The Faraday Effect

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1 Introduction

In the diary of Michael Faraday the following entry appears dated 13th September, 1845.[1]

'Today worked with lines of magnetic force, passing them across different bodies (transparent in different directions) and at the same time passing a polarised ray of light through them . . .

A piece of heavy glass which was 2 inches by 1.8 inches, and 0.5 of an inch thick, being a silico borate of lead, and polished on the two shortest edges, was experimented with. It gave no effects when the same magnetic poles or the contrary poles were on opposite sides (as respects the course of the polarized ray)—nor when the same poles were on the same side, either with the constant or intermitting current—BUT, when contrary magnetic poles were on the same side, there was an effect produced on the polarized ray, and thus magnetic force and light were proved to have relation to each other. This fact will most likely prove exceeding fertile and of great value in the investigation of both conditions of natural force.'

With this and subsequent experiments, Faraday and later workers demonstrated that the plane of polarisation of linearly polarised light is rotated on passage through any substance placed in a magnetic field with non-zero component in the direction of the light beam. In brief, a longitudinal magnetic field made all substances appear optically active.

Although these first observations were made over a century ago, the Faraday effect has until very recently found relatively little application to chemical systems, at least in comparison with natural optical activity which had early triumphs in both organic and inorganic chemistry and has enjoyed tremendous popularity in recent years with the development of techniques for making measurements over a wide range of frequencies, particularly through absorption bands. It is the purpose of this Review to emphasise the recent revival of interest in Faraday effect studies and to demonstrate in some detail that such studies can be a very powerful means for clarifying spectroscopic assignments and characterising the symmetry and angular momentum properties of both ground and excited states of molecules and ions. We shall confine our attention to the visibile–u.v. spectral region and chiefly to molecules and ions of 'chemical interest'. Thus we will not discuss applications to systems such as ferrites, semiconductors and metals nor the use of the effect in light modulation.

[1] Faraday's Diary, vol. IV, G. Bell and Sons Ltd., London, 1933.

References 2—5 give reviews of the extensive early Faraday work. A detailed theoretical understanding of the effect, especially through the work of Rosenfeld, Kramers, and Serber, came only with the development of quantum mechanics. However, these workers confined their attention to regions outside absorption bands. Only much more recently have treatments of regions of absorption appeared.[6-9] The most detailed are those of Stephens[8] and Shen.[9] An excellent review article on the Faraday effect by Buckingham and Stephens has recently appeared.[10] These authors give a detailed theoretical treatment of the dispersion of the Faraday effect through absorption bands and cover the literature through most of 1965. Despite the recent date of the Buckingham and Stephens article, another review seems timely because there has been a great burst of activity which has clearly confirmed their assertion that the dispersion of the Faraday effect through absorption bands, 'should become an important tool in spectral analysis and the investigation of molecular structure'. The present article will concentrate on the work done since the above-mentioned article.

Before developing the theory of the Faraday effect in molecules, we digress for a moment to compare and contrast the Faraday effect with other phenomena. Although substances in a magnetic field appear to be optically active, the relationship with natural optical activity is not straightforward. In both phenomena the same quantities are measured as a function of frequency, namely, the difference in the refractive indices for left and right circularly polarised light (which manifests itself as the angle of rotation of plane polarised light) or the difference in absorption coefficients for left and right circularly polarised light. The former is the optical rotatory dispersion (o.r.d.) and the latter is the circular dichroism (c.d.). In natural optical activity the dissymmetry of the molecules causes the electrons to move in a helical path on excitation[11] which may then absorb left circularly polarised light to a greater or lesser extent than right depending upon the 'handedness' of the helix. In magnetic optical activity, left and right circularly polarised photons no longer interact equivalently with an absorbing medium in the presence of a magnetic field. Thus we should not anticipate the same direct relation between magnetic optical activity and molecular stereochemistry which we find in natural optical activity.

The Faraday effect is however closely related to another well-known phenomenon which arises from the interaction of magnetic fields with matter, namely the Zeeman effect. As an illustration, let us consider the Zeeman effect

[2] R. W. Wood, 'Physical Optics,' Macmillan, New York, 1934, 3rd edn., ch. 21.

[3] W. Schütz, 'Magnetooptik (Handbuch der Experimental physik)', Akademische Verlagsgesellschaft, Leipzig, 1936, vol. 16.

[4] J. R. Partington, 'An Advanced Treatise on Physical Chemistry', Longmans Green, London, 1953, vol. 4, pp. 592–632.

[5] T. M. Lowry, 'Optical Rotatory Power', Dover Publications, New York, 1964, ch. 12.

[6] A. M. Clogston, *J. Phys. Radium*, 1959, **20**, 151.

[7] M. L. Sage, *J. Chem. Phys.*, 1961, **35**, 969.

[8] P. J. Stephens, 'Theoretical Studies of Magneto-Optical Phenomena', Doctoral Thesis, Oxford University, 1964.

[9] Y. R. Shen, *Phys. Rev.*, 1964, **133**, A511.

[10] A. D. Buckingham and P. J. Stephens, *Ann. Rev. Phys. Chem.*, 1966, **17**, 399.

[11] S. F. Mason, *Quart. Rev.*, 1963, **17**, 20.

for a system with a spherically symmetric potential, *e.g.*, an atom.[12] The angular momentum in such systems is specified by the quantum numbers J and M_J which represent the eigenvalues of total angular momentum and z-component of total angular momentum respectively. In the absence of the field a state specified by an angular momentum J is $2J + 1 -$ fold degenerate, this degeneracy corresponding to the number of distinct eigenvalues, $M_J = J$, $J - 1$, $J - 2$, ... $- J$. In a magnetic field this degeneracy is lifted, the relative energies being determined by the Lande g-factor.

We now consider the selection rules governing the absorption of electric dipole radiation for a transition between the states $J = 0$ and $J = 1$. These are shown schematically in Figure 1. We note that the $\Delta M_J = 0$ transition is
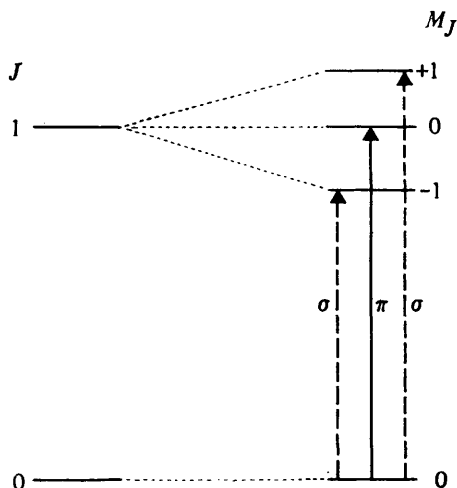

Figure 1 *Zeeman splitting of eigenstates of total angular momentum $J = 0$, $J = 1$ in a magnetic field and polarisation of transitions. π indicates transition allowed for radiation polarised with electric vector parallel and σ for radition polarised perpendicular to the field*

polarised parallel to the field (the z-direction) whereas those corresponding to $\Delta M_J = \pm 1$ are polarised in the x, y plane. Thus instead of a single $J = 0 \rightarrow J = 1$ transition, in the presence of the field we see three lines, one polarised parallel (π) and the other two perpendicular to the applied magnetic field. These selection rules may be derived in a straightforward manner using standard quantum mechanical methods. Similarly we may derive the selection rules for left and right circularly polarised light for the same system and these are shown in Figure 2. We may however obtain these selection rules by the consideration of the angular momentum associated with photons.[13] That

[12] See for example G. Herzberg, 'Atomic Spectra and Atomic Structure', Dover Publications, New York, 1944.
[13] A. S. Davydov, 'Quantum Mechanics', Pergamon Press, Oxford, 1965, sect. 135.

photons possess angular momentum follows from the experimental fact that a system must change by at least one unit of total angular momentum in order that radiation be emitted. From the laws of conservation of angular momentum, this same angular momentum is associated with the photon. Thus we may show that left and right circularly polarised light correspond to electric dipole photons having $J = 1$ and $M_J = -1$ and $+1$ respectively and it follows that the absorption of one of these photons by a system must cause the system to change in total angular momentum by $+1$ and in z-component of angular momentum by $+1$ for right and -1 for left circularly polarised radiation.
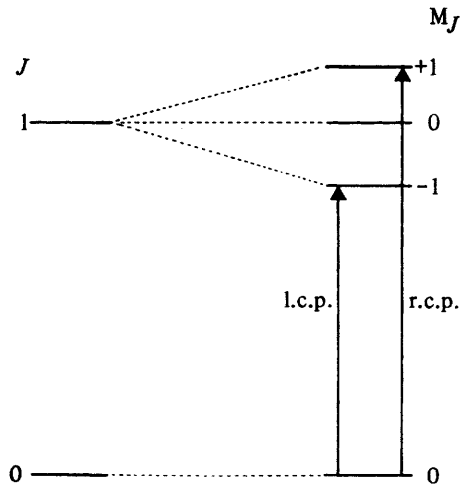

Figure 2 *Selection rules for left and right circularly polarised* (l.c.p. *and* r.c.p.) *radiation to* M_J *states split by a magnetic field*

From these selection rules for circularly polarised light in atomic systems we may build up a pictorial description of the main features of the Faraday effect. A more rigorous description for generalised molecular systems follows in the section on theory. Note that for experimental and theoretical reasons discussed later we shall discuss mainly c.d. rather than o.r.d.

Let us first consider a transition from a ^1S state ($J = 0$) to a ^1P state ($J = 1$). This is shown diagrammatically in Figure 3 together with the appropriate selection rules. If we measure separately the absorption of left and right circularly polarised light we see one line for each, separated by the Zeeman splitting of the excited state as shown in 3(c), and a measurement of the c.d. ($\epsilon_L - \epsilon_R$) would clearly lead to a lineshape of the form shown in 3(d), provided that the Zeeman splitting is less than the linewidth. A dispersion of this form is known as a Faraday A term,[14] and can only arise if a state with $J > 0$ is involved. Note that

[14] R. Serber, *Phys. Rev.*, 1932, **41**, 489.
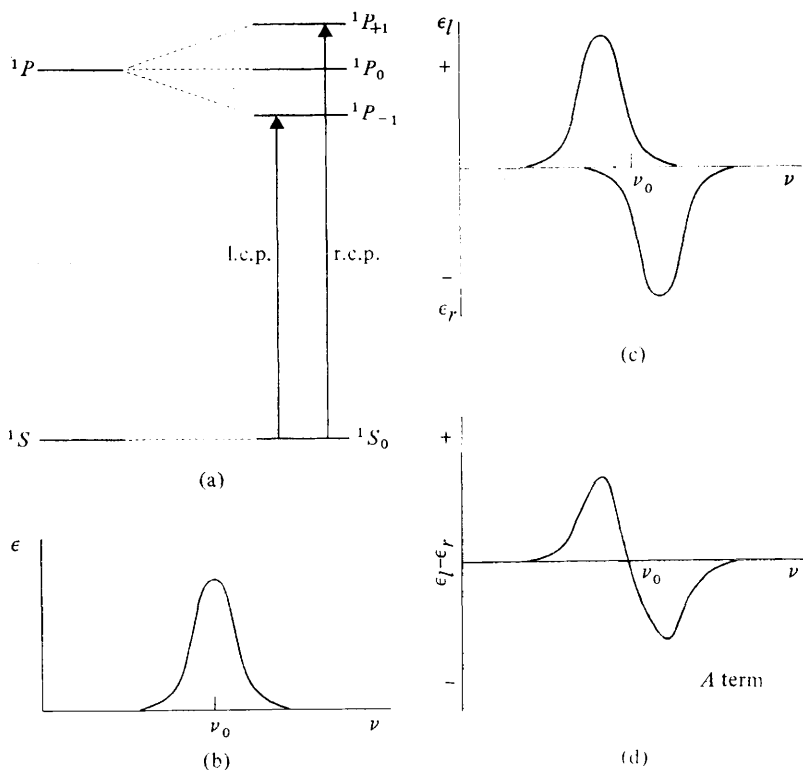
Figure 3 (a) *Effect of a magnetic field on atomic* ^1S *and* ^1P *states and selection rules for circularly polarised light for the transition* $^1S \rightarrow {}^1PM_J$. (b) *Absorption of light plotted as a function of frequency in the absence of the field;* $\nu_\bullet$ *is the resonance frequency.* (c) *Absorption of left circularly polarised light* (*plotted* $+ve$) *and right circularly polarised light* (*plotted* $-ve$) *when* ^1P *excited state is split by the field. Note that the two transitions occur with equal probability.* (d) *Resultant magnetic circular dichroism curve showing Faraday A term line shape*

the sign of the observed A term (*i.e.* whether it is positive or negative at short wavelengths) depends on the sign of the Zeeman splitting and the selection rules for circularly polarised light, and hence from a measurement, plus a knowledge of one, we may determine the other.

