Librons Observed in Liquid Acetonitrile by Hyper-Rayleigh Scattering

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Hyper-Rayleigh scattering intensity ratios I_{VV}/I_{VH} in the range 9–26 are observed for liquid acetonitrile (CH_3CN), inconsistent with localized modes of motion in an isotropic fluid. The observations are consistent with propagating orientational modes (librons) with frequency $\nu = 2$ cm^{-1}, which scatter 71% of the light.

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Hyper-Rayleigh scattering (HRS) has recently become one of the principal methods for measuring the nonlinear optical properties of molecules in solution [1]. In this method the intensity of frequency-doubled light scattered from a liquid sample is measured, and the magnitude of the molecular first hyperpolarizability β is obtained based on the assumption that the molecules are randomly oriented. While this assumption may be justified for a dilute solution of strong chromophores, for pure liquids orientational correlation between molecules can alter the HRS intensity by a large factor [2]. This sensitivity to orientational correlation is a problem for accurate hyperpolarizability determinations, but it makes HRS a potentially powerful tool in the study of the molecular dynamics of fluids.

The usual picture of the molecular motions in simple liquids is that of local modes, where molecular position and orientation correlations extend over only a few molecular diameters, and vibrations are just perturbed versions of the normal modes of the molecules in the gas phase. However, the compressional sound waves (longitudinal acoustic phonons) observed in Brillouin spectroscopy are widely recognized collective modes of molecular motion in liquids [3], and linear light scattering experiments have also observed shear waves (transverse acoustic phonons) in viscous liquids [4]. Furthermore, the polar vibrational excitations in molecular fluids have been shown by hyper-Raman scattering experiments to have a strongly delocalized character [5]. Collective modes of molecular reorientation have not been observed in simple liquids even though both diffusive and propagating hydrodynamic modes of condensed matter systems are allowed [6].

In this Letter we present HRS measurements which show that molecular orientation in liquid acetonitrile has a delocalized, collective mode (libron) which coexists with the localized orientational diffusion mode. This mode is analogous to spin waves in magnetic materials or propagating director distortions in liquid crystals. The support for this conclusion comes from observations of the variation of HRS intensity with light polarization and scattering angle, which are consistent with delocalized modes but not localized modes.

The experimental apparatus and methods used in this work have been previously described [7]. The beam from a pulsed Nd:YAG laser operating at $\lambda = 1064$ nm is focused into a filtered sample of liquid acetonitrile contained in a fused silica fluorimeter cuvette, and the scattered light near $\lambda = 532$ nm is collected and analyzed with a grating spectrometer. The polarization of the incident laser beam is controlled using a prism polarizer and a Babinet-Soleil compensator, while the polarization of the collected light is analyzed using a sheet polarizer (in some cases the polarizer was followed by a quartz wedge polarization scrambler). The scattering geometry is defined in Fig. 1, and the HRS spectrum is shown in Fig. 2. The HRS spectrum has a strong narrow central peak and broad weak wings. This work focuses on the central peak. Measurements were made at two scattering angles, $\theta = 90°$ and $45°$, using standard 1 cm cuvettes with square and triangular cross sections, respectively. The HRS polarization ratios are corrected for the effects of finite collection angle (0.2 sr), polarizer extinction ratio, and spectrometer polarization selectivity. The finite collection angle corrections are weakly dependent on the assumed form of the angular dependence of the HRS intensity. The corrections increase the polarization ratios by no more than 15%, 5%, and 10% for I_{VV}/I_{HV}, I_{VV}/I_{VH}, and I_{VV}/I_{HH}, respectively.
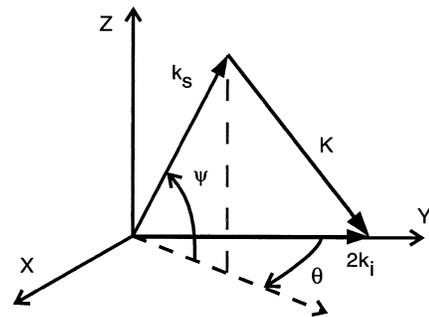
FIG. 1. Laser light with wave vector $\mathbf{k}_i$ is incident along Y, and scattered light with wave vector $\mathbf{k}_s$ is collected close to the X-Y plane. The incident polarization vector is along Z or X (V or H polarized). A component of the scattered light is selected with polarization either in the $\mathbf{k}_s$-Z plane (V polarized) or parallel to the X-Y plane (H polarized). The polarization combinations considered are labeled VV, HV, VH, and HH, where the incident polarization is given by the first letter and the scattered polarization is given by the second letter.
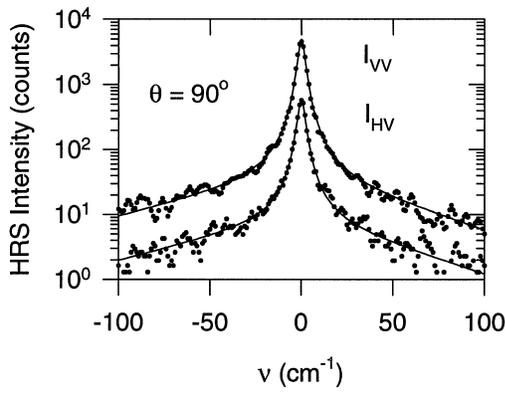
FIG. 2. HRS spectral intensity for CH_3CN is plotted versus frequency difference ν measured from the laser second harmonic frequency $2\nu_0 = 18\,800$ cm^{-1}, and the fits are performed as previously described [7]. The fitted curves are the sum of a Lorentzian with 4 cm^{-1} full width at half maximum, and an exponential profile with slope parameter 55 cm^{-1}. The Lorentzian component accounts for 90% (80%) of the integrated intensity of the VV (HV) spectrum.

