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## **Intracavity Enhancement of Raman Peaks Inside the Cavity of a Dye Laser**

P. H. Young<sup>a</sup>; H. W. Latz<sup>a</sup>

<sup>a</sup> Department of Chemistry, Ohio University, Athens, Ohio

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INTRACAVITY ENHANCEMENT OF RAMAN PEAKS INSIDE  
THE CAVITY OF A DYE LASER

Key Words: Dye Laser, Intracavity Raman Spectroscopy

P. H. Young and H. W. Latz

Department of Chemistry  
Ohio University  
Athens, Ohio 45701

ABSTRACT

A Nitrogen pumped dye laser using coumarin 515 as the lasing medium is used as an excitation source to measure Raman scatter inside the cavity of the dye laser. When a Raman active sample is placed inside the resonator cavity, the Raman scatter is enhanced due to the multipass effect inside the resonator cavity. This enhancement allows for easier detection of the Raman bands.

INTRODUCTION

The main advantage of using a dye laser is its inherent ability to be tuneable over all of the wavelengths of the fluorescent dye. This advantage allows the laser to be tuned away from interferences, such as fluorescence from the sample.

To date, most of the intracavity research has been done with the absorption effect.<sup>1-4</sup> This is done by tuning the laser to a wavelength of excitation for the sample of interest. Then placing the sample inside the resonator cavity and scanning the emission spectrum of the dye.

The intracavity Raman effect was accomplished by Porto and co-workers in 1963 using a continuous wave helium neon laser with photographic detection.<sup>5</sup> In 1964 Porto and co-workers accomplished the same experiment but using photoelectric detection for such solvents as carbon tetrachloride, carbon disulfide, and benzene.<sup>6</sup> Porto and co-workers have also shown, using a continuous wave helium neon laser, the intracavity enhancement of Raman bands for gases.<sup>7</sup>

This paper describes the use of a nitrogen pumped dye laser to measure the intracavity Raman spectra of some common Raman active solvents.

## EXPERIMENTAL

### Apparatus

A Laser Energy Company pulsed N2-50 nitrogen pumped dye laser was used with a typical dye laser output of 0.2 millijoules. The dye was tuneable in the wavelength range of 480 nm to 520 nm. The monochromator used was a 0.5 meter Jarrell-Ash single grating scanning monochromator with an IP-28 photomultiplier tube and a Jarrell-Ash A/C amplifier as the detection system. The recorder used was a Sargent Welch stripchart recorder. The entrance slit to

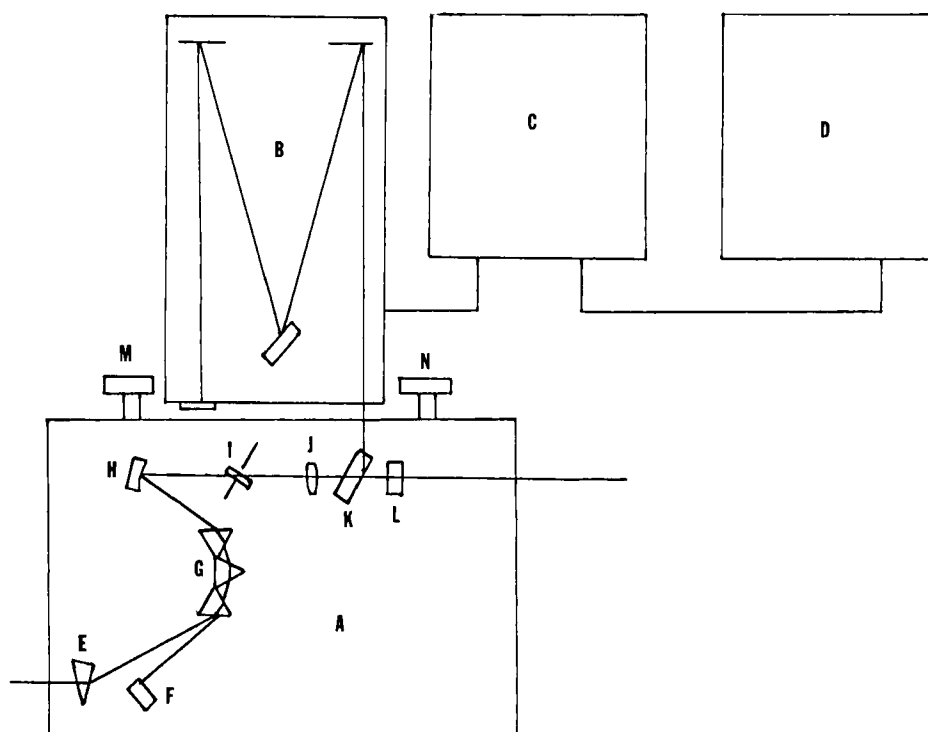


FIG. 1: Block Diagram of the Experimental Setup for the Intra-cavity Raman Spectrometry. A) Dye Laser, B) Monochromator, C) A/C Amplifier, D) Recorder, E) Prism, F) 100% Reflecting tuning Mirror, G) Prisms H) Mirror, I) Dye Cell, J) Lens, K) Sample Cell, L) 99% Reflecting Mirror, M) and N) Knobs to Align Baseplate.

