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The Interpretation of Optically Detected ENDOR in Zero Field
and their relationship to [14]N Nuclear Quadrupole Interactions

in $^3(\pi\pi^*)$ States of Quinoline and Quinoxaline.

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Abstract

It is shown that the proper assignment of ^{14}N ENDOR transitions

in azaaromatic π,π^* triplet states must take into consideration the

contribution of the electron magnetic moment operator to the intensity

of a given transition. In quinoline and quinoxaline, the electron magnetic

moment operator is found to give the dominate contribution to ENDOR

intensities, and to a high degree of accuracy the nuclear moment operator

may be neglected. An erroneous ENDOR assignment of quinoxaline is corrected

on this basis, and the ENDOR of quinoline is assigned. In particular,

we find for these molecules that the dominant ENDOR transitions do not

yield the ^{14}N quadrupole parameters e^2qQ and η independently, but only

the value of $3\,e^2qQ(1 - \eta/3)/4$.

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I. Introduction

Optical detection of electron spin resonance in zero field of azaaromatic $\pi\pi^*$ triplets was first reported by Van der Waals and Schmidt on quinoxaline.[1] Later, Tinti, El-Sayed, Maki, and Harris[2] further refined the optical zero field detection technique by using a high resolution grating spectrometer to observe the magnetic resonance effect in individual vibronic bands. The fine structure of the zero field transitions were quantitatively explained independently for the quinoxaline triplet[3] and for the 2,3-dichlorquinoxaline triplet[4,5].

The first successful optical ENDOR experiment in zero field was published by Harris, Tinti, El-Sayed and Maki on 2,3-dichloroquinoxaline.[4,5] It was shown by these authors that the ENDOR transitions could be understood quantitatively in terms of a Hamiltonian incorporating the ^{14}N nuclear quadrupole coupling and hyperfine interactions in the excited state. Subsequently, Chan, Schmidt, and van der Waals[6] reported similar experiments on quinoxaline in its triplet state.

Although, the _experimental_ results of both groups are in substantial agreement for these two similar molecules, the interpretation of the ENDOR transitions put forth is quite different. The correct assignment of the observed ENDOR transitions depends upon the choice of the proper transition moment operator. Since the nuclear and electron spin states are mixed by the hyperfine interaction, the most general expression for the intensity of an ENDOR transition should include the interaction of both the electron and nuclear dipole moments with the applied rf magnetic field[7]. It is the purpose of this communication to demonstrate that the use of a transition moment operator which includes _only_ the nuclear dipole moment may lead to an incorrect assignment of the ENDOR transitions resulting in an erroneous

the
interpretation of \nuclear quadrupole interaction. In addition it will
be shown that major features of the ENDOR transitions and associated
quadrupole interactions can be understood quantitatively using only the
transition moment operator of the electron dipole moment.

II. Discussion

The fine structure in the optically detected zero field transition
of phosphorescent triplet states, as well as the frequencies and
intensities of the ENDOR transitions can be understood in terms of the
spin-Hamiltonian.

$$\mathcal{H} = \mathcal{H}_{ss} + \sum_{n}\left[(\mathcal{H}_Q)_n + (\mathcal{H}_{HF})_n\right] \tag{1}$$

where $\mathcal{H}_{ss}$ is the zero field splitting Hamiltonian,

$$\mathcal{H}_{ss} = -(X S_x^2 + Y S_y^2 + Z S_z^2), \tag{2}$$

and $(\mathcal{H}_Q)_n$ and $(\mathcal{H}_{HF})_n$ are the nuclear quadrupole interaction and the
electron-nuclear hyperfine interaction of the $\underline{n}$th nucleus. We will discuss
the ENDOR transitions reported in azanaphthalenes[4,5,6]

