Hyper-Rayleigh scattering measurements of hyperpolarizabilities for tetrahedral molecules

Robby D Pyatt
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HYPER-RAYLEIGH SCATTERING MEASUREMENTS
OF HYPERPOLARIZABILITIES FOR
TETRAHEDRAL MOLECULES

by

Robby D. Pyatt
Bachelor of Science
University of Nevada, Las Vegas
1998

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Examination Committee Chair

Dean of the Graduate College

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ABSTRACT

Hyper-Rayleigh Scattering Measurements of Hyperpolarizabilities for Tetrahedral Molecules

by

Robby D. Pyatt

Dr. David Shelton, Examination Committee Chair
Professor of Physics
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First hyperpolarizabilities $\beta$ of carbon tetrachloride, carbon tetrafluoride, deuterated methane, and methane have been measured by hyper-Rayleigh scattering in gas and liquid phases. The gas-phase results for the coefficient $\beta_{xyz}$ (atomic units) are $11.0\pm0.9$ (CCl$_4$), $5.4\pm0.4$ (CF$_4$), $7.0\pm0.6$ (CD$_4$), $7.1\pm0.7$ (CH$_4$). Ab initio calculations are consistent with the measured values for CCl$_4$ and CF$_4$. A discrepancy between theory and experiment remains for CH$_4$, and is likely due to higher-order vibrational effects not accounted for in calculations. While the effective, liquid-phase $\beta$ for CCl$_4$ is 200% higher than in the gas phase due to collective scattering modes, the liquid environment has little effect on $\beta$ for the other molecules. CD$_4$ and CH$_4$ liquids exhibit free-rotor behavior. Liquid-gas comparisons for CF$_4$, CD$_4$, and CH$_4$ show evidence that the Lorentz local-field corrections are inadequate in nonlinear optics. Through z-scan measurements, thermal-lensing and/or absorption coefficients have been obtained for six molecules.
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CHAPTER 1

INTRODUCTION

The concern of this work is the measurement of nonlinear properties of molecules. When an electric field is applied to a molecule the resultant induced dipole typically varies linearly with the field strength. This linear response is described by the polarizability ($\alpha$), the proportionality constant between the induced dipole and the field. In nonlinear optics, the concern is induced dipoles that are proportional to the second and higher powers of the field. The first hyperpolarizability ($\beta$) specifies the first-order nonlinearity between the induced dipole and an applied field, and this quantity is of interest in the present work.

Nonlinear optical properties of materials give rise to a variety of effects that can, in turn, be used to measure the properties. These include the Kerr and Pockels effects and harmonic generation. The electric-field-induced, second-harmonic generation (EFISH) experiment typically produces accurate values of $\beta$. In the case of second-harmonic generation (SHG), light scattered from a molecular sample provides the desired information about molecular properties. Molecular nonlinearities are usually small enough that scattering is very weak. EFISH has the advantage of being a coherent scattering process, so larger signals are possible. The production of coherence effects depends on phase matching for incident and scattered waves, as well as macroscopic order in the sample produced by permanent molecular dipole moments and an applied static electric field. However, this method is complicated, and spectral information is not easily obtained. The measured quantity also depends on molecular
properties other than $\beta$. Above all, the EFISH experiment cannot be used to measure $\beta$ for nondipolar molecules.

Hyper-Rayleigh scattering (HRS) is the method that was first used to observe nonlinear light scattering in fluids and is important for several reasons. Spectral information, which gives insight into molecular dynamics, is easily obtained. It is possible to analyze the polarization of the scattered light, and there are also other advantages such as flexibility and simplicity\(^1,2\). For molecules of tetrahedral symmetry ($T_d$ point group), use of HRS is essential because there is no dipole moment.

Interest in nonlinear optics has greatly increased since the tools necessary to observe nonlinear effects have become available. In typical materials, nonlinear-optical properties show themselves only with very strong applied fields. Although nonlinear light scattering was mentioned as early as the 1920s\(^3,4\), with some theoretical development in the following decades, much of the early work was forgotten\(^5\) until the early 1960s. By that time, lasers had been invented, facilitating the famous demonstration by Franken et al. that ruby laser light incident in a quartz crystal is scattered in the form of ultraviolet light\(^6\). Many authors consider this to be the birth of nonlinear optics. Subsequent advances in lasers and other instrumentation have made HRS experiments more practical, particularly in the case of weakly scattering molecules.

Parallel to instrumentation development, there have been dramatic advances in theoretical methods and computational power. Theoretical treatments of molecular nonlinearities are of intrinsic interest and also important because measurements are usually difficult and not always feasible. Although first-principles calculations of nonlinear properties were done by the 1960s, they are very computationally intensive. Computers now facilitate calculations of much higher accuracy, in which vibrational effects, high degrees of electron correlation, and frequency and basis-set dependences are taken into account. The refinement of ab initio methods has also been aided by
comparison with measured values, and the potential for a critical test of theoretical calculations has motivated the present study.

Bishop et al. have calculated $\beta$ for a series of $T_d$ molecules\cite{7}: carbon tetrachloride (CCl$_4$), carbon tetrafluoride (CF$_4$), and methane (CH$_4$). These molecules are small enough that first-principles calculations of very high quality should be possible. Molecules of $T_d$ symmetry have other computational advantages. Only one coefficient is needed to determine $\beta$, and calculation of a single bond length specifies the equilibrium molecular geometry. In the present work, measurements of $\beta$ are reported for liquid and gaseous CCl$_4$, CF$_4$, CH$_4$, and deuterated methane (CD$_4$). These are the only measurements available for CF$_4$ and CD$_4$, and the most precise for CH$_4$. HRS spectra have also been obtained. Since these spectra should be calculable for the gas phase, the spectral measurements provide for an additional comparison between theory and experiment.

HRS in CCl$_4$ has been studied many times, but there are two reasons for returning to it. First, the liquid was previously established as a reference material for HRS\cite{2} and has been used extensively for this purpose in the present measurements. Second, the gas-phase value previously measured using the same apparatus as in the current work\cite{2} strongly disagreed with the theoretical prediction already mentioned\cite{7}. Electron correlation and basis set effects were suspected as the cause of the discrepancy, because of the large number of electrons in the chlorine atoms.

One motivation for looking at CF$_4$ and CH$_4$ is that they have the same structure as CCl$_4$ and the HRS technique is nearly the same, while the reduced number of electrons should facilitate more accurate theoretical predictions. Thus, calculations of $\beta$ for CF$_4$ and CH$_4$ should agree better with experiment. CD$_4$ is interesting since its electronic structure is the same as for CH$_4$, while the spectrum and vibrational contributions to $\beta$ are different. All three are weak scatterers, liquids at cryogenic
temperatures, and gases at room temperature, so much of the preparatory work in the apparatus and other experimental aspects is similar. The weakness of their HRS signals and difficulty of both gas and liquid measurements has previously made them unattractive candidates for measurements of $\beta$.

$\text{CH}_4$ is the first gas in which HRS was observed. Maker et al. were able to observe vibrational and pure-rotational bands in HRS spectra and extract a value for $\beta$. However, several things make a new study of $\text{CH}_4$ desirable. Instrumentation has improved in the last few decades, and much better spectral resolution is possible. The uncertainty for the previous experiment was 300%, preventing a critical comparison with theory. Lastly, there is dispersion in $\beta$. While Maker et al. made measurements at the ruby wavelength (694.3 nm), the current experiments have been done in the near infrared, at 1064 nm. It is interesting that $\text{CH}_4$, as a very early example of HRS, has returned—35 years later—to provide an important evaluation of theoretical accuracy.

Acetonitrile ($\text{CH}_3\text{CN}$) has also been used as a reference in both gas and liquid phases. The advantages of $\text{CH}_3\text{CN}$ are a large scattering signal and the availability of previously-established values of $\beta$ for both gas and liquid phases. In the present experiments, similar sample-handling techniques were required for $\text{CH}_3\text{CN}$ and $\text{CCl}_4$, and measurements were done on either hot-vapor samples or room-temperature, liquid samples.

This work has been defined and motivated in the present chapter. Theoretical and experimental contexts for issues surrounding the measurements and analysis are provided in Chapters 2 and 3. In Chapters 4 and 5, the experimental results and considerations particular to each molecule are presented. In Chapter 6, \textit{ab initio} calculations of $\beta$ are compared with the measured results and conclusions are drawn. Although the liquid-phase measurements were done before the gas-phase work, the presentation of this entire work is done in reverse order. Since theoretical aspects of
the gases are more easily understood, gas-phase theory is used as a base case, and liquids are then discussed to see how they differ in behavior from simple, dense gases. Similarly, the gas-phase apparatus, nearly the same as in previous experiments, is treated as a base case, while modifications necessary for the liquid-phase work are mentioned afterward.
CHAPTER 2

THEORETICAL BACKGROUND

This chapter contains the theoretical points necessary to put the experiment into context. First, $\beta$ will be defined, followed by an explanation of the relationship between $\beta$ and the observed scattering. The notion of isotropic averaging and its implications will then be discussed. Lastly, some essential quantum aspects of HRS and the reasons for doing spectral studies are reviewed.

2.1 The $\beta$ tensor

When electric fields are applied to materials, they become polarized. The polarization could be examined in terms of the electric susceptibilities $\chi^{(1)}, \chi^{(2)}, \chi^{(3)}, \ldots$ and polarization field $\vec{P}$. The $\chi^{(i)}$ specify the induced polarization in successively higher powers of the applied field $\vec{E}$. They are macroscopic quantities involving the field response, averaged over a region much larger than molecular dimensions. Alternatively, the molecular polarizabilities $\alpha, \beta, \gamma, \ldots$ are used to relate the dipole moment $\vec{\mu}$ induced in a molecule to the field $\vec{E}$ when the individual molecular properties are of interest. The object of the current work was to measure properties of individual molecules, so molecular dipoles and polarizabilities are dealt with in this discussion.

The dipole moment induced in a molecule can be expressed as a Taylor series expansion in the applied field:

$$\mu_i = \alpha_{ij} E_i + \frac{1}{2} \beta_{ijk} E_i E_j + \frac{1}{6} \gamma_{ijkl} E_i E_j E_k + \ldots .$$  

Eqn. (2.1) is for the static case, so frequency arguments are unnecessary. The sub-
scripts index the Cartesian components of the tensors in this expression. One must sum over all repeated indices (the Einstein summation convention) to get the total response. The first-order (linear) response is determined by $\alpha$. The coefficients $\beta_{ijk}$ of Eqn. (2.1) determine the second-order response. The polarizabilities are tensor quantities because the induced dipoles generally depend on the orientation of the molecule with respect to the field. The tensor $\beta$ is of third rank and has $3^3 = 27$ elements.

The symmetry of a given molecule is reflected in the structure of $\beta$, in that all molecules of the same symmetry group (point group) have the same vanishing components and similar relationships among nonzero components. Many examples of this are given by Butcher and Cotter and by Boyd. For the case of $T_d$ molecules, $\beta$ is of octupolar symmetry, $\beta_{xyz}$ being the only independent, nonzero component:

$$\beta = \beta_{xyz} = \beta_{xyz} = \beta_{yxz} = \beta_{yzx} = \beta_{zxy} = \beta_{zyx}.$$ (2.2)

The electric fields of interest in HRS experiments are optical fields, which oscillate in time with frequencies characteristic of the light. Dipoles induced by optical fields will, therefore, tend to oscillate. When the applied field is optical, the above expression can become much more complicated, because (i) there can be components of the induced dipole oscillations at sum and difference frequencies (see following discussion), (ii) the frequency dependence of the polarizabilities would also necessitate that all frequency arguments be explicitly shown, and (iii) there can be applied fields of more than one frequency. The simplest, non-trivial example of induced dipoles oscillating at sum and difference frequencies is found in the effect of a single, one-dimensional applied field of frequency $\omega$. The field can be written as

$$E = E_o \left( \frac{e^{i\omega t} + e^{-i\omega t}}{2} \right) = E_o \cos \omega t.$$ (2.3)

The frequency-dependent first hyperpolarizability will then result in a contribution
to $\mu$ varying as the square of the field:

$$E^2 = E_o^2 \left( \frac{e^{2i\omega t} + e^{-2i\omega t} + 2}{4} \right) = \frac{1}{2} E_o^2 (1 + \cos 2\omega t) . \quad (2.4)$$

Eqn. (2.4) shows that if $\beta \neq 0$, the effect of the quadratic term will be to add components to $\mu_i$ at frequencies 0 and $2\omega$, corresponding to the difference ($\omega - \omega$) and sum ($\omega + \omega$), respectively. Similarly, the linear term is responsible for oscillations at $\omega$ and the cubic term produces fluctuations at $\omega$ and $3\omega$.

The essential point in the current work is that the component $\mu_i^{(2\omega)}$ of the induced dipole moment fluctuating at frequency $2\omega$ is proportional to both $\beta$ and $E^2$. In HRS measurements, there is only a single applied field of frequency $\omega$. Under this condition, and ignoring the (much weaker) interactions of higher order than $\beta$, the tensorial relationship for the frequency-doubled component of the dipole moment can be written as

$$\mu_i^{(2\omega)} = \frac{1}{2} \beta_{ijk} (-2\omega; \omega, \omega) E_j(\omega) E_k(\omega) , \quad (2.5)$$

where summation over $j$ and $k$ is implied and the frequency dependence of $\beta$ is shown explicitly.

2.2 Isotropic averaging

Without static applied fields or orientational correlations between neighboring molecules, scattering in fluids results from randomly-oriented molecules. In this case, the fluid will be macroscopically isotropic, and the dipole moments induced in the laboratory (space-fixed) coordinates can be related to the molecular polarizabilities through isotropic averaging, giving all possible molecular orientations equal weight. A distinction must now be made between the hyperpolarizabilities in space-fixed and molecule-fixed coordinates. The ultimate quantity of interest is $\beta_{xyz}$, the property
of a single molecule given in terms of a reference frame fixed with respect to the molecule. Because of molecular motion, the molecule-fixed axes rotate with respect to the space-fixed, modifying the average induced dipole in the space-fixed frame and the scattering intensity. The space-fixed axes and scattering geometry for the present experiments are shown in Fig. (2.1).

The averaged molecular hyperpolarizability $\langle \beta^2 \rangle^{1/2}$ in the space-fixed frame is the quantity more directly measured. It is $\beta^2$ that must be orientationally averaged since the scattering intensity varies as the averaged squared induced dipoles at the molecular scale. The measured component of the averaged dipole moment varies with the beam polarization and collection angle, so the space-fixed hyperpolarizability can be written as $\langle \beta_{VV}^2 \rangle^{1/2}$ to further specify scattering geometry. The first subscript $V$ denotes incident light polarized along the $Z$ axis (vertically), and the second, selection of the $Z$-polarized component of the scattered light. An $H$ in either position would imply the same respective propagation direction, but with perpendicular (horizontal) respective polarization. The space-fixed $\beta$ is still a tensor, and the quantities $\langle \beta_{VV}^2 \rangle$ and $\langle \beta_{VH}^2 \rangle$ can be written as $\langle \beta_{ZZZ}^2 \rangle$ and $\langle \beta_{XZZ}^2 \rangle$, respectively. Capital letters $X$, $Y$, and $Z$,
Y, and Z in the subscripts indicate the space-fixed reference frame. For convenience, \( \beta_{VV} \) will be used to denote \( <\beta_{VV}^2>^{1/2} \) throughout this work.

