

## Collision induced hyper-Rayleigh light scattering in $\text{CCl}_4$

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Measurements of hyper-Rayleigh scattering in carbon tetrachloride liquid and vapour indicate that interaction induced contributions account for more than half of the scattered intensity from the liquid phase. The spectral characteristics of hyper-Rayleigh scattering from carbon tetrachloride are influenced by the effects of hindered rotation, orientational correlations, and dipole-induced-dipole and octupole-induced-dipole interactions, as well as the usual local field factors. The unimolecular contribution is associated with the narrow Lorentzian feature of the hyper-Rayleigh spectrum. The first hyperpolarizability  $\beta$  determined from the intensity of just the narrow Lorentzian feature of the liquid hyper-Rayleigh spectrum agrees with the gas phase value of  $\beta$ , but is 1.57 times smaller than the value obtained by including the entire liquid hyper-Rayleigh spectrum.

### 1. Introduction

Hyper-Rayleigh scattering (HRS) in carbon tetrachloride ( $\text{CCl}_4$ ) has been investigated several times since the original measurements of Terhune *et al.* in 1965 [1–6]. In previous experiments, the spectral profile of HRS from liquid  $\text{CCl}_4$  was analysed as a sum of narrow and broad Lorentzians. The narrow component was interpreted in terms of rotational diffusion of the molecule, and the broad component was attributed to molecular interactions [3, 5, 6]. A discrepancy, which is attributed to molecular interactions, remains between the theoretically predicted value  $I_{\text{VV}}^{2\omega}/I_{\text{HV}}^{2\omega} = 3/2$  for a molecule of tetrahedral symmetry and the experimentally observed polarization ratios of 1.8–2.9 for the second harmonic scattered light [1–4, 6]. Here  $I_{\text{HV}}^{2\omega}$  indicates the vertically polarized second harmonic scattered intensity at  $2\omega$  induced by the horizontally polarized incident radiation. Kielich *et al.* [7–9] have given several theoretical discussions of HRS scattering from both isolated and interacting molecules. The case of  $\text{CCl}_4$  has also been discussed previously by Weinberg [2] and Bersohn *et al.* [10]. In the present work, we have made measurements of the HRS spectrum of liquid and gas phase  $\text{CCl}_4$  in order to test these theoretical predictions and quantitatively assess the role of molecular interactions in HRS. Such an assessment is in order since measurements of the integrated HRS intensity recently have become an important method for determining absolute values of the first hyperpolarizability  $\beta$  [11].

### 2. Experimental details

Carbon tetrachloride (spectroscopic grade) was filtered through a 0.2  $\mu\text{m}$  micro-pore filter directly into a 1 cm spectroscopic fused silica cuvette enclosed in a thermostatted aluminium block. The source radiation at 1064 nm was obtained from

an acousto-optically Q-switched Nd:YAG laser (Quantronix 116) and focused into the sample cell with a  $4\times$  microscope objective lens. The laser produced trains of  $\approx 150$  ns, 1 mJ pulses at a repetition rate of 1–3 kHz. The input power level and polarization were selected by two Glan-Laser polarizers followed by a Soleil-Babinet compensator. The scattered light was collected at  $90^\circ$  with  $f/1.8$  optics and focused into a spectrometer (Jobin-Yvon Ramanor U 1000), with polarization selection by a sheet polaroid. The lineshape measurements were made with spectral slit widths of  $1.2\text{ cm}^{-1}$  (liquid) and  $13\text{ cm}^{-1}$  (vapour). The dispersed light was detected by a cooled photon counting photomultiplier tube (Hamamatsu R943), and data were acquired with a multichannel scaler (Nucleus PCA). More details of the experimental apparatus are given elsewhere [12].

