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A Quarter century of stimulated Raman scattering†

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Abstract - A brief description of the development of stimulated Raman scattering is presented.

EARLY REMINISCENCES

It is twenty-four years ago that the field of stimulated Raman scattering was born and received its name. Woodbury and Ng had been studying the output of the ruby laser (ref. 1) at the Hughes Research Laboratories, where the device was invented by Maiman (ref. 2). The operation of the ruby laser in the Q-switched mode had been introduced in the same laboratories (ref. 3). One way to obtain Q-switching was by means of a Kerr cell filled with nitrobenzene. Woodbury and Ng discovered (ref. 1) that the output of light at 694 nm actually diminished at higher pump power levels. Detailed studies showed that in this case considerable power was generated in the infrared. The Stokes shift corresponded to a Raman active mode of the nitrobenzene molecule. Woodbury presented a detailed account (ref. 4) of the events leading to the discovery of the stimulated Raman effect at the Third International Conference on Quantum Electronics, held in Paris in February 1963.

I was co-chairman (with P. Grivet) of that conference, and in September 1962 I received a call from Malcolm Stitch, then a group leader at Hughes Research Laboratories, that they had observed these new effects in the output frequencies of a ruby laser, Q-switched with a nitrobenzene cell. At that time the Hughes group was not yet sure whether it was a new fluorescent emission or a Raman effect. Gisela Eckardt proposed the explanation in terms of stimulated Raman scattering and in due time a patent was issued (ref. 5). In the fall of 1962 a group at Hughes Research Laboratories carried out a series of experiments (ref. 6) which demonstrated convincingly that the explanation in terms of SRS was correct. A theoretical description was developed by Hellwarth (ref. 7).

Before any of these results had been published, I had independently arrived at a theoretical framework for SRS in October 1962. I had been working on the problem of incorporating effects of damping into the theory of the nonlinear susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$. I realized that the density matrix formalism afforded a straightforward way of doing this. The nonlinear susceptibilities would thus be complex quantities. At the time I received the above-mentioned telephone call, I immediately realized that the imaginary part of the Raman susceptibility would lead to exponential gain at the Stokes frequency. This results was mentioned in a paper (ref. 8) submitted in October 1962. At the third ICQE in Paris I presented further details on the calculation of the complex Raman susceptibility. This paper (ref. 9) was presented in French, and had been carefully edited by my French graduate student at that time, Jacques Ducuing. Perhaps because of the French language, and also because the proceedings of the conference were published a year later, this particular contribution has hardly ever been quoted. Permit to translate here from the concluding paragraph,

> "It is therefore possible to define complex susceptibilities of different orders with positive or negative imaginary parts. One may incorporate the corresponding polarizations in Maxwell's equations and obtain simultaneously maser effects, and nonlinear parametric and Raman effects."

Further theoretical details were worked out in a joint paper with Y. R. Shen (ref. 10). At the same conference there was also a theoretical paper by Zeiger and Tannenwald (ref. 11) on the stimulated Raman effect in crystals. Only a few months later, at a meeting of the American Physical Society, in the spring of 1963, Terhune announced the observation of coherent anti-Stokes radiation. He correctly interpreted this effect (refs. 12,13) in

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terms of the complex nonlinear susceptibility $\chi^{(3)}$. This quantity generally describes the coupling between four electromagnetic waves (ref. 14), each characterized by a frequency, wave vector amplitude, phase and polarization mode. It followed readily in all these formalisms that the Raman gain coefficient at frequency $\omega_L - \omega_{vib}$ is proportional to the laser intensity $|E(\omega_L)|^2$ and to the population difference, $N_a - N_b$,

$$g_s = (N_a - N_b)(\partial\sigma^R_{sp}/\partial\Omega)(c^3 n_L^2/\Gamma_{ab}^2\ \nu_s^2\ 4\pi n_s^3)|E_L|^2$$

$$= 8\pi(\omega_s/n_s c)(-\chi''^{(3)}_{Raman})|E_L|^2. \qquad (1)$$

There is a corresponding loss coefficient (ref. 15) at the anti-Stokes frequency $\omega_L + \omega_{vib}$. The gain and loss would be reversed, if the vibrational population were inverted.

An important contribution was made by Loudon (ref. 16) and Garmire, Pandarese and Townes (ref. 17) who called explicit attention to the vibrational excitation in the stimulated Raman effect. The vibration is coherently driven in the presence of two light waves, at ω_1 and ω_2, respectively, with $\omega_1 - \omega_2 = \omega_{vib}$.