First, we will focus on the triplet $\pi\pi^*$ phosphorescent state of
quinoline (1 - azanaphthalene), with the following simplifications:
(a) ignore the proton hyperfine interactions in the Hamiltonian, (e.g.
equation 1), (b) assume that the principle axes of the three tensor
interactions, $\mathcal{H}_{ss}$, $\mathcal{H}_Q$, and $\mathcal{H}_{HF}$, coincide, and (c) assume the y and
z components of $\mathcal{H}_{HF}$ may be neglected. Approximation (c) is justified

in so far as single crystal EPR measurements of quinoline[8,9] and similar

molecules has shown that $A_{xx} > A_{yy}$, A_{zz} for the ^{14}N hyperfine interaction.[8,9]

Approximation (c) makes (b) irrelevant as far as $\mathcal{H}_{HF}$ is concerned since

the "approximate" hyperfine tensor has cylindrical symmetry and because

the X-axis is normal to the molecular plane and therefore a common

principle axis. It is also reasonable to assume that the principle axis of

$\mathcal{H}_Q$ will be close to the direction of the nitrogen lone pair orbital

(approximately along the molecular Y-axis). The principle Y-axis of $\mathcal{H}_{ss}$

is known from single crystal measurements[8] to deviate only a few

degrees from the lone pair direction in the molecule, so approximation

(b) is not too serious even for $\mathcal{H}_Q$. For quinoline (n = 1) these simplifications

allow us to write

$$\mathcal{H}_Q = \sum_k \epsilon_k I_k^2 \qquad (k = x, y, z) \qquad (3)$$

and

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

The simple product functions, $|uv> = \tau_u \chi_v$, form a set of eigenfunctions

which diagonalize $\mathcal{H}_{ss}$ and $\mathcal{H}_Q$. τ_u and χ_v are the electron and nuclear

spin functions while u and v correspond to x, y and z. With this choice

of basis functions only $\mathcal{H}_{HF}$ is off diagonal in the Hamiltonian matrix;

thus, it maybe dealt with easily by first order perturbation theory. This

approach and nomenclature has been used by Chan, Schmidt, and van der Waals[6],

and an energy level diagram appropriate to quinoline is given as figure 3

in their communication[6]. The zero field energies are arranged in the

order $E_z > E_y > E_x$. The principle result of using $\mathcal{H}_{HF}$ as a perturbing

Hamiltonian is a shift of the $|zz\rangle$ and $|zy\rangle$ levels to higher energies

and a shift of the $|yz\rangle$ and $|yy\rangle$ levels to lower energies by an amount

$\alpha = A_{xx}^2/(E_z - E_y)$. Satellites occurring in the zero field magnetic resonance

$\tau_x \rightarrow \tau_z$ multiplet gain intensity from mixing the states $|yy\rangle$ with $|zz\rangle$

and $|yx\rangle$ with $|zy\rangle$ via $\mathcal{H}_{HF}$. The satellites are thus transitions

$|(xy)'\rangle \rightarrow |(zz)'\rangle$, and $|(xz)'\rangle \rightarrow |(zy)'\rangle$, occuring at $E_z - E_x + \alpha \pm (\epsilon_z - \epsilon_y)$.

The primes indicate the perturbed basis functions resulting from the

perturbation $\mathcal{H}_{HF}$. These satellites are separated by $2\nu_-$ where

$\nu_- = 3 \, e^2qQ \, [1 - \eta/3]/4$ assuming η is positive. e^2qQ and η are the ^{14}N

nuclear quadrupole coupling constant and asymmetry parameter respectively

in the $\pi\pi^*$ triplet state. Thus, the positions of the satellites relative

to $E_z - E_x$ are determined only by α and the value of ν_- which is the

frequency of $\underline{one}$ of the pure ^{14}N nuclear quadrupole transitions.

Saturation of either satellite leads to a non-Boltzmann distribution

of nuclear levels in the τ_x and τ_z manifolds. Thus, $\underline{in\ principle}$, ENDOR

becomes possible in both manifolds. However, in order to properly assign

the ENDOR transitions which might be observed it is necessary to estimate

their relative intensities from the theoretical model which has been

developed. It is in this context that we[4,5] differ from the interpretation

put forth by Chan, Schmidt and van der Waals.[6]

