

# Long range dipole–dipole correlations in nitrobenzene–benzene solutions

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Hyper-Rayleigh scattering (HRS) from liquid nitrobenzene–benzene solutions with nitrobenzene mole fraction in the range  $0.001 < x_{NB} < 1$  was measured for several combinations of linear polarized incident and scattered light, for scattering angles near  $90^\circ$ . Polar collective modes are identified by their distinctive HRS polarization dependence. At all concentrations the nitrobenzene HRS intensity is dominated by the transverse polar collective mode contribution and the longitudinal collective mode contribution is near zero. The transverse polar mode HRS is due to long range dipole–dipole orientation correlations between the nitrobenzene molecules, such that the molecular dipoles are oriented transverse to the wave vector for each spatial Fourier component of the orientation distribution. © 2010 American Institute of Physics. [doi:10.1063/1.3517221]

## I. INTRODUCTION

Hyper-Rayleigh scattering (HRS) is a second harmonic light scattering mediated by the molecular first hyperpolarizability  $\beta$  and is widely employed to measure  $\beta$  of organic chromophores in solution.<sup>1–6</sup> It is usually assumed that the molecules are independent and randomly oriented, so that the observed HRS signal from the sample is the result of incoherent addition of HRS from each individual molecule. The  $\beta$  tensor components for a molecule are then obtained from experimental measurements of the HRS intensity and its polarization dependence by applying theoretical expressions relating HRS to the orientation averaged molecular  $\beta$  tensor.<sup>6–9</sup> Although HRS experiments studying neat molecular liquids have found significant effects due to both nearest neighbor and longer range intermolecular interactions and correlations,<sup>10,11</sup> the assumption of an independent random molecular orientation is thought to be valid when applied to dilute chromophore solutions. This issue was recently explored for nitrobenzene–methanol solutions by Chen and Wong, with the conclusion that the coherent contribution due to nitrobenzene intermolecular correlations rapidly vanishes as the nitrobenzene molecules are diluted with methanol.<sup>12</sup>

The present HRS study of nitrobenzene–benzene solutions was undertaken to further explore the correlation between the nitrobenzene molecules as a function of intermolecular distance. The ideal experiment would measure nitrobenzene HRS as the intermolecular spacing is varied by diluting the nitrobenzene with solvent molecules that do not contribute to the HRS signal. Benzene was chosen as the solvent since HRS from the centrosymmetric benzene molecules is much weaker than HRS from the nitrobenzene molecules (the nonvanishing HRS from liquid benzene is mainly due to the small fluctuating  $\beta$  induced in each molecule by the quadrupole electric fields of nearest neighbor benzene molecules<sup>13,14</sup>). HRS intensities were measured in the  $90^\circ$  scattering geometry with linearly polarized incident and scattered light selected. Configurations with incident and scat-

tered light polarized either perpendicular or parallel to the horizontal scattering plane are denoted VV, HV, VH, and HH, where V denotes vertical polarization, H denotes horizontal polarization, and the first and second letters refer to the incident and scattered light, respectively. Macroscopic isotropy requires that HRS intensities obey the relation  $I_{HV} = I_{VH}$  in the case of a liquid with only local intermolecular correlations. Violation of this equality indicates contributions from delocalized collective modes and long range correlations, where  $I_{HV}/I_{VH} = 2$  for a transverse polar mode and  $I_{HV}/I_{VH} = 0$  for a longitudinal polar mode.<sup>11,15,16</sup> The present work probes the long range intermolecular correlations using measurements of the ratio  $I_{HV}/I_{VH}$  as a function of nitrobenzene concentration.

Some of the experimental results of this work reproduce observations previously reported by Chen and Wong,<sup>12</sup> and the new observations in this work are also consistent with their observations. However, the conclusion of the present work is opposite. The experimental results presented below show the persistence of strong orientation correlations between nitrobenzene molecules in dilute solution.

## II. THEORY

The theory for HRS from independent randomly oriented molecules is well established.<sup>6–9</sup> The theory for HRS from polar collective modes has been developed more recently<sup>15,16</sup> and has been most recently applied in a study of neat liquid nitrobenzene.<sup>11</sup> The interpretation of the present experiment is based on the following expressions for HRS at  $90^\circ$  scattering angle, including contributions from both the randomly oriented molecules and from the polar collective modes,<sup>11,16</sup>

$$I_{VV} = A_0 P^2 + A_T R^2, \quad (1)$$

$$I_{HV} = A_0 + A_T, \quad (2)$$

$$I_{VH} = I_{HH} = A_0 + \frac{(A_T + A_L)}{2}, \quad (3)$$

where  $A_0$ ,  $A_T$ , and  $A_L$  are intensity coefficients for HRS due to local, transverse, and longitudinal modes, respectively.

