Supplementary Materials for

Attosecond interferometry of shape resonances in the recoil frame of CF₄

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1 Theoretical methodology

1.1 Quantum-scattering Calculations

The calculation of the CF$_4$ photoionization matrix elements $M_{1h_{u_*e}}^{\Gamma_0}(E_{SB}, \vartheta, \varphi)$ has been performed using the ePolyScat molecular scattering codes described in Refs. [52,53]. The electronic structure of CF$_4$ has been calculated with the Hartree-Fock (HF) method using a cc-pVTZ basis set. The single-center partial-wave expansion in the scattering calculations has been truncated at $l_{\text{max}} = 60$, which ensures converged results. Given the set of matrix elements

![Fig. S1. Calculated angle-resolved sidebands for the 1t, HOMO of CF$_4$. Theoretically predicted sideband intensity for SB12 (A), SB14 (B), and SB16 (C), displayed as a function of the emission angle $\vartheta$ and the XUV-IR delay $\tau$. The black dots signify the position of the extremal phase $\Phi_{\text{Mol}}(E_{SB}, \vartheta)$ at each angle.](image)
Fig. S2. Calculated angle-resolved sidebands for the 4t_2 HOMO-1 of CF_4. Theoretically predicted sideband intensity for SB12 (A), SB14 (B), and SB16 (C), displayed as a function of the emission angle $\vartheta$ and the XUV-IR delay $\tau$. The black dots signify the position of the extremal phase $\Phi_{Mol}(E_{SB}, \vartheta)$ at each angle.

$I_{lm\mu}(E)$ output by ePolyScat, the emission- and orientation-angle-dependent photoionization matrix elements have been calculated via:

$$M_{h\nu}^{\Gamma_0}(E, \vartheta, \varphi) = \sum_{lm\mu} I_{lm\mu}^{\Gamma_0} Y_{lm}(\vartheta, \varphi) Y_{1\mu}(\beta, \alpha) \quad (1)$$

The molecular frame employed in the theoretical calculation is depicted in Fig. S3 and Fig. 3 of the main text. The molecular $z$-axis corresponds to the emission angle $(\vartheta, \varphi) = (0, 0)$, i.e. $(\vartheta = 0, \varphi = 0)$ points along the (dissociating) C–F bond. For illustrative purposes, in Fig. 3 we also plot the squared amplitude of a selected MF-angle-resolved matrix element at $\alpha = 0, \beta = 0$. This quantity corresponds to the molecular-frame photoelectron angular distribution, MFPAD.

To assess the accuracy of the ePolyScat calculations used in our work, MFPADs obtained with the photoionization matrix elements described above have been compared to previous calculations and experimental data presented in Ref. [34]. Figure S4 displays the MFPADs for photoionization from the HOMO and Figure S5 from the HOMO-1 of CF_4. The direct comparison of Figs. S5 and S validates the accuracy of our calculations.

1.2 Laboratory-Fame angular resolved delays

In Figure 2 of the main text we show laboratory frame angular resolved delays for an emission angle of 0-18°. This angle was chosen, because it is the angular range with the most electron
Fig. S3. Calculated MFPAD for photoionization from the $4t_2$ (HOMO-1) channel. The shown MFPAD corresponds to an electron kinetic energy of $E_{kin} = 3.2$ eV. The Euler angles are set at $\alpha = 0^\circ$, $\beta = 0^\circ$, i.e. the laboratory and the molecular frames coincide. The black spheres show the positions of the fluorine atoms.
Fig. S4. Calculated MFPADs. The MFPADs for the 1t₁ (HOMO) channel shown in this figure have been calculated with ePolyScat, i.e. the same methodology used for the calculation of the time delays.

Fig. S5. Calculated MFPADs. Same as Fig. S4 for the 4t₂ (HOMO-1) channel. The overall very good agreement with, both, experimental MFPADs and more sophisticated multi-channel calculations based on the complex Kohn variational method [34], both shown in Fig. S6, demonstrate the accuracy of the ePolyScat calculations.