   If we let $\mathcal{H}_{rf}(t)$ represent the time-dependent perturbation

Hamiltonian due to the rf field used to induce the ENDOR transitions,

then the intensity of an ENDOR transition is given by

$$\mathcal{I}_{vw}^u \sim |\langle (uv)' | \mathcal{H}_{rf}(t) | (uw)' \rangle|^2 \qquad (5)$$

with

$$\mathcal{H}_{rf}(t) = \vec{H}_2(t) \cdot (\gamma_n \vec{I} + \gamma_e \vec{S}) \qquad (6)$$

where u labels the electron spin manifold; v and w refer to nuclear states.
In equation 6, $\vec{H}_2(t)$ is the rf magnetic field, γ_n is the magnetogyric
ratio of ^{14}N, and γ_e is the electron magnetogyric ratio. In equation 5
the states $|(uv)'\rangle$ are eigenfunctions of the spin-Hamiltonian, <u>including</u>
<u>the perturbation</u> $\mathcal{H}_{HF}$. Consequently, they are not pure electron spin
states which diagonalize $\mathcal{H}_{ss}$. If they were, the second term in equation 6
would not contribute to the intensity of the ENDOR transitions, and that
term could be ommitted, as in fact it was by Chan, Schmidt and van der Waals[6].
For quinoline, in the approximation we are using, the lowest spin manifold,
τ_x, is not admixed with the others; whereas the τ_y and τ_z manifolds are
mixed together by $\mathcal{H}_{HF}$. Therefore, the intensity of an ENDOR transition
in the τ_z manifold is

$$\mathcal{I}^z_{yz} \sim 4\beta^2 \gamma_e^2 + 4\beta \gamma_e \gamma_n + \gamma_n^2 \tag{7}$$

where $\beta = A_{xx}/(E_z - E_y) \simeq 2 \times 10^{-2}$. On the other hand, in the τ_x manifold

$$\mathcal{I}^x_{xy} \sim \gamma_n^2 \tag{8}$$

It may immediately be seen by inserting numbers for the constants
in equations 7 and 8 that $\mathcal{I}^z_{yz}/\mathcal{I}^x_{xy} \simeq 4\beta^2 \gamma_e^2/\gamma_n^2 \simeq 2 \times 10^5$.

The ratio depends on the polarization of $\mathcal{H}_2(t)$ since $|xx\rangle \rightarrow |xy\rangle$
is Z-polarized while $|(zy)'\rangle \rightarrow |(zz)'\rangle$ is X-polarized. For quinoline
dissolved in durene, however, the effect of polarization is not important
because of the relative orientation of the two sites in durene[10].

The contribution of the electron magnetic moment to the intensity of an ENDOR transition is seen to be many orders of magnitude greater than the contribution of the nuclear magnetic moment operator. It can be easily shown that the $\tau_z \chi_y \to \tau_z \chi_z$ transition is the only ENDOR transition of any appreciable intensity having an energy level in common with either of the weak satellites of the $\tau_x \to \tau_z$ microwave transition. The ENDOR transition in fact connects levels common to both satellites. All other ENDOR transitions in both the τ_z and τ_x manifolds would be many orders of magnitude weaker. In practice, therefore, no ENDOR transition in the τ_x manifold is expected to have appreciable intensity. The contribution of the nuclear magnetic moment of ^{14}N to ENDOR intensities is insignificant. Even the small mixing of electron spin states due to previously ignored matrix elements of $\mathcal{H}_{HF}$ (i.e. A_{yy}, A_{zz}) would be more effective by a factor of $\sim 10^3$ in inducing ENDOR transitions in the τ_x manifold than a simple consideration of the nuclear moment. It is thus no oversimplification to state that in azaaromatic $\pi\pi^*$ triplets such as quinoline and quinoxaline, the intensities of ENDOR transitions of ^{14}N can be understood by considering only the electron magnetic moment operator[4,5]. If weak ENDOR transitions are observed, they may be assigned correctly by considering a more exact version of $\mathcal{H}_{HF}$ or a refinement of some of the other approximations in the model which may lead to intensity enhancement of the ENDOR.

