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NONLINEAR RAYLEIGH AND RAMAN LIGHT SCATTERING BY ATOMIC AND MOLECULAR SUBSTANCES[x]

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[x] The present paper is dedicated to the memory of Marian Smoluchowski, born 100 and deceased 55 years ago.

SUMMARY

Theoretical and experimental studies on nonlinear light scattering processes of the Rayleigh and Raman kinds resulting from the interaction between intense electromagnetic waves with individual electrons, atoms and molecules, and with assemblages of correlated molecules in dense matter, are reviewed.

1. LINEAR LIGHT SCATTERING

1.1. Molecular Rayleigh Scattering

Over a century has elapsed since the pioneering work of John Tyndall [1] and Lord Rayleigh [2] on the scattering of light on optical inhomogeneities in material media. Opaque and colloidal systems are intense scatterers. We shall not be dealing here with this light scattering process known as Tyndall's effect, but shall rather concentrate on the scattering which emerges from optically transparent and macroscopically homogeneous media, such as atomic and molecular gases and liquids and their mixtures as the result of various statistical fluctuations /we have in mind fluctuations of density, concentration, anisotropy, and so forth/. This in fact is what is known as molecular light scattering, the theoretical fundamentals of which are due to Lord Rayleigh [2], Smoluchowski [3], and Einstein [4].

Lord Rayleigh, when studying the azure of the sky, established the fundamental fact that the intensity I^S of light scattered by individual /nonabsorbing/ atoms or molecules is inversely proportional to the fourth power of the incident light wavelength $\lambda = 2\pi c/\omega$ and directly proportional to the incident intensity I :

$$I^S(\omega) \simeq \lambda^{-4} I \quad . \qquad /1/$$

This then is elastic scattering, also referred to as Rayleigh scattering, in which the incident and scattered wavelength is the same. Quantum-mechanically, Rayleigh scattering consists in the absorption of a photon of incident light by an atom or molecule and the simultaneous emission of a photon of the same energy though not necessarily the same direction.

Smoluchowski [3] showed that on a microscopic scale no medium is truly homogeneous, since random thermal motion gives rise to spontaneous fluctuations in density in elements of volume of linear dimensions less than the light wavelength. In accordance with the Lorentz-Lorenz relation [5], these thermal fluctuations in density entail local variations of the refractive index and, consequently, optical inhomogeneity. In this way Smoluchowski was able to prove that the true reason of molecular light scattering /and thus of the blue colour of the sky/ resides in fluctuations in density. These fluctuations increase immensely as one approaches the critical point of a substance causing the effect of critical opalescence. Einstein [4], extending the ideas of Lord Rayleigh and Smoluchowski, proposed a quantative thermodynamical theory of light scattering by liquids and solutions taking into account, besides fluctuations in density, fluctuations in concentration of solutions.

Further extensions of the theory of Rayleigh light scattering dealt with the rôle of fluctuations in the anisotropy of polarisability of molecules [6-9], translational fluctuations [10,11], as well as translational-orientational fluctuations [12]. Information concerning the linear optical polarisability of individual molecules and the anisotropy of their polarisability is obtained from studies of the depolarisation of light scattered by gaseous systems [6,13] and of the depolarized component from dilute solutions [14]. The investigation of light scattering on liquids and solutions moreover provides data relating to the structure of short-range ordering, both radial and orientational [12,15].

1.2. Raman Scattering

In the general case elastic scattering at unchanged wavelength is accompanied by inelastic scattering involving a change in the light wavelength discovered by Raman and Krishnan [16] in liquids and by Landsberg and Mandelshtam [17] in crystals. This process of Raman scattering, also referred to as modulation or combination scattering /in Russian: kombinatsionnoye rasseyanye/ consists in the following: an atom or molecule in the act of light scattering undergoes a transition from an initial energy state to another, arbitrary discrete quantum state. This quantal picture had already been predicted by Smekal [18], according to whom there is apparent a scattering at an oscillation frequency $\omega_s = \omega - \omega_{\alpha\beta}$ less than that of the incident light wave /a Stokes frequency line/ and at an oscillation frequency $\omega_{as} = \omega + \omega_{\alpha\beta}$ larger than that of the incident wave /an anti-Stokes line/. Here, $\omega_{\alpha\beta} = (E_\beta - E_\alpha)/\hbar$ is the oscillation frequency related with the transition between the energy levels E_α and E_β. Stokes Raman scattering is more strongly favoured than anti-Stokes scattering, since the latter involves a transition from an upper state, the population of which /for a given temperature/ falls off exponentially with increasing energy separation of the two quantum states [19]. Raman spectroscopy rapidly developed into a separate discipline and provides information complementary to that obtained from infrared spectroscopy [19-22].

2. NONLINEAR SCATTERING PROCESSES OF LIGHT

2.1. Three-photon Scattering Processes

The quantum-mechanical theory of electromagnetic radiation as initiated by Dirac [23], allows one to compute the probability of various processes involving the emission, absorption or scattering of light quanta [24]. In general, such processes can occur in two- or many-quantum acts. In the visible region, simultaneous absorption and emission of two quanta was dealt with by Goeppert-Mayer [25]. Blaton [26], by second-order quantum mechanical perturbation theory, showed that a system of atoms subjected to irradiation with frequency ω emits waves of double frequency 2ω. This light scattering at double frequency was subsequently investigated by Güttinger [27], Neugebauer [28], Kielich [29], and Li [30]. Namely, the object of study was a nonlinear process of the Rayleigh kind, when two quanta of the frequencies ω_1 and ω_2 are incident on a molecular system, which scatters elastically a new quantum of the summation frequency $\omega_1 + \omega_2$ or the difference frequency $\omega_1 - \omega_2$. In the particular case when the two incident photons have the same frequency, $\omega_1 = \omega_2 = \omega$, the summation process yields Rayleigh scattering at double frequency. Kielich [31] proposed the study of this novel Rayleigh scattering for the determination of the second-order nonlinear polarisabilities of molecules not possessing a centre of symmetry. The method became promising when Terhune, Maker and Savage [32], using a giant pulsed ruby laser, performed the first measurement of nonlinear light scattering.

Güttinger [27] and Kielich [29] carried out a theoretical investigation of the general case of three-photon inelastic scattering, when a molecular system goes over from a quantum state α to a state β under the effect of two incident photons of frequencies ω_1 and ω_2 and scatters a third photon, of a frequency $\omega_3 = \omega_1 + \omega_2 \pm \omega_{\alpha\beta}$.

2.2. Hyper-Raman Scattering

For two incident photons of the same frequency, one has double-photon Raman scattering at the Stokes type frequencies $\omega_s = 2\omega - \omega_{\alpha\beta}$ and anti-Stokes type frequencies $\omega_{as} = 2\omega + \omega_{\alpha\beta}$. The selection rules for this new scattering effect were first studied for all molecular point groups by Cyvin, Rauch and Decius [33], to whom is due the term Hyper-Raman Effect /derived from that of molecular hyperpolarisability [34] /. Recently, Peticolas et all [35] extended these studies to molecules of biological polymers. Akhmanov and Klysko [36], and recently Long and Stanton [37], discussed the enhancement of hyper-Raman scattering intensity through resonance processes. Maker et all [38] lately developed a technique of hyper-Raman spectroscopy in the gas phase.

The selection rules for hyper-Raman activity are quite different /and rather less restrictive/ from those for infrared and ordinary Raman activity, numerous Raman and infrared inactive modes being hyper-Raman active. Thus, this novel kind of nonlinear light scattering spectroscopy offers a method for the direct investigation of molecular frequencies previously regarded as spectroscopically inaccessible and is thus of very considerable interest. For a clear and highly stimulating presentation of these matters, we refer the Reader to the excellent articles by Long [39] as well as the review articles by Brandmüller and Schrötter [22] covering linear as well as nonlinear Raman spectroscopy.

2.3. Co-operative Hyper-Rayleigh Scattering

Kielich [40], in his formulation of the semi-macroscopic theory of elastic second-harmonic scattering of light, showed that beside the above-discussed incoherent hyper-Rayleigh scattering due to individual molecules without a centre of symmetry, co-operative scattering can be caused in dense matter by centrosymmetric molecules once the molecular centre of symmetry is destroyed by local time and space fluctuations of molecular electric fields. Recently, indeed, such co-operative second-harmonic scattering by neighbouring molecules has been detected by Lalanne, Martin and Kielich [41] in liquids such as cyclohexane, benzene and the like. Obviously, as has been shown by Bersohn et all [42] and Kielich [41,43], in liquids with not centro-symmetric molecules one has in addition to incoherent scattering by single molecules coherent double-photon scattering by neighbouring molecules, whose positions and orientations are correlated. However, the experimental work of Weinberg [44] points to a rather weak influence of orientation molecular correlations on second-harmonic scattering in liquids. Nevertheless, Freund [45] has reported observations of intense second-harmonic scattering by fluctuations in angular orientation in NH_4Cl for temperatures in the immediate vicinity of the second-order phase transition.

Quite recently, Strizhevsky and Obukhovsky [46], as well as Jha and Woo [47], proposed a theory of nonlinear light scattering from phonons in crystals, which opens up new possibilities in the study of ionic motion.

2.4. The Advantages and Limitations of Applying Lasers as Light Sources

For reasons which are quite obvious, the experimental observation of nonlinear scattering processes became feasible only thanks to laser techniques, or rather since the time of the first, truly magnificent experiment of Franken et all [48] in 1961 in which they proved that ruby laser light of wavelength λ_{ω}=6943 Å, focused within a quartz crystal, gave rise to the second harmonic of coherent light at the wavelength $\lambda_{2\omega}$= 3471.5 Å. Lasers operating continuously or pulsewise emit a parallel beam of monochromatic light, coherent in space and time, and conveying a flux of immense energy density. It was precisely this high intensity of laser light, inachievable in usual conditions, that permitted the induction in matter of new nonlinear optical phenomena like harmonics generation and self-focusing [49-54], including the previously discussed hyper-Rayleigh and hyper-Raman scatterings, as well as stimulated Raman and Brillouin scatterings [55,56] which, however, will not be dealt with in this article.

