Optical Spectra of Chlorophyll a and b Molecules and Complexes in PMMA and MTHF

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The optical spectra of chlorophyll a and chlorophyll b in PMMA and MTHF were studied over a wide range of concentration (8×10^{-6}–1×10^{-3} mole/l in PMMA, and 10^{-6}–10^{-1} mole/l in MTHF). In the absorption spectra it is possible to identify bands which originate from chlorophyll disolvates and chlorophyll monosolvates in MTHF as well as bands which are most probably due to isolated chlorophyll molecules in PMMA. In high-concentration samples of chlorophyll in MTHF some bands may be assigned to aggregates, but based on optical results only, no particular model can be proposed. The emission spectra are strongly influenced by reabsorption and energy transfer processes. However, the so-called Q_y band of isolated molecules in PMMA and of chlorophyll monosolvates in MTHF as well as the Q_x and the Q_y bands of chlorophyll disolvates in MTHF can be identified unequivocally in the fluorescence spectra.

1. Introduction

In two previous papers [1, 2] we have presented results of the investigation of the ESR spectra of chlorophyll a and chlorophyll b molecules in their metastable triplet state in matrices of polymethylmethacrylate (PMMA) and of methyltetrahydrofurane (MTHF). From the concentration dependence of these spectra we have concluded that the observed spectra can be assigned to isolated chlorophyll molecules, to chlorophyll mono- or disolvates, or to complexes thereof. In MTHF at concentrations below 10^{-3} m ($= 10^{-3}$ mole/l) only chlorophyll disolvates are observed. At higher concentrations chlorophyll monosolvates and isolated chlorophyll molecules show up in the ESR spectra gradually, whereas at 10^{-1} m (the highest concentration which was studied) pairs of chlorophyll monosolvates and of isolated chlorophyll molecules could be identified. In this work we present the optical spectra obtained from the same samples in an attempt to find correlations between these spectra and the related ESR spectra and possibly to assign optical bands to different chlorophyll complexes. Such an assignment would be quite valuable since there exist many investigations of optical spectra of in-vivo systems [3–7] which might be interpreted using the correlation of ESR and optical spectra discussed in this work.

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2. Experimental

The preparation of the samples has been described previously [1]. For the optical measurements the PMMA samples were cut into slices of about 1.3 mm thickness whereas for the MTHF samples, which are liquid at room temperature, we used thin quartz cuvettes of different thickness depending on the chlorophyll concentration.

For the measurement of the emission spectra we used a standard setup with excitation and detection beams at right angles. The samples were cooled by helium gas as a heat exchanger to about 80 K. Optical excitation was achieved using a Xenon high pressure arc (XBO 150 W or XBO 450 W, Osram, for fluorescence and phosphorescence respectively) with suitable interference filters or filter combinations. The emitted light was analyzed with a 1-m spectrograph (Jarell-Ash) in the case of fluorescence emission in combination with a cooled photomultiplier (9658 R, EMI) with a modified S-20 cathode and an electrometer (model 602, Keithley). In the case of phosphorescence emission a 0.25-m monochromator (Bausch & Lomb) was used with a cooled photomultiplier with S-1 characteristic (9684, EMI). In the latter case both, the excitation and the detection beam were chopped alternatingly at a frequency of 100 Hz in order to remove scattered excitation light from the detection beam.

Absorption spectra were recorded between 4.2 K and 300 K using a double-beam spectrophotometer (model 14, Cary).

Most of the spectra reported in this work are presented as obtained, i.e. in a scale linear with

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respect to the wavelength and not corrected for the spectral sensitivity of the detection scheme. Only the fluorescence spectra obtained on the MTHF samples were computer-processed in order to correct them for the spectral sensitivity and to convert them to a linear frequency scale. In this case we attempted to deconvolute the spectra into a minimum number of distinct, symmetrical Gaussian shaped bands. However, since this quite tedious procedure did not yield essential results we did not apply it to the other spectra. In the figures presented in the following sections the scale on the bottom of the figure is always linear, whereas the scale on the top gives the conversion to the inverse units to facilitate the comparison of different figures.

3. Fluorescence Spectra

3.1. Concentration Dependence of the Fluorescence Spectra

The observed fluorescence spectra depend both on the concentration and on the wavelength of the light used for the excitation. We have studied these dependencies in the range of chlorophyll concentrations from 8×10^{-6} m to 1×10^{-3} m for the PMMA samples and 1×10^{-6} m to 1×10^{-1} m for the MTHF samples. The wavelength of the exciting light was selected using interference filters at (405 ± 9) nm, (434 ± 12) nm, (446 ± 12) nm, (490 ± 7) nm and (546 ± 8) nm. In some cases also the entire spectrum of the XBO 150 W at wavelengths below 550 nm was used for excitation. In this section we present some typical spectra and discuss the observed influence of these parameters.

