a. REPORT
| 14-05-2011 |
| Final Report |

b. ABSTRACT
Potential for terahertz/optical, two color non-linear sensing of liquid biochemical agents

5a. CONTRACT NUMBER
W911NF-06-1-0241

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
306033

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of California - Santa Barbara
Office of Research
The Regents of the University of California
Santa Barbara, CA 93106 -2050

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
48949-EL-CDP.6

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
A high-sensitivity setup for the observation of X(2)-based, terahertz/optical, sum and difference frequency generation in liquids is presented. It relies on launching wavefront modulated terahertz radiation into a liquid traversed by an optical beam. Phase matching and polarization selection rules can be tuned to support three wave mixing via either chiral allowed electric dipole processes or higher order quadrupole/magnetic dipole processes. Under nonresonant excitation, hyperpolarizabilities from quadrupole/magnetic dipole processes are measured.

15. SUBJECT TERMS
terahertz, optical mixing, secondorder nonlinearity, liquid

16. SECURITY CLASSIFICATION OF:
a. REPORT
UU
b. ABSTRACT
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c. THIS PAGE
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17. LIMITATION OF ABSTRACT
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18. SECURITY CLASSIFICATION OF: 

19a. NAME OF RESPONSIBLE PERSON
Silas Allen

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805-893-7134
ABSTRACT
A high-sensitivity setup for the observation of X(2)-based, terahertz/optical, sum and difference frequency generation in liquids is presented. It relies on launching wavefront modulated terahertz radiation into a liquid traversed by an optical beam. Phase matching and polarization selection rules can be tuned to support three wave mixing via either chiral allowed electric dipole processes or higher order quadrupole/magnetic dipole processes. Under nonresonant excitation, hyperpolarizabilities from quadrupole/magnetic dipole processes are measured. Since this approach does not require terahertz transmission through macroscopic thicknesses of water, it has the potential to open a new window on the terahertz dynamics of water solvated molecules.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)
Number of Papers published in peer-reviewed journals: 1.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)
Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations
Number of Presentations: 0.00
Non Peer-Reviewed Conference Proceeding publications (other than abstracts):
Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0
Peer-Reviewed Conference Proceeding publications (other than abstracts):
Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts
Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded
Awards

Feodor Lynen Fellowship (for Thomas Feil)

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### Graduate Students

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### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

- The number of undergraduates funded by this agreement who graduated during this period: ...... 0.00
- The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00
- Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00
- Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ...... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

### Names of Personnel receiving masters degrees

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Names of personnel receiving PHDs

| NAME | Total Number: |

Names of other research staff

| NAME | PERCENT_SUPPORTED | FTE Equivalent: | Total Number: |

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

We succeeded for the first time to observe sum and difference frequency mixing between optical and terahertz radiation from a liquid. Although we anticipated that this would be allowed only in molecules that have chiral symmetry, and thus be a signature of biological molecules, we discovered that the dominant mechanism was electric quadrupolar allowed sum and difference frequency mixing.

Technology Transfer
Terahertz/optical sum and difference frequency generation in liquids

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(Received 18 June 2010; accepted 18 January 2011; published online 9 February 2011)

A high-sensitivity setup for the observation of $\chi^{(2)}$-based, terahertz/optical, sum and difference frequency generation in liquids is presented. It relies on launching wavefront modulated terahertz radiation into a liquid traversed by an optical beam. Phase matching and polarization selection rules can be tuned to support three wave mixing via either chiral allowed electric dipole processes or higher order quadrupole/magnetic dipole processes. Under nonresonant excitation, hyperpolarizabilities from quadrupole/magnetic dipole processes are measured. Since this approach does not require terahertz transmission through macroscopic thicknesses of water, it has the potential to open a new window on the terahertz dynamics of water solvated molecules. © 2011 American Institute of Physics. [doi:10.1063/1.3552964]

