Polarized hyper-Rayleigh light scattering measurements of nonlinear optical chromophores

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Hyper-Rayleigh light scattering measurements at incident wavelengths of 1064 and 1319 nm are reported for several organic nonlinear optical chromophores in solution with approximately 5%–10% uncertainty in the relative first hyperpolarizabilities. The measured chromophores include representatives from $C_1$, $C_2$, $C_{2v}$, and $D_3$ molecular point groups and include both neutral and ionic compounds. The measurements were made with 2–5 cm$^{-1}$ spectral resolution and include polarization analysis of the incident and scattered light. Polarization ratios were measured with 2%–3% uncertainty for each molecule, and relative magnitudes of the hyperpolarizability components were deduced. Two-photon induced fluorescence from several chromophores was observed to overlap with the scattered second harmonic light spectrum. The use of a scanning monochromator, however, generally allows the separation of these two sources of photons. The measured first hyperpolarizabilities are consistent with previous electric field induced second harmonic generation measurements of the same compounds, provided that the standard reference value for the nonlinear susceptibility of quartz is taken to be $d_{11}=0.30\pm0.02$ pm/V at 1064 nm.

I. INTRODUCTION

Until recently, the only method in widespread use for measuring the second order nonlinear optical (NLO) properties of organic molecules was the electric field induced second harmonic generation (EFISHG) experiment. Due to the use of a static electric field in this experiment, the compounds investigated by the EFISHG method are restricted to neutral dipolar species. As other authors have indicated, there exist many potentially interesting molecules whose NLO properties cannot be assessed by this experiment because of symmetry constraints or because they exist as ionic species. The quantity measured in the EFISHG experiment is proportional to

$$\left(\gamma + \frac{\mu \beta z}{5kT}\right),$$

where the first and second hyperpolarizabilities are given by $\beta$ and $\gamma$. The molecular dipole moment is $\mu$ and the projection of $\beta$ in the direction of the dipole moment is given by $\beta_z$. $T$ is the temperature, with $k$ Boltzmann’s constant. This experiment requires an extensive set of physical and optical measurements characterizing the density, refractive index, dielectric constant, and EFISHG amplitudes and coherence lengths on a series of solutions of graded concentration. For accurate work, additional third harmonic or other measurements assessing the magnitude of the second hyperpolarizability are required in order to obtain the first hyperpolarizabilities of the compounds. Temperature dependent EFISHG studies provide an accurate separation of the first and second hyperpolarizabilities, however, such measurements are only feasible in the gas phase. In contrast, the hyper-Rayleigh scattering (HRS) experiment is dependent only upon $\beta$ and requires only an efficient detection system to collect the scattered second harmonic light.

In spite of the seemingly simple experimental requirements of the HRS apparatus, the results obtained by the HRS method have occasionally been significantly different than those obtained by the EFISHG experiment (when a direct comparison is possible). In particular, for compounds such as $N,N$-dimethylaninonitrostilbene (DANS), the NLO properties are expected to be essentially one dimensional and the two NLO characterization methods are expected to yield equivalent results. It has become apparent that the anomalous HRS results are due to two-photon induced fluorescence from some of these molecules. The presence of this two-photon induced fluorescence overlaps with the HRS spectrum and has prevented the previous authors from making an accurate assessment of the scattered second harmonic intensity. With the use of a scanning monochromator in the HRS apparatus to isolate the second harmonic signal, we find that consistent results are obtained from the HRS method and the EFISHG experiment for a determination the molecular $\beta$ of these compounds. Calibration of the absolute $\beta$ values was accomplished with respect to a HRS measurement of carbon tetrachloride, which has been previously characterized. Except for measurements on molecular liquids, previous HRS measurements have not provided any spectral information, as the spectral selectivity was achieved with interference filters.

The polarization of the incident and scattered light is analyzed in this work. As all components of the hyperpolarizability tensor $\beta$ can contribute to HRS, detailed polarization studies of the sample are able to provide information on several components of $\beta$. We provide expressions for the HRS for several molecular point groups assuming elliptically polarized incident light and detection of the second harmonic scattered light at 90° to the input light. These expressions provide a means of assessing the relative magnitudes of the
The molecules investigated in this work are listed in Table I. All compounds were obtained from Aldrich Chemical except for DANS, which was purchased from Acros Chemical (a division of Fisher Scientific) and LDS 722, which was purchased from Exciton, Inc. The purity of the compounds was typically greater than 95% and they were used as received. All the compounds were prepared as dilute solutions in 1,4 dioxane, which has negligible HRS signal for the selected compounds. Normal 1 cm spectroscopic fused silica cuvettes were used for measurements and in typical experiments a 1.0 cm$^3$ volume of liquid was sufficient. The solutions were filtered through a 0.2 μm micro pore filter to remove dust particles that could be a source of spurious second harmonic signal. When comparing chromophores in different solvents, the second harmonic signal was corrected for the effects of thermal lensing. The maximal HRS signal was limited due to strong thermal absorption from absorption at 1064 or 1319 nm by a C–H vibrational overtone.

A schematic diagram of the experimental apparatus is shown in Fig. 1. The incident radiation at 1064 or 1319 nm was obtained from an acousto-optically Q-switched Nd:YAG laser (Quantronix 116) operating in a near Gaussian TEM$_{00}$ mode with a measured $M^2$=1.1. The laser produced trains of $\approx$150 ns, 1 mJ pulses at a repetition rate of 3 kHz at 1064 nm and $\approx$400 ns, 0.1 mJ pulses at a repetition rate of 1 kHz at 1319 nm. The input power level and polarization were selected by two Glan–Laser polarizers followed by a Soleil–Babinet compensator. The incident laser beam was focused into the sample cell with a 4X microscope objective lens and positioned to pass at a distance of 2 mm from the inside of the cell wall facing the collecting lens. The scattered light was collected at 90° with f/1.8 optics and focused into a spectrometer (Jobin–Yvon Ramanor U 1000), with polarization selection by a sheet polaroid. The relative spectral response of the complete spectrometer was calibrated with respect to the graybody radiation emitted from a tungsten filament lamp, see Fig. 2. The entrance slits of the spectrometer were closed to provide a spectral slit width of 2–5 cm$^{-1}$. The spectrally dispersed light was detected by a cooled photon counting photomultiplier tube.

