

## Linear and Nonlinear Light Scattering from the Surfaces of Liquids\*

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### Abstract

The linear optical properties of matter, e.g. the refractive index, the absorption coefficient and the reflectivity, can be interpreted in terms of the oscillating charge and current densities induced by the optical field. For most purposes, it is sufficient to consider the oscillating dipole moment  $\mu = \alpha E = \alpha E^{(0)} \exp(-i\omega t + i\mathbf{k} \cdot \mathbf{r})$ , where  $\alpha$  is the mean polarisability of a molecule, or of a unit cell, in a plane wave propagating with wave vector  $\mathbf{k}$ , angular frequency  $\omega$  and amplitude  $E^{(0)}$ . A static electric field  $F$  polarises the material and may affect the reflected light linearly in  $F$ . If  $F$  is in the plane of incidence there is a change of phase of the reflected light, and if  $F$  is perpendicular to the plane of incidence there is a change in polarisation and intensity. If the intensity of the optical field is high, nonlinear scattering is observed from the surface of a liquid. The surface breaks the symmetry of the fluid, leading to partial molecular orientation and hence to a non-vanishing first hyperpolarisability  $\beta$  that gives the induced dipole at the frequency  $2\omega$  proportional to the square of  $E$ . With intense laser sources a molecular monolayer or sub-monolayer can be detected. Surface selectivity can be achieved by tuning an infrared laser of frequency  $\omega_{\text{IR}}$  to a vibrational frequency of the monolayer and detecting a coherent beam at the sum frequency  $\omega + \omega_{\text{IR}}$ , when the surface is simultaneously subjected to pulses at  $\omega$  and  $\omega_{\text{IR}}$ .

### 1. Introduction

The optical properties of matter are attributable to the oscillations in the charge and current densities induced by the electromagnetic field associated with the light beam. The dominant contribution generally comes from the oscillating induced electric polarisation  $P(t)$  which is proportional to the electric field strength  $E(t)$ :

$$P(t) = \chi^{(1)} \cdot E(t) = N\bar{\mu}(t) = N\alpha \cdot E(t), \quad (1)$$

where  $\chi^{(1)}$  is the electric susceptibility,  $N$  the number density,  $\mu(t)$  the induced dipole moment, and  $\alpha$  the mean polarisability of a molecule (or of a unit cell) comprising the material;  $\chi^{(1)}$  and  $\alpha$  are functions of the angular frequency  $\omega$  of the optical field and are symmetric second-rank tensors.

The refractive index and absorption coefficient of a gas are determined by the real and imaginary parts of the symmetric tensor  $\alpha_{\alpha\beta}$  (Born and Huang

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1954), and the intensities of Rayleigh and Raman scattering are proportional to the square of the transition polarisability  $\langle \Psi_f | \alpha_{\alpha\beta} | \Psi_i \rangle$ , where  $\Psi_i$  and  $\Psi_f$  are the initial and final states of the molecule (Placzek 1934).

Some optical phenomena are not accounted for by equation (1). For example, the Faraday effect (i.e. magnetic optical rotation and magnetic circular dichroism) comes from the anti-symmetric polarisability  $\alpha'_{\alpha\beta} = -\alpha'_{\beta\alpha}$  which gives the dipole induced by  $\dot{\mathbf{E}}_\beta(t) = \partial E_\beta(t)/\partial t$  (Buckingham and Stephens 1966);  $\alpha'_{\alpha\beta}$  is induced by a static magnetic field  $\mathbf{B}$  in the direction of propagation and is an optical property possessed by all matter. Natural optical activity is due to the electric dipole moment induced by  $\dot{\mathbf{B}}(t)$ , the time-derivative of the magnetic field of the light beam, and to the magnetic dipole moment  $\mathbf{m}(t)$  induced by  $\dot{\mathbf{E}}(t)$  (Condon 1937). Nonlinear optical phenomena, such as second-harmonic generation, are also not accounted for by equation (1) but are related to the nonlinear susceptibilities  $\chi^{(2)}$ ,  $\chi^{(3)}$ , etc. that give the electric polarisation proportional to  $\mathbf{E}^2$ ,  $\mathbf{E}^3$ , etc. (Bloembergen 1965; Shen 1984).

Section 2 of this paper is concerned with predictions of the effects of a static electric field  $\mathbf{F}$  on the reflection of light from the surface of a fluid or solid. Section 3 is devoted to a brief discussion of nonlinear light scattering from the surface of a liquid, and in particular to the technique of sum frequency generation (Hunt *et al.* 1987).

