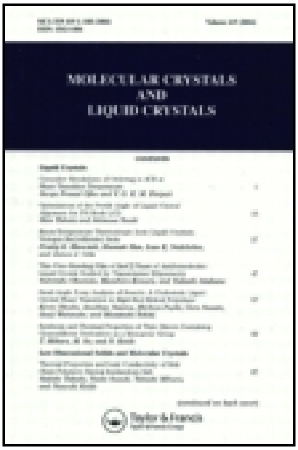

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Microwave-Optical Double Resonance Investigation of the ESR of Metastable Triplet States

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Microwave-Optical Double Resonance Investigation of the ESR of Metastable Triplet States

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Abstract—X band microwave-optical double resonance studies of the metastable triplet states of naphthalene–d_8 and quinoxalene are presented and the amplitudes and linebreadths of the signals examined. It is noted that the amplitudes of the lines are consistently an order of magnitude or more smaller than expected on the basis of a simple theory; the discrepancy is shown to arise in part from the long triplet spin-lattice relaxation times which prevailed under the conditions of the measurements. *K* band microwave optical double resonance results for quinoxalene support this analysis and indicate that the double resonance method can be extended to permit study of the ESR of triplet systems of photochemical interest which are too short-lived to be observable by conventional ESR methods. A successful application of the double resonance method to triplet cyclopentanone is reported.

Introduction

Somewhat over a year ago, we reported[1] the first results of a simultaneous investigation of the phosphorescence and electron spin resonance of the triplet state of naphthalene-d_8 molecules oriented in a host lattice of biphenyl. In that experiment, we observed that microwave saturation of any of the three ESR transitions between the triplet sublevels of the naphthalene–d_8 was accompanied by a change in the intensity of its phosphorescence. It was thus proven experimentally that, as anticipated theoretically,[2,3,4] the phosphorescence matrix elements of the triplet manifold were different for different substates of the manifold. Inasmuch, moreover, as the influence of the microwave irradiation of the sample upon its phosphorescence was never discerned unless an ESR transition were simultaneously observed, the experiment also showed that the occurrence of the resonance condition could be deduced with certainty from observed alterations of the phosphorescence. One expects, therefore, that complete information on the ESR spectrum of a phosphorescent state can be obtained from a study of the phosphorescence alone, it being unnecessary to observe the ESR by the usual methods.

It is with this second aspect of these results that we are presently concerned. Our concern is a practical one; we need only take cognizance of the many types of luminescent triplet species which are too short-lived to be observable by conventional ESR methods and yet whose spin distributions are of great interest to the theoretical chemist or to the photochemist. With this problem area in mind, we shall examine the suitability of the optical detection methods for examination of the ESR of short-lived luminescent states. We shall find that in principle the method will be generally useful. We shall also point out some practical factors which may obstruct the application of the method and shall attempt to devise means of circumnavigating them. We shall begin with a review of the optical detection scheme.

Principles of the Method

The origin of the optical effect in ESR is illustrated in Figs. 1 and 2. The first of these is a state and energy diagram of the naphthalene triplet spin system in a magnetic field. The scale on the vertical axis indicates the smallness of the magnetic contribution to the energies of the states. The electronic ground state of the molecule has an energy some 21000 cm^{-1} lower than those shown and would have to be placed a kilometer or so below these if it were to be included in the diagram. Ordinarily, the emission lines are many cm^{-1} broad, and the individual transitions from the triplet sublevels to the ground state cannot be resolved.‡

Figure 1 has been drawn for the case in which the external magnetic field H_0 has been applied in the direction of the y-axis (short axis)

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‡ The individual transitions may sometimes be resolved in the case of very pure crystals. See reference 5.

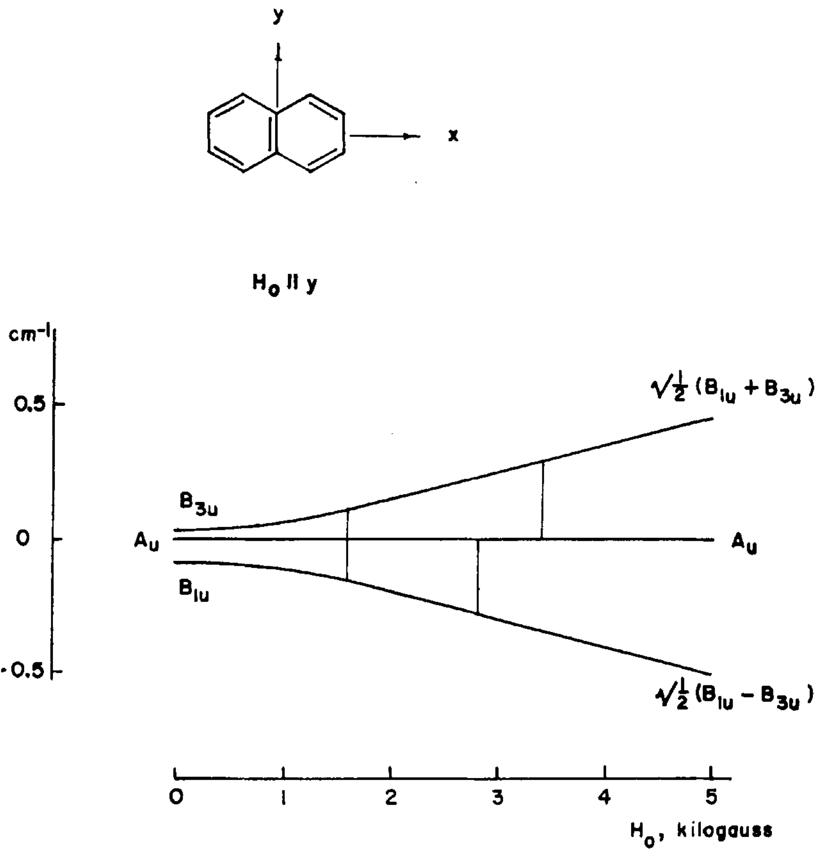

Figure 1. State and energy diagram for the naphthalene molecule in an external magnetic field directed along the y-axis. The positions of the three ESR transitions at 9020 MHz are indicated.

