## SHOCK TUBE STUDY OF HIGH TEMPERATURE ABSORPTION

## SPECTROSCOPY OF CH AT 431 nm

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An experimental survey of CH absorption near the $Q_{2d}(7)$ and $Q_{1c}(7)$ lines of the $\{A^2\Delta \ (v=0) \leftarrow X^2\Pi \ (v=0)\}$ band was obtained at 2840°K, 0.2 atm using a remotely located cw ring dye laser source and a shock tube. Mixtures of methane and argon were shock heated to provide reproducible peak concentrations of CH, and narrow-line absorption was measured in repeated experiments with the laser set at different wavelengths. The spectral absorption data were interpreted with a theoretical model in order to verify the measurements and establish the sensitivity of this technique as an in situ absorption diagnostic for CH at 431.132 nm (vac.).

INTRODUCTION

The species CH is of interest in combustion. Its characteristic blue emission spectrum can be observed in the reaction zone of most premixed flames [1]. The spectral characteristics of CH have been studied in detail [2], and absolute absorption measurements of its concentration in combustion environments were made possible by the publication of reliable data on its oscillator strength [3,4]. Relative measurements of CH in flames using laser-induced-fluorescence have also been reported [5]. Useful studies of spectral line assignments were reported by Fagerholm, who studied the $^2\Sigma^- \leftarrow \ ^2\Pi$ and the $^2\Delta \leftarrow \ ^2\Pi$ systems of CH and CD [6], and by Gero [7]. In addition, Kiess and Broida provide a useful overview of spectroscopic data on CH [8].

In this study, a laser absorption technique previously demonstrated in this laboratory for the quantitative measurement of NCO [9] was applied as a diagnostic of CH behind incident shock waves. Mixtures of methane dilute in argon were shock heated to generate reproducible levels of CH under specified conditions of pressure (0.2 atm) and temperature (2840°K) in the shock tube. The narrow-linewidth absorption spectrum in the vicinity of the $Q_{1c}(7)$ and $Q_{2d}(7)$ lines of the $(A^2\Delta(v=0) \leftarrow X^2\Pi(v=0))$ band of CH was mapped out by conducting a series of nearly identical experiments, each at a different laser wavelength. Using the known spectroscopic parameters of CH, detection limits were inferred from the present experimental conditions and extrapolated to other temperatures.

Experimental spectra reported by Fagerholm [6] and Gero [7] indicate the accidental coincidence of the $Q_{2d}(7)$ and $Q_{1c}(7)$ lines, which belong to different branches of the $[A^2\Delta(v=0) \leftarrow X^2\Pi(v=0)]$ band. The present diagnostic takes

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advantage of this coincidence and is therefore characterized by higher absorption levels than would be obtained on a single line. In this paper, the experimental facility and optical techniques will first be described, then the spectroscopic models and results will be presented.

## EXPERIMENT

The experiments were conducted behind incident shock waves in a 15.24 cm internal diameter pressure-driven shock tube. Shock speeds varied between 1.79 and 1.84 mm/µsec, with attenuation of 0.5%/m or less. Typical leak plus outgassing rates were $10^{-4}$ torr/min. Methane was obtained from a commercial cylinder (Liquid Carbonic) with 99% purity. The absorption from the $Q_{1c}(7)$ and $Q_{2d}(7)$ lines of CH around 431.13 nm (vac.) was observed using the optical setup shown in Fig. 1. This system was described in detail elsewhere [10,11]. It consisted of an $Ar^+$-pumped ring dye laser with an output power of 40 mW. The performance of the stilbene S3 dye degraded rapidly at this wavelength and required the use of fresh dye each day of laser operation. Amplitude stabilization was necessary for this ring laser operating near threshold to prevent excessive amplification of $Ar^+$ laser power fluctuations. Verification of the single mode operation of the visible dye laser beam was obtained using a confocal interferometer (Spectra-Physics Model 470, free spectral range 2 GHz), but proved difficult at this wavelength as a result of finesse degradation. The component of the laser power rejected by the amplitude stabilizer was sufficient to drive the wavemeter (Burleigh model WA-10) used for setting the laser wavelength. It was necessary to correct the displayed wavelength for the change in the index of refraction of air between the helium-neon reference wavelength at 632.991 nm and the blue wavelengths around 431.13 nm (correction = actual - displayed wavelength = +0.0019 nm).