### Table I. Chromophore acronyms.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>pNA</td>
<td>p-Nitroaniline</td>
</tr>
<tr>
<td>oMA</td>
<td>o-Nitroaniline</td>
</tr>
<tr>
<td>mNA</td>
<td>m-Nitroaniline</td>
</tr>
<tr>
<td>DAB</td>
<td>4-Dimethylaminobenzaldehyde</td>
</tr>
<tr>
<td>MNA</td>
<td>2-Methyl, 4-nitroaniline</td>
</tr>
<tr>
<td>DAC</td>
<td>4-Dimethylaminocinnamaldehyde</td>
</tr>
<tr>
<td>MK</td>
<td>(Michler’s Ketone)</td>
</tr>
<tr>
<td>DBASA</td>
<td>trans, trans-Bis[4-(dimethylamino)benzylidene]acetone</td>
</tr>
<tr>
<td>DABMN</td>
<td>Dimethylaminobenzylidenemalononitrile</td>
</tr>
<tr>
<td>DANS</td>
<td>4-(Dimethylamino)-4’-nitrostilbene</td>
</tr>
<tr>
<td>Coumarin</td>
<td>334: 2,3,5,6 1H,4H-Tetrahydro-9-acetylquinoxilinolizin-9,9a,1-p-coumarin</td>
</tr>
<tr>
<td>DCM</td>
<td>4-Dicyanmethylen-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran</td>
</tr>
<tr>
<td>DR1</td>
<td>(Disperse Red 1) 4-[N-ethyl-N-(2-hydroxyethyl)] amino-4’-nitroazobenzene</td>
</tr>
<tr>
<td>LDS 722</td>
<td>1-Ethyl-4-(4-(dimethylamino)phenyl)-1,3-butadienyl)-pyridinium Perchlorate</td>
</tr>
<tr>
<td>Styrly</td>
<td>7: 2-[4-(4-(dimethylaminophenyl)-1,3-butadienyl]-3-ethylbenzothiazolium p-toluene sulfate</td>
</tr>
<tr>
<td>DIA</td>
<td>N,N Dimethylindoliniline</td>
</tr>
<tr>
<td>RB</td>
<td>Rhodamine B: 2-[6-Diethylylamino]-3-(diethylylma-3H-xanthen-9-yl] benzoic acid</td>
</tr>
<tr>
<td>CV</td>
<td>Crystal Violet</td>
</tr>
<tr>
<td>BG</td>
<td>Brilliant Green</td>
</tr>
<tr>
<td>BTB</td>
<td>Bromothymol Blue</td>
</tr>
</tbody>
</table>

first hyperpolarizability components that are needed for an accurate assessment of $\beta$ from HRS measurements. We conclude that HRS measurements are capable of the same or better level of accuracy as EFISHG measurements, with the benefit of being able to probe a wider variety of molecules and different hyperpolarizability components.

### II. EXPERIMENT

The molecules investigated in this work are listed in Table I. All compounds were obtained from Aldrich Chemical except for DANS, which was purchased from Acros Chemical (a division of Fisher Scientific) and LDS 722, which was purchased from Exciton, Inc. The purity of the compounds was typically greater than 95% and they were used as received. All the compounds were prepared as dilute solutions in 1,4 dioxane, which has negligible HRS signal for all polarization geometries. Approximately 5% methanol was added to the solutions of the molecular salts to aid in the dissolution of these compounds. Normal 1 cm spectroscopic fused silica cuvettes were used for measurements and in typical experiments a 1.0 cm$^3$ volume of liquid was sufficient. The solutions were filtered through a 0.2 μm micro pore filter to remove dust particles that could be a source of spurious second harmonic signal. When comparing chromophores in different solvents, the second harmonic signal was corrected for the effects of thermal lensing. The maximal HRS signal was limited due to strong thermal absorption from absorption at 1064 or 1319 nm by a C–H vibrational overtone.

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III. THEORY

Hyper-Rayleigh or second harmonic light scattering denotes a process in which two photons of frequency $\omega$ incident upon a noncentrosymmetric molecule or ensemble of molecules are absorbed and simultaneously 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 $E_0(\omega)$,

$$\mu_i = \alpha_i E_i + \frac{1}{2} \beta_{ijk} E_i E_j + \cdots,$$

where the molecular tensors $\alpha$ and $\beta$ describe the linear and lowest order nonlinear optical properties of the molecules, respectively. Note, that many experimentalists, especially those using the EFISHG technique, use a series expansion of the induced dipole moment without the factors of $1/n!$ in the definitions of the molecular hyperpolarizabilities. If the incident light is assumed to be travelling in the $x$ direction, the polarization of the incident electric field, $\mathbf{E}(\omega)$, can be described by the following equation:

$$\mathbf{E}(\omega) = E_0(\omega) \{ \cos \psi \cos \omega t e_x + \sin \psi \cos (\omega t + \delta) e_y \},$$

where $\psi$ and $\delta$ are arbitrary angles. Circularly polarized light is described by $\psi = \pi/4$ and $\delta = \pi/2$ and linearly polarized light by $\psi = 0$ (horizontal) or $\psi = \pi/2$ (vertical).

The second harmonic light intensity for a collection of $N$ noninteracting molecules without orientational correlations is given by $I^{2\omega}_N \approx N(\mu_0(2\omega)\mu_0(2\omega))$, 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. The ensemble averaging over the molecular motions indicated by the brackets will involve products of components of the first hyperpolarizability tensor $\beta$ of the form $\langle \beta_{1jk}\beta_{LMN} \rangle$. Assuming the scattered HRS signal is collected at $90^\circ$ along the $y$ direction, the polarization dependence of the second harmonic signal is given by

$$I^{2\omega}_E \approx \langle \mu_0^2 \rangle \times (\beta_{YYY}^2) \cos^4 \psi + (\beta_{ZZZ}^2) \sin^4 \psi$$

$$+ \sin^2 \psi \cos^2 \psi ((\beta_{YZZ} + \beta_{ZYY})^2 + 2\beta_{ZZZ} \beta_{YZZ} \cos 2\delta),$$

$$I^{2\omega}_H \approx \langle \mu_0^2 \rangle \times (\beta_{ZZZ}^2) \sin^4 \psi + (\beta_{XYY}^2) \cos^4 \psi$$

$$+ \sin^2 \psi \cos^2 \psi ((\beta_{XYZ} + \beta_{XZY})^2 + 2\beta_{XZZ} \beta_{XYX} \cos 2\delta),$$

where the subscripts $V$, $H$, and $E$ indicate vertically, horizontally, and elliptically polarized light, respectively. The macroscopic averages $\langle \beta_{1jk}\beta_{LMN} \rangle$ are quadratic forms of the microscopic molecule-fixed-axis hyperpolarizability components, $\beta_{ijk}$. These products may be calculated for molecules of any point group by using, for example, Table I and Eqs. (34)–(34) of Bersohn et al. or Table II and Eqs. (11)–(13) from Cyvin et al. In the general case, assuming that the first hyperpolarizability tensor is real, at most five invariants of the molecular hyperpolarizabilities may be determined, depending upon the molecular symmetry. Consequently, elliptically polarized light is required to obtain full information on these invariants when the detected scattered harmonic light is restricted to be linearly polarized. Subsequent work has shown that other polarization geometries may be required if the first hyperpolarizability tensor has an imaginary component.

