Title
OPTICALLY DETECTED NUCLEAR QUADRUPOLE RESONANCE AND TRANSFERRED HYPERFINE COUPLING VIA GUEST - HOST INTERACTIONS IN MOLECULAR CRYSTALS

Permalink
https://escholarship.org/uc/item/3551353h

Authors
Fayer, M.D.
Harris, C.B.
Yuen, D.A.

Publication Date
1970-09-01
Submitted as a communication to
Journal of Chemical Physics

RECEIVED
LAWRENCE
RADIATION LABORATORY
OCT 15 1970

LIBRARY AND
DOCUMENTS SECTION

OPTICALLY DETECTED NUCLEAR QUADRUPOLE RESONANCE
AND TRANSFERRED HYPERFINE COUPLING VIA GUEST-HOST
INTERACTIONS IN MOLECULAR CRYSTALS

M. D. Fayer, C. B. Harris, and D. A. Yuen

September 1970

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY
This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Optically Detected Nuclear Quadrupole Resonance and Transferred Hyperfine Coupling via Guest-Host Interactions in Molecular Crystals

M. D. Fayer, C. B. Harris and D. A. Yuen

Department of Chemistry, University of California and the Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, California 94720

Recent optically detected zero field electron spin resonance experiments on $^3\pi\pi^*$ 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. 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 and in the external heavy atom affect on phosphorescent radiative and radiationless decay, 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 pyrazine 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 previously\(^3\). 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 \(|E|\) and \(D + |E|\) zero field transitions\(^{11}\) 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 orientation $^{12}$ 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 $^{35}\text{Cl}$ nuclear quadrupole transitions for tetrachlorobenzene $^{13,14}$ (77°K, 36.8 and 36.9 MHz) and
paradichlorobenzene$^{15,16}$ ($77^\circ$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 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-isomorphous$^{17}$ substitution of the guest and possibly from crystallographic twinning$^{18}$. The spectrum of pyrazine in paradichlorobenzene exhibits narrower chlorine satellites to the extent that the $^{35}$Cl and $^{37}$Cl isotopic splittings are resolved. This is consistent with Kwiram's$^4$ 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.
References

11. D and |E| are the conventional ESR zero field parameters.
Figure Captions

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

Figure lb. The optically detected zero field spectrum of pyrazine in 1,4 dichlorobenzene at high microwave power.
Figures 1a and 1b
LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.