The Magnetic Circular Emission Spectrum of Zinc Octaethyl Porphyrin

By ROBERT A. SHATWELL and ANTHONY J. MCCAFFERY*
(*School of Molecular Sciences, University of Sussex, Falmer, Brighton* BN1 9QJ)

Summary The difference of intensity of left and right circularly polarised emission from zinc octaethyl porphyrin in a magnetic field at low temperature enables the evaluation of the magnetic moment of the fluorescent and phosphorescent states; attention is drawn to the potential of this technique in studying energy transfer processes.

THE technique of magnetic circular dichroism (m.c.d.) is now well established[1] and, to date, has involved the study of the difference in *absorption* coefficients for left and right circularly polarised light. The related experiment namely the difference of circular intensity of emitted radiation from excited molecules in a magnetic field (which we shall abreviate as magnetic circular emission. m.c.e.) also potentially contains much new data on electronic states of molecules. For example the symmetry and magnetic moment of the emitting state may be obtained and, further, information on internal conversion and intersystem crossing processes is available from studies of the conservation of angular momentum. It should also be possible to study the dynamics of transitions between the components of an emitting doublet or triplet thus providing information similar to that obtained from microwave-optical double resonance experiments.[2]

So far the experimental detection of m.c.e. has only been reported briefly as a contributed paper at a symposium.[3] In this communication we report the observation of the m.c.e. spectrum of zinc octaethyl porphyrin (ZnOEP) at *ca.* 15 K in a magnetic field of up to 2·5 Tesla.

In the experiment, the sample consisted of ZnOEP dissolved in a rigid matrix of polymethyl methacrylate.[4] It was mounted in the bore of a super-conducting magnet which was in contact with liquid helium, and was excited by the 5145 Å line of a Spectra Physics 4 w argon ion laser. The emitted radiation was analysed using a photoelastic modulator[5] followed by a calcite polariser. The modulated radiation was wavelength analysed by a grating monochromator, the signal detected by a photomultiplier and amplified by means of a phase-sensitive detector.

The emission spectrum of ZnOEP is shown in the upper part of the figure. Both the fluorescence and phosphorescence spectra of zinc porphyrins are well known.[6,7] We note here that our spectrum is that of a rigid solution and thus the lines observed in both absorption and emission of ZnOEP in polymethyl methacrylate are broadened by the multiplicity of sites in the matrix. This contrasts the sharp line spectra found in hydrocarbon matrices by Canters *et al.*[7] In some respects this is a distinct advantage since we do not expect the polymer lattice to cause the marked crystal field splitting observed by these authors. Whilst much useful information may be derived from studies in hydrocarbon matrices, these relatively minor lattice and zero field effects tend to obscure the overall molecular processes taking place. If necessary they can be dealt with by taking moments of the line shapes.[8] The spectrum shows both the fluorescence and phosphorescence bands. The strong peaks at 17,450 and 16,000 cm^{-1} in the emission spectrum are assigned as transitions from the origin of the excited ^1E_u state to the vibrational ground state of the $^1A_{1g}$ ground electronic level and to the $\nu = 1$ vibrational level in the totally symmetric mode respectively. The structure between these two represents transitions to other excited vibrational levels and is analogous to the structure found in the absorption and m.c.d. spectra of ZnOEP in polymethyl methacrylate at low temperatures by Gale *et al.*[4] The phosphorescence peak occurs at *ca.* 14,360 cm^{-1} and is close in energy to that observed in the hydrocarbon matrix at 4·2 K.[7]

