

7 Supplementary Information

7.1 Precursor-Specific Partial Ionization Cross Sections

Table SI1: Absolute PS-PICS of PF₃ as a function of ionizing electron energy E . Subscripts indicate ionisation level ($n = 1,2,3$) responsible for production of a particular ion. Values are given in the form $a(b)$ which represents a cross section of $(a \pm b) \text{ \AA}^2$

E/eV	PF ₃ ⁺ $\sigma_1[\text{X}^+]$	F ⁺ $\sigma_1[\text{X}^+]$	F ⁺ $\sigma_2[\text{X}^+]$	F ⁺ $\sigma_3[\text{X}^+]$	P ⁺ $\sigma_1[\text{X}^+]$
50	0.87(2)	0.081(9)	0.021(4)	0.0013(3)	0.29(2)
60	0.86(3)	0.124(4)	0.060(3)	10(1) x10 ⁻⁴	0.38(1)
75	0.84(3)	0.146(6)	0.134(6)	0.0011(5)	0.42(2)
85	0.83(3)	0.152(6)	0.178(7)	0.0038(6)	0.43(2)
100	0.79(3)	0.151(7)	0.232(9)	0.012(1)	0.42(2)
125	0.75(3)	0.094(4)	0.34(2)	0.028(2)	0.39(2)
150	0.70(3)	0.073(4)	0.37(2)	0.050(2)	0.36(2)
175	0.66(3)	0.063(3)	0.38(2)	0.061(4)	0.34(2)
200	0.62(3)	0.053(3)	0.37(2)	0.071(4)	0.32(2)
E/eV	P ⁺ $\sigma_2[\text{X}^+]$	P ⁺ $\sigma_3[\text{X}^+]$	F ₂ ⁺ $\sigma_1[\text{X}^+]$	F ₂ ⁺ $\sigma_2[\text{X}^+]$	PF ⁺ $\sigma_1[\text{X}^+]$
50	2.2(8) x10 ⁻⁴	4.0(9) x10 ⁻⁴	0.0013(6)	2(1) x10 ⁻⁵	0.357(8)
60	0.006(8)	2.9(8) x10 ⁻⁴	0.0017(1)	8(2) x10 ⁻⁵	0.37(1)
75	0.042(2)	2(2) x10 ⁻⁴	0.0020(2)	1.6(3) x10 ⁻⁴	0.38(1)
85	0.069(3)	8(2) x10 ⁻⁴	0.00207(9)	1.8(4) x10 ⁻⁴	0.37(1)
100	0.101(4)	0.0029(7)	0.0022(3)	2.3(2) x10 ⁻⁴	0.36(2)
125	0.141(7)	0.0069(5)	0.0021(2)	2.6(2) x10 ⁻⁴	0.34(1)
150	0.153(9)	0.012(1)	0.0020(2)	2.7(2) x10 ⁻⁴	0.31(1)
175	0.157(8)	0.017(1)	0.0019(1)	2.6(4) x10 ⁻⁴	0.29(1)
200	0.152(8)	0.019(1)	0.0018(2)	2.2(3) x10 ⁻⁴	0.28(1)
E/eV	PF ⁺ $\sigma_2[\text{X}^+]$	PF ⁺ $\sigma_3[\text{X}^+]$	PF ₂ ⁺ $\sigma_1[\text{X}^+]$	PF ₂ ⁺ $\sigma_2[\text{X}^+]$	F ₂ ⁺ $\sigma_2[\text{X}^{2+}]$
