

Enhancement of the Scattering Intensity for the Hyper-Raman Effect in Connection with Statistical Properties of the Excitation Light Source

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The scattering intensity for the hyper-Raman effect is found to depend on statistical properties of the excitation light source. In close correspondence to the two-photon absorption process also for the hyper-Raman effect there arises an amplification factor of $3/2$ up to 2 for the superposition of two or an infinite number, respectively, of incoherent light waves, polarized parallel. This result is derived in semiclassical terms so that the origin of the effect can be followed more clearly than in quantum electrodynamical calculations. It is shown that natural light in nonlinear optics can be represented mathematically alternatively by superposing linearly or circularly polarized light waves as in linear optics, but with the important modification that one should superpose an infinite number of incoherent components instead of only two of them. A new experimental method is proposed to observe the hyper-Raman effect using the mode locking technique. It is shown that the scattering intensity can be increased in this way by a factor of approximately $\frac{2}{3} M$ where M is the number of modes coupled together with a constant frequency separation $\Delta\omega$.

Introduction

The hyper-Raman effect (HRE) is a nonlinear optical phenomenon observed when a high intensity laser light beam is scattered by a quantized material system, for example a molecular gas. The elementary process involved in the hyper-Raman effect consists in annihilation of two incident photons and creation of a single scattered photon (3 photon process). In general the two incident photons can have different frequencies, that is, the gas sample can be irradiated by two lasers with frequencies ω_1 and ω_2 . During the scattering process the material system also can undergo a transition into a different energy state resulting in a frequency shift of the scattered photon so as to conserve energy. If we denote the initial and final molecular states by H and H' , respectively, and the energy difference between them by

$$E_H - E_{H'} = \hbar \omega_{HH'}$$

the hyper-Raman scattered photon frequencies ω_s according to a quantum mechanical calculation are given by

$$\omega_s = \begin{cases} 2\omega_1 + \omega_{HH'}, \\ 2\omega_2 + \omega_{HH'}, \\ \omega_1 \pm \omega_2 + \omega_{HH'}. \end{cases} \quad (1)$$

Usually the special case when no frequency shift occurs ($\omega_{HH'} = 0$) is called hyper-Rayleigh scattering or second harmonic generation. In what follows we shall leave out of our considerations the scat-

tering process $\omega_1 - \omega_2 + \omega_{HH'}$ near the difference frequency, although this effect would have many interesting aspects both experimentally and theoretically.

In terms of classical electrodynamics the hyper-Raman effect can be described by considering the electric field strength \mathbf{E} associated with the incident radiation. The field \mathbf{E} interacts with the material system and induces a time dependent dipole moment $\boldsymbol{\mu}$ which then acts as the source of the scattered electromagnetic radiation. The induced dipole moment $\boldsymbol{\mu}$ may be expanded into a power series in the applied electric field \mathbf{E}

$$\mu_i = \sum_j \alpha_{ij} E_j + \frac{1}{2} \sum_{jk} \beta_{ijk} E_j E_k + \frac{1}{6} \sum_{jkl} \gamma_{ijkl} E_j E_k E_l + \dots \quad (2)$$

Here the indices i, j, k, l refer to space-fixed Cartesian coordinate axes. The coefficients α_{ij} , β_{ijk} , γ_{ijkl} are Cartesian tensors of second, third and fourth order. The first term in the expansion (2) controls the well known ordinary Raman effect, see Placzek¹, Koningstein² or Sushtchinskij³. The second term, being quadratic in the field strength, oscillates at frequencies $2\omega_1$, $2\omega_2$, and $\omega_1 \pm \omega_2$ and describes the hyper-Raman effect to be discussed in this paper. In 1964, Kielich⁴ and Li⁵ published quantum mechanical calculations of the hyper-Raman polarizability tensor matrix elements using the same semiclassical approach as was used by Placzek¹ in his pioneer work on the ordinary Raman effect. This treatment describes the electromagnetic field classically and only the material system quantum mechanically. The effect of the ra-

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diation on the system is to induce a perturbation. The perturbed wave functions of the molecular system are calculated to second order in time dependent perturbation theory. These wave functions are then used to calculate the time dependent dipole moment matrix elements $\langle \bar{H}' | \mu | \bar{H} \rangle$, where $|\bar{H}'\rangle$ and $|\bar{H}\rangle$ denote the perturbed states, which result from the unperturbed states $|H'\rangle$ and $|H\rangle$, respectively, during the irradiation process. The terms constituting these matrix elements can be arranged according to their frequency dependence and especially those terms with frequencies given in Eq. (1) may be written as

$$\begin{aligned} & (\mu^{(2\omega_1)})_{HH'}^{H'} \exp \{ -i(2\omega_1 + \omega_{HH'})t \}, \\ & (\mu^{(2\omega_2)})_{HH'}^{H'} \exp \{ -i(2\omega_2 + \omega_{HH'})t \}, \\ & (\mu^{(\omega_1 + \omega_2)})_{HH'}^{H'} \exp \{ -i(\omega_1 + \omega_2 + \omega_{HH'})t \} \end{aligned} \quad (3)$$

$$\text{where } (\mu_i^{(\omega_1 + \omega_2)})_{HH'}^{H'} = \frac{1}{2} \sum_{jk} (\beta_{ijk}^{(\omega_1 + \omega_2)})_{HH'}^{H'} A_j^{(1)} A_k^{(2)} \quad (4)$$

with $\varrho, \sigma = 1, 2$. $A_j^{(\varrho)}$ are the components of the complex amplitude vector $\mathbf{A}^{(\varrho)}$ in terms of which the real electric field strength is defined by

$$\begin{aligned} \mathbf{E}^{(\varrho)} &= \mathbf{A}^{(\varrho)} \exp \{ -i(\omega_\varrho t + \varphi_\varrho) \} \\ &+ \mathbf{A}^{(\varrho)*} \exp \{ i(\omega_\varrho t + \varphi_\varrho) \}, \quad \varrho = 1, 2. \end{aligned} \quad (5)$$

For the purposes to be discussed later the phase factors $e^{-i\varphi_\varrho}$ and the amplitudes are supposed to be also time dependent, but with time variations that are slow compared with the frequency factors. Equation (5) covers generally elliptical polarized light waves by properly choosing the components of $\mathbf{A}^{(\varrho)}$, see ^{1-3, 24}.

