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C. B. Harris and Robert J. Hoover

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Quadrature Phase Relationships in
Phosphorescence Microwave Double Resonance Spectroscopy

by

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Abstract

The functional dependence of the phase shift of a time-dependent phosphorescence intensity change relative to a repetitive delta-function microwave perturbation is given in terms of the triplet state kinetic parameters and the perturbation repetition rate. This extension of quadrature measurements to the phosphorescence microwave double resonance (PMDR) technique is found to be particularly useful since the phase shift is independent of the degree of spin alignment of the magnetic sublevels, the degree of microwave saturation, and the polarization of the microwave transition moment. It is shown that the symmetries of vibronic bands in the phosphorescence can be distinguished by measuring the phase shift. Experimental results are reported for p-dichlorobenzene and s-tetrachlorobenzene.

[†] Alfred P. Sloan Fellow

Introduction

As a consequence of spin-orbit coupling, phosphorescence from the lowest triplet state of a molecule to the ground state vibrational manifold is selective from the individual magnetic sublevels and can be thought of as a sum of three components, one from each of the zero field magnetic sublevels, τ_x , τ_y and τ_z . The amplitude of each component is determined by the radiative rates and the populations which are in turn determined by intersystem crossing rates, total decay rates, and spin lattice relaxation effects. Advantage has been taken of these facts in the method of phosphorescence-microwave double-resonance (PMDR) spectroscopy which isolates two of the magnetic sublevels with a microwave field and monitors the change in phosphorescence it induces at low temperatures (1.3-2°K). The sublevels active in emission and the degree of spin alignment in the lowest triplet state can be determined via standard PMDR techniques.¹ This information is useful in determining triplet state properties such as the relative rates and routes of intersystem crossing as well as the specific spin level contributions to vibronic bands.

In some cases the magnetic sublevels active to a particular vibrational progression can be analyzed in greater detail by polarized PMDR² yielding information lost in standard techniques. Depending upon the specific case under investigation, the polarized components from the individual magnetic sublevels of the triplet may only be resolved to a varying degree. The same basic information can be obtained by time resolved techniques such as that developed by van der Waals et al.;³

however as a diagnostic tool for simply determining which sublevels are active in emission to particular vibrational bands it is usually more time consuming than relatively straightforward PMDR techniques. In this communication we would like to outline an additional PMDR method which retains the basic features of standard PMDR techniques but adds the advantages of time resolved spectroscopy.

Quadrature PMDR

It is well known that time-resolved spectroscopy can be executed in two ways. First is simply to measure the amplitude of a signal which has one or more sources as a function of time and decompose the signal into its frequency components. The second method is to measure the phase shift of a signal as a function of frequency. One standard example of the latter is called quadrature detection and is simply the measurement of the in-phase and out-of-phase components of a signal relative to a periodic perturbation. The application of quadrature methods to the determination of kinetic parameters in photochemical processes has been extensively developed by Johnston and co-workers.⁴ As will be demonstrated, it can be valuable in resolving phosphorescence components in much the same vein since the emission amplitude is intrinsically kinetically determined.

Let us treat the kinetics of a microwave induced change in triplet phosphorescence resulting from the saturation or inversion of the populations of two of the three triplet spin sublevels. Consider explicitly the case when the microwave pulse is short compared to any radiative or radiationless process and is applied repeatedly

every τ seconds in the presence of continuous exciting optical radiation. At the time of the pulse the phosphorescence intensity will acquire a new value because of the microwave induced population change and will relax back to some boundary value, determined by τ , as a function of the time, t , after the pulse. Differential equations of the intensity of phosphorescence induced by a microwave field connecting two spin sublevels τ_x and τ_y , under such condition can be solved and the solutions are given by Eqs. 1 through 2f.

$$I_{xy}(t) = k_x^r N_x(t) + k_y^r N_y(t). \quad (1)$$

With $0 < t < \tau$,

$$N_x(t) = c_1 e^{-k_x t} + \frac{k_x^I}{k_x} N_s, \quad (2a)$$

and

$$N_y(t) = c_2 e^{-k_y t} + \frac{k_y^I}{k_y} N_s, \quad (2b)$$

where the constants for saturation of the sublevel populations are

$$\begin{aligned} c_1 &= \alpha \Delta^{ss} / (1 + \alpha), \\ c_2 &= -\Delta^{ss} / (1 + \alpha); \end{aligned} \quad (2c)$$

