could be maintained to within ±10° throughout the length of the column and up to a maximum of 400°. The column was packed with 228 g of active alumina (No. KA-201) generously donated by the Kaiser Aluminum Corp. Temperatures were measured using iron–constantan thermocouples with ice water as a reference and a Leeds and Northrup potentiometer.

In experiments using protio material, the catalyst as obtained from the manufacturer was found to be too active giving undesirable side products. Consequently, the catalyst was further deactivated by treating the column with anhydrous pyridine at 250° under a nitrogen stream. Such treatment eliminated the undesirable side reactions.

Dehydration of deuterated material was accomplished after the catalyst had been treaed at 250° and a nitrogen flow of 200 ml/min with 50 ml of deuterium oxide, 50 ml of anhydrous pyridine, and 30 ml of deuterium oxide. The column was baked out overnight under the same conditions. A trapping system was attached to the outlet end of the column and consisted of two pentane-slush traps held at $-140°$ and a heptane-slush trap held at $-90°$. The exit end of the trapping system was connected to a flow meter. The olefinic alcohol (10.7 g, 0.111 mol) was added to the top of the column using a pressure equalizing addition funnel while maintaining the system at 250 ± 10° and the nitrogen flow at 200 ml/min. The reactant was added dropwise over a 15-min period and product collection was continued for 4 hr. A total of 6.9 g of material was collected in the traps. The volatile components were distilled into another trap cooled in Dry Ice–acetone. A small portion (0.25 g) of lithium aluminum deuteride was added to the distillate and the component boiling below 50° was removed by distillation through a 15-cm Vigreux column into a flask cooled to $-40°$. Redistillation through a similar column gave 4.4 g (53%) of a hydrocarbon fraction boiling at 40–41°. This was taken as the piperylene-d_8 fraction. The major part of the 2.5-g residue was found to be unreacted starting material, the remainder being water. Higher temperatures are believed necessary to achieve better yields in the dehydration step using deuterated materials although temperatures of 250° gave nearly quantitative yields with protio alkenol.

Analysis by vpc using a 25 ft × $^3/_8$ in. 25% β,β'-oxydipropionitrile–5% silver nitrate column at 35° and 60 ml/min showed that the distillate consisted of 18% pentene-d_{10} (mixture of 1 and 2 isomers with *cis*-2-pentene being the major component), 29% *cis*-1,3-pentadiene-d_8, and 53% *trans*-1,3-pentadiene-d_8. The components were identified by coinjection with protio isomers of each of the compounds. Mass spectroscopic analysis revealed that the isotopic purity of the piperylenes was approximately 82% d_8 and 18% d_7 with possibly some of the d_6 isomer also being present.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF49(638)-1479.

Lowest Triplet State of Substituted Benzenes. II. Phosphorescence Microwave Double Resonance Studies on the $^3\pi\pi^*$ State of *p*-Dichlorobenzene

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Abstract: Phosphorescence microwave double resonance (pmdr) spectra of *p*-dichlorobenzene have been obtained monitoring low temperature (~1.3°K) trap phosphorescence and used to make symmetry assignments of various vibronic bands present in the spectra. In addition, ratios of radiative rate constants of individual triplet spin sublevels to several vibrational states, the intrinsic lifetimes of all three triplet spin sublevels, and selective polarized phosphorescence from individual spin sublevels in various vibronic transitions have been measured. An analysis of these data is presented along with explicit considerations of the *p*-chlorine perturbation on the aromatic ring. Finally, the relationships between the orbital symmetries and the sign and magnitude of the zero-field electron spin dipolar interactions in the triplet state are presented for several halobenzenes and on these bases an assignment of the orbital symmetry of the lowest excited triplet state of *p*-dichlorobenzene is made.

The classification of the orbital symmetry of excited triplet states of aromatic and substituted aromatic molecules is a problem which has received a considerable amount of attention from theoreticians and experimentalists alike. Early investigators, while attempting to establish the assignment of the lowest triplet state of benzene from a vibrational analysis of the phosphorescence, concluded that the transition was essentially dipole forbidden and that the weak phosphorescence activity originated from a vibronic coupling of the e_{2g} vibrations.[2a] This vibronic coupling of the e_{2g} modes has been cited as evidence for either a $^3B_{1u}$ or $^3B_{2u}$ state.[2] Theorists have generally agreed that a $^3B_{1u}$ state would be lowest in energy.[3] In a classic study, Albrecht has set down the possible routes by which dipole-allowed character might find its way into the benzene $T_1 \rightarrow S_0$ transition.[4] His findings, along with the oscillator strengths and phosphorescence polarization, allowed him to propose the $^3B_{1u}$ assignment which has since gained wide acceptance.

In addition to benzene, substituted benzenes such as hexachloro-, tetrachloro-, *p*-dichloro- and *p*-dibromobenzene have been studied. A $^3B_{2u}$ assignment has

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(1) Alfred P. Sloan Fellow.

(2) (a) H. Shull, *J. Chem. Phys.*, **17**, 295 (1949); (b) D. S. McClure, *ibid.*, 17, 665 (1959); D. P. Craig, *ibid.*, **18**, 236 (1950).

(3) M. Goeppert-Mayer and A. L. Sklar, *ibid.*, **6**, 645 (1938); C. C. J. Roothaan and R. S. Mulliken, *ibid.*, **16**, 118 (1948); C. C. J. Roothaan and R. G. Parr, *ibid.*, **17**, 1001 (1949); R. G. Parr, D. P. Craig, and I. G. Ross, *ibid.*, **18**, 1561 (1950); K. J. Niira, *ibid.*, **20**, 1498 (1952); *J. Phys. Soc. Jap.*, **8**, 630 (1953); J. A. Pople, *Proc. Phys. Soc., London, Sect. A*, **68**, 81 (1955); R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956); N. S. Ham and K. Ruedenberg, *ibid.*, **25**, 1 (1956); D. R. Kearns, *ibid.*, **36**, 1608 (1962); J. R. Platt, *J. Mol. Spectrosc.*, **9**, 288 (1962); J. W. Moskowitz and M. P. Barnett, *J. Chem. Phys.*, **39**, 1557 (1963); J. M. Schulman and J. W. Moskowitz, *ibid.*, **43**, 3287 (1965).

(4) A. C. Albrecht, *ibid.*, **33**, 156 (1960); **33**, 169 (1960); **38**, 354 (1962).

been proposed for the lowest triplet state of hexachlorobenzene on the basis of polarized phosphorescence spectra,[5] while single-crystal polarized $T_1 \leftarrow S_0$ absorption spectra led Castro and Hochstrasser to propose an identical assignment for the para-dihalogenated benzenes.[6]

It is not generally possible, because of the spin-forbidden nature of phosphorescence, to unambiguously assign the triplet orbital symmetry without a complete knowledge of the spin–orbit symmetries of all three triplet spin sublevels. Two techniques have been recently developed to determine these symmetries through an analysis of the spin sublevel origins in the vibronic transitions of the phosphorescence spectrum.