Figures 1 A and B present the fluorescence spectra observed on PMMA samples with various chlorophyll a or b concentrations at an excitation wavelength of 405 nm. Figures 2 A and B show the corresponding results obtained on MTHF samples. They illustrate the following statements, which can be made on the concentration dependence regardless of the excitation wavelength:

a) Chlorophyll a and chlorophyll b in PMMA (Fig. 1 A and 1 B)

- The maximum of the chlorophyll fluorescence shifts towards longer wavelengths with increasing chlorophyll concentrations.
- Several spectra (e.g. Fig. 1 B) indicate that the principal emission band is not a single band but consists of a superposition of at least two bands.

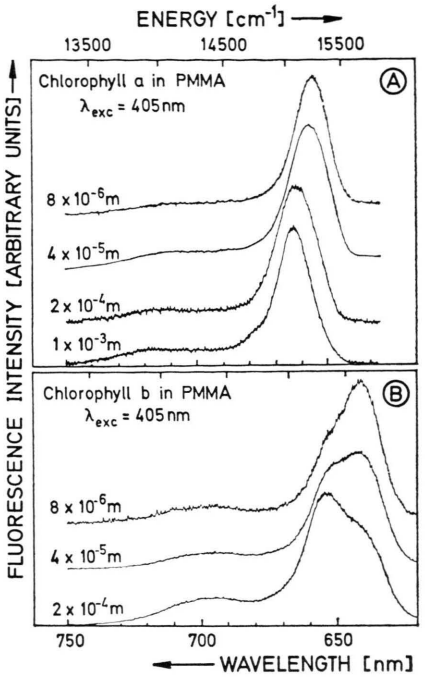

Fig. 1. Concentration dependence of the fluorescence of chlorophyll in PMMA. $T = 80$ K, $\lambda_{exc} = 405$ nm. A) chlorophyll a, B) chlorophyll b.

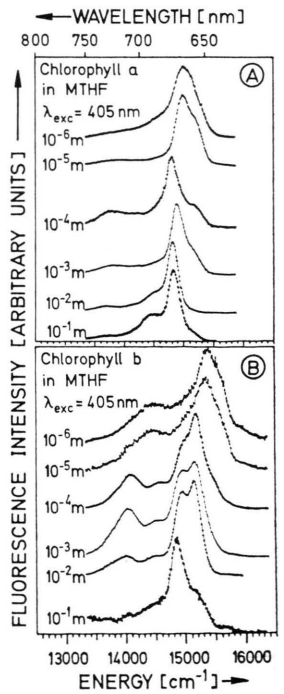

Fig. 2. Concentration dependence of the fluorescence of chlorophyll in MTHF. $T = 80$ K, $\lambda_{exc} = 405$ nm. A) chlorophyll a, B) chlorophyll b.

- The relative intensity of the long-wavelength emission (at about 700 nm) increases with increasing concentration.

b) Chlorophyll a in MTHF (Fig. 2A)

In this case the fluorescence spectra depend on the concentration differently, if the excitation wavelength is below 450 nm (excitation into the Soret band) or above. In the first case the following observations are made:

- The principal emission band splits and shifts towards longer wavelengths with increasing concentration.
- There is one important exception from this statement: at a concentration of 10^{-4} m the position of the main emission band is clearly at the longest wavelength (~ 678 nm) observed in all samples and the band itself is relatively narrow.
- Also at this concentration the long wavelength contribution (~ 725 nm) has its maximum intensity.

If the excitation wavelength is longer than 480 nm the spectrum changes drastically with increasing concentration. The long wavelength contribution in this case has its maximum intensity at a concentration of about 10^{-3} m.

c) Chlorophyll b in MTHF (Fig. 2B)

Similarly to the results obtained for chlorophyll a in MTHF the concentration dependence of the fluorescence spectra of chlorophyll b in MTHF depends on the range of the excitation wavelength. However, the distinction of the different ranges is not as evident as in the case of chlorophyll a. Again there is a pronounced red shift with increasing concentration. The long wavelength contribution at 710 nm has its maximum intensity at concentrations of 10^{-4} m to 10^{-3} m.

3.2. Dependence of the Fluorescence Spectra on the Excitation Wavelength

a) Chlorophyll a and Chlorophyll b in PMMA (Fig. 3)

Figure 3 presents the fluorescence spectra of chlorophyll a and chlorophyll b in PMMA at different excitation wavelengths.