### 3. HRS from fluctuations in molecular fluids

Hyper-Rayleigh or second harmonic light scattering denotes a process in which two photons of frequency  $\omega$  incident upon a non-centrosymmetric molecule or ensemble of molecules are absorbed and a third photon of frequency  $2\omega$  is emitted. The nonlinear optical response of an isolated molecule irradiated with light of high intensity is usually written as a Taylor series expansion of the induced dipole moment  $\mu$  in terms of the applied electric field  $E_i(\omega)$ ,

$$\mu_i = \alpha_{ij}E_j + \frac{1}{2}\beta_{ijk}E_jE_k + \frac{1}{6}\gamma_{ijkl}E_jE_kE_l + \dots, \quad (1)$$

where the molecular tensors  $\alpha$ ,  $\beta$ , and  $\gamma$  describe the linear polarizability and the first and second hyperpolarizabilities of the molecules, respectively. Note that some experimentalists use a series expansion without any numerical coefficients. The second harmonic light intensity for a collection of  $N$  non-interacting molecules without orientational correlations, in the electric dipole approximation, is given by  $I^{2\omega} \propto N \langle \mu_i(2\omega) \mu_i^*(2\omega) \rangle$ , where the brackets indicate averaging over all possible molecular orientations. The total intensity is simply the sum of the intensities scattered by the individual molecules because the phase of the scattered light, which depends on the orientation of the molecule, varies randomly from one molecule to the next. Spatial fluctuations of molecular orientation are responsible for the non-vanishing intensity of incoherent HRS from molecular fluids, while temporal fluctuations of molecular orientation govern the spectral distribution of HRS.

Interaction between molecules in a dense fluid alters the motions of the individual molecules and introduces correlations between the positions and orientations of neighbouring molecules. The free rotation of an isolated molecule is replaced by rotational diffusion (on time scales longer than the interval between collisions), and the discrete spectrum collapses to a Lorentzian band. Correlations in position have little direct effect on HRS, but orientational correlations between molecules will strongly modify the HRS intensity. While the angular and polarization dependence of HRS is not altered by short range orientational correlations in the case of molecules of  $T_d$  symmetry, the spectrum arising from orientational correlations between molecules will be distinct from the unimolecular spectrum since the respective correlation functions have different time dependences.

The interaction between molecules distorts the molecules as well as altering their distribution. The fluctuating molecular field seen by the interacting molecules leads to

a perturbed first hyperpolarizability  $B_{ijk}^{2\omega}$ , which can be written in terms of the molecular polarizabilities and hyperpolarizabilities  $\alpha$ ,  $\beta$ , and  $\gamma$  as [8, 9]

$$B_{ijk}^{2\omega} = \sum_{p=1}^N \left\{ \alpha_{i\epsilon}^{2\omega(p)} \frac{\partial^2 F_{\epsilon}^{(p)}}{\partial E_j \partial E_k} + \beta_{i\epsilon\eta}^{2\omega(p)} \left( \delta_{\epsilon j} + \frac{\partial F_{\epsilon}^{(p)}}{\partial E_j} \right) \left( \delta_{\eta k} + \frac{\partial F_{\eta}^{(p)}}{\partial E_k} \right) + \gamma_{i\epsilon\eta\kappa}^{2\omega(p)} F_{0l}^{(p)} + \dots \right\}, \quad (2)$$

where the molecular field  $\mathbf{F}_0$  is due to the other  $N - 1$  molecules of the medium in the absence of an externally applied electric field, and the field  $\mathbf{F}$  is due to dipoles induced when an external field is present. In general, the molecular field  $\mathbf{F}_0$  due to the permanent molecular multipole moments is

$$F_{0i}^{(p0)} = - \sum_{\substack{q=1 \\ q \neq p}}^N \left\{ T_{ij}^{(pq)} \mu_j^{(q)} - \frac{1}{3} T_{ijk}^{(pq)} \Theta_{jk}^{(q)} + \frac{1}{15} T_{ijkl}^{(pq)} \Omega_{jkl}^{(q)} + \dots \right\}, \quad (3)$$

where  $\mu$ ,  $\Theta$  and  $\Omega$  are, respectively, the permanent electric dipole, quadrupole, and octupole moments of the molecule [8, 13]. The tensors  $T_{ij}^{(pq)}$ ,  $T_{ijk}^{(pq)}$ , and  $T_{ijkl}^{(pq)}$  represent the binary (pairwise) interactions between molecules  $p$  and  $q$  of the dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole kinds, respectively, and differ from zero for  $p \neq q$ . For the case of tetrahedral molecules such as  $\text{CCl}_4$  the lowest order nonzero term in equation (3) is the octupole term. The field  $\mathbf{F}$  due to induced dipoles is