Obviously, for each material there exists a well-defined limit with regard to the application of giant power lasers upward of which some destruction sets in [57], making it impossible to continue the observation of this or that nonlinear process. But laboratories now have at their disposal a wide range of lasers, from normal pulsed lasers of a power of 10^5 W to Q-switched 10^8 W lasers and the recently constructed picosecond pulsed lasers providing as much as 10^{12} W in a peak [57,58]. Generally, at powers upward of 10^8 W, parasitical processes perturb the investigation of nonlinear scattering [59]. In those critical conditions, many-photon ionisation occurs in gases [60], or optical breakdown, or emission of neutrons from plasma arising in the focus of the laser beam [58]. These and other processes of interaction between the electrons and intense laser fields are the subject of other Reports at the present Conference.

Laser light sources have revolutionized Raman spectroscopy for at least two reasons: firstly, their high intensity and very narrow linewidth have greatly improved the achievable sensitivity and resolution; secondly, the collimation and polarisation of the laser beam permit the separation of the polarisation component and also allow analyses of the angular dependence of Raman scattering, usual and nonlinear [40, 61-63]. Experimental studies on scattering processes resort to at least 4 types of lasers:

/1/ the He-Ne gas laser / λ = 6328 Å, CW power 0.1 W/,
/2/ the Ar-ion gas laser / λ = 4880 or 5145 Å, CW power 2 W/,
/3/ the CO_2 gas laser / λ = 106000 Å, CW power 10-5000 W/,
/4/ the Nd:YALG solid-state laser / λ =106000 Å, CW power 1 - 250W/.

These types of continuously operating lasers, used in linear scattering spectroscopy, can be applied as sources of the light beam analyzing various nonlinear changes in scattering processes. When studying nonlinear scattering processes, we make use of giant pulsed lasers, thus the giant pulsed ruby laser [32,41,64,65] / λ = 6943 Å, 10^6-10^7 W peak power in a pulse of 10^{-7} sec half-width/, and the Q-switched Nd:glass laser [41,59] / λ = 106000 Å, mean power 10^6-10^7 W/.

2.5. Higher-order Scatterings of Intense Light

In gases, three-photon scattering processes can take place in the dipole approximation only if the molecules do not possess a centre of symmetry. Accordingly, Kielich [29,66] developed a quantum-mechanical theory of four-photon scattering processes, which are less sensitive to molecular symmetry and can take place in the case of atoms also. Here, three photons with the frequencies ω_1, ω_2, ω_3 are incident upon an atom or molecule giving rise to a fourth photon, of one of the frequencies

$\omega_4 = \omega_1 \pm \omega_2 \pm \omega_3$ at elastic scattering, or

$\omega_4 = \omega_1 + \omega_2 + \omega_3 \pm \omega_{\alpha\beta}$ at inelastic scattering. The symmetry relations and selection rules for these scatterings have been discussed by various authors [67-69]. A particular case of this is third-harmonic scattering, as discussed in detail for gases by Kozierowski [70] and for liquids by Kielich and Kozierowski [71]. The possibilities for observing third-harmonic scattering are not particularly good, though it may be worth mentioning that lately Ward and New [72] succeeded in producing a third harmonic in the neutral gases.

In general, one has nonelastic processes with n photons of frequencies ω_1, ω_2, ... ω_n incident on the molecule, which if making a transition from quantum state α to β, scatters an /n+1/-th photon with frequency [62]:

$$\omega_{n+1} = \sum_{i=1}^{n} \omega_i \pm \omega_{\alpha\beta} \pm \cdots \qquad /2/$$

When considering these multi-harmonic scattering processes, one has to take into account not only the commonly considered electric dipole type transition but moreover transitions of higher orders e.g. the electric quadrupole transition, magnetic dipole transition [73], and quite generally all electric and magnetic multipole transitions [66].

Restricting ourselves for the sake of simplicity to elastic scattering of the electric dipole kind, one can define as follows the tensor of scattered light intensity [29]:

$$I_{ij}^{S} = \left\langle \frac{\partial^2 M_i}{\partial t^2} \left(\frac{\partial^2 M_j}{\partial t^2} \right)^{*} \right\rangle , \qquad /3/$$

where $M_i(t)$ stands for the i-th component of the electric dipole moment induced in the scattering medium by the electric field $E(\omega)$ of a light wave oscillating at the frequency ω. The symbol $\langle \; \rangle$ in Eq./3/ denotes classical or quantal statistical averaging in the presence of the radiation field.

If the light beam incident on the medium is of a sufficiently high intensity I, as is the case with giant lasers, linear as well as higher-order scatterings occur, whence /3/ can be expanded in a series [74]:

$$I_{ij}^{S} = \sum_{n=1}^{\infty} I_{ij}^{(n)} , \qquad /4/$$

where the tensor

$$I_{ij}^{(n)} = \sum_{k=1}^{n} (k\omega)^4 \left\{ F_{k\omega}^{(n)} I \delta_{ij} + G_{k\omega}^{(n)} I_{ij} \right\} I^{n-1} \qquad /5/$$

defines elastic scattering of the n-th order. The quantities $F_{k\omega}^{(n)}$ and $G_{k\omega}^{(n)}$ are factors characterizing the isolated molecule optically and the scattering medium structurally and thermodynamically, and are in general implicite functions of the harmonic frequencies ω, 2ω, ... $k\omega$. For $k = n$, the tensor

/5/ defines n-harmonic scattering, which can be resolved from among the other nonlinear scattering processes /$k < n$/ in experiments bearing not only on frequency-dependence but also on temperature-dependence, since $F^{(n)}_{n\omega}$ and $G^{(n)}_{n\omega}$ depend to a much lesser degree on temperature than is the case for $F^{(n)}_{k\omega}$ and $G^{(n)}_{k\omega}$. Above, $2 \leq k < n$ [75].

The tensor /5/, which with regard to /3/ defines many-quantum processes generally involving n+1 photons, splits into a part independent of the state of polarisation of the incident intensity I and a part depending on its polarisation as given by the intensity tensor I_{ij}. In this respect, Eq. /5/ represents the general expression for the angular dependence of nonlinear light scattering observation.

In particular, for first-order scattering we have by /5/:

$$I^{(1)}_{ij} = \omega^4 \left\{ F^{(1)}_{\omega} I \delta_{ij} + G^{(1)}_{\omega} I_{ij} \right\}, \qquad /6/$$

which is the well-known formula for linear Rayleigh scattering with the ground frequency ω. The factors $F^{(1)}_{\omega}$ and $G^{(1)}_{\omega}$ depend on the linear optical properties of the atoms or molecules as well as on their various correlations in dense media [12].

For second-order scattering, Eq. /5/ yields :

$$I^{(2)}_{ij} = \omega^4 \left\{ F^{(2)}_{\omega} I \delta_{ij} + G^{(2)}_{\omega} I_{ij} \right\} I + (2\omega)^4 \left\{ F^{(2)}_{2\omega} I \delta_{ij} + G^{(2)}_{2\omega} I_{ij} \right\} I . \qquad /7/$$

Quite generally, this expression points to the presence of nonlinear scattering at the ground frequency ω as well as at the second-harmonic frequency 2ω, as observed experimentally by Terhune et all [32]. The microscopic mechanisms of the two processes in gases are entirely different: whereas the one depends essentially on optical orientation of anisotropic linearly polarizable molecules [75] , the second-harmonic process is due directly to second-order nonlinear polarisation, which can occur only in molecules in the ground state without a centre of inversion [29] . Condensed media involve considerable dependence on a variety of radial and angular pairwise and triple molecular correlations [40,42], which can give rise to light scattering even in substances consisting of centrosymmetric molecules [41] . A closer statistical-molecular analysis of the factors $F^{(2)}_{2\omega}$ and $G^{(2)}_{2\omega}$ shows moreover that second-harmonic scattering is more highly sensitive to molecular symmetry and the statistical structure of the medium than is linear Rayleigh scattering, Eq. /6/.

By /5/, the third-order scattering intensity tensor is:

$$I^{(3)}_{ij} = \omega^4\left\{F^{(3)}_{\omega} I \delta_{ij} + G^{(3)}_{\omega} I_{ij}\right\} I^2 + (2\omega)^4\left\{F^{(3)}_{2\omega} I \delta_{ij} + G^{(3)}_{2\omega} I_{ij}\right\} I^2 + (3\omega)^4\left\{F^{(3)}_{3\omega} I \delta_{ij} + G^{(3)}_{3\omega} I_{ij}\right\} I^2 \qquad /8/$$

involving in general three distinct processes. Those occurring at the frequency ω and 3ω depend more weakly on the molecular symmetry than does second-harmonic scattering; it is essential that they can result from isolated atoms or isotropic molecules by nonlinear third-order polarisation [29] . However, the light intensity is less affected by third-order than by second-order scattering processes. In fact, $I^{(2)}/I^{(1)}$ is of the order of $/10^{-11} - 10^{-12}/I$ and is now accessible to measurement by laser techniques [32,41]. But $I^{(3)}/I^{(1)}$, which is of the order of $/10^{-22} - 10^{-24}/I^2$, would only be detectable experimentally with laser beam intensities upward of 10^8 e.s.u., that is to say, at near-threshold conditions for multi-photon photoionisation [60].

Similarly, Eq. /5/ permits the calculation of scattering processes of orders higher than the third. Their respective probabilities are extremely small, since $I^{(n+1)}/I^{(n)}$ is of the order of $/10^{-11} - 10^{-12}/^n I^n$. From quantum-mechanical considerations [29,66], it should be possible to detect these many-photon processes near resonance regions, where nonlinear variations of the tensor /5/ are large. Surely, extensive studies of higher-order scattering processes will provide better insight into the fine electro-magnetic structure of atoms and molecules, their nonlinear properties, and correlations in dense media, than was hitherto possible within the limitations of linear molecular optics.

