

OPTICAL MOLECULAR REORIENTATION IN SECOND-HARMONIC LIGHT SCATTERING*

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Since nonlinear light scattering requires the use of an intense laser beam, optical reorientation of the molecules affecting the intensity and depolarisation of the scattered light can occur. The paper contains a detailed analysis of the variations in second harmonic light scattering, calculated by classical statistics for weak molecular reorientation as well as for complete optical alignment. The experimental study of these variations is for the first time proposed as a method for direct determinations of the anisotropy of second-order nonlinear polarizability of noncentrosymmetric molecules.

1. Introduction

Molecules in the electric field of a light wave of appropriately high intensity scatter light with the fundamental frequency ω and multiple frequencies 2ω , 3ω , ... Elastic scattering at the fundamental frequency, referred to as linear Rayleigh scattering, has of late gained in importance owing to developments in laser technique [1]. It will be remembered that an intense electric field acting on a substance composed of molecules gives rise, at the least, to two processes: a Voigt process, consisting in nonlinear polarisation of the atoms, or molecules, and a Langevin process, consisting in reorientation of anisotropic molecules by the field vector [2]. Equivalent molecular processes take place in the electric field of a light wave [3, 4] leading, among others, to variations in intensity of the scattered light [5-8].

In this paper, we shall be dealing with variations in Second Harmonic Light Scattering (SHS) [6] due to optical reorientation of molecules [3, 4]. Previous measurements of SHS by Maker and Terhune [9] and Kielich, Lalanne and Martin [10] failed to make apparent a considerable effect of molecular reorientation, though such attempts have been made in molecular liquids by having resort to strong ruby lasers [11].

It has nevertheless been shown that the collimated beam of a giant laser can cause an

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observable reorientation of the molecules [12] and even their complete ordering (alignment) i. e. optical saturation [13]. Saturation of optical alignment of macromolecules in solution can lead to considerable variations in anisotropic Rayleigh scattering [14]. SHS can also be expected to undergo measurable changes by optical reorientation of molecules and macromolecules [15].

Since our primary concern here will lie with the assessment of the order of magnitude of the effect of optical molecular reorientation on SHS, the present theory will not cover intermolecular correlations. This will largely simplify the results. We shall moreover assume the molecular scattering substance as optically transparent and homogeneous. In a first step, we shall perform calculations for weak optical reorientation leading to results generally valid for molecules of arbitrary symmetry not having a centre of symmetry. In a second step, we shall make calculations for arbitrarily strong optical reorientation, however restricting ourselves to certain simpler and at the same time more important molecular symmetries. In the limit, the results comprise the case of complete molecular alignment i. e. optical saturation, for which the final formulae assume a simple form well adapted to numerical evaluations.

2. Fundamentals of the theory

We consider a system consisting of N like anisotropic microsystems (molecules, macromolecules) in a sphere of volume V . To the centre of V is attached the origin of laboratory co-ordinates $\{X_i\}$, $i = x, y, z$. To each microsystem is attached a molecular co-ordinate system $\{X_\alpha\}$, $\alpha = 1, 2, 3$, in a manner to make the 3-axis coincide with the symmetry axis of the microsystem. Transitions from molecular to laboratory co-ordinates are performed by way of the transformation matrix:

$$(C_{i\alpha}) = \begin{pmatrix} \cos \vartheta \cos \varphi \cos \psi - \sin \varphi \sin \psi, & -\cos \vartheta \cos \varphi \sin \psi - \sin \varphi \cos \psi, & \sin \vartheta \cos \varphi \\ \cos \vartheta \sin \varphi \cos \psi + \cos \varphi \sin \psi, & -\cos \vartheta \sin \varphi \sin \psi + \cos \varphi \cos \psi, & \sin \vartheta \sin \varphi \\ -\sin \vartheta \cos \psi, & \sin \vartheta \sin \psi, & \cos \vartheta \end{pmatrix}, \quad (1)$$

where ϑ , φ , ψ are Euler angles defining the orientation of the molecular system of co-ordinates with respect to that of laboratory co-ordinates.

We assume for simplicity the positions and orientations of the molecules as mutually uncorrelated. As a model fulfilling this condition, we can consider a rarefied gas or a dilute solution of anisotropic molecules in a solvent the molecules of which are isotropic.

An intense beam of laser light, linearly polarized with electric vector \vec{E}^ω vibrating at the frequency ω :

$$E_i^\omega = E_0 e_i \cos \omega t, \quad (2)$$

(\vec{e} — unit vector in the polarisation direction; E_0 — vibration amplitude), incident on the medium, causes two effects of interest here: (i) harmonic light scattering, and (ii) optical reorientation.

2.1. Nonlinear polarizability and SHS

Strong electric fields cause a distortion of the electron shell of the molecule inducing in the latter an electric dipole moment \vec{m} , which is a nonlinear function of the field intensity (1) and can be expressed, with an accuracy sufficient for our aims, in the form of the expansion [5, 8]:

$$m_i = a_{ij}^0 e_j E_0 \cos \omega t + \frac{1}{4} (b_{ijk}^0 e_j e_k E_0^2 + b_{ijk}^{2\omega} e_j e_k E_0^2 \cos 2\omega t) + \dots, \quad (3)$$

where a_{ij} is the tensor of linear polarizability and b_{ijk} that of nonlinear polarizability.

We note that in addition to the first, linear term, varying in pace with the variations of the electric field (2), there appear two nonlinear terms: a second term, constant in time, and a third term vibrating with the frequency 2ω . The last term is responsible for the emergence of radiation with the doubled frequency in the spectrum of light scattered by the microsystem [6, 8].

Observation of SHS is carried out through an analyzer which transmits only radiation with an electric vector vibrating along the direction of the unit vector \vec{n} . Hence, in the wave zone beyond the analyzer, the intensity of SHS from unit volume is given by the expression:

$$I_n^{2\omega} = I_{ij}^{2\omega} n_i n_j, \quad (4)$$

where $I_{ij}^{2\omega}$ is the tensor of SHS intensity, of the following form (in Gauss units) [8]:

$$I_{ij}^{2\omega} = \frac{1}{4\pi c^3} \frac{N}{V} \left\langle \frac{d^2 m_i^{2\omega}}{dt^2} \frac{d^2 m_j^{2\omega}}{dt^2} \right\rangle_{I_0}. \quad (5)$$

The symbol $\langle \dots \rangle_{I_0}$ stands for statistical averaging in the presence of the light beam of intensity I_0 , and \dots^t denotes the average over one period of vibration.