The years 1963 and 1964 were, however, characterized by many serious discrepancies between theory and experiment. In particular, the Raman gain was usually anomalously large and anomalously low thresholds for Raman oscillation were the rule rather than the exception. These anomalies disappeared, when it was shown by several groups that self-focusing of laser light caused them, and the experimental thresholds were really the threshold to produce self-focusing within the Raman cell. The first quantitative agreement between theoretical and experimental Raman gain was obtained in hydrogen gas. A more complete historical account of the first years of SRS may be found in a review article (ref. 18).

MAJOR DEVELOPMENTS

Since 1967 the subject of SRS has grown rapidly in importance and has led to a number of applications. A large number of review articles on SRS and CARS is now available (refs. 19-24), and three recent monographs (refs. 25-27) also devote detailed attention to the subject. In these few pages only an enumeration of some of the more important developments can be given. The selection is incomplete and reflects predilections of the author.

Coherent Raman spectroscopy

Perhaps the most significant development in the seventies was the use of tunable dye lasers in SRS. If a sample is subjected to two incident collinear laser beams, at frequencies ω_1 and $\omega_2 < \omega_1$, respectively, and the difference frequency $\omega_1 - \omega_2$ is tuned through Raman resonances, a small Raman gain at ω_2 is observable with cw dye laser beams. Owyoung (ref. 24) has developed this technique to obtain unprecedented resolution in Raman spectra of complex molecules in gases.

CARS (coherent anti-Stokes Raman spectroscopy)

With two tunable pulsed lasers, a signal at the anti-Stokes frequency $\omega_4 = 2\omega_1 - \omega_2$ is created. The signal is maximized, if the phase matching condition $k_4 = k_1 + k_1' - k_2$ is satisfied as shown in Fig. 1. The two beams at ω_1 and ω_1', which need not be the same, may also have different directions $k_1 \neq k_1'$. The three wave vectors need not be coplanar. One speaks of "boxcars" and "folded boxcars" in these more general phase matching conditions. The intensity $I(\omega_4)$ is observed as a function of the tuning $\omega_1 - \omega_2$. Discrimination in frequency and spatial direction largely suppresses fluorescent and scattered light background. CARS techniques are therefore useful to monitor composition and temperature profiles in flames, in jet and combustion engines, and other hostile environments (refs. 25,26).

Resonant SRS and CARS

It is possible to enhance the Raman gain coefficient of a particular vibrational transition by tuning ω_1 (or ω_2) close to the resonance of a one-photon electronic transition, shown in Fig. 2. Thus the contribution of a solute molecule with a particular absorption band may be enhanced over the background of solvent molecules. Thus ω_1 is tuned in the vicinity of the electronic absorption band and $\omega_1 - \omega_2$ is tuned through the Raman resonance (ref. 23). This has been applied successfully to biological molecules.

Polarization effects in SRS and CARS

In CARS there is always a non-resonant contribution χ^{NR}, even if $\omega_1 - \omega_2$ is far from any Raman resonance. This background signal may be reduced by paying attention to the

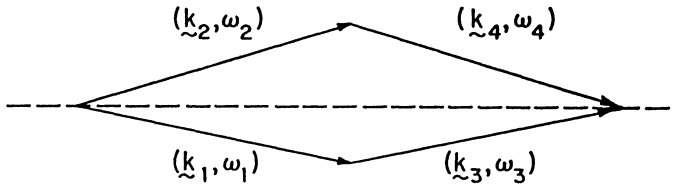

Fig. 1. Wave vector or momentum matching in four-wave mixing, $k_4 = k_1 + k_2 - k_3$, $\omega_4 = \omega_1 - \omega_2 + \omega_3$. Some frequency and wave vectors may be chosen equal. In conventional CARS $k_1 = k_3$ and $\omega_1 = \omega_3$. In boxcars, $k_1 \neq k_3$, but $\omega_1 = \omega_3$. The page may be creased along the dotted line to obtain the three-dimensional geometry of folded boxcars.

