

Article

Continuous-Wave Molecular Modulation Using a High-Finesse Cavity

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Abstract: We demonstrate an optical modulator at a frequency of 90 THz that has the capability to modulate any laser beam in the optical region of the spectrum. The modulator is constructed by placing deuterium molecules inside a high-finesse cavity and driving a vibrational transition with two continuous-wave laser beams. The two beams, the pump and the Stokes, are resonant with the cavity. The high intra-cavity intensities that build up drive the molecules to a coherent state. This molecular coherence can then be used to modulate an independent laser beam, to produce frequency up-shifted and down-shifted sidebands. The beam to be modulated is not resonant with the cavity and thus the sidebands are produced in a single pass.

Keywords: stimulated Raman scattering; Raman lasing; optical modulators; ultrafast physics; subfemtosecond pulses

1. Introduction

Over the last two decades, we have witnessed an explosion of interest and progress in ultrafast science [1]. Femtosecond time scale molecular dynamics (vibrational and rotational) are now routinely probed using commercially available laser systems. The advances in femtosecond lasers have also allowed the generation of soft X-ray subfemtosecond pulses using the technique of high harmonic generation (HHG) [2,3]. The frontiers of ultrafast science have now moved comfortably into the

subfemtosecond domain and electronic processes on these time scales are currently being studied. Despite this great progress, many researchers (including us) feel that key ingredients of ultrafast physics remain missing. We cannot yet produce optical waveforms with the same precision and flexibility with which we can produce electronic waveforms. We also have not yet been able to produce a coherent optical spectrum with a large number of precise laser beams that simultaneously cover the infrared, visible, and ultraviolet regions of the electromagnetic spectrum. Constructing such a device, typically referred to as an arbitrary optical waveform generator [4], has been one of the biggest unmet challenges in the field since the invention of the laser in 1960. This device would ideally produce fully coherent radiation ranging from 200 nanometers all the way up to 10 microns in wavelength (a “white-light” laser).

We believe that, if constructed, such a device would have important applications in a broad range of research areas, such as the following examples. (i) By phase locking the spectral components, one can synthesize subfemtosecond pulses in the optical region of the spectrum [5–8]. Although, as mentioned above, subfemtosecond pulses are now routinely produced in the soft X-ray region of the spectrum using HHG, synthesizing such pulses in the more accessible optical region will increase their utility and impact. (ii) By appropriately adjusting the phases and the amplitudes of the Fourier components, one can synthesize arbitrary optical waveforms, such as a square waveform or a sawtooth waveform, on subfemtosecond time scales. Such sub-cycle pulse shaping will likely extend the horizons of coherent and quantum control to a completely new regime [9–11]. (iii) A continuous-wave (CW) white-light laser with narrow linewidth spectral components would allow precision spectroscopy of a large number of molecular and atomic species [12]. Furthermore, the whole spectrum could be locked to a reference so that the absolute frequency of each component is known to a high precision. Using this approach, it may be possible to construct optical clocks in different regions of the spectrum or to generate a broad absolute frequency reference with components covering the full optical region.

One of the most promising techniques for the construction of an arbitrary optical waveform generator is the technique of *molecular modulation* [13–17]. This technique utilizes coherent vibrations and rotations in molecules to produce a broad Raman spectrum covering many octaves of bandwidth. A subset of such a spectrum has recently been used to synthesize optical waveforms with sub-cycle resolution [18–20]. In this technique, the molecules are driven to a highly coherent state using two intense laser beams, the pump and the Stokes. Because of the high intensities required for efficient modulation, experiments have traditionally been performed using Q-switched pulsed lasers. The extension of the molecular modulation technique to the CW domain would allow for each spectral component to have a very narrow frequency linewidth. Such precision is required in spectroscopy and many other applications. Over the last five years, we have been working towards accomplishing this goal. To achieve the intensities required by the molecular modulation technique with CW lasers, our approach has been to place the molecules inside a cavity with a high finesse at the pump and at the Stokes wavelengths [21–27]. Our prior experiments have demonstrated CW stimulated Raman scattering in a previously inaccessible regime: at very low gas pressures with an established CW molecular coherence more than two orders of magnitude larger than previously achieved [28]. Of particular importance, we have demonstrated for the first time that this approach can produce a broad spectrum in wavelength regions where the cavity mirrors are not reflective [29–31].

In this paper, building on our earlier work, we report two experimental results. (i) We have constructed an optical modulator that can modulate any laser in the optical region of the spectrum with a modulation frequency of 90 THz. The modulator is prepared by driving a vibrational transition in molecular D₂ using the resonant pump and the Stokes beams in the cavity. With the molecules coherently prepared, a separate laser beam passes through the molecular gas cell and is modulated in a single pass. (ii) We have achieved locking of two independent laser beams to the cavity (the pump and the Stokes) and observed Raman generation as we varied the two-photon detuning. This is the first experiment where a CW molecular modulator is prepared using two independent laser beams. These results show considerable promise for fully extending the molecular modulation technique to the CW domain. Specifically, they open up the prospect of using a molecular modulator to broaden the spectrum of a broadband laser (such as a Ti:sapphire femtosecond oscillator), which we will discuss below.

