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D. Pichler
(Ph.D. Thesis)

November 1990

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Nonlinear Optical Spectroscopy of Ce$^{3+}$ Ions in Insulating Crystals
(Ph. D. dissertation)

by
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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.
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by

David Matthew Piehler

Abstract

Coherent anti-Stokes Raman spectroscopy (CARS) involving electronic states of rare earth ions in insulating crystals has shown only limited success, unlike CARS involving vibrational transitions. The major problem is that $\chi^{(3)E}$, the contribution to the third order susceptibility from the electronic states of the rare earth ions, is often obscured by $\chi^{(3)NR}$, the contribution from the bulk crystal which can be orders of magnitude larger. Previous CARS experiments in pure rare earth crystals gave values of $C = |\chi^{(3)E}/\chi^{(3)NR}|_{\text{max}}$ no greater than 0.5.

The quantity $\chi^{(3)E}$ increases as the frequencies of the input lasers approach the energies of the parity-allowed $4f \rightarrow 5d$ electric dipole transitions of the rare earth ions. Among the trivalent rare earth ions, Ce$^{3+}$ with its single $4f$ electron has the lowest energy excited $5d$ configuration. Electronic CARS resonances involving Stark components of the $2F_{5/2}$ and $2F_{7/2}$ manifolds of the Ce$^{3+}$ ion have been measured in two crystals at liquid helium temperature. In the pure crystal, CeF$_3$, the levels of $5d$ configuration range from about 40000 to 50000 cm$^{-1}$ and strong CARS resonances ($C > 3$) were seen when using visible ($\lambda_1 = 476$ nm, $\lambda_2 = 532$ nm) or near ultraviolet ($\lambda_1 = 355$ nm, $\lambda_2 = 385$ nm) lasers. Approximating the virtual intermediate states by a degenerate $5d$ level at 45000 cm$^{-1}$ accounted for both the absolute magnitude and dispersion properties of $|\chi^{(3)E}|_{\text{max}}$. In the dilute crystal, LuPO$_4$ doped with 0.06 mol % Ce$^{3+}$, strong CARS resonances ($C > 15$)
were observed only when the anti-Stokes signal was nearly resonant with the onset of the lowest 5d band at 30460 cm$^{-1}$ (328 nm).

The applicability of these experiments to other rare earth systems as well as the prospects for stimulated electronic Raman gain are discussed.

Additionally, polarized two-photon absorption spectra originating in the 4f ground state and terminating in the 5d levels in the Ce$^{3+}$:LuPO$_4$ crystal, gave the energies and symmetries of the zero-phonon lines of the two lowest 5d bands. The zero-phonon lines, which are labeled by the irreducible representations of the $D_{2d}$ double group, are at 30460 cm$^{-1}$ ($\Gamma_7$) and 39715 cm$^{-1}$ ($\Gamma_6$).
Although he wrote to his brother Charles that the prospect of painting Peggy’s mural was “exciting as hell,” Jackson’s procrastination was evidence of his terror at the thought of executing a work so large “with no strings attached as to what or how I paint.” He sat on a keg and stared at the huge blank canvas for a month. ... After months of indecision about the subject of his mural, Pollock decided to let his mode of creation constitute his theme.

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### References
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Norm Edelstein has been responsible for both financial and scientific support of this work. Norm is fond of saying "Pa$^{4+}$ is just like Ce$^{3+}$." After our long collaboration, my response is now "OK Norm, you may be right, but I’d rather work with cerium."

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Introduction

As a group, insulating crystals containing trivalent rare earth ions are noteworthy for their unique optical properties, as well as their practical applications in such devices as lasers. Among these ions, (sometimes referred to as lanthanide or $4f^n$ ions), two properties of the trivalent cerium ion make it an especially attractive system to study. One is that $\text{Ce}^{3+}$ has a single optically active electron $(n = 1)$. This simplifies calculations, and consideration of many-body interactions within the electronic configuration is unnecessary. The other is that the first excited configuration ($4f^{(n-1)}5d^1$) is lower in energy than for any other trivalent rare earth ion. This relatively low $5d$ configuration creates experimental opportunities not available in other trivalent rare earth systems. This dissertation reports on efforts to exploit these opportunities in two $\text{Ce}^{3+}$ systems – the dilute $\text{Ce}^{3+}:\text{LuPO}_4$, and the fully concentrated $\text{CeF}_3$.

Nonlinear wave mixing spectroscopy is a most appropriate method for studying the electronic structure of trivalent cerium ions in insulating crystals. The electronic energy levels of the ground $4f$ configuration lie in the infrared (0 – 3000 cm$^{-1}$), while the states of the first excited configuration, $5d$, are usually in the ultraviolet (30000 – 50000 cm$^{-1}$). An insulating crystal containing the $\text{Ce}^{3+}$ ion usually remains transparent throughout the visible region of the electromagnetic spectrum. Wave mixing spectroscopy enables access to these
high- and low-lying energy levels with visible lasers. The mixing of lightwaves at optical frequencies is allowed by the fact that the complex electronic susceptibility of a material deviates from a linear relationship with the applied electric field at sufficiently high intensities. In this dissertation, pulsed lasers produce these high intensities. As a form of wave mixing, two-photon absorption enables a visible laser to probe ultraviolet electronic levels by creating a material excitation wave whose frequency is twice that of the input lightwave. (See Figure I.1 (b).) In another form of wave mixing, material resonances are detected when the difference in frequency between two input lightwaves is equal to the energy of a low-lying state. This is known as coherent anti-Stokes Raman spectroscopy (CARS). (See Figure I.1 (a).)

The experiments are:

- **Electronic Coherent Anti-Stokes Raman Spectroscopy.** CARS is a form of four-wave mixing in which two input lasers at frequencies $\omega_1$ and $\omega_2$ interact within a nonlinear medium to produce a third coherent beam at frequency $\omega_3 = 2\omega_1 - \omega_2$. Resonances are observed in the signal at $\omega_3$ as $(\omega_1 - \omega_2)$ is swept through the electronic energy levels of the Ce$^{3+}$ ion. For most rare earth crystals, these resonances are very weak due to the inherently small cross section for spontaneous electronic Raman scattering. The strength of these resonances may be increased by using lasers near the strong $4f \rightarrow 5d$ parity allowed electric dipole transitions. When using near ultraviolet lasers ($\lambda_1 = 355$ nm, $\lambda_2 = 385$ nm), Ce$^{3+}$:LuPO$_4$ exhibits strong CARS resonances when the anti-Stokes signal $(\omega_3)$ is nearly resonant with the lowest level of the $5d$ configuration at 30360 cm$^{-1}$. These resonances are an order of magnitude greater than those seen in pure rare earth crystals which contain 2000 times more rare earth ions per unit volume. Due to the relatively low energy of the $5d$ configuration in CeF$_3$, electronic CARS experiments with visible lasers ($\lambda_1 = 476$ nm, $\lambda_2 = 532$ nm) show resonances an order of magnitude greater than in other rare earth crystals containing approximately the same number of rare earth ions per unit
volume. The absolute strengths of these resonances were accurately predicted using the Axe theory of two-photon processes with $4f \rightarrow 5d$ absorption data. These experiments are detailed in chapters 2 and 4.

- **$4f \rightarrow 5d$ Two-photon Absorption.** The simplest and most direct way to investigate the nature of the $5d$ configuration in $\text{Ce}^{3+}:\text{LuPO}_4$ is by two-photon absorption. Although two-photon transitions between the $4f$ and $5d$ configurations are formally parity forbidden ($\Delta l = 1$), they are allowed in second order by the odd parity components of the crystal field. The intensity of the resulting $5d \rightarrow 4f$ fluorescence as a function of laser frequency and polarization determines the energies and symmetries of zero-phonon lines of the $5d$ configuration. Results are given in Chapter 3.

- **Simulated Electronic Raman Scattering.** One of the original motivations for this work was to determine if electronic Raman processes in rare earth crystals could be strong enough for the observation of stimulated electronic Raman scattering. Stimulated electronic Raman scattering has been observed in atomic vapors, but not never involving ions in crystals. No stimulated electronic Raman processes were observed in $\text{CeF}_3$. This is discussed briefly in an appendix to Chapter 4.
Figure 1.1. Schematic diagram of wave mixing processes. (a) CARS. (b) Two-photon absorption.
Chapter One

Optical Properties of Ce$^{3+}$:LuPO$_4$ and CeF$_3$

This chapter introduces the optical properties of Ce$^{3+}$:LuPO$_4$ and CeF$_3$ which are the samples used in experiments described in later chapters. A survey of the Ce$^{3+}$ free ion begins the chapter followed by sections dealing with the effects of introducing the Ce$^{3+}$ free ion into a crystalline environment. Finally, the optical properties of two specific Ce$^{3+}$ systems – the CeF$_3$ crystal and Ce$^{3+}$ doped into the LuPO$_4$ crystal are given.

1.1 The Ce$^{3+}$ Free Ion

In order to understanding the Ce$^{3+}$ ion in the condensed state, it is informative to first review the properties of the Ce$^{3+}$ free ion.

The rare earth elements span the periodic table from lanthanum ($Z = 57$) to lutetium ($Z = 71$). In a solid state system containing rare earth ions, the rare earth ion usually exists in the trivalent state. The electronic configuration of the trivalent rare earth ion in its ground
The state is [Xe]4f

\(n = 0, \ldots, 13\). The first excited configuration is 4f\(^{(n-1)}5d^1\) which usually lies in the vacuum ultraviolet region (50000 cm\(^{-1}\) – 100000 cm\(^{-1}\)). The 4f\(^{(n-1)}6s^1\) and the 4f\(^{(n-1)}6p^1\) configurations usually lie above 100000 cm\(^{-1}\). Figure 1.1 shows the lowest levels of the various 4f\(^{(n-1)}5d^1\) electronic configurations of the free trivalent rare earth ions as one moves across the rare earth series. At the beginning of the series, the Ce\(^{3+}\) ion has the lowest energy excited 4f\(^{(n-1)}5d^1\) configuration.

The Ce\(^{3+}\) ion has a single optically active electron and its behavior is described by a single electron free ion Hamiltonian \(H_{FI}\):

\[
H_{FI} = H_0 + \zeta_{nl} L \cdot S
\]

(1.1)

where \(H_0\) is the Hamiltonian which governs the interaction of the electron with the spherically symmetric Xe core. \(H_0\) determines the relative energies of the configurations labeled by \(nl\). The term \(\zeta_{nl} L \cdot S\) characterizes the spin-orbit interaction. Since there is only a single electron to deal with, \(L-S\) coupling is valid, and the free ion states may be labeled by the Russell-Saunders terms \((2S+1)L_J\).

Lange [1] measured the energy levels of the Ce\(^{3+}\) free ion and the results are in Table 1.1. Note the fairly large spin-orbit interaction \((\zeta_{4f} = 643.7 \text{ cm}^{-1}, \zeta_{5d} = 995.6 \text{ cm}^{-1}\)\), as is typical for the heavier ions and atoms. For comparison, \(\zeta_{3p} = 11.5 \text{ cm}^{-1}\) for the yellow D emission lines of Na.

Figure 1.2 shows the radial wavefunctions for the Ce\(^{3+}\) free ion. The radial wavefunctions are the key to understanding the behavior of rare earth ions in solids, as will be discussed in this chapter. The 4f wavefunction lies primarily within the filled 5s\(^2\)5p\(^6\) shells of the Xe core. The 5d electron, on the other hand, extends beyond the 5s\(^2\)5p\(^6\) shells of the Xe core.
1.2 The Ce$^{3+}$ Ion in a Crystalline Environment

The spectroscopy of the $4f^n$ configuration of rare earth ions in crystals may be divided into two parts - classical and modern. Classical rare earth spectroscopy deals with the rare earth ion in a static crystalline environment. Atomic-like free-ion wavefunctions describe the quantum state of the rare earth ion. The addition of a crystal field Hamiltonian to the free ion Hamiltonian accounts for the introduction of the rare earth ion into a crystal lattice. This classical model successfully explains energy level structures as well as intensities of one- and two-photon optical transitions. Books by Judd [2], Wyborne [3], and Dieke [4] review this classical approach which is essentially an extension of atomic physics. Modern rare earth spectroscopy is a branch of solid state physics. Such topics as line broadening, electron-phonon interactions, energy transfer, and ion-ion interactions view the rare earth ion as part of a collective solid state system. Books by Hufner [5], and Kaplyanskii and Macfarlane [6] deal with these topics. The distinction between modern and classical spectroscopy is somewhat artificial. For the practicing experimentalist, both aspects are relevant.

The spectroscopy of the excited $4f^{(n-1)}5d^1$ configuration of rare earth ions in crystals is less well known. There are two reasons for this. First, Figure 1.1 indicates that these levels are in the ultraviolet region where many crystals are opaque. Secondly, interconfigurational $4f \leftrightarrow 5d$ transitions consist of broad ($> 1000$ cm$^{-1}$), sometimes overlapping bands making the exact location of $4f^{(n-1)}5d^1$ levels a difficult task. In fact, the Ce$^{3+}$ ion with $n=1$, has the only really tractable $4f^{(n-1)}5d^1$ configuration. It has not only the lowest energy configuration, but also is split into at most five levels by the effects of the crystalline electric field. On the other hand, the number of levels in the $4f^{(n-1)}5d^1$ configuration increases rapidly as one moves toward the center of the rare earth series. For example, a
crystalline electric field may split the $4f^{(n-1)}5d^1$ configuration of the Pr$^{3+}$ ion ($n=2$) into as many as 140 levels.

### 1.2.1 The 4f Configuration

Figure 1.2 shows the radial extent of the $4f$ wavefunction. The $4f$ electron exists primarily within the filled $5s^2$ and $5p^6$ shells of the Xe core. This fact explains the success of classical rare earth spectroscopy. Since the $4f$ electron is shielded from its local environment, the effects of the crystal lattice are small, and the crystal field acts as a small perturbation on the free ion states.

The crystal field Hamiltonian models the effect of introducing the free ion into the crystal lattice. In the crystal field model, the Ce$^{3+}$ ion is surrounded by a distribution of charges which produce an electrostatic field at the site of the Ce$^{3+}$ ion. The binding between the ion and the surrounding ligands is assumed to be purely ionic and the ion does not share charge with the surrounding ligand. The energy levels of the free ion are split by the Stark effect. The effect of the crystal field on the $4f$ electron is small. Typical Stark splittings are on the order of hundreds of cm$^{-1}$. This accounts for a remarkable property of rare earth crystals. The energy levels of the $4f^n$ electrons are approximately the same in any crystal environment – with the exception of the small crystal field (Stark) splittings.

The crystal field Hamiltonian for a $4f$ electron may be written as [3]

$$H_{CF} = \sum_{k,q} B^k_q C^k_q \quad k = 2, 4, 6; \quad q = -k, \ldots, k$$

(1.2)

where $B^k_q$ are the crystal field parameters, and the operator $C^k_q$ is defined in terms of spherical harmonics.
\[ C_q^k = \left( \frac{4\pi}{2k + 1} \right)^{\frac{1}{2}} Y_q^k(\theta, \phi) \]  

and only acts upon angular variables. The full Hamiltonian describing the system is now

\[ H = H_{FI} + H_{CF} \]

The crystal field is presumed to be small, and \( H_{CF} \) is treated as a perturbation on the free ion Hamiltonian. Since \( H_{CF} \) does not commute with the total angular momentum, \( J \) is no longer a good quantum number. Depending on the symmetry of the site of the Ce\(^{3+} \) ion in the crystal, \( H_{CF} \) will split and reduce the degeneracy of the \((2J + 1)\)-fold degenerate free ion states. The crystal field Hamiltonian transforms according to the the point group which describes the point symmetry of the rare earth ion in the crystal. For systems such as Ce\(^{3+} \) with half-integral \( J \), the Stark components are labeled by the irreducible representations of double group of the point group of the crystal field. The Stark components split from a single free ion state are called a manifold. Additionally, since \( H_{CF} \) connects states of different \( J \), the crystal field states are said to be \( J \)-mixed. Since each state no longer has definite \( J \) values, the \( \Delta J = 0, \pm 1 \) (0\( \rightarrow \)0 forbidden) selection rules for electronic transitions are relaxed. Rigorous selection rules for electronic transitions are defined by the symmetry labels of the crystal field states.

The point group symmetry of the rare earth site restricts the number of non-zero \( B_q^k \) s. Only two crystal field parameters, \( B_0^4 \) and \( B_0^6 \) are needed to describe the crystal field at a site of cubic symmetry. At a site of very low symmetry, such as \( C_2 \), 14 crystal field parameters are needed to model the crystal field. The number of Stark components into which the crystal field splits a \((2J + 1)\)-fold degenerate free ion state depends on the point group of the crystal field and the value of \( J \). Generally, the number of Stark components
increases as the symmetry of the crystal field is lowered. For systems with an odd number of electrons (half-integral \( J \)) such as \( \text{Ce}^{3+} \), Kramers' theorem demands that Stark levels have \textit{at least} two-fold degeneracy in any crystal field. Hence, a crystal field may split a \( J \) state of a Kramers ion into a maximum of \((2J + 1)/2\) doubly degenerate levels. These doubly degenerate levels are called Kramers doublets. Only the application of a magnetic field (which destroys time-reversal symmetry) can split a Kramers doublet.

If the \( \text{Ce}^{3+} \) ion lies at a site in a crystal with a point group symmetry lower than cubic, the crystal field will split the free ion ground state, \( ^{2}F_{5/2} \), into three Kramers doublets, and the \( ^{2}F_{7/2} \) free ion state into four Kramers doublets. (See Figure 1.3.) Even though \( J \) is no longer a good quantum number (the wavefunctions of the Stark components of the \( ^{2}F_{5/2} \) manifold may now be 98\% \( J=5/2 \) and 2\% \( J=7/2 \) in character), each manifold is labeled by the dominant \( J \)-component. The irreducible representations of the double group describing the crystal field label each Stark component.

Crystal field theory can explain the location, symmetries, and number of Stark components in terms of the addition of a small crystal field Hamiltonian to the free ion Hamiltonian. No \textit{ab initio} method of calculating crystal field parameters has yet proved satisfactory. Crystal field parameters are derived from a least squares fit of the crystal field Hamiltonian to experimental data. Using free ion wavefunctions as the basis set, the crystal field Hamiltonian is diagonalized yielding a set of crystal field parameters and angular wavefunctions for the Stark components. In the crystal field theory, the \( 4f \) radial wavefunction of the free ion is unchanged, since the crystal field does not act upon radial variables.
1.2.2 The 5d Configuration

The radial wave function of the 5d electron extends much further beyond the filled $5s^25p^6$ shells of the Xe core than does the 4f electron. (See Figure 1.2.) This results in a much stronger interaction between the 5d electron and the crystal lattice. Crystal field theory may be applied to the 5d electron much as it is applied to the 4f electron.

$$H_{CF} = \sum_{k,q} B_q^k C_q^k$$

(for a d electron $k$ only goes as high as four since a spherical tensor of rank six cannot connect two $l = 2$ states by the Wigner-Eckhart theorem). For the 5d electron, the crystal field is the dominant interaction ($H_{CF} > \zeta_{nl} L \cdot S$) and $J$-mixing of the free ion states is fairly complete. The $J$ labels of the free ion states are not even approximate quantum numbers for the 5d crystal field levels. As with the 4f levels, the irreducible representations of the double group which describes the symmetry at the site of the Ce$^{3+}$ ion in the host crystal label the 5d states. If the symmetry of the Ce$^{3+}$ site is less than cubic, the combined effect of the spin-orbit interaction and crystal field split the 5d configuration into five Kramers doublets.

Figure 1.4 shows the 5d levels for a Ce$^{3+}$ ion in several different host crystals. Four important features to notice are:

- The crystal field splitting of the 5d electron is quite large compared to the 4f electron. The total splitting of the 5d configuration may be as great as 20000 cm$^{-1}$, about 50 times that of the 4f configuration.
- The energies of the 5d levels depend strongly on the host crystal. The crystal field parameters of the particular crystal are now the dominant factor determining the energy levels. These parameters are very sensitive to the host crystal and are
responsible for the wide variation of $5d$ spectra. The onset of the $5d$ configuration varies from about 21000 cm$^{-1}$ in YAG ($Y_3Al_5O_{12}$) [7] to 38700 cm$^{-1}$ in LaF$_3$ [8].

- Unlike the $4f$ levels, the $5d$ levels are broad (> 1000 cm$^{-1}$) bands. This is due to the stronger coupling of the $5d$ electron to the phonons of the host crystal. This is explained in detail in the next section.

- In a simple model where a distribution of point charges represent the crystal lattice, one expects the center of gravity of the $5d$ configuration to increase since the radially extended $5d$ electron is attracted to the positively charged neighbors. In real rare earth systems, the center of gravity of the $5d$ configuration is lower in a crystalline environment than in the free ion. A key issue then is the inadequacy of the description of the neighboring ligands by a purely electrostatic crystal field. The interaction between the Ce$^{3+}$ ion and the neighboring ligands is actually a good deal more complicated, and the reader is referred to articles by Aull and Jenssen [9, 10] for more details.

One may expect the crystal field model to be less satisfactory in describing the $5d$ configuration than the $4f$ configuration. Ionic bonding is a good approximation for the shielded $4f$ electron, but the radially extended $5d$ electron may share charge with the surrounding ligands. For $d$ electron systems (usually transition metal ions), ligand field theory is often used and the electronic charge may transfer between the metal ion and the neighboring ligands. In this case, the ligand field states are a linear combination of the $d$ electron and the ligand states, and the distinct $I = 2$ character of the crystal field state is lost [11]. In this dissertation, the $5d$ states are modeled by the empirical crystal field theory since it less complicated, and it provides a convenient starting point for the treatment of the $5d$ electron.
1.2.3 4f ↔ 5d Transitions

The two main differences between intra-configurational 4f ↔ 4f transitions and inter-configurational 4f ↔ 5d transitions are in strength and linewidth.

Electric dipole transitions between states in the same electronic configuration are forbidden by parity. If a rare earth ion sits at a crystal site that lacks inversion symmetry, the odd components of the crystal field Hamiltonian can mix excited states of opposite parity (such as the 5d) with the 4f states to allow relatively weak second-order "forced electric dipole" transitions. These transitions typically have oscillator strengths on the order of $10^{-6}$ to $10^{-8}$ which are still large enough to dominate over magnetic dipole transitions which have oscillator strengths on the order of $10^{-8}$. Electric dipole transitions between the 4f and 5d configurations are parity allowed ($\Delta l = 1$). Thus, 4f ↔ 5d transitions have large oscillator strengths ($10^{-1}$ to $10^{-2}$) and the 5d states have a correspondingly short radiative lifetime ($\sim 10^{-8}$ s). 4f states have much longer radiative lifetimes ($10^{-3}$ to $10^{-6}$ s) which make crystals containing rare earth ions good materials for Q-switched lasers operating on 4f ↔ 4f transitions.

The rest of this section deals with the spectral features of 4f ↔ 5d transitions. Unlike 4f ↔ 4f transitions which are characterized by relatively narrow (< 10 cm$^{-1}$) spectral lines, 4f ↔ 5d transitions are broad band (> 1000 cm$^{-1}$) and exhibit a Stokes shift between the peaks of the absorption and emission band. These features may be understood in terms of the configurational coordinate model.

The configurational coordinate model takes into account the interaction between the electronic states of the impurity ion and the vibrations (phonons) of the host crystal. For simplicity, only the totally symmetric "breathing mode" of the lattice is considered. This is the motion in which the surrounding lattice moves in and out about the impurity ion and
may be described by a single normal coordinate $Q$. The interaction of the electronic states with this mode is usually much greater than with the other vibrational modes [12].

Figure 1.5 shows the configurational coordinate diagram in which the electronic and vibrational energy levels are shown. In the ground electronic state ($4f$), the configurational coordinate has an equilibrium value $Q_0$. When the ion is in the $5d$ state, the configurational coordinate average value is $Q_0'$. The difference between $Q_0$ and $Q_0'$ is related to the relative sensitivity of the $5d$ and $4f$ states to the motion of the host lattice. Again refer to Figure 1.2. The $4f$ electron is shielded, and it is not very sensitive to changes in the crystal environment. Figures 1.2 and 1.4 indicate that the radially extended $5d$ electron is quite sensitive to changes in the local environment.

