Dynamics via Attosecond Four-Wave Mixing

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Abstract Attosecond four-wave mixing spectroscopy is a relatively new technique for studying ultrafast dynamics of highly excited states with exquisite temporal precision and spectral resolution. The attosecond four-wave mixing technique, as described in this paper, uses non-collinear beam geometries of one attosecond pulse together with two optical pulses to obtain background-free, spatially isolated emission signals in the extreme ultraviolet range that directly resolve coherent dynamics in the time domain. This method is advantageous by avoiding the strong spectral modulations that often complicate the interpretation of collinear attosecond transient absorption studies while also enabling greater control over the spatial and temporal characteristics of each light-matter interaction used to probe the ultrafast processes. This paper describes a broad range of attosecond four-wave mixing experiments performed in gas phase atoms and molecules, and a recent extension into solids.

Keywords Attosecond · Four wave mixing · Atomic and molecular dynamics

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1   Introduction

As the methods for generating light pulses of sub-femtosecond durations with broadband extreme ultraviolet (XUV) photon energies are becoming routinely achievable, exciting new uses of these pulses to investigate photophysical and photochemical processes have accelerated. Attosecond transient absorption (ATA) spectroscopy is widely used to study attosecond and femtosecond (fs) photochemical dynamics in atoms, molecules, and solids [1, 2]. While ATA spectroscopy has proven extremely valuable for monitoring ultrafast dynamics with simultaneous high temporal and spectral resolution, strong spectral modulations on-axis can obfuscate and overwhelm underlying temporal dynamics of interest [3–5]. Although the origin of the spectral modulations, such as AC Stark effects and Autler-Townes splittings, are interesting topics in their own right, it is also important to disentangle direct time-domain measurements of ultra-short lived coherent dephasing dynamics and highly excited state lifetimes. Attosecond Four-Wave Mixing (FWM) spectroscopy using a non-collinear geometry is realized as a method that circumvents the strongly modulated ATA spectral features measured on-axis, providing direct access to the lifetimes and coherent dynamics of highly excited states [6]. The development of attosecond FWM spectroscopy in the Leone and Neumark groups is detailed in this paper with emphasis on how technique developments have revealed new ways to measure chemical dynamics with increasing precision.

1.1   Attosecond Four-Wave Mixing (FWM) Spectroscopy

Attosecond FWM spectroscopy falls within a family of third order nonlinear spectroscopies used to probe the macroscopic polarization that is created in a sample following a series of three incident light-matter interactions. Many popular techniques within this class of experiments use pulses with photon energies in the ultraviolet, visible, infrared and terahertz regimes. The attosecond FWM technique combines one attosecond pulse with XUV photon energies (11–35 eV in the experiments discussed here) with two few-cycle near-infrared (NIR) pulses that have broadband spectra spanning the visible/NIR (1.25–2.25 eV) region. The third-order polarization of interest is the third term in the expansion:

$$P = \epsilon_0 \left(\chi^{(1)} E_1 + \chi^{(2)} E_1 E_2 + \chi^{(3)} E_1 E_2 E_3 + \cdots \right) \tag{1}$$

where the vacuum permittivity is given by ϵ_0, the nth order susceptibility is $\chi^{(n)}$, and each sequentially incident electric field is given by E_i (i = 1, 2, or 3 for third order processes). The attosecond FWM experiment uses various pulse sequences; here E_1 is taken to be an XUV attosecond pulse train or isolated attosecond pulse produced on a tabletop apparatus by high harmonic generation (HHG) – this pulse can come first, simultaneously, or last – and $E_{2,3}$ are sub-6 fs NIR pulses (see Fig. 1). The
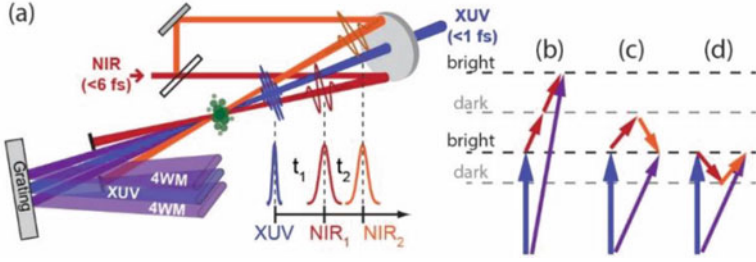
Fig. 1 Principle of Attosecond Four-Wave Mixing Spectroscopy. (**a**) Simplified experimental schematic of the beams overlapping at the sample; translation stages not shown in NIR beam path. Several wave-mixing pathways are shown in (**b**)–(**d**). The "ladder up" coupling scheme is shown in (**b**), the "Λ" coupling scheme is shown in (**c**), and the "V" coupling scheme is shown in (**d**)

