Total fluorescence spectra of free base chlorin and its photo-product in polyvinylbutyral at liquid helium temperatures

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Abstract

The total fluorescence spectra of free base chlorin and its photoproduct in polyvinylbutyral at liquid helium temperatures were investigated. Five electronic origins $(\pi\pi^*)$ of chlorin were identified. For the photoproduct, the $S_1 \leftarrow S_0$ $(\pi\pi^*)$ origin and three possible Soret bands were found. The energy selection phenomenon upon $S_1 \leftarrow S_0$ excitation was observed for both tautomers. In the case of free base chlorin, energy selection for the $S_3 \leftarrow S_0$ excitation was also observed. The broad spectral features corresponding to the $S_1 \leftarrow S_0$ transition of the photoproduct suggest that there is strong interaction between its electronic transition and the matrix, and its large Stokes shift supports the contention that there is a substantial change in geometry in its first excited state.

1. Introduction

Free base chlorin (2,3-dihydroporphin: H_2Ch) is a derivative of free base porphin in which a peripheral double bond on one pyrrole ring has been reduced [1]. At room temperature chlorin exists predominantly in the form shown in Fig. 1(a); at low temperatures, in addition to this form, a photo-induced tautomer (H_2Ch^*:Fig. 1(b)) is also stable [2].

High-resolution spectroscopic studies of free base chlorin have been made by Völker et al. [3, 4]. They investigated the photochemical holeburning of chlorin in n-alkanes, the so-called Shpolskii matrices, and showed that very narrow holes (~ 40 MHz) can be burned into the inhomogeneously broadened lines of both tautomers. The spectrum of an impurity molecule embedded in a solid matrix is inhomogeneously broadened because of the different environments surrounding the individual chromophores. If the absorbing molecule undergoes a phototransformation upon excitation by narrow-band laser, and the new form of the molecule is stable and absorbs at a frequency different from the original one, a spectral hole is left in the absorption band. By tuning the laser to different frequencies over this inhomogeneously broadened envelope, potentially thousands of holes can be burned in it at cryogenic temperatures. As a result of this, it has been suggested that persistent

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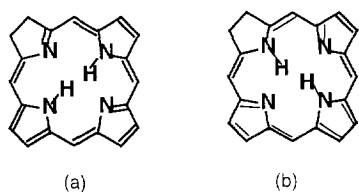
Fig. 1. Molecular formulas of (a) free base chlorin, and (b) the photoproduct of free base chlorin.

spectral holeburning (PSHB) could be used to store information in the frequency domain [5, 6].

The basic parameters to determine the suitability of a material for data storage are its Debye–Waller factor (DWF), the homogeneous linewidth of the zero phonon line (ZPL) of the impurity molecule and its inhomogeneous bandwidth. The larger the DWF, the narrower the homogeneous line width of the ZPL and the broader the inhomogeneous bandwidth, the more data that could be stored by the sample. Free base chlorin in polyvinylbutyral (PVB) is a promising material for this use since the $S_1 \leftarrow S_0$ ($\pi\pi^*$) transition of H_2Ch has a relatively high DWF (0.55 at 7 K [7]), a narrow homogeneous line width (160 MHz at 1.7 K [8]) and a large inhomogeneous broadening (400 cm^{-1} at 4.2 K [9]); consequently, H_2Ch/PVB samples have already been used in a series of experiments to demonstrate principles of optical data storage and processing [6, 10, 11].

The direct photoreaction of H_2Ch at low temperatures occurs with a quantum yield of 10^{-3}–10^{-4}, whereas the efficiency of back photoreaction is ~ 100 times higher. High photoreaction quantum yield would be an advantage in certain fast data storage applications, however, our experiments show that only very broad holes can be burned in the photoproduct band. It is therefore desirable to obtain a clearer understanding of chlorin's electronic spectroscopy. In order to do this, we set out to investigate the low-temperature total fluorescence spectra of H_2Ch and H_2Ch^* in PVB.

Total fluorescence spectroscopy (TFS) [12, 13] is a useful tool for characterizing molecules on the basis of their excitation and emission spectra. It measures the fluorescence intensity as a function of both excitation and emission frequencies. TFS is especially suitable for investigating systems whose

emission spectra are dependent on the excitation frequencies. Total fluorescence spectroscopy of organic molecules in solid matrices at room and low temperatures upon $S_1 \leftarrow S_0$ excitation has been described in detail by Locher [14] and Hofstraat et al. [15]; however, we will briefly discuss some salient features here.

