Attosecond photoionisation time delays reveal the anisotropy of the molecular potential in the recoil frame

H. Ahmadi1,2,9, E. Plésiat3,4,9, M. Moioli1, F. Frassetto5, L. Poletto5, P. Decleva6, C. D. Schröter7, T. Pfeifer7, R. Moshammer7, A. Palacios3,8, F. Martin3✉ & G. Sansone1✉

Photoionisation time delays carry structural and dynamical information on the target system, including electronic correlation effects in atoms and molecules and electron transport properties at interfaces. In molecules, the electrostatic potential experienced by an outgoing electron depends on the emission direction, which should thus lead to anisotropic time delays. To isolate this effect, information on the orientation of the molecule at the photoionisation instant is required. Here we show how attosecond time delays reflect the anisotropic molecular potential landscape in CF4 molecules. The variations in the measured delays can be directly related to the different heights of the potential barriers that the outgoing electrons see in the vicinity of shape resonances. Our results indicate the possibility to investigate the spatial characteristics of the molecular potential by mapping attosecond photoionisation time delays in the recoil-frame.
Molecular systems are characterized by complex potential landscapes determined by their chemical composition and by the spatial arrangement of their constituents. In general, the electronic potential presents a non-spherical shape, which plays a key role in the stereo-dynamics of atom-molecule collisions and molecule–molecule interactions.

As explained in textbooks, the effect and the spatial gradient of a potential can be unveiled by monitoring the motion of a probe charge immersed in that potential. In atoms and molecules, this charge can be one of the electrons contained in the system, which must absorb enough energy from an external source to overcome the ionisation potential and to acquire the necessary kinetic energy to explore the potential landscape, while staying long enough in the molecular surroundings to sample its relevant features. This is ideally possible by using ultraviolet radiation, i.e. photon energies of a few tens eV. In a classical picture, an electron with 10 eV energy takes about 53 as to travel through the typical molecular extension of 1 Å. The extremely short timescale of this motion calls for the application of attosecond pulses, which can efficiently generate photoelectron wave packets and provide the necessary time resolution.

The dynamics of photoionising wave packets is usually investigated by means of pump-probe experiments, in which an isolated or a train of attosecond pulses in the extreme ultraviolet (XUV) range set the photoelectron wave packet free and a synchronised infra-red (IR) pulse probes the instant at which the electron enters the continuum. Using this approach, the role of electronic correlation effects in the photoionisation of atoms has been investigated in real-time and. Attosecond time delays have also been reported in photoionisation in molecular systems, showing the relevance of nuclear motion in hydrogen and the role played by shape resonances in N₂O and nitrogen. Moreover, the role of the localisation of the initial wave function and of a functional molecular group has also been demonstrated.

In atomic systems, the photoionisation time delays are usually decomposed into a term specific of the atomic potential (usually indicated as Eisenbud–Wigner–Smith delay) and a measurement-induced contribution due to the action of the IR probe pulse on the photoelectron wave packet moving in the long-range Coulomb potential. In the long run, the influence of the latter term can be usually quantified through simple formulas independent of the specific target and its angular dependence has been characterised, in molecules the effect of the IR field on the measured time delays has not been characterised yet. In general, in the case of molecular systems, the contributions of the two terms cannot be disentangled, which requires a more involved analysis.

A fundamental prerequisite for the characterisation of the combined effect of the anisotropic molecular landscape and of the IR field is to have access to the orientation of the molecule at the photoionisation instant. This can be done by measuring the emission direction(s) of ionic fragment(s) after the interaction with the XUV radiation, which defines the recoil frame. Symmetric molecules consisting of only a few atoms are ideal to test these effects in this frame. On the one hand, small molecules present a limited number of photoionisation and photofragmentation pathways, making feasible the identification of the electronic level of the outgoing photoelectron and, under suitable conditions, the determination of the molecular orientation during the interaction with the ionising radiation. On the other hand, the symmetry of the molecule gives the opportunity to identify specific privileged directions in the recoil frame and to characterise the effect of the molecular potential along them.

