

Preliminary Note

Nanosecond time resolved emission spectroscopy of isolated molecules: styrenes

K. P. GHIGGINO, D. PHILLIPS, K. SALISBURY and M. D. SWORDS

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

(Received March 10, 1977)

An apparatus for recording time resolved emission spectra on a nanosecond time scale is described and further results on styrenes excited in the 1L_a band in the isolated molecule limit are reported.

The dual fluorescence observed can be explained on the basis of a short lived component arising from high vibrational levels of the S_1 (1L_b) state produced on internal conversion from S_2 and a long lived component from a state which arises through twisting of the 1L_a state about the olefinic bond. If such twisting motion is suppressed, as in the caged styrene phenylnorbornene, the long lived component of fluorescence disappears, in support of the hypothesis.

Introduction

The recording of simultaneously time and spectrally resolved emission curves affords considerably more information than is obtained from either CW pumped spectrally resolved emission or time resolved total emission alone can give. In the case of molecules "isolated" in the low pressure limit, the appearance of different spectral distributions of photons observed coincident with or close to the pump pulse from those observed at a later time provides unequivocal evidence of two (or more) emitting states, and such evidence can be invaluable for the detailed understanding of the photophysics of such species. In an earlier brief report an apparatus was described capable of such time and spectral resolution on a nanosecond time scale [1], and preliminary results on *trans*-1-phenylpropane were reported [2]. We describe the apparatus in more detail here and give further results on the parent compound styrene and on related molecules.

Experimental

A block diagram of the apparatus is shown in Fig. 1. The system uses conventional Ortec single-photon counting detection equipment [3], and a Spectraphysics Model 164 argon ion laser fitted with the Model 366 mode-

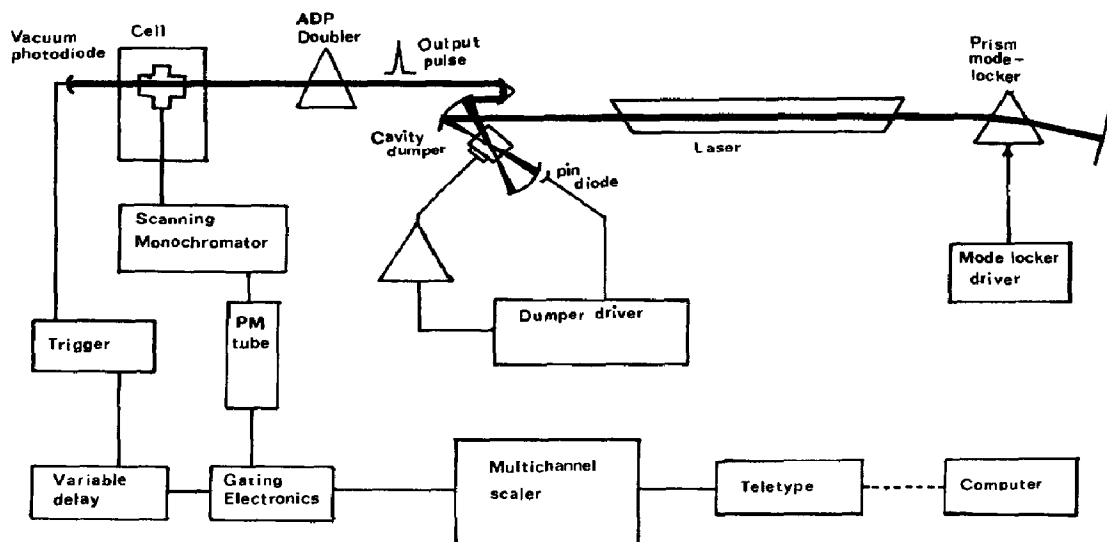


Fig. 1. Block diagrams of time resolved spectral apparatus.