Eqs (5) and (3) yield [6]:

$$I_{ij}^{2\omega} = \frac{\rho}{2} \frac{\pi(2\omega)^4}{c^5} I_0^2 \langle b_{ikm}^{2\omega} b_{jin}^{2\omega} \rangle_{I_0} e_k e_l e_m e_n, \quad (6)$$

where $\rho = N/V$ is the number density of molecules, and $I_0 = I_{ii} = \text{Tr } I_{ij}$ the incident light intensity, with:

$$I_{ij} = \frac{c}{4\pi} \overline{E_i^\omega E_j^\omega} = \frac{c}{8\pi} E_0^2 e_i e_j = I_0 e_i e_j. \quad (7)$$

2.2. Optical reorientation

A molecule in the electric field \vec{E}^ω possesses the potential energy $U(\Omega, \vec{E}^\omega)$ in general dependent on the orientation Ω . In a sufficient approximation, $U(\Omega, \vec{E}^\omega)$ can be expressed in the form [3, 4]:

$$U(\Omega, \vec{E}^\omega) = -\mu_i E_i^\omega - \frac{1}{2} a_{ij} E_i^\omega E_j^\omega - \frac{1}{6} b_{ijk} E_i^\omega E_j^\omega E_k^\omega - \frac{1}{24} c_{ijkl} E_i^\omega E_j^\omega E_k^\omega E_l^\omega - \dots \quad (8)$$

Above, μ_i is the permanent electric dipole of the molecule, and c_{ijkl} the fourth-rank tensor of its nonlinear polarizability.

If the vibration period ω^{-1} of the electric field \vec{E}^ω strongly exceeds the relaxation time τ of the molecules i. e. if $\omega^{-1} \gg \tau$, a state of equilibrium sets in. On omitting intermolecular interactions, this state of equilibrium conforms in a good approximation to a Boltzmann distribution function with potential energy (8) averaged over the period of vibrations of the molecule [14]:

$$f(\Omega, I_0) = \frac{\exp(-\beta U_I)}{\int \exp(-\beta U_I) d\Omega}, \quad (9)$$

where $\beta = 1/kT$; $d\Omega = \sin \vartheta d\vartheta d\varphi d\psi$ is the element of body angle; and [3]:

$$U_I = \overline{U(\Omega, \vec{E}^\omega)} = -\frac{2\pi}{c} a_{ij} e_i e_j I_0 - \left(\frac{\pi}{c}\right)^2 c_{ijkl} e_i e_j e_k e_l I_0^2 - \dots \quad (10)$$

A microsystem in the intense electric field of a light wave tends to assume an orientation minimalizing its average potential energy (10). This process is obviously perturbed by thermal motion of the molecules. As a result, a state with some degree of ordering is established. This state has been predicted theoretically as the "optical Kerr effect" [3, 4] and subsequently observed in experiment [12]. To Kielich [5, 14] is moreover due the investigation of the influence of optical molecular ordering on Rayleigh light scattering.

3. SHS at weak optical reorientation of the microsystems

The chief problem in determining the intensity of SHS taking into account molecular reorientation by laser light resides in statistical averaging with the distribution function (9).

On the assumption of relatively weak reorientation, $U < kT$, Eq. (9) can be satisfactorily expanded applying statistical perturbation calculus [15]:

$$f(\Omega, I_0) = f_0 + f_1 + f_2 + \dots \quad (11)$$

f_0 is a distribution function specifying the molecular distribution in the absence of the laser field of intensity I_0 , whereas

$$f_1 = -\beta f_0 (U_I - \langle U_I \rangle_0) \quad (12)$$

and

$$f_2 = \frac{1}{2} \beta^2 f_0 [U_I^2 - \langle U_I^2 \rangle_0 - 2(U_I - \langle U_I \rangle_0) \langle U_I \rangle_0], \quad (13)$$

are I_0 -dependent terms of the distribution function. The symbol $\langle \dots \rangle_0$ denotes the isotropic average over all molecular orientations with the unperturbed distribution function f_0 .

On restricting ourselves to the first two terms of (11) and taking the first term of (10), we obtain:

$$f_1 = \frac{2\pi}{c} \beta f_0 I_0 (a_{ij}^\omega e_i e_j - a_\omega), \quad (12a)$$

where we have written the trace of the tensor a_{ij}^ω as:

$$a_{ii}^\omega = 3a_\omega,$$

and use has been made of the relation: $\langle e_i e_j \rangle_0 = \frac{1}{3} \delta_{ij}$.

With regard to Eqs (6), (11) and (12a), Eq. (4) becomes:

$$I_n^{2\omega} = I_{n0}^{2\omega} + I_{n1}^{2\omega} + I_{n2}^{2\omega} + \dots, \quad (14)$$

where the expansion terms of the zero-th and first orders are of the form:

$$I_{n0}^{2\omega} = S^{2\omega} \langle b_{ikm}^{2\omega} b_{jln}^{2\omega} \rangle_0 n_i n_j e_k e_l e_m e_n, \quad (15a)$$

$$I_{n1}^{2\omega} = S^{2\omega} \frac{2\pi}{c} \beta I_0 [\langle b_{ikm}^{2\omega} b_{jln}^{2\omega} a_{pq}^\omega \rangle_0 e_p e_q - \langle b_{ikm}^{2\omega} b_{jln}^{2\omega} \rangle_0 a_\omega] n_i n_j e_k e_l e_m e_n. \quad (15b)$$

In the preceding two expressions, we have introduced the notation:

$$S^{2\omega} = \frac{\rho}{2} \frac{\pi(2\omega)^4}{c^5} I_0^2. \quad (16)$$

The isotropic averages of tensor products occurring in Eqs (15a) and (15b) can be replaced by the isotropic averages of the respective products of unit vectors \vec{n} and \vec{e} by applying the well known formula [16]:

$$\begin{aligned} \langle \underbrace{n_i n_j e_k e_l \dots e_q}_{2k} \rangle_0 &= \frac{1}{2(2k+1)!!} \{ [2k+1] [1 - (\vec{n} \cdot \vec{e})^2] \delta_{ij} \sigma_{kl\dots q} + \\ &+ [3(\vec{n} \cdot \vec{e})^2 - 1] \sigma_{ijkl\dots q} \}, \end{aligned} \quad (17)$$

where:

$$\sigma_{ijkl} = \delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk},$$

and

$$\sigma_{ijklmn} = \delta_{ij} \sigma_{klmn} + \delta_{ik} \sigma_{jlmn} + \delta_{il} \sigma_{jkmn} + \delta_{im} \sigma_{jkl n} + \delta_{in} \sigma_{jklm}, \text{ etc.}$$

