STARK EFFECT ON THE $S_1 \leftarrow S_0$ TRANSITION OF THE TWO TAUTOMERIC FORMS OF CHLORIN STUDIED BY PHOTOCHEMICAL HOLE-BURNING IN n-HEXANE AND n-OCTANE SINGLE CRYSTALS AT 1.2 K

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Stark experiments are reported on the $S_1 \leftarrow S_0$ 0–0 transitions of chlorin (7,8-dihydroporphin) and its photoisomer in different sites in n-hexane and n-octane single crystals by photochemical hole-burning at 1.2 K. For chlorin $\Delta\mu = +0.23$ D with $\Delta\mu \| \mu(S_0)$. For the photoproduct we estimate $\mu(S_1) = 2.2$ D with a site-dependent angle between $\mu(S_1)$ and $\mu(S_0)$ of up to 24°.

1. Introduction

Free-base chlorin (7,8-dihydroporphin, H_2Ch) is a derivative of free-base porphin (H_2P) in which an exterior double bond in one of the pyrrole rings has been reduced. As a result, the molecular symmetry is lowered from D_{2h} to C_{2v} and the molecule is expected to possess a permanent ground-state dipole moment, μ.

Recently we have used photochemical hole-burning to measure Zeeman shifts of the $S_1 \leftarrow S_0$ transition of H_2Ch and its photoisomer (H_2Ch*) in n-hexane host crystals [1,2]. In the present study we demonstrate that a similar technique may be used to measure the Stark effect on the $S_1 \leftarrow S_0$ transition in n-hexane (n-C_6) and n-octane (n-C_8) single crystals.

From the Stark shifts we expect to obtain the magnitude and direction of the change in dipole moment $\Delta\mu$ of the $S_1 \leftarrow S_0$ transition for H_2Ch and H_2Ch*. While the magnitude $|\Delta\mu|$ is directly related to the charge redistribution in the molecule on excitation to S_1, the direction of $\Delta\mu$ might give us further insight into the orientation of the chlorin guests in the host lattices. When chlorin is incorporated into n-C_6, for instance, the 0–0 transitions of H_2Ch and H_2Ch* are split into Shpolskii multiplets with four major components [3], which from earlier Zeeman experiments [1,2] are known to originate from guest molecules in type A sites [4]. The results of the Stark experiments then might indicate how these four sub-sites differ with respect to the orientation of the molecular dipole moment in the substitutional plane.

In section 2 of this paper we describe the Stark experiments. The method used, in which the crystal is rotated between the electrodes, is somewhat different from those previously employed for Stark effect studies of crystal spectra [5]. The chief advantage of our procedure is that all measurements can be made on the same crystal and yield the direction of $\Delta\mu$ with respect to the crystal axes. In section 4 we discuss the data. For H_2Ch, where $\Delta\mu \| \mu$, the situation is straightforward; however, for H_2Ch* the ground- and excited-state dipole moments are no longer parallel and the orientation of $\Delta\mu$ relative to μ here depends on the site.

2. Experimental

Free-base chlorin was prepared by reduction of free-base porphin [3] or by the method of Eisner and

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Linstead [6]. A saturated solution of H_2Ch in n-alkane was diluted 80:1, degassed, sealed in a pyrex tube and slowly crystallized by lowering into liquid nitrogen. Single-crystal pieces ($1.5 \times 1.5 \times 4.0$ mm) were cut and then oriented under a polarizing microscope. The two hosts, n-C_6 and n-C_8 have a similar crystal structure, triclinic with one molecule per unit cell [7]. The crystal a axis corresponds to the direction of growth and the ab and ac planes could be assigned via their extinction angles ($18 \pm 3°$ and $30 \pm 5°$, respectively).

The oriented crystal was placed at the center of a pyrex ball (diameter 9.0 mm) in a 1.5×1.5 mm axial slot running through the ball with the crystal a axis parallel to the slot. The ball was then attached to a Teflon seat by means of a thin string around its circumference so that the ball could be rotated about the slot axis (i.e. the a axis of the crystal), horizontally placed in the liquid-helium immersion dewar. In addition, the insert holding the ball could be rotated

a full 360° about a vertical axis during the experiment. This apparatus thus allowed us to make electric field measurements at all angles of rotation in two perpendicular planes (for constructional details see fig. 1).