Fig. S6. Experimental and calculated MFPADs of the 4t₂ (HOMO-1) channel from previous work. MFPADs adapted from Larsen et al. [34], shown here to demonstrate the agreement of our calculations with previous experimental and theoretical data. (A) $E_{\text{kin}}=2.1$ eV, (B) $E_{\text{kin}}=3.2$ eV, (C) $E_{\text{kin}}=4.3$ eV and (C) $E_{\text{kin}}=5.2$ eV.

yield and also with the best energy resolution. Nevertheless, the question arises how much the delays caused from the shape resonances depend on the choice of emission angle. In Fig. S7 we show the ionization delays of CF₄ for both HOMO and HOMO-1 referenced to argon,
with an electron emission angle of 25°-55°. The black solid line shows the calculated RABBIT delays for the same angular range and reference. It can be seen, that also in this angular range the agreement between theory and experiment is good. Further, there is no qualitative difference of the delays observed for the angular range of 0-18°, shown in Figure 2. Due to the choice of electric and magnetic field parameters, we are unable to access delays for full angular integration.

**Fig. S7 Laboratory-Frame Photoionization delays.** Delays for channel (A) 1t₁ and (B) 4t₂. Black filled circles show the experimental values, the black solid line shows the calculated RABBIT delays. Both experimental and theoretical delays are for electrons emitted 25°-55° with respect to the XUV polarization and are referenced to argon using the same angular integration range. The emission angle is visualized in the inlet of (A), where the green shaded area shows the angular range and the purple double arrow indicates the XUV polarization. The error bars show the standard deviation of the delays extracted from multiple data sets.

### 1.3 Partial wave analysis of the RABBIT delays

In this section, we present a detailed analysis of the photoionization cross sections and RABBIT delays discussed in this work on the basis of a partial wave decomposition. This approach clarifies the key mechanisms underlying the photoelectron trapping in the shape resonances and its manifestation in the measured RABBIT delays.

We first discuss the HOMO channel. Figure S8 shows the cross section of the 1t₁ → k₄t₂ photoionizing transition. It clearly reveals the presence of a shape resonance at a kinetic energy
of \( \sim 2.3 \text{ eV} \), which is dominated by an f-wave \((l = 3)\) contribution. No shape resonances have been found in the relevant energy range in the other continuum symmetries \((a_2, e\) and \(t_1)\).

The HOMO-1 channel features two shape resonances, one of \(a_1\) symmetry (Fig. S9A) and one of \(t_2\) symmetry (Fig. S9B). The two resonances lie close in energy and overlap within their respective widths. Both of them are dominated by f-wave contributions, as in the case of the HOMO channel. The \(a_1\) shape resonance additionally has contributions from s- \((l = 0)\) and g- \((l = 4)\) waves, whereas the \(t_2\) shape resonance has p- \((l = 1)\) and d- \((l = 2)\) wave contributions. We note that p- and d-waves do not contain the totally symmetric irreducible representation and are therefore excluded from contributing to the \(a_1\) shape resonance by symmetry.

To determine the lifetimes of the respective resonances we fit the symmetry-resolved cross sections using the Fano formalism [54]

\[
f(x) = A \frac{(q + \frac{x - E_0}{\Gamma/2})^2}{1 + \left(\frac{x - E_0}{\Gamma/2}\right)^2} + B,
\]

where \(q\) is the Fano parameter, \(\Gamma\) the linewidth, \(E_0\) the resonance position, \(A\) an amplitude and \(B\) an offset. The lifetime is then calculated with the relation \(\tau = \hbar/\Gamma\). In Table S1 we show the resonance lifetimes together with the fit parameters.
Fig. S9 Partial-wave decomposition of the HOMO-1 cross sections. For channels (A) HOMO-1→ka₁ and (B) HOMO-1→kt₂.

| Channel          | Lifetime τ / as | Width Γ / eV | Resonance Position E₀ / eV | Fano Parameter q |
|------------------|-----------------|--------------|---------------------------|-----------------|
| 1t₁ → kt₂        | 650             | 1.01         | 2.43                      | 26.8            |
| 4t₂ → ka₁        | 457             | 1.44         | 3.91                      | -7.6            |
| 4t₂ → kt₂        | 370             | 1.78         | 3.02                      | 6.67            |

Table S1. Lifetimes and Fano-fit parameters of shape resonances.

