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# THE DETERMINATION OF MOLAR ABSORPTION COEFFICIENTS OF METASTABLE STATES

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## Summary

A computer controlled spectrophotometer is described which allows spectroscopic and kinetic measurements on a sample which is simultaneously irradiated with strong monochromatic light. Data gathering routines and methods to calculate the molar absorption coefficients of metastable species are discussed. The triplet–triplet absorption spectrum of fluorenacene is reported.

## Introduction

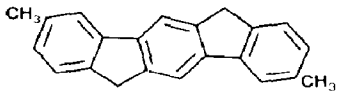
The absorption spectra of metastable states are commonly studied by observing the response of the system with respect to pulsed [1 - 3], modulated [4 - 6], or stationary state [7 - 9] excitation. These methods and their applications to the identification of triplet–triplet transitions of organic molecules have been recently discussed by Labhart and Heinzelmann [10]. In most cases only partial conversion to the metastable state can be achieved and the spectroscopic measurement has to be done on a mixture of ground and metastable state molecules. The determination of the molar absorption coefficient of the pure metastable state will therefore depend on a determination of its concentration and involve a correction for ground state absorption.

In the first part of this paper the design of a computer controlled spectrophotometer is outlined. Kinetic and spectroscopic measurements can be performed while the sample is irradiated with monochromatic light. An irradiation unit consisting of a high-pressure xenon lamp, a high intensity monochromator, and a light shutter have been added to an existing spectrophotometer [11, 12]. Absorption spectra of the ground state and the spectra needed to determine the molar absorption coefficients of the metastable states can be measured under identical conditions.

A main advantage of a computer controlled instrument consists in the great flexibility introduced by software control. For the present purpose two new measurement routines had to be implemented into the existing

software [11] package. The first one (SEUV) is used to measure the change in absorbance which is observed when a sample reaches a photostationary state. It involves two wavelength scans with and without illumination. The second procedure (MEUV) being the more sensitive one combines elements of a slow modulation and a stationary state technique and is especially suited for metastable species having a lifetime in the range from 10 to 1000 ms. It involves the successive determination of the change of absorbance at fixed wavelength settings.

In the second part the treatment of experimental data on a large computer is discussed. Three methods are used to estimate the concentration of the metastable species. The first one involves a calculation of the ratio of the observed change in absorbance and the ground state absorbance. It can be used to obtain a lower limit for the fractional population of the metastable state. In the second method molar absorbance curves for the metastable species are calculated assuming different stationary state concentrations. The disappearance of structure in regions of sharp ground state absorption bands indicates the correct photostationary concentration [13]. The third method depends on an analysis of the kinetic behaviour of the illuminated system [14, 15]. It can also be used if just a limited spectral region which does not overlap with ground state absorption is studied. For sufficient accuracy it requires, however, that an appreciable fractional population of the metastable state can be achieved under photostationary conditions. The absorption coefficients of the triplet states of fluorenacene (I) [16] are reported in this paper. Applications to the study of photochromic systems will be given elsewhere [17].




I

*Trans*-fluorenacene

## The spectrophotometer

*Optical system*

A schematic drawing of the optical system is shown in Fig. 1. The probing light passes through a monochromator ($MO_1$). Spherical mirrors ($MR_1$ - $MR_4$) form a real image of the output slit of the monochromator ($MO_1$) onto the input slit of a second monochromator ($MO_2$). A mirror ($BS_1$) splits the beam into two parts of equal intensity while $BS_2$ recombines the light beams. A mechanical chopper (CH) modulates the sample beam at a frequency of 3.6 kHz and the reference beam at 2.8 kHz.

Excitation of the sample is achieved by a 1600 W xenon high pressure lamp (EL). A fused quartz lens ($L_1$) focuses the light on the entrance slit of a high energy grating monochromator ($MO_3$ blazed at 250 nm). A water filter (WF) of 20 cm length absorbs the strong infra-red radiation and prevents