Bersohn et al. give a clear explanation of this isotropic averaging of \( \beta \) for an arbitrary molecule\(^{13}\). Their tabulated results can be used to show that

\[
<\beta_{zzz}^2> = <\beta_{VV}^2> = \frac{12}{35} \beta_{xyz}^2
\]

(2.6)

\[
<\beta_{xzz}^2> = <\beta_{VH}^2> = \frac{8}{35} \beta_{xyz}^2
\]

(2.7)

for a \( T_d \) molecule. Eqns. (2.6) and (2.7) relate the molecular property \( \beta_{xyz} \) to the space-fixed quantities actually measured.

2.3 Scattering intensity and depolarization ratios

The magnitude of \( \beta \) for a given molecule is extracted from HRS intensity measurements, so it is necessary to see how the nonlinearity and the scattering intensity are related. Oscillating dipoles produce radiation of the oscillation frequency. Since incident radiation at frequency \( \omega \) produces a dipole at \( 2\omega \), it will also produce scattered radiation at \( 2\omega \). This is the process defining SHG, and is the basis for measuring \( \beta \).

The intensity \( S \) of scattered radiation is always proportional to the square the dipole moment producing it, and the intensity of an incident beam is proportional to the square of its field. Linear scattering due to \( \alpha \) is therefore proportional to the incident intensity, while scattering at \( 2\omega \) due to \( \beta \) is proportional to the square of the incident intensity. From these considerations and from the work in reference 13, it is clear that the scattering intensities can be written

\[
S_{VV}^{(2\omega)} \propto <(\mu^{(2\omega)})^2> \propto <\beta_{VV}^2>
\]

(2.8)

\[
S_{VH}^{(2\omega)} \propto <(\mu^{(2\omega)})^2> \propto <\beta_{VH}^2>
\]

(2.9)

where the induced dipoles have been isotropically averaged.
Since scattering intensities depend on the polarization of the incident light and the relative direction of scattering collection, these issues must also be reviewed. In the (nominally) 90° experimental scattering geometry for the current work (see Fig. 2.1), the incident light travels along the X direction, and only the light scattered into a small solid angle about the Y axis is observed.

The directional dependence of the HRS intensity has been treated by Altmann and Strey⁵ and by Bersohn¹³ et al. The important results in the case of vertically polarized incident light are that (i) the scattered intensity will be isotropic in the XY plane and (ii) a maximum in scattering intensity in the YZ plane typically occurs for a scattering wave vector $k_{\omega}$ along the Y axis. All further theoretical and experimental considerations will be based on this geometry unless otherwise stated. For $T_d$ molecules, all information about $\beta$ can be obtained by observing scattering with this 90° geometry. For molecules of low symmetry, incident light of linear, circular, and elliptical polarizations must be used to obtain information about all tensor components¹³. However, because there is just a single independent nonzero tensor component for $T_d$ molecules, use of vertically polarized light and observation of the vertical component of the scattered light yields all the necessary information.

The results given in Eqns. (2.6) and (2.7) imply a depolarization ratio of

$$\frac{S_{\text{VH}}}{S_{\text{VV}}} = \frac{2}{3}$$

for $T_d$ molecules in the 90° scattering geometry. This same result follows from the work of others¹⁴.

2.4 Quantum aspects of HRS

The classical picture of scattering given earlier in this chapter is useful in understanding the electrodynamic origins of HRS. However, the quantum treatment
of scattering gives an indication of the expected spectral shapes, which result from molecular dynamics, transition selection rules, and nuclear spin statistics. The purpose of this section is to state the theoretical results and considerations necessary to predict the scattering spectra.

A second-harmonic photon of frequency $2\omega$ carries twice as much energy as a single, incident photon. In the quantum process underlying SHG, two photons are incident on a molecule and a single photon of twice the energy and frequency is produced. The scattering frequency can be different from the second-harmonic frequency if the internal energy of the molecule simultaneously changes. For example, in linear optics, the well-known Rayleigh scattering becomes inelastic Raman scattering when there is a difference between the incident and scattered photon energies corresponding to a change in internal molecular energy levels. In the same way, internal vibrational or rotational transitions can occur during nonlinear scattering processes. The degree of inelasticity of the scattering determines whether the process is called hyper-Rayleigh or hyper-Raman scattering. Many authors have used hyper-Rayleigh scattering to refer to processes involving no vibrational transitions. This convention is followed in this work, where the pure rotational spectra of concern are called hyper-Rayleigh spectra.

The principles involved in calculating rotational Raman spectra are well known. Rotational HRS spectra are calculated in the same manner, except that the matrix elements and selection rules are different. Calculations of HRS spectra are particularly simple in the case of $T_d$ molecules. The moment of inertia is the same with respect to any axis passing through the center of mass, eliminating the need for averaging over different rotations. The selection rules for two-photon scattering processes have been treated by several authors\textsuperscript{14,15} for the case of $T_d$ molecules. They are

$$\Delta J = 0, \pm 1, \pm 2, \pm 3$$ (2.11)
where \( J \) and \( J' \) are the quantum numbers for the initial and final rotational states. Thus, seven overlapping branches must be calculated and summed to predict the total spectrum. Altmann and Strey show that each branch is given by

\[
I_{VV}^{2\omega} |_{J \rightarrow J'} \propto (2J + 1)(2J' + 1) \exp[-BJ(J + 1)/kT]
\] (2.13)

where \( B \) is the rotational constant for the molecule and \( BJ(J + 1) \) is the energy of the rotational level in cm\(^{-1}\). The factor \((2J + 1)(2J' + 1)\) accounts for the spatial degeneracies of the initial and final states, as well as the matrix element for the transition. The quantity \( \exp[-BJ(J + 1)/kT] \) is the Boltzmann factor weighting each degenerate state of the initial level \( J \) by its relative thermal population. Altmann and Strey neglect the nuclear spin degeneracies \( g_s^{J,J'} \) of the initial and final states, which multiply the right side of Eqn. (2.13). These degeneracy factors have been calculated for some \( T_d \) molecules by Wilson.

Shelton has written Mathematica code to calculate HRS spectra for \( T_d \) molecules, and this code is found in Appendix A. Nuclear spin degeneracies have been included in calculating both populations and matrix elements. A table within the code lists values of \( B \) and the nuclear spin \( s \) for each of the four \( T_d \) molecules studied in this work. The code also contains an algorithm to convolve the calculated spectra with the instrumental response function applicable to the current experiments. All of the calculated spectra shown in this work have been convolved in this way to compare with measured HRS spectra. The calculated and measured gas-phase spectra are compared in Chapter 4.
2.5 HRS in the liquid phase

The liquid phase is different from the gas phase in several ways. First, the rotational structure of the spectrum is fundamentally related to the molecular motion, so any change from free-rotor motion of the molecules will change the spectrum. In most liquids, rotational motion of the molecules is strongly damped, and the free-rotor quantum states describing gas-phase molecules are no longer valid. Such hindered rotation or "libration" gives rise to a narrow Lorentzian band instead of the discrete spectrum expected in the gas phase. Second, orientational correlations between molecules can give rise to coherence effects, increasing or decreasing the scattered radiation. Third, collective scattering modes can alter the HRS intensity and make the liquid-phase depolarization ratio different from the gas-phase value. In CCl$_4$(l), for example, all three of these effects occur, and the depolarization ratio $S_{HV}/S_{VV} < \frac{2}{3}$ and varies across the HRS spectrum$^{17}$. Another example is CH$_3$CN liquid, for which 71% of the HRS intensity is due to librons, and in which the measured depolarization ratio is outside of the bounds allowed for local-mode scattering and varies over the spectrum$^{18}$.

Because of these intermolecular interactions, the effective liquid-phase $\beta$ can be quite different from the gas-phase value. In addition, the liquid-phase spectrum is usually not calculable based on first principles. However, some indications preliminary to measurement indicate that for the cryogenic liquids, these intermolecular effects could be much smaller. The octupole-induced dipole contribution to HRS was found to be large for CCl$_4$(l). However, the quantity $(\gamma \Omega/\beta)^2$, which controls this contribution ($\Omega$ is the molecular octupole moment), is lower for the cryogenic liquids by nearly a factor of 1000, so this type of scattering would not be expected in CF$_4$, CD$_4$, or CH$_4$. The cryogenic liquids also have smaller refractive indices, smaller molecular sizes, and fewer electrons than CCl$_4$, all suggesting the possibility of smaller intermolecular
interactions. Thus, one purpose of this research was to determine whether CF$_4$, CD$_4$, and CH$_4$ scatter independently and exhibit free-rotor behavior in the liquid phase.

The role of intermolecular interactions was assessed experimentally by observing how $\beta$ and the HRS spectrum change when going from the gas phase to the liquid. These comparisons are shown in Chapters 5 and 6. The depolarization ratios for the cryogenic liquids were not studied due to the weakness of their HRS signals, but changes in the effective $\beta$ in the liquid (after local-field corrections) could still indicate nonlocal scattering modes.
CHAPTER 3

EXPERIMENTAL AND ANALYTICAL METHODS

In this chapter, the apparatus and methods used to obtain and analyze data are set forth. The gas-phase apparatus is described in Sec. 3.1, followed by an explanation of modifications for the liquid-phase measurements in Sec. 3.2. The reduction of the raw data and extraction of molecular hyperpolarizabilities is treated in Sec. 3.3.

3.1 Gas-phase apparatus and method

For the gas-phase experiments, most of the apparatus remained the same as previously reported\(^1,2\). It is described here for convenience and completeness, and some minor differences are mentioned. Sample preparation for the hot-vapors was very different from that for the room-temperature gases, and the methods for these sample types are discussed separately. The gas-phase apparatus is shown schematically in Fig. 3.1. The incident light at wavelength \(\lambda = 1064\) nm was provided by a Nd:YAG laser (Quantronix 116) with \(1\) cm\(^{-1}\) stability. The laser was continuously pumped with a krypton arc lamp and acousto-optically Q-switched to give \(\approx 100\) ns pulses of \(\approx 0.7\) mJ energy. A repetition rate \(R = 1.5\) kHz was used throughout the gas-phase measurements. The \(\text{TEM}_{00}\) beam of 4 mm diameter passed through two Glan-laser polarizers used for polarization selection and attenuation. The Soleil-Babinet compensator was set to rotate the polarization plane and produce a vertically polarized input beam. A visible-blocking filter (Schott RG-850) prevented second-harmonic light generated along the beam path from entering the sample region. Lenses of focal...
lengths 5.0, 3.8, and 3.0 cm were used at various times to focus the incident beam to a \( \approx 15\,\mu\text{m} \) diameter inside the sample. Samples were held in 1 cm fused-silica cuvettes, which in turn were held in an aluminum block mounted on translation stages. With the stages, the position of the collection window could be adjusted with respect to the laser beam with 0.1 mm precision. The block was thermostatted, equipped with heaters, and had openings on all four sides for incident and scattered light and for observation of the incident beam with a CCD camera. Light scattered from the sample was collected at f/1.8 and focused by a 5 cm camera lens into the entrance slit of a tandem-grating spectrometer (Jobin-Yvon Ramanor U 1000). A sheet polaroid (extinction ratio \( 5 \times 10^{-4} \) at 532 nm) was usually placed between the collection lens and spectrometer slit to select the vertically polarized component of the scattered light. Unlike the previous experiments, a calibrated polarization scrambler was sometimes placed after the sheet polaroid to nullify the effect of the polarization-dependent spectrometer response.

The spectral slit width was set at 25 cm\(^{-1}\) (as large as possible) because of the weakness of the HRS signals. Photons selected by the spectrometer were detected

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with a cooled PMT (Hamamatsu R943). Pulses were then sent through an ampli­fier/discriminator. An electronic gate passed only pulses occurring simultaneously with the laser flashes, and these pulses were then counted by a Nucleus PCA multi­channel scaler (MCS), whose scans were synchronized with those of the spectrometer. The ungated countrate from the PMT was typically 1 count per second (cps), and with gating this was reduced to $2.4 \times 10^{-4}$ cps.

Some care was required to ensure that the scattered light was imaged onto the entrance slit of the spectrometer. This was done by narrowing and shortening the spectrometer entrance slit and positioning the focusing and collection lenses using the precision translation stages on which they were mounted. Alignment was done with the reference liquid samples because of their strong HRS signals ($\approx 100$ cps at line center). When switching to another sample of different refractive index, there were differences in the position of the focus for the incident beam and the magnification of the scattering region by the collection lens. The lenses were displaced by precalculated amounts to compensate for these differences, as described in reference 1.

3.1.1 Preparation of hot-vapor samples

Reagent-grade CH$_3$CN and CCl$_4$ were used for these experiments. Hot-vapor samples were prepared by using a 0.2 $\mu$m micropore filter and syringe to fill a 1 cm fused-silica cuvette with a liquid-sample reservoir about 1 cm high. Air was left in with the vapor. The atomic and diatomic components of air have no dipole-allowed SHG, and the presence of air as a buffer is thought to suppress some types of background problems. The thermostatted block was heated to produce liquid temperatures of 50–75° C and sample vapor pressures of 380–730 Torr. Microscope slides were used to cover the openings on the four vertical sides of the block during the hot-vapor measurements, thereby avoiding condensation on the cell windows near the openings.

For the hot-vapor samples, knowledge of the liquid temperatures was critical in
obtaining accurate vapor pressures and densities. Separate experiments were done to directly measure the liquid temperature as a function of block temperature. A 0.003 in. thermocouple wire was inserted into the cuvette, with the thermocouple positioned near the cuvette center and just under the liquid surface. The Teflon cap still sealed the opening, and the block was heated to a given temperature. After reaching equilibrium, the block and liquid temperatures were compared. At room temperature, they were the same; at typical experimental temperatures, the liquid was 3–4°C lower than at the position where the block temperatures were measured. The liquid temperatures were used to calculate vapor pressures and densities, and virial corrections based on the pure vapors were taken into account. Vapor pressures, liquid densities, and virial coefficients were obtained from references 19 and 20.

The liquid samples used as references during the gas-phase measurements were prepared in the same way, except that the cuvettes were raised so the laser beam passed through the liquid, and all liquid reference spectra were taken at room temperature.

3.1.2 Preparation of room-temperature gas samples

CF₄ and CH₄ were obtained from ultra-high-purity bottles. CD₄ (minimum deuterium content 99%) was obtained from Isotec. Because of the weak scattering and wider spectra of these molecules, it was necessary to have samples of higher pressure. A 1 cm fused-silica cuvette with a graded seal was connected to a shutoff valve using a glass-to-metal seal and Swagelok connectors. The cuvette was cleaned by rinsing with filtered methanol and by heating in an oven. The cuvette assembly was then attached to a manifold, to which pressure gauges and gas supply lines were also connected. The CF₄ and CH₄ were sent through a 0.5 μm in-line dust filter before entering the manifold.