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Given the values for  $P^2$  and  $R^2$ , ratios of the intensity coefficients  $A_0$ ,  $A_T$ , and  $A_L$  may be determined from ratios of HRS intensities,  $I_{VV}/I_{HV}$  and  $I_{HV}/I_{VH}$ , using the following expressions:

$$\frac{A_0}{A_T} = \frac{R^2 - \left(\frac{I_{VV}}{I_{HV}}\right)}{\left(\frac{I_{VV}}{I_{HV}}\right) - P^2}, \quad (4)$$

$$\frac{A_L}{A_T} = 2 \left[ \frac{\frac{A_0}{A_T} + 1}{\left(\frac{I_{HV}}{I_{VH}}\right)} - \frac{A_0}{A_T} - \frac{1}{2} \right]. \quad (5)$$

The parameter  $P^2$  for independent randomly oriented molecules is  $P^2 = \langle \beta_{ZZZ}^2 \rangle / \langle \beta_{XXX}^2 \rangle$ , where the squared lab-frame components of  $\beta$  averaged over all molecular orientations,  $\langle \beta_{ZZZ}^2 \rangle$  and  $\langle \beta_{XXX}^2 \rangle$ , can be expressed in terms of the components of  $\beta$  in the molecular frame.<sup>6-9</sup> The molecular  $\beta$  tensor may be given as a Cartesian tensor or as the direct sum of irreducible spherical tensors.<sup>9</sup> In the case that Kleinman symmetry holds (full permutation symmetry of the spatial indices of the Cartesian tensor  $\beta_{ijk}$ ) the spherical tensor direct sum is  $\beta = \beta^{(1)} \oplus \beta^{(3)}$ , with  $P^2 = 9$  for  $\beta^{(1)}$  (the first rank, dipolar term) and  $P^2 = 3/2$  for  $\beta^{(3)}$  (the third rank, octupolar term). The parameter  $R^2$  for a transverse polar mode also has the value  $R^2 = 9$  in the zero frequency limit where Kleinman symmetry is exact. In the case that the applied field frequency is nonzero and Kleinman symmetry is not exact, both  $R^2$  and  $P^2$  for  $\beta^{(1)}$  can deviate from 9.

Both  $\beta^{(1)}$  and  $\beta^{(3)}$  for a molecule are usually nonzero so that  $3/2 \leq P^2 \leq 9$ . For an isolated nitrobenzene molecule one obtains  $P^2 = 3.60$  from the *ab initio* calculated static electronic  $\beta$  components  $\beta_{zzz} = -193.6$ ,  $\beta_{zyy} = 4.7$  and  $\beta_{zxx} = 27.4$  (atomic units; permanent dipole  $\mu_z < 0$ ).<sup>17</sup> However, the previous study of HRS from neat liquid nitrobenzene gave the parameter values  $P^2 = 1.5$  and  $R^2 = 9.7 \pm 0.3$ .<sup>11</sup> These results are interpreted as follows. The value  $R^2 = 9.7$  is consistent with HRS from a polar collective mode with a small deviation from Kleinman symmetry, while the value  $P^2 = 1.5$  is consistent with incoherent scattering from the octupolar term  $\beta^{(3)}$ . The polar collective mode HRS is due to orientation correlations acting to give coherent scattering over an extended volume for the vector term  $\beta^{(1)}$ , but these correlations do not result in coherent scattering for the octupolar term  $\beta^{(3)}$ . It is not necessary to include a separate incoherent contribution for the vector term  $\beta^{(1)}$  since an arbitrary vector distribution can be represented by an appropriate superposition of transverse and longitudinal modes. In the case that the transverse and longitudinal mode intensities are equal the result would be indistinguishable from incoherent scattering from the vector term  $\beta^{(1)}$ , where  $R^2 = 9.7$  instead of 9 again indicates a deviation from Kleinman symmetry. Adhering to this interpretation, Eqs. (4) and (5) will be evaluated using experimentally measured values for the HRS intensity ratios (“polarization ratios”) obtained from this work and the parameter values  $P^2 = 1.5$  and  $R^2 = 9.7$  obtained from the previous study of neat nitrobenzene.<sup>11</sup> Thus, the intensity coefficient  $A_0$  in Eqs. (1)–(3) will represent incoherent HRS from  $\beta^{(3)}$ ,

while the intensity coefficients  $A_T$  and  $A_L$  account for incoherent and coherent HRS from  $\beta^{(1)}$ .

HRS intensities for different samples are usually compared assuming that the measured HRS intensity is related to the effective molecular hyperpolarizability by<sup>3</sup>

$$I_{2\omega} \propto \rho F \beta^2 I_{\omega}^2, \quad (6)$$

where  $\rho$  is the molecular number density and  $F$  accounts for other sample-dependent factors and is given by

$$F = L_{\omega}^4 L_{2\omega}^2 T_{\omega}^2 T_{2\omega} n_{\omega} / n_{2\omega}^2. \quad (7)$$

In this equation  $n$  is the sample refractive index,  $L$  is the Lorentz local field factor, and  $T$  is the Fresnel transmission factor. The HRS contributions from the components of the solution are assumed to be additive.