A Soleil–Babinet compensator is used in our apparatus to create elliptically polarized light from the incident horizontally polarized light. The polarization of the light leaving the compensator can be written as

$$\mathbf{E}(\omega) = E_0(\omega) \left\{ \cos \frac{\Gamma}{2} \mathbf{e}_h - i \sin \frac{\Gamma}{2} \mathbf{e}_v \right\}.$$
5.0× greater intensity for vertically polarized as compared to horizontally polarized light from harmonic scattering at 1064 nm and 16.3× greater intensity at 1319 nm, as shown in Fig. 2.

The measured HRS intensities are strongly affected by the solution refractive indices, \( n \), as the amount of incident and scattered light passed through the cell will depend strongly upon these values. The transmission coefficient through a cell wall is

\[
T_{L,o} = \frac{1}{2} \left( 1 - \frac{1}{n_w - n_L} \right)^2 \left( \frac{n_w + n_L}{n_L} \right)^2,
\]

with window, \( n_w \), and liquid, \( n_L \), refractive indices at frequency \( \omega \), and where \( L = S \) (sample) or \( R \) (reference). Provided the laser focusing lens and the light collection lens are correctly repositioned to account for different focal geometries in different solutions, the relation between the relative HRS signal from the sample and reference is given by

\[
\frac{I_{S}^{2\omega}}{I_{R}^{2\omega}} = \frac{n_{R,S}^2}{n_{S,R}^2} \frac{T_{S,2\omega}^2}{T_{R,2\omega}^2} \frac{T_{S,2\omega}^2}{T_{R,2\omega}^2} \frac{N_S}{N_R} \left( \frac{\beta_S^2}{\beta_R^2} \right),
\]

where the factors account for effective scattering source length, collection solid angle, refraction losses, local fields, sample number density, and molecular hyperpolarizability, in that order. The Lorentz local field for sample \( S \) at frequency \( \omega \) is assumed to be given by

\[
\mu_S = \frac{n^2 + 2}{2n} \mu_{\text{th}}.
\]

All the HRS measurements of the samples reported in this work [except for a solvent dependence study of \( p \)-nitroaniline (pNA), see below] were made under nearly the same solvent conditions (1,4 dioxane), these factors due to the molecular environment are expected to be constant. A standard solution of pNA in 1,4 dioxane served as a secondary external reference standard for the comparison of the harmonic scattering from different NLO chromophores.

The comparison of different chromophores is based on the HRS measurements of the sample solutions in the VV polarization geometry. In this case, the second harmonic intensity of the sample, \( I_{VV}^{2\omega} \), is given by

\[
I_{VV}^{2\omega} = N(I_{VV}^{2\omega})(\omega^2)^4 \times 10^{-10},
\]

where the absorbance, \( A = \varepsilon_{2\omega}cL \), accounts for the absorption losses at the second harmonic wavelength (532 or 660 nm). The extinction coefficient is \( \varepsilon_{2\omega} \), the concentration of the solution is given by \( c \), and the distance from the laser beam to the cell wall is \( L \) (2 mm). As the reference and the sample chromophores were measured under nearly the same solvent conditions, the first hyperpolarizability of the sample, \( \beta_{VV}^S \), can be obtained from the following equation:

\[
\beta_{VV}^S = \sqrt{\frac{C_{VV}}{C_{VV}}} \sqrt{\frac{I_{VV}^{2\omega}}{I_{VV,R}^{2\omega}}} \sqrt{\frac{N_R}{N_S}} \beta_{VV}^R,
\]

where the subscript VV indicates the appropriate average of the molecule-fixed coefficient of the first hyperpolarizability in the VV polarization geometry. The coefficient \( C_{VV} \) is a numerical factor obtained from the spatial averaging of \( \langle \beta_{VV}^S \rangle \). In the next section we calculate these factors for some of the molecular point groups of the chromophores investigated in this work, along with the polarization ratios for elliptically polarized light as given by Eqs. (4a)–(4c).

### IV. HRS DEPOLARIZATION RATIOS FOR SELECTED POINT GROUPS

The macroscopic averages \( (\beta_{UV} \beta_{LMN}) \) that determine the amount of HRS scattering in Eqs. (4a)–(4c) were calculated by using Eqs. (34)–(44) and Table I of Bersohn et al. The nonzero components of \( \beta \) were taken from standard compilations of NLO susceptibility component tables. The coefficients \( \beta_{VV} \) and \( C_{VV} \) are then obtained by setting \( \psi = \pi/2 \) in the equations below for \( I_{UV}^{2\omega} \). Some of these polarization ratios and their coefficients have been determined previously for selected polarization geometries. However, as noted above, in order to correct for the finite collection angle of the detection optics, complete expressions for the dipole moment averages of \( \langle \mu_i^2 \rangle \) including their polarization dependences are required for a determination of \( \beta \) by the HRS measurement.

#### A. Molecules of \( D_{3h} \) symmetry

**One independent nonzero coefficient, \( \beta_{yyy} \)**

\[
I_{VV}^{2\omega} \propto \langle \mu_i^2 \rangle \propto \frac{8}{35} \beta_{yyy}^2 \left[ 1 + \frac{5}{3} \cos^2 \psi - 2 \cos^4 \psi \right],
\]

(9a)

\[
I_{VV}^{2\omega} \propto \langle \mu_i^2 \rangle \propto \frac{16}{105} \beta_{yyy}^2 \left[ 1 + \cos^2 \psi - \cos^4 \psi \right],
\]

(9b)

\[
\langle \mu_i^2 \rangle \propto \frac{16}{105} \beta_{yyy}^2 \left[ 1 + \frac{7}{2} \cos^2 \psi - 3 \cos^4 \psi \right],
\]

(9c)

\[
\frac{I_{VV}^{2\omega}}{I_{VV}^{2\omega}} = \frac{3}{2},
\]

(9d)

\[
\beta_{VV} = \beta_{yyy} \quad \text{and} \quad C_{VV} = \frac{8}{35}.
\]

(9e)

#### B. Molecules of \( T_d \) symmetry

**One independent nonzero coefficient, \( \beta_{xyz} \)**

The equations obtained from Eqs. (4a)–(4c) for molecules of \( T_d \) symmetry have been given previously. The results are the same for molecules of \( D_{3h} \) symmetry, with

\[
\frac{I_{VV}^{2\omega}}{I_{VV}^{2\omega}} = \frac{3}{2},
\]

but with the exception that

\[
\beta_{VV} = \beta_{xyz} \quad \text{and} \quad C_{VV} = 12/35.
\]