Chan, Schmidt, and van der Waals [6] used only the nuclear magnetic moment operator, i.e. $\mathcal{H}_{rf}(t) = \mathcal{H}_2(t) \cdot \gamma_n \vec{I}$, and predicted four ENDOR transitions of comparable intensity common to each satellite, two of these transitions being degenerate. As has been demonstrated, only one ENDOR transition should have any appreciable intensity. This is in fact observed experimentally. Specifically one ENDOR transition has been detected at ~ 3.0 MHz [6]. Our model allows us to assign this ENDOR transition energy

to ν_- (i.e. $\sim 3.0 = 3\,e^2qQ(1-\eta/3)/4$) as $|zy> \rightarrow |zz>$ if the

$\tau_x\,\chi_z \rightarrow \tau_z\,\chi_y$ or $\tau_x\,\chi_y \rightarrow \tau_z\,\chi_z$ microwave satellite is being saturated.

Furthermore, Mr. Fayer and Mr. Yuen[11] in our laboratories have observed an ENDOR transition

~ 3.1 MHz while saturating the $\tau_y\,\chi_z \rightarrow \tau_z\,\tau_y$ satellite[‡][†] as predicted by

our model. It can be shown that this ENDOR transition is the only allowed

transition via the electron magnetic moment operator in the τ_y manifold

and it is degenerate with the $|zy> \rightarrow |zz>$ transition in the τ_z

manifold and again equal to ν_-. Consequently, e^2qQ and η cannot be obtained

independently unless at least one other $\mathcal{H}_{HF}$ element, A_{zz} and/or A_{yy},

contributes intensity to additional ENDOR transitions related to

$\nu_+ = 3e^2qQ(1+\eta/3)/4$ and/or $\nu_o = e^2qQ\cdot\eta/2$ respectively[4,5].

We now reexamine briefly the interpretation of the ENDOR transitions

associated with the $\tau_x \rightarrow \tau_z$ microwave transition of quinoxaline (1,4-

diazanaphthanlene). The approximations remain the same as for quinoline

but now the nuclear Hamiltonian contain interactions of two equivalent

^{14}N nuclei. Thus

$$\sum_n [(\mathcal{H}_Q)_n + (\mathcal{H}_{HF})_n] = \sum_{k=x,y,z} \epsilon_k\,(I_{1k}^2 + I_{2k}^2) + A_{xx}\,S_x\,(I_{1x} + I_{2x}) \qquad (9)$$

The set of twenty seven functions $\tau_u\,\chi_{1v}\,\chi_{2v}$, and $\tau_u(\chi_{1v}\,\chi_{2w} \pm \chi_{1w}\,\chi_{2v})$ defined a:

$\tau_u(\chi_{1v}\,\chi_{2w})^\pm$ (u, v, w correspond to x, y, and z) diagonalize the first

‡ Data from 10^{-3} M quinoline in Durene at 1.6°K in the 0-0 phosphorescent

emmission.

† Two sites are resolved in the $\tau_y \rightarrow \tau_z$ microwave transitions with $E_z - E_y$

differing by ~ 5.9 MHz. We observed the ENDOR transition on the low

energy site ($E_z - E_y = 998.9$ MHz) where the second order hyperfine

splitting between $|yx> \rightarrow |zx>$ and the degenerate pair $|yz> \rightarrow |zz>$:

$|yy> \rightarrow |zy>$ is resolved. The value obtained for A_{xx} from the second

order splitting is ~ 21.2 MHz.

two terms of the Hamiltonian (equation 1). These may be used as basis

functions with $\mathcal{H}_{HF}$ as a perturbation Hamiltonian. As in the case of

quinoline the states of the τ_x manifold are not mixed with states of the τ_y

and τ_z manifolds, but the states of the latter manifolds are mixed together by

$\mathcal{H}_{HF}$. Because two 3 x 3 matrices each involving two basis states of the same

electron spin manifold occur when the 27 x 27 matrix is reduced the

complete solution cannot be obtained by first order perturbation theory.