In the case of chlorophyll a the maximum of the dominant fluorescence band shifts monotoneously towards longer wavelengths with increasing excitation wavelength. The shape of the principal band

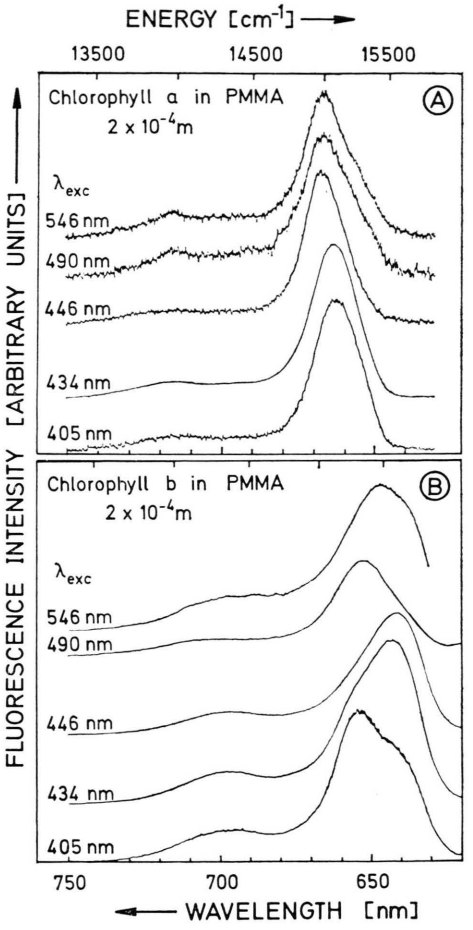

Fig. 3. Influence of the excitation wavelength on the fluorescence spectrum of chlorophyll in PMMA. $T = 80$ K, concentration: 2×10^{-4} m.
A) chlorophyll a, B) chlorophyll b.

indicates that it results from a superposition of at least three different bands.

In the case of chlorophyll b in PMMA the behaviour is more complicated: At excitation wavelengths of 434 nm and 446 nm (into the Soret bands) one observes the maximum of the principal fluorescence band at about 640 nm, whereas at other excitation wavelengths one finds additional emission bands between 650 nm and 665 nm, indicating that the principal band consist of a superposition of several components.

b) Chlorophyll a in MTHF (Figs. 4A, B, C)

The dependence of the chlorophyll-a fluorescence in MTHF samples on the excitation wavelength is illustrated by Figs. 4A, B and C. Two different ranges of concentration must be distinguished in

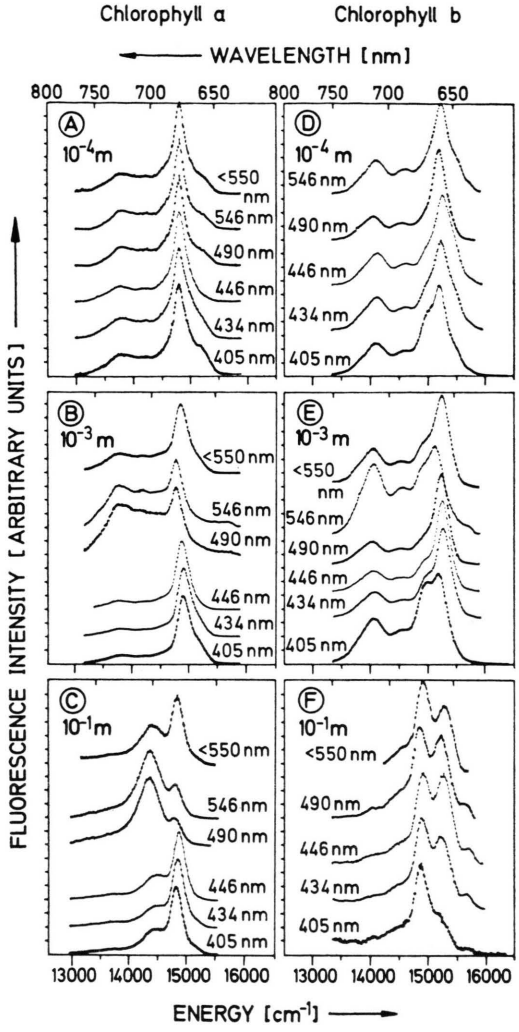

Fig. 4. Influence of the excitation wavelength on the fluorescence spectrum of chlorophyll in MTHF. $T = 80$ K. A) chlorophyll a, 10^{-4} m; D) chlorophyll b, 10^{-4} m; B) chlorophyll a, 10^{-3} m; E) chlorophyll b, 10^{-3} m; C) chlorophyll a, 10^{-1} m; F) chlorophyll b, 10^{-1} m.

these samples. Below 10^{-4} m the observed spectra are almost independent of the excitation wavelength. At higher concentrations (10^{-3} m to 10^{-1} m) one observes two different types of spectra depending on whether the excitation takes places within the Soret bands (405 nm, 434 nm, 446 nm) or beyond (490 nm, 546 nm, <550 nm) (Figs. 4B and Fig. 4C).

c) Chlorophyll b in MTHF (Fig. 4D, E, F)

In samples with 10^{-4} m chlorophyll b in MTHF, the fluorescence spectra depend only very weakly on the excitation wavelength. At lower concentrations however (10^{-5} m, 10^{-6} m) there are again two groups of excitation wavelengths which yield comparable results depending on whether the excitation takes place within the Soret bands (434 nm, 446 nm, 490 nm) or at other wavelengths (405 nm or 546 nm). A similar distinction between these two groups is observed in the high concentration samples (10^{-3} m to 10^{-1} m, Figs. 4E, F).

