

## Short Communication

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### Fluorescence excitation spectroscopy of styrene vapour: further evidence for dual emission

K. P. GHIGGINO, K. HARA, K. SALISBURY and D. PHILLIPS

*Department of Chemistry, The University, Southampton SO9 5NH, Hants. (Gt. Britain)*

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The role of rotation about essentially double bonds in the excited states of aryl-substituted olefins is a subject which has attracted much attention recently [1 - 7]. Studies in this laboratory have centred on an examination of the photochemistry and photophysics of styrenes [3 - 7]. Time resolved spectroscopy using a cavity-dumped frequency-doubled argon ion laser (excitation wavelength 257.25 nm) showed that styrene and its derivatives with structures allowing twisting about the olefinic double bond have a dual fluorescence [4 - 7]. Only a single fluorescence component is present for phenyl norbornene in which any rotation about the double bond is structurally impossible [5, 6]. For those derivatives exhibiting a dual fluorescence, the component of emission with a long lifetime was observed to be blue shifted with respect to the shorter lifetime component [4 - 6]. The short lived fluorescence was attributed to emission occurring mainly from high vibrational levels of the first excited singlet state  $^1L_b$ , while it was suggested that long lived fluorescence was due to emission from a "twisted" excited state attained by rotation about the olefinic double bond [4 - 6].

It was previously shown [4, 7] that changing the excitation wavelength from the  $^1L_b$  to the  $^1L_a$  bands of styrene resulted in the appearance of non-exponential fluorescence decay kinetics owing to the appearance of the dual emission, and in this paper further evidence for dual fluorescence, obtained from an examination of the excitation spectra of styrene vapour, is presented.

A 150 W xenon lamp, a double grating monochromator (Hilger and Watts D330/331) and a Hilger and Watts D330 single grating monochromator were used as the excitation source and excitation and observation monochromators respectively. 45° front surface observation of fluorescence was employed using a sample cell supplied with a Rayleigh horn to prevent excitation scatter. The single-photon counting light detection system has been described elsewhere [6]. Correction factors for the wavelength dependence of excitation intensity were obtained using sodium salicylate [8, 9] (deposited from a methanol solution sprayed onto a quartz optical flat in