(10b)

#### C. Molecules of \( D_3 \) symmetry

**Two independent nonzero coefficients, \( \beta_{xxx} \) and \( \beta_{xyz} \)**

\[
I_{VV}^{2\omega} \propto \langle \mu_i^2 \rangle \propto \frac{8}{35} \beta_{xxx}^2 \left[ 1 + \frac{5}{3} + \frac{6}{R^2} \right] \cos^2 \psi - 2 \cos^4 \psi,
\]

(11a)
For where

\[ C \] of Kleinman symmetry breaking for the \( R_5 \) structure, so that Kleinman symmetry, which implies

\[ b \]

coefficients, corresponding expressions for \( D_3 \) and

\[ \beta_{2\text{nn}} \]

\[ \beta_{2\text{nn}} = \frac{6}{4 + 7R^2}, \]

where \( R = \beta_{2\text{nn}}/\beta_{2\text{nn}} \) and

\[ \beta_{2\text{nn}} = \beta_{2\text{nn}} \] and \( C_{2\text{nn}} = 8/35. \]

For \( D_3 \) symmetry, Kleinman symmetry implies \( \beta_{2\text{nn}} = 0 \) and \( R = 0 \), so with Kleinman symmetry Eqs. (11a)–(11e) reduce to the same expressions as for \( D_3h \) symmetry, Eqs. (9a)–(9e).

D. Molecules of \( C_{2\text{v}} \) symmetry

The molecule is taken to be in the \( z-y \) plane with \( z \) the two-fold symmetry axis. There are five nonzero independent coefficients, \( \beta_{zzz}, \beta_{zxy}, \beta_{xzz}, \beta_{xyy}, \) and \( \beta_{yyz} \). We assume Kleinman symmetry, which implies \( \beta_{zxy} = \beta_{xyz} \) and \( \beta_{xxz} = \beta_{zxx} \). Also, we assume an essentially two-dimensional structure, so that \( \beta_{xxz} = \beta_{zxx} = 0 \). In this case Eqs. (4a)–(4c) give

\[ I_{\text{HH}}^{2\text{w}} \propto \frac{1}{105} \beta_{zzz}^2 \left[ 15 + 18R + 27R^2 - (24 + 68R + 4R^2) \right] \]

\[ \times \cos^4 \psi + (12 + 48R - 12R^2) \cos^4 \psi \],

(12a)

\[ I_{\text{VV}}^{2\text{w}} \propto \frac{1}{105} \beta_{zzz}^2 \left[ 3 - 2R + 11R^2 - (4 + 16R - 4R^2) \cos^2 \psi \right] \]

\[ + (4 + 16R - 4R^2) \cos^4 \psi \],

(12b)

\[ \langle \mu^2 \rangle \propto \frac{1}{105} \beta_{zzz}^2 \left[ 3 - 2R + 11R^2 + (-28R + 28R^2) \cos^2 \psi \right] \]

\[ + (12 + 48R - 12R^2) \cos^4 \psi \].

(12c)

\[ I_{\text{HV}}^{2\text{w}} = \frac{15 + 18R + 27R^2}{3 - 2R + 11R^2}, \]

(12d)

where \( R = \beta_{zxy}/\beta_{zxy} \) and

\[ \beta_{2\text{nn}} = \beta_{2\text{nn}} \] and \( C_{2\text{nn}} = 15 + 18R + 27R^2 \]

\[ 105. \]

(12e)

Note that when \( R = -1 \), Eqs. (12a)–(12e) reduce to the corresponding expressions for \( D_3h \) symmetry, Eqs. (9a)–(9e), as expected. Algorithms that include the possibility of Kleinman symmetry breaking for the \( C_{2\text{v}} \) point group or groups of lower symmetry are straightforward to program. Generally, however, the equations are indeterminate as there are usually more nonzero coefficients than can reasonably be determined by HRS measurements.

V. RESULTS AND DISCUSSION

In order to calibrate the results of the HRS experiment, a reference standard is required. Carbon tetrachloride was found to be useful for this purpose as it has a reasonably large signal for a small molecule, has only one nonzero coefficient of the first hyperpolarizability, \( \beta_{yyz} \), exhibits no significant absorption in the near infrared, and has been fully characterized in a previous communication. This determination of \( \beta_{yyz} \) of CCl\(_4\) was based on an analysis of the intra and intermolecular interactions of the molecular multipole moments and hyperpolarizabilities of CCl\(_4\). Of the total HRS observed from CCl\(_4\), approximately 40% of the HRS intensity is due to the intrinsic molecular contribution from \( \beta_{yyz} \), for which we find a value of 19 au at 1064 nm. Preliminary results from a more direct comparison between gas phase EFISHG and HRS, liquid HRS measurements, and theoretical calculations of hyperpolarizabilities of a number of molecular liquids are in good agreement with this value for \( \beta_{yyz} \) of CCl\(_4\).

Recently, Morrison et al. address some of the difficulties that can occur regarding the use of a pure solvent such as CCl\(_4\) as a HRS reference. These problems however, are not applicable to our experimental setup. The beam waist radius in our apparatus is \( \approx 7 \mu m \) compared to \( \approx 82 \mu m \) in that of Morrison et al. and the confocal beam length is about 260× smaller. Consequently, the effective scattering source volume in our apparatus is \( \approx 3000 \)× smaller than that of Morrison et al. and hence we are much less likely to have scattering from any residual dust in the sample. Also, the gated electronics in our photon counting apparatus accept at most one count per laser pulse, which limits the number of counts due to a possible dust scattering event. Finally, as we do a frequency scan of the scattered radiation, any residual background scattering can be subtracted off from the SHG signal.