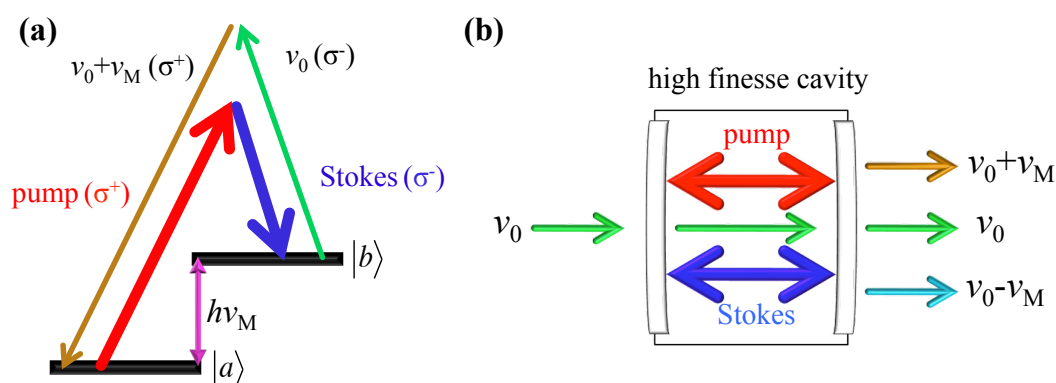
2. Molecular Modulation

The technique of molecular modulation differs from traditional stimulated Raman scattering [32–37] in that it relies on Raman generation in the regime of near maximal coherence. Figure 1a shows a simplified energy level diagram for a typical molecular system (for example, D₂). Here state $|a\rangle$ is the ground rotational-vibrational state of the molecule and state $|b\rangle$ is a particular excited rotational-vibrational state. The two excitation lasers (the pump and the Stokes) drive the coherence (off-diagonal density matrix element ρ_{ab}) of the Raman transition. When the driving lasers are sufficiently intense, it becomes possible to coherently transfer almost half of the population to the excited state, thus approaching the state of maximum coherence, $|\rho_{ab}| \approx 1/2$. The concept of maximum coherence has gained considerable attention over the last two decades. It is now understood that for nonlinear mixing processes, the generation efficiency is maximized for a maximally coherent state [38–41]. Furthermore, because the generation process is almost complete in a single coherence length, phase-matching is unimportant and new beams are generated collinearly.

When the molecules are driven to a highly coherent state, they act as an efficient frequency mixer with the modulation frequency determined by the oscillation frequency of the molecules, $\nu_M = \nu_{\text{pump}} - \nu_{\text{Stokes}}$. For linearly polarized driving laser beams, the driving lasers themselves can be modulated to produce higher-order Stokes and anti-Stokes sidebands through four-wave mixing. In addition to the driving lasers, the system can also be used to modulate any other laser beam. As shown in Figure 1, a separate laser (called the mixing beam) with frequency ν_0 can be modulated to produce frequency upshifted (anti-Stokes) and downshifted (Stokes) sidebands at frequencies $\nu_0 + \nu_M$ and $\nu_0 - \nu_M$, respectively. If the process is highly efficient or a multi-pass configuration is used, a very broad Raman spectrum can be produced with frequencies of the form $\nu_0 + q\nu_M$ (q is an integer). Using the molecular modulation technique with pulsed lasers, several groups have demonstrated the generation of a wide spectrum in molecular H₂ and D₂ [14–17] and have synthesized the first optical pulses to break the single-cycle barrier [18–20]. These experiments currently hold the world record for the shortest pulses ever synthesized in the optical region of the spectrum. When the driving laser beams are opposite circularly polarized, as is the case in Figure 1a, the generation of sidebands from the driving lasers themselves is suppressed due to angular momentum conservation rules [42]. In this regime, a frequency

upshifted or downshifted sideband from an appropriately-polarized mixing beam will be produced, and the molecular medium can be used as an efficient frequency converter. Further details regarding the molecular modulation technique can be found in a number of review articles [43–45].

Figure 1. (a) Simplified energy level diagram. Two intense lasers, the pump and the Stokes, drive the Raman transition and establish the molecular coherence, ρ_{ab} . The molecules can then be used to modulate any other mixing laser with frequency ν_0 to produce frequency upshifted or downshifted sidebands at frequencies $\nu_0 + \nu_M$ and $\nu_0 - \nu_M$, respectively. With the polarization configuration as shown, only a frequency upshifted sideband is produced. (b) Molecular modulation with CW laser beams. The molecules are placed inside a cavity with a high finesse at the pump and at the Stokes wavelengths. For a sufficiently large molecular coherence, any mixing laser incident on the cavity will be modulated. The mixing beam does not need to be resonant with the cavity as the modulation is produced in a single pass through the system.



