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14. ABSTRACT The goal of the project is to assess the feasibility of Femtosecond Adaptive Spectroscopic Technique applied to coherent anti-Stokes Raman spectroscopy (FAST CARS) for a real time remote detection of hazardous microparticles in atmosphere and to evaluate the range of distances for typical species and the parameters of laser system that drive the limits of applicability. We will formulate a semiclassical theory of nonlinear scattering to estimate the number of detectable photons from a prototype molecule at a distance.					
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I. SUMMARY

The goal the project was to assess the feasibility of Femtosecond Adaptive Spectroscopic Technique applied to coherent anti-Stokes Raman spectroscopy (FAST CARS) for a real time remote detection of hazardous microparticles in atmosphere and to evaluate the range of distances for typical species and the parameters of laser system that drive the limits of applicability. We formulated a semiclassical theory of nonlinear scattering to estimate the number of detectable photons from a prototype molecule at a distance. The theory incorporated enhanced quantum coherence built in the system by femtosecond pulses and nonlinear optical processes.

The implementation of quantum control methods in combination with optical frequency combs in CARS for remote detection presents a fundamentally new approach. We estimated the main factors that provided an intense FAST CARS in the backward direction and understood the scope of distances and the laser system parameters relevant for typical species. The completed theoretical work advanced understanding of the limits of experimental real-

ization of FAST CARS for the remote detection of hazardous air contaminants. It paved the path to the next step comprised of a rigorous theoretical and experimental demonstration of long standoff detection in collaboration with Dr. Francesco Narducci from Naval Postgraduate School. The obtained results were reported in [1].

II. MAIN RESULTS

Based on a semiclassical approach [2], we estimated the feasibility of FAST CARS for real time remote detection of hazardous microparticles in atmosphere, evaluated the range of distances for typical species and the parameters of laser system that drive the limits.

We made use of a semiclassical theory of nonlinear scattering presented in [2] to estimate the number of detectable photons from a prototype molecule at a distance. The theory incorporates enhanced quantum coherence built in the system by femtosecond pulse trains and nonlinear optical processes. We investigated methanol as a prototypical molecule. This molecule has two Raman active vibrational modes: the symmetric 2837cm^{-1} (85.05THz) mode and asymmetric 2942cm^{-1} (88.20THz) stretch mode. The frequency of these vibrational modes is slightly different allowing to test the chemical selectivity of detection. We estimated the density of photons scattered in the backward direction and calculate the irradiance that can be detected by a detector placed 1 km away from the molecule. The ratio of the backscattered number of photons to the number of probe photons is

$$\frac{n_4(\mathbf{R}, \omega_{ac})}{n_3} = \frac{\epsilon}{2\pi} \left(\frac{d}{w}\right)^2 \int_0^{2\pi} \frac{\mathcal{I}_4(\mathbf{R}, \omega_{ac})_{\Theta=0(\pi)}}{\mathcal{I}_3(\omega_{ac})} d\Phi, \quad (1)$$

where ϵ is the detector efficiency, d is the detector diameter, w is the laser beam diameter and the intensity ratio is

$$\frac{\mathcal{I}_4(\mathbf{R}, \omega_{ac})_{\Theta=0(\pi)}}{\mathcal{I}_3(\omega_{ac})} = u \left(\frac{3}{8\pi R} \lambda \frac{\gamma_r}{\gamma_{ac}} N |\bar{\rho}_{bc}(0)| F \right)^2. \quad (2)$$

Here $u = |\hat{\epsilon}_4|^2$, ϵ_4 is the polarization of the signal field, R is the distance between detector and target, λ is the anti-Stokes wavelength, γ_r is the radiative decay rate and γ_{ac} is the decoherence rate, N is the number of target molecules and $|\bar{\rho}_{bc}|$ is the coherence between vibrational levels.