The matrix elements $(\beta_{ijk}^{(\omega_1 + \omega_2)})_{HH'}^{H'}$ were calculated by Kielich ⁴ and Li ⁵ to be

$$\begin{aligned} & (\beta_{ijk}^{(\omega_1 + \omega_2)})_{HH'}^{H'} \\ &= \frac{2}{\hbar^2} \sum_{FF'} \left\{ \frac{\langle H' | \mu_i | F \rangle \langle F | \mu_j | F' \rangle \langle F' | \mu_k | H \rangle}{(\omega_{F'H} - \omega_2)(\omega_{FH} - \omega_1 - \omega_2)} \right. \\ &+ \frac{\langle H' | \mu_i | F \rangle \langle F | \mu_k | F' \rangle \langle F' | \mu_j | H \rangle}{(\omega_{F'H} - \omega_1)(\omega_{FH} - \omega_1 - \omega_2)} \\ &+ \frac{\langle H' | \mu_k | F \rangle \langle F | \mu_i | F' \rangle \langle F' | \mu_j | H \rangle}{(\omega_{F'H} - \omega_1)(\omega_{FH'} + \omega_2)} \\ &+ \frac{\langle H' | \mu_j | F \rangle \langle F | \mu_i | F' \rangle \langle F' | \mu_k | H \rangle}{(\omega_{F'H} - \omega_2)(\omega_{FH'} + \omega_1)} \\ &+ \frac{\langle H' | \mu_k | F \rangle \langle F | \mu_j | F' \rangle \langle F' | \mu_i | H \rangle}{(\omega_{F'H'} + \omega_1 + \omega_2)(\omega_{FH'} + \omega_2)} \\ &\left. + \frac{\langle H' | \mu_j | F \rangle \langle F | \mu_k | F' \rangle \langle F' | \mu_i | H \rangle}{(\omega_{F'H'} + \omega_1 + \omega_2)(\omega_{FH'} + \omega_1)} \right\}. \end{aligned} \quad (6)$$

The same result was obtained later also by Christie and Lockwood ⁶, who used a diagrammatic perturbation technique. It is important to note that the appropriate expressions $(\beta_{ijk}^{(2\omega)})_{HH'}^{H'}$ for the scattering process at the doubled frequencies $2\omega_1$ or $2\omega_2$ can not be obtained from Eq. (6) by simply taking the limit $\omega_\varrho \rightarrow \omega \neq 0$ ($\varrho = 1, 2$), but only by dividing additionally the right hand side of Eq. (6) by a factor of 2, so that

$$(\beta_{ijk}^{(2\omega)})_{HH'}^{H'} = \frac{1}{2} \lim_{\omega_1, \omega_2 \rightarrow \omega} (\beta_{ijk}^{(\omega_1 + \omega_2)})_{HH'}^{H'} \quad (7)$$

holds, as was stated explicitly by Akhmanov and Klyshko ⁷. To our knowledge this important fact has not been given any further attention in the literature on the hyper-Raman effect. It is therefore one of the main purpose of our paper to interpret this equation and discuss its implications on the hyper-Raman scattering intensity in connection with statistical properties of the incident light beams.

Inspection of Eq. (6) shows that for $\omega_1 \neq \omega_2$ the β -tensor does not exhibit any permutational symmetry of its indices i, j and k . If, however, $\omega_1 = \omega_2$, the β -tensor becomes symmetric in its last two indices j and k , that is $\beta_{ijk}^{(2\omega)} = \beta_{ikj}^{(2\omega)}$. Long and Stanton ⁸ derived an expression for $\beta^{(2\omega)}$ which seems not to show this symmetry in j and k , compare their Equation (5.2). However, this expression is incomplete since it is impossible to extract the β -tensor unequivocally from Eq. (3.22) in ⁸ without previously having made use of the relation $A_j A_k = A_k A_j$ and thus symmetrizing the expression in the field components. After this has been done one obtains six terms for β instead of three, with symmetry properties as stated above and with the factor 1/2 to appear for $\beta^{(2\omega)}$.

§ 2. Scattering Intensities for the Hyper-Raman Effect with Incident Light Beams Polarized in Parallel and Perpendicular Directions

According to the classical version of the theory of interaction between light and matter the total scattering intensity (energy rate irradiated in all space directions) can be calculated using the classical radiation formula

$$I = \frac{2}{3c^3} \langle |\ddot{\mu}|^2 \rangle, \quad \left[\frac{\text{energy}}{\text{time}} \right], \quad (8)$$

supplemented by Kleins rule ^{1, 9}.

In Eq. (8) the angular brackets $\langle \rangle$ indicate the average over a time interval which is supposed to be

long compared with the coherence time of the incident light waves. According to Klein's rule the expressions (3) plus their complex conjugate parts have to be inserted into Equation (8). This yields

$$I^{(\omega_q+\omega_\sigma)}(H \rightarrow H') = \frac{4}{3} \frac{\omega_s^4}{c^3} \langle |\mu^{(\omega_q+\omega_\sigma)}_{H'}|^2 \rangle \quad (9)$$

with

$$\omega_s = \omega_q + \omega_\sigma + \omega_{HH'}. \quad (9a)$$

Using Eq. (4) this becomes

$$I^{(\omega_q+\omega_\sigma)}(H \rightarrow H') = \frac{\omega_s^4}{3 c^3} \sum_{ijk} (\beta_{ijk}^{(\omega_q+\omega_\sigma)})_{H'}^{H'} (\beta_{ijk'}^{(\omega_q+\omega_\sigma)})_{H'}^{H'*} \cdot \langle A_j^{(q)} A_j^{(q)*} A_k^{(\sigma)} A_k^{(\sigma)*} \rangle. \quad (10)$$

The brackets $\langle A_j^{(q)} A_j^{(q)*} A_k^{(\sigma)} A_k^{(\sigma)*} \rangle$ in general depend in a complicated manner on statistical properties of the incident light so that they can only be calculated explicitly having additional information on the experimental characteristics of the incident light beam. The simplest idealization of course arises assuming monochromatic light waves, for which the amplitudes $\mathbf{A}^{(q)}$ are constant in time. For this case the incident intensity (energy rate per unit area) depends on the amplitude vector defined in Eq. (5) as follows

$$I_0^{(q)} = \frac{c}{2\pi} \langle |\mathbf{A}^{(q)}|^2 \rangle = \frac{c}{2\pi} |\mathbf{A}^{(q)}|^2. \quad (11)$$

Using polarization unit vectors

$$\boldsymbol{\varepsilon}^{(q)} = \mathbf{A}^{(q)} / |\mathbf{A}^{(q)}| \quad (12)$$

the scattered light intensity can then be written simply as

$$I^{(\omega_q+\omega_\sigma)}(H \rightarrow H') = Q^{(\omega_q+\omega_\sigma)}(H \rightarrow H') I_0^{(q)} I_0^{(\sigma)} \quad (13)$$

with

$$Q^{(\omega_q+\omega_\sigma)}(H \rightarrow H') = \frac{4\pi^2 \omega_s^4}{3 c^5} \sum_{ijk} (\beta_{ijk}^{(\omega_q+\omega_\sigma)})_{H'}^{H'} \cdot (\beta_{ijk'}^{(\omega_q+\omega_\sigma)})_{H'}^{H'*} \varepsilon_j^{(q)} \varepsilon_j^{(q)*} \varepsilon_k^{(\sigma)} \varepsilon_k^{(\sigma)*}. \quad (14)$$

The dimension of $Q^{(\omega_q+\omega_\sigma)}(H \rightarrow H')$ is unit area per unit of incident intensity. We propose to call Q a normalized scattering probability in order to avoid confusion with the ordinary Raman effect where a similar quantity Q has dimension of unit area and is named a cross section.