2.1. Molecular Modulation with CW Lasers

Despite these exciting experiments, molecular modulation technique as demonstrated in these experiments has significant limitations and has not yet made a big impact on other research areas. The required laser intensities for preparing the molecules into a maximally coherent state is quite high, exceeding 100 MW/cm^2 . As a result, all of those molecular modulation experiments described in the previous paragraph have been performed using Q-switched pulsed lasers, which have important limitations. The duty cycle of these lasers is low, less than 1 part in 10^7 , which severely restricts data rates. Furthermore, each sideband has a minimum linewidth that is determined by the duration of the Q-switched pulse, $1/(10 \text{ ns}) \approx 100 \text{ MHz}$. This is an important limitation for precision spectroscopy experiments where the transitions studied may have linewidths on the Hz level. To overcome these limitations, it is important to extend the molecular modulation technique to the CW domain.

For extending the technique to the CW domain, two approaches are promising. One approach is to utilize the tight confinement of hollow-core photonic crystal fibers, an approach that has been studied by Benabid and colleagues [46]. In contrast, our approach is to place the molecules inside a cavity with high finesse at the pump and at the Stokes wavelengths, as shown in Figure 1b. When the cavity resonance condition is simultaneously satisfied for both laser beams, high intensities build up inside the cavity and the molecules are driven to a highly coherent state. If the pump and the Stokes beams are

linearly polarized, higher-order Stokes and anti-Stokes beams from the driving lasers will be produced. A separate weaker mixing laser can also be modulated in a single pass through the system. Our scheme was motivated by the recent pioneering experiments of Carlsten and colleagues that have demonstrated CW Raman lasing of the Stokes beam inside a high-finesse cavity [21–26,35]. We have extended these experiments to the regime of sufficiently high coherence such that significant modulation can be produced in a single pass through the system. As a result, the mixing beam does not need to be resonant with the cavity, and any optical wavelength can be modulated. This broadband modulation capability is critical, as it may allow for the broadening of the already broad spectrum of a Ti:sapphire oscillator.

3. Experiment: 90 THz CW Modulator

In this section, we discuss our optical modulator with a modulation frequency of 90 THz that is capable of modulating any beam in the optical region of the spectrum. Optical modulators typically utilize nonlinear optical processes in crystals, such as electro-optic and acousto-optic effects. Such modulators have recently achieved modulation rates approaching 100 GHz; yet, due to intrinsic limitations of electronic components, crystal-based approaches may remain unable to achieve much higher modulation rates. In contrast, we have recently demonstrated a modulator at a frequency of 17.6 THz using a rotational transition in molecular H_2 [30]. The experiment that we describe in this section extends our earlier result to a higher modulation rate of 90 THz by using a vibrational transition in molecular D_2 .

A schematic of our experiment is shown in Figure 2. We prepare the molecules to a highly coherent state inside a high-finesse cavity with two intense laser fields, the pump and the Stokes, at wavelengths of 1.064 μm and 1.555 μm , respectively. The experiment starts with locking the pump laser beam to one of the cavity modes. For sufficiently high intra-cavity pump laser intensity, the Stokes laser beam is produced through Raman lasing into a cavity mode. We utilize the $|\nu = 0, J = 0\rangle \rightarrow |\nu = 1, J = 0\rangle$ vibrational Raman transition in D_2 , which has a transition frequency of 90 THz. With the molecules prepared in a coherent state, a third, weaker laser beam at a wavelength of 785 nm passes through the system. This mixing beam is modulated to produce frequency up-shifted and down-shifted sidebands at wavelengths of 636 nm and 1026 nm, respectively. The mirrors of the cavity do not have a high reflectivity at 785 nm, thus the modulation is produced in a single pass through the system.

To produce the desired high power pump laser beam, we start with a custom-built external cavity diode laser (ECDL) with an optical power of 20 mW and a free-running linewidth of about 0.5 MHz. We amplify the ECDL output with an ytterbium fiber amplifier centered at 1.064 μm . The amplifier produces a linearly-polarized, single-spatial and single frequency mode output with a maximum power of 20 W. The amplified beam is then coupled to the TEM_{00} mode of the high-finesse cavity using a mode matching lens (MML). The mirrors of the high-finesse cavity have high damage threshold coatings with high reflectivity near wavelengths of 1.06 μm and 1.55 μm . The transmittance of the mirrors at the two wavelengths are about 50 parts per million (ppm) and the total scattering and absorption losses are at the level of 100 ppm. One of the cavity mirrors is mounted on a piezoelectric transducer to allow for slight adjustments of the cavity length. We use the Pound–Drever–Hall (PDH) technique to lock the amplifier output to the cavity [47]. For this purpose, the ECDL passes through an electro-optic modulator (EOM)

and the cavity reflected signal is picked off with a glass slide (GS) to produce electronic feedback to the ECDL frequency and the cavity length. The mirrors are housed in a vacuum chamber, which is machined from stainless steel with an inner tube diameter of 5 cm. The central 50 cm-long region of the chamber is surrounded by a liquid N₂ reservoir. Cooling the molecules reduces Doppler broadening and greatly increases the population of the ground rotational level [14]. The mixing beam is produced by a separate 785 nm ECDL whose output is amplified by a semiconductor tapered amplifier. The optical power in the mixing beam before the cavity is about 100 mW. The motivation for amplifying the mixing beam is to increase the optical power of the generated sidebands to more easily detectable levels.

