D. C. Hanna M. A. Yuratich D. Cotter

Nonlinear Optics of Free Atoms and Molecules

D. C. Hanna M. A. Yuratich D. Cotter

Nonlinear Optics of Free Atoms and Molecules

With 89 Figures

Springer-Verlag Berlin Heidelberg New York 1979

DAVID C. HANNA, Ph. D.
MICHAEL A. YURATICH, Ph. D.

Department of Electronics, The University of Southampton
Highfield, Southampton S09 5NH, Great Britain

DAVID COTTER, Ph. D.

Max-Planck-Institut für biophysikalische Chemie
Abt. Laserphysik, D-3400 Göttingen, Fed. Rep. of Germany

Editorial Board

ISBN 3-540-09628-0 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-09628-0 Springer-Verlag New York Heidelberg Berlin

Library of Congress Cataloging in Publication Data. Hanna, David C, 1941-. Nonlinear optics of free atoms and molecules. (Springer series in optical sciences; v. 17) Bibliography: p. Includes index. 1. Nonlinear optics. 2. Atoms. 3. Molecules. I. Yuratich, Michael A., 1952- joint author. II. Cotter, David, 1950- joint author. III. Title. QC 446.2.H36 535'.2 79-19828

Printed in Germany

Offset printing: Beltz Offsetdruck, Hemsbach/Bergstr. Bookbinding: J. Schäffer oHG, Grünstadt.
2153/3130-543210

Preface

Laser physics and nonlinear optics are fields which have been intimately connected from their beginning. Nonlinear optical effects such as second-harmonic generation fulfil vital functions in many laser systems. Conversely advances in laser development quickly lead to progress in nonlinear optics. Of particular importance has been the development of tunable visible and uv lasers. With the ability to tune the laser frequency into close resonance with atomic transition frequencies, one can produce a large resonance enhancement of the nonlinearity. This permits the observation of a great variety of nonlinear optical processes in dilute media such as atomic vapours. In recent years much of the research effort in nonlinear optics has been directed towards the use of such media, and it is this area which forms the subject of the present book.

We review a wide range of nonlinear optical processes in atomic vapours, molecular gases and cryogenic liquids. At the same time we have tried to treat the subject in sufficient depth to be useful to research workers in the field. To achieve this, a measure of selectivity has been introduced by emphasising those nonlinear processes which are seen to have applications as sources of tunable coherent radiation. Thus we have not discussed in any detail those nonlinear processes whose main applications are in spectroscopy, such as Doppler-free two-photon absorption. However, much of the background is appropriate to just such topics as these and we believe that the book should therefore be of use to people working in a number of fields where lasers are involved.

The book divides broadly into two parts; general theory (Chaps.2 and 3) and experimental aspects (Chaps.4-8). In the theoretical chapters we start by considering the nonlinear optical susceptibilities which form the cornerstone of most discussions of nonlinear optics. Then, other approaches to the theory of the nonlinear polarisation are introduced; for example, the ideas of adiabatic ("dressed") states and multiphoton Bloch equations and vector models. The latter approaches emphasise the resonant nature of the process

and are a natural extension of ideas developed originally for resonant interactions in two-level atoms.

The close connection between these apparently diverse descriptions is explored in some detail. The other main task of the theoretical section, dealt with in Chap.3, is a consideration of the propagation behaviour of the interacting fields, thus leading to expressions for experimentally important quantities, such as the intensity of the generated radiation. An underlying aim throughout the theoretical section has been to provide a consistent and full description of the notations employed and to give the various formulae in a form suitable for use in calculations. In keeping with modern conventions we use SI-units throughout; the relations between SI and esu definitions are collected in an appendix.

Some readers may not wish to go deeply into the theory at first, and the experimental chapters have been written with this in mind. Thus the formulae given in the experimental chapters usually take a simpler form than their more general counterparts in the theory section. Chapters 4-6 deal with experimental aspects of atomic vapours as nonlinear media. Chapter 7 deals with molecular gases and also molecular cryogenic liquids, drawing extensively on the principles established in earlier sections. Thus attention is focused on the main differences vis à vis atomic vapours, primarily the much richer energy level structure in molecules, the much higher number densities involved, and the fact that resonances occur in the infrared.