The problem was solved using a computer program for diagonalizing the

secular determinant, generating the perturbed wavefunctions and computing

the transition moments of all the magnetic dipole transitions using the

electron magnetic moment operator. An energy level diagram for the

nine nuclear states comprising the τ_z manifold of quinoxaline is drawn

to scale in figure 1 and Table I gives the states which are mixed with

each dominate state of the τ_z manifold upon diagonalizing the secular

determinant. The spin Hamiltonian parameters used for the numerical

calculation were $\nu_- = 3\ e^2qQ\ (1 - \eta/3)/4 = 2.938$ MHz, while all other

parameters were those obtained by Chan, Schmidt and van der Waals[6].

We will justify our choice of ν_- below. These parameters indeed predict

a strong central multiplet for the $\tau_x \to \tau_z$ microwave transition which is

flanked by two pairs of satellites in agreement with the observed spectrum

and interpretation put forth by Schmidt and van der Waals[1,3]. For

consistency with the nomenclature adopted by these authors we number these

lines 1-5 in order of increasing frequency. The nuclear states of the

τ_z manifold associated with transitions within each of these satellites

are numbered in figure 1.

Chan, Schmidt, and van der Waals[6] observed three strong ENDOR

transitions with the microwave frequency fixed on lines 2 or 4. The

frequencies of these transitions were the same for each satellite. We

label these ENDOR transitions ν_1', ν_2', and ν_3' in order of increasing

frequency. From the arguments given above in connection with quinoline,

these transitions gain their intensity from the electron magnetic

moment operator. Since there is no mixing of the τ_x manifold in our

approximation we assign these three ENDOR transitions to the τ_z manifold .

Three strong ENDOR transitions are found within the τ_z manifold from

our calculation and are indicated in figure 1 as ν_1, ν_2 and ν_3. It

may be verified that these transitions gain intensity from the electron

magnetic moment operator by examining the mixture of states given in

Table I. Furthermore, each transition connects a state associated with

line 2 with one associated with line 4, and hence all three ENDOR

transitions should occur on each line. To a high degree of approximation

the doubly degenerate transition labeled ν_2 in figure 1 occurs at the

pure ^{14}N nuclear quadrupole frequency ν_-. If we identify ν_2 with the

observed frequency ν_2', we obtain excellent agreement of all transition

frequencies as shown in Table II. We have indeed assigned all of the

intense ENDOR lines using only the ν_- pure nuclear quadrupole transition

frequency. In fact we have found that in the approximation A_{yy}, $A_{zz} = 0$,

there is no feature in the microwave multiplet or in the ENDOR spectrum

which changes with $\mathcal{H}_Q$ as long as ν_- remains invarient. We have recomputed

the microwave spectrum and the ENDOR transitions (ν_1, ν_2 and ν_3)

varing η between 0 and 1.0 while keeping ν_- constant. All transition frequencies and intensities in the calculation remain unchanged. The invariant of the ENDOR transitions is not surprising if one notes in figure 1 that these transitions each involve the flip of a single nucleus between the χ_y and χ_z nuclear states. The change in quadrupole energy is thus $h\nu_- = \epsilon_z - \epsilon_y$ in each case. The fact that three frequencies occur is entirely a result of the electron-nuclear hyperfine perturbation.

By failing to recognize the importance of the electron magnetic moment operator in determining the intensity of an ENDOR transition Chan, Schmidt and van der Waals were led to a misassignment of an ENDOR transition. This is not surprising since the use of only the nuclear magnetic moment operator in the transition moment predicts a host of ENDOR transitions of comparable but extremely weak intensity. They assigned the ν_3' transition to $\nu_+ = 3\ e^2qQ\ (1 + \eta/3)/4$, and thus came to the erroneous conclusion that e^2qQ and η could be obtained independently from the three intense ENDOR frequencies. These authors also report the observation of other extremely weak ENDOR signals. These signals are probably attributable to nuclear transitions which gain intensity from the small hyperfine components A_{zz} and A_{yy} via the electron magnetic moment operator. A generalization which can be made for azaaromatic $\pi\pi^*$ triplet states is that a hyperfine tensor element A_{ii} gives rise to intensity for ^{14}N nucleus transitions in the plane normal to i. Correct assignment of the weak ENDOR transitions would allow e^2qQ and η to be obtained independently since they would be related to $\nu_+ = 3\ e^2qQ(1 + \eta/3)/4$ and $\nu_o = e^2qQ\ \eta/2$.