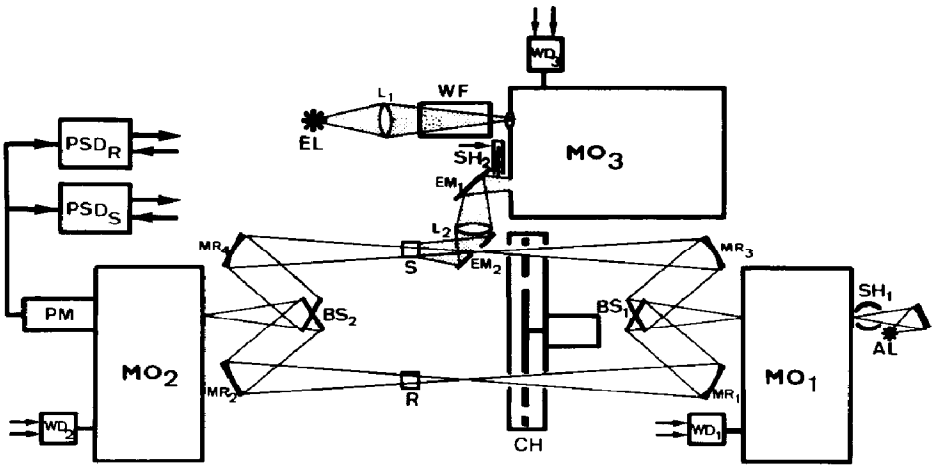



Fig. 1. Optical system of the spectrophotometer.

damage to the grating. The field lens at the entrance slit forms an image of the lens ($L_1$) on the collimating mirror of $MO_3$. The output slit is imaged onto the sample cell (S) using a lens ($L_2$) and plane mirrors ($EM_1$ and $EM_2$). The latter has a small rectangular aperture through which the analyzing light passes without attenuation. An electromagnetic shutter ($SH_2$) has an opening time of 5 ms and allows a modulation of the excitation light at a maximum rate of 10 Hz.

Excitation along the axis of the spectroscopic beam offers several advantages. The same cell types as in ordinary absorption spectroscopy can be used. More important the exciting light produces a concentration gradient of the transient species in direction of the investigation beam only. It can easily be shown that such a distribution does not affect the validity of the Lambert–Beer law and that the concentration determined from an absorption measurement corresponds exactly to the mean concentration of the transient species in the cell. No excitation light reaches the entrance slit of $MO_2$ directly; the rectangular opening in $EM_2$ is exactly in the central focal plane of the sample beam and it is imaged onto the entrance slit of $MO_2$. Residual stray light which is due to scattering in the probe is not modulated and its contribution to the signal is eliminated by the lock-in amplifier.

A curve of the light intensity as a function of wavelength which can be used to excite the sample is given in Fig. 2. The spectral bandwidth of the monochromator $MO_3$ was 14 nm and an area of about 2 $cm^2$ was illuminated at the position of the sample cell. A radiant flux meter (Hewlett–Packard, model 8330 A) was used to measure the light intensity. The maximum occurs near 22,500 $cm^{-1}$ at 28 $mW/cm^2$. This corresponds approximately to $10^{-7}$ Einstein $cm^{-2}$ $s^{-1}$.

The sample cell used for triplet–triplet absorption measurements has a path length of 1 or 2 cm and consists of a copper block with indium sealed quartz windows. It is located in a cryostat. Evaporation of liquid nitrogen in