Chiral sum and difference frequency generation (SDFG) has been shown to be a competitive tool for the vibrational spectroscopy of liquids and solutions in the infrared frequency band. To explore the lowest frequency macro- molecular modes of biomolecules, which occur at terahertz frequencies, in life’s natural environment—water, we have developed a high-sensitivity approach for detecting nonlinear mixing of terahertz and optical radiation in liquids. This approach is motivated by the difficulty encountered doing conventional terahertz absorption spectroscopy caused by the overwhelming absorption of the water solvent.\textsuperscript{1,2} Furthermore, we wish to exploit the fact that nonlinear, sum and difference frequency generation, a $\chi^{(2)}$-process, is largely suppressed in liquids but may be activated by the intrinsic chiral symmetry of biomolecules.\textsuperscript{3} The approach described in the following letter has the potential for circumventing the strong terahertz absorption of the solvent, potentially select for chiral biomolecules, and be doubly resonant with electronic excitations and macromolecular vibrations.

A configuration that optimizes SDFG in the face of strong terahertz absorption by water is shown in Fig. 1. A metal grating (gold) of period $d=2\pi/k_G$ is fabricated on top of a terahertz transparent substrate (here semi-insulating GaAs). This substrate is surrounded by a cuvette, which contains the liquid. Terahertz radiation (electric field vector $E_{\text{THz}}$) from the UCSB free electron laser (FEL) is focused onto the plane of the gold grating with a diameter equal to the width of the cuvette opening. At the same time, visible radiation, provided by a 532 nm multimode, flashlamp pumped yttrium-aluminum-garnet (YAG) laser (electric field vector $E_0$), is guided through the liquid just above the grating surface. With reference to the schematic drawing in Fig. 1(b), the optical beam has an elliptical cross section $z_0 = 50$ $\mu$m high $\times$ 1 $\text{mm}$ wide. Alignment is critical and is achieved by blocking the optical beam by a piece of etched GaAs. The surface of the 2 mm thick GaAs in contact with the grating has a 50 $\mu$m deep trough 2 $\text{mm}$ wide, forming a 50 $\mu$m high “tunnel” at the grating surface. Alignment is tested by assuring that 90% of the aforementioned elliptical beam passes through the tunnel, especially as the grating is rotated.

The two lasers overlap in the liquid above the metal grating. Efficient nonlinear conversion requires phase matching\textsuperscript{9} according to $k_{\pm} - \delta = 0$, where $k_0$ and $k_{\pm}$ are the wavevectors of the incoming 532 nm light and the sum or difference frequency radiation (electric field vector $E_{\pm}$), respectively. For the current planar process, this results in the following equations [cf. Fig. 1(c)]:

$$k_G \cos(\theta_G - \theta) + n_0 k_0 = n_G k_{\pm} \cos(\delta \theta),$$

$$k_G \sin(\theta_G - \theta) = n_0 k_{\pm} \sin(\delta \theta).$$

By allowing the grating to rotate in the $x$-$y$-plane, $\theta_G$ can be adjusted to meet these conditions for a (well) chosen grating period $d$. As the cuvette rotates with the grating, the incident radiation is refracted through an angle $\theta$ and the effective grating angle is $\theta_G = \theta - \theta_G = \arcsin(n_0) / n_s$, where $n_s$ is the optical refractive index of the liquid. The visible laser excitation has a very narrow spatial width of 50 $\mu$m perpendicular to the grating (1 $\text{mm}$ in the grating plane). This essentially confines the nonlinear process to the $x$-$y$-plane. The sideband radiation, very nearly collinear with the exciting radiation ($\delta \theta$ is very small), is collected and spectrally resolved in a double monochromator. As shown in Fig. 1(b), the sideband radiation is polarized perpendicular to that of the incoming beam. Therefore, a set of crossed polarizers [Pol 1 and Pol 2 in Fig. 1(b)] around the mixing chamber

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\textsuperscript{a}Electronic mail: tfeil@phys.ethz.ch.
allows one to suppress the exciting 532 nm light by four to five orders of magnitude before it enters the spectrometer. This, combined with very narrow spectrometer slits, delivers a signal to background ratio for the strongest observed sidebands of about 100. While the remaining background is negligible, we are nonetheless able to observe nonresonant, $\chi^{(2)}$, based, terahertz/visible SDFG in liquids. The signal is detected with a photomultiplier tube by photon counting or averaged, time resolved, current transients. Under the conditions described in Eqs. (1) and (2), the entire interaction volume defined by the overlap of the terahertz and optical beams is phase matched to optimize the power radiated at the sum or difference frequency.

