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Frequency Comb Spectroscopy from IR to XUV

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14. ABSTRACT

Key research highlights arising from the AFOSR funding support in 2017 include the following:
(1) Achieving phase-matching condition for high repetition rate XUV frequency comb generation. We recently submitted a paper titled 'Phase-matched extreme-ultraviolet frequency-comb generation' to Nature Photonics and it is accepted for publication now.
Laser-driven high-order harmonic generation (HHG) provides tabletop sources of broadband extreme-ultraviolet (XUV) light with excellent spatial and temporal coherence. These sources are typically operated at low repetition rates, less than 100 kHz, where phase-matched frequency conversion into the XUV is readily achieved.
However, there are many applications that demand improved counting statistics or frequency-comb precision afforded by operation at high repetition rates, > 10 MHz. Unfortunately, at such high repetition rates, phase matching is prevented by the accumulated steady-state plasma in the generation volume, setting stringent limitations on the XUV average power.
We have now solved this problem and reached, for the first time, phase matched XUV generation at high repetition rate. Specifically, we use gas mixtures at high temperatures as the generation medium to increase the translational velocity of the gas, thereby reducing the steady-state plasma in the laser focus. This allows phase-matched XUV emission inside a femtosecond enhancement cavity at a repetition rate of 77 MHz, enabling a record generated power of 2 mW in a single harmonic order.
This power scaling opens up many demanding applications, including XUV frequency-comb spectroscopy of few-electron atoms and ions for precision tests of fundamental physical laws and constants.
(2) A major accomplishment on frequency comb is the marriage of frequency comb spectroscopy with cold molecules. Cavityenhanced
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Final report to AFOSR on Grant FA9550-15-1-0111
"Frequency Comb Spectroscopy from IR to XUV"

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Abstract

Key research highlights arising from the AFOSR support for this research project are described in the following paragraphs. We note that all of the cited publications acknowledge the funding support from this AFOSR grant.

(A) Achieving phase-matching condition for high repetition rate XUV frequency comb generation. A key paper on "Phase-matched extreme-ultraviolet frequency-comb generation" has been published in Nature Photonics [1]. Laser-driven high-order harmonic generation (HHG) provides tabletop sources of broadband extreme-ultraviolet (XUV) light with excellent spatial and temporal coherence. These sources are typically operated at low repetition rates, less than 100 kHz, where phase-matched frequency conversion into the XUV is readily achieved. However, there are many applications that demand improved counting statistics or frequency-comb precision afforded by operation at a repetition rate that is higher than 10 MHz. Unfortunately, at such high repetition rates, phase matching is prevented by the accumulated steady-state plasma in the generation volume, setting stringent limitations on the XUV average power.
We have now solved this problem and reached, for the first time, phase matched XUV generation at high repetition rate. Specifically, we use gas mixtures at high temperatures as the generation medium to increase the translational velocity of the gas, thereby reducing the steady-state plasma in the laser focus. This allows phase-matched XUV emission inside a femtosecond enhancement cavity at a repetition rate of 77 MHz, enabling a record generated power of 2 mW in a single harmonic order.
This power scaling opens up many demanding applications, including XUV frequency-comb spectroscopy of few-electron atoms and ions for precision tests of fundamental physical laws and constants.

To accomplish this goal, we came up with a novel design of a continuous gas flow nozzle designed for high-power high-harmonic generation. We manufactured this nozzle in our own machine shop. In order to gain robustness against laser ablation, the nozzle is made of fused-silica glass. The small orifice enables high local pressures of up to 124 bars in the resulting supersonic beam. Moreover, the nozzle can be heated to high temperatures. All those features create an ideal gas environment for high-repetition rate high-harmonic generation, enabling to the highest ever harmonic yield reported. We published this work in Rev. of Scientific Instruments describe all the technical aspects, including systematic exploration of the final performance of high-harmonic generation in terms of maximum pressure and temperature [2].

(B) A major accomplishment on frequency comb is the marriage of frequency comb spectroscopy with cold molecules. Cavity-enhanced frequency comb spectroscopy in mid-infrared has demonstrated the powerful capability of combining high resolution, high sensitivity, and broad spectral coverage for molecule detections. Thus, frequency comb spectroscopy in our lab has provided fundamental understandings for large molecules where challenging questions remain for large amplitude motion and intramolecular vibrational coupling. This experimental platform also has the potential to open new molecular species and new kinetics for precise investigations, including the study of collisions of complex molecules, weakly bound clusters, and cold chemistry.

