Nuclear Magnetic Double-Resonance Spectrum of a Strongly Coupled Two-Spin System

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The density-matrix theory of double resonance is applied for a detailed analysis of the frequency-sweep nuclear magnetic double-resonance spectra of the strongly coupled two-proton system in 2-bromo-5-chloro-thiophene under various conditions of irradiation. These spectra show significant relaxation and coherence effects. The results of the theory are very sensitive to the relaxation mechanisms assumed for the system, indicating the possibility of deriving significant information about the relaxation of the system by this method. Comparison of the observed and theoretical double-resonance spectra shows that the proton relaxation in this molecule is due, in large measure, to external interactions with a high degree of correlation between the interactions with the two protons. An approximation proposed by Bloch for simplifying the calculations is found to be applicable even when the irradiation frequency is close to some single-resonance transition frequencies.

INTRODUCTION

THE technique of nuclear magnetic double resonance has been used effectively to simplify complex single-resonance spectra and to derive relative signs of some of the spin-spin coupling constants. In most of such applications only the effects of the strong radio-frequency perturbation on the spin Hamiltonian need be considered. These effects have been analyzed under various conditions by transforming the spin Hamiltonian into a coordinate system rotating at the angular frequency of the irradiating field.[1-3] The irradiating field, however, may introduce significant changes in the populations and lifetimes of the different energy levels. Thus, depending on the relaxation of the system, intensity and linewidth changes may occur which are not predicted by the above calculations.[4,5] The analysis of these features requires a complete description of the double-resonance problem including the relaxation mechanisms in the system, and thus may provide significant information about the latter. Density-matrix techniques provide a convenient method of describing relaxation effects in double-resonance spectra.[6,7]

A general method, based on the density-matrix formalism given by Bloch[6] and using the notational simplicity of Redfield,[8] for analyzing relaxation and coherence effects in nuclear magnetic double resonance

has been described in an earlier paper.[9] The method consists of deriving the complete spin density matrix in the steady state, under the influence of the irradiating and observing fields (H_2 and H_1) in a coordinate system rotating at the angular frequency of H_2. It is convenient to use a representation in which the stationary part of the spin Hamiltonian is diagonal in the rotating frame of reference. It was also shown that an approximation, useful in simplifying these calculations, originally proposed by Bloch[6] is applicable to systems with weak relaxation under a wide range of experimental conditions. In the present work this method has been applied to the analysis of frequency-sweep double-resonance spectra of a strongly coupled two-spin (AB) system. These spectra were obtained under several different conditions of irradiation and contain features that are not predicted by a simple calculation. The analysis was made by assuming various relaxation mechanisms for the system. The approximation proposed by Bloch was shown to be applicable to this molecule. A comparison of the results obtained for different relaxation mechanisms yields considerable information on the relaxation in the system.

THEORY

The equation of motion of the spin density matrix $\tilde{\sigma}$, for the double-resonance problem, in a coordinate system rotating at the angular frequency $-\omega_2 \mathbf{k}$, is given by[9]

$$\frac{d\tilde{\sigma}}{dt} = -i[\mathcal{3C}_0{}^R + \tilde{\mathcal{3C}}_1(t), \tilde{\sigma}] - \Gamma(\tilde{\sigma} - \sigma_0),\qquad(1)$$

where the operators in the rotating frame are recognized by putting a tilde ($\sim$) on top; $\mathcal{3C}_0{}^R$ and $\tilde{\mathcal{3C}}_1(t)$ are the stationary and time-dependent parts of the spin Hamil-

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tonian, expressed in angular frequency units, in that frame of reference; and $\Gamma(\bar{\sigma}-\sigma_0)$ is the relaxation term. $\mathcal{3C}_0{}^R$ and $\mathcal{3C}_1(t)$ are given by

$$\mathcal{3C}_0{}^R = 2\pi\{A_iI_z(i)+\sum_{i<j} J_{ij}\mathbf{I}(i)\cdot\mathbf{I}(j)\}+(D_{2+}+D_{2-}),\quad (2)$$