## 2. Reflection from a Polarised Surface

Reflectivity of electromagnetic waves from a surface results from the coherent scattering of light by the oscillating charge and current densities induced near the surface by the electromagnetic field. Since the complex polarisability  $\alpha_{\alpha\beta}$  is unaffected by a reversal of the orientation of the molecule, and since reversal of an externally applied electric field  $\mathbf{F}$  reverses the mean orientation of molecular dipoles, it might be expected that there is no *linear* effect of  $\mathbf{F}$  on the optical properties of a fluid. However, there is a small linear effect of  $F_x$  on the intensity of circularly polarised light propagating in the  $z$  direction that is scattered in the  $y$  direction (Buckingham and Raab 1975; Buckingham and Shatwell 1980). This differential scattering—of the order of 1 part per million in a field of  $10^6 \text{ V m}^{-1}$ —comes from the interference of the radiation from the induced electric dipole with that from the induced magnetic dipole and electric quadrupole in the polarised fluid. The phase of the light reflected from the surface of a fluid has been predicted to change linearly with  $F_z$ , the field strength perpendicular to the fluid (Buckingham 1982). These effects come from the higher-order polarisabilities  $G'_{\alpha\beta}$  and  $A_{\alpha\beta\gamma}$  which give the electric dipole moment induced by  $\dot{\mathbf{B}}(t)$  and the electric field gradient  $\nabla \mathbf{E}(t)$  respectively (Buckingham 1967a):

$$\mu_\alpha(t) = \alpha_{\alpha\beta} E_\beta(t) + \omega^{-1} G'_{\alpha\beta} \dot{\mathbf{B}}_\beta(t) + \frac{1}{3} A_{\alpha\beta\gamma} \nabla_\beta E_\gamma(t) + \dots, \quad (2)$$

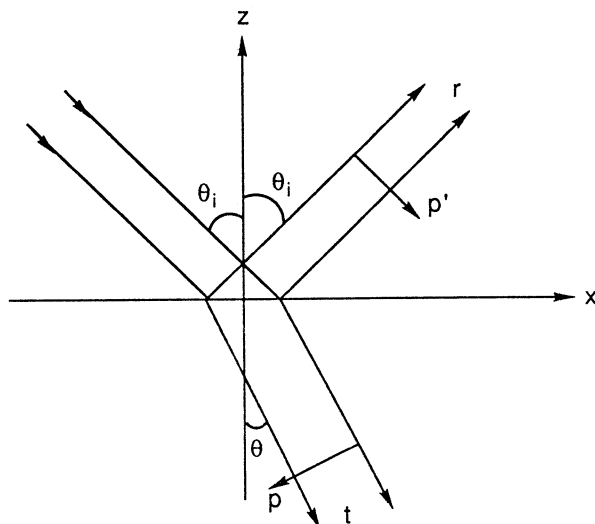
$$m_\alpha(t) = -\omega^{-1} G'_{\beta\alpha} \dot{E}_\beta(t) + \dots, \quad (3)$$

$$\Theta_{\alpha\beta}(t) = A_{\gamma\alpha\beta} E_\gamma(t) + \dots, \quad (4)$$

where  $\mathbf{m}(t)$  and  $\boldsymbol{\Theta}(t)$  are the oscillating magnetic dipole moment and electric quadrupole moment of the molecule in the electromagnetic field. The time-

derivatives of  $\mathbf{B}(t)$  and  $\mathbf{E}(t)$  in equations (2) and (3) are necessary to achieve symmetry under time-reversal  $\hat{\theta}$ . The molecular property tensors  $\alpha$ ,  $\mathbf{G}'$  and  $\mathbf{A}$  are symmetric under  $\hat{\theta}$ ;  $\alpha$  is also even under parity  $\hat{P}$  while  $\mathbf{G}'$  and  $\mathbf{A}$  are odd under  $\hat{P}$ . Thus for centrosymmetric molecules  $\mathbf{G}' = \mathbf{0}$  and  $\mathbf{A} = \mathbf{0}$  if the centre of symmetry is chosen as the origin.

