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DETERMINATION OF THE ABSOLUTE SIGN OF THE ELECTRON SPIN
DIPOLAR AND NUCLEAR QUADRUPOLEAR INTERACTIONS
IN MOLECULAR EXCITED TRIPLET STATES

by

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ABSTRACT

A simple method for determining the absolute sign of the principal component of the zero field tensor or the sign of the nuclear quadruple coupling constant in molecular excited triplet states is outlined for molecules containing half integral nuclear spins where $I > \frac{1}{2}$.

INTRODUCTION

Optical detection of electron spin resonance in zero field is being increasingly used to measure electron spin splittings and electron nuclear spin interactions in excited triplet states.¹ In addition to the zero field spin dipolar parameters $|D|$ and $|E|$, interactions due to ^{14}N in azaaromatic² and $^{35,37}\text{Cl}$, ^{79}Br , and ^{81}Br in aromatic^{3,4,5} $\pi\pi^*$ triplet states have been observed and analyzed to yield the out-of-plane component of the nuclear electron spin hyperfine tensor and more importantly the nuclear quadrupole splitting parameters in the lowest excited triplet states. Zero field experiments have not however provided reliable estimates of the in-plane components of the hyperfine tensor nor of the field gradient asymmetry parameter η for $^3\pi\pi^*$ states because of the out-of-plane orientation of the principle axis of the electron spin dipolar tensor.

In the following we would like to extend the information available from an analysis of zero field electron spin resonance in excited triplet states by pointing out how the sign of the quadrupole splitting parameter or the absolute ordering of the principal axis of the electron spin sublevel manifold can be easily and readily deduced from the observed zero field electron spin resonance spectra in cases where the molecule contains quadrupolar nuclear spins. The analysis is outlined for p-dichlorobenzene although it is quite general to the whole class of mono, di, tri and tetra halo substituted aromatics or for that matter to any substituted aromatic containing a nonintegral nuclear spin with $I > \frac{1}{2}$.

RESULTS

The spin Hamiltonian describing the triplet state is taken³ to be

$$\mathcal{H} = \mathcal{H}_{ss} + \sum_i \mathcal{H}_Q + \sum_i \mathcal{H}_{HF} \quad (1)$$

where the summation is over the two chlorine nuclei and

$$\mathcal{H}_{ss} = -\left(XS_x^2 + YS_y^2 + ZS_z^2\right) \quad (2)$$

$$\mathcal{H}_Q = \frac{e^2qQ}{12} \left\{ 3I_z^2 - \frac{15}{4} \right\} \quad (3)$$

$$\mathcal{H}_{HF} = A_{xx} S_x I_x \quad (4)$$

with the principal axes system chosen so that the x-axis is normal to the molecular plane and the z-axis is the long in-plane axis coincident with the carbon chlorine bonds. The asymmetry term in $\mathcal{H}_Q$ has been neglected. Other assumptions inherent in this Hamiltonian have been discussed elsewhere³ and all terms have their conventional meanings.

The product functions $\tau_u \chi_1 \chi_2$ form a convenient starting bases set where $\tau_u = X, Y, \text{ or } Z$ is the electron spin function and $\chi_i = \pm\frac{1}{2}, \pm\frac{3}{2}$ is the nuclear spin function of the i-th chlorine nucleus. These zero-th order spin functions diagonalize $\mathcal{H}_{ss}$ and $\mathcal{H}_Q$ but leave $\mathcal{H}_{HF}$ off-diagonal. Consequently $\mathcal{H}_{HF}$ mixes the nuclear-electron spin states of the Y and Z manifolds in first order. The X manifold contains four states, two being degenerate and the other two being symmetrically split from the degenerate pair by $\frac{1}{2}e^2qQ$ as a result of the zero-th order chlorine quadrupole interaction.

Since $\mathcal{H}_{\text{HF}}$ only connects states in different electron spin manifolds with $\Delta I_z = \pm 1$, the Hamiltonian matrix for the Y and Z manifolds reduces to block-diagonal form containing two identical 16 x 16 blocks. Each level remains at least doubly degenerate and thus only one of the Kramers pairs need be considered. A suitable bases for more complete factorization employs the appropriate linear combinations of the degenerate $\tau_u \chi_1 \chi_2$ states listed in Table I. Using these, each Kramers pair reduces to one 6 x 6, two 4 x 4, and one 2 x 2 matrices. The states mixed in this new bases by $\mathcal{H}_{\text{HF}}$ are shown in Table II.

Applying second-order perturbation theory and including all non-vanishing terms, the following energy corrections on the states in parentheses are obtained.

$$\Delta E \left(\langle Z_{\frac{1}{2}}^{1+} | \right) = \frac{4A_{\text{xx}}^2}{Z-Y} + \frac{\frac{3}{2}A_{\text{xx}}^2}{Z-Y - \frac{1}{2}e^2qQ} \quad (5)$$

$$\Delta E \left(\langle Z_{\frac{1}{2}}^{1-} | \right) = \frac{\frac{3}{2}A_{\text{xx}}^2}{Z-Y - \frac{1}{2}e^2qQ} \quad (6)$$

$$\Delta E \left(\langle Z_{\frac{3}{2}}^{\pm} | \right) = \frac{\frac{3}{2}A_{\text{xx}}^2}{Z-Y + \frac{1}{2}e^2qQ} \quad (7)$$

One notes that the out-of-plane hyperfine interaction causes a splitting between the $\langle Z_{\frac{1}{2}}^{1+} |$ and $\langle Z_{\frac{1}{2}}^{1-} |$ states. Similar results are obtained for the Y manifold. Thus, the $\langle Z_{\frac{1}{2}}^{1\pm} |$ and the $\langle Y_{\frac{1}{2}}^{1\pm} |$ levels each split by an amount $4A_{\text{xx}}^2 / (Z-Y)$, whereas the $\langle Z_{\frac{3}{2}}^{\pm} |$ and $\langle Y_{\frac{3}{2}}^{\pm} |$ levels show no splitting to second-order. The importance of these small but finite and measurable splittings

is that either the sign of e^2qQ or the absolute ordering of the X electron spin manifold relative to the Y and Z manifolds can be readily obtained from the zero field electron spin resonance spectrum.