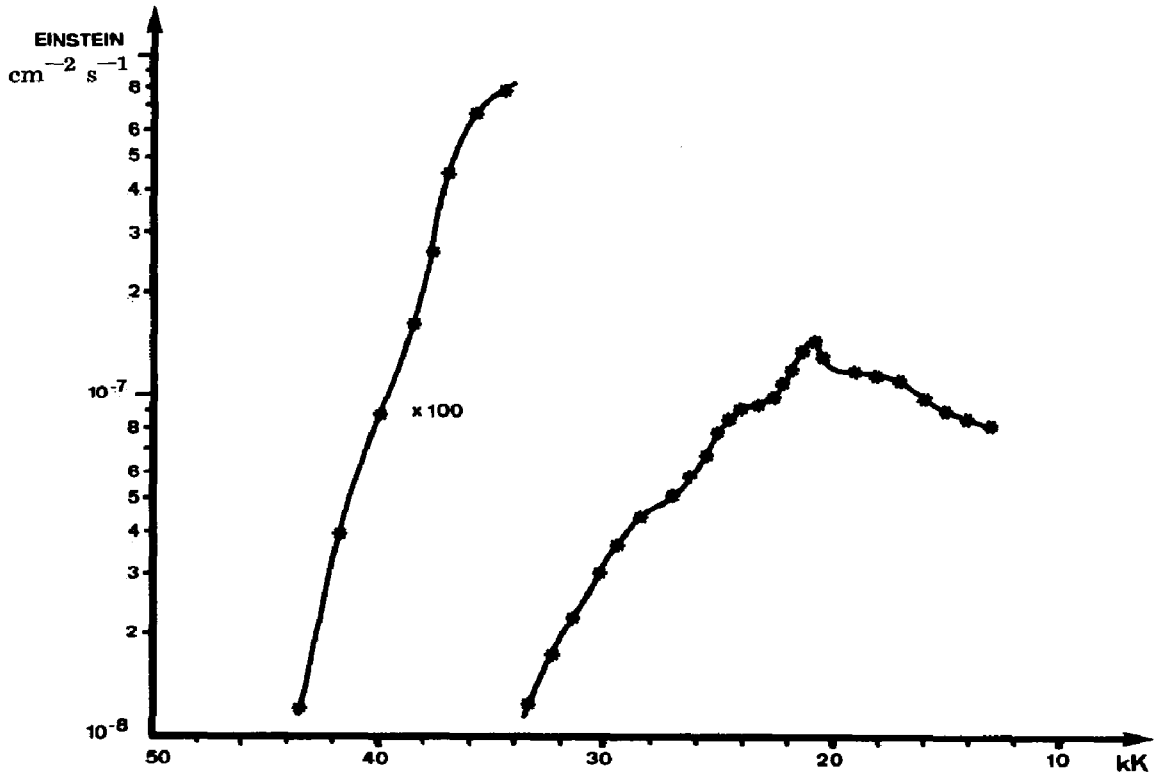



Fig. 2. Intensity of the excitation light at the sample position. Spectral bandwidth 14 nm.

a heat exchanger combined with a P-I-D controlled heating element allows temperature regulation from 70 K to 300 K with a stability of ± 1 °C.

*Electronic system*

A PDP-8/I small computer (Digital Equipment Corporation DEC) with 8 K memory is used to control the spectrophotometer and to store data. The interfacing and the electronic system using two phase sensitive detectors ($PSD_R$ and $PSD_S$) locked to the sample and the reference channel frequencies has been fully described in ref. [11]. For the present purposes a step-motor ($WD_3$) (Slowsyn SS 50) which sets the wavelength of the excitation monochromator and an electromagnetic light shutter ($SH_2$) (Uniblitz, model 325B, Vincent Associate) had additionally to be interfaced to the computer.

## Data recording

The programs for the PDP-8/I small computer have been written in the assembly language PAL8 and occupy the lower half of the 8 K memory. The upper half is used for data storage. The software developed earlier [11] could be fully used and only two relatively small subroutines which handle the newly added hardware and two subroutines which control the sequence of the events in the two new methods of data collection: SEUV (steady state

excitation with u.v. light) and MEUV (modulated excitation with u.v. light) had to be added. Experimental results obtained in various stages of development of this system have been reported by Wild *et al.* [18], Kreibich *et al.* [19] and Wild [20].

Let us consider a completely reversible photoreaction [21]. Irradiation of A forms the photoproduct B which may completely return to the educt A:

$$A \xrightarrow[\omega\phi]{h\nu} B \qquad \begin{array}{l}\text{light induced generation of B}\\ (\omega = \text{transition probability}, \phi = \text{light intensity})\end{array} \tag{1}$$

$$B \xrightarrow[k]{\Delta} A \qquad \begin{array}{l}\text{thermal back reaction}\\ (k = \text{rate constant})\end{array} \tag{2}$$

The absorbance of the samples before irradiation is given by:

$$D(\tilde{\nu}) = A_0 \cdot \epsilon_A(\tilde{\nu}) \cdot l = -\log I_S/I_R \tag{3}$$

where $A_0$ represents the concentration of the educt, $\epsilon_A(\tilde{\nu})$ its molar absorption coefficient and $l$ the cell length. $D(\tilde{\nu})$ is obtained from a transmittance measurement on the double beam spectrophotometer. $I_S$ and $I_R$ represent the light intensities of the spectroscopic light beams after the sample and reference cells. If the excitation light is switched on the concentration of the metastable species will rise from zero to the steady state value $B_\infty = xA_0$. Simultaneously the concentration of A will decrease from $A_0$ to $A_0 - xA_0$, where $x$ stands for the fractional population of the metastable state. The absorbance $D^*(\tilde{\nu})$ in the photostationary state is given by:

$$D^*(\tilde{\nu}) = (A_0 - xA_0) \cdot \epsilon_A(\tilde{\nu}) \cdot l + xA_0 \cdot \epsilon_B(\tilde{\nu}) \cdot l = -\log I_S^*/I_R^* \tag{4}$$

and the difference $\Delta D(\tilde{\nu})$ is obtained from:

$$\begin{aligned}\Delta D(\tilde{\nu}) &= D^*(\tilde{\nu}) - D(\tilde{\nu}) = xA_0[\epsilon_B(\tilde{\nu}) - \epsilon_A(\tilde{\nu})]l \\ &= -\log (I_S^* \cdot I_R)/(I_R^* \cdot I_S) = -\log T(\tilde{\nu})\end{aligned} \tag{5}$$

In a SEUV experiment $\Delta D(\tilde{\nu})$ is derived from a first scan consisting of measurements at 256 fixed wavelength settings giving $D(\tilde{\nu})$ and a second scan with the probe in the photostationary state yielding $D^*(\tilde{\nu})$.

