

Overtone spectra of styrene and polystyrene in the visible and near infrared regions

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Abstract. Vibrational overtone spectra of styrene (liquid) and polystyrene (solid), studied by the laser-induced thermal lens (for $\Delta V = 6$) and the conventional near infrared absorption (for $\Delta V = 3-5$) techniques, are reported. For polystyrene, the overtone energy-bond length correlation predicts that the aryl CH bonds are $\sim 0.0005 \text{ \AA}$ longer than that in benzene, while no such conclusions could be drawn on styrene. The sp^3 CH overtones in polystyrene are observed on the low energy side of the aryl CH overtones.

Keywords. Overtone spectroscopy; CH bond lengths; thermal lens technique.

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1. Introduction

Overtone spectroscopy of CH local modes has been used for studying the influence of various substituents on the benzene ring CH bonds (Mizugai and Katayama 1980a; Mizugai *et al* 1981; Gough and Henry 1983, 1984; Nakagaki and Hanazaki 1984; Ahmed and Henry 1986; Ahmed *et al* 1987; Rasheed *et al* 1987). From such studies it has been inferred that electron withdrawing substituents cause shortening and electron donating substituents cause lengthening of the ring CH bonds. In the present paper we report of CH overtone spectra of styrene (liquid) and polystyrene (solid) obtained by the dual beam thermal lens ($\Delta V = 6$) and conventional absorption ($\Delta V = 3-5$) techniques, and compare them with those of benzene. The thermal lens effect in solids and liquids has been studied theoretically and experimentally (Gupta *et al* 1980; Fang and Swofford 1983) and the technique has been widely used for recording the overtone spectra of several organic liquids. However to the authors' knowledge this is the first report of the thermal lens overtone spectrum of a solid as well as that of a polymer.

2. Experimental

High purity (>99%) styrene (Fluka AG, Germany) and cross-linked polystyrene (Polypenco, UK) are used for the present experiments. The dual beam thermal lens

technique (Fang and Swofford 1983) uses a rhodamine 6G CW dye laser (Spectra Physics 380A) pumped by an argon ion laser (Spectra Physics 171-17). The chopped dye laser beam (50-100 mW) creates a pulsating thermal lens in the sample (path lengths—1 cm for styrene and 2 cm for polystyrene). The intensity modulations on a probe He-Ne beam (2 mW) passing through the sample is synchronously detected and normalized for laser power variations. The details of our thermal lens experimentation are given elsewhere (Rasheed *et al* 1987). The near infrared absorption spectra are recorded in a Hitachi 330 UV-VIS-NIR Spectrophotometer at $26 \pm 1^\circ\text{C}$ (path lengths—1 cm for styrene and 2 cm for polystyrene) with air as the reference.

3. Results and discussion

The thermal lens and NIR spectra are shown in figures 1-4. The observed peak positions of the two compounds and their assignments are given in table 1. The experimental uncertainties in peak positions are $\pm 2 \text{ cm}^{-1}$ ($\Delta V = 3$), $\pm 8 \text{ cm}^{-1}$ ($\Delta V = 4$), $\pm 7 \text{ cm}^{-1}$ ($\Delta V = 5$) and $\pm 9 \text{ cm}^{-1}$ ($\Delta V = 6$). A comparison between the spectra of styrene and polystyrene reveals that the main peaks in both the compounds arise from aromatic CH overtones. In addition to aryl CH overtones the NIR spectrum of polystyrene shows the overtone bands of the CH bonds of the side chain.

Styrene molecule contains aromatic and olefinic CH bonds. The overtones of both these types of CH bonds appear generally in the same spectral regions (Wong and Moore 1982; Nakagaki and Hanazaki 1981) and could not be separately identified. In fact the olefinic CH bonds are masked by the more intense aryl CH overtones. A comparison of the aryl CH overtones' peak positions of the two compounds with those of benzene (Patel *et al* 1979) shows that the shifts in peak positions are

