PHYSICAL REVIEW A VOLUME 25, NUMBER 2 FEBRUARY 1982

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Anti-Stokes Raman laser

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(Received 28 October 1981)

The first observation of nonresonant, stimulated anti-Stokes Raman emission is reported. A metastable Tl($6p\ ^2P^o_{3/2}$) inversion is created by selective photodissociation of TlCl. Raman scattering from the Tl metastable state to ground using 532- and 355-nm pump lasers resulted in stimulated emission at 376 and 278 nm, respectively. Conversion efficiencies up to 10% are reported.

An anti-Stokes Raman laser may be defined as stimulated anti-Stokes Raman emission induced by a pump laser between two levels of the same parity in which a population inversion exists between the upper and lower Raman states. Such laser devices are particularly attractive since they are tunable by tuning the pump laser and, because the upper Raman state is often a metastable level, large inversion densities and high anti-Stokes output energies are possible. Early workers[1] in this area were able to demonstrate measurable gain in inverted I atoms, where the $I^*(5p^5\ ^2P^o_{1/2})$ state was populated by flash photolysis of trifluoromethyliodide (CF_3I). The anti-Stokes Raman signal was observed by pumping this inversion with the fundamental of a Nd:YAG (yttrium aluminum garnet) laser at 1.06 μm and probing with a broad-band dye laser; however, superfluorescent emission at the nonresonant anti-Stokes wavelength was not observed.

This Communication reports what we believe to be the first observation of a stimulated, nonresonant, anti-Stokes Raman laser. Thallium vapor which was inverted by selective photodissociation of TlCl was used as the Raman medium. Using the second (532-nm) and third (355-nm) harmonics of a Nd:YAG laser as pump sources, stimulated anti-Stokes emission from the Tl($6p\ ^2P^o_{3/2}$) to the Tl($6p\ ^2P^o_{1/2}$) state was observed at 376 and 278 nm, respectively.

Over the past few years a wide variety of lasers and population inversions along dipole-allowed transitions have been created in various metals by selective photodissociation of metal compounds, in particular metal halides.[2–6] The possibility of using a similar technique to create a population inversion in the Tl($6p\ ^2P^o_{3/2}$) metastable state with respect to the ground state was first considered by White and Zdasiuk[7] by selective TlBr photodissociation at 266 nm. Although a population inversion was found not to exist in this case, more recent work by VanVeen *et al.*[8] using a time-of-flight analysis of the photofragments of Tl salts produced by excimer laser irradiation has suggested that an inversion in the Tl($6p\ ^2P^o_{3/2}$) state could be created by photodissociation of TlCl. In the present experiments absorption of an ArF excimer laser photon at 193 nm results in photodissociation along the paths

$$\mathrm{TlCl} + \gamma(193\ \mathrm{nm}) \rightarrow \mathrm{Tl}^*(6p\ ^2P^o_{3/2}) + \mathrm{Cl}$$
$$\rightarrow \mathrm{Tl}^*(6p\ ^2P^o_{3/2}) + \mathrm{Cl}^*,$$

where, since the splitting of the Cl ground state is small, both Cl and Cl* are probably produced in an undetermined ratio. Since no Tl($6p\ ^2P^o_{1/2}$) ground-state atoms are produced by this process, the $6p\ ^2P^o_{3/2}$ metastable state is inverted with respect to ground.

Absorption of a strong pumping field tuned near a dipole-allowed state with opposite parity may connect the metastable and ground states via a two-photon, anti-Stokes Raman scattering process. If the input field is sufficiently strong, stimulated emission at the anti-Stokes wavelength will result. A schematic energy-level diagram illustrating this concept is shown for the Tl atom in Fig. 1. In the present experiments anti-Stokes Raman emission was observed at 376 and 278 nm with 532- and 355-nm pumping lasers, as shown in Figs. 1(a) and 1(b), respectively.