In the Born-Oppenheimer approximation, $|\psi\rangle|\chi_n\rangle$ describes the state of the ion-lattice system. The ket $|\psi\rangle$ describes the electronic state and $|\chi_n\rangle$ describes the vibrational state of the lattice which may be treated as a harmonic oscillator with quantum number $n$. In this simple model, one assumes that the oscillator force constant is the same for both the ground and excited states. In the Condon approximation, the electric dipole matrix element may be written as

$$\langle 4f | \langle \chi_n | r | \chi_m \rangle | 5d \rangle = \langle 4f | r | 5d \rangle \langle \chi_n | \chi_m \rangle$$

(1.6)

If $(Q_0 - Q_0') = 0$ (which is a good approximation for the case when both the ground and excited states are in the $4f$ configuration), then $\langle \chi_n | \chi_m \rangle$ is non-zero only when $n = m$. When $Q_0$ and $Q_0'$ are different, $\langle \chi_n | \chi_m \rangle$ may be non-zero for a range of $m$ and $n$ values, resulting in transitions between different vibrational quantum numbers.

If the temperature of the system is zero, only the $|4f\rangle|\chi_{n=0}\rangle$ state is populated. The absorption spectrum (Figure 1.5) shows a zero-phonon line corresponding to the purely electronic ($n = 0 \rightarrow m = 0$) transitions, and a vibronic sideband corresponding to $n$
= 0 \rightarrow m > 0 \text{ transitions}. The shape of the absorption band depends on the Franck-Condon factors $\langle \chi_n | \chi_m \rangle$, which depend on $(Q_0 - Q_0')$, which depends on the difference in sensitivity between the electronic states to the vibrating local environment.

After absorption at zero temperature, the excitation rapidly decays to the lowest vibrational level of the excited electronic state. The emission spectrum is the mirror image of the absorption with a zero-phonon line and a vibronic sideband. The difference between the peaks of the absorption and emission spectra is called the Stokes shift. The greater the difference in vibronic coupling between the ground and excited states, the greater the Stokes shift.

The vibrations of the totally symmetric mode usually dominate, but all even parity phonons (both acoustic and optical, throughout the Brillouin zone) contribute to the $4f \leftrightarrow 5d$ vibronic sideband. Thus, the use of a single breathing mode vibration to represent the full spectrum of lattice phonons is crude. Actual vibronic sidebands are more complex (and perhaps more interesting) than those shown in Figure 1.5, reflecting the richness of the full phonon spectrum.

1.3 Line Broadening in Rare Earth Systems

The line broadening of the Stark levels occur due to mechanisms which have their source in the nature of the crystal lattice. This section reviews both homogeneous and inhomogeneous line broadening mechanisms since they will be important for interpreting the results of later chapters. The reader is referred to review articles by Macfarlane [13], and Macfarlane and Shelby [14] for further detail.

In systems which are inhomogeneously broadened, individual ions (or atoms) have slightly different energy levels, thereby broadening the overall linewidth of the system as a
whole without increasing the linewidth of the individual ions. A narrow band laser may selectively excite only a subset of ions in the collection, and "burn a hole" in the inhomogeneously broadened spectrum. The most familiar form of inhomogeneous broadening is Doppler broadening, in which each atom has a different resonant frequency depending on its relative velocity.

Crystal imperfections are the major source of inhomogeneous broadening in rare earth crystals. In an imperfect crystal, each rare earth ion may see a slightly different crystal field, and consequently undergo a slightly different Stark splitting. The extreme case is an impurity ion in a glass. Here there is no long range order and each impurity may be surrounded by a very different charge distribution. The resulting inhomogeneous linewidths may be as great as hundreds of cm\(^{-1}\) – greater than the Stark splitting. The random introduction of an impurity ion into the host crystal actually destroys the crystal symmetry. As the doping increases, some impurity ions may experience a crystal field which may be perturbed by the presence of another nearby impurity ion. If the impurity ion is not same size as the ion for which it substitutes, the crystalline lattice may be distorted at the site of the impurity. These effects may be minimized in very dilute crystals. If nearest impurity neighbors are separated by several lattice sites, they have a small effect on the crystal field, and the effect of random strain on the lattice by size mismatch is local and constant. Typical inhomogeneous linewidths for \(4f \leftrightarrow 4f\) transitions in dilute rare earth crystals are 1 to 10 GHz (0.03 to 0.3 cm\(^{-1}\)). Since this inhomogeneous "strain" broadening is related to the strength of the crystal field, \(5d\) electrons should have much larger (~50 times) inhomogeneous linewidths.

The previous section indicates that \(4f \leftrightarrow 4f\) electric dipole transitions have lifetimes on the order of \(10^{-3}\) to \(10^{-6}\) s. This implies a (homogeneous) lifetime broadening between 1 kHz and 1 MHz, much smaller than the inhomogeneous strain broadening. In real systems at finite temperatures, non-radiative effects shorten the lifetimes. In fact, all experiments
reported in this dissertation are performed at low temperature (~3.8 to 10 K) to minimize line broadening due to non-radiative effects.

Consider the two levels system in Figure 1.6. If the system is coupled to a crystal lattice, transitions between \(a\) and \(b\) may occur via absorption and emission of phonons. For transitions from \(b\) to \(a\) the transition probability is

\[
W_{b \rightarrow a} = W(T = 0)(n + 1)
\]

where \(n\) is the occupancy number of phonons with frequency \(\omega\), and \(W(T = 0)\) is the spontaneous emission probability at zero temperature. For transitions from \(a\) to \(b\) the transition probability is

\[
W_{a \rightarrow b} = W(T = 0) n
\]

As \(T \to 0\), \(n \to 0\) and spontaneous emission from \(b\) to \(a\) dominates. State \(b\) is lifetime broadened to a much greater extent than state \(a\).

The factor \(W(T = 0)\) is proportional to the phonon density of states. The phonon density of states has a major influence on non-radiative decay processes. In the Debye approximation, the density of states for acoustic phonons has a cutoff, and \(W(T=0)\) is zero for \(\omega > \omega_{\text{Debye}}\). Typical Debye energies are in the range of hundreds of cm\(^{-1}\). If \(a\) and \(b\) are separated by more than \(\hbar \omega_{\text{Debye}}\), the lifetime of \(b\) will be fairly long, since decay can occur only by the simultaneous emission of two or more acoustic phonons, a rarer process.

Unlike the acoustic phonon density of states which is a continuum, the optical phonons usually exist in several well defined energy ranges. Additionally, optical phonons often have energies greater than the Debye energy. Optical phonons may have energies as high as thousands of cm\(^{-1}\).
Figure 1.7 illustrates the lifetimes for a generic rare earth system at low temperature. Two manifolds \((2S+1)L_J\) and \((2S'+1)L'_J\) may be separated by several thousand cm\(^{-1}\). In each manifold the upper states decay rapidly to the lowest state by the spontaneous emission of a phonon. Intra-manifold non-radiative decay is usually dominated by acoustic phonons. Inter-manifold non-radiative transitions are dominated by the higher energy optical phonons. If the manifolds are separated by more than the energy of a single optical phonon, non-radiative decay may take place by the spontaneous emission of two or more optical phonons. The decay rate is related to the effective number of optical phonons involved in the transition. If the number is high then non-radiative decay is unlikely, and radiative decay (fluorescence) dominates. If the number is low (usually below three), then non-radiative decay dominates. In other words, fluorescence may only be observed between manifolds that are separated by more than a few optical phonon energies. The result is that the lowest state in a manifold will have little lifetime broadening compared to the upper levels of the same manifold. Typical inhomogeneous linewidths for the upper levels range from tenths to tens of cm\(^{-1}\). The lowest level in the manifold may then be a metastable state, and primarily inhomogeneously broadened by crystal imperfections.

As the concentration of rare earth ions in a crystal increase, ion-ion interactions increase homogeneous broadening for all Stark levels. This type of broadening is similar to collisional broadening in atomic systems. These ion-ion interactions, which arise from magnetic dipole fluctuations among nearby rare earth ions, lead to homogeneous linewidths on the order of one to five cm\(^{-1}\) in pure rare earth crystals.
1.4 Ce$^{3+}$:LuPO$_4$

Ce$^{3+}$:LuPO$_4$ is the first cerium system which I investigated. Compared to other rare earth crystals, relatively little work has been done on this system. Traditionally, Ce$^{3+}$ doped crystals have not been of great interest to rare earth spectroscopists since they are transparent in the visible. The host crystal, LuPO$_4$, is uncommon since lutetium, one of its constituent elements, is quite expensive. More common is the naturally occurring xenotime crystal (YPO$_4$). The ionic radii of Y$^{3+}$ (0.93 Å) and Lu$^{3+}$ (0.93 Å) are nearly equal and the crystal structures are very nearly the same. Since the nearby PO$_4^{3-}$ complexes have the most influence on the crystal field experienced by the impurity ion, the electronic structure of the Ce$^{3+}$ ions in both host crystals is similar.

The host crystal, LuPO$_4$, is uniaxial with the tetragonal zircon structure. The space group of the lattice is $D_{4h}^{19}$ and the point group symmetry of the Lu$^{3+}$ site is $D_{2d}$ [15]. The $z$-axis is parallel to the highest symmetry crystal axis. All Lu$^{3+}$ sites are equivalent. The nearest neighbors of the Lu$^{3+}$ ion are eight O$^{2-}$ ions. (See Figure 1.8.) Four of the O$^{2-}$ ions are at a distance of 2.263 Å, while the other four are at a distance of 2.346 Å [16]. The nearest neighbor Lu$^{3+}$ ion is 3.708 Å away. The density of LuPO$_4$ is 6.508 g cm$^{-3}$ [17], and the number density of Lu$^{3+}$ ions is $1.465 \times 10^{22}$ cm$^{-3}$.

Because LuPO$_4$ is not a common crystal, the optical properties have not been thoroughly studied. However, LuPO$_4$ should not be very different from the more common YPO$_4$ and YVO$_4$ crystals. LuPO$_4$ is an insulator with a band gap of $\sim 70000$ cm$^{-1}$ [18], and is birefringent with $n_e (= n_z) = 1.728$ and $n_o (= n_x = n_y) = 1.694$ at 520.8 nm [19]. The energies of optical phonons in LuPO$_4$ may be as high as $\sim 1100$ cm$^{-1}$, due to the local vibrational modes of the phosphate complex [20]. The Debye energy of LuPO$_4$ at 300 K is 300 cm$^{-1}$ [19].
Early experiments by Hoshina and Kuboniwa [21] and Nakazawa and Shinoya [22] measured the electronic structure of Ce\(^{3+}\) doped into LuPO\(_4\) from 5d → 4f emission and excitation spectra. Since the emission bands to the various 4f Stark levels overlap, there was some confusion as to the energies and symmetries of the 4f levels. More recently, Williams, et al. [23–25] made a detailed examination of the ground 4f configuration by electronic Raman scattering and the excited 5d configuration by absorption measurements. Their results are shown in Table 1.2. They also fit the energy levels of the 4f and 5d configuration to the empirical crystal field Hamiltonian, and derived angular wavefunctions for levels of both the 4f and 5d configurations.

The Ce\(^{3+}\) ion has a larger ionic radius (1.07 Å) than Lu\(^{3+}\). Due to this size mismatch the high doping concentrations of the Ce\(^{3+}\) ion tend to change the LuPO\(_4\) crystal structure. The crystal Ce\(_x\)Lu\(_{1-x}\)PO\(_4\) has the tetragonal zircon structure for small \(x\) and the monoclinic “monazite” structure for \(x\approx 1\). At low concentrations, the Ce\(^{3+}\) ions substitute for the Lu\(^{3+}\) ions at sites of \(D_{2d}\) symmetry. Since the Ce\(^{3+}\) ion has an odd number (one) of optically active electrons, the Stark components are labeled by the irreducible representations of the double group of \(D_{2d}\), \(\Gamma_6\) and \(\Gamma_7\). Each Stark component is a Kramers doublet.

Selection rules for electric dipole transitions between states in \(D_{2d}\) symmetry are:

\[
\begin{align*}
\Gamma_7 &\leftrightarrow \Gamma_7 \quad \text{allowed when electric field is polarized in the } x (= y) \text{ direction.} \\
\Gamma_6 &\leftrightarrow \Gamma_6 \quad \text{allowed when electric field is polarized in the } x (= y) \text{ direction.} \\
\Gamma_6 &\leftrightarrow \Gamma_7 \quad \text{allowed when electric field is polarized in the } z \text{ or } x (= y) \text{ direction.}
\end{align*}
\]

The nature of the lowest 5d band is of primary importance in the experiment described in Chapter 2. The absorption spectrum is shown in Figure 1.9. This is very similar to that recorded by Hoshina and Kuboniwa[21]. They measured the zero-phonon
line at 30472 cm$^{-1}$, which compares well to measurements by Williams [23] and this work of 30460 cm$^{-1}$. They also correlated the peaks in the vibronic sideband with the phonons of host crystal. By the above selection rules, the $^2F_{5/2} (\Gamma_6) \rightarrow 5d (\Gamma_7)$ is allowed in both $z$ and $x$ polarizations. Only a small difference in the vibronic sideband between the $x$ and $z$ polarizations is observed. (See Appendix 1.1 for experimental details of the absorption data.) Chapter 3 describes measurements of the two lowest 5$d$ levels by two-photon absorption.

Consistent with the strong oscillator strength of the 5$d \rightarrow 4f$ transition is a fast radiative decay. The lifetime of the lowest 5$d$ band is 20 ns. Appendix 1.2 gives the details of this measurement.

M. M. Abraham and L. A. Boatner of Oak Ridge National Laboratory supplied the crystals used in this work. The crystals are about $1 \times 1 \times 5$ mm with the crystal ($z$) axis parallel to the longest dimension. X-ray fluorescence analysis indicates that 0.0604 mol % of the Lu$^{3+}$ ions have been replaced by Ce$^{3+}$ ions and the number density of Ce$^{3+}$ ions is then $8.71 \times 10^{19}$ cm$^{-3}$. The natural crystal faces in the $xz$ and $yz$ planes are of good optical quality, and were not polished. There are no good crystal faces in the $xy$ plane. All experiments used light which propagated perpendicular to the $z$-axis.

1.5 CeF$_3$

LaF$_3$ is among the most widely used host crystals for studies of trivalent rare earth ions [26, 27]. It is an insulator with a band gap of $\sim 80000$ cm$^{-1}$ [28]. Ce and La lie next to each other in the periodic table and their trivalent ionic radii are nearly the same. In the crystal Ce$_x$La$_{(1-x)}$F$_3$, the cerium concentration may be varied from $x = 0$ to 1 without
altering the crystal structure. Tysonite, a naturally occurring mineral, with \( x = 0.5 \) is found in the Pikes Peak region in Colorado [29].

The crystal CeF\(_3\) (as well as LaF\(_3\)) has the trigonal space group \( D_{3d}^4 \) [30]. The site symmetry of the Ce\(^{3+}\) ion is \( C_2 \) with three two-fold \( C_2 \) axes perpendicular to the three-fold \( C_3 \) crystal axis. (See Figure 1.10.) All Ce\(^{3+}\) ions experience the same \( C_2 \) crystal field, however there are three distinct \( C_2 \) axes. The three-fold crystal axis defines the \( z \) direction and the \( x \) and \( y \) axes are chosen arbitrarily. The Ce\(^{3+}\) ion has nine F\(^-\) neighbors at distances between 2.400 to 2.631 Å [31]. The nearest Ce\(^{3+}\) neighbor is at 4.08 Å. The number density of Ce\(^{3+}\) ions is \( 1.88 \times 10^{22} \text{ cm}^{-3} \) [17].

Along with the spin-orbit interaction, the \( C_2 \) crystal field should split the 5\( d \) configuration into five levels and the 4\( f \) configuration into seven levels. The irreducible representation of the \( C_2 \) double group of labels the levels which are all Kramers doublets. Each level has the same symmetry label, and there are no selection rules for radiative transitions. Therefore, all transitions are allowed.

In 1934, Van Velck and Hebb [32] studied Faraday rotation in pure CeF\(_3\), and assigned the broad absorption at \( \sim 250 \) nm to the 4\( f \rightarrow 5d \) transition. Buchanan \textit{et al.} [33] measured the levels of the 4\( f \) configuration by infrared absorption at liquid helium temperature. The four Stark components of the \( 2^F_{7/2} \) manifold were located at 2180, 2240, 2635 and 2845 cm\(^{-1}\) with the highest two levels having quite broad (\( \sim 30 \) cm\(^{-1}\)) spectra. Higher temperature spectra indicated possible absorption from an electronic level at \( \sim 150 \) cm\(^{-1}\), but a third \( 2^F_{5/2} \) level was not found. Most recently, experiments by Gerlinger and Schaak [34] resolved the problem of the missing \( 2^F_{5/2} \) Stark component. By coincidence, the Stark components of the \( 2^F_{5/2} \) manifold are nearly resonant with the optical phonons of the crystal. This results in a hybridization of the electronic states of the Ce\(^{3+}\) ion with the phonon states to form new vibronic states. The low temperature Raman spectrum in this region shows broad (\( \sim 100 \) cm\(^{-1}\)) features, where one might expect separate narrow Raman
lines for the optical phonons and the electronic levels. Table 1.3 gives the energies of the 4f levels from the data of Gerlinger and Schaak who also detected the levels of the $^2F_{7/2}$ manifold by electronic Raman scattering.

The 5d configuration of Ce$_x$La$_{(1-x)}$F$_3$ has been studied with various Ce$^{3+}$ concentrations [8, 28, 35–38]. These investigations showed five 5d levels with the peaks of the levels at roughly the same energies. As the concentration of Ce$^{3+}$ increases, the absorption peaks remain approximately the same; however the 5d bands broaden, and the onset of the 5d band becomes lower. Presumably this additional broadening is due to the ion-ion interaction. Note that the radial wavefunction of 5d electron may overlap with the radial wavefunction of its nearest neighbor at 4.08 Å. (See Figure 1.2.) Elias et al. [35], showed that the 5d band begins at ~35000 cm$^{-1}$ in pure CeF$_3$ at 100 K. Unlike the dilute crystals, the lowest 5d absorption band does not begin abruptly with a zero-phonon line, but gradually. The peaks in the absorption of the 5d levels measured in a thin single crystal film of CeF$_3$ at room temperature are given in Table 1.3 [28].

CeF$_3$ is birefringent. Figure 1.11 shows the ordinary and extraordinary indices of refraction from the near ultraviolet to the near infrared [39]. The nonlinear index of refraction is between 1.3 and $1.55 \times 10^{-13}$ esu at 1.06 μm [40, 41]. Raman scattering shows that there are no optical phonons in the CeF$_3$ lattice with energies greater than ~350 cm$^{-1}$ [42]. The Debye energy of CeF$_3$ is 272 cm$^{-1}$ [43].

R. W. Sparrow of Optovac, Inc. (North Brookfield, Massachusetts) supplied the CeF$_3$ crystal. It is a 1 cm$^3$ cube, polished on all six sides. The optic axis is parallel to the sides of the cube.
Appendix 1.1 Measurement of the $^{2}F_{5/2} (\Gamma_6) \rightarrow 5d (\Gamma_7)$ Absorption Spectrum in Ce$^{3+}$:LuPO$_4$

Figure 1.12 shows the experimental apparatus used to measure the absorption spectrum of the lowest 5d band from the ground state ($^{2}F_{5/2} (\Gamma_6) 0 \text{ cm}^{-1}$). In order to measure the lowest 5d band, a 60 W D$_2$ lamp illuminated the sample and the transmitted light was directed into a SPEX 1403 double monochromator which operated in second order. (The SPEX 1403 cannot scan beyond 31000 cm$^{-1}$ in first order.) A Corning 7–54 filter (which passes the near ultraviolet, but cuts off red) prevented the first order red emission from the lamp from overlapping the second order ultraviolet signal. The sample was masked so that all light had to pass through 1.1 mm of crystal. The crystal was cooled to $\sim$ 10 K in Janis Supertran cyrostat. A cooled Hamamatsu 943–02 photomultiplier tube detected the transmitted light. A personal computer recorded the output from the photon counting electronics, and controlled the frequency scanning of the monochromator. The transmission spectra of an undoped LuPO$_4$ crystal was used to obtain a background spectrum and was used to subtract out the instrumental response. The intensity of light as a function of wave number yielded the absorption spectrum of the first 5d band as shown in Figure 1.9. The instrumental resolution was about 2 cm$^{-1}$.

The x and z polarized spectra were nearly identical in both line shape and intensity. The only asymmetry in the spectra is at the peak in the vibronic sideband at $\sim$ 305 cm$^{-1}$ above the zero-phonon line [23].

Figure 1.9 shows small peaks to the left of the zero-phonon line. At higher resolution, the spectrum showed that these peaks have counterparts to the right of the zero phonon line, with which they form symmetric pairs about the zero phonon line. Thus, the (lower energy) peaks on the left are assigned to absorption from populated vibrational levels of the ground electronic state. The mechanism for population may be from the 5d $\rightarrow$
4f fluorescence excited by the D$_2$ lamp or from the radiation of the D$_2$ lamp heating the crystal. [No absorption losses were seen in the CARS signal when the CARS output frequency matched these peaks. Since the CARS process does not change the quantum state of the system, there is no mechanism by which the vibrational levels may be populated.]

Appendix 1.2 Measurement of the 5d→4f Radiative Lifetime in Ce$^{3+}$:LuPO$_4$

A pulsed laser ($\Delta t = 5$ ns), a fast photomultiplier tube (time resolution < 2 ns) and a 500 MHz oscilloscope allowed measurement of the 20 ns lifetime of the lowest 5d level in Ce$^{3+}$:LuPO$_4$.

Figure 1.13 shows schematically the setup used to measure the lifetime of the lowest 5d state. The output of a Q-switched Nd:YAG laser is doubled and used to pump a pulsed dye laser. The dye medium is DCM and the dye laser produces tunable radiation in the 15000 cm$^{-1}$ to 16000 cm$^{-1}$ range. The output of the dye laser is frequency doubled in a KD*P crystal to produce tunable radiation in the near ultraviolet. The 5d band is pumped above the zero-phonon line and the system non-radiatively decays to the lowest vibrational state of the excited electronic states as shown in Figure 1.5. A portion of the 5d→4f emission is focused on the slits of the double monochromator. The monochromator was set to the frequency of the 5d → $^2F_{5/2}$ emission band, and the signal from the RCA 1P28A photomultiplier tube was recorded on a Tektronix 11302 analog oscilloscope with a 500 MHz Tektronix 11A71 amplifier. A digitizing camera (Tektronix DCS–01) recorded the fluorescence output from each laser shot. Figure 1.14 shows the averaged signal from 100 laser shots. Also shown is the exciting laser pulse in the time domain. The fluorescence-
decay is fit to an exponential curve giving a lifetime of 20 ns. The accuracy of this measurement is about ± 1 ns.

The crystal was held in a cryostat at ~ 10 K. Measurements of the fluorescence lifetime did not change at room temperature.

At ~ 10 K, $5d \rightarrow 4f$ stimulated emission originating from the 30460 cm$^{-1}$ zero-phonon line was observed. As the pump energy reached a threshold (~ 100 µJ/pulse), the $5d(\Gamma_7) \rightarrow ^2F_{7/2}(\Gamma_6, 2179 \text{ cm}^{-1})$ transition (at 28281 cm$^{-1}$) suddenly increased greatly in intensity, and no longer showed a 20 ns exponential decay, but was a 5 ns pulse just as the exciting laser pulse. The stimulated emission was highly directional in the direction of the input pulse. The stimulated emission could be collimated, separated from the pump pulse by a quartz prism, and projected on a fluorescent screen. At higher pump intensities, the glow on the fluorescent screen resulting from the stimulated emission was visible to the naked eye. The energy of the stimulate emission was estimated to be about 0.1% of the pump pulse. The stimulated emission at 28281 cm$^{-1}$ was polarized parallel to the z axis. At a higher threshold, x polarized stimulated emission was observed on the $5d(\Gamma_7) \rightarrow ^2F_{7/2}(\Gamma_7, 2220 \text{ cm}^{-1})$ transition at 28240 cm$^{-1}$. No attempt was made to enclose the sample in a laser cavity (with the exception of the natural faces of the crystal). For the purposes of this section (lifetime measurement), stimulated emission is a parasitic effect.