When a molecule is excited to a higher electronic state, S_n ($n > 1$), the $S_1 \rightarrow S_0$ fluorescence shows a different pattern from that obtained from the $S_1 \leftarrow S_0$ excitation. There are two limiting cases which lead to distinct total fluorescent spectra when the excitation–emission process involves three electronic states (S_n, S_1 and S_0). The first one occurs when the homogeneous line width of the absorption bands is larger than the inhomogeneous broadening of the spectrum. Under these conditions, the line shape and the maximum position of the fluorescence spectrum are independent of the excitation frequency, and the total fluorescence spectrum is obtained by simply taking the product of the emission and excitation spectral line shapes. The second case (energy selection) occurs when the inhomogeneous broadening of the spectrum is much larger than the homogeneous line width. In this situation, the emission spectrum does, in general, depend on the excitation frequency. This results because only a subset of chromophore molecules whose transition energies are resonant with the energy of the excitation light can be selected. The resulting $S_1 \rightarrow S_0$ fluorescence frequencies from these selected molecules will also possess some selectivity. But, those selected frequencies will have a distribution since the transition energies of different electronic transitions are accidentally degenerate; however, this distribution generally has a narrower width than the whole inhomogeneous line width. Different $S_n \leftarrow S_0$ excitation energies correspond to the different distributions of the $S_1 \rightarrow S_0$ emission energy. Suter et al. [16, 17] have previously observed energy selection spectra of 1,4-diazatriphenylene (DAT) at low temperature in glasses of isopentane and in glasses of 3-methylpentane; in these samples the $T_1 \rightarrow S_0$ phosphorescence spectrum was dependent on the $S_1 \leftarrow S_0$ excitation frequency.

In this research, we set out to locate and characterize the $S_n(\pi\pi^*)$ electronic states of both H_2Ch

and H_2Ch^*. Our investigation has covered the fluorescence spectrum and the excitation spectrum from the $S_1 \leftarrow S_0$ transition through the Soret bands. The spectral patterns obtained provide further insight to excited state properties.

2. Experimental

Free base chlorin was synthesized using the method of Egorova et al. [18]. The H_2Ch/PVB samples were made by dissolving H_2Ch and PVB separately in dichloromethane (CH_2Cl_2), then mixing the two solutions and finally evaporating (6 days) the solvent. A thin (0.2 mm) H_2Ch/PVB film was obtained; its room temperature optical density was about 0.7 at 635 nm.

The photoproduct (H_2Ch^*) was produced by illuminating the sample at 10 K with a slide projector's light that had been passed through a narrow bandpass filter. The spectral range of the filter was 620 nm ($\sim 16\,129\,cm^{-1}$) to 640 nm ($\sim 15\,625$ cm^{-1}); this corresponds to the $S_1 \leftarrow S_0$ absorption band of H_2Ch.