On assuming complete permutational symmetry of the tensors a_{ij}^ω and $b_{ijk}^{2\omega}$, we have:

$$I_{n0}^{2\omega} = S^{2\omega} \frac{1}{105} [(4b_{ijk}^{2\omega} b_{ijk}^{2\omega} - b_{ijj}^{2\omega} b_{ikk}^{2\omega}) + (\vec{n} \cdot \vec{e})^2 (2b_{ijk}^{2\omega} b_{ijk}^{2\omega} + 10b_{ijj}^{2\omega} b_{ikk}^{2\omega})], \quad (18a)$$

$$\begin{aligned} I_{n1}^{2\omega} &= S^{2\omega} \frac{2\pi}{105} \frac{\beta I_0}{c} \{ [(2b_{ijk}^{2\omega} b_{iji}^{2\omega} - b_{iik}^{2\omega} b_{jji}^{2\omega}) a_{ki}^\omega + (b_{ijj}^{2\omega} b_{ikk}^{2\omega} - 2b_{ijk}^{2\omega} b_{ijk}^{2\omega}) a_\omega] + \\ &+ (\vec{n} \cdot \vec{e})^2 [(2b_{ijk}^{2\omega} b_{iji}^{2\omega} + 4b_{ijj}^{2\omega} b_{iki}^{2\omega} + 3b_{iik}^{2\omega} b_{jji}^{2\omega}) a_{ki}^\omega - (2b_{ijk}^{2\omega} b_{ijk}^{2\omega} + 7b_{ijj}^{2\omega} b_{ikk}^{2\omega}) a_\omega] \}. \end{aligned} \quad (18b)$$

$I_{n0}^{2\omega}$ is the SHS intensity in the absence of molecular reorientation. $I_{n1}^{2\omega}$ is the contribution to SHS due to some degree of reorientation of the molecules.

We now introduce "relative variations in scattered light", defined as follows [14, 17]:

$$\delta I_n^{2\omega} = \frac{I_n^{2\omega} - I_{n0}^{2\omega}}{I_{n0}^{2\omega}}. \quad (19)$$

Since we restrict our considerations here to the first approximation in the expansion (14), we are justified in writing:

$$\delta I_{n1}^{2\omega} = \frac{I_{n1}^{2\omega}}{I_{n0}^{2\omega}}. \quad (19a)$$

Let us specify the observation set-up. Assume observation of SHS to be performed perpendicularly to the propagation direction of incident light. The plane defined by these two directions will be termed the plane of observation. The scattered intensity will be denoted by V or H according to whether the vector n is vertical (V) or horizontal (H) to the plane of observation. Lower indices v and h will denote, respectively, that the incident light wave is polarized perpendicularly, or parallel, to the plane of observation.

The expressions (18a) and (18b) derived by us above are quite general. However, with regard to the high complexity of such generally valid results, we prefer to perform our further calculations for molecules of the higher symmetries only. We consider only molecules for which the tensor $a_{\alpha\beta}^{\omega}$ has two mutually independent elements: $a_{11}^{\omega} = a_{22}^{\omega} \neq a_{33}^{\omega}$ and the tensor $b_{\alpha\beta\gamma}^{2\omega}$ at the most two independent elements. These conditions are met, among others, by molecules belonging to the groups: D_{2d} , D_{3h} , D_3 , C_{3h} , C_4 , C_{4v} , C_5 , C_{5v} , C_6 , C_{6v} , C_{∞} , $C_{\infty v}$. In all these cases, the tensor a_{ij}^{ω} is of the form:

$$a_{ij}^{\omega} = a_{\omega}[(1 - K_a)\delta_{ij} + 3K_a C_{i3} C_{j3}], \quad (20)$$

where:

$$a_{\omega} = \frac{1}{3}(2a_{11}^{\omega} + a_{33}^{\omega}), \quad K_a = \frac{1}{3a_{\omega}}(a_{33}^{\omega} - a_{11}^{\omega}).$$

3.1. Molecules having the symmetries D_3 , D_{3h} and C_{3h}

For D_3 , the tensor $b_{ijk}^{2\omega}$ is of the form [6]:

$$b_{ijk}^{D_3} = b_{111}^{2\omega}(C_{i1}C_{j1}C_{k1} - C_{i1}C_{j2}C_{k2} - C_{i2}C_{j1}C_{k2} - C_{i2}C_{j2}C_{k1}). \quad (21)$$

For D_{3h} , it is [6]:

$$b_{ijk}^{D_{3h}} = b_{222}^{2\omega}(C_{i1}C_{j1}C_{k1} - C_{i2}C_{j1}C_{k1} - C_{i1}C_{j2}C_{k1} - C_{i1}C_{j1}C_{k2}). \quad (22)$$

For the symmetry C_{3h} , the tensor $b_{ijk}^{2\omega}$ can be expressed as the sum:

$$b_{ijk}^{C_{3h}} = b_{ijk}^{D_3} + b_{ijk}^{D_{3h}}. \quad (23)$$

On insertion of (21), (22) or (23) into Eqs (18a), (18b) and having resort to Eq. (19a), we get:

$$\delta I_{n1}^{2\omega} = -\frac{1}{3} \frac{1 + (\vec{n} \cdot \vec{e})^2}{2 + (\vec{n} \cdot \vec{e})^2} (\pm q), \quad (24)$$

where

$$(\pm q) = \pm \frac{2\pi |a_{33}^{\omega} - a_{11}^{\omega}|}{ckT} I_0 \quad (25)$$

is a dimensionless reorientation parameter [14]. The sign “+” refers to positive optical anisotropy, $a_{33}^o - a_{11}^o > 0$, as is the case for prolate (rodlike) molecules. The sign “—” refers to negative optical anisotropy, $a_{33}^o - a_{11}^o < 0$, exhibited by oblate (disklike) ones. Thus,

$$\frac{3}{4} \delta V_{v1}^{2\omega} = \delta H_{v1}^{2\omega} = \delta V_{h1}^{2\omega} = \delta H_{h1}^{2\omega} = -\frac{1}{6} (\pm q). \quad (26)$$

For these three types of symmetry, the relative variations in SHS intensity (in a first approximation) have a sign opposite to the sign of the anisotropy of first-order polarizability.