of the naphthalene molecule. (A similar diagram applies, with some relabelling of axes and states, to the triplet state of quinoxalene.) Under these circumstances the energy of the state labelled A_u in the diagram is unaffected by the magnetic field, and there is no mixing of this state with others. The states labelled B_{1u} and B_{3u} mix strongly when the field is applied, and both the paramagnetic and optical properties of the triplet manifold are affected as a result. The ESR transition between the highest and lowest triplet sublevels, which is allowed in the absence of a magnetic field, becomes forbidden (corresponding to a $\Delta m = \pm 2$ transition) in the high-field region. Optically, the scrambling of the B_{1u} and B_{3u} states is manifested by a change in the angular distribution of the phosphorescence and by changes in its polarization and total intensity.[3,4] At very low temperatures, in fact, where kT is small compared to the spacing between the lowest level in the diagram and the next higher level, the phosphorescence will occur only from the lowest of the states. In the limit of zero external magnetic field, the phosphorescence would be characteristic of an oscillating dipole moment oriented along the x-direction (long axis) of the molecule, the emission occurring mainly in the directions lying near the yz plane and with its electric vector polarized essentially parallel to the x-axis.‡ If a strong magnetic field is applied, without changing kT, the emission will contain, in addition, a component characteristic of a dipole moment oscillating in the molecular x-direction (normal to the molecular plane), and z-polarized light propagating in the x-direction will then be observed. If the z-oriented dipole moment is larger than the x-oriented dipole moment, the total emission intensity will be observed to be larger when the magnetic field is present than when it is not.

While polarization effects may be observed in the optical detection of ESR, the optical scheme depends, in its crudest form, only upon alterations in the total intensity of the phosphorescence. In analyzing the effect quantitatively, we refer to Fig. 2. We shall abandon our supposition that in thermal equilibrium only the lowest of the three triplet levels if populated; it suffices to require only that at thermal equilibrium the populations be significantly different. This stipulation is easily met with temperatures in the liquid helium range and fields of several kilogauss. For fields of this magnitude, the highest and lowest states of naphthalene–d_8 are both mixtures of roughly equal amounts of B_{1u} and B_{3u} character, and the emission intensities of the highest and lowest states will be roughly equal.§ In the interest of simplicity we shall treat them as being precisely equal. Since electric dipole radiation from the A_u state is symmetry-forbidden, the total phosphorescence intensity will be proportional

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‡ We here assume that the phosphorescence is caused by an electric dipole radiative process. This may not always be the case, however. See reference 6.

§ A more precise treatment would take into account the interference between the contributions of the B_{1u} and the B_{3u} states to the radiative matrix elements.

to the sum of the populations of the lowest and highest energy triplet sublevels.

Two types of population distributions may be imagined. In the first type, the triplet spin system is in thermal equilibrium with the crystal lattice, and the populations of the triplet sublevels are described by a Boltzmann distribution appropriate to the temperature of the lattice. The numbers in the center portion of Fig. 2 pertain to the values $\mu_0 H = 0.3\ \text{cm}^{-1}$, $T = 1.8\,^\circ\text{K}$, which were employed in most of the work reported here. The total radiative intensity, in appropriate units, is 1.61. The second case arises when one of the ESR transitions of Fig. 1 is strongly excited by a microwave field of the appropriate frequency. Under microwave saturation of this transition, the populations of the levels which it connects become very nearly equal. If we imagine that the middle transition of Fig. 1 is saturated momentarily, and then the microwave field turned off, we would have, at the next instant, a situation depicted

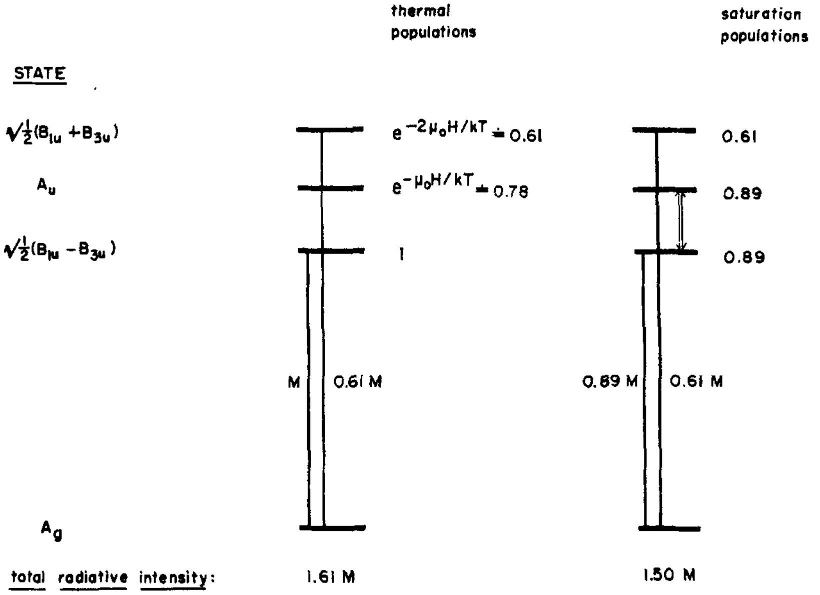

Figure 2. Radiation diagram illustrating the origin of the MODOR effect. *M* is the radiative transition probability of the lowest or highest triplet sublevels.