The values of the measured first hyperpolarizabilities have long been known to be strongly dependent on the effects of the solvent on the chromophore solute. This effect has also been observed in a systematic measurement of pNA in various solvents by the EFISHG experiment. Due to the simplicity of the local field factors in the HRS experiment in comparison with the EFISHG measurement, an assessment of NLO chromophores in various solvents by the HRS technique should give an intrinsically more accurate means of measuring the changes in \( \beta \) due to different solvent conditions. The results of these measurements for the pNA molecule are collected in Table II. The value of \( \beta_{zzz} \) of pNA was determined through use of Eq. (6) and Eqs. (12a)–(12e). Qualitatively, the same trends observed in the EFISHG experiment are also observed in the results of the HRS experiment. However, when comparing the \( \beta \) values obtained from HRS experiment to those obtained from the EFISHG experiment, we find that the HRS values are 0.631 ± 0.035× the values obtained from the EFISHG measurement. Note, that
the EFISHG determination of $\beta$ for pNA is also typically 
$\approx 5\%$ too large due to neglect of the third order contribution 
[recall Eq. (1)]. As the reference standard used in the 
EFISHG experiments was a quartz crystal with an assumed 
SHG coefficient of $d_{11} = 0.5$ pm/V, our results from the HRS 
experiment imply that the quartz reference value should be 
$d_{11} = 0.30 \pm 0.02$ pm/V. This value is in agreement with the 
conclusions of Roberts, recent measurements by Mito 
and Bethea.28

As has been noted previously, many chromophores of 
interest for applications in nonlinear or electro-optics also 
exist a large two-photon induced fluorescence effect.8 In 
fact, many of the chromophores listed in Table I are also 
used as laser dyes and/or fluorescent probes. Previous au-


tors have overestimated the values for $\beta$ obtained from 
HRS measurements, as the two-photon induced fluorescence 
typically overlaps with the HRS spectrum to a significant 
extent.8,29 This is illustrated in Fig. 3 for the DANS chromo-
phore for HRS with excitation at a fundamental wave-
length of 1064 nm. For comparison, HRS from pNA is also 
shown in Fig. 3, from which there is a negligible amount of 
two-photon induced fluorescence. Evidence that this is a 
two-photon process is shown in Fig. 4 which illustrates the 
power dependence of the fluorescence for the case of DANS 
with two-photon fluorescence emission maximum at 
$16500 \text{ cm}^{-1}$ (606 nm). The power law coefficient of $m = 2.02$ 
indicates that the fluorescence is excited by a two-photon 
absorption process. The results from the other chromophores

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**TABLE II.** A comparison of the solvent dependence of the first hyperpolarizability $\beta_{zzz}$ of pNA from the HRS measurements (referenced to $\beta_{zzz}$ of CCl$_4$ = 19 au) with the EFISHG measurements. The hyperpolarizabilities are given in atomic units (1 au = $3.206 \times 10^{-35}$ C$^2$ m$^3$ J$^{-2}$ = $3.6213 \times 10^{-42}$ m$^4$ V$^{-1}$ = $8.6392 \times 10^{-33}$ esu, with $\mu = 1/2 BE^2$). The ratio of $\beta_{zzz}^{\text{HRS}}$ to $\beta_{zzz}^{\text{EFISHG}}$ is nearly constant at 0.631$\pm$0.038. After adjusting this ratio by 
subtracting the third order hyper-polarizability contribution to the liquid EFISHG signal (~5%) we conclude 
that the reference value for quartz is $d_{11} = 0.30 \pm 0.02$ pm/V at 1064 nm. The values of the zero frequency 
hyper-polarizabilities, $\beta_{zzz}$, are calculated by the two-level model from the HRS measurements, except for 
the vapor phase results, which are extrapolated from the EFISHG measurements.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_0$ [nm]</th>
<th>$\beta_{zzz}^{\text{HRS}}$ [au]</th>
<th>$\beta_{zzz}^{\text{EFISHG}}$ [au]</th>
<th>Ratio</th>
<th>$\beta_{zzz}$ [au]</th>
</tr>
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<td>vapor</td>
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<td>1808</td>
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<td>1201</td>
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<tr>
<td>CDCl$_3$</td>
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<td>2630</td>
<td>3774</td>
<td>0.654</td>
<td>1344</td>
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<tr>
<td>1,4 dioxane</td>
<td>354</td>
<td>2470</td>
<td>3913</td>
<td>0.631</td>
<td>1225</td>
</tr>
<tr>
<td>CH$_3$CN</td>
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<td>4430</td>
<td>6760</td>
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<td>2057</td>
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<tr>
<td>CH$_3$OD</td>
<td>370</td>
<td>4540</td>
<td>7987</td>
<td>0.568</td>
<td>2061</td>
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</tbody>
</table>

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8P. Kaatz and D. P. Shelton (unpublished).
TABLE III. Optical and nonlinear optical properties of selected chromophores at 1064 nm. The absorption maximum and the two-photon induced fluorescence maximum are given by $\lambda_0$ and $\lambda_F$, respectively. The integrated two-photon induced fluorescence intensity (photon flux) and the integrated HRS intensity are indicated by $I_F$ and $I_{HRS}$. The uncertainty in the measured depolarization ratio of $I_{C\nu V}/I_{HRS}$ is in the range of 2%-3%. The ratio of hyperpolarizability components $R$ is obtained by inverting the expression for the polarization ratio as a function of $R$. Figure 6 shows a graph of Eq. (12d) which expresses this relation in the case of $C_{2v}$ symmetry. The uncertainty of $R$ depends on the slope of the graph and for values of $I_{C\nu V}/I_{HRS}$=5 the relative uncertainty of $R$ is approximately $\pm 0.015$ (see the inset of Fig. 6). Absolute values of the first hyperpolarizability $\beta$ were obtained by comparison with $\beta_{1zz}$ of CCl$_4$, which has a value of 19 au at $\lambda_0=1064$ nm (Ref. 10). Values for the first hyperpolarizabilities $\beta$ are given in relative units (relative to $\beta_{1zz}$ of pNA) and absolute atomic units (au) (see Table II for a list of conversion factors to other units). The zero frequency hyperpolarizability, $\beta_0$, is calculated by the two-level model from the measurements at 1064 nm.