locker cavity dumper together with a Coherent Radiation Model 144 frequency doubler provides the excitation pulses at 257.25 nm. The system may also be used in the visible region at 488 nm or 514.5 nm by excluding the frequency doubler, and is capable of providing tunable visible pulses if used to pump synchronously a dye laser. Pulse shapes operating cavity dumped (Figs. 2(a), 2(b)) and mode locked (Fig. 2(C)) are shown. The maximum repetition rate of dumped pulses is 5 MHz. It will be noted that frequency doubling shortens the pulse duration by a factor of $\sqrt{2}$. In the present experiments the doubled output at 257.25 nm only was used and, because of some instability in operating mode locked for long periods of time, the non-mode-locked cavity dumped pulses were employed. These had a width at half height of 7 ns and a decay of some 3 ns. Pulse profiles were exactly reproducible over many hours of operation, as was the repetition rate and the time between pulses. This is particularly advantageous for single-photon counting detection, which in normal operation utilizes an excitation pulse to initiate a counting sequence in the form of a voltage ramp in a time-to-amplitude converter (TAC), the sequence terminating at the end of a fixed period of time or upon observation of a single emitted photon. The dead time in the TAC/MCA combination is such that in this mode of operation any attempt to utilize start-pulse repetition rates in excess of 200 kHz causes instrumental paralysis, and thus the full capacity of the 5 MHz rate of the laser is not realized. The problem can be overcome in the present case, however, by inverting the normal arrangement in the TAC, with emitted photons acting as start pulses and the next laser pulse acting as the stop pulse. Because of the reproducibility of the interval between laser pulses it is valid to count back one pulse to obtain the desired time elapsing between excitation and emission, and thus every emitted photon can be utilized below a

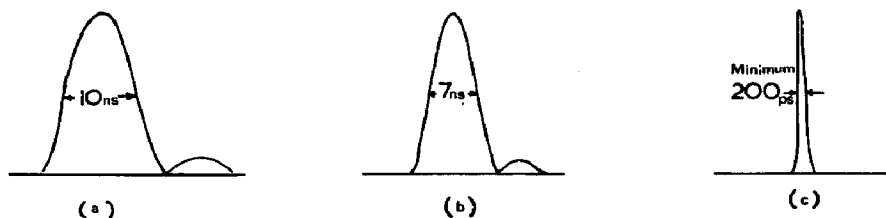


Fig. 2. Pulse profiles from an argon ion laser: (a) cavity dumped only; (b) cavity dumped, frequency doubled; (c) mode locked.

5% duty factor to prevent photon pile-up. This method may not be used if the interval between excitation pulses is variable, as in spark discharge lamps. For the measurement of decay times of total fluorescence data acquisition times are extremely rapid (of the order of minutes) with this method compared with other excitation methods.

The object of this experiment is to select photons arriving within a gate of finite temporal dimensions, which can be moved across the decay profile of total emission (Fig. 3(a)), and spectrally to disperse these. Using the TAC in the manner described above upper and lower level discriminators (Fig. 3(b)) may be used to provide such a gate, with gate width Δt variable from 100 ps to 80 μ s and time delay from 0 s to ∞ . For conventional use of the TAC with excitation pulses providing the start pulse, limitation of operating frequency to 200 kHz is prohibitive, and a home-built gated comparator has been used to replace the TAC.

Spectral dispersion was obtained with a Rank Precision Monospek 1000 monochromator with reciprocal dispersion of 8 $\text{\AA} \text{ mm}^{-1}$. In time resolved experiments slit widths were used to give a spectral resolution of 1 \AA .

Results and discussion

Preliminary results using a conventional discharge lamp for excitation of styrene, *trans*-1-phenylpropene and indene at low pressures (0.1 Torr) in the vapour phase showed that for excitation into the first excited singlet state 1L_b total fluorescence decay times were single exponential with lifetimes decreasing as excitation energy increased [2]. Upon excitation to the S_2 (1L_a) levels, however, non-exponential decay (or at least two components of fluorescence) was observed, and for *trans*-1-phenylpropene the presence of two emitting states was demonstrated using the time resolved emission spectroscopy technique.

