

Optical frequency conversion by a rotating molecular wave plate

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We demonstrate efficient four-wave mixing in low-pressure molecular deuterium without the need for phase matching. We use two laser fields with opposite circular polarizations to produce a strong excitation of a rovibrational transition at a frequency of 3167 cm^{-1} . The coherent molecular motion, in turn, modulates a third laser field (also circularly polarized) and results in highly efficient single-sideband conversion. © 2001 Optical Society of America

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Four-wave mixing in atomic and molecular gases has served, for more than 30 years, as an efficient tool for producing coherent radiation at desired wavelengths.¹ An important development in this area was the invention of nonlinear optics at maximal coherence,^{2,3} which allowed 100% frequency conversion without the need for phase matching, under conditions in which the nonlinear susceptibility is of the order of the linear susceptibility. This technique relied on all-resonant laser-pulse propagation in an atomic medium (Λ scheme) and utilized electromagnetically induced transparency.⁴

Recently it was demonstrated that the ideas of electrically induced transparency and nonlinear optics at maximal coherence can be extended to molecular systems.⁵ In such systems the laser detunings from electronic states are very large ($\sim 60,000\text{ cm}^{-1}$), but a Raman transition can still be adiabatically prepared in a maximal-coherence state by use of two single-mode laser fields at a finite Raman detuning. When this coherence is established, the molecular motion modulates light in the same way as a conventional optical modulator but at a frequency that is many orders of magnitude higher.^{6,7} In recent experiments, strongly driven molecular vibrations were used to produce frequency modulation with an ultrabroad bandwidth.⁸⁻¹¹ In particular, collinear generation of 17 mutually coherent Raman sidebands, ranging in wavelength from $2.94\text{ }\mu\text{m}$ in the infrared to 195 nm in the vacuum ultraviolet, was demonstrated.^{9,10} For many applications, however, single-sideband conversion is preferred. In this Letter we show how the molecular modulation technique can be modified to yield efficient frequency conversion into a single sideband.

It is known that a rotating birefringent wave plate will modulate circularly polarized light to produce a single sideband, shifted by twice the rotational frequency of the wave plate. For a diatomic molecule (D_2 in our case), the polarizability depends on the orientation of the molecular axes; thus we can create a rotating wave plate by aligning all the molecules in the D_2 cell and making them rotate in unison. This is done by coherent excitation of an ensemble of molecules that are initially in the ground molecular

state ($\nu'' = 0, J'' = 0$) into a superposition of molecular vibration and rotation ($\nu' = 1, J' = 2$). We use two strong laser fields with opposite circular polarizations, slightly detuned from the Raman resonance to excite coherent molecular oscillation.^{12,13} This oscillation, in turn, mixes with a third circularly polarized (potentially widely tunable) laser field and generates a single Raman sideband. In this case the single-sideband conversion is required by angular-momentum conservation. Unlike in previous molecular modulation experiments,⁶ no further generation will occur when only the two strong circularly polarized drive fields are applied.

Our experimental setup is shown in Fig. 1. We use two transform-limited laser pulses at wavelengths of $1.0645\text{ }\mu\text{m}$ and 796.12 nm , such that the laser-frequency difference is approximately equal to the frequency of the $(\nu' = 1, J' = 2) \rightarrow (\nu'' = 0, J'' = 0)$ molecular transition in D_2 . The first laser is a Quanta-Ray GCR-290 Q-switched injection-seeded