The cause of the predicted phase shift on reflection due to the normal component  $F_z$  may be visualised as arising from a movement of the source of the molecular scattering due to the reorientation caused by  $F_z$ . For example, consider a molecule such as  $\text{CH}_3\text{Br}$  where the main contributor to the molecular polarisability may be thought of as coming from the heavy bromine atom; the dipole moment of  $\text{CH}_3\text{Br}$  has the sense  $^+\text{H}_3\text{CBr}^-$  so a field  $F_z$  out from the surface tends to place the  $\text{H}_3\text{C}$  groups at the top while  $-F_z$  tends to put the Br atoms at the surface and thereby shorten the optical path of the reflected light. The field  $F_z$  may affect the structure of the surface layer, thus complicating the interpretation of measurements of the linear effect of  $F_z$  on the phase of the reflected light (Galwas 1983), but also providing a new tool for probing the structure of the surface. In this paper expressions are derived for the changes in the reflected field due to an electrostatic field  $F_y$  parallel to the surface. Since any change to the surface structure must be an even function of  $F_x$  and  $F_y$  (though not of  $F_z$ ), the full linear effects of  $F_x$  and  $F_y$  may be attributed to molecular distortion and orientation.



**Fig. 1.** Reflection from the surface of a fluid. The surface is the  $xy$  plane with  $z$  the outward normal and  $y$  into the paper. The plane of incidence is  $xz$ , the angles of incidence and refraction being  $\theta_i$  and  $\theta$ . The directions of propagation of the transmitted and reflected beams are  $t$  and  $r$ .

Fig. 1 shows the axis system chosen to describe the reflection. Optical polarisation of the boundary causes the extinction of the incident wave in the medium and the creation of the refracted and reflected waves (Born and Wolf 1959).

The electric field of the reflected wave may be obtained from that radiated by the induced electric dipole moment  $\overline{\boldsymbol{\mu}(t)}$ , augmented by the radiation from the oscillating magnetic dipole  $\overline{\boldsymbol{m}(t)}$  and electric quadrupole moment  $\overline{\boldsymbol{\Theta}(t)}$  of a molecule or of some appropriate microscopic region in the fluid in the optical field (Buckingham and Raab 1975):

$$E_{\alpha}(t) \propto \overline{\ddot{\mu}_{\alpha}(t)} - \hat{k}_{\alpha} \hat{k}_{\beta} \overline{\ddot{\mu}_{\beta}(t)} - \frac{n}{c} \epsilon_{\alpha\beta\gamma} \hat{k}_{\beta} \overline{\ddot{m}_{\gamma}(t)} + \frac{n}{3c} (\overline{\ddot{\Theta}_{\alpha\beta}(t)} \hat{k}_{\beta} - \hat{k}_{\alpha} \overline{\ddot{\Theta}_{\beta\gamma}} \hat{k}_{\beta} \hat{k}_{\gamma}) + \dots, \quad (5)$$

where  $\hat{\mathbf{k}}$  is the unit vector in the direction of propagation of the radiation,  $n$  is the index of refraction ( $n = \sin\theta_i/\sin\theta$ ), and the bars denote a statistical average.

A static electric field  $\mathbf{F}$  will distort the molecules and orient them through the torque  $\boldsymbol{\mu}^{(0)} \times \mathbf{F}$  acting on their permanent electric dipole moment  $\boldsymbol{\mu}^{(0)}$ . The mean value of  $\cos\Omega_a$ , where  $\Omega_a$  is the angle between the arbitrary molecular axis  $a$  and the field  $\mathbf{F}$ , is

$$\overline{\cos\Omega_a} = \frac{3\epsilon}{2\epsilon+1} \frac{\langle\mu_a\rangle F}{3kT} \equiv \frac{\mu_a^{(0)} F}{3kT}, \quad (6)$$

where  $\langle\mu_a\rangle$  is the mean component in the  $a$ -direction of the dipole moment of a molecule and its neighbours in a microscopic sphere of arbitrary radius, and  $\epsilon$  is the static dielectric constant of the fluid. Equation (6) is exact within the confines of classical statistical mechanics (Buckingham 1967*b*). To first order in the field strength  $\mathbf{F}$  we have

$$\overline{\alpha_{\alpha\beta}} = \alpha\delta_{\alpha\beta}, \quad (7)$$

$$\overline{G'_{\alpha\beta}} = G'\delta_{\alpha\beta} + \epsilon_{\alpha\beta\gamma} g F_{\gamma}, \quad (8)$$

$$\overline{A_{\alpha\beta\gamma}} = (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} - \frac{2}{3} \delta_{\alpha\delta} \delta_{\beta\gamma}) a F_{\delta}, \quad (9)$$

where

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \equiv \frac{1}{3}\alpha_{\beta\beta}, \quad (10)$$

$$G' = \frac{1}{3}(G'_{xx} + G'_{yy} + G'_{zz}) \equiv \frac{1}{3}G'_{\beta\beta}, \quad (11)$$

$$g = \frac{1}{6}\epsilon_{\alpha\beta\gamma}(G'_{\alpha\beta\gamma} + G'_{\alpha\beta\gamma}\mu_{\gamma}^{(0)}/kT), \quad (12)$$

$$a = \frac{1}{10}(A_{\alpha\alpha\beta\beta} + A_{\alpha\alpha\beta}\mu_{\beta}^{(0)}/kT). \quad (13)$$