FWM pulse sequence can be completed or initiated by two light-matter interactions from a single NIR pulse or two independently controlled and timed NIR pulses; several scenarios have been realized and are discussed below.

Similar to other nonlinear spectroscopies, a phase-matching condition due to momentum conservation of all three input wavevectors distinguishes the attosecond FWM signals of interest as a fourth XUV wave that is emitted. The attosecond FWM phase matching condition is

$$\mathbf{k}_{signal} = \mathbf{k}_{XUV} \pm \mathbf{k}_{NIR1} \pm \mathbf{k}_{NIR2} \qquad (2)$$

where $\mathbf{k}_{XUV}$ is the XUV wavevector and $\mathbf{k}_{NIR1}$ ($\mathbf{k}_{NIR2}$) specifies the first (second) NIR wavevector of the incident light-matter interactions. The phase matching condition may be satisfied by one NIR photon from each NIR laser beam, or by two NIR photons from one NIR laser beam. Three of the possible wavevector combinations shown in Fig. 1 produce different wave-mixing signals (e.g., $\mathbf{k}_{XUV} + \mathbf{k}_{NIR1} - \mathbf{k}_{NIR2}$ known as "Λ-type" coupling, $\mathbf{k}_{XUV} - \mathbf{k}_{NIR1} + \mathbf{k}_{NIR2}$ known as "V-type" coupling, and $\mathbf{k}_{XUV} + \mathbf{k}_{NIR1} + \mathbf{k}_{NIR2}$ known as "ladder up" coupling, which can also be ladder down, not shown). In the fully non-collinear geometry, all three light matter interactions have distinct spatial components of the wavevector in the laboratory frame, giving rise to a background free, spatially-isolated signal. The XUV-NIR1 and XUV-NIR2 overlap angles (θ_1 and θ_2, respectively) can be separately controlled during the FWM signal emission, which is emitted at an angle $\theta_{emission}$ expressed as

$$\theta_{emission} \approx \frac{\omega_{NIR1}\theta_1 + \omega_{NIR2}\theta_2}{\omega_{XUV}} \qquad (3)$$

for the V-type and Λ-type pathways, with the photon frequencies of the incident photons specified as ω_{XUV}, ω_{NIR1}, and ω_{NIR2}. By controlling the relative timings of the three incident pulses, different types of FWM experiments can be performed to probe the evolution of different states. In what is referred to as a "bright state"

scan, the $\mathbf{k}_{XUV}$ pulse arrives first and $\mathbf{k}_{NIR1}$ and $\mathbf{k}_{NIR2}$ pulses occur simultaneous to each other while the delay between $\mathbf{k}_{XUV}$ and the two NIR interactions is scanned to measure the evolution of the XUV-bright states. In what is known as the "dark state" scan, the $\mathbf{k}_{XUV}$ and $\mathbf{k}_{NIR1}$ pulses are temporally coincident first, exciting XUV-dark states, which are scanned by the delay between the $\mathbf{k}_{NIR1}$ and $\mathbf{k}_{NIR2}$ pulses. In a transient grating mode, a spatial grating can be generated by two NIR pulses arriving first, for example, to create a grating composed of altered carrier densities in a solid.

