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Liquid Crystals

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Transient excited-state absorption of the liquid crystal CB15 [4-(2-methylbutyl)-4-cyanobiphenyl] in its isotropic phase

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Transient excited-state absorption of the liquid crystal CB15 [4-(2-methylbutyl)-4-cyanobiphenyl] in its isotropic phase

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Liquid crystals are known to possess large electronic optical non-linearities. Transient photo-induced absorption is not commonly applied to liquid crystals, but it is a powerful technique by which to examine the excited-state absorption (ESA) and hence the non-linear absorption of molecular systems. We show that measurements of this kind can give an insight into the dominant mechanisms of picosecond non-linear optical response in liquid crystals, and together with semi-empirical quantum chemical calculations appropriate assignments of the absorptions can be made. In particular, we report measurements of the transient ESA of the liquid crystal CB15 [4-(2-methylbutyl)-4-cyanobiphenyl] in its isotropic phase using femtosecond pump-probe spectroscopy in the wavelength range from 400 to 1000 nm. By pumping directly into the first excited state (S_1), we identify at least four transient ESAs which contribute to the non-linear response up to a time of 1 ns after excitation. These features show a linear dependence with pump intensity. There also exists weak two-photon absorption (TPA) into S_1 at 650 nm, giving a similar ESA. Furthermore, we show that a semi-empirical quantum-chemical treatment of a single molecular unit of CB15 using the AM1 Hamiltonian gives good agreement with the observed spectra, and implies that the dominant ESA in the picosecond regime can be attributed principally to singlet–singlet transitions from monomer units; but there is also a possible contribution to the ESAs by excimer absorption. On the time scale of our experiment we see no evidence of triplet–triplet absorptions, and we have also measured a fluorescence quantum yield of 20%.

1. Introduction

The non-linear optical properties of liquid crystals have generated considerable interest in recent years, see [1] and references therein. Their large optical non-linearities make them candidates for use in a wide variety of optoelectronic devices such as second harmonic generators, photonic switches and optical limiters [2]. The cyanobiphenyl family of mesogenic liquid crystals is one of the most stable and widely studied groups, see [3] and references therein.

In particular, the 4-*n*-alkyl-4-cyanobiphenyl (or *n*-CB) family has a high transparency in the visible spectral region from blue to near infrared, whilst exhibiting large non-linear refraction and absorption in this range; this has made it especially interesting for optoelectronic devices. The *z*-scan method has been used to determine successfully the non-linear optical absorption and refraction coefficients for a series of *n*-CBs [4–6], and inferences have been made about the dominant mechanism for non-linearities on time scales from picoseconds to milliseconds. On the picosecond time scale, the dominant mechanism is thought to be due to electronic contributions [7], and in this regime the use of transient-grating spectroscopy has been used to differentiate between electronic and nuclear Kerr effects. Two-photon absorption (TPA) into the first excited state, followed by one-photon absorption into higher excited states, has been observed at excitation wavelengths in the visible spectral region in 5-CB using transient grating spectroscopy [8] and pulse-probe techniques [9]. The fluorescence decay of *n*-CBs and their related polymers in both solution and the neat form has been extensively studied [10–13]. However, the fluorescence spectra do not generally give direct information about higher excited-states in these molecules. Transient absorption spectroscopy is a powerful technique whereby the excited-state absorptions (ESAs) can be measured, giving a direct insight into the origin of the electronic non-linear absorptions as measured by other techniques. A better understanding of the excited-state absorptions in these molecules will

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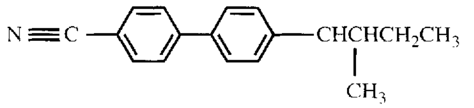
therefore be of direct relevance to their application in non-linear optical devices. Unlike fluorescence spectroscopy this technique has not been applied extensively to liquid crystals.

Recently, nanosecond transient absorption measurements were reported on the liquid crystal 5-CB, dissolved in cyclohexane [14] which demonstrated that on the nanosecond time scale singlet–singlet absorptions, triplet–triplet absorptions and exciplex absorptions contributed to the electronic non-linear absorption over a spectral range from 380 to 870 nm. No transient absorption was detected at wavelengths greater than 620 nm.

