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Published in:
Optics Letters

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
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Download date: 12. Jul. 2023
Time-resolved four-wave-mixing spectroscopy for inner-valence transitions

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Received XX Month XXXX; revised XX Month, XXXX; accepted XX Month XXXX; posted XX Month XXXX (Doc. ID XXXXX); published XX Month XXXX

Non-collinear four-wave mixing (FWM) techniques at near-infrared (NIR), visible, and ultraviolet frequencies have been widely used to map vibrational and electronic couplings, typically in complex molecules. However, correlations between spatially localized inner-valence transitions among different sites of a molecule in the extreme ultraviolet (XUV) spectral range have not been observed yet. As an experimental step towards this goal we perform time-resolved FWM spectroscopy with femtosecond NIR and attosecond XUV pulses. The first two pulses (XUV-NIR) coincide in time and act as coherent excitation fields, while the third pulse (NIR) acts as a probe. As a first application we show how coupling dynamics between odd- and even-parity inner-valence excited states of neon can be revealed using a two-dimensional spectral representation. Experimentally obtained results are found to be in good agreement with ab initio time-dependent R-matrix calculations providing the full description of multi-electron interactions, as well as few-level model simulations. Future applications of this method also include site-specific probing of electronic processes in molecules.

OCIS codes: (190.0190) Nonlinear optics; (020.3690) Line shapes and shift; (300.2570) Four-wave mixing; (300.6240) Spectroscopy, coherent transient; (320.7110) Ultrafast nonlinear optics; (300.1030) Absorption.

With the development of coherent femtosecond-duration laser pulses nonlinear (third-order) four-wave-mixing (FWM) spectroscopy has become a versatile tool for the investigation of ultrafast dynamics in molecules and other material samples. A large body of experimental approaches for time-resolved molecular spectroscopy has been developed based on FWM phenomena, such as photon echo [1], coherent anti-Stokes Raman scattering [2], transient grating [3], and many more. The spectroscopically most comprehensive implementation of FWM is the so-called two-dimensional spectroscopy (2DS) with three temporally independent pulses which allows the correlation of excitation- and nonlinear-response spectra to directly measure couplings between quantum states [4,5]. 2DS in the infrared, visible, and ultraviolet spectral ranges has enabled the exploration of vibrational [6], electronic [7] and vibronic [8] coupling dynamics in complex molecular systems. The extension of 2DS into the extreme ultraviolet (XUV) and X-ray spectral regions aims to map coupling dynamics between spatially localized inner-valence or core transitions among different sites of a quantum system. It has been theoretically discussed by Mukamel and coworkers [9,10] and is a long-awaited goal. In principle, modern free-electron laser (FEL) and high-harmonic generation (HHG) based coherent XUV and X-ray light sources can provide appropriate pulses for 2DS experiments, but key challenges are both the increased technical demands to create appropriate multipulse geometries in this photon energy range, as well as the intrinsically low photon flux of laboratory based sources. Nevertheless, first steps are being made, as demonstrated in recent experiments that explore NIR- and XUV-induced transient gratings that emphasize both the spectroscopic element selectivity [11] and the enhanced spatial resolution [12] capabilities of the XUV domain.

Meanwhile, an all-optical two-color pump-probe technique utilizing weak attosecond XUV pulses and strong few-cycle NIR pulses—often referred to as attosecond transient absorption spectroscopy (ATAS)—has opened a direct route to the measurement and control of the XUV spectral response of bound electronic transitions [13–21]. With both the XUV-NIR time delay τ and the NIR intensity I_NIR as continuously tunable control parameters, ATAS has a multi-dimensional experimental anatomy [22]. Two-dimensional (2D) time-domain spectra S(τ, ω) measured as a function of both the XUV photo-excitation frequency ω...
Here we extend ATAS (typically a VUV/XUV and a single time-delayed laser pulse) into a time-resolved FWM technique, where excitation and probing by an NIR laser pulse occurs at two different times. As we will show, this allows the spectroscopy on both dipole-allowed and forbidden XUV-excited inner-valence transitions. The first two pulses (XUV and weak NIR) coincide in time (with locked zero-delay timing and a fixed phase relation between fundamental field and higher harmonics) and are temporally separated from the strong (non-perturbative) third (NIR) pulse by the time delay ρ. The interaction of a sample with the first two pulses (XUV and NIR) creates a polarization, i.e., the coherent superposition of ground and both odd- and even-parity excited states. This two-color pump step extends the coherent excitation onto states the transition into which would be forbidden by a single XUV photon from the ground state. After the excited system has evolved freely during the time delay ρ, the interaction with the strong NIR pulse generates a nonlinear (third-order) response signal by again coupling between XUV-dipole-allowed and forbidden excited states. We have chosen the 2s-3p-inner-valence excited states 2s−13s(1S0), 2s−13d(1D0) and 2s−13p(1P0) of neon (henceforth denoted as 3s, 3d, and 3p) as a target to perform first such proof-of-principle FWM experiments. Neon provides an appropriate electronic energy-level structure for investigating resonant transitions between XUV-dipole-allowed and forbidden states which cannot be accessed by conventional ATAS methods.

