified 4.7 Tesla Bruker/Spectrospin FT-ICR CMS47X mass spectrometer\textsuperscript{1–5} equipped with a Bruker infinity cell\textsuperscript{6} and laser vaporisation source.\textsuperscript{7,8} Briefly, a frequency-doubled Litron Nano S 60-30 Nd:YAG laser (532 nm, 5 mJ/pulse, 30 Hz) is focussed onto a rotating solid disc of manganese producing a plasma. This plasma is then entrained into a pulse of the desired gas mixture (H\textsubscript{2}O in helium) produced \textit{via} a homebuilt piezoelectric valve. The ensuing pulse is cooled \textit{via} supersonic jet expansion into the source chamber. The gas pulse traverses through a skimmer (forming the molecular beam), and ions are guided \textit{via} an electrostatic lens set-up into the center of the ICR cell. Ions are then stored and mass-selected within the 4.7 T magnetic field\textsuperscript{9} under ultra-high vacuum conditions (ca. 5 x 10\textsuperscript{−10} mbar). The ICR cell is surrounded by a copper jacket, whereby the temperature of the cell can be controlled and cooled to ca. 87 K \textit{via} liquid nitrogen,\textsuperscript{10,11} minimising the effects of black body infrared radiative dissociation (BIRD).\textsuperscript{12–17} In each case \textit{either} the measurements were recorded at room temperature, or cooling of the ICR cell \textit{via} liquid nitrogen was employed.

On the opposite side of the magnet, the output radiation of a tunable IR OPO laser system (EKSPLA NT277/273-XIR) is aligned into the cell through a CaF\textsubscript{2} window.\textsuperscript{18} Absorption of infrared photons, leading to photodissociation events are measured \textit{via} mass spectroscopy.\textsuperscript{19} Monitoring the precursor and fragment abundance channels as a function of wavenumber yields the infrared spectrum of the complex of interest. Infrared spectra were recorded in i) the 2250–4000 cm\textsuperscript{−1} wavelength region, probing in the O–H symmetric and asymmetric stretching region, and ii) the 1450–1950 cm\textsuperscript{−1} region, probing the water bend and Mn–H stretch. Specific details on the laser setup can be found in previous publications.\textsuperscript{18,20} Infrared spectra of size-selected clusters was recorded \textit{via} action spectroscopy, reaction 1:
\[
\text{Mn}^+(\text{H}_2\text{O})_n + m \ h\nu \rightarrow \text{Mn}^+(\text{H}_2\text{O})_{n-x} + x(\text{H}_2\text{O})
\] (1)

Typical irradiation times are between 0.2–20.0 s at 1000 Hz repetition rate. The normalized IRMPD Yield is calculated from the precursor ion and BIRD-corrected fragment ion intensities along with considerations given to the laser power. First, ion intensities are normalized so that the precursor ion intensity is 100%. In the next step, the fragment intensities are BIRD corrected by subtracting the fragment intensities form a control experiment without laser irradiation, but identical residence time in the ICR cell. IRMPD yields are then calculated as \((\text{sum over BIRD corrected fragment intensities})/(\text{sum over BIRD corrected fragment intensities and precursor intensity})/(\text{laser power})\) and re-normalized for graphical display so that the maximum IRMPD yield in the spectrum is 100%.

The laser power is measured after every mass spectrum to account for small fluctuations. The laser power drops in the range 3500 – 3520 cm\(^{-1}\). Due to the complex kinetics of the IRMPD process, this may lead to small artifacts in the IRMPD yield at these wavelengths even after power correction.

In conjunction with the IRMPD measurements, BIRD experiments were also performed on the \(\text{Mn}^+(\text{H}_2\text{O})_8\) complex. Figure S1a shows a typical mass spectrum recorded during an experimental run, presenting \(\text{Mn}^+(\text{H}_2\text{O})_n\) clusters, \(n = 4–15\). Figure S1a-e presents a sequence of mass spectra used to record the IRMPD spectrum presented in Figure 1b in the main article. First, the \(\text{Mn}^+(\text{H}_2\text{O})_8\) complex is mass-selected (Figure S1b), and is heated by room temperature black-body radiation from the ICR cell walls for 20 s (Figure S1c). The \([\text{Mn}_4(\text{H}_2\text{O})_4]^+\) complex is mass-selected (Figure S1d) and subject to IR radiation at 3680 cm\(^{-1}\), leading to water loss, Figure S1e. To construct the IRMPD spectrum in Figure 1b, the whole process is repeated, changing the irradiation wavenumber in Figure S1e. A series of mass spectra like the
one in Figure 1e, measured with the irradiation wavenumber changed sequentially, is obtained to generate IRMPD spectra.

In addition to using BIRD to dissociate the Mn\(^+\)(H\(_2\)O)\(_8\) complex, IR radiation from the OPO laser system was also employed. The IRMPD spectrum of Mn\(^+\)(H\(_2\)O)\(_8\), Figure 1c, shows a strong broad band at ca. 3200 cm\(^{-1}\). This band was used to photodissociate the Mn\(^+\)(H\(_2\)O)\(_8\) complex, forming [Mn\(_4\)(H\(_2\)O)\(_4\)]\(^+\). The IRMPD spectrum shown in Figure 1e was generated as follows: the mass-selected Mn\(^+\)(H\(_2\)O)\(_8\) complex was irradiated for 3.0 s with IR light at 3200 cm\(^{-1}\), leading to loss of 4 H\(_2\)O. The resulting [Mn\(_4\)(H\(_2\)O)\(_4\)]\(^+\) complex was mass-selected and subject to IR radiation for 0.3 s, generating the IRMPD spectrum in Figure 1e.
Figure S1: Representative mass spectra outlining the experimental procedure used to construct BIRD+IRMPD spectra. (a) mass spectrum obtained from the ion source, (b) mass-selected Mn\(^+(H_2O)_8\) cluster, (c) mass distribution after 20 s irradiation with black-body infrared radiation, (d) mass-selected Mn\(^+(H_2O)_4\) cluster, and (e) mass spectrum recorded after irradiation with infrared light at 3680 cm\(^{-1}\) for 0.3 s. Arrows indicate that mass spectra, a–e, were measured sequentially.
Table S1: Irradiation times and temperatures used in the experiment.

| Cluster          | OH Region | Temperature / K | Irradiation time / s |
|------------------|-----------|-----------------|----------------------|
| \(\text{Mn}^+(\text{H}_2\text{O})_4\) | Stretch   | 87              | 0.2                  |
|                  | Bend      | 298             | 0.3                  |
| \(\text{Mn}^+(\text{H}_2\text{O})_8\) | Stretch   | 87              | 0.2                  |
|                  | Bend      | 298             | 1.0                  |
| \(\text{Mn}^+(\text{H}_2\text{O})_4 \leftrightarrow \text{Mn}^+(\text{H}_2\text{O})_8\) | Stretch   | 87              | 3.0 @3200 cm\(^{-1}\)/0.3 |
|                  | Bend      | 298             | 20.0/0.3             |
|                  |           |                 | 20.0/10.0            |

Figure S2. a) Experimental IRMPD spectrum of \(\text{Mn}^+(\text{H}_2\text{O})_4\) recorded at \(\approx 298\) K. b) Experimental IRMPD spectrum of \(\text{Mn}^+(\text{H}_2\text{O})_4\) recorded, and mass-selected, after \(\text{Mn}^+(\text{H}_2\text{O})_8\) was subject to 20.0 s of blackbody-infrared-radiative dissociation (BIRD), at \(\approx 298\) K. c) Experimental IRMPD spectrum of \(\text{Mn}^+(\text{H}_2\text{O})_8\) recorded at \(\approx 298\) K. In d–f), simulated infrared spectra were modelled at the BHandHLYP/aug-cc-pVDZ level with a scaling factor of 0.96.
**Computational Data**

**Figure S3.** Interpolation between septet and quintet Mn\(^{2+}\)(H\(_2\)O\(_2\))\(_2\) minima optimized at the CCSD/aug-cc-pVDZ level at different computational levels using the aug-cc-pVDZ basis set. State average of one quintet and one septet state was used for multi-reference calculations.

