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Theory of Photoselection for Zeeman Split Phosphorescence

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General equations applicable to photoselection experiments for Zeeman split phosphorescence are derived. The general equations are also extended to the cases where excitation and observation are effected with unpolarized light, and expressions for the ratio of phosphorescence intensities of the three split subcomponents are obtained. Some comments on experimentation are made.

As reported previously,[1,2] we have succeeded in observing the Zeeman splitting of the phosphorescence of pyrazine. By measuring the phosphorescence intensities of the three Zeeman split components, one is able to obtain matrix elements connecting the ground state and all of the three triplet subcomponents. An example of such treatment has been given in a previous paper for the pyrazine phosphorescence.[2] For more detailed analyses, an experiment under polarized light is necessary. Such polarization measurements, conjoined with the Zeeman effect, will provide us with invaluable information on the nature of spin subcomponents, the manner in which the triplet state acquires the singlet character, effect of coupled vibrations, and so on.

The methods for polarization measurements are divided into two major classes. In one method one uses an oriented sample such as single crystal. In the other, called the method of photoselection, samples of random orientation are used. The former method is usually considered superior in a sense that it provides the polarization nature uniquely. However, the use of single crystals, the very necessary condition for this method, limits the actual application for the following reasons: First, the crystal structure, especially the arrangement of molecules in a unit cell, is not known for a majority of organic molecular crystals. Second, it is extremely difficult to retain a relatively large single crystal uncracked at liquid helium temperature. Finally, most important and crucial of all, many organic molecules do not exhibit phosphorescence in pure crystalline states. This is especially relevant for molecules whose lowest triplet state is of π, π^* nature.[3] Any molecular phosphorescence for molecules of this class should therefore be investigated in solutions or in mixed crystals. Because of the three difficulties associated with the single crystal experiments the method of photoselection acquires greater importance. The general equations which have been used for photoselection work are, however, not valid when external magnetic field is applied. It is consequently required that the theory of photoselection be extended to include the effect of magnetic field. In this paper, general equations applicable to photoselection experiments for the Zeemen split phosphorescence are derived. The general equations and the manner of their derivation are of importance not only for the polarization work but also for ordinary Zeeman effect experiments with unpolarized light because the latter should be treated as a special case of the former.

Theoretical

1) Effect of Magnetic Field on the Phosphorescence Intensities. The effect of magnetic field on the triplet state of organic molecules was treated in a previous paper;[2] consequently, only the essence is outlined here.

Let the lowest triplet state be produced by an excitation of an electron from a molecular orbital ϕ_a to a molecular orbital ϕ_b. We choose the following zeroth order triplet eigenfunctions.

$$\left.\begin{aligned} |T_x> &= 2^{-1/2}(|\overline{\phi}_a\overline{\phi}_b| - |\phi_a\phi_b|) \\ |T_y> &= 2^{-1/2}(|\overline{\phi}_a\overline{\phi}_b| + |\phi_a\phi_b|) \\ |T_z> &= 2^{-1/2}(|\phi_a\overline{\phi}_b| + |\overline{\phi}_a\phi_b|) \end{aligned}\right\} \tag{1}$$

The Hamiltonian for Zeeman effect is represented by

$$\mathscr{H} = g\beta H(lS_x + mS_y + nS_z) \tag{2}$$

where l, m, and n are direction cosines of molecular axes, x, y and z, respectively, with the field direction. Further, the zero field splitting parameters D and E are neglected. This assumption

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[1] T. Azumi, Y. Udagawa, M. Ito and S. Nagakura, *J. Chem. Phys.*, **47**, 4850 (1967).

[2] T. Azumi, M. Ito and S. Nagakura, This Bulletin, **42**, 685 (1969).

[3] H. Sternlicht, G. C. Nieman and G. W. Robinson, *J. Chem. Phys.*, **38**, 1326 (1963).

may roughly be justified for many organic molecules when magnetic field is larger than, say, 15 kG. (See a previous paper[2]) When magnetic field is applied, triplet wave functions $|T_1>$, $|T_0>$ and $|T_{-1}>$ are now represented in terms of (1) as

$$\begin{pmatrix} |T_1> \\ |T_0> \\ |T_{-1}> \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1-l^2}{2}} & \frac{n+ilm}{\sqrt{2(1-l^2)}} & \frac{-(nl+im)}{\sqrt{2(1-l^2)}} \\ l & im & n \\ \sqrt{\frac{1-l^2}{2}} & \frac{n-ilm}{\sqrt{2(1-l^2)}} & \frac{-(nl-im)}{\sqrt{2(1-l^2)}} \end{pmatrix} \begin{pmatrix} |T_x> \\ |T_y> \\ |T_z> \end{pmatrix} \tag{3}$$

