

High-Speed High-Resolution Gas-Phase Raman Spectroscopy

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A new Raman spectrometer has been developed that can produce a complete high-resolution gas-phase vibrational spectrum during the time period of a single laser pulse. Conventional gas-phase Raman spectroscopy uses a single narrow-band laser to produce signals that are weak, requiring relatively long collection times. This spectrometer uses a degenerate OPO as a broad-band source that covers a continuous range of $>3000\text{ cm}^{-1}$. When a beam from this broad-band source is added to a narrow-band laser beam, the intensity of the Raman signal is amplified by the nonlinear optical effect. The resulting instrument can generate spectra with high-spectral ($<1\text{ cm}^{-1}$), spatial ($<0.05\text{ mm}^2$), and temporal resolution ($<1\text{ s}$).

As a form of vibrational spectroscopy, Raman spectroscopy is a useful tool for accurately identifying molecules and studying their structures. During recent years, the use of multichannel array detectors, such as charge coupled devices (CCDs), has provided the ability to generate Raman spectra quickly without the need to scan a monochromator or interferometer. Some advantages of Raman over its closest competitor, infrared spectroscopy, include easy acquisition of spectra from aqueous samples, the ability to boost the Raman effect by resonance enhancement or surface enhancement, and the ability to obtain higher spatial resolution through the use of visible light instead of infrared light. The most challenging disadvantage of Raman spectroscopy is often the inherent weakness of the incoherent scattering effect, which can make the technique susceptible to spectral interference from stronger processes, such as laser-induced fluorescence.

Although many applications of Raman spectroscopy involve condensed-phase samples, gas-phase analysis is important for studies ranging from fundamental molecular spectroscopy to challenging applications, such as the diagnostics of combustion, plasmas, chemical vapor deposition, and gas-phase dynamics. These applications may involve high temperatures, hostile environments, transient species, and sensitive flow fields that preclude the use of a physical probe for sensing or collecting samples. The use of laser light has emerged as an effective tool for probing such systems in situ.

Not all laser techniques have the ability to obtain the information needed for characterization of such systems. Figures of merit include universality, reliability, and the ability to obtain information with a high degree of spectral, spatial, and temporal resolution. In some cases, the information may be needed to create two- or three-dimensional images that provide spatially resolved distribu-

tions of species, concentration, and temperature. The large amount of information associated with creating spectroscopic images requires that the acquisition rate be sufficiently rapid to complete the measurement before the sample changes.

For gas-phase systems, Raman spectroscopy provides several potential advantages over other forms of spectroscopy. Laser induced fluorescence is a powerful technique with typical detection limits in the subparts-per-million range. However, fluorescence is not a universal technique and is sensitive to the environment. For example, not all species fluoresce, and those that do may have a wide range of excitation and emission wavelengths, requiring additional time to adjust the wavelength of the laser and the detection system. The quenching of fluorescence is highly dependent upon temperature and species, and the process of correcting for the effect of quenching limits the reliability and scope of the measurement.

Infrared spectroscopy is a very widely used tool for condensed-phase chemical analysis, but gas-phase Fourier transform infrared (FT-IR) has several limitations when compared to gas-phase Raman spectroscopy. First, homonuclear species (e.g., O_2 , N_2 , C_2 , and H_2) are often important in studies such as combustion analysis; however, these species do not appear in infrared spectra. Second, the infrared spectrum of a given molecule in one physical state or matrix may change considerably when in a different state or matrix.¹ Gas-phase infrared spectra are often strongly affected by rotational band-broadening, but Raman spectra tend to be dominated by sharp Q branches from totally symmetric vibrations.² Consequently, FT-IR detectors for gas chromatography usually have a resolution of no better than 4 cm^{-1} , which is considered adequate to record peaks with bandwidths that are typically broadened to $10\text{--}20\text{ cm}^{-1}$ wide.³ Third, as is the case with condensed-phase infrared spectroscopy, the spatial resolution in gas-phase infrared spectroscopy tends to be poorer than that for gas-phase Raman spectroscopy as a result of the lack of broadly tunable infrared lasers and the fact that visible beams of light can be focused more tightly than infrared beams. Finally, multichannel detection offers some advantages over multiplex detection (used in FT-IR spectrometers), such as less susceptibility to noise from the light source.