Now we discuss the converse situation, namely, a transition from a ^1P state to ^1S. This is shown in Figure 4(a). The splitting pattern and selection rules are the same. Again we expect an A term, and this will be of the same sign as in the previous example. However, a new feature now appears because in the presence of the field the $^1P_{-1}$ state will have a higher population than the $^1P_{+1}$ determined by the appropriate Boltzman factor. Transitions from $^1P_{-1}$ will therefore have a higher intensity and ϵ_L will be greater than ϵ_R. The resultant
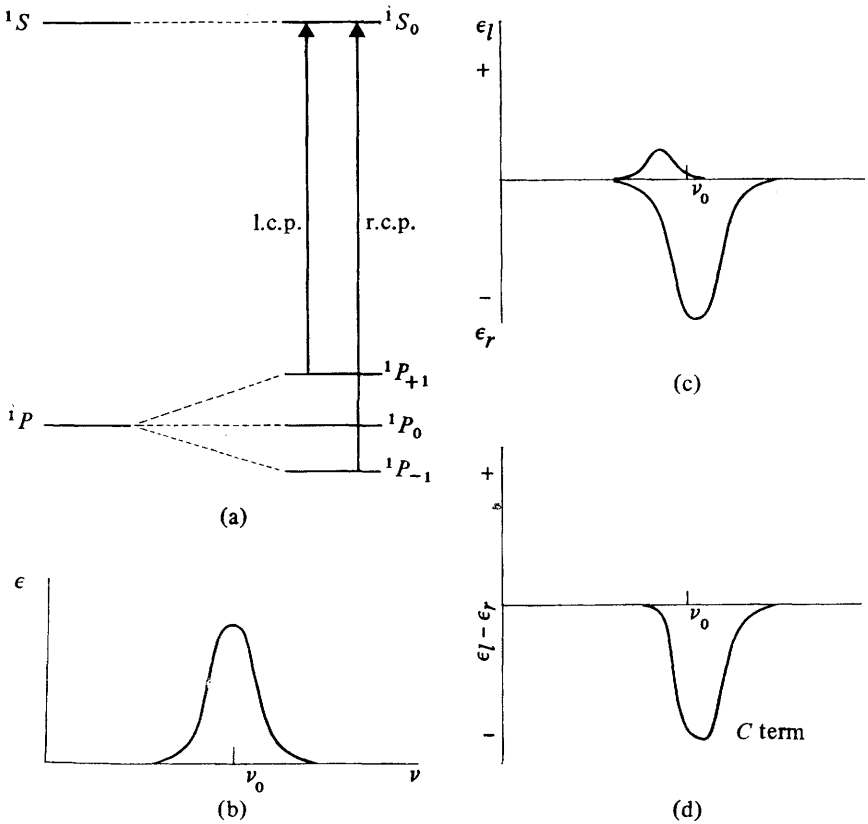
Figure 4 (a) *Splitting of levels in a magnetic field and polarisation of transitions for* $^1PM_J \to$ ^1S. (b) *Absorption in the absence of the field.* (c) *Absorption of left circularly polarised (plotted* $+ve$) *and right circularly polarised (plotted* $-ve$) *light in the presence of the field. Note that the relative intensities of these depends on a Boltzmann factor which reflects the number of atoms in the* $M_J = -1$ *and* $M_J = +1$ *sublevels.* (d) *Resultant magnetic circular dichroism showing Faraday C term line shape. Note that there is also an A-term which is generally small compared to C and which is not shown in the resultant m.c.d. The Faraday B term has the same lineshape as the C term.*

c.d. is shown in 4(d), this lineshape being known as the Faraday C term. Note that the sign of the C term depends on the sign of the Zeeman splitting and on the selection rules and again, one may be determined from an experiment and a knowledge of the other. The magnitude of the C term is dependent on the inverse of the absolute temperature and the magnitude of the Zeeman splitting.

The A and C terms are a consequence of the splitting of levels by the magnetic field. The third Faraday parameter, the B term, arises from the mixing of levels by the field. In the situation shown in Figure 5 the field causes the states

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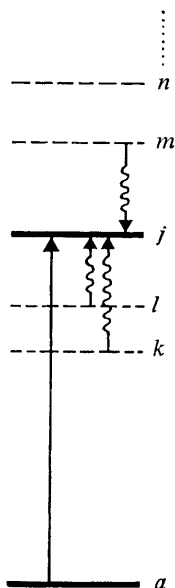
Figure 5 *States k, l, m, n . . . of the molecule which may be mixed into states a or j by the magnetic field. Note that in order for the mixing to occur the states must be connected by a magnetic dipole transition moment (shown by a wavy arrow to j)*

k, l, m . . . to be mixed with state j (or a) owing to the presence of a magnetic dipole transition moment between k, l, m, . . . and j, the amount of mixing being inversely proportional to the energy separation. The B term then is analogous to the temperature-independent paramagnetic term in the theory of paramagnetic susceptibilities.[15] As will be shown later, this leads to a lineshape which is identical to that of the C term but is not temperature dependent.

2 Theory[16]

The Faraday effect in its simplest form may be expressed by the equation,*

$$\phi = VHl \tag{1}$$

* Note that this treatment concerns only the 'normal' Faraday effect and excludes the quadratic Faraday effect where the angle of rotation is proportional to the square of the field strength and which may occur only in optically active molecules. We also exclude the optical Faraday effect in which circular birefringence is induced by an intense beam of circularly polarised light. These two phenomena have recently been discussed in detail by Atkins and Miller.[17, 18]

[15] J. H. Van Vleck, 'The Theory of Electric and Magnetic Susceptibilities', Oxford University Press, 1932.

[16] Based on ref. 8 and on lectures given by P. J. Stephens at the University of Virginia in July 1966.

[17] P. W. Atkins and M. H. Miller, *Mol. Phys.*, 1968, **15**, 503.

[18] P. W. Atkins and M. H. Miller, *Mol. Phys.*, 1968, **15**, 491.

where ϕ is the angle of rotation of the plane of polarisation of a linearly polarised light beam when it travels through a sample of thickness l parallel to a magnetic field H, V is the Verdet constant-characteristic of a given substance and a function of concentration, temperature, and frequency. As is well known, equation (1) is a complete description only in transparent regions of the spectrum. In regions of absorption, the rotation of the plane of polarisation is accompanied by the development of an ellipticity of the originally linearly polarised light. Phenomenologically the situation is identical to natural optical activity, and very clear discussions have appeared in the recent literature.[11,20] A compact generalisation of equation (1) may be written.

$$\hat{\Phi} = \phi - i\theta = \frac{\pi l}{\lambda}(\hat{n}_- - \hat{n}_+) = \hat{V}\int_0^l H(l)\,dl \tag{2}$$

$\hat{\Phi}$ is the complex (magnetic) rotation[19] whose real part (ϕ) is the rotation and whose imaginary part (θ) is the ellipticity.[11, 19] $\hat{n}_-$ is the complex refractive index for left circularly polarised (l.c.p.) light and is defined by, $\hat{n}_- = n_- - iK_-$ where n_- is the real refractive index for l.c.p. light and K_- is the corresponding absorption index.[19] An analogous definition applies for n_+ where the subscript ($+$) designates right circularly polarised (r.c.p.) light. The integral in equation (2) emphasises the fact that the magnetic field need not be homogeneous along the direction of the light beam. It follows immediately from equation (2) that the rotation (ϕ) is proportional to ($n_- - n_+$) and the ellipticity (θ) to ($K_- - K_+$). It is for this reason that the ellipticity is commonly referred to as the circular dichroism (c.d.) in natural optical activity. The obvious nomenclature for this quantity in magnetic work is magnetic circular dichroism (m.c.d.). Finally, it should be noted that due to the analytic properties of $\hat{\Phi}$, ϕ and θ are related by Kramers–Kronig transforms.[20] The explicit relationships have been discussed in some detail by Moscowitz.[19] In principle, then, it is only necessary to determine one quantity (but at all frequencies) to know both.

In order to extract useful chemical information from the Faraday effect, it is necessary to relate the experimentally observed quantity (θ or ϕ) to molecular properties. This can be done in several different ways. Conceptually the simplest is to calculate ($K_- - K_+$) directly using the conventional time-dependent perturbation techniques used in calculating absorption coefficients. It is directly analogous to the method used by Condon, Altar, and Eyring[21] for natural c.d., though our treatment does not give the term for natural c.d.

The electric field vector of a circularly polarised light wave travelling in the positive z direction can be written

$$\vec{E}_\pm = {}^1/_{\sqrt{2}}\,(\vec{i} \pm \vec{ij})\,E_0\exp[2\pi i\nu(t - n_\pm z/c)] \tag{3}$$

where the subscripts $+$ and $-$ denote r.c.p. and l.c.p. respectively, $\vec{i}$ and $\vec{j}$

[19] A. Moscowitz, *Adv. Chem. Phys.*, 1962, **4**, 67.
[20] For an excellent introduction to this topic see L. D. Landau and E. M. Lifshitz, 'Electro-dynamics of Continuous Media', Pergamon Press, Oxford, 1960, sect. 62.
[21] E. U. Condon, W. Altar, and H. Eyring, *J. Chem. Phys.*, 1937, **5**, 753.

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are unit vectors along the x- and y-axes of a righthanded co-ordinate system, $i = \sqrt{-1}$ and the other symbols have the usual significance. Proceeding in the usual manner,[22] the energy of interaction between the light wave and a molecule is given by $-\bar{m} . \vec{E}_{\pm}$, where $\bar{m} = \sum_i e_i \bar{r}_i$ is the electric dipole moment operator. Following the standard derivation†[22, 23] we obtain for the absorption coefficient $\alpha_{\pm}$ associated with a transition from state a to higher state j,

$$\alpha_{\pm} = \frac{4\pi^3}{hc} (N_a - N_j) \, \mathrm{f}(\nu, \nu_0) \, |\langle a | m_{\pm} | j \rangle|^2 \qquad (4)$$

where N_a and N_j are the numbers of molecules per unit volume in the states a and j respectively, $\nu_0 = (E_j - E_a)/h$, $\mathrm{f}(\nu, \nu_0)$ is a frequency function defining the shape of the absorption line $[\int(\mathrm{f}/\nu) \, d\nu = 1]$, and $m_{\pm} = m_x \pm im_y$. α is defined in the usual way[20] from Lambert's law,

$$I = I_0 \, \mathrm{e}^{-\alpha l} = I_0 \, \mathrm{e}^{-4\pi\nu K l/c} \qquad (5)$$

Since we are dealing with electronic transitions, in most cases $N_j \approx 0$, and it then follows from equations (2), (4), and (5) that for the transition $a \to j$

$$\theta = \tfrac{1}{4}(\alpha_- - \alpha_+) = \pi^3/ch \sum_{a \to j} N_a \mathrm{f}(\nu, \nu_0)$$

$$[|\langle a | m_- | j \rangle|^2 - |\langle a | m_+ | j \rangle|^2] \qquad (6)$$

where the sum is over all degenerate components of the transition.

If a constant magnetic field, H_z is applied along the z-axis, the wavefunctions and energy levels of the system are perturbed, the perturbing energy being

$$-\mu_z H_z = \beta (\mathbf{L}_z + 2\mathbf{S}_z) H_z \qquad (7)$$

where μ_z is the z-component of the magnetic dipole moment operator, β is the Bohr magneton and $\mathbf{L}_z$ and $\mathbf{S}_z$ are the z-components of the total orbital and spin angular momentum operators respectively measured in units of $h/2\pi$.

Provided care is taken, in degenerate cases, to use wavefunctions diagonal in μ_z, by the use of perturbation theory, explicit expressions for the energy and wavefunction of any state $|k\rangle$ may be obtained correct to first order in the magnetic field; namely

$$E_k = E^0{}_k - \langle k^0 | \mu_z | k^0 \rangle H_z \qquad (8)$$

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† In this derivation we must note that, unlike the real quantities m_x etc, for which $|\langle a | m_x | j \rangle|^2 = |\langle j | m_x | a \rangle|^2$, that $|\langle a | m_- | j \rangle|^2 = |\langle j | m_+ | a \rangle|^2$ and $|\langle a | m_+ | j \rangle|^2 = |\langle j | m_- | a \rangle|^2$.

