Optical Kerr-effect study of trans- and cis-1,2-dichloroethene: liquid-liquid transition or super-Arrhenius relaxation

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The evidence that a molecular liquid in its thermodynamically-stable state can undergo a liquid-liquid transition (LLT) is still uncertain. Therefore, trans-1,2-dichloroethene is of interest due to reports of a LLT above the melting point [S. Kawanishi, et al, J. Phys. Soc. Jpn. 1982, 51, 1579; S. Rzoska, et al, J. Phys.-Condes. Matter 2008, 20, 24142; K. Merkel, et al, J. Chem. Phys. 2008, 129, 074503]. Ultrafast optical Kerr-effect (OKE) spectroscopy enables accurate measurement of the low-frequency modes arising from interactions in liquids and therefore should be sensitive to the change in liquid structure inherent in such a transition. In the OKE data presented here, no sharp transitions are discernible, nor are there any in calorimetry data. However, the same data do reveal that neither trans- or cis-1,2-dichloroethene are simple liquids: a non-Arrhenius temperature dependence (with a Debye lineshape) is observed for the $\alpha$ relaxation. This dependence can be fitted by the Vogel-Fulcher-Tammann (VFT) law over the measurable temperature range suggesting that at low temperature, cooperative relaxation, due to the formation of clusters or structure, is present. OKE measurements are also presented for cis-1,2-dichloroethene showing very similar behaviour. Accurate analysis of the OKE spectrum in the terahertz region is generally limited by approximations inherent in the models. Here the diffusional modes are convoluted with librational modes to give a more physically meaningful approximation to the inertial response.

1. Introduction

It was first suggested by Frank that supercooling can be explained as the frustration of crystallisation through cluster formation.1 Much theoretical work has since suggested that structure is a general property even for simple liquids. The possibility of a (phase) transition between the randomly organised and the structured phases, or between two different structures is therefore a possibility and is naturally of interest as it challenges the widely held view that a liquid can have only a single phase.2 Tanaka and co-workers have proposed that the liquid-liquid transition (LLT) should be a general property of liquids,3,4 and numerical simulations of supercooled water,5,6 carbon,7 silicon,8 gallium,9 nitrogen,10 and simple liquids11 support this view. There is strong experimental evidence for multiple liquid phases in supercooled Y$_2$O$_3$–Al$_2$O$_3$,12 and for single-component liquids, LLTs have been reported for phosphorus,13 AgI,14 nitrogen,15 gallium,16 silicon,17 germanium,18 and bismuth,19 although a number of these transitions are reported to be intramolecular transformations (e.g., polymerisations) as opposed to transformations in the liquid structure.
Temperature-induced transitions in thermodynamically-stable liquids at atmospheric pressure are expected to be exceptionally unlikely, however, LLTs have been reported in a number of single-component organic molecular liquids: acrylonitrile,\textsuperscript{20} α,β-trifluoroacrylonitrile,\textsuperscript{21} methyl acetate,\textsuperscript{22} quinoline and its derivatives,\textsuperscript{23} \textit{trans}-1,2-dichloroethene (tDCE),\textsuperscript{24-27} triphenyl phosphite (TPP),\textsuperscript{28} n-butanol,\textsuperscript{4} TPP-based mixtures,\textsuperscript{29} 2-biphenyl methanol,\textsuperscript{30} and glycerol.\textsuperscript{31} That in TPP is perhaps the best studied and appears to be a transformation from a deeply supercooled state of the normal liquid to a glassy state that has a different structure. The transition occurs on a timescale of hours, the precise nature of the glassy state is not known, and the experimental confirmation of a LLT in a supercooled liquid such as this is made difficult due to the possibility of mixed liquid/microcrystalline states.\textsuperscript{32} In water, a hypothetical LLT in the physically inaccessible phase region, associated with a second critical point and a Widom line, has been postulated to explain anomalous thermodynamic properties,\textsuperscript{5,33} and a fragile to strong transition has been measured in nanoconfined supercooled water.\textsuperscript{34}

The possibility of a LLT in a single component liquid is therefore still controversial, particularly for molecular liquids. For one to occur at atmospheric pressure above the melting temperature would be particularly interesting. For \textit{trans}-1,2-dichloroethene, the suggestion of a liquid-liquid transition was first made following the observation of a weak discontinuity (at \textit{ca.} 257 K) in the temperature dependence of the \textit{T}_1 relaxation time measured by NMR. It was suggested that a quasi-nematic phase arising from interactions of the quadrupole moment was responsible.\textsuperscript{25} More recently, a sharp discontinuity in the mid-infrared absorption spectrum was observed at 247 K.\textsuperscript{26} This behaviour was attributed to “molecular ordering” originating from electrostatic interactions. Contemporary to this, a study of specific heat capacity, x-ray diffraction, and nonlinear dielectric effect spectroscopy also observed, in each case, an anomaly at the same temperature.\textsuperscript{27}

Optical Kerr-effect (OKE) spectroscopy has now been applied effectively to the study of dynamics in the low frequency (up to \textit{ca.} 1000 cm\textsuperscript{-1}) region in a wide range of transparent liquids.\textsuperscript{35-39} It is directly sensitive to the low-frequency modes arising from fluctuations in intermolecular coordination and can therefore distinguish structure as has been demonstrated in studies of weakly interacting liquids,\textsuperscript{40} water,\textsuperscript{41} aromatic molecular liquids,\textsuperscript{42,43} and more complex systems.\textsuperscript{39,44}

