

276. Triplet-Triplet Absorption Spectra of Aromatic Hydrocarbons: I. Naphthalene¹⁾

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Summary. The difference between the triplet-triplet and singlet-singlet absorption spectrum of naphthalene has been measured at 90°K using a newly developed computer controlled spectrograph. Good spectral resolution has been obtained and a strong band was found in the ultraviolet region. Recent calculations are compared with the triplet-triplet spectrum of naphthalene.

1. Introduction. – Triplet-triplet spectra of many aromatic hydrocarbons are well known in the visible part of the spectrum and have been studied by many authors²⁾. Typical spectra measured by flash photolysis are given by *Porter & Windsor* [3], and *Astier & Meyer* [4] [20]. *Craig & Ross* [5], *McClure* [6] and *Henry & Kasha* [7] have used a photostationary method. Modulation techniques have been applied by *Labhart & Heinzelmann* [8], by *Slifkin & Walmsley* [9] and by *Zhmyreva et al.* [10].

The computer controlled spectrograph described in this work combines features of photostationary and modulation techniques and is especially suited for the study of metastable states having a lifetime of a few milliseconds to several seconds. The software developed to run the spectrograph is described in [11].

2. The Spectrograph. – 2.1. The principle of measurement is illustrated in Fig. 1. At a given wavelength the transmitted intensity *I* of the sample SA in the non irradiated state is measured. Individual readings with a 1:4000 resolution are taken in 200 μs intervals. Summing the individual readings represents digital filtering and leads to improved accuracy. Then the exciting light EL is turned on, and after a short waiting period the transmitted intensity *I** of the sample in the photostationary state is measured in the same way. The whole cycle is repeated at the next chosen wave-length. A single scan consists of 512 such cycles.

2.2. The block diagram of the spectrograph is shown in Fig. 2. A PDP 8/I small computer forms the basis of the system. The computer does not only serve as a data acquisition facility, but controls the whole experiment through an interface IF. The experimenter enters all parameters such as specific timing and spectral region through a teletype TTY.

The analysing light AL is chopped mechanically by a chopper disk CH in order to eliminate stray light and luminescence contributions. It passes through a hole in the excitation mirror SM through the sample SA and through the monochromator MONO. The monoenergetic light is converted into a current signal SIG1 by the photomultiplier PM. From SIG1 and the reference signal REF the phase sensitive detector PSD forms a dc signal SIG2, which is digitized by an analog to digital converter and fed into the computer.

The opening and closing of the shutter SH is initiated by a pulse P1. The pulses P2 and P3 increase and decrease respectively the wavelength of the analysing monochromator MONO in steps. The pulses P4 and P5 vary the supply voltage of the photomultiplier tube PM. A digital feedback loop adjusts this voltage such that the output signal SIG2 of the phase sensitive detector PSD has an optimum value at each wavelength.

1) Part of the thesis of *U. B. R.*, the experimental results of which were presented at the Euchem Conference on Primary Photoprocesses, Elmau Germany, Oct. 25-30, 1970.

2) cf. Ref. in [1] and [2].

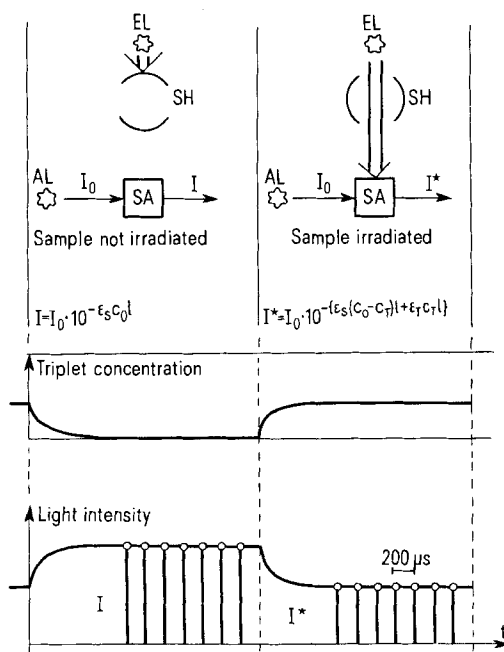


Fig. 1. Principle of measurement

AL:	analysing light source
SA:	sample
EL:	excitation light source
SH:	light shutter
I_0, I, I^* :	light intensities
each circle:	one digitising process
ϵ_s	singlet extinction coefficient
ϵ_T :	triplet extinction coefficient
c_0	total concentration of the solution = $c_s + c_T$
c_s, c_T :	singlet resp. triplet state concentration
l :	cell length

2.3. The data $I(\tilde{\nu})$ and $I^*(\tilde{\nu})$ are used to calculate the change in optical density $\Delta D(\tilde{\nu})$ which occurs in the irradiated state of the sample:

Optical density in the non irradiated state:

$$D(\tilde{\nu}) = \log \frac{I_0(\tilde{\nu})}{I(\tilde{\nu})} = \epsilon_s(\tilde{\nu}) \cdot c_0 \cdot l \quad (1)$$

Optical density in the irradiated state:

$$D^*(\tilde{\nu}) = \log \frac{I_0(\tilde{\nu})}{I^*(\tilde{\nu})} = \{\epsilon_s(\tilde{\nu}) \cdot (c_0 - c_T) + \epsilon_T(\tilde{\nu}) \cdot c_T\} \cdot l \quad (2)$$

Change in optical density:

$$\begin{aligned} \Delta D(\tilde{\nu}) &= D^*(\tilde{\nu}) - D(\tilde{\nu}) \\ &= \log \frac{I(\tilde{\nu})}{I^*(\tilde{\nu})} = \{\epsilon_T(\tilde{\nu}) - \epsilon_s(\tilde{\nu})\} \cdot c_T \cdot l \end{aligned} \quad (3)$$

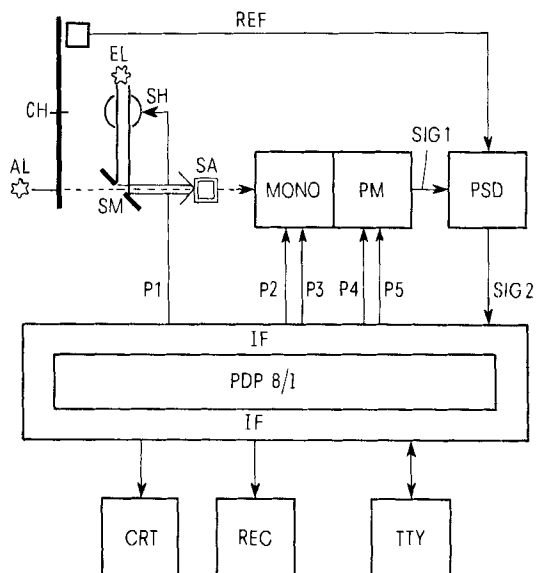


Fig. 2. Block diagram of the computer controlled single beam spectrograph

AL:	analysing light source
CH:	mechanical light chopper (1500 Hz)
SM:	sample irradiating mirror with an aperture through which the analysing light passes
SA:	sample
MONO:	monochromator (Zeiss M4Q II) with stepmotor drive
PM:	photomultiplier tube (S1 or S13), high voltage power supply with stepmotor drive
PSD:	phase sensitive detector (Brookdeal 411)
IF:	computer interface
EL:	excitation light source (1600 W Xe high pressure)
SH:	mechanical shutter (max. 50 Hz) with stepmotor drive
CRT:	x-y oscilloscope
REC:	x-y pen recorder
TTY:	Teletype reader/printer/punch

For small changes in optical density, i. e. $\Delta D(\tilde{\nu}) \ll 1$:

$$\Delta D(\tilde{\nu}) = \log \frac{I(\tilde{\nu})}{I^*(\tilde{\nu})} \approx \frac{I(\tilde{\nu}) - I^*(\tilde{\nu})}{2.3 I^*(\tilde{\nu})} \quad (4)$$

Positive values of $\Delta D(\tilde{\nu})$ occur when $\epsilon_T(\tilde{\nu}) > \epsilon_S(\tilde{\nu})$ and represent triplet-triplet absorption bands. Negative values occur due to singlet depletion at the positions of singlet absorption bands.

The small computer allows an immediate display of $\Delta D(\tilde{\nu})$ calculated with the approximate formula (4) on a oscilloscope CRT. The data punched on paper tape are transferred to a large computer which allows smoothing and plotting of $\Delta D(\tilde{\nu})$ calculated with formula (3) as a linear function of wavenumbers.

3. Experimental. Naphthalene was spectroscopic grade (*J. T. Baker Chemical Co.*) and used without further purification. The measurements were made in a methylcyclohexane/isopentane 4:1 glass (HCIP) at 90°K. The concentration of the solution was 1.4×10^{-6} M. The excitation light

was peaked at $31,000\text{ cm}^{-1}$ with a spectral half width of $15,000\text{ cm}^{-1}$. The path length in the cell was 1 cm .

4. Results and Discussions. – Experiment I.1. shows the well known bands in the range from $20,000\text{ cm}^{-1}$ to $30,000\text{ cm}^{-1}$ (Fig. 3). In addition to the main bands 1, 3, 5, additional vibrational lines 2, 4, 6, 7 are resolved. These weak lines have also been observed by *Hunziker* [12] in gas-phase work.