[22] L. Pauling and E. B. Wilson jun., 'Introduction to Quantum Mechanics', McGraw-Hill, New York, 1935, sect. 40b.
[23] E. B. Wilson jun., J. C. Decius, and P. C. Cross, 'Molecular Vibrations', McGraw-Hill, New York, 1955, sect. 7–9.

$$| k \rangle = | k^0 \rangle - \sum_{j \neq k} \frac{\langle j^0 | \mu_z | k^0 \rangle H_z}{E^0{}_k - E^0{}_j} | j^0 \rangle \qquad (9)$$

where a superscript zero indicates the unperturbed state. Assuming a Boltzmann distribution, the following equation may be obtained:

$$N_a = N_a{}^0 \exp \left[- (E_a - E_a{}^0)/kT \right] \approx$$

$$N_a{}^0 \left[1 + \langle a^0 | \mu_z | a^0 \rangle \frac{H_z}{kT} + \dots \right] \qquad (10)$$

where in the last expression the exponential has been expanded and only the first power in H_z retained. This approximation will hold good provided $\langle a^0 | \mu_z | a^0 \rangle H_z/kT \ll 1$, a condition which is generally met in practice except at very low temperatures. Finally, if we require an explicit description through absorption lines, a form for $f(\nu, \nu_0)$ must be assumed, *e.g.*:

$$f(\nu, \nu_0) = \left(\frac{2}{\pi} \right) \frac{\nu^3 \Gamma}{(\nu_0^2 - \nu^2)^2 + \nu^2 \Gamma^2} \qquad (11)$$

which is often referred to as the damped oscillator model.[24] The $(2/\pi)$ is a normalising factor such that $\int_0^\infty [f(\nu, \nu_0)/\nu] \, d\nu = 1$, and Γ is the approximate linewidth at half height. The exact form chosen for $f(\nu, \nu_0)$ is not of great importance. Equation (11) clearly has the correct qualitative form and its use has the virtue that it will be possible to write explicit algebraic expressions for both θ and ϕ, something which is not possible if a Gaussian expression is used, for example.

Recalling that $\nu_0 = (E_j - E_a)/h$ and using equation (8), we obtain

$$\nu_0 = \nu_0^0 - H_z/h \left[\langle j^0 | \mu_z | j^0 \rangle - \langle a^0 | \mu_z | a^0 \rangle \right] \equiv \nu_0^0 - H_z \nu_0' \qquad (12)$$

where $\nu_0^0 = (E_j{}^0 - E_a{}^0)/h$. We now substitute equation (12) into equation (11) and expand $f(\nu, \nu_0)$ in powers of H_z again retaining terms only through first order. The result is,

$$\frac{\pi}{2} f(\nu, \nu_0) = \frac{\nu^3 \Gamma}{(\nu_0^{02} - \nu^2)^2 + \nu^2 \Gamma^2} + \frac{4\nu_0^0 \nu_0' H_z (\nu_0^{02} - \nu^2) \nu^3 \Gamma}{[(\nu_0^{02} - \nu^2)^2 + \nu^2 \Gamma^2]^2} + \dots \qquad (13)$$

It can be shown[8] that retention of terms only through first order is justified provided $\nu_0' H_z \ll \Gamma/2$. Since the left hand side of the inequality is the Zeeman splitting, the expansion to first order is seen to be valid only if the Zeeman splitting is much less than the line width.

If we now substitute equations (9), (10), and (13) into equation (6) and keep only terms linear in H_z, the final result is,

$$\theta = - \frac{8\pi^2 H_z N}{3ch} \left[f_1 A + f_2 (B + C/kT) \right] \qquad (14)$$

[24] W. Heitler, 'The Quantum Theory of Radiation', Oxford University Press, 1954, 3rd edn., p. 35.

where $N (\equiv N_a d_a)$ is the total number of molecules per unit volume in the ground state a, d_a is the corresponding degeneracy of this state and,

$$A = 3/d_a \sum_{a \to j} [\langle j | \mu_z | j \rangle - \langle a | \mu_z | a \rangle] \operatorname{Im} \{\langle a | m_x | j \rangle\langle j | m_y | a \rangle\} \tag{15}$$

$$B = 3/d_a \sum_{a \to j} \operatorname{Im} \{ \sum_{k \neq a} [\langle k | \mu_z | a \rangle/(E_k - E_a)]$$

$$[\langle a | m_x | j \rangle\langle j | m_y | k \rangle - \langle a | m_y | j \rangle\langle j | m_x | k \rangle]$$
$$+ \sum_{k \neq j} [\langle j | \mu_z | k \rangle / (E_k - E_j)]$$

$$[\langle a | m_x | j \rangle\langle k | m_y | a \rangle - \langle a | m_y | j \rangle\langle k | m_x | a \rangle] \} \tag{16}$$

$$C = 3/d_a \sum_{a \to j} \langle a | \mu_z | a \rangle \operatorname{Im} \{\langle a | m_x | j \rangle\langle j | m_y | a \rangle \} \tag{17}$$

$$f_1 = \frac{4\nu_0\nu^3 (\nu_0^2 - \nu^2)\,\Gamma}{h\,[(\nu_0^2 - \nu^2)^2 + \nu^2\Gamma^2]^2} \tag{18}$$

$$f_2 = \frac{\nu^3\Gamma}{(\nu_0^2 - \nu^2)^2 + \nu^2\,\Gamma^2} \tag{19}$$

(It should be noted that $\sum_{a \to j} \operatorname{Im}\{\langle a | m_x | j \rangle\langle j | m_y | a \rangle \} = 0$ which

follows directly from the fact that any unperturbed ket and its complex conjugate belong to the same degenerate set.[8]) We have now dropped the superscript zero notation so that all quantities in equations (14)—(19) must be understood to refer to unperturbed (*i.e.* $H_z = 0$) states. Im means imaginary part. This result now applies for a single, isolated, absorption line of an oriented molecule in a magnetic field along the (space-fixed) z-axis. For a medium which is isotropic in the absence of the field (*e.g.*, a solution), an average over orientation can be performed to obtain expressions in terms of molecule-fixed axes.[10]

For the special case of an isotropic molecule (*e.g.*, point group O), equations (14)—(19) are correct as they stand for molecule-fixed axes. Finally, if we convert to molar ellipticity ($[\theta]_m$) per unit magnetic field in the conventional units[11, 19] of natural optical activity (degree deciliter decimeter^{-1} mole^{-1}), and express A in units of square Debye $\times \beta$ and $(B + C/kT)$ in square Debye $\times \beta$ per cm^{-1} (β = Bohr magneton), the result is:

$$[\theta]_m = -\,21.3458\,\{f_2\,[B + C/kT] + f_1 A\} \tag{20}$$

A number of points should be made regarding this treatment. First, this simplified derivation does not give the (usually) much smaller magnetic terms[8, 10] arising from the interaction of the wave magnetic field with the molecule. Second, the corresponding expression for $[\phi]_m$, the magnetic optical rotatory dispersion (m.o.r.d.), may be obtained by explicitly performing the Kramers–Konig transform[19] on equation (20). The expression for $[\phi]_m$ is given

in refs. 8, 10, and 25. Third, the sign convention used here is opposite to that used in the older Faraday literature. Thus, when the light beam is moving in the positive direction of the magnetic field, the sign convention is the same as for natural optical activity. With this convention, the Verdet constant of water is negative. This sign convention is now used by virtually all workers. As a fourth point, we note that if low-lying excited states are thermally accessible (for example, levels arising from spin–orbit splitting of the ground state), the derivation given may be modified in a straightforward way by removing the restriction, $N_j = 0$.

A very important and rather subtle problem concerns the generalisation of equations (14)—(19) to absorption bands. This has been discussed in some detail by Buckingham and Stephens.[10] For resolved individual lines (generally found only in gases or crystals at low temperatures), the situation is relatively simple. If the linewidth is large compared to the Zeeman splitting, the above equations apply. If this condition is not met, the expansion shown in equation (13) is not appropriate, but then equation (6) can be used to fit the two components of θ individually.[10] For an individual vibronic band in solution whose width is attributed to librational motion, equations (14)—(19) may reasonably be used, but now Γ is interpreted as the width of the band and the matrix elements refer to the vibronic states involved in the transition.[10] The use of the damped oscillator model is now a strictly *ad hoc* representation of the band shape and other shapes may be better, there being some indication, for example, that a Gaussian is often preferable.[26]

The most difficult case is the solution band which is a composite of many unresolved vibronic bands, since each vibronic component may have its own characteristic shape and matrix elements. However, for an allowed electronic transition (and even for a forbidden transition under certain circumstances) it can be argued[10] that A, B, and C have the same shape for every vibronic component with the same Franck–Condon overlap factors governing the Faraday and absorption band shapes. Equations (14)—(19) are again valid for the overall band, and the matrix elements now refer to purely electronic states. These arguments require the usual Franck–Condon approximation for allowed transitions, namely that the electric-dipole transition matrix element can be written as a product of an electronic part and a vibrational overlap. If, for example, the electronic transition moment is a strong function of vibrational state, the argument fails.

The most promising approach for circumventing many of these difficulties is the method of moments first applied to m.c.d. by Henry, Schnatterly, and Slichter.[27] In this approach, which will be discussed in a later section, various integrals over the experimental m.c.d. are used. These integral quantities are found to be independent of many of the details of the vibronic structure of the band.

[25] P. J. Stephens, W. Suëtaka, and P. N. Schatz, *J. Chem. Phys.*, 1966, **44**, 4592.
[26] G. N. Henning, 'The Faraday Effect of Charge-Transfer Transitions in Transition Metal Hexahalides', Ph.D. Dissertation, University of Virginia, 1968.
[27] C. H. Henry, S. E. Schnatterly, and C. P. Slichter, *Phys. Rev.*, 1965, **137**, A583.

3 Experimental

The techniques required for Faraday measurements through absorption bands are well-developed, and the experiments involve no exceptional difficulties. Clearly, one simply needs to interface appropriately a magnetic field with an apparatus for measuring optical activity. In natural optical activity one can measure the dispersion of either the optical rotation or circular dichroism through the absorption band, and excellent commercial instruments have become available in recent years for doing either or both. In principle, the same information is obtained from either measurement though each has its own practical advantages.[28-30] In magnetic work however, m.c.d. has a compelling experimental advantage. This arises because the Faraday effect is universal. Hence, for m.o.r.d. measurements, not only the molecule of interest contributes a rotation, but cell windows and solvent contribute as well; and these latter rotations are often much larger than that of the solute. Therefore some technique to cancel or compensate for this effect is needed. This is further complicated by the fact that compensation at one wavelength does not assure compensation at all wavelengths because each substance has its own characteristic dispersion form and these diverge rapidly towards the u.v. Hence the m.o.r.d. of even a pure substance through an absorption band will be superimposed on a more or less rapidly changing background. All of these problems disappear if one measures m.c.d. because, provided transparent windows and solvent are used, only the solute exhibits a circular dichroism, and then only in regions of absorption. Thus the m.c.d. of a solution is run first with solute and then without, the latter trace providing the (generally flat) m.c.d. baseline. If it is not possible to run pure solvent under identical conditions, a satisfactory baseline can usually be obtained by running the sample at zero magnetic field. Because of this very great practical advantage we shall frame our entire discussion in terms of m.c.d.

The techniques for the measurement of c.d. are well known.[29] Linearly polarised light is converted alternately to left and right circular polarisation by the use of a quarter-wave plate which maintains $\pi/2$ phase retardation over a wide range of frequencies, such as a Fresnel rhomb, or an electro-optic modulator (a Pockels cell) or a stress modulated plate.[31] This light is then passed through the sample and the difference in absorption between l.c.p. and r.c.p. light is amplified and recorded as a function of wavelength.

To measure m.c.d., it is only necessary to apply a longitudinal magnetic field to the sample in the c.d. spectrophotometer. An extremely convenient way to do this is to mount the sample in the optical channel of a superconducting solenoid which is fitted directly into the sample compartment of the spectrophotometer. The superconducting solenoid has the very great advantages of

[28] C. Djerassi, 'Optical Rotatory Dispersion', McGraw-Hill, New York, 1960.
[29] L. Velluz, M. Legrand, and M. Grosjean, 'Optical Circular Dichroism', Academic Press, London, 1965.
[30] P. Crabbe, 'Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry', Holden-Day, London, 1965.
[31] M. Billardon and J. Badoz, *Compt. rend.*, 1966, **263**, 139.

compactness and high field. A detailed discussion of such a system in use at the University of Virginia with a description of its application to both m.o.r.d. and m.c.d. may be found in the article by Schatz *et al.*[32]

4 Faraday Parameters

The functional form of the m.c.d. through an absorption band is shown separately for A, B, and C terms in Figures 3 and 4. A quantitative understanding of each of these effects can be obtained by following through in detail the algebra which gives rises to equations (14)—(19) when equations (9), (10), and (13) are substituted in equation (6). The important qualitative points are: (i) *A* terms change sign at the absorption maximum whereas *B* and *C* terms peak at this wavelength; (ii) *C* terms are inversely proportional to absolute temperature; (iii) *A* terms are possible only if either the ground or excited state in the transition is degenerate;† (iv) *C* terms are possible only if the ground state (strictly any thermally accessible state) is degenerate; (v) *B* terms are generally present for all transitions in molecules; (vi) unlike absorption coefficients, Faraday parameters can occur with either sign.