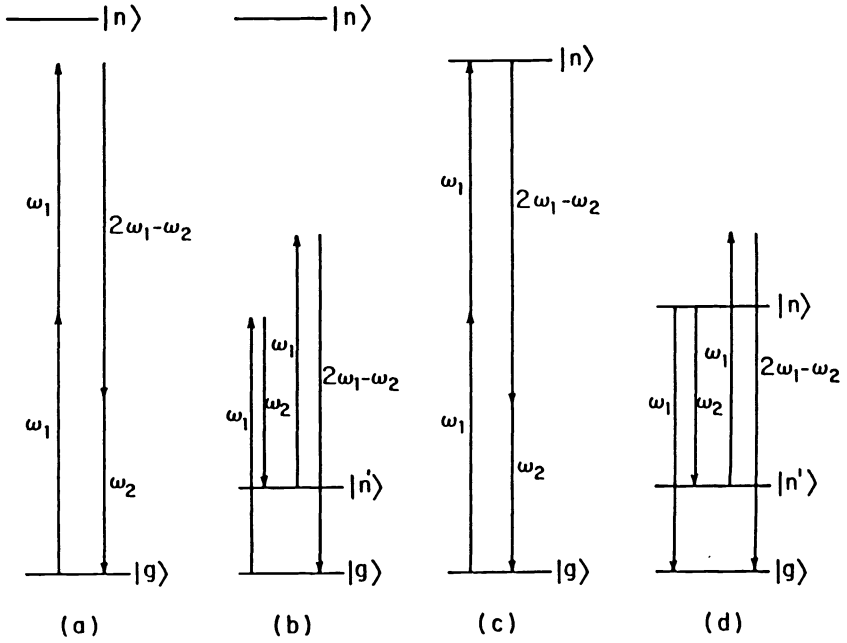

Fig. 2. The creation of a new beam at $2\omega_1 - \omega_2$ by three incident beams at $\omega_1 = \omega_3$ and ω_2, respectively. a) Nonresonant mixing; b) Intermediate Raman resonance (CARS); c) Intermediate two-photon absorption resonance; d) One-photon resonantly enhanced CARS.

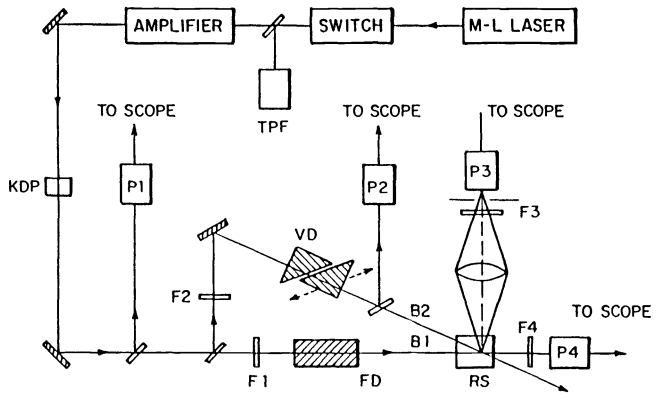

Fig. 3. Schematic of experimental arrangement to measure relaxation times of vibrational excitations. The pump pulse B_1 at $\lambda = 1.06$ μm excites the vibration, the probe pulse B_2 at $\lambda = 0.53$ μm measures this excitation for variable delays VD. CARS excitation is detected by photodetector P_4. Spontaneous anti-Stokes scattering is detected by P_3. $F_1 - F_4$ are appropriate filters. (After A. Laubereau, D. von der Linde and W. Kaiser, Phys. Rev. Lett., 28, 1162, 1972).

polarization of the incident beams at ω_1 and ω_2 and the polarization of the signal beam at $2\omega_1 - \omega_2$ for CARS. The change of polarization of the four-wave mixing signal at $2\omega_1 - \omega_2$ through a Raman resonance was first noted by Levenson and Bloembergen (ref. 28). The method was generalized and developed into Raman active ellipsometry by Akhmanov et al (ref. 22).

In SRS the polarization of the output signal ω_2 may be different from polarization of the input at ω_2. The change depends on the polarization of the beam at ω_1. This effect has received the name of RIKE, Raman Induced Kerr Effect (refs. 20,25,26).

