Matrix Isolation Spectroscopic and Relativistic Quantum Chemical Study of Molecular Platinum Fluorides $\text{PtF}_n$ ($n = 1–6$) Reveals Magnetic Bistability of $\text{PtF}_4$

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Dedicated to Professor Helge Willner on the occasion of his 75th birthday

Abstract: Molecular platinum fluorides $\text{PtF}_n$, $n = 1–6$, are prepared by two different routes, photo-initiated fluorine elimination from $\text{PtF}_6$ embedded in solid noble-gas matrices, and the reaction of elemental fluorine with laser-ablated platinum atoms. IR spectra of the reaction products isolated in rare-gas matrices under cryogenic conditions provide, for the first time, experimental vibrational frequencies of molecular $\text{PtF}_n$. Photoysis of $\text{PtF}_6$ enabled a highly efficient and almost quantitative formation of molecular $\text{PtF}_n$, whereas both $\text{PtF}_5$ and $\text{PtF}_4$ were formed simultaneously by subsequent UV irradiation of $\text{PtF}_6$. The vibrational spectra of these molecular platinum fluorides were assigned with the help of one- and two-component quasirelativistic DFT computation to account for scalar relativistic and spin–orbit coupling effects. Competing Jahn-Teller and spin–orbit coupling effects result in a magnetic bistability of $\text{PtF}_6$, for which a spin-triplet ($^3B_{2g}, D_{3h}$) coexists with an electronic singlet state ($^1A_{1g}, D_{5h}$) in solid neon matrices.

Introduction

The most common oxidation states for platinum are $+2$ and $+4$, but $\text{PtF}_2$ and the ions $\text{PtF}_4^-$ and $\text{PtF}_2^{2-}$ are probably the best known and most investigated binary platinum fluoride species.$^{[1]}$ Unlike the solid mixed-valence trifluoride ($\text{Pt}^{4+}\text{Pt}^{6+}\text{F}_3$)$^{[2]}$ and solid tetrafluoride,$^{[3]}$ platinum pentafluoride is a low-melting (m.p. 80 °C), deep-red solid that disproportionates readily to yield $\text{PtF}_4$ and $\text{PtF}_2$ upon heating.$^{[3c,4]}$ The deep-red platinum hexafluoride combines high volatility (m.p. 61.3 °C)$^{[5]}$ with the highest electron affinity ($\text{EA} = 7.09$ eV)$^{[6]}$ of the known metal hexafluorides. Thus, $\text{PtF}_6$ is a useful and extremely strong one-electron oxidizer that has found its place in chemical history as the first species that enabled the synthesis of a stable dioxygenyl salt, $[\text{O}_2]^+ [\text{PtF}_6]^-$, and of the first xenon compounds, likely $[\text{FXe}]^+ [\text{PtF}_6]^-$ and $[\text{FXe}]^+ [\text{Pt}_2\text{F}_{11}]^-$.$^{[1a,b,7]}$

There are numerous investigations on molecular $\text{PtF}_6$ (see ref. [1b] and references therein), but only very few spectroscopic investigations on molecular fluorides of platinum in lower oxidation states. Platinum monofluoride ($\text{PtF}$) has been studied by microwave$^{[6]}$ laser absorption$^{[8]}$ and laser-induced fluorescence spectroscopy.$^{[9]}$ Very recently we have reported the infrared stretching frequencies of $\text{PtF}$ and $\text{PtF}_2$ embedded in solid neon and argon matrices.$^{[7]}$ $\text{PtF}_5$ ($n = 2–4$) were studied by means of high-temperature Knudsen cell mass spectroscopy and their thermochemistry has been explored.$^{[10]}$ However, experimental spectroscopic investigations on the molecular platinum fluorides $\text{PtF}_n$, $\text{PtF}_4$, and $\text{PtF}_6$ are not yet available.

In this work, we present vibrational spectra and UV transitions of molecular $\text{PtF}_6$ embedded in cryogenic solid neon and argon matrices. We also report on a first systematic investigation of the molecular platinum fluorides $\text{PtF}_n$, $n = 1–6$, formed independently by two different routes, the reaction of laser-ablated platinum atoms with elemental fluorine and the selective photodecomposition of $\text{PtF}_6$. We were also interested in the IR spectroscopic detection of non-classical $\text{PtF}_5$, $n = 4, 5$ complexes. The existence of such complexes has so far only been predicted computationally, for example for AuF$_2$F$_3$ (AuF$_{3}^+$)$^{[11]}$ and $[\text{PtF}_4]^- [\text{PtF}_2]$,$^{[11]}$ but has never been verified experimentally. One possible access to such non-classical difluoride complexes of $\text{PtF}_4$ could be the photochemically initiated elimination of $\text{F}_2$ from $\text{PtF}_6$ in a solid noble-gas matrix. Our experimental results are supplemented by ab initio CCSD(T) calculations, one-component quasirelativistic DFT computations$^{[14]}$ that include (spin-free) scalar relativistic (SR)
effects, as well as two-component quasirelativistic DFT computations\cite{16} including spin–orbit coupling (SOC) effects (for experimental and computational details see the Supporting Information).