by the right side of Fig. 2. The populations of the two lowest levels are equalized by the microwave pulse, that of the highest level remaining unchanged from before because spin-lattice relaxation mechanisms have not yet had time to redistribute the populations. The total radiative intensity is now 1.50, some 6% lower than in the case of the Boltzmann distribution. (If the high-field transition of Fig. 1 had been saturated instead, the phosphorescence intensity would have *in*creased by about the same amount.) If one were to impose, then, a pulsed or " chopped " microwave field upon the spin system, alternately saturating one of the high-field ESR transitions and allowing it to relax, one would expect a synchronous modulation of about 6% (peak to peak) to occur in the intensity of the phosphorescence. Conversely, one might use the occurrence of such modulation to locate the magnetic field positions of the ESR transitions of the system.

Because the phosphorescence of any level may be viewed as a radiative transition induced by resonance between this transition and an appropriate Fourier component of the zero-point electromagnetic field, the effect of ESR saturation on the intensity of the phosphorescence is analogous to the effect of NMR saturation upon the ESR signal in an ENDOR experiment. The phenomenon we have been discussing might just as well be dubbed " Microwave-Optical Double Resonance ", or " MODOR ", for short. The power of the technique derives basically from the same " quantum magnification " which is exploited in ENDOR. The quanta one detects in MODOR carry an energy roughly 10^4 larger than those of the microwave field used to induce resonance, and it should accordingly take 10^4 fewer optical quanta/sec to overcome noise in a detector than microwave quanta. One therefore expects the optical detection method to be considerably more sensitive, in the case of short-lived phosphorescent paramagnetic systems, than conventional microwave methods of detecting ESR.

Experimental Results

A block diagram of the apparatus employed in our early MODOR work appears in Fig. 3. The system consists of three main parts: a high intensity ultraviolet source for producing metastable triplet molecules, a largely conventional ESR setup for exciting transitions

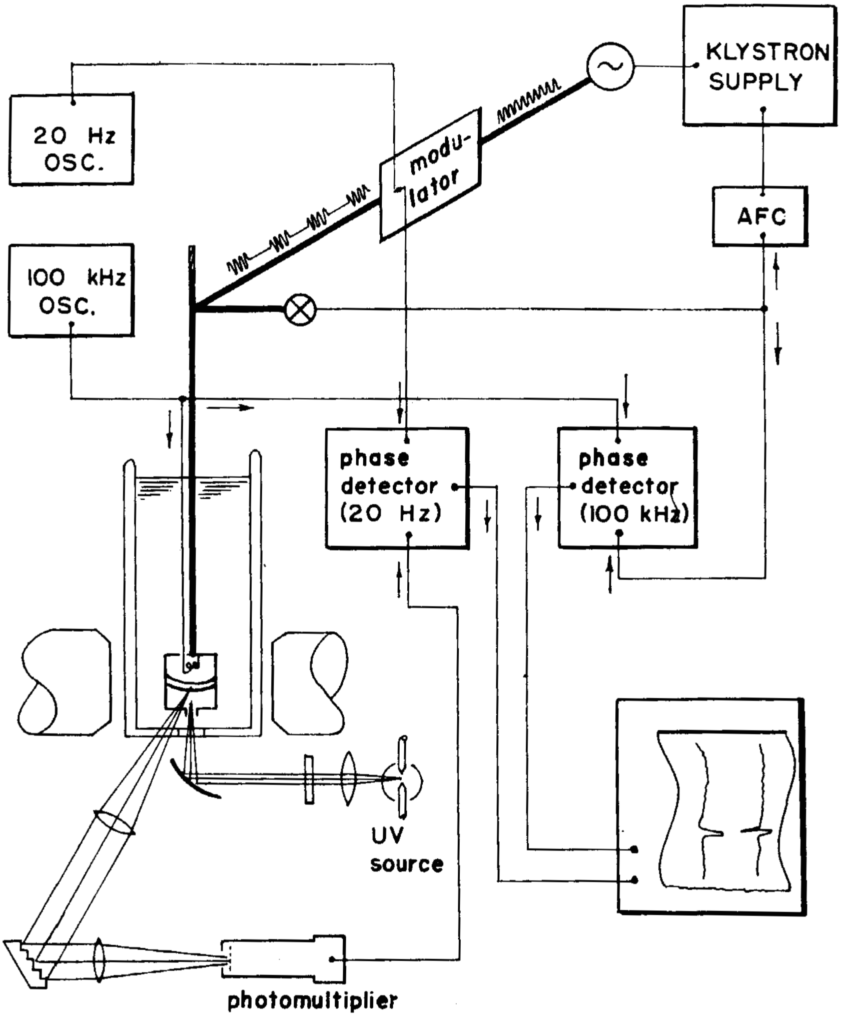

Figure 3. Block diagram of the X-band MODOR apparatus.

between the triplet sublevels, and a spectrograph—low-resolution monochromator plus photomultiplier—for monitoring the phosphorescence of the sample. The microwaves incident upon the sample cavity are modulated on and off by a ferritic modulator, which is driven by a 20 Hz square wave. The magnetic field at the sample is sinusoidally modulated at 100 kHz by means of a modulation coil placed inside the cylindrical cavity, which resonates in the TE_{011} mode at 9020 MHz and which has a loaded Q, at liquid helium temperatures, of approximately 15 000. The filtered ultraviolet[1] excitation light passes through a hole in the bottom of the cavity and comes to a focus on the sample, which is placed at the center. A portion of the sample's phosphorescence passes through an azimuthal slot in the cylindrical sidewall of the cavity and corresponding window on the liquid helium dewar and into the monochromator. The aperture of this system is $f/3.5$. The slot subtends an angle of 180° at the axis of the cavity, and the angular dependence of the ESR and MODOR can be studied by rotating the waveguide assembly about a vertical axis.