The cuvette was outgassed, typically filled to 3000 Torr, disconnected from the
manifold, and placed in the sample holder. After each HRS experiment, the pressure was remeasured by reconnecting the cuvette to the manifold. Expansion experiments in the manifold and cuvette yielded volume ratios needed to accurately assess post-HRS gas pressures. For most of the experiments, the cuvette was leak-tight, as indicated by the pressure measurements and a helium leak detector. During a few measurements, there was a slow leak, and gas densities were then based on an exponential time curve that gave effective densities not much lower than straight averages. Estimated uncertainties due to this are reflected in the error bars.

3.2 Liquid-phase apparatus

In comparison with the gas-phase apparatus, the principal difference for the liquid-phase measurements was that the liquid samples were contained in an optical cryostat. A top-loading cryostat (Oxford Optistat DN) was used for both samples and references. A custom stand was built to hold the cryostat in the same place as for the gas-phase samples. The stand allowed for adjustment and clamping in all three translational and one rotational dimension. A set of translation stages for one dimension allowed positioning of the collection window with respect to the laser beam with 0.01 mm precision. A 1 cm fused-silica cuvette with a graded seal was suspended inside the cryostat on a stem of pyrex tubing. This cuvette assembly was clamped into the O-ring seal at the top of the cryostat. The pyrex tubing was connected to the manifold with copper tubing and flexible bellows tubing. Two vacuum systems were used, one for the manifold and sample tube, and the other for the cryostat chambers.

Gases were filtered into the manifold and condensed into a cold pyrex reservoir tube connected to the manifold, after which they were vacuum distilled into the cuvette and typically held at 100 K. The room-temperature, liquid references were also vacuum distilled into the cuvette from a second pyrex reservoir, but these measure-
ments were done at 290–295 K. One advantage of the vacuum distillation was the lack of disturbances to the sample tube position between sample and reference measurements. Lens positions were adjusted between sample and reference measurements to compensate for image shifts due to the change in refractive index. As the vacuum apparatus had several O-rings, which can absorb large quantities of solvent vapor, care was taken to degas the system by prolonged pumping each time CH$_3$CN or CCl$_4$ was removed from the sample tube. Continuous monitoring of vapor pressures and liquid temperatures were possible. Densities of the cryogenic liquids were obtained from references 19, 21, and 22, and molecular number densities of CD$_4$ were assumed to be the same as for CH$_4$.

All of the liquid-phase measurements were done with VV scattering geometry and with the polarization scrambler. All were done with CH$_3$CN liquid as the reference, with the exception of the first CH$_4$ measurement, for which CCl$_4$ liquid was used. Although stimulated Brillouin and stimulated Raman scattering are possible in liquids at high input intensities, even the peak intensities in these experiments ($\approx 1$ GW/cm$^2$) were orders of magnitude smaller than typical thresholds$^{12}$.

3.3 Analysis of data

Before proceeding to the experimental results, it is convenient to consider the reduction of raw data to produce the quantities of interest. The raw results of each experiment are the measured, integrated scattering intensities for sample and reference. In this section, sample-dependent corrections to these intensities are discussed and the final expressions used to extract $\beta$ for each molecule are given. Evaluation of thermal-lensing effects and the necessary corrections for them are discussed in Chapter 5 with the liquid-phase measurements.
3.3.1 Sample-dependent $G$ factors

Some factors other than $\beta$ affect the measured intensities. We can collect these factors into a single factor $G$ and write

$$S^{2\omega} \propto G \rho \beta^2,$$  \hspace{1cm} (3.1)

where

$$G = \frac{L^4 L_{2\omega}^2 T^2 T_{2\omega} n_{\omega}}{n_{2\omega}^2}. \hspace{1cm} (3.2)$$

These $G$ factors are the same as the $F$ factors discussed in reference 2, except that the molar sample densities $\rho$ are not included in $G$. For noninteracting molecules, the scattering intensity increases linearly with $\rho$. In Eqn. (3.2), $n$ is the sample refractive index and $L = (n^2 + 2)/3$ is the Lorentz local-field factor. The Fresnel transmission factors $T$ account for sample-dependent transmission at a sample/fused-silica (sa-si) interfaces of the cuvette, and are given by

$$T = 1 - \frac{(n_{\text{si}} - n_{\text{sa}})^2}{(n_{\text{si}} + n_{\text{sa}})^2}. \hspace{1cm} (3.3)$$

The factor $n_{\omega}/n_{2\omega}$ in Eqn. (3.2) accounts for changes in incident beam focusing and the collection solid angle, as fully described in references 1 and 2. A summary of the material parameters necessary to calculate $G$ for each molecule is found in Table 3.1.

3.3.2 Spectral considerations

The CF$_4$ and CCl$_4$ HRS spectra are narrow, and the frequency region scanned was wide enough to see the full spectra. The CD$_4$ and CH$_4$ spectra, however, are much wider, so in order to improve collection times and signal-to-noise ratios, the far wings were not scanned. Corrections to the CD$_4$ and CH$_4$ integrated intensities were based on the calculated spectra (see Chapters 4 and 5). For the gas-phase measurements,
Table 3.1. Summary of densities and $G$ factors. Changes in $G$ factors for different gas refractive indices were negligible, so a common $G$ was used for all gases.

<table>
<thead>
<tr>
<th>molecule</th>
<th>temp. (K)</th>
<th>$\rho$ (mol/L)</th>
<th>$n_1$</th>
<th>$n_2$</th>
<th>$n_3$</th>
<th>$G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CN(l)</td>
<td>295</td>
<td>$^{d}19.13$</td>
<td>$^{e}1.3376$</td>
<td>$^{e}1.3456$</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>CCl$_4$(l)</td>
<td>295</td>
<td>$^{d}10.4$</td>
<td>$^{e}1.4500$</td>
<td>$^{e}1.4630$</td>
<td>4.51</td>
<td></td>
</tr>
<tr>
<td>CF$_4$(l)</td>
<td>100</td>
<td>$^{d}20.7$</td>
<td>$^{c}1.23$</td>
<td>$^{c}1.233$</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>CD$_4$(l)</td>
<td>100</td>
<td>27.4</td>
<td>$^{a}1.273$</td>
<td>$^{b}1.284$</td>
<td>2.40</td>
<td></td>
</tr>
<tr>
<td>CH$_4$(l)</td>
<td>100</td>
<td>$^{d}27.4$</td>
<td>$^{a}1.276$</td>
<td>$^{b}1.287$</td>
<td>2.40</td>
<td></td>
</tr>
<tr>
<td>gases</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.905</td>
</tr>
<tr>
<td>fused silica</td>
<td>295</td>
<td></td>
<td>1.450</td>
<td>1.461</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Based on fit of data from reference 23 to Cauchy equation and extrapolation to 1064 nm.
$^b$Reference 23
$^c$Estimated from references 24 and 25.
$^d$From references 19 and 22.

the resulting corrections were 8% (for CD$_4$) and 6% (for CH$_4$). For the liquid phase, no corrections were necessary because the calculated and experimental spectra were within the scanned regions.

The spectral response variation of the spectrometer was evaluated over the widest scan region. A calibrated quartz-tungsten-halogen lamp (Oriel 200 W Model 63355 S/N 7-1054) provided the light, which was allowed to enter an integrating sphere placed at the usual sample position. The integrating sphere was used for attenuation and to homogenize spatial and angular dependences of the light entering the spectrometer. The results indicated an upper limit of 0.1% for the intensity corrections, so the effect was simply ignored.

3.3.3 Background assessment

Because of the low signal-to-noise ratios in the gas-phase experiments, accurate corrections for background were particularly important. It was straightforward to calculate the gated background count rates based on the measured, ungated background...
count rates and gating factor. This method is accurate if the timing of all background counts is independent of the laser pulse and gate opening, a condition met by thermionic emission from the PMT photocathode and any ambient light leaking into the spectrometer. Such background is independent of whether or not the laser beam passes through the sample, and this will subsequently be referred to as "calculated" background. The accuracy of calculated background was verified in two ways. First, the gating factor was directly measured. Second, the gated background was measured separately during some experiments for comparison with the calculated background. The measurement was done by modifying the gating circuit to open the gate twice as often as usual. Each time the oscilloscope produced a gating pulse during a laser firing, a delayed, twin gating pulse was also sent to the gate. The twin gating pulse fell between laser firings, and any photons detected during the twin pulse were counted by a separate MCS. The distribution of counts and the total in the second MCS were used to verify that random background was equal to the calculated value.

Any counts produced by the laser pulses and not originating from HRS in the sample, however, are synchronized with the gate, just as the HRS counts, and will result in background over and above what is calculated. This enhancement will be referred to as "spurious" background. Evidence suggests that dust and two-photon fluorescence were sources during the measurements of room-temperature gases. For the hot vapors, there were spurious background sources that behaved in a very different way than dust and fluorescence. Evaluation of these spurious background sources was crucial in extracting correct scattering intensities, and is discussed in Secs. 3.3.3.1-3.3.3.4.

3.3.3.1 Dust

There is strong evidence that during the measurements of room-temperature gases, dust particles passed through the focused laser beam and were incinerated, resulting in
broadband thermal radiation synchronized with the laser pulses. This type of spurious signal was discovered when anomalous signal bursts were observed. One example was a series of four counts observed within a fraction of a second during a measurement of average countrate $1.4 \times 10^{-3}$ cps. The signal increased greatly when the sample cell was removed from the aluminum block and the beam passed through open air in the sample region. The problem remained when a different focusing lens was used, but ceased completely when the lenses were removed and the beam passed through the sample area unfocused. Over time, visible debris accumulated on the bottom of the cuvette, and was removable by repeated flushings with filtered methanol.

This problem was controlled by carefully cleaning the sample cell, pressurizing the sample cell slowly, and placing the sample cell in the block and waiting before starting measurements. It is interesting to note that Maker had a broadband “fluorescence” problem in his CH$_4$ measurements, and the problem disappeared as the gas pressure in his sample cell was reduced to zero\textsuperscript{8}.

3.3.3.2 Two-photon fluorescence

One source of spurious background in the measurements of room-temperature gases was consistent with two-photon fluorescence occurring in some material on the surface of the sample cell. The source was very constant over time. In one attempted measurement, for example, a large, broadband, spurious background signal produced an average signal of $(6.8 \pm 0.3) \times 10^{-3}$ cps. After 28 hours with the cuvette undisturbed, this signal was the same at $(6.8 \pm 0.8) \times 10^{-3}$ cps. After a 90\textdegree rotation of the cuvette, the signal was lower by a factor of two, consistent with a contaminant unevenly distributed on the cuvette surface. After cleaning the input and output surfaces of the cuvette, the countrate dropped by a factor of 27 to the level expected for the calculated background and HRS from the sample. A thin layer of fluorescent material on the windows could certainly produce enough counts to overwhelm the
signal because cross sections for two-photon fluorescence are orders of magnitude larger than for HRS. Additionally, the spectrum of the suspected fluorescence was flat over the 600 cm\(^{-1}\) region examined. Two-photon fluorescence can be very broadband and can extend hundreds of cm\(^{-1}\) above the two-photon energy.

The source of the contamination on the outside of the cuvette was suspected to be either plastic bags wrapped around the cuvette from time to time or the Kimwipes used to clean the cuvette surfaces. Cleaning the outside of the sample cell with methanol eliminated the problem.

3.3.3.3 Spurious background in CCl\(_4\)(g) measurements

Although dust and two-photon fluorescence could cause problems in the hot-vapor measurements, the major spurious background for these measurements was very different in behavior. There were sporadic occurrences of spurious count rates, sometimes much larger than in the cases of dust or fluorescence, on time scales much longer than dust incinerations but without the persistency of two-photon fluorescence. As well as could be determined, the spectrum was flat, just as for dust and fluorescence. An example of a spectrum discarded because of this problem can be seen in Fig. 3.2. The spectrum in the Fig. 3.2 was taken over the course of 10 hours, but the peak with \(\approx 20\) counts (marked by the arrow) was directly observed to occur during a 40 s period. The other bursts probably occurred in a similar way, and there is also a flat spurious background.

The source of the problem was not determined, but could have resulted from a molecular breakdown or reaction catalyzed by the laser radiation or by incineration of a dust particle. One advantage of having the liquid reservoir was the continual renewal of the vapor sample. There was a problem with condensation on the cuvette surfaces during trial CCl\(_4\)(g) measurements; though this could have affected the observed HRS intensities, it is thought to be unrelated to the spurious background.
Fig. 3.2. Spurious background in HRS spectrum of CCl₄ vapor. Though the spectrum was taken over a 10 hour period, the peak marked by an arrow accumulated during a 40s period.

problems. Use of a carefully-cleaned cuvette eliminated this type of spurious background. Spectra with obvious problems were discarded in the final analysis, and the remaining spectra showed consistent intensities. No problem of this nature occurred during the CH₃CN(g) measurements.

3.3.3.4 Measurement of spurious background

Several different methods were employed to quantify spurious background problems. Measurements in which there were large spurious background problems were discarded, and the methods described in this section were used measure spurious background when small. No single method was used for every measurement or gave conclusive results alone. It was quite impossible to find every spurious count, so a demonstration of measurement repeatability and small spurious countrates was important.

Null measurements were used to estimate spurious background for the room-
temperature gases. In all aspects, they were identical to measurements of the room-
temperature gases, except that the sample cell was filled with ultra-high-purity N\textsubscript{2} instead of with the other gases. Since \(\beta\) is identically zero for N\textsubscript{2}, there is no dipole-
allowed HRS produced, and quadrupole-allowed HRS is orders of magnitude too small
to observe. Any counts observed, therefore, were due to background. The calculated
background was compared to the observed number of counts to estimate the number
of spurious counts. Null measurements were taken before and/or after some of the
measurements of room-temperature gases, using the same sample tube. These mea-
surements provided estimates of the small, spurious background contributions from
dust or two-photon fluorescence and proved that there was no observable collection
of HRS produced in the windows of the fused-silica sample cell.

The gated-background method was used before and/or after measurements of both
room-temperature gases and hot vapors. In this case, the sample cell was prepared
and situated for a measurement. At first, the spectrometer was not set to scan but
to look very far from line center, where there was no HRS from the sample. Since
all known sources of spurious background were independent of wavenumber in the
observed regions, spurious background could be measured far from line center just
as well as within the scanning region. The measured, gated countrate was then
compared with the value calculated from the ungated countrate to check for any
spurious background.

The method of change in count rate was used for the measurements of room-
temperature gases, in which dust was a problem. Over the course of a measurement,
counts due to dust would be expected to diminish with time. In the absence of gas
leaks or power drifts, a decrease in countrate could indicate how many counts were
due to dust. This method had the advantage that spurious counts recorded as single
counts within a channel were just as detectable as larger bursts.
The method of statistically improbable counts involved examination of the MCS-binned spectrum to determine whether occurrences of two or more counts in a single MCS channel were likely due to dust. An illustration will make this clear. The Poisson probability for observing \( r \) randomly-occurring events in a given time interval is

\[
P_r = \frac{\lambda^r e^{-\lambda}}{r!},
\]

where \( \lambda \) is the average rate of occurrence. In one of the CD\(_4\) measurements, there were 54 measured counts in the 248-channel region of the MCS used. If the spectrum were flat, \( \lambda = 54/248 \text{ cts} \) would be expected in each channel, on average. This gives \( P_3 = 0.14\% \). One would expect to see a total of 3 counts in \( 0.0014 \times 248 = 0.35 \) channels; given the spectral shape, \( P_3 \) would be larger near the center of the spectrum and smaller in the wings. One occurrence of 3 counts in a channel in the wings indicated that it was probably due to dust. The disadvantage of this method is that single counts due to dust or two-photon fluorescence are generally not seen, and it is less useful in the central part of the spectrum.