The first, based upon the high-field Zeeman effect employed by Hochstrasser and Lin,[7] has been effectively used to determine the magnitudes and signs of the zero-field parameters. Additionally, in cases where the applied magnetic field affects a resolvable splitting of the spin sublevels, this technique could be used to determine the symmetry of higher excited triplet states. The technique has the virtue of not restricting investigations to only the lowest triplet state since it can be applied to $T \leftarrow S_0$ absorption spectra.

A second technique has evolved recently from the application of optically detected magnetic resonance[8] (odmr) studies to molecules in phosphorescent triplet states. Odmr techniques have proven quite useful for the determination of a number of properties associated with excited triplet states, such as the zero-field splittings and nuclear-electron hyperfine and nuclear quadrupole interactions. Indeed, knowledge of these properties can shed light on the orbital nature of the triplet state. These techniques provide experimentalists with a powerful new tool, yielding data which, when incorporated into the wealth of spectroscopic data available, can remove the present ambiguities in the assignment of the orbital symmetries of excited triplet states in many molecules. For instance, it is well known that the magnitude of the zero-field parameter D is related to the spatial distribution of the electron spins[9] in the triplet state and can therefore be used to distinguish between an $n\pi^*$ and a $\pi\pi^*$ state. In addition to parameters directly related to the electron distribution in the triplet state, odmr can be used to determine explicitly the intrinsic lifetimes of individual triplet spin sublevels and also their relative radiative activity in various vibronic transitions present in the phosphorescence spectrum.[8,10] It is precisely these sorts of data which are necessary for the unambiguous assignment of triplet state orbital symmetries. We have therefore applied odmr techniques to the problem of determining the orbital symmetry of the lowest triplet state in *p*-dichlorobenzene (DCB).

Experimental Results

A. Sample. Samples of Eastman Organic *p*-dichlorobenzene (DCB) were degassed and extensively zone refined (200 passes at 2 in./hr). Single crystals of DCB were grown by Bridgman techniques and mounted inside a helical slow wave structure which was suspended in a liquid helium dewar. When polarized data were collected crystals were aligned coniscopically to detect phosphorescence from the crystallographic bc face. The exciting light was incident on the a′b face and was incident from a direction perpendicular to the bc face. Temperatures lower than 4.2°K were obtained by pumping on the liquid helium.

B. Phosphorescence Microwave Double Resonance Spectroscopy (Pmdr). Pmdr spectra were obtained in a manner similar to that previously reported.[11] Unpolarized phosphorescence emission was monitored at 90° to the exciting source, focused through appropriate filters, and isolated by a Jarrell-Ash 0.75-m Czerney-Turner spectrometer equipped with a cooled (−20°) EMI 6256S photomultiplier. The three zero-field transitions of DCB were observed at 5.362, 3.605, and 1.758 GHz, as reported by Buckley and Harris.[12]

In addition to the reported exciton phosphorescence[13] in DCB (origin = 27890 cm^{-1}), emission from a shallow trap which will be referred to as the x trap (origin = 27865 cm^{-1}) and a deep trap which will be referred to as the y trap (origin = 27807 cm^{-1}) was observed. The DCB sample was found to be extremely sensitive to its recent thermal history. The emission of both the exciton and the x trap was observed at 4.2°K with approximately equal intensity. Upon cooling the sample to 1.3°K only the x trap emission was observed. If the temperature of the DCB crystal was lowered to 4.2°K rapidly (approximately 20 min), exciton emission was not observed, but the emission from the y trap was observed in addition to that from the x trap. Upon cooling the sample below 4.2°K, the intensity of the x trap emission increased while the intensity of the y trap emission decreased until at 1.3°K only the x trap emission was observed. The y trap emission is believed to be due to triclinic inclusions in the monoclinic DCB lattice. This was tested by preparing a triclinic sample of DCB which contained approximately 0.01 mol %*p*-dimethoxybenzene as an impurity to stabilize the triclinic form at helium temperatures. Since the same phosphorescence origin as well as the same odmr transition frequencies were observed for both the y trap and the triclinic form of DCB, the y trap is *presumably* due to triclinic inclusions.

We will concentrate in the remaining discussion on the monoclinic form, *i.e.*, the x trap. Each of the pmdr spectra illustrated in Figure 1 was obtained while saturating one of the three microwave zero-field transitions. The microwave field was amplitude modulated at 25 cps and the spectra were obtained by standard phase

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(5) D. W. Olds, *J. Chem. Phys.*, **35**, 2248 (1961).

(6) G. Castro and R. M. Hochstrasser, *ibid.*, **46**, 3617 (1967).

(7) R. M. Hochstrasser and T.-S. Lin, *ibid.*, **49**, 4929 (1968).

(8) M. Sharnoff, *ibid.*, **46**, 3263 (1967); A. L. Kwiram, *Chem. Phys. Lett.*, **1**, 272 (1967); J. Schmidt, I. A. M. Hesselmann, M. S. de Groot, and J. H. van der Waals, *ibid.*, **1**, 434 (1967); J. Schmidt and J. H. van der Waals, *ibid.*, **2**, 640 (1968); **3**, 546 (1969); I. Y. Chan, J. Schmidt, and J. H. van der Waals, *ibid.*, **4**, 269 (1969); C. B. Harris, D. S. Tinti, M. A. El-Sayed, and A. H. Maki, *ibid.*, **4**, 409 (1969); M. J. Buckley, C. B. Harris, and A. H. Maki, *ibid.*, **4**, 591 (1970); M. A. El-Sayed, D. S. Tinti, and D. Owens, *ibid.*, **3**, 339 (1969); M. A. El-Sayed, *J. Chem. Phys.*, **52**, 6432 (1970); D. S. Tinti and M. A. El-Sayed, *ibid.*, **54**, 2529 (1971); M. A. El-Sayed, *ibid.*, **52**, 6432 (1970); M. D. Fayer, C. B. Harris, and D. A. Yuen, *ibid.*, **53**, 4719 (1970); C. B. Harris, *ibid.*, **54**, 972 (1971); A. H. Francis and C. B. Harris, *Chem. Phys. Lett.*, **9**, 181 (1971); J. Schmidt, V. C. van Dorp, and J. H. van der Waals, *ibid.*, **8**, 345 (1971); M. Sharnoff, *ibid.*, **2**, 498 (1968); R. F. Clements and M. Sharnoff, *ibid.*, **7**, 4 (1970).

(9) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, pp 115–127.