An expression for the nitrobenzene contribution  $I_{VV,NB}$  to the HRS intensity from a solution with nitrobenzene mole fraction  $x_{NB}$  and benzene mole fraction  $x_B = (1 - x_{NB})$ , based on this additive model, is

$$I_{VV,NB} = I_{VV,S} - x_B I_{VV,B}, \quad (8)$$

where  $I_{VV,S}$  is the HRS intensity measured for the solution and  $I_{VV,B}$  is the HRS intensity measured for neat benzene under the same conditions. This expression ignores the distinction between  $\rho F$  for the solution and for neat benzene, which is a good approximation for the dilute nitrobenzene solutions where the benzene contribution is the most significant. Similar expressions for ratios of the nitrobenzene HRS intensity contributions in the solution are

$$\left(\frac{I_{VV}}{I_{HV}}\right)_{NB} = \frac{(1-x)y}{1 - \frac{xy}{z}} \quad (9)$$

and

$$\left(\frac{I_{HV}}{I_{VH}}\right)_{NB} = \frac{(1-t)u}{1 - \frac{tu}{v}}, \quad (10)$$

where

$$x = x_B \frac{I_{VV,B}}{I_{VV,S}}, \quad (11)$$

$$y = \left(\frac{I_{VV}}{I_{HV}}\right)_S, \quad (12)$$

$$z = \left(\frac{I_{VV}}{I_{HV}}\right)_B, \quad (13)$$

$$t = \frac{xy}{z}, \quad (14)$$

$$u = \left(\frac{I_{HV}}{I_{VH}}\right)_S, \quad (15)$$

$$v = \left(\frac{I_{HV}}{I_{VH}}\right)_B. \quad (16)$$

### III. EXPERIMENT

The HRS experimental apparatus and methods are similar to those previously described.<sup>11,18,19</sup> Linearly polarized pulses from an injection-seeded single-longitudinal-mode

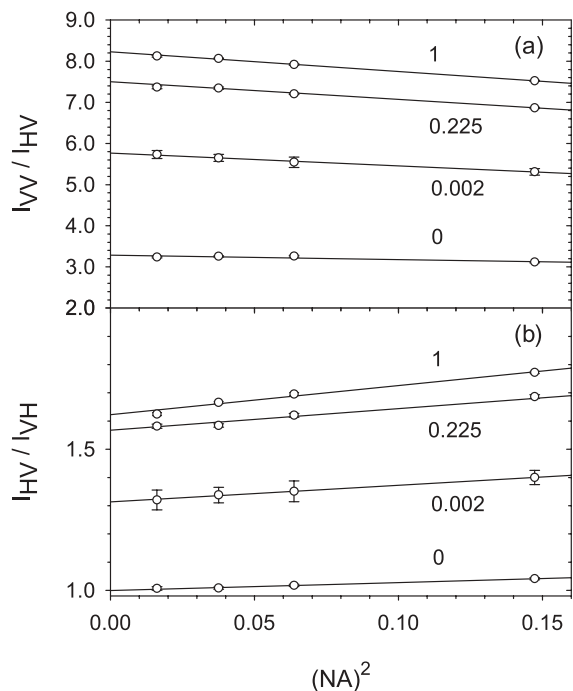


FIG. 1. Typical measurements of (a) VV/HV and (b) HV/VH for nitrobenzene-benzene solutions showing the extrapolation to  $NA = 0$ . The measurements are made with  $\Delta\nu = 0.3 \text{ cm}^{-1}$  for samples with  $x_{NB}$  as shown by the labels on the fitted lines.

Nd:YAG (yttrium aluminum garnet) laser (operating at  $\lambda = 1064 \text{ nm}$ , 4.3 kHz repetition rate, 100 ns pulse duration) are focused into the liquid sample contained in a 1 cm fused silica spectroscopic cuvette. Light scattered near the  $90^\circ$  scattering angle is collected and collimated by a lens, analyzed by a polarizing beam splitter, focused by another lens into an optical fiber, and fiber coupled to spectral filters and the photon counting detector. The sample temperature was  $T = 25.0 \text{ }^\circ\text{C}$  for all measurements, and the laser beam average power in the sample was typically  $P_{av} = 1.5 \text{ W}$ . The sample solutions were prepared from deuterated nitrobenzene ( $\text{C}_6\text{D}_5\text{NO}_2$ , Isotec, 99.5 at. % D), benzene ( $\text{C}_6\text{D}_6$ , Aldrich, 99.6 at. % D), and methanol ( $\text{CD}_3\text{OD}$ , Aldrich, 99.8 at. % D) to minimize thermal lens effects due to absorption of the laser beam. Thermal defocusing due to residual laser absorption by  $\text{C}_6\text{D}_6$  causes the normalized, dead-time corrected HRS photon count rate  $S_{\text{HRS}}/P_{av}^2$  to decrease ( $-2.4\%/W$ ), while self-focusing by  $\text{C}_6\text{D}_5\text{NO}_2$  causes  $S_{\text{HRS}}/P_{av}^2$  to increase ( $+3.5\%/W$ ). The reported HRS intensities are  $S_{\text{HRS}}/P_{av}^2$  extrapolated to  $P_{av} = 0$ .