2.6. Related Scattering Processes

In addition to the above-discussed nonlinear scatterings on atomic and molecular media, yet other nonlinear scattering processes are accessible to observation when resorting to other scatterers, such as free [76-78] and bonded [79,86] electrons, plasma [81], isolated atoms [82-85], macromolecules [35,86,87], and colloidal particles [88]. Karplus and Neuman [89], and McKenna and Platzman [90], developed a theory of light scattering on light in vacuum, whereas Rosen and Whitmore [91] proposed experiments for the observation of the vacuum scattering of light by light. The processes of interaction between photons in vacuum and in material media are discussed in the review articles of Gardner [92]. At present, these processes are of theoretical significance as concrete examples, or problems, in nonlinear quantum electrodynamics [93-95] and of the general problem of the interaction between an intense electromagnetic field and molecular electric or magnetic multipoles [66,96,97]. The scattering processes discussed above are largely determined, on the one hand, by the statistical-fluctuational properties of the medium [98,99] and, on the other, by the coherence and statistics of intense photonic fluxes [100, 101].

3. RESULTS AND CONCLUSIONS

We now proceed to a concise presentation of the results and conclusions from the study of nonlinear scattering processes in relation to the information provided by the investigation of other nonlinear optical effects.

3.1. Nonlinear Optical Polarizabilities of Atoms and Molecules

When an atom or molecule is acted on by the electric field $E(\omega_1)$ of a not excessively intense light wave, the dipole moment induced at frequency ω_2 /first-order moment/ is in a first approximation:

$$m_i^{(1)}(\omega_2) = a_{ij}(-\omega_2,\omega_1)\,E_j(\omega_1), \qquad /9/$$

where $a_{ij}^{\omega_2} \equiv a_{ij}/-\omega_2,\omega_1/$ is a second-rank tensor defining the linear molecular polarizability at frequency ω_2. The linear relation /9/ between the dipole moment and the electric field inducing it is a direct result of Lorentz's classical theory [5] of harmonic electron vibrations, as well as of the first approximation of quantum-mechanical perturbation calculus [19].

Eq./9/ accounts for linear optical processes, such as optical refraction and usual Rayleigh scattering.

If molecular systems are acted on by a sufficiently intense electric field, not only the linear dipole moment /9/ but also moments of higher orders are induced. In the classical theory of Lorentz, these moments are the result of anharmonicity in the electron vibrations [7] ; in quantum theory, they stem from higher orders of perturbation calculus [102]. Now, in particular, if a molecule interacts simultaneously with two waves of the oscillation frequencies ω_1 and ω_2, the second-order dipole moment induced at frequency $\omega_3 = \omega_1 + \omega_2$ can be expressed formally as follows:

$$m_i^{(2)}(\omega_3) = b_{ijk}(-\omega_3, \omega_1, \omega_2)\, E_j(\omega_1)\, E_k(\omega_2) \quad , \qquad /10/$$

where the third-rank tensor $b_{ijk}^{\omega_3} \equiv b_{ijk}(-\omega_3, \omega_1, \omega_2)$ describes nonlinear molecular polarizability of the second order (often referred to as the first hyperpolarizability [34]).

At $\omega_1 = \omega$ and $\omega_2 = 0$, the tensor $b_{ijk}^{\omega} \equiv b_{ijk}(-\omega, \omega, 0)$ is accessible to determination from static Kerr effect studies [7,34] or from molecular light scattering in liquids [12]. In the case when $\omega_1 = \omega_2 = \omega$, the tensor $b_{ijk}^{2\omega} \equiv b_{ijk}(-2\omega, \omega, \omega)$ describes the above discussed second-harmonic Rayleigh scattering process [31,32]/or first hyper-Rayleigh effect/ as well as second-harmonic generation by a gas or liquid subjected to the action of a DC electric field [103,104] .

When a molecule interacts with three waves /oscillation frequencies ω_1, ω_2, ω_3 / simultaneously, a third-order moment is induced in it which at the frequency $\omega_4 = \omega_1 + \omega_2 + \omega_3$

is given by the expression:

$$m_i^{(3)}(\omega_4) = c_{ijkl}\left(-\omega_4,\omega_1,\omega_2,\omega_3\right) E_j(\omega_1)\, E_k(\omega_2)\, E_l(\omega_3), \qquad /11/$$

where the fourth-rank tensor $c_{ijkl}^{\omega_4} \equiv c_{ijkl}(-\omega_4,\omega_1,\omega_2,\omega_3)$ describes nonlinear molecular polarizability of the third order /the second hyperpolarizability [34]/.

For the case $\omega_1 = \omega$ and $\omega_2 = \omega_3 = 0$, the tensor $c_{ijkl}^{\omega} \equiv c_{ijkl}(-\omega,\omega,0,0)$ describes the quadratic Voigt effect in Kerr's process [7,8] and can be determined numerically from studies on atomic and molecular gases [34]. For $\omega_1 = \omega$ and $\omega_2 = -\omega_3 = \omega_L$, the tensor $c_{ijkl}(-\omega,\omega,\omega_L,-\omega_L)$ describes the nonlinear electronic contribution to the optical birefringence induced in a gas or liquid by intense laser light of the frequency ω_L [105]. On the other hand, for $\omega_1 = \omega_2 = \omega$ and $\omega_3 = 0$, the tensor $c_{ijkl}^{2\omega} \equiv c_{ijkl}(-2\omega, \omega,\omega, 0)$ describes co-operative hyper-Rayleigh scattering in a liquid [40,41] and DC electric field induced second-harmonic scattering in gases [103,104,106]. Finally, for $\omega_1 = \omega_2 = \omega_3 = \omega$, the tensor $c_{ijkl}^{3\omega} \equiv c_{ijkl}(-3\omega,\omega,\omega,\omega)$ accounts for third-harmonic scattering and generation by gases and liquids [53,70-72].

In appropriately chosen experimental conditions, the phenomena discussed above permit the determination of the numerical values of the nonlinear polarizability tensors b_{ijk} and c_{ijkl}. When aiming at this, particular attention should be given to the measuring of laser light-induced birefringence [106,108], DC electric field-induced second-harmonic generation [103,106] and third-harmonic generation [53,43,72] /besides studies of hyper-Rayleigh scattering [107]/. Quantum-mechanical theories of the nonlinear polarizability tensors b_{ijk} and c_{ijkl} have been worked out [29,66,109] . Symmetry relations have been discussed and the number of mutually independent tensor elements determined by group theory for all point groups [33,68,110] /see Table I/. For atoms and some simple molecules, numerical computations of the tensor elements b_{ijk} and c_{ijkl} have moreover been carried out by various theoretical methods [34,54,111,112] for the respective frequencies. The results of these calculations of nonlinear atomic and molecular polarizabilities, together with the values determined from the previously discussed nonlinear processes, are listed in Table II.

3.2. Depolarisation of Hyper-Rayleigh Scattering

When considering only pure harmonic scattering, the order of the scattering in Eq. /5/ coincides with the ordinal number of the harmonic, so that with regard to the n-th harmonic of elastic scattering we can write [62] :

$$I_{ij}^{n\omega} = (n\omega)^4 \left(F_{n\omega} I \delta_{ij} + G_{n\omega} I_{ij} \right) I^{n-1} \quad . \qquad /12/$$

If experimental conditions are chosen so that the incident light wave is polarized vertically, Eq. /12/ leads to the following expression for the depolarisation ratio of the n-th harmonic of scattered light [62] :

$$D_v^{n\omega} = \frac{F_{n\omega}}{F_{n\omega} + G_{n\omega}} \quad . \qquad /13/$$

In particular, for the second scattered harmonic, this leads to:

$$D_V^{2\omega} = \frac{F_{2\omega}}{F_{2\omega} + G_{2\omega}} \quad . \qquad /14/$$

In the present case, the structural parameters $F_{2\omega}$ and $G_{2\omega}$ are dependent on the tensor $b_{ijk}^{2\omega}$, occurring in Eq. /10/ . Assuming for simplicity the tensor $b_{ijk}^{2\omega}$ as totally symmetric /as in fact it is in the absence of electron dispersion and absorption/, and on neglecting interactions between the molecules, we get [29,40] :

$$F_{2\omega} = \frac{N}{840\ V}\left(4\, b_{ijk}^{2\omega}\, b_{ijk}^{2\omega} - b_{ijj}^{2\omega}\, b_{ikk}^{2\omega}\right) ,$$

$$G_{2\omega} = - F_{2\omega} + \frac{N}{280\ V}\left(2 b_{ijk}^{2\omega}\, b_{ijk}^{2\omega} + 3 b_{ijj}^{2\omega}\, b_{ikk}^{2\omega}\right) , \qquad /15/$$

where N is the number of molecules per volume V of the scattering medium.

In the particular case of molecules having the tetrahedral symmetry T_d , one has:

$$F_{2\omega} + G_{2\omega} = \frac{3}{2}\ F_{2\omega} = \frac{3N}{70V}\left(b_{123}^{2\omega}\right)^2 \quad , \qquad /15a/$$

and the depolarisation ratio /14/ amounts to [31] :

$$D_V^{2\omega} = \frac{2}{3} \quad . \qquad /14a/$$

Formulas /15/ describe non-coherent elastic second-harmonic scattering /hyper-Rayleigh effect/ by molecules not possessing a centre of symmetry. The first to detect this type of scattering in carbon tetrachloride, water, etc. were Terhune et all [32], using laser technique. Recently, Maker [64] reported extensively on spectral broadening of elastic second-harmonic light scattering in a number of liquids. The broadening arises principally from rotational molecular motions, and such studies provide information about the time-dependence of the orientation-dependent molecular pair diatribution function of liquids, as does the investigation of linear scattering [113].