Figure 2. The simplified schematic of our experiment. We start the experiment by locking a high-power pump laser beam to one of the axial modes of the cavity. With the pump laser locked, the Stokes beam is produced through Raman lasing. The pump and the Stokes beams drive the molecular coherence, which can then be used to modulate a separate 785-nm laser beam in a single pass. ECDL: external cavity diode laser, EOM: electro-optic modulator, Yb FA: ytterbium fiber amplifier, PBS: polarizing beam splitter, GS: glass slide, PD: photo-diode, MML: mode-matching lens, HFC: high-finesse cavity, TA: tapered amplifier, DM: dichroic mirror, G: grating, BB: beam block.

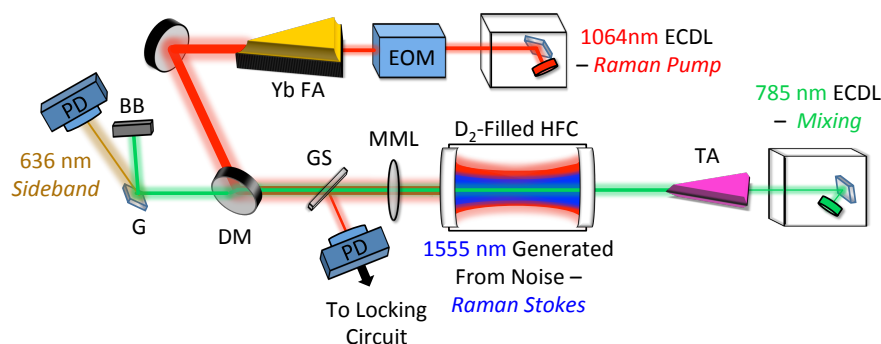
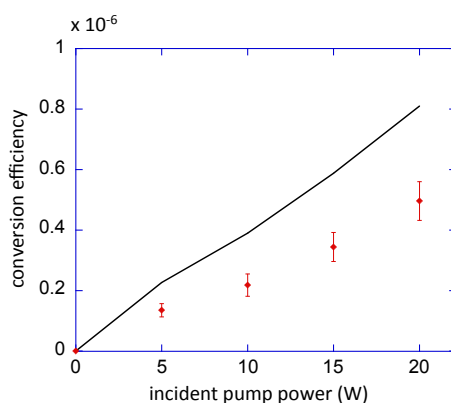


Figure 3 shows the power conversion efficiency from the mixing beam to the frequency up-shifted sideband at a wavelength of 636 nm, as the incident pump power is varied. For this measurement, the D₂ pressure is held constant at 0.3 atm. The highest conversion efficiency that we achieve is 0.5×10^{-6} . Although the conversion efficiency is low, this is the first time CW modulation of an independent laser at such a high rate has been demonstrated. In addition to the measurement of Figure 3, as we vary the incident pump power, we also measure the transmitted pump and Stokes powers through the cavity. Similar to our previous experiments, the transmitted pump power stays constant at about 1 mW, whereas the transmitted Stokes power increases linearly to a maximum of about 7 mW as we increase the input pump power. From the transmitted power measurements, we can calculate the intra-cavity circulating intensities for the pump and the Stokes beams using the mirror transmittance and the known cavity mode size. The maximum calculated intra-cavity intensities for the pump and Stokes lasers are 10 kW/cm² and 62 kW/cm², respectively. The solid line in Figure 3 shows the calculated conversion efficiency using the estimated intra-cavity pump and Stokes intensities. There are no adjustable parameters in this calculation; *i.e.*, all parameters that are used are experimentally measured. We observe reasonable agreement between the experimental data points and the calculations. The disagreement is likely due

to the imperfect spatial overlap of the 785-nm beam with the TEM₀₀ mode of the cavity. This spatial overlap is difficult to measure precisely in our experiment and the calculations do not take this effect into account. The predicted largest value for the molecular coherence that we achieve in this experiment is $|\rho_{ab}| = 2.5 \times 10^{-5}$.

Figure 3. The conversion efficiency from the mixing beam to the 636 nm anti-Stokes sideband as the incident pump power is varied at a constant D₂ pressure of 0.3 atm. The solid line is a theoretical calculation without any adjustable parameters, based on the measured transmitted powers of the pump and the Stokes beams through the cavity.