As we shall show in our discussion of applications, these qualitative features alone are often a very powerful tool for clarifying spectroscopic interpretations. However, to obtain the maximum of information, it is essential to extract quantitative values for *A*, *B*, and *C* from the experimental data. One obvious method is to fit the experimental data to equation (20) using a least-squares procedure assuming a specific band shape, for example equation (11), which leads directly to equations (18) and (19), or a Gaussian shape.[25] This approach has been used by the present reviewers and co-workers quite extensively for *A* terms and has been discussed in detail.[32] Results obtained in this way are at least of semi-quantitative value if one type of term dominates [A or $(B + C/kT)$]. Thus the damped oscillator and Gaussian models will usually give values agreeing within a factor of *ca.* 2. (In fact, based on comparisons with the method of moments discussed below and other evidence, it appears that the fitting procedure based on a Gaussian band shape is usually very good.) When both *A* and $(B + C/kT)$ contributions are comparable, the results obtained by fitting are less reliable, and if one term dominates, the value obtained for the non-dominant term by fitting is devoid of significance. Nevertheless, in many complicated overlapping situations, and certainly when data can be obtained only part way through a band, the fitting procedure seems to be the only practical alternative.

A much more powerful technique for extracting Faraday parameters is the method of moments, first applied to the Faraday effect by Henry, Schnatterly,

† Note that degeneracy is a necessary requirement for a Zeeman splitting (and hence *A* and *C* terms) because only such states are capable of possessing angular momentum.[33]

[32] P. N. Schatz, A. J. McCaffery, W. Suëtaka, G. N. Henning, A. B. Ritchie, and P. J. Stephens, *J. Chem. Phys.*, 1966, **45**, 722.

[33] This follows because the angular momentum operator is pure imaginary and non-degenerate eigenfunctions are necessarily real (except possibly for a trivial phase factor). Thus a non-zero angular momentum for a non-degenerate state would necessarily imply a non-real expectation value.

and Slichter.[27] In this method, moments are computed by numerically integrating the m.c.d. and absorption data in accordance with the formulae:[34]

$$\langle \epsilon \rangle_n \equiv \int_{\text{band}} (\epsilon/\nu) \, \nu^n \, d\nu \; ; \; \langle \theta \rangle_n \equiv \int_{\text{band}} ([\theta]_m/\nu)\nu^n \, d\nu \tag{21}$$

which are referred to respectively as the nth moments of the absorption and m.c.d. As a first illustration of this approach, consider the zeroth moment of the m.c.d. which satisfies the relation:

$$\int_{\text{band}} ([\theta]_m/\nu) \, d\nu = - 33 \cdot 53 \, (B + C/kT), \tag{22}$$

where we have assumed that the band arises from the vibronic transitions corresponding to a single allowed electronic transition. The matrix elements in A, B, and C are purely electronic. [In the general case of a band composed of many transitions, the same relation applies provided the right-hand side of equation (22) is summed over all the transitions.] This relation was derived by Stephens[8, 10] and has been used extensively by him and the present reviewers and co-workers. The great utility of this relationship is twofold. First, the values of Faraday parameters are obtained independent of any assumption of band shape and hence fitting procedures. Second, the A term contribution integrates to zero. Thus one can extract $(B + C/kT)$ in the presence of a sizable A term, the circumstance under which fitting procedures are least reliable. Results have also been published for electronically allowed transitions from a non-degenerate ground state to a degenerate excited state. To a good approximation, the results are:[34]

$$\langle \theta \rangle_0 = - 33.53 \, B$$
$$\langle \theta \rangle_1 = 33.53 \, (A - B\bar{\nu}) \tag{23}$$
$$\bar{\nu} = \langle \epsilon \rangle_1/\langle \epsilon \rangle_0$$

Thus both A and B can be extracted by simple numerical integrations of the experimental data. Moreover, the results are independent of all details of the vibronic structure of the excited state, *e.g.*, Jahn–Teller or solvent interactions. Additional information is also available from higher moments.[27] The method is clearly not applicable if data are not available completely through a band, and the expressions will involve sums of Faraday parameters if several overlapping bands are involved. However, when applicable the method is clearly of great power and utility.

5 Examples

We shall first make some general comments on applications and then discuss individually examples of the use of A, B, and C terms. In the expressions for A, B, and C [equations (15)—(17)], matrix elements of the form

$$\langle a \mid m_x \mid j \rangle \langle j \mid m_y \mid a \rangle$$

[34] P. J. Stephens, *Chem. Phys. Letters*, 1968, **2**, 241.

occurred. This product will in general be proportional to the dipole strength D defined by

$$D = \frac{1}{d_a} \sum_{a-j} | \langle a | \vec{m} | j \rangle |^2 \tag{24}$$

and D in turn is related to the integrated intensity of the transition by

$$D = \frac{9.1834 \times 10^{-3}}{\nu_0} \int \epsilon \, d\nu \tag{25}$$

where D is in square Debye, ν_0 is the resonance frequency, and ϵ is the molar extinction coefficient.[35] We will thus often be able to replace these products of electric-dipole matrix elements by D multiplied by a known proportionality constant, and thus we can reduce our theoretical discussion to ratios of a Faraday parameter to dipole strength (A/D, B/D, C/D). Further, D may easily be evaluated experimentally from equation (26). This procedure has two extremely important advantages. First, it eliminates the need to calculate electric-dipole transition moment integrals accurately, a notoriously difficult problem. Second it eliminates the need to consider solvent corrections, at least as a first approximation, because these enter into A, B, C, and D in the same way,[8] and hence cancel if ratios are discussed. Thus the magnitude of C/D is determined by the ground-state magnetic moment, a quantity which very often is either known experimentally or is easy to calculate, and its sign by the overall symmetry of the transition. This can make the observation of C terms a very powerful diagnostic tool for the determination of the symmetry of transitions, since the sign alone will often be sufficient to distinguish among various possibilities. In addition, the C term is sensitive to interactions which quench ground-state angular momentum, such as Jahn–Teller distortions, low-symmetry crystal-field perturbations, and exchange interactions, and m.c.d. may be used to investigate these effects, particularly if a wide range of temperatures is available. Similarly A/D is determined by two parameters, namely the ground- and excited-state magnetic moments, the sign being determined by the overall symmetry of the transition and by the ground and excited state magnetic moment factor in equation (15). Qualitatively, the appearance of an A term is unambiguous proof that at least one of the states involved in the transition is degenerate. This is an especially useful tool for identifying degenerate excited states when the ground state is known to be non-degenerate. Such identifications are not easily made in other ways since one must either resort to single crystal spectroscopy or use stress, Stark, or Zeeman experiments which are applicable only to sharp line spectra. Quantitative extraction of the A value will permit an experimental determination of the excited-state magnetic moment, a quantity not easily determined in other ways and one of considerable value in testing molecular wavefunctions. For forbidden transitions, the same basic considerations apply, but it is necessary to consider the details of the intensity mechanism to perform a complete analysis. Stephens[36] has discussed the vibronically allowed $d \rightarrow d$ transitions in d^6 Co^{III}

[35] J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Molecules', Methuen, London, 1963, ch. 1.
[36] P. J. Stephens, *J. Chem. Phys.*, 1966, **44**, 4060.

complexes and has shown that the excited-state vibrational symmetry of a resolved vibronic line can be determined if the excited-state electronic symmetry is known and *vice versa*.

The theoretical analysis of B terms is very much less promising for a simple reason—the existence of sums over all excited states including the continuum [equation (16)]. In fact, unless one or a very few states are known to dominate the mixing process [equation (9)] because they are very close in energy, the theoretical analysis will be exceedingly complicated and it will be impossible even in principle to work out any simple expression for B/D. An application involving the analysis of B terms in $CoCl_4^{2-}$ has been given by Stephens[37] though in this particular case it is likely that the C terms arising from spin–orbit coupling which were neglected are of decisive importance.

It seems highly probable that a much more empirical approach will be necessary in using B terms than is the case for A and C terms, and it is an unfortunate fact that B terms are generally present for all transitions and hence may obscure C and A terms.
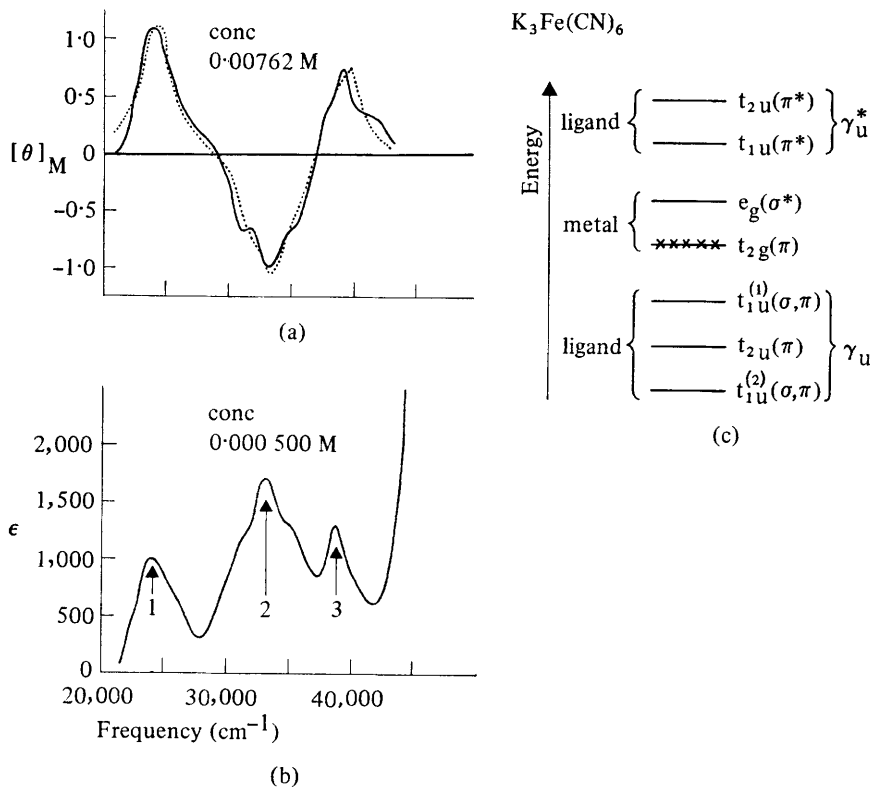
A. Use of C terms.—An excellent illustration of the use of C terms is provided by the charge-transfer spectra of octahedral d^5 complex ions. We consider first the case of $Fe(CN)_6^{3-}$ in aqueous solution.[38, 32] The visible–u.v. absorption and m.c.d. spectra are shown in Figure 6. The detailed arguments are given elsewhere,[32] but it is clear that the three absorption bands are allowed charge-transfer transitions involving the transfer of a ligand t_u electron to the vacancy in the $t_{2g}d$ shell [Figure 6(c)]. Hence, the three absorption bands correspond to the three transitions $^2T_{2g} \to \, ^2T_{2u}$, $^2T_{1u}(\pi + \sigma)$, $^2T_{1u}(\sigma + \pi)$. The question which cannot be answered on the basis of the absorption spectrum is which of the three transitions is $^2T_{2g} \to \, ^2T_{2u}$. Observation of the m.c.d. spectrum settles this question with ease. Note that the three m.c.d. bands are C terms since the m.c.d. shows $1/T$ dependence down to liquid helium temperatures.[39] Now it is only necessary to calculate (C/D) for each transition. The results (derived in the appendix of ref. 32) are $C/D = -0.5 \, \beta$ for $^2T_{2g} \to \, ^2T_{1u}$ and $C/D = +0.5 \, \beta$ for $^2T_{2g} \to \, ^2T_{2u}$ ($\beta =$ Bohr magneton). Noting that a positive C term corresponds to a negative m.c.d. and *vice versa* [see equation (21)], it is now clear by inspection of Figure 6(a) that band 2 must correspond to the $^2T_{2g} \to \, ^2T_{2u}$ transition. We emphasise that this result is symmetry determined except for the ground-state magnetic moment calculation. That in turn is done quite reliably (certainly without any doubt as to sign) by assuming that the metal t_{2g} orbitals are pure d. The C/D values obtained experimentally are in reasonable quantitative agreement with the theoretical predictions.[32]

As a second example of a d^5 system, we consider the $IrCl_6^{2-}$ ion. The first three intense bands again correspond to the same ligand t_u to metal t_{2g} charge-

[37] P. J. Stephens, *J. Chem. Phys.*, 1965, **43**, 4444.
[38] P. J. Stephens, *Inorg. Chem.*, 1965, **4**, 1690.
[39] A. J. McCaffery, to be published.