(10) J. Schmidt, W. S. Veeman, and J. H. van der Waals, *Chem. Phys. Lett.*, **4**, 341 (1969).

(11) D. S. Tinti, M. A. El-Sayed, A. H. Maki, and C. B. Harris, *ibid.*, **3**, 343 (1969).

(12) M. J. Buckley and C. B. Harris, *J. Chem. Phys.*, **56**, 137 (1972).

(13) G. A. George and G. C. Morris, *Mol. Cryst. Liquid Cryst.*, **11**, 61 (1970).

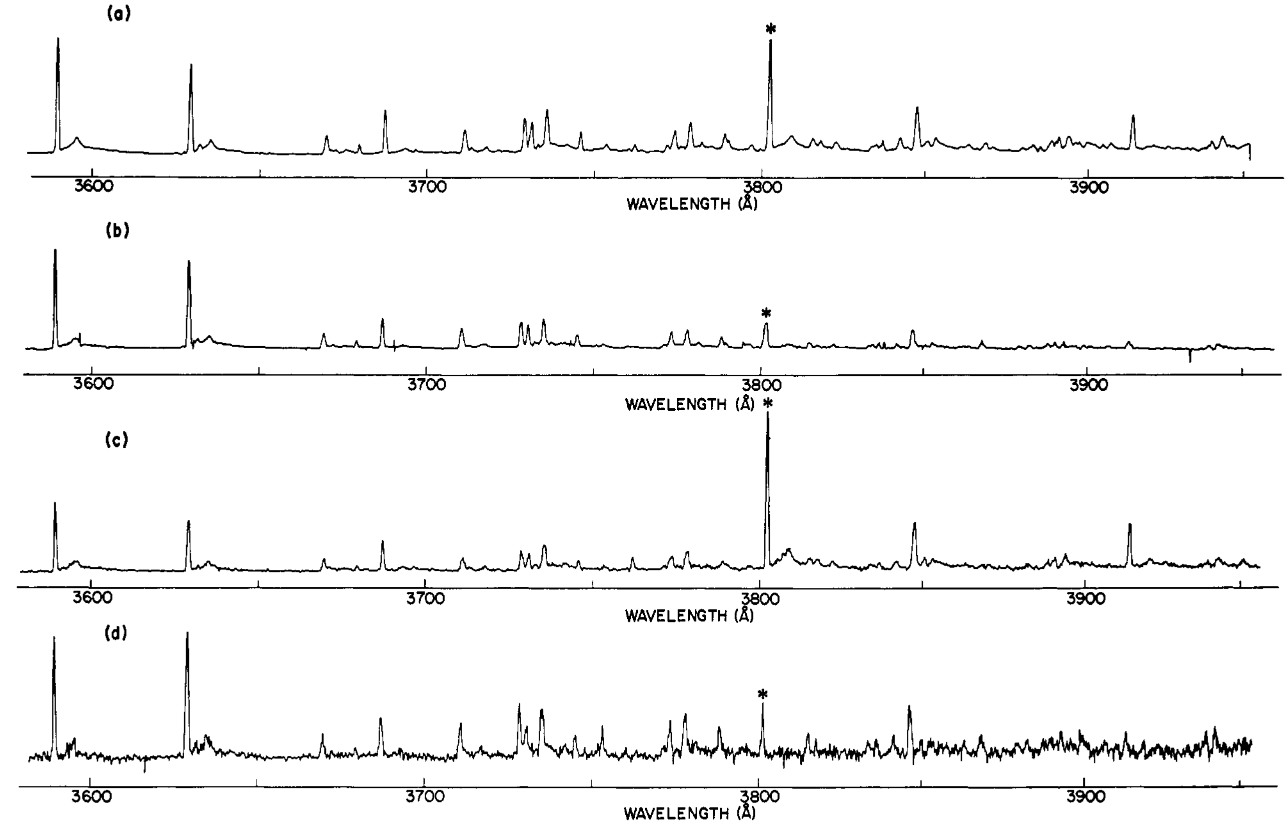

Figure 1. (a) Unpolarized phosphorescence spectrum in *p*-dichlorobenzene. (b) The 5.362-GHz ($D + |E|$) zero-field pmdr spectrum. (c) The 3.604-GHz ($D - |E|$) zero-field pmdr spectrum. (d) The 1.758-GHz ($2\,|E|$) zero-field pmdr spectrum. All spectra were obtained at 1.3°K.

detection techniques. All of the vibronic transitions increase in intensity for each of the pmdr experiments. Since a lock-in amplifier was used, any decrease in intensity while monitoring the emission to a vibrational level of the ground state would have caused the pmdr transition to go negative rather than positive. The relative increase in intensity of the vibronic transition at 0,0 + 1579 cm^{-1} (denoted by an asterisk in Figure 1) compared to the origin is striking. The relative increase in intensity is greatest while saturating the 3.604-GHz transition, while the relative increase in intensity of the origin is greatest for the 5.362-GHz transition. Other vibrations which have been assigned as a_g behave in a manner similar to the origin and therefore it is clear that the vibration at 0,0 + 1583 cm^{-1} is not exclusively an a_g vibration as previously assigned, since all vibrations with the same symmetry should maintain a constant intensity ratio within all three pmdr spectra.

C. Adiabatic Inversion. The inversion experiments were conducted at 1.3 ± 0.05°K employing essentially the same procedure reported elsewhere (ref 14). Microwave power was obtained from a Hewlett-Packard Model 8690-B sweep oscillator, amplified *via* a 20-W traveling wave tube, and was applied to the sample through a rigid coaxial line terminated with a slow wave helix. The frequency sweep required to invert the triplet sublevels was obtained by applying a ramp voltage to the FM input of the microwave sweep generator. The ramp voltage was adjusted so that at V_0 the microwave frequency was ω_0, the center of the epr transition being used for inversion. The FM voltage was swept linearly from $V_0 - {}^1/_2V$ to $V_0 + {}^1/_2V$ in a time τ so that the microwave frequency changed from $\omega_0 - {}^1/_2\delta$ to $\omega_0 + {}^1/_2\delta$ in a time τ. Maximum inversion was achieved by adjusting the power, the time τ ($\sim$100 μsec), and the ramp voltage V. Optimum inversion was obtained at a rate of $\sim$10 MHz/100 μsec.

