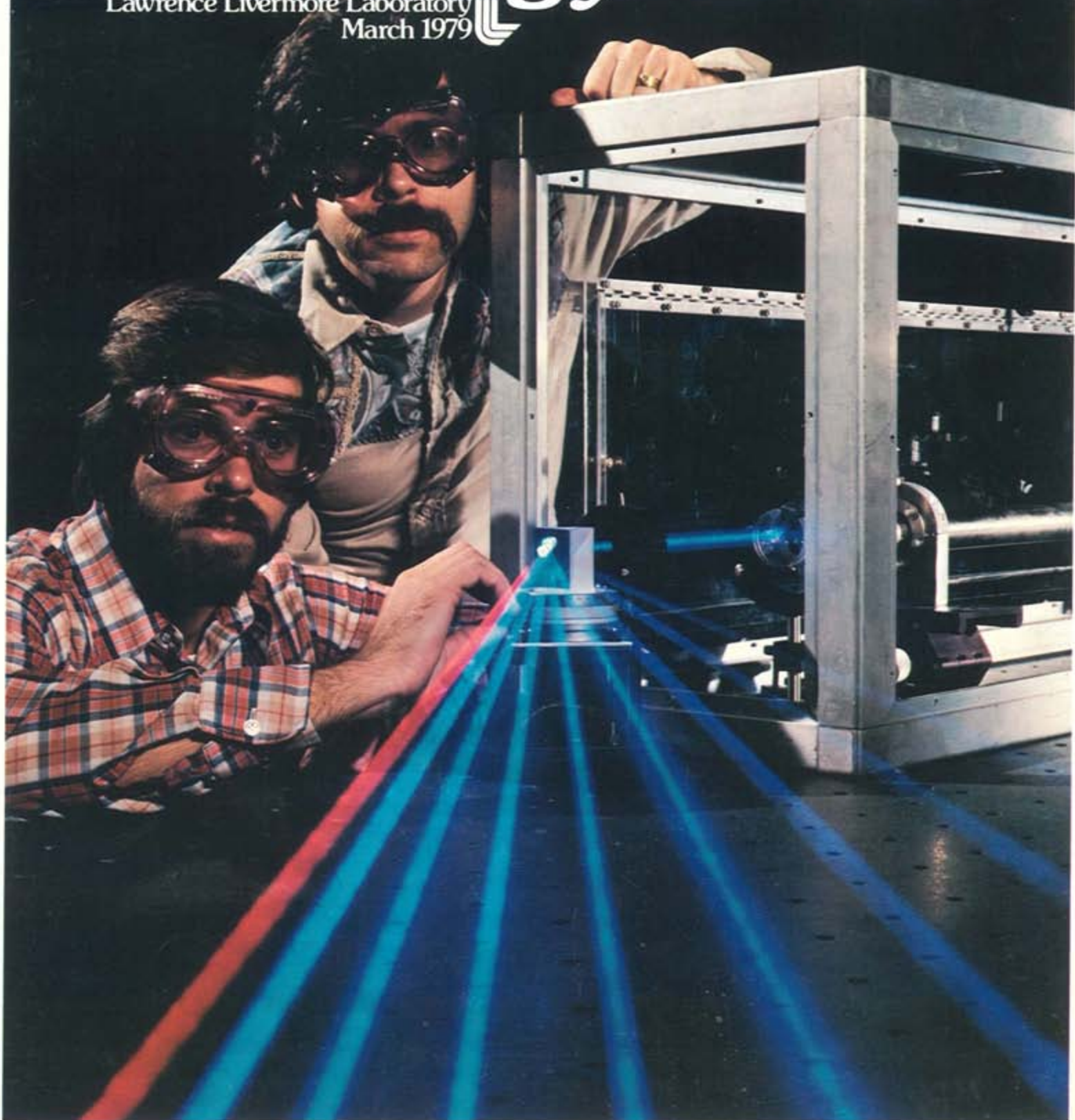


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A tunable laser system for the ultraviolet, visible, and infrared regions



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We have developed a laser system that produces tunable, coherent beams of radiation covering the electromagnetic spectrum from below 200 nm in the ultraviolet to above 1000 nm in the infrared. This system uses a tunable dye laser in the visible region and converts the laser light to shorter and longer wavelengths by stimulated Raman scattering in molecular hydrogen or deuterium gas. For example, in the ultraviolet region, we have generated wavelengths as short as 171.3 nm. Tunable ultraviolet beams can be applied to atomic and molecular spectroscopy as well as to isotopic and chemical analyses.