The polarization and angular dependence of HRS from a collection of randomly oriented molecules is summarized in the first columns of Table I. For the polarization geometries used here, $\langle \beta_{ZZZ}^2 \rangle$ and $\langle \beta_{XZZ}^2 \rangle$ are the only two observables [8]. The quantity $\langle \beta_{JKL}^2 \rangle$ is the ensemble average of a space-fixed component of the molecular β tensor, and can be expressed in terms of the molecule-fixed components of β. For scattering in the X-Y plane the intensities I_{VV}, I_{HV}, and I_{VH} are independent of scattering angle, and $I_{VV}/I_{HV} = I_{VV}/I_{VH} = \langle \beta_{ZZZ}^2 \rangle / \langle \beta_{XZZ}^2 \rangle$. The ratio $P^2 \equiv \langle \beta_{ZZZ}^2 \rangle / \langle \beta_{XZZ}^2 \rangle$ is restricted to the range $3/2 \leq P^2 \leq 9$. This can be seen by expressing β as the sum of first and third rank irreducible spherical tensors, where $\langle \beta^2 \rangle = [\beta^{(1)}]^2 + [\beta^{(3)}]^2$. The polarization ratios are $P^2 = 9$ for $[\beta^{(1)}]^2$ and $P^2 = 3/2$ for $[\beta^{(3)}]^2$, so the ratio P^2 for their sum falls between these limits. This restriction on the possible values of P^2 requires only that the medium is isotropic on the scale of the light wavelength and that correlations are short range. For the specific case of the acetonitrile molecule, the value $P^2 = 6.074$ is obtained using the β tensor components from an *ab initio* static calculation, in which electron correlation is treated by the coupled cluster method including all single and double excitations and a perturbation estimate of connected triple excitations [CCSD(T)] [9].

HRS from a delocalized mode is mediated by the macroscopic susceptibility $\chi_{JKLM}(-2\omega + \Omega; \omega, \omega, \Omega)$, where the polarization indices $JKLM$ correspond to the frequency arguments: 2ω-Ω for the induced polarization, ω, ω for the applied optical fields, and Ω for the mode of molecular motion. The tensor χ_{JKLM} must be isotropic because the liquid it represents is isotropic, and it is symmetric in its middle two indices because the two field frequency arguments are equal. The independent nonvanishing tensor components χ_{ZZZZ}, χ_{XZZX}, and $\chi_{XZXZ} = \chi_{XXZZ}$ obey the relation $\chi_{ZZZZ} = \chi_{XZZX} + 2\chi_{XZXZ}$, and the response of the medium can be described by two independent quantities χ_{XZZX} and $R \equiv \chi_{ZZZZ}/\chi_{XZZX}$. If χ_{JKLM} is symmetric in all indices, then $R = 3$. The tensor χ_{JKLM} vanishes unless the mode of molecular motion is odd under inversion (i.e., a dipole mode). Using symmetry arguments and the dipole approximation [10], one sees that dipolar delocalized modes contribute to HRS, but do not contribute to linear light scattering processes such as Raman scattering in an isotropic medium. Modes of motion even under inversion, such as compressional sound waves, contribute to linear light scattering (e.g., the Brillouin spectrum) but not to HRS.