Simple phosphorescence decay studies at 1.3°K show that the DCB triplet state possesses two short-lived sublevels and one relatively long-lived sublevel. Using the inversion technique the lifetimes of all three sublevels were measured in the same manner as reported by Schmidt, Veeman, and van der Waals.[10] The experiment depends upon an examination of the time evolution of the emission intensity to a particular vibration in the phosphorescence spectrum. The event sequence occurred as follows. The excitation source, a 100-J flash lamp ($\sim$20 μsec duration), was triggered first, with the excitation light focused on the sample through a water filter and a Schott 3100-Å interference filter. A PAR waveform eductor was triggered a short time after the excitation flash ($\sim$100 μsec) and the population inversion operation[14] was performed after a variable delay which was adjusted to allow the two short-lived spin sublevels to decay. The waveform eductor served to store output from successive event sequences and thereby improve the signal-to-noise ratio. Successive event sequences were separated by a 4-sec delay to ensure complete decay of the triplet sublevels; however only the first 1 sec of each sequence was sampled and stored in the waveform eductor. These observations confirm the simple decay data, yield sublevel 1/e life-

(14) C. B. Harris, *J. Chem. Phys.*, **54**, 972 (1971); C. B. Harris and R. J. Hoover, *ibid.*, **56**, 2199 (1972).

times of 13 ± 1.5, 46 ± 3, and about 600 msec, and further establish the long-lived sublevel to be common to both the 5.362- and 3.604-GHz transitions. Inversion was observed at times as long as several seconds after excitation, thereby establishing that at very low temperatures (~1.3°K) spin-lattice relaxation may be neglected.

Figure 2 illustrates the phosphorescence to the electronic origin in the inversion experiment described above. Following the excitation flash, the two short-lived spin sublevels decay, thus depleting their populations. The inversion operation is triggered after a time long compared to the short lifetimes (~90 msec) thereby placing population from the long-lived sublevel selectively into one of the now almost empty short-lived sublevels. In this manner one can obtain ratios of radiative rate constants from the ratio of intensity of the inversion signal at τ = 90 msec (5.362/3.604 GHz).

From pmdr spectra, vibronic transitions of varying symmetries were identified. A systematic series of the 5.362- and 3.604-GHz inversions were also applied to several of the prominent vibrations in the phosphorescence spectrum which yielded the data listed in Table I.

Table I. Relative Inversion Heights (Normalized to Phosphorescence Intensity)

	$D+\|E\|$	$D-\|E\|$	Ratio: $\frac{D+\|E\|}{D-\|E\|}$[b]
Origin (0,0)	0.50	0.12	4.1:1
b_{1g}(0,0 + (1579 + 309) cm^{-1})[a]	0.47	0.18	2.6:1
b_{2g}(0,0 + 309 cm^{-1})	0.53	0.12	4.6:1
b_{3g}(0,0 + 1579 cm^{-1})[a]	0.40	0.28	1.4:1

[a] See text for discussion of assignments of these bands. [b] These ratios are approximately equal to the radiative rate constant ratios (τ_y/τ_z) in the bands listed.

Monitoring emission from the crystallographic[15] bc face, polarization ratios obtained for this same series of inversions are reported in Table II.

Table II. Polarized Inversion Heights (b/c Ratio)

	$D+\|E\|$	$D-\|E\|$
Origin (0,0)	0.49	1.45
b_{1g}(0,0 + (1579 + 309) cm^{-1})	0.95	1.38
b_{2g}(0,0 + 309 cm^{-1})	0.83	1.67
b_{3g}(0,0 + 1579 cm^{-1})	0.65	1.00

In addition, polarization of emission from the long-lived spin sublevel was measured by eliminating the inversion operation and monitoring the polarized emission in the tail of the phosphorescence decay to vibronic transitions at 3629 and 3849 Å. Table III illustrates these data.

Table III. b/c Polarization Ratios in the Phosphorescence Decay[a]

	Origin	b_{1g}	b_{2g}	b_{3g}
τ_y,τ_z (0–25 msec)	0.7	1.4	1.4	0.7
τ_x (200 msec–1 sec)	0.5	0.8	1.1	0.6

[a] The a'c face shows similar a'/c ratios.

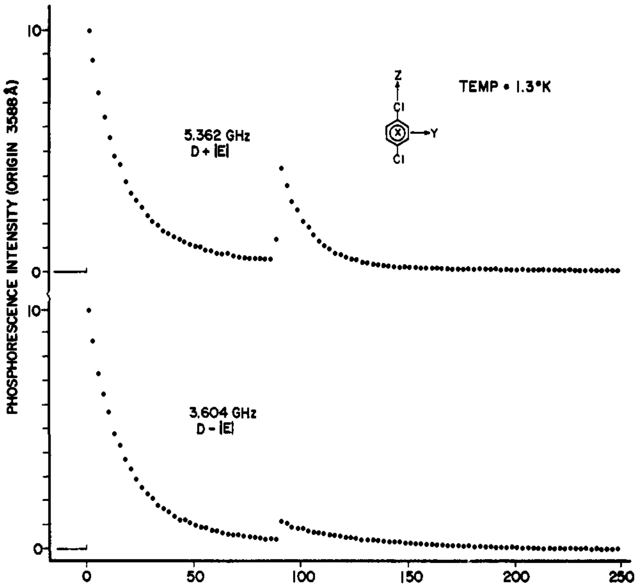

Figure 2. The phosphorescence decay and microwave induced inversion monitoring the x-trap origin at 1.3°K in *p*-dichlorobenzene from 168 accumulations in a 100-channel averager. The fraction of inversion in both transitions was 0.85.

Discussion

The $T_1 \rightarrow S_0$ phosphorescence, because of its spin-forbidden nature, derives its transition probability from singlet states admixed into the triplet state *via* spin–orbit coupling.[16] It has been shown that within molecules of relatively high point symmetries the triplet state spin sublevels generally exhibit selective spin–orbit coupling with excited singlet states; consequently, one and sometimes two spin sublevels contribute the majority of phosphorescence intensity.[17]

A completely unambiguous assignment of the orbital symmetry of the triplet states requires, in addition to the polarization of the phosphorescence from the active spin sublevels, a knowledge of the magnetic orientation of these spin sublevels relative to the molecular axes. An explicit consideration of the spin–orbit symmetries for *p*-dichlorobenzene (DCB) in both a $^3B_{1u}$ and a $^3B_{2u}$ state will easily demonstrate this requirement.

Zeroth-order wave functions for each triplet sublevel, taken as a product of spatial (orbit) and spin functions, transform as the direct product of the irreducible representations of each part. Eigenfunctions of the spin angular momentum operator transform, in zero magnetic field, as rotations which in the point group D_{2h} are $B_{1g}(R_z)$, $B_{2g}(R_y)$, and $B_{3g}(R_x)$. Table IV outlines the total spin–orbit symmetry of the sublevels for the above orbital symmetries for the lowest triplet state of *p*-dichlorobenzene (DCB) in D_{2h}.

An examination of Table IV reveals that the only differences between the $^3B_{1u}$ and the $^3B_{2u}$ assignments are: (1) the spin–orbit symmetry of the τ_x spin sublevel and (2) the magnetic orientation of the B_{3u} and A_u (τ_z or τ_y) spin–orbit states.

