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Publication Date

1970-09-01

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INTERACTIONS IN MOLECULAR CRYSTALS

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September 1970

AEC Contract No. W-7405-eng-48

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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 $3_{n\pi^*}$ 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}N and $^{35,37}\text{Cl}$ nuclear quadrupole coupling constants^{2,3,5,6}. 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 excitons⁷ and in the external heavy atom affect on phosphorescent radiative and radiationless decay⁸, 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 phenomena, which we will refer to as transferred

hyperfine, has in fact been observed in the proton ENDOR of organic triplets by Hutchinson, et al.⁹ and in carbon-13 and deuteron ENDOR by Kwiram et al.¹⁰ We wish to report positive evidence for transferred hyperfine to ^{35}Cl and ^{37}Cl nuclei and an additional phenomenon which results from guest to host transferred hyperfine, specifically the detection of the ground state nuclear quadrupole coupling constants 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 $^3_{\pi\pi^*}$ state of pyrazine⁴ in 1,4 dichlorobenzene.

All materials were extensively purified and single crystals, 10^{-2} m quinoline and 10^{-3} m pyrazine in tetrachlorobenzene and dichlorobenzene respectively were grown by Bridgeman techniques. The experimental setup was identical to that published previously³. Quinoline was detected using continuous wave techniques while pyrazine 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 1a and 1b show the $2|E|$ and $D + |E|$ zero field transitions¹¹ for quinoline and pyrazine 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 37 MHz. The satellites are 13 MHz wide at half height and show some poorly resolved structure. The spectrum of pyrazine 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^{4,5,6} 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 orientation¹² of the host's principle 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 MHz 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 Figure 1a and 1b are simply the nuclear quadrupole coupling constants of the chlorine containing host molecules in the ground state. This borne out by a comparison of the known ³⁵Cl nuclear quadrupole transitions for tetrachlorobenzene^{13,14} (77°K, 36.8 and 36.9 MHz) and

paradichlorobenzene^{15,16} (77°K, 34.78 MHz, 4°K, 34.8MHz). 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 drawback of the method appears to be the line widths of the chlorine satellites. In tetrachlorobenzene the line width probably results from multiple chlorine sites due to non-isomorphous¹⁷ substitution of the guest and possibly from crystallographic twinning¹⁸. The spectrum of pyrazine in paradichlorobenzene exhibits narrower chlorine satellites to the extent that the ³⁵Cl and ³⁷Cl isotopic splittings are resolved. This is consistent with Kwiram's⁴ 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 "labelled" with a non-quenched phosphorescing triplet.