As was already shown by Placzek¹ not only the total scattering intensity, but also the spacial distribution of the scattered light can be calculated using the appropriate classical radiation formula. In this

way the energy scattered by a molecule per unit time into direction \mathbf{r} within the solid angle $d\Omega$ can be calculated from the equation

$$dI^{(\omega_q+\omega_\sigma)}(\mathbf{r}, H \rightarrow H') = \frac{\omega_s^4}{2\pi c^3} \langle |\mu^{(\omega_q+\omega_\sigma)}_{H'}|^2 \rangle \sin^2 \vartheta d\Omega. \quad (15)$$

Here ϑ is defined as the angle between the direction of observation \mathbf{r} and the dipole moment vector

$$(\mu^{(\omega_q+\omega_\sigma)})_{H'}^{H'} + c.c.$$

If the scattering is from a gas of molecules in thermodynamical equilibrium then of course the gas density and the population probability of the initial state also have to be accounted for. Furthermore, if there are no external fields present, it is necessary to sum over all degenerate magnetic sublevels of the interacting states H and H' and divide by $2J+1$, the magnetic degeneracy of the initial state. Since, however, in the present paper we are not interested in the details of the rotational structure of vibration-rotation hyper-Raman bands, but shall discuss only the overall scattering intensity, in what follows we shall treat the scattering process as if it were from a single molecule placed at the origin of the coordinate system.

At first glance the calculation of scattering intensity given above and previously carried out in a similar manner also by other authors^{4, 10} seems not to bear any problems. The Eqs. (13) and (14), however, lead to difficulties when considering the limit $\omega_2 \rightarrow \omega_1$, that is, when the two laser frequencies become equal. To see this one could arrange an experiment with two laser beams, each with intensity $I_0/2$, and with only slightly different frequencies $\omega_2 \neq \omega_1$ chosen far away from resonances of the material system. Adding together all scattering intensities for this experiment one would get one term for $2\omega_1$, another one for $2\omega_2$ and a third one for $\omega_1 + \omega_2$

$$I(H \rightarrow H') = Q^{(2\omega_1)}(H \rightarrow H') I_0^{(1)^2}/4 + Q^{(2\omega_2)}(H \rightarrow H') I_0^{(2)^2}/4 + Q^{(\omega_1 + \omega_2)}(H \rightarrow H') I_0^{(1)} I_0^{(2)}/4. \quad (16)$$

In order to be able to compare these three terms explicitly we further suppose $\mathbf{A}_1 = \mathbf{A}_2$ and take the limit $\omega_2 \rightarrow \omega_1$.

Using Eq. (7) this gives

$$\lim_{\omega_2 \rightarrow \omega_1} I(H \rightarrow H') = \frac{3}{2} Q^{(2\omega_1)} I_0^{(1)^2}. \quad (17)$$

On the other hand one could of course perform another experiment with only one single mode laser beam and irradiate the gas sample with twice the intensity that was used before for each of the beams. This time the scattered light intensity would be

$$I^{(2\omega_1)}(H \rightarrow H') = Q^{(2\omega_1)} I_0^{(1)^2} \quad (18)$$

with a proportionality factor of 1 only instead of $3/2$ as before; a result that seems to contradict Equation (17). The origin of this contradiction is that in deriving Eqs. (13) and (14) we have not taken any account of the statistical properties of the two incident light beams relative to each other. In order to clarify this point further we shall calculate the scattering intensity yet in another way, namely by first superposing the two incident light waves and only then calculating the scattering intensity with the help of the original Eq. (10) which is true for arbitrary statistical properties of the incident light.

With $\mathbf{A}_1 = \mathbf{A}_2$ superposition of the two light waves (5) yields

$$\begin{aligned} \mathbf{E}^{(1,2)} = \{ & 2\mathbf{A} \exp \{ -i [(\omega_1 + \omega_2)t \\ & + \varphi_1 + \varphi_2] / 2 \} + \text{c.c.} \} \\ & \times \cos \frac{1}{2} [(\omega_1 - \omega_2)t + \varphi_1 - \varphi_2] . \end{aligned} \quad (19)$$

As a result one again gets a harmonic light wave with an amplitude

$$\mathbf{A}^{(1,2)} = 2\mathbf{A} \cos \frac{1}{2} [(\omega_1 - \omega_2)t + \varphi_1 - \varphi_2] \quad (20)$$

which is modulated at half the beat frequency $|\omega_1 - \omega_2| \neq 0$. When this amplitude $\mathbf{A}^{(1,2)}$ is inserted into Eq. (10) one is coming out with an additional time dependent factor

$$4 \{ \cos \frac{1}{2} [(\omega_1 - \omega_2)t + \varphi_1 - \varphi_2] \}^4$$

which has to be averaged over time.

The result for $\omega_1 \neq \omega_2$ and arbitrary phase conditions is a proportionality factor of $3/2$ in agreement with Eq. (17) and not with Equation (18). We shall now discuss the limit $\omega_2 \rightarrow \omega_1$ using Eqs. (19) and (20). As long as $\omega_2 \neq \omega_1$ holds the resulting amplitude for arbitrary phase conditions will underly variations in time described by Equation (20).

Averaging over one period of oscillation only (short time average, see for example Loudon¹¹, § 5.5) one finds the intensity to vary at the beat frequency $|\omega_2 - \omega_1|$. However, since the scattering intensity in hyper-Raman effect depends quadratically on the incident intensity, the long time aver-

age leads, as we have seen, to an overall amplification of the scattering process by a factor of $3/2$ compared with what could be expected using only one classical monochromatic light wave, see Eqs. (17) and (18). At the limit $\omega_2 = \omega_1$ the superposition amplitude $\mathbf{A}^{(1,2)}$ depends only on the phase difference $(\varphi_1 - \varphi_2)/2$. If the two light waves are statistically independent, this phase difference can take all values between 0 and 2π with equal probability. Averaging over time Eq. (10) therefore leads to the same result as for $\omega_2 \neq \omega_1$. If, on the other hand, $\varphi_1 - \varphi_2$ is constant in time, the superposition process yields one new classical monochromatic light wave. For this case it is not possible to distinguish two separate beams with definite intensities any more. Instead the amplitude of the new light wave has to be normalized according to the intensity that results after superposition. Consequently Eq. (18) has to be used in order to calculate the scattering intensity. These arguments within semiclassical theory lead us to the notion of distinguishable wave trains. Two classical wave trains as given in Eq. (5) are defined distinguishable

- a) for arbitrary frequencies, if the phases $\varphi_o(t)$ are statistically independent
- and moreover
- b) for wave trains with a constant phase difference, if there frequencies are different (distinguishable).

We are aware that this notion in quantum electrodynamics will experience some restrictions for example in situations where uncertainly relations are important, but nevertheless it seems to us to be the key-word that allows to give a consistent and satisfactory description of many aspects of the theory of scattering intensities in hyper-Raman effect which previously led to severe contradictions. With these reservations as to the definition of distinguishable wave trains in mind it is now possible to give a more precise interpretation of Equation (7). Whereas in conventional derivations of Eq. (7) it could seem that this equation is true in the limit $\omega_2 \rightarrow \omega_1$ regardless of the statistical properties of the two light beams involved the preceding semiclassical discussion that follows Eq. (20) makes it clear that it can only be applied when the two superposed light waves are distinguishable. Coming back to Eqs. (16) and (17) it is seen now that their validity must also be restricted to the case of superposition

of two distinguishable light waves whereas for indistinguishable light waves Eq. (18) applies. Later on we shall give a direct semiclassical proof also for the case of two perpendicularly polarized light waves so that the interpretation of Eq. (7) given above can be claimed to be generally true within semiclassical theory.