Our early MODOR work was concerned with two molecules, naphthalene-d_8 and quinoxalene, with very similar metastable triplet states[7,8] and phosphorescence characteristics,[9,10] but with triplet state lifetimes differing by two orders of magnitude, being 18 sec and 0.2 sec, respectively. While we have used both biphenyl and durene as host lattices, we will be mainly concerned here with the durene crystal, whose cleavage plane is within 7° of perpendicularity to the y-axes of all the naphthalene or quinoxalene guest molecules.[7,8] When H_0 is directed along the normal to this plane, the conditions assumed in Figs. 1 and 2 are, in large measure, fulfilled for all the molecules of the sample.

Figure 4 shows a pair of ESR and MODOR signal tracings obtained with H_0 oriented perpendicular to the cleavage plane of a mixed crystal of naphthalene-d^8 and durene. The ESR lines have shapes indicative of severe saturation, as expected, since the signal information is carried during the " microwaves on " portion of the cycle, where saturation is intended. Another prominent feature of these signals—linebreadths of as much as 40 gauss, was not to be expected. Nor was it foreseen that the linebreadths of the MODOR signals should be twice as large as those of the ordinary ESR signals, although this is observed to be the case for the high field, $\Delta m \pm 1$ transitions. Other workers[11,12] have recently observed similar effects. At present their origin is not understood in detail.

In Figs. 5 and 6 we have a closer look at the low field and high field lines, obtained under somewhat different microwave power levels and with a different crystal. In Figs. 7 and 8 we present

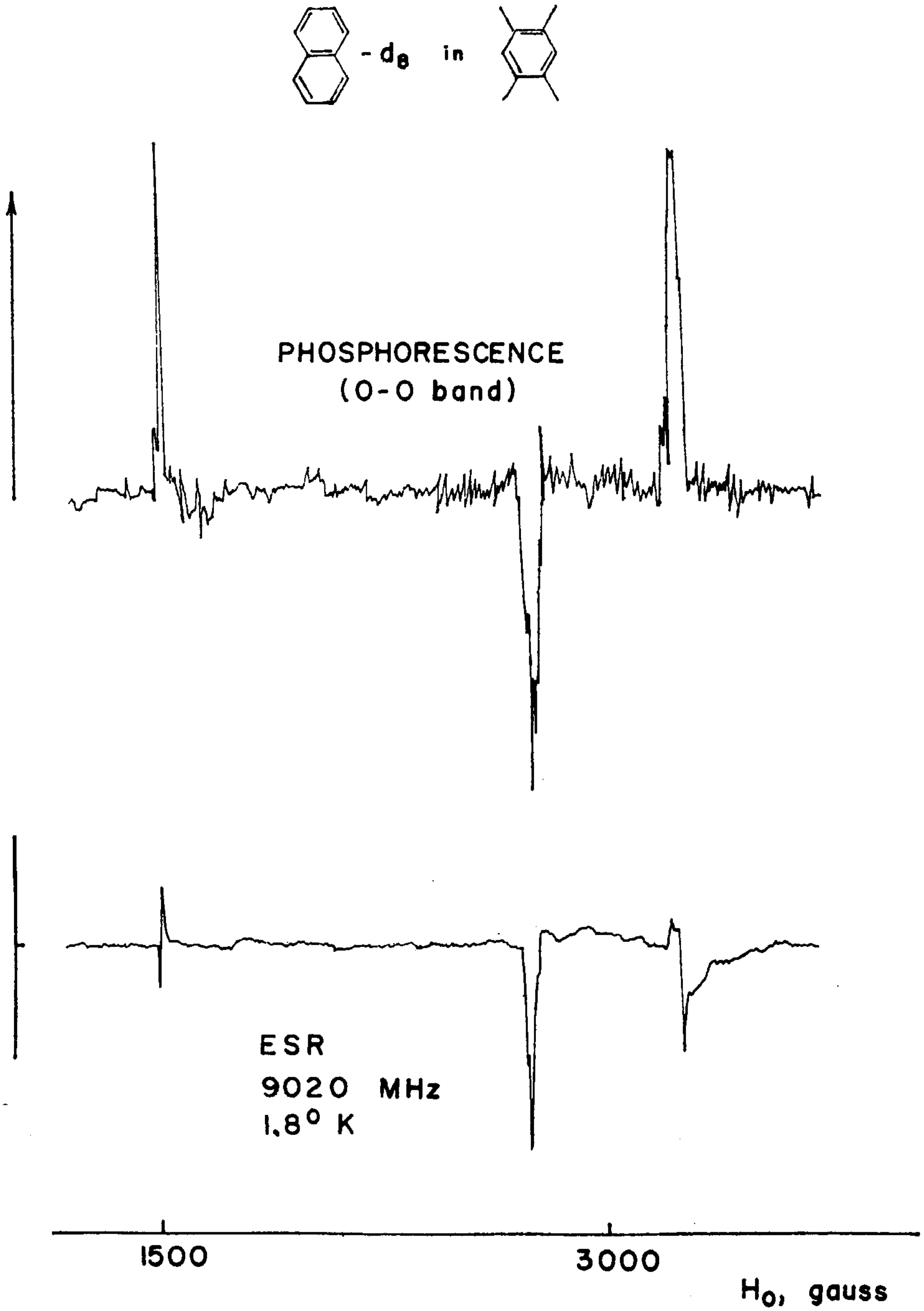

Figure 4. ESR and MODOR signals for naphthalene–d_8 in durene.

