Hyper-Rayleigh scattering spectrum of liquid nitromethane

David P. Shelton[a)]

Department of Physics, University of Nevada Las Vegas, Las Vegas, Nevada 89154-4002

The vertical vertical (VV), horizontal vertical (HV), and vertical horizontal (VH) hyper-Rayleigh scattering (HRS) spectra were measured for liquid CH_3NO_2 at $T = 300$ K. The main HRS spectral component has a width $\nu_1 = 1.28 \pm 0.04$ cm^{-1}, which gives an orientation relaxation time $\tau = 4.1 \pm 0.1$ ps in good agreement with other experiments. However, the VH spectrum also contains a previously unobserved strong narrow peak at zero-frequency shift, absent from the VV and HV spectra, which is due to a slowly relaxing longitudinal orientation mode. The upper bound on the width of this peak is 5 MHz, which corresponds to a relaxation time $\tau > 30$ ns. © *2005 American Institute of Physics.* [DOI: 10.1063/1.2036974]

Recent hyper-Rayleigh scattering (HRS) experiments studying liquid water[1,2] and acetonitrile[3,4] found a narrow peak in the depolarized vertical horizontal (VH) HRS spectrum which is absent from the vertical vertical (VV) and horizontal vertical (HV) HRS spectra. It is suggested that this narrow peak is due to long-lived polar domains, and that such domains may be present in any dipolar liquid for which $\rho\mu_0^2 > 9\varepsilon_0 kT = 49$ D^2 M at $T = 300$ K.[3] A survey of dipolar liquids is needed to determine the prevalence of this phenomenon. Nitromethane is a liquid composed of small molecules with a large dipole moment ($\mu_0 = 3.46$ D), where the dipole density $\rho\mu_0^2 = 224$ D^2 M exceeds the predicted threshold for the formation of polar domains.[5] The first motivation for the present measurements of the HRS spectrum of nitromethane is to find whether the predicted narrow peak is present in the VH spectrum. If this peak due to the conjectured polar domains is observable, then one also expects that the hyperpolarizability tensor β will contain a large dipolar irreducible tensor part. However, previous HRS measurements for nitromethane found a low value for the polarization ratio I_{VV}/I_{HV}, which appears to be incompatible with a large first-rank irreducible spherical tensor part for β.[6] The second motivation for studying nitromethane is to try to understand this apparent discrepancy. To address these questions the HRS spectra for nitromethane were measured with VV, HV, and VH polarizations over wide and narrow frequency scans at low and high resolutions.

The apparatus was the same as previously described.[1–3] The beam from an injection-seeded, single longitudinal mode, pulsed Nd: yttrium aluminum garnet (YAG) laser at $\lambda = 1064$ nm was focused into the liquid sample contained in a 1-cm fused silica fluorimeter cuvette placed in a thermostatic enclosure at $T = 27.0\,^\circ$C. The scattered light near $\theta = 90^\circ$ and $\lambda = 532$ nm was collected with a $f/1.8$ lens and analyzed by a grating spectrometer with calibrated spectral response. A confocal Fabry-Perot interferometer with 1.0-GHz free spectral range (FSR) was added in series with the grating spectrometer for the highest resolution measure-

ments. The incident beam in the sample had a waist diameter of 6 μm, and the pulses had a 2.2-kHz repetition rate, 90-ns duration, and 0.6-mJ energy. Strong focusing of the laser beam reduces thermal lensing, allows better coupling to the Fabry-Perot, and prevents damage at the cell windows, but increases the peak intensity at the focus to 50 GW/cm^2. The spectrophotometric grade samples were filtered through a 0.2-μm micropore filter. The polarization of the incident laser beam was controlled using a prism polarizer and an electronically controlled liquid-crystal wave plate, while the polarization of the collected light was analyzed using a sheet polarizer mounted to allow the polarization axis to be rotated rapidly by 90°. A liquid-crystal 45° rotator placed between the analyzing polarizer and the grating spectrometer equalized the response for H and V polarizations. The measured deviations from constant response were less than 5% for both polarizations over the 100-cm^{-1} spectral range used in this work. The measured spectra were corrected for the instrument response and the polarization mixing[2,7] due to the finite collection angle. The grating spectrometer scans were made in multiple pairs, VV and HV or VH and HV, with the HV scans serving as the common reference. For the Fabry-Perot measurements the VH HRS spectrum and the reference spectrum of the second-harmonic light generated in a potassium titanyl phosphate (KTP) crystal were recorded on alternate scans of the interferometer. The peak HRS count rate for the grating spectrometer scans was in the range of 0.2-3 counts/s, while it was 0.05 counts/s with the Fabry-Perot. The background due to the gated photomultiplier dark count rate was 9×10^{-4} counts/s.