The FWM apparatus for many of the experiments discussed here utilized a Femtopower Ti:sapphire laser (1 kHz repetition rate, 1.7 mJ, 22 fs, 780 nm center wavelength) with a hollow core fiber compressor and chirped mirrors to spectrally broaden and temporally compress the amplifier output down to pulses with <6 fs durations and a spectrum spanning 500–1000 nm. Typically ~70% of the beam is split off for the HHG process while the remaining portion is used to drive the NIR light matter interactions. The XUV pulses formed by HHG are optionally filtered using a thin metallic foil filter to remove the collinear NIR driving field before the XUV beam is focused to the sample area by a toroidal mirror. The other ~30% of the NIR beam not used for HHG is routed through piezo driven computer-controlled translation stages to adjust the relative time delay with respect to the XUV pulse. In the fully non-collinear geometry, this NIR beam is split again by a 50:50 beamsplitter to produce the $\mathbf{k}_{NIR1}$ and $\mathbf{k}_{NIR2}$ pulses. The NIR beams are spatially and temporally overlapped on the sample with $\mathbf{k}_{XUV}$ using an annular mirror to produce the FWM signals. A thin metallic foil filter is used after the sample to remove residual NIR scatter from the detector, the signals are spectrally dispersed by a grazing incidence concave XUV-grating onto a two-dimensional CCD camera to collect a spectrum. The vertical dimension is the angular divergence of the signal due to the wave vector matching, while the horizontal direction is the XUV spectrally resolved dimension. See references for specific experimental configurations used in each experiment.

2   Discovering Phase-Matched Wave-Mixing Signals with Attosecond XUV Pulses and Few-Cycle NIR Pulses

The initial observations of phase-matched attosecond FWM signals arose from an experimental configuration used for ATA spectroscopy on Ne atoms consisting of one NIR beam and one XUV beam in a collinear geometry [6]. Clear phase-matched wave-mixing signals from ladder-type upconversion pathways were revealed in this collinear experiment using selective XUV wavelength-filtering to suppress the 13th harmonic in the XUV beam. In a follow-up experiment, the first non-collinear geometry with one non-collinear NIR pulse was implemented in Ne, generating the first "off-axis" signal shown in Fig. 2a. Necessarily, the only signals detectable off-axis from $\mathbf{k}_{XUV}$ in this configuration were the ladder-type. Another non-collinear experiment was promptly done to begin exploring the new wave-mixing based
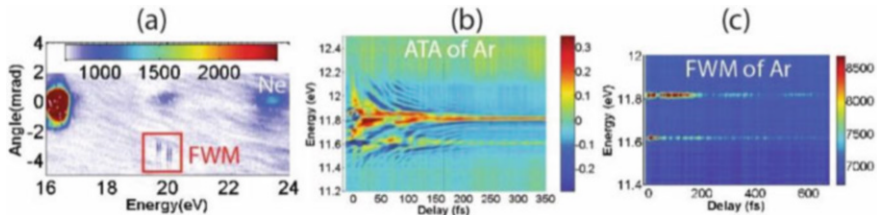
Fig. 2 Initial FWM demonstrations: Ne and Ar. (**a**) The off-axis FWM signal of Ne $2p^{-1}ns/nd$ coupled through ladder-type pathways is observed at -3 mrad. For comparison, the ATA signals of Ar $3p^{-1}ns/nd$ are shown in (**b**) and the off-axis FWM signals are shown in (**c**). (Reprinted with permission from [4], copyright 2016 by the American Physical Society)

spectroscopy [4]. Realizing the phase-matched wave-mixing signals enabled the disentanglement of complex transition pathways in highly excited states, generating deeper insight into coherent dynamics of gas phase atoms and molecules.