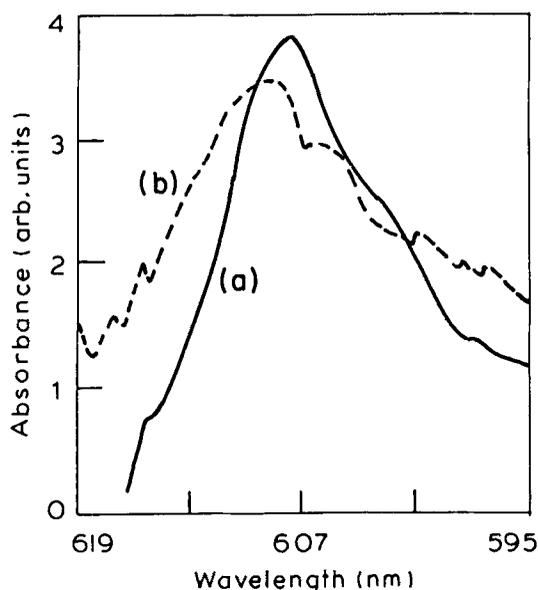


Figure 1. Aryl CH overtone spectrum in the $\Delta V = 6$ region recorded by the dual beam thermal lens technique (a) pure styrene, (b) polystyrene block.

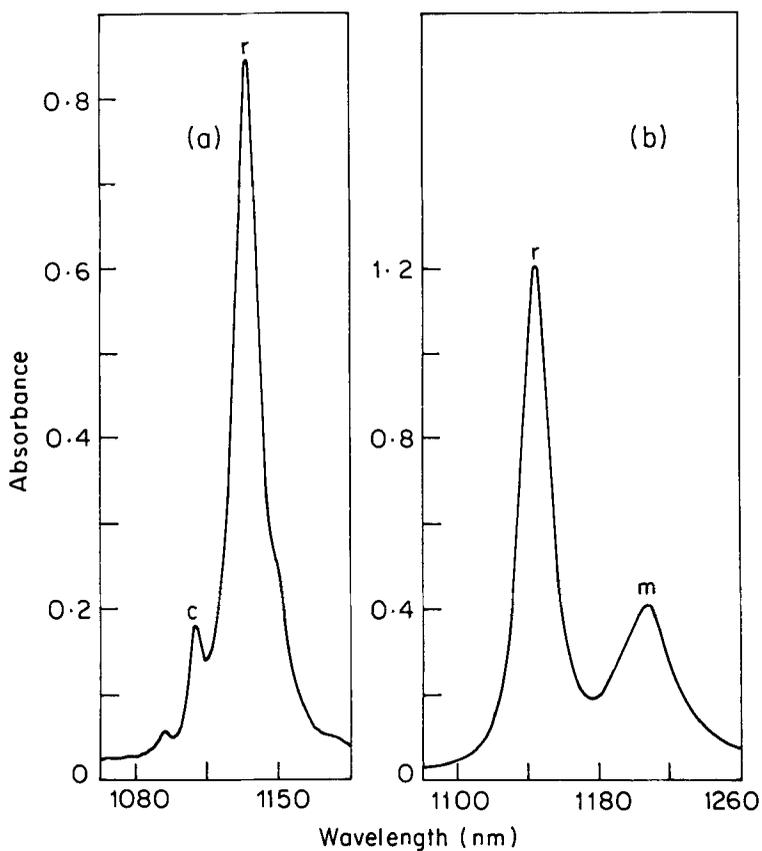


Figure 2. Overtone spectrum of (a) pure styrene and (b) polystyrene block in the $\Delta V = 3$ region (r) aryl CH band (m) methylenic CH band (see text).

