THE ACTIVE "INGREDIENT" IN CANLUB

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ABSTRACT

There is evidence that formation of $Cs(Zr_xI_yC)$ compounds is the chemical step involved in preventing stress-corrosion cracking (SCC) of fuel sheathing. One of the recent key findings is that SCC of unirradiated Zircaloy sheathing is observed only when CANLUB was "over-baked". This result appears to be consistent with results obtained by various analytical techniques that show that if one of the key components in CANLUB was decomposed then SCC would occur. Since there is a possible link between fuel oxidation and graphite coating, the synthesis of $Zr_6I_{12}C$ compounds using a different type of coating (without graphite) was also investigated.

These results will assist in improving CANLUB specifications which will result in improvements in manufacturers' process controls, so that CANLUB continues to be effective. An increased understanding of CANLUB chemistry is also needed to improve the coating for advanced CANDU fuels that will be irradiated to extended burnups.

INTRODUCTION

The CANLUB graphite layer between the Zircaloy sheath and the fuel pellets is an essential component to the performance of CANDU fuel. The continued successful operation of CANDU reactors, which includes routine power-ramping of CANDU fuel, depends on the continued role of CANLUB in preventing stress-corrosion cracking (SCC). A subtle change in the current DAG-154 CANLUB product could adversely affect the coating's ability to prevent SCC, resulting in a defect excursion in CANDU reactors. Although CANLUB has proven successful within the normal operating envelope of the natural UO_2 fuel cycle, its performance at extended burnups, typical of advanced fuel cycles, has been shown to deteriorate (1,2).

The objective of this work is to understand the mechanism by which CANLUB prevents SCC and the parameters which influence this mechanism. This will allow 1) the current DAG-154 product to be better specified at the manufacturing level, thereby ensuring the continued successful operation of CANDU reactors, and 2) the development of advanced SCC-prevention coatings that will be utilized in the development of advanced fuel cycles

operating to extended burnups.

Specimens of DAG-154 and binder baked at various temperatures were characterized by ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Judging from the NMR data, the active ingredient in CANLUB coating was identified after standard curing at 350°C. This active component was found to be essential to form Zr_xI_yC compounds; those compounds could not be formed using pure graphite or CANLUB cured at high temperatures (3). It is important to ensure that CANLUB continues to protect the sheathing against SCC. Therefore, it is essential to identify the effective components that are critical to the function of CANLUB (4), and to develop a routine analytical tool to monitor those components.

EXPERIMENTAL

Characterization of CANLUB

To demonstrate the dependence of SCC threshold on the active ingredient in CANLUB, specimens of DAG-154 baked at 320, 330, 340, 350, 360, 365, 370, 375, 380, 385, 390, 400, 420 and 440°C for two hours in vacuum (10^{-2} to 10^{-3} torr), were characterized by Raman spectroscopy. The reactivity/capacity of the baked CANLUB specimens were evaluated (qualitatively) by scanning electron microscopy (SEM) after reaction with I_2 (200 mg) and Zircaloy-4 sheathing at 600°C in vacuum (5).

C-ring SCC tests were performed at 320°C for the specimens of CANLUB baked onto the sheathing at various temperatures. Rings cut from these CANLUB-coated fuel sheaths were split longitudinally and loaded to a stress of ~300 MPa at 320°C, in evacuated capsules (10^{-3} torr) filled with iodine (at a concentration of ~ 0.02g I_2 per cm^2) for 24 hours.

Instrumentation

Specimens of DAG-154 baked at various temperatures were characterized by Raman spectroscopy. Raman spectra were excited using 50 mW of 647.1 nm radiation. Laser plasma lines were removed by passing the laser beam through a narrow bandpass filter. Spectra were collected using a SPEX 1000M single monochromator equipped with a liquid-nitrogen-cooled Spectrum One CCD detector. High rejection of the Rayleigh scatter was achieved by placing a holographic notch filter in front of the spectrometer slits. Several areas on the specimens were characterized. The measured spectra were baseline corrected and cosmic-ray spikes were removed, then the areas of the peaks were measured. The area of the graphite peak at 1580 cm^{-1} was used to normalize the intensities of the C-H stretching bands (originated from the active component of CANLUB), to remove variations of laser power, laser focus, and collection optics alignment.