We shall now continue on these lines and consider the case of natural linear polarized light (also called chaotic light in the literature) which we shall represent mathematically by a superposition of M statistically independent wave trains each of which has intensity I_0/M and then letting M tend to infinity ($M \rightarrow \infty$). In order to calculate the scattering intensity for this case Eq. (16) can be generalized with the result

$$I(H \rightarrow H') = \lim_{\text{natural, linear}} \left\{ M Q^{(2\omega)} + \frac{M(M-1)}{2} Q^{(\omega+\omega')} \right\} \frac{I_0^2}{M^2} \\ = \lim_{M \rightarrow \infty} \{ 2M^2 - M \} Q^{(2\omega)} \frac{I_0^2}{M^2} = 2 Q^{(2\omega)} I_0^2. \quad (21)$$

The distinction between ω and ω' in (21) has only been made in order to account for the statistical independence of the M incident modes which allows Eq. (7) to be applied in the second line. The conclusion to be drawn from this simple calculation is that natural linear polarized light should be expected to be scattered twice as effectively as coherent light by the hyper-Raman effect. This result has been obtained by more sophisticated quantum electrodynamical methods already by Shen¹²; see also Welsh¹³. The value of our derivation is that it is carried out in simple semiclassical terms and that it allows to follow more clearly the origins of this rather unexpected phenomenon. The amplification factor of 2 is seen in this way to result from the fact that the number of terms $Q^{(\omega+\omega')}$ overbalances the $Q^{(2\omega)}$ terms by a factor of M and that additionally $Q^{(\omega+\omega')} \rightarrow 4 Q^{(2\omega)}$ holds in the limit. It is therefore a straight-forward consequence of the factor 2 in Equation (7). Equation (21) allows also to judge on how fast the amplification factor approaches its limiting value 2 with increasing number M of independent modes used in the experiment. For $M=10$ the amplification is already 1.9 and for $M=100$ it is 1.99 and so on.

It should not be surprising that these findings are in close correspondence to the two-photon absorption process, see Loudon¹¹. Both the scattering intensity in hyper-Raman effect as well as the absorp-

tion rate for the two-photon absorption process depend on coherence properties of the incident light.

In Loudon's book it is shown that a calculation of the two-photon absorption process based on quantum electrodynamics leads to an expression which contains the second order coherence function $g_{12}^{(2)}$, see § 12 in¹¹.

But also in our present semiclassical treatment $g_{12}^{(2)}$ is easily introduced. Let for instance the incident light wave be polarized in x -direction. Then in Eq. (10) one is left with a single term

$$\langle A_x A_x^* A_x A_x^* \rangle.$$

Using the definition

$$g_{12}^{(2)} = \frac{\langle E^*(\mathbf{r}_1, t_1) E^*(\mathbf{r}_2, t_2) E(\mathbf{r}_2, t_2) E(\mathbf{r}_1, t_1) \rangle}{\langle |E(\mathbf{r}_1, t_1)|^2 \rangle \langle |E(\mathbf{r}_2, t_2)|^2 \rangle} \quad (22)$$

as given for example in the textbook by Loudon¹¹, Eq. (5.99), where the amplitudes E correspond to our complex amplitudes \mathbf{A} (up to a complex time dependent factor) and taking into account that for hyper-Raman scattering produced by a single monochromatic light wave $\mathbf{r}_2 = \mathbf{r}_1$ and $t_2 = t_1$, one obtains the relation

$$\langle A_x^* A_x^* A_x A_x \rangle = g^{(2)} (4\pi^2/c^2) I_0^2. \quad (23)$$

From this it is seen that the scattering intensity for linearly polarized incident light with statistical properties whatsoever can be expressed generally as

$$I^{(2\omega)}(H \rightarrow H') = g^{(2)} Q^{(2\omega)}(H \rightarrow H') I_0^2. \quad (24)$$

It is known that for purely coherent light

$$g^{(2)} = 1 \quad (25)$$

in accordance with our Equation (18).

For natural linear polarized light, on the other hand

$$g^{(2)} = 2 \quad (26)$$

holds in accordance with our previous semiclassical derivation that led to Equation (21).

It is satisfactory to see that both of these approaches, the simple semiclassical one and also the more fastidious quantum electrodynamical one lead to consistent results if only the semiclassical language is carefully developed. The notion of distinguishable wave trains introduced in this paper in quantum electrodynamics seems to correspond to the notion of distinguishable photon states. This is elucidated best using the diagrammatic technique in

order to derive the β -matrix elements^{6, 14, 15}. This method clearly shows that if the two incident photons stem from different photon states one has to sum up twice as many diagrams as for the case of two photons from the same state, since for the latter case the interchange of the two "incident" vertices does not produce a new diagram as they both refer to the same perturbation.

So far we have discussed the superposition of two parallel light waves with various statistical properties relative to each other and also the superposition of a large number of M ($M \rightarrow \infty$) parallel wave trains with randomly distributed phases. As a result we have found that the scattered intensity is increased by a factor of $3/2$ or 2 for two or M ($M \rightarrow \infty$) independent light waves, respectively, compared with what one would get using an equivalent single mode coherent light beam.

We shall now proceed and analyze the case of light waves polarized perpendicularly and with $\omega_2 = \omega_1$. Let us first suppose two light waves polarized in the x - and y -directions each having intensity $I_0/2$ and with no phase correlations between them. They both are thought to impinge simultaneously in z -direction on the molecule placed in the origin of the coordinate system. The phase condition can be formulated as

$$A_x = A_y e^{-i\varphi(t)}$$

where $\varphi(t)$ can take all values between 0 and 2π with equal probability. Starting from the general Eq. (10) and taking the average over time all terms with mixed indices cancel with the exception of $(\beta_{ixy}^{(2\omega)})_{H'}^{H'} (\beta_{ixy}^{(2\omega)})_{H'}^{H'*}$ and three additional terms which arise from the first one by permutation of its second and third indices. Since the β -tensor for $\omega_2 = \omega_1$ is symmetric with respect to these indices the scattering intensity for this case becomes

$$I(H \rightarrow H') = \frac{\pi^2 \omega_s^4}{3 c^5} \sum_i \{ |(\beta_{ixx}^{(2\omega)})_{H'}^{H'}|^2 + 4 |(\beta_{ixy}^{(2\omega)})_{H'}^{H'}|^2 + |(\beta_{iyy}^{(2\omega)})_{H'}^{H'}|^2 \} I_0^2. \quad (27)$$

The same result can also be obtained by applying Eq. (16), which for $\omega_2 \neq \omega_1$ gives

$$I(H \rightarrow H') = \frac{\pi^2}{3 c^5} \omega_s^4 \sum_i \{ |(\beta_{ixx}^{(2\omega)})_{H'}^{H'}|^2 + |(\beta_{ixy}^{(\omega_1+\omega_2)})_{H'}^{H'}|^2 + |(\beta_{iyy}^{(2\omega_2)})_{H'}^{H'}|^2 \} I_0^2. \quad (28)$$

Now, using Eq. (7), this is seen to be identical with Eq. (27) for the limit $\omega_2 \rightarrow \omega_1$. Since Eq. (27) has

been derived directly from the general Eq. (10) and not referring to Eq. (7) in any way, the agreement between Eq. (27) and (28) confirms Eq. (7) for the special case of two perpendicularly polarized and statistically independent light waves.