The most reliable method involved looking at the wings of the pure-rotational spectra. To use this method, the calculated background was subtracted from a spectrum as a flat contribution. The wings of the measured, gas-phase spectra were then examined in the region where the average intensity should be zero, as indicated by the calculated spectrum. Any average, residual background in the wings was assumed to be the same as in the center of the spectrum, and an estimate of the spurious background for the spectrum was thus determined. This method was useful only for CF\(_4\) and CCl\(_4\), the molecules with narrow spectra.

### 3.3.4 Other corrections

The measured spectrometer response is five times greater for light of vertical polarization than for horizontal. Most of the measurements were done in the VV
scattering geometry, but some gas-phase measurements in which CCl$_4$(l) was used as a reference were done by collecting over both polarization components of the scattered light; this geometry is denoted herein as VX (VV + VH). For VX measurements, the polarization scrambler shown in Fig. 3.1 was used without the sheet polarizer. Since the depolarization ratio for the tetrahedral molecules is 2/3 in the gas phase, a comparison of any two of them in the same scattering geometry (VV, VH, or VX) should yield an intensity ratio equal to the vertical scattering ratio, so the ratios are always reported as VV ratios. The only correction necessary to report VX ratios as VV ratios is for CCl$_4$(l), which was used as the reference for the gas-phase measurements. The integrated depolarization ratio for CCl$_4$(l) (measured in the current work) is 0.435 < 2/3, so the intensities $S_{VX}^{CCl_4(l)}$ were corrected to the VX intensities that would be observed if the depolarization ratio were the same as in the gas phase. This was done by multiplying the VX intensities by $(1 + 2/3)/(1 + 0.435)$, where the vertical scattering intensity is normalized to one.

Dead-time corrections were necessary for the reference measurements, in which the HRS signals were large. This was due to the collection electronics, which were set up to measure at most one count per laser pulse. Based on the laser repetition rate $R$, the corrected signal $S_1$ was obtained from the raw signal $S_o$ according to the expression $S_1 = -R \ln(1 - S_o/R)$, which is discussed in references 1 and 26.

Very small intensity corrections were necessary to account for the difference between the classical orientational average calculated in ab initio treatments and the quantum rotors actually measured. This correction was found by using the code in Appendix A. The calculated scattering intensities found in the code were normalized so that each branch of the HRS spectrum gave unit intensity in the classical limit of large $J, J'$. The calculated totals were then compared with the classical intensities. Even in the worst case (for CD$_4$ at 100 K), the necessary correction to $\beta$ was only
0.46%, too small to see given the precision of the reported measurements. The corrections tended to be progressively smaller at higher temperatures and for the heavier molecules, for which higher rotational states are populated.

3.3.5 Calibration method

The use of CCl$_4$(l) as a reference throughout the gas-phase measurements requires that its accuracy as a reference standard be evaluated. It has several advantages including its lack of absorption at 1064 nm and ease of use at room temperature. Its strong HRS signal is important experimentally, providing fast reference measurements, good statistics, and an easy way to align the collection optics and check for changes in laser performance. It has been studied extensively and established as an HRS reference standard using the same apparatus as in the current work.$^{2,17}$ The chain of measurements previously used to calibrate $\beta_{VV}^{\text{CCl}_4(l)}$ can be represented schematically as

$$
\beta_{\text{EFISH}}^{\text{Ref(g)}} \Rightarrow \beta_{\text{HRS}}^{\text{Ref(g)}} \Rightarrow \beta_{\text{HRS}}^{\text{Ref(l)}} \Rightarrow \beta_{\text{HRS}}^{\text{CCl}_4(l)} ,
$$

where $\beta_{\text{EFISH}}$ and $\beta_{\text{HRS}} = \beta_{VV}$ are distinct quantities involving different combinations of tensor components. For each of seven dipolar reference (Ref) molecules, $\beta_{\text{EFISH}}^{\text{Ref(g)}}$ was measured and theoretical calculations were used to relate $\beta_{\text{HRS}}^{\text{Ref(g)}}$ to $\beta_{\text{EFISH}}^{\text{Ref(g)}}$. Using the gas HRS value thus derived, the gas and liquid were directly compared in HRS experiments to obtain $\beta_{\text{HRS}}^{\text{Ref(l)}}$. Finally, Ref(l) and CCl$_4$(l) were compared to obtain $\beta_{\text{HRS}}^{\text{CCl}_4(l)}$. The values of $\beta_{\text{HRS}}^{\text{CCl}_4(l)}$ obtained through the dipolar reference molecules were averaged to establish CCl$_4$(l) as an HRS reference standard.

The value $\beta_{\text{HRS}}^{\text{CCl}_4(l)}$ was recalibrated during the current experiments, using CH$_3$CN(g) as a reference. The value of $\beta_{\text{HRS}}^{\text{CH}_3\text{CN}(g)}$ used was the same as before, but CH$_3$CN(g) and CCl$_4$(l) were directly compared in the current HRS experiments to obtain $\beta_{\text{HRS}}^{\text{CCl}_4(l)}$. 

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Thus, the current calibration scheme is

$$\beta^{\text{CH}_3\text{CN}(g)}_{\text{EFISH}} \Rightarrow \beta^{\text{CH}_3\text{CN}(g)}_{\text{HRS}} \Rightarrow \beta^{\text{CCl}_4(l)}_{\text{HRS}}.$$  (3.5)

The results for the current experiments have been based upon this latest calibration because (i) signal-to-noise ratios are improved in the current experiments, (ii) spurious background has been studied more extensively, (iii) the current calibration chain is slightly more direct, and (iv) the accuracy of gas-phase measurements based on the current calibration does not depend on how correct the Lorentz local-field factors are. Consideration (iv) can be understood since \(\text{CH}_3\text{CN}(g)\) is being used to directly calibrate \(\text{CCl}_4(l)\), which in turn is used to directly calibrate the current gas-phase measurements of other molecules. In any gas-liquid-gas calibration chain, use of an arbitrary local-field factor when comparing the first gas and the liquid will give an incorrect result for the liquid, but there will be a cancellation effect when the liquid is compared with the second gas via the same factor. The previous and current calibration results are summarized in Chapter 5 with the \(\text{CCl}_4(l)\) results.

In the case of the liquid-phase measurements, the current calibration for \(\text{CCl}_4(l)\) was still used for consistency. However, an additional step was required because \(\text{CH}_3\text{CN}(l)\) was used as the direct reference. This is done using the ratio of integrated intensities for \(\text{CCl}_4(l)\) and \(\text{CH}_3\text{CN}(l)\) measured previously.²

3.3.6 Presentation of measurement results

Measured ratios of integrated scattering intensities for samples and references are reported since they are closely related to the raw measurements. Throughout Chapters 4 and 5, these ratios are examined before the results for \(\beta\) are given. However, there is a need to compare different measurements of these ratios for the same molecules, but with varying corrections for dead time, background, and thermal lensing. These corrections were made to the raw, integrated, scattered intensities \(S\) to
produce the corrected intensities $S'$. The sample and reference measurements were normalized to the same spectral scan speed when the ratios $(S')_{\text{Samp}}^{\text{VV}} / (S')_{\text{Ref}}^{\text{VV}}$ were formed. For gas-phase measurements in which the VX geometry was used, the corrected CCl$_4$(l) intensities $S'$ include the polarization correction already mentioned.

Densities also varied among gas-phase samples, so intensities were normalized for comparison by dividing by the molar densities. The intensity ratios presented herein for both gas- and liquid-phase measurements are always of form

$$\frac{I_{\text{Samp}}^{\text{VV}}}{I_{\text{Ref}}^{\text{VV}}} = \frac{(S')_{\text{Samp}}^{\text{VV}}}{(S')_{\text{Ref}}^{\text{VV}}} \frac{\rho_{\text{Ref}}}{\rho_{\text{Samp}}}.$$  

(3.6)

This form keeps measured values as close as possible to the raw data while allowing internal comparisons of measurements. Despite this density normalization, these ratios do not represent molecule-for-molecule comparisons of scattered light intensities for sample and reference because of changes in laser beam parameters and light collection. These differences for sample and reference are reflected in the $G$ factors, which are taken into account only after the final, averaged values of the integrated intensity ratios in Eqn. (3.6) are found. The space-fixed $\beta_{\text{VV}}^{\text{Samp}}$ are extracted from the measured intensity ratios according to

$$\beta_{\text{VV}}^{\text{Samp}} = \beta_{\text{VV}}^{\text{Ref}} \sqrt{\frac{I_{\text{Samp}}^{\text{VV}}}{I_{\text{Ref}}^{\text{VV}}} \frac{G_{\text{Ref}}}{G_{\text{Samp}}}}.$$  

(3.7)

Liquid-phase results are left in this form, while $\beta_{\text{xyz}}$ is calculated for gas-phase $T_d$ molecules according to Eqn. (2.6).

Throughout the text, atomic units have been used in reporting values of $\beta$ (1 a.u. $= 1 e^2 a_0^3 E_H^{-1} = 3.20636 \times 10^{-53} \text{C}^3 \text{m}^3 \text{J}^{-2} = 8.6392 \times 10^{-33} \text{esu}$, where $e$ is the electron charge, $a_0^3$ is the Bohr radius, and $E_H$ is the Hartree energy).
CHAPTER 4

GAS-PHASE MEASUREMENTS

The measurement results for the molecules in the gas phase are presented in this chapter. CCl$_4$(l) was used as the reference throughout the gas-phase experiments, so the measured intensity ratios $I_{VV}^{\text{Samp}} / I_{VV}^{\text{CCl}_4(l)}$ are reported for each sample molecule in Secs. 4.1-4.4. Discussion of spurious background corrections is given for each molecule. The use of CCl$_4$(l) as a reference is discussed in Sec. 4.5, and the gas-phase intensity ratios and extracted $\beta_{xyz}^{\text{Samp}}$ are summarized in Sec. 4.6.

4.1 CCl$_4$ results

During the first hot-vapor measurements, condensation on the cuvette windows was sometimes a problem. This was eliminated by adjusting the liquid level to be farther below the windows in the aluminum block. This problem could increase the signal if there were drops of liquid on the laser input or output window, or decrease the signal if there were drops on the collection window. All measurements involving known or suspected condensation problems were eliminated from the final analysis, though they largely support it. The integrated intensity ratio was first evaluated considering only the calculated background. Fig. 4.1(a) summarizes the results. The weighted average of $(26.3 \pm 1.5) \times 10^{-3}$ was extracted from the four measurements with no fog problems. All measured values without obvious background problems agree with the weighted average to within their error bars, with the exception of one measurement involving fog problems and a ratio four times higher than those shown.
Fig. 4.1. CCl$_4$(g) intensity ratios and spectrum. (a) Measured ratios $I_{VV}^{\text{CCl}_4(g)}/I_{VV}^{\text{CCl}_4(l)}$. Only the calculated background has been subtracted. (b) Sum of measured spectra with only the calculated background (2.1 counts per point) subtracted as a flat contribution. The calculated spectrum is scaled to match the integrated intensity of the measured spectrum. The calculation was done at the average measurement temperature.
The sum of measured spectra is shown in Fig. 4.1(b). The measurements were done at temperatures between 50° and 75° C. The width of the calculated spectrum was insensitive to the temperature, so the one shown in Fig. 4.1(b) was calculated for an average measurement temperature. Only the calculated background was subtracted, being taken as a flat contribution. Although the measurements with condensation problems were not considered in calculating the best-estimate intensity ratio, the two shown in Fig. 4.1(a) were not significantly different from the best-estimate ratio, and were included in the spectral sum [Fig. 4.1(b)]. The statistical uncertainty for each datum point in the spectrum is $\sqrt{N}$, where $N$ is the sum of the datum point shown in the spectrum and the calculated background indicated in the figure caption.

Little information about spurious background was extracted from the individual CCl₄ gas measurements; estimates from two of the measurements gave reductions of the intensity ratios by 4% and 9%, respectively. The final estimate of spurious background was based on the wing method described in Sec. 3.3.3. This was applied collectively to the four measurements with no condensation or other problems. This method resulted in a reduction of the intensity ratio by $16 \pm 4\%$, yielding the best estimate $I_{VV}^{CCl_4(g)} / I_{VV}^{CCl_4(l)} = (22.1 \pm 2.6) \times 10^{-3}$.

4.2 CF₄ results

No CF₄ results were excluded from the final analysis; based on the spectral features and consistency of results, there do not appear to have been any CF₄ measurements with large spurious background. The results found by subtracting only the calculated background from intensities and spectra are summarized in Fig. 4.2. The weighted average intensity ratio of $(4.88 \pm 0.26) \times 10^{-3}$ was based on all measurements. Only the calculated background has been subtracted to determine the ratios and the spectrum shown. The scattering geometry was VV for the last three measured values (on the
Fig. 4.2. CF₄(g) intensity ratios and spectrum. (a) Measured ratios \( I_{\text{VV}}^{\text{CF}_4(g)}/I_{\text{VV}}^{\text{CCl}_4(l)} \) based on calculated background. (b) Calculated spectrum vs. sum of measured spectra. The calculated background (3.0 counts per point) was subtracted as flat contribution. The calculated spectrum is scaled to match the integrated intensity of the measured spectrum.
right of Fig. 4.2(a)) and VX for the first two. The internal agreement of all values is quite satisfactory.

Spurious background was estimated for individual measurements by using several different methods, yielding 10%, 4%, and 0% intensity reduction estimates for three of the measurements; for the other two, the available information was insufficient to make estimates. The wing method indicated negligible average spurious background, but with a much larger error bar than in the case of CCl₄(g). The spurious background found in the three individual measurements was assumed to be the total for all. The corresponding correction factor applied to the weighted average intensity ratio was 4.5%, with 100% uncertainty assumed for the correction. This process resulted in a final estimate of $I_{\text{VV}}^{\text{CF}_4(g)} / I_{\text{VV}}^{\text{CCl}_4(l)} = (4.66 \pm 0.33) \times 10^{-3}$ for the intensity ratio.

4.3 CD₄ results

There were two CD₄ measurements, and evaluation of the intensity ratio $I_{\text{VV}}^{\text{CD}_4} / I_{\text{VV}}^{\text{CCl}_4}$ yielded values (based on the calculated background only) of (i) $(12.2 \pm 2.0) \times 10^{-3}$ and (ii) $(8.13 \pm 0.76) \times 10^{-3}$, in clear disagreement with one another. Even if no information about spurious background were available, it would be justified to accept the smaller of the two values as correct, based on the knowledge that spurious background can be large at times and that it is almost always present in small degree. Moreover, a gated background assessment after the first measurement indicated a spurious count rate 10–20 times larger than the calculated background, large enough to overwhelm the HRS counts. This measurement was done after stopping the experiment and disturbing the cuvette, so there was uncertainty about how high the spurious count rate was during the experiment. Because of the probable spurious background and a laser power drift during the first measurement, the first value was disregarded during the
Fig. 4.3. CD$_4$(g) measured spectrum vs. calculation. Only the calculated background (1.9 counts per point) was subtracted, taken as a flat contribution. The calculated spectrum is scaled to match the integrated intensity of the measured spectrum.

final analysis. The first measurement is additional evidence of the possible magnitude of spurious background.