To eliminate the effect of laser power fluctuations and drift, a typical experimental polarization ratio measurement consisted of HRS photon counts recorded for two different polarization configurations while alternating between the two configurations at 10 s intervals for several hundred cycles. Polarization ratio measurements were made with four values of the collection numerical aperture ( $NA = 0.127, 0.194, 0.253$ , and  $0.384$ ) and extrapolated to  $NA = 0$  using a function linear in  $NA^2$  fit to the data as shown in Fig. 1. One additional larger aperture stop had been used in the previous work<sup>11</sup> but better results are obtained by restricting the maximum aperture to eliminate the uncertainty in the effective  $NA$  due to lens aber-

ration. Spectral analysis was performed by an interference filter just before the detector to select a band centered at 532 nm with bandwidth  $\Delta\nu = 60 \text{ cm}^{-1}$  (FWHM, full width at half maximum) and a fiber-coupled, dual-etalon filter that was inserted to narrow the selected spectral band to  $0.3 \text{ cm}^{-1}$  (the average transmission of this filter outside the nominal pass-band was 6% of the peak transmission). Higher spectral resolution (13 MHz) was obtained by inserting a fiber-coupled, scanning confocal Fabry–Perot interferometer as previously described.<sup>18,19</sup>

The HRS intensities and polarization ratios were measured with a spectral bandwidth  $\Delta\nu = 0.3 \text{ cm}^{-1}$  to select the narrow central peak of the nitrobenzene HRS spectrum and minimize the contribution of the spectrally broad benzene HRS to the measured signal. However, the spectral width of the central peak increases as the nitrobenzene is diluted and the reduced transmission through the  $0.3 \text{ cm}^{-1}$  filter reduces the apparent intensity of the nitrobenzene HRS. The overlap of the HRS spectrum with the  $0.3 \text{ cm}^{-1}$  filter function was assessed by measuring the ratio of HRS signals with and without the filter inserted, normalized to the filter peak transmission measured in the same way using second harmonic light generated by a KTP (potassium titanyl phosphate) crystal. For each solution, the fraction of the nitrobenzene HRS spectrum that overlaps the  $0.3 \text{ cm}^{-1}$  filter function,  $T_{NB}$ , is given in terms of the measured values for the solution,  $T_S$ , and for neat benzene,  $T_B$ , by the expression

$$T_{NB} = \frac{T_S}{\left[1 + \left(1 - \frac{T_S}{T_B}\right) \frac{w}{(1-w)}\right]}, \quad (17)$$

where

$$w = \frac{I_{VV,B}}{I_{VV,S}}. \quad (18)$$

The longitudinal polar mode contribution due to dissolved ions was assessed by scanning the VH spectrum with 13 MHz resolution. The high resolution VH HRS spectrum consists of a narrow unresolved spike riding on a broad, flat background, where the spike is the longitudinal mode contribution induced by the ions.<sup>18</sup> The polarization ratio with the VH spike subtracted,  $(I_{HV}/I_{VH})_S$ , is given by the expression

$$\left(\frac{I_{HV}}{I_{VH}}\right)_S = \left[1 + \left(\frac{S}{B}\right)_{\text{VH}}\right] \left(\frac{I_{HV}}{I_{VH}}\right), \quad (19)$$

where  $(S/B)_{\text{VH}}$  is the relative integrated intensity of the VH spike and background and  $(I_{HV}/I_{VH})$  is the directly measured ratio for the solution.

## IV. RESULTS AND DISCUSSION

The first result of this work is the HRS measurement for a nitrobenzene–methanol solution ( $x_{NB} = 0.46$ , methanol volume fraction 0.32), intended to reproduce the observation by Chen and Wong from which it was concluded that the delocalized mode seen in nitrobenzene is destroyed by dilution with methanol at a volume ratio as small as 1:1.<sup>12</sup> The result  $I_{HV}/I_{VH} = 0.84 \pm 0.01$  from the present work is consistent with the result  $I_{HV}/I_{HH} = 0.89 \pm 0.21$  obtained

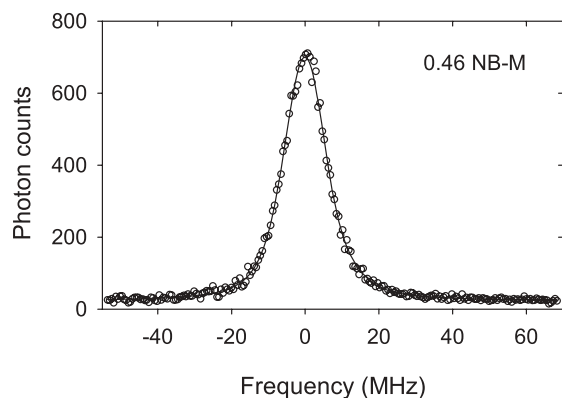


FIG. 2. High resolution VH HRS spectrum for  $x_{NB} = 0.46$  nitrobenzene-methanol solution showing the spike due to dissolved ions. The open circles are the data, while the fitted curve is the sum of a flat background and the scaled instrument response function (13 MHz FWHM) convolved with a Lorentzian broadening function ( $0.0 \pm 0.2$  MHz FWHM). The free spectral range of the Fabry-Perot interferometer is 750 MHz, and from this spectrum the relative integrated intensity of the spike and background is  $(S/B)_{VH} = 0.72 \pm 0.03$ .