RESULTS AND DISCUSSION

Characterization of CANLUB

Graphite is a major ingredient of the CANLUB coating. Figure 1 shows a Raman spectra of pure graphite in the spectral range of 200-3600 cm^{-1}. The spectrum of graphite indicated strong bands at 1332, 1582 and 2682 cm^{-1}, and weak bands at 2465, 2924 and 3241 cm^{-1}, as well as several shoulders on the strong bands. The Raman spectrum of pure crystalline graphite was expected to contain two Raman active bands, based on the symmetry of the graphite unit cell. A group theoretical analysis of graphite (6) led to the following irreducible representation for the optical modes:

$$\Gamma_{opt} = 2E_{2g} + E_{1u} + A_{2u} + 2B_{2g}$$

The two E_{2g} modes were Raman active and reported at 42 and 1581 cm^{-1}. This accounted for only one of the Raman bands observed in Figure 1 (at 1582 cm^{-1}). The strong band at 1332 cm^{-1} had often been reported in the literature and was attributed to the presence of microcrystalline materials (7,8). The Raman bands at 2465, 2682, 2924 and 3241 cm^{-1} were also reported, but their origin was not clear. The band at 2924 cm^{-1} was in the same spectral region as the C-H stretching bands of aliphatic hydrocarbons. Therefore, this could potentially interfere with the detection of the active components in CANLUB.

Raman spectra of the CANLUB-coated samples were measured in the spectral regions containing the major graphite peak (1200-1700 cm^{-1}) and the hydrocarbon C-H stretching peak (2700-3000 cm^{-1}). Figure 2 shows a typical Raman spectrum of the CANLUB coating (DAG-154). Similar to the graphite specimen shown in Figure 1, strong bands were observed at 1330 and 1581 cm^{-1}. Figure 3 shows the Raman spectrum of the C-H stretching bands obtained from the same CANLUB-coated specimen. It is clear that the active component from CANLUB can be detected by Raman spectroscopy. It must be emphasized that using Raman spectroscopy to measure the active component in CANLUB is still in the developmental stage, and further work is required (and has been planned for 1995/96) before a definite correlation between the C-H peak intensity and active ingredient concentration can be made.

One of the recent key findings is that SCC of unirradiated Zircaloy sheathing occurs when CANLUB is over-baked at high temperatures (Figure 4). This result agrees with the previous ^{13}C NMR (3) and Raman results (see Figure 5) which showed that the key ingredient in CANLUB decomposed and disappeared at certain temperatures. $Zr_6I_{12}C$-type compounds could not be synthesized when CANLUB was baked at high temperatures. In fact, the formation of the Zr_xI_yC compounds could not be achieved using pure graphite either.

These results suggest that 1) the formation of $Cs(Zr_xI_yC)$ compounds is the chemical step involved in preventing SCC of fuel sheathing, and 2) for CANLUB to work, the active ingredient in CANLUB has to be remained after baking.

CONCLUSIONS

Evidence has been obtained suggesting that:

1) The organic carbon left after standard curing is required for the formation of Zr_xI_yC compounds. These compounds could not be formed using pure graphite or CANLUB cured at high temperatures.

2) Zircaloy sheathing is more susceptible to SCC when DAG-154 CANLUB is over-baked.

3) Raman spectroscopy can be used to monitor the active component CANLUB.