$K_3Fe(CN)_6$

(a)

conc
0·00762 M

$[\theta]_M$

1·0
0·5
0
-0·5
-1·0

ligand $\left\{ \begin{array}{l} ——— \quad t_{2u}(\pi^*) \\ ——— \quad t_{1u}(\pi^*) \end{array} \right\} \gamma_u^*$

metal $\left\{ \begin{array}{l} ——— \quad e_g(\sigma^*) \\ \text{✳✳✳✳} \quad t_{2g}(\pi) \end{array} \right.$

ligand $\left\{ \begin{array}{l} ——— \quad t_{1u}^{(1)}(\sigma,\pi) \\ ——— \quad t_{2u}(\pi) \\ ——— \quad t_{1u}^{(2)}(\sigma,\pi) \end{array} \right\} \gamma_u$

Energy

(c)

conc
0·000 500 M

ϵ

2,000
1,500
1,000
500
0

1
2
3

20,000 30,000 40,000
Frequency (cm^{-1})

(b)

Figure 6 $K_3Fe(CN)_6$: (a) *Molecular ellipticity per unit magnetic field. Solid line is experimental result and dotted line is a computer fit.* (b) *Molar extinction coefficient.* (c) *Orbital energy diagram for* $M(CN)_6^{n-}$. *Crosses denote electrons in the highest occupied shell in* $Fe(CN)_6^{3-}$. *The order within* γ_u *and* γ^*_u *is arbitrarily chosen* (Reproduced, with permission, from *J. Chem. Phys.*, 1966, **45**, 722)

transfer transitions.[40] The important difference from the $Fe(CN)_6^{3-}$ case is the fact that spin–orbit coupling is large and must be considered explicitly. Figure 7(a) shows the situation schematically using Griffith's[41] double group notation (E' and E'' are two dimensional, U' is a four dimensional irreducible representation). The spin–orbit splitting of the ground state is *ca.* 3000 cm^{-1} and hence only the E_g'' ground state is populated at room temperature. Again *C* terms dominate, and the calculated *C* and *D* values are shown in Figure 7(a). We note that these parameters are calculated exactly as in the last example. It is only necessary to use the appropriate double group coupling tables in Griffith.[41] Figure 7(b) shows the experimental m.c.d. and absorption spectra

[40] G. N. Henning, A. J. McCaffery, P. N. Schatz, and P. J. Stephens, *J. Chem. Phys.*, 1968, **48**, 5656.
[41] J. S. Griffith, 'The Theory of Transition-Metal Ions', Cambridge Univ. Press, Cambridge, 1964.
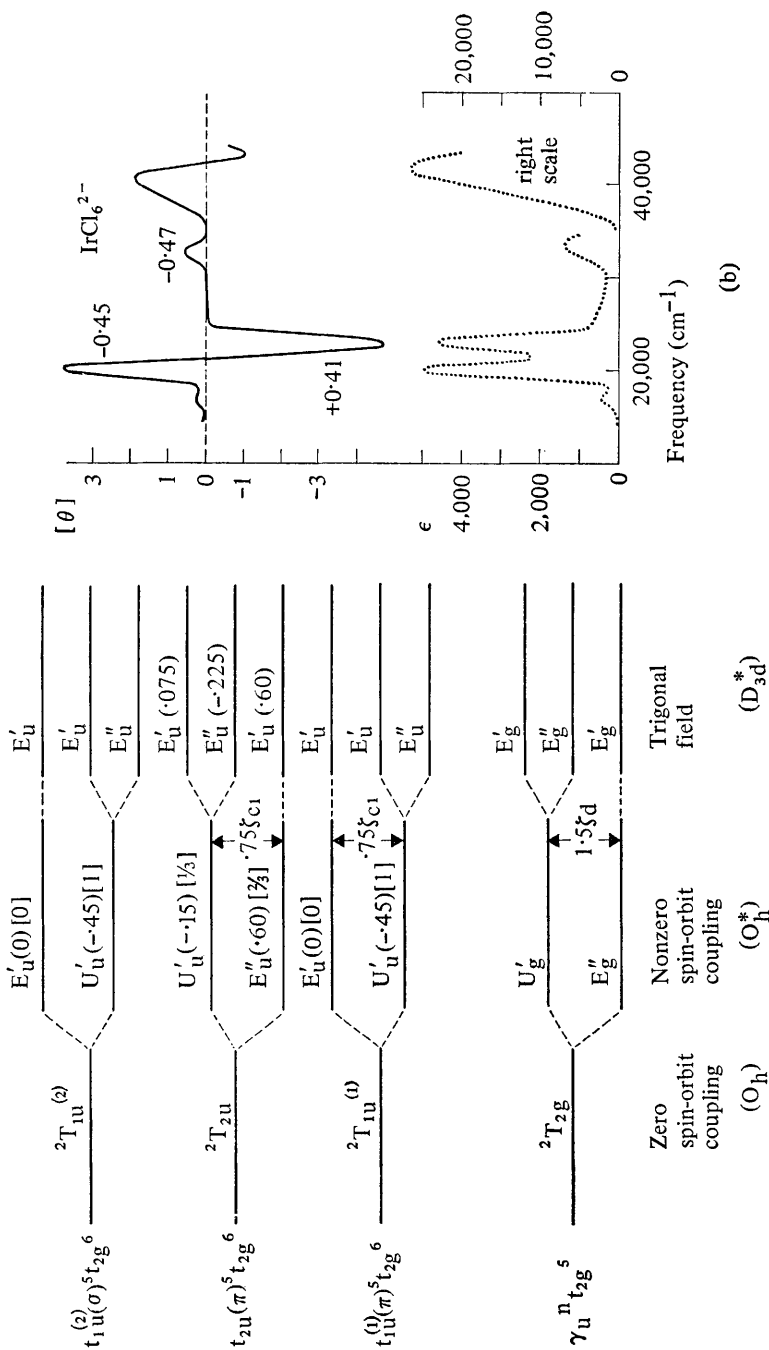
Figure 7 $IrCl_6^{2-}$: (a) States of $\gamma_u^n t_{2g}^5$ and $\gamma_u^{n-1} t_{2g}^6$ configurations. The numbers in parentheses are the theoretically calculated C values and the numbers in square brackets are the corresponding D values. C and D are expressed in terms of the same reduced matrix element.[a] C/D is in units of Bohr magnetons. (b) Absorption spectrum and m.c.d. of $IrCl_6^{2-}$ in dichloroethane. $[\theta]_M$ is the molar ellipticity (defined as in natural optical activity in degrees decilitre decimetre^{-1} mole^{-1}) per gauss in the direction of the light beam. ε is the molar extinction coefficient. The experimental C/D values are indicated for each band (Reproduced, with permission, from *J. Chem. Phys.*, 1968, **48**, 5656)

in solution with the experimental C/D values given under each band. Comparison with Figure 7(a) shows immediately that the first band at 20,200 cm^{-1} is $E_g'' \rightarrow U_u'$ [$^2T_{1u}(\pi)$] and the second at 22,700 cm^{-1} is $E_g'' \rightarrow (E_u'' + U_u')(^2T_{2u})$, the small spin–orbit splitting in the excited state (due to the Cl ligands) being undetected in solution, and the third at 32,300 cm^{-1} is most probably $E_g'' \rightarrow U_u'$ [$^2T_{1u}(\sigma)$].

Figure 8 illustrates the increased information which may be obtained on studying the same ion in the crystalline state at low temperatures. Vibrational structure becomes apparent and the bands become much sharper. A detailed
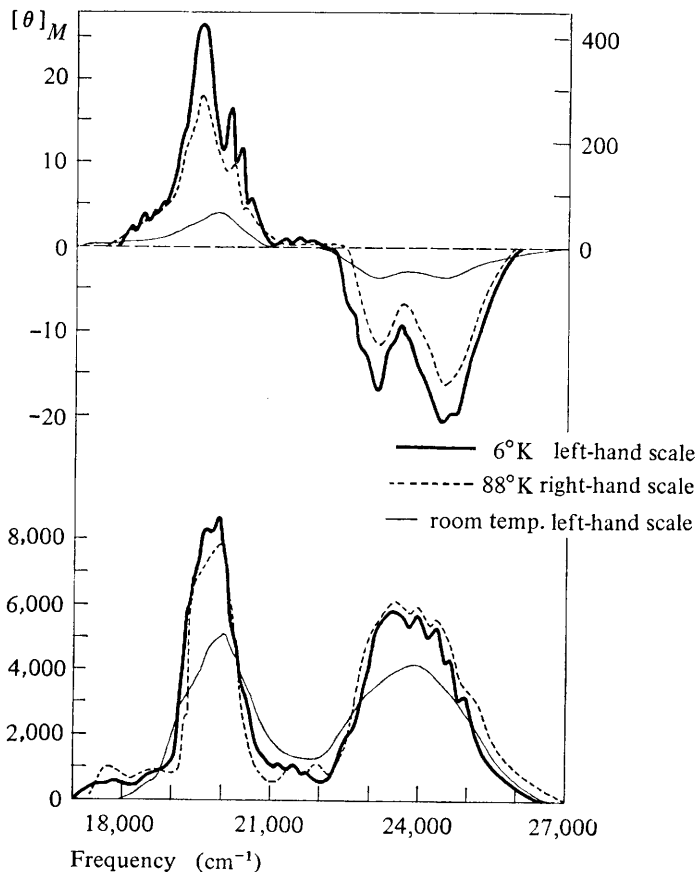
Figure 8 (MeNH$_3$)$_2$SnCl$_6$: Ir^{4+}. *M.c.d. and absorption spectra at* 300 K, 88 K (*left hand ellipticity scale*) *and* 6.0 K (*right hand ellipticity scale*) (Reproduced, with permission, from *J. Chem. Phys.*, 1969, **50**, 379)

discussion of these spectra is given in ref. 42 but the main features are as follows. The 20,000 cm^{-1} band shows a negative C term corresponding to the $E_g'' \to U_u'$ [$^2T_{1u}(\pi)$] transition. In the second main band (23,000—25,000 cm^{-1}) however we note a striking difference from the solution and room temperature crystal results in that the m.c.d. shows a pronounced cleft which does not correlate with any obvious feature in the absorption spectrum. Since the band arises from transitions to two closely spaced spin–orbit components with C terms of opposite sign[42] it seems likely that the cleft is the sharper $E_g' \to U_u'$ component bisecting the larger $E_g' \to E_u''$ band. Further discussion of this feature together with detailed comments on the vibrational structure may be found in ref. 42. The main point is that the Faraday parameters (C terms in the present example) can occur with either sign and hence are inherently capable of giving more information than the corresponding absorption spectrum. The m.c.d. of $(MeNH_3)_2 SnCl_6 : Ir^{4+}$ was found experimentally to have the $1/T$ dependence characteristic of C terms in the range 300—6° K. This indicates that magnetic exchange interactions are unimportant in this system since these would produce marked deviations from $1/T$ dependence.

B. Use of A terms.—The above examples have shown some typical uses to which C terms have been put and we now turn our attention to cases in which only the excited state of the transition is degenerate.