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Despite these potential advantages, the weak intensity of the incoherently scattered Raman signal remains the major impediment to the use of Raman spectroscopy for rapid gas-phase spectroscopy. One potential problem is spectral interference from strong sources of light, such as fluorescence or ambient light from the samples themselves (e.g., combustion or plasma systems). Even in the absence of spectral interference, however, long collection times (minutes or even hours) are often required to obtain spectra with satisfactory resolution and signal-to-noise ratios. These collection times may be even longer for applications requiring high spectral resolution; increasing the resolution requires reducing the slit widths (causing reduced throughput) if using a monochromator or increasing the travel distance of the interferometer if using a Fourier transform Raman spectrometer. These long collection times may prohibit the use of gas-phase Raman spectroscopy for studying dynamical systems and for experiments in which large amounts of data need to be collected (e.g., imaging).

Several potential methods for increasing Raman signals and decreasing the collection time include the use of surface enhancement,^{4,5} resonance enhancement,⁶ or giant pulsed lasers.^{7,8} Surface enhancement provides a means for increasing the condensed-phase Raman signal by 3–6 orders of magnitude and has been used for detecting single molecules on surfaces. However, surface enhancement requires adsorbing the analyte onto a metal surface, a process that changes the state of the molecule and can perturb the system under study. The surface enhancement effect is also not universal. Resonance enhancement uses strong coupling between vibrational and electronic levels to increase the size of the Raman signal by 2–6 orders of magnitude. Since different molecules have electronic levels at different wavelengths, the universality of resonance enhancement is unfortunately limited by the choice of the laser wavelength. Since the Raman signal intensity increases linearly with the laser intensity, giant pulsed lasers have been used with multichannel detection as a means for increasing the Raman signal and obtaining single-shot spectra. These systems usually require using very wide entrance slits on the monochromator to maximize throughput, resulting in spectra with very low spectral resolution (e.g., spectral bandwidth >100 cm⁻¹). Consequently, such systems are suitable for systems with a small number of known molecules rather than for general chemical analysis. Resonance enhancement and giant pulsed laser approaches may also be susceptible to strong laser induced fluorescence and sample decomposition.

One universal method for increasing the intensity of the Raman signal and overcoming spectral interference (e.g., fluorescence) is to use a nonlinear variation of Raman spectroscopy called coherent anti-Stokes Raman spectroscopy (CARS). CARS is a well-established nonlinear optical method that involves the use of two or more intense beams of light in order to generate an output Raman signal as an intense narrow-band coherent beam that is blue-shifted (anti-Stokes) relative to the input beams. Spectra may be produced by gradually changing the frequency of one or more

of the laser beams while recording the intensity of the generated beam. Applications in the gas-phase include combustion diagnostics and high-resolution spectroscopy. Detection limits are around 0.1%.

Conventional CARS requires a gradual change in the wavelength of a tunable laser, which is not practical for generating Raman spectra at high speeds. In the past, a major obstacle has been that the tuning range of dye lasers is roughly an order of magnitude below that needed to produce complete vibrational spectra. A recent solution to this problem has been to use an optical parametric oscillator (OPO) as an exceptionally broadly tunable source for CARS.⁹ However, the time required to gradually change the frequency over the required range is still prohibitive for applications requiring rapid analysis. For example, using a pulsed laser with a 10 Hz repetition rate, the time required to produce a single vibrational spectrum covering a range of 3000 cm⁻¹ with a 0.2 cm⁻¹ step size would be 25 min, which is not a significant improvement over conventional gas-phase Raman spectroscopy. Furthermore, many researchers consider CARS to be experimentally complicated because it requires not only tuning of the detection system but also long-range tuning of one of the input beams. In contrast, conventional Raman spectroscopy using a fixed frequency laser and a monochromator with a CCD requires no such tuning and can benefit from multichannel detection.

