

## Optically Detected Nuclear Quadrupole Resonance and Transferred Hyperfine Coupling via Guest-Host Interactions in Molecular Crystals

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Recent optically detected zero-field electron spin resonance experiments on  ${}^3\pi\pi^{*1-3}$  and  ${}^3n\pi^{*4}$  states of azaaromatic compounds doped in molecular crystals have provided the triplet zero-field parameters, nuclear-electron hyperfine interactions and the first measurement of excited state  ${}^{14}\text{N}$  and  ${}^{35,37}\text{Cl}$  nuclear quadrupole coupling constants.<sup>2,3,5,6</sup> In these experiments only intramolecular interactions have been considered. However, in molecular crystals the importance of intermolecular interactions is evident in the transfer of energy via excitons<sup>7</sup> and in the external heavy atom effect on phosphorescent radiative and radiationless decay,<sup>8</sup> to cite only two examples. It is not surprising then to expect the triplet wavefunction of an optically excited guest molecule to overlap the ground-state wavefunction of the adjacent host molecules in doped molecular crystals and thereby transfer a small but finite spin density to the host. This phenomenon, which we will refer to as transferred hyperfine, has in fact been observed in the proton ENDOR of organic triplets by Hutchinson *et al.*<sup>9</sup> and in carbon-13 and deuterium ENDOR by Kwiram *et al.*<sup>10</sup> We wish to report positive evidence for transferred hyperfine to  ${}^{35}\text{Cl}$  and  ${}^{37}\text{Cl}$  nuclei and an additional phenomenon which results from guest to host transferred hyperfine, specifically the detection of the ground-state nuclear quadrupole coupling con-

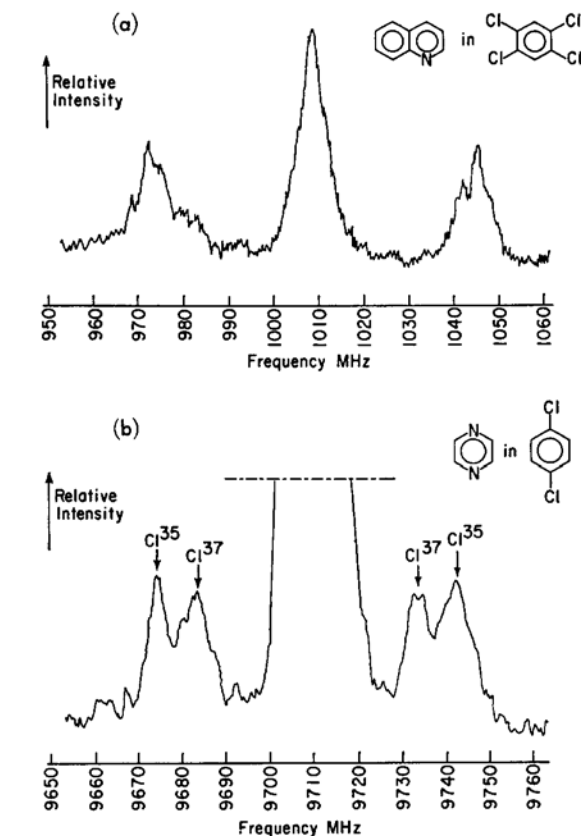


FIG. 1. (a) The optically detected zero-field spectrum of quinoline in 1,2,4,5-tetrachlorobenzene at high microwave power. (b) The optically detected zero-field spectrum of pyrazine- $d_4$  in 1,4-dichlorobenzene at high microwave power.<sup>16</sup>

stants of the host molecules via the optically detected zero-field magnetic resonance of the triplet state of the guest. The two systems studied were the  ${}^3\pi\pi^*$  state of quinoline doped in 1,2,4,5-tetrachlorobenzene and the  ${}^3n\pi^*$  state of pyrazine- $d_4$  in 1,4-dichlorobenzene.

