High-resolution, terahertz-driven atom probe tomography

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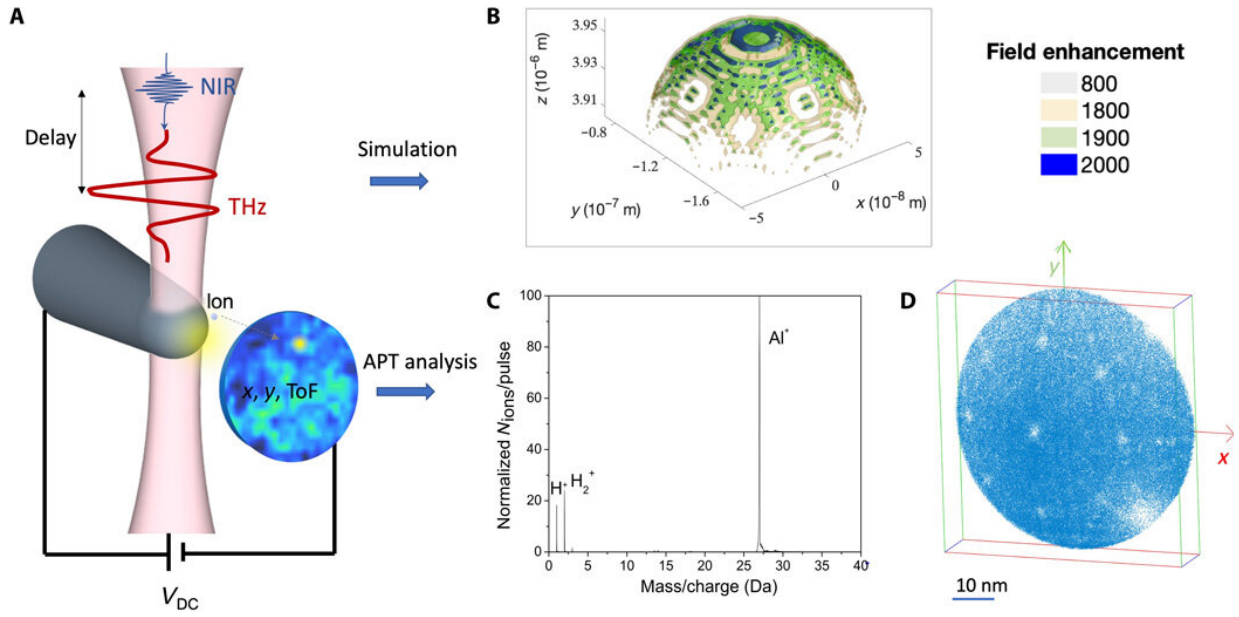


Ion field evaporation triggered by terahertz in a tomographic atom probe. (A) Ultrashort terahertz (red) pulses are focused onto a metallic nanotip inside a high vacuum chamber. The high voltage applied to the metallic tip translates into an intense electric field at the specimen apex. The evaporated ions are projected toward a time-sensitive detector and a PSD located at 10 cm from the nanotip. A NIR pulse (blue) can be combined to the terahertz pulse with a variable delay to probe the interaction mechanisms. ToF, time of flight. (B) Isosurface plots of the three-dimensional (3D) field distributions calculated numerically for the excitation frequency of 2 THz and for different values of the field enhancement factor. (C) Mass spectrum as measured from a terahertz-assisted atom probe analysis of a pure aluminum specimen. The datasets consist of around 105 ions collected at a bias voltage VDC = 8.7 kV and an evaporation rate of 0.01 ion per

pulse at T = 50 K. (D) 3D reconstruction of a pure aluminum specimen. Credit: Science Advances, doi: 10.1126/sciadv.abd7259