$$\mathcal{3C}_1(t) = D_{1+}\exp(i\omega't)+D_{1-}\exp(-i\omega't),\quad (3)$$

with

$$A_i = v_{0i}+\omega_2/2\pi,\quad (4)$$

$$v_{ki} = -(\gamma_iH_k/2\pi)\quad k=0,1,2,\quad (5)$$

$$D_{k\pm} = \pi\sum_i v_{ki}I_{\pm}(i)\quad k=1,2,\quad (6)$$

$$\omega' = \omega_1-\omega_2,\quad (7)$$

where $\mathbf{I}(i)$ and γ_i are the spin and gyromagnetic ratio including chemical shift of nucleus i; J_{ij} is the spin-spin coupling constant of nucleus i with nucleus j; H_0, H_1, and H_2 represent the static magnetic field $\mathbf{H}_0=H_0\mathbf{k}$ and the two radio-frequency fields $\mathbf{H}_k=H_k\cos\omega_k t\mathbf{i}-H_k\sin\omega_k t\mathbf{j}(k=1,2)$, respectively. The quantities J_{ij} and $v_{ki}(k=0,1,2)$ are expressed in cps. The relaxation term $\Gamma(\bar{\sigma}-\sigma_0)$ is defined by its matrix elements in a basis $\alpha,\alpha'\cdots$ such that $\mathcal{3C}_0{}^R|\alpha\rangle=E_\alpha|\alpha\rangle\cdots$, through the relations

$$\langle\alpha|\Gamma(\bar{\sigma}-\sigma_0)|\alpha'\rangle = -\sum_{\beta\beta'}R_{\alpha\alpha'\beta\beta'}(\bar{\sigma}-\sigma_0)_{\beta\beta'},\quad (8)$$

with

$$R_{\alpha\alpha'\beta\beta'} = J_{\alpha\beta\alpha'\beta'}-\delta_{\alpha'\beta'}\sum_\gamma \tfrac{1}{2}J_{\gamma\beta\gamma\alpha}-\delta_{\alpha\beta}\sum_\gamma \tfrac{1}{2}J_{\gamma\alpha'\gamma\beta'},\quad (9)$$

and

$$J_{\alpha\beta\alpha'\beta'} = \langle\langle\alpha|\mathcal{3C}'(t)|\beta\rangle\langle\alpha'|\mathcal{3C}'(t)|\beta'\rangle^*\rangle_{\mathrm{av}}2\tau_c,\quad (10)$$

where $\mathcal{3C}'(t)$ is the relaxation Hamiltonian. The $\langle\ \rangle_{\mathrm{av}}$ represents an ensemble average, and τ_c is the correlation time. σ_0 is given by

$$\sigma_0 = (1/N)-q\mathcal{3C}_0,\quad (11)$$

where $\mathcal{3C}_0$ is the stationary part of the spin Hamiltonian in the laboratory frame of reference, N is the number of its eigenvalues and $q=\hbar/NkT$. A number of assumptions are made in the derivation of Eq. (1) including especially the assumption of extreme narrowing or $|\mathcal{3C}_0\tau_c|\ll1$. The relaxation Hamiltonian $\mathcal{3C}'(t)$ may conveniently be written as[10]

$$\mathcal{3C}'(t) = \sum_q F^{(q)}(t)A^{(q)},\quad (12)$$

where $F^{(q)}$ are random functions of lattice operators and $A^{(q)}$ are spin operators expressed in irreducible form. The functions $F^{(q)}$ are in general complex and the operators $A^{(q)}$ are in general non-Hermitian and the Hermi-

ticity of $\mathcal{3C}'(t)$ is obtained through the relations

$$F^{(q)} = F^{(-q)*},$$
$$A^{(q)} = A^{(-q)\dagger}.\quad (13)$$

With this form for $\mathcal{3C}'(t)$ the correlation functions for most of the relaxation mechanisms simplify through the relation

$$\langle F^{(q)*}(t)F^{(q')}(t)\rangle_{\mathrm{av}} = \delta_{qq'}\langle|F^{(q)}(t)|^2\rangle_{\mathrm{av}}.\quad (14)$$

Equations (12), (13), and (14), together with the fact that the matrix elements of $A^{(q)}$ are all real allow, Eq. (10) to be written as

$$J_{\alpha\beta\alpha'\beta'} = 2\tau_c\sum_q\langle|F^{(q)}|^2\rangle_{\mathrm{av}}\langle\alpha|A^{(q)}|\beta\rangle\langle\alpha'|A^{(q)}|\beta'\rangle.\quad (15)$$