In a previous computational study, only even-numbered molecular platinum fluorides PtF$_{2n}$ ($n = 1$–4) were studied by scalar relativistic density functional and coupled-cluster methods.\cite{15} However, more recent studies on PtF$_6$ \cite{17,18} PtF$_8$ \cite{19} PtX$_4$ ($X = F, Cl, Br$)\cite{20} and the related PdF$_e$\cite{21} have shown that SOC effects have a dramatic impact on their electronic structure and spectra. SOC effects can open electronic decay channels, which were closed in non-relativistic calculations.

For the neutral PtF$_6$ and PtF$_4$, molecules, which are most relevant in this work, ligand field theory predicts a triplet $^3T_{2g}$ ground state for the $t_{2g}^1e_g^6$ configuration of octahedral PtF$_6$ ($O_h$) and a $^6E_g$ ground state associated with the $a_{1g}^2e_g^4b_{2g}^1$ occupancy of a square planar PtF$_4$ ($D_{2h}$)\cite{22} (see Figure 1, and ref. [21] for the d-orbital splitting in octahedral and square planar transition metal complexes). The singly occupied molecular orbitals (MOs) in both molecules are predominantly Pt(5d) orbitals with some $\pi^*$ antibonding Pt–F character. The Jahn-Teller (JT) theorem predicts a geometrical distortion from the high-symmetry configuration for degenerate electronic states of such nonlinear molecules, that lowers the symmetry and lifts the degeneracy.\cite{23}

Hence, nonrelativistic and scalar-relativistic electronic structure computations for PtF$_6$ predict JT-distorted $D_{3h}$ or $D_{4h}$ molecular structures\cite{24,25} but relativistic computations including SOC\cite{26} give, in accordance with experimental structural and spectroscopic data, a diamagnetic octahedral molecule with a closed-shell singlet ground state (Figure 1).\cite{16} Thus, PtF$_6$ represents the rare case where relativistic spin–orbit splitting leads to a qualitative change of molecular and electronic structure in a stable molecule.\cite{16}

### Results and Discussion

#### Conversion of PtF$_6$ to PtF$_4$

We have studied the photochemistry of PtF$_6$ isolated in solid noble-gas matrices. PtF$_6$ was prepared according to the original protocol of Weinstock et al.\cite{27} and its vapor was co-deposited onto the matrix support together with an excess of pure neon and argon, respectively. In solid neon, the two IR active fundamentals of octahedral PtF$_6$ are observed at $\nu_1 = 705.6$ cm$^{-1}$ (Figure 2) and $\nu_4 = 274.6$ cm$^{-1}$ (Figure S2.3 in the Supporting Information), where the former is accompanied by a weaker matrix site at 709.1 cm$^{-1}$ (Figure 2). These frequencies are close to previously reported values for PtF$_6$ in a solid Ar matrix ($\nu_1 = 705.2$ cm$^{-1}$, $\nu_4 = 274.2$ cm$^{-1}$),\cite{28} and reported vapor-phase frequencies (705, 273 cm$^{-1}$).\cite{29}

Upon irradiation of this deposit with blue LED light ($\lambda = 470$ nm) the red color of matrix-isolated PtF$_6$ diminished and the deposit became almost colorless (Figure S2.1). In the Pt–F stretching region four closely spaced new IR bands appeared at wavenumbers between 710 and 717 cm$^{-1}$ (Figure 2). A similar band pattern occurred in all subsequent photolysis experiments, which indicates that these bands are likely associated with a single new species. It is assumed that the photodecomposition of PtF$_6$ either cleaves a single Pt–F bond to give a fluorine free radical and PtF$_4$, or it leads to the elimination of F$_2$ and molecular PtF$_6$. For square pyramidal PtF$_4$ (Figure 3) at least two different Pt–F stretching bands, a strong equatorial asymmetric PtF$_4$ stretching mode and a much weaker axial Pt–F' stretch, can be expected, while a square planar PtF$_4$ species will show only a single IR-active Pt–F stretching band. As mentioned above, the predicted $^6E_g$ ground state for a square planar PtF$_4$ ($D_{2h}$; Figure 1) will be subject to a Jahn-Teller (JT) distortion,\cite{16} that lowers the symmetry and lifts the