In this work we investigate the photoionisation dynamics induced by a train of attosecond XUV pulses on CF₄ molecules by means of photoelectron-photoion coincidence spectroscopy. The advantage of this approach is the possibility to derive information on the molecular orientation at the instant of photoionisation by measuring in coincidence the momenta of the emitted electron and the fragment ions resulting from the subsequent dissociation of the molecular cation. In this way, we have been able to unambiguously identify individual ionisation channels and obtain time-resolved recoil-frame photoelectron angular distributions (RFPADs) from which the variations of photoionisation delays with the electron emission direction have been extracted. The measured delays are in very good agreement with those obtained from calculated time-resolved RFPADs, where all the transitions induced by the attosecond pulse train and the IR probe, are taken into account in a time-dependent formalism. The agreement confirms the validity of our experimental approach and opens the route to orientation-specific exploration and understanding of molecular photoionisation delays.

Results

Recoil frame and XUV spectroscopy of CF₄. We focus on photoelectrons emitted from the Highest-Occupied Molecular Orbital of CF₄, which is triply degenerate and belongs to the irreducible representation T₁ of the point group T₂₃ (see Fig. 1a). The xz plane represents the molecular frame, where one fluorine atom (1) is positioned along the negative z-axis and a second fluorine atom (2) is contained in the xz plane (the carbon atom occupies the centre). In the molecular frame, the common direction of the polarisation vectors of the collinear XUV and IR fields (indicated as a magenta arrow in Fig. 1a) is identified by the angles β (polar angle) and α (azimuthal angle).

Photoelectrons and photoions emitted after the interaction with an attosecond pulse train generated in argon and krypton and a synchronised IR field were measured using a Reaction Microscope. This approach usually called RABBITT (Reconstruction of attosecond beating by two-photon transitions) allows one to combine temporal and spectral resolution, which turns out to be advantageous for identifying the different fragmentation channels or yields involved in the experiment. The output used in the measurements is described in ref. 26. For XUV photon energies in the range 20–46 eV photoionisation of neutral CF₄ into five different cationic states (X2T₁, A2T₂, B²E, C²T₂, D²A₁) is energetically possible. While the first three predominantly lead to the formation of CF₃⁺ ions, the last two lead to the formation of CF₂⁺ ions (see Supplementary Figs. 1 and 2 and Supplementary Table 1). The parent molecular ion CF₄⁺ was not observed, in agreement with previous spectroscopic measurements. Additional correlation between the kinetic energy release (KER) of the ions and the photoelectrons gives the possibility to isolate the contribution of the photoelectrons associated with the X2T₁ state from those associated with the A2T₂ and B²E states (see Supplementary Figs. 1 and 3 and 4).

Photoionisation from the ground state (leading to cations in the X2T₁ state) results in fast dissociation and emission of CF₃⁻ fragments with 100% probability, giving access to the relative orientation of the polarisation direction of the external fields with respect to the polar angle β (the azimuthal angle α cannot be determined in our measurements) at the instant of photoionisation using the recoil approximation.

The validity of the approximation is further confirmed by the good agreement between the measured photoelectron angular distributions (PADs) for this state and those calculated by assuming a fixed nuclei configuration (see below). Because the position of the fluorine atoms in the tripod is not determined in the experiment, the measured PADs are plotted as a function of the θ angle, i.e.
The spectra are thus retrieved capturing only photoelectrons in coincidence with the momentum of the dissociating CF\textsubscript{4} molecule and deidentified in the molecular frame by the angles $\alpha$ and $\beta$. The emission direction of the photoelectron in the molecular frame (cyan arrow) is defined by the angles $\theta$ and $\varphi$. RABBITT traces obtained for the parallel ($0^\circ \leq \beta \leq 45^\circ$ and $135^\circ \leq \beta \leq 180^\circ$) b and perpendicular ($60^\circ \leq \beta \leq 120^\circ$) c configurations. The angles $\alpha$ and $\varphi$ cannot be determined in our measurements.