Time-resolved SRS and CARS

The existence of pulsed high power and tunable dye picosecond laser sources has opened up the field of transient Raman spectroscopy (ref. 29). A prototype arrangement is shown in Fig. 3. An incident pulse at $\lambda_1 = 1.06$ μm creates a vibrational excitation in the Raman sample RS. This Raman active excitation is probed by a delayed pulse at $\lambda = 0.53$ μm with a variable time delay $t_d = t_1 - t_3$. The coherent anti-Stokes signal detected by P_4 at $\omega_3 + \omega_{vib}$ measures the strength of coherent mode as a function of time, or the transverse relaxation time T_2. Spontaneous anti-Stokes scattering in arbitrary transverse directions detected by P_3 measures the decay of the population in the excited vibrational state, or the longitudinal relaxation time T_1. The rate of transfer of vibrational energy to other vibrational modes, or to other degrees of freedom, has thus been determined for various solvent and solute molecules.

It is not necessary to rely on Raman laser action to excite the Raman-active material. One may use a laser pulse at ω_1, and a second synchronous pulse, derived from a tunable dye laser, at $\omega_2 = \omega_1 - \omega_{vib}$, to excite the material parametrically. A third pulse at another frequency ω_3 is then used to measure the coherent excitation with a variable time delay. Similar arrangements can also measure properties of excitations in solids, including excitons, optical phonons, polaritons, spin waves, etc. In principle, both frquency ($\omega_1 - \omega_2$) and spatial ($k_1 - k_2$) dispersion can be observed. More recently, femtosecond pulses have become available. Therefore, the time resolution can be pushed to the limit set by the uncertainty principle, $\Delta t(\omega_1 - \omega_2) \cong 1$.

A somewhat unusual example of time-resolved CARS is the investigation of a Raman-active mode ν_1 in SF_6, following the excitation of this molecule by a CO_2 laser pulse (refs. 30,31). This mode initially excites levels $n_3 = 1,2,3,4$ and higher levels of the ν_3 mode. Due to anharmonic coupling with the ν_1 mode satellites appear in the CARS spectrum of the ν_1 resonance as shown in Fig. 4. The study of the time evolution of this spectrum has given information about intermolecular (collisional) relaxation processes. It is of considerable interest to improve the time resolution of such type of experiments so that intramolecular vibrational energy redistribution of highly excited molecules may be followed before collisions take place (ref. 32).

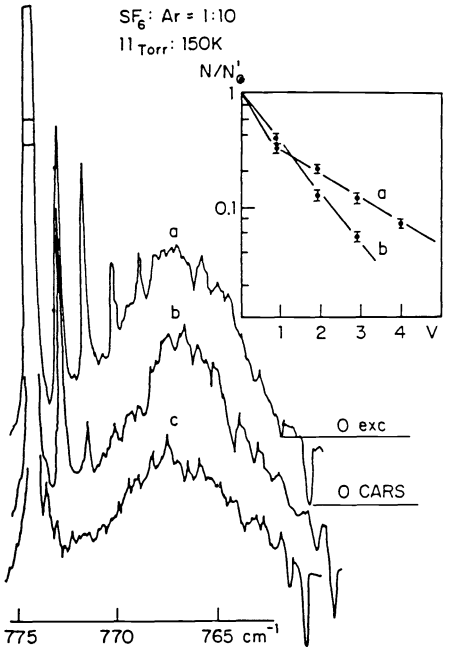

Fig. 4. CARS spectra of SF_6 (1 torr) with Argon buffer gas (10 torr) after excitation with a CO_2 laser pulse with a fluence of 0.2 J/cm^2 for various delay times τ_d.

a) $\tau_d = 100$ ns;
b) $\tau_d = 200$ ns;
c) $\tau_d = 2\mu$s.

The inset shows the distribution of the lowest levels of the excited ν_3 mode. (After ref. 30).

Tunable Raman light sources

A large field of application is the extension of domain of frequency tunability of dye lasers by Raman shifting. The most often used gases are hydrogen, deuterium and methane, which have large Stokes shifts, characteristic of the vibration of the hydrogen atom. The tunability of dye lasers can be extended to the far infrared, by first, second or third order Stokes shifting (ref. 33). There was e.g. considerable interest (refs. 34,35) to obtain a tunable line source near $\lambda = 16$ μm to cover the ν_3 absorption line feature of UF_6, for possible use in laser isotope separation. Starting with a suitable CO_2 laser line and a rotational $\Delta J = 2$ transition of the hydrogen molecule, the desired frequency interval can be reached. An alternative is to start with a parametric optical down converter of $LiNbO_3$ oscillating in the near infrared and using the vibrational Stokes shift of hydrogen.