Finally, a number of further topics are covered in Chap.8: multipole processes, laser-induced inelastic collisions and phase conjugation. These topics give a good illustration of the variety of possible nonlinear effects, and while they do not fit readily into the earlier experimental sections, they share with these the same theoretical background.

In writing this book we have benefited greatly from discussions with many colleagues, too numerous to mention individually. However, a special word of thanks should go to Mrs. Sue Meen, who typed the draft manuscript with patience and good humour. MAY held a Ramsay Memorial fellowship during the period of writing the book and wishes to thank the trustees for their support. DCH, who spent a sabbatical year in Munich during the final stage of completion of the book wishes to thank the Alexander von Humboldt foundation for its support, and Professor Herbert Walther for his hospitality.

Finally, we all wish to thank our wives for tolerating our long periods of distractions and for giving us so much encouragement.

October 1979 *David C. Hanna, Michael A. Yuratich, David Cotter*

Contents

1. Introduction

Soon after the invention of the laser it was demonstrated that the intense light flux available could produce nonlinear optical effects in various media. The first such demonstration was by FRANKEN et al. [1.1], in which radiation at the second harmonic of the ruby laser was produced when a ruby laser beam was focussed into a quartz crystal. A phenomenological description of this and other nonlinear effects can be given by expressing the polarisation P induced in the medium as a series in ascending powers of the applied field E,

$$P = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(2)} E^2 + \varepsilon_0 \chi^{(3)} E^3 + \ldots \quad . \tag{1.1}$$

The first term, containing the first-order susceptibility, describes the familiar linear optical property of an index of refraction. Franken's experiment confirmed the existence of the second term and showed that with the optical field strengths available from lasers, effects due to $\chi^{(2)}$ could become significant. At about the same time, KAISER and GARRETT [1.2] observed another nonlinear optical effect produced by a laser beam – two-photon absorption. This arises from the $\chi^{(3)}$ term.

Following these experiments, there was a rapid growth of interest in the new field of nonlinear optics. There have been three main motivations. First, there is the possibility of exploiting the nonlinear behaviour in various devices. The most important of these are frequency converters, in which laser radiation at one frequency is converted, for example by harmonic generation, sum-frequency generation or difference-frequency generation, into coherent radiation at a new frequency, often with a high efficiency. Because the converted radiation may be at a frequency that is not directly available from a laser source, these frequency-conversion techniques provide an important means of extending the spectral range covered by coherent sources. A second reason for studying nonlinear optical processes is that they set a limit to the light flux that can be passed through a medium. For example, two-photon absorption, stimulated Raman and Brillouin scattering

can lead to depletion of the incident light, and self-focussing leads to distortion of the incident-beam profile. Too high an intensity may even lead to irreversible changes in the medium (e.g., damage in the case of solids). A third interest in nonlinear optical effects lies in their use as a means of obtaining information about the microscopic properties of the atoms or molecules that constitute the nonlinear medium. Examples of this are the use of two-photon absorption and coherent anti-Stokes Raman scattering to study energy levels that are inaccessible by single-photon absorption.

Although much of the early nonlinear optics work was on condensed matter, more recently there has been a shift of interest towards gaseous media. The object of this book is to review the progress made in the nonlinear optics of vapours and gases. The theoretical background is presented in a general way, but in discussing uses of these nonlinear effects we place strong emphasis on frequency-conversion applications. We shall also examine a number of other nonlinear processes that compete with and, therefore, impose limitations on the efficiency of the desired frequency-conversion process. First, however, we examine the reasons for the shift of interest from crystals to vapours.

At first crystalline nonlinear media were seen to offer the greatest device potential. The reasons for this view were twofold. First it can be shown by a simple symmetry argument that $\chi^{(2)}$ in (1.1) is zero unless the medium lacks a centre of symmetry. Nonlinear effects in centrosymmetric media (such as atomic vapours and non optically active molecular liquids and gases) would thus depend on higher-order, and therefore presumably smaller, nonlinear terms. Second, it was shown by BASS et al. [1.3], GIORDMAINE [1.4] and MAKER et al. [1.5], that the birefringence of a crystalline medium could be used to match the phase velocities of fundamental and harmonic radiation by compensating the material dispersion. With this "phase-matching", a long interaction length (or coherence length) of up to a few centimetres became possible, and harmonic-conversion efficiencies could then easily reach tens of percent. These promising results were a considerable spur to activity, and at about this time a search began in a number of laboratories for suitable nonlinear crystals. The qualities looked for were many and demanding, including 1) large $\chi^{(2)}$, 2) sufficient birefringence to permit phase matching, 3) good optical quality over a crystal dimension of ~1cm, 4) ability to withstand high optical intensity and 5) good transparency to the incident and generated radiation. The results of this extensive research effort on crystal nonlinear optical devices are covered in a number of review articles