All materials were extensively purified and single crystals,  $10^{-2}$  mole% quinoline and  $10^{-3}$  mole% pyrazine in tetrachlorobenzene and dichlorobenzene, respectively, were grown by Bridgeman techniques. The experimental setup was identical to that published previously.<sup>3</sup> Quinoline was detected using continuous wave techniques while pyrazine- $d_4$  was detected using 20-Hz amplitude modulation of the microwave field. All experiments were performed at 1.8°K while optically detecting emission to the (0,0) state of the guest.

Figure 1(a) and 1(b) show the  $2|E|$  and  $D+|E|$  zero-field transitions<sup>11</sup> for quinoline and pyrazine- $d_4$ , respectively. The quinoline spectrum consists of a main peak at 1009.0 MHz flanked by a pair of satellites split symmetrically from the main peak by 36 MHz. The satellites are 13 MHz wide at half-height and show some poorly resolved structure. The spectrum of pyrazine- $d_4$  consists of a main peak at 9708.1 MHz and two pairs of symmetrical satellites split 27.0 MHz and 34.8 MHz from the center peak. Each has a width at

half-height of 7 MHz. The above results can be understood in terms of intramolecular and intermolecular interactions.

The description of zero-field transitions involving only intramolecular interactions in triplet states of molecules that contain quadrupole nuclei is basically<sup>4-6</sup> as follows. Since the zero field and the nuclear quadrupole Hamiltonian depend on the  $S^2$  and  $I^2$  operators, respectively, the nuclear quadrupole splittings appear in *first* order on the zero-field transitions as satellites split off from the main zero-field transition by the nuclear quadrupole frequency. The presence of a finite hyperfine interaction at the quadrupole nuclei provides the intensity in these transitions and a small *second*-order shift in energy.

Consider now the chlorine nuclear quadrupole and chlorine transferred hyperfine resulting from intermolecular interactions. The presence of a chlorine nuclei on host molecules is no different from a chlorine on a guest as far as the basic interactions are concerned. The major differences are that the elements of the chlorine hyperfine tensor are expected to be greatly reduced in the intermolecular interaction, and generally one does not know *a priori* the molecular orientation of the guest relative to the host molecules. The latter restriction is not however too serious because in zero field the *first*-order chlorine splittings of the host on the zero-field transitions of the guest are independent of the orientation<sup>12</sup> of the host's principal field gradient tensor relative to the zero-field tensor of the guest. Second-order energy shifts of the chlorine satellites can occur but these are expected to be less than a few tenths of a megahertz since they are dependent upon a very small transferred chlorine hyperfine interaction. If the chlorine asymmetry parameters are zero the separation of chlorine satellites in Fig. 1(a) and 1(b) are simply the nuclear quadrupole coupling constants of the chlorine containing host molecules in the ground state. This is verified by a comparison of the known <sup>35</sup>Cl nuclear quadrupole transitions for tetrachlorobenzene<sup>13,14</sup> (77°K, 36.8 and 36.9 MHz) and paradichlorobenzene<sup>15,16</sup> (77°K, 34.78 MHz, 4°K, 34.8 MHz). It is important to stress that the chlorine satellites acquire their intensity by transferred hyperfine. This then is positive evidence for such interactions.

The most serious draw-back of the method appears to be the linewidths of the chlorine satellites. In tetrachlorobenzene the linewidth probably results from multiple chlorine sites due to nonisomorphous<sup>17</sup> substitution of the guest and possibly from crystallographic twinning.<sup>18</sup> The spectrum of pyrazine-*d*<sub>4</sub> in paradichlorobenzene exhibits narrower chlorine satellites to the extent that the <sup>35</sup>Cl and <sup>37</sup>Cl isotopic splittings are resolved. This is consistent with Kwiram's<sup>4</sup> low-field optically detected ESR study which reports a two-site substitution of pyrazine in paradichlorobenzene.

Finally, the above method for determining nuclear quadrupole coupling constants may be valuable in large

molecules if the molecules can be "probed" or "labeled" with a nonquenched phosphorescing triplet.

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