**Table S2** - Relative stability of Mn\(^{2+}\)(H\(_2\)O\(_2\))\(_2\) in septet spin multiplicity compared to the quintet analogue (in kJ mol\(^{-1}\)), negative values indicate that the ion in septet spin multiplicity is more stable. The structures were optimized in both spin multiplicities at the respective level using the aug-cc-pVDZ basis set, energies include zero-point correction. For the CCSD(T) value, the CCSD zero-point correction was used.

| Method      | ΔE  |
|-------------|-----|
| B3P86       | 4.7 |
| B3LYP       | 21.6|
| BHandHLYP   | -7.1|
| BMK         | 14.3|
| CAM-B3LYP   | 27.1|
| M06         | 57.3|
| M06L        | 33.3|
| M11         | -0.9|
| MN15        | 32.2|
| O3LYP       | 15.3|
| ωB97XD      | 29.2|
| CCSD        | -35.1|
| CCSD(T)     | -28.7|
Table S3 – Relative energies of Mn\(^{+}(H_{2}O)_{2}\) and HMnOH\(^{+}(H_{2}O)\) isomers as optimized at different levels of theory using the aug-cc-pVDZ basis set (in kJ mol\(^{-1}\)). See Figure S4 for the respective isomers.

| Isomer | CCSD | BHandHLYP | B3LYP | M11 |
|--------|------|-----------|-------|-----|
| \(^{7}\)Ila | 0.0  | 0.0       | 0.0   | 0.0 |
| \(^{7}\)Ilb | 25.1 | 22.5      | 19.3  | 23.3|
| \(^{5}\)Iic | 35.1 | 7.1       | -21.6 | 0.9 |
| \(^{5}\)Ild | 81.4 | 61.7      | 52.8  | 74.1|
| \(^{5}\)Ile | 134.7| 120.7     | 41.7  | 82.2|

Figure S4. Selected low-energy structures of Mn\(^{+}(H_{2}O)_{2}\) and HMnOH\(^{+}(H_{2}O)\).

Figure S5. IR spectra of selected Mn\(^{+}(H_{2}O)_{n}\) clusters, \(n = 2–4\), in the O–H stretching region using various methods along with the aug-cc-pVDZ basis set. Scaling factors of 0.92, 0.96, and 0.95 were used for BHandHLYP, B3LYP, and CCSD, respectively.
Figure S6. IR spectra of selected Mn$^\text{7+}$(H$_2$O)$_n$ clusters, $n = 2$–$4$, in the H$_2$O scissoring region using various methods along with the aug-cc-pVDZ basis set. Scaling factors of 0.96, 1.00 and 0.98 were used for BHandHLYP, B3LYP and CCSD, respectively.
Figure S7. Calculated IR spectra of six selected Mn\(^{\text{II}}\)(H\(_2\)O\(_8\)) isomers at the BHandHLYP/aug-cc-pVDZ level of theory.

Table S4 – Position (in cm\(^{-1}\)) and intensity (in km mol\(^{-1}\), in parenthesis) of the Mn–H vibration for the most stable HMnOH\(^{\text{II}}\)(H\(_2\)O)\(_n\), \(n = 1–3\), isomers. The frequencies are unscaled. The aug-cc-pVDZ basis set was used.

| method       | \(^5\)lc | \(^5\)lle | \(^5\)lll | \(^5\)llle |
|--------------|---------|----------|----------|----------|
| CCSD         | 1466 (49.0) | 1598 (17.4) | 1701 (7.1) | –        |
| BHandHLYP    | 1444 (127.9) | 1519 (40.6) | 1638 (4.2) | 1610 (4.2) |
| B3LYP        | 1722 (6.5) | 1759 (3.5) | 1792 (32.2) | 1769 (52.7) |
| B3P86        | 1768 (3.9) | 1798 (4.6) | 1828 (39.0) | 1808 (59.9) |
| BMK          | 1662 (16.7) | 1751 (4.1) | 1827 (36.2) | 1806 (65.2) |
| CAM-B3LYP    | 1704 (14.7) | 1763 (3.0) | 1812 (24.8) | 1790 (43.1) |
| M06          | 1696 (13.9) | 1754 (4.7) | 1777 (12.0) | 1754 (25.5) |
| M06L         | 1773 (4.3) | 1780 (5.0) | 1811 (36.0) | 1791 (55.4) |
| M11          | 1610 (21.0) | 1690 (5.1) | 1767 (16.9) | 1742 (29.4) |
| MN15         | 1723 (3.2) | 1777 (3.5) | 1830 (32.8) | 1797 (49.1) |
| O3LYP        | 1698 (5.0) | 1723 (2.2) | 1742 (26.2) | 1717 (41.5) |
| \(\omega\)B97XD | 1764 (4.3) | 1808 (6.3) | 1829 (39.4) | 1807 (62.9) |
**Table S5** – Mn-H bond length (in Å) for the most stable HMnOH*(H2O)n, n = 0–3, isomers. The aug-cc-pVDZ basis set was used.

| method          | 5lc | 5lIe | 5llI | 5lVe |
|-----------------|-----|------|------|------|
| CCSD            | 1.639 | 1.609 | 1.599 | 1.601 |
| BHandHLYP       | 1.643 | 1.618 | 1.604 | 1.608 |
| B3LYP           | 1.578 | 1.574 | 1.577 | 1.581 |
| B3P86           | 1.564 | 1.562 | 1.568 | 1.571 |
| BMK             | 1.589 | 1.580 | 1.581 | 1.586 |
| CAM-B3LYP       | 1.575 | 1.568 | 1.572 | 1.575 |
| M06             | 1.597 | 1.590 | 1.596 | 1.599 |
| M06L            | 1.584 | 1.582 | 1.589 | 1.593 |
| M11             | 1.585 | 1.572 | 1.573 | 1.577 |
| MN15            | 1.564 | 1.560 | 1.563 | 1.569 |
| O3LYP           | 1.580 | 1.577 | 1.581 | 1.585 |
| ωB97XD          | 1.569 | 1.566 | 1.572 | 1.576 |

**Table S6** – Position (in cm⁻¹) and intensity (in km mol⁻¹, in parenthesis) of several vibrations in HMnOH*(H₂O). The frequencies are unscaled. The aug-cc-pVDZ basis set was used.