Here  $G'_{\alpha\beta\gamma}$  and  $A_{\alpha\beta\gamma\delta}$  describe the changes in the molecular properties  $G'_{\alpha\beta}$  and  $A_{\alpha\beta\gamma}$  of a fixed molecule due to distortion by the static field  $\mathbf{F}$ :

$$G'_{\alpha\beta}(\mathbf{F}) = G'_{\alpha\beta} + G'_{\alpha\beta\gamma} F_{\gamma} + \dots,$$

$$A_{\alpha\beta\gamma}(\mathbf{F}) = A_{\alpha\beta\gamma} + A_{\alpha\beta\gamma\delta} F_{\delta} + \dots \quad (14)$$

From equations (8) and (9) we see that in a field  $F_y$  parallel to the surface, the only non-vanishing elements of  $(\overline{G_{\alpha\beta}} - G'\delta_{\alpha\beta})$  are  $\overline{G_{zx}} = -\overline{G_{xz}} = gF_y$ , and of  $\overline{A_{\alpha\beta\gamma}}$  they are

$$\overline{A_{xxy}} = \overline{A_{xyx}} = \overline{A_{zzy}} = \overline{A_{zyz}} = \frac{3}{4}\overline{A_{yyy}} = -\frac{3}{2}\overline{A_{yxx}} = -\frac{3}{2}\overline{A_{yzz}} = aF_y.$$

We can now evaluate the electric fields  $\mathbf{E}^{(t)}$  and  $\mathbf{E}^{(r)}$  of the transmitted and reflected waves coming from the oscillating charge and current distribution in the surface layer polarised by the electrostatic field  $F_y$ . From equation (5) we get

$$E_p^{(t)} \propto \overline{\mu_p} + \frac{n}{c}\overline{m_y} + \frac{n}{3c}\overline{\Theta_{pt}} + \dots \quad (15)$$

$$= \alpha E_p - \frac{2n}{c\omega} G' \dot{E}_y + \dots, \quad (16)$$

$$E_y^{(t)} \propto \overline{\mu_y} - \frac{n}{c}\overline{m_p} + \frac{n}{3c}\overline{\Theta_{yt}} + \dots \quad (17)$$

$$= \alpha E_y + \frac{2n}{c\omega} G' \dot{E}_p + \dots, \quad (18)$$

$$E_{p'}^{(r)} \propto -\overline{\mu_{p'}} - \frac{n}{c}\overline{m_y} - \frac{n}{3c}\overline{\Theta_{p'r}} - \dots \quad (19)$$

$$= \alpha \cos(\theta_i + \theta) E_p + \frac{n}{c\omega} \dot{E}_y [ \{1 - \cos(\theta_i + \theta)\} G' + (\overline{G_{zx}} + \frac{1}{3}\omega \overline{A_{xxy}}) \sin(\theta_i + \theta) ] + \dots, \quad (20)$$

$$E_y^{(r)} \propto -\overline{\mu_y} + \frac{n}{c}\overline{m_{p'}} - \frac{n}{3c}\overline{\Theta_{yr}} - \dots \quad (21)$$

$$= -\alpha E_y - \frac{n}{c\omega} \dot{E}_p [ \{1 - \cos(\theta_i + \theta)\} G' - (\overline{G_{zx}} + \frac{1}{3}\omega \overline{A_{xxy}}) \sin(\theta_i + \theta) ] + \dots \quad (22)$$