2.1 Electronic and Vibronic Coherences in Atoms and Molecules

Utilizing an attosecond pulse train in the 15–25 eV range, Cao et al. [6] found that once the $2s^2 2p^5$ $[^2P_{3/2,1/2}]3s/3s'$ states in Ne were excited near 16.8 eV, a two-NIR-photon transition could resonantly couple the XUV-excited states to the *ns/nd* states located around 20 eV. A coherent emission of XUV light was observed at -3 mrad divergence from the $\mathbf{k}_{XUV}$ beam, simultaneously imaged on the CCD and shown to be a phase-matched nonlinear signal over a range of Ne gas pressures, see Fig. 2a. Ladder coupling pathways ($\mathbf{k}_{XUV} + \mathbf{k}_{NIR1} + \mathbf{k}_{NIR1}$) drove the transition resonantly through XUV-dark 3p states. Notably, very strong oscillations were observed as the time delay between the XUV and NIR interactions was scanned. Two principal electronic coherences were identified for the bound electronic wavepacket, corresponding to a strong 3s/3s' state spin-orbit splitting (~0.17 eV) and the weaker "which-way" interference of the one- and three-photon transition pathways (~3 eV) [6].

A rich and direct view of coherent dynamics was then measured by performing a similar experiment on the Ar $3s^2 3p^5[^2P_{3/2,1/2}]ns/nd$ states using 11–16 eV excitation, only now with a non-collinear NIR beam [4]. The comparison to on-axis ATA signals demonstrated the enhanced clarity of time-dependent signals in FWM (see Fig. 2b, c), avoiding the strong AC-Stark effect spectral modulations seen in ATA. The FWM signal complexity increased with two different ladder-coupled pathways observed above ($+\theta_{emission}$) and below ($-\theta_{emission}$) $\mathbf{k}_{XUV}$, corresponding to emission from the $3p^{-1}$ 4s/4s' states and the $3p^{-1}$ 4d/4d' and 5d/5d' states, respectively, which resonantly coupled through dark 4p states. The 4s/4s' emission in Fig. 2c comprises multiple coherent oscillation frequencies in the 0–0.5 eV range

representing the interference of many wave-mixing pathways initiated by launching the XUV wavepacket. Further control over the NIR-couplings was achieved by allowing the NIR pulse that is collinear with the XUV and drives the HHG process to provide one of the NIR interactions. This experimental adjustment enabled higher orders of diffraction (i.e., six-wave mixing) to be viewed and showed off-axis V- and Λ-couplings for the first time. Dynamics of very long-lived (>600 fs) 4p dark states were then accessible, capturing electronic coherences among the spin-orbit split 4p states.

To extend FWM to molecular dynamics investigations, the vibronic wavepacket dynamics of XUV-excited H_2 were measured [7]. A vibronic wavepacket was created by exciting the B′ and D states in addition to vibrational progressions supported in these states. The complex evolution of the wavepacket propagation was directly resolved by Fourier transform analysis of the ladder-type, Λ-type, and V-type coupling pathways. Many types of coherences are disentangled in this experiment, providing an in-depth tomographic perspective of complex wavepacket evolution involving multiple vibrations, electronic states, and truly vibronic coherences.

3 Increasing Resolution: Fully Non-Collinear Wave-Mixing

Implementing the collinear NIR field used for the HHG process to also serve as the k_{NIR1} wavevector increased the versatility of attosecond FWM spectroscopy by enabling Λ- and V-type pathways to be measured off-axis. However, this geometry inherently restricts the timing control between k_{XUV} and k_{NIR1}. Consequently, additional developments led to two independent NIR beamlines, each with temporal control, to maximally interrogate the generated nonlinear signals in space and time using a fully non-collinear beam geometry. These two NIR beams are experimentally recombined above and below the XUV beam in a vertically stacked fashion.

3.1 Exploring the Fully Non-Collinear Geometry

Similar to transient-grating spectroscopy, an attosecond FWM experiment having both NIR beams non-collinearly aligned with respect to the XUV pulse can be thought of as forming a grating during the phase-matching process. The parameter space of the temporal delays is a distinguishing factor for FWM from other transient-grating spectroscopies. The FWM signals of interest in many of the experiments considered here are those that use the grating as a 'probe' of the XUV-excited dynamics and deliberately scan each of the pulse delays to target dynamics of interest. The grating can also be written first, for future measurements, for example, of transient carrier dynamics in solids.