Some interest has been focused upon the possibility of lasers based on $4f^{(n-1)}5d^1 \rightarrow 4f^n$ transitions in trivalent rare earth crystals. These transitions are broad band, and might lead to tunable ultraviolet solid state lasers. Stimulated emission and/or laser action has been observed in Ce$^{3+}$:LiYF$_4$ at 326 nm [44, 45], Ce$^{3+}$:LaF$_3$ at 286 nm [38] and Nd$^{3+}$:LaF$_3$ at 172 nm [46]. Other Ce$^{3+}$ systems do not show stimulated emission due to excited state absorption (Ce$^{3+}$:YAG [47]), or the production of photochromic centers by the ultraviolet pump (Ce$^{3+}$:CaF$_2$ [48]). Thus, Ce$^{3+}$:LuPO$_4$ is the third cerium system to exhibit
5d → 4f stimulated emission. A more quantitative investigation is needed to determine the suitability of Ce$^{3+}$:LuPO$_4$ as a (room temperature) solid state laser material.
TABLE 1.1. Energy levels of the Ce$^{3+}$ free ion. From Ref [1].

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<th>term symbol</th>
<th>energy (cm$^{-1}$)</th>
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TABLE 1.2. Energy levels for Ce$^{3+}$:LuPO$_4$. All levels are labeled by the irreducible representations of the double group of $D_{2d}$. Energy values for the 5$d$ levels refer to the zero-phonon lines. From Williams [23, 25] unless otherwise noted. Notes: (a) Measured by two-photon absorption (Chapter 3), disagrees with Williams' value of 39930 cm$^{-1}$. (b) Measured by two-photon absorption, agrees with Williams' value. (c) Williams' value is 2221 cm$^{-1}$.

<table>
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<th>configuration</th>
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</tbody>
</table>
TABLE 1.3. Energy levels of Ce$^{3+}$ in CeF$_3$. All levels have the same symmetry label. Energy levels of the 5d configuration refer to the peaks of the absorption bands. Absorption for the lowest 5d band begins at $\sim$ 35000 cm$^{-1}$. Energy levels for the 5d configuration are from Ref. [28], and the 4f from Ref. [34]. Note: (a) The states of the $^{2}F_{5/2}$ manifold are coupled to the near-resonant optical phonons, giving very broad vibronic states.
FIGURE 1.1. The energy levels of the lowest states of the first excited configurations (4f(^{n-1})5d^1) of the trivalent rare earth ions. From the data of Ref. [49].

FIGURE 1.2. Radial distribution for the 4f, 5s, 5p and 5d orbitals of the Ce^{3+} free ion (From a Hartree-Fock calculation [50].) \( P_{nl}(r) = r^2 \langle r | nl \rangle^2 \)
FIGURE 1.3. Schematic diagram illustrating the spin-orbit and Stark splitting of a 4f electron. The irreducible representations of the double group of the crystal field label each Stark component.
FIGURE 1.4. Locations of the 5d crystal field levels of the Ce$^{3+}$ ion in several different crystal matrices. Only four of the five 5d levels are observed below the band gap of $Y_3Al_5O_{12}$ which begins at $\sim$ 50000 cm$^{-1}$. References: LuPO$_4$ [23, 25]; LaF$_3$ [38]; $Y_3Al_5O_{12}$ [7]; YAIO$_3$ [51]; BaY$_2$F$_8$ [52].
FIGURE 1.5. Configurational coordinate model which shows vibronic energies with respect to a single normal coordinate. At right are the absorption and emission spectra at $T = 0$ K.

\[
\begin{align*}
W_{a \rightarrow b} &= W(T = 0) n \\
W_{b \rightarrow a} &= W(T = 0) (n + 1)
\end{align*}
\]

FIGURE 1.6. Model illustrating dephasing in a two level system. For simplicity, both states are degenerate. $n = $ phonon occupancy number.
\[ (2S' + 1)L' \}
\[ T \approx 10^{-9} - 10^{-12} \text{ s} \]
\[ T \approx 10^{-3} - 10^{-6} \text{ s} \]

(metastable)

\[ (2S + 1)L_j \}
\[ \approx 100 \text{ cm}^{-1} \]

FIGURE 1.7. Generic 4f levels of a rare earth ion in a crystal at low temperature. Dashed lines represent non-radiative decay (spontaneous phonon emission). (After Ref. [13].)
FIGURE 1.8. Model illustrating $D_{2d}$ symmetry at the site of the Lu$^{3+}$ ion in LuPO$_4$. The Lu$^{3+}$ ion is at the center of the model, and the circles represent the oxygen ions of the phosphate complexes. The z-axis is parallel to the LuPO$_4$ crystal axis. The local axes ($x', y', z$) are transformed to the macroscopic crystal axes ($x, y, z$) by a 45° rotation in the xy plane.
FIGURE 1.9. Low temperature absorption spectrum of the lowest 5d level in Ce$^{3+}$:LuPO$_4$. The small peaks to the left of the zero-phonon line (ZPL) are due to absorption from excited vibrational states.
FIGURE 1.10. Partial view of the CeF$_3$ structure. Only the Ce$^{3+}$ ions are shown. The smaller circles indicate depth. Each Ce$^{3+}$ ion is surrounded by F$^-$ ions in such a way that there is a $C_2$ symmetry axis perpendicular to the $C_3$ axis. (a) Looking down the $C_3$ crystal axis. White ions are on the top layer, grey on the bottom. (b) View from the side.
FIGURE 1.11. Indices of refraction for birefringent CeF$_3$. From a Sellmeier equation fit to the data of Ref. [39]. These data are used for the phase matching calculations of Chapter 4.
FIGURE 1.12. Schematic diagram of the $4f \rightarrow 5d$ absorption measurement apparatus.
FIGURE 1.13. Schematic diagram of the 5d lifetime measurement apparatus.
FIGURE 1.14. Intensity of $5d \rightarrow 4f$ fluorescence as a function of time. Also shown are the temporal profile of the exciting laser pulse and a convolution of the laser pulse with a 20 ns decaying exponential function.
Chapter Two

Doubly Resonant Coherent Anti-Stokes Raman Spectroscopy of Ce$^{3+}$ in LuPO$_4$

This chapter describes a doubly resonant four-wave mixing experiment in a dilute rare earth doped crystal – Ce$^{3+}$ in LuPO$_4$.

I measured coherent anti-Stokes Raman spectra between Stark components of the $^2F_{5/2}$ and $^2F_{7/2}$ manifolds of the Ce$^{3+}$ ion diluted in LuPO$_4$. The anti-Stokes signal is nearly resonant with the lowest level of the $5d$ configuration at 30460 cm$^{-1}$. (See Figure 2.1.) For a LuPO$_4$ crystal doped with 0.06 mol % Ce$^{3+}$, enhancements of the third order susceptibility $|\chi^{(3)R}/\chi^{(3)WR}|$ are as high as 15. This enhancement is over 30 times larger than seen previously in singly resonant experiments in pure rare earth crystals which contain 2000 times as many rare earth ions per unit volume.

The reader is invited to review section 1.5 which specifies the optical properties of Ce$^{3+}$:LuPO$_4$. This chapter is organized as follows:

Section 2.1 introduces nonlinear optical wave mixing processes in general, and coherent anti-Stokes Raman spectroscopy (CARS) in particular. Although a physically
distinct process, CARS is related to spontaneous Raman scattering. Section 2.2 discusses spontaneous Raman scattering involving the electronic states of rare earth ions in crystals. Section 2.3 contains estimates for the magnitudes of electronic CARS processes in rare earth crystals based upon spontaneous electronic Raman scattering cross sections. A brief examination of CARS selection rules may be found in section 2.4. The experimental apparatus and procedure used to measure CARS resonances are given section 2.5. Section 2.6 presents the experimental results. Finally, section 2.7 contains a discussion and analysis of the experimental results.

2.1 Wave Mixing Spectroscopy

2.1.1 Optical Wave Mixing

Wave mixing involves the interaction of one or more modes of an electromagnetic field within a material which possesses optical properties which vary with the strength of the electromagnetic field. In the linear optical approximation, one plane wave with a definite polarization, wavevector, and frequency will propagate freely and independently of another distinct plane wave which may differ in polarization, wavevector, or frequency. (Any arbitrary electromagnetic wave may be decomposed into a linear superposition of plane waves.) The fact that the dielectric constant is not a linear function of the electric field intensity will couple the Maxwell equations for the individual plane waves. Hence one can no longer speak of truly distinct plane waves. Now the behaviors of all waves are tied to each other. Where waves overlap in time and space they will influence the behavior of each other. Even a single plane wave may interact with itself.

The polarization of a medium depends on the applied field as:
\[ P = \chi^{(1)} \cdot E + \tilde{\chi}^{(2)} : E \cdot E + \dot{\chi}^{(3)} : E \cdot E \cdot E + \ldots \] (2.1)

The first term in the above equation is the usual linear electronic susceptibility \( \chi = (1 + 4\pi \chi^{(1)}) \). The real part is related to the linear index of refraction, and the imaginary part corresponds to the linear absorption coefficient. The quantity \( \chi^{(1)} \) is dimensionless and typical values in transparent condensed matter are in the \( 10^{-1} \) range. The second order susceptibility, \( \chi^{(2)} \), is responsible for such phenomena as second harmonic generation, and in a commercial nonlinear crystal such as KD\(^2\)P (K\(_2\)D\(_2\)PO\(_4\)), \( \chi^{(2)} \) has a magnitude of \( \sim 10^{-8} \) esu. The third term is responsible for effects such as the nonlinear index of refraction (optical Kerr effect), two-photon absorption and four-wave mixing. In transparent solids, \( \chi^{(3)} \) is on the order of \( 10^{-14} \) esu [53]. Nonlinear effects become important when the electric field is sufficiently intense or when lightwaves are allowed to interact coherently over long distances. A pulsed laser (\( \Delta t = 10 \) ns) with an energy of 1 mJ per pulse focused on a 100 \( \mu \)m diameter spot produces an electric field of \( |E| = 3 \times 10^3 \) esu (= 10\(^7\) V/m). With this intensity the second and third order induced polarizations, while still not as large as the first order polarization, are now large enough to produce measurable effects.

This chapter reports on experiments which involve the interaction of three light waves which produce a nonlinear polarization at optical frequencies via the third order susceptibility. Under the right circumstances, this induced polarization may generate a fourth lightwave. This process is called four-wave mixing. This process may be explained by applying the Maxwell equations to a medium with a third order nonlinear polarization. The reader is directed to books by Shen [54], and Levenson and Kano [55] for a more in depth discussion of wave propagation in nonlinear media.

In general, a closed form solution of the coupled wave equations in a nonlinear medium is not possible. Some approximations are necessary to demonstrate wave mixing.
The first approximation is treating all interacting waves as plane waves. One begins by assuming that one or more input waves induce a nonlinear polarization according to equation (2.1). Generally, the nonlinear polarization is a traveling wave with frequency $\omega_p$ and wave vector $k_p$:

$$P^{NL}(r, t) = \frac{1}{2} P^{NL}(r, \omega_p) e^{i(k_p \cdot r - \omega_p t)} + c. c. \tag{2.2}$$

The next approximation is that of negligible pump depletion. The intensity of the generated wave is small compared to the input waves, and energy transfer between the pump waves and generated wave may be neglected. In this case, the input waves propagate without interference, and the amplitude of the induced polarization is constant throughout the medium. ($P^{NL}(r, \omega_p) = P^{NL}(\omega_p)$) The behavior of the generated signal wave, $E_s$, may be described by the wave equation with the nonlinear polarization as a source term:

$$\nabla \times \nabla \times E_s(r, t) + \frac{n^2(\omega_s)}{c^2} \frac{\partial^2}{\partial t^2} E_s(r, t) = -\frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} P^{NL}(r, t) \tag{2.3}$$

The frequency of the generated wave is that of the induced polarization ($\omega_s = \omega_p$). The $z$ direction may be chosen to lie in the direction of the generated wave such that

$$E_s(r, t) = \frac{1}{2} E_s(z) e^{i(k_z z - \omega_s t)} + c. c. \tag{2.4}$$

Then equation (2.3) may be written as

$$\frac{\partial^2}{\partial z^2} E_s(z) e^{i k_z z} + \frac{n^2(\omega_p) \omega_p^2}{c^2} E_s(z) e^{i k_z z} = -\frac{4\pi \omega_p^2}{c^2} P^{NL}(\omega_p) e^{i k_p \cdot z} \tag{2.5}$$

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The next simplification is the slowly varying amplitude approximation, in which one assumes that \( E_s(z) \) does not change much over distances on the scale of a wavelength. This is equivalent to the inequality

\[
\left| \frac{\partial^2}{\partial z^2} E_s(z) \right| \ll \left| \frac{1}{k_s} \frac{\partial}{\partial z} E_s(z) \right|
\]  

(2.6)

Now equation (2.5) is transformed into an easily solved first order differential equation:

\[
\frac{\partial}{\partial z} E_s(z) = \frac{2\pi i \omega_p}{n(\omega_p) c} P^{NL}(\omega_p) e^{i\Delta k \cdot z}
\]

(2.7)

where \( \Delta k = k_p - k_s \). Integration of the above equation with the boundary condition \( E_s(z = 0) = 0 \) gives

\[
E_s(z) = \frac{2\pi i \omega_p}{n(\omega_p) c} P^{NL}(\omega_p) \frac{\sin(\Delta k \cdot z / 2)}{\Delta k \cdot z / 2}
\]

(2.8)

The above equation indicates that \(|E_s|\) is a maximum when \( \Delta k = 0 \) and falls to zero when \( \Delta k \cdot z = 2\pi \). The requirement that \( \Delta k = 0 \) is called phase matching. As will be discussed in the next section, phase matching often presents the greatest experimental challenge in wave mixing. Physically, phase matching insures that the electric field generated throughout the nonlinear medium adds coherently to the signal wave. If phase matching is not achieved, the generated wave can interfere destructively with itself and the signal may be low. Assuming phase matching, the intensity of the output wave after it has traversed a distance \( l \) in the nonlinear medium is
Again note that the above equation is valid only in the small signal regime, since the signal intensity cannot exceed the intensity of the input lightwaves as \( I \rightarrow \infty \). The above description illustrates how an induced polarization at optical frequencies may generate a new lightwave. No mention has been given to the relationship between the induced polarization and the input lightwaves. This point is considered in the next section.

### 2.1.2 Coherent Anti-Stokes Raman Spectroscopy (CARS)

The above section has shown how wave mixing in a nonlinear medium can generate a signal wave from the nonlinear polarization generated from one or more input waves. When the generated wave is derived from a third-order nonlinear polarization, the process is called *four-wave mixing*. Coherent anti-Stokes Raman spectroscopy (CARS) is one form of four-wave mixing. (The origin of the name will follow.) In CARS, two input lightwaves at frequencies \( \omega_1 \) and \( \omega_2 \) generate a third order polarization at frequency \( \omega_3 = 2\omega_1 - \omega_2 \) via the third order susceptibility tensor:

\[
P_i^{(3)}(\omega_3) e^{-i\omega_3 t} = 3 \chi_{ijk}^{(3)} (-\omega_3, \omega_1, \omega_1, -\omega_2) \times E_j(\omega_1)E_j(\omega_1)E_k^*(\omega_2) e^{-i(2\omega_1 - \omega_2)t}
\]  

(2.10)

In the Maker-Terhune notation [56], the frequency arguments of \( \chi^{(3)} \) add to zero and the factor of three in the equation results from the permutation degeneracy of the input frequencies. Figure 2.2 shows schematic diagrams of the CARS process in the frequency and spatial domains. Only if the index of refraction is independent of frequency, can
phase matching be satisfied by collinear beams. That is, \( \omega_3 = 2\omega_1 - \omega_2 \) implies that \( |k_3| = 2|k_1| - |k_2| \). Generally, the index of refraction is dispersive, and the phase matching condition is satisfied when the input beams cross at an angle \( \theta \). (See Figure 2.2(c).)

Thus far I have focused on the fact that wave mixing produces new lightwaves at new frequencies. The most common application of wave mixing is second harmonic generation in which light may be frequency doubled by wave mixing in a medium with a non-zero \( \chi^{(2)} \).

Four-wave mixing may be used as a spectroscopic tool when the intensity of the signal wave is dependent on the frequencies of the input lightwaves. According to equations (2.9) and (2.10)

\[
I_3 \propto \omega_3^2 |\chi^{(3)}|^2 I_1^2 I_2
\]

where \( I_n \) is the intensity of the \( n \)th lightwave. Note that the intensity of the signal, \( I_3 \), varies linearly with the intensity of \( \omega_2 \) and quadratically with the intensity of \( \omega_1 \). A measurement of \( I_3 \) as a function of \( \omega_1 \) and \( \omega_2 \) yields the frequency dependence of the quantity \( |\chi_{ijk}^{(3)}(-\omega_3, \omega_1, \omega_1, -\omega_2)|^2 \). This quantity may contain useful spectroscopic information.

Both the linear and nonlinear susceptibilities are characteristic properties of a material, and may be calculated from quantum mechanical principles. The macroscopic polarization of a material is

\[
\langle P \rangle = N \langle \mu \rangle = -Ne \langle r \rangle
\]

where \( N \) is the number density of constituents (atoms, ions, molecules, etc.) of the material, and \( \mu \) is the dipole moment of each constituent. The brackets indicate that the
ensemble average of the dipole moment is used. The density matrix, $\rho$, is used to calculate the ensemble average \[57\]:

\[ \langle P \rangle = \text{Tr}(\rho P) \quad (2.13) \]

The Liouville equation governs the behavior of the density matrix.

\[ \frac{\partial \rho}{\partial t} = \frac{1}{i\hbar} [H, \rho] \quad (2.14) \]

where

\[ H = H_0 + e \mathbf{r} \cdot \mathbf{E} + H_{\text{relax}} \quad (2.15) \]

$H_0$ is the Hamiltonian for the material, $e \mathbf{r} \cdot \mathbf{E}$ describes the interaction of light and matter in the electric dipole approximation, and $H_{\text{relax}}$ is a phenomenological Hamiltonian added to account for relaxation effects (e.g. lifetime broadening).

Typically, $\rho$ is expanded in a power series in the electric field, and (2.14) is solved by successive perturbations \[54\]. $\langle P \rangle$ is derived from equation (2.13).

\[ \chi_{ijkl}^{(3)}(-\omega, \omega_a, \omega_b, -\omega_c) = \frac{\langle P_i \rangle}{D \ E_j(\omega_a)E_k(\omega_b)E_l(\omega_c)} \quad (2.16) \]

where $D$ is the Maker-Terhune degeneracy factor. The full expression for $\chi_{ijkl}^{(3)}$ has 48 terms.

For a particular wave mixing experiment, the 48 terms may be divided into two parts. The nonresonant part, $\chi_{ijkl}^{(3)NR}$, has negligible frequency dependence, while the resonant part, $\chi_{ijkl}^{(3)R}$, varies considerably over the frequency domain of the experiment.
The resonant third order susceptibility tensor governing singly resonant CARS (shown schematically in Figure 2.3(a)) is [54, 58]

\[
\chi^{(3)}_{ijkl}(-\omega_3, \omega_1, \omega_1, -\omega_2) = \frac{-N\Lambda}{12\hbar} \sum_f \frac{\alpha_{ij}(\omega_3, \omega_1)\alpha_{kl}(\omega_1, \omega_2)}{(\omega_1 - \omega_2 - \omega_{gf} - i\Gamma_{gf})} \tag{2.17}
\]

where

\[
\alpha_{uv}(\omega_x, \omega_y) = \frac{1}{\hbar} \sum_n \left[ \frac{\langle g \mid e_{x_n} \mid n \rangle \langle n \mid e_{y_f} \mid f \rangle}{(\omega_x - \omega_{gn})} - \frac{\langle g \mid e_{y_n} \mid n \rangle \langle n \mid e_{x_f} \mid f \rangle}{(\omega_y + \omega_{gn})} \right] \tag{2.18}
\]

is the usual (non-resonant) Raman tensor. The indices \(i, j, k\) and \(l\) denote the polarizations of the \(\omega_3, \omega_1, \omega_1,\) and \(\omega_2\) beams respectively. The kets \(|g\rangle, |f\rangle,\) and \(|n\rangle\) correspond to the ground, low lying, and intermediate states with energies zero, \(\hbar\omega_{gf},\) and \(\hbar\omega_{gn}.\) The number density of scatterers is \(N,\) and \(\Gamma_{gf}\) is the Lorentzian linewidth (HWHM) of the \(|g\rangle \rightarrow |f\rangle\) transition. The term \(\Lambda = ((n^2 + 2)/3)^4,\) where \(n\) is the refractive index, contains the local field corrections.

Note that \(\chi^{(3)}_{ijkl}\) varies rapidly in both magnitude and phase as \(\omega_1 - \omega_2\) is scanned through \(\omega_{gf}.\) The other terms vary only slightly with changing \(\omega_1 - \omega_2,\) and are collected into \(\chi^{(3)WR}_{ijkl},\) which is treated as a (real) constant.

The fact that the matrix element for this wave mixing process is related to the spontaneous Raman tensor is responsible for the name of this process – Coherent Anti-Stokes Raman Spectroscopy (CARS). Anti-Stokes comes from the right two arrows in Figure 2.2(a) which look like a diagram for spontaneous anti-Stokes Raman scattering. It is important to emphasize at this point that CARS and spontaneous Raman scattering are physically distinct processes. As a form of wave mixing, CARS may be understood in
terms of classical electromagnetic waves. Spontaneous Raman scattering may be explained only within the framework of a quantized electromagnetic field [59].

The intensity of the CARS signal, \( I_3 \), at \( \omega_3 = 2\omega_1 - \omega_2 \) is proportional to the square of the induced polarization (equation (2.9)), which is proportional to the total third order susceptibility tensor (equation (2.10)).

\[
I_3 = |\chi^{(3)R} + \chi^{(3)NR}|^2
\] (2.19)

where for simplicity, the tensor indices are suppressed. In addition, the factor \( \omega_3^2 \) in equation (2.9) may be treated as a constant since \( \omega_3^2 \) does not change much over a typical CARS scan. If one considers only a single low lying level, \( |f\rangle \), and notes that the Raman tensors are essentially independent of \( \omega_1 \) and \( \omega_2 \) as \( (\omega_1 - \omega_2) \) is swept through \( \omega_{gf} \), one may write equation (2.17) as

\[
\frac{\chi^{(3)R}}{\chi^{(3)NR}} = \frac{-A}{\delta - i\Gamma}
\] (2.20)

where \( A \) is a constant, and \( \delta = \omega_1 - \omega_2 - \omega_{gf} \). The intensity of the CARS signal normalized to the off-resonance intensity is

\[
\frac{I_3}{I^{NR}_3} = \frac{|\chi^{(3)R} + \chi^{(3)NR}|^2}{|\chi^{(3)NR}|^2} = 1 - \frac{2A\delta}{\delta^2 + \Gamma^2} + \frac{A^2}{\delta^2 + \Gamma^2}
\] (2.21)

Figure 2.4 shows each term in the above equation. At \( \delta = 0 \), \( |\chi^{(3)R}/\chi^{(3)NR}| \) reaches a maximum value of \( A/\Gamma \). One sees that as \( A/\Gamma \rightarrow 0 \), the first term dominates and the CARS signal is constant and frequency independent. In order to observe the resonance against the background, the quantity \( C = |\chi^{(3)R}/\chi^{(3)NR}|_{\text{max}} = A/\Gamma \) should be greater than the
experimental noise to signal ratio. *One may consider the quantity C to be a figure of merit for CARS experiments.* Systems with larger values of C yield better information. Figure 2.5 shows the CARS signal in a system with C = 0.05. Here the weak resonance may be unobservable if the background signal is noisy. Figure 2.6 shows the calculated CARS spectrum for the 992 cm\(^{-1}\) vibrational mode in benzene (C = 18.8). Here the resonance peak is about 350 times as intense as the non-resonant background. The dynamic range (\(I_{\text{max}}/I_{\text{min}}\)) of the signal is about \(10^5\). This large dynamic range is one of the most appealing aspects of CARS experiments.