Fortunately, CARS collection times may be dramatically reduced using multiplex CARS, in which tunable lasers are replaced by broad-band lasers. The generated output beam contains multiple wavelengths over a range that depends on the convoluted bandwidth of the broad-band input beam(s). Like conventional Raman spectroscopy, this output beam is then dispersed onto a multichannel detector that allows simultaneous measurement of multiple wavelengths. Multiplex CARS has served as an attractive tool for combustion diagnostics and pump-probe spectroscopies because of its ability to rapidly capture a portion of the vibrational spectrum in turbulent or dynamic systems without needing to tune laser wavelengths. Eckbreth and co-workers have developed several multiplex CARS mixing schemes, including dual-Stokes CARS and dual-broad-band CARS, both requiring the use of two separate broad-band beams and one narrow-band beam, and dual-pump CARS, which uses two separate narrow-band beams and one broad-band beam.¹⁰ For example, in dual-broad-band CARS, two broad-band sources are used to provide the first two photons of the CARS process, with the third photon coming from a narrow-band source. All vibrational frequencies that can be created by a photon from the first broad-band source minus a photon from the second broad-band source will appear in the generated spectrum. The resulting range of vibrational frequencies that may be probed depends not on the central frequencies of the broad-band sources but on their bandwidths.¹¹ To simplify the experiment, a single broad-band laser beam may be used for both broad-band sources. Using this dual-broad-band approach, the spectral range is, therefore, determined by the bandwidth of the broad-band source(s), and the spectral resolution is determined by the bandwidth of the narrow-band source (or the spectrograph). Fundamental differences

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between multiplex CARS and conventional Raman include the following: (1) the ability to obtain information with high 3D spatial resolution (if the input beams are crossed in the sample), (2) the generation of the Raman signal as an intense beam, (3) the presence of a nonresonant background, (4) signals that vary with the square of the concentration, and (5) no tradeoff between spectral resolution and throughput (usually found when using a monochromator). The fifth difference is possible because the generated CARS beam is coherent and can be tightly focused to a spot at the entrance of the monochromator that is smaller than the width of the pixels on the CCD.

A persistent obstacle for multiplex CARS, however, has been the difficulty in producing an adequate broad-band source of light. The traditional method for generating intense broad-band light has been through the use of a broad-band dye laser. Unfortunately, the bandwidth of a typical dye is only a few hundred wavenumbers, which is an order of magnitude below that needed to produce a complete vibrational spectrum. Recently, Toleutaev, Tahara, and Hamaguchi were able to increase this range to $\sim 1000\text{ cm}^{-1}$ using a mixture of dyes;¹² however, this range is still significantly narrower than the $\sim 3000\text{ cm}^{-1}$ range needed to cover the vibrational region. Goldberg and co-workers have explored the use of white light generation as a means for producing a broad-band source for CARS;¹³ however, white light generation requires pumping with extremely high peak powers,¹⁴ and the mode-locked lasers used to achieve these high peak powers have ultrashort pulse lengths that are not suitable for high-resolution spectroscopy. Without an adequate broad-band source that can provide the ability to generate a complete high-resolution vibrational spectrum, multiplex CARS has been limited as a technique for qualitative analysis. Although used for analysis of specific species known to exist in the sample, it has not been used as a general technique for the detection and identification of unknown species.

Recently, several groups have begun investigating the use of OPOs as solid-state alternatives to broad-band dye lasers.^{15,16} An OPO is a nonlinear optical device that is pumped by a laser and generates two laser-like beams. The higher-frequency beam is called the signal beam, the lower-frequency beam is called the idler beam, and the relationship between the two is $\omega_{\text{pump}} = \omega_{\text{signal}} + \omega_{\text{idler}}$. The nonlinear medium inside of an OPO is typically a birefringent crystal. Due to phase-matching constraints, a given crystal orientation usually produces only one set of signal and idler frequencies. Unless narrowed by some other method (e.g., using a diffraction grating or injection seeding¹⁷), the bandwidths of the free-running OPO signal and idler beams depend (oppositely) upon the slope of the phase-matching curve $d\theta/d\lambda$. For nonlinear materials, such as BBO (β -barium borate), the moderately small value of $d\theta_{\text{phase-matching}}/d\lambda$ allows a moderately wide range of wavelengths to be simultaneously phase-matched, resulting in moderately broad-band behavior. By combining the output of a free running BBO OPO with a narrow-band beam, multiplex

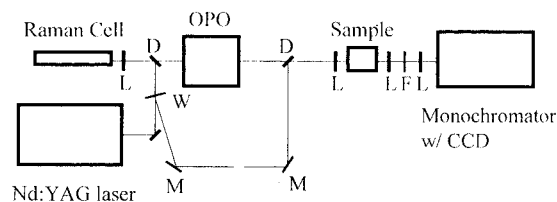


Figure 1. Simplified layout of the multiplex OPO CARS spectrometer. The symbols are as follows: D, dichroic mirror; F, filters; L, lens; M, mirror; and W, wedged window.