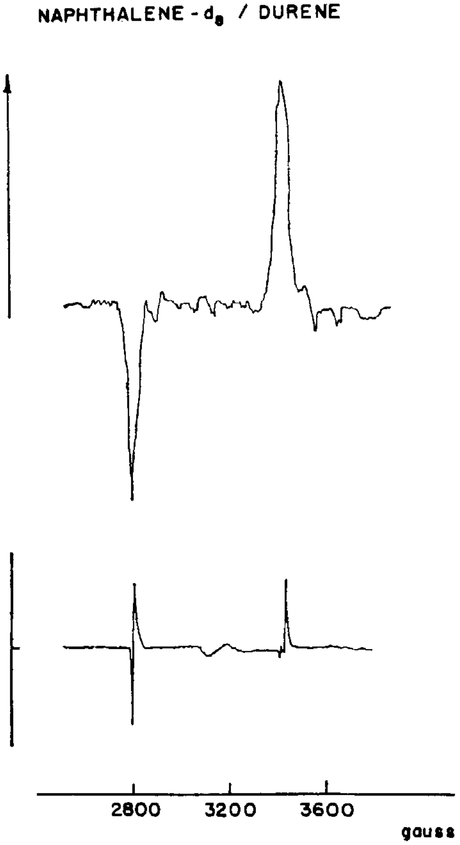

Figure 5. The $\Delta m = \pm 1$ transition of naphthalene–d_8 in durene. The amplitudes of the MODOR lines are approximately 0.3% of the total phosphorescence.

similar results, this time for quinoxalene in durene, while in Fig. 9 we present for comparison the $\Delta m = \pm 2$ transition in the MODOR of quinoxalene randomly oriented in EPA. We see repeated, in these figures, the tendency of the high field, $\Delta m = \pm 1$ transitions to be significantly broader than the low field, $\Delta m = \pm 2$ transitions and the tendency of the MODOR signals to have the same width as the ESR signals in the case of the $\Delta m = \pm 2$ transition but larger widths in the case of the $\Delta m = \pm 1$ transitions. This pattern is not unique to the naphthalene/durene or quinoxalene/durene system, but prevails also when the host lattice is biphenyl.

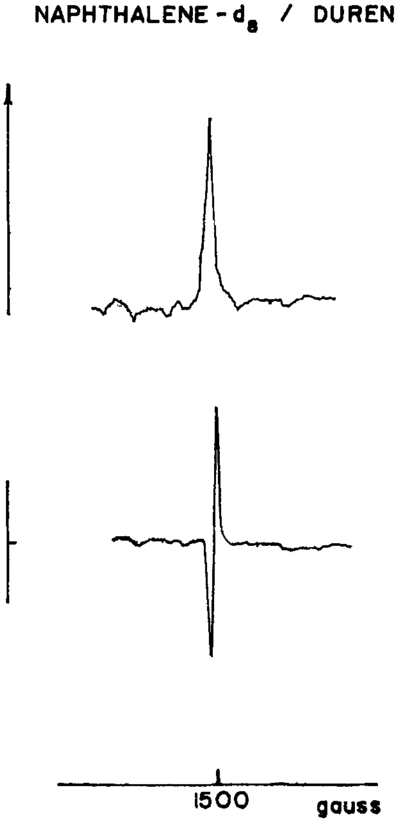

Figure 6. The $\Delta m = \pm 2$ transition of naphthalene–d_8 in durene. The modulation depth of the MODOR line is approximately 0.3%.

Two further features characterize these results. Firstly, while the conventional ESR signals are vastly weaker (or not visible at all) in the case of the quinoxalene molecule, the MODOR signals of quinoxalene are actually comparable, in photons/sec, to those for naphthalene–d_8 studied under parallel conditions. Secondly, the MODOR signals are *without exception* an order of magnitude weaker than would be expected on the basis of the foregoing analysis. We shall analyze these features in turn.

In the first instance, we note that—apart from considerations of linewidth and of relaxation time—the strengths of the ESR signals are proportional to the concentrations of molecules producing them.