For transient intermediates having a lifetime in the region from 10 to 1000 ms the MEUV method is preferred. A timing diagram of this type of experiment is shown in Fig. 3. A single measurement at a fixed wavelength setting requires the following actions: (a) the intensities $I_S$ and $I_R$ of the sample and reference beam are measured; (b) the shutter ($SH_2$) is opened and the concentration of the metastable species starts to build up. After a delay time TAU 1 the photostationary state concentration is reached; (c) the intensities $I_S^*$ and $I_R^*$ are measured; (d) the shutter ($SH_2$) is closed. After a delay time TAU 0 which allows complete decay of the metastable species, the sequence (a) to (d) may be repeated; (e) the monochromators ($MO_1$ and $MO_2$) are set to the next wavelength position; (f) a digital feedback loop adjusts the high voltage power supply of the photomultiplier (PM) such that the larger of the two intensities $I_S$ or $I_R$ lies in the interval NORM.

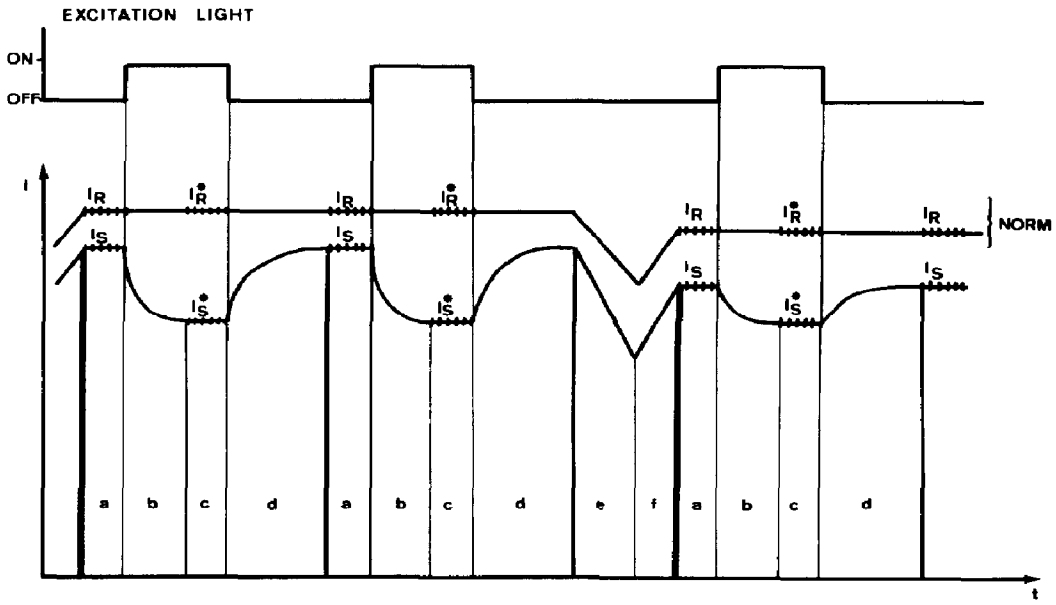



**Fig. 3. Timing diagram for a MEUV (modulated excitation with ultraviolet light) experiment.**

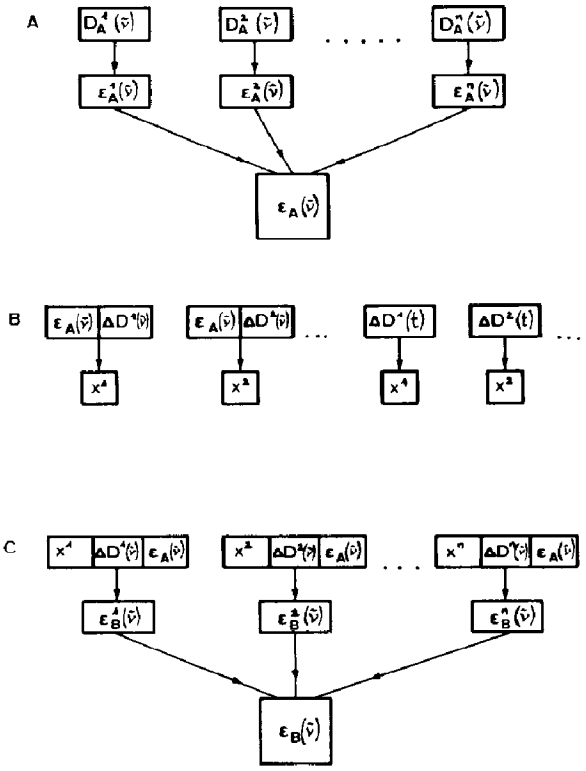
The measurements of $I_S$ and $I_R$ or $I_S^*$ and $I_R^*$ involve conversions of the output signals of the two phase sensitive detectors $PSD_S$ and $PSD_R$ (Fig. 1) to digital values with 12 bit accuracy. By repeating these conversions at 200 $\mu$s intervals for about three lifetimes of the transient species a significant improvement of the signal-to-noise ratio is achieved. The information gathered by the small computer is punched on paper tape and transferred to a mass storage device of a CDC 6400/6500 computer system.