Eq. (15) yields the equalities

$$J_{\alpha\beta\alpha'\beta'} = J_{\alpha'\beta'\alpha\beta} = J_{\beta\alpha\beta'\alpha'} = J_{\beta'\alpha'\beta\alpha},\quad (16)$$

which are in turn reflected in the following relations for the R elements:

$$R_{\alpha\alpha'\beta\beta'} = R_{\beta\beta'\alpha\alpha'} = R_{\alpha'\alpha\beta'\beta} = R_{\beta'\beta\alpha'\alpha},\quad (17)$$

and

$$\sum_\beta R_{\alpha\alpha'\beta\beta} = 0.\quad (18)$$

The deviation from σ_0 caused in the density matrix by the two rf fields $\mathbf{H}_1$ and $\mathbf{H}_2$ is written explicitly through the equation

$$\bar{\sigma} = \sigma_0+\bar{\chi}+\bar{\eta}(t),\quad (19)$$

where $\bar{\chi}$ is the effect of $\mathbf{H}_2$ in the absence of $\mathbf{H}_1$ and $\bar{\eta}(t)$ is the effect of $\mathbf{H}_1$ on the resulting system. When $\mathcal{3C}_1(t)=0$, $\bar{\eta}(t)=0$ and Eq. (1) for the steady-state condition, becomes

$$[\mathcal{3C}_0{}^R,\bar{\chi}+\sigma_0]-i\Gamma(\bar{\chi}) = 0.\quad (20)$$

For a system of two spins A and B each with spin $\tfrac{1}{2}$, and where J_{AB} is of the same order of magnitude as $|v_{0A}-v_{0B}|$, if v_{0A} and $v_{0B}\gg|v_{0A}-v_{0B}|$, Eq. (20) becomes

$$[\mathcal{3C}_0{}^R,\bar{\chi}]-i\Gamma(\bar{\chi}) = -(2\pi qv_0)(\pi v_2)\sum_i[I_+(i)-I_-(i)].\quad (21)$$

Taking matrix elements of Eq. (21) in the $\alpha,\alpha'\cdots$ basis and using Eq. (17) and the fact that $\bar{\chi}$ is Hermitian yields the following set of N^2 simultaneous equations in the matrix elements of $\bar{\chi}$:

$$(E_\alpha-E_{\alpha'})\,\mathrm{Re}(\bar{\chi}_{\alpha\alpha'})$$
$$-\sum_{\beta<\beta'}(R_{\alpha\alpha'\beta\beta'}-R_{\alpha\alpha'\beta'\beta})\,\mathrm{Im}(\bar{\chi}_{\beta\beta'})$$
$$= -(2\pi qv_0)(\pi v_2)\sum_i[I_+(i)-I_-(i)]_{\alpha\alpha'},\quad (22)$$

$$(E_\alpha-E_{\alpha'})\,\mathrm{Im}(\bar{\chi}_{\alpha\alpha'})+\sum_{\beta<\beta'}(R_{\alpha\alpha'\beta\beta'}+R_{\alpha\alpha'\beta'\beta})$$
$$\times\mathrm{Re}(\bar{\chi}_{\beta\beta'})+\sum_\beta R_{\alpha\alpha'\beta\beta}\bar{\chi}_{\beta\beta} = 0,\quad (23)$$

[10] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), p. 278.

with $\alpha < \alpha'$ and when $\alpha = \alpha'$

$$2 \sum_{\beta < \beta'} R_{\alpha\alpha\beta\beta'} \, \mathrm{Re}(\tilde{\chi}_{\beta\beta'}) + \sum_{\beta} R_{\alpha\alpha\beta\beta} \tilde{\chi}_{\beta\beta} = 0. \quad (24)$$

For a two-spin system $N=4$, Eqs. (22) and (23) each represent six equations, and Eq. (24) represents four equations. The set of Eqs. (24) can be shown to be linearly dependent by virtue of Eq. (18) and one of these must be replaced by the relation

$$\sum_{\beta} \tilde{\chi}_{\beta\beta} = 0 \quad (25)$$

to obtain a nontrivial solution of $\tilde{\chi}$.