The total fluorescence spectra were recorded with a moderately high-resolution, computer-controlled spectrometer using photon-counting detection. The resolution of the spectra in Figs. 2 and 3 is $60\,cm^{-1}$; this was determined by the monochromator stepwidth. The resolution of the spectra in Figs. 4(a) and (b) is $5\,cm^{-1}$; this was determined by the slitwidth of the monochromator. The excitation source was a 2.5 kW high-pressure xenon lamp whose output was passed through a Spex 1402 double monochromator (dispersion, 0.5 nm/mm). The resulting fluorescence signal went through a second Spex 1402 double monochromator and was detected by a cooled, RCA 31034 photomultiplier tube. A front surface excitation geometry was used. The spectra were corrected for the wavelength dependence of the excitation light's intensity by the use of a quantum counter (350–690 nm) and a Hamamatsu R928 photomultiplier tube. All the measurements were controlled by a DEC PDP 11/73A computer. The sample was cooled in an Oxford Instruments CF204 cryostat. The total fluorescence spectroscopic technique has been described more fully elsewhere [12].
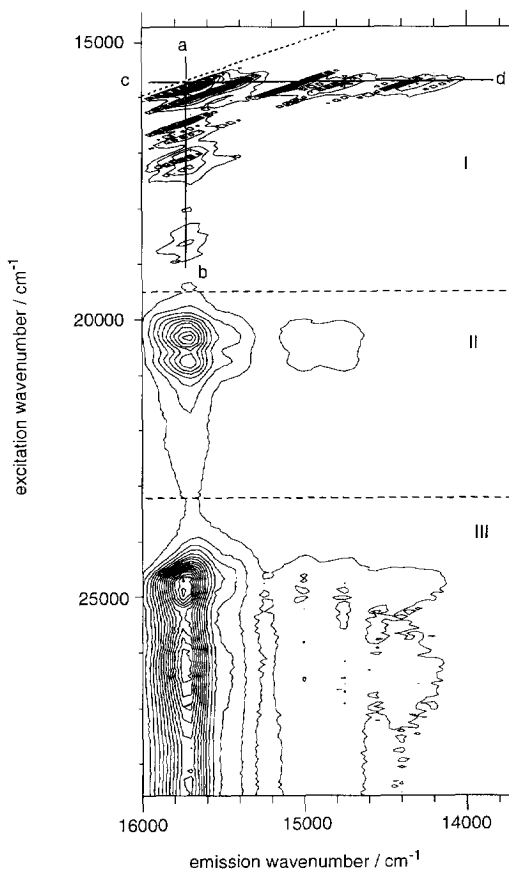

Fig. 2. Total fluorescence spectrum of free base chlorin in PVB film at 12K. Note the differing scales of the excitation and emission axes. On the dotted line the excitation frequency is equal to the emission frequency. Region I corresponds to $S_1 \leftarrow S_0$ excitation. Region II corresponds to $S_2 \leftarrow S_0$ excitation. Region III corresponds to $S_3 \leftarrow S_0$, $S_4 \leftarrow S_0$, and $S_5 \leftarrow S_0$ excitations or Soret region.

3. Results and discussion

3.1 Total fluorescence spectrum of H_2Ch in PVB

Fig. 2 shows the total fluorescence spectrum of chlorin in PVB at 12 K. It has been divided into three regions according to the characteristic features along the excitation axis.

Region I extends from 15 250 to 19 500 cm^{-1}. This portion of the spectrum corresponds to the $S_1 \leftarrow S_0$ ($\pi\pi^*$) excitation. The bands exhibit the
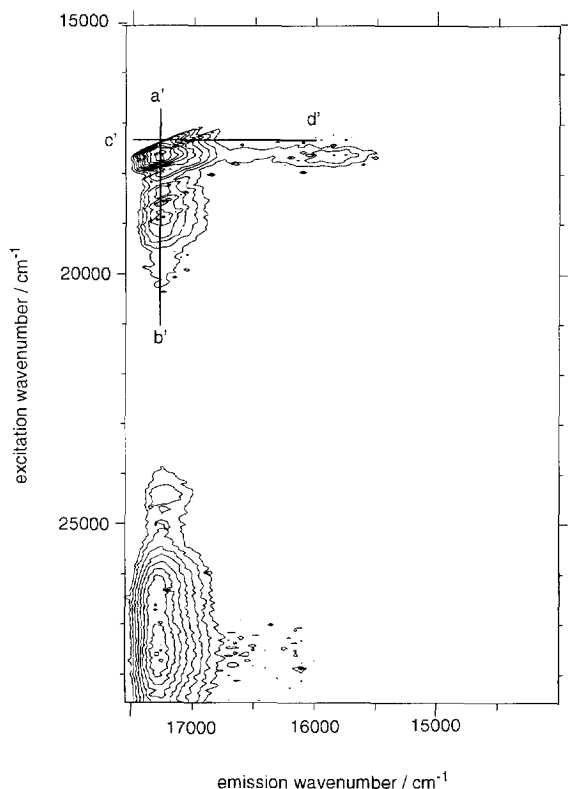
Fig. 3. Total fluorescence spectrum of the photoproduct of chlorin in PVB at 7 K. It was obtained by subtracting the spectrum of H_2Ch from the spectrum produced after photo-tautomerization and then plotting the positive components.