The spin-orbit interaction which allows spin-forbidden triplet-singlet transitions is approximated as

$$\mathscr{H}_{so} = \sum_i \xi_i l_i S_i \tag{4}$$

where two electron operators are neglected. Then, the singlet state which may mix with the triplet state is only of the type

$$|S> = 2^{-1/2}(|\phi_a\overline{\phi_c}| + |\phi_c\overline{\phi_a}|) \tag{5}$$

The matrix elements for the spin-orbit interaction betwen the singlet and the triplet states are now obtained as follows:

$$\begin{pmatrix} <S|\mathscr{H}_{so}|T_1> \\ <S|\mathscr{H}_{so}|T_0> \\ <S|\mathscr{H}_{so}|T_{-1}> \end{pmatrix} = \frac{\hbar}{2}\xi \begin{pmatrix} -\sqrt{\frac{1-l^2}{2}} & i\,\frac{n+ilm}{\sqrt{2(1-l^2)}} & \frac{nl+im}{\sqrt{2(1-l^2)}} \\ -l & -m & -n \\ -\sqrt{\frac{1-l^2}{2}} & i\,\frac{n-ilm}{\sqrt{2(1-l^2)}} & \frac{nl-im}{\sqrt{2(1-l^2)}} \end{pmatrix} \begin{pmatrix} <\phi_c|l_x|\phi_b> \\ <\phi_c|l_y|\phi_b> \\ <\phi_c|l_z|\phi_b> \end{pmatrix} \tag{6}$$

Let the phosphorescence intensities from the three subcomponents, $|T_1>$, $|T_0>$ and $|T_{-1}>$ be denoted by I_1 I_0, and I_{-1}. Then from (6)

$$\begin{pmatrix} I_1/g_1 \\ I_0/g_0 \\ I_{-1}/g_{-1} \end{pmatrix} = c \begin{pmatrix} \frac{1-l^2}{2} & \frac{1-m^2}{2} & \frac{1-n^2}{2} \\ l^2 & m^2 & n^2 \\ \frac{1-l^2}{2} & \frac{1-m^2}{2} & \frac{1-n^2}{2} \end{pmatrix} \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix} \tag{7}$$

where c is a proportionality constant, g's represent the Boltzmann populations of the respective components, and further, u_x, u_y and u_z represent the contribution to intensity from l_x, l_y and l_z in spin-orbit coupling (4).

2) Theory of Photoselection: Incorporation of the Effect of Magnetic Field. Theory of photoselection was presented in an elegant manner by Albrecht.[4] We shall closely follow his presentation, and here merely incorporate the effect of magnetic field.

We choose the two coordinate sets, the molecule-fixed set (x, y, z) and the laboratory-fixed set (a, b, c). Assigning these a common origin we then specify the orientation of a molecule in laboratory using Eulerian angles, θ, ϕ and ψ. The cosines of the angles between the axes of the two coordinates are

	x	y	z
a	$\cos\theta$	$\sin\theta\sin\psi$	$\sin\theta\cos\psi$
b	$\sin\theta\sin\phi$	$\cos\phi\cos\psi-\cos\theta\sin\phi\sin\psi$	$-\cos\phi\sin\psi-\cos\theta\sin\phi\cos\psi$
c	$-\sin\theta\cos\phi$	$\sin\phi\cos\psi+\cos\theta\cos\phi\sin\psi$	$-\sin\phi\sin\psi+\cos\theta\cos\phi\cos\psi$

These nine direction cosines are abbreviated as, for example, t_{ax}.

The experimental arrangement is shown schematically in Fig. 1. Namely, excitation is effected with the light incident along b axis onto ac face, polarized along a axis by an amount p and along c axis 1-p. The magnetic field is applied along c axis. The emitted phosphorescence may be viewed along a axis or along c axis. In the latter case, the Faraday rotarion may affect the polarization values. Hence, we had better avoid observation from c axis when magnetic field is large enough to cause the Faraday rotation.

We assume that at a given wavelength absorption takes place in x, y and z axes of the molecule

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[4] A. C. Albrecht, *J. Mol. Spectroscopy*, **6**, 84 (1961).

