Doubly-resonant two-photon-absorption-induced four-wave mixing in Tb(OH)3 and LiTbF4
by David Adams Ender

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Physics
Montana State University
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Abstract:
Doubly-resonant two-photon-absorption-induced four-wave mixing has been observed for the first time in a rare earth insulator. The generation of the nonlinear signal exhibits strong intermediate and two-photon resonances in crystalline Tb (OH)3 and LiTbF4 This provides a novel method for high resolution measurements of intermediate $4f^n$ configurations and excited configurations of rare earth ions.

The intermediate resonance showed spectral line narrowing up to ten times narrower than the corresponding inhomogeneously broadened absorption. In LiTbF4, laser-limited line widths were obtained and in Tb(OH)3, a homogeneous limit corresponding to $T_2 = 50$ psec may have been reached. The qualitative behavior of the narrowing is explained by the dispersion of the anamalous index of refraction and its effect on phase matching. Direct measurement of the anamalous dispersion was made to test the model. Results indicate nonlinear contributions to the refractive index may have been present.

The two-photon resonance in Tb(OH)3 was measured to be a 230 cm^-1 wide crystal field component of the broad $4f^n$ 5d excited configuration. Thus high resolution UV spectroscopy with tunable visible lasers is demonstrated.

Applications are discussed including the extraction of homogeneous line widths from inhomogeneously broadened spectra, coherent transient measurements, and UV and VUV spectrosocpy. The latter uses different selection rules than linear absorption methods and allows study of transitions between excited states.

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iii

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TABLE OF CONTENTS

v

LIST OF TABLES

LIST OF FIGURES

List of Figures, Continued

Abstract

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Chapter 1

HISTORY AND SURVEY

The propagation of an intense laser beam in matter often generates light at frequencies different than that of the laser itself. Several laser beams can create light at a mixture of frequencies. In addition, such light mixing can interact coherently with the medium of propagation as well as exhibit resonant behavior. The branch of optics describing these phenomena is called nonlinear optics.

The subject of this thesis deals with the first observation of two nonlinear optical effects: (1) doubly-resonant two-photon absorption-induced four-wave mixing (TPAFWM) in rare earth insulators (specifically $Tb(OH)_3$ and $LiTbF_4$), and (2) phase matching induced line narrowing.

The initial observation of the TPAFWM signal was made by Rufus Cone and Joel Friedman at Bell Telephone Laboratories, Murray Hill.[1] Light at $\omega_4 = \omega_1 + \omega_2 - \omega_3$ was observed upon application of beams at frequencies ω_1, ω_2 and ω_3. The ω_4 beam intensity exhibits resonant behavior as the input beams are tuned relative to transitions of the crystal, making this technique highly useful for spectroscopy.

The surprising thing found at Murray Hill was the extreme spectral narrowing exhibited by the ω_4 signal

inside the corresponding ω_1 absorption line shape (see Figure 1.1). Subsequent observations at Montana State University showed that the narrowed line could be driven from one side of the ω_1 resonance to the other upon variation of the beam crossing angles.[2] This report confirms this as a TPAFWM process and explains the nature of the narrowing, the peculiar shape, and its spectral motion. Utilization of this process as a spectroscopic tool will also be discussed.[3]

History

The field of nonlinear optics was ushered in by the classic experiment done in July of 1961 by Franken, Hill, Peters, and Weinreich[4] in which second harmonic generation (SHG) was first measured. Light from a ruby laser at 6943 Å was focused into a crystalline quartz sample as in Figure 1.2. The resultant beam was spectrally analyzed yielding photographic plates showing not only light at 6943 A but also a faint spot at 3471.5 Å. The conversion efficiency was 10^{-8}. Today, efficiencies close to one are routinely achieved.[5]

Nonlinear optical effects arise from higher order terms of the induced polarization of a medium which is

(a.)

(b.)