As discussed above, the CARS susceptibility is related the spontaneous Raman tensor. According to equations (2.17) and (2.18), when the laser frequencies are far below the intermediate states, \(|\chi^{(3)R}|\) takes a maximum value

\[
|\chi^{(3)R}|_{\text{max}} = \frac{N\Lambda |\alpha|^2}{12\hbar\Gamma} \tag{2.22}
\]

The Raman tensor is related to the total Raman cross section, \(\sigma\), by

\[
\sigma = \frac{8\pi\Lambda \omega_s^4 |\alpha|^2}{3c^4} \tag{2.23}
\]

where \(\omega_s\) is the Stokes frequency (the frequency of the scattered light). The total Raman cross section is proportional to the differential Raman cross section:

\[
\sigma = \frac{8\pi}{3} \frac{d\sigma}{d\Omega} \quad (\theta = 90^\circ) \tag{2.24}
\]

The above equations allow a knowledge of the spontaneous Raman cross section, the linewidth and the magnitude of \(\chi^{(3)WR}\) to predict the CARS figure of merit, C. Conversely,
if $A$ and $\Gamma$ are measured in a CARS experiment, and $\chi^{(3)WR}$ is known, the spontaneous Raman cross section may be determined. This is done in Chapter 4.

Since the size of the CARS resonance is related to the spontaneous Raman cross section, the next section deals with spontaneous Raman scattering involving electronic states of rare earth ions in crystals.

An historical note: Maker and Terhune [56] performed the first four-wave mixing experiment in which lasers at frequencies $\omega_1$ and $\omega_2$ produced light at $2\omega_1 - \omega_2$. Wynne [60] first demonstrated that this process could be used as a spectroscopic tool when the four-wave mixing signal is measured as a function of $(\omega_1 - \omega_2)$. In rare earth crystals, there have been many degenerate wave mixing experiments, but relatively few experimenters have reported wave mixing with lasers of two or more colors. The work of Shand [61] and Traar [62] involved singly resonant CARS in pure rare earth crystals and will be discussed in section 2.3.1. Cone and co-workers have measured multiresonant two-photon absorption induced four-wave mixing in Tb(OH)$_3$, LiTbF$_4$, and TbF$_3$ crystals [63–66]. Recently, Mosharay et al. observed three-level photon echoes in Pr$^{3+}$:LaF$_3$ [67].

2.2 Electronic Raman Scattering in Rare Earth Crystals

Spontaneous Raman scattering is an inelastic light scattering process. An incident photon with energy $\hbar \omega_i$ produces a scattered photon with energy $\hbar \omega_s$, and the material undergoes a change in energy of $\hbar (\omega_i - \omega_s)$. If $\omega_i > \omega_s$, then $\omega_s$ is called the Stokes frequency and the system absorbs an energy of $\hbar (\omega_i - \omega_s)$. If $\omega_s > \omega_i$, then $\omega_s$ is called the anti-Stokes frequency and the system is put into a lower energy state. (See Figure 2.7.) The excitation may be electronic, vibrational, or rotational in nature. Raman and Krishnan first discovered vibrational Raman scattering in liquid solutions in 1928 [68].
Independently, Landsberg and Mandelstamm discovered vibrational Raman scattering in transparent crystals in the same year [69].

Hougen and Singh [70] first reported Raman scattering between electronic states of rare earth ions in a crystal in 1963. Unlike electric dipole transitions between crystal field states of the ground $4f^n$ configuration, which are parity forbidden in first order, Raman transitions between states of the same electronic configuration are parity allowed. The primary use of electronic Raman scattering (ERS) has been to locate and determine the symmetry of low-lying Stark levels [71]. The main experimental problem associated with ERS in rare earth crystals is due to the magnitude of ERS cross sections which are usually much smaller than those encountered in vibrational Raman scattering. For example: the total Raman cross section of the 992 cm$^{-1}$ vibrational mode in benzene [72] is $2.7 \times 10^{-28}$ cm$^2$/molecule while electronic Raman cross sections for rare earth ions in crystals [73, 74] range from $5 \times 10^{-29}$ to $1 \times 10^{-33}$ cm$^2$/ion. Crystals with dilute concentrations of rare earth ions will have even smaller effective cross sections. If the energies of the electronic levels are close to the optical phonons of the crystal, the phonon Raman signal may overwhelm the ERS signal. In addition, electronic linewidths increase rapidly with temperature, necessitating the use of a cryogenic cooling system for the crystals.

For these reasons, coherent electronic Raman spectroscopy in rare earth crystals [61, 62] has shown only limited success unlike coherent vibrational Raman spectroscopy [75, 76]. The intensity of the signal from coherent anti-Stokes Raman spectroscopy (CARS) is proportional to the square of the third order electronic susceptibility, $|\chi^{(3)}|^2$ (equation (2.19)). The complex quantity $\chi^{(3)}$ is the sum of a non-resonant part ($\chi^{(3)NR}$) which is due to the bulk crystal, and a resonant, frequency dependent part ($\chi^{(3)R}$) which contains the spectroscopic information (equation (2.17)). Since $\chi^{(3)R}$ is roughly proportional to the spontaneous Raman cross section, one has
The resonant susceptibility for electronic CARS, $\chi_{el}^{(3)R}$, is often so small that it is obscured by $\chi^{(3)NR}$ which can be orders of magnitude larger. This is especially true for dilute rare earth crystals, since $\chi_{el}^{(3)R}$ is proportional to the number density of rare earth ions in the crystal.

Experiments [77–83] have shown that ERS cross sections in rare earth crystals can be resonantly enhanced when the frequency of the exciting laser is near the energy of an electronic level of the rare earth ion. These studies included inter- and intra-configurational resonances. In the case of intra-configurational resonant ERS, the intermediate state is within the same electronic configuration as the initial and final state, i.e., $4f^n$ for the rare earth ions. The ERS cross sections involve electric dipole matrix elements between the initial and final states to the intermediate states. Electric dipole transitions are parity forbidden in first order, but the odd components of the crystal field mix excited states of opposite parity (such as the $4f^{(n-1)}5d^1$) with the $4f^n$ crystal field states to allow relatively weak second order "forced electric dipole" transitions. Inter-configurational resonant ERS directly use excited states of opposite parity ($4f^{(n-1)}5d^1$), and the enhancement of the ERS signal is much stronger. As indicated in Chapter 1, most of these excited configurations of the trivalent rare earth ions have energies greater than 50,000 cm$^{-1}$, and are inaccessible to conventional spectroscopic sources.

Due to the small ERS cross sections, studies in very dilute crystals involve inter-configurational resonances. Keil and Scott [77] observed ERS between levels of the ground $4f 5d$ configuration of 10$^{-3}$ mol % Ce$^{2+}$ in CaF$_2$ crystals. They used a laser in resonance with the excited $4f^2$ configuration. Piehler, et al. [83] detected ERS between Stark components of the $5f$ configuration of $\sim 0.1$ mol% Pa$^{4+}$ in Cs$_2$ZrCl$_6$ crystals using a laser 525 cm$^{-1}$ below the lowest level of the $6d$ configuration. Most recently, Cone et al.
observed ERS in Tb$^{3+}$:LiYF$_4$ and LiTbF$_4$ using a laser in near resonance with the $4f^25d$ configuration of the Tb$^{3+}$ ion at about 39000 cm$^{-1}$.

Among the trivalent rare earth ions, the Ce$^{3+}$ ion with its single $4f$ electron, is not only the simplest ion to analyze, but also has the lowest energy $4f^{(n-1)}5d^1$ configuration. In Ce$^{3+}$:LuPO$_4$, the lowest crystal field level of the $5d$ configuration begins at 30460 cm$^{-1}$.

Williams et al. [23, 25] took advantage of the relatively low energy of the $5d$ configuration in a 0.6 mol% Ce$^{3+}$:LuPO$_4$ crystal and measured ERS intensities between the ground state and excited crystal field states of the $^2F_{5/2}$ and $^2F_{7/2}$ manifolds. They performed this experiment with lasers at 354.7 nm (28192 cm$^{-1}$) and 514.5 nm (19430 cm$^{-1}$). A change of laser source from 514.5 nm to 354.7 nm resulted in the enhancement of the ERS intensity by a factor an order of magnitude larger than could be accounted for by the $\omega^4$ dependence of the Raman cross section.

In the spirit of resonant ERS, this chapter reports on doubly resonant electronic CARS experiments on a 0.06 mol% Ce$^{3+}$:LuPO$_4$ crystal. Use of a frequency-tripled Nd$^{3+}$:YAG laser (28192 cm$^{-1}$) and a tunable dye laser operating in the 26000 cm$^{-1}$ range, satisfies two resonance conditions. When the difference in energy between the two lasers is equal to the energy of the lower crystal field levels of the $^2F_{7/2}$ manifold, the CARS signal will be in the the 30400 cm$^{-1}$ range, less than 100 cm$^{-1}$ below the lowest $5d$ band. (See Figure 2.1.) With this extra resonance, the resonant susceptibility is large enough to compete with $\chi^{(3)NR}$, even in a dilute crystal.
2.3 Estimating the Magnitude of Electronic CARS Resonances

In this section, the figures of merit are estimated for singly resonant electronic CARS in rare earth crystals, and doubly resonant electronic CARS in Ce$^{3+}$:LuPO$_4$.

2.3.1 Singly Resonant CARS

The size of singly resonant CARS resonances in rare earth crystals may be estimated by using equations (2.23) and (2.24), and a knowledge of the both the spontaneous Raman cross section and the non-resonant susceptibility. For a typical pure rare earth crystal at low temperature, $N = 10^{22}$ cm$^3$, $\Gamma/2\pi c = 2$ cm$^{-1}$, and the intermediate states of opposite parity lie above 50000 cm$^{-1}$. (A pure rare earth crystal is one in which the rare earth ion is a full stoichiometric component, e.g. PrF$_3$, Tb$_3$Al$_5$O$_{12}$ etc.) A typical Stokes frequency is $\omega_J/2\pi c = 20000$ cm$^{-1}$. Using the earlier cited figures for ERS cross sections (section 2.2), one finds that $|\chi^{(3)R}|_{\text{max}}$ for singly resonant electronic CARS should vary between $5 \times 10^{-14}$ esu and $5 \times 10^{-18}$ esu. For a dilute rare earth crystal such as the crystal discussed in this chapter, $N = 10^{19}$ cm$^3$ and $\Gamma/2\pi c = 0.2$ cm$^{-1}$. This implies that $|\chi^{(3)R}|_{\text{max}}$ will vary from $5 \times 10^{-16}$ esu to $5 \times 10^{-20}$ esu. For most transparent solids $\chi^{(3)NR} = 10^{-14}$ esu [53], and $|\chi^{(3)R}|_{\text{max}}$ will be the same order of magnitude or smaller than $\chi^{(3)NR}$. One may conclude that in singly resonant CARS, the enhancement of $\chi^{(3)}$ due to resonances between electronic states of rare earth ions will be modest at best. For dilute rare earth crystals, $C \ll 1$, and detection of singly resonant CARS will be difficult, if not impossible.

Experiments by Shand [61] and Traar [62] are consistent with this conclusion. Both selected favorable rare earth systems to obtain the highest values of $C$. Shand
measured electronic CARS resonances between Stark components of the ground $^7F_6$ manifold and the $^7F_5$ manifold of the Tb$^{3+}$ ion in Tb$_3$Al$_5$O$_{12}$ at 80 K, and found $C \leq 0.4$. Traar investigated electronic CARS resonances from the $^3H_4 \leftrightarrow ^3F_2$ transitions of Pr$^{3+}$ in PrF$_3$ at 2 K, and found $C \approx 0.5$. Figure 2.8 shows the results of their experiments. Additionally, Shand [61] reported that no CARS resonances were detected for Nd$^{3+}$ doped into several host crystals (Gd$_3$Ga$_5$O$_{12}$, Y$_3$Al$_5$O$_{12}$, and La$_2$Be$_2$O$_5$.)

### 2.3.2 Doubly Resonant CARS

For doubly resonant CARS, the resonant third order susceptibility tensor corresponding to Figure 2.3 (b) is [54]

$$
\chi^{(3)R}_{ijkl}(-\omega_3, \omega_1, \omega_1, -\omega_2) = \frac{-N\Lambda}{12\hbar^3} \sum_f \frac{1}{(\omega_1 - \omega_2 - \omega_{gf} - i\Gamma_{gf})} \times \sum_n \frac{\langle g | er \rangle \langle n | er \rangle \langle f \rangle}{(\omega_3 - \omega_n - i\Gamma_n)} \times \sum_{n'} \frac{\langle g | er \rangle \langle n' | er \rangle \langle f \rangle}{(\omega_1 - \omega_{n'} - i\Gamma_{n'})}
$$

(2.26)

In the above equation, both summations, $n$ and $n'$, are over all intermediate states. Double resonance is a route by which $\chi^{(3)R}$ may be increased to compete favorably with $\chi^{(3)NR}$. Equation (2.26) indicates that $|\chi^{(3)R}_{ijkl}|_{\text{max}}$ will increase as $\hbar\omega_3$ and $\hbar\omega_1$ approach the energies of the intermediate states, $\hbar\omega_n$ and $\hbar\omega_{n'}$. For this reason, I chose to work with a crystal containing Ce$^{3+}$ ions whose $5d$ configuration lies in the near ultraviolet. Using the 514.5 nm line of an argon ion laser (19430 cm$^{-1}$), Williams, et al. [23, 25] measured absolute values for the ERS cross sections between the ground state and the crystal field levels of the $^2F_{7/2}$ manifold. These ranged from $(0.14 \text{ to } 2.5) \times 10^{-29}$ cm$^2$/ion which are on the high end of the range of rare earth ERS cross sections. The low lying $5d$ configuration in
Ce$^{3+}$:LuPO$_4$ accounted for its large spontaneous ERS cross section. Using the methods of the section 2.3.1, I estimate that for singly resonant CARS in dilute Ce$^{3+}$:LuPO$_4$, $|\chi^{(3)}R|_{\text{max}} \approx 2.5 \times 10^{-16}$ esu.

The lowest 5d band in Ce$^{3+}$:LuPO$_4$ begins at 30460 cm$^{-1}$. (See Figure 1.9.) By using the frequency tripled output of a Nd$^{3+}$:YAG laser (28192 cm$^{-1}$) and a tunable light source in the 26000 cm$^{-1}$ region, a CARS resonance between the ground state and the lowest level of the $^2F_{7/2}$ manifold at 2179 cm$^{-1}$ produces a signal at $\omega_3/2\pi c = 30371$ cm$^{-1}$. (See Figure 2.1.) If one assumes that the lowest 5d level is most important for the Raman cross section, one can estimate the enhancement of $|\chi^{(3)}R|_{\text{max}}$ relative to its singly resonant value. (i.e. at $\omega_1/2\pi c = 19430$ cm$^{-1}$) According to Equation (2.26),

$$|\chi^{(3)}R|_{\text{max}} \approx \frac{1}{\Gamma_{gf}} \sum_n \frac{1}{(\omega_3 - \omega_{gn})} \sum_{n'} \frac{1}{(\omega_1 - \omega_{gn'})}$$

(2.27)

if $|\omega_3 - \omega_{gn}| \gg \Gamma_{gf}$. Since the entire lowest 5d band contributes, I replace the summations in the above equation by integrals weighted by the absorption data of Figure 1.9. Numerical integration gives an enhancement factor of about 97. Now $|\chi^{(3)}R|_{\text{max}}$ may be as great as $2.5 \times 10^{-14}$ esu for the dilute Ce$^{3+}$:LuPO$_4$ crystal. By going from singly to doubly resonant CARS, the figure of merit changes from $C \ll 1$ to $C \geq 1$ for a dilute rare earth crystal. This is the primary point of this chapter.

### 2.4 Selection Rules

The symmetry of the crystal field levels imposes selection rules on the electronic Raman tensors [73]. The symmetry properties of the tensor $\chi^{(3)}_{ijkl}$ are that of the product of Raman tensors $\alpha_{ij} \cdot \alpha_{kl}$. In the experiments described in this chapter, all polarizations are
parallel so that $\chi^{(3)}_{iii}^R$ is of interest. For electronic CARS resonances ($| g \rangle \leftrightarrow | f \rangle$), the following selection rules apply: (Recall that the ground state has symmetry $\Gamma_6$.)

$$\Gamma_6 \leftrightarrow \Gamma_6 \quad \chi^{(3)}_{iii}^R \text{ allowed for } i = x, y, z,$$
$$\Gamma_6 \leftrightarrow \Gamma_7 \quad \chi^{(3)}_{iii}^R \text{ allowed for } i = x, y \ (\chi^{(3)}_{zzz} = 0).$$

2.5 The Experimental Apparatus and Procedure

The experimental CARS setup is displayed schematically in Figure 2.9.

2.5.1 The Light Sources

The ultimate source of coherent radiation in this experiment is a $Q$-switched Spectra-Physics DCR–1 Nd$^{3+}$:YAG laser. The Nd$^{3+}$:YAG laser generates laser pulses which are about 10 ns in length with energies up to 0.5 J at a wavelength of 1.064 $\mu$m (9379.2 cm$^{-1}$). The laser operates at a repetition rate of 10 Hz. The pulses may be frequency doubled in a type II KD*P crystal to produce green light at 532.1 nm (18794.3 cm$^{-1}$). (KDP is an abbreviation for potassium di-hydrogen phosphate, a common nonlinear material. The star indicates that deuterium substitutes for hydrogen.) This green light may be frequency mixed in another type II KD*P crystal with the original 1.064 $\mu$m beam to generate frequency-tripled light at 355.6 nm (28191.5 cm$^{-1}$). The energy of the 10 ns 355 nm pulse may be as high as 22 mJ. The output is linearly polarized.

Individual laser shots could be measured in the time domain by digitizing the shots as they appeared on an oscilloscope screen (as in Appendix 1.2.) Figure 2.10 shows oscilloscope tracings of five individual laser shots along with the average of 100 laser
shots. The RCA 1P28A photomultiplier tube (PMT) has a listed time response of < 2 ns. The PMT produces electronic pulses which were viewed on a Tektronix 11302 analog oscilloscope with a 11A71 plug-in amplifier. The frequency response of the oscilloscope-amplifier combination is 500 MHz (2 ns). Therefore, the time resolution in Figure 2.10 is between 2 and 3 ns. The temporal shape of the individual pulses vary greatly, but the average pulse length (defined as the FWHM of the averaged pulse envelope) is about 10 ns. Rankin et al. [85] have studied the 355 nm output from a Q-switched Nd³⁺:YAG laser with a streak camera with 40 ps resolution. The results show a complex temporal structure not detectable on a nanosecond scale. The output consists of irregular bursts of pulses with widths of 100 to 700 ps.

Measurement of the emission lines from a low pressure Hg lamp showed that the bandwidth of SPEX 1403 double monochromator was about 0.25 cm⁻¹ when the entrance and exit slits were opened to 10 μm and the intermediate slits were open to 20 μm. The line profile is approximately gaussian with a FWHM bandwidth of 0.8 ± 0.1 cm⁻¹ (24±3 GHz). Immediately evident is the fact that the pulses are not fourier transform limited. A cursory inspection shows that Δω_laser Δt_laser = 2000.

The fundamental, doubled, and tripled laser output are more or less collinear after passing through the KD²P crystals. This beam passes through a series of dispersing prisms which separate the frequencies. The 1.06 μm and 532 nm beams head toward a beam dump while the 355 nm beam is saved for further use. The beam from the prism harmonic separator passes through a quartz plate as shown in figure 2.9. About 8% of the beam is picked off at a right angle while the rest of the beam pumps a Spectra-Physics PDL-1 dye laser. This laser operates with Quinolon 390 laser dye to provide a source of radiation continuously tunable from 382–396 nm (~26200 to 25250 cm⁻¹). The dye laser oscillator is of the Littman design where a grating in the seventh order is used as the tuning element. As with the Nd³⁺:YAG laser, the pulsed dye laser is multimode. The average
pulse length is 5 ns and the linewidth is \(0.6 \pm 0.1\) cm\(^{-1}\). When operated at full power (with both pre-amplifier and amplifier operational) the pulsed dye laser is capable of producing 500 \(\mu\)J pulses at 384 nm (=26000 cm\(^{-1}\)).

### 2.5.2 The CARS Setup

The polarizations of both \(\omega_1\) and \(\omega_2\) were parallel. An optical delay line insured that the pulses from both the Nd\(^{3+}\):YAG laser and the dye laser overlapped in time at the sample. A 25 cm focal length lens focused both beams onto a 100 \(\mu\)m spot on the sample. The sample size was about \(1 \times 2 \times 5\) mm with the laser light passing through about 1 mm of material. The crystal was mounted in a Janis liquid helium Supertran Cryostat, and cooled to about 10 K. The sample could be oriented such that the \(z\)-axis was either parallel or perpendicular to the polarization of the input beams \(\omega_1\) and \(\omega_2\). This facilitated measurement of \(|\chi^{(3)}_{zzzz}|^2\) and \(|\chi^{(3)}_{xxxx}|^2\). Since the crystal is uniaxial \(\chi^{(3)}_{xxxx} = \chi^{(3)}_{yyyy}\). The energy per pulse was 200 \(\mu\)J for each beam.

The prism which directs \(\omega_2\) into the 25 cm lens was mounted on a translation stage in order to adjust the phase matching angle. Optimal signal was detected when the angle between \(\omega_1\) and \(\omega_2\) was 48 mrad outside of the crystal. At this angle phase matching was satisfied for \((\omega_1 - \omega_2)/2\pi c = 2000\) to 2400 cm\(^{-1}\).

A SPEX 1403 double monochromator analyzed the CARS signal at \(\omega_3 = 2\omega_1 - \omega_2\), and an RCA 1P28A photomultiplier tube detected the signal. The slits on the monochromator were opened such that bandwidth was about 10 cm\(^{-1}\). In addition, a biased silicon photodiode (EG&G SCG-100A) detected attenuated light from beam \(\omega_2\). A pair of Stanford Research Systems SR250 boxcar integrators measured the pulses from both the photomultiplier and the photodiode.
A IBM–PC clone personal computer collected individual measurements of the CARS signal, normalized this signal to \( \omega_2 \) for each laser shot, and averaged these values over 75 laser shots. After collecting each set of data, the computer scanned the dye laser to a new value of \( \omega_2 \) and adjusted the monochromator to maintain the relationship 
\[
\omega_{\text{MONOCHROMATOR}} = 2\omega_1 - \omega_2.
\]
The data were saved on floppy disks and transferred to Macintosh IIx computer for analysis.

### 2.5.3 Noise

For any experiment, one would prefer to have a signal to noise ratio that is as great as possible. In this experiment, the overwhelming cause of noise in the data is the laser source. The Nd\(^{3+}\):YAG laser operated on more than one longitudinal mode. This affects both the temporal and frequency characteristics of the laser pulse [86]. Figure 2.10 shows that the output from the Nd\(^{3+}\):YAG laser varies both in energy and pulse shape from shot to shot. The complex temporal structure of the laser pulses \( \omega_1 \) and \( \omega_2 \) are uncorrelated, and vary randomly from pulse to pulse. The CARS signal for a given pulse is proportional to the integral of \( I^2(\omega_1, t) \times I(\omega_2, t) \) over time. In other words, the main source of noise is the fact that the random spiking in both pulses causes the temporal overlap of the two pulses to vary wildly from shot to shot. The normalization procedure cannot account for the random variation in the signal since the signal is normalized to the time integrated intensity of \( I(\omega_2, t) \) over each shot. In fact, the shot to shot normalization does not improve the signal to noise ratio much. Normalization does, however, account for the variation in the gain of the dye laser over the spectral range of the experiment. Averaging the signal over a large number (\( \sim 75 \)) of laser shots helps to improve the signal to noise ratio.
2.6 The Data

I measured enhancements in the third order susceptibility due to electronic transitions between the ground \( \Gamma_6 \) state and the two lower levels of the \( ^2F_{7/2} \) manifold at 2179 cm\(^{-1}\) (\( \Gamma_6 \)) and 2220 cm\(^{-1}\) (\( \Gamma_7 \)). I did not observe the two upper levels of the \( ^2F_{7/2} \) manifold because the CARS signals from these two levels are within the 5\( d \) absorption band. Figures 2.11 and 2.12 show the intensities of the signals normalized to the off resonance intensities as a function of frequency and polarization. As expected from the selection rules, I observed no resonance between the \( \Gamma_6 \) ground state and the \( \Gamma_7 \) level at 2220 cm\(^{-1}\) in the \( z \) polarization.

