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TIME-RESOLVED INFRARED SPECTRAL PHOTOGRAPHY, (U)
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TIME-RESOLVED INFRARED SPECTRAL PHOTOGRAPHY

LEVEL III

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Introduction

A new technique was recently developed [1] which allows broadband infrared absorption spectra to be photographed with ≈ 5 nsec time resolution, even under some conditions, in a single-shot. Experimental details and theoretical aspects of this method are discussed at length in [2]. Briefly, the technique utilizes third order nonlinearities of alkali metal vapors to achieve two objectives: (1) generation of a pulsed, broadband, infrared continuum beam (ν_{ir}) 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.

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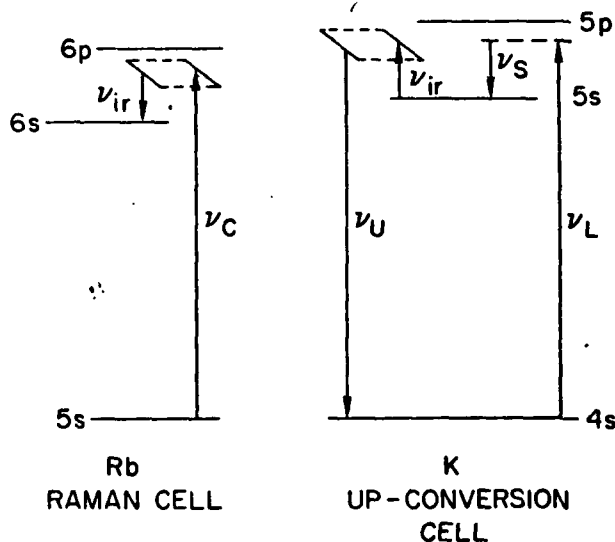


Figure 1 Level diagrams for the Raman generation and four-wave upconversion processes.

Generation of ν_{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 ($\Delta\nu \sim 1000 \text{ cm}^{-1}$) visible dye laser beam ν_c , originates from a mirrorless, superfluorescent dye cell (C_1 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

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having approximately the same spectral width and pulse duration ($\approx 5\text{nsec}$) as ν_c . The i.r. spectral range spanned by ν_{ir} depends on both ν_c and the energy of the final electronic state involved in the Raman transition. For Rb, with ν_c in the vicinity of the 6p resonance lines, the infrared generated falls in the $2.7\mu\text{m}$ 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 $30\mu\text{m}$, 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 ν_L , injected into HP2 via a silicon wafer (Si_2), generates by SERS a narrow-band Stokes beam ν_S . Beams ν_L , ν_S and ν_{ir} beat together in HP2 to produce an upconverted beam ν_U by means of the resonantly enhanced four-wave mixing process shown in Fig. 1. The intensity of a given spectral component of ν_U is linearly proportional to its corresponding ν_{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.