Materials scientists must be able to exert ultrafast control of matter using a strong electromagnetic field on the atomic scale to understand the ionization dynamics and excitations in solids. Researchers can couple picosecond duration terahertz pulses to metallic nanostructures to generate extremely localized and intense electric fields. In a new report now on *Science Advances*, Angela Vella and a research team at the CNRS and the University Institute of France controlled field ion emission across from metallic nanotips. The terahertz near-field induced an athermal ultrafast evaporation of surface atoms as ions on the subpicosecond timescale with the tip acting as a field amplifier. The ultrafast terahertz-ion interaction offered unprecedented control on ultrafast free-ion pulses to image, analyze and manipulate matter at atomic scales. In this work, Vella et al. demonstrated terahertz atom probe microscopy as a new platform for microscopy with atomic and chemical resolution.

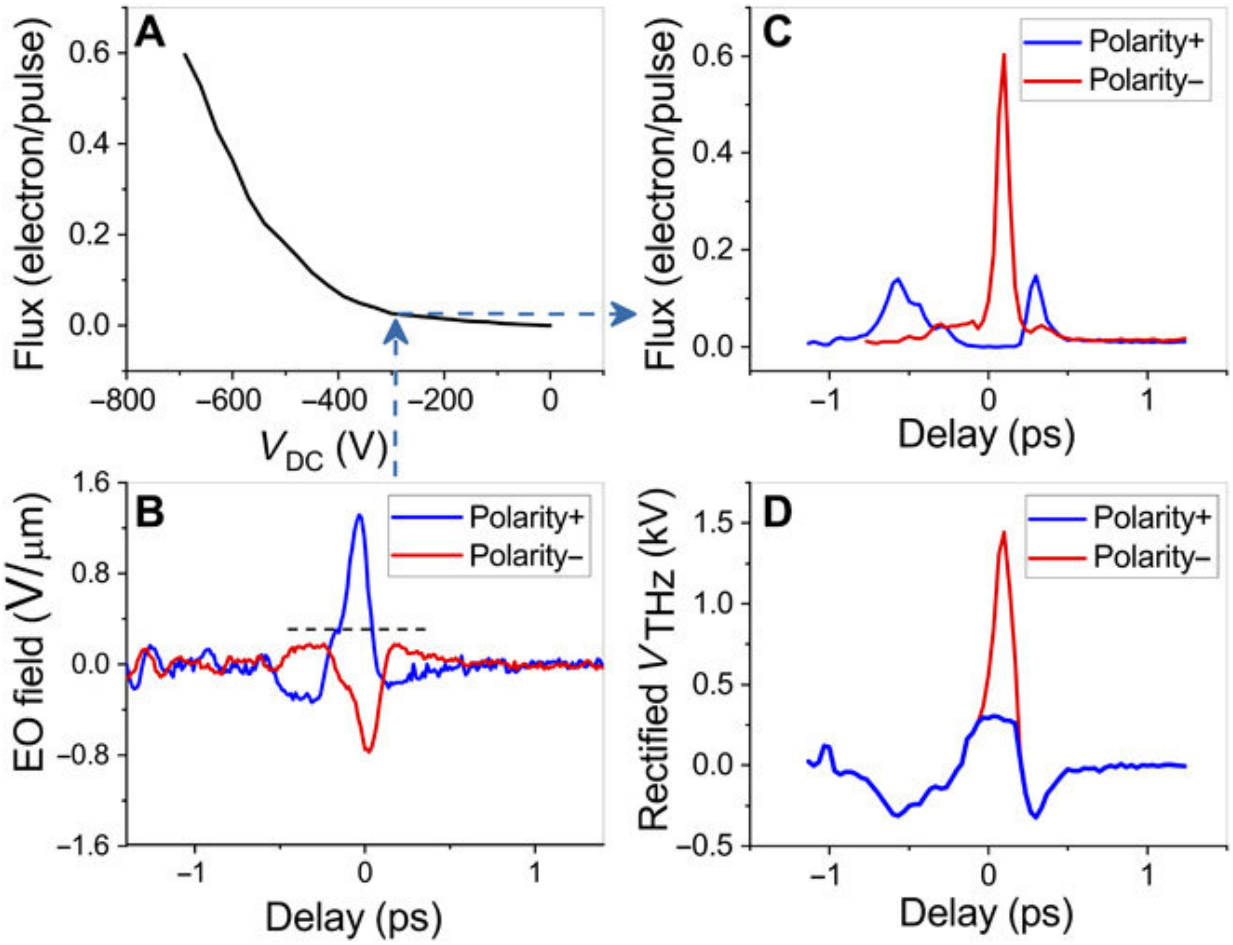
The basics of atom probe tomography

The ability to couple electromagnetic fields to solid-state nanostructures to control the basic properties of matter at the nanoscale is increasingly attracting interest for a variety of applications including chemistry, catalysis, gas-sensing and ultrafast electron microscopy and imaging. The basic principle of atom probe tomography (APT) involves the field emission of positive ions from a sharp tip as an imaging technique based on controlled field evaporation of atoms from a nanometric needle-shaped sample under a strong electric field. The technique was attractive due to its capability to provide sub-nanometer spatial resolution in the three dimensions of space, with high chemical sensitivity across whole

periodic elements and their isotopes.

Laser-assisted atom probe tomography