or alternatively for adiabatic inversion of the sublevel populations,⁵

$$\begin{aligned} c_1 &= -\alpha f \Delta^{ss} / [\alpha(1-f) e^{-k_x \tau} - f e^{-k_y \tau} - \alpha], \\ c_2 &= f \Delta^{ss} / [\alpha(1-f) e^{-k_x \tau} - f e^{-k_y \tau} - \alpha]; \end{aligned} \quad (2d)$$

where

$$\Delta^{ss} = \left(\frac{k_y^I}{k_y} - \frac{k_x^I}{k_x} \right) N_s, \quad (2e)$$

$$\alpha = \frac{(1 - e^{-k_y \tau})}{(1 - e^{-k_x \tau})}, \quad (2f)$$

and f is the fraction of inversion, k_x^r and k_y^r are the radiative rate constants from the sublevels τ_x and τ_y respectively, k_x and k_y are the total triplet decay rate constants, k_x^I and k_y^I are the intersystem crossing rate constants, N_s is the excited singlet state population, and τ is the period between microwave pulses. Dividing the period τ into four equal parts of duration $\tau/4$, we define integrated microwave induced intensities in these periods as

$$q_1 = \int_0^{\tau/4} I_{xy}(t) dt, \quad (3)$$

$$q_2 = \int_{\tau/4}^{2\tau/4} I_{xy}(t) dt, \quad (4)$$

$$q_3 = \int_{2\tau/4}^{3\tau/4} I_{xy}(t) dt, \quad (5)$$

and

$$q_4 = \int_{3\tau/4}^{\tau} I_{xy}(t) dt. \quad (6)$$

Combinations of the quadrants q_1 through q_4 can be constructed which subtract random noise that is present and subtract all emission except that induced by the microwave field. Two such combinations are

$$Q_{0^\circ}^{xy} = q_1 + q_2 - q_3 - q_4 \quad (7)$$

and

$$Q_{90^\circ}^{xy} = -q_1 + q_2 + q_3 - q_4 \quad (8)$$

and represent two signals displaced by 90° from each other. From these two signals a general phase angle, ϕ , can be defined as

$$-\phi_v^{xy} = \tan^{-1} \left(Q_{0^\circ}^{xy} / Q_{90^\circ}^{xy} \right) \quad (9a)$$

$$= \tan^{-1} (\lambda) \quad (9b)$$

where the subscript v denotes the particular vibrational level in the ground singlet manifold to which phosphorescence is being monitored and the superscript denotes the two triplet spin sublevels being periodically perturbed with the microwave field. The phosphorescence intensity changes and the quadrants q_1 through q_4 are shown schematically in Figure 1.

The importance of these phase relationships in PMDR spectroscopy is that they are expected to be the same for measurements made monitoring phosphorescence to vibrational states of the same overall symmetry. They are also independent of microwave power, and hence to the degree of saturation of the magnetic sublevels, and to the polarization of the microwave transition moment. The difference in the magnitude of the phase angle and its functionality in τ for phosphorescence to singlet vibronic states of different symmetries is easily obtained.

Substitution of equations 1 and 2 into 3 through 6 and integration yields a closed analytic form for λ of Eq. 9b as:

$$\lambda = \frac{-C_x/C_y(1+e^{-k_x\tau}-2e^{-k_x\tau/2}) + (1+e^{k_y\tau}-2e^{-k_y\tau/2})}{\frac{C_x}{C_y}(e^{-k_x\tau}-2e^{-3k_x\tau/4}+2e^{-k_x\tau/4}) - (e^{-k_y\tau}-2e^{-3k_y\tau/4}-2e^{-k_y\tau/4} - 1)} \quad (10)$$

where

$$\frac{C_x}{C_y} = \alpha \left(\frac{k_x^r}{k_y^r} \frac{k_y}{k_x} \right) \quad (11)$$

The above equations assume the spin sublevels to be isolated and therefore neglect any spin-lattice relaxation effects. The same result (Eq.10) is obtained for saturating microwave pulses and inversion pulses as is expected in quadrature techniques since the phase angle is independent of the amplitude of a repetitive signal. This means that the phase angle is also independent of the extent of spin alignment in the magnetic sublevels. The important feature of Equations 10 and 11 is that the functionality of the phase angle is restricted to only ratios of radiative rate constants from the magnetic sublevels being connected by the microwave field since the total depletive rates k_x and k_y can be considered constant at any one temperature. Naturally C_x/C_y is different for vibrations of different overall symmetries because of selective spin-orbit plus vibronic and/or spin-vibronic coupling.