The visible output of the laser system was transported 65 m via a 200 µm optical fiber to the shock tube facility where it was double-passed through the shock tube test section. The incident and return beams were filtered (FWHM: 40 nm, center at 450 nm) and monitored on separate detectors. The signals were electronically balanced prior to each experiment using small dc offset and gain adjustments on one of the differential amplifiers. The difference ($i_o - i$) and reference ($i_o$) signals were recorded on two separate channels of a digital storage oscilloscope (Nicolet Explorer III, dc coupled through a 100 kHz upper frequency cut-off filter). The data were subsequently transferred to a computer for analysis. Six runs were conducted with the following mixtures and conditions: $CH_4$ = 4.95 ± 0.15% dilute in argon, $T_2$ = 2840 ± 45°K, $p_2$ = 0.22 atm, $\rho_{21}$ = 4.25 ± 0.02 ($\rho_{21}$ is the density ratio across the shock and also the ratio of particle time to laboratory time), and wavelengths in the range 431.129 < $\lambda$ < 431.134 nm (vac.). A test was conducted with the laser blocked to monitor possible spontaneous emission interferences from the test gas, but these emission levels were found to be insignificant.

## RESULTS AND INTERPRETATION

The fractional transmission of the laser system is related to the mole fraction of CH through the Lambert-Beer law,

$$i/i_o = \exp\left[- \beta(\lambda)p \; x_{CH}L\right] \; ,$$

where $i/i_o$ is the fractional transmission, $\beta(\lambda)$ the absorption coefficient at wavelength $\lambda$, $x_{CH}$ the mole fraction of CH, p the total pressure and L the optical path length (30.5 cm). Under the present experimental conditions, it

was assumed that the dilute mixtures of $CH_4$ could provide reproducible levels of CH. By running nearly identical experiments and recording the absorption of CH at the peak concentration, relative absorption coefficients of CH as a function of wavelength were measured. A typical absorption trace obtained in these experiments is shown in Fig. 2. Note that the present methane mixtures produced small amounts of soot, causing a small level of extinction from light scattering, at late times in the experiments.

The peak absorption levels recorded in the six shock tube experiments were corrected for slight variations in the initial conditions and plotted as a function of wavelength in Fig. 3. The solid line is a theoretical profile assuming Doppler broadening (FWHM = 0.246 $cm^{-1}$ at 2840°K), which can be expected under these high temperature shock tube conditions. Good agreement is found between the Doppler model and the experimental points. In addition, the inferred line peak lies at 23194.76 $cm^{-1}$, in reasonable agreement with Fagerholm, who reported the $Q_{1c}(7) + Q_{2d}(7)$ lines at 23194.81 $cm^{-1}$.

In order to assess the sensitivity of the present laser diagnostic, the relative absorption coefficient of the individual CH lines can be calculated using [11]

$$\frac{\beta}{f_{oo}} = \left(\frac{\Pi e^2}{m_e c^2}\right) \times \frac{(2J'' + 1) \exp\left[-\frac{hc}{kT} F(J'')\right]}{Q_{rot} Q_{vib} Q_{el}} \times \frac{N}{RT} \times \frac{S}{(2J'' + 1)} \times \phi \ ,$$

where $\beta$ is the absorption coefficient ($cm^{-1}$ $atm^{-1}$) at line center; $f_{oo}$ is the oscillator strength of the $[A^2\Delta (v=0) + X^2\Pi(v=0)]$ band; $F(J'')$ is the rotation energy of the lower state ($cm^{-1}$); R is the universal gas constant (82.1 atm $cm^3$/mole/°K); N is Avogadro's number; $Q_{rot}$, $Q_{vib}$ and $Q_{el}$ are the rotational, vibrational and electronic partition functions, respectively; S is the rotational line strength; and $\phi$ is the Doppler line shape factor (cm) evaluated at line center,

$$\phi = 2(\ln2/\Pi)^{1/2}/\Delta\omega_D \ ,$$

where $\Delta\omega_D$ = 0.246 $cm^{-1}$ is the Doppler width. The quantities $(\Pi e^2/m_e c^2)$ and $hc/k$ are equal to 8.826 $10^{-13}$ cm and 1.4388°K cm, respectively.

The partition functions are evaluated using the approximate expressions

$$Q_{rot} \simeq \frac{kT}{hcB_o''} \ , \qquad Q_{vib} \simeq \left[1 - \exp\left(-\frac{hc}{kT} \omega_e\right)\right]^{-1} \ ,$$

and $Q_{el} \simeq 4$. (There are two levels arising from electronic spin, and two levels arising from the possible orientations of the electronic orbital angular momentum.) By convention, the lower energy level of a given rotational transition is defined such that its degeneracy is equal to $(2J'' + 1)$. As a consequence, the normalization rule for the rotational line strengths must read for a given J''

$$S(Q_{1c}) + S(R_{1dc}) + S(P_{1dc}) = S(Q_{2d}) + S(R_{2cd}) + S(P_{2cd}) = 2J'' + 1 \ .$$

The corresponding rotational line strengths were taken from Kovacs [12].