As a first example let us consider the d^{10} systems $SbCl_6^-$ and $SnCl_6^{2-}$ both of which exhibit a moderately intense absorption in the u.v.[43] The two most probable one-electron excitations are [Figure 9(a)] $t_{1u}(\pi) \to a_{1g}$ and $e_g \to t_{1u}^*$ each of which gives rise to a transition to a T_{1u} excited state from the A_{1g} ground state. For this transition we find, using group theory alone, that
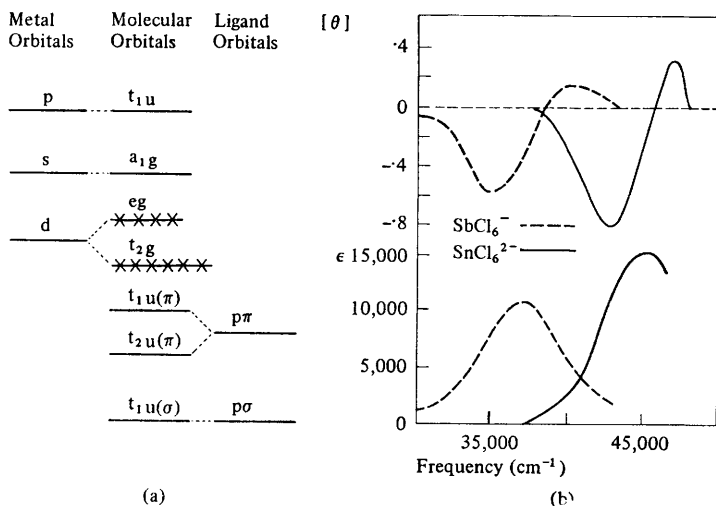
$$A/D = - i\langle T_{1u}x \mid \mu_z \mid T_{1u}y\rangle$$

and, making certain simplifying assumptions,[43] we may calculate that $A/D = + \beta/2$ and $- \beta/2$ respectively for the two choices. The experimental m.c.d. is shown in Figure 9(b) and we see immediately that A/D is positive. We are thus able to choose the assignment $t_{1u}(\pi) \to a_{1g}$ by a simple qualitative observation (the sign of the A term) and our confidence in this choice is further reinforced by the fact that the observed A/D value is also quantitatively in reasonable agreement with theory.[43]

Coronene is the second example and the highest occupied and lowest vacant π MO's are shown in Figure 10 together with the spectroscopic states arising from the first one-electron excitation. The commonly accepted order of states is $^1B_{2u}$, $^1B_{1u}$, $^1E_{1u}$, exactly analogous to the benzene molecule most of whose spectrum lies outside the range of present m.c.d. instrumentation. However, this order has not been unanimously agreed upon, some calculations predicting that a $^1E_{2g}$ level is lower than $^1B_{1u}$ and others that the $^1E_{1u}$ level is significantly

[42] A. J. McCaffery, P. N. Schatz, and T. E. Lester, *J. Chem. Phys.*, 1969, **50**, 379.
[43] P. N. Schatz, P. J. Stephens, G. N. Henning, and A. J. McCaffery, *Inorg. Chem.*, 1968, **7**, 1246.

Metal Orbitals	Molecular Orbitals	Ligand Orbitals
p	t_{1u}	
s	a_{1g}	
d	e_g	
	t_{2g}	
	$t_{1u}(\pi)$	
	$t_{2u}(\pi)$	$p\pi$
	$t_{1u}(\sigma)$	$p\sigma$

(a)

(b)

Figure 9 (a) *Schematic MO diagram for octahedral d^{10} metal hexachloride complexes* (b) *Absorption spectrum and m.c.d. of* $SnCl_6^{2-}$ *in 12N HCl (solid line) and* $SbCl_6^{-}$ *in 12N HCl (dashed line)* (Reproduced, with permission, from *Inorg. Chem.*, 1968, **7**, 1246)

split by a Jahn–Teller distortion. These points are discussed in greater detail in ref. 44. The experimental absorption and m.c.d. spectra are shown in Figure 10 and the m.c.d. is found to support the conventional assignment. Thus the first band ($^1B_{2u}$) shows complex vibrational structure in both absorption and m.c.d. indicating contributions to the intensity either from degenerate vibronic states or from overlapping vibrations having opposite signed m.c.d.'s. The second band also shows considerable structure but no indication of the overall *A* term which would be expected if the transition were $^1A_{1g} \rightarrow {}^1E_{2g}$. Here however we must emphasise that the absence of an *A* term does not disprove this assignment since it could conceivably be small and obscured by the (always present) *B* term. The intense band (33,000 cm^{-1}) shows a very distinct *A* term consistent with the $^1A_{1g} \rightarrow {}^1E_{1u}$ assignment and in contradiction to the suggestion of a large Jahn-Teller splitting. In ref. 44 an experimental value of the magnetic moment of the $^1E_{1u}$ state of coronene was obtained and the ability of various quantum mechanical models to predict this quantity was tested. MO models of varying degrees of sophistication using Slater orbitals were found to be uniformly unsuccessful although the use of a basis set of orthogonalised orbitals at least gave the correct sign. Interestingly the free-electron model gives good results for both coronene and triphenylene though it fails for the non-

[44] P. J. Stephens, P. N. Schatz, A. B. Ritchie, and A. J. McCaffery, *J. Chem. Phys.*, 1968, **48**, 132.
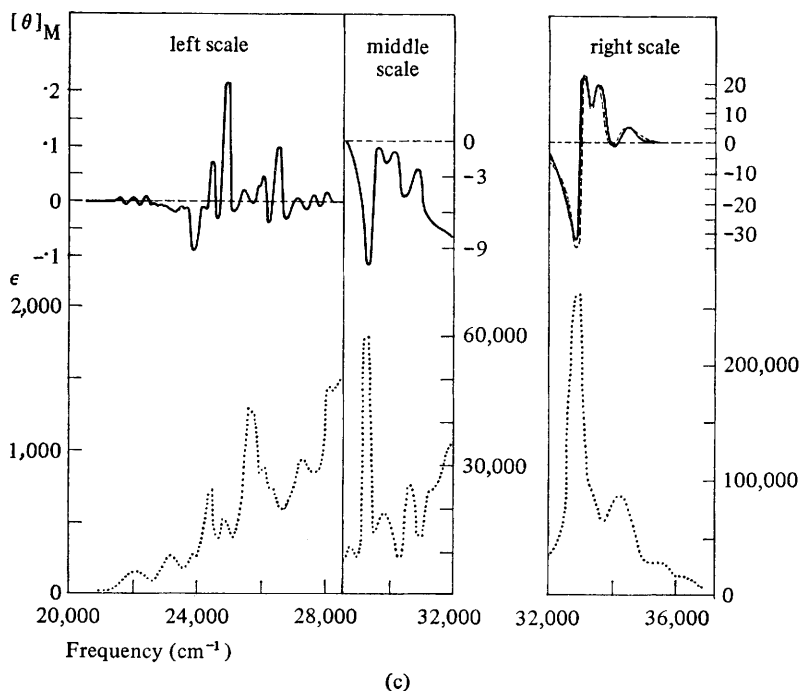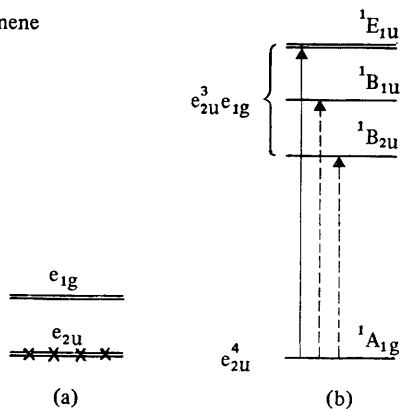
Figure 10 (a) *Highest occupied and lowest unoccupied MO's for coronene. Crosses indicate electrons in the ground state.* (b) *Lowest singlet states of coronene. Solid and dashed lines denote allowed and forbidden transitions, respectively.* (c) *M.c.d. and absorption spectra of coronene. The dashed line shows the computer best fit of the 32—36,000 cm⁻¹ band system* (Reproduced, with permission, from *J. Chem. Phys.*, 1968, **48**, 132)

alternant tropylium ion[45] as do the MO models using either orthogonalised or non-orthogonal orbitals.

C. Use of B terms.—The selection rules for B terms may be derived from equation (16) and from the analogous expressions for the non-isotropic case.[10] Consider the mixing of state k with state j to give a B term in the m.c.d. of the transition $a \rightarrow j$ in Figure 5. For the B term to be non-zero, states j and k must be connected by the magnetic dipole operator; *i.e.*, the direct product of the irreducible representations of j and k must contain a component of the magnetic dipole operator (μ). Furthermore states a and j, and k and a must be connected by components of the electric dipole moment operator which are mutually perpendicular and whose vector product contains a component parallel to $\langle j \mid \mu \mid k \rangle$. Hence if the direct product of j and k contains only the n-component of angular momentum, the product of a and j must contain the z-component of the electric moment, and the product of k and a the y-component of the electric moment, or *vice versa*. The closer states k and j are in energy the greater is the mixing and hence the larger the contribution to the B term [equations (9) and (16)].

Foss and McCarville[46] examined the m.c.d. of a series of cata-condensed aromatic hydrocarbons and reported data for the two longest wavelength transitions ($^1A_{1g} \rightarrow {}^1B_{2u}$ and $^1A_{1g} \rightarrow {}^1B_{1u}$). The authors assumed that the dominant contribution to the m.c.d. was from the field-induced mixing of the two excited states and it can be readily ascertained that these fulfil the symmetry requirements outlined above. In this work the magnitude of the m.c.d. is related to the separation of the excited $^1B_{1u}$, $^1B_{2u}$ states and increases markedly as the two bands approach one another. The sign of the m.c.d. is said to depend on the polarisation of the $a \rightarrow j$ transition being positive when the band is transversely polarised. A similar account of the symmetry properties of B terms was given by Briat and co-workers[47] in an investigation of the m.c.d. of derivatives of [10]-annulene. In a later paper, Foss and McCarville[48] carried over this treatment to the $^1A_{1g} \rightarrow {}^1B_{2u}$ band of substituted benzenes and found a correlation between the sign of the m.c.d. and the nature of the substituent. A o,p-directing group gives a positive m.c.d. and a *meta*-directing group a negative one, and a plot of m.c.d. versus Hammet σ *para* values for 17 monsubstituted benzenes gave a reasonable straight line. In disubstituted benzenes the dominant substituent determines the sign of the m.c.d. Since there exists a rather limited number of stable, highly symmetrical molecules it seems likely that considerable future effort will be devoted to a study of the factors influencing the sign and magnitude of B terms in the transitions of molecules having low symmetry. The success of Foss and McCarville indicates that this is potentially a useful chemical tool.

[45] A. B. Ritchie, Ph.D. Dissertation, University of Virginia, 1968.
[46] J. G. Foss and M. E. McCarville, *J. Chem. Phys.*, 1966, **44**, 4350.
[47] B. Briat, D. A. Schooley, R. Records, E. Bunnenberg, C. Djerassi, and F. Vogel, *J. Amer. Chem. Soc.*, 1968, **90**, 4691.
[48] J. G. Foss and M. E. McCarville, *J. Amer. Chem. Soc.*, 1966, **89**, 30.

6 Survey of Recent Work
The final portion of this Review will be a survey of recent m.c.d. experiments. This appears worthwhile since much important work has been done since the only previous recent review, that of Buckingham and Stephens.

We have somewhat arbitrarily divided the systems studied into five main (sometimes overlapping) categories depending on (i) the symmetry of the molecule, *i.e.* whether the analysis involves *A*, *B*, and *C* or only *B* terms, (ii) the nature of the compound, *viz.* organic or inorganic, (iii) the conditions of the experiment, *i.e.* crystals at low temperatures, solutions at room temperature, gases at high resolution. These are listed in the Table (end of Review).

A. Solids.—Perhaps the most important fundamental new work is that done on absorption bands in solids at low temperatures. In this situation the orientation of the molecules is known and at low temperatures the bands become sharper and vibrational fine structure may be resolved. This is potentially of great value, since we may then apply our previous analysis to individual vibronic lines with the possibility of obtaining magnetic moments and vibrational symmetries of individual vibronic states. This should be a very powerful tool for the investigation of Jahn–Teller and other vibronic interactions.

In this category the most extensively investigated absorption bands in solids are the colour centres in alkali halide crystals. These are very interesting systems from a theoretical viewpoint because of their relative simplicity. The *F*-centre for example consists of an electron trapped at a negative ion vacancy in say KF or KCl and has a broad absorption band in the visible. The ground and excited states are ^2S and ^2P respectively, the latter being split by spin–orbit interaction into $^2P_{3/2}$ and $^2P_{1/2}$. Transitions to these give rise to the characteristic colour of the *F*-centre. The m.c.d. of the *F*-centre in KBr was first reported by Margerie and co-workers[49] followed by measurements on NaCl, NaBr, KCl, and caesium halides.[50] Lüty and co-workers[51, 52] measured the m.o.r.d. of *F*-centres in KCl, NaCl, KBr, KI, RbBr, and CsBr and separated out the contributions due to the ground and excited states. They showed that the spin–orbit splitting of ^2P in the *F*-centre is opposite in sign to that of the free alkali atom and that the magnitude of splitting is determined by both the metal and halogen ions.