$$F_i^{(p)} = - \sum_{\substack{q=1 \\ q \neq p}}^N T_{ij}^{(pq)} \{ \alpha_{jk}^{(q)} E_k + \frac{1}{2} \beta_{jkl}^{(q)} E_k E_l \} + \sum_{\substack{q=1 \\ q \neq p}}^N \sum_{\substack{r=1 \\ r \neq q}}^N T_{ij}^{(pq)} \alpha_{jk}^{(q)} T_{kl}^{(qr)} \alpha_{lm}^{(r)} E_m - \dots \quad (4)$$

The summations in equations (3) and (4) extend formally over the entire sample, but only the near neighbours of a molecule are considered explicitly, while distant molecules are treated in the continuum approximation. For the case of non-polar molecules such as  $\text{CCl}_4$  the induced dipole fields of the distant molecules are accounted for by the usual Lorentz local field factors. The interaction between the nearest neighbours varies rapidly with distance, so molecular motion causes  $B_{ijk}^{2\omega}$  to fluctuate rapidly and gives rise to a broad ‘collision induced’ HRS spectral component.

The following theoretical expression for the HRS intensities  $I_{\text{VV}}^{2\omega}$  and  $I_{\text{HV}}^{2\omega}$  including the contributions due to interacting molecular pairs but neglecting the first term of equation (2), was given by Kielich *et al.* [7, 8]:

$$\frac{I_{\text{VV}}^{2\omega}}{I_{\text{HV}}^{2\omega}} = \frac{3}{2} \frac{\beta^2 + C\beta^2 + \frac{74}{5} \left( \frac{\beta\alpha}{4\pi\epsilon_0} \right)^2 \langle r^{-6} \rangle + \frac{28}{3} \left( \frac{\gamma\Omega}{4\pi\epsilon_0} \right)^2 \langle r^{-10} \rangle}{\beta^2 + C\beta^2 + \frac{31}{2} \left( \frac{\beta\alpha}{4\pi\epsilon_0} \right)^2 \langle r^{-6} \rangle + \frac{14}{9} \left( \frac{\gamma\Omega}{4\pi\epsilon_0} \right)^2 \langle r^{-10} \rangle}. \quad (5)$$

Here  $\alpha = \alpha_{ii}/3$  is the mean molecular polarizability, and  $\beta$  and  $\Omega$  denote  $\beta_{xyz}$  and  $\Omega_{xyz}$  the only independent nonzero molecule-fixed components of the first hyperpolarizability and octupole moment tensors of a tetrahedral molecule. The statistical averages  $\langle r^{-n} \rangle$  are given by

$$\begin{aligned} \langle r^{-n} \rangle &= 4\pi\rho \int_0^\infty r^{2-n} g(r) dr \\ &= 4\pi\rho\sigma^3 \int_0^\infty x^{2-n} \exp\left[-\frac{U(x)}{kT}\right] dx, \end{aligned} \quad (6)$$

where  $\rho$  is the number density of molecules,  $g(r)$  is the radial distribution function,  $U(x)$

is the intermolecular pair potential, and  $x = r/\sigma$ , where  $\sigma$  is the molecular diameter. The  $\beta^2$  terms in equation (5) are due to scattering from the intrinsic  $\beta$  of single molecules. The  $C\beta^2$  terms account for the effect of the orientational correlation of neighbouring molecules. The  $(\beta\alpha)^2$  terms are the result of the field of the induced dipole on molecule 2 acting on molecule 1 (lowest order 'dipole-induced-dipole' or DID). The  $(\gamma\Omega)^2$  terms account for the interaction-induced increment in  $\beta$  of molecule 1 due to the octupole field of molecule 2 acting on the second hyperpolarizability of molecule 1 ('octupole-induced-dipole'). Equation (5) forms the basis for an assessment of the role of molecular interactions in HRS from  $\text{CCl}_4$ , as will be discussed further below.