The rotational energy of the ground state was evaluated using the Hill and Van Vleck formulae [2]

$$F'' = B''_0 \left[ (J'' + 1/2)^2 - \Lambda^2 \right] \pm B''_0 \left[ (J'' + 1/2)^2 + \frac{1}{4} Y'' (Y'' - 4) \Lambda^2 \right]^{1/2}$$

$$- D''_0 K''^2 (K'' + 1)^2 , \quad (cm^{-1})$$

where $\Lambda = 1$; in the present case, the + sign corresponds to $Q_{2d}$ and the − sign to $Q_{1c}$. An additional correction was introduced to account for $\Lambda$-doubling of the ground state, namely − 0.85 cm$^{-1}$ for $Q_{2d}(7)$ and + 0.54 cm$^{-1}$ for $Q_{1c}(7)$. Using $B''_e = 14.1961$ cm$^{-1}$, $D''_0 = 1.48 \times 10^{-3}$ cm$^{-1}$ [6] and $Y''(Y''-4) \approx -4$, $\omega_e = 2868.5$ cm$^{-1}$ [8], it follows that: $F'' = 774.27$ cm$^{-1}$ and $S = 6.56$ for $Q_{2d}(7)$; and $F'' = 777.58$ cm$^{-1}$ and $S = 7.56$ for $Q_{1c}(7)$. Finally, the relative absorption coefficient at the center of the superposed $Q_{1c}(7)$ and $Q_{2d}(7)$ lines can be written as a function of temperature, assuming a Doppler width $\Delta\omega_D = 0.0046 \, T^{1/2}$ (cm$^{-1}$),

$$\frac{\beta}{f_{oo}} = \frac{\beta(Q_{2d}) + \beta(Q_{1c})}{f_{oo}} \approx 9.52 \times 10^{13} \times \frac{1 - e^{-4130/T}}{T^{5/2}} \times e^{-1120/T} \quad (cm^{-1} atm^{-1}) .$$

A plot of $\beta/f_{oo}$ vs. temperature is given in Fig. 4. At the present experimental temperature (2840°K), $\beta/f_{oo} \approx 114000$ cm$^{-1}$atm$^{-1}$. Using the oscillator strength of Sawada and Kamada [3] and the Franck-Condon factor of Liszt and Smith [4], $f_{oo} \approx 0.0065$ and $\beta$ (2840°K) $\approx 740$ cm$^{-1}$ atm$^{-1}$. From Fig. 3, the measured line-center absorption at 431.132 nm is $(1 - 1/I_0) \approx 4.9\%$. This value corresponds to a CH mole fraction of about 20 ppm.

From the experimental record of Fig. 2, the minimum detected absorption level is seen to be quite low, a few tenths of a percent, and this is attributed primarily to scattering interferences from soot particles. Without any correction for scattering, the inferred value of CH is about ± 2 ppm, suggesting this as a "detection limit" for present conditions. It is clear that a proper account of soot scattering could further reduce the minimum detectable level of CH. Such account could be taken by simultaneously monitoring non-resonant scattering of laser light, and subtracting the scattering extinction trace from the resonant absorption signal. The resulting detection limit of CH should be below 1 ppm at 3000°K.

In conclusion, we believe that the present diagnostic has significant potential for high temperature studies of CH kinetics and spectroscopy in a shock tube.