If, on the other hand, phase correlations are present between the two perpendicularly polarized light waves a separate discussion is necessary. For a constant phase difference the superposition process is known to yield a new harmonic wave which in general is polarized elliptically and in special cases also linearly. However, it is not possible in these situations to distinguish two separate beams with definite intensities any more. Instead, again, as for the case of two parallel polarized beams discussed previously, the amplitude of the new light beam has to be normalized according to the intensity that results after superposition. Having done this the scattering intensity must be calculated with the help of a formula analogous to Equation (18). The question of how to treat the general case of arbitrary phase correlations and whether it is possible to introduce also for this case a generalized g -factor will be analyzed elsewhere.

§ 3. Hyper-Raman Scattering Intensity for Natural Light

In text books on optics (see for instance Born and Wolf¹⁶) a superposition of two perpendicularly polarized light waves with no phase correlation between them, as described just before, usually is declared as the mathematical realization of natural light, see § 10.8 in¹⁶. Equivalently natural light can also be thought of as the superposition of two circularly polarized light waves with opposite sense of rotation and again lacking any phase correlation between them see § 10.8.2 in¹⁶. Indeed, these two definitions of natural light ensure that the intensity of its components in any direction perpendicular to the direction of propagation is the same; and moreover, this intensity is not affected by any previous retardation of one of the components relative to the other. These two properties up to now have been thought to give a completely sufficient description of thermally excited, or in other words, natural light. The question arises, however, whether the definitions given above also meet all requirements of nonlinear optics. If this were so, one would expect the hyper-Raman scattering intensity for two

perpendicularly polarized incoherent light waves, as discussed in Eq. (27) to be equal with the result for two circular incoherent light waves, one right-handed and the other left-handed. In Appendix 1 it is shown, however, that these two results in fact are different.

The important conclusion to be drawn in this situation is, that in nonlinear optics the definition of possible mathematical representations of natural light should be modified. Obviously this is a consequence of the fact that in nonlinear optics not only phase fluctuations but also intensity fluctuations become important, so that for example the scattering intensity for the hyper-Raman process depends on the correlation degree of second order rather than on that of first order.

In order to account for this we shall define natural light as the superposition of a large number ($2M$, with M tending to infinity) of wave trains polarized perpendicularly in x - and y -direction as before and all mutually independent statistically. Each of them is supposed to have intensity I_0/M so that the overall intensity incident on the molecule is $2I_0$.

Generalization of Eq. (16) then gives

$$I_{\text{nat}}(H \rightarrow H') = \lim_{M \rightarrow \infty} \frac{4\pi^2}{3c^5} \omega_s^4 \sum_i \left\{ M |(\beta_{ixx}^{(2\omega)})_{H'}^H|^2 + M |(\beta_{iyy}^{(2\omega)})_{H'}^H|^2 + \frac{M(M-1)}{2} |(\beta_{ixx}^{(\omega+\omega')})_{H'}^H|^2 + \frac{M(M-1)}{2} |(\beta_{iyy}^{(\omega+\omega')})_{H'}^H|^2 + M^2 |(\beta_{ixy}^{(\omega+\omega')})_{H'}^H|^2 \right\} \frac{I_0^2}{M^2}$$

where again the distinction between ω and ω' is meant symbolically only in order to keep in mind the statistical independence of all modes.

Taking the limit $\omega' \rightarrow \omega$ and using Eq. (7) gives

$$I_{\text{nat}}(H \rightarrow H') = \frac{4\pi^2 \omega_s^4}{3c^5} 2 \sum_i \left\{ |(\beta_{ixx}^{(2\omega)})_{H'}^H|^2 + 2 |(\beta_{ixy}^{(2\omega)})_{H'}^H|^2 + |(\beta_{iyy}^{(2\omega)})_{H'}^H|^2 \right\} I_0^2. \quad (29)$$

It is important to note that the same result can be obtained by composing natural light out of $2M$ ($M \rightarrow \infty$) circularly polarized, statistically independent light waves, half of them right handed and the other half left handed. This is shown also in Appendix 1. Therefore, also in nonlinear optics natural light can be represented alternatively by superposing linearly or circularly polarized light waves, but with the important modification that one should superpose an infinite number of independent com-

ponents instead of only two of them as in linear optics.

Equation (29) can also be confirmed starting out from Eq. (27) and taking into account, according to the g -factor in Eq. (26), that chaotic linearly polarized light is scattered twice as efficient as an equivalent single mode light beam. Adding therefore an additional factor of 2 to the terms $|\beta_{ixx}|^2$ and $|\beta_{iyy}|^2$ in Eq. (27) one again comes out with Equation (29). It should be mentioned that formula (29) leads to a depolarization ratio ρ for natural light which is different from that given by Cyvin, Rauch and Decius¹⁷. It will be shown in a subsequent paper that ρ is within the limits $1/6 \leq \rho \leq 13/18$ instead of $1/5 \leq \rho \leq 4/5$ as in¹⁷.

Bancewicz, Ożgo and Kielich¹⁸ write the scattering intensity formula in the form of a scattering tensor

$$I_{ij}^{(2\omega)} \sim b_{ikm}^{(2\omega)} b_{ilm}^{(2\omega)} I_{kl} I_{mn}$$

where $b_{ikm}^{(2\omega)}$ corresponds to our β -tensor and I_{kl} is the so called "intensity tensor of the incident light", defined as

$$I_{kl} \sim \langle A_k A_l^* \rangle.$$

Although this formula gives exactly the same results as our Eq. (10) for the special case of a linearly polarized classical monochromatic light wave it would lead into difficulties when applied to the more general case of two light beams with more complicated statistical properties and especially also for natural light. This is because the tensor of incident light suggests that the time average to be taken in Eq. (10) over the incident amplitudes should be separated into two parts so that

$$I^{(\omega+\omega\sigma)} \sim \sum_{\substack{ijk \\ j'k'}} (\beta_{ijk})_{H'}^H (\beta_{ij'k'})_{H'}^{H'*} I_{jj'}^{(g)} I_{kk'}^{(\sigma)}$$

with

$$I_{jj'}^{(g)} = \frac{c}{2\pi} \langle A_j^{(g)} A_{j'}^{(g)*} \rangle.$$

For the case of two perpendicularly polarized light waves with irregular phase fluctuations between them this would result in an expression

$$I \sim \sum_i \left\{ |(\beta_{ixx}^{(2\omega)})_{H'}^H|^2 + 2 |(\beta_{ixy}^{(2\omega)})_{H'}^H|^2 + |(\beta_{iyy}^{(2\omega)})_{H'}^H|^2 \right\} I_0^2$$

with a factor of 2 in front of the cross term instead of 4 as in our Equation (27). On the other hand, for natural light, in Kielich's formula an overall factor of 2 would be missing, since although it treats the two incident photons independently as it should be, the calculation is in close correspondence

to linear optics, where only phase fluctuations are taken into account and not also intensity fluctuations. These were seen to give rise to the amplification factor of 2.