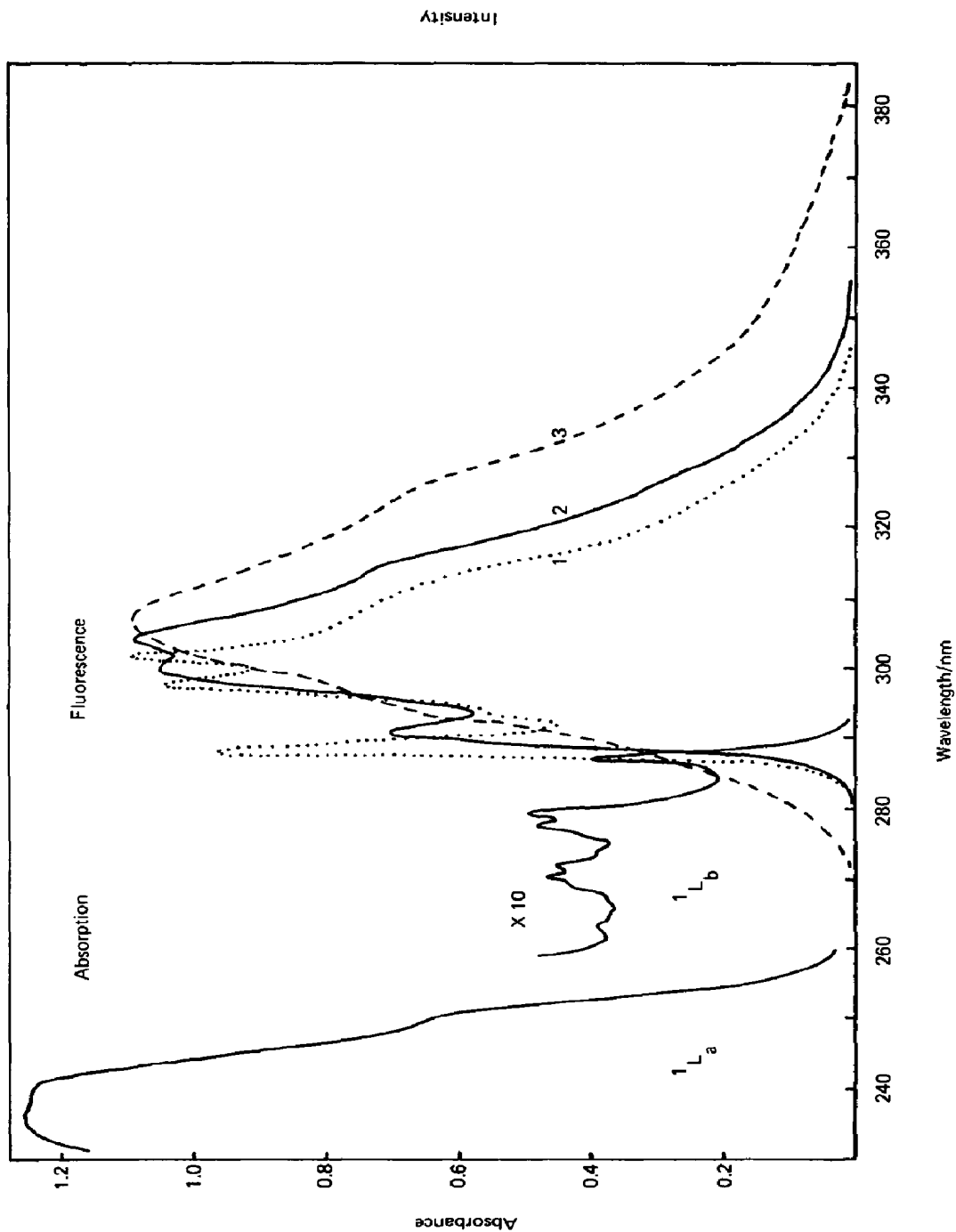


Fig. 1. Absorption spectrum of styrene in the gas phase at 0.2 Torr and the normalized fluorescence spectra (0.5 Torr) for different excitation wavelengths: curve 1, 287 nm; curve 2, 282 nm; curve 3, 257 nm.