In experiment I.2., around $45,000\text{ cm}^{-1}$ an extremely strong and broad absorption band can be seen. The isosbestic point between the singlet-singlet and triplet-triplet spectrum at $44,000\text{ cm}^{-1}$ represents the most interesting feature of this region. Due to

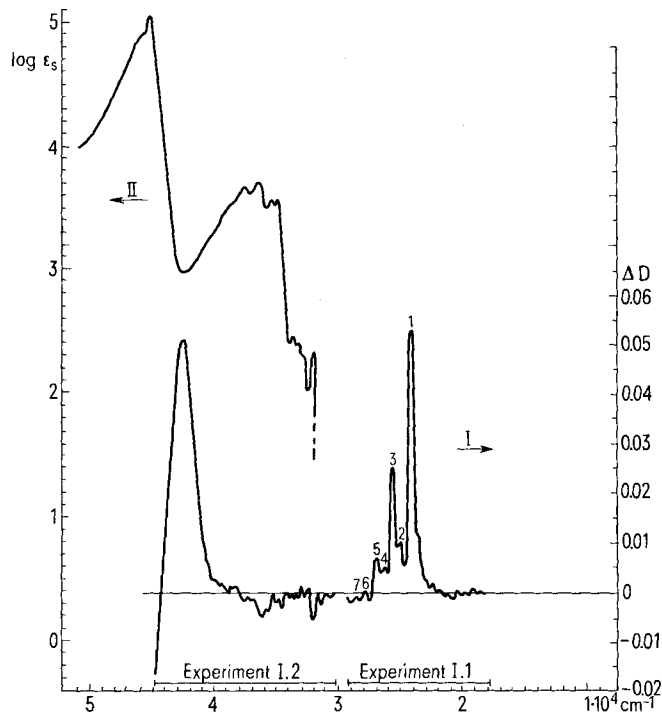


Fig. 3. *Naphthalene*

I: $\Delta D(\tilde{\nu})$ at 90°K in MCIP
 II: $\log \epsilon_s(\tilde{\nu})$ at room temperature in n-hexane^{a)}

^{a)} DMS UV. Atlas of Organic Compounds, Butterworth, Verlag Chemie, 1966 (vol. I) – 1971 (vol. V).

the sharp rise of the singlet absorption, we can only estimate that the peak absorption of this triplet band occurs little above $44,000\text{ cm}^{-1}$. The peak in the experimental curve at $42,000\text{ cm}^{-1}$ is approximately 10 times stronger than the singlet depletion band at $36,400\text{ cm}^{-1}$. This band has an ϵ_s of $5600\text{ mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$ at room temperature. The ϵ_T of the UV. band is therefore at least $56,000\text{ mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$. Since the ϵ_s value of the singlet band may be larger due to band sharpening at low temperature and $42,000\text{ cm}^{-1}$ may not be the maximum of the triplet band, a value up to $100,000\text{ mol}^{-1}\cdot\text{l}\cdot\text{cm}^{-1}$

may be expected for this band⁴). The triplet-triplet spectrum of naphthalene may be interpreted with the aid of *Pariser-Parr-Pople* type calculations. In Table I the results of the original work by *Pariser* (C) and two calculations (A, B) which we have performed using the *Mataga* [14] approximation for the electron repulsion integrals, are given.

These three calculations only involve triplet configurations which are singly excited with respect to the singlet ground state S_0 . A more elaborate configuration interaction, also including configurations which are doubly excited with respect to S_0 , has been taken into account by *Orloff* (D), and by *deGroot & Hoiijtink* (E)⁵).

Not all of the symmetry allowed transitions however carry oscillator strength. It is interesting that additional selection rules apply in this system. This is nicely demonstrated in the calculation A which only includes first order configuration interaction between degenerate configurations. First using the generalized *Coulson-Rushbrooke* theorem [17] [18] a classification of the configurations in + and – configurations may be achieved and only transitions between unlike signs are allowed. Transitions which are forbidden by this rule are given in () parentheses (cf. Table I). Secondly, only transitions between the lowest triplet configuration T_1 and configurations which are singly excited with respect to T_1 are allowed. This selection rule eliminates for instance transitions from T_1 to triplet configurations which are obtained from orbital promotion $4 \rightarrow 8$ and $3 \rightarrow 7$. Forbidden bands of this type are listed in



The states S_i and T_j are linear combinations of configurations. The symbol following the state number indicates for first order interaction all the configurations used, whereas for the other calculations it indicates the main configurational components. A singly excited configuration ($i \rightarrow k$) is generated from the ground state function by replacing the orbital i by the virtual orbital k . In the doubly excited configuration $\begin{pmatrix} s \rightarrow t \\ u \rightarrow v \end{pmatrix}$ both orbitals s and u are replaced by the virtual orbitals t and v

a: G. J. Hoiijtink [21]

b: cf. [17], [18]