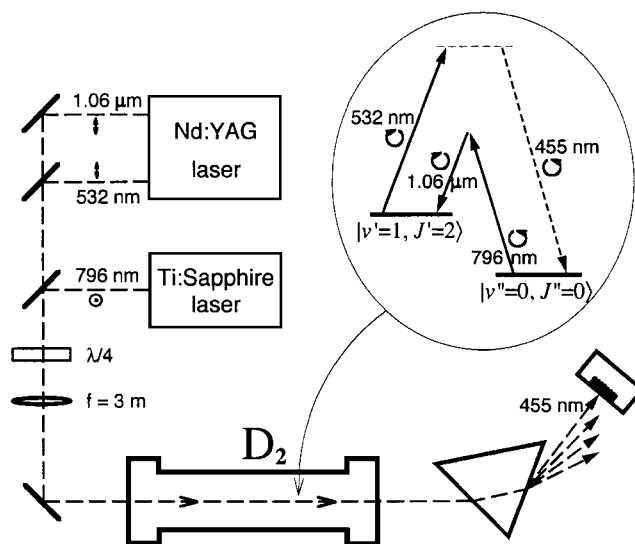


Fig. 1. Experimental setup and energy-level diagram for frequency conversion in D_2 . We use two laser fields ($1.06\text{ }\mu\text{m}$ and 796 nm), with opposite circular polarizations, to produce rovibrational excitation, which converts a third field (532 nm) into a single sideband (455 nm).

Nd:YAG laser, producing 150-mJ, 10-ns, transform-limited pulses at a 10-Hz repetition rate. The second laser is a custom-made Ti:sapphire system, injection seeded from an external-cavity laser diode and pumped by the second harmonic of a separate Q-switched Nd:YAG laser. This laser produces 75-mJ, 14-ns pulses at the (tunable) seeding laser wavelength, which is monitored by a Burleigh WA-1500 wavemeter (resolution, 50 MHz). The two driving laser pulses are synchronized by adjustment of the delay between the two Nd:YAG laser Q-switch trigger pulses. The third (weak) laser pulse (0.8 mJ, 7 ns) at 532 nm is obtained from the second harmonic of the first Nd:YAG laser and is thus automatically synchronized with the two driving pulses. Initially all three beams are linearly polarized, with the polarization of the 1.06- μm and 532-nm beams in the horizontal plane and the polarization of the 796-nm beam in the vertical plane. The laser beams are combined with dichroic beam splitters and sent through a $\lambda/4$ Fresnel rhomb, which produces opposite circular polarizations for orthogonal linear polarizations at the input. The beams are focused into the D₂ cell; the 1.06- μm laser spot size is 460 μm , the 796-nm laser spot size is 395 μm , and the 532-nm laser spot size is 195 μm . The D₂ cell is cooled by liquid nitrogen to $T = 77$ K, such that 60% of the molecules are in the ground rotational state. The length of the cooled region is 48 cm, and the pressure is 103 Torr.

We observe collinear generation of a single sideband at 455 nm. The polarization of the sideband is expected to be circular and orthogonal to the polarization of the 532-nm beam. We disperse the sidebands with a prism and use a Moletron J4-09 pyroelectric detector to measure the generated pulse energy. Figure 2(a) shows the pulse energy at 455 nm as a function of the Raman detuning of the driving fields. Zero detuning is determined from the position of the generation peak at reduced driving intensities. For comparison, Fig. 2(b) shows the depletion of the 532-nm beam. Each point in the plots is an average over 10 laser shots, with error bars showing the standard deviation of each data set. To within the error bars, the number of photons absorbed from the 532-nm beam is equal to the number of photons generated at 455 nm. This result demonstrates single-sideband frequency conversion, with a peak conversion efficiency of 15.4% (the photon conversion efficiency is 13.2%).

There has been significant research done in the areas of Raman processes and four-wave mixing in both atoms and molecules.¹ Oudar and Shen have discussed in detail how four-wave mixing can be used for spectroscopy,¹⁴ and Begley *et al.* have demonstrated coherent anti-Stokes Raman spectroscopy as an effective spectroscopic tool.¹⁵ Frey *et al.*¹⁶ and Loy *et al.*¹⁷ have demonstrated four-wave mixing by use of vibrational transitions in molecules to obtain tunable infrared generation. Our technique differs significantly from that described in past work. Our conversion process occurs collinearly, at low pressure, off line center, without the need for phase matching, and results in good spatial and temporal coherence of the generated field. As opposed to traditional

Raman scattering, our generation process is linear in the pump (532-nm) field intensity and allows efficient conversion of radiation from a weak pump.

Our technique requires preparation of high molecular coherence. In that sense our work is related to the research on ultrafast coherent excitation of superposition states in molecules performed by Laubereau *et al.*¹⁸ They demonstrated four-wave mixing by superposition of molecular vibrations and employed it to measure the coherence time of the vibrational state. In contrast with our work, in their work coherence was achieved nonadiabatically, through the application of an intense broadband short pulse.