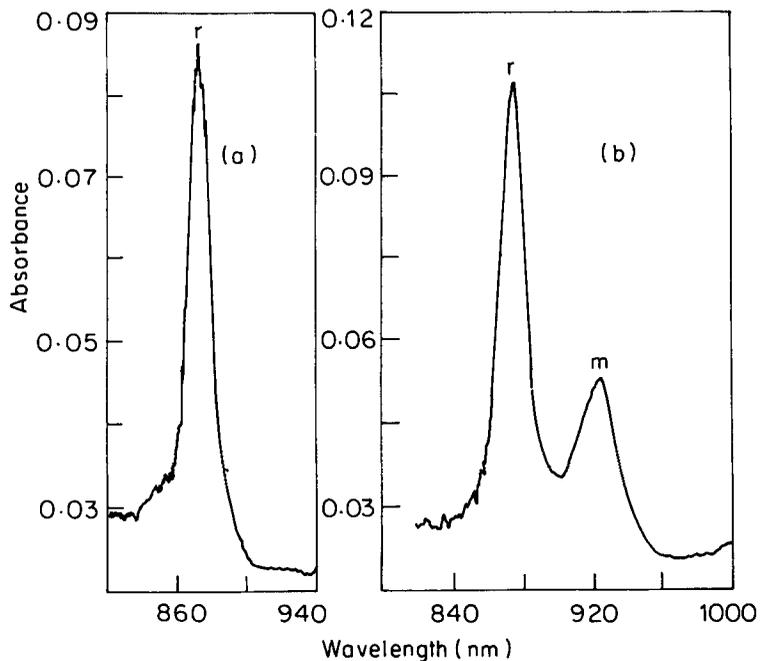


Figure 3. Overtone spectrum of (a) pure styrene and (b) polystyrene block in the $\Delta V = 4$ region (r) aryl CH band (m) methylenic CH band (see text).

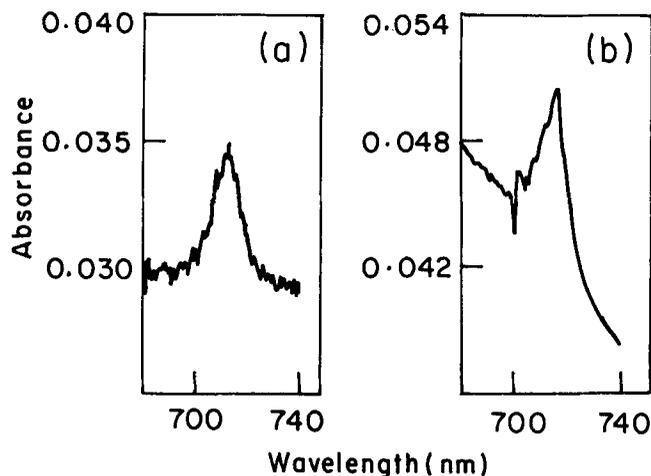


Figure 4. Overtone spectrum of (a) pure styrene and (b) polystyrene block in the $\Delta V = 5$ region. Only aryl CH bands could be detected.

Table 1. Observed overtone energies (cm^{-1}), mechanical frequencies X_1 (cm^{-1}), anharmonicities X_2 (cm^{-1}) and least square correlation coefficients for aryl CH local modes in styrene and polystyrene.

Molecule	$\Delta V = 3$	$\Delta V = 4$	$\Delta V = 5$	$\Delta V = 6$	X_1	X_2	γ
Benzene*	8760	11442	14015	16467	3148.1	-57.6	—
Styrene	8757	11435	14035	16449	3153 ± 9	-58 ± 2	-0.99910
Polystyrene	8741	11429	13986	16430	3149 ± 6	-59 ± 2	-0.99996

*From Patel *et al* 1979

-3 cm^{-1} ($\Delta V = 3$), -7 cm^{-1} ($\Delta V = 4$), $+20 \text{ cm}^{-1}$ ($\Delta V = 5$) and -18 cm^{-1} ($\Delta V = 6$) for styrene and -19 cm^{-1} ($\Delta V = 3$), -13 cm^{-1} ($\Delta V = 4$), -29 cm^{-1} ($\Delta V = 5$) and -37 cm^{-1} ($\Delta V = 6$) for polystyrene. The shifts in the styrene peaks are comparable to the experimental uncertainties in peak positions. Also there is no regularity in the magnitude and sign of the shifts. Thus we are unable to reach a conclusion on the effect of the $-\text{CH}=\text{CH}_2$ group on the aryl CH bonds. The polystyrene spectrum, on the other hand shows increasing negative shifts with respect to benzene towards higher overtones. Even if the shifts are small, the good least square correlation of the Birge-Sponer plot (table 1) and the regularity in the magnitude and sign of the shifts clearly indicates that there is a small but detectable effect on ring CH bonds. There exists an excellent correlation between shift in overtone energy and CH bond length (Wong and Moore 1982; Mizugai and Katayama 1980b). Wong and Moore (1982) have shown that even though absolute bond length determination to a great precision may not be possible, bond length changes as small as 10^{-4} \AA can be detected using overtone absorption spectra. The correlation between aryl CH bond length and the shift in overtone energy from benzene reads

