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Vibrational Spectroscopy 24 2000. 109–123

http://www.sciencedirect.com/science/article/pii/S0924203100000849

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Vibrational Spectroscopy 24 (2000) 109–123

VIBRATIONAL SPECTROSCOPY

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A comparative study of confined organic monolayers by Raman scattering and sum-frequency spectroscopy

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Received 4 August 1999; received in revised form 25 January 2000; accepted 24 February 2000

Abstract

The structure of a Langmuir–Blodgett (LB) monolayer of Zn arachidate at the solid–solid interface has been studied by Raman scattering and sum-frequency (SF) spectroscopy. The monolayer was confined in the contact between a CaF_2 prism and a MgF_2 lens at an average pressure of 60 MPa. This is the first report of an unenhanced Raman spectrum of an organic monolayer at the solid–solid interface. The Raman and SF spectra both show that the deposited monolayer is conformationally ordered and that the monolayer retains this order when placed between the prism and the lens. The relative intensity of the Raman spectra of the Zn arachidate monolayer at the CaF_2/air and CaF_2/MgF_2 interfaces can be explained in terms of the strength of the interfacial electric fields. The relative intensities of the SF spectra at the two interfaces cannot be interpreted in this manner. Deviations from the expected intensities are discussed in terms of structural changes in the monolayer.

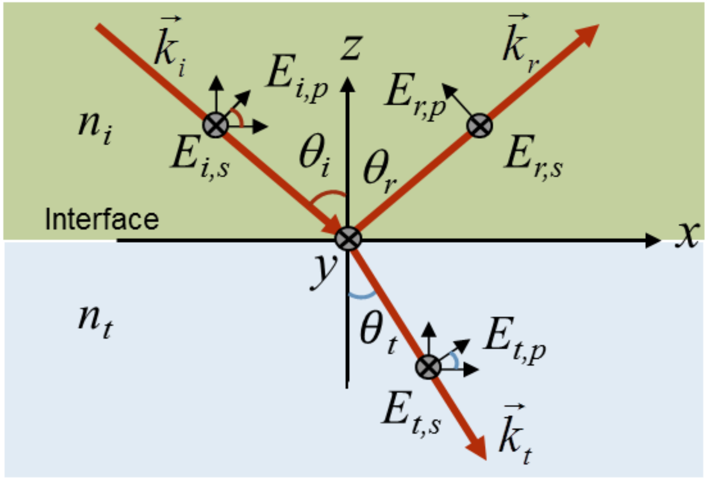
Keywords: Raman scattering; Sum-frequency spectroscopy; Monolayer; Tribology; Total internal reflection

Fresnel coefficients

???

- $K_{p,x} = \frac{2n_i cos\theta_i cos\theta_t}{n_t cos\theta_i + n_i cos\theta_t}$
- $K_{s,y} = \frac{2n_i cos\theta_i}{n_i cos\theta_i + n_t cos\theta_t}$
- $K_{p,z} = \frac{2n_i cos\theta_i sin\theta_t}{n_t cos\theta_i + n_i cos\theta_t}\left(\frac{n_t}{n'}\right)^2$

the refractive indices:
n_i → of the incident media
n_t → of the transmitted media
n' → of the monolayer
Snell's Law: $\sin\vartheta_t = (n_i/n_t)\sin\vartheta_i$.