Here the OKE spectrum of \textit{trans}-1,2-dichloroethene is measured over a temperature range of 210–300 K. No discontinuities or sharp transitions are apparent, but the structural relaxation becomes super-Arrhenius at low temperature and over this limited temperature range can be described by the Vogel-Fulcher-Tammann (VFT) law. As it has been suggested that the LLT has its origins in liquid-crystal-like ordering through the planar centrosymmetric conformation specific to that of the \textit{trans} conformer,\textsuperscript{25} we have also made OKE measurements on \textit{cis}-1,2-dichloroethene (cDCE) for comparison.

2. Experimental

The OKE setup is essentially standard. A Coherent Mira-SEED Ti:sapphire oscillator provided 8 nJ \textasciitilde 20 fs pulses at a repetition rate of 76 MHz. After pre-compensation for group-velocity dispersion in a homosil prism pair, the beam was split into (90%) pump and (10%) probe beams. A high-speed optical delay line (Newport IMS600LM) in the pump beam path controlled the pump-probe relative delay with sub-fs resolution. The two beams were then co-focused by a 10-cm-focal-length achromatic lens into the sample. The transmitted probe beam was recollimated and then analysed by the combination of an achromatic quarter-wave retarder, Wollaston prism, and balanced photodiode detector which measure the ellipticity of the polarisation of the beam induced by the transient birefringence of the sample (optical-heterodyne detection). The optical material in each beam was equalised in order to match the optical dispersion.
In this setup, where, with balanced detection, the probe intensity is nulled, the principal sources of noise are due to fluctuations that cause transient unbalancing of the detector. Fluctuations in the path of the probe beam are minimised by using beam tubes, but a second stronger noise source was found to be small wavelength fluctuations from the laser, which unbalance the analyser via chromaticity in the quarter-wave plate. These were removed by employing a Fresnel “rhomb” as the quarter-wave retarder. This optic inconveniently introduces a beam displacement, but it is inherently achromatic. In addition, fluctuations and drift in the signal intensity can be significantly reduced by ensuring that the pump and probe beams undergo an equivalent set of reflections before the sample, thus stabilising the overlap of the two beams. To this end, the corner-cube retroreflector employed on the delay stage is matched by a similar optic in the probe beam. To minimise spurious signals from scattered pump light, both pump and probe beams were mechanically chopped at rates of ca. 3 kHz in the ratio of 5:7 with lock-in demodulation at the difference frequency. Chopping the probe beam normally introduces transient out-of-balance signals and to minimise these, and to allow high modulation rates, each chopper was placed at the focus of a 1:1 ($f = 16 \text{ cm}$) telescope.

**Sample purity**

Liquid *trans*-1,2-dichloroethene was supplied by Sigma-Aldrich at a stated purity of >98%. Although we are not aware of any evidence that low levels of impurity influence structural behaviour, this possibility was explored through further purification. Initially, dissolved atmospheric gases were removed through freeze-thaw cycling under vacuum. Infrared absorption analysis then suggested that the principal impurity was the *cis* conformer. To quantify this, a further 1% (vol) of neat *cis*-1,2-dichloroethene (Sigma-Aldrich, >97%) was added to the supplied sample. The FTIR spectrum shows an intense band at 1588 cm$^{-1}$ due to the *cis* conformer (Figure 1). This band increases by a factor of ~3 in the mixture allowing the concentration of the impurity in the supplied sample to be estimated at ~0.5%. There was no trace of the spectrum of either 1,1-dichloroethene or water.

Although the standard method of separation is fractional distillation, the boiling temperatures of the *cis* and *trans* conformers at 333 K and 321 K respectively, suggest that this would be inefficient. There is a rather greater difference in the melting temperatures (193 K and 223 K) and differential crystallisation proved to be a successful approach. Thus, 3 ml of the liquid was frozen thoroughly at 200 K and then placed under vacuum for ca. 15 min. After remelting, this was repeated twice and the spectrum then remeasured (Figure 1). The impurity peak is reduced to a very low level. Without a reference spectrum for the 100% pure liquid it is impossible to quantify, but attempts at further purification made no visible difference. The level of impurity is therefore estimated at less than 0.02%. Other low melting temperature impurities, such as the trace level amylene stabilisers (m.p. ~139 K) present in the supplied liquids, should also be removed by this process.
Figure 1. Infrared absorption analysis of sample purity of trans-1,2-dichloroethene (1 mm pathlength). The spectrum in black is as supplied, red is following the addition of 1% neat cis-1,2-dichloroethene, and green is following purification (note the shoulder at 1580 cm\(^{-1}\) (labelled \(\ast\)) is from \(\text{dDCE}\)).