The librons with wave vector $\mathbf{K}$ are a pair of degenerate transverse optical (TO) modes with polarization perpendicular to $\mathbf{K}$, and a longitudinal optical (LO) mode with polarization parallel to $\mathbf{K}$. Momentum conservation in the scattering process gives $\mathbf{K} = 2\mathbf{k}_i - \mathbf{k}_s$. The components of the induced polarization $\boldsymbol{\mu}$ are of the form $\mu_J = \chi_{JKKJ} E_K^2 Q_J$, where Q_J is the J component of the (TO or LO) mode with amplitude Q propagating with wave vector $\mathbf{K}$. Expressions for the polarization and angle dependence of HRS from a libron are derived following the methods in Bersohn *et al.* [8]. The results for scattering in the X-Y plane from TO and LO modes are summarized in the last two columns of Table I. One feature which distinguishes nonlocal from local mode HRS is that $I_{HV} \neq I_{VH}$ for delocalized modes. Another distinctive feature is that the polarization ratio I_{VV}/I_{VH} is outside the range $3/2$ to 9 required for local modes.

HRS polarization ratio measurements for acetonitrile are shown in Table II, both at line center and integrated over the HRS spectrum (using narrow and wide spectral slit widths, respectively). The first line of Table II shows

TABLE I. Comparison of the angular dependence of local, TO, and LO mode HRS. For $\psi = 0$ scattering occurs in the X-Y plane.

Polarization	$I_{\text{local}}/\langle \beta_{XZZ}^2 \rangle$ $\psi \neq 0$	$I_{\text{local}}/\langle \beta_{XZZ}^2 \rangle$ $\psi = 0$	$I_{TO}/(\chi_{XZZX})^2$ $\psi = 0$	$I_{LO}/(\chi_{XZZX})^2$ $\psi = 0$
VV	$\sin^2\psi + P^2 \cos^2\psi$	P^2	R^2	0
HV	$\cos^2\theta \sin^2\psi + \cos^2\psi$ $+ P^2 \sin^2\theta \sin^2\psi$	1	1	0
VH	1	1	$\sin^2(\theta/2)$	$\cos^2(\theta/2)$
HH	$\sin^2\theta + P^2 \cos^2\theta$	$\sin^2\theta + P^2 \cos^2\theta$	$[1 - (R-1)\cos\theta]^2 \sin^2(\theta/2)$	$[1 + (R-1)\cos\theta]^2 \cos^2(\theta/2)$

TABLE II.   HRS polarization ratios measured for CH_3CN over narrow and wide spectral intervals $\Delta \nu$ centered at $\nu = 0$ cm^{-1}. The polarization ratios for HRS from local modes must all fall in the range from 3/2 to 9.

θ (deg)	$\Delta \nu$ (cm^{-1})	I_{VV}/I_{HV}	I_{VV}/I_{VH}	I_{VV}/I_{HH}
90	2.5	9.2 ± 0.1	11.6 ± 0.2	11.6 ± 0.4
90	18	9.0 ± 0.1	12.5 ± 0.2	
45	2.5	8.4 ± 0.8	8.5 ± 0.1	
45	18	7.1 ± 0.9	12.0 ± 0.2	

that the polarization ratio at line center for 90° scattering in CH_3CN follows the pattern $I_{VV}/I_{HV} \neq I_{VV}/I_{VH} = I_{VV}/I_{HH} > 9$. Comparison with the results in Table I shows that these measurements are consistent with HRS from TO modes and inconsistent with LO or local modes. The HRS spectrum was scanned with 2.5 cm^{-1} resolution to investigate the spectral variation of the polarization ratios. Figures 3 and 4 show the spectral intensities and intensity ratios measured with VV, HV, and VH polarizations. The most striking result is that the ratio I_{VV}/I_{VH} shows a minimum at line center, increases to a maximum at about ± 3 cm^{-1}, and everywhere falls outside the bounds for local mode HRS. The $\sin^2(\theta/2)$ dependence of I_{VH} for TO modes leads one to expect larger values of the ratio I_{VV}/I_{VH} at smaller scattering angles, and this is confirmed by the data in Figs. 3 and 4.