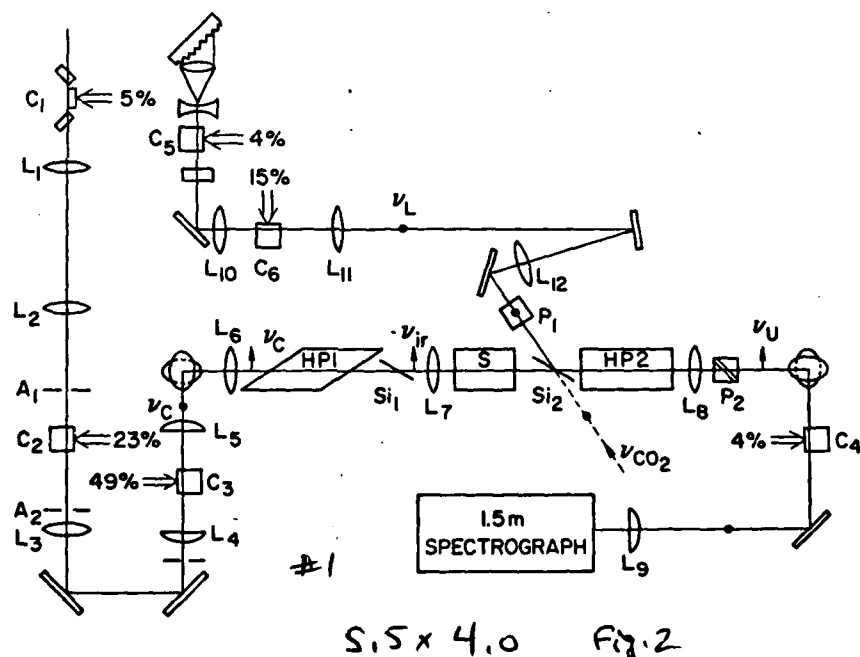


Figure 2 Diagram of experimental apparatus.

Experimental

The dye cells depicted in Fig. 2 were all transversely pumped by the third harmonic of a Quanta-Ray $\text{Nd}^{3+}:\text{YAG}$ laser. Up to 100mj of pulse energy is

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available at this frequency. This was apportioned to the various dye cells as indicated in the diagram. The basic pulse width was ~ 5 nsec.

The polarizations of the various beams were chosen as shown in Fig. 2. This allowed the narrow-band laser beam ν_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 $5s \rightarrow 6p \rightarrow 6s$ Raman scheme (shown in Fig. 1) to generate ν_{ir} . 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 $\sim 4,000\text{cm}^{-1}$ 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 ν_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.

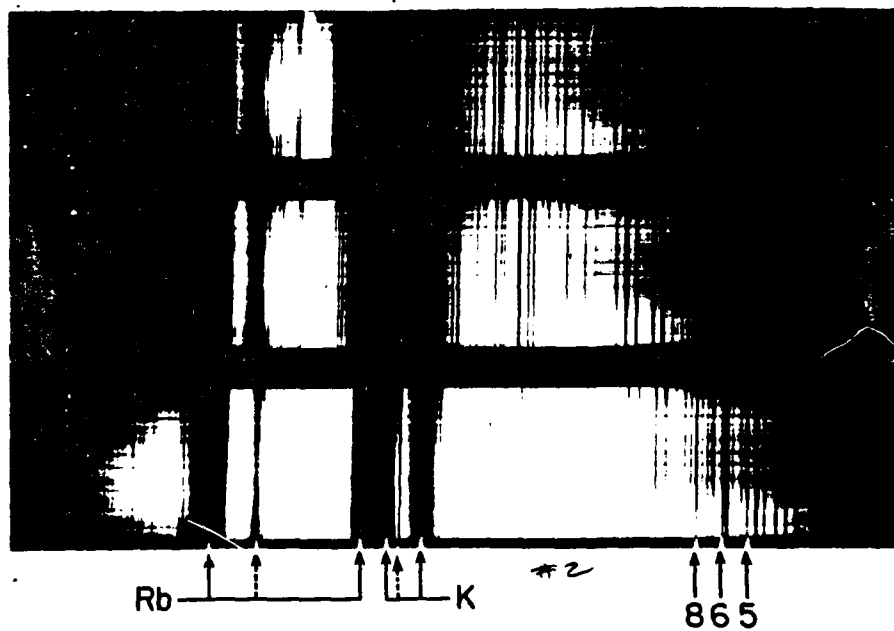
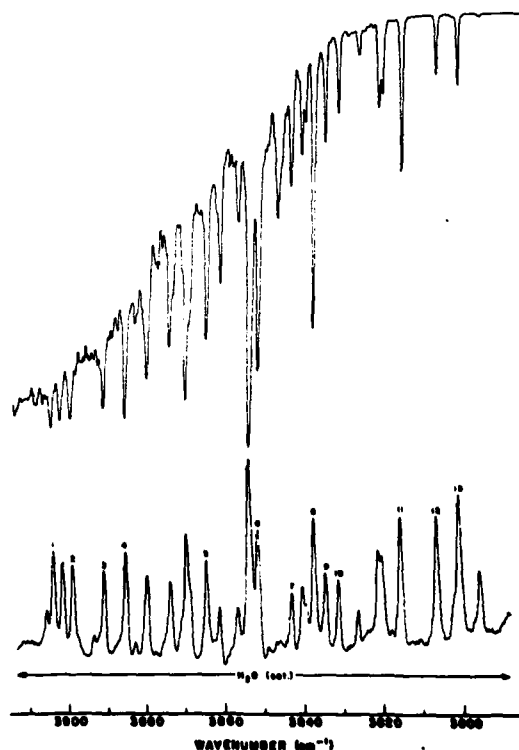


Figure 3 Upconverted POPOP Rb-K spectrum (second order, sample cell removed); increasing exposures (top to bottom). The numbers 8,6,5 refer to numbered peaks in the IUPAC calibration spectrum given in Fig. 4.