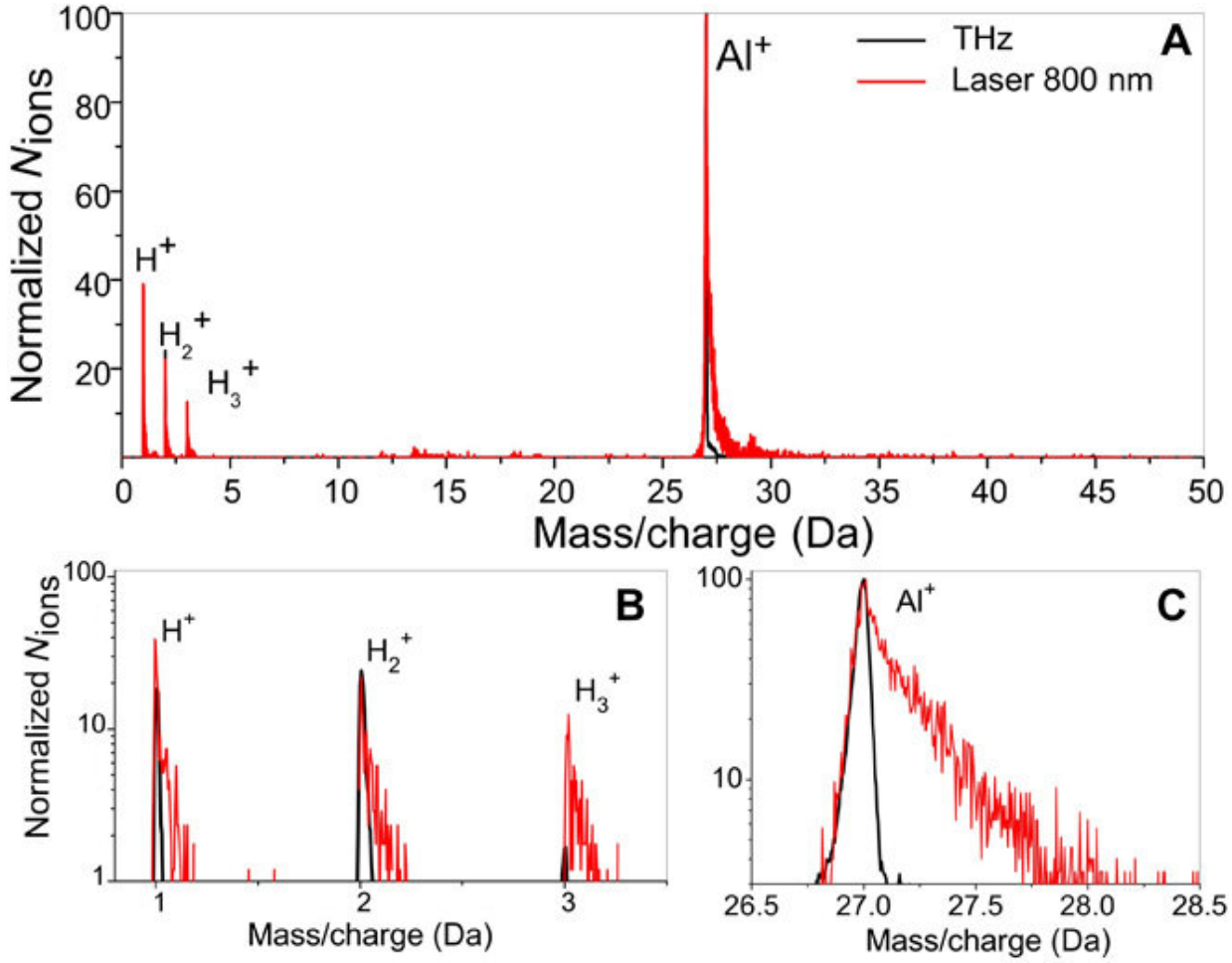
At first, the atom probe tomography method was restricted to conductive materials due to the use of high-voltage pulses to trigger ion evaporation. The development of the laser-assisted atom probe tomography (La-APT) allowed the analysis of semiconducting and dielectric materials. During La-APT, the scientists evaporated the sample atom by atom via the combined actions of a high DC field and an ultrashort laser pulse. Due to existing limits, the potential for terahertz-based APT to perform high-resolution imaging was very promising although essential to acquire deeper awareness of the underlying physics of terahertz-pulse-matter interactions. The researchers showed the enhancement of terahertz fields in positively biased nanotips to trigger the emission of positively charged ions from the nanostructure surface to present a high chemical and space resolution terahertz-assisted APT instrument.