What is not so obvious, however, are the reasons why the phase angle is expected to be independent of a particular vibration being monitored so long as the overall symmetry of the vibrations remains constant.

Within the framework of the Born-Oppenheimer approximation, the ratio of the radiative rate constants (k_x^v/k_y^v) to vibrations of the same total symmetry are equal, since vibronic coupling within the triplet manifold affects all three spin sublevels equally and any differences in the nuclear potential functions of the spin sublevels caused by spin-orbit interactions are extremely small. Thus the Franck-Condon factors (f_i^v) in the ratio $k_x^v/k_y^v = k_x^{e\Gamma} f_x^v / k_y^{e\Gamma} f_y^v$ cancel and the ratio is determined by the ratio of the electronic contributions to the transition moment ($k_i^{e\Gamma}$) for a given symmetry Γ and polarization. Thus the ratios are independent of the particular vibration being monitored in PMDR provided the overall symmetry of the transition remains unchanged. Measurement of the phase angle should then allow one to separate vibrations according to their symmetries.

Experimental and Results

Trap phosphorescence from single crystals (zone refined - 200 passes at 2 inches/hr) of paradichlorobenzene (whose electronic origin at 1.3°K is 3588.3 Å) and s-tetrachlorobenzene (doped with 1% paradichlorobenzene to enhance Y-trap emission⁶) were investigated. The microwave perturbation used consisted of a frequency-modulated pulse (see Fig. 1) which resulted in an inversion of the magnetic sublevel populations via adiabatic fast passage. Larger signal changes could be obtained via inversion than by saturation. The duration of the pulse was only 100 μsec in order to ensure that the microwave perturbation could be considered

like a delta function as was assumed in Equation 2. The crystals were placed in a helical slow-wave structure to which microwaves of the appropriate frequency were applied. The crystal was continuously irradiated through the windings with the 2800 Å region of a Hg short arc isolated by a Schott uv 280 interference filter. The helical slow wave structure was supported in a dewar that was pumped to 1.2-1.3°K. The phosphorescence to the vibrational band under investigation was isolated at 90° angle to the incident exciting source by a 3/4 meter Jarrell-Ash spectrometer equipped with a cooled EMI 9856-QB photomultiplier. The photomultiplier was terminated in a 50 Ω load to insure a fast rise time to facilitate photon counting. Standard photon counting threshold-discriminated signals were gated such that four quadrants of Equations 3-6 could be obtained on separate channels. Reversible up-down counters then performed the additions and subtractions of Equations 7 and 8 and the differences were displayed on separate channels of a dual recorder after averaging for a suitable prescribed number of periods of length τ . In this manner the absolute errors could be determined from photon counting statistics.

For convenience the values of λ are presented rather than the phase angle (Cf. Equation 9) because the observed differences are numerically larger. The errors listed in Table I are the standard deviations obtained from counting statistics. Errors for the 25 ms period are higher due to greater fluctuations in the exciting source intensity at frequencies ~ 40 cps and the fact that the absolute intensity change due to the microwave perturbation is small at high modulation frequencies (see Eq. 2).

Table I

The values of λ (Eq. 9b) obtained for various phosphorescence bands and τ values.

paradichlorobenzene (D- E) ⁷					
$\lambda(\text{\AA})$	$\Gamma_{D_{2h}}^v$	$\tau(\text{ms})$			
		25	50	100	200
3586	$a_1 (0,0)$	8.80 ± 0.14	4.04 ± 0.03	-	-
3688	a_1	8.46 ± 0.10	3.98 ± 0.03	-	-
3628	b_{2g}	9.34 ± 0.16	4.37 ± 0.04	-	-
3711	b_{2g}	9.07 ± 0.12	4.26 ± 0.04	-	-
3804	b_{3g}	10.25 ± 0.35	4.80 ± 0.04	-	-
s-tetrachlorobenzene (D+ E) ⁶					
2754	a_1	6.16 ± 0.37	3.11 ± 0.03	1.60 ± 0.01	0.87 ± 0.01
3821	$a_1(2xb_{2g})$	6.92 ± 0.18	3.40 ± 0.02	1.83 ± 0.01	1.11 ± 0.01
3788	b_{2g}	7.76 ± 0.10	3.66 ± 0.10	2.12 ± 0.01	1.18 ± 0.01
3888	b_{2g}	7.31 ± 0.15	3.51 ± 0.05	1.88 ± 0.01	1.17 ± 0.01

The data in Table I for paradichlorobenzene clearly show the separation of bands of different symmetry via quadrature PMDR even though the lifetimes of the two connected levels are quite different (35 ms and 700 ms). The data for s-tetrachlorobenzene are not as good in terms of separation or constancy for a given symmetry. This is probably in part due to the fact that the populations of the trap sublevels are dependent to a great extent on exciton deactivation.⁸ This results in a non-exponential decay (and buildup) for the traps while Eqs. 1 and 2 are derived assuming simple exponential behavior.

