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Orientational dynamics of molecular liquid oxygen

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The orientational behavior of liquid oxygen is studied by probing its molecular dynamics with a picosecond birefringence technique. Temperature-dependent measurements provide a means to distinguish orientational relaxation processes from intermolecular collisional effects. The results are compared with a hydrodynamic model which reveals the importance of bimolecular forces on the rotational dynamics.

Before the advent of ultrafast optical pulses, indirect techniques such as light scattering or nuclear magnetic resonance were employed to observe dynamical liquid phenomena at the molecular level. Recently, it has been demonstrated that short optical pulses can be used to study liquid behavior in real time with subpicosecond resolution.[1-3] Transient birefringence measurements in particular have been shown to be a powerful probe of molecular orientational dynamics and intermolecular interaction times.[2-4] However, there is often some ambiguity regarding the interpretation of such data, since in general there are several mechanisms through which birefringence may be optically induced.

We have studied the transient birefringence of liquid oxygen, and have been able to distinguish between orientational and collision-related responses by observing the evolution of the response with changing temperature and liquid viscosity. Since the liquid phase of oxygen exists over a large temperature range, the liquid dynamics may be studied over a wide variation in viscosity. Liquid oxygen is particularly interesting because of the peculiar bimolecular interactions associated with the optical transitions[5] which give oxygen its blue color and which are responsible for a number of interesting magnetic properties.[6] These transitions are unusual in the sense that one photon simultaneously excites electronic transitions in two molecules, and vibrational excitations in one or both.

Research-grade oxygen was condensed into a copper and brass optical cell, mounted inside a variable temperature optical cryostat. Over the full 35-K range of the liquid phase, the temperature stability of the experimental cell could be maintained to within 5 mK of a set temperature. A transient birefringence of the liquid was induced and probed by optical pulses of 500 fs duration. These pulses were obtained at a 76-MHz repetition rate from a dual-jet dye laser, synchronously pumped by a mode-locked argon-ion laser. The dye-laser wavelength was tuned to 584 nm, far enough from the oxygen bimolecular absorption line at 577 nm to avoid any significant absorption of energy by the liquid, but close enough to obtain a significant enhancement in the magnitude of the induced birefringence. An acousto-optic shutter was used in order to keep the average power below 3 mW while maintaining a high peak intensity. In this fashion any thermal disturbances were avoided. The train of linearly polarized pulses from the dye laser was split into pump and probe beams with an intensity ratio of 10:1. A variable delay was added along the path of the probe beam and its polarization rotated by 45° relative to that of the pump before the two beams were recombined and focused in the liquid to a common spot of about 50 microns in diameter. The pump-induced birefringence and its subsequent decay were monitored by measuring the induced component of circular polarization in the probe pulses as a function of their time delay relative to the pump pulses. A complete description of the technique and optical system will be presented elsewhere.[7]

The transient birefringent response of liquid oxygen was studied over the temperature range from $T=90$ K to just above its freezing point, at $T=54.4$ K. A sample of the data is displayed in Fig. 1, at a temperature of 65 K. The time-resolved birefringence is plotted along with an inset showing the data after smoothing and deconvolving with the measured pulse shape. Over more than a decade, the response is exponential with a time constant, in this case, of 1.42 psec. The size of the induced birefringence is large enough to allow an accurate measurement of its decay time, so that temperature-dependent effects can be observed in detail. Figure 2 shows a summary of the data, where the error bars include systematic as well as statistical errors. The results are consistent with the various existing data in the literature. A time of $1.1\pm.5$ psec has been measured at $T=77$ K through Rayleigh light scattering[8] and $\gtrsim 1$ psec at $T=90$ K through optical birefringence techniques.[3] Finally, the long relaxation times disappear when the system is cooled into the solid phase below the freezing point of the liquid.