We have neglected to consider the two other possible symmetry assignments for the lowest triplet state in

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(15) U. Croatto, S. Bezzi, and E. Bua, *Acta Crystallogr.*, **5**, 825 (1952).

(16) D. S. McClure, *J. Chem. Phys.*, **20**, 682 (1952).

(17) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

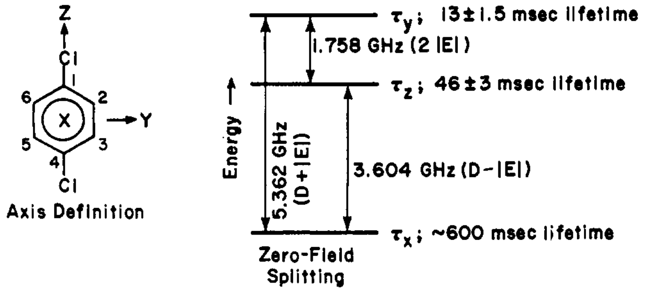

Figure 3. *p*-Dichlorobenzene zero-field splittings for the phosphorescent triplet state in the coordinate system illustrated.

DCB (^3A_u) and ($^3B_{3u}$), since they correspond to nπ^* or $\sigma\pi^*$ configurations. Experimental evidence indicates a $\pi\pi^*$ configuration is correct. Early support for this contention came from the observation that the DCB $T_1 \leftarrow S_0$ absorption spectrum exhibits a significant amount of out-of-plane polarization.[6,13] Furthermore, the experimental values for the zero-field parameters D and D^* ($D^* = (D^2 + 3E^2)^{1/2}$) of DCB differ by only a few per cent from those of benzene.[12,18] Finally, measurement of the chlorine hyperfine interaction[12] indicates that the *p*-chlorines of DCB possess a much smaller spin density than might be expected for a ^{3}nπ^* state.[19]

Table IV. Spin-Orbit Symmetries of the Individual Magnetic Sublevels in *p*-Dichlorobenzene in the States $^3B_{1u}$ and $^3B_{2u}$

Orbital symmetry	Magnetic sublevel	Spin-orbit symmetry	Vibrational band—Polarization[a] a_g	b_{1g}	b_{2g}	b_{3g}
$^3B_{1u}$ ($\pi\pi^*$)	τ_y	B_{3u} (nπ^*)	X	Y	Z	
	τ_z	A_u (nπ^*)		Z	Y	X
	τ_x	B_{2u} ($\pi\pi^*$)	Y	X		Z
$^3B_{2u}$ ($\pi\pi^*$)	τ_z	B_{3u} (nπ^*)	X	Y	Z	
	τ_y	A_u (nπ^*)		Z	Y	X
	τ_x	B_{1u} ($\pi\pi^*$)	Z		X	Y

[a] Z and Y are in-plane long and short axes, respectively, according to the coordinate system in Figure 3, while X is out of plane.

By analogy to benzene[18,20] and from previous studies of aromatic molecules in $\pi\pi^*$ triplet states,[21-29] it is reasonable to assume that in DCB the largest component of the electron spin-spin tensor in its principal axis system is along the molecular axis normal to the plane. In the coordinate system illustrated in Figure 3, the lowest energy triplet sublevel would then be τ_x.

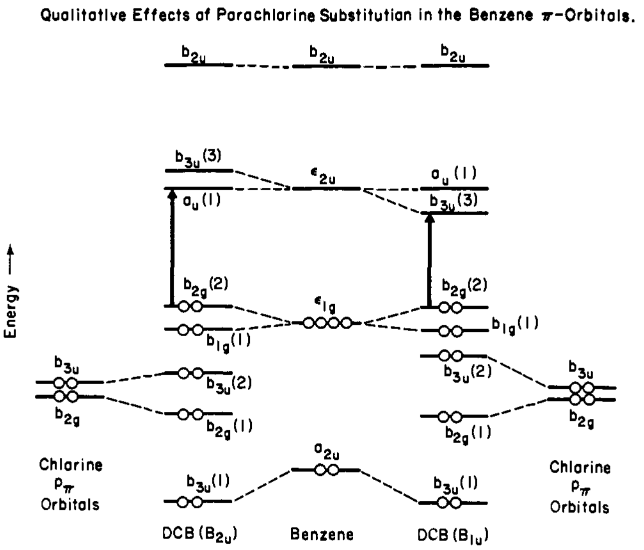

Figure 4. The one-electron π molecular orbitals of benzene and *p*-dichlorobenzene with a qualitative assessment of two possible effects of the *p*-chlorine substitution.

The observation that the long-lived (~600 msec) spin sublevel is common to both the 3.604-GHz ($D - |E|$) and 5.362-GHz ($D + |E|$) zero-field transitions, together with the above considerations, allows us to assign the lowest energy sublevel as the long-lived sublevel. The remaining spin sublevels, τ_y and τ_z, are then associated with spin eigenfunctions of the zero-field Hamiltonian asymmetry parameter E.

The zero-field splitting parameter E is a measure of the anisotropy of the triplet electron spin distribution in the molecular plane and should be equal to zero if the molecular plane possesses a rotational symmetry greater than C_2.[18] In such cases τ_y and τ_z would be degenerate. If the spin sublevels are ordered $\tau_y > \tau_z$, E is negative, whereas if $\tau_z > \tau_y$ E is positive. From a simple spin dipole argument, in the absence of appreciable spin-orbit coupling contributions to the zero-field splittings, the sign and magnitude of E in substituted benzene triplet states can be easily determined, with little ambiguity, from the one-electron molecular orbitals that form the basis for the excited state. Figure 4 illustrates two possible perturbations that can occur with chlorine para substitution. The chlorine out-of-plane p orbitals (π) form linear combinations that transform as b_{2g} and b_{3u} in D_{2h}. Since the energies of these orbitals would be somewhere between the benzene[29,30] a_{2u} and e_{1g} orbitals, first-order perturbation theory requires that the $b_{2g}(2)$ MO derived from the benzene e_{1g} MO be raised in energy while the predominantly chlorine $b_{2g}(1)$ MO be lowered. The b_{3u} interactions unfortunately cannot be easily predicted from perturbation theory. Two orders are possible depending upon the magnitude of the chlorine–benzene interactions. First, the $b_{3u}(3)$ orbital derived from the benzene e_{2u} MO could be lowered *via* chlorine interactions. This would depend upon many factors, few of which can be even qualitatively estimated. The other possibility is for the $b_{3u}(3)$ MO to increase in energy *via* carbon–chlorine bonding. In either of the above cases the symmetry of the *lowest* occupied MO in the ground state of DCB is expected to be $b_{2g}(2)$; therefore two excited state orbital symmetries can arise. $^3B_{1u}$ is derived from a $b_{2g} \rightarrow b_{3u}$ transition while the state $^3B_{2u}$ is derived from the transition $b_{2g} \rightarrow$

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(18) M. S. de Groot, I. A. M. Hesselmann, and J. H. van der Waals, *Mol. Phys.*, 16, 45 (1969).