The form of equation (22) shows that if the incident beam is polarised in the  $y$ -direction then the beam reflected from the polarised surface has a right or left circularity proportional to  $\overline{G_{zx}} + \frac{1}{3}\omega \overline{A_{xxy}}$  and this is proportional to  $F_y$  and could therefore be modulated. Alternatively, Rayleigh's reciprocity principle (Perrin 1942; de Figueredo and Raab 1980; Graham 1980), based on time-reversal symmetry, means that if the field components  $E_p$  and  $E_y$  are those of a circularly polarised beam  $\mathbf{E}^\pm = E^{(0)}(\mathbf{p} \cos \omega t \mp \mathbf{j} \sin \omega t)$ , where  $\mathbf{p}$  and  $\mathbf{j}$  are unit vectors in the  $p$  and  $y$  directions and  $\mathbf{E}^+$  and  $\mathbf{E}^-$  are right and left circularly polarised fields, respectively, then, from equations (20) and (22)

$$E_{p'}^{(r)\pm} = E^{(0)} \cos \omega t \left( \alpha \cos(\theta_i + \theta) \mp \frac{n}{c} \{ (1 - \cos(\theta_i + \theta)) G' + (\overline{G_{zx}} + \frac{1}{3}\omega \overline{A_{xxy}}) \sin(\theta_i + \theta) \} \right), \quad (23)$$

$$E_y^{(r)\pm} = \pm E^{(0)} \sin \omega t \left( \alpha \pm \frac{n}{c} \{ (1 - \cos(\theta_i + \theta)) G' - (\overline{G_{zx}} + \frac{1}{3}\omega \overline{A_{xxy}}) \sin(\theta_i + \theta) \} \right). \quad (24)$$

At the Brewster angle of incidence,  $\theta_i + \theta = \pi/2$  and equations (23) and (24) simplify to

$$E_{p'}^{(r)\pm} = \mp \frac{n}{c} E^{(0)} \cos \omega t [G' + (\overline{G'_{zx}} + \frac{1}{3} \omega \overline{A_{xxy}})], \quad (25)$$

$$E_y^{(r)\pm} = \pm E^{(0)} \sin \omega t \left( \alpha \pm \frac{n}{c} \{G' - (\overline{G'_{zx}} + \frac{1}{3} \omega \overline{A_{xxy}})\} \right). \quad (26)$$

It may be noted that at the Brewster angle the reflected electric field polarised in the plane of incidence,  $E_{p'}^{(r)\pm}$  in equation (20), does not go completely to zero as is usual but has a weak component proportional to  $\dot{E}_y$ . The terms in  $\overline{G'_{zx}} + \frac{1}{3} \omega \overline{A_{xxy}}$  go to zero for normal incidence.

The boundary conditions for the oscillating electric and magnetic fields, i.e. the tangential components of  $\mathbf{E}$  and the normal components of  $\mathbf{B}$  are continuous, can be satisfied for nonzero  $G'$  and  $\overline{G'_{zx}} + \frac{1}{3} \omega \overline{A_{xxy}}$  if the transmissivity depends upon  $G'$  and  $\overline{G'_{zx}} + \frac{1}{3} \omega \overline{A_{xxy}}$ .

The field-dependent reflectivity is determined by  $\overline{G'_{zx}} + \frac{1}{3} \omega \overline{A_{xxy}}$  which is independent of the choice of origin in the molecule or unit cell (Buckingham and Longuet-Higgins 1968), as it must be for an observable property. If  $F_y$  is modulated at an audio-frequency  $f$  so that  $F_y = F^{(0)} \cos(2\pi ft)$ , then the intensity of light modulated at the frequency  $f$  transmitted by a polariser in the path of the reflected beam with  $y$  polarisation is

$$I_y^{(r)\pm}(f) = \mp \frac{n}{c} (E^{(0)})^2 \sin(\theta_i + \theta) [\alpha^* (\overline{G'_{zx}} + \frac{1}{3} \omega \overline{A_{xxy}}) + \text{c.c.}], \quad (27)$$

where  $\alpha^*$  is the complex conjugate (c.c.) of  $\alpha$ . If  $\omega$  is near an absorption frequency then  $\alpha$  becomes complex, as does  $G'_{\alpha\beta}$  and  $A_{\alpha\beta\gamma}$ .

The best means of measuring the new optical property  $g + \frac{1}{3} \omega a$  may be to examine the interference of the reflected beam with a weak probe beam that propagates at the same frequency and in the same direction. That would permit the observation of the real and imaginary parts of  $g + \frac{1}{3} \omega a$ . It would be desirable to study the field-induced reflection as a function of the frequency  $\omega$  of the incident and probe beams.

