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Time-resolved optical Kerr effect experiments on supercooled benzene and test of mode-coupling theory

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ABSTRACT

We have performed time-resolved optical Kerr effect experiments with heterodyne detection on benzene. We succeeded in supercooling benzene by 21 K below the melting point $T_m = 279$ K, and we investigated the full range of existence from the supercooled phase up to the boiling point $T_b = 353$ K. Our time-resolved data show clearly the complex relaxation pattern of benzene that is characterized by different time scales. These dynamic features, common to many other molecular liquids, to date have not been addressed and there is not a unique theoretical model able to explain them, even in a simple molecular liquid such as benzene. We compare our data with the predictions of a schematic mode-coupling model, fitting the experimental relaxations with a numerical solution of the time-dependent correlation functions. Although the temperature range investigated is clearly outside the asymptotic scaling regime, we found the mode-coupling model able to describe properly the measured dynamics in large time and temperature ranges.

§1. INTRODUCTION

The dynamics of both simple and less simple molecular liquids show several common characteristics. These recurrent features suggest a possible 'universal' scenario characterizing the structure and dynamics of these liquids (Loughnane *et al.* 1999). The experimental spectra, or decays, demonstrate the presence of three main time scales. A *fast time scale* (typically up to 10^{-12} s) where the driving processes are the intramolecular vibrations; the intermolecular dynamics on this time scale also have a vibrational character. In fact, on the short time scale the molecules are vibrating around their equilibrium position since it should be a valid approximation to take the liquid structure as static. On the *intermediate time scale* (few picoseconds) the liquid structure cannot be taken as static since the diffusion processes start to be

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effective, producing a structural redefinition. On this time scale the intermolecular vibrations couple strongly with the structural relaxation rearrangement. Finally, on the *slow time scale* (that can vary from 10^{-11} to 10^{-9} s, depending on the liquid viscosity), the leading effect is the structural relaxation.

This dynamic scenario still lacks a comprehensive physical model and even single processes are not elucidated in many aspects. Therefore condensed-matter researchers still accord much attention to this problem from either an experimental or a theoretical point of view.

There is quite a large literature about the physics of molecular liquids (Berne and Pecora 1976, Rothschild 1984, Wang 1985) where the dynamics have been described through different models.

However, according to a simplified scheme where we do not include a model based on computer calculation, the dynamic theoretical models can be addressed along three main lines.

(i) Several physicists are working on generalized hydrodynamics models (GHMs) with the aim of giving a more comprehensive picture of relatively slow molecular liquid dynamics. The interest in this theoretical research has recently been renewed by studies on supercooled and glass-former liquid dynamics (Franosch *et al.* 2001, 2003, Pick *et al.* 2003). The GHMs are powerful models that normally describe properly the slow dynamics but hardly reproduce the faster dynamics. Furthermore they retain only some of the principal molecular aspects.

(ii) A series of different approaches focused on the liquid local properties, which we shall here call the local vibrational models (LVMs), have been used with the aim of identifying the vibrational and diffusive processes present in the relatively fast dynamics. The LVMs are a natural progression of the long-standing problem of cage structures in molecular liquids (Mukamel 1995, Polimeno and Freed 1995, Moro and Polimeno 1997). These models are able to address some of the molecular aspects present in the dynamics but they introduce a strong hypothesis about the interaction of the diffusive and intermolecular processes.

(iii) A different approach has been introduced to describe the dynamics of supercooled liquids: the mode-coupling theory (MCT) (Götze and Sjögren 1992, Götze 1999). These models, based on memory function methods, have been able to reproduce the relaxation properties in a large time window, from the fast to the slow time scale. Furthermore the asymptotic solutions of the MCT are able to predict several critical properties of the supercooled phase of glass formers. Recently, the MCT has been proved to also be a valid model for the liquid phase (over the melting point) of glass formers (Torre *et al.* 2000, Prevosto *et al.* 2002, Ricci *et al.* 2002). So potentially the MCT could give a valuable interpretation of simple molecular liquids (non-glass-forming liquids) (Wiebel and Wuttke 2002) overcoming some of the limitations intrinsic to the GHMs and LVMs.

