Research Highlight #200

Alexandre Dazzi, Ph.D.

Tenure Professor, Université Paris-Saclay, Orsay, France

Professor Alexandre Dazzi has always possessed a desire to discover and a fascination with physics, a combination that carried him through a doctorate in the field of optics, a postdoc in a chemistry lab, and the invention and continued development of photothermal AFM-IR.

Combining Theory and Experiments

> "I've always been sensitive to the materials aspect, solid state physics. And I was always excited about lasers and light. So, I focus on the interaction between light and matter."

With a double diploma in physics and materials engineering, Dazzi developed a foundation in using theoretical concepts to inform practical applications. His doctoral work focused on the use of perovskite crystals for optical computing, and the goal of his experimental setup was to mix laser waves in the crystals to create an optical amplifier. To inform his experimental setup, Dazzi used Maxwell's equation to model the propagation of the waves and wrote a program to predict the mode inside of the waveguide.

> "I'm not a pure theoretician. I like to use the theory and apply it to my experiments."

For his postdoctoral work, Dazzi ended up in a chemistry lab after the company he was initially supposed to work for closed. This twist of fate led him to become more familiar with chemistry and helped him to become confident in his expertise as a physicist and engineer. This postdoctoral work involved designing and implementing a setup for plasmonic detection, where there is a plasmon shift when a molecule adsorbs onto an electrode irradiated by a laser.

After his postdoctoral work was completed, Dazzi became an Associate Professor at the Institut de Chimie Physique (ICP) of the Université Paris-Saclay. The ICP was searching for someone to design a high-resolution infrared (IR) microscope at their synchrotron facility. At the time, scanning near-field optical microscopy (SNOM) was the only technique of that kind available, so SNOM was what Dazzi was hired to improve. After four years of work with a colleague, they had created a SNOM that was, as he puts it, "disappointing." More importantly, the SNOM theory he developed showed that the

ABOUT THE RESEARCHER

Alexandre Dazzi is a tenure professor at the Université Paris-Saclay in Orsay, France. He and his research group are a part of the Institut de Chimie Physique, which is a joint research unit of the French National Center for Scientific Research (CNRS) and Paris-Saclay University. Within his laboratory, he has four Bruker nanoIR™ instruments.

Awards:

2010: nanoIR made the R&D 100 Award list, with Dazzi as a developer.

2011: nanoIR was named Microscopy Today's Innovation Award winner, with Dazzi as one of the developers.

2014: Dazzi was awarded the prestigious Ernst Abbe Memorial Award by the New York Microscopical Society for his pioneering work in the field of nanoscale IR spectroscopy.

2023: Dazzi became the Materials Sciences Laureate of the Raimond Castaing Grand Prize from the Sfµ (Société Française des Microscopies) for his remarkable contributions to microscopy.

Website: Institute of Physical Chemistry - Institut de Chimie Physique (universite-paris-saclay.fr)

IR spectra were not similar to Fourier-transform infrared spectroscopy (FTIR) and were more a mix of absorbance and reflectance. So regardless of how much the technique or microscope were improved, the theory said that the absorbance cannot be isolated and therefore the spectra will never be comparable to FTIR. But given his love for problem-solving and discovery, this challenge was just another opportunity for Dazzi.

Inventing Photothermal AFM-IR

When the attempt to create a high-quality SNOM was relatively unsuccessful, Dazzi kept searching for a way to perform IR microscopy locally with high precision and with a tool able to output IR spectra directly comparable to FTIR. During that time, another scientist at the lab developed a sub-micron IR spectroscopy and imaging (optical photothermal infrared microscopy, O-PTIR) system, where an IR laser was used to irradiate the sample, and the deflection of visible probe laser caused by sample heating was measured and analyzed.

Dazzi, inspired, added an AFM to directly detect the thermal expansion instead of using laser deflection angle.

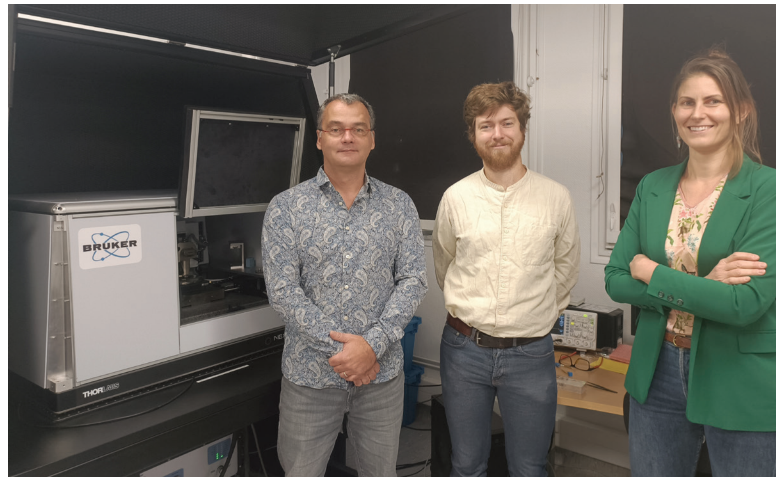
> "Let's buy an AFM and we will detect the expansion. AFM-IR was born, just by this idea."

In 2005, Dazzi published a paper on his AFM-IR system, and subsequently received a call from an American start-up asking if he would be interested in working towards a patent. They were awarded this U.S. patent in 2007, and the company Anasys Instruments was formed. Anasys went on to release the first nanoIR system in 2010; this and its follow-up systems led to the acquisition of Anasys by Bruker in 2018.