Finally, our assignment predicts that only one intense ENDOR transition should be observed on each of the outer satellities. The transition ν_3 should occur on line 1 while the transition ν_1 should occur on line 5.

Table I

State of Figure 1	Principle States	Admixed States
$\lvert zxx\rangle'$	$\tau_z\, \chi_{1x}\, \chi_{2x}$	
$\lvert zxz\rangle'$, $\lvert zzx\rangle'$	$(\tau_z\, \chi_{1x}\, \chi_{2z})^{\pm}$	$(\tau_y\, \chi_{1x}\, \chi_{2y})^{\pm}$
$\lvert zzz\rangle'$	$\tau_z\, \chi_{1z}\, \chi_{2z}$	$(\tau_y\, \chi_{1y}\, \chi_{2z})^{+}$, $\tau_z\, \chi_{1y}\, \chi_{2y}$
$\lvert zyz\rangle'$	$(\tau_z\, \chi_{1y}\, \chi_{2z})^{+}$	$\tau_y\, \chi_{1y}\, \chi_{2y}$, $\tau_y\, \chi_{1z}\, \chi_{2z}$
$\lvert zxy\rangle'$, $\lvert zyx\rangle'$	$(\tau_z\, \chi_{1x}\, \chi_{2y})^{\pm}$	$(\tau_y\, \chi_{1x}\, \chi_{2z})^{\pm}$
$\lvert zzy\rangle'$	$(\tau_z\, \chi_{1y}\, \chi_{2z})^{-}$	
$\lvert zyy\rangle'$	$\tau_z\, \chi_{1y}\, \chi_{2y}$	$(\tau_y\, \chi_{1y}\, \chi_{2z})^{+}$, $\tau_z\, \chi_{1z}\, \chi_{2z}$

Table II

Calculated and observed ENDOR frequencies and Intensities

for Quinoxaline

Calculated		Observed[†]	
Frequency (MHz)	Intensity[*‡]	Frequency (MHz)	Intensity[*]
ν_1 2.239	3.4, 3.4	ν_1' 2.2393	3.8, 3.5
ν_2 2.936	2.7, 2.7	ν_2' 2.9384	10.0, 10.0
ν_3 3.850	2.0, 2.0	ν_3' 3.7900	2.7, 8.1

[*] First entry line 2, second entry line 4.

[†] Reference 6.

[‡] Calculated where 10^3 is the intensity of a fully allowed electron spin transition.

References

(1) J. Schmidt and J. H. van der Waals, Chem. Phys. Letters $\underline{2}$ (1968) 640.

(2) D. S. Tinti, M. A. El-Sayed, A. H. Maki and C. B. Harris, Chem. Phys. Letters $\underline{3}$ (1969) 343.

(3) J. Schmidt and J. H. van der Waals, Chem. Phys. Letters $\underline{3}$ (1969) 546.

(4) C. B. Harris, D. S. Tinti, M. A. El-Sayed and A. H. Maki UCRL-19053, July, 1969.

(5) C. B. Harris, D. S. Tinti, M. A. El-Sayed and A. H. Maki, Chem. Phys. Letters $\underline{4}$ (1969) 409.

(6) I. Y. Chan, J. Schmidt and J. H. van der Waals, Chem. Phys. Letters $\underline{4}$, (1969) 269.

(7) A. Abragram, Nuclear Magnetism (The Clarendon Press, Oxford, 1961) p. 193.

(8) J. S. Vincent and A. H. Maki, J. Chem. Phys., $\underline{42}$, 865 (1965); Y. Gondo and A. H. Maki, J. Chem. Phys. $\underline{50}$, 3270 (1969).

(9) J. S. Vincent and A. H. Maki, J. Chem. Phys. $\underline{39}$, 3088 (1963).

(10) J. M. Robertson, Proc. Roy. Sco. (London), $\underline{A141}$, 594 (1933); $\underline{A142}$, 659 (1934).

(11) M. D. Fayer, C. B. Harris and D. Yuen, unpublished results.