The sample temperature was maintained to within 0.01 K by a cryostat (Oxford Instruments, Optistat DN). To maintain high sample purity the apparatus was made gas-tight by fusing a 30-cm-long glass tube onto the opening of a 2 mm path length gradient-seal quartz cuvette (Starna Optiglass). This assembly was placed in the cryostat with the tube extending through the top entry port to a gas line. The line was evacuated, and the purified liquid distilled into the cuvette, fractionally distilled in the case of the neat liquids. In addition to further purifying the sample, distillation removes dust particles that otherwise are a source of noise peaks. For the measurements made on cis-1,2-dichloroethene, the samples were distilled only. The apparatus was then sealed to prevent reabsorption of atmospheric gases and the measurements were therefore made at the vapour pressure, \textit{i.e.} along the liquid–vapour coexistence line. The trans-1,2-dichloroethene samples crystallised at \textit{ca.} 205 K \((T_m = 223 \text{ K})\) and the measurements were taken from 210 K to the upper limit of the cryostat at 300 K. Typical cryostat heating and cooling rates were \textit{ca.} 2 K min\(^{-1}\).

At the start of the OKE time-domain scan, 100 points were measured before time-zero to provide an accurate measure of the baseline. Then, through the instantaneous peak and up to a delay of 2 ps, the step size was 5 fs and thereafter logarithmically increased for a further 400 points to give a total scan of 100–200 ps depending on the temperature. For each temperature, typically eight complete scans were averaged. Prior to analysis, the signals were resampled (by linear interpolation) to a linear timescale. The use of an unamplified laser oscillator results in a relatively weak signal in the relaxation but means that the entire signal can be measured in a single scan.

OKE spectroscopy measures the derivative of the polarisability-polarisability time-correlation function in the time domain and is sensitive to the square of the anisotropic part of the many-body polarisability tensor, \(\hat{\Pi}_{xy}\),

\[
S_{\text{OKE}}(\tau) \propto \frac{1}{k_B T} \frac{d}{d\tau} \langle \hat{\Pi}_{xy}(\tau) \hat{\Pi}_{xy}(0) \rangle.
\]  

The deconvoluted spectrum is equivalent to the (Bose-Einstein population-corrected) depolarised Raman spectrum. The slowest components of this spectrum are normally assigned to rotational modes that report on structural relaxation, but trans-
Translational motions may make substantial contributions through the collision-induced spectrum and, where rotations result in only a weak change in the total polarisability, translational modes can dominate the spectrum.\textsuperscript{37,46}

3. Analysis and fitting

Time vs. frequency domain fitting

Where only the low frequency diffusional modes are considered, OKE data are frequently fitted in the time domain. In the time domain, the noise is normally distributed and the difficulties and possible compromises of a numerical Fourier transform are avoided. Alternatively, fitting in the frequency domain allows deconvolution of the signal (correcting for the effects of the finite bandwidth of the laser pulse) and gives valuable insight into the nature of the spectrum.\textsuperscript{47} Here reconvoluted fitting was performed by generating the (complex) fit function in the frequency domain and fitting in the time domain through a numerical Fourier transform. Provided that the bandwidth extends to the highest frequencies generated in the fit-function, no artifacts are introduced and this approach gives the greatest flexibility in the choice of fitting functions. For example, the Cole-Cole function which has no analytical Fourier transform, can be employed and compared to the similar stretched exponential function.\textsuperscript{37,38,48} In the region below a few THz, where broad overlapped bands are encountered, fitting a complete model at once to the entire signal should yield the highest accuracy.

Relaxations

Generally, it is found that the low-frequency spectra of liquids can be analysed through a simple phenomenological model.\textsuperscript{38} The essential features are evident when plotted on a logarithmic frequency scale and these are outlined in Figure 2. At the lowest frequency is the fundamental relaxation representing the decay of correlation over the longest scales of space and time. In OKE spectroscopy, this “α relaxation” is normally reported through single-molecule rotations and can be described generally, as a function of angular frequency, by the Debye function,

\[
S_D(\omega) = A_D/(1 + i\omega \tau),
\]

(2)

which is equivalent to an exponential decay, with time constant $\tau$, in the time domain.

Typically, the α relaxation is accompanied by one or more β relaxations. These are often associated with motions originating from cage-rattling, but without detailed modelling their origins may be unclear. The β relaxation is generally inhomogeneously broadened by the large-scale fluctuations associated with the α relaxation and can often be modelled by the Cole-Cole function\textsuperscript{38}

\[
S_{CC}(\omega) = \frac{A_{CC}}{1 + (i\omega \tau)^\beta}, (0 < \beta < 1).
\]

(3)

where the exponent $\beta$ acts as a broadening parameter. Because the α relaxation imposes an upper limit on the lifetime of the inhomogeneity of the β relaxation (i.e., the components of the β relaxation cannot be slower than the structural α relaxation), the β relaxation is, ideally, terminated such that it never becomes slower than the Debye relaxation.\textsuperscript{38} This leads to the modified Cole-Cole function

\[
S'_{CC}(\omega) = \frac{A_{CC}}{1 + (i\omega \tau + \tau_\alpha/\tau_\alpha)^\beta}.
\]

