

Applications of Nuclear Quadrupole Double Resonance Spectroscopy

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Since its discovery in 1951, Nuclear Quadrupole Resonance (NQR) spectroscopy has been used to study the electronic environment around quadrupolar nuclei. However, the low sensitivity of direct methods for detecting the transitions of lighter quadrupolar nuclei (^2H , $^{10,11}\text{B}$, ^{17}O , ^{25}Mg , etc.) has severely limited the usefulness of NQR spectroscopy. Drastic improvements in the sensitivity and spectroscopic range of the NQR technique were made with the advent of double resonance NQR techniques [1]. Quadrupolar nuclei previously inaccessible to traditional methods are now detectable at concentrations of 10^{-6} of the abundant nuclear spin, making NQR spectroscopy an important tool for the study of the solid state electronic structure of molecules.

NQR spectroscopy measures the interaction of a nucleus, possessing an electronic quadrupole moment Q , with the electric field gradient produced at the nucleus by its local electronic environment. As a result, the NQR technique provides information on the ground state charge distribution in the vicinity of the quadrupolar nucleus.

In this work the ^{14}N and ^{17}O NQR spectra for a series of substituted aromatic amine oxides was utilized to probe the electronic nature of the N-O group. Aromatic amine oxides have elicited considerable chemical [2], pharmacological [3], and theoretical interest [4]. Fundamental to their chemistry is the dual pi electron, donor-acceptor role of the NO moiety. With the aid of ^{13}C CP-MAS NMR [5,6] the orientation of electric field gradient (efg) tensor of the N-O group has been determined. Using a modified Townes-Dailey model [7], analyses of the hydrogen bonding, coordination, and ring substitution effects on the nature of the N-O group are interpreted in terms of the nitrogen valence p orbital population. Further, the Z axis of the ^{17}O efg tensor has been shown to lie along the N-O bond. Analysis of the ^{17}O NQR results of the oxide group oxygen for a series of substituted pyridine-N-oxides proves a quantitative measure of the sensitivity of the pi-bond order to variations in the para substituent. Changes in the solid state N-O pi-bond order correlate with shifts in the N-O stretching frequency [8], as well as with ^{17}O and ^{15}N NMR chemical shifts in solution [9,10].

The ^2H and ^{14}N NQR spectra for a series of urea adducts were studied to develop a better understanding of the nature and extent of charge transfer that occurs in the peptide linkage, $-\text{CONH}_2$, upon the formation of N-H---O and O-H---O hydrogen bonds. Urea, a basic biological building block, was chosen for study because of its ability to form a large variety of adducts which exhibit varying degrees of hydrogen bonding. The NQR results along with crystallographic data [11] show the existence of a correlation between H---O contact distance and the C-O bond length. There is lengthening of the C-O bond with decreasing O---H contact distance. In terms

of classical valence bond theory, other canonical forms become increasingly important with increasing protonation of the carbonyl oxygen. Crystallographic data indicate the presence of an inverse relationship between C-O and C-N bond lengths, through a range of 1.30-1.40Å and 1.30-1.20Å respectively. A variation of ~0.1Å (about 0.5 bond order) indicates a dramatic variation in the electronic structure of the amide framework. The ^2H and ^{14}N NQR data provide quantitative measures of electronic changes as well as the variations in valence shell orbital populations that occur with changing hydrogen bond order.

References

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