For molecules having a centre of symmetry in their ground state, the tensor $b^{2\omega}_{ijk}$ as well as the structural parameters /15/ vanish, ruling out this type of second-harmonic scattering. In liquids, however, one has to take into account the temporally and spatially fluctuating molecular field $\vec{F}(\vec{r},t)$ of electric multipoles. Its field strength in regions of near-range ordering considerably exceeds that of the electric field $\vec{E}(\vec{r},t)$ of light waves. This molecular field $\vec{F}(\vec{r},t)$ lowers the molecular symmetry by causing some additional nonlinear distortion of the electron shells and interatomic bonds. Thus, if the molecule possesses a symmetry centre in its ground state, the molecular field $\vec{F}(\vec{r},t)$ removes it thus endowing the molecule with the capacity to cause double photon scattering. We have moreover to take into consideration that the molecular field not only modifies the symmetry of the molecule by a nonlinear distortion described by the effective tensor

$$b^{2\omega}_{ijk}(\vec{F}) = b^{2\omega}_{ijk}(0) + c^{2\omega}_{ijkl}\ F_l + \dots, \qquad /16/$$

/where the term in the tensor $c^{2\omega}_{ijkl}$ contains non-zero compponents for molecules of all symmetries/ but in addition induces an electric anisotropy in regions of near ordering. As a consequence, the molecular fluctuational regions /the dimensions of which are small in comparison with the incident wavelength λ / do not as a whole possess a centre of symmetry and, accordingly, act as sources of co-operative second-harmonic scattering, determined by the following structural parameters [41,59]:

$$F_{2\omega}=\frac{1}{840}\left\langle\sum_{p=1}^{N}\sum_{q=1}^{N}\left\{4\,c_{ijkl}^{2\omega(p)}\,c_{ijkm}^{2\omega(q)}\right.\right. -$$

$$\left.\left.-\,c_{ijjl}^{2\omega(p)}\,c_{ikkm}^{2\omega(q)}\right\}F_l^{(p)}\,F_m^{(q)}\exp\left[i\left(\Delta\vec{k}\cdot\vec{r}_{pq}\right)\right]\right\rangle ,$$

$$G_{2\omega}+F_{2\omega}=\frac{1}{280V}\left\langle\sum_{p=1}^{N}\sum_{q=1}^{N}\left\{2\,c_{ijkl}^{2\omega(p)}\,c_{ijkm}^{2\omega(q)}\right.\right. +$$

$$\left.\left.+\,3\,c_{ijjl}^{2\omega(p)}\,c_{ikkm}^{2\omega(q)}\right\}F_l^{(p)}\,F_m^{(q)}\exp\left[i\left(\Delta\vec{k}\cdot\vec{r}_{pq}\right)\right]\right\rangle , \qquad /17/$$

where $\Delta\vec{k}=\vec{k}_{2\omega}-2\vec{k}_{\omega}$, with $\vec{k}_{\omega}$ denoting the wave vector of incident light and $\vec{k}_{2\omega}$ that of the second-harmonic scattered wave; $\vec{r}_{pq}$ is the vector connecting the centres of the two scattering molecules p and q.

On neglecting, in a first approximation, the anisotropic part of the nonlinear tensor $c_{ijkl}^{2\omega}$, the following relation holds between the structural parameters [41] :

$$F_{2\omega}+G_{2\omega}=9\,F_{2\omega}=\frac{N}{27\,V}\,c_{2\omega}^{2}\left\langle F^{2}\right\rangle , \qquad /18/$$

where, for molecules possessing the symmetry of the point groups D_{6h} and $D_{\infty h}$, we have the mean second-order nonlinear polarisability:

$$c_{2\omega}=c_{iijj}^{2\omega}/5=\left(3c_{3333}^{2\omega}+12\,c_{3311}^{2\omega}+8\,c_{1111}^{2\omega}\right)/15 . \qquad /19/$$

The mean statistical value of the square of the molecular field, $\langle F^2 \rangle$, in general differs from zero. In the particular case of axially-symmetric molecules having a quadrupole moment Θ, it is given as follows [40]:

$$\langle F^2 \rangle = 3\,\Theta^2 \left\langle \sum_{q=p}^{N} r_{pq}^{-8} \right\rangle \quad . \qquad /20/$$

In the isotropic approximation of Eq. /18/, the depolarisation ratio /14/ assumes the following numerical value [40]:

$$D_v^{2\omega} = \frac{1}{9} \simeq 0.11 \quad . \qquad /21/$$

On taking into account the anisotropic part of the tensor $c_{ijkl}^{2\omega}$, we obtain in place of /21/ the expression:

$$D_v^{2\omega} = \frac{1}{9} \; \frac{1 + \Delta_{2\omega}^2}{1 - \Delta_{2\omega}^2} \quad , \qquad /22/$$

where in particular for axially-symmetric molecules and on neglecting their angular correlations we have in approximation [41]:

$$\Delta_{2\omega}^2 = \frac{51}{175} \left(\frac{c_{3333}^{2\omega} - c_{1111}^{2\omega}}{c_{3333}^{2\omega} + 2c_{1111}^{2\omega}} \right)^2 \quad . \qquad /23/$$

The results of measurements of $D_v^{2\omega}$ for liquids consisting of molecules without a centre of symmetry, as well as of centrosymmetric molecules, are listed in Table III.

A measuring circuit for the study of co-operative hyper-Rayleigh scattering [41,65] is shown in Fig.1. Figs 2 and 3 give experimental results of Lalanne et all [59] for liquid benzene obtained using a Q-switched Nd:glass laser with high-transmission optical system. Zone /I/ belongs to co-operative hyper-Rayleigh scattering, in which no parasitical signal is recorded beyond the hyper-Raman effect region /$\pm$ 3000 cm^{-1}/. Zone /III/ corresponds to optical breakdown of the liquid. The intermediary zone /II/ originates from a not easily definable source; maybe we are dealing here with a pre-breakdown region, characterized by luminescent ionisation of several molecules and their subsequent recpmbination.

Formulas /22/ and /23/ permit the statement that studies of the depolarisation ratio of hyper-Rayleigh scattering provide direct information concerning the anisotropy of nonlinear third-order polarizability of centrosymmetric molecules. Formulas /17/ and /18/, on the other hand, provide a first method for direct determinations of the mean value of the square of the molecular field $\langle F^2 \rangle$ in the fluctuational region in a liquid.

3.3. Laser Hyper-Raman Spectroscopy.

At inelastic scattering, the tensor of the light intensity scattered at frequency $2\omega \pm \omega_{\alpha\beta}$ for the transition $\alpha \rightarrow \beta$ is given [29] by the following expression:

$$I_{ij}^{\alpha\beta}(2\omega) = \frac{1}{2}\left(2\omega \pm \omega_{\alpha\beta}\right)^4 \left\langle b_{ikl}^{\alpha\beta}(-2\omega)\, b_{jmn}^{\alpha\beta}(2\omega)\right\rangle I_{km} I_{ln} \quad , /24/$$

where I_{km} is the tensor of incident light intensity. The frequency-dependence of the nonlinear second-order polarizability tensor for the transition $\alpha \rightarrow \beta$ is of the form [29,96]:

$$b^{\alpha\beta}_{ijk}(-2\omega) = \frac{2}{\hbar^2}\sum_{\gamma\delta}\left\{ \frac{\langle\alpha|m_i|\gamma\rangle\langle\gamma|m_j|\delta\rangle\langle\delta|m_k|\beta\rangle}{(\omega_{\gamma\beta}+2\omega+i\Gamma_{\gamma\beta})(\omega_{\delta\beta}+\omega+i\Gamma_{\delta\beta})} + \frac{\langle\alpha|m_k|\delta\rangle\langle\delta|m_i|\gamma\rangle\langle\gamma|m_j|\beta\rangle}{(\omega_{\delta\alpha}-\omega-i\Gamma_{\delta\alpha})(\omega_{\gamma\beta}+\omega+i\Gamma_{\gamma\beta})} + \frac{\langle\alpha|m_j|\gamma\rangle\langle\gamma|m_k|\delta\rangle\langle\delta|m_i|\beta\rangle}{(\omega_{\gamma\alpha}-\omega-i\Gamma_{\gamma\alpha})(\omega_{\delta\alpha}-2\omega-i\Gamma_{\delta\alpha})} \right\}, \quad /25/$$

where $\langle\alpha|m_i|\gamma\rangle$ is the matrix element of the electric dipole moment operator for the transition $\alpha\rightarrow\gamma$ with the relaxation time $\Gamma^{-1}_{\alpha\gamma}$ /related with the damping of radiation/.

The nonlinear polarizability tensor /25/ is non-zero whenever $\alpha = \beta \pm 1$, or $\alpha=\beta$. At $\alpha=\beta+1$ we have Stokes and at $\alpha=\beta-1$ anti-Stokes hyper-Raman scattering, whereas $\alpha=\beta$ corresponds to hyper-Rayleigh scattering.

Apart of this quantum-mechanical description of hyper-Raman scattering consisting in an extension of the well-known Kramers - Heisenberg theory [114], one can proceed by the classical description, based on Placzek's linear theory of polarizability [19]. The latter theory was initially extended to nonlinear inelastic scattering by Kielich [29], and the approach was subsequently developed by a number of authors [33,37,61]. To take account of the atomic vibrations, the successive polarizability tensors are expanded in power series of the vibrational normal co-ordinates:

$$Q_\mu = Q^0_\mu \cos(\omega_\mu t + \varphi_\mu) \quad ,$$

the nuclear vibrational frequencies ω_μ being assumed to be very small as compared with the frequencies ω of the incident light wave.

Relevant to our considerations is the scattering process of the second order described by formula /10/, where the tensor b_{ijk} is now expressed in the form of an expansion on the assumption that the vibrations of the nuclei lead to a small distortion of the electron shell of the molecule [29] :

$$b_{ijk} = b^0_{ijk} + \sum_{\mu} \left(\frac{\partial b_{ijk}}{\partial Q_\mu} \right)_0 Q_\mu + + \frac{1}{2} \sum_{\mu\nu} \left(\frac{\partial^2 b_{ijk}}{\partial Q_\mu \partial Q_\nu} \right)_0 Q_\mu \, Q_\nu + \dots \qquad /26/$$

where the derivatives are evaluated at the equilibrium values of the normal co-ordinates.

The matrix elements of the tensor /26/ are commonly calculated with wave functions separated into an electron part and a nuclear part, and finally summation is performed over the relevant vibrational states [37,61] .