A steady-state solution for $\tilde{\eta}(t)$ may be obtained by assuming that the diagonal elements of $\tilde{\eta}$ are constant in time and the off-diagonal elements vary with time as

$$\tilde{\eta}_{\alpha\alpha'} = Y_{\alpha\alpha'}{}^{+} e^{i\omega' t} + Y_{\alpha\alpha'}{}^{-} e^{-i\omega' t}. \quad (26)$$

The value of H_1 is usually kept small enough not to cause saturation effects so that $\tilde{\eta}_{\alpha\alpha}$ may be assumed to be zero. Further, if there are no coincident transitions in the double-resonance spectrum, only one off-diagonal element of $\tilde{\eta}$ is important at one time. Under these conditions a solution for $\mathrm{Re}(Y_{\alpha\alpha'}{}^{\pm})$ and $\mathrm{Im}(Y_{\alpha\alpha'}{}^{\pm})$ can be obtained in a closed form as

$$\mathrm{Re}(Y_{\alpha\alpha'}{}^{\pm}) = \frac{-(\pm\omega' + E_\alpha - E_{\alpha'})[D_{1\pm'}(\mathrm{Re}\tilde{\chi} + \sigma_0)]_{\alpha\alpha'} + R_{\alpha\alpha'\alpha\alpha'}[D_{1\pm'} \, \mathrm{Im}\tilde{\chi}]_{\alpha\alpha'}}{(\pm\omega' + E_\alpha - E_{\alpha'})^2 + R_{\alpha\alpha'\alpha\alpha'}{}^2}, \quad (27)$$

$$\mathrm{Im}(Y_{\alpha\alpha'}{}^{\pm}) = \frac{-R_{\alpha\alpha'\alpha\alpha'}[D_{1\pm'}(\mathrm{Re}\tilde{\chi} + \sigma_0)]_{\alpha\alpha'} - (\pm\omega' + E_\alpha - E_{\alpha'})[D_{1\pm'} \, \mathrm{Im}\tilde{\chi}]_{\alpha\alpha'}}{(\pm\omega' + E_\alpha - E_{\alpha'})^2 + R_{\alpha\alpha'\alpha\alpha'}{}^2}. \quad (28)$$

The signal intensity S in a nuclear induction experiment is given by

$$S \propto \frac{d}{dt} \sum_i \gamma_i \, \mathrm{Tr}\langle I_y(i)\sigma \rangle. \quad (29)$$

If only one off-diagonal element of $\tilde{\eta}$ is important at one time, the absorption-mode signal intensity at the frequency ω_1 may be derived from Eq. (29) as[7,9]

$$S_{\alpha\alpha'}{}^{\pm} \propto \mp \sum_i \gamma_i I_\pm(i)_{\alpha\alpha'} \, \mathrm{Im}(Y_{\alpha\alpha'}{}^{\pm}), \quad (30)$$

where the two alternative signs refer to the two situations $(\pm\omega' + E_\alpha - E_{\alpha'}) \gtreqless 0$. Substituting for $\mathrm{Im}(Y_{\alpha\alpha'}{}^{\pm})$ when $(\pm\omega' + E_\alpha - E_{\alpha'}) = 0$ gives

$$S_{\alpha\alpha'}{}^{\pm} \propto \mp \frac{1}{R_{\alpha\alpha'\alpha\alpha'}} \sum_i \gamma_i I_\pm(i)_{\alpha\alpha'} \times [D_{1\pm'}(\mathrm{Re}\tilde{\chi} + \sigma_0)]_{\alpha\alpha'}. \quad (31)$$

The occurrence of significant signal intensity for both the conditions $(\pm\omega' + E_\alpha - E_{\alpha'}) \approx 0$ is a result of the coherence induced by the rf field H_1, which is implicit in Eq. (26).