The results of the grating spectrometer scans are shown in Fig. 1, where intensity is plotted as a function of the frequency shift ν from the second harmonic of the laser (the Stokes side of the spectrum is shown with a negative frequency shift). Figure 1(c) clearly shows that there is a narrow peak in the VH HRS spectrum of nitromethane. The analysis of the spectra in Fig. 1 is modeled on the analysis of the HRS spectra previously measured for water and acetonitrile.[2,3] For each polarization the spectrum is represented as the sum of four components of the form

---
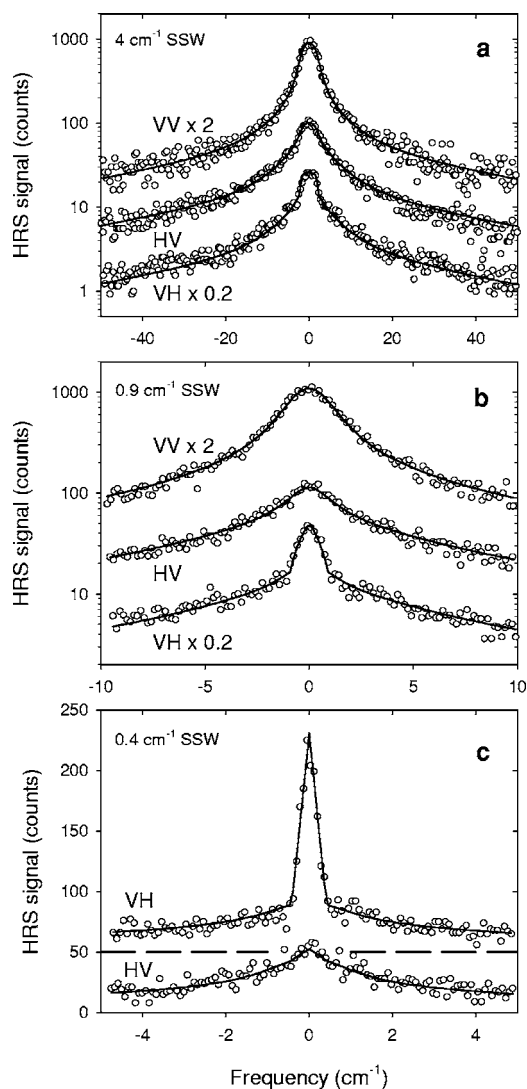[a)]Electronic mail: shelton@physics.unlv.edu

123, 111103-1

FIG. 1. VV, HV, and VH HRS spectra for nitromethane at $T=27.0\,^{\circ}$C scanned at successively higher resolution [spectral slit width (SSW), full width at half maximum (FWHM)]. In panels a and b the VV spectra are shifted up by a factor of 2 and the VH spectra are shifted down by a factor of 5 for clarity. In panel c the VH spectrum is shifted up by 50 counts and the baseline for the VH spectrum is shown by the dashed line. The curves are the simultaneous fit of Eqs. (1) and (2a)–(2d) to all the spectra.

$$I(\nu) = A/[1 + (\nu/\nu_1)^2] + B/[1 + (\nu/\nu_2)^2]$$
$$+ C\exp[-|\nu/\nu_3|] + D\delta(\nu), \qquad (1)$$