[1.6-10]. Despite the considerable successes of this research, disappointingly few materials have proved capable of satisfying the list of requirements above. Infrared and ultraviolet absorption in crystals are major limitations and these, with other shortcomings, have been the driving force behind attempts to exploit optical nonlinearities in gases and vapours.

A number of significant advantages are offered by gases and vapours. They can be easily prepared, with good optical quality over large dimensions. They do not suffer irreversible (and costly) damage at high intensities, and have good uv and ir transparency. The disadvantages of vapours are their low number densities compared with condensed matter and the fact that because these media have inversion symmetry, the most important nonlinear effects are due to the $\chi^{(3)}$ term. (This remark will need to be qualified when we consider magnetic-dipole and electric-quadrupole contributions to the nonlinear polarisation.) To observe effects due to $\chi^{(3)}$ comparable in magnitude to those due to $\chi^{(2)}$ in the better nonlinear crystals, one of two conditions must be met. Either a very large field strength E is required (for example by using intense mode-locked laser pulses) or the magnitude of $\chi^{(3)}$ must be made resonantly large by choosing the frequencies of the interacting waves to be close to resonance with transition frequencies of the medium.

Pioneering investigations into the nonlinear properties of gases were made by NEW and WARD [1.11], who generated third-harmonic radiation in several atomic and molecular gases (see also [1.12,13]). The conversion efficiencies were very low, however, because the fundamental frequency (provided by a ruby laser) and its third harmonic were well away from any resonance, and also, as the process was not phase-matched, the coherence length was short. HARRIS and MILES [1.14] then made a proposal which overcame these limitations. This involved the use of a metal vapour as the nonlinear medium, with a buffer gas to provide the necessary dispersion for phase matching [1.15]. Metal vapours can provide resonance transitions close to the laser frequencies commonly used; this leads to a much larger susceptibility. Thus, HARRIS and his co-workers went on to demonstrate experimentally [1.16] a value for $\chi^{(3)}$ in rubidium vapour which was 10^6 greater than the $\chi^{(3)}$ measured in He by WARD and NEW [1.12]. This result indicated that high conversion efficiencies should be possible for third-harmonic generation. With a high-power mode-locked Nd:YAG laser as the fundamental source, third-harmonic efficiencies of several percent have now been achieved [1.17,18]. By using harmonics of the Nd:YAG laser output, and then generating harmonics and sum frequencies from these [1.19-21] high powers have been generated at a number of discrete uv and vuv wavelengths.

For many applications, however, tunable uv and vuv sources are required and harmonic generation can provide this if a tunable fundamental source is used. Dye lasers offer the most convenient source of tunable visible radiation, although in their more simple and unsophisticated forms, the peak power available is considerably less than that from a mode-locked Nd:YAG laser. The disadvantage of lower power can, however, be compensated by the tunability, which, besides offering tunability of the generated harmonic, brings with it the possibility of also tuning the dye laser to a frequency at which $\chi^{(3)}$ is resonantly enhanced. For example, using two-photon resonant enhancement (i.e., with the dye laser tuned so that its frequency is half that of an allowed two-photon transition), HODGSON et al. [1.22] obtained significant powers over a wide range in the vuv by sum-frequency generation in Sr vapour of the outputs from two dye lasers pumped by a N_2 laser. Two other reports of the two-photon resonance technique were made around the same time [1.23,24]. BLOOM et al. [1.24] described an experiment in Na vapour in which they showed that with modest laser powers, "up-conversion" from ir to uv photons occurred with an efficiency of 50% (a power-conversion efficiency of ~1600%). Results like these suggest that third-harmonic generation and sum-frequency generation in vapours are likely to play an important role among future sources of coherent uv, vuv and even soft-X-ray radiation [1.25]. We have therefore devoted a whole chapter (Chap.4) to this topic.

