



ChemPhys Perspective

## Uncovering molecular relaxation processes with nonlinear spectroscopies in the deep UV


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### ABSTRACT

Nonlinear laser spectroscopies in the deep UV spectral range are motivated by studies of biological systems and elementary processes in small molecules. This perspective article discusses recent technical advances in this area with a particular emphasis on diffractive optic based approaches to four-wave mixing spectroscopies. Applications to two classes of systems illustrate present experimental capabilities. First, experiments on DNA components at cryogenic temperatures are used to uncover features of excited state potential energy surfaces and vibrational cooling mechanisms. Second, sub-200 fs internal conversion processes and coherent wavepacket motions are investigated in cyclohexadiene and  $\alpha$ -terpinene. Finally, we propose new experimental directions that combine methods for producing few-cycle UV laser pulses in noble gases with incoherent detection methods (e.g., photoionization) in experiments with time resolution near a single femtosecond. These measurements are motivated by knowledge of extremely fast non-adiabatic dynamics and the resolution of electronic wavepacket motions in molecules.

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### 1. Introduction

Time-resolved laser spectroscopies have long been central to the understanding of chemical dynamics in condensed phases [1,2]. Beginning with early flash photolysis techniques, the spectroscopic methods used to understand chemical reactions have steadily progressed with advances in laser technology [3]. The last decade has seen tremendous growth in nonlinear femtosecond laser spectroscopies inspired by NMR methods. One general class of techniques utilizes high-order Raman nonlinearities to uncover dynamics ranging from intermolecular motions in liquids to intramolecular charge transfer [4–11]. Two-dimensional (2D) Fourier transform spectroscopies have also impacted the understanding of a variety of processes in condensed phases [12–18]. The inner workings of photosynthetic complexes and molecular aggregates are now understood to be far more intricate than previously thought [19–28]. Direct observations of chemical equilibrium exchange dynamics in liquids are another breakthrough with transformative implications [29–31]. It is envisioned that 2D spectroscopy will one day achieve widespread use in biological and materials science [32,33].

For technical reasons, 2D Fourier transform measurements were first applied and matured most rapidly at infrared wavelengths [34–39]. Solutions to challenges including high-precision

control over pulse delays and interferometric phase stability enabled subsequent applications in the visible wavelength range [40–42]. Further extension of 2D spectroscopy to the deep ultraviolet, hereafter termed 2DUV, is primarily motivated by biological systems whose lowest frequency resonances are found in this spectral range (200–300 nm) [43–49]. Such experiments must contend with several problems including the attainment of adequate laser bandwidth, interferometric phase stability, and the suppression of undesired nonlinearities in solutions (e.g., photoionization of solute and solvent). A variety of approaches have been demonstrated in the past few years. Traditional four-pulse laser beam geometries [44,50] and pulse shaping methods [51,52] have both been implemented. Another innovative new approach utilizes a birefringent delay line [53]. Specialized second harmonic generation methods in BBO crystals [49,54,55], self-phase modulation in  $\text{CaF}_2$  [52], and nonlinearities in noble gases [56,57] have all been leveraged to enhance the laser bandwidths employed in 2DUV experiments. Because of these technical advances, biologically interesting applications to DNA and proteins are now on the horizon [44,46,47,49,57].

This perspective article considers present technical frontiers involving nonlinear spectroscopies in the deep UV wavelength range. We begin by discussing technical issues with a particular emphasis on the diffractive optic based experiments employed in our laboratory. Applications to two classes of systems that exhibit sub-ps internal conversion processes are then used to illustrate our experimental capabilities. First, potential energy landscapes and solute–solvent interactions are investigated in studies of small

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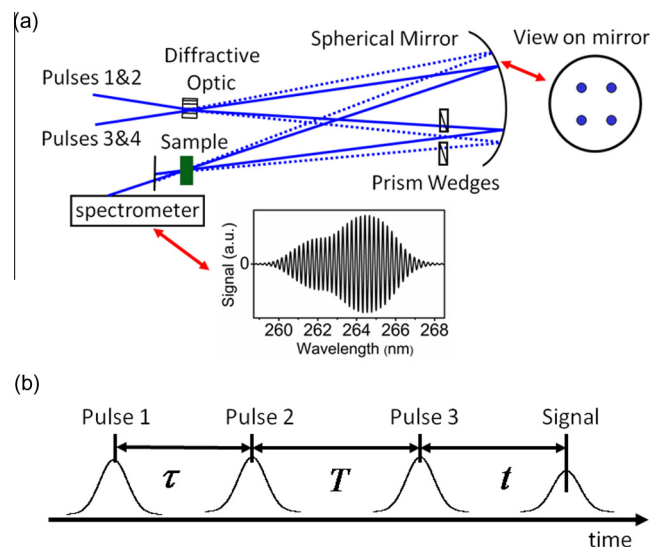
DNA components (e.g., nucleobases, nucleosides, dinucleotides) at temperatures ranging from 100 to 300 K. Second, sub-200 fs internal conversion transitions are directly resolved in cyclohexadiene and a closely related derivative,  $\alpha$ -terpinene. Observations of vibrational coherences in these ring-opening systems provide insights into the excited state potential energy gradients that drive their photochemistries. Our efforts to extend interferometric four-wave mixing spectroscopies from 270 to 200 nm are then discussed within the context of the limitations imposed by technical challenges [57]. Finally, we propose new experimental directions that combine wavelength regimes and time scales not typically employed in chemical physics research. The basic idea is to combine methods for producing short laser pulses in noble gases with incoherent detection methods (e.g., photoelectrons, molecular fragments) in experiments with time resolution between that which is typically associated with attosecond and femtosecond spectroscopies. Such measurements are motivated by knowledge of extremely fast non-adiabatic dynamics and the resolution of electronic wavepacket motions in molecules.