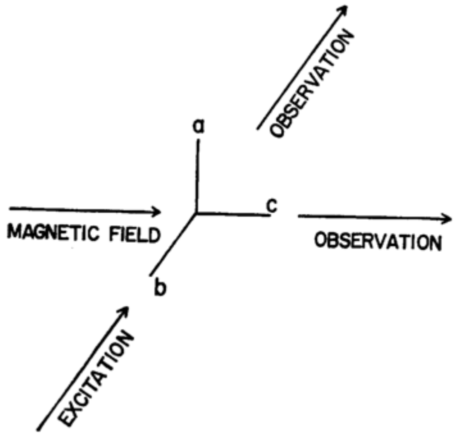

Fig. 1. Experimental arrangement.

with the fraction of r_x, r_y and r_z, respectively. Similarly, we assume that at a given wavelength the phosphorescence is polarized along x, y, and z axes with the fraction of q_x, q_y and q_z, respectively.

Now, the probability that a molecule at θ, ϕ and ψ is photoexcited is given by

$$p[r_x t_{ax}^2 + r_y t_{ay}^2 + r_z t_{az}^2] + (1-p)[r_x t_{cx}^2 + r_y t_{cy}^2 + r_z t_{cz}^2]$$

and the probability for viewing with light polarized, say, along a is

$$q_x t_{ax}^2 + q_y t_{ay}^2 + q_z t_{az}^2$$

with analogous expressions for viewing along b and c axes. Unsplit phosphorescence intensities are proportional to the product of these two expressions. In the presence of magnetic field, these quantities are split up according to (7). Namely, for I_1 and I_{-1} the above product is further multiplied by

$$g_{\pm1}\left[\frac{1-l^2}{2}u_x + \frac{1-m^2}{2}u_y + \frac{1-n^2}{2}u_z\right]$$

and for I_0

$$g_0[l^2 u_x + m^2 u_y + n^2 u_z]$$

where $l = t_{cx}$, $m = t_{cy}$ and $n = t_{cz}$. In the sample of random orientation we integrate the product of the three expressions over Eulerian angles:

$$\int_0^{2\pi} \mathrm{d}\phi \int_0^{2\pi} \mathrm{d}\psi \int_0^{\pi} \sin\theta \,\mathrm{d}\theta$$

3) Results. Integration of the expressions described above yields the following results. Here, A, B, and C denote the phosphorescence intensities polarized along a, b and c axes, respectively. The subscript $+1$, 0 and -1 indicate the phosphorescence subcomponents.

