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## Relativistic Contribution: An Electronic Explanation to the Thermal Disproportionation of $\text{PtF}_5$

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**Abstract** In the present work, is performed a computational thermochemical study of platinum tetrafluoride ( $\text{PtF}_4$ ) and platinum pentafluoride ( $\text{PtF}_5$ ). The results are compared to those previously [1] obtained to  $\text{PtF}_6$  as well as experimental data. It is concluded that in gaseous phase  $\text{PtF}_4$  and  $\text{PtF}_5$  retain their structures and number of unpaired electrons exhibited in the solid phase. Furthermore, is proposed that the generally accepted  $t_{2g}^5 e_g^0$  configuration to  $\text{Pt}^{5+}$  is not correct. Based on the calculated results, an energy diagram is proposed to  $\text{PtF}_5$ , which explain why, upon heating, platinum pentafluoride disproportionates readily [7]:  $2\text{PtF}_5 \rightarrow \text{PtF}_4 + \text{PtF}_6$ , providing a clear, elegant and straightforward explanation to the thermal instability of  $\text{PtF}_5$  as consequence of the electronic configuration.

**Keywords** Thermochemistry,  $\text{PtF}_4$ ,  $\text{PtF}_5$ , formation enthalpy, relativity, molecular structure, disproportionation.

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### Introduction

Platinum fluorides are chemically instable (they are highly reactive) and high volatile compounds, making them difficult to be studied by the many experimental techniques.

As shown to  $\text{PtF}_6$  [1], thermochemical data can be of paramount importance to a fully understanding of the properties of such compounds. It was proved that whereas solid state  $\text{PtF}_6$  is paramagnetic, gas phase platinum hexafluoride is, indeed, diamagnetic, because a relativistic effect [1].

In this context/connection, in the present work, it is performed a computational thermochemistry study of gas phase platinum tetrafluoride ( $\text{PtF}_4$ ) and platinum pentafluoride ( $\text{PtF}_5$ ).

All computations were performed by using Spartan'16 [2]. Thermochemical calculations were performed by semi-empirical (PM6) method. The SE-PM6 approach was chose taking into account its minor computation time consuming and its reliability, as verified for  $\text{PtF}_6$  [1].

Platinum tetrafluoride is a diamagnetic yellowish brown solid [3]. It was modelled as a trimer (Figure 1). The calculated value for  $\Delta_f H_{(g)}^0 = -528.43 \text{ kJmol}^{-1}$ , is in very good agreement with the experimental value of  $-524 \pm 25 \text{ kJmol}^{-1}$  obtained by Knudsen cell mass spectrometry. The trimeric  $\text{PtF}_4$  was modelled with none unpaired electrons. So, it is concluded that gas phase  $\text{PtF}_4$  is, as the solid, diamagnetic. Initially, It was assumed that  $\text{PtF}_4$  exhibited a tetrahedral geometry but it is now known that the Pt chemical environmental in such compound is, in fact, octahedral, with  $\text{PtF}_4$  been a polymeric compound, with a diamagnetic configuration: ( $d^6: t_{2g}^6 e_g^0$ ).



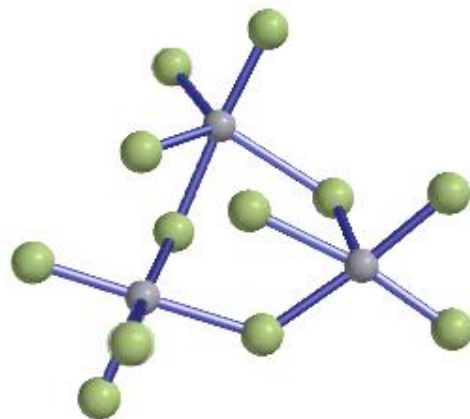


Figure 1: Modelled  $PtF_4$  trimer

As is well known,  $PtF_5$  is a dark red solid, with a tetrameric structure and magnetic moment of 2.05 BM [3]. Such magnetic moment is compatible with a  $d^5$ :  $t_{2g}^5 e_g^0$  configuration, with one unpaired electron (calculated spin only magnetic moment = 1.73 BM).

The gas phase  $PtF_5$  was modelled as a tetramer (Figure 2) and the calculated gas phase formation enthalpy,  $\Delta_f H_{(g)}^0 = -775.43$  (zero unpaired electrons),  $-747.76$  (2 unpaired electrons) and  $-725.43$  (4 unpaired electrons). The experimental  $\Delta_f H_{(g)}^0$  for  $PtF_5$  is  $-693.60 \text{ kJmol}^{-1}$ , calculated from the following experimental data [4-6] ( $\text{kJmol}^{-1}$ ):  $PtF_4(s)$ ,  $\Delta_f H = -740$ ;  $PtF_6(g) = \Delta_f H = -676$  and  $PtF_4(s) + PtF_6(g) \rightarrow Pt_2F_{10}(g)$ ,  $\Delta_r H = 28.8$ .

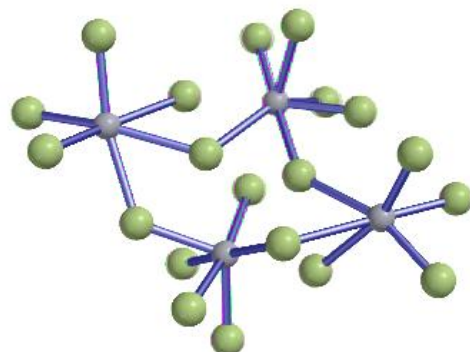


Figure 2: Modelled  $PtF_5$  tetramer

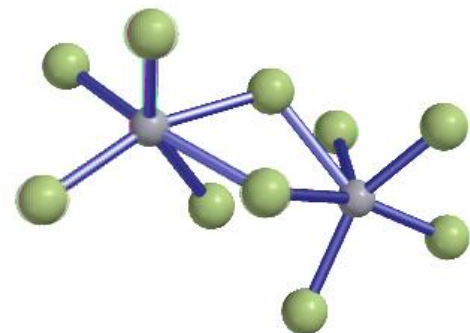


Figure 3: Modelled  $PtF_5$  dimer

As can be verified, considering the tetrameric structure, the calculated  $\Delta_f H_{(g)}^0$  value for  $PtF_5$  in better agreement with the experimental value (+ 4.6%) is the one to a four unpaired electrons compound.