CARS spectra have been produced covering a range of around 40 cm^{-1} .^{18,19}

More recently, this range has been increased to $\sim 1000\text{ cm}^{-1}$ through the use of a near-degenerate OPO.²⁰ As the birefringent crystals in a type I phase-matching OPO are tilted so that $\omega_{\text{signal}} = \omega_{\text{idler}}$ (the degeneracy point), the slope $d\theta/d\lambda$ approaches 0, causing the bandwidth to increase. For example, a BBO OPO pumped at 532 nm and set near degeneracy ($\omega_{\text{signal}} \approx \omega_{\text{idler}}$) can produce broad-band light that is centered at 1064 nm and can cover a range of roughly 1000 cm^{-1} . When the output from this broad-band OPO is mixed with a separate narrow-band beam to produce light at $\omega_{\text{broad-band OPO}} - \omega_{\text{broad-band OPO}} + \omega_{\text{narrow-band beam}}$ (dual broad-band CARS), the resulting coherent Raman spectra cover a range of $\sim 1000\text{ cm}^{-1}$.

In this paper, we describe a new multiplex CARS spectrometer using an OPO CARS system that can cover the entire vibrational spectrum in a single laser pulse. The degenerate OPO used in this system is pumped at 683 nm by a backward stimulated Raman scattering beam from a hydrogen Raman shifter. Because of the wide range over which the slope $d\theta/d\lambda$ is ~ 0 for type I phase-matching BBO pumped at this wavelength, the light generated by this OPO covers a continuous range of $>3000\text{ cm}^{-1}$. When mixed with a narrow-band beam using the dual broad-band approach, the resulting spectral range is sufficient to cover the entire vibrational region.

EXPERIMENTAL SECTION

Figure 1 shows a simplified drawing of the instrument. The frequency doubled beam ($\lambda = 532\text{ nm}$) from an injection seeded Q-switched Nd:YAG laser (Spectraphysics GCR-230) was used to pump a 1-m-long stainless steel Raman cell (Taitech, Inc.) filled with H_2 at a pressure of 400 psi. The generated beam of light at 683 nm, produced by backward stimulated Raman scattering (SRS), is spatially similar to that of the 532-nm beam and provides a high-quality pump source for the OPO. The custom-built OPO (Laservision, Inc.) contains two BBO crystals (type I phase-matching) and produces a broad-band output beam with wavelengths covering a continuous range from 1020 to 1800 nm. Measurements of the shot-to-shot fluctuations in the energy of the OPO beam taken over a series of fixed wavelengths (1100–1700 nm in steps of 100 nm) yielded a relative standard deviation of 5–10% for each wavelength over this range.

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Typically, a 532-nm pump beam with a pulse energy of ~ 160 mJ produces a ~ 50 mJ beam of 683-nm light, which in turn produces ~ 6 mJ of broad-band light. The intensity of the backward SRS beam is enhanced by a factor of 2–3 by tilting the Raman cell so that the focused pump beam collides with the side of the Raman cell near the focal point. The origin for this enhancement is not fully understood, but it appears to be relatively insensitive to the pump wavelength (as observed when pumped by an OPO (Spectraphysics MOPO 730) that allowed the pump wavelength to be tuned gradually from 502 to 557 nm). Furthermore, this enhancement is not observed when hydrogen is replaced with methane.

