Doped liquid nitrobenzene is ferroelectric

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The high resolution hyper-Rayleigh light scattering spectrum for liquid nitrobenzene doped with triflic acid (CF_3SO_3H) shows a narrow spike at zero frequency shift which has the polarization signature of a polar longitudinal collective mode. This spectral spike disappears for pure nitrobenzene. The spectral spike is interpreted as due to ferroelectric domains in the liquid. The dopant molecules appear to induce ferroelectric organization of the nitrobenzene molecules which is otherwise absent in the pure liquid. Estimated domain size is 34 nm and relaxation time is 50 ns. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2800561]

The structure of polar molecular liquids is an unsolved problem of long standing. Strongly interacting, dense dipolar liquids are a difficult problem because the dipole interaction is long range and anisotropic. Recently this problem has received renewed attention in the form of theoretical calculations and model simulations, and ferroelectric phases are found for the simplest dense model dipolar fluids composed of hard or soft spherical particles with a point dipole at the center of each particle.[1–13] The structures found in simulations of such model fluids include chains of head-to-tail dipoles,[3–7] columnar ferroelectric phases,[9] bubble domains,[10] and dipoles with vortex orientational order.[11,12] These calculations are suggestive but do not establish the existence of ferroelectric phases for real liquids, since the molecules in real dipolar fluids exhibit strong anisotropic short range interactions in addition to the long range dipole interaction. Furthermore, recent large-scale molecular dynamics simulations for liquid water[14] and acetonitrile,[15] employing realistic intermolecular interaction potentials, failed to find evidence for ferroelectric ordering of the molecules.

Experimental evidence for ferroelectric molecular order in liquid water,[16] acetonitrile,[17] and nitromethane[18] comes from recent hyper-Rayleigh scattering (HRS) measurements. These experiments measured the spectrum of the light scattered by the liquid, near the second-harmonic frequency of the incident laser beam, for several combinations of incident and scattered light polarizations. A narrow spike is observed at zero frequency shift in the VH depolarized HRS spectrum (where V denotes vertical linear incident-electric-field polarization, H denotes horizontal linear scattered-electric-field polarization, and the scattering plane is horizontal). This spike is not present in the VV or HV HRS spectra, which identifies it as due to a longitudinal polar collective mode.[17,19] The spectral width of the spike is <10 MHz, which corresponds to a relaxation time >30 ns for this mode,[16,18] very long compared to the picosecond molecular reorientation time scale. This long-lived collective mode with polar molecular order is ascribed to slowly relaxing ferroelectric domains in the liquid. The size of these domains

in nitromethane is 3.4 nm based on HRS measurements for nitrobenzene-nitromethane solutions.[20]

Nitrobenzene (NB) is a strongly dipolar molecular liquid with a very strong HRS signal, which should make it a good system for HRS studies of ferroelectric domains in polar liquids. However, VH spike intensity measurements for nitrobenzene were initially very erratic, apparently due to some contaminant in the nitrobenzene. The work reported here was motivated by this problem and finds that the HRS spectrum of nitrobenzene is extremely sensitive to dissolved acid. HRS measurements are presented below for a series of nitrobenzene-triflic acid solutions.

The experimental apparatus and procedure for measuring the high resolution VH HRS spectrum of nitrobenzene are similar to those previously described.[20] Linearly polarized pulses (1064 nm wavelength, 0.1 mJ pulse energy, 100 ns pulse duration, 4 kHz repetition rate) from an injection-seeded single-longitudinal-mode Nd: yttrium aluminum garnet laser are focused into the liquid sample (6 μm beam waist diameter) contained in a 1 cm spectroscopic cuvette. Light scattered around the 90° scattering angle is collected and collimated by a 0.62 numerical aperture lens, analyzed by a dichroic linear polarizer, fiber coupled to a scanning confocal Fabry-Pérot (FP) interferometer [free spectral range (FSR)=1000 MHz], and then fiber coupled to an interference filter (532 nm peak, 60 cm^{-1} bandwidth) and the photon counting detector (GaAsP photomultiplier). The instrument spectral response function (reference spectrum) was measured by scanning the second-harmonic light generated by a potassium titanyl phosphate crystal. The reference spectrum has typical width of 32 MHz (full width at half maximum intensity) due to the combined effects of FP resolution and drift. Several thousand scans of the reference and the HRS signal were alternated for each sample measurement. All spectra were acquired at $T=27.0$ °C sample temperature.