The parameter F is the geometrical and orientation factor, which depends on the target area volume and the phase mismatch. If we choose a perfect phase matching condition,

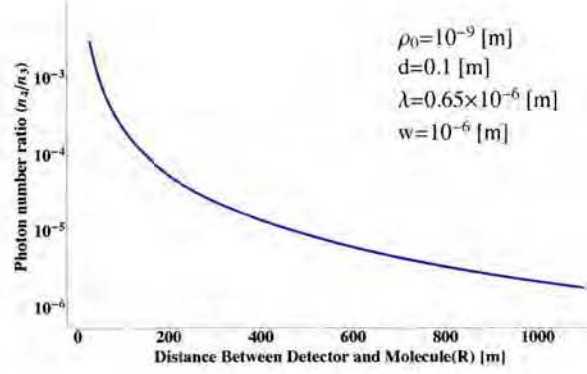


FIG. 1: The ratio of the number of the incident to the anti-Stokes backscattered photons as a function of the distance between the detector and the molecule (R).

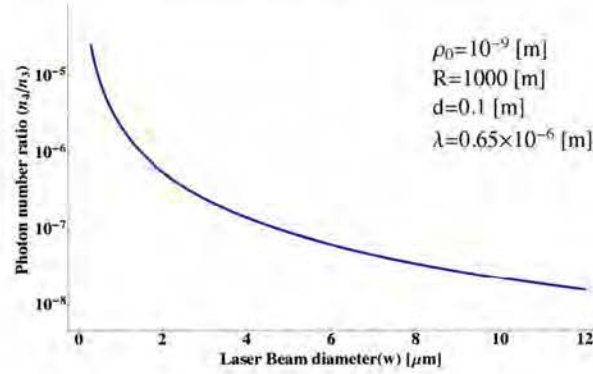


FIG. 2: The ratio of the number of the incident to the anti-Stokes backscattered photons as a function of the laser beam diameter (w).

we could consider $F = 1$. To achieve this condition, we choose parameters relevant for the methanol molecule - the target molecular diameter $\rho_0 = 10^{-9}m$ and the anti-Stokes wavelength $\lambda = 0.65 \mu m$. We have made a series of test calculations to analyze the dependence of the ratio of the incident to the backscattered photons as a function of the distance between the detector and the molecule (R), the laser beam diameter (w), and the detector diameter (d). The results are presented in the figures below.

Based on the above calculations we have made the following estimates. Suppose, the detector has a diameter $d = 0.1 m$ and it is placed $R = 1 km$ away. The detector efficiency is $\epsilon = 0.1$, radiative decay is $\gamma_r = 10^8 s^{-1}$, decoherence rate is $\gamma_{ac} = 2.5 \times 10^{13} s^{-1}$, the number of molecules $N = 5 \times 10^8$ and the laser beam diameter is $w = 1 \mu m$ [2]. The coherence

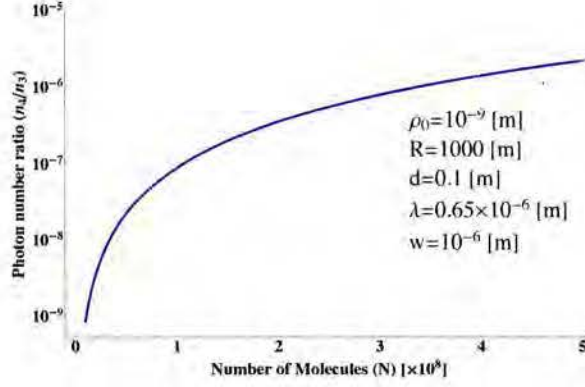


FIG. 3: The ratio of the number of the incident to the anti-Stokes backscattered photons as a function of the number of molecules N along the laser path.

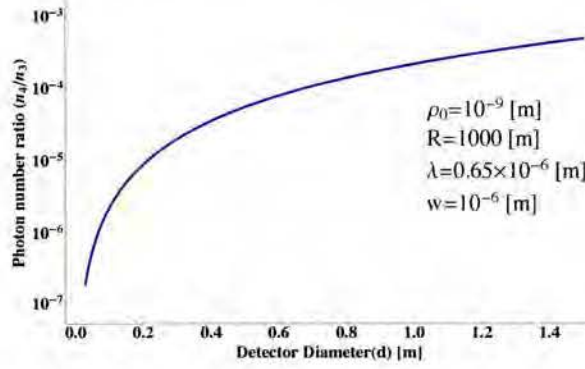


FIG. 4: The ratio of the number of the incident to the anti-Stokes backscattered photons as a function of the detector diameter (d).