Rectified terahertz voltage at the tip apex. (A) Current-voltage characteristic of electron emission obtained from an aluminum tip (apex radius of 70 nm) under laser illumination at INIR = 2.3 GW/cm2. (B) Two terahertz transients with inverted field directions (polarity) measured by EO sampling outside the atom probe chamber. (C) Photocurrent modulation for the terahertz waveforms corresponding to the EO traces of (B) at VDC = −300 V and INIR = 2.3 GW/cm2. (D) Rectified terahertz pulse reconstructed from (A) and (C). Credit: Science Advances, doi: 10.1126/sciadv.abd7259

The experiments: near-terahertz field characterization and calibration

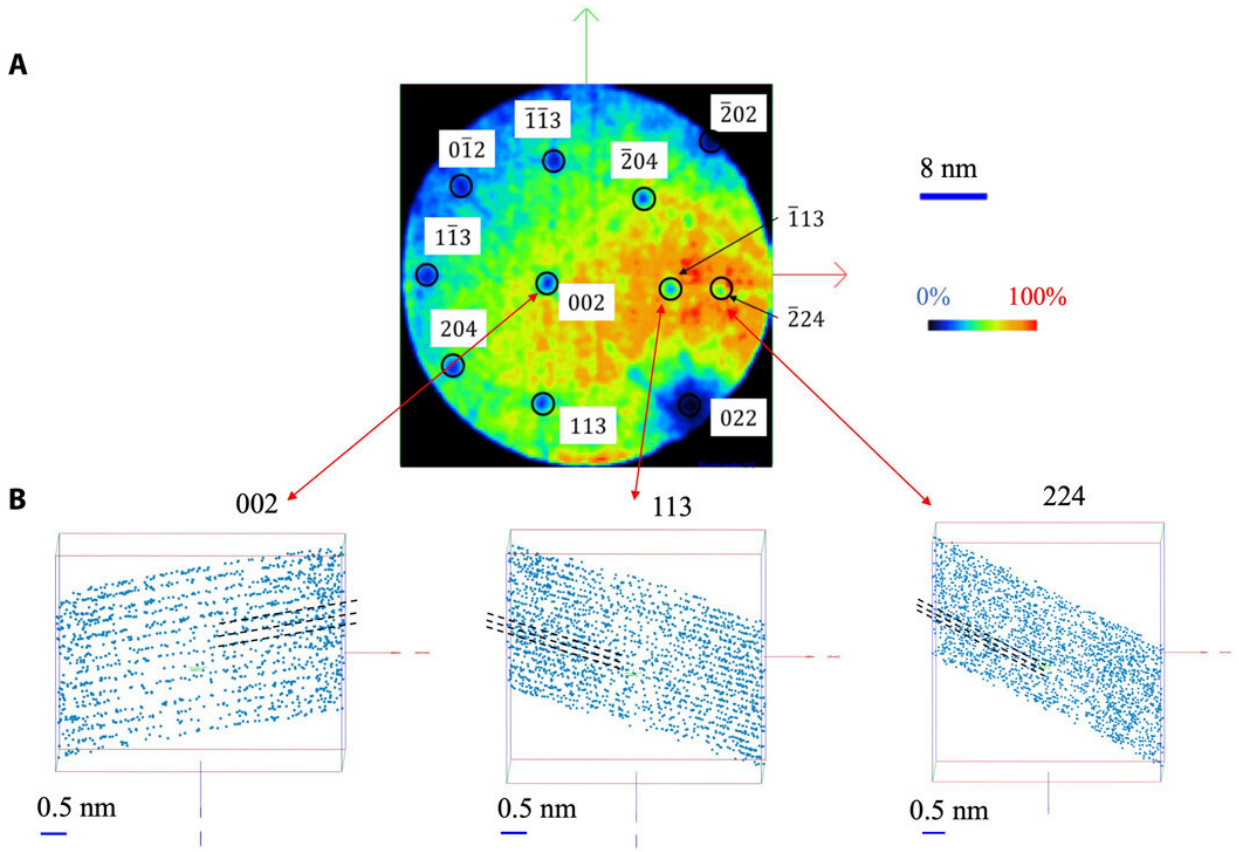
During the experiments, the team focused on a single-cycle strong terahertz field generated from two-color air plasma on an aluminum tip-biased at several kilovolts. They combined a near-infrared (NIR) pulse with the terahertz pulse and colinearly focused it on an aluminum tip biased at several kilovolts. Using time-of-flight measurements, they retrieved the mass/charge ratio, and from the impact position on the detector system they reconstructed the evaporated volume using a reverse projection law. The researchers noted the temporal traces of the generated terahertz pulses for two inverted field directions or polarities measured by electro-optic sampling outside the atom probe chamber. Vella et al. measured the terahertz field at the apex of the sample using this field to drive electron emission from the negatively biased aluminum tip under NIR illumination to show how the tip functioned as an ultrafast rectifying diode. The team noted the same deviation from the incident terahertz pulse due to the antenna response to the tip. The results indicated the amplitude of the terahertz pulse to be about 2000 times higher than the incident terahertz field. To compare the field enhancement factor, the team used finite-difference time-domain commercial software Lumerical to take the tip geometry into account. The team increased the amplitude of the terahertz field to its maximum of 5.5 V/nm to perform ion field emission using terahertz pulses. They then experimentally checked this value of the terahertz near-field using electron energy filtering.