In the process of third-harmonic generation (and sum- or difference-frequency generation) the atoms of the nonlinear medium are left, after the scattering process, in their initial state. Such processes are known as "parametric" processes. Characteristically, they need to be phase matched if they are to be efficient. There is another important class of nonlinear processes, which are termed "nonparametric", in which the final state of the atoms after scattering is different from the initial state. Such processes do not involve phase matching. [This distinction between parametric and nonparametric processes is rather loose. It will need qualification later (Chap.3), when we consider some processes that cannot be so clearly categorised.] Two-photon absorption and emission, and stimulated Raman scattering are important examples of nonparametric processes. In stimulated Raman scattering (SRS) a powerful pump wave at frequency ω_p produces a high gain at a Stokes frequency ω_s, where the frequency $\omega_p - \omega_s$ coincides with a Raman-active transition of the medium. Stokes photons generated by spontaneous Raman scattering and travelling in the direction of the pump beam undergo avalanche multiplication, thus creating a Stokes beam that propagates

in the same direction as the pump beam, of a power approaching that of the pump beam. SRS is one of the more venerable nonlinear optical processes, being first observed quite unexpectedly by WOODBURY and NG [1.26], as an emission from the nitrobenzene in the Kerr-cell used to Q-switch their ruby laser. In fact, SRS is certainly one of the most easily demonstrated nonlinear optical effects. A number of factors combine to make this so. For example, it can occur in any medium (it is described by a third-order susceptibility $\chi^{(3)}$); furthermore, there is no phase-matching requirement. This means that very long interaction lengths can be achieved. By using a liquid or a high-pressure gas, a high number density is ensured and, despite involving a third-order process, the susceptibility per molecule is high. This is because the pump and Stokes frequencies are in two-photon resonance with the initial and final levels [i.e., $\hbar(\omega_p - \omega_s) = E_f - E_g$; see Fig.1.1]. Thus resonance is automatically achieved without the need, as in two-photon absorption, for a coincidence between twice the incident laser frequency and a transition frequency of the medium.

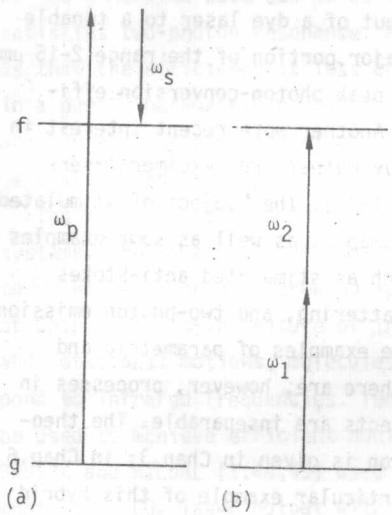

Fig.1.1a,b. Two-photon resonance. (a) Raman scattering $\hbar(\omega_p - \omega_s) = E_f - E_g$ (b) Two-photon absorption $\hbar(\omega_1 + \omega_2) = E_f - E_g$

Before the discovery of tunable dye lasers, SRS from ruby-laser radiation provided the nearest thing to tunable coherent radiation. A large number of organic liquids, and some high-pressure gases, each with different vibrational Stokes shifts, from a few hundred to a few thousand wave numbers, were found capable of SRS, thus providing high-power sources at many wavelengths in the near infrared region. With the arrival of dye lasers, this use of SRS declined. However, even before dye lasers became available the wavelengths