(4)
The derivative of the stretched exponential \( \exp\left[-\left(t/\tau\right)^\alpha\right] \) gives a similar range of behaviour but is more usually associated with complexity in the \( \alpha \) relaxation mode particularly at temperatures below the melting point.\(^{49}\) Unfortunately, neither the Cole-Cole nor stretched exponential function has an analytical Fourier transform. In studies of supercooled and glass-forming liquids the \( \alpha \) relaxation is widely modelled by the Cole-Davidson function.\(^{50}\) However, it is frequently found that as the glass-transition temperature is approached, this mode resolves into the combination of an \( \alpha \) relaxation and a Cole-Cole \( \beta \) relaxation.\(^{50}\) The simple model described here – of the Debye + Cole-Cole combination, with the former terminating the latter – appears to be capable of reproducing this whole range of behaviour and lends itself to a meaningful physical interpretation. In more complex systems where mesoscopic structure exists, the \( \alpha \) relaxation can be broadened concomitant with the appearance of a sub-\( \alpha \) mode.\(^{39}\) Relaxational modes are generally characterised by their temperature dependence, which in simple cases is Arrhenius while non-Arrhenius behaviour generally appears in the supercooled region where single-molecule relaxation gives way to cooperative behaviour.\(^{49}\)

![Figure 2. Simple model for molecular liquids shown in the frequency domain. The fundamental structural \( \alpha \) relaxation (eqn (2)) at low frequency is accompanied by an unresolved \( \beta \) relaxation \( \beta \) (eqn (3)). At higher frequencies, additional processes including librations and low-frequency intramolecular modes libr+ (eqn (5) or eqn (6) occur. The effect of inertial rise modifications and \( \alpha \) termination (see text) can be seen by comparison with the unmodified functions (dotted).](image)

**Librations**

At frequencies above the relaxational modes, the spectra of liquids at room temperature are generally continuous up to the librational region, which typically occurs at 1–3 THz (Figure 2). Librational modes arise from single molecule, cage-constrained, rocking and translational motions that, unlike the \( \beta \) relaxation, are essentially temperature-independent. This part of the spectrum presents the greatest challenge to a simple analysis due typically to the presence of multiple broad overlapped modes, but this reflects the indistinct nature of the motions, which are to some extent concerted and thus introduce cross-terms. This complexity is beyond a simple analysis. A more comprehensive model should be provided by mode-coupling theory, which has been successful in the analysis of the relaxational modes of supercooled and glass-forming liquids, but no practical method of applying it to the behaviour presented here is yet available. Therefore, in general, the librational modes are fitted by either the Brownian (damped harmonic) oscillator
\[ S_n(\omega) = \frac{A_n\omega_0^2}{\omega_0^2 - \omega^2 - i\gamma}, \]  

(5)

or the Gaussian oscillator,\(^{35}\) which is usually defined as,

\[ \text{Im}[S_n(\omega)] = A_n \exp\left(-\frac{(\omega - \omega_0)^2}{\gamma^2}\right) - A_n \exp\left(-\frac{(\omega + \omega_0)^2}{\gamma^2}\right), \]  

(6)

where, in each case, \(\omega_0\) is the undamped resonance (angular) frequency, and \(\gamma\) is the damping rate.

**Inertial rise**

It is well known that as models of relaxation, the Debye and its variants are unphysical in that they assume an instantaneous rise of the response in the time domain.\(^{31,52}\) The rotational diffusion mode represents the decay to equilibrium from a partial alignment of the polarisability tensors due to the incident (pump) field. In the OKE experiment, this interaction creates an instantaneous change in the angular velocity of the particles, rather than their position (as implied by the derivative in eqn (1)). The position (orientation) cannot change instantaneously due to the inertia of the particle. The result is an inertial rise form and the Debye function must be modified to take this into account (when the contribution of the fast dynamics is considered). As free rotation does not normally take place, the alignment process occurs on the timescale of the cage-constrained librational (rocking) motions.

In previous OKE and related studies, an exponential prefactor, \(1 - \exp(-k_{RT}t)\) or equivalent, has been employed as a correction in the time-domain\(^{47,52,53}\) or more complex models have been sought.\(^{54}\) The rise rate, \(k_{RT}\), is associated with the first moment or the mean of the librational rise times, \(e.g., \) similar to \(\pi/\langle \tau_L \rangle\) where \(\tau_L\) is the librational period. We showed previously how this modification can be generalised for the Havriliak-Negami function.\(^{38}\)

Often this approximation is satisfactory and the value of \(k_{RT}\) appears uncritical because inaccuracies can be concealed by latitude in the amplitude and shape of the librational modes themselves. However, we found recently that for simple liquids\(^{48}\) the exponential prefactor could not provide an accurate inertial rise profile for the collision-induced spectrum, and instead substituted a Gaussian inertial rise form, \(1 - \exp(-k^2_{RT}t^2)\).

This arbitrariness is unsatisfactory. A more complete approach would allow the diffusional mode to rise as the envelope of the librational mode(s) and this can be achieved by generating the mode through a convolution of the relaxational function with the librational function(s), \(i.e., D(t) \propto (D \otimes L)(t)\). If the fit function originates in the frequency domain, the convolution is simply a product of the two functions. This approach is perhaps more physically meaningful, and eliminates the parameter \(k_{RT}\). It does not, however, solve the problem of knowing through which librational modes the relaxation arises, but this is simply an inevitable reflection of the complexity of behaviour of the liquid.