$$\left.\begin{aligned}
A_0 = g_0\boldsymbol{r}\bigg[u_x\bigg\{p\begin{bmatrix}6&4&4\\4&18&6\\4&6&18\end{bmatrix} + (1-p)\begin{bmatrix}4&20&18\\6&2&6\\4&6&4\end{bmatrix}\bigg\} + u_y\bigg\{p\begin{bmatrix}18&4&6\\4&6&4\\6&4&18\end{bmatrix}\\
+ (1-p)\begin{bmatrix}6&2&6\\16&8&18\\6&4&4\end{bmatrix}\bigg\} + u_z\bigg\{p\begin{bmatrix}18&6&4\\6&18&4\\4&4&6\end{bmatrix} + (1-p)\begin{bmatrix}4&6&4\\6&4&4\\18&18&6\end{bmatrix}\bigg\}\bigg]\boldsymbol{q}\\
B_0 = g_0\boldsymbol{r}\bigg[u_x\bigg\{p\begin{bmatrix}4&4&6\\4&8&16\\6&16&6\end{bmatrix} + (1-p)\begin{bmatrix}4&20&18\\6&2&6\\4&6&4\end{bmatrix}\bigg\} + u_y\bigg\{p\begin{bmatrix}4&8&16\\8&0&6\\16&6&6\end{bmatrix}\\
+ (1-p)\begin{bmatrix}6&2&6\\16&8&18\\6&4&4\end{bmatrix}\bigg\} + u_z\bigg\{p\begin{bmatrix}6&16&6\\16&6&6\\6&6&2\end{bmatrix} + (1-p)\begin{bmatrix}4&6&4\\6&4&4\\18&18&6\end{bmatrix}\bigg\}\bigg]\boldsymbol{q}\\
C_0 = g_0\boldsymbol{r}\bigg[u_x\bigg\{p\begin{bmatrix}4&6&4\\20&2&6\\18&6&4\end{bmatrix} + (1-p)\begin{bmatrix}34&2&6\\2&10&2\\6&2&6\end{bmatrix}\bigg\} + u_y\bigg\{p\begin{bmatrix}6&16&6\\2&8&4\\6&18&4\end{bmatrix}\\
+ (1-p)\begin{bmatrix}2&10&2\\10&26&6\\2&6&6\end{bmatrix}\bigg\} + u_z\bigg\{p\begin{bmatrix}4&6&18\\6&4&18\\4&4&6\end{bmatrix} + (1-p)\begin{bmatrix}6&2&6\\2&6&6\\6&6&30\end{bmatrix}\bigg\}\bigg]\boldsymbol{q}\\
A_{\pm1} = g_{\pm1}\boldsymbol{r}\bigg[u_x\bigg\{p\begin{bmatrix}18&5&5\\5&12&4\\5&4&12\end{bmatrix} + (1-p)\begin{bmatrix}5&4&5\\11&6&11\\12&11&5\end{bmatrix}\bigg\} + u_y\bigg\{p\begin{bmatrix}12&5&4\\5&18&5\\4&5&12\end{bmatrix}\\
+ (1-p)\begin{bmatrix}4&13&11\\6&3&5\\11&12&5\end{bmatrix}\bigg\} + u_z\bigg\{p\begin{bmatrix}12&4&5\\4&12&5\\5&5&18\end{bmatrix} + (1-p)\begin{bmatrix}5&11&12\\11&5&12\\5&5&4\end{bmatrix}\bigg\}\bigg]\boldsymbol{q}\\
B_{\pm1} = g_{\pm1}\boldsymbol{r}\bigg[u_x\bigg\{p\begin{bmatrix}5&12&11\\12&3&6\\11&6&4\end{bmatrix} + (1-p)\begin{bmatrix}5&4&5\\11&6&11\\12&11&5\end{bmatrix}\bigg\} + u_y\bigg\{p\begin{bmatrix}5&10&6\\10&7&11\\6&11&4\end{bmatrix}\\
+ (1-p)\begin{bmatrix}4&13&11\\6&3&5\\11&12&5\end{bmatrix}\bigg\} + u_z\bigg\{p\begin{bmatrix}4&6&11\\6&4&11\\11&11&6\end{bmatrix} + (1-p)\begin{bmatrix}5&11&12\\11&5&12\\5&5&4\end{bmatrix}\bigg\}\bigg]\boldsymbol{q}\\
C_{\pm1} = g_{\pm1}\boldsymbol{r}\bigg[u_x\bigg\{p\begin{bmatrix}5&11&12\\4&6&11\\5&11&5\end{bmatrix} + (1-p)\begin{bmatrix}4&6&4\\6&16&6\\4&6&18\end{bmatrix}\bigg\} + u_y\bigg\{p\begin{bmatrix}4&6&11\\13&3&12\\11&5&5\end{bmatrix}\\
+ (1-p)\begin{bmatrix}20&2&6\\2&8&4\\6&4&18\end{bmatrix}\bigg\} + u_z\bigg\{p\begin{bmatrix}5&11&5\\11&5&5\\12&12&4\end{bmatrix} + (1-p)\begin{bmatrix}18&6&4\\6&18&4\\4&4&6\end{bmatrix}\bigg\}\bigg]\boldsymbol{q}
\end{aligned}\right\} \qquad (8)$$

where

$$\boldsymbol{r} = [r_x \ r_y \ r_z]$$

and

$$\boldsymbol{q} = \begin{bmatrix} q_x \\ q_y \\ q_z \end{bmatrix}$$

Hence of cource

$$\boldsymbol{r}\begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix}\boldsymbol{q} = \begin{array}{l} c_{11}r_xq_x + c_{12}r_xq_y + c_{13}r_xq_z \\ +c_{21}r_yq_x + c_{22}r_yq_y + c_{23}r_yq_z \\ +c_{31}r_zq_x + c_{32}r_zq_y + c_{33}r_zq_z \end{array}$$

Extension to Unpolarized Work

The general equations derived above may readily be extended to the cases where both excitation and observation are made with unpolarized light. The results for two different observations are as follows.