Table II shows an example of a quantitative comparison of experimental and calculated data (Eq. 10) for the s-tetrachlorobenzene $2|E|$ transition monitoring the origin. The value of k_x^r/k_y^r for the origin was experimentally determined by decay techniques³ to be ~5, indicating mixed emission. The data were calculated using this value and various combinations of lifetimes, with values of ~20 ms giving the best overall fit. These lifetimes are shorter than those experimentally determined (~25 ms) by decay techniques.³ The overall fit is good with the largest error at high modulation frequencies.

Discussion

As a routine technique for distinguishing vibrational symmetries and determining rate constants, the method suffers some shortcomings. These can be illustrated by considering two limiting cases of Eq. 10. If the total lifetimes of the two magnetic sublevels being connected

Table II

λ -value for s-tetrachlorobenzene 2|E| Transition ⁶

$\tau(\text{ms})$	Calculated ^a	Observed
25	6.49	5.71
50	3.32	3.16
100	1.81	1.85
200	1.18	1.20

^a $\tau_x = 18 \text{ ms}$, $\tau_y = 19.5 \text{ ms}$, and $k_x^r, k_y^r = 4.5$; see Eqs. 10 and 11.

by a microwave field are equal or very different, i.e., $k_x \gg k_y$, Eq. 10 is reduced to

$$\lambda = \frac{-(1 + e^{-k_y \tau} - 2e^{-k_y \tau/2})}{(e^{-k_y \tau} - 2e^{-3k_y \tau/4} + 2e^{-k_y \tau/4} - 1)} \quad (12)$$

and unfortunately is independent of any radiative rate constant ratios.

This means that the phase angle is the same for all vibrations.

In many aromatic molecules, particularly those with higher symmetries, the rate process in phosphorescence approaches the limits leading to Eq. 12; consequently, great care must be exercised in measuring the phase angle since the differences are expected to be small. Large differences in the phase angle are expected, however, in intermediate cases.

Although the factors described above may limit the utility of quadrature techniques in PMDR, the general form of the τ dependence of ϕ can yield useful information. As the modulation period τ is made longer than the sublevel lifetimes the value of λ (Eq. 9b) approaches unity; however, the value of ϕ for a given τ will be larger for emission from a sublevel with a short lifetime than from one with a long lifetime. This can provide information as to which sublevel is most active in emission. This information used in conjunction with polarization data can be useful in determining assignments. Such information may be difficult to obtain from simple decay measurements in cases where the lifetimes of the levels are nearly equal. In these cases quadrature techniques are particularly attractive since ϕ is independent of the magnitude of the population differences between sublevels. Thus

data obtained from all three zero field microwave transitions can be compared without worrying about the complications introduced by the lack of uniform microwave induced population changes. This is only true, however, when the spin sublevels can be considered independent. This is equivalent to neglecting spin-lattice relaxation effects. If spin-lattice relaxation is included in the derivation of Eq. 10, the phase angle ϕ is found to be dependent on the degree of spin alignment since the rate of population equilibration depends on the population difference between sublevels. Thus, one expects to find a dependence of ϕ on the degree of saturation or inversion. The equations describing ϕ are complex and will not be presented here. We wish only to point out that the quadrature method may provide a new tool for directly studying spin-lattice relaxation effects or other phenomena such as exciton averaging of triplet state sublevel populations. A study of ϕ versus saturating power, for example, may show deviations which would indicate whether or not such relaxation processes are important. Quantitative evaluation, however, of these effects is made difficult by the complexity of the differential equations describing coupled spin sublevels.

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Figure Caption

- Figure 1 . (a) Periodic modulation of phosphorescence intensity (I_p) caused by delta-function microwave pulses at $t = n\tau$, $n = 1, 2, \dots$.
- (b) Breakdown of the modulation period τ into four quadrants. The perturbing microwave pulse is applied during a short time (heavy vertical line) at the beginning of each cycle.

Fig. 1

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