Bloch[6] proposed that for systems with weak relaxation the calculations may be made by assuming $(\tilde{\chi} + \sigma_0)$ to be diagonal in the $\alpha, \alpha' \cdots$ basis. It can be seen from Eq. (20) that the off-diagonal elements of $(\tilde{\chi} + \sigma_0)$ are very small if

$$|E_\alpha - E_{\alpha'}| \gg |\langle \alpha | \Gamma(\tilde{\chi}) | \alpha' \rangle| \quad (32)$$

for all $\alpha \neq \alpha'$. $(E_\alpha - E_{\alpha'})$ reaches its lowest value, which is of the order of the strength of irradiation, when the irradiating frequency is equal to the corresponding single-resonance frequency. The off-diagonal matrix elements of $\Gamma(\tilde{\chi})$ are of the order of the linewidths in the spectrum. If the strength of irradiation is large com-

pared to the linewidths in the spectrum, Bloch's approximation is applicable even when irradiation is done close to a single-resonance transition.[9] The use of this approximation reduces the total number of simultaneous equations [Eqs. (22)–(25)] to N. The validity of the approximation has to be tested for individual cases. An alternative condition for this is found to be[9]

$$\mathrm{Re}(\tilde{\chi})_{\alpha\alpha'} \gg \mathrm{Im}(\tilde{\chi})_{\alpha\alpha'} \quad (33)$$

for all α and α' if a calculation is attempted using Eqs. (22) through (25).

EXPERIMENTAL

The frequency-sweep double-resonance experiments were performed using a spin decoupler[11] with the Varian high-resolution NMR spectrometer operating at 60 Mc/sec. The spectrometer frequency and magnetic field are locked to the proton resonance of tetramethyl silane, using the low-frequency sideband obtained by modulating the magnetic field at 1000 cps with a tuning fork oscillator. Two other modulation frequencies are used for irradiation and detection purposes. The output is lock-in detected at the observing frequency which is swept by a motor-drive. The index of modulation is kept well below saturation at the observing and locking frequencies, while it is considerably larger at the irradiating frequency. The experiment was performed on the strongly coupled two-proton system (AB) in 2-bromo-5-chlorothiophene:
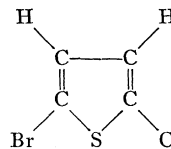
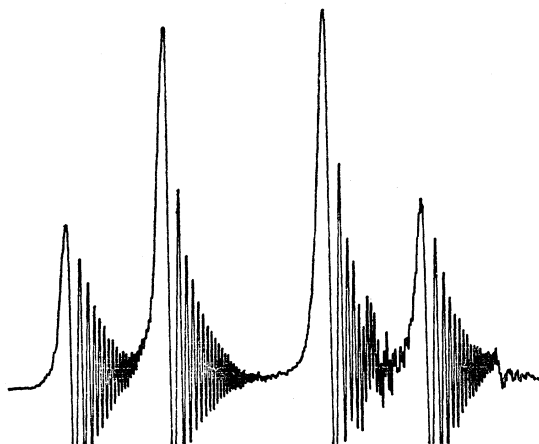[11] J. H. Noggle, Rev. Sci. Instr. 35, 1166 (1964).

FIG. 1. The proton resonance spectrum of 2-bromo-5-chlorothiophene at 60 Mc/sec.

RESULTS AND DISCUSSION

The proton resonance spectrum of 2-bromo-5-chloro-thiophene at 60 Mc/sec is shown in Fig. 1. The spectrum can be analyzed in a straightforward manner[12] to obtain the following values for the chemical shift δ and the spin-spin coupling constant J between the two protons: $\delta = 9.6 \pm 0.2$ and $J = 3.9 \pm 0.2$ cps. These values agree with those obtained by Anderson[13] for this molecule. Double-resonance spectra were obtained with three different frequencies of irradiation. If the low-field half of the spectrum is assigned to the B nucleus, these three frequencies correspond to $A_B = -1.55$, 2.35, and 3.95 cps [see Eq. (4)]. In the first two cases the irradiating frequency is made to coincide with the inner and outer lines of the B spectrum, respectively, and in the third case it is set on the low-field side of the spectrum. In each case the strength of irradiation has been determined by calculating the double-resonance frequencies $(E_\alpha - E_{\alpha'})$ for different values of v_2 and comparing with the observed spectrum. The values of v_2 thus obtained, corresponding to the three values of A_B given above, are $v_2 = 9.4$, 9.6, and 9.5 cps, respectively.