TABLE 1

The Most Intense Raman Bands of the Four Solvents Studied

<u>Solvent</u>	<u>Raman band (<math>\text{cm}^{-1}</math>)</u>			
Acetonitrile	384	926	2260	2960
Methylene Chloride	301	718	2983	
Tetrahydrofuran	280	909	1230	2870
Hexane	792	2865	2880	2900

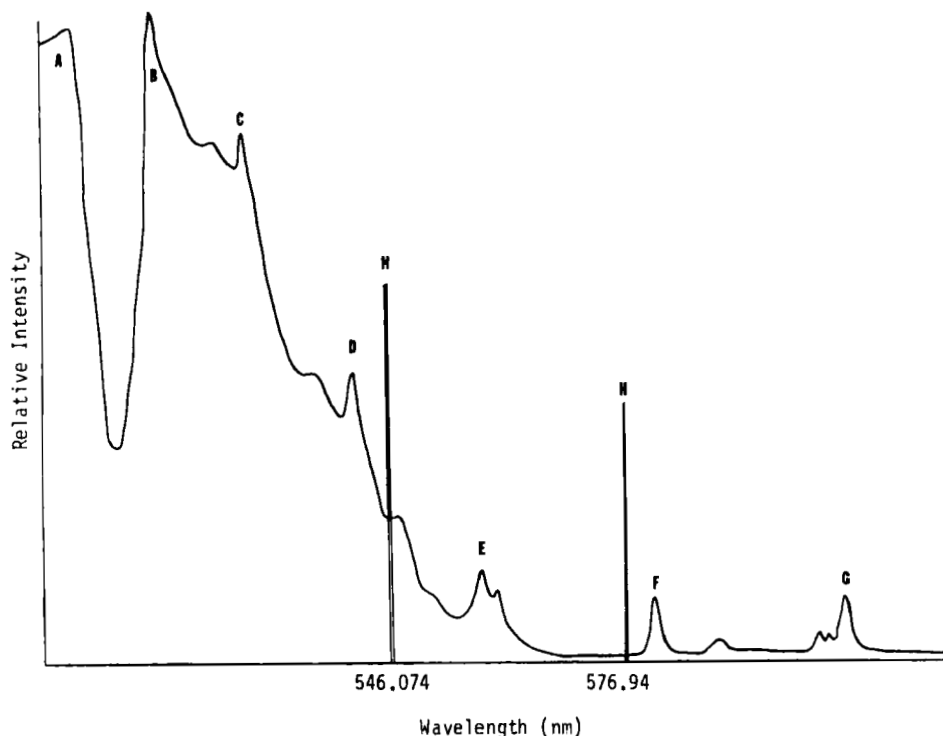


FIG. 2: Intracavity Raman Spectrum of Acetonitrile. A) Fluorescence Maximum, B) Laser Maximum, C)  $384\text{ cm}^{-1}$ , D)  $926\text{ cm}^{-1}$ , E)  $1380\text{ cm}^{-1}$ , F)  $2260\text{ cm}^{-1}$ , G)  $2960\text{ cm}^{-1}$ , H) Mercury Emission Lines.

the monochromator was 150 microns and the exit slit was 100 microns. The sample cell was a three centimeter quartz cell oriented to brewster's angle inside the resonator cavity. The monochromator was aligned at ninety degrees with respect to the dye laser to detect the Raman scattered radiation. The experimental setup is shown in figure 1.

### Solvents

All solvents were ACS grade except for hexane which was HPLC grade and were used without further preparation.