The VH HRS spectrum of nitrobenzene is composed of a sharp spike riding on top of a broader spectrum composed of successively weaker components of widths of 0.16, 1.1, and 19 cm^{-1} due to molecular reorientation and intermolecular collision.[20] Figure 1 shows a typical nitrobenzene VH HRS spectrum obtained in this experiment, which consists of a

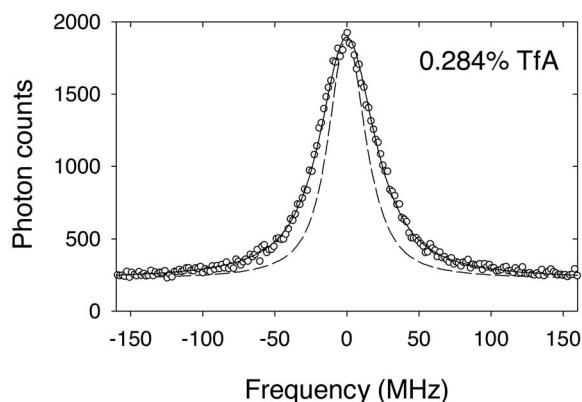a)Electronic mail: shelton@physics.unlv.edu

FIG. 1. VH HRS spectrum showing the instrumentally broadened spike riding on a flat background. The solid curve is the fit to the data, while the dashed curve shows the sum of the background term and the scaled reference peak for comparison. The fitted peak is the convolution of this reference peak and the Lorentzian function $L(\nu)=A/[1+(\nu/\nu_0)^2]$.

TABLE I. VH HRS measurements for nitrobenzene-triflic acid solutions.

x	S/B	$(S+B)/B_0$	ν_0 (MHz)
6.15×10^{-8}	0.005 ± 0.001[a]	1.01 ± 0.03	3.7 ± 1.8
1.70×10^{-7}	0.019 ± 0.001[b]	1.01 ± 0.02	4.6 ± 0.9
4.34×10^{-7}	0.047 ± 0.002[c]	0.99 ± 0.03	2.7 ± 0.5
1.21×10^{-6}	0.146 ± 0.003[b]	1.10 ± 0.02	3.5 ± 0.3
3.52×10^{-6}	0.271 ± 0.008[c]	1.24 ± 0.04	2.8 ± 0.4
8.43×10^{-6}	0.375 ± 0.005[b]	1.34 ± 0.03	3.3 ± 0.2
2.40×10^{-5}	0.479 ± 0.010[c]	1.46 ± 0.04	3.4 ± 0.3
5.78×10^{-5}	0.503 ± 0.006[b]	1.43 ± 0.03	3.2 ± 0.2
1.66×10^{-4}	0.517 ± 0.011[c]	1.46 ± 0.04	3.5 ± 0.3
4.07×10^{-4}	0.524 ± 0.007[b]	1.45 ± 0.03	4.3 ± 0.2
1.15×10^{-3}	0.508 ± 0.012[c]	1.43 ± 0.04	5.2 ± 0.3
2.84×10^{-3}	0.522 ± 0.008[b]	1.45 ± 0.03	8.1 ± 0.2
7.91×10^{-3}	0.497 ± 0.008[c]	1.49 ± 0.05	15.2 ± 0.3
1.94×10^{-2}	0.449 ± 0.005[b]		29.4 ± 0.3
2.64×10^{-2}	0.448 ± 0.016[d]		36.1 ± 1.0