The difficulty of defining the inertial rise response is often avoided by considering only the final relaxation, but, as inspection of the frequency domain spectrum normally shows (\(e.g., \) Figure 3), above the melting point spectra are continuous with relaxational modes extensively overlapped with the librational region. The accuracy of the analysis is therefore likely to be highest when the entire spectrum (or time-domain signal) is fit at once. This final convolution approach is used to fit the data presented here and since for these liquids there is a single dominant librational mode, the process is straightforward.
4. Results and discussion

The trans-1,2-dichloroethene molecule is rigid, planar, and centrosymmetric. It has C\textsubscript{2h} symmetry and is to a good approximation a prolate symmetric top.\textsuperscript{35} With no intramolecular rotational modes, a rather simple spectrum is therefore expected. OKE measurements are shown in Figure 3. In the time domain, the instantaneous hyperpolarisability response reflects the autocorrelation of the laser pulse. After \textit{ca.} 20 fs, a librational response is visible accompanied by a much higher-frequency underdamped intramolecular vibration. These modes then evolve into the final diffusional decay. In the frequency domain, the lowest frequency mode can be seen to be Debye-like and this appears to extend smoothly into the librational region.

![Figure 3. OKE measurements for tDCE in the time domain showing, on logarithmic axes, five sets of data measured at 210, 230, 250, 270, and 300 K. The instrument response (autocorrelation) is also shown (dashed). The inset shows the signals at the lowest and highest temperatures in the frequency domain.](image)

As expected, these data can be fit with a relatively simple empirical model. Figure 4 shows the fit in the frequency domain at 220 K. Peaking at \textit{ca.} 0.01 THz is the $\alpha$ relaxation fitted by a Debye function. This is accompanied by a secondary ($\beta$) relaxation, which is fitted by a Cole-Cole function broadened by an exponent of \textit{ca.} 0.7. The $\beta$ relaxation is terminated by the $\alpha$ relaxation mode, while both modes have the inertial rise modification by convolution with the dominant librational mode that appears just above 1 THz and which has a Gaussian lineshape. A second weaker libration is present at 3 THz. This and the intramolecular vibration at 10.5 THz are modelled as Brownian oscillators (eqn (5)).

Whereas the Brownian oscillator\textsuperscript{56} is derived from the model of an oscillator frictionally-damped by a thermal bath, the Gaussian function implies an inhomogeneous lineshape, as appears in the Lynden-Steele model through the distribution of librational frequencies in the cage model,\textsuperscript{57} and often appears to be a better model of the principle librational mode\textsuperscript{39,43,53,58} as is the case here. OKE cannot distinguish homogeneous from inhomogeneous broadening, and the two functions are generally used as empirical models. Higher order spectroscopies could ideally make this distinction, but currently provide much poorer signal-to-noise ratios.
Figure 4. Deconvoluted frequency domain spectrum measured for trans-1,2-dichloroethene at 220 K ($T_m = 223$ K). The fit is also shown (but is almost indistinguishable from the data) and is decomposed into the Debye function (D) at lowest frequency, accompanied by a secondary (Cole-Cole) relaxation (CC). Above 1 THz is the overdamped Gaussian librational mode (G), and a secondary libration or overdamped vibration B1. A weak mode at $\sim$7.1 THz is not visible on this scale. Inset is detail of the librational region showing the difference in the lineshape (purple shaded region) between the Cole-Cole function modified by the inertial rise function (solid purple line), and the unmodified Cole-Cole (dashed purple line). The modification to the Debye function is less pronounced.

The data are fit in the time domain as shown in Figure 5.

Figure 5. The fit to the data for tDCE at 220 K shown on logarithmic axes in the time domain. The data are indistinguishable from the fit except where the noise is apparent after 50 ps. The principal components of the fit are shown: the instrument cross-correlation (dashed), the Gaussian mode (G), the Debye $\alpha$ relaxation (D), and the Cole-Cole function (CC). The latter two are modified by the inertial rise function and the Cole-Cole is terminated by the Debye. The residuals of the fit are shown above.

Selected fit parameters for the temperature range studied are given in Table 1. Because of the large degree of overlap, the lineshape of the (nominally Cole-Cole) $\beta$ relaxation mode is determined primarily by the two modifications: the $\alpha$ termination
and the inertial rise form. The parameters of the Cole-Cole function therefore are not very meaningful and therefore the first moment of the fitted function and its integral (in the imaginary spectrum) are given. Normally, the Gaussian lineshape (eqn (6)) is determined by the two parameters, $\omega_0$, the undamped resonance frequency, and $\gamma$, the damping rate. However, for $\omega_0 < \gamma$, the function is in the overdamped limit where (on a log frequency scale) the lineshape effectively becomes independent of both $\omega_0$ and $\gamma$. The frequency of the mode maximum is then equal to $\gamma$, and the amplitude becomes linearly dependent on $\omega_0$. This is the case here, and therefore $\omega_0$ was fixed at an arbitrary low frequency ($\omega_0 = 1$). The mode is then defined by just two parameters: $\gamma$ and $A'_c = A_c \omega_0$. Although this fit reproduces the data very well, the spectrum in this region, as is usually the case, is composed of multiple overlapping bands. This naturally introduces a great deal of uncertainty in the parameters for the modes around 1 THz. Multiple measurements were made on separately prepared samples to minimise the effects of any systematic errors.