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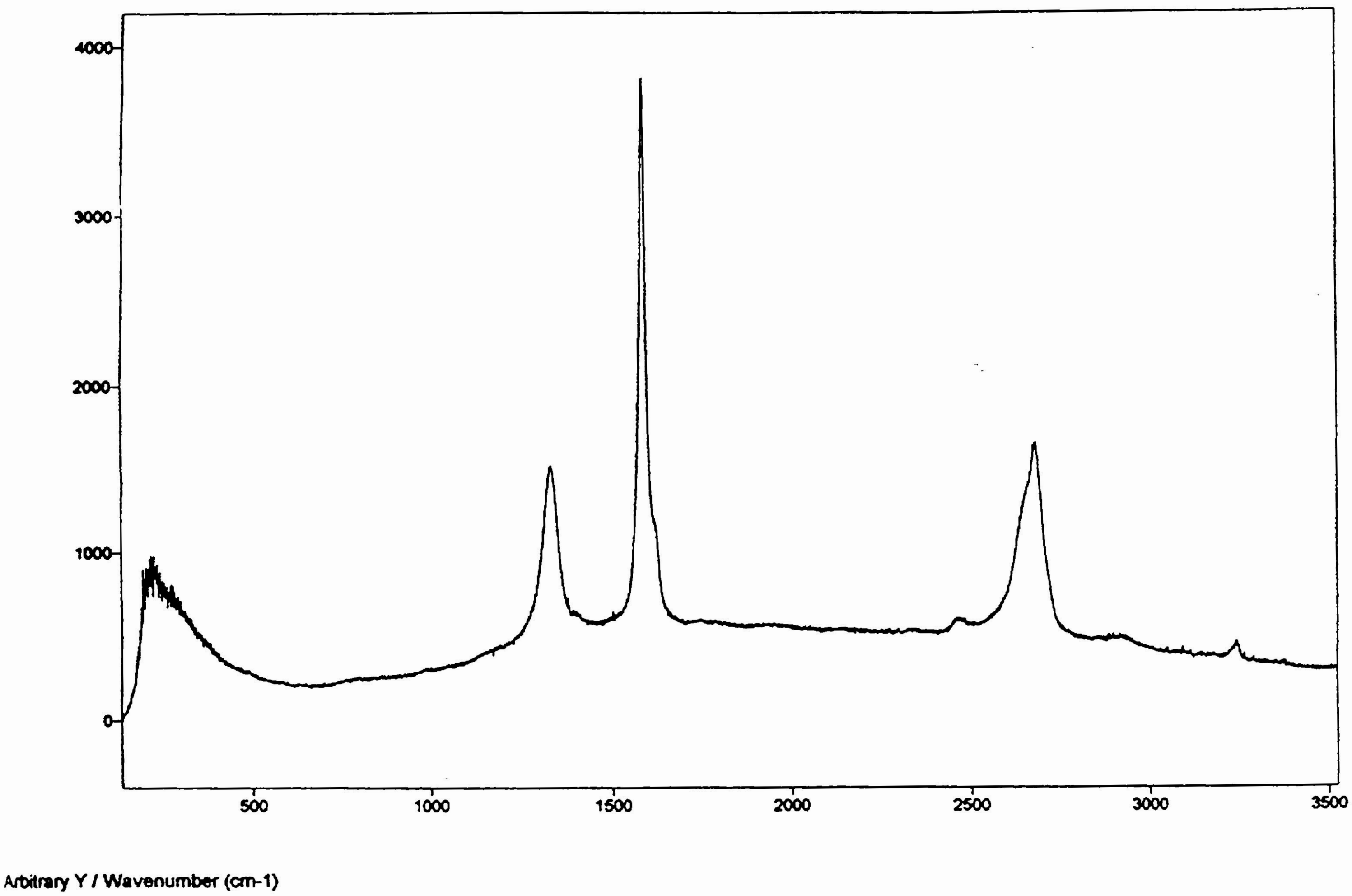

FIGURE 1: RAMAN SURVEY SPECTRUM OBTAINED FROM PURE GRAPHITE.

