**Supporting Information for**

# Matrix Infrared Spectroscopic and Theoretical Study on the $Pt(SF_4)$ and $PtF_2SF_2$ Complexes with Multiple Pt-S Bonding Characters

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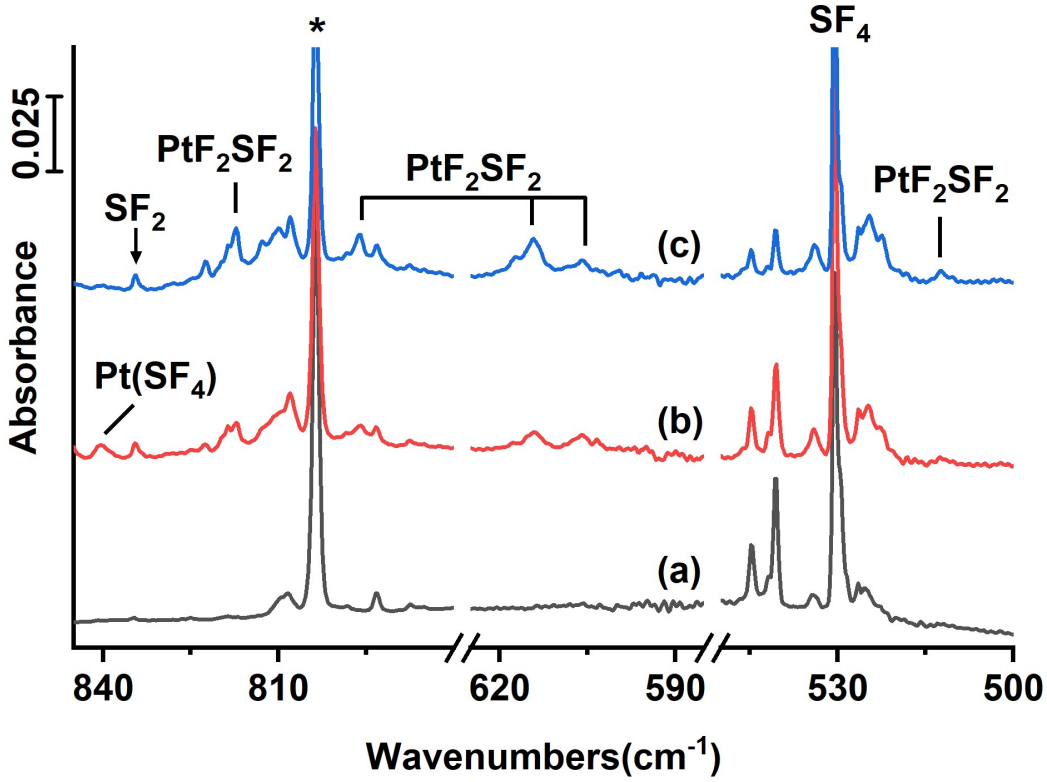


**Figure S1.** Infrared spectra in the 845-780, 625-585 and 550-500 $cm^{-1}$ regions: (a) 0.2% $SF_4$ deposited in excess neon at 4 K, (b) co-deposit of laser-ablated platinum atoms and 0.2% $SF_4$ in excess neon followed by 8 K annealing, (c) co-deposit of laser-ablated platinum atoms and 0.2% $SF_4$ in excess neon followed by $\lambda > 280$ nm irradiation and 10 K annealing. The asterisk denotes the absorption of $SOF_2$.