As it has been suggested that the LLT is specific to the trans conformer of dichloroethene and is associated with liquid-crystal-like ordering, measurements were also made on cis-1,2-dichloroethene for comparison. Despite the very different symmetry and presence in the latter of a permanent dipole of 1.9 D,59 the intermolecular contributions to the OKE spectrum are very similar. The fit for cis-1,2-dichloroethene is shown in the frequency domain in Figure 6. The $\alpha$ relaxation here has a weaker intensity and decays $\sim$33% faster than in trans-1,2-dichloroethene at the same temperature. Below ca. 200 K this simple fit starts to fail due to the $\alpha$ relaxation mode broadening as is commonly observed in supercooled liquids.49 A stretched exponential is then an improvement, but the difference is relatively small and for easier comparison of the parameters the Debye fit is retained. In the librational region the spectrum is even less well defined than that of trans-1,2-dichloroethene and the parameters are presented for only the $\alpha$ relaxation.

Figure 6. Deconvoluted frequency domain spectrum measured for cis-1,2-dichloroethene at 210 K. The fit is also shown (orange) and is decomposed into the Debye function at lowest frequency, accompanied by a secondary (Cole-Cole) relaxation, the predominant (Gaussian) librational mode (shaded) and above 1 THz a pair of librational modes. The aliasing referred to in the text can be seen as an oscillation in the data, extending up to $\sim$2 THz.
Table 1. Parameters for the fit for trans-1,2-dichloroethene from 210 K to 300 K at 10 K intervals.

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<td>10^4 A B1 (a.u.)</td>
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<td>2.7</td>
<td>3.0</td>
<td>3.2</td>
<td>3.3</td>
<td>3.5</td>
<td>3.9</td>
<td>4.1</td>
<td>4.2</td>
<td>4.3</td>
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<tr>
<td>ω B1/2π (THz)</td>
<td>3.52</td>
<td>3.46</td>
<td>3.40</td>
<td>3.38</td>
<td>3.36</td>
<td>3.31</td>
<td>3.25</td>
<td>3.22</td>
<td>3.23</td>
<td>3.21</td>
</tr>
<tr>
<td>γ B1/2π (THz)</td>
<td>2.4</td>
<td>2.7</td>
<td>3.0</td>
<td>3.2</td>
<td>3.3</td>
<td>3.5</td>
<td>3.9</td>
<td>4.1</td>
<td>4.1</td>
<td>4.2</td>
</tr>
<tr>
<td>ω B2/2π (THz)</td>
<td>10.49</td>
<td>10.50</td>
<td>10.49</td>
<td>10.49</td>
<td>10.49</td>
<td>10.48</td>
<td>10.48</td>
<td>10.48</td>
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<td>10.47</td>
</tr>
<tr>
<td>γ B2/2π (THz)</td>
<td>0.19</td>
<td>0.19</td>
<td>0.21</td>
<td>0.22</td>
<td>0.23</td>
<td>0.25</td>
<td>0.27</td>
<td>0.29</td>
<td>0.28</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Notes: (1) A(D) is the amplitude of the α relaxation mode, where this has been scaled to represent a simple Debye fit to the spectrum. (2) A CC is the integral of the Cole-Cole (β) relaxation. (3) ω CC is the 1st moment of the Cole-Cole (β) relaxation. G refers to the Gaussian mode and B1 are the Brownian oscillators for which critical damping occurs for γ/2 = ω0. A weak mode at 7.1 THz (237 cm⁻¹), (γ = 0.7, A ≈ 10⁻⁴) is temperature independent within the experimental precision. This and the higher frequency modes that can be observed at 22.8 THz (761 cm⁻¹) and 25.4 THz (847 cm⁻¹) have been assigned previously. The increasing step size above 2 ps introduces aliasing so the parameters for B1 and B2 were determined by optimising the fit in the range ~50 fs to 2 ps. Estimations (joint confidence interval) of the uncertainty in the fit parameters appear too small so the precision in the values relates, very approximately, to their scatter.

Table 2. Parameters for the α relaxation of cis-1,2-dichloroethene from 170 K to 280 K.

<table>
<thead>
<tr>
<th>T /K</th>
<th>τ D /ps</th>
<th>A D (a.u.)</th>
<th>T /K</th>
<th>τ D /ps</th>
<th>A D (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>170</td>
<td>34</td>
<td>0.081</td>
<td>230</td>
<td>6.9</td>
<td>0.053</td>
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<tr>
<td>180</td>
<td>24</td>
<td>0.074</td>
<td>240</td>
<td>5.7</td>
<td>0.051</td>
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<tr>
<td>190</td>
<td>17</td>
<td>0.071</td>
<td>250</td>
<td>4.9</td>
<td>0.047</td>
</tr>
<tr>
<td>200</td>
<td>13</td>
<td>0.064</td>
<td>260</td>
<td>4.2</td>
<td>0.046</td>
</tr>
<tr>
<td>210</td>
<td>11</td>
<td>0.060</td>
<td>270</td>
<td>3.7</td>
<td>0.044</td>
</tr>
<tr>
<td>220</td>
<td>8.5</td>
<td>0.057</td>
<td>280</td>
<td>3.3</td>
<td>0.042</td>
</tr>
</tbody>
</table>

Figure 7 shows the parameters that appear to be temperature dependent. The fits are normalised to the integral of the instantaneous signal (i.e., to the bulk polarisability), so are corrected for trivial changes such as drift in laser intensity, pulse duration, and the change of density with temperature. The intensity of the α relaxation mode falls almost linearly with temperature and this might imply an increase in molecular ordering that would allow collective polarisation enhancement, however similar trends are seen in many other liquids and their origins are obscure. Although the Gaussian librational mode also weakens, the intensity of both the Cole-Cole function and B1 increase with temperature. The frequency of the Gaussian mode...
(indicated by $\gamma$) and that of $B_1$ falls with temperature, consistent with a weakening of structure of the solvent cage, while the damping of the C–Cl bending mode, $B_3$, increases, suggesting that inhomogeneous broadening is the dominant effect here.