3.3. Deconvolution of the Fluorescence Spectra of the MTHF Samples

In order to obtain a quantitative description of the observed spectra it was attempted to fit the experimentally observed spectra with a superposition of a minimum number of Gaussian shaped lines. Figure 5 presents an example of the result of such a fitting procedure for 10^{-4} m chlorophyll b in MTHF with excitation at 434 nm. In Table 1 the

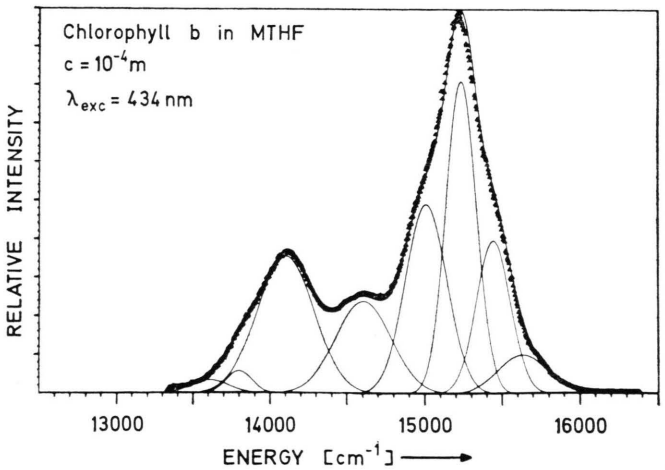

Fig. 5. Deconvolution of the fluorescence spectrum of chlorophyll b in MTHF. $T = 80$ K, concentration: 10^{-4} m, $\lambda_{exc} = 434$ nm.

Table 1. Deconvolution parameters for the fluorescence spectrum of 10^{-4} m chlorophyll b in MTHF at excitation with 434 nm light at 77 K.

Band position [cm^{-1}]	Halfwidth [cm^{-1}]	Relative intensity [%]
13 621	298	1.4
13 813	199	2.4
14 117	431	14.4
14 613	423	9.7
15 029	314	19.7
15 253	232	32.5
15 461	260	15.8
15 653	386	4.1

fitting parameters (band positions, half widths and relative intensities) are compiled for this particular example.

Corresponding deconvolution data were obtained for the fluorescence spectra of the MTHF samples for the entire range of concentrations and excitation wavelengths [8]. However, since the spectra are strongly influenced by reabsorption and energy transfer processes, it was not possible to assign the bands obtained from this procedure to specific chlorophyll systems. The parameters should be considered only as a device to describe the observed spectra. Therefore we have not incorporated all of them in this paper and have also not processed the PMMA spectra in a similar fashion.

4. Absorption Spectra

4.1. Concentration Dependence

Figure 6 presents the room-temperature absorption spectra of chlorophyll a and b in PMMA (5×10^{-5} m) and in MTHF (1×10^{-3} m), respectively. In PMMA substantial differences between the chlorophyll a spectrum and that of chlorophyll b are observed, whereas the differences between the corresponding spectra in MTHF are comparatively small. The structure of none of these spectra at room temperature depends significantly on the chlorophyll concentration over the entire accessible range (10^{-5} to 10^{-3} m in PMMA and 10^{-5} to 10^{-2} m in MTHF). Table 2 summarizes the absorption bands observed at room temperature.

Table 2. Room-temperature absorption-band maxima of chlorophyll a and chlorophyll b in PMMA and MTHF.

Chlorophyll a	Chlorophyll b
PMMA	
656 nm (15 244 cm^{-1})	640 nm (15 625 cm^{-1})
610 nm (16 393 cm^{-1})	589 nm (16 978 cm^{-1})
428 nm (23 364 cm^{-1})	455 nm (21 978 cm^{-1})
407 nm (24 570 cm^{-1})	430 nm (23 256 cm^{-1})
MTHF	
663 nm (15 083 cm^{-1})	654 nm (15 291 cm^{-1})
615 nm (16 260 cm^{-1})	598 nm (16 722 cm^{-1})
572 nm (17 483 cm^{-1})	560 nm (17 857 cm^{-1})
526 nm (19 011 cm^{-1})	526 nm (19 011 cm^{-1})
428 nm (23 364 cm^{-1})	435 nm (22 989 cm^{-1})
408 nm (24 510 cm^{-1})	413 nm (24 213 cm^{-1})