Our procedure for orienting the crystal, commonly used in ESR and other experiments in a magnetic field [8], does not seem to have been used before in electric field studies. It has two advantages over the usual "sandwich" cell technique for Stark measurements. First, it allows one to obtain all electric field data on the same crystal. Second, both the magnitude and direction of $\Delta\mu$ can be determined. Three perpendicular electric field measurements yield $|\Delta\mu|$ and the absolute values of its direction cosines, but not the quadrant of these cosines. By making Stark measurements at least every 30° in two mutually perpendicular planes one can identify maximum and minimum positions and from these one is able to determine the direction of $\Delta\mu$ with respect to the crystal axes.
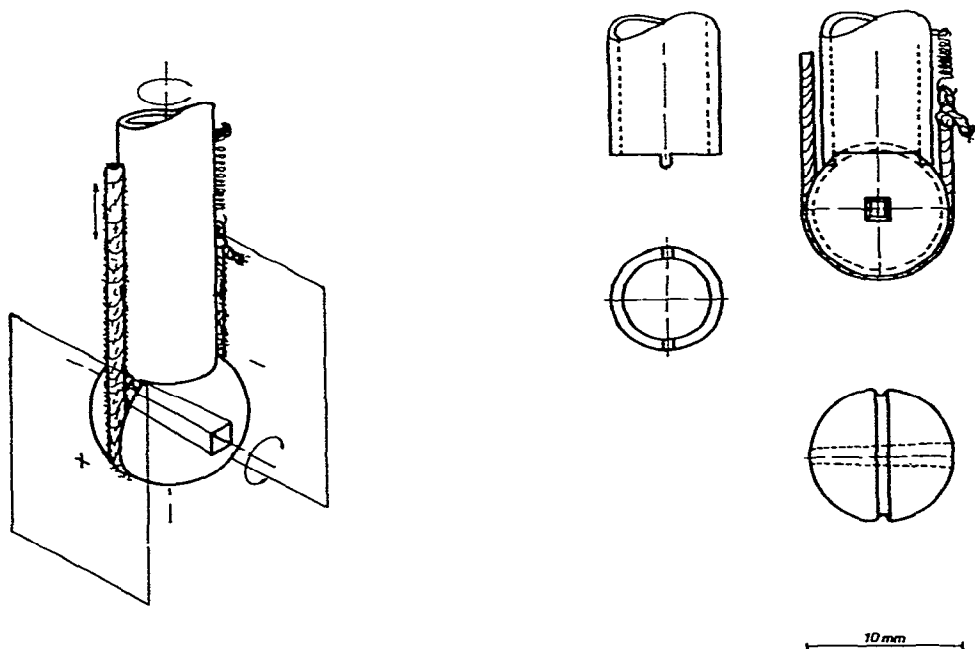

Fig 1 View and projection of Stark cell constructed by J.A.J.M. Disselhorst and L. van As. The crystal holder consists of a glass ball held against a cylindrical teflon tube by means of a cotton thread; two protrusions on the cylinder fit into a groove along the equator of the ball. By pulling on the thread via a mechanism at the top of the cryostat, the ball is rotated about tapered axial slot holding the crystal; in addition the entire sample holder may be rotated about a vertical axis by means of the teflon tube. The ball was fabricated by pushing a small section of pyrex capillary tubing onto a tapered copper pin covered with wax. This piece of glass is transformed into a spherical ball by melting in a flame and, subsequently, the groove at the equator is cut on a lathe with the aid of a copper wire covered with a slurry of Carborundum powder.