## Data treatment

Each experiment performed on the small computer is labelled by a number and contains a text, a parameter and a data section. The three programs to be described form part of a general spectroscopic software system [22]. The concepts employed are based on statistical treatment of experimental data and have been discussed by Känzig *et al.* [12].

The determination of the molar absorption coefficients of a metastable state may be carried out in three distinct steps (Fig. 4). First (A) the molar absorption coefficients of the ground state are calculated from a set of absorption measurements $D_A^{(i)}(\tilde{\nu})$ recorded in different or overlapping regions using appropriate concentrations and cell length. The detailed procedure has been described by Känzig *et al.* [12]. The molar absorption curve of fluorenacene at 77 K in a 3-methylpentane glass is given in Fig. 5. It has been derived from seven absorption measurements with concentrations varying from $2 \times 10^{-6}$ to $3 \times 10^{-5}$ mol/l and a cell length of 2 cm.

In a second step (B) the fractional population $x^{(i)}$ of the metastable state is estimated using one or more of the three methods described below.



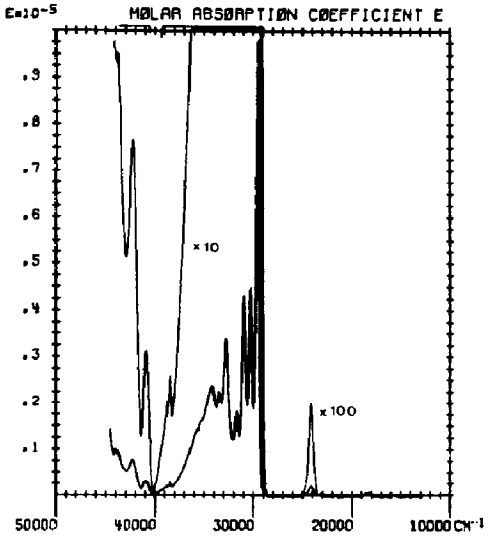



Fig. 4. The determination of molar absorption coefficients of metastable states.

Fig. 5. Absorption spectrum of fluorenacene $\epsilon_A(\tilde{\nu})$.

The molar absorption coefficients $\epsilon_B(\tilde{\nu})$ of the metastable species are calculated in a third step (C):

$$\epsilon_B^{(i)}(\tilde{\nu}) = \epsilon_A(\tilde{\nu}) + \Delta D^{(i)}(\tilde{\nu})/(x^{(i)} \cdot A_0^{(i)} \cdot l^{(i)}) \tag{6}$$

$$\sigma_B^{2(i)}(\tilde{\nu}) = \sigma_A^2(\tilde{\nu}) + (x^{(i)} \cdot A_0^{(i)} \cdot l^{(i)})^2 \cdot \sigma_{\Delta D}^{2(i)}(\tilde{\nu}) \tag{7}$$

where $\epsilon_A(\tilde{\nu})$ represents the molar absorption coefficient of the ground state A. $A_0^{(i)}$ and $l^{(i)}$ refer to the total concentration and the cell length of the experiment giving $\Delta D^{(i)}(\tilde{\nu})$ with the fractional population $x^{(i)}$. A weighted average is calculated from the individual estimates $\epsilon_B^{(i)}(\tilde{\nu})$ by taking into account their statistical precision $\sigma_B^{(i)}(\tilde{\nu})$.

