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## LETTER TO THE EDITOR

# The femtosecond optical Kerr effect in molten caesium chloride

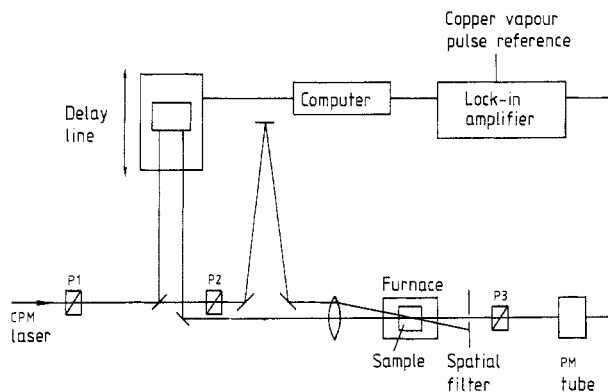
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**Abstract.** Femtosecond time-resolved measurements of the optical Kerr effect in molten caesium chloride have been made. Amplified laser pulses of 115 fs duration and 1  $\mu$ J energy were used to induce a birefringence. The transmission of a weak probe pulse of the same duration gives a value of 180 fs for the relaxation time of the induced birefringence; this value is consistent with that expected for binary ionic collisions. The magnitude of the Kerr coefficient is estimated to be  $\approx 3 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$  ( $3 \times 10^{-15}$  esu).

It is now well established that simple ionic molten salts possess substantial local ordering which extends over distances of 10–20 Å [1]. Neutron diffraction studies have shown, for example, that molten alkali halides display charge ordering with a coordination number that depends on relative ionic sizes: CsCl has octahedral coordination, whereas LiCl has tetrahedral coordination [2]. This ordering of ions within the melt gives rise to complex dynamical properties. Inelastic light and neutron scattering measure a broad power spectrum which extends to frequencies well above the optical vibrational frequencies of the crystal [3, 4]. At low frequencies the ionic motion is primarily diffusive but modified by the structural correlation; ions may have uncorrelated motion within separate ordered regions, but they can hop to vacant sites within neighbouring units. At intermediate frequencies the motion is collective, showing structure which arises from ‘remnant’ optical modes of the crystal. At high frequencies the scattering arises from single-particle processes in which the motion of the ions may be more appropriately described as Brownian or gas-like. The characteristic timescales of these processes may be estimated from their respective frequencies, and range from  $\approx 100$  fs for Brownian motion to  $\geq 1$  ps for diffusive motion.

The purpose of the present work has been to measure the dynamics of molten salts directly in the time domain. It is well known that the third-order dielectric susceptibility which determines the form of the depolarised Raman spectrum can also be probed using optical Kerr effect (OKE) [5]. The electric field of an intense pulse of plane-polarised light induces an anisotropy in the refractive index of the medium, and this birefringence may be detected as an ellipticity induced in a plane-polarised probe pulse. The non-linear polarisation may be electronic, in which case the onset and decay are extremely rapid, or it may be atomic as for example in the field-induced orientation of asymmetric molecules, in which case the decay is relatively slow. Measurement of the decay time of the induced birefringence has been used extensively to study molecular re-orientation in liquids, which occurs mainly in the picosecond range [6]. More recently it has been



**Figure 1.** A schematic diagram of the experimental arrangement used to measure the optical Kerr effect. P1, P2, P3 are polarising prisms, PM is the photomultiplier. The colliding pulse laser (CPM) is amplified and focused to produce a pump pulse electric field of  $4 \times 10^8 \text{ V m}^{-1}$ .

used to investigate dynamics of rare-gas liquids [7]; in these materials an asymmetry in the polarisability is induced by inter-molecular collisions, and it has been measured to decay in approximately 500 fs. In this Letter we report OKE experiments on molten CsCl in the femtosecond range. The ions have the rare-gas electronic configuration, and Raman measurements have revealed a high depolarisation ratio (i.e. anisotropic polarisability) [8]. Our results show that there is an ionic non-linear susceptibility which has the same order of magnitude as the purely electronic contribution, and which decays with a characteristic relaxation time of 180 fs.

The optical arrangement used in the experiment is shown in figure 1. Femtosecond pulses were generated in a colliding pulse mode-locked (CPM) ring dye laser [9], and subsequently amplified in a copper vapour laser-pumped dye amplifier [10]. Pulses of up to  $5 \mu\text{J}$  energy at a repetition frequency of 6.5 kHz and 115 fs duration are produced at a wavelength of 620 nm. After vertically polarising the amplified beam (P1), 5% of the light was split off to provide the probe pulse. Time delay was introduced using a computer-controlled optical delay line. The remainder of the amplified beam formed the pump pulse, which is polarised (P2) at  $45^\circ$  to the probe beam. Both pump and probe beams were focused into the melt using a 100 mm focal length lens such that they crossed at the focus, giving an overlap region of 1.2 mm in length and  $120 \mu\text{m}$  in diameter. The probe beam was then spatially filtered to prevent unwanted scatter from the pump pulse, and subsequently passed through a polarisation analyser (P3) crossed with respect to P1. Light emerging from the crossed polariser arrangement was detected by a photomultiplier, and the resulting signal processed in a lock-in amplifier tuned to the repetition rate of the pulses.