Table 1

Frequencies of the 0–0 transition, direction cosines and resultant value of the change in dipole moment $\Delta\mu$ for H_2Ch and H_2Ch^* (primed labels) in a number of sites in n-C_6 and n-C_8, and the angle Φ between $\Delta\mu(H_2Ch)$ and $\Delta\mu(H_2Ch^*)$. The $\Delta\mu$ vectors are represented graphically in figs. 3 and 4

Line	Frequency (cm^{-1})	Directions cosines			Resultant $\|\Delta\mu\|$ (D)	Φ (deg)
		$\|a$	$\|b'$	$\|c'$		
n-C_6						
1	15790	0 189	−0 595	−0 780	0 21	
2	15769	0 412	−0 804	0.429	0.20	
3	15762	0.415	−0 716	0.562	0.18	
4	15758	0 091	−0 586	−0.805	0.23	
1	17415	0.038	−0.778	−0 627	0.43	16 4
2	17284	0 014	0.204	0.979	0.98	74.8
3'	17259	0 026	0 017	1.000	0.89	55 9
4	17353	0 239	−0.910	−0 339	0 52	34.1
n-C_8						
1	15755	0 059	0 853	0 520	0.25	
2a	15749	0 194	−0 600	0.775	0.25	
2b	15748	0 000	−0 881	−0 473	0 25	
2c	15747	0 038	−0.897	−0 440	0.26	
4	15728	0 186	−0 595	0 782	0 26	
1'	17311	0 010	0 707	0 707	0 51	14 3
2a	17339	0 021	0 614	0 789	0 92	75.8
2b'	17307	0 196	−0.957	0 215	0.75	42 1
2c	17303	0.186	−0 982	0.035	0.62	29.2
4	17305	0 098	0.390	0 916	0 66	59 9

The ball was situated between two tin oxide coated quartz electrodes (diameter 10 0 mm) separated by 12.0 mm. A dc field was applied with an Oltronix regulated high voltage (0–3 kV) power supply and measured with a Fluke 8000A digital multimeter via a high-voltage probe. All measurements were carried out at 1 2 K. The holes were burned and probed as previously described [1,2].

3 Results

Excitation and emission spectra of H_2Ch and H_2Ch^* in n-C_6 and n-C_8 have been shown elsewhere [1,5]. The major 0–0 peaks in n-C_6 are labelled as before, 1–4, the corresponding photoproduct bands are indicated by primes For n-C_8 we have also used the earlier numbering scheme, with the exception of line 2, at high resolution it was found to be composed of three bands, which we have numbered 2a, 2b and 2c. Line 3 was not present in our single-crystal sample.

Table 1 gives the frequencies of the 0–0 bands measured.

The Stark measurements in three orthogonal directions were made with the electric field (E) parallel to the a, b' and c' axes of the crystal. The b' axis is perpendicular to the a axis and in the ab plane; the c' axis is perpendicular to the a and b' axes. Under the influence of the field a photochemical hole burnt at zero field splits into two components. The splittings were measured in a series of fields and found to be linear with respect to E (fig. 2). The resulting values of the dipole moment change were calculated using an isotropic Lorentz internal field correction L approximated by $L = (n^2 + 2)/3$ (e.g. ref. [9]). With a value $n = 1.4$ for the n-alkane refractive index [10] we obtain $E(\text{local}) = 1.3 E(\text{applied})$. Because of the experimental symmetry there is no correction due to the pyrex ball. This was further verified by making Stark measurements on a crystal mounted half inside and half outside the Pyrex crystal holder; no difference in the Stark effect in the two parts was observed.
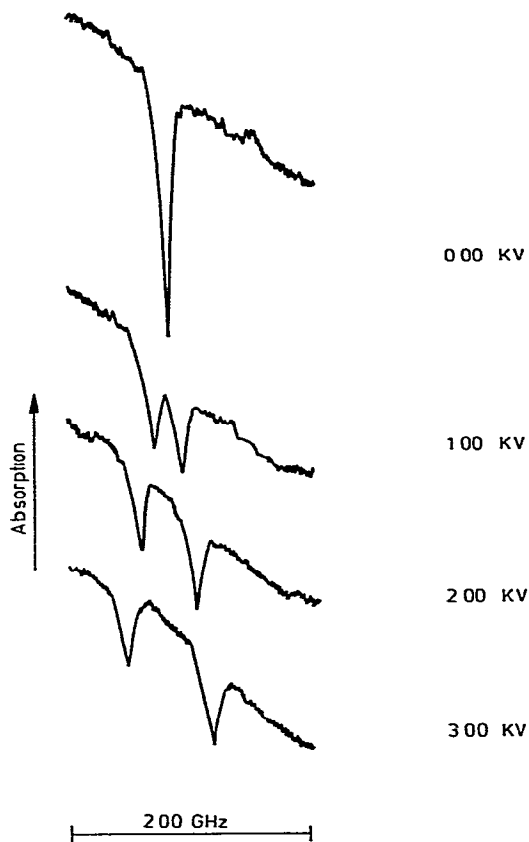
Fig. 3. Stereographic projection showing the orientation of the change in dipole moment, $\Delta\mu$, of the $S_1 \leftarrow S_0$ 0–0 transition of chlorin in an n-C_6 single crystal. The unprimed numbers refer to the stable tautomer (H_2Ch) and the primed ones to the photoproduct (H_2Ch^*). a, b and c are the crystallographic axes, b' and c' are defined in section 3. The alkane chain direction is indicated by r and z is perpendicular to the approximation to the chlorin plane (the drawn circle). All points are plotted on the upper half of the sphere. Note that 1,4 and 2,3 form groups separated by 90° and that each group is roughly 45° away from r. Note that $\Delta\mu(H_2Ch^*)$ is rotated in-plane with respect to $\Delta\mu(H_2Ch)$.