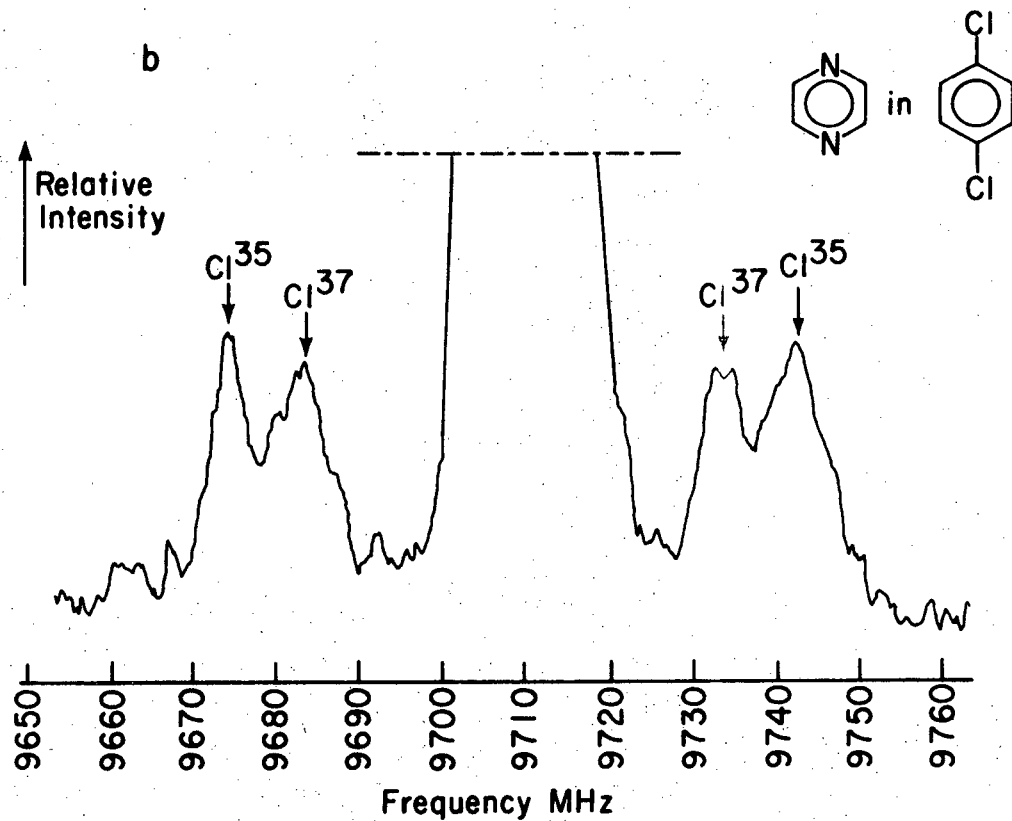
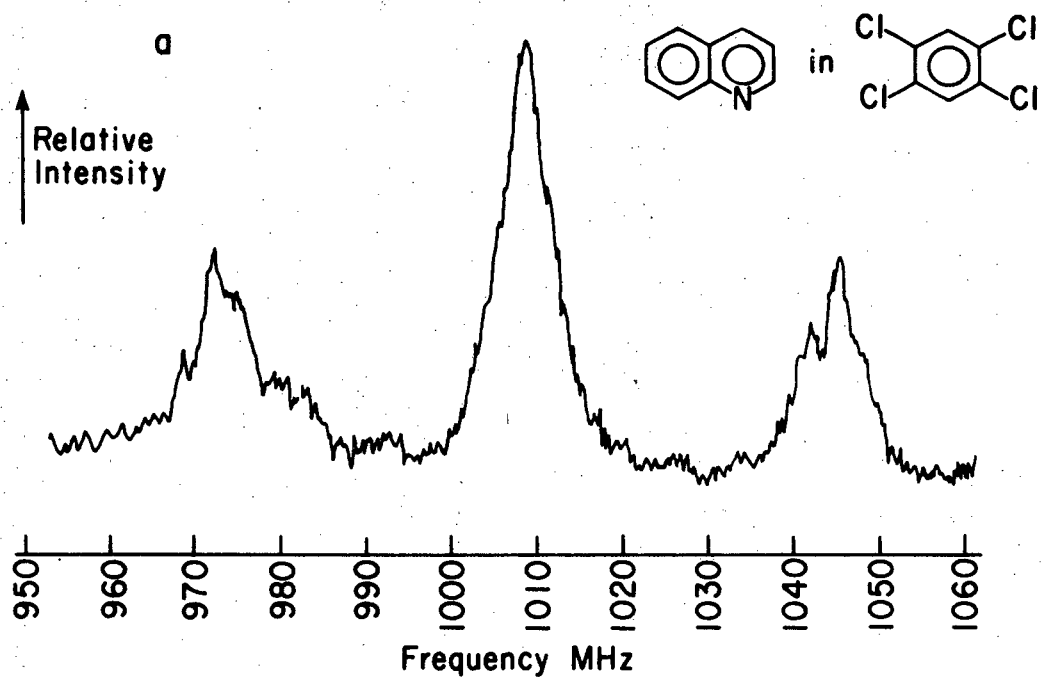
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Figure Captions

Figure 1a. The optically detected zero field spectrum of quinoline in 1,2,4,5 tetrachlorobenzene at high microwave power.

Figure 1b. The optically detected zero field spectrum of pyrazine in 1,4 dichlorobenzene at high microwave power.¹⁶



XBL 709-6566

Figures 1a and 1b

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