The problem of coherent scattering of the pump beam into the probe beam can be effectively eliminated by chopping the probe beam and locking the detection system to the chopping frequency. Having assessed by this test that there was no significant contribution from coherent scattering, we used the arrangement shown in figure 1 because of the improved signal-to-noise ratio.

Our sample consisted of high-purity CsCl contained in a quartz cell and maintained at temperatures of around 1000 K in a temperature-controlled optical furnace. This material is particularly convenient to study because of its relatively low melting temperature (918 K), high stability and negligible chemical reactivity.

In the limit where the characteristic relaxation time of the induced non-linearity is very much shorter than the laser pulse width, and the induced ellipticity is small, the present experimental arrangement measures the third-order intensity correlation function of the laser pulse [11]. The function can be asymmetric if the pulse itself is asymmetric. The CPM laser is expected to produce symmetric pulses  $I(t) \sim \text{sech}^2(1.76t/\tau_p)$ , where  $\tau_p$  is the pulse width. No significant asymmetry was observed when a crystalline sample exhibiting only an electronic non-linearity was measured.

The transmission of the probe beam through P3 as a function of time delay is shown in figure 2 for a sample temperature of 970 K. A marked asymmetry is clearly visible, which decays in approximately 150 fs. The profile is qualitatively similar to that obtained by Greene and co-workers [7] for the rare-gas liquids. However, we do not observe any transmission at times  $\geq 300$  fs after the peak of the excitation pulse. The transmission profile was not found to change appreciably with temperature in the range 920–1000 K. In order to make a quantitative analysis of the birefringence we must integrate the induced transmission over the duration of the pump pulse. The effect sampled by the probe beam is the convolution of the decay of induced retardation with the pump pulse profile. The crossed polariser arrangement of figure 1 gives a  $\sin^2(\varphi/2)$  transmission function, where  $\varphi$  is the optically induced retardation angle. Assuming the retardation to decay exponentially with time with a characteristic time constant  $\tau$  gives

$$\varphi(t') = A \int_{-\infty}^{t'} I_{\text{pump}}(t'') \exp[-(t' - t'')/\tau] dt'' \quad (1)$$

where

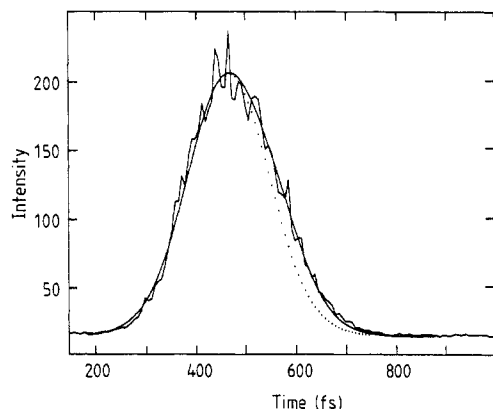
$$A = 2\pi l B_K / \lambda \tau. \quad (2)$$

$l$  is the interaction length and  $B_K$  is the kerr coefficient. Equation (1) assumes instantaneous polarisation, i.e. that there is no inertia opposing the applied field. Convolution of the transmission function with the probe pulse gives the transmitted intensity  $T$ :

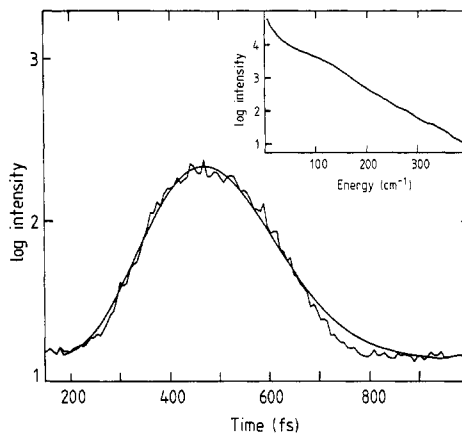
$$T(t) = T_0 \int_{-\infty}^{\infty} I_{\text{probe}}(t' - t) \sin^2(\varphi(t')/2) dt' \quad (3)$$

where  $T_0$  is a constant. We have made a computer fit of this function to the data assuming  $\text{sech}^2$  pulse shapes for  $I_{\text{pump}}$  and  $I_{\text{probe}}$ , using the birefringence decay time  $\tau$  as a variable parameter. The smooth curve in figure 2 is the calculated transmission obtained with  $\tau = 180$  fs.