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 $\chi^{(3)}_{xyy}$ for K in the upconverter cell and in $\chi^{(3)}_{xxx}$ 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 C_1 , C_2 , and C_3 is demonstrated. The bright line at the left

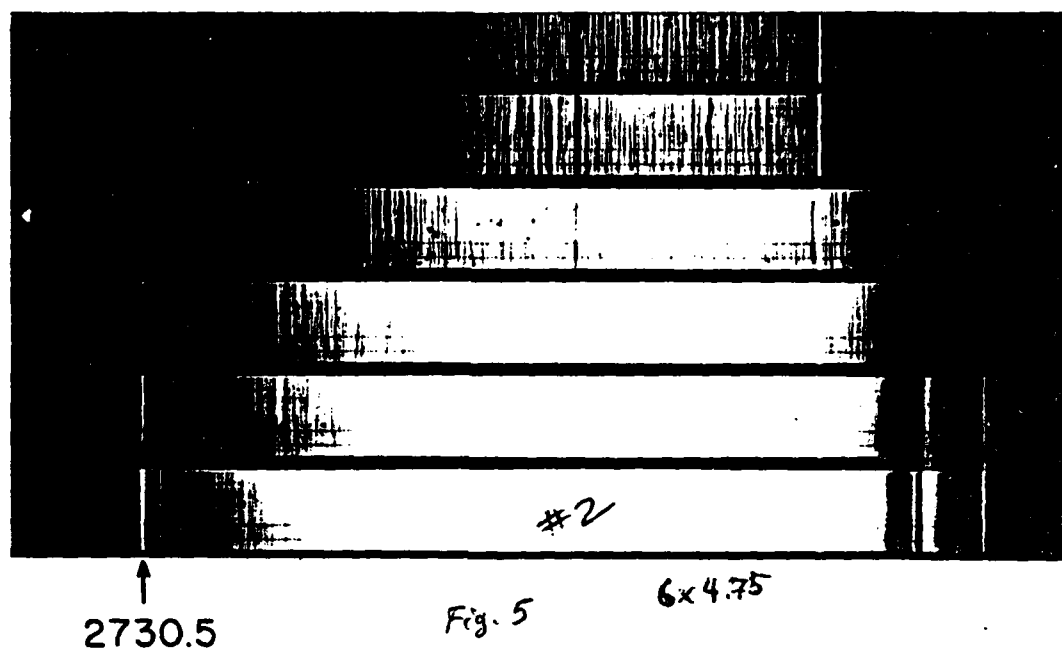


Figure 5 Upconverted dimethyl POPOP Rb-K spectra with accumulated shots per exposure of 1,3,5,7,9 and 20 (top to bottom). No upconverted beam amplifier was used.

of the lower spectra results from upconversion of a 2730.5cm^{-1} lasing transition ($6s_{1/2} \rightarrow 5p_{1/2}$) in the K cell HP2. The bright line seen at the right of the upper spectra is the narrow-band laser beam ν_L , which remains fixed in frequency in all of the spectra shown in Fig. 5. From spectra such as those shown in Fig. 5, we observe that phase-matching appears to play no important role in the Raman-driven upconverter, since there is no obvious intensity peaking of upconverted light at the wavelength (ν_L) that corresponds to the exact phase-matching i.r. wavelength. The very striking broadband nature of the upconversion process, together with its observed high efficiency[1], is further evidence of this. A possible explanation for this is that the SERS process has very high gain (several hundred cm^{-1}). This may give a short "active region", where the Stokes wave ν_S grows rapidly while the intensity of the pump wave ν_L falls. If this region were only a few millimeters long, fairly large wavevector mismatch-

ing could be tolerated. Tuning of ν_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 3607cm^{-1} . Thus, a spectral region $\sim 1000\text{cm}^{-1}$ 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 600cm^{-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 $\sim 3208\text{cm}^{-1}$ 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 ν_L passes through HP2.