| Method          | Mn-H  | H₂O scissoring | OH stretch |
|-----------------|------|----------------|------------|
| CCSD            | 1598 (17.4) | 1674 (109.6) | 3769 (189.5) | 3858 (238.4) | 3876 (273.7) |
| BHandHLYP       | 1519 (40.6) | 1696 (125.9) | 3876 (227.0) | 3959 (274.0) | 4001 (312.5) |
| B3LYP           | 1759 (3.5) | 1637 (107.5) | 3726 (216.0) | 3811 (279.1) | 3812 (263.9) |
| B3P86           | 1798 (4.6) | 1637 (108.2) | 3757 (221.0) | 3843 (313.5) | 3845 (235.4) |
| BMK             | 1751 (4.1) | 1653 (124.8) | 3815 (245.1) | 3898 (288.6) | 3938 (341.0) |
| CAM-B3LYP       | 1763 (3.0) | 1637 (120.3) | 3752 (230.6) | 3833 (272.7) | 3860 (320.1) |

**Figure S8.** Selected low-energy structures of Mn⁺(H₂O)₄ and HMnOH⁺(H₂O)₃. Relative energies in kJ mol⁻¹ were evaluated at the CCSD(T)/aug-cc-pVDZ//BHandHLYP/aug-cc-pVDZ level of theory.
Figure S9. Selected low-energy structures of Mn\(^+\)(H\(_2\)O\(_8\)) and HMnOH\(^+\)(H\(_2\)O\(_7\)). Relative energies in kJ mol\(^{-1}\) were evaluated at the CCSD(T)/aug-cc-pVDZ//BHandHLYP/aug-cc-pVDZ level of theory.

Figure S10. Interpolation between \(5\text{IVh}\) and \(7\text{IVc}\) minima optimized at the BHandHLYP/aug-cc-pVDZ level and single-point recalculated at the CCSD(T)/aug-cc-pVDZ level. Calculated points are shown as crosses, splines are included to guide the eye.
Calculated Structures and IR Spectra

Cartesian coordinates (in Å) of structures optimized at the BHandHLYP/aug-cc-pVDZ level along with zero-point corrected energies (in a.u.)

| Structure | E (a.u.) | Mn (Å) | O (Å) | H (Å) |
|-----------|---------|--------|-------|-------|
| 7IIa      | -1303.560921 | 0.000000 | 0.746126 | 0.000000 |
|           |         | 1.523974 | -0.827323 | 0.000000 |
|           |         | -1.500634 | -0.905893 | 0.000000 |
|           |         | -2.016449 | -1.161965 | 0.766977 |
|           |         | 1.373818 | -1.773738 | 0.000000 |
|           |         | 2.472361 | -0.689762 | 0.000000 |

| Structure | E (a.u.) | Mn (Å) | O (Å) | H (Å) |
|-----------|---------|--------|-------|-------|
| 5IIb      | -1379.940160 | -0.008482 | -0.365981 | -0.000002 |
|           |         | -1.775979 | -0.563327 | -0.000087 |
|           |         | 2.241391 | -1.395456 | 0.000050 |
|           |         | 0.431783 | 1.707654 | 0.000081 |
|           |         | 2.017654 | -0.199271 | -0.000012 |
|           |         | 0.236621 | -1.951862 | 0.000093 |
|           |         | 2.613825 | 0.954878 | 0.000039 |
|           |         | 2.544109 | 0.691861 | 0.000045 |
|           |         | -0.032782 | 2.575950 | -0.000195 |
|           |         | -1.387460 | 1.808934 | 0.000086 |

| Structure | E (a.u.) | Mn (Å) | O (Å) | H (Å) |
|-----------|---------|--------|-------|-------|
| 5IIIb     | -1456.369339 | -1.477640 | -0.794265 | 1.366107 |
|           |         | -1.029356 | 0.008690 | -0.677134 |
|           |         | -0.215311 | 1.793396 | 0.371788 |
|           |         | 0.867980 | -1.047527 | -0.435071 |
|           |         | 3.206628 | 0.031840 | 0.283348 |
|           |         | 2.357691 | -0.867572 | 1.735091 |
|           |         | 0.963845 | -1.521319 | 1.718368 |
|           |         | -0.137918 | 1.866040 | 1.321190 |
|           |         | -0.030949 | 2.673864 | -0.002155 |
|           |         | 1.722989 | -0.645671 | -1.80534 |
|           |         | 3.786911 | -0.346526 | 0.940490 |
|           |         | 3.763444 | 0.537757 | -0.384678 |
H 1.070690 -1.799728 -0.988798

7IVc
E = -1456.366345
O 0.004253 1.732777 0.758682
Mn -0.000589 0.009299 -0.672864
O -2.306575 -0.263760 -0.142287
H 0.003613 2.660712 0.528877
H -0.776301 -1.766333 1.399978
H 0.773768 -1.765573 1.400408
H -2.854550 0.406201 0.267178
H -2.838712 -0.647485 -0.839913

O 2.305343 -0.267492 -0.143149
H 2.836656 -0.657036 -0.838166
H 2.853965 0.405541 0.260350

5IVd
E = -1456.367513
O 2.098955 0.071238 0.000471
Mn 0.493322 -1.397725 -0.000067
O -0.774430 0.306399 -0.000064
H 3.041461 -0.084366 0.000502
H -0.452078 1.212677 -0.000840
H -1.752105 0.309248 -0.000241
H 1.016107 3.154626 -0.762040
H 1.014926 3.154762 0.761862
H 1.934939 1.025599 -0.000082
O -3.992605 0.206887 -0.756355

5IVe
E = -1456.352768
O -1.828309 -0.080628 -0.597301
Mn -0.957302 2.579151 -0.000082
O -0.094161 -0.084366 0.000050
H -0.452078 1.212677 -0.000840
H -1.752105 0.309248 -0.000241
H 1.016107 3.154626 -0.762040
H 1.014926 3.154762 0.761862
H 1.934939 1.025599 -0.000082
O -3.992605 0.206887 -0.756355

7IVd
E = -1456.35713
O 2.099855 0.071238 0.000471
Mn 0.957302 2.579151 -0.000082
O -0.774430 0.306399 -0.000064
H 3.041461 -0.084366 0.000502
H -0.452078 1.212677 -0.000840
H -1.752105 0.309248 -0.000241
H 1.016107 3.154626 -0.762040
H 1.014926 3.154762 0.761862
H 1.934939 1.025599 -0.000082
O -3.992605 0.206887 -0.756355

5IVf
E = -1456.364577
O 1.821515 -0.850601 -0.000037
Mn 0.000032 -0.000991 -0.000035
O -1.821477 0.850601 -0.000051
H 2.693478 -0.394536 0.000036
H -2.693528 0.394325 0.000008
H -1.972213 1.793881 -0.000864
H -4.674448 -0.551166 0.768564

5IVg
E = -1456.362308
Mn 0.826976 -0.270552 0.00134
O -0.952326 -1.400432 -0.001756
H 2.817113 0.359330 -0.001108
H -0.593154 1.416628 -0.000887
H -0.409225 2.353266 -0.002285
H -1.550084 1.294453 -0.000156
H 3.375379 0.277640 -0.776891
H 3.377325 0.282054 0.773724
H -1.018252 -2.352287 -0.001411
H -1.841090 -1.019772 -0.001135
O -3.163356 0.279641 0.000460
H -3.737502 0.343732 -0.762152
H -3.737243 0.343378 0.763293