In the following, the SDFG process is characterized through the geometry and phase matching dependencies in the setup using enantiomeric and racemic limonene as a medium. In completely identical geometries, all measured sidebands disappear without the liquid. The FEL is tuned to frequencies around 0.65 THz and delivers output powers of about 1–2 kW in a narrow, $\sim 1–3 \mu$m, pulse at a repetition rate of the order of $\sim 1$ Hz. Figure 2(a) shows scans across the sum and difference frequency sidebands around the 532 nm (18 795.2 cm$^{-1}$) YAG line generated in S-limonene by 0.61 THz (20.3 cm$^{-1}$). The rotation angle was 27°. At each point, 500 mixing events are averaged. Due to the narrow monochromator slit widths (50 $\mu$m), individual features of the multimode line of the YAG laser are partially resolved. In the following, signals are extracted as the integral of the total sideband line.

Sum frequency sidebands for both S-limonene and a racemic limonene mixture are compared in Fig. 2(b). Within the accuracy of the experiment, there is no appreciable difference. Since the racemic mixture is nonchiral, the observed sidebands can originate from a $\chi^{(2)}$ origin beyond the dipole approximation or be due to higher even order polarizations. The linear power dependences of the limonene sideband, shown in Fig. 2(c), excludes the latter. The nonlinear polarization is thus caused by magnetic dipolar or quadrupolar processes.

It is important to distinguish volume from surface generated nonlinear polarization. Molecules in a surface layer may not enjoy the full rotational invariance of the liquid and may turn on a $\chi^{(2)}$ process. In addition, the abrupt termina-

tion of the three radiation fields at the surface can activate quadrupole or magnetic dipole processes at the surface. Indeed, much published work has focused on distinguishing three wave mixing due to surface molecular layers and bulk quadrupole and magnetic dipole effects that are caused by the surface boundary conditions of the three waves.

We performed two control measurements to discriminate against mixing at interfaces. We do so by scanning the interaction volume defined by the terahertz and optical beam overlap. Before doing so, we independently established the size of the terahertz and optical beams. First, the terahertz spot was scanned along the x-axis in the volume above the grating [see arrow Fig. 1(a)]. The strong signal at the grating center in the top inset of Fig. 2(c) precludes mixing on the vertical cuvette sidewalls, consistent with a volume effect. To explore the possibility that the SDFG arises from the surface of the grating, we measured the signal as a function of the height of the optical beam above the grating [dashed line in Fig. 1(b)]. The results are displayed and compared to two models in the lower inset in Fig. 2(c). One model assumes that the mixing occurs in molecules adsorbed on the surface. Signals from these molecules will decay at a rate controlled by the vertical Gaussian width of the optical beam. The predicted decay is very much faster than that observed (a ratio of $2.5 \times 10^{-7}$ at $\Delta z = 50 \mu$m). The other model assumes that the drop off of sideband intensity is due to the decay of the grating induced spatial modulation of the terahertz field in the quasistatic limit $\lambda_{THz} > d$, SDFG $\propto \exp(-4\pi \cos(\theta_C)(\Delta z / d))$. It predicts a just slightly faster attenuation than observed. However, we are strictly not in the quasistatic limit ($\lambda_{THz} \sim d$) and more rigorous models that capture shadowing would lead to a slower decay of the spatially modulated intensity. The measured decay when compared with these two models strongly supports mixing in the bulk, a volume effect.