We have performed femtosecond pump-probe measurements on the closely related CB15 liquid crystal at 298 K in its isotropic phase; the molecular structure is shown in figure 1. CB15, unlike CB5 (5-CB), is isotropic at room temperature and has a melting point at 4°C. This, combined with its high optical clarity, makes it a suitable candidate for optoelectronic devices. Transient ESAs are observed from 400 to 1000 nm which shows that non-linear absorption can occur over the entire visible spectral range. We present both spectrally-resolved and time-resolved data, up to 1 ns after excitation, which show the ultrafast excited-state dynamics and non-linear absorptions of CB15. At least four distinct ESAs are observed and are assigned to predominantly singlet–singlet excitations from monomeric units. There exists weak TPA at 650 nm and the excited-state absorptions from the TPA excited-state appear to follow the one-photon excited-state spectrum. The one-photon (325 nm) pumped ESA features show a linear dependence with pump intensity which indicates that on the picosecond time scale, the dominant mechanisms for non-linear absorptions are driven by effective third-order processes. Our assignments of the ESA have been assisted by a semi-empirical quantum-chemical analysis using the AM1 Hamiltonian [15] which gives good agreement with our observed spectra.

2. Experimental

Our sample of CB15 is commercially available from Merck Industrial Chemicals, Poole and was used without further purification or degassing. The sample was placed in a suprasil quartz glass cuvette of 1 mm light path, available from Hellma. All measurements were taken at 298 K, so that the CB15 sample was in its isotropic phase. The number density of CB15 molecules was approximately $2{\cdot}4 \times 10^{21}$ cm^{-3} [9].



4'-(2-methylbutyl)-4-cyanobiphenyl
CB15

Figure 1. The molecular structure of 4-(2-methylbutyl)-4-cyanobiphenyl, CB15.

Measurements of the linear optical absorption were taken using a Perkin Elmer λ9 spectrophotometer. Steady-state fluorescence was measured using a xenon lamp as excitation source, and was detected using a spectrograph coupled to an Oriel Instapec CCD camera system. The fluorescence quantum yield was measured by means of an integrating sphere [16] with a multi-line UV excitation from a cw argon-ion laser.

Ultrafast optical measurements were taken using the pump-probe technique with parallel, linearly polarized light. The experimental set up is shown in figure 2. The laser system used to take these measurements is based on a synchronously-pumped, hybridly-modelocked, GVD-compensated dye laser [17], which produces 100 fs pulses at 650 nm with 800 pJ energies at 76 MHz repetition rate. The second harmonic of a Nd:YAG regenerative amplifier with a repetition rate of 1 kHz is used to amplify the dye laser pulses in a three-stage dye amplifier. In this way, a train of 1 kHz pulses with energies of 1 μJ are used to produce a white light supercontinuum which extends from 400 to 1000 nm.

A portion of this continuum is spectrally filtered to provide the pump beam at 650 nm. This beam is then focused into a 0·2 mm BBO crystal in order to produce the doubled 325 nm pump, following which the excess of 650 nm beam is suppressed using a UG11 Schott glass filter. The remaining white light is passed through a BG12 Schott glass filter to suppress the dominant 650 nm spectral component of the continuum and is used as the probe pulse. The probe is further split into two beams, one of which passes through the sample excitation region via an adjustable delay line (from 0 to 1 ns with respect to the pump); the other is used as a reference beam. The pump beam is mechanically chopped at 500 Hz which allows the transmission of the sample to be measured both when it is excited with the pump beam and when it is not. The pump diameter at the focus was approximately 1·5 times that of the probe (which was 100 μm), and the energy of the pump pulse was approximately 0·1 μJ. The pump pulse width was approximately 300 fs. This was measured by a cross-correlation of the 650 nm pump and monochromatic probe at the sample position. The pump and probe beam crossed at an angle of 5° external to the cuvette. The two probe beams were spectrally dispersed and imaged onto a Wright Instruments CCD camera [18], enabling spectra to be taken from 400 to 1000 nm.

The AM1 calculations were carried out using the 1993 version of the quantum-chemical package MOPAC [19].