3.2. For the symmetry D_{2d} , the hyperpolarizability tensor is of the form [6, 8]:

$$b_{ijk}^{2\omega} = b_{123}^{2\omega} (C_{i1} C_{j2} C_{k3} + C_{i1} C_{j3} C_{k2} + C_{i2} C_{j1} C_{k3} + C_{i2} C_{j3} C_{k1} + C_{i3} C_{j1} C_{k2} + C_{i3} C_{j2} C_{k1}). \quad (27)$$

On insertion into (18a), (18b) and with regard to Eq. (19a), we obtain in a first approximation:

$$\delta I_{n1}^{2\omega} = 0. \quad (28)$$

3.3. Molecules having the symmetries $C_4, C_{4v}, C_5, C_{5v}, C_6, C_{6v}, C_{\infty}, C_{\infty v}$.

The hyperpolarizability tensor now is [6, 15]:

$$b_{ijk}^{2\omega} = \frac{3}{5} b_{2\omega} [(1 - K_b) (\delta_{ij} C_{k3} + \delta_{ik} C_{j3} + \delta_{jk} C_{i3}) + 5K_b C_{i3} C_{j3} C_{k3}], \quad (29)$$

with:

$$b_{2\omega} = \frac{1}{3} (2b_{113}^{2\omega} + b_{333}^{2\omega}), \quad K_b = \frac{1}{3b_{2\omega}} (b_{333}^{2\omega} - 3b_{113}^{2\omega}).$$

By Eqs (29), (18a), (18b) and (19a), we have:

$$\delta I_{n1}^{2\omega} = \frac{2}{15} \frac{(-7 + 24K_b + 8K_b^2) + (\vec{n} \cdot \vec{e})^2 (133 + 84K_b + 8K_b^2)}{(7 + 8K_b^2) + 4(\vec{n} \cdot \vec{e})^2 (14 + K_b^2)} (\pm q), \quad (30)$$

whence

$$\delta V_{v1}^{2\omega} = \frac{4}{45} \frac{63 + 54K_b + 8K_b^2}{21 + 4K_b^2} (\pm q), \quad (30a)$$

and

$$\delta H_{v1}^{2\omega} = \delta V_{h1}^{2\omega} = \delta H_{h1}^{2\omega} = \frac{2}{15} \frac{-7 + 24K_b + 8K_b^2}{7 + 8K_b^2} (\pm q). \quad (30b)$$

The slope of the straight lines (30a) and (30b) is defined by the value and sign of the anisotropy of hyperpolarizability K_b and the sign of the reorientation parameter q (Figs 1a and 1b).

For positive q , the steepness of $\delta V_{v1}^{2\omega}$ attains a maximum amounting to $q^{-1}\delta V_{v1\max}^{2\omega} = 0.488$ for $K_b = 1.995$ and a minimum of $q^{-1}\delta V_{v1\min}^{2\omega} = -0.0434$ for $K_b = -2.712$; the slope of

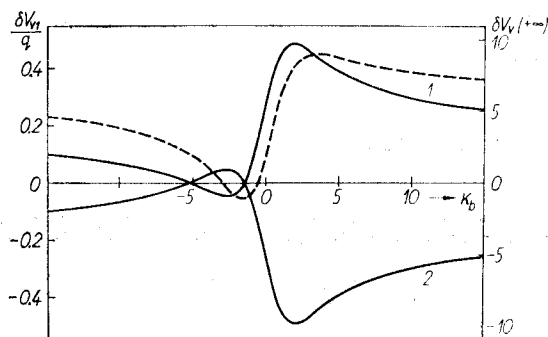


Fig. 1a. Slope of $\delta V_{v1}^{2\omega}$ vs the anisotropy of hyperpolarizability K_b (Eq. (30a)): 1 — for $(+q)$; 2 — for $(-q)$, and graph of the asymptote of $\delta V^{2\omega} (+\infty)$ vs K_b (Eq. (46a)) (dashed line) for molecules having the point group symmetries $C_4, C_{4v}, C_5, C_{5v}, C_6, C_{6v}, C_{\infty}, C_{\infty v}$

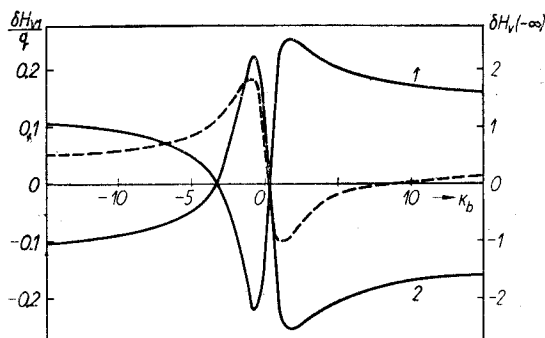


Fig. 1b. Slope of $\delta H_{v1}^{2\omega}$ vs the anisotropy of hyperpolarizability K_b (Eq. (30b)): 1 — for $(+q)$; 2 — for $(-q)$, and graph of the asymptote of $\delta H^{2\omega}(-\infty)$ vs K_b (Eq. (47b)) for molecules having the point group symmetry $C_4, C_{4v}, C_5, C_{5v}, C_6, C_{6v}, C_{\infty}, C_{\infty v}$

$\delta H_{v1}^{2\omega}$ attains a maximum of $q^{-1}\delta H_{v1\max}^{2\omega} = 0.2520$ for $K_b = 1.686$, and a minimum equalling $q^{-1}\delta H_{v1\min}^{2\omega} = -0.2520$ at $K_b = -0.513$. For negative values of the reorientation parameter q the slope values assume opposite signs; thus, for those values of K_b for which they attained their maximal values, they now are minima, and vice versa.

Moreover, $\delta V_{v1}^{2\omega} = 0$ for $q \neq 0$ at $K_b = -5.25$ and $K_b = -1.5$ whereas $\delta H_{v1}^{2\omega} = 0$ for $q \neq 0$ at $K_b = -3.27$ and $K_b = 0.27$.

Numerical values of K_b for some linear molecules are given in Table I.