from their work (0.5 methanol volume fraction,  $4 \text{ cm}^{-1}$  bandwidth, nonzero  $NA$ ). However, adding methanol allows dissociation of ionic impurities dissolved in the nitrobenzene. Figure 2 shows the narrow spike due to dissolved ions in the high resolution scan of the VH HRS spectrum for this solution. The observed VH spike intensity  $(S/B)_{VH} = 0.72 \pm 0.03$  can be accounted for by about  $10^{-5}$  M of dissociated ions. Subtracting the VH spike contribution using Eq. (19) gives  $(I_{HV}/I_{HH})_S = 1.44 \pm 0.03$ , close to the results for neat nitrobenzene.<sup>11,12</sup> It is most probable that the previous observations with nitrobenzene-methanol solutions were confounded by the appearance of the VH spike due to ions and do not indicate destruction of the delocalized mode by dilution as previously concluded.<sup>12</sup> An advantage of the nitrobenzene-benzene solutions used in the remainder of this work is that the nonpolar benzene suppresses dissociation of dissolved ionic impurities.

The results of the HRS measurements for nitrobenzene-benzene solutions are shown in Table I, and the results extracted for the nitrobenzene component of each solution using Eqs. (4), (5), (8)–(19) are shown in Table II. These experimental results are also plotted as functions of nitrobenzene

concentration in Fig. 3. The effect of the benzene HRS contribution is small for  $I_{VV}$  but large for  $I_{VV}/I_{HV}$  and  $I_{HV}/I_{VH}$  at  $x_{NB} < 0.01$ . With the benzene contribution subtracted, the experimental results for  $(I_{HV}/I_{VH})_{NB}$  in Fig. 3(c) clearly indicate that the nitrobenzene delocalized mode is present in even the most dilute solution studied. The nitrobenzene intermolecular distance is 5.5 nm for the most dilute solution (10 mM,  $x_{NB} = 0.001$ ), small compared to the 250 nm wavelength for the mode probed in this experiment (determined by the scattering wave vector).

The HRS data for  $I_{VV}$  can be fit by a simple model based on Eqs. (6) and (7), as shown by the curves in Fig. 3(a). Ignoring the frequency dependence of  $n$ , Eq. (7) for  $F$  reduces to  $F = L^6 T^3 / n$ , where  $n = 1.50005 + 0.06583x_{NB} - 0.01573x_{NB}^2$  is obtained from a fit to refractive index measurements for nitrobenzene-benzene solutions,<sup>20</sup> the Lorentz local field factor is  $L = (n^2 + 2)/3$ , and the Fresnel transmission factor for the solution interface with the fused silica cuvette is  $T = 1 - (n - 1.46)^2 / (n + 1.46)^2$ . Since volume is additive to within 0.2% for nitrobenzene-benzene solutions, an adequate expression for the molecular number density for the solution is  $\rho = (x_{NB}/\rho_{NB}^* + x_B/\rho_B^*)^{-1}$ , where  $\rho_{NB}^* = 9.74$  M and  $\rho_B^* = 10.00$  M are the densities for the neat liquids.<sup>21–23</sup> The HRS intensity for the solution is  $I_{VV,S} = I_{VV,B} + I_{VV,NB}$ , where the following expressions for  $I_{VV,B}$  and  $I_{VV,NB}$  are constructed to agree at  $x_{NB} = 0$  and 1 with the measured HRS intensities for the neat liquids,  $I_{VV,B}^*$  and  $I_{VV,NB}^*$ , respectively:

$$I_{VV,B} = \left( \frac{x_B \rho}{\rho_B^*} \right) \left( \frac{F}{F(x_{NB} = 0)} \right) I_{VV,B}^*, \quad (20)$$

$$I_{VV,NB} = \left( \frac{x_{NB} \rho}{\rho_{NB}^*} \right) \left( \frac{F}{F(x_{NB} = 1)} \right) \left( \frac{T_{NB}}{T_{NB}(x_{NB} = 1)} \right) \times \left( \frac{1 + c_1 x_{NB}}{1 + c_1} \right) I_{VV,NB}^*. \quad (21)$$

The expression for  $I_{VV,NB}$  differs from Eq. (6) by the introduction of two factors. The factor containing  $T_{NB}$  simply accounts for the variation of the apparent HRS intensity due to the change in spectral width and transmitted

TABLE I. HRS measurements for  $C_6D_5NO_2 / C_6D_6$  solutions with  $\Delta\nu = 0.3 \text{ cm}^{-1}$ . The polarization ratios  $I_{VV}/I_{HV}$  and  $I_{HV}/I_{VH}$  are the measurements extrapolated to  $NA = 0$ , while  $I_{VV}$ ,  $T_{VV}$ , and  $(S/B)_{VH}$  are the values measured with  $NA = 0.253$ .