To illustrate this feature we consider explicitly transitions involving the triplet electrons and one or more chlorine nuclei and restrict the discussion to one chlorine isotope although extension to multiple nuclear isotopes is self-evident. The highest and lowest frequency transitions in a given electron spin multiplet will involve simultaneous electron spin plus two chlorine nuclear spin flips.³ These transitions are $\langle Z_2^{1\pm} | \leftrightarrow \langle X_2^{3\pm} |$ and $\langle Z_2^{3\pm} | \leftrightarrow \langle X_2^{1\pm} |$ for, say, the $Z \leftrightarrow X$ multiplet and appear as satellites split from the central electron spin only transition by approximately the Cl nuclear quadrupole coupling constant. Since the X manifold is split only by the first-order quadrupole interaction, any splitting (or extra broadening) in one of the above satellite transitions is associated with the Z manifold and in particular the $\langle Z_2^{1\pm} |$ states. If the absolute ordering of the Z and X manifolds is known independently, then the sign of e^2qQ follows directly from the assignment of either the high or low frequency transition to involvement of the $\langle Z_2^{1\pm} |$ states via a splitting or broadening of one of the two transitions. Alternately and perhaps more importantly, taking e^2qQ to be negative for covalently bonded chlorine from other considerations,⁶ the assignment allows the absolute sign of (Z-X) to be obtained. Similar conclusions obviously apply to the corresponding transitions of the $Y \leftrightarrow X$ multiplet. One cannot however obtain the sign of the zero field parameter E from the spectrum since both the

highest and lowest frequency transitions in the $Z \leftrightarrow Y$ multiplet involve $\frac{1}{2}^{\pm}$ nuclear spin states so that both show a splitting or are broadened.

Figure 1 illustrates the 5.36 GHz transition in p-dichlorobenzene with the features at ca. ± 70 MHz from the central portion expanded. In the 5.36 GHz spectrum the transition at +70 MHz is clearly broadened when compared to that at -70 MHz and even shows some signs of splitting. The 3.60 GHz transition resembles the 5.36 GHz transition insofar as line shapes are concerned whereas in the 1.76 GHz spectrum the ± 70 MHz transitions have nearly equal breadths (not shown). Since $Y > Z > X$ is indicated in p-dichlorobenzene from a combination of theoretical and experimental studies,⁷ the above observations definitely lead to a negative sign for e^2qQ as would be expected.⁶ Conversely, if $e^2qQ < 0$ is assumed; then the observations lead immediately to $X < Z, Y$; that is, $D > 0$. In addition to the sign of D , the value for the out-of-plane hyperfine interaction can be obtained from the expanded spectrum of the +70 MHz region of the 5.36 GHz transition where a splitting of about 1.0 MHz is discernable.⁸ From perturbation theory it can be shown that this splitting, Δ , is given by:

$$\Delta = \frac{4A_{xx}^2}{(|Y-Z|)}, \quad (8)$$

and yields an $A_{xx} = 22$ MHz.

This is in exact agreement with the value obtained earlier by Buckley and Harris³ from fitting the entire spectrum by a complete diagonalization of the spin Hamiltonian. Similarly it can be shown that the frequency separation (Δ') between the peaks of the ± 70 MHz transitions of the ^{35}Cl isotope

in the 5.36 GHz spectrum to second order equals

$$\Delta' = \frac{4A_{xx}^2}{(|Y-Z|) - 2|e^2qQ|} \quad (9)$$

from which $e^2qQ = -64.5$ MHz. Again this is in excellent agreement with the more exact earlier value.³

DISCUSSION

The perturbation approach used above for p-dichlorobenzene has been confirmed by complete diagonalization of the Hamiltonian including the asymmetry term. The latter only leads to small energy shifts (≤ 10 kHz) and introduces no new splittings. Hence, the main assumptions used to obtain the sign of D from the zero field spectra are that $e^2qQ < 0$ and that $A_{xx} \gg A_{yy}, A_{zz}$. Both conditions are expected to be generally true for chlorine covalently bonded to aromatic rings if the molecule remains planar and the excited state symmetry is $\pi\pi^*$. It is not unreasonable then to expect that the sign of D should be obtainable in other haloaromatics from identical consideration. Furthermore, even in mono-chlorobenzene or mono-bromobenzene where no splittings in the satellite transitions arise from $\mathcal{H}_{HF}$, the sign of D can be experimentally deduced from the zero field spectra when the perturbation on the quadrupole satellites are explicitly considered since the quadrupole satellites at ca. ± 35 MHz from the central electron spin only transition are slightly shifted in the Y-Z, X-Z, and X-Y multiplets in a predictable manner. Again

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