The experimental setup (see Fig. 1a), as previously described in Ref. [17], involves a commercial Ti:Sapphire multipass amplifier with hollow-core fiber and chirped-mirror compression stages for the generation of NIR (central photon energy ~1.6 eV) sub-7 fs pulses delivered at a 4 kHz repetition rate and ~0.4 mJ pulse energy. These pulses act as driver pulses for HHG in an argon gas-filled cell (~75 mbar backing pressure) yielding short trains of atto-second pulses that are inherently phase-locked to the fundamental field. HHG spectra obtained extend continuously over the autoionizing resonance region of neon between 43 eV and 50 eV covering the full 2s−1np Rydberg series (cf. the HHG absorption spectrum in Fig.1b). A piezo-driven two-component split mirror (inner, dynamic part: gold coating; outer part: silver coating) is employed to introduce a time delay between the co-propagating atto-second XUV and femtosecond NIR pulses. The NIR pulse intensity is controlled by a piezo-controlled iris aperture. Spatial beam separation between XUV and NIR is achieved by a two-part spectral band-pass filter in annular geometry where the outer, annular, part consists of a 2 μm thin nitrocellulose membrane (1.2 mm central hole) and the inner part is a single layer of 0.2 μm thin aluminum foil (1.2 mm diameter). Importantly, for the results shown in this work, the central part transmits a residual NIR-photon intensity on the order of 1 − 10 %, which can be considered as a perturbative NIR replica pulse which remains locked in temporal overlap with the XUV. The NIR transmission is due to small holes or other imperfections in the extremely fragile foil (e.g. created during the manufacturing process and/or mechanical strain while assembling the custom-made filter arrangement). After passing the band-pass filter, the NIR-pulse delay (with respect to the NIR-XUV excitation step) and intensity-controlled laser beams are focused into the neon gas-filled target cell (~35 mbar backing pressure). The transmitted XUV light contains the sample’s dipole response which is detected by a high-resolution XUV spectrometer (~20 mEeV Gaussian standard deviation near 45 eV, see Ref. [16] for details).

For comparison with our experimental results, calculations based on the R-matrix with time-dependence (RMT) approach [28] were performed for the neon atom. RMT is an ab initio, non-perturbative computational technique for the description of general multi-electron atomic/ionic systems interacting with a strong laser field. By employing the standard R-matrix division of space [29] a tractable solution of the time-dependent Schrödinger equation can be obtained affording a full account of multi-electron effects, and a comprehensive treatment of detailed atomic structure. In order to describe both the core- and doubly-excited states of neon under investigation, the calculations comprise all single-, double- and triple-excitations of the 2s and 2p electrons into 3p, 3s, 3d, (spectroscopic) 4s and 4p (pseudo)-orbitals, which are determined as described in Ref. [30]. This leads to an expansion over 152 multi-electron configurations. Additionally, to account for the various ionization pathways, six residual ion states of Ne+ are included in the calculation. This yields energies within 0.09 eV of the literature values, for the states under investigation [31–33]. Using RMT we compute d(t): the time-dependent expectation value of the dipole operator. The absorption spectrum is then given by [34]

$$\sigma(\omega) = 4\pi \frac{\omega}{c} \text{Im} \left[ \frac{d(\omega)}{E(\omega)} \right]$$

(1)

where ω is the photon energy, c the speed of light, and d(ω) and E(ω) are the Fourier transform of d(t) and the electric field, respectively.