*The quotient method*

Let us calculate the following ratio:

$$Q^{(i)}(\tilde{\nu}) = \Delta D^{(i)}(\tilde{\nu})/(A_0^{(i)} \cdot \epsilon_A(\tilde{\nu}) \cdot l^{(i)}) = x^{(i)} \cdot (\epsilon_B^{(i)}(\tilde{\nu})/\epsilon_A(\tilde{\nu}) - 1) \tag{8}$$

For physical reasons $x^{(i)}$, $\epsilon_A(\tilde{\nu})$, and $\epsilon_B^{(i)}(\tilde{\nu})$ must be positive. $Q^{(i)}(\tilde{\nu})$ is therefore always larger than $-x^{(i)}$. It is easily seen that in regions where $\epsilon_B(\tilde{\nu}) \ll \epsilon_A(\tilde{\nu})$ the quotient $Q^{(i)}(\tilde{\nu})$ approximates the negative fractional population $-x^{(i)}$. If $Q^{(i)}(\tilde{\nu})$ approximates the same value in two or more spectral regions one can be reasonably sure that $-Q^{(i)}(\tilde{\nu})$ represents a good estimate for $x^{(i)}$.

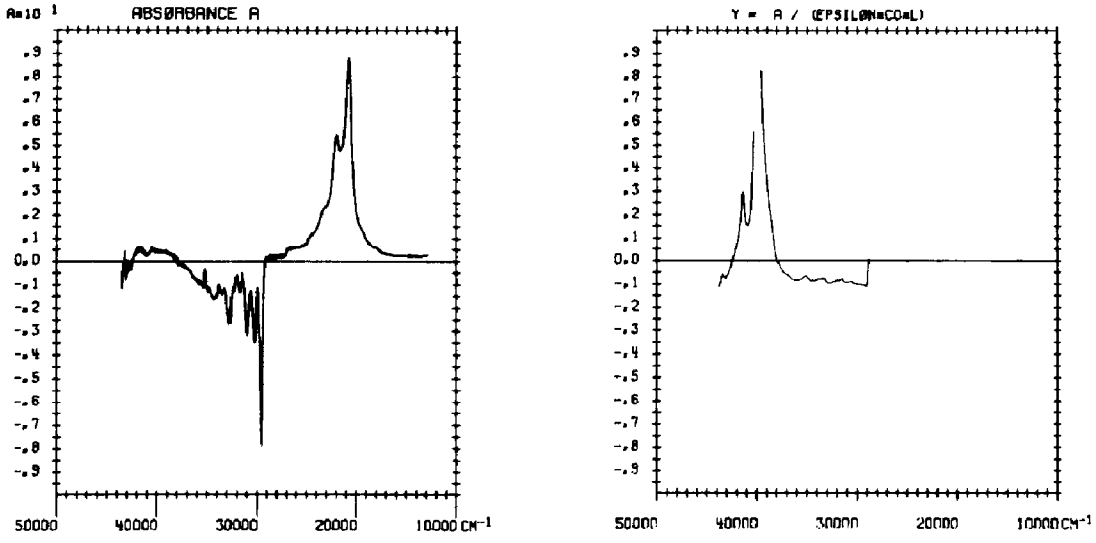



Fig. 6. $\Delta D^{(i)}(\tilde{\nu})$ of fluorenacene ($6.1 \times 10^{-6}$ mol/l) recorded at 77 K in 3-methylpentane in a 2 cm cell. Excitation occurred at 33,000 $cm^{-1}$ with a light flux of $1.0 \times 10^{-8}$ Einstein $cm^{-2}$ $s^{-1}$.

Fig. 7. Quotient $Q^{(i)}(\tilde{\nu}) = \Delta D^{(i)}(\tilde{\nu})/(A_0^{(i)} \cdot \epsilon_A(\tilde{\nu}) \cdot l^{(i)})$ calculated from experimental data given in Figs. 5 and 6.

The division of two spectra is a particularly delicate operation. If the statistical precision of the quotient is not considered properly, very unreasonable results may occur.

One of a series of $\Delta D^{(i)}(\tilde{\nu})$ spectra recorded at 77 K in 3-methylpentane is shown in Fig. 6. The sample ($6.1 \times 10^{-6}$ mol/l) was excited at 33 000 $cm^{-1}$ with a light flux of $1.0 \times 10^{-8}$ Einstein $cm^{-2}$ $s^{-1}$. The corresponding quotient $Q^{(i)}(\tilde{\nu})$ is given in Fig. 7. A minimum of about —0.11 is assumed throughout the range extending from 36 000 - 30 000 $cm^{-1}$. Even though the singlet spectrum is strongly structured in this range, the quotient remains practically constant. It can therefore be concluded that the value 0.11 is a good estimate for the fractional population of the triplet state.