Indeed, we have recently broken new ground in demonstrating high-resolution quantum-state resolved spectroscopy of buckminsterfullerene C_{60} using an infrared frequency comb. A rotationally resolved spectrum of C_{60} has to date remained elusive, despite the very intense research into this molecule's chemical and physical properties since its discovery in 1985. Our approach utilizes cyrogenic buffer gas cooling of the output of a 1000 K effusive oven to prepare cold gas phase C_{60} molecules. We subsequently probe these with a frequency comb tuned to the 8.5 μm IR active fundamental. The combination of a high finesse absorption enhancement cavity and Fourier transform interferometry read-out provide sensitive, broadband detection, while retaining the high spectral resolution of the frequency comb light. Our initial results point to successful ground state vibrational cooling and observation of resolved rotational fine structure. We will soon undertake experimental modifications that we expect to improve the C_{60} number density and internal state cooling efficiency. However, the study of different buffer gas for cooling C_{60} is already an interesting topic. Because of its large total rovibrational energy (~5 eV) at room temperature, for C_{60} we have so far seen that helium is far less effective as a cooling gas than argon or neon. It will be important to understand these atom-molecule collisional processes so that we can cool C_{60} further down to 4 K. A scientific paper reporting these results was published in the journal Science in 2019 [3].

With the very active development of the optical frequency comb spectroscopy into valuable tools for broadband molecular diagnostics, we have seen remarkable advances for the measurement of complicated molecular spectra by improving the resolution, accuracy, sensitivity, and measurement times of spectrometric approaches. At the invitation of the chief editor of the Journal of Molecular Spectroscopy, we wrote a feature article where we trace some recent developments relevant to high-resolution spectroscopy of molecules, especially in the mid-infrared spectral region [4]. We discuss examples that harness the emerging techniques of cavity-enhanced frequency comb spectroscopy and dual-comb spectroscopy and we conclude with a perspective of forthcoming opportunities and challenges.

(C) We recently developed a powerful capability of time-resolved transient absorption at high spectral resolution based on the use of a mid-infrared optical frequency comb, making this technique invaluable for detecting transient chemical species with simultaneously high resolution in both the time and spectral domains. We applied this technique to the study of one of the most fundamental reactions, OH + CO, important for

both atmospheric and combustion chemistry. The reaction is complex due to the formation of the HOCO intermediate. With our transient comb spectroscopy we now directly detect *trans*-DOCO and *cis*-DOCO, the deuterated analogue of *trans*- and *cis*-HOCO, and their respective product yields at room temperature. Together with measurements of the $D+CO_2$ products, the measurement completes the understanding of this multistep reaction. With real-time measurements of the reaction kinetics, we now have direct access to the formation rate coefficients and branching ratios of all chemically accessible product species for this important reaction from beginning to end. Quantitative and mechanistically detailed understanding of the OH+CO reaction is a long sought-after goal in chemical kinetics. This reaction is comprised of multiple elementary chemical reactions that produce two transient intermediates (*trans*-HOCO and *cis*-HOCO) and products ($H+CO_2$) along the reaction path on a multidimensional potential energy surface. Despite intense and long-standing efforts from the physical chemistry community, the direct observation of *trans*-DOCO from OD+CO at thermal reaction conditions was only recently achieved and reported in Ref. [5]. That work represented the first experimental confirmation of the HOCO formation mechanism. To understand the full reaction mechanism we need to also observe *cis*-HOCO radical during this reaction process. Our new experimental observation now completes this chapter, as reported in Ref. [6].

Finally, to provide a complete spectroscopy description of these recently observed reaction transients, we use time-resolved, mid-IR direct frequency comb spectroscopy to obtain high-resolution rovibrational spectra of products produced from the OD + CO reaction. We present spectral analyses for isotopologues of the transient DOCO radicals from this reaction in the OD stretch region. The analyses were performed with the aid of two different theoretical approaches based on both perturbation theory and variational calculations used for prediction of rovibrational spectra of polyatomic molecules. This provides a basis to discuss the advantages and challenges of the current approach for studying spectroscopy and dynamics of transient molecules. The work reporting this result was published as a Cover for Molecular Physics [7].

(D) We have also just constructed a phase-stabilized 100 mW frequency comb near 10 μm. This is based on the development of a synchronously pumped femtosecond optical parametric oscillator (OPO) that produces an IR optical frequency comb with the highest average power in this wavelength region. A manuscript is in press that describes the detailed design of the frequency comb, and discusses potential applications for precise and sensitive direct frequency comb spectroscopy. This light source will be an invaluable tool for the scientific goals of high-resolution spectroscopy of large molecules and time-resolved detection of transient molecules [8].

We have also published an article on “comb-resolved spectroscopy with immersion grating in long-wave infrared” [9]. We report on the development of a novel dispersive spectrometer based on an immersion grating, a tool originally developed for infrared astronomy, applied to direct frequency comb spectroscopy at the long-wave infrared region of 8-10 μm. We report the detailed characterization of the spectrometer and discuss its current and potential applications for precise and sensitive molecular

spectroscopy. We have achieved the highest frequency resolution using a grating spectrometer in the long-wave infrared region and also demonstrated the capability for comb mode-resolved imaging. Considering the rapid development of frequency comb sources in the long wave infrared, and thanks to the broadband capability (λ = 2 to 11 μm) and high efficiency of the immersion grating, this spectrometer forms a critical component for future high-resolution spectroscopy and time-resolved detection of transient molecules when combined with cavity-enhancement and molecular cooling techniques.

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