In this work we present the study of the relaxation processes in a simple molecular liquid, benzene, by time-resolved optical spectroscopy and we investigate the MCT interpretation of the dynamic features of this liquid. We have chosen benzene, consisting of perfectly symmetric molecules, as a particularly simple and meaningful example. The time-resolved optical Kerr effect (OKE) data on benzene

are obtained in the full accessible temperature range from the supercooled state (we succeeded in supercooling benzene by about 20 K below the melting point $T_m = 279$ K) up to the boiling point $T_b = 353$ K. The experimental results have been compared with the F_{12} two-component schematic MCT model (Götze and Voigtmann 2000).

§2. Experiments and results

The time-resolved OKE spectroscopy measures the birefringence relaxation of the system directly in the time domain. The excitation pulse creates an optical anisotropy in the sample. The decay of the induced anisotropy is monitored with an additional probe pulse, delayed optically. In a heterodyne-detected optical Kerr effect (HD-OKE) experiment, the signal is given by the convolution of the second-order pulse intensity autocorrelation $G^{(2)}(t)$ with the material response function $R(t)$, according to

$$S(\tau) = \int G^{(2)}(t) R(t - \tau) \, dt, \qquad (1)$$

$$R(t) \propto -\frac{\partial}{\partial t} \phi(q, t), \qquad (2)$$

with

$$\phi(q, t) = \frac{\langle \varepsilon_{xy}(q, t) \varepsilon_{xy}(-q, 0) \rangle}{\langle |\varepsilon_{xy}(q, 0)|^2 \rangle},$$

where $\phi(q, t)$ is the correlation function of the dielectric constant. Note that, in an OKE experiment, the excited anisotropy is characterized by a zero wave vector, so that we must consider $q \approx 0$ in equation (2).

The present study is performed with the experimental equipment and laser system that has been described in detail elsewhere (Bartolini *et al.* 1999). With respect to the experimental procedure reported by Bartolini *et al.* (1999), we have introduced an experimental improvement that allows us to measure the long-time part of the relaxation process (Prevosto *et al.* 2002, Ricci *et al.* 2002). The fast relaxation part (0–2 ps) is measured with an ultrafast laser pulse of about 60 fs. In the temporal region from 2 ps to the end of the decay, the OKE experiment is performed with stretched pulses of about 400 fs, which allows us to transfer a larger quantity of energy to the system without increasing the instantaneous intensity of the pulse. This larger quantity of energy is then released in the signal detected, which is characterized by a better signal-to-noise ratio.

Benzene ($T_m = 279$ K; $T_b = 353$ K) was bought from Sigma Aldrich (99% puriss p.a.), unpacked under inert gas and sealed into a Duran cuvette. We used a cylindrical cuvette, without sharp corners in order to reduce the crystallization effects. This cuvette is placed into a square cell with glycerol as the matching liquid to compensate the cylindrical (lens) aberration induced by the cuvette. The cell was hold in a cryostat system, cooled with Peltier cells; this enabled temperature control to better than ± 0.1 K. Thus the sample could be supercooled up to 258 K, where it remained liquid for several hours. The HD-OKE data are collected at different temperatures from 350 to 258 K. In figure 1 we show all OKE signals in a logarithmic plot; for
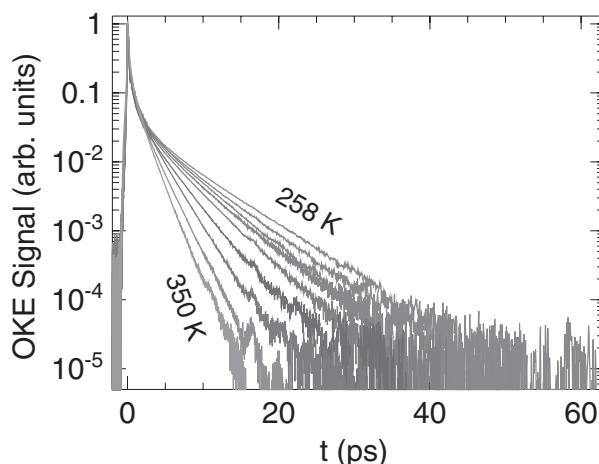
Figure 1. HD-OKE signal of liquid benzene measured at different temperatures, from top to bottom, 258, 264, 269, 274, 279, 293, 310, 330 and 350 K ($T_m = 279$ K).

