# SUPPLEMENTARY MATERIALS

## Dimer Rhenium Tetrafluoride with a Triple Bond Re-Re: Structure, Bond Strength

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Table S1. Disagreement factor $R_f$ and calculated vibration amplitude *l*(F5…F10) versus the torsion vibration frequency of the $Re_2F_8$ molecule.

| $\nu_{tors}$ | 20 см$^{-1}$ | 30 см$^{-1}$ | | 40 см$^{-1}$ | 50 см$^{-1}$ |
|---|---|---|---|---|---|
| $R_f$, % | 5.061 | 4.832 | | 5.145 | 5.491 |
| | $l_{calc}$[1] | $l_{calc}$ | $l_{exp}$ | $l_{calc}$ | $l_{calc}$ |
| F5…F10, Å | 0.432 | 0.314 | 0.315(15) | 0.260 | 0.231 |

[1] Calculated (using different values of the torsion force constant and frequency) and experimental vibration amplitudes of the $Re_2F_8$ molecule.

Table S2. The calculated and experimental structural characteristics of the $[Re_2X_8]^{2-}$ (X=F, Cl, Br).

| | | r(Re-Re), Å | r(Re-X), Å | α(XReRe),° | ν(Re-Re), cm$^{-1}$ | $\nu_{tors}$ cm$^{-1}$ | ν(Re-X) [a] cm$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $[Re_2F_8]^{2-}$ | calc<br>exp [15] | 2.231<br>2.188(3) | 1.977<br>1.92 - 1.96(3) | 104.2<br>99.9 - 102.6(4) | 337<br>317 | 66 | 485 - 579<br>525 - 568 |
| $[Re_2Cl_8]^{2-}$ | calc<br>exp [13] | 2.216<br>2.224(1) | 2.357<br>2.330(2) | 104.5<br>103.4(5) | 292<br>274 [12] | 44 | 267 - 336<br>361 [12] |
| $[Re_2Br_8]^{2-}$ | calc<br>exp [13] | 2.225<br>2.226(4) | 2.512<br>2.467(4) | 105.2<br>104.6(4) | 287<br>276 [12] | 25 | 159 - 224<br>211 [12] |

[a] the range of eight stretching Re-X vibration frequencies.

Table S3. Conditions of the synchronous GED/MS experiments.

| Nozzle-to plate distances, mm | **338** | **598** |
|---|---|---|
| Number of recorded plates | 7 | 7 |
| Electron beam current, μA | 2.7 | 0.6 |
| Wavelength of electrons, Å | 0.04329(8) | 0.04335(8) |
| Temperature of the effusion cell, K | 471(5) | 471(5) |
| Average exposure time, s | 180 | 105 |
| Residual gas pressure in diffraction chamber, Torr | $1.3 \cdot 10^{-6}$ | $3.1 \cdot 10^{-6}$ |
| s-range/Δs, Å$^{-1}$ | 2.4-23.3/0.1 | 1.1-15.0/0.1 |
| Ionization voltage, V | 50 | 50 |

Table S4. The vibrational frequency values of the molecule $Re_2F_8$ obtained in three variants DFT.

| Frequency, $cm^{-1}$ | PBE0/qRECP-1 | B3LYP/qRECP-2 | PBE/RECP-3 |
|---|---|---|---|
| $\omega_1(a_{1g})$ | 749 | 710 | 704 |
| $\omega_2(e_u)$ | 711 | 687 | 677 |
| $\omega_3(a_{2u})$ | 699 | 672 | 665 |
| $\omega_4(e_g)$ | 689 | 668 | 657 |
| $\omega_5(b_{1g})$ | 670 | 642 | 638 |
| $\omega_6(b_{2u})$ | 617 | 594 | 597 |
| $\omega_7(a_{1g})$ | 370 | 345 | 338 |
| $\omega_8(b_{2g})$ | 325 | 309 | 312 |
| $\omega_9(b_{1u})$ | 312 | 296 | 304 |
| $\omega_{10}(a_{2u})$ | 272 | 271 | 265 |
| $\omega_{11}(e_g)$ | 221 | 207 | 217 |
| $\omega_{12}(a_{1g})$ | 193 | 198 | 185 |
| $\omega_{13}(e_u)$ | 213 | 197 | 207 |
| $\omega_{14}(e_g)$ | 193 | 186 | 186 |
| $\omega_{15}(b_{1g})$ | 170 | 183 | 161 |
| $\omega_{16}(b_{2u})$ | 172 | 177 | 173 |
| $\omega_{17}(e_u)$ | 131 | 147 | 125 |
| $\omega_{18}(a_{1u})$ | 40 | 10 | 43 |