Analyzing aluminum nanotip in terahertz-assisted APT. (A) Mass spectra as measured from a terahertz-assisted atom probe analysis (black) and a NIR laser–assisted atom probe analysis (red) of a pure aluminum specimen. The datasets consist of around 105 ions collected at a bias voltage Ubias = 9 kV, NIR laser intensity INIR = 2.3 GW/cm2, and an evaporation rate of 0.01 ion per pulse at T = 50 K. (B) Zoom on H+, H+2, and H+3 mass peaks using semilog scale. (C) Zoom on Al+ mass peak using semilog scale. Credit: Science Advances, doi: 10.1126/sciadv.abd7259

Studying the aluminum tip in terahertz-assisted APT and its dual-frequency excitation

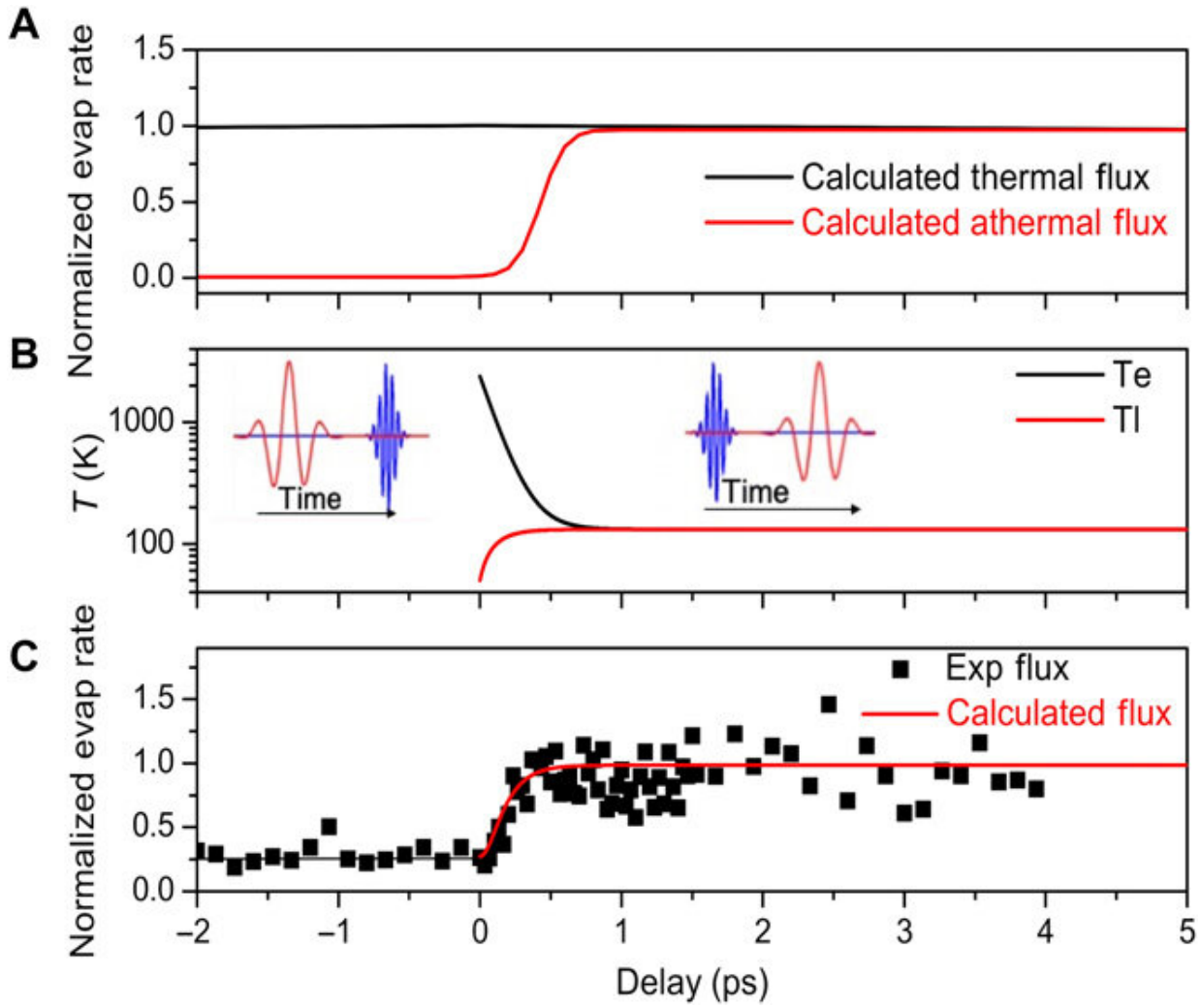
To perform ion field evaporation using terahertz pulses, Vella et al. positively biased the aluminum tip at 9 kV and set the terahertz pulse with positive polarity to its maximum amplitude of 5.5 V/μm corresponding to a near field of 10.5 V/nm. The scientists presented the mass spectra obtained at the same bias using terahertz and NIR laser pulses. The 3-D reconstruction of the evaporated volume showed well-resolved atomic planes for three crystallographic directions as discerned using NIR analysis. The team obtained the image reconstruction of APT using field erosion and calculated the spatial resolution of 3-D images using the Fourier transform approach. Using dual-frequency excitation of the aluminum tip, they recorded the evaporation rate as a function of the delay between the NIR and terahertz laser pulses.