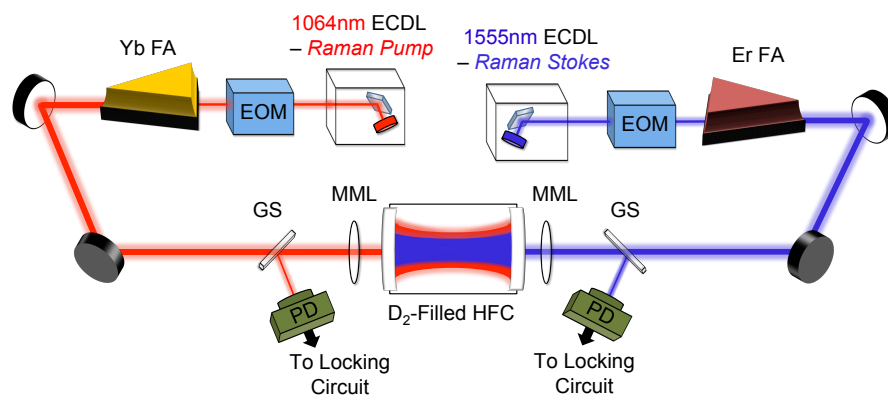
Currently, the conversion efficiency in this experiment is limited by the intra-cavity pump and Stokes laser intensities. One drawback of the current experiment is that we rely on Raman lasing to generate the Stokes beam. As a result, the pump and the Stokes intra-cavity intensities are limited by the dynamics of Raman lasing. This drawback can be overcome by locking two independent laser beams to the cavity, rather than relying on Raman lasing, an approach we discuss in the next section.

4. Experiment: Preparing Molecules with Two Independent CW Laser Beams

In this section, we discuss our experiment where we have prepared the molecular coherence by using two independent laser beams. Figure 4 shows the simplified schematic of this experiment. Similar to the pump laser, the Stokes laser system starts with an ECDL, but now near a wavelength of 1.55 μm . We amplify the Stokes ECDL output to 20 W with an erbium-doped fiber amplifier. A PDH setup similar to that of the pump laser keeps the Stokes beam resonant with the cavity. When we lock both lasers to the cavity and adjust the frequency difference of the two lasers to within about a GHz of the Raman transition resonance, $\nu_{\text{pump}} - \nu_{\text{Stokes}} \approx \nu_{ab}$, the two beams efficiently drive the molecular coherence. The established molecular coherence then mixes with the driving lasers to produce the anti-Stokes and second Stokes sidebands at wavelengths of 807 nm and 2.94 μm , respectively. These sidebands are only observed when the lasers are tuned to within about 1 GHz of the Raman transition. For these experiments, we reduce the gas pressure to a sufficiently low value such that Raman lasing on the vibrational Stokes beam is negligible; *i.e.*, if we lock only the pump laser to the cavity there is no substantial Raman generation. The Raman lasing needs to be suppressed because the Stokes beam generated through Raman lasing interferes with the cavity lock of the 1.55 μm beam. Figure 5 shows the power of the generated 807 nm

anti-Stokes beam as a function of the two-photon detuning at a molecular gas pressure of 0.01 atm. This pressure value is about three orders of magnitude lower than those traditionally used in stimulated Raman scattering experiments. It is important to note that, just as in the 90 THz mixing experiment described above, the cavity mirrors do not have a high reflectivity at the anti-Stokes wavelength, so the 807 nm beam is generated in a single pass through the system. We generate a maximum CW anti-Stokes power exceeding 1 mW, which is an order of magnitude larger than our previous experiments that relied on Raman lasing to generate the Stokes beam [30]. The predicted established molecular coherence in this experiment is more than an order of magnitude higher than what was achieved in the mixing experiment, $|\rho_{ab}| \approx 1 \times 10^{-3}$. Although the established molecular coherence in this experiment is much higher, we have not yet been able to translate this increase into an increase in the mixing efficiency experiment of the previous section. When we increase the molecular gas pressure, the dynamics of Raman lasing and instabilities in the locking performance substantially reduce the intra-cavity intensities for the pump and the Stokes beams.

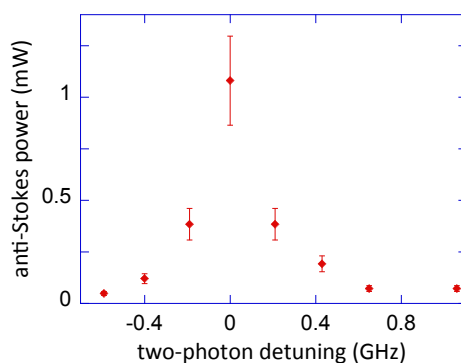
Figure 4. Simplified schematic for the two-beam experiment. We start with two external cavity diode lasers at the pump and at the Stokes wavelengths. Each beam is amplified to an output power of 20 W using a fiber amplifier. The amplified beams are then coupled to the high-finesse cavity using mode matching lenses. We use the Pound–Drever–Hall technique to lock the amplifier outputs to the cavity. ECDL: external cavity diode laser, EOM: electro-optic modulator, Yb FA: ytterbium-doped fiber amplifier, Er FA: erbium-doped fiber amplifier, GS: glass slide, MML: mode matching lens, PD: photo-diode, HFC: high-finesse cavity.