energy selection phenomenon; the emission frequencies depend on the excitation frequencies. The spectral bands, which are inhomogeneously broadened due to the different environmental surrounding produced by the host molecules, represent various vibronic excitations and emissions of the $S_1 \rightleftharpoons S_0$ transitions. The inhomogeneous width, full width at half maximum (fwhm), of the $S_1 \leftarrow S_0$ origin band is about 300 cm^{-1} for chlorin in PVB; in an n-octane matrix this value is about 1.5 cm^{-1} [3, 4]. In region I the two spectral bands just below the dotted line, on which excitation frequencies equal emission frequencies, are attributed to the phonon sideband and one local vibration. The bands with excitation frequencies in the 15 300 16 200 cm^{-1} range arise from the 0–0 excitation and then emission to the nonzero vibrational states of S_0. The spectral bands whose emission frequencies lie between 15 400 and 16 000 cm^{-1} result from the 0–0 emission with excitation to the vibrational states of S_1. In region I, the intensity I of the emission to the nonzero vibrational states of S_0, upon excitation to nonzero vibrational states of S_1, was much weaker than the emission to the zero vibrational state. We estimated the relative intensity along line cd in Fig. 2, $I_{0\to0}/I_{1\to0} = 10$, and the relative intensity along line ab, $I_{0\leftarrow0}/I_{1\leftarrow0} = 20$, [7] for a relatively strong mode. If the intensities of the excitation and emission 0–0 bands were
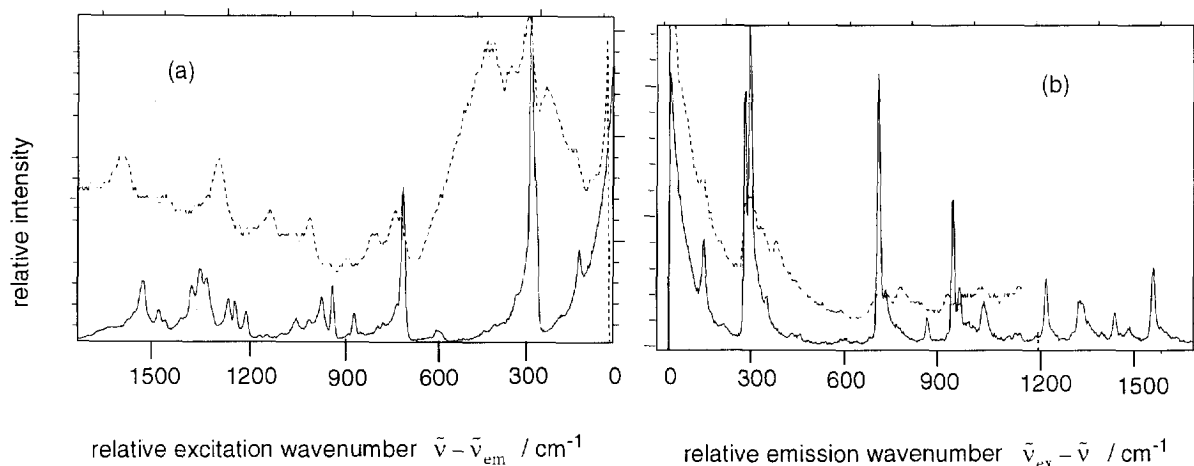

Fig. 4. Comparison of the excitation and emission spectra of the two tautomers. (a) Excitation spectra of chlorin (solid line, emission at 15 730 cm^{-1}, line ab in Fig. 2) and the photoproduct (dotted line, emission at 17 300 cm^{-1}, line a′b′ in Fig. 3). $\tilde{\nu}_{em}$ is the fixed emission wave number. (b) Emission spectra of chlorin (solid line, excitation at 15 730 cm^{-1}, line cd in Fig. 2) and the photoproduct (dotted line, excitation at 17 300 cm^{-1}, line c′d′ in Fig. 3). $\tilde{\nu}_{ex}$ is the fixed excitation wavenumber.

each assigned a value of one, we have $I_{1 \to 0} = 0.1$, and $I_{1 \leftarrow 0} = 0.05$. Thus, the relative intensity of the emission into the vibrational S_0 states produced by excitation light in resonance with the vibrational components in S_1, is 0.005 (0.1×0.05). Therefore, these emissions do not show up in the figure. This indicates that the probability of the 0–0 transition is much larger than that of the 0–f ($f = 1, 2 \ldots$) transition for the H_2Ch molecule. This can be rationalized by assuming that the minimum positions of the S_0 and S_1 potential surfaces are very near to each other; the Stokes shift is very small. The purely electronic zero phonon line has the largest intensity among all of the vibronic zero phonon transitions; this property is also important for data storage, since narrow and deep spectral holes can only be obtained under this condition.