5IVh
E = -1456.361415
Mn 0.000759 0.063342 -0.000189
O 0.018703 2.235667 -0.00068
O -0.018571 -2.111039 -0.00028
H 2.198044 -0.192867 0.000707
H -2.200768 -0.156110 0.000426
H -2.743419 0.130455 0.771715
H -2.742947 0.135535 -0.771089
H 0.024367 2.798414 -0.775282
H 0.024635 2.799601 0.774273
H 2.742806 -0.035013 0.772580
H 2.744464 -0.033335 -0.770360
H 0.749947 -2.680069 -0.001471
H -0.797179 -2.664956 -0.000660

5IVi
E = -1456.361189
O 2.189132 -1.240563 -0.369315
Mn 0.459655 -0.158682 0.204120
O -1.468230 0.082846 0.813652
O 1.894902 1.521885 -0.291766
H 3.010064 -0.798498 -0.586284
H 2.343406 -2.183337 -0.373206
H 1.809341 2.053385 -1.084327
H 2.240328 2.100553 0.389259
H -1.726581 0.046999 1.735131
H -2.283380 0.049018 0.268831
O -3.678825 -0.015859 -0.619111
H -4.144259 -0.804203 -0.888979
H -4.242115 0.724748 -0.831290

5IVj
E = -1456.361543
O 3.126926 0.000242 -0.000050
Mn 1.074686 0.000143 0.000017
O -0.905073 0.000005 0.000173
O -2.375082 -2.214299 -0.000493
S15

H 3.687307 0.777039 -0.008496
H -1.468462 -0.797912 -0.000030
H -1.468803 0.777649 0.000044
O 0.276190 2.213740 0.000195
H -2.768037 2.627922 -0.765012
H -2.767842 2.627001 0.766001

5IVk
E = -1456.348268
O 0.885378 -1.355818 -0.000201
Mn -0.858521 -0.336280 -0.000353
O 0.353926 1.378818 0.001662
O -2.314843 0.679144 -0.001201
O 2.983783 0.350662 -0.000610
H -0.065565 2.238991 0.001588
H 1.311244 1.463050 -0.000095
H -3.211571 0.356555 0.000537
H 0.977067 -2.306526 0.002188
H 1.757872 -0.924246 0.000539
H 3.557950 0.431668 0.761336
H 3.557823 0.429392 -0.762889
H -1.687745 -1.704330 0.008438

5IVl
E = -1456.356783
O -0.004780 1.922148 -0.142755
Mn 0.001958 -0.287186 0.458927
O 2.148192 -0.381031 -0.000122
O -1.497862 -1.277720 0.000125
O -2.786430 1.213958 0.000011
H -0.417773 0.288415 -0.486300
H 0.764085 1.303709 -0.061314
H 1.663497 3.452590 -0.492418
H 1.230977 3.95512 0.964846
H -2.671365 -0.144415 -0.419284
H -2.184567 0.69468 -1.877327
H -0.697656 -0.220616 0.622957
H -4.609879 0.505937 0.929323
H -4.592730 -1.009865 0.741210

5IVm
E = -1456.344540
O -0.446723 -1.354652 -0.086293
Mn 0.629924 0.410330 -0.036029
O -0.835000 1.452235 0.011852
O 2.344980 -0.691235 0.109945
O -2.831865 -0.512710 0.033810
O -0.775559 2.403845 0.001623
H 3.222110 -0.308064 0.086740
H 2.418113 -1.602605 0.393993
H -0.328584 2.151313 -0.599183
H -1.428754 -1.180947 -0.000238
H -3.626178 -0.702379 0.526272
H -2.651163 0.429012 0.089834
H 1.570779 1.705089 -0.152833

TS1
E = -1456.363170
O 2.677246 1.145571 0.000111
Mn 0.688450 -0.937897 -0.00058
O 0.002349 1.093801 -0.000122
O -1.497862 -1.277720 0.000125
O -2.786430 1.213958 0.000011
H 3.252394 1.230964 -0.759059
H 3.252265 1.230964 0.759374
H 0.679011 1.771972 -0.000068
H -0.886202 1.464821 -0.000091
H -3.282264 1.512824 0.761629
H -3.282322 1.512723 -0.761608
H -2.150861 -0.565600 0.000107
H -1.955712 -2.116076 0.000177

TS2
E = -1456.369392
O 3.105931 -0.030471 0.289145
H 0.338340 1.779355 1.261443
H 0.696188 -0.500380 0.874968
H 3.661074 0.524232 -0.255411
H 1.661126 -0.710801 -0.301710
H 0.796602 -1.067668 -0.586409
H 0.969759 -1.757476 -1.224592
H -1.066555 0.073509 -0.629485
O -1.394537 -0.845623 1.383903
H -0.937601 -1.643387 1.631722
H -2.230840 -0.842756 1.849808
O -0.051845 1.773213 0.387111
H -0.149777 2.683937 0.111599

TS3
E = -1456.364319
O 2.473049 0.086495 0.069146
H -0.220274 -0.044305 -0.735543
O -0.157473 1.722133 0.676841
H 0.418870 -1.540256 0.738271
H -2.246039 -0.271814 0.303029
H -2.394943 -0.860745 1.849198
H -3.067755 -0.203163 -0.173765
H -0.943790 1.944325 1.175310
H 0.298377 2.542385 0.492338
H 0.281588 -2.484908 0.684539
H 1.362936 -1.387732 0.846654
H 2.935309 0.671912 0.667689

S15
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| Mn      | -0.358247 | -0.333416 | -0.308974 |
| O       | 0.700602  | 0.110158  | 1.497030  |
| O       | 1.033881  | -1.210016 | -1.212982 |
| O       | -0.499034 | -3.065615 | 0.814361  |
| H       | -2.030293 | 0.314976  | 0.680504  |
| H       | 0.918318  | -1.411922 | -2.128710 |
| Mn      | -1.295944 | -0.533846 | -1.600155 |
| O       | 0.700602  | 0.110158  | 1.497030  |
| O       | 1.033881  | -1.210016 | -1.212982 |
| O       | -0.499034 | -3.065615 | 0.814361  |
| H       | -2.030293 | 0.314976  | 0.680504  |
| H       | 0.918318  | -1.411922 | -2.128710 |
| O       | 1.449766  | 0.729041  | 1.438495  |
| O       | 1.107940  | 2.053575  | -0.369539 |
| O       | 0.133801  | 2.211827  | -1.564788 |
| O       | 0.864874  | 2.940986  | 0.283156  |
| H       | -1.217987 | -2.878225 | 1.169905  |
| O       | -1.899790 | 0.917047  | 1.418107  |
| H       | -2.908677 | 0.485522  | 0.289575  |
| H       | 0.976956  | -0.649709 | 2.005540  |
| H       | -1.295944 | -0.533846 | -1.600155 |
| H       | 0.494441  | -0.586718 | -0.414611 |
| O       | 0.932284  | -2.601474 | 0.113728  |
| O       | -1.552627 | -1.990956 | -0.954063 |
| H       | 0.243191  | -0.113487 | 0.839527  |
| H       | 0.451233  | 0.772891  | -0.297147 |
| H       | -4.701286 | 1.358498  | -1.007459 |
| H       | -5.247941 | 0.333953  | -0.009209 |