Raman shifts may also be used to extend the domain of tunability of excimer lasers, or of frequency doubled dye lasers, in the UV region. An important application of Raman lasers is the achievement of high brightness in the UV. Higher power excimer lasers are often multimode. Several modules of multimode excimer lasers may be used to pump one diffraction limited mode of a high pressure hydrogen Raman cell. The power conversion into the first Stokes mode may approach one hundred percent quantum efficiency.

Finally, mention is made of the infrared spin flip Raman laser (ref. 36) in InSb, which is tunable by the application of an external magnetic field. A good discussion of this device with ample references to the vast literature may be found in Shen's monograph (ref. 27).

High order and surface Raman processes

The transient time-resolved picosecond techniques to probe dynamic vibrational excitation have been extended by Flytzanis et al. (refs. 37,38) to study vibrational overtones and two-phonon excitation states in liquids and solids. In principle, such higher order excitations may also be probed by active four-wave mixing techniques.

Other possible applications concern the investigation of Raman-active surface excitations (ref. 39) and the coherent excitations in very small droplets (ref. 40) (Mie spheres). The appreciable Raman gain in long glass fibers and other optically guided structures should also be mentioned (ref. 41).

Stimulated Raman scattering in the atmosphere

This subject has been active for about two decades, and receives increased current attention because of the interest in propagating high intensity laser beams through the atmosphere. Soviet work (ref. 42) demonstrated that the rotational Raman transition has the larger gain at pressures below one atmosphere. This is explained by the fact that the line width of the rotational line decreases with decreasing pressure, as it is collisionally broadened. By contrast, the line width of the vibrational Q band broadens at lower pressures, as individual J-transitions are resolved. At higher pressures, the collisional frequency is so high that the Q-band narrows to the position appropriate for the average J-value. The rotational gain is maximum for circularly polarized laser light, with the Stokes circularly polarized in the opposite sense, corresponding to a $\Delta J = \pm\Delta m = +2$ transition. These polarizations prevent a joint coupling of the Stokes and anti-Stokes modes.

At room temperature, the gain is maximum for the $S_{00}(8)$ transition of N_2, and is independent of atmospheric pressures below one atmosphere (ref. 43), as the product of population difference in the vibrational ground state, between J = 8 and J = 10 rotational states and the line width is independent of pressure. The Raman gain coefficient for the $S_{00}(8)$ transition of N_2 is about $\gamma = 4.2$ cm/TW, i.e., $g_g = 4.2$ cm^{-1} for 10^{12} Watts/cm^2. There is good agreement between recent theoretical (ref. 43) and experimental values (ref. 44). This value should hold down to an atmospheric pressure of about one torr, corresponding to a height of h = 45 km. Above this altitude the line width becomes constant, and is determined by the very small Doppler width for forward rotational Stokes scattering. The gain coefficient will then drop with the density and becomes exponentially smaller at increasing altitudes. Thus the overall Raman gain for vertical propagation through the atmosphere may be put equal to exp(gh). When $gh \geq 25$, the amplified spontaneous emission will lead to about one percent conversion. This occurs for beam intensity of 2.5 MW/cm^2. Above this "threshold" value nearly all the laser power will be converted into Stokes light. Since the rotational Stokes shift is small (75 cm^{-1}) for $S_{00}(8)$), the total power loss is negligible. The problem is, however, that the amplified Stokes light will be emitted into a much larger solid angle than the high power laser beam. Assume that the latter emerges in a diffraction limited mode from a 3 m aperture. For $\lambda \sim 0.3$ μm the diffraction angle is 10^{-7} radian. The Stokes gain is roughly the same for any direction contained in a cylinder of 3 m diameter and 45 km height. Thus the Stokes light will fill a cone with apex angle on the order of 10^{-4} radian. Thus the geometry is now just the reverse of the case discussed in the section Tunable Raman light sources. There many pump modes feed energy into a single Stokes mode of a Raman oscillator. Here a single pump mode amplified the spontaneous emission in many Stokes modes.

A PATHOLOGICAL CASE OF CARS

In this section a development of the last decade will be reviewed, which may be regarded as a CARS experiment in an atom, where the two levels of the Raman-active transition are two Zeeman sublevels of the ground state atomic configuration. Conventional wisdom holds that the Raman-type susceptibilities are proportional to the population difference between the two levels involved in the Raman-type transition as is also evident from Eq. (1). Consequently, the gain or loss is expected to vanish and no CARS-type four-wave mixing should occur. The usual treatment, of which Eq. (1) is a particular result, is however based on an approximate and rather ad hoc treatment of damping effects.