Region II extends from 19 500 to 23 200 cm^{-1}. This is presumably the $S_2 \leftarrow S_0$ ($\pi\pi^*$) transition area. The total fluorescence spectral pattern in this interval shows that the line shapes and the positions of the maxima of the emission spectra are independent of the excitation frequencies. The spectral bands are broad and featureless; this can be interpreted by assuming that the homogeneous line widths of the absorption spectrum are larger than the inhomogeneous broadening. In such a case, if a monochromatic excitation source is tuned through the absorption band, at each wavelength all the molecules will be excited with comparable probability. Consequently, there is no energy selection. When the molecules are excited to the higher electronic excited states, they most probably will first relax to S_1 via fast internal conversion without emitting light; then they either undergo further radiationless decay to the ground state, to a triplet state, or emit fluorescence. The lifetimes of higher excited states are generally shorter than that of the first excited state; these short times can be of the order of 10^{-13}–10^{-14}s, which leads to homogeneous broadenings of 50–400 cm^{-1}. Based on the above argument, we assign the band at 20 325 cm^{-1} as the origin of $S_2 \leftarrow S_0$ ($\pi\pi^*$) and the band at 20 700 cm^{-1} as a vibrational satellite of $S_2 \leftarrow S_0$ transition.

Region III covers the remainder of the spectrum, which corresponds to the Soret bands. The

first of these spectral features is in the excitation range of 23 200–25 300 cm^{-1}. On the low energy ($\sim 24 500$ cm^{-1}) side of this band the energy selection phenomenon was observed. Also, on its high-energy side an excitation independent emission pattern was seen. To explain this unusual feature, we assume that this band consists of two $\pi\pi^*$ electronic origins. The first is located at about 24 680 cm^{-1} and has a relatively long lifetime, which leads to a narrower homogeneous line width compared with the inhomogeneous broadening. The second origin is at about 24 900 cm^{-1} and has a shorter lifetime, which leads to a broader homogeneous line width compared to the inhomogeneous broadening. The bandwidths (fwhm) of the two transitions are about 650 and 1000 cm^{-1}, respectively; since the distance between these two states is small (~ 200 cm^{-1}), the bands have substantial overlap. (The positions and bandwidths of these origins were determined by making vertical cuts through the total fluorescence spectrum.) These two $\pi\pi^*$ bands are assigned as the $S_3 \leftarrow S_0$ and $S_4 \leftarrow S_0$ origins. The calculated spectrum of free base chlorin by Petke et al. [19] agrees with our assignments; they found two $\pi\pi^*$ transitions in this region.

It is interesting to note that energy selection is also observed in the $S_3 \leftarrow S_0$ excitation. This would not occur in this three energy level (S_3, S_1, S_0) excitation–emission process unless the homogeneous broadening in the excitation spectrum was significantly less than that of the inhomogeneous broadening. The pattern is similar to what Suter et al. [16, 17] observed for the 1,4-diazatriphenylene in low-temperature matrices of isopentane and 3-methylpentane. In their results, the initially excited state, S_1, had a relatively long lifetime, which lead to a very small homogeneous broadening of the absorption spectrum; such a spectral pattern implies that the $S_1 \leftarrow S_0$ excitation energy corresponds to a distribution of the $T_1 \to S_0$ emission energy. But the width of this distribution is narrower than that of the whole distribution of the emission energy. Consequently, our TFS results on the $S_3 \leftarrow S_0$ excitation of H_2Ch imply that the lifetime of the S_3 state could be of the order of picoseconds or even longer. (Detailed discussion about the TFS and excitation line shapes in three

energy level excitation–emission process can be found in Refs. [16, 17].)

In Fig. 2, the excitation band at $26\,200\,\text{cm}^{-1}$ exhibits the excitation - independent emission pattern. If it is examined carefully, it looks slightly asymmetric; this can be seen even more clearly in vertical cuts of the total fluorescence spectrum. Possibly, this arises from the presence of two major components. We assign the lower energy component as the $S_5 \leftarrow S_0\ (\pi\pi^*)$ origin.