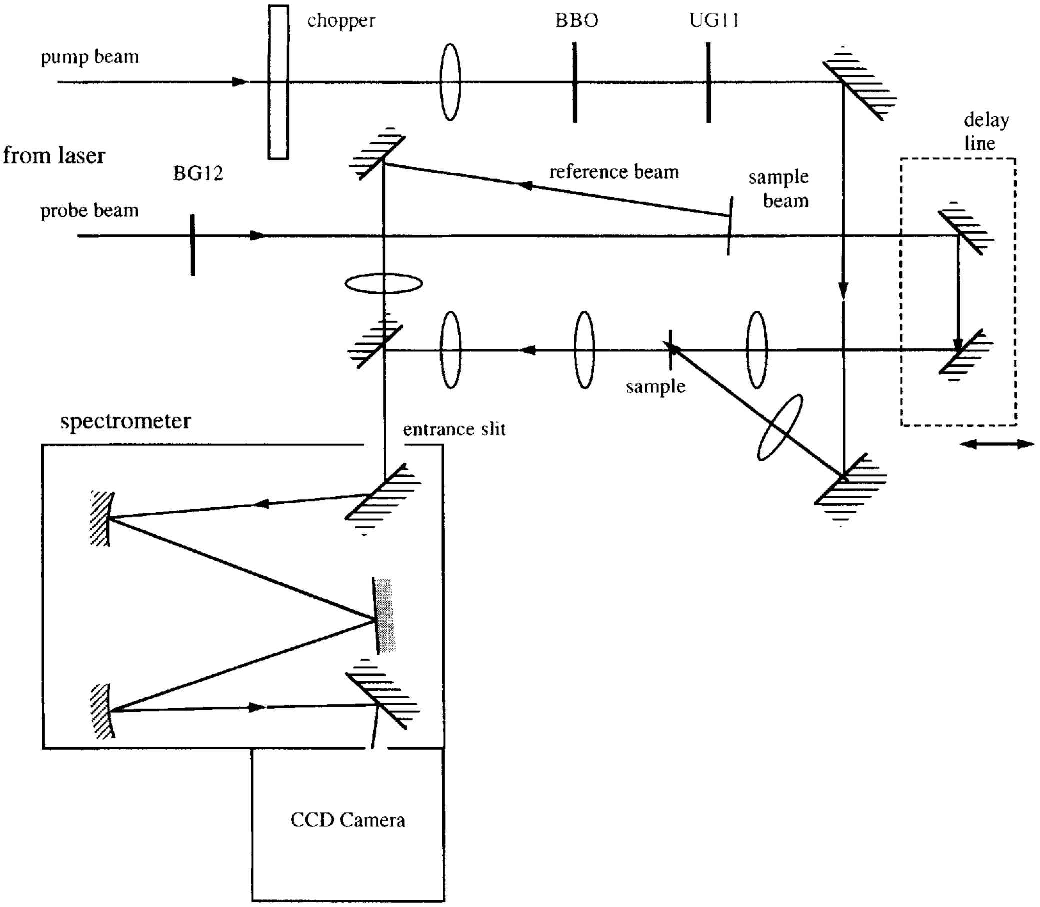


Figure 2. Schematic diagram showing the experimental set-up.

3. Results

The linear absorption spectrum for CB15 and the steady-state fluorescence spectrum for an excitation wavelength of 325 nm are shown in figure 3. The linear absorption spectrum was taken using a dilute solution of CB15 in chloroform; the dilution was necessary because neat CB15 has an absorbance too large to be measured using the spectrophotometer. The linear spectrum exhibits a broad absorption, peaking at 283 nm, with a FWHM of 42 nm. This represents the $S_0 \rightarrow S_1$ transition, which can be associated with optical excitations of the low energy vibrations of the phenyl rings [20]. The fluorescence spectrum peaks at 390 nm, FWHM 80 nm, with evidence of a shoulder at 360 nm. The fluorescence quantum yield of CB15 excited with the multi-line UV wavelengths of a cw argon-ion laser was measured to be 20·0 ± 5·0%. This is likely to be an under estimate since the pump wavelengths spectrally overlap a part of the luminescence, which hinders accurate calculation of the quantum efficiency. Therefore it can be assumed that the fluorescence quantum efficiency is likely to be greater than 20%.