The correct inclusion of damping into the equation of motion for the density matrix (ref. 45) or the double-sided Feynman diagrams (refs. 21,46), which describe the evolution of the system of atom and radiative fields, leads to a large number of correction terms for higher order susceptibilities. These have often simply been ignored and cannot be obtained by any procedure that starts from the evolution without damping and then afterwards makes the ad hoc assumption that some frequencies occurring in the resonant dominators are complex. The correction terms which were first explicitly displayed by Lynch et al. (ref. 45) lead to extra induced resonances (ref. 47). The CARS-type susceptibility describing the Raman-type resonance between two equally populated Zeeman levels of the ground state (ref. 48) contains a term proportional to the sum of these populations and proportional to the damping of the virtual optical transition from the ground to an excited electronic configuration

$$\chi^{(3)}(-2\omega_1 + \omega_2;\ \omega_1,\ -\omega_2, \omega_1) = \int_{-\infty}^{+\infty} \frac{\mu_{ge}\mu_{eg'}\mu_{g'e}\mu_{eg} N_0 (+i\Gamma)}{\hbar^3 \Delta^3 [\omega_{g'g} - (\omega_1 - \omega_2) - (k_1 - k_2)\cdot \bar{v} + i\Gamma_{g'g}]} f(\bar{v})\, d\bar{v}. \qquad (2)$$

can be made quite large by choosing the detuning Δ of the laser frequencies from the optical resonance small, but still larger than the damping Γ, the Doppler width of the optical resonance, and the optical Rabi frequency. N_0 is the sum of the populations in the Zeeman states.

Figure 5 shows a CARS-type four-wave mixing signal in Na vapor. The Zeeman-type resonance occurs when $\omega_1 - \omega_2 = g\hbar^{-1}\beta H_0$. One may either vary ω_2, i.e., $\omega_1 - \omega_2$, or H_0 to scan the resonance. The integrated signal intensity is proportional to the square of the buffer gas pressure. Furthermore, the line width is inversely proportional to the buffer gas pressure. This behavior is explained by collisional narrowing of the Doppler width $(k_1 - k_2)\cdot v_{at}$. The atomic thermal velocity must then be replaced by the diffusive velocity $\bar{v}$. The two beams at $\omega_1 - \omega_2$ induce a Zeeman coherence grating in the Na vapor. This grating has a long life time if the diffusion of Na atoms is impeded by a high buffer gas pressure. Up to 20 atmospheres of He, Ar, Xe have been used. The grating is probed by a third beam at ω_1, and leads to a diffracted wave at $2\omega_1 - \omega_2$. The degenerate frequency case, $\omega_2 = \omega_1$, is of special interest (ref. 49). In this case, three incident light beams are derived from a single dye laser. Two beams produce a stationary coherence grating, which is probed by the third beam. Since all frequencies are equal, a phase conjugate backward wave geometry may be used, as shown in Fig. 6. The CARS-type resonance is probed by varying an external magnetic field, produced by Helmholtz coils, through zero. An ultra-narrow Hanle resonance with a width of about 10 kHz has been obtained, as shown in Fig. 7.

It is instructive to consider this collision-induced Hanle resonance as a limiting case of four-wave CARS-type mixing. It uses the features of polarization discrimination, of electronic one-photon near resonance enhancement and of collisional Doppler narrowing. Most importantly, however, the proportonality of signal to the square of the buffer gas prssure proves unambiguously the correct procedure (refs. 45,46) of incorporating damping into the formalism of Raman-type susceptibilities. The paradox that collisions can cause the appearance of a new coherent light beam created by four-wave mixing is resolved as follows. There are many contributions to the nonlinear susceptibility. In the absence of damping mechanisms different Feynman-type diagrams interfere destructively to give a vanishing contribution to the Zeeman- and Hanle-type resonances. The collisions destroy this particular destructive interference.