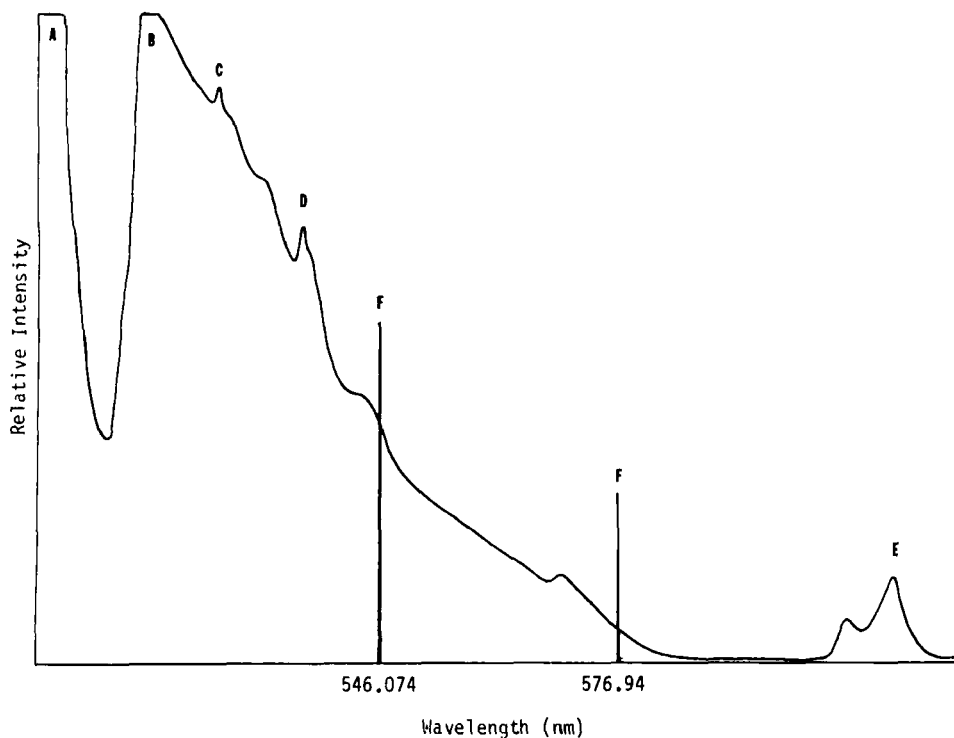


FIG. 3: Intracavity Raman Spectrum of Methylene Chloride. A) Fluorescence Maximum, B) Laser Maximum, C) 301 cm<sup>-1</sup>, D) 718 cm<sup>-1</sup>, E) 2983 cm<sup>-1</sup>, F) Mercury Emission Lines.

### RESULTS AND DISCUSSION

The laser pulse times were optimized as to give a maximum signal output from the A/C amplifier. For wavelength calibration purposes, the 549.074 nm and 576.94 nm emission lines of mercury were superimposed on each Raman Spectrum. All spectra were recorded in nanometers and then converted to wavenumbers for simplicity.

Table 1 shows a summary of the most intense Raman bands for each of the solvents under study. These bands were then used to characterize each of the Raman spectra shown below.

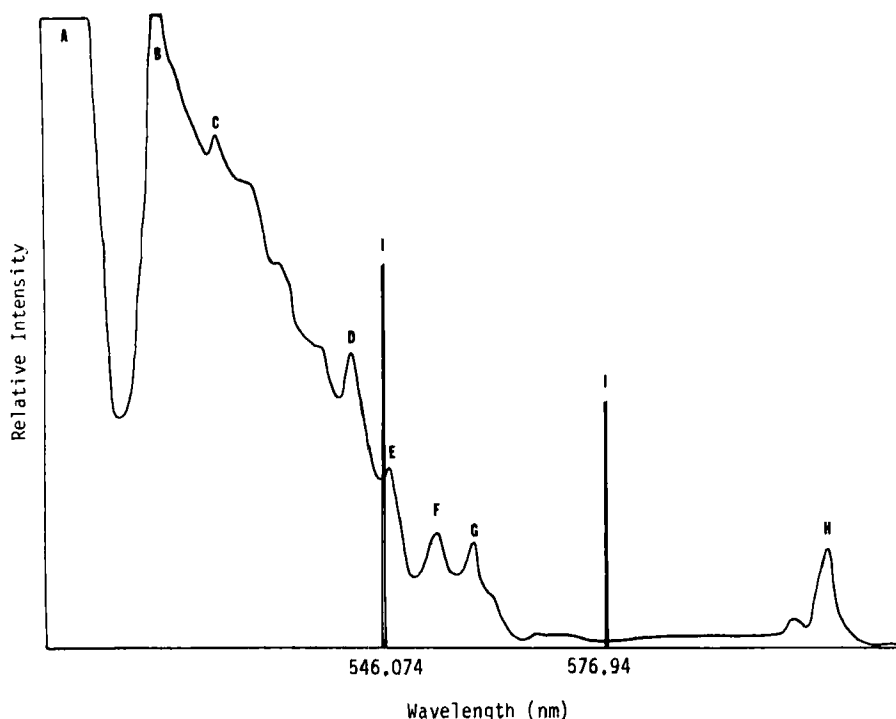


FIG. 4: Intracavity Raman Spectrum of Tetrahydrofuran. A) Fluorescence Maximum, B) Laser Maximum, C) 280  $\text{cm}^{-1}$ , D) 909  $\text{cm}^{-1}$ , E) 1020  $\text{cm}^{-1}$ , F) 1230  $\text{cm}^{-1}$ , G) 1450  $\text{cm}^{-1}$ , H) 2870  $\text{cm}^{-1}$ , I) Mercury Emission Lines.