The broad-band beam from the OPO is combined collinearly with an ~ 5 mJ beam of 532-nm light using a dichroic mirror that reflects 532 nm and passes light from 1000 to 2000 nm. The two overlapped beams (both horizontally polarized) are then focused into an 8-in.-long quartz cell using a 20-cm focal length lens. The spatial resolution of the system is determined by the diameter of the focused 532-nm beam, which is ~ 250 μm . After the cell, the pump beams are removed using a KG3, a BG40, and a 532-nm holographic notch filter, and the broad-band output beam containing spectral information is sent to a SPEX 1250m (1.25 m) monochromator with a CCD (1024 \times 256 elements, 27 μm pixels). Two gratings are available: a 150 g/mm grating that allows coverage of a 146-nm range at 0.143 nm (5–7 cm^{-1})/pixel, and a 1200 g/mm grating covering a range of 18 nm at 0.0176 nm (0.6–0.9 cm^{-1})/pixel.

The spectral resolution of the instrument is determined by both the bandwidth of the narrow-band beam (532 nm) and the resolution of the monochromator and CCD system. However, since the bandwidth of the 532-nm beam is negligible (<0.003 cm^{-1} as a result of injection seeding of the Nd:YAG laser), the instrumental resolution is effectively determined solely by the monochromator w/CCD. As will be discussed below, the factor that limits the resolution is the size of the pixels in the CCD.

RESULTS AND DISCUSSION

Several experiments were conducted in order to study the instrument's shot-to-shot stability, speed, resolution, range, and general quality of spectra. Spectra were also taken using a Fourier transform infrared spectrometer (Perkin-Elmer Paragon 1000) for comparison reasons. Results from these experiments are shown in Figures 2–5 and discussed below.

Figure 2 shows a series of successive spectra of cyclohexane vapor taken at room temperature. Three peaks at 459.9 (2949 cm^{-1}), 461.7 (2863 cm^{-1}), and 510.3 nm (801 cm^{-1}) are from cyclohexane itself, and two other peaks at 473.4 (2330 cm^{-1}) and 492.0 nm (1556 cm^{-1}) are due to nitrogen and oxygen in air. The spectra were produced using the low-density 150 g/mm grating, which allowed full vibrational spectra to be obtained quickly without needing to change the monochromator wavelength. The CCD exposure time was set to 0.1 s in order to match the 10 Hz repetition rate of the Nd:YAG laser. The relatively low spectral resolution of this grating caused two close peaks in the cyclohexane C–H region (at 459.91 (2949 cm^{-1}) and 460.20 nm (2936 cm^{-1})) to be unresolved.

Figure 2 shows that the shot-to-shot stability is somewhat poor. The stability of the system should depend on two different types of fluctuations in the pump beams: changes in absolute intensity

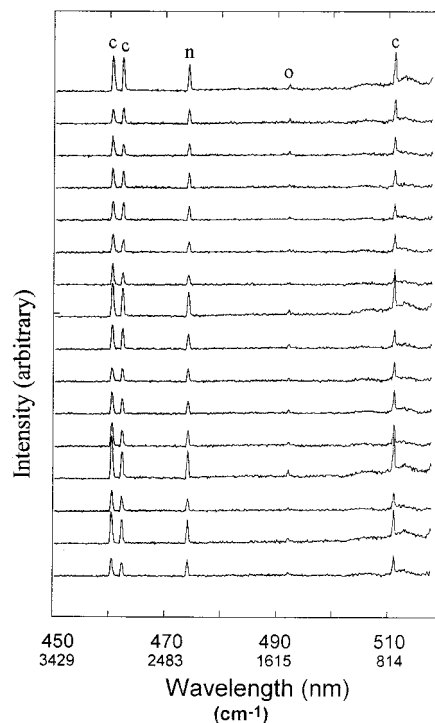


Figure 2. Successive uncorrected CARS spectra of cyclohexane vapor taken with the 150 g/mm grating and 0.1-s exposure times. The peaks are labeled as follows: cyclohexane, c; nitrogen, n; and oxygen, o.