Those results were analysed in a most important paper by Henry, Schnatterly, and Slichter[27] who were concerned with the validity of the approximation that only electronic states need be considered, despite the fact that absorption lines are known to be much broadened by vibronic interactions which may be one or two orders of magnitude larger than splittings due to the magnetic field. The technique used was an extension of that derived by Van Vleck[53] for the calculation of magnetic resonance line shapes and is known as the method of

[49] N. V. Karlov, J. Margerie, and Y. Merle-d'Aubigne, *J. Phys. Radium*, 1963, **24**, 717.
[50] R. Romestain and J. Margerie, *Compt. rend.*, 1964, **258**, 2525, 4490.
[51] F. Lüty and J. Mort, *Phys. Rev. Letters*, 1964, **12**, 45.
[52] F. Lüty, J. Mort, and F. C. Brown, *Phys. Rev.*, 1965, **137**, *A*, 566.
[53] J. H. Van Vleck, *Phys. Rev.*, 1948, **74**, 1168.

moments (see also previous discussion in Sections 3 and 4). Since the lineshape of an electronic transition is the sum of a large number of vibronic components it is very difficult to calculate. Van Vleck has shown however that the moments of the lineshape can be derived rigorously since they are expressed as diagonal sums which may be evaluated in any system of quantisation. The optical case of a transition from a non-degenerate ground state to a degenerate excited state split by spin–orbit coupling and electron–lattice interactions, was treated by Henry *et al.*[27] These authors deduced rigorous formulae for the moments of absorption of linearly and circularly polarised light in the presence of external perturbations due to stress or magnetic or electric fields. The change of the first moment of absorption of left or right circularly polarised light on 'switching on' the magnetic field could be expressed in terms of a spin–orbit parameter Δ, as could the change in the second moment. This gave two independent determinations of Δ. From the second moment of the absorption and the change in the third moment of absorption Henry *et al.* were able to evaluate contributions to the broadening of the F-band by cubic and non-cubic vibrational modes. For these determinations the experimental data of Romestain and Margerie[49, 50] were used.

The same method of analysis was used by Shepherd[54] in a measurement of the m.c.d. of the R-centre in KCl and KF. The R-centre is an equilateral triangle of F-centres in the (111) crystal plane, thus resembling the hypothetical triatomic hydrogen molecule in electronic structure, and it has a ^2E ground state, with transitions to $^2A_2$ (R_2) and ^2E (R_1). Shepherd found that the zeroth moment (band area) of the zero-phonon line m.c.d. was strongly affected by internal strains in the sample but the change in the first moment is independent of strain. The first moment was measured as a function of temperature and a direct evaluation of the reduction of the angular momentum and spin–orbit coupling by Jahn–Teller interactions was obtained. Simultaneously, Burke[55] has made the same measurements and analysis of the R-centre including the broad R_1R_2 bands, the results confirming those of Shepherd. The same system has also been examined by Merle D'Aubigne and Duval.[56] As might be expected, there has been a very rapid increase in the number of m.c.d. experiments on colour centres. Ingels and Jacob[57] recorded the m.c.d. and absorption spectra of the U_2 centre in KCl, KBr, and KI and from this evaluated the excited state spin–orbit splittings. Chemically this is a very interesting system since it is an interstitial H atom and thus is the tetrahedral HX_4^{4-} molecule. Other measurements include the F-centre in CaO by Kemp *et al.*,[58] where the authors have evaluated the magnitude of the Jahn–Teller quenching of the ground-state magnetic moment by use of the moments technique of analysis, the Z_2 centre in Sr-doped KCl,[59] and the A-band in Tl^+ and Pb^{2+}-doped potassium halides.[60]

[54] I. W. Shepherd, *Phys. Rev.*, 1968, **165**, 985.
[55] W. Burke, *Phys. Rev.*, 1968, **172**, 866.
[56] Y. Merle D'Aubigne and P. Duval, *J. Phys. Radium*, 1968, **29**, 896.
[57] J. Ingels and G. Jacob, *Physica status solidi*, 1968, **30**, 163.
[58] J. C. Kemp, W. M. Zinkiker, and J. A. Glaze, *Phys. Letters*, 1966, **22**, 37.
[59] G. Gehrer, W. Bock, and E. Lüscher, *Physica status solidi*, 1969, **31**, K13.
[60] R. Onaka, T. Mabuchi, and A. Yoshikawa, *J. Phys. Soc. Japan*, 1967, **23**, 1036.

These latter systems are related to the post-transition $d^{10}s^2$ hexahalides and the authors have evaluated g-factors and assigned the first main absorption as $^1S_0$ to $^3P_1$.

Relatively little other work has been published to date on solids at low temperatures. Pisarev and co-workers[61] have indicated how m.c.d. may be utilised to study magnetic exchange interactions in an examination of the hexagonal ferrimagnet $RbNiF_3 : Co^{2+}$. Denning[62] measured the m.c.d. of $(+)$—Co en_3^{3+} in [Rh en_3Cl_3]$_2$NaCl,$6H_2O$ at *ca.* 5 K and found that the excited-state magnetic moment was quenched to less than 0.05 of its expected value, which was attributed to the dynamic Jahn–Teller distortion of the excited state. A single crystal of K_2PtCl_4 at *ca.* 5 K was examined by McCaffery, Stephens, and Schatz[63] who found that the A term observed in the solution m.c.d. of K_2PtCl_4 at *ca.* 30,000 cm^{-1} and due to the $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition is mainly in-plane polarised since it appears almost unchanged in the axial m.c.d. Vibrational structure was not resolved in the m.c.d. however and no further information was deduced concerning the position of the d_{z^2} orbital in the MO scheme. Margerie[64] has looked at the m.c.d. of the rare-earth ion Sm^{2+} doped into the cubic CaF_2 lattice down to 1.87 K and has evaluated excited-state magnetic moments for the $4f^6 \rightarrow 4f^55d$ transitions as an aid to the interpretation of the spectrum.

Work on $IrCl_6^{2-}$ in $(MeNH_3)_2SnCl_6$[42] is described in section 5A. In this paper the authors identified the spin–orbit split components of the excited states from the m.c.d. spectrum and were able to establish the $1/T$ dependence of the C term in the range 300—6 K and to show that no appreciable exchange coupling took place in this particular host lattice. Results are also available on $IrBr_6^{2-}$ in both $(EtNH_3)_2SnBr_6$ and K_2SnBr_6[65] and here the spin–orbit splitting is much larger since in the d^5 configuration, excited-state spin–orbit coupling is due almost entirely to the ligands. Furthermore, the m.c.d. seems to indicate a strong trigonal distortion in the ethyl ammonium crystal which is absent in the potassium salt. Weakliem[66] and co-workers have examined the m.c.d. of thulium doped into CaF_2 at 2.0 K and established that the $4f \rightarrow 5d$ bands are mainly $G_{3/2}$ in character. A preliminary account of more extensive research by Weakliem *et al.*[67] on the m.c.d. of divalent rare-earths in CaF_2 has appeared and several groups of workers have published m.c.d. spectra of di- and tri-valent rare-earths in CaF_2 and SrF_2.[68–71]

[61] R. V. Pisarev, I. G. Siny, N. N. Nestarova, G. A. Smolensky, and P. P. Syrnikov, *Physica status solidi*, 1968, **30**, 367.
[62] R. G. Denning, *Chem. Comm.*, 1967, 120.
[63] A. J. McCaffery, P. J. Stephens, and P. N. Schatz, *J. Amer. Chem. Soc.*, 1968, **90**, 5730.
[64] J. Margerie, *Physica*, 1967, **33**, 238.
[65] T. E. Lester, A. J. McCaffery, J. R. Dickinson, and P. N. Schatz, to be published.
[66] C. H. Anderson, H. A. Weakliem, and E. S. Sabisky, *Phys. Rev.*, 1966, **143**, 223.
[67] C. H. Anderson and H. A. Weakliem in 'Optical Properties of Ions in Crystals' ed. H. M. Crosswhite and H. W. Moos, Interscience, New York, 1966.
[68] L. A. Alexseyeva and P. P. Feofilov, *Optics and Spectroscopy*, 1967, **22**, 545.
[69] L. A. Alexseyeva and N. V. Starostin, *Optics and Spectroscopy*, 1968, **24**, 72.
[70] L. A. Alexseyeva, N. V. Starostin, and P. P. Feofilov, *Optics and Spectroscopy*, 1967, **23**, 140.
[71] T. Inari, *J. Phys. Soc. Japan*, 1968, **25**, 639.

B. Gases.—High-resolution gas-phase work is also of fundamental importance in that it provides a test of the theory in cases where sharp lines are resolved having widths of the same order as, or much smaller than, the Zeeman splitting. Stalder and Eberhardt[72] have carried out a thorough investigation of the m.o.r.d. and m.c.d. of the rotational fine structure of the $^1\sum^+ \rightarrow {}^3\Pi$ electronic absorption of ICl, and they have calculated the expected m.o.r.d. and m.c.d. patterns treating the Zeeman component of each line separately. *A* Terms arising from excited rotational state degeneracies together with *B* terms from the mixing of adjacent levels by the field were evaluated and compared with the experimental spectrum. They concluded that the agreement between calculated and observed m.c.d. gave support to the Buckingham–Stephens equations for the dispersion of the Faraday effect through absorption bands, provided that in the case where narrow lines are resolved, each Zeeman component of each zero-field line is treated separately.

Magnetic rotation spectra and Zeeman effect experiments in gases provide related information but space limitations do not permit these to be discussed here.

C. High-symmetry Inorganic Compounds.—By far the greatest amount of work in this category has been done by Schatz and co-workers at the University of Virginia who have demonstrated that it is a most fruitful area for m.c.d. by virtue of the availability of many systems of high symmetry and the success of ligand field theory in interpreting the spectra. The first investigations of these workers[32] concerned the charge-transfer transitions in MnO_4^-, CrO_4^{2-}, and $Fe(CN)_6^{3-}$. In the two d^0 oxyions, magnetic moments from the *A* terms of the allowed transitions were compared with those calculated by use of wavefunctions which corresponded to a variety of bonding situations. Confirmation of the first band assignment as $t_1 \rightarrow e$ was obtained but unambiguous assignments of the other bands was not possible although $t_2 \rightarrow e$ could be excluded. The results obtained on $Fe(CN)_6^{3-}$ have been discussed earlier. Other work on allowed transitions by this group includes the previously discussed $IrCl_6^{2-}$ spectrum and the related compounds $IrBr_6^{2-}$ and $RuBr_6^{3-}$;[40] the d^6 hexahalides $PtCl_6^{2-}$, $PdCl_6^{2-}$, $RhCl_6^{3-}$, $PtBr_6^{2-}$, $IrCl_6^{3-}$, $IrBr_6^{3-}$, and PtI_6^{2-},[26, 73] and the d^{10} hexahalides, $SnCl_6^{2-}$ and $SbCl_6^-$.[26, 43] From the sign and magnitudes of the *A* terms in the d^6 halides the main absorption bands were tentatively assigned as $t_{1u}(\pi) \rightarrow e_g(d)$ and $t_{1u}(\sigma) \rightarrow e_g(d)$ in the chlorides. The hexabromides have more complicated m.c.d. spectra due probably to increased spin–orbit coupling. The d^{10} halides have been discussed in section 5(B).

Work on d–d transitions has not tended to produce information as decisive as that on allowed transitions. McCaffery, Stephens, and Schatz[74] examined Co^{3+} complexes with a wide variety of ligands and symmetries and found that

[72] A. F. Stalder and W. H. Eberhardt, *J. Chem. Phys.*, 1967, **47**, 1445.
[73] G. N. Henning, P. N. Schatz, and A. J. McCaffery, to be published.
[74] A. J. McCaffery, P. J. Stephens, and P. N. Schatz, *Inorg. Chem.*, 1967, **6**, 1614.

excited-state magnetic moments appear to be very much reduced. However, certain spin-forbidden transitions showed a very pronounced m.c.d. particularly the intraconfigurational quartet $\rightarrow$ doublet excitations of Cr^{3+}, which dwarfed the spin-allowed m.c.d. in some cases. $Mn(H_2O)_6^{2+}$ also showed large spin-forbidden m.c.d. More success was obtained with the square planar d^8 halides. Martin *et al.*[75] first demonstrated the degeneracy of the $^1A_{1g} \rightarrow {}^1E_g$ transition in $PtCl_4^{2-}$ by m.c.d. and this was extended to other members of this series by McCaffery *et al.*[63] The latter authors showed in addition that the two strong bands in the u.v. spectrum of these compounds are probably the charge-transfer transitions $^1A_{1g} \rightarrow {}^1A_{2u} + {}^1E_u (\pi)$ and $^1A_{1g} \rightarrow {}^1E_u (\sigma)$, except for $PtCl_4^{2-}$ where there is evidence for a $5d \rightarrow$ metal $6p_z$ transition.