#### 4. Liquid phase HRS measurements

The HRS spectrum of liquid  $\text{CCl}_4$  is shown in figure 1. The main features are a narrow Lorentzian peak superimposed on a broad exponential wing. The Lorentzian lineshape is readily understood as HRS from rotationally diffusing  $\text{CCl}_4$  molecules [3, 14]. The broad exponential wing strongly suggests collision induced HRS, since a nearly exponential profile is typical of collision induced light scattering [15]. For comparison, figure 2 shows the depolarized Rayleigh wing spectrum of liquid  $\text{CCl}_4$ , which is entirely collision induced.

The terms in equation (5) have been evaluated for liquid  $\text{CCl}_4$  using the parameter values in table 1 with a Lennard-Jones model for the interaction potential, giving the result

$$I_{\text{VV}}^{2\omega} \propto \beta^2 [1 + C + 0.42 + 1.01]. \quad (7)$$

A limitation of equation (5) is that it includes only pair interactions and pair correlations. The difference between  $g(r)$  in equation (6) and the true radial distribution function for the liquid is one source of error. A more serious error for the DID interaction giving rise to the third term in equation (5) is that the effects of triplet and quadruplet correlations at liquid densities almost exactly cancel out the pair contribution. This is seen in the case of collision induced depolarized Rayleigh scattering. Calibrating the intensity in figure 2 using a Raman band, we find that the scattered intensity from the liquid is just  $0.01 \times$  the calculated DID pair contribution, in agreement with previous determinations [20]. This cancellation occurs for DID because the local environment of a colliding molecule in the liquid is more symmetrical than in a low density gas, and the orientations of the induced dipoles are highly correlated. The fourth term of equation (5) is immune to this cancellation effect due to many-body spatial correlations, because it is the result of the mean-square electric field of surrounding octupoles whose orientations are in the first approximation uncorrelated.

When the  $\beta^2$ ,  $C\beta^2$ ,  $(\beta\alpha)^2$  and  $(\gamma\Omega)^2$  terms of equation (5) are considered separately the polarization ratios  $I_{\text{VV}}^{2\omega}/I_{\text{HV}}^{2\omega}$  are  $3/2$ ,  $3/2$ ,  $222/155 \approx 1.43$ , and  $9$ , respectively. This allows a partial separation of the four contributions to  $I_{\text{VV}}^{2\omega} = I_1 + I_2 + I_2' + I_3$  by combining the  $I_{\text{VV}}^{2\omega}$  and  $I_{\text{HV}}^{2\omega}$  spectra as follows:

$$\frac{9}{5}(I_{\text{HV}}^{2\omega} - \frac{1}{9}I_{\text{VV}}^{2\omega}) = I_1 + I_2 + \frac{1173}{1110}I_2', \quad (8a)$$

$$\frac{9}{5}(\frac{2}{3}I_{\text{VV}}^{2\omega} - I_{\text{HV}}^{2\omega}) = -\frac{7}{222}I_2' + I_3. \quad (8b)$$

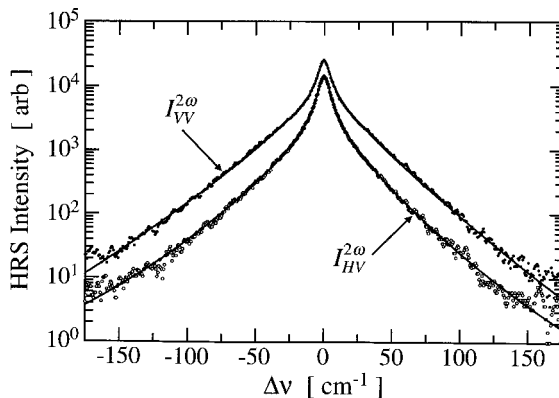


Figure 1. HRS from  $\text{CCl}_4$  at 22 °C with irradiation at 1064 nm. The Lorentzian contributes 40% of the total scattering for  $I_{VV}^{2\omega}$  and 60% for  $I_{HV}^{2\omega}$ . Integration of the total scattering gives a polarization ratio  $I_{VV}^{2\omega}/I_{HV}^{2\omega} = 2.32 \pm 0.05$ , whereas integration of the Lorentzian term gives a ratio  $I_{VV}^{2\omega}/I_{HV}^{2\omega} = 1.54 \pm 0.05$ , as predicted for scattering from molecules of  $T_d$  symmetry.