TABLE I

Numerical values of the hyperpolarizability* and hyperpolarizability anisotropy elements for linear molecules ($C_{\infty v}$)

Molecule	b_{333}	$b_{113} = b_{223}$	$b = \frac{1}{3}(2b_{113} + b_{333})$	$K_b = \frac{b_{333} - 3b_{113}}{3b}$
Co	0.0731	-0.0635	-0.0180	-4.8905
NO	0.0831	-0.0120	0.0197	2.0152
LiF	0.1980	0.262	0.2407	-0.8144
FCCH	-0.199	0.157	0.0383	-5.8261
HF	-0.0865	0.0193	-0.0160	3.0146
BF	-0.0624	-0.2930	-0.2161	-1.2594

* The absolute values of b_{333} and b_{113} are taken from Hush and Williams [20], who give them in Si units $C^3m^3J^{-2} \times 10^{-50}$. Multiplication by 2.6944×10^{20} converts them to units of the Gauss system. We have refrained from doing so as we were interested only in determining the numerical variability interval of the dimensionless parameter K_b of hyperpolarizability anisotropy.

It is worth noting that, if K_b is defined as in Eq. (20), its value is not subject to restriction by any condition since b_{113} and b_{333} can be positive as well as negative, whereas the linear anisotropy K_a is restricted numerically to the interval $-0.5 \leq K_a < 1$.

4. Influence of strong molecular reorientation on SHS

Provided one refrains from considering intermolecular interactions, the problem of nonlinear variations in SHS intensity due to strong optical reorientation of the microsystems can be solved strictly for the above considered point group symmetries by having resort to the methods applied in the case of Rayleigh scattering [14].

In addition to our previous assumption concerning the observation set-up, we shall assume that the incident light beam propagates in the direction of the y -axis of laboratory co-ordinates, and shall choose the z -axis as parallel to the polarisation vector \vec{e} of the beam.

In those cases when the tensor $a_{\alpha\beta}^{\omega}$ possesses two mutually independent elements, $a_{11}^{\omega} = a_{22}^{\omega} \neq a_{33}^{\omega}$, the time-averaged potential energy (10) can be written as follows:

$$U_I = U(0, I_0) - \frac{2\pi}{c} I_0 (a_{33}^{\omega} - a_{11}^{\omega}) C_{z3}^2, \quad (31)$$

where $U(0, I_0) = -2\pi/c a_{11}^{\omega} I_0$ is the orientation-independent part of U_I . Besides, in Eq. (31), we have invoked the initially made assumptions concerning the choice of laboratory co-ordinates.

By Eqs (31), (1) and (25), the distribution function (9) can be replaced by a function of the following form [14]:

$$f(\Omega, I_0) = f(\vartheta, I_0) f_0(\varphi) f_0(\psi), \quad (32)$$

where

$$f(\vartheta, I_0) = \frac{\exp(\pm q \cos^2 \vartheta)}{\int_0^{\pi} \exp(\pm q \cos^2 \vartheta) \sin \vartheta d\vartheta}$$

Above, $f_0(\varphi)$ and $f_0(\psi)$ are distribution functions in the variables φ and ψ independent of the intensity of laser light. Consequently, averaging over the angles φ and ψ is isotropic, to be performed with the usual formulae [14]:

$$\langle \sin^n \varphi \rangle_0 = \langle \cos^n \varphi \rangle_0 = \langle \sin^n \psi \rangle_0 = \langle \cos^n \psi \rangle_0 = \begin{cases} \frac{(2k-1)!!}{2^k} & \text{for } n = 2k \\ 0 & \text{for } n = 2k+1. \end{cases} \quad (33)$$

However, averaging over the angle ϑ is carried out with the distribution function (32) and involves generalized Langevin functions of even order, defined as follows:

$$L_{2n}(\pm q) = \frac{\int_0^\pi \cos^{2n} \vartheta \exp(\pm q \cos^2 \vartheta) \sin \vartheta d\vartheta}{\int_0^\pi \exp(\pm q \cos^2 \vartheta) \sin \vartheta d\vartheta}. \quad (34)$$

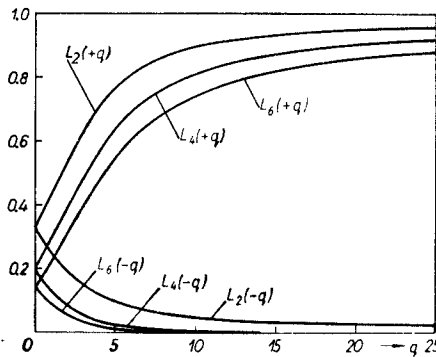


Fig. 2. Graphs of the generalized Langevin functions (Eq. (34)) for positive and negative reorientation parameter q

Methods for their calculation are due to Kielich [14]. For their shape, see Fig. 2. Langevin functions can be applied as well to cases of weak reorientation ($q < 1$) in the form of the following power series expansion [14]:

$$L_{2n}(\pm q) = \sum_{k=0}^n C_k^n (\pm q)^k, \quad (35)$$

where the expansion coefficients are given by:

$$C_k^n = \frac{1}{k!(2k+2n+1)} - \sum_{m=1}^k \frac{C_{k-m}^n}{m!(2m+1)}.$$

From the preceding formulae, we obtain:

$$\begin{aligned}
 L_2(\pm q) &= \frac{1}{3} \pm \frac{4}{45} q + \frac{8}{945} q^2 \mp \dots, \\
 L_4(\pm q) &= \frac{1}{5} \pm \frac{8}{105} q + \frac{16}{1575} q^2 \mp \dots, \\
 L_6(\pm q) &= \frac{1}{7} \pm \frac{4}{63} q + \frac{104}{10395} q^2 \mp \dots.
 \end{aligned}
 \tag{36}$$

For the point group symmetries considered above, we obtain the following results describing the influence of strong reorientation of the molecules on the intensity of SHS.