All of these problems were corrected in the second measurement. The cuvette was cleaned, and the laser was very stable. The spurious background was evaluated more carefully and in three different ways, all indicating that its contribution was small. An intensity correction of 4% was estimated (2% in the calculated $\beta$), and 100% uncertainty was assumed for the correction, resulting in a final intensity ratio $I_{\text{CD}_4}^{\text{VV}} / I_{\text{CCl}_4}^{\text{VV}} = (7.80 \pm 0.77) \times 10^{-3}$.

The spectrum from the second measurement is shown in Fig. 4.3. Only the calculated background was subtracted, being taken as a flat contribution.
4.4 CH₄ results

The CH₄ measurement was the most difficult. The smaller moment of inertia results in an HRS spectrum much wider than those of the other T₄ molecules. Based on best estimates for intensity ratios and the assumption of constant calculated- and spurious-background countrates, the expected signal-to-noise ratio would be lower than for CF₄ by 10% for CD₄ and 60% for CH₄. In addition, CH₄ was the first molecule studied, and some discarded measurements were done while background problems were still being solved. All of the measured intensity ratios $I_{\text{CH}_4}^{\text{CH}_4}/I_{\text{CCl}_4}^{\text{CCl}_4}$ are shown in Fig. 4.4(a), with the exception of measurements aborted due to obvious spurious-background problems. Six of the measurements shown were finally rejected because spurious background was not adequately assessed.

Only the calculated background was subtracted in the ratios shown. A weighted average of $(8.80 \pm 0.64) \times 10^{-3}$ was extracted from the four measured ratios used in the final analysis. Estimates of spurious background were again obtained for the individual measurements, resulting in an estimated correction of 9% in the intensity (5% in beta), with an uncertainty of 100% assumed in the correction. The final estimate of the intensity ratio is $I_{\text{CH}_4}^{\text{CH}_4}/I_{\text{CCl}_4}^{\text{CCl}_4} = (8.00 \pm 0.98) \times 10^{-3}$.

The observed spectra are summed and compared with the calculated spectrum in Fig. 4.4(b). Only the calculated background has been subtracted from the spectrum, being taken as a flat contribution. The spectra from all measurements shown in Fig. 4.4(a) were included in the spectral sum, with the exception of the measurement with the largest ratio of $16.5 \times 10^{-3}$, in which spurious background appears to have contributed to a greater extent. The spurious background remaining in Fig. 4.4(b) (estimated at 10–15% of the integrated intensity) will have the effect of reducing the amplitudes of the measured spectral peaks relative to the less intense portions of the spectrum.
Fig. 4.4. CH$_4$(g) intensity ratios and spectrum. (a) Measured ratios $I_{\text{VV}}^\text{CH}_4 / I_{\text{VV}}^\text{CCL}_4$ based on calculated background. Measurements are shown in the order taken, from left to right. The last two measurements were done in the VV scattering geometry, and the others were done in the VX geometry. (b) Sum of measured spectra vs. calculation. All measurements used in the final analysis and some others without suspected background problems are included. Only the calculated background (3.9 counts per point) has been subtracted, taken as a flat contribution. The calculated spectrum is scaled to match the integrated intensity of the measured spectrum.
4.5 Gas-phase summary

The measured intensity ratios and extracted $\beta_{xyz}$ for the four $T_d$ molecules are summarized in Table 4.1. The measured values of $\beta_{xyz}$ shown in the table were extracted from the best-estimate intensity ratios as indicated by Eqns. (2.6) and (3.7).

Table 4.1. Summary of gas-phase results. All values of $\beta$ are given in atomic units.

<table>
<thead>
<tr>
<th>molecule</th>
<th>$I_X^{(g)} / I_{VV}^{\text{CCl}_4(t)}$ $(10^{-3})$</th>
<th>measured $\beta_{xyz}$</th>
<th>ab-initio $\beta_{xyz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl$_4$</td>
<td>22. ± 2.</td>
<td>11.0 ± 0.9</td>
<td>13.6</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>4.7 ± 0.4</td>
<td>5.4 ± 0.4</td>
<td>4.34</td>
</tr>
<tr>
<td>CD$_4$</td>
<td>7.8 ± 0.8</td>
<td>7.0 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>8.0 ± 0.9</td>
<td>7.1 ± 0.7</td>
<td>9.17</td>
</tr>
</tbody>
</table>

*From Bishop et al., reference 7.*

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LIQUID-PHASE MEASUREMENTS

The major analytical emphasis for the liquid-phase measurements was thermal lensing rather than background. There were no observable problems with spurious background in the cryogenic-liquid samples. Although the distillation process created dusty liquid samples, no incineration appeared to occur, possibly because of the increased thermal conductivities and low temperatures of the cryogenic liquids. Dust created problems at times in vacuum-distilled CCl$_4(l)$ samples, but CCl$_4(l)$ was not used as a reference after the first measurement. The cuvette was inside the cryostat and isolated most of the time, diminishing the possibility of fluorescent surface contaminants. Much better signal-to-noise ratios (10–100) were possible for the liquid-phase experiments, with count rates of order 0.1 cps for the cryogenic liquids. However, absorption at 1064 nm by a C–H vibrational overtone causes thermal lensing in CH$_3$CN, CH$_4$ and CD$_4$. Corrections for this effect can be large, and the correction methods are discussed in Sec. 5.1.

The results of the liquid-phase measurements are reported in Secs. 5.2–5.4. For all except one of the liquid-phase measurements, CH$_3$CN(l) was used as the reference, and the intensity ratios $I_{V^V}^{Samp(l)}/I_{V^V}^{CH_3CN(l)}$ are the raw results reported. The results of the liquid-phase measurements, along with comparisons of $\beta$ in liquid and gas phases, are summarized in Sec. 5.5.
5.1 Thermal-lensing corrections

If a medium absorbs some of the incident laser radiation, there will be some heating. For liquids, which have large thermal expansion coefficients, this typically decreases the density and refractive index. The Gaussian beam profile and heat transport combine to create transverse temperature and refractive index gradients and an effective diverging lens. This causes the laser beam to be more weakly focused and less intense. For a linear light-scattering experiment, the signal is proportional to the intensity, so this effect does not change the scattering intensity; the beam is less intense, but extends over a larger cross-sectional area. However, in a nonlinear light-scattering process, the signal is proportional to the square of the intensity, and thermal lensing decreases the average squared incident intensity and the HRS intensity.

To compare the HRS signals of two liquids and relate them to molecular properties, then, it is necessary to correct the observed intensity ratios to those that would be seen in the absence of thermal lensing, or in the limit of zero input power. Corrections for this effect can be large, so the correction methods are discussed here. The HRS extrapolation method used to find thermal lensing corrections in strongly scattering liquids is explained in Sec. 5.1.1. The method required for the weakly-scattering liquids is more elaborate and involves experimental, theoretical, and computational work. These considerations are explained in several steps in Secs. 5.1.2–5.1.4.

5.1.1 HRS extrapolation method

The simplest way to determine the thermal-lensing correction is purely empirical. The quantity HRS/P^2 is measured as a function of the power P, and both previous\(^1\) and current measurements show that this relationship is linear. A linear fit to the data and extrapolation to zero power give the intensity in the absence of the lensing effect. This method was used to find the thermal-lensing corrections only for the room-temperature liquids, which have nonlinearities large enough to produce...
appreciable signals at low power. There is no measurable thermal lensing in CCl$_4$(l), but the strong lensing in CH$_3$CN(l) is demonstrated by the measurement shown in Fig. 5.1. Use of this method for CH$_3$CN(l) resulted in intensity corrections of 20–40%, depending on the average power.

This method was not used for the cryogenic liquids because the signals were too weak at low powers to give reliable results. One alternative is to scale the known correction factor for CH$_3$CN(l) by the relative thermal-lensing strengths in other liquids. In the following sections, this method is described.

5.1.2 Thermal-lens theory for the cw case

The work of Gordon et al. yields an expression for the focal length of a thermal lens under the condition of conductive heat transport. For a cw laser beam of power $P$ and beam radius $w$ passing through a layer of liquid of small length $\Delta L$, thermal conductivity $k$, absorption coefficient $b$, unperturbed refractive index $n_0$, and change

![Fig. 5.1. HRS extrapolation method for CH$_3$CN(l). The extrapolation to zero power gives the expected signal in the absence of thermal lensing.](image-url)
of index with temperature \( dn/dT \), the self-induced lens has focal length

\[
F = \frac{k \pi n_0 w^2}{b P \Delta L \frac{dn}{dT}}. \quad (5.1)
\]

Gupta et al. give an analogous expression for a pulsed laser beam.\(^{29}\)

Eqn. (5.1) can be inverted (giving the focal power or lens strength) and broken into three factors to understand it phenomenologically:

\[
\frac{1}{F} \propto \frac{b P \Delta L}{1} \times \frac{1}{\frac{k w^2}{2}} \times \frac{1}{\frac{n_0}{dT}}. \quad (5.2)
\]

Factor 1 gives the heat absorbed, to which the lens strength is proportional. Factor 2 accounts for conductive thermal transport and transverse beam geometry. As the thermal conductivity of the medium increases, the thermal gradient and lens strength decrease; moreover, the gradient and lens strength are proportional to the beam intensity, which varies as \( 1/w^2 \). Factor 3 accounts for the response of the medium to a given thermal gradient. A larger variation of refractive index with temperature results in an increase in lens strength, and division by \( n_0 \) makes factor 3 the relative change in index.

The laser beam parameters in Eqn. (5.1) are known, so if the material parameters are also known, one has an expression giving the focal length of a thin layer of the medium. The sample can then be divided into many layers and the beam numerically propagated through the medium to find its solution both within the medium and in the far-field region. Several things can be calculated as a function of beam power \( P \), including the average squared intensity in the liquid (proportional to the HRS produced) and the far-field beam parameters \( I \) (the central beam intensity) and \( \theta \) (the divergence angle of the beam). The only parameter necessary for these calculations but not available from the literature is \( b \), and the z-scan method described in the next section can be used to extract it.
5.1.3 Z-scan method

Small changes in near-field beam geometry translate into large effects in the far-field region. Observations of far-field beam profiles were introduced by Sheik-Bahae et al. as a sensitive method of measuring nonlinear optical interactions\(^{30}\). Their method, referred to as a “z-scan”, has been adapted here to provide an experimental basis for determining relative strengths of thermal lenses in the liquids.

The z-scan experiment is illustrated in Fig. 5.2(a). The sample is moved along the beam direction, which is typically designated as the z direction, hence the term “z-scan.” As the sample is moved, the variation in \( \theta \) or \( I \) is examined, and sharp minima and maxima in these parameters are the signature of a z-scan experiment. To illustrate this, the result of a beam propagation calculation is shown in Fig. 5.2(b).

The far-field angle \( \theta \) was calculated as a function of the distance \( Z \). The position for maximum intensity \( I_{\text{max}} \) corresponds to the position for minimum angle \( \theta_{\text{min}} \), and vice versa. The behavior shown in Fig. 5.2(b) can be understood in terms of two competing effects of near-field thermal lensing: (i) past the focal plane of the beam, a thermal lens, being negative, simply increases the beam divergence and the far-field angle \( \theta \) by some amount \( \delta \theta \); and (ii) a similar defocusing effect before the focal plane will decrease beam diffraction in the focal region, with a consequential decrease in \( \theta \). Which effect dominates will depend on the relative liquid distances traversed by the two regions of the beam. Extrema occur when the focal plane is near either the output or input side of the sample, so that the thinnest part of the beam goes through the sample and only one of the competing effects is acting.

The minimum and maximum in the far-field parameters are convenient reference values since they can be found easily in both calculations and experiments and used as a common ground for the two. Even more useful than the minima and maxima are their ratios, which can be related to the lens strengths in the following way. If
Fig. 5.2. Z-scan method. (a) Position of sample with respect to beam focus is specified by parameter $Z$, which is changed to see the corresponding variation in far-field parameters. (b) Calculated variation of far-field beam angle $\theta$ as a function of $Z$. The calculation was done for a confocal parameter $z_0 = 4.58$ mm (in the liquid), beam power $P = 0.9$ W, and CH$_3$CN material parameters.
thermal lensing is perturbative and no convection occurs, \( \theta_{\text{min}} \) and \( \theta_{\text{max}} \) should vary linearly with the lens strength, which is proportional to \( P \):

\[
\begin{align*}
\theta_{\text{min}} &= \theta_0 (1 - cP) \\
\theta_{\text{max}} &= \theta_0 (1 + cP),
\end{align*}
\]

where the far-field angle \( \theta_0 \) is the value unperturbed by a thermal lens (in the limit \( P \to 0 \)) and \( c \) is a small constant specific to a given set of material and beam parameters. Since \( I_{\text{min}} \propto \theta_{\text{max}}^{-2} \) and \( I_{\text{max}} \propto \theta_{\text{min}}^{-2} \), we can write

\[
\frac{I_{\text{max}}}{I_{\text{min}}} = \frac{\theta_{\text{max}}^2}{\theta_{\text{min}}^2} = \frac{(1 + cP)^2}{(1 - cP)^2} \approx (1 + cP)^4
\]

or

\[
\left( \frac{I_{\text{max}}}{I_{\text{min}}} \right)^{1/4} = 1 + cP.
\]

The coefficient \( c \) is proportional to the set of material parameters \( (bdn/dT)/(kn_0) \) from Eqn. 5.2.

In the present z-scan experiments, the sample was moved with respect to the focal plane of the beam in order to find \( I_{\text{max}} \) and \( I_{\text{min}} \). The ratio \( (I_{\text{max}}/I_{\text{min}})^{1/4} \) was then measured as a function of beam power, which was corrected to the power inside the sample to compare with calculations. The laser was operated in cw mode and a 20 cm focusing lens was used to make the experiment more sensitive. When the cryostat was used, the lens was moved with respect to the sample because of the difficulty of moving the sample, but because of the long focal length of the lens and other geometric considerations, the systematic error incurred in the intensity measurements was negligible. Plots of the measured ratio as a function of \( P \) are shown for several molecules in Fig. 5.3. In both propagation calculations and z-scan experiments, these plots deviated from linearity at higher powers, where thermal lensing can be nonperturbative and convection can be significant. The nonlinear
Fig. 5.3. Z-scan measurements for several molecules. The fitted lines were constrained to 1.0 at $P = 0$, and the slopes $c$ are shown in $W^{-1}$. Solid symbols distinguish CD$_4$ and CD$_3$CN.

regions were avoided when extracting slopes. The absorption coefficient for CH$_3$CN was found by adjusting it to make the calculated z-scan slope fit the experimental slope. For CH$_4$, $b$ was then found by scaling the CH$_3$CN quantity $(b\,dn/dT)/(\kappa n_0)$ by the relative z-scan slope $c_{CH_4}/c_{CH_3CN}$ and then using the known CH$_4$ parameters from the literature to isolate $b$. A similar process was used for CD$_4$. Table 5.1 summarizes the extracted $b$ and the literature values of the other material parameters for CH$_3$CN, CD$_4$, and CH$_4$.