2.7 Analysis

2.7.1 Calculation of \( \chi^{(3)R} \)

In order to fit the observed spectra, the form of \( \chi^{(3)R} \) as a function of \( \omega_1, \omega_2 \) and \( \omega_3 \) must be known. I assume the same form \( \chi^{(3)R}/\chi^{(3)NR} = -A/(\delta - i\Gamma) \) (equation (2.20)) as used for singly resonant CARS with a single low lying level. Since this is a doubly resonant experiment with a number of Raman active electronic levels, this choice must be justified with respect to Equation (2.26).

The two lowest crystal field levels of the \( ^2F_{7/2} \) manifold are separated by 41 cm\(^{-1}\). Since this separation is much greater than the linewidths of either level, I may treat these levels separately, and the susceptibilities for each level will not interfere with each other.
In a doubly resonant CARS experiment [87], the line shape of the signal changes as \( \omega_3 \) moves through resonance with the intermediate state \( |n\rangle \). In terms of equation (2.26) this occurs for two reasons. First, \( i\Gamma_{gn} \) may become comparable in magnitude to \( (\omega_3 - \omega_{gn}) \) adding an additional phase to \( \chi^{(3)}R \). In addition, the quantity \( (\omega_3 - \omega_{gn}) \) may vary considerably throughout the scan, shifting both the magnitude and phase of \( \chi^{(3)}R \). For the conditions of the experiment reported here, both of these effects are small and may be safely ignored as demonstrated below.

All 5\(d\) bands (zero phonon lines and vibronic sidebands) act as intermediate states for the CARS process, and one must sum over the entire 5\(d\) configuration in equation (2.26). If the coupling between the Ce\(^{3+}\) ion and the host lattice is not too strong, the intermediate states may be described by the Born-Oppenheimer approximation, and written as the product

\[
|n\rangle \rightarrow |n_e\rangle \mid \chi_v\rangle
\]  

(2.28)

where \( |n\rangle \) labels the \( n\)th 5\(d\) band (\( n=1 \) to 5), \( |n_e\rangle \) labels the \( n\)th electronic state of the Ce\(^{3+}\) ion 5\(d\) configuration, and \( |\chi_v\rangle \) labels the vibrational state of the crystal. Then

\[
\omega_{gn} \rightarrow \omega_{gn_e} + \omega_{\chi}
\]

(2.29)

where \( \hbar\omega_{gn_e} \) is the energy of the \( n\)th zero phonon line (purely electronic transition), and \( \hbar\omega_{\chi} \) corresponds to the phonon states. The Stark components of the 4\(f\) configuration involved in the CARS experiment all have same vibrational quantum number, namely \( |0_v\rangle \).

In the Condon approximation

\[
\langle g | er_i | n\rangle \langle n | er_i | f \rangle = \langle g_e | er_i | n_e \rangle \langle n_e | er_i | f_e \rangle \times |\chi_v | 0_v\rangle^2
\]

(2.30)
If \( \omega_1 \) is far enough below the 5d bands, the following approximation holds for the final summation in Equation (2.26)

\[
\sum_{n'} \frac{\langle g | e_r | n' \rangle \langle n' | e_r | f \rangle}{(\omega_1 - \omega_{gn'})} \approx \sum_{\text{all 5d bands}} \frac{\langle g_e | e_r | n'_e \rangle \langle n'_e | e_r | f_e \rangle}{(\omega_1 - \bar{\omega}_{gn'})} \tag{2.31}
\]

where \( \bar{\omega}_{gn'} \) are the centers of gravity of the five 5d bands. Since only \( \chi_{iii}^{(3)} \) is of interest, all tensor indices are the same.

For the second summation in Equation (2.26), only the lowest 5d band contributes appreciably. The absorption coefficient, \( a(\omega_{gn}) \), for the ground state to the lowest 5d level is

\[
a(\omega_{gn}) \propto |\langle g_e | e_r | 1_e \rangle|^2 \times |\langle \chi_{\nu} | 0_{\nu} \rangle|^2 \tag{2.32}
\]

The intensity of the absorption spectrum of the lowest 5d band shows very little polarization behavior. Hence, \( |\langle g_e | e_r | 1_e \rangle|^2 \) may be treated as a constant, independent of \( i \).

Then equations (2.30) and (2.32) allow the following change to be made to the second summation in equation (2.26):

\[
\sum_{n} \frac{\langle g | e_r | n \rangle \langle n | e_r | f \rangle}{(\omega_3 - \omega_{ gn } - i\Gamma_{ gn })} \approx \langle g_e | e_r | n_e \rangle \langle n_e | e_r | f_e \rangle \times \int_{\text{first 5d band}} \frac{a(\omega_{gn})}{(\omega_3 - \omega_{gn})} d\omega_{gn} \tag{2.33}
\]

Note that the \( i\Gamma_{ gn } \) term has been disregarded. This is justified in our experiment because \( |\omega_3 - \omega_{ gn }| / 2\pi c \) is always \( \geq 50 \text{ cm}^{-1} \), which is much larger than \( \Gamma_{ gn } / 2\pi c \) for the individual levels which make up the 5d band.
Now Equation (2.26) may be written as

\[ \chi_{iii}^{(3)R} \propto \frac{1}{\delta - i\Gamma} \times \langle g_e | e_{r_i} | n_e \rangle \langle n_e | e_{r_i} | f_e \rangle \]

\[ \times \int_{\text{first } 5d \text{ band}} \frac{a(\omega_{gn})}{(\omega_3 - \omega_{gn})} d\omega_{gn} \]

\[ \times \sum_{\text{all } 5d \text{ bands}} \frac{\langle g_e | e_{r_i} | n'_{e} \rangle \langle n'_{e} | e_{r_i} | f_e \rangle}{(\omega_1 - \omega_{gn'})} \] (2.34)

The frequency-tripled Nd\textsuperscript{3+}:YAG laser provides \( \omega_1 \) which is a constant. The absorption coefficient, \( a(\omega_{gn}) \), is plotted in Figure 1.9. Numerical evaluation of the above integral shows that its value changes only slightly as \( \omega_3 \) varies throughout each resonance. The value of the integral varies by only 1% over the line profiles in Figure 2.12 and by about 5% over Figure 2.11. For this reason, I treat the integral as a constant over each resonance. I therefore fit the data to

\[ \frac{\chi_{iii}^{(3)R}}{\chi_{iii}^{(3)NR}} = \frac{-A}{\delta - i\Gamma} \] (2.35)

Measurement of \( \chi_{xxxx}^{(3)NR} / \chi_{zzzz}^{(3)NR} = 1.48 \pm 0.15 \) in a pure LuPO\textsubscript{4} crystal allows comparison of all observed resonances. Williams, et al. [23, 24] have calculated angular wavefunctions for all electronic levels of the 4\( f \) and 5\( d \) configurations. Using the absorption data of Figure 1.9, relative values of \( A \) may be calculated according to Equation (2.34) and compared with experiment. Since the features to the left of the zero phonon line in Figure 1.9 are not connected to the ground state, I did not include them in the
calculation. The results of the calculation are given in Table 2.2. The basis of the calculations rests on the assumption that the $5d$ states may be described by the Born-Oppenheimer approximation. The Born-Oppenheimer approximation does not, however, affect the choice of Equation (2.35) as an appropriate functional form for $\chi^{(3)}R$.

### 2.7.2 Deconvolution of the Spectra

Ideally, one would like to fit the data of Figures 2.11 and 2.12 to equation (2.21). However, the actual spectra must be deconvolved, in order to take into account the finite bandwidths of the input lasers. The output intensity is written as

$$I(\omega_3) \propto \int |\chi^{(3)}(-\omega_3, \omega_1, \omega_1, -\omega_2) + \chi^{(3)}(-\omega_3, \omega_1', \omega_1', -\omega_2)|^2$$

$$\times g_1(\omega_1)g_1(\omega_1')g_2(\omega_2) \delta(\omega_3 - \omega_1' - \omega_1 + \omega_2) \ d\omega_1 d\omega_1' d\omega_2$$

(2.36)

where $g_i(\omega)$ is the normalized intensity of beam $\omega_i$ centered at $\omega_i^0$. Since the input lasers have finite linewdiths, the output $I(\omega_3)$ will have a frequency distribution centered at $\omega_3^0 = 2\omega_1^0 - \omega_2^0$. The detector bandwidth is greater than that of $I(\omega_3)$ so the data corresponds to

$$I(\omega_3^0 = 2\omega_1^0 - \omega_2^0) \propto \int I(\omega_3) d\omega_3$$

(2.37)

Our lasers have approximately gaussian lineshapes with FWHM 0.8 cm$^{-1}$ for $\omega_1$ and 0.6 cm$^{-1}$ for $\omega_2$. The accuracy of the laser line width measurements is $\pm 0.1$ cm$^{-1}$. With gaussian intensity profiles for the input lasers, the above equations cannot be evaluated in closed form. The CARS signals in Figures 2.11 and 2.12 may be fit by
numerically computing $I(\omega_0^0)$. A least squares fit is obtained by treating $A$ and $\Gamma$ as variable parameters. Table 2.1 summarizes these results. The fitted curves are drawn as solid lines in Figures 2.11 and 2.12. The major effect of using lasers with linewidths greater than the $\text{Ce}^{3+}$ linewidths is a general broadening of the spectra, especially when $\Delta\omega_{\text{laser}} > 2\Gamma$. Perhaps most noticeable is the suppression of the “dip” in the CARS signal in Figures 2.12(a) and (b). Here the normalized intensity does not fall far below one as in a typical CARS intensity profile. In Figure 2.11(b), $\Delta\omega_{\text{laser}} < 2\Gamma$, and the effect is less.

According to Teets [88], the above convolution (equation (2.36)) is superior to that introduced by Yuratich [89] which is the standard equation used in the field. In a publication based on the work in this chapter [90], the Yuratich convolution was used and gave similar results.

2.7.3 Analysis

Although the above analysis strictly applies only to homogeneously broadened lines, I view $\Gamma$ as a phenomenological parameter which may include contributions from both homogeneous and inhomogeneous broadening. The use of broad band lasers hampers the ability to accurately measure these quantities. The fourth column of Table 2.1 lists the linewidths for the various levels. The linewidth of the lowest crystal field level in the $^2F_{7/2}$ manifold is much narrower than the higher level. This is expected since the higher level may decay by the spontaneous emission of a phonon. Reed and Moos [91] investigated multi-phonon inter-manifold relaxation in YPO$_4$ crystals doped with various rare earth ions. (The phonon spectra of LuPO$_4$ and YPO$_4$ are very similar.) They found that manifolds with energy gaps $\leq 2500$ cm$^{-1}$ do not fluoresce but decay non-radiatively. An extrapolation of their data indicates that the nonradiative decay rate from the 2179 cm$^{-1}$
level to the 429 cm\(^{-1}\) level should be less than \(10^7 \text{s}^{-1}\). This rate corresponds to homogeneous linewidths less than 10 MHz (\(3 \times 10^{-4} \text{ cm}^{-1}\)). As a consequence, the 2220 cm\(^{-1}\) state is lifetime broadened, while the linewidth of the 2179 cm\(^{-1}\) level may be primarily attributed to crystal strain broadening. These measured linewidths are typical of those found in dilute rare earth crystals at low temperatures as discussed in Chapter 1.

The fifth column of Table 2.1 gives the value of \(C\) for the different resonances. The bandwidths and noise levels of the lasers place limits on how weak a resonance can be detected. The experimental noise to signal ratio is about 5%. For a resonance with \(\Gamma/2\pi c = 0.045 \text{ cm}^{-1}\), the lower limit of detection is \(C < 0.5\). For a resonance with \(\Gamma/2\pi c = 0.45 \text{ cm}^{-1}\), the lower limit of detection is \(C < 0.05\). When I performed this experiment with visible lasers (\(\omega_1/2\pi c = 18792 \text{ cm}^{-1}\), \(\omega_2/2\pi c = 16600 \text{ cm}^{-1}\)), I observed no CARS resonances. Therefore, by going from singly to doubly resonant CARS, \(C\) increases by at least a factor of 31.

The third column of Table 2.1 gives the experimental values of \(A\). Table 2.2 compares the ratios of the \(A\) values for both calculation and experiment. Agreement is fair since both the calculation and experiment predict that the 2220 cm\(^{-1}\) \(xxxx\) and 2179 cm\(^{-1}\) \(zzzz\) -polarized resonances will be several times larger than the 2179 cm\(^{-1}\) \(xxxx\) polarized resonance.

The use of broad band lasers masks the true size of the resonance for narrow lines. Had I used lasers with sub-gigahertz bandwidths, the signal peak in Figure 2.12(a) would be about 150 times as large as the off resonance intensity. Figure 2.13 shows the data of Figure 2.12(a) along with the CARS signal calculated from equation (2.21) (which neglects the finite laser linewidths) using the parameters in Table 2.1. The use of broad band lasers has a smaller effect on the 2220 cm\(^{-1}\) resonance, and the CARS "dip" is visible.
2.7.4 Summary

Calculations in section 2.3 indicated that the figure of merit \((C)\) for singly resonant electronic CARS experiments in pure rare earth crystals may be expected to be modest at best. By going from singly resonant CARS to doubly resonant CARS (where the second resonance involves the strong \(4f \rightarrow 5d\) transition) the figure of merit may be enhanced to such an extent that \(C\) may be large even for a dilute rare earth crystal.

I have demonstrated doubly resonant CARS involving electronic states in a dilute rare earth crystal – Ce\(^{3+}:\)LuPO\(_4\). The signals produced are an order of magnitude larger than those seen previously in singly resonant CARS in pure rare earth crystals which contain 2000 times as many rare earth ions per unit volume. Two factors account for the large values of

\[
C = \left| \chi^{(3)R} / \chi^{(3)NR} \right|_{\text{max}} = A / \Gamma.
\]

First and most important is the enhancement due to the signal being in near resonance with the lowest \(5d\) band. In addition, the narrow linewidth of the lowest level of the \(^2F_{7/2}\) manifold gives \(C\) an extra boost.

The use of doubly resonant CARS should be applicable to high resolution spectroscopy of other dilute rare earth systems. Requirements are, in order of importance, accessible \(5d\) levels, electronic transitions with narrow linewidths, and lasers with bandwidths narrower than the material resonances. Crystals doped with divalent rare earth ions are attractive candidates. The \(5d\) bands of divalent rare earths are in the visible and near infrared. At low temperatures electronic linewidths of metastable states in dilute crystals are ultimately limited by inhomogeneous broadening. Dilute single crystals usually have inhomogeneous broadening (FWHM) in the 1 to 10 GHz range [13]. Finally, in order to accurately measure the resonance, and to avoid deconvolution of spectra, narrow band lasers should be employed.
TABLE 2.1. Summary of data with estimated uncertainties. $C = |\chi_{iii}^{(3)R} / \chi_{iii}^{(3)WR}|_{max} = A/\Gamma$. $\chi_{xxxx}^{(3)WR} / \chi_{zzzz}^{(3)WR} = 1.48 \pm 0.15$.

<table>
<thead>
<tr>
<th>polarization</th>
<th>$\omega/2\pi c$ (cm$^{-1}$)</th>
<th>$A/2\pi c$ (cm$^{-1}$)</th>
<th>$\Gamma/2\pi c$ (HWHM) (cm$^{-1}$)</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>zzzz</td>
<td>2179</td>
<td>0.70±0.20</td>
<td>0.045±0.015</td>
<td>15.5</td>
</tr>
<tr>
<td>zzzz</td>
<td>2220</td>
<td>&lt;0.03</td>
<td>–</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>xxxx</td>
<td>2179</td>
<td>0.18±0.04</td>
<td>0.040±0.015</td>
<td>4.5</td>
</tr>
<tr>
<td>xxxx</td>
<td>2220</td>
<td>0.55±0.10</td>
<td>0.40±0.10</td>
<td>1.4</td>
</tr>
</tbody>
</table>

TABLE 2.2. Ratios of $A$ values for the different CARS resonances in different polarizations calculated from Equation (2.34).

<table>
<thead>
<tr>
<th>$\omega/2\pi c$ (cm$^{-1}$)</th>
<th>2220</th>
<th>2179</th>
<th>2220</th>
<th>2179</th>
</tr>
</thead>
<tbody>
<tr>
<td>polarization</td>
<td>zzzz</td>
<td>xxxx</td>
<td>xxxx</td>
<td>zzzz</td>
</tr>
</tbody>
</table>

| calculated | 0 : 1 : 5.67 : 8.33 |
| experiment  | 0 : 1 : 3.1±1.0 : 3.8±1.3 |
FIGURE 2.1. Schematic diagram of doubly resonant CARS in Ce$^{3+}$:LuPO$_4$. $\omega_1/2\pi c = 28192$ cm$^{-1}$, $\omega_2/2\pi c = 26013$ cm$^{-1}$, $(2\omega_1 - \omega_2)/2\pi c = 30371$ cm$^{-1}$, $\Delta = 89$ cm$^{-1}$ and $D = 2268$ cm$^{-1}$. 
\[ \omega_3 = 2\omega_1 - \omega_2 \]

**FIGURE 2.2.** Schematic diagrams of CARS in frequency and spatial domains. (a) Relation between the input (straight arrows) and output (curved arrow) in frequency. (b) Relationship between input and output beams. (subscripts indicate polarization.) (c) Phase matching condition. For small \( \theta, \phi = \theta. \)
FIGURE 2.3. Schematic diagram of singly (a) and doubly (b) resonant CARS. The dashed lines are not real states, and are drawn to aid the eye.
FIGURE 2.4. Individual terms in equation (2.21) Calculated with $A/2\pi c = 1$ cm$^{-1}$ and $\Gamma/2\pi c = 1$ cm$^{-1}$. ($C = 1$.)
FIGURE 2.5  CARS signal calculated from equation (2.21) with low figure of merit ($C = 0.05$, $A/2\pi c = 0.05$ cm$^{-1}$, and $\Gamma/2\pi c = 1$ cm$^{-1}$) Note the small dynamic range of the signal ($I_{\text{max}}/I_{\text{min}} = 1.1$).
FIGURE 2.6. Normalized CARS signal for the 992 cm$^{-1}$ vibrational mode in benzene. Calculated using the parameters $\chi^{(3)WR} = 1.6 \times 10^{-14}$ esu, $\Gamma/2\pi c = 1.2$ cm$^{-1}$, and $|\chi^{(3)}|_{\text{max}} = 30.0 \times 10^{-14}$ esu from Ref. [92]. ($C = 18.8$.) Note that the signal has a dynamic range of $\sim 10^5$. 

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FIGURE 2.7. Schematic diagrams of spontaneous Raman scattering. The frequency of the exciting laser is $\omega_l$. (a) Stokes scattering. (b) Anti-Stokes scattering.
FIGURE 2.8. Previously detected electronic CARS resonances in (a) Tb$_3$Al$_5$O$_{12}$ at 80 K (from Ref. [61]) and (b) PrF$_3$ at 2 K (from Ref. [62]). Note that the signal does not exceed 1.5 times the background. Figures of merit: (a) $C \leq 0.4$, (b) $C = 0.5$. 

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FIGURE 2.9. Schematic diagram of the CARS apparatus.
FIGURE 2.10. Temporal profiles of individual shots from the frequency tripled Nd\textsuperscript{3+}: YAG laser and the average of 100 shots. Time resolution is between two and three ns.
FIGURE 2.11 (a). Intensity of CARS signal at frequency $\omega_3$ as a function of $\omega_1 - \omega_2$ with the lasers polarized in the z direction. No resonance is seen because $\chi^{(3)R}_{zzzz} = 0$ for resonances between the $\Gamma_6$ ground state and the $\Gamma_7$ level at 2220 cm$^{-1}$. 
FIGURE 2.11 (b). Intensity of CARS signal at frequency $\omega_3$ as a function of $(\omega_1 - \omega_2)$ normalized to the off resonance intensity. The solid line is a fitted curve with the parameters listed in Table 2.1. The lasers are polarized in the $x$ direction.
FIGURE 2.12 (a). Intensity of CARS signal at frequency $\omega_3$ as a function of $(\omega_1 - \omega_2)$ normalized to the off resonance intensity. The solid line is a fitted curve with the parameters listed in Table 2.1. The lasers are polarized in the $z$ direction.
FIGURE 2.12 (b). Intensity of CARS signal at frequency $\omega_3$ as a function of $(\omega_1 - \omega_2)$ normalized to the off resonance intensity. The solid line is a fitted curve with the parameters listed in Table 2.1. The lasers are polarized in the $x$ direction.
FIGURE 2.13. Calculated CARS signal \((\chi_{zzzz}^{(3)} / \chi_{zzzz}^{(3)WR})^2\) using the data of Table 2.1, and assuming that the input lasers have zero linewidth. For comparison, the data of Figure 2.12 (a) are also shown.
Chapter Three

$4f \rightarrow 5d$ Two-photon Absorption in Ce$^{3+}$:LuPO$_4$

My motivation for investigating the $4f \rightarrow 5d$ two-photon absorption (TPA) spectra of the Ce$^{3+}$ ion in the LuPO$_4$ crystal was to locate and determine the symmetry of the crystal field components of the $5d$ configuration. Knowledge of the nature of the $5d$ states is vital to understanding electronic Raman processes. The calculations of relative CARS intensities in Chapter 2 (Table 2.2) require accurate electronic wavefunctions for the $5d$ levels. Williams et al. calculated electronic wavefunctions from a crystal field fit of the $5d$ configuration. They used single-photon absorption spectra to locate the $5d$ levels. They experimentally located the zero-phonon line and determined its symmetry for only the lowest $5d$ level. The energies of zero-phonon lines in the higher crystal field levels were not observed – they were estimated, and the symmetries of the higher levels were derived from the crystal field fit.
By measuring polarized TPA spectra, I confirmed that the zero-phonon line of the lowest $5d$ level is at $30460 \text{ cm}^{-1}$, and its symmetry is $\Gamma_7$. This is consistent with results from single-photon absorption spectra. Additionally the two-photon spectra shows the next crystal field level has its zero-phonon line at $39715 \text{ cm}^{-1}$, with symmetry is $\Gamma_6$. The two-photon spectra of higher lying levels do not reveal any information.

This chapter is organized as follows: Section 3.1 introduces the theory of two-photon absorption in the context of four-wave mixing. Section 3.2 reviews previous $4f \rightarrow 5d$ TPA experiments. Section 3.3 briefly reviews TPA selection rules. The apparatus for detection of TPA is described in section 3.4. Section 3.5 presents and discusses the results.

3.1 Theory of Two-photon Absorption

In 1931 Goeppert-Mayer predicted the TPA process using time-dependent perturbation theory [93]. In the TPA process, a state with energy $2\hbar\omega$ is populated by the simultaneous absorption of two quanta of energy $\hbar\omega$. The two-photon absorption coefficient is proportional to the square of the intensity of the incident light. As a result of this nonlinear intensity dependence, it was not until after the invention of the laser that this process was actually observed [94]. TPA allows access to energy levels which may be out of the frequency range of available light sources. (See Figure 3.1.) In addition, selection rules for two-photon transitions may differ from those of single photon transitions. As a consequence, TPA spectroscopy may be used to compliment single photon spectroscopy, and to determine the symmetry labels of energy levels.

