1. Introduction: Zeolite Structural Problems

The open framework structures of molecular sieves(1),(2) are well illustrated by the structure of zeolite-Y (Figure 1.) which was determined by diffraction techniques and clearly shows the large central cavity and the channel system by which it is accessed. However, materials of this general type pose particular problems because of their microcrystalline nature where the small particle sizes often preclude the application of single-crystal diffraction techniques and recourse must be made to the much more limited powder X-ray diffraction data (3). Although substantial improvements may be made by the use of synchrotron based X-ray sources and the implementation of Rietveld refinement techniques (4), at present the structures of many zeolites are unknown and the powder X-ray experiments must be combined with data from other experiments. In this regard, solid-state NMR has emerged in recent years as a powerful complementary method to X-ray diffraction (5). While the latter is most sensitive to long range ordering and periodicities in the three dimensional structure, NMR is most sensitive to short and medium range effects. Additional structural information which would be useful includes:

1. Independent information on the topography and structure e.g. the numbers and occupancies of the independent T-sites and the bonding network between them.
2. The distribution of Si and Al atoms over the T-sites.
3. Nature and mobilities of molecules and ions present within the host structure.
4. The effect of organic molecules and other variables on the host structure: Information on size and shape selectivity.
5. The monitoring of the progress of catalytic reactions "in situ".

In fact, progress has been made in the application of solid-state NMR spectroscopy in all of these different areas. In this and the following lecture, we will discuss the development and background of the technique with particular emphasis on recently developed areas of current activity.
Conventional high-resolution NMR spectroscopy in solution yields spectra with narrow resonances whose positions (frequencies) are characteristic of the local magnetic (or chemical) environments and whose relative intensities reflect the numbers of nuclei in the different environments. By contrast, solid-state NMR spectra of stationary solid samples typically show very broad, often featureless absorptions. The critical difference is that in the solid-state the nuclei are fixed in position and the spectra reflect the angular and distance dependences of the different interactions for all possible orientations as will be found in a powdered sample. In solution, the fast and random tumbling of the molecules produces the average values of these interactions yielding the conventional "high-resolution" NMR spectrum. The most important interactions together with their isotropic averages are:

a. The direct dipole-dipole interaction. This is most important for protons which have large magnetic moments and a high natural abundance so many such interactions can occur. Its solution average is zero.

b. Chemical Shift Anisotropy (CSA). This describes the three-dimensional shielding of the nucleus and will be important for spin 1/2 nuclei such as $^{31}$P, $^{13}$C, $^{29}$Si. Where such nuclei interact with protons, these will be a $^1$H-X dipolar interaction, but this can be removed by irradiation at the proton resonance frequency leaving the CSA of the dilute nucleus.

c. Quadrupolar Interactions: These arise from the interaction of the nuclear charge with an unsymmetrical electric field gradient and are important for nuclei with spins > 1/2. These include deuterium $^2$D with I = 1 and nuclei with non-integral spins such as $^{27}$Al, I = 5/2, $^7$B, I = 3/2 and $^{17}$O, I = 5/2.