The frequency-sweep double-resonance spectra of 2-bromo-5-chlorothiophene for the three cases (i) $A_B = -1.55$, $v_2 = 9.4$; (ii) $A_B = 2.35$, $v_2 = 9.6$; and (iii) $A_B = 3.95$, $v_2 = 9.5$ are shown in Figs. 2, 3, and 4, respectively. All these spectra contain a beat pattern centered at the irradiating frequency. This occurs since the strong signal at the irradiating frequency is passed by the lock-in detector tuned to the observing frequency when the two frequencies are nearly equal. All these spectra also show some transitions below the baseline as opposed to above the baseline for a normal spectrum. These transitions are located symmetrically about the irradiating frequency with respect to some of
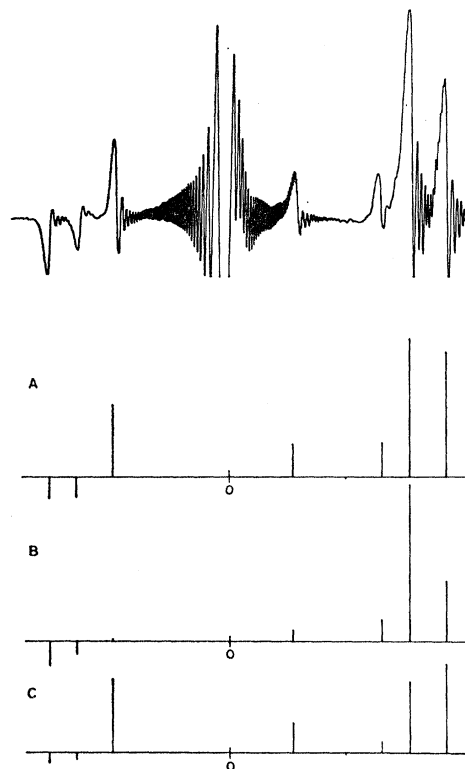
[12] J. A. Pople, H. J. Bernstein, and W. G. Schneider, *High Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959), p. 119.
[13] W. A. Anderson, Phys. Rev. **102**, 151 (1956).

FIG. 2. Observed and calculated proton-proton double-resonance spectra of 2-bromo-5-chlorothiophene with $A_B = -1.55$ cps and $v_2 = 9.4$ cps. The theoretical spectra, A, B, and C represent the results for the three relaxation mechanisms RFC, RFUC, and DD, respectively.

the transitions above the baseline. Such inverted transitions obtain in the density matrix description of the problem when the coherence in the motion of the spins induced by the rf field is considered [Eq. (31)].

Three different mechanisms are considered for the relaxation of the two-proton system for the purpose of theoretical calculation of the spectrum:

(A) Relaxation due to an isotropic random field with complete correlation between the interactions with the two protons (RFC—random field correlated):

$$\mathfrak{IC}'(t) = \tfrac{1}{2} F^+(t)[I_-(A) + I_-(B)]$$
$$+ F^z(t)[I_z(A) + I_z(B)]$$
$$+ \tfrac{1}{2} F^-(t)[I_+(A) + I_+(B)], \quad (34)$$

with

$$\tfrac{1}{2} \langle |F^+(t)|^2 \rangle_{av} = \tfrac{1}{2} \langle |F^-(t)|^2 \rangle_{av} = \langle |F^z(t)|^2 \rangle_{av}, \quad (35)$$

and $F^\pm = F^x \pm i F^y$.

(B) Relaxation due to an isotropic random field without any correlation between the interactions with the two protons (RFUC—random field uncorrelated):

$$\mathfrak{IC}'(t) = \tfrac{1}{2} F_A{}^+(t) I_-(A) + F_A{}^z(t) I_z(A) + \tfrac{1}{2} F_A{}^-(t) I_+(A)$$
$$+ \tfrac{1}{2} F_B{}^+(t) I_-(B) + F_B{}^z(t) I_z(B) + \tfrac{1}{2} F_B{}^-(t) I_+(B), \quad (36)$$

with

$$\tfrac{1}{2}\langle|F_A{}^+(t)|^2\rangle_{av}=\tfrac{1}{2}\langle|F_A{}^-(t)|^2\rangle_{av}=\langle|F_A{}^z(t)|^2\rangle_{av}$$
$$=\tfrac{1}{2}\langle|F_B{}^+(t)|^2\rangle_{av}=\tfrac{1}{2}\langle|F_B{}^-(t)|^2\rangle_{av}=\langle|F_B{}^z(t)|^2\rangle_{av}, \quad (37)$$

and

$$\langle F_A{}^{(q)}(t)^* F_B{}^{(q')}(t)\rangle_{av}=\delta_{qq'}\delta_{AB}\langle|F_A{}^{(q)}(t)|^2\rangle_{av}. \quad (38)$$