$$\gamma_{\text{CH}}^0 (\text{\AA}) = 1.084 - 8 \times 10^{-5} \frac{\Delta\omega}{V} (\text{cm}^{-1}). \quad (1)$$

This correlation predicts that the aryl CH bonds in polystyrene are $\sim 0.0005 \text{ \AA}$ longer

than that in benzene. Except for $\Delta V = 4$, other overtone data predict the same change in CH bond length. In principle, the ortho, meta and para CH bonds are differently affected by a substituent, the ortho being affected most. However the present condensed phase spectrum gives only the average effect over the three different types of CH bonds.

The transition energies of the overtones obey the well-known Birge-Sponer relation

$$\Delta E_{v \leftarrow 0} = V(A + VB) \quad (2)$$

where the mechanical frequency of the C–H bond is $X_1 = (A - B)$ and the anharmonicity is $X_2 = B$. A plot $\Delta E/V$ versus V gives X_1 and X_2 . Table 1 shows these local mode parameters and the correlations of the least square fit. Since the shifts in the overtone energies from those of benzene are very small, the aryl CH local mode parameters of styrene and polystyrene are very close to those of benzene.

In the $\Delta V = 3$ and 4 regions of the polystyrene spectra, a band appears on the low energy side of the aryl CH bands. The peak positions of these bands are 8295 cm^{-1} and 10811 cm^{-1} respectively. These values are close to the overtone transition energies of secondary CH oscillators of alkanes (Fang and Swofford 1980) and are thus identified to be the overtones of the $sp^3 \text{ CH}_2$ moiety of the side chain. The overtones of the isolated CH bond may also be contributing to these bands. The above bands clearly distinguish the overtone spectrum of polystyrene from that of styrene and hence can be used to probe polymerization as has been established in polymerization of ethylene (Siesler and Moritz 1980).

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References

- Ahmed M K and Henry B R 1986 *J. Phys. Chem.* **90** 1737
- Ahmed M K, Swanton D J and Henry B R 1987 *J. Phys. Chem.* **91** 293
- Fang H L and Swofford R L 1983 *Ultrasensitive laser spectroscopy* (ed.) D S Klinger (New York: Academic Press) p. 175
- Fang H L and Swofford R L 1980 *J. Chem. Phys.* **73** 2607
- Gough K M and Henry B R 1983 *J. Phys. Chem.* **87** 3433
- Gough K M and Henry B R 1984 *J. Phys. Chem.* **88** 1298
- Gupta M C, Hong S D, Gupta A and Moacanin J 1980 *Appl. Phys. Lett.* **37** 505
- Mizugai Y and Katayama M 1980a *J. Am. Chem. Soc.* **102** 6424
- Mizugai Y and Katayama M 1980b *Chem. Phys. Lett.* **73** 240
- Mizugai Y, Katayama M and Nakagawa N 1981 *J. Am. Chem. Soc.* **103** 5061
- Nakagaki R and Hanazaki I 1981 *Chem. Phys. Lett.* **83** 512
- Nakagaki R and Hanazaki I 1984 *Spectrochem. Acta* **A40** 57
- Patel C K N, Tam A C and Kerl R J 1979 *J. Chem. Phys.* **71** 1470
- Rasheed T M A, Moosad K P B, Nampoori V P N and Sathianandan K 1987 *J. Phys. Chem.* **91** 4228
- Siesler H W and Moritz K H 1980 *Infrared and Raman spectroscopy of polymers* (New York: Merceel Dekker Inc.) p. 331
- Wong J S and Moore C B 1982 *J. Chem. Phys.* **77** 603