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Abstract. Femtosecond impulsive stimulated scattering (ISS) experiments were performed on liquid carbon disulphide as a function of pressure at room temperature in a diamond anvil cell. The subpicosecond response of the liquid becomes weakly oscillatory as pressure is raised from one atmosphere to several kilobars, indicating microscopic dynamics that is vibrational in character at short times. Molecular dynamics simulations were performed to study the contribution to the ISS signal from single-molecule reorientational motion. Even at very high densities the reorientation of single molecules in the computer liquid is insufficient to explain the oscillations in the ISS signal.

1. Introduction

Recently, it has become possible to use optical pulses to study subpicosecond microscopic motions in liquids directly in the time domain via femtosecond time-resolved impulsive stimulated scattering (ISS) [1, 2]. Previously we published ISS measurements of liquid carbon disulphide as a function of temperature. The data showed weakly oscillatory dynamics at temperatures below 190 K. Here we present complementary ISS data from liquid carbon disulphide obtained as a function of pressure at room temperature. The ISS response is again oscillatory in the high density liquid, suggesting the occurrence of intermolecular libration. We also present results of molecular dynamics simulations of a model of CS_2. The simulations were undertaken to determine whether correlated librations can be observed for short times in molecular reorientational motions.

2. Experimental details

The ISS experiment has been described extensively elsewhere [1]. Excitation pulses of 80 fs FWHM were overlapped in a transient grating geometry inside a diamond anvil cell. A photodiode was used to record the Bragg diffracted light from a variably delayed probe pulse incident on the grating created by the excitation pulses. Liquid carbon disulphide was contained inside the diamond anvil cell within a hole of 1 mm diameter drilled in a stainless stell gasket 1 mm thick. The corrosive action of high pressure CS_2 on the gasket material prevented us from taking scans at pressures greater than 5 kbar.
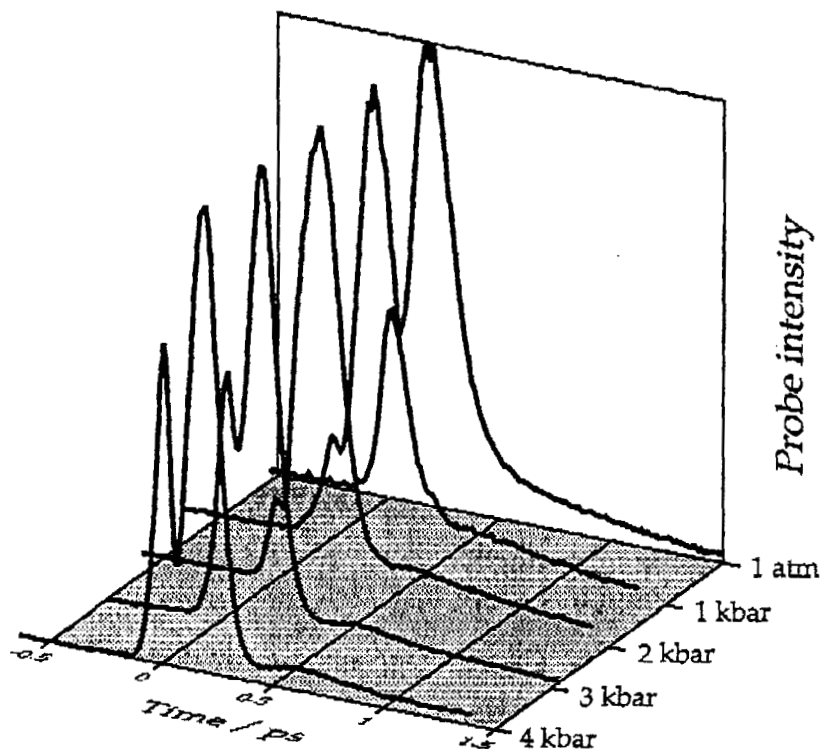
Figure 1. ISS scans from liquid carbon disulphide as a function of pressure at 293 K.

The linear polarizations of all beams were set to minimize the contribution to the signal from the instantaneous electronic optical non-linearity of the liquid [3].

To our knowledge these are the shortest pulses ever used in an optical experiment with a diamond anvil cell. Cross correlations of the femtosecond pulses after passage through the diamonds showed no pulse broadening.