TPA may also be described within the framework of four-wave mixing as in section 2.1. Assume that a plane wave, polarized in the $i$ direction, is traveling in the $z$ direction.
\[ E(\mathbf{r}, t) = \frac{1}{2} \mathbf{E}(z) e^{i(kz - \omega t)} + \text{c. c.} \] (3.1)

and that the plane defined by \( z = 0 \) is the boundary between vacuum and a nonlinear medium. Within the medium, there is a nonlinear polarization generated via the third-order susceptibility tensor \( \chi_{iiii}^{(3)}(-\omega, \omega, \omega, -\omega) \):

\[ P_{NL}^i = \chi_{iiii}^{(3)} (-\omega, \omega, \omega, -\omega) \mathbf{E}_i \mathbf{E}_* e^{i(kz - \omega t)} \] (3.2)

Note that the induced polarization travels in phase with the incident wave. This means that phase matching is automatically satisfied. Use of the same methods and approximations as in section 2.1.1 yields

\[ \frac{\partial}{\partial z} E_i(z) = \frac{2\pi i \omega}{n(\omega) c} \left[ \chi_{iiii}^{(3)}(-\omega, \omega, \omega, -\omega) |E_i|^2 E_i \right] \] (3.3)

(Compare with equation (2.7).) Since the intensity, \( I \), of the wave is given by

\[ I = \frac{n(\omega) c}{8\pi} |E_i|^2 \] (3.4)

equation (3.3) may be rearranged as

\[ \frac{\partial}{\partial z} I(z) = - \left[ \frac{32\pi^2}{n^2(\omega) c^2} \text{Im}\chi_{iiii}^{(3)}(-\omega, \omega, \omega, -\omega) \right] \omega I^2(z) \] (3.5)

Thus for TPA, attenuation of the intensity is proportional to the square of the intensity and the imaginary part of the susceptibility. Since the nonresonant part of the susceptibility is a
real number, one only needs to be concerned with the resonant susceptibility. From Ref. [54],

\[ \text{Im } \chi_{iii}^{(3)R} = N \pi |M_{ii}|^2 g(\hbar(2\omega - \omega_{gf})) \] (3.6)

where

\[ M_{ii} = \sum_n \frac{1}{\hbar} \left[ \frac{\langle g |er_i| n \rangle \langle n |er_i| f \rangle}{(\omega - \omega_{gn})} \right] \] (3.7)

and \( g(\hbar(2\omega - \omega_{gf})) \) is a normalized Lorenztian function with linewidth \( \hbar\Gamma_{gf} \). The kets \( |g\rangle \), \( |f\rangle \), and \( |n\rangle \) correspond to the ground, final, and intermediate states with energies zero, \( \hbar\omega_{gf} \), and \( \hbar\omega_{gn} \). (See Figure 3.1.) The number density of ions is \( N \), and \( \Gamma_{gf} \) is the Lorentzian linewidth (HWHM) of the \( |g\rangle \rightarrow |f\rangle \) transition. Equation (3.6) predicts that the TPA will peak when \( 2\omega = \omega_{gf} \). Note that the TPA matrix element \( M_{ii} \) is very similar to the Raman tensor in equation (2.18). It is evident from equation (3.7) that if the states \( |g\rangle \) and \( |f\rangle \) are parity eigenstates, then TPA from \( |g\rangle \) to \( |f\rangle \) can occur only if both states have the same parity.

### 3.2 4f→5d Two-photon Absorption

In the first order, two-photon transitions between the 4f and 5d configurations are parity forbidden (\( \Delta l = 1 \)). In a crystal, the odd parity components of a non-centrosymmetric crystal field or the odd parity lattice vibrations may relax the parity selection rules, and 4f→5d two-photon absorption may be observed. Gayen, et al. have
extensively studied $4f \rightarrow 5d$ two-photon transitions in $\text{Ce}^{3+}:\text{CaF}_2$ [95–98]. They measured the TPA cross section for the zero-phonon line of the lowest $5d$ level to be $5 \times 10^{-54} \text{ cm}^4 \text{ s}$. Typical TPA cross sections for parity allowed two-photon transitions range from $10^{-49}$ to $10^{-51} \text{ cm}^4 \text{ s}$. Leavitt [99] and Sztucki and Strcek [100] have contributed to a theoretical understanding of $4f \rightarrow 5d$ two-photon absorption.

The first observation of TPA involved the $4f^7 \rightarrow 4f^65d$ transition in $\text{Eu}^{2+}:\text{CaF}_2$ [94]. With the exception of the work by Gayen, et al. and Bayer and Schaak [101], most subsequent TPA experiments in rare earth crystals [102] concentrated on the sharp, parity allowed $4f^n \rightarrow 4f^n$ transitions.

### 3.3 Selection Rules

The TPA matrix element in equation (3.7) has the same selection rules as the Raman tensor. Therefore, the selection rules for the TPA susceptibility tensor are the same as the CARS selection rules (section 2.4):

\[
\Gamma_6 \rightarrow \Gamma_6 \quad \chi^{(3)R}_{iii} \text{ allowed for } i = x, y, z.
\]

\[
\Gamma_6 \rightarrow \Gamma_7 \quad \chi^{(3)R}_{iii} \text{ allowed for } i = x, y \quad (\chi^{(3)R}_{zzz} = 0).
\]

In this case $i$ is the polarization of the incident radiation. Recall that the ground state in $\text{Ce}^{3+}:\text{LuPO}_4$ has symmetry $\Gamma_6$.

### 3.4 Experimental Details

Figure 3.2 shows the experimental apparatus.
A frequency doubled (tripled) Nd$^{3+}$:YAG laser (Spectra-Physics DCR-1) pumped a pulsed dye laser which used DCM (LD489) laser dye to provide tunable radiation in the 14900 to 16500 cm$^{-1}$ (18800 to 21200 cm$^{-1}$) range. The pulsed dye laser linewidth was about 0.5 cm$^{-1}$. These frequency ranges allowed the two-photon investigation of the lowest 5$d$ level (DCM) and the next two higher 5$d$ levels (LD489). (Table 1.2 lists the 5$d$ levels of Ce$^{3+}$:LuPO$_4$.) The energy per pulse of the incident radiation was about 500 µJ. The light from the pulsed dye laser was focused on the sample by a 15 cm lens. The focused laser light passed through about 2 mm of the sample. A Spectra-Physics 310-21 broadband polarization rotator allowed measurements to be made with the incident light polarized in the $z$ and $x$ directions. The transmitted light was attenuated and detected by a biased photodiode (EG&G 100A). The sample was cooled to ~10 K in a Janis Supertran cryostat as in Chapter 2.

Two-photon absorption can be a weak process. Rather than attempt to detect the minute attenuation in the laser beam as it passes through the sample, the 5$d$ $\rightarrow$ 4$f$ fluorescence which results from the two-photon excitation was measured. (See Figure 3.3.) This actually is a much more sensitive measure of absorption, since the background is zero. The fluorescence from the lowest 5$d$ level to the 4$f$ levels is in the ultraviolet (27000 - 30000 cm$^{-1}$) while the laser excitation is in the visible. Therefore, two ultraviolet filters (Corning 7-54) which pass ultraviolet, while blocking the visible were used to discriminate the fluorescence from the excitation. An RCA 1P28A photomultiplier tube covered with the two filters was placed at the window of the cryostat in order to collect the greatest amount of light. The 5$d$ $\rightarrow$ 4$f$ fluorescence has a lifetime of 20 ns. The signal from the PMT was detected with a SRS 250 boxcar averager with a 30 ns gate. The boxcar gate was delayed by 10 ns after the 5 ns laser pulse to further discriminate the fluorescence signal from the laser (see Figure 3.4). Another boxcar measured the signal from photodiode. As in Chapter 2, a personal computer collected individual measurements of
the $5d \rightarrow 4f$ fluorescence signal, normalized this signal to the square of the intensity for each laser shot, and averaged these values over 75 laser shots. After collecting each set of data, the computer scanned the dye laser to a new frequency. This yielded the two-photon excitation spectra in Figures 3.5, 3.6 and 3.7.

3.5 Results and Discussion

3.5.1 $^2F_{5/2} (\Gamma_6) \rightarrow 5d (\Gamma_7)$

Figure 3.5 shows the two-photon excitation spectra of the lowest $5d$ level in both the $x$ and $z$ polarizations. The $x$ polarized spectrum is much more intense than the $z$ polarized spectra leading to the assignment of this level as $\Gamma_7$. The $z$ polarized spectra is probably due to some polarization leakage. The single photon spectra [23] shows very little polarization dependence and is also consistent with the assignment of $\Gamma_7$. Figure 3.6 shows the $x$ polarized two-photon spectrum along with the single photon spectrum from Figure 1.9. Note that both spectra show the zero-phonon line at 30460 cm$^{-1}$. Additionally, many peaks in the two-photon vibronic sidebands correlate with the single photon sideband. Probably the most interesting feature is the intensity of the zero-phonon line compared to the vibronic sideband. The zero-phonon line is much more prominent in the two-photon spectrum than in the single photon spectrum. Gayen et al. observed the same feature in Ce$^{3+}$:CaF$_2$ [95, 97].
The two-photon spectra of the higher 5d levels differed from the lowest 5d levels. Figure 3.7 shows the only distinct feature in the excitation spectra from scanning the laser from 18800 to 21200 cm\(^{-1}\) (corresponding to two-photon energies of 37600 to 42400 cm\(^{-1}\)). I interpret this as the zero-phonon line of the of the second 5d level. Since it was detected in both z and x polarizations, the \(\Gamma_6\) symmetry label is assigned to this level.

Another possible explanation for this feature is as follows: If an impurity ion with an energy level at 19857 cm\(^{-1}\) exists within the host crystal, an incident photon may populate this level. With this level populated, the higher 5d level of the Ce\(^{3+}\) ion may be populated by another 19857 cm\(^{-1}\) photon in an energy transfer process. There are two reasons to doubt this. Both the Ce\(^{3+}\) and the impurity ion have very low concentrations making energy transfer unlikely. Additionally, no rare earth ion doped into LuPO\(_4\) has an energy level at 19857 cm\(^{-1}\).

The signal for the two-photon spectra of the zero-phonon line at 39715 cm\(^{-1}\) was weaker than the zero-phonon line of the lowest 5d level, and there was a non-zero background. This non-zero background may be a continuation of the vibronic sideband of the lowest 5d level, or, alternatively, ultraviolet fluorescence may be excited by multi-(greater than two)-photon absorption into the crystal band gap.

Using calibrated filters, I determined that the fluorescence resulting from the two-photon excitation of the higher levels originates in the lowest 5d level. Therefore, excitation non-radiatively decays from the higher 5d levels to the lowest 5d level. (see Figure 3.2(b).) The zero-phonon line of the third 5d level was not observed. Presumably, this level is extremely broadened by non-radiative decay to second 5d level. It is not surprising that no vibronic sideband was observed in the second 5d level since the peaks of the sideband are probably much weaker than the zero-phonon line.
The symmetry assignments for the two lowest 5d levels are at odds with those reported by Karanjikar and Niak [103] for Ce$^{3+}$ in YPO$_4$. Since the structure of YPO$_4$ and LuPO$_4$ are nearly identical, one expects the spectra of Ce$^{3+}$:LuPO$_4$ and Ce$^{3+}$:YPO$_4$ to be very similar. Indeed, the 5d energy levels reported for Ce$^{3+}$:YPO$_4$ are quite close to those listed for Ce$^{3+}$:LuPO$_4$ in Table 1.2. The symmetry assignments of Karanjikar and Niak are extrapolated from the work of Nakazawa and Shinoya [22] and are probably in error. The symmetry assignments of the two lowest 5d levels in this work rely on the fact that the ground state has symmetry $\Gamma_6$. The electronic Raman work of Williams et al. [23, 25] has demonstrated this to be the case with no ambiguity.

3.6 Summary

I have demonstrated the use of two photon absorption to locate and determine the symmetry of 4f $\rightarrow$ 5d zero-phonon lines in Ce$^{3+}$:LuPO$_4$ at low temperature. Two-photon absorption has some advantages over single photon absorption. (1) Ultraviolet levels can be easily accessed with visible lasers. (2) Zero-phonon lines seem to be easily distinguished from the vibronic sideband.
FIGURE 3.1. Schematic diagram of two-photon absorption.
FIGURE 3.2. Apparatus for measuring two-photon spectra.
FIGURE 3.3. Schematic diagram illustrating inter-configurational TPA. (Compare to Figure 1.5 which illustrates $4f \rightarrow 5d$ single photon absorption.) The dashed line indicates non-radiative decay. (a) TPA to the lowest $5d$ level. (b) TPA to the second $5d$ level.
FIGURE 3.4. Timing diagram for two-photon absorption measurement.
FIGURE 3.5. Polarized two-photon excitation spectra of lowest 5d level of Ce$^{3+}$:LuPO$_4$ at $\sim$ 10 K. (Intensity of the 5d $\rightarrow$ 4f ultraviolet fluorescence intensity as a function of the wave number and polarization of the incident radiation.)
FIGURE 3.6. Two-photon absorption (solid line) versus single photon absorption (dashed line). Single photon absorption data is from Figure 1.9. Resolution of single photon data is about 2 cm$^{-1}$.
FIGURE 3.7. Two-photon excitation spectra of the zero-phonon line of the second 5d level. Note that the horizontal scale differs greatly greatly from Figures 3.5 and 3.6. This peak was the only feature seen in the 18800 to 21200 cm$^{-1}$ spectral region.
Chapter Four

Electronic Coherent Anti-Stokes Raman Spectroscopy in CeF₃

This chapter reports on CARS resonances detected between the $^2F_{5/2}$ ground state and the 2161 cm⁻¹ and 2239 cm⁻¹ Stark components of the $^2F_{7/2}$ manifold of the Ce³⁺ ion in the CeF₃ crystal at 3.8 K. The reader is invited to review section 1.6 which discusses the properties of the CeF₃. In Chapter 2, I demonstrated that strong electronic CARS resonances ($C > 15$) could be detected in a dilute crystal (0.06 mol % Ce³⁺ doped into LuPO₄) only when the anti-Stokes signal was nearly resonant with the onset of the lowest 5$d$ level at 30460 cm⁻¹. This chapter reports the observation of singly resonant electronic CARS in a fully concentrated cerium crystal – CeF₃. In CeF₃, the levels of 5$d$ configuration range from about 40000 to 50000 cm⁻¹. This rather low energy 5$d$ configuration is responsible for a relatively large electronic Raman cross section. This large cross section leads to a high figure of merit, and the detection of strong CARS resonances ($C > 1$) with visible lasers should be possible.
Measurements were made with both the visible ($\lambda_1 = 476$ nm, $\lambda_2 = 532$ nm) and near ultraviolet ($\lambda_1 = 355$ nm, $\lambda_2 = 385$ nm) lasers. The enhancement of the third order susceptibility due to the electronic resonances $C = \chi^{(3)R}/\chi^{(3)NR}$ is as great as 4.8. This represents an order of magnitude increase over singly resonant electronic CARS experiments in other pure rare earth crystals. The CARS data also allowed accurate measurement of the Ce$^{3+}$ electronic Raman cross sections. In the visible region, $\sigma_{zz} (2161$ cm$^{-1}) = (5.0\pm1.1) \times 10^{-30}$ cm$^2$, and $\sigma_{zz} (2239$ cm$^{-1}) = (1.9\pm0.7) \times 10^{-30}$ cm$^2$. Both the absolute magnitude and dispersion of $\chi^{(3)R}$ could be calculated by modeling the virtual intermediate states as a single degenerate $5d$ state at 45000 cm$^{-1}$.

In the CeF$_3$ crystal, the spectra of both the ground $4f$ and excited $5d$ configurations [8, 28, 32–38] as well as the linear [39] and nonlinear [40, 41] refractive indices have been characterized. From the linear and nonlinear refractive indices, $\chi^{(3)NR}$ may be estimated. Experimental CARS measurements yield $|\chi^{(3)R}/\chi^{(3)NR}|_{\text{max}}$ which lead to an absolute measurement of $|\chi^{(3)R}|_{\text{max}}$. The spontaneous Raman cross section may be derived from $|\chi^{(3)R}|_{\text{max}}$.

In the appendix of this chapter, $|\chi^{(3)R}|_{\text{max}}$ is calculated using the Axe [104] theory of two-photon processes which follows the Judd-Ofelt [105, 106] theory for $4f^n \rightarrow 4f^n$ single photon intensities. Both involve summations over intermediate states of excited electronic configurations whose parity is opposite that of the ground $4f^n$ configuration. In both theories, calculations are simplified by assuming that all electronic states within each excited configuration are degenerate in energy. Absolute two-photon intensities may be calculated if the energies $\hbar \omega_{nl}$ of the excited $nl$ configurations and radial integrals $\langle 4f | r | nl \rangle$ are known. Usually, the $4f^{(n-1)}5d^1$ configuration is expected make the major contribution to the intensity since other excited states of opposite parity (e.g. $4f^{(n-1)}ng^1$) are too high in energy to contribute appreciably. Most previous work [102] on two-photon $4f^n \rightarrow 4f^n$ transitions (two-photon absorption and electronic Raman scattering) in rare earth crystals.
measured relative intensities, and application of the Axe theory did not require knowledge of $\delta \omega_{5d}$ and $\langle 4f|15d \rangle$. Chase and Payne [107], however, measured absolute two-photon absorption cross sections of the Nd$^{3+}$ ion in YAG and LiYF$_4$ crystals. They found a significant difference in cross sections between the host crystals which suggested that $\delta \omega_{5d}$ and $\langle 4f|15d \rangle$ differ from their free ion values and vary according to the host crystal.

For most trivalent rare earth ions, the $4f^{(n-1)}5d^1$ configuration lies in the vacuum ultraviolet. When the ion is introduced into a crystal lattice, these states are often well above the crystal band gap, and experimental evaluation of $\delta \omega_{5d}$ and $\langle 4f|15d \rangle$ is impossible. For Ce$^{3+}$ systems, however, the states the 5d configuration are usually in the 20000 to 60000 cm$^{-1}$ range, and $\delta \omega_{5d}$ and $\langle 4f|15d \rangle$ may be derived from absorption measurements. This allows an independent test of the Axe theory, which uses the same approximations as the more familiar Judd-Ofelt theory. (The quantities which characterize absolute single photon intensities in the Judd-Ofelt theory are related to the odd parity components of the crystal field, and cannot be measured in an independent experiment.)

Williams et al. [23, 24] studied the Ce$^{3+}$ ion in LuPO$_4$, and related the observed absolute electronic Raman cross sections to observed $4f \rightarrow 5d$ oscillator strengths and a reduction of $\langle 4f|15d \rangle$ relative to its free ion value.

In this chapter, both $\langle 4f|15d \rangle$ and $\delta \omega_{5d}$ for CeF$_3$ have been derived from $4f \rightarrow 5d$ absorption measurements. $|\chi^{(3)}_R|_{\text{max}}$ is then calculated from the Axe theory, and compared with experimental measurements. In Ce$^{3+}$:LuPO$_4$ the 5d configuration is split into five levels which range from

There are two main conclusions to be drawn from this chapter. One is that the electronic CARS signals in rare earth crystals may be significantly greater than reported in earlier experiments. Additionally, both the magnitude and dispersion of $|\chi^{(3)}_R|_{\text{max}}$ agree with the predictions of the Axe theory in which the states of the excited 5d configuration are the dominate intermediate states.
Section 4.1 compares the resonant and nonresonant third-order susceptibilities for electronic CARS in CeF₃, and gives an estimate of $C$. Section 4.2 outlines the experimental procedure which is essentially that of Chapter 2, with a few modifications. Section 4.3 presents the experimental data and analysis. Section 4.4 summarizes the CARS experiment. Section 4.5 discusses the applicability of these results to stimulated electronic Raman scattering. In the appendix to this chapter, $|\chi^{(3)R}/\chi^{(3)NR}|$ is calculated using the Axe theory of two-photon transition intensities in atomic systems. The second appendix to this chapter deals with stimulated electronic Raman gain.

4.1 The Resonant and the Nonresonant Susceptibility

The optical properties of the CeF₃ crystal outlined in section 1.6 allow the calculation of both $\chi^{(3)R}_{zzzz}$ and $\chi^{(3)NR}_{zzzz}$.

4.1.1 The Resonant Susceptibility

For the CARS measurements with visible lasers, a frequency-doubled Nd³⁺:YAG laser provides $\omega_2/2\pi c = 18794.3$ cm⁻¹. A tunable laser operating in the 21000 cm⁻¹ region provides $\omega_1$. The CARS signal at $\omega_3 = 2\omega_1 - \omega_2$ is then in the $\omega_3/2\pi c = 23200$ cm⁻¹ region. (See Figure 4.1.) The magnitude of the resonant third-order susceptibility tensor peaks when $\hbar(\omega_1 - \omega_2)$ is equal to $\hbar\omega_{gf}$, the energy of the Raman transition. In the appendix, the maximum value of $|\chi^{(3)R}_{zzzz}(-\omega_3, \omega_1, \omega_1, -\omega_2)|$, is calculated using the Axe theory of two-photon processes. This calculation is based on the following assumptions:

- The 5$d$ intermediate states are the dominant intermediate states for the calculation of the Raman tensor. Additionally, the 5$d$ intermediate states are treated as if all
have the same energy (following the work of Judd [105], Ofelt [106] and Axe [104]).

- The 4f levels are treated in the zero crystal field limit, meaning that the states have spherical (i.e. atomic) symmetry.
- The quantity $\langle 4f| r | 5d \rangle$ is derived from oscillator strength measurements in Ce$^{3+}$:LaF$_3$.

In addition, the methods used in the appendix are also used to calculate the total spontaneous electronic Raman cross section, $\sigma_{zz}$. (The indices correspond to the polarizations of the incident and scattered light, respectively.)

The results given in the appendix show that for a CARS resonance between the ground state of the $^2F_{5/2}$ manifold and one of the four Stark components of the $^2F_{7/2}$ manifold, the maximum of resonant third-order susceptibility is

$$|\chi_{zzzz}^{(3)}|_{max} (^2F_{5/2} \leftrightarrow ^2F_{7/2}) \approx \frac{1.3 \times 10^{-14} \text{ esu}}{\Gamma'}$$

(4.1)

where $\Gamma'$ is the linewidth (HWHM) of the Raman transition in cm$^{-1}$. The linewidths for electronic Raman transitions between Stark components in rare earth crystals at low temperature should range from about 0.5 to 10 cm$^{-1}$. The lowest (metastable) level in a manifold usually has the smallest linewidth. As discussed in section 2.3.1, the value in equation (4.1) is on the high end for electronic CARS in fully concentrated rare earth crystals.
4.1.2 The Nonresonant Susceptibility

In a CARS experiment the nonresonant susceptibility is responsible for the constant background in the signal. The nonresonant susceptibility is related to the product of the linear ($n$) and nonlinear ($n_2$) indices of refraction [108]:

$$\chi^{(3)NR}_{zzzz}(-\omega_3, \omega_1, \omega_1, -\omega_2) = \chi^{(3)NR}_{zzzz}(-\omega_1, \omega_1, \omega_1, -\omega_1) = \frac{n(\omega_1) n_2(\omega_1)}{12\pi}$$ (4.2)

Using the data of Ref. [39] for $n$ and that of Refs. [40] and [41] for $n_2$ yields $\chi^{(3)NR} = 6.1 \times 10^{-15}$ esu at 1.06 $\mu$m. The quantity $\chi^{(3)NR}$ is slightly dispersive, and changes (slowly) with increasing frequency. Sheik-Bahae, et al. [109] have shown that the dispersion of $n_2$ is a consequence of two-photon absorption to the crystal band gap, just as the dispersion of $n$ is a consequence of single photon absorption. They applied a Kramers-Kronig analysis to a two-parabolic-band model to arrive at

$$n_2 \propto \frac{G_2(\hbar\omega / E_g)}{nE_g^4}$$ (4.3)

where

$$G_2(x) = \frac{-2 + 6x - 3x^2 - \frac{3}{4}x^4 - \frac{3}{4}x^5 + 2(1 - 2x)^{3/2}\Theta(1 - 2x)}{64x^6}$$ (4.4)

$E_g$ is the energy of the crystal band gap, and $\Theta$ is the unit step function. Empirically, they have shown that this model is applicable to a wide range of solids, from wide-gap insulating crystals to semiconductors. One may be tempted to use the energy of the $4f \rightarrow$
5d band gap in CeF$_3$ as $E_g$. However, as discussed in Chapter 3, $4f \rightarrow 5d$ two-photon absorption is forbidden in first order since $\Delta l = 1$. Gayen et al. have measured the $4f \rightarrow 5d$ two-photon absorption cross section of Ce$^{3+}$ in CaF$_2$ [95]. Assuming that $4f \rightarrow 5d$ two-photon cross section of Ce$^{3+}$ in CeF$_3$ is similar to Ce$^{3+}$ in CaF$_2$, the two-photon absorption contribution to $n_2$ due to the Ce$^{3+}$ $4f \rightarrow 5d$ band gap should be negligible. Ultraviolet reflectance spectra shows the onset of the valence band to conduction band transition at $\sim 10$ eV in CeF$_3$ [28]. (LaF$_3$, which has nearly the same linear and nonlinear refractive indices as CeF$_3$ [39-41], also shares nearly identical optical properties in the $8 - 34$ eV range.) Using $E_g = 10$ eV, and the measured value of $n_2$ at 1.06 $\mu$m, $\chi^{(3)NR}$ has the following values in the following spectral regions:

<table>
<thead>
<tr>
<th>Wavenumber ($\text{cm}^{-1}$)</th>
<th>Wavelength ($\mu$m)</th>
<th>$\chi^{(3)NR}_{zzzz}$ ($\text{esu}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9397</td>
<td>1.06</td>
<td>$6.1 \times 10^{-15}$ esu</td>
</tr>
<tr>
<td>21000</td>
<td>476</td>
<td>$8.0 \times 10^{-15}$ esu</td>
</tr>
<tr>
<td>28192</td>
<td>355</td>
<td>$9.7 \times 10^{-15}$ esu</td>
</tr>
</tbody>
</table>

Therefore, one may expect from equation (4.1) a figure of merit of $C = |\chi^{(3)R}/\chi^{(3)NR}|_{\text{max}} = 2$ in the visible region if the linewidths are about 1 cm$^{-1}$. While there is some uncertainty in this figure, one can expect that electronic CARS resonances in CeF$_3$ at low temperature should be readily observable.