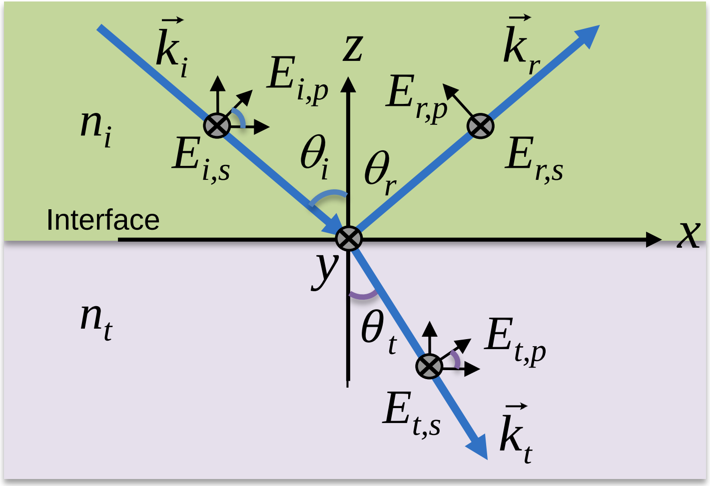


Fresnel coefficients

- $L_{xx} = \frac{E_{t,p}}{E_{i,p}}\frac{cos\theta_t}{cos\theta_i} = t_p \frac{cos\theta_t}{cos\theta_i} = \frac{2n_i cos\theta_i}{n_i cos\theta_t + n_t cos\theta_i}\frac{cos\theta_t}{cos\theta_i} = \frac{2n_i cos\theta_t}{n_i cos\theta_t + n_t cos\theta_i} \Rightarrow$
- $L_{yy} = t_s = \frac{2n_i cos\theta_i}{n_i cos\theta_i + n_t cos\theta_t}$
- $L_{zz} = \frac{E_{t,p}}{E_{i,p}}\frac{sin\theta_t}{sin\theta_i}\cdot\zeta = t_p \frac{sin\theta_t}{sin\theta_i}\cdot\zeta = \frac{2n_i cos\theta_i}{n_i cos\theta_t + n_t cos\theta_i}\frac{sin\theta_t}{sin\theta_i}\cdot\zeta \Rightarrow$

$$\therefore\ n_i\ sin\theta_i = n_t sin\theta_t$$

- $L_{xx} = \frac{2n_i cos\theta_t}{n_i cos\theta_t + n_t cos\theta_i}$
- $L_{yy} = \frac{2n_i cos\theta_i}{n_i cos\theta_i + n_t cos\theta_t}$
- $L_{zz} = \frac{2n_t cos\theta_i sin\theta_t}{n_i cos\theta_t + n_t cos\theta_i}\left(\frac{n_i}{n}\right)^2$



Fresnel coefficients at TIR

$$\therefore\ cos\theta_t = \sqrt{1-\sin^2\theta_t} = \sqrt{1-\left(\frac{n_i}{n_t}\right)^2\sin^2\theta_i} = \frac{\sqrt{n_{ti}^2-\sin^2\theta_i}}{n_{ti}} = \frac{i\sqrt{\sin^2\theta_i-n_{ti}^2}}{n_{ti}}$$

$$sin\theta_t = \left(\frac{n_i}{n_t}\right)\sin\theta_i$$

$$n_{ti} = \frac{n_t}{n_i}$$

$$K_{p,x} = \frac{2n_i cos\theta_t}{n_t cos\theta_i + n_i cos\theta_t} \Rightarrow$$

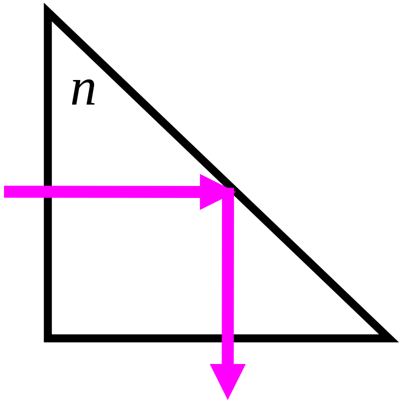
$$Re(K_{p,x}) = \frac{2\,(\sin^2\theta_i-n_{ti}^2)}{n_{ti}^4\cos^2\theta_i+\sin^2\theta_i-n_{ti}^2},\ Im(K_{p,x}) = \frac{2n_{ti}^2 cos\theta_i(\sin^2\theta_i-n_{ti}^2)^{1/2}}{n_{ti}^4\cos^2\theta_i+\sin^2\theta_i-n_{ti}^2}$$

$$K_{s,y} = \frac{2n_i cos\theta_i}{n_i cos\theta_i + n_t cos\theta_t} \Rightarrow$$

$$Re(K_{s,y}) = \frac{2\cos^2\theta_i}{1-n_{ti}^2},\quad Im(K_{s,y}) = \frac{-2cos\theta_i(\sin^2\theta_i-n_{ti}^2)^{1/2}}{1-n_{ti}^2}$$

$$K_{p,z} = \frac{2n_i cos\theta_i}{n_t cos\theta_i + n_i cos\theta_t}\left(\frac{n_t}{n'}\right)^2 \Rightarrow$$

$$Re(K_{p,z}) = \frac{2n_{ti}^2\cos^2\theta_i}{n_{ti}^4\cos^2\theta_i+\sin^2\theta_i-n_{ti}^2},\ Im(K_{p,z}) = \frac{-2cos\theta_i(\sin^2\theta_i-n_{ti}^2)^{1/2}}{n_{ti}^4\cos^2\theta_i+\sin^2\theta_i-n_{ti}^2}$$