As mentioned above, there is a strong similarity between our technique and that of nonlinear optics at maximum coherence in atomic lead (Pb).^{2,3} Although the preparation and the nature of the coherence in the molecular system differ from that in Pb, the generation equations are nearly the same and predict the possibility of 100% photon conversion from the third applied field to the generated field. The results of this experiment are below the ideal limit by a factor of 7.6. We believe that this discrepancy is due to a lower-than-expected coherence of the rovibrational transition, most likely caused by dephasing of the rovibrational state ($\nu' = 1, J' = 2$). By using shorter pulses or operating at lower pressures with a longer interaction length (perhaps with a multipass cell), we expect to approach the theoretical maximum.

In contrast with the technique used with Pb, our technique does not require a single-photon resonance for the two driving fields, and the third applied field

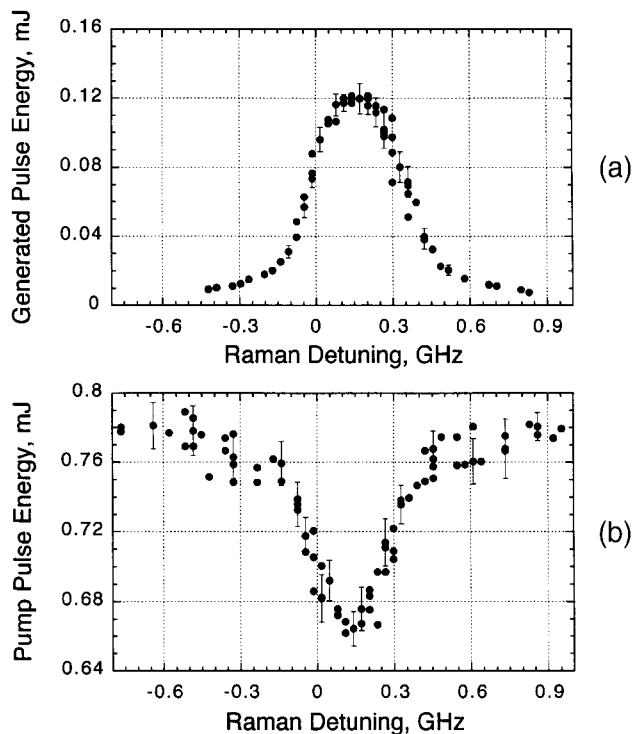


Fig. 2. Tuning characteristics of the molecular frequency converter: (a) pulse energy, generated at 455 nm, (b) pulse energy in the 532-nm pump field. The energy-conversion efficiency is 15.4%, and, within error bars, the pump depletion is equal to the generated energy.

is detuned far from the upper electronic states. The large detuning should result in a conversion efficiency that is relatively insensitive to the bandwidth or the wavelength of the applied third source. This leads to an important potential application of this technique, the generation of tunable far-infrared radiation.^{19,20} With this configuration (Fig. 1), instead of using 532-nm radiation, one can apply tunable near-infrared radiation (3 to 4 μm) of correct polarization to downshift to tunable far-infrared radiation (30 to 300 μm). Under the assumption of large single-photon detunings, at a fixed density and length the energy-conversion efficiency will decrease as the square of the frequency of the generated field but, to our knowledge, still has the possibility of being larger than that of any other technique. Moreover, the same method can be used to convert laser pulses from far infrared to near infrared, thereby making their detection much more efficient. This idea was anticipated by the time-resolved infrared spectral photography of Bethune *et al.*²¹ We imagine building an infrared spectrometer that utilizes molecular modulation to generate far-infrared radiation, sends that radiation through the test medium, and then converts it back into more easily detectable radiation through the same molecular system.

In summary, in this Letter we have demonstrated efficient laser-frequency conversion (15.4%) into a single sideband in a low-pressure molecular gas. The frequency shift of 3167 cm^{-1} is provided by a strongly driven rovibrational transition in D_2 that is excited by two quasi-monochromatic laser fields with opposite circular polarizations. A potential application of this technique is the generation and detection of far-infrared radiation.

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