**Discussion**

Overall the experimental and theoretical photoemission delays are in good agreement. The experimental attosecond time delays for the parallel case exhibit a minimum around $\theta = 90^\circ$, while they are relatively independent of $\theta$ in the perpendicular case (see also Supplementary Figs. 9 and 10). The minima present negative values (on the order of a few hundreds of attoseconds), indicating that the maxima of the sidebands oscillations observed at these angles occur at earlier time delays. The theoretical data reproduce these trends, with the minimum at $90^\circ$ for the parallel configuration and a smooth evolution as a function of the photoelectron emission angle for the perpendicular configuration.

For the parallel case (left panels in Fig. 2), the minimum observed around $\theta = 90^\circ$ can be attributed to the interaction with the IR field (see Supplementary Figs. 11–13). In Fig. 2a–c, three different regions are highlighted corresponding to the intervals $\theta_a = [0^\circ - 29^\circ]$, $\theta_b = [60^\circ - 75.5^\circ]$, and $\theta_c = [151^\circ - 180^\circ]$ centred around the directions $A (\theta = 15^\circ)$, $B (\theta = 68^\circ)$ and $C (\theta = 165^\circ)$, respectively. Photoelectrons leaving the molecule along these three directions, experience significant differences in the molecular landscape, as shown in Fig. 3a, which reports the molecular potential resulting from the simulations and the three escape directions A, B, and C (indicated with dot-dashed lines). For a better visualisation, two-dimensional cuts of the potential are plotted in each plane. The nearly opposite directions A and C correspond to photoelectrons emitted (almost) parallel or
antiparallel to the ion emission direction. For these directions, the molecular potentials exhibit barriers with quite different heights, as shown in Fig. 3b. On the contrary, the direction B corresponds to photoelectrons escaping the molecule along a direction characterised by a barrier, whose height is close to that along the C direction. The photoionisation cross-sections along the three directions are also reported in Fig. 3c, indicating the existence of shape-resonances in the photon-energy range \( \approx 28-33 \text{ eV} \) for the three directions.

The anisotropic molecular potential influences the photoionisation dynamics, as demonstrated in Fig. 4a, b, which present the difference of the time delays measured along the directions A and C (\( \Delta \tau_{A-C} = \tau_A - \tau_C \)) and B and C (\( \Delta \tau_{B-C} = \tau_B - \tau_C \)), respectively. The experimental values (red squares) were determined integrating the photoelectrons emitted in the parallel configuration over the emission angles \( \theta \) in the intervals \( \theta_A = [0 - 29^\circ] \), \( \theta_B = [60 - 75.5^\circ] \), and \( \theta_C = [151 - 180^\circ] \) along the directions A, B, and C, respectively. The theoretical values (black circles) were obtained from the calculated RABBITT spectra in the same way. The delay difference \( \Delta \tau_{A-C} \) presents a minimum in the experimental as well as in the theoretical as data around 34 eV photon energy, which approximately matches the maximum of the shape resonance for the direction C observed in Fig. 3c. For photon energies beyond the shape-resonance regions of both directions, the absolute value of the difference \( \Delta \tau_{A-C} \) becomes smaller.