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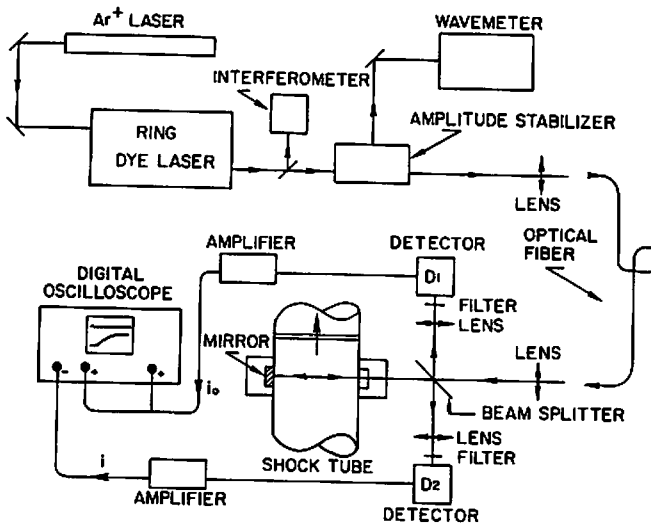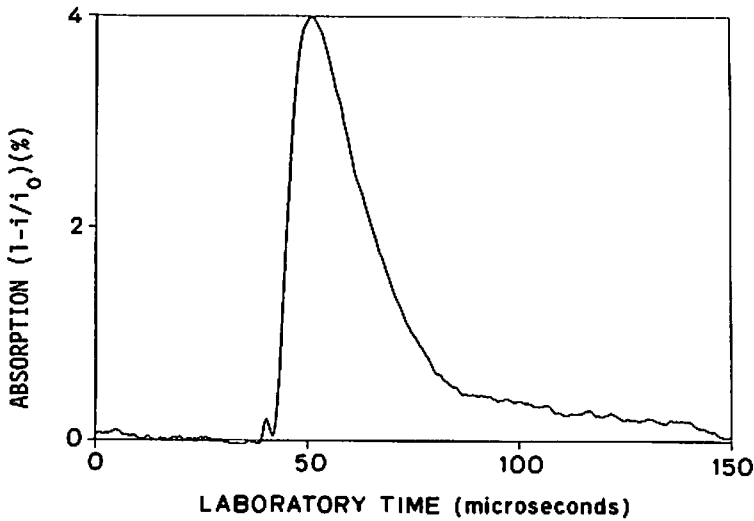
Fig. 1    Shock tube laser absorption diagnostic



Fig. 2    A typical laser absorption $(1 - i/i_o)$ record at 431.133 nm, with the conditions $T_2 = 2830°K$, $p_2' = 0.22$ atm, $\rho_{21} = 4.28$, $CH_4 = 4.95\%$ dilute in argon. The initial spike results from a Schlieren effect, useful in defining the shock arrival time. The absorption level at late times is attributed to a small amount of soot formation.
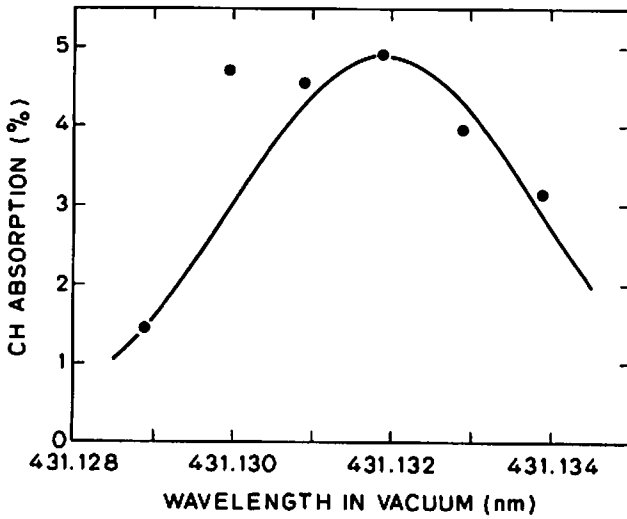
Fig. 3. CH absorption levels around 431.131 nm (vac.). The conditions are $T_2$ = 2840 ± 45°K, $p_2$ ≈ 0.22 atm, $CH_4$ ≈ 4.95 ± 0.15% dilute in argon, path length L = 30.5 cm. The inconsistency of the experimental point at 431.130 nm may be attributed to a mode hop of the ring laser.
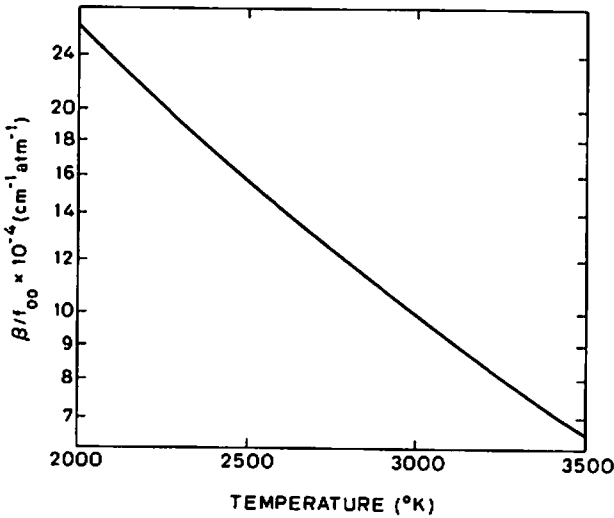


Fig. 4. Theoretical temperature dependence of the relative absorption coefficient of CH. The calculation is performed at the center of the superposed $Q_{1c}(7)$ + $Q_{2d}(7)$ lines and assumes a Doppler-broadened line shape function.