One of our immediate goals is to increase the established molecular coherence and operate at higher pressures in the two-beam setup and thereby increase the mixing efficiency. We believe that the intra-cavity intensities in our experiment are currently limited by the large free-running linewidths of the ECDLs (about 0.5 MHz) and by imperfect locking electronics. Due to these limitations, we are able to couple at best 10% of the incident power in each laser beam to the cavity. To overcome these limitations, we plan to pursue the following technical improvements in our setup in the near future: (i) constructing better ECDLs with free-running linewidths of about 50 kHz [48]; (ii) pre-stabilizing the ECDLs with separate low-finesse cavities so that their free-running linewidths are considerably reduced [49]; and (iii) increasing the bandwidth of the locking electronics and better understanding the limitations of the feedback circuit [50,51]. With these improvements, our goal will be to achieve intra-cavity intensities

approaching the damage threshold of the mirror coatings (about 100 MW/cm²). CW optical intensities exceeding 100 MW/cm² inside a high-finesse cavity have recently been experimentally demonstrated for high-quality dielectric coatings [52]. Our experience with these coatings has been consistent with this recent experiment since we have been able to routinely obtain intensities exceeding 10 MW/cm² in an empty chamber (without any molecular gas) without any apparent degradation in mirror performance. With both the pump and the Stokes beams locked to the cavity with circulating intensities of about 100 MW/cm², the established molecular coherence will be $|\rho_{ab}| \approx 0.01$, more than an order of magnitude higher than what we have achieved to date. We can then use the system to modulate a separate weak mixing laser to produce frequency upshifted and downshifted sidebands. We would then have a 90 THz modulator with a single-pass conversion efficiency approaching 10% over much of the optical region of the spectrum. As described in the next section, such an efficient broadband modulator has exciting potential applications.

Figure 5. The power of the 807 nm anti-Stokes beam as a function of two-photon Raman detuning, $(\nu_{\text{pump}} - \nu_{\text{Stokes}}) - \nu_{ab}$, at a D₂ gas pressure of 0.01 atm. At these low pressures, Doppler broadening is the dominant contribution to the linewidth. The two-photon detuning is varied by locking either the pump or the Stokes beam to a different cavity mode. As a result, the data points are spaced in frequency by the free spectral range of the cavity, which is 200 MHz.

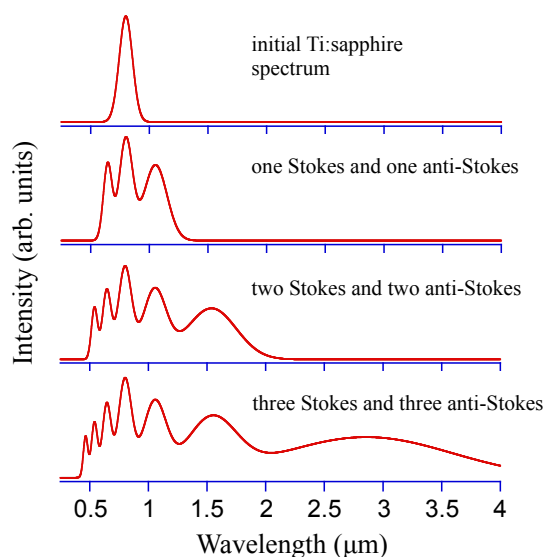


5. Modulation of a Femtosecond Ti:sapphire Oscillator

One of the main motivations for extending molecular modulation to the CW domain is that it would allow combining this technique with femtosecond Ti:sapphire laser technology. The idea is that the modulator can be used to efficiently generate sidebands on a femtosecond oscillator to produce a broad spectrum with a large number of spectral components. This scheme was first suggested by Kien *et al.* [53], and was later experimentally demonstrated with Q-switched pulsed lasers by Marangos and colleagues [54–56]. Consider a broadband laser with power spectral density $F(\nu)$. If this laser goes through a molecular medium that is prepared in a highly coherent state, modulation produces sideband “replicas” of the spectrum spaced from the original by the modulation frequency. The first Stokes and anti-Stokes sidebands will produce replicas $F(\nu - \nu_M)$ and $F(\nu + \nu_M)$, the second orders will produce $F(\nu - 2\nu_M)$ and $F(\nu + 2\nu_M)$, and this process could continue until the spectrum fills the full optical

range. Figure 6 shows how the scheme works for a typical broadband Ti:sapphire laser oscillator with a spectrum that spans from about 700 nm to 900 nm in wavelength. In this qualitative calculation, we use the vibrational transition in D_2 ($\nu_M = 90$ THz) to produce sidebands and broaden the Ti:sapphire spectrum. To show the effect more clearly, we assume 60% conversion efficiency to each sideband, although as mentioned above, in the near future, we will aim for about 10% conversion efficiency with $|\rho_{ab}| \approx 0.01$. Intensity spectra (in linear scale) for the incident Ti:sapphire beam and for first, second, and third order modulation are shown.