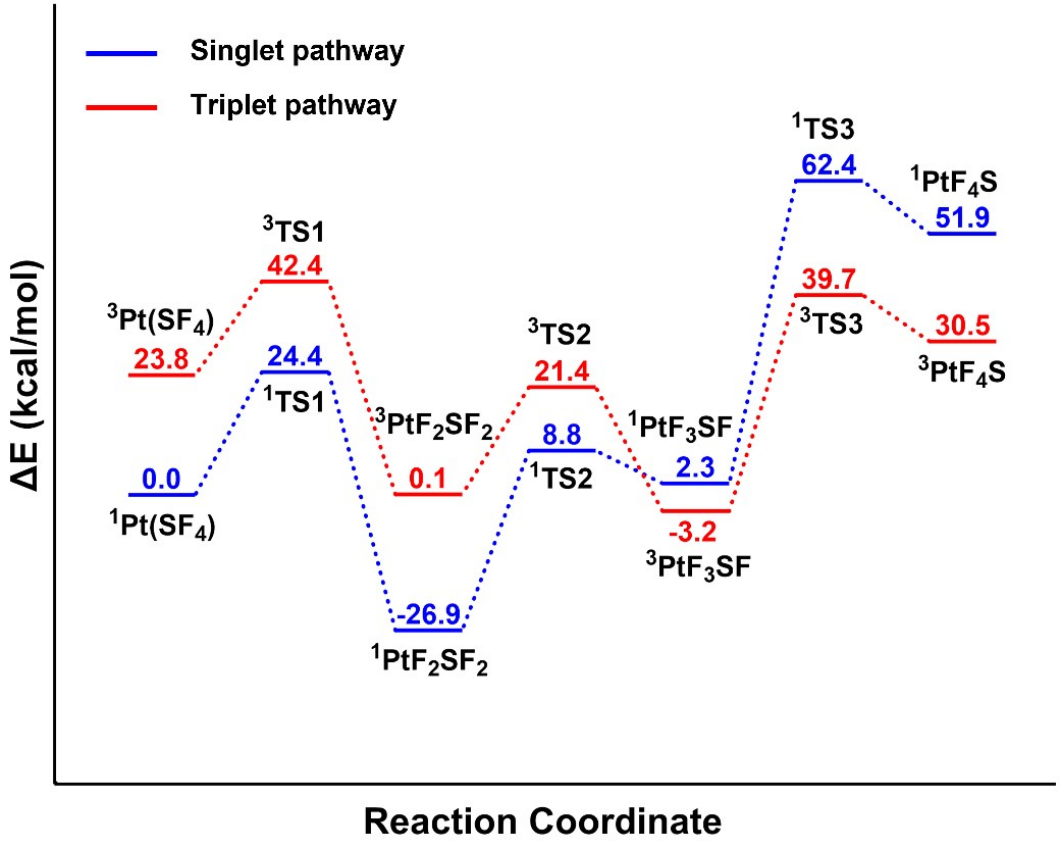


**Figure S2.** Potential energy profile for the fluorine transfer process from $Pt(SF_4)$ to $PtF_4S$ at the PBE0/6-311+G(3df)/SDD level of theory.

**Table S1.** Experimental infrared absorptions ($cm^{-1}$) of $PtF_2SF_2$, $Pt(SF_4)$ and their isotopomers in solid neon.

| | mode | $SF_4$ | $^{34}SF_4$ |
|---|---|---|---|
| $PtF_2SF_2$ | $\nu_s$(F-S-F) | 817.2 | 809.2 |
| | $\nu_{as}$(F-S-F) | 796.1 | 786.6 |
| | $\nu_{as}$(F-Pt-F) | 614.3 | 614.2 |
| | $\nu_s$(F-Pt-F) | 605.9 | 605.8 |
| | $\nu$(Pt-S) | 512.2 | 499.1 |
| $Pt(SF_4)$ | $\nu_s(SF_{2,eq})$ | 861.2[a] | 845.4 |
| | $\nu_{as}(SF_{2,eq})$ | 840.6 | 829.0 |
| | $\nu_{as}(SF_{2,ax})$ | 712.7[a] | 700.9 |

[a] Determined from the infrared difference spectrum.

**Table S2.** Calculated vibrational frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) of $Pt(SF_4)$, $PtF_2SF_2$ and their isotopomers at the PBE0/6-311+G(3df)/SDD level.

| $Pt(SF_4)$ | | $Pt(^{34}SF_4)$ | | $PtF_2SF_2$ | | $PtF_2{}^{34}SF_2$ | |
|---|---|---|---|---|---|---|---|
| freq | int | freq | int | freq | int | freq | int |
| 861.8 | 504 | 847.6 | 477 | 828.7 | 213 | 819.1 | 205 |
| 837.4 | 120 | 826.0 | 116 | 805.8 | 150 | 796.2 | 147 |
| 735.5 | 337 | 723.4 | 325 | 618.6 | 142 | 618.5 | 141 |
| 588.0 | 15 | 584.5 | 16 | 610.1 | 18 | 610.0 | 19 |
| 562.4 | 4 | 560.9 | 5 | 514.3 | 43 | 501.1 | 41 |
| 527.2 | 39 | 526.3 | 42 | 401.3 | 5 | 398.5 | 5 |
| 493.7 | 0 | 493.7 | 0 | 264.1 | 4 | 263.7 | 4 |
| 424.4 | 1 | 421.3 | 1 | 230.1 | 1 | 228.7 | 1 |
| 270.6 | 2 | 269.9 | 2 | 197.7 | 7 | 197.7 | 7 |
| 222.8 | 0 | 222.7 | 0 | 170.3 | 3 | 170.3 | 3 |
| 218.2 | 1 | 217.1 | 1 | 90.2 | 0 | 90.1 | 0 |
| 129.6 | 1 | 129.2 | 1 | 24.0 | 0 | 23.9 | 0 |