Similar results have now been obtained for the parent compound styrene, but with much improved spectral resolution (Fig. 4(a)). It is clear that the early gated spectrum, which shows considerable vibrational structure, decays on a nanosecond time scale into a structureless spectrum, which, rather unusually, has a maximum that is blue shifted with respect to that of the early gated spectrum. This point is reinforced by a consideration of fluorescence decay times measured by selecting photons within a narrow wavelength range, as shown in Fig. 5(a). It is clear that, as the emitted wavelength under observation is progressively shortened, there is an increasing contribution to

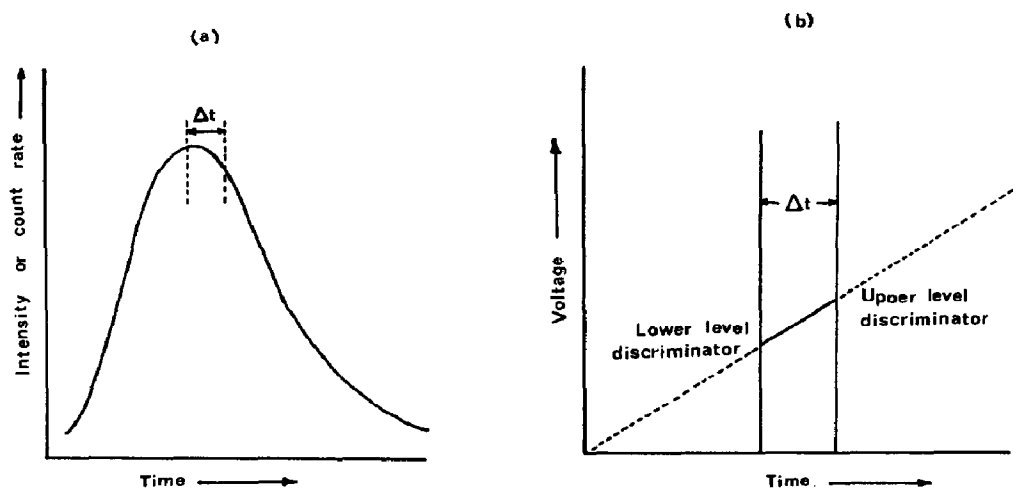


Fig. 3. (a) Gating for time resolved spectroscopy. (b) Arrangement using upper and lower level discriminators and time-to-amplitude converter (TAC).

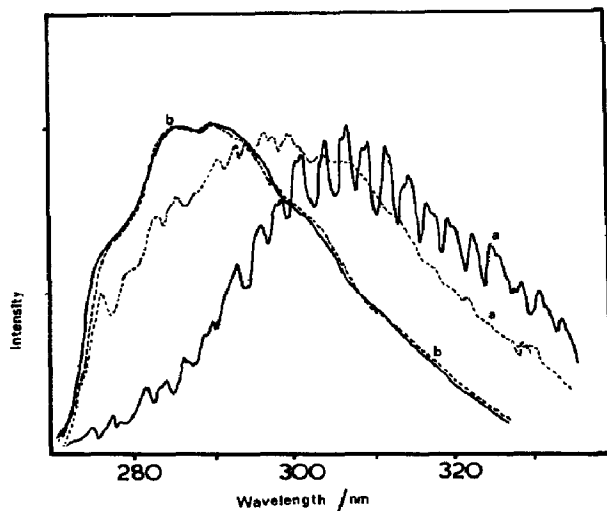


Fig. 4. Time resolved fluorescence spectra of (a) styrene, (b) phenylnorbornene: — early gated spectra obtained with gate positioned on leading edge of pump pulse; - - - - late gated spectra obtained with gate delayed 35 ns from pump pulse.

the decay curve of a long lived component of fluorescence. Decay times of these two components of fluorescence for styrene and related compounds are shown in Table 1 for laser excitation at 257.25 nm.