(19) L. T. Cheng and A. L. Kwiram, *Chem. Phys. Lett.*, 4, 457 (1969).

(20) M. Godfrey, C. W. Kern, and M. Karplus, *J. Chem. Phys.*, 44, 4459 (1966).

(21) M. Gouterman and W. Moffitt, *ibid.*, 30, 1107 (1959).

(22) M. Gouterman, *ibid.*, 30, 1369 (1959).

(23) B. Smaller, *ibid.*, 37, 1579 (1962).

(24) H. Hameka, *ibid.*, 31, 315 (1959).

(25) Y. N. Chin, *ibid.*, 39, 2736 (1963).

(26) C. A. Hutchinson, Jr., and B. W. Mangum, *ibid.*, 34, 908 (1961).

(27) N. Hirota, C. A. Hutchinson, Jr., and P. Palmer, *ibid.*, 40, 3717 (1964).

(28) C. A. Hutchinson, Jr., J. V. Nicholas, and G. W. Scott, *ibid.*, 53, 1906 (1970).

(29) C. E. Moore, *Nat. Bur. Stand.* (*U. S.*), *Circ.*, 467 (1949 and 1952).

(30) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966.

Table V

Molecule	Triplet state	Predicted spin sublevel order (spin–orbit symmetry)	E value	Approximate carbon spin densities 1	2	3	4	5	6
DCB	$^3B_{1u}$ ($b_{2g} \rightarrow b_{3u}$)	$\tau_y > \tau_z \gg \tau_x$ ($B_{3u} > A_u \gg B_{2u}$)	"Large" negative	0.67[a]	0.165	0.165	0.67[a]	0.165	0.165
DCB	$^3B_{2u}$ ($b_{2g} \rightarrow a_u$)	$\tau_z > \tau_y \gg \tau_x$ ($B_{3u} > A_u \gg B_{1u}$)	"Small" positive	0.33[a]	0.33	0.33	0.33[a]	0.33	0.33
TCB	$^3B_{1u}$ ($b_{1g} \rightarrow a_u$)	$\tau_z > \tau_y \gg \tau_x$ ($A_u > B_{3u} \gg B_{2u}$)	"Large" positive	~0	0.5[a]	0.5[a]	~0	0.5[a]	0.5[a]
TCB	$^3B_{2u}$ ($b_{1g} \rightarrow b_{3u}$)	$\tau_y > \tau_z \gg \tau_x$ ($A_u > B_{3u} \gg B_{1u}$)	"Small" negative	0.33	0.33[a]	0.33[a]	0.33	0.33[a]	0.33[a]

[a] Indicates appropriate chlorine positions. At these positions spin density values are a maximum since any spin delocalization on chlorines bonded to these carbons would reduce the carbon spin densities.

a_u. If we consider the triplet states with one of the unpaired electrons in the $b_{2g}(2)$ MO and the other in an $a_u(1)$ or $b_{3u}(3)$ MO, the sign and the magnitude of the spin dipolar term E can be anticipated in each case knowing that the para substitution does not appreciably affect the value of D. The D value of DCB is within a few per cent of that of benzene.[12] Since both the $a_u(1)$ and $b_{1g}(3)$ MO's (*cf.* Figure 5) have a nodal plane through the 1 and 4 positions the one-electron spin density in these MO's would be concentrated on positions 2, 3, 5, and 6. In the b_{2g} and b_{3u} MO's the para carbons have four times the spin density of the others. Naturally the chlorine affects these values to a degree by delocalizing a *small* amount of spin density as evidenced by the out-of-plane chlorine hyperfine coupling constant (~25 MHz).[12] Figure 5 summarizes the spin densities on each carbon and the symmetries for the appropriate one-electron MO's (Table V).

Consider explicitly the $^3B_{1u}$ state. The magnetic dipole–dipole forces between the two unpaired spins, one in $b_{2g}(2)$ and the other in $b_{3u}(3)$, arise principally from spin density on carbons 1 and 4 (4/12) with that on carbons 2, 3, 5, and 6 (1/12) as illustrated in Figure 5. There are eight such nearest neighbor dipole–dipole interactions between $b_{2g}(2)$ and $b_{3u}(3)$. In the principal axes which diagonalize the zero-field tensor these contributions result in almost (1.83) twice as much dipolar repulsion along Y as along Z. The remaining non-nearest neighbor contributions are greatly reduced because of the $(1/r^3)$ dependence between spins. Moreover these interactions when combined with the small nearest neighbor terms between spins on only carbons 2, 3, 5, and 6 are about equally distributed along the Y and Z axes so their contribution to the zero-field splitting parameter E is negligible. The net result, considering all the above terms, is to raise the energy of the τ_y spin sublevel substantially above τ_z and give rise to a *large* negative value for E. On the other hand, if the orbital symmetry in DCB were $^3B_{2u}$, the expected value for E would be zero when all nearest neighbor spin dipole terms are explicitly considered with one electron in $b_{2g}(2)$ and the other in $a_u(1)$. A small positive E value might be expected experimentally since the chlorines would delocalize a small amount of spin from carbons 1 and 4 in the $b_{2g}(2)$ MO thereby lowering the energy of τ_y relative to τ_z. These same arguments can be extended to *s*-tetrachlorobenzene (TCB) (*cf.* Table IV).

The *measured E* values in both molecules are large. In fact, in DCB[12] it is 65% of its maximum allowed value and in TCB[31] it is 70% of its maximum allowed value before the principal coordinate system of the zero-field Hamiltonian must be changed.[9] This we believe is more than enough anisotropy in the zero-field splitting to provide evidence for a $^3B_{1u}$ assignment for both DCB and TCB. The application of an external magnetic field could in principle confirm the sublevel order. Such an experiment has been attempted on DCB in this laboratory, but the unfavorable orientation of the Y and Z axes in the two molecules of the DCB unit cell[15] prevented us from obtaining conclusive data by a low magnetic field odmr study. Attempts made in this laboratory to observe the odmr spectra of DCB