(1) Straight view (observation along b axis)

$$\left.\begin{aligned} I_0 &= g_0\boldsymbol{r}\left\{u_x\begin{bmatrix} 24 & 16 & 16 \\ 16 & 16 & 10 \\ 16 & 10 & 16 \end{bmatrix} + u_y\begin{bmatrix} 16 & 16 & 10 \\ 16 & 24 & 16 \\ 10 & 16 & 16 \end{bmatrix} + u_z\begin{bmatrix} 16 & 10 & 16 \\ 10 & 16 & 16 \\ 16 & 16 & 24 \end{bmatrix}\right\}\boldsymbol{q} \\ I_{\pm1} &= g_{\pm1}\boldsymbol{r}\left\{u_x\begin{bmatrix} 16 & 13 & 13 \\ 13 & 20 & 16 \\ 13 & 16 & 20 \end{bmatrix} + u_y\begin{bmatrix} 20 & 13 & 16 \\ 13 & 16 & 13 \\ 16 & 13 & 20 \end{bmatrix} + u_z\begin{bmatrix} 20 & 16 & 13 \\ 16 & 20 & 13 \\ 13 & 13 & 16 \end{bmatrix}\right\}\boldsymbol{q} \end{aligned}\right\} \quad (9)$$

(2) Side view (observation along c axis)

$$\left.\begin{aligned} I_0 &= g_0\boldsymbol{r}\left\{u_x\begin{bmatrix} 9 & 24 & 23 \\ 10 & 15 & 17 \\ 9 & 17 & 16 \end{bmatrix} + u_y\begin{bmatrix} 17 & 8 & 17 \\ 22 & 11 & 23 \\ 17 & 9 & 16 \end{bmatrix} + u_z\begin{bmatrix} 16 & 17 & 9 \\ 17 & 16 & 9 \\ 23 & 23 & 10 \end{bmatrix}\right\}\boldsymbol{q} \\ I_{\pm1} &= g_{\pm1}\boldsymbol{r}\left\{u_x\begin{bmatrix} 16.5 & 12.5 & 13 \\ 19.5 & 13.5 & 16 \\ 20 & 16 & 13 \end{bmatrix} + u_y\begin{bmatrix} 12.5 & 20.5 & 16 \\ 13.5 & 15.5 & 13 \\ 16 & 20 & 13 \end{bmatrix} + u_z\begin{bmatrix} 13 & 16 & 20 \\ 16 & 13 & 20 \\ 13 & 13 & 16 \end{bmatrix}\right\}\boldsymbol{q} \end{aligned}\right\} \quad (10)$$

The above equations determine the ratio of the three split phosphorescence subcomponents when neither polarizer nor analyser is used. It is to be noted that the ratio is not simply a ratio of the Boltzmann populations.

An Example: Predictions for Pyrazine Phosphorescence

Because of the complexity of the general equations it may not be very clear as to how the polarization is affected by magnetic field. From this viewpoint, we shall take pyrazine phosphorescence as an example and illustrate how the phosphorescence intensities are divided among the three subcomponents and how the polarization values are affected by magnetic field.

Group theoretical consideration²⁾ predicts $u_y=1$ and $q_z=1$ for 0, 0 band of the pyrazine phosphorescence. (For details see a previous paper.²⁾) Polarization observed by Krishna and Goodman⁵⁾ is in agreement with this prediction. The molecular axes are defined as recommended by Mulliken.⁶⁾ Namely, z axis lies in the molecular plane on the N-N axis and x axis is normal to the molecular plane. We consider two different wavelength regions of excitation, one for $^1B_{2u}$ (π, π^*) state (at 37839 cm^{-1}) and the other for $^1B_{3u}$ (n, π^*) state (at 30776 cm^{-1}). Further, we consider the case in which the exciting light is polarized either along a axis (vartical excitation) or along c axis (horizontal excitation).