While the relative cw thermal lens strengths were found to within 2% in most cases, the absolute accuracy of the extracted absorption coefficients is almost certainly worse. An ad hoc estimate of 30% accuracy for all absorption coefficients was based on the difference between CH$_3$CN results from two different methods. One method was the z-scan process already described. In the other method, the HRS was calculated as a function of power in beam propagation calculations, with $b$ treated
Table 5.1. Material parameters relevant to thermal-lensing calculations. The estimated uncertainty in $b$ is 30%. The parameters $dn/dT$ and $k$ for CD$_4$ are assumed to be the same as for CH$_4$, while $\rho$ and $c_p$ are corrected to account for the difference in molecular mass.

<table>
<thead>
<tr>
<th>liquid</th>
<th>$a - dn/dT$</th>
<th>$b_k$</th>
<th>$c_\rho$</th>
<th>$b_{c_p}$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10^{-4}K^{-1})</td>
<td>(10^{-3}W cm^{-1})</td>
<td>(gm cm^{-3})</td>
<td>(J gm^{-1} K^{-1})</td>
<td>(10^{-3}cm^{-1})</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>4.5</td>
<td>1.877</td>
<td>0.782</td>
<td>2.227</td>
<td>1.91</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>9.2</td>
<td>2.081</td>
<td>0.439</td>
<td>3.373</td>
<td>0.64</td>
</tr>
<tr>
<td>CD$_4$</td>
<td>(9.2)</td>
<td>(2.081)</td>
<td>(0.549)</td>
<td>(2.698)</td>
<td>0.60</td>
</tr>
</tbody>
</table>

*aBased on references 23 and 26.
*bFrom reference 19.
*cFrom references 19 and 22.

as the free parameter necessary to make the calculated HRS reduction match the directly measured reduction. This latter method involved calculations of pulsed thermal lensing, which are discussed further in the next section.

The typical difference between deuterated and hydrogenated molecules is illustrated by the slopes for CH$_3$CN and CD$_3$CN in Fig. 5.3. The C-D vibrational frequencies are lower than those for C-H bonds, usually resulting in much lower absorption for deuterated molecules. One surprising result of these measurements is that thermal-lens strengths are so similar for CH$_4$ and CD$_4$.

In order to use the absorption coefficients found by the z-scan method, the difference between cw and pulsed thermal lensing must be taken into account, and this is done in the next section.

5.1.4 Pulsed vs. cw thermal lensing

Relative thermal-lensing strengths in the case of a pulsed beam of average power $P$ are not necessarily the same as for a cw beam of the same power. This is because different material parameters can be important. For example, in the cw case, the
temperature gradient for a given $P$ is controlled by the thermal conductivity $k$ of the medium. However, in the pulsed case, the heat capacity $c_p$ controls the temperature gradient in the limiting case of a single pulse much shorter than the time for diffusion across the beam. The relative strength for CH$_4$ in the cw case is $c_{CH_4}/c_{CH_3CN}$. A first guess of what the relative strength might be in this limiting pulsed case is

$$\frac{c_{CH_4}}{c_{CH_3CN}} \frac{k_{CH_4}}{k_{CH_3CN}} \frac{(\rho c_p)_{CH_3CN}}{(\rho c_p)_{CH_4}} = 0.76,$$

or a factor of 1.3 times larger than for the cw case.

The real case is intermediate between the cw and the limiting pulsed cases because during each pulse there is a residual gradient left from the previous pulses. A self-consistent solution can be found numerically. Code was written to solve the diffusion equation in cylindrical coordinates, under the approximation that heat transfer occurred only by conduction and transverse to the beam propagation direction. The boundary conditions were similar to those used by Gordon et al., and absolute calculated temperatures in the cw case were within 1% of those given in their paper\textsuperscript{28}. Since the strength of the lens is proportional to the curvature of the transverse temperature profile at the center of the beam, this curvature was calculated for different material parameters, laser repetition rates, and beam widths to determine (i) the curvature in the cw case for a given $P$ and beam waist $w$, (ii) the curvature of a pulse under the same conditions, and (iii) the self-consistent, residual curvature just before each pulse under pulsed conditions. Residual curvatures were then expressed as fractions of full cw curvatures. An expression for the focal length of a pulsed thermal lens was obtained from the work of Gupta et al., and the effective fraction of the full, pulsed lens strength present during the peak of HRS production was estimated at 0.5, based on the temporal intensity profile of the laser pulses. The effect of both the residual cw lens strength and fractional pulsed strength were then combined in the propagation calculations previously explained to calculate HRS production as a function of
power. The results for CH$_3$CN, CD$_4$, and CH$_4$ are shown in Fig. 5.4(a). The thermal
lensing corrections for CD$_4$ and CH$_4$ were based on the calculated curves shown in
the figure. The accuracy of the curves was judged by comparing the calculated HRS
for CH$_3$CN to two different fitted experimental curves involving the same conditions.
These curves, shown in Fig. 5.4(b), agree at lower powers but not at higher powers.
(The CH$_3$CN thermal-lensing corrections were based on the experimental curves.)
The agreement between theory and experiment is expected to be better for CD$_4$ and
CH$_4$ since their cw thermal-lensing strengths are only half as large as for CH$_3$CN. The
expected agreement for $P = 1.5$ W in CH$_4$, for example, should correspond to the
agreement observed in CH$_3$CN at $P = 0.9$ W. In addition, the sign of the observed
error in Fig. 5.4(b) is consistent with convective effects at higher powers in CH$_3$CN,
and these would be diminished in CD$_4$ and CH$_4$ due to their larger kinematic vis­
cosities. The uncertainty in the thermal-lensing correction factors for CD$_4$ and CH$_4$
influences was estimated at 5%.

5.1.5 Thermal-lensing summary

Through a combination of theoretical, experimental, and computational work,
the thermal-lensing corrections have all been determined with 5% precision. The
thermal-lensing correction was measured empirically for CH$_3$CN, which has a strong
HRS signal and the strongest lensing effect of any of the liquids used in the HRS exper­
iments. For the weakly scattering liquids, empirical measurements are not effective.
However, the relative cw thermal-lensing strengths were measured using the z-scan
method, and the far-field parameters behaved as predicted by theory. The z-scan ex­
periments also yielded absorption coefficients because the other relevant parameters
are known. Using the measured absorption coefficients and supplemental information
from thermal-relaxation calculations, the laser beam was then numerically propagated
through media with different material parameters, under the influence of both pulsed
Fig. 5.4. HRS as a function of power. (a) Calculations for CH$_3$CN, CD$_4$, and CH$_4$, done for beam parameters corresponding to the experimental conditions. Corrections for CD$_4$ and CH$_4$ were based on the curves shown. (b) Comparison of theory and experiment for CH$_3$CN.
and steady-state thermal-lensing contributions. These propagation calculations were used to calculate HRS intensities as a function of power and make thermal-lensing corrections for CD$_4$ and CH$_4$. The accuracy of the overall method was judged by comparing HRS results from the propagation calculation and the empirical measurement for CH$_3$CN. Thermal lensing in CCl$_4$ and CF$_4$ is negligible.

5.2 CCl$_4$ results

There are some differences between the measurements reported in this section and those for the other liquids. CCl$_4$($l$) was measured against CH$_3$CN($g$) instead of CH$_3$CN($l$). This provided the necessary calibration for CCl$_4$($l$), as described in Sec. 3.3.5. In addition, the measurements of CCl$_4$($l$) vs. CH$_3$CN($g$) were done with the gas-phase apparatus.

The intensity ratios and a typical spectrum are shown in Fig. 5.5. There were no known problems with spurious background in the CH$_3$CN($g$) spectra, so the final weighted average of $I_{VV}^{\text{CCI}_4(l)}/I_{VV}^{\text{CH}_3\text{CN}(g)} = 18.4 \pm 0.8$ was based on the calculated background.

The previous and current calibration procedures for $\beta_{VV}^{\text{CCI}_4(l)}$ were described in Sec. 3.3.5, and the results are summarized in Table 5.2.

Table 5.2. Summary of CCl$_4$(l) calibration results. All results for $\beta$ are given in atomic units.

<table>
<thead>
<tr>
<th>$\beta_{\text{efish}}^{\text{CH}_3\text{CN}(g)}$</th>
<th>$(\beta_{VV}/\beta_{\text{efish}})_{\text{theory}}^{\text{CH}_3\text{CN}(g)}$</th>
<th>$\beta_{VV}^{\text{CH}_3\text{CN}(g)}$</th>
<th>$\beta_{VV}^{\text{CCI}_4(l)}$ (previous)</th>
<th>$\beta_{VV}^{\text{CCI}_4(l)}$ (current)</th>
<th>$I_{VV}^{\text{CCI}<em>4(l)}/I</em>{VV}^{\text{CH}_3\text{CN}(g)}$ (current)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$17.9 \pm 1.1$</td>
<td>$0.606 \pm 0.007$</td>
<td>$10.85 \pm 0.68$</td>
<td>$18.6 \pm 0.7$</td>
<td>$20.9 \pm 1.4$</td>
<td>$18.4 \pm 0.8$</td>
</tr>
</tbody>
</table>

$^a$From reference 2.
Fig. 5.5. CCl₄(l) intensity ratios and spectrum. (a) Measured ratios $I_{VV}^{CCl_4(l)}/I_{VV}^{CH_3CN(g)}$, based on calculated background for CH₃CN(g). (b) CCl₄(l) spectrum from a single measurement vs. gas-phase calculation. The spectrum includes the dead-time correction for each point. Background was negligible. The calculated spectrum is scaled to match the integrated intensity of the measured spectrum. Both the calculated and measured spectra are convolved with the 25 cm⁻¹ instrumental response function. The width of the measured spectrum shown is a factor of 2 larger (full width at half maximum) than the resolved spectrum, for which the width is 11.7 cm⁻¹.
5.3 CF₄ results

Three measurements were made for CF₄, and the intensity ratios are summarized in Fig. 5.6(a). The final weighted average of \((7.38 \pm 0.16) \times 10^{-3}\) is based on the last two measurements alone. Apart from the strong disagreement with the other values, the first measurement (left) was one of the first liquid measurements, and several major experimental problems occurring in the time between the sample and reference measurements could have lead to a decrease in the reference intensity and the observed increase in the intensity ratio. The error bars shown in Fig. 5.6(a) assume counting statistics only. In addition, the last two measurements, unlike the first, were done in reference-sample-reference format, giving better control over laser drifts and other possible problems.

The sum of CF₄(ℓ) spectra from the last two measurements is shown in Fig. 5.6(b). The calculated background has been subtracted. These measurements were done at 93 K and 100 K and are compared with the 100 K gas-phase calculation.

5.4 CD₄ and CH₄ results

One measurement was made for CD₄(ℓ) (at 100 K), with a final extracted intensity ratio \(I_{VV}^{\text{CD}_4(ℓ)}/I_{VV}^{\text{CH}_3\text{CN}(ℓ)} = (15.24 \pm 0.51) \times 10^{-3}\). The measured spectrum is compared with the calculated gas spectrum in Fig. 5.7.

Four measurements were made for CH₄, all between 97 and 100 K. The measured intensity ratios are summarized in Fig. 5.8(a). The four measured ratios were used to find the final weighted average \(I_{VV}^{\text{CH}_4(ℓ)}/I_{VV}^{\text{CH}_3\text{CN}(ℓ)} = (13.63 \pm 0.28) \times 10^{-3}\).

The measured spectrum is shown in Fig. 5.8(b). This sum includes only half of the measured spectra because of a slight spectrometer calibration error in the others.
Fig. 5.6. $\text{CF}_4(l)$ intensity ratios and spectrum. (a) Ratios $\frac{I_{VV}^{\text{CF}_4(l)}}{I_{VV}^{\text{CH}_2\text{CN}(l)}}$ for the three measurements. The first measurement (on left) was disregarded in the weighted average. (b) Sum of $\text{CF}_4(l)$ spectra from the last two measurements vs. 100 K gas-phase calculation. The calculated background varied across the spectrum due to ambient light, so background ($\approx 10\%$ of the raw measured integrated intensity) has subtracted on a per-point basis. The calculated spectrum has been scaled to match the integrated intensity of the measured spectrum.
Fig. 5.7. CD$_4$(l) spectrum: measurement vs. gas-phase calculation. Both experiment and calculation were done at 100 K, and the calculated background (0.12 counts per point) has been subtracted from the measured spectrum. The calculated spectrum has been scaled to match the integrated intensity of the measured spectrum.
Fig. 5.8. CH$_4$(l) intensity ratios and spectrum. (a) Summary of intensity ratios $I_{VV}^{CH_4(l)}/I_{VV}^{CH_3CN(l)}$. All were included in the weighted average. (b) Sum of several measured spectra vs. 100 K gas-phase calculation. The calculated background (0.15 counts per point) has been subtracted. The calculated spectrum has been scaled to match the integrated intensity of the measured spectrum.
The calculated background has been subtracted, and the measured spectrum is compared with the 100 K gas-phase calculation.

5.5 Liquid-phase summary

A summary of the liquid-phase intensity ratios and hyperpolarizabilities is given in Table 5.3. The quantity $\beta^{(l)}/\beta^{(g)}$ is a measure of the effect of the liquid environment on $\beta$. The error for this quantity excludes calibration uncertainties common to both liquid- and gas-phase measurements.

Table 5.3. Summary of liquid-phase results. The errors for the ratios in the last column exclude calibration uncertainty common to both liquid and gas. All values of $\beta$ are in atomic units.

<table>
<thead>
<tr>
<th>molecule</th>
<th>$I_{VV}^{(l)}/I_{VV}^{CH_3CN(l)}$ (10^{-2})</th>
<th>$I_{VV}^{(l)}/I_{VV}^{CH_3CN(g)}$</th>
<th>$\beta_{VV}^{(l)}$</th>
<th>$\beta_{VV}^{(l)}/\beta_{VV}^{(g)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl$_4$</td>
<td>a90. ± 3.</td>
<td>b18.4 ± 0.8</td>
<td>21. ± 1.</td>
<td>3.0 ± 0.3</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>0.74 ± 0.02</td>
<td>0.122 ± 0.007</td>
<td>2.5 ± 0.2</td>
<td>0.80 ± 0.09</td>
</tr>
<tr>
<td>CD$_4$</td>
<td>1.61 ± 0.05</td>
<td>0.27 ± 0.02</td>
<td>3.4 ± 0.3</td>
<td>0.83 ± 0.09</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1.43 ± 0.03</td>
<td>0.24 ± 0.02</td>
<td>3.2 ± 0.3</td>
<td>0.77 ± 0.09</td>
</tr>
</tbody>
</table>

* Taken from reference 2 and converted to the type of intensity ratio used in the current work.
* This is the only value in this column that was directly measured. All others were converted from the measured values in the previous column.
CHAPTER 6

COMPARISON OF THEORY AND EXPERIMENT

In this chapter, theoretical and experimental values for $\beta$ are compared, observed differences between gas- and liquid-phase $\beta$ and HRS spectral widths are examined, and conclusions are drawn from this work. Our method will first be reviewed. The ultimate reference is CH$_3$CN($g$) for all the measurements. A gas-phase reference provides particular advantages for the gas-phase experiments since beam and collection geometries are identical for sample and reference. This advantage is not negated when using a liquid transfer standard. As described in Chapter 3, the accuracy of local-field factors is not important in extracting $\beta$ for gas-phase molecules with the current calibration method. Spurious background was a major experimental concern in the gas measurements, but it was assessed using many different methods, producing a best guess for each intensity ratio with an error bar that takes into account all reasonable estimates of its magnitude. The agreement of measured and calculated gas-phase spectra gives further evidence that the magnitude of spurious background was small.