The experimental points are in good agreement with the theoretical curve (except for the point corresponding to sideband 20). The stereo Wigner time delay\(^{22,32,33} \) obtained from the one-photon (XUV) dipole matrix elements and integrated over the corresponding angle intervals is also reported (blue triangles) and indicates a minimum in the same energy region. The deviations between the difference of the stereo Wigner time delays and the corresponding time delays obtained for the two-colour simulations, support the conclusion that the delay in photoionisation of molecules cannot be decomposed, in general, into the sum of a contribution due to the Wigner delay and one associated with the continuum-continuum delay\(^{22} \). The latter, indeed, should cancel out when subtracting the delay estimated along the directions A and C. In any case, the overall evolution of the delay is qualitatively similar suggesting the relevance of the differences in the position of the shape resonances along the directions A and C in the photoionization process. Differently from the previous case, the experimental data for the delay difference \( \Delta \tau_{B-C} \) (red square) do not show any significant variation of the delay as a function of the photon energy, as expected. The theoretical values (black circle) are in good agreement with the experimental data, indicating only a moderate linear increase of the delay. The absence of any remarkable variation of the delay as a function of the sidebands for these two directions can be attributed to the similar heights of the trapping potentials, as shown in Fig. 3b. In this condition, the evolution of the stereo Wigner time delays (blue triangles) is close to the experimental one.
We have demonstrated that the anisotropic molecular landscape affects the stereo-photoemission time delays. In particular, different heights of the trapping potentials introduce different delays in the emission of the photoelectron wave packet into the continuum. Our results indicate the importance of coincidence spectroscopy to disentangle the information on the photoemission process from different electronic states and for different molecular orientations. Extension of this approach would be beneficial also for larger and more complex molecular systems.

**Methods**

**Experimental setup.** The experiment was performed using a 10 kHz laser Ti:sapphire system providing 30-fs laser pulses centred at 800 nm with a pulse energy of 1 mJ. The input pulse first passes through a 1-mm-thick glass plate with a 3-mm-diameter hole at the centre splitting the beam into two parts (annular and central part), which are spatially separated and temporally delayed. Then, the input beam is focused by a 25-cm-focal-length parabolic mirror into a high-harmonic gas cell filled with argon (Ar) or krypton (Kr) to generate XUV photons (20–46 eV) consisting of odd multiples of the input pulse frequency.

In our work, the XUV photons were generated by the annular beam. By using an iris before the gas cell and blocking the annular beam, we ensure that the central beam, after focusing it into the gas cell, is not contributing to the XUV emission. After the gas cell, another 1-mm-thick glass plate, centred with respect to the first plate, is placed to synchronise the XUV and IR probe pulses. The delay between XUV and IR probe pulse is varied precisely by tilting the second, drilled plate. The IR probe pulse is part of the input beam which is going through the hole of the first plate and glass of the second one. The delay between XUV and IR probe pulse is varied precisely by tilting the second, drilled plate. For the XUV-only measurements, an aluminium filter is introduced into the beam propagation direction after the high-order harmonic generation cell in order to block the co-propagating IR pulse. Then, the XUV and probe pulses are refocused by a toroidal mirror into the interaction region inside a 3D momentum imaging detector.
spectrometer leading to dissociative photoionisation of CF$_4$ at an ion count rate of about 0.1 per XUV pulse. The resulting ions and electrons are guided using a homogeneous electric field (E) $\approx 313$ V/m and a weak magnetic field (B) $\approx 9.4$ G towards time- and position-sensitive detectors located at the opposite ends of the spectrometer.

**Theoretical methods.** In brief, theoretical RABBITT spectra have been obtained by solving the time-dependent Schrödinger equation (TDSE) within the static-exchange approximation [13,14]. In this method, the time-dependent wave function is expanded in a basis set of N-electron stationary wave functions, built from anti-symmetrized products of an (N−1) electron-wave function for the bound electrons and a one-electron continuum wave function for the electron ejected into the continuum. The (N−1) electron wave functions are built from B-spline representations of the lowest Kohn-Sham (KS) orbitals resulting from the diagonalization of the KS hamiltonian of density functional theory, excluding the orbital from which the electron is ejected to the continuum, and the one-electron continuum wave functions are obtained from an inverse iterative procedure in the former KS orbital basis for each photoelectron energy. All dipole matrix elements describing the transitions between all bound and continuum states as well as between continuum states have been included in the solution of the TDSE, which is essential to describe the bound-continuum and continuum–continuum transitions leading to the RABBITT spectra. We have restricted all simulations to the equilibrium geometry (fixed-nuclei approximation). More details can be found in the Supplementary Information.