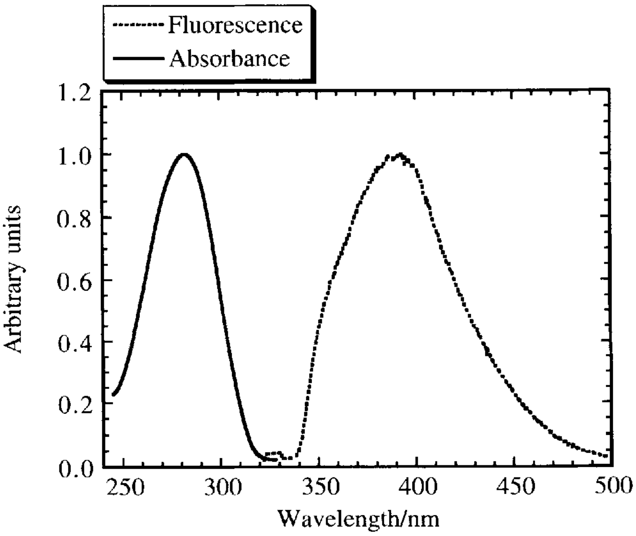
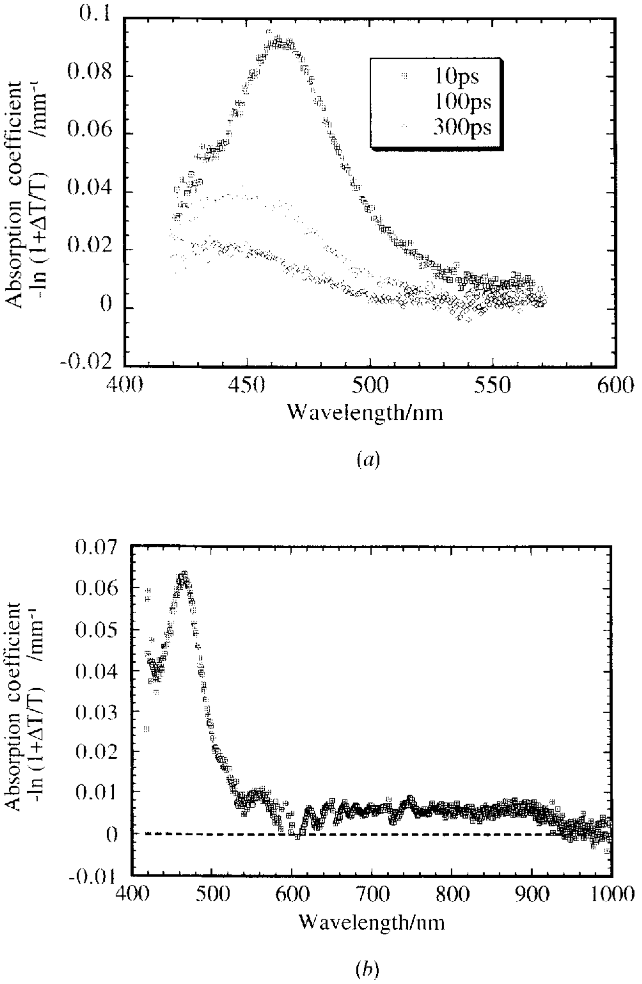


Figure 3. The normalized linear absorption spectrum of CB15 and the normalized fluorescence spectrum of CB15 at an excitation of 325 nm.

Figure 4 (*a*) shows excited-state absorption spectra from 400 to 550 nm taken at 10, 100 and 300 ps after excitation with the 325 nm pump. Figure 4 (*b*) shows a spectrum from 400 to 1000 nm at 10 ps after excitation. The non-linear absorption coefficient, α, has been plotted against wavelength, where α has been calculated from our spectral data by the following relation,

$$\alpha = -\frac{1}{l}\ln\left[1+\frac{\Delta T}{T}\right] \qquad (1)$$

where l is the path length of the light through the sample, and $\Delta T/T$ is the fractional change in transmission of the sample. The absorption features rise within the time scale of the temporal width of the pump pulse, which suggests that the excited states giving rise to these new absorptions are populated on a time scale of 300 fs. The dominant absorption occurs at 465 nm, FWHM of approximately 80 nm. This absorption decays significantly within 100 ps. There appears to be an underlying absorption, peaking at 450 nm, which spreads from 400 to 520 nm, which is much more long-lived. In addition, there is a smaller absorption peaking at 570 nm, FWHM of approximately 40 nm, and a large broad-band absorption from 610 to 1000 nm. This absorption is relatively small, with maximum $\Delta T/T \leqslant 0{\cdot}01$, and therefore the resolution of separate transitions in this range was not possible. However, these absorptions persist to the limit of our time delay, indicating life times of order nanoseconds. The triplet–triplet absorptions in *n*-CBs can compare in magnitude with the singlet–singlet absorptions [14]. Slowly rising absorptions on a time scale of nanoseconds are characteristic of triplet–triplet absorptions because inter-system crossing must occur before triplet states can be populated. However, no significant absorptions arose within the 1 ns time scale of our experiment. We can therefore infer from our data that the inter-system crossing time for this molecule is greater than 1 ns. Inter-system crossing times of greater than 1 ns are typical for *n*-CBs [21].



(*a*)

(*b*)

Figure 4. (*a*) Ultrafast spectra taken at 10 ps (squares), 100 ps (circles) and 300 ps (diamonds) after excitation at 325 nm; (*b*) a spectrum taken at 10 ps after excitation at 325 nm showing the entire spectral range from 400 to 1000 nm.

