Introduction

A new technique was recently developed which allows broadband infrared absorption spectra to be photographed with 500-nsec time resolution, even under some conditions, in a single-shot. Experimental details and theoretical aspects of this method are discussed at length in [1]. Briefly, the technique utilizes third order nonlinearities of alkali metal vapors to achieve two objectives: (1) generation of a pulsed, broadband, infrared continuum beam which can probe the absorption of a sample and (2) subsequent conversion of this i.r. beam, with its encoded spectral information about the sample, to the visible, where it can be photographically or photoelectrically recorded. The two principal nonlinear processes involved are diagrammed in Fig. 1.

Figure 1 Level diagrams for the Raman generation and four-wave upconversion processes.

Generation of \( v_{\text{ir}} \) is accomplished by broadband stimulated electronic Raman scattering (SERS) in a first alkali metal vapor heat-pipe oven (HP1 in Fig. 2). A broadband (\( \Delta v \sim 1000 \text{cm}^{-1} \)) visible dye laser beam \( v_{\text{C}} \) originates from a mirrorless, superfluorescent dye cell (C1 in Fig. 2) and is subsequently amplified to the level of a few millijoules and focused into HP1. This visible beam, the primary beam for the SERS process, is converted to an infrared Stokes beam.
having approximately the same spectral width and pulse duration (≈5nsec) as \( \nu_c \). The i.r. spectral range spanned by \( \nu_{ir} \) depends on both \( \nu_c \) and the energy of the final electronic state involved in the Raman transition. For Rb, with \( \nu_c \) in the vicinity of the 6p resonance lines, the infrared generated falls in the 2.7\( \mu \)m range. With the use of dye laser continua spectrally located near other alkali resonance lines, generation of broadband i.r. in several different regions, extending out to at least 30\( \mu \)m, should be possible.[1]

The second nonlinear process diagrammed in Fig. 1 is responsible for the upconversion that occurs in the second heat-pipe oven (HP2 in Fig. 2). A narrow band laser beam \( \nu_L \), injected into HP2 via a silicon wafer (Si\(_2\)), generates by SERS a narrow-band Stokes beam \( \nu_S \). Beams \( \nu_L \), \( \nu_S \) and \( \nu_{ir} \) beat together in HP2 to produce an upconverted beam \( \nu_U \) by means of the resonantly enhanced four-wave mixing process shown in Fig. 1. The intensity of a given spectral component of \( \nu_U \) is linearly proportional to its corresponding \( \nu_{ir} \) component. Thus infrared spectra are simply translated to the visible by the fixed Raman energies of the alkali metal atoms in HP2. This procedure allows one to take advantage of the fact that detectors with high inherent spectral resolution exist for the visible region.

![Diagram of experimental apparatus](image)

Figure 2 Diagram of experimental apparatus.

Experimental

The dye cells depicted in Fig. 2 were all transversely pumped by the third harmonic of a Quanta-Ray Nd\(^{3+}\):YAG laser. Up to 100mj of pulse energy is
available at this frequency. This was apportioned to the various dye cells as indicated in the diagram. The basic pulse width was \( \sim 5\text{ nsec} \).

The polarizations of the various beams were chosen as shown in Fig. 2. This allowed the narrow-band laser beam \( r_L \) to be conveniently nulled by polarizer \( P_2 \), while the orthogonally polarized upconverted beam is transmitted.

For most of our work thus far we have utilized the Rb 5s→6p→6s Raman scheme (shown in Fig. 1) to generate \( r_p \). Using dyes such as POPOP, Bis-MSB, and dimethyl POPOP in p-dioxane, and Stilbene 420 in mixtures of water and methanol, i.r. continua covering the range from \( \sim 4000\text{ cm}^{-1} \) to \( \sim 2600\text{ cm}^{-1} \) have been produced. At the longer i.r. wavelengths, the cross-section for the Raman process shown in Fig. 1 becomes less resonantly enhanced, requiring \( \nu_c \) pump energies of a few millijoules to exceed SERS thresholds.

For the Raman-driven upconverter we have exclusively employed K vapor and the scheme shown in Fig. 1. DPS in p-dioxane is used in both the narrow-band oscillator and amplifier cells (\( C_5 \) and \( C_6 \)). In some instances an upconverted beam amplifier cell \( C_4 \) was also utilized.

**Discussion of Spectra**

The upconverted spectra shown in Fig. 3 are typical of our first results.

![Figure 3 Upconverted POPOP Rb-K spectrum (second order, sample cell removed); increasing exposures (top to bottom). The numbers 8,6,5 refer to numbered peaks in the IUPAC calibration spectrum given in Fig. 4.](image)
Here the combination of a 5 torr Rb cell and a continuum beam based on solutions of POPOP in p-dioxane was used to generate an i.r. continuum, and the sample cell S was completely removed. Dark bands correspond to \(4s \rightarrow 5p_{3/2,1/2}\) resonance absorptions of K atoms in the second cell and to absence of i.r. light at the exact \(6p_{3/2,1/2} \rightarrow 6s\) frequencies of Rb. Between each of these absorption line pairs is a dark line, due to interference nulls in \(\chi^{(3)}_{xxx}\) for K in the upconverter cell and in \(\chi^{(3)}_{xxxx}\) for Rb in the Raman cell.[1]

The myriad of sharp, dark lines on the high frequency side of the spectrum results from residual water vapor in the optical path between the two vapor cells. A densitometer trace of a portion of the spectrum in Fig. 3 is shown in the upper portion of Fig. 4. The correspondence with a published IUPAC water vapor spectrum[3] (lower trace) is apparent.

Figure 4 Comparison of densitometer trace of portion of spectrum shown in Fig. 3 (upper) with IUPAC calibration spectrum (lower).