![Figure 1. Simplified scheme of Jahn-Teller (JT) distortion and spin–orbit coupling (SOC) on the platinum 5d orbital splitting of singlet octahedral PtF$_6$ ($O_h$; left) and triplet square planar PtF$_4$ ($D_{2h}$; right). JT and $\Delta SO$ indicate the Jahn-Teller and spin–orbit splitting of degenerate orbitals in the high-symmetry configuration, respectively, and $\Delta CF$ that due to crystal field splitting.](image1)

![Figure 2. Pt–F stretching band region of Ne matrix-isolation IR spectra of PtF$_6$ and molecular PtF$_4$. a) precursor PtF$_6$ seeded in excess Ne and co-deposited for 85 min at 6 K, and b) after irradiation at $\lambda = 470$ nm (LED) for 70 min. Impurity bands are marked by an asterisk.](image2)
degeneracy.\(^{[22]}\) JT distortions of tetragonal \(D_{4h}\) molecules have been studied much less frequently than those of trigonal or octahedral molecules.\(^{[20]}\) Generally, for centrosymmetric molecules JT effects will preserve the inversion symmetry, and the non-degenerate vibrational modes \(b_{1u}\) and \(b_{2u}\) are JT active in \(D_{4h}\) molecules.\(^{[22]}\) As a consequence, JT distortion of square planar PtF\(_4\) will lead to a splitting of the single degenerate Pt–F mode and therefore two closely spaced vibrational Pt–F bands of almost equal intensity are expected to appear in the IR spectrum. Such a two-band spectrum is indeed shown in Figure 2 for the observed photo-dissociation product of PtF\(_4\) where both bands reveal an additional matrix-site splitting like the PtF\(_4\) precursor band. This spectrum already provides strong evidence for the formation of JT distorted planar PtF\(_4\) \((D_{4h}\) symmetry). After prolonged irradiation, the photo-initiated transformation of PtF\(_4\) to PtF\(_6\) is almost quantitative and surprisingly selective, since no other bands occurred in the Pt–F stretching region. This allowed us to additionally measure several much weaker bands of PtF\(_6\) such as two combination bands at 1281.8 and 1393.5 cm\(^{-1}\) (Figure S2.2), as well as three weak bands in the far-IR region at 270.5, 248.1, and 221.1 cm\(^{-1}\) (Table 1, Figure S2.3). The combination band positions in the infrared spectrum provide useful estimates for the two infrared-active Pt–F stretching modes of PtF\(_4\) \((a_{1g} + b_{2g})\). For example, the corresponding two combination bands observed for PtF\(_4\) in solid Ne at 1305.8 cm\(^{-1}\) \((v_1 +v_3)\) and 1361.0 cm\(^{-1}\) \((v_1 +v_3)\) (Figure 2), provide upper limits for the Raman bands of \(v_2 = 600\) cm\(^{-1}\) \((e_g)\) and \(v_1 = 655\) cm\(^{-1}\) \((a_{1g})\), which are close to the reported Raman bands of PtF\(_4\) at 601 and 655 cm\(^{-1}\), respectively.\(^{[25]}\) Accordingly, from the two combination bands of PtF\(_4\) we estimate upper limits for two unobserved Raman bands of 677 cm\(^{-1}\) \((v_1)\) and 569 cm\(^{-1}\), in good agreement with the combination bands observed in solid argon (Table 2).

Investigating the photo-decomposition of PtF\(_4\) in a solid argon matrix we found a different photo-behavior than in solid neon. In solid argon the PtF\(_4\) band is also depleted by green light LED radiation of \(\lambda = 528\) nm (Figure S2.4). This photo-decomposition is much less efficient than the blue light charge-transfer (CT) excitation (Figure 2), and a new band occurred at 679.8 cm\(^{-1}\) (Figure S2.4). The new feature is assigned to the degenerate \(e\)-type Pt–F stretching mode of molecular PtF\(_4\) based on the observed band positions and its photo-behavior in further experiments (see below and Tables 2 and S5.1). For the lowest-energy electronic state of PtF\(_4\) \((B_g, C_{3v})\), a slightly distorted square pyramidal structure with an axial and four longer equatorial Pt–F bonds is predicted (Figure 3). The much weaker computed axial Pt–F stretching vibration of PtF\(_4\) (Table S5.2) was not detected experimentally. Under subsequent blue light radiation (\(\lambda = 455\) nm) PtF\(_4\) was formed again and the bands due to PtF\(_4\) and PtF\(_6\) diminished simultaneously (Figure S2.4). The frequency shift between the two Pt–F stretching bands of PtF\(_4\) isolated in solid argon (Table 2) is smaller than that in neon, which likely indicates a smaller distortion of the PtF\(_4\) molecule from the high-symmetry \(D_{4h}\) structure in the argon matrix.

