Stimulated Stokes downconversion in liquid and solid parahydrogen

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We report the results of our preliminary investigations into the suitability of condensed-phase parahydrogen as a Raman-shifting medium for infrared cavity ringdown laser absorption spectroscopy. We have observed the conversion of ~10-ns pulses of 532-nm radiation into first-, second-, and third-order vibrational Stokes radiation in bulk liquid and solid parahydrogen after a single 11-cm pass. Unexpectedly, we find that liquid H_2 yields more efficient conversion than solid H_2 with certain focal geometries, and that in the case of the solid, a collimated or loosely focused pump geometry is more efficient than a tight focus. © *2003 American Institute of Physics.*
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Cavity ringdown laser absorption spectroscopy (CRLAS) is a versatile spectroscopic tool[1–3] that offers high sensitivity ($\Delta I/I \sim 10^{-6}$) without the requirements of source- or sample-based modulation schemes. In this technique, the decay (ringdown) of radiation in a cavity formed by two high-reflectivity mirrors is measured to directly yield the absorption coefficient of the material within the cavity. Most conveniently, widely tunable pulsed lasers can be used as the source of the radiation, although cw lasers tuned to a cavity resonance can also be used for higher sensitivity.

CRLAS has found wide application at visible wavelengths, where pulsed dye lasers offer high power and stability. However, the extension of this technique into the infrared has been more challenging due to the lack of commercially available pulsed-laser sources of sufficiently high resolution. In Berkeley, we have been using a high-pressure cell of gaseous H_2 and a multipass configuration[4] to downconvert visible light from dye and Alexandrite lasers into the infrared through multiple orders of stimulated Raman scattering. This configuration produces ample third-Stokes pulse energies (~100 μJ/pulse) to perform IR-CRLAS at wavelengths shorter than 5 μm. However, accessing the 5–10-μm range requires higher pump energies (due to the decrease in Raman conversion efficiency with wavelength), which in turn requires Herriott-cell mirrors with extremely high damage thresholds. The difficulty of obtaining such mirrors with adequate reflectivity has prompted us to investigate the suitability of condensed-phase parahydrogen as a Raman-shifting medium.

Solid parahydrogen is expected to be substantially more efficient than gaseous hydrogen, because the solid has a higher number density of $n \sim 2.6 \times 10^{22}$ cm^{-3} and a small Raman linewidth[5] of $\Gamma \lesssim 7$ MHz (the Raman gain is directly proportional to n and inversely proportional to Γ). The extensive measurements of Hakuta's group[6] have demonstrated that the Raman-gain coefficient of the solid is 7000 times greater than that of the gas at the optimum pressure. The stimulated Raman effect has been studied in liquid hydrogen by Stoicheff,[7] who did not report a Raman gain. However, the Raman gain of liquid hydrogen is expected to be lower than that of solid hydrogen due to its greater Raman linewidth[8] of ~1500 MHz. In this letter, we discuss our initial studies of Stokes downconversion in both liquid and solid parahydrogen samples.

In our experiments, industrial-grade hydrogen was converted into parahydrogen using Apache catalyst in a liquid helium bath. The converted hydrogen was removed from the converter by raising the temperature to approximately 17 K. The parahydrogen (~99.95%) released into the vapor phase at this temperature was then transferred into an evacuated cylindrical cell housed in a helium cryostat. The sample cell consists of a copper cylinder (11-cm length, 2-cm inner diameter) with windows (BaF_2 or sapphire) sealed with indium gaskets. Solid hydrogen crystals were grown at about 9–11 K from the vapor and then cooled to 4 K, as in previous work in Chicago[9] and Kyoto.[10] The crystal grows with its c-axis normal to the wall, and while it is not possible to fill the entire sample cell with a single-domain crystal, spectroscopic evidence[9] along optically transparent paths shows that it is a single crystal locally where the laser radiation probes. These crystals were mostly transparent, except for an unfilled opaque region near the center of the cylinder. For the liquid experiments, the crystals were melted at a temperature of about 15 K while periodically pumping on the cell to remove excess pressure. The resulting liquid was completely transparent.