[a]Solvent $S/B=(2.3\pm0.7)\times10^{-3}$.
[b]Solvent $S/B=(3.8\pm0.8)\times10^{-3}$.
[c]Solvent $S/B=(8.9\pm0.7)\times10^{-3}$.
[d]Solvent $S/B=(59.7\pm1.5)\times10^{-3}$.

narrow peak riding on a flat background. The narrow peak is the instrumentally broadened spike. The flat background is formed from the broader components of the nitrobenzene HRS spectrum by the overlap of 1800 successive spectral orders of the FP interferometer which fall within the 60 cm^{-1} bandpass of the interference filter. One FSR contains the integrated intensity of the HRS spectrum. The HRS spectrum is fitted with a function composed of a constant background term added to the peak obtained by convolving the reference spectrum with the Lorentzian function $L(\nu)=A/[1+(\nu/\nu_0)^2]$. The principal results obtained from each spectrum are S/B, the ratio of the integrated intensities of the peak (S) and the background (B), and ν_0, the spectral width of the spike.

Samples of nitrobenzene (Fluka, ACS grade; Acros, electronic grade) gave S/B in the range of 0.02-0.08 when used as received, and preliminary experiments suggested that this variability was due to traces of nitric and sulfuric acids remaining in the nitrobenzene. Nitrobenzene was purified by freeze-pump-thaw cycles (frozen at $-196\,^{\circ}$C and then $0\,^{\circ}$C) to remove volatile contaminants, followed by vacuum distillation (at $110\,^{\circ}$C with 4 Torr argon buffer gas) to leave behind less volatile impurities. Such purified nitrobenzene samples gave S/B as low as 5×10^{-4}. Adding sulfuric acid increased S/B back to 0.1, but the actual concentration of H_2SO_4 in the nitrobenzene was uncertain since H_2SO_4 preferentially partitions into the aqueous phase when dilute acid is mixed with nitrobenzene, whereas concentrated acid reacts with the nitrobenzene. Therefore, nitrobenzene samples doped with triflic acid (TfA, CF_3SO_3H) were used instead. Triflic acid is a strong, non-nucleophillic, nonoxidizing acid which dissolves readily in nitrobenzene. Samples were prepared by adding triflic acid (Sigma-Aldrich, reagent grade) to nitrobenzene, and then successively diluting this concentrated solution. Solution concentrations were determined by weighing the components, and samples were measured within 1 day of preparation. Solutions with >4 mole % TfA darkened visibly within 1h, and continued to darken more slowly for several days, as a broad absorption band extending across the visible appeared (absorbance=0.5 at 460 nm,

0.1 at 600 nm, 0.04 at 750 nm for 1 cm of 8 mole % TfA). No darkening was observed with <1% TfA.

Results of the HRS measurements are summarized in Table I and displayed in Fig. 2. Ferroelectric order of the liquid is indicated by the ratio S/B, which increases and then saturates as the mole fraction x of triflic acid dissolved in the nitrobenzene increases. The variation of S/B seen in Fig. 2(a) is described by a curve of the form

$$f(x)=(S/B)_{\max}[1-\exp(-x/x_0)], \qquad (1)$$

with coefficients $(S/B)_{\max}=0.501$ and $x_0=4.45\times10^{-6}$ (the saturation mole fraction). A saturating function of this form is obtained if each added dopant molecule may seed formation of a ferroelectric domain with a probability proportional to the remaining unseeded volume fraction of the liquid. Thus, at low dopant concentration, the liquid contains isolated domains of characteristic volume V_D and the number of domains is proportional to x, while at high dopant concentration, the domains fill the entire liquid volume. The observations are consistent with $S/B=0$ and no ferroelectric domains for pure NB. The S/B values observed for nominally pure NB can be accounted for by acid concentration $x=4\times10^{-7}$ in NB before purification and $x=4\times10^{-9}$ in the most pure NB sample. Solution samples were prepared from NB of varying purity (solvent S/B, see Table I), and the tabulated results have been corrected for the effect of the residual impurity of the NB solvent using the expression $S/B=$(solution S/B)$-$(solvent S/B)$\exp(-x/x_0)$. This expression assumes that the effect of the residual impurities in the NB is the same as the effect of a small added increment of acid.

