

Optical spectroscopy of chiral liquids

The effect of a non-depolarizing anisotropic media on the polarisation of light can be described by the Jones Matrices r in reflection and t in transmission, where

$$r = \begin{pmatrix} \tilde{r}_{pp} & \tilde{r}_{ps} \\ \tilde{r}_{sp} & \tilde{r}_{ss} \end{pmatrix} \quad \text{and} \quad t = \begin{pmatrix} \tilde{t}_{pp} & \tilde{t}_{ps} \\ \tilde{t}_{sp} & \tilde{t}_{ss} \end{pmatrix} .$$

The BIL Picometer measures the quantities x and y . In the standard configuration x and y are functions of the complex quantity r . In terms of the matrix elements of t and the orientation of the polariser (P) and analyser (A) (as measured s direction)

$$t = \frac{t_{pp} + t_{ps} \cot A}{t_{sp} + t_{ss} \cot A}$$

With the configuration $A = 90^\circ$ and $P = 45^\circ$ the measured ellipticity parameters x and y become

$$x = -\frac{2 \operatorname{Re}(t)}{1 + |t|^2}, \quad y = -\frac{2 \operatorname{Im}(t)}{1 + |t|^2} .$$

the minus signs in x and y due to transmission rather than usual reflection geometry.

The optical properties of a chiral material can be expressed in terms of two complex refractive indices $n_{c+} = n_+ + ik_+$ and $n_{c-} = n_- + ik_-$ which describe the response of the material to left-hand and right-hand circularly polarised light. At normal incidence Lekner (Optical properties of isotropic chiral media, Pure and Applied Optics vol 5, 417 (1996)) gives the transmission coefficients of a chiral medium of thickness l as

$$t_{pp} = t_{ss} = c(Z_+ + Z_-),$$

$$t_{ps} = -t_{sp} = ic(Z_+ - Z_-),$$

where the factor c appearing in both equations is the same function of the coefficients t .

$Z_\pm = \exp(iq_\pm d)$, and $q_\pm = n_{c\pm}$, and d is the sample thickness in units of $2\pi l / \lambda$. The \pm signs refer to the propagation of right and left handed waves. Then

$$t = \frac{t_{ps}}{t_{ss}} = i \frac{Z_+ + Z_-}{Z_+ - Z_-} = i \frac{\exp(in_+ d) + \exp(in_- d)}{\exp(in_+ d) - \exp(in_- d)} = \cot\left(\frac{Dqd}{2}\right).$$

Here $Dqd = (n_{c+} - n_{c-})d = (Dn + iDk)d$. Substituting t into the above equations for x and y we find

$$x = -\frac{\sin(Dnd)}{\cosh(Dkd)}, \quad y = -\tanh(Dkd).$$

When both Dnd and Dkd are small we find $x \sim -Dnd$ and $y \sim -Dkd$.

Chemistry notation:

Atkins calls the variation of the angle of polarisation rotation Optical Rotary Dispersion, with $Dq = (n_R - n_L)d = Dnd$, and the difference in absorption intensities Circular Dichroism.