4.1. Symmetries D_3 , D_{3h} and C_{3h}

On insertion into Eq. (6) of the hyperpolarizability tensors (21) for D_3 , (22) for D_{3h} , and (23) for C_{3h} , and on averaging over the angles φ and ψ in accordance with formula (33) and over ϑ in accordance with (34), we obtain:

$$V_v^{2\omega} = I_{zz}^{2\omega} = S^{2\omega} \beta_{2\omega}^2 \frac{1}{2} [1 - 3L_2(\pm q) + 3L_4(\pm q) - L_6(\pm q)], \tag{37a}$$

$$H_v^{2\omega} = H_h^{2\omega} = I_{yy}^{2\omega} = V_h^{2\omega} = I_{xx}^{2\omega} = S^{2\omega} \beta_{2\omega}^2 \frac{1}{4} [1 - L_2(\pm q) - L_4(\pm q) + L_6(\pm q)], \tag{37b}$$

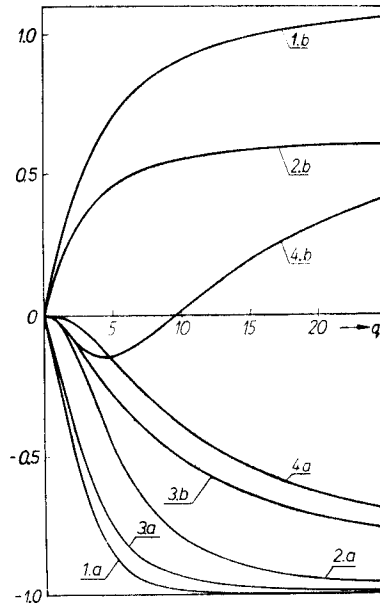


Fig. 3. Relative variations of SHS light intensity vs the degree of reorientation. The graphs 1 and 2 are for molecules having the symmetries D_{3h} , D_3 , C_{3h} (Eqs (39a, b)). The graphs 3 and 4 are for molecules having the symmetry D_{2d} (Eqs (42a, b)). The graphs 1 and 3 represent the components $\delta V_v^{2\omega}$; the graphs 2 and 4 represent the components $\delta H_v^{2\omega} = \delta V_h^{2\omega} = \delta H_h^{2\omega}$, a and b denote the sign of the reorientation parameter, “+” and “-”, respectively. (The function 4b is plotted in 10-fold magnification)

with

$$\begin{aligned}\beta_{2\omega}^2 &= (b_{111}^{2\omega})^2 \quad \text{for } D_3, \\ \beta_{2\omega}^2 &= (b_{222}^{2\omega})^2 \quad \text{for } D_{3h}, \\ \beta_{2\omega}^2 &= (b_{111}^{2\omega})^2 + (b_{222}^{2\omega})^2 \quad \text{for } C_{3h}.\end{aligned}$$

On taking the first terms of the expansion (36), we find:

$$V_{v0}^{3\omega} = \frac{8}{3^5} S^{2\omega} \beta_{2\omega}^2, \quad (38a)$$

$$H_{v0}^{2\omega} = H_{h0}^{2\omega} = V_{h0}^{2\omega} = \frac{1}{10^5} S^{2\omega} \beta_{2\omega}^2. \quad (38b)$$

Hence, insertion of (37a), (37b) and (38a), (38b) into (19) yields:

$$\delta V_v^{2\omega} = \frac{1}{16} [19 - 105L_2(\pm q) + 105L_4(\pm q) - 35L_6(\pm q)], \quad (39a)$$

$$\delta H_v^{2\omega} = \delta H_h^{2\omega} = \delta V_h^{2\omega} = \frac{1}{64} [41 - 105L_2(\pm q) - 105L_4(\pm q) + 105L_6(\pm q)]. \quad (39b)$$

The functions (39a) and (39b) are plotted in Fig. 3.

4.2. Symmetry D_{2d}

We have to insert into Eq. (6) the hyperpolarizability tensor (27) and to perform the averaging procedure indicated by formulae (33) and (34). This yields:

$$V_v^{2\omega} = S^{2\omega} (b_{123}^{2\omega})^2 \frac{9}{2} [L_2(\pm q) - 2L_4(\pm q) + L_6(\pm q)], \quad (40a)$$

$$H_v^{2\omega} = H_h^{2\omega} = V_h^{2\omega} = S^{2\omega} (b_{123}^{2\omega})^2 \frac{1}{4} [1 - 3L_2(\pm q) + 11L_4(\pm q) - 9L_6(\pm q)]. \quad (40b)$$

In the absence of reorientation, we obtain:

$$V_{v0}^{2\omega} = \frac{3 \cdot 6}{10^5} S^{2\omega} (b_{123}^{2\omega})^2, \quad (41a)$$

$$H_{v0}^{2\omega} = H_{h0}^{2\omega} = V_{h0}^{2\omega} = \frac{8}{3^5} S^{2\omega} (b_{123}^{2\omega})^2. \quad (41b)$$

Hence

$$\delta V_v^{2\omega} = \frac{1}{8} [-8 + 105L_2(\pm q) - 210L_4(\pm q) + 105L_6(\pm q)], \quad (42a)$$

and

$$\delta H_v^{2\omega} = \delta H_h^{2\omega} = \delta V_h^{2\omega} = \frac{1}{32} [3 - 105L_2(\pm q) + 385L_4(\pm q) - 315L_6(\pm q)]. \quad (42b)$$

The functions (42a) and (42b) are shown graphically in Fig. 3.

4.3. Symmetries C_4 , C_{4v} , C_5 , C_{5v} , C_6 , C_{6v} , C_∞ , $C_\infty v$

Insertion of (29) into (6) and averaging yields:

$$\begin{aligned}V_v^{2\omega} &= S^{2\omega} b_{2\omega}^2 \frac{9}{5} \{9L_2(\pm q) - 6K_b[3L_2(\pm q) - 5L_4(\pm q)] + \\ &\quad + K_b^2[9L_2(\pm q) - 30L_4(\pm q) + 25L_6(\pm q)]\},\end{aligned} \quad (43a)$$

and

$$\begin{aligned}H_v^{2\omega} &= H_h^{2\omega} = V_h^{2\omega} = S^{2\omega} b_{2\omega}^2 \frac{9}{50} \{1 - L_2(\pm q) - 2K_b[1 - 6L_2(\pm q) + \\ &\quad + 5L_4(\pm q)] + K_b^2[1 - 11L_2(\pm q) + 35L_4(\pm q) - 25L_6(\pm q)]\}.\end{aligned} \quad (43b)$$