Table 1. Observed and computed vibrational frequencies [cm\(^{-1}\)] of PtF\(_4\) \((D_{4h})\).

| \(v_i\) \((1\rightarrow 9)\) | Exp. \(^a\) | Calcd. (Int.) \(^b\) | Modes \(^c\) |
|---|---|---|---|
| \(v_1\) \((B_{2u})\) | 716.6 (714.4) | 712 (93) | \(v_{6u}\) (PtF), antisym. stretch (x) |
| \(v_2\) \((B_{2u})\) | 712.7 (710.5) | 707 (97) | \(v_{6u}\) (PtF), antisym. stretch (y) |
| \(v_3\) \((A_{1g})\) | 677 \(^d\) | 685 (0) | \(v_{6u}\) (PtF), antisym. stretch (x) |
| \(v_4\) \((B_{1g})\) | 569 \(^d\) | 426 (0) | \(v_{6u}\) (PtF), antisym. stretch (y) |
| \(v_5\) \((A_{1g})\) | n. o. | 272 (0) | \(v_{6u}\) (PtF), antisym. stretch (x) |
| \(v_6\) \((B_{2u})\) | 270.5 | 256 (5) | \(v_{6u}\) (PtF), antisym. stretch (y) |
| \(v_7\) \((B_{2u})\) | 248.1 (247.1) | 223 (8) | \(v_{6u}\) (PtF), antisym. stretch (x) |
| \(v_8\) \((A_{1g})\) | 221.1 | 234 (6) | \(v_{6u}\) (PtF), antisym. stretch (y) |
| \(v_9\) \((A_{1g})\) | n. o. | 165 (0) | \(v_{6u}\) (PtF), antisym. stretch (x) |

\(^a\) In parentheses: symmetry species for the \(D_{4h}\) symmetry. \(^b\) Ne matrix, 6 K, matrix-site bands are given in parentheses, n.o. = not observed. \(^c\) Values calculated at the 1c- and 2c-X2C-TPSSH levels; relative intensities are given in parentheses. \(^d\) Tentative mode description. \(^e\) Estimated from the combination bands \(v_3 + v_4 = 1281.8\) cm\(^{-1}\) and \(v_1 + v_3 = 1393.5\) cm\(^{-1}\) \((B_{2g})\) state neglecting anharmonicity (Figure S2.2).
structure with an averaged vibrational spacing of 498 ± 10 and 551 ± 12 cm⁻¹, respectively (Table S3.1). These frequencies were previously assigned to the totally symmetric stretching modes in the corresponding excited states.²¹,²⁶ The UV spectrum obtained for PtF₂ is very similar to that of PtF₄ (Figure 4b). There are two strong CT bands blue shifted from the PtF₂ bands with λ_max = 325 nm and 272 nm. The lower-wavelength band revealed a well-resolved vibrational progression with an average spacing of 542 ± 15 cm⁻¹ (Figure S2.6, Table S4.1).

Quantum-chemical calculations on PtF₆ and PtF₄

To support our assignments, quasi-relativistic DFT (density functional theory) calculations were carried out on the molecular platinum fluorides PtF₆ (n = 1–6) at scalar relativistic one-component (1c-X2C)²⁴ and two-component (2c-X2C and 2c-ZORA)²₅,²₆ levels to include spin–orbit coupling (SOC) effects (for computational details see the Supporting Information). Our computed structures and vibrational frequencies at the 2c-X2C level for the PtF₆ ground state (O₁₅) are fully consistent with previous results (Table S3.2).²₄,²₅ We note that SOC splits the degenerate spin-free τ₁₂ MOs into a fourfold degenerate HOMO ([2g₂] configuration) and an unoccupied twofold degenerate LUMO (e₁₁g) level (Figure 1). Based on 2c-X2C and 2c-ZORA TDDFT calculations the observed two strong CT bands of PtF₆ (Figures 4 and S2.6) are assigned to threefold degenerate (E₁₃) excitations involving transitions from occupied fluorine lone-pair (π(F)) levels to the lowest unoccupied level (e₁₁g LUMO) of PtF₆ (Table S3.4). The longer-wavelength band centered at 436 nm accounts for the reddish color and the observed photo-decomposition of PtF₆ under the λ = 470 nm irradiation to yield PtF₄. Further low-energy HOMO-LUMO excitations give rise to additional weak absorptions down to the near-IR (Table S3.1).²¹,²₄