(C) Relaxation through direct dipole-dipole interaction between the two protons in the system (DD):

$$\mathcal{3C}'(t)=\sum_{q=-2}^{2} F^{(q)}A^{(q)}, \quad (39)$$

with

$$F^{(0)}=\frac{1-3\cos^2\theta}{r^3} \qquad A^{(0)}=\alpha\{-\tfrac{2}{3}I_z(A)I_z(B)+\tfrac{1}{6}[I_+(A)I_-(B)+I_-(A)I_+(B)]\},$$

$$F^{(1)}=\frac{\sin\theta\,\cos\theta e^{-i\phi}}{r^3} \qquad A^{(1)}=\alpha\{I_z(A)I_+(B)+I_+(A)I_z(B)\},$$

$$F^{(2)}=\frac{\sin^2\theta e^{-2i\phi}}{r^3} \qquad A^{(2)}=\tfrac{1}{2}\alpha I_+(A)I_+(B),$$

and

$$F^{(-q)}=F^{(q)*}, \quad A^{(-q)}=A^{(q)\dagger}, \quad \text{and} \quad \alpha=-\tfrac{3}{2}\gamma_A\gamma_B\hbar. \quad (40)$$

Spectra were calculated using an IBM 1620 computer for the three different conditions of irradiation assuming the above relaxation mechanisms and following the steps indicated in the theory section. The relaxation
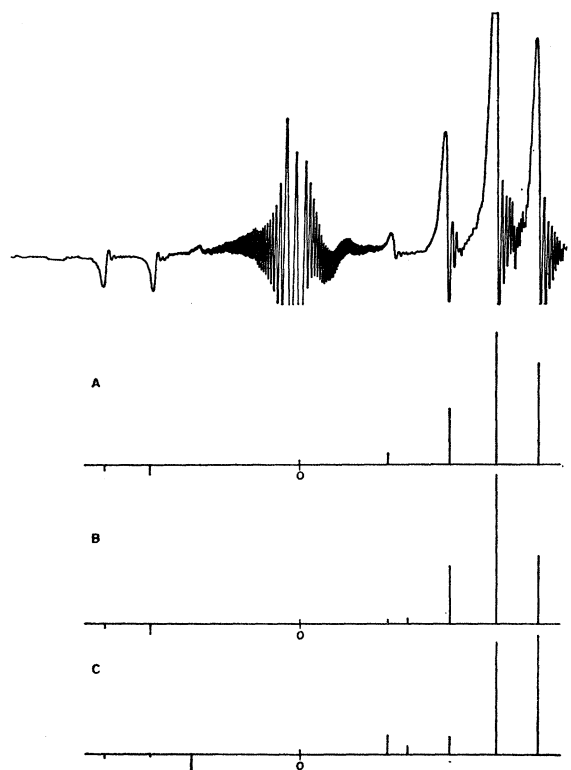
matrix elements are all calculated within a proportionality constant.[14] In all the cases it was found that $\mathrm{Re}(\bar{\chi})_{\alpha\alpha'}\gg\mathrm{Im}(\bar{\chi})_{\alpha\alpha'}$ for all α and α' and that $(\mathrm{Re}\bar{\chi}+\sigma_0)$
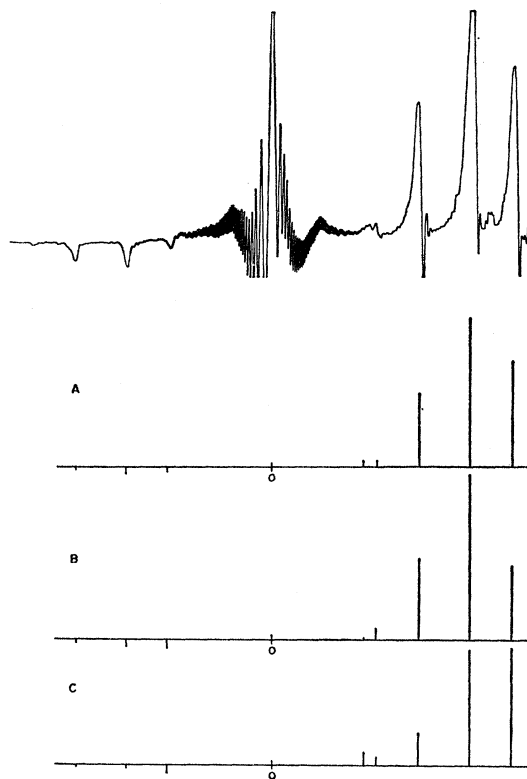