The normalized integrated VH HRS intensities, given by $(S+B)/B_0$ in Table I and Fig. 2(b), were obtained from measurements made with the FP interferometer bypassed. The normalized intensity $(S+B)/B_0$ is the ratio of the integrated intensity $S+B$ measured for the solution sample and the integrated intensity B_0 similarly measured for pure NB. The
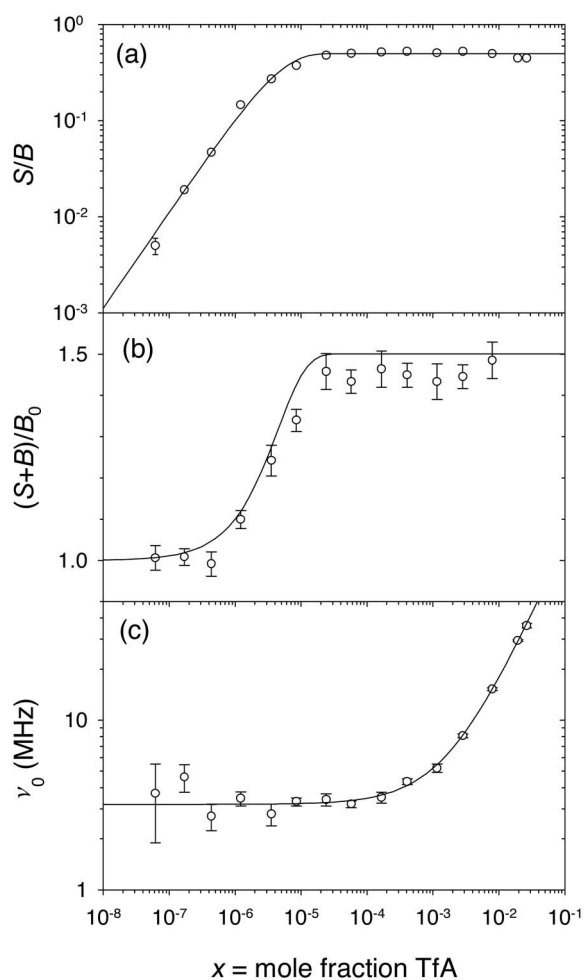
FIG. 2. VH HRS measurements for nitrobenzene-triflic acid solutions plotted vs triflic acid mole fraction x. (a) The solid curve is the fit of Eq. (1) to the S/B data from Table I. (b) The solid curve is $1+S/B$ generated using the curve in (a) for S/B, and the circles are integrated intensity measurements normalized to the integrated intensity for pure nitrobenzene. (c) The VH HRS spectral width ν_0 is obtained from fits to spectra such as that shown in Fig. 1. The fitted curve is given by $\nu_0(x)=a(1+bx^c)$ with $a=3.2$ MHz, $b=246$, and $c=0.86$.

VH HRS intensity increases for acid doped NB, and the data are in fair agreement with the relation

$$(S+B)/B_0 = 1 + S/B \tag{2}$$

expected to hold for vortex ferroelectric domains. This relation is shown by the solid curve in Fig. 2(b), constructed using the fitted curve from Fig. 2(a) for S/B. For such domains, only the molecules which reside in the vortex core are oriented with net polar order, and the spike in the spectrum is due to coherent scattering from these few molecules. Since the vortex core contains only a small fraction of the molecules, the background of incoherent scattering from the remaining molecules is expected to be almost unchanged by domain formation ($B=B_0$).

Figure 2 shows that the spectral width of the spike in the VH HRS spectrum, ν_0, is independent of x until well past the point where domains are fully formed. The Lorentzian width $\nu_0=3.2$ MHz for the spike at low x corresponds to an exponential relaxation time $\tau=(2\pi\nu_0)^{-1}=50$ ns for the domains.

At large values of x, the spectral width increases and the relaxation time falls, so it appears that while the dopant induces domain formation at low concentration, it disrupts the domains at high concentration.