Figure 6 shows increasing exposures of upconverted spectra with ~ 300 torr of CH_4 in the 18cm 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]

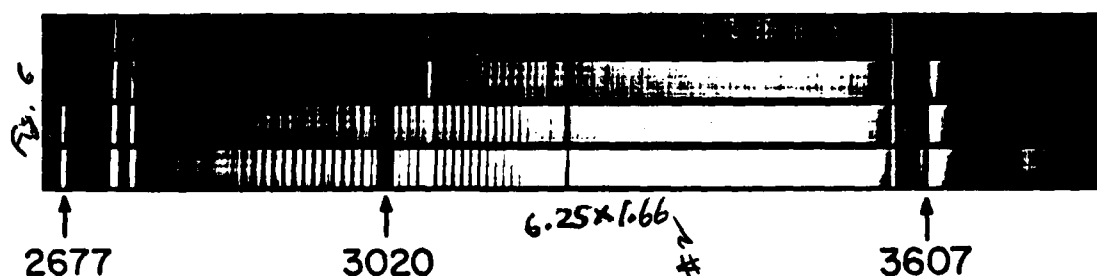


Figure 6 Methane spectra (second order, 300 torr). Shots per exposure are 10, 20, 30 and 50 (top to bottom). Cells C_1 , C_2 and C_3 contain 5×10^{-4} molar solutions of Stilbene 420 in 1:1 $\text{H}_2\text{O}-\text{CH}_3\text{OH}$.

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

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 23.7kcal/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_2 TEA laser radiation, tuned to coincide with the ν_4 band of the CH_3NC molecule.[6]

The ν_1 band of CH_3NC , associated with the symmetric stretch of the CH_3 group, lies near 2966cm^{-1} . The top strip in Fig. 7 shows the upconverted spectrum of CH_3NC in this region. In agreement with an earlier study by Thompson and Williams[7], the P, Q, R branch contours of the ν_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 ν_1 band belong to the ν_5 band. The isomerization product CH_3CN also has a ν_1 band centered at 2955cm^{-1} , but the absorption band is too weak to be observed here.