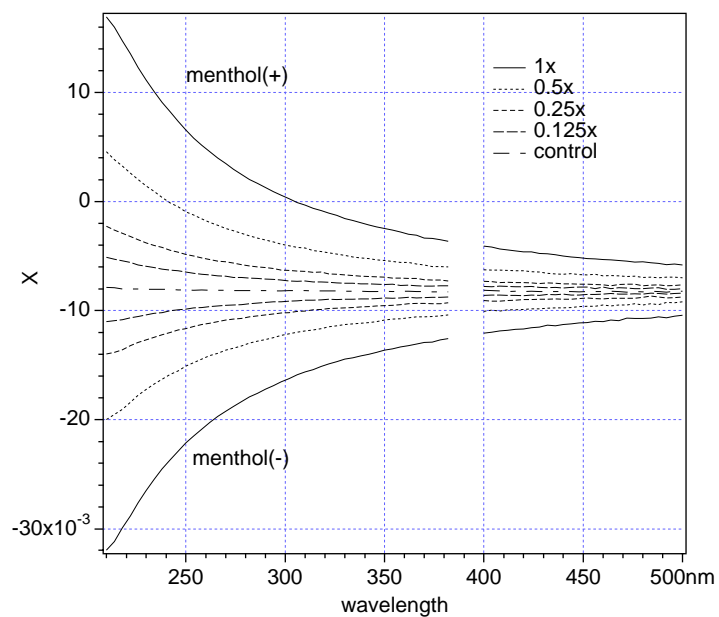
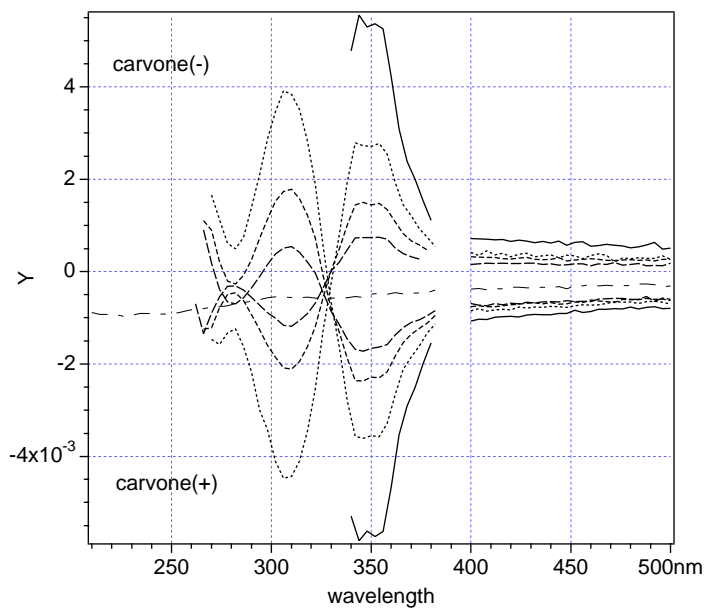
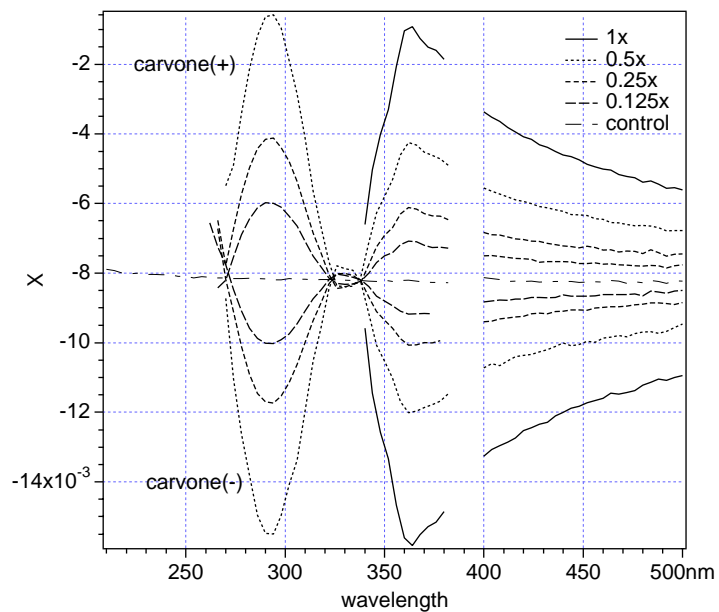
The specific rotation is then Dq/cl , where c is concentration in g/mL and l is the length of the cell in dm. If the change in absorption is small $DA = cl = Dkd$, where c is the concentration in g/mL and l is the path length in dm.