The data in Table II and Figs. 3 and 4 were analyzed assuming a superposition of local and TO modes, using the expressions

$$I_{VV}/P^2 = A + B(R^2/P^2), \qquad (1)$$

$$I_{HV} = A + B, \qquad (2)$$

$$I_{VH} = A + B \sin^2(\theta/2), \qquad (3)$$

where $P^2 = 6.074$ is assumed from *ab initio* calculations [9], R^2 is expected to be near 9, and $A = A(\nu, \theta)$ and $B = B(\nu, \theta)$ are spectral functions for the local and TO modes, respectively. The quantities R^2, A, and B are determined by solving Eqs. (1)–(3) for given values of I_{VV}, I_{HV}, and I_{VH}. The best estimate of R^2 obtained from the polarization ratio data in Table II is $R^2 = 11.4 \pm 0.8$, and this value is used in the subsequent analysis. The values $\int B \, d\nu / \int A \, d\nu = 1.30$ and 0.63 are obtained from the data in Table II for $\theta = 90°$ and $45°$, respectively. The fraction of scattered light in the central 18 cm^{-1} due to the TO mode ranges from 71% of I_{VV} at $\theta = 90°$ to 8% of I_{VH} at $\theta = 45°$. Suitable linear combinations of the VV, HV, and VH spectra are used to obtain the TO mode HRS spectral profiles. Subtracting the HV and VH spectra in Fig. 3 ($\theta = 90°$) gives $I_{HV} - I_{VH} = B/2 = I_{VH,TO}$. Subtracting the VV and VH spectra in Fig. 4 ($\theta = 45°$) and using $R^2/P^2 = 1.877$ gives $(I_{VV}/P^2 - I_{VH})[1 - \sin^2(\theta/2)/(R^2/P^2)]^{-1} = (R^2/P^2)B = I_{VV,TO}/P^2$. Note that the VH spectrum in
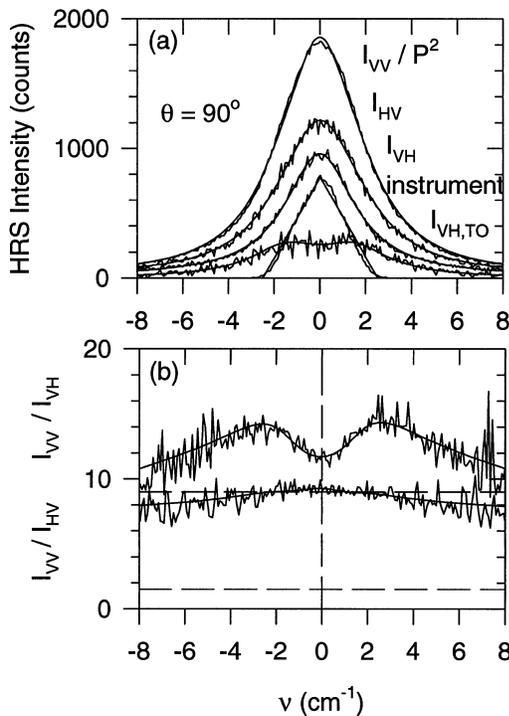
FIG. 3.   Measured and fitted curves are plotted for the HRS (a) spectral intensities and (b) polarization ratios versus frequency at $\theta = 90°$. The horizontal dashed lines in (b) mark the bounds for local mode HRS.
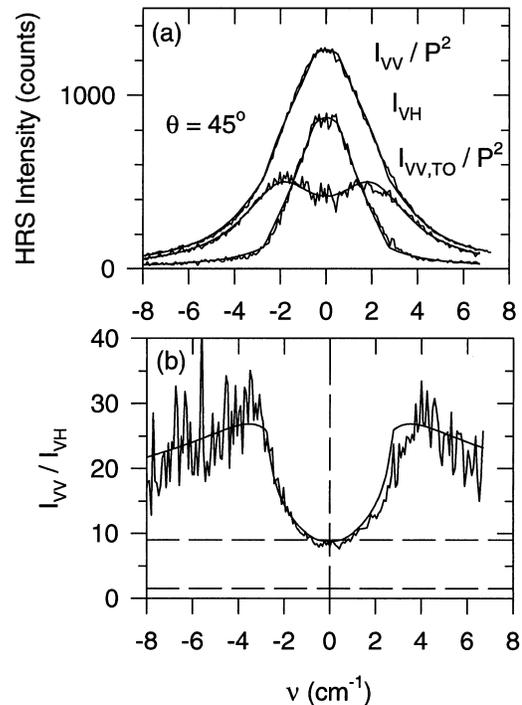
FIG. 4.   Measured and fitted curves are plotted for the HRS (a) spectral intensities and (b) polarization ratios versus frequency at $\theta = 45°$. The horizontal dashed lines in (b) mark the bounds for local mode HRS.