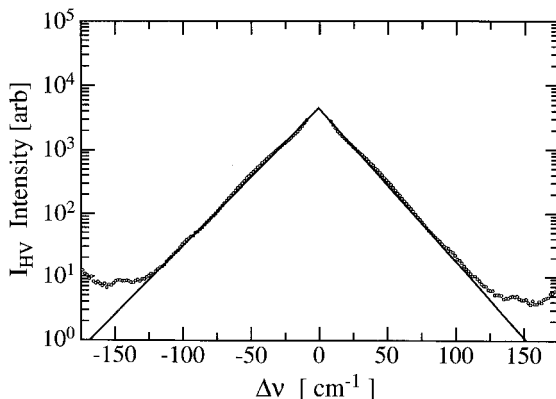


Figure 2. Depolarized  $I_{HV}$  Rayleigh wing scattering from  $\text{CCl}_4$  at 22 °C with irradiation at 514.5 nm from an  $\text{Ar}^+$  laser. A fit of the Rayleigh wing scattering to an exponential gives  $\nu_R = 19 \pm 1 \text{ cm}^{-1}$ . Superimposed on the exponential is a broad feature at  $\Delta\nu \approx \pm 50 \text{ cm}^{-1}$  and a Raman combination band ( $\nu_4 - \nu_2$ ) at  $\Delta\nu \approx \pm 100 \text{ cm}^{-1}$ . Above  $\Delta\nu = 150 \text{ cm}^{-1}$  the scattered intensity rises due to the approach of the  $\nu_2$  Raman band at  $\Delta\nu \approx 218 \text{ cm}^{-1}$ .

If one assumes that the  $I_{\mathcal{D}}$  intensity is negligible because of the DID cancellation effect, then equation (8a) is governed by molecular reorientation and intermolecular orientational correlation, while equation (8b) is governed by the octupole-induced-dipole interaction. The 'octupolar' spectrum of equation (8a) should consist of a Lorentzian and a single exponential, while the 'dipolar' spectrum of equation (8b) should consist of a single exponential. Figure 3 shows the experimental spectra constructed according to equation (8a, b), and indeed they have the expected form. In particular, both a Lorentzian and an exponential component are necessary to fit the octupolar spectrum adequately.

The spectral profile of collision induced HRS is determined mainly by the modulation of the scattered intensity during a collision because of the  $r^{-m}$  dependence of the interaction. The DID HRS spectrum is expected to be the same as the

Table 1. Molecular parameters for  $\text{CCl}_4$ .

Parameter	Value	Ref.
$\alpha$	$1.17 \times 10^{-39} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$	[16]
$\beta^a$	$6.0 \times 10^{-52} \text{ C}^3 \text{ m}^3 \text{ J}^{-2}$	See text
$\gamma^b$	$1.23 \times 10^{-60} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$	[17]
$\Omega$	$5.3 \times 10^{-49} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$	[18]
$\varepsilon/k^c$	327 K	[19]
$\sigma^c$	0.588 nm	[19]
$\rho$	$6.24 \times 10^{27} \text{ m}^{-3}$	
$\langle r^{-6} \rangle$	$2.6 \times 10^{56} \text{ m}^{-6}$	
$\langle r^{-10} \rangle$	$1.1 \times 10^{93} \text{ m}^{-10}$	

<sup>a</sup> Fitted value of  $\beta \propto \gamma \Omega$ .

<sup>b</sup> Measured by dc Kerr effect at 632.8 nm. Equation (5) requires the static value of  $\gamma$ , which will be larger due to vibrational contributions.

<sup>c</sup> Lennard-Jones 6,12 potential.