$x_{NB}$ (%)	$I_{VV}$ ( $\text{s}^{-1} \text{ W}^{-2}$ )	$T_{VV}$	$I_{VV}/I_{HV}$	$I_{HV}/I_{VH}$	$(S/B)_{VH}$ (%)
0	$0.37 \pm 0.01$	$0.073 \pm 0.002$	$3.285 \pm 0.022^a$ $3.287 \pm 0.070$	$0.999 \pm 0.004^a$	$0.0 \pm 0.1$
0.10	$1.01 \pm 0.03$	$0.128 \pm 0.002$	$4.974 \pm 0.083$	$1.195 \pm 0.023$	–
0.20	$1.94 \pm 0.04$	$0.167 \pm 0.004$	$5.768 \pm 0.079$	$1.314 \pm 0.026$	–
0.60	$4.42 \pm 0.06$	$0.193 \pm 0.002$	$6.236 \pm 0.062$	$1.400 \pm 0.013$	–
2.5	$18.0 \pm 0.2$	$0.233 \pm 0.002$	$6.816 \pm 0.044$	$1.474 \pm 0.014$	$0.0 \pm 0.6$
6.1	$50.7 \pm 0.6$	$0.257 \pm 0.002$	$7.054 \pm 0.041$	$1.499 \pm 0.011$	$0.0 \pm 0.3$
22.5	$259 \pm 3$	$0.323 \pm 0.002$	$7.470 \pm 0.018$	$1.563 \pm 0.008$	$0.2 \pm 0.3$
100	$2570 \pm 26$	$0.529 \pm 0.001$	$8.228 \pm 0.013^b$	$1.622 \pm 0.009^b$	$2.2 \pm 0.2^b$

<sup>a</sup>Measured with  $\Delta\nu = 60 \text{ cm}^{-1}$ .

<sup>b</sup>Reanalyzed data from Ref. 11.

TABLE II. The  $C_6D_5NO_2$  contributions to the HRS results for  $C_6D_5NO_2 / C_6D_6$  solutions.

$x_{NB}$ (%)	$I_{VV,NB}$ ( $s^{-1} W^{-2}$ )	$T_{VV,NB}$	$(I_{VV}/I_{HV})_{NB}$	$(I_{HV}/I_{VH})_{NB}$	$(A_0/A_T)_{NB}$	$(A_L/A_T)_{NB}$
0.10	$0.64 \pm 0.03$	$0.229 \pm 0.008$	$7.077 \pm 0.341$	$1.579 \pm 0.106$	$0.469 \pm 0.090$	$-0.08 \pm 0.14$
0.20	$1.57 \pm 0.05$	$0.235 \pm 0.006$	$7.025 \pm 0.164$	$1.562 \pm 0.059$	$0.483 \pm 0.044$	$-0.07 \pm 0.08$
0.60	$4.05 \pm 0.06$	$0.227 \pm 0.003$	$6.793 \pm 0.084$	$1.514 \pm 0.019$	$0.548 \pm 0.025$	$-0.05 \pm 0.03$
2.5	$17.6 \pm 0.2$	$0.244 \pm 0.002$	$6.970 \pm 0.047$	$1.505 \pm 0.018$	$0.498 \pm 0.013$	$-0.01 \pm 0.03$
6.1	$50.4 \pm 0.6$	$0.262 \pm 0.002$	$7.110 \pm 0.042$	$1.510 \pm 0.013$	$0.461 \pm 0.011$	$0.01 \pm 0.02$
22.5	$259 \pm 3$	$0.324 \pm 0.002$	$7.480 \pm 0.018$	$1.569 \pm 0.009$	$0.370 \pm 0.004$	$0.006 \pm 0.010$
100	$2570 \pm 26$	$0.529 \pm 0.001$	$8.228 \pm 0.013$	$1.659 \pm 0.009$	$0.218 \pm 0.002$	$0.033 \pm 0.008$

fraction for the nitrobenzene HRS peak. The function  $T_{NB} = 0.2305 + 0.4585x_{NB} - 0.1596x_{NB}^2$  is a fit to the measurements in Table II. An earlier depolarized light scattering study of nitrobenzene–benzene solutions found nitrobenzene spectral widths consistent with  $T_{NB}$  measured in this work and also found negligible benzene spectral width variation.<sup>24</sup>

The factor in Eq. (21) containing the adjustable parameter  $c_1$  represents the only essential deviation from Eq. (6). It is included since the HRS intensity observed for neat nitrobenzene is 35% higher than predicted by extrapolation of dilute solution values using Eq. (6). Including this factor gives an excess intensity proportional to the number of nearest neighbor nitrobenzene molecules and accounts for the effect of short range correlations and interactions between the molecules. The parameter value  $c_1 = 0.35$  results in good agreement between the calculated curves and the measurements, as seen in Fig. 3(a) and suggests that the local interaction effects become negligible for  $x_{NB} < 0.1$ .

The fit function Eq. (21) was derived assuming incoherent HRS from independent randomly oriented molecules except at the highest nitrobenzene concentration, and the nearly linear intensity variation with nitrobenzene concentration for this fit function is consistent with the  $I_{VV,NB}$  observations. However, this does not rule out HRS from nitrobenzene molecules with long range orientation correlations. For example, nearly linear concentration dependence for  $I_{VV,NB}$  would also result if the correlation volume varied inversely with nitrobenzene concentration so that the number of nitrobenzene molecules in the correlation volume remained constant. Such orientation correlations would also account for the concentration-independent enhancement of  $(I_{VV}/I_{HV})_{NB}$  and  $(I_{HV}/I_{VH})_{NB}$  as seen in Figs. 3(b) and 3(c).