delay times shorter than 5 ps the curves have a complex profile, with a highly non-exponential character, while for long delay times the decay shows an almost exponential behaviour over more than three decades of signal intensity. So we can identify three different processes: at very short delays (0.1–1 ps), there is evidence of an oscillatory behaviour of the signal, superimposed as a fast quasiexponential decay. No intramolecular vibration of benzene is low enough to be directly excited within the pulse bandwidth (Ricci *et al.* 2002); the origin of the oscillation is then to be found in the intermolecular vibrations. This oscillating signal is followed by a residual intermediate decay taking place up to 4–5 ps. Finally, the slow relaxation process appears and it extends, for the lower-temperature data, up to 40 ps. In some recent work the LVM scenario combined with molecular dynamics simulation has been used to address these relaxation processes (Chelli *et al.* 2001, Ricci *et al.* 2001, Ratajaska-Gomska 2002). In these papers the slow or structural relaxation is attributed (as expected for molecular liquid formed by anisotropic molecules) to a pure orientational diffusion that, in a single-molecule interpretation, has been compared with the Debye–Stokes–Einstein hydrodynamic model. The fast and intermediate dynamics are explained on the basis of local intermolecular vibration. According to these studies, two main groups of vibrational modes are present: the first group is made up of under-dumped modes (UDMs) characterized by an approximate frequency of 1.2 THz and the second group consists of over-dumped modes (ODMs) of about 360 GHz. The UDMs describe the fast vibrational dynamics; the ODMs reproduce the intermediate relaxation processes. A comparison with the molecular dynamic simulation and with a quasicrystalline model suggests a mixed rotational–translational nature of these modes; nevertheless a definite assignment of these has not been worked out. These LVM approaches consider a basic hypothesis to be valid, namely that the structural relaxation has self-determining dynamics and that it interacts with the local modes by the modification of the local liquid structure; and vice versa the local modes do not contribute to defining the structural relaxation. This hypothesis is in many respects an oversimplification of the dynamic problem that hardly applies to a molecular liquid such as benzene where all the dynamic

features are characterized by similar time scales. Nevertheless, the LVM allows a sensible connection between the measured relaxation and some microscopic features of the molecular liquid.

The dynamic models of molecular liquids are still an open problem and even 'simple' molecular liquids, such as benzene, have been not fully described. As we have discussed briefly, the theoretical models for these liquids are often oversimplified and based on arbitrary decoupling of the motions present in the dynamic systems. It would be extremely interesting to have a theoretical model able to describe the whole complex relaxation pattern, without any doubtful time scale separation.

Recently the MCT has been introduced as a possible valid model to describe the dynamics of the molecular liquids (Wiebel and Wuttke 2002). The MCT has been shown to describe properly the dynamic scenario of many molecular liquids showing a glass transition (Götze 1999). Indeed the MCT models are able to describe the relaxation features up to temperature well above the critical temperature (Torre *et al.* 2000, Prevosto *et al.* 2002, Ricci *et al.* 2002, Pratesi *et al.* 2003).

This suggests that the MCT should be tested as a theory that describes the dynamics of molecular liquids even if they do not show a glass transition and are characterized by rather low viscosities. To describe these liquids we cannot use the asymptotic solution of the MCT, since they hold only for temperatures relatively close to T_c. Also, the schematic models of the MCT are valid in an extended temperature range that can span substantially above the critical temperature T_c.

In the present work we shall compare our data with the schematic 'two-correlator' F_{12} MCT model that, as described in several papers (Alba-Simionesco and Krauzman 1995, Götze and Voigtmann 2000), is able to describe properly the light scattering spectra of many glass-forming liquids including the high-frequency region (1–2 THz). In this model we introduce two correlators $\phi_{q0}(t)$ and $\phi_{qs}(t)$, the 'master' and 'slave' correlators respectively. $\phi_0(t)$ models the intrinsic dynamics of the system; $\phi_s(t)$ correlator is connected to a coupled physical observable of the system. Its time derivative will be interpreted as the correlation function observed by the OKE.