During temporal overlap of all three pulses and in the first few femtoseconds of the XUV-NIR time delay, Fidler et al. [8] showed that the grating formation in atomic He results in a time-dependence of the diffraction orders measured off-axis. Up to the third diffraction order – labeled m = −3, indicating eight-wave-mixing – was experimentally characterized and theoretically simulated for He 1snp resonances around 21.2 eV and nearby 3s-, 3d-, 4s-, and 2s + light-induced states. In this experiment, the two non-collinear NIR pulses were held at relative temporal overlap while the delay between the XUV pulse and the two NIR pulses was scanned. A delay-dependent emergence of FWM signals for increasing diffraction orders was observed while lower diffraction orders showed enhanced spectral shifting. Theoretical investigation of these phenomena using an AC Stark phase grating model attributed the effects to the diffraction orders accumulating AC Stark phase and lower orders formed more rapidly. Broadly, this showed that AC Stark effects can still influence spectral features in FWM spectra, especially for light-induced states.

The fully non-collinear geometry has proven fruitful for investigating complex molecular potential energy landscapes where relative timing of the light-matter interactions is key. As an example, Warrick et al. [9] were successful in mapping out the potential energy surface of the a″ $^1\Sigma_g^+$ double-well dark state in N_2 using judicious timing of the NIR pulses in the FWM pulse sequence (see Fig. 3). An attosecond XUV pulse first excited the b′ $^1\Sigma_u^+$ valence state around 14 eV with an excess of vibrational quanta, launching a vibronic wave packet that propagated toward greater internuclear distances. The relative orientation of the b′ and a″ potential energy surfaces are such that the b′ Franck-Condon region overlaps with the inner well of the a″ dark state and the b′ outer turning point overlaps with the second outer well of the a″ dark state; both wells are accessible with one NIR photon. To characterize the inner well of the a″ dark state, k_{XUV} and k_{NIR1} were held at temporal overlap while the delay between k_{NIR1} and k_{NIR2} was scanned. The observed coherences in the FWM signals identified a primary 0.267 eV oscillation
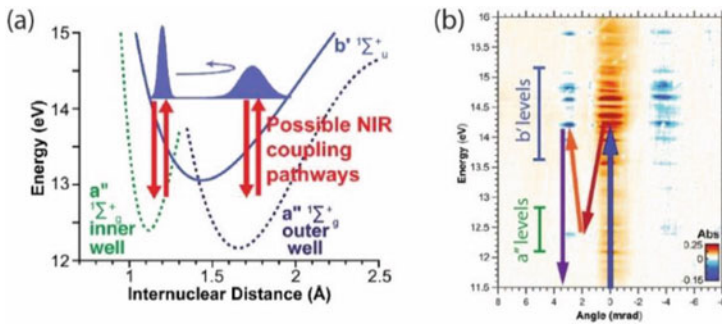

Fig. 3 Non-Collinear FWM in N_2. (**a**) A schematic potential of the bright b′ state and the dark a′ state probed selectively using the fully non-collinear FWM pulse sequence. (**b**) The CCD image of the FWM signal at time zero relating the bright and dark states

frequency, matching very well with known vibrational levels of the a″ inner well dark state. By adjusting the $\mathbf{k}_{NIR1}$ pulse to be delayed 25 fs from the b′ state excitation, corresponding to a half vibrational period of the b′ state, a substantially lower coherence frequency of 0.1 eV is observed while the 0.267 eV oscillations of the a″ inner well are diminished. The a″ outer well vibrational frequency agrees well with calculated values and is expected to be lower than the inner well due to extended internuclear separations. This is a salient example of where the background free FWM signal and fully controllable non-collinear beam geometry enabled a high resolution and temporally precise spectroscopic investigation of a complex excited state molecular dynamics.