In Figs. 2(a) and (2b), we present time-delay-resolved absorption measurements for a scanned time delay ρ between XUV-NIR pump and NIR-probe fields, obtained from experiment and RMT calculations. Time-resolved absorption changes can be observed across all the reso-
Fig. 2. Time-resolved 2D absorption spectra $S(t, \omega)$ at $\sim 10^{12}$ W/cm$^2$ NIR-probe intensity obtained from (a) experiment and (b) full $ab$ initio calculations assuming Gaussian pulses and for the NIR-pump 10% of the NIR-probe intensity (also see Dataset 1 in Ref. [43]). Strong periodic full-cycle modulations are imprinted on the 3p resonance which give rise to diagonal, line-like peaks at $\sim 1.6$ eV Fourier energy in the 2DAS, $S(v, \omega)$ (lower panels c and d, respectively), indicating coherent coupling pathways. Vertically aligned peaks are due to time-delay dependent NIR intensity variations in the temporal overlap region. The energetic position of the dipole-forbidden and thus spectroscopically hidden 3s and 3d coupling partners ($h\omega_{3p} = 43.7$ eV and $h\omega_{3d} = 47.0$ eV) are indicated by the dashed lines as a guide to the eye. Besides the excellent agreement between experiment and RMT calculations, remaining discrepancies are likely due to uncertainties in the exact experimental pulse shapes. The 3s and 3d resonances are assigned based on Ref. [32].

Resonance lines shown in Figs. 2(a) and 2(b). Our focus here is on the absorption changes occurring near the 3p state at $h\omega_{3p} = 45.55$ eV photo-excitation energy in order to understand the two-photon XUV-NIR-induced wave-packet dynamics created by the superposition of two coherently excited states with opposite parities. The time-domain absorption spectra $S(t, \omega)$ (Figs. 2a and 2b) are Fourier analyzed ($\tau \rightarrow v$) to decompose the temporal beat patterns for each resonance into distinct peaks on a 2DAS, $S(v, \omega)$, spectral representation (Figs. 2c and 2d). Peak position, shape, and orientation allow the characterization of coherent coupling and transition pathways analogous to the case previously described for XUV-only excitation and a single time-delayed NIR probe pulse [23]. For the case presented here, the additional weak NIR pulse locked to the XUV excitation pulse near time zero plays a crucial role, as it coherently excites states that would otherwise be dipole-forbidden for an XUV-only excitation. The basic structures observed in the time-domain spectra $S(t, \omega)$ (Figs. 2a and 2b) have been seen in several related ATAS studies with XUV-only excitation fields [13–19,22,23] and can in general be decoupled into three interfering sub-structures [23]: (i) a slow, $r$-dependent modulation following a hyperbolic geometry near resonance lines which corresponds to a fork-like feature with elliptically-shaped peaks with slope 1 originating at zero Fourier energy in the 2DAS $S(v, \omega)$, (ii), a fast $r$-dependent rippling-type pattern, which gives rise to line-like Fourier peaks of slope 1 at non-zero Fourier energies. According to dipole-selection rules such Fourier peaks at even-numbered multiples of the NIR-photon energy indicate transitions between identical-parity states mediated by an even number of NIR photons. Such features [half- and quarter-cycle modulations] have been observed and interpreted recently [13,18,22]. In Figs. 2c and 2d we observe these Fourier features, however, at one NIR-photon energy, $\sim 1.6$ eV (full-cycle modulations), evidencing a coherent excitation and time-dependent coupling of opposite-parity states. We identify the even-parity 3s and 3d states as the coupling partners of the 3p state by analyzing the orientation of the two dominant line-like peaks appearing at $h\omega_{3p} = 45.55$ eV photo-excitation energy and $\sim 1.6$ eV Fourier energy, which extrapolate towards the coupled resonance energies on the photo-excitation energy axis at $h\omega_{3p} = 43.7$ eV and $h\omega_{3d} = 47.0$ eV [32]. It is important to note that the two-color XUV-NIR pump step for the coherent excitation of both XUV-dipole-allowed and dipole-forbidden (allowed by the absorption of an additional NIR photon near time zero) transitions to final states 3p and 3s, 3d is the key mechanism to observing Fourier features at odd-numbered multiples of the NIR-photon energy. To further confirm this understanding we present in Fig. 3 few-level model (FLM) simulations based on the approach previously described in Ref.[16] assuming $2 \times 10^{11}$ W/cm$^2$ NIR-pump and $2 \times 10^{12}$ W/cm$^2$ NIR-probe intensities. The numerical parameters (resonance energies, line widths, asymmetry $q$-parameters) used to model the three states (3p, 3s, 3d) above the ground state are taken from Refs. [32,38]. The $N = 1$ ionization con-

![Fig. 2](image-url)

![Fig. 3](image-url)
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