NMR SPECTRA OF FIVE SPIN SYSTEMS—I

The NMR Spectrum of Nitrobenzene

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ABSTRACT

The analysis of the NMR spectra of five nuclei each with spin \( \frac{1}{2} \) has been undertaken. For such systems the nuclei may be arranged in groups of different symmetry. The proton magnetic resonance spectrum of nitrobenzene is an example of \( A_2B_2C \) type. From the analysis of this spectrum the values of various coupling constants and chemical shifts have been determined.

INTRODUCTION

From a high resolution NMR spectrum it is possible to determine the values of chemical shifts and coupling constants and thereby draw conclusions about the structure of the molecule. This procedure is relatively simple for molecules having only a few interacting nuclei or where nuclei can be divided into simple groups of two or three nuclei, not interacting with any of the nuclei of the other group. The analysis of the NMR spectra of the \( A_2B_3C \) type (four non-equivalent nuclei with spin \( \frac{1}{2} \)) has been reported earlier by Dharmatti et al. (1962) and Govil et al. (1961). Among the five spin systems, spectra of three types have been observed and analysed. Mc Garvey and Slomp (1959) have reported the spectra of the \( A_2B_3 \) type. Spectra of the type \( ABX_3 \) were examined by Fessenden and Waugh (1959). The spectrum of pyridine an example of \( AB_2X_2 \) type was analysed by Schneider, Bernstein and Pople (1957) using the method of isotopic substitution. Lately spectra of the type \( A_2B_2X \) have been analysed by Kimura et al. (1960).

Here we present the analysis of the NMR spectrum of nitrobenzene (Fig. 1), an example of the \( A_2B_2C \) type without the use of isotopic substitution. The spectrum of this compound, at relatively lower resolution, was

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first obtained by Corio and Dailey (1956). They did not rigorously analyse the spectrum but just estimated the values of the chemical shifts of the ortho, meta and para protons. They assumed the chemical shift of the para proton at the position of the peak with the highest intensity. This assumption was not reasonably correct and our detailed analysis shows that the chemical shift of para proton is at a lower field than that of the peak of maximum intensity.

**Theoretical**

Assuming the steady magnetic field in the negative Z-direction, the complete quantum mechanical Hamiltonian involving the scalar products of the spin vectors of all pairs of magnetic nuclei can be written as

\[ H = \sum_i v_i I_z (i) + \sum_{i<j} J_{ij} \vec{I}_i \cdot \vec{I}_j \]

where \( \vec{I}_i \) is the spin vector of the nucleus \( i \) whose resonance frequency is \( v_i \), \( I_z (i) \) is the z component of the spin and \( J_{ij} \) is the nuclear spin-spin interaction between the nuclei \( i \) and \( j \).

The basic product functions can be written in the irreducible form after making use of the symmetry in the molecule. The diagonal and the off-diagonal matrix elements of the Hamiltonian with respect to these functions can be calculated by standard methods (Pople et al., 1959). These are given in Table I. The secular equation for this system gets factorised into two 1 x 1, two 2 x 2, two 3 x 3, two 4 x 4 and two 6 x 6 matrices.

Once these matrices are solved one gets the energy values and the stationary state wave functions. These quantities enable us to calculate the spectrum in terms of \( J_s \) and \( v_s \). The frequency corresponding to the transition \( q \rightarrow q' \) is given by \( E_q - E_{q'} \) and the intensity is proportional to \( |\langle q' | \sum_i I_x (i) | q \rangle|^2 \). The calculated spectrum is given in Table II in terms of \( E_s \) and the coefficient \( C_s \) of the various product functions in the stationary state function \( \phi_q \).

There are nine unknown parameters to be determined from the high resolution spectrum taken relative to a particular standard. These are the 3 chemical shifts and 6 coupling constants. There are 110 possible transitions out of which 24 belong to group A, 24 to B and 20 to C and the remaining are combination transitions. Out of these only nine transition frequencies are required to determine uniquely all these parameters.