3.2. Total fluorescence spectrum of the H_2Ch photoproduct in PVB

Fig. 3 illustrates the total fluorescence spectrum of the photoproduct of free base chlorin (H_2Ch^*) in PVB at 7 K. It was obtained by subtracting the total fluorescence spectrum of H_2Ch from the spectrum made after phototautomerization and then plotting only the part with positive intensity. The fluorescence resulting from the excitation range of $17\,000$–$20\,000\ \text{cm}^{-1}$ shows distinct energy selection; it can be attributed to the $S_1 \leftarrow S_0\ (\pi\pi^*)$ excitation of H_2Ch^*. Surprisingly, there is no sign of the $S_2 \leftarrow S_0\ (\pi\pi^*)$ transition, which from earlier work by Dicker et al. [20] was expected to be just above the $S_1 \leftarrow S_0$ origin. We assign the higher energy area ($24\,000$–$28\,600\ \text{cm}^{-1}$) as the Soret region. In this interval three excitation bands can be identified; they are located at $25\,000$, $26\,050$ and $27\,500\ \text{cm}^{-1}$, respectively.

Fig. 4 shows slices of the total fluorescence excitation and emission spectra of the $S_1 \leftrightharpoons S_0$ region for H_2Ch (solid lines) and H_2Ch^* (dotted lines). The H_2Ch^* homogeneous bandwidths in the $S_1 \leftarrow S_0$ excitation region are broader than those of H_2Ch. This can be explained by assuming that the interaction between the photoproduct's electronic transition and the matrix is considerably stronger than that of H_2Ch and the matrix; therefore, the Debye–Waller factor of H_2Ch^* is small. As a consequence of this, H_2Ch^*/PVB should not be a good holeburning material. When we tried to burn holes, only very shallow ones were obtained [7]; therefore, the photoproduct in PVB is not suitable for data storage.

The vibronic excitation and emission spectra of H_2Ch exhibit mirror symmetry (Fig. 4) which indi-

cates that the geometry of the molecule does not change in the course of the electronic transition. In contrast to H_2Ch, the excitation and emission spectra of H_2Ch^* show almost no mirror symmetry. This implies that upon electronic excitation the photoproduct undergoes a substantial configurational change. This was also observed by Dicker et al. [20], who studied the Stark effect on the $S_1 \leftarrow S_0$ transition of the two tautomers of chlorin by photochemical holeburning in n-hexane and n-octane single crystals at 1.2 K. They found that in the case of H_2Ch^* the ground and excited state dipole moments are no longer parallel, which suggests that the molecular geometry is changed upon the electronic excitation. They also concluded that the photoproduct's S_1 and S_2 states are only 400–$700\ \text{cm}^{-1}$ apart [21]. This small gap could be associated with the absence of mirror symmetry, since the $S_1 \leftarrow S_0$ excitation spectrum will be distorted by non-adiabatic interaction. However, if the $S_2 \leftarrow S_0$ origin is just above the $S_1 \leftarrow S_0$ origin we would expect to have observed either a very broad band in this region, or if the $S_2 \leftarrow S_0$ origin band were narrow, to observe $S_2 \rightarrow S_0$ fluorescence. In our results none of these were observed and we see no indications of the $S_2 \leftarrow S_0$ transition.

A comparison of the vibrational frequencies of H_2Ch^* in the S_1 state with those of the H_2Ch in the S_1 state (Fig. 4(a)) shows that they are quite different. This also supports the idea that the geometries of two tautomers in their respective first electronic excited state differ considerably. Conversely, the two emission spectra (Fig. 4(b)) show that a number of the vibrational frequencies in the ground state are similar for both tautomers, for example, the vibrations with frequencies of 153, 309 and $721\ \text{cm}^{-1}$. The vibrational modes are expected to be very similar for both molecular geometries in the ground state. Using the normal coordinate analysis of free base porphin [22] as a guide, those vibrations can be assigned to the totally symmetric modes.

Finally, we point out that the Stokes shift of the photoproduct's $S_1 \leftrightharpoons S_0$ transition is about $300\ \text{cm}^{-1}$ while the value for H_2Ch is only about $40\ \text{cm}^{-1}$. (These values were determined from vertical cuts in the excitation and emission portions of the total fluorescence spectra.) This large Stokes

shift in the spectrum of H_2Ch^* also implies that there is a significant change in its geometry during the $S_1 \leftarrow S_0$ transition.