50	0.0030(7)	2.1(6) x10 ⁻⁴	2.03(5)	0.018(3)	3(2) x10 ⁻⁵
60	0.0158(8)	1.4(1) x10 ⁻⁴	2.26(7)	0.038(1)	-
75	0.033(1)	1(1) x10 ⁻⁴	2.45(9)	0.055(3)	1(2) x10 ⁻⁵
85	0.042(2)	6(1) x10 ⁻⁴	2.5(1)	0.062(2)	-
100	0.051(2)	0.0013(2)	2.6(1)	0.068(3)	4(2) x10 ⁻⁵
125	0.057(3)	0.0016(2)	2.6(1)	0.071(3)	1.1(4) x10 ⁻⁵
150	0.058(3)	0.0027(2)	2.5(1)	0.071(4)	1.1(7) x10 ⁻⁴
175	0.060(3)	0.0024(2)	2.5(1)	0.071(3)	1.9(6) x10 ⁻⁴
200	0.059(3)	0.0028(4)	2.4(1)	0.068(3)	3.0(4) x10 ⁻⁴
E/eV	F ₂ ²⁺ $\sigma_3[\text{X}^{2+}]$	P ²⁺ $\sigma_2[\text{X}^{2+}]$	P ²⁺ $\sigma_3[\text{X}^{2+}]$	PF ₂ ²⁺ $\sigma_2[\text{X}^{2+}]$	PF ₂ ²⁺ $\sigma_3[\text{X}^{2+}]$
50	9(17) x10 ⁻⁷	0.0044(6)	1.4(9) x10 ⁻⁵	0.014(3)	1.6(8) x10 ⁻⁵
60	1(9) x10 ⁻⁸	0.013(1)	2.8(8) x10 ⁻⁶	0.042(2)	4(1) x10 ⁻⁵
75		0.029(1)	8(3) x10 ⁻⁵	0.070(2)	1.5 x10 ⁻⁴
85	1(2) x10 ⁻⁶	0.037(2)	2.9(2) x10 ⁻⁴	0.084(3)	6.1(7) x10 ⁻⁴
100	2(2) x10 ⁻⁶	0.046(2)	0.0017(1)	0.098(4)	0.0019(1)
125	4(2) x10 ⁻⁵	0.054(3)	0.0060(3)	0.106(5)	0.0045(2)
150	1.45(7) x10 ⁻⁴	0.053(3)	0.0120(7)	0.109(5)	0.0064(3)
175	2.4(3) x10 ⁻⁴	0.055(3)	0.0143(7)	0.109(5)	0.0069(4)
200	2.9(3) x10 ⁻⁴	0.053(3)	0.0182(9)	0.107(9)	3(3) x10 ⁻⁴
E/eV	PF ₂ ²⁺ $\sigma_2[\text{X}^{2+}]$	PF ₂ ²⁺ $\sigma_3[\text{X}^{2+}]$	PF ₃ ²⁺ $\sigma_2[\text{X}^{2+}]$		
50	0.0058(9)	1.8(8) x10 ⁻⁵	0.002(1)		
60	0.0123(6)	3.5(8) x10 ⁻⁵	0.004(2)		
75	0.0176(7)	1.2(5) x10 ⁻⁴	0.007(2)		
85	0.0199(8)	1.7(4) x10 ⁻⁴	0.0097(6)		
100	0.022(1)	2.9(3) x10 ⁻⁴	0.010(2)		
125	0.022(1)	4.3(7) x10 ⁻⁴	0.010(4)		
150	0.023(1)	5.3(5) x10 ⁻⁴	0.014(5)		
175	0.022(1)	5.5(7) x10 ⁻⁴	0.012(4)		
200	0.022(1)	5.7(4) x10 ⁻⁴	0.011(2)		