### 3. Nonlinear Scattering from the Surface of a Liquid

If the intensity of the optical field is high, nonlinear scattering from the surface of a liquid may be observed. Second-harmonic generation originates from the first hyperpolarisability  $\beta_{\alpha\beta\gamma}$  giving the dipole proportional to the square of the incident electric field  $E^{(0)} \exp(-i\omega t)$  which oscillates at the harmonic frequency  $2\omega$ . Since  $\overline{\beta_{\alpha\beta\gamma}}$  is zero for an isotropic fluid, all the second-harmonic radiation must come from the surface region where molecular orientation may occur. The technique is therefore surface-specific. It was first investigated by Bloembergen and Pershan (1962) and has recently been reviewed by Shen (1989). Second-harmonic generation at surfaces has sufficient sensitivity to permit the detection of a submonolayer of molecules (Brown and Matsuoka 1969; Chen *et al.* 1973).

An interesting new nonlinear optical technique for studying surfaces is *sum frequency generation* (SFG). It utilises two pulsed lasers, one of which is tunable in the vicinity of an infrared absorption frequency of the molecules

in the surface layer. In the presence of synchronised laser pulses at  $\omega$  and  $\omega_{\text{IR}}$ , coherent radiation at the sum frequency  $\omega + \omega_{\text{IR}}$  may be detected as a result of a near-resonant  $\bar{\beta}_{\alpha\beta\gamma}$  for the molecules at the surface. When  $\omega_{\text{IR}}$  is near the infrared absorption frequency for the transition  $0 \rightarrow \nu$ , the oscillating dipole at the sum frequency  $\omega + \omega_{\text{IR}}$  is

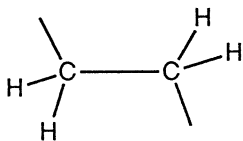
$$\mu_{\alpha}(\omega + \omega_{\text{IR}}) = \frac{1}{2} \beta_{\alpha\beta\gamma} E_{\beta}(\omega) E_{\gamma}(\omega_{\text{IR}}), \quad (28)$$

where

$$\begin{aligned} \beta_{\alpha\beta\gamma} \approx \sum_j & \left( \frac{\langle 0 | \mu_{\alpha} | j \rangle \langle j | \mu_{\beta} | \nu \rangle}{\hbar(\omega_j - \omega - \omega_{\text{IR}})} + \frac{\langle 0 | \mu_{\beta} | j \rangle \langle j | \mu_{\alpha} | \nu \rangle}{\hbar(\omega_j + \omega)} \right) \\ & \times \langle \nu | \mu_{\gamma} | 0 \rangle [\hbar(\omega_{\nu} - \omega_{\text{IR}})]^{-1}, \end{aligned} \quad (29)$$

where  $|0\rangle$  is the ground state,  $|\nu\rangle$  is the excited vibrational level of the ground electronic state, and  $|j\rangle$  is an excited electronic state whose excitation energy from the ground state is  $\omega_j$ . The expression in large parentheses in (29) is the Raman transition polarisability, while  $\langle |\mu_{\gamma}| 0 \rangle$  is the infrared transition dipole moment. If the vibrational transition  $0 \rightarrow \nu$  is active in the infrared and Raman spectra of the monolayer, then  $\beta_{\alpha\beta\gamma}$  will be large and the sum frequency can be detected. However, if the molecule has a centre of symmetry then  $\beta_{\alpha\beta\gamma}$  is zero.

The SFG technique has been used to study the CH vibrations of monolayers of methanol and pentadecanoic acid on glass and water (Hunt *et al.* 1987; Guyot-Sionnest *et al.* 1987), and of octadecyl thiol adsorbed on gold (Harris *et al.* 1987).



**Fig. 2.** Trans configuration of the  $-(\text{CH}_2)_{17}-$  chain.

Dr C. D. Bain has constructed apparatus in Cambridge for recording SFG and has successfully applied it to the study of monolayers of octadecyl thiol  $[\text{CH}_3(\text{CH}_2)_{17}\text{SH}]$  adsorbed on silver and gold surfaces. The infrared reflectance spectrum of this system has been recorded by Dr R. G. Nuzzo of the AT&T Bell Laboratories, Murray Hill, New Jersey; it shows strong absorption near  $2900 \text{ cm}^{-1}$  due to CH stretching vibrations, and these include resolved lines due to  $-\text{CH}_3$  and  $\text{>CH}_2$ . The SFG spectrum recorded by C. D. Bain shows lines due to  $-\text{CH}_3$  only. This can be explained by the trans configuration of the  $-(\text{CH}_2)_{17}-$  chain shown in Fig. 2, making the CH stretching modes very weak in SFG because of the approximate centre of symmetry.

The technique of SFG clearly has the sensitivity and specificity to make it a useful tool for studying interfaces.

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