

Electronic Supplementary Information

Auger electron angular distributions following excitation or ionization from the Xe 3d and F 1s levels in xenon difluoride

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Table S1

Calculated ionization energies^(a) and population^(b) of XeF₂ orbitals.

Orbital Labelling		Ionization energy (eV) ^(a)	Atomic contribution to molecular orbitals ^(b)								
Atomic	Molecular		Xe 3d	Xe 4s	Xe 4p	Xe 4d	Xe 5s	Xe 5p	F 1s	F 2s	F 2p
Xe 3d	σ_g	715.84	1.0								
	π_g	715.75	1.0								
	δ_g	715.49	1.0								
F 1s	σ_g	714.39							1.0		
	σ_u	714.39							1.0		
Xe 4s	σ_g	217.94		1.0							
Xe 4p	σ_u	168.09			1.0						
	π_u	167.50			1.0						
Xe 4d	σ_g	80.27				1.0					
	π_g	79.95				1.0					
	δ_g	79.28				1.0					
Valence Orbitals											
	$8\sigma_g$	42.616								0.925	
	$5\sigma_u$	42.445								0.966	
	$9\sigma_g$	29.535					0.855				
	$6\sigma_u$	20.109						0.249			0.714
	$4\pi_u$	18.369						0.246			0.745
	$3\pi_g$	17.511									0.972
	$10\sigma_g$	15.038									0.836
	$5\pi_u$	13.539						0.761			0.235

^(a) Koopmans Theorem values: RHF/DGVDZP calculation for core levels; RHF/def2-QZVP (with ECP) for valence orbitals^(b) Mulliken population analysis: MP2/DGVPDZ calculation for core levels; MP2/def2-QZVP for valence orbitals. F atom contributions are shown as the sum of the two equivalent individual F atom populations.

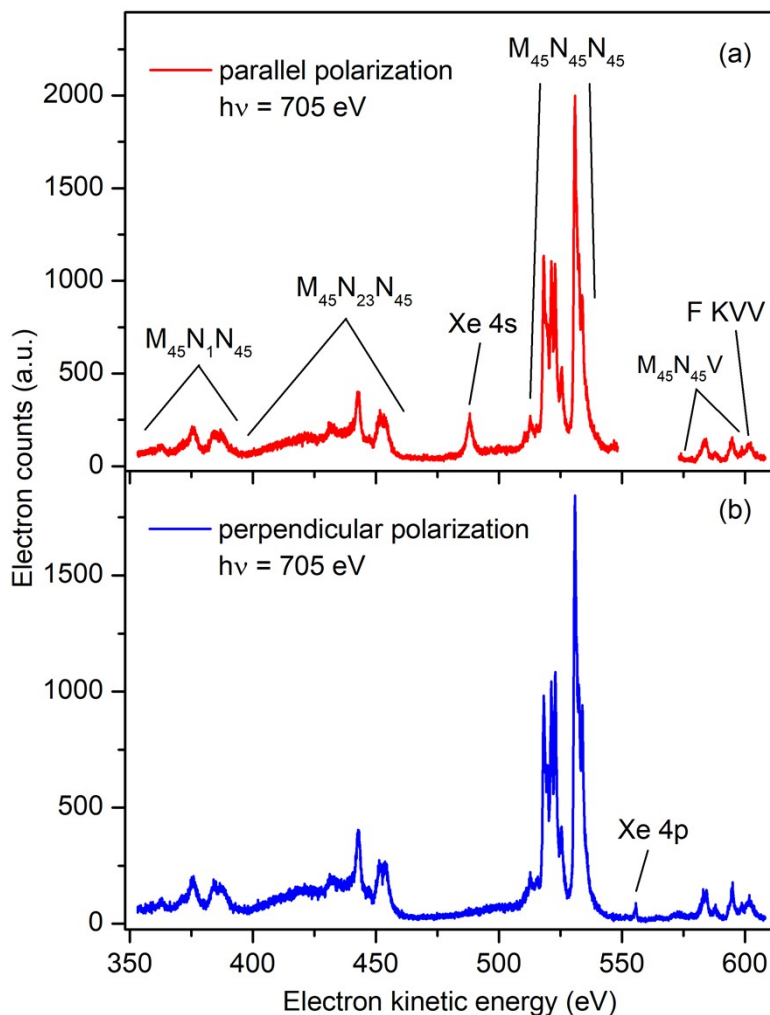


Figure S1

The non-resonant Auger electron spectrum of XeF₂ recorded at a photon energy of 705 eV using parallel (a) and perpendicularly (b) polarized radiation. Most of the structure is associated with the M₄₅N₁N₄₅, M₄₅N₂₃N₄₅, M₄₅N₄₅N₄₅, and M₄₅N₄₅V transitions, although one peak is attributed to the F KVV transition. Peaks arising from direct ionization from the Xe 4s and Xe 4p levels are observed in the spectra recorded with parallel (a) and perpendicularly (b) polarized radiation, respectively.