Fig. 4, which is almost pure local mode, is much narrower than the *VV* spectrum, whereas the TO mode spectrum is broad and double peaked.

The TO mode spectra were fit with a double-peaked Lorentzian function: $\{1 + [(\nu - \nu_1)/\nu_2]^2\}^{-1} + \{1 + [(\nu + \nu_1)/\nu_2]^2\}^{-1}$, with splitting $2\nu_1$ and width $2\nu_2$. The splitting and width obtained are $2\nu_1 = 3.0$ cm^{-1} and $2\nu_2 = 3.8$ cm^{-1} at $\theta = 90°$, and $2\nu_1 = 4.0$ cm^{-1} and $2\nu_2 = 4.1$ cm^{-1} at $\theta = 45°$ (uncorrected for the 2.5 cm^{-1} instrumental linewidth). The local mode spectra were fit with the sum of Lorentzian and exponential functions centered at $\nu = 0$. The parameters of the weak, broad exponential components were determined from the wings of the spectra in Fig. 2. A single Lorentzian function with width 3.7 cm^{-1} FWHM was adequate for the fit to the $\theta = 90°$ local mode spectrum. An adequate fit to the $\theta = 45°$ local mode spectrum requires a weak, wide Lorentzian plus a strong, unresolved, instrumentally broadened component. This is consistent with the pair of Lorentzians with 6:1 width ratio expected for the rotational diffusion spectrum of a C_{3V} molecule [11]. The fitted curves for the HRS spectral intensities are plotted in Figs. 3(a) and 4(a). The polarization ratio fitted curves plotted in Figs. 3(b) and 4(b) are ratios of these fitted spectral intensity curves. The fitted curves adequately represent the spectral and polarization ratio data.

The coupled mode of librating dipolar molecules and an electromagnetic wave is a polariton, which has a dispersion relation $\omega^2\varepsilon(\omega) = c^2K^2$ with two branches [5]. For a TO mode with $\nu_{TO} = 2$ cm^{-1}, the lower branch is an almost purely mechanical TO polariton with frequency $\omega \approx \omega_{TO}$ independent of K. The upper branch is an LO mode with $\omega \propto K$, which is too weak and too high in frequency to observe. The observed splitting in the HRS spectrum shows no significant K dependence, in agreement with the TO polariton dispersion relation. The phase velocity of the TO mode is $v = \omega/K \approx 10^{-4}c = 30$ km/s, as compared to 1.3 km/s for compressional waves [12].

This work indicates that most of the HRS intensity for liquid acetonitrile is due to propagating waves of molecular reorientation rather than orientational diffusion of the molecules. Such librons may be important features of the molecular dynamics of most liquids, not just acetonitrile. These librons have not been observed before because they are invisible in linear scattering experiments with isotropic media. Their discovery in acetonitrile is due to the exceptionally high HRS polarization ratio in that liquid, which cannot be explained in any other way. Now having recognized that such delocalized polar modes may be present, the I_{HV}-I_{VH} HRS difference spectrum can be used to search for and characterize the librons in a wide range of molecular liquids.

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