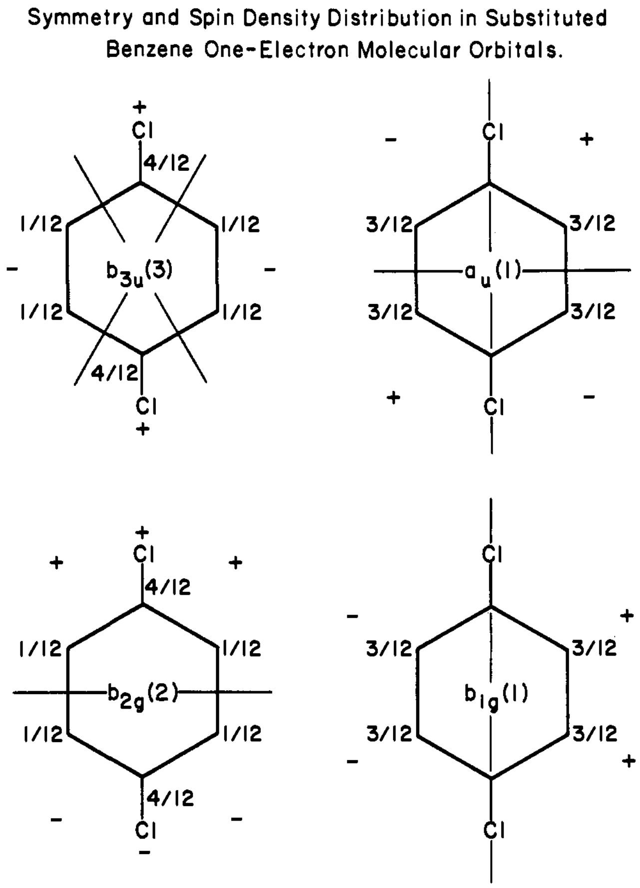

Figure 5. The symmetries of various benzene one-electron molecular orbitals in D_{2h} along with approximate spin density distributions on the individual carbon atoms in the appropriate molecular orbitals.

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(31) A. H. Francis and C. B. Harris, *Chem. Phys. Lett.*, 9, 188 (1971).

doped into other suitable hosts (known crystal structure and an absence of heavy atoms) have as yet proved unsuccessful.

It is noteworthy that in either symmetry $^3B_{1u}$ or $^3B_{2u}$ the *spin-orbit* symmetry associated with the highest spin sublevel is B_{3u} in DCB and A_u in TCB. This is consistent with the observation that phosphorescence to the origin in DCB (see below) and in TCB[32] originates from the upper (B_{3u}) and middle (B_{3u}) spin sublevels, respectively, in DCB and TCB. In DCB this has been determined by measuring which spin sublevel has the largest radiative dipole activity to the phosphorescence origin. Since in D_{2h} the spin sublevel that transforms as A_u is formally dipole forbidden, the principal activity should be from the spin sublevel that transforms as B_{3u}. In the $^3B_{1u}$ or $^3B_{2u}$ states this would correspond to τ_y or τ_z, respectively. Delayed adiabatic inversion data illustrated in Figure 2 and Table I demonstrate that the principal activity is from the upper spin sublevel. The important point of Figure 2 is that the ratio of the radiative rates (τ_y/τ_z) is much greater than unity. These data establish the symmetry of the upper spin sublevel (τ_y) as B_{3u}. The spin-orbit symmetry of the lowest spin sublevel (τ_x) can be determined by polarization measurements (*cf.* Table III) taken while monitoring emission from the DCB crystallographic bc face[15] in the tail of the phosphorescence decay to vibronic transitions at 3529 Å (0,0 + 309 cm^{-1}) and 3849 Å (0,0 + (1579 + 309) cm^{-1}) which have been assigned as a b_{2g} fundamental[6,33] and a $b_{1g}(b_{3g} \times b_{2g})$ combination band,[34] respectively. These measurements indicate that emission from the long-lived sublevel (τ_x) is out-of-plane polarized to b_{1g} while polarization is mixed to b_{2g}. In addition, phosphorescence from τ_x to b_{1g} is about 2.5 times as intense as that to the b_{2g} when the emission is normalized to their respective total phosphorescence intensity. These data point to a B_{2u} spin-orbit symmetry for the τ_x sublevel consistent with the $^3B_{1u}$ orbital assignment (*cf.* Table IV).

It is apparent from both the pmdr data and adiabatic inversion data that the B_{3u} and A_u spin-orbit states contribute most to the dipole activity in DCB phosphorescence. This activity and our observation that the lowest triplet state of DCB possesses two short-lived (lifetimes: 13 ± 1.5 and 46 ± 3 msec) and one relatively long-lived spin sublevel (~600 msec) can be better understood when further aspects of the chlorine perturbations are considered more explicitly.

Intrinsic emission lifetimes of the triplet sublevels are inversely proportional to the radiative and/or radiationless transition probability and thereby proportional to the amount of singlet character mixed into the triplet state primarily by spin-orbit coupling. The measured magnitudes of the DCB sublevel lifetimes (τ_y and τ_z) are about a factor of 10^3 shorter than those of benzene.[35] This observation points to a significant amount of spin-orbit coupling presumably due to the addition of two chlorine nuclei to the benzene ring. A natural assumption is that the most effectively spin-orbit coupled singlet states would be those states which include to a large degree the atomic orbitals of the two *p*-chlorines. The symmetries of these possible chlorine perturbing orbitals using all chlorine valence electrons except the out-of-plane p_π are b_{1u}, a_g, b_{2u}, b_{3g}. In DCB singlet states fashioned from the combinations of these orbitals and $b_{3u}(3)$ or $a_u(1)$ will transform as the direct products of their respective irreducible representations. Singlet states which might admix any electric dipole character into the triplet sublevels must be antisymmetric with respect to inversion. This restriction limits the consideration of possible perturbing singlet states to only $^1B_{3u}$ ($b_{3g} \times a_u(1)$; $a_g \times b_{3u}(3)$) and ^1A_u ($a_g \times a_u(1)$; $b_{3g} \times b_{3u}(3)$) or those states responsible for the electric dipole activity from τ_y and τ_z. The presence of carbon–chlorine bonds (as opposed to carbon–hydrogen bonds) would lower the energy of some $\sigma\pi^*$ states of ^1A_u and $^1B_{3u}$ symmetry relative to those in benzene augmenting their importance in chlorobenzenes. Because the A_u and B_{3u} states have one-center spin-orbit coupling matrix elements with the τ_z and τ_y sublevels while the $^1\pi\pi^*$ character associated with τ_x arises only from two center spin-orbit terms,[17] one expects most of the phosphorescence to originate from τ_y and τ_z as the experimental data demonstrate. The pmdr data and the adiabatic inversion data show that the principal route in phosphorescence in all transitions is from $\tau_y(B_{3u})$. This can be seen from the ratios reported in Table I which are approximately equal to the spin sublevel radiative rate constant ratios for the vibrational transitions listed. The vibronic origin found at 3804 Å (0,0 + 1579 cm^{-1}) is most perplexing in this respect. It has been assigned as an a_g fundamental by some investigators.[6,36,37] Pmdr spectra (Figure 1) clearly show that it behaves differently than other a_g vibrations. A tentative b_{3g} assignment was therefore made on the basis of reported laser Raman studies;[33] however, the microwave inversion data subsequently failed to display the expected b_{3g} behavior for this transition. Any b_{3g} vibration in the phosphorescence spectrum would be expected to exhibit a reversal of activity from spin sublevels τ_y and τ_z compared to the origin (or any totally symmetric vibration). Even taking into account a slight relaxation of symmetry restrictions we would expect most of its intensity to be derived from the τ_z ($A_u \times b_{3g} = B_{3u}$) sublevel. Our observations, in fact, show a marked increase in emission from the τ_z sublevel in the pmdr's. However, most of the emission remains from τ_y, as evident from the radiative rate constant ratios from τ_y and τ_z, *i.e.*, ${k_{r\tau_y}}^{(0,0+1579)}$: ${k_{r\tau_z}}^{(0,0+1579)} = 1.4{:}1$. These anomalous characteristics allow us to *suggest* that the (0,0 + 1579) band is, in actuality, associated with both an a_g and a b_{3g} vibration which our instruments were unable to resolve.