The short lived (red) component of fluorescence can be identified with emission from high vibrational levels of the S_1 state produced upon internal conversion from the initially populated S_2 state and to a small extent directly by absorption. Thus projection of decay time data obtained conventionally as a function of excitation wavelength for S_1 excitation to excess energies equivalent to the laser excitation wavelength used here gives results in essential agreement with the short lived component of fluorescence measured. Since the early gated spectrum shown in Fig. 4(a) thus corresponds to emission from

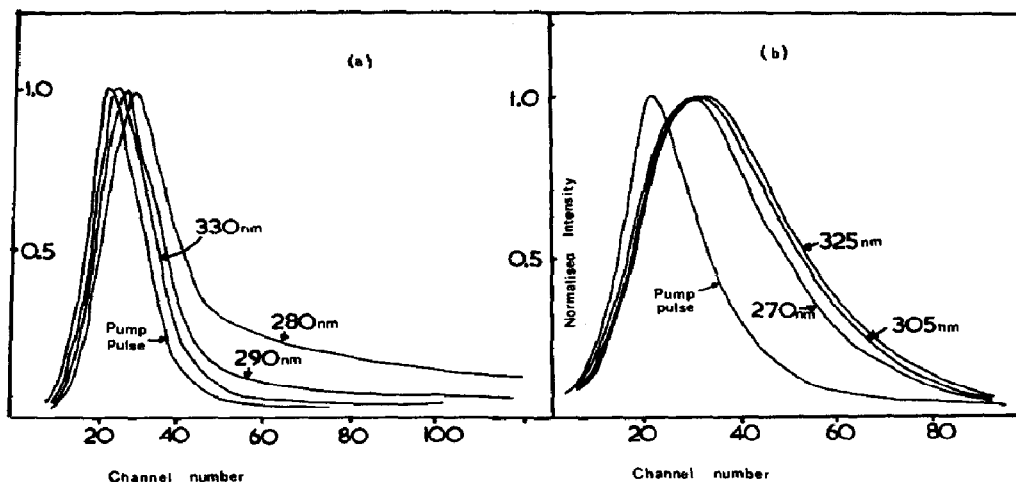


Fig. 5. Fluorescence decay profiles as function of emission wavelength monitored: (a) styrene, (b) phenylnorbornene. Emission wavelength monitored is shown in the diagram.

TABLE 1

Dual fluorescence decay times for isolated styrenes excited at 257.25 nm^a

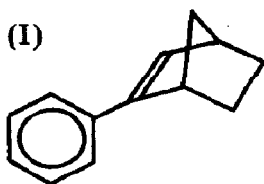
Compound	$\tau(\text{short})^b$ (ns)	$\tau(\text{long})^b$ (ns)
Styrene	1.5 (330)	50 (280)
<i>trans</i> -1-Phenylpropene	2.0 (330)	45 (270)
Phenylnorbornene (I)	4.5 (325)	—

^aStyrene pressure 0.1 Torr.

^bWavelength (in nm) at which decay monitored shown in parentheses.

high vibrational levels of the S_1 state to correspondingly high levels of the ground state detailed analysis of the spectrum and vibrational assignment is difficult because of the effect of anharmonicities, the more so since band assignments have not been published for these compounds.

The excited states of simple olefins minimize potential energy by twisting about the olefinic double bond, and it has been argued that the long lived component of emission in simple styrenes corresponds to emission from a state which has a shallow potential minimum at some small angular displacement along this normal coordinate [2]. If such motion were totally restricted, the long lived component of fluorescence observed in styrene would not be expected to be observed. Support for the above hypothesis is thus obtained from the time resolved spectra of phenylnorbornene



in which rotation about the olefinic double bond is completely frozen out. As seen in Fig. 4(b), early gated and late gated spectra are identical, and this point is amplified in Fig. 5(b), from which it can be seen that fluorescence decay times are constant across the total fluorescence spectrum.

Nanosecond time resolved emission spectroscopy thus supports the hypothesis concerning the nature of dual fluorescence in styrene vapour. Further support for these ideas is being provided by extensive work using other techniques, and a full report of these experiments will be forthcoming.

Acknowledgments

We are extremely grateful to the Science Research Council for financial support.

- 1 M. D. Swords and D. Phillips, *Chem. Phys. Lett.*, 43 (1976) 228.
- 2 R. P. Steer, M. D. Swords, P. M. Crosby, D. Phillips and K. Salisbury, *Chem. Phys. Lett.*, 43 (1976) 461.
- 3 P. A. Hackett and D. Phillips, *J. Phys. Chem.*, 78 (1974) 671.