By rotating the plane of polarisation of the probe beam in the absence of induced birefringence we calibrated the detection system and obtained an absolute value for the maximum induced transmission. From (2) we obtain a value for  $B_K = 3 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$  ( $3.2 \times 10^{-13}$  esu). The third-order electronic non-linear susceptibilities of a number of crystalline alkali halides have been measured, although to our knowledge CsCl has not been measured so far. Values obtained for the chlorides are  $7 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$  for NaCl and  $4 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$  for KCl [12]; extrapolation of this trend of decreasing third-order non-linear susceptibility with increasing number of electron orbitals leads us to estimate a value of around  $10^{-22} \text{ m}^2 \text{ V}^{-2}$  ( $10^{-13}$  esu) for CsCl. This extrapolated crystal value of  $B_K$  is purely electronic in origin and cannot be directly compared with our experimental value of  $B_K$  which includes electronic and ionic contributions. In order to estimate the magnitude of the electronic contribution we have extended (1) to include a second exponential term constrained to have a decay time comparable with that expected for



**Figure 2.** Probe transmission as a function of time delay between excite and probe pulses. The dotted curve is to guide the eye and is symmetric with the rising edge of the data. The smooth curve is a fit to the data assuming an exponential decay of the induced non-linearity with a time constant  $\tau = 180$  fs.



**Figure 3.** Probe transmission (as in figure 2) plotted on a logarithmic scale. The smooth curve is a fit to the data assuming a Lorentzian time dependence of the induced non-linearity with a time constant  $\tau = 120$  fs. The Raman spectrum of molten CsCl is shown inset [8].

electronic non-linear processes ( $\approx 10$  fs); we deduce that the electronic contribution is less than or roughly equal to the ionic contribution. In the case of anisotropic molecules the electronic and orientational non-linear susceptibilities are found to be typically of the same order of magnitude. In liquid xenon Greene and co-workers [7] measured the electronic effect and found it to be larger by almost an order of magnitude.

The depolarised Raman spectrum of molten CsCl is shown inset in figure 3 [8]. It shows an exponential decrease of intensity with increasing energy,  $I(\omega) \sim \exp - \omega/\omega_0$ , with  $\omega_0 = 50 \text{ cm}^{-1}$ . The mean value for the depolarisation ratio over this frequency range is  $\rho \approx 0.53$  which has led to the suggestion that the Cs ions in the melt are distorted, or that there is octahedral coordination within spatially correlated regions. The dynamical process which gives rise to the exponential wing has not so far been identified, and possibly a number of different processes contribute. The increase in scattered intensity observed at the transition from the solid to the molten state tends to rule out the possibility of two-phonon scattering processes [8]. It has also been noted by Mitchell and Raptis [8] that the ionic plasma frequency in CsCl is  $\approx 20 \text{ cm}^{-1}$ , which suggest the possibility that the exponential wing in the Raman spectrum is due to light scattering from a heavily damped plasma. Fleury and co-workers [13] have studied the high-frequency exponential wing in the Raman spectra of rare-gas liquids, and attribute its presence to isolated binary collisions of the gas molecules. In this model  $\omega_0$  is approximately  $3(k_B T/m\sigma^2)^{1/2}$  where  $\sigma$  is the Lennard-Jones length parameter. For CsCl this expression yields  $\omega_0 \approx 43 \text{ cm}^{-1}$ , which is in remarkably good agreement with the Raman data. In this model the Kerr effect is predicted to have a Lorentzian dependence on time, rather than the exponential decay in (1). We have used this approach and obtain a fit to the data given by the smooth curve in figure 3. The result is plotted on a logarithmic scale in order to emphasise the low-intensity signal detected at later times. The best fit yields  $\tau = 120$  fs; it is fairly good for intensities down to about 10% of the maximum,

but the Lorentzian lineshape clearly gives an intensity at later times that is higher than the experimental measurement.

A comparison of the magnitude of  $B_K$  with the total Raman cross section can be made via the relation [14]:

$$I_{\text{tot}} = [(2\pi)^3/N\lambda^4 4\pi\epsilon_0]n_0k_B TB_K \quad (\text{SI units}) \quad (4)$$

where  $N$  is the number density of ions and  $n_0$  is the refractive index. This relation gives  $I_{\text{tot}} \approx 2 \times 10^{-29} \text{ cm}^2 \text{ sr}^{-1}$  which is in good agreement with the Raman cross section measurements of Mitchell and Raptis [8] who obtained for depolarised scattering a value of  $I_{\text{tot}} \approx 10^{-29} \text{ cm}^2 \text{ sr}^{-1}$ .

These results show that the time-resolved OKE in molten caesium chloride measures a non-linear response that is similar to that measured in the frequency domain by inelastic light scattering. The major contribution to the OKE appears to arise from collision-induced anisotropy in the polarisability of ions within the melt. The anisotropy decays on a timescale of  $\approx 180$  fs due primarily to binary collisions between the ions. The measurements do not give any direct information about dynamical effects of correlated regions within the melt; there is no evidence of processes with timescales  $\geq 1$  ps which has been identified in the Raman spectra. Further measurements on other alkali halides will be useful in helping to establish the systematics of dynamical behaviour in molten salts and in elucidating the origin of the fast non-linear process reported here.

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