§ 4. Enhancement of the Scattering Intensity with the Help of the Mode-Locking Technique

Although the ideas described above would allow the scattering intensity in hyper-Raman effect to be increased by a factor of 2, they nevertheless seem to be only of some theoretical interest since the hyper-Raman effect is known to be extremely weak and correspondingly difficult to observe experimentally. Another more effective method, well known in modern laser applications^{19, 20}, of increasing the HRE scattering signal could be the mode locking technique, which causes the intensity to consist of a periodic train of extremely short pulses for which high peak intensities can be realized. Coupling together $M = 2N + 1$ modes with a constant frequency separation $\Delta\omega$ and phases φ_M all forced to maintain their relative value (for simplicity they are made equal to zero and also the amplitudes are all taken equal $\mathbf{A}^{(\omega)} = \mathbf{A}$) the resulting electric field strength is as follows

$$\mathbf{E}(t) = \sum_{\varrho = -N}^N \{ \mathbf{A} \exp \{ -i(\omega + \varrho \Delta\omega)t \} + \text{c. c.} \} \quad (30)$$

$$= \{ \mathbf{A} e^{-i\omega t} + \text{c. c.} \} \frac{\sin M(\Delta\omega/2)t}{\sin(\Delta\omega/2)t}, \quad M = 2N + 1,$$

see for instance Yariv¹⁹, Eq. (11.24) or Brunner, Radloff and Junge²⁰, Equation (4.65). The resulting amplitude therefore again has a definite time dependence in analogy with Equation (19). Putting this into Eq. (10) the additional factor

$$\left(\frac{\sin M(\Delta\omega/2)t}{\sin(\Delta\omega/2)t} \right)^4 \quad (31)$$

arises and has to be averaged over time.

This makes it necessary to calculate the integral

$$\frac{1}{2\pi} \int_0^{2\pi} \left(\frac{\sin Mx}{\sin x} \right)^4 dx \quad (32)$$

which is not trivial. It can not be found in standard tables of integrals, see for instance Gradshteyn and Ryzhik²¹, where only the integral with the second power of the trigonometrical integrand $\sin Mx/\sin x$ is given. The underlying physics of our problem, however, suggests a simple method for calculating

the value of (32) allowing at the same time also a deeper insight into the problem. Equation (30) allows to extract the identity

$$\sum_{\varrho = -N}^N \exp \{ -i(\omega + \varrho \Delta\omega)t \} \quad (33)$$

$$= \exp \{ -i\omega t \} \frac{\sin M(\Delta\omega/2)t}{\sin(\Delta\omega/2)t}, \quad M = 2N + 1.$$

It is seen from this equation that the desired integrand (31) can be obtained by taking first the square of (33) and then ones more the absolute square in order to abandon at the same time the $e^{-i\omega t}$ factor. The first step leads to

$$\left(\sum_{\varrho = -N}^N \exp \{ -i(\omega + \varrho \Delta\omega)t \} \right)^2 = \exp \{ -i2\omega t \} \cdot \{ \exp \{ i2N\Delta\omega t \} + 2 \exp \{ i(2N-1)\Delta\omega t \} + 3 \exp \{ i(2N-2)\Delta\omega t \} + \dots + 2N \exp \{ i\Delta\omega t \} + (2N+1) + 2N \exp \{ -i\Delta\omega t \} + \dots + 2 \exp \{ -i(2N-1)\Delta\omega t \} + \exp \{ -i2N\Delta\omega t \} \}. \quad (34)$$

The physical content of Eq. (34) is that it can be interpreted as the Fourier-analysis of the hyper-Raman transition moment defined in Equation (4). In order to see this one can look at the expression

$$\mathbf{A} \frac{\sin(N + \frac{1}{2})\Delta\omega t}{\sin(\Delta\omega/2)t}$$

as the new time dependent amplitude \mathbf{A}' of the multimode wave train defined in Eq. (30) and insert this amplitude into Equation (4). This would give an expression for the induced dipole moment just as in Equation (34). It should be mentioned by the way that the same result could have been obtained also by a straightforward quantum mechanical calculation. For carrying through such a calculation one would have to introduce the electric field strength, as given in Eq. (30), into the perturbation hamiltonian. The weightfactors 1, 2, ..., $(2N+1)$, ..., in Eq. (34) would then appear as the appropriate weights of the β -tensor analogous to Equation (7). A detailed treatment of this subject will be given elsewhere.

The next step is now to take the absolute square of Eq. (34) and average over time. All mixed terms make no contribution to the integral and so the result is

$$\left\langle \left| \left(\sum_{\varrho = -N}^N \exp \{ -i(\omega + \varrho \Delta\omega)t \} \right)^2 \right|^2 \right\rangle$$

$$= 1^2 + 2^2 + \dots + (2N)^2 + (2N+1)^2 + (2N)^2 + \dots + 2^2 + 1^2 = \frac{1}{3}(2M^3 + M). \quad (35)$$

On the other hand this time average is just the desired integral (32). We obtain therefore *

$$\frac{1}{2\pi} \int_0^{2\pi} \left(\frac{\sin Mx}{\sin x} \right)^4 dx = \frac{1}{3} (2M^3 + M). \quad (36)$$

According to Eq. (10) the total scattering intensity for coupled modes is thus given by

$$I^{(2\omega)}(H \rightarrow H') = Q^{(2\omega)}(H \rightarrow H') \frac{1}{3} (2M^3 + M) I_0^2 \quad (37)$$

where $Q^{(2\omega)}(H \rightarrow H')$ is defined through Eq. (14) with $\varrho = \sigma$. It is supposed that the mode separation $\Delta\omega$ is small enough to guarantee that the dependence of the β -tensor on the mode frequencies can be neglected. I_0 is the intensity of each mode so that the mean total incident intensity is MI_0 .

Comparing this with Eq. (24) gives the second order coherence for the case of mode coupling

$$g^{(2)} = \frac{1}{3} \left(2M + \frac{1}{M} \right). \quad (38)$$

Besides this summary result the r.h.s. of Eq. (35) gives also the relative intensities with which each of

the individual modes is present in the scattered light. The intensity increases quadratically towards the central frequency, which has a proportionality factor of M^2 . This means that the central scattering frequency 2ω by itself would show the same intensity, as if the total incident intensity MI_0 would have been concentrated in the central mode. The net intensity gain that can be attained by the use of the mode coupling technique results from the additional scattering intensity provided by the remaining mode frequencies on both sides of the central frequency. But of course, concentration of the total intensity MI_0 into one mode only would not be very realistic. Normally one will be faced with the situation, that the intensity is distributed among several (M) modes but with phases statistically independent. In Eq. (33) this can be accounted for giving each term under the summation symbol an additional time dependent phase factor. Calculating then expression (34) only those terms which have equal frequency and phase factors can be put together. Thus Eq. (34) for independent modes is to be replaced by the following