(i.e., due to shot-to-shot variations in the intensity of the pump beams) and changes in the spectral distribution of the OPO (e.g., due to spectral shifting of the broad-band beam). One way to study these two types of fluctuations would be to use a spectrometer equipped with a near-infrared array detector to obtain shot-to-shot spectra of the degenerate OPO. The analysis of the results would involve creating a model that describes how these fluctuations would affect the resulting CARS spectra. In contrast to other multiplex CARS processes (i.e., Dual Pump CARS) in which the spectral profile of the broad-band source simply and directly affects the resulting spectra, the spectral profile of the broad-band source for dual broad-band CARS has a more complex (convoluted) effect on the resulting spectra.²⁰ The effect of the convolution is to smooth out artifacts in the spectrum of the broad-band source. More specifically, the dual broad-band approach used in this instrument involves the mixing of the broad-band source with itself (the broad-band source is used for both ω_1 and ω_2), which smooths out any potentially detrimental structure. Evidence for the resulting smoothness appears as a lack of fine structure and relative smoothness of the nonresonant background of broad spectra, such as those shown in Figure 2–4 (ignoring effects from stray Rayleigh scattered light and the holographic notch filter at the low-wavenumber portion of the spectra). Instead of contributing directly to structure within the spectrum, fine structure in the broad-band OPO tends to contribute to the gradual downward sloping of the nonresonant background from low-frequency shift to high-frequency shift.

Since our laboratory is not equipped with a near-infrared array detector, we instead chose to directly examine the resulting spectra themselves. Evaluation of the two most widely separated peaks from Figure 2 yielded relative standard deviations of 32

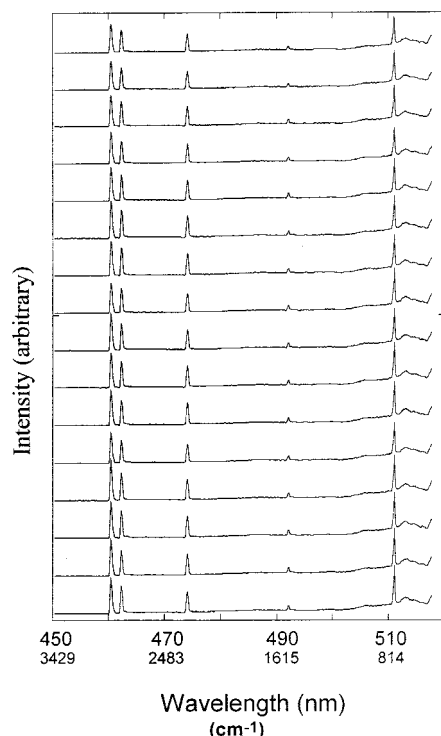


Figure 3. Successive uncorrected CARS spectra of the same sample as in Figure 2 taken with the 150 g/mm grating and 1-s exposure times.

(459.9 nm) and 38% (510.3 nm). The ratio of the two peaks had a standard deviation of 18%, indicating that the use of an internal standard would be somewhat effective in reducing the fluctuations. The experiment was then repeated using the high-resolution (1200 g/mm) grating so that a similar analysis could be carried out using two closely spaced peaks. The relative standard deviation for the two tallest peaks in the CH region were 32 (459.9 nm) and 42% (461.8 nm), and the relative standard deviation of the ratio was 27%.

Next, the measurement was repeated after increasing the acquisition times from 0.1 (single laser pulse) to 1 s (accumulation of 10 laser pulses) in order to investigate the potential benefit of averaging. Figure 3 shows the resulting spectra, which show a significant improvement in stability from exposure to exposure compared to Figure 2. The relative standard deviations of the same three peaks (at 459.9, 461.8, and 510.3 nm) decreased to 9, 6, and 6%, respectively, and the relative standard deviations of the ratios were 7% for both the 459.9:461.8 and the 459.9:510.3 nm ratios. The improvements are roughly consistent with that predicted (an improvement factor of $10^{1/2}$). These results suggest that one may be able to significantly improve precision without sacrificing temporal resolution by using a higher repetition rate laser.