3.2 Direct Time-Domain Characterization of Highly Excited States

Attosecond FWM spectroscopy can enable accurate time-domain lifetime measurements of highly excited states with very short lifetimes. The autoionizing $4s^2 4p^5$ [$^2P_{1/2}$] *ns/nd* Rydberg states of Kr were studied with FWM spectroscopy by Fidler et al. [10] where the background-free signals were essential to accurately characterize the lifetimes. The autoionizing $4p^{-1}$*ns/nd* lifetime dynamics in the ATA measurement are dramatically overwhelmed with AC Stark induced spectral modulation, rendering the time-domain characterization nearly impossible. However, the off-axis FWM signals directly resolve the autoionization lifetimes unobscured by strong spectral modulations. Strong coherent oscillations are present in the FWM signals, reflecting the evolution of a Rydberg wavepacket excited with the attosecond XUV pulse. Despite these complex oscillations, the underlying decay dynamics were fitted for the $4s^{-1}$[$^2P_{1/2}$]6d, 7d, and 8d states as 22 ± 8 fs, 33 ± 6 fs, and 49 ± 6 fs, respectively, which agrees with frequency-domain linewidth data (see Fig. 4a). These *nd* states are also embedded in near degenerate *ns* states but are clearly separable in the time domain due to the *ns* states having picosecond lifetimes. These are the first short-lived lifetime measurements of atoms in the time-domain using attosecond FWM spectroscopy.

In systems with complex manifolds of near-degenerate excited states, direct time-domain measurements can be desirable to separate different excited state dynamics when spectral congestion renders linewidth measurements difficult. Additionally, when states undergo competing decay mechanisms, high temporal resolution measurements may be useful to investigate specific relaxation channels. An excellent example of this is in the Rydberg series converging to the O_2^+ c $^4\Sigma_u^+$ state, which can decay both through predissociation of vibrational levels *via* tunneling and through autoionization. Lin et al. [11] used attosecond FWM spectroscopy to measure the 3s Rydberg state dynamics in this series for the v = 0 and v = 1 vibrational levels to be 5.8 ± 0.5 fs and 4.5 ± 0.7 fs, respectively (see Fig. 4b). The fully non-collinear beam geometry was crucial to the success of this experiment, as
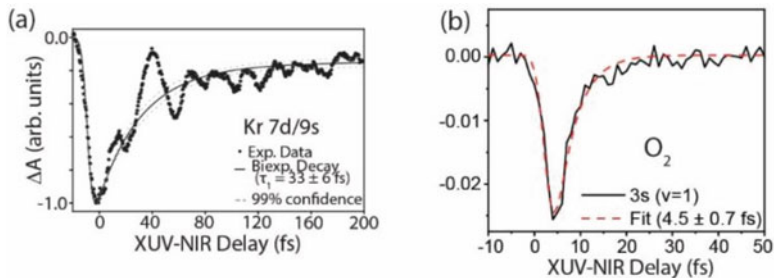
Fig. 4 Time-domain Lifetime Measurements with FWM. (**a**) The 33 ± 6 fs autoionization decay time of the Kr $4p^{-1}7d/9s$ resonance is accurately measured in the time-domain. (Reprinted from [10] with permission of AIP Publishing). (**b**) The $v = 1$ decay time of the O_2 3s Rydberg state measured as 4.5 ± 0.7 fs. (reproduced from [11] with permission from the Royal Society of Chemistry)

each of the two NIR beams required different overlap angles with the XUV beam to further separate FWM signals from Λ-type and ladder-type coupling pathways. With accompanying theoretical work, electron-nuclear couplings were identified as playing a major role in the relaxation of the O_2 3s Rydberg state. The more rapid decay of the $v = 1$ state was shown to be largely due to electronic autoionization, rather than due to different predissociation rates for $v = 0$ and $v = 1$. Interestingly, the autoionization rate was found to be very sensitive to the O-O internuclear distance, depending upon the vibrational level of the excited O_2 3s Rydberg state.