between vibrational levels is the maximum, $|\rho_{bc}| = 0.5$. For these values of parameters, the ratio between the number of incident photons and backscattered anti-Stokes photons n_4/n_3 is about 10^{-5} . For the pulse, which we will be using in experiments, having pulse energy 0.6 nJ and wavelength $\lambda = 800 \text{ nm}$, the number of backscattered photons is

$$N_{3 \text{ per pulse}} = \frac{E_0}{h \cdot \frac{c}{\lambda}} = 2 \times 10^9. \quad (3)$$

So that the number of anti-Stokes photons per pulse is about $n_{4 \text{ per pulse}} = 2 \times 10^4$. If the pulse repetition rate is 1 GHz , the number of anti-Stokes photons per second is about 2×10^{13} giving 2 microwatts power, which is sufficient for detection.

In the Eq.(1) for the ratio of the incident to anti-Stokes backscattered photons, one of the key parameters is the coherence between vibrational levels $|\bar{\rho}_{bc}|$. This parameter can

be controlled by a input pulse and its value can be maximized. To demonstrate that for the parameters of the pulsed radiation available in Dr. Narducci's laboratory it is possible to reach a maximum vibrational coherence in the methanol molecule, we have performed a series of calculations for the dynamics in this molecule. Consider a three level system consisting of two vibration states of the ground electronic state and one excited electronic-vibrational state in a molecule. This molecule interacts with the pump and Stokes pulses, which induce molecular dynamics and population transfer. The pulses are chosen to be transform-limited since at this point we estimate the field intensity and frequency only; they read

$$E_{p(s)} = E_{p(s)0} e^{-\frac{t^2}{\tau^2}} \cos(\omega_{p(s)} t), \quad (4)$$

where $E_{p(s)0}$ is the peak value of the field amplitude, τ is the pump and Stokes pulse duration and $\omega_{p(s)}$ is the carrier frequency of the pump and Stokes pulse. The light-matter Hamiltonian in the interaction representation reads,

$$\hat{H} = \hbar \begin{pmatrix} 0 & 0 & \frac{\Omega_p(t)}{2} e^{i\omega_1 t} \\ 0 & 0 & \frac{\Omega_s(t)}{2} e^{-i(\omega_p - \omega_s - \omega_s)t} \\ \frac{\Omega_p^*(t)}{2} e^{-i\omega_1 t} & \frac{\Omega_s^*(t)}{2} e^{i(\omega_p - \omega_s - \omega_s)t} & \omega_3 - \omega_p \end{pmatrix} \quad (5)$$

Here $\Omega_{p(s)} = -\frac{\mu}{\hbar} E_{p(s)0} e^{-\frac{t^2}{\tau^2}}$ is the Rabi frequency and μ is the transition dipole moment, which we assume to be the same for both transitions. If the field and the three-level system parameters satisfy the condition that the one-photon detuning $\Delta \gg \Omega_{p(s)}$, where $\Delta = \omega_{31} - \omega_p$, then the excited level is hardly populated at all times. It means the change of probability amplitude in time is negligible, $\dot{C}_3 = 0$. Then the excited state can be adiabatically eliminated and the system reduces to the effective two-level system, for which the Hamilton reads

$$\hat{H}_{eff} = \hbar \begin{pmatrix} -\frac{|\Omega_p(t)|^2}{4\Delta} & -\frac{\Omega_p(t)\Omega_s^*(t)}{4\Delta} e^{i\delta t} \\ \frac{\Omega_p^*(t)\Omega_s(t)}{4\Delta} e^{-i\delta t} & -\frac{|\Omega_s(t)|^2}{4\Delta} \end{pmatrix} \quad (6)$$

Here, $\delta = (\omega_p - \omega_s - \omega_2 + \omega_1)$ is the two-photon detuning. The coherence between the vibrational levels can be studied by solving the time-dependent Schrödinger equation numerically. To simplify the example, we choose the two-photon resonance condition ($\delta = 0$) and assume the peak values of the Rabi frequency are the same for both the pump and