T = 1.3K

1 cm^{-1}
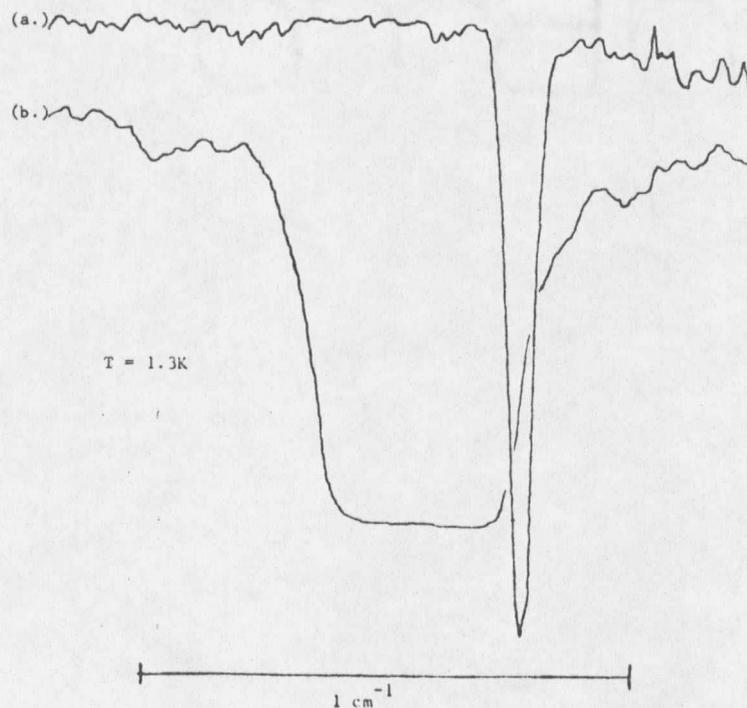
Figure 1.1.(a.) Four-wave mixing signal, and (b.) corres-
ponding absorption for the $^5D_4\Gamma_1$ state of
LiTbF$_4$. ω_3 = 17422 cm^1. Crossing angle
θ = 1.50°.

written as an expansion in powers of E/E_{at}:

$$P = \chi E (1 + C_1 \frac{E}{E_{at}} + C_2 (\frac{E}{E_{at}})^2 + \dots) \qquad (1.1)$$

The C_i are expansion coefficients of order one and $E_{at} \sim$
$\frac{e}{a_o^2}$ = 1.7 x 10^7 statvolts/cm is the typical atomic field
an electron sees in a transparent insulator (a_o = one Bohr
radius).

Figure 1.2. Second harmonic generation in crystalline quartz. The ruby laser emits at 6943.0Å. The sample generates light at 3471.5Å.
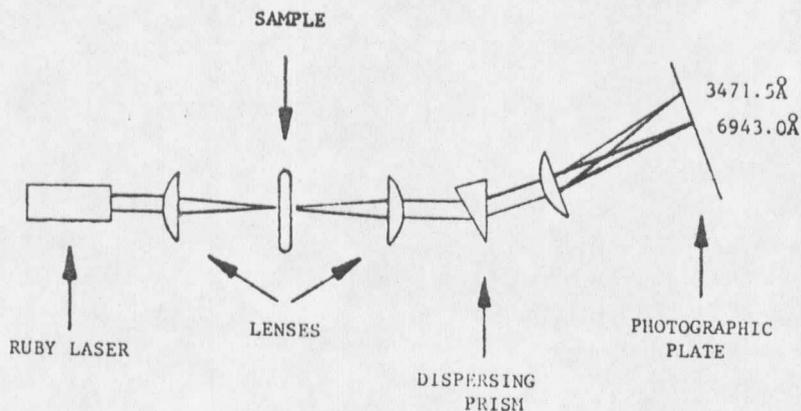
This oscillating polarization acts as a source term in Maxwell's equations generating light at the various frequencies given by a Fourier decomposition of P.

One usually rewrites Equation (1.1) as

$$\vec{P} = \varepsilon_0 \chi^{(1)} \cdot \vec{E} + \chi^{(2)} : \vec{E}\vec{E} + \chi^{(3)} \vdots \vec{E}\vec{E}\vec{E} + \ldots, \qquad (1.2)$$

where the tensor coefficients of the electric field are referred to as the linear ($\chi^{(1)}$) and nonlinear ($\chi^{(2)}$, $\chi^{(3)}$, ...) electric susceptibilities of the medium.

