I. INTRODUCTION

In the previous two chapters, we have discussed the use of relatively classical techniques to characterize engine combustion deposits. Elemental analysis shows the deposits to contain 60 to 69 wt.% carbon, 20 to 27 wt.% oxygen, and 3 to 5 wt.% hydrogen, with varying amounts of nitrogen, sulfur, and lube-derived inorganic elements. Both thermogravimetric analysis and insertion probe mass spectroscopy show the presence of volatile materials, and the mass spectroscopy suggests these volatile materials to contain, in part, polynuclear aromatic hydrocarbons. Infrared spectroscopy shows that the oxygen functionality includes ketones (possibly as anhydrides) and aryl and alkyl ethers. However, one very significant question remains unanswered: What kind of carbon holds the backbone of the deposit matrix together?

To answer this, we have performed experiments to investigate the $^{13}$C nuclear magnetic resonance of solid state deposits, using the technique of cross polarization/magic angle spinning (CP/MAS). Different types of carbon resonate at different spectral positions, allowing a distinction between aliphatic ($sp^3$) and aromatic ($sp^2$) carbons. We briefly discuss in the next section some of the past work in this field.
II. BACKGROUND

In 1976, the combination of sensitivity-enhanced cross-polarization nuclear magnetic resonance with magic angle sample spinning allowed the generation of liquid-like high-resolution rare-spin nuclear magnetic resonance spectra of solids. Applied most frequently to the $^{13}$C (rare spin)/$^1$H (abundant spin) pair of nuclei, this technique has gained widespread popularity in the interpretation of structure of typical organic solids. The isotropic chemical shifts obtained under these conditions are essentially equivalent to those observed in the liquid-state, with little evidence for problems associated with "solid-state effects." In fact, magic angle spinning has even been applied to liquid specimens to eliminate bulk susceptibility shifts.

CP/MAS $^{13}$C NMR has been especially useful in the characterization of coal and coal-derived materials, and one notes that combustion deposits are similar to coals with respect to abundances of carbon and hydrogen. In this context, various studies have been made on the quantitative reliability of the technique, especially in samples of low hydrogen abundance. Schaefer has suggested that, if the protons in a sample are more or less uniformly distributed in a rigid organic solid, concentrations as low as 5% will generate cross-polarization spectra of representative carbon intensities. Alemany, Grant, Pugmire, Alger, and Zilm have noted that carbon atoms four or more bonds from the nearest intramolecular proton cannot be fully polarized before $T_{1p}$ (H) effects begin to dominate the proton magnetization. Rapid molecular motion aggravates the problem because of motional attenuation of the dipolar interaction. One way of assessing the significance of these potential complexities is to compare CP/MAS results with data from a simple $^{13}$C 90° pulse without cross-polarization. Although data accumulation time will be lengthened, the results will not be dependent on the proton $T_{1p}$. As it happens, one of the more serious problems in analyzing engine deposits by CP/MAS arises from the presence of ferromagnetic impurities, as discussed in the next section.

III. OBTAINING THE CP/MAS SPECTRUM

Solid-state cross polarization/magic angle spinning experiments were performed on a JEOL FX-60QS solid-state spectrometer.