The optical experiments (see Fig. 1) utilized the direct output of a doubled Nd:YAG laser (532 nm) with ~10-ns pulse length, operating at a 20-Hz repetition rate. The output pulse energy was varied by adjusting the flashlamp voltage and the Q-switch delay. In our initial experiments, some fundamental (1064-nm) light was present in the pump beam. We corrected our results for this effect, as described later, and

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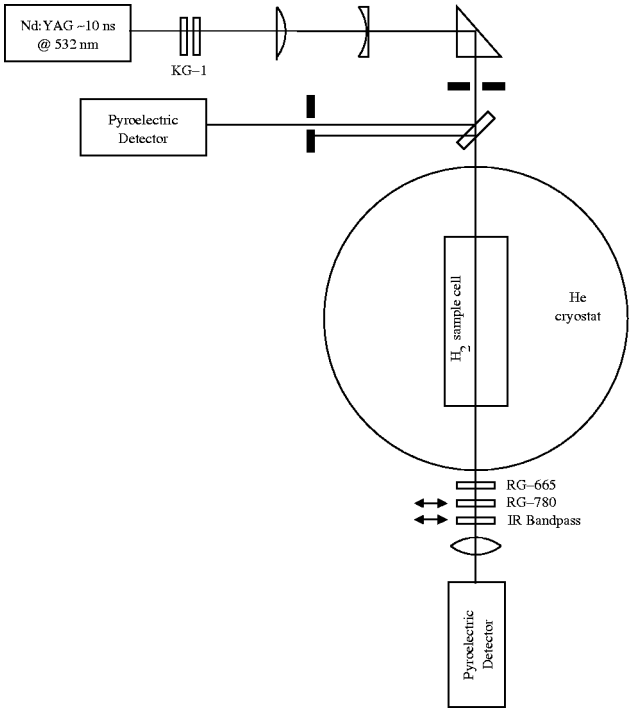

FIG. 1. Experimental configuration for Raman shifting measurements.

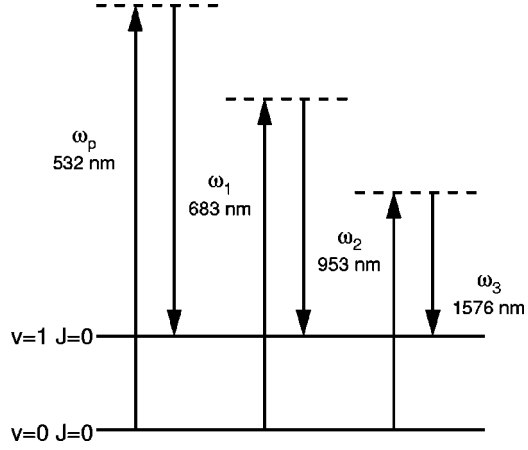

FIG. 2. Energy-level diagram of the stimulated Raman scattering process.

also conducted a second set of experiments using dichroic mirrors and Schott KG-1 glass to filter out the 1064-nm radiation.

Three different pump geometries were tested. The first (depicted in Fig. 1) is a collimated beam (~1-mm diameter) achieved with a Galilean telescope consisting of a 300-mm-focal-length planoconvex lens and a −50-mm-focal-length planoconcave lens. The second geometry was a loosely focused configuration, using a compound lens of focal length ~85 cm. The last geometry was a more tightly focused beam, using a compound lens of focal length ~46 cm.

After passing through the collimating or focusing optics, the pump beam was sent through an iris in order to remove the outer portions of the beam that would not cleanly pass through the opening of the cryostat. The beam was sampled by a calcium fluoride beamsplitter, the primary reflection of which was sent to a pyroelectric detector in order to monitor the pump power incident on the cryostat. The pump beam then traveled into the cryostat and through the solid or liquid hydrogen sample. The output radiation (consisting of the pump, Stokes, and anti-Stokes beams) exited the cryostat, passed through various filters, and was then focused onto a pyroelectric detector.

An energy level diagram depicting the Raman conversion process is given in Fig. 2. We performed our power measurements using a set of filters described in Table I. For each pump power setting, we performed three measurements: first, with a Schott RG-665 filter alone; second, with the RG-665 and RG-780; and third, with the RG-665 and an infrared bandpass filter (''IRB''). After correcting for the filter transmittances, these measurements yield independent measurements of each order of the Stokes radiation. When 1064-nm light was present in the pump beam (in our initial experiments), some of it passed through all of these filters. We corrected for this by assuming that no third-Stokes radiation had been detected (i.e., that the light passing through the IRB filter was entirely 1064 nm). By applying the measured transmittances of each of the filters at 1064 nm, we were then able to numerically remove the contribution of 1064-nm light to the first- and second-Stokes measurements. These corrections yielded results in very good agreement with the second set of experiments, in which the 1064-nm light was filtered out before the cryostat.