These correlators obey the following integrodifferential equations:

$$\frac{\partial^2}{\partial t^2}\phi_{q0}(t) + \gamma_0 \frac{\partial}{\partial t}\phi_{q0}(t) + \Omega_0^2 \phi_{q0}(t) + \Omega_0^2 \int_0^t m_{q0}(t-t')\frac{\partial}{\partial t'}\phi_{q0}(t')\,\mathrm{d}t' = 0, \qquad (3)$$

with $m_{q0}(t) = V_1 \phi_{q0}(t) + V_2 \phi_{q0}^2(t)$;

$$\frac{\partial^2}{\partial t^2}\phi_{qs}(t) + \gamma_s \frac{\partial}{\partial t}\phi_{qs}(t) + \Omega_s^2 \phi_{qs}(t) + \Omega_s^2 \int_0^t m_{qs}(t-t')\frac{\partial}{\partial t'}\phi_{qs}(t')\,\mathrm{d}t' = 0, \qquad (4)$$

with $m_{qs}(t) = V_s \phi_{q0}(t)\phi_{qs}(t)$.

The model contains seven parameters, two frequencies Ω and Ω_s characterizing the ballistic short time motion, two damping coefficients γ and γ_s representing the fast contributions to the memory kernel and three coupling coefficients V_1, V_2 and V_s. These parameters are all expected to vary smoothly and monotonically with temperature. To fit our OKE data we solve numerically equations (3) and (4) then we compare the time derivative of the calculated correlation function with the experimental decay. The fitting routine is made by an inner loop that calculates $\phi_0(t)$ and

$\phi_s(t)$ by iteratively solving equation (3) in the time domain; then $\phi_s(t)$ is obtained by equation (4) and its time derivative is fitted to the experimental data. This loop is repeated, adjusting the model parameters until a nonlinear least-squares minimization is reached. This procedure is performed independently for each of the nine temperatures. In an attempt to reduce the number of free parameters we find that the microscopic frequency of the slave correlator can be kept at a constant value $\Omega_s = 1$ THz. We show in figure 2 the good agreement between the experimental data and the fits for all the time window, both for the high-temperature decay and for the data in the supercooled region. The other parameter values, obtained by the fit, show
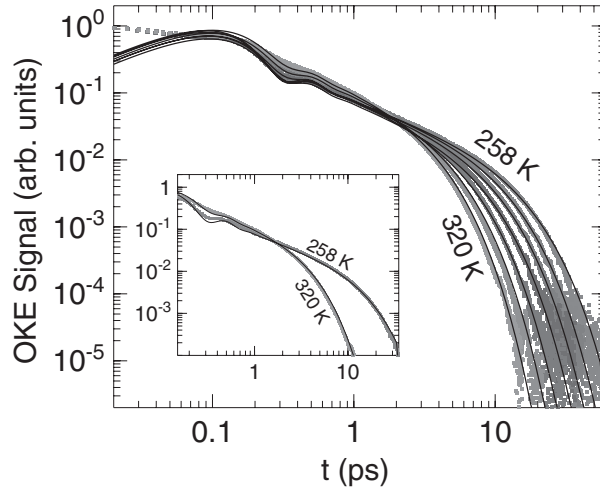

Figure 2. Fit of the HD-OKE signal with the mode-coupling two-correlator F_{12} model (——).
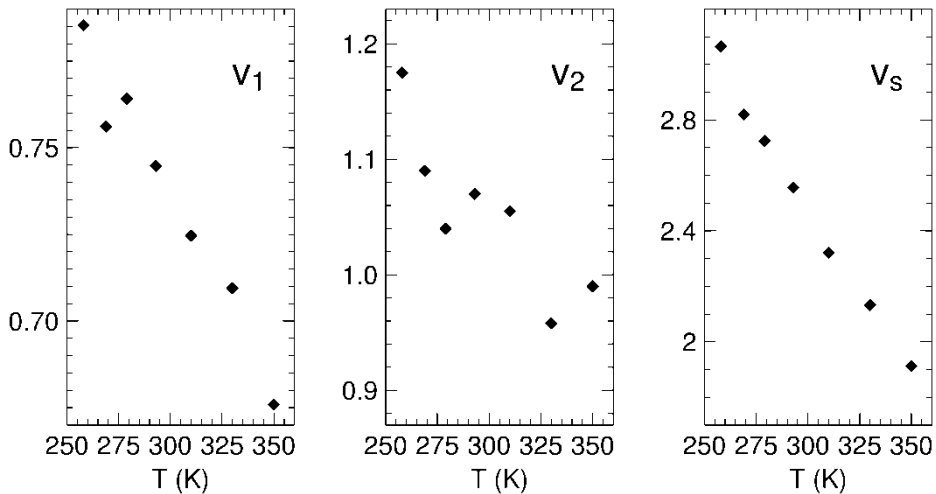