In Fig. 2 are shown predicted phosphorescence intensities polarized either along a, b, or c axis under the four different modes of excitation. The length of the vertical lines and the numbers specified indicate the phosphorescence intensities divided by the population of the upper level. It is immediately seen how zero field intensities are split up into three subcomponents under the presence of magnetic field. Shown also in Fig. 2 are the values of polarization for straight view and for

TABLE 1. PREDICTED INTENSITY RATIO OF THE THREE PHOSPHORESCENCE SUBCOMPONENTS FOR PYRAZINE

	$I_1 : I_0 : I_{-1}$	
Excitation	Straight view	Side view
$^1B_{3u}(n, \pi^*)$	$16g_1 : 10g_0 : 16g_{-1}$	$16g_1 : 17g_0 : 16g_{-1}$
$^1B_{2u}(\pi, \pi^*)$	$13g_1 : 16g_0 : 13g_{-1}$	$13g_1 : 23g_0 : 13g_{-1}$
$^1B_{1u}(\pi, \pi^*)$	$20g_1 : 16g_0 : 20g_{-1}$	$13g_1 : 16g_0 : 13g_{-1}$

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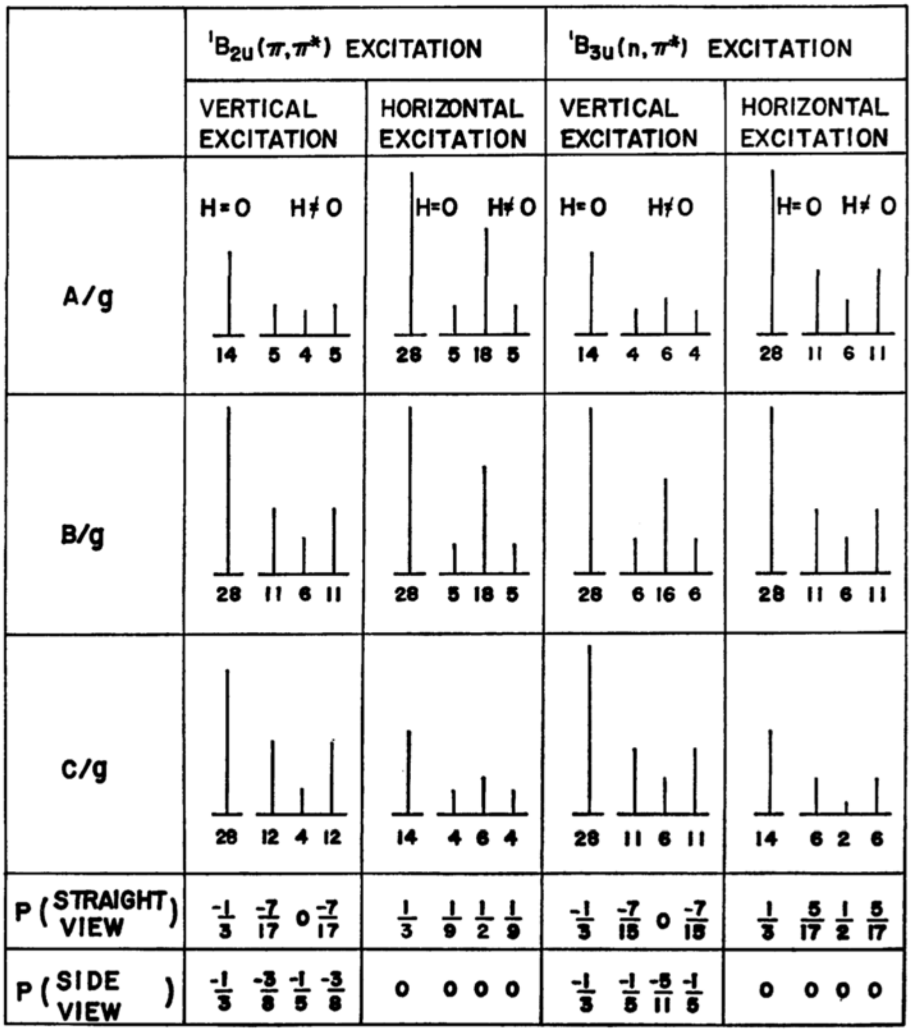
5) V. G. Krishna and L. Goodman, *J. Chem. Phys.*, **36**, 2217 (1961).

6) R. S. Mulliken, *ibid.*, **23**, 1997 (1955).