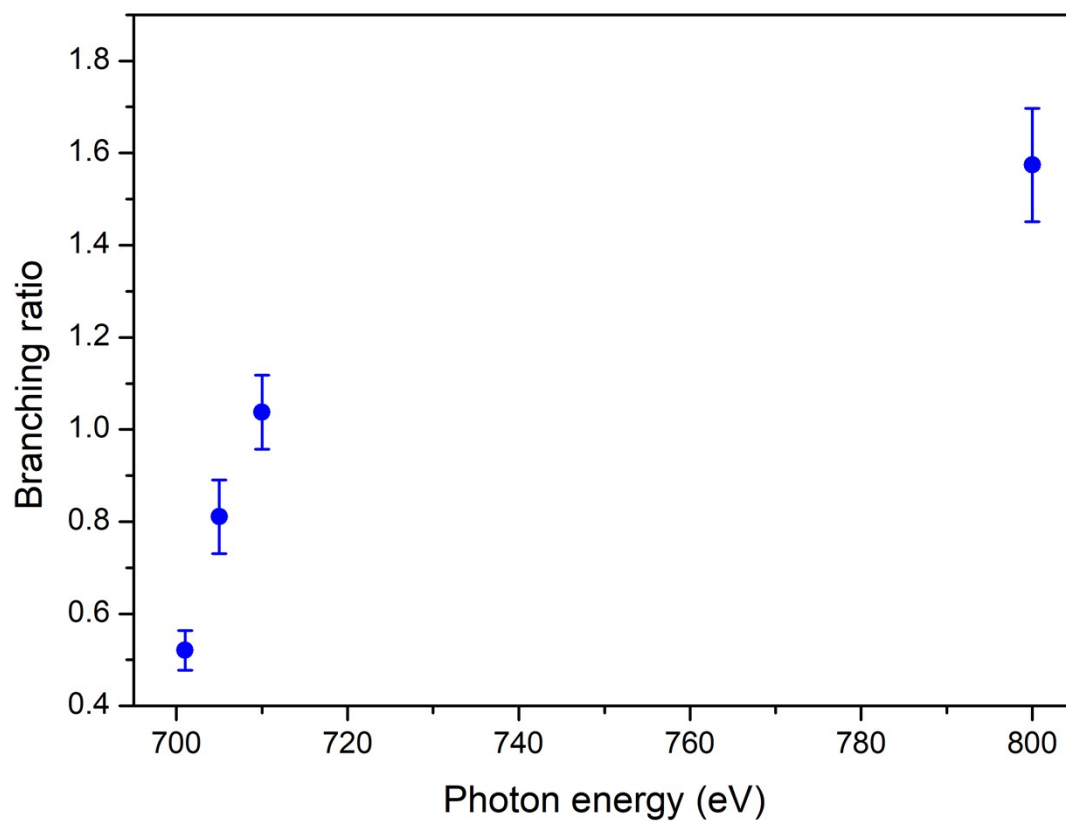


Figure S2

The $M_4N_{45}N_{45}:M_5N_{45}N_{45}$ intensity branching ratio obtained from the fits of the non-resonant Auger spectra.