The beamlike output of the CARS signal makes this technique better than conventional Raman for simultaneously obtaining both high resolution and high throughput. In conventional Raman, maximum resolution can be achieved by reducing the size of the entrance slit so that it approaches the distance between pixels in the CCD (e.g., 27 μm). However, since incoherently scattered light is imaged at the entrance slit, reducing the width of the slit also reduces the amount of light that enters the monochromator. Since coherent light can be focused to a spot size that is smaller than

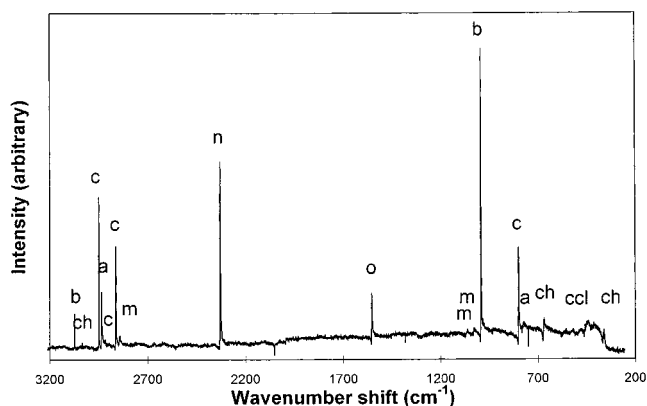


Figure 4. Spectrum of a mixture of eight species in the gas phase: benzene, b; acetone, a; carbon tetrachloride, ccl; chloroform, ch; cyclohexane, c; methanol, m; nitrogen, n; and oxygen, o.

that of incoherent light, the entire CARS signal can pass through a 27- μm -wide monochromator entrance slit. Therefore, maximum resolution can be achieved without loss of any of the CARS signal. When used in this manner, the resolution of the instrument (limited by the 27- μm pixel width of the CCD and using the 1200 g/mm grating) corresponds to 0.018 nm pixel-to-pixel.

Experimentally, the difference between coherent and incoherent light can also be observed by varying the size of the entrance slit. As the entrance slit is increased to values above 27 μm , peaks from incoherent light (e.g., ambient room light from fluorescent light bulbs that contain mercury vapor) grow broader, but peaks from the CARS signal remain sharp and narrow.

To determine the maximum range of this technique, we added hydrogen gas to the cell. Hydrogen's Raman shift at $\sim 4160\text{ cm}^{-1}$ is the highest frequency possible from a molecular species. The instrument was able to measure this peak with reasonably good signal to noise ($S/N = 20$ for a 10-s exposure), indicating that the instrument can be used to cover a range of more than 4000 cm^{-1} .

Finally, Figure 4 shows a spectrum taken with this instrument of a mixture of benzene, acetone, carbon tetrachloride, chloroform, cyclohexane, and methanol vapor, with two additional peaks from nitrogen and oxygen. This spectrum was taken using the 1200 g/mm grating. To produce this spectrum, 4 separate exposures, each lasting 10 s (100 laser pulses) and covering a different wavelength region, were combined so that the entire vibrational region from 3200 to 250 cm^{-1} could be displayed. The low wavenumber shift cutoff in this spectrum was determined to be $\sim 350\text{ cm}^{-1}$ as a result of the holographic notch filter. This value may be further reduced by either angle-tuning an appropriate holographic notch filter or by tuning the wavelength of the narrow-band beam. In past work, using an earlier version of this OPO that had a narrower bandwidth, use of the second approach resulted in a low wavenumber shift limit of 71 cm^{-1} .²⁰ Further reduction in this number (e.g., for generating pure rotational spectra) could be achieved using techniques such as folded or planar BOXCARs.²¹

Aside from the merging of the four exposures, the spectrum shown is not corrected for the wavelength response of the