3. Results and discussion

In figure 1 the ISS response of liquid CS_2 is shown at several pressures. At zero delay time all scans show a peak due to the effectively instantaneous electronic non-linear polarizability of the liquid. The differing heights of this feature relative to the subsequent signal maximum due to the nuclear non-linear polarizability from scan to scan result from partial depolarization by the diamond anvils in the high pressure cell and are not significant. The scans have been scaled so that the maximum of the nuclear response of each scan has equal magnitude.

All scans show a rise in the signal after zero delay time which reaches a maximum after 180 fs. This is due at least in part to orientational motions of molecules which occur in response to the impulsive torques exerted by the excitation pulses. The inertial rise in signal reflects the time necessary for the heavy CS_2 molecules to continue their motion away from their initial starting values toward partial orientational alignment.

The decay of the signal at later times reflects the return of the molecules to their isotropic orientations. At atmospheric pressure the decay shows two components, a rapid decline from the signal maximum out to approximately 500 fs followed by a much slower decay. As the pressure is increased the dynamics become considerably richer with the appearance of a weak oscillation around 650 fs. The overall appearance of the data at high density is qualitatively similar to the response at low temperature and atmospheric pressure [1, 2]. Thus increasing the density of the liquid, whether by lowering the temperature at constant pressure or by increasing the pressure at constant temperature, results in an ultrafast response which appears vibrational in character.

4. Molecular dynamics simulations

ISS signal arises from polarizability variations driven coherently by the ultrashort optical excitation pulses. Polarizability fluctuations induced by thermal energies are probed by light scattering, and the connection between ISS and light scattering has been discussed in detail [4]. The same difficulties met in constructing a microscopic theory of light scattering from molecular liquids are encountered in determining microscopic dynamical information from an ISS signal. At the simplest level of analysis, only single-molecule polarizabilities are considered. Through these, the excitation pulses exert impulsive torques on molecules and the probe pulse is scattered by the resulting partial orientational alignment. In a dense liquid, correlated motions of pairs, triplets, etc. of molecules will also be driven to some extent, and will lead to scattering of the probe pulse, through interaction-induced (II) polarizabilities. Here we calculate the ISS signal arising solely from the orientational motions of single molecules in a computer simulation of liquid CS_2, neglecting signal contributions from pair orientational correlations and from II polarizabilities. This permits us to test whether single-molecule orientational correlations become oscillatory (i.e. librational) at short times in a computer model of liquid CS_2. Various models of reorientation in dense liquids predict librational motion at short times, due to the oscillatory motions of molecules in transient potential wells or cages created by their neighbours [5].

Molecular dynamics (MD) simulations of CS_2 were performed at a variety of densities at room temperature to model the ISS signal arising solely from single-molecule reorientation. The Lennard-Jones interaction site potential suggested by Madden and Tildesley [6] was used to model the effective pair interactions of a system of 108 molecules. The centre of mass motion was solved by the Verlet leapfrog algorithm [7] while the rotational motion was solved using the Singer algorithm [8]. At all state points trajectories were calculated for at least 100 ps. Molecular orientations were saved approximately every 10 fs for the calculation of the correlation functions described below.

In general, the ISS signal is given by

$$I_{ISS}(t) = \int_{-\infty}^{+\infty} d\tau \, I^p(t - \tau) \left(\int_{-\infty}^{\tau} dt' \, G^{\varepsilon\varepsilon}(\tau - t') I^e(t') \right)^2 \qquad (4.1)$$