Figure 7. Temperature dependence of the fit parameters for tDCE. The notation follows Table 1.

The data shown in Table 1 and Figure 7 refer to the purified trans-1,2-dichloroethene samples. However, neither the sample as received nor the sample with 1.5% cis impurity (which was measured without further purification) resulted in any measurable change in behaviour.

Qualitative analysis of the temperature dependence of the librational band can be made if the diffusional modes are subtracted. Figure 8 compares this “reduced” spectrum at five temperatures along with that of the cis conformer at the lowest of these temperatures. To do this accurately, the entire signal was first fitted in the time domain and the $\alpha$ relaxation (Debye function with the inertial rise modification) was then subtracted. The resultant (baseline) signal was then cropped to $\sim 25$ ps to remove noise, then zero-padded by a factor of four. The numerical Fourier transform was then calculated and deconvoluted from the fitted autocorrelation function. The increasing step size above 2 ps normally introduces aliasing (visible in the residuals in Figure 5). Increasing the step size logarithmically helps by spreading the resulting artefacts across the spectrum but there is still a visible ripple in the spectrum of Figure 6. This becomes pronounced in the reduced spectrum, and being influenced by temperature, masks the true temperature dependence. To eliminate this problem, the data in Figure 8 were measured by jittered stepping; a method of time-interleaved sampling that will be described in a future publication.
Figure 8. Spectra for tDCE at five temperatures and cDCE at 210 K after subtraction of the fitted α relaxation Debye function.

The reduced spectra for trans-1,2-dichloroethene confirm the very weak temperature dependence of these modes, showing that, surprisingly, additional diffusive modes, such as the translations that would appear through the collision-induced spectrum, are not observable or have only a weak temperature dependence. The complexity of this region prevents more accurate analysis due to parameter intercorrelation that is evident in the fit. However, with increasing temperature, the peak of this band falls from ca. 0.95 THz at 210 K to ca. 0.73 THz at 290 K. This is due to the blue shift of the Cole-Cole function combined with the slight red shift of the Gaussian librational mode as seen in Table 1.

The temperature dependence of the Debye time constants of the α relaxation for the trans and cis conformers is shown on an Arrhenius plot in Figure 9. There is no evidence of any discontinuity but in each case the data cannot be fit by the Arrhenius function with a single activation energy, even in the temperature range above $T_m$. Fitting to the higher temperature region, it is apparent that the relaxation becomes super-Arrhenius at low temperature. In OKE studies the appropriate form of the Arrhenius expression is

$$\tau_c(T) = \frac{A}{T} \exp\left(\frac{E_a}{k_B T}\right)$$

and fitting to the high temperature region yields very similar activation energies of 6.0 kJ mol$^{-1}$ for trans and 5.8 kJ mol$^{-1}$ for cis. These values are between the values for end-over-end rotation (8.1 kJ mol$^{-1}$) and $c_2$ axis rotation (3.5 kJ mol$^{-1}$) calculated for trans-1,2-dichloroethene from infrared vibrational bandwidths. In studies of glass-forming liquids, super-Arrhenius relaxation rates are commonly observed and are associated with relaxation over increasing length scales in the supercooled region where the formation of Fisher clusters or similar structure is expected. In such studies it is generally found that the temperature dependence can be modelled by the Vogel-Fulcher-Tammann (VFT) expression, which for the OKE response can be written,

$$\tau = \frac{\tau_0}{T} \exp\left(\frac{D T_o}{T - T_o}\right)$$

Although in glass-forming liquids this expression is typically applied to relaxation below a crossover temperature similar to $T_m$, here, perhaps due to the limited degree of supercooling, it describes the data very well over the entire measured temperature range. For trans-1,2-dichloroethene, $T_0 = 70$ K, and for cis-1,2-dichloroethene, $T_0 = 54$ K although these values are very approximate due to the very limited extent of supercooling, particularly for trans-1,2-dichloroethene. In glass-forming liquids, $T_0$ is generally much higher, typically ca. 50 K above the glass transition temperature. Over this limited range, of less than a decade in $T$, detailed interpretation of the VFT expression would be of doubtful validity. The important observation is
that the relaxation time constant changes smoothly and becomes super-Arrhenius before the melting temperature is reached implying an increasing length scale, \textit{i.e.}, cooperativity in the relaxation.

Figure 9. Arrhenius plot of the time constant of the \( \alpha \) relaxation for \( t \text{DCE} \) and \( c \text{DCE} \). The two dotted lines are Arrhenius fits to the data at high temperature. The solid red curve is the fit of the VFT law, eqn.(7).