4 New Advancements: Techniques and Applications

The advantages of driving the FWM process resonantly with full temporal and spatial control over each light-matter interaction in the fully non-collinear geometry are clearly illustrated by the above examples. Namely, greater precision in the measurement is obtained to investigate the atomic or molecular response of interest. The advancements discussed below lay the foundations for FWM with phase-sensitivity using heterodyned detection and, in NIR-resonant cases, for gaining NIR-frequency specific FWM pathway information using pulse shaping methods. In addition to technical advancements, the application of attosecond FWM to exciton dynamics in solid state materials is opening new fields of inquiry.

4.1 Technique Developments

The background-free signals generated in the attosecond FWM experiment are homodyne-detected signals, meaning that the signals are detected without a ref-

erence field to provide phase-sensitive detection through interference. The intensity of the FWM signal is given by $|E_{signal}|^2$ where E_{signal} is the electric field of the background-free FWM emission. In the presence of a reference field, referred to as a "local oscillator", the interference of the signal field and the reference field produces cross terms that enable the relative phase of the signal field to be measured and provide signal enhancement. This detection scheme is often referred to as heterodyned detection. In attosecond FWM spectroscopy, an XUV-replica local oscillator is needed to perform a self-heterodyned detection scheme, which is widely used in other nonlinear spectroscopies in the optical and infrared regions. Such a scheme was demonstrated by Fidler et al. [12] on the FWM signals in 1s*nl* Rydberg states of He by deliberately optimizing the HHG process to favor an angularly diffuse $\mathbf{k}_{XUV}$ beam with a divergence of ~ ± 2 mrad in the CCD imaging plane. The implementation of the self-heterodyned detection scheme allowed eight light-induced states to be observed in total, while the homodyned case could only detect one, showing the enhanced sensitivity of features with comparably small cross sections. Further improvement and implementations of heterodyned detection schemes in attosecond FWM spectroscopy will enable detailed electronic dynamics investigations in increasingly complex systems.

Multidimensional spectroscopies are widely implemented in the optical and infrared regions to give greater insight into photoexcited dynamics and photo-chemical pathways. These methods increase the spectral dimensionality of the measured signals by resolving the frequency dependence of multiple transitions in an experimental pulse sequence. In a key development, Marroux et al. [13] translated this methodology into the realm of attosecond XUV science by implementing a spatial light modulator into one of the NIR beamlines of the non-collinear FWM geometry. The NIR-frequency dependence of FWM pathways in the Ar $3s^2 3p^5$ [$^2P_{3/2,1/2}$] *ns/nd* excited states were mapped by using pulse sequences with narrow-band (1.4–2.2 meV) amplitude and phase slices altered in the broadband NIR pulse bandwidth (Fig. 5a). The resulting two-dimensional XUV-NIR spectrum directly relates the relative energetic locations of the XUV-forbidden dark states with respect to the XUV emission from the FWM pathways. Coherent superpositions detected as quantum beats in the FWM emission from interfering pathways are also decomposable through this multidimensional method by selecting specific transition pathways to follow in a time-dependent manner. Moving forward, two-dimensional XUV-NIR spectroscopy holds promise for disentangling resonant wave-mixing phenomena in highly congested excited state manifolds to accurately characterize state-specific energies and lifetimes.