Tunable dye lasers in the visible region have opened up large areas of scientific study and, in particular, have become important analytical tools.¹ However, in the ultraviolet (uv) region below 220 nm, convenient, continuously tunable, coherent light sources have been sought for many years with little success. Although there have been many recent advances in tunable uv and vacuum ultraviolet (vuv) generation below 220 nm, the methods used generally require unusual materials or techniques, and the wavelength coverage is generally very limited.

Continuously tunable uv light can be generated by frequency-doubling the output of a continuously tunable dye laser operating in the visible region. This frequency-doubling is accomplished through the use of a nonlinear, birefringent crystal. Although

wavelengths as short as 185 nm have been produced in this manner, they have been generated efficiently only at wavelengths longer than 220 nm. As a result of our recent work, there is now a new, satisfactory method of generating continuously tunable light from the infrared through the visible to the ultraviolet to wavelengths below 220 nm.

Our simple and versatile method is based on the so-called anti-Stokes stimulated Raman scattering (SRS) in molecular hydrogen gas. We have successfully and efficiently generated continuously tunable wavelengths as short as 171.3 nm. To our knowledge, this is the shortest wavelength ever produced by stimulated Raman scattering. We believe that this technique can be further extended to wavelengths as short as 130 nm.

Stimulated Raman scattering

Stimulated Raman scattering was extensively studied in the earliest days of quantum electronics. In fact, the high-order Raman processes we use were first observed over a decade ago.

The physics of the Raman process is illustrated in the energy level scheme depicted in Fig. 1a. The pump laser pulse at frequency ν_p is incident upon a molecule in an initial state, i , and can promote it to a virtual state, indicated by the dashed line in Fig. 1a. If enough transitions are induced, a population inversion can result in the gas between the virtual level and a final level, f . In a molecule such as hydrogen, the initial state is the ground-state vibrational level, and the final state is the first vibrational level. Stimulated emission occurs at a longer wavelength corresponding to the frequency $\nu_p - (\nu_f - \nu_i) = \nu_p - \nu_R$. For hydrogen, the Raman frequency, ν_R , is simply its fundamental vibrational frequency ($\nu_R = 4155 \text{ cm}^{-1}$, and $1 \text{ cm}^{-1} = 30 \text{ GHz}$). The fraction of the pump laser light that is converted in this

Raman process is said to be “Stokes-shifted,” and this particular output is called “first Stokes radiation,” denoted S_1 .

