störende Linien mit hohen Drehimpulsquantenzahlen J unterdrückt werden, wenn das statische Feld E_{st} und die Radiofrequenz ν_R auf einen Übergang mit niedrigem J abgestimmt ist, da wegen der meist geringeren Stark-Aufspaltung von Niveaus mit höherem J ein Doppelresonanzeffekt dort nicht möglich ist. Bei Mikrowellenspektren mit einer hohen Liniendichte kann dadurch die Zuordnung erleichtert werden. Auch eine genaue Dipolmomentbestimmung erscheint möglich.

Details des Effekts, andere Zellgeometrien und Anwendungen werden zur Zeit untersucht und später mitgeteilt.

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ESR, Dielectric and Optical Absorption of Manganese (II) Chloro Complexes in DMF and DMA Solution

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The tetrahedral complex $MnCl_4^{2-}$ in solution exhibits a characteristic absorption spectrum (yellow instead of pink colour) [1, 2] as well as a characteristic ESR spectrum with a smaller hfs splitting than other Mn^{2+} complexes [3]. We have investigated solutions containing tetrahedral complexes, among others, to find out if characteristic optical and ESR spectra appear together or if there are differences to distinguish further between special complex species. The experiments were carried out with solutions of hydrated manganous chloride ($MnCl_2 \cdot 4\,H_2O$) in dimethylformamide (DMF) and dimethylacetamide (DMA) in a medium concentration range (0.05 ... 0.5 mol/l). Solutions in dimethylsulfoxide (DMSO) give results similar to DMF. Hydrated salt was used because of the stability of the solutions in contact with air.

In addition to ESR and optical spectra, dielectric absorption was used as third tool indicating but special complexes. The data, as shown in Fig. 1, are divided by the manganese concentration c to indicate the concentration dependence of the fraction of complex species deteted by the various methods.

Optical absorption of the yellow solutions was measured in the visible and near UV region. The maxima are the same (at 22 550, 23 400 and 28 100 cm^{-1}) as reported for the tetrahedral $MnCl_4^{2-}$ and mixed tetrahedral species [1, 2]. Beer's law is not obeyed. At higher concentrations, nevertheless, the molar extinction E/c depends only slightly on the concentration.

Dielectric absorption measurements were made in the 300 to 1800 MHz range. From the total imaginary part of the dielectric constant (ε'') was substracted the extrapolated conductive part (ε_1'') and the contribution of the pure solvent (ε_3''). The remaining ε_2'' is due to absorption by ionic dipoles alone [4]. Solutions of pure water, corresponding to the water concentration of the hydrated salt, show negligible ε_2'' in the frequency band used.

Taking into account measurement errors, ε_2'' follows an absorption curve broader than a Debye curve [approximately a Fröhlich curve [5] with $\ln(\tau_1/\tau_2) = 2.5$], indicatinig several relaxation times or a continuous distribution. $\varepsilon''_{2\max}/c$ is only slightly concentration dependent in both solvents. The mean relaxation time τ is 280 ($\pm$ 50) ps im DMF, also independent of concentration, while in DMA $\tau \approx 280$ ps at 0.1 mol/l and about 200 ps at 0.5 mol/l.

The ESR spectra of both solutions are quite different. In DMF, at low concentrations the spectrum is well resolved and exhibits more than the usual six lines (Fig. 2) [6]. In the whole concentration range it may be described as superposition of two spectra with equal g-factor and intensities, but different hfs splitting ($A_2 = 0.84\ A_1$). The "anomalous" splitting A_2 is in agreement with the splitting observed on $MnCl_4^{2-}$ complexes [3]. — In DMA, at low concentrations the well resolved spectrum consists of six hfs components of equal linewidth, with the same splitting A_1 as observed in other manganous solutions (e. g. water, $A_1 = 95$ Oe). — Adding excess chloride (with diamagnetic cations), both spectra approach a uniform anomalous spectrum with A_2.

Related to the concentration, the signal intensity is relatively too weak in both solutions. From intensity and observed linewidth one deduces the relative spin number N/N_0, which is the fraction of species detected by ESR. N/N_0 increases with increasing concentration, especially in DMF solutions. At higher concentrations an additional broad (and therefore very weak) background spectrum becomes indicable, which may be attributed to the lacking spins, not represented by N/N_0.

The limiting linewidth at dilution, $\varDelta H$, in DMF is the same as with other salts in this solvent (e. g. nitrate, perchlorate): $\varDelta H/A_1 = 0.26$ (for the smallest line). In DMA, the hfs components of chloride ($\varDelta H/A_1 = 0.38$) are somewhat broader than those of other salts (0.31).