The optical absorption in oxygen is the result of bimolecular processes, where one photon simultaneously excites electronic transitions in a pair of molecules. Three such transitions dominate the visible spectrum of oxygen since no allowed single-molecule transitions lie in this range. In addition, each electronic transition is accompanied by vibrational subbands associated with the creation of additional vibrational quanta. The optical absorption of a pair of molecules will depend on the orienta-

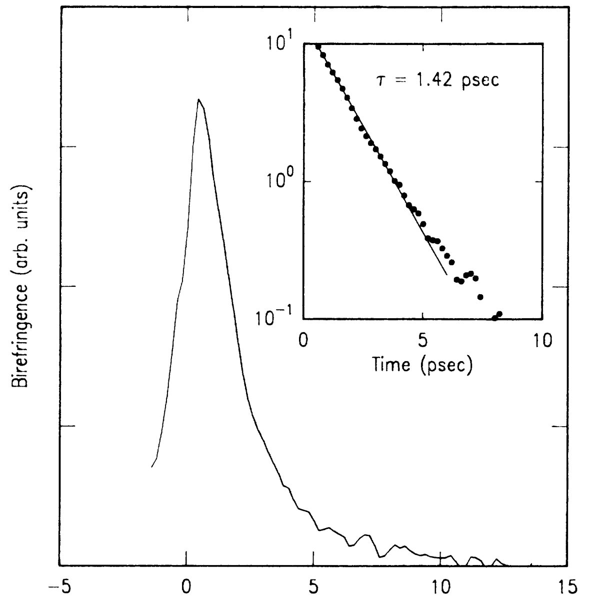

FIG. 1. Time-resolved optically induced birefringence in liquid oxygen at a temperature of 65 K. The inset shows a semilog plot of the deconvolved data, and the solid line is a single exponential fit.

tions of the molecules involved,[5] so that one might expect reorientational birefringence effects to be strongest near the absorption bands. This effect was in fact observed as the laser wavelength was tuned toward the low-energy side of band at 577 nm. This particular wavelength corresponds to the ($^1\Delta^1\Delta \leftarrow {}^3\Sigma^3\Sigma$) electronic transition with the

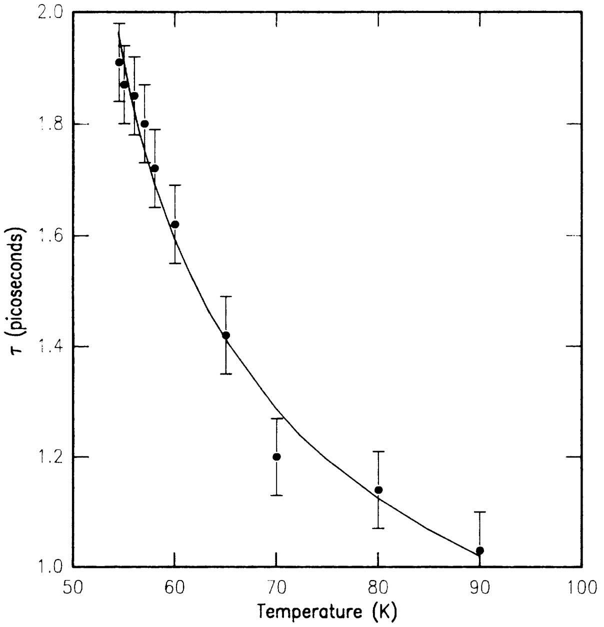

FIG. 2. Birefringence relaxation time as a function of temperature. The solid curve is a fit as described in the text.

additional creation of one vibrational quantum.