**SVIIIe**

E = -1761.956073

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| Mn      | 0.899417  | -0.483129 | -0.183938 |
| O       | 0.797907  | 1.501366  | 0.781905  |
| O       | 2.689898  | 0.653610  | -1.84676  |
| O       | -0.113384 | 0.012808  | -1.719592 |

**SVIIIg**

E = -1761.959040

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| Mn      | -0.999465 | -1.333605 | 0.529355  |
| O       | 0.119890  | -0.059688 | 1.951071  |
| Mn      | 0.494441  | -0.586718 | -0.414611 |
| O       | 0.932284  | -2.601474 | 0.113728  |
| O       | -1.552627 | -1.990956 | -0.954063 |
| H       | 0.243191  | -0.113487 | 0.839527  |
| H       | 0.451233  | 0.772891  | -0.297147 |
| H       | -4.701286 | 1.358498  | -1.007459 |
| H       | -5.247941 | 0.333953  | -0.009209 |

**SVIIIf**

E = -1761.957827

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| Mn      | 2.332732  | -2.48534  | 0.013011  |
| O       | 0.743088  | -0.75655  | 1.467344  |
| Mn      | 1.473254  | 1.759822  | -0.263984 |
| O       | 0.639252  | -1.863394 | -1.089224 |
| H       | 1.386983  | 1.055419  | 2.071708  |
| H       | -1.203150 | 2.394363  | -0.333867 |
| H       | 2.033858  | 2.506249  | -0.462813 |
| Element | X  | Y  | Z   |
|---------|----|----|-----|
| H       | 0.547673 | 2.040375 | -0.364780 |
| H       | 1.357755  | -1.591475  | -2.279640  |
| H       | 0.094789  | -1.498708  | -1.367935  |
| H       | 0.133858  | 0.160497   | 1.785380   |
| H       | 0.314295  | -1.410436  | 1.659884   |
| H       | -1.531482  | 1.574820   | 2.858990   |
| H       | -1.457773  | 1.655679   | 1.315877   |
| H       | -1.466975  | 3.300818   | -0.479286  |
| H       | -1.684238  | 1.855077   | -0.993365  |
| H       | -1.978798  | -2.676175  | -1.457672  |
| H       | -1.849484  | -1.879787  | -0.139833  |
| O       | 0.238177  | 0.697347   | -2.066662  |
| H       | -3.106976  | 0.784002   | -2.618618  |
| H       | -2.265604  | -0.239541  | -1.817471  |
| O       | -1.981397  | 1.656553   | 1.613899   |
| H       | -2.578551  | -2.167539  | 2.153867   |
| H       | -2.076560  | -0.734924  | 1.879633   |

5VIII

**E = -1761.953598**

| Element | X  | Y  | Z   |
|---------|----|----|-----|
| O       | 1.903665  | -0.557737  | 0.888075  |
| Mn      | 0.095042  | -0.124315  | 0.625381  |
| O       | -1.847652  | 0.538491   | 0.643586  |
| O       | 0.560802   | 1.585364   | -0.465777 |
| O       | -0.452195  | -1.466556  | -0.970526 |
| O       | -1.931834  | 2.938760   | -0.785212 |
| O       | 3.084552   | 1.778636   | 0.000990  |
| O       | -3.228314  | -1.787294  | 0.106363  |
| H       | 1.894218   | -2.606783  | -1.049032 |
| H       | -2.070475  | 1.324633   | 0.127204  |
| H       | -2.515904  | -0.147539  | 0.503293  |
| H       | 2.147722   | -0.939612  | 1.726614  |
| H       | -0.036021  | 2.284488   | -0.733875 |
| H       | 1.499230   | 1.876066   | -0.461797 |
| H       | -1.255488  | -1.980876  | -0.893925 |
| H       | 0.293107   | -2.051890  | -1.208226 |
| H       | -4.004760  | -1.876455  | -0.443702 |
| H       | -3.373457  | -3.274161  | 0.847258  |
| H       | -2.146610  | 3.724717   | -0.294763 |
| H       | -2.314635  | 3.055820   | -1.652206 |
| H       | 3.922862   | 1.873249   | -0.440912 |
| H       | 3.031369   | 0.888823   | 0.377325  |
| H       | 2.242913   | -1.974493  | -0.481436 |
| H       | 2.684340   | -2.884641  | -1.611161 |
| H       | -0.270846  | -1.009923  | 1.916793  |

5VIIIj

**E = -1761.952832**

| Element | X  | Y  | Z   |
|---------|----|----|-----|
| Mn      | -0.362854  | 0.254244  | -0.992286 |
| H       | -2.798344  | 0.279035   | -1.353871 |
| O       | 0.096807   | 1.014430   | 0.868055  |
| O       | 1.521996   | 0.747864   | -1.542502 |
| O       | 0.222206   | -1.813899  | -0.360854 |
| H       | 0.442859   | 2.435890   | -1.049902 |
| H       | -0.578224  | -2.161866  | 0.097640  |
| O       | -2.065294  | -2.163383  | 0.793902  |
| H       | -2.475116  | -1.482495  | 0.362037  |
| H       | -2.733386  | -2.821941  | 0.959121  |
| O       | -2.194160  | 0.202892   | -0.620965 |
| H       | -0.682527  | 0.042758   | -2.551717 |

7VIIIj

**E = -1761.953392**

| Element | X  | Y  | Z   |
|---------|----|----|-----|
| O       | 1.953395  | -1.878646  | 0.334847  |
| Mn      | 0.172176   | -0.457513  | 0.689746  |
| O       | 1.598463   | 0.976296   | -0.011103 |
| O       | -1.425038  | 1.238479   | -0.082906 |
| O       | -0.482597  | -1.339186  | -1.215837 |
| O       | -3.114448  | -0.794655  | -1.444269 |
| O       | 4.168497   | -0.238426  | -0.288480 |
| O       | -3.506427  | -0.109999  | 1.290290  |
| H       | -2.194412  | 1.076555   | 0.477720  |
| H       | -1.736487  | 1.037625   | -0.968894 |
| H       | 2.083709   | -2.617176  | 0.926124  |
| H       | 2.821640   | -1.499804  | 0.150923  |
| H       | -1.429628  | -1.342170  | -1.428984 |
| H       | -0.083078  | -2.136116  | -1.555220 |
| H       | 1.369601   | 1.911734   | -0.156488 |
| H       | 2.534156   | 0.830879   | -0.161167 |
H -4.278572 0.127737 1.800838
H -2.943458 -0.620075 1.877409
H -3.527088 -0.750857 -0.575879
H -3.788996 -1.050431 -2.067947
H 4.597384 -0.302726 -1.140252
H 4.865185 -0.048841 0.337869
O 0.466592 3.341737 -0.393377
H 0.558542 4.241601 -0.093926
H -0.420787 3.050290 -0.178645