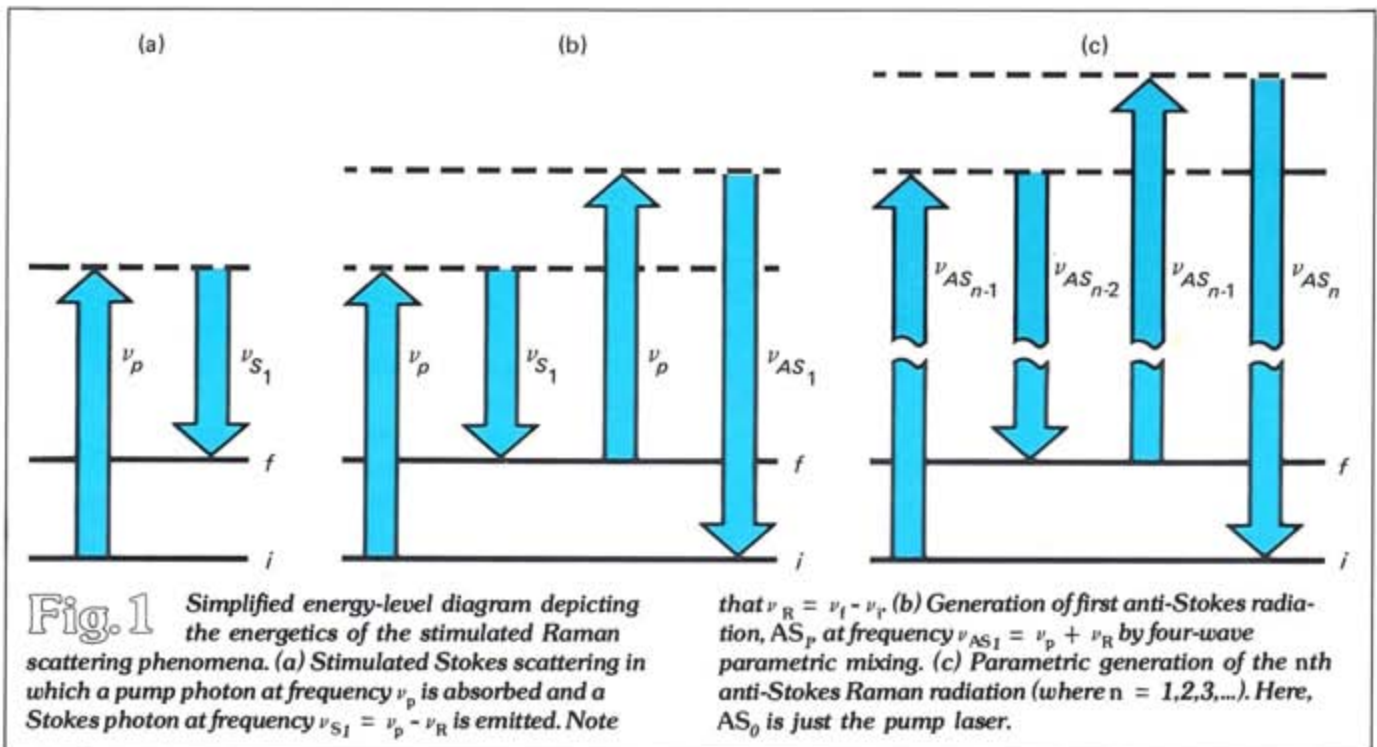
As in conventional lasing, first Stokes emission has a flux-density (or intensity) threshold. Below this threshold, no S_1 radiation appears, but once the pump laser flux density exceeds the threshold, S_1 grows exponentially in intensity as the pump intensity increases. As a result, two intense waves (the pump and the S_1) propagate in phase through the molecular gas. Since these two waves are in phase, they harmonically beat against one another and produce an electronic polarization in the gas at the Raman frequency, ν_R . This induced polarization induces a high-frequency sideband on the light. This conversion of light to a higher frequency ($\nu_p + \nu_R$) is called the

“first anti-Stokes radiation,” denoted AS_1 . The energetics of this process are depicted in Fig. 1b.

Raman generation of AS_1 is sometimes called parametric four-wave mixing because four waves (two at ν_p , one at ν_{S_1} , and one at ν_{AS_1}) participate in the process. Unlike first Stokes generation, this process has no threshold once S_1 radiation appears. Higher-order anti-Stokes frequencies ($\nu_p + n\nu_R$, for $n = 2, 3, 4, \dots$) are produced in an equivalent way as depicted in Fig. 1c. Parametric generation of higher-order Stokes frequencies also occurs.

Anti-Stokes scattering in molecular hydrogen

Molecular hydrogen is an excellent gas for Raman scattering because it has a very large Raman cross section. In addition, it has



widely spaced vibration levels ($\nu_R = 4155 \text{ cm}^{-1}$) so that large frequency shifts can be obtained using the SRS process. Isotopic substitution of deuterium for hydrogen extends the wavelength coverage to different ranges because the Raman shift in deuterium is $\nu_R = 2991 \text{ cm}^{-1}$. Furthermore, hydrogen can withstand high optical fields before it breaks down. This allows the propagation of waves at those intensities needed to produce the high-order, nonlinear Raman processes we have discussed.