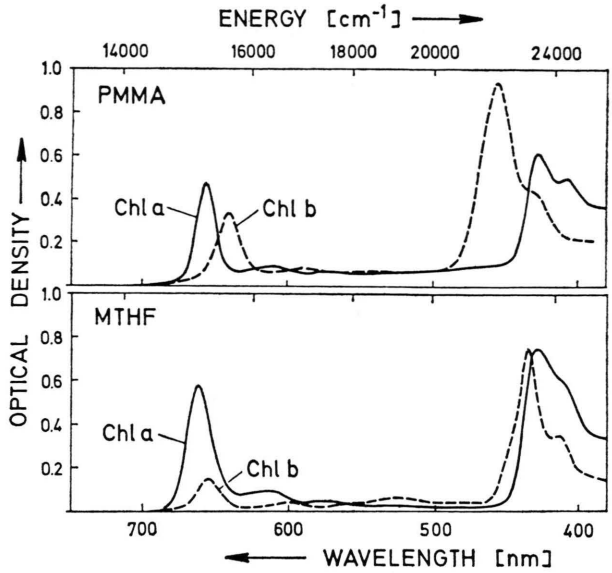

Fig. 6. Room-temperature absorption spectrum of chlorophyll. Top: PMMA, $c = 5 \times 10^{-5}$ m, sample thickness: 1.2 mm. Bottom: MTHF, $c = 1 \times 10^{-3}$ m, sample thickness: 0.3 mm.

4.2. Temperature Dependence

The absorption spectra of the chlorophyll-a-PMMA samples do not change significantly, if the samples are cooled from 300 K to 77 K. Contrary to this observation there are marked changes in the chlorophyll-a-MTHF spectra in the same range of

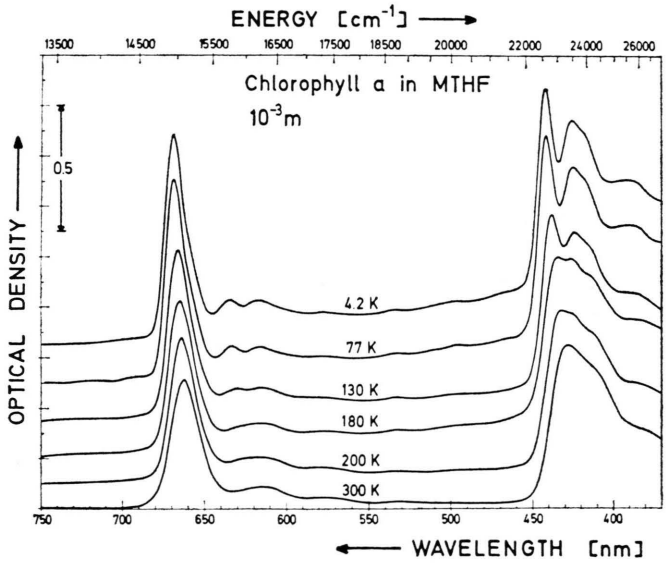

Fig. 7. Influence of the temperature on the absorption spectrum of chlorophyll a in MTHF. $c = 1 \times 10^{-3}$ m, sample thickness: 0.3 mm.

temperature (Fig. 7): When lowering the temperature a distinct splitting of the room-temperature absorption bands is observed with a resulting complicated structure of the low-temperature spectra. Below 77 K no further changes are detected. The principal features of the low-temperature absorption spectrum of 10^{-3} m chlorophyll a in MTHF can be summarized in the following way:

- The principal absorption band in the long wavelength region is situated at 667 nm (14993 cm^{-1}). It has a shoulder at 656 nm (15244 cm^{-1}).
- The absorption band observed at 615 nm at room temperature is split into two approximately equally intense bands at 616 nm (16234 cm^{-1}) and 634 nm (15773 cm^{-1}).
- In the range of the Soret bands several distinct bands are observed at 438 nm (22831 cm^{-1}), 423 nm (23641 cm^{-1}), 413 nm (24213 cm^{-1}), and 387 nm (25840 cm^{-1}). From the parallel behaviour at different experimental conditions it may be concluded that the 423-nm band is due to the same species as the weak band at 656 nm.
- Finally an additional very weak absorption band occurs at 694 nm (14409 cm^{-1}). This band can be traced also in the room-temperature spectra, if a modified experimental technique is used [8].