A: This work; only first order configuration interaction between degenerate configuration has been taken into account

B: This work; configuration interaction between all 25 singly excited configurations has been considered

C: *Pariser* [13]

D: *Orloff* [15]

E: *deGroot et al.* [16]

⁴) This band has independently been observed by *Astier et al.* [20]. They found with the technique of flash photolysis a maximum at $42,500 \text{ cm}^{-1}$ with an ϵ_T of $60,000 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$. Their experiments have been performed in an alcohol solution at 113°K , with high ground state depletion. Note added in proof: In a very recent paper [22] *Y. H. Meyer, R. Astier & J. M. Leclercq* have given a thorough discussion of the triplet-triplet spectroscopy of Polyacenes.

⁵) We would like to thank *R. L. de Groot* for making the original computer outputs available to us.

States	Nomenclature		Polarisation	Transition energies (cm ⁻¹)/oscillator strengths				
	a	b		experiment	A	B	C	D
$S_0 \rightarrow S_n$								
S_0	reference	$^1A_g^-$	-	-	-	-	-	-
S_1	(5 → 7) - (4 → 6)	$^1B_{3u}^-$ (x)	32,200	34,800/0	33,800/0	32,400/0	-	-
S_2	(5 → 6)	$^1B_{2u}^+$ y	35,000	37,800/0.53	36,400/0.25	36,200/0.26	-	-
S_3	(5 → 7) + (4 → 6)	$^1B_{3u}^+$ x	45,300	47,400/1.82	47,200/2.08	47,900/2.11	-	-
$T_1 \rightarrow T_n$								
T_1	(5 → 6) ref.	$^3B_{2u}^-$	-	-	-	-	-	-
T_2	(5 → 8) + (3 → 6)	$^3B_{1g}^+$ (x)	-	6,900/0	9,800/0	10,000/0	-	9,500/0
T_3	(5 → 9) + (2 → 6)	$^3A_g^+$ (y)	-	20,300/0	18,800/0	18,200/0	-	16,400/0
T_4	(4 → 8) + (3 → 7)	$^3A_g^+$ [(y)]	-	24,300/0	31,500/0	31,000/0	-	26,200/0
T_5	(5 → 8) - (3 → 6)	$^3B_{1g}^-$ x	24,000	26,900/0.61	33,500/0.42	30,700/0.45	26,400/0.83	26,500/0.10
T_6	(4 → 8) - (3 → 7)	$^3A_g^-$ [y]	-	29,700/0	33,600/0.06	28,500/0.08	-	27,000/0.03
T_7	(5 → 9) - (2 → 6)	$^3A_g^-$ y	38,500	34,600/0.52	43,400/0.31	41,700/0.36	34,200/0.58	37,900/0.16
T_8	$\begin{pmatrix} 5 \rightarrow 6 \\ 5 \rightarrow 7 \end{pmatrix} + \begin{pmatrix} 5 \rightarrow 6 \\ 4 \rightarrow 6 \end{pmatrix}$	$^3B_{1g}^+$ (x)	-	-	-	-	41,900/0	42,100/0
T_9	$\begin{pmatrix} 5 \rightarrow 6 \\ 5 \rightarrow 7 \end{pmatrix} - \begin{pmatrix} 5 \rightarrow 6 \\ 4 \rightarrow 6 \end{pmatrix}$	$^3B_{1g}^-$ x	45,000	-	-	-	50,200/1.00	46,000/0.27

[] parentheses. Such transitions become however weakly allowed through further configuration interaction.

The assignment of the observed 24,000 cm⁻¹ triplet band system to a ${}^3B_{1g}^- \leftarrow {}^3B_{2u}^+$ transition seems firmly established. All calculations give a band in this region. *Pavlopoulos* [19] has furthermore shown that this band has the correct long axis polarisation. *Porter* [3] found at 38,500 cm⁻¹ the onset of a strong UV. band. He assigned this band on the basis of the available *Pariser* data to the ${}^3A_g^- \leftarrow {}^3B_{2u}^+$ transition. Our work shows an extremely strong band above 44,000 cm⁻¹ which is predicted by *Orloff* [15] & *deGroot* [16]. It seems definitely necessary to include doubly excited configurations with respect to S₀ which are singly excited with respect to T₁ into the calculations. It is still puzzling that the band ${}^3A_g^- \leftarrow {}^3B_{2u}^+$ starting at 38,500 cm⁻¹ which should have appreciable oscillator strength according to all calculations is quite weak in our spectrum. Further work which we plan to do in the UV. region will involve polarisation studies on this band.

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