Fig 2 Stark doubling of a photochemical hole in line 2b of H_2Ch in n-C_8 at 1.2 K. First the hole is burnt and then probed at zero electrical field E. In a series of fields the splittings are found to be linear with respect to E. The width of the absorption line is ≈ 20 GHz. The frequency in zero field is 15748 cm^{-1}. The width of the holes is ≈ 100 MHz.

The value of $|\Delta\mu|$ and the direction cosines of $\Delta\mu$ with respect to the a, b' and c' axes are listed in table 1 for H_2Ch and H_2Ch^*. The resulting directions of $\Delta\mu$ in n-C_6 and n-C_8 are plotted in the stereonets of figs. 3 and 4, respectively.

An indication of the sign of $\Delta\mu$ for H_2Ch was obtained from room-temperature solution and thin-film spectra. In an n-hexane solution the $H_2Ch\ S_1 \leftarrow S_0$ transition is at 636.2 nm; in a thin film it is at 647.0 nm. This "red"-shift of 262 cm^{-1} implies that in this excitation the molecular dipole moment has increased [11].
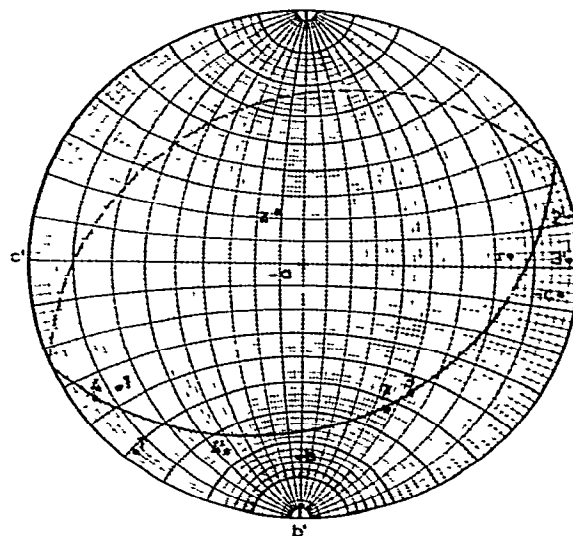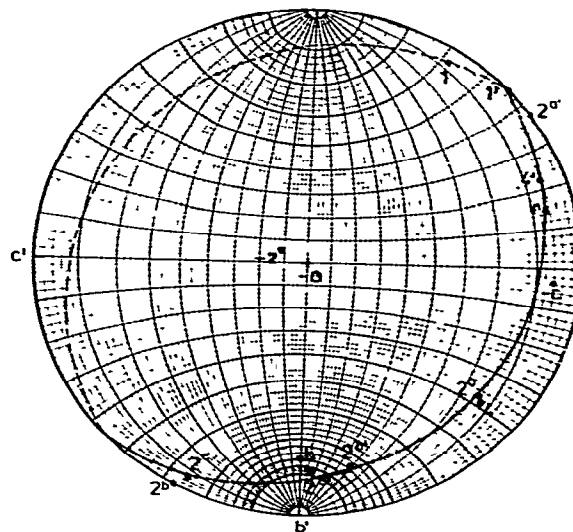
Fig. 4. Stereonet indicating the directions of $\Delta\mu$ of H_2Ch and H_2Ch^* in n-C_8. The representation is similar to that used in fig. 3. Here 1, 2b, 2c and 2a, 4 form groups