4.2. Experimental

The experimental apparatus is very similar to that used in Chapter 2. The major difference is in the size of the crystal. The Ce$^{3+}$:LuPO$_4$ crystal is a $\sim 1 \times 1 \times 5$ mm natural crystal while the CeF$_3$ crystal is a 1 cm$^3$ polished cube. A Oxford CF1204 helium gas flow
cryostat is used to cool the CeF$_3$ crystal to 3.8 K. This is a better cooling system than the cold-finger dewar used in Chapters 2 and 3. Low pressure helium gas provides a direct contact between the sample and the cryogenic fluid, and a temperature probe at the sample site provides accurate temperature measurements.

CARS resonances were observed in the visible region by the use of the Nd$^{3+}$:YAG laser second harmonic (18794.3 cm$^{-1}$, linewidth = 0.52 cm$^{-1}$ (FWHM)) to provide $\omega_2$. Frequency-tripled light from the same laser pumped a dye laser operating with Coumarin 500 ($\sim$ 21000 cm$^{-1}$, linewidth = 0.25 cm$^{-1}$) which provided a variable $\omega_1$. At each laser shot, the signal was normalized to the square of the intensity of beam $\omega_1$. The energy of each beam was about 100 $\mu$J/pulse. Both $\omega_1$ and $\omega_2$ were polarized parallel to the optical (z) axis of CeF$_3$. The optimal signal was seen when the angle between $\omega_1$ and $\omega_2$ was $\sim$ 50 mrad. This yielded measurements of $|\chi^{(3)}_{zzzz}|^2$. Figures 4.2 and 4.3 show CARS resonances at $(\omega_1 - \omega_2)/2\pi c = 2161$ cm$^{-1}$ and 2239 cm$^{-1}$, respectively. A measure of the success of this experiment is that it now makes sense to plot the data on a logarithmic intensity scale. In Figure 4.2, the normalized intensity ranges from 0.09 to 9.5 for a dynamic range of about $10^2$. (The dynamic range for previous electronic CARS measurements in pure rare earth crystals did not exceed 2 [61, 62].) CARS resonances involving the two highest Stark components of the $^2F_{7/2}$ manifold were not observed. This is probably due to the large linewidths of these levels.

CARS resonances were also detected using the ultraviolet laser frequencies used in Chapter 2. The frequency tripled light from the Nd$^{3+}$:YAG laser at $\omega_1/2\pi c = 28191.5$ cm$^{-1}$ provided one beam, and also pumped a dye laser to provide tunable radiation in the $\omega_2/2\pi c = 26000$ cm$^{-1}$ range. As in Chapter 2, the linewidths of the lasers were $\Delta \omega_1/2\pi c = 0.80$ cm$^{-1}$ and $\Delta \omega_2/2\pi c = 0.60$ cm$^{-1}$. Table 4.1 displays the characteristics of the lasers used in this chapter. Measurements were taken with the polarizations of both $\omega_1$ and $\omega_2$ parallel to the z axis to yield $|\chi^{(3)}_{zzzz}|^2$. Additionally, measurements were made with the polarizations of
and \( \omega_1 \) and \( \omega_2 \) perpendicular to each other. A 354.7 nm half-wave plate could be inserted into beam \( \omega_1 \) to rotate the polarization by 90°. In the case of non-parallel polarizations in a birefringent medium, a detailed calculation is necessary to determine the possibility of phase matching, and if so the phase matching angle.

The CARS phase matching requirement is

\[
k_3 = 2k_1 - k_2 \quad \text{when} \quad \omega_3 = 2\omega_1 - \omega_2
\]

(4.5)

In a nondispersive medium \((n = \text{constant})\), phase matching would be satisfied with all wave vectors collinear. In a dispersive medium, phase matching is non-collinear. Figure 4.4 is a pictorial diagram of this requirement. It is evident that phase matching is impossible if \(|k_3| + |k_2| < 2|k_1|\). The solution for the phase matching angle, \( \Theta \), is

\[
\cos \Theta = \frac{4k_1^2 + k_2^2 - k_3^2}{4k_1k_2}
\]

(4.6)

and the magnitude of the wave vector \( k_i \) is proportional to the product of the frequency and the index of refraction.

\[
k_i = \frac{\omega_i n(\omega_i)}{c}
\]

(4.7)

Equation (4.24) determines the phase matching angle and may be solved using the data for the index of refraction for both \( x (o) \) and \( z (e) \) polarized lightwaves as a function of frequency given in Figure 1.11. There are three cases to consider.

- \( \chi^{(3)}_{zzzz} \): All beams are polarized parallel to the \( z \) axis. An application of equation (4.6) gives a phase matching angle of 33 mrad.
- $\chi^{(3)}_{xxzz}$: $\omega_1$ is polarized parallel to the $x$ axis, $\omega_2$ is polarized parallel to the $z$ axis and the signal $\omega_3$ is polarized parallel to the $z$ axis. Equation (4.6) gives an imaginary phase matching angle (0.108 i mrad). This corresponds to the situation illustrated in Figure 4.4(b). The wave vectors $k_2$ and $k_3$ are now too short to complete the triangle as in Figure 4.4(a). This may be understood by referring to the index of refraction data of Figure 1.11. $\omega_2$ and $\omega_3$ are e-rays and have a smaller index of refraction than the o-ray $\omega_1$. No phase matching exists, and no signal was observed at $\omega_3$.

- $\chi^{(3)}_{zzxx}$: $\omega_1$ is polarized parallel to the $z$ axis, $\omega_2$ is polarized parallel to the $x$ axis and the signal $\omega_3$ is polarized parallel to the $x$ axis. Equation (4.6) gives a phase matching angle of 112 mrad. This relatively large phase matching angle may also be understood by referring to the index of refraction data in Figure 1.11. Now $\omega_1$ is an e-ray and has a lower index of refraction than o-rays $\omega_2$ and $\omega_3$. The wave vector $k_1$ is now fairly short and and a larger phase matching angle $\theta$ is required to complete the triangle in Figure 4.4(c). Since CeF$_3$ is uniaxial ($n_x = n_y = n_0$), this analysis applies equally to $\chi^{(3)}_{zyzy}$.

The phase matching angle is the angle at which the beams cross inside the nonlinear medium. (See Figure 4.5.) The angle between beams $\omega_1$ and $\omega_2$ outside the medium, $\theta'$, is related to the phase matching angle, $\theta$, by Snell’s law:

$$n \sin (\theta/2) = \sin (\theta'/2)$$  \hspace{1cm} (4.8)

Since $n_o = n_e = 1.63$, 33 mrad inside the sample corresponds to 46 mrad ($2.6^\circ$) outside the sample, and 112 mrad inside the sample corresponds to 182 mrad ($10.5^\circ$). The four cm diameter 25 cm focal length lens used in Chapter 2 cannot converge two parallel beams at an angle of 182 mrad. A four cm diameter 10 cm focal length lens is then used to focus both beams on the sample at an angle of 182 mrad (or 46 mrad).
The results are shown in Figures 4.6, 4.7, 4.8. Fairly strong CARS resonances were observed at 

\((\omega_1 - \omega_2)/2\pi c = 2161 \text{ cm}^{-1}\) in the zzzz, xzzx, and yzzy polarizations. The signal from the xzzx and yzzy polarizations are nearly identical. A weak CARS resonance at 

\((\omega_1 - \omega_2)/2\pi c = 2239 \text{ cm}^{-1}\) was seen only in the zzzz polarization. Again, no resonances were observed for the two highest states of the \(^2F_{7/2}\) manifold.

4.3 Analysis

The data are fit to a third order susceptibility as in Chapter 2:

\[
\frac{\chi_{ijij}^{(3)R}}{\chi_{ijij}^{(3)NR}} = \frac{-A}{(\omega_1 - \omega_2 - \omega_{gf}) - i\Gamma}
\]

As in Chapter 2, the finite bandwidths of the input lasers are taken into account by convolving the spectrum as in equations (2.36) and (2.37). The effect of laser bandwidth are not as extreme as in Chapter 2. The dilute Ce\(^{3+}\):LuPO\(_4\) crystal at low temperature had very narrow linewidths compared the concentrated crystal CeF\(_3\). A best fit of the data in Figures 4.2 and 4.3 gives values for \(A, \Gamma\) and \(C\) given in Table 4.2. The best fits of the data from the ultraviolet lasers in Figures 4.6, 4.7 and 4.8 also give values for \(A, \Gamma\) and \(C\) in Table 4.2. The fitted curves are drawn as solid lines in the figures.

Unlike the case of Ce\(^{3+}\):LuPO\(_4\), resonances were detected using visible lasers. (See Table 4.1.) Since the visible lasers have narrower linewidths than the ultraviolet lasers, they may be expected to yield better data. Additionally, since the magnitude of the nonresonant susceptibility is extrapolated from its value at 1.06 \(\mu\)m, the value of \(\chi_{zzzz}^{(3)NR}\) is likely to be more accurate for the visible frequencies. The dynamic range for the 2161 cm\(^{-1}\)
resonance was much higher than the 2239 cm\(^{-1}\) resonance. As a result the 2161 cm\(^{-1}\) resonance may be expected to yield better data than the 2239 cm\(^{-1}\) resonance. The linewidths should be the same when measured with either laser setup. The difference in measured linewidths between the visible and ultraviolet spectra (0.55 and 0.60 cm\(^{-1}\) for the 2161 cm\(^{-1}\) resonance and 3.5 and 4.5 cm\(^{-1}\) for the 2239 cm\(^{-1}\) resonance) are indicative of the accuracy of the measurements. Estimated uncertainties in the data are included in Table 4.2.

Note that the peak CARS intensities are similar for 2161 cm\(^{-1}\) resonances. The ultraviolet spectrum has a greater figures of merit \((C = 4.8)\) compared to the visible spectrum \((C = 3.5)\). The ultraviolet spectra were recorded with broader linewidth lasers, and the effect is that the CARS peaks are suppressed to a greater degree than in the visible spectra which were recorded with narrower band lasers. The spectra do differ in the difference between maxima and minima. The difference between maxima, \((\omega_1 - \omega_2)_+\), and minima, \((\omega_1 - \omega_2)_-\), in the limit of zero-linewidth lasers is [54]:

\[
[(\omega_1 - \omega_2)_+ - (\omega_1 - \omega_2)_-]^2 = A^2 + 4\Gamma^2 \tag{4.10}
\]

The ultraviolet resonances have a larger difference between peak and valley than do the visible resonances due to a larger value of \(A\). Figure 4.9 shows the CARS resonances calculated using the data of Table 4.2, and assuming that the input lasers have negligible linewidth.

The linewidth of the higher lying level at 2239 cm\(^{-1}\) is much greater than the level at 2161 cm\(^{-1}\). The higher state may decay to the lower state by the spontaneous emission of a single phonon and is lifetime broadened. This broadening is enhanced by the existence of a 78 cm\(^{-1}\) optical phonon in the CeF\(_3\) crystal [42]. The lower level, on the other hand, requires the relatively unlikely simultaneous emission of several phonons to decay to the
ground $^2F_{5/2}$ manifold. The $\Gamma/2\pi c = 0.55$ cm$^{-1}$ linewidth of the lower level is probably due to ion-ion interactions which occur in fully concentrated rare earth crystals.

The quantity $|\chi^{(3)R}|_{\text{max}}$ may be calculated from Table 4.2. For the experiment with visible lasers, $|\chi^{(3)R}|_{\text{max}} \cdot \Gamma' = 1.5 \times 10^{-14}$ esu for the 2161 cm$^{-1}$ resonance and $0.6 \times 10^{-14}$ esu for the 2239 cm$^{-1}$ resonance. These values agree quite well with the prediction of the Axe theory given in equation (4.1). Because the calculation in the appendix neglected crystal field effects, the value given in equation (4.1) is the average value of $|\chi^{(3)R}|_{\text{max}}$ for the four Stark components of the $^2F_{7/2}$ manifold.

The parameter $A$ is related to the total spontaneous Raman cross section by (from equations (2.20), (2.23) and (2.24))

$$\sigma_z = \frac{32\pi \epsilon_0 c^4}{N c^4} A \chi^{(3)NR}_{zzzz}$$

where $\omega_z$ is the frequency of the scattered light (the Stokes frequency). The Raman cross sections (assuming $\omega_z = \omega_1$) are listed in Table 2. The Raman cross section in the visible region compares well with the estimated values in the appendix (equation (4.32)). The value in equation (4.32) is the sum of the Raman cross sections of the four levels of the $^2F_{7/2}$ manifold. The major uncertainty in the experimental values are due to the uncertainty in the non-resonant susceptibility (or equivalently, the nonlinear index of refraction). An accurate measurement of $n_2$ in CeF$_3$ in the $z$ polarization in at 476 nm and 355 nm would allow a more accurate absolute Raman cross section measurement.

Assuming that the 5$d$ levels are degenerate, and that the 5$d$ configuration dominates the electronic Raman processes, the dispersion of the maximum value of the resonant susceptibility is given in equations (4.15) and (4.17) of the appendix:

$$|\chi^{(3)R}_{zzzz}(-\omega_3, \omega_1, \omega_1, -\omega_2)|_{\text{max}}$$
This allows a comparison of values of $A$ for the visible and ultraviolet experiments. For the visible experiments, $\omega_1/2\pi c = 21000 \text{ cm}^{-1}$, $\omega_2/2\pi c = 18794.3 \text{ cm}^{-1}$ and $\omega_3/2\pi c = 23200 \text{ cm}^{-1}$. For the ultraviolet experiments, $\omega_1/2\pi c = 28191.5 \text{ cm}^{-1}$, $\omega_2/2\pi c = 26000 \text{ cm}^{-1}$ and $\omega_3/2\pi c = 30400 \text{ cm}^{-1}$. In the Axe approximation, $\omega_{5d}/2\pi c = 45000 \text{ cm}^{-1}$. Then

$$A_{uv} = \frac{\chi_{vis}^{(3)NR}}{\chi_{vis}^{(3)NR}} \left[ \frac{1}{(\omega_3 - \omega_{5d})} - \frac{1}{(\omega_1 + \omega_{5d})} \right] \left[ \frac{1}{(\omega_1 - \omega_{5d})} - \frac{1}{(\omega_2 + \omega_{5d})} \right]$$

or, upon inserting the above values (along with the nonresonant susceptibilities)

$$\frac{A_{uv}}{A_{vis}} = 1.43 \pm 0.21$$

The uncertainty in the above figure comes from the uncertainty in $\chi_{vis}^{(3)NR}/\chi_{uv}^{(3)NR}$. The experimental ratios, from Table 4.2, are $(A_{uv}/A_{vis}) (2161 \text{ cm}^{-1}) = 1.46 \pm 0.16$ and $(A_{uv}/A_{vis}) (2161 \text{ cm}^{-1}) = 2.23 \pm 0.95$. This agreement is quite good. In their analysis of the asymmetries in electronic Raman transitions in ErPO$_4$ and TmPO$_4$, Becker et al. [110] indicated that intermediate states of $d$ and $g$ electronic configurations make contributions of "equal significance." The above results indicate that the $5d$ configuration alone accounts for the dispersion of $|\chi^{(3)R}|_{\text{max}}$ in CeF$_3$.  

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4.4 Summary

Strong electronic CARS resonances have been observed in CeF$_3$. Figures of merit, $C = |\chi^{(3)}R/\chi^{(3)W}|_{\max} = A/\Gamma$, are an order of magnitude larger than measured previously in other pure rare earth crystals. This is due to the fairly large electronic Raman cross section which is, in turn, due to the relatively low 5$d$ configuration of the Ce$^{3+}$ ion. The absolute strengths of these resonances were accurately predicted using the Axe theory of two-photon processes and along with 4$f \rightarrow 5$d absorption data. Approximating the intermediate states by a single degenerate 5$d$ level at 45000 cm$^{-1}$ accounted for both the absolute magnitude and dispersion properties of $|\chi^{(3)}R|_{\max}$.

Appendix 4.1 Calculation of $|\chi^{(3)}R|_{\max}$ and $\sigma_{zz}$

A4.1.1 Application of the Axe Theory of Two-photon Processes

The quantity $|\chi^{(3)}_{zzzz}|_{\max}$ is calculated for an electronic CARS experiment in CeF$_3$ using visible lasers. A frequency-doubled Nd$^{3+}$:YAG laser provides $\omega_2/2\pi c = 18794.3$ cm$^{-1}$. A tunable laser operating in the 21000 cm$^{-1}$ region provides $\omega_1$. The CARS signal at $\omega_3 = 2\omega_1 - \omega_2$ is then in the $\omega_2/2\pi c = 23200$ cm$^{-1}$ region. (See Figure 4.1.) The quantity $|\chi^{(3)}_{zzzz}(-\omega_3, \omega_1, \omega_1, -\omega)|_{\max}$ for singly resonant CARS may be derived from equation (2.17):

$$|\chi^{(3)R}_{iii}|_{\max} = \frac{N A |\alpha_{ii}(\omega_3, \omega_1)\alpha_{ii}(\omega_1, \omega_2)|}{12 E_{\Gamma}}$$

(4.15)
where
\[
\alpha_{uv}(\omega_x, \omega_y) = \frac{1}{\hbar} \sum_n \left[ \frac{\langle g | e_r | n \rangle \langle n | e_r | f \rangle}{(\omega_x - \omega_{sn})} - \frac{\langle g | e_r | n \rangle \langle n | e_r | f \rangle}{(\omega_y + \omega_{sn})} \right]
\]

(4.16)

is the usual (nonresonant) Raman tensor (equation 2.18).

The first approximation is the assumption that the intermediate states, \(|n\rangle\), are dominated by the 5d levels at \(\omega_{5n}/2\pi c = 40000\) to \(50000\) cm\(^{-1}\). Other excited states of opposite parity are presumed to be too high in energy to contribute appreciably. The next approximation is originally due to Judd [105] and Ofelt [106], and was first applied to two-photon processes by Axe [104]. If the denominators do not cause the quantities in the summation to change rapidly as a function of \(n\), the denominators may be removed from the summation. This is equivalent to setting the energies of all the 5d levels to the same energy. That is, \(\omega_{5n}/2\pi c = \omega_{5d}/2\pi c = 45000\) cm\(^{-1}\). Equation (4.16) may now be written as

\[
\alpha_{ii}(\omega_x, \omega_y) = \frac{e^2}{\hbar} \left[ \frac{1}{(\omega_x - \omega_{5d})} - \frac{1}{(\omega_y + \omega_{5d})} \right] \sum_{all\ 5d\ states} \langle g | r_i | 5d \rangle \langle 5d | r_i | f \rangle
\]

(4.17)

The initial and final states are in the 4f configuration and the intermediate states are 5d.

Using the methods of Axe [104], the above summation simplifies to

\[
\sum_{all\ 5d\ states} \langle 4f \psi JM | z | 5d \rangle \langle 5d | z | 4f \psi J'M' \rangle
\]

\[
= \langle l = 3 \ | \ {C^{(1)}} | \ l = 2 \rangle^2 \ | 4f | r | 5d \rangle^2
\]

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\[ \times \sum_{\lambda = 0,2} (2\lambda + 1) \left( \begin{array}{c} 1 \\ 0 \end{array} \right) \left( \begin{array}{c} \lambda \\ 3 \end{array} \right) \left( \begin{array}{c} 1 \\ 2 \end{array} \right) \left( \begin{array}{c} 1 \\ 3 \end{array} \right) \langle 4f \psi J M | U_0^{(\lambda)} | 4f \psi J' M' \rangle (4.18) \]

The above equation may be evaluated if angular wavefunctions are available for both the initial and final states, and the quantity \( |\langle 4f | r | 5d \rangle| \) is known. Unfortunately, the 4f - 5d radial overlap varies from crystal to crystal, and accurate angular wavefunctions for Ce\(^{3+}\) in CeF\(_3\) (or LaF\(_3\)) are not known. As demonstrated below, an effective measure of \( |\langle 4f | r | 5d \rangle| \) may be derived from the 4f \( \rightarrow \) 5d absorption spectrum of Ce\(^{3+}\) in LaF\(_3\). For the 4f wavefunctions, those of the free Ce\(^{3+}\) ion are used.

A4.1.2 Calculating \( |\langle 4f | r | 5d \rangle| \) for Ce\(^{3+}\) in CeF\(_3\)

In the crystal field model, the crystal field Hamiltonian acts only upon angular variables. The radial wavefunctions are presumed to be unaffected by the crystal field interaction. However, studies [23, 25, 107, 111, 112] indicate that the 5d radial wavefunction may be sensitive to the local crystal environment, and the quantity \( |\langle 4f | r | 5d \rangle| \) can vary considerably from crystal to crystal. The 4f wavefunction has no radial node while the 5d radial wavefunction has two nodes, one near the maximum of the 4f radial wavefunction. (See Figure 4.10.) Since the interaction of the the 5d electron with the host lattice is much greater than the 4f electron, a small change in the 5d radial wavefunction can significantly alter the radial overlap. Therefore, a calculation of \( |\langle 4f | r | 5d \rangle| \) from the free ion wavefunctions cannot be applied to this work. An effective measurement of \( |\langle 4f | r | 5d \rangle| \) may be derived from the 4f \( \rightarrow \) 5d oscillator strength of the Ce\(^{3+}\) ion in the (Ce,La)F\(_3\) environment.