Continuing the analysis, a good fit to the  $A_0/A_T$  measurements shown in Fig. 3(d) is obtained using the function

$$\frac{A_0}{A_T} = c_2 \left( \frac{T_{NB}(x_{NB} = 1)}{T_{NB}} \right) \quad (22)$$

with parameter value  $c_2 = 0.222$ . Due to the choice  $P^2 = 1.5$  and  $R^2 = 9.7$  in the evaluation of Eq. (4),  $A_0$  measures HRS from octupolar  $\beta^{(3)}$  and  $A_T$  measures HRS from dipolar  $\beta^{(1)}$ . Equation (22) is obtained if short range interactions and correlations between nitrobenzene molecules result in narrowing of the dipolar spectrum but not the octupolar spectrum as  $x_{NB}$  increases, so that the increased transmission through

the  $0.3 \text{ cm}^{-1}$  filter for the dipolar spectrum causes a decrease in  $A_0/A_T$ . (Since  $T_{NB}$  is obtained from the measurements of  $I_{VV,NB}$  which is dominated by the  $A_T$  contribution, it is essentially a measure of the transmission for the dipolar spectrum.)

The  $A_L/A_T$  measurements shown in Fig. 3(d) are insignificantly different from zero except for neat nitrobenzene and are fit by a function

$$\frac{A_L}{A_T} = c_3 x_{NB} \quad (23)$$

with  $c_3 = 0.03$ . The deviation from  $A_L = 0$  at the highest nitrobenzene concentration is interpreted as nearest neighbor interactions beginning to disrupt the long range correlations.

The curves for  $I_{VV}/I_{HV}$  and  $I_{HV}/I_{VH}$  calculated using the above model are in good agreement with the corresponding measurements, as shown in Figs. 3(b) and 3(c). The curves for  $(I_{VV}/I_{HV})_{NB}$  and  $(I_{HV}/I_{VH})_{NB}$  were calculated using Eqs. (1)–(3) with the fit functions given by Eqs. (22) and (23) for  $(A_0/A_T)_{NB}$  and  $(A_L/A_T)_{NB}$ . The calculations for  $(I_{VV}/I_{HV})_S$  and  $(I_{HV}/I_{VH})_S$  also used the fitted functions for  $I_{VV,NB}$  and  $I_{VV,B}$  given by Eqs. (21) and (20) and the measured values for  $(I_{VV}/I_{HV})_B$  and  $(I_{HV}/I_{VH})_B$ . The effects of HRS from the benzene solvent and spectral narrowing of the nitrobenzene peak cause  $I_{VV}/I_{HV}$  and  $I_{HV}/I_{VH}$  to vary with  $x_{NB}$  but the strength of the transverse polar mode in the model is independent of  $x_{NB}$ .

The vector part of  $\beta$  transforms just like the dipole moment of a polar molecule, so an explanation for the near zero contribution of the longitudinal mode to the HRS peak is suggested by considering theoretical results for the dielectric properties of a dense fluid of nonpolarizable dipolar molecules with number density  $\rho$  and dipole moment  $\mu$ .<sup>25</sup> The pair distribution function for the dipolar molecules can be expressed as the sum of a function  $g^S$  including short range orientation correlations extending only a few molecular diameters and a function  $g^L$  including only the long range correlations due to dipole–dipole interactions. For wavevector  $k \rightarrow 0$ , large static permittivity  $\epsilon(0)$ , and  $g^S = 1$ , the mean square transverse and longitudinal Fourier components of the sample dipole moment density are  $\langle |M_X(\mathbf{k})|^2 \rangle = \frac{1}{2} \rho \mu^2$  and  $\langle |M_Z(\mathbf{k})|^2 \rangle = \frac{1}{2} \rho \mu^2 / \epsilon(0)$ , and in the rotational diffusion limit the transverse and longitudinal relaxation times are  $\tau_D$  and  $\tau_D / \epsilon(0)$ , respectively, where  $\tau_D$  is the Debye relaxation time.<sup>25</sup> The dipoles in the liquid are arranged as large amplitude transverse modes and small amplitude longitudinal modes due to the long range dipole–dipole interactions and