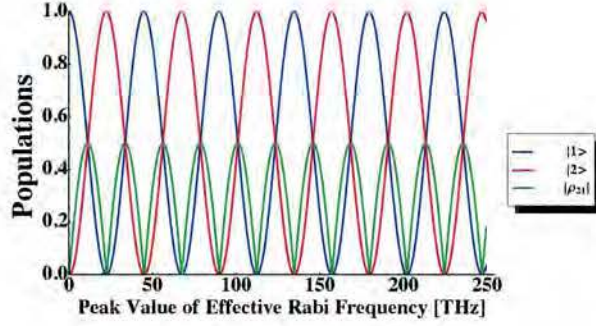


FIG. 5: Population dynamics in the effective two-level system. The single pulse duration is $\tau = 55.8fs$, the one photon detuning $\Delta = 1000THz$, the two-photon detuning $\delta = 0$.

Stokes pulses ($\Omega_{p0} = \Omega_{s0}$). We define the effective Rabi frequency as $\Omega_{eff} \equiv \frac{\Omega_p(t)\Omega_s^*(t)}{4\Delta}$. The population dynamics in the effective two-level system is shown in (Fig.5) as a function of the peak effective Rabi frequency Ω_{eff} . It demonstrates Rabi oscillations with periodic complete population transfer to the upper vibrational state following the pulse area solution. The first complete oscillation happens at $\Omega_{eff0} = 22.5THz$. The effective pulse area is $\pi/2$. This figure also shows the points of the maximum coherence between two vibrational states, which are exactly at the crossings of two populations at their value equal to $1/2$.

The peak value of the Rabi frequency of both pump and Stokes pulse at the first oscillation is $\Omega_R = 300 THz$. The peak field amplitude related to $300THz$ is $9.48 * 10^7 V/cm$. The peak value of the Ti-Sapphire laser in Dr. Narducci's laboratory is $2.275 * 10^7 V/cm$ (the peak Rabi frequency is $72 THz$). For such field the maximum coherence is achieved by a pulse train pulse train of 8 pulses, while full population transfer occurs after 17 pulses, see Fig.(6).

The results presented above demonstrate that the Ti-Sapphire laser available in Dr. Narducci's laboratory possesses parameters sufficient for generation of Raman signal from test molecules such as methanol and iodine. For the pulse repetition rate $1GHz$, the number of anti-Stokes photons per second may be sufficient for remote detection at distances up to $1 km$. To increase the number of photons in the backward direction several parameters can be varied, such as the laser beam diameter, the detector diameter and the pulse repetition rate.

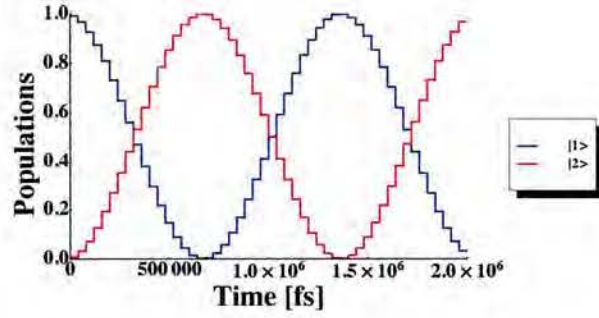


FIG. 6: The population dynamics in the effective two-level system as a function of time for peak value of the field amplitude 2.275×10^7 V/cm. The single pulse duration is $\tau = 55.8$ fs, the one photon detuning $\Delta = 1000$ THz, the two-photon detuning $\delta = 0$. The crossing of populations indicating the maximum coherence occurs after 7 pulses.

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- [1] Gengyuan Liu, Frank A. Narducci, Svetlana A. Malinovskaya, “Limits to remote molecular detection via coherent anti-Stokes Raman spectroscopy using a maximal coherence control technique”, App. Optics. submitted (2017).
 - [2] C.H.R. Ooi, G. Beadie, G.W. Kattawar, J.F. Reinjes, Y. Rostovtsev, M.S. Zubairy, M.O. Scully, “Theory of femtosecond coherent anti-Stokes Raman backscattering enhances by quantum coherence for standoff detection of bacterial spores,” Phys. Rev. A **72**, 023807 (2005).