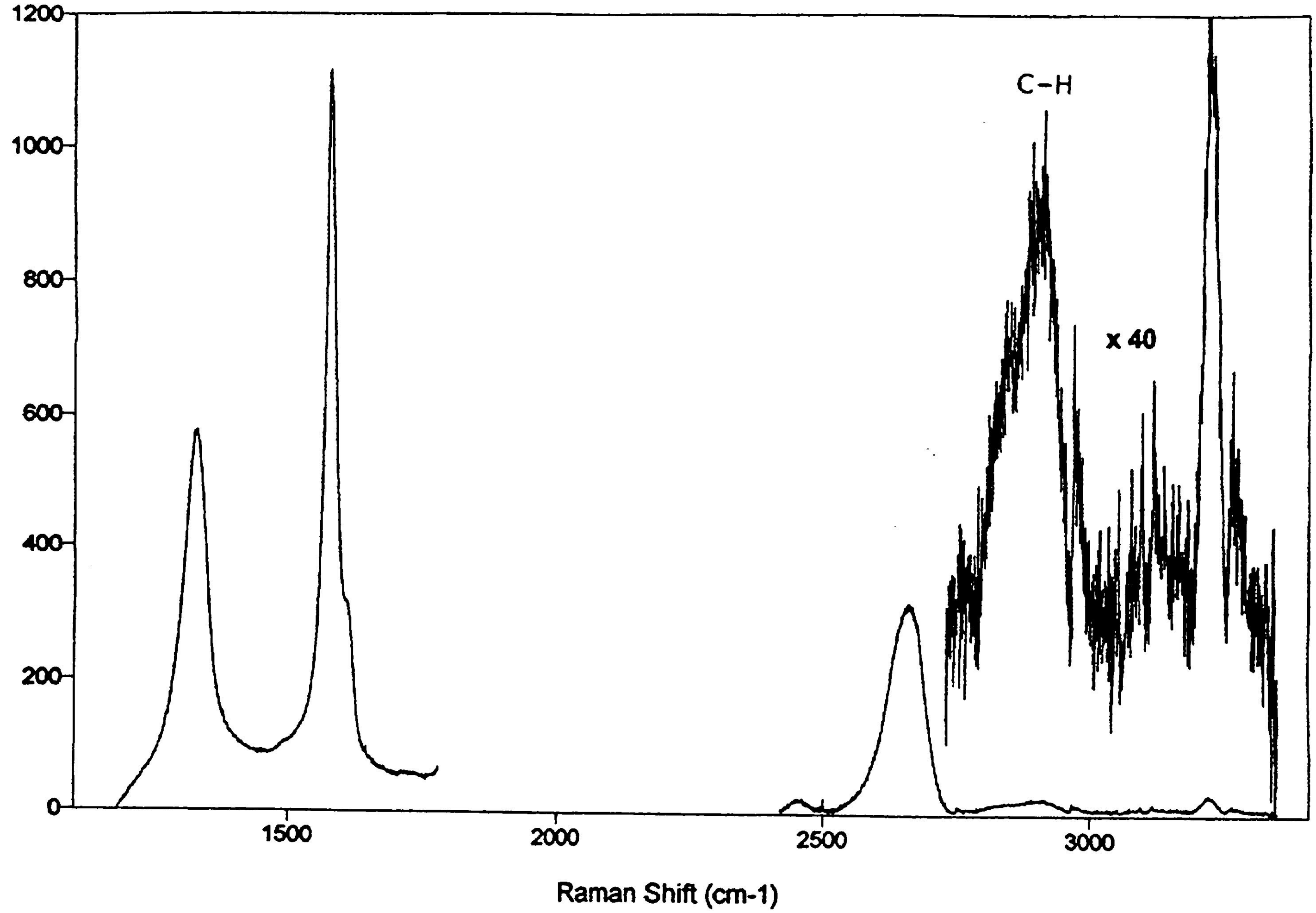

FIGURE 2: RAMAN SURVEY SPECTRUM OBTAINED FROM CANLUB (DAG-154).

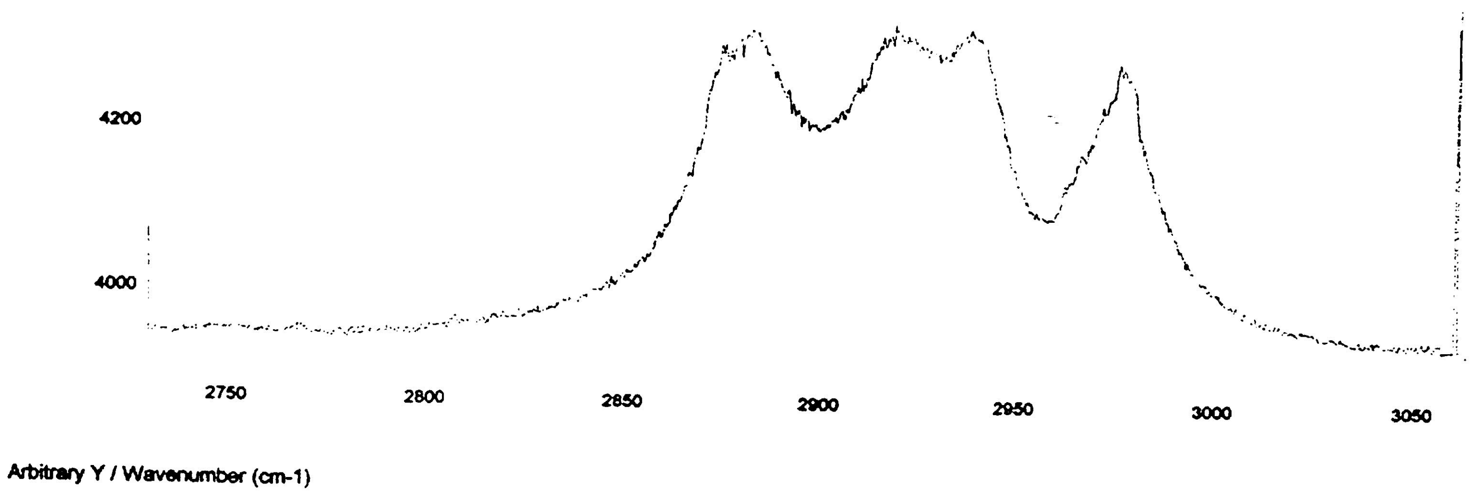

FIGURE 3: RAMAN C-H STRETCHING BANDS OBTAINED FROM CANLUB (DAG-154).