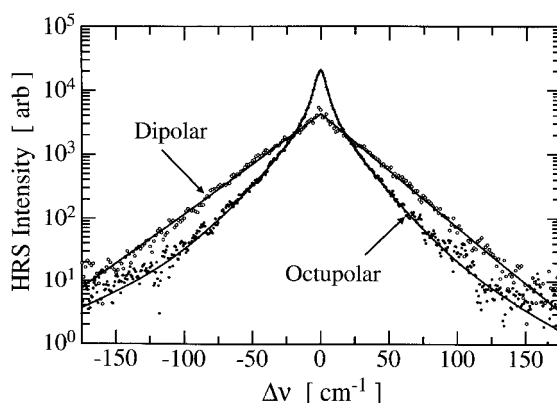


Figure 3. Decomposition of the HRS spectra of  $\text{CCl}_4$  at 22 °C into the dipolar and octupolar contributions, as in equation (8). The dipolar spectrum is due entirely to collision induced scattering. The fit to an exponential decay gives  $\nu_3 = 26 \pm 1 \text{ cm}^{-1}$ . The octupolar spectrum contains both a Lorentzian with  $\text{FWHM} = 9.2 \pm 0.3 \text{ cm}^{-1}$  and an exponential term with  $\nu_2 = 17 \pm 1 \text{ cm}^{-1}$ .

DID Rayleigh spectrum since the molecular trajectories and the  $r^{-3}$  dependence of the induction mechanism are the same for both. The spectral width scales as  $[(m^2+6)\langle x^{-2m+2} \rangle / \langle x^{-2m} \rangle]^{1/2}$  for collision induced scattering in the gas phase, so one may estimate that the octupole-induced-dipole interaction, which varies as  $r^{-5}$ , gives a spectrum that is  $1.5 \times$  wider than the DID spectrum [21]. The dynamics of the orientational correlations are unknown, but one may guess that the correlations vary as an inverse power of  $r$  and that they produce a spectrum roughly similar to the DID spectrum.

The experimental spectra were fitted with the following expression:

$$I_{\text{VV}}^{2\omega}(\Delta\nu) = \left\{ I_1 \frac{\nu_1/\pi}{\Delta\nu^2 + \nu_1^2} \left[ \frac{2}{1 + \exp|\Delta\nu/\nu_0|} \right] + I_2 \frac{\exp - |\Delta\nu/\nu_2|}{2\nu_2} + I_3 \frac{\exp - |\Delta\nu/\nu_3|}{2\nu_3} \right\} \exp(-\Delta\nu/2kT), \quad (9)$$

where  $I_1, I_2, I_3$  are the integrated intensities of the components of  $I_{VV}^{2\omega}$  ( $I_2$  and  $I_3$  are combined into the  $I_2$  term). The frequency shift  $\Delta\nu$  is measured from the second harmonic of the incident laser frequency (negative  $\Delta\nu$  for the Stokes side). The final exponential factor accounts for the Stokes/anti-Stokes intensity asymmetry ( $2kT = 410 \text{ cm}^{-1}$  at  $22 \text{ }^\circ\text{C}$ ). The Lorentzian function in equation (9) has its far wings clipped; for large  $|\Delta\nu|$  it becomes an exponential. For  $CCl_4$  the transition is expected to occur at about  $100 \text{ cm}^{-1}$ , corresponding to a time of about  $0.05 \text{ ps}$ , because the re-orientational motion is ballistic rather than diffusive at times shorter than the mean time between collisions. The Raman spectrum of liquid  $Br_2$  provides experimental evidence for this clipped Lorentzian lineshape [22].

The values of  $\nu_0, \nu_1, \nu_2, I_1$ , and  $I_2$  are determined by fitting the octupolar spectrum in figure 3 using a clipped Lorentzian and a single exponential, while the values of  $\nu_3$  and  $I_3$  are determined by fitting the dipolar spectrum in figure 3 to a single exponential. The spectra were corrected for the effect of the finite collection angle  $\theta_0$  on  $I_{VV}^{2\omega}$  by using