4. Conclusion

Total fluorescence spectra of both free base chlorin and its photoproduct were investigated. For H_2Ch we were able to assign the five lowest electronic singlet–singlet $(\pi\pi^*)$ transitions by their TFS patterns. The large inhomogeneous broadening and sharp ZPL of H_2Ch in PVB potentially lead to a substantial capacity for data storage. For H_2Ch^*, the location of the $S_1 \leftarrow S_0$ $(\pi\pi^*)$ transition and three Soret bands were identified. The lack of the mirror symmetry of the vibronic excitation and emission spectra of the molecule implies that the geometry of the photoproduct is changed considerably as a result of the $S_1 \leftarrow S_0$ excitation. The broad line width of the H_2Ch^* spectrum in the $S_1 \leftarrow S_0$ excitation region indicates a strong coupling between the electronic transition and PVB. The excitation spectra of the two tautomers in the $S_1 \leftarrow S_0$ region are very different and this also implies that the geometry of H_2Ch^* is different from that of H_2Ch in the first excited state. From our results we have concluded that the H_2Ch photoproduct in this matrix is not suitable for use in data storage.

Acknowledgements

References

[1] C.B. Storm and Y. Teklu, J. Amer. Chem. Soc. 94 (1972) 1745.
[2] C.B. Storm, Y. Teklu and E.A. Sokoloski, Ann. N.Y. Acad. Sci. 206 (1973) 631.
[3] S. Völker and R.M. Macfarlane, J. Chem. Phys. 73 (1980) 4476.
[4] S. Völker and R.M. Macfarlane, IBM J. Res. Dev. 23 (1979) 547.
[5] G. Castro, D. Haarer, R.M. Macfarlane and H.P. Trommsdorff, U.S. Patent 4, 101, 976 (1978).
[6] U.P. Wild, A. Renn, C. DeCaro and S. Bernet, Appl. Opt. 29 (1990) 4329.
[7] W.Y. Huang, Diss. ETH No. 10461 (1994).
[8] F.A. Burkhalter, G.A. Suter, U.P. Wild, V.D. Samoilenko, N.V. Rasumova and R.I. Personov, Chem. Phys. Lett. 94 (1983) 483.
[9] U.P. Wild, S.E. Bucher and F.A. Burkhalter, Appl. Opt. 24 (1985) 1526.
[10] U.P. Wild, A. Renn, R. Locher and A.J. Meixner, Proc. Int. Symp. on Optical Memory, (1987); Jpn. J. Appl. Phys. 26 (Suppl. 4) (1987) 233.
[11] U.P. Wild, S. Bernet, B. Kohler and A. Renn, Pure Appl. Chem. 64 (1992) 1335.
[12] G.W. Suter, A.J. Kallir and U.P. Wild, Chimia 37 (1983) 413.
[13] A.J. Kallir, G.W. Suter, S.E. Bucher, E. Meister, M. Lüönd and U.P. Wild, Acta Phys. Polon. A71 (1987) 755.
[14] R. Locher, Diss. ETH No. 9384 (1991).
[15] J.W. Hofstraat, R. Locher and U.P. Wild, Appl. Spectrosc. 44 (1990) 1317.
[16] G.W. Sutter and U.P.Wild, Chem. Phys. 102 (1986) 205.
[17] G.W. Suter and U.P. Wild, Chem. Phys. 120 (1988) 131.
[18] G.D. Egorova, K.N. Soloveu and A.M. Shulga, Zh. Obsch. Khim. 37 (1967) 357.
[19] J.D. Petke, G.M. Maggiora, L.L. Shipman and R.E. Chistoffersen, J. Mol. Spectrosc. 73 (1978) 311.
[20] A.I.M. Dicker, L.W. Johnson, M. Noort and J.H. van der Waals, Chem. Phys. Lett. 94 (1980) 14.
[21] A.I.M. Dicker, M. Noort, H.P.H. Thijssen, S. Völker and J.H. van der Waals, Chem. Phys. Lett. 78 (1981) 212.
[22] L.L. Gladkov and K.N. Solovyov, Spectrochim. Acta 41A (1985) 1437.