*The sum method*

If one assumes a fractional population $\tilde{x}^{(i)}$ of the metastable state, the optical density $\tilde{D}_B^{(i)}(\tilde{\nu})$ can be calculated in the following way:

$$\begin{aligned}\tilde{D}_B^{(i)}(\tilde{\nu}) &= \Delta D^{(i)}(\tilde{\nu}) + x^{(i)}(A_0^{(i)} \cdot \epsilon_A(\tilde{\nu}) \cdot l^{(i)}) \\ &= x^{(i)} \cdot A_0^{(i)} \cdot \epsilon_B^{(i)}(\tilde{\nu}) \cdot l^{(i)} + (\tilde{x}^{(i)} - x^{(i)}) A_0^{(i)} \cdot \epsilon_A(\tilde{\nu}) \cdot l^{(i)} \end{aligned} \quad (9)$$

where $x^{(i)}$ represents the true fractional population of the metastable state observed in the experiment (i) giving $\Delta D^{(i)}(\tilde{\nu})$. The total concentration is $A_0^{(i)}$ and the cell length $l^{(i)}$. It is readily seen from eqn. (9) that, if $x^{(i)}$ is chosen to be equal to the true $x^{(i)}$ value, the spectrum $\tilde{D}_B^{(i)}(\tilde{\nu})$ will represent the absorption which results from the pure metastable species. In Fig. 8(a) a set of curves assuming $x = 0.0; 0.05; 0.1; 0.2$ are plotted. By visual inspec-

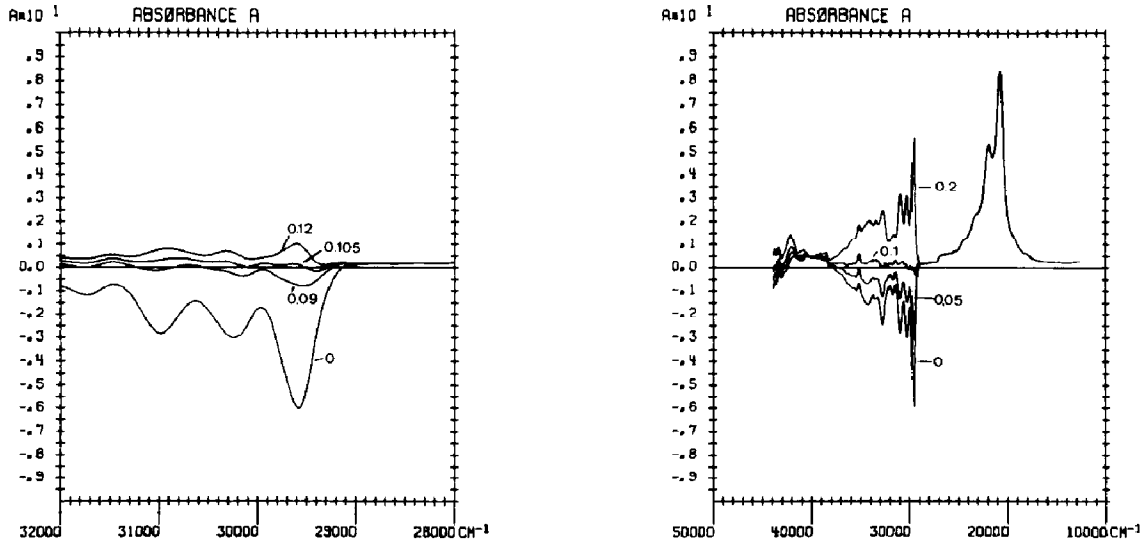



Fig. 8(a). A set of $\tilde{D}_B^{(i)}(\tilde{\nu})$ curves (see text) assuming $x$ = 0.0; 0.05; 0.1; 0.2; in the range 50,000 - 10,000 $cm^{-1}$. (b). A set of $\tilde{D}_B^{(i)}(\tilde{\nu})$ curves assuming $x$ = 0.0; 0.09; 0.105; 0.12; in the range 32,000 - 28,000 $cm^{-1}$.

tion it is easy to estimate that the correct $x^{(i)}$ must lie in the neighbourhood of 0.1. A second set (Fig. 8b) calculated in a smaller wavelength interval with $x$ = 0.0; 0.09; 0.105; 0.12 helps to narrow down the range for $x^{(i)}$, the best estimate being 0.105. The main criterion used requires the absorption spectrum $\tilde{D}_B^{(i)}(\tilde{\nu})$ to look as simple as possible. Specifically it should be possible to eliminate "structure" in $\tilde{D}_B^{(i)}(\tilde{\nu})$ in regions where the spectrum of A has sharp absorption bands. While it is extremely boring to calculate trial functions $\tilde{D}_B^{(i)}(\tilde{\nu})$ by hand, computer plots can be obtained at little cost with high spectral resolution.