Perhaps the most important property of molecular hydrogen gas, however, is its very low optical dispersion. We recall from the discussion in the previous section that high-order Raman processes (S_n and AS_n , for $n = 1, 2, 3, \dots$) occur because the waves at two different frequencies travel in phase through

the medium. Optical dispersion would destroy this condition, because the mixing waves would propagate through the gas at different velocities. The larger the optical dispersion, the shorter the distance over which the waves can interact and produce the high-order Raman processes. Ultimately, the number of short-wavelength AS sideband-component frequencies generated is limited by the optical dispersion. Fortunately, the conversion efficiency to the Raman-generated waves increases dramatically with frequency and tends to offset this effect in molecular hydrogen.

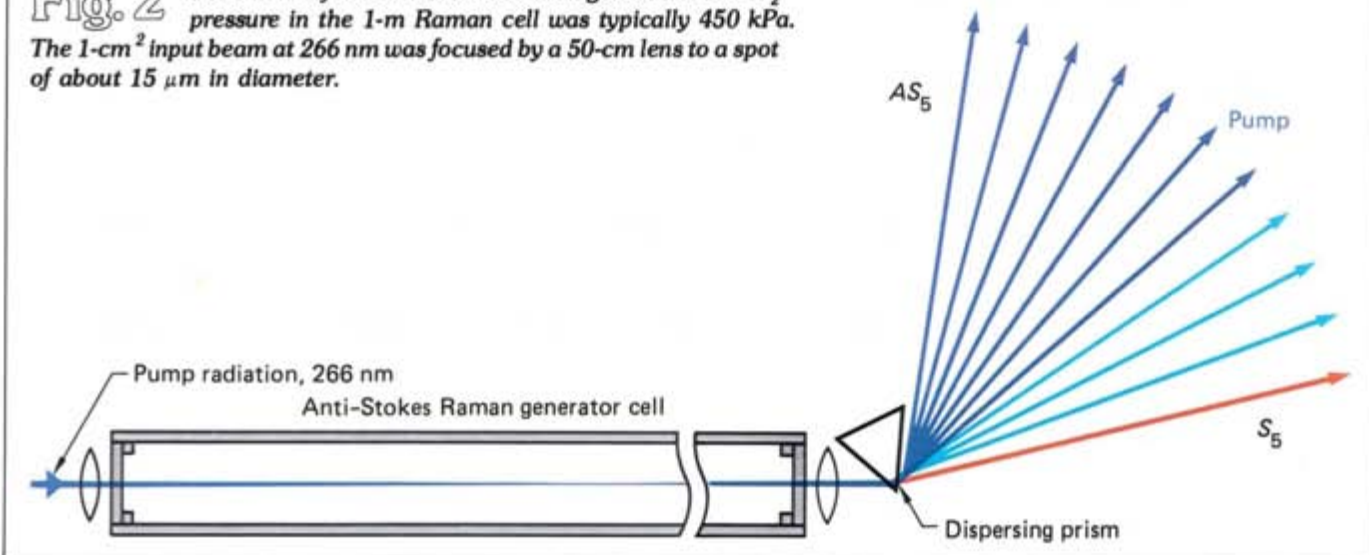
Generation of anti-Stokes ultraviolet radiation

Fixed wavelengths. We have exploited the SRS method using the experimental setup illustrated

in Fig. 2. Starting with the fourth harmonic of a neodymium-yttrium-aluminum-garnet (Nd-YAG) laser at 266 nm we have generated quite easily at least five anti-Stokes and five Stokes components under modest pumping conditions. In this case, the AS_4 wave occurs at 184.4 nm and the AS_5 wave at 171.3 nm. Although the AS_6 occurs at 159.9 nm, it was not observed because it was totally absorbed by the suprasil dispersing prism used in these studies. All the beams emerge collinearly from the Raman cell, and a simple prism was used to disperse the separate component waves.