where the intensity coefficients are assumed to obey the relations

$$aA_{VV} = A_{HV} = bA_{VH}, \qquad (2a)$$

$$cB_{VV} = B_{HV} = B_{VH}, \qquad (2b)$$

$$cC_{VV} = C_{HV} = C_{VH}, \qquad (2c)$$

$$D_{VV} = D_{HV} = 0, \qquad (2d)$$

and the frequencies $\nu_1, \nu_2,$ and ν_3 are independent of polarization. The A term is due to isotropic and transverse reorientation modes, the B and C terms are due to short-duration intermolecular collisions, and the D term is the narrow peak due to slow longitudinal reorientation. To obtain a spectrum which may be directly compared with the measured spectrum, Eq. (1) is multiplied by the factor $(\nu_s/\nu_0)^3 \times \exp(-hc\nu/2kT)$, where ν_s and ν_0 are the scattered and incident light frequencies, multiplied by the instrumental response function (accounting for frequency dependence of the instrument frequency band pass, transmission, and detection efficiency) and convolved with the trapezoidal or triangular instrument function. Finally, the mixing of the VV, HV, and VH spectra is accounted for, and the detector background is added. The largest polarization mixing effects due to the finite collection angle are an increase by 3% for the A_{HV} term and mixing 5% of the D_{VH} term into the VV and HV spectra. All the spectra in Fig. 1 were simultaneously fitted with Eqs. (1) and (2a)–(2d) modified by these instrumental effects, giving the fit parameters shown in Table I and the curves shown in Fig. 1.

Table I shows that $A_{VV}/A_{HV}=7.8\pm0.3$, close to the dipolar limit of 9, indicating that β is dominated by its dipolar irreducible tensor part. This is similar to the results for water and acetonitrile where $A_{VV}/A_{HV}=8.46$ and 9.2 ± 0.1, respectively.[2,4] The ratio $A_{HV}/A_{VH}=1.25\pm0.07$ for nitromethane is close to the value 1 for isotropic modes and indicates that the transverse-mode contribution is only 25%. The orientation relaxation time corresponding to the Lorentzian width $\nu_1=1.28\pm0.04$ cm^{-1} for this mode is $\tau=4.1\pm0.1$ ps, in good agreement with $\tau=3.8$ ps obtained from dielectric relaxation and depolarized Rayleigh experiments.[8] The normalized integrated intensity D for the narrow VH peak in nitromethane is eight times larger than the corresponding value for acetonitrile.[3] Table I shows that the B and C terms representing the collision-induced spectrum account for more than 60% of the VV integrated intensity and almost 90% of the HV and VH integrated intensities for nitromethane. Table II shows that the width, shape, and polarization of the collision-induced HRS

TABLE I. HRS spectral fit parameters for Eqs. (1) and (2a)–(2d) for liquid nitromethane at $T=27.0\,^{\circ}$C. The intensities are normalized to the HV intensity for the A term.

		Peak intensity			Integrated intensity		
	ν_i(cm^{-1})	VV	HV	VH	VV	HV	VH
A	1.28 ± 0.04	7.8 ± 0.3	1	0.80 ± 0.05	7.8 ± 0.3	1	0.80 ± 0.05
B	6.6 ± 0.3	0.99 ± 0.06	0.56 ± 0.03	0.56 ± 0.03	5.1 ± 0.4	2.9 ± 0.2	2.9 ± 0.2
C	51 ± 5	0.34 ± 0.04	0.19 ± 0.02	0.19 ± 0.02	8.5 ± 1.3	4.8 ± 0.7	4.8 ± 0.7
D	<0.0002	0	0	>3000	0	0	0.53 ± 0.03

TABLE II. Comparison of collision-induced HRS spectral fit parameters for several liquids.

Molecule	$\nu_2(cm^{-1})$	$\nu_3(cm^{-1})$	C/B	B_{VV}/B_{HV}	B/A
CH_3NO_2[a]	6.6±0.3	51±5	0.34±0.4	1.79±0.03	0.55±0.03
D_2O[b]	8.8	70	0.30	2.32	0.018±0.002
C_2Cl_4[c]	6.1±0.7	69±13	0.64±0.08	3.5±0.2	⋯
CH_3CN	⋯	35,[c] 55[d]	⋯	3.5,[c] 4[d]	0.031±0.004[c]

[a]This work.
[b]Reference 2.
[c]Reference 3.
[d]Reference 4.

spectrum for nitromethane are similar to that measured for other molecules, but the relative intensity is 20 times larger. The low value 3.0±0.1 of the previous VV/HV polarization ratio measurement is accounted for by the strong collision-induced contribution within the 25-cm^{-1} spectral window for that measurement.[6]