| Chromophore | Group | $\lambda_0$ [nm] | $\lambda_F$ [nm] | $I_F/I_{HRS}$ | $I_{C\nu V}/I_{HRS}$ | $R$ | $\beta_{1zz}$ [au] | $\beta_{0}$ [au] |
|-------------|-------|------------------|------------------|----------------|---------------------|----------------|-------------------|
| pNA         | $C_{2v}$ | 354               | <2               | 7.1            | 4.9                 | -0.008          | 1                 | 2470             |
| oNA         | $C_{2}$  | 370              | 5.8, 3.0$^a$     | 6.1            | +0.14, +0.60        | 0.2 – 0.3       | 620              | 300              |
| mNA         | $C_{2}$  | 397              | ~15              | 6.5            | +0.048             | 0.82            | 2020             | 1100             |
| DAB         | $C_{2v}$ | 329              | 6.5, 5.6         | +0.060         | 0.92               | 2270            | 1090             |
| MNA         | $C_{2v}$ | 361              | 6.8, 5.2         | +0.018         | 2.9                | 7260            | 3280             |
| DAC         | $C_{2v}$ | 371              | 8.7              | -0.280         | 0.85               | 2100            | 1220             |
| MK          | $C_{2v}$ | 322              | 8.7              | -0.330         | 0.60               | 1480            | 750              |
| DBCP        | $C_{2v}$ | 345, 359$^b$     | 8.7              | 6.3, 5.6       | +0.015             | 14              | 34600            | 10400            |
| BDABA       | $C_{2v}$ | 426              | 8.5, 3.0         | -0.230         | 5.3                | 13100           | 3960              |
| DABMN       | $C_{2v}$ | 420              | 7.3              | -0.033         | 4.8                | 11800           | 3760             |
| DANS        | $C_{2v}$ | 426              | 6.9              | +0.015         | 14                 | 36400           | 10400            |
| Coumarin 334| $C_{2v}$ | 438              | 7.6              | -0.070         | 4.7                | 11700           | 3130             |
| DCM         | $C_{2v}$ | 455              | 6.4              | +0.073         | 19                 | 46900           | 10300            |
| DRI         | $C_{2v}$ | 474              | 6.8              | +0.021         | 33                 | 81500           | 13400            |
| LDS 722     | $C_{2v}$ | 489              | 7.1              | -0.013         | 50                 | 123000          | 15100            |
| Styril 7    | $C_{2v}$ | 563              | 7.5              | -0.005         | 92                 | 227000          | 10600            |
| DIA         | $C_{2v}$ | 566              | 7.0              | +0.002         | 19                 | 46900           | 4400             |
| RB          | $C_{2v}$ | 562              | <2               | 7.0            | 5.0                 | +0.002          | 19               | 46900           |
| CV          | $D_{3h}$ | 589              | 4.4              | 1.5            | 27                 | 66700           | 10400            |
| BG          | $C_{2v}$ | 632              | 7.6              | 2.1            | -0.300$^c$        | 17              | 42000            | 11200            |
| BTB (acid)$^d$ | $C_1$  | 420              | 7.6              | 4.3            | -0.072             | 2.5             | 6160             | 1960             |
| BTB (base)$^d$ | $C_1$  | 613              | 7.5              | 4.4            | -0.062             | 26              | 64200            | 14100            |

$^a$The polarization data for oNA can be fit assuming $C_{2v}$ symmetry with $R=+0.14$ or +0.60. See Fig. 9 and the related discussion.
$^b$Shoulder at 359 nm.
$^c$The polarization data for BG cannot be fitted assuming Kleinman symmetry at 1064 nm. See Fig. 7 and the related discussion.
$^d$The polarization data for BTB is fitted assuming $C_{2v}$ symmetry.

FIG. 5. The spectrum of the two-photon induced fluorescence from DANS with irradiation at 1064 nm. The spectrum is similar to the single-photon-induced fluorescence spectrum. The measured spectrum is corrected for the spectral response of the spectrometer, see Fig. 2. The HRS peak at $2\omega=18797$ cm$^{-1}$ seen in Fig. 3 is undetectable here because of the low spectral resolution.
TABLE IV. Optical and nonlinear optical properties of selected chromophores at \(\lambda_b = 1319\) nm. See Table I for a listing of the chromophore acronyms. The remaining notation is the same as that used in Table III. Absolute values of the first hyperpolarizability were obtained by comparison with \(\beta_0\) of CCl\(_4\) which was assumed to have a value of 18 au at \(\lambda_b = 1319\) nm. Values for the first hyperpolarizabilities \(\beta\) are given in units to \(\beta_0\) of pNA and absolute atomic units (au), see Table II for conversion factors to other commonly used units. The zero frequency hyperpolarizability, \(\beta_0\) is calculated by the two-level model from the measurements at 1319 nm.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>Group</th>
<th>(\lambda_b) [nm]</th>
<th>(\lambda_f) [nm]</th>
<th>(I_p/I_{HRS})</th>
<th>(1/C_{VV})</th>
<th>(\Delta n/\Delta n_{IV})</th>
<th>(R)</th>
<th>(\beta_{HRS})</th>
<th>(\beta_{HRS}) [au]</th>
<th>(\beta_0) [au]</th>
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<tbody>
<tr>
<td>pNA</td>
<td>C(_{2V})</td>
<td>354</td>
<td>&lt;2</td>
<td>6.5</td>
<td>5.6</td>
<td>+0.063</td>
<td>1</td>
<td>1.850</td>
<td>4.2000</td>
<td>1.225</td>
</tr>
<tr>
<td>DABMN</td>
<td>C(_{2V})</td>
<td>420</td>
<td>6.5</td>
<td>+0.058</td>
<td>3.8</td>
<td>7.030</td>
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<tr>
<td>DANS</td>
<td>C(_{2V})</td>
<td>426</td>
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<td>+0.026</td>
<td>8.8</td>
<td>16.300</td>
<td>8.520</td>
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<tr>
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<tr>
<td>LDS 722</td>
<td>C(_{2V})</td>
<td>489</td>
<td>6.8</td>
<td>+0.025</td>
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<td>24.600</td>
<td>10.400</td>
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<td>Styril 7(^a)</td>
<td>C(_{2V})</td>
<td>563</td>
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<td>25</td>
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<td></td>
<td></td>
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<tr>
<td>DIA</td>
<td>C(_{2V})</td>
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<td>&lt;2</td>
<td>7.0</td>
<td>5.0</td>
<td>+0.006</td>
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<td>107.000</td>
<td>6.730</td>
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<tr>
<td>BTB (base)(^b)</td>
<td>C(_1)</td>
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<td>24</td>
<td>44.400</td>
<td>4.740</td>
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<td></td>
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</tbody>
</table>

\(^a\)The HRS at 1319 nm from Styril 7 is masked by the intense two-photon induced fluorescence.

\(^b\)The polarization data for BTB is fitted assuming C\(_{2V}\) symmetry.

ence. And in the extreme case of Styril 7 with excitation at 1319 nm, it is not even possible to separate the contribution of the two-photon induced fluorescence from the scattered second harmonic light with our apparatus.

Also indicated in Tables III and IV are the extrapolated zero frequency values of the first hyperpolarizabilities obtained by applying the two-level model to the HRS measurements at 1064 and 1319 nm. The two level model can be described in terms of the transition frequency, \(\omega_{eg}\), (the corresponding wavelength \(\lambda_b\) is given in Tables III and IV) of the highest occupied-lowest unoccupied energy level transition.\(^4,30\) The frequency response of \(\beta\) can then be modeled as

\[
\beta(-2\omega, \omega, \omega) = \frac{\omega_{eg}^4}{(\omega_{eg}^2 - 4\omega^2)(\omega_{eg}^2 - 4\omega^2 - 3\omega^2)} \beta_0, \quad (13)
\]

where \(\beta_0\) is given by

\[
\beta_0 = \frac{3}{2}\frac{\Delta \mu \cdot \mu_{eg}^2}{\omega_{eg}^2}. \quad (14)
\]

The difference between excited and ground state electric dipole moments is given by \(\Delta \mu\) and \(\mu_{eg}\) is the transition dipole moment between the ground and excited state. We estimate \(\beta_0\) using the two-level model by substituting the measured values of \(\beta\), \(\lambda\), and \(\lambda_f\) into Eq. (13).