D. High-symmetry Organic Compounds.—Included in this group are compounds such as the metalloporphyrins which may also be thought of as metal complexes. For simplicity of calculations however, the metal is generally ignored, and a satisfactory account of the electronic properties is usually obtained. Several groups of authors have investigated the magnetic optical activity of porphyrins, phthalocyanins, and related compounds, the most comprehensive account being that of Stephens, Suëtaka, and Schatz.[76] These authors analysed the m.o.r.d. data of Shashoua[77] and were able to confirm that the visible Q_0, Q_1 bands in zinc haematoporphyrin and magnesium phthalocyanine are indeed the vibronic components of one $^1A_{1g} \rightarrow {}^1E_u$ electronic transition and that the Soret band is another $^1A_{1g} \rightarrow {}^1E_u$ transition. In free base coproporphyrin II and phthalocyanine, the degenerate Q_0 and Q_1 bands are split into their x and y polarised components which may be identified by the sign of the m.c.d. Stephens *et al.* also compared the experimental excited-state magnetic moments with those calculated from current theoretical models and found that the free-electron model of Simpson[78] and the MO wavefunctions of Gouterman and co-workers[79] in which extensive configuration interaction is included give results in good agreement with experiment. The simple MO treatment of Longuet-Higgins[80] *et al.* does not agree well with experiment.

A somewhat different experimental approach was taken by Malley *et al.*[81] who measured the absorption of left circularly polarised light by zinc coproporphyrin I and then superimposed on the same trace the absorption of right circularly polarised light, both in the presence of a 100 kG magnetic field. The absorption maximum of the two peaks were then subtracted to yield directly the energy of splitting of the excited state. As the authors point out,

[75] D. S. Martin jun., J. G. Foss, M. E. McCarville, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, 1966, **5**, 491.
[76] P. J. Stephens, W. Suëtaka, and P. N. Schatz, *J. Chem. Phys.*, 1966, **44**, 4592.
[77] V. E. Shashoua, *J. Amer. Chem. Soc.*, 1965, **87**, 4044.
[78] W. T. Simpson, *J. Chem. Phys.*, 1949, **17**, 1218.
[79] C. Weiss, H. Kobayashi, and M. Gouterman, *J. Mol. Spectroscopy*, 1965, **16**, 415.
[80] H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, 1950, **18**, 1174.
[81] M. Malley, G. Feher, and D. Mauzerall, *J. Mol. Spectroscopy*, 1968, **26**, 320.

this avoids the approximations inherent in the earlier fitting techniques,[32] though these are also eliminated by use of the method of moments,[27, 34] However, the technique requires other assumptions concerning what constitutes a measure of the energy difference between electronic states when transitions from thermally populated vibrational states contribute to the overall band shape. The spectra of Malley *et al.* show a loss of intensity on the red sides of the bands on cooling to 77 K. Therefore the low-temperature value of the Zeeman splitting would be more reliable and there is very good agreement between the 77 K magnetic moment of Malley *et al.* and that obtained by Stephens *et al.* using fitting techniques.[25]

Briat and co-workers have accumulated much data on systems related to the porphyrins including some optically active chlorins[82] and cyclic polyenes related to [18]-annulene[83] and [10]-annulene.[47] The value of m.c.d. as an analytic tool is stressed since the m.c.d. is larger and more detailed at 50 kG than the natural c.d. of the chlorins. It also confirms rather well the assignments of chlorin spectra given by Gouterman.[84] The annulene spectra have several interesting features and theoretical work on the m.c.d. results would be very desirable. For example the sign of the A term under the $^1A_{1g} \rightarrow {}^1E_u$ transition in [18]-annulene is opposite in sign to that observed in coronene[44] and metal porphyrins.[76] Further experimental work is also indicated. Gouterman and Wagniere[85] obtained greatly increased information from the absorption spectra at 77 K which enabled them to resolve the B_{2u} and B_{1u} bands. Low-temperature m.c.d. studies might well throw some light on the puzzling question of bond alternation in the cyclic polyenes.

The comprehensive account of the m.c.d. of benzene triphenylene and coronene by Stephens *et al.*[44] has been discussed in an earlier section. The authors used the experimental excited-state magnetic moments to test current theories of π-electrons in aromatic hydrocarbons.

E. Low-symmetry Organic Compounds.—Foss'[46, 48] work on the chemical factors influencing the sign of B terms has been mentioned earlier. McCaffery *et al.*[86] failed to find any obvious correlations analogous to the Octant Rule in natural optical activity on examining the $n - \pi^*$ m.c.d. of series of ketones, the effects in most cases being very small. Voelter *et al.*[87a] found m.c.d. more sensitive than natural c.d. as an analytic tool for purines, pyrimidines, and

[82] B. Briat, D. A. Schooley, R. Records, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, 1967, **89**, 6170.
[83] B. Briat, D. A. Schooley, R. Records, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, 1967, **89**, 7062.
[84] M. Gouterman, *J. Mol. Spectroscopy*, 1961, **6**, 138.
[85] M. Gouterman and G. Wagniere, *J. Chem. Phys.*, 1962, **36**, 1188.
[86] A. J. McCaffery, G. N. Henning, P. N. Schatz, A. B. Ritchie, H. P. Perzanowski, O. R. Rodig, A. W. Norvelle jun., and P. J. Stephens, *Chem. Comm.*, 1966, 520.
[87a] W. Voelter, R. Records, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, 1969, **91**, 6191.

nucleosides. Foss and McCarville's[87b] most recent work suggests an explanation for the very striking sign change of the $^1A_{1g} \rightarrow {}^1B_{2u}$ m.c.d. of substituted benzenes on going from electron-donating to electron-withdrawing substituents. In this the $^1B_{1u}$ transition is re-assigned as a charge-transfer absorption either from or to the ring depending upon whether the substituent is a donor or acceptor. The change in sign in the energy denominator of the B term expression thus accounts for the change in sign.

The authors thank Professor S. F. Mason for helpful comment.

Table

Compound	References
1. Solids	
F-centre in NaCl, KBr, KCl, KI, RbBr, CsBr	49, 54, 55, 52
R-centre in KCl, KF	54, 55, 56
$[\text{Rh en}_3\text{Cl}_3]_2\text{NaCl},6\text{H}_2\text{O} : \text{Co}^{3+}$	62
$K_2\text{PtCl}_4$	63
$(\text{MeNH}_3)_2\text{SnCl}_6 : \text{Ir}^{4+}$	42
$(\text{EtNH}_3)_2\text{SnBr}_6 : \text{Ir}^{4+}$	65
$Al_2O_3 : Cr^{3+}$	45, 92, 93, 98
$CaF_2 : Sm^{2+}$	64
$CaF_2 : Tm^{2+}$	66
$CaF_2 : Ho^{2+}, Eu^{2+}, Pr^{2+}, Er^{2+}, Dy^{2+}, Sm^{2+}, Nd^{2+}$	67
$Al_2O_3 : Mn^{2+}, MgO : Mn^{2+}$	94
$CaF_2 : U^{4+}, Ho^{3+}$ glass	97
U_2-centre in KCl, KBr, KI	57
F-centre in MgO	58
Z_2-centre in KCl : Sr^{2+}	59
A-band in KCl : Pb^{2+}, KBr : Pb^{2+}, KBr : Tl^+, KI : Tl^+	60
$RbNiF_3 : Co^{2+}$	61
$CaF_2 : Tm^{2+}, Ho^{2+}, Dy^{2+}, SrF_2 : Tm^{2+}$	68, 70
$CaF_2 : Ce^{3+}$	69
$CaF_2 : Ho^{2+}, Ho^{3+}$	71
2. Gases	
ICl	72
Pyrazine	88
3. Liquids and Solutions	
(i) *Inorganic*	
$MnO_4^-, CrO_4^{2-}, Fe(CN)_6^{3-}$	32, 38
$IrCl_6^{2-}, IrBr_6^{2-}, RuBr_6^{3-}$	40
$SnCl_6^{2-}, SbCl_6^-$	43

[87b] J. G. Foss and M. E. McCarville, to be published.

Table—*continued*

Compound	References
$PtCl_6^{2-}$, $PdCl_6^{2-}$, $RhCl_6^{3-}$, $IrCl_6^{3-}$, $PtBr_6^{2-}$, $IrBr_6^{3-}$, PtI_6^{2-}	26, 73
$Co(H_2O)_6^{2+}$, $Ni(H_2O)_6^{2+}$, $Cr(NH_3)_6^{3+}$, $Cr(H_2O)_6^{3+}$	
$Co(NH_3)_6^{3+}$, $Co(CN)_6^{3-}$, $Mn(H_2O)_6^{2+}$, $Co(NH_3)_5Cl^{2+}$,	74
trans-Co en$_2$Cl$_2$$^+$, *cis*-Co en$_2Cl_2$$^+$, cis-$Co(NH_3)_4(H_2O)_2^{3+}$	
$PtCl_4^{2-}$, $PdCl_4^{2-}$, $PdBr_4^{2-}$, $AuCl_4^-$, $AuBr_4^-$, $Pd(NH_3)_4^{2+}$	75, 63
$CoCl_4^{2-}$, $CoBr_4^{2-}$, CoI_4^{2-}	89
$EuCl_3$, $ErCl_3$, $HoCl_3$, $SmCl_3$, $TbCl_3$, $GdCl_3$, $TmCl_3$, $CeCl_3$	96
$ErCl_3$, $TmCl_3$, $EuCl_3$	97

(ii) *Organic*

Coproporphyrin-II tetramethylester, haematoporphyrin, zinc haematoporphyrin, phthalocyanine, magnesium-, copper-, zinc-phthalocyanine	76, 77
Zinc coproporphyrin I tetramethyl ester	81
Methyl pheophorbide *a*, pyromethyl pheophorbide *a*, *meso*-pyro methyl pheophorbide *a*, 9-desoxopyromethylpheophorbide *a* chlorin e_6 trimethyl ester, rhodochlorin dimethyl ester isochlorin e_5 dimethyl ester	82
Cytochrome C	90
1,7,13-Tridehydro[18]-annulene, [18]-Annulene, [18]-Annulene trioxide, [18]-annulene dioxide sulphide, [18]-annulene disulphide oxide, [18]-annulene trisulphide, monodehydro[14]-annulene, 1,8-bisdehydro[14]-annulene, *trans*-15,16-dimethyl dihydropyrene, 1,9-bisdehydro[16]-annulene, [16]-annulene, [8]-annulene	83
1,6-Imino-cyclodecapentaene (cdp), 1,6-oxy-cdp., *N*-methyl-1,6-imino-cdp., 1,6-methano-cdp., 11-bromo-1,6-methano-cdp., 2,7-dibromo-1,6-methano-cdp., *N*-acetyl-1,6-imino-cdp., 1,6-methanocycloundecapentaenylfluoborate.	47
Benzene, coronene, triphenylene	44
Xanthosine, xanthine, guanosine, guanine, inosine hypoxanthine, adenosine, adenine, uridine, uracil, thymidine, thymine, α- and β-2′-deoxy-5-(trifluoromethyl)uridine, cytidine, cytosine.	87
Toluene, naphthalene, anthracene, tetracene	46
NN-dimethylamino, amino, hydroxy, methoxy, methyl, ethyl, chloro, bromo, iodo, carboxycarbonylcyano, sulphonic, sulphonyl chloride, mono-substituted benzene. σ-Aminohydroxy, *m*-aminochloro, *m*-aminobromo, *m*-hydroxymethyl, *p*-hydroxymethyl, σ-*p*- and -*m*-dimethyl, *p*-nitrocarbonyl, *p*-chlorosulphonic, *p*-methyl acetyl, disubstituted benzenes.	48

Table—*continued*

Compound	*References*
Pentamethyl and hexachloro-benzene. Benzene, anilinium σ- and *m*-methyliodo, m-bromofluoro, σ-carboxy hydroxy, 1,3,5-trimethyl, hexaethyl- and *p*-carboxyamino benzene. Acetone, ethyl methyl-, isopropyl methyl-, isobutyl methyl-ketone, cyclobutanone, 2-bromocyclobutanone, cyclopentanone, cyclohexanone, 2-methyl-, 4-methyl-cyclohexanone cyclododecanone, tetramethyl cyclobutane-1, 3-dione, isophorone, dicyclopropyl-, dicyclobutyl ketone, *cis*-2-decalone, norcamphor, acetophenone; *p*-methyl-, *p*-methoxy-, p-chloro-, *p*-bromo-acetophenone, benzophenone, thiobenzophenone.	86, 91
Naphthalene, 1,4,5,8-tetrachloronaphthalene, anthracene, phenanthrene, 1-methyl-phenanthrene, benzo(*c*)phenanthrene, 1-methylbenzo(*c*)phenanthrene, 1-fluoro-12-methyl-benzo(*c*)phenanthrene, fluorene, triphenylene, fluoranthrene, perylene.	95

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