	$^1B_{2u}(\pi,\pi^*)$ EXCITATION		$^1B_{3u}(n,\pi^*)$ EXCITATION	
	VERTICAL EXCITATION	HORIZONTAL EXCITATION	VERTICAL EXCITATION	HORIZONTAL EXCITATION
	H=0　H≠0	H=0　H≠0	H=0　H≠0	H=0　H≠0
A/g	14　5 4 5	28　5 18 5	14　4 6 4	28　11 6 11
B/g	28　11 6 11	28　5 18 5	28　6 16 6	28　11 6 11
C/g	28　12 4 12	14　4 6 4	28　11 6 11	14　6 2 6
P (STRAIGHT VIEW)	$\frac{-1}{3}$　$\frac{-7}{17}$ 0 $\frac{-7}{17}$	$\frac{1}{3}$　$\frac{1}{9}$ $\frac{1}{2}$ $\frac{1}{9}$	$\frac{-1}{3}$　$\frac{-7}{15}$ 0 $\frac{-7}{15}$	$\frac{1}{3}$　$\frac{5}{17}$ $\frac{1}{2}$ $\frac{5}{17}$
P (SIDE VIEW)	$\frac{-1}{3}$　$\frac{-3}{8}$ $\frac{-1}{5}$ $\frac{-3}{8}$	0　0 0 0	$\frac{-1}{3}$　$\frac{-1}{5}$ $\frac{-5}{11}$ $\frac{-1}{5}$	0　0 0 0

Fig. 2. Predicted phosphorescence intensities and polarizations for pyrazine phosphorescence under different modes of excitation (see the text).

side view. It is amazing to see how fertile informations are obtained by applying magnetic field. It is exactly for this reason that the polarization measurements under magnetic field are recommended. The predicted ratio of the phosphorescence intensities for unpolarized work is summarized in Table 1. A part of this result has been already presented in a previous paper.

Some Comments on Experimentation

The present paper aims only at presenting general equations which may be of use in ideal photoselection experiments. Whether or not ideal conditions for photoselection experiments are satisfied in reality and how to solve any difficulties that might occur is another question. We have not made any considerable effort in this regard so far; however, in the following, we point out our views on experimentation.

One of the difficulties inherent to polarization experiments is due to improper polarization caused by the apparatus. This difficulty is readily overcome in a similar manner to Azumi and McGlynn,⁷⁾ and Russel and Albrecht⁸⁾ calibrated their apparatus for improper polarization effect in ordinary (*i. e.*, without magnetic field) photoselection experiments. The correction involves a repetition of the experiment keeping everything unchanged except for the excitation which is effected horizontally and emission is observed from the side. Theoretically, the emission should in this case be unpolarized. This is easily seen

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7) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).

8) P. G. Russell and A. C. Albrecht, *ibid.*, **41**, 2536 (1964).

from the fact that in the general equations (8) equating p to zero necessarily yields $A=B$ for all three phosphorescence subcomponents. Any observed polarization should, consequently, be regarded as due to instrumentation, and is served for the correction factor. Further, by observing this correction factor by varying the strength of magnetic field, one may be able to see, though indirectly, the effect of Faraday rotation.

Another difficulty in photoselection experiment is that one has to work with samples of random orientation. Further, the sample should be strain-free. In this connection, it is noted that in the Zeeman effect experiment, one has to lower the temperature to liquid helium temperature to narrow the bandwidth, since the Zeeman splitting at 50 kG may only amount to 5—6 cm^{-1}. Rigid glass solvents which may be used at liquid helium temperature are shown in Table 2. These media have been reported to form transparent glass at 4.2°K, but it is uncertain whether or not they are strain-free. Furthermore, it is doubtful if bandwidth becomes sufficiently narrow in these media. In fact, according to Armstrong,⁹⁾ in the isopentane-3-methylpentane mixed solvent no significant band narrowing has been attained by lowering temperature down to 4.2°K. In this regard, one may also try some rare gas matrices such as neon and xenon¹⁰⁾ and also so called "Shpolskii's solvents" such as cyclohexane and carbon tetrachloride¹¹⁾ even though they are best considered polycrystalline.

TABLE 2. RIGID GLASS SOLVENTS AT 4.2°K

Solvent	Reference
Isopentane + 3-Methylpentane (6 : 1 in volume)	9
Silicone (Dow-Corning 200 with 10^6 cs viscosity)	9
Trifluorobromomethane	12

Test of various solvents for use of photoselection experiments at liquid helium temperature is being attempted and will be reported in future publications.

We wish to express our appreciation to Professor Mitsuo Ito for constant encouragement and invaluable discussions.

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9) A. T. Armstrong, private communications to T. A. (1968).

10) G. W. Robinson, *J. Mol. Spectroscopy*, **6**, 58 (1961).

11) E. V. Shpol'skii, *Soviet Phys. Usp.*, **5**, 522 (1963).

12) F. E. Dörr, *Angew. Chem.*, **78**, 457 (1966).