Figure 6. Broadening the spectrum of a Ti:sapphire laser using the vibrational transition in D_2 with $\nu_M = 90$ THz. Starting with a typical broadband laser with power spectral density, $F(\nu)$, replicas of the spectrum spaced by the Raman transition frequency are produced. Here we follow the process up to three Stokes and anti-Stokes sidebands, *i.e.*, the final spectrum includes contributions from $F(\nu - 3\nu_M)$, $F(\nu - 2\nu_M)$, ..., $F(\nu + 3\nu_M)$. In this calculation, we assume 60% conversion efficiency to each sideband.



A key advantage of this approach, and the feature that sets it apart from similar previous work, is that since the molecules are prepared with two CW lasers, the linewidth of the molecular oscillations can be made very narrow. When the two driving lasers are locked to the high-finesse cavity, their linewidths can be narrowed to values much smaller than 1 kHz. This also sets the linewidth of the molecular oscillations (*i.e.*, the precision in the value of ν_M). As a result, the mixing process will not significantly affect the spectral characteristics of the individual comb lines of the Ti:sapphire oscillator. Many of the ideas and experiments that use stable Ti:sapphire comb lines may be performed with the much broader spectrum of Figure 6. We also note that the broad output spectrum of Figure 6 can form a phase-stabilized frequency comb. This can be accomplished by adjusting the modulation frequency ν_M to be an exact integer multiple of the comb-spacing of the Ti:sapphire laser. The modulation frequency is precisely set by the frequencies of the pump and the Stokes laser beams, $\nu_M = \nu_{\text{pump}} - \nu_{\text{Stokes}}$. The pump and Stokes laser beams can, for example, be locked to two teeth of a separate phase-stabilized frequency-comb oscillator.

We note that throughout this section, we have assumed the Ti:sapphire laser to be sufficiently weak such that it does not interfere with the molecular state preparation. This assumption is satisfied for a

typical femtosecond oscillator (1 nanojoule energy per pulse, 20 femtosecond pulse width, 100 MHz repetition rate). For many applications such as quantum control, nanojoule per pulse level energies will not be sufficient. For such applications, an amplified Ti:sapphire system (larger than 1 microjoule energy per pulse, about 10 kHz repetition rate) can be used as a mixing laser. The peak power of such lasers is quite high, and these pulses would interfere with the molecular state preparation by the pump and the Stokes laser beams. To overcome this problem, one idea would be to chirp the pulse so that its peak power is greatly reduced. In the spirit of the technique of *chirped pulse amplification*, peak power can be dramatically reduced by stretching the pulses to picosecond times scales. Also, for modulating amplified Ti:sapphire systems, pulsed molecular modulators such as those utilizing photonic crystal fibers may be used [57].

We conclude this section by noting that there are other schemes that can be used to broaden the spectrum of a Ti:sapphire laser. Early experiments used nonlinear self-phase modulation inside a photonic crystal fiber to broaden the Ti:sapphire spectrum [58,59]. Recently, multi-octave broadband spectra and single-cycle pulse synthesis have been demonstrated using a number of approaches including coherently combining the supercontinuum output from multiple highly nonlinear fibers and using multiple optical parametric amplifiers seeded by a common laser source [5–8]. These are exciting developments that may eventually allow for the synthesis of arbitrary optical waveforms. However, we believe that the simplicity and the coherent nature of the molecular modulation process make it the most promising route for constructing an arbitrary optical waveform generator. As mentioned before, the molecular modulation technique was the first to synthesize single-cycle pulses and this technique still holds the world record for the shortest pulses that have ever been synthesized in the optical region of the spectrum [18–20].

6. Conclusions and Future Directions

In conclusion, we have discussed constructing an optical modulator at a frequency of 90 THz that has the capability of modulating any laser in the optical region of the spectrum. We also have discussed the initial results of our efforts to prepare the molecular modulator using two independent lasers locked to the modes of a high-finesse cavity. These results are significant steps towards extending the molecular modulation technique to the CW domain. The long-term goal of our project is to use the molecules to frequency broaden the spectrum of a Ti:sapphire oscillator as shown in Figure 6. If successful, this approach may produce a broad CW spectrum covering the full optical region with millions of spectral components. We next discuss some of the exciting potential applications of such a source.