*The kinetic method*

The change in optical density $\Delta D(\tilde{\nu}_0,t)$ is measured at a fixed position $\tilde{\nu}_0$ where a large effect occurs as a function of time. The kinetic curve which shows the build-up of the metastable species after the excitation light is switched on is given in Fig. 9(a). The corresponding decay function is displayed in Fig. 9(b). An estimate of the fractional population $x$ = 0.156 can be calculated from the rise ($\tau_r$) and fall ($\tau_d$) time constants:

$$x = (\tau_d - \tau_r)/\tau_d \qquad (10)$$

The values $\tau_r$ = 2.304 s and $\tau_d$ = 2.732 s were obtained from a least squares fit to the experimental curves assuming first order kinetics. Strictly speaking first order kinetics is only observed in an optically dense sample if it is irradiated at an isosbestic point of the A and B spectra. Reliable $x$ values can only be obtained with this method if rather large populations of the metastable state can be achieved. It has, however, the distinct advantage that it does not depend on any observation of ground state depletion.

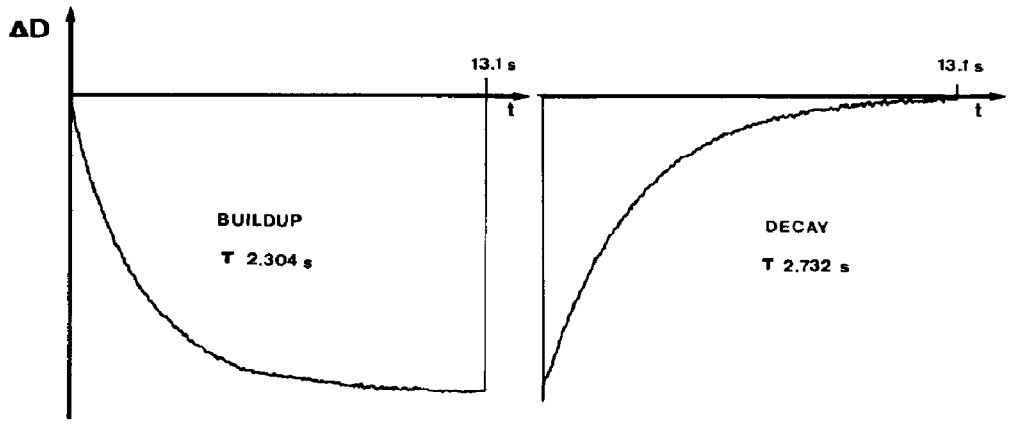



Fig. 9. Kinetic curves of the build-up and the decay of the metastable state.

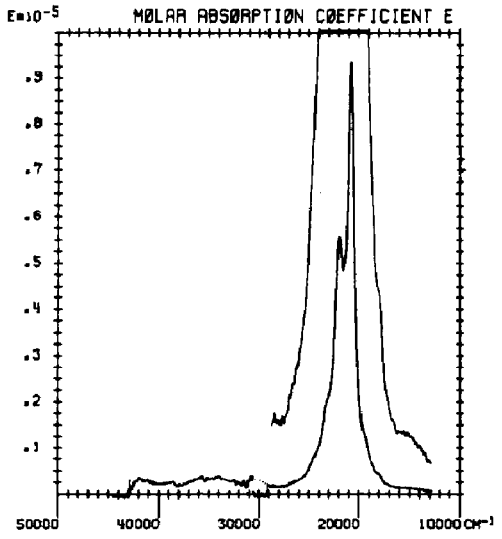



Fig. 10. Molar absorption spectrum of the triplet state of fluorenacene, $\epsilon_B(\tilde{\nu})$.

*The molar absorption coefficients of the triplet state of fluorenacene*

In Fig. 10, the complete molar absorption spectrum $\epsilon_B(\tilde{\nu})$ of the triplet state of fluorenacene is presented. It was calculated from $\epsilon_A(\tilde{\nu})$ and from five $\Delta D^{(i)}(\tilde{\nu})$ measurements assuming for each curve an optimized parameter $x^{(i)}$. Two strong peaks are observed at 21,900 and 20,800 $cm^{-1}$ having molar absorption coefficients of 55,600 ± 3500 and 93,500 ± 4300 $mol^{-1} \cdot l \cdot cm^{-1}$. There are no strong triplet–triplet bands hidden under the singlet spectrum. From the stationary state triplet concentration and the intensity of the excitation light one may estimate the quantum yield of triplet formation [13] to be 0.05.

## Acknowledgements

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