$$\begin{aligned} & \left(\sum_{\varrho=-N}^N \exp \left\{ -i [(\omega + \Delta\omega \varrho) t + \varphi_{\varrho}(t)] \right\} \right)^2 \\ &= \exp \left\{ -2i\omega t \right\} \left\{ \exp \left\{ i[2N\Delta\omega t - 2\varphi_{-N}(t)] \right\} + 2 \exp \left\{ i[(2N-1)\Delta\omega t - \varphi_{-N}(t) - \varphi_{-N+1}(t)] \right\} \right. \\ & \quad + \exp \left\{ i(2N-2)\Delta\omega t \right\} \left[\exp \left\{ -2i\varphi_{-N+1}(t) \right\} + 2 \exp \left\{ -i(\varphi_{-N}(t) + \varphi_{-N+2}(t)) \right\} \right] \\ & \quad + \dots + \exp \left\{ -i2\varphi_0(t) \right\} + 2 \sum_{\varrho=1}^N \exp \left\{ -i(\varphi_{\varrho}(t) + \varphi_{-\varrho}(t)) \right\} + \dots \\ & \quad \left. + 2 \exp \left\{ -i[(2N-1)\Delta\omega t + \varphi_N(t) + \varphi_{N-1}(t)] \right\} + \exp \left\{ -i(2N\Delta\omega t + 2\varphi_N(t)) \right\} \right\}. \end{aligned} \quad (39)$$

Again the time average of the absolute square of (39) has to be calculated. In this way all terms for which the phase factors do not cancel are seen to give no contribution to the result. The remaining terms yields

$$\begin{aligned} & \left\langle \left| \sum_{\varrho=-N}^N \exp \left\{ -i [(\omega + \varrho \Delta\omega) t + \varphi_{\varrho}(t)] \right\} \right|^2 \right\rangle \\ &= 1^2 + 2^2 + (1^2 + 2^2) + (2^2 + 2^2) + (1^2 + 2^2 + 2^2) + \dots + 2^2 N + (1 + 2^2 N) + 2^2 N + \dots + 2^2 + 1^2 \\ &= 2N + 1 + 16 \sum_{r=1}^{N-1} r + 12N = 8N^2 + 6N + 1 = 2M^2 - M. \end{aligned} \quad (40)$$

At is should be this result is identical with the second line of Equation (21). Comparison of Eq. (40) and (35) shows that the overall scattering intensity

for independent modes is weaker by a factor of $\approx M/3$ ($M \gg 1$) than it is for coupled modes. Besides that the right hand side of Eq. (40) gives the relative intensity distribution among the scattering frequencies $2\omega - 2N\Delta\omega$ up to $2\omega + 2N\Delta\omega$. As can be seen from Eq. (40) for independent modes the intensity increases approximately linear towards the central frequency, which has the weight factor

* In the same way Eq. (34) gives the integral

$$\frac{1}{2\pi} \int_0^{2\pi} \left(\frac{\sin Mx}{\sin x} \right)^2 dx = M.$$

$1 + 4N$. The intensity of the central scattering frequency therefore turns out to be weaker by a factor of about $M/2$ (for $M \gg 1$) for independent modes than for phase-coupled modes. Figure 1 shows the scattering intensity for 51 phase coupled modes (upper curve) in comparison with that for independent modes (lower curve). Besides the effect of considerable intensity enhancement Fig. 1 reveals also a remarkable change in the HRE scattered light line profile compared with that of the incident light where it was supposed that the intensity is distributed equally among all modes. It is seen from Fig. 1 that for independent modes the line profile changes through HRE into a triangle and that for phase coupled modes the scattering process produces an even narrower line with a line width that is only about half of that for independent modes. All this is in contrast to the ordinary Raman effect where neither the scattering intensity nor the line profile can be influenced by statistical properties of the incident light.

The considerations so far were based on the assumption that all modes coupled together have

equal intensities. Experimentally a more realistic approach of course would be to suppose for example a Lorentzian intensity distribution. But this would have prevented a simple analytical treatment of the HRE scattering process and would have not allowed also to give a simple formula for the intensity enhancement that can be obtained in this way. (For solving these more realistic problems it will be necessary to develop numerical procedures.) This and also the quantum mechanical confirmation of the modelocking technique applied to HRE will be given in subsequent publications.

The arguments presented here suggest that the mode coupling technique could be an important tool in the effort of trying to overcome the enormous experimental difficulties in observing the hyper-Raman effect which so far have prevented this effect to become a more powerful spectroscopic method of practical interest with a broader domain of applications. It is also important to mention that the enhancement effect studied in this paper for the HRE should also be present for the two-photon absorption process.

Appendix 1

Hyper-Raman Scattering Intensity for Natural Incident Light Represented by Circularly Polarized Wave Trains

In order to calculate the scattering intensity for circularly polarized incident light it is convenient to transform the Cartesian components of the β -tensor into spherical components. For a vectorial quantity, as for example the electric field strength \mathbf{E} , this transformation according to well known text books, see for instance Landau-Lifshitz²² or Fano and Racah²³ can be written as

$$\begin{aligned} E_0 &= i E_z, \\ E_{\pm 1} &= \mp \frac{i}{\sqrt{2}} (E_x \pm i E_y). \end{aligned} \quad (\text{A1})$$

Here E_x , E_y and E_z are Cartesian components in a space-fixed coordinate system and E_q , ($q = -1, 0, 1$), are spherical components. Symbolically these equations may be written as follows

$$E_q = \sum_{k=1}^3 E_k(k|1q), \quad q = -1, 0, 1, \quad (\text{A2})$$

where the transformation coefficients $(k|1q)$ from a unitary matrix. Since the β -tensor transforms as

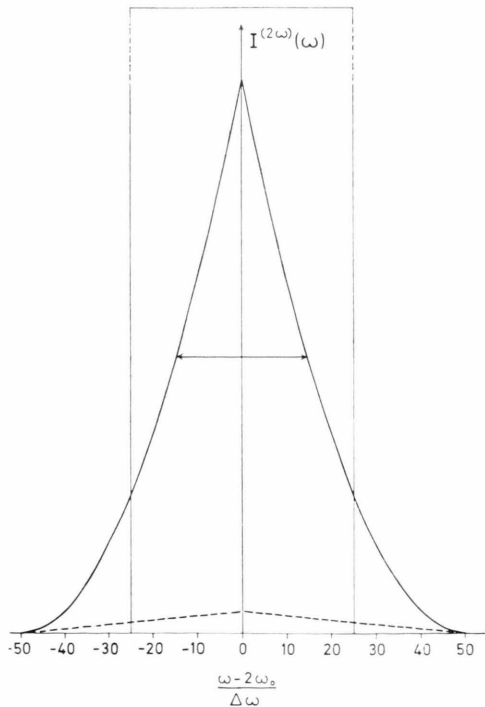


Fig. 1. Scattering intensity enhancement in hyper-Raman effect using the mode-locking technique. The rectangular curve indicates the incident intensity distribution around ω_0 . The broken curve gives the scattering intensity for independent modes and the full curve for coupled modes.