FIGURE 4: SCC-TESTS OF CANLUB-COATED ZIRCALOY-4 SHEATHING WITH BAKING TEMPERATURES RANGING FROM 320 to 440°C. A TYPICAL FRACTURE SURFACE OBTAINED FROM SHEATHING WITH CANLUB BEING OVER-BAKED.

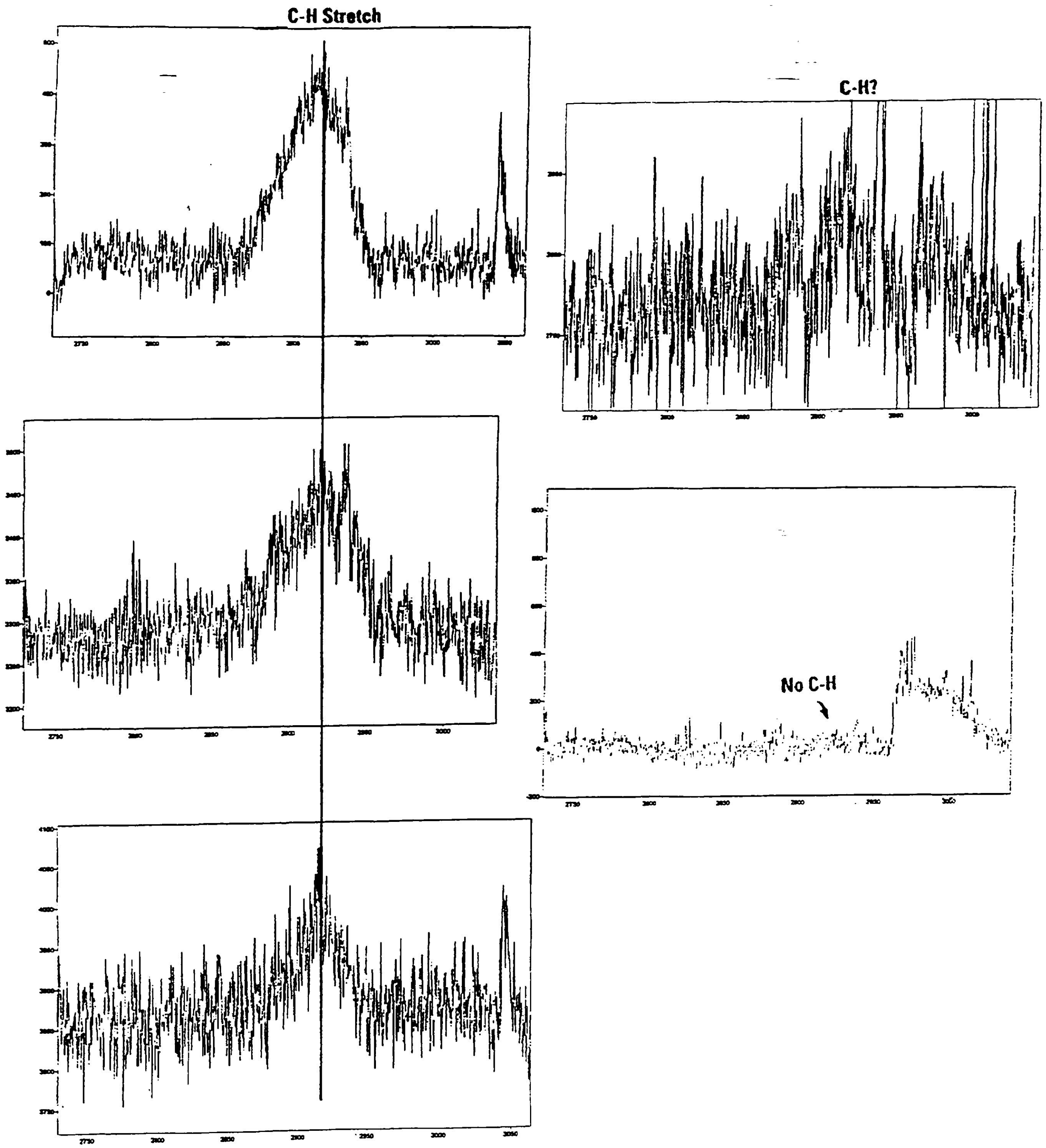

FIGURE 5: RAMAN SPECTRA OBTAINED FROM CANLUB (DAG-154 COATING) BAKED AT TEMPERATURES RANGING FROM 320 TO 440°C. THE TWO ON THE RIGHT HAND SIDE WERE AT THE HIGHEST TEMPERATURES.