Time-resolved data for these absorption features were extracted from the spectral data. Figure 5 (*a*) shows the decay of the ESA at 460 nm and figure 5 (*b*) shows the decay with time of the 470 nm peak. The data were fitted to bi-exponential functions of the form,

$$\alpha = A\exp(-t/t_0) + B\exp(-t/t_1) \qquad (2)$$

with time constants t_0 and t_1 and pre-exponential factors A and B. Time constants t_0 and t_1 of 42 ± 7 ps, and $1{\cdot}0 \pm 0{\cdot}2$ ns, respectively, were determined for the 460 nm decay, and 42 ± 6 ps and $1{\cdot}6 \pm 0{\cdot}7$ ns, respectively, were determined for the 470 nm decay. These time constants agree with each other within the accuracy of the fits, which is expected since the ESAs at 460 and 470 nm originate from the same spectral feature centred at 465 nm. We associate the fast decay with the ESA centred at 465 nm and the slower decay with the underlying ESA centred at 450 nm. Figure 5 (*c*) shows the decay of the ESA at 710 nm which, although noisy, suggests that there is only one decay component of approximately $1{\cdot}1 \pm 0{\cdot}1$ ns. Table 1 shows the results of exponential and bi-exponential fits to the decays at several wavelengths. Each of the four observed ESAs appears to have different decay dynamics, implying that the absorptions originate from different electronic states or different molecular species such as excimers. The broad infrared transition appears to have roughly the same decay time of approximately 1 ns, and the transition at 560 nm is mono-exponential, with a decay time of approximately 460 ps.

The intensity dependence of the ESAs was measured with the time delay fixed at 10 ps after excitation. We used a Newport AV2 filter wheel, with an optical density

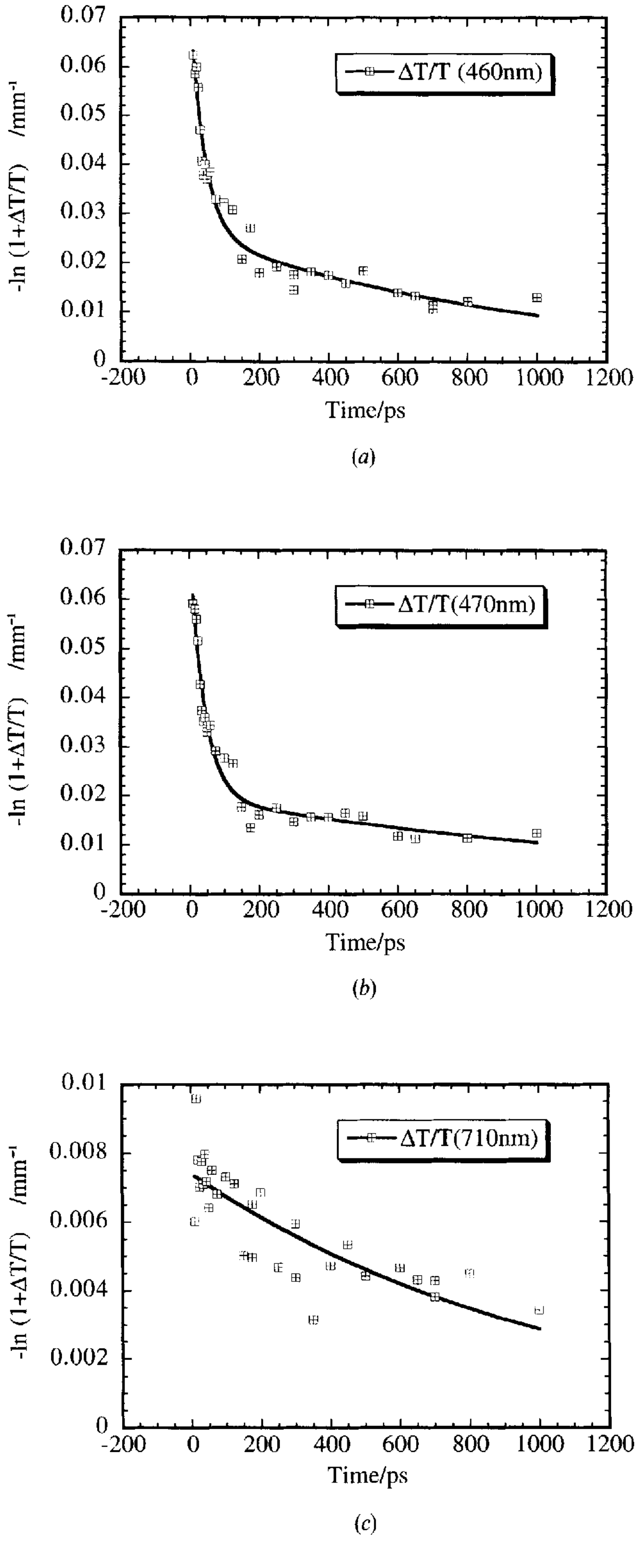


Figure 5. Time resolved data showing the evolution of the spectral features at (*a*) 460 nm, (*b*) 470 nm and (*c*) 710 nm, together with exponential fits to the data.

Table 1. The results of mono-exponential and bi-exponential fits to the decays of the spectral features shown in figure 5.