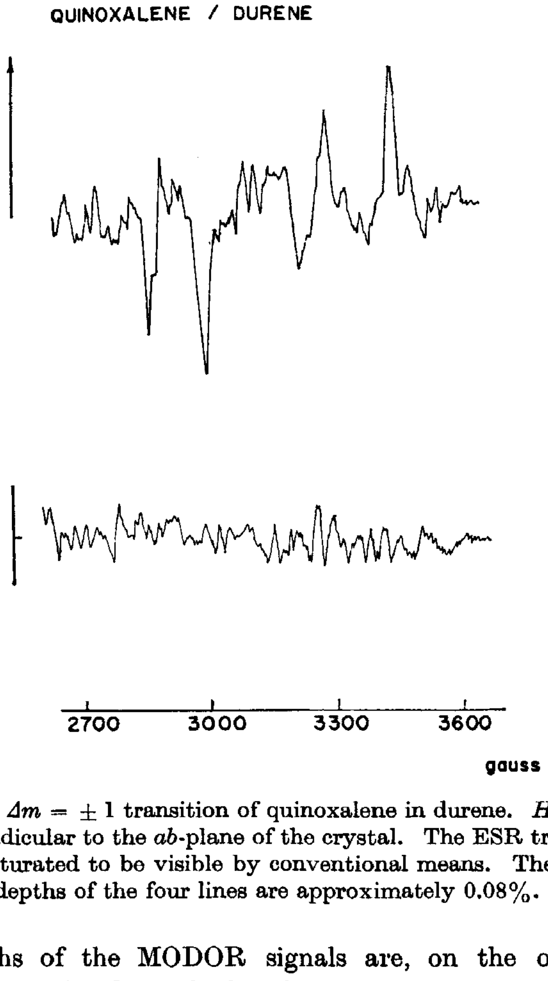

Figure 7. The $\Delta m = \pm 1$ transition of quinoxalene in durene. H_0 is approximately perpendicular to the *ab*-plane of the crystal. The ESR transitions are too heavily saturated to be visible by conventional means. The modulation depths of the four lines are approximately 0.08%.

The strengths of the MODOR signals are, on the other hand, proportional to the flux of phosphorescence quanta (and to the modulation depth which occurs during ESR saturation). While the comparatively short radiative lifetime of the quinoxalene has the effect of limiting the concentration of quinoxalene triplet states obtainable in the sample and thereby reducing the triplet state ESR signal, it does ensure that a given steady concentration of quinoxalene triplets will produce more phosphorescence quanta than an equal concentration of naphthalene-d_8 triplets. In the idealized case in which non-radiative de-excitation of triplets does not occur, and in which the efficiency of crossing from the singlet excited by the ultraviolet beam

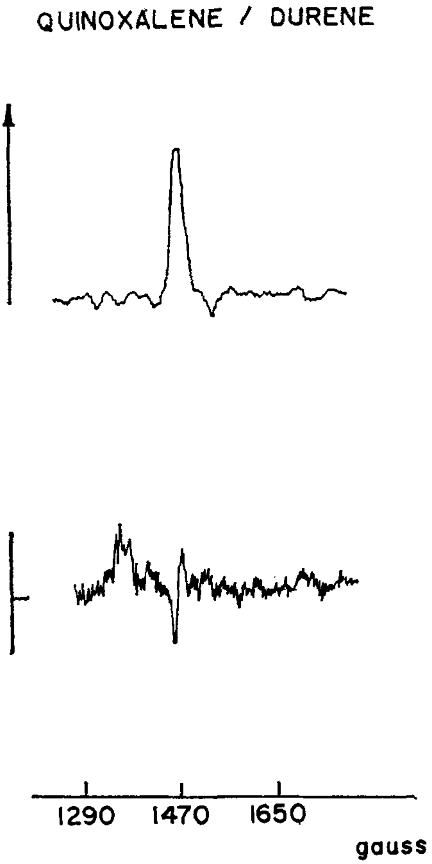

Figure 8. The $\Delta m = \pm 2$ transition of quinoxalene in durene. The modulation depth is approximately 0.2%.

to the metastable triplet state approaches unity, the intensity of the phosphorescence is independent of the triplet state lifetime and depends only upon the rate at which quanta are absorbed from the UV beam. These conditions are approximately fulfilled for the triplet species in question here, and in retrospect it is clear why the MODOR signals of quinoxalene and naphthalene are similar.

The implication of this result for the study of short-lived photochemically active triplets is clear; the short triplet lifetime of these species is no obstacle for the MODOR technique, so long as the lifetime is determined radiatively rather than limited by deactivation through tunnelling or quenching via chemical reaction.

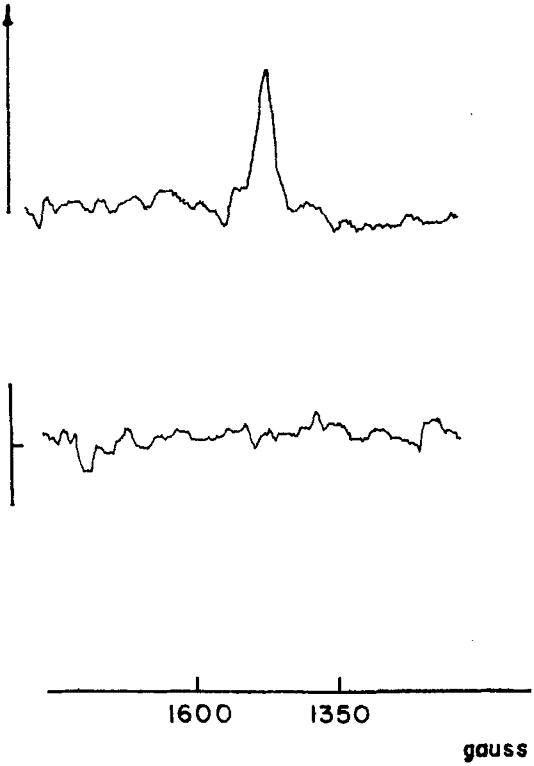

Figure 9. MODOR of quinoxalene randomly oriented in EPA.

The second characteristic feature of our data gives us some cause for concern, however. To orient ourselves towards the discrepancy, we ask what would happen to the phosphorescence modulation if the chop period of the microwave power were shorter than the characteristic spin-lattice relaxation times of the spin system. In such circumstances, the transition in question will not relax to thermal equilibrium during the quiescent portion of the microwave cycle, and the net change in phosphorescence intensity will be smaller—roughly by a factor of $(1 - \exp(-\tau/2T_1))$, where τ and T_1 are chop period and spin-lattice relaxation time, respectively—than anticipated earlier.