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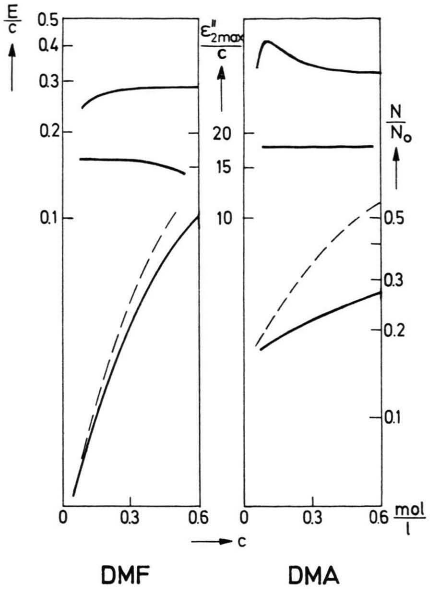

← Fig. 1. Decadic extinction coefficient, E/c, at 28 000 cm^{-1} (top); Maximum of ionic dipole part of dielectric absorption, $\varepsilon''_{2\max}/c$ (middle); Spin fraction, N/N_0, of resolved ESR spectra (below); versus manganese concentration c. ———: $MnCl_2 \cdot 4\,H_2O$; – – –: $MnCl_2$.

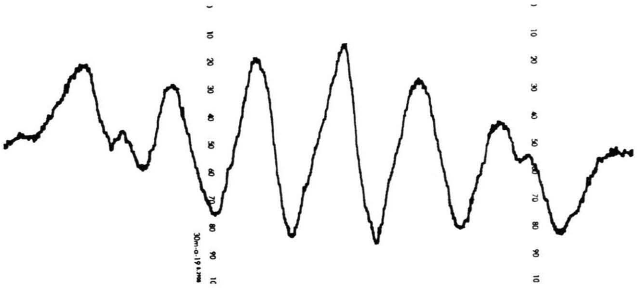

Fig. 2. ESR spectrum of 0.06 mol/l $MnCl_2 \cdot 4\,H_2O$ in DMF.

For comparison, Fig. 1 shows also ESR results on water-free salts, with a noteworthy increase of the detected spin fraction in the DMA solution.

The discussion is based on the assumption of an equilibrium between various species, belonging to at least two coordination types. Their ionic composition may be represented by

A, AB, AB_2 ...	octahedral,
... AB_3, AB_4	tetrahedral.

(The free sites of the first coordination sphere may be occupied by solvent or water molecules. Coordination of anions in the second sphere is also possible, at least in the octahedral case.) The three measuring methods are selective for special species: The "yellow" optical spectrum detects all tetrahedral species (also with mixed coordination [2]). The dielectric absorption detects species with an electric moment, thus all except A and AB_4. Complementary to the dielectric measurements, the ESR spectrum (its well resolved part) detects species of high symmetry, namely A and AB_4.

The initial question is to be answered as follows: "Yellow" spectrum and "anomalous" hfs splitting are not necessarily related. In spite of a similar optical spectrum, both solutions show different ESR spectra and different concentration dependence of extinction and spin fraction N/N_0.

To describe the species in the solution, mention must be made of the steep decrease of equivalent conductivity with increasing concentration, far below the concentrations used here, which (as well as the spin number) proofs the fraction of species A to be small. – Since dielectric relaxation may be attributed to rotational orientation, the mean effective radius of the relaxing units may be estimated from the relaxation time by comparison with other dielectric data [7]; it is found to be about 6.5 Å. Therefore the dielectrically detected species must be solvated. The absorption curves (ε'' versus frequency) indicate that different types may be present, but a detailed analysis would not be significant. Since the electric moments of the various polar species as well as their relaxation times may be in the same order of magnitude, we conclude from the $\varepsilon''_{2\max}$ values, as a rough approximation, the total fraction of these species to be nearly concentration independent. The same follows from optical data (in a certain concentration range) for the total fraction of tetrahedral species. Thus AB_4 is the only species of the above list to be detected by ESR, and for balance its spin fraction should also be only slightly concentration dependent, in contrast to our results.

Therefore the observed ESR spectrum has to be attributed to an additional species, not listed above. We conclude from the nearly 1 : 1 composition of the spectrum in DMF that it may be a higher (presumably solvated) complex of the $A \cdot AB_4$ ionic type, e. g. composed of two molecules ($MnCl_2$) in a way that one cation is surrounded by four anions, the second cation remaining outside the tetrahedron. Such a complex would exhibit "yellow" optical absorption as well as dielectric absorption. This assumption is supported by the ESR behaviour in DMA: In nearly all other cases of well resolved Mn^{2+} solution spectra, the outer hfs components are broadened because they are composed from five lines, which do not coincide perfectly. But in our case, all six hfs lines have equal linewidth. This may be the result of a slow spin exchange process (exchange frequency about 30 MHz) or a superexchange process via Cl^-. A possibility for those exchange processes is given by the proposed dimeric complex.