The anti-Stokes Raman gain cross section, σ_R,

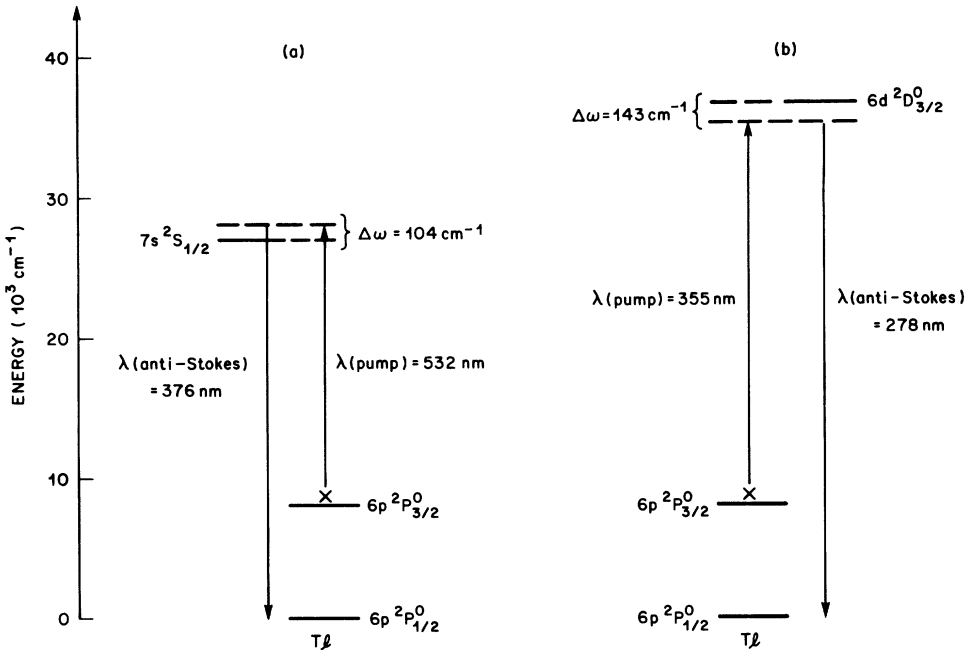

FIG. 1. Pertinent energy levels for anti-Stokes Raman lasing from inverted Tl($6p\ ^2P^0_{3/2}$) atoms. (a) Raman emission at 376 nm using a 532-nm pump source. (b) Raman emission at 278 nm using a 355-nm pump source.

may be readily calculated assuming a near-resonant, three-level approximation. For the Tl case one has, in mks units[9]

$$\sigma_R = \frac{e^4 f_1 f_2 \nu_R}{32\pi^3 \epsilon_0^2 m^2 hc^2 \nu_1 \nu_2 \Delta\nu^2 \sqrt{2}\Delta}, \quad (1)$$

where f_1 and f_2 are the oscillator strengths connecting the intial and final states to the intermediate level, ν_1 and ν_2 are the respective frequencies, ν_R is the anti-Stokes frequency, $\Delta\nu$ is the virtual detuning, and Δ is the pump laser linewidth. With 532-nm pumping as in Fig. 1(a), one has $f_1 = 0.135$, $f_2 = 0.125$, $\nu_R = 8.0\times10^{14}$ sec^{-1}, $\nu_1 = 7.9\times10^{14}$ sec^{-1}, $\nu_2 = 5.6\times10^{14}$ sec^{-1}, $\Delta\nu = 3.1\times10^{12}$ sec, and $\Delta = 3.0\times10^{10}$ sec^{-1}, yielding an anti-Stokes gain cross section of σ_R (376 nm) $= 1.8\times10^{-24}$ cm^4/W. Similarly for 355-nm pumping one has $f_1 = 0.036$, $f_2 = 0.145$, $\sigma_R = 1.1\times10^{15}$ sec^{-1}, $\nu_1 = 1.1\times10^{15}$ sec^{-1}, $\nu_2 = 8.5\times10^{14}$ sec^{-1}, $\Delta\nu = 4.3\times10^{12}$ sec^{-1}, and $\Delta = 3.0\times10^{10}$ sec^{-1}, which gives σ_R (278 nm) $= 1.9\times10^{-25}$ cm^4/W. The anti-Stokes Raman gain is then calculated as $N\sigma_R Il$, where N is the population inversion density, I is the pump laser intensity, and l is the effective length of the medium.