For the liquid-phase measurements, one additional intensity-comparison step was required in the calibration chain. However, this comparison was in scattering intensities, so the only local-field factors of importance were those for the sample liquids being measured. While beam and collection geometries were not identical for the liquid-phase measurements, it was previously shown$^1$ that differences in beam and collection geometries for gases and liquids have been adequately accounted for. The thermal-lensing effect was the major analytical concern for the liquid-phase measure-
ments. Corrections for this effect were made to CH₃CN, CD₄, and CH₄ intensities. The estimated systematic uncertainty in the correction for each liquid was included in the final error bar.

Since the experimentally-derived β varies as the square root of the measured intensity, uncertainties in β are only half as large as for the intensity ratios. When calibration uncertainty is included, the final uncertainty in β is about 10% for each molecule.

In the ensuing discussion, we will refer to Table 6.1, where theoretical and experimental information about β is resummarized and the measured, liquid-phase linewidths are compared with the calculated, gas-phase linewidths. As mentioned

<table>
<thead>
<tr>
<th>molecule</th>
<th>aβ calc</th>
<th>βₓᵧᵧ</th>
<th>βₓᵧᵧ/βₓᵧᵧ</th>
<th>width(ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>13.6</td>
<td>11.0±0.9</td>
<td>3.0±0.3</td>
<td>b0.66±0.02</td>
</tr>
<tr>
<td>CF₄</td>
<td>4.34</td>
<td>5.4±0.4</td>
<td>0.80±0.09</td>
<td>b0.59±0.04</td>
</tr>
<tr>
<td>CD₄</td>
<td>7.0±0.6</td>
<td>0.83±0.09</td>
<td>c1.1±0.1</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>9.17</td>
<td>7.1±0.7</td>
<td>0.77±0.09</td>
<td>c1.1±0.1</td>
</tr>
</tbody>
</table>

Table 6.1. Theoretical and experimental summary for the four T₄ molecules. All values of β are in atomic units. The width comparison in the last column is based on the instrumentally broadened spectra (for both calculation and experiment) shown in Chapter 5.

"^Extracted from Bishop et al., reference 7.
^Full width at half maximum (FWHM).
^Root mean square (rms).

in Sec. 3.3.4, quantum corrections to the intensities are too small to see given the precision of our measured values of β.

All ab initio calculations mentioned in this chapter refer to the work of Bishop et al. unless otherwise specified. In their work, β is calculated by summing the electronic contribution βₑ, the zero-point vibrational-averaging (ZPVA) correction
$\Delta \beta_{ZPVA}$, and the pure-vibrational contribution $\beta^v$ to get the total effective first hyperpolarizability $\beta^{tot}$.

6.1 Calculation vs. measurement for CCl$_4$ and CF$_4$.

The value of $\beta_{xyz}^{CCl_4} = 13.6$ a.u. shown in Table 6.1 was calculated at $\omega = 0.04$ atomic units using different basis sets for the various contributions to $\beta$. At the same $\omega$, a value of $\beta_{xyz} = 8.6$ a.u. was calculated using consistent but smaller basis sets, and Bishop et al. conclude that the theoretical $\beta$ at the MP2 level lies somewhere between these two values. The dispersion correction (from interpolating Bishop's values) in going from $\omega = 0.040$ to 0.043 a.u. ($\lambda = 1064$ nm) is -0.03 a.u., insignificant compared to the difference between the two theoretical estimates of $\beta$. The calculated value therefore agrees with the experimental value of $11.0 \pm 0.9$ a.u. to the extent of comparison allowed by theory. The spectral narrowing and dramatic increase in the effective $\beta_{VV}$ in the liquid phase have been thoroughly examined previously, establishing that there are strong contributions to the scattering from intermolecular interactions.$^{17}$

The value $\beta_{xyz}^{CF_4} = 4.34$ a.u. at $\lambda = 1064$ nm is obtained by interpolating the calculated MP2 results of Bishop et al. In addition, their MP2 static value of $\beta^e = 4.08$ a.u. for CF$_4$ can be compared with Maroulis’ best estimate$^{31}$ of $\beta^e = 6.0$ a.u. at the MP4 level. This difference suggests that the dynamic value of Bishop et al. could rise to $\beta_{xyz}^{CF_4} = 6.2$ a.u. with a more highly-correlated treatment. The measured gas-phase value $\beta_{xyz}^{CF_4} = 5.4 \pm 0.4$ a.u. lies between these two estimates from theory. The measured liquid $\beta_{VV}$ is 20% lower than the measured gas-phase value. The liquid-phase spectrum is significantly narrower than the calculated gas-phase spectrum at the same temperature, indicating that rotational diffusion occurs in the liquid, as it does for CCl$_4$. Despite rotational diffusion, the liquid-phase $\beta$ can still be the same
as in the gas phase, as long as no collective scattering modes or coherence effects are present. As stated in Sec. 2.5, octupole-induced-dipole scattering should be negligible for CF$_4$(l), and this would, in any case, increase the effective liquid $\beta$. However, it is quite possible that orientational correlations in the liquid result in destructive interference of scattering waves, decreasing observed scattering and the effective liquid $\beta$. The observed rotational diffusion suggests that intermolecular interactions are strong enough for destructive orientational correlations to be plausible. An alternative explanation for the difference between the extracted liquid and gas $\beta$ involves the local-field factors and is presented in Sec. 6.3.

6.2 Calculation vs. measurement for CH$_4$.

The *ab initio* results for $\beta_{xyz}$ agree with the measured gas-phase values better for CCl$_4$ and CF$_4$ than for CH$_4$. The calculated value of $\beta_{xyz}$ for CH$_4$ is $29 \pm 10\%$ larger than the measured value. This is the most surprising result of this work since the quality of the *ab initio* calculations should be the best for CH$_4$. It should be noted that use of the previously-established reference value$^2$ for $\beta_{VV}^{\text{CCl}_4(l)}$ would result in a smaller value yet for $\beta_{xyz}^{\text{CH}_4(g)}$. It should be reemphasized that (*i*) thermal lensing is not a consideration for sample or reference in the gas-phase measurements, (*ii*) 100% uncertainty was assumed in the spurious-background correction for CH$_4(g)$, and (*iii*) any background problems unaccounted for would tend to *increase* the experimentally-extracted $\beta$, while the observed discrepancy between experiment and theory is of opposite tendency.

No calculation was done for CD$_4$, but $\beta$ should be nearly the same as for CH$_4$ because (*i*) the calculation shows that $\beta^e$ is the dominant contribution and (*ii*) $\Delta\beta^{Z\text{PVA}}$ is small, opposite in sign, and both expected to decrease for CD$_4$.

One might argue that a calculation with higher-order correlation or a larger basis
set is necessary to determine \( \beta^e \) more accurately, particularly in light of the similarity in measured \( \beta \) for the two molecules. However, a comparison of Bishop's calculation with Maroulis' work\(^{32} \) provides evidence that the discrepancy is not due to \( \beta^e \). Maroulis calculated \( \beta \) for \( \text{CH}_4 \) in the static-frequency limit, in the equilibrium geometry, at the MP4 and coupled cluster single double (triple) CCSD(T) levels of electron correlation. He thoroughly investigated basis-set and correlation effects to get a best estimate of \( \beta^e = 8.31 \) a.u., compared with a static value of \( \beta^e = 8.1 \) a.u. from the MP2 calculation of Bishop et al. Maroulis also investigated sensitivity of \( \beta^e \) to bond length, from which a rough estimate of \( \Delta \beta^{ZPVA} \approx 0.8 \) a.u. follows, to be compared with the MP2 static value \( \Delta \beta^{ZPVA} = 1.1 \) of Bishop et al. These considerations indicate that the convergence of Bishop's dynamic value of \( \beta^e \) is satisfactory.

Contributions to \( \beta^\nu \) that have not been calculated are a more likely explanation of the discrepancy between theory and experiment. Although the pure-vibrational contribution was calculated, only fundamental vibrations were taken into account. \( \text{CH}_4 \) and \( \text{CD}_4 \) are different from the other \( T_d \) molecules in that vibrational overtone and combination bands of relatively low order fall near the laser wavelength. References 33–35 show overtone absorption spectra for \( \text{CD}_4 \) and \( \text{CH}_4 \). The overtones of lower order, which are strongest and below the laser frequency, would give contributions to \( \beta^\nu \) of the same sign as the fundamental contributions. Since \( \beta^e \) and \( \beta^\nu \) are of opposite sign, the calculated magnitude of \( \beta^{tot} = \beta_{xyz} \) should decrease with the added contributions, as required to achieve agreement with experiment. The overtones are at lower-lying frequencies for \( \text{CD}_4 \), so it might seem unlikely that the same large contribution to \( \beta^\nu \) could exist for both molecules. For the same reason, one expects the absorption coefficient to be much smaller for \( \text{CD}_4 \) than for \( \text{CH}_4 \). However, the observed fact is that the absorption coefficients are almost the same for the deuterated and hydrogenated versions (see Sec. 5.1.3), and it could be that the overtone
and combination bands give similar, large contributions to both the absorption and the hyperpolarizability. A major advantage of Bishop’s calculations over previous work is that they are frequency-dependent and take into account vibrational effects. Ironically, it may be that for CH₄, vibrational contributions are more critical, so that even overtone and combination bands must be taken into account.

The question of vibrational overtones could be solved theoretically by calculating matrix elements for the vibrational bands of higher order than the fundamental and including the contributions of these in calculating βᵽ. This could also be addressed experimentally by doing measurements with a fundamental frequency in the visible, so as to make pure-vibrational contributions negligible.

6.3 Local-field factors

It is curious that for all three cryogenic liquids, β is ≈ 20% lower in the liquid than in the gas. One explanation for the consistency of the difference is that the Lorentz local-field factors are invalid for nonlinear-optical processes. Wortmann and Bishop suggest that the correct local-field factor for the generated, second harmonic is (2n₂w + 1)/3n₂w times the Lorentz local-field factor. If β is really the same in both liquid and gas phases for CF₄, CD₄, and CH₄; and if the modified local-field factors are correct; then the error incurred by use of the Lorentz factor would effectively be multiplication of β⁽⁽⁾⁾/β⁽⁾⁾ ≈ 1 by (2n₂w + 1)/3n₂w ≈ 0.86, a result not significantly different from the liquid-to-gas ratios shown in Table 6.1. An alternative way to examine the effect of the modified field factors is to analyze the experimental data and obtain β⁽⁽⁾⁾ and β⁽⁽⁾⁾/β⁽⁾⁾ based on the modified factors instead of the Lorentz factors. This was done, and the results are summarized in Table 6.2. The present measurements of CF₄, CD₄, and CH₄ do not prove that the modified form of the local-field factors is correct, but these molecules are certainly good examples to look at for
Table 6.2. Experimental values derived with modified local-field factors. The modified results in the last two columns were obtained by multiplying the values in Table 6.1 by the first column of this table. Values for $\beta$ are in atomic units.

<table>
<thead>
<tr>
<th>molecule</th>
<th>$3n^2/(2n^2 + 1)$</th>
<th>$\beta_{\nu\nu}$</th>
<th>$\beta_{\nu\nu}/\beta_{\nu'\nu'}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl$_4$</td>
<td>1.216</td>
<td>26. ±1.</td>
<td>3.6±0.4</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>1.129</td>
<td>2.8±0.2</td>
<td>0.9±0.1</td>
</tr>
<tr>
<td>CD$_4$</td>
<td>1.151</td>
<td>3.9±0.3</td>
<td>1.0±0.1</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1.152</td>
<td>3.7±0.3</td>
<td>0.9±0.1</td>
</tr>
</tbody>
</table>

Evidence of whether the modified form is correct. One way to assess local-field effects would be to look at molecules for which little effect of intermolecular interactions is expected in the liquid phase. Collision-induced scattering would not be expected in any of the cryogenic liquids. Moreover, the measured HRS spectra for CD$_4$ and CH$_4$ indicate that free-rotor behavior remains in the liquid phase, making coherence effects very unlikely.

6.4 Conclusion

While the HRS experiments necessary to measure $\beta$ for weakly scattering gas molecules and cryogenic liquids are difficult, values of $\beta$ have been successfully obtained in both liquid and gas phases for four tetrahedral molecules. With error bars under 10% in all cases, critical comparisons with the latest *ab initio* calculations were possible, which was the primary goal of this work. Because of the relatively few electrons in CH$_4$, calculations were expected to be more accurate than those for CCl$_4$ and CF$_4$. However, to the degree that the calculated and experimental gas-phase values of $\beta$ can be compared, they agree for CCl$_4$ and CF$_4$, while a fairly large discrepancy remains for CH$_4$. It appears most likely that this is due to vibrational effects that are unimportant for other molecules, and it would be interesting to see a calculation.
of the magnitude of these effects. The gas-phase HRS spectra for these molecules appear to be entirely calculable as far as experimental statistics and resolution permit comparisons.