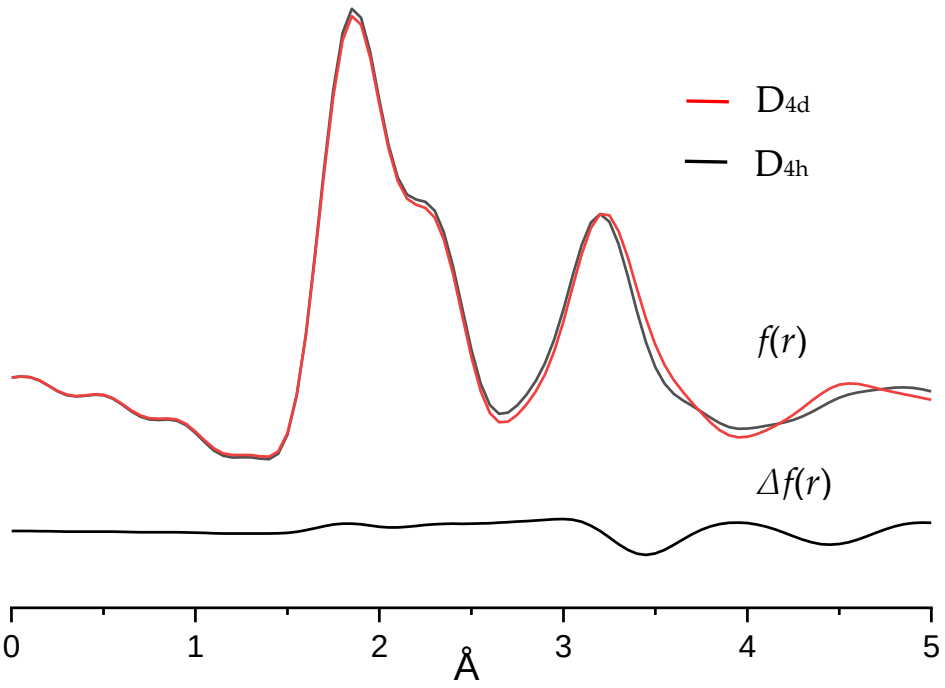


Figure S1. Theoretical functions f(r) for models $D_{4h}$ and $D_{4d}$ of the $Re_2F_8$ molecule and difference curve Δf(r).

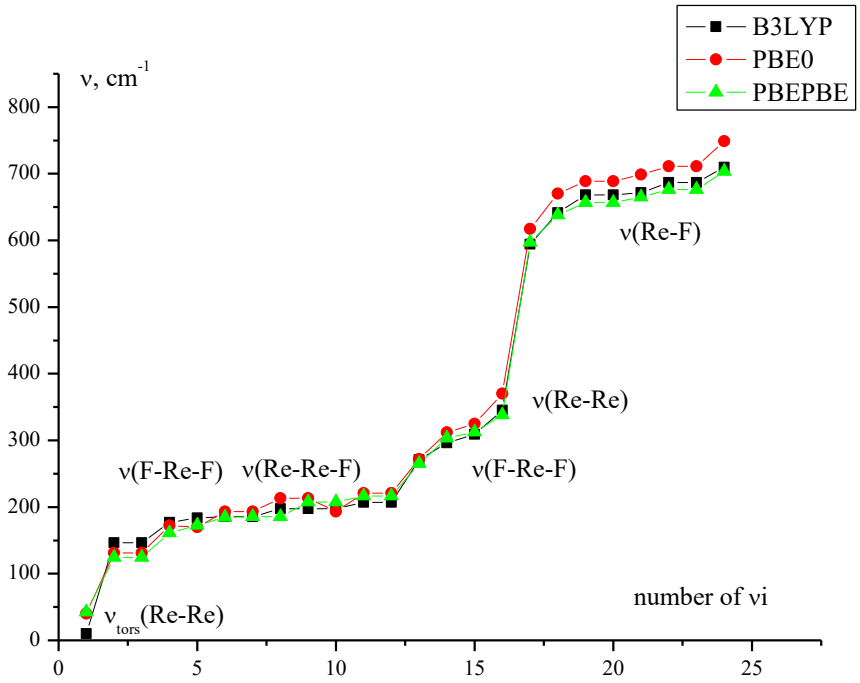


Figure S2. The values of vibrational frequencies of the molecule $Re_2F_8$ obtained in three variants DFT.