Since their earliest experiment, Terhune et all [32] observed both elastic and inelastic second-harmonic scattering. The experimental set-up used by them is shown in Fig.4. Spectra were excited with a pulsed ruby laser providing a plane-polarized, up to 10^6 W peak power, 80 nsec half-width and 10^{-3} radian divergence output beam at a two-per-minute repetition rate. The laser beam was focused at f/10 and the scattering collected at f/1. All measurements were carried out just below the threshold for dielectric breakdown or Raman laser action in the sample. This method permitted the obtaining of the nonlinear scattering spectra for water and fused quartz [32] as well as for methane pressurized to 100 atmospheres [115] . Maker and Savage [38] introduced certain modifications into the set-up of Terhune [32] /see Fig.4/ and Maker [64] in order to record the hyper-Raman spectra in a shorter time through the use of a multi-channel photon counting detector involving an image intensifier television camera--multi-channel scaler. The spectrum thus obtained for methane by Verdieck et all [38] is shown in Fig.5. The two prominent lines, centered at $\Delta = 100\ \mathrm{cm}^{-1}$ and $3050\ \mathrm{cm}^{-1}$, represent 510 and 4222 photoevents respectively. The first band corresponds to hyper-Rayleigh scattering /the methane molecule has T_d symmetry thus causing incoherent elastic double-photon scattering/ whereas the other band belongs to the hyper-Raman shift.

Fig.6 shows the hyper-Raman spectrum of ethane, the molecule of which in the ground state has the symmetry D_{3d} /consequently, being centrosymmetric, it cannot cause elastic double-photon scattering/. A hyper-Rayleigh line is totally absent, and the strong band located at $\Delta = 2950\ \mathrm{cm}^{-1}$ corresponds to hyper-Raman scattering, due to the torsional oscillation of ethane. We have here a highly instructive example of the fact that for highly symmetric molecules some vibrational spectra are forbidden in both infrared absorption and in usual Raman scattering; however, some of these vibrational transitions are allowed in hyper-Raman spectroscopy /in centrosymmetric molecules the vibrations can remove the centre of symmetry/.

Lately, Peterson [116] applied nonlinear scattering spectroscopy to the study of hyper-Rayleigh and hyper-Raman scattering as well as to that of the delayed fluorescence decay after laser excitation.

3.4. Critical Second-Harmonic Scattering in Powdered Samples

Lajzerowicz [117] predicted that second-harmonic scattering could take place on fluctuations in critical states. Freund [45] was the first to study second-harmonic scattering by NH_4Cl in the temperature region immediately above the lambda-point transition at $T_\lambda \simeq 242.6^oK$ /second-order phase transition involving rotational disordering of the tetrahedral NH_4^+ ions/. In the low-temperature phase, neighbouring NH_4^+ ions have parallel orientations, whereas in the high-temperature phase they are distributed randomly. The disordered phase has an effective microscopic centre of symmetry and does not exhibit second-harmonic generation. In the vicinity of the critical temperature /$T > T_\lambda$ /, fluctuations in angular orientation away from complete randomness permit the observation of second-harmonic generation, referred to by Freund as critical harmonic scattering. Freund established the fact that the harmonic scattering intensity decreases exponentially with temperature for $T > T_\lambda$, and varies but slowly with the temperature below T_λ Experiments of this kind /see Fig.7/ are sensitive to ordering over regions comparable in size or less than the coherence length for optical frequency doubling [51] , which in this instance is about 27 microns. Such studies permit evaluations of the long range correlation length, particularly when resorting to small-angle second-harmonic scattering, as was done recently by Freund and Kopf [118] , and can serve for reaching decisions when chosing between various controversial models in studies of second-order transitions; moreover, they can disclose the behaviour of the pairwise correlation function in the critical region [119] and, generally, permit comparisons with the results of other studies [120].

Noteworthy in this context is the highly interesting suggestion, put forward by Rabin [121], to apply second-harmonic generation to the study of defects in centrosymmetric solids. Lattice defects, introduced into a crystal, may alter the local point symmetry in the medium, and in fact may convert local inversion symmetry to that of a non-centrosymmetric point group.

3.5. Harmonics in the Scattering of Light by Electrons.

Laser technique has provided the basis for the investigation of interactions of intense light with electrons [60,77] apparent also as scattered light harmonics. Various aspects of the theory of harmonic light scattering by free electrons have been studied classically and quantum-mechanically, including relativistic and radiative corrections, by Vachaspati [76] and Ehlotzky [78]. The problem was dealt with in regard to elastically bound electrons by Bali and Dutt [79] and to anharmonically bound electrons by Goyal and Prakash [80].

Salat [81] developed the theory of nonlinear incoherent light scattering in a homogeneous plasma and showed that with a suitable choice of the difference frequency, enhanced light scattering occurs near the plasma frequency and on thermal ion density fluctuations.

3.6. Nonlinear Light Scattering by Optical Reorientation of Microsystems.

In matter composed of anisotropic microsystems /molecules, micromolecules, colloid particles / a sufficiently intense laser light beam will cause —— in addition to harmonic scatterings directly related with nonlinear electron distortion of the scattering centres —— a nonlinear scattering process due to reorientation of the microsystems by the electric field of the light wave [75] . Such optical reorientation of the microsystems should cause light intensity-dependent changes in the depolarisation ratio [122]. Lalanne's [123] attempt to detect these changes in molecular liquids proved inconclusive owing to the circumstance that, as nonlinearity of scattering became apparent, the liquid underwent destruction with growing laser light intensity. Numerical evaluations show that nonlinear changes in scattered light intensity can be predicted to occur by way of reorientation of macromolecules in solution in molecular liquids and of colloid particles in suspension [87] .In such systems, as has been shown by Kielich [87,88] , the relative changes in the vertical and horizontal components of scattered light intensity are given /at vertically polarized incident light/ by the formulas:

$$\delta V_v \left(1+\tfrac{4}{5}\kappa^2\right) = 4\kappa\, \Phi(\pm q) + \tfrac{8}{5}\kappa^2 \left\{ Q(\pm q) + T(\pm q) \right\}, \qquad /27/$$

$$\delta H_v = -Q(\pm q) \ ,$$

where $q = \frac{|a_{33} - a_{11}|}{2kT} I_v$ is the reorientation parameter of a macromolecule having the optical anisotropy $\kappa = (a_{33} - a_{11})/(a_{33} + 2a_{11})$ immersed in the electric field of a light wave of intensity I_v.

The reorientation functions $\Phi(\pm q)$, $Q(\pm q)$ and $T(\pm q)$ occurring in Eqs /27/ are plotted versus q in Fig.8, where the sign "plus" refers to cigar-like particles with positive optical anisotropy and the sign /minus" refers to disc-like particles with negative optical anisotropy. Eqs /27/ enable us to investigate nonlinear scattering arising not only from weak reorientation of the particles but moreover to study optical saturation of this reorientation —— an ordered state when all the particles are aligned into the oscillation direction of the electric vector of the intense light wave. Nonlinear Rayleigh light scattering studies, especially at optical saturation, constitute a simple method for determining the shape of macromolecules and colloid particles as well as the sign of their optical anisotropy. A similar method, involving the use of a DC electric field as orienting agent, was proposed by Stoylov [124].

3.7. Nonlinear Light Scattering on Optical Inhomogeneities.

Recently, experimental work has been reported from the USSR concerning the nonlinear scattering of an intense laser beam by optically inhomogeneous media. Chastov and Lebedyev [125] observed nonlinear light scattering from suspensions containing particles with dimensions smaller than the light wavelength, the scattered intensity growing with increasing intensity of the laser beam /Fig.9/. These authors, after Askaryan [126], attribute this nonlinear scattering to bubbles formed thermally around the absorbing particles. Danileyko et all [127] observed nonlinear scattering on small optical inhomogeneities in corundum crystals and explained it phenomenologically as being due to optical Kerr effect, electrostriction, and heating.

Askaryan [126] was the first to consider in general nonlinear scattering processes caused by thermal and acoustical perturbations at inhomogeneities. Of late, he and his co-workers [128] have drawn attention to the practical significance of effects of nonlinear light scattering by halos near inhomogeneities in natural media /air, water/ and in optical and laser elements /platinum particles in neodymium glass, carbon particles in ruby, particles in liquid media, etc./ which limit the transmission of high beam intensities.

The experimental results of Chastov and Lebedyev [125] represented by the graphs of Fig.9 would not, however, appear to admit of an explanation of the steep rise in scattered intensity and of its tendency to saturation by invoking thermal effects alone. Maybe a process of orientation of the particles contained within the bubbles intervenes here, leading in conformity with the theoretical curves of Fig.8 to optical saturation at sufficiently high intensities of the laser beam /provided the pulse duration is sufficiently long to permit this/.

4. SUGGESTIONS FOR FUTURE STUDIES

Since the time of Blaton [26] and Güttinger's [27] far-reaching theoretical anticipations of three-photon scatterings by nigh 35 years elapsed until the detection of those processes in the magnificent, highly imaginative experiment of Terhune, Maker and Savage [32]. During the past 10 years numerous theoretical papers have appeared in which various aspects of nonlinear light scatterings in a variety of media are analyzed, providing solid foundations for the new nonlinear spectroscopy of atoms and molecules down to picosecond pulse durations inclusively [129]. In fact, we are on the eve of operating a junction between the statistics of matter [40, 98, 99] and the statistics of photons [100,101].

The recent perfections of laser technique have led to much progress in hyper-Raman spectroscopy [38,39] and have moreover permitted the detection of critical harmonic scattering [45], co-operative hyper-Rayleigh scattering [41], and the inception of studies on nonlinear scattering by optical inhomogeneities [125-128]. These novel scattering processes will certaintly very soon attain the status of methods for the investigation of the nonlinear electro-magnetic properties of isolated atoms, molecules, macromolecules and particles as well as of the microscopic structure of liquids and solids, including phase transitions, critical and numerous other phenomena. Originating in the work of Smoluchowski on the statistical-fluctuational behaviour of matter, co-operative nonlinear scattering [41] and nonlinear diffraction processes [130] have become a highly effective and sensitive instrument for gaining insight into the various mechanisms of molecular correlations [131], periodic spatial modulation of nonlinear susceptibilities [130], long-range order [119], order-disorder transitions [119], and interactions between photons and phonons [46,47].