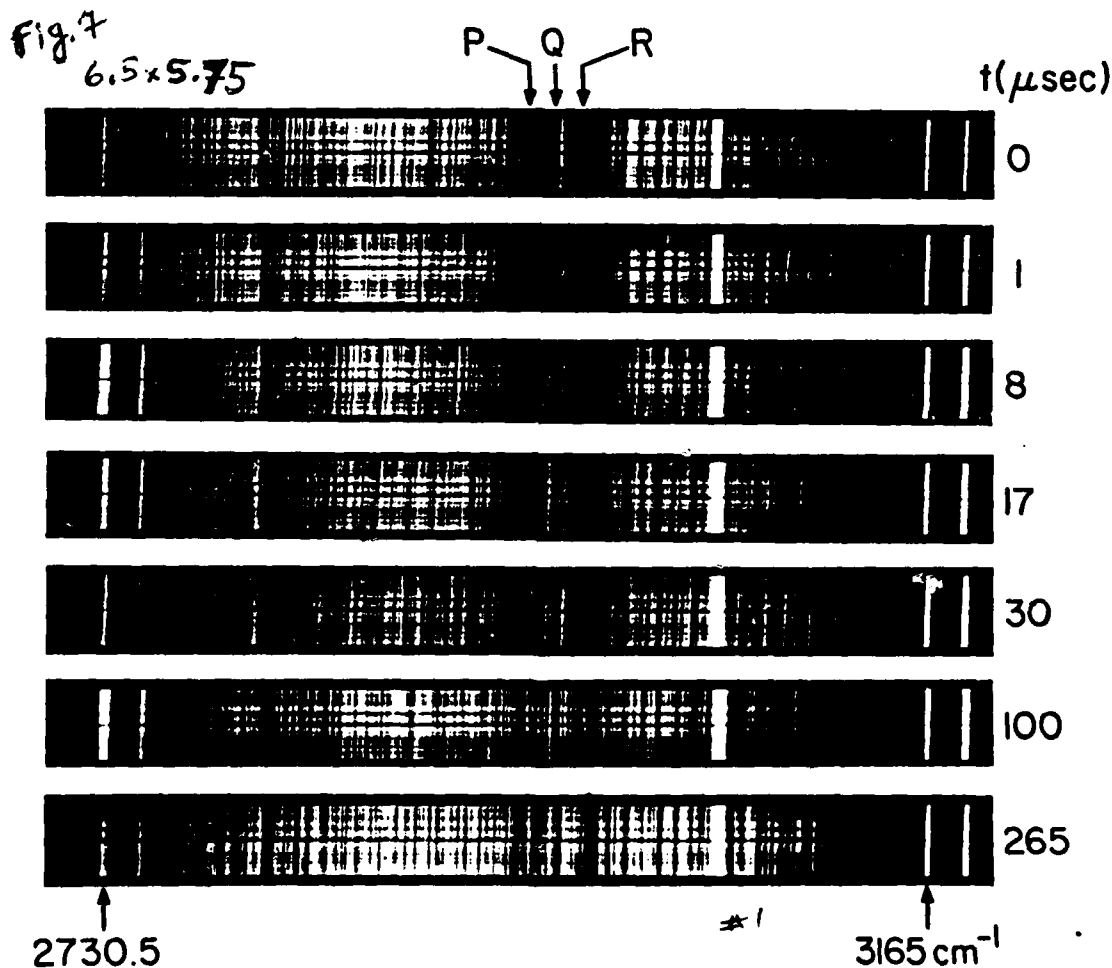
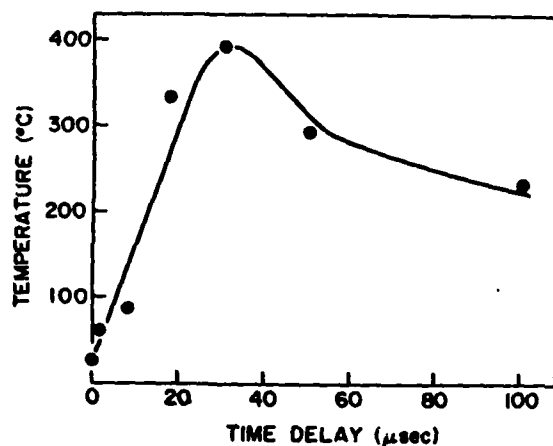


Figure 7 Changes in the upconverted spectra of 100 torr CH_3NC as it thermally explodes (isomerizes), various times after the application of an unfocused 0.5J pulse of CO_2 TEA laser radiation ($\nu_{\text{CO}_2}=960\text{cm}^{-1}$). Each spectrum represents 16 superimposed shots.

Figure 7 shows time-resolved upconverted spectra of CH_3NC (100 torr initial pressure) taken at intervals of 1,8,17,30,100 and 265 μsec , 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 ν_1 absorption band weakens as time increases. Second, the absorption band contours of the P and R branches broaden substantially, with maximum broadening occurring 30 μsec 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 ν_1 band of CH_3NC), 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 Temperature of the reacting CH_3NC gas as a function of time, determined from the separation of the P and R branches.



About 30 μsec 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_3CH ; this is in reasonable agreement with thermal data.[9] Molecules of CH_3NC hotter than this threshold temperature rapidly isomerize to CH_3CN and are thus not detected by the i.r. probe. A true determination of the kinetic temperature could be made by seeding the CH_3NC gas with a small amount of stable foreign gas (such as HCN) that has strong i.r. bands in a convenient range.

Acknowledgements

This work is partly supported by the U. S. Army Research Office and the Office of Naval Research. We would like to thank our colleague, Dr. J. Ors, for preparation of the CH_3NC sample.

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