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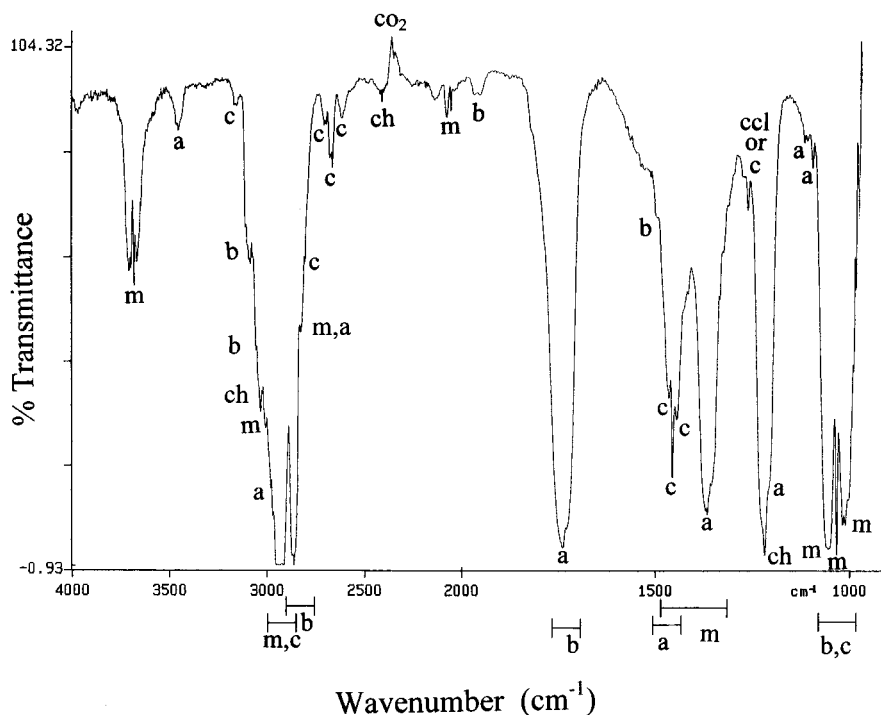


Figure 5. FT-IR spectrum of the same species shown in Figure 4. The peaks are labeled with the same notation as in Figure 4. The labels below the x axis are for species that have peaks in the vicinity that are not apparent due to severe spectral congestion.

detection system. One advantage of coherent spectroscopies is that they have a nonzero nonresonant background that can be used to help correct for the wavelength dependencies of lasers, optics, detectors, and even the sample or sample holder. When the spectrum shown in Figure 4 was corrected so that the nonresonant background was flat, the resulting Raman cross section for the symmetric ring mode (992 cm^{-1}) was 1.2 times larger than the cross section for the CH stretch (3070 cm^{-1}). This value is similar to a ratio of 1.5 found in a literature reference for gas-phase Raman cross sections.²²

The multiplex CARS spectrum shown in Figure 4 is dominated by sharp narrow Q branches, and the average line width of the eight tallest peaks is 2.5 cm^{-1} (standard deviation, 0.7 cm^{-1}). All of the peaks are fully resolved, with the exception of overlapping peaks from acetone and cyclohexane at 2936 cm^{-1} . Figure 5 shows an FT-IR spectrum taken of the same vapor-phase compounds, taken with a resolution of 4 cm^{-1} . The resulting FT-IR peaks are much more rotationally broadened, resulting in severe spectral congestion.

CONCLUSION

A high-resolution multiplex CARS spectrometer has been built that can take complete gas-phase vibrational Raman spectra in a single laser pulse. This spectrometer uses a degenerate OPO as an exceptionally broad band source, generating light that covers a range sufficient to cover the entire vibrational region. The $<1\text{ cm}^{-1}$ resolution, which is limited by the monochromator grating and CCD, is useful for generating gas-phase Raman spectra with peaks that are narrow and relatively free from spectral congestion. Accumulation of signal over 1 s (10 laser pulses) improves stability so that the relative standard deviation of successive exposures is 5–10%, which is probably acceptable for most applications.

Although the generation of the broad-band source involves the use of a pump laser, Raman shifter, and OPO, the remainder of the experimental setup is not significantly more complicated than that of a conventional Raman experiment. The only major difference is that a broad-band beam is collinearly added to that of the "normal" narrow-band laser beam. Furthermore, it is possible that continuing rapid advances in laser technology may provide a simpler way of generating broad-band light.

The ability to capture the entire vibrational spectrum using a rapid and experimentally simple system may promote the use of CARS as a standard analytical technique. In the past, experimental complexity and the inability to generate complete spectra have relegated CARS to specialized problems involving specific vibrational peaks from predicted molecules. For the first time, it may be both possible and practical to consider CARS as a candidate for general qualitative and quantitative analysis, especially in applications that may benefit from high spectral, spatial, and temporal resolution. Such applications may include spectroscopic imaging, combustion diagnostics, pump-probe spectroscopy, Raman spectroscopy of dynamical systems, hazardous gas monitoring, and as a detector in flowing systems (e.g., industrial monitoring and chromatographic separation detection).

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