For PtF₆, the lowest-energy singlet and triplet configurations were evaluated at 1c-X2C and 2c-X2C levels. At both levels, the JT distorted open-shell triplet configuration (B₁₂g) of D₂₅ symmetry (Figure 3) was found to be slightly lower in energy than the square-planar closed-shell A₁₂g state (D₄h, Table S4.2). Generally, JT interactions (of electrostatic origin) and SOC (of relativistic origin) compete with each other,²₅,²₆ and SOC reduces the singlet-triplet energy gap for PtF₆ considerably from 56 kJ mol⁻¹ in the spin-free 1c-X2C computation to about 11 kJ mol⁻¹ in the two-component 2c-X2C computations (TPSSh level, Table S4.2). However, in contrast to PtF₄, in which SOC completely suppresses the expected JT distortion, the JT distortion of PtF₆ in its lowest-energy triplet state is only partly quenched by SOC. The effect of JT distortion and SOC on the platinum d orbital splitting of planar PtF₆ is illustrated in Figure 5. The D₄h→D₂₅ distortion of the triplet state increases the gap between the highest occupied and the lowest unoccupied MOs, while this gap is further increased by SOC. As expected, the experimentally observed splitting of the degener-

Table 2. Observed and computed IR active Pt–F stretching frequencies [cm⁻¹] for PtF₆ (n = 1–6).

| Sym. | State | Ne | Exp. [d] | Ar | 1c-X2C | 2c-X2C |
|------|-------|----|----------|----|--------|--------|
| PtF₆ | Cᵥ     | 2Σ⁺ | 605.6    | 590.0 | 618 (100) | 620 (100) |
| PtF₄ | Dᵥ     | 3Σ⁺ | 710.1 (706.1) | 695.6 | 735 (100) | 710 (100) |
| PtF₂ | Cᵥ     | 2Σ⁺ | (685.7) 682.4 (680.5) | (671.5) 669.4 | 690 (100) | 684 (100) |
| PtF₄ | Dᵥ     | 3Σ⁺ | 635.3    | 645 (16) | 624 (23) |
| PtF₂ | Cᵥ     | 2Σ⁺ | 691.2    | 679.8 | 685 (100) | 684 (100) |
| PtF₂ | O₁₄   | 1Σ⁺ | (709.1) 705.6 | 705.5 (701.8) | 698 (100) |

[a] Matrix sites are given in parentheses. [b] Values calculated at one and two-component X2C-TPSSh level, respectively. [c] Computed frequencies and relative intensities (in parentheses) of ν₁ (195 Pt–F), ν₂, ν₃, ν₄, ν₅, ν₆ are at 665 cm⁻¹ (O, 1c-X2C) and 670 cm⁻¹ (3, 2c-X2C), respectively.

Figure 4. UV/Vis spectra (resolution: 0.1 nm) of a) PtF₆ and b) PtF₄ in the range from 667 to 210 nm. Spectrum (a) was recorded from PtF₄ isolated in solid neon after deposition at 6 K for 36 min and spectrum (b) was obtained after irradiation of the initial deposit with blue LED light (λ = 470 nm) for 75 min.
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Distortion in the triplet ground state from states of PtF

Figure 5.

on the orbital splitting of square planar PtF

two states can be easily distinguished by their different UV/Vis

TDDFT level (Tables S4.7 and S4.8). As expected, the UV/Vis

bands are predicted at the 1c-ZORA TDDFT level and their

spectra. For the triplet state, four low-energy CT excitation

λ

vibrationally resolved excitation at shorter wavelengths, which

transitions of the singlet isomer. This is particularly true for the

photo-destruction of PtF

isomer of PtF

is clearly dominated by transitions of the singlet isomer. This is particularly true for the

vibrationally resolved excitation at shorter wavelengths, which

is predicted to be more intense. On the other side, the higher

intensity of the experimental transition around 325 nm

(10nm) (Figures 4 and S2.6) can probably be attributed to a super-

position of excitations of both isomers. The singlet isomer, on

the other hand, is difficult to detect in the experimental IR

spectrum. Because of similar bond lengths and vibrational

frequencies of these isomers, the strong degenerate Pt±F

stretching band of the minor isomer is predicted within the

region of the two closely spaced stretching bands of the triplet

isomer, and the much weaker deformation bands of the minor

isomer (Tables 1 and S4.6) are difficult to detect experimentally

anyway.