$$\left(\frac{I_{VV}^{2\omega}}{I_{HV}^{2\omega}}\right)_{\text{corr}} = \frac{\left\langle \frac{\sin^4 \theta \sin^2 \phi \cos^2 \phi}{1 - \sin^2 \theta \cos^2 \phi} \right\rangle + \left\langle \frac{\sin^2 \theta \cos^2 \theta \cos^2 \phi}{1 - \sin^2 \theta \cos^2 \phi} \right\rangle + \left(\frac{I_{VV}^{2\omega}}{I_{HV}^{2\omega}}\right)_{\text{exp}} \langle 1 - \sin^2 \theta \cos^2 \phi \rangle}{\left\langle \frac{\sin^4 \theta \sin^2 \phi \cos^2 \phi}{1 - \sin^2 \theta \cos^2 \phi} \right\rangle + \left(\frac{I_{VV}^{2\omega}}{I_{HV}^{2\omega}}\right)_{\text{exp}} \left\langle \frac{\sin^2 \theta \cos^2 \theta \cos^2 \phi}{1 - \sin^2 \theta \cos^2 \phi} \right\rangle + \langle 1 - \sin^2 \theta \cos^2 \phi \rangle}, \quad (10)$$

where  $\langle \cdot \rangle$  is the average over the collection aperture, and  $\theta, \phi$  are the usual polar coordinates [10, 12]. With the present collection optics, this gives a corrected polarization ratio that is about 1.5% higher than the experimentally measured ratio. The experimental values of the width parameters are consistent with the estimates given previously:  $\nu_0 = 80 \text{ cm}^{-1} \approx 100 \text{ cm}^{-1}$ ,  $\nu_2 = 17 \text{ cm}^{-1} \approx 19 \text{ cm}^{-1}$  and  $\nu_3 = 26 \approx 1.5 \times 19 \text{ cm}^{-1}$ . The Lorentzian width  $\nu_1 = 4.6 \text{ cm}^{-1}$  (HWHM) corresponds to an orientational relaxation time of  $1.15 \text{ ps}$ . The measured magnitudes of  $I_1, I_2$ , and  $I_3$  give

$$I_{VV}^{2\omega} \propto \beta^2 [1 + (0.47 \pm 0.07) + (1.01 \pm 0.05)]. \quad (11)$$

The last term of equation (11) is exactly the same as the last term in equation (7) because the ratio of the  $\beta^2$  and  $(\gamma\Omega)^2$  terms has been used to determine the value of  $\beta$  in table 1. The middle contribution in equation (11) could be due to either orientational correlations or uncanceled DID interactions, since the spectral and polarization signatures for the two effects would be practically indistinguishable. This term should be compared with  $C + 0.42$  in equation (7), realizing that the value 0.42 should be considered an upper bound on the DID contribution because of possible strong cancellation effects. It is probable that the middle contribution in equation (11) is dominated by orientational correlation effects.

As a check of the polarization analysis, functions with the form of equation (9) were fitted to the  $I_{VV}^{2\omega}$  and  $I_{HV}^{2\omega}$  spectra separately. The width parameters were set to the previously determined values, but the intensity parameters were free to vary. The polarization ratios obtained,  $1.54 \pm 0.05$  for the Lorentzian component and  $1.3 \pm 0.3$  and  $8 \pm 2$  for the exponentials, are consistent with the predicted values,  $1.5$ ,  $\approx 1.5$ , and 9.

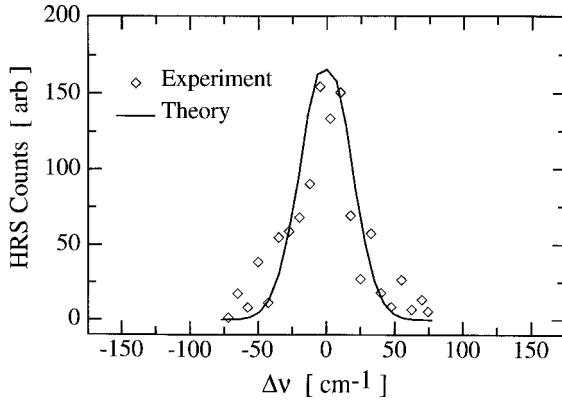


Figure 4. HRS  $I_{VV}^{20}$  spectrum from  $\text{CCl}_4$  vapour at  $62^\circ\text{C}$ . The theoretical curve was calculated with  $B = 0.057\text{ cm}^{-1}$ ,  $T = 62^\circ\text{C}$ , and convolved with the instrument response function.