**Cartesian coordinates for the optimized geometries of the species in Figure S2 at the PBE0/6-311+G(3df)/SDD level of theory.**

**$Pt(SF_4)$ singlet 0**

| **Atom** | **X** | **Y** | **Z** |
|---|---|---|---|
| S | 0.000000 | 0.000000 | -1.082236 |
| Pt | 0.000000 | 0.000000 | 0.991652 |
| F | 0.000000 | 1.626104 | -1.267103 |
| F | 1.211829 | 0.000000 | -2.068070 |
| F | -1.211829 | 0.000000 | -2.068070 |
| F | 0.000000 | -1.626104 | -1.267103 |

**$Pt(SF_4)$ triplet +23.8 kcal/mol**

| **Atom** | **X** | **Y** | **Z** |
|---|---|---|---|
| S | 0.090440 | -1.218092 | 0.000000 |
| Pt | 0.064306 | 1.045804 | 0.000000 |
| F | 0.064306 | -1.293441 | 1.642466 |
| F | -1.426674 | -1.573950 | 0.000000 |
| F | 0.579956 | -2.737306 | 0.000000 |
| F | 0.064306 | -1.293441 | -1.642466 |

**$Pt(SF_4)$ quintet +92.0 kcal/mol**

| Atom | X | Y | Z |
|---|---|---|---|
| S | 0.000000 | 0.000000 | -1.269068 |
| Pt | 0.000000 | 0.000000 | 1.119695 |
| F | 0.000000 | 1.655069 | -1.280856 |
| F | 1.128465 | 0.000000 | -2.443095 |
| F | -1.128465 | 0.000000 | -2.443095 |
| F | 0.000000 | -1.655069 | -1.280856 |

**$PtF_2SF_2$ singlet 0**

| Atom | X | Y | Z |
|---|---|---|---|
| S | 0.597643 | 1.375412 | 0.000000 |
| Pt | -0.049250 | -0.579444 | 0.000000 |
| F | -0.158912 | -0.832377 | 1.912935 |
| F | -0.158912 | 2.120712 | -1.159444 |
| F | -0.158912 | 2.120712 | 1.159444 |
| F | -0.158912 | -0.832377 | -1.912935 |

**$PtF_2SF_2$ triplet +26.9 kcal/mol**

| Atom | X | Y | Z |
|---|---|---|---|
| S | 1.647854 | -0.495039 | -0.320146 |
| Pt | -0.682409 | 0.055207 | 0.011130 |
| F | -1.069515 | -1.810368 | -0.250827 |
| F | 2.320450 | 0.865852 | -0.715624 |
| F | 2.192378 | -0.585172 | 1.152782 |
| F | -0.458619 | 1.931300 | 0.286354 |

**$PtF_2SF_2$ quintet +84.8 kcal/mol**

| Atom | X | Y | Z |
|---|---|---|---|
| S | -0.212331 | -2.214203 | 0.000000 |
| Pt | 0.306831 | 0.782616 | 0.000000 |
| F | 2.097463 | 0.320308 | 0.000000 |
| F | -1.459730 | -2.238989 | 1.102762 |
| F | -1.459730 | -2.238989 | -1.102762 |
| F | -1.459730 | 1.311357 | 0.000000 |

**$PtF_3SF$ singlet +5.5 kcal/mol**

| Atom | X | Y | Z |
|---|---|---|---|
| F | -0.248127 | 1.960630 | -0.089624 |
| F | -0.438121 | -1.921530 | -0.274533 |
| F | -1.993148 | -0.002465 | 0.779119 |
| S | 1.669802 | 0.484130 | -0.024057 |
| F | 2.541691 | -0.728836 | 0.474223 |
| Pt | -0.326634 | -0.019439 | -0.097664 |