$$K_{p,x}=\frac{2n_i cos\theta_t}{n_t cos\theta_i+n_i cos\theta_t}=\frac{2i\sqrt{\sin^2\theta_i-n_{ti}^2}}{n_{ti}^2 cos\theta_i+i\sqrt{\sin^2\theta_i-n_{ti}^2}}=\frac{2i\sqrt{\sin^2\theta_i-n_{ti}^2}\left(n_{ti}^2 cos\theta_i-i\sqrt{\sin^2\theta_i-n_{ti}^2}\right)}{n_{ti}^4 cos^2\theta_i+\sin^2\theta_i-n_{ti}^2}$$

$$\Rightarrow\ Re\left(K_{p,x}\right)=\frac{2\,(\sin^2\theta_i-n_{ti}^2)}{n_{ti}^4\cos^2\theta_i+\sin^2\theta_i-n_{ti}^2},\ \ Im\left(K_{p,x}\right)=\frac{2n_{ti}^2 cos\theta_i\left(\sin^2\theta_i-n_{ti}^2\right)^{1/2}}{n_{ti}^4\cos^2\theta_i+\sin^2\theta_i-n_{ti}^2}$$

$$K_{s,y}=\frac{2n_i cos\theta_i}{n_i cos\theta_i+n_t cos\theta_t}=\frac{2n_i cos\theta_i}{n_i cos\theta_i+n_t\frac{i\sqrt{\sin^2\theta_i-n_{ti}^2}}{n_{ti}}}=\frac{2cos\theta_i}{cos\theta_i+i\sqrt{\sin^2\theta_i-n_{ti}^2}}\times\frac{cos\theta_i-i\sqrt{\sin^2\theta_i-n_{ti}^2}}{cos\theta_i-i\sqrt{\sin^2\theta_i-n_{ti}^2}}=$$

$$=\frac{2cos\theta_i\left(cos\theta_i-i\sqrt{\sin^2\theta_i-n_{ti}^2}\right)}{cos^2\theta_i+\sin^2\theta_i-n_{ti}^2}$$

$$\Rightarrow\ Re\left(K_{s,y}\right)=\frac{2\cos^2\theta_i}{1-n_{ti}^2},\quad Im\left(K_{s,y}\right)=\frac{-2cos\theta_i\left(\sin^2\theta_i-n_{ti}^2\right)^{1/2}}{1-n_{ti}^2}$$

$$K_{p,z}=\frac{2n_i cos\theta_i}{n_t cos\theta_i+n_i cos\theta_t}\left(\frac{n_t}{n'}\right)^2=\left(\frac{n_t}{n'}\right)^2\frac{2n_i cos\theta_i}{n_t cos\theta_i+n_i\frac{i\sqrt{\sin^2\theta_i-n_{ti}^2}}{n_{ti}}}=\left(\frac{n_t}{n'}\right)^2\frac{2cos\theta_i\left(n_{ti}^2 cos\theta_i-i\sqrt{\sin^2\theta_i-n_{ti}^2}\right)}{n_{ti}^4 cos^2\theta_i+\sin^2\theta_i-n_{ti}^2}$$

$$\Rightarrow Re\left(K_{p,z}\right)=\frac{2n_{ti}^2\cos^2\theta_i}{n_{ti}^4\cos^2\theta_i+\sin^2\theta_i-n_{ti}^2},\ \ Im\left(K_{p,z}\right)=\frac{-2cos\theta_i\left(\sin^2\theta_i-n_{ti}^2\right)^{1/2}}{n_{ti}^4\cos^2\theta_i+\sin^2\theta_i-n_{ti}^2}$$

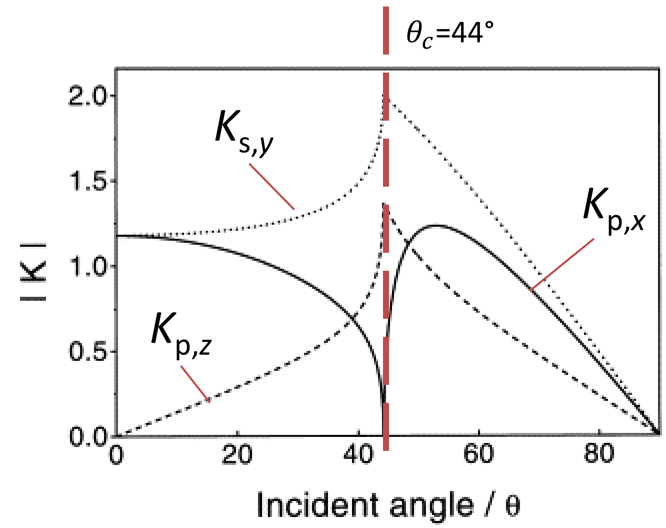
$$L_{s,y}^{r} = 4\pi i \frac{\omega_{sum}}{c} \frac{1}{n_i cos\theta_r + n_t cos\theta_t}$$