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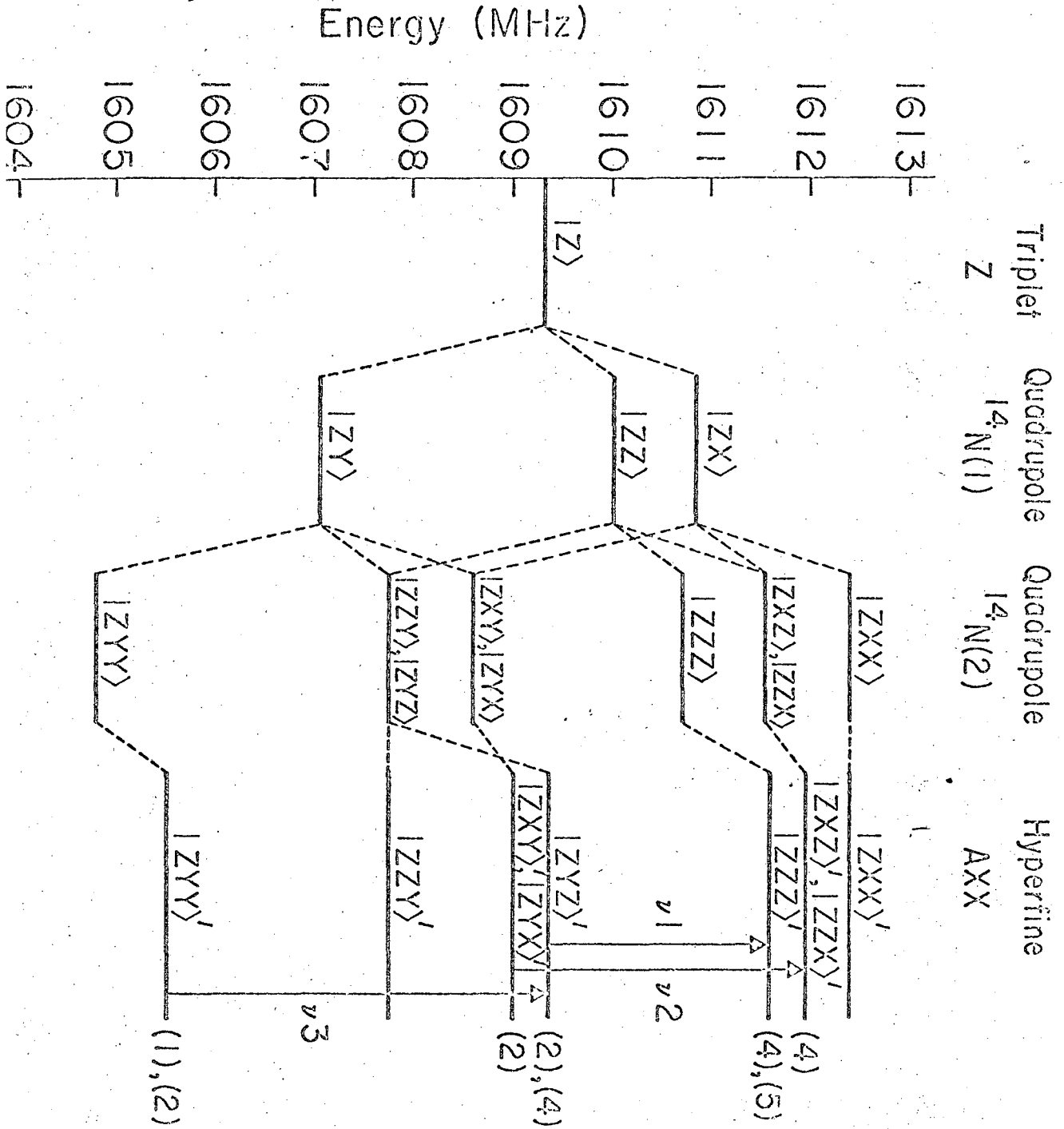
Figure 1. Energy levels of the τ_z electron spin manifold of quinoxaline. See Table I for the identification of the primed states.