Fig. 3. Observed and calculated proton-proton double-resonance spectra of 2-bromo-5-chlorothiophene with $A_B=2.35$ cps and $v_2=9.6$ cps. The theoretical spectra, A, B, and C represent the results for the three relaxation mechanisms RFC, RFUC, and DD, respectively.

Fig. 4. Observed and calculated proton-proton double-resonance spectra of 2-bromo-5-chlorothiophene with $A_B=3.95$ cps and $v_2=9.5$ cps. The theoretical spectra, A, B, and C represent the results for the three relaxation mechanisms RFC, RFUC, and DD, respectively.

[14] This constant is determined by assuming that the linewidth $R_{\alpha\alpha'\alpha\alpha'}$ of a transition $\alpha \to \alpha'$ is 0.3 cps in the limit of $J\ll|v_{0A}-v_{0B}|$ and $v_2=0$. If Bloch's approximation is valid and the calculations are done by assuming only one relaxation mechanism, the relative intensities in the double-resonance spectrum are independent of this proportionality factor in the calculation of R.

is diagonal in the $\alpha, \alpha' \cdots$ representation to an excellent approximation. Bloch's approximation is thus found to be valid irrespective of whether irradiation is done close to some single-resonance transitions as in cases (i) and (ii) or away from these transitions as in case (iii).

The results of the theoretical calculation using the three relaxation mechanisms are plotted in juxtaposition for comparison with the observed spectra and are shown in Figs. 2, 3, and 4 for the three conditions of irradiation. A comparison of the results for the three mechanisms in any of the three cases clearly indicates that the theoretical spectrum depends strongly on the relaxation mechanism assumed for the system. In all three cases the results obtained for mechanism (C), the internal dipole-dipole interaction, are in clear disagreement with the observed spectra. Comparison of the results for mechanisms (A) and (B), correlated and uncorrelated external relaxation, respectively, with the observed spectra shows several features of (B) in disagreement while the remaining may agree reasonably well. The results of (A) show the best over-all agreement with the observed spectra in all three cases and reproduce all the features of these spectra. On the basis of these results it is therefore possible to rule out the choice of mechanisms (B) and (C) as exclusive or dominating mechanisms of relaxation for this system. Mechanism (A) appears to be the most important. The results, however, do not permit the conclusion that (A) is the exclusive relaxation mechanism of the system. Small contributions of mechanisms (B) and (C) cannot be ruled out. The dependence of the intensities of the transitions on a combination of relaxation mechanisms is not straightforward and a complete calculation has to be done for each mixture of relaxation mechanisms. The accuracy with which the intensities in the spectrum are known in the present case is not sufficient to justify a detailed fitting of the observed spectrum with a combination of the mechanisms. It can be concluded, however, that the system relaxes primarily through external interactions and that the interactions of the two protons with the external field causing relaxation are correlated to a high degree. This is in agreement with the results of Noggle[15] obtained from transient experiments on a similar molecule, 2-3-dibromothiophene, for which a correlation factor of 0.75 is estimated for relaxation of the protons by external interactions.

SUMMARY

A density matrix description of relaxation and coherence effects of nuclear magnetic double resonance[9] is applied to the spectra of 2-bromo-5-chlorothiophene obtained under different conditions of irradiation. The approximation proposed earlier by Bloch[6] is found to be applicable to this case even when the irradiation frequency is close to single-resonance transition frequencies. The results of the calculations assuming different mechanisms of relaxation for the system show significant differences and indicate the possibility of determining the relative contributions of various mechanisms for any system using this method, if the intensities in the spectra are known to a high degree of accuracy. The proton relaxation in 2-bromo-5-chlorothiophene is found to be largely due to external interactions. The interactions of the two protons with these external fields are highly correlated.

ACKNOWLEDGMENTS

[15] J. H. Noggle, Ph.D. thesis, Harvard University, Cambridge 38, Massachusetts, 1964 (unpublished).