Collisions can also give rise to a Raman-type resonance between two initially unpopulated excited states. In fact, the resonance at $\omega_1 - \omega_2 \cong 17$ cm^{-1} between the excited doublet $^2P_{1/2} - {}^2P_{3/2}$ in Na vapor was the first experiment (ref. 47) on collision-induced coherence. The same effect has been explored in solids at low temperature, where lattice phonon interactions can make the resonance in an excited doublet observable (ref. 50). Stochastic fluctuations in the incident light beams can also induce such Raman-type resonance (ref. 51), and this has recently been confirmed experimentally in Sm-vapor (ref. 52). The field of collision-induced coherence gives a new handle on the nature of collisional processes and is now in an active stage of exploration.

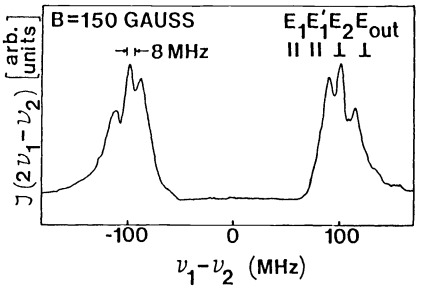

Fig. 5

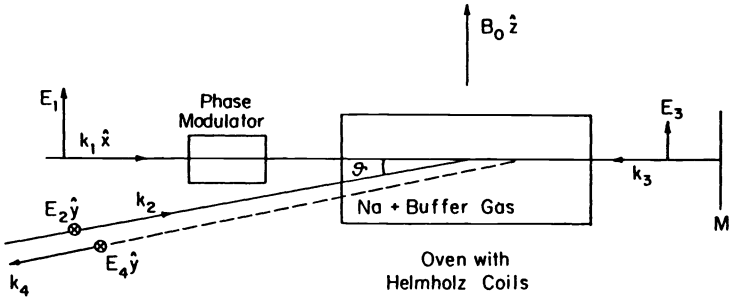

Fig. 6

Fig. 5. Collision-induced CARS-type Zeeman resonance in Na vapor in an external magnetic field of 150 gauss. The helium buffer gas pressure was 700 torr. The detuning Δ = 30 GHz below the $3^2S_{1/2}$ - $3^2P_{3/2}$ resonance. (After ref. 48).

Fig. 6. Experimental arrangement for frequency degenerate CARS to demonstrate the collision-induced Hanle resonance in zero magnetic field. Note the polarization directions of the light beams with respect to the scanning magnetic field. (After ref. 49).

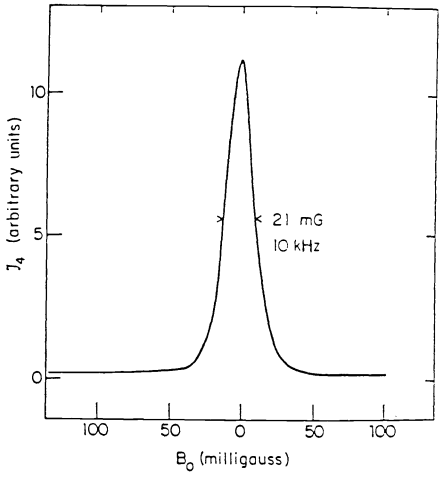

Fig. 7. An experimental Hanle-type resonance in Na vapor obtained with the arrangement of Fig. 6, under the following conditions: v = 0.3°, Na vapor saturated at 294°C, Ar buffer gas pressure 8400 torr, detuning Δ = 50 GHz below $3^2S_{1/2}$ - $3^2P_{1/2}$ resonance, intensity in interaction region 0.1 W/cm^2 for each beam. (After ref. 49).

CONCLUDING REMARKS

To round out a quarter century of SRS the timing of this writing (1986) requires a look ahead of only one year into the future. The proceedings of the 10th International Conference on Raman Spectroscopy present a rather comprehensive picture of current activity. Further progress will be made in time-resolved spectroscopy with subpicosecond resolution, in the study of hyper-Raman and other higher order effects with CARS, in extension of resonant Raman excitation in the UV region of spectrum, and in the development of Raman laser sources. During the past few years extensive theoretical investigations (refs. 53,54) have been made for four-wave light mixing in the case of one or more very strong light beams. The perturbation approach for those fields ceases to be valid. If only one light field is strong, the usual approach is to make a transformation to a rotating coordinate system so that the strong Hamiltonian for this light field becomes time-independent. Very recently these techniques have been extended to the case of two or more strong fields (refs. 54,55) CARS-type experiments with strong beams are likely to receive more attention. Extrapolation of the current activities instills confidence in the vitality of stimulated Raman scattering for the foreseeable future.

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