Combining two-dimensional infrared spectroscopy with atomic force microscopy

Atomic force microscopy (AFM) is coupled with time-domain two-dimensional infrared (2DIR) spectroscopy to develop AFM-2DIR nanospectroscopy, which combines the spatial precision of AFM with the rich spectroscopic information provided by 2DIR spectroscopy. Application of this method reveals the anharmonicity of a carbonyl vibrational mode and the possible energy transfer pathways of hyperbolic phonon polaritons in isotope-rich hexagonal boron nitride.

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The question

Advances in infrared (IR) spectroscopy have focused on improving spatial resolution and expanding the spectroscopic information that can be obtained. When exposed to light, the sharp metal-coated tip of an atomic force microscope (AFM) localizes and enhances the optical field underneath the tip, making the spatial resolution independent of the incident wavelength. Exploiting the benefits of tip enhancement, atomic force microscopy-based instruments for super-resolution IR imaging have been created, including scattering-type scanning near-field optical microscopy (s-SNOM)[1] with optical detection and AFM-IR microscopy with photothermal mechanical detection[2]. Meanwhile, the development of time-domain two-dimensional IR (2DIR) techniques, which involves the sequential emission of precisely timed femtosecond IR pulses, has provided intricate spectroscopic information of molecular interactions, such as the anharmonicities and couplings of vibrational modes of molecules, and the energy transfer processes of polaritons in hyperbolic materials[3]. However, the spatial resolution of 2DIR is usually restricted by Abbe's diffraction limit. Merging the tip-enhancement of AFM with 2DIR could enable Abbe's diffraction limit to be surpassed, allowing for nanoscale spatial resolution, while also offering the rich spectroscopic information of 2DIR spectroscopy.

The solution

We constructed an AFM-2DIR apparatus (Fig. 1a) that consists of three main components: a home-built interferometer assembly for generating a femtosecond IR pulse sequence, an AFM with a metallic tip, and a photothermal signal extraction mechanism based on peak force infrared (PFIR) microscopy[4]. The collective absorption of the IR pulse sequence and subsequent non-radiative decay contribute to the photothermal signal. The timing between the first and the second pump pulses (t_1) and between the second and third (probe) pulses (t_2) are scanned during the measurement while recording the photothermal signal (S). The spectrogram $S(t_1, \omega_2)$ is obtained from fast Fourier transform (FFT) of $S(t_1, t_2)$ along the fast scan axis of t_2 (Fig. 1b). An additional FFT is performed along t_1 on $S(t_1, \omega_2)$ to obtain $S(\omega_1, \omega_2)$, the 2D-PFIR spectrum (where ω_1 and ω_2 are the frequency axes of the probe and pump, respectively, resolved from sequential FFTs).

Using our AFM-2DIR method, aided by finite element simulations of the tip-enhancement field, we investigated the anharmonicity of a carbonyl vibrational mode of azide functionalized poly(methyl methacrylate) (PMMA-N_3) and the possible energy transfer pathways of phonon polaritons in isotope-rich hexagonal boron nitride (h-^{10}BN) (ref. 5).

The 2D-PFIR spectrum of the carbonyl vibrational mode from a 50-nm thick PMMA-N_3 film shows ground-state depletion, excited-state absorption and successive overtone absorptions (Fig. 1c), as well as revealing the anharmonicity of the vibrational mode to be 19 cm^{-1}.

Application of AFM-2DIR to h-^{10}BN revealed the energy transfers between available IR resonances. We observed energy transfer pathways from hyperbolic phonon polariton modes to a phonon mode, as well as energy transfers between the polariton modes. Subsequently, we formulated a frequency domain relationship for energy transfers between hyperbolic phonon polaritons based on a constraint of spatial overlap of polariton waves.

Future directions

The AFM-2DIR approach developed here aims to bridge the gap between traditional 2DIR spectroscopy constrained by the diffraction limit and the AFM-IR technique, which is independent of incident wavelength. AFM-2DIR nanospectroscopy could facilitate studies of IR energy transfer and mode coupling in nanoscale heterogeneous materials and structures. Exploring the anharmonicity and energy transfer of vibrational modes is also useful for studying reactive compounds and intermediates within heterogeneous catalytic processes. This method has the potential to be used for diverse applications, ranging from the examination of spatial and spectral properties of the secondary structures of proteins to exploration of the energy transfer of polaritons in custom-tailored hyperbolic materials, even at cryogenic temperatures.

Nevertheless, although we have demonstrated the application of AFM-2DIR spectroscopy, there is room for improvement. Currently, data acquisition from the stacked interferometer is a time-consuming process. Overcoming this limitation would enable more efficient time-resolved studies.