7VIIIm
E = -1761.954747
O -2.167641 -2.160891 0.956482
Mn -1.866996 -0.450763 -0.770700
O -2.189647 0.692937 1.111262
O 0.117170 -1.064391 -0.060484
O -0.680707 1.315047 -1.577604
O 0.024699 1.882106 1.996618
O 1.645837 2.475300 -0.307444
H 0.098808 1.761988 -1.218631
H -0.953034 1.768819 -2.371352
H -2.548465 -1.723942 1.718214
H -2.716235 -2.922328 0.774559
H -1.417957 1.160351 1.489723
H -2.930981 1.292221 1.162671
H 1.029171 -0.897557 -0.335195
O 0.098922 -1.803733 0.543192
H 2.184788 2.960203 -0.517523
H 2.187138 1.360746 -0.467551
H 0.685947 2.049999 1.330483
H 0.194034 2.423820 2.761443
O 0.703381 -0.359185 -0.826772
H 2.896981 -0.541020 -1.744055
H 3.447263 -0.730433 -0.322792
O 4.784399 -1.404726 0.568442
H 4.958302 -2.329920 0.731886
H 5.568279 -0.938553 0.848435

7VIIIo
E = -1761.950529
O -1.958896 2.994714 -0.580825
Mn -0.710847 -0.590041 -0.446632
O -0.166414 -1.089749 1.605881
O 2.823074 -1.075261 -2.032364
O 2.501736 0.519719 0.141497
O 0.392133 1.435540 0.141522
O 3.066343 0.897250 -0.222209
H 1.330246 1.388271 -0.107845
H 0.460416 1.612679 0.183190
H -2.815583 0.515466 1.043755
H -2.487513 1.452933 -0.149840
H -1.006694 2.969053 -0.671177
H -2.291548 3.682614 -1.150728
H 3.343642 -1.471260 -2.726786
H 1.901710 -1.241572 -2.240228
H 0.690257 -0.778915 1.957490
H -0.376777 -1.930097 2.005368
H 3.760597 1.525646 -0.404167
H 3.122644 0.280869 -0.908252
O -2.256152 -2.321147 -0.117978
H -3.173003 -2.081451 -0.252591
H -2.129400 -3.155723 -0.567421
H 2.691601 0.290868 1.521194
O 2.117830 0.108536 2.275887
H 2.675124 0.007010 3.042560

5VIIIp
E = -1761.948660
O -2.063489 -1.374169 0.806629
Mn -0.318023 -0.285486 0.628028
O 0.264915 -1.401266 -1.117746
O 1.525749 1.173252 -0.262871
O 1.095123 0.882498 0.739718
O 0.242087 2.991343 -0.699432
O 2.857503 -1.205893 -1.512853
O -4.116014 -0.176447 -0.509025
O 3.965343 -0.024220 0.826124
H 1.943524 0.595446 1.070502
H -2.245001 -1.994182 1.507726
H -2.896402 -1.050457 0.425152
H 1.215907 -1.319743 -1.351999
H -0.022395 -2.273724 -1.371480
H -1.047483 1.991529 -0.535489
H -2.360725 1.080140 -0.716343
H 4.372146 -0.641213 1.431221
H 4.544596 0.734920 0.806818
H 3.324403 -0.757658 -0.799037
H 3.319973 -1.010271 -2.322650
H -4.828379 0.273692 -0.057220
H -4.513507 -0.585835 -1.276024
H 0.308762 3.887670 -0.383589
H 0.809236 2.435248 -0.140338
O  -2.040031  1.001485  -1.538039
O   2.764258  -1.503912   0.032268
H   3.493577   1.225087  -0.039692
H   3.108888  -1.425502   1.172928
H   0.376863  -1.017796   2.356577
O  -1.698464  1.766098  -1.305987
H   4.021639   1.636334   0.645489
H   3.850698   1.550134  -0.867491
O  -3.048187  -1.408975  -0.670245
O   3.426550  -2.192166  -0.029246
H   0.451701  -1.106794  -1.487119
H   0.449025  -0.932487  -2.430053
H  -1.519470  -1.521039  -0.543642
Mn   0.000183  -0.089442  -0.041242
O   1.517874   1.522676  -0.544584
O   1.481413   1.466144  -0.258687
O  -1.480739   1.466911  -0.257742
O   -3.905667   0.009665  -1.036355
O   0.001885   3.759415   0.551626
H   1.289598   2.358244   0.043185
H   2.412185   1.262926  -0.129387
O  -1.345922  -2.962468  -0.182347
O  -1.288259   2.359019   0.043561
Mn   0.000183  -0.089442   0.041242
O   1.517874   1.522676   0.544584
O   1.481413   1.466144   0.258687
O  -1.480739   1.466911   0.257742
O   -3.905667   0.009665  -1.036355
O   0.001885   3.759415   0.551626
O  -2.391041   1.465354  -0.170500
Mn   0.749126   -0.021640   0.255555
O   0.620199   -1.740478  -0.127440
O   0.421045   1.175687  -1.407350
O  -2.015243   -1.019531   1.518905
Mn   2.770388   1.493252  -0.032043
O   3.461966   -1.242467   0.386822
H   1.582968   -1.641650  -0.111040
H  -2.293115   2.396292  -0.181960
O   -3.021021   1.391855   0.735733
O   1.319888   1.439042  -1.162977
H   0.379611   1.072020  -2.355711
H   -1.642986   -1.227494   2.389443
H   -2.571862   -1.774724   1.283884
O  -4.010470   -1.664664  -0.623657
Mn   3.781204   -1.568938   0.881768
O   3.228862   0.642699  -0.029394
O   3.438588   2.175758  -0.028955
O   0.463313   1.081617   1.491979
O   0.477830   0.847978   2.422400
H   1.354304   1.360262   1.239727
H   0.413075   -2.478410   0.457068
O   -1.785270   -0.941281  -1.704074
H   -1.577308   -1.837047  -1.976184
H   -2.694407   -0.769188  -1.952697

S21
IR frequencies (in cm⁻¹, without shift) and intensities (KM/mole) for structures optimized at the BHandHLYP/aug-cc-pVDZ level

7IIa
30.7313 1.5476
87.9991 0.8598
236.9107 2.3411
276.1865 20.9571
304.3383 4.7
345.2992 225.8488
385.3786 226.5671
484.8917 14.853
491.3515 60.4095
1679.5964 125.2825
1689.8342 104.4727
3889.1754 180.4236
3982.5449 0.0
3983.862 432.272

7IIb
64.4194 0.4304
150.5894 17.4743
259.569 66.7381
284.6552 240.7681
287.456 104.8601
356.195 9.1429
425.3049 29.3894
677.675 16.1289
958.016 116.8184
1671.4813 110.3169
1712.0438 24.4526
3262.5427 1644.2576
3940.0512 1851.9349
3953.7438 432.272
4037.4487 172.1753

5IId
72.5571 0.5696
142.1434 17.5368
266.7639 235.5138
272.7132 91.5338
275.9713 61.8532
362.6967 14.853
469.074 8.3496
709.2875 14.1721
979.872 105.0031
1671.0543 118.7193
1707.7235 31.6763
3188.5029 189.9172
3939.3482 78.4426
3955.0165 162.7554
4037.4487 172.1753

7IIIa
73.8619 1.2155
85.5225 15.9741
260.9292 9.1429
264.1715 401.5665
326.3575 0.0
348.8574 15.2654
513.9258 8.953
518.7483 0.0
1672.7284 293.1942
1675.6326 0.0
3888.8677 0.0
3889.1754 180.4236
3982.5449 0.0
3983.862 432.272

5IIe
108.1392 8.1895
127.2444 1.6808
161.2034 14.1344
244.1491 95.7888
376.4654 316.9314
386.8627 4.0363
471.2303 21.3701
612.767 55.9616
648.012 95.7626
755.4344 60.3741
1518.7647 40.5962
1696.1539 125.873
3876.0383 226.9629
3958.9199 273.9858
4001.3882 312.5054