**$PtF_3SF$ triplet 0 kcal/mol**

| Atom | X | Y | Z |
|---|---|---|---|
| F | -1.842354 | -0.015842 | 0.000000 |
| F | 1.850848 | 0.718833 | 0.000000 |
| F | -0.385004 | 2.215332 | 0.000000 |
| S | 0.605410 | -1.769214 | 0.000000 |
| F | -0.699774 | -2.657437 | 0.000000 |
| Pt | 0.000000 | 0.332813 | 0.000000 |

**$PtF_4S$ singlet +21.4 kcal/mol**

| Atom | X | Y | Z |
|---|---|---|---|
| F | 0.000000 | 1.925597 | 0.251677 |
| F | -1.809997 | 0.000000 | 0.666490 |
| F | 1.809997 | 0.000000 | 0.666490 |
| F | 0.000000 | -1.925597 | 0.251677 |
| Pt | 0.000000 | 0.000000 | 0.180174 |
| S | 0.000000 | 0.000000 | -1.911288 |

**$PtF_4S$ triplet 0 kcal/mol**

| Atom | X | Y | Z |
|---|---|---|---|
| F | 0.000000 | 1.901068 | 0.415574 |
| F | -1.901068 | 0.000000 | 0.415574 |
| F | 1.901068 | 0.000000 | 0.415574 |
| F | 0.000000 | -1.901068 | 0.415574 |
| Pt | 0.000000 | 0.000000 | 0.196320 |
| S | 0.000000 | 0.000000 | -1.892103 |

**TS1 singlet (-166.37 $cm^{-1}$)**

| Atom | X | Y | Z |
|---|---|---|---|
| S | 1.276599 | -0.038881 | 0.250572 |
| Pt | -0.987867 | -0.080913 | 0.018218 |
| F | 0.274297 | 1.662353 | 0.131770 |
| F | 2.809092 | 0.520760 | 0.428073 |
| F | 1.454767 | 0.152501 | -1.299701 |
| F | 1.753848 | -1.565242 | 0.136510 |

**TS1 triplet (-121.55 $cm^{-1}$)**

| Atom | X | Y | Z |
|---|---|---|---|
| S | -1.384936 | -0.006128 | -0.261084 |
| Pt | 1.012053 | -0.101948 | -0.011058 |
| F | -0.106469 | 1.735808 | -0.225948 |
| F | -2.977609 | 0.389964 | -0.381540 |
| F | -1.482244 | 0.304246 | 1.261599 |
| F | -1.742696 | -1.535577 | -0.094127 |

**TS2 singlet (-129.63 $cm^{-1}$)**

| Atom | X | Y | Z |
|---|---|---|---|
| S | 1.600213 | -0.382978 | -0.507131 |
| Pt | -0.346881 | -0.037576 | 0.007320 |
| F | -1.373349 | -1.617807 | 0.119961 |
| F | 0.779174 | 1.663349 | -0.066113 |
| F | 2.577211 | -0.179792 | 0.706918 |
| F | -1.821556 | 1.140755 | 0.077357 |

**TS2 triplet (-102.81 $cm^{-1}$)**

| Atom | X | Y | Z |
|---|---|---|---|
| S | 1.557798 | 0.000046 | -0.654785 |
| Pt | -0.378067 | -0.000184 | 0.195343 |
| F | -0.621068 | -1.887337 | 0.398948 |
| F | -0.623466 | 1.886561 | 0.399643 |
| F | 2.622015 | 0.001517 | 0.513989 |
| F | -0.870317 | 0.000769 | -1.841494 |

**TS3 singlet (-324.96 $cm^{-1}$)**

| Atom | X | Y | Z |
|---|---|---|---|
| F | -0.241564 | 1.924166 | 0.194991 |
| F | -1.853508 | 0.001783 | -0.755039 |
| F | 1.363046 | -0.003180 | 1.355816 |
| F | -0.245813 | -1.923842 | 0.192245 |
| Pt | -0.191594 | 0.000141 | 0.116158 |
| S | 1.484056 | -0.000085 | -1.122028 |

**TS3 triplet (-368.53 $cm^{-1}$)**

| Atom | X | Y | Z |
|---|---|---|---|
| F | -0.365980 | -1.907462 | -0.282849 |
| F | -1.874383 | 0.001355 | 0.836682 |
| F | 1.726920 | -0.000830 | -0.919548 |
| F | -0.362363 | 1.907808 | -0.283044 |
| Pt | -0.252375 | 0.000076 | -0.107033 |
| S | 1.722968 | -0.000860 | 0.886715 |