Even if the solid matrix confinement and host-guest

interactions in a Ne-matrix site at 6 K prevent a structural

rearrangement from D

s

to D

s

symmetry, it cannot be ruled out

that the DFT calculations overestimate the energy difference of

these spin isomers. Thus, the combination of JT distortion and

SOC leads to two co-existing configurations with different

magnetic spin states (magnetic bistability) for molecular PtF.

The considerable SOC effects observed for the fluorides PtF

and PtF

are remarkable. It has also been shown that the

strength of SOC in related platinum complexes depends on the

nature of the ligands. Computational studies on the diatomic

PtX

+ F

(X=F, Cl) and PtX

+ Br

(X=F, Cl, Br) have shown that

SOC effects are most dramatic in the fluorides (X=F). This

is caused by the high platinum 5d orbital dominance of the

corresponding partially occupied π* MOs in the fluorides and

due to the redox-innocent character of the fluorine ligand in

these complexes.

The experimental observations in the solid Ar matrix

suggest a stepwise elimination of F atoms from PtF

via PtF

to yield PtF

according to the Equations (1) and (2), where both

steps can be triggered successively by selective irradiations.

In contrast to this, the PtF

intermediate was not detected during the

photo-decomposition of PtF

in the Ne matrix. It can, however, not be ruled out that the F atom initially formed in

solid neon by Pt±F bond cleavage (Eq. (1)) during irradiation

abstracts a second F ligand from the PtF

intermediate and

reacts irreversibly to PtF

+ F (Eq. (2)), and that a multistate

process is involved.

PtF

1

hv

PtF

2

F

(1)

PtF

2

F

1

hv

PtF

1

+ F

(2)

From a purely ground-state thermochemical perspective,

process 2 is clearly feasible (Table 3), as addition of a fluorine

atom to PtF

to form PtF

(Table 3, reaction 5) generates more

free energy than needed for subsequent F

elimination (Table 3,

reaction 9).

Photochemistry of PtF

As the chemistry of the molecular platinum fluorides is still

largely unknown, we carried out additional experiments to

explore the photochemistry of PtF

and the reaction of IR laser-
The dissociation of PtF₅ obtained with laser-ablated platinum atoms with elemental fluorine gas diluted in the rare gases neon and argon. For irradiation of PtF₅ we used a λ = 266 nm laser to avoid a simultaneous excitation of the broad PtF₅ CT bands. However, mainly the strong Pt–F stretching bands of PtF₅ and PtF₃ increased at the expense of the PtF₃ bands under the 266 nm radiation. Analogous to the above described Ar-matrix spectrum (Figure S2.4), for molecular PtF₅ only the intense degenerate e-type Pt–F stretching band at 691.2 cm⁻¹ (accompanying by a weaker matrix site at 694.8 cm⁻¹) could be safely assigned in this experiment (Table 2). In addition, much weaker Pt–F stretching bands appeared at 682.4, 635.3 and 617.9 cm⁻¹ (Figure 6). Similar results were obtained with λ = 254–400 nm broad-band UV or 254±5 nm radiation (Figure S2.7). These observations suggest a photo-dissociation of F₂ molecules rather than a Pt–F bond cleavage of PtF₅ followed by a stepwise fluorination of PtF₅ to PtF₆ (reactions 4 and 5, Table 3). These experiments support our previous assignment of the PtF₅ stretching band and provide Pt–F band positions for the hitherto unknown molecular PtF₅ (Tables 2 and S7.5). For PtF₃ in its 3Aₑ ground state a T-type structure with one shorter and two longer Pt–F bonds has been computed at the 2c-X2C DFT level (Figure 3, Table S7.4). Photo-dissociation of F₂ is also efficient under λ = 375 ± 10 nm UV–LED radiation and the F-atoms thus formed react with PtF₃ and PtF₅ back to PtF₅ and traces of PtF₆ (Figure 6c). Because of their limited mobility in a solid neon matrix, F-atoms are very efficient fluorinating agents under matrix isolation conditions.[29] The addition of a fluorine radical is strongly exothermic for the lower platinum fluorides (Table 3) and is expected to proceed without activation barrier.