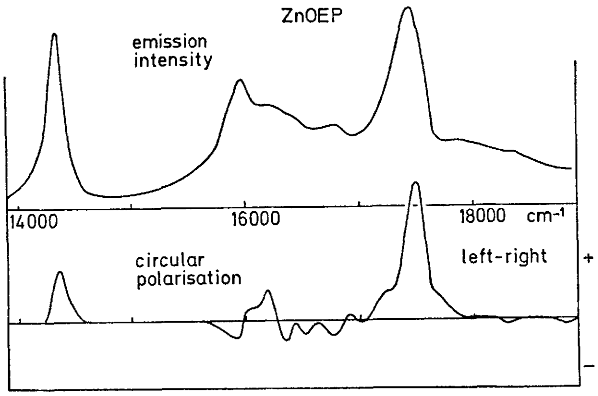

FIGURE. *The unpolarised emission (top curve) and the circular intensity differential (lower curve) of zinc octaethyl porphyrin in polymethyl methacrylate at* ca. 20 K. *The m.c.e. sign is defined from knowledge of the sign of the Zeeman splitting of the* $^1E_u{}^1$ *state of ZnOEP and assumption of a Boltzmann distribution of molecules within the Zeeman components of this state. The sign convention is thus in accord with that currently used in m.c.d. spectroscopy. Noise level on the emission spectrum is less than the pen width. That on the m.c.e. spectrum is approximately twice the pen width.*

The m.c.e. spectrum is displayed beneath the emission. Note that the sign convention used here is consistent with that used in m.c.d. spectroscopy and was determined by means of a Fresnel rhomb. We have checked that the signal is zero in the absence of magnetic field and is exactly reversed by reversing the field. Further we have determined that the sample does not significantly depolarise light. We are therefore confident that this represents a true measure of the difference of intensity of the circularly polarised emitted components and is not an artefact.

Using the nomenclature established for m.c.d. spectroscopy[1] we expect to see Faraday C terms due to the *initial* state degeneracy in the transition $^1E_u \rightarrow {}^1A_{1g}$. The fluorescence origin m.c.e. has band shape conforming to this expectation as has the phosphorescence m.c.e. We expect shortly to have accurate temperature measurements and temperature variation results to confirm this point and to enable the calculation of reliable excited state magnetic moments. One feature of interest occurs in the region between the fluorescence and phosphorescence peaks which shows variable sign m.c.e. Clearly the interpretation is not as simple as that previously outlined and, transitions occur to excited vibrational levels of more than one symmetry. The composite nature of the analogous region in the excited state was noted in the low temperature absorption and m.c.d. spectra.[4]

One final point concerns the question of angular momentum conservation mentioned earlier. If the molecule is pumped with circularly polarised radiation, which has a well defined M_J value, then non-Boltzmann populations of the Zeeman sublevels of the emitting states may be attained. This requires (i) relatively slow spin-lattice relaxation and (ii) conservation of angular momentum through the internal conversion and intersystem crossing process. It should be manifest in a change of circular polarisation of the *emitted* radiation upon irradiation with circularly polarised light and a study of this phenomenon could throw light on the nature of these energy transfer processes. Preliminary measurements of this type have been made on the porphyrin system but no conclusive result was obtained. Although spin lattice relaxation is slow in polymer matrices, the polymers are also very poor conductors of heat and thus the excited molecules may well be at high temperatures. This preliminary experiment is therefore inconclusive and this important point concerning conservation of angular momentum must await further experimental developments.

(*Received, 6th June* 1973; *Com.* 811.)

---

[1] P. N. Schatz and A. J. McCaffery, *Quart. Rev.*, 1969, **23**, 552.
[2] J. Schmidt, D. A. Antheunis, and J. H. van der Waals, *Mol. Phys.*, 1971, **22**, 1.
[3] A. Boccara, B. Briat, J. Badoz, and M. Billardon, Columbus Symposium on Molecular Spectra and Structure, Columbus, Ohio, 1969.
[4] R. Gale and A. J. McCaffery, *J.C.S. Dalton*, 1972, 596.
[5] Morvue Electronic Systems, Tigard, Oregon.
[6] R. S. Becker and J. B. Allison, *J. Phys. Chem.*, 1963, **67**, 2662.
[7] G. Canters, J. Van Egmond, T. J. Schaafsma, and J. H. Van der Waals, *Mol. Phys.*, 1972, **24**, 1203.
[8] P. J. Stephens, *J. Chem. Phys.*, 1970, **52**, 3489.