4 Discussion

Our results show that the method used is very suitable for Stark experiments. Not only could we use relatively low electric field strengths (<3 kV/cm), we were also able to obtain the directions of $\Delta\mu$ with respect to the crystallographic axes

In the stereonets for n-C_6 (fig 3) and n-C_8 (fig 4) we have plotted the directions of $\Delta\mu$ of H_2Ch (the numbers without primes) and the direction of the alkane chains (r) for each crystal. The half-solid, half-dashed curve represents the plane through the $\Delta\mu$s of H_2Ch This plane in n-C_8 is parallel to that of the molecular plane of the porphin nucleus in site A in the same host as determined from earlier ESR experiments [12]. In n-C_6 the drawn plane also corresponds to an A site, within the accuracy with which the samples can be mounted. These findings lead us to consider the drawn planes as a good approximation to the chlorin molecular plane.

In both hosts the experiments on H_2Ch yield results for $\Delta\mu$ that fall into two groups (n-C_6, 1,4 and 2,3; n-C_8 1, 2b, 2c and 2a, 4) related by a rotation in the molecular plane of $\approx 90°$ and making angles of $\approx 45°$ with r. A comparison with ESR experiments on H_2P in n-C_8 [13] yields that the directions of $\Delta\mu$ coincide within 5° with the H_2P molecular axes running through the nitrogens, see fig 2b of ref. [14] which shows the N–N axes of H_2P to make angles of roughly 45° with r. Because of the agreement between the measured $\Delta\mu$ directions for the H_2Ch $S_1 \leftarrow S_0$ excitation and those predicted from the H_2P orientation, we conclude that the directions of the H_2Ch ground- and excited-state dipole moments are parallel, in agreement with C_{2v} symmetry of the molecule

The fact that the Stark effect causes a doubling of the hole provides additional insight into the incorporation of chlorin in the alkane host. For every dipole in a given site there is another in the opposite direction and thus the inversion symmetry of the crystal is maintained.

The average values of $|\Delta\mu|$ for H_2Ch in n-C_6 and n-C_8 are 0 21 ± 0.02 D and 0.255 ± 0.005 D, respectively. The results are in agreement with an ab initio SCF calculation by Petke et al. [15] who predicted that chlorin would have $\Delta\mu = 0.26$ D for its $S_1 \leftarrow S_0$ transition. Even though the difference between the

results for the two hosts is marginally significant, it is tempting to attribute it to the change in site on going from n-C_6 to n-C_8.

For the photoisomer the results are less clear-cut. In the stereonets we also have plotted $\Delta\mu$ for the $S_1 \leftarrow S_0$ excitation of H_2Ch^* (numbers with primes): however, the directions are considerably different from those of the corresponding lines of H_2Ch. There is an apparent in-plane rotation (angle Φ) between the measured $\Delta\mu$s of H_2Ch and H_2Ch^*. Also, the magnitude of $|\Delta\mu|$ for H_2Ch^* varies considerably from site to site in the two hosts (e.g. n-C_6, 0.43–0.98 D). In table 1 $|\Delta\mu|$ for each site is listed with the direction cosines of $\Delta\mu$ and the change in direction (Φ) of $\Delta\mu$ relative to H_2Ch.

It is apparent that in the case of the photoproduct the ground- and excited-state dipole moments are no longer parallel Since it is highly implausible that the molecule actually rotates in the lattice in the photo-isomerization step, we explain the data by making the assumption that the dipole moment of H_2Ch^* in the ground state remains parallel to that of H_2Ch and that it changes direction on excitation to the state S_1. In order to evaluate the magnitude of the dipole moment $\mu(S_1)$ of H_2Ch^* and its direction we need an estimate of the photoisomer ground-state dipole mo-
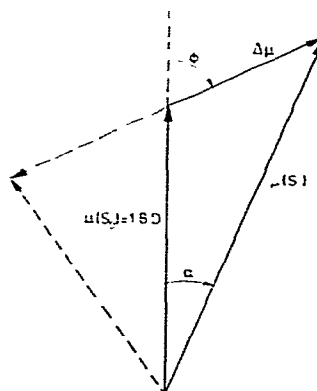