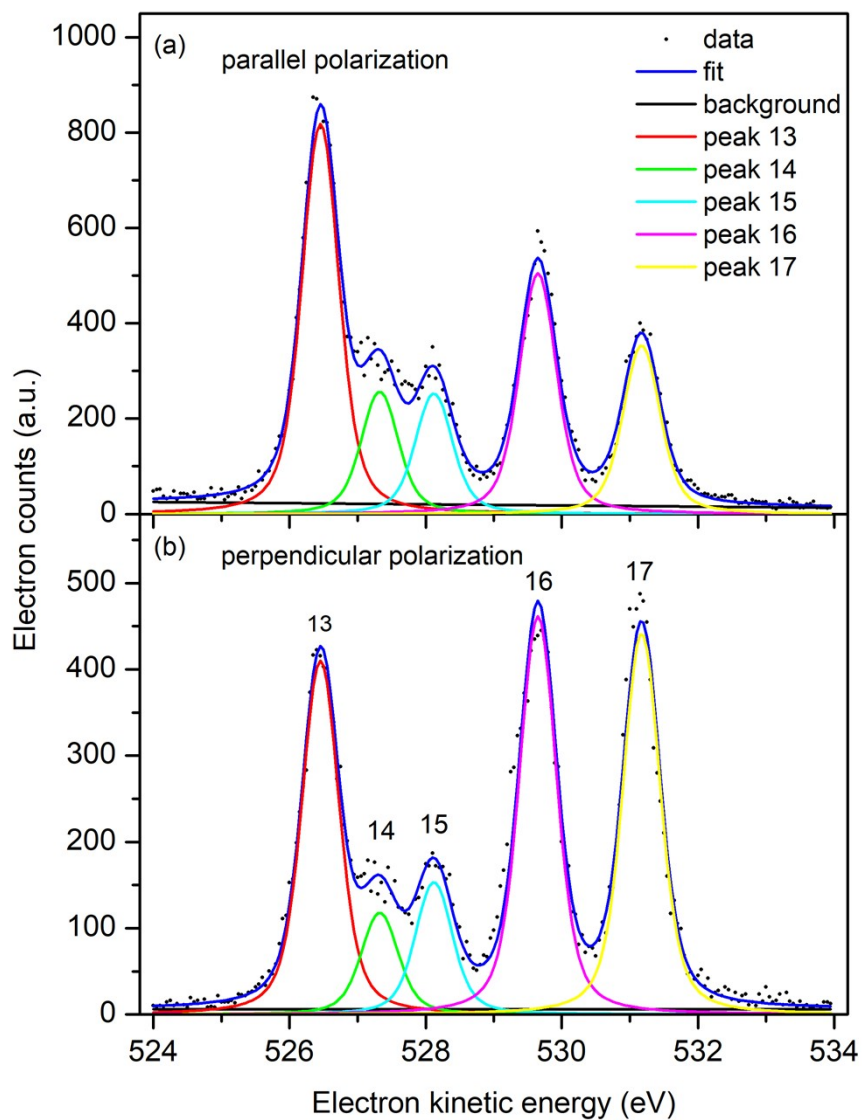


Figure S3

Resonantly excited $M_5N_{45}N_{45}$ Auger spectra, measured at a photon energy of 669.9 eV, coinciding with the $Xe\ 3d_{5/2} \rightarrow \sigma^*$ transition. The spectra were recorded with parallel (a) and perpendicularly (b) polarized radiation. The raw and the fitted data are shown. The kinetic energies of the peaks numbered 13-17 are given in Table 2.

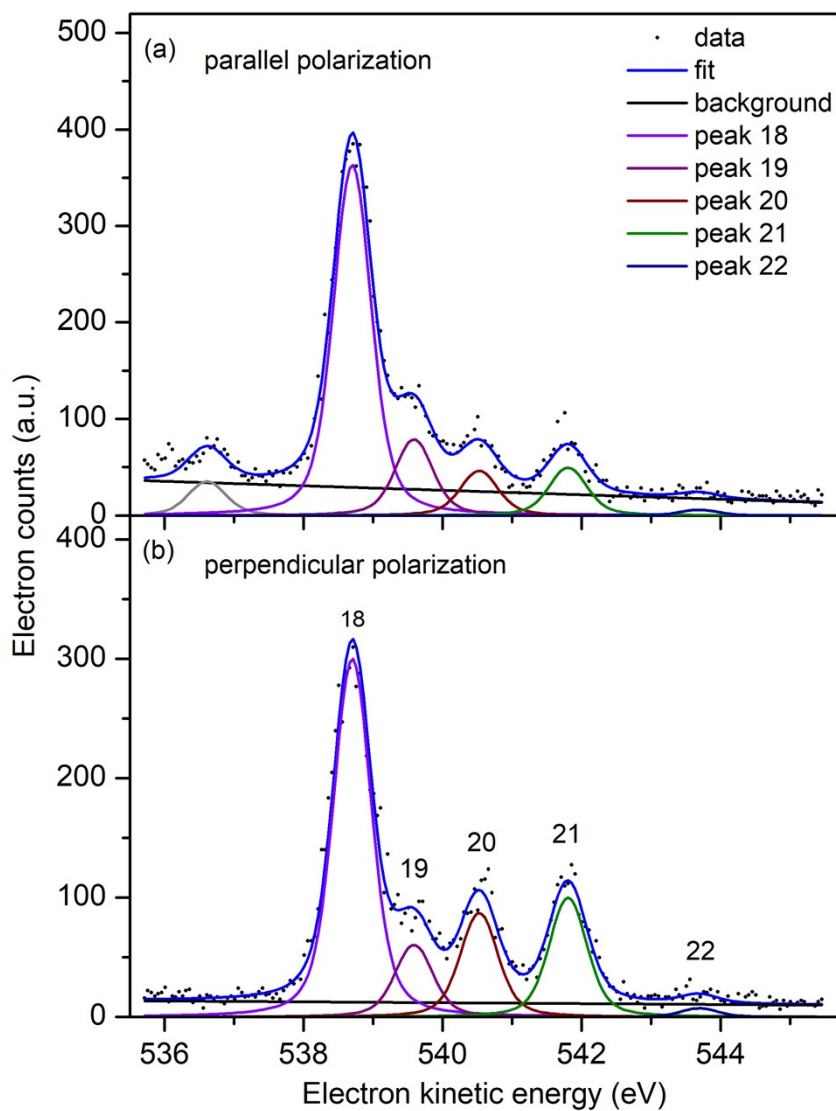


Figure S4

Resonantly excited $M_4N_{45}N_{45}$ Auger spectra, measured at a photon energy of 682.8 eV, coinciding with the overlapping Xe $3d_{3/2} \rightarrow \sigma^*$ and F $1s \rightarrow \sigma^*$ transitions. The spectra were recorded with parallel (a) and perpendicularly (b) polarized radiation. The raw and the fitted data are shown. The kinetic energies of the peaks numbered 18-22 are given in Table 2.