A nonlinear quadrupolar process $^{[11]}$ in an isotropic medium produces a local polarization, $d\vec{P}$, at the sum or difference frequency that is proportional to the following vector product $^{[12]}$ (the radiation from a second term $\propto \vec{E}_0$ is suppressed by the cross polarizers):

$$d\vec{P}(\omega_{THz} \pm \omega_0) \propto [(\vec{k}_G + \vec{k}_0) \cdot \vec{E}_0] E_{THz}^G.$$  (3)

Here, $E_{THz}^G$ is the terahertz electric field above and in the near field of the grating [see inset in Fig. 3(a)]. It is spatially modulated at the grating period and there are spatially modulated components both perpendicular to the grating surface as well as along the grating wavevector; there are none along the grating lines. As the relative orientation of the incident terahertz field, $\vec{E}_{THz}$, and grating wavevector, $\vec{k}_G$, are altered, the magnitude of the modulated terahertz field will vary as $|E_{THz}^G| \propto |\vec{k}_G \cdot \vec{E}_{THz}|$.

While the phase matching conditions are the same for the chiral and quadrupolar processes, the angle dependence for the quadrupole process is such that the intensity vanishes when the grating wavevector is parallel to the incident optical radiation. Ignoring the phase matching requirements, the angular dependence [see Fig. 1(c)] of the radiated sideband power, $P_\pm$, will appear as follows:

$$P_\pm \propto |\cos(\theta_C - \theta_T)\sin(\theta_C)|^2.$$
The observed signal is not unique to limonene but has also been observed in several other polar and nonpolar liquids. Table I compares the experimentally observed hyperpolarizabilities $\beta = (1000N_Ac_i/\varepsilon_0)^{-1}\chi^{(2)}$ for limonene, carbon tetrachloride ($\text{CCl}_4$), and water, where $N_A$ is the Avogadro’s constant, $\varepsilon_0$ is the dielectric constant, and $c_i$ is the molar concentration of the liquid. We keep the interaction volume the same but have not corrected for different terahertz absorption coefficients. This correction is most important for water and can be as large as factors of 2–3. The absolute values were determined from a comparison to the terahertz/optical sideband generation measured in a bismuth germanate crystal, placed directly onto the grating, in the same setup ($\chi^{(2)} = 5 \times 10^{-12} \text{ m/V}$). For limonene and $\text{CCl}_4$, the measured signal reaches values similar to hyperpolarizabilities found for chiral dipole allowed SDFG of resonantly excited C–H bonds.\(^1\)

An estimate based on the work in Ref. 13 of the strength of chiral, electric dipole terahertz/visible SDFG gives hyperpolarizabilities about 20–1000 times larger than in Table I for single and double resonant excitation, respectively. This should place even protein solutions with molarities in the range of $10^{-3}$–$10^{-4}$ above our detection limit and thus provide a direct spectroscopy tool for macromolecular vibrations of biopolymers.

T.F. would like to thank the Alexander von Humboldt Foundation for the financial support. We gratefully acknowledge the help of Kevin Plaxco with all things touching (bio)chemistry. This work was supported by the (U.S.) Army Research Office under Contract No. W911NF0610241 and by the William M. Keck Foundation under Contract No. SB080017.

\(^11\)Chiral and magnetic dipole processes are very similar in nature and we do not attempt to distinguish them here.

### Table I. Measured hyperpolarizabilities.

| Liquid       | $M$ (mol/l) | $|\beta_{\text{quad}}|^{1}$ (m$^2$ C/V$^2$) |
|--------------|-------------|---------------------------------|
| Limonene     | 6.17        | $1.0 \times 10^{-53}$          |
| $\text{CCl}_4$ | 10.27       | $0.5 \times 10^{-53}$          |
| Water        | 55.35       | $0.05 \times 10^{-53}$         |

\(\theta_G\) is the dielectric constant, and $c_i$ is the molar concentration of the liquid. We keep the interaction volume the same but have not corrected for different terahertz absorption coefficients. This correction is most important for water and can be as large as factors of 2–3. The absolute values were determined from a comparison to the terahertz/optical sideband generation measured in a bismuth germanate crystal, placed directly onto the grating, in the same setup ($\chi^{(2)} = 5 \times 10^{-12} \text{ m/V}$). For limonene and $\text{CCl}_4$, the measured signal reaches values similar to hyperpolarizabilities found for chiral dipole allowed SDFG of resonantly excited C–H bonds.\(^1\)

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