Fig. 5 Vector model to interpret the H_2Ch^* results. The ground-state dipole moment $\mu(S_0)$ for H_2Ch^* is assumed to be parallel to $\Delta\mu(H_2Ch)$ and equal to 1.8 D. $\Delta\mu$ is the measured change in dipole moment of H_2Ch^* and Φ the angle between $\Delta\mu(H_2Ch^*)$ and $\Delta\mu(H_2Ch)$ as listed in table 1 The solid vectors represent the plus combination which yields values of $\mu(S_1)$ for H_2Ch^* and of the angle α subtended by this vector and $\Delta\mu(H_2Ch)$ listed in table 2 The dashed vectors represent the minus combination

Table 2

Direction cosines and resultant value of the dipole moment of H_2Ch^* in the S_1 state for a number of sites in n-C_6 and n-C_8 These values have been calculated assuming that $\mu(S_0)$ is parellel to the change in dipole moment of the stable tautomer $(\Delta\mu(H_2Ch))$ and has a value of 1.8 D. α represents the angle between $\mu(S_1)$ and $\Delta\mu(H_2Ch)$

Host	Line	Direction cosines of $\mu(S_1)$			$|\mu(S_1)|$ (D)	α (deg)
		$\|a$	$\|b'$	$\|c'$		
n-C_6	1'	0.161	0 636	−0.756	2.18	4.0
	2'	0.334	−0.553	0.763	2.28	24.5
	3'	0.319	−0.529	0 786	2.45	17.6
	4'	0.128	0.680	−0.722	2.21	7.4
n-C_8	1'	0 049	0 825	0 564	2.27	2 1
	2a'	0.167	−0 237	0.957	2.24	23.6
	2b'	0.062	−0.957	−0.283	2.38	12.4
	2c'	0.078	−0 942	−0.325	2 34	7.7
	4'	0.181	−0 371	0.911	2.23	14.8

ment, $\mu(S_0)$, for which neither an experimental nor theoretical value is available. For the stable isomer, however, values for $\mu(S_0) = 1.5-1.7$ D have been calculated [15,16], while earlier calculations in this laboratory [1] have indicated that $\mu(S_0)$ should be slightly larger for $H_2Ch^*_+$ than for H_2Ch. In the analysis of our data we have therefore, made the tentative assumption that $\mu(S_0) = 1.8$ D for H_2Ch^*. Using this assumed value we calculated the direction and magnitude of the H_2Ch^* excited-state dipole moment, $\mu(S_1) = \mu(S_0) + \Delta\mu$, and the angle α between $\mu(S_0)$ and $\mu(S_1)$ (fig. 5).

The results of this computation are in table 2. Since we did not know the sign of $\Delta\mu$ we evaluated the two possible combinations. It seems reasonable to expect that $\mu(S_1)$ should be roughly constant for the different sites. The plus combinations listed reflect this expectation, while the minus combinations did not. (In each host there was one site for which the minus combinations predict a slight increase in dipole moment, while for the other sites a decrease of ≈ 0.5 D is calculated.) All of the plus combination $\mu(S_1)$ fall into a relatively narrow range and the angles α are of a size which may be physically realistic.

The site-dependent rotation of μ on excitation of H_2Ch^* to state S_1 by as much as $24°$ may seem remarkable at first sight. We think this effect is closely related to the near degeneracy of S_1 and S_2 in this molecule. As discussed in ref. [2] the energy separation $E_2 - E_1$ between the two origins is thought to vary between about 400 and 700 cm^{-1} for sites $1'$–$4'$

of H_2Ch^* in n-C_6. It is believed that the two orbital states are mixed by the crystal field and vibronic coupling [1]. Consequently, for H_2Ch^* it is probably not appropriate to describe the transition studied on the basis of a pure upper electronic state S_1, but rather as one which involves a site-dependent combination of S_1 and S_2.

Acknowledgement

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