θ_r is the angle of emission of the SF light

Above the critical angle, the real and imaginary parts of $L_{s,y}$ are given by:

$$Re(L_{s,y}^{r}) = 4\pi \frac{\omega_{sum}}{c} \frac{\left(\sin^2\theta_r - n_{ti}^2\right)^{1/2}}{n_{ti}(1-n_{ti}^2)}$$

$$Im(L_{s,y}^{r}) = 4\pi \frac{\omega_{sum}}{c} \frac{cos\theta_i}{n_{ti}(1-n_{ti}^2)}$$



$$L_{s,y}^{r} = 4\pi i \frac{\omega_{sum}}{c} \frac{1}{n_i cos\theta_r + n_t cos\theta_t} = 4\pi \frac{\omega_{sum}}{c} \frac{i}{n_i cos\theta_r + n_t cos\theta_t}$$

Snell's law: $sin\,\theta_t = \left(\frac{n_i}{n_t}\right) sin\,\theta_i = \frac{sin\theta_i}{n_{ti}}$

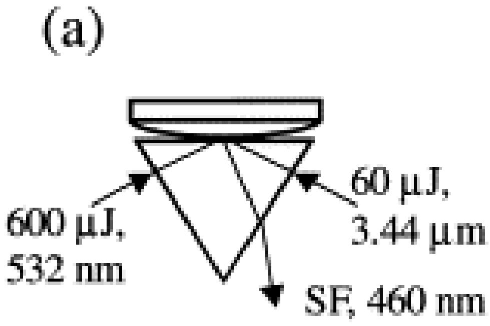
$$L_{s,y}^{r} = 4\pi i \frac{\omega_{sum}}{cn_i}\left[\frac{1}{cos\theta_r + n_{ti}\sqrt{1-\left(\frac{sin\theta_i}{n_{ti}}\right)^2}}\right] = 4\pi \frac{\omega_{sum}}{cn_i} \frac{i}{cos\theta_r + \sqrt{n_{ti}^2 - \sin^2\theta_t}} =$$

$$= 4\pi \frac{\omega_{sum}}{cn_i} \frac{i}{cos\theta_r + \sqrt{n_{ti}^2 - \sin^2\theta_t}} = 4\pi \frac{\omega_{sum}}{cn_i} \frac{i}{cos\theta_r + i\sqrt{\sin^2\theta_t - n_{ti}^2}} = 4\pi \frac{\omega_{sum}}{cn_i} \frac{icos\theta_r + \sqrt{\sin^2\theta_t - n_{ti}^2}}{\cos^2\theta_r + \sin^2\theta_t - n_{ti}^2} =$$

$$= 4\pi \frac{\omega_{sum}}{cn_i} \frac{icos\theta_r + \sqrt{\sin^2\theta_t - n_{ti}^2}}{1 - n_{ti}^2} = 4\pi \frac{\omega_{sum}}{cn_i} \frac{(\sin^2\theta_t - n_{ti}^2)^{1/2}}{1 - n_{ti}^2} + 4\pi \frac{\omega_{sum}}{cn_i} \frac{icos\theta_r}{1 - n_{ti}^2}$$

Since each Fresnel coefficient is at least a factor of 2 larger at θ_c than at normal incidence, it is evident that TIR at the critical angle can lead to very large increases in signal.

The TIR geometry



- plano-convex MgF_2 lens
  - a diameter of 25.4 mm
  - radius of curvature of 59.9 mm
- equilateral CaF_2 prism
  - dimensions of 15×15 mm^2