the direct product of three vectors the corresponding transformation law for β into its spherical components $\beta_{\lambda\mu\nu}$ is given by

$$\beta_{\lambda\mu\nu} = \sum_{ijk} \beta_{ijk} (i|1\lambda) (j|1\mu) (k|1\nu), \quad (\text{A3})$$

$$\lambda, \mu, \nu = -1, 0, 1.$$

This in principle allows to express also the induced dipole moment in Eq. (4) in terms of spherical components

$$(\mu_{\lambda}^{(\omega_0+\omega\sigma)})_{H'}^{H} = \frac{1}{2} \sum_{\mu\nu} (\beta_{\lambda\mu\nu}^{(\omega_0+\omega\sigma)})_{H'}^{H} A_{[\mu]}^{(o)} A_{[\nu]}^{(\sigma)}. \quad (\text{A4})$$

Here $A_{[\mu]}$ is the standard set of amplitudes, see Fano and Racah²³, defined by

$$A_{[\mu]} = \sum_k A_k (k|1\mu)^*. \quad (\text{A5})$$

Equation (A4) can be verified directly inserting (A3) and (A5), using the unitarity of the matrix $(k|1\mu)$ and comparing with Eq. (4) and (A2).

In this way the scattering intensity, see Eq. (10), can be converted into

$$I^{(\omega_0+\omega\sigma)}(H \rightarrow H') = \frac{\omega_s^4}{3c^3} \sum_{\substack{\lambda\mu\nu \\ \mu'\nu'}} (\beta_{\lambda\mu\nu}^{(\omega_0+\omega\sigma)})_{H'}^{H} (\beta_{\lambda\mu'\nu'}^{(\omega_0+\omega\sigma)})_{H'}^{H'*} \\ \times \langle A_{[\mu]}^{(o)} A_{[\mu']}^{(o)*} A_{[\nu]}^{(\sigma)} A_{[\nu']}^{(\sigma)*} \rangle. \quad (\text{A6})$$

In the same manner also expression (14) for the scattering probability can be converted.

With the help of Eq. (5) it can be seen that right – or left-handed circular-polarized light propagating along the z-axis can be represented by taking only the spherical component $A_{[-1]} = A_1$ or $A_{[1]} = A_{-1}$ respectively, different from zero. Thus, for example, the scattering probability for a right-handed circularly polarized classical monochromatic light wave is given by

$$Q^{(2\omega)}(H \rightarrow H') = \frac{4\pi^2}{3c^5} \omega_s^4 \sum_{\lambda} |(\beta_{\lambda-1-1}^{(2\omega)})_{H'}^{H}|^2, \quad (\text{A7})$$

and the same holds also for a left-handed circularly polarized light wave because of the equation

$$\sum_{\lambda} |(\beta_{\lambda 11}^{(2\omega)})_{H'}^{H}|^2 = \sum_{\lambda} |(\beta_{\lambda-1-1}^{(2\omega)})_{H'}^{H}|^2. \quad (\text{A8})$$

We proceed now to calculate the scattering intensity for the case when two circularly polarized light waves, one right-handed and the other left-handed with irregular phase fluctuations between them, impinge simultaneously on the molecule. Both are supposed to have intensity I_0 . Again the calculation can be carried out in two different ways. On the one hand one can use Eq. (A6) and analyse which of the products $\langle A_{[\mu]} A_{[\mu']}^* A_{[\nu]} A_{[\nu']}^* \rangle$ remain different from zero after having calculated the time average. On the other hand one can also use Eqs. (16) and (7). Both of these calculations lead to the same result

$$I^{(2\omega)}(H \rightarrow H') = \frac{8\pi^2}{3c^5} \omega_s^4 \sum_{\lambda} \{ |(\beta_{\lambda 11}^{(2\omega)})_{H'}^{H}|^2 + 2 |(\beta_{\lambda 1-1}^{(2\omega)})_{H'}^{H}|^2 \} I_0^2. \quad (\text{A9})$$

In order to compare with Eq. (27) this expression now has to be converted into Cartesian components by means of Equation (A3). A straightforward calculation gives

$$\sum_{\lambda} |(\beta_{\lambda 11})_{H'}^{H}|^2 = \frac{1}{4} \sum_i \{ |(\beta_{ixx})_{H'}^{H}|^2 + |(\beta_{iyy})_{H'}^{H}|^2 + 4 |(\beta_{ixy})_{H'}^{H}|^2 - [(\beta_{ixx})_{H'}^{H} (\beta_{iyy})_{H'}^{H'*} + \text{c. c.}] \},$$

and

$$\sum_{\lambda} |(\beta_{\lambda 1-1})_{H'}^{H}|^2 = \frac{1}{4} \sum_i \{ |(\beta_{ixx})_{H'}^{H}|^2 + |(\beta_{iyy})_{H'}^{H}|^2 + [(\beta_{ixx})_{H'}^{H} (\beta_{iyy})_{H'}^{H'*} + \text{c. c.}] \}. \quad (\text{A10})$$

Inserting this into Eq. (A9) one obtains finally

$$I^{(2\omega)}(H \rightarrow H') = \frac{4\pi^2}{3c^5} \omega_s^4 \sum_i \{ \frac{3}{2} |(\beta_{ixx})_{H'}^{H}|^2 + \frac{3}{2} |(\beta_{iyy})_{H'}^{H}|^2 + 2 |(\beta_{ixy})_{H'}^{H}|^2 + \frac{1}{2} [(\beta_{ixx})_{H'}^{H} (\beta_{iyy})_{H'}^{H'*} + \text{c. c.}] \} I_0^2. \quad (\text{A11})$$

As can be seen this result is different from Equation (27). Thus, in contrast to the ordinary Raman effect, for the hyper-Raman effect two contrarotating circularly polarized light waves with mutual phase independence would give a different scattering inten-

sity than two independent light waves polarized linearly in perpendicular directions!

Another situation arises if one composes the two circularly polarized light waves out of many ($M \rightarrow \infty$) independent waves trains, each of intensity I_0/M .

The same arguments as were used in deriving Eq. (29) lead now to the result, that the first term in Eq. (A9) under these circumstances must be multiplied by an extra factor of 2. Calculating the intensity by means of Eqs. (A10) it is seen that this time the square brackets cancel and moreover that the result becomes exactly identical with Eq. (29) derived for natural light.

This proves the statement of § 3 that also in nonlinear optics natural light can be represented alternatively by superposing linearly or circularly polarized light waves.

It is possible to generalize these results for elliptically polarized light waves. In this way it can be shown that natural light can also be composed out of $2M$ ($M \rightarrow \infty$) statistically independent contra-rotating wave trains, each of which should be po-

larized elliptically with ellipses orientated at right angle relative to each other, see ²⁴. In order to carry through the calculation it is convenient to introduce elliptical components

$$A_{\bar{1}} = \frac{1}{\sqrt{1+a^2}} (a A_x + i A_y),$$

$$A_{-\bar{1}} = \frac{1}{\sqrt{1+a^2}} (A_x - i a A_y) \quad (\text{A12})$$

where a describes the semiaxes-ratio of the polarization ellipse. It can be shown that the scattering intensity in hyper-Raman effect is independent on the parameter a , see Altmann ²⁵.

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