While the odmr techniques employed in this study have helped remove the primary ambiguities (*i.e.*, spin sublevel origins of phosphorescence), the present observations of DCB phosphorescence show quite clearly a relaxation of D_{2h} symmetry. Specifically, both the polarized and nonpolarized inversion data (Tables I and II) show some emission from $\tau_z(A_u)$ to the electronic origin. The D_{2h} symmetry restrictions require that emission to any totally symmetric vibration should

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(32) A. H. Francis and C. B. Harris, *J. Chem. Phys.*, in press.

(33) M. Suzuki and M. Ito, *Spectrochim. Acta, Part A*, **25**, 1017 (1969).

(34) See later text for discussion of this band. We suggest that this band is actually a $b_{1g}(b_{3g} \times b_{2g})$ combination band coincident with a $b_{2g}(a_g \times b_{2g})$ combination band.

(35) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

(36) A. Stojiljkovic and D. H. Whiffen, *Spectrochim. Acta*, **12**, 47 (1958).

(37) J. R. Scherer and J. C. Evans, *ibid.*, **19**, 1739 (1963).

originate from the $\tau_y(B_{3u})$ sublevel, while the $\tau_z(A_u)$ sublevel should be completely inactive to such vibrations. The measured value of the radiative rate constant ratio for $\tau_y(B_{3u}):\tau_z(A_u)$ to the origin (Table I) is about 4:1. The emission from τ_y shows predominantly out-of-plane polarization as expected and emission from τ_z, the symmetry restricted sublevel, displays a slight in-plane polarization. In fact, the pmdr spectra shown in Figure 1 clearly reveal that some mixed emission is apparent in all transitions since all optical transitions are coupled by all three microwave transitions.

A definitive explanation for the mixed phosphorescence observed in DCB is beyond the scope of data currently available. We have, however, considered various possibilities. Explicit considerations of the crystal field effects focused on the surrounding chlorine atoms, since the reduction of molecular symmetry D_{2h} to C_i site symmetry would occur in all likelihood *via* either chlorine crystal field contributions (*e.g.*, the heavy atom effect) or explicit trap characteristics. An analysis of the DCB crystal structure[15] shows that the sum of weighted ($1/|r|^2$) vectors from each of the 24 nearest chlorine atoms surrounding any DCB molecule yields a resultant vector $0.87\hat{x} + 0.31\hat{y} + 0.38\hat{z}$, relative to the DCB molecular axes. Such a field vector could mix both the in-plane zero-field spin sublevels and the out-of-plane spin sublevel with each in-plane spin state. Obviously, this chlorine-field vector possesses suitable geometry to account for the mixed DCB phosphorescence, but a quantitative assessment of the strength of the external chlorine influence and the trap effects would be necessary before we can venture any definite conclusions. Aside from crystal effects, the relaxation of symmetry restrictions observed in DCB trap phosphorescence might also be due to a distortion of the molecule itself. The question of the exact nature of this distortion remains as yet unanswered. The distortion may be caused by a rearrangement of the nuclear skeleton either under the influence of the excited state electronic potential or as an inherent characteristic of the trap. It is noteworthy, however, that the chlorine field gradient in the excited state is substantially lower than in the ground state. As has been discussed[12] this can be due in part to a distortion and in part to increased carbon–chlorine π bonding in the excited state. The average decrease in chlorine field gradients in $\pi\pi^*$ states in those molecules thus far investigated where no distortion is suspected is about 3% (8-chloroquinoline,[38] 1,2,4,5-tetrachlorobenzene,[32] and 1,4-dichloroquinoxaline[39]). An average decrease of 3% may well represent the increased π character of the C–Cl bond. DCB, on the other hand, shows an 8% decrease in the chlorine field gradient. Perhaps the additional 5% decrease is due to an out-of-plane chlorine distortion. The pmdr and inversion data do not exclude this possibility. Further experiments are needed to resolve this question adequately.

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(38) M. J. Buckley and C. B. Harris, *Chem. Phys. Lett.*, **5**, 205 (1970).

(39) M. J. Buckley and C. B. Harris, unpublished work.

Theoretical and Practical Considerations for Measurements of the Efficiencies of Chemiluminescent Electron-Transfer Reactions[1]

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Abstract: Digital simulation methods and a kinetic analysis have been used to define a concise set of parameters which quantitatively describe the efficiencies of the simplest types of energy-sufficient and energy-deficient chemiluminescent electron-transfer processes. Techniques for data acquisition and analysis are discussed in both theoretical and practical terms for the triple-potential-step generation of luminescence. It is shown that excited state yields of electron transfer are experimentally accessible from the analysis of luminescence decay curves and that total quantum output data can provide a measure of the overall efficiency of chemiluminescence. The effects of reactant instability on these determinations are also considered and rendered accountable.

Although the phenomenon of electrogenerated chemiluminescence (ecl) was first reported about eight years ago,[2] there have been very few investigations of the absolute quantum yields of these processes, largely because appropriate instruments have been lacking. Moreover, each report of the absolute output of an ecl process has introduced a new method for

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(1) Mechanisms of Chemiluminescent Electron-Transfer Reactions. III. For the previous paper in this series, see D. J. Freed and L. R. Faulkner, *J. Amer. Chem. Soc.*, **93**, 3565 (1971).

(2) (a) R. E. Visco and E. A. Chandross, *ibid.*, **86**, 5350 (1964); (b) D. M. Hercules, *Science*, **145**, 808 (1964); (c) K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **87**, 139 (1965).