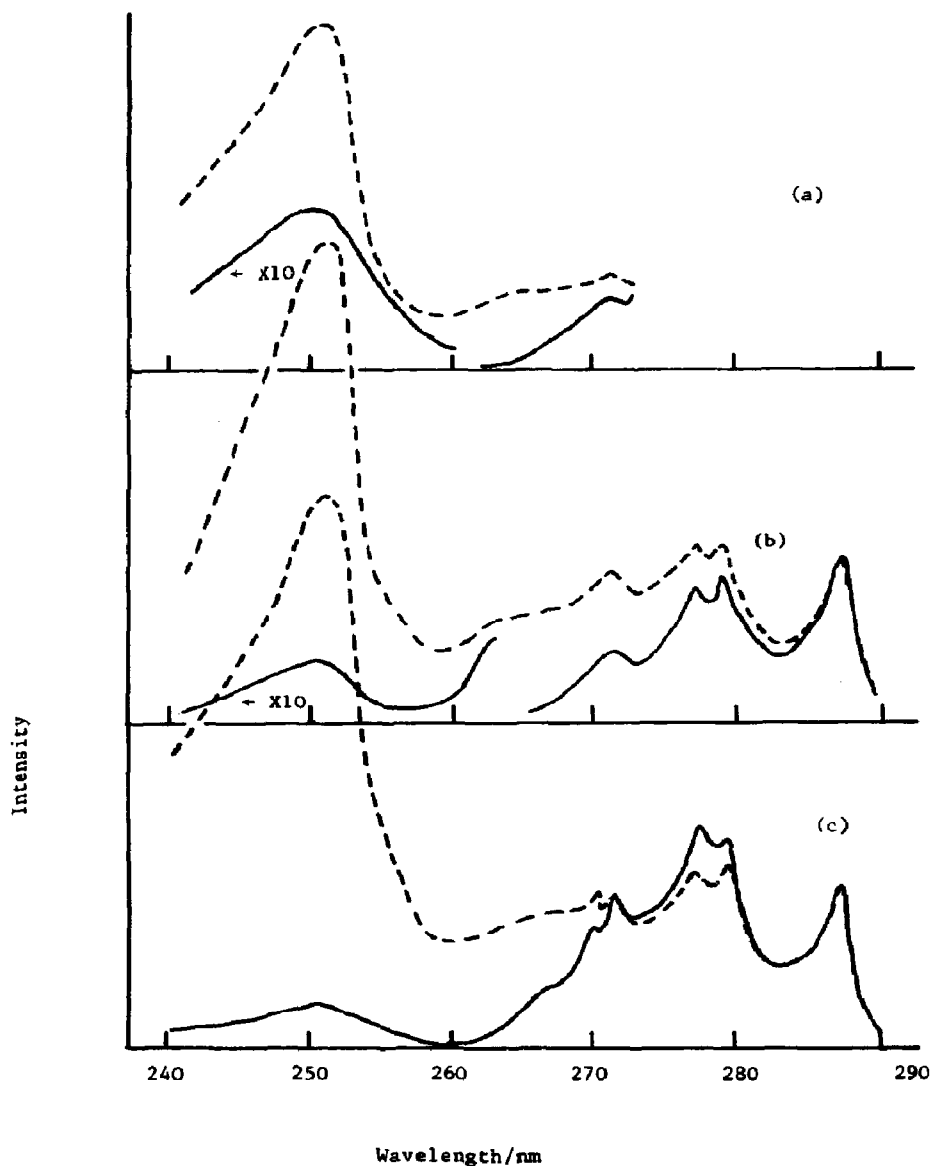


Fig. 2. Corrected excitation spectra of styrene (0.5 Torr) with (broken curve) and without (solid curve) 700 Torr butane for different emission wavelengths: (a) 282 nm; (b) 303 nm; (c) 370 nm. The excitation spectra observed at 282 nm are shown in the wavelength region where no light scattering effect is observed.

place of the cell window). Styrene was purified by preparative gas-liquid chromatography and butane, purchased from BDH Ltd., was used without further purification. For the present work a spectral resolution of 1 nm was used on the monochromators.

The absorption and fluorescence spectrum of low pressure styrene vapour is shown in Fig. 1. At the pressure of 0.5 Torr used the fluorescence from styrene molecules can be considered to be in the collision-free region

[7]. It should be noted that the fluorescence spectrum obtained with excitation at 287 nm (0-0 band of absorption) is structured, but with excitation into shorter wavelengths the fluorescence spectrum becomes broader and red shifted. Such spectral behaviour is well known in gas phase fluorescence [10] but attention is also drawn to a short wavelength tail which appears near 280 nm in the fluorescence when 257 nm excitation is used.

In order to investigate further the different radiative processes occurring on excitation at the different wavelengths, the excitation spectra depicted in Fig. 2 were obtained. Since it has been postulated [4 - 6] that the blue-shifted emission is emission from a twisted excited state populated via  $S_2$ , it would be expected that  $S_2$  excitation would result in relatively more emission appearing at 282 nm than would  $S_1$  excitation compared with observation at 303 nm. This is clearly the case as Figs. 2(a) and 2(b) indicate. The higher emission intensity at 370 nm (red-shifted emission) obtained on excitation to  $S_2$  and high vibrational levels of  $S_1$  (compare Figs. 2(c) and 2(b)) may be the result of radiative relaxation from high vibrational levels of  $S_1$ .

Turning to the effects of added vibrational quencher on the excitation spectra and looking only at the contributions from  $S_2$  excitation, the following points can be made.

(i) An overall increase in intensity occurs in each case (Figs. 2(a) - 2(c)). This is almost certainly a consequence of the quenching of some non-radiative processes [11 - 13] (fragmentation etc.) which occur on excitation into  $S_2$  [7].

(ii) The magnitude of the effect of the vibrational quencher seen in the case of 370 and 282 nm emission is small compared with the effect on 303 nm emission. A likely explanation for this observation is that relaxation to low levels of  $S_1$ , from which the blue-shifted and red-shifted emissions are weak, predominates in the presence of a foreign gas whatever the initial level excited. Thus the evidence obtained from the fluorescence excitation spectra for the appearance of the blue-shifted and red-shifted emissions upon excitation into the  $S_2$  band of styrene vapour is consistent with our previous time resolved studies [4 - 7].

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