Platinum pentafluoride was also modelled as a dimer (Figure 3), and the calculated gas phase formation enthalpy are  $\Delta_f H^\theta_{(g)} = -568.67$  (zero unpaired electrons),  $-648.74$  (2 unpaired electrons) and  $-629.36$  (4 unpaired electrons). In this case, the better agreement with the experimental value (-6.5%) is to the compound with two unpaired electrons. Since solid  $PtF_5$  has one unpaired electron, the dimer must have 2, and the tetramer, 4, as predicted by the obtained results. So, can be concluded that in gas phase,  $PtF_5$  has the same number of unpaired electrons of the solid state compound.

Such results are in contrast with those obtained to gas phase  $PtF_6$ , which is paramagnetic in the solid state and diamagnetic in the gas phase [1].

It is well known that upon heating, platinum pentafluoride disproportionates readily [7]:  $2PtF_5 \rightarrow PtF_4 + PtF_6$ . Furthermore, as is well known, Pt(VI) has four unpaired electrons ( $t_{2g}^3 e_g^1$ ), exhibiting a Jahn-Teller distortion [8]. That is, two mols of a solid compound with one unpaired electron ( $PtF_5$ ) produces one mol of a compound with none unpaired electron ( $PtF_4$ ) and one mol of a compound with four unpaired electrons ( $PtF_6$ ). This sounds like a little strange conclusion. Seems more natural that two mols of a compound with one unpaired electron ( $PtF_5$ ) produces two mols of compounds with none unpaired electron (one mol of  $PtF_4$  and one mol of  $PtF_6$ ), as suggests the energy diagram shown in Figure 4.

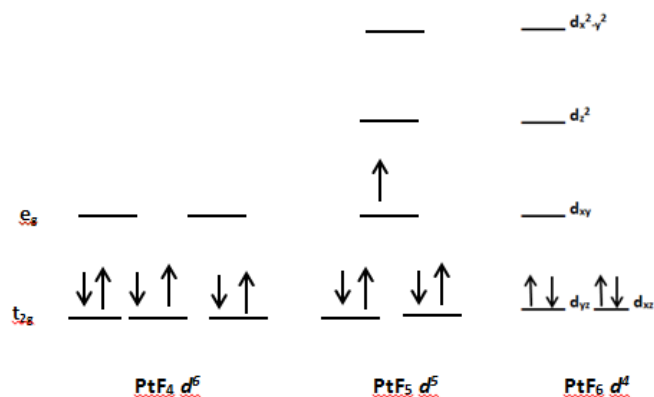


Figure 4: Proposed energy diagrams to gas phase  $PtF_4$ ,  $PtF_5$  and  $PtF_6$

This proposal is in agreement with the fact that the calculated energy spectra and electron distributions for  $PtF_6$  (taking into account the relativistic contributions) suggest that the triplet state  $t_{2g}$  is split in the tetragonal field into a singlet and a lower lying doublet, with four  $5d^4$  electrons occupying the  $5d_{xz}$  and  $5d_{yz}$  atomic orbitals in the spin paired state. Such diamagnetic nature for  $PtF_6$  was also predicted based on four components Dirac molecular Hartree-Fock and density functional theory (DFT) and the two component zeroth order regular approach (ZORA) including spin orbit interaction calculations, despite the fact that some criticism was expressed for such conclusion [9-13].

So, disregarding the energetics of structural rearrangements, etc., the enthalpy of the reaction  $Pt_2F_{10}(g) \rightarrow PtF_4(s) + PtF_6(g)$ ,  $\Delta_r H = -28.8 \text{ kJmol}^{-1}$ , is related with the energetic of a doublet ( $PtF_5$ ) to singlet ( $PtF_4$  and  $PtF_6$ ) transition, that is,  $-14.4 \text{ kJmol}^{-1}$  per electron.

Based on the obtained results, the energy diagrams shown in Figure 4 is proposed for gas phase  $PtF_4$ ,  $PtF_5$  and  $PtF_6$ . Such diagram is in agreement with the fact that two mols of a solid compound with one unpaired electron ( $PtF_5$ ) produces two mols of compounds with none unpaired electron (one mol of  $PtF_4$  and one mol of  $PtF_6$ ). So, the traditionally accepted statement that gas phase  $PtF_5$  has the configuration  $d^5: t_{2g}^5 e_g^0$  (which explain the presence of an unpaired electron, of course) is not correct. Hence, can be concluded that the same relativistic contributions that operated on  $PtF_6$  [1, 9-13], is prominent in  $PtF_5$ , and responsible to the electron configuration shown in Figure 4.

Furthermore, such electron configuration provides a clear, elegant and straightforward explanation to the disproportionation of  $PtF_5$  under heating: as the temperature increases, the system try to "compensate" such thermal



energy gain lowering the electronic energy of the system, by “lowering” two unpaired electrons (two mols of  $\text{PtF}_5$ ) to lower energy levels (one electron in  $\text{PtF}_4$  and one electron in  $\text{PtF}_6$ ).

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