Further progress in nonlinear spectroscopy technique will permit the obtaining of hyper-Raman spectra of high quality which, in conjunction with infrared and usual Raman spectra /thus, using a single light source, one type of sample cell and a single spectrometer and detector [39]/ will disclose the finer details of molecular structure than was hitherto possible with usual spectroscopy. Also, much interesting information bearing on the relaxational mechanisms in resonance effects of electrons, ions, atoms and molecules in the optical spectral region will surely become available. Similarly with regard to the collision-induced light scattering studies recently initiated in gases by Birnbaum et all [132] /see also [13, 133] /, frequency-broadening of the second harmonic can be expected to be observable experimentally. One is hopeful that, quite soon, certain delicate experiments resulting from interaction of intense coherent laser beams with free electrons /e.g. revealing an intensity-dependent frequency shift in Compton scattering [77] etc. /as well as from pure interaction between photons [91] will be successfully performed. The experiments proposed, once performed, will resolve a variety of as yet controversial theoretical problems, especially in the domain of quantum electrodynamics theory [134].

Considerable importance will accrue to the studies of local electric field induced double photon scattering in atomic fluids suggested theoretically by Kielich [134] and of late put to effect experimentally by Maker [136] in the liquids nitrogen, argon, oxygen, etc Thus, co-operative elastic second harmonic light scattering can be said, to provide a new tool for the study of the neighbourhood of atoms and molecules in dense matter [137].

The vast amount of information provided by studies on nonlinear light scattering processes will supplement that derived from the study of other phenomena of nonlinear molecular optics [134] and will give us a deeper understanding of numerous problems of fundamental, theoretical and practical, significance, as well as of the truly astounding properties revealed by laser light.

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Table I. Number of non-zero elements (N) and of mutually independent elements (I) of the symmetric polarizability tensor a_{ij}, b_{ijk} and c_{ijkl} for all point groups.

Group	a_{ij}		b_{ijk}		c_{ijkl}	
	N	I	N	I	N	I
C_1	9	6	27	10	81	15
C_i	9	6	0	0	81	15
C_s	5	4	14	6	41	9
C_2	5	4	13	4	41	9
C_{2h}	5	4	0	0	41	9
C_{2v}	3	3	7	3	21	6
D_2	3	3	6	1	21	6
D_{2h}	3	3	0	0	21	6
C_4	3	2	7	2	29	5
S_4	3	2	12	2	29	5
C_{4h}	3	2	0	0	29	5
C_{4v}	3	2	7	2	21	4
D_{2d}	3	2	6	- 1	21	4
D_4	3	2	0	0	21	4
D_{4h}	3	2	0	0	21	4
C_3	3	2	15	4	53	5
S_6	3	2	0	0	53	5
C_{3v}	3	2	11	3	37	4

Table I. /cont./

D_3	3	2	4	1	37	4
D_{3d}	3	2	0	0	37	4
C_{3h}	3	2	8	2	21	3
C_6	3	2	7	2	21	3
C_{6h}	3	2	0	0	21	3
D_{3h}	3	2	4	1	21	3
C_{6v}	3	2	7	2	21	3
D_6	3	2	0	0	21	3
D_{6h}	3	2	0	0	21	3
T	3	1	6	1	21	2
T_h	3	1	0	0	21	2
T_d	3	1	6	1	21	2
O	3	1	0	0	21	2
O_h	3	1	0	0	21	2
$C_{\infty v}$	3	2	7	2	21	3
$D_{\infty h}$	3	2	0	0	21	3
K_h	3	1	0	0	21	1
K	3	1	0	0	21	1
D_{4d}	3	2	0	0	21	3
D_{5h}	3	2	0	0	21	3
D_{5d}	3	2	0	0	21	3
D_{6d}	3	2	0	0	21	3

Table II. Numerical values of linear and nonlinear polarizabilities of atoms and molecules. Only mean values are given: $a = a_{ii}/3$, $b = b_{ii3}/3 = b_{333}$ /for the axial symmetry/, $b \equiv b_{123}$ /for tetrahedral symmetry/ and $c = c_{iijj}/5 = C_{3333}$.

Units	10^{-24} cm^3	10^{-30} cm^5 esu^{-1}	10^{-36} cm^7 e.s.u.$^{-2}$		
Atom or molecule	a^{ω}	$b^{2\omega}$	c^{ω}	$c^{2\omega}$	$c^{3\omega}$
He	0.205	0	0.022 [34]	0.023 [111]	0.024 [111]
Ne	0.394	0	0.051 [34]	0.24 [106]	0.214 [72]
Ar	1.66	0	0.59 [34]	2.74 [106]	3.024 [72]
Kr	2.52	0	1.4 [34]	6.69 [106]	9.264 [72]
Xe	4.11	0	3.9 [34]	18.52 [106]	23.496 [72]
H_2	0.79	0	0.28 [34]	0.36 [103]	1.920 [72]
O_2	1.60	0		0.64 [103]	
CO	1.95			1.81 [103]	
CO_2	2.65	0	4.5 [34]		2.744 [72]
CH_4	2.6	0.01 115	2.6 [54]	1.48 [103]	
CCl_4	10.5	0.03 32	3.3 [108]	2.1 [103]	
CHF_3	1.81	-0.06 103	0.9 [34]	0.27 [103]	
$CHCl_3$	8.23	0.33 103	4.8 [105]	4.4 [103]	
C_2H_6	4.47		1.9 [34]	4.8 [103]	
CH_3I	7.28	0.84 103		8.0 [103]	
SF_6	4.47		1.2 [34]	0.26 [103]	

Table III. Experimental values of the depolarisation ratio of linear scattering D_v^{ω} and second-harmonic scattering $D_v^{2\omega}$ for some liquids.

Liquid	Point group of the molecule	D_v^{ω}	$D_v^{2\omega}$	
Water	C_{2v}	0.057	0.116	32
Carbpn tetrachloride	T_d	0.02	0.345	32
			0.51	64
			0.45	41
Chloroform	C_{3v}	0.11	0.65	64
Acetonitrile			0.10	32
Diethylether		0.038	0.16	64
Methylcyclohexane		0.058	0.10	64
Methanol		0.025	0.17	64
n-propanol		0.025	0.45	64
Isopropanol		0.02	0.21	64
Cyclohexane	D_{3d}	0.025	0.12	41
Tetrachlorethylene	D_{2d}		0.20	41
Trans - 1,2 - dichloroethylene	C_{2h}	0.25	0.24	41
Benzene	D_{6h}	0.27	0.17	41
Carbon disulphide	$D_{\infty h}$	0.48	0.21	41

Table IV. Activity of fundamental vibrations in infrared, Raman and hyper-Raman scattering [33].

Point group	Symmetry species	Tensor elements of:		
		dipole moment d_i	polarizability a^{ω}_{ij}	hyperpolarizability $b^{2\omega}_{ijk}$
D_{3d} (e.g. C_2H_6)	A_{1g}		$a_{11}+a_{22}$, a_{33}	
	A_{2g}			
	E_g		$a_{11}-a_{22}$, a_{12} a_{23}, a_{31}	
	A^g_{1u}			$b_{111}-3b_{122}$
	A^g_{2u}	d_3		$b_{222}-3b_{112}$, $b_{223}+b_{311}$, b_{333}
	E_u	d_1, d_2		$b_{111}+b_{122}$, $b_{222}+b_{112}$ $b_{223}-b_{311}$, b_{123}, b_{331}, b_{233}
D_{6h} (e.g. C_6H_6)	A_{1g}		$a_{11}+a_{22}$, a_{33}	
	A_{2g}			
	B_{1g}			
	B_{2g}			
	E_{1g}		a_{23}, a_{31}	
	E_{2g}		$a_{11}-a_{22}$, a_{12}	
	A_{1u}			
	A_{2u}	d_3		$b_{223}+b_{311}$, b_{333}
	B^f_{1u}			$b_{111}-3b_{122}$
	B^f_{2u}			$b_{222}-3b_{112}$
	E_{1u}	d_1, d_2		$b_{111}+b_{122}$, $b_{222}+b_{112}$, b_{331}, b_{233}
	E_{2u}			$b_{223}-b_{311}$, b_{123}

Figure Captions

Fig. 1. Schematic diagram of cooperative Rayleigh scattering measurements of Lalanne [41].

Fig. 2. Dependence of the SHLS intensity $V_v^{2\omega}$ on the reference signal I^2 for benzene. $\lambda_L = 1.06\mu$, $L/2 = 0.53$. Detection bandwidth about 500 cm^{-1} /Lalanne et al. [59]/.

Fig. 3. Dependence of the SHLS intensity $H_v^{2\omega}$ on the reference signal I^2 for benzene. $\lambda_L = 1.06\mu$, $L/2 = 0.53$. Detection bandwidth about 500 cm^{-1} /Lalanne et al. [59]/.

Fig. 4. Arrangement for observation of nonlinear scattering according to Terhune, Maker and Savage [32]. The polarization properties of the scattered light were determined with the laser both plane and circularly polarized. The signal from a 1P28 phototube which measured the scattered radiation through the monochromator, along with that from a monitor of the laser beam, was displayed on a dual-beam oscilloscope. Individual photoelectrons could be detected. Spurious signals occurred during the laser pulse about once in every 200 pulses.

Fig.5. Hyper-Raman spectrum of methane according to Maker et al. [38]. Horizontal scale is the hyper-Raman shift, $\Delta = 2\nu_{laser} - \nu_{scattered}$, and vertical scale is the number of counts accumulated divided by that of laser shots.

Fig.6. Hyper-Raman spectrum of ethane according Verdieck et al. [38]; /scales as in Fig.5/.

Fig.7. Diagram of the experimental arrangement for critical second-harmonic scattering in NH_4Cl according to Freund and Kopf [118].