7.2 Structure of the collision complex $[\text{Ar-PF}_3]^{2+}$

To support the inference, from experiment, that the chemical reaction of PF_3^{2+} with Ar to generate ArF^+ proceeds via a collision complex, the computational methodology described in the main text, was used to identify and characterize any accessible $[\text{Ar-PF}_3]^{2+}$ stationary points. A single stable C_{3v} geometry was found for the singlet complex, involving a P-Ar bond. The F-P bond length is 1.47 Å and the P-Ar bond length is 2.11 Å. The F-P-F angle is 116° and the F-P-Ar angle is 102°. This singlet minimum lies 2.5 eV below the singlet reactant asymptote.

The triplet dication yielded one stable lower symmetry $[\text{PF}_3\text{-Ar}]^{2+}$ geometry, as illustrated in Figure S11. This complex lies 3.7 eV below the triplet reactant asymptote. The geometric parameters for this stationary point are given in Table S12.

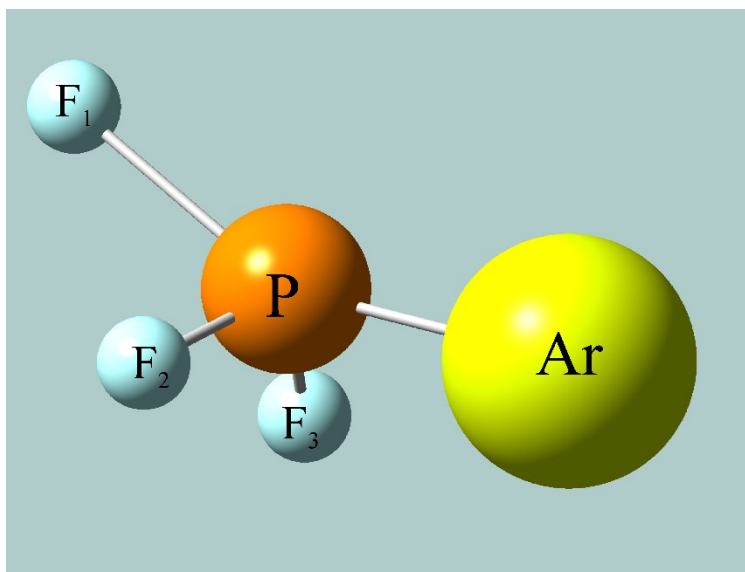


Figure S11 Calculated geometry of a $\text{PF}_3^{2+} + \text{Ar}$ bound state. This low symmetry structure is found for the triplet dication state. See text for details.

Table S12: Geometric parameters for the triplet $[\text{PF}_3\text{-Ar}]^{2+}$ complex. See text and Figure S11 for details.

Atom	N_A	N_B	N_C	$r/\text{Å}$	Angle/deg	Dihedral/deg	$x/\text{Å}$	$y/\text{Å}$	$z/\text{Å}$
P							-0.313	-0.000	-0.076
F ₂	P			1.49			-0.502	-1.249	0.712
F ₃	P	F ₂		1.49	114		-0.502	1.249	0.712
F ₁	P	F ₂	F ₃	2.12	93	-94	-2.319	0.000	-0.748
Ar	P	F ₂	F ₃	2.24	100	106	1.921	0.000	-0.275

7.3 Preparation of PF₃

The preparation was conducted on a gas handling manifold equipped with greaseless Young's taps and an electronic (capacitive) vacuum gauge. Anhydrous ZnF₂ (Sigma-Aldrich) was used as received. PCl₃ was purified by trap-to-trap distillation on a vacuum line under static vacuum.

In a glove box anhydrous ZnF₂ (12.6 g, 0.12 moles) was loaded into a large Schlenk flask containing a magnetic stirrer follower. After removal from the box, anhydrous acetonitrile (100 ml) was added to the flask under nitrogen. The flask was then equipped with a pressure-equalizing addition funnel loaded with PCl₃ (8.0 g, 0.058 moles). The assembly was then transferred to the gas handling line, evacuated, and maintained under static vacuum. A 300 cm³ capacity ampoule equipped with a Young's tap was now attached to the line and evacuated before cooling to liquid nitrogen temperature. The vacuum manifold was now isolated from the pump to leave the receiving flask under static vacuum. With the flask isolated from the line, PCl₃ was added cautiously to the well-stirred ZnF₂ suspension. A steady reaction ensued and the temperature was seen to rise; the reaction was controlled by periodically immersing the flask in an ice bath. The stopcock on the reaction flask was opened periodically to transfer PF₃ into the receiving flask where it was collected as a snow-white solid. The addition of PCl₃ was continued over approximately 60 minutes during which time a dense precipitate of ZnCl₂ was observed in the reaction flask. When no further gas evolution was observed, the reaction flask was disconnected and the cold receiver flask was briefly put under dynamic vacuum to remove any non-condensable gas.

To purify the product a new 300 cm³ capacity ampoule was attached to the line and cooled to liquid nitrogen temperature. The solid sample was now allowed to warm in a dry ice/acetone bath allowing the PF₃ to transfer across into the new ampoule. This operation was then repeated with a third flask. The final bulb was allowed to warm to room temperature ready for further experiments. Approximately 1 dm³ of PF₃ at 600 mmHg was obtained.