where $G^{\varepsilon\varepsilon}$ is the impulse response function (Green function) for the dielectric tensor of the liquid to the impulsive driving force of the ultrashort optical pulses, and I^e, I^p are
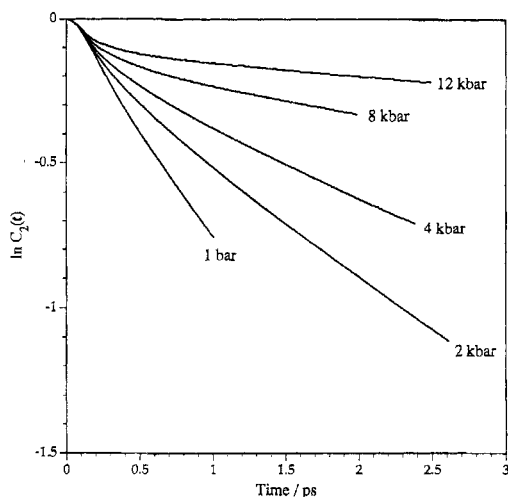
Figure 2. Natural logarithm of $C_2(t)$ orientational correlation functions showing inertial behaviour at short times and single exponential decay at later times. Curves are labelled by the experimental pressure corresponding to the density used in each MD run.
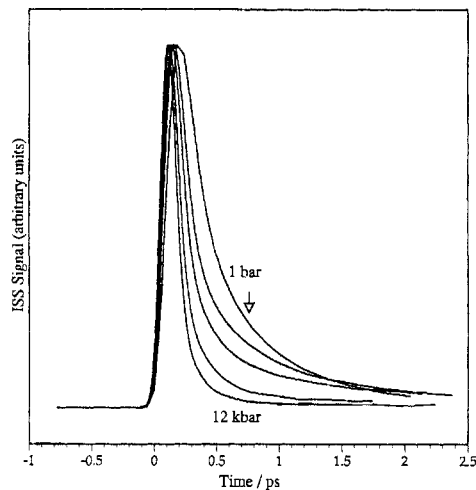
Figure 3. Simulated ISS signal calculated from isothermal MD runs using equation (4.1) with excitation and probe pulse durations of 80 fs. From top to bottom the experimental pressures corresponding to the liquid density used in the MD runs are: 1 bar, 2 kbar, 4 kbar, 8 kbar and 12 kbar, respectively.

the intensity profiles of excitation and probe pulses respectively. The impulse response function for $t > 0$ can be written as [1]

$$G^{\varepsilon\varepsilon}(t > 0) = -(4/k_B T)\, dC^{\varepsilon\varepsilon}(t)/dt \qquad (4.2)$$

where $C^{\varepsilon\varepsilon}(t)$ is a time correlation function of the collective polarizability of the liquid. Using this relation it is straightforward to model the ISS signal from an equilibrium MD simulation. Neglecting II polarizabilities and orientational correlations between pairs of molecules, we set $C^{\varepsilon\varepsilon}(t) \approx C_2(t)$ where $C_2(t)$ is the orientational correlation function of the unit vector, $\boldsymbol{u}$, directed along the CS_2 symmetry axis.

$$C_2(t) = \sum_i \langle P_2[\boldsymbol{u}_i(0) \cdot \boldsymbol{u}_i(t)]\rangle = \sum_i \tfrac{1}{2}\langle 3[\boldsymbol{u}_i(0) \cdot \boldsymbol{u}_i(t)]^2 - 1\rangle. \qquad (4.3)$$

In figure 2 the logarithm of $C_2(t)$, calculated from the stored MD trajectory data, is plotted at several state points. After the initial inertial part, the correlation functions decay exponentially at all state points.

The simulated ISS responses given by equations (4.1) and (4.2) were calculated assuming Gaussian pulse profiles of 80 fs FWHM. The results are shown in figure 3 at five densities spanning the entire liquid range at room temperature. The simulated ISS response curves reproduce the delayed maximum in the signal (the inertial effect) and the two decay times (a faster one, followed by a slower one) at later times. But even at the very high densities simulated, the response never reproduces the weak oscillation seen in the experimental data. The wiggles in the curves in figure 3 are within the statistical noise of these calculations. For this particular intermolecular potential we

conclude that molecular libration does not occur at room temperature even at very high densities.

5. Conclusions

We have measured the femtosecond ISS response of liquid carbon disulfide as a function of pressure at constant temperature in a diamond anvil cell. The most striking feature of the data is the appearance at high pressures of a broad oscillation at about 650 fs. Molecular dynamics simulations were performed over a wide range of densities for a Lennard-Jones interaction site model of the liquid to study single-molecule reorientation dynamics. For the potential used, the reorientation of single molecules evolves smoothly from inertial motion to diffusional motion (indicated by single exponential decay of $C_2(t)$) without any occurrence of libration, even at very high liquid densities. Despite clear evidence of an oscillatory component to the ultrafast molecular dynamics of liquid carbon disulphide at high densities, a definitive interpretation of this distinctive feature in terms of specific molecular motions is not yet possible.

Acknowledgments

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