Methods for producing short UV laser pulses in noble gases have largely been developed by the optical physics community. More than a decade ago, Kapteyn and Murnane generated 8 fs pulses near 270 nm in hollow core fibers filled with argon [58,59]. Bradforth and co-workers later used a similar waveguide to achieve wavelength-tunable 30 fs laser pulses throughout the deep UV [60,61]. Laser filamentation has also been employed to obtain short laser pulse durations in this spectral range [62–65]. Such filamentation techniques have been leveraged in gas phase studies of molecular dynamics for extraordinary insights [66,67]. In these investigations, 10–15 fs pulses at the 3rd and 5th harmonics of a Ti:Sapphire laser were produced via filamentation in argon then directed into photoionization mass spectrometry experiments without transmissive optics. One key to the success of these measurements is that UV laser pulses emerge fairly well-compressed from filaments provided that transform-limited near infrared pulses are used to drive the nonlinearity [64]. Thus, the key experimental challenge amounts to delivering the UV pulse to the sample medium without imparting dispersion.

Improvements in pulse generation methods and experimental techniques continue to expand the scope of scientific inquiry. For instance, it was recently shown that bandwidths capable of supporting 1.0 fs laser pulses are attainable between 200 and 300 nm [64]. This exciting demonstration raises questions about what is ultimately possible. Can experiments with 0.5–1.0 fs laser pulse durations be realized in experiments carried out in the gas phase? Can experiments with 1.0 fs time resolution provide interesting new physical insights? One of the central interests in attosecond physics is the resolution of electronic wavepacket motions in molecules [68,69]. It is our view that efforts to interrogate these dynamics in the deep UV may be complementary to work now carried out in the extreme UV and X-ray spectral regions [70–72].

## 2. Diffractive-optic based four-wave mixing spectroscopies in the deep UV

The experiments conducted in our laboratory make use of a diffractive optic based four-wave mixing interferometer for which the basic design is now relatively widespread [41,70,73,74]. Our particular setup has been described elsewhere, so the details are kept brief here [44,75]. As shown in Fig. 1, the pump and probe laser beams are split into  $\pm 1$  diffraction orders with a diffractive optic at the entrance to the interferometer. The four resulting laser beams are relayed onto the sample with a single aluminum coated spherical mirror to minimize loss in laser intensity. Three of the



**Fig. 1.** (a) Schematic of diffractive optic based interferometer used to conduct 2DUV experiments in our laboratory. (b) Pulse sequence used in TG and 2DUV spectroscopies. The system absorbs light during the delay,  $\tau$ ; non-radiative dynamics occur in the delay,  $T$ ; the signal is emitted in the time interval,  $t$ . The absorptive part of the TG signal field provides information equivalent to a conventional transient absorption experiment, whereas 2DUV shows how correlations in the excitation and emission frequencies,  $\omega_\tau$  and  $\omega_t$ , vary with respect to  $T$ . This figure is reproduced from Ref. [75].

incoming pulses induce the third-order polarization that radiates the signal, whereas the fourth is used as a reference field for interferometric signal detection [76,77]. The arrival times of the first two pulses are controlled with attosecond precision by translating thin prism wedges in the paths of the laser beams [41]. This use of transmissive optics is potentially problematic if the system under investigation possesses narrow line widths, because the difference in the durations of the first two pulses can become significant when  $\tau$  is scanned over a long range. However, in the experiments presented below, the signals fully decay by  $|\tau| < 40$  fs so the difference in the two pulse durations is never more than 0.02 fs. Alternate all-reflective approaches have been developed for applications in which the use of prism wedges is not a viable option [50].

In the language of perturbation theory, the first two field-matter interactions in the four-wave mixing process, which are associated with light absorption, occur with the pair of pulses derived from the pump beam. The non-radiative dynamics of interest (e.g., internal conversion, nuclear relaxation) take place in the delay between the second and third pulse,  $T$ . This is the delay normally scanned in a pump-probe experiment. Finally, signal emission is induced by the pulse 3. 2D Fourier transform spectroscopy differs from TG in that it additionally resolves the waveform associated with light absorption by scanning the experimentally controlled delay,  $\tau$ . Thus, dimensions corresponding to both light absorption,  $\omega_\tau$ , and signal emission,  $\omega_t$ , are obtained by Fourier transformation. TG experiments set  $\tau = 0$ , so the absorptive component of the TG signal field provides information equivalent to a conventional transient absorption experiment [12,13].

Sensitivity is one of the primary motivations for combining TG spectroscopy with interferometric detection instead of carrying out a traditional two-pulse transient absorption experiment. The central issue is that both the solute and solvent are readily ionized at excessive intensities when deep UV light is employed [78–80]. Fortunately, the signal of interest scales to a lower order in the incident light intensity than the undesired (multi-photon) photoionization processes. Thus, contributions of photoionization can be suppressed by using sufficiently low fluences. It has been shown

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