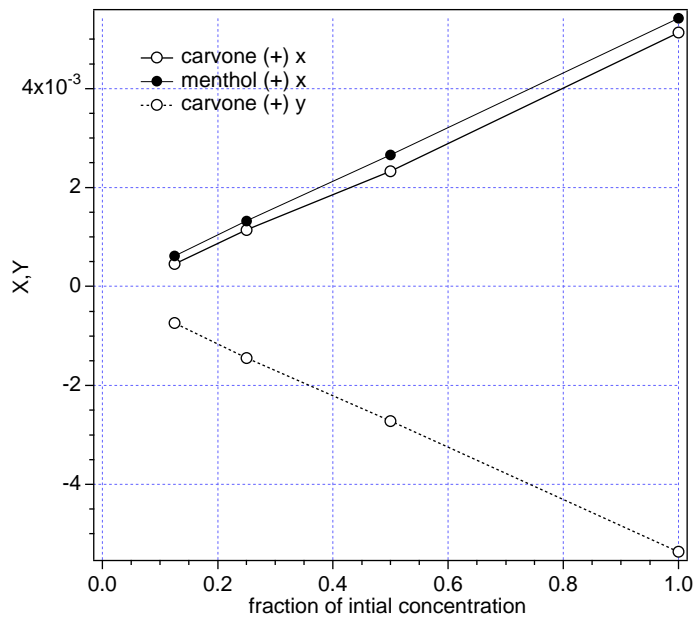
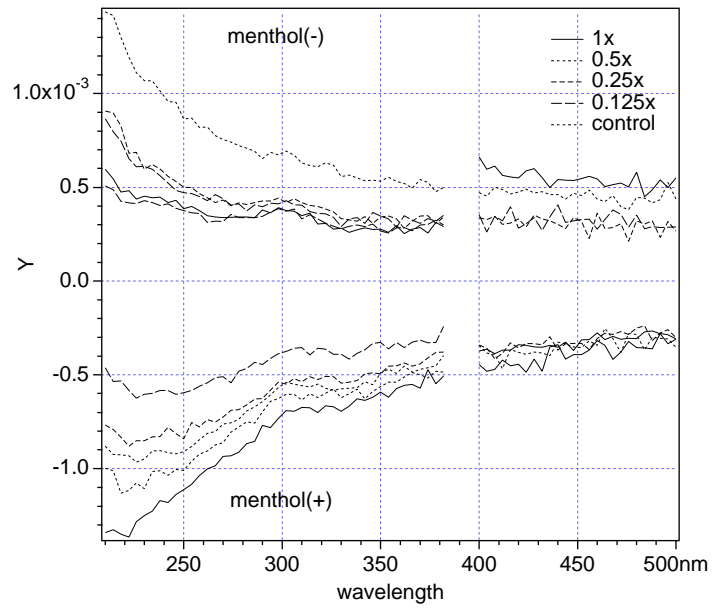
Comments on Data

The signal corresponding to positive values of the ellipsometry quantities x and y are set in the ellipsometer calibration procedure. However signs of the theoretical expressions depend upon angle definitions, rotation definitions etc.

The measurements show that x varies through two positive peaks as a function of decreasing wavelength for both the carvone (+) and menthol(+) solutions, while y initially increases negatively as part of an oscillation with equal amplitudes on either side of zero. Figure 1 has made a simple interpretation of the data, using the simple oscillator model for the absorption and refractive index variation. Two different cases are shown, with different oscillator widths.

The y variation is consistent with two absorption peaks as shown in Figure 1, with that for the - circular polarisation lying at longer wavelengths than the peak for the + polarisation. The cross-over point at 325nm is the point where the k_- absorption equals the k_+ absorption. The x variation is not the same as shown in the chiral model of Figure 1. We need to understand chiral theory better!