4.2   New Applications in Materials

With the success of the attosecond FWM technique in characterizing short-lived dynamics of highly excited states in gaseous atoms and molecules, this approach was recently extended to study highly localized "atomic-like" core-level excitons in solids. Gaynor et al. [14] used attosecond FWM spectroscopy to characterize the
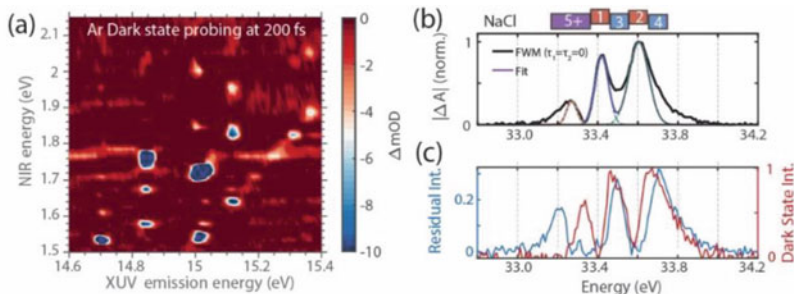
Fig. 5 Advancements in attosecond FWM spectroscopy. (**a**) The fully non-collinear FWM geometry enabled NIR-pulse-shaping based two-dimensional spectra, demonstrated by mapping out Ar $3p^{-1}np$ dark states. (Reproduced from [13] with permission from AAAS). (**b**, **c**) The deconvolution of the Na^+ $L_{2,3}$-edge spectrum for crystalline NaCl showing at least five core-excitons. (Reprinted with permission from [14], copyright 2021 by American Physical Society). (**b**) The time-zero FWM spectrum is fit to the three prominent bright core-excitons measured in the FWM bright state scan. (**c**) The residual of the fit identifies more core-excitons measured separately by the dark state scan

spectral and temporal dynamics of these core-level excitons localized on Na^+ in polycrystalline NaCl thin films. Here, an atomic-like Na^+ $2p^{-1}3s$ state is formed by XUV excitation around 33.5 eV where the 3s electron remains Coulombically bound with the core-level hole in the 2p level, forming the core-exciton. In this study, the inhomogeneous broadening of the Na^+ core-exciton spectrum was deconvolved, identifying at least five distinct core-exciton features that underlie the linear absorption, all of which were observed to decay on sub-10 fs timescales (Fig. 5b).

The physical relaxation mechanisms of the core-excitons were ascribed to electron-electron interactions due to the presence of many energetically overlapping core-excitons and ultrafast decay times that outpace the reported timescales of longitudinal-optical phonons and Auger decay in the literature. This study demonstrated that attosecond FWM spectroscopy can be a viable technique for studying ultrafast phenomena in materials, and it suggests that the atomic spectroscopic intuition applied to the gas phase FWM studies may also be productively applied to more complex materials systems.

5 On the Horizon

The simultaneous high-temporal precision and high spectral resolution afforded by the background-free signal generation of attosecond FWM spectroscopy makes it advantageous for studying ultrashort dynamics of highly excited states in atoms, molecules, and materials. Nearly all of the atomic and molecular attosecond FWM studies to-date have benefitted from NIR-resonant dark states for a resonantly enhanced wave-mixing pathway. The possibility for non-resonantly driven FWM

experiments is known at free electron laser experiments [15] and should be explored further. To understand the non-resonant effects of the FWM experiment better will help broaden the understanding and applications of the technique [16].

Future studies of core-excited state dynamics in small molecules will allow for unambiguous exploration of few-fs electronic and vibrational decay channels with more localized reporting from the element-specific core-level transitions accessed by higher photon energy attosecond light sources. Incorporating UV photon energies into the non-collinear wave-mixing pulses will enhance the background-free isolation of FWM signals and enable UV-resonant FWM pathways that can involve valence-level transitions in small organic molecules. In some cases, using an actinic pump pulse to photo-initiate a dynamical process of interest, which is then probed by the attosecond FWM pulse sequence, may prove particularly exciting. An example is where bond-length dependent electronic dynamics are approachable by triggering photodissociation or photoisomerization.

As the solid-state materials studies\enlargethispage*{12pt} using attosecond FWM are still very new, many directions in this research area are wide open and unexplored. Combining time-dependent theoretical simulations with attosecond FWM experiments is a difficult challenge but will be very helpful for the field. A systematic understanding of how localized excitations in solids form, evolve in time, and play a role in specific material properties – especially in correlated electronic behaviors and topological states – is an exciting potential research direction. On a fundamental level, attosecond FWM spectroscopy seems to be sensitive to atomically localized excitations. However, a comparison of dynamics measured by FWM to those dynamics measured by other means and interpreted in the typical delocalized band structure picture will be particularly instructive.

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