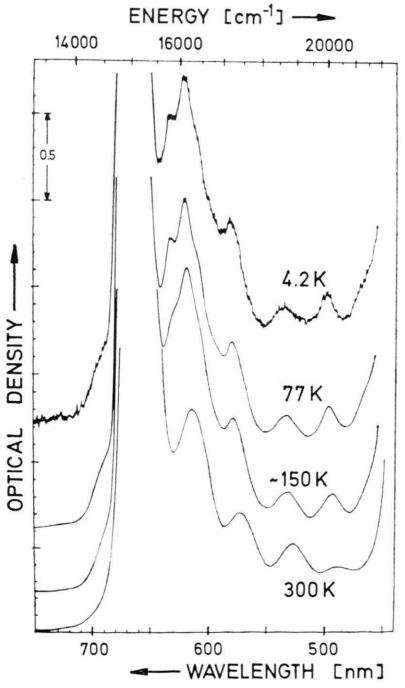

Fig. 8. Influence of the temperature on the absorption spectrum of chlorophyll a in MTHF, $c = 5 \times 10^{-2}$ m, sample thickness: 0.3 mm.

If the chlorophyll-a concentration is increased to about 5×10^{-2} m, the results are similar, qualitatively. However three important changes should be noted:

- The structure on the high energy shoulder of the principal absorption band at 667 nm (14993 cm^{-1}) becomes quite pronounced (Figure 8). At least three bands can be identified at low temperatures in the wing of this band at 632 nm (15823 cm^{-1}), 619 nm (16155 cm^{-1}) and 608 nm (16447 cm^{-1}). The intensity of the 619-nm band is substantially more intense than the band at 632 nm, whereas in the low-concentration samples the corresponding bands (616 nm and 634 nm, respectively) are equal in intensity. (Additional bands are observed between the principal long-wavelength band and the Soret band at 580 nm (17241 cm^{-1}), 533 nm (18762 cm^{-1}) and at 495 nm (20202 cm^{-1}). They will not be discussed in this work.)
- An additional shoulder on the low energy wing of the Soret band is observed at 465 nm (21505 cm^{-1}).
- The absorption band at 694 nm (14409 cm^{-1}) shows up quite clearly in the high-concentration sample.

Only the temperature dependence of the absorption spectra of chlorophyll a in PMMA and in MTHF was studied in this work. The reason for this restriction was that in general chlorophyll a in solution has been investigated more thoroughly than chlorophyll b [4, 5].

On the other hand the ESR spectra of chlorophyll b in MTHF yielded more information about complex formation. Therefore the corresponding temperature dependence of the absorption spectra of chlorophyll b are also of interest. Such experiments are currently in preparation but not yet accomplished.

5. Discussion

Optical absorption spectra of chlorophyll a and chlorophyll b in various solvents have been studied by several authors [4—5, 9—11]. A comparison with their results allows it to identify the principal absorption bands observed in the PMMA samples at 656 nm (15244 cm^{-1}) for chlorophyll a and at 640 nm (15625 cm^{-1}) for chlorophyll b as the so-

called Q_y bands. Based on the ESR results on the same samples [1, 2] it is reasonable to assign these bands to isolated chlorophyll molecules. This assignment is supported by the observation that the Q_y bands in PMMA are higher in energy than in a large number of other polar and nonpolar solvents. The Q_y bands in MTHF are observed at 663 nm (15083 cm^{-1}) for chlorophyll a and at 654 nm (15291 cm^{-1}) for chlorophyll b.

A number of authors [11—15] have found evidence that chlorophyll a and also bacteriochlorophyll in various polar solvents forms mono- and disolvates. The ESR results on the chlorophyll-MTHF samples [1, 2] confirm these observations. In the case of chlorophyll b in MTHF they also indicate the existence of dimers of zero- and monosolvates. Combining these results with the absorption spectra presented in Sect. 4 it may be concluded that the absorption bands at 656 nm (15244 cm^{-1}), 619 nm (16155 cm^{-1}) and at 423 nm (23641 cm^{-1}) originate from chlorophyll-a monosolvates and that the absorption bands at 667 nm (14993 cm^{-1}), 632 nm (15823 cm^{-1}) and at 438 nm (22831 cm^{-1}) are due to chlorophyll-a disolvates.

The interpretation of the fluorescence spectra is more difficult. Reabsorption and energy transfer processes may strongly influence the observed spectra at least in the highly concentrated samples. In view of this fact the spectra which are presented in Sect. 3 and in particular the deconvolution data should be considered merely as a documentation of the spectra obtained on the different samples. It is not yet possible to assign specific emission bands to particular chlorophyll arrangements. However in combination with the absorption results a few statements about the emission spectra can be made:

- The emission bands observed in the PMMA samples at 656 nm (15244 cm^{-1}) and 640 nm (15625 cm^{-1}) are the 0,0 bands of the Q_y transition of isolated chlorophyll a and chlorophyll b molecules, respectively.
- Similarly in the low-concentration MTHF samples the Q_y bands of the disolvates and the monosolvates can be identified. Their respective spectral positions are at 667 nm (14993 cm^{-1}) and at 656 nm (15244 cm^{-1}) for chlorophyll a, and at 650 nm (15385 cm^{-1}) and 640 nm (15625 cm^{-1}) for chlorophyll b.
- The emission band at 634 nm (15773 cm^{-1}), which was observed at excitation photon energies less than required for the Soret transition ($\lambda_{exc} = 490$ nm and 546 nm, Fig. 4B), for chorophyll a in MTHF is assigned to the Q_x transition of the disolvates. An analogous assignment is possible for the 627-nm (15949 cm^{-1}) band observed for chlorophyll b in MTHF.
- The long-wavelength emission bands observed in the high-concentration MTHF samples at 694 nm (14409 cm^{-1}) for chlorophyll a and at 673 nm (14859 cm^{-1}) for chlorophyll b are probably due to aggregates of unknown structure. In the case of chlorophyll b they might be assigned to the complexes which were identified using the ESR spectra of the high-concentration samples.
- Most of the low-energy satellites can be interpreted as vibronic sidebands of the principal bands with a splitting of $\bar{\nu} = 1039$ cm^{-1}.

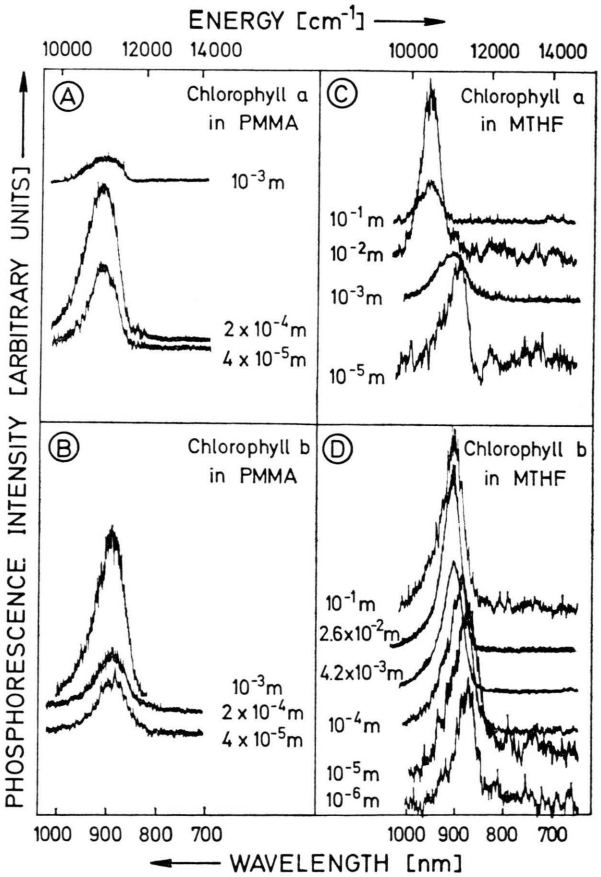

Fig. 9. Phosphorescence spectrum of chlorophyll, $T = 77$ K, 645 nm $\leqq \lambda_{exc} \leqq$ 750 nm.
A) chlorophyll a in PMMA, B) chlorophyll b in PMMA, C) chlorophyll a in MTHF, D) chlorophyll b in MTHF.

6. Phosphorescence

Several authors have studied the phosphorescence spectra of chlorophyll in vitro [10, 16—21]. It was pointed out by Krasnovsky and coworkers [20, 21] that the disagreeing results of previous studies may be due to the fact that the phosphorescenc originates from different triplet species depending on the concentration and the excitation wavelength. In order to obtain a complete set of spectroscopic data of the samples studied in this work in Fig. 9 the phosphorescence spectra obtained at 77 K for chlorophyll a or chlorophyll b in PMMA or MTHF at various concentrations are presented. The samples were excited in the wavelength range 645 nm $< \lambda_{exc} <$ 750 nm using a Xenon high-pressure lamp (XBO 450 W, Osram) with a filter combination (RG 645, Schott and 750/6441, Coherent Radiation).

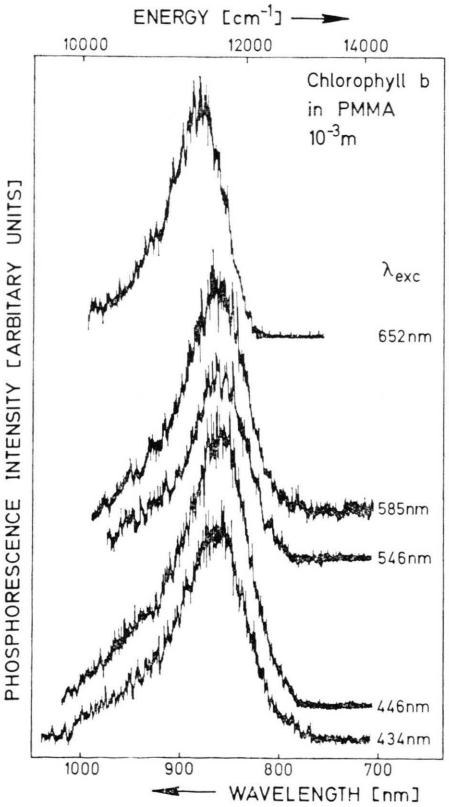

Fig. 10. Influence of the excitation wavelength on the phosphorescence spectrum of chlorophyll b in PMMA. $T = 77$ K, $c = 10^{-3}$ m.