**Data availability**

The data that support the findings of this study are available on reasonable request from the corresponding author G.S.(giuseppe.sansone@physik.uni-freiburg.de). Requests for data will be processed within 1 week. The data are not publicly available due to further analysis on the findings conducted by the authors of this manuscript.

**Code availability**

Analysis codes used in this study are available on reasonable request from the corresponding author G.S.(giuseppe.sansone@physik.uni-freiburg.de). Requests for codes will be processed within one week.

Received: 14 October 2021; Accepted: 4 February 2022; Published online: 10 March 2022

**References**

1. Klein, A. et al. Directly probing anisotropy in atom-molecule collisions through quantum scattering resonances. Nat. Phys. 13, 35–38 (2017).
2. Ascenzi, D. et al. Stereodynamical effects by anisotropic intermolecular forces. Front. Chem. 7, 390 (2019).
3. Jackson, J. D. Classical Electrodynamics. 3rd edn (Wiley, New York, NY, 1999).
4. Kaptyn, H. et al. Harnessing attosecond science in the quest for coherent X-rays. Science 317, 775–778 (2007).
5. Corkum, P. B. & Ivanov, F. Attosecond science. Nat. Phys. 3, 381–387 (2007).
6. Krausz, F. & Ivanov, M. Attosecond physics. Rev. Mod. Phys. 81, 163–234 (2009).
7. Nisoli, M. et al. Attosecond electron dynamics in molecules. Chem. Rev. 117, 10760–10825 (2017).
8. Paul, P. M. et al. Observation of a train of attosecond pulses from high harmonic generation. Science 292, 1689 (2001).
9. Schultz, M. et al. Delay in photoemission. Science 328, 1658 (2010).
10. Sansone, G., Pfeifer, T., Smeonić, K. & Kuleff, A. I. Electron correlation in real time. ChemPhysChem 13, 661–680 (2012).
11. Isinger, M. et al. Photoionization in the time and frequency domain. Science 356, 889–893 (2017).
12. Cattaneo, L. et al. Attosecond coupled electron and nuclear dynamics in dissociative ionization of H$_2$. Nat. Phys. 14, 733–738 (2018).
13. Huppert, M. et al. Attosecond delays in molecular photoionization. Phys. Rev. Lett. 117, 093001 (2016).
14. Haessler, S. et al. Phase-resolved attosecond near-threshold photoionization of molecular nitrogen. Phys. Rev. A 80, 014405 (2009).
15. Nandi, S. et al. Attosecond timing of electron emission from a molecular shape resonance. Sci. Adv. 6, eaab7762 (2020).
16. Vos, J. et al. Orientation-dependent stereo Wigner time delay and electron localization in a small molecule. Science 360, 1326–1330 (2018).
17. Biswas, S. et al. Probing molecular environment through photoemission delays. Nat. Phys. 16, 778–783 (2020).
18. Wigner, E. P. Lower limit for the energy derivative of the scattering phase shift. Phys. Rev. 98, 145–147 (1955).
19. Pazourek, R., Nagele, S. & Burdgjerfer, J. Attosecond chronoscopy of photoemission. Rev. Mod. Phys. 87, 765–802 (2015).
20. Dahlstrom, J. M., L’Héulier, A. & Maquet, A. Introduction to attosecond delays in photoionization. J. Phys. B: At. Mol. Opt. 45, 183001 (2012).
21. Heuser, S. et al. Angular dependence of photoemission time delay in helium. Phys. Rev. A 94, 063409 (2016).
22. Baykusheva, D. & Wörner, H. J. Theory of attosecond delays in molecular photoionization. J. Chem. Phys. 146, 124306 (2017).
23. Dorner, R. et al. Cold Target Recoil Ion Momentum Spectroscopy: a ‘momentum microscope’ to view atomic collision dynamics. Phys. Rep. 330, 95–192 (2000).
24. Lebec, M., Houyer, J. C. & Dowek, D. Ion-electron velocity vector correlations in dissociative photoionization of simple molecules using electrostatic lenses. Rev. Sci. Instr. 73, 1866–1874 (2002).
25. Ullrich, J. et al. Recoil-ion and electron momentum spectroscopy: reaction-microscopes. Rep. Prog. Phys. 66, 1463–1545 (2003).
26. Ahmadl, H. et al. Collinear setup for delay control in two-color attosecond measurements. J. Phys.-Photonics 2, 024006 (2020).
27. Creasey, J. C. et al. Fragmentation of Valence Electronic States of CF$_4$ and SF$_6$. Studied by Threshold Photoelectron Photon Coincidence Spectroscopy. Chem. Phys. 174, 441–452 (1993).
28. Brehm, B. et al. Kinetic energy release in ion fragmentation: N$_2$, O$_2$, COS$^+$ and CF$_4$ decays. Int. J. Mass Spectr. Ion Phys. 13, 251–260 (1974).
29. Zhang, W., Cooper, G., Ikuki, T. & Brion, C. E. Excitation and ionization of free molecules. I. Absolute oscillator strengths for the photoabsorption (12–740 eV) and the ionic photofragmentation (15–80 eV) of CF$_4$, Chem. Phys. 137, 391–405 (1989).
30. Larsen, K. A. et al. Resonance signatures in the body-frame valence photoionization of CF$_4$, Phys. Chem. Phys. Chem. 20, 21075–21084 (2018).
31. Pleija, E. et al. Real-time imaging of ultrafast charge dynamics in tetrafuranorhodamine from attosecond pump-probe photoelectron spectroscopy. Chem. Eur. J. 24, 12061–12070 (2018).
32. Chacon, A., Lein, M. & Ruiz, C. Asymmetry of Wigner’s time delay in a small molecule. Phys. Rev. A 89, 053427 (2014).
33. Chacón, A. & Ruiz, C. Attosecond delay in the molecular photoionization of asymmetric molecules. Opt. Express 26, 4548–4562 (2018).