The oscillator strength, \( f \), is related to the absorption coefficient, \( a \), by [113]
\[ f = \frac{mc^2}{\pi e^2 N} \int a(\sigma) \, d\sigma \quad (4.19) \]

where \( \sigma = 1/\lambda \). The oscillator strength is related to the dipole matrix element between the initial state \( |i\rangle \) and final state \( |f\rangle \) by [105]

\[ f = \frac{2m \omega (n^2 + 2)^2}{\hbar} \frac{1}{9n} |\langle i | r | f \rangle|^2 \quad (4.20) \]

Both Erlich et al. [38] and Elias et al. [36] have measured the ultraviolet absorption spectra of Ce\(^{3+}\):LaF\(_3\). Integration of the total spectra according to equation (4.19) yields a total oscillator strength for the ground state to \( 5d \) configuration transition. The oscillator strength should not depend on Ce\(^{3+}\) concentration, so that the Ce\(^{3+}\):LaF\(_3\) values should apply to CeF\(_3\). Erlich et al. measured the spectra of 0.05 mol % Ce\(^{3+}\) in LaF\(_3\) at room temperature. Measurement of the area under the \( 4f \rightarrow 5d \) absorption spectrum gave \( f = 2.2 \times 10^{-2} \). Elias et al. measured the absorption spectra of 0.01 mol % Ce\(^{3+}\) in LaF\(_3\) at 100 K. The area under the spectrum gave \( f = 1.8 \times 10^{-2} \), and there was no polarization dependence. For the purposes of this calculation, we shall assume that all levels of the \( ^2F_{5/2} \) manifold contribute equally to the absorption spectrum to give a \( 4f \rightarrow 5d \) oscillator strength of \( f = 2 \times 10^{-2} \). From equation (4.20) and \( f = 2 \times 10^{-2} \)

\[ \sum_{\text{all } 5d \text{ states}} |\langle i | z | 5d \rangle|^2 = 9.1 \times 10^{-19} \text{ cm}^2 \quad (4.21) \]

Since all levels of the \( ^2F_{5/2} \) manifold are assumed to be equally occupied, the initial state is
\[ |i\rangle = |F_{5/2}\rangle = \frac{1}{\sqrt{6}} 2F \langle 5/2, \pm 5/2 \rangle + |5/2, \pm 3/2 \rangle + |5/2, \pm 1/2 \rangle \]  

(4.22)

and the small amount of J-mixing is ignored. The summation in equation (4.21) may be calculated with the aid of equation (4.18) and the quantities \( \langle 3 \parallel C^{(1)} \parallel 2 \rangle = 31/2 \), and

\[ \langle 4f \psi JM | U_0^{(0)} | 4f \psi' J'M' \rangle = \frac{1}{\sqrt{7}} \delta(\psi JM, \psi' J'M') \]  

(4.23)

to give

\[ \sum_{\text{all } 5d \text{ states}} |\langle i \mid z \mid 5d \rangle|^2 = \frac{1}{7} \langle 4f \mid r \mid 5d \rangle|^2 \]  

(4.24)

(The \( \lambda = 2 \) term in equation (4.18) is zero when summed over all \( M \).) Judd [114] has derived an equivalent result. Combining equation (4.21) with (4.24) gives

\[ |\langle 4f \mid r \mid 5d \rangle| = 0.25 \text{ Å} \]  

(4.25)

This compares with a value calculated for the free ion radial wavefunctions of \( |\langle 4f \mid r \mid 15d \rangle| = 0.441 \text{ Å} \) [24]. (Recently, Lyu and Hamilton [115] have calculated \( |\langle 4f \mid r \mid 15d \rangle| = 0.29 \text{ Å} \) from lifetime measurements of Ce\(^{3+} \) in LaF\(_3 \).

**A4.1.3 Wavefunctions for Ce\(^{3+} \) in CeF\(_3 \)**

Accurate wavefunctions for the electronic states of the 4f configuration of the Ce\(^{3+} \) ion in CeF\(_3 \) are not available. Fourteen crystal field parameters are needed to characterize the Stark splitting of a 4f electron at a site of \( C_2 \) symmetry. Crystal field parameters are...
determined by a least squares fit of the energy levels to the crystal field Hamiltonian, and the angular wavefunctions are the eigenstates of the Hamiltonian. In the case of Ce$^{3+}$, the seven energy levels of the $4f$ configuration are insufficient to uniquely determine the fourteen crystal field parameters. Additionally, as discussed earlier, the only well determined energy levels of the $4f$ configuration are the the four Stark components of the $2F_{7/2}$ manifold. Attempts to model the Ce$^{3+}$:LaF$_3$ crystal field by assuming a higher symmetry such as $C_{2v}$ or $D_{3h}$ (which decreases the number of crystal field parameters), have proven unsatisfactory [34].

Without wavefunctions of the initial and final states, equation (4.18) cannot be exactly solved. Approximations are necessary. As before, we assume that there is no $J$-mixing. For $4f$ electrons, a weak crystal field only mixes the $J$ character of the $4f$ levels slightly. Additionally, we assume that the wavefunctions of the Stark components have spherical (i.e. atomic) symmetry as in the free ion. This is equivalent to a zero crystal field approximation. Thus,

$$|^2F_{5/2}\rangle = \frac{1}{\sqrt{6}} \, 2^F (|5/2, \pm 5/2\rangle + |5/2, \pm 3/2\rangle + |5/2, \pm 1/2\rangle)$$

(4.26a)

$$|^2F_{7/2}\rangle = \frac{1}{\sqrt{8}} \, 2^F (|7/2, \pm 7/2\rangle + |7/2, \pm 5/2\rangle + |7/2, \pm 3/2\rangle + |7/2, \pm 1/2\rangle)$$

(4.26b)

The zero crystal field approximation is likely to be better for a Ce$^{3+}$ ion at a site of low symmetry (such as $C_2$) than at a site of high symmetry. Like the free ion wavefunctions, the angular wavefunction for a Stark component of a low symmetry ion will contain all $M$ ($|M| \leq J$) values, and no selection rules exist. Additionally, the crystal field has only a second-order influence on the electronic Raman process. That is, the
crystal field is responsible for the distribution of Raman intensity among the Stark components of a given manifold. Use of equation (4.18), $\langle 2F_{5/2} \parallel U^{(2)} \parallel 2F_{7/2} \rangle = 0.350$, the Wigner-Eckart theorem, and the orthogonality relation

$$
\langle \psi J' | \mathcal{M}_{q}^{(k)} | \psi' J'M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k \\ -M & q \end{pmatrix} \begin{pmatrix} J' \\ M' \end{pmatrix} \langle \psi J || \mathcal{T}^{(k)} || \psi' J' \rangle
$$

(4.27)

and the orthogonality relation

$$
\sum_{j_1, j_2, k} \begin{pmatrix} j_1 & j_2 & k \\ m_1 & m_2 & q \end{pmatrix} \begin{pmatrix} j_1 & j_2 & k' \\ m_1 & m_2 & q' \end{pmatrix} = \frac{1}{(2k+1)} \delta(k, k') \delta(q, q')
$$

(4.28)

gives

$$
\left| \sum_{\text{all } 5d \text{ states}} \langle 2F_{5/2} \parallel z \parallel 5d \rangle \langle 5d \parallel z \parallel 2F_{7/2} \rangle \right|^2 = 6.06 \times 10^{-3} \left| \langle 4f \parallel r \parallel 5d \rangle \right|^4
$$

(4.29)

Now the quantity $|\chi_{zzzz}^{(3)R}|_{\text{max}}$ may be estimated for $2F_{5/2} \leftrightarrow 2F_{7/2}$ Raman transitions. Use of equations (4.15), (4.17), (4.25) and (4.29) gives $|\chi_{zzzz}^{(3)R}|_{\text{max}} = 5.1 \times 10^{-14}$ esu. This value is actually the sum of $|\chi_{zzzz}^{(3)R}|_{\text{max}}$ for the four Stark components of the $2F_{7/2}$ manifold (if one assumes that each level has a linewidth $\Gamma/2\pi c = 1$ cm$^{-1}$). One might then expect that for each Stark level

$$
|\chi_{zzzz}^{(3)R}|_{\text{max}} (2F_{5/2} \leftrightarrow 2F_{7/2}) \approx \frac{5.1 \times 10^{-14} \text{ esu}}{4 \times (\text{HWHM linewidth in cm}^{-1})}
$$

(4.30)

This value is on the high end of resonant susceptibilities for singly resonant electronic CARS experiments in rare earth crystals as discussed in section 2.3.1.
A4.1.4 Calculation of the Raman Cross Section

The above analysis also applies to the calculation of the total spontaneous Raman cross section for transitions from the $2^2F_{5/2}$ ground state to the Stark levels of the $2^2F_{7/2}$ manifold. The total (not differential) Raman cross section is related to the Raman in tensor equation (4.16) by

$$\sigma_{zz} = \frac{8 \pi \Lambda \omega_s^4 |\alpha_{zz}|^2}{3 c^4}$$

(4.31)

where $\omega_s$ is the frequency of scattered light (the Stokes frequency). This leads to a Raman cross section of (assuming $\omega_s/2\pi c = 21000$ cm$^{-1}$)

$$\sigma_{zz}(2^2F_{5/2} \leftrightarrow 2^2F_{7/2}) = 1.6 \times 10^{-29}$ cm$^2$ (4.32)

Again, the above expression is the sum of Raman cross sections for the four Stark components of the $2^2F_{7/2}$ manifold. This is on the high end of the range of ERS cross sections [73]. For comparison, Williams et al. [23, 25] measured $\sigma_{zz} = 1.4 \times 10^{-29}$ cm$^2$ for the four $2^2F_{7/2}$ Stark components in Ce$^{3+}$:LuPO$_4$. 

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Appendix 4.2  Stimulated Electronic Raman Gain

A4.2.1  Introduction

Finally, I discuss stimulated electronic Raman scattering in rare earth crystals. The data collected in the electronic CARS experiments in CeF$_3$ enables a calculation of the stimulated Raman gain coefficient. I observed no electronic stimulated Raman gain in CeF$_3$. This was due to mainly to the low crystal damage threshold.

Stimulated electronic Raman scattering has been observed in atomic vapors, but never involving the electronic states of ions in crystals. While the energies of molecular vibrations are limited to the infrared, the energies of electronic transitions may be in the infrared, visible or ultraviolet. As a consequence, electronic stimulated Raman scattering may shift the frequency of an input laser by tens of thousands of cm$^{-1}$, while vibrational stimulated Raman scattering only shifts frequencies by thousands of cm$^{-1}$. Since CeF$_3$ has a large electronic Raman cross section (for a rare earth system), it is a good system on which to begin the investigation of stimulated electronic Raman gain in crystals.

Like CARS and two-photon absorption, stimulated Raman scattering may be viewed within the framework of four-wave mixing. In the stimulated Raman effect, the presence of a lightwave at frequency $\omega_p$ causes a lightwave at frequency $\omega_s$ to be amplified when $\delta(\omega_p - \omega_s)$ is equal to the energy of a Raman transition. The initial growth of the Stokes wave, $I_s$, compared to its initial value $I_s(0)$ is given by [54]

$$I_s = I_s(0) \exp \left[ g_R ll_p \right]$$  \hspace{1cm} (4.33)
where \( g_R \) is the Raman Gain coefficient, \( l \) is the distance over which both lightwaves interact, and \( I_p \) is the intensity of the lightwave at \( \omega_p \) (the "pump" frequency). The Raman gain coefficient is related to the spontaneous Raman cross section, \( \sigma \), by [54]:

\[
g_R = \frac{3N \pi c^2 n_p \sigma}{\omega_p \omega^2 n^2 \Gamma}
\]  

This quantity may be calculated from the linewidths and electronic Raman cross sections listed in Table 4.2. For \( \omega_p/2\pi c = 28192 \text{ cm}^{-1} \), the Raman gain for the 2161 cm\(^{-1}\) level at 3.8 K is

\[
g_R = 0.52 \frac{\text{cm}}{\text{GW}}
\]  

(4.35)

For \( \omega_p/2\pi c = 21000 \text{ cm}^{-1} \), the Raman gain is for the 2161 cm\(^{-1}\) level is

\[
g_R = 0.21 \frac{\text{cm}}{\text{GW}}
\]  

(4.36)

Since \( g_R \) is inversely proportional to the linewidth, the gain for the other states of the 4f configuration will be much smaller. Recall that the Stark components of the \( ^2F_{5/2} \) manifold are vibronically broadened by \( \sim 100 \text{ cm}^{-1} \).

Equation (4.34) gives a value of \( g_R = 1.9 \text{ cm/GW} \) for the 992 cm\(^{-1}\) vibration in benzene in the visible region \((N = 7 \times 10^{21} \text{ cm}^{-3}, \Gamma/2\pi c = 1.2 \text{ cm}^{-1}, \sigma = 2.7 \times 10^{-28} \text{ at } \omega_p/2\pi c = 21000 \text{ cm}^{-1} [72])\). For the 1085 cm\(^{-1}\) vibrational mode in a calcite (CaCO\(_3\)) crystal, a measurement of the Raman gain gave 13 cm/GW [116]. Thus, the calculated electronic Raman gain in CeF\(_3\) at low temperature is several times smaller than vibrational Raman gain in common materials.
A4.2.2 Experimental

The apparatus used to detect Raman Gain is shown in Figure 4.11. A laser pulse of frequency $\omega_p$ is focused on the sample with a 15 cm lens. The light passes through 1 cm of the sample. Spontaneous Raman scattering produces photons of energy $\hbar \omega_s = \hbar (\omega_p - \omega_R)$. The photons of frequency $\omega_s$ which travel along the path of the pump beam are amplified according to equation (4.33). The iris blocks off-axis scattered light which consists primarily of spontaneous Raman photons. A lens collimates the light, and a prism separates $\omega_s$ and $\omega_p$. The Stokes beam is focused into the SPEX 1403 double monochromator. The Stokes signal is detected with the same photomultiplier tube and electronics as in Chapter 2. A variety of pump sources (frequency-doubled and tripled Nd$^{3+}$:YAG, pulsed dye lasers, and frequency-doubled pulsed dye lasers) were used to cover the range $\omega_p/2\pi c \sim 18000 \text{ cm}^{-1}$ to $\sim 33000 \text{ cm}^{-1}$. A nonlinear relationship between the intensity of the pump and the Stokes intensity indicates stimulated Raman gain.

In benzene and calcite samples ($\sim 1 \text{ cm thickness at room temperature}$) stimulated vibrational Raman gain was easily observed. In both cases stimulated Raman gain was observed at pump energies of $\sim 100 \mu J/pulse$. (The low threshold in benzene is due to self-focusing of the pump beam [54].) At slightly higher energies, a fair fraction of the pump beam was converted to a coherent beam at the Stokes frequency, and the signal was clearly visible to the naked eye.

No stimulated electronic Raman gain was observed in CeF$_3$ at 3.8 K. The pump beam could be polarized either parallel or perpendicular to the crystal axis. The frequency of the input light ranged from $\sim 18000 \text{ cm}^{-1}$ to $\sim 33000 \text{ cm}^{-1}$. When the frequency-tripled Nd$^{3+}$:YAG was used as the pump ($\omega_p/2\pi c = 28191.5 \text{ cm}^{-1}$), the threshold for crystal
damage was $\sim 700 \mu J/pulse (\sim 1 \text{ GW/cm}^2)$. At higher pump frequencies, the damage threshold was lower. No stimulated electronic Raman gain was seen below the onset of crystal damage.

A4.2.3 Analysis

The experimental apparatus described above is adequate for the demonstration of stimulated Raman gain if the gain coefficient is high enough. Since the spatial profile of the pump beam as it passes through the sample is not well known, it is difficult to put an upper limit on the electronic Raman gain coefficient of CeF$_3$. Other experimental arrangements permit accurate quantitative measurements. The best methods use stable cw pump and probe beams, and detect the small change in the probe intensity induced by the pump beam [55].

Optical fibers are perhaps the most appropriate structures for stimulated Raman scattering since they provide beam confinement and long interaction lengths. In a silica glass fiber, the maximum vibrational Raman gain coefficient is $\sim 0.01 \text{ cm/GW}$ [117], and stimulated Raman scattering, Raman amplification, and Raman lasing have been observed. If one assumes that the linewidth of the 2161 cm$^{-1}$ electronic level in CeF$_3$ increases by an order of magnitude at room temperature, then $g_R \sim 0.01 \text{ cm/GW}$ (from equation (4.36)). If a CeF$_3$ single crystal fiber were fabricated, one then may expect to observe electronic Raman gain at room temperature.
<table>
<thead>
<tr>
<th></th>
<th>visible</th>
<th>ultraviolet</th>
</tr>
</thead>
</table>
| $\omega_1$ | Coumarin 500 dye  
$\omega_1/2\pi c \approx 21000 \text{ cm}^{-1}$ (tunable)  
$\Delta \omega_1/2\pi c = 0.25 \text{ cm}^{-1}$ | tripled Nd$^{3+}$:YAG  
$\omega_1/2\pi c = 28191.5 \text{ cm}^{-1}$ (fixed)  
$\Delta \omega_1/2\pi c = 0.80 \text{ cm}^{-1}$ |
| $\omega_2$ | Nd$^{3+}$:YAG 2nd harmonic  
$\omega_2/2\pi c = 18794.3 \text{ cm}^{-1}$ (fixed)  
$\Delta \omega_2/2\pi c = 0.52 \text{ cm}^{-1}$ | Quinolon 390 dye  
$\omega_2/2\pi c = 26000 \text{ cm}^{-1}$ (tunable)  
$\Delta \omega_2/2\pi c = 0.60 \text{ cm}^{-1}$ |

**TABLE 4.1.** Characteristics of the lasers used in this chapter. Linewidths are FWHM.
<table>
<thead>
<tr>
<th></th>
<th>$\omega/2\pi c$</th>
<th>$ijji$</th>
<th>$A/2\pi c$</th>
<th>$\Gamma/2\pi c$</th>
<th>$C$</th>
<th>$\sigma_{zz}$</th>
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<tr>
<td>(cm$^{-1}$)</td>
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<td>($\text{cm}^{-1}$)</td>
<td>($\text{cm}^{-1}$)</td>
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<td>(cm$^2$)</td>
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<tr>
<td>$\omega_1 = 21000\text{ cm}^{-1}$</td>
<td>2161</td>
<td>$zzzz$</td>
<td>1.95$\pm$0.10</td>
<td>0.55$\pm$0.03</td>
<td>3.5</td>
<td>$(5.0\pm1.1) \times 10^{-30}$</td>
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<tr>
<td>$\omega_2 = 18794.3\text{ cm}^{-1}$</td>
<td>2239</td>
<td>$zzzz$</td>
<td>0.72$\pm$0.22</td>
<td>3.5$\pm$1.0</td>
<td>0.21</td>
<td>$(1.9\pm0.7) \times 10^{-30}$</td>
</tr>
<tr>
<td>$\chi^{(3)NR}_{zzzz} =$</td>
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<td></td>
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<tr>
<td>$(8.0\pm2.0) \times 10^{-15}\text{ esu}$</td>
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<tr>
<td>$\omega_1 = 28191.5\text{ cm}^{-1}$</td>
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<td>$zzzz$</td>
<td>2.85$\pm$0.29</td>
<td>0.60$\pm$0.06</td>
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<td>$(2.9\pm0.9) \times 10^{-29}$</td>
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<tr>
<td>$\omega_2 = 26000\text{ cm}^{-1}$</td>
<td>2239</td>
<td>$zzzz$</td>
<td>1.6$\pm$0.5</td>
<td>4.52$\pm$1.4</td>
<td>0.36</td>
<td>$(1.6\pm0.7) \times 10^{-29}$</td>
</tr>
<tr>
<td>$\chi^{(3)NR}_{zzzz} =$</td>
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<td></td>
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</tr>
<tr>
<td>$(9.7\pm2.9) \times 10^{-15}\text{ esu}$</td>
<td>2161</td>
<td>$zzzz$</td>
<td>2.35$\pm$0.25</td>
<td>0.50$\pm$0.05</td>
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</tr>
<tr>
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<td>0.50$\pm$0.05</td>
<td>4.7</td>
<td>-</td>
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</tr>
<tr>
<td>2239</td>
<td>$yyzy$</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 4.2. Summary of the data and estimated uncertainties. ($C = |\chi_{ijji}^{(3)R}/\chi_{ijji}^{(3)NR}|_{\text{max}} = A/\Gamma$). The total spontaneous Raman cross section, $\sigma_{zz}$, is related to $A$ and $\chi_{zzzz}^{(3)NR}$ through equation (4.11).
FIGURE 4.1. Schematic diagram of singly resonant electronic CARS in CeF$_3$ using visible lasers. A frequency doubled Nd$^{3+}$:YAG laser provides a fixed $\omega_2/2\pi c = 18794$ cm$^{-1}$. A tunable dye laser provides $\omega_1/2\pi c = 21000$ cm$^{-1}$. Energy levels are not drawn to scale. Only the energy levels measured in this chapter are drawn.
FIGURE 4.2.(a). Linear intensity scale: Intensity of CARS signal, normalized to the off resonance intensity, at frequency $\omega_3$ as a function of $\omega_1 - \omega_2$ with the visible lasers polarized in the z direction. Solid line is a fit to the parameters listed in Table 4.2. ($A/2\pi c = 1.95 \text{ cm}^{-1}, \Gamma/2\pi c = 0.55 \text{ cm}^{-1}$)
FIGURE 4.2.(b). Logarithmic intensity scale: Intensity of CARS signal, normalized to the off resonance intensity, at frequency $\omega_3$ as a function of $\omega_1 - \omega_2$ with the visible lasers polarized in the $z$ direction. Solid line is a fit to the parameters listed in Table 4.2. ($A/2\pi c = 1.95 \text{ cm}^{-1}, \Gamma/2\pi c = 0.55 \text{ cm}^{-1}$)
FIGURE 4.3. Intensity of CARS signal, normalized to the off resonance intensity, at frequency $\omega_3$ as a function of $\omega_1 - \omega_2$ with the visible lasers polarized in the $z$ direction. Solid line is a fit to the parameters listed in Table 4.2. ($A/2\pi c = 0.72 \text{ cm}^{-1}$, $\Gamma/2\pi c = 3.47 \text{ cm}^{-1}$).
FIGURE 4.4. (a) Phase matching condition for CARS: $k_3 = 2k_1 - k_2$. (b) Phase matching impossible for CARS in CeF$_3$ in zxxz polarization. (c) Phase matching for CARS in CeF$_3$ in the xzzx polarization.

FIGURE 4.5. $\theta'$ is the angle between $\omega_1$ and $\omega_2$ outside of the medium with index of refraction $n$. Inside the medium the angle is $\theta$. $\theta$ and $\theta'$ are related by Snell's law: $n \sin (\theta/2) = \sin (\theta'/2)$. 
FIGURE 4.6.(a). Linear intensity scale: Intensity of CARS signal, normalized to the off resonance intensity, at frequency $\omega_3$ as a function of $\omega_1 - \omega_2$ with the ultraviolet lasers polarized in the $z$ direction. Solid line is a fit to the parameters listed in Table 4.2. ($A/2\pi c = 2.85$ cm$^{-1}$, $\Gamma/2\pi c = 0.60$ cm$^{-1}$)
FIGURE 4.6.(b) Logarithmic intensity scale: Intensity of CARS signal, normalized to the off resonance intensity, at frequency $\omega_3$ as a function of $\omega_1 - \omega_2$ with the ultraviolet lasers polarized in the $z$ direction. Solid line is a fit to the parameters listed in Table 4.2. ($A/\pi c = 2.85 \text{ cm}^{-1}, \Gamma/\pi c = 0.60 \text{ cm}^{-1}$)
FIGURE 4.7. Intensity of CARS signal, normalized to the off resonance intensity, at frequency $\omega_3$ as a function of $\omega_1 - \omega_2$ with the ultraviolet lasers polarized in the $z$ direction. Solid line is a fit to the parameters listed in Table 4.2. ($A/2\pi c = 1.61 \text{ cm}^{-1}$, $\Gamma/2\pi c = 4.52 \text{ cm}^{-1}$)
FIGURE 4.8. Intensity of CARS signal, normalized to the off resonance intensity, at frequency $\omega_3$ as a function of $\omega_1 - \omega_2$. Closed squares refer to $\chi^{(3)}_{xzzx}$ and open squares refer to $\chi^{(3)}_{yzzy}$. Solid line is a fit to the parameters listed in Table 4.2.
Figure 4.9. CARS resonances calculated from the data of Table 4.2, assuming that the input lasers have negligible bandwidths ($\Delta\omega_{\text{laser}} < 2\Gamma$).
FIGURE 4.10. Radial wavefunctions \( r \langle nl \mid r \rangle \) as a function of \( r \) for the Ce\(^{3+}\) free ion. From a Hartree-Fock calculation [50].
FIGURE 4.11. Schematic diagram of apparatus used to investigate stimulated electronic Raman gain in CeF$_3$. The frequency of the incident light is $\omega_p$, and $\omega_R/2\pi c = 2161$ cm$^{-1}$. 
References


[50] N. Edelstein (private communication).


[58] The factor of 12 is added to conform to the notation of Maker and Tehrune (Phys. Rev. 137, A801 (1965)).