The basic experimental apparatus is illustrated in Fig. 2. The 193-nm radiation used to dissociate the TlCl was generated using a commercial ArF excimer laser. Approximately 80 mJ of 193-nm light was focused into the salt heat pipe oven with a CaF_2 lens. The ArF laser pulse was ~15 nsec in duration and was focused to an area of about 3×10^{-2} cm^2 over 25 cm in the TlCl cell. The second and third harmonics of a Nd:YAG laser were used as pump sources and were generated using potassium dihydrogen phosphate (KDP) crystals, yielding pulse energies of up to 300 mJ at 532 nm and 180 mJ at 355 nm. These beams had pulse lengths of approximately 7 nsec at 532 nm and 5–6 nsec at 355 nm. The pump beams were focused with a separate lens and combined with the ArF laser using a dichroic mirror. The Nd:YAG harmonics were overlapped spatially with the ArF beam and focused to an area of 1×10^{-2} cm^2 over the 25-cm TlCl hot zone. In this configuration the pump laser beam area served to define the interaction region and the effective volume for the anti-Stokes Raman laser. Temporal overlap of the two laser beams was controlled using a precision delay generator stable to 1 nsec, thereby allowing the dissociation and pump lasers to be readily synchronized or delayed with respect to one another. The TlCl cell was a simple stainless-steel oven with cold, unaligned CaF_2 windows. Argon buffer gas at 30 Torr was used to prevent TlCl vapor condensation on the windows. The cell was operated at 450 °C providing a TlCl vapor density of about 6.9×10^{16} molecules/cm^3; however, observation of the stimulated Raman effect did not depend critically on this choice of operating conditions. The anti-Stokes lasers were studied using either a 0.5-m scanning monochrometer and photomultiplier tube combination or were dispersed using

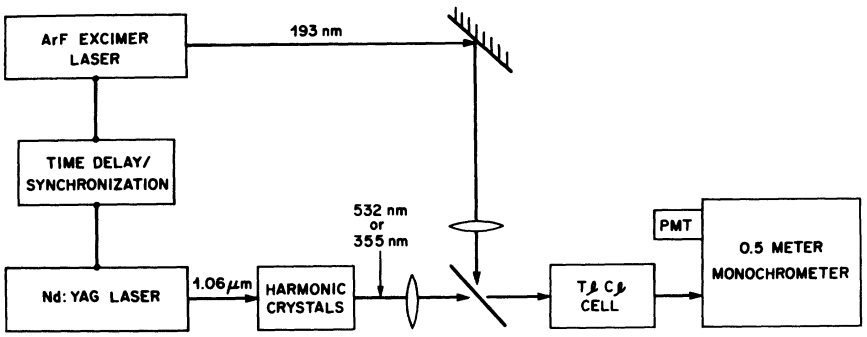

FIG. 2. Experimental apparatus used to observe stimulated anti-Stokes Raman emission.

quartz prisms for easy energy measurements.