**Acknowledgements**

This work was performed under the European COST Action CA18222 AttocChem and funded by the Ministerio Español de Ciencia e Innovación (MICINN) through the projects PID2019-105488RA-I00, the Severo Ochoa Programme for Centres of Excellence in R&D (SEV-2016-0686) and the Maria de Maeztu Programme for Units of Excellence in R&D (CEX2018-000805-M), and the Comunidad de Madrid through the project FULMATE. All calculations were performed at the Mare Nostrum Supercomputer Centre of the Red Española de Supercomputación (RES) and the Centro de Computación Científica at the Universidad Autónoma de Madrid (CCC-UAM). Financial support by the Italian Ministry of Research (Project FIRB No. RBID08CRXXK) is gratefully acknowledged. This project has received also funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no. 641789 MEDEA. G.S. acknowledges support by the Deutsche Forschungsgemeinschaft (DFG) INST 39/1079 (High-Repetition-Rate Attosecond Source to Coincidence Spectroscopy), INST 39/1078 (High-Energy Attosecond Source)). Funding from the Bundesministerium för Bildung und Forschung (Project 05K19VF1) is gratefully acknowledged.

**Author contributions**

H.A., E.P., A.P., F.M. and G.S. conceived the present study. H.A., M.M. and G.S. conducted the experiment. H.A. analysed the experimental data. C.D.S., T.P. and R.M. contributed to the design and construction of the Reaction Microscope used in the experiment. F.F. and L.P. contributed to the design and implementation of the XUV spectrometer. E.P., A.P. and P.D. have developed the codes to simulate the RABBITT experiment. E.P. performed the theoretical calculations under the guidance of A.P., P.D. and F.M. contributed the theoretical research. H.A., E.P., A.P., F.M. and G.S. drafted the manuscript. H.A. acknowledges useful discussion with Maurizio Reduzzi and Arne Sønstebø. All authors discussed the experimental results and the final version of the manuscript.

**Funding**

Open Access funding enabled and organized by Project DEAL.

**Competing interests**

The authors declare no competing interests.