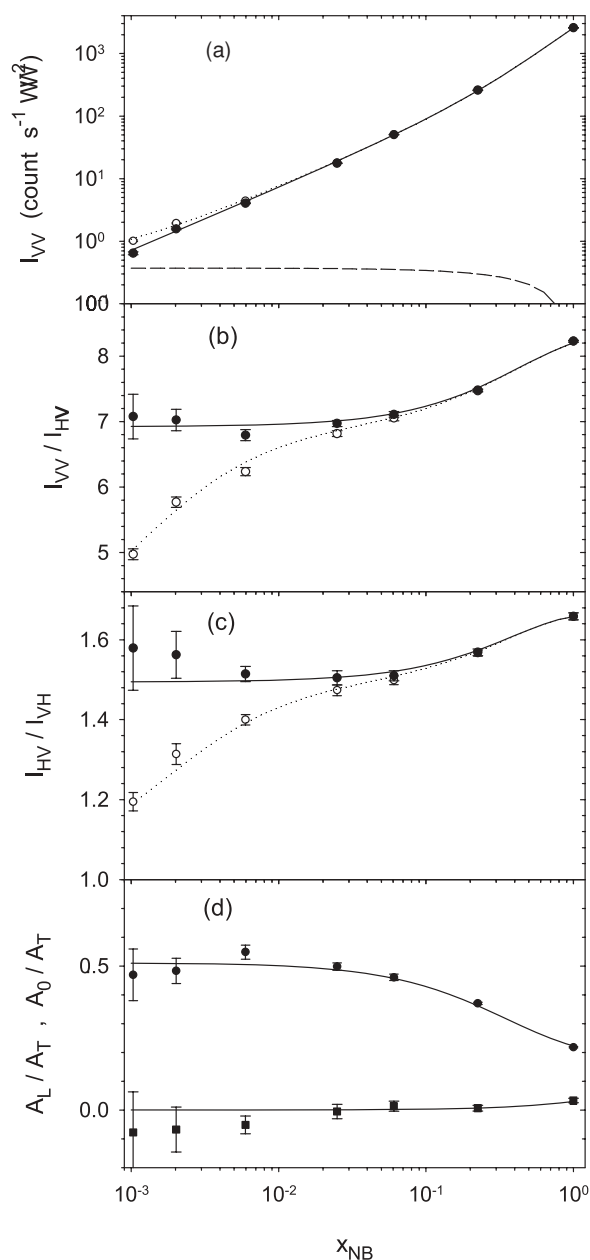


FIG. 3. (a) HRS intensity, (b), (c) polarization ratios, and (d) local and delocalized mode intensity ratios from Tables I and II are plotted versus nitrobenzene mole fraction. The HRS measurements for nitrobenzene-benzene solutions are shown by the open circles, while the contributions due to the nitrobenzene molecules in the solution are shown by the filled symbols. The calculated results for the nitrobenzene and benzene components and for the solution are shown by the solid, dashed and dotted curves, respectively. In (c) the VH spike contribution due to ionic contamination has been subtracted from the solution measurements and in (d) the  $A_0/A_T$  and  $A_L/A_T$  measurements are plotted as filled circles and squares, respectively.

the temporal fluctuations result in a narrow spectral peak for the transverse modes and a much broader peak for the longitudinal modes. This theory suggests  $A_L/A_T = 1/\epsilon(0)$  for the HRS integrated intensity and  $A_L/A_T \approx 1/\epsilon^2(0)$  for the measurements made with a narrow spectral bandwidth which discriminates against the  $A_L$  contribution. For neat nitrobenzene where  $\epsilon(0) = 35$ ,<sup>23</sup> the predicted range  $0.001 < A_L/A_T < 0.03$  is close to the observed value  $0.033 \pm 0.008$ . However, for dilute nitrobenzene-benzene solutions where  $\epsilon(0)$  is

close to the value  $\epsilon(0) = 2.27$  for neat benzene,<sup>23</sup> the predicted range  $0.2 < A_L/A_T < 0.4$  is inconsistent with the observed result  $A_L/A_T < 0.03$ . The theoretical results for a pure fluid of rigid dipoles without short range orientation correlations may be correct but inapplicable in the case of a real liquid solution of polar and nonpolar polarizable molecules.

Polar liquids remain a difficult theoretical problem due to the anisotropy and long range of the dipole interaction. An unresolved problem of long standing is the possibility of orientationally ordered states of dipolar liquids, such as the ferroelectric phase for the Stockmayer and other model dipolar fluids found in some but not all theoretical calculations and simulations.<sup>26</sup> Short range correlations may have a decisive effect on the existence of such ordered states.<sup>26</sup> Conversely, standard continuum electrostatic treatments of liquid dielectrics may fail since they do not properly account for the long range transverse correlations between dipoles in molecular liquids and the consequent nonlocality of the microscopic material response.<sup>27</sup>

## V. SUMMARY

The observed density dependence of the HRS intensity for nitrobenzene-benzene solutions is consistent with an expression derived assuming incoherent HRS from independent randomly oriented molecules, with small deviations appearing at the highest nitrobenzene concentrations. However, the observed density dependence does not rule out HRS from molecules with long range orientation correlations. Furthermore, the observed polarization dependence of HRS from nitrobenzene-benzene solutions is not consistent with randomly oriented molecules or molecules with only local orientation correlations. The HRS observations support a model where the dipole-dipole interactions in polar liquids result in long range transverse orientation correlations of the molecules which are impressed on HRS from the vector term  $\beta^{(1)}$  but do not affect HRS from the octupolar term  $\beta^{(3)}$ . The model fitting the observations indicates that the transverse polar orientation correlation of the nitrobenzene molecules is undiminished by dilution to 0.001 mole fraction nitrobenzene.

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