With only the 193-nm dissociating laser present, laser emission along the Tl($7s\ ^2S_{1/2}$–$6p\ ^2P^o_{1/2}$) resonance line at 377 nm was observed. No laser emission along the Tl($7s\ ^2S_{1/2}$–$6p\ ^2P^o_{3/2}$) transition was observed consistent with the data that the primary photofragment is the Tl($6p\ ^2P^o_{3/2}$) atom. Approximately 100 μJ was observed at 377 nm, indicating that 2–3% of the Tl atoms were left in the $7s\ ^2S_{1/2}$ state after the dissociation. At low (i.e., $\lesssim$15 mJ/pulse) 532-nm pump energies, the anti-Stokes Raman rate was not sufficient to compete with the alternate channels which resulted in premature filling of the Tl ground state. At a 532-nm energy of about 15 mJ the Raman process was stimulated and the 377-nm resonance emission disappeared. Above this threshold the Raman laser grew and saturated at a pump energy above approximately 25 mJ. Accounting for the stimulated emission from both ends of the cell, a pulse energy at 376 nm of 1.8 mJ was measured. The anti-Stokes laser followed the 532 nm pump and had a pulse width of $\sim$7 nsec. The observed output energy implies a Tl($6p\ ^2P^o_{3/2}$) storage density of approximately 4×10^{16} atoms/cm^3 was created by the photodissociation step.

Since, in principle, all the stored energy can be extracted by increasing the pump laser intensity to saturation, the conversion efficiency is best defined in terms of the efficiency of the pumping process. In this manner one may define the efficiency as the ratio of the anti-Stokes output energy to the 193-nm energy absorbed in the active volume. Approximately 26 mJ of the 193-nm pump was absorbed in the active volume, implying an efficiency of $\sim$7%.

The 532-nm laser could be delayed 30–40 nsec after the dissociating laser and still maintain Raman lasing. Under ideal conditions the $6p\ ^2P^o_{3/2}$ level is metastable for a considerably longer time; however, other competing processes, such as the 377-nm laser, tend to fill up the ground state and destroy the population inversion. The use of other dissociating wavelengths may give a more favorable distribution of photofragments and increase the effective storage time.[8]

Two separate tests were performed to verify that the 376-nm emission was indeed an anti-Stokes Raman laser and not due to the four-wave parametric mixing in the Tl atom. First, the 376-nm light was verified to occur both in the co-propagating and counter-propagating directions from the cell. In addition, if the four-wave parametric mixing were to account for the strong 376-nm emission, either the 193- or 532-nm lasers would need to generate a coherent emission via Stokes scattering from the ground state to the $6p\ ^2P^o_{3/2}$ state resulting in radiation at 228 or 910 nm, respectively. No such emission was observed, indicating a true population inversion did exist between the $6p\ ^2P^o_{3/2}$ and $6p\ ^2P^o_{1/2}$ levels.

Similar behavior for the 278-nm Raman laser using 355 nm as the pump wavelength [Fig. 1(b)] was observed. The anti-Stokes Raman emission followed the pump pulse and was 5 nsec in duration. With an input energy of $\sim$100 mJ/pulse at 355 nm, the output energy at 278 nm from both cell ends was approximately 2.5 mJ/pulse. The 278-nm laser was verified to occur from both ends of the cell and again no evidence of the four-wave parametric mixing and the corresponding frequencies this would imply was found. The conversion efficiency in this case was 10%.

Anti-Stokes Raman lasers, due to their tunability and relatively high conversion efficiency could be useful for up-converting a variety of laser sources. Up-converters for CO_2 lasers could be constructed in alkali atoms to yield radiation in the 400-nm range. The present system using metastable Tl atoms is attractive for shifting various excimer lasers, and with a high brightness ArF laser[10] as a pump, one could envision resonant coupling to the Tl($6p^2\ ^2D$) autoionizing level to yield a tunable laser at 168 nm. Since one is typically a few hundred to a thousand wave numbers detuned from the intermediate state, dispersion should be minimum, and the anti-Stokes laser should prove a useful means of up-converting very short pulse length lasers.

A variety of other pumping methods might be utilized to create the necessary population inversions. Incoherent, flash photolysis has already been demonstrated to create very large metastable I populations,[1] and such techniques could be readily applied to metal salts. Laser-induced collisional pumping[11] has been proposed as a method of inverting metastable levels and selective autoionization pumping[12] should permit the creation of metastable inversions in ions.

The authors gratefully acknowledge helpful discussions with A. M. Johnson.

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