---

$\hbar$ is Planck's constant divided by 2π

thus obtained yielded some close coincidences with allowed transitions in alkali atoms and opened the way to observation of a wealth of nonlinear effects [1.27-31]. One of these effects was stimulated electronic Raman scattering (SERS) [1.32-34]. The word electronic is added to emphasise that the scattering transition is between the purely electronic levels of an atom rather than between the vibrational or rotational levels of a molecule. SERS in atoms differs from SRS in molecules in two important respects. The Stokes shifts are large ($\sim 10^4 cm^{-1}$ typically) and this means that the Stokes wavelength can be well into the infrared for pump wavelengths in the visible region. Also the pump wavelength can be close to an intermediate level; the Raman cross section is then very large (resonant Raman scattering). This in turn implies that the threshold for SERS is reached with a relatively low pump intensity, well within the capabilities of typical dye lasers. With a dye laser as the pump, its wavelength can be tuned to take full advantage of the resonant enhancement. More importantly, it means that the Stokes wavelength can be tuned. SERS, therefore, provides an extremely simple way of directly converting the tunable visible output of a dye laser to a tunable infrared output [1.35-40]. In this way, a major portion of the range 2-15 μm has been covered; over parts of this range, peak photon-conversion efficiencies as nigh as 50% have been achieved. Another more recent interest in SERS is in the efficient conversion of the uv output from excimer lasers into the visible region of the spectrum [1.41-43]. The subject of stimulated electronic Raman scattering is reviewed in Chap.5, as well as some examples of other related nonparametric processes such as stimulated anti-Stokes Raman scattering, stimulated hyper-Raman scattering, and two-photon emission.

The processes dealt with in Chaps.4,5 are examples of parametric and nonparametric interactions, respectively. There are, however, processes in which both parametric and nonparametric effects are inseparable. The theoretical background for this type of situation is given in Chap.3; in Chap.6 we review the experimental results for a particular example of this hybrid process which has been used for the generation of tunable infrared radiation [1.35]. Briefly, the process may be described as four-wave mixing, i.e., a scheme in which three frequencies ω_1, ω_2, ω_3 are mixed to generate a fourth, ω_4, given in this case by $\omega_4 = \omega_1 - \omega_2 - \omega_3$. The effect is enhanced by arranging that ω_1, ω_2 satisfy a two-photon resonance of the Raman type, i.e., $\omega_1 - \omega_2$ is equal to a Raman transition frequency of the medium (see Fig.1.2). However, instead of supplying ω_2 externally from a laser, it is also generated within the medium by stimulated Raman scattering of the powerful pump wave ω_1. Thus, the overall process can be thought of as a combination of

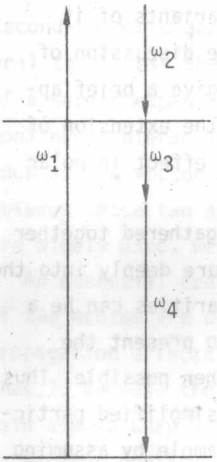

Fig.1.2. Generation of $\omega_4 = \omega_1 - \omega_2 - \omega_3$ by four-wave Raman-resonant difference mixing

nonparametric generation (of ω_2 by SRS) and parametric generation of $\omega_4 = \omega_1 - \omega_2 - \omega_3$ by four-wave mixing. In addition the two-photon absorption of the generated wave has to be considered, because $\omega_3 + \omega_4$ $(= \omega_1 - \omega_2)$ also satisfies two-photon resonance. An interesting result of this type of process is that the efficiency is less critically dependent on phase matching than in a purely parametric process. Although this technique has resulted in generation over wide ranges of the infrared, the observed efficiencies have generally been rather low.

The results reviewed in Chaps.4-6 refer to experiments on atomic-vapour systems. The same ideas of two-photon resonant enhancement can also be applied to molecules; there is growing activity in this field. This is the subject of Chap.7. The main feature of interest is that, owing to their vibrational and rotational motions, molecules have energy-level spacings that correspond to infrared frequencies. Two-photon resonant enhancement can, therefore, be used to achieve efficient nonlinear generation in the ir. For example, BRUECK and KILDAL [1.44,45] used this technique to generate the third harmonic of a CO_2 laser output with an efficiency of ~4%. This is several orders of magnitude more efficient than the best THG conversion efficiency for the CO_2 laser, using the third-order susceptibility of nonlinear crystalline media [1.46]. There is also a revival of interest in SRS in high-pressure molecular gases (such as H_2, D_2 and CH_4) as a means of efficient tunable ir generation [1.47-54], tunable uv generation [1.55,56], efficient Raman shifting of excimer lasers [1.57,58] and high energy pulse compression [1.59,60].

Because the subject of SRS in gases has been extensively covered in the early literature, we shall not discuss this any further in Chap.7. There have also been recent demonstrations of Raman-resonant four-wave mixing in H_2,

using a scheme analogous to that described in Chap.6 or variants of it [1.61-65]. Because the results of this work complement the discussion of Chap.6 (and the common theoretical ideas of Sect.3.4) we give a brief appraisal in Sect.7.5. One further topic concludes Chap.7; the extension of SRS generation to the far infrared by the resonance Raman effect in polar molecules [1.61,67].