Result

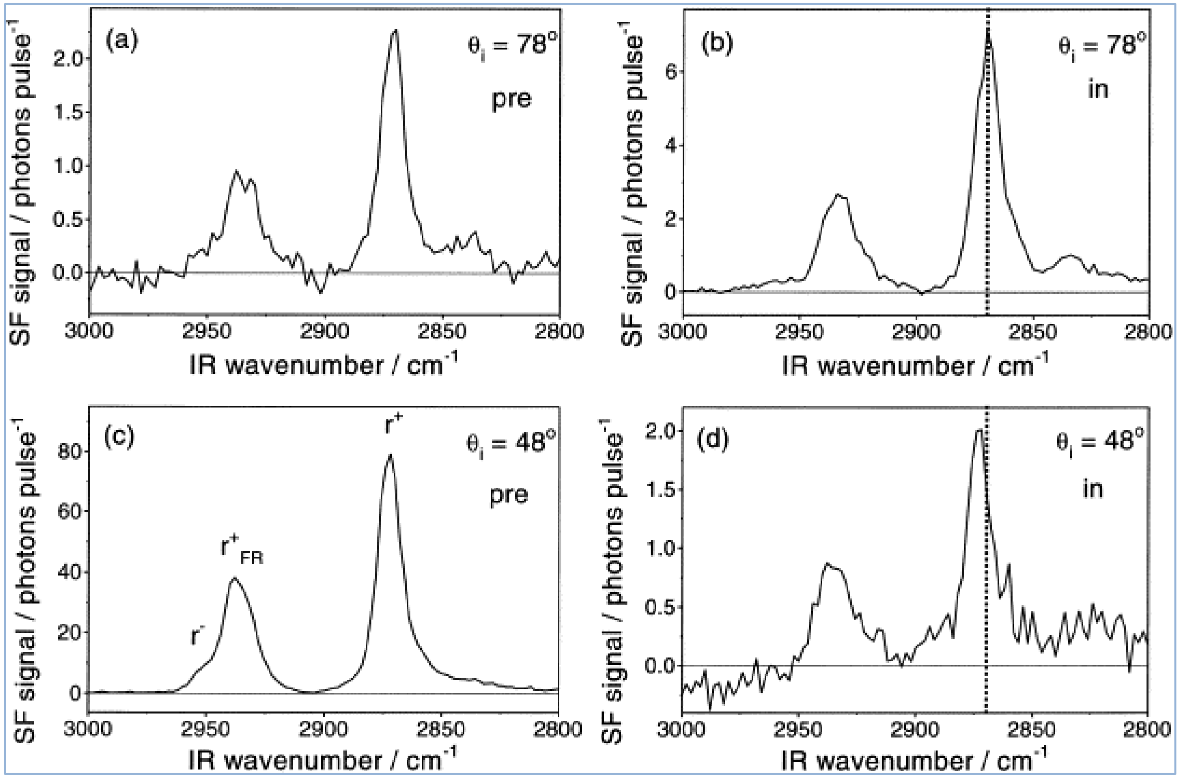


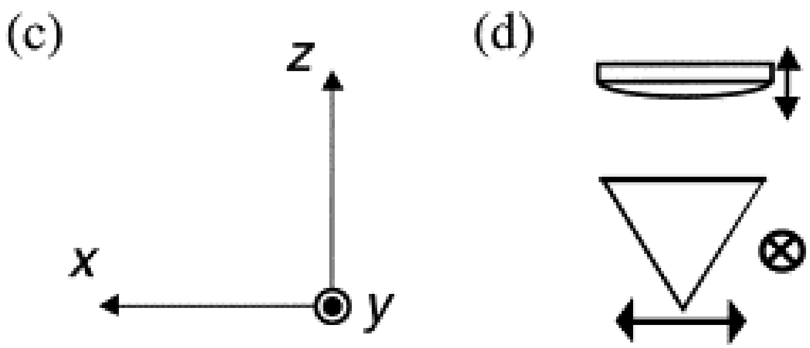
Fig. 6. TIR SF spectra of Zn arachidate at the CaF_2/air and CaF_2/MgF_2 interfaces: (a) ϑ_i=78°, pre-contact, (b) ϑ_i=78°, in-contact, (c) ϑ_i=48°, pre-contact, and (d) ϑ_i=48°, in-contact. All spectra were recorded with an acquisition time of 30 s at each data point except (c), which was recorded with an acquisition time of 5 s at each data point. Laser powers used for spectra (a) and (b) were 300 μJ $pulse^{-1}$ at 532 nm and 40 μJ $pulse^{-1}$ in the IR. Laser powers used for spectra (c) and (d) were 500 μJ $pulse^{-1}$ at 532 nm and 60 μJ $pulse^{-1}$ in the IR.

Peak	78°	48°
	Ratio	Ratio
SFS		
r^+(2874 cm^{-1})	3.45	0.023
r_{FR}^+ (2936 cm^{-1})	2.78	0.032

Summary

- TIR
- Fresnel coefficients at TIR

The TIR geometry used for the SF



$$p_m = \frac{4Ea}{3\pi R} \Rightarrow$$

R – the radius of curvature of the lens

E – the reduced Young's modulus of the two materials

$$\frac{1}{E} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}$$

ν_i – the Poisson ratio

E_i – the Young's modulus of material i

a – the radius of the contact spot