We can see immediately that the oscillation of the parent electric field at frequency ω in Franken's SHG

experiment will generate a polarization in the medium oscil-lating at 2ω for nonzero $\chi^{(2)}$. Likewise, higher order terms will produce other harmonics and for situations involving input waves of distinct frequencies various sum and difference frequencies will be generated. Nonlinear optics is a colorful subject.

Nonlinear effects in the polarization have been studied since the nineteenth century (Pockels and Kerr effects).[6] However, it wasn't until the advent of the laser in July of 1960 that the ability was obtained to generate light waves intense enough to utilize the higher order terms in the expanded polarization.[7]

Consequently, little motivation existed to develop a global theoretical approach to the many nonlinear optical effects awaiting discovery. The years from 1961 to the present have been spent primarily laying the theoretical framework, fitting new observations into it, and working out the finer details of the theory.

While the future still holds promise for the discovery of new effects, the majority of workers in the field are directing their research more toward device applications[8] or applications of nonlinear optical spectroscopy. The latter topic is considered important enough that Nicholaas

Bloembergen and Arthur Schawlow won the 1981 Nobel prize in physics for their work in the field.[9] In particular, it is Bloembergen's work in four-wave mixing that forms the background for this thesis.

Nonlinear Spectroscopy

Several general reviews exist on the field of nonlinear optical spectroscopy. Bloembergen has written several excellent articles on nonlinear optics for which two are exceptionally comprehensive.[10] Hänsch,[11] Levenson,[12] and Brewer[13] each have short topical articles with good reference lists on some of the more important subfields on nonlinear optical spectoscopy. More recent reviews are given by Levenson and Song[14] and Laubereau and Kaiser[15] on coherent Raman spectroscopy and coherent time domain Raman spectroscopy respectively. The former is worthwhile on the basis of its reference list alone.

Nonlinear laser spectroscopy provides information in both frequency and temporal domains. In many cases it offers distinct advantages over linear spectroscopy. These include higher resolution and signal sensitivity. Dynamics of collective excitations, both coherent and incoherent, can be studied, and multiphoton processes enable different

sets of selection rules to be used.

Frequency Domain Spectroscopy

Many methods have been developed for spectroscopy in the frequency domain. Use of the third order susceptibility $\chi^{(3)}$ provides such techniques as stimulated Raman scattering (SRS),[14,16,17] coherent antistokes Raman spectroscopy (CARS),[12,14,18] coherent Stokes Raman spectroscopy (CSRS),[19,20] two-photon-absorption-induced four-wave mixing (TPAFWM),[21,22,23] and degenerate four-wave mixing (DFWM).[24,25,26] A chief advantage of these techniques lies in the fact that the output signal is generally separated spatially from the input beams and is of a different frequency. Thus easy signal discrimination is obtained.

The ability to measure homogeneous linewidths inside of inhomogeneously broadened[27] spectral lines is a topic of much interest. By measuring the width of the homogeneous line one obtains the associated relaxation time. This provides insight into the dynamics of the excited state. Certain nonlinear techniques can extract this information where linear techniques fail.

One such method, saturation or hole-burning spectroscopy,[28,29] involves saturating the narrower homogeneous

part of the inhomogeneous line with a strong pump laser,
then probing the absorption profile with a weaker probe
beam. When the probe frequency comes into the saturated
part of the absorption, it is no longer absorbed. Thus, an
absorption profile with a "hole" is mapped out. The hole
provides a measure of the homogeneous linewidth.

Doppler-free two-photon spectroscopy[11,30] comple-
ments single photon spectroscopy in that it provides spectral
information between states of the same parity. It is espe-
cially valuable in studying gases where the photon
frequencies are Doppler shifted as viewed by molecules
traveling with different velocities. This inhomogeneously
broadens the transition. By utilizing photons traveling
in opposite directions, the first order Doppler shifts
cancel yielding nearly homogeneous line shapes in the
fluorescence spectrum.

Nonlinear polarization spectroscopy[11,31,32] is
closely related to saturation spectroscopy. However, rather
than monitoring the probe's absorption, the polarization is
examined. The pump laser induces a birefringence in the
sample which changes the polarization of the probe. By
placing the sample between crossed polarizers, very high
signal-to-noise ratios are possible. When the pump and