7IIIb
32.2178 0.0
84.9665 11.5522
85.5225 15.9741
260.9292 9.1429
264.1715 401.5665
326.3575 0.0
438.8574 15.2654
513.9258 8.953
518.7483 0.0
1672.7284 293.1942
1675.6326 0.0
3888.8677 0.0
3889.1754 180.4236
3982.5449 0.0
3983.862 432.272
| 374.2774  | 295.3887 |
| 377.5165  | 151.9465 |
| 377.8763  | 151.7147 |
| 469.8298  | 15.7541  |
| 469.9987  | 15.7772  |
| 495.4699  | 133.0868 |
| 1677.694  | 157.9717 |
| 1677.7737 | 157.7355 |
| 1678.8535 | 50.3446  |
| 3897.8261 | 83.9487  |
| 3897.8793 | 84.0586  |
| 3898.4833 | 7.7427   |
| 3995.5277 | 143.954  |
| 3995.8322 | 174.1667 |
| 3995.8998 | 175.0731 |
| 5IIIb     |          |
| 39.9443   | 0.2566   |
| 137.7076  | 6.5883   |
| 138.6667  | 1.0098   |
| 186.3595  | 7.116    |
| 199.8761  | 22.2406  |
| 278.438   | 121.1408 |
| 351.2413  | 17.6098  |
| 353.5917  | 42.8807  |
| 389.0305  | 2.5379   |
| 397.9657  | 345.9156 |
| 441.6536  | 178.763  |
| 455.5254  | 116.4886 |
| 455.7145  | 40.8246  |

| 5IVa      |          |
| 42.9684   | 7.521    |
| 45.1123   | 4.9006   |
| 94.2161   | 0.4003   |
| 122.5136  | 12.6196  |
| 186.3595  | 7.116    |
| 199.8761  | 22.2406  |
| 278.438   | 121.1408 |
| 351.2413  | 17.6098  |
| 353.5917  | 42.8807  |
| 389.0305  | 2.5379   |
| 397.9657  | 345.9156 |
| 441.6536  | 178.763  |
| 455.5254  | 116.4886 |
| 455.7145  | 40.8246  |

| 5IVb      |          |
| 19.5168   | 3.0178   |
| 42.6985   | 1.336    |
| 69.557    | 1.3089   |
| 78.5286   | 0.3916   |
| 98.9587   | 1.6959   |
| 121.5735  | 6.0782   |
| 149.4596  | 11.4349  |
| 213.2874  | 8.5387   |
| 247.9119  | 29.9935  |
| 263.5666  | 22.7448  |
| 268.5113  | 192.3799 |
| 282.9537  | 28.0317  |
| 310.0129  | 168.2474 |
| 321.2488  | 60.7979  |
| 340.662   | 109.935  |
| 361.3521  | 14.209   |
| 374.4941  | 151.0492 |
| 460.8868  | 29.7108  |
| 477.1243  | 48.7172  |
| 617.9543  | 72.3425  |
| 881.2137  | 102.5294 |
| 1671.4088 | 135.491  |
| 1673.4047 | 118.7798 |
| 1677.6679 | 132.9661 |
| 1711.997  | 42.9563  |
| 3499.9625 | 113.5282 |
| 3904.6508 | 53.0451  |
| 3907.5688 | 39.7513  |
| 3946.2533 | 50.8363  |
| 3976.4224 | 128.7237 |
| 4005.4004 | 157.5912 |
| 4010.2682 | 153.7353 |
| 4044.3099 | 145.4817 |

| 7IVc      |          |
| 54.0779   | 5.4163   |
| 64.9725   | 1.0025   |
| 74.8696   | 0.1122   |
| 80.0936   | 0.8656   |
| 98.9242   | 1.2561   |
| 152.5145  | 0.5326   |
| 176.223   | 1.778    |
| x     | y     | x     | y     | x     | y     |
|-------|-------|-------|-------|-------|-------|
| 184.1201 | 5.9933 | 198.6998 | 0.2392 | 248.8043 | 12.6683 |
| 255.1553 | 0.385  | 282.1176 | 194.8212 | 290.2213 | 2.7854 |
| 366.2371 | 0.2549 | 373.7828 | 218.3584 | 380.3769 | 35.2781 |
| 387.6279 | 152.2468 | 397.6579 | 207.6486 | 4011.8939 | 154.2561 |
| 4024.1055 | 147.0971 | 43.5677 | 1.8151 | 46.0031 | 0.8551 |
| 76.8039 | 7.9126 | 115.2282 | 0.6609 | 121.8842 | 0.9161 |
| 203.3622 | 129.171 | 216.0635 | 151.7201 |
| 261.7982 | 33.7986 | 263.1669 | 0.0007 | 265.7518 | 59.9836 |
| 303.004 | 55.566 | 312.6232 | 16.5709 | 324.8286 | 28.2735 |
| 460.5175 | 22.186 | 464.4597 | 158.1741 | 601.1006 | 122.2547 |
| 630.1918 | 37.1428 | 733.7736 | 170.7535 | 750.6448 | 83.1769 |
| 882.8722 | 93.2025 | 1663.8138 | 125.3614 | 1679.1095 | 94.8195 |
| 1681.3577 | 85.8534 | 1714.1317 | 1.4444 | 3498.5837 | 1309.5113 |
| 3693.5433 | 453.2755 | 3833.0983 | 591.7939 | 3924.8967 | 31.2302 |
| 3952.0663 | 48.3787 | 3989.8578 | 188.0712 | 4014.1241 | 154.1246 |
| 4052.3723 | 148.634 | 51.7498 | 1.9164 | 76.2926 | 7.6453 |
| 92.2267 | 1.0046 | 109.2214 | 1.0926 | 168.6119 | 1.0583 |
| 174.7699 | 8.5842 | 224.3427 | 97.4097 | 231.9229 | 23.2782 |
| 282.0973 | 37.2427 | 302.036 | 1.0713 | 319.4474 | 22.9073 |
| 345.656 | 133.3019 | 356.7796 | 24.0056 | 374.9136 | 84.849 |
| 415.0821 | 152.1158 | 457.329 | 389.9039 | 497.9115 | 30.2685 |
| 539.1565 | 3.0702 | 591.7115 | 138.4476 | 664.015 | 79.3901 |
| 667.5775 | 92.554 | 757.4491 | 32.1734 | 1610.4642 | 4.1794 |
| 1671.3643 | 158.6301 | 1676.2725 | 142.3698 | 1686.9227 | 89.0073 |
| 3880.937 | 105.2335 | 3914.9822 | 178.0841 | 3920.0775 | 67.8628 |
| 4002.586 | 141.9144 | 4005.9328 | 249.0783 | 4021.6249 | 170.3057 |
| 4026.9378 | 167.4577 | 51.7498 | 1.9164 | 104.9497 | 2.4788 |
| 109.8402 | 2.6424 | 143.8706 | 2.6316 | 176.2974 | 8.5456 |
| 240.3235 | 11.2215 | 248.2196 | 6.1937 | 259.2606 | 20.2835 |
| 310.534 | 3.4907 | 351.1647 | 1.0521 | 370.4094 | 27.6365 |
| 386.8653 | 101.7293 | 395.05 | 352.2192 | 420.6617 | 2.9036 |
| 500.5231 | 159.1732 | 599.5056 | 58.292 | 609.5015 | 58.6038 |
| 644.7412 | 88.9177 | 709.2615 | 205.5215 | 749.2148 | 107.8348 |
| 765.3785 | 3.9502 | 807.5329 | 134.966 |
| Value 1 | Value 2 | Value 3 |
|--------|--------|--------|
| 1635.0347 | 156.1902 | 1669.5699 |
| 1677.2874 | 71.1979 | 1710.8261 |
| 3587.9117 | 840.1542 | 3836.9848 |
| 3914.4335 | 49.6618 | 3983.3130 |
| 5VIIIa | 56.1836 | 2.8279 |
| 82.6794 | 5.4571 | 87.9952 |
| 106.2764 | 7.797 | 113.3035 |
| 126.3205 | 0.6609 | 128.4093 |
| 143.9006 | 1.8382 | 155.1619 |
| 161.7271 | 4.6362 | 169.3527 |
| 179.0415 | 48.1226 | 181.1201 |
| 208.2822 | 32.1122 | 216.0418 |
| 219.8302 | 8.4345 | 227.0355 |
| 250.6329 | 30.9867 | 252.6946 |
| 278.5071 | 96.6289 | 279.0589 |
| 326.3223 | 14.6932 | 349.3986 |
| 362.629 | 66.053 | 381.7001 |
| 399.0197 | 7.3065 | 412.8615 |
| 458.1746 | 28.1758 | 457.5497 |
| 523.0303 | 95.9834 | 550.2326 |
| 527.9529 | 72.4698 | 562.042 |
| 560.842 | 75.8904 | 596.1288 |
| 576.6586 | 66.3455 | 600.6034 |
| 596.1288 | 39.2398 | 596.1288 |
| 605.9842 | 162.9757 | 893.2001 |
| 891.8891 | 108.5766 | 1584.9211 |