Analyzing aluminum nanotip in terahertz-assisted APT. (A) Spatial distribution

of Al+ ions on the detector for the terahertz-assisted atom probe analysis. (B) 3D images resulting from the terahertz-assisted atom probe analysis showing Al atomic planes along the , , and crystallographic directions; black dotted lines are guides to the eye. Credit: Science Advances, doi: 10.1126/sciadv.abd7259

In situations where the terahertz pulse preceded the NIR pulse, the evaporation rate was deemed stable and its value equal to that obtained only by terahertz pulses and therefore unaffected by NIR laser excitation. Temporal overlap between the NIR and the THz pulse maintained unchanged evaporation rates. When the NIR pulses preceded the terahertz pulse, the evaporation rate increased up to its maximum in less than 0.5 picoseconds. The underlying physical evaporation mechanism contributed to the chemical and space resolution of the atom probe assisted by terahertz pulses compared to NIR pulses. The results of the dual-frequency excitation in the AI nanotip contributed experimental proof of the athermal ion evaporation by terahertz pulses.



Following NIR laser heating in the nanotip apex via terahertz field emission. (A) Normalized evaporation rate calculated considering a thermal (black) or athermal (red) evaporation mechanism for the terahertz pulse and a thermal mechanism for the NIR laser pulse as a function of the delay between these two pulses as sketched in Fig. 1A. (B) Electronic and lattice temperatures computed in a two-temperature model for parameters of the measurement in (C). (C) Transient terahertz field evaporation (black squares) as a function of the delay between the NIR and the terahertz pulses. The datasets consist of around 103 ions per step collected at VDC = 8.9 kV, NIR laser intensity INIR = 0.5 GW/cm2, and an evaporation rate of 0.01 ion per pulse using only terahertz pulses and 0.001 ion per pulse using only NIR laser pulses, at T = 50 K. Credit: Science Advances, doi: 10.1126/sciadv.abd7259

Outlook

In this way, Angela Vella and colleagues showed how ultrafast, nonthermal field evaporation of surface atoms as ions by tip-enhanced single-cycle terahertz pulses paved the path for material analysis with spatial and chemical resolutions. The method can also facilitate time-resolved chemistry in high electric fields to open new ways in field-induced chemistry. The narrow energy spread of the field-evaporated ions by single-cycle terahertz pulses will open the way to use charged particle beams for imaging, analysis and matter modification from the microscale to the nanoscale.

More information: Vella A. et al. High-resolution terahertz-driven atom probe tomography, *Science Advances*, 10.1126/sciadv.abd7259

Sadeghian B. et al. Ultralow-voltage field-ionization discharge on whiskered silicon nanowires for gas-sensing applications. *Nature Materials*, doi.org/10.1038/nmat2944

Blavette D. et al. An atom probe for three-dimensional tomography. *Nature*, doi.org/10.1038/363432a0