The values for \(\beta_0\) of pNA in selected solvents are also tabulated in Table II. The two-level model predicts an approximate second order dependence of \(\beta_0\) with \(\lambda_b\), from Eq. (14). This power law prediction has generally been verified in studies of the relationship of \(\beta\) with respect to the conjugation dependencies (length) of different chromophores.\(^31-33\) The \(\beta_0\) value implied from our HRS results, however, indicates that pNA in 1,4 dioxane gives within experimental error the same \(\beta_0\) value as the vapor phase ElishG measurement of pNA, whereas the two-level model predicts that \(\beta_0\) should increase by \(\approx 40\%\). The values for \(\beta_0\) of pNA in more polar solvents such as acetonitrile (CH\(_3\)CN) or methanol (CH\(_3\)OD) are in approximate agreement with the two-level model prediction of an \(\approx 70\%\) increase of \(\beta_0\) with respect to the corresponding value obtained from the vapor phase ElishG measurement. These HRS results are in agreement with the previous ElishG measurements.\(^25\)

The adequacy of the two-level model for a constant chromophore/solvent system can be assessed by comparing the corresponding \(\beta_0\) values in Tables III and IV. In general, we find that the two-level model adequately describes the measured increase in \(\beta\) as the incident wavelength decreases from 1319 to 1064 nm for the single ring systems such as pNA, as the agreement in \(\beta_0\) from Tables III and IV indicates. For the larger two ring or central atom systems however, the value of \(\beta_0\) obtained from a measurement at 1064 nm typically provides an unreliable prediction of the value of \(\beta\) obtained from a measurement at 1319 nm.

The results of Tables III and IV are generally in reasonable agreement with the ElishG results on the same molecules. Occasionally, however, there are significant differences. For example, after correcting for the differences in the definition of \(\beta\), quartz reference value (\(d_{11}\)), and accounting for dispersion via the two level model, we obtain nearly the same value for \(\beta_{HRS}\) of DANS by the HRS measurement as do Cheng et al.\(^5\) by the ElishG experiment. In comparing the same measurements of DR1, however, the results of Cheng et al. are 53\% lower than our HRS measurements. For DR1, the HRS measurements at 1319 nm are not expected to be resonantly enhanced, so the two measurement procedures should yield equivalent values for \(\beta_0\) but they do not. Such discrepancies can lead to large differences in the measured values of \(\beta\) from various groups, as the ElishG results have occasionally been used to calibrate the results from HRS measurements.\(^34-37\)

Most of the chromophores investigated in this work have at least quasi C\(_{2V}\) symmetry. The nonlinear optical properties of these chromophores have traditionally been assumed to be one-dimensional, primarily because the ElishG experiment is incapable of assessing the relative magnitude of hyperpolarizability components. In contrast, HRS measurements are
able to give some insight into the magnitude of other components. Figure 6 shows the dependence of the ratio \( R = \frac{\beta_{y2}}{\beta_{zz}} \) for \( C_{2v} \) symmetry as a function of the measured polarization ratio \( \frac{I_{VV}^{02}}{I_{VV}^{00}} \), as calculated from Eq. (12d). Most of the molecules in Tables III and IV have approximately \( C_{2v} \) symmetry with a polarization ratio \( \frac{I_{VV}^{02}}{I_{VV}^{00}} \) in the range of 4.2–5.8. The inset shows that the relation between the polarization ratio and values of \( R \) obtained from Eq. (12d) are approximately linear in this range. Although in principle, \( R \) is double valued for measured values of \( \frac{I_{VV}^{02}}{I_{VV}^{00}} > 5 \), most of the molecules with \( C_{2v} \) symmetry investigated in this work have a strong charge transfer axis. The component of the first hyperpolarizability along this axis, \( \beta_{zz} \), is expected to dominate the nonlinear response. Exceptions are the "lambda" molecules, for which \( R \approx -0.30 \).

FIG. 6. The value of \( R = \frac{\beta_{y2}}{\beta_{zz}} \) for \( C_{2v} \) symmetry as a function of the measured polarization ratio, \( \frac{I_{VV}^{02}}{I_{VV}^{00}} \), as calculated from Eq. (12d). Most of the molecules in Tables III and IV have approximately \( C_{2v} \) symmetry with a polarization ratio \( \frac{I_{VV}^{02}}{I_{VV}^{00}} \) in the range of 4.2–5.8. The inset shows that the relation between the polarization ratio and values of \( R \) obtained from Eq. (12d) are approximately linear in this range. Although in principle, \( R \) is double valued for measured values of \( \frac{I_{VV}^{02}}{I_{VV}^{00}} > 5 \), most of the molecules with \( C_{2v} \) symmetry investigated in this work have a strong charge transfer axis. The component of the first hyperpolarizability along this axis, \( \beta_{zz} \), is expected to dominate the nonlinear response. Exceptions are the "lambda" molecules, for which \( R \approx -0.30 \).

FIG. 7. The measured polarization ratios \( \frac{I_{VV}^{02}}{I_{VV}^{00}} \) of BG with irradiation at 1064 nm (solid squares) and at 1319 nm (open squares) as a function of the retardation angle \( \psi \). At 1319 nm, the polarization data can be fitted assuming Kleinman symmetry for a molecule of \( C_{2v} \) symmetry with \( R = -0.340 \) (solid curve). At 1064 nm, however, where the second harmonic occurs in the absorption band of the molecule, the data cannot be fitted assuming Kleinman symmetry. The dashed curve through the data at 1064 nm is drawn assuming \( C_{2v} \) symmetry with parameter values \( \beta_{y2}/\beta_{zz} = \beta_{x2}/\beta_{zz} = -0.300 \), \( \beta_{xt}/\beta_{zz} = +0.330 \), and \( \beta_{xt}/\beta_{zz} = 0 \). The fit at 1064 nm is optimized assuming that the values for \( \beta_{y2} \) and \( \beta_{xz} \) change relatively little from their values at 1319 nm (see text).
reported for the CV molecule, with widely different results.22,23,41,45 Our own results off resonance at 1319 nm compare best with the long wavelength measurements of Stadler et al.37 At 1319 nm we obtain a value for \( \beta_{zyy} \) of CV that is 1.20 times smaller than that of DR1, while Stadler et al. find a value of 1.35 times smaller at 1500 nm. We disagree on the absolute value of DR1, however, for reasons discussed previously. The possibility of residual scattering as discussed by Morrison et al.23 may explain the difference in the results as Stadler et al. use an unfocused beam in their HRS apparatus, which provides a much larger scattering source volume. The results at other wavelengths likely involve differences in accounting for absorption, excess scattering, and/or the method used to infer a \( \beta \) value.