By integrating a more intricate pulse sequence and employing the increasingly popular pulse-shaping technique used in 2DIR, it could be possible to increase the ability of AFM-2DIR nanospectoscopy to discern the timing of energy transfer processes. For investigating electronic states and energy transfers in photoactive materials, including photovoltaics, a comparable photothermal detection mechanism based on AFM could be applied to visible pulse sequences.

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EXPERT OPINION

"I appreciate the methodological advances presented in this work. The combination of AFM-based IR spectroscopy and time-domain two-dimensional IR spectroscopy — AFM-2DIR nanospectroscopy — is indeed notable progress in the field. This method has been demonstratively used to elucidate the anharmonicity of a carbonyl vibrational mode and the energy transfers of h-BN phonon polaritons." **Qing Dai, National Center for Nanoscience and Technology of China, Beijing, China.**

FIGURE

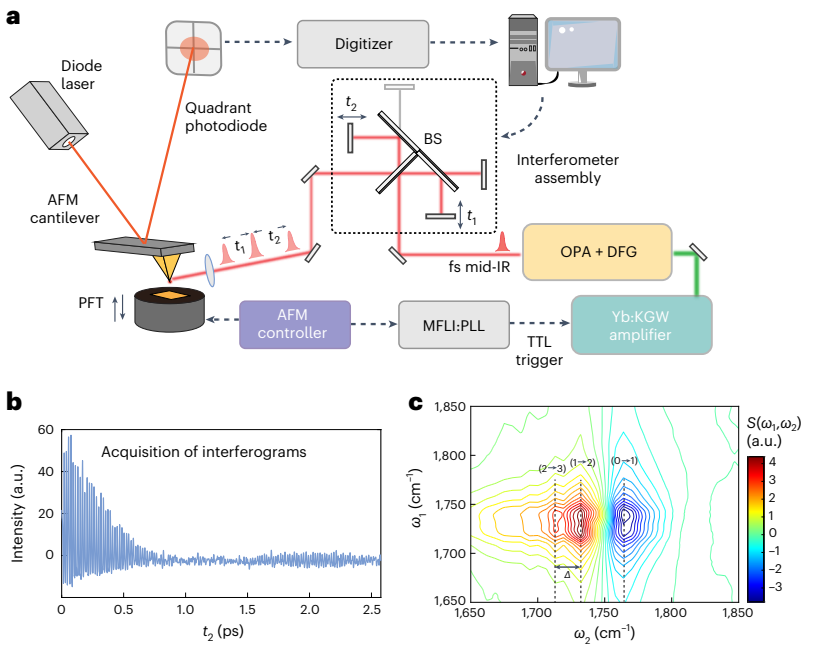

Fig. 1 | Experimental setup for AFM-2DIR spectroscopy and application to a carbonyl vibrational mode. a, The femtosecond laser is triggered by the peak force tapping (PFT) frequency of the AFM using a phase lock loop (PLL) to generate a transistor-to-transistor logic (TTL) waveform. Three IR pulses, created by interferometers and with time separations t_1 and t_2, are guided into the AFM tip–sample region. The highly localized light field induces photothermal expansions of the sample, which cause the AFM cantilever to oscillate. The cantilever vertical deflection waveform containing the photothermal signal is read out through a quadrant photodiode and sent to a digitizer together with the scanned timings to form a series of interferograms of photothermal signals. **b**, Example interferogram along the fast-scanning axis. **c**, Real part of the 2D-PFIR spectrum collected from a carbonyl vibrational mode showing ground state depletion, excited state absorption and successive overtones. The anharmonicity (Δ) of 19 cm^{-1} was estimated from the spacing between overtone absorptions. BS, beam splitter; DFG, difference frequency generation; MFLI, lock-in amplifier; OPA, optical parametric amplifier.

BEHIND THE PAPER

The work was encouraged by Gilbert C. Walker and Martin T. Zanni, both of whom had been postdoctoral fellows of Robin Hochstrasser — the pioneer of 2DIR spectroscopy. When I was a postdoctoral fellow at the University of Toronto in Gilbert C. Walker's group we often had discussions on how to combine scattering near-field microscopy with 2DIR spectroscopy. However, that near-field route had been shown to be difficult. Later, as a PI, my group developed PFIR — a type of photothermal AFM-IR with narrow-band IR lasers. At the Fall 2022 American Chemical Society Meeting in Chicago, I met with Martin T. Zanni, and we discussed the possibility and potential impact of combining photothermal AFM-IR with 2DIR with femtosecond laser pulses. After building several explorative apparatuses within a year, my PhD student, Q.X., and I were finally able to make the method work, and we now present our results here. **X.G.X.**

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FROM THE EDITOR

"This is a striking example of an innovative experimental approach, through which the combination of two established techniques provides a new capability useful for the exploration of the nanoscale." **Benjamin Heinrich, Senior Editor, *Nature Nanotechnology*.**