In the Debye-Stokes-Einstein model, the single molecule rotational relaxation time constant for a simple (prolate or oblate) particle is related to the shear viscosity by

\[
\tau_0 = \frac{V_{\text{eff}}}{k_B T} + \tau^0,
\]

where \( \tau^0 \) is the zero viscosity intercept. The viscosity of trans-1,2-dichloroethene was measured over the accessible range of \(-10^\circ\text{C} \text{ to } 30^\circ\text{C} \) (using a Cambridge Viscosity, Viscolab 3000) and over this very limited range was found to be Arrhenius with an activation energy of \( E_A = 0.13 \text{ kJ mol}^{-1} \).

Despite its simplicity, the DSE expression has been shown to be good for a very wide range of liquids. Here the measured single-exponential OKE relaxation suggests that trans-1,2-dichloroethene behaves as a simple (oblate) ellipsoid. OKE measures \( \tau_c \), the collective rotational Debye time-constant, and this is related to single molecule rotation \( \tau_r \) through

\[
\tau_c = g_2 \tau_r / j_2
\]

where \( g_2 \) is introduced as a static pair correlation term and \( j_2 \) is a dynamic angular momentum correlation term. For simple liquids \( g_2 \) and \( j_2 \) are normally close to unity, in which case eqn (8) allows the effective volume of the rotationally relaxing particle to be estimated. In Figure 10, the line fit returns an effective volume of \( 24.4 \pm 0.4 \text{ Å}^3 \), and \( \tau^0 = 1.47 \pm 0.05 \text{ ps} \). This value is low compared to a molar volume of \( 128 \text{ Å}^3 \) calculated from a density of \( 1.257 \text{ g cm}^{-3} \) at \( 25^\circ\text{C} \), but might itself imply fractional Stokes-Einstein behaviour as results from Fischer-cluster induced structure in supercooled liquids.
Figure 10. Agreement with the Debye-Stokes-Einstein dependence eqn (8), of the $\alpha$ relaxation time-constant (obtained from the VFT fit) and the viscosity.

Reported calorimetry measurements suggest that the LLT appears as a peak in the specific heat capacity. To investigate this we made similar measurements using a Perkin-Elmer Diamond differential scanning calorimeter (DSC). Samples of trans-1,2-dichloroethene were measured both as received, after freeze-thaw degassing, and after purification. The temperature scan rate was varied between 10 and 100 K min$^{-1}$. Normal crystallisation (around 200 K, depending on the sample) and melting (224 K) peaks were measured, but no trace of any additional transitions could be observed. Figure 11 shows typical DSC data with three cooling runs in which only typical non-reproducible artefacts appear above crystallisation. Additional measurements were carried with ca. 30 min holds at a series of constant temperatures following cooling from 280 K to check for the presence of a slow transition, but none was measurable.

Figure 11. Calorimetry (DSC) data for trans-1,2-dichloroethene showing the absence of phase transitions above the melting temperature. Above (black) is a typical heating and cooling trace at 20 K min$^{-1}$ showing both the crystallisation and melting transitions. Below are three cooling traces with the heat flow scale expanded until the normal baseline noise is visible.
5. Conclusions

The OKE response derives from the low frequency rotations, translations, and vibrations that are characteristic of and determined by molecular interactions. It would be surprising then if the OKE spectrum was not sensitive to a liquid-liquid transition that implied a change in structure of the liquid as suggested previously. However, in the OKE data presented here, there is no visible discontinuity in the temperature dependence of the \( \tau_\alpha \) relaxation time constant. There is a deviation from simple Arrhenius behaviour, but for these data it is more reasonable to treat the dependence as continuous as shown by the agreement with the Vogel-Fulcher-Tammann law. Two possible conclusions naturally arise from this observation – either \textit{trans}-1,2-dichloroethene undergoes no LLT in this temperature range, or the LLT has no discernable influence on \( \tau_\alpha \). However, it would be surprising if a change in structure had no influence on the rate of rotational relaxation. The NMR studies that originally reported the LLT also measured rotational relaxation as \( T_1 \), however the magnitude of the transition was comparable to the scatter in the data. The absence of a thermodynamic transition would seem to be confirmed by our DSC measurements. There are nonlinearities in the temperature dependences of the parameters for the OKE fits as shown in Figure 7, but these are comparable in magnitude to the significant scatter that arises from the relatively weak signal measured in \textit{trans}-1,2-dichloroethene, and the large degree of mode overlap, and no consistent transition is apparent in the different parameters.

The absence of sharp temperature-induced changes in the OKE spectra does not disprove the LLT, but it shows that the structural change does not influence the intermolecular spectrum. Even exploring the possibility that the time scale of the LLT is very slow has not yielded clear evidence. However, as these liquids are heated or cooled heterogeneities appear that introduce some light scattering. These can also be observed in other simple liquids. Whether these are simply due to temperature (and consequent density) gradients induced by the temperature changes, or are evidence of structural heterogeneities, will be the subject of a subsequent study.

The super-Arrhenius temperature dependence of \( \tau_\alpha \) and the relatively large range of facile supercooling does suggest that both \textit{trans}- and \textit{cis}-1,2-dichloroethene should not be described as simple liquids, and is also consistent with the presence of locally-preferred structure and hence frustrated crystallisation such as is found for water, as well as in liquids that associate through \( \pi \) bonds such as benzene.

6. Acknowledgements

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