In the following, we study the angle dependence of the photoionization delays in the molecular frame and analyze the contributions of individual partial waves. When the analysis is restricted to a single partial wave, we always obtain delays that are forward-backward symmetric along the dissociation axis. Any asymmetry is therefore the signature of the interference of at least two partial waves. In the following, we hence chose different subsets of partial waves and displayed the corresponding molecular-frame RABBIT delays. For all partial-wave resolved delays shown, the cc-contribution and the argon reference delays are omitted. The partial-wave analysis of the RABBIT delays in the HOMO channel is shown in Fig. 3 of the main text. Here, we present the corresponding analysis of the HOMO-1 channel.

As shown in Fig. S9 and Fig. 2 of the main text, the HOMO-1 channel contains two overlapping shape resonances of symmetries a₁ and t₂, respectively. Here, we discuss the partial-wave decomposition of the angle-resolved photoionization delays for each continuum symmetry sep-
arately first, before showing the results of the complete calculation.

Figures S10 and S11 show the delays obtained from a calculation that is restricted to the $a_1$ continuum symmetry and $l = 0, 3$ or $l = 0, 3, 4$, respectively. Note that $l = 1, 2$ are not contributing to the $a_1$ continuum symmetry. The comparison of the two figures shows that the qualitative asymmetry of the delays is already captured by $l = 0, 3$ alone. In SB12, the addition of $l = 4$ has a large effect, both on the angular variation and the absolute values of the delays, whereas it has only a minor effect in the case of SB14 and SB16.

Fig. S10 Partial-wave-resolved RABBIT delays of the HOMO-1 channel with continuum symmetry $a_1$. Restricted to the contributions of partial waves with $l=0$ and 3 for (A) $E_{\text{kin}}^{\text{CF}_4} = 1.55$ eV for SB12, (B) SB14 and (C) SB16. All delays are referenced to argon.

Fig. S11 Partial-wave-resolved RABBIT delays of the HOMO-1 channel with continuum symmetry $a_1$. Restricted to the contributions of partial waves with $l=0, 3$ and 4 for (A) $E_{\text{kin}}^{\text{CF}_4} = 1.55$ eV for SB12 (B) SB14 and (C) SB16. All delays are referenced to argon.
Figures S12 and S13 show the delays obtained from a calculation that is restricted to the $t_2$ continuum symmetry and $l = 2, 3$ or $l = 1, 2, 3$, respectively. Note that $l = 0$ is not contributing to the $t_2$ continuum symmetry. The comparison of the two figures again shows that most features in the angular dependence of the delays are already captured by $l = 2, 3$ alone. In SB12, the addition of $l = 1$ has a visible effect on the angular variation of the delays, whereas it has only a minor effect in the case of SB14 and SB16.

**Fig. S12** Partial-wave-resolved RABBIT delays of the HOMO-1 channel with continuum symmetry $t_2$. Restricted to the contributions of partial waves with $l= 2$ and 3 for (A) $E_{\text{kin}}^{\text{CF}_4}=1.55$ eV for SB12, (B) SB14 and (C) SB16. All delays are referenced to argon.

**Fig. S13** Partial-wave-resolved RABBIT delays of the HOMO-1 channel with continuum symmetry $t_2$. Restricted to the contributions of partial waves with $l=1, 2$ and 3 for (A) $E_{\text{kin}}^{\text{CF}_4}=1.55$ eV for SB12, (B) SB14 and (C) SB16. All delays are referenced to argon.

Figure S14 shows the angle-resolved delays obtained by including all continuum symme-
tries and all significantly contributing partial waves \( (l = 0 - 4) \). The comparison with Figs. S11 and S13 shows that the total delays are not a simple linear combination of the delays obtained for specific continuum symmetries. The importance of interference phenomena is further supported by the direct comparison of the results of a coherent and incoherent addition of the symmetry-resolved photoionization matrix elements in Fig. 4 of the main text.