Focusable power is essential so that the threshold for Stokes generation can be exceeded and the efficient generation of shorter wavelengths can be achieved. In the experiment depicted, the

Fig. 2 Schematic of the anti-Stokes Raman generator. The H_2 pressure in the 1-m Raman cell was typically 450 kPa. The 1-cm^2 input beam at 266 nm was focused by a 50-cm lens to a spot of about $15 \mu\text{m}$ in diameter.



intensity at the focus of the pump radiation was about 10^{12} W/cm^2 . We found that thresholds for S_1 generation and the associated parametric anti-Stokes processes below 200 nm were less than 2 mJ (in a 5-ns pulse) under the conditions shown in Fig. 2. This laser power condition is easily met by commercially available lasers, both tunable and fixed-frequency.

We have observed pump-wave energy depletions of greater than 75%. The energy partitioning favors the lower-order Stokes and anti-Stokes waves, but an adequate efficiency is achieved in the higher

orders, for example, about 1% energy or about 0.7% photon conversion in the AS_4 wave. With 15 μJ of pump energy at 266 nm, we have measured 150 μJ in the AS_4 at 184.4 nm and 5 μJ in the AS_5 at 171.3 nm.

Tunable anti-Stokes radiation. For a tunable uv laser, we must use a tunable pump laser in the visible region. With a commercially available dye laser pumped by an Nd-YAG laser, we have obtained results similar to those just described. Using a 560-nm pump at fluxes of 20 mJ in a 5-ns pulse, we have observed AS_8 (195.7 nm)

to S_2 (1048 nm); and with 280-nm pump radiation we have observed AS_4 (191.1 nm) to S_6 (927.9 nm). The generation of anti-Stokes waves at even higher orders probably occurs, although they could not be observed in this particular experiment because of the particular output window of the Raman cell. In another test using 65-mJ pulses (~ 5 ns long) from the dye laser at 560 nm, we measured more than 25 μJ at AS_8 (195.7 nm).

The linewidth of the uv radiation is another important parameter that influences the usefulness of