Wavelength/nm	t_0/ps	t_1/ps	A	B
460	42 ± 7	1000 ± 200	0·048	0·026
470	42 ± 6	1600 ± 700	0·052	0·02
560	460 ± 60	n/a	0·009	n/a
710	1100 ± 200	n/a	0·007	n/a
755	1000 ± 200	n/a	0·007	n/a
775	1300 ± 400	n/a	0·006	n/a

varying from 0·05 to 2·0, in order to attenuate the pump energy. Care was taken to ensure that the overlap of pump and probe beams was not altered on rotation of the wheel. Figure 6 shows a plot of relative pump intensity, I/I_0, against the absorption coefficient, α, at 460, 490 and 560 nm together with linear fits to the data. The peak intensity is estimated to be 1·3 GW cm^{-2}. The curves are fitted by linear functions, all with regression coefficients, r, greater than 0·95.

The weak linear absorption at 325 nm suggests that at 650 nm, two-photon absorption (TPA) should be possible into the S_1 state, since it is suggested that the TPA spectrum essentially follows the one-photon absorption spectrum [8]. Therefore a transient absorption experiment was performed using the 650 nm pump and we obtained the spectrum at 2 ps after excitation shown in figure 7. To achieve a reasonable signal-to-noise ratio we focused the pump beam tightly such that it was comparable in diameter to the probe. The TPA was very weak at 650 nm, as the excited-state spectrum demonstrates. However, it follows the one-photon excitation spectra to a certain extent. There is clearly a relatively large ESA in the range 400 to 600 nm, as has been observed in 5-CB [21]. Furthermore, our absorption appears to peak at approximately 460 nm,

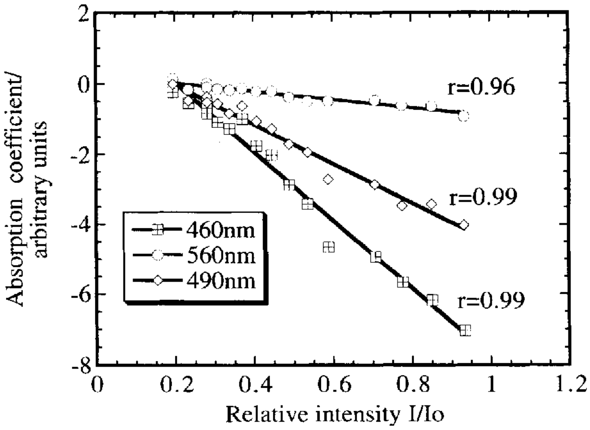


Figure 6. Intensity dependence of spectral features at 460 nm (squares), 560 nm (circles) and 490 nm (diamonds), together with linear fits to the data.

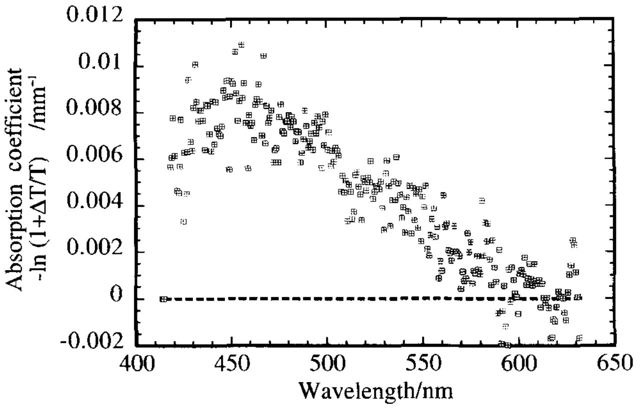


Figure 7. A TPA spectrum taken at 2 ps after excitation with an intense 650 nm beam.

Table 2. The results of the AM1 calculation of the energy levels of the CB15 molecule. The first 11 calculated singlet states are shown below. The first three states are nominally labelled S_0, S_1 and S_2.

Singlet State	Wavelength/nm	Energy/eV
1st (S_0)	0	0
2nd (S_1)	295	4·21
3rd (S_1)	282	4·4
4th (S_1)	281	4·42
5th (S_2)	248	5·01
6th	218	5·69
7th	209	5·94
8th	208	5·98
9th	195	6·38
10th	180	6·91
11th	178	6·96

which coincides with the peak of the one-photon ESA shown in figure 4. However, in the range from 600 to 1000 nm, any absorptions above the level of noise could not be resolved. TPA measurements warrant further investigation, but it would be better to pump at half the wavelength of the peak of the linear absorption where two-photon coupling into the first excited-state is likely to be greater. This is beyond the scope of our experiment at present.