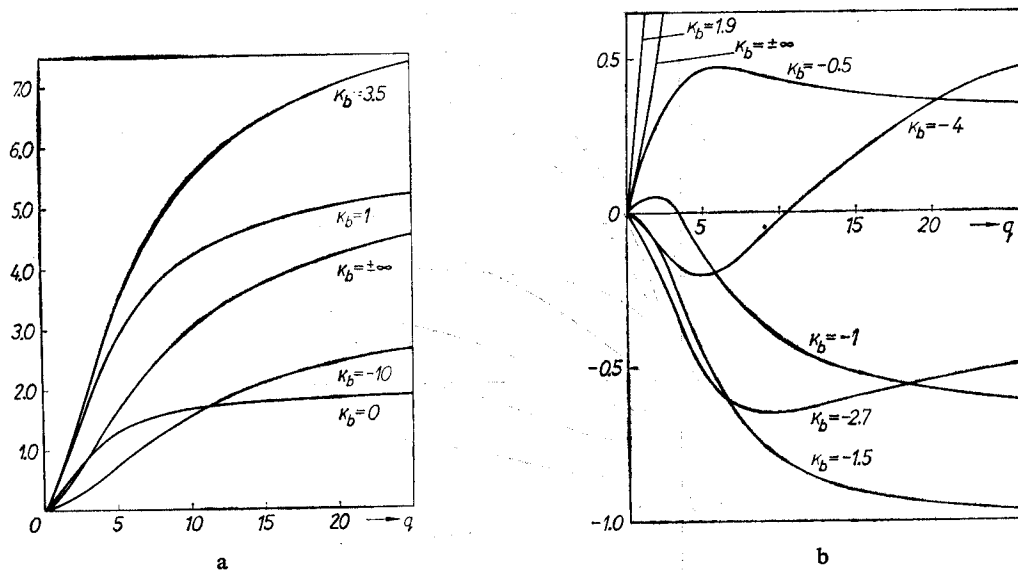


Fig. 4a, b. Graph of $\delta V^{2\omega}$ vs the reorientation parameter $+q$ for various values of the anisotropy K_b (Eq. (45a)). Figs 4a–4c are for molecules of the symmetries C_4 , C_{4v} , C_5 , C_{5v} , C_6 , C_{6v} , C_{∞} , $C_{\infty v}$

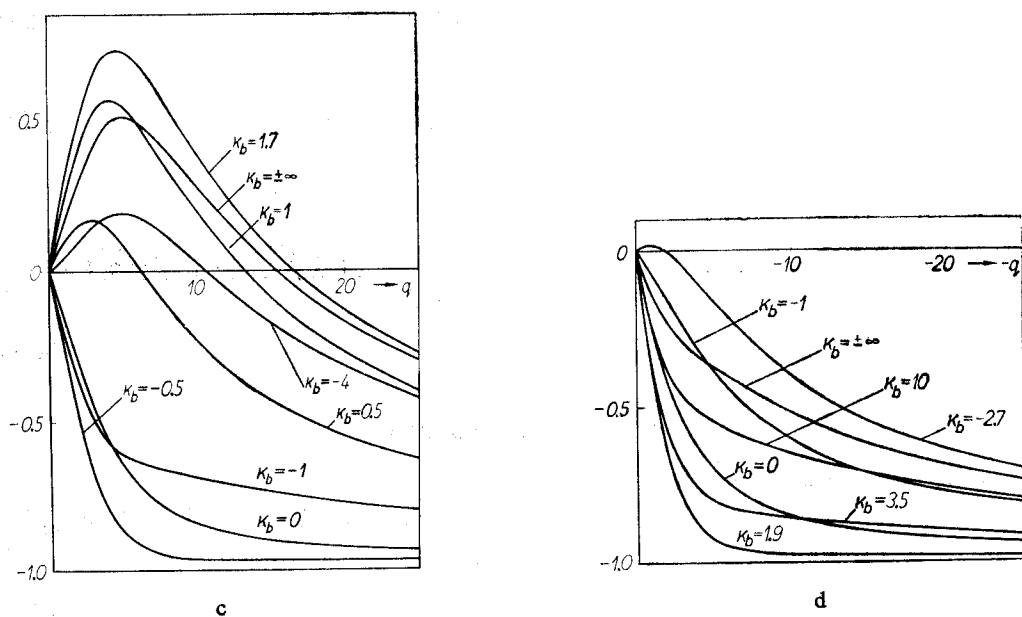


Fig. 4c. Graph of $\delta H_v^{2\omega}$ vs the reorientation parameter $+q$ for various values of the anisotropy K_b (Eq. (45b))
 Fig. 4d. Graph of $\delta V_v^{2\omega}$ vs the reorientation parameter $-q$ for various values of the anisotropy K_b (Eq. (45a))

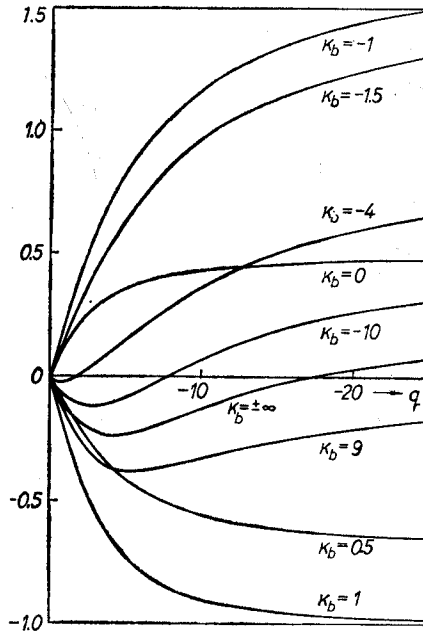


Fig. 4e. Graph of $\delta H_v^{2\omega}$ vs the reorientation parameter $-q$ for various values of the anisotropy K_b (Eq. (45b))

In the absence of reorientation, we have:

$$V_{v0}^{2\omega} = S^{2\omega} b_{2\omega}^2 \frac{27}{25} \left(1 + \frac{4}{21} K_b^2\right), \tag{44a}$$

and

$$H_{v0}^{2\omega} = H_{h0}^{2\omega} = V_{h0}^{2\omega} = S^{2\omega} b_{2\omega}^2 \frac{3}{25} \left(1 + \frac{8}{7} K_b^2\right). \tag{44b}$$

We consequently have:

$$\delta V_v^{2\omega} = \frac{-21 + 63L_2(\pm q) - K_b[126L_2(\pm q) - 210L_4(\pm q)] - K_b^2[4 - 63L_2(\pm q) + 210L_4(\pm q) - 175L_6(\pm q)]}{21 + 4K_b^2}, \tag{45a}$$

and

$$\begin{aligned} \delta H_v^{2\omega} &= \delta H_h^{2\omega} = \delta V_h^{2\omega} = \\ &= \frac{7 - 21L_2(\pm q) - K_b[42 - 252L_2(\pm q) + 210L_4(\pm q)] + K_b^2[5 - 231L_2(\pm q) + 735L_4(\pm q) - 525L_6(\pm q)]}{14 + 16K_b^2}. \end{aligned} \tag{45b}$$

The functions (45a) and (45b) are plotted in Figs 4a–4e for various values of the hyperpolarizability anisotropy K_b .