The spectral position of both, chlorophyll-a and chlorophyll-b phosphorescence in PMMA is almost independent of the concentration over the entire accessible range. However, it depends strongly on the excitation wavelength. For instance, if the range of excitation wavelengths is extended to 550 nm $< \lambda_{exc} <$ 750 nm, the phosphorescence maximum shifts to shorter wavelengths by an amount of roughly 25 nm. Figure 10 shows, as an example, the shift of the chlorophyll-b phosphorescence band in PMMA, if the excitation wavelength is varied from 434 nm to 652 nm.

In MTHF the spectral position of the phosphorescence maximum depends much less on the excitation wavelength. On the other hand there is a substantial shift towards longer wavelengths, if the concentration is increased from 10^{-6} m to 10^{-1} m (roughly 50 nm for chlorophyll a and 30 nm for chlorophyll b).

Similarly to the fluorescence spectra the phosphorescence spectra evidently result from a superposition of various bands, the relative intensities and positions of which depend on the concentration as well as on the excitation wavelength. However, because of the above mentioned difficulties (reabsorption, energy transfer) it is not possible to assign distinct phosphorescence bands to particular chlorophyll triplet species.

7. Conclusion

The most reliable information on chlorophyll in matrices like PMMA or MTHF, which is accessible by optical spectroscopy, is obtained using absorption spectroscopy. Whereas emission spectra are always complicated because of reabsorption and energy-transfer processes, various solvate complexes and maybe aggregates can be identified in the absorption spectra. It therefore seems to be worthwile to study the full concentration dependencies of the absorption spectra systematically, by using a deconvolution technique. Such investigations are currently in preparation.

Acknowledgement

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[1] W. Hägele, D. Schmid, and H. C. Wolf, Z. Naturforsch. **33a**, 83 (1978).
[2] W. Hägele, D. Schmid, and H. C. Wolf, Z. Naturforsch. **33a**, 94 (1978).
[3] Govindjee, Bioenergetics of Photosynthesis, Academic Press, New York 1975.
[4] G. P. Gurinovitch, A. N. Sevchenko and K. N. Solov'ev, Spectroscopy of Chlorophylls and Related Compounds, AEC Technical Report No. 7199, National Technical Information Service, Springfield, Va. (1968).
[5] J. B. Thomas, Einführung in die Photobiologie, Georg-Thieme-Verlag, Stuttgart 1968.
[6] L. P. Vernon and G. R. Seely (eds.), The Chlorophylls, Academic Press, New York 1966.
[7] F. Drissler, W. Hägele, D. Schmid, and H. C. Wolf, Z. Naturforsch. **32a**, 88 (1977).
[8] W. Hägele, Dissertation, Universität Stuttgart 1977.
[9] J. M. Lhoste, Bull. Soc. Franc. Physiol. Végét. **14**, 379 (1968).
[10] R. L. Amster, Photochem. Photobiol. **9**, 331 (1969).
[11] T. M. Cotton, Dissertation, Northwestern University, Evanston, Ill. (1976).
[12] S. Freed and K. M. Sancier, J. Amer. Chem. Soc. **76**, 198 (1954).
[13] T. A. Evans and J. J. Katz, Biochim. Biophys. Acta **396**, 414 (1975).
[14] J. C. Goedheer, Biochim. Biophys. Acta **275**, 169 (1972).
[15] T. M. Cotton, A. D. Trifunac, K. Ballschmiter, and J. J. Katz, Biochim. Biophys. Acta **368**, 181 (1974).
[16] M. Calvin and G. D. Dorough, Science **105**, 433 (1947).
[17] J. Fernandez and R. S. Becker, J. Chem. Phys. **31**, 467 (1959).
[18] S. Singh and R. S. Becker, J. Amer. Chem. Soc. **82**, 2083 (1960).
[19] S. B. Broyde and S. S. Brody, J. Chem. Phys. **46**, 3334 (1967).
[20] A. A. Krasnovsky jr., N. N. Lebedev, and F. F. Litvin, Dokl. Akad. Nauk SSSR, ser. fiz. **209**, 965 (1973).
[21] N. N. Lebedev, J. Nauš, and A. A. Krasnovsky jr., Biofizika **21**, 381 (1976).