The AM1 Hamiltonian was used to optimize the molecular geometry of a monomeric unit of CB15 with its phenyl rings held in a planar configuration with respect to one another. Using the optimized geometry, a multi-electron configuration interaction (CI) calculation was performed. This, considered as a basis, set microstates with all of the electronic configurations possible by using the highest four filled and the lowest four unfilled molecular orbitals, giving a total of 4900 possible electronic configurations. The results of the CI calculation gave us the singlet energy levels of the CB15 molecule. Table 2 shows the results of the CI calculation. The first three states are labelled S_0 (0 nm), S_1 (295, 282, 281 nm) and S_2 (248 nm), representing the ground state and the first excited state, respectively. We have included the three states at 295, 282 and 281 nm within the S_1 manifold because the experimental linear absorption shows the $S_0 \rightarrow S_1$ transition as a broad feature centred at 283 nm which envelopes these theoretical states. It should be noted that the oscillator strengths for the theoretical transitions are not known, and therefore the calculations are useful in the sense that they provide supporting evidence that the experimental assignments of the observed transitions are correct.

4. Discussion

Our results provide detailed information on the origins of picosecond electronic optical non-linearities in the liquid crystal CB15. The ESA features all rise instantaneously within the time scale of the pump pulse. This implies that these ESAs are very likely to be the result of singlet–singlet absorptions from the first excited-state manifold, S_1. We detected no spectral shift in the absorption peaks on an ultrafast time scale, which implies that relaxation from higher vibronic levels in S_1 occurs in less than our temporal resolution of 300 fs. Spectral shifts are more apparent in time-resolved fluorescence studies [10–13] of *n*-CBs in solution, which can be explained due to the creation of a solvent-stabilized intramolecular charge transfer (CT) excited-state. However, in the isotropic phase, the CT complex will not be stabilized and we see no evidence of its creation in the ESA spectra.

As already discussed, triplet–triplet absorptions are not observed on the time scale of our experiment, but have been seen on nanosecond time scales in 5-CB [14]. We can therefore assume that the inter-system crossing time for CB15 is much greater than 1 ns. This, coupled with the fact that the fluorescence quantum yield is at least 20% implies that the triplet yield may not be very high in this molecule. We can also assume that, since the triplet–triplet absorption grows in on a time scale of several nanoseconds, the dominant mechanism for electronic non-linear absorption in the picosecond regime is due to singlet excitations, whereas the electronic non-linear absorption in the nanosecond regime is probably due to both singlet–singlet and triplet–triplet absorptions.

Table 3 shows the energies and wavelengths of transitions possible from the first excited state S_1 (295 nm) to higher excited states, and transitions from the other states within the S_1 manifold (281, 282 nm) to higher excited states. These were calculated from the energy levels calculated by the AM1 Hamiltonian, shown in table 2. There is excellent agreement between the observed transitions and those calculated for S_1

Table 3. The energies and wavelengths of transitions possible from the first excited state S_1 at 295 nm and 281 nm to the higher excited states.

S_1 (295 nm)		S_1 (281 nm)	
ΔE (S_1–S_n)/eV	Wavelength/nm	ΔE (S_1–S_n)/eV	Wavelength/nm
0·19	–	0	–
0·21	–	0·02	–
0·8	1552	0·59	–
1·48	839	1·67	744
1·73	718	1·92	647
1·77	701	1·96	634
2·17	572	2·36	526
2·7	460	2·89	430
2·75	451	2·94	422

(295 nm)–S_n transitions in table 2. There are transitions predicted at 450, 460 and 572 nm which virtually coincide with our observed transitions. There are also predicted transitions in the near infrared of 701, 718 and 839 nm. These infrared transitions are consistent with the broad infrared ESA that is observed. It is therefore concluded that the four distinct ESAs we observe are principally due to excitations into different excited singlet states, as the spectral and time-resolved data imply. The transitions from states higher in the S_1 manifold (281, 282 nm) to S_n do not agree with the observed spectra as well as the S_1 (295 nm)–S_n transitions. However, since the excitation is at 325 nm, we are exciting electrons low into the first excited-state manifold and therefore we would expect the dominant contributions to the excited-state transitions to originate from lower energy states.