Optically induced birefringence in liquids is generally the result of a superposition of different physical processes, each with a characteristic relaxation time. In our case, the most relevant times are the molecular interaction time τ_i and the molecular reorientation time τ_r. The interaction time τ_i is historically associated with the collision-induced part of the depolarized light scattering spectrum, where electronic contributions are important. Since τ_i is not expected to be very temperature or viscosity dependent,[9] the temperature-dependent effects in the birefringence relaxation can be associated with changes in the reorientation time τ_r. Ambiguities which arise[10] when trying to separate τ_r and τ_i can thus be avoided. The general viscosity and temperature dependence of τ_r is well described by the equation[11,12]

$$\tau_r = C\left[\frac{\eta}{T}\right] + \frac{2\pi}{9}\left[\frac{I}{k_B T}\right]^{1/2}, \tag{1}$$

where C is a constant, T the temperature, η the liquid viscosity, I the molecule's moment of inertia, and k_B is the Boltzmann constant. The first term represents the resistance to rotation from the surrounding liquid, and the second term is a free rotor orientation time. A fit of the data to this form yields the solid curve shown in Fig. 2, where the constant C and moment of inertia are obtained from the fit, using the measured viscosity of liquid oxygen.[13] We find that $C = 50$ psec K cP^{-1}. The nonzero value of C implies that the orientational dynamics are linked with the hydrodynamical properties of the liquid. This experiment result may be compared to the predictions of classical calculations of rotational diffusion for a particle in a viscous fluid. The simplest such calculation leads to the Stokes-Einstein equation,[14] from which we find that $C = V/k$, where V is the molecular volume. Estimating the volume from the 2.95-Å Leonard-Jones length for oxygen[10] gives $C \sim 970$ psec K cP^{-1}. The discrepancy between this result and the experimental value is not too surprising since the Stokes-Einstein equation was derived for a large particle and assumes that the fluid near the surface of the particle is dragged along as the particle rotates. Other hydrodynamic models which allow the molecule to slip through the fluid as it rotates predict much smaller values for C, depending on the exact shape of the molecule.[11] Thus the experimentally determined value of C is not inconsistent with a hydrodynamic model of molecular reorientation.

It is also interesting to extrapolate the reorientational time τ_r to zero viscosity. The usual interpretation of this limit is in terms of a free rotor orientation time. Proceeding along this line, the effective moment of inertia is obtained through fitting the data to Eq. (1) as described earlier. We find that $I = 130$ amu Å^2. This is far from the expected value of about 12 amu Å^2 estimated for a single molecule by calculating the moment of a rigid rotor consisting of two point masses (16 amu each) separated by the 1.24-Å internuclear distance in an oxygen molecule.[10] However, the experimental value of I is quite close to the 140-amu Å^2 moment for a two molecule rotor, assuming point masses of 32 amu each separated by a distance equal to the Leonard-Jones length.[10] Comparison of this value to the experimental result indicates that I is not a simple free rotor moment of inertia and suggests that the relatively long reorientational time can be interpreted as the response from coupled pairs of rotors. The orientational relaxation is then a consequence of the strong pairwise intermolecular interaction between molecules in this system rather than simply that of one noninteracting molecule. The fact that the amplitude of the relaxation signal increases near the absorption energy supports this interpretation, as oriented molecules are more likely to electronically couple and respond in a bimolecular fashion. This situation can be contrasted with that of liquid nitrogen, where the molecular size, shape, and mass are similar, but the strong bimolecular interaction is absent. Experimentally, it is found that $\tau \sim 0.35$ psec,[8] close to the free rotor time for an isolated nitrogen molecule.

In conclusion, we have studied the viscosity and temperature dependence of the picosecond molecular reorientational dynamics in liquid oxygen, thereby probing the liquid on a microscopic scale. A viscosity dependence of the reorientation time was observed, implying that the reorientation is linked to the hydrodynamic properties of the liquid. However, the viscosity dependence was found to be poorly described by the Stokes-Einstein equation as a result of the simple hydrodynamic assumptions implicit in that equation. In addition, we have also presented evidence that the observed transient birefringence is bimolecular in nature, and is associated with the reorientation of molecular pairs. Thus the bimolecular properties which are seen through static optical and magnetic measurements must be considered when interpreting the dynamical behavior of the fluid. Studies of diluted oxygen solutions could serve to provide a more complete description of the dynamics of these pairs.

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