The significant spectral narrowing observed in CCl₄ and CF₄ liquids is absent in CD₄ and CH₄, which appear to behave as free rotors even in the liquid phase. Unlike the CCl₄ case, there is little difference between gas- and liquid-phase β for CF₄, CD₄, and CH₄. The liquid-gas comparisons for these molecules provide evidence that the Lorentz local-field factors require modification for experiments in nonlinear optics. Another interesting byproduct of this work has been the demonstration of a z-scan technique to measure absorption coefficients.
APPENDIX A

MATHEMATICA CODE FOR SPECTRAL CALCULATIONS

(* spectrum.m  D.P. Shelton  rev.10/2000 *)

(* Compute the deltaJ = 0, +-1, +-2, +-3 branches *)
(* of the rotational hyper-Raman spectrum for XY4, *)
(* with selection rule J + J' >= 3. *)
(* Include nuclear statistical weights. *)
(* Points every 1 cm-1 from 1-npts/2 to +npts/2 cm-1. *)
(* The output spectrum has 1 cm-1 resolution. *)
(* kT = 208.50 cm-1 at T = 300 K *)

(* molecule nuclear spin E(cm-1) *)
(* CH4  1/2  (H)  5.24104 *)
(* CD4  1   (D)  2.63264 *)
(* CF4  1/2  (F)  0.185    *)
(* CC14 3/2 (35Cl)  0.0572  *)
(*                      3/2 (37Cl) *)

B = 5.24 ;  T = 295 ;  jmax = 25 ;  npts = 1000 ;

kT = 208.50 * T / 300. ;
cntr = npts/2 ;
s = Table[0, {n, npts}] ;
z = 0. ;
gszero = {1,0,0,1,1,0} ;
gshalf = {5,3,5,11,13,11} ;
gsone = {15,18,30,51,63,66} ;

(* Spherical Top rotational states |J,M,K> have *)
(* degeneracy (2J+1)^2 for level J, and squared *)
(* octupolar transition matrix element (2J'+1)/(2J+1) *)
(* for J -> J', averaged over M,K and summed over M',K'*)
(* *)
(* Symmetry Adapted Functions are linear combinations *)
(* of the Spherical Top rotational wavefunctions, *)
(* accounting for nuclear spin statistics and symmetry.*)
(* Matrix elements between SAF's are computed following*)
(* with the corrections given in*)
(* Corrections to average transition matrix elements*)
(* calculated by x3jjp.m and wigner.m are stored in*)
(* x3jjp.dat [Jmax+1,4].*)

(* Switch spin statistics by commenting out appropriate*)
(* lines for: f and ff . *)

x3jjp = << x3jjp.50 ;

Do[
   j = m - 1 ;
   q = Mod[ j , 6 ] ;
   qq = q + 1 ;
   (* Count states and compute partition function Z. *)
   (* f = (2 j + 1) ; distinguishable nuclei *)
   (* f = (j-q)/6 + gszero[[qq]] ; spin 0 nuclei *)
   f = 16(j-q)/6 + gshalf[[qq]] ; (* spin 1/2 nuclei *)
   (* f = 81(j-q)/6 + gsone[[qq]] ; spin 1 nuclei *)
   pop = N[ (2 j + 1) f Exp[ -j (j+1) B / kT ] ];
   z = z + pop ;
   (* ff = correction factor for average matrix element *)
   ff = Table[ 1, {n,4} ] ;
   (* ff = ff ; distinguishable nuclei *)
   ff = ( 1 + (1/4) x3jjp[[j+1]] )
        (4/3) (2j+1)/f ; (* spin 1/2 *)
   (* ff = ( 1 + (1/9) x3jjp[[j+1]] )
        (27/4) (2j+1)/f ; spin 1 *)
   (* J -> J *)
   deltaE = 0 . ;
   intens = pop ff[[1]] ;
   intens = If[ (2 j) < 3 , 0 , intens ] ;
   n = cntr + Round[ deltaE ] ;
\[ s[[n]] = s[[n]] + \text{intens} \]

(* J -> J+1 *)
\[ \text{deltaE} = 2 (j+1) B \text{ff}[[2]] \]
\[ \text{intens} = \text{pop} \left( \frac{2 \ j + 3}{2 \ j + 1} \right) \]
\[ \text{intens} = \text{If} \left[ (2 \ j + 1) < 3, 0, \text{intens} \right] \]
\[ n = \text{cntr} + \text{Round}[\text{deltaE}] \]
\[ s[[n]] = s[[n]] + \text{intens} \]

(* J+1 -> J *)
\[ \text{intens} = \text{intens} \text{Exp}[-\text{deltaE} / kT] \]
\[ \text{deltaE} = -\text{deltaE} \]
\[ n = \text{cntr} + \text{Round}[\text{deltaE}] \]
\[ s[[n]] = s[[n]] + \text{intens} \]

(* J -> J+2 *)
\[ \text{deltaE} = 4 (j + 3/2) B \text{ff}[[3]] \]
\[ \text{intens} = \text{pop} \left( \frac{2 \ j + 5}{2 \ j + 1} \right) \]
\[ \text{intens} = \text{If} \left[ (2 \ j + 2) < 3, 0, \text{intens} \right] \]
\[ n = \text{cntr} + \text{Round}[\text{deltaE}] \]
\[ s[[n]] = s[[n]] + \text{intens} \]

(* J+2 -> J *)
\[ \text{intens} = \text{intens} \text{Exp}[-\text{deltaE} / kT] \]
\[ \text{deltaE} = -\text{deltaE} \]
\[ n = \text{cntr} + \text{Round}[\text{deltaE}] \]
\[ s[[n]] = s[[n]] + \text{intens} \]

(* J -> J+3 *)
\[ \text{deltaE} = 6 (j+1) B \text{ff}[[4]] \]
\[ \text{intens} = \text{pop} \left( \frac{2 \ j + 7}{2 \ j + 1} \right) \]
\[ \text{intens} = \text{If} \left[ (2 \ j + 3) < 3, 0, \text{intens} \right] \]
\[ n = \text{cntr} + \text{Round}[\text{deltaE}] \]
\[ s[[n]] = s[[n]] + \text{intens} \]

(* J+3 -> J *)
\[ \text{intens} = \text{intens} \text{Exp}[-\text{deltaE} / kT] \]
\[ \text{deltaE} = -\text{deltaE} \]
\[ n = \text{cntr} + \text{Round}[\text{deltaE}] \]
\[ s[[n]] = s[[n]] + \text{intens} \]

 total = 0. ;
 Do[ s[[n]] = s[[n]] / z ;

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total = total + s[[n]] ; 
,\{n,npts\} ] ;

(* Integrated intensity for the spectrum = "total". *) 
(* In the classical limit each of the 7 branches is *) 
(* equally intense and total = 7. *) 

ListPlot[ s, PlotJoined->True ] ;
 s >> spectrum.81 ;

(* UNIX command to "translate" the Mathematica format *) 
(* into a simple list suitable for SigmaPlot is: *)
(* b b b b b b b b b b b b b b b b b b b b b b b b b b b b *)
(* tr ",\~v\~j\" "\~v\~j <filename >newfilename *)
(* *)
(* tr "..." "..." replaces first string with second *)
(* \~v = CNTRL-v "protects" the carriage return \~j *)
(* blank spaces required as shown; 3 after 2nd \~v\~j *)
(* *)
(* UNIX command to change e.g. 1.23*-6 to 1.23e-6 *)
(* sed -e 's/\*/-/e/' <filename >newfilename *)
(* *)
(* 'substitute/string1/by string2/' *)
(* where string1 = \~ and \ protects \~ *)

(* Convolve with fwhm-point wide trapezoidal window. *)
(* Choose fwhm = odd and 2 cm-1 wide rise and fall. *)
(* The window function is stored in "w". *)
(* The convolved spectrum is returned in "t". *)
fwhm = 25 ;
w = Table[ 1, {n, fwhm} ] ;
w[[1 ]] = 0.5 ;
w[[fwhm]] = 0.5 ;
norm = fwhm - 1. ;
t = Table[ 0, {n, npts} ] ;
top = npts - fwhm + 1 ;

Do[
  Do[
    p = m + n - 1 ;
    q = m + (fwhm-1)/2 ;
    t[[q]] = t[[q]] + w[[n]] * s[[p]] ;
    ,\{n,fwhm\} ] ;
\[ t[[q]] = t[[q]] / \text{norm} ; \]

\[ ,\{m,\text{top}\} ; \]

\text{ListPlot[} t, \text{PlotJoined->True}] ;
\text{t} >> \text{spectrum.83} ;

\text{(* x3jjp.m \hspace{1cm} D.P. Shelton \hspace{1cm} rev.10/2000 \hspace{1cm} *)}

\text{(* Compute correction term } X3 = [42\phi(J,J')-1] \text{ \hspace{1cm} *)}
\text{(* for } J = 0 \text{ to } J_{\text{max}} \text{ and } J'-J = 0,1,2,3 \text{. \hspace{1cm} *)}
\text{(* Table of matrix elements } djkl \text{ for } J = 0 \text{ to } J_{\text{max}}+3, \text{\hspace{1cm} *)}
\text{(* for positive } K,L \text{ only, is required from wigner.m . \hspace{1cm} *)}
\text{(* \hspace{1cm} *)}
\text{(* } X3 \text{ is from Eq. 88 and Eqs. 40,75,76,79,80,85 in \hspace{1cm} *)}
\text{(* Ozier & Fox, JCP 52, 1416 (1970). \hspace{1cm} *)}
\text{(* \hspace{1cm} *)}

\text{<<wigner.m} ; \text{ (* set: } J_{\text{max}}(\text{wigner.m}) = J_{\text{max}}(\text{here}) + 3 \text{ \hspace{1cm} *)}
\text{Jmax = 50 ;}

\text{x3jjp} = \text{Table[} N[0], \{J,1,J_{\text{max}}+1\},\{Jp,1,4\} \} ;
\text{Delta[a_,b_] := If[a==b, 1, 0] ;}
\text{Eps[a_] := 1/Sqrt[1 + Delta[a,0]] ;}

\text{(* Compute } x3jjp \text{ for } J = 0 \text{ to } J_{\text{max}} \text{ and } Jp = J \text{ to } J+3 \text{. \hspace{1cm} *)}
\text{Do[}

\text{(* Four-fold sum over even positive values of } K,L \text{ and } K',L'\text{\hspace{1cm}*)}
\text{(* the initial and final projection quantum numbers. \hspace{1cm} *)}
\text{(* Sum } K,L = 0 \text{ to } J \text{ for } J = \text{ even, \hspace{1cm} *)}
\text{(* or } K,L = 2 \text{ to } J-1 \text{ for } J = \text{ odd. \hspace{1cm} *)}
\text{(* Same ranges for } K',L', \text{ but with } |K'-K'|,|L'-L'| = 2. \hspace{1cm} *)
\text{(* Inversion index rho = 1 or 2(=0) restricts allowed } K,L. \hspace{1cm} *)
\text{(* } J+rho = \text{ even allows } K,L=4n, J+rho = \text{ odd allows } K,L=4n+2 \hspace{1cm} *)
\text{(* } J' \text{ and } rho' \text{ similarly restrict } K',L'. \hspace{1cm} *)
\text{(* Parity change for transition requires odd } J+rho \text{ change, \hspace{1cm} *)}
\text{(* and follows from } |K'-K|=2 . \hspace{1cm} *)
\text{(* Scan } K,K',L,L' \text{ and discard disallowed combinations. \hspace{1cm} *)}

\text{KLstart = If[ EvenQ[J], 0, 2 ] ;}
\text{KLend = If[ EvenQ[J], J, J-1 ] ;}
Do[
    rho = Mod[J + K/2, 2] ; (* rho=0,1: 0 = 2 modulo 2 *)
    rhop = Mod[Jp+Kp/2, 2] ;
    KpLpmin = If[ EvenQ[Jp], 0, 2 ] ;
    term = If[ 3<=J+Jp
        && KpLpmin<=Kp<=Jp
        && KpLpmin<=Lp<=Jp
        && Mod[J+rho+Jp+rhop,2]==1
        && Mod[J+rho,2]==Mod[L/2,2]
        && Mod[Jp+rhop,2]==Mod[Lp/2,2] ,

        ( Eps[Kp] Eps[K] )^-1
        ( ThreeJSymbol[{Jp,Kp},{3, 2},{J,-K}]
          - ThreeJSymbol[{Jp,Kp},{3,-2},{J,-K}] )
        (Eps[Lp] Eps[L] )^-1
        ( ThreeJSymbol[{Jp,Lp},{3, 2},{J,-L}]
          - ThreeJSymbol[{Jp,Lp},{3,-2},{J,-L}] )
        ( Delta[Kp,Lp]/3 + (-1)^-(Jp+rhop) (4/3)
          Eps[Kp] Eps[Lp] djk1[[Jp+1,Kp+1,Lp+1]] )
        ( Delta[K,L]/3 + (-1)^-(J+rho) (4/3)
          Eps[K] Eps[L] djk1[[J+1,K+1,L+1]] )

        , 0 ] ;

    x3jjp[[J+1,Jp-J+1]] = x3jjp[[J+1,Jp-J+1]] + term ;

    , {K,KLstart,KLend,2}, {Kp,K-2,K+2,4},
    {L,KLstart,KLend,2}, {Lp,L-2,L+2,4} ] ;

    , {J,0,Jmax}, {Jp,J,J+3} ] ] ;

    x3jjp = 42 x3jjp - 1 ;

    x3jjp >> x3jjp.50 ;

(* wigner.m D.P. Shelton rev.10/2000 *)

(* Compute a table of matrix elements of the *)
(* Wigner rotation matrices DJKL(alpha,beta,gamma). *)
(* where the arguments of DJKL are the Euler angles. *)
(* Mathematica array indices for JKL are {J+1,K+1,L+1}.*

(* Compute djk1 = DJKL(0,Pi/2,0) *)

(* using recursion from Fox & Ozier, JCP 52, 5044 (1970). *)
(* Recursion Eq.65 started with Eq.60 and also Eqs.28-30. *)
(* Exponential error growth requires numerical precision *)
(* of about J digits to ensure accuracy even in the worst *)
(* case, which is dJJJJ constructed by J-fold recursion. *)

Jmax = 53;
digits = 100;
djk1 = Table[ 0, {J, 1, Jmax + 1}, {K, 1, Jmax + 1}, {L, 1, Jmax + 1} ];

(* Compute each matrix djk1 up to order Jmax. *)
Do[
 (* Fill in row dJKO and column dJOK for K = 1 to J. *)
 Do[
  djk1[[J + 1,K + 1,1]] = N[ Sqrt[4 Pi/(2J+1)]
  SphericalHarmonicY[J,K,Pi/2,0] , digits] ;
  djk1[[J+1,1,K+1]] = N[ (-1)^K djk1[[J+1,K+1,1]] , digits] ;
  ,{K,0,J} ] ;
 (* Calculate dJIK and dKJ1 for K in steps of 2. *)
 Kstart = If[ EvenQ[J] , 2, 1 ] ;
 Do[
  djk1[[J+1,K+1,2]] = N[ (-K/Sqrt[(J+1)J]) djk1[[J+1,K+1,1]] , digits] ;
  djk1[[J+1,2,K+1]] = N[ (-1)^K djk1[[J+1,K+2,1]] , digits] ;
  ,{K,Kstart,J,2} ] ;
 (* Fill in the skipped elements dJIJ and dJKJ. *)
 Kstart = If[ EvenQ[J] , 1, 2 ] ;
 Do[
  djk1[[J+1,2,K+1]] = N[ ( Sqrt[(J+K+1)(J-K)] djk1[[J+1,2,K+2]]
  + Sqrt[(J-K+1)(J+K)] djk1[[J+1,2,K]] ) /(-2) , digits] ;
  djk1[[J+1,K+1,2]] = N[ (-1)^K djk1[[J+1,2,K+1]] , digits] ;
  ,{K,Kstart,J-1,2} ] ;
 (* Fill in the remaining elements dJKL. *)
 Do[
  djk1[[J+1,K+1,L+2]] = N[ (-2 K djk1[[J+1,K+1,L+1]]]
- Sqrt[(J-L+1)(J+L)] djkl[[J+1,K+1,L]]

/ Sqrt[(J+L+1)(J-L)] , digits] ;

djkl[[J+1,L+2,K+1]] = N[ (-1)^-(K-L+1) djkl[[J+1,K+1,L+2]]

, {K,2,J}, {L,1,K-1} ] ;

, {J,0,Jmax} ] ;

djkl = N[ djkl ] ; (* Convert back to machine precision. *)

(* djkl >> djkl.dat ; *)
REFERENCES


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