While it is tempting to ascribe our discrepancy to unfavorable relaxation times, we must also recognize that the simple theory developed earlier assumed tacitly that all the spins in a given resonance line were saturated during each " microwaves on " pulse.

Now the data already presented were taken by using 100 kHz magnetic field modulation of about 8 gauss peak to peak. The high field lines being some 40 to 50 gauss broad, this assumption was not well fulfilled. We might expect that the observed modulation depths would have been about 5 times larger had the entire line been modulated over. Tentatively, then, we ascribe to the MODOR $\Delta m = \pm 1$ lines a "corrected" modulation depth of 1.5% for naphthalene–d_8 and 0.8% for quinoxalene.‡

Returning now to the relaxation time problem, we found that raising the microwave chop frequency from 20 Hz to 40 Hz diminished the naphthalene–d_8 MODOR signals by a factor of $2\frac{1}{2}$, while lowering the chop frequency from 20 Hz to 4 Hz augmented the signals by an equal factor. We conclude from these data that the relaxation time of deuteronaphthalene in durene at about 3000 gauss and 1.8 °K is about 0.05 sec when H_0 is perpendicular to the *ab*-plane. Multiplying our earlier "corrected" modulation amplitude by $2\frac{1}{2}$ produces modulation depths of 4%, which may be considered to be consistent with our earlier theory. If it be assumed that quinoxalene would also be described by the simple theory, we conclude that the relaxation times of quinoxalene are about twice as long as those of the naphthalene–d_8, or about 0.1 sec under the conditions just given.

Relaxation times of this magnitude are not too disturbing when one is dealing with long-lived aromatics which have lifetimes on the order of seconds; one may always use a sufficiently low microwave chop frequency so that relaxation effects no longer limit the MODOR modulation depths. It is not generally possible to skirt the relaxation problem in this way, however. In the case of species of photochemical interest, whose triplet lifetimes are in the millisecond range, or shorter, spin lattice relaxation times of 0.1 seconds would limit the MODOR modulation depths to about 1% of those foreseen by our simple theory, and the MODOR method would probably not have sensitivity sufficient for detection of the species. While this conclusion would be void if a photochemical triplet ensemble happened to be created in a state of net spin polarization[13] the existence of such an ensemble cannot be taken for granted. There are few cases on record in which optical spin polarization has been observed in

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‡ In the case of quinoxalene, the lines of each doublet have been lumped together, as though H_0 had been strictly perpendicular to the *ab*-plane.

triplets, and in any case one would wish to be able to avoid having to wrestle with the caprices of Nature. It is therefore imperative that a way of overcoming the general limitation of long relaxation times be developed.

Fortunately, such a way is close at hand. Electron spin-lattice relaxation times are strikingly dependent upon temperature and upon magnetic field.[14] In the temperature range accessible with liquid helium, we expect the spin-lattice relaxation of organic triplet states to be controlled by the rates at which the states are capable of absorbing or emitting a single phonon. The spin-lattice relaxation times characteristic of this so-called " direct " process vary inversely with the temperature and inversely with the square of the field. By raising the temperature from 1.8° to 4.2°, and by raising the microwave frequency and magnetic field at resonance by a factor of three, one diminishes the relaxation times by a factor of 21. Triplets which might have had spin-lattice relaxation times of 0.1 sec under the experimental conditions of our early MODOR work would have relaxation times of 5 msec at *K* band and 4.2°! One has, then, a realistic expectation of being able to do MODOR work at *K* band on photochemical species.

We have verified this conclusion by means of a MODOR setup whose microwave portion operates in the neighborhood of 26 000 MHz. In our first experiment with this apparatus we examined the MODOR of a quinoxalene/durene crystal cleaved from the same block as those used in our *X* band experiments. Figure 10 shows a tracing obtained with this crystal. The modulation depths of the lines are 0.4% and 0.7%, respectively, of the total phosphorescence. While a theoretical value of about 8% was expected in this instance, it must be recalled that only about 15% of either line was brought into saturation at any one time. The " corrected " modulation depths, 3% and 5%, are satisfactory. The spin-lattice relaxation time apparently no longer interferes with the MODOR method.

As a further test of our expectations, we mention the case of the MODOR of a species of photochemical interest, cyclopentanone.[15] At 77 °K, this molecule has a phosphorescence lifetime in EPA of only 1.1 msec.[16] We have been able to observe the MODOR of cyclopentanone in a durene host; a typical recorder tracing appears in

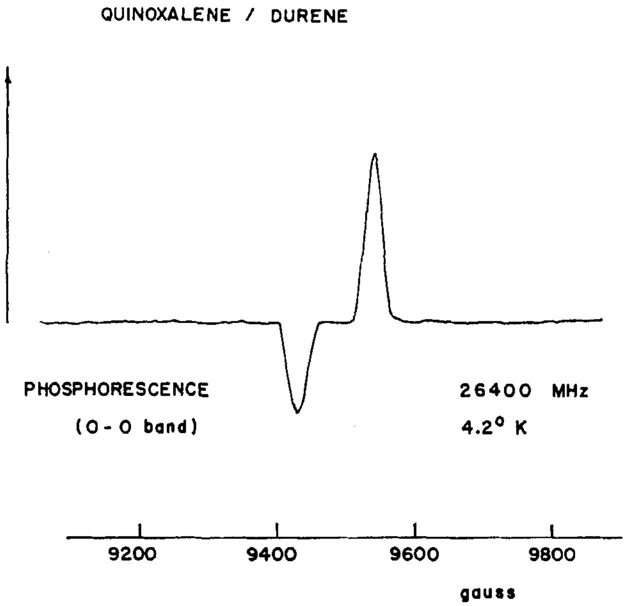

Figure 10. MODOR signals of quinoxalene in durene observed with a K-band microwave source. H_0 is parallel to the b-axis of the crystal.