However, broad excited-state absorptions of excimers have been observed in concentrated 5-CB solutions [14] at room temperature on a picosecond to nanosecond time scale. The absorptions in our sample could well be broadened by underlying excimer absorptions. The steady-state fluorescence shows a shoulder at 360 nm and a main peak at 390 nm which have been assigned in *n*-CBs to monomer fluorescence, and excimer fluorescence, respectively [23]. This implies that excimers are formed in significant population in isotropic CB15, and that there remains a large amount of local order even in the isotropic phase. Due to this local order the formation of excimers may be relatively fast, and has been measured to be of the order of 200 ps in isotropic CB5 [23], which is a much shorter time than the corresponding triplet inter-system crossing time for this molecule. Therefore we conclude that there may be underlying excimer absorptions contributing to the ESAs. The excimer absorptions would presumably grow in at longer times, since excimer formation is likely to be more significant at times greater than 1 ns, and therefore we believe that the underlying excimer absorptions are smaller than the monomer absorptions at times less than 1 ns, as has been shown for 5-CB [14]. However, since the ESA peaking at 465 nm is dominant at short times, it is not easy to discern whether the underlying ESA peak at 450 nm rises with time. The infrared ESAs rise immediately and are most likely to be predominantly monomer ESAs, but the ESA at 450 nm could well be significantly contributed to by excimer absorption. Therefore the two-component decay of 42 ps and 1·5 ns at 450 nm can be explained in terms of a fast decay from a purely monomeric species and a slower decay which is due to both monomeric and excimeric species. We note that the two-component decay is unlikely to be due to molecular reorientation, since two-component decays are not observed over the entire spectrum and the high viscosity of the liquid crystal implies that molecular reorientation times should occur on a longer time scale. We would presumably be able to discern the excimer contributions to our ESAs at much longer times (e.g. after 10 ns) when the singlet–singlet monomer absorptions have decayed significantly. However, we believe that the dominant ESAs observed within 1 ns are mainly due to singlet–singlet excitations from monomers, as our calculations appear to show.

The discrepancy between the observed and theoretical predictions are principally due to the following reasons. We have calculated gas phase results for a single molecule and have not taken into account intermolecular interactions such as excimer formation which would presumably broaden the transitions. It should also be noted that our analysis has taken into account only one geometry of the CB15 molecule, namely a planar configuration of the phenyl rings, whereas in the isotropic phase the phenyl rings are orientated at random angles with respect to one another, and the alkyl tail also has a random orientation. These effects are also likely to broaden the observed transitions. Other relatively smaller discrepancies may be due to the method of calculation itself. We are employing a large, but finite, CI calculation which means that there is often a systematic error in the calculated optical transition energies, as has been observed in calculations on similar organic molecules [22]. This is likely to be due to the amount of electron–electron correlation energy included in the calculated state energies in a given CI calculation. As the size of the CI increases, this error decreases and is smaller for open-shell configurations, which have similar correlation energies, than the ground-state with its closed-shell configuration. Therefore the $S_0 \rightarrow S_1$ transition (i.e. the linear absorption) is likely to be less accurate than $S_1 \rightarrow S_n$ transitions. This seems to be what we observe.

The intensity-dependent measurements on our ESA features (see figure 6) show convincing linear relationships. The absorption coefficient is defined as,

$$\alpha = \alpha_0 + \beta I, \tag{3}$$

where α_0 is the linear absorption coefficient. A linear dependence of α with intensity, I, implies that β, the non-linear absorption coefficient, is independent of intensity and that the non-linear absorption in the picosecond regime is due to an effective third-order process. That is, there is linear absorption followed by linear excited-state absorption. This conflicts with time-resolved z-scan determinations of the non-linear absorption [8] of 5-CB at 532 nm, where a fifth-order process is inferred. It could be that these measurements of the non-linear absorption also included triplet–triplet or exciplex absorptions which may have grown in with time. These measurements were also performed using the nematic phase of 5-CB, and therefore intermolecular interactions would have been much more important. It may also be likely that contributions by two-photon absorption are larger at 532 nm. We conclude that in CB15, in its isotropic phase, the principal electronic non-linear absorptions in the picosecond regime are due to effective third-order processes.

5. Conclusion

We have shown that by transient absorption spectroscopy the picosecond optical electronic non-linearities can be related to the transient excited-state absorptions in the liquid crystal CB15 in its isotropic phase. ESAs have been observed across more than the entire visible spectral range extending from 400 to 1000 nm and can be assigned to singlet–singlet absorptions. The peak absorption occurs at 465 nm and decays quickly with a time constant of approximately 46 ps. The other absorptions are longer lived with nanosecond decays. Excimer absorptions could possibly contribute to the ESAs within the time scale of our experiment. A relatively high fluorescence quantum yield of $20{\cdot}0 \pm 5{\cdot}0\%$ has been reported, and triplet–triplet absorptions are not observed on a 1 ns time scale, indicating an inter-system crossing time much greater than 1 ns. Intensity dependent measurements using the 325 nm pump show that the non-linear absorptions are linear functions of intensity implying that they are due to effective third-order processes. Weak TPA is observed at 650 nm and appears to follow the one-photon ESA spectrum. Furthermore, quantum-chemical calculations using the AM1 Hamiltonian verify that the observed ESAs are likely to be due to absorptions from S_1 into different excited singlet states, and that optical excitations of monomeric units of CB15 can describe the observed spectra to a satisfactory level.

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