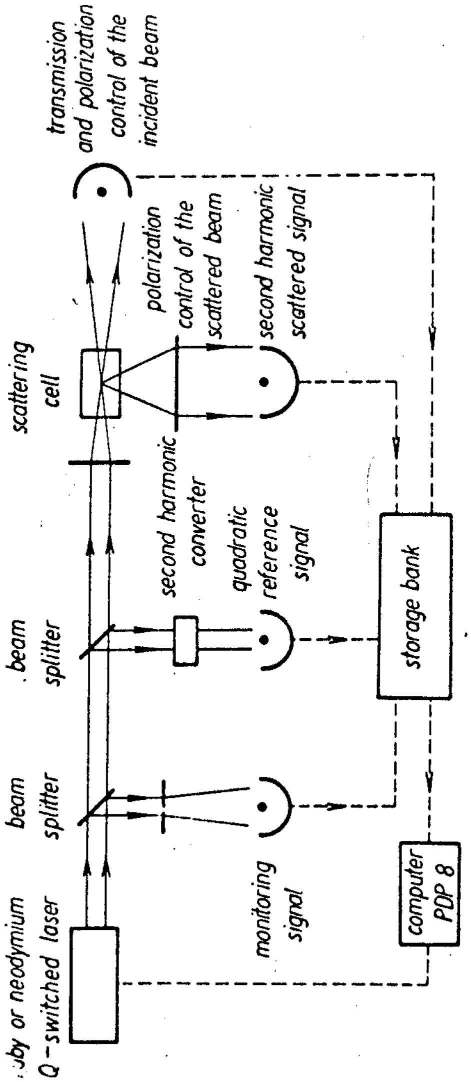
Fig.8. Reorientation functions /27/ of nonlinear scattering, describing the degree of alignment of the particles versus the parameter q, according to Kielich [37].

Fig.9. Dependence of the amount of light scattered at 90° on the incident intensity, for the following solutions: (according to Chastov and Lebedyev [125]):

1 - adducts of aluminium chloride phtalocyanine and aluminium bromide in dichlorobenzene solution,

2 - copper 2,3-naphtalocyanine in quinoline,

3 - platinum 1,2-naphtalocyanine in quinoline.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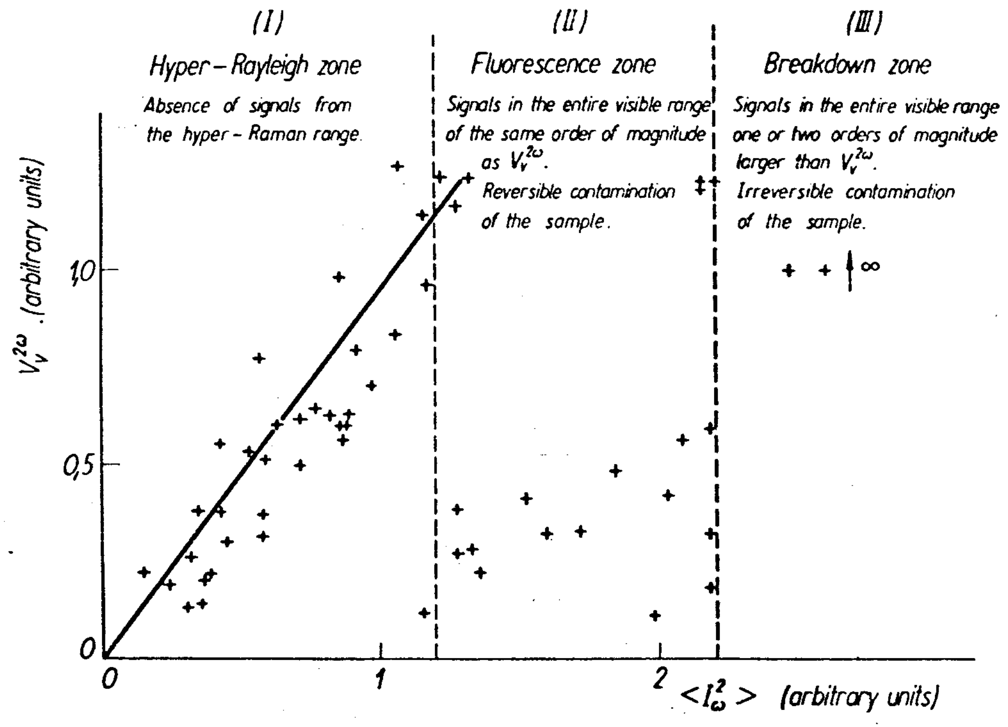
splitter
beam
splitter
scattering
cell
transmission
and polarization
control of the
incident beam
polarization
control of the
scattered beam
second harmonic
scattered signal
second harmonic
converter
quadratic
reference
signal
monitoring
signal
storage bank
computer
PDP 8

Fig. 1


(I)
Hyper–Rayleigh zone
Absence of signals from the hyper – Raman range.
(II)
Fluorescence zone
Signals in the entire visible range of the same order of magnitude as $V_v^{2\omega}$.
Reversible contamination of the sample.
(III)
Breakdown zone
Signals in the entire visible range one or two orders of magnitude larger than $V_v^{2\omega}$.
Irreversible contamination of the sample.
∞
$V_v^{2\omega}$. (arbitrary units)
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0,5
0
0
1
2
$<I_\omega^2>$ (arbitrary units)

Fig. 2

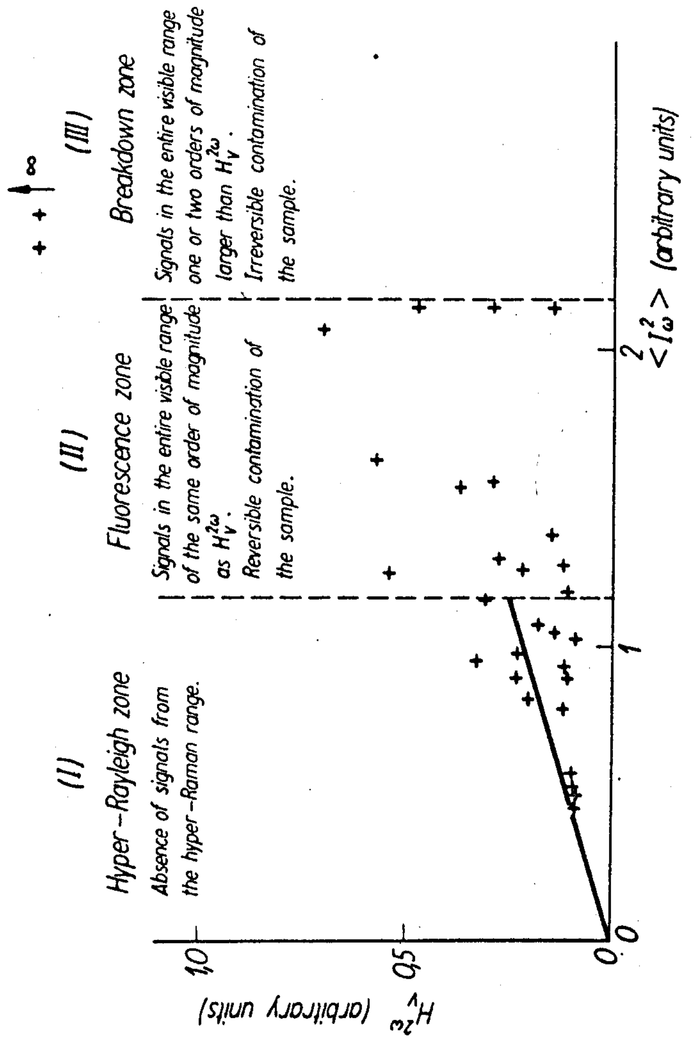
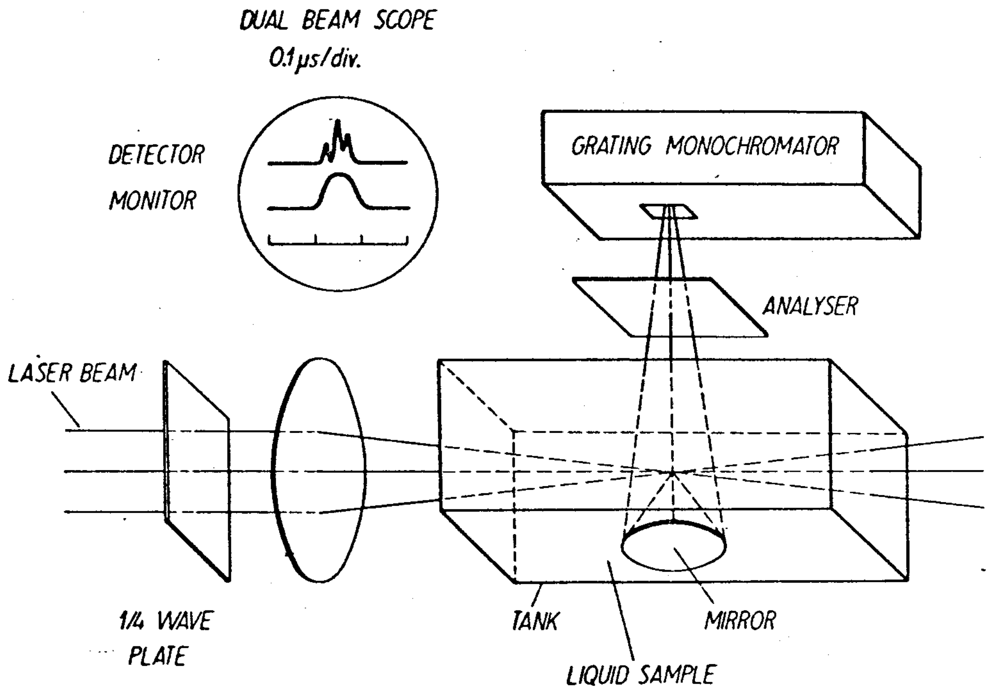

(I)
Hyper–Rayleigh zone
Absence of signals from the hyper–Raman range.
(II)
Fluorescence zone
Signals in the entire visible range of the same order of magnitude as $H_V^{2\omega}$.
Reversible contamination of the sample.
(III)
Breakdown zone
Signals in the entire visible range one or two orders of magnitude larger than $H_V^{2\omega}$.
Irreversible contamination of the sample.
∞
$H_V^{2\omega}$ (arbitrary units)
1,0
0,5
0
0
1
2
$<I_\omega^2>$ (arbitrary units)