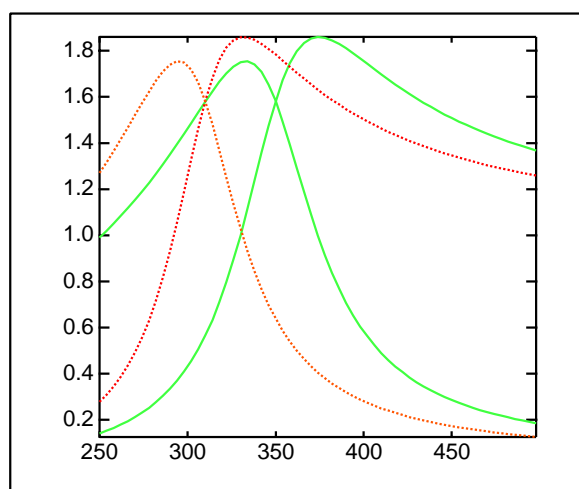
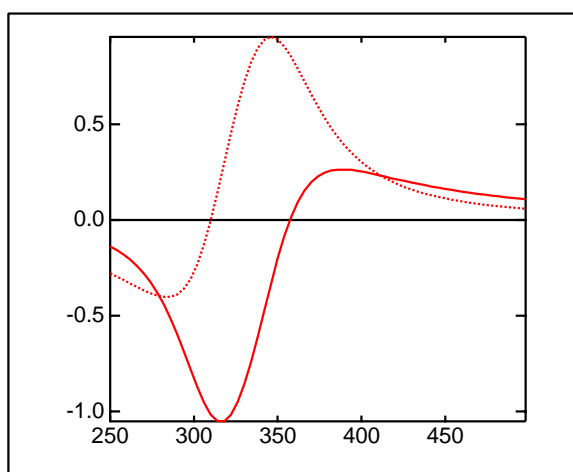
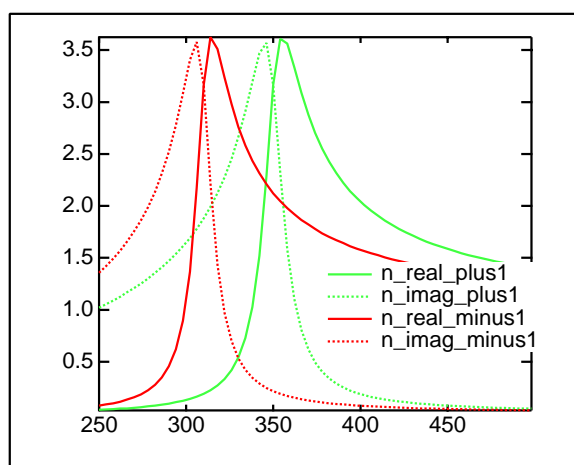
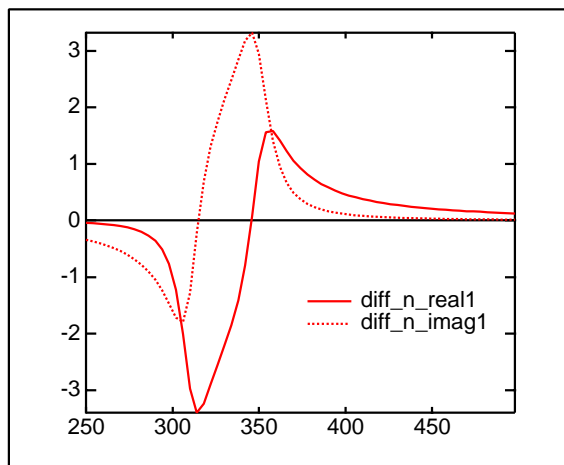
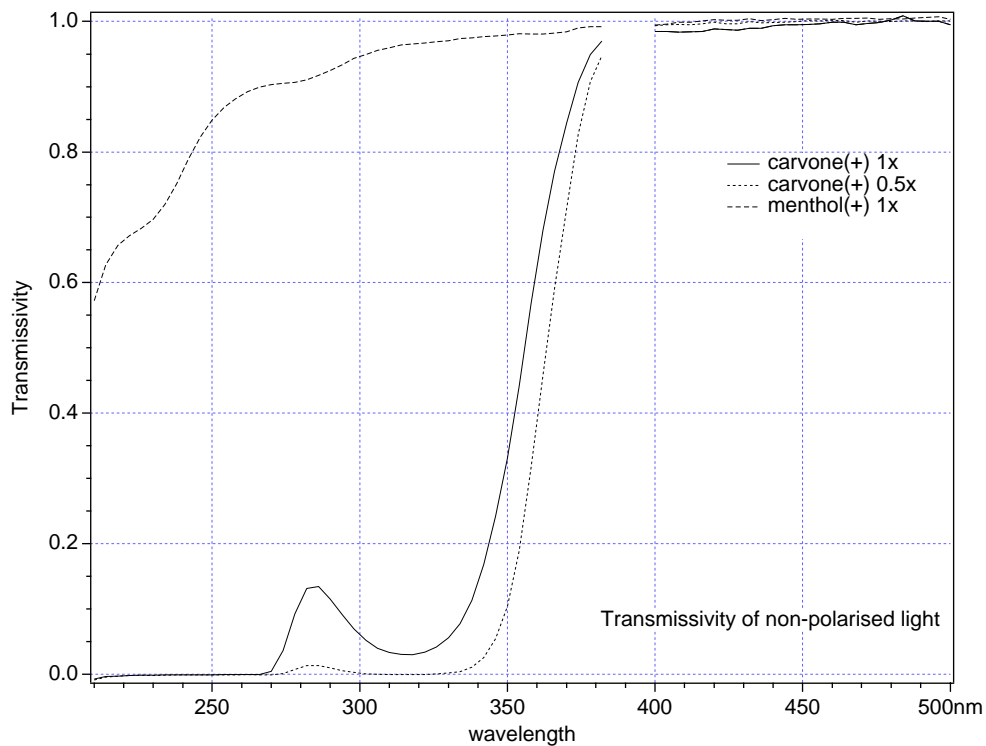


Figure 1: Chiral model with the absorption modeled by + and - Lorentzians, to give the spectral variation of D_n and D_k . Top narrow Lorentzians, bottom wide Lorentzians