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Characteristics of a Tunable Travelling Wave Dye Ring Laser

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A flashlamp pumped dye ring laser using 4 Abbé prisms of constant 90 degree deviation has been built. Travelling wave operation is obtained when the counterclockwise wave is fed back by a beam-splitting output prism. The laser emission offers remarkable frequency stability when narrowed down to a linewidth of 7 pm by the use of an intracavity solid Fabry-Perot etalon.

Introduction

Various methods are known for the achievement of tunable, narrowband emission from organic dye lasers [1–3]. By inserting frequency selective elements — based on dispersion, rotational dispersion or interferometry — into the cavity, the spectral output can be reduced from some ten nanometers to a fiew picometers. Tunable narrowband laser emission down to a linewidth of 50 pm was reported by Schäfer and Müller [4] using a six-prism ring laser. In the present work, we describe the properties of a ring laser using 4 Abbé or Pellin-Broca prisms whose emission was additionally spectrally narrowed by the insertion of a Fabry-Perot etalon into the laser resonator.

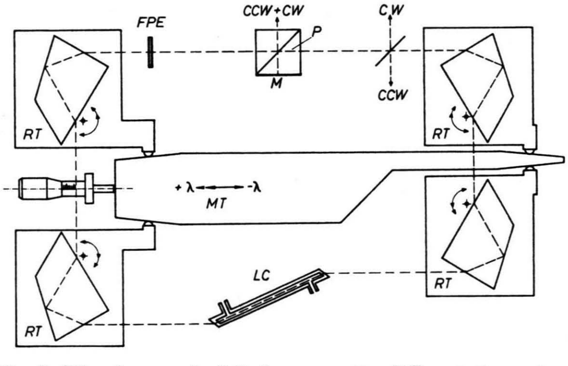

Fig. 1. Ring laser unit; LC: laser cuvette; RT: rotating prism table with Abbé prisms, axis and sense of rotation indicated; MT: movable table; FPE: Fabry-Perot etalon; P: beam splitting output prism with high reflectivity mirror M, for clarity the output prism has been rotated by 90° around the beam axis; G: glass sampling plate for separate measurement of CW and CCW output.

Dye Laser Construction

The flashlamp pumped dye laser consisted of a Brewster angled, 80 mm long, 2 mm internal diameter quartz glass dye cell within an elliptical cylinder reflector. It was optically pumped by a linear flashlamp (pump energy 200 J, ILC dye laser flashlamp type 4D3). The ring-shaped resonator (Fig. 1) was made of 4 highly dispersive (Schott SF 10 glass) Abbé prisms of constant 90° deviation arranged at Brewster's angle to avoid reflection losses. The wavelength tuning was achieved by simultaneous counter rotation of the 4 mechanically coupled prisms. To change the wavelength from 436 m to 656 nm a prism rotation of 2.4° was necessary [5]. One advantage of the arrangement lies in the fact that the lateral displacement of the beam does not exceed 0.1 mm for a 220 nm wavelength interval. In addition, only a single prism set is necessary for tuning throughout the whole visible and near infrared spectral region. The simultaneous counter rotation of the 4 prisms was accomplished by means of the linear motion of a table equipped with roller bearings of high mechanical precisions.

Power was extracted from the ring laser by a dielectric beam splitting prism of 25% reflectivity. Three faces of this prism were antireflection coated whereas the fourth face was provided with a high reflectivity coating. The latter served to increase the output and to force the laser into unidirectional, travelling wave operation, by partially reflecting the counterclockwise (CCW) wave back onto itself [6]. For further spectral narrowing of the laser emission an intracavity solid Fabry-Perot etalon (FPE) was employed. It consisted of a multilayer coated quartz plate of 0.25 mm thickness with a free spectral range of about 0.58 nm at 660 nm (further details cf. [7]) * and had a reflectivity of 78%. By tilting the FPE around a horizontal axis, the emision wavelength could be shifted by a few picometers.

Results

Figure 2 shows the peak output power obtained from various dyes within the wavelength range 550 nm to

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* The Fabry-Perot etalon was kindly put at our disposal by Dr. W. Schmidt, Carl Zeiss, Oberkochen.