Fig. 3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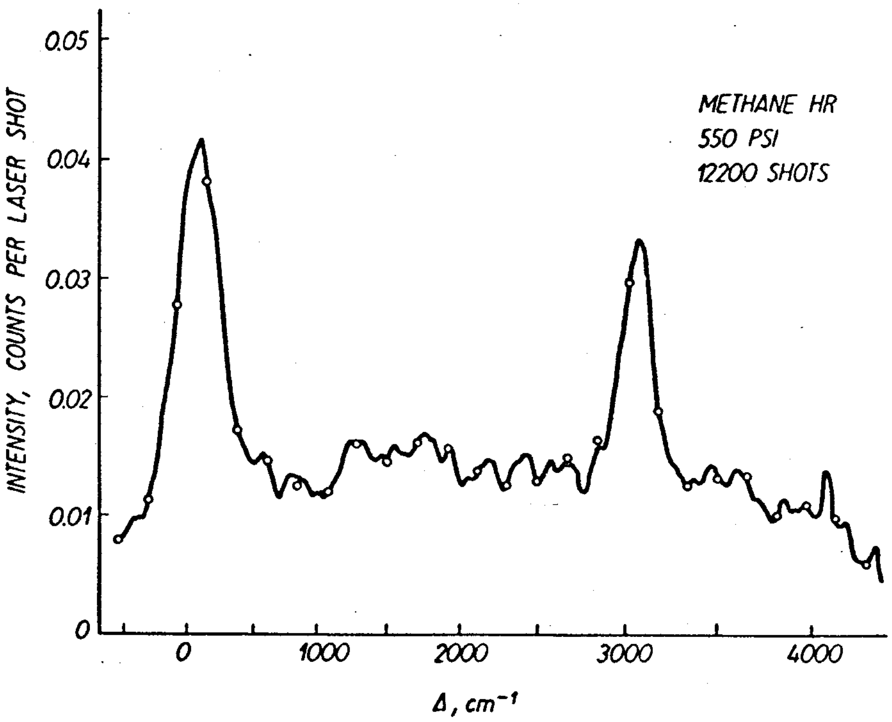
DETECTOR
MONITOR
GRATING MONOCHROMATOR
ANALYSER
LASER BEAM
1/4 WAVE PLATE
TANK
MIRROR
LIQUID SAMPLE

Fig. 4


METHANE HR
550 PSI
12200 SHOTS
INTENSITY, COUNTS PER LASER SHOT
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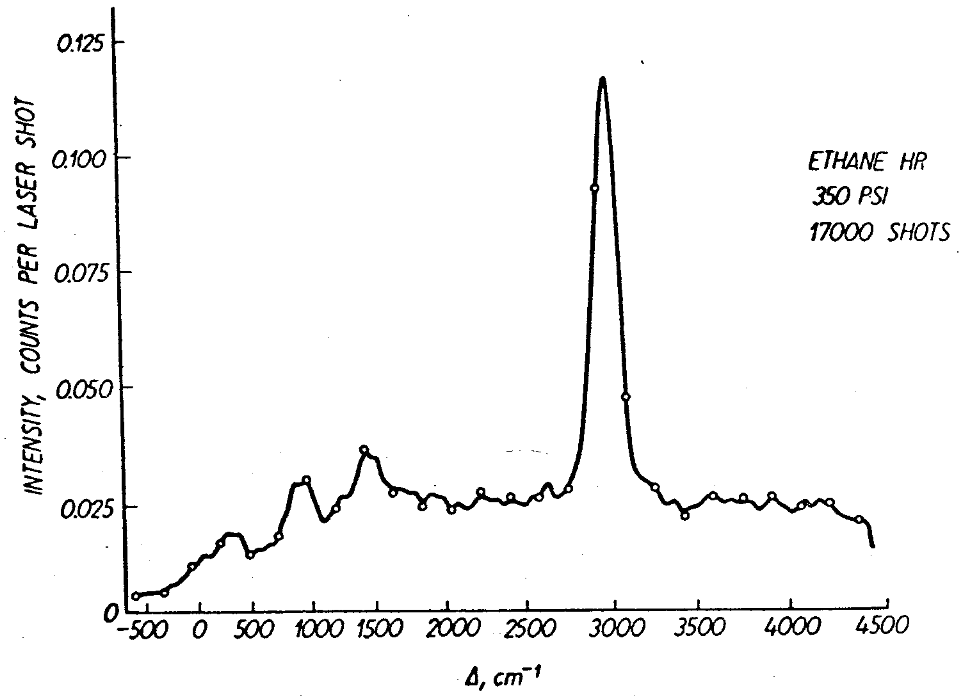
0
0
1000
2000
3000
4000
Δ, cm⁻¹

Fig. 5


ETHANE HR
350 PSI
17000 SHOTS
INTENSITY, COUNTS PER LASER SHOT
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0.075
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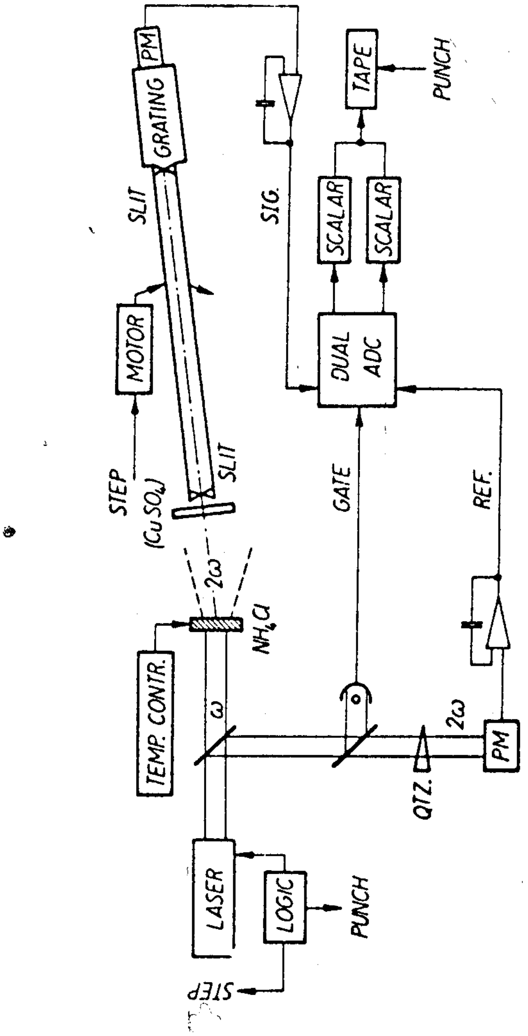
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Δ, cm⁻¹

Fig. 6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LOGIC
PUNCH
STEP
TEMP. CONTR.
ω
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($CuSO_4$)
STEP
SLIT
MOTOR
SLIT
GRATING
PM
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SCALAR
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DUAL ADC
GATE
REF.
QTZ.
2ω
PM

Fig. 7

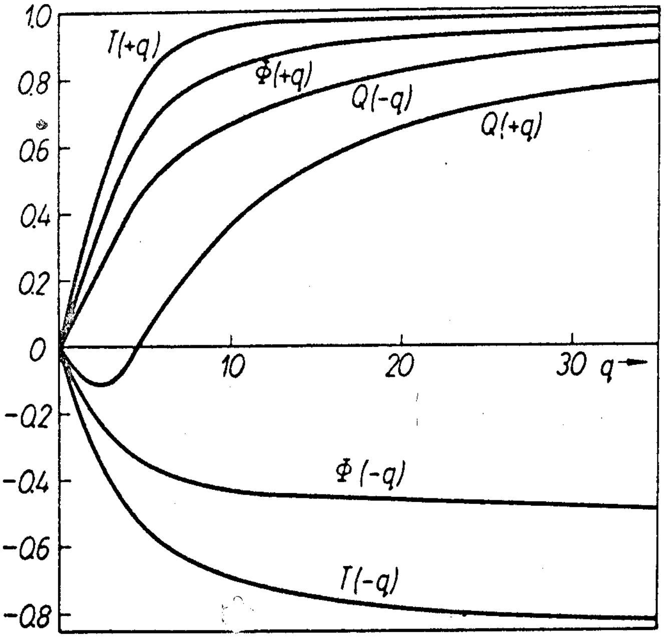

Fig. 8

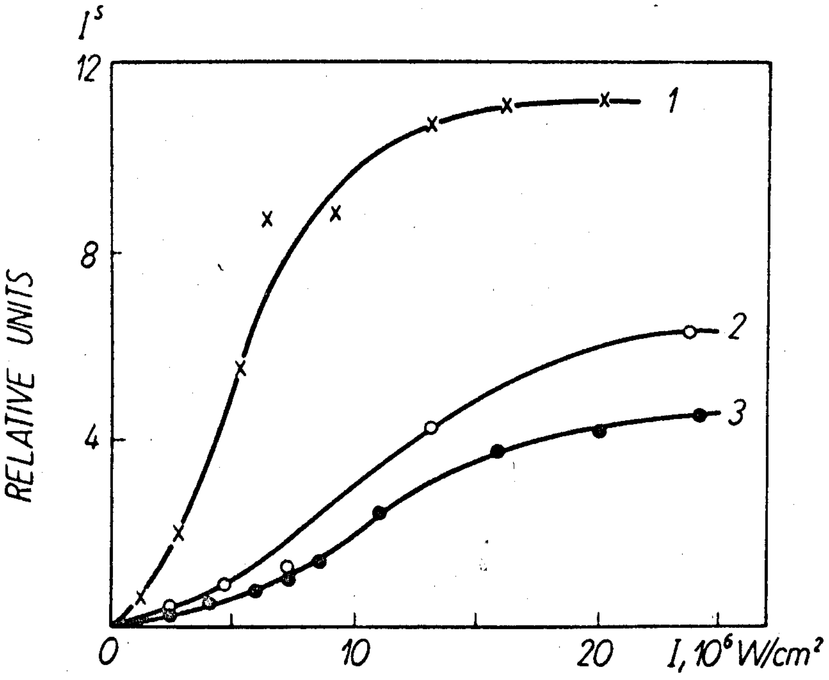

Fig. 9