The academic community was eager to adopt this new capability. There was now the possibility to localize easy-to-understand FTIR-like spectra in which (unlike optical near-field techniques) the imaginary part of the refractive index could be isolated from the real part. Dazzi's goal of building a tool to make IR spectroscopy accessible at the nanoscale had become reality.

What is AFM-IR?

AFM-IR is infrared spectroscopy that is conducted in an AFM. Results can be directly compared with more ubiquitous IR techniques such as FTIR. In AFM-IR, light absorption is indirectly measured by way of cantilever deflection. When the material being irradiated by an IR laser absorbs the incident energy, heat is generated within that irradiated volume. Heat generation induces a very quick volume change in the sample, as the laser is pulsed, which is measured through deflection of the AFM cantilever that is mechanically coupled to the surface. The way the light is absorbed (seen via output spectra) can be used to determine local chemical information about the sample at a resolution limited by the size of the AFM tip.



Dazzi and his research team with their beta-model Dimension Icon-IR™. From left: Alexandre Dazzi, Jeremie Mathurin (CNRS Researcher), and Ariane Deniset-Besseau (Associate Professor).

Advancing and Using AFM-IR

Since the first 2010 nanoIR system was released, Dazzi has been involved in a number of important advances in the technology:

- Top-down illumination (replacing transmission) to eliminate the thin-sample limitation*
- Resonance-enhanced AFM-IR, which uses a quantum-cascade laser (QCL) to take advantage of cantilever resonance to improve signal and greatly increase resolution (from 50 nm to just a few nanometers) – initially published by Professor Belkin from the University of Texas at Austin*
- Tapping mode compatibility to allow for measurements on fragile samples*
- Surface sensitive mode (newly patented) to probe only the surface of a sample and not the bulk

Alexandre Dazzi (materials sciences) and Alain Brisson (life sciences) are awarded the Castaing Prize by Société Française des Microscopies leaders.

These and other improvements to AFM-IR will continue to increase measurement capabilities and expand relevant application spaces, and Dazzi is eager to see where his research and that of his colleagues will take the technology in the future.

Looking Back

Reflecting on his career thus far, he has no regrets. Due to the whole of his experiences, including the unexpected ones, he is now able to focus on a technique he loves in a position that fascinates him. He does add, however, that if given the chance to go back and start over, he might have become a mathematician. His current work is full of applied math, but he also has an ever-growing appreciation for the beauty of pure mathematics.

> "I'm like a kid with science. I'm always excited by what I'm looking at.… If you have the spirit of the kid, I think everything is interesting."

Since the commercialization of AFM-IR, Dazzi has continually received collaboration requests from other researchers. This has resulted in a publication history that showcases a wide variety of samples and the use of photothermal AFM-IR for diverse purposes. When asked about his favorite project or sample from this collection, he said the cultural heritage and astrochemistry samples really stand out. Overall, what he enjoys most is the journey of establishing a successful sample preparation and experimental setup, then being able to answer interesting research questions.

> "It is quite fun to study samples from a famous painter and from the dust of stars. I'm not an expert in these types of samples. But what is very fun is to participate, to answer a question."

NOTE: *The lead researcher on the indicated nanoIR commercial developments was Dr. Craig Prater.

Select publications examining samples using AFM-IR:

1. Yabuta, H., Cody, G. D., Engrand, C., et al. (2023). Macromolecular organic matter in samples of the asteroid (162173) Ryugu. *Science, 379*(6634). https://doi.org/10.1126/science.abn9057
2. Dartois, E., Kebukawa, Y., Yabuta, H., et al. (2023). Chemical composition of carbonaceous asteroid Ryugu from synchrotron spectroscopy in the mid- to far-infrared of Hayabusa2-returned samples. *Astronomy & Astrophysics, 671*, A2. https://doi.org/10.1051/0004-6361/202244702
3. Reynaud, C., Thoury, M., Dazzi, A., et al. (2020). In-place molecular preservation of cellulose in 5,000-year-old archaeological textiles. *Proceedings of the National Academy of Sciences, 117*(33), 19670–19676. https://doi.org/10.1073/pnas.2004139117

Select publications on AFM-IR technology:

4. Mathurin, J., Deniset-Besseau, A., Bazin, D., et al. (2022). Photothermal AFM-IR spectroscopy and imaging: Status, challenges, and trends. *Journal of Applied Physics, 131*(1), 010901. https://doi.org/10.1063/5.0063902
5. Kurouski, D., Dazzi, A., Zenobi, R., & Centrone, A. (2020). Infrared and Raman chemical imaging and spectroscopy at the nanoscale. *Chemical Society Reviews, 49*(11), 3315–3347. https://doi.org/10.1039/C8CS00916C
6. Dazzi, A., & Prater, C. B. (2017). AFM-IR: Technology and Applications in Nanoscale Infrared Spectroscopy and Chemical Imaging. *Chemical Reviews*, *117*(7), 5146–5173. https://doi.org/10.1021/acs.chemrev.6b00448
7. Dazzi, A., Glotin, F., & Carminati, R. (2010). Theory of infrared nanospectroscopy by photothermal induced resonance. *Journal of Applied Physics, 107*(12), 124519. https://doi.org/10.1063/1.3429214

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