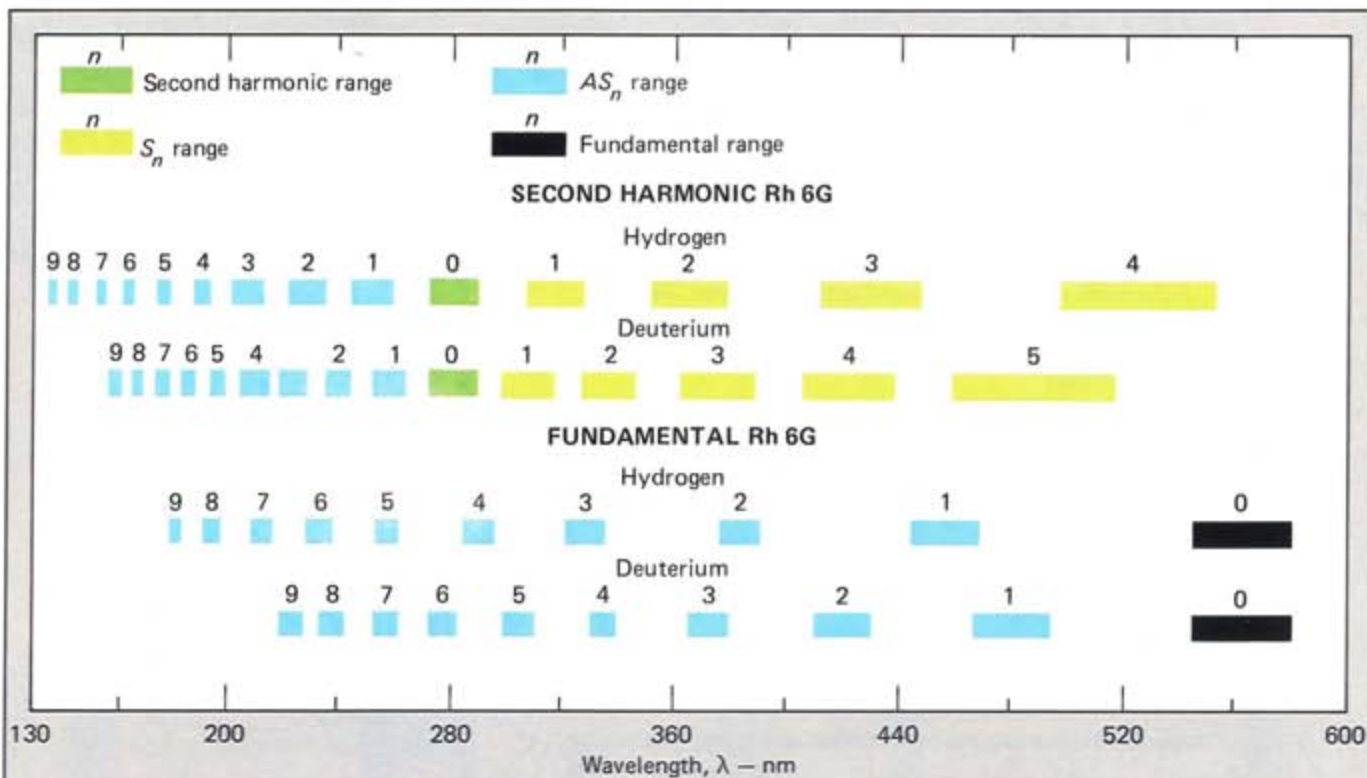


Fig. 3 Wavelength coverage possible between 130 and 600 nm, using a Raman-shifted rhodamine 6G dye laser. We have observed AS_8 to S_2 using the fundamental and AS_5 to S_6 using the second harmonic of the rhodamine 6G dye laser.

this radiation. In general the linewidth of the Raman radiation depends both on the linewidth of the pump and on the details of the stimulated Raman scattering. If the Raman processes are purely parametric as mentioned above, the spectral linewidth, $\Delta\nu$, of the anti-Stokes (Stokes) emissions is simply that of the pump. Indeed, we have observed that the linewidth of AS_8 at 195.7 nm tracks the 0.5-cm^{-1} linewidth at the 560-nm pump wavelength. As a result, optical resolutions, $\Delta\lambda/\lambda$, of 10^{-5} to 10^{-6} even below 220 nm are routinely obtained.

Other important characteristics of the uv beams are their polarizations and divergences. Because the Raman scattering is purely vibrational [Q(1) mode], the scattered radiation is linearly polarized with the pump radiation. Circular polarization of the pump is to be avoided, since it would induce rotational Raman components [S(1) and S(0) modes] that would reduce the conversion efficiency to the vibrational Raman lines.

The output beams are close to being diffraction-limited. We attribute this to the diffraction-limited pump and the relatively low pressures (<790 kPa) at which we operate the hydrogen cell.

Full-spectrum coverage

With the output powers available from commercial dye lasers, spectral coverage in the uv range can be achieved to below 175 nm using SRS with only a few dyes. In fact, as illustrated in Fig. 3, this tuning range can be almost entirely spanned by using a rhodamine 6G dye laser alone if we include also the frequency-doubled output from such a laser.

In one example where we desired large spectral coverage in the uv, we used the AS_7 component of the output of a rhodamine 6G dye laser to excite molecular nitric-oxide vapor in a photoacoustic cell. When the AS_7 radiation is tuned to resonance with a nitric-oxide transition, the excited molecule deposits some of its

energy into the gas. The resulting pressure wave induces a signal in a small microphone transducer in the cell. Figure 4 is a trace of the microphone signal versus the scanned wavelength. This spectrum covers a portion of the rotational spectrum of the $\gamma(1,0)$ band in nitric oxide. It is a spectral region previously inaccessible using other