Most of the necessary theoretical background has been gathered together in Chaps.2,3. Many readers will probably not wish to venture deeply into the theory (the complexity of notation for high-order nonlinearities can be a powerful repellant). An attempt has therefore been made to present the experimental work of Chaps.4-7 in a self-contained way, when possible. Thus, the formulae used in the experimental sections are often simplified particular cases of more general results from Chaps.2,3, for example by assuming all interacting waves to be linearly polarised in the same direction. Nevertheless, we have felt it worthwhile to devote considerable space to the theory for a number of reasons. First, we have set out to establish unambiguously the notation we use for nonlinear susceptibilities, because difficulties have been compounded by different authors using different units and definitions. The most notorious offenders have been factors of two; in discussing second-order susceptibilities ROBINSON [1.68] said of these different conventions that "in particularly fertile ground, these various factors can luxuriate and blossom as factors of 8 in the final answer". Of course, these problems become even greater with higher-order susceptibilities. Expressions for these susceptibilities have been derived by a number of authors using time-dependent perturbation theory [1.69-71]. With some modification of notation to bring it into line with the now more common conventions (including the use of SI units) we adopt BUTCHER's [1.70] expressions for the n'th order susceptibilities as the starting point of Chap.2. (The relations between SI and esu definitions are presented in an appendix.) From these general expressions, we then derive susceptibilities for the particular processes to be discussed in later sections, e.g., third-harmonic generation, sum- and difference-frequency generation, stimulated Raman and hyper-Raman scattering, two-photon absorption, etc.

Roughly half of Chap.2 is given to this task of providing the expressions needed in the subsequent experimental sections. The other main aim we have pursued in Chap.2 is to relate the susceptibility formalism of nonlinear optics to the very different approaches that address themselves to the resonant interaction of radiation with a two-level or three-level atom. In the early days of nonlinear optics, when nonresonant phenomena such as

second-harmonic generation in crystals were the major interest, it was natural to express the nonlinear behaviour in terms of susceptibilities, by use of a series expansion, as in (1.1). The more recent interest in resonant nonlinear interactions has seen a growing use of nonperturbative treatments, such as the vector model of FEYNMAN et al. [1.12]. Because the relationship between these two approaches is not always obvious and yet both approaches are widely used, we have given a fairly lengthy discussion of this topic.

An essential feature of nonlinear optics is that the physical dimensions of the medium are usually large compared to the optical wavelength. Wave-propagation effects are therefore important; this forms the subject of Chap.3. Because the emphasis of this review is on device applications, the main aim in Chap.3 has been to produce expressions for the power generated in various nonlinear processes. The analysis is restricted to a plane-wave treatment in Chap.3, although the fact that the fields are confined to a beam can entail important modifications to the results of the plane-wave analysis. For example, in third-harmonic generation the use of focussed gaussian beams modifies the phase-matching condition. In stimulated Raman scattering, a tightly focussed pump beam can lead to a large diffraction loss for the Stokes wave; the threshold condition is then greatly modified. Rather than treat these topics in Chap.3, we have left them to the experimental sections (Chaps.4,5, respectively) where their significance can be made more apparent.

In evaluating possible applications of a nonlinear optical process it is obviously important to know of limiting effects to which the process might be subject. These limiting effects are common to many processes; we have, for convenience, concentrated our discussion of them in Sects.4.6, 5.4. Where possible, we give rough estimates of their magnitudes. These estimates are necessarily rough, because the conditions appropriate to efficient nonlinear generation involve high vapour pressures (high by the standards of typical spectroscopic experiments) and high incident intensities of resonant laser radiation. Under these conditions, a multitude of processes manifest themselves simultaneously, such as multiphoton ionisation, amplified spontaneous emission, various sum- and difference-frequency mixing processes, radiation trapping, level shifts, and so on. Considerable further work is needed to unravel this complex behaviour.

Finally, in Chap.8, some less familiar nonlinear optical effects are briefly described. They provide further illustration of the wide variety of phenomena that may be observed under resonance conditions.