Figure 3. Coupling coefficients used in the schematic F_{12} mode-coupling fits. The coefficients V_1 and V_2 control the intrinsic dynamics of the liquid, represented by the correlation function $\phi(t)$; the 'slave correlator' $\phi_s(t)$, which represents the experimental observable, couples to $\phi(t)$ by means of V_s. In agreement with the MCT theory these coefficients decrease with increasing temperature.
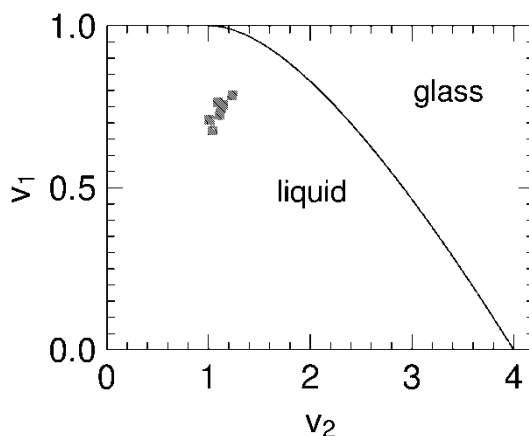
Figure 4. Mode-coupling coefficients V_1 and V_2 in a phase diagram of the F_{12} model: (——), ideal glass transition singularity.

a weak regular temperature dependence, as can be seen in figure 3. In figure 4 the coupling coefficients V_1 and V_2 obtained from our fits are shown as full squares in a phase diagram. For larger values of V_1 and V_2, the F_{12} model becomes a glass. The phase boundary corresponding to the idealized liquid–glass transition is indicated in figure. In benzene the coupling coefficients fall clearly in the liquid phase; from the available V_1 and V_2 it is not even possible to extrapolate a hypothetical trajectory by which benzene would approach the glass transition if it could be further supercooled. Therefore it is impossible to indicate a meaningful value of the asymptotic line-shape parameter λ.

§4. CONCLUSION

We studied the dynamics of liquid benzene over a wide temperature range (including its supercooled phase) by measuring the correlation function of the anisotropic fluctuations of the dielectric constant by time-resolved OKE experiments. The three typical time scales of molecular liquids have been confirmed by the present experiments on benzene and no critical phenomena have been detected even in the supercooled phase. So, as benzene is also considered to be a highly symmetric, simple and stiff molecular structure (in fact the intramolecular dynamics do not contribute on the interesting time scales), it has proved to be an excellent prototype of a 'simple' molecular liquid. We found a fast decay process, with clear vibrational features, taking place on the 0.1–1 ps time window; an intermediate process taking place from about 1 ps up to 4–5 ps (for the lower-temperature data) and a slow relaxation process that extends up to 40 ps.

We investigated the MCT ability to reproduce the benzene dynamics. Since the asymptotic solutions do not apply to simple molecular liquid, we utilized the F_{12} schematic model that has the potentiality to explain such a dynamic problem. The numerical solution of this model is indeed able to fit properly the benzene decays with consistent values of the parameters. What is striking is the ability to fit the whole relaxation pattern from 0.1 to 40 ps without any arbitrary separation of the time scales and of the dynamic processes. In the MCT the structural relaxation and the vibrational dynamics are solution of the equations of motion; so the fast vibrational processes and the slow relaxation are intrinsically included and

coupled. The vibrational dynamics are characterized by a frequency of about 1 THz in reasonable agreement with the UDM frequency, introduced in the LVM approach. The crossover from the fast to the slow processes correctly describes the intermediate relaxation, so that no ODMs are needed to describe the relaxation. According to this interpretation the intermediate relaxation is simply the merging of the (probably local) vibrational dynamics into the slow collective diffusive process. This merging is not trivial, as has already been proved in glass-former liquids, because on this intermediate time scale the two processes are strongly coupled.

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