These results suggest that the photochemistry of the system described is dominated by the photo-dissociation of F₂ and F-atom reactions rather than the photo-destruction of molecular PtF₅. Due to the restrictions of the matrix environment, the F₂ fragment formed by the initial photolysis of PtF₅ remains close to the PtF₅ molecules or could even be trapped within the same matrix cage together with PtF₆. In this latter case a PtF₅:F₂ complex could possibly be formed that reacts under near-UV photolysis back to PtF₅. This led us to compute PtF₂:F₂ complexes in both side-on and end-on coordination to platinum (Figure 7), comparing the lowest triplet and singlet states. The interaction energies for these complexes are small. They are dominated by dispersion interactions (for details see the Supporting Information), consistent with weak van-der-Waals complexes, and the side-on complex was found to be somewhat lower in energy at all levels (Table S6.1). Computed structural and vibrational data for the side-on and end-on PtF₅:F₂ complexes, respectively, at various 1c- and 2c-levels (Tables S6.2–S6.5) show only small vibrational frequency shifts (by < 3 cm⁻¹ at 2c-X2C level using the TPSSh functional and D3 dispersion corrections) compared to free PtF₅, which corroborates the relatively weak interactions.

Results for PtF₂:F₂ and the previously detected AuF₅:F₂ (AuF₅) complex[13] prompted us also to consider complexes of PtF₅ with F₂. In contrast to PtF₆, an end-on bent C₂v-symmetrical coordination with a F–Pt–F angle of around 112–115° (Figure 7, Table S6.6) has been found to be energetically favored over a C₁v-symmetrical side-on coordination in this case (by about 37 kJ/mol at B3LYP 1c-X2C level). Here the larger interaction is not anymore dominated by dispersion contributions. Indeed, optimization at TPSSh-D3 level leads to dissociation of the F–F bond. While the interaction is thus more pronounced, the spectra provided no evidence for the formation of this complex.

**Reaction of Pt atoms with fluorine**

The initially formed product of the exothermic reaction between laser-ablated platinum atoms and F₂ is expected to be the linear PtF₂.[11] Due to a low concentration of F₂ gas diluted in the corresponding noble gas (1:1000–1:200) and, owing to the short reaction time prior to solidification of the deposit on the matrix support, the formation of higher platinum fluorides is suppressed. However, fluorine atoms are also obtained from

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**Table 3. Reaction enthalpies (ΔH) and free energies (ΔG) (calculated for T=5 K and p=1 bar) for the F atom and F₂ addition to PtF₅ (n=2–6)[a]**

| Reaction          | ΔH [kJ/mol] | ΔG [kJ/mol] |
|-------------------|-------------|-------------|
| 1. PtF + F → PtF₆ | -424.4      | -424.1      |
| 2. PtF₂ + F → PtF₅ | -214.0      | -213.7      |
| 3. PtF₃ + F → PtF₄ | -285.7      | -285.3      |
| 4. PtF₄ + F → PtF₃ | -120.0      | -119.7      |
| 5. PtF₅ + F → PtF₂ | -181.5      | -181.2      |
| 6. PtF₆ + F → PtF₁ | -490.9      | -490.6      |
| 7. PtF₁ + F₂ → PtF₃ | -352.2      | -351.9      |
| 8. PtF₂ + F₂ → PtF₄ | -258.3      | -257.9      |
| 9. PtF₃ + F₂ → PtF₅ | -154.1      | -153.7      |

[a] Electronic energies have been obtained at the 2c-X2C-DFTB3LYP level.
the noble gas/fluorine stream by dissociation of F₂ within the hot plasma plume and also by the broad-band radiation produced by the laser ablation of metals. These fluorine atoms allow for a successive fluorination of the initially formed Pt atoms and of PtF₂ during condensation of the gas mixture on the cold matrix support. Although the noble gases neon and argon are considered to be inert matrix hosts, they differ in their specific host–guest interactions and often also in terms of the observed reaction products. In fact, infrared spectra of the reaction products of laser-ablated Pt atoms with F₂ in neon and argon matrices (Figure 8) appear rather different at first glance, and the Ar-spectrum of the Pt–F stretching region is much simpler. This is partly because of stronger argon–guest interactions, which give rise to significant neon-to-argon matrix shifts, particularly for the lower platinum fluorides PtF (Δν = −15.6 cm⁻¹) and PtF₂ (Δν = −14.5 cm⁻¹) compared to a much smaller shift of the strong PtF₂ stretching band of <4 cm⁻¹ (Table 2). Substantial neon-to-argon matrix shifts have also been observed for AuF (Δν = +18.7 cm⁻¹, ArAuF in solid Ne compared to NeAuF) and AuF₂ (Δν = −24.7 cm⁻¹ for pure Ar and Ne matrices, respectively).\