At optical saturation, $q = +\infty$, the variations in SHS intensity become:

$$\delta V_v^{2\omega}(+\infty) = \frac{42 + 84K_b + 24K_b^2}{21 + 4K_b^2}, \quad (46a)$$

and

$$\delta H_v^{2\omega}(+\infty) = -1, \quad (46b)$$

whereas at $q = -\infty$ they become:

$$V_v^{2\omega}(-\infty) = -1, \quad (47a)$$

and

$$\delta H_v^{2\omega}(-\infty) = \frac{7 - 42K_b + 5K_b^2}{14 + 16K_b^2}. \quad (47b)$$

It is found that in some cases the relative variations in SHS intensity tend to zero at saturation; thus,

$$\delta V_v^{2\omega} \xrightarrow{q \rightarrow +\infty} 0 \quad \text{for} \quad K_b = -2.9 \quad \text{and} \quad K_b = -0.6$$

and

$$H_v^{2\omega} \xrightarrow{q \rightarrow -\infty} 0 \quad \text{for} \quad K_b = 0.17 \quad \text{and} \quad K_b = 8.23.$$

The way in which the asymptotes, to which $\delta V_v^{2\omega}$ and $\delta H_v^{2\omega} = \delta H_h^{2\omega} = \delta V_h^{2\omega}$ tend at $q \rightarrow \pm\infty$ (Eqs (46a) and (47b)) depend on the value of the parameter K_b , is shown in Figs 1a and 1b. The graphs of Figs 1a and 1b show that in certain cases the sign of the asymptote differs from that of the slope of $\delta I_n^{2\omega}$ in the point $q = 0$. This is apparent from Figs 4a, 4c–4e as well.

5. Conclusions

The steadily progressing studies of nonlinear properties of molecules come up against considerable experimental and theoretical difficulties even with regard to the numerical determination of the tensor elements of second-order nonlinear polarizability b_{ijk} [19, 20]. The difficulties increase considerably with regard to the determination of those of the tensor c_{ijkl} [21, 22]. The method proposed here for the study of variations in SHS under the effect of optical reorientation can be helpful, at least for their assessment. In principle, this holds for molecules of the groups C_4 , C_{4v} , C_5 , C_{5v} , C_6 , C_{6v} , C_∞ and $C_{\infty v}$. For molecules of the groups D_3 , D_{3h} , D_{2d} , and C_{3h} , the parameters of nonlinear polarizability are not accessible to determination from variations in SHS. Nevertheless, in the latter 4 cases too, optical molecular reorientation can be decisively relevant e. g. in measurements of the depolarisation ratio of SHS (as it obviously is with regard to the 8 previously stated symmetries).

The study of molecules having the symmetries C_4 , C_{4v} , C_5 , C_{5v} , C_6 , C_{6v} , C_∞ and $C_{\infty v}$ appear to be of especial interest since the determination of the sign of the parameter K_b is not possible in usual (i. e. reorientation-less) SHS. Now the study of the sign of variations in SHS, even at weak reorientation, permits to determine the sign of K_b at certain values of $|K_b|$ (Figs 1a and 1b) provided the sign of the reorientation parameter q is known. Investigations of the behaviour of the SHS components up to complete optical molecular alignment should yield still fuller data, permitting the assessment of the value and sign of the hyperpolarizability anisotropy (Figs 4a-4c).

When comparing the shapes of Rayleigh and hyper-Rayleigh scattering versus the degree of reorientation, we note in the first place that the variations $\delta H_v^{2\omega} = \delta H_h^{2\omega} = \delta V_h^{2\omega}$ are functions of the anisotropy K_b , whereas in Rayleigh scattering they are independent of the anisotropy in linear polarizability K_a [14] and tend to -1 with $q \rightarrow \pm \infty$. Moreover, in SHS, at fixed sign of q , one of the components $\delta V_v^{2\omega}$ or $\delta H_v^{2\omega} = \delta H_h^{2\omega} = \delta V_h^{2\omega}$ always tends to -1 at saturation (complete alignment) for arbitrary K_b while the other component is a function of K_b and can attain the value -1 only in the following two cases: $\delta V_v^{2\omega}(+\infty) = 1$ for $K_b = -1.5$, or $\delta H_v^{2\omega}(-\infty) = -1$ for $K_b = 1$. The former case occurs if $b_{333}^{2\omega} = 0$ at $a_{33}^{\omega} > a_{11}^{\omega}$. The latter case occurs if $b_{113}^{2\omega} = 0$ at $a_{33}^{\omega} < a_{11}^{\omega}$. A comparison of the values of the asymptotes leads to the following conclusions:

$\delta V_v^{2\omega}(+\infty)$ lies within the interval $(-1, 9)$ and $\delta H_v^{2\omega}(-\infty)$ within the interval $(-1, 1.8)$, whereas [14] $\delta V_v^{2\omega}(+\infty)$ belongs to the interval $(0, 4)$ and $\delta V_v^{2\omega}(-\infty)$ to the interval $(0, 0.875)$, whence we see that the maximal changes in scattered intensity are much larger in SHS and can be negative also for the component $\delta V_v^{2\omega}$.

As to the feasibility of inducing optical reorientation, the matter has been dealt with in previous papers [14, 15]. It is to be presumed that saturation (complete alignment) is achievable in media involving macromolecules upwards of 100 \AA in size. By having recourse to the focussed beam of a giant laser, it still may be possible [15] to attain the threshold of strong reorientation ($q = 1$) in molecular media; the chief obstacle in the way of complete saturation resides in the destructive effect of giant optical fields.

We consider that the experimental detection of the influence of optical reorientation on SHS can be the most easily performed in measurements of variations in depolarisation ratio, since here the quantity measured depends on the intensity of the incident beam only by way of the reorientation parameter [23].

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