Since the leading terms in the square brackets in equations (7) and (11) are the intrinsic molecular contribution whereas the remaining terms are interaction induced contributions, we may define the effective hyperpolarizability of molecules in the liquid as

$$\beta_L = \beta(I_{VV}^{20}/I_1)^{1/2}, \quad (12)$$

where  $\beta_L/\beta = [1 + 0.47 + 1.01]^{1/2} = 1.57 \pm 0.04$ . This estimate of  $\beta_L/\beta$  may be tested by comparing liquid and gas phase HRS integrated intensities.

### 5. Vapour phase HRS measurements

Vapour phase HRS measurements were made in the same spectroscopic cell above the liquid, at a temperature of  $62^\circ\text{C}$ . The HRS signal is reduced by about  $10^4$  for the vapour compared with the liquid. The HRS spectrum for molecules of  $T_d$  symmetry is given by [23]:

$$I_{VV}^{20}|_{J \rightarrow J'} \propto (2J+1)(2J'+1) \exp(-BJ(J+1)/kT), \quad (13)$$

with selection rules  $\Delta J = 0, \pm 1, \pm 2, \pm 3$  and  $J+J' \geq 3$ . A comparison of the theoretical HRS spectrum and the experimental results is shown in figure 4.

For a quantitative intensity comparison, the vapour and liquid measurements of  $I_{VV}^{20}$  were made in the same cell with the same focusing and collection optics and the same spectral slit width. Between liquid and vapour measurements, the focusing lens, cuvette, and collection lens are repositioned using calibrated translation stages to compensate for image shifts due to the change in the refractive index of the sample. The effective hyperpolarizability  $\beta_L$  of  $\text{CCl}_4$  molecules in the liquid, obtained from the ratio of HRS intensities for liquid (L) and vapour (G) samples measured in a fused silica (S) cuvette, is

$$\left(\frac{\beta_L}{\beta_G}\right)^2 = \frac{I_L^{20} \rho_G (\mathcal{Z}_G^{20})^2 (\mathcal{Z}_G^\omega)^4 (T_G^{20}) (T_G^\omega)^2 (n_L^\omega)^2 n_G^\omega}{I_G^{20} \rho_L (\mathcal{Z}_L^{20})^2 (\mathcal{Z}_L^\omega)^4 (T_L^{20}) (T_L^\omega)^2 (n_G^\omega)^2 n_L^\omega}. \quad (14)$$

The factors following the measured intensity ratio and the sample density ratio in equation (14) are functions of the refractive indices  $n$ . Respectively, these factors



account for local fields ( $\mathcal{L} = (n^2+2)/3$ ), transmission across the silica-sample interfaces ( $T_X = 1 - (n_S - n_X)^2 / (n_S + n_X)^2$ ), collection solid angle, and length of the focal region in the sample. The result of this measurement is  $(\beta_V/\beta_G) = 1.53 \pm 0.10$ , which is in good agreement with  $(I_{VV}^0/I_V)^{1/2} = 1.57 \pm 0.04$  obtained from analysis of the liquid HRS spectrum.

## 6. Conclusion

The HRS intensity is more than doubled by the interactions between nearest neighbour molecules in liquid  $\text{CCl}_4$ . This conclusion is supported by the results of both spectral analysis and direct intensity comparison. The measured HRS spectral distribution, polarization, and integrated intensity are all consistent with a theoretical treatment which includes the rotational diffusion and angular correlation of undistorted molecules, as well as the distorting effects of the permanent and induced multipolar electric fields of the surrounding molecules. The large exponential component of the octupolar HRS spectrum indicates that strong, short duration intermolecular orientational correlations exist in liquid  $\text{CCl}_4$ . The interaction effects seen in liquid  $\text{CCl}_4$  must be considered to obtain reliable estimates of the intrinsic molecular first hyperpolarizabilities from HRS measurements.

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