S25
| Value 1 | Value 2 |
|--------|--------|
| 212.3145 | 6.209  |
| 219.5235 | 6.8502 |
| 237.4034 | 40.3167|
| 252.116  | 12.5469|
| 260.6788 | 32.5974|
| 273.6764 | 4.4652 |
| 279.449  | 81.459  |
| 288.3607 | 46.629  |
| 306.9081 | 11.5836 |
| 314.6349 | 17.6027 |
| 330.3155 | 17.0222 |
| 350.6962 | 7.0456 |
| 365.4091 | 34.5248 |
| 374.7828 | 204.9829|
| 385.7183 | 8.8052 |
| 411.4814 | 14.4445 |
| 420.5612 | 75.7705 |
| 462.788  | 198.7232|
| 487.4739 | 18.2222 |
| 506.5942 | 55.2512 |
| 543.9267 | 5.3379 |
| 583.2721 | 72.9249 |
| 607.6409 | 113.7286|
| 648.4915 | 153.9599|
| 665.3655 | 107.4823|
| 710.0712 | 94.0263 |
| 740.9246 | 297.4551 |
| 762.5138 | 36.0303 |
| 827.3995 | 31.6383 |
| 875.9369 | 184.294 |
| 108.1373 | 1.5141 |
| 115.5768 | 3.934 |
| 127.8249 | 4.8666 |
| 149.5447 | 3.8025 |
| 151.526  | 4.1923 |
| 169.4226 | 6.0828 |
| 182.8688 | 2.6347 |
| 198.4364 | 125.787 |
| 266.0648 | 51.5012 |
| 215.5309 | 50.9608 |
| 237.572  | 13.8914 |
| 239.9132 | 34.8144 |
| 272.4414 | 46.2683 |
| 278.922  | 14.5741 |
| 292.0876 | 118.7396|
| 302.2137 | 62.031  |
| 316.1474 | 24.5717 |
| 318.2483 | 17.7465 |
| 332.9461 | 17.0885 |
| 365.9241 | 51.8961 |
| 368.2267 | 62.1888 |
| 384.964  | 89.3352 |
| 396.9832 | 30.4865 |
| 430.8961 | 112.5027|
| 434.8346 | 348.3364|
| 468.3361 | 10.1053 |
| 487.3263 | 34.1793 |
| 530.9574 | 35.5362 |
| 541.6015 | 64.2345 |
| 567.863  | 15.7021 |
| 593.856  | 145.954 |
| 616.2489 | 18.0209 |
| 656.9221 | 259.4174|
| 692.3595 | 32.9955 |
| 733.201  | 270.7121 |
| 737.8507 | 148.1251|
| 761.2398 | 37.4377 |
| 838.6419 | 36.2401 |
| 873.2222 | 170.3138 |
| 893.1063 | 112.2466|
| 937.7181 | 75.5455 |
| 1516.8739| 12.5315 |
| 1642.4099| 80.9084 |
| 1661.0224| 98.1885 |
| 1674.0517| 148.9232|
| 1681.9538| 135.211 |
| 1697.0587| 68.365 |
| 1762.3612| 53.4237 |
| 1726.4131| 5.0126 |
| 1804.4875| 332.5328|
| 1847.1905| 1030.9306|
| 1872.5962| 522.5168|
| 1893.1992| 891.9697 |
| 3687.6788| 983.031 |
| 3754.6562| 448.862 |
| 3926.448  | 101.559 |
| 3997.4647 | 194.926 |
| 4005.1914| 48.3467 |
4009.0102 169.4377
4015.2688 108.7967
4018.9573 139.5471
4025.5714 183.5996
4034.4058 124.3278
4038.8560 195.6519

5VIIIg
19.1493 5.0972
29.7920 1.06
35.964 4.9159
41.7009 0.693
53.3881 2.1232
57.6729 0.4791
80.3761 0.8264
97.4741 7.5928
107.4439 1.7912
109.2036 0.6733
122.1422 1.1444
127.1349 6.5156
153.7851 1.1768
155.2860 68.8678
173.8331 4.8784
189.9604 71.7761
192.6165 26.332
202.8694 162.8109
214.3370 65.0791
218.8506 77.4018
230.6922 46.6529
263.7473 9.0374
270.2147 10.7719
277.5581 19.2261
302.6749 18.7495
316.0735 6.9734
328.6444 35.0115
349.8983 27.4359
377.6002 12.4494
388.0885 54.1246
398.1797 13.3936
444.0543 136.8775
456.6165 74.7829
523.0103 42.0591
608.1108 42.0591
620.7414 141.878
622.0042 66.4018
645.815 33.116
699.0647 226.8559
704.6638 155.2827
708.131 49.4275
811.6154 152.3909
816.6266 167.201
881.7702 47.4243
1670.1691 125.7279
1672.7373 18.1924
1678.2198 204.15
1682.1804 107.6207
1695.5989 62.6176
1697.0210 39.3709
1713.9447 16.3507
1721.3673 12.6427
3562.8917 965.8073
3628.1143 976.5264
3643.0297 344.9133
3720.9604 523.4102
3744.8127 231.8459
3814.2385 813.5149
3833.5044 228.8297
3851.3615 683.6023
3930.8797 10.5185
3957.1525 35.2266
4002.9724 100.7719
4009.14 195.7355
4016.8027 90.7186
4021.7775 147.0779
4032.1818 177.2857
4058.9382 129.7427

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