The typical Intracavity Raman spectra obtained are shown in figures 2, 3, 4, and 5. Figure 2 shows the spectrum obtained for Acetonitrile. Characteristic bands are the nitrile stretch at 2260  $\text{cm}^{-1}$  and the carbon hydrogen stretch at 2960  $\text{cm}^{-1}$ . Figure 3 shows the spectrum obtained for Methylene Chloride which shows the characteristic carbon chlorine stretch at 718  $\text{cm}^{-1}$  and its carbon hydrogen stretch at 2960  $\text{cm}^{-1}$ . Figure 4 shows the spectrum obtained for Tetrahydrofuran. Characteristic bands are the ring

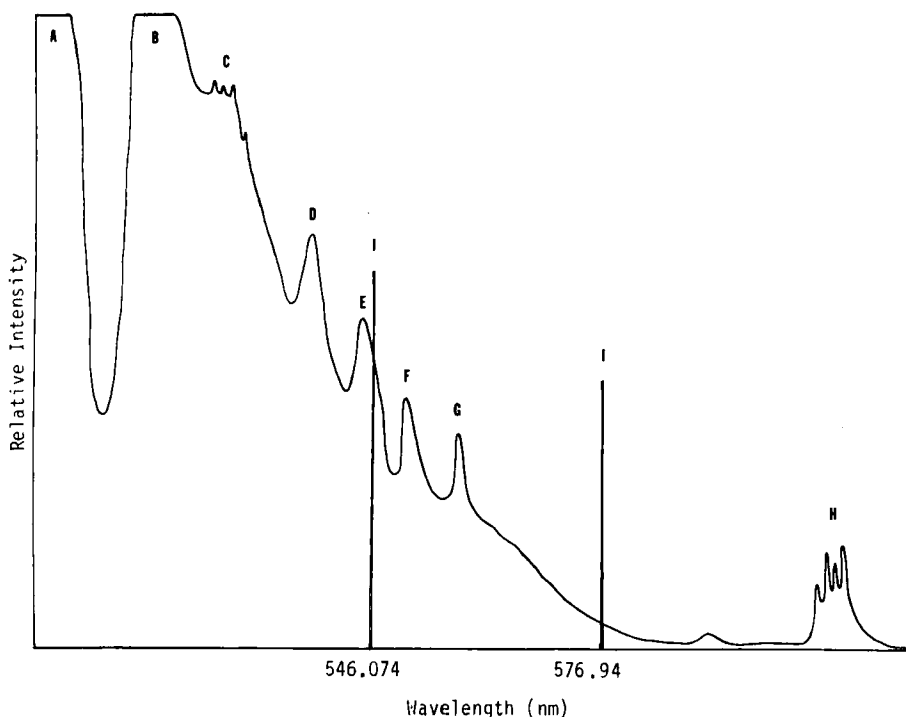


FIG. 5: Intracavity Raman Spectrum of Hexane. A) Fluorescence Maximum, B) Laser Maximum, C)  $380\text{ cm}^{-1}$ , D)  $830\text{ cm}^{-1}$ , E)  $1050\text{ cm}^{-1}$ , F)  $1300\text{ cm}^{-1}$ , G)  $1450\text{ cm}^{-1}$ , H)  $2865\text{ cm}^{-1}$ - $2940\text{ cm}^{-1}$  Multiplet, I) Mercury Emission Lines.

breathing at  $909\text{ cm}^{-1}$  and the carbon hydrogen stretch at  $2870\text{ cm}^{-1}$ . Figure 5 shows the spectrum obtained for Hexane which shows the  $\text{CH}_2$  twist at  $1300\text{ cm}^{-1}$ , the  $\text{CH}_3$  deformation at  $1450\text{ cm}^{-1}$ , and the characteristic multiplet at  $2920\text{ cm}^{-1}$ . All of the Intracavity Raman spectra suffered interference from fluorescence scatter from the lasing dye. But since this fluorescence was constant, it did not cause any difficulty in assigning the Raman bands.

The main drawback of these experiments was the presence of background light due to spurious scattering of the Rayleigh line



inside the monochromator and background from the Nitrogen laser. Much of the spurious scattering may be decreased by using a double grating monochromator and the Nitrogen laser background may be decreased by placing it at ninety degrees with respect to the dye laser instead of coaxially.

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