The results of our first-Stokes measurements are shown in Fig. 3. Quite unexpectedly, we observed substantially higher conversion from the liquid parahydrogen than from the solid, in the tightly focused pump geometry. The solid performed considerably better in either the loosely focused or collimated pump beam conditions, compared to the tight focus. We were unable to observe any first-Stokes output from the liquid with a collimated pump beam, up to a pump energy of 6 mJ (at which energy the liquid yielded over 0.5 mJ with a tightly focused pump).

We also observed second-Stokes output from both liquid and solid parahydrogen. A tightly focused pump geometry in the liquid, and a loosely focused pump in the solid, equivalently yielded the best results: about 100 μJ of second-Stokes with ~70 mJ of pump. The tightly focused beam in the solid yielded only ~40 μJ with the same pump energy. We obtained very little third-Stokes output: 0.5 μJ from the liquid and 0.2 μJ from the solid, both under the tight focusing conditions with ~70 mJ of pump. (The loosely focused and collimated pump geometries were part of our initial experiments, which were contaminated with 1064-nm light, so they did not provide useful third-Stokes measurements.)

We note that the conversion efficiencies obtained in this experiment are somewhat lower than those obtained in similar experiments (on the solid only) in Kyoto.[10] The Kyoto experiments also showed significant variability in efficiency from run to run, which suggests that there is some aspect of

TABLE I. Filter transmittances.

λ (nm)	RG-665	RG-780	IRB
532	$<10^{-5}$	$<10^{-5}$	⋯
683	77%	$<10^{-5}$	$<10^{-4}$
953	91%	90%	$<10^{-3}$
1064	91%	90%	6%
1576	91%	90%	85%

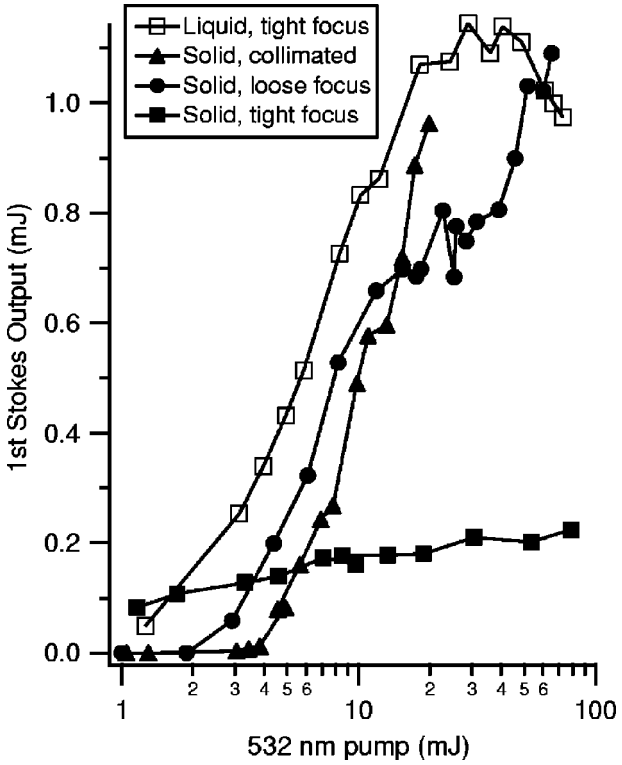

FIG. 3. First-Stokes measurements for liquid and solid parahydrogen.

this system which is not being optimized and which could lead to considerably higher conversion efficiency if understood. Some possibilities include the crystal quality, the pump-beam geometry, the pump-beam mode quality, and the pulse length of the pump beam. Two additional observables that may provide information helpful to maximizing higher-order Stokes output are the anti-Stokes intensity and the first-Stokes backward scattering intensity. We did not make quantitative measurements of these parameters, but note that we observed them to be strong in some cases and nearly absent in others.

At present, a single pass through liquid or solid parahydrogen is not able to compete with a multipass, high-pressure, gaseous hydrogen cell, in terms of third-Stokes output usable for IR-CRLAS. However, the higher Raman-gain coefficient of the condensed phase suggests that we should be able to obtain much higher conversion efficiency than we have thus far. Followup experiments are planned in Berkeley to pursue the potential of the condensed phase for Raman shifting.

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