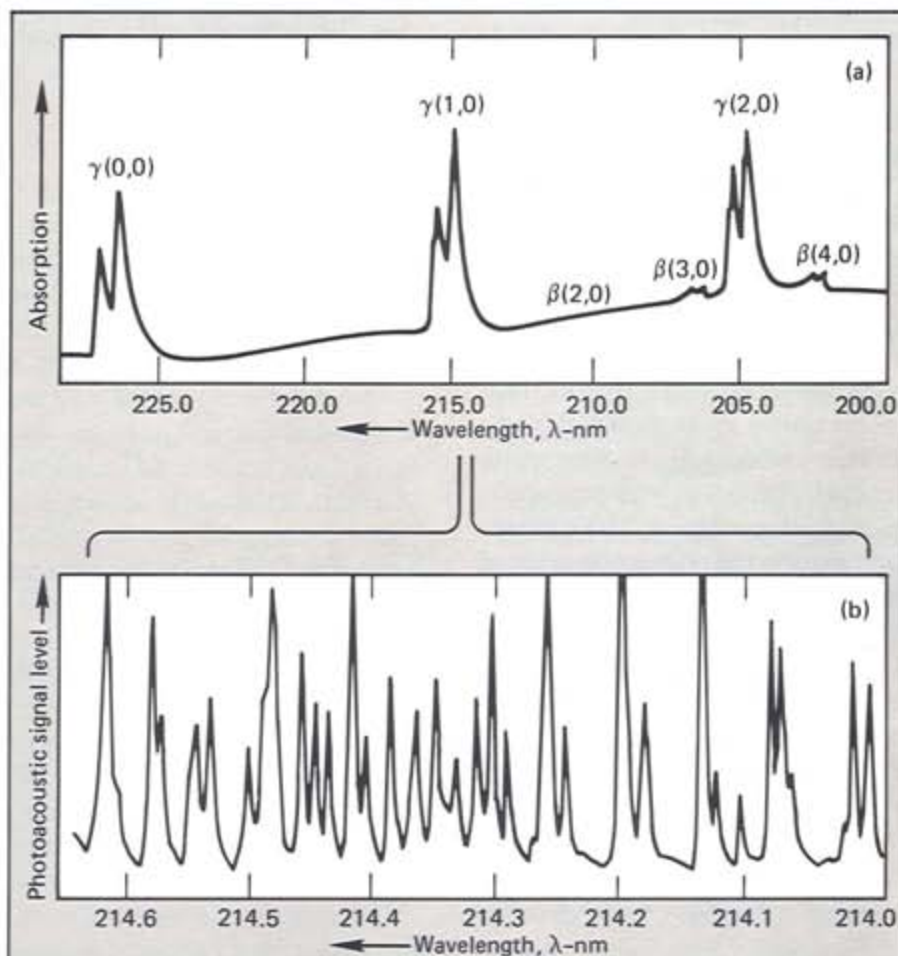


Fig. 4 Nitric-oxide absorption spectrum taken around 215 nm. (a) The upper trace is an absorption spectrum taken at low resolution. The three major bands correspond to transitions between the $v'' = 0$ vibrational level of the ground electronic state, $X^2\Pi_{1/2}$, and the $v' = 0, 1, 2$ vibrational levels of the excited electronic state, $2\Sigma^+$. (b) The lower trace is a portion of the resolved rotational spectrum of $v' = - v'' = 0$ taken photoacoustically with the anti-Stokes stimulated Raman source described in the text and illustrated in Fig. 2.

laser methods. With our laser running at 10 pulses per second, this spectrum was recorded in only 5 minutes.

Potential applications

The extremely versatile properties of this laser system make it applicable to the evaluation of advanced isotope separation schemes and technology and to photochemical studies. In addition, it is suitable for quantum electronics applications. The excellent spectral and spatial properties of the scattered radiation make anti-Stokes generation an ideal signal source for injection-locking short-wavelength excimer lasers. Furthermore, since SRS gain increases with the pump frequency, the parametric processes should have progressively lower thresholds at shorter wavelengths in spite of increased dispersion and potential breakdown problems. The ultimate limit may be the absorption edge of H_2 (<130 nm). One possibility for achieving tunable output to 130 nm may be by using an ArF-based system. AS_5 of the ArF output at 193.3 nm would occur at 137.9 nm, while AS_6 would occur at 130.4 nm. We plan to explore these intriguing possibilities in the near future.

Key words: anti-Stokes radiation; coherent radiation; infrared radiation; laser systems; stimulated Raman scattering; Stokes radiation; uv radiation; visible radiation.

Notes and references

1. See, for example, "High-Resolution Dual-Laser Flow Cytometry," in the December 1978 *Energy and Technology Review* (UCRL-52000-78-12), p. 27, and "Laser Excitation and Probing: New Directions in Photochemistry," in the January 1979 *Energy and Technology Review* (UCRL-52000-79-1), p. 24.