6.1. Temporal Waveform Synthesis

Once a very broad spectrum with millions of spectral components is produced, the next challenge will be to synthesize temporal waveforms using pulse-shaping techniques [60,61]. The full optical spectrum (from 200 nm to 10 microns) is much broader than the typical spectra used in pulse-shaping experiments. Because of the large bandwidth of the spectrum, arbitrary temporal waveform synthesis will likely be a challenging task, and there are a number of open questions. To adjust the phases and the amplitudes of components over such a broad spectrum, one approach would be to use piezo-driven moveable metal

mirrors [62–64] and to work with a reflective geometry. These mirrors have a high reflection coefficient over the full optical region, and recent advances in fabrication allow for a large number of individually adjustable pixels. For the infrared region of the spectrum where the wavelength is large, the limited range of piezo-motion might be an issue. To overcome this limitation, an acousto-optic pulse shaper may be used for the infrared wavelengths [65]. A key component of pulse-shaping techniques is a nonlinear detector that allows measurement of the synthesized waveform through correlation studies. This is traditionally a thin nonlinear crystal where the second harmonic signal as a function of time delay reveals the temporal structure. However, for a very broad spectrum, crystals cannot be used; a nonlinear detector with a wide bandwidth is required. The nonlinear processes in noble gases have a sufficiently large bandwidth for this purpose. For example, the experiments of the Harris group used multi-photon ionization and sum frequency generation in Xe atoms to characterize ultrafast pulses [18].

6.2. Frequency Reference and Precision Time-Keeping

There is a growing demand for constructing clocks with improved precision. Recent advances in optical clocks have yielded frequency stabilities exceeding 1 part in 10^{15} , surpassing the precision of Cs atomic clocks [66–68]. Optical clocks utilize ultra-stable lasers that are locked to very narrow atomic transition lines. With a CW molecular modulator, it may be possible to extend the frequency stability of an optical clock to the full optical spectrum. As previously mentioned, a key advantage is that since the molecules are prepared with two CW lasers, the linewidth of the molecular oscillations can be made very narrow. The frequencies of the two driving laser beams, ν_{pump} and ν_{Stokes} , can in principle be locked to optical reference lines (such as to two teeth of a stabilized, frequency-comb Ti:sapphire laser). As a result, the absolute frequency of the molecular oscillations, $\nu_M = \nu_{\text{pump}} - \nu_{\text{Stokes}}$, would be known to a very high precision (potentially approaching a precision at the level of 1 part in 10^{15}). The idea then would be to use a frequency stabilized mixing beam so that all mixing orders with frequencies $\nu_0 + q\nu_M$ have an absolute frequency stability on the 1 part in 10^{15} level. As discussed above, we could also use a Ti:sapphire laser as a mixing beam. For this case, if the Ti:sapphire laser is absolute frequency stabilized (a frequency comb), the generated spectrum of Figure 6 will be an absolute frequency reference covering the full optical region. We believe this would constitute a light source with many exciting applications in a number of research areas. For example, one can perform precision spectroscopy of a large number of atomic and molecular species from a single source. One would also be able to construct optical clocks in regions of the spectrum that are currently inaccessible.

6.3. Coherent Control

Over the last decade, quantum and coherent control has emerged as an exciting sub-field of atomic, molecular, and optical physics [69–71]. It is now understood that efficient control of a quantum system requires laser light with a broad spectrum with frequencies that match as many transitions in the system as possible [72]. Using arbitrary optical waveforms with a spectrum ranging from 200 nm to 10 μm in wavelength, one can simultaneously control the electronic, vibrational, and rotational coordinates of molecules. This will facilitate the understanding of various couplings between different coordinates of the system. For example, one possibility is to study the ionization of a molecule as a function of the

vibrational coordinate. This cannot be done with only the soft X-ray pulses provided by HHG since their spectrum does not have the infrared wavelengths that are needed to efficiently control the slow vibrational coordinate.

The ability to shape the pulse beyond the slowly-varying envelope approximation will likely extend the ideas of coherent control to a completely new regime. Currently, because of the limited bandwidth of laser sources, coherent control experiments are done in the quasi-steady-state regime, in which the electric field of the laser light cycles back and forth many times before its envelope changes. Sub-cycle pulse shaping allows true manipulation of the electric field itself instead of just the envelope, providing a completely new tool. Up until now, sub-cycle pulses have only been available in the THz region of the spectrum. These pulses have been used for many pioneering experiments in Rydberg atoms in which the Rydberg wave-packets are precisely controlled [73,74]. Extending sub-cycle pulses to the optical region of the spectrum will extend these experiments to electronic wave-packets with much shorter characteristic time scales. As demonstrated by the recent exciting experiments from the HHG community [75], there remains much to be understood about the ultrafast dynamics of electronic motion and its coupling to other coordinates.

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Author Contributions

D. D. Yavuz supervised the research, designed the experiments, and wrote the text. D. C. Gold and J. J. Weber performed the experiments, took the data, and edited the text. All authors contributed to the interpretation of the experimental results.

Conflicts of Interest

The authors declare no conflict of interest.

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