**Fig. S14 Partial-wave-resolved RABBIT delays of the HOMO-1 channel with all continuum symmetries.** Restricted to the contributions of partial waves with \( l = 0, 1, 2, 3 \) and 4 for (A) \( E_{\text{kin}}^{CF_2} = 1.55 \) eV for SB12, (B) SB14 and (C) SB16. All delays are referenced to argon.
1.4 Graphical representations of the shape-resonance wavefunctions

In this section, we discuss the continuum wave functions at the energies of the three relevant shape resonances in more detail. These wavefunctions were obtained using the resonance-search algorithm implemented in ePolyScat [52,53]. These calculations use a single-active-electron approximation and are therefore slightly less accurate than the regular ePolyScat calculations used throughout the remainder of this work. They nevertheless have the benefit of providing the energy positions, lifetimes and single-electron continuum wavefunctions of the shape resonances, which offer an intuitive understanding of their spatial and temporal properties.

Both the initial orbitals as well as the resonant wavefunctions are calculated in a coordinate system where the C-F bonds span a tetrahedron with vertices given by \((\pm r_{CF} \cos \alpha/2, \pm r_{CF} \cos \alpha/2, \pm r_{CF} \cos \alpha/2)\) with \(\alpha = \arccos 1/3\). Choosing the electric field vector to lie along one of the C-F bonds (e.g. \((1,1,1)\)) will thus create a superposition of all three degenerate wavefunction components:

\[
\frac{1}{\sqrt{3}}(1t_1^{(x)} + 1t_1^{(y)} + 1t_1^{(z)}).
\]

Figure S15 shows the wave functions of the bound 1t_1 and 4t_2 orbitals, as well as the continuum wave functions of the three shape resonances that were studied in this work. Two of these continuum wavefunctions are also shown in Fig. 2C,D of the main text. Here, we note that the t_2 shape resonances in both channels have nearly identical wave functions, which suggests that they are actually closely related to each other, although accessed from different initial orbitals. This is a remarkable observation because the two t_2 resonances are located at different photon energies in the two channels and have different lifetimes. Specifically, the 4t_2 \(\rightarrow t_2\) resonance lies higher in photon energy and has a shorter lifetime than the 1t_1 \(\rightarrow t_2\) resonance.

The isocountour values chosen in Fig. S15 have the advantage of emphasizing the nature of the shape resonances, i.e. the molecular cage effect, but the disadvantage of not clearly displaying the continuum character of the corresponding wave functions. We therefore chose
**Fig. S15 3-dimensional orbital wavefunctions.** (A) Orbital wavefunctions for the 1\textsubscript{t\textsubscript{1}} HOMO (bottom) and the t\textsubscript{2} continuum wavefunction at the resonance energy (top). (B) same as (A) for the 4t\textsubscript{2} HOMO-1 and the a\textsubscript{1}, as well as t\textsubscript{2} resonant wave functions. The position of the atoms is indicated with black/blue spheres for C/F, respectively. Contour levels used are: 0.8, 0.7, 0.35, 0.15 and 0.09.

A different set of isocontour values for the same wavefunctions in Fig. S16. Here, the bound character of the molecular orbitals and the infinite extension of the continuum wave functions is more clearly visualized.
Fig. S16 3-dimensional orbital wavefunctions with lower isocontour values. Same as Fig. S15, but with lower isocontour values to emphasize the diffuse contributions to the shape-resonant wave functions. Contour levels used are: 0.8, 0.6, 0.4, 0.22, 0.0145.
1.5 Calculation of the potential energy surfaces of CF$_4^+$

The potential-energy surfaces shown in Fig. 1A of the main text were obtained as follows. First, one of the C-F bond lengths was fixed to one of 25 values in a constrained structure optimization of CF$_4^+$ with unrestricted DFT employing the BP86 functional and the def2-TZVP basis set. For each of these structures, the six lowest-lying electronic states were calculated at the SA-CASSCF(23,16) level of theory using the relativistic X2C Hamiltonian and the ANO-RCC basis set with triple-zeta contraction. This active space contains all valence orbitals except for the energetically well-separated 2s-orbitals of the fluorine atoms.
Fig. S17. Phase retrieval from overlapping photoelectron signals of CF₄. (A) Laboratory-frame angle-resolved RABBIT spectrum with an angle between electron direction and XUV polarization of 0-18°. (B) Fitted energy spectrum of CF₄. The electron energies from the three energetically accessible states are fitted according to their cross section and XUV intensities using Gaussians. (C) Amplitude at 2ω of a Fourier Transformation of the RABBIT spectrum shown in (A). (D) Phase at 2ω of the same Fourier Transformation.
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