Fig. 11. From the magnitudes of the modulation depths—roughly 0.2%—we may surmise that the relaxation times are probably somewhat longer than the triplet state lifetime.

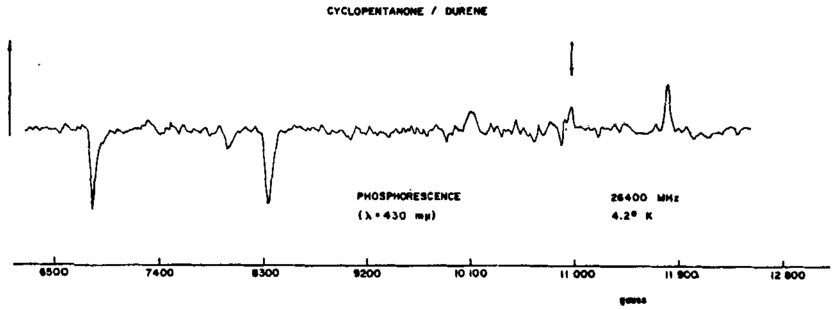

Figure 11. MODOR signals of cyclopentanone in durene. H_0 lies in the ab-plane, making an angle of 51° with the b-axis. The arrow indicates a line partially obscured by noise in this tracing but clearly visible in other data.

Concluding Remarks

The use of a high magnetic field and microwave frequency to lower the spin-lattice relaxation times was probably crucial to the success of this experiment. Another reason for preferring the use of high microwave frequencies is apparent from the large spacing of the lines of Fig. 11. The zero field splittings in cyclopentanone are larger than the microwave quanta used in a typical X-band experiment, and not all of the resonances of the system would have been observable in X-band MODOR.

If the choice of high frequency and field has an important bearing on MODOR work, that of the host lattice is equally crucial. The ESR–MODOR lines we have reported here have been systematically too broad to permit resolution of hyperfine structure, the observation of which was a principal aim of our investigations. The results suggest that the host lattices are responsible for this failure, that the guest molecules have a narrow but continuous distribution of possible orientations within the host lattices we have used. Such a distribution of orientations, conjoined with the magnetic anisotropy of the triplet molecules, would give rise to a continuous distribution of resonance lines which would look like a discrete set of anomalously broad lines. The $\Delta m = \pm 1$ lines would be several times as broad as the $\Delta m = \pm 2$ line,[17] a feature much in evidence here. A width of just 1° in orientation distribution would suffice to explain the linewidths reported here, both for naphthalene-quinoxalene and for cyclopentanone in durene. It would appear that the guest molecules are executing hindred motion which is slow enough to be manifested as a line-broadening mechanism. Whether or not hindered motion is at the bottom of things, it is apparent that in future MODOR work much attention must be given to the matching of host and guest.

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REFERENCES

1. Sharnoff, M., *J. Chem. Phys.* **46**, 3263 (1967).
2. McClure, D. S., *J. Chem. Phys.* **17**, 665 (1949)
3. Albrecht, A. C., *J. Chem. Phys.* **38**, 354 (1963).
4. Azumi, T., O'Donnell, C. M. and McGlynn, S. P., *J. Chem. Phys.* **45**, 2735 (1966).
5. Azumi, T., Udugawa, Y., Ito, M. and Nagakura, S., *J. Chem. Phys.* **47**, 4850 (1967).

6. Sharnoff, M., " On Magnetic Dipole Contributions to the Intrinsic $S_0 \leftrightarrow T_1$ Transition in Simple Aromatics " in *The Triplet State*, A. B. Zahlan, ed., Cambridge University Press, New York, 1967.
7. Hutchison, C. and Mangum, B. W., *J. Chem. Phys.* **34**, 908 (1961).
8. Vincent, J. S. and Maki, A. H., *J. Chem. Phys.* **39**, 3088 (1963).
9. Chaudhuri, N. K. and El-Sayed, M. A., *J. Chem. Phys.* **44**, 3728 (1966).
10. Chaudhuri, N. K. and El-Sayed, M. A., *J. Chem. Phys.* **43**, 1423 (1965).
11. Kwiram, A. H., *Chem. Phys. Letters* **1**, 272 (1967).
12. Schmidt, J., Hesselmann, I. A. M., De Groot, M. S. and Van Der Waals, J. H., *Chem. Phys. Letters* **1**, 434 (1967).
13. Schwoerer, M. and Wolf, H. C., XIV th Colloque Ampere, Ljubljana, 1966.
14. Pake, G. E., *Paramagnetic Resonance*, W. A. Benjamin, Inc., New York, 1962.
15. Dunion, P. F., *The Photolysis of Cyclopentanone*, Ph.D. Thesis, University of Delaware, 1965 (unpublished).
16. LaPaglia, S. R. and Roquitte, B. C., *J. Phys. Chem.* **66**, 1739 (1962)
17. Van der Waals, J. H. and De Groot, M. S., *Mol. Physics* **2**, 333 (1959).