Figure 2 shows the result of scanning the VH HRS spectrum with the Fabry-Perot interferometer (the grating spectrometer served as a prefilter selecting a spectral interval of 1.6 cm^{-1}=48×FSR)). The HRS spectrum was fitted by the sum of a flat background and the convolution of the reference spectrum with a narrow Lorentzian $\{f(\nu) = [1+(\nu/\nu_4)^2]^{-1}\}$. The best fit is obtained with a Lorentzian of zero width, as shown by the curve in Fig. 2. At the 99% confidence level the Lorentzian width is $\nu_4 < 5$ MHz, with corresponding relaxation time $\tau > 30$ ns. This is an unexpectedly long time for reorientation of molecules in room-temperature liquid nitromethane. Based on the fit parameters in Table I, the narrow D component comprises 48% of the VH HRS light within the central 1.6-cm^{-1} interval. As a check for artifacts, the peak in Fig. 2 is expected to be 19 times higher than the HRS background when the Fabry-Perot transmission function is taken into account, which is in good agreement with the observed result. The HRS spectrum
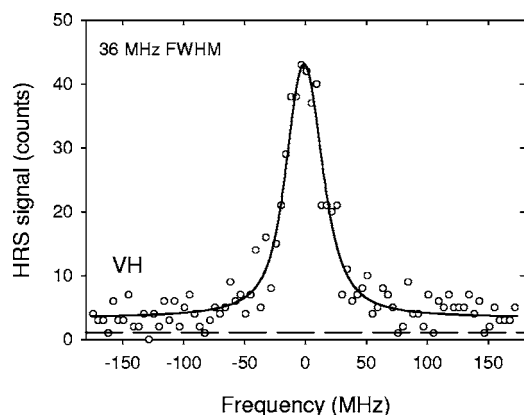

FIG. 2. VH HRS spectrum for nitromethane at $T=27.0\,^\circ$C scanned with 36-MHz resolution (FWHM). The fitted curve is the sum of the instrument spectral response function and a constant background. The dashed line marks the level of the background due to the detector dark count rate.

clearly shows that a slowly relaxing longitudinal mode attributed to polar domains is present in nitromethane.

A puzzling result is the low intensity of the nitromethane HRS spectrum compared with that for acetonitrile. Previous measurements found that the VV HRS integrated intensity is 4.4 times larger for acetonitrile, from which it is estimated that $|\beta|$ is 2.2 times larger for acetonitrile in the liquid phase.[9] However, the gas phase value for β measured by electric-field-induced second harmonic (EFISH) is 1.9 times larger for nitromethane and has the opposite sign (with respect to μ_0).[9] The gas phase values of the dipole moment μ_0 and hyperpolarizability γ, the number density of the liquid ρ, and the product $\mu_0\gamma\rho$, all differ by less than 10% between nitromethane and acetonitrile.[9] In the liquid the field F due to the other molecules will induce an increment γF in β, and if there are orientation correlations between the molecules the average value of β will be shifted by an increment approximately proportional to $\mu_0\gamma\rho$. Due to the different sign for β in gas phase nitromethane, the same increment $\Delta\beta$ which will double β for acetonitrile will also halve β for nitromethane, which would account for the observed liquid HRS intensities. Short-range orientation correlations are sufficient for this effect. This effect is seen in detailed calculations for water, and in that case the increment $\Delta\beta$ is twice as large as β.[10]

The main result of this work is the observation of a strong narrow peak in the VH HRS spectrum of nitromethane, similar to that already observed in water and acetonitrile. This narrow peak may be due to long-lived polar domains in the liquid.

[1] D. P Shelton, Phys. Rev. B **72**, 020201 (2005).
[2] D. P. Shelton, J. Chem. Phys. **117**, 9374 (2002); **121**, 3349(E) (2004).
[3] D. P. Shelton, J. Chem. Phys. **123**, 084502 (2005).
[4] D. P. Shelton and P. Kaatz, Phys. Rev. Lett. **84**, 1224 (2000).
[5] R. C. Weast, *CRC Handbook of Chemistry and Physics*, 68th ed. (CRC, Boca Raton, 1987).
[6] D. P. Shelton, Chem. Phys. Lett. **325**, 513 (2000).
[7] D. P. Shelton, J. Opt. Soc. Am. B **17**, 2032 (2000).
[8] M. G. Giorgini, P. Foggi, R. S. Cataliotti, M. R. Distefano, A. Morresi, and L. Mariani, J. Chem. Phys. **102**, 8763 (1995).
[9] P. Kaatz, E. A. Donley, and D. P. Shelton, J. Chem. Phys. **108**, 849 (1998).
[10] A. V. Gubskaya and P. G. Kusalik, Mol. Phys. **99**, 1107 (2001).