The size of the domains may be estimated from the dopant saturation mole fraction x_0, assuming that each dopant molecule induces formation of a domain and the domains fill the liquid. Thus, the number of nitrobenzene molecules in a domain is $M=x_0^{-1}=2.25\times10^5=(60.8)^3$ molecules, occupying a volume $V_D=3.90\times10^4$ nm$^3=(33.9$ nm$)^3$. The ratio of coherent to incoherent scattering for this domain is $(S/B)_{max}=N^2/(M-N)\approx N^2/M$, where N is the number of coherently scattering molecules in the domain. Therefore, $N\approx[(S/B)_{max}M]^{1/2}=336$ molecules. If the domain is cubical, a vortex core of 336 molecules will be 61 molecules long and its cross section will contain 5.5 molecules. Assuming $\mu=4.22$ D for the nitrobenzene molecular dipole moment (the gas phase value)[21] gives total dipole moment of 1418 D for this core of 336 aligned molecules. The electric field energy of the domain can be reduced by placing countercharges at each end of the polarized core of the domain. One TfA molecule per domain, dissociated into a charge pair separated by the 34 nm length of the core, gives a dipole moment of 1626 D. This single charge pair may stabilize the domain by compensating the dipole moment of the core.

In the simplest model the dipoles independently orient in response to the mean field of all the dipoles. Ferroelectric order for the Langevin model occurs for dipole coupling parameter $D>1$, where $D=\rho\mu^2/9\varepsilon_0kT$ and ρ is the molecular number density. The coupling $D=3.57$ at $T=300$ K for NB ($\mu=4.22$ D) is far above the ferroelectric threshold for this model. A more realistic model is the Stockmayer fluid (SF) consisting of particles which have a point dipole at their center and also interact by a 12-6 Lennard-Jones potential. Estimates of the threshold coupling for ferroelectric order in the SF obtained from molecular dynamics simulations are in the range $D=4.2-7.4$,[2] which places NB below threshold. However, the dipole moment of a polarizable molecule in a liquid will be increased above its gas phase value by interactions with its neighbors. Using the dipole enhancement factor $(n^2+2)/3$ estimated from continuum electrostatics,[22] where $n=1.55$ is the refractive index for NB, gives the above-threshold value $D=7.69$ for liquid NB. However, molecular dynamics simulations for liquid NB show antiparallel face-to-face pairing of NB molecules,[23] and this short range orientation correlation has the effect of reducing the effective dipole coupling strength. This suggests that the occurrence of ferroelectric order in NB is decided by the combined effects of local environmental enhancement of the molecular dipole moment, competition between short range and long range molecular correlations, and boundary conditions enforced by redistribution of mobile charges.

Similar considerations may account for the discrepancy between the HRS experiments for acetonitrile[17] and the recent, realistic, very large scale (28 000 molecules) molecular dynamics simulation of liquid acetonitrile which found no evidence for ferroelectric order.[15] The gas phase value $\mu=3.92$ D for acetonitrile[21] gives dipole coupling strength $D=5.98$ for the liquid, which is within the range of the ferro-

electric threshold values seen for the SF.[2] However, the strong orientation correlations for nearest neighbor molecules observed for simulated acetonitrile[15] will reduce the effective coupling parameter, and this evidently puts it below threshold. This simulation did find ferroelectric order when the particles were morphed to make them more like Stockmayer particles while keeping their dipole moment constant.[15] This suggests that both simulated fluids are close to the ferroelectric threshold, and that the effect of increasing the acetonitrile model dipole moment to account for the polarizability of the real fluid should be investigated. The apparent discrepancy between simulation and experiment might be resolved if simulated acetonitrile with a larger dipole moment is found to be ferroelectric.

In summary, it is found that liquid nitrobenzene doped with acid is ferroelectric even though the pure liquid is not. The estimated size and relaxation time for the ferroelectric domains induced by acid doping are 34 nm and 50 ns, respectively.

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