The spectra of Fig. 3 represent superpositions of dozens of shots taken with the lower power apparatus of [1]. One result of this averaging is that a random spectral noise that we have since repeatedly encountered (side infra) is effec-
tively averaged out, leaving well-resolved i.r. bands with apparently correct intensity distributions.

In Fig. 5 the wide range of i.r. covered with the use of dimethyl POPOP in cells C₁, C₂, and C₃ is demonstrated. The bright line at the left
ing could be tolerated. Tuning of $\nu_L$ over a wide range is observed to have no strong effect on the upconverted spectra, in line with the above comments.

At the right of the bottom spectrum of Fig. 5 are seen again diffuse dark lines corresponding to the Rb 6p$\rightarrow$6s transitions and also a sharp dark line between them representing the Rb Raman null. The latter occurs approximately at 3607 cm$^{-1}$. Thus, a spectral region $\sim$1000 cm$^{-1}$ in width can be spanned with a single continuum dye solution, provided several shots per plate exposure are allowed. Because of insufficient exposure, the single-shot spectrum covers only approximately 600 cm$^{-1}$.

The top few spectra display the granular spectral character of the upconverted light, mentioned earlier. To obtain a reasonably accurate spectrum comprising narrow absorption lines generally requires averaging ten shots or so. Even so, in Fig. 5 a dark line at $\sim$3208 cm$^{-1}$ is clearly evident in the top most (single-shot) exposure. This dark line appears in virtually all spectra covering this region. Its frequency coincides with the K 4d-5f transitions. Potassium atoms in the 4d states are probably produced by photodissociation of K$_2$ dimers as the beam $\nu_L$ passes through HP2.

Figure 6 shows increasing exposures of upconverted spectra with $\sim$300 torr of CH$_4$ in the 18 cm long sample cell. The CH$_4$ Q-branch is marked. The P and R branches are also clearly seen. Upconverted spectra have also been recorded with NH$_3$ and various other organics in the sample cell.[2]

Figure 6 Methane spectra (second order, 300 torr). Shots per exposure are 10, 20, 30 and 50 (top to bottom). Cells C$_1$, C$_2$ and C$_3$ contain $5\times10^{-4}$ molar solutions of Stilbene 420 in 1:1 H$_2$O-CH$_3$OH.

Example of a Time-Resolved Spectrum: CH$_3$NC$\rightarrow$CH$_3$CN

To demonstrate the transient capability of the new technique, the isomerization of methyl isocyanide to methyl cyanide was studied. This well-known isomerization, exothermic by 23.7 kcal/mole[4], has been suggested as an ideal unimolecular reaction for testing thermal explosion theories.[5] Recently we observed
that this thermal isomerization can be initiated by single pulses of CO\textsubscript{2} TEA laser radiation, tuned to coincide with the \( \nu_4 \) band of the CH\textsubscript{3}NC molecule.[6]

The \( \nu_1 \) band of CH\textsubscript{3}NC, associated with the symmetric stretch of the CH\textsubscript{3} group, lies near 2966 cm\(^{-1}\). The top strip in Fig. 7 shows the upconverted spectrum of CH\textsubscript{3}NC in this region. In agreement with an earlier study by Thompson and Williams[7], the P, Q, R branch contours of the \( \nu_1 \) band are clearly shown, but the P and R lines are not resolved. The sharp lines on the high-frequency side of the R branch of the \( \nu_1 \) band belong to the \( \nu_5 \) band. The isomerization product CH\textsubscript{2}CN also has a \( \nu_1 \) band centered at 2955 cm\(^{-1}\), but the absorption band is too weak to be observed here.

Figure 7 Changes in the upconverted spectra of 100 torr CH\textsubscript{3}NC as it thermally explodes (isomerizes), various times after the application of an unfocused 0.5J pulse of CO\textsubscript{2} TEA laser radiation (\( \nu_{\text{CO}_2} = 960 \text{ cm}^{-1} \)). Each spectrum represents 16 superimposed shots.
Figure 7 shows time-resolved upconverted spectra of CH$_3$NC (100 torr initial pressure) taken at intervals of 1, 8, 17, 30, 100 and 265µsec, respectively, after the unfocused 0.5J CO$_2$ laser pulse, applied to the sample cell via Si$_2$ (Fig. 2), has initiated the thermal isomerization. Two effects can be clearly seen from these spectra. First, the intensity of the $\nu_1$ absorption band weakens as time increases. Second, the absorption band contours of the P and R branches broaden substantially, with maximum broadening occurring 30µsec after the laser pulse. This broadening is due to the increase in temperature from the energy released in the isomerization process. As shown by Gerhard and Dennison[8], for a parallel band transition in a symmetric rotator (e.g., the $\nu_1$ band of CH$_3$NC), the separation between the maxima of the P and R branch contours is proportional to the square root of the absolute temperature. Using this relation and the measured separations between P and R bands, we obtain the instantaneous temperature as a function of time, plotted in Fig. 8.

![Figure 8](image)

Figure 8 Temperature of the reacting CH$_3$NC gas as a function of time, determined from the separation of the P and R branches.

About 30µsec after the laser pulse, the temperature rises to about 673K; it then gradually cools. The maximum measured temperature of 673K indicates this to be the approximate "threshold temperature" for thermal isomerization to CH$_3$CH; this is in reasonable agreement with thermal data.[9] Molecules of CH$_3$NC hotter than this threshold temperature rapidly isomerize to CH$_3$CN and are thus not detected by the i.r. probe. A true determination of the kinetic temperature could be made by seeding the CH$_3$NC gas with a small amount of stable foreign gas (such as HCN) that has strong i.r. bands in a convenient range.

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References