For reasons of symmetry, both the ground and excited state dipole moments are identically zero for octupolar molecules. Thus the two-level model is not applicable to these molecules, as is evident from Eq. (14). The \( \beta_0 \) values in Tables III and IV for CV are obtained from a three-level model with nearly degenerate excited states.41 The frequency dependence of \( \beta \) for this model is exactly the same as the two-level model result given by Eq. (13). At 1064 nm the measured \( \beta \) value of CV is comparable to that of DR1. However, as indicated previously, the resonantly enhanced value of \( \beta \) from the HRS measurement at 1064 nm provides an unreliable prediction of the value of \( \beta_0 \), as this value of \( \beta_0 \) is more than twice as high as the value for \( \beta_0 \) derived from the HRS measurement at 1319 nm.

A number of theoretical calculations exist for hyperpolarizability components of pNA.46–49 Some of these calculations are collected in Table V and compared with our HRS and EFISHG measurements. In general, the calculated polarization ratios, \( I_{VV}/I_{HV} \), are significantly lower than our measured ratios. Moreover, we find that there is considerable dispersion in \( \beta_{zyy} \) for pNA. At 1064 nm we find \( R = -0.008 \pm 0.015 \), while at 1319 nm \( R = +0.063 \pm 0.015 \). The results of the HRS measurements at 1064 nm are shown in Fig. 9 with the corresponding fit to \( C_{2V} \) symmetry using Eqs. (12a)–(12e).

The polarization ratio \( I_{VV}/I_{HV} \) of pNA measured at 1064 nm in this work is significantly higher (about 9%) than previous results.35,50 Lower values obtained by previous authors may be partly due to a neglect of the effect of the finite aperture of the collection optics used in the apparatus of their HRS experiments. As an indication of the size of such effects with the apparatus used in this work, the uncorrected measured polarization ratio \( I_{VV}/I_{HV} \) is predicted to be about 8% smaller than the corrected measured ratio \( I_{VV}/I_{HV} \) for pNA, whereas, the corrected polarization ratios must be equal. This was experimentally verified for pNA at both incident wavelengths (1064 and 1319 nm). As this finite aperture effect is more important for larger HRS polarization ratios, a comparison of HRS measurements with other "standard" 

![Graph](image)

FIG. 8. The measured polarization ratios \( I_{VV}/I_{HV} \) of CV with irradiation at 1064 nm (solid squares) as a function of the retardation angle \( \psi \). The curve shows that the HRS polarization data can be fit assuming CV has \( D_{3h} \) symmetry, or equivalently, assuming \( D_3 \) symmetry with \( R = \beta_{zyy}/\beta_{yy} = 0.0 \pm 0.015 \). The HRS polarization results from irradiation at 1319 nm are similar.

### Table V. Experimental and theoretical first hyperpolarizability components of pNA.

<table>
<thead>
<tr>
<th>Method</th>
<th>( \lambda_0 ) [nm]</th>
<th>( \beta_{zzz} ) [au]</th>
<th>( \beta_{zzz} ) [au]</th>
<th>( \beta_{zyy} ) [au]</th>
<th>( \beta_0 ) [au]</th>
<th>( I_{VV}/I_{HV} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFISHG</td>
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<td>1808</td>
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<td></td>
<td></td>
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<tr>
<td>EFISHG</td>
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<td>EFISHG</td>
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<td>HRS</td>
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<td>4.9 ± 0.1</td>
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<td>1967</td>
<td>5.6 ± 0.1</td>
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<td>1029</td>
<td>-23</td>
<td>-39</td>
<td>967</td>
<td>4.44</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Results from a vapor phase EFISHG measurement.
*Extrapolated by the two-level model using the vapor phase measurement at 1064 nm.
*Results from measurement in 1,4 dioxane.
TABLE VI. Experimental and theoretical first hyperpolarizability components of oNA.

<table>
<thead>
<tr>
<th>Method</th>
<th>(\lambda_0) [nm]</th>
<th>(\beta_{zzz}) [au]</th>
<th>(\beta_{\gamma\gamma}) [au]</th>
<th>(\beta_{\gamma\gamma}) [au]</th>
<th>(\beta_{\gamma\gamma}) [au]</th>
<th>(R)</th>
<th>(R_{VV}^2/R_{HV}^2)</th>
<th>(\text{Ref.})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRS(^a)</td>
<td>1064</td>
<td>709</td>
<td>0</td>
<td>0</td>
<td>+100</td>
<td>809</td>
<td>+0.14</td>
<td>6.1±0.1</td>
</tr>
<tr>
<td>HRS(^b)</td>
<td>1064</td>
<td>510</td>
<td>0</td>
<td>0</td>
<td>+306</td>
<td>816</td>
<td>+0.60</td>
<td>6.1±0.1</td>
</tr>
<tr>
<td>EFISHG(^b)</td>
<td>1907</td>
<td>404(^b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>INDO</td>
<td>1313</td>
<td>132</td>
<td>−360</td>
<td>235</td>
<td>1560</td>
<td>+0.18</td>
<td>5.3</td>
<td>51</td>
</tr>
</tbody>
</table>

\(^a\)Results from measurement in 1,4 dioxane.
\(^b\)For comparison with the HRS measurements, the extrapolated value (2-level model) of \(\beta\) is 730 au at 1064 nm.

VI. CONCLUSIONS

In contrast to previous work on HRS measurements from NLO chromophores, we find it essential to incorporate a scanning monochromator to analyze the properties of the scattered light. Quite often molecules of interest for nonlinear optical and electro-optic applications also exhibit two-photon induced fluorescence that can interfere with the analysis of the second harmonic scattered light. Interference filters are usually inadequate for selecting just the second harmonic photons. The existence of the strong two-photon induced fluorescence in many of these chromophores also has implications for potential SHG devices, as prolonged two-photon induced fluorescence usually leads to eventual bleaching of the NLO chromophores.\(^{52,53}\)

The HRS technique is a useful alternative to the well-established EFISHG measurement for the determination of the molecular \(\beta\) of NLO chromophores. The HRS measurement generally provides more information on a number of independent \(\beta\) components and is also applicable to molecular salts and molecules of low symmetry. The EFISHG experiment does have advantages for the measurement of chromophores that absorb far into the red, however. We find that the HRS measurement yields results for \(\beta\) that are generally consistent with the previous EFISHG measurements, provided that the NLO susceptibility of the quartz reference typically used to calibrate these measurements is taken to be \(d_{11}=0.30±0.02 \text{ pm/V}\).