In the Ne spectrum (Figure 8b–d), the intense IR bands of the species with linear Pt–F bonds (PtF₂, PtF₄, and PtF₆) are grouped together in the spectral region between 705–717 cm⁻¹ (Figure 8b–d). However, their assignment is made possible by their different photo-behaviors. Interestingly, the higher platinum fluorides PtF₃ and PtF₅ were not observed in laser ablation experiments using argon as a host gas (Figure 8a). This can probably be explained by the slower condensation rate of neon (25 K f.p.) on a 6 K surface compared to that for argon (84 K f.p.), leaving more time for the successive fluorination of the initially formed PtF₂ during condensation of neon gas onto a solid matrix. Fluorination by photo-mobilized F atoms is also more efficient in solid neon than in solid argon. A list of all observed Pt–F stretching frequencies for the observed PtFₙ (n = 1–6) species is given in Table 2, where they are compared to computed frequencies at the one and two-component X2C-TPSSh level, from which the influence of SOC effects on these frequencies can be evaluated. We note that the computed Pt–F bond lengths of PtF₂ (1.837 Å), PtF₄ (B₃¹g: 1.852 Å) and PtF₆ (1.861 Å, Figure 3) increase slightly within this series. This trend
correlates well with computed frequencies for the antisymmetric stretching modes of their linear F–PtF–F units (PtF$_2$: 710 cm$^{-1}$; PtF$_4$: ($B_{2u}$) averaged value: 705 cm$^{-1}$; PtF$_6$: 698 cm$^{-1}$; 2c-X2C-TPSH results, Table 2), and there is an excellent agreement between these computed and the experimentally observed frequencies in the solid Ne matrix: PtF$_2$: 710 cm$^{-1}$; PtF$_4$: ($B_{2u}$): 715 cm$^{-1}$ (average value), and PtF$_6$: 706 cm$^{-1}$ (Table 2), considering that the largest matrix-shift compared to the gas-phase value is expected for the low-valent PtF$_2$ species.

Computed natural (NPA) atomic charges and Pt-orbital populations (Table S7.6) indicate decreasing charge on the platinum atom along the series with PtF$_2$ (0.456) and PtF$_6$ (0.525), PtF$_4$ (8.03, Table S7.6) and, PtF$_6$ (–0.384, 2c-X2C-B3LYP), and they follow the same trend on average for PtF$_3$ and PtF$_5$. As previously discussed for other examples, the computed atomic charges of platinum show the expected correlation with its formal oxidation numbers (Figure S2.9). While the computed natural electron population of the 5d orbitals of PtF$_2$ (8.03, Table S7.6) corresponds well to a formal d$^8$ configuration of a Pt$^4+$ compound, that of PtF$_4$ (5d population: 7.57) and PtF$_6$ (7.24) differ significantly from a formal d$^6$ (Pt$^{II}$) and d$^4$ (Pt$^{IV}$) configuration. In addition, these calculations also reveal significant 6s-populations, particularly for PtF$_2$ (0.88, Table S7.6), thus indicating 5d, 6s-hybridization. Thus, the fully ionic approximation appears to be a worse bonding model for these binary platinum fluorides, for which the degree of covalency increases significantly along the series.

Conclusion

We have presented a systematic spectroscopic study of the series of molecular platinum fluorides PtF$_n$ (n = 1–6) and, for the first time, vibrational frequencies of the molecules PtF$_2$, PtF$_4$, and PtF$_6$. These species were prepared by a photo-initiated defluorination of PtF$_6$ and the reaction of fluorine atoms or F$_2$ molecules with laser-ablated platinum atoms, respectively, and were isolated under cryogenic conditions in rare-gas matrices. The platinum fluorides produced in the laser-ablation experiments depend on the noble-gas host. However, it was found that the formation of PtF$_2$ by blue-light (λ = 470 nm) irradiation of PtF$_6$ is almost quantitative in both solid neon and argon. PtF$_5$ and PtF$_6$ were formed simultaneously by subsequent UV irradiation of PtF$_6$. The assignment of their vibrational spectra is supported by one- and two-component quasirelativistic DFT computations, which account for scalar relativistic (SR) and SOC effects. Computations at the lowest-energy triplet and singlet surfaces of PtF$_2$ show competing JT and SOC effects, which result in a magnetic bistability with the co-existence of $^3\text{B}_2$ and $^1\text{A}_1$ electronic states having $D_{2h}$ and $D_{6h}$ symmetry, respectively. The presence of both of these states in the solid neon matrices has been spectroscopically: five fundamental and two combination bands of the lowest-energy triplet state of PtF$_4$ were assigned in its IR spectrum, whereas the UV/Vis spectrum is dominated by the CT bands of singlet PtF$_2$. Although further calculations predict structures and IR spectra of PtF$_4$ and PtF$_5$ complexes with F$_2$ at 1